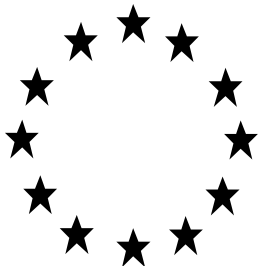
Draft Renewal Assessment Report
under Regulation (EC) 1107/2009



CLOPYRALID

Volume 3 – B.8 (AS)

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B.8. ENVIRONMENTAL FATE AND BEHAVIOUR

Most data on the fate and behaviour of clopyralid in soil, water and air were evaluated during the Annex I inclusion process in 2002-2005. This dRAR therefore focuses on those environmental fate studies which were not evaluated in the DAR and its addenda. However, a number of new studies were submitted by the Notifier to fulfil the current requirements, and only these data are presented and evaluated in detail in this dRAR.

For a better overview, existing data and their evaluation resulting from the process of Annex I inclusion are briefly mentioned and amended by new data generated in order to fulfil current requirements. The numbering and the headlines correspond to latest EU requirements.

All AIR3 data on the fate and behaviour of clopyralid in the environment was generated and owned by the Notifier, and no publicly available literature was submitted.

B.8.1. FATE AND BEHAVIOUR IN SOIL

B.8.1.1. Route and rate of degradation in soil

B.8.1.1.1. Aerobic degradation in soil

Two studies to address this point were presented in the dossier for the Approval of Clopyralid submitted in 30 April 2002, evaluated in the DAR (2003) and peer review at EU level. The data were deemed acceptable following evaluation, and are still valid for decision making.

CA 7.1.1.1.1/1 - Clopyralid Technical - Aerobic degradation in soil

Report	[IIA 7.1.1.1/01], Baloch, R. & Grant, R. 1991.
Report title	Degradation and metabolism of Clopyralid in soil under aerobic conditions.
DAS Study number	GHE-P-2398R, Ref. K45.
Guidelines	BBA Part IV, 4-1 (1991) Apart from minor deviations, the study also meets the requirements of the SETAC-Europe Guideline, Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, Part 1, Section 1.1 (1995)
GLP	Yes (certified laboratory)

Methods

The route of aerobic degradation of [2,6-pyridinyl-^{14}C]-clopyralid as monoethanolamine salt was investigated in a total of five European soils under laboratory conditions at 20 °C for up to 12 months. Additionally, a lower temperature (10 °C), three different moisture levels (10%, 40% and 60% of maximum moisture holding capacity, MHC) as well as three different concentrations (0.05, 0.3 and 1 mg/kg) were investigated in three of the soils. The application rate in the main study, 225 g a.i./ha, corresponded to the concentration of 0.3 mg clopyralid/kg dry soil. The soils are characterized in Table 8.1-1.

Table 8.1-1 The soils used to investigate the aerobic degradation of clopyralid

Soil name	Parabraunerde	Marcham	Castle Rising	Speyer 2.1 *)	Speyer 2.2 *)
Country of origin	Germany	UK	UK	Germany	Germany
Texture (%)					
Sand	5	63	69	91	88
Silt	81	17	22	6	8
Clay	14	20	9	3	4

Textural classification USDA (quoted) UK BBA	Silty loam Silty loam Medium clayey silt	Sandy loam Sandy clay loam Strongly sandy loam	Sandy loam Sandy loam Medium loamy sand	Sand Sand Pure sand	Loamy sand Sand Pure sand
Bulk density (g/cm^3)	1.11	1.11	0.43	1.35	1.08
pH	7.7	8.3	8.0	6.5	6.3
Organic matter content (%)	1.74	3.19	27.6	1.28	3.84
Organic carbon (%) calculated as OM/1.724	1.01	1.85	16.01	0.74	2.23
Cation exchange capacity (mEq/100 g)	9.2	17.8	53.3	2.4	7.6
MHC determined by capillary saturation (% w/w dry soil)	13.4	22.0	38.8	7.2	14.1
Microbial biomass (µg C/g soil)	47	170	313	Not detected	110

*) The two Speyer soils were not used in the additional testing with lower incubation temperature, different moisture contents or different application rates.

The soils were incubated in biometer flasks in dark. The moisture content of the soils was adjusted by addition of distilled water. NaOH traps were used to collect the evolved CO_2 during the incubation. Oxygen was added to the flasks throughout the study to ensure aerobic conditions were maintained.

In the main test (5 soils, 20 °C, 40 % of MHC) the soils were sampled 0, 1, 3, 7, 14 and 28 days and 3, 6, 9 and 12 months after the application. In other parts of the test the three soils were sampled at 0, 7, 14, 28, 92 and 184 days of incubation. Prior to extraction the radioactivity content of the soil samples was quantified by combustion of aliquots in oxygen using a sample oxidiser. The soil samples were extracted with calcium chloride solution, acidified acetone and sodium hydroxide solution. Extracts and washings were quantified by liquid scintillation counting (LSC) and the extracts of soils were characterised by co-chromatography with known reference compounds by thin layer chromatography (TLC).

The DT_{50} and DT_{90} values were calculated in the original study using the Timme-Frehse programme in two ways: by using the data points up to three months and using all data points up to six months or a year. It was noted that using the data from all measurements, the DT_{50} and DT_{90} values were generally much higher than those calculated with the data points of first three months. It was also discussed if data from measurements of all extracts should or should not be used in the calculations.

In the EU dossier the Notifier has recalculated the DT_{50} and DT_{90} values using the Solver function in a Microsoft Excel spreadsheet in order to find a better fit between the observed experimental data and the first order rate equation by minimising the sum of squares of the residuals between the actual data and the best fit line. Contrary to the earlier calculation, the radioactivity in combined extracts was taken into account.

Results

The overall **recoveries of the radioactivity** were acceptable in all parts of the test. In all parts of the test the mass balances were between 74.88 and 113.24 % of the applied radioactivity (AR) throughout the sampling periods. In the main test (5 soils, 20 °C, 40 % of MHC) the mean recovery of radioactivity was 99.3 % of AR, whereas the mean recoveries were 99.0 % of AR for testing the effect of temperature, 102.2 % of AR for testing the effect of soil moisture and 103.4 % of AR for testing the use rate. All recoveries indicate a complete mass balance.

For the **main part of the study** the distribution of applied radioactivity between extractable, NER and volatile components was similar for all soil types. The level of radioactivity extractable from the soil declined from between 95.5 and 103.3% AR initially to between 28.1 and 80.1% AR after 28 days and declined further to < 10% AR in all soil types by 275 days. The level of NER increased to between 11.2 and 35.1% AR after 92 days and subsequently plateaued in the Marcham sandy loam soil and slowly declined in the four remaining soils. The level of volatile radioactivity recovered in the side-arm trap steadily increased throughout the study to between 11.1 and 42.0% AR by 28 days, 47.5 and 65.5% AR after 92 days and to between 72.9 and 83.3% AR after 374 days. The amount of additional radioactivity recovered in the flask rinse was typically < 0.5% AR on all occasions. The similarity observed between the duplicate samples of the Parabraunerde silty loam soil indicated that the results to the whole experiment were reproducible.

At 10 ºC the radioactivity extractable from the soil declined from between 95.5 and 101.9% AR initially to between 49.4 and 76.8% AR after 28 days and further declined to between 10.8 and 53.5% AR by 184 days. The level of NER generally increased steadily throughout the incubation period and reached a maximum of between 9.9% and 26.9% AR after 92 to 184 days, however, for one soil type the level of NER detected had started to decline by the end of the study. The level of volatile radioactivity recovered in the side-arm trap steadily increased throughout the study and consisted of between 18.5 and 25.9% AR by 92 days and between 36.3 and 55.6% AR after 184 days. The amount of additional radioactivity recovered in the flask rinse was typically < 0.5% AR. At the lower temperature of 10°C, the decline in the level of extractable radioactivity and the corresponding increase in the level of evolved CO_2 occurred at a lower rate. The level of accumulated NER was not as significant as for similarly treated soil samples at 20°C.

At the lower **moisture content** the level of radioactivity extractable declined only slightly over the duration of the study and comprised of between 95.3% and 99.3% AR at the end of the incubation period (184 days). The level of NER only accumulated to between 4.7 and 10.1% AR after 184 days and the level of evolved CO_2 detected was < 0.1% AR on all occasions. The amount of additional radioactivity recovered in the flask rinse was < 0.2% AR on all occasions. At the higher moisture content the level of radioactivity extractable from the soil declined to between 3.6 and 79.6% AR after 28 days and further declined to between 1.3 and 5.3% AR by 184 days. The level of NER increased to a maximum of between 16.4 and 33.0% AR after 28 to 92 days and subsequently declined in all soils to between 14.1% and 26.8% AR by the end of the study. The volatile radioactivity steadily increased throughout the study to between 16.3% and 66.9% AR by 28 days and between 75.6% and 81.7% AR after 184 days. The amount of additional radioactivity recovered in the flask rinse was typically < 0.5% AR. At the lower moisture content the rate of decline in the level of extractable radioactivity had slowed considerably compared to 40% MHC. At the higher moisture content the decline in the level of extractable radioactivity and the corresponding increase in the level of evolved CO_2 occurred at a slightly higher rate than that at 40% MHC.

At the lower **application rate** the level of radioactivity extractable from the soil samples declined from between 89.7 and 97.7% AR initially to between 13.4% and 33.6% AR after 28 days and further declined to between 3.8% and 4.6% AR by the end of the study. The level of NER increased to a maximum of between 18.2% and 38.4% AR after 28 days and subsequently declined in all soils to between 17.1% and 21.8% AR after 184 days. The level of evolved CO_2 steadily increased throughout the study to between 45.3% and 52.6% AR by 28 days and to between 72.3% and 86.2% AR after 184 days. The amount of additional radioactivity recovered in the flask rinse was < 0.1% AR. At the higher application rate the level of radioactivity extractable from the soil samples declined to between 77.6% and 94.9% AR after 28 days and further declined to between 30.4% and 55.6% AR by 184 days. The level of NER generally increased steadily throughout the incubation period to between 9.0% and 30.4% AR after 184 days. The level of volatile radioactivity recovered steadily increased throughout the study to between 4.4% and 5.7% AR by 28 days and increased further to between 35.9% and 70.0% AR after 184 days. The amount of additional radioactivity recovered in the flask rinse was typically < 0.5% AR. The decline in the level of extractable radioactivity and the corresponding increase in the level of evolved CO_2 was slower at the higher application rate.

TLC analysis of the calcium chloride extracts demonstrated that in all cases the only material observed was clopyralid. Analysis of the concentrated acetone extracts indicated the presence of clopyralid and material at the origin. However, further investigations concluded that the origin material observed was due to matrix effects occurring during analysis and that if these were minimised, further parent material was released. It was, therefore, concluded that the origin material was an artefact of the analysis procedure and that clopyralid was the only component detected i.e. no metabolites were produced at all the temperatures, moisture contents and treatment

rates investigated. The levels of clopyralid recorded were, therefore, taken as the sum of the calcium chloride and acidified acetone extracts.

Although the NER was not investigated extensively, an extraction with sodium hydroxide (0.5M) was conducted which would normally separate the humic acid and fulvic acid fractions from the insoluble humin fraction. As the majority of the radioactivity remained unextractable it can be concluded that the NER was associated mostly with the humin fraction and was deeply incorporated into the soil structure.

The **DT_{50} and DT_{90} values** recalculated by the Notifier on the basis of the data obtained in this study are presented in Tables 8.1-2 – 8.1-5.

Table 8.1-2 $DT_{50(lab)}$ and $DT_{90(lab)}$ values for the rate of aerobic degradation of clopyralid at a treatment rate of 0.3 mg/kg in five soils at 20°C and 40% MHC

Soil name	Soil type	Data range (days)	$DT_{50(lab)}$ (days)	$DT_{90(lab)}$ (days)	Regression parameters		
					C_0	K	R^2
Parabraunerde	Silty loam	0 – 374	45	150	107.24	0.0153	0.984
Marcham	Sandy loam	0 – 374	36	120	102.23	0.0192	0.988
Castle Rising	Sandy loam	0 – 374	28	93	98.44	0.0247	0.984
Speyer 2.1	Sand	0 – 374	65	217	103.78	0.0106	0.989
Speyer 2.2	Loamy sand	0 – 184	16	54	99.387	0.0424	0.978

Table 8.1-3 Effect of temperature: $DT_{50(lab)}$ and $DT_{90(lab)}$ values for the rate of aerobic degradation of clopyralid at a treatment rate of 0.3 mg/kg in three soils at 10°C & 40% MHC

Soil name	Soil type	Data range (days)	$DT_{50(lab)}$ (days)	$DT_{90(lab)}$ (days)	Regression parameters		
					C_0	K	R^2
Parabraunerde	Silt loam	0 - 184	198	657	101.59	0.0035	0.967
Marcham	Sandy clay loam	0 - 184	100	331	100.24	0.0070	0.969
Castle Rising	Sandy loam	0 - 184	73	244	98.27	0.0095	0.963

Table 8.1-4 Effect of moisture: $DT_{50(lab)}$ and $DT_{90(lab)}$ values for the rate of aerobic degradation of clopyralid at a treatment rate of 0.3 mg/kg in three soils at 20°C and 10, 40 and 60% MHC

Soil name	Moisture level, % MHC	Data range (days)	$DT_{50(lab)}$ (days)	$DT_{90(lab)}$ (days)	Regression parameters		
					C_0	K	R^2
Parabraunerde	10%	0 - 184	n/c	n/c	n/c	n/c	n/c
	40%[1]	0 - 374	45	150	107.24	0.0153	0.984
	60%	0 - 184	42	141	112.18	0.0163	0.959
Marcham	10%	0 - 184	n/c	n/c	n/c	n/c	n/c
	40%[1]	0 - 374	36	120	102.23	0.0192	0.988
	60%	0 - 184	32	105	107.38	0.0220	0.980
Castle Rising	10%	0 - 184	n/c	n/c	n/c	n/c	n/c
	40%[1]	0 - 374	28	93	98.44	0.0247	0.984
	60%	0 - 184	7	24	95.03	0.0967	0.992

n/c = not calculated, no significant degradation occurred over 184 days, DT_{50} > 1 year.
[1] Values included for reference, see Table 8.1-2.

Table 8.1-5 Effect of application rate: $DT_{50(lab)}$ & $DT_{90(lab)}$ values for the rate of aerobic degradation of clopyralid at treatments of 0.05, 0.3 & 1.0 mg/kg in three soils at 20°C & 40% MHC

Soil name	Application rate, mg/kg	Data range (days)	$DT_{50(lab)}$ (days)	$DT_{90(lab)}$ (days)	Regression parameters		
					C_0	K	R^2
Parabraunerde	0.05	0 - 184	23	77	106.33	0.0299	0.947
	0.3[1]	0 - 374	45	150	107.24	0.0153	0.984
	1.0	0 - 184	215	715	103.66	0.0032	0.917
Marcham	0.05	0 - 184	14	45	102.12	0.0508	0.967
	0.3[1]	0 - 374	36	120	102.23	0.0192	0.988
	1.0	0 - 184	120	398	102.51	0.0058	0.963
Castle Rising	0.05	0 - 184	18	59	101.03	0.0392	0.892
	0.3[1]	0 - 374	28	93	98.44	0.0247	0.984
	1.0	0 - 184	57	189	103.33	0.0121	0.943

[1] Values included for reference, see Table 8.1-2.

The mean $DT_{50(lab)}$ at 20 °C and 40 % MHC in five soils was 38 days, and correspondingly the mean of $DT_{90(lab)}$ was 127 days. At lower temperature the degradation rate declined remarkably, with the mean $DT_{50(lab)}$ of 124 days in three soils. The rate of degradation of clopyralid correlated well to first-order kinetics.

Comments

The study was well performed and reported clearly and was in compliance with GLP. All mass balances were acceptable. The DT_{50} and DT_{90} values were recalculated by the notifier using all measurement points and another PC programme. The results of the recalculation were presented only in Document MIII of the Dossier, no separate research paper was attached. However, in the dossier the reasons for the recalculation were discussed in detail and the procedure is acceptable to the rapporteur. The recalculated DT_{50} and DT_{90} values are some longer compared to those in the original study, providing thus a better safety margin in the PEC calculations.

The soils used in the additional parts of the study have all a very high pH, and are thus not typical to Northern European conditions, where a low soil pH prevails. Therefore the soils tested may be more representative to the Southern European conditions? However, the DT_{50} values did not correlate with the pH, organic carbon content or texture of the soils and therefore this has no impact on the validity of the study.

Due to the complete mineralisation of clopyralid to CO_2 in soils, no other degradation products could be found. Therefore the degradation pathway of clopyralid cannot be described according to this study. However, this is acceptable as the study indicates a complete mineralisation in all conditions, and the fraction of non-extractable residue was low throughout the inclubation period.

The mean DT_{50} of 38 days from this study (corrected as 36 days for soil moisture content at field capacity) was used in the first tier FOCUS ground water modelling for calculating the PEC_{gw} (ref.K80).

CA 7.1.1.1.1/2 - Clopyralid Technical - Aerobic degradation in soil

Report	[IIA 7.1.1.1/02], Skinner, W., Jao, N. & Smith, J.K. 1995.
Report title	Aerobic soil metabolism of [^{14}C] clopyralid.
DAS Study number	GH-C 3598. Ref. K64.
Guidelines	US EPA Pesticide Assessment Guidelines, Subdivision N, Paragraph 162-1 (1982). Apart from minor deviations, the study also meets the requirements of the SETAC-Europe Guideline, Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, Part 1, Section 1.1 (1995)
GLP	Yes (certified laboratory)

Methods

The route of aerobic degradation of [2,6-pyridinyl-^{14}C]-clopyralid was investigated in a silt loam soil from USA (Marshall county) under laboratory conditions at 25°C. The soil contained 6 % sand, 68 % silt and 26 % clay. Its pH was 6.0, its organic matter content was 2.62 % and organic carbon content 1.52 %. The cation exchange capacity was 11.92 mEq/100 g and the bulk density was 1.34 g/cm^3. The moisture holding capacity was 31.22 % at 0.33 bar suction and 34.6 % at 0.1 bar suction.

The soil was sieved (2 mm) prior to use to remove debris and to ensure homogeneity. The microbial biomass of the soils was determined at the start, middle and end of the study period.

Soil samples (50 g dry weight equivalent) were added to biometer type flasks. The side-arms to the flasks were charged with potassium hydroxide solution (40 ml, 10%) to collect evolved CO_2. The moisture content of the soil samples was adjusted to 75% of the MHC at 1/3 bar suction by addition of distilled water. The flasks were sealed and incubated at 20°C wrapped in tin foil to protect from the light.

[2,6-pyridinyl-^{14}C]-Clopyralid was applied to the soil samples at a rate of 0.28 mg ai/kg dry soil (equivalent to an application rate of 210 g ai/ha in a soil depth of 5 cm. The radiopurity was confirmed prior to commencing the study by HPLC analysis.

All soil samples were incubated in the dark at 25°C. The potassium hydroxide solution in the side-arms to the flasks was removed and replenished on occasions throughout the incubation period to avoid saturation.
At pre-defined sampling intervals over a period of 78 days duplicate whole soil samples were taken for analysis. The soil was extracted with an acidified acetone solution. Extracts and washings were quantified by LSC and stored in a freezer at –20°C prior to chromatographic analysis. The level of NER remaining in the soil after extraction was determined by drying the post-extracted soil residue and combusting aliquots in oxygen.

Soil extracts were analysed by HPLC without the requirement for prior concentration.
The volatile radioactivity recovered in the trapping solutions was confirmed as CO_2 by barium carbonate precipitation. Whenever significant amounts of applied radioactivity remained in the extracted soil residue this was further fractionated into humic acids, fulvic acids and humin components.

Results

The mean **recovery of radioactivity** was 99.6 % of AR, indicating that a complete mass balance was achieved.

The level of radioactivity **extractable** from the soil declined from 100.1% AR initially to 46.5% AR after 14 days and declined further to 8.0% AR after 78 days. The level of **NER** increased to 19.1% AR after 28 days and subsequently plateaued at a level between 19% and 21% AR. The level of volatile radioactivity recovered in the side-arm trap steadily increased throughout the study to 73.6% AR after 78 days. Good reproducibility was observed between the replicate samples. By day 78, 73.6 % of AR evolved to **CO_2**.

In addition to the analysis performed at each sampling interval the **NER was further fractionated** in to humic acid, fulvic acid and humin soil fractions where it had accumulated to significant levels (i.e. > 10% AR). The fractions of humic acid and fulvic acid remaided constant at all sampling times (1.1-1.4 % and 6.4 – 7.5 % of AR, respectively). At all sampling intervals the majority of the NER was associated with the humin soil fraction indicating that these components were deeply incorporated in to the soil structure.

The **chromatographic profile** of the soil extracts by HPLC analysis indicated that the level of clopyralid detected declined steadily from 97.4% AR initially to 67.0% AR by 7 days, and further to 0.3% AR by 43 days.

Degradation of clopyralid gave rise to the formation of several minor regions of **unidentified radioactive components** (as detected by HPLC analysis). None of the regions detected amounted to levels greater than 10% AR on any occasion. The most significant was region 2 (aromatic ring still intact and some form of exchangeable hydrogen attached to the ring) which comprised a maximum of 7.7% AR after 14 days and declined to <2 % of applied by 78 days, but could not be fully identified. This component was not found in the previous study. Region 1 (max. 6.0 % of AR at day 7) consisted of polar unretained material and was shown to comprise of multiple components. Regions 3 and 4 were found not to exceed 1.8% AR.

The **DT_{50} and DT_{90}** values were recalculated in the Document MIII of the dossier similarly to the previous study. The degradation of clopyralid was found to correlate well to first-order kinetics.

Table 8.1-6 $DT_{50(lab)}$ and $DT_{90(lab)}$ values for the rate of aerobic degradation of clopyralid in one US soil at 25°C and 75% of the 1/3 bar MHC

Soil name	Soil type	Data range (days)	$DT_{50(lab)}$ (days)	$DT_{90(lab)}$ (days)	Regression parameters		
					C_0	K	R^2
Marshall County	Silt loam	0 - 78	9	29	102.15	0.0789	0.991

Comments

The study was in compliance with GLP, well performed and reported clearly. Despite the numerous methods of isolation and characterization used, the degradates could not be fully identified because of the low levels of radioactivity in the extracts. The degradation rate obtained in this study appears to be in line with the results of the previous study (Ref.K45). The recalculation of DT_{50} and DT_{90} values gave a slightly longer half-life and thus a better margin of safety, and is therefore acceptable.

RMS comments and evaluation:

The studies on the aerobic degradation of clopyralid were evaluated in the DAR (2003) as commented above and the results were used in the risk assessment presented in the EFSA conclusion on clopyralid (EFSA Scientific Report 2005: 50). The outcomes as used in the kinetic evaluation (Schubert 2015) are still valid and therefore the studies are not reviewed here again. No other comments, studies are acceptable and adequate for the renewal for the approval of clopyralid.

In the AIR3 dossier of clopyralid one additional new study on the aerobic degradation of clopyralid was attached, which has not been evaluated before in the context of regulation 1107/2009. This study is reviewed below, and the results are used in the risk assessment together with the two previously evaluated studies.

CA 7.1.1.1.1/3 - Clopyralid Technical - Aerobic degradation in soil

Report	[IIA 7.1.1.1/03], Wardrope, L. 2009
Report title	The Degradation of [14C]-Clopyralid in Soil under Aerobic Conditions
DAS Study number	Charles River; Lab Study No. 808711; DAS Study No. 29902; 26 February 2009
Guidelines	OECD 307 (2002) US EPA OSCPP 835.4100, OPPTS 835.4100
GLP	Yes

Materials and methods:

The degradation of [2,6-pyridinyl-^{14}C]-Clopyralid was studied in four agricultural soils in the dark under aerobic conditions at 20 ± 2°C for 90 days. The soils used were as presented in Table 8.1.7.

Table 8.1.7. Soil properties in the laboratory degradation study of clopyralid (Wardrope 2009).

Soil Group	Texture Class USDA*	Origin	pH (water) *	Organic Carbon (%)*
A	sandy loam	Ryton Organic Gardens, Warwickshire, UK.	6.2	2.0
B	clay loam	Chapel Farm, Evesham, Worcs., UK.	7.6	1.7
C	clay loam	Farditch Farm, Chelmorton, Buxton, UK.	5.6	4.1
D	loam	Pas de Calais, France	7.5	2.7

*Determined by CEMAS as a separate GLP study, results are taken from report CEMS-4200

The moisture content of the soils was determined and adjusted to *ca* 42-43% of maximum water holding capacity. The soils were allowed to acclimatize to test conditions for seven days prior to test item application. [^{14}C]-Clopyralid was applied to the soil at a nominal rate of 0.27 µg/g dry weight soil (nominal application rate of 0.2 kg as/ha based on distribution in the top 5 cm soil with bulk density 1.5 g/mL). The application of [^{14}C]-Clopyralid in Milli-Q water (1 mL) adjusted the soils to *ca* 45% of maximum water holding capacity.

The test system consisted of a flow through apparatus where the soils (50 g oven dry weight equivalent) were incubated in Erlenmeyer flasks connected to a series of individual traps containing ethanediol and sodium hydroxide, for the collection of non-specific ^{14}C-volatile organic compounds and $^{14}CO_2$, respectively. Single replicate samples were removed for each soil type at zero time (immediately following application), 1, 3, 7, 14, 21, 30, 60 and 90 days. Trapping solutions were sampled at the time of sample termination and sampled and replenished at 30 day intervals. At each sampling occasion, single samples for each soil type were removed from the incubation apparatus and extracted. Extractions (Day 1-Day 90) were performed by adding a solution of acetonitrile: 2M hydrochloric acid (4: 1 v/v, 100 mL) to each sample, shaking for *ca* 1 hour, followed by centrifugation *(ca* 3500 rpm; *ca* 15 min).

The extract was decanted, the total volume measured and aliquots submitted for liquid scintillation counting (Extract 1). The procedure was repeated twice for soil groups A, B and C (Extracts 2 and 3) and three times for soil group D (Extracts 2, 3 and 4). The extracts for each sample were combined and concentrated to a small volume prior to HPLC analysis. Extractable soil radioactivity was quantified using liquid scintillation counting (LSC). Radioactive components in soil extracts were quantified using reverse-phase HPLC with on-line radiochemical detection. The identity of [^{14}C]-Clopyralid was confirmed by TLC. Non-extractable ^{14}C-residues were quantified using LSC following combustion. The test conditions outlined in the study protocol were maintained throughout the study.

Results:

Material balance, calculated as the percent of applied radioactivity (% AR), was maintained from Day 0-Day 90 as presented in the table below. The amounts of radioactivity in each of the components of the system at Day 90 are also summarized in Table 8.1.8.

Table 8.1.8. The radioactive material balance in the soils.

Soil Group	**Texture Class USDA***	**Extractable at Day 90 (%AR)**	**Non-Extractable at Day 90 (%AR)**	**Evolved $^{14}C0_2$ at Day 90 (%AR)**	**Overall Material Balance Range (%AR)**
A	sandy loam	4.00	22.34	70.27	91.18-103.85
B	clay loam	3.63	28.12	68.55	94.24-101.36
C	clay loam	3.01	23.89	64.94	91.82-105.77
D	loam	4.83	28.14	65.33	94.51-104.49

The amount of [^{14}C]-Clopyralid in soil extracts declined from quantitative levels at Day 0 to values of 4.74%, 4.00%, 1.40% and 3.64% AR, at Day 60, for soil groups A, B, C and D, respectively. Group C soil extractability had dropped to below *ca* 5% AR at Day 60 however, for consistency with the other soil groups, the group C Day 60 soil extracts were analysed by HPLC. At Day 90 the extractability in all soil groups was below 5% AR therefore no HPLC analysis of Day 90 extracts was carried out. One minor polar degradation product was observed in all soil types. This component did not exceed *ca* 3% in any soil type and was observed at one sampling interval in soil groups A and B and two sampling intervals (not consecutive) in soil groups C and D.

The major degradation product in all soil types was $^{14}CO_2$ reaching maximum levels of 70.27% and 68.55% AR in soil groups A and B at Day 90 and 74.31 % and 68.21 % AR in soil groups C and D at Day 60. Non-extractable residues reached maximum values of24.42%, 28.57%, 32.86% and 32.24% AR in soil groups A, B, C and D, respectively and had declined slightly in all soil types by Day 90. The DT_{50} and DT_{90} of Clopyralid were calculated using the simple first-order (SFO) model. The kinetic modelling results are summarized in Table 8.1.9.

Table 8.1.9. Kinetic modelling of laboratory degradation of clopyralid in four soils.

Soil Group	Texture Class (USDA)	DT_{50} (days)	DT_{90} (days)	Chi^2 error	r^2

A	sandy loam	16.6	55.0	4.9	0.99
B	clay loam	23.1	76.7	6.9	0.96
C	clay loam	4.9	16.3	12.9	0.97
D	loam	10.0	33.2	11.3	0.96

Conclusions:

- Based on the results of this study, it is concluded that [^{14}C]-Clopyralid is rapidly mineralised to $^{14}CO_2$ as the majority of the radioactivity was recovered as $^{14}CO_2$. The maximum % AR recovered as $^{14}C_2$ in soil groups A (sandy loam), B (clay loam), C (clay loam) and D (loam) was 70.27%, 68.55%, 74.31 % and 68.21 %, respectively.

- Soil extractability decreased over the course of the study (Day 0-Day 90) to 4.00%, 3.63%, 3.01 % and 4.83% AR in group A, B, C and D soils, respectively.

- Soil extracts were analysed, using HPLC, and contained [^{14}C]-Clopyralid and one minor polar metabolite which did not exceed *ca* 3% in any soil type and was observed at a maximum of two sampling intervals (not consecutive) in soil groups C and D.

- Non-extractable residues accounted for 22.34%, 28.l2%, 23.89% and 28.14% AR in group A, B, C and D soils by Day 90, respectively. The maximum non-extractable residue recovered over the duration of the study was 32.86% AR for the group C soil at Day 21.

- The rate of degradation in soils A-D was calculated on the basis of above results. The best fit endpoints for DT_{50} (50% decline time) of [^{14}C]-Clopyralid, using SFO are shown in Table 8.1.10.

Table 8.1.10. Degradation rate of [^{14}C]-Clopyralid

Soil Group	Soil type	DT_{50} (days)	DT_{90} (days)	Chi^2 error	r^2
A	Sandy loam	16.6	55.0	4.9	0.99
B	Clay loam	23.1	76.7	6.9	0.96
C	Clay loam	4.9	16.3	12.9	0.97
D	loam	10.0	33.2	11.3	0.96

- The study did not consider the degradation at 10 °C, since the degradation rate at different temperatures may be calculated. Neither was the degradation of metabolites considered, as no metabolites were formed.

RMS comments and evaluation:

The study was new and not evaluated before in the context of regulation 1107/2009. The study was well performed according to the test guideline and GLP, clearly reported and of good quality. It is noted that on three occasions slight deviations from the incubation temperature range were observed, but only for short periods of time. It is assessed that this had no detrimental effect on the validity of the study. The results are in line with the earlier studies evaluated during the Annex I inclusion of clopyralid, and thus can be used to add the knowledge on the rate of aerobic degradation of clopyralid in soil, as presented in the kinetic evaluation below. The study is acceptable and the data is adequate for risk assessment, no further data on this endpoint are required.

B.8.1.1.2. Anaerobic degradation in soil

Two supplementary studies considering the anaerobic degradation and photolysis of clopyralid in soil were presented in the dossier for the Approval of Clopyralid submitted in 30 April 2002, evaluated in the DAR (2003) and peer review at EU level. The data were deemed acceptable following evaluation, and are still valid for decision making.

CA 7.1.1.1.2/1 - Clopyralid Technical - Anaerobic degradation in soil

Report	[IIA 7.1.1.1.2/01], Allan, J., Lowrie, C. & Hall, B.E. 2002.
Report title	The Degradation of [^{14}C] clopyralid in soil under anaerobic conditions.
DAS Study number	GHE-P-9563. Ref. K76.
Guidelines	SETAC-Europe Guideline, Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, Part 1, Section 1.2 (1995)
GLP	Yes (certified laboratory)

Methods

The rate and route of anaerobic degradation of [2,6-pyridinyl-^{14}C]-clopyralid was investigated in soil under laboratory conditions at 20°C.

The characterisation of the test soil is summarised in Table 8.1-11. The soil was classified as a sandy clay loam (UK classification) and displayed similar properties to previous batches of the same soil used for other studies i.e. the investigation of aerobic degradation. The soil was sieved (2 mm) and stored at 4°C prior to use. Before dispensing in to the incubation flasks, the moisture content and microbial biomass of the soil was determined. The moisture content was determined by oven drying and the microbial biomass.

Table 8.1-11. Characterisation data for soil used to investigate the anaerobic degradation of clopyralid

Soil name, origin	Marcham, UK
Textural analysis (%)	
Sand (63-2000 µm)	56.5
Silt (2-63 µm)	20.7
Clay (<2 µm)	22.8
Soil textural classification (UK)	Sandy clay loam
pH (H_2O)	7.8
pH (0.1M KCl)	7.2
pH (0.01M $CaCl_2$)	7.4
Organic matter (%)	2.2
Organic carbon (%)	1.3
Cation exchange capacity (CEC, mEq/100 g)	22.5
MHC (% w/w dry soil)	
0.33 bar suction (pF 2.5)	20.2
0.001 bar suction (pF 0)	59.6

Soil samples (100 g dry weight equivalent) were weighed into Erlenmeyer incubation flasks (250 mL) and flooded to create a water layer (3 cm, *ca* 150 g) covering the soil surface. The flooded soil samples were pre-equilibrated, prior to application of the test substance under a nitrogen atmosphere for a period of 47 days in the dark at 18.5-20.8°C. Over the pre-equilibration period the redox potential of a control sample was monitored to ensure anaerobic conditions were established.

Once anaerobic conditions had been established the flooded soil samples were treated with [2,6-pyridinyl-^{14}C]-clopyralid augmented with non-radiolabelled clopyralid at a rate equivalent to a field application of 300 g ai/ha. The test substance was applied to the surface of the water layer in a dropwise fashion in a small volume (100 µL) of water. The samples were then incubated over a period of 120 days under a stream of moist, oxygen-free nitrogen at 20°C in the dark. Evolved volatile components were passed through a set of ethanediol and ethanolamine traps, in series, and over a copper II oxide catalyst to convert any remaining volatile components to CO_2. The trapping solutions were collected, replenished at regular intervals to avoid saturation and quantified by LSC.

At pre-selected intervals (0, 7, 14, 30, 60, 90 and 120 days) single flooded soil samples were taken for analysis. At each sampling interval the redox potential of the removed sample and the control sample was determined to ensure that anaerobic conditions had been maintained. At each sampling interval the surface water was carefully decanted from the soil. The surface water was subjected to analysis by HPLC and TLC without any further processing. The soil layer was extracted by shaking twice with acetonitrile. An additional acidified acetonitrile extraction was performed at the later sampling intervals (i.e. for 60, 90 and 120 days). The levels of radioactivity in the surface water and soil layer extracts were quantified by LSC. The radioactivity remaining in the post extracted soil residue, following air-drying and thorough mixing, was quantified by combustion analysis. The soil layer extracts were concentrated by rotary evaporation prior to analysis by HPLC and TLC.

To recover any residual radioactivity after removal of the surface water and soil, the incubation flasks were soaked with acetone and the washings quantified by LSC.

HPLC analysis was conducted using a reverse phase gradient system with in-line UV and radiodetection. Non-radiolabelled clopyralid was used as authentic reference standard and was admixed with the samples for co-chromatography. TLC analysis was conducted using precoated silica gel plates developed in ethyl acetate:methanol:acetic acid. Non-radiolabelled clopyralid was co-chromatographed under each sample and visualised using UV light (254 nm).

Results

Measurements of the **redox potential** during the pre-equilibration period confirmed that anaerobic conditions had been established prior to treatment of the test substance. Also, the microbial biomass determination of the soil samples confirmed that the soil was viable at the start of the study.

The recovery and distribution of radioactivity from the flooded soil samples is summarised in Table 8.1-12.

The overall **recovery of radioactivity** was between 101% and 106% AR (mean 103% AR) for all samples indicating a complete mass balance. In a preliminary study, the potential for clopyralid to adsorb to glassware was shown to be negligible.

Table 8.1-12. Recovery and distribution of radioactivity from flooded soil samples under anaerobic conditions at 20°C

Sampling interval (days)	Surface water (% AR)	Soil components (% AR)			Apparatus wash (% AR)	Volatile components (% AR)		Mass balance (% AR)
		Extracts	NER	(sub-total)		Polar	CO_2	
0	98.48	3.60	0.90	4.50	0.01	NS	NS	102.99
7	64.64	27.19	9.64	36.83	0.01	0.01	0.03	101.52
14	57.10	33.00	11.08	44.08	0.01	0.02	0.04	101.25
30	61.34	31.23	13.35	44.58	0.05	0.03	0.09	106.09
60	54.21	36.00	10.80	46.80	0.03	0.04	0.15	101.23
90	54.68	35.02	12.18	47.20	0.01	0.03	0.18	102.10
120	54.24	37.05	11.20	48.25	0.03	0.04	0.19	102.75

NS = no sample

Initially, the majority of the radioactivity was recovered from the surface water which contained 98% AR at 0 days. The **partitioning of the radioactivity** between the surface water and soil layers equilibrated over a period of 14 days following treatment. After 14 days, the levels of radioactivity detected in the surface water and soil layers were 57% and 33% AR, respectively. Thereafter, the levels remained reasonably constant over the remainder of the study (120 days) at between 54 and 61% AR for the surface water and between 31% and 37% AR for the soil layer. The level of NER from the soil layer increased to 10% AR after 7 days and, thereafter, remained reasonably consistent between 11% and 13% AR. The level of polar volatile components and CO_2 detected was very low (≤0.04% and ≤0.2% AR, respectively) throughout the entire study.

Analysis of the surface waters and soil extracts by **HPLC** indicated that **minimal degradation occurred** under anaerobic conditions. The chromatographic profile of the water and soil phases, as determined by HPLC analysis is summarised in Table 8.1-13. The surface waters and combined acetonitrile extracts were found to contain exclusively clopyralid. The additional extracts performed using acidified acetonitrile contained clopyralid and a small amount (< 1% AR) of a polar metabolite.

Analysis of the surface waters and soil extracts by **TLC** generally confirmed the results obtained by HPLC. Minor discrepancies between the two analytical methods included firstly some origin bound material detected by TLC in the surface water samples (probably due to either matrix effects and/or problems that can be caused by applying large volumes of aqueous based samples to reverse-phase TLC plates). And secondly, the minor metabolites observed by HPLC in the acidified acetonitrile extracts of the soil layer were not confirmed by TLC. However, these metabolites comprised of < 1% AR is not considered significant.

Table 8.1-13. Profile of radioactivity recovered from flooded soil samples incubated at 20°C under anaerobic conditions

Sampling interval (days)	Phase	Clopyralid (% AR)	Others (% AR)
0	Water	98.48	ND
	Soil	<5.00	ND
	Total	*98.48*	*ND*
7	Water	64.64	ND
	Soil	27.20	ND
	Total	*91.84*	*ND*
14	Water	57.10	ND
	Soil	33.00	ND
	Total	*90.10*	*ND*
30	Water	61.34	ND
	Soil	31.23	ND
	Total	*92.57*	*ND*
60	Water	54.21	ND
	Soil	36.00	ND
	Total	*90.21*	*ND*
90	Water	54.68	ND
	Soil	34.54	0.48
	Total	*89.22*	*0.48*
120	Water	54.24	ND
	Soil	36.14	0.92
	Total	*90.38*	*0.92*

ND = not detected

Degradation of clopyralid under anaerobic conditions was slow, with less than 10% AR having degraded after 120 days. Due to the limited degradation observed, the degradation rate was not calculated, however, it can be estimated that the $DT_{50(lab)}$ for clopyralid under anaerobic conditions was > 1 year.

Comments

The study was new, in compliance with GLP, well performed and reported clearly. Two different analytical methods were used to confirm the identification of the radioactivity in soil extracts. The anaerobic degradation of clopyralid is negligible. The study is acceptable.

RMS comments and evaluation:

The study on the anaerobic degradation of clopyralid was evaluated in the DAR (2003) as presented above and the results were used in the risk assessment presented in the EFSA conclusion on clopyralid (EFSA Scientific Report 2005: 50). The outcomes are still valid and therefore the study is not reviewed here again. No other comments, study is acceptable.

B.8.1.1.3. Photolytic degradation on soil

CA 7.1.1.1.2/2 - Clopyralid Technical - Photolysis in soil

Report	[IIA 7.1.1.1.2/02], Batzer, F.R., Concha, M. & Shepler, K. 1994.
Report title	Photodegradation of [^{14}C] clopyralid in/on soil by natural sunlight.
DAS Study number	GH-C 3496. Ref. K71.
Guidelines	US EPA Pesticide Assessment Guidelines, Subdivision N, Paragraph 161-3 (1982). Apart from minor deviations, the study also considered to meet the requirements of the SETAC-Europe Guideline, Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, Part 1, Section 2 (1995)
GLP	Yes (certified laboratory)

Methods

The route of photodegradation of [2,6-pyridinyl-^{14}C]-clopyralid was investigated on soil under natural summer sunlight conditions (latitude 37.45°N) at *ca* 25°C. The characterisation of the test soil is summarised in Table 8.1-14. The soil was classified as a silt loam (USDA classification). The soil was sieved prior to use. Soil samples (3.1 g dry weight equivalent) were weighed into Petri dishes. Deionised water was added to each to form a slurry and the slurries were allowed to air-dry to form a thin soil layer. The application rate of [2,6-pyridinyl-^{14}C]-clopyralid corresponded to a concentration of 35 mg/kg soil.

Table 8.1-14. Characterisation data for soil used to investigate the photodegradation of clopyralid

Soil name, origin	Calloway, Mississippi, US
Textural analysis (%)	
Sand	6.0
Silt	68.0
Clay	26.0
Soil textural classification (USDA)	Silt loam
pH	6.0
Organic matter (%)	2.62
Cation exchange capacity (CEC, mEq/100 g)	11.92
MHC at 1/3 bar suction (% w/w dry soil)	31.22
Bulk density (g/mL)	1.34

A total of 22 soil dishes were prepared to allow for duplicate samples to be taken at zero-time, and further duplicates at 2, 5, 15, 20 and 30 days after application from both light-exposed and dark control samples. The test apparatus consisted of a stainless steel chamber sealed with either a quartz-glass plate for light-exposed samples, or with a blackened glass plate for the dark controls.

Each chamber was equipped with a circulating jacket through which coolant was passed to maintain a constant temperature of *ca* 25°C. This was monitored at 10-20 minute intervals throughout the study using themocouples attached to the soil surface in both irradiated and dark conditions. Humidified air was drawn through sterile filters into the chamber containing the treated soil samples, and then through an ethylene glycol trap to collect organic volatiles, and through two 10% NaOH traps for evolved $^{14}CO_2$.

The exposure phase was carried out in Richmond, California, US at latitude 37.45°N between 15 June and 15 July, 1994. Sunlight intensity and cumulative energy were recorded at 10-20 minute intervals throughout the study using a radiometer.

Duplicate soil samples were taken from both the exposed and dark control sample sets for analysis at the previously defined timepoints. At these sampling intervals the trapping solutions were also sampled, quantified by LSC analysis and replenished. Soil samples were extracted and analysed by LSC. After extraction, the soil residues were weighed and aliquots taken for combustion analysis to determine the levels of NER. The soil extracts were analysed by HPLC, and additionally representative samples (light-exposed and dark control) at 30 days were also analysed by 2D TLC analysis. The areas of radioactivity were located using a plate scanner to confirm the HPLC results.

Results

The majority of the radioactivity in the **irradiated soil samples**, at all sampling occasions, was extracted from the soil. This initially accounted for *ca* 95% AR and remained at this level throughout the 30 day study. The level of NER reached a maximum of only *ca* 5% AR. The levels of evolved volatile components were low with little radioactivity (≤ 0.5% AR) being detected in the ethylene glycol trap, and only *ca* 3% AR in the sodium hydroxide traps as carbon dioxide after 30 days. Overall, the amount of material recovered ranged from 93.9% to 104.8% AR indicating a mass balance for the irradiated samples. For the **dark controls**, a similar pattern was seen, though less carbon dioxide was formed. Overall the amount of material recovered ranged from 96.1% to 103.4% AR indicating a mass balance for the dark control samples.

For the irradiated soil samples, the levels of clopyralid detected remained approximately constant throughout the study (>89% AR). Several small bands of unidentified radioactivity were also seen in the **HPLC** profile, but these reached up to only *ca* 3% AR in total, with no single component being greater than 1.7% AR. For the dark controls, a similar pattern was again seen, but with smaller amounts of the unidentified radioactivity (1.4% AR or less in total).
The **2D TLC** analysis of the 30 day samples (exposed and dark controls) confirmed the HPLC findings in showing that clopyralid was the only significant component present.

Under exposed conditions, the **half-life of clopyralid** was calculated to be > 12 years using pseudo first-order kinetics ($R^2 = 0.006$). The lack of degradation seen in both the light exposed and dark control samples is reflected in the long half-life and the poor correlation co-efficient for the data set, and therefore this half-life must only be considered as an estimate.

Comments

The study was in complaince with GLP, well performed and reported clearly. The irradiation conditions (latitude) in this study are comparable to Southern Mediterranean area. Two different analytical methods were used to confirm the identification of radioactivity in soil extracts. Photolysis appears not to be a significant route of dissipation of clopyralid in soil, and therefore the latitude has no impact. The study is acceptable.

RMS comments and evaluation:

The study on photolysis of clopyralid on soil was evaluated in the DAR (2003) as presented above and the results were used in the risk assessment presented in the EFSA conclusion on clopyralid (EFSA Scientific Report 2005: 50). The outcomes are still valid and therefore the study is not reviewed here again. No other comments, study is acceptable.

Data to address this point were presented in the dossier submitted in April 2002 for the Active Approval and were deemed acceptable following evaluation and peer review at EU level. These data are still valid for decision making. In addition a complete new photodegradation study was conducted according to the current guidelines, as presented below, and evaluated by the RMS.

CA 7.1.1.1.2/3 - 14C-Clopyralid: Photodegradation on Soil by Xenon lamp

Report	[IIA 7.1.1.1.2/03], Ponte, M. 2014
Report title	^{14}C-Clopyralid: Photodegradation on Soil by Xenon lamp
DAS Study number	PTRL West, Hercules, California, USA; Lab Study No. 2605W; DAS Study No. 140076; 16 December 2014
Guidelines	OECD Draft Document (2002) Phototransformation of Chemicals on Soil Surfaces; US EPA OCSPP 835.2410, OPPTS 835.2410
GLP	Yes

Materials and methods

The photodegradation of ^{14}C-clopyralid was studied in one sandy loam soil (62 % sand, 23 % silt, 15 % clay, org. C 2,1 % and pH of 5.4) originating from Greene county, Iowa, USA under continuous radiation of a Xenon lamp with light intensity of 374 W m^{-2} and spectral distribution comparable to natural sunlight at 37.45 °N latitude for 16 days. The soil was maintained at 75% field moisture capacity (FMC) at 1/3 bar and at the temperature of 20 ± 2 °C.

Soil samples were extracted at 0, 1, 3, 7, 11, and 16 DAT and the soil extracts were radioassayed and chromatographed on the day of collection. Volatiles traps were measured (volume) and radioassayed on the day of sampling. Aliquots of the extracted soil samples were combusted to determine level of unextracted residues.

The entire soil sample was extracted with 10 mL of acetone/2N H_2SO_4 (20/4, v/v). The soil extract was used to aid the transfer of soil from the sample dish to the centrifuge tubes. The samples were shaken on a Wrist-Action shaker for 30 minutes followed by centrifugation for 5 minutes at 4,000 rpm. The extracts were decanted and the extraction procedure was repeated twice with 10 mL extraction solvent each time. All three extracts were combined and measured before taking the aliquots (3 x 200 µL) for radioassay by LSC. Aliquots of the extracts were evaporated under nitrogen to remove acetone, then diluted with an aliquot of acetonitrile and microfuged. The volumes of the resulting concentrates were measured and aliquots taken for LSC radioassay for concentration efficiency determination prior to HPLC analysis.

Following decant of final extract, the centrifuge tubes (with caps) were weighed and recorded on the sampling worksheet to determine post-extracted soil (PES) weight and aliquots were combusted to determine the levels of unextracted radiocarbon. Approximately 4 x 0.2-g sub-samples of each extracted residue pellet were weighed and combusted using a Harvey biological oxidizer. The generated $^{14}CO_2$ was then collected in Harvey scintillation cocktail and assayed by LSC.

All radioassays of extracts and solutions utilized 5 mL or 15 mL of Safety Solve scintillation cocktail (Research Products International Corp.) in 7 mL or 20 mL standard polyurethane counting vials and Beckman LS 5000 CE or LS 6000 IC liquid scintillation spectrometers. Computer-constructed quenched curves, derived from a series of ten sealed quenched standards, automatically converted cpm to dpm. Typical parameters are as follows: counting efficiency, 96%; background, 35 DPM; counting time, 1 to 5 minutes.

The efficiency of the oxidizer was determined daily, beginning with spiking vials of Harvey scintillation cocktail with a known volume of a ^{14}C standard (vial spikes). Aliquots of the same standard were then spiked into cellulose and combusted. Each day, two cellulose spikes were combusted on each oxidizer and compared to two vial spikes prior to combustion of samples. The daily efficiency for each oxidizer was calculated by taking the average of the cellulose spike results

and dividing it by the average of the results of the two direct spikes. Acceptable oxidizer recoveries were between 90 and 110%.

High performance liquid chromatography (HPLC) analyses of all sample extracts were accomplished for quantitation using a Capcell C-18 column (250 x 4.6 mm i.d., 5.0 μm; 1.0 mL/min; UV detection at 254 nm) and a linear gradient with 1% trifluoroacetic acid in water and acetonitrile.

The % AR represented by 10 dpm above background (20 dpm) and 40 dpm (2X background) for each sample phase (caustic layer, room temperature organic extract, and combustions) were calculated as presented in Table 8.1.15.

Table 8.1.15. The detection limits (LOD, LOQ) for clopyralid for each sample phase.

Matrix	LOD (%AR)	LOD (dpm)	LOQ (%AR)	LOQ (dpm)
Caustic trap	0.0009	30	0.001	40
Extract	0.0009	30	0.001	40
HPLC	0.4	129	0.8	258

Soil samples were extracted and analyzed for radioactivity activity by LSC the same day of sacrifice. HPLC analyses of soil extracts were conducted within 1 day of sampling; therefore, determination of storage stability was unnecessary.

Results

Dark control samples were maintained in the dark at 20 °C in a constant temperature chamber for up to 16 days after treatment. Irradiated samples were maintained at a constant temperature of 20 °C by submerging the soil dishes in a water bath maintained at this temperature via a circulating bath. The sample moistures were measured gravimetrically throughout the study to determine the need for soil moisture adjustment. The soil moisture was monitored and adjusted over the course of the study as needed.

The mass balance of total radiocarbon recovery was 100.9 ± 2.8% and 101.3 ± 1.8% of the applied amount in the dark and in the irradiated samples, respectively, as presented in Table 8.1.16.

Table 8.1.16. Phototransformation of Clopyralid, expressed as percentage of the applied radioactivity (mean ± std dev.) on soil

Compound		Sampling times (days)					
		0	t1	t2	t3	t4	t5
Parent compound	irradiated	100.1	100.3	101.0	94.3	99.7	96.2
	dark	100.1	100.4	97.6	96.3	102.2	100.5
Total extractable residues	irradiated	100.1	100.3	101.0	94.3	99.7	96.2
	dark	100.1	100.4	97.6	96.3	102.2	100.5
Non-extractable residues	irradiated	0.5	0.8	0.8	2.8	1.7	4.3
	dark	0.5	0.5	0.7	1.3	1.5	1.6
CO_2	irradiated	0.0	0.0	0.2	0.5	1.3	2.1
	dark	0.0	0.0	0.1	0.2	0.7	1.4
Volatile organics*	irradiated	0.0	0.0	0.0	0.6	0.2	0.3
	dark	0.0	0.0	0.0	0.0	0.0	0.0
Total % recovery	irradiated	100.6	101.1	102.0	98.2	102.8	102.9
	dark	100.6	100.9	98.4	97.7	104.3	103.5

At test termination, 96.2% and 100.5% of the applied radioactivity remained as the parent in the light and dark samples, respectively. At study termination, the evolved CO_2 in the irradiated and dark samples amounted to 2.1% and 1.4% of the applied amount, respectively.

Extractable [^{14}C]-residues were >96% of applied dose in irradiated and dark control samples throughout the study. Bound residues represented an average of 4.3% in irradiated samples and 1.6% in dark samples at test termination.

The degradation rates of Clopyralid for the dark and the irradiated soil samples, using single first-order kinetics are presented in Table 8.1.17.

Table 8.1.17. Degradation rate of clopyralid in the photolysis study

Compound	Degradation rate (DAT^{-1})	Equation	R^2
clopyralid			
Dark	7.54E-10	$\frac{d(parent)}{dt} = -k[parent]$	0.1377
Irradiated (total)	0.002498	$\frac{d(parent)}{dt} = -k[parent]$	0.2981
Photolysis	0.002498	$k_{photolysis} = k_{total}$	

[a] where $\frac{d(parent)}{dt} = -k_{[parent]}$

[b] where $\frac{d(parent)}{dt} = -k_{[parent]}$

[c] where $k_{photolysis} = k_{total}$ or $k_{photolysis} = k_{total} - k_{dark\backslash}$

Conclusions

- No significant photodegradation was observed in a sandy loam soil exposed to light using Xenon lamp as a light source or dark control samples throughout the study period. Unextracted residues represented <5% of the applied dose in all samples and radiocarbon.

- The expected half-life and the DT_{90} values for clopyralid soil photolysis at 40° N latitude in the summer sun were 553 and 2040 days, respectively. Clopyralid did not degrade in the dark control samples either. The degradation rate constant for clopyralid in dark control samples was 7.54 $x10^{-10}$ $days^{-1}$.

RMS comments and evaluation:

The new study on photolysis of clopyralid on soil was not evaluated before in the context of regulation 1107/2009. The study was well performed according to the test guideline and GLP, clearly reported and of good quality.

The study design deviated slightly from the SETAC Europe guidelines. The SETAC guidelines suggest an air-dried soil be irradiated or incubated at 20 ± 3 ºC. The EPA guidelines suggest the soil be maintained at 75% of 1/3 bar and an experimental temperature between 18 and 30 ºC. The experimental design for this study maintained the soil at 75% of 1/3 bar with an experimental temperature of 20 ºC. It is noted that on three occasions slight deviations from the incubation temperature range were observed, but only for short periods of time, and the deviations were well reported. It is assessed that this had no detrimental effect on the validity of the study.

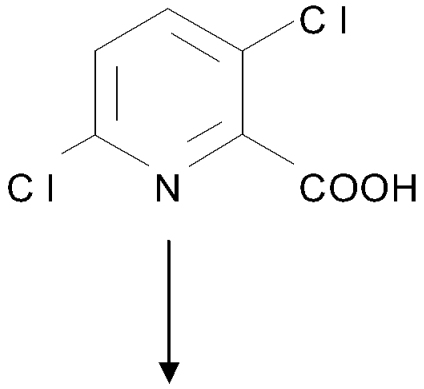
The results are in line with the earlier studies evaluated during the Annex I inclusion of clopyralid and confirming the conclusion that photolysis is not a significant route of degradation of clopyralid in soil.

The study is acceptable and the data is adequate for the risk assessment. Data requirement is fulfilled and no further data on this endpoint are required.

Overall conclusions on the route of degradation of clopyralid in soil:

- Clopyralid is readily degraded in soil under aerobic conditions. No metabolites, other than CO_2, were detected. The levels of CO_2 steadily increased to a maximum of ca 80 % AR indicating that ultimately clopyralid is completely mineralised. NER levels reached up to 35 % AR and subsequently declined in most soils. At lower application rates clopyralid is degraded more rapidly. At low moisture contents no significant degradation was observed, indicating that the route of degradation was largely microbial.
- Some minor, unidentified metabolites were observed in an aerobic study using a US soil and conditions, but the levels did not exceed 7.7 % AR.
- Degradation of clopyralid under (flooded) anaerobic conditions was not as extensive as under aerobic conditions. By the end of the study the applied radioactivity was evenly distributed between the soil and water phases. Minimal degradation was observed and no significant metabolites were detected. NER levels reached up to 13.4 % AR. No volatile components were evolved. (<0.2 % AR total).
- In two soil photolysis studies, little or no degradation of clopyralid occurred on soil under natural summer sunlight at latitude 37.45 ºN at ca 25ºC and 20 ºC, and only very minor degradation products, including CO_2, were formed. Therefore, soil photolysis is not a significant route of degradation for clopyralid.
- Based on these findings, the route of degradation of clopyralid in soil is proposed in Figure 8.1.

Figure 8.1. Route of the degradation of clopyralid in soil



Incorporation into humin soil fraction (NER)
and/or
Mineralisation to CO_2

B.8.1.1.4. Laboratory studies on the rate of degradation in soil

The rate of degradation of clopyralid in soil under aerobic conditions was determined from studies Baloch & Grant (1991, K45) and Skinner & al. (1995, K64) using radiolabelled test substance which were also used to investigate the route of degradation described under chapter 8.1.1.1. The DT_{50} and DT_{90} calculations were presented in the dossier for the Approval of Clopyralid submitted in 30 April 2002, evaluated in the DAR (2003) and peer review at EU level. The data were deemed acceptable following evaluation, and are still valid for decision making.

Recently, a new study (Wardrope, L. 2009) was added to the AIR3 dossier of clopyralid. This study was evaluated as presented above, and the results of all three studies were used in a new kinetic evaluation of the laboratory degradation rate of clopyralid in soil (Schubert 2015). As a summary of the laboratory studies available, following overview conclusions can be made on the degradation properties of clopyralid.

- Clopyralid was readily degraded in soil under aerobic conditions according to first-order kinetics.
- The $DT_{50(lab)}$ values for earlier evaluated EU soils (20 °C, 40 % MHC) ranged from 16 to 65 days (mean 38 days), whilst at 10 °C and 40 % MHC, the $DT_{50(lab)}$ values were 73 to 198 days (mean 124 days). In addition, the $DT_{50(lab)}$ value for a US soil (25 °C, 75% of 1/3 bar MHC) was 9 days, which confirmed that degradation readily occurs in soil.
- Clopyralid degraded more rapidly at lower treatment rates and higher moisture contents.
- Since the maximum $DT_{50(lab)}$ under standard conditions exceeded 60 days at 20 °C, this triggered the need for soil dissipation studies under field conditions (see Point IIA, 7.1.1.2.2).
- No major aerobic degradation products >10 % AR, other than CO_2, are observed (see Point IIA, 7.1.1.1.1). Therefore, rate of degradation data for any metabolites is not required and has not been determined.
- Clopyralid was not significantly degraded under either anaerobic conditions (first oder $DT_{50(lab)}$ > 1 year) or photodegraded in soil (first-order half-life > 12 years). These potential degradation routes are much slower than under aerobic conditions.

The kinetic calculation on the degradation behaviour of clopyralid in soil under laboratory conditions was performed on the results from the studies of Baloch and Grant (1991; CA 7.1.1.1/1), Skinner et al. (1995; CA 7.1.1.1/2), and Wardrope (2009; CA 7.1.1.1/3). The goal of the kinetic evaluation is to derive persistence and modelling endpoints according to FOCUS (2006).

CA 7.1.2.1.1/4 – Kinetic evaluation of aerobic soil degradation studies with clopyralid

Report	[IIA 7.1.2.1.1/04], Schubert, S. 2015
Report title	Evaluation of kinetic endpoints for clopyralid from laboratory soil degradation studies.
DAS Study number	151039; 27 July 2015
Guidelines	FOCUS (2006). Guidance document on estimating persistence and degradation kinetics from environmental fate studies on pesticides in EU registration. Version 2.0.
GLP	None

Materials and methods

Data: Standard procedures recommended by FOCUS (2006) were followed in this report. The initial pesticide concentration was set to the value of the total mass balance at this time point. With the exception of soil D of Wardrope (2009) the only component being added to the initial pesticide concentration was the "Non extractable residue" fraction. Soil D of Wardrope (2009) exhibits a small percentage of an unknown polar fraction at time zero (1.73% of applied radioactivity). This percentage was added to the initial parent concentration. Data as used in the kinetic evaluation are shown in Tables 8.1.18 - 8.1.20 below.

Normalisation to standard conditions: If necessary modelling endpoints derived from the kinetic evaluation were normalised to standard temperature (20°C) and/or to soil moisture content at field capacity (pF2). Normalisation procedure followed FOCUS groundwater guidance (FOCUS, 2014).

Software: The evaluation was conducted using the software package CAKE version 3.1.

Table 8.1.18. Data of Baloch and Grant (1991) as used in the kinetic evaluation

Parabraunerde		**Marcham**		**Castle Rising**		**Speyer 2.1**		**Speyer 2.2**	
DAT	Clopyralid (% AR)	DAT	Clopyralid (% AR)	DAT	Clopyralid (% AR)	DAT	Clopyralid (% AR)	DAT	Clopyralid (% AR)
0	0	0	102.68	0	105.48	0	105.71		
0	0	1	98.15	1	96.44	1	95.26	0	100.7
1	101.1	3	100.03	3	98.55	3	103.64	1	95.38
1	100	7	91.33	7	71.46	7	96.33	3	86.14
3	104.2	14	82.49	14	76.6	14	94.96	7	77.57
3	102.2	28	62.72	28	49.39	28	80.06	14	52.49
7	98.55	92	8.68	92	7.11	92	32.51	28	28.1
7	98.62	184	5.29	184	4.14	184	14.72	92	13.59
14	93.82	275	4.53	275	2.87	275	9.95	184	9.76
14	93.11	374	3.72	374	2.27	374	6.56		
28	73.55								
28	80.06								
92	14.97								
92	15.11								
184	11.41								
184	5.4								
275	4.26								
275	3.99								
374	2.97								
374	3.27								

Table 8.1.19. Data of Skinner et al. (1995) as used in the kinetic evaluation

Mississippi	
DAT	Clopyralid (% AR)
0	102.3
0	100.9
1	94.6
1	93.8
3	83.5
3	82.8
7	65.4
7	68.5
14	28.5
14	36.2
21	8.3
21	21.3
28	1.2
28	16.1
43	0.3
43	0.4
59	0.3
59	0.4
78	0.2
78	0.3

Table 8.1.20. Data of Wardrope (2009) as used in the kinetic evaluation

Soil A		Soil B		Soil C		Soil D	
DAT	Clopyralid (% AR)	DAT	Clopyralid (% AR)	DAT	Clopyralid (% AR)	DAT	Clopyralid (% AR)
0	93.16	0	95.69	0	92.32	0	94.51
1	94.42	1	99.6	1	93.3	1	100.51
3	84.72	3	96.26	3	75.57	3	87.65
7	68.29	7	86.92	7	29.83	7	59.81
14	61.19	14	73.12	14	8.81	14	48.52
21	37.63	21	56.23	21	7.01	21	13.04
30	25.55	30	44.73	30	6.82	30	8.23
60	4.74	60	4	60	1.4	60	3.64

Results and discussion

Evaluation for persistence endpoints: Both models, SFO and FOMC, produced visually acceptable fits for each soil. With the exception of soil Speyer 2.2 SFO yields a lower Chi^2 error. However, the FOMC model shows a negative lower boundary of the 95th percentile confidence interval for parameter beta. A negative value is outside the acceptable range for this parameter. Therefore, the fit is not acceptable. All SFO fits show robust estimates for model and parameters. Therefore, SFO is selected as the appropriate model for the evaluation of persistence for each soil.

Evaluation for modelling endpoints: SFO yield robust and visually acceptable fits for each soil. Therefore, SFO is selected as the appropriate model for deriving modelling endpoints.

Table 8.1.21. Clopyralid laboratory soil data against SFO kinetic model

				Estimated model parameters		Model statistics		Lower boundary 95th percentile confidence interval		Upper boundary 95th percentile confidence interval	
Study	**Soil**	**DT 50**	**DT90**	**Parent_0**	**k_parent**	**Chi2**	**r2**	**Parent_0**	**k_parent**	**Parent_0**	**k_parent**
Baloch and Grant (1991)	Parabraunerde	44.4	147.3	108.4	0.01563	6.796	0.9855	104	0.01295	112.813	0.018
	Marcham	34.5	114.7	104.4	0.02007	5.478	0.9925	98.91	0.01571	109.793	0.024
	Castle Rising	26.3	87.3	101.5	0.02637	8.284	0.9844	93.51	0.01812	109.501	0.035
	Speyer 2.1	64.6	214.6	104.4	0.01073	5.466	0.9892	98.88	0.008424	109.836	0.013
	Speyer 2.2	16.2	53.8	99.87	0.04281	7.78	0.9887	89.74	0.02791	110.006	0.058
Skinner et al. (1995)	Mississippi	8.6	28.5	95.96	0.0807	6.49	0.9842	98.97	0.07059	109.1	0.091
Wardrope (2009)	A	16.5	54.8	104	0.04198	4.856	0.9871	89.72	0.03421	102.19	0.05
	B	23.0	76.4	103.2	0.03016	6.767	0.9674	93.41	0.02127	112.971	0.039
	C	4.9	16.2	100.7	0.142	12.73	0.973	86.89	0.09017	114.433	0.194
	D	9.8	32.4	102.6	0.07101	10.17	0.9689	89.95	0.04785	115.222	0.094

Table 8.1.22. Clopyralid laboratory soil data against FOMC kinetic model

				Estimated model parameters			Model statistics		Lower boundary 95th percentile confidence interval			Upper boundary 95th percentile confidence interval		
Study	**Soil**	**DT50**	**DT90**	**Parent_0**	**alpha**	**beta**	**Chi2**	**r2**	**Parent_0**	**alpha**	**beta**	**Parent_0**	**alpha**	**beta**
Baloch and Grant (1991)	Parabraunerde	29.2	97.5	113.671	167.945	7061.087	7.164	0.9853	106.395			120.9		
	Marcham	24.9	83.4	108.783	77.677	2772.201	5.753	0.9925	103.221			114.3		
	Castle Rising	25.9	91.6	101.8154	13.3625	487.2213	8.682	0.9841	92.3482	-122.6328	-4679.28	111.3	149.4	5653.7
	Speyer 2.1	62.2	230.7	104.9127	7.4981	641.7989	5.578	0.9891	98.3891	-22.333	-2160.92	111.44	37.33	3444.52
	Speyer 2.2	15.3	105.7	102.1022	1.29792	21.59976	5.506	0.9886	93.02638	0.04782	-9.15598	111.178	2.548	52.356
Skinner et al. (1995)	Mississippi	6.7	22.3	109.076	633.62	6110.857	6.84	0.9864	101.7			116.5		
Wardrope (2009)	A	14.1	46.9	98.965	205.114	4149.568	5.202	0.987	89.34			108.6		
	B	17.7	59.3	108.1	94.17	2395	7.217	0.9674	76.76	-17820		139.4	18006.9	
	C	3.7	12.4	105.825	1264.28	6808.419	13.58	0.973	86.039	-1577.219	-12746.7	125.6	4105.8	26363.5
	D	8.0	26.5	106.615	1157.71	13321.55	10.85	0.9689	89.495	670.607	9786.15	123.7	1644.8	16856.9

Normalisation of modelling endpoints to standard conditions

Table 8.1.23. Normalisation of modelling endpoints

Study		Soil	Texture (ADAS)	Actual SFO-DT_{50}	Study temp. (°C)	Study moisture content (% w/w)	Gravimetric water content at pF2 (% w/w) [d]	Temperature correction factor	Moisture correction factor [e]	SFO-DT_{50} at 20°C/pF2
Baloch and Grant (1991)		Parabraun-erde	silt loam	44.4	20	18.63[a]	27	1	0.77	34.2
		Marcham	sandy clay loam	34.5	20	20.19 [a]	22	1	0.94	32.4
		Castle Rising	sandy loam	26.3	20	65.13 [a]	19	1	1	26.3
		Speyer 2.1	sand	64.6	20	12.58 [a]	12	1	1	64.6
		Speyer 2.2	sand	16.2	20	18.56 [a]	12	1	1	16.2
Skinner et al. (1995)		Mississippi	silty clay loam	8.6	25	23.42 [b]	30	1.61	0.84	11.6
Wardrope (2009)		A	sandy loam	16.5	20	24.28 [c]	19	1	1	16.5
		B	clay	23.0	20	28.05 [c]	48	1	0.69	15.9
		C	clay loam	4.9	20	48.17 [c]	28	1	1	4.9
		D	clay loam	9.8	20	35.30 [c]	28	1	1	9.8
									Geomean:	**18.4**

[a] Reported soil moisture: 40% of maximum WHC

[b] Reported soil moisture: 75% of 1/3 bar WHC

[c] Reported soil moisture: 45% WHC

[d] FOCUS default for soil texture (ADAS)

[e] = (study moisture / gravimetric moisture at pF2)$^{0.7}$

Conclusion

The available data on clopyralid laboratory soil degradation was evaluated for persistence and modelling endpoints according to FOCUS (2006). SFO was the appropriate model for all soils. The degradation endpoints are summarized in Table 8.1.24. below.

Table 8.1.24. Summary of clopyralid persistence and modelling soil degradation endpoints

Study	Soil	Kinetic model	Actual DT50 (days)	Actual DT90 (days)	DT50 at 20°C/pF2 (days)
Baloch and Grant (1991)	Parabraunerde	SFO	44.4	147.3	34.2
	Marcham	SFO	34.5	114.7	32.4
	Castle Rising	SFO	26.3	87.3	26.3
	Speyer 2.1	SFO	64.6	214.6	64.6
	Speyer 2.2	SFO	16.2	53.8	16.2
Skinner et al. (1995)	Mississippi	SFO	8.6	28.5	11.6
Wardrope (2009)	A	SFO	16.5	54.8	16.5
	B	SFO	23.0	76.4	15.9
	C	SFO	4.9	16.2	4.9
	D	SFO	9.8	32.4	9.8
		Maximum:	**64.6**	**Geomean:**	**18.4**

RMS comments and evaluation:

The kinetic calculation of the soil degradation endpoints of clopyralid presented by the Notifier was assessed. The DT_{50} and DT_{90} values were derived from three different studies on ten soils with an adequate variety of properties. The studies are acceptable and all individual values are valid, thus allowing an appropriate risk assessment. The kinetic calculation was performed according to FOCUS guidance, and the outcomes as summarized above are considered acceptable. Single First-Order kinetics appears to appropriately describe the degradation of clopyralid in soils. The data is adequate for the renewal for the approval of clopyralid, and no further data are required.

B.8.1.1.5. Field studies on the rate of degradation in soil

The rate of aerobic degradation of clopyralid in soil has been determined in laboratory studies as presented above. The actual $DT_{50(lab)}$ values were in the range of 5 to 65 days and the $DT_{90(lab)}$ values from 16 to 215 days in ten soils. Since the $DT_{50(lab)}$ value was > 60 days, five soil dissipation trials in Northern Europe (including one in the Nordic region) have been carried out to represent a worst-case for dissipation. The field dissipation reports of clopyralid in soil were presented in the dossier for the Approval of Clopyralid submitted in 30 April 2002. Two trials were conducted in spring (in the UK and DK) and three of the trials were applied in the autumn (two in Northern France and one in Germany). All studies are considered valid for assessing kinetics in the field as they provide a range of conditions likely to result in a rigorous assessment. The trials were conducted using an aqueous formulation of clopyralid as the monoethanolamine salt (LONTREL 100) containing 100 g a.s./L, with a nominal application rate of 125-300 g a.s./ha made to bare soil.

The method of calculation of the $DT_{50(field)}$ and $DT_{90(field)}$ values for clopyralid from these trials was explained in the original DAR of clopyralid, and evaluated and peer reviewed at EU level. The data were deemed acceptable following evaluation, and are still valid for decision making. Therefore the details of the studies of Rawle & Yon (2002a-b) are only briefly presented here again.

CA 7.1.1.2.2/1 - Clopyralid Technical - Field dissipation in soil

Report	[IIA 7.1.1.2.2/01], Rawle, N.W. & Yon, D. 2002a.
Report title	The Dissipation of clopyralid in soil following a single application of Lontrel (EF-1136), Denmark and UK - 2000.
DAS Study number	GHE-P-9370. Ref. K81.
Guidelines	BBA Part IV, 4-1 (1986), Part V (1993). SETAC-Europe Guideline, Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, Part 1, Section 3.1 (1995)
GLP	Yes (certified laboratory)

CA 7.1.1.2.2/2 - Clopyralid Technical - Field dissipation in soil

Report	[IIA 7.1.1.2.2/02], Rawle, N.W. & Yon, D. 2002b.
Report title	The Degradation of [^{14}C] clopyralid in soil under anaerobic conditions.
DAS Study number	GHE-P-9371. Ref. K82.
Guidelines	BBA Part IV, 4-1 (1986), Part V (1993). SETAC-Europe Guideline, Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, Part 1, Section 3.1 (1995)
GLP	Yes (certified laboratory)

Methods

The trials were conducted using an aqueous formulation of clopyralid as the monoethanolamine salt (LONTREL 100) containing 100 g as/L, with a nominal application rate of 125-300 g as/ha made to bare soil. The applications were made either in spring (UK, Denmark) or in autumn (France, Germany). The characteristics of the soils (0-10 cm layer) used in these trials are summarised in Table 8.1-25.

Table 8.1-25. Characterisation data for soils used in EU field dissipation trials (0-10 cm depth)

Location	Sand (%)	Silt (%)	Clay (%)	Classification (ADAS)	pH (water)	Organic carbon (%)	CEC (mEq/100g)	Ref.
Spalding, UK	23.79	56.56	19.65	Clay loam	7.8	1.1	11.3	K81
Middlefart, Denmark	53.30	27.26	19.44	Sandy clay loam	7.5	1.7	16.1	K81
Ansonville, N. France	5.94	64.78	29.28	Silty clay loam	8.2	1.5	22.8	K82
Mainbervilliers, N. France	32.74	43.19	24.07	Clay loam	7.1	1.1	18.9	K82
Oederquart, Germany	18.88	53.33	27.80	Silty clay loam	7.5	1.7	15.8	K82

UK – Spalding

Clopyralid, formulated as LONTREL (EF-1136), was applied to a bare soil plot (3 m x 41.5 m) at an agricultural site at Spalding, Lincolnshire, UK, on 16 May 2000 at a rate of 304 g as/ha. The soil was classified as a clay loam. Soil cores (5 cm i.d.) were collected to a depth of 30 cm at regular intervals. Twenty cores were taken at each timepoint and these were divided into 0-10 and 10-20 cm horizons. The twenty samples from each respective horizon were combined for analysis, and any soil below 20 cm depth was discarded. A sub-sample from each composited horizon was then analysed for residues of clopyralid. The method had a lowest validated level (LVL) of 0.0005 mg/kg. All residues equivalent to <20% of the LVL (i.e. <0.0001 mg/kg) are classified as not detected (ND).

Denmark – Middlefart
Clopyralid, formulated as LONTREL (EF-1136), was applied to a bare soil plot (3 m x 66 m) at an agricultural site at Rojleskovvej 18, 5500 Middlefart, Denmark, on 11 May 2000 at a rate of 300 g as/ha. The soil was classified as a sandy clay loam. Soil cores were collected, processed and analysed as for Spalding.

Northern France – Ansonville
Clopyralid, formulated as LONTREL (EF-1136), was applied to a bare soil plot (3 m x 41.5 m) at an agricultural site at Ansonville, Loiret, 38, Northern France on 10 November 2000 at a rate of 128-130 g as/ha. The soil was classified as a silty clay loam. Soil cores were collected, processed and analysed as for Spalding.

Northern France – Mainbervilliers
Clopyralid, formulated as LONTREL (EF-1136), was applied to a bare soil plot (3 m x 41.5 m) at an agricultural site at Mainbervilliers, Seine-et-Marne, 77, Northern France on 14 November 2000 at a rate of 125-127 g as/ha. The soil was classified as a clay loam. Soil cores were collected, processed and analysed as for Spalding.

Germany – Oederquart
Clopyralid, formulated as LONTREL (EF-1136), was applied to a bare soil plot (6 m x 33 m) at an agricultural site at Oederquart, 21734 Lower Saxonia, Germany on 29 September 2000 at a rate of 123 g as/ha. The soil was classified as a silty clay loam. Soil cores were collected, processed and analysed as for Spalding.

The $DT_{50(field)}$ and $DT_{90(field)}$ values for clopyralid from these trials were calculated by the Notifier using non-linear regression and the Solver function in a Microsoft Excel spreadsheet to find the best fit between the observed experimental data and the first order rate equation, as below:

$$C_T = C_0 \times \exp^{-KT}$$

The line of best fit was determined by minimising the sum of the squares of the residuals between the actual concentrations and the best fit line. This was achieved using the Solver function to change the values of C_0 and K and converge on a minimum value for the sum of the squares of the residuals. The rate constant, K, was then used to determine the DT_{50} (from LN(2)/K) and DT_{90} (from LN(10)/K) values. The calculations were described only in the Documents MII and MIII of the dossier. In the original study reports no DT_{50} values were presented.

Results

The measured concentrations of clopyralid in soils at five locations are presented in Tables 8.1-26 to 8.1-30.

Table 8.1-26. Clopyralid concentrations in the top 20 cm of soil following spring application of LONTREL (EF-1136) – Spalding, UK – 2000 (Ref. K81)

Sampling time (days after appn.)	Clopyralid concentration (mg/kg dry weight)		
	0-10 cm	10-20 cm	Mean 0-20 cm*
Pre-appn.	<0.0005	<0.0005	<0.0005
0	0.2859	0.0009	0.1434
3	0.1061	<0.0005	0.0532
7	0.1084	<0.0005	0.0543
15	0.0855	0.0337	0.0596
29	0.0304	0.0030	0.0167
62	0.0071	<0.0005	0.0037

- For residues <0.0005 mg/kg, a value of 0.00025 mg/kg was used for the calculation of the mean residue

Table 8.1-27. Clopyralid concentrations in the top 20 cm of soil following spring application of LONTREL (EF-1136) – Middlefart, Denmark – 2000 (Ref. K81)

Sampling time (days after appn.)	Clopyralid concentration (mg/kg dry weight)		
	0-10 cm	10-20 cm	Mean 0-20 cm*
Pre-appn.	<0.0005	<0.0005	<0.0005
0	0.1900	<0.0005	0.0951
4	0.1485	<0.0005	0.0744
7	0.1682	<0.0005	0.0842
14	0.1563	0.0021	0.0792
28	0.0790	0.0012	0.0401
61	0.0132	<0.0005	0.0067
124	0.0027	<0.0005	0.0015
183	0.0007	<0.0005	0.0005

** For residues <0.0005 mg/kg, a value of 0.00025 mg/kg was used for the calculation of the mean residue*

Table 8.1-28. Clopyralid concentrations in the top 20 cm of soil following autumn application of LONTREL (EF-1136) – Ansonville, Northern France - 2000 (Ref. K82)

Sampling time (days after appn.)	Clopyralid concentration (mg/kg dry weight)		
	0-10 cm	10-20 cm	Mean 0-20 cm*
Pre-appn.	<0.0005	<0.0005	<0.0005
0	0.2090	<0.0005	0.1046
3	0.0498	0.0032	0.0265
7	0.0379	0.0036	0.0208
14	0.0063	0.0074	0.0069
28	0.0011	0.0011	0.0011
56	<0.0005	<0.0005	<0.0005
122	<0.0005	<0.0005	<0.0005
177	<0.0005	<0.0005	<0.0005

- *For residues <0.0005 mg/kg, a value of 0.00025 mg/kg was used for the calculation of the mean residue*

Table 8.1-29. Clopyralid concentrations in the top 20 cm of soil following autumn application of LONTREL (EF-1136) – Mainbervilliers, Northern France - 2000 (Ref. K82)

Sampling time (days after appn.)	Clopyralid concentration (mg/kg dry weight)		
	0-10 cm	10-20 cm	Mean 0-20 cm*
Pre-appn.	<0.0005	<0.0005	<0.0005
0	0.0983	0.0010	0.0497
3	0.0570	0.0016	0.0293
7	0.0476	0.0041	0.0259
14	0.0227	0.0046	0.0137
28	0.0052	0.0018	0.0035
56	0.0011	<0.0005	0.0007
122	<0.0005	<0.0005	<0.0005
177	<0.0005	<0.0005	<0.0005

** For residues <0.0005 mg/kg, a value of 0.00025 mg/kg was used for the calculation of the mean residue*

Table 8.1-30. Clopyralid concentrations in the top 20 cm of soil following autumn application of LONTREL (EF-1136) – Oederquart, Germany - 2000 (Ref. K82)

Sampling time (days after appn.)	Clopyralid concentration (mg/kg dry weight)		
	0-10 cm	10-20 cm	Mean 0-20 cm*
Pre-appn.	<0.0005	<0.0005	<0.0005
0	0.0785	<0.0005	0.0394
3	0.0536	<0.0005	0.0269
7	0.0613	<0.0005	0.0308
14	0.0433	0.0020	0.0227
27	0.0188	0.0014	0.0101
59	0.0020	0.0022	0.0021
119	0.0012	0.0006	0.0009

** For residues <0.0005 mg/kg, a value of 0.00025 mg/kg was used for the calculation of the mean residue*

The **$DT_{50(field)}$ and $DT_{90(field)}$ values** of clopyralid at five locations in Europe, calculated by the Notifier on the basis of these results are presented in Table 8.1-31.

Table 8.1-31. $DT_{50(field)}$ and $DT_{90(field)}$ values for clopyralid from dissipation trials

Location, Application date	Clopyralid			Ref.
	R^2	$DT_{50(field)}$ (days)	$DT_{90(field)}$ (days)	
Spalding, UK	0.715	8	28	K81
Middlefart, Denmark	0.953	24	79	K81
Ansonville, N. France (10 Nov 00)	0.968	2	6	K82
Mainbervilliers, N. France (14 Nov 00)	0.976	7	24	K82
Oederquart, Germany (29 Sep 00)	0.954	16	54	K82
	Mean	*11*	*38*	

The **correlation coefficient** (R^2) values indicate that the dissipation data in five locations fitted well to first-order kinetics in four locations of the five studied. The only exception was Spalding, UK, where a lower correlation coefficient was found.

Comments

The field and analytical parts of the studies were well performed and reported in the original study reports. The studies were in compliance with GLP. The DT_{50} and DT_{90} calculations were presented only in the Documents MII and MIII of the dossier of clopyralid, and the reporting of the method and outcome of the calculation was rather brief, however sufficient. This was probably due to the late submission of the data. Based on the data obtained, the dissipation of clopyralid in field is rapid. The studies are acceptable and no further studies are required.

RMS comments and evaluation:

The studies on the field dissipation of clopyralid in soil were evaluated in the DAR (2003) as presented above and the results were used in the risk assessment presented in the EFSA conclusion on clopyralid (EFSA Scientific Report 2005: 50). The outcomes are still valid and therefore the studies are not reviewed in detail here again. The results can be used to assess the degradation kinetics of clopyralid in field, as presented below by the Notifier. The results of these studies were used in the recalculation of $DT_{50field}$ values of clopyralid (Robinson 2016). No other comments, studies are acceptable and adequate for the renewal for the approval of clopyralid.

Additionally, new European soil dissipation studies were submitted in the context of the renewal of approval of clopyralid, which have not been evaluated before. The evaluations of the new studies are presented below.

CA 7.1.1.2.2/3 - Clopyralid Technical - Field dissipation in soil

Report	[IIA 7.1.1.2.2/03], Kröger, F. 2015a
Report title	Soil dissipation study with one spring application of GF-1966 (Clopyralid) at three sites to bare soil in Europe in 2013-2015.
DAS Study number	Eurofins Agroscience Services, Stade, Germany; Eurofins Study S13-00312. DAS Study No. 130673.
Guidelines	Guideline 7029/VI/95 (rev. 5) to Directive 91/414/EEC and Regulations (EU) 544/2011 and 545/2011 implementing Regulation (EC) 1107/2009. SANCO/3029/99 rev. 4. SETAC 1995 (excluded calculation of DT50).
GLP	Yes

Materials and methods

A field dissipation study was conducted with clopyralid on bare ground test plots in Northern Europe from 2013 to 2014. Three different sites were considered: Bargstedt, Germany, Wilson, UK, and Sermaises, Northern France. At each site one plot divided into three sub-plots was installed.

Table 8.1.32. Soil properties: Bargstedt, Northern Germany

		0-30 cm depth	30 – 60 cm depth	60 – 100 cm depth
Soil type (USDA) [%]	Sand:	78.3	74.3	74.8
	Silt:	14.9	16.9	9.4
	Clay:	6.9	8.9	15.8
pH –value ($CaCl_2$)		4.86	5.40	4.44
pH –value (H_2O)		4.26	4.54	4.77
Cation Exchange Capacity [meq/100g]		5.9	3.7	5.1
TC [%]		1.6	0.40	< 0.3
TOC [%]		1.5	0.39	< 0.3
C org [%]		2.6	0.67	< 0.5
USDA classification		loamy sand	sandy loam	sandy loam

Table 8.1.33. Soil properties: Wilson, UK

		0-30 cm depth	30 – 60 cm depth	60 – 100 cm depth
Soil type (USDA) [%]	Sand:	40.1	45.9	49.3
	Silt:	42.2	40.1	35.5
	Clay:	17.8	14.0	15.3
pH –value ($CaCl_2$)		6.92	7.10	7.30
pH –value (H_2O)		6.24	6.46	6.82
Cation Exchange Capacity [meq/100g]		9.3	6.2	5.9
TC [%]		1.8	0.83	1.0
TOC [%]		1.3	0.38	< 0.3
C org [%]		2.2	0.66	< 0.5
USDA classification		loam	loam	loam

Table 8.1.34. Soil properties: Sermaises, Northern France

		0-30 cm depth	30 – 60 cm depth	60 – 100 cm depth
Soil type (USDA) [%]	Sand:	2.8	2.2	5.1
	Silt:	65.6	61.6	56.4
	Clay:	31.7	36.3	38.6
pH –value ($CaCl_2$)		6.80	7.13	7.51
pH –value (H_2O)		6.98	7.27	7.56
Cation Exchange Capacity [meq/100g]		17.0	16.4	22.6
TC [%]		1.5	0.55	0.89

TOC [%]	1.3	0.55	0.41
C org [%]	2.2	0.95	0.71
USDA classification	silty clay loam	silty clay loam	silty clay loam

Irrigation was performed in correlation against long term monthly rainfall. Missing amounts were applied in the following month in order to ensure precipitation higher or equal to long term values. Daily weather data was measured on site. Additionally, taking into account concerns raised by the EFSA PPR Panel (EFSA Journal 2010; 8(12):1936) regarding potential surface losses after application, plots were irrigated with 10 mm after application but before the 0 DAA sample.

Clopyralid was applied formulated as GF-1966 at a nominal application rate of 200 g ae/ha. The German and UK sites were sprayed on 14 May 2013, whereas the French site one week earlier, on 07 May 2013. In order to verify application results 12 deposition trays (30 x 30 x 3 cm) filled with 1 kg of top soil (0-10 cm) were placed in the plot (4 per subplot). Therefore the soil was sieved through a 3.5 mm mesh to produce a homogenous sample of uniform texture. On the day of application the soil was evenly distributed and levelled over the surface of the tray. Immediately after application, the soil from each tray was filled in polythene container, closed and double wrapped in polythene bags to prevent any potential losses due to breaking. The deposition trays were stored deep frozen after end of application.

Soil samples were collected following the sampling schema as presented in Table 8.1.35. After collection, the soil residue samples were stored deep frozen at the test site until frozen shipment to the lab sample preparation test site.

Table 8.1.35. Soil residue sample collection dates

Site	Days after application
Bargstedt, Germany	-1, 0, 1, 3, 7, 10, 15, 21, 28, 58, 90, 115, 181, 360
Wilson, UK	-1, 0, 1, 3, 7, 9, 13, 20, 27, 58, 87, 127, 183, 370
Sermaises, Northern France	-1, 0, 1, 3, 7, 10, 14, 21, 27, 62, 91, 121, 177, 377

The frozen soil cores (0-30 cm & 0-100 cm) were cut in 10 cm layers in deep frozen stage (only the top 30 were first cut, deeper horizons were only cut on request of the Study Director; remaining soil cores after removal of the top 30 cm were labelled with the original sample code and addition of the remaining depth; e.g. 30-100). For homogenisation, the acetate liners of the frozen cores were opened and the total weight of the 6 cores per subplot for each 10 cm layer recorded before homogenisation. The soil core layers were then homogenised by grinding and sieving two consecutive times with dry ice. One aliquot of at least 400 g frozen homogenised soil was taken and stored deep frozen for analysis. The remaining soil should be stored deep frozen as retained sample. This was not done for all samples; for some samples only a second aliquot of about 400 g was stored. The remaining liners and caps were stored deep frozen.

Sample extraction and determination of residues was performed according to the analytical method described in Dow AgroSciences Study No. 120612 as provided by Dow AgroSciences LLC. Quantification was performed by use of LC-MS/MS detection. The limit of quantification (LOQ) of the analytical method for soil was 0.5 µg/kg with a limit of detection (LOD) set at 0.15 µg/kg (30 % of the LOQ). All 0-10 cm, 10-20 cm and 20-30 cm horizons were analysed. If detectable residues were found in 20-30 cm horizon, then the following deeper horizon was analysed.

Results

Bargstedt, Northern Germany

On sample collections dates 0 and 1 DAA soil cores were only taken from the 0-30 cm layer. It had not been expected that clopyralid residue would be found in the 20-30 cm layer. However, residue was found in this layer for 0 and 1 DAA. It can be speculated that the irrigation right after application has caused this transfer downwards. 10 mm of irrigation may be too much for a mobile compound like clopyralid. However, on the two following sample collection dates, 3 and 7 DAA, no residue could be detected in the 30-40 cm layer. Therefore, it can be concluded that no further vertical transfer of clopyralid had occurred on 0 and 1 DAA.

Starting with 10 DAA movement below 30 cm could be observed. The peak vertical residue level occurs 21 DAA with concentrations up to 23 µg/kg in the 40-50 cm layer in one subplot. While residues could be detected below 50 cm these were very low. 120 DAA was the last sample collected date with residue detected.

On three sample collection dates residue was detected in the deepest sampled layer (90-100 cm): 14, 21, and 60 DAA. However, the maximum residue concentration found was 0.8 % of initial concentration.

The observed leaching pattern can be explained by the combination of an unusually wet spring and a sandy soil texture. Average monthly precipitation is 63 mm for May (DWD weather station Freiburg/Elbe, Station ID 1451, time period 1981-2010, station within 5 km of study site). From application on 13 May 2013 until 31 May 2013 130 mm were observed. Adding 10 mm of irrigation right after application yields a total 140 mm of rain. Hence, in only half a month more than twice as much rain as usually observed in a month occurred. Especially the period between 3 DAA and 14 DAA received heavy rainfall (100 mm for the period after 3 DAA and before 14 DAA).

Wilson, UK

On sample collections dates 0 and 1 DAA soil cores were only taken from the 0-30 cm layer. Like in the German trial it had not been expected that clopyralid residue would be found in the 20-30 cm layer. Interestingly 10 mm of irrigation right after application did not cause lateral movement. However, additional 3.6 mm of rain between 0 and 1 DAA caused downward movement.

Starting with 3 DAA movement below 30 cm could be observed. However, the levels detected were very low. Very low levels (< 0.5 µg/kg) could be observed in the lowest sampled layer (90-100 cm).

Like in Germany it was an unusually wet spring in the UK. While total precipitation amounts were not as high as in Germany, they still exceeded the long term average (13-31 May 2013: 72 mm long term versus 26 mm actual). However, residue levels found in deeper layers were lower than in Germany. The heavier soil texture in the UK may have contributed to these differences.

Sermaises, Northern France

On sample collections dates 0 and 1 DAA soil cores were only taken from the 0-30 cm layer. Like in Germany and the UK residue had been detected in the 20-30 cm layer.

While leaching to deeper layers occurred, residue levels were lower than in Germany and in the UK. The deepest layer with residue being detected is 70-80 cm.

While precipitation amounts where similar to the UK trial in May, less lateral movement could be observed. This could be explained by the soil texture at the Northern French site, which is more clayey compared to the two other sites.

Conclusion

The degradation behaviour of clopyralid was studied at three sites across Northern Europe. At all three sites movement of clopyralid out of the top layer could be observed. The leaching pattern can be explained by soil texture and precipitation amounts at the respective sites.

Table 8.1.36. Field residues of clopyralid in Bargstedt, Northern Germany

		Residues of clopyralid [µg/kg] at sample collection dates[1, 2, 3]													
Depth [cm]	**Subplot**	**0-7 DBA**	**0**	**1**	**3**	**7**	**10**	**14**	**21**	**30**	**60**	**90**	**120**	**180**	**365**
0-10	1	<0.5	104	4.3 101 112	7.2 44 53	126 104 123	14 14	3.9 3.2	1.1 2.3	2.3 2.1	<0.5	2.7	1.6	n.d.	n.d.
	2	n.d.	110	4.8 114 115	60	84 107 90	7.1	2.7 3.3	2.4 8.2	1.7 2	<0.5	5.1	0.6	n.d.	n.d.
	3	< 0.5	108	3.1 106 96	73	109 107 102	20 18	4.2 3.9	2.8 2	1 1.1	<0.5	0.8	<0.5	n.d.	n.d.
10-20	1	n.d.	0.9 <0.5 <0.5	0.8 <0.5 <0.5	<0.5 1.8 2.1	<0.5 <0.5	48 51	7.5 7.7	7.7 14	1.7 2	n.d.	6.7	<0.5	n.d.	n.d.
	2	n.d.	<0.5 <0.5 <0.5	21 n.d. n.d.	<0.5	2 0.5	7.8	9.3 7.5	4 2.5	3 3.5	n.d.	6.3	<0.5	n.d.	n.d.
	3	n.d.	2 <0.5 <0.5	3.7 n.d. <0.5	n.d.	0.9 0.6	31 36	8.1 8.9	9.6 8.7	2.4 2.2	n.d.	<0.5	<0.5	n.d.	n.d.
20-30	1	n.d.	9.5 <0.5 <0.5	16 <0.5 <0.5	4.2 <0.5 n.d.	<0.5 n.d.	29 31	13 12	17 9.5	10 12	n.d.	1.2	n.d.	n.d.	n.d.
	2	n.d.	1.7 n.d. n.d.	10 n.d. n.d.	3.2	<0.5 n.d.	3.2	19 19	2.3 9	3.1 3	n.d.	2.9	<0.5	n.d.	n.d.
	3	n.d.	32 0.6 <0.5	22 n.d. n.d.	<0.5	<0.5 n.d.	39 37	27 13	4.6 14	1.6 1.4	n.d.	<0.5	n.d.	n.d.	n.d.

		Residues of clopyralid [µg/kg] at sample collection dates[1, 2, 3]												
Depth [cm]	**Subplot**	**0-7 DBA**	**0**	**1**	**3**	**7**	**10**	**14**	**21**	**30**	**60**	**90**	**120**	**180**	**365**
30-40	1				n.d.	n.d.	1.5	18	15	7.8	<0.5	n.d.	n.d.		
	2				n.d.	n.d.	1.5	8.5	11	9	<0.5	n.d.	n.d.		
	3				n.d.	n.d.	1	22	20	9.1	<0.5	n.d.	n.d.		
40-50	1						n.d.	7.2	11	<0.5	2.6	n.d.	n.d.		
	2						n.d.	11	9.3	2.2	2.7	n.d.	n.d.		
	3						n.d.	6.7	23	2.8	2.6	n.d.	n.d.		
50-60	1							2.6	0.8	0.8	5	<0.5	n.d.		
	2						n.d.	6.6	2.6	0.8	4.3	n.d.	0.6		
	3							1.5	3	0.6	2.9	<0.5	n.d.		
60-70	1							2.2	0.5	<0.5	3.4	n.d.	n.d.		
	2							3.3	3.9	n.d.	1.9	<0.5	<0.5		
	3							0.7	1.2	n.d.	3.9	0.6	n.d.		
70-80	1							1.3	n.d.	n.d.	1.8	0.6	n.d.		
	2							0.8	2.5	n.d.	1.2	<0.5	n.d.		
	3							<0.5	0.6	n.d.	0.9	0.8	<0.5		
80-90	1							<0.5	<0.5	n.d.	<0.5	n.d.	n.d.		
	2							<0.5	1	n.d.	<0.5	<0.5	n.d.		
	3							0.6	n.d.	n.d.	<0.5	0.9	<0.5		
90-100	1							n.d.	n.d.		n.d.	n.d.	n.d.		
	2							n.d.	<0.5		n.d.	0.6	n.d.		
	3							<0.5	n.d.	n.d.	n.d.	0.9	n.d.		

1 More than one residue concentrations for a subplot-sample date combination indicate analytical replicates. These are not true replicates.

2 n.d. = not determined

3 On sample collection dates 0-7 DBA, 0 DAA, and 1 DAA only 30 cm soil cores had been drawn.

Table 8.1.37. Field residues of clopyralid in Wilson, UK

		Residues of clopyralid [µg/kg] at sample collection dates[1, 2, 3]												
Depth [cm]	**Subplot**	**0-7 DBA**	**0**	**1**	**3**	**7**	**9**	**13**	**20**	**27**	**58**	**87**	**127**	**183**	**370**
0-10	1	n.d.	100	29 53	38	36	28	30	14	8.4	0.5	<0.5	<0.5	<0.5	<0.5
	2	<0.5	123	11 61	45	48	43	35	16	<0.5	<0.5	<0.5	<0.5	n.d.	<0.5
	3	n.d.	102	20 62	61	41	58	42	14	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
10-20	1	<0.5	n.d.	19	26	36	23	15	18	9.3	n.d.	0.6	n.d.	n.d.	<0.5
	2	n.d.	n.d.	26	23	18	12	19	15	n.d.	n.d.	n.d.	<0.5	n.d.	n.d.
	3	n.d.	n.d.	17	7.6	18	14	8.2	23	n.d.	<0.5	<0.5	n.d.	<0.5	<0.5
20-30	1	n.d.	n.d.	0.9	<0.5	3.7	8	3.6	5.9	4.3	<0.5	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	0.7	3.3	2	5.9	2.5	7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	3	<0.5	n.d.	1.8	0.5	1.2	2.9	4.6	10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
30-40	1				<0.5	1.4	0.6	n.d.	2	n.d.	n.d.				
	2				0.9	n.d.	1.4	n.d.	2	0.9	n.d.				
	3				<0.5	0.7	n.d.	n.d.	2.4	1.6	<0.5				
40-50	1				n.d.	0.6	<0.5	n.d.	1.6	0.6	n.d.				
	2				<0.5	<0.5	<0.5	n.d.	1.6	1.2	n.d.				
	3				n.d.	<0.5	n.d.	n.d.	0.6	2.2	<0.5				
50-60	1				n.d.	<0.5	0.7	n.d.	1.3	n.d.	n.d.				
	2				<0.5	<0.5	<0.5	n.d.	1.2	1.1	n.d.				
	3				n.d.	0.6	n.d.	n.d.	0.5	3.3	< 0.5				

		Residues of clopyralid [µg/kg] at sample collection dates[1, 2, 3]												
Depth [cm]	**Subplot**	**0-7 DBA**	**0**	**1**	**3**	**7**	**9**	**13**	**20**	**27**	**58**	**87**	**127**	**183**	**370**
60-70	1					<0.5	0.5		1		n.d.				
	2				<0.5	<0.5	n.d.		0.7	<0.5	n.d.				
	3					0.9			n.d.	2.6	n.d.				
70-80	1					<0.5	1.4		<0.5		n.d.				
	2				<0.5	n.d.	n.d.		<0.5	0.6	n.d.				
	3					<0.5				1.2	n.d.				
80-90	1					n.d.	1.2		n.d.		n.d.				
	2				<0.5				<0.5	<0.5	n.d.				
	3					0.5				n.d.	n.d.				
90-100	1					n.d.	n.d.				n.d.				
	2				<0.5				<0.5	n.d.	n.d.				
	3					<0.5				<0.5	n.d.				

1 More than one residue concentrations for a subplot-sample date combination indicate analytical replicates. These are not true replicates.

2 n.d. = not determined

3 On sample collection dates 0-7 DBA, 0 DAA, and 1 DAA only 30 cm soil cores had been drawn.

Table 8.1.38. Field residues of clopyralid in Sermaises, Northern France

		Residues of clopyralid [µg/kg] at sample collection dates[1, 2, 3]													
Depth [cm]	**Subplot**	**0-7 DBA**	**0**	**1**	**3**	**7**	**10**	**14**	**21**	**27**	**62**	**91**	**121**	**177**	**377**
0-10	1	n.d.	101	45 96	98	105	76	18	13	4.4	<0.5	<0.5	n.d.	n.d.	<0.5
	2	n.d.	81	93 100	84	94	93	18	6.9	8.6	<0.5	0.8	n.d.	n.d.	n.d.
	3	n.d.	106	2.8 94	84	70	68	37	20	6.8	<0.5	11	n.d.	<0.5	n.d.
10-20	1	<0.5	1.2	4.5	17	7.1	3.5	11	9.9	6.5	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	3.9	0.6	6	6.5	1.7	12	6	8.8	n.d.	n.d.	n.d.	n.d.	n.d.
	3	<0.5	2.8	3.4	5.2	5.2	3.8	29	11	4.6	<0.5	<0.5	n.d.	n.d.	n.d.
20-30	1	n.d.	1.1	1.3	4.9	1.5	1.5	5.9	2.4	2.1	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	1.8	1	2	1.8	0.6	8.2	3.2	1.4	n.d.	n.d.	n.d.	n.d.	<0.5
	3	n.d.	<0.5	2.9	1.4	1.6	2	6.5	2.2	2	n.d.	<0.5	n.d.	n.d.	n.d.
30-40	1				1.8	0.8	<0.5	6.5	4.6	0.7	n.d.	n.d.			
	2				1.5	0.8	<0.5	6.6	3.7	0.9	n.d.	n.d.			n.d.
	3				0.9	0.8	-[4]	2.2	2.5	n.d.	n.d.	n.d.			
40-50	1				n.d.	<0.5	n.d.	2	4	n.d.	n.d.	n.d.			
	2				n.d.	<0.5	n.d.	1.6	5	<0.5	n.d.	n.d.			
	3				n.d.	<0.5	-[4]	0.6	2.9	n.d.	n.d.	n.d.			
50-60	1				n.d.	n.d.	n.d.	n.d.	1.2	n.d.	n.d.	n.d.			
	2				n.d.	<0.5	n.d.	n.d.	4.5	n.d.	n.d.	n.d.			
	3				n.d.	<0.5	-[4]	<0.5	0.6	n.d.	n.d.	n.d.			

		Residues of clopyralid [µg/kg] at sample collection dates[1, 2, 3]													
Depth [cm]	**Subplot**	**0-7 DBA**	**0**	**1**	**3**	**7**	**10**	**14**	**21**	**27**	**62**	**91**	**121**	**177**	**377**
60-70	1							n.d.	<0.5	n.d.	n.d.	n.d.			
	2					n.d.		n.d.	2.5	n.d.	n.d.	n.d.			
	3					<0.5		n.d.	n.d.	n.d.	n.d.	n.d.			
70-80	1							n.d.	n.d.	n.d.	n.d.	n.d.			
	2					n.d.		n.d.	n.d.	n.d.	n.d.	n.d.			
	3					<0.5		n.d.	n.d.	n.d.	n.d.	n.d.			
80-90	1														
	2														
	3					n.d.									

1 More than one residue concentrations for a subplot-sample date combination indicate analytical replicates. These are not true replicates.

2 n.d. = not determined

3 On sample collection dates 0-7 DBA, 0 DAA, and 1 DAA only 30 cm soil cores had been drawn.

4 Soil sample 10 DAA, 30 – 100 cm has been lost.

RMS comments and evaluation:

The new field dissipation study on clopyralid was evaluated by the RMS. The study was well conducted according to the guidelines and the GLP, clearly reported and the results are valid to be used in the kinetic evaluation and risk assessment. The application rate on bare soil, ignoring the crop interception, was slightly higher than ends up to the soil from the maximum use of the representative formulation GF-1374 on pasture (up to 160 g clopyralid/ha). There were several slight deviations from the study protocol during the study period, e.g. adjustments of sampling times due to local holidays, but they were assessed as not been affected to the outcome significantly. The study is considered as acceptable and adequate for the renewal for the approval of clopyralid.

The field data available enabled the kinetic evaluation in Northern and Central European conditions, as presented by the Notifier (Robinson 2015, below). Southern European conditions are addressed in two separate studies (Kröger 2016 a-b) with a separate kinetic assessment (Robinson 2016).

CA 7.1.1.2.2/4 - Clopyralid Technical - Kinetic evaluation of field dissipation studies

Report	[IIA 7.1.1.2.2/04], Robinson, P. 2015
Report title	Estimation of kinetic endpoints for clopyralid from soil dissipation studies.
DAS Study number	Dr. Knoell Consult Report number 102664-1. DAS Study No. 150296.
Guidelines	FOCUS Kinetics (2006, 2014) EFSA Guidance Document for evaluating laboratory and field dissipation studies to obtain DegT50 values of active substances of plant protection products and

	transformation products of these active substances in soil. EFSA Journal 2014;12(5): 3662.
GLP	No

The aim of this evaluation was to conduct a kinetic modelling analysis for clopyralid using residue data from field soil dissipation studies, in order to derive persistence endpoints that can be used for comparison against regulatory trigger values, and modelling endpoints that can be used for calculating predicted environmental concentrations (PECs) in various environmental compartments.

Materials and methods

The evaluation was based on residue data from a new tailored study, which included three field soil dissipation trials in Europe (Kröger, 2015). In addition, a legacy study, which included five European field trials (Rawle & Yon, 2002a, 2002b), was re-evaluated according to the most recent guidance (FOCUS, 2006, 2014; EFSA, 2014). For all trials clopyralid was applied as a test substance.

Values between the LOQ and LOD were set to ½(LOQ+LOD). Values below LOD were replaced by half the LOD. If the concentrations of the applied substance in soil declined to values below LOD, the curve was cut off after the first value below LOD, unless detections above LOQ were made later in the experiment (FOCUS, 2006, 2014). These corrections were performed along the time course as well as with depth along the soil layers. Since changes in soil density with depth could be neglected, the measured residues (µg/kg) of clopyralid in the different soil layers were simply summed up to provide total residue values.

According to FOCUS (2006, 2014), true replicates at each sampling point should be used for the kinetic evaluation if available. In each study there were three field sub-plots; these were considered to be true replicates. Where multiple values at a sub-plot were given for a single depth interval, these were regarded as analytical replicates and averaged prior to summing residues.

The evaluation for persistence endpoints followed the recommendations of FOCUS (2006, 2014). Persistence endpoints were evaluated according to best-fit kinetics. The evaluation for modelling endpoints followed the recommendations of FOCUS (2006, 2014) and EFSA (2014). For modelling endpoints, a time step normalisation method was applied to the data (standard reference conditions of 20°C and 100% field capacity). For persistence endpoints, the best-fit model was selected (lowest χ^2 error) according to FOCUS (FOCUS, 2006, 2014).

Samples taken prior to 10 mm cumulative rainfall/irrigation were excluded. This applied only to the legacy studies Rawle and Yon (2002a, b). The most recent study Kröger (2015) was irrigated with 10 mm right after application but before the 0 DAA sample.

Weather data had not been recorded on site for the trials of Rawle and Yon (2002a, b). However, for all sites but one official weather stations were available within 20 km distance from the study sites: Daily average soil temperature was available for Spalding, UK and Mainbervilliers, France. These data had been used directly in the day-length normalisation. For the other sites daily min/max air temperature was available. For site Middlefart, Denmark, no temperature measurements were available within 20 km distance from the site. Therefore, air temperature data was obtained from the 25 km MARS data set. Daily total rainfall was available for all sites from official weather close by (within 20 km distance). Soil temperature, when not available from measurements, and soil moisture were generated with the aid of the model PERSIST (Walker and Barnes, 1981. Simulation of herbicide persistence in soil; a revised computer model. Pesticide Science; 12(2):123-132).

Results

Persistence endpoints

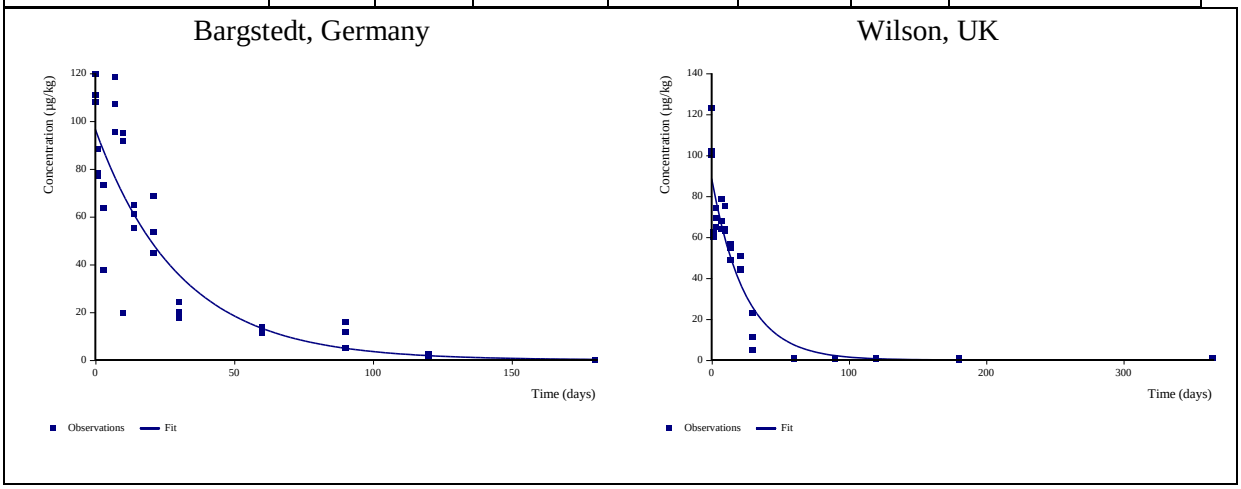
All three trials of Kröger (2015) can best be described by SFO kinetics. While χ^2 is above 15% the models can still describe the data successfully. Therefore, all three endpoints are considered as valid.

Four of five sites of Rawle and Yon (2002a, b) can be described successfully by kinetic models. Statistics are robust. The only exception is site Spalding, UK. A fairly high χ^2 error is accompanied by a dissatisfactory visual fit. Therefore, only the endpoints of the other four sites are considered as valid.

The $DT_{50(field)}$ values resulting from different kinetics for evaluating the persistence at different locations and studies are summarized in Table 8.1.39.

Table 8.1.39. Comparison of the various models for persistence

Trial	SFO		FOMC		DFOP		Best-fit persistence model
	DT_{50}	**χ^2**	**DT_{50}**	**χ^2**	**DT_{50}**	**χ^2**	
Kröger (2015)							
Bargstedt, Germany	**21.0**	**23.9**	16.8	24.8	20.8	25.9	SFO
Wilson, UK	**16.7**	**22.6**	13.0	23.4	16.7	24.3	SFO
Sermaises, France	**16.3**	**19.3**	11.7	20.2	16.3	21.2	SFO
Rawle and Yon (2002 a,b)							
Ansonville, France	1.87	19.9	1.13	9.95	**0.16**	**5.36**	DFOP
Spalding, UK	8.38	32.1	2.19	21.9	**0.61**	**16.8**	DFOP
Mainbervilliers, France	7.24	11.8	6.25	11.5	6.04	7.22	DFOP
Oederquart, Germany	**16.2**	**12.0**	14.1	13.0	16.2	14.3	SFO
Middlefart, Denmark	**23.7**	**13.1**	16.7	14.0	23.7	15.1	SFO



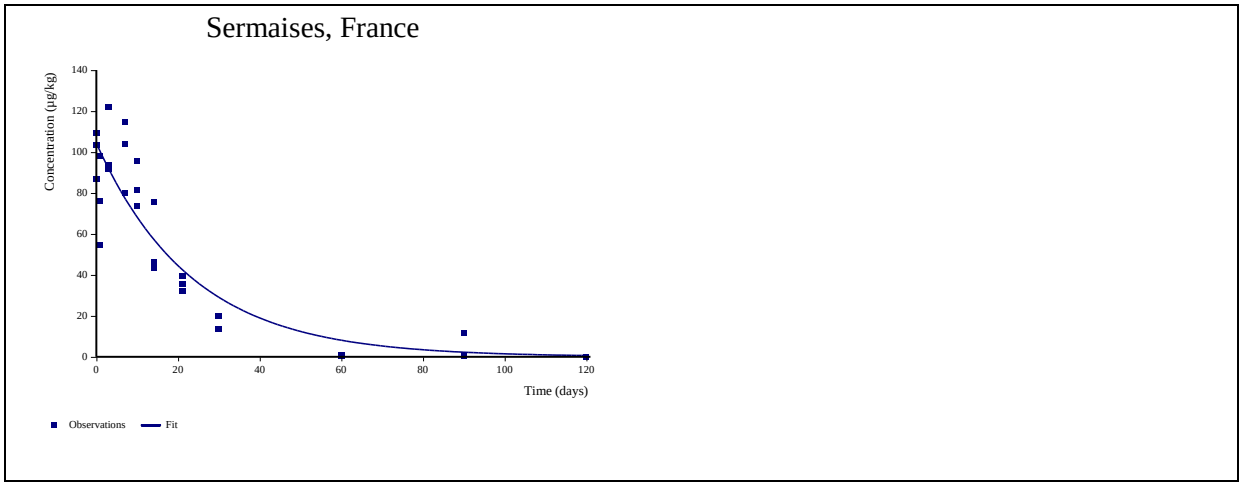
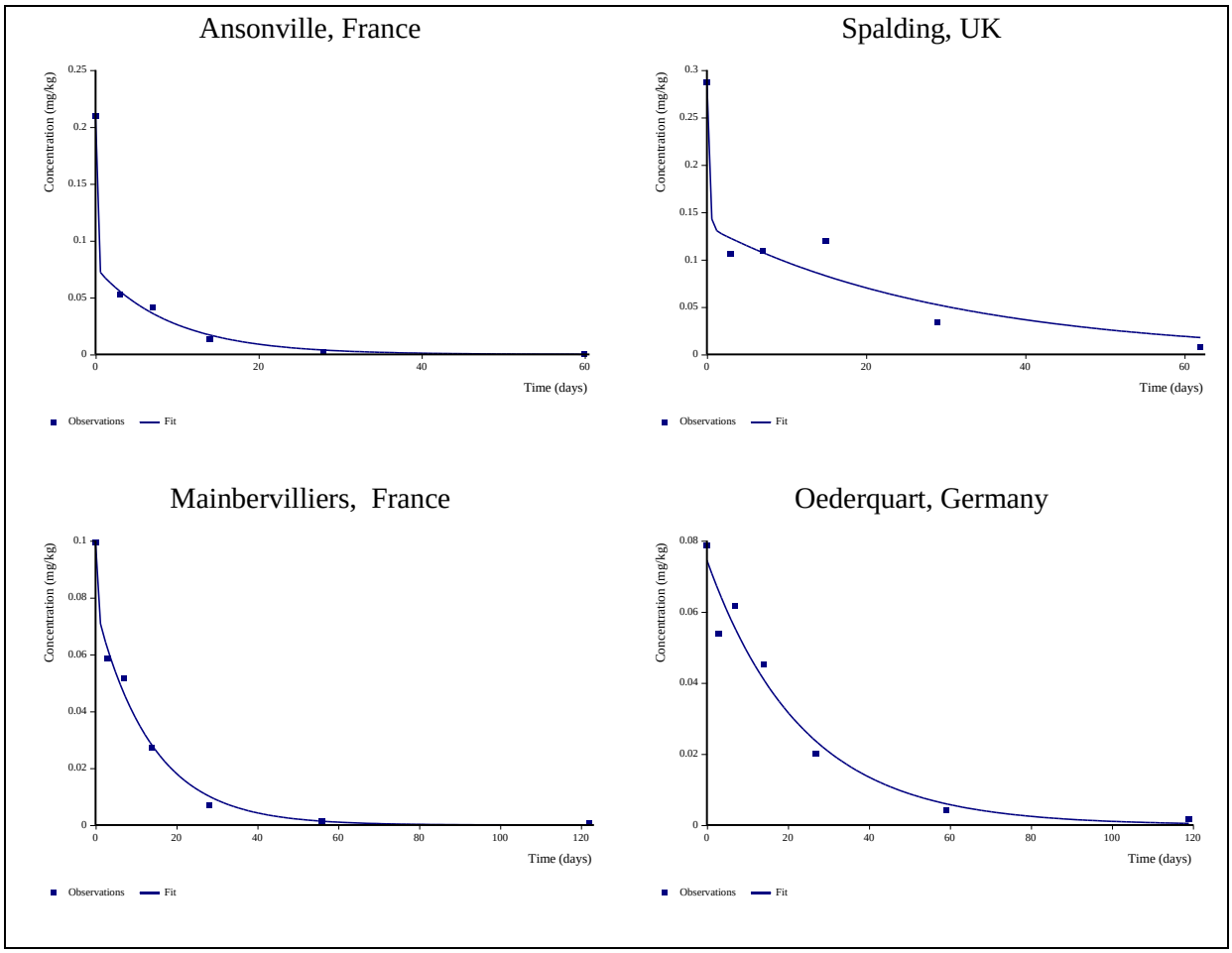


Figure 8.2. Persistence endpoint best-fit kinetics (Kröger, 2015)



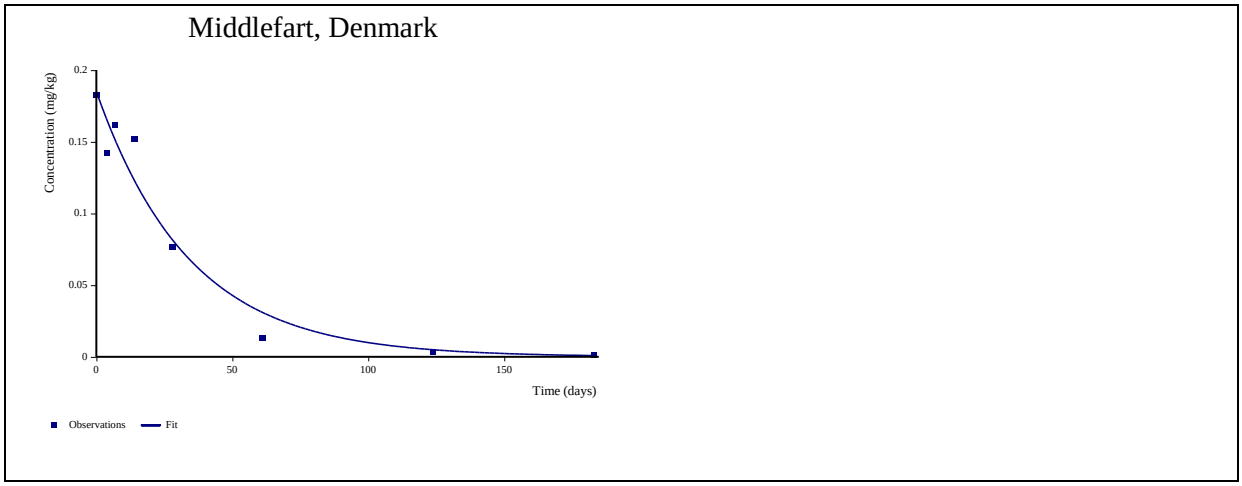


Figure 8.3. Persistence endpoint best-fit kinetics (Rawle and Yon, 2002a,b)

Table 8.1.22. Summary of the best-fit models for persistence

Trial	Model	DT_{50} (d)	DT_{90} (d)
Kröger (2015)			
Bargstedt, Germany	SFO	21.0	69.6
Wilson, UK	SFO	16.7	55.6
Sermaises, France	SFO	16.3	54.0
Rawle and Yon (2002a,b)			
Ansonville, France	DFOP	0.16	12.1
Spalding, UK	DFOP	[a]	[a]
Mainbervilliers, France	DFOP	6.04	28.3
Oederquart, Germany	SFO	16.2	53.9
Middlefart, Denmark	SFO	23.7	78.7

[a] No statistically reliable fit

Modelling endpoints

The $DT_{50(field)}$ values resulting from different kinetics normalised for soil moisture and temperature, to be used for modelling are summarized in Table 8.1.40.

Table 8.1.40. Comparison of the various models for modelling

Trial	SFO		FOMC		DFOP		Selected model for modelling endpoint
	DT_{50}	χ^2	DT_{50}	χ^2	DT_{50}	χ^2	
Kröger (2015)							
Bargstedt, Germany	13.0	23.4	[a]	[a]	[a]	[a]	SFO
Wilson, UK	13.5	21.5	[a]	[a]	[a]	[a]	SFO
Sermaises, France	7.50	19.9	[a]	[a]	[a]	[a]	SFO
Rawle and Yon (2002 a,b)[b]							
Ansonville, France	2.07	11.4	-	-	-	-	SFO
Spalding, UK	[a]	[a]	[a]	[a]	[a]	[a]	[a]
Mainbervilliers, France	2.70	3.65	-	-	-	-	SFO
Oederquart, Germany	5.69	3.37	-	-	-	-	SFO
Middlefart, Denmark	8.46	2.37	-	-	-	-	SFO
Geomean	**6.21**						

[a] No statistically reliable fit

[b] kinetic fit for DAA > 10 mm rainfall according to EFSA, 2014

'-' = model not tested since SFO was deemed to be acceptable according to FOCUS, 2006, 2014

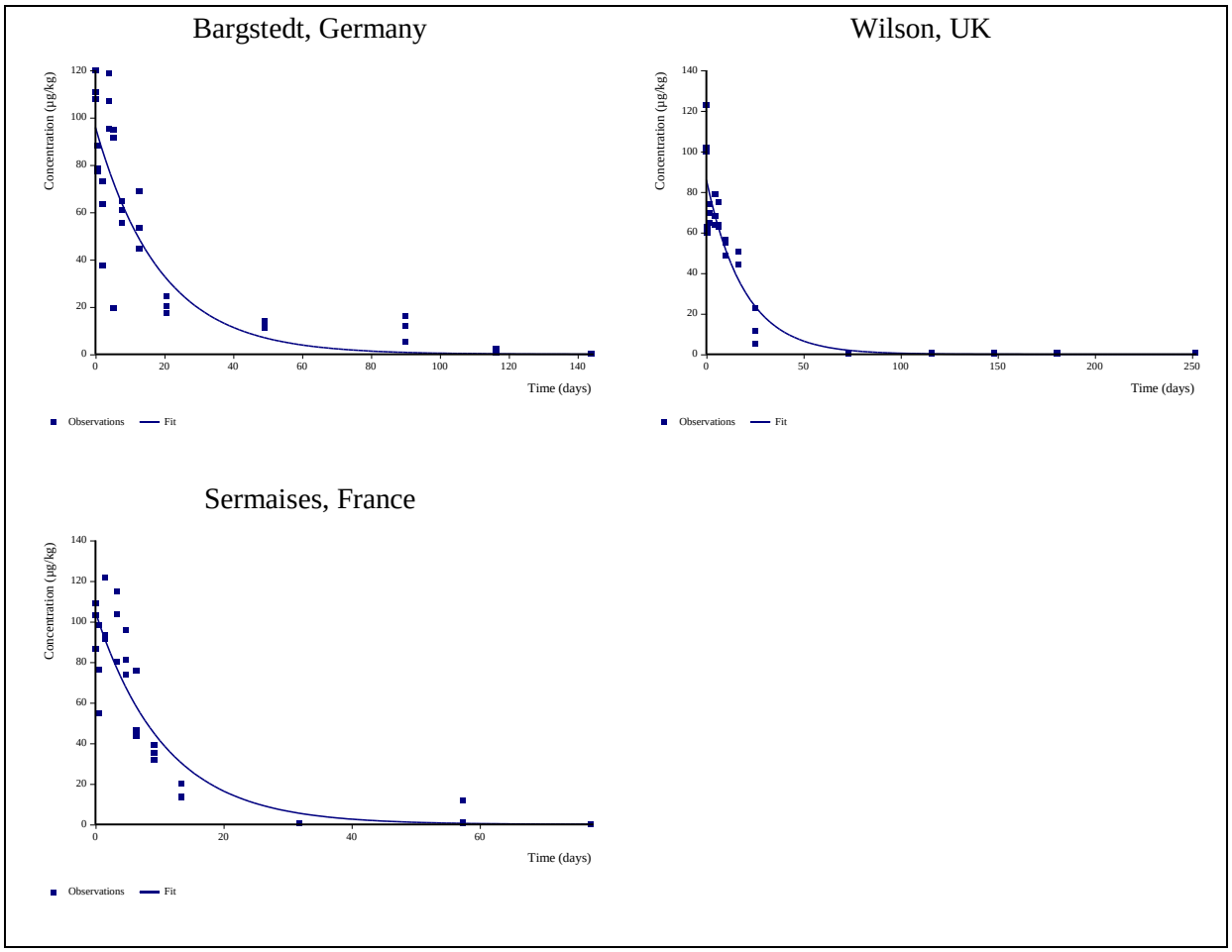


Figure 8.4. Modelling endpoint kinetics (Kröger, 2015)

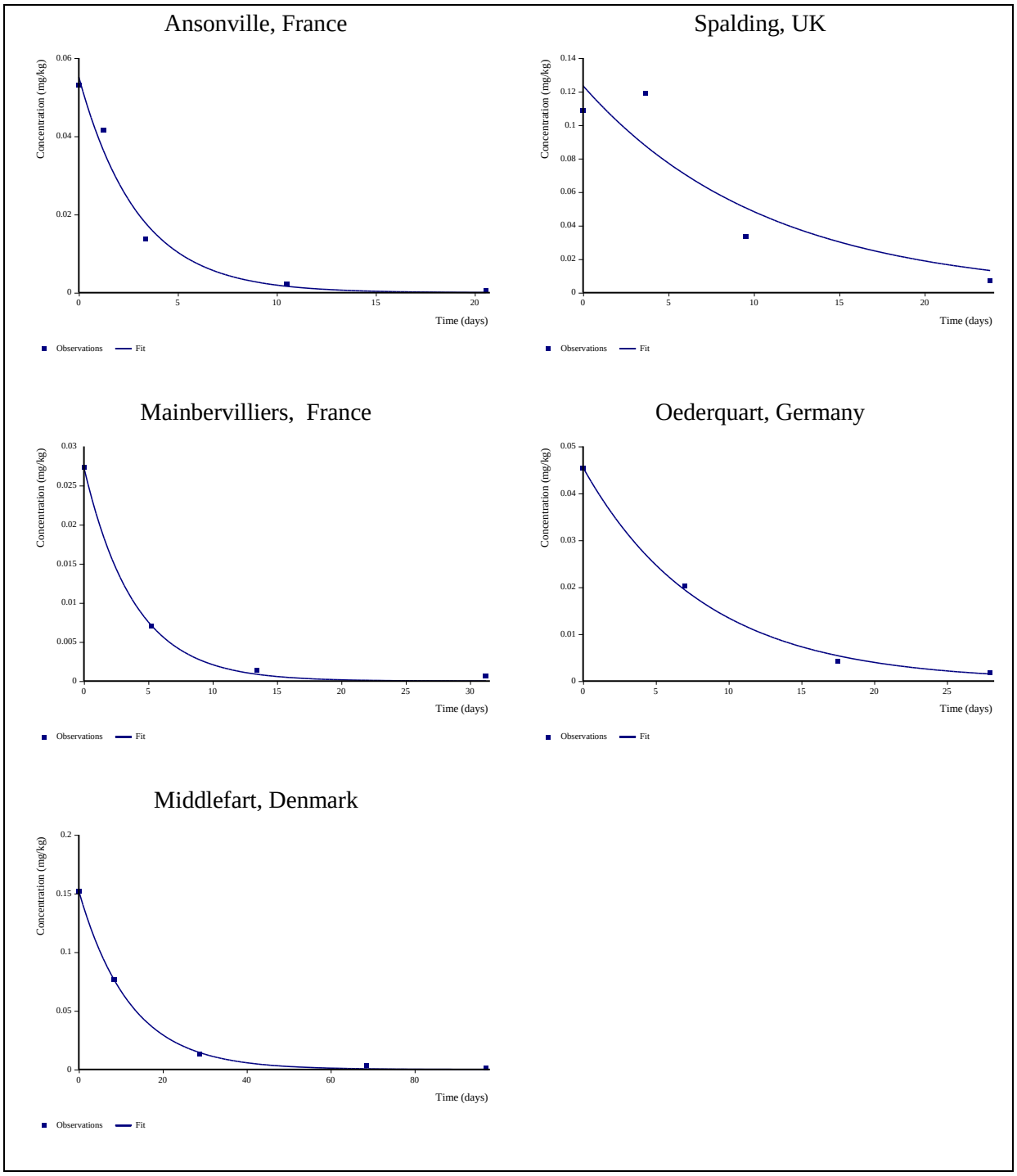


Figure 8.5. Modelling endpoint kinetics (Rawle and Yon, 2002a,b)

RMS comments and evaluation:

The kinetic calculation of the field dissipation endpoints of clopyralid in Northern and Central European conditions, as presented by the Notifier, was assessed by the RMS. The DT_{50} and DT_{90} values were derived from three different studies on eight locations and address adequate variety of climate and soil conditions in Northern and Central parts of the Europe. The studies are acceptable and all individual values are valid, thus allowing an appropriate risk assessment. The kinetic

calculation was performed according to FOCUS guidance, and the outcomes as summarized above are considered acceptable. The recalculated $DT_{50field}$ values are somewhat shorter (with geomean of 6.2 days) than originally obtained during the first evaluation of clopyralid (mean $DT_{50field}$ of 11 days from the studies Rawle & Yon 2002a-b). However, the individual values at different locations remain within the same range in all studies. The data is adequate for the renewal for the approval of clopyralid, and no further data are required.

Because the results of separate field dissipation studies in Southern European conditions were not available when the dossier was prepared, the kinetic evaluation of these studies is performed separately (Robinson 2016). No further data is required.

To address the conditions in Southern EU, two new field dissipation studies with clopyralid were conducted in Spain and Southern France. The Notifier updated the dossier in March 2016 to provide final reports of these studies. The updated reports were evaluated by the RMS. Cosequently, the kinetic evaluation of the results was submitted as a separate report by Robinson (2016; see 7.1.1.2.2/7).

CA 7.1.1.2.2/5 - Clopyralid Technical - Field dissipation in soil - Spain

Report	[IIA 7.1.1.2.2/05], Kröger, F. 2016a
Report title	Soil dissipation study with one spring application of GF-1966 (Clopyralid) at one site to bare soil in South Europe in 2015.
DAS Study number	Eurofins Agroscience Services, Stade, Germany; Eurofins Study S15-02991. DAS Study No. 150672.
Guidelines	SETAC 1995 (excluded calculation of DT50) SANCO/3029/99 rev. 4: EU guidance document for generating and reporting methods of analysis in support of pre-registration data requirements. Regulations (EU) 283/2013 and 284/2013 implementing Regulation (EC) 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC. EFSA Guidance Document for evaluating laboratory and field dissipation studies to obtain DegT50 values of active substances of plant protection products and transformation products of these active substances in soil. EFSA Journal 2014;12(5): 3662. ISO 10381-6:2009 (handling & storage soil for assessment of microbial biomass) OECD 217 US EPA (Oct 2008). Fate, Transport and Transformation Test Guidelines. OPPTS 835.6100. Terrestrial Field Dissipation
GLP	Yes

Materials and methods

A field dissipation study was conducted with clopyralid on bare ground test plots in Spain in 2015. One site was considered: Canals, Spain. One plot divided into three sub-plots was installed. The soil was characterised as presented in Table 8.1.41.

Table 8.1.41. Soil properties: Canals, Spain

		0-30 cm depth	30 – 60 cm depth	60 – 100 cm depth
Soil type (USDA) [%]	Sand:	23.9	24.5	18.8
	Silt:	45.5	37.9	51.6
	Clay:	30.6	37.7	29.7
pH –value ($CaCl_2$)		7.56	7.70	7.72
pH –value (H_2O)		8.04	7.95	7.97
Cation Exchange Capacity [meq/100g]		17.3	18.5	19.6
TC [%]		1.9	2.2	1.5
TOC [%]		0.40	<0.3	<0.3
C org [%]		0.69	<0.5	<0.5
USDA classification		clay loam	clay loam	silty clay loam

The product GF-1966, containing 950 g/kg nominal of the active ingredient (a.i.) Clopyralid-olamine, which is equivalent to 720 g/kg of the acid equivalent (a.e.) Clopyralid, was applied at the field site to bare soil on the treated plot using a calibrated boom sprayer. The nominal application rate was 277.78 g product/ha (equivalent to 200 g Clopyralid/ha nominal) with a target water volume of 400 L/ha. To verify the spray application, deposition trays were placed on the soil surface. The actual application rates determined by quantifying the amount of spray discharged ranged from values of 198.2 to 211.7 g a.e./ha.

Immediately after application of the test item and before subsequent soil sampling, the control plot and the treated plot were covered with a thin layer of sand to minimise potential surface processes. Further, immediately after application of the sand cover and the first soil sampling at least 5 mm were irrigated to the treated plot to minimise potential surface processes. No tillage or fertilization was performed during the period of the study and no crops were grown throughout any of the trials. The plots were kept generally free of weeds via the application of glyphosate.

Irrigation of both the treated and the untreated plot was performed, in case of dryer than normal conditions or when weather conditions resulted in excessive drying out of the soil. Actual rainfall was checked three times per month (about every 10 days) and compared to ET_0-values. Each 10 day's deficit ≥ 3 mm was generally compensated by irrigation with well water or water from water courses along the field. The amount irrigated must has been verified by rain measuring devices (generally at least 5 placed in each treated subplot and 3 placed on the control plot; except for four irrigation events, where only 2 rain measuring devices have been used in each treated subplot). All measured values and their mean as well as their approximate position in the plot have been recorded. For calculation of required irrigation for every approximately 10 day period the formula below was used:

$$Irrigation = (0.55 \times \sum_{\sim 10 days} ET_0) - \sum_{\sim 10 days} precipitation$$

Irrigation was generally homogenously applied and did not exceed 20 mm per event. The total amount of irrigation (average) was 428.9 mm.

Daily values of air temperature, soil temperature (at approx. 10°cm and 30 cm depth), volumetric soil moisture (at approx. 10 cm and 30 cm depth), wind speed, solar radiation, air humidity as well as rainfall were recorded by an on-site weather station. The air and soil temperature as well as the soil moisture was recorded as daily minimum, maximum and average. The rain was recorded as sum per day, the volumetric soil moisture as average percent water content and all other data as daily mean values.

The long term averages (air temperature and rainfall) were obtained from a close by weather station (from 2002-2011). The daily ET_0 values and the daily precipitation were used as basis for the calculation of irrigation. The data loggers recorded daily values based on half hourly measured values, hence reported averages are based on up to 48 single values. Daily minima and maxima are based on the total of up to 48 values per day. Soil temperature was measured at 10 cm and 30 cm depth with a

10 kΩ thermistor sensor. Soil moisture was measured at 10 cm and 30 cm depth with a volumetric water content sensor. The soil sensors for measuring soil temperature and moisture were buried inside one of the treated plot. Rainfall was measured with a tipping gauge sensor measuring 0.2 mm per tip. Air temperature was measured with a 2 kΩ thermistor.

Clopyralid was applied formulated as GF-1966 at a nominal rate of 200 g ae/ha on 19 May 2015. In order to verify application results 15 deposition trays (30 x 30 x 3 cm) filled with 1 kg of top soil (0-10 cm) were placed in the plot (5 per subplot). Therefore the soil was sieved through a 2 mm mesh to produce a homogenous sample of uniform texture. On the day of application the soil was evenly distributed and levelled over the surface of the tray. Immediately after application, each tray was closed with a metal lid and double bagged and labelled to prevent any potential losses due to breaking. The deposition trays were stored deep frozen on dry ice immediately (within 5 minutes) after end of application.

To exclude surface dissipation processes (EFSA, 2014), 5 mm irrigation was applied after application but before the 0 DAA sample collection. Only 5 mm were chosen because leaching into lower layers should be prevented. However, to ensure that surface dissipation processes are eliminated plots were covered with an additional 1-1.7 cm sand layer after application.

Untreated soil residue samples were taken 1 DBA from the future treated plot. After application soil residue samples were taken immediately after application and at 1, 3, 7, 9, 15, 20, 30, 43 and 62 days after application (DAA).

Soil cores from 0-100 cm were taken using a hydraulic soil corer fitted with a liner of 4.8 cm inner diameter and 100 cm length. To penetrate the soil, a metal tip of 4.5 cm inner diameter was used, leading to an inner diameter of 4.5 cm of the soil cores. Soil cores from 0-30 cm were taken using a manual corer fitted with a liner of 4.9 cm inner diameter and 30 cm length.

The frozen soil cores (0-30 cm and 0-100 cm) were cut in 10 cm layers in deep frozen stage and the resulting layers were stored deep frozen. For homogenisation the acetate liners of the frozen 0-10 cm, 10-20 cm and 20-30 cm horizons were opened and the total weight of the 10 cores per subplot for each 10 cm layer were recorded before homogenisation. The soil core layers then were homogenised by grinding and sieving two consecutive times with dry ice. One aliquot of at least 400 g frozen homogenised soil was stored deep frozen for analysis. A second aliquot of at least 400 g was stored deep frozen as retained sample.

Sample extraction and determination of residues was performed according to the analytical method described in DOW AgroSciences Study No. 120612 as provided by Dow AgroSciences LLC. Quantification was performed by use of LC-MS/MS detection. The limit of quantification (LOQ) of the analytical method for soil was 0.5 µg/kg with a limit of detection (LOD) set at 0.15 µg/kg (30 % of the LOQ). All 0-10 cm, 10-20 cm and 20-30 cm horizons were analysed. If detectable residues were found in 20-30 cm horizon, then the following deeper horizon was analysed.

Results

Residue levels decline steadily to below 10% of initial residue within 30 days. Only little transfer into lower layers occurred. The residue concentrations in Spanish soil are presented in Table 8.1.41.

Table 8.1.41. Residues of clopyralid in Canals, Spain

		Residues of clopyralid [µg/kg] at sample collection dates[1, 2, 3]											
Depth [cm]	**Subplot**	**0-7 DBA**	**0**	**3**	**7**	**9**	**15**	**20**	**30**	**43**	**62**	**90**	**120**
0-10	1	n.d.	83.272	60.684	80.529	40.911	40.313	13.29	< 0.5	< 0.5	< 0.5	n.d.	n.d.
	2		88.226	95.12	73.077	84.747	34.13	9.837	< 0.5	0.661	n.d.	n.d.	n.d.
	3		110.86	90.145	102.94	84.951	32.842	15.024	0.558	0.798	1.236	0.789	n.d.
10-20	1	n.d.	< 0.5	< 0.5	< 0.5	0.601	17.573	12.49	0.502	0.708	n.d.	n.d.	n.d.
	2		< 0.5	< 0.5	< 0.5	0.559	29.658	24.277	0.7	< 0.5	0.598	n.d.	n.d.
	3		n.d.	< 0.5	< 0.5	4.133	36.93	18.702	1.335	< 0.5	1.222	n.d.	n.d.
20-30	1	n.d.	n.d.	n.d.	n.d.	n.d.	< 0.5	n.d.	1.168	< 0.5	0.533	n.d.	n.d.
	2		n.d.	n.d.	n.d.	n.d.	< 0.5	1.101	0.944	n.d.	0.574	n.d.	n.d.
	3		n.d.	n.d.	n.d.	n.d.	< 0.5	3.323	0.776	< 0.5	1.875	n.d.	n.d.
30-40	1						< 0.5.		1.456	n.d.	n.d.		
	2						n.d.	n.d.	0.816		n.d.		
	3						n.d.	n.d.	n.d.	n.d.	n.d.		
40-50	1						n.d.		0.597	n.d.	n.d.		
	2						n.d.	n.d.	0.695		n.d.		
	3						n.d.	n.d.	n.d.	n.d.	n.d.		
50-60	1								n.d.				
	2								< 0.5				
	3							n.d.					
60-70	1								n.d.				
	2								n.d.				
	3												
80-90	1								n.d.				
	2								n.d.				
	3												
90-100	1								n.d.				
	2								n.d.				
	3												

1 More than one residue concentration for a subplot-sample date combination indicates analytical replicates. These are not true replicates.

2 n.d. = not determined

3 On sample collection dates 0-7 DBA and 0 DAA, only 30 cm soil cores had been drawn.

RMS comments and evaluation:

The new field dissipation study on clopyralid in Spain was evaluated by the RMS. Several slight deviations from the study protocol during the study period were reported, e.g. adjusting the plot preparation, but it was assessed that the deviations had no impact on the study outcome. It is considered appropriate to use the earlier single formulation GF-1966 containing clopyralid as the only active substance in field dissipation studies instead of the current, more complex formulation GF-1374. The final report of the study was submitted in March 2016.

The study was evaluated by the RMS as well conducted in accordance with test guidelines and the GLP, clearly reported and the results are considered as valid for the kinetic evaluation and risk assessment, as presented in a separate report of Robinson 2016 (IIA 7.1.1.2.2./07) below.

Similarly to the previous study, another new field dissipation study on clopyralid in Southern France was submitted by the Notifier to address the Southern EU conditions. This report was evaluated by the RMS.

CA 7.1.1.2.2/6 - Clopyralid Technical - Field dissipation in soil - S France

Report	[IIA 7.1.1.2.2/06], Kröger, F. 2016b
Report title	Soil dissipation study with one spring application of GF-1966 (Clopyralid) at one site to bare soil in South Europe in 2015.
DAS Study number	Eurofins Agroscience Services, Stade, Germany; Eurofins Study S15-02992. DAS Study No. 150673.
Guidelines	SETAC 1995 (excluded calculation of DT50) SANCO/3029/99 rev. 4: EU guidance document for generating and reporting methods of analysis in support of pre-registration data requirements. Regulations (EU) 283/2013 and 284/2013 implementing Regulation (EC) 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC. EFSA Guidance Document for evaluating laboratory and field dissipation studies to obtain DegT50 values of active substances of plant protection products and transformation products of these active substances in soil. EFSA Journal 2014;12(5): 3662. ISO 10381-6:2009 (handling & storage soil for assessment of microbial biomass) OECD 217 US EPA (Oct 2008). Fate, Transport and Transformation Test Guidelines. OPPTS 835.6100. Terrestrial Field Dissipation
GLP	Yes

A field dissipation study was conducted with clopyralid on bare ground test plots in Southern France in 2015. One site was considered: Elne, France. One plot divided into three sub-plots was installed. The soil was characterised as presented in Table 8.1.42.

Table 8.1.42. Soil properties: Elne, Southern France

		0-30 cm depth	30 – 60 cm depth	60 – 100 cm depth
Soil type (USDA) [%]	Sand:	29.2	23.2	22.7
	Silt:	56.1	56.6	59.8
	Clay:	14.7	20.2	17.5
pH –value ($CaCl_2$)		6.72	7.23	7.15
pH –value (H_2O)		6.32	7.24	4.76
Cation Exchange Capacity [meq/100g]		11.7	14.2	14.5
TC [%]		1.3	0.30	0.32
TOC [%]		1.1	<0.3	<0.3
C org [%]		1.9	<0.5	<0.5
USDA classification		silt loam	silt loam	silt loam

Clopyralid was applied formulated as GF-1966 at a nominal rate of 200 g ae/ha on 29 May 2015. The product GF-1966, containing 950 g/kg nominal of the active ingredient (a.i.) Clopyralid-olamine which is equivalent to 720 g/kg of the acid equivalent (a.e.) Clopyralid, was applied at the field site to bare soil on the treated plot using a calibrated boom sprayer. The nominal application rate was 277.78 g product/ha (equivalent to 200 g Clopyralid/ha nominal) with a target water volume of 400 L/ha. To verify the spray application, deposition trays were placed on the soil surface. The actual application rates were determined by quantifying the amount of spray discharged ranged from average values of 199.4 to 216.5 g a.e./ha.

Immediately after application of the test item and before subsequent soil sampling, the control plot and the treated plot were covered with a thin layer of sand to protect the applied product from the sun. Immediately after application of the sand cover and the first soil sampling 5.1 mm were irrigated to the treated and untreated plot to minimize potential surface processes.

No tillage or fertilization was performed during the course of the study and no crops were grown throughout the trial. The plots were kept generally free of weeds via the application of glyphosate. Rainfall was supplemented with irrigation to compensate the precipitation compared to ET0 values in case of dryer than normal conditions. The total amount of irrigation (average) was 188.1 mm.

After application on 29 May 2015 soil residue samples were taken immediately after application and at 3, 7, 10, 13, 21, 28, 45, 60, 94, 117, 152 and 180 DAA. Since no residues could be detected in the 117 DAA samples, the sample preparation and analytical phase was stopped after the 117 DAA samples and study data is only reported up to and including the 117 DAA sampling (sampled on 23 Sep 2015).

Residue analysis was performed according to the analytical method of Dow AgroSciences LLC. Quantification was performed by use of LC-MS/MS detection. The limit of quantification (LOQ) of the analytical method was 0.5 µg/kg a limit of detection (LOD) set at 0.15 µg/kg (30 % of the LOQ).

Results

The residues in soil samples are presented in Table 8.1.43. With the exception of 0 DAA and one replicate sample at 21 DAA no transfer below 20 cm had occurred. However, the data shows a large variation. First analyses at 0 DAA showed low levels. Analysis of the retain samples yielded higher though still lower than could be expected. Comparison with the tray samples could not show that application of test substance had been irregular. The following to sampling dates, 3 and 7 DAA, show a steady decline to low residue levels. However, at 10 DAA residue levels increase again and peak at 13 DAA. Afterwards residue declines again. This pattern cannot be explained. All samples had been re-analysed but initial results had been confirmed. It could not been shown that samples had been interchanged accidentally, nor that test substance could have entered the field via drift from neighbouring fields.

Table 8.1.43. Residues of clopyralid in Elne, France

		Residues of clopyralid [µg/kg] at sample collection dates[1, 2, 3]											
Depth [cm]	**Subplot**	**0-7 DBA**	**0**	**3**	**7**	**9**	**15**	**20**	**30**	**43**	**62**	**90**	**120**
0-10	1	0.572 n.d.	61.132 73.699	7.885 8.982	5.751 5.880	19.062 19.399	102.582 102.005	49.458	35.947	44.305 41.276	9.387	*2.075*	n.d.
	2		62.238 88.517	55.569 62.005	5.465 6.654	37.457 35.672	74.786 76.711	37.08	21.063	12.915	35.168 39.562	*3.385*	n.d.
	3		39.897 71.745	31.32 41.396	18.753 23.082	14.139 15.134	65.636 82.407	68.461 53.104	34.445	62.392 53.645	9.02	*11.838*	n.d.
10-20	1	n.d.	0.967 1.043	< 0.5	n.d. n.d.	< 0.5	n.d. n.d.	1.171	n.d.	n.d.	n.d.	n.d.	n.d.
	2		1.425 1.673	n.d. n.d.	n.d. n.d.	n.d. n.d.	n.d. n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	3		0.717 0.855	1.383 1.667	n.d. n.d.	n.d. n.d.	n.d. n.d.	n.d.	n.d.	n.d.	n.d.	< 0.5	n.d.
20-30	1	n.d.	1.049 0.885	n.d. n.d.	n.d. n.d.	n.d. n.d.	n.d. n.d.	2.869	n.d.	n.d.	n.d.	n.d.	n.d.
	2		0.879 1.289	n.d. n.d.	n.d. n.d.	n.d. n.d.	n.d. n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	3		< 0.5	n.d. n.d.	n.d. n.d.	n.d. n.d.	n.d. n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
30-40	1			n.d.	< 0.5	n.d.	n.d.	< 0.5					
	2			n.d.	n.d.	n.d.	n.d.	n.d.					
	3			n.d.	n.d.	n.d.	n.d.	n.d.					
40-50	1			n.d.	< 0.5	n.d.	n.d.	n.d.					
	2			< 0.5	n.d.	n.d.	n.d.	n.d.					
	3			n.d.	n.d.	n.d.	n.d.	n.d.					
50-60				n.d.	< 0.5	n.d.	n.d.						
				n.d.	n.d.	n.d.	n.d.						
				n.d.	n.d.	n.d.	n.d.						
60-70				n.d.	n.d.	n.d.	n.d.						
				n.d.	n.d.	n.d.	n.d.						
				n.d.	n.d.	n.d.	n.d.						

1 More than one residue concentration for a subplot-sample date combination indicates analytical replicates. These are not true replicates.

2 n.d. = not determined

3 On sample collection dates 0-7 DBA and 0 DAA, only 30 cm soil cores had been drawn.

RMS comments and evaluation:

The new field dissipation study on clopyralid in Southern France was evaluated by the RMS. For the test conditions, reference was made to a similar ongoing field study in Spain (Kröger 2016a), but a summary is presented above. Several slight deviations from the study protocol during the study period were reported, e.g. delayed precipitation compensation by irrigation due to a malfunction of weather data connection for several days, but it was assessed that the deviations had no impact on the study outcome so far. It is considered appropriate to use the earlier single formulation GF-1966 containing clopyralid as the only active substance in field dissipation studies instead of the current, more complex formulation GF-1374. The fluctuation of the concentrations in the topsoil could not be explained, and the statistical fit of the endpoints from this study is not acceptable and the DT_{50} value obtained not appropriate to be used in the risk assessment.

The field data available enabled the kinetic evaluation in Southern European conditions, as presented by the Notifier below (Robinson 2016; see 7.1.1.2.2/7). No further data in addition to the final reports mentioned above are required.

CA 7.1.1.2.2/7 - Clopyralid Technical - Kinetic evaluation of field dissipation studies

Report	[IIA 7.1.1.2.2/07], Robinson, P. 2016
Report title	Estimation of kinetic endpoints for clopyralid from soil dissipation studies from soil dissipation studies (Southern Europe).
DAS Study number	Dr. Knoell Consult Report number 104115-1 DAS Study No. 160486.
Guidelines	FOCUS Kinetics (2006, 2014) EFSA Guidance Document for evaluating laboratory and field dissipation studies to obtain DegT50 values of active substances of plant protection products and transformation products of these active substances in soil. EFSA Journal 2014;12(5): 3662.
GLP	No

The aim of this evaluation was to conduct a kinetic modelling analysis for clopyralid using residue data from the two field soil dissipation studies in Southern EU, in order to derive persistence endpoints that can be used for comparison against regulatory trigger values, and modelling endpoints that can be used for calculating predicted environmental concentrations (PECs) in various environmental compartments.

Materials and methods

Two tailored field dissipation studies to derive DegT50 were considered for the evaluation: in Spain (Kröger 2016a; 7.1.2.2.1/5) and in Southern France (Kröger, 2016b; 7.1.2.2.1/6). Values between the LOQ and LOD were set to ½(LOQ+LOD). Values below LOD were replaced by half the LOD. If the concentrations of the applied substance in soil declined to values below LOD, the curve was cut off after the first value below LOD, unless detections above LOQ were made later in the experiment (FOCUS, 2006, 2014). These corrections were performed along the time course as well as with depth along the soil layers. Changes in soil density with depth were accounted for using the measurements of the weight of moist cuttings (10 cm segments) of the soil cores from each sub-plot and their respective moisture contents. Total core residues (µg/kg) were converted to total aerial concentrations (g/ha) for each sub-plot and sample time using details of the specific borer liner's cross-sectional area.

According to FOCUS (2006, 2014), true replicates at each sampling point should be used for the kinetic evaluation if available. In each study there were three field sub-plots; these were considered to be true replicates. Where multiple values at a sub-plot were given for a single depth interval, these were regarded as analytical replicates and averaged prior to summing residues.

The evaluation followed the recommendations of FOCUS (2006, 2014). Persistence endpoints were evaluated according to best-fit kinetics. The evaluation for modelling endpoints followed the recommendations of FOCUS (2006, 2014) and EFSA (2014). A time step normalisation method was applied to the data (standard reference conditions of 20°C and 100% field capacity). For the new tailored field study trials (Kröger, 2016a, 2016b), actual daily soil moisture and temperature data were measured at the field sites. These data were used in the time step normalisation.

Results

Persistence endpoints

As presented in Table 8.1.44 and Figure 8.6, the dissipation of clopyralid in the two trials (Kröger, 2016a, 2016b) can best be described by SFO kinetics. However, as the visual and statistical fit (χ^2 = 49.3%) for the trial from Southern France (Kröger, 2016b) is very poor, only the persistence endpoint obtained from the Spanish soil (Kröger, 2016a) was considered as valid.

Table 8.1.44. Comparison of the various models for persistence

Trial	SFO		FOMC		DFOP		Best-fit persistence model
	DT_{50}	χ^2	DT_{50}	χ^2	DT_{50}	χ^2	
Kröger (2016a)							
Canals, Spain	**13.7**	**19.2**	10.3	20.0	13.7	21.0	SFO
Kröger (2016b)							
Elne, Southern France	***(49.3)[a]***	***(49.3)[a]***	*(40.9)[a]*	*(51.5)[a]*	*(26.1)[a]*	*(52.0)[a]*	*(SFO)*

[a] Model fit not statistically or visually acceptable (according to FOCUS, 2006, 2014)

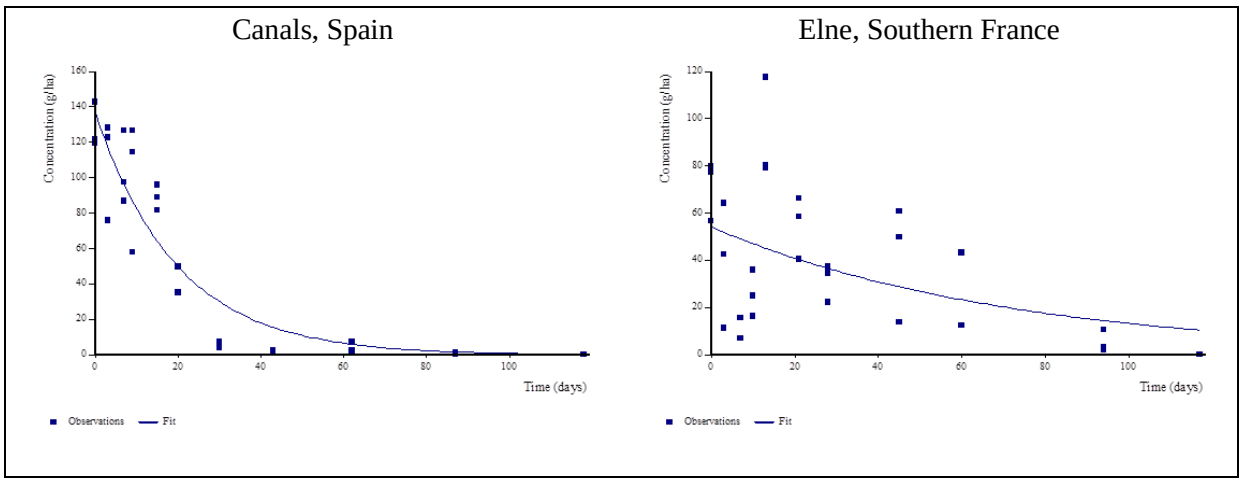


Figure 8.6. Persistence endpoint best-fit kinetics (Kröger, 2016a, 2016b)

Thus, the persistence endpoints of clopyralid in Southern European conditions can be summarized as presented in Table 8.1.45.

Table 8.1.45. Summary of the best-fit models for persistence

Trial	Model	DT_{50} (d)	DT_{90} (d)
Kröger (2016a)			
Canals, Spain	SFO	13.7	45.4
Kröger (2016b)			
Elne, Southern France	*(SFO)*[a]	*(49.3)*[a]	*(164)*[a]

[a] Model fit not statistically or visually acceptable (according to FOCUS, 2006, 2014)

Modelling endpoints

The modelling endpoints derived from field dissipation studies conducted in Spain and Southern France are presented in Table 8.1.46 and illustrated in Figures 8.7 and 8.8.

Table 8.1.46. Comparison of the various models for modelling

Trial	SFO		FOMC		DFOP		Selected model for modelling endpoint
	DT_{50}	χ^2	DT_{50}	χ^2	DT_{50}	χ^2	
Kröger (2015)							
Canals, Spain	12.3	14.4	-	-	-	-	SFO
Kröger (2016b)							
Elne, Southern France	*(57.1)*[a]	*(49.1)*[a]	*(16.9)*[a]	*(54.4)*[a]	*(28.6)*[a]	*(51.6)*[a]	*(72.6)*[a]

[a] Model fit not statistically or visually acceptable (according to FOCUS, 2006, 2014)
'-' = model not tested since SFO was deemed to be acceptable according to FOCUS, 2006, 2014

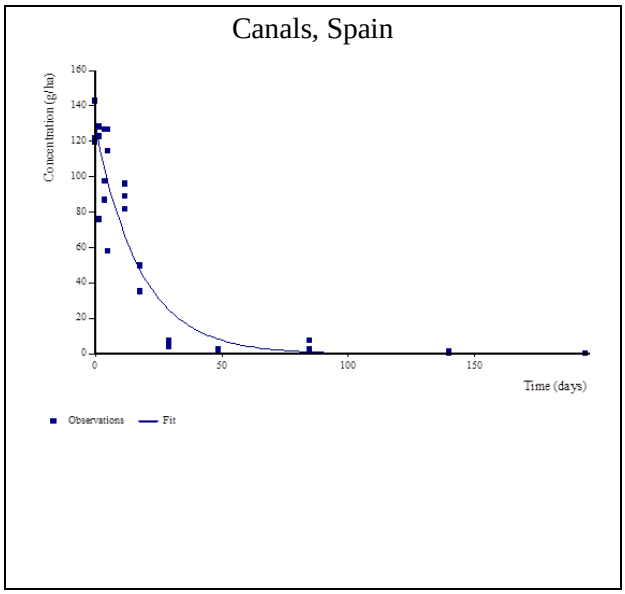


Figure 8.7. Modelling endpoint kinetics in Spain (Kröger, 2016a)

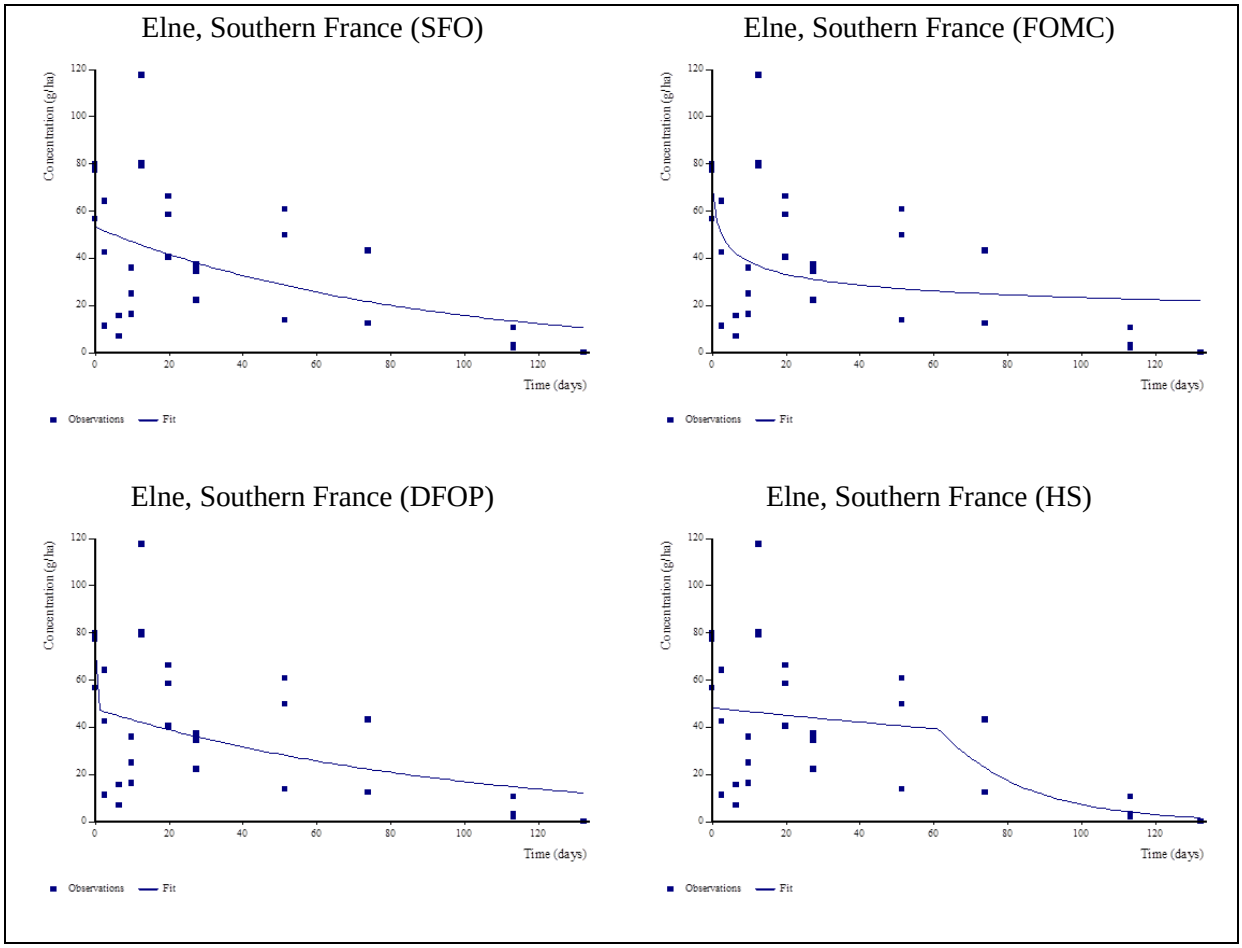


Figure 8.8. Modelling endpoint kinetics in Southern France (Kröger, 2016b)

RMS comments and evaluation:

Because the results of separate field dissipation studies in Southern European conditions were not available when the dossier was prepared, the kinetic evaluation of these studies is performed separately. The kinetic calculation of the field dissipation endpoints of clopyralid in Southern European conditions, as presented by the Notifier was assessed by the RMS. The kinetic calculation was performed according to FOCUS guidance, and the outcomes as summarized above are considered acceptable.

The DT_{50} and DT_{90} values could reliably be derived from the Spanish data, while the fluctuation of the concentrations found in the French soil could not be explained, and therefore the endpoint values are considered not valid and inappropriate for risk assessment. The $DT_{50field}$ values in Southern European conditions are in line with those obtained in Northern and Central Europe, as originally presented during the first evaluation of clopyralid (mean $DT_{50field}$ of 11 days from the studies Rawle & Yon 2002a-b), recently amended by Kröger (2015) and recalculated by Robinson (2015). The individual values at different locations remain within the same range in all studies. The data is adequate for the renewal for the approval of clopyralid, and no further data are required.

No further data are required other than the final reports of the field dissipation studies in Spain and Southern France, as mentioned above.

Overall conclusions on the field dissipation of clopyralid in soil

Based on the first evaluation of clopyralid (2003), following conclusions were made on the field dissipation of clopyralid in European conditions:

- The $DT_{50(field)}$ and $DT_{90(field)}$ values for clopyralid in five dissipation trials following spring and autumn application in Northern Europe (which was considered to represent a worst-case for dissipation) ranged from 2 to 24 days (mean 11 days), and from 6 to 79 days (mean 38 days), respectively.
- The correlation co-efficients (R^2 = 0.715-0.976) meant that the dissipation data was a reasonable to good fit to first-order kinetics.
- The soil dissipation studies have shown that the $DT_{90(field)}$ is less that 1 year so the potential for clopyralid to accumulate in soil following successive application is not necessary to be investigated further.

For the renewal of the approval of clopyralid, three new studies were added to the data base, with field degradation data from three more locations in Northern and Central European conditions, and from two locations in Southern Europe. This data was added to the knowledge base, and the kinetic evaluations were performed according to latest guidance, separately for the N and C EU and for the S EU field conditions. Based on the recalculations, following conclusions can be made:

- Dissipation half lives (persistence endpoints) ranged from 0.16 to 23.7 days (DT_{50}), with the DT_{90} of 12 - 70 days in Northern and Central European conditions.
- Degradation half lives (modelling endpoints) ranged from 2.07 to 13.5 days ($DegT_{50matrix}$), with a geometric mean value of 6.2 days in Northern and Central European conditions.
- Dissipation half life of 14 days with the DT_{90} of 45 days (persistence endpoint) and DT_{50} of 12 days to be used in modelling was obtained in Spain, while the Southern French data were not appropriate for deriving valid DT_{50} and DT_{90} values.
- SFO kinetics characterise the degradation of clopyralid in soil.
- These data indicate that clopyralid would be readily degraded in the field.

RMS comments and evaluation:

No field dissipation data with the current representative formulation GF-1374 are available, but field dissipation studies with clopyralid formulated as GF-1966 (earlier formulation representative to support the original Annex I inclusion of clopyralid, containing clopyralid as the only active substance) were conducted as presented above. This is considered acceptable, as the current representative formulation is a mixture of three active substances and thus more complex for assessing the environmental fate of the active substance than the earlier single active formulation.

Because the results of separate studies in Southern European conditions were not available when the dossier was prepared, separate reports on kinetic evaluations were submitted for different parts of Europe. No further data in addition to the final reports mentioned above are required.

In January 2017 the Dow AgroSciences informed the RMS about two new field dissipation studies in Markgröningen, Germany, and Meauzac, S-France, for which the final study reports are expected in March, 2017, and offered to update the risk assessments accordingly. The two new trials consolidate the existing data package. After consultation with EFSA, the RMS could not postpone submitting the dRAR in order to include these sites in the kinetic evaluation of soil dissipation studies at this stage, but recognized that further data exists, which should be taken into account later, for which an appropriate evaluation period has to be ensured. The expected workload will be unmanageable during the limited time period offered for reflecting the peer review comments.

(Ahrens, C. and Kröger, F. 2017: Field soil dissipation study with one spring application of GF-1966 (Clopyralid) at one site in North EU and one site in South EU to bare soil in 2016 – 2017. DAS Study ID 160394)

The soil degradation data available indicate that clopyralid is readily degraded in the field in various conditions throughout the Europe.

B.8.1.1.6. Soil residue studies

Soil residue studies are required when the $DT_{50(lab)}$ is greater than one third of the period between application and harvest and where uptake by the succeeding crop is possible. The mean $DT_{50(lab)}$ for clopyralid is 38 days which will likely be less than one third of the application to harvest period. Therefore, information on soil residues would not normally be required. However, should any data be required, it is considered that soil residues at the time of sowing or planting of a succeeding crop can be reliably estimated from the soil dissipation data generated in Europe, and, consequently, additional soil reissue studies have not been carried out.

RMS comments and evaluation:

The justification presented by the Notifier is acceptable and no further studies are required to support the renewal for the approval of clopyralid.

B.8.1.1.7. Soil accumulation studies

The soil dissipation studies have shown that the $DT_{90(field)}$ is <1 year so the potential for clopyralid to accumulate in soil following successive applications has not been investigated further.

RMS comments and evaluation:

The justification presented by the Notifier is acceptable and no further studies are required to support the renewal for the approval of clopyralid.

B.8.2. ADSORPTION, DESORPTION AND MOBILITY IN SOIL

B.8.2.1. Adsorption and desorption in soil

Two studies to address this point were presented in the dossier for the Approval of Clopyralid submitted in 30 April 2002, evaluated in the DAR (2003) and peer review at EU level. One of the studies did not fulfill the GLP requirements and had some deficiencies, and thus was not considered as valid for AIR3 evaluation. The other study (Reeves & Mittelstaedt 2002) is acceptable, and the results are still valid for decision making. As the study was evaluated in the DAR, the evaluation is not repeated here.

CA 7.1.3.1. Adsorption/Desorption of Clopyralid in Soil

Report	IIA 7.1.3.1/01, Reeves, G. L. & Mittelstaedt, W., 2002
Report title	Adsorption/Desorption of Clopyralid in Soil: Corrections to Final Report of Study DW 2/92 from August 1993
DAS Study number	GHE-P-9762
Guidelines	OECD 106 (1981)
GLP	Yes

Methods

The sorption of [2,6-pyridinyl-^{14}C]-clopyralid has been investigated in four agricultural soils using the batch equilibrium technique. The characterisation data for the soils used for the main study (0-30 cm depth) are summarised in Table 8.2-1. The soils selected displayed a range of parameters, i.e. sand 4-72%, clay 5-42%, pH 5.3-7.2, and organic carbon content 0.89-2.06%. Soils were sieved (2 mm) prior to use.

Table 8.2-1 Characterisation data for European soils used to investigate the sorption of clopyralid

Country of origin	Germany	Germany	Germany	Germany
Location	Merzenhausen	Kaldenkirchen	Lanna	Overhetfeld
Soil textural classification (quoted BBA)	Silt loam	Loamy sand	Clay loam	Loamy sand
Textural analysis (%)				
Sand (63-2000 µm)	4.1	71.8	14.6	71.6
Silt (2-63 µm)	81.6	22.8	43.5	22.7
Clay (<2 µm)	14.3	5.4	41.9	5.7
Textural classification (UK)	Silt loam	Sandy loam	Clay	Sandy loam
pH ($CaCl_2$)	7.19	5.34	6.62	6.49
Organic matter (%)[1]	1.72	1.69	3.55	1.60
Organic carbon (%)	1.00	0.98	2.06	0.93
CEC (mEq/100 g)	10.08	3.31	18.64	5.56

[1] *Calculated as organic carbon x 1.724*

The definitive study was conducted by equilibrating soil slurries, containing 20 mL sterile 0.01M calcium chloride and 20 g soil (dry weight) i.e. a 1:1 soil/solution ratio, at 25°C in the dark for 16 hours. The soil slurries were pre-equilibrated with blank calcium chloride solution prior to addition of the test compound. Adsorption isotherms were determined by treating the calcium chloride solutions with [2,6-pyridinyl-^{14}C]-clopyralid (ref no.GHD-1235-94b, specific activity 5095.21 kBq/mg, RCP 98.5%), augmented with non-radiolabelled clopyralid (batch AGR 228018, purity 99%), at nominal concentrations of 0.001, 0.01, 0.10 and 1.0 µg/mL.

After the equilibration period the soil slurries were separated using centrifugation and filtration. The radioactivity in the aqueous layer was quantified by LSC. The radioactivity content of the soil layer was determined indirectly by subtracting the amount in the aqueous layer from the total radioactivity applied.

No desorption steps were carried out as the level of clopyralid adsorption was too low.

To ascertain the stability of clopyralid over the study period, sub-samples of the aqueous layer were analysed by TLC at the end of the study. Also at the end of the study, at the top concentration for each soil the soil layer was dried and quantified by combustion analysis to obtain a mass balance.

In a preliminary study, prior to the definitive adsorption study, the equilibration time (i.e. the time taken for the adsorption process of the test compound to plateau in the soil slurries) was determined for all soils. Soil slurries were prepared with 20 mL 0.01M calcium chloride containing clopyralid at a single concentration (1.0 mg/L nominal). At pre-defined intervals over a period of 48 hours whole samples were taken for analysis by LSC and the amount of test compound adsorbed determined as a percentage of the initial concentration. As part of this investigation control samples containing clopyralid in the absence of soil were also processed to ascertain the level of clopyralid adsorbed to the containers.

In the preliminary study the optimal soil/solution ratio was investigated by mixing varying amounts of soil (20, 10, 4 and 2 g dry weight) with 20 mL sterile 0.01M calcium chloride containing clopyralid at a single concentration (1.0 mg/L nominal). The slurries were shaken over a period of 48 hours. At intervals of 24 and 48 hours the slurries were centrifuged and aliquots removed from the aqueous layer for quantification by LSC.
In a supplementary study, the effect of pH on adsorption of clopyralid to soil was investigated. Selected soil samples were augmented by addition of HCl and re-subjected to the adsorption test described above.

The original experimental data is presented in Ref. K60, and the updated report K79 contains the recalculation of the results. According to the Notifier, the recalculation was necessary due to a number of errors in th original report.

Results

Quantification of the 0.01M calcium chloride solutions showed actual concentrations of clopyralid of 0.0011, 0.0113, 0.1135 and 1.0233 mg/L.

The results of the **preliminary study** with regards to the optimal equilibration time and soil to solution ratio were inconclusive. The levels of the clopyralid measured in the aqueous layer of the soil slurries after shaking were greater than the initial concentration of the stock solutions. This was probably due to the low amounts adsorbed by the soil and errors involved with the small aliquot size taken from the aqueous layer for quantification by LSC. For the definitive study, a soil/solution ratio of 1:1 was used based on the low amounts adsorbed, and an equilibration time of 16 hours was arbitrarily selected. Based on the results of other studies (Ref. K46) an equilibration time of 16 hours should be sufficient in order for the soil slurries to equilibrate.

Freundlich adsorption isotherms were determined for the four soils from the Ap soil layer and recalculated in the new report K79. The adsorption of clopyralid was found to give a good correlation to the Freundlich equation (R^2 = 0.90 to 0.99). The soil partition coefficient (K_d) for adsorption ranged from 0.032 to 0.151 mL/g for all soils at all concentrations used for this study. Normalised for organic carbon content, the adsorption coefficient (K_{OC}) was 3.43 to 7.34 mL/g. The Freundlich adsorption coefficient K_f for adsorption was determined to be 0.0054 to 0.0267 mL/g, and the Freundlich exponent (1/n) was 0.3881 to 0.8602. The **recalculated results** for the adsorption phase are summarised in Table 8.2-2.

Table 8.2-2. Soil adsorption parameters for clopyralid in four European soils

Soil name	K_d (mL/g)	K_f (mL/g)	Freundlich exponent (1/n)	R^2	K_{OC} (mL/g)
Merzenhausen	0.051	0.0057	0.5577	0.99	5.06
Kaldenkirchen	0.048	0.0267	0.8602	0.99	4.76
Lanna	0.151	0.0054	0.3881	0.90	7.34
Overhetfeld	0.032	0.0125	0.7830	0.99	3.43
Mean	*0.071*	*0.0126*	*0.6473*	-	*5.15*

Adsorption of clopyralid to soil was low for all soil types. There appeared to be no significant correlation between adsorption and silt or clay content, organic carbon content or soil pH. The sorption data indicated that clopyralid would be **classified as very mobile** according to most classification schemes.

For the **supplementary investigation into the effect of pH**, the Kaldenkirchen soil from the Bv 3 horizon (original pH 6.12) and the Lanna soil from the Ap horizon were supplemented with HCl. For the Kaldenkirchen soil, adsoprtion increased substantially at lower pH values. For the Lanna soil, additions of acid had minimal effect on the soil pH, however, a wide range of values were obtained for the Freundlich soil adsorption coefficient (Table 8.2-3).

Table 8.2-3. Investigation of pH effect on soil adsorption of clopyralid

Soil name	pH	K_d (mL/g)	K_f (mL/g)	Freundlich exponent (1/n)	R^2	K_{OC} (mL/g)
Kaldenkirchen (Bv3 horizon)	4.06	0.059	0.0587	0.9984	0.99	98.64
	5.63	0.032	0.0385	1.0426	0.99	52.65
Kaldenkirchen (Ap horizon) [1,2]	5.34	0.048	0.0267	0.8602	0.99	4.76
Lanna (Ap horizon)	6.21	0.301	0.0720	0.7121	0.99	14.61
	6.68	0.232	0.0355	0.6552	0.97	11.25
Lanna (Ap horizon) [1]	6.62	0.151	0.0054	0.3881	0.90	7.34

[1] *Result from main study included for comparison*
[2] *Soil sample relates to a different soil horizon*

As part of the isotherm determination the recovery of clopyralid was quantified for three out of the four soils used. The **mass balance** obtained ranged from 87.9% to 105.0% AR (mean 98% AR) indicating a complete recovery of the test compound under the conditions of the study. As part of the preliminary study, control samples containing clopyralid in the absence of soil were processed. Although no results are reported it is assumed that any significant adsorption to the containers would have been highlighted. It is, therefore, assumed that in conjunction with the complete recovery of the test compound, adsorption to the containers under the conditions of the study was negligible.

TLC analysis of the aqueous layer at the end of the study indicated that clopyralid was stable under the conditions of the test over the study period.

Comments

The updated report (K79) contains a recalculation of the sorption data for clopyralid since the original data presented in report GHE-P-3531 (Ref. K60) was found to contain a number of errors. According to the author, it was not possible to recalculate the data by using the original report, and so the raw data had to be used. The report K79 therefore supersedes the original report and presents the newly calculated values, but it does not contain any new experimental data.

The original study appeared well performed and reported, however due to the errors the calculation of the results was not reliable. The study was in compliance with GLP. The recalculation report was also well prepared, in compliance with GLP and acceptable.

Although soil samples were also taken from deeper soil horizons for the Kaldenkirchen (Bv3) and Overhetfeld (Ah/Bv + Sw/Bv, Sd/Bt1 and Cv) soils, no further results on these soils were reported. This data is, however, not required, since this is additional work to the guideline requirement.

The adsorption of clopyralid in soils is very low.

RMS comments and evaluation:

The study was previously evaluated in the DAR (2003), as presented above. The results are in line with the new study, considered as valid and can thus be used in the risk assessment together with

new data available. Therefore the knowledge base available on the sorption of clopyralid in a variety of soils is adequate.

The Notifier submitted a new adsorption/desorption study for the AIR3 evaluation of clopyralid. This study is evaluated below.

CA 7.1.3.1. [14C]-Clopyralid: Adsorption to and Desorption from Five Soils

Report	IIA 7.1.3.1/02, Buntain, I., Simmonds, M. 2015
Report title	[^{14}C]-Clopyralid: Adsorption to and Desorption from Five Soils
DAS Study number	Battelle UK Ltd., Chelmsford, Essex, UK; Lab Study No. YR/13/016 DAS Study No. 130699; 25 February 2015
Guidelines	OECD 106 US EPA OSCPP 835.1230, OPPTS 835.1230
GLP	Yes

Materials and methods

The adsorption and desorption of clopyralid-2,6-^{14}C was studied in five soils from the EU and the USA. The test substance was radioactively labeled as illustrated in Figure 8.9. The radiochemical purity of the test substance was 99.0 %, and its specific radioactivity was 35.0 mCi/mmol (6.68 MBq mg-1).

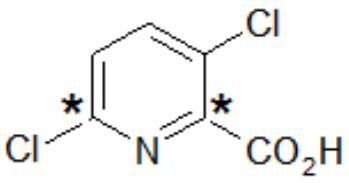


Figure 8.9. The Position of labelling (*) of clopyralid used in the adsorption/desorption test.

The details of the soil collection and storage are given in Table 8.2.4. and the properties of the soils are characterized in Table 8.2.5.

Table 8.2.3. Description of soil collection and storage

Description	Calke sandy loam	Longwoods sandy loam	LUFA 2.1 loamy sand	Quilen loam	DU-L-PF clay loam
Geographic location	Calke, Derbyshire, UK. 52°47.419'N 1°27.940'W	Longwoods, Lincolnshire, UK. 53°7'6.6''N 0°25'26.7''W	Dudenhofen, Rheinland-Pfalz, Germany	Quilen, Pas de Calais, France. 50°31'45.2''N 1°55'34.4''E	Grand Forks, North Dakota, USA. 47°44.842N 97°46.512W
Pesticide use history at the collection site	None used for several years				
Collection procedures	By spade from shelf cut into topsoil	By spade from shallow pit in topsoil	No details provided	Soil sampled from LRA soil nursery (stored under grass at 20cm)	By shovel
Sampling depth (cm)	10-20 cm	5-20 cm	*ca* 20 cm	10-20 cm	0-6 inches
Storage conditions	Ambient				
Storage length	< 3 months prior to use				
Soil preparation (e.g. 2 mm sieved; air dried etc.)	Sieved to 2 mm prior to use				

Table 8.2.4. Properties of the soils

Property	Calke sandy loam	Longwoods sandy loam	LUFA 2.1 loamy sand	Quilen loam	DU-L-PF clay loam
Soil texture (USDA)	sandy loam	sandy loam	loamy sand	loam	clay loam
% sand	75	73	85	40	39
% silt	14	14	10	39	33
% clay	11	13	5	21	28
Soil texture (ADAS)	sandy loam	sandy loam	loamy sand	clay loam	clay loam
% sand	71	69	85	38	37
% silt	18	18	10	41	35
% clay	11	13	5	21	28
pH (water)[1]	5.9	7.6	5.3	7.0	6.5
pH (calcium chloride)[2]	5.7	7.4	4.9	6.9	6.3
Organic carbon (%)	3.15	3.13	0.68	4.02	6.47
CEC (meq/100 g)	10.6	17.2	4.3	17.7	25.0
Moisture at 1/3 atm (%)	14.3	13.0	4.8	26.4	44.7
Bulk density (g/cm^3)	1.08	1.22	1.46	0.98	0.85
Biomass (mg microbial C/100 g or CFU or other)	not determined	not determined	not determined	not determined	not determined

[1] Determined with pH electrode in a 1:1 soil: water suspension (NUT.02.05)
[2] Determined with pH electrode in a 1:2 soil: 0.01M $CaCl_2$ suspension (NUT.02.80)

Preliminary (Tier 1 and Tier 2) tests were conducted to assess the sorption of the test item to the test vessels; to determine the background activity on the soil and the measurement of aqueous pH after contact with the soil; to determine the appropriate soil/solution ratio, the adsorption equilibration time and the amount of test material absorbed at equilibrium, the desorption equilibrium time and the stability of the test materials during the tests. All preliminary tests were conducted on the Lufa 2.1 loamy sand and Quilen loam soils, with the test material at a nominal concentration of 0.3 µg/mL.

The experimental conditions of the definitive study are described in Table 8.2.5. below for the adsorption phase, and in Table 8.2.6. for the desorption phase.

Quantitative measurement of radioactivity was carried out by liquid scintillation counting (LSC) following solubilisation of the samples in a suitable LSC cocktail (Irgasafe, Perkin Elmer Life Sciences (UK) Ltd). Samples were counted for 5 minutes or until 40,000 counts were accrued, whichever occurred first. Sample counts were automatically corrected for background from the scintillant and solvents present, and for quenching using pre-calibrated quench correction curves to convert cpm to quench-corrected dpm.

Table 8.2.5. Study design for the adsorption phase

Parameters		Description (for all soils)
Condition of soil (air dried/fresh)		Fresh, Soils were sieved to ≤ 2 mm. Before application soils were pre-equilibrated with 0.01M CaCl2 solution overnight
Have these soils been used for other laboratory studies? (specify which)		Not known
Soil (g/replicate, oven-dry weight)		Each test was performed in duplicate. 20 g ode of soil was used for each of the five soils.
Equilibrium solution used (name and concentration; eg: 0.01N $CaCl_2$)		0.01M aqueous $CaCl_2$ solution
Control used (with salt solution only) (Yes/No)		Controls without soil or test item were used in the preliminary studies only.
Test material concentrations	Nominal application rates (mg a.i./kg soil)	0.3, 0.1, 0.03, 0.01 and 0.003 mg L^{-1}
	Analytically measured concentrations (mg a.i./kg soil)	For Calke, LUFA 2.1 and Quilen soils: 0.27, 0.09, 0.028, 0.009 and 0.0028 mg L^{-1}. For Longwoods and DU-L-PF soils: 0.28, 0.10, 0.029, 0.010 and 0.0028 mg L^{-1}
Identity and concentration of co-solvent, if any		≤ 0.1% v/v acetonitrile
Soil:solution ratio		1:1 for all five soils. (20 g ode soil to 20 mL solution)
Initial pH of the equilibration solution, if provided		pH of 0.01M CaCl2 solution; 7.02-7.12: pH with soil but without test item; 5.51-7.23
No. of replications	Controls	None
	Treatments	Duplicate
Equilibration	Time	Pre-equilibration overnight (minimum 12 hours)
	Temperature (□C)	20 ± 2°C
	Darkness (Yes/No)	Yes
	Shaking method	End-over-end shaker
	Shaking time	24 hours for all soils
Method of separation of supernatant (eg., centrifugation)		Centrifugation
Centrifugation	Speed (rpm or g)	4000 rpm (3756 g)
	Duration (min)	10 minutes
	Method of separation of soil and solution	Decanting

Table 8.2.6. Study design for the desorption phase

Parameters		Description (for all soils)
Were the soil residues from the adsorption phase used?		Yes
Amount of test material present in the adsorbed state/adsorbed amount (mg a.i./kg soil)		0.0-38.8% depending on soil type and concentration
Number of desorption cycles		1
Equilibration solution and quantity used per treatment for desorption (eg., 0.01M $CaCl_2$)		The decanted solution was replaced by an approximately equal volume of fresh 0.01 M aqueous CaCl2 solution
Soil:solution ratio		1:1 for all five soils.
Replications	Controls	None
	Treatments	Duplicate
Desorption equilibration	Time	24 hours
	Temperature (□C)	20 ± 2°C
	Darkness	Yes
	Shaking method	End-over-end shaker
	Shaking time	24 hours for all soils
Centrifugation	Speed (rpm or g)	4000 rpm (3756 g)
	Duration (min)	10 minutes
	Method of separation of soil and solution	Decanting
Second desorption	Indicate if the method is the same as the first desorption cycle. Briefly describe the method, if different.	Non-applicable
n^{th} desorption	Indicate if the method is the same as the first desorption cycle. Briefly describe the method, if different.	Non-applicable

Following desorption, all tubes from the first experimental run with Calke, LUFA 2.1 and Quilen soils were solvent extracted. Approximately 20 mL of acetonitrile was added to each tube and the tubes weighed. The tubes were placed on the end-over-end shaker for ca 30 minutes, removed, reweighed, centrifuged for 10 minutes and the supernatants decanted. This procedure was repeated twice with 20 mL portions of acetonitrile/water/formic acid (50:50:1). The Quilen loam was additionally extracted with one portion of acetone/1N hydrochloric acid. Following removal of the extraction supernatant, the tube and soil pellet were re-weighed to enable the weight of each supernatant to be calculated. Aliquots of each supernatant were weighed and the radioactivity determined by LSC. All tubes containing soil were then allowed to air dry and reweighed without the cap prior to homogenisation and combustion. In Longwoods and DU-L-PF soils no solvent extraction was performed. At the end of the desorption phase the soils were combusted as for the first three soils but without any pre-drying.

HPLC analyses of all sample extracts were accomplished using the following conditions as described in Table 8.2.7.

Table 8.2.7. HPLC analysis of the soil samples in adsorption/desorption test.

Column	Kromasil C18, 5µm 250 x 4.6 mm i.d.		
Mobile Phase	A) Water + 0.2% phosphoric acid		
	B) Acetonitrile		
Gradient:	Time (min)	%A	%B
	0	95	5
	10	95	5
	30	0	100
	31	95	5
	35	95	5
Injection Volume	10 – 1000 µL		
Flowrate	1 mL min^{-1}		
Run Length	35 minutes		
Wavelength	230 nm		
Scintillant	Flologic, flowrate 1.5 mL min^{-1}		
[^{14}C]-Detection	Radiomatic 525TR or 625TR Radiodetector fitted with a 0.5 mL liquid flow cell utilising FLO-LOGIC 1:1 Liquid Scintillation cocktail at 1.5 mL per minute.		

Mass spectral analysis (LC/MS) for identification of the test item was accomplished in conditions as outlined in Table 8.2.8.

Table 8.2.8. Conditions of the LC/MS analysis of the soil samples in adsorption/desorption test.

HPLC conditions	Instrument	Agilent 1290 series consisting of Binary Pump, Thermostatic autosampler, Temperature controlled column oven and variable wavelength detector		
	Column	Kromasil C8 5 µm (250 x 4.6 mm)		
	Mobile Phase [A]	0.2% Acetic acid in water		
	Mobile Phase [B]	0.2% Acetic acid in acetonitrile		
	HPLC Gradient	Time	%A	%B
		0	80	20
		5	0	100
		12	0	100
		12.1	80	20
		15	80	20
	Flow Rate	1 mL/min with *ca* 100 µL/min into MS ion source.		
	Injection Volume	20 µL		
	UV Wavelength	254 nm		
	[^{14}C]-Detection	LabLogic β-Ram Model 3 Radiodetector fitted with a 0.5 mL liquid flow cell utilising FLO-LOGIC 1:1 Liquid Scintillation cocktail at 1.5 mL per minute.		
LC-MS conditions	Instrument	Thermo Q-Exactive Orbitrap Mass Spectrometer		
	Calibration	ESI +/- calibration performed at 3 day intervals using solutions provided by the instrument supplier.		
	Tune Parameters:			
	Ion Source	HESI (Heated Electrospray Ionisation)		
	Capillary Temperature	300ºC		
	Sheath Gas	65 (arbitrary unit)		
	Aux Gas	25 (arbitrary unit)		
	Probe Heater Temp.	350ºC		
	S-Lens RF Level	55 (arbitrary unit)		

The Detection limits (LOD, LOQ) for the Parent compound were calculated as described below.

LSC: LSC assays are background corrected. For the LSC counters used in this study, and when using a 5 minute counting time, this background has been shown to vary by ± 2.5 cpm for ten replicate assays of a single background vial. The expected variation in background corrected sample cpm is therefore:

For a typical quench of > 70%, this is also the expected variation in dpm. A background corrected LSC value of 3 x 3.5 dpm ~ 10 dpm therefore represents the limit of quantification.

The limit of Quantification as % AR equates to:

$$\frac{\text{LOQ}}{\text{specific activity}} = \frac{10 \text{ dpm x } 1{,}000{,}000 \text{ ng mg}^{-1}}{402{,}600{,}000 \text{ dpm mg}^{-1}} = 0.025 \text{ ng}$$

In this study a 1 g aliquot of each sample extract was taken for LSC. Therefore the LOQ in each extract is 10 dpm g^{-1}.

This equates to a concentration in the sample of:

$$\frac{10 \text{ dpm g}^{-1} \text{ x } 1{,}000 \text{ µg mg}^{-1}}{402{,}600{,}000 \text{ dpm mg}^{-1}} = 0.000025 \text{ µg g}^{-1}$$

At each treatment concentration this LOQ corresponds to nominal concentrations as presented in Table 8.2.9.

Table 8.2.9. The LOQ corresponding to nominal concentrations in each treatment rates.

Treatment rate	Nominal Concentration	LOQ as % Applied	
1	0.3 µg g^{-1}	= 100 x 0.000025 /0.3	0.008%
2	0.1 µg g^{-1}	= 100 x 0.000025 /0.1	0.025%
3	0.03 µg g^{-1}	= 100 x 0.000025 /0.03	0.08%
4	0.01 µg g^{-1}	= 100 x 0.000025 /0.01	0.25%
5	0.003 µg g^{-1}	= 100 x 0.000025 /0.003	0.8%

HPLC: HPLC analysis was used to check the purity of the test item. The limits of quantification have therefore been expressed in terms of percent of applied radioactivity. The standard deviation of the radio detector signal was determined for a background region of a suitable radio chromatogram. The noise level (standard deviation for the selected background region) was then used to calculate the LOD and LOQ.

LOD (peak area cpm) = 3 × noise level (background standard deviation in cpm) = 29 cpm

LOQ (peak area cpm) = 6 × noise level (background standard deviation in cpm) = 58 cpm

Standard Deviation for background region = 9.7 cpm

LOD (peak area cpm) = 29cpm

LOQ (peak area cpm) = 58cpm

The % Applied was then calculated by: ROI/Area (cpm) x LOD (cpm) or LOQ (cpm)

The peak of interest represented 0.39% ROI and area of 97.27 cpm

The LOD therefore equates to: 0.39/97.27 x 29 = 0.1% AR

The LOQ therefore equates to: 0.39/97.27 x 58 = 0.2% AR

Storage stability was not of concern for this study as all adsorption supernatants, desorption supernatants and soil extracts analysed during the preliminary and definitive experiments were profiled by HPLC within a maximum of two days from generation. When not in the process of being analysed, solutions and extracts were stored frozen (ca -20 °C).

Results and discussion

The radiochemical stability of each test substance throughout the various tests was demonstrated by HPLC analysis of representative samples of the various phases. No significant degradation was observed in any of the supernatants analysed for either the preliminary or the definitive phases, with [^{14}C]-clopyralid representing ≥99.5% of the radiochromatogram in all solutions analysed

Mass balance was calculated for each definitive sample as the sum of the radioactivity recovered from the adsorption supernatant, the desorption supernatant, the organic extract (where applicable), and combustion of the extracted soil pellet. The overall material balance for individual samples was in the range of 91.8-102.2% for the Calke sandy loam (mean 96.5%), 94.9-106.2% for the Longwoods sandy loam (mean 101.4%), 97.1-102.3% for the LUFA 2.1 loamy sand (mean 99.5%), 94.6-100.0% for the Quilen loam (mean 96.9%) and 101.1-106.1% for the DU-L-PF clay loam (mean 104.1%).

The mass balances for individual samples are presented in Table 8.2.10. The concentrations of [^{14}C]-Clopyralid, in the solid and liquid phases at the end of adsorption equilibration period are presented in Table 8.2.11, and the obtained adsorption and desorption constants in the soils studied are presented in Table 8.2.12.

Table 8.2.10. Recovery of [^{14}C]-Clopyralid, expressed as percentage of the applied radioactivity, in soil after adsorption/desorption

Soil	Rep	% Adsorb Solution	% Desorb Solution	% Extract	% NER	% Total
Calke						
0.3	1	48.76	24.43	21.05	3.63	97.86
0.3	2	49.35	23.09	22.34	2.78	97.56
0.1	1	48.73	21.03	23.10	3.85	96.72
0.1	2	48.52	21.60	23.55	3.82	97.48
0.03	1	45.56	19.13	24.38	6.53	95.59
0.03	2	45.66	19.80	24.86	7.54	97.85
0.01	1	42.97	20.31	24.84	6.44	94.57
0.01	2	38.34	17.39	26.54	10.86	93.13
0.003	1	42.57	18.82	31.79	9.01	102.20
0.003	2	34.53	15.48	28.37	13.45	91.83
Longwoods						
0.3	1	53.99	21.67	n/a	19.20	94.86
0.3	2	57.05	22.63	n/a	20.50	100.18
0.1	1	54.70	26.19	n/a	20.43	101.32
0.1	2	53.69	24.56	n/a	21.21	99.46
0.03	1	56.18	23.35	n/a	25.28	104.81
0.03	2	65.29	21.00	n/a	17.18	103.47
0.01	1	55.43	23.87	n/a	18.96	98.26
0.01	2	59.56	25.84	n/a	19.34	104.74
0.003	1	56.20	22.41	n/a	22.24	100.85
0.003	2	55.11	23.22	n/a	27.85	106.18
Lufa 2.1						
0.3	1	64.78	22.10	9.63	0.55	97.05
0.3	2	66.85	20.84	9.91	0.46	98.06
0.1	1	66.93	21.66	10.44	0.56	99.59
0.1	2	65.72	21.93	10.83	0.64	99.13
0.03	1	66.11	21.19	10.35	0.67	98.31
0.03	2	65.67	21.54	10.33	1.19	98.73
0.01	1	67.91	20.80	11.17	0.85	100.73
0.01	2	66.02	20.57	11.27	2.04	99.89
0.003	1	66.82	19.78	11.06	3.27	100.93
0.003	2	65.50	20.49	11.53	4.81	102.32
Quilen						
0.3	1	38.66	21.63	32.64	3.97	96.89
0.3	2	40.25	21.55	32.17	3.78	97.75
0.1	1	39.61	20.03	33.90	4.70	98.24
0.1	2	39.30	20.01	33.60	5.13	98.05

Soil	Rep	% Adsorb Solution	% Desorb Solution	% Extract	% NER	% Total
0.03	1	36.74	17.66	33.87	7.15	95.42
0.03	2	37.40	17.08	33.30	9.26	97.04
0.01	1	35.38	14.50	31.26	13.41	94.55
0.01	2	34.77	16.50	34.17	9.73	95.18
0.003	1	29.31	13.74	33.62	18.69	95.36
0.003	2	31.72	13.68	34.19	20.39	99.98
DU-L-PF						
0.3	1	37.51	27.10	n/a	40.46	105.08
0.3	2	38.11	26.80	n/a	37.62	102.53
0.1	1	37.22	26.22	n/a	42.63	106.08
0.1	2	37.41	26.00	n/a	42.56	105.96
0.03	1	34.67	24.93	n/a	45.85	105.45
0.03	2	35.97	25.22	n/a	43.15	104.34
0.01	1	33.35	24.44	n/a	47.56	105.35
0.01	2	33.76	24.09	n/a	44.71	102.57
0.003	1	36.37	24.63	n/a	41.18	102.18
0.003	2	28.04	21.08	n/a	51.96	101.09
					average	99.66
					SD	3.69
					Maximum	106.18
					Minimum	91.83

Table 8.2.11. Concentration of [^{14}C]-Clopyralid, in the solid and liquid phases at the end of adsorption equilibration period

Nominal Concentration (mg L^{-1})	Soil (mg kg^{-1})	Solution (mg L^{-1})	% Adsorbed (± range)
Calke sandy loam			
0.3	0.008	0.259	2.9 ± 0.4
0.1	0.004	0.088	3.9 ± 0.3
0.03	0.003	0.025	9.4 ± 0.4
0.01	0.001	0.007	16.8 ± 4.1
0.003	0.001	0.002	24.3 ± 2.8
Longwoods sandy loam			
0.3	0.016	0.232	5.7 ± 0.2
0.1	0.006	0.084	5.8 ± 0.2
0.03*	0.0003	0.025	9.1 ± 0.0
0.01	0.0003	0.009	3.2 ± 1.6
0.003	0.0002	0.002	7.1 ± 2.9
LUFA 2.1 loamy sand			
0.3	0.010	0.268	3.7 ± 0.4
0.1	0.003	0.092	3.3 ± 0.2
0.03	0.001	0.027	3.7 ± 0.3
0.01	0.0004	0.009	3.9 ± 0.4
0.003	0.0002	0.003	6.3 ± 2.1
Quilen loam			
0.3	0.053	0.223	19.9 ± 2.5
0.1	0.018	0.073	19.4 ± 0.6
0.03	0.006	0.021	23.4 ± 0.7
0.01	0.003	0.006	28.9 ± 3.7
0.003	0.001	0.002	37.3 ± 1.1
DU-L-PF clay loam			
0.3	0.034	0.224	11.6 ± 1.6
0.1	0.017	0.073	16.4 ± 0.4
0.03	0.006	0.020	20.2 ± 1.3
0.01	0.002	0.007	23.3 ± 0.9
0.003	0.001	0.002	24.0 ± 9.0

Table 8.2.12. Adsorption and desorption constants of [^{14}C]-clopyralid in the soils

Soil	Adsorption				Desorption			
	K_F	K_{Foc}	1/n	r^2	K_F	K_{Foc}	1/n	r^2
Calke sandy loam	0.01	0.5	0.489	0.991	0.02	0.5	0.424	0.864
Longwoods sandy loam	0.08	2.5	1.047	0.947	0.12	3.9	0.903	0.909
LUFA 2.1 loamy sand	0.03	4.1	0.889	0.991	0.01	2.1	0.653	0.984
Quilen loam	0.16	3.9	0.804	0.996	0.18	4.6	0.715	1.000
DU-L-PF clay loam	0.14	2.1	0.829	0.993	0.26	4.0	0.857	0.999

K_F - Freundlich adsorption and desorption coefficients
K_{Foc} - Coefficient adsorption per organic carbon (K_F x 100/% organic carbon)
1/n -Slope of Freundlich adsorption/desorption isotherms
r^2 - Correlation coefficient of Freundlich equation

Adsorption

The amount of applied test material adsorbed ranged from 2.9 to 24.3% in the Calke sandy loam, 3.2 to 9.1% in the Longwoods sandy loam, 3.3 to 6.3% in the LUFA 2.1 loamy sand, 19.4 to 37.3% in the Quilen loam and 11.6 to 24.0% in the DU-L-PF clay loam. The calculated adsorption constants (K_F) of the Freundlich isotherms for the soils (with soil concentrations corrected for total recovery of the [^{14}C]-clopyralid Test Item) ranged from 0.01 mL g^{-1} in the Calke sandy loam to 0.16 mL g^{-1} in the Quilen loam (mean 0.08 mL g^{-1}). Corresponding K_{FOC} values ranged from 0.5 mL g^{-1} in the Calke sandy loam to 4.1 mL g^{-1} in the LUFA 2.1 loamy sand (mean of 2.6 mL g^{-1}).

Desorption

The desorption K_{Fdes} values ranged from 0.01 mL g-1 in the LUFA 2.1 loamy sand to 0.26 mL g^{-1} in the DU-L-PF clay loam (mean value of 0.12 mL g^{-1}). Corresponding K_{FOCdes} values ranged from 0.5 mL g^{-1} in the Calke sandy loam to 4.6 mL g^{-1} in the Quilen loam, with a mean value of 3.0 mL g^{-1}.

Correlation to Soil pH

There was no clear correlation between the K_F or K_{FOC} values obtained with the soil pH or any of the other soil parameters.

Conclusion

The K_{FOC} values obtained ranged from 0.5 to 4.1 mL g^{-1} (mean 2.6 mL g^{-1}). The Freundlich exponents (1/n) were significantly < 1 in four out of the five soils tested, suggesting a non-linear relationship between sorption and concentration (a higher degree of sorption to soil at lower concentrations) in these soils.

The K_{FOCdes} values ranged from 0.5 to 4.6 mL g^{-1} (mean 3.0 mL g^{-1}). The determined K_{FOC} values indicated that [^{14}C]-clopyralid can be classified as being very mobile in soil according to the Briggs classification and as having very high mobility in soil according to the McCall classification.

RMS comments and evaluation:

The study presented by the Notifier in the AIR3 dossier was new and not evaluated before in the context of the regulation 1107/2009. The study was well conducted according to the current test

guideline and the GLP, well reported and overall acceptable. The results are in line with the earlier study, considered as valid and can thus be used in the risk assessment together with the data already available. Therefore the knowledge base available on the sorption of clopyralid in a variety of soils is adequate, as summarized below in Table 8.2.13. The data requirement is fulfilled and no further studies on the adsorption and desorption in soil are required to support the renewal of the approval of clopyralid.

Table 8.2.13. Summary of the adsorption data of clopyralid.

Soil name	Soil type	OC (%)	pH ($CaCl_2$)	$K_{f,ads}$ (mL/g)	K_{foc} (mL/g)	Modelling 1/n[a] (-)	Study
Merzenhausen	Silt loam[b]	1.00	7.19	0.006	0.57[c]	0.9	Reeves & Middelstaedt, 2002 (CA 7.1.3.1.1/1)
Kaldenkirchen	Loamy sand[b]	0.98	5.34	0.027	2.72[c]	0.9	
Lanna	Clay loam[b]	2.06	6.62	0.005	0.26[c]	0.9	
Overhetfeld	Loamy sand[b]	0.93	6.49	0.013	1.34[c]	0.9	
Calke	Sandy loam[d]	3.15	5.7	0.01	0.5	0.489	Buntain & Simmonds, 2015 (CA 7.1.3.1.1/2)
Longwoods	Sandy loam[d]	3.13	7.4	0.08	2.5	0.9	
LUFA 2.1	Loamy sand[d]	0.68	4.9	0.03	4.1	0.9	
Quilen	Loam[d]	4.02	6.9	0.16	3.9	0.804	
DU-L-PF	Clay loam[d]	6.47	6.3	0.14	2.1	0.829	
Geometric mean					**1.41**	**-**	
Arithmetic mean					**-**	**0.836**	

[a] according to reliability criterion presented in the OECD 106 guideline
[b] BBA classification
[c] calculated based on RMS, 2005
[d] USDA classification

An assessment of the modelling endpoints was given by the Notifier, as presented below.
From these two studies the geomean Koc and arithmetic mean Freundlich coefficient (1/n) are to be derived. Before this can be done two data issues have to be addressed first:

1) The previous EFSA Conclusion Report for clopyralid (EFSA, 2005. 50:1-65) quotes Kd,oc values as Koc values (e.g. presented Koc values are Kd values normalised by organic carbon content) for study Reeves and Mittelstaedt (2002; CA 7.1.3.1.1/1). However, for modelling Kf,oc is required (e.g. Kf values normalised by organic carbon content).

2) Both studies, Reeves and Mittelstaedt (2002; CA 7.1.3.1.1/1) and Buntain and Simmonds (2015; CA 7.1.3.1.1/2), exhibit a wide range of values for the Freundlich exponent. To address a potential discussion on the typical range of the exponent, the following guidance is applied here:

   According to *Generic Guidance for Tier 1 FOCUS Ground Water Assessments, version 2.2, May 2014, page 40*, a default value of 0.9 is to be used for 1/n for a soil if it was not possible to determine a reliable value in the experiment.

According to *OECD 106 – Adsorption, 21 January 2000, page 12*, the reliability criterion for a Freundlich relationship is the product of the Kd with the soil/solution ratio. In the case of an indirect method (measurements are based concentration decrease in the aqueous phase) the product should be > 0.3. In the case of a direct method (both phases are analysed) > 0.1.

Both soil adsorption studies, Reeves and Mittelstaedt (2002) and Buntain and Simmonds (2015), are evaluated against the OECD 106 reliability criterion, as presented below.

1) Calculation of $K_{f,oc}$ values in Reeves and Mittelstaedt (2002), as presented in Table 8.2.14.

Table 8.2.14. Calculation of K_{foc} values in the study of Reeves and Mittelstaedt (2002).

Soil	Organic carbon (%)	K_f (mL/g)	$K_{f,oc}$ (mL/g)
Merzenhausen	1.00	0.0057	0.57
Kaldenkirchen	0.98	0.0267	2.72
Lanna	2.06	0.0054	0.26
Overhetfeld	0.93	0.0125	1.34

2) Reliability check for 1/n

The study has employed the indirect method and a soil/solution ratio of 1. Therefore, the reliability criterion can be stated as K_d > 0.3. The results are checked against this criterion in Table 8.2.15 below.

Table 8.2.15. Check against OECD 106 reliability criterion

Soil	K_d (mL/g)	OECD 106 reliability criterion met	Study Freundlich exponent 1/n (-)	Modelling Freundlich exponent 1/n (-)
Merzenhausen	0.051	No	0.5577	0.9
Kaldenkirchen	0.048	No	0.8602	0.9
Lanna	0.151	No	0.3881	0.9
Overhetfeld	0.032	No	0.7830	0.9

Calculation of K_{foc} values of Buntain and Simmonds (2015) is not required, as the study report quotes K_{oc} values correctly as K_{foc} values. The study has employed the direct method and soil/solution ratio of 1. Therefore, the reliability criterion can be stated as K_d > 0.1. The study report does not report the K_d value. Therefore, K_d values are calculated below in Tables 8.2.16 - 8.2.18, and the data are checked against the OECD 106 reliability criterion in Table 8.2.19.

Table 8.2.16. Calculation of K_d values for soils Calke and Longwoods

Calke				**Longwoods**			
Tube no.	**Cw1 (µg/g)**	**Cs1 (µg/g)**	**K_d (mL/g)**	**Tube no.**	**Cw1 (µg/g)**	**Cs1 (µg/g)**	**K_d (mL/g)**
40	0.2588	0.0089	0.034389	90	0.2276	0.015	0.065905
41	0.2599	0.0069	0.026549	91	0.2356	0.0169	0.071732
42	0.087	0.0039	0.044828	92	0.0848	0.0059	0.069575
43	0.0886	0.0033	0.037246	93	0.0833	0.0054	0.064826
44	0.0244	0.0024	0.098361	94	0.0246	0.0027	0.109756
45	0.0249	0.0027	0.108434	95*	0.0287	-0.0021	
46	0.0077	0.0011	0.142857	96	0.0082	0.0005	0.060976
47	0.0069	0.0018	0.26087	97	0.009	0.0002	0.022222
48	0.0022	0.0006	0.272727	98	0.0025	0.0001	0.04
49	0.0019	0.0007	0.368421	99	0.0025	0.0003	0.12
		Mean:	**0.139468**			**Mean:**	**0.069444**

Table 8.2.17. Calculation of K_d values for soils Lufa 2.1 and Quilen

Lufa 2.1				**Quilen**			
Tube no.	**Cw1 (µg/g)**	**Cs1 (µg/g)**	**K_d (mL/g)**	**Tube no.**	**Cw1 (µg/g)**	**Cs1 (µg/g)**	**K_d (mL/g)**
60	0.2678	0.011	0.04108	70	0.2254	0.0463	0.20541
61	0.2674	0.009	0.03366	71	0.22	0.06	0.27273
62	0.092	0.0029	0.03152	72	0.0736	0.0175	0.23777
63	0.0916	0.0032	0.03493	73	0.0721	0.0186	0.25798
64	0.0275	0.0011	0.04000	74	0.0204	0.0065	0.31863
65	0.0275	0.001	0.03636	75	0.0207	0.0062	0.29952
66	0.0092	0.0003	0.03261	76	0.0065	0.0022	0.33846
67	0.009	0.0004	0.04444	77	0.0064	0.0029	0.45313
68	0.0028	0.0001	0.03571	78	0.0016	0.001	0.62500
69	0.0027	0.0002	0.07407	79	0.0018	0.001	0.55556
		Mean:	**0.04044**			**Mean:**	**0.35642**

Table 8.2.18. Calculation of K_d values for soil DU-L-PF

DU-L-PF			
Tube no.	**Cw1 (µg/g)**	**Cs1 (µg/g)**	**K_d (mL/g)**
100	0.2224	0.0396	0.17806
101	0.2246	0.0291	0.12956
102	0.0735	0.0163	0.22177
103	0.0725	0.0172	0.23724
104	0.0202	0.0065	0.32178
105	0.0207	0.0056	0.27053
106	0.0065	0.0024	0.36923
107	0.0065	0.0022	0.33846
108	0.0021	0.0004	0.19048
109	0.0016	0.0009	0.56250
		Mean:	**0.28196**

Table 8.2.19. Check against OECD 106 reliability criterion (Buntain and Simmonds (2015)

Soil	**K_d (mL/g)**	**OECD 106 reliability criterion met**	**Study Freundlich exponent 1/n (-)**	**Modelling Freundlich exponent 1/n (-)**
Calke	0.139	Yes	0.489	0.489
Longwoods	0.069	No	1.047	0.9
Lufa 2.1	0.040	No	0.889	0.9
Quilen	0.356	Yes	0.804	0.804
DU-L-PF	0.282	Yes	0.829	0.829

The following table summarises both studies. A geomean K_{foc} of 1.42 mL/g and an arithmetic mean Freundlich exponent of 0.836 are proposed for the modelling.

Table 8.2.20. Proposed modelling endpoints for K_{foc} and 1/n of clopyralid

Study	Soil	K_d (mL/g)	K_{foc} (mL/g)	Study Freundlich exponent 1/n (-)	Modelling Freundlich exponent 1/n (-)
Reeves and Mittelstaedt (2002; CA 7.1.3.1.1/1)	Merzenhausen	0.051	0.57	0.5577	0.9
	Kaldenkirchen	0.048	2.72	0.8602	0.9
	Lanna	0.151	0.26	0.3881	0.9
	Overhetfeld	0.032	1.34	0.7830	0.9
Buntain and Simmonds (2015; CA 7.1.3.1.1/2)	Calke	0.139	0.5	0.489	0.489
	Longwoods	0.069	2.5	1.047	0.9
	Lufa 2.1	0.040	4.1	0.889	0.9
	Quilen	0.356	3.9	0.804	0.804
	DU-L-PF	0.282	2.1	0.829	0.829
Modelling endpoints:		**Geomean:**	**1.41**	**Arithmetic mean:**	**0.836**

RMS comments and evaluation:

The calculation presented by the Notifier is acceptable and the data is appropriate to be used in the modelling of clopyralid. No further data to derive the adsorption and desorption endpoints are required to support the renewal for the approval of clopyralid.

B.8.2.2. Adsorption and desorption of metabolites, breakdown and reaction products

There are no metabolites, breakdown or reaction products of clopyralid that meet the criteria laid down in Regulation 1107/2009 and require investigation. Therefore no data on adsorption and desorption of metabolites, breakdown and reaction products are available.

RMS comments and evaluation:

The justification presented by the Notifier is acceptable and no further studies are required to support the renewal for the approval of clopyralid.

B.8.2.3. Aged sorption

The sorption behaviour of Clopyralid was determined in the batch equilibrium studies described in CA 7.1.3.1.1. Therefore, aged residue column leaching studies are not required.

RMS comments and evaluation:

The justification presented by the Notifier is acceptable and no further studies are required to support the renewal for the approval of clopyralid.

B.8.2.4. Mobility in soil

B.8.2.4.1. Column leaching studies of the active substance

The column leaching study submitted for the Annex I inclusion of clopyralid, evaluated originally in the DAR (2003), was assessed as not valid, and therefore not considered here. No further column leaching studies have been submitted nor required, as other data are available. The sorption behaviour of clopyralid was determined in the batch equilibrium studies described in CA 7.1.3.1.1. Therefore, column leaching studies with the active substance are not required.

RMS comments and evaluation:
The justification presented by the Notifier is acceptable and no further column leaching studies are required to support the renewal for the approval of clopyralid. The mobility can be assessed reliably by modelling, for which appropriate mobility endpoints have been submitted according to the data requirement regulation 283/2013.

B.8.2.4.2. Column leaching of metabolites, breakdown and reaction products

The degradation studies of clopyralid in soil revealed that no significant metabolites, breakdown and reaction products are formed from clopyralid. The mobility of the active substance was determined in the batch equilibrium studies described in CA 7.1.3.1.1. Therefore, any column leaching studies with the metabolites or the active substance are not required.

RMS comments and evaluation:
No significant amounts of metabolites, breakdown and reaction products others than CO_2 are formed from clopyralid in soils. Therefore it is not relevant to require column leaching studies with the metabolites to support the renewal for the approval of clopyralid. The justification of the Notifier is agreed and no data are required.

B.8.2.4.3. Lysimeter studies

The mobility of Clopyralid and its metabolites in soil will be assessed with FOCUS groundwater modelling tools using the degradation data described under CA 7.1.1 and CA 7.1.2 and the sorption data described in CA 7.1.3.1.1 and CA 7.1.3.1.2. Therefore, lysimeter studies are not required.

However, lysimeter studies were presented in the dossier submitted in April 2002 for the Active Approval and were deemed acceptable following evaluation and peer review at EU level. These data are still valid as supporting information, although the uses considered in these studies are no longer supported by the Notifier for the renewal of authorization of clopyralid. As the data was evaluated in the DAR (2003), the evaluation is not repeated here again, although the studies are briefly mentioned below.

CA 7.1.4.2/1- Spring application oilseed rape lysimeter

Report	IIA 7.1.3.3/1, Schnöder, F., 2004.
Report title	[14C] Clopyralid: Leaching in outdoor lysimeters following spring application to oilseed rape – Final report
DAS Study number	000136
Guidelines	In accordance with BBA Guidelines Part IV, Section 4-3, 1990 and the modification thereof, 1991.
GLP	Yes

RMS comments and evaluation:

This final report of the study was evaluated in the Addendum 1 of the DAR (2004). The study was considered as acceptable, however the use rate tested not representing the worst case GAP for oilseed rape in Europe. Use on oilseed rape is no longer supported as a representative use of clopyralid in the AIR3 evaluation of clopyralid, and therefore the study is not reviewed in more detail here.

CA 7.1.4.2/2- Autumn application oilseed rape lysimeter

Report	IIA 7.1.3.3/2, Dust, M., Führ, F., 1994.
Report title	Degradation and leaching of clopyralid monoethylamine salt after post emergence application of LONTREL 100 to winter rape in German lysimeters
DAS Study number	GHE-P-4037
Guidelines	In accordance with BBA Guidelines Part IV, Section 4-3, 1990 and the modification thereof, 1991.
GLP	Yes

RMS comments and evaluation:

This study was evaluated in the DAR (2003). The study was considered as acceptable. Use on oilseed rape is no longer supported as a representative use of clopyralid in the AIR3 evaluation of clopyralid, and therefore the study is not reviewed in more detail here.

CA 7.1.4.2/3- Post-emergence application sugar beet lysimeter

Report	IIA 7.1.3.3/3, Brumhard, B., Führ, F., Baloch, R., 1994.
Report title	Behaviour of [2,6 14C] Clopyralid (LONTREL*) in a sandy Pseudogley Braunerde after post-emergence application to sugar beet
DAS Study number	GHE-P-2908
Guidelines	In accordance with BBA Guidelines Part IV, Section 4-3, 1990 and the modification thereof, 1991.
GLP	Yes

RMS comments and evaluation:

This study was evaluated in the DAR (2003). The study was considered as acceptable, however the use rate tested not representing the worst case GAP for sugar beet in Europe. Use on sugar beet is no longer supported as a representative use of clopyralid in the AIR3 evaluation of clopyralid, and therefore the study is not reviewed in more detail here.

CA 7.1.4.2/4- Post-emergence application sugar beet lysimeter

Report	IIA 7.1.3.3/4, Brumhard, B., Baloch, R., Führ, F., 1994.
Report title	Behaviour of [2,6 14C] clopyralid formulated as LONTREL 100 in Parabraunerde (Orthic Luvisol) after post emergence application to sugar beet lysimeters
DAS Study number	GHE-P-2580
Guidelines	In accordance with BBA Guidelines Part IV, Section 4-3, 1990 and the modification thereof, 1991.
GLP	Yes

RMS comments and evaluation:

This study was evaluated in the DAR (2003). The study was considered as acceptable, however the use rate tested not representing the worst case GAP for sugar beet in Europe. Use on sugar beet is no longer supported as a representative use of clopyralid in the AIR3 evaluation of clopyralid, and therefore the study is not reviewed in more detail here.

B.8.2.4.4. Field leaching studies

The mobility of Clopyralid and its metabolites in soil will be assessed with FOCUS groundwater modelling tools using the degradation data described under CA 7.1.1 and CA 7.1.2 and the sorption data described in CA 7.1.3.1.1 and CA 7.1.3.1.2. Therefore, field leaching studies are not required.

RMS comments and evaluation:

The justification presented by the Notifier is acceptable and no field leaching studies are required to support the renewal for the approval of clopyralid.

B.8.3. PREDICTED ENVIRONMENTAL CONCENTRATIONS IS SOIL (PECS)

$PEC_{soil,ini}$ was assessed for clopyralid considering an application rate of the representative formulation GF-1374 of 80 g a.s/ha on winter cereals (BBCH 13) and of 120 g a.s./ha on established grassland. The resulting $PEC_{soil, ini}$ were calculated to be 0.107 mg/kg and of 0.016 mg/kg, respectively. A worst case $PEC_{soil, ini}$ of 2.08 mg/kg was calculated for formulation GF-1374 considering a maximum application rate of 1.5 L/ha. As no degradation products other than CO_2 are formed from clopyralid, it

is not relevant to calculate the PECsoil of metabolites. The details of the PECsoil calculations are presented in the dRAR Part 19 Vol. 3 Chapter 8.

B.8.4. FATE AND BEHAVIOUR IN WATER AND SEDIMENT

B.8.4.1. Route and rate of degradation in aquatic systems (abiotic degradation)

B.8.4.1.1. Hydrolytic degradation

One study to address this point was presented in the dossier for the Approval of Clopyralid submitted in 30 April 2002, evaluated in the DAR (2003) and peer review at EU level. The data was deemed acceptable following evaluation, and is still valid for decision making.

CA 7.2.1.1/1 - Hydrolysis of ^{14}C Clopyralid in Water

Report	IIA 7.2.1.1/1, Smith-Drake, J.K. 2000
Report title	Hydrolysis of ^{14}C Chlopyralid in Natural Water and Buffered Water as a Function of pH.
DAS Study number	000132, Ref. K70.
Guidelines	EC Directive 92/69 Method C.7 and OECD 111
GLP	Yes

Methods

The rate of hydrolytic degradation of [2,6-pyridinyl-^{14}C]-clopyralid was investigated in aqueous sterile buffer solutions at pH values of 4, 7 and 9, and in natural water under laboratory conditions. Solutions of aqueous buffers (0.05M) prepared at pH values of 4, 7 and 9 were sterilised by autoclaving. The sterility and pH of the buffers solutions was checked. A sample of natural water was collected from Indianapolis (Indiana, USA), the characteristics are summarised in Table 8.4-1.

Individual sub-samples of the buffer solutions and natural water, sufficient to allow duplicate sampling at intervals of 0, 2, 4, 24 and 120 hours (5 days), were treated with [2,6-pyridinyl-^{14}C]-clopyralid (batch no. INV1535, RCP >99%, specific activity 30.9 mCi/mmole) at a nominal level of 0.50 mg/l (this is well below the clopyralid aqueous solubility of *ca* 1000 mg/l). The sub-samples were incubated at 50°C in the dark, with no headspace, in amber sterile vials.

At each sampling interval duplicate samples were removed for analysis. Aliquots (50 µl) of the buffer solutions were taken for quantification by LSC. Further aliquots were taken for chromatographic analysis either by HPLC or TLC. As a result of the findings of the preliminary study described above no further testing was carried out.

Table 8.4-1 Characterisation details of natural water sample

Parameter	Value
pH	8.0
Hardness (mg equivalent $CaCO_3$/l)	393
Conductivity (mmhos/cm)	2.06
Total suspended solids (mg/l)	24
Alkalinity (mg $CaCO_3$/l)	284
Dissolved oxygen (mg/l)	7.5

Results

The **recovery of radioactivity** was determined to be between 95.4 % to 106.3 % AR (mean 102 % AR) for the buffer solutions and between 96.1% and 109.8 % AR (mean 104 % AR) for the natural water samples indicating a complete mass balance. Adsorption to glassware was, therefore, negligible.

Microbial analysis showed that the **sterility** of the buffer solutions was maintained throughout the test. The recovery of the applied radioactivity and the amount of clopyralid, as determined by HPLC analysis, in the buffer solutions and natural water samples is summarised in Tables 8.4-2 and 8.4-3, respectively.

Table 8.4-2 Recovery and concentrations of clopyralid in sterile buffer solutions at 50ºC

Incubation time (hours)	pH 4		pH 7		pH 9	
	Mass balance (% AR)	Clopyralid (% AR)	Mass balance (% AR)	Clopyralid (% AR)	Mass balance (% AR)	Clopyralid (% AR)
0	100.0	100.0	100.0	98.7	100.0	100.0
2	104.4	104.4	99.8	99.8	96.2	96.2
4	103.6	103.6	95.8	95.8	95.4	95.4
24	106.3	106.3	102.5	102.0	100.8	100.8
120	106.0	106.0	102.4	102.4	101.8	101.7

Values are means of duplicate determinations

Table 8.4-3 Recovery and concentrations of clopyralid in natural water at 50ºC

Incubation time (hours)	Natural water	
	Mass balance (% AR)	Clopyralid (% AR)
0	100.0	99.1
2	96.1	96.1
4	106.9	106.9
24	109.8	107.8
120	106.6	106.6

Values are means of duplicate determinations

Clopyralid is **hydrolytically stable** in sterile aqueous buffer between pH 4 and pH 9 and in natural waters at temperatures up to 50°C over a period of 5 days. Since <10 % degradation of clopyralid was observed at 50°C, this is equivalent to an environmental half-life of > 1 year. Therefore, hydrolysis is not expected to be a significant route of dissipation of clopyralid in the environment and no further testing is required.

Comments

The study was new and well performed according to the test guideline and in compliance with GLP. Only the preliminary test at 50 ºC for 5 days was performed, and as no degradation was observed, the definite test at 20 ºC for 30 days was not carried out, as recommended in the guideline. This is acceptable, as clopyralid appears to be hydrolytically stable at higher temperature than naturally occurs at European conditions.

RMS comments and evaluation:

The study on the hydrolytic degradation of clopyralid was evaluated in the DAR (2003) as presented above and the result was used in the risk assessment presented in the EFSA conclusion on clopyralid (EFSA Scientific Report 2005: 50). Hydrolysis is not a relevant pathway of the degradation of clopyralid. No other comments, the study is acceptable and the data is adequate for the renewal for the approval of clopyralid.

B.8.4.1.2. Direct photochemical transformation in water

Two studies are available to address this point. The first one (Concha & Shepler 1994) was submitted for the Approval of Clopyralid submitted in 30 April 2002, evaluated in the DAR (2003) and peer review at EU level. The data was deemed acceptable following evaluation, and is still valid for decision making. In addition, a complete new study (Ponte 2014) was conducted according to the current guidelines.

CA 7.2.1.2/1 - Photolysis of ^{14}C Clopyralid in Water

Report	IIA 7.2.1.2/1, Concha, M. & Shepler, K. 1994
Report title	Photodegradation of [^{14}C] clopyralid in buffered aqueous solution at pH 7 by natural sunlight.
DAS Study number	ENV 94048, Ref. K69.
Guidelines	US EPA Pesticide Assessment Guidelines, Subdivision N, Paragraph 161-2 (1982). Apart from minor deviations, the study also meets the requirements of the SETAC-Europe guideline, Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, Part 1, Section 10 (1995).
GLP	Yes (certified laboratory), with the only exception that sunrise/sunset data was obtained from a local newspaper.

Methods

The photodegradation of [2,6-pyridinyl-^{14}C]-clopyralid was investigated in sterile aqueous buffer solutions at pH 7 under natural sunlight at 25°C. Solutions of [2,6-pyridinyl-^{14}C]-clopyralid (batch A903-14, specific activity 31.5 mCi/mmole, RCP 98.1%) were prepared at a concentration of 2 mg/l in a phosphate buffer at pH 7. The buffer solution was sterilised by filtration (0.22 µm) and the pH re-determined (pH 6.98). Treated solutions in quartz tubes were exposed to natural sunlight for a period of 30 days.

The outdoor experiment was conducted in Richmond, California, US (latitude 37.45°N, longitude 122.26°W). Similarly treated samples were wrapped in tin foil to exclude light and used as dark controls. The temperature of the samples was maintained at 25°C by use of a water bath. The average daily sunlight energy was 11.56 W min/cm^2. The sample tubes were connected to trapping solutions to collect evolved volatile products. Whole samples, exposed and dark controls, were taken for analysis over a period of 30 days. The buffer and trapping solutions were quantified by LSC and analysed by HPLC. Confirmatory analysis was conducted on selected samples by 2D-TLC.

Results

The **recovery and distribution of the applied radioactivity** in the buffer solutions for the exposed samples and dark controls is summarised in Table 8.4-4. The overall recovery ranged from 98.8 % to 103.8 % AR indicating a complete mass balance. The recovered radioactivity was virtually all detected in the aqueous samples, the level

of evolved volatile components was minimal (≤ 2 % AR). Analysis of the buffer solutions at each sampling interval indicated that the pH and sterility were maintained throughout the study.

Table 8.4-4 Recovery and distribution of radioactivity from aqueous buffers exposed to natural sunlight (and dark controls)

Incubation time (days)	Recovery (% AR)			Total recovery (% AR)
	Aqueous sample	Sodium hydroxide	Ethylene glycol	
Exposed samples				
0	101.2	NA	NA	101.2
7	103.4	0.4	< 0.1	103.8
15[1]	97.9	0.8	0.1	98.8
21	101.0	1.4	0.1	102.5
30[1]	96.6	2.0	0.2	98.8
Dark controls				
0	101.0	NA	NA	101.0
15[1]	98.9	0.1	0.1	99.1
30[1]	99.2	0.1	0.1	99.4

NA = not applicable
[1] Values are means of duplicate determinations

The profile of the radioactive components is summarised in Table 8.4-5. **Minimal degradation** was observed and clopyralid was the major component detected in all samples. The level of clopyralid detected in the exposed samples declined from 99.4 % AR initially to 92.7 % AR after 30 days. Low levels of minor degradation products were observed which comprised of a combined total of 4.1 % AR after 21 days and consisted of several components each of which were < 2 % AR.

The rate of observed photodegradation of clopyralid was slow and did not correlate well to first-order kinetics. However, the corresponding **DT_{50} and DT_{90}** values were determined using the methodology described in soil degradation studies. The results obtained are summarised in Table 8.4-6. The rate of photodegradation of clopyralid in aqueous buffer at pH 7 was *ca* 271 days. The degradation rate in the exposed samples was not corrected for the rate observed in the dark controls due to the insignificant degradation observed.

No significant degradation products were observed. Due to the low photodegradation rate the quantum yield was not determined. Photodegradation of clopyralid in water is not expected to be a significant environmental degradation pathway.

Table 8.4-5 Recovery and distribution of radioactivity from aqueous buffers exposed to natural sunlight (and dark controls)

Incubation time (days)	Radioactive component (% AR)				Total recovery (% AR)
	Clopyralid	Others	Sodium hydroxide	Ethylene glycol	
Exposed samples					
0	99.4	1.8	NA	NA	101.2
7	101.5	1.9	0.4	< 0.1	103.8
15[1]	95.1	2.9	0.8	0.1	98.8
21	96.9	4.1	1.4	0.1	102.5
30[1]	92.7	3.9	2.0	0.2	98.8
Dark controls					
0	99.5	1.5	NA	NA	101.0
15[1]	97.7	1.2	0.1	0.1	99.1
30[1]	97.8	1.4	0.1	0.1	99.4

NA = not applicable
[1] Values are means of duplicate determinations

Table 8.4-6. $DT_{50(lab)}$ and $DT_{90(lab)}$ values for the rate of photodegradation of clopyralid in aqueous solution

System type	Data range (days)	$DT_{50(lab)}$ (days)	$DT_{90(lab)}$ (days)	Regression parameters		
				C_0	K	R^2
Sterile pH 7 buffer	0 - 30	271	901	100.78	0.0026	0.583

Comments

The study was well performed according to the guideline and in compliance with GLP. The irriadiation conditions are comparable to the Southern Mediterranean area. The DT_{50} was obviously again recalculated by the Notifier, as in the original report a DT_{50} of 261 days (R^2 = 0.702) was reported. The DT_{90} was not reported in the original study, but was calculated by the Notifier in the Dossier. This is however acceptable, as the recalculation does not significantly change the conclusion based on the original report. Photodegradation does not appear to be a significant degradation pathway of clopyralid in aquatic environment.

RMS comments and evaluation:

The study on the photolytic degradation of clopyralid was evaluated in the DAR (2003) as presented above and the result was used in the risk assessment presented in the EFSA conclusion on clopyralid (EFSA Scientific Report 2005: 50). Therefore the study was not re-evaluated in more detail here again.

The Notifier submitted a new study for the renewal of authorization of clopyralid, which is evaluated below.

CA 7.2.1.2/2 - Photolysis of ^{14}C Clopyralid in Water

Report	IIA 7.2.1.2/2, Ponte, M. 2014
Report title	Direct Aqueous Photodegradation of [14C] Clopyralid in ph 7 Buffer.
DAS Study number	PTRL West, Hercules, California, USA; Lab Study No. 2606W; DAS Study No. 140077; 16 December 2014
Guidelines	OECD 316 US EPA OCSPP 835.2240, OPPTS 835.2240
GLP	Yes

Materials and methods

The degradation of Clopyralid-2,6-^{14}C with a radiochemical purity of 98.0 % and specific radioactivity of 32.8 mCi/mmol was studied in buffer solutions that were made with HPLC grade water, as presented in Table 8.4.7. below. The samples were artificially illuminated, and the details of the light source are described in Table 8.4.8. The comparison of the artificial light source with natural sunlight is presented in Figure 8.10. and in Table 8.4.9. No preliminary study was conducted.

Table 8.4.7. Description of buffer solutions

pH	Type and final molarity of buffer	Composition
7	0.01 M Phosphate Buffer	50 mL of 0.1M potassium phosphate and 29.6 mL 0.1 M NaOH, diluted to 1.0 L with HPLC water and adjusted to pH 7 using concentrated phosphoric acid

Table 8.4.8. Details of the artificial light source

Property	Details
Type of lamp used	xenon lamp in Suntest CPS+
Emission wavelength spectrum	below
Light intensity	489 W m 2
Filters used	quartz with infra-red coating (CIRA), soda lime
Relationship to natural sunlight	wavelength distribution determined using spectroradiometer and intensity determined using chemical actinometer

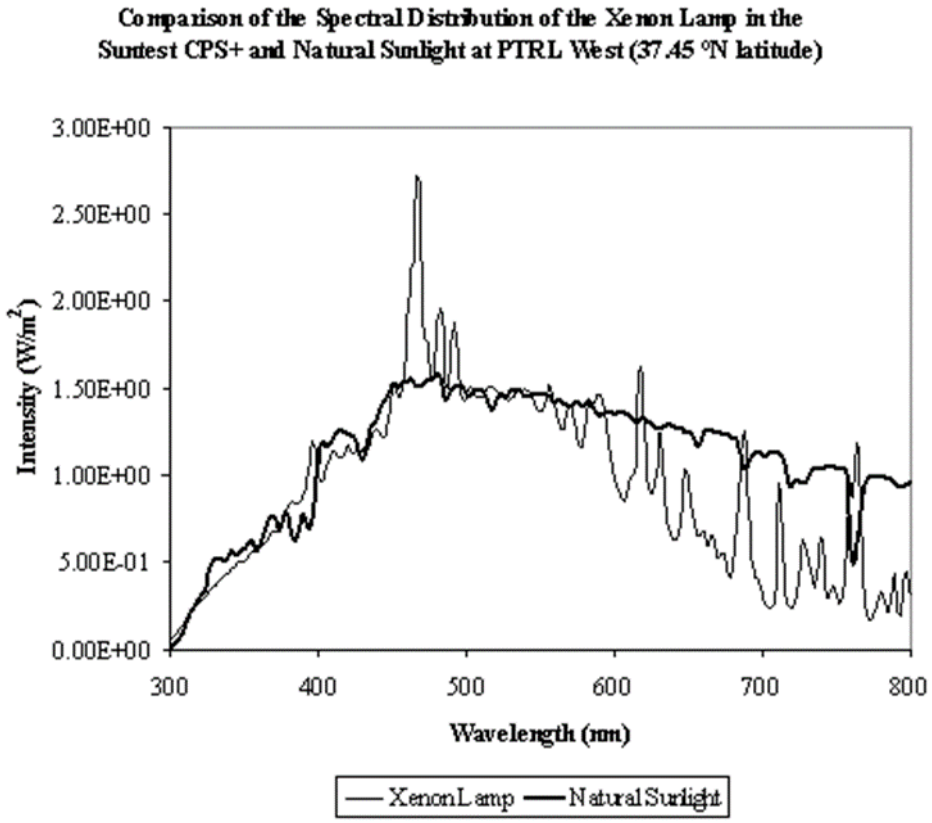


Figure 8.10. Comparison of xenon light source and natural sunlight

Table 8.4.9. Total light energy

	Summer solstice	Initial xenon lamp	Final xenon lamp	Average xenon lamp
Sum (W/(m^2 nm))		507.6	471.3	489

The experimental parameters are presented in Table 8.4.10., and sampling scheme is presented in Table 8.4.11.

Table 8.4.10. Experimental parameters

Parameter		Description
Duration of test		0 to 16 days after treatment
Test concentrations	nominal:	2 mg/L
	measured:	1.80 mg/L
Dark control used		yes
Number of replicates	Dark: Irradiated:	2 2
Preparation of test medium (bulk preparation)	volume per treatment:	5 mL
	method of sterilization:	autoclave
	co-solvent, if any (name/concentration):	acetonitrile, ≤0.1%
Test apparatus		Suntest CPS+ for light exposed, biological incubator for dark controls quartz tubes for light exposed and Pyrex tubes for dark controls (11 mm id) Samples connected to traps for volatiles via Teflon tubing, peristaltic pump used to draw sterile air continuously over sample headspace
Details of traps for CO_2 and volatile organics		10% NaOH traps, ethylene glycol
Test material sorption to walls of apparatus		no
Experimental conditions	Temperature:	25 ± 2 °C
	Light source:	Xenon lamp
	Duration of light/darkness:	continuous light
Light Source Characterization		chemical actinometery and spectroradiometer
Actinometer(s)		PNAP/pyridine
Other details, if any		NA

Table 8.4.11. Sampling details

Parameter		Details
Sampling intervals		0, 1, 3, 5, 7, 11 and 16 DAT
Sampling method		Check sterility of samples (last sampling and T0). Check pH. Transfer sample to graduated cylinder, rinse sample tube with methanol, combine with sample. Measure volume. Count triplicate aliquots of samples to determine recoveries. Sample analyzed directly by HPLC.
Sampling procedures for all actinometer samples		Transfer sample to labeled amber vial and store in refrigerator. Sample analyzed directly by HPLC following completion of sample kinetics.
Method of sampling volatile compounds, if any		Continuous trap system. Trap solutions measured (volume) and triplicates radioassayed by LSC.
Sampling interval times	pH measurement	Checked at each sample time
	Sterility checks	Checked at T0 and last sampling time
	Other	N/A
Sample storage before analysis, if any		Samples analyzed on the day of sampling (see below) and kept in a refrigerator when not in use
Other observations		NA

Analytical Methodology

For the Total ^{14}C measurement, all radioassays utilized 5 mL or 15 mL of scintillation cocktail or Harvey cocktail in 7 mL or 20 mL standard polyethylene counting vials and Beckman LS 6500 or LS 6000IC liquid scintillation counters. Computer-constructed quench curves, derived from a series of ten sealed quenched standards, automatically converted cpm to dpm. Typical parameters are as follows: counting efficiency, 96%; background, 25 dpm; counting time, 1 minute. Scintillation cocktail was added to each sample before counting. Samples were generally counted for 1 minute; however samples that were expected to have low amounts of radioactivity were often counted for 5 minutes or longer.

For quantitation, HPLC analyses of all samples were accomplished using a Capcell C-18 column (250 x 4.6 mm i.d., 5.0 µm; 1.0 mL/min; UV detection at 254 nm) and a linear gradient with 1% trifluoroacetic acid in water and acetonitrile.

To determine the detection limits (LOD, LOQ) for the parent compound, the % AR represented by 10 dpm and 40 dpm for each sample phase (caustic layer, EG, aqueous sample) is calculated and presented in Table 8.4.12.

Table 8.4.12. The detection limits for the parent compound

Matrix	LOD (%AR)	LOD (dpm)	LOQ (%AR)	LOQ (dpm)
Caustic trap	0.0009	30	0.001	40
Extract	0.0009	30	0.001	40
HPLC	0.4	129	0.8	258

The photodegradation rate of the clopyralid in pH 7 buffer was calculated using KinGUI ver 2.12.1 (Bayer CropScience) according to FOCUS Kinetics Guidance (2006) on estimating persistence and degradation kinetics from Environmental Fate Studies. In order to estimate DT_{50} and DT_{90} values,

Single First-Order (SFO) kinetic model was fitted to the degradation data. Input data sets for modelling were derived from individual data for each time-point. All data points were unweighted. DT_{50} and DT_{90}, chi-square and r^2 values were calculated directly by the software.

Samples were typically analysed on the day of sacrifice. HPLC analysis for % AR determination was completed the same day of sampling so no storage stability determination was necessary.

Results and discussion

The pH of each sample was assayed at sample sacrifice and sterility was checked at the beginning and the end of the exposure. Sample pH was unchanged throughout the study and sterility was maintained during the study period.

Total radiocarbon recovery was 100.7 ± 4.5% and 101.4 ± 1.1% of the applied amount in the dark and in the irradiated samples, respectively. The mass balance is presented in Table 8.4.13. below.

Table 8.4.13. Phototransformation of clopyralid, expressed as percentage of the applied radioactivity (mean ± std dev.)

Compound		Sampling times (days)						
		0	t1	T3d	T5d	T7d	T11d	T16d
Clopyralid	irradiated	101.0	101.1	101.4	101.5	102.5	100.1	98.3
	dark	NA	100.6	104.1	103.4	100.4	102.6	93.1
Others	irradiated	0.0	0.0	0.0	0.0	0.4	0.4	1.9
	dark	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CO_2	irradiated	NA	0.0	0.1	0.1	0.2	0.2	0.4
	dark	NA	0.0	0.0	0.0	0.0	0.0	0.1
Volatile organics*	irradiated	NA	0.0	0.1	0.1	0.1	0.2	0.3
	dark	NA	0.0	0.1	0.0	0.0	0.0	0.0
Total % recovery	irradiated	101.0	101.1	101.5	101.7	103.2	100.9	100.9
	dark	101.0	100.6	104.2	103.4	100.4	102.6	93.2

No transformation of clopyralid occurred during the study. At study termination 93.1% of the applied radioactivity remained as the parent in the dark samples and 100.2% in irradiated samples.

The half-life/DT_{50} (50% decline time) of clopyralid for the dark and the irradiated samples, using single first-order kinetics, are shown in in Table 8.4.14.

Table 8.4.14. Observed aqueous photodegradation rate of clopyralid in pH 7 Buffer (uncorrected for light intensity)

Conditions	Degradation rate (DAT^{-1})	Equation	R^2
Dark	N/A	$\frac{d(parent)}{dt}$ = - k[parent]	
Irradiated (total)	1.61 x 10-3	$\frac{d(parent)}{dt}$ = - k[parent]	0.3627
Photolysis	1.61 x 10-3	kphotolysis = ktotal or kphotolysis = ktotal - khydrolysis	0.3627

The predicted environmental photolytic half-life of clopyralid, derived from the measured half-life in laboratory under artificial lamp, was calculated to be 431 continuous day(s) of irradiation.

The degradation rates for clopyralid presented here are those observed under continuous exposure to xenon light. The degradation rates corrected to sunlight are presented below.

Table 8.4.15. Clopyralid aqueous photolysis degradation rates calculated as a function of latitude and season

Latitude	Season	$\Sigma\varepsilon_{c\lambda}L_{\lambda}$	Degradation rate	
			(k)	DT_{50} (days)
0 N	Spring	1.74E+01	1.76E-05	39375
10 N	Spring	1.80E+01	1.82E-05	38077
20 N	Spring	1.74E+01	1.76E-05	39375
30 N	Spring	1.60E+01	1.76E-05	42778
40 N	Spring	1.37E+01	1.38E-05	50217
50 N	Spring	1.11E+01	1.12E-05	61875
60 N	Spring	8.36E+00	8.44E-06	82109
0 N	Summer	1.63E+01	1.65E-05	42000
10 N	Summer	1.79E+01	1.81E-05	38287
20 N	Summer	1.89E+01	1.91E-05	36283
30 N	Summer	1.86E+01	1.88E-05	36862
40 N	Summer	1.76E+01	1.78E-05	38933
50 N	Summer	1.60E+01	1.62E-05	42778
60 N	Summer	1.39E+01	1.40E-05	49500
0 N	Fall	1.78E+01	1.80E-05	38500
10 N	Fall	1.61E+01	1.63E-05	42515
20 N	Fall	1.63E+01	1.65E-05	42000
30 N	Fall	1.08E+01	1.09E-05	63578
40 N	Fall	7.64E+00	7.72E-06	89767
50 N	Fall	4.50E+00	4.55E-06	152308
60 N	Fall	2.03E+00	2.05E-06	338049
0 N	Winter	1.66E+01	1.68E-05	41250
10 N	Winter	1.39E+01	1.40E-05	49500
20 N	Winter	1.07E+01	1.08E-05	64167
30 N	Winter	7.23E+00	7.30E-06	94932
40 N	Winter	4.01E+00	4.05E-06	171111
50 N	Winter	1.65E+00	1.67E-06	414970
60 N	Winter	4.18E-01	4.22E-07	1642180

Quantum Yield

The quantum yield of the PNAP/PYR actinometer was 3.9 x 10-5, based on the concentration of pyridine used (2.31 x 10-3 M). The quantum yield for clopyralid was determined as 1.01 x 10-6.

Conclusion

The expected half-life value for clopyralid photolysis at 40° N latitude in the summer sun was 38,933 days. There were no significant degradation products observed in the aqueous samples for light exposed or dark control samples throughout the study period. The CO_2 concentrations reached a maximum of 0.4%AR at 16 DAT.

RMS comments and evaluation:

The study on the photolytic degradation of clopyralid was well performed, according to the current guidelines and the GLP, clearly reported and overall acceptable. The findings of this study confirm the previous understanding of the photolytic stability of clopyralid in water. The data requirement is fulfilled and no further data is required.

B.8.4.1.3. Indirect phototransformation in water

This study is not required according to the EU guidance 1107/2009.

RMS comments and evaluation:

The justification presented by the Notifier is acceptable.

B.8.4.2. Route and rate of biological degradation in aquatic systems

B.8.4.2.1. Ready biodegradability

Data to address this point were presented in the dossier submitted in April 2002 for the Active Approval and were deemed acceptable following evaluation and peer review at EU level. These data are still valid for decision making.

CA 7.2.2.1/1 - LONTREL T: Assessment of its Biodegradability – Modified Sturm Test

Report	IIA 7.2.2.1/01, Jenkins, W. R., 1991
Report title	LONTREL T: Assessment of its Biodegradability - Modified Sturm Test
DAS Study number	GHE-P-2522, Ref. A12.
Guidelines	EC directive 84/449EEC Annex V, C.5 and C.6 OECD 301B and 301D
GLP	yes

Methods

The ready biodegradability of technical grade clopyralid (Lontrel T 95 % w/w, batch RMM 1434, purity 96.4 % w/w) has been investigated using the Modified Sturm Test (EEC method C.5, OECD no. 301B). The investigation was preceded by the determination of the Total Organic Content, the Dissolved Organic Content (TOC and DOC respectively), the chemical oxygen demand (COD) and a five-day bacterial inhibition assay of the test compound conducted using the Closed Bottle test (EEC method C.6, OECD no. 301D). The COD of clopyralid was determined by oxidation with an acid-dichromate mixture at 150 °C and compared to the calculated theoretical oxygen demand. The TOC and DOC contents of solutions containing clopyralid (20 mg/L) in distilled water and in the mineral salt medium employed in the Modified Sturm test were determined using an organic carbon analyser.

The bacterial inhibition assay was conducted by adding clopyralid to mineral salt medium inoculated with an extract prepared from unfertilised soil, with and without sodium benzoate (2 mg/l), at nominal concentrations of 2 and 10 mg/l. The concentration of dissolved oxygen in duplicate bottles was measured initially and after incubation at 20 °C for a period of 5 days.

The Modified Sturm test was conducted by adding clopyralid, at nominal concentrations of 10 and 20 mg/L, to vessels containing the mineral salt medium inoculated with an extract of unfertilised soil. Control vessels were also prepared containing the mineral salt medium, with and without, sodium benzoate (20 mg/l). The vessels were aerated for 28 days with carbon dioxide free air. The CO_2 produced was trapped in a series of Drechsel bottles containing barium hydroxide. The residual barium hydroxide was determined at intervals by titration with hydrochloric acid using phenolphthalein indicator. The concentrations of dissolved organic carbon (DOC) of control, reference and test mixtures were also determined at the start of the test and after 27 days.

Results

In the **preliminary tests** the COD of clopyralid was determined to be 0.73 mgO_2/mg, which was 103 % of the calculated theoretical oxygen demand of 0.71 mg O_2/mg. This indicated that under the conditions of the test clopyralid was completely oxidised. In addition the TOC and DOC of clopyralid in distilled water were determined to be 93 and 96 % of the theoretical organic carbon content, indicating that clopyralid was fully oxidised under the conditions of the analysis and that all the carbon measured by TOC was in solution.

In the **bacterial inhibition test** the reference substance, sodium benzoate, was readily degraded to 48 % of the theoretical maximum oxygen demand after 5 days in the control vessels. The presence of clopyralid at 2 or 10 mg/l had no significant effect on the degradation of the reference substance. Therefore it was concluded that clopyralid was not inhibitory to the bacterial inoculum.

In the **Modified Sturm test** the reference material, sodium benzoate, was degraded to 60 % of its theoretical CO_2 production after 7 days and 91 % after 28 days. Analysis of the DOC indicated that the reference material was 98 % degraded. In the control vessels cumulative CO_2 production after 28 days amounted to 20.5 mg CO_2 compared to a theoretical maximum of 50 mg CO_2. The acceptable level of CO_2 production in the controls and effective degradation of the reference material indicated that the inoculum was viable over the duration of the study period.

In the vessels containing clopyralid at concentrations of 10 and 20 mg/l, **cumulative CO_2 production** was 10 % and 5 % of theoretical maximum levels respectively after 27 days. The DOC level of these solutions was 92% of theoretical levels at the start of the test and had declined by 9 % and 3 % by the end of the test in the solutions containing 10 and 20 mg clopyralid/l respectively, independently confirming the levels of CO_2 production observed.

The results are summarised in Table 8.4-16.

Substances are considered to be readily degradable if CO_2 production is equal to or greater than 60% of the theoretical value after 28 days in this test. Therefore **clopyralid cannot be considered to be readily degradable**.

Table 8.4-16. Cumulative CO_2 production from degradation of clopyralid and reference material from a Modified Sturm Test

Incubation time (days)	Sodium benzoate (20 mg/l)		Clopyralid (10 mg/l)		Clopyralid (20 mg/l)	
	mg CO_2	% TCO_2 [1]	mg CO_2	% TCO_2 [1]	mg CO_2	% TCO_2 [1]
2	4.5	4	0.0	0	1.7	2
3	38.7	30	0.5	1	2.2	3
4	60.6	47	--	--	--	--
5	70.2	55	0.5	1	2.2	3
7	77.5	60	1.1	3	3.3	4
10	89.3	70	1.1	3	3.3	4
16	101.1	79	1.7	4	3.3	4
25	111.2	87	2.3	6	3.3	4
27	115.1	90	4.0	10	3.9	5
28	117.4	91	4.0	10	3.9	5

[1] *Theoretical CO_2 production*

Comments

The study was well performed and reported, according to the guidelines and in compliance with GLP. Clopyralid is not readily biodegradable under the thest conditions. The test is acceptable. Based on the result of this study, a classification as R52/53 according to the directive 67/548/EEC is proposed.

RMS comments and evaluation:

The ready biodegradability study of clopyralid was evaluated in the DAR (2003) as valid and the result was used in the risk assessment presented in the EFSA conclusion on clopyralid (EFSA Scientific Report 2005: 50). Therefore the evaluation was not repeated here again. Clopyralid is not readily biodegradable. The data requirement is fulfilled and no further data are required.

B.8.4.2.2. Aerobic mineralisation in surface water

This is a new data requirement under Regulation 1107/2009 therefore no data have previously been considered. A new study was submitted by the Notifier, which is evaluated below.

CA 7.2.2.2/1 - Aerobic mineralization of clopyralid in surface water

Report	CA 7.2.2.2/01, Ponte, M. & Hiler, T. 2015
Report title	[14C] Clopyralid: Aerobic Mineralization in Surface Water
DAS Study number	PTRL West; Lab Study No. 2067W DAS Study No. 140078; 26 May 2015
Guidelines	OECD 309
GLP	yes

Materials and methods

The aerobic mineralization of Clopyralid-2,6-^{14}C with a radiochemical purity of 98.0 % and a specific radioactivity of 32.8 mCi/mmol was studied in a natural surface water from Lake Tuckahoe, MD (pH 7.2). The experimental conditions are summarized in Table 8.4.17, and the test apparatus is illustrated in Figure 8.11. below.

Table 8.4.17. Experimental parameters

Parameter		Description
Duration of definitive test		60 days
Test concentrations	nominal, low dose	10 µg/L
	nominal, high dose	80 µg/L
	measured, low dose	10.3 µg/L
	measured, high dose	80 µg/L
Number of replicates		Duplicates of the radiolabel at each time point
Preparation of test medium	Volume per sample	100 mL
	Method of sterilisation	Autoclave
Test item application	Co-solvent	NA
	Volume of application solution used/treatment	0.2 mL
	Application Method	Syringe, to water surface
Test apparatus		250 mL Erlenmeyer glass flasks
Continuous stirring		Yes using a mechanical shaker
Method of aeration		Moistened air flowed over samples
Traps for CO_2 and volatile organics		Foam plug for volatiles, 10% NaOH (14CO2)
Test item sorption to walls of apparatus?		Accounted for during analysis
Experimental conditions	Temperature °C	20.0 ± 2.0
	Lighting	Dark
Method to determine microbial activity of test water		[^{14}C]Clopyralid mineralization
Other details		None

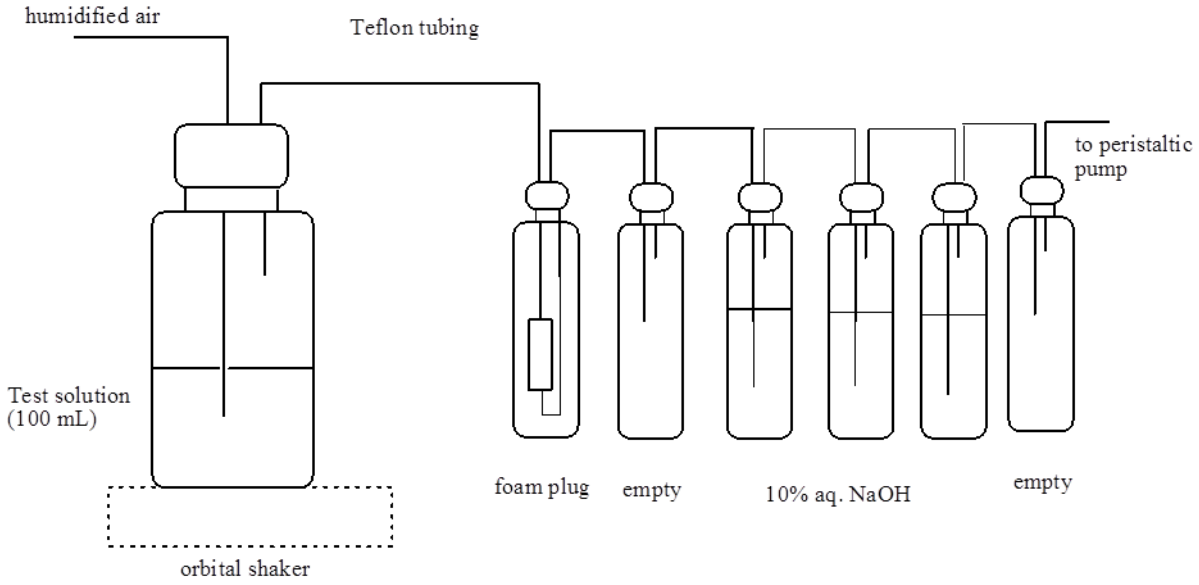


Figure 8.11. Test apparatus

Sampling

A total of 52 samples were prepared for the viable sample sets (46 dosed samples) and 10 samples for the sterile set. All samples received 100 mL of natural water (or sterile natural water as applicable). The experimental design was as follows:

- 22 treated samples to be dosed at the high concentration, sufficient for 9 sampling intervals in duplicate and two extras

- 22 treated samples to be dosed at the low concentration, sufficient for 9 sampling intervals in duplicate and two extras

- 4 treated samples to be dosed with [14C]benzoic acid as controls

- 10 sterile treated samples dosed at the high concentration, sufficient for 5 sampling intervals in duplicate

- remaining samples prepared but not dosed

All samples (except for sterile set) were connected to individual sets of traps containing polyurethane foam plug and three 10% aqueous NaOH traps in series.

The sampling details are presented in Table 8.4.18. below.

Table 8.4.18. Sampling details – definitive test

Criteria	Details
Sampling intervals for the parent/transformation products	0, 3, 7, 14, 28, 38, 48 and 60 days after treatment (DAT)
Sampling method	Aqueous samples were decanted to measure total volume. Aliquots were taken for assessment of 14C by LSC and/or HPLC
Sampling methods for the volatile compounds, if any	Foam plugs were soaked in 20 mL acetonitrile for 2 hours, then aliquots (1 mL) were radioassayed by LSC.
Sampling intervals/times for:	
pH measurement	Days 0, 3, 7, 14, 28, 38, 48 and 60 DAT
sterility check	Days 0, 3, 7, 14, 28, 38, 48 and 60 DAT
Sample storage before analysis	None, except Day 28 (5 days)
Other observation, if any (e.g., precipitation, colour change, etc.)	N/A

Analytical Methodology

The pH and oxygen concentration of the water was monitored (pH 330i & Oxi 330i, WTW GmbH, Weilheim, Germany) in the samples and in a control sample (probes were inserted prior to sampling and the reading recorded after stabilisation of the signal). Measurements were taken for the high dose, high dose (sterile) and low dose samples.

At each sampling interval, the volume of the water phase recorded and the radioactivity present determined by LSC. Aliquots of the samples were taken at each sampling interval for direct HPLC analysis.

For the total ^{14}C measurement, all radioassays utilized 5 mL or 15 mL of scintillation cocktail or Harvey cocktail in 7 mL or 20 mL standard polyethylene counting vials and Beckman LS 6500 or LS 6000IC liquid scintillation counters. Computer-constructed quench curves, derived from a series of ten sealed quenched standards, automatically converted cpm to dpm. Typical parameters are as follows: counting efficiency, 96%; background, 25 dpm; counting time, 1 minute. Scintillation cocktail was added to each sample before counting. Samples were generally counted for 1 minute; however samples that were expected to have low amounts of radioactivity were often counted for 5 minutes or longer.

For quantitation, HPLC analyses of all sample were accomplished using a Capcell C-18 column (250 x 4.6 mm i.d., 5.0 µm; 1.0 mL/min; UV detection at 254 nm) and a four step, non-linear gradient.

Mass spectral analysis (LC/MS) was conducted to identify the transformation products. Initial metabolite identification was accomplished by co-chromatography with available reference standards using HPLC.

To determine the detection limits (LOD, LOQ) for the parent compound, samples were normally counted for 1 minute. Typical background levels were 20 dpm. The LOD was defined as 10 dpm above background and LOQ was defined as 2X background.

β-RAM Chromatograms: The limit of quantitation observed in the HPLC chromatograms was determined by an experiment in which varying volumes of 14C material were injected, and the DPM detected was compared to the actual injected DPM. Based on the results of the experiment, the smallest injection which obtained acceptable recoveries was 258 dpm (limit of quantitation, LOQ). Thus, for a sample size of 30,000 dpm injected of a matrix containing 80 µg/mL:

$$\frac{258 \text{ dpm}}{30000 \text{ dpm injected}} \times 80 \,\mu g/L = 0.69 \,\mu g/L$$

Table 8.4.19. The detection limits (LOD, LOQ) for the parent compound

		LOD		LOQ	
		High dose	Low dose	High dose	Low dose
LSC	Water	0.001% AR	0.007% AR	0.0013% AR	0.01% AR
	Volatiles	0.001% AR	0.007% AR	0.0013% AR	0.01% AR
	NaOH	0.001% AR	0.007% AR	0.0013% AR	0.01% AR
HPLC	Water	0.67% AR	---	0.86% AR	---

The degradation rate of the test item in surface water was calculated using KinGUI ver 2.12.1 (Bayer CropScience) according to FOCUS Kinetics Guidance (2006) on estimating persistence and degradation kinetics from Environmental Fate. In order to estimate DT_{50} and DT_{90} values, Single First-Order (SFO) kinetic model was fitted to the degradation data. Input data sets for modelling were derived from individual data for each time-point. All data points were unweighted. DT_{50} and DT_{90}, chi-square and r^2 values were calculated directly by the software.

Samples were typically analysed on the day of sacrifice. HPLC analysis for % AR determination was completed within 3 days of the sampling time point.

Results and discussion

Oxygen concentrations measured in the surface water of treated samples confirmed aerobic conditions during the incubation period. The pH values during incubation showed stability of the system. Similar values were measured in the control samples, indicating that the test item had no significant effects on the physico-chemical parameters of the test system. The mean temperature during incubation was 20 ± 2 °C for all systems.

Microbial Viability of the Natural Water: Within 14 days of incubation, the decline of the radiocarbon in the water layer declined to only 2.8% AR and recoveries of radioactive carbon dioxide was quantitative. As more than 90% of benzoic acid degraded within 14 days, the test water can be considered as microbially active.

Total radiocarbon recovery ranged from 94.2 to 100.0 % of the applied amount in the high dose samples, 95.3 to 104.6 % of the applied amount in the low dose samples, and 95.1 to 99.9 % of the applied amount in the sterile samples. The material balance in the high and low dose samples as well as in the sterile samples is presented in Tables 8.4.20. - 8.4.23.

Table 8.4.20. Degradation of Clopyralid, expressed as percentage of the applied radioactivity (mean ± std dev.) in the high dose samples

Compound		Sampling times (days)								
		0	3	7	14	21	28	38	48	60
Water		97.1	99.6	97.2	97.8	96.5	95.7	94.4	95.2	95.3
Volatiles	CO_2	NA	0.0	0.0	0.1	0.2	0.4	0.5	0.4	1.0
	volatile organic	NA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Total	NA	0.0	0.0	0.1	0.2	0.4	0.5	0.4	1.0
Total % recovery		97.1	99.6	97.2	97.8	96.7	96.1	94.8	95.5	96.3

Table 8.4.21. Degradation of Clopyralid, expressed as percentage of the applied radioactivity (mean ± std dev.) in the low dose samples

Compound		Sampling times (days)								
		0	3	7	14	21	28	38	48	60
Water		100.8	100.7	96.4	95.9	97.3	98.2	97.3	97.8	98.4
Volatiles	CO_2	NA	0.1	0.1	0.1	0.2	0.0	0.1	0.1	0.1
	volatile organic	NA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Total	NA	0.1	0.1	0.1	0.2	0.0	0.1	0.1	0.1
Total % recovery		100.8	100.8	96.5	96.0	97.5	98.2	97.4	97.9	98.5

Table 8.4.22. Degradation of Clopyralid, expressed as percentage of the applied radioactivity (mean), sterile

Compound		Sampling times (days)				
		7	28	38	50	60
Water		98.9	95.8	96.6	96.3	99.4
Volatiles	(not trapped)	NA	NA	NA	NA	NA
Total % recovery		98.9	95.8	96.6	96.3	99.4

Greater than 93.8% of the applied ^{14}C was associated with the parent compound at test termination, indicating the stability of clopyralid in aqueous environments. At high dose, the major transformation product was CO_2, where an average of 98.2% of the parent clopyralid was present after 60 days. No significant difference in the degradation was observed between the high dose, low dose and sterile samples.

The rate of degradation for clopyralid in surface water was calculated using single first-order (SFO) kinetics. The calculated dissipation half-life (DT_{50}) and DT_{90} values obtained are shown in Table 8.4.23. below.

Table 8.4.23. Degradation rate of Clopyralid

Test item	Conditions	DT_{50} (days)	DT_{90} (days)	Model used	χ^2 error %
parent	High dose	1107	3676	SFO	0.7547

Conclusions

The expected half-life of clopyralid in natural water under aerobic conditions was >1100 days. There were no significant degradation products observed in the aqueous samples high concentration or sterile samples throughout the study period. The CO_2 concentrations reached a maximum of 1.0%AR at 60 DAT in high concentration samples.

RMS comments and evaluation:
The aerobic mineralization study of clopyralid in surface water was well performed according to the guidelines and the GLP, clearly reported and acceptable. The aerobic degradation of clopyralid in surface waters is very slow, and no degradation products other than CO_2 were found. The study is valid and the data can be used in the risk assessment. The data requirement is fulfilled and no further data are required.

B.8.4.2.3. Degradation in water/sediment systems

Data to address this point were presented in the dossier submitted in April 2002 for the Active Approval and were deemed acceptable following evaluation and peer review at EU level. These data are still valid for decision making.

CA 7.2.2.3/1 - Degradation of [^{14}C] Clopyralid in water/sediment systems

Report	IIA 7.2.1.3.2, Hall, B.E., Allan, J. & Lowrie, C. 2002
Report title	The aerobic degradation of [^{14}C]-clopyralid in natural waters and their associated sediments.
DAS Study number	GHE-P-9564, Ref. K77.
Guidelines	BBA, Part IV, Section 5.1 (1990) SETAC-Europe, Part 1, Section 8,2 (1995)
GLP	yes

Methods

The route and rate of aquatic degradation of [2,6-pyridinyl-^{14}C]-clopyralid was investigated in two representative water/sediment systems (of EU origin) under aerobic laboratory conditions. Application was made to the surface water to mimic introduction into aquatic systems via spray-drift.

Two water/sediment systems consisting of loamy sand and sandy silt loam sediments and associated waters were sampled from Chatsworth, UK and Lombardy, Italy, respectively and stored at 4 °C prior to use. The characterisation details of the water/sediment systems are summarised in Table 8.4-8. The associated water samples were screened for pesticide and chemical contamination prior to use.

Sediment samples were loosely added to borosilicate glass cylinders to a depth of 2.5 cm. The corresponding associated water was added to a further depth of 6 cm (100 ml). The resulting ratios of dry sediment to water weights were 1:2 and 1:5 for the sandy loam and sandy silt loam sediments respectively.

A stream of moist CO_2-free air was introduced into the cylinder via a dip-tube extending to just above the surface of the water phase. Air was drawn out of the cylinders through a set of trapping solutions designed to separately collect evolved organic volatile components and CO_2. The volatile trapping solutions were sampled and replenished at regular intervals to avoid saturation.

The water/sediment systems were incubated at a temperature of 20 °C in the dark and pre-equilibrated for a period of 21 days. During the pre-equilibration period the oxygen content, pH and redox potential of the surface water was monitored.

The water/sediment systems were treated with [2,6-pyridinyl-^{14}C]-clopyralid (batch no. F0571 42a, specific activity 30.9 mCi/mmol, RCP 99.2 %) added dropwise onto the water surface. Approximately 9.83 µg clopyralid was added to each water/sediment system, equivalent to a surface water concentration of 100 µg/l. The treatment rate corresponded to the direct over-spray of a water body with an application rate of 300 g a.s./ha and assumes uniform distribution in 30 cm depth. The studied concentration corresponded to ca 36 times the calculated worst case initial PEC_{sw}.

At intervals over 100 days, duplicate samples from each system type were taken and the water and sediment phases separated. The sediment phase was extracted twice with acetonitrile (100 ml) by shaking end-over-end. At later sampling intervals (60 and 100 days) an additional extraction was performed with acidified acetonitrile (acetonitrile:2M hydrochloric acid, 8:2 v/v). The sediment extracts were concentrated under vacuum at ambient temperature. The water phase and the concentrated sediment extracts were quantified by LSC and analysed by both HPLC and TLC. Following extraction the sediment residue was allowed to air dry prior to quantification by combustion analysis.

Table 8.4-24. Summary of characterisation data for water/sediment systems

Water/sediment system	Swiss Lake, Chatsworth, UK	Rivalta sul Mincio, Lombardy, Italy
Sediment		
Textural analysis (%)		
Sand (63-2000 µm)	82.5	34.7
Silt (2-63 µm)	14.8	48.6
Clay (<2 µm)	2.8	16.7
Textural classification (UK)	Loamy sand	Sandy silt loam
pH (H_2O)	5.5	7.7
pH (KCl)	4.9	7.4
pH (0.01M $CaCl_2$)	5.0	7.3
Organic matter (%)[1]	1.21	6.38
Organic carbon (%)	0.7	3.7
Total nitrogen (%)	0.12	0.48
Total phosphorous (%)	0.02	0.14
Dry matter content of air-dried sediment (% w/w dry soil)	99.6	97.9
Parameter taken at time of sampling		
Redox potential at 5 cm (U_H, mV)	24	-63
Associated water		
pH	6.5	8.1
Parameter taken at time of sampling		
Redox potential (U_H, mV)	364	408
O_2 content (%)	90.6	75.5
Conductivity (µS/m)	ND	447
Temperature (°C)	8.5	12.0
pH	6.14	6.6

[1] *Calculated as organic carbon x 1.724*
ND = not determined

Results

The recovery and distribution of the applied radioactivity from the water/sediment systems is summarised in Table 8.4-25.

The overall **recovery of radioactivity** from the non-sterile samples was between 97.5 % and 102.4 % AR indicating a complete mass balance. The distribution of the applied radioactivity was similar for both water/sediment systems.

The amount of radioactivity in the **water phase** steadily declined from between 98.7 % and 100.1 % AR at 0 days following application to between 56.0 % and 67.2 % AR after 100 days. The radioactivity slowly dissipated to the **sediment phase** which comprised of < 1 % AR initially to maximum levels between 28.6 % and 36.4 % AR over the period 60 to 100 days. The majority of the radioactivity was extractable from the sediment phase. The level of NER observed increased slowly to maximum levels between 6.2 % and 7.3 % AR after 30 days incubation and then declined to between 2.0 % and 5.9 % AR. The amount of **volatile** radioactivity evolved was minimal throughout the study, the amount of CO_2 detected slowly increased to between 2.3 % and 5.3 % AR after 100 days. The amount of other organic volatile material recovered comprised of < 0.1 % AR on all occasions.

The recovery of radioactivity from the **sterile samples** ranged from 99.5 % to 102.3 % AR. The distribution of the applied radioactivity observed for the sterile samples was similar to that observed for the non-sterile samples except that the level of CO_2 formation detected in the sterile samples was even lower than that observed in the non-sterile samples. Therefore the results to the sterile samples are not discussed further.

The chromatographic profile as determined by **HPLC analysis** of the water phase and the extractable radioactivity from the sediment phase is summarised in Table 8.4-10. For the majority of cases clopyralid was the only component observed during analysis. Minor metabolites were observed but only in the acidified acetonitrile sediment extracts for the loamy sand water/sediment system at later sampling intervals. The minor metabolites observed consisted of at least three unidentified components, all more polar than clopyralid and comprised of a combined maximum amount of 5.4 % AR.

The levels of clopyralid detected in the **system as a whole** slowly declined from between 98.7 % and 100.1 % AR initially to between 86.6 % and 88.6 % AR after 100 days. The DT_{50} value for clopyralid was not calculated due to the low rate of degradation observed.

The levels of clopyralid detected in the **separate water phase** declined steadily throughout the study and comprised between 56.0 % to 67.2 % AR after 100 days. Correspondingly, the levels of clopyralid detected in the sediment phase increased steadily to between 21.4 % and 30.5% AR by the end of the incubation period.

Table 8.4-25. Recovery and distribution of radioactivity from BBA guideline study design following application to the water

Sampling interval	Water phase (% AR)	Sediment phase (% AR)			Volatile components (% AR)		Mass balance[1] (% AR)
		Extract	NER	(Sub-total)	Organic volatiles	CO_2	
Loamy sand							
0 days	100.13	0.39	0.11	0.50	NS	NS	100.67
6 hours	98.03	1.94	0.63	2.57	0.01	0.01	100.67
1 day	95.30	4.05	1.47	5.52	< 0.01	0.01	100.86
2 days	92.28	5.84	2.22	8.06	< 0.01	0.03	100.38
7 days	84.46	10.11	5.08	15.19	0.01	0.05	99.69
14 days	80.18	13.77	5.53	19.30	0.03	0.10	99.61
30 days	78.27	16.47	7.28	23.75	0.02	0.34	102.39
60 days	69.49	26.82	1.76	28.58	0.04	0.85	98.95
100 days	67.24	23.76	1.95	25.71	0.09	2.27	98.33
30 days sterile	76.03	18.88	4.91	23.79	0.03	0.13	100.65
100 days sterile	74.06	19.86	5.27	25.13	0.04	0.23	99.50
Sandy silt loam							
0 days	98.69	0.82	0.17	0.99	NS	NS	99.71
6 hours	88.94	7.14	1.29	8.43	0.01	0.02	97.48
1 day	89.65	7.32	1.37	8.69	< 0.01	0.02	98.45
2 days	81.99	13.98	2.81	16.79	0.01	0.06	99.08
7 days	77.90	17.31	3.89	21.20	0.01	0.09	99.22
14 days	70.76	23.28	4.55	27.83	0.02	0.18	98.82
30 days	69.11	25.95	6.21	32.16	0.02	0.92	102.24
60 days	60.86	28.09	5.79	33.88	0.05	2.93	97.73
100 days	56.04	30.55	5.85	36.40	0.07	5.30	97.83
30 days sterile	73.24	22.66	5.47	28.13	0.03	0.15	101.55
100 days sterile	75.32	21.46	5.09	26.55	0.06	0.36	102.31

All figures are means of duplicate samples
NS = no sample
[1] Includes up to 0.36% AR recovered as part of an apparatus wash

Table 8.4-26. Profile of extractable radioactivity from BBA guideline study design following application to the water

Sampling interval/ sample type		Radioactive components (% AR)			
		Loamy sand		Sandy silt loam	
		Clopy-ralid	Others	Clopy-ralid	Others
0 day	Aq.	100.13	n.d	98.69	n.d
	Sed.	--	--	--	--
	Total	100.13	n.d	98.69	n.d
6 hour	Aq.	98.03	n.d	88.94	n.d
	Sed.	--	--	7.13	n.d
	Total	98.03	n.d	96.07	n.d
1 day	Aq.	95.30	n.d	89.65	n.d
	Sed.	--	--	7.31	n.d
	Total	95.30	n.d	96.95	n.d
2 days	Aq.	92.28	n.d	81.99	n.d
	Sed.	5.84	n.d	13.95	n.d
	Total	98.12	n.d	95.94	n.d
7 days	Aq.	84.46	n.d	77.90	n.d
	Sed.	10.10	n.d	17.30	n.d
	Total	94.55	n.d	95.20	n.d
14 days	Aq.	80.18	n.d	70.76	n.d
	Sed.	13.76	n.d	23.90	n.d
	Total	93.94	n.d	94.04	n.d
30 days	Aq.	78.27	n.d	69.11	n.d
	Sed.	16.46	n.d	25.95	n.d
	Total	94.73	n.d	95.05	n.d
60 days	Aq.	69.49	n.d	60.86	n.d
	Sed.	22.14	4.69	28.09	n.d
	Total	91.62	4.69	88.94	n.d
100 days	Aq.	67.24	n.d	56.04	n.d
	Sed.	21.39	5.37	30.54	n.d
	Total	88.63	5.37	86.57	n.d
Sterile					
30 days	Aq.	76.63	n.d	73.24	n.d
	Sed.	18.88	n.d	22.66	n.d
	Total	95.50	n.d	95.90	n.d
100 days	Aq.	74.06	n.d	75.32	n.d
	Sed.	19.85	n.d	21.45	n.d
	Total	93.91	n.d	96.76	n.d

All figures are mean of duplicate samples
-- Not analysed
n.d = not detected

The rate of dissipation of clopyralid from the water phase to the sediment phase did not correlate well to first-order kinetics. However, the corresponding **DT_{50} and DT_{90}** values were determined by the Notifier using the methodology described before under soil degradation studies. The results obtained are summarised in Table 8.4-27. Clopyralid dissipated from the water phase with a first-order half-life of between 128 and 167 days.

Table 8.4-27. $DT_{50(lab)}$ and $DT_{90(lab)}$ values for the rate of dissipation of clopyralid from the water phase to the sediment phase

System type	Data range (days)	$DT_{50(lab)}$ (days)	$DT_{90(lab)}$ (days)	Regression parameters		
				C_0	K	R^2
Loamy sand	0 - 100	167	556	93.02	0.0041	0.764
Sandy silt loam	0 - 100	128	425	86.41	0.0054	0.731

Comments

The study was new and well performed and reported, according to the guidelines and in compliance with GLP. The Notifier has again recalculated the DT_{50} and DT_{90} values as described previously. No reason for the recalculation was given. In the original report the respective DT_{50} values of water phase of 182 days for loamy sand system and 143 days for sandy silt loam system (R^2 = 0.81) were calculated with a slightly better fit (R^2 = 0.81 for both systems). No DT_{90} values were calculated in the original report, however.

Movement of clopyralid to the sediment from water did not fully reach equilibrium throughout the 100 day incubation period. Clopyralid dissipated slowly from the water phase to the sediment. Minimal degradation was observed and no major metabolites >10 % of AR were formed in 100 days of incubation.

Clopyralid is very slowly degradable in water/sediment systems according to this study.

Comment from the Notifier on the draft monograph:

The reason for recalculating the kinetics is the same provided for the soil compartment, but was not repeated here. In essence, first-order kinetics based upon log-transformed data were used in the original report, whilst the recalculation was done using first-order kinetics but using non-transformed data which is deemed to give a better fit to the data.

RMS comments and evaluation:

The first order DT_{50} values of 128 - 167 days and DT_{90} values of 425 - 556 days were obtained for the dissipation from the water phase to the sediment in two water/sediment systems within 100 days.

This water/sediment study of clopyralid was evaluated in the DAR (2003) as valid and the result was used in the risk assessment presented in the EFSA conclusion on clopyralid (EFSA Scientific Report 2005: 50). Therefore the evaluation was not repeated here again. Clopyralid is very slowly degradable in water/sediment systems. The outcome is consistent with the other data available on the aquatic degradation of clopyralid. The data requirement is fulfilled and no further data are required.

B.8.4.3. Degradation in the saturated zone

Due to its low leaching potential, no studies on degradation of Clopyralid in the saturated zone have been conducted. No data are provided as currently no guidance or validated methods exist.

RMS comments and evaluation:

It is not agreed that the leaching potential of clopyralid would be low. Although the adsorption potential of clopyralid and the anaerobic degradation DT50 in soil > 1year indicate that the degradation in saturated zones would not be rapid, appropriate use instructions and risk mitigation options allow a safe use with regard to releases into saturated zones, as demonstrated by the PECgw calculations available. With appropriate use instructions that include cautionary measures the leaching risk can be mitigated adequately to prevent significant releases into saturated zones, as addressed with PECgw calculations in Chapter B.8.6.1. No further studies on the degradation in the saturated zone are required to fulfill this data requirement to support the renewal for the approval of clopyralid.

B.8.4.4. Summary of studies on fate and behaviour in water

Concerning the chemical and photochemical degradation of clopyralid in aquatic systems, the EFSA conclusion on the peer review of Clopyralid (EFSA Scientific Report (2005) 50, 1-65) was summarized as:

"In sterile buffer solutions at 50 ºC clopyralid was found to be stable for five days to hydrolysis at environmental relevant pH 4 to 9. Therefore, clopyralid is expected to be stable to hydrolysis for more than 30 d at 20 ºC.

The photochemical degradation of clopyralid in water was investigated in sterile aqueous buffer solutions at pH 7under natural sunlight at 25 ºC. Minimal degradation was observed indicating that photodegradation will not be an environmental significant degradation pathway for clopyralid.

A ready biodegradability test indicated that clopyralid should be classified as a non-ready biodegradable substance. However, the RMS informed the meeting that has proposed to ECB not to classify with R53 based on the ecotoxicological assessment."

A new aqueous photodegradation study according to the current test guideline was submitted in the AIR3 dossier, and the outcome of this study confirms the current understanding of the insignificant role of chemical pathways in the aquatic degradation of clopyralid. In this study the predicted environmental photolytic half-life, derived from the measured half-life in laboratory under artificial lamp (determined using KinGUI software, version 2.12.1), was calculated to be over 38000 days at 40° N latitude in summer sunlight. The quantum yield of clopyralid photolysis was 1.01 $x10^{-6}$. No transformation occurred in the irradiated samples. At study termination, in the irradiated samples, the evolved CO_2 and volatile organics amounted to 0.3% and 0.4% of the applied amount, respectively. The total unidentified radioactivity was 1.9% of the applied radioactivity in the irradiated samples.

The route and rate of biological degradation in aquatic systems was summarized by EFSA, (EFSA Scientific Report (2005) 50, 1-65, Conclusion on the peer review of Clopyralid, 14 December 2005) as follows:

"A study with two water sediment systems is available. Clopyralid partitions slowly from water to the sediment ($DT_{50\ water}$ = 128 d – 167 d) and reaches a maximum of 30.6 % AR after 100 d into the sediment. There is practically no degradation of clopyralid in the water sediment system and up to 91 % AR remains as clopyralid at the end of the experiment after 100 d (extrapolated $DT_{50\ whole\ system}$ > 500 d). Non extractable radioactivity in te sediment amounted at the end of the study (100 d) to 5.85 % AR. The amount of CO_2 formed slowly increased to 2.3 % and 5.3 % AR after 100 d."

A new aerobic mineralization study in surface water was submitted in the AIR3 dossier. The following information has not been previously reviewed for Annex I inclusion: The expected half-life of clopyralid in natural water under aerobic conditions was >1100 days. There were no significant degradation products observed in the aqueous samples high concentration or sterile samples throughout the study period. The CO_2 concentrations reached a maximum of 1.0%AR at 60 DAT in high concentration samples.

As a conclusion, new studies confirmed the previous knowledge on the fate and behaviour of clopyralid in aquatic environments. Its degradation pattern is determined by microbial degradation, resulting to formation of no other degradation products than CO_2, while chemical pathways of degradation are insignificant in the aquatic environments.

B.8.5. IMPACT ON WATER TREATMENT PROCEDURES

Essentially no new information was provided since the first EU evaluation of clopyralid.

RMS comments and evaluation:
The justification by the Notifier of not presenting data is acceptable. Clopyralid is not expected to contaminate groundwater as drinking water source, if appropriate caution, appropriate risk mitigation measures and Good Agricultural Practices are followed. As the uses of GF-1374 formulation, containing clopyralid as one of its active substances, are not intended to greenhouses or otherwise connected to sewage systems, the exposure of sewage treatment plants is not likely and no risk is anticipated.

B.8.6. PREDICTED ENVIRONMENTAL CONCENTRATIONS IN SURFACE WATER AND IN GROUND WATER (PEC_{SW}, PEC_{GW})

B.8.6.1. Predicted environmental concentrations in ground water

GF-1374 was not the representative formulation for the first approval of clopyralid in 2005. For the AIR3 dossier, GF-1374 was changed as the representative formulation, containing less clopyralid and causing a lower environmental exposure compared to the previous formulation representative for the approval of clopyralid in the EU. Therefore a new PEC_{gw} calculation was necessary resulting from the uses of the product GF-1374 on cereals and pasture. The details and evaluation of the PEC_{gw} calculation provided by the Notifier are presented in the dRAR Part 19 Vol. 3 Chapter 8.

B.8.6.2. Predicted environmental concentrations in surface water (PEC_{sw}) and sediment (PEC_{sed})

For the AIR3 dossier, GF-1374 was changed as the representative formulation, containing less clopyralid and causing a lower environmental exposure compared to the previous representative formulation. Therefore a new PEC_{sw} and PEC_{sed} calculation was necessary. Predicted environmental concentrations in surface water and sediment resulting from the uses of GF-1374 were not evaluated as part of the first Active Approval of clopyralid in 2005. The details of the PECsw and PECsed calculations are presented in the dRAR Part 19 Vol. 3 Chapter 8.

B.8.7. FATE AND BEHAVIOUR IN AIR

B.8.7.1. Volatilisation

One study on the volatility of clopyralid from soil and plant surfaces was submitted and evaluated for the Annex I inclusion in the DAR (2003), and considered as valid in the EFSA conclusion. Therefore the study is not re-evaluated here again.

CA7.3.1/1 - The evaporation of clopyralid acid from soil and leaf surfaces following application of LONTREL 100

Report	[IIA 7.2.2/01], Day, S. R. and Rudel, H., 1994
Report title	The evaporation of clopyralid acid from soil and leaf surfaces following application of LONTREL 100
DAS Study number	GHE-P-3507. Ref. K58.
Guidelines	German BBA Guidelines
GLP	Yes

Methods

The volatility of [2,6-pyridinyl-^{14}C]-clopyralid from plant and soil surfaces was investigated in the laboratory using a wind tunnel apparatus. Spray applications of [2,6-pyridinyl-^{14}C]-clopyralid (batch A903-14, specific activity 31.5 mCi/mmol, 6070 kBq/mg, RCP 97.6 %), formulated as the LONTREL 100 EC formulation, were made at a rate of 100 g ai/l (1.2 l product/ha, spray volume 400 l/ha).

The characterisation details of the soil used are summarised in Table 8.7-1. Soil samples were adjusted to 60% MHC and a soil layer of 3 cm was used contained in stainless steel bowls (44.5 cm x 31.5 cm, surface area 0.14 cm^2) prior to spraying with the test compound in an enclosed spray chamber.

Plant experiments were conducted using french beans (*Phaseolus vulgaris*) in the state of flowering. The beans were grown in stainless steel bowls (29.5 cm x 30.0 cm) to an approximate height of 35 cm using a soil with > 70% sand and organic carbon content of ≤ 1.5%. During treatment the soil surface of the plant samples was covered to ensure that evaporation losses were due to volatilisation from the plant surfaces. The samples were placed in an air stream in a volatilisation chamber. The air stream was maintained at *ca* 1-1.2 m/s at a relative humidity of 40% and at 20-21°C. The losses of clopyralid due to evaporation were measured by continuously trapping volatile

material in the air exhaust using polyurethane foam plugs. Plugs were collected after 0-1, 1-3, 3-6 and 6-24 hours and extracted using acetone:acetic acid (8:2 v/v).

Table 8.7-1 Characterisation data for soil used to investigate the volatilisation of clopyralid from soil surfaces

Soil name	Borstel
Country of origin	Germany
Textural analysis (%)	
Sand	76
Silt	18
Clay	6
Soil textural classification (USDA quoted)	Sandy loam/ loamy sand[1]
Soil textural classification (UK)	Sandy loam/ loamy sand[1]
Soil textural classification (BBA)	Silty sand
PH	6.0
Organic matter (%)[2]	2.6
Organic carbon (%)	1.5
MHC (% w/w dry soil)	28.8

[1] *Borderline textural classification*
[2] *Calculated as organic carbon x 1.724*

Results

The **recovery of the applied radioactivity** from the soil and plant samples are summarised in Tables 8.7-2 and 8.7-3 respectively. The overall recovery of radioactivity was between 94 % and 100 % AR indicating a complete mass balance.

The loss of clopyralid due to evaporation was calculated based on the amount of radioactivity recovered from the air samples as a percentage of the total applied radioactivity, less the non-incident radioactivity recovered from the spray chamber.

Following application, **losses due to evaporation** accounted for < 2 % and ≤ 4 % AR from soil and plant surfaces respectively after 24 hours.

Based on these results, clopyralid is not expected to be present in air in significant quantities for longer periods.

Table 8.7-2 Evaporation behaviour of clopyralid from a soil surface

Treatment	Applied material				Recovered material			Total recovery (% AR)
	Total used (mg)	Rinsing of sprayer (mg)	Recovery from spray chamber (mg)	Actual amount applied (mg)	Extract from soil (mg)	NER (mg)	Air sampling (mg)	
1	11.7	0.4	0.7	10.6	9.2 (87%)	0.7 (7%)	0.1 (1%)	10.0 (94%)
2	11.4	2.1	3.9	5.4	4.8 (89%)	0.4 (7%)	< 0.1 (< 2%)	5.3 (99%)

Table 8.7-3 Evaporation behaviour of clopyralid from a plant surface

Treatment	Applied material				Recovered material			Total recovery (% AR)
	Total used (mg)	Rinsing of sprayer (mg)	Recovery from spray chamber (mg)	Actual amount applied (mg)	Rinse of plant surfaces (mg)	Plant residue (mg)	Air sampling (mg)	
1	12.2	0.5	3.3	8.4	7.8 (93%)	0.5 (6%)	0.2 (2%)	8.4 (100%)
2	11.9	0.5	6.5	4.9	4.3 (88%)	0.2 (4%)	0.2 (4%)	4.7 (98%)

Comments

The study was well performed and reported, according to the German guideline and in compliance with GLP. As a conclusion of the results, volatilisation of clopyralid from soil and leaf surfaces is a very minor route of dissipation in the environment. The study is acceptable.

RMS comments and evaluation:

The evaporation data was evaluated in the DAR (2003) as presented above, considered valid and adequate for the Annex I inclusion of clopyralid. Volatilisation of clopyralid from plant and soil surfaces is a very minor route of dissipation of clopyralid. This outcome is still valid and no further studies are required to support the renewal for the approval of clopyralid.

B.8.7.2. Route and rate of degradation in air

Data to address this point were presented in the dossier submitted in April 2002 for the Active Approval and were deemed acceptable following evaluation and peer review at EU level. These data are still valid for decision making.

CA 7.3.1/2 - Photochemical oxidation of clopyralid in air

Report	[IIA 7.2.2/02], Madsen, S. 2002
Report title	Calculation of the Stability in Air of Clopyralid - Photochemical Degradation
DAS Study number	LLC NAFST; Ref. A63
Guidelines	US EPA, AOPWIN v. 1.90 calculation
GLP	Yes

Methods

The stability of clopyralid in air was estimated using the Atmospheric Oxidation Program provided by the U.S. Environmental Protection Agency (AOPWIN v. 1.90, © 2000 U.S.EPA). The estimation methods used were based upon the structure-activity relationships developed by Dr. Roger Atkinson and co-workers. The software provided estimates of the rate constant and half-life for the atmosphere gas-phase reaction between the test substance and average atmospheric concentrations of hydroxyl radicals and ozone.

The structure of clopyralid was inputted into the software using SMILES (Simplified Molecular Input Line Entry System) notation, and the estimated results were calculated.
Results

The hydroxyl radical rate constant was calculated to be 0.5481 x 10^{-12} cm^3 / molecule-sec. Assuming a hydroxyl radical concentration of 1.5 x 10^{-6} OH / cm^3 in air and a 12-hour day, a half-life of 19.513 days was obtained.

Comments

The calculation was well reported and acceptable. The photochemical degradation of clopyralid is slow if compared to the criterion of 2 days for persistent organic pollutants (POP) set by UN-ECE.

RMS comments and evaluation:

The photochemical oxidative degradation in air for clopyralid is slow, with a calculated half-life of 19.5 days (Atkinson method, AOPWIN v1.90). The calculation was considered valid and adequate for the Annex I inclusion of clopyralid in the DAR (2003), as presented above. No further studies are required to support the renewal for the approval of clopyralid.

B.8.7.3. Transport via air

The photochemical oxidation of clopyralid in atmosphere is slow (DT50 19.5 days) and it has a low vapour pressure of 1.02 x 10^{-5} mm Hg at 25°C (CA 2.2). In this respect clopyralid fulfils the UN-ECE POP criteria of potential long-range atmospheric transport. However, the other POP criteria (persistence, toxicity, bioaccumulation) are not met. According to experimental data on volatilisation, its evaporation from soil and plant surfaces is minimal, and therefore it is not expected to be present in air in significant quantities. Its Henry's law constant (3.28 x 10^{-10} Pa m^3 /mol) also indicates that its partitioning into air is negligible. Therefore it can be concluded that the potential for long-range transport of clopyralid via air might be considered as minimal, and no further evaluation is required.

RMS comments and evaluation:

The data on the fate and behavior of clopyralid in air is still valid and acceptable, and no further studies are required to support the renewal for the approval of clopyralid.

B.8.7.4. Local and global effects

This is a new data requirement under Regulation 1107/2009 therefore no data have previously been considered. The evaluation of local and global effects is only required for a substance applied in high amounts. This does not apply to Clopyralid and no further evaluation is required. It was concluded that clopyralid is anticipated not to be present in air in significant quantities due to low vapour pressure, low Henry's Law Constant, and experimental data on volatilisation. Due to experimental data on volatilisation of clopyralid, the potential for long-range transport via air might be considered as minimal.

As Summarized by EFSA, (EFSA Scientific Report (2005) 50, 1-65, Conclusion on the peer review of Clopyralid, 14 December 2005):

"Concentration of clopyralid in the air compartment and transport through it is not expected to be significant. Although photochemical oxidation in atmosphere is slow (DT_{50} = 19.5d) has a low vapour pressure and its Henry's law constant indicates that its partitioning into air is negligible. According to one available study, evaporation of clopyralid from soil and plant surfaces is minimal."

RMS comments and evaluation:

The data on the fate and behavior of clopyralid in air is still valid and acceptable, and no further studies are required to support the renewal for the approval of clopyralid.

B.8.7.5. Summary of fate and behaviour in air

Clopyralid is not expected to evaporate significantly from canopy after application. The vapour pressure of Clopyralid does not exceed the trigger for volatilisation. The concentration of clopyralid in the air compartment and transport through it is not expected to be significant from the intended uses of the product GF-1374, if the use instructions and the GAPs are followed.

RMS comments and evaluation:

The justification of the Notifier is agreed and acceptable, and no further studies are required to support the renewal for the approval of clopyralid.

B.8.8. ESTIMATION OF CONCENTRATIONS FOR OTHER ROUTES OF EXPOSURE

No further data are required, as no other routes of environmental exposure are anticipated in addition to those as evaluated above.

RMS comments and evaluation:

The justification of the Notifier is agreed and acceptable, and no further studies are required to support the renewal for the approval of clopyralid.

B.8.9. DEFINITION OF RESIDUE

B.8.9.1. Definition of the residue for risk assessment

Components included in the residue definition for risk assessment purposes are presented below:

Compartment	Component
Soil	Clopyralid
Groundwater	Clopyralid
Surface water	Clopyralid
Sediment	Clopyralid
Air	Clopyralid is not volatile and it is not expected that any of the metabolites formed in soil, water or sediment will be volatile. Therefore, it is unlikely that there will be any environmental or toxicological risk resulting from residues of active or its degradation products in air. In the absence of official guidance no residue definition is proposed for air.

B.8.9.2. Definition of the residue for monitoring

Components included in the residue definition for monitoring purposes are presented below:

Compartment	Component
Soil	Clopyralid
Groundwater	Clopyralid
Surface water	Clopyralid
Sediment	Clopyralid
Air	Clopyralid is not volatile and it is not expected that any of the metabolites formed in soil, water or sediment will be volatile. Therefore, it is unlikely that there will be any environmental or toxicological risk resulting from residues of active or its degradation products in air. In the absence of official guidance no residue definition is proposed for air.

RMS comments and evaluation:

The definitions of the residue for risk assessment and monitoring purposes presented by the Notifier are agreed and acceptable, and no further data are required to support the renewal for the approval of clopyralid.

B.8.10. MONITORING DATA CONCERNING FATE AND BEHAVIOUR OF THE ACTIVE SUBSTANCE, METABOLITES, DEGRADATION AND REACTION PRODUCTS

Two monitoring reports to address this point were available. The first of them (Wright & Horth 2002) was presented in the dossier submitted in April 2002 for the Active Approval and was deemed acceptable following evaluation and peer review at EU level. A summary from the DAR (2003) is presented below. These data are still valid for decision making.

CA7.5. - Monitoring of clopyralid in groundwater and surface water

Report	[IIA 7.4/1], Wright, K. & Horth, H. 2002
Report title	Review of monitoring and occurrence of clopyralid in groundwater and surface water in Europe.
DAS Study number	Water Research Council, Wallingford, Oxon, UK GHE-P-9757, Ref. K75.
Guidelines	Local sampling and measurement guidelines are likely variable
GLP	No

Methods

A survey was undertaken by WRc Medmenham, Henley Road, Medmenham, Marlow, Bucks, UK of clopyralid monitoring programmes and occurrence data across Europe (15 EU Member States, as well as Norway and Switzerland). The survey focused on data for surface waters and groundwater, although some drinking water data were also included. The information was obtained from professional contacts across Europe (government departments and research organisations), in-house data and published studies.

Only a small amount of data for clopyralid in European waters was found and the search should not be considered complete. An attempt was also made to classify the data in terms of their reliability (Categories I to III, where III = the most reliable), although a low category assignment does not necessarily mean the data are unreliable. For example, there may have been inadequate information given in the source reports to assign a higher category.

Data were available for Denmark, Germany, Sweden and the UK only. Data were also available from the EU COMMPS dataset. Data from a total of 7503 samples from 1081 sites were obtained.

Results

Clopyralid was found in groundwater in Denmark, Germany and the UK in a small proportion of samples (0.3% of about 2000 samples and almost 700 sites). A concentration of 0.1 µg/l was exceeded in 2 samples in Denmark only.

Some surface water data were available for Germany, Sweden and the UK. Clopyralid was found at low concentrations at one site in Germany (maximum concentration 0.1 µg/L) but some high concentrations were reported from Sweden and the UK (maxima at 10 µg/L and 14 µg/L, respectively). These may have been relatively short-term pollution incidents. The COMMPS database only contained data from one site in Germany.

For drinking water, several cases of non-compliance with the drinking water standard of 0.1 µg/L have been reported from the UK, where remedial measures were required in at least 100 water supply zones of two water companies.

To provide an overview, the data are summarised in Table 8.10.1.

Table 8.10.1. Summary of clopyralid monitoring data

Country	Date	No. sites	No. samples	Detected (samples)		Samples >0.1 µg/l		Max.	LoD (LoDtm)	Cat.
				No.	%	No.	%	µg/l	µg/l	
Groundwater										
Denmark	93-99	226	427	2	0.5	2	0.5	0.12	<0.1	II
Germany	93-94	275	1,246	4 sites	0.3	0	-	0.09	0.01-0.3 (0.02–0.1)	I
UK	96/99	193	332	1	0.3	0	-	0.02	0.02	II
Total*	***93-99***	***694***	***2,005***	***7***	***0.3***	***2***	***0.1***	***0.12***	***0.01-0.3 (0.02–0.1)***	***I-II***
Surface water										
Germany	93-94	19	238	0	-	0	-	-	0.01-0.3 (0.01-1.0)	I
Sweden	92-96	2	253	14	5.5	14	5.5	10	(0.3)	III
UK	95 96/99	? 66	191 606	15 41	8 6.8	10 >1	5 -	0.08** 14	0.02-0.2 ?	II II
Total*	***93-99***	***86***	***1,309***	***71***	***5.3***	***>25***	***>1.8***	***14***	***0.01-0.3 (0.01-1.0)***	***I-III***
EU-COMMPS (Germany only)	97	1	21	1 site	4.8	0	-	0.1	?	I
Drinking water										
Germany	93-94	201	537	1 site	0.2	0	0	0.1	0.01-0.3 (0.02–0.1)	I
UK	91-97	100	3,652	18	0.5	18	-	>0.1	0.01	III
Total	***91-97***	***301***	***4,189***	***19***	***0.5***	***18***	***2.4***	***>0.1***	***0.01-0.3 (0.02–0.1)***	***I-III***
All water types										
Total*	***91-99***	***1,081***	***7,503***	***97***	***1.3***	***>45***	***0.6***	***14***	***0.01-0.3 (0.01-1.0)***	***I-III***

LoD = limit of detection (LoDtm = limit of determination)
** = sites have not been added where there may be overlap, i.e. the total represents a minimum number*
*** = 95th percentile*
? = no information

Comments

The survey was new and well reported. As currently no guidance is available on how to harmonise the performance of the monitoring, the methods may have varied a lot in different countries and laboratories, and therefore the results are difficult to compare.The reliability categorisation of the data is helpful for the rapporteur in evaluating the data. The survey of monitoring data over Europe is valuable for evaluating the risk of clopyralid to ground and surface waters and for deciding on the acceptability of clopyralid into Annex I.

Clopyralid seems not to be one of the most frequently monitored pesticidal active substances in Europe. However, in a few countries monitoring programmes include clopyralid, and the drinking water standard 0.1 µg/l was exceeded or close to be exceeded in a few cases. Taking into account also other mobility data, risk mitigation measures for protecting drinking water sources may be warranted at Member State level.

RMS comments and evaluation:

The summary of monitoring data in Europe was originally evaluated as valid in the DAR (2003) and the data are still valid for the risk assessment. A more recent study report with a wider coverage over Europe was submitted by the Notifier to support the AIR3 evaluation of clopyralid, and the study is evaluated below.

CA7.5. - Monitoring of clopyralid in groundwater and surface water

Report	CA 7.5/1; Aldous, E., Johnson, I. And Keirle, R. 2015
Report title	Review of monitoring and occurrence of clopyralid in surface freshwater, groundwater and drinking water in Europe.
DAS Study number	WRc plc, Swindon, UK. WRc Report Reference: UC10779.02. DAS Report No. 150295.
Guidelines	Local sampling and measurement guidelines are likely variable
GLP	No

Survey methods

National governmental departments, national or regional authorities and/or research institutes in each of the relevant countries were approached for data obtained through relevant research projects and / or national or regional monitoring programmes. A comprehensive list of contacts is provided in the study report. Organisations approached but which did not provide a response are also named in this report. In addition, thorough internal (WRc) and external (e.g. Science Direct) literature searches were performed for academic papers/journals and reports containing relevant data. Websites of selected institutions were also searched for relevant information.

A critical assessment of the data is provided, where possible, from the available information, including details of:

- Type of sample (focusing on surface water and groundwater, but including well water, soil and sediment where the information is readily available);
- Method of analysis;

- Number and type of sampling sites;
- Number of samples analysed, sampling frequency, seasonal sampling;
- Number of positive findings (numerical value where possible), negative findings (with indication of limit of detection, if available);
- Any indications concerning correlation with pesticide application, accidental spillage, or other explanations for positive findings;
- Information on quality assurance programmes and analytical quality control (QA/AQC); and
- Information on whether data forms part of a national, regional or other spatial form of monitoring programme.

The quality of the data in this report has been assessed on a preliminary basis to determine its reliability with the categorisations being broadly consistent with previous reports. However a new category to accommodate studies where insufficient evidence to assess reliability has been added. These four categorisations are now more reflective of the Klimisch codes used in European Chemical Agency (ECHA) guidelines for assessing data reliability (ECHA, 2011). Descriptions of the categories are given below.

Category III: Reliable

Studies or data generated according to validated methods that are internationally recognised by laboratories that are accredited (e.g. ISO, GLP). The methodology and test parameters used are well documented and complete.

Category II: Reliable with restrictions

Studies or data generated in which the studies do not comply with national or international guidelines but are well documented and based on sound scientific principles. This may include data generated before the establishment of standardised guidelines or studies conducted in laboratories that are not accredited.

Category I: Unreliable

Studies or data generated using an unorthodox methodology that may introduce uncertainties and negate scientific precision and accuracy. This may also include inconsistent or biased methodologies or studies where insufficient controls were used.

Category X: Insufficient data

Studies where insufficient or limited data (including that on the analytical methodology) are provided and the data cannot be classified. This is not to say that the studies are considered reliable or unreliable. Studies include data located in secondary sources that are insufficiently referenced as to locate the original data.

Category III and II data are of a standard that can be considered to be reliable. Data from category I and X are not considered to be suitable for use. However, data assigned category X may be used in a supporting manner to contribute towards a ‘weight of evidence’ approach.

It is worth noting that some laboratories make a distinction between limit of detection (usually the method limit of detection established by analysing standards) and the limit of determination or quantification (where the sample matrix is taken into consideration). The latter is usually somewhat higher and gives a better indication of the true limit, particularly in surface water samples where there

is normally significant 'background noise' in analytical determinations. However, the difference between the two limits may be insignificant in groundwater analyses. Most studies do not distinguish between these, and it is often not clear which limit is reported. In such cases, we have quoted the given limits as limits of detection (LoD), whereas limits of quantification (LoQ) are presented, only where specific reference has been made to this limit in the reported studies.

A concentration value of 0.1 µg l^{-1} is often used as a baseline value for pesticide contamination of waters in monitoring programmes, although such low levels do not usually reflect concentrations of concern in terms of potential human or ecological effects. For example, Environmental Quality Standards or Objectives (EQS, EQO) in surface waters are usually higher than this value.

The reason for applying this low value is in the use of such the waters as sources for drinking water supplies. A limit of 0.1 µg l^{-1} applies for individual pesticides in drinking water (0.5 µg l^{-1} for the sum of pesticides) in the European Union (EU Drinking Water Directive 1998, 98/83/EC and the previous, 1980, Directive 80/778/EC). The latter standard is not based on toxicological considerations, but compliance with this limit is a legal requirement.

Keeping pesticide concentrations below the standard is considered particularly important in the case of groundwater, which is often supplied to consumers after minimal treatment. In contrast, more extensive treatment is usually required for surface waters, sometimes including advanced treatment techniques (e.g. activated carbon adsorption, advanced oxidation techniques), which typically result in the removal of pesticides, along with other raw water contaminants. However, it is sometimes necessary to install additional treatment processes, specifically to remove pesticides, in order to achieve the prescribed drinking water quality limits. Consequently, where data for pesticide concentrations in drinking water have been reported, it must be stressed that such results may not reflect the pesticide concentrations of untreated water sources.

It is also worth noting that pesticide concentrations are much more variable in surface waters, compared with groundwater, which tends to exhibit relatively constant levels over a considerable period of time (many years). In surface waters, short-term peaks may occur, for example due to run-off after application of pesticides followed by rainfall, and produce seasonal patterns linked to pesticide application. Hence, a higher sampling frequency is required to provide a conclusive picture of the extent of pesticide concentrations in river waters. However, groundwater requires a much longer period for recovery, once contaminated.

In some cases, where the reason for a result (such as an isolated positive finding or an unusually high concentration of a pesticide) is not clear in terms of its significance to water contamination, it may be worth trying to obtain some further follow-up information. However, such detailed investigations are outside the scope of this study.

Results

Overall, there are monitoring data from 23 individual European countries (the United Kingdom includes separate reporting for England, Wales, Scotland and Northern Ireland). It is difficult to summarise and compare all the data because of the variety of ways in which the data have been made available. For example, observed concentrations were sometimes reported in ranges only and limits of detection or quantification (LoDs/LoQs) were not always explicitly reported. Moreover, these were found to vary between laboratories used in different countries or regions and from year to year. The LoDs/LoQs are not reported in some original source data so the 'less than' sign (<) has been used indicating that the value is less than the analytical method can measure. Where reported, the LoQs are mainly below the drinking water limit of 0.1 µg l^{-1}. However, due to the number of different laboratories, analytical methods used and reporting techniques there are data above the 0.1 µg l^{-1} limit. The LoD/LoQ groundwater data range from 0.003 – 1.0 µg l^{-1}, the surface freshwater range from 0.002 – 200 µg l^{-1} and the drinking water data range from 0.001 – 0.2 µg l^{-1}. The higher groundwater

and surface freshwater LoDs have been in the United Kingdom (Scotland in 2008/9), but no explanation for using the high limit was provided. In some cases where there was no information about the LoD/LoQs, it was possible to infer them from the available data (e.g. the LoQ was less than the lowest reported values).

The scope of the project was to report publically available data for clopyralid. In some cases, where the reason for a result (such as an isolated positive finding or an unusually high concentration of a pesticide) is not clear in terms of its significance to water contamination, some effort to obtain explanatory or contextual information has been made where this is feasible. However, such detailed investigations on all such values are beyond the scope of this study.

Clopyralid is approved for use in 26 countries and there are twelve countries that have monitored clopyralid in groundwater, surface freshwater and drinking water: Austria, Belgium, Czech Republic, Finland, France, Ireland, Norway, Slovakia, Sweden, Switzerland, the Netherlands and the United Kingdom.

For all the water types (groundwater, surface freshwater and drinking water), data were reported for over 7,181 sites and 87,107 samples, of which ≤4.92% of the total (≤4,287 samples) were above the drinking water limit of 0.1 µg l^{-1}. However, this figure is higher than the actual number due to laboratories using Limits of Detection or Quantification >0.1 µg l^{-1} especially when analysing surface freshwater (France, Ireland, Slovakia, Sweden and the United Kingdom).

Groundwater monitoring data showed that clopyralid was only monitored in groundwater in eight countries (Austria, Belgium (Wallonia), Czech Republic, Ireland, Norway, Slovakia, Sweden and the United Kingdom). There were greater than 4,459 sites and over 24,538 samples. Clopyralid was detected and exceeded the 0.1 µg l^{-1} drinking water limit in ≤0.35% of groundwater samples (≤85 samples). Maximum concentrations in excess of 0.1 µg l^{-1} were reported in Belgium (Wallonia), Czech Republic, Slovakia, Sweden and the United Kingdom (England and Wales). A maximum clopyralid concentration of 17.1 µg l^{-1} was reported in the Czech Republic.

Surface freshwater monitoring data showed that clopyralid was monitored in eleven countries (Austria, Belgium (Wallonia), Czech Republic, Finland, France, Norway, Slovakia, Sweden, Switzerland, the Netherlands and the United Kingdom). It was generally more frequently found and at higher concentrations than in groundwater, though with more variability as is typical of surface freshwater. There were greater than 1,678 sites monitored and 21,159 samples analysed. Clopyralid was detected and exceeded 0.1 µg l^{-1} in ≥4,172 samples which represented ≤19.71% of all samples. However, there were LoDs >0.1 µg l^{-1} and this has exaggerated the number of samples exceeding the limit. Maximum concentrations in excess of the 0.1 µg l^{-1} drinking water limit were reported in the Czech Republic, Finland, France, Norway, Slovakia, Sweden, Switzerland and the United Kingdom (England, and Scotland).

Drinking water monitoring data showed that clopyralid was only monitored in four countries (Czech Republic, Ireland, Sweden and the United Kingdom). There were 1,044 sites although this is an underestimate of sites as data for England and Wales is reported from single Water Companies and the number of sites was not reported and 41,410 samples analysed. There were 30 samples which had clopyralid concentrations above 0.1 µg l^{-1}, representing 0.07% of the total with the maximum reported concentration being in the range 0.0005 – 0.3 µg l^{-1}.

It must be noted that, whilst the presence of pesticides in drinking water indicates their presence in the source water, their concentration or absence in drinking water does not necessarily reflect their concentration or absence in the source waters, as they may be removed during water treatment.
The highest reported concentrations were in surface freshwater with 1,980 µg l^{-1} detected in 2014 in England (Anglian Region) and groundwater in the Czech Republic with a concentration of 17.1 µg l^{-1}. In both instances, there are no supporting data to indicate the reason for the high concentrations.

Where information is provided on analytical methodologies and/or analytical quality control (AQC), the data are considered reasonably reliable, falling under Category II. However, many datasets were provided with no accompanying methodology and some reports which lacked sufficient detail on this subject were classified as Category X.

The monitoring data of clopyralid in ground waters, surface waters and drinking waters over Europe is summarized in Table 8.10.2.

Table 8.10.2. Summary of available Clopyralid monitoring data in groundwater, surface freshwater and drinking water in Europe

Country	Year	No. of sites	No. of samples	Detected (samples)		Samples with values >0.1 µg l^{-1}		Max. conc.[a]	LoD[b]	LoQ[b]	Quality Category [1]
				No.	% of total	No.	% of total	µg l^{-1}	µg l^{-1}	µg l^{-1}	
Groundwater (GW)											
Austria	2008	204	46	0	0	0	0	<0.03	0.03	-	X
	2010		201	0	0	0	0	<0.015	0.015	-	X
Belgium (Flanders)	-	-	-	-	-	-	-	-	-	-	-
Belgium (Wallonia)	2009 - 2013	424	1,854	190	10.25	3	0.16	0.336	-	0.005	X
Bulgaria	-	-	-	-	-	-	-	-	-	-	-
Croatia	-	-	-	-	-	-	-	-	-	-	-
Cyprus	-	-	-	-	-	-	-	-	-	-	-
Czech Republic	2009 - 2014	≥665	6,425	50	0.78	20	0.31	0.48 – 17.1	-	0.03 – 0.09	X
Denmark	-	-	-	-	-	-	-	-	-	-	-
Estonia	-	-	-	-	-	-	-	-	-	-	-
Finland	-	-	-	-	-	-	-	-	-	-	-
France	-	-	-	-	-	-	-	-	-	-	-
Germany	-	-	-	-	-	-	-	-	-	-	-
Greece	-	-	-	-	-	-	-	-	-	-	-
Hungary	-	-	-	-	-	-	-	-	-	-	-
Ireland	2014	NR	205	0	0	0	0	<0.005	-	0.005	I
Italy	-	-	-	-	-	-	-	-	-	-	-
Latvia	-	-	-	-	-	-	-	-	-	-	-
Lithuania	-	-	-	-	-	-	-	-	-	-	-
Luxembourg	-	-	-	-	-	-	-	-	-	-	-
Malta	-	-	-	-	-	-	-	-	-	-	-
Norway	2007 - 2012	>28	199	0	0	0	0	-	-	-	X
Poland	-	-	-	-	-	-	-	-	-	-	-
Portugal	-	-	-	-	-	-	-	-	-	-	-
Romania	-	-	-	-	-	-	-	-	-	-	-
Slovakia	2008 - 2013	171	904	1	0.11	1	0.11	<0.02 – 0.96	-	0.02	X
Slovenia	-	-	-	-	-	-	-	-	-	-	-
Spain	-	-	-	-	-	-	-	-	-	-	-
Sweden	2008 - 2013	≥16	369	2	0.54	0	0	<0.003 – 0.027	0.003 – 0.02	-	X
	2008 - 2014	114	1,136	7	0.62	2	0.18	0.009 – 5.2	-	0.005 – 0.2	X

Country	Year	No. of sites	No. of samples	Detected (samples)		Samples with values >0.1 µg l^{-1}		Max. conc.[a]	LoD[b]	LoQ[b]	Quality Category [1]
				No.	% of total	No.	% of total	µg l^{-1}	µg l^{-1}	µg l^{-1}	
Switzerland	-	-	-	-	-	-	-	-	-	-	-
The Netherlands	-	-	-	-	-	-	-	-	-	-	-
United Kingdom:											
England	2008 - 2015	2,486	10,471	106	1.01	58	0.55	<0.01 – 2.46	0.01 – 0.2	-	II
Wales	2010 - 2015	149	712	6	0.84	1	0.14	0.555	0.01 – 0.1	-	II
Scotland	2008 - 2013	202	2,016	6	0.30	0	0	<0.025 - <1.0	<0.025 - <1.0	-	II
Northern Ireland	-	-	-	-	-	-	-	-	-	-	-
Total GW	***2007 - 2015***	***≥4,459[c]***	***24,538***	***368***	***1.50***	***85***	***0.35***	***<0.003 – 17.1***	***0.003 – 1.0***	***0.005 – 0.2***	***I, II, X***
Surface freshwater (FW)											
Austria	2008	8	6	0	0	0	0	<0.03	0.03	-	X
	2010		6	0	0	0	0	<0.015	0.015	-	X
Belgium (Flanders)	-	-	-	-	-	-	-	-	-	-	-
Belgium (Wallonia)	2009 - 2013	10	171	11	6.43	0	0	0.002 – 0.007	-	0.005	X
Bulgaria	-	-	-	-	-	-	-	-	-	-	-
Croatia	-	-	-	-	-	-	-	-	-	-	-
Cyprus	-	-	-	-	-	-	-	-	-	-	-
Czech Republic	2009	111	466	8	1.71	≤8	≤1.71	0.4	-	0.05	X
	2012	21	NR	NR	NR	NR	NR	NR	-	NR	X
Denmark	-	-	-	-	-	-	-	-	-	-	-
Estonia	-	-	-	-	-	-	-	-	-	-	-
Finland	2007 - 2012	≤39	506	40	7.91	-	-	0.44	-	0.05 – 0.1	X
	2008 - 2012	15	255	136	53.33	≤43	≤16.86	0.025 – 0.44	-	0.05 – 0.1	X
France	2008	596	3,446	2	0.06	(≤216[d])	(≤6.27[d])	0.025 – 0.25	-	0.05 – 0.5	X
Germany	-	-	-	-	-	-	-	-	-	-	-
Greece	-	-	-	-	-	-	-	-	-	-	-
Hungary	-	-	-	-	-	-	-	-	-	-	-
Ireland	2011	1	2	2	100	1	50	0.125	-	0.25	X
Italy	-	-	-	-	-	-	-	-	-	-	-
Latvia	-	-	-	-	-	-	-	-	-	-	-
Lithuania	-	-	-	-	-	-	-	-	-	-	-
Luxembourg	-	-	-	-	-	-	-	-	-	-	-
Malta	-	-	-	-	-	-	-	-	-	-	-
Norway	2008 - 2013	≥9	492	43	8.74	21	4.27	0.3 – 2.4	-	<0.05 - <0.065 [e]	X
Poland	-	-	-	-	-	-	-	-	-	-	-
Portugal	-	-	-	-	-	-	-	-	-	-	-

Country	Year	No. of sites	No. of samples	Detected (samples)		Samples with values >0.1 µg l^{-1}		Max. conc.[a]	LoD[b]	LoQ[b]	Quality Category[1]
				No.	% of total	No.	% of total	µg l^{-1}	µg l^{-1}	µg l^{-1}	
Romania	-	-	-	-	-	-	-	-	-	-	-
Slovakia	2008 - 2013	198	3,026	14	0.46	(≤2,979[d])	(≤92.3[d])	<0.08 – 4.9	-	0.08 – 0.35	X
	2008 - 2012	34	698	0	0	(≤554[d])	(≤79.37[d])	0.04 – 0.35	-	0.08 – 0.35	X
Slovenia	-	-	-	-	-	-	-	-	-	-	-
Spain	-	-	-	-	-	-	-	-	-	-	-
Sweden	2008 - 2013	4	569	248	43.59	102	17.93	0.011 – 2.2	0.004 – 0.02	0.002 – 0.05	X
	2008 - 2013	2	108	50	46.30	10	9.26	0.01 – 0.18	0.005 – 0.03	0.01 – 0.05	X
	2008 - 2014	64	455	60	13.19	14	3.08	0.007 – 0.7	0.003 – 0.5	-	X
	2010 - 2012	2	54	27	50	≤27	50	0.025 – 0.48	-	0.02 – 0.05	X
Switzerland	2012	5	45	0	0	0	0	<LoD	NR	-	II
The Netherlands	2008 - 2013	286	NR	NR	NR	NR	NR	<75	NR	-	II
United Kingdom:											
England	2008 - 2015	160	4,609	234	5.08	143	3.1	<0.01 – 1,980	0.01 - 100	-	II
Wales	-	-	-	-	-	-	-	-	-	-	-
England & Wales	2006 - 2012	6	2,700	-	-	37	1.37	0.59	0.01 – 0.04	-	II
Scotland	2008 - 2013	104	2,899	18	0.62	7	0.24	0.025 – 0.384 (<1.0)	0.025 – 1.0	-	II
Northern Ireland	-	-	-	-	-	-	-	-	-	-	-
Great Britain	2010 - 2012	3	646	10	1.55	≤10	≤1.55	0.005 – 0.2	-	0.01 – 0.1	X
Total FW	***2006 - 2015***	***≥1,678[c]***	***21,159***	***903***	***4.27***	***(≤4,172[d])***	***(≤19.71[d])***	***0.002 – 1,980***	***0.002 – 1.0***	***0.002 – 0.35***	***II, X***
Drinking water (DW)											
Austria	-	-	-	-	-	-	-	-	-	-	-
Belgium	-	-	-	-	-	-	-	-	-	-	-
Bulgaria	-	-	-	-	-	-	-	-	-	-	-
Croatia	-	-	-	-	-	-	-	-	-	-	-
Cyprus	-	-	-	-	-	-	-	-	-	-	-
Czech Republic	2013-2014	95	122	0	0	0	0	<0.03 – <0.05	0.03	0.05	X
Denmark	-	-	-	-	-	-	-	-	-	-	-
Estonia	-	-	-	-	-	-	-	-	-	-	-
Finland	-	-	-	-	-	-	-	-	-	-	-
France	-	-	-	-	-	-	-	-	-	-	-
Germany	-	-	-	-	-	-	-	-	-	-	-
Greece	-	-	-	-	-	-	-	-	-	-	-
Hungary	-	-	-	-	-	-	-	-	-	-	-
Ireland	2009 - 2013	714	797	NR	NR	0	0	0.0005 – 0.014	0.001 – 0.1	-	X

Country	Year	No. of sites	No. of samples	Detected (samples)		Samples with values >0.1 µg l^{-1}		Max. conc.[a]	LoD[b]	LoQ[b]	Quality Category [1]
				No.	% of total	No.	% of total	µg l^{-1}	µg l^{-1}	µg l^{-1}	
Italy	-	-	-	-	-	-	-	-	-	-	-
Latvia	-	-	-	-	-	-	-	-	-	-	-
Lithuania	-	-	-	-	-	-	-	-	-	-	-
Luxembourg	-	-	-	-	-	-	-	-	-	-	-
Malta	-	-	-	-	-	-	-	-	-	-	-
Norway	-	-	-	-	-	-	-	-	-	-	-
Poland	-	-	-	-	-	-	-	-	-	-	-
Portugal	-	-	-	-	-	-	-	-	-	-	-
Romania	-	-	-	-	-	-	-	-	-	-	-
Slovakia	-	-	-	-	-	-	-	-	-	-	-
Slovenia	-	-	-	-	-	-	-	-	-	-	-
Spain	-	-	-	-	-	-	-	-	-	-	-
Sweden	2008 - 2014	115	1,709	2	11.70	0	0	0.007 - <0.1	0.005 – 0.2	-	X
Switzerland	-	-	-	-	-	-	-	-	-	-	-
The Netherlands	-	-	-	-	-	-	-	-	-	-	-
United Kingdom:											
England	2008 - 2014	24[h]	36,357	NR	NR	25	0.07	NR	NR	-	III
Wales	2008 - 2014	1[h]	268	NR	NR	0	0	NR	NR	-	III
Scotland	-	-	-	-	-	-	-	-	-	-	-
Northern Ireland	2008 - 2015	45[c, f]	235	NR	NR	0	0	<0.0057 – 0.077	0.001 – 0.066		III
	2008 - 2015	50[c, g]	1,922	NR	NR	5	0.26	<0.016 – 0.3	0.001 – 0.04	-	III
Total DW	***2008 - 2015***	***1,044*** [c]	***41,410***	***2***	***0.04***	***30***	***0.07***	***0.0005 – 0.3***	***0.001 – 0.2***	***0.05***	***III, X***

Notes: a = Where results from more than one year are reported for a country, the range of maxmum concentrations encountered is reported with the lowest and highest annual maxmimum concentrations separated by a hyphen. Where a range is reported for a water category (surface water, groundwater and drinking water), the lowest and highest annual maximum across all countries reporting within that category is reported separated by a hyphen.

b = Where data from a range of years is reported with different LoD or LoQ, the range of the LoD or LoQ used is presented as the minimum and the maximum value for the LoD or LoQ separated by a hyphen

c = Duplicate sites removed over the monitoring period.

d = LoD/LoQ is > 0.1 µg l^{-1} and therefore the number of samples with concentrations > 0.1 µg l^{-1} cannot be determined exactly. The value reported is the largest number of samples that could possibly exceed 0.1 µg l^{-1} and as such represents a worst case scenario. Consequently, the value is presented in parentheses.

e = LoQ not specified, therefore reported as lower than the lowest detected level.

f = Raw drinking water supplies.

g = Final drinking water supplies

h =Water Utility Companies supplying drinking water.

[1] = Quality category scale I to III, where III is the most reliable, with an additional category, X being used where there was inadequate information to classify the data.

< = The term has been used when data taken from the original source has used a 'less than' sign (<), indicating that the value is less than the analytical method can measure. It has also been used in the totals column if it has been used in the section previously.

NR = Not reported.

RMS comments and evaluation:

The effort of the Notifier to report on the monitoring activities is appreciated. The recent monitoring data from 23 individual countries in Europe was more comprehensive compared to the survey that was submitted for the Annex inclusion of clopyralid in 2002. The survey was well reported. As currently no harmonized guidance is available on how the monitoring should be performed, a variety of sampling and analysis methods was recognized, and the reliability of specific studies was assessed as variable. However, the survey gave a comprehensive overview on the aquatic load resulting from the uses of clopyralid over the Europe. Though the number of countries where monitoring data is available has increased since the 2002 survey, there are still many Member States, where plant protection products containing clopyralid are in use, but which are not organizing any monitoring activities on this active substance.

The survey of monitoring data over Europe is valuable for evaluating the environmental load, and especially the adequacy and appropriateness of the risk mitigation measures proposed as a condition for the approval of clopyralid. Compared to the previous survey (Wright & Horth 2002), the percentages of findings and also the concentrations found in groundwater, surface waters and drinking water were similar or in certain locations even higher than reported in 2002, indicating that overall the risk mitigation measures currently in use have not significantly reduced its releases into aquatic environment in Europe. The survey clearly indicates that risk mitigation is necessary for protecting drinking water sources and other aquatic environments at Member State level. The attempt of the Notifier to mitigate the environmental load by changing the representative formulation to one with a lower content of clopyralid and reducing its application rate is supported.

The monitoring data submitted is overall of acceptable quality and valid, and no further studies are required to support the renewal for the approval of clopyralid.

B.8.11. REFERENCES RELIED ON

Data owner: DAS = Dow AgroSciences.

Data Point	Author(s)	Year	Title Compagny Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
CA 7.1.1.1/1 CA 7.1.2.1.1/1	Baloch, R.;Grant, R.	1991	Degradation and metabolism of Clopyralid in Soil under Aerobic Conditions DAS Report No.GHE-P-2398R Agricultural Research and Development Center, DowElanco Limited, Letcombe Laboratory, Letcombe Regis, Wantage, Oxon, U.K. GLP/GEP (Y/N): Yes Published (Y/N): No	No	No	N/A	DAS	DAR 2003
CA 7.1.1.1/2 CA 7.7.2.1.1/2	Skinner, W.; Jao, N.; Smith, J. K.	1995	Aerobic Soil Metabolism of [^{14}C]Clopyralid DAS Report No.GHE-C-3598 PTRL West, Inc. 4123-B Lakeside Drive, Richmond, CA 94806 GLP/GEP (Y/N): Yes Published (Y/N): No	No	No	N/A	DAS	DAR 2003
CA 7.1.1.1/3 CA 7.1.2.1.1/3	Wardrope, L.	2009	The Degradation of (14C)-Clopyralid in Soil Under Aerobic Conditions DAS Report No.808711 Charles River Laboratories, Tranent, East Lothian, United Kingdom GLP/GEP (Y/N): Yes Published (Y/N): No	No	Yes	Active substance data submitted with an application under Article 15 of the Regulation (renewal) and with the application for renewal of authorisation of the corresponding product. Applies also to data	DAS	Submitted for the purpose of renewal

Data Point	Author(s)	Year	Title Compagny Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
						submitted with applications for authorisation for products containing AIR2 substances (Regulation (EU) No 1141/2010).		
CA 7.1.1.2/1 CA 7.1.2.1.3/1	Allan, J.; Lowrie, C. ; Hall, B. E.	2002	The Degradation of C14 Clopyralid in Soil Under Anaerobic Conditions DAS Report No.GHE-P-9563 Inveresk Research International, Tranent, East Lothian, United Kingdom GLP/GEP (Y/N): Yes Published (Y/N): No	No	No	N/A	DAS	DAR 2003
CA 7.1.1.3/1	Ponte, M.	2014	14C-Clopyralid: Photodegradation on Soil by Xenon lamp DAS Report No.140076 PTRL West, Hercules, California, USA GLP/GEP (Y/N): Yes Published (Y/N): No	No	Yes	Active substance data submitted with an application under Article 15 of the Regulation (renewal) and with the application for renewal of authorisation of the corresponding product. Applies also to data submitted with applications for authorisation for	DAS	Submitted for the purpose of renewal

Data Point	Author(s)	Year	Title Compagny Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
						products containing AIR2 substances (Regulation (EU) No 1141/2010).		
CA 7.1.2.1.1/4	Schubert, S.	2015	Evaluation of kinetic endpoints for clopyralid from laboratory soil degradation studies DAS Report No. 151039 Dow AgroSciences, Milton Park, UK GLP/GEP (Y/N): No Published (Y/N): No	No	Yes	Active substance data submitted with an application under Article 15 of the Regulation (renewal) and with the application for renewal of authorisation of the corresponding product. Applies also to data submitted with applications for authorisation for products containing AIR2 substances (Regulation (EU) No 1141/2010).	DAS	Submitted for the purpose of renewal
CA 7.1.2.2.1/1	Rawle, N.; Yon, D.	2002	The dissipation of clopyralid in soil following a single application of LONTREL (EF-1136), Denmark and the UK – 2000 DAS Report No. GHE-P-9370 CEMAS	No	No	N/A	DAS	DAR 2003

Data Point	Author(s)	Year	Title Compagny Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
			GLP/GEP (Y/N): Yes Published (Y/N): No					
CA 7.1.2.2.1/ 2	Rawle, N.; Yon, D.	2002	The dissipation of clopyralid in soil following a single application of LONTREL (EF-1136), Germany and Northern France – 2000 DAS Report No. GHE-P-9371 CEMAS GLP/GEP (Y/N): Yes Published (Y/N): No	No	No	N/A	DAS	DAR 2003
CA 7.1.2.2.1/ 3	Kröger, F.	2015	Soil dissipation study with one spring application of GF-1966 (Clopyralid) at three sites to bare soil in Europe in 2013-2015 Eurofins Agroscience Services, Stade, Germany Eurofins Study S13-00312 DAS Study No. 130673 GLP/GEP (Y/N): Yes Published (Y/N): No	No	Yes	Active substance data submitted with an application under Article 15 of the Regulation (renewal) and with the application for renewal of authorisation of the corresponding product. Applies also to data submitted with applications for authorisation for products containing AIR2 substances (Regulation (EU) No 1141/2010).	DAS	Submitted for the purpose of renewal

Data Point	Author(s)	Year	Title Compagny Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
CA 7.1.2.2.1/ 4	Robinson, P.	2015	Estimation of kinetic endpoints for clopyralid from soil dissipation studies. Dr Knoell Consult Ltd., Cardiff, UK DAS Study No. 150296 GLP/GEP (Y/N): No Published (Y/N): No	No	Yes	Active substance data submitted with an application under Article 15 of the Regulation (renewal) and with the application for renewal of authorisation of the corresponding product. Applies also to data submitted with applications for authorisation for products containing AIR2 substances (Regulation (EU) No 1141/2010).	DAS	Submitted for the purpose of renewal
CA 7.1.2.2.1/ 5	Kröger, F.	2016	Soil dissipation study with one spring application of GF-1966 (Clopyralid) at one site to bare soil in South Europe in 2015. Eurofins Agroscience Services, Stade, Germany Eurofins Study S15-02991 DAS Study No. 150672 GLP/GEP (Y/N): Yes Published (Y/N): No	No	Yes	Active substance data submitted with an application under Article 15 of the Regulation (renewal) and with the application for renewal of authorisation of	DAS	Submitted for the purpose of renewal

Data Point	Author(s)	Year	Title Compagny Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
						the corresponding product. Applies also to data submitted with applications for authorisation for products containing AIR2 substances (Regulation (EU) No 1141/2010).		
CA 7.1.2.2.1/ 6	Kröger, F.	2016	Soil dissipation study with one spring application of GF-1966 (Clopyralid) at one site to bare soil in South Europe in 2015. Eurofins Agroscience Services, Stade, Germany Eurofins Study S15-02992 DAS Study No. 150673 GLP/GEP (Y/N): Yes Published (Y/N): No	No	Yes	Active substance data submitted with an application under Article 15 of the Regulation (renewal) and with the application for renewal of authorisation of the corresponding product. Applies also to data submitted with applications for authorisation for products containing AIR2 substances (Regulation (EU) No 1141/2010).	DAS	Submitted for the purpose of renewal

Data Point	Author(s)	Year	Title Compagny Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
CA 7.1.2.2.1/7	Robinson, P.	2016	Estimation of kinetic endpoints for clopyralid from field soil dissipation studies (Southern Europe). Dr Knoell Consult Ltd., Cardiff, UK DAS Study No. 160486 GLP/GEP (Y/N): No Published (Y/N): No	No	Yes	Active substance data submitted with an application under Article 15 of the Regulation (renewal) and with the application for renewal of authorisation of the corresponding product. Applies also to data submitted with applications for authorisation for products containing AIR2 substances (Regulation (EU) No 1141/2010).	DAS	Submitted for the purpose of renewal
CA 7.1.3.1.1/1	Reeves, G. L. & Mittelstaedt, W.	2002	Adsorption/Desorption of Clopyralid in Soil: Corrections to Final Report of Study DW 2/92 from August 1993 DAS Report No.GHE-P-9762 Forschungszentrum Julich GmbH, Julich, Germany GLP/GEP (Y/N): Yes Published (Y/N): No	No	No	N/A	DAS	DAR 2003
CA 7.1.3.1.1/2	Buntain, I., Simmonds, M.	2015	[14C]-Clopyralid: Adsorption to and Desorption from Five Soils DAS Report No.130699	No	Yes	Active substance data submitted with an	DAS	Submitted for the purpose of renewal

Data Point	Author(s)	Year	Title Compagny Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
			Battelle UK Ltd., Chelmsford, Essex, UK GLP/GEP (Y/N): Yes Published (Y/N): No			application under Article 15 of the Regulation (renewal) and with the application for renewal of authorisation of the corresponding product. Applies also to data submitted with applications for authorisation for products containing AIR2 substances (Regulation (EU) No 1141/2010).		
CA 7.1.4.2/1	Schnöder, F.	2004	[14C] Clopyralid: Leaching in outdoor lysimeters following spring application to oilseed rape – Final report DAS Report No.000136 Covarance Laboratories, Germany GLP/GEP (Y/N): Yes Published (Y/N): No	No	No	N/A	DAS	DAR addendum 1, 2004
CA 7.1.4.2/2	Dust, M., Führ, F.	1994	Degradation and leaching of clopyralid monoethylamine salt after post emergence application of LONTREL 100 to winter rape in German lysimeters DAS Report No.GHE-P-4037 Forschungszentrum Julich GmbH, Julich, Germany	No	No	N/A	DAS	DAR 2003

Data Point	Author(s)	Year	Title Compagny Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
			GLP/GEP (Y/N): Yes Published (Y/N): No					
CA 7.1.4.2/3	Brumhard, B., Führ, F., Baloch, R.	1994	Behaviour of [2,6 14C] Clopyralid (LONTREL*) in a sandy Pseudogley Braunerde after post-emergence application to sugar beet DAS Report No.GHE-P-2908 Forschungszentrum Julich GmbH, Julich, Germany GLP/GEP (Y/N): Yes Published (Y/N): No	No	No	N/A	DAS	DAR 2003
CA 7.1.4.2/4	Brumhard, B., Baloch, R., Führ, F.	1994	Behaviour of [2,6 14C] clopyralid formulated as LONTREL 100 in Parabraunerde (Orthic Luvisol) after post emergence application to sugar beet lysimeters DAS Report No.GHE-P-2580 Forschungszentrum Julich GmbH, Julich, Germany GLP/GEP (Y/N): Yes Published (Y/N): No	No	No	N/A	DAS	DAR 2003
CA 7.2.1.1/1	Smith-Drake, J. K.	2000	Hydrolysis of 14C Clopyralid in Natural Water And Buffered Water as a Function of pH DAS Report No.000132 Dow AgroSciences LLC, Indianapolis, Indiana, United States GLP/GEP (Y/N): Yes Published (Y/N): No	No	No	N/A	DAS	DAR 2003
CA 7.2.1.2/1	Concha, M. & Shepler, K.	1994	Photodegradation of [14C] Clopyralid in Buffered Aqueous Solution at pH 7 by Natural Sunlight DAS Report No. ENV 94048 DowElanco, Indianapolis, USA GLP/GEP (Y/N): Yes	No	No	N/A	DAS	DAR 2003

Data Point	Author(s)	Year	Title Compagny Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
			Published (Y/N): No					
CA 7.2.1.2/2	Ponte, M.	2014	Direct Aqueous Photodegradation of [14C]Clopyralid in pH 7 Buffer DAS Report No.140077 PTRL West, Hercules, California, USA GLP/GEP (Y/N): Yes Published (Y/N): No	No	Yes	Active substance data submitted with an application under Article 15 of the Regulation (renewal) and with the application for renewal of authorisation of the corresponding product. Applies also to data submitted with applications for authorisation for products containing AIR2 substances (Regulation (EU) No 1141/2010).	DAS	Submitted for the purpose of renewal
CA 7.2.2.1/1	Jenkins, W. R.	1991	LONTREL T: Assessment of its Biodegradability - Modified Sturm Test Life Science Research, Eye, Suffolk, UK DAS Report No. GHE-P-2522 GLP/GEP (Y/N): Yes Published (Y/N): No	No	No	N/A	DAS	DAR 2003

Data Point	Author(s)	Year	Title Compagny Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
CA 7.2.2.2/1	Ponte, M., Hiler, T.	2015	[14C]Clopyralid: Aerobic Mineralization in Surface Water DAS Report No.140078 PTRL West, Hercules, CA, USA GLP/GEP (Y/N): Yes Published (Y/N): No	No	Yes	Active substance data submitted with an application under Article 15 of the Regulation (renewal) and with the application for renewal of authorisation of the corresponding product. Applies also to data submitted with applications for authorisation for products containing AIR2 substances (Regulation (EU) No 1141/2010).	DAS	Submitted for the purpose of renewal
CA 7.2.2.3/1	Hall B.E.; Allen, J.; Clements B.	2002	The Aerobic Degradation of [14]-Clopyralid in Natural Waters and their Associated Sediments DAS Report No.GHE-P-9564 Inveresk Research International, Tranet, East Lothian, UK Published (Y/N): No	No	No	N/A	DAS	DAR 2003
CA 7.3.1/1	Day, S. R.; Rudel, H.	1994	The evaporation of Clopyralid acid from soil and leaf surfaces following application of LONTREL 100 DAS Report No. GHE-P-3507	No	No	N/A	DAS	DAR 2003

Data Point	Author(s)	Year	Title Compagny Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
			Fraunhofer Institute, D-57392 Schmallenberg, Grafschaft/Hochsauerland, Germany GLP/GEP (Y/N): Yes Published (Y/N): No					
CA 7.3.1/2	Madsen, S.	2002	Calculation of the Stability in Air of Clopyralid - Photochemical Degradation. DAS Report No. LLC NAFST GLP/GEP (Y/N): No Published (Y/N): No	No	No	N/A	DAS	DAR 2003
CA 7.5/1	Wright, K. & Horn, H.	2002	Review of monitoring and occurrence of clopyralid in groundwater and surface water in Europe. DAS Report No. GHE-P-9757 Water Research Council, Wallingford, Oxon, UK GLP/GEP (Y/N): No Published (Y/N): No	No	No	N/A	DAS	DAR 2003
CA 7.5/2	Aldous, E.; Johnson, I.; Keirle, R.	2015	Review of monitoring and occurrence of clopyralid in surface freshwater, groundwater and drinking water in Europe. WRc plc, Swindon, UK WRc Report Reference: UC10779.02. DAS Report No. 150295 GLP/GEP (Y/N): No Published (Y/N): No	No	Yes	Active substance data submitted with an application under Article 15 of the Regulation (renewal) and with the application for renewal of authorisation of the corresponding product. Applies also to data submitted with applications for authorisation for	DAS	Submitted for the purpose of renewal

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						products containing AIR2 substances (Regulation (EU) No 1141/2010).		
CP 9.2.4/1	Robinson, P.	2016	Predicted environmental concentrations of clopyralid in groundwater (PECgw) following the application to winter cereals and grassland - a modelling assessment for Europe using FOCUS PEARL, FOCUS PELMO and FOCUS MACRO DAS Report No. 151156, 25.2.2016. Dr. Knoell Consult Report 104115-2. GLP/GEP (Y/N): No Published (Y/N): No	N	Y	Active substance data submitted with an application under Article 15 of the Regulation (renewal) and with the application for renewal of authorisation of the corresponding product. Applies also to data submitted with applications for authorisation for products containing AIR2 substances (Regulation (EU) No 1141/2010).	DAS	Submitted for the purpose of renewal
CP 9.2.4/2	Robinson, P.	2016	Predicted environmental concentrations of clopyralid in groundwater (PECgw) following the application to winter cereals and grassland - a modelling assessment for Europe using FOCUS PEARL, FOCUS PELMO and FOCUS MACRO DAS Report No. 151156, revision 04.05.2016	N	Y	Active substance data submitted with an application under Article 15 of the Regulation	DAS	Submitted for the purpose of renewal

Data Point	Author(s)	Year	Title Compagny Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
			Dr. Knoell Consult Report 104115-7. GLP/GEP (Y/N): No Published (Y/N): No			(renewal) and with the application for renewal of authorisation of the corresponding product. Applies also to data submitted with applications for authorisation for products containing AIR2 substances (Regulation (EU) No 1141/2010).		
CP 9.2.5/1	Robinson, P.	2015	Predicted environmental concentrations of clopyralid in surface water and sediment (PECSW and PECSED) following the application to winter cereals and grassland - a modelling assessment for Europe using the FOCUS surface water scenarios at Steps 1-3 DAS Report No. 151157 16.10.2015. Dr. Knoell Consult Report 02664-2. GLP/GEP (Y/N): No Published (Y/N): No	N	Y	Active substance data submitted with an application under Article 15 of the Regulation (renewal) and with the application for renewal of authorisation of the corresponding product. Applies also to data submitted with applications for authorisation for	DAS	Submitted for the purpose of renewal

Data Point	Author(s)	Year	Title Compagny Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
						products containing AIR2 substances (Regulation (EU) No 1141/2010).		
CP 9.2.5/2	Robinson, P.	2016	Predicted environmental concentrations of clopyralid in surface water and sediment (PECSW and PECSED) following the application to winter cereals and grassland - a modelling assessment for Europe using the FOCUS surface water scenarios at Steps 1-3 DAS Report No. 151157, revision 04.05.206 Dr. Knoell Consult Report 104115-8. GLP/GEP (Y/N): No Published (Y/N): No	N	Y	Active substance data submitted with an application under Article 15 of the Regulation (renewal) and with the application for renewal of authorisation of the corresponding product. Applies also to data submitted with applications for authorisation for products containing AIR2 substances (Regulation (EU) No 1141/2010).	DAS	Submitted for the purpose of renewal