BASF Aktiengesellschaft	Chlorfenapyr (BAS 306 I)	Doc III - A7.1.2(01)
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## Section A7.1.2(01) Rate and route of degradation in aquatic systems

### Annex Point IIIA XII.2.1

had insufficient radiocarbon in the water to determine the DT <sub>50</sub> . A summary of DT <sub>50</sub> values, the order of the best fit, and the associated r <sup>2</sup> values is given in Table A7 _ 2(01)-9  4.1.4 Degradation of TS in abiotic control  4.1.5 Intermediates/ degradation products  CL 312,094 was the only metabolite found, increasing to 19% of TAR in the sediment and 4% in the water of the sand system at 103 days and 6% TAR in the sediment and 4% in the water of the sand system at 101 days.  4.1.6 Bound Residues  Bound residues increased throughout the study for both systems, reaching maximums of 3% and 7% in the sand and loam systems, respectively.  4.1.7 Mineralization to CO <sub>2</sub> was insignificant, accounting for less than 1% of TAR at all sampling intervals.  5 APPLICANT'S SUMMARY AND CONCLUSION  The distribution and degradation of chlorfenapyr was studied in two natural water/sediment systems. \(^{12}\)C for up to 100 days. The water was partitioned with dichloromethane and the sediment extracted with methanol, followed by combustion. Extracts were analyzed by LSC, HPLC, and TLC.  5.2 Results and discussion  Chlorfenapyr moved rapidly from the water into the sediment. Chlorfenapyr was slowly degraded with a DT <sub>50</sub> in the whole systems of 223 to 226 days. CL 312,094 was the only metabolite, reaching 19% of the applied radiocarbon in sterile systems. The DT <sub>50</sub> for chlorfenapyr in aquatic systems where it is microbially metabolized. CL 312,094 was the only metabolite accounting for more than 1% of the radiocarbon dose. The DT <sub>50</sub> for chlorfenapyr in the whole system was 223 to 226 days.				
sand/water system and 226 days in the loam/water system. The DT <sub>50</sub> in sediment was 258 and 222 days for the sand and loam, respectively, and the DT <sub>50</sub> in water was 97 days for the sand system. The loam system had insufficient radiocarbon in the water to determine the DT <sub>50</sub> . A summary of DT <sub>50</sub> values, the order of the best fit, and the associated r <sup>2</sup> values is given in Table A7_1_2(01)-9  4.1.4 Degradation of TS in abiotic control  4.1.5 Intermediates/ degradation	4.1.2	Graph	is shown in Figures A7_1_2(01)-1, -2, and -3 for the sand/water system. The degradation in sediment and the total system is shown in Figures	
in abiotic control  original chlorfenapyr recovered after 101 days of incubation.  4.1.5 Intermediates/ degradation products  Bound Residues  Bound residues increased throughout the study for both systems, reaching maximums of 3% and 7% in the sand and loam systems, reaching maximums of 3% and 7% in the sand and loam systems, respectively.  4.1.7 Mineralization to CO2  Mineralization to CO2 was insignificant, accounting for less than 1% of TAR at all sampling intervals.  5 APPLICANT'S SUMMARY AND CONCLUSION  The distribution and degradation of chlorfenapyr was studied in two natural water/sediment systems. I*C labeled chlorfenapyr was applied to pre-equilibrated water/sediment systems. Systems were analyzed after incubation in the dark at 20 ± 1°C for up to 100 days. The water was partitioned with dichloromethane and the sediment extracted with methanol, followed by combustion. Extracts were analyzed by LSC, HPLC, and TLC.  5.2 Results and discussion  Chlorfenapyr moved rapidly from the water into the sediment. Chlorfenapyr was slowly degraded with a DT <sub>50</sub> in the whole systems of 223 to 226 days. CL 312,094 was the only metabolite, reaching 19% of the applied radiocarbon in the loam/water systems and 6% of the dose in the sand/water system at 100days. The importance of microbes in the degradation in sterile systems.  Chlorfenapyr moves rapidly to sediments in aquatic systems where it is microbially metabolized. CL 312,094 was the only metabolite accounting for more than 1% of the radiocarbon dose. The DT <sub>50</sub> for chlorfenapyr in the whole system was 223 to 226 days.	4.1.3	$DT_{50}/DT_{90}$	sand/water system and 226 days in the loam/water system. The $DT_{50}$ in sediment was 258 and 222 days for the sand and loam, respectively, and the $DT_{50}$ in water was 97 days for the sand system. The loam system had insufficient radiocarbon in the water to determine the $DT_{50}$ . A summary of $DT_{50}$ values, the order of the best fit, and the associated $r^2$	X
degradation products in the sediment of the loam system at 103 days and 6% TAR in the sediment and 4% in the water of the sand system at 101 days.  4.1.6 Bound Residues  Bound residues increased throughout the study for both systems, reaching maximums of 3% and 7% in the sand and loam systems, respectively.  4.1.7 Mineralization to CO2  Mineralization to CO2  TAR at all sampling intervals.  5 APPLICANT'S SUMMARY AND CONCLUSION  The distribution and degradation of chlorfenapyr was studied in two natural water/sediment systems. Systems were analyzed after incubation in the dark at 20 ± 1°C for up to 100 days. The water was partitioned with dichloromethane and the sediment extracted with methanol, followed by combustion. Extracts were analyzed by LSC, HPLC, and TLC.  5.2 Results and discussion  Chlorfenapyr moved rapidly from the water into the sediment. Chlorfenapyr was slowly degraded with a DT <sub>50</sub> in the whole systems of 223 to 226 days. CL 312,094 was the only metabolite, reaching 19% of the applied radiocarbon in the loam/water system and 6% of the dose in the sand/water system at 100days. The importance of microbes in the degradation of chlorfenapyr in aquatic systems was shown by no degradation in sterile systems.  5.3 Conclusion  Chlorfenapyr moves rapidly to sediments in aquatic systems where it is microbially metabolized. CL 312,094 was the only metabolite accounting for more than 1% of the radiocarbon dose. The DT <sub>50</sub> for chlorfenapyr in the whole system was 223 to 226 days.	4.1.4			X
reaching maximums of 3% and 7% in the sand and loam systems, respectively.  4.1.7 Mineralization to CO <sub>2</sub> was insignificant, accounting for less than 1% of TAR at all sampling intervals.  5 APPLICANT'S SUMMARY AND CONCLUSION  5.1 Materials and methods  The distribution and degradation of chlorfenapyr was studied in two natural water/sediment systems. <sup>14</sup> C labeled chlorfenapyr was applied to pre-equilibrated water/sediment systems. Systems were analyzed after incubation in the dark at 20 ± 1°C for up to 100 days. The water was partitioned with dichloromethane and the sediment extracted with methanol, followed by combustion. Extracts were analyzed by LSC, HPLC, and TLC.  5.2 Results and discussion  Chlorfenapyr moved rapidly from the water into the sediment. Chlorfenapyr was slowly degraded with a DT <sub>50</sub> in the whole systems of 223 to 226 days. CL 312,094 was the only metabolite, reaching 19% of the applied radiocarbon in the loam/water system and 6% of the dose in the sand/water system at 100days. The importance of microbes in the degradation of chlorfenapyr in aquatic systems was shown by no degradation in sterile systems.  5.3 Conclusion  Chlorfenapyr moves rapidly to sediments in aquatic systems where it is microbially metabolized. CL 312,094 was the only metabolite accounting for more than 1% of the radiocarbon dose. The DT <sub>50</sub> for chlorfenapyr in the whole system was 223 to 226 days.  5.3.1 Reliability  1	4.1.5	degradation	in the sediment of the loam system at 103 days and 6% TAR in the	X
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natural water/sediment systems. <sup>14</sup> C labeled chlorfenapyr was applied to pre-equilibrated water/sediment systems. Systems were analyzed after incubation in the dark at 20 ± 1°C for up to 100 days. The water was partitioned with dichloromethane and the sediment extracted with methanol, followed by combustion. Extracts were analyzed by LSC, HPLC, and TLC.  5.2 Results and discussion  Chlorfenapyr moved rapidly from the water into the sediment. Chlorfenapyr was slowly degraded with a DT <sub>50</sub> in the whole systems of 223 to 226 days. CL 312,094 was the only metabolite, reaching 19% of the applied radiocarbon in the loam/water system and 6% of the dose in the sand/water system at 100days. The importance of microbes in the degradation of chlorfenapyr in aquatic systems was shown by no degradation in sterile systems.  5.3 Conclusion  Chlorfenapyr moves rapidly to sediments in aquatic systems where it is microbially metabolized. CL 312,094 was the only metabolite accounting for more than 1% of the radiocarbon dose. The DT <sub>50</sub> for chlorfenapyr in the whole system was 223 to 226 days.  5.3.1 Reliability  1			5 APPLICANT'S SUMMARY AND CONCLUSION	
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Annie Alexandra	5.3	Conclusion	microbially metabolized. CL 312,094 was the only metabolite accounting for more than 1% of the radiocarbon dose. The DT <sub>50</sub> for	
F12 Deficiency	5.3.1	Reliability	1	
5.5.2 Denciencies No	5.3.2	Deficiencies	No	

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## Rate and route of degradation in aquatic systems

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	Evaluation by Competent Authorities
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted
	EVALUATION BY RAPPORTEUR MEMBER STATE
Date	20/05/2005
Materials and Methods	Comments:
	Title: According to the standard formats of TNsG the title should be "Rate and route of degradation in aquatic systems including identification of metabolites and degradation products". Since the identification of metabolites and degradation products is reported.
	The ring labeling designation in 3.1, should be " <sup>14</sup> C-pyrolle-ring labeled AC 303,630" instead of " <sup>14</sup> C-pyrrole and labeled AC 303,630".
	In 3.3.1, should be referd, not only the place were the samples were collected by also, there kind: "The water/sediment systems were taken from the "Altensenne lake near Paderborn and the "Mülenteich" brooklet near Scmallenberg-Grafschaft, for sandy/water and loam/water system, respectively."

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### Rate and route of degradation in aquatic systems

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#### Results and discussion Comments:

In the table A7\_1\_2(01)-9, mentioned in **4.1.3**, the whole system and sediment references are switched out of place. It should be replace by:

Table A7\_1\_2(01)-9:Degradation rates of Chlorfenapyr in water/sediment systems

system	DT <sub>50</sub> [days]	order	r²
Sand/water system			
sediment	258.0 d	1 <sup>st</sup>	0.82
water	96.9 d	Root 1.5st	0.86
whole system	222.6 d	1 <sup>st</sup>	0.88
Loam/water system		*	
sediment	222.0 d	2 <sup>nd</sup>	0.95
water	1	1.75	-
whole system	226.0 d	2 <sup>nd</sup>	0.96

<sup>1</sup> not determinable due to low levels and noise

According to the original study report, in **4.1.4**, the % of chlorfenapyr recovered was 82 to 87%, instead of 87 to 88%.

In the same subheading, for a better study results approach, the information about degradation of TS in abiotic control, should included:

In the sterilized samples of the sand/water systems approximately 92% of the AR was recovered in the whole system; with approximately 82%AR in the sediment extracts and 2% AR was NER in the sediment. The water contained a total of 7% AR, with 6% AR extractable. The test substance accounted for 82% AR in the sediment extract at the end of the study.

In the sterilized loam/water samples approximately 94% of the AR was recovered in the whole system; with approximately 87%AR in the sediment extracts and 5% AR was NER in the sediment. The water contained a total of 2% AR. The test substance accounted for 87% AR in the sediment extract at the end of the study.

In 5.2, the warning see table A7\_1\_2(01)-7 and A7\_1\_2(01)-8, should be included, since these tables represent the extraction of chlorfenapyr and metabolites from sediments and water.

**Conclusion** The RMS adopt the applicant's conclusion.

1

Reliability

Acceptability Acceptable

Remarks Despite there is no standard formats for study summaries in TNsG, the proposed by the applicant gives all the relevant information for study assessment.

COMMENTS FROM ...

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Date	Give date of comments submitted
Materials and Methods	Discuss additional relevant discrepancies referring to the (sub)heading numbers and to applicant's summary and conclusion.  Discuss if deviating from view of rapporteur member state
Results and discussion	Discuss if deviating from view of rapporteur member state
Conclusion	Discuss if deviating from view of rapporteur member state
Reliability	Discuss if deviating from view of rapporteur member state
Acceptability	Discuss if deviating from view of rapporteur member state
Remarks	

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Table A7\_1\_2(01)-1: Reference substances for co-chromatography

	Batch No.	purity
Chlorfenapyr	AC 8503-32A	97.3%
CL 312094	AC 8535-41B	98%
2-(p-chlorophenyl)-1-ethoxymethyl)-5- (trifluoromethyl)-pyrrole-3-carbonitrile		

Table A7\_1\_2(01)-2: Characterization of the water/sediment systems

Designation Origin		Loam/water system		Sand/water system		
		sediment	water	sediment	water	
Sediment	sand [%]	16		99		
	silt [%]	27		Sales Si		
	clay [%]	57		1		
	pH (CaCl <sub>2</sub> )	6.6		8.4		
	organic C	6.7%	<0.05mg/L	0.2%	34 mg/L	
	total N	6.3 g/kg	<0.05mg/L	< 0.05	<0.05mg/L	
	total P [mg/kg]	899 mg/kg	<0.05mg/L	36 mg/kg	<0.05mg/L	
	CEC [mVal/100g]	24		< 0.05		
	Calcium	5-2.1	15 mg/L	- 2500000	23 mg/L	
	Magnesium		2.7 mg/L		0.9 mg/L	

Table A7\_1\_2(01)-3: TLC conditions

Stationary phase	Silica gel F254 (20 x20 cm, 0.25 mm Merck)					
Mobile phase	Toluene:hexane 2:1 (v:v)					
The labeled compour 284/285	nds were detected with a Berthold TLC linear analyzer, type LB					
$R_f$	Chlorfenapyr – 0.42					
	CL 312,094 – 0.31					

Table A7\_1\_2(01)-4: HPLC Conditions

Pump Gynkothek, Modell M 480				
Detector	<sup>14</sup> C Berthold radioactivity Monitor Modell 506A			
Integrator	PC with "14C Berthold" software			
Control	PC with Gynkosoft			
Column	Hypersil ODS, 250 x 4.6 mm, 5 µm			
Solvent	acetonitrile: water 80:20 (v:v)			
Flow rate	1 mL/min			
Retention time	Chlorfenapyr - 6.3 min CL 312,094 - 5.4 min			

Table A7\_1\_2(01)-5: Material balance and distribution of radioactivity after application of [14C]-chlorfenapyr to water/sand system

DAT	%TAR						
	water			sediment		volatiles	
	CH <sub>2</sub> Cl <sub>2</sub>	remaining H <sub>2</sub> O	MeOH	non- extractable	CO <sub>2</sub>	others	
0	12	1	72	1	<1	<1	86
0	12	1	77	1	<1	<1	91
0.25	16	Î	76	1	<1	<1	94
0.25	17	1	77	1	<1	<1	96
1	13	1	81	1	<1 <1 <1 <1	<1	96
1	13	1	76	1	<1	<1	91
2	11	1	77	1		<1	90
2	11	1	80	1	<1	<1	93
7	12	1	80	1	<1	<1	94
7	10	1	79	1	<1	<1	91
14	8	1	78	1	<1	<1	88
14	10	A C	77	1		<1	89
30	9	1	75	1	<1	<1	86
30	10	1	72	1	<1	1	85
60	10	2	75	2	<1 <1 <1 <1 <1	1 2	91
60	10	2 2 2	76	3	<1	1	92
101	10	2	65	2	<1	10	89
101	11	2	65	2	<1	12	92

Table A7\_1\_2(01)-6: Material balance and distribution of radioactivity after application of  $[^{14}C]$ -Chlorfenapyr to water/loam system

	%TAR					
DAT	water		sediment	volatiles		material balance
		МеОН	non- extractable	CO <sub>2</sub>	others	
0	1	91	4	. 44	100	96
0	2 2	94	4	₽<	i <del>a.</del>	100
0.25	2	94	5	<1	<1	101
0.25	3	96	5	<1	<1	104
1	3 2 2 2 2 2	89	5 5 4	<1 <1 <1	<1 <1	96
1	2	91	4	<1	<1	97
2	2	91	5	<1	<1	98
2	2	88	5	<1	<1	95
7	2	88	5	<1	<1	95
7	2	90	5	<1	<1	97
14	2 2 1	89	5	<1	<1	96
14	1.	86	5 5 5 6	<1	<1 1	92
30	1	82	5	<1 <1 <1	1	89
30	2 1	78	6	<1	<1	86
60	1	85	6		<1 5 3	97
60	1	86	6	<1	3	96
100	2	82	7	<1	5	96
100	2	81	7	<1	2	92

Table A7\_1\_2(01)-7:

Chlorfenapyr and metabolites in the methanol extracts of the sediments

	%TAR			
DAT	AC 303,630	CL 312,094	unknowns	
Sand/water sys	tem		Į.	
0	74	<1	1	
0.25	77	<1	<1	
1	79	<1 <1 <1 <1	<1	
2	79	<1	<1 <1 <1 <1	
7	80		<1	
14	78	<1	<1.	
30	71	2	1	
60	72	2	(1	
101	58	6	<u>. "1</u>	
Loam/water sy	stem	70	*	
0	91	<1	2	
0.25	95	<1 <1	2 <1 <1	
1	90	<1	<1	
2	90	<1	<1	
7	89	1	<1	
14	84	1 2	2	
30	74	6	1	
60	73	12	1	
101	62	19	1	

Table A7\_1\_2(01)-8:

Chlorfenapyr and metabolites in the dichloromethane extracts of the water

	%TAR			
DAT	AC 303,630	CL 312,094	unknowns	
Sand/water sys	tem			
0	12	<1	<1	
0.25	17	<1	<1	
1	13	<1	<1	
2	11	<1	<1	
7	11	<1	<1	
14	8	<1	<1	
30	8	1	<1	
60	8	2	<1	
101	6	4	1	
Loam/water sy	stem			
	Insufficient rad	ioactivity for HPLC		

Table A7\_1\_2(01)-9:

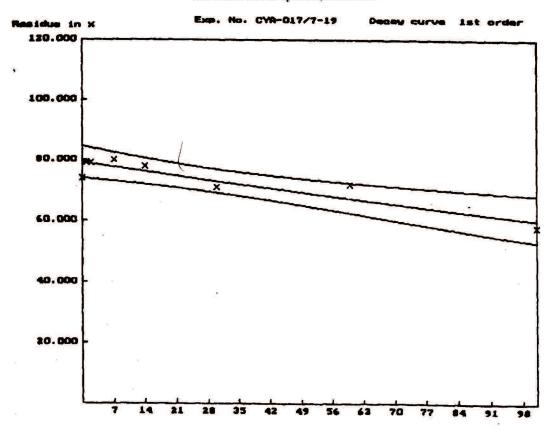
Degradation rates of Chlorfenapyr in water/sediment systems

system	DT <sub>50</sub> [days]	order	r²
Sand/water system			
whole system	258.0 d	1 <sup>st</sup>	0.82
water	96.9 d	Root 1.5st	0.86
sediment	222.6 d	$1^{\rm st}$	0.88
Loam/water system	•		
whole system	222.0 d	2 <sup>nd</sup>	0.95
water	- L	5-27	
Sediment	226.0 d	$2^{\mathrm{nd}}$	0.96

<sup>&</sup>lt;sup>1</sup> not determinable due to low levels and noise

Figure A7\_1\_2(01)-1:

Experimental data and calculated degradation curve for chlorfenapyr in the sand/water system, sediment



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Figure A7\_1\_2(01)-2:

Experimental data and calculated degradation curve for chlorfenapyr in the sand/water system, water

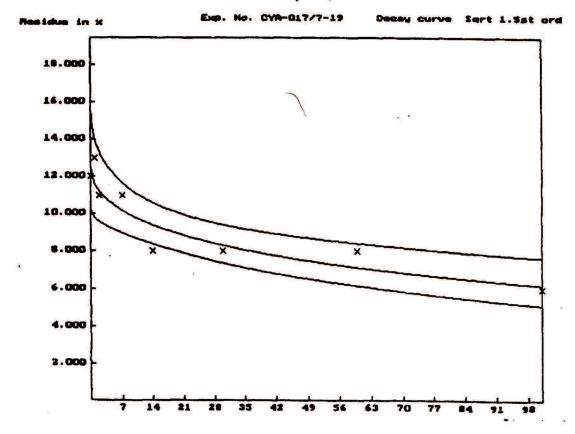


Figure A7\_1\_2(01)-3:

Experimental data and calculated degradation curve for chlorfenapyr in the sand/water system, whole system

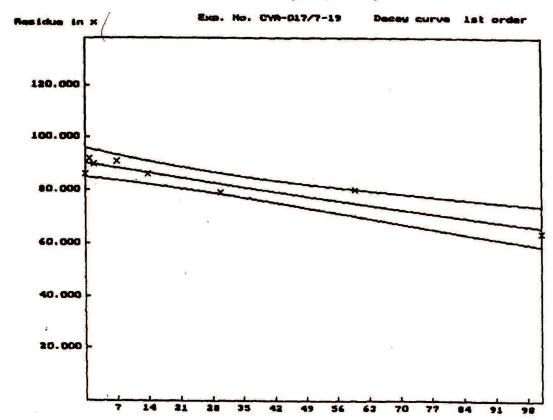


Figure A7\_1\_2(01)-4:

Experimental data and calculated degradation curve for chlorfenapyr in the loam/water system, sediment

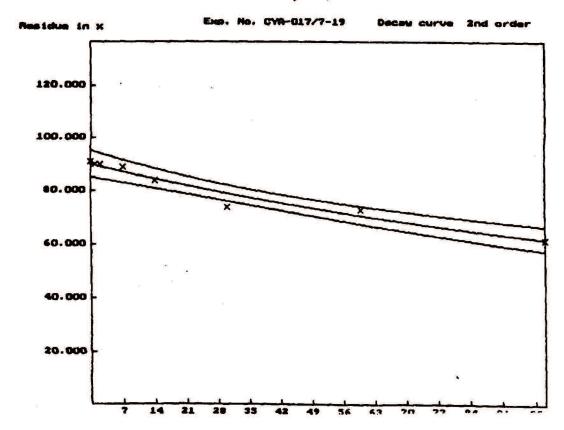
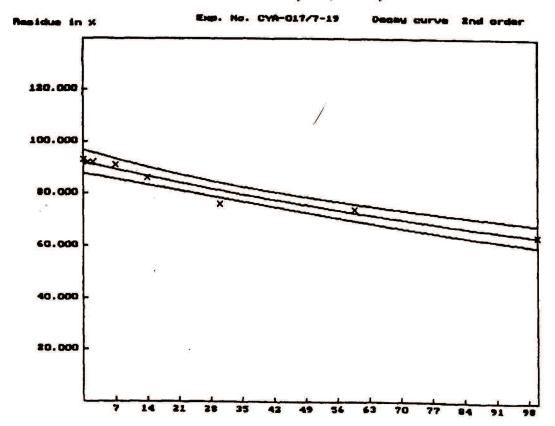


Figure A7\_1\_2(01)-5:

Experimental data and calculated degradation curve for chlorfen apyr in the loam/water system, whole system



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Official use only 1 REFERENCE 1.1 Reference 1.2 **Data protection** Yes 1.2.1 Data owner 1.2.2 1.2.3 Criteria for data Data submitted to the MS after 13 May 2000 on existing a.s. for the protection purpose of its entry into Annex I / authorization 2 GUIDELINES AND QUALITY ASSURANCE 2.1 Guideline study Yes BBA Guideline, Part IV, 5-1 2.2 GLP Yes 2.3 Deviations No 3 MATERIALS AND METHODS <sup>14</sup>C-phenyl-ring labeled AC 303,630 3.1 Test material Lot/Batch number 3.1.1 AC 8877-78 3.1.2 Specification Deviating from specification given in section 2 as follows: 3.1.3 Radiolabeling 3.1.4 Purity 97.8% radiopure, 97.3% chemically pure 3.1.5 Specific Activity 64.6 µCi/mg 3.1.6 Further relevant The solubility of AC 303,630 in de-ionized water at 20°C is 0.14 mg/L. properties 3.1.7 Composition of Not applicable Product 3.1.8 TS inhibitory to No microorganisms 3.2 Reference Reference substances used for co-chromatography are shown in Table substance A7\_1\_2(02)-1. 3.3 **Testing procedure** 3.3.1 The distribution and degradation of chlorfenapyr was studied in two Test system X natural systems of water and sediment. The water/sediment systems

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were taken from the "Altensenner" lake near Paderborn and the "Mülenteich" brooklet near Scmallenberg-Grafschaft. Characteristics of the water/sediment systems are given in Table A7 $_12(02)$ -2. The study was performed using an open gas flow system with a trapping device for volatiles. The test vessels were filled with a 2 $_2$ -2.5 cm sediment layer (ca. 30g dry weight for loamy sediment, 82 g dry weight for sandy sediment) and a 6 cm water layer (ca 145 mL), which were allowed to equilibrate for six to eight weeks before treatment.

 $^{14}$ C-phenyl-ring labeled AC 303,630 in 100 μL of acetone (<0.1% in the system) was applied to the water at a rate of 20 μg a.s. per test vessel. Two flasks per system were heat sterilized (121°C, 30 min) prior to application of the test substance.

Incubation was done in the dark at a temperature of  $20 \pm 2^{\circ}$ C for up to 100 days after treatment. Duplicate samples were taken from each water/sediment system at 0h, 6h, and 1, 2, 7, 14, 30, 60, and 100 or 101 days after treatment.

# 3.3.2 Analytical procedures

The entire water/sediment system was transferred to centrifuge tube and centrifuged at 650 G for 20 minutes. The water was decanted and analyzed by LSC. Water samples which contained more than 10% of the applied radiocarbon were extracted with methylene chloride and the extract was analyzed by LSC and HPLC using the conditions in Table A7\_1\_2(02)\_3. The sediment was extracted with MeOH and the extract was analyzed by LSC and HPLC. Unextractable radiocarbon remaining in the soil was determined by combustion and LSC.

### 3.3.3 Intermediates/ degradation products

Metabolites were identified by co-chromatography using HPLC with radiodetection.

# 3.3.4 Controls

Two flasks per system were heat sterilized (120°C, 20 min) prior to application of the test substance.

### 3.3.5 Statistics

The best-fit functions for the decrease in AC 303,630 in the water, sediment, and whole system were determined and  $DT_{50}$  values were calculated.

#### 4 RESULTS

# 4.1 Degradation of test substance

### 4.1.1 Distribution of Radiocarbon and Mass Balance

The distribution of radiocarbon and mass balance for each interval is shown in Table A7 $_12(01)$ -4 for the sand/water system and Table A7 $_12(01)$ -5 for the loam/water system. The overall mass balance ranged from 89% to 98% with an average of 94% for the sand system and from 92% to 103% with an average of 98% for the loam system.

4.1.2 Graph

The degradation of chlorfenapyr in the sediment, water and total system is shown in Figures A7 $_1$ 2(01)-1, -2, and -3 for the sand/water system. The degradation in sediment and the total system is shown in Figures A7 1 2(01)-4 and -5 for the loam/water system.

4.1.3  $DT_{50}/DT_{90}$ 

The  $DT_{50}$  for chlorfenapyr in the whole systems was 218 days in the sand/water system and 418 days in the loam/water system. The  $DT_{50}$  in sediment was 248 and 402 days for the sand and loam, respectively, and

X

X

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5.3.1

5.3.2

Reliability

Deficiencies

1

No

		the $DT_{50}$ in water was 114 days for the sand system. The loam system had insufficient radiocarbon in the water to determine the $DT_{50}$ . A summary of $DT_{50}$ values, the order of the best fit, and the associated $r^2$ values is given in Table A7_1_2(01)-8	
4.1.4	Degradation of TS in abiotic control	No degradation occurred in the sterilized systems, with 81 to 88% of the original chlorfenapyr recovered after 101 days of incubation.	X
4.1.5	Intermediates/ degradation products	CL 312,094 was the only metabolite accounting for more than 1% of the radiocarbon dose, reaching maximums of 6% and 20% in the sand and loam sediments, respectively, and 5% in the water from the sand/water system.	
4.1.6	Bound Residues	Bound residues increased throughout the study for both systems, reaching maximums of 3% in the sand/water system and 7% in the loam/water system.	
4.1.7	Mineralization to CO <sub>2</sub>	Mineralization to CO <sub>2</sub> was insignificant, accounting for less than 1 % of the applied radiocarbon at all intervals.	
		5 APPLICANT'S SUMMARY AND CONCLUSION	
5.1	Materials and methods	The distribution and degradation of chlorfenapyr was studied in two natural water/sediment systems. Pyrrole- $^{14}$ C labeled chlorfenapyr was applied to pre-equilibrated water/sediment systems. Systems were analyzed after incubation in the dark at $20 \pm 1^{\circ}$ C for up to 100 days. The water was partitioned with dichloromethane and the sediment extracted with methanol, followed by combustion. Extracts were analyzed by LSC and HPLC.	X
5.2	Results and discussion	Chlorfenapyr moved rapidly from the water into the sediment. Chlorfenapyr was slowly degraded with a $DT_{50}$ in the whole systems of 218 to 418 days. CL 312,094 was the only metabolite, reaching 20% of the applied radiocarbon in the loam/water system and 11% of the dose in the sand/water system at 100 days. The importance of microbes in the degradation of chlorfenapyr in aquatic systems was shown by no degradation in sterile systems.	
5.3	Conclusion	Chlorfenapyr moves rapidly to sediments in aquatic systems where it is microbially metabolized. CL 312,094 was the only metabolite accounting for more than 1% of the radiocarbon dose. The $DT_{50}$ for chlorfenapyr in the whole system was 218 to 418 days.	

	<b>Evaluation by Competent Authorities</b>
	Use separate "evaluation boxes" to provide transparency as to the comments and views submitted
	EVALUATION BY RAPPORTEUR MEMBER STATE
Date	20/05/2005

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## Section A7.1.2(02)

## Rate and route of degradation in aquatic systems

### Annex Point IIIA XII.2.1

Materials and Methods	Comments:
	Title: According to the standard formats in TNsG the title should be "Rate and route of degradation in aquatic systems including identification of metabolites and degradation products". Since the identification of metabolites and degradation products is reported.
	In 3.3.1, should be refered, not only the place were the samples were collected bu also, there kind: "The water/sediment systems were taken from the "Altensenner lake near Paderborn and the "Mülenteich" Brooklet near Scmallenberg-Grafschaft, for sandy/water and loam/water system, respectively."

### Section A7.1.2(02)

### Rate and route of degradation in aquatic systems

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#### Results and discussion

#### Comments:

In the table Table A7\_1\_2(02)-8, mentioned in **4.1.3**, the whole system and sediment references are switched out of place. It should be replace by:

Table A7\_1\_2(02)-8: Degradation rates of Chlorfenapyr in water/sediment systems

system	DT <sub>50</sub> [days]	order	r <sup>2</sup>
Sand/water system			
sediment	247.6 d	1 <sup>st</sup>	0.91
water	113.6 d	2 <sup>nd</sup>	0.86
whole system	217.9 d	1 <sup>st</sup>	0.96
Loam/water system			
sediment	401.0 d	Root 1st	0.97
water	2.1	<u>late</u>	55 <sub>h</sub>
whole system	417.6 d	Root 1st	0.98

<sup>1</sup> not determinable due to low levels and noise

In 4.1.4, for a better study results approach, information about degradation of TS in abiotic control, should included:

In the sterilized samples of the sand/water systems approximately 91% of the AR was recovered in the whole system, with approximately 82%AR in the sediment extracts and 2% AR was NER in the sediment. The water contained a total of 8% AR, all of which was extractable into dichlormethane. The test substance accounted for 81% AR in the sediment extract at the end of the study.

In the sterilized loam/water samples approximately 92% of the AR was recovered in the whole system; with approximately 83%AR in the sediment extracts and 8% AR was NER in the sediment. The water contained a total of 2% AR. The test substance accounted for 81% AR in the sediment extract at the end of the study.

In 5.1, the ring designation is switch off, this study was preformed with the phenyl-ring not with the pyrrole-ring

In 5.2, the warning see table A7\_1\_2(01)-6 and A7\_1\_2(01)-7, should be included, since these tables represent the extraction of chlorfenapyr and metabolites from sediments and water.

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Conclusion	The RMS adopt the applicant's conclusion.
Reliability	1
Acceptability	Acceptable
Remarks	Despite there is no standard formats for study summaries in TNsG, the proposed by the applicant gives all the relevant information for study assessment.
	COMMENTS FROM
Date	Give date of comments submitted
Materials and Methods	Discuss additional relevant discrepancies referring to the (sub)heading numbers and to applicant's summary and conclusion.
	Discuss if deviating from view of rapporteur member state
Results and discussion	Discuss if deviating from view of rapporteur member state
Conclusion	Discuss if deviating from view of rapporteur member state
Reliability	Discuss if deviating from view of rapporteur member state
Acceptability	Discuss if deviating from view of rapporteur member state
Remarks	

### Table A7\_1\_2(02)-1: Reference substances for co-chromatography

	Batch No.	purity
Chlorfenapyr	AC 8503-32A	97.3%
CL 312094	AC 8535-41B	98%
2-(p-chlorophenyl)-1-ethoxymethyl)-5- (trifluoromethyl)-pyrrole-3-carbonitrile		

Table A7\_1\_2(02)-2: Characterization of the water/sediment systems

Designation Origin		Loam/water system		Sand/water system	
		sediment	water	sediment	water
Sediment	sand [%]	16		99	
	silt [%]	27		**	
	clay [%]	57		1	
	pH (CaCl <sub>2</sub> )	6.6		8.4	
	organic C	6.7%	<0.05mg/L	0.2%	34 mg/L
	total N	6.3 g/kg	<0.05mg/L	< 0.05	<0.05mg/L
	total P [mg/kg]	899 mg/kg	<0.05mg/L	36 mg/kg	<0.05mg/L
	CEC [mVal/100g]	24		< 0.05	
	Calcium		15 mg/L		23 mg/L
	Magnesium		2.7 mg/L		0.9 mg/L

Table A7\_1\_2(02)-3: HPLC Conditions

Pump	Gynkothek, Modell M 480		
Detector	<sup>14</sup> C Berthold radioactivity Monitor Modell 506A		
Integrator	PC with "14C Berthold" software		
Control	PC with Gynkosoft		
Column	Hypersil ODS, 250 x 4.6 mm, 5μm		
Solvent	acetonitrile: water 80:20 (v:v)		
Flow rate	1 mL/min		
Retention time	Chlorfenapyr - 6.3 min		
	CL 312,094 - 5.4 min		

Table A7\_1\_2(02)-4:

Material balance and distribution of radioactivity after application of  $[^{14}\mathrm{C}]\text{-chlorfenapyr}$  to sand/water system

DAT	%TAR						
	water		sediment		volatiles		material balance
	CH <sub>2</sub> Cl <sub>2</sub>	remaining H <sub>2</sub> O	МеОН	non- extractable	CO <sub>2</sub>	others	
0	13	1	78	1	<1	<1	93
0	12	1 2 <1	80	1	<1	<1	95
0.25	15	<1	82	1	<1	<1	98
0.25	14	1	81	1		<1	97
1	1.1	1	80	1	<1	<1	93
Ī	11	1	82	1	<1	<1	95
2	13	1	79	1	<1	<1	94
2	13	1	79	1	<1	<1	94
7	11	I	82	1	<1	<1	95
7	12	1	84	1	<1	<1	98
14	13	1	77	1	<1	<1	92
14	11	1	80	1	<1	<1	93
30	11	1	81	1 2	ব ব ব ব ব ব	<1	95
30	9	1	82	2	<1	<1	94
60	13	1 2	70	2 2	<1	5	92
60	10	1	71	2	<1	10	94
101	15	<1	67	3	<1	3	89
101	11	2	68	3	<1	7	92

Table A7\_1\_2(02)-5:

Material balance and distribution of radioactivity after application of  $[^{14}\mathrm{C}]\text{-}\mathrm{Chlorfenapyr}$  to loam/water system

	%TAR						
DAT	water		sediment volatiles			material balance	
		МеОН	non- extractable	CO <sub>2</sub>	others		
0 '	1	94	4	<1	<1	99	
0	3	93	4	<1	<1	100	
0.25	2	97	4	<1 <1 <1	<1 <1 <1	103	
0.25	2	96	4	<1	<1	102	
1	3 2 2 2 2 2 2	93	4	<1	<1 <1 <1	99	
1	2	92	4	<1	<1	98	
2	2	90	5	<1	<1	97	
2	2	90	5	<1	<1	97	
7	2	90		<1	<1	97	
7	1	86	4	<1	<1	92	
14	1.	89	5	<1	<1	95	
14	1	91	5 5 6	<1		97	
30	1	86	6	<1	<1 2 3	95	
30	1."	88	5	<1 <1 <1	3	97	
60	2	92	6	<1	2	102	
60	1	81	7	<1	6	95	
100	1	87	7	<1	1	96	
100	2	86	7	<1	2	97	

Table A7\_1\_2(02)-6:

Chlorfenapyr and metabolites in the methanol extracts of the sediments

	%TAR				
DAT	AC 303,630	CL 312,094	unknowns		
Sand/water sys	tem				
0	79	<1	<1		
0.25	82	<1	<1		
1	81	<1 <1 <1 <1	<1 <1		
2	79	<1	<1		
7	82	<1	1		
14	77	2	1		
30	79	2	1		
60	67	3	(1		
101	61	6	<u>. "1</u>		
Loam/water sy	stem	h	*		
0	94	<1	<1		
0.25	97	<1 <1	<1 <1		
1	93	<1	<1		
2	90	<1	<1		
7	86	2	<1		
14	87	4	<1		
30	80	6	1		
60	74	12	1		
101	66	20	1		

Table A7\_1\_2(02)-7:

Chlorfenapyr and metabolites in the dichloromethane extracts of the water

	%TAR				
DAT	AC 303,630	CL 312,094	unknowns		
Sand/water sys	tem				
0	12	<1	<1		
0.25	14	<1	<1		
1	11	<1	<1		
2	13	<1	<1		
7	11	<1	<1		
14	10	2	<1		
30	9	2	1		
60	9	3	i.		
101	6	5	2		
Loam/water sy	stem				
	Insufficient radi	ioactivity for HPLC			

Table A7\_1\_2(02)-8:

Degradation rates of Chlorfenapyr in water/sediment systems

system	DT <sub>50</sub> [days]	order	r <sup>2</sup>
Sand/water system	12 153341		
whole system	247.6 d	1 <sup>st</sup>	0.91
water	113.6 d	2 <sup>nd</sup>	0.86
sediment	217.9 d	1 <sup>st</sup>	0.96
Loam/water system	•		
whole system	401.0 d	Root 1st	0.97
water	_1		20
sediment	417.6 d	Root 1st	0.98

<sup>1</sup> not determinable due to low levels and noise

Figure A7\_1\_2(02)-1:

 $\label{lem:continuous} \textbf{Experimental data and calculated degradation curve for chlorfen apyr in the sand/water system, sediment$ 

