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Document Title

Summary of the fate and behaviour in the environment for

Thiacloprid

Data Requirements

EU Regulation 1107/2009 & EU Regulation 283/2013
Document MCA
Section 7: Fate and behaviour in the environment

According to the guidance document, SANCO 10181/2013, for preparing dossiers for the approval of a chemical active substance

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Date	Data points containing amendments or additions[1] and brief description	Document identifier and version number

[1] It is suggested that applicants adopt a similar approach to showing revisions and version history as outlined in SANCO/10180/2013 Chapter 4 How to revise an Assessment Report.

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CA 7 FATE AND BEHAVIOUR IN THE ENVIRONMENT

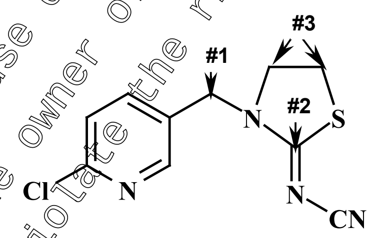
Data on the fate and behaviour of Thiacloprid in soil, water, sediment and air were submitted within the EU Dossier (Baseline Dossier), which resulted in the Annex I inclusion under Directive 91/414/EEC in 2004 (SANCO/4347/2000 – Final; 13 May 2004). In the Supplemental Dossier for renewal of approval of Thiacloprid only those environmental fate studies which were not submitted within the Baseline Dossier are described in sections 7.1 to 7.5. However, for a better understanding of the behaviour of Thiacloprid in soil, water and sediment, and air, short summaries including the results of all environmental fate studies which were considered relevant during the first EU evaluation (summarised in the EU Monograph Annex B8) are given additionally in this summary in sections CA 7.1, CA 7.2 and CA 7.3. To differentiate between studies already evaluated during the last Annex I listing and new studies, the references or author(s) given in tables are written in grey for studies already evaluated and in black for new studies.

The proposed residue definitions for each compartment are given in CA 7.4.

For Thiacloprid no new studies were performed with respect to monitoring of soil, surface water, ground/drinking water, sediment and air. From the studies found in published literature one article with respect to monitoring of surface water is regarded as providing adequate supportive information (see CA 7.5). In this literature study, the detected concentration of Thiacloprid in surface water was lower than the predicted environmental concentrations for the representative uses of Thiacloprid.

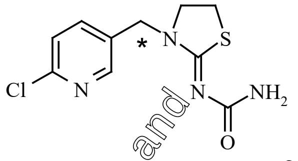
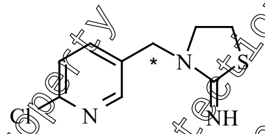
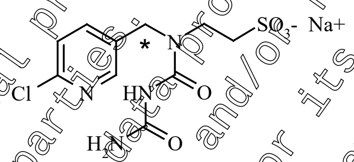
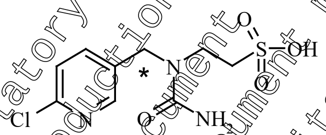
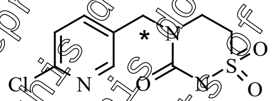
The studies concerning the fate and behaviour of Thiacloprid in the environment were conducted using radiolabelled as well as unlabelled parent compound. The three different radiolabel positions used are regarded as adequate to define the route of degradation of Thiacloprid.

The structure of Thiacloprid and the ^{14}C-radiolabelling used is as follows:

Thiacloprid (YRC 2894) #1 : [methylene-^{14}C] labelling position #2: [thiazolidine-2-^{14}C] labelling position #3: [thiazolidine-4,5-^{14}C] labelling position	

The results of studies are summarized in the following sections, the proposed degradation pathways in soil, water and sediment are given in Figure 7.1.1.1-1 and Figure 7.2- 1, respectively.

In addition, studies have been performed with the following radiolabelled or non-labelled major degradation products: YRC 2894-amide (M02), YRC 2894-des-cyano (M29), YRC 2894-sulfonic acid⁻ Na⁺ (M30), YRC 2894-sulfonic acid amide (M34) and YRC 2894-thiadiazine (M46). If applicable, the labelling position used is indicated by *:

YRC 2894-amide (M02) KKO2254 Structural formula:	
YRC 2894-des-cyano (M29) AE 1303449 Structural formula:	
YRC 2894- sulfonic acid$^-$ Na$^+$ (M30, free acid) WAK6999, BCS-AB54351, Structural formula:	
YRC 2894-sulfonic acid amide (M34), KTS 9815, AE 1303058 Structural formula:	
YRC 2894-thiadiazine (M46) BCS-CJ16425, Z5 Structural formula:	

In original reports study authors may have used different names or codes for degradation products of Thiacloprid. In this summary, a single name or a single code is used for each degradation product.
A full list containing structural formula, various names, short forms, codes and occurrences of degradation products is provided as Document N3.

CA 7.1 Fate and behaviour in soil

The route of degradation of Thiacloprid in soil has been investigated in a set of three laboratory studies using different soils. Thiacloprid was found to be rapidly degraded and thoroughly metabolised in soil under aerobic conditions. The formed major metabolites YRC 2894-amide (M02), YRC 2894-des-cyano (M29), and YRC 2894-sulfonic acid$^-$ Na$^+$ (M30) are further degraded to carbon dioxide and NER, and, therefore, do not accumulate in soil. The compounds YRC 2894-sulfonic acid amide (M34) and YRC 2894-thiadiazine (M46) found in the leachates of lysimeter studies is included in the residue definition for ground water risk assessment although it was not found as a major metabolite in the route of degradation studies.

Anaerobic and photolytic experiments were performed with [^{14}C]-Thiacloprid in soil. However, these routes of degradation do not change the before-mentioned residue definition for soil and ground water risk assessment. Under anaerobic soil conditions Thiacloprid disappears quickly to form YRC 2894-amide which degraded only moderately and no further major metabolite occurs. Photo-degradation on soil surface has no relevance compared to the fast degradation in the dark.

The proposed degradation pathway in soil is shown by Figure 7.1.1.1-1. For a summary of kinetics of degradation in soil see Table 7.1- 1 and Table 7.1- 2.

An updated kinetics evaluation of the field dissipation studies performed with Thiacloprid (6 trials performed in Northern Europe, 2 trials in Southern Europe) according to FOCUS kinetics (2006) is submitted in order to derive kinetic parameters suitable for modelling purposes and environmental risk assessments. This data are also included in Table 7.1- 1 and Table 7.1- 2.

In general no difference between lab and field degradation data was indicated. Therefore, it was justified to combine both data sets for the overall evaluation.

DT_{50} values and maximum occurrences of Thiacloprid and its major degradation products in soil to be used as modelling input values for the calculation of PEC_{soil} values are summarized in Table 7.1- 1. Since for such calculations the overall worst case values should be taken a worst case non-normalized field DT_{50} value of 13.7 and 321.1 days is used to describe the degradation of Thiacloprid and M02 in such calculations.

Table 7.1- 1: Key substance specific input parameters of Thiacloprid and its metabolites for calculating PEC_{Soil}

Compound	Worst case DT_{50} non-normalized [days]	Maximum occurrence in soil [%]	Molar mass [g/mol]	Molar mass correction factor
Thiacloprid	13.7)*	100	252.7	1
YRC 2894-amide (M02)	321.1)*	86.7)1	270.7	1.0712
YRC 2894-sulfonic acid (M30)	97.6)*	19.7)2	336.8	1.3328
YRC 2894-des-cyano (M29)	789.3)#	33.2)1	227.7	0.9011

*: worst case non-normalized field DT_{50} value.
#: worst case non-normalized laboratory DT_{50} value.
)1: [redacted], N.; 2011;)2: [redacted], R., [redacted], W.

The data on adsorption and desorption of Thiacloprid and its major degradation products in soil are given in section CA 7.1.3.1. Table 7.1- 2 summarizes the adsorption parameters in soil to be used for modelling purposes. On the basis of the batch adsorption studies Thiacloprid is classified as moderately to slightly mobile, and there is no evidence that it dissociates at environmentally relevant pH. YRC 2894-amide (M02) is classified as moderately mobile and YRC 2894-sulfonic acid (M30) is classified as very mobile to mobile. There is no evidence that soil pH influences the adsorption of either Thiacloprid or the metabolites YRC 2894-amide (M02) and YRC 2894-sulfonic acid (M30).
On the basis of new batch adsorption studies YRC 2894-des-cyano (M29) is classified as having low mobility, YRC 2894-sulfonic acid amide (M34) and YRC 2894-thiadiazine (M46) are classified as being very mobile in soil.

The key substance parameters to be used for the calculation of PEC_{GW} values are summarized in the following Table 7.1- 2. For groundwater exposure assessments the lysimeter metabolites YRC 2894-sulfonic acid amide (M34) and YRC 2894-thiadiazine (M46) are also considered. This was concluded during the first data evaluation by the EU, which resulted in the Annex I inclusion under Directive 91/414/EEC in 2004 (SANCO/4347/2000 – Final, 13 May 2004).

Table 7.1- 2: Key substance specific input parameters of Thiacloprid and its metabolites for calculating PEC_{GW}

Compound	Formation fraction	DT_{50} [days]	Koc)2 [mL/g]	Kom)2 [mL/g]	FREUNDLICH)2 exponent
Thiacloprid	1.0	5.4)1	615.0	357.0	0.880
YRC 2894-amide (M02)	0.61)2	41.3)1	293.0	170.0	0.830
YRC 2894-sulfonic acid (M30)	0.80)2	15.6)1	20.2	11.7	0.940
YRC 2894-thiadiazine (M46)	0.44)5	19.8)3	9.6	5.6	0.960
YRC 2894-des-cyano (M29)	0.23)2	140.7)3	371.0	215.0	0.840
YRC 2894-sulfonic acid amide (M34)	0.56)2	48.8)4	7.0	4.1	1.000

)1: Median of complete data set of normalized lab and field DT_{50} values.
)2: Arithmetic mean of data set.
)3: Geometric mean of lab data set.
)4: Worst case of lab data set.
)5: Worst case assumption that M30 can only degrade to M34 and M46.

CA 7.1.1 Route of degradation in soil

The route of degradation of Thiacloprid in soil has been investigated in a set of three laboratory studies using different soils. Thiacloprid was found to be fast degraded and thoroughly metabolised in soil under aerobic conditions. The formed major metabolites YRC 2894-amide (M02), YRC 2894-des-cyano (M29) and YRC 2894-sulfonic acid^{-} Na^{+} (M30) are further moderately degraded to carbon dioxide and non-extractable residues (NER), and, therefore, do not accumulate in soil. The compounds YRC 2894-sulfonic acid amide (M34) and YRC 2894-thiadiazine (M46) found in the leachates of lysimeter studies are included in the residue definition for ground water risk assessment even though they were not detected as major metabolites in the route of degradation studies.

Anaerobic and photolytic experiments were performed with [^{14}C]-Thiacloprid in soil. However, both that routes of degradation do not change the residue definition for soil and ground water risk assessment. Under anaerobic soil conditions Thiacloprid disappears rapidly to form YRC 2894-amide (M02) which is moderately degraded and no further major metabolite occurs. Photo-degradation on soil surface has no relevance compared to the fast degradation in the dark.

The proposed degradation pathway in soil is shown by Figure 7.1.1.1-1, a compilation of formation fractions for the metabolites derived from the different data sets is given by Table 7.1.2.1.2-10.

CA 7.1.1.1 Aerobic degradation

The route of degradation of Thiacloprid in soil under aerobic conditions in the laboratory was evaluated during the Annex I inclusion (compare EU Monograph, Annex B8) and was accepted by the European Commission (SANCO/4347/2000 – Final; 13 May 2004). The following study included in the Baseline Dossier was regarded as relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted], R., [redacted], W.	1998	M-001076-02-1

Summary of study performed by [redacted], R., [redacted], W.: 1998

The study conducted under standardized laboratory conditions in 4 different soils (sand, loamy sand, loamy silt, and sandy loam) with [methylene-^{14}C]-Thiacloprid at rates equivalent to 300 to 350 g as/ha.

Thiacloprid was found to be thoroughly metabolised in soil and rapidly degraded to $^{14}CO_2$ under aerobic conditions. The total mineralisation of Thiacloprid steadily increased in all soils, although the microbial biomass was markedly reduced during the incubation period. Depending on the type of soil the mineralisation reached 6.5% to 33.6% of the applied amount after 100 days and 24.7% after 365 days in the sandy loam. Other volatile metabolites have not been found. The total recovery of radioactivity ranged from 91.9 to 103.8% of the applied amount.

The test substance was metabolised via formation of the amide and cleavage of the thiazolidine ring to $^{14}CO_2$. During the incubation period more than 8 intermediates were observed. Five metabolites were identified. Major metabolites (> 10% of the applied radioactivity, AR) were the YRC 2894-amide (M02) and YRC 2894-sulfonic acid (M30). All other degradation products accounted for less than 5.7% of AR during the course of the study. The metabolite YRC 2894-des-cyano (M29) formed at a maximum of 5.7% in this study is newly included in the residue definition.
Depending on the soil type YRC 2894-amide (M02) made up a maximum of 73.8% of the AR. In the sandy soil (BBA 2.1) YRC 2894-sulfonic acid (M30) accounted for 19.7% of AR. However, in the other soils this metabolite did not exceed a maximum value of 8.5% of AR.

The degradation of Thiacloprid is essentially based on hydrolysis and oxidation reactions. Breakdown of the molecule starts by addition of water to the nitrile group under formation of the amide. Cleavage of the thiazolidine ring is also a major degradation step probably by addition of water to the imino group and ring opening followed by rapid oxidation of the sulphur to form the sulfonic acid. Desalkylation of the tertiary amino group results in M32 which is hydrolysed to the urea compound M31. Oxidation at the methylene bridge also occurs (M33), and is certainly a general reaction for the formation of 6-chloronicotinic acid (M03) which was however not detected in the main study, but could also be formed from M29 and M31. In combination with other study data and evaluations (see in the following) the metabolic pathway shown in Figure 7.1.1.1-1 is proposed.

The study evaluated in the base-line dossier was not regarded as sufficient to describe the route of Thiacloprid degradation in soil. To determine whether a different route of degradation was observed in the lysimeter studies a further study has been performed using the lysimeter soil as test system (see [redacted], E.; 2003). This study is submitted within this Supplementary dossier.

Additionally, a new core metabolism study performed with the radiolabel placed in the 2nd ring of parent molecule was regarded as necessary. It is submitted within this Supplemental Dossier for the Thiacloprid renewal of approval (see [redacted], N.; 2011). Resulting from the new studies no further degradation products were found, however the amount of metabolites formed was different in the new route of degradation study. To enable groundwater risk assessment additional rate of degradation studies with some metabolites were performed.

Based on all performed studies the definition of major soil degradation products in this Supplemental Dossier has been concluded, and the metabolic pathway shown in Figure 7.1.1.1-1 is proposed.

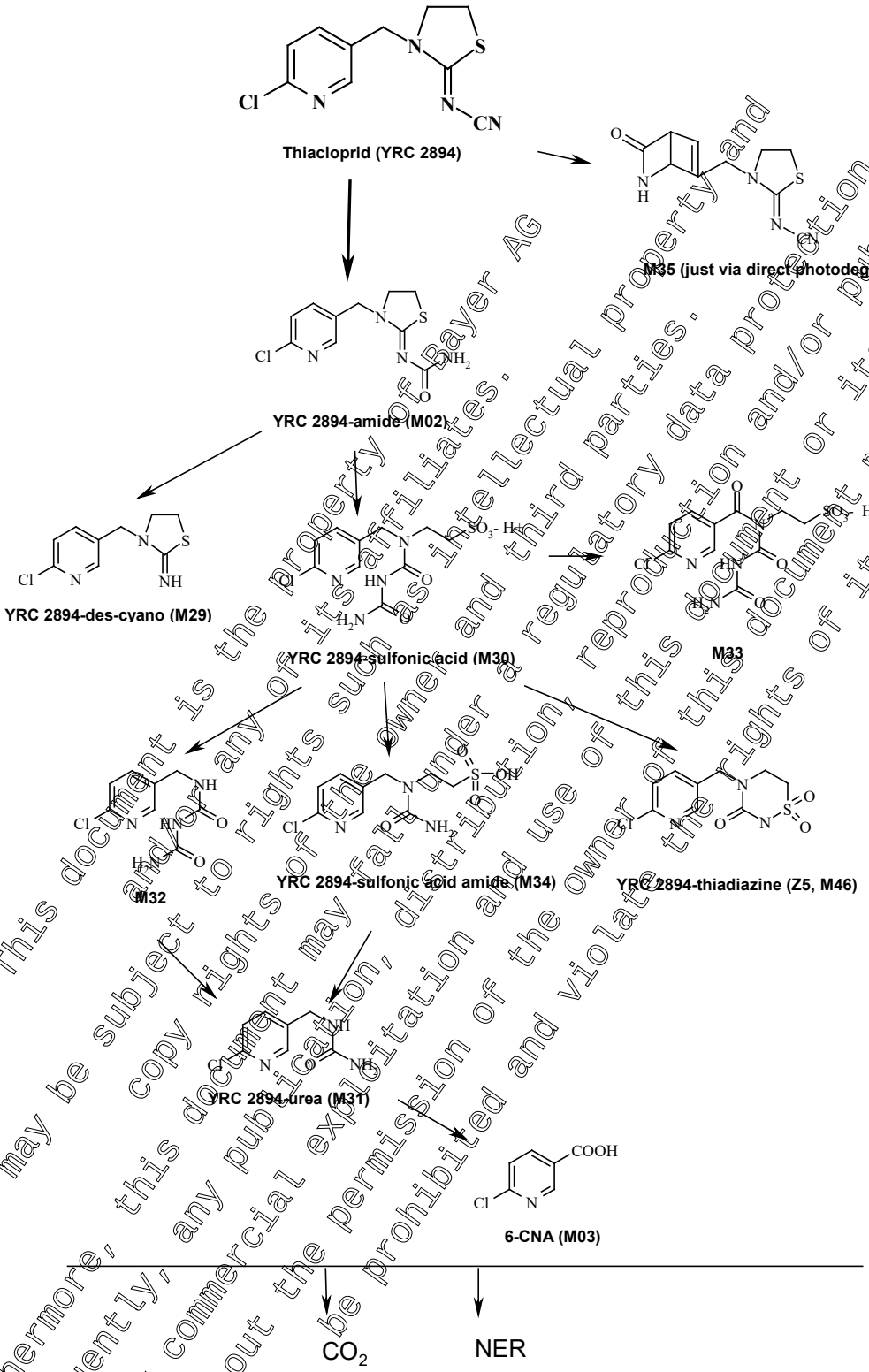


Figure 7.1.1.1-1: Proposed degradation pathway of Thiacloprid in soil under laboratory conditions considering all routes of soil degradation and lysimeter studies.

Report:	**KCA 7.1.1.1 /03; [redacted], E.; 2003**
Title:	Aerobic Degradation/Metabolism of Thiacloprid (YRC2894) in Soil [redacted]AXXa.
Report No:	MR-433/02
Document No:	M-106754-01-1
Guidelines:	Official Journal of the European Communities, No. L 172 (EN), July 22, 95. Commission Directive, 95/36/EC, amending Council Directive 91/414/EEC, 7171/VI/94-EN, 7.1.1 Route and Rate of Degradation. SETAC-Europe: Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, March 1995, Part 1, Section 1.1 German BBA Guideline, Part IV, 4-1, 1986
GLP:	Yes

EXECUTIVE SUMMARY

The route and rate of [methylene-^{14}C]-Thiacloprid degradation was studied in one soil under aerobic conditions in the dark in the laboratory for 120 days at 20±1°C and 49% of respective maximum water holding capacity. The test was conducted in soil [redacted]AXXa (sandy loam, pH_{CaCl_2} 6.3, OC 1.02%), which was used in the lysimeter study, also (see Section CA 7.1.4.2). The study application rate was 51.6 µg as/100g soil (dry weight), equivalent to the highest field application rate of about 400 g as/ha. The test was performed in static systems consisting of 300-mL Erlenmeyer flasks each containing 100 g soil (dry weight equivalents) and equipped with traps for the collection of carbon dioxide and volatile organic compounds. Duplicate samples were processed and analysed 0, 1, 2, 5, 12, 28, 49, 69, 90 and 120 days after treatment (DAT).

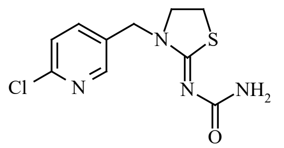
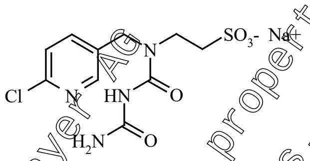
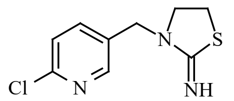
At each sampling interval, the soil was extracted 3 times by shaking with methanol at room temperature, and additionally, due the low extractability, portions were further extracted with methanol/water (50/50) for about 1 hour under reflux conditions. The radioactivity was determined in all samples and the extracts analysed by TLC- and HPLC-radio-detection methods. Metabolites were identified by mass-spectroscopy and by comparison with authentic reference compounds. Volatile radioactivity was trapped using soda lime and released for measurement by adding HCl for $^{14}CO_2$ (identified by Grignard reaction) or extracting the foam plugs with ethyl acetate for radio assaying by LSC.

Investigation of the route of degradation showed that Thiacloprid is well degraded and mineralised in the tested soil incubated under standardised aerobic laboratory conditions in the dark. Complete material balances found at the sampling intervals demonstrated that there was no significant loss of radioactivity from the test systems or during sample processing. During the study the total recovery of radioactivity (RA) in individual test vessels ranged from 103.8% to 97.1% of applied radioactivity (AR), and the mean was 100.0% (SD 1.6%).

The total mineralisation of [methylene-^{14}C]-Thiacloprid to carbon dioxide reached 10.2% of AR during the testing period of 120 days. Formation of volatile organic compounds (VOC) was insignificant. The non-extractable residues (NER) exceeded a maximum portion of 28.0% at DAT-49, and declined to 24.9% of AR until DAT-120. Since relevant proportions of steadily increasing $^{14}CO_2$ and NER were observed this indicates that the NER formed from the parent is a major part of its entire route of degradation in soil, and that NER formation is not caused by an inadequate extraction of parent from the soil matrix.

The comparatively fast degradation resulted in the following degradation products in soil:

Table 7.1.1.1- 1: Identified degradation products (mean maximum amounts, % of AR)

<table>
<tr><td colspan="2">CO_2 (10.2%, DAT-120)
NER (28.0%, DAT-49)</td></tr>
<tr><td>YRC 2894-amide (KKO 2254)
(70.2%, DAT-5)
  </td><td>YRC 2894-sulfonic acid (WAK 6999) (11.3%, DAT-120)
  </td></tr>
<tr><td>YRC 2894-des-cyano (KTU 3072)
(5.5%, DAT-120)
  </td><td></td></tr>
</table>

It is concluded from this study that Thiacloprid is degraded rapidly in soil [redacted] AXXa with a simple first order DT_{50} of 1.3 days when incubated under aerobic conditions at 20°C. The formed major metabolites (YRC 2894-amide (M02), YRC 2894-sulfonic acid (M29) and YRC 2894-des-cyano (M30)) are further moderately degraded and, therefore, do not accumulate in soil. For more details on kinetics of degradation see Section CA 7.1.2.1.

Formation of significant amounts of non-extractable residues and carbon dioxide indicates a participation in the natural carbon cycle of soil and the potential for a complete mineralisation of Thiacloprid. Thiacloprid and its degradation products have no potential for accumulation in the environment.

I. MATERIALS AND METHODS

A. Test Item

[Methylene-^{14}C]-YRC 2894:	BECH 0527 (synthesis: KML 2358)
Specific Radioactivity:	3.77 MBq/mg (102 µCi/mg)
Radiochemical Purity:	>98% (acc. to radio-HPLC and TLC, protocol BECH 0527)
Chemical purity:	97.6% (acc. to HPLC-UV at 210 nm, protocol BECH 0527)

B. Test System

The study was carried out using soil [redacted] AXXa which was used in the lysimeter study, also (see Section CA 7.1.4.2). The soil was taken from an agricultural use area. The plant protection product use history of the soil is known for at least 5 years. The characteristics of test soil are given in following table.

Table 7.1.1.1- 2: Physico-chemical characteristics of test soil [redacted]AXXa

Parameter	Results/Units
Texture Class (USDA)	Sandy loam
Sand (2,000 - 50 µm) Silt (<50 - 2 µm) Clay (<2 µm)	72.4% 22.6% 5.0% (64% Illite, 19% Kaolinite, 17% Vermiculite/Chlorite)
pH	7.2 (water), 6.3 ($CaCl_2$), 6.4 (KCl)
Organic Matter[1)]	1.75%
Organic Carbon	1.02%
Microbial Biomass Activity[2)] [mg microbial C /kg dry wt]	Initial (DAT-0): 499 (without a.s.), 330 (with a.s.) Final (DAT-120): 129 (without a.s.), 186 (with a.s.)
Cation Exchange Capacity	8 meq/100 g
WHC_{max}	34.42 g water / 100 soil (DM)
Bulk Density (disturbed)	2.5 g/cm³

[1)] % organic matter = % organic carbon x 1.724.
[2)] Determinations were performed using wet soil.

II. STUDY DESIGN

A. Experimental Conditions

The soils were sampled freshly from the fields (upper horizon of 0 to 20 cm) and sieved to a particle size of ≤ 2 mm. Description of soil collection and storage is given in Appendix 2 of the report.

Static test systems (300-mL Erlenmeyer glass flasks) for degradation in soil under aerobic conditions were used as incubation vessels. Each flask was fitted with a trap attachment (permeable for oxygen) containing soda lime for absorption of carbon dioxide and a polyurethane (PU) foam plug for adsorption of volatile organic compounds (VOC).

For preparation of the test systems, 100 g dry weight equivalents of the sieved soils were weighed into each flask. Soil moisture was adjusted to approx. 49% of the maximum water holding capacity (MWHC) for the individual test systems by addition of de-ionized water, taking into account the water content of the application solution. The flasks were then fitted with above-mentioned trap attachments. The untreated test systems were equilibrated to study conditions for some days prior to application. For detailed information on experimental design see also Table 2 and Table 3 of report.

A study application rate of 51.6 µg per 100 g soil dry weight was applied. An aliquot of 147 µL of aqueous [^{14}C]-Thiacloprid application solution finally containing 7.2% of organic solvent (ACN) was applied drop-wise onto the soil surface of the respective equilibrated test systems using a pipette.
After application, the test vessels (except DAT-0 samples) were fitted with trap attachments and placed into a temperature-controlled walk-in climatic chamber for incubation. The soil moisture was maintained since water loss from evaporation (determined by re-weighing of flasks) was replaced in interval (for details see Table 4 of report). Soil microbial biomass was determined at the beginning and at end of the study in untreated test systems (DAT-0 and DAT-120, see Table 7.1.1.1- 2).

B. Sampling

Duplicate treated flasks were taken and processed completely for analyses at the following sampling dates: 0, 1, 2, 5, 12, 28, 49, 69, 90 and 120 days after treatment (DAT).

C. Analytical Procedures

Prior to opening an incubated test system for processing of soil, volatiles possibly still present in the head space of the test system were purged into the trap attachment. Afterwards, the trap attachment was removed and the soil was extracted completely. The soil was extracted immediately after

sampling of the flasks. The total soil portion of each test flask was transferred (using the extraction solvent) into a centrifuge beaker. The mean efficiency of "cold" extraction at DAT-0 was 89.8%, only. Thus, after drying and homogenising the extracted soil a further extraction was performed with 25-g-aliquots in a ®Soxtec equipment (45' boiling and 15' rinsing). Volume and the radioactivity of the combined extracts (-E and HE) was determined. Chromatographic analyses of soil extracts by the primary method were performed not later than on the day after preparation. The analysed extracts were stored in a freezer for further investigations, if necessary. The paper filters used for filtration were cut into pieces (usually 3 to 4), combusted completely, and the evolved radioactivity was regarded as not extracted radioactivity.

The amount of degradation products in the combined soil extract was determined by liquid scintillation counting (LSC) and by TLC/radiodetection analysis. The amount of volatiles and non-extractable residues was determined by LSC and combustion/LSC, respectively (for more details see section 3.6.1 of report). Degradation products were identified by mass-spectroscopy and by comparison with authentic reference compounds.

III. RESULTS AND DISCUSSION

Results indicated that the anticipated standardized aerobic laboratory conditions were maintained during the entire incubation period in the dark. Maintenance of aerobic conditions was achieved by using an "open" test system (so-called bio-meter flasks permeable for air) incubated in a large air-conditioned room. The anticipated standardised soil temperature was maintained during the study. The average temperature was 19.99 °C, (max / min = 20.70 / 19.65 °C). The anticipated standardised soil moisture was maintained during the study. In absolute terms, the water loss between two sampling intervals was low. Between sampling intervals the soil moisture decreased on average from 49% to 46.3% of WHCmax, only. Viable soil was used within this study. The measured values for microbial biomass were found to be in the usual range expected of soils taken from agricultural fields. As it is usual for such laboratory studies the microbial biomass determined at the end of the incubation was significantly lower. In the soil samples treated with Thiacloprid similar values were determined. Thus, the parent compound did not affect the microbial biomass of the test soil.

A. Data

The amount of applied test item for the degradation samples was determined to be 195.66 kBq (equal to 51.6 µg of test item, considering the radio-purity) with a RSD of 0.72%, and this was set to 100% of applied radioactivity [% of AR]. It was confirmed that the application was homogeneous during the application procedure. The calculations for radioactivity (as % of applied radioactivity) in the soil and the respective trap attachment for volatiles are listed in Table 7.1.1.1- 3, the conclusive overview was presented in Table 7.1.1.1- 1, already.

Complete material balances found at the sampling intervals demonstrated that there was no significant loss of radioactivity from the test systems or during sample processing. During the study the total recovery of radioactivity (RA) in individual test vessels ranged from 103.8% to 97.1% of applied radioactivity (AR), and the mean was 100.0% (SD 1.6%).

B. Method Validation

Verification of Sample Processing Method

The mean efficiency of "cold" plus "hot" extraction at interval DAT-0, i.e. about 2 hours after treatment of soil, was 98.9% of AR (see data in Table 7.1.1.1- 3). Thus, the extraction procedure was well suitable to extract the applied [^{14}C]-Thiacloprid from the soil matrix.

Table 7.1.1.1- 3: Material balance of radioactivity in soil [redacted] AXXa (expressed as percentage of applied radioactivity, % AR)

Incubation time [days]		0.1	1	2	5	12	28
Volatiles	Soda lime		0.1	0.3	2.2	4.5	6.8
	PU-foam		<0.1	<0.1	<0.1	<0.1	<0.1
	Subtotal volatiles		**0.1**	**0.3**	**2.2**	**4.5**	**6.8**
Soil							
Extracted	Organic extract	89.8	86.2	83.9	74.5	62.7	49.7
	Hot extract	9.1	13.5	14.1	16.9	22.6	20.3
	Subtotal extracted	**98.9**	**99.7**	**98.1**	**91.4**	**85.3**	**70.0**
NER	Soil	1.7	1.2	2.2	5.7	9.9	21.4
	Filter	0.9	0.1	0.1	0.4	0.4	3.9
	Subtotal not extracted	**2.6**	**1.3**	**2.3**	**6.1**	**10.3**	**25.3**
	Total	**101.5**	**101.1**	**100.7**	**99.8**	**100.0**	**102.1**
	Mean deviation	+/- 0.5	+/- 0.2	+/- 0.7	+/- 1.0	+/- 0.4	+/- 1.8

Incubation time [days]		49	69	90	120
Volatiles	Soda lime	7.7	8.4	9.1	10.2
	PU-foam	0.1	<0.1	0.1	<0.1
	Subtotal volatiles	**7.7**	**8.4**	**9.1**	**10.2**
Soil					
Extracted	Organic extract	40.5	34.2	32.2	27.7
	Hot extract	23.1	28.7	32.3	35.7
	Subtotal extracted	**63.5**	**62.9**	**64.5**	**63.3**
NER	Soil	24.3	25.3	24.2	24.4
	Filter	3.5	1.6	0.8	0.5
	Subtotal not extracted	**28.0**	**26.9**	**25.0**	**24.9**
	Total	**99.2**	**98.2**	**98.7**	**98.4**
	Mean deviation	+/- 0.2	+/- 1.1	+/- 1.3	+/- 0.6

Table 7.1.1.1- 4: Residues of ^{14}C- Thiacloprid in extract of soil [redacted] AXXa (expressed as % of AR; mean of duplicates)

Compound	DAT (Days after treatment)									
	0.1	1	2	5	12	28	49	69	90	120
Origin	0.5	0.5	0.4	0.2	0.6	0.4	< LOQ	0.1	< LOQ	0.5
Thiacloprid	95.5	63.5	39.7	12.4	6.7	5.0	3.4	2.7	2.8	3.5
-amide (M02)	1.6	32.7	52.5	70.2	60.0	46.3	45.1	43.2	37.8	28.5
-sulfonic acid (M30)	< LOQ	0.1	0.3	0.5	3.5	5.0	6.8	8.7	10.5	11.3
Zone D	0.1	0.4	0.6	1.4	2.1	1.5	1.3	1.1	1.1	2.0
Zone E	< LOQ	< LOQ	< LOQ	0.7	1.1	0.7	< LOQ	< LOQ	< LOQ	< LOQ
Zone F	0.5	0.6	1.5	2.4	1.4	0.6	< LOQ	0.2	< LOQ	< LOQ
-des-cyano (M29)	< LOQ	0.2	0.3	0.9	1.5	3.2	2.1	2.5	4.7	5.5
Zone H	< LOQ	< LOQ	< LOQ	0.1	0.9	0.8	1.0	0.8	2.3	2.8
Zone R_f 0.15	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	1.8	3.0	3.6
Zone R_f 0.77	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.4	0.5	1.0

Zone X: region of interest set for TLC analysis
LOQ = 0.1% of AR

Verification of Chromatographic Procedures

Using the TLC chromatographic method A the recovery of Thiacloprid amounted to 99.5% of AR. These results indicated that the radio-thin-layer chromatographic method (A) was well suitable to analyse the applied [^{14}C]-Thiacloprid.
The TLC limit of quantification (LOQ) for a single peak in the combined organic extracts was 0.1% of AR.

C. Degradation of Test Item

A synopsis on biotransformation of Thiacloprid in aerobic soil is shown by Table 7.1.1.1-1; the results were included in the proposed pathway of degradation in soil (see Figure 7.1.1.1-1). More detailed data (expressed as percent of AR) are summarized in Table 7.1.1.1- 4.

Volatiles, i.e. Mineralisation to $^{14}CO_2$

The amount of RA trapped in the individual test flasks (raw data and expressed as % of AR) was given in Table 7.1.1.1- 3. At all sampling intervals no volatile organic compounds (VOC) were measured in the polyurethane foam (each VOC value was <0.1% of AR).

The RA found in the soda lime of the trap attachments was $^{14}CO_2$ (see Table 7.1.1.1- 3). A steady increase of the portion of $^{14}CO_2$ was measured during the entire study period. At the termination of the experiment (at day 120) the amount of $^{14}CO_2$ was 10.2% of AR.

Test Item and Degradation Products in Soil Extracts

Until study termination (DAT-120) extractable residues decreased to 63.3% of AR. In the same time period the portion of RA recovered by the "cold" extract decreased from approx. 90% to approx. 28%, whilst that recovered by the "hot" extract increased from approx. 9% to approx. 36%.

The disappearance of Thiacloprid was quite fast: for kinetics of degradation see Section CA 7.1.2.1.

Degradation of Thiacloprid was accompanied by the formation of several degradation product zones with the observed amounts shown in Table 7.1.1.1- 4; the respective degradation products and its maximum amounts observed were summarized in Table 7.1.1.1- 4.

Non-Extractable Residues

Non-extractable residues (NER) steadily increased to max. 28.0% of AR at DAT-49, slightly declining to 24.9% of AR until DAT-120 (end of study). Since relevant proportions of $^{14}CO_2$ were observed, also, this indicates that the NER formed from the parent is a major part of its entire route of degradation in soil, and that NER formation is not caused by an inadequate extraction of parent from the soil matrix.

Kinetic Analysis of Data

It is concluded from this study that Thiacloprid is degraded rapidly in soil [redacted]AXXa (compare Table 7.1.1.1- 3 and Table 7.1.1.1- 4) with a simple first order DT_{50} of 1.3 days when incubated under aerobic conditions at 20°C. The formed major metabolites (i.e. M02, M29 and M30) are further moderately degraded and, therefore, do not accumulate in soil. For more details on kinetics evaluation of degradation see Section CA 7.1.2.1.

Degradation Pathway

Based on the results of current study, combined with that from the other performed route of degradation studies, the pathway of degradation of Thiacloprid in soil presented by Figure 7.1.1.1-1 is proposed.

IV. CONCLUSIONS

Investigation of the route of degradation showed that Thiacloprid is well degraded and mineralized in the lysimeter soil incubated under standardized aerobic laboratory conditions in the dark. The quite fast degradation leads to the major degradation products shown in Table 7.1.1.1- 1. Formation of significant amounts of non-extractable residues and carbon dioxide indicates a participation in the natural carbon cycle of soil and the potential for a complete mineralization of Thiacloprid.

The outcome is included pathway of degradation as well as in the summary of the degradation rates of Thiacloprid and its major degradation products in soil in the laboratory given in section CA 7.1.1 and in Table 7.1- 1 and Table 7.1- 2.

Report:	**KCA 7.1.1.1 /04; [redacted], N.; 2011**
Title:	[Thiazolidine-2-^{14}C]-Thiacloprid: Aerobic metabolism/degradation in a European soil.
Report No:	MEF-10/140
Document No:	M-404822-01-1
Guidelines:	OECD Guideline for Testing of Chemicals, No. 307, Aerobic and Anaerobic Transformation in Soil, 2002 US EPA Fate, Transport and Transformation Test Guidelines, OPPTS 835.4100 and OPPTS 835.4200, Aerobic and Anaerobic Soil Metabolism, 2008 Commission Directive 95/36/EC amending Council Directive 91/414/EEC (Annexes II and III, Fate and Behaviour in the Environment), 1995
GLP:	Yes

EXECUTIVE SUMMARY

The route and rate of [thiazolidine-2-^{14}C]-Thiacloprid degradation was studied in a silt loam ([redacted]4a, OC = 2.4%, pH_{CaCl2} 6.3; [redacted], Germany) for 120 days under aerobic conditions in the dark at 20 ± 1°C and 55 ± 5% WHCmax (maximum water holding capacity). An amount of 16 µg Thiacloprid/100 g soil dry weight was applied in this study, corresponding to the single use rate of 120 g Thiacloprid/ha.
The test was performed in static systems consisting of 300-mL Erlenmeyer flasks each containing 100 g soil (dry weight equivalents) and equipped with traps for the collection of carbon dioxide and volatile organic compounds (VOC). Duplicate samples were processed and analysed 0, 0.25, 1, 2, 4, 7, 14, 21, 30, 45, 72 and 120 days after treatment (DAT).

At each sampling date the soil samples were extracted four times by shaking at ambient temperature and with respect to the formation of non-extractable residues by hot (microwave) extraction with acetonitrile/water solution mixtures. The extracts were analysed and quantified by HPLC. Test item and major metabolites were identified by HPLC-MS and HPLC-MS/MS and/or confirmed by co-chromatography with the corresponding characterized reference substances. AMD-TLC was used as confirmation method.

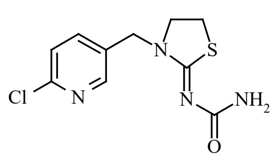
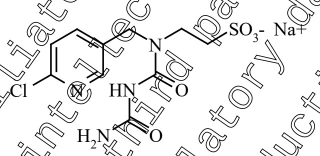
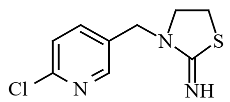
Investigation of the route of degradation showed that Thiacloprid is well degraded and mineralised in the tested soil incubated under standardised aerobic laboratory conditions in the dark. Complete material balances found at the sampling intervals demonstrated that there was no significant loss of radioactivity from the test systems or during sample processing. During the study the total recovery of radioactivity (RA) in individual test vessels ranged from 97.6% to 101.8% of the applied radioactivity (AR).

The total mineralisation of [thiazolidine-2-^{14}C]-Thiacloprid to carbon dioxide reached 41.5 % of AR recovered at study termination (DAT-120). Formation of volatile organic compounds (VOC) was insignificant.

The non-extractable residues (NER) steadily increased from 0.6 % of AR at DAT-0 to 29.4 % at study end (DAT-120). A further characterization (fractionation into humin, humic acids and fulvic acids) was shown for the DAT-72 interval. Since relevant proportions of steadily increasing $^{14}CO_2$ and NER were observed this indicates that the NER formed from the parent is a major part of its entire route of degradation in soil, and that NER formation is not caused by an inadequate extraction of parent from the soil matrix.

The comparatively fast degradation resulted in the following degradation products in soil:

Table 7.1.1.1- 5: Identified degradation products (mean maximum amounts, % of AR)

CO_2 (41.5%, DAT-120) **NER** (29.4%, DAT-120)	
YRC 2894-amide (KKO 2254) (86.6%, DAT-2) 	**YRC 2894-sulfonic acid** (WAK 6999) (15.1%, DAT-21) 
YRC 2894-des-cyano (KTU 3072) (33.0%, DAT-72) 	

Remark: compare with Table 7.1.1.1- 1: the same major degradates were found using the [methylene-^{14}C]label.

In the course of the study up to 7 radioactive HPLC peaks indicating degradation products were observed and quantified in addition. The maximum concentration of an assigned, unidentified, HPLC peak (ID: u1) was 3.9 % of AR (DAT-30). The very minor peaks were calculated as sum and were in the range of 0.2 to 1 % of AR. Altogether the unknown extracted radioactivity achieved a maximum value of 6.1 % of AR.

It is concluded from this study that Thiacloprid is degraded rapidly in soil [redacted]AXXa with a best fit kinetics according to FOCUS (double first order in parallel, DFOP, for trigger evaluation) as 0.35 days under aerobic conditions at 20°C in the dark. The formed major metabolites (i.e. M02, M29 and M30) are further moderately degraded and, therefore, do not accumulate in soil. For more details on kinetics of degradation see Section CA 7.1.2.1.

Formation of significant amounts of non-extractable residues and carbon dioxide indicates a participation in the natural carbon cycle of soil and the potential for a complete mineralisation of Thiacloprid. Thiacloprid and its degradation products have no potential for accumulation in the environment.

The results received within this [thiazolidine-2-^{14}C]-Thiacloprid metabolism/degradation study were in good agreement with the proposed aerobic soil degradation pathway of Thiacloprid (see Figure 7.1.1.1-1) known from the corresponding metabolism/degradation studies using the [methylene-^{14}C]label (see both studies summarized earlier. No new metabolite specific for the [thiazolidine-2-^{14}C]label was found.

I. MATERIALS AND METHODS

A. Test Item

[Thiazolidine-2-^{14}C]YRC 2894:	KATH 6633
Specific Radioactivity:	4.12 MBq/mg (111.3 µCi/mg)
Radiochemical Purity:	> 99 % (HPLC, radiodetector)
Chemical purity:	> 99 % (HPLC, UV-detector, 210 nm)

B. Test System

The study was carried out using soil [redacted]4a. The soil was taken from an agricultural use area. The plant protection product use history of the soil is known for at least 5 years. The characteristics of test soil are given in following table.

Table 7.1.1.1- 6: Physico-chemical characteristics of test soil [redacted]4a

Parameter	**Results/Units**	**Methods**
Geographic Location (City / State / Country)	[redacted] /North Rhine-Westphalia / Germany	
Soil Taxonomic Classification (USDA)	Loamy, mixed, mesic Typic Argudalfs	
Soil Series	N/A	
Soil Mapping Unit	[redacted]	
Texture Class (USDA)	Silt Loam	Hydrometer method *
Sand Silt Clay	42 % 51 % 7 %	Sieve analysis *
pH in 0.01 M $CaCl_2$ (soil/$CaCl_2$ 1/2) pH in water (soil/water 1/1) pH in water (saturated paste) pH in 1 N KCl	6.3 6.5 6.6 6.0	pH-electrode suspension method or pH in saturated paste *
Organic Matter	4.1 %	Calculated: % org. matter = % org. carbon x 1.724
Organic Carbon	2.4 %	Combustion analysis *
Initial & Final Soil Biomass or Microbial Activity	see Table 2 of report	Part of current study
Cation Exchange Capacity (CEC)	12.8 meq/100 g	Sum of cations (extracted with 1N CH_3COONH_4) and hydrogen (pH measurement in Adams-Evans buffer solution) *
Water Holding Capacity 0.33 bar (pF 2.5)	23.4 g H_2O *ad* 100 g DW	Moisture remained when water saturated soil is placed under 1/3 bar pressure
Maximum Water Holding Capacity (WHC_{max})	64.6 g H_2O *ad* 100 g DW	Cylinder drip-off method (BCS-D-EnSa-MeA/Efate)
Bulk Density (disturbed)	0.99 g/cm^3	Determined by weighing a known volume of dried and ground soil *

Sampling Date	DAT-0	DAT-30	DAT-30$^+$	DAT-120	DAT-120$^+$
Microbial Biomass (mg microbial carbon per kg of soil dry weight)	1011	833	855	550	620

$^+$ Samples applied with acetonitrile/water 1/20 (solvent of application solution).
* References to soil characterization methods used by “AGVISE”, USA.

II. STUDY DESIGN

A. Experimental Conditions

The soils were sampled freshly from the fields (upper horizon of 0 to 20 cm) and sieved to a particle size of ≤ 2 mm. Description of soil collection and storage is given in Appendix 2 of the report.

Static test systems (300-mL Erlenmeyer glass flasks) for degradation in soil under aerobic conditions were used as incubation vessels. Each flask was fitted with a trap attachment (permeable for oxygen) containing soda lime for absorption of carbon dioxide and a polyurethane (PU) foam plug for adsorption of volatile organic compounds (VOC).

For preparation of the test systems, 100 g dry weight equivalents of the sieved soils were weighed into each flask. Soil moisture was adjusted to 55% of the maximum water holding capacity (MWHC) for the individual test systems by addition of de-ionized water, taking into account the water content of the application solution. The flasks were then fitted with above-mentioned trap attachments.
The untreated test systems were equilibrated to study conditions for some days prior to application. For detailed information on experimental design see also Table 3 and Table 4 of report.

A study application rate of 0.16 mg per 100 g soil dry weight was applied. An aliquot of 1000 µL of aqueous [^{14}C]-Thiacloprid application solution was applied drop-wise onto the soil surface of the respective equilibrated test systems using a pipette.
After application, the test vessels (except DAT-0 samples) were fitted with trap attachments and placed into a temperature-controlled walk-in climatic chamber for incubation. The soil moisture was maintained since water loss from evaporation (determined by re-weighing of flasks) was replaced in interval (see Appendix 3 of report). Soil microbial biomass was determined in test systems at DAT-0, DAT- 29 and DAT-120 (see Table 7.1.1.1- 6).

B. Sampling

Duplicate treated flasks were taken and processed completely for analyses at the following sampling dates: 0, 0.25, 1, 2, 4, 7, 14, 21, 30, 45, 72 and 120 days after treatment (DAT).

C. Analytical Procedures

Prior to opening an incubated test system for processing of soil, volatiles possibly still present in the head space of the test system were purged into the trap attachment. Afterwards, the trap attachment was removed and the soil was extracted completely. The soil was extracted immediately after sampling of the flasks. The total soil portion of each test flask was transferred (using the extraction solvent) into a centrifuge beaker. The extraction procedures for all intervals were as follows:

Solvent	Volume	Duration	Temperature	Cycles	Combine extracts
Acetonitrile/water 50/50 (v/v)	100 mL	30 min shaking	ambient*	1	yes
Acetonitrile/water 80/20 (v/v)	100 mL	30 min shaking	ambient*	3	
Acetonitrile/water 80/20 (v/v)	100 mL	12 min microwave	70°C	1	-

* further called cold extract

After each extraction step, the suspension was centrifuged for 10 minutes at 5000 x *g*, and the clear supernatant was decanted. The four organic cold extracts were combined. The organic microwave extract was analysed separately. Volume and radioactivity contents were determined. Aliquots (10 mL) of the combined organic cold extracts and microwave extracts were spiked with 20 µl Dobanol® and concentrated to approximately 1.0 – 1.5 mL using a SpeedVac concentrator. 100 µl acetonitrile were added to the concentrated extracts.

Volume and the radioactivity of the combined extract were determined. Chromatographic analyses of soil extracts by the primary method were performed not later than on the day after preparation. The analysed extracts were stored in a freezer for further investigations, if necessary. The paper filters used for filtration were cut into pieces (usually 3 to 4), combusted completely, and the evolved radioactivity was regarded as not extracted radioactivity.
The amount of degradation products in the combined soil extract was determined by liquid scintillation counting (LSC) and by HPLC/radiodetection analysis. The amount of volatiles and non-extractable residues was determined by LSC and combustion/LSC, respectively. Test item and major metabolites were identified by HPLC-MS and HPLC-MS/MS and/or confirmed by co-chromatography with the corresponding characterized reference substances. AMD-TLC was used as confirmation method.

III. RESULTS AND DISCUSSION

Results indicated that the anticipated standardized aerobic laboratory conditions were maintained during the entire incubation period in the dark. Maintenance of aerobic conditions was achieved by using an "open" test system (so-called bio-meter flasks permeable for air) incubated in a large air-conditioned room. The anticipated standardised soil temperature was maintained during the study. The average temperature was 20.0 °C (range = 19.8 – 20.6 °C). The anticipated standardised soil moisture of 55% of WHCmax was maintained during the study. Viable soil was used within this study. The measured values for microbial biomass were found to be in the usual range expected of soils taken from agricultural fields. As it is usual for such laboratory studies the microbial biomass determined at the end of the incubation was significantly lower.

A. Data

The amount of applied test item for the degradation samples was determined to be 15.8 µg/vessel, which is equivalent to 65083 Bq. This was set to 100% of applied radioactivity [% of AR]. It was confirmed that the application was homogeneous during the application procedure.
The calculations for radioactivity (as % of applied radioactivity) in the soil and the respective trap attachment for volatiles are listed in Table 7.1.1.1- 7, the conclusive overview was presented in Table 7.1.1.1- 5, already.

Complete material balances found at the sampling intervals demonstrated that there was no significant loss of radioactivity from the test systems or during sample processing. During the study the total recovery of radioactivity (RA) in individual test vessels ranged from 103.1% to 97.3% of applied radioactivity (AR), and the mean was 100.5% (SD 1.5%).

B. Method Validation

Verification of Sample Processing Method

Mean DAT-0 material balance was 101.7% of AR; the test item was stable under the conditions of extraction and sample processing, i.e. the DAT-0 recovery of 101.1 % of AR found in the organic cold and microwave extracts was just the parent compound (Table 7.1.1.1- 8). These results demonstrate that the extraction method was well suitable to extract the applied [thiazolidine-2-^{14}C]-Thiacloprid from the soil matrix.

Verification of Chromatographic Procedures

Using HPLC, the complete recovery of injected radioactivity was confirmed for both methods using samples from DAT-0 and DAT-14. The minimum limit of quantification (LOQ) by HPLC for a single peak was estimated as three times LOD (0.2% of AR) and was in the soil extracts in the range of 0.6% of AR. Peaks between LOD and LOQ were used in calculations as given values. Representative HPLC chromatograms showing the separation of parent and transformation products can be found in Figure 8 to Figure 11 of report. These results indicated that the HPLC method was well suitable to analyse the applied [^{14}C]-Thiacloprid as well as the degradation products.

In order to confirm the results of the HPLC method, extracts were investigated with a second separation method (AMD-TLC). A comparison of both methods is given in Appendix 8 of report. The test item and the metabolites were well separated and no additional metabolite was detected in significant amounts (>5% AR).

Table 7.1.1.1- 7: Material balance of radioactivity in soil [redacted]4a (expressed as percentage of applied radioactivity, % AR)

	Replicate	DAT											
	No.	**0**	**0.25**	**1**	**2**	**4**	**7**	**14**	**21**	**30**	**45**	**72**	**120**
Volatiles													
$^{14}CO_2$	1	n.a.	<0.1	0.1	0.2	0.82	1.90	4.56	8.1	12.9	18.5	29.1	41.3
	2	n.a.	<0.1	0.1	0.2	0.8	1.9	4.8	7.8	13.0	20.1	28.4	41.7
	Mean			**0.1**	**0.2**	**0.8**	**1.9**	**4.7**	**8.0**	**13.0**	**19.3**	**28.8**	**41.5**
Volatile organics	1	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	2	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1
	Mean								**0.1**	**0.1**			**0.1**
Total	1	n.a.	<0.1	0.1	0.2	0.8	1.9	4.6	8.3	12.9	18.5	29.1	41.3
	2	n.a.	<0.1	0.1	0.2	0.8	1.9	4.8	7.8	13.1	20.1	28.4	41.8
	Mean			**0.1**	**0.2**	**0.8**	**1.9**	**4.7**	**8.1**	**13.0**	**19.3**	**28.8**	**41.5**
Extractable Radioactivity													
Cold extract	1	98.9	97.8	98.6	93.0	87.5	81.1	69.8	61.6	56.4	47.8	34.1	24.2
	2	101.1	101.2	95.7	93.2	89.1	83.2	71.4	63.6	57.3	46.4	34.7	24.5
	Mean	**100.0**	**99.5**	**97.1**	**93.1**	**88.3**	**82.2**	**70.6**	**62.6**	**56.9**	**47.1**	**34.4**	**24.3**
Microwave extract	1	1.1	1.1	1.9	3.4	3.3	3.7	6.2	6.1	5.6	5.9	5.5	5.1
	2	1.2	1.2	1.4	3.1	3.3	3.8	5.5	5.4	6.1	6.1	5.4	5.0
	Mean	**1.1**	**1.1**	**1.6**	**3.2**	**3.3**	**3.8**	**5.9**	**5.8**	**5.9**	**6.0**	**5.5**	**5.1**
Total	1	99.9	98.9	100.4	96.3	90.8	84.9	76.1	67.8	62.1	53.7	39.6	29.2
	2	102.3	102.4	97.1	96.3	92.4	87.0	76.9	69.0	63.4	52.5	40.1	29.6
	Mean	**101.1**	**100.7**	**98.8**	**96.3**	**91.6**	**86.0**	**76.5**	**68.4**	**62.7**	**53.1**	**39.8**	**29.4**
Bound Residue	1	0.6	0.7	2.4	5.4	9.2	13.1	18.9	23.4	24.3	26.5	29.2	29.4
	2	0.5	0.7	2.8	5.2	9.2	13.0	19.0	23.9	24.3	26.6	28.7	29.4
	Mean	**0.6**	**0.7**	**2.6**	**5.3**	**9.2**	**13.0**	**18.9**	**23.7**	**24.3**	**26.5**	**28.9**	**29.4**
Material Balance	1	100.5	99.6	102.9	101.9	100.9	99.8	99.5	99.5	99.3	98.7	97.9	99.8
	2	102.8	103.1	100.0	101.7	102.4	101.8	100.7	100.7	100.7	99.2	97.3	100.8
	Mean	**101.7**	**101.4**	**101.5**	**101.8**	**101.7**	**100.8**	**100.1**	**100.1**	**100.0**	**98.9**	**97.6**	**100.3**

n.d. : not detected, n.a. : not analyzed, DAT : day after treatment

Balance	**Min**	**97.3**
	Max	**103.1**
	Mean	**100.5**
	rel. standard deviation	**1.5%**

Table 7.1.1.1- 8: Residues of ^{14}C-Thiacloprid in extract of soil [redacted]4a (expressed as % of AR)

Compound	Replicate No.	DAT 0	0.25	1	2	4	7	14	21	30	45	72	120
Thiacloprid	Mean	101.1	64.6	12.2	3.0	1.6	1.1	0.8	0.6	0.4	0.4	n.d.	n.d.
	SD	±1.2	±1.7	±0.5	±0.1	±0.1	±0.1	±0.0	±0.1	±0.2	±0.2		
-amide	Mean	n.d.	36.1	83.2	86.6	75.5	61.9	45.1	38.4	25.1	15.0	3.0	5.3
	SD		±0.0	±1.2	±0.1	±0.8	±0.4	±0.5	±0.8	±0.4	±0.5	±0.0	±0.0
-sulfonic acid	Mean	n.d.	n.d.	1.2	3.3	7.0	10.9	13.6	15.1	12.8	8.9	2.1	3.3
	SD			±0.1	±0.1	±0.2	±0.2	±0.6	±0.0	±0.1	±0.3	±0.0	±0.0
DIJ10739	Mean	n.d.	n.d.	0.6	0.5	0.8	0.7	0.6	0.3	n.d.	n.d.	n.d.	n.d.
	SD			±0.1	±0.1	±0.1	±0.0	±0.1	±0.3				
u1	Mean	n.d.	n.d.	0.7	0.9	1.9	2.5	2.9	3.1	3.9	3.7	1.1	3.7
	SD			±0.0	±0.3	±0.1	±0.0	±0.2	±0.2	±0.3	±0.3	±0.1	±0.2
-des-cyano	Mean	n.d.	n.d.	0.9	2.0	4.2	8.1	12.2	9.0	18.4	23.6	33.0	16.2
	SD			±0.0	±0.0	±0.0	±0.5	±0.0	±0.0	±0.4	±0.3	±0.2	±0.3
u3	Mean	n.d.	n.d.	n.d.	n.d.	0.6	0.9	1.3	1.9	2.2	1.6	0.4	n.d.
	SD					±0.1	±0.1	±0.0	±0.0	±0.0	±0.1	±0.0	
Sum u4-u7	Mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.2	1.0
	SD											±0.1	±0.2
Sum unidentified radioactivity	Mean	n.d.	n.d.	0.7	0.9	2.5	3.4	4.2	5.1	6.1	5.3	1.7	4.7
	SD			±0.0	±0.3	±0.0	±0.1	±0.2	±0.2	±0.2	±0.1	±0.1	±0.4
Total extractable residues	Mean	101.1	100.7	98.8	96.3	91.6	86.0	76.5	68.4	62.7	53.1	39.8	29.4
	SD	±1.2	±1.7	±1.7	±0.0	±0.8	±1.1	±0.4	±0.6	±0.6	±0.6	±0.3	±0.2
$^{14}CO_2$	Mean	n.a.	<0.1	0.1	0.2	0.8	1.9	4.7	8.0	13.0	19.3	28.8	41.5
	SD			±0.0	±0.0	±0.0	±0.0	±0.1	±0.1	±0.0	±0.8	±0.3	±0.2
Volatile organics	Mean	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.1	<0.1	<0.1	0.1
	SD								±0.1	±0.1			±0.1
Non-extractable residues	Mean	0.6	0.7	2.6	5.3	9.2	13.0	18.9	23.7	24.3	26.5	28.9	29.4
	SD	±0.0	±0.0	±0.2	±0.1	±0.0	±0.1	±0.0	±0.3	±0.0	±0.1	±0.3	±0.0
Total % recovery	Mean	101.7	101.4	101.5	101.8	101.7	100.8	100.1	100.1	100.0	98.9	97.6	100.3
	SD	±1.1	±1.7	±1.5	±0.1	±0.8	±1.0	±0.6	±0.6	±0.7	±0.3	±0.3	±0.5

n.d.: not detected, n.a.: not analyzed, DAT: day after treatment, SD: standard deviation, u: unknown, u2: -des-cyano

Unidentified radioactivity: maximum component 3.9 % of AR at DAT-30 (u1); none increasing towards study end.
DIJ10739 = YRC 2894-urea (see M31 in Figure 7.1.1.1-1).

C. Degradation of Test Item

A synopsis on biotransformation of Thiacloprid in aerobic soil is shown by Table 7.1.1.1- 5; the results were included in the proposed pathway of degradation in soil (see Figure 7.1.1.1-1). More detailed data (expressed as percent of AR) are summarized in Table 7.1.1.1- 8.

Volatiles, i.e. Mineralisation to $^{14}CO_2$

The amount of RA trapped in the individual test flasks (raw data and expressed as % of AR) was given in Table 7.1.1.1- 7, already. At all sampling intervals not any volatile organic compounds (VOC) were measured in the polyurethane foam (each VOC value was <0.1% of AR).

Amount of RA found in the soda lime of the trap attachments was addressed as $^{14}CO_2$ (again see Table 7.1.1.1- 7). A steady increase of the portion of $^{14}CO_2$ was measured during the entire study period. At the termination of the experiment (at day 120) the amount of $^{14}CO_2$ yielded 41.5% of AR.

Test Item and Degradation Products in Soil Extracts

Until study termination (DAT-120) extractable residues decreased to 29.4% of AR. In the same time period the portion of RA recovered by the "cold" extract had decreased from 100% to 24.3% of AR. In general the portions recovered by hot extraction remained on a low level (max 6.0% of AR).

The disappearance of Thiacloprid was quite fast: for kinetics of degradation see Section CA 7.1.2.1.

Degradation of Thiacloprid was accompanied by the formation of several degradation product zones with the observed amounts shown in Table 7.1.1.1- 8; the respective degradation products and its maximum amounts observed were summarized by Table 7.1.1.1- 5.

Non-Extractable Residues

Non-extractable residues (NER) steadily increased to max. 29.4% of AR at DAT-120 (end of study). Since high proportions of $^{14}CO_2$ were observed, also, this indicates that the NER formed from the parent is a major part of its entire route of degradation in soil, and that NER formation is not caused by an inadequate extraction of parent from the soil matrix.

Kinetic Analysis of Data

It is concluded from this study that Thiacloprid is degraded very rapidly in soil [redacted] 4a (see Table 7.1.1.1- 7 and Table 7.1.1.1- 8) with a best fit DT_{50} of 0.35 days when incubated under aerobic conditions at 20°C in the dark. The formed major metabolites (i.e. M02, M29 and M30) are further moderately degraded and, therefore, do not accumulate in soil. For more details on kinetics evaluation of degradation see Section CA 7.1.2.1.

Degradation Pathway

Based on the results of current study, combined with that from the other performed route of degradation studies, the pathway of degradation of Thiacloprid in soil presented by Figure 7.1.1.1-1 is proposed.

IV. CONCLUSIONS

Investigation of the route of degradation showed that Thiacloprid is well degraded and mineralized in soil incubated under standardized aerobic laboratory conditions in the dark. The rapid degradation leads to the major degradation products shown in Table 7.1.1.1- 5. Formation of significant amounts of non-extractable residues and carbon dioxide indicates a participation in the natural carbon cycle of soil and the potential for a complete mineralization of Thiacloprid.

The results received within this [thiazolidine-2-^{14}C]-Thiacloprid metabolism/degradation study were in good agreement with the proposed aerobic soil degradation pathway of Thiacloprid (see Figure 7.1.1.1-1) known from the corresponding metabolism/degradation studies using the [methylene-^{14}C]label (see both studies summarized earlier. No new metabolite specific for the [thiazolidine-2-^{14}C] radio-label was found.

The outcome is included pathway of degradation as well as in the summary of the degradation rates of Thiacloprid and its major degradation products in soil in the laboratory given in section CA 7.1.1 and in Table 7.1-1 and Table 7.1- 2.

CA 7.1.1.2 Anaerobic degradation

The significance of the route of degradation of Thiacloprid in soil under anaerobic conditions in the laboratory was evaluated during the Annex I inclusion (compare EU Monograph, Annex B8), and was accepted by the European Commission (SANCO/4347/2000 – Final; 13 May 2004). The following was stated in the list of endpoints:
No data provided, not required for the currently requested uses (summer application).

Since in general an exposure under anaerobic conditions cannot be excluded and the study is stated as a current data requirement under 1107/2009, a new study performed with [thiazolidine-2-^{14}C]-Thiacloprid is submitted within this Supplemental Dossier for the Thiacloprid renewal of approval.

Report:	**KCA 7.1.1.2 /01; [redacted], H.-P.; [redacted], T.; 2014**
Title:	[Thiazolidine-2-^{14}C]-Thiacloprid: Anaerobic Metabolism / Degradation in Soil.
Report No:	EnSa-13-0490
Document No:	M-484954-01-1
Guidelines:	OECD Guideline for Testing of Chemicals, No. 307, Aerobic and Anaerobic Transformation in Soil, 2002
GLP:	Yes

EXECUTIVE SUMMARY

The route and rate of [thiazolidine-2-^{14}C]-Thiacloprid degradation was studied in a silt loam ([redacted] 4a, OC = 1.9%, pH$_{CaCl2}$ 6.4, [redacted], Germany) at 19.8 °C in the dark under flooded anaerobic conditions following a short aerobic incubation phase. A test concentration of 356 µg per kg soil dry weight was applied based on the single field use rate of 120 g Thiacloprid/ha.
The test was performed in static systems consisting of 300-mL Erlenmeyer flasks each containing 100 g soil (dry weight equivalents). During the aerobic study phase, air-permeable traps were attached for the collection of carbon dioxide and volatile organic compounds (static test systems). At start of the anaerobic study phase, the traps for volatile components were replaced by sealable two-valve glass stoppers connected with plastic gas sampling bags. Following application of [^{14}C]-Thiacloprid to soil the samples were incubated under aerobic conditions in the dark at about 20 °C and 55% of maximum water holding capacity. After 1 day of incubation the soil samples were flooded with oxygen-depleted, de-ionized water (approx. 3 cm layer above soil level) and set under an atmosphere of argon. The water-logged samples were maintained under anaerobic conditions at approximately 20 °C in the dark for 125 days. Duplicate test systems were analysed immediately after application and after 1 day of aerobic incubation. Further samples were taken directly after water logging (day 1) and 5, 8, 13, 35, 63, 91 and 126 days after treatment (DAT), corresponding to 0, 4, 7, 12, 34, 62, 90 and 125 days after soil flooding (DASF).

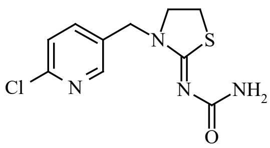
Soil and water layer were separated by centrifugation to allow for separate analysis of the phases with the water being analysed directly. Afterwards the soil was extracted three times at ambient temperature using acetonitrile/water 4/1 (v/v). Furthermore, one microwave extraction step was performed using acetonitrile/water 1/1 (v/v) at 70 °C. The amounts of test item and degradation products in soil extracts were determined by liquid scintillation counting (LSC) and by HPLC/radio-detection analysis. The amounts of volatiles and non-extractable residues were determined by LSC and combustion/LSC, respectively. Test item and degradation products were identified by HPLC-MS(/MS) including accurate mass determination and by co-chromatography with reference items.

Complete material balances found at the sampling intervals demonstrated that there was no significant loss of radioactivity from the test systems or during sample processing. During the study the mean total recovery of radioactivity in individual test vessels was 99.0% of AR (range of 97.3 to 100.5% of AR).

During the short aerobic phase, the maximum amount of carbon dioxide was 0.1% of AR, only. This carbon dioxide formation stopped after flooding and during anaerobic incubation. Formation of volatile organic compounds (VOC) was insignificant as demonstrated by values of < 0.1% of AR at all samplings intervals in the aerobic and anaerobic incubation phase. Non-extractable radioactivity (NER) in soil slightly increased from 1.7 to 3.1% of AR (mean). Later, in the course of the anaerobic incubation period, the NER increased to 27.0% of AR until study end.

The comparatively fast degradation resulted in the following degradation products in soil kept under flooded anaerobic conditions following a short aerobic incubation phase:

Table 7.1.1.2- 1: Identified degradation products (mean maximum amounts, % of AR)

YRC 2894-amide (M02) (85.1%, DASF-7) 	**NER** (27.0%, DASF-125)

DASF: days after flooding.

Investigation of the route of degradation showed that Thiacloprid is well degraded during the short aerobic phase of study. The amount of Thiacloprid decreased rapidly from 97.6% to 30.4% of AR (mean values), thus the DT_{50} value was already exceeded. At the same time the amount of YRC 2894-amide (M02) increased to 63.7% of AR. During the following flooded state (i.e. a progressing anaerobic incubation) the amount of Thiacloprid decreased to < LOD at study end, and M02 increased to 85.1% of AR at DAT-8 (corresponding to DASF-7). However, after flooding and set-up of anaerobic conditions, the further degradation of the major primary metabolite YRC 2894-amide (M02) was slowed down. From DAT-8 towards study termination the amount of M02 decreased slowly to 64.4% AR (mean values), but none of the secondary metabolites shown in pathway of the aerobic degradation in soil (see Figure 7.1.1.1-1) nor the terminal metabolite carbon dioxide were found.

The experimental data of the anaerobic degradation of Thiacloprid could be well described by a first order multi-compartment (FOMC) kinetic model. The anaerobic half-life of Thiacloprid after flooding and shift to anaerobic conditions was 1 day. For more details on kinetics of degradation see Section CA 7.1.2.1.3 and CA 7.1.2.1.4.

The results received within this study showed that no new metabolite specific for anaerobic conditions is to be expected in soil. Whenever a treated plot becomes anaerobic (e.g. after flooding by a heavy rainfall), residues of Thiacloprid will be degraded fast, mainly to YRC 2894-amide (M02). If thereafter the soil status turns back to normal aerobic conditions, the degradation of M02 in soil will proceed following the pathway according to Figure 7.1.1.1-1.

I. MATERIALS AND METHODS

A. Test Item

[Thiazolidine-2-^{14}C]-YRC 2894:	KML 9290
Specific Radioactivity:	4.12 MBq/mg (111.30 µCi/mg)
Radiochemical Purity:	> 98% (HPLC with radioactivity detector) > 98% (TLC, scan)
Chemical purity:	> 99% (HPLC with UV-detector, 210 nm)

B. Test System

The study was carried out using soil [redacted] 4a. The soil was taken from an agricultural use area. The plant protection product use history of the soil is known for at least 5 years. The characteristics of test soil are given in following table.

Table 7.1.1.2- 2: Physico-chemical characteristics of test soil [redacted] 4a

Parameter	Results/Units	Method
Geographic Location (City / State / Country)	[redacted] /North Rhine-Westphalia / Germany	
Soil Taxonomic Classification (USDA)	Loamy, mixed, mesic Typic Argudalfs	
Soil Series	N/A	
Soil Mapping Unit	[redacted]	
Texture Class (USDA)	Silt Loam	Hydrometer method *
Sand Silt Clay	20 % 66 % 14 %	Sieve analysis *
pH in 0.01 M $CaCl_2$ (soil/$CaCl_2$ 1/2) pH in water (soil/water 1/1) pH in water (saturated paste) pH in 1 N KCl	6.4 6.6 6.7 6.2	pH-electrode suspension method or pH in saturated paste *
Organic Matter	3.3 %	Calculated: % org. matter = % org. carbon x 1.724
Organic Carbon	1.9 %	Combustion analysis *
Initial & Final Soil Biomass or Microbial Activity	see Table 2 of report	Part of current study
Cation Exchange Capacity (CEC)	11.3 meq/100 g	Sum of cations (extracted with 1N CH_3COONH_4) and hydrogen (pH measurement in Adams-Evans buffer solution) *
Water Holding Capacity 1/10 bar (pF 2.0)	38.9 g H_2O *ad* 100 g DW	Moisture remained when water saturated soil is placed under 1/10 bar pressure
Maximum Water Holding Capacity (WHC_{max})	54.5 g H_2O *ad* 100 g DW	Cylinder drip-off method (BCS-D-EnSa-MeA/Efate)
Bulk Density (disturbed)	1.12 g/cm³	Determined by weighing a known volume of dried and ground soil *

Sampling Date	DAT-0	DAT-0[+]
Microbial Biomass (mg microbial carbon per kg of soil dry weight)	992	1042
Anaerobic Plate Count Assay DASF-125, replicate 1 DASF-125, replicate 2	Dilution 10^{-3}: 9.33 x 10^3 CFU/g soil 8.67 x 10^3 CFU/g soil	Dilution 10^{-4}: 2.00 x 10^4 CFU/g soil 3.33 x 10^4 CFU/g soil

[+] Application solvent control.
* References to soil characterization methods used by "AGVISE", USA.

II. STUDY DESIGN

A. Experimental Conditions

The soils were sampled freshly from the fields (upper horizon of 0 to 20 cm) and sieved to a particle size of ≤ 2 mm. Description of soil collection and storage is given in Appendix 3 of the report.

Static test systems (300-mL Erlenmeyer glass flasks) for degradation in soil under aerobic conditions were used as incubation vessels. Each flask was fitted with a trap attachment (permeable for oxygen) containing soda lime for absorption of carbon dioxide and a polyurethane (PU) foam plug for adsorption of volatile organic compounds (VOC).

For preparation of the test systems, 100 g dry weight equivalents of the sieved soils were weighed into each flask. Soil moisture was adjusted to 55% of the maximum water holding capacity (MWHC) for the individual test systems by addition of de-ionized water, taking into account the water content of the application solution. The flasks were then fitted with above-mentioned trap attachments.
The untreated test systems were equilibrated to study conditions for some days prior to application.

A study application rate of 35.6 mg per 100 g soil dry weight was applied. An aliquot of 400 µL of [^{14}C]-Thiacloprid application solution (methanol/water 1/1, v/v), was applied drop-wise onto the soil surface of the respective equilibrated test systems using a pipette.
After application, the test vessels (except DAT-0 samples) were fitted with trap attachments and placed into a temperature-controlled walk-in climatic chamber for incubation. Soil microbial biomass was determined in test systems at DAT-0 (see Table 7.1.1.2-2).

1 day after test item application (DAT-1 = DASF-0) the soil of each flask was flooded with 150 mL of oxygen-depleted de ionized water. The flasks were then sonicated for a few seconds to eliminate gas bubbles. The trap attachment of all remaining test flasks was removed and replaced by air-tight plastic gas sampling bag, which had been flushed with argon gas before. The argon was purged out of the bags and the valves were set to connect flask headspace and gas sampling bag, but closing the system from the outer atmosphere. Such setup allowed for pressure-less closed-flask incubation. To ensure maintenance of oxygen-free conditions, the test systems were placed in a box flushed by nitrogen within the walk-in incubation chamber. Anaerobic bacteria were determined at DASF-125.

For detailed information on experimental design see also Table 3 and Table 4 of report.

B. Sampling

Duplicate treated flasks were taken and processed completely for analyses at the following aerobic sampling dates: DAT-0 and DAT-1 (DAT = days after treatment).
Duplicate treated flasks were taken and processed completely for analyses at the following anaerobic sampling dates, 1, 5, 8, 13, 35, 63, 91 and 126 days after treatment (DAT), corresponding to 0, 4, 7, 12, 34, 62, 90 and 125 days after soil flooding (DASF).

C. Analytical Procedures

Prior to opening an incubated test system for processing of soil, volatiles possibly still present in the head space of the vessel were purged into the trap attachment (aerobic phase) or gas sampling bag (anaerobic phase). Afterwards, the trap attachment or gas sampling bag was removed and the soil was extracted completely. The soda lime from the trap attachments of the aerobic phase was transferred into flasks and stored before processing at < -18 °C in the dark for 6 weeks. The PU foam was processed immediately after sampling. The soda lime was stored before processing at < -18 °C in the dark for a maximum period of 5 weeks.

The gas sampling bag of the anaerobic phase was processed immediately after sampling. It was connected to a combustion oven unit intended for volatiles. Thereby the volatiles present in the gas sampling bag were slowly purged using a stream of nitrogen over a soda lime trap for absorption of $^{14}CO_2$, through the catalytic oven for oxidative combustion of organic volatiles (e.g. methane), and

finally through three liquid scintillation flasks filled with alkaline LSC cocktail, for absorption of $^{14}CO_2$ from combustion exhaust. Afterwards, the scintillation cocktails were directly analysed by LSC; the soda lime was further processed as described in Section 3.6.1.3 of report.

In the flooded soils (DASF-0 to DASF-125) the oxygen content of the water, redox potential of water and of soil, and pH of the water were determined by electrode measurements. The water layer was separated from the soil layer by centrifugation (10 min. at 4550 x *g*). After determination of the volume the radioactivity content was determined by LSC.

The entire soil of each test vessel was extracted three times at ambient conditions using a mechanical shaker followed by an accelerated extraction using a microwave with a magnetic stirrer. The extraction procedure is summarized in the following table:

Solvent	Volume	Minimum Duration	Temperature	Cycles
ACN/H_2O 4/1 (*v/v*)	80 mL	30 min, shaking	ambient	3
ACN//H_2O 1/1 (*v/v*)	80 mL	10 min, stirring	microwave, 70 °C	1

After each extraction step, extract and soil were separated by centrifugation (approx. 10 minutes at 4550 x *g*) and decantation. The volumes of the combined ambient extracts and the microwave extract were determined. The radioactivity content of these extracts was determined by LSC. The exhaustive extracted soils were air-dried, homogenized by a planetary mill and NER were determined by combustion/LSC.

The first analysis of soil extracts with the primary chromatographic method was usually done within one day after sampling. The total soil portion of each test flask was transferred (using the extraction solvent) into a centrifuge beaker. After analysis, soil extracts were stored at < -18 °C in the dark. Due to concentration recovery issues without using Dobanol®, all samples were re-analysed after addition of Dobanol®. The maximum sample storage period was 64 days (for storage stability see Section 3.6.2.3 of report).

At each sampling interval aliquots of the combined ambient and both microwave soil extracts were combined, concentrated and characterized by the primary chromatographic method (see Section 3.6.2.2.1 of report). A HPLC/radiodetection system using a phenyl-hexyl-phase column was used for quantitation and identification by co-chromatography. Peak setting and integration was done manually by selecting the peak start and stop times. Peaks were evaluated as “regions of interest”. No chromatographic analyses were performed for the PU foam plug extracts, because they contained less than 0.1% AR. Test item and degradation products were identified by HPLC-MS(/MS) including accurate mass determination and by co-chromatography with reference items.

III. RESULTS AND DISCUSSION

Results indicated that the anticipated standardized aerobic/anaerobic laboratory conditions were maintained during the entire incubation period in the dark. Maintenance of aerobic conditions was achieved by using an “open” test system (so-called bio-meter flasks permeable for air) incubated in a large air-conditioned room. Progressing anaerobic test conditions were received by flooding the test flask after approx. one DT_{50} of Thiacloprid (i.e. 1 day) with oxygen free air and incubating the air-tight closed flasks in an oxygen free chamber.

The temperature was maintained during the study. The average temperature was 19.8 °C (max / min = 18.9 – 20.4 °C). The standardised soil moisture of 55% of WHCmax was maintained during the 1st day of study. Viable soil was used within this study. The measured values for aerobic microbial biomass were found to be in the usual range expected of soils taken from agricultural fields. An anaerobic microbial biomass was successfully built up (see Table 7.1.1.2- 2).

A. Data

The amount of applied test item for the degradation samples was determined at DAT-0 as 146779 Bq (equal to 35.6 µg) with a RSD of 0.8% and was set to 100% of applied radioactivity [% of AR]. It was confirmed that the application was homogeneous during the application procedure. The calculations for radioactivity (as % of AR) in the soil and the respective trap attachment for volatiles are listed in Table 7.1.1.2- 3, the conclusive overview was presented in Table 7.1.1.2- 1, already.

Complete material balances found at all sampling intervals for each soil demonstrated that there was no significant loss of radioactivity from the test systems or during sample processing. During the study the total recovery of radioactivity (RA) in individual test vessels ranged from 97.3 to 100.5% of AR, and the mean was 99.0% of AR.

B. Method Validation

Verification of Sample Processing Method

The mean DAT-0 recovery for the test item was 97.6% of AR for the tested soil (see Table 7.1.1.2- 3). The concentration recovery for the water samples and the combined soil extracts were between 99.7 and 102.0% of AR. These results demonstrate that the sample processing methods was well suited.

Verification of Chromatographic Procedures

The primary chromatographic method (HPLC/radiodetection) was well suited for the quantitative analysis of the samples of this study, as demonstrated by a mean HPLC recovery of 100.1% and a good linear fit for injected amounts of [thiazolidine-2-^{14}C]-Thiacloprid from 9.0 to 917.0 Bq absolute on column ($R^2 > 0.9993$). The LOD of the primary chromatographic method was determined as 9.0 Bq absolute on column or 0.8% of AR.

C. Degradation of Test Item

A synopsis on biotransformation of Thiacloprid in aerobic soil is shown by Table 7.1.1.2- 1; the results were included in the proposed pathway of degradation in soil (see Figure 7.1.1.1-1). More detailed data (expressed as percent of AR) are summarized in Table 7.1.1.2- 4.

Volatiles, i.e. Mineralisation to $^{14}CO_2$

During the short aerobic phase (1 day), the maximum amount of carbon dioxide was 0.1% of AR, only. This carbon dioxide formation stopped after flooding and during anaerobic incubation. Formation of volatile organic compounds (VOC) was insignificant as demonstrated by values of < 0.1% of AR at all samplings intervals in the aerobic and anaerobic incubation phase.

Test Item and Degradation Products in Soil Extracts

Extractable residues decreased from DAT-0 to DAT-126 (corresponding to DASF-125) from 98.1 to 59.9% of AR. The amount of Thiacloprid in the soil extracts decreased from DAT-0 to DAT-126 (corresponding to DASF-125) from 97.6% of AR to < LOD in soil [redacted]4a.
Within the aerobic phase of the study, the amount of the test item Thiacloprid in the entire test systems decreased rapidly from 97.6 to 30.4% of AR (mean values). During the following anaerobic incubation period (i.e. flooded state) the amount of Thiacloprid decreased to < LOD at study end.
The amounts of the degradation product YRC 2894-amide (M02) in the entire system increased to 63.7% of AR during the aerobic incubation period of one day and further to 85.1% of AR at DAT-8 (corresponding to DASF-7). From DAT-8 towards study termination the amount of M02 decreased to 64.4% of AR (mean values). The degradation product YRC 2894-sulfonic acid (M30) could be detected in single samples in very low amounts only. The total unidentified residues in the entire systems reached values not higher than 3.8% of AR. Maximum levels of individual unidentified minor transformation products in the entire system were not higher than 3.0% of AR.

Table 7.1.1.2- 3: Material balance of radioactivity in soil [redacted] under aerobic/anaerobic conditions (expressed as percentage of applied radioactivity, % of AR)

			Sampling Times									
Days after Treatment			0	1	1	5	8	13	35	63	91	126
Days after Soil Flooding			N/A		0	4	7	12	34	62	90	125
Volatiles												
Volatiles of Aerobic Incubation Phase												
	Carbon Dioxide	A	n.a.	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
		B	n.a.	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
		Mean	**n.a.**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**
	Volatile Organic Compounds	A	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
		B	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
		Mean	**n.a.**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**
	Total Volatiles Aerobic	A	n.a.	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
		B	n.a.	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
		Mean	n.a.	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Volatiles of Anaerobic Incubation Phase												
	Carbon Dioxide	A	N/A		n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
		B	N/A		n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
		Mean	**N/A**		**n.a.**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**
	Volatile Organic Compounds	A	N/A		n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
		B	N/A		n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
		Mean	**N/A**		**n.a.**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**
	Total Volatiles Anaerobic	A	N/A		n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
		B	N/A		n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
		Mean	N/A		n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Total Carbon Dioxide		A	n.a.	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
		B	n.a.	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
		Mean	**n.a.**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**
Total Volatile Organic Compounds		A	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
		B	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
		Mean	**n.a.**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**
Total Volatiles		A	n.a.	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
		B	n.a.	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
		Mean	**n.a.**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**
Water and Soil Extractable Residues												
Water		A	N/A		21.1	20.3	17.6	14.9	11.7	11.4	11.2	10.2
		B	N/A		22.5	20.9	16.6	15.8	11.6	11.2	11.3	10.4
		Mean	**N/A**		**21.8**	**20.6**	**17.1**	**15.4**	**11.6**	**11.3**	**11.3**	**10.3**
Soil Extractable Residues												
	Ambient Extract	A	94.5	91.5	70.8	67.3	67.2	63.2	54.7	50.3	48.1	48.0
		B	95.0	93.2	70.6	62.0	67.4	64.1	56.6	50.1	49.0	47.0
		Mean	**94.8**	**92.4**	**70.7**	**64.6**	**67.3**	**63.7**	**55.6**	**50.2**	**48.6**	**47.5**
	Microwave Extract	A	3.5	4.1	3.9	5.9	7.3	9.2	13.0	14.1	13.0	12.2
		B	3.3	4.9	4.3	8.2	7.4	9.1	12.5	13.9	13.0	12.7
		Mean	**3.4**	**4.9**	**4.1**	**7.1**	**7.3**	**9.1**	**12.8**	**14.0**	**13.0**	**12.4**
	Total Soil Extractable Residues	A	98.0	96.5	74.7	73.2	74.5	72.4	67.7	64.4	61.2	60.2
		B	98.3	98.0	74.9	70.3	74.8	73.2	69.1	64.0	62.0	59.7
		Mean	**98.1**	**97.3**	**74.8**	**71.8**	**74.6**	**72.8**	**68.4**	**64.2**	**61.6**	**59.9**
Total Water and Soil Extractable Residues		A	98.0	96.5	95.8	93.6	92.1	87.3	79.4	75.8	72.4	70.4
		B	98.3	98.0	97.4	91.2	91.4	89.0	80.7	75.2	73.3	70.0
		Mean	**98.1**	**97.3**	**96.6**	**92.4**	**91.8**	**88.2**	**80.0**	**75.5**	**72.9**	**70.2**
Non-Extractable Residues		A	2.8	3.2	2.8	6.1	7.7	10.5	17.9	22.7	24.6	26.7
		B	1.6	3.1	2.9	8.3	7.9	10.6	18.4	23.3	25.0	27.4
		Mean	**1.7**	**3.1**	**2.9**	**7.2**	**7.8**	**10.6**	**18.2**	**23.0**	**24.8**	**27.0**
Material Balance		A	99.8	99.8	98.6	99.8	99.9	97.9	97.4	98.6	97.0	97.1
		B	99.9	101.2	100.4	99.6	99.4	99.7	99.1	98.6	98.4	97.5
		Mean	**99.8**	**100.5**	**99.5**	**99.7**	**99.7**	**98.8**	**98.3**	**98.6**	**97.7**	**97.3**

N/A: not applicable, n.d. not detected, not analysed

Table 7.1.1.2- 4: Residues of ^{14}C-Thiacloprid in extract of soil [redacted]4a (expressed as % of AR; mean ± SD)

			Sampling Times									
		DAT	**0**	**1**	**1**	**5**	**8**	**13**	**35**	**63**	**91**	**126**
Compound	**Source**	**DASF**	**N/A**		**0**	**4**	**7**	**14**	**34**	**62**	**90**	**125**
Thiacloprid	Entire System	Mean SD	97.6 ± 0.6	30.4 ± 0.0	27.5 ± 0.6	6.1 ± 0.2	4.7 ± 0.0	3.3 ± 0.1	1.4 ± 0.2	1.1 ± 0.2	0.9 ± 0.0	< LOD
YRC 2894-sulfonic acid (M30) [3]	Entire System	Mean SD	n.d.	n.d.	< LOD	< LOD	< LOD	< LOD	< LOD	n.d.	n.d.	< LOD
Unknown 2 [3]	Entire System	Mean SD	n.d.	< LOD	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD	< LOD
YRC 2894-amide (M02)	Entire System	Mean SD	n.d.	63.7 ± 0.4	66.5 ± 0.2	82.8 ± 1.5	85.1 ± 0.2	82.7 ± 0.8	76.6 ± 0.7	72.4 ± 0.7	68.8 ± 0.1	64.4 ± 0.9
Unknown 4	Entire System	Mean SD	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD	1.0 ± 0.1	1.5 ± 0.1	1.6 ± 0.3	3.0 ± 0.2
Diffuse residues	Entire System	Mean SD	< LOD	2.9 ± 1.4	1.5 ± 0.4	1.5 ± 0.2	< LOD	< LOD	< LOD	< LOD	0.9 ± 0.0	< LOD
Total extractable residues [1]	Entire System	Mean SD	98.0 ± 0.1	97.6 ± 1.1	95.6 ± 0.7	90.4 ± 1.2	90.3 ± 0.4	86.5 ± 0.4	79.0 ± 0.4	75.0 ± 0.7	72.3 ± 0.4	68.6 ± 0.6
Carbon dioxide [2] (sum aerobic and anaerobic)		Mean SD	n.a.	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0
Volatile organic compounds (VOC)[2] (sum aerobic and anaerobic)		Mean SD	n.a.	< 0.1 ± 0.0	< 0.1 ± 0.0	< 0.1 ± 0.0	< 0.1 ± 0.0	< 0.1 ± 0.0	< 0.1 ± 0.0	< 0.1 ± 0.0	< 0.1 ± 0.0	< 0.1 ± 0.0
Non-extractable residues [2] (NER)		Mean SD	1.7 ± 0.1	3.1 ± 0.0	2.9 ± 0.1	7.2 ± 0.1	7.8 ± 0.1	10.6 ± 0.0	18.2 ± 0.2	23.0 ± 0.3	24.8 ± 0.2	27.0 ± 0.3
Total recovery [1]		Mean SD	99.8 ± 0.0	100.2 ± 1.0	98.5 ± 0.8	97.7 ± 0.1	98.2 ± 0.3	97.1 ± 0.5	97.2 ± 0.6	98.1 ± 0.3	97.1 ± 0.6	95.7 ± 0.3

n.d.: not detected, n.a.: not analysed, DAT: days after treatment, DASF: days after soil flooding, SD: standard deviation
[1] Difference to Material Balance values due to rounding errors as well as clean up and chromatographic losses
[2] Values taken from Material Balance
[3] Signals could be detected in some cases (single samples) in HPLC chromatograms but were below the calculated limit of detection

Non-Extractable Residues

In the short aerobic incubation phase, NER in soil increased from 1.7 to 3.1% of AR (mean values), only. During the following anaerobic incubation period NER increased to 27% of AR at study end. NER was further characterized for the samples of DAT-126 (corresponding to DASF-125).

Kinetic Analysis of Data

The disappearance of Thiacloprid was quite fast: for details on kinetics of degradation see Section CA 7.1.2.1.3. The half-life for Thiacloprid was 1 day in the tested soil under anaerobic conditions.

Degradation Pathway

Based on the results of current study it is obvious that under anaerobic conditions the pathway of degradation of Thiacloprid in soil (presented by Figure 7.1.1.1-1) is slowed down at the stage of YRC 2894-amide (M02).

IV. CONCLUSIONS

The results obtained within this study showed that no new metabolite specific for anaerobic conditions is to be expected in soil. Whenever a treated plot turns to anaerobic status, e.g. after flooding by a heavy rainfall, residues of Thiacloprid will be degraded fast, mainly to YRC 2894-amide (M02). Thereafter, if the soil status turns back to normal aerobic soil condition, the degradation of M02 in soil will proceed following the pathway according to Figure 7.1.1.1-1.

CA 7.1.1.3 Soil photolysis

The route of photo-degradation of Thiacloprid on soil surface was evaluated during the Annex I inclusion (compare EU Monograph, Annex B8), and was accepted by the European Commission (SANCO/4347/2000 – Final; 13 May 2004). The following study included in the Baseline Dossier was regarded as relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted], E.	1998	M-001245-01-1

EU conclusion of study performed by [redacted], E.; 1998:

Photo-degradation of Thiacloprid on soil surface is negligible since the dissipation rate in the irradiated samples was comparable to that in the dark controls. The phototransformation product M35 (YRC 2894-Dewar pyridone) observed at a maximum formation of <5% of AR during irradiation is shown in the route of degradation of Thiacloprid in soil as given in Figure 7.1.1.1-1. However, it is not regarded as relevant for soil and groundwater risk assessments since photo-degradation of Thiacloprid on soil surfaces will not significantly contribute to primary degradation of the parent compound under real use conditions.

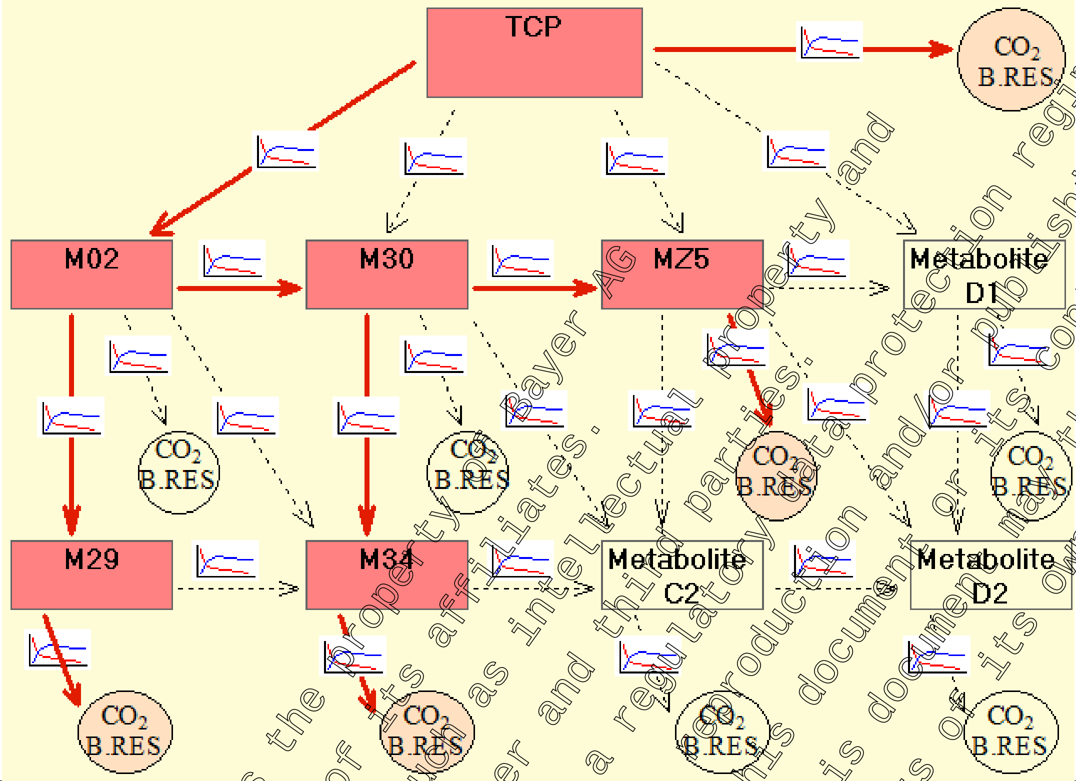
No additional studies are submitted within this Supplemental Dossier for the Thiacloprid renewal of approval..

CA 7.1.2 Rate of degradation in soil

Thiacloprid was well degraded in soil under aerobic conditions in the laboratory (Section CA 7.1.2.1) and in the field (Section CA 7.1.2.2). The data sets of Thiacloprid and its major degradation products and the respective kinetics modelling evaluations to be used for modelling purposes (acc. to FOCUS kinetics (2006)[1] are summarized in sections CA 7.1.2.1.1 and CA 7.1.2.1.2, and are submitted within this Supplemental Dossier for the Thiacloprid renewal of approval. An overview of results is presented by Table 7.1- 1 and Table 7.1- 2.

For modelling purposes, the overall metabolic scheme (Figure 7.1.1.1-1) was transformed into a multi-compartmental model, based on measured data and kinetic evaluations of [redacted], L.; [redacted], S.; 2014, and [redacted], L.; [redacted], S.; 2013). This model is summarised by Figure 7.1.2-2.

[1] FOCUS kinetics (2006): "Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration", Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference Sanco/10058/2005 version 2.0, 434 pp.



TCP = thiacloprid M02 = YRC 2894-amide M29 = YRC 2894-des-cyano	M30 = YRC 2894-sulfonic acid M34 =YRC 2894-sulfonic acid amide MZ5 = YRC 2894-thiadiazine (M46)

Figure 7.1.2-2: Compartmental model used for the modelling of soil degradation of Thiacloprid (example implementation in FOCUS PELMO).

In order to select the relevant population to calculate the modelling input DT_{50}, the null hypothesis that laboratory and field values are equal was tested (EFSA, 2014)[2].The statistical significance of differences in the laboratory and field DT_{50} values for Thiacloprid, YRC 2894-amide (M02) and YRC 2894-sulfonic acid (M30) was checked with Student's t-test at a 25% significance level. As the t-test value (t) was lower than the t-quantile of t-distribution (tdf, 1-α), the null hypothesis was not rejected for Thiacloprid and YRC 2894-amide (M02). Hence, as the null hypothesis that laboratory and field half-lives are equal is not rejected, and the relevant population of half-lives consists of more than four values, half-lives were pooled from both laboratory and field studies. The resulting first-order DT_{50} values are given in Table 7.1.2- 1 for Thiacloprid, and in Table 7.1.2- 2 for YRC 2894-amide (M02). For M30 the null hypothesis was to be rejected, thus the half-lives were not pooled and only field degradation data is taken into account (see Table 7.1.2- 3 for M30 data).
A median DT_{50} value of 5.4 days is proposed to describe the degradation of Thiacloprid in the modelling calculations, i.e. for PEC_{GW}. A median DT_{50} value of 41.3 days is proposed to describe the degradation of YRC 2894-amide (M02) in calculations, together with an arithmetic mean formation fraction from parent of 0.61. Geometric mean DT_{50} value of 15.6 days is proposed to describe the degradation of YRC 2894-sulfonic acid (M30) in calculations, together with arithmetic mean formation fraction from YRC 2894-amide of 0.80 (for compilation of data see Table 7.1- 2).

[2] EFSA Guidance Document for evaluating laboratory and field dissipation studies to obtain $DegT_{50}$ values of active substances of plant protection products and transformation products of these active substances in soil. EFSA Journal, 2014, 12 (5), 3662.

Table 7.1.2- 1: First-order soil DT_{50} values of Thiacloprid

Soil	DT50 [days]
BBA 2.1 & b)	2.96
BBA 2.2 & b)	2.16
[redacted] im Tal & b)	0.66
[redacted] & b)	5.39
[redacted] AXXa § b)	1.83
[redacted] 4a @ b)	0.35
[redacted] # c)	2.9
[redacted] # c)	6.6
[redacted] # c)	5.7
[redacted] # c)	6.8
[redacted] # c)	9.5
[redacted] # c)	7
[redacted] $ c)	1 a)
[redacted] $ c)	7.2
Geometric mean	3.4
Median	5.4

a) no valid value could be determined
b) evaluation of laboratory degradation studies ([redacted] & [redacted]; 2013a)
c) evaluation of field degradation studies ([redacted] & [redacted]; 2013b)
& study [redacted] & [redacted]; 1998
§ study [redacted]; 2003
@ study [redacted]; 2011
# study [redacted]; 1997
$ study [redacted]; 1998

Table 7.1.2- 2: First-order soil DT_{50} and formation fraction values of YRC 2894-amide (M02)

Soil	DT_{50} [days]	Formation fraction
BBA 2.1 [& b)]	41.3	0.74
BBA 2.2 [& b)]	85.7	0.82
[redacted] im Tal [& b)]	33.78	0.77
[redacted] [& b)]	121.47	0.79
[redacted] AXXa [§ b)]	- [a)]	0.72
[redacted] 4a [@ b)]	15.11	0.89
[redacted] [# c)]	24.1	- [a)]
[redacted] [# c)]	72.4	0.5353
[redacted] [# c)]	38.7	0.2447
[redacted] [# c)]	133.4	0.4078
[redacted] [# c)]	53.8	0.3477
[redacted] [# c)]	28.8	0.6552
[redacted] [$ c)]	76.4	0.5345
[redacted] [$ c)]	39.9	0.5005
Geometric mean	49.0	-
Median	41.3	-
Arithmetic mean	-	0.61

a) no valid value could be determined
b) evaluation of laboratory degradation studies ([redacted] & [redacted]; 2013a)
c) evaluation of field degradation studies ([redacted] & [redacted]; 2013b)
& study [redacted] & [redacted]; 1998
§ study [redacted]; 2003
@ study [redacted]; 2011
# study [redacted]; 1997
$ study [redacted]; 1998

Table 7.1.2- 3: First-order soil DT_{50} and formation fraction values of YRC 2894-sulfonic acid (M30)

Soil	DT_{50} [days]	Formation fraction
BBA 2.1 [& b)]	36.29	0.82
BBA 2.2 [& b)]	- [a)]	- [a)]
[redacted] im Tal [& b)]	- [a)]	- [a)]
[redacted] [& b)]	- [a)]	- [a)]
[redacted] AXXa [§ b)]	110.78	- [d)]
[redacted] 4a [@ b)]	9.99	0.55
BBA 2.1 [= b)]	65.55	- [d)]
BBA 2.2 [= b)]	19.71	- [d)]
[redacted] [= b)]	19.14	- [d)]
[redacted] AXXa [* b)]	18.84	- [d)]
[redacted] [# c)]	12	- [a)]
[redacted] [# c)]	7.1	0.8794
[redacted] [# c)]	16	1
[redacted] [# c)]	16.7	1
[redacted] [# c)]	7	1
[redacted] [# c)]	- [a)]	0.5054
[redacted] [$ c)]	13.8	1
[redacted] [$ c)]	8.6	0.4116
Geometric mean (field data only)	15.6 [e)]	-
Arithmetic mean	-	0.80 [f)]

a) no valid value could be determined
b) evaluation of laboratory degradation studies ([redacted] & [redacted]; 2013a)
c) evaluation of field degradation studies ([redacted] & [redacted]; 2013b)
d) direct application of the metabolite
e) value based on field studies only
f) value based on both laboratory and field studies
& study [redacted] & [redacted]; 1998
§ study [redacted]; 2003
@ study [redacted]; 2011
= study [redacted]; 1998
* study [redacted]; 2003
# study [redacted]; 1997
$ study [redacted]; 1998

CA 7.1.2.1 Laboratory studies

Thiacloprid was well degraded in soil under aerobic conditions in the laboratory. The degradation of parent compound and its metabolites in soil has been investigated in several laboratory degradation studies after soil treatment by parent compound Thiacloprid (see section CA 7.1.1.1) or by the metabolites YRC 2894-sulfonic acid (M30), YRC 2894-des-cyano (M29) or YRC 2894-thiadiazine (M46) as summarized in section CA 7.1.2.1.2). The set of soil degradation data originating from these studies was evaluated in order to derive kinetic parameters to be used for predictions of environmental concentration of Thiacloprid, M02, M29, M30, M34 and M46. The evaluation was performed following the guideline given by the report of the FOCUS group on kinetic evaluation (FOCUS 2006, 2012). The kinetic models and DT_{50} values in soil of Thiacloprid and its major degradation products used for modelling purpose and trigger evaluation (best-fit) as well as the formation fractions in soil for major degradation products are summarized in sections CA 7.1.2.1.1 and CA 7.1.2.1.2.

Modelling input values derived from laboratory studies and their kinetic evaluations, then proposed for the calculation of predicted environmental concentrations of Thiacloprid and its major degradation products in soil, groundwater and surface water were included in Table 7.1-1 (for PEC_{Soil}), Table 7.1-2 (for PEC_{GW}) and in Table 7.2- 1 and Table 7.2- 2 (for PEC_{SW}). They are submitted within this Supplemental Dossier for the Thiacloprid renewal of approval.

CA 7.1.2.1.1 Aerobic degradation of the active substance

The rate of degradation of Thiacloprid in soil under aerobic conditions in the laboratory was evaluated during the Annex I inclusion (compare EU Monograph, Annex B8), and was accepted by the European Commission (SANCO/4347/2000 – Final; 13 May 2004). The following studies included in the Baseline Dossier were regarded as relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted], R., [redacted] W.	1998	M-001076-02-1
[redacted], H.	1998	M-001290-01-1

Summary of study performed by [redacted], R., [redacted], W.; 1998

The study conducted under standardized laboratory conditions in 4 different soils (sand, loamy sand, loamy silt, and sandy loam) with [methylene-^{14}C]-Thiacloprid was performed at an average concentration of 37.1 µg as/100g soil (dry weight), i.e. equivalent to a recommended field application rate of about 300 to 350 g as/ha. A summary of these data kinetically evaluated by [redacted], H., 1998, is shown by Table 7.1.2.1.1- 1.

Table 7.1.2.1.1- 1: Summary of DT_{50} values of Thiacloprid by [redacted], H.; 1998

Compound	DT_{50} Range at 20°C (persistence values)	DT_{50} (geomean 20 °C, normalised to FC)
Thiacloprid	0.7 - 4.7 days	1.3 days (n = 4)
YRC 2894-amide (M02)	32 - 142 days	41.7 days (n = 4)

No additional "rate of degradation study for the active substance" is submitted within this Supplemental Dossier for the Thiacloprid renewal of approval.

However, the new route of Thiacloprid degradation studies by [redacted], E.; 2003, and [redacted], N.; 2011 (see below), can also be evaluated for degradation kinetics. Further due to changes in the requirements for kinetic fitting, the data evaluation by [redacted], L.; [redacted], S.; 2014, included an updated kinetic evaluation of the study performed by [redacted], R., [redacted], W.; 1998, according to

FOCUS kinetics (2006) to derive kinetic parameters suitable for modelling purpose and environmental risk assessment.

Report:	**KCA 7.1.2.1.1 /03; [redacted], E.; 2003**
Title:	Aerobic Degradation/Metabolism of Thiacloprid (YRC2894) in Soil [redacted] AXXa.
Report No:	MR-433/02
Document No:	M-106754-01-1
Guidelines:	Official Journal of the European Communities, No. L 172 (EN), July 22, 95: Commission Directive, 95/36/EC, amending Council Directive 91/414/EEC, 7171/VI/94-EN, 7.1.1 Route and Rate of Degradation. SETAC-Europe: Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, March 1995, Part 1, Section 1.1 German BBA Guideline, Part IV, 4-1, 1986
GLP:	Yes

EXECUTIVE SUMMARY

The details on study performed by [redacted], E.; 2003, were summarized in the route of Thiacloprid degradation section CA 7.1.1.1.

Report:	**KCA 7.1.2.1.1 /04; [redacted], N.; 2011**
Title:	[Thiazolidine-2-^{14}C]thiacloprid: Aerobic metabolism/degradation in an European soil.
Report No:	MEF-10/140
Document No:	M-404822-01-1
Guidelines:	OECD Guideline for Testing of Chemicals, No. 307, Aerobic and Anaerobic Transformation in Soil, 2002 US EPA Fate, Transport and Transformation Test Guidelines, OPPTS 835.4100 and OPPTS 835.4200, Aerobic and Anaerobic Soil Metabolism, 2008 Commission Directive 95/36/EC amending Council Directive 91/414/EEC (Annexes II and III, Fate and Behaviour in the Environment), 1995
GLP:	Yes

EXECUTIVE SUMMARY

The details on study performed by [redacted], N.; 2011, were summarized in the route of Thiacloprid degradation section CA 7.1.1.1.

Report:	**KCA 7.1.2.1.1 /05; [redacted], L.; [redacted], S.; 2014**
Title:	Kinetic evaluation of laboratory aerobic soil degradation of Thiacloprid (YRC 2894) and its metabolites according to FOCUS kinetics **Thiacloprid (YRC 2894)** YRC 2894-amide (KKO 2254) YRC 2894-thiazolidinimine (KTU 3072) YRC 2894-sulfonic acid (WAK 6999) YRC 2894-sulfonic acid amide (KTS 9815) YRC 2894-thiadiazine (BCS-CJ16425, MZ5)
Report No:	EnSa-13-0290
Document No:	M-454544-02-1
Guidelines:	FOCUS (2011): Generic guidance for estimating persistence and degradation kinetics from environmental fate studies on pesticides in EU registration. Version 1.0, 23 November 2011
GLP:	No (modelling calculation)

EXECUTIVE SUMMARY

The set of soil degradation data originating from the relevant aerobic soil degradation studies with the insecticide Thiacloprid and its degradation products in soil, i.e. YRC 2894-amide (M02), YRC 2894-des-cyano (M29), YRC 2894-sulfonic acid (M30), YRC 2894-sulfonic acid amide (M34), and YRC 2894-thiadiazine (M46), was evaluated in order to derive kinetic parameters to be used for predictions of environmental concentration of the substances. The evaluation was performed following the guideline given by the report of the FOCUS group on kinetic evaluation. For modelling purposes the resulting degradation half-lives were normalised to reference conditions, 20 °C and 100% field capacity using a Q_{10} value of 2.58 for the temperature normalisation and a Walker coefficient of 0.7 for the moisture normalisation.

In this chapter, the evaluations for parent compound Thiacloprid are summarized, only. For those of the degradation products in soil see next chapter CA 7.1.2.1.2.

Key parameters of soils and study conditions are summarised in following Table 7.1.2.1.1- 2.

Table 7.1.2.1.1- 2: Properties of the soils used in laboratory studies with Thiacloprid (YRC 2894)

Reference	Soil	Texture class (USDA)	Sand content [%]	Clay content [%]	Organic carbon [%]	pH ($CaCl_2$)	CEC [meq/100 g]
[redacted], R., [redacted], W.; 1998	BBA 2.1	sand	89.4	0.1	0.57	5.3	)[a]
	BBA 2.2	loamy sand	80.5	7.2	2.48	6.3	)[a]
	[redacted]im Tal	loamy silt	3.6	15.6	2.4	5.8	)[a]
	[redacted]	sandy loam	65.7	7.9	1.12	6.7	)[a]
[redacted], E.; 2003	[redacted]AXXa	sandy loam	72.4	5.0	1.02	6.3	8.0
[redacted], N.; 2011	[redacted]4a	silt loam	42.0	7.0	2.4	6.3	12.8

)[a] value not available

The compilation of non-normalised modelling DT_{50} values (at study conditions) for Thiacloprid (YRC 2894) derived from the different available data sets is shown by Table 7.1.2.1.1- 3.

Table 7.1.2.1.1- 3: Compilation of non-normalised modelling DT_{50} values (at study conditions) for Thiacloprid (YRC 2894) derived from the different data sets

Study Soil	Model used for parent)[a]	Thiacloprid DT_{50} [days]
[redacted], R., [redacted], W.; 1998		
BBA 2.1	FOMC	2.96
BBA 2.2	FOMC	2.16
[redacted] im Tal	FOMC	0.70
[redacted]	FOMC	6.78
[redacted], E.; 2003		
[redacted] AXXa	FOMC	1.99
[redacted], N.; 2011		
[redacted] 4a	SFO	0.35
Median		**2.08**
Geometric mean		**1.66**

)[a] if necessary, parent DT_{50SFO} was back-calculated from DT_{90FOMC} / 3.32 or from slow phase (k_2) of HS

The compilation of normalised modelling DT_{50} values (at study conditions) for Thiacloprid (YRC 2894) derived from the different available data sets is shown by Table 7.1.2.1.1- 4.

Table 7.1.2.1.1- 4: Compilation of normalised modelling DT_{50} values for Thiacloprid (YRC 2894) derived from the different data sets

Study Soil	Model used for parent)[a]	Thiacloprid DT_{50} [days]
[redacted], R., [redacted] W.; 1998		
BBA 2.1	FOMC	2.96
BBA 2.2	FOMC	2.16
[redacted] im Tal	FOMC	0.66
[redacted]	FOMC	5.39
[redacted], E.; 2003		
[redacted] AXXa	FOMC	1.83
[redacted], N.; 2011		
[redacted] 4a	SFO	0.35
Median		**2.00**
Geometric mean		**1.56**

)[a] if necessary, parent DT_{50SFO} was back-calculated from DT_{90FOMC} / 3.32 or from slow phase (k_2) of HS

The geometric mean non-normalized half-life is 1.7 days; the geometric mean normalized half-life is 1.6 days for Thiacloprid in soil.

CA 7.1.2.1.2 Aerobic degradation of metabolites, breakdown and reaction products

The rate of degradation of Thiacloprid degradation products in soil under aerobic conditions in the laboratory was evaluated during the Annex I inclusion (compare EU Monograph, Annex B8), and was accepted by the European Commission (SANCO/4347/2000 – Final; 13 May 2004). The following studies/reports included in the Baseline Dossier were regarded as relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted], E.	1998	M-001112-01-3
[redacted], H.	1998	M-001290-01-1

[redacted], T.	2002	M-042056-01-1

Summary of study performed by [redacted], E.; 1998

An aerobic soil degradation study for the sulfonic acid metabolite M30 was conducted with three soils according to BBA (Part IV, 4-1) and SETAC guidelines. [^{14}C]-M30 was added in methanol and water at a concentration of 0.194 mg a.s./kg dry soil. All incubation vessels (300 mL) were closed with trap attachments for CO_2 and organic volatiles (soda lime and glass wool, respectively) and aerobically incubated at 20 ± 1°C in the dark for a maximum of 101 days with soil maintained at 45% WHC. After 0, 2 hours, 3, 7, 14, 30, 56, 77 and 101 days of incubation, radioactivity from replicate soil samples was extracted with water and then water/methanol/1N HCl (800 + 200 + 2 parts by volume) before quantification by LSC and identification by TLC against authentic samples, MS and NMR.

The DT_{50} values were reached in all soils within the test period of 101 days, even the DT_{90}-values in the sandy loam and loamy sand soils were reached during the incubation period. The test substance was metabolized to $^{14}CO_2$, and two intermediates were identified. $^{14}CO_2$ accounted for 49% (sandy loam), 19% (sand) and 86% (loamy sand) of the applied radioactivity after 101 days. Thus carbon dioxide was the main degradation product in terms of quantity. Besides $^{14}CO_2$ two further metabolites were observed (M32 and M34), which were identified by spectroscopy. M32 was the main metabolite in the sandy loam soil; it made up a maximum of 18.1% of the applied radioactivity. In the other two soils M34 was the dominating degradate accounting for 22.7% at maximum.

These results of study were kinetically evaluated study by the report below.

Summary of kinetic data evaluation performed by [redacted], H.; 1998

The degradation behaviour of the amide metabolite (M02) was quantified using data from aerobic laboratory degradation studies with the parent compound ([redacted], R., [redacted], W.; 1998) for four soils. First-order kinetics was applied to the two individual steps of the degradation pathway (transformation of Thiacloprid to M02, degradation of M02) with the simplifying assumption that degradation of Thiacloprid followed first order kinetics. DT_{50} and DT_{90} values were obtained by non-linear fitting using the software ACSL Optimize. A summary of the results listed in Table B.8.3 in the Monograph, also reported in the list of endpoints, SANCO/4347/2000 – Final; 13 May 2004, is shown by Table 7.1.2.1.1- 1.

Summary of kinetics evaluation performed by [redacted], T.; 2002

In the before-mentioned aerobic soil degradation study on YRC 2894-sulfonic acid (M30) using three soils the YRC 2894-sulfonic acid amid (M34) was generated in significant amounts. Therefore, both compounds could be kinetically evaluated. A summary of the results for M30 was listed in Table B.8.5 in the Monograph, also reported in the list of endpoints, SANCO/4347/2000 – Final; 13 May 2004, is shown by Table 7.1.2.1.2- 1 below.

The summary of DT_{50} evaluation on M34 was just contained in the list of endpoints, SANCO/4347/2000 – Final; 13 May 2004 and are summarised in the table below:

Table 7.1.2.1.2- 1: Degradation kinetics of M30 and M34 in soils under aerobic conditions (data from study by [redacted], E.; 1998

Compound	DT_{50} Range at 20°C (persistence values)	DT_{50} (geomean 20 °C, normalised to FC)
YRC 2894-sulfonic acid (M30)	16 - 79 days	23.4 days (n = 3)
YRC 2894-sulfonic acid amide (M34)	8 - 52 days	15.1 days (n = 3)

The following additional aerobic soil degradation study on YRC 2894-sulfonic acid (M30) using [redacted] AXXa soil was performed to be able to evaluate the findings from lysimeter studies.

Report:	**KCA 7.1.2.1.2 /05; [redacted], J.; 2003**
Title:	Aerobic Degradation of YRC 2894-Sulfonic Acid (WAK6999) in Soil [redacted] AXXa.
Report No:	MR-526/02
Document No:	M-084208-01-1
Guidelines:	OECD Guideline for Testing of Chemicals, No. 307, Aerobic and Anaerobic Transformation in Soil, 2002 SETAC-Europe: Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides Commission Directive 95/36/EC amending Council Directive 91/414/EEC (Annexes II and III, Fate and Behaviour in the Environment), 1995
GLP:	Yes

EXECUTIVE SUMMARY

The degradation test was conducted in on one soil ([redacted] AXXa, the same soil which was used in the lysimeter study (see Section CA 7.1.4.2) with [methylene-^{14}C]-WAK 6999 at an average concentration of 15.6 µg as/100 g soil (dry weight). This was equivalent to the highest field application rate of about 400 g as/ha and assuming 30% conversion factor of Thiacloprid metabolized to WAK 6999. The calculation was based on a soil depth of 0-5 cm, and a soil density of 1.5 g/cm³. The soil samples were treated directly as it would happen during a spray application. All soils were adjusted to 40% of their maximum water holding capacity. The radioactivity determined in the appropriate amount of the application solution was defined as the totally applied amount at time zero. These values were the basis for further calculations. The flasks were incubated in the dark under aerobic conditions at 20 ± 0.5 °C for 120 days. The evaporated amount of water was determined and replenished. Samples were taken for analysis at days 0, 3, 7, 14, 31, 62, 90 and 120 post-treatment. The soil characteristics are given by Table 7.1.2.1.2- 2.

Table 7.1.2.1.2- 2: Characteristics of soil used

Soil Designation	Soil Type[a)] and Origin	Sand (%)	Silt (%)	Clay (%)	Org. C (%)	pH ($CaCl_2$)
[redacted] AXXa	Sandy loam, GER	72.4	22.6	5.0	1.02	6.3

Note a) = according to USDA scheme

Soil samples were extracted 2 times by shaking with 50 mL water, and additionally the solid residues were extracted 2 times with 50 mL of methanol/water/1N HCl (800/200/2 v:v:v). All extracts steps were carried out for about 30 minutes and at room temperature. The radioactivity was determined in all samples and paper filters used, and the extracts analysed by radio-TLC-methods. Metabolites were identified by co-chromatography with authentic reference compounds. Volatile radioactivity was trapped using soda lime and released for measurement by adding HCl for $^{14}CO_2$ (identified by Grignard reaction) or extracting the foam plugs with ethyl acetate for radio assaying by LSC. The degradation curve and regression analysis was calculated with the evaluation program ®ModelManager (Environmental Kinetics), Version 1.1, developed and published by Cherwell Scientific Ltd, Oxford, UK. The model was run in the mode "use standard data" as well as "use existing parameter estimates".

In soil [redacted] AXXa YRC 2894-sulfonic acid (M30) was degraded with a simple first order DT_{50} of 25.9 days (DT_{90} of 86.0 days) when incubated under aerobic conditions at 20°C. The statistical evaluation of the degradation is given in Table 7.1.2.1.2- 3.

Table 7.1.2.1.2- 3: Statistical evaluation of degradation of M30 in [redacted] AXXa soil

Compound	K (1/days)	Statistical evaluation				
		DT_{50} as (d)	DT_{75} as (d)	DT_{90} as (d)	Order	R^2
YRC 2894-sulfonic acid (M30)	0.0268	25.9	51.8	86.0	1st	0.992

In the test the amount of $^{14}CO_2$ increased over the entire study period. At the end of the study about 59% of AR was measured as $^{14}CO_2$. Thus carbon dioxide was the main degradation product in terms of quantity. Along with the overall metabolism of test substance NER was formed (maximum of 35% of AR, then decreasing to 33% at study termination). Besides CO_2 two further metabolites were observed and identified as YRC 2894-sulfonic acid amide (M34) and YRC 2894-diamide (M32), max. 5.3 % of AR and 5.8 %, respectively. No further degradation product >10% of AR was found in this study. The results concerning the recovery of radioactivity and the distribution of the test compound and the degradation products are summarised in Table 7.1.2.1.2- 4c.

Table 7.1.2.1.2- 4: Mass balance and distribution of radioactivity after incubation of [^{14}C]-WAK 6999 in aerobic soil at 20°C (expressed as % of AR)

Soil	DAT [a]	M30	M32	M34	$^{14}CO_2$	Volatile compounds	Extracted	NER	Recovery
[redacted] AXXa	0	90.7	n.d.	n.d.	n.p.		91.1	9.4	100.4
	3	82.4	n.d.	2.7	1.0	< 0.1	85.5	14.3	100.8
	7	73.8	n.d.	5.3	2.4	< 0.1	79.2	18.9	100.5
	14	64.9	n.d.	4.7	6.5	< 0.1	69.6	25.3	101.4
	31	44.7	1.5	3.6	19.8	< 0.1	49.7	28.8	98.3
	62	14.9	5.8	1.7	39.3	< 0.1	24.1	34.5	97.9
	90	3.0	5.3	0.7	52.7	< 0.1	9.3	34.9	96.9
	120	2.2	3.8	0.5	58.7	< 0.1	6.6	32.9	98.3

[a] days after treatment; n.p. = not performed, n.d. = not detected

The current laboratory study demonstrated that M30 is degraded in microbial active soil. Residues of M30 were steadily eliminated from the soil by mineralization to the major degradation product CO_2. The resulting DT_{50} for M30 was well in the range of the earlier study (compare Table 7.1.2.1.2- 1).

The following aerobic soil degradation study on YRC 2894-des-cyano (M29) was needed to evaluate its behaviour in soil and to perform the groundwater risk assessment.

Report: **KCA 7.1.2.1.1/06; [redacted], M.; 2013**
Title: Thiacloprid-des-cyano: Aerobic degradation in four European soils.
Report No: S12-00015
Document No: M-447080-01-1
Guidelines: OECD Guideline for Testing of Chemicals, No. 307, Aerobic and Anaerobic Transformation in Soil, 2002
US EPA Fate, Transport and Transformation Test Guidelines, OPPTS 835.4100 and OPPTS 835.4200, Aerobic and Anaerobic Soil Metabolism, 2008
GLP: Yes

EXECUTIVE SUMMARY

The degradation of the YRC 2894-des-cyano (M29) was investigated in four different soils of European origin ([redacted] AXXa, [redacted] II, [redacted] 4a and

[redacted]Hof under aerobic conditions at 20°C in the dark. The study was performed with non-labelled YRC 2894-des-cyano, a soil degradation product of Thiacloprid, over a period of 120 days (sampling intervals 0, 1, 2, 7, 14, 29, 59 and 120 days). The soil characteristics are given by Table 7.1.2.1.2- 5.

Table 7.1.2.1.2- 5: Characteristics of soils used

Soil Designation	Soil Type[a)] and Origin	Sand (%)	Silt (%)	Clay (%)	Org. C (%)	pH (CaCl2)
[redacted] AXXa	Loamy sand, GER	82	9	9	1.6	6.4
[redacted] II	Clay loam, GER	38	33	29	5.0	7.2
[redacted] 4a	Silt loam, GER	22	59	19	1.7	6.3
[redacted]	Sandy loam, GER	52	29	19	2.9	5.4

a) = according to USDA scheme

For the test vessels 100 g of soil (dry weight basis) were used. The average soil moisture content was 55 ± 5% of the maximum water holding capacity (MWHC) over the entire period of the study. The biological activity was checked directly after treatment, 59 days after application and at the end of the incubation period.

The actual application rate was 9.62 µg YRC 2894-des-cyano per test vessel, which was equivalent to 0.0962 mg YRC 2894-des-cyano/kg soil (dry weight). Duplicate test vessels were taken for analysis per sampling interval. The entire sample was processed by extraction three times at ambient temperature and once under microwave conditions. The combined extracts were analysed for YRC 2894-des-cyano residues by reversed phase (LC_{18}) high performance liquid chromatography coupled with mass spectrometry (HPLC-MS/MS) in multiple reaction monitoring (MRM) mode using YRC 2894-des-cyano standards in pure solvent for calibration.

The extraction efficiency during the study was demonstrated by concurrent recovery samples. This was demonstrated by fortification of untreated samples of [redacted] soil with YRC 2894-des-cyano at LOQ level (corresponding to 5% of the application rate) and at 22-fold LOQ level (corresponding to 110% of the application rate), respectively. The mean recoveries of all concurrent recovery samples were between 85.3 - 102.2 % of the applied amount.

Residues of YRC 2894-des-cyano declined to 78.7% in [redacted] soil, to 34.1% in [redacted] soil, to 61.6% in [redacted] soil and to 75.9% in [redacted] soil during 120 days of incubation. The total applied amount determined directly after application was 101.4% in [redacted] soil, 99.5 % in [redacted] soil, 92.0% in [redacted] soil and 99.9% in [redacted] soil.

The dissipation times (DT_{50} and DT_{90}) of the test item were calculated for each soil. While the fit resulting from first order multi compartment (FOMC) calculation could be derived as the best fit for [redacted] soil. The fits were best from applying double first order in parallel (DFOP) kinetic models for the other three soils. The dissipation of YRC 2894-des-cyano (M29) from aerobic soil under laboratory conditions resulted in half-lives of 54.7 to 813 days for the respective soils (see Table 7.1.2.1.2- 6 below).

Table 7.1.2.1.2- 6: Statistical evaluation of degradation of YRC 2894-des-cyano (M29) in four soils

Soil (Soil type)	Best Fit Kinetic Model	DT_{50} [d]	DT_{90} [d]	ε [%]	Visual Assessment *
Soil AX (loamy sand)	DFOP	456.6	n/a	2.2	+
Soil DD (clay loam)	FMOC	54.7	n/a	10.8	+
Soil HaH (silt loam)	DFOP	247.4	990.8	2.0	+
Soil HH (sandy loam)	DFOP	813.0	n/a	1.2	+

* Visual Assessment: + = good, o = moderate, - = poor; n/a: not applicable

The following aerobic soil degradation study on YRC 2894-thiadiazine (M46) was needed to evaluate its behaviour in soil, with respect to groundwater exposure assessment.

Report:	**KCA 7.1.2.1.2 /07; [redacted], A.; 2013**
Title:	Thiacloprid-thiadiazine: Aerobic degradation in four soils.
Report No:	S12-00014
Document No:	M-448295-01-1
Guidelines:	OECD Guideline for Testing of Chemicals, No. 307, Aerobic and Anaerobic Transformation in Soil, 2002 US EPA Fate, Transport and Transformation Test Guidelines, OPPTS 835.4100 and OPPTS 835.4200, Aerobic and Anaerobic Soil Metabolism, 2008
GLP:	Yes

EXECUTIVE SUMMARY

The degradation of YRC 2894-thiadiazine (M46) was investigated in four different soils ([redacted] AXXa), [redacted] II, [redacted] 4a, and [redacted] under aerobic conditions at 20°C in the dark. The study was performed with non-labelled YRC 2894-thiadiazine, a soil degradation product of Thiacloprid, over a period of 96 days. The soil characteristics are given by Table 7.1.2.1.2- 7.

Table 7.1.2.1.2- 7: Characteristics of soils used

Soil Designation	Soil Type[a] and Origin	Sand (%)	Silt (%)	Clay (%)	Org. C (%)	pH ($CaCl_2$)
[redacted] AXXa	Loamy sand, GER	78	14	8	1.7	6.4
[redacted] II	Loam, GER	36	38	26	5.1	7.1
[redacted] 4a	Silt loam, GER	20	62	18	1.9	6.4
[redacted]	Silt loam, GER	34	52	14	2.9	5.5

Note [a] = according to USDA scheme

For the test systems 100 g soil (dry weight basis) were used. The average soil moisture content was 55 ± 5% of the maximum water holding capacity (MWHC) over the entire period of the study. The application rate of YRC 2894-thiadiazine (M46) was 3.6 µg per vessel and 100 g soil (dry weight), which was equivalent to 0.036 mg YRC 2894-thiadiazine/kg soil (dry weight). Duplicate test systems were worked-up per sampling interval. The entire soil per flask was extracted three times at ambient temperature followed by one time under hot conditions by microwave extraction. The combined extracts were analysed for YRC 2894-thiadiazine residues by reversed phase high performance liquid chromatography/mass spectrometry (HPLC-MS/MS).
Method development and validation was performed successfully within this study. In addition, the extraction efficiency during the study was demonstrated by concurrent recovery samples. Therefore untreated [redacted] soil samples were fortified at each sampling interval with YRC 2894-thiadiazine at the LOQ level (corresponding to 5% of the application rate) and at 22-fold LOQ level (corresponding to 110% of the application rate). The mean recoveries of all concurrent recovery samples were 92.5% of the applied amount at the LOQ level and 96.7% at the 22-fold LOQ level.

YRC 2894-thiadiazine was degraded within 96 days to 10.8% and 10.5% of the applied amount in [redacted] and [redacted] soils. In the other two soils YRC 2894-thiadiazine decreased to 6.3% ([redacted]) and 9.2% ([redacted]) of the applied amount 71 days after treatment, already.

The dissipation times (DT_{50} and DT_{90}) of the test item were calculated for each soil. The best fit kinetic models are shown in the following table (see Table 7.1.2.1.2- 8 below). YRC 2894-thiadiazine (M46) dissipated from soils under aerobic laboratory conditions, with typical half-lives between 9.5 and 28.0 days. Therefore, the compound is unlikely to accumulate in a viable soil environment.

Table 7.1.2.1.2- 8: Statistical evaluation of degradation of YRC 2894-thiadiazine (M46) in four soils

Soil (soil type)	Best Fit Kinetic Model	DT_{50} [d]	DT_{90} [d]	ε [%]	Visual Assessment*
[redacted] AXXa (loamy sand)	DFOP	25.1	95.3	2.2	+
[redacted] II (clay loam)	SFO	9.5	31.7	2.5	+
[redacted] (silt loam)	DFOP	28.0	101.8	2.3	+
[redacted] (sandy loam)	SFO	21.0	69.6	1.6	+

* Visual Assessment: + = good, o = moderate, - = poor.

The set of soil degradation data originating from the old and new studies was evaluated by [redacted], L.; [redacted], S.; 2014, in order to derive kinetic parameters to be used for predictions of environmental concentration of the substances. In the following the respective evaluation of the degradation products is summarized. The evaluation of parent compound was summarized in Section CA 7.1.2.1.1.

Report:	**KCA 7.1.2.1.2 /08: [redacted], L.; [redacted], S.; 2014**
Title:	Kinetic evaluation of laboratory aerobic soil degradation of Thiacloprid (YRC 2894) and its metabolites according to FOCUS kinetics Thiacloprid (YRC 2894) **YRC 2894 amide (KKO 2254)** **YRC 2894 thiazolidinimine (KTU 3072)** **YRC 2894 sulfonic acid (WAK 6999)** **YRC 2894 sulfonic acid amide (KTS 9815)** **YRC 2894 thiadiazine (BCS-CJ16425, MZ5)**
Report No:	EnSa-13-0290
Document No:	M-454544-02-1
Guidelines:	FOCUS (2011): Generic guidance for estimating persistence and degradation kinetics from environmental fate studies on pesticides in EU registration. Version 1.0, 23 November 2011
GLP:	No (modelling calculation)

EXECUTIVE SUMMARY

The soil degradation of the insecticide Thiacloprid (YRC 2894) and its metabolites YRC 2894-amide (M02), YRC 2894-des-cyano (M29), YRC 2894-sulfonic acid (M30), YRC 2894-sulfonic acid amide (M34), and YRC 2894-thiadiazine (M46) has been investigated in several laboratory degradation studies after application of either Thiacloprid [redacted], R., [redacted], W., 1998; [redacted], E.; 2003; [redacted], N.; 2011), YRC 2894-sulfonic acid (M30; [redacted], E., 1998; [redacted], J.; 2003), YRC 2894-des-cyano (M29; [redacted], M.; 2013) or YRC 2894-thiadiazine (M46; [redacted], A.; 2013) to different soils. The set of soil degradation data originating from these studies was evaluated in order to derive kinetic parameters to be used for prediction of environmental concentration of the substances.

The evaluation was performed following the guideline given by the report of the FOCUS group on kinetic evaluation. For modelling purposes the resulting degradation half-lives were normalised to reference conditions 20 °C and 100% field capacity using a Q_{10} value of 2.58 for the temperature normalisation and a Walker coefficient of 0.7 for the moisture normalisation.

The geometric mean non-normalised half-lives are 49.5 days for M02, 152.4 days for M29, 31.8 days for M30, 30.2 days for M34, and 19.8 days for M46, which are presented in Table 7.1.2.1.2- 9.

The formation fractions resulting from the evaluation for the relevant Thiacloprid metabolites M02, M29, M30, M34, and M46 are presented in Table 7.1.2.1.2- 10.

The geometric mean normalised half-lives are 46.6 days for M02, 140.7 days for M29, 29.3 days for M30, 28.4 days for M34, and 19.8 days for M46 (see Table 7.1.2.1.2- 11).

Table 7.1.2.1.2- 9: Non-normalised DT_{50} values for the relevant Thiacloprid metabolites derived from the different data sets

Study / Soil	Model used for test item)c	M02	M29	M30	M34	M46
[redacted], R., [redacted], W.; 1998						
BBA 2.1	FOMC	41.42	-)a	36.40	---	---
BBA 2.2	FOMC	85.70	34.55	-)a	---	---
[redacted] im Tal	FOMC	36.25	)a	-)a	---	---
[redacted]	FOMC	152.72	110.44	-)a	---	---
[redacted], E.; 2003, M-106754-01-1						
[redacted] AXXa	FOMC	-)a	-)b	120.33	---	---
[redacted], N.; 2011						
[redacted] 4a	SFO	15.11	-a	9.99	---	---
[redacted], E.; 1998 (M30 applied as test item)						
BBA 2.1	SFO	---	---	73.83	54.93	---
BBA 2.2	SFO	---	---	19.71	16.57	---
[redacted]	SFO	---	---	22.14	-)a	---
[redacted], J.; 2003 (M30 applied as test item)						
[redacted] AXXa	SFO	---	---	23.39	---	---
[redacted], M.; 2013 (M29 applied as test item)						
[redacted] II	SFO	---	83.37	---	---	---
[redacted] 4a	HS	---	309.16	---	---	---
[redacted] Hof	HS	---	835.32	---	---	---
[redacted] AXXa	-)b	---	-)b	---	---	---
[redacted], A.; 2013 (M46 applied as test item)						
[redacted] II	SFO	---	---	---	---	9.54
[redacted] 4a	SFO	---	---	---	---	29.25
[redacted] Hof	SFO	---	---	---	---	20.96
[redacted] AXXa	SFO	---	---	---	---	26.19
Median		41.42	110.44	23.39	35.75	23.58
Geometric mean		49.49	152.39	31.82	30.17	19.78

)a No reliable half-life obtained due to poor visual fit; for details see chapters 7.1 to 7.18 of report.
)b No reliable half-life obtained due to failed t-test for degradation rate k_x.
)c if necessary, parent DT_{50SFO} was back-calculated from DT_{90FOMC}/3.32 or from slow phase (k_2) of HS.
--- = substance not observed in respective study/soil.

Table 7.1.2.1.2- 10: Compilation of formation fractions derived from the different data sets

Study / Soil	YRC 2894 → M02	M02 → M29	M02 → M30	M30 → M34
[redacted], R., [redacted], W.;1998				
Soil BBA 2.1	0.74	(0.18)[b]	0.82	---
Soil BBA 2.2	0.82	0.22	(0.78)[b]	---
Soil [redacted] im Tal	0.77	(0.14)[c]	(0.29)[c]	---
Soil [redacted]	0.79	0.23	(0.77)[c]	---
[redacted], E.; 2003				
Soil [redacted] AXXa	0.72	(0.11)[c]	(0.33)[c]	---
[redacted], N.; 2011				
Soil [redacted] 4a	0.89	(0.30)[b]	0.55	---
[redacted], E.; 1998				
Soil BBA 2.1	---	---	---	0.70
Soil BBA 2.2	---	---	---	0.42
Soil [redacted]	---	---	---	(0.34)[b]
Arithmetic mean)[a]	**0.79**	**0.22)[a]**	**0.69)[a]**	**0.56)[a]**

)[a] values in brackets were not considered reliable and were excluded from averaging.
)[b] modelled formation phase did not reach peak concentration of emerging substance.
)[c] overall poor visual fit of either precursor or emerging substance.
--- = pathway not observed in respective study/soil.

Table 7.1.2.1.2- 11: Normalised DT_{50} values for the relevant Thiacloprid metabolites derived from the different data sets

Study / Soil	Model used for test item	M02	M29	M30	M34	M46
[redacted], R., [redacted], W.; 1998						
BBA 2.1	FOMC	41.30	-)[a]	36.29	---	---
BBA 2.2	FOMC	85.70	34.55	-)[a]	---	---
[redacted] im Tal	FOMC	33.78	-)[a]	-)[a]	---	---
[redacted]	FOMC	121.47	87.84	-)[a]	---	---
[redacted], E.; 2003						
[redacted] AXXa	FOMC	-)[a]	-)[a]	110.78	---	---
[redacted], N.; 2011						
[redacted] 4a	SFO	15.11	-)[a]	9.99	---	---
[redacted], E.; 1998 (M30 applied as test item)						
BBA 2.1	SFO	---	---	65.55	48.77	---
BBA 2.2	SFO	---	---	19.71	16.57	---
[redacted]	SFO	---	---	19.14	-)[a]	---
[redacted], J.; 2003 (M30 applied as test item)						
[redacted] AXXa	SFO	---	---	18.84	---	---
[redacted], M.; 2013 (M29 applied as test item)						
[redacted] II	SFO	---	78.76	---	---	---
[redacted] 4a	HS	---	292.07	---	---	---
[redacted]	HS	---	789.33	---	---	---
[redacted] AXXa	-)[b]	---	-)[b]	---	---	---
[redacted], A.; 2013 (M46 applied as test item)						
[redacted] II	SFO	---	---	---	---	9.54
[redacted] 4a	SFO	---	---	---	---	29.25
[redacted]	SFO	---	---	---	---	20.96
[redacted] AXXa	SFO	---	---	---	---	26.19
Median		**41.30**	**87.84**	**19.71**	**32.67**	**23.58**
Geometric mean		**46.59**	**140.68**	**29.34**	**28.43**	**19.78**

)[a] No reliable half-life obtained due to poor visual fit; for details see chapters 7.1 to 7.18 of report.
)[b] No reliable half-life obtained due to failed t-test for degradation rate k_x.
--- = substance not observed in respective study/soil.

CA 7.1.2.1.3 Anaerobic degradation of the active substance

The rate of degradation of Thiacloprid in soil under anaerobic conditions in the laboratory was not yet evaluated during the Annex I inclusion (see EU Monograph, Annex B8; European Commission (SANCO/4347/2000 – Final; 13 May 2004).

Since in general an exposure under anaerobic conditions cannot be excluded, a e new study performed with [thiazolidine-2-^{14}C]-Thiacloprid is submitted within this Supplemental Dossier for the Thiacloprid renewal of approval.

Report:	**KCA 7.1.2.1.3 /01; [redacted], H.-P.; [redacted], T.; 2014**
Title:	[Thiazolidine-2-^{14}C]-Thiacloprid: Anaerobic Metabolism / Degradation in Soil
Report No:	EnSa-13-0490
Document No:	M-484954-01-1
Guidelines:	OECD Guideline for Testing of Chemicals, No. 307, Aerobic and Anaerobic Transformation in Soil, 2002
GLP:	Yes

EXECUTIVE SUMMARY

For detailed summary of study see Section CA 7.1.1.2 earlier.

The experimental data of the anaerobic degradation of Thiacloprid could be well described by a first order multi-compartment (FOMC) kinetic model. The anaerobic half-life of Thiacloprid after flooding and shift to anaerobic conditions was 1 day. The table below summarizes the best fit results of the DT_{50} and DT_{90} calculations.

Table 7.1.2.1.3- 1: Best fit DT_{50} evaluation for Thiacloprid degradation in soil after flooding and set-up of anaerobic conditions at 20 °C in the dark

Soil (Soil Type)	Best Fit Kinetic Model [1]	DT_{50} [d]	DT_{90} [d]	ε [%]	Visual Assessment [2]
[redacted] 4a (Silt loam)	FOMC	0.9	15.0	2.0	+

[1] FOMC: First order multi compartment
[2] Visual assessment: + good

CA 7.1.2.1.4 Anaerobic degradation of metabolites, breakdown and reaction products

No studies are submitted and required.

From the study performed with Thiacloprid by [redacted], H.-P.; [redacted], T.; 2014 , it is indicated that after flooding and set-up of anaerobic conditions the degradation of YRC 2894-amide (M02), the major primary metabolite of Thiacloprid, is slowed down. From DAT-8 towards study termination the amount of M02 decreased from 85.1 to 64.4% of AR (mean values, see Table 7.1.1.2- 4). The results of the study showed that no new metabolite specific for anaerobic conditions is to be expected in soil.

CA 7.1.2.2 Field studies

The behaviour of Thiacloprid in soil under field conditions was evaluated during the Annex I inclusion (compare EU Monograph, Annex B8, SANCO/4347/2000 – Final; 13 May 2004). Two field soil dissipation studies were performed and evaluated (see next Section). No additional experimental studies are submitted within this Supplemental Dossier for the Thiacloprid renewal of approval.

CA 7.1.2.2.1 Soil dissipation studies

The dissipation of Thiacloprid in soil under field conditions was evaluated during the Annex I inclusion (compare EU Monograph, Annex B8), and was accepted by the European Commission (SANCO/4347/2000 – Final; 13 May 2004). The following studies included in the Baseline Dossier were regarded as relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted], H.	1998	M-001025-01-2
[redacted], H.	1997	M-001007-01-1

Further, two storage stability investigations on soil samples were included. They confirmed a sufficient storage stability of the residues in soil.

Author(s)	Year	Document No.
[redacted], H.	1998	M-002218-01-1
[redacted], H.	1998	M-002220-01-1

EU conclusion of study performed by [redacted], H.; 1998:

Two field dissipation trials were conducted in southern Europe according to BBA guidelines (Part IV, 4-1). Non-radiolabelled YRC 2894 (480 SC) was applied to bare soil at an application rate of 0.6 kg/ha (0.288 kg as/ha) in spring 1995. A single application was conducted in two different typical agricultural regions of France and Spain. The application rate was 0.288 kg as/ha.

The following kinetics results were stated in the list of endpoints for Southern Europe:

DT_{50f} of Thiacloprid: 10 – 16 days (n = 2, r² = 0.90 – 0.99)
DT_{50f} of M02: 68 – 107 days (n = 2)

DT_{90f} of Thiacloprid: 35 – 53 days (n = 2)
DT_{90f} of M02: 226 – 357 days (n = 2)

EU conclusion of study performed by [redacted], H.; 1997:

Six field dissipation trials were conducted in northern Europe according to BBA guidelines (Part IV, 4-1). Non-radiolabelled YRC 2894 was sprayed in spring (11 April to 3 May 1995) or summer (French site only, 24 July 1995) on bare soil at six sites selected as typical of agricultural regions of France, Germany and the UK. Following the single application (equivalent rate of 288 g a.s./ha as 480 SC formulation) with a water rate of 200-300 L/ha, three sites were cropped with grass whilst the three others were kept bare by manual or mechanical weed control.

The following kinetics results were stated in the list of endpoints for Northern Europe:

DT_{50f} of Thiacloprid: 9 – 27 days (n = 6, r² = 0.82 – 0.96)
DT_{50f} of M02: 46 – 314 days (n = 6)

DT_{90f} of Thiacloprid: 31 – 91 days (n = 6)
DT_{90f} of M02: 153 – 1047 days (n = 4)

No additional studies are submitted within this Supplemental Dossier for the Thiacloprid renewal of approval. However, due to changes in requirements updated kinetic evaluations of the degradation behaviour of Thiacloprid in soil under field conditions have been performed according to FOCUS kinetics (2006) to derive kinetic parameters suitable for modelling purpose and environmental risk assessment. This report is summarized as follows.

Report:	**KCA 7.1.2.2.1 /07; [redacted], L.; [redacted], S.; 2013**
Title:	Kinetic evaluation of field dissipation studies with Thiacloprid (YRC 2894) and its metabolites YRC 2894-amide (KKO 2254, M02) and YRC 2894-sulfonic acid (WAK 6999, M30) under European conditions
Report No:	EnSa-13-0429
Document No:	M-468397-01-1
Guidelines:	FOCUS (2011): Generic guidance for estimating persistence and degradation kinetics from environmental fate studies on pesticides in EU registration. Version 1.0, 23 November 2011
GLP:	No (modelling calculation)

EXECUTIVE SUMMARY

The experimental data from eight field dissipation trials ([redacted], H.; 1998, [redacted], H.; 1997) were evaluated in order to determine kinetic parameters for Thiacloprid (YRC 2894) and its metabolites YRC 2894-amide (M02) and YRC 2894-sulfonic acid (M30) that are suitable for comparison against trigger values and as inputs for environmental fate models.

The evaluations were performed following guidance given by the FOCUS report and the EFSA opinion on kinetic evaluation. The evaluations were based on both non-normalized data at field conditions and data normalized to standard reference conditions for soil temperature (20°C) and soil moisture (100% field capacity, pF2) using the time-step method. For this, daily temperature and soil moisture values were determined for each site by simulations with PEARL 4.4.4, using site-specific soil properties and weather data. For the temperature normalization a Q_{10}-value of 2.58 was used.

Based on a visual and statistical quality check, the kinetic parameters derived from all but one field study were deemed to be reliable persistence triggers and appropriate inputs for environmental fate models.

Non-normalized DT_{50} values (see Table 7.1.2.2.1- 1) ranged from 5.3 days to 13.7 days for Thiacloprid (geo_{mean} = 8.9 days), from 24.9 days to 321.1 days for M02 (geo_{mean} = 79.0 days), and from 12.8 days to 97.6 days for M30 (geo_{mean} = 27.9 days). The formation fractions of M02 and M30 are provided by Table 7.1.2.2.1- 2.

Normalized DT_{50} values (see Table 7.1.2.2.1- 1) ranged from 2.9 days to 9.5 days for Thiacloprid (geo_{mean} = 6.2 days), from 24.1 days to 133.4 days for M02 (geo_{mean} = 50.5 days), and from 7.1 days to 76.7 days for M30 (geo_{mean} = 15.6 days).

Modelling endpoints derived from normalized field dissipation studies following EFSA Guidelines ranged from 4.1 days to 14.0 days for Thiacloprid (Table 7.1.2.2.1- 3). The geometric and arithmetic mean (n = 6) was 7.9 and 8.8 days, respectively.

In conclusion, the field dissipation DT_{50} data of parent, M02 and M30 are in good agreement with the laboratory data, and are included in the overall summary of modelling input data listed by Table 7.1- 1 and Table 7.1- 2.

Table 7.1.2.2.1- 1: First-order DT_{50} values of Thiacloprid, YRC 2894-amide (M02) and YRC 2894-sulfonic acid (M30), derived from field dissipation studies under European conditions, following FOCUS (2006, 2011).

	Thiacloprid		M02		M30	
Location	**DT_{50})[1]**	**DT_{50ref})[2]**	**DT_{50})[1]**	**DT_{50ref})[2]**	**DT_{50})[1]**	**DT_{50ref})[2]**
	(days)		(days)		(days)	
[redacted]	5.9	2.9	24.9	24.1	)[3]	14.0
[redacted]	6.4	6.6	153.1	72.4	97.6	7.1
[redacted]	13.1	5.7	27.5	38.7	25.3	16.9
[redacted]	11.6	6.8	321.1	133.4	19.1	76.7
[redacted]	10.8	9.5	165.1	53.8	)[3]	)[3]
[redacted]	5.3	7.0	)[3]	28.8	)[3]	)[3]
[redacted]	)[3]	)[3]	)[3]	76.4	)[3]	13.8
[redacted]	13.7	7.2	43.1	39.9	12.8	8.6
Geometric mean	8.9	6.2	79.0	50.5	27.9	15.6

)[1] based non-normalized residue data and best-fit kinetic model
)[2] corrected to reference conditions of 20°C and 100% field capacity (pF2); re-calculated $DT50_{SFO}$ for use in exposure models
)[3] data did not allow to determine a reliable value

Table 7.1.2.2.1- 2: Formation fractions (ff) of M02 and M30, derived from field dissipation studies under European conditions, following FOCUS (2006, 2011).

	M02)[4]		M30)[5]	
	ff)[1]	**ff_{ref})[2]**	**ff)[1]**	**ff_{ref})[2]**
[redacted]	0.4501	)[3]	1	)[3]
[redacted]	0.5323	0.5253	0.8365	0.8794
[redacted]	0.2430	0.2447	1	1
[redacted]	0.4095	0.4078	1	1
[redacted]	0.3141	0.3477	1	1
[redacted]	)[3]	0.6552	)[3]	0.5054
[redacted]	)[3]	0.5345	)[3]	1
[redacted]	0.5713	0.5005	0.2874	0.4116
Arithmetic mean	0.4201	0.4608	0.8540	0.8281

)[1] based on pathway kinetics for non-normalized residue data and best-fit kinetic model
)[2] based on pathway kinetics for corrected residue data to reference conditions of 20°C and 100% field capacity (pF2); for use in exposure models
)[3] data did not allow to determine a reliable value
)[4] formation from Thiacloprid (YRC 2894)
)[5] formation from M02.

Table 7.1.2.2.1- 3: Summary of modelling endpoints derived from normalised field residue data following EFSA Guidance (EFSA, 2010).

	Thiacloprid (YRC 2894)	
	$DegT_{50matrix}$ (days)	**Kinetic model**
[redacted]	4.1	SFO
[redacted]	n.r.)[1]	
[redacted]	4.2	SFO
[redacted]	n.r.)[1]	
[redacted]	11.4)[2]	HS
[redacted]	10.3	SFO
[redacted]	14.0)[2]	HS
[redacted]	8.6	SFO
Geometric mean	4.9	
Arithmetic mean	8.8	

)[1] no reliable $DegT50_{matrix}$ was achieved
)[2] back-calculated from k_2 of HS

CA 7.1.2.2.2 Soil accumulation studies

Field accumulation and soil residue studies have not been performed and are not required for Thiacloprid.
As stated by the evaluation during the Annex I inclusion (compare LoEP in SANCO/4347/2000 – Final; 13 May 2004) metabolite M02 could accumulate in Northern Europe. This is considered when taking the proposed input values for calculation of $PEC_{Soil\ Plateau}$ listed in Table 7.1- 1, i.e. a DT_{50} of 321.1 days for degradation of M02.

CA 7.1.3 Adsorption and desorption in soil

CA 7.1.3.1 Adsorption and desorption

The adsorption and desorption behaviour of Thiacloprid and its M02, M30 and M34 in soil was evaluated during the Annex I inclusion (compare EU Monograph, Annex B8), and was accepted by the European Commission (SANCO/4347/2000 – Final; 13 May 2004).

Since not any adsorption and desorption data were stated in the LoEP for the metabolites M29 and M46, respective new studies performed and are submitted within this Supplemental Dossier for the Thiacloprid renewal of approval.

The following Table 7.1.3.1- 1 summarizes the adsorption constants $K_{OC(ads)}$ in soils to be used for modelling purposes:

Table 7.1.3.1- 1: Overall summary of adsorption constants $K_{OC(ads)}$ in soils of Thiacloprid and degradation products relevant for leaching assessments

Compound	**Koc)[1] [mL/g]**	**Kom)[1] [mL/g]**	**FREUNDLICH[1] exponent 1/n**
Thiacloprid	615.0	357.0	0.88
YRC 2894-amide (M02)	293.0	170.0	0.83
YRC 2894- sulfonic acid (M30)	20.2	11.7	0.94
YRC 2894-thiadiazine (M46)	9.6	5.6	0.96
YRC 2894-des-cyano (M29)	371.0	215.0	0.84
YRC 2894-sulfonic acid amide (M34)	7.0	4.1	1.00

)[1]: Arithmetic mean of available data set.

On the basis of the batch adsorption studies Thiacloprid is classified as moderately to slightly mobile, and there is no evidence that it dissociates at environmentally relevant pH. YRC 2894-amide (M02) is classified as moderately mobile and YRC 2894-sulfonic acid (M30) is classified as very mobile to mobile. YRC 2894-des-cyano (M29) is classified as low mobile, YRC 2894-sulfonic acid amide (M34) and YRC 2894-thiadiazine (M46) are classified as very mobile in soil. There is no evidence that soil pH influences the adsorption of either Thiacloprid or the metabolites.

CA 7.1.3.1.1 Adsorption and desorption of the active substance

The adsorption and desorption behaviour of Thiacloprid and its residues in soil was evaluated during the Annex I inclusion (compare EU Monograph, Annex B8), and was accepted by the European Commission (SANCO/4347/2000 – Final; 13 May 2004). The following adsorption studies for thiacloprid included in the Baseline Dossier were regarded as relevant during the Annex I inclusion:

Author(s)	Year	Document No
[redacted], J.	1994 (revised 1997)	M-002086-03-2

Summary of study performed by [redacted], J; 1994

The adsorption of Thiacloprid was investigated in batch equilibrium experiments with six soils. Arithmetic mean K_{OC} (K_{OM}) value is used to quantify the sorption of Thiacloprid in PEC calculations, together with arithmetic mean FREUNDLICH exponent: K_{OC} = 615 mL/g, K_{OM} = 357 mL/g, 1/n = 0.88.

Table 7.1.3.1.1- 1: Adsorption data of Thiacloprid

Soil	Koc [mL/g]	Kom [mL/g]	FREUNDLICH exponent 1/n
[redacted]	393	228	0.86
[redacted]	753	437	0.84
[redacted]	522	303	0.94
[redacted]	572	332	0.91
[redacted]	870	505	0.87
[redacted]	582	338	0.83
Arithmetic mean	**615**	**357**	**0.88**
Geometric mean	**596**	**346**	**-**

No additional studies are submitted within this Supplemental Dossier for the Thiacloprid renewal of approval.

CA 7.1.3.1.2 Adsorption and desorption of metabolites, breakdown and reaction products

The adsorption and desorption behaviour of the Thiacloprid metabolites M02, M30 and M34 in soil was evaluated during the Annex I inclusion (compare EU Monograph, Annex B8), and was accepted by the European Commission (SANCO/4347/2000 – Final; 13 May 2004). The following studies included in the Baseline Dossier were regarded as relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted], R.	1995	M-000683-01-2
[redacted], B.	1998	M-001114-02-1
[redacted], H.-P.	2002	M-063807-01-1

Additional studies required for groundwater risk assessment have been performed with additional metabolites and are included in this Supplemental Dossier.

Summary of study performed by [redacted], R.; 1994

The adsorption of YRC 2894-amide (M02) was investigated in batch equilibrium experiments with five soils. An additional study investigating the adsorption of YRC 2894-amide (M02) on lysimeter soil [redacted] AXXA was performed. This further study by [redacted], B.; [redacted], U.; 2003 was not in the baseline dossier and is summarized later. The respective results were included in following summary Table 7.1.3.1.2- 1.

The following arithmetic mean values are used to quantify the sorption of YRC 2894-amide in PEC calculations: K_{OC} = 293 mL/g (K_{OM} = 170 mL/g; 1/n = 0.83).

Table 7.1.3.1.2- 1: Adsorption data of YRC 2894-amide (M02)

Soil	Koc [mL/g]	Koc [mL/g]	FREUNDLICH exponent 1/n
[redacted] a)	223	129	0.81
[redacted] a)	302	175	0.81
[redacted] a)	313	182	0.91
[redacted] a)	166	96	0.76
[redacted] a)	438	254	0.81
[redacted] AXXa b)	313	182	0.85
Arithmetic mean	**293**	**170**	**0.83**
Geometric mean	**280**	**162**	-

a) data from study by [redacted], R.; 1995
b) data from study by [redacted], B.; [redacted], U.; 2003

Summary of study performed by [redacted], B.; 1998

The adsorption of YRC 2894-sulfonic acid (M30) was investigated in batch equilibrium experiments with five soils. An additional study investigating the adsorption of YRC 2894-sulfonic acid (M30) on lysimeter soil [redacted] AXXA was performed. This further study [redacted], B.; [redacted], R.; 2003, was not in the baseline dossier and is summarized later. The respective results were included in following summary Table 7.1.3.1.2- 2.

The following arithmetic mean values are used to quantify the sorption of YRC 2894- sulfonic acid in PEC calculations: K_{OC} = 20.2 mL/g, (K_{OM} = 11.7 mL/g, 1/n = 0.94).

Table 7.1.3.1.2- 2: Adsorption data of YRC 2894-sulfonic acid (M30)

Soil	Koc [mL/g]	Koc [mL/g]	FREUNDLICH exponent 1/n
[redacted] a)	15.4	8.9	0.98
[redacted] a)	26.2	15.2	0.92
[redacted] a)	17.4	10.1	0.97
[redacted] a)	11.9	6.9	0.91
[redacted] a)	28.2	16.4	0.92
[redacted] AXXa b)	22.0	12.8	0.93
Arithmetic mean	20.2	11.7	0.94
Geometric mean	19.3	11.2	-

a) data from study by [redacted], B.; 1998
b) data from study by [redacted], B.; [redacted], R.; 2003

Summary of study performed by [redacted], H.-P.

The adsorption of YRC 2894-sulfonic acid amide (M34) was investigated in batch equilibrium experiments with four soils. The results are summarized in Table 7.1.3.1.2- 3.

Due to the very low affinity of YRC 2894-sulfonic acid amide to soil, no definitive studies to establish Freundlich isotherms were performed according to the OECD test guideline. However, based on the pre-tests with about 1 mg test substance/mL, a soil to water partition coefficient was calculated for each soil. The resulting K_{OC} values were in the range of 2.9 to 6.3 mL/g (mean 5.0 mL/g). Using classifications for the estimation of the mobility of crop protection agents in soil based on K_d and/or K_{OC} values, YRC 2894-sulfonic acid amide (M34) is to be classified as very mobile in soil.

Table 7.1.3.1.2- 3: Adsorption data of YRC 2894-sulfonic acid amide (M34)

Soil	Soil type	K_d [mL/g]	FREUNDLICH exponent 1/n	K_{OC} [mL/g]
BBA 2.2	Loamy sand	0.10	Not measurable	5.16
[redacted]/AXXa	Sandy loam	0.06		6.27
LUFA Speyer	Sandy loam	0.08		5.70
[redacted]	Silty clay	0.05		2.94
Arithmetic mean		0.07	--	5.02

Since for a low adsorbing compound like M34 batch equilibrium experiments are not the preferred test method (compare OECD TG 106), a new column leaching study was performed in order to get more precise adsorption constants for modelling purposes (see [redacted], E.; 2014 in Section CA 7.1.4.1.2).

The following two studies not yet included in the Baseline Dossier give additional valid information about the adsorption/desorption behaviour of YRC 2894-amide (M02) and YRC 2894-sulfonic acid (M30) on a lysimeter soil (compare Section CA 7.1.4.2).

Report:	**KCA 7.1.3.1.2 /04; [redacted], B.; [redacted], U.; 2003**
Title:	Adsorption/desorption of KKO 2254 (YRC 2894-amide) on soil [redacted] AXXa
Report No:	MR-500/02
Document No:	M-085123-01-1
Guidelines:	OECD Guideline for Testing of Chemicals No. 106, Adsorption/Desorption, 2000 EPA Pesticide Assessment Guidelines, Subdivision N, Chemistry: Environmental Fate § 163-1, Leaching and Adsorption/Desorption Studies

GLP:	Yes

EXECUTIVE SUMMARY

The test was conducted by using a batch equilibrium procedure in one soil (lysimeter soil [redacted] AXXa) with [methylene-^{14}C]KKO 2254 (M02): Purity control BECH 0677, radiochemical purity > 99%; chemical purity: > 99% HPLC-UV detection at 210 nm; specific radioactivity 3.53 MBq/mg (95.3 µCi/mg).
After air-drying the test soil was screened to a particle size of ≤ 2 mm. The characteristics of the soils are given in the following Table 7.1.3.1.2- 4:

Table 7.1.3.1.2- 4: Characteristics of test soil used

Soil designation	Soil type[a)], origin	Sand (%)	Silt (%)	Clay (%)	Org. C (%)	pH ($CaCl_2$)
[redacted] AXXa	Sandy loam, GER	72.4	22.6	5.0	1.02	6.3

[a)] according to USDA scheme.

Test container: Centrifuge tubes with screw cap, volume: 43 mL, material: Teflon®.
Temperature: Climate cabinet, (room 164), 20.1 ± 0.1 °C.
Agitation: Mechanical overhead shaker, 29 ± 2 rpm.
Parallel batches: 2 replicates.
Separation: Centrifuge (Beckmann J2-21 with Rotor JA-20, about 10000 g).

The air-dried soil was weighed into centrifuge tubes (6.1 g fresh weight, corresponding to 6.0 g dry weight in the definitive test), and 17.9 mL of stock solution 1 (aqueous 0.01 M $CaCl_2$ solution) were added. After pre-equilibration for about 24 hours, 2 mL of the respective application solution were added. The tubes were closed and the suspension was agitated with an overhead shaker for 24 hours at constant temperature in the dark. The suspension was centrifuged and the supernatant was investigated by LSC and in case of the highest concentration of the test substance also by TLC.

For the desorption experiment, the supernatant from the adsorption experiment was completely removed, and a corresponding volume of aqueous $CaCl_2$ solution (0.01 M) was added to the soil. After agitation and centrifugation, the supernatant was analysed as described before.

For calculation of the mass balance, the supernatant resulting from the desorption step was completely decanted. The remaining RA in soil was analysed by combustion of aliquots of the soil.

The partition of the radioactivity between supernatant and soil was determined using five concentrations of the test substance covering three orders of magnitude. All experiments were performed in duplicate.

Important parameters like stability of the test substance, adsorption to vessel surface, soil to solution ratio and equilibration time were already known or determined in orientating pre-tests.

For more information about the experimental design see also Table 2 of report.

After completion of the shaking process the gross weight of the centrifuge tubes was determined and the containers were centrifuged for 20 min at 10000 g. The clear supernatant was decanted into 20-mL scintillation vessels. Aliquots were taken from the clear supernatant for LSC measurement (3 x 100 µL for conc. A to D) or 3 x 500 µL for conc. E) and the pH of the supernatant was determined. Aliquots of 10 µL were removed for TLC analysis with two different methods (highest concentration only). The amount of supernatant was determined by weighing. The removed supernatant was replaced by fresh 0.01 M $CaCl_2$ solution (stock solution I) for desorption investigations. The containers were sealed, shaken for another 24 hours and processed as described in the adsorption experiment above.

The remaining soil was air-dried, ground and the radioactivity in the soil was determined by combustion of each three aliquots of about 1 g of the soil samples. After the desorption test TLC

analysis was performed with supernatant of the highest test concentration in order to confirm the stability of the test substance during the experiment.

In a pre-experiment, the necessary equilibration time was established. In the definitive test, the soil was pre-equilibrated for 24 hours with 0.01 M $CaCl_2$ solution. The soil to solution ratio was 1:3.33. After application of the test substance, the system was equilibrated for 24 hours at 20.1 ± 0.1 °C in the dark.

Referring to individual samples, the total recovery of AR was in the range of 96 to 99%. The RA material balance comprising all sampling intervals demonstrated that no significant amount of radioactively-labelled test item dissipated as volatile compounds or was lost during processing.

After application of the test compound at concentrations of 5.0, 1.0, 0.2, 0.04 and 0.005 mg per litre $CaCl_2$ solution (i.e. covering three orders of magnitude) the percentage of the chemical adsorbed to the soil phase varied between 43 and 71% of applied. The adsorption constant K_d, calculated by means of the FREUNDLICH adsorption isotherm, as well as the organic carbon content based K_{OC} are shown in Table 7.1.3.1.2- 5.

The desorption tests showed that from the soil between 18 and 39% of the adsorbed KKO 2254 (M02) were desorbed again. On basis of this study the mobility of KKO 2254 (M02) in soil is to be classified as low.

Table 7.1.3.1.2- 5: Adsorption and desorption of [methylene-^{14}C]KKO 2254 (M02) in lysimeter soil [redacted] AXXa

Soil Designation	Soil Type	pH (0.01 M $CaCl_2$)	OC (%)	Adsorption			Desorption		
				K_d (mL/g)	1/n	K_{OC} (mL/g)	K_d (mL/g)	1/n	K_{OC} (mL/g)
[redacted] AXXa	Sandy loam	6.3	1.02	3.188	0.8477	313	5.247	0.8518	514

Report: **KCA 7.1.3.1.2 /05; [redacted], B.; [redacted], R.; 2003**
Title: Adsorption/desorption of WAK 6999 (YRC 2894-sulfonic acid) on soil [redacted] AXXa.
Report No: MR-499/02
Document No: M-082767-01-1
Guidelines: OECD Guideline for Testing of Chemicals No. 106, Adsorption/Desorption, 2000
EPA Pesticide Assessment Guidelines, Subdivision N, Chemistry: Environmental Fate § 163-1, Leaching and Adsorption/Desorption Studies
GLP: Yes

EXECUTIVE SUMMARY

The test was conducted by using a batch equilibrium procedure in soil (lysimeter soil [redacted] AXXa) with [methylene-^{14}C]-WAK 6999 (M30): Purity control BECH 0674, radiochemical purity > 98%; chemical purity > 98% HPLC-UV detection at 210 nm; specific radioactivity 3.33 MBq/mg (90.1 µCi/mg).
After air-drying the soil was screened to a particle size of ≤ 2 mm. The characteristics of the soils are given in the following table:

Table 7.1.3.1.2- 6: Characteristics of test soil used

Soil designation	Soil type[a], origin	Sand	Silt	Clay	Org. C	pH

		(%)	(%)	(%)	(%)	($CaCl_2$)
[redacted] AXXa	Sandy loam, GER	72.4	22.6	5.0	1.02	6.3

[a)] according to USDA scheme.

Test container: Centrifuge tubes with screw cap, volume: 43 mL, material: Teflon®.
Temperature: Climate cabinet, (room 164), 20.1 ± 0.1 °C.
Agitation: Mechanical overhead shaker, 29 ± 2 rpm.
Parallel batches: 2 replicates.
Separation: Centrifuge (Beckmann J2-21 with Rotor JA-20; about 10000 g).

The air-dried soil was weighed into centrifuge tubes (25.4 g fresh weight, corresponding to 25.0 g dry weight in the definitive test), and 17.6 mL of stock solution 1 (aqueous 0.01 M $CaCl_2$ solution) were added. After pre-equilibration for about 24 hours, 2 mL of the respective application solution were added. The tubes were closed and the suspension was agitated using an overhead shaker for 24 hours at constant temperature in the dark. The suspension was centrifuged and the supernatant was analysed by LSC and in case of the highest concentration of the test substance by TLC as well.

For the desorption experiment, the supernatant from the adsorption experiment was completely removed, and a corresponding volume of aqueous $CaCl_2$ solution (0.01 M) was added to the soil. After agitation and centrifugation, the supernatant was analysed as described before.

For calculation of the mass balance, the supernatant resulting from the desorption step was completely decanted. The remaining RA in soil was analysed by combustion of aliquots of the soil.

The partition of the radioactivity between supernatant and soil was determined using five concentrations of the test substance covering three orders of magnitude. All experiments were performed in duplicate.

Important parameters like stability of the test substance, adsorption to vessel surface, soil to solution ratio and equilibration time were already known or determined in orientating pre-tests.

For more information about the experimental design see also Table 2 of report.

After completion of the shaking process the gross weight of the centrifuge tubes was determined and the containers were centrifuged for 20 min at 10000 g. The clear supernatant was decanted into 20-mL scintillation vessels. Aliquots were taken from the clear supernatant for LSC measurement (3 x 100 µL for conc. A to D) or 3 x 500 µL for conc. E) and the pH of the supernatant was determined. Aliquots of 10 µL were removed for TLC analysis with two different methods (highest concentration only). The amount of supernatant was determined by weighing. The removed supernatant was replaced by fresh 0.01 M $CaCl_2$ solution (stock solution 1) for desorption investigations. The containers were sealed, shaken for another 24 hours and processed as described in the adsorption experiment above.

The remaining soil was air-dried, ground and the radioactivity in the soil was determined by combustion of each three aliquots of about 1 g of the soil samples. After the desorption test TLC analysis was performed with supernatant of the highest test concentration in order to confirm the stability of the test substance during the experiment.

In a pre-experiment, the necessary equilibration time was established. In the definitive test, the soil was pre-equilibrated for 24 hours with 0.01 M $CaCl_2$ solution. The soil to solution ratio was 1:0.8. After application of the test substance, the system was equilibrated for 24 hours at 20.1 ± 0.1 °C in the dark.

Referring to individual samples, the total recovery of AR was in the range of 97 to 100%. The RA material balance comprising all sampling intervals demonstrated that no significant amount of radioactively-labelled test item dissipated as volatile compounds or was lost during processing.

After application of the test compound at concentrations of 5.0, 10.0, 2.0, 0.4 and 0.005 mg per litre $CaCl_2$ solution the percentage of the chemical adsorbed to the soil phase varied between 20 and 29% of applied after 24 hours. The adsorption constant K_d, calculated by means of the FREUNDLICH adsorption isotherm, as well as the organic carbon content based K_{OC} are shown in Table 7.1.3.1.2- 7.

The desorption tests showed that from the soil between 33 and 36% of the adsorbed M30 were desorbed again. On basis of this study the mobility of WAK 6999 in soil is to be classified as mobile.

Table 7.1.3.1.2- 7: Adsorption and desorption of [methylene-^{14}C]-WAK 6999 (M30) in lysimeter soil [redacted] AXXa

Soil Designation	Soil Type	pH (0.01 M $CaCl_2$)	OC (%)	Adsorption			Desorption		
				K_d (mL/g)	1/n	K_{OC} (mL/g)	K_d (mL/g)	1/n	K_{OC} (mL/g)
[redacted] AXXa	Sandy loam	6.3	1.02	0.227	0.9343	22.0	1.482	0.9870	145

The following performed two new studies not yet included in the Baseline Dossier were necessary to obtain data on adsorption/desorption of the degradation products YRC 2894-des-cyano (M29) and YRC 2894-thiadiazine (M46) in soil for the groundwater risk assessment.

Report:	**KCA 7.1.3.1.2 /06; [redacted], W.; [redacted], A.; 2013**
Title:	[pyridinyl-methyl-^{14}C]BCS-AA48007: Adsorption/desorption in five different soils.
Report No:	AS246
Document No:	M-447091-01-1
Guidelines:	OECD Guideline for Testing of Chemicals No. 106, Adsorption/Desorption, 2000 EPA Pesticide Assessment Guidelines, Subdivision N, Chemistry: Environmental Fate § 163-1, Leaching and Adsorption/Desorption Studies
GLP:	Yes

EXECUTIVE SUMMARY

The adsorption/desorption characteristics of [pyridinyl-methyl-^{14}C]BCS-AA48007 (YRC 2894-des-cyano, M29) were studied in five soils by batch equilibrium experiments. After air-drying the soils were screened to a particle size of ≤ 2 mm. The characteristics of the soils are given in the following table:

Table 7.1.3.1.2- 8: Characteristics of test soils used

Soil designation	Soil type[a], origin	Sand (%)	Silt (%)	Clay (%)	Org. C (%)	pH ($CaCl_2$)
[redacted]	Sandy loam, GER	57	30	13	2.0	5.1
[redacted] 4a	Silt loam, GER	27	60	13	2.9	6.3
[redacted]II	Loam, GER	37	40	23	4.4	7.3
[redacted] AXXa	Loamy sand, GER	77	16	5	2.0	5.9
[redacted]	Silt loam, GER	31	54	15	2.9	5.2

[a] according to USDA scheme.

The adsorption phase of the study (definitive test) was carried out at concentrations of nominal 1.00, 0.30, 0.10, 0.03, and 0.01 mg/L in the dark at 20 °C ± 2 °C for 24 hours. The equilibration solution

used was 0.01 M aqueous $CaCl_2$ solution. After the preliminary test I a soil to solution ratio of 1:8 was defined to all soils. Desorption phase of the study was carried out by supplying pre-adsorbed soil specimens with fresh 0.01 M aqueous $CaCl_2$ solution for one desorption cycle. The aqueous supernatant after adsorption was separated by centrifugation and the [pyridinyl-methyl-^{14}C]BCS-AA48007 residues in the supernatant were analysed by liquid scintillation counting (LSC). The adsorption parameters were calculated using the FREUNDLICH adsorption isotherm. Test systems without soil were used as control in preliminary test and did not show adsorption to the vessels or degradation.

For all soils the parental mass balance after 72 hours showed that >90% of applied [pyridinyl-methyl-^{14}C]BCS-AA48007 could be recovered. This demonstrates that the test item was sufficient stable for the test.

The mass balance in the definitive test of the soils was determined by LSC of the supernatants after adsorption / desorption and by combustion of the remaining soils. The overall material balance for all concentrations for individual specimens was in the range of 97.2-99.3%, 92.9-100.5%, 87.1-98.0%, 97.4-102.7% (one replicate 137.9% - not used for the determination of FREUNDLICH isotherm), and 85.3-103.7% of the applied radioactivity in soils [redacted], [redacted]4a, [redacted]II, [redacted] AXXa and [redacted], respectively.

In the definitive adsorption test 47.6-69.5%, 61.1-78.4%, 70.1-83.7%, 50.4-69.8%, and 62.3-78.9% of the applied test material was adsorbed in soils [redacted], [redacted]4a, [redacted]II, [redacted] AXXa, [redacted], respectively.

The calculated adsorption constant $K_F^{(ads)}$ of the FREUNDLICH isotherms for the five test soils ranged from 6.7 mL/g to 16.0 mL/g. The FREUNDLICH exponent 1/n was in the range of 0.8330 to 0.8521, indicating that the concentration of the test item did affect the adsorption behaviour.

At the end of one adsorption and one desorption phase, 23.0-38.9%, 16.3-30.1%, 11.1-22.0%, 21.9-37.0%, and 14.7-27.5% of the initially adsorbed amount were desorbed in soils [redacted], [redacted]4a, [redacted]II, [redacted] AXXa, [redacted], respectively.

The mean desorption $K_F^{(des)}$ ranged from 7.9 – 18.2 mL/g, and the normalized $K_{F,OC}^{(des)}$ ranged from 392.7 – 479.2 mL/g, thus were 1.13 – 1.18 times higher than those obtained for adsorption phase. The following Table 7.1.3.1.2- 9 summarizes the key soil properties and results from the study:

On basis of this study the mobility of YRC 2894-des-cyano (M29) in soil is to be classified as low mobile.

Table 7.1.3.1.2- 9: Adsorption and desorption of [methylene-^{14}C]-YRC 2894-des-cyano (M29) in five soils

Soil Designation	Soil Type	pH (0.01 M $CaCl_2$)	Org. C (%)	Adsorption K_f (mL/g)	$K_{f,OC}$ (mL/g)	1/n
[redacted]	Sandy loam	5.1	2.0	6.7	338.2	0.83
[redacted] 4a	Silt loam	6.3	2.9	11.1	383.0	0.85
[redacted]II	Loam	7.3	4.4	16.0	364.2	0.85
[redacted] AXXa	Loamy sand	5.9	2.0	7.2	361.0	0.83
[redacted]	Silt loam	5.2	2.9	11.8	407.2	0.84
				Arithmetic mean	**371**	**0.84**

Report:	**KCA 7.1.3.1.2 /07; [redacted], W.; [redacted], A.; 2012**
Title:	[Pyridinyl-methyl-^{14}C]-BCS-CJ16425: Adsorption/desorption in five different soils.
Report No:	AS242
Document No:	M-445982-01-1
Guidelines:	OECD Guideline for Testing of Chemicals No. 106, Adsorption/Desorption, 2000 EPA Pesticide Assessment Guidelines, Subdivision N, Chemistry: Environmental Fate § 163-1, Leaching and Adsorption/Desorption Studies
GLP:	Yes

EXECUTIVE SUMMARY

The adsorption/desorption characteristics of [pyridinyl-methyl-^{14}C]-BCS-CJ16425 (YRC 2894-thiadiazine, M46) were studied in five soils by batch equilibrium experiments. After air-drying the soils were screened to a particle size of ≤ 2 mm. The characteristics of the soils are given in the following table:

Table 7.1.3.1.2- 10: Characteristics of test soils used

Soil designation	Soil type [a], origin	Sand (%)	Silt (%)	Clay (%)	Org. C (%)	pH ($CaCl_2$)
[redacted]	Sandy loam, GER	57	30	13	2.0	5.1
[redacted] 4a	Silt loam, GER	27	60	13	2.9	6.3
[redacted] II	Loam, GER	37	40	23	4.4	7.3
[redacted] AXXa	Loamy sand, GER	77	16	5	2.0	5.9
[redacted]	Silt loam, GER	31	54	15	2.9	5.2

[a] according to USDA scheme.

The adsorption phase of the study (definitive test) was carried out at concentrations of nominal 1.00, 0.30, 0.10, 0.03, and 0.01 mg/L in the dark at 20 °C ± 2 °C for 24 hours. The equilibration solution used was 0.01 M aqueous $CaCl_2$ solution. After the preliminary test I a soil to solution ratio of 1:1 was defined to all soils. Desorption phase of the study was carried out by supplying pre-adsorbed soil specimens with fresh 0.01 M aqueous $CaCl_2$ solution for one desorption cycle. The aqueous supernatant after adsorption was separated by centrifugation and the [pyridinyl-methyl-^{14}C]-BCS-CJ16425 residues in the supernatant were analysed by liquid scintillation counting (LSC). The adsorption parameters were calculated using the FREUNDLICH adsorption isotherm. Test systems without soil were used as control in preliminary test and did not show adsorption to the vessels or degradation. The mass balance of the soils was determined by LSC of the supernatants after adsorption and desorption and by combustion of the remaining soils.

For all soils the parental mass balance after 72 hours showed that >90% of applied [pyridinyl-methyl-^{14}C]-BCS-CJ16425 could be recovered. This demonstrates that the test item was sufficient stable for the test.

The overall material balance for all concentrations for individual specimens was in the range of 94.9-99.3%, 93.0-98.8%, 91.5-97.2%, 97.7-108.6%, and 97.8-103.7% of the applied radioactivity in soils [redacted], [redacted] 4a, [redacted] II, [redacted] AXXa, and [redacted], respectively.

In the definitive adsorption test 17.8-23.0%, 16.8-21.4%, 19.9-27.5%, 14.9-18.4%, and 28.1-36.2% of the applied test material was adsorbed in soils [redacted], [redacted] 4a, [redacted] II, [redacted] AXXa, and [redacted], respectively.

The calculated adsorption constant $K_F^{(ads)}$ of the FREUNDLICH isotherms for the five test soils ranged from 0.18 mL/g to 0.41 mL/g. The FREUNDLICH exponent 1/n was in the range of 0.9427 to 0.9990, indicating that the concentration of the test item did affect the adsorption behaviour.

At the end of one adsorption and one desorption phase, 27.9-35.5%, 24.5-34.1%, 19.3-27.9%, 32.0-45.3% and 23.3-27.8% of the initially adsorbed amount were desorbed in soils [redacted], [redacted] 4a, [redacted] II, [redacted] AXXa, and [redacted], respectively.

The mean desorption $K_F^{(des)}$ ranged from 0.25 – 0.49 mL/g, and the normalized $K_{F,OC}^{(des)}$ ranged from 7.8 – 16.8 mL/g, thus were 0.67 - 0.85 times higher than those obtained for adsorption phase.

The following Table 7.1.3.1.2- 11 summarizes the key soil properties and results from the study.

On basis of this study the mobility of YRC 2894-thiadiazine (M46) in soil is to be classified as very mobile to mobile.

Table 7.1.3.1.2- 11: Adsorption and desorption of [methylene-[14]C]-YRC 2894-thiadiazine (M46) in five soils

Soil Designation	Soil Type	pH (0.01 M $CaCl_2$)	Org. C (%)	Adsorption K_f (mL/g)	$K_{f,oc}$ (mL/g)	1/n
[redacted]	Sandy loam	5.1	2.0	0.22	11.2	0.95
[redacted] 4a	Silt loam	6.3	2.9	0.23	7.9	1.00
[redacted] II	Loam	7.3	4.4	0.26	5.8	0.95
[redacted] AXXa	Loamy sand	5.9	2.0	0.18	9.0	0.96
[redacted]	Silt loam	5.2	2.9	0.41	14.3	0.94
				Arithmetic mean	**9.6**	**0.96**

CA 7.1.3.2 Aged sorption

No studies submitted, and no studies are required. The leaching behaviour is evaluated by the adsorption/desorption data shown in the Section CA 7.1.3.1, in combination with accepted and agreed model calculations of predicted environmental ground water concentration (PEC_{GW}) for parent and its major metabolites. Therefore, new studies were not performed and are not required under Commission Regulation (EU) No 283/2013 in accordance with Regulation (EC) No 1107/2009.

CA 7.1.4 Mobility in soil

Some studies on mobility of Thiacloprid and its residues in soil were evaluated during the Annex I inclusion (see EU Monograph Annex B8, and European Commission, SANCO/4347/2000 – Final; 13 May 2004).

Under current requirements the leaching behaviour is evaluated by the adsorption/desorption data shown in the Section CA 7.1.3.1, in combination with accepted and agreed model calculations of predicted environmental ground water concentration (PEC_{GW}) for parent and its major metabolites. Therefore, new studies were not performed and are not required under Commission Regulation (EU) No 283/2013 in accordance with Regulation (EC) No 1107/2009. Due to the characteristics of the metabolite YRC 2894- sulfonic acid (M30) the sorption can hardly be determined from the adsorption data, and for this metabolite a column leaching study has been performed.

CA 7.1.4.1 Column leaching studies

CA 7.1.4.1.1 Column leaching of the active substance

The following study was included in the Baseline Dossier and evaluated during the Annex I inclusion. However, the outcome was not used for deriving end points as these are derived from sorption studies listed under Section CA 7.1.3.1 or CA 7.1.4.1.2.

Author(s)	Year	Document No.
[redacted], J.	1995	M-002045-04-1

Summary of study performed by [redacted], J.; 1995

Thiacloprid (YRC 2894) is classified as extremely rapidly degradable in soil. The investigations showed that after ageing due to the rapid degradation no transport of the test compound takes place. The same also holds true for the main metabolite (M02). Only the highly polar sulfonic acid metabolite (M30) is almost completely washed out of the soil column and hence transported into the leachate. Based on the classification of McCall et al. (1980), YRC 2894 has to be classified as immobile after ageing in soil.

No further column leaching studies were performed for Thiacloprid since that requirement is covered by the adsorption/desorption studies performed with the active substance (see Section CA 7.1.3.1.1).

CA 7.1.4.1.2 Column leaching of metabolites, breakdown and reaction products

A new column leaching study not yet included in the baseline Dossier was performed to obtain more precise adsorption constants for modelling purposes of the metabolite YRC 2894-sulfonic acid amide (M34) (compare study and data by [redacted], H. P.; 1998).

Report:	**KCA 7.1.4.1.2 /01; [redacted], E.; 2014**
Title:	[Methylene-^{14}C]-YRC 2894-sulfonic acid amide: Soil Column Leaching
Report No:	EnSa-13-1056
Document No:	M-488355-01-1
Guidelines:	OECD 312 (2004), OPPTS 835.1240 (2008). European Commission: Opinion of the scientific committee on plants on methods for the determination of the organic carbon adsorption coefficient (Koc) for a plant protection product active substance in the context of council directive 91/414/EC, 18.07.2002. SCP/KOC/002-Final. (Today: Commission Regulation (EU) No 283/2013 in accordance with Regulation (EC) No 1107/2009).
GLP:	Yes

EXECUTIVE SUMMARY

The soil adsorption behaviour of [methylene-^{14}C]-YRC 2894-sulfonic acid amide (M34) was investigated in the dark at 20 °C by column leaching experiments performed on four test soils. The characteristics of the soils are given in Table 7.1.4.1.2- 1.

Each 2.53 µg of test item was applied to the surface of bulk-packed soil columns (30 cm long, 5 cm inner diameter; duplicate columns for each soil) that had been saturated with 0.01 M aqueous $CaCl_2$ solution before. Then, the treated columns were irrigated with 393 mL of $CaCl_2$ solution at a constant flow (setting of pump was 8.2 mL/h) over 48 hours, which equals 200 mm of simulated constant rainfall. Column elution was done under saturated flow conditions throughout the experiment. The column eluates were collected in time intervals to collect approximately 20 - 25 mL per fraction, and radio-assayed by LSC. After draining, the soil columns were deep-frozen. However, since for the test item under investigation the majority of ^{14}C applied had been leached through the soil columns, the stored soil columns were not processed and radio-assayed further.

Table 7.1.4.1.2- 1: Characteristics of test soils used

Soil designation	Soil type[a)], origin	Sand (%)	Silt (%)	Clay (%)	Org. C (%)	pH ($CaCl_2$)
[redacted] II (DD)	Loam, GER	37	38	25	5.2	7.4
[redacted] 4a (HF)	Silt loam, GER	25	58	17	1.9	6.6
[redacted] AXXa (AX)	Loamy sand, GER	77	16	7	2.0	6.3
[redacted] (HN)	Loam, GER	33	50	17	2.9	5.7

[a)] according to USDA scheme.

$K_{d/Koc}$ values were calculated using computer software ®Microsoft Excel spread sheet representing a so-called "leaching case". This sheet was developed for the transformation of column parameters and leaching data into the respective values using published mathematics described for the chromatographic theory by Ketelle et al and Swoboda et al), i.e. for test items showing no to low adsorption.

In addition, the soil columns were treated with 258 µg carbofuran, a mobile reference item, in order to check the quality of test conditions. The measured column leaching k_{OC} value obtained for carbofuran under similar test conditions in soil AX was found to be 15 mL/g. As in the current study only minor portions of applied carbofuran (1.0% of applied for DD, 6.5% of applied for HF, 2.0% of applied for AXE, 6.8% for HN) could be recovered (determined by HPLC-UV detection) within the total collected leachate until termination of leaching test, whereas the leachates contained at least 50% of applied YRC 2894-sulfonic acid amide. From that finding it was to be concluded that the K_{OC} for test the item should fall clearly below 15 or even lower than 10 mL/g in the current study.
The following table summarizes the key data and results of this study. A mean K_{OC} of 7.0 mL/g resulted for the test item YRC 2894-sulfonic acid amide (M34). Since that value is regarded more appropriate than that of the batch equilibrium study by [redacted], H.-P.; 1998 (i.e. 5.0 mL/g), it is included in summary Table 7.1.3.1- 1 and used for exposure calculations.

On basis of this study YRC 2894-sulfonic acid amide (M34) is classified as very mobile in soil.

Table 7.1.4.1.2- 2: Key data and results of column leaching tests with [^{14}C]-YRC 2894-sulfonic acid amide (M34)

Soil Designation	Soil Type	pH (0.01 M $CaCl_2$)	Org. C (%)	Adsorption		
				K_d (mL/g)	K_{OC} (mL/g)	1/n
[redacted] II	Loam	7.4	5.2	0.19	3.6	1.0 (default)
[redacted] 4a	Silt loam	6.6	1.9	0.15	7.7	
[redacted] AXXa	Loamy sand	7.3	4.4	0.15	7.3	
[redacted]	Loam	5.9	2.0	0.28	9.7	
				Arithmetic mean	**7.0**	

CA 7.1.4.2 Lysimeter studies

The mobility of Thiacloprid and its residues in soil, investigated by a three-year outdoor lysimeter study, was evaluated during the Annex I inclusion (compare EU Monograph, Annex B8), and was accepted by the European Commission (SANCO/4347/2000 – Final; 13 May 2004). The following lysimeter study by [redacted], B. included in the Baseline Dossier was regarded as relevant during the Annex I inclusion. The outcome and respective conclusions were reported in Appendix II (End Points and Related Information) on page 13 of SANCO/4347/2000 – Final; 13 May 2004, also. This includes those of the other related reports by [redacted], J., [redacted], M., [redacted], F., [redacted],

J.P.E., [redacted], H.-P., [redacted], J.; [redacted], R., which clarified and evaluated the findings in the leachates of the lysimeters.

Author(s)	Year	Document No.
[redacted], B.	1998	M-002182-01-1
[redacted], J.	2001	M-075099-01-1 KCA 7.1.1.1
[redacted], M.	1995	M-001013-01-2 KCA 8.2.6.1
[redacted], F.	1995	M-001002-01-2 KCA 8.2.4.1
[redacted], J.P.E.	1996	M-001011-02-1 KCA 8.2.6.1
[redacted], H.-P.	2002a	M-063642-01-1
[redacted], H.-P.	**2002b**	M-078775-01-1 KCA 7.1.4.2
[redacted], H.-P.	2002c	M-053688-02-1
[redacted], J.; [redacted], R.	2002	M-062583-01-1

No additional studies are submitted within this this Supplemental Dossier for the Thiacloprid renewal of approval.

Summary of lysimeter study performed by [redacted], B.; 1995

A three-year (May 1994 to December 1997) lysimeter study investigated leaching of YRC 2894 following applications in two successive years to a grass cover in accordance with BBA guidelines (Part IV, 4-3). Although grass is not a proposed use for YRC 2894, the grass cover was chosen to reflect a realistic worst-case situation for the worst-case proposed use (pome fruits). Other uses such as those on fruiting vegetables do not include repeated applications in successive years.
Undisturbed cores (surface area 1 m^2, depth 1.25 m) of a sandy loam over sand (texture according to USDA, topsoil pH 7.0, OC 1.41%) were buried on a lysimeter facility at [redacted], Germany in 1993. Two lysimeters (A and B) were cropped with grass sown in April 1994 and 1995 and cultivated according to common agricultural practice (cuts to 8-10 cm when height reached 20-25 cm). The grass was incorporated into the subsoil in March 1995 and sown again in April 1995 to keep test conditions identical for the two years of application. Two post-emergence applications (total amount split into two equal treatments separated by a 15-day interval) of [^{14}C]YRC 2894 were sprayed onto the two lysimeters (treated surface area 0.81 m^2) in May 1994 and May 1995 at total rates of 0.400 kg a.s./ha (1994) and 0.365 kg a.s./ha (1995). Formulations of YRC 2894 differed between the two years of application (SC 600 for the first year, SC 480 for the second). Other pesticide and fertilizers were also applied to the lysimeters according to normal agricultural practice.

Following relevant results were listed in Appendix II (End Points and Related Information) on page 13 of SANCO/4347/2000 – Final; 13 May 2004:
Average annual precipitation (mm): 869
Average annual leachate volume (mm): 372
% of applied radioactivity in leachate: 3%

Peak annual average concentrations (µg/L):
Total radioactivity: 2.31 µg a.s. equivalent/L
Parent compound YRC 2894: not detected
YRC 2894-amide (M02): not detected

YRC 2894-sulfonic acid (M30)	2.4 µg/L
YRC 2894-sulfonic acid amide (M34):	0.27 µg/L
Unidentified Z5:	0.15 µg a.s. equivalent/L
Z5, later identified by [redacted], H.-P.; 2002 as YRC 2894-thiadiazine (M46):	0.16 µg/L

The outcome of lysimeter study was not used for deriving distinct modelling end points since that can better be done by the studies listed under Section CA 7.1.3.1 or CA 7.1.4.1.2, in combination with accepted and agreed model calculations of predicted environmental ground water concentration (PEC_{GW}) for parent and its major metabolites.

Conclusion of position paper given by [redacted], 1998

YRC 2894-sulfonic acid amide (M34) is a minor soil metabolite always accompanying YRC 2894-sulfonic acid (M30). As the presence of M30 at concentration levels measured for the leachate of a lysimeter study is of no toxicological, ecotoxicological or biological concern, the same applies for its direct degradate M34 which will occur at concentrations significantly lower than those of M30.

Conclusion of studies performed by [redacted], H.-P.; 2002a, b, c

The structure of unknown metabolite Z5 found in lysimeter leachate was identified as YRC2894-thiadiazine (M46).

Conclusion of position paper given by [redacted], J.; [redacted], R., 2002, well considering the studies performed by [redacted], M., [redacted], F., [redacted], J.P.E..

The metabolites found in the lysimeter leachate are not of ecotoxicological or toxicological relevance.

CA 7.1.4.3 Field leaching studies

No relevant studies are included in the baseline dossier, since such were not required. No additional studies are submitted within this this Supplemental Dossier for the Thiacloprid renewal of approval.

CA 7.2 Fate and behaviour in water and sediment

The route of degradation of Thiacloprid in the aqueous environment, which was investigated in a set of laboratory studies performed under pure aqueous conditions (hydrolysis; photolysis) as well as under more realistic environmental conditions, i.e. in the presence of natural water and sediment containing oxygen and organic material, can be well explained (see Figure 7.2- 1).

Thiacloprid is stable to hydrolysis at pH 5, 7, and 9 and quite stable to photo-transformation. Therefore, these processes are not relevant for its dissipation in the environment, and no metabolites have to be considered from these routes of degradation.

Thiacloprid is classified as not readily biodegradable. Regardless of its concentration, Thiacloprid biodegrades slowly in natural surface water, with a lag phase of approx. 14 days. Thereafter, degradation and formation of the major metabolite YRC 2894-amide (M02) starts and is faster at a low dose than at a high dose. The primary metabolite YRC 2894-amide M02 is known from the pathway of degradation in soil. However, prior to starting biodegradation, a biological matrix (bio-film, etc.) has to be formed in the test flasks.

In contrast to the findings from abiotic test systems Thiacloprid disappears rapidly in biologically active water and sediment systems. Thereby, YRC 2894-amide (M02) occurs as a major metabolite in water and sediment with maximum concentrations in water and sediment on day 35. The second main metabolite is YRC 2894-sulfonic acid (M30) which is predominantly formed after M02 had reached its maximum. None of the metabolites accumulated in the test systems. The degradation of Thiacloprid in an anaerobic water/sediment system followed a route similar to that established for aerobic conditions, although it is more slowly degraded.

The results of aerobic water/sediment study have been kinetically evaluated, and the respective degradation parameters in water and sediment have been determined.

In the following Table 7.2- 1 and Table 7.2- 2 a summary of substance input data for Thiacloprid and its metabolites is given, well considering the respective new kinetic evaluations by [redacted] et al (i.e. [redacted], L.; 2010, on degradation in aerobic water/sediment systems according to FOCUS kinetics guidance), in order to be used for surface water and sediment exposure assessments.

In general, the results on parent compound and M02 from the outdoor mesocosm studies performed with Thiacloprid confirmed the estimations received from the respective exposure modelling studies.

Figure 7.2- 1: Proposed bio-degradation pathway of Thiacloprid (YRC 2894) in the aquatics

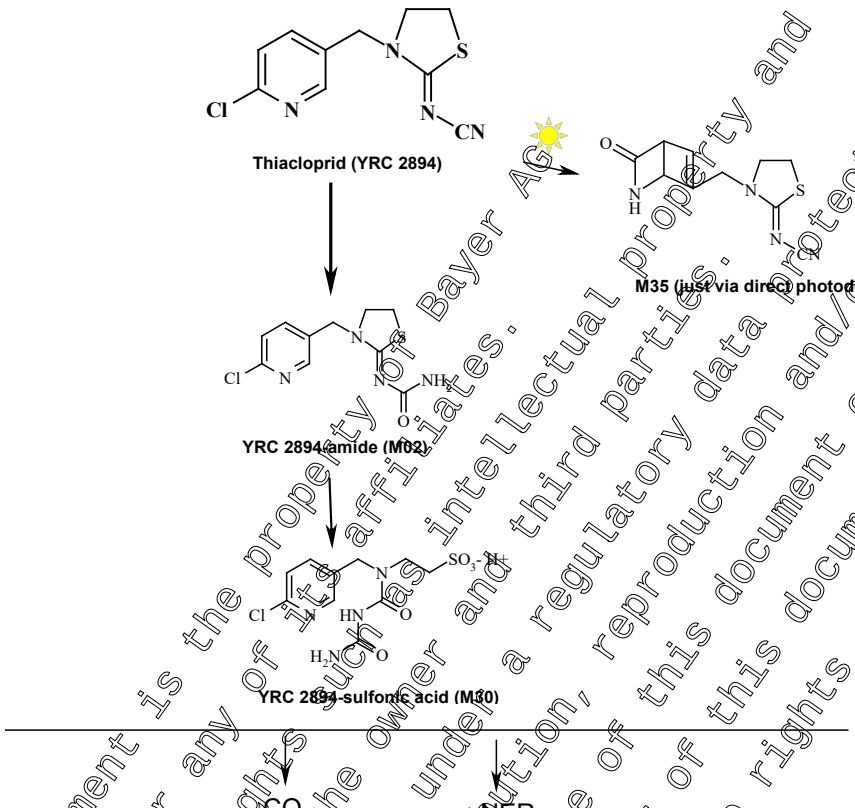


Table 7.2- 1: Substance parameters proposed for Thiacloprid and its metabolites at Steps 1-2 level PEC calculations

Parameter	Unit	Thiacloprid	M02	M29	M30
Molar Mass	g/mol	252.7	270.7	227.7	336.8
Water Solubility	mg/L	159	660	57000	56000
Koc	mL/g	615	293	371	20.2
Degradation					
Soil	days	5.4	41.3	140.7	15.6
Total System	days	15.8	99.2	1000 *	1000 *
Water	days	15.8	99.2	1000 *	1000 *
Sediment	days	15.8	99.2	1000 *	1000 *
Max Occurrence					
Water / Sediment	%	100	69	0.0001	9.7
Soil	%	100	86.7	33.2	19.7

* Default value used

Table 7.2- 2: Additional substance parameters proposed for Thiacloprid and its metabolites at Steps 3/4 level PEC calculations

Parameter	Unit	Thiacloprid	M02	M29
Vapour Pressure	Pa	3.0E-10	3.4E-10	1.1E-04
Plant Uptake Factor		0.0	0.0	0.0
Wash-Off Factor PRZM	1/cm	0.5	0.5	0.5
Wash-Off Factor MACRO	1/mm	0.05	0.05	0.05
Degradation				
Soil	days	5.4	41.3	140.7
Form. Frac. PRZM	molar basis	-	0.010	0.230
Form. Frac. MACRO	molar basis	-	0.653	0.207
Aquatic Metabolite				
Molar Mass Corr. Factor		-	1.07123	-
Max Occ.	%	-	69	-
Tot. Corr. Factor		-	0.73915	
Max Occ. at Day		-	35	

CA 7.2.1 Route and rate of degradation in aquatic systems (chemical and photochemical degradation)

CA 7.2.1.1 Hydrolytic degradation

The hydrolytic degradation of Thiacloprid was evaluated during the Annex I inclusion (compare EU Monograph, Annex B8), and was accepted by the European Commission (SANCO/4347/2000 – Final; 13 May 2004). The following study included in the Baseline Dossier was regarded as relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted] B.	1998	M-001109-01-1

No additional studies are submitted within this this Supplemental Dossier for the Thiacloprid renewal of approval.

Summary of study performed by [redacted], B.; 1998

Thiacloprid is stable at pH 5, 7, and 9. Under the experimental conditions the test substance was recovered from solution at constant levels throughout the test (95 to 98 % of the applied amount). In the investigated pH-range formation of two minor hydrolysis products was only observed at pH 9. Each of them amounted to less than 2 % of the applied radioactivity. Since no hydrolysis products were detected in the studies with the parent compound, no further studies are necessary.

CA 7.2.1.2 Direct photochemical degradation

The direct photochemical degradation of Thiacloprid was evaluated during the Annex I inclusion (compare EU Monograph, Annex B8), and was accepted by the European Commission (SANCO/4347/2000 – Final; 13 May 2004). The following studies included in the Baseline Dossier were regarded as relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted], E.	1995	M-000677-01-2 KCA 7.2.1.2
[redacted], J., [redacted], W.	1998	M-001109-01-1 KCA 7.2.1.1

Summary of study performed by [redacted], E.; 1995

No degradation of YRC 2894 was observed during the irradiation period of 500 minutes and no photoproducts were detected. The mean quantum yield of the direct photodegradation of YRC 2894 in water as calculated from the UV-Vis absorption and degradation kinetics was low (Φ = 0.000352). Environmental half-lives for all scenarios considered (different seasons and latitudes) were predicted to be >1000 days.

Summary of study performed by [redacted], J., [redacted], W.; 1998

Total recovery was 101-107% AR. YRC 2894 was degraded throughout the course of the experiment in illuminated samples only, and accounted for 84% AR after 18 days of irradiation. A minor photoproduct accounting for a maximum of 5.4% AR (day 18) was identified as M35. The mean DT_{50} of YRC 2894 was calculated as 79.7 days continuous irradiation (equivalent to 324 solar summer days for Phoenix, Arizona, USA) for illuminated samples (r^2 = 0.91). No degradation of YRC 2894 was observed in the dark controls.

No additional studies are submitted within this this Supplemental Dossier for the Thiacloprid renewal of approval.

CA 7.2.1.3 Indirect photochemical degradation

Since this topic was not a core data requirement and thus not evaluated by the European Commission during the last Annex I inclusion of Thiacloprid, no respective study is included in the Baseline Dossier (see EU Monograph, Annex B8 and SANCO/4347/2000 – Final; 13 May 2004).

The following study is now submitted within this Supplemental Dossier for the Thiacloprid renewal of approval. The study was carried out according to MAFF test guideline laboratory conditions in order to fulfill special data requirements for registration approvals in Japan. Photo-degradation in natural waters in mainly driven by indirect photo-transformation processes for any compound which is stable to hydrolysis and direct photo-transformation (i.e. for Thiacloprid).

Report:	**KCA 7.2.1.3/01; [redacted], K., [redacted], W.; 1997**
Title:	Photodegradation of YRC 2894 in Natural Water.
Report No:	PF4272
Document No:	M-000676-01-1
Guidelines:	MAFF/Japan: Guideline for Testing Method of the Photolysis of Agrochemicals in Water (Temporary, 1990). US EPA, 161-2: Photodegradation in Water, 1982 (which refers to photolysis in pure buffer water)

GLP:	Yes

EXECUTIVE SUMMARY

The present study describes the degradation behaviour of [methylene-^{14}C]YRC 2894 in natural water (Rhine river water, for characteristic data see Table 7.2.1.3- 1) at irradiation with artificial sunlight. The water (6 L) was freshly collected from Rhine River on June 22, 1995 at 1:30 p.m. The collection site was in D-[redacted] (GER) at km-position 714 near the [redacted]. The water was sampled from the surface water near the bank, filled in polyethylene flasks and stored under darkness in a refrigerator.

Table 7.2.1.3- 1: Key data of test water used (taken from Rhine River)

Parameter	Result	pH: Day of determination	pH: Mean of duplicates
TOC [mg/L] [1)]	4	0 [1)]	8.2
DOC [mg/L] [1)]	4	1	9.6
Nitrite [mg/L] [1)]	<0.1	2	9.7
Nitrate [mg/L] [1)]	2.7	4	9.9
Total phosphate [mg/L] [1)]	0.13	7	9.6
Conductivity, 25°C [µS/cm] [1)]	509	14	8.7 9.3 (dark)
Total water hardness [°DH] [1)]	11.1	28	6.3
Dissolved O_2 [%] [1)] [%] [2)] [%] [2)], dark	90 85 88	42	6.4 5.5 (dark)

[1)] : Prior to the start of study
[2)] : At the end of study

After application (the pH-value of the application solution was 8.4) of the maximum recommended dose rate of 350 g a.i./ha, which corresponds to a concentration of 0.7 mg a.i./L with reference to a theoretically water depth in a paddy rice field of 5 cm, the test systems were incubated at a temperature of 25 °C over a period of 42 days of continuous irradiation with artificial sunlight. At each sampling time the test solutions were analysed as well by means of high performance liquid as by thin layer chromatography. The content of radioactivity was determined by liquid scintillation measurement. Material balances were established at each sampling interval.

The material balance was in a range of 96.0% and 104.2% of applied radioactivity, the mean value was 100.4% of AR, demonstrating that no significant loss occurred during the testing period.

Under the experimental conditions used, YRC 2894 degraded in the Rhine River water with an experimental half-life of 42.5 irradiation days, which corresponds to a calculated long environmental half-life of 178 days under intensive solar conditions in Phoenix, AZ (USA). One main metabolite was observed during the course of the experiment with a maximum of about 19.3% of AR. The structure of this main metabolite was identified as YRC 2894-Dewar pyridone (M35), a photo-isomer of YRC 2894 after chlorine-hydroxy group exchange at the pyridyl ring. Besides this main metabolite another metabolite was observed. This second metabolite was 6-Chloronicotinic acid (M03) and amounted to 9.9% of AR at the end of the study. Furthermore, formation of $^{14}CO_2$ (about 6.2% of applied radioactivity) and a third polar minor metabolite (about 6.1% on day 42) were determined at study termination.
There was no degradation observed in the dark control samples.

CONCLUSION

The rate of degradation of YRC 2894 was faster in natural water (caused by indirect photo-transformation) than that observed in pure sterile buffer solutions caused by direct photo-transformation. However the only degradate exceeding 10% under these conditions was < 10% until day 28 of illumination, equivalent to 117 days of intense summer sunlight in Pheonix, Arizoan.

Therefore the general conclusion drawn by the earlier studies (see Section CA 7.2.1.2) is not to be changed: photo-transformation processes are not relevant for its dissipation in the environment, and no metabolites have to be considered from these routes of degradation (EU Monograph, Annex B8 and SANCO/4347/2000 – Final; 13 May 2004).

CA 7.2.2 Route and rate of biological degradation in aquatic systems

CA 7.2.2.1 "Ready biodegradability"

With respect to the "ready biodegradability" of Thiacloprid a statement was given as a conclusion in the list of end points of Annex I inclusion by the European Commission (SANCO/4347/2000 – Final; 13 May 2004):
No data submitted, therefore not readily biodegradable.

No additional studies are submitted within this this Supplemental Dossier for the Thiacloprid renewal of approval.

CA 7.2.2.2 Aerobic mineralisation in surface water

Since this topic (a new data requirement under 1107/2009) was not a data requirement the data was available at the Annex I inclusion of Thiacloprid, therefore no study is included in the Baseline Dossier. The following new study is submitted within this Supplemental Dossier for the Thiacloprid renewal of approval.

Report:	**KCA 7.2.2.2 /01; [redacted], D.; 2013**
Title:	[Thiazolidine-2-^{14}C]-Thiacloprid - Aerobic mineralisation in surface water - Simulation biodegradation test.
Report No:	20120136
Document No:	M-456839-01-1
Guidelines:	OECD Guideline for the Testing of Chemicals, Guideline 309, April 13, 2004. DG Sanco 11802/2010/rev 1 amending the Regulation (EC) No. 1107/2009.
GLP:	Yes

EXECUTIVE SUMMARY

Aerobic mineralisation of [thiazolidine-2-^{14}C]-Thiacloprid in surface water was investigated under defined laboratory conditions in the dark. For this purpose the radiolabelled test item was applied to 100 mL of natural pond water (for key water data see Table 7.2.2.2- 1) at concentrations of 0.1 and 0.01 mg/L. Additionally, the high concentration experiment was performed under sterile conditions in order to gain information about abiotic degradability of the test item.
The test flasks were incubated for a period of 62 days at 21.0 ± 0.1 °C under aerobic conditions by gently stirring the water. Radiolabelled benzoic acid was used as reference substance to check the sufficiency of microbial activity of the test water. Sufficient activity is reached if at least 90% of the acid degrades within 14 days of incubation.
The freshly collected water samples were passed through a 0.2 mm sieve and filled into 350 mL conical flask. After treatment, the flasks were incubated under continuous ventilation with moistened air. The exiting air was passed through a trapping system consisting of ethylene glycol and sodium hydroxide flasks in series.

Table 7.2.2.2- 1: Key data of test water used

Origin/Source		[redacted], [redacted], France
Batch No.		[redacted] 11/12
Sampling depth [1]	[cm]	0 - 10
Temperature [1]	[°C]	7.7
pH [1]		7.47
Redox Potential [1]	[mV]	91
Oxygen content [1]	[mg/L]	11.90
Colour		greenish
Turbidity		visibility through water layer down to about 20 cm
Total organic carbon (TOC)[2]	[mg/L]	5.41
Dissolved organic carbon (DOC)[2]	[mg/L]	4.92
NO_3 [2]	[mg/L]	2.93
NO_2 [2]	[mg/L]	< 0.82
N tot [2]	[mg/L]	1.00
P tot [2]	[mg/L]	0.88
Ammonium (NH^{4+}) [2]	[mg/L]	0.21

1 measured at field sampling.
2 determined by AgroLab GmbH, 6037 Root, Switzerland (non GLP).
Note: Redox potential was measured with platinum/silver chloride electrode (not corrected for pH). In order to obtain redox potential of the hydrogen electrode, +211 mV have to be added to the measured values.

Duplicate samples (replicate A and B) per system were then worked up to incubation day 0, 3, 7, 14, 28, 40 and 62. After sampling, the pH and the oxygen concentration in water were determined together with the total radioactivity present in the water layer and in the volatile traps. Aliquots of water samples were then analysed, directly or after a concentration step, by HPLC for parent and metabolites. Radioactive carbon dioxide dissolved in the water layer was extracted from the water layer by adding soda lime followed by acidification and trapping the released carbon dioxide.

The oxygen concentration measured in the water phase ranged from 6.01 to 8.32 mg/L in the high dose, from 6.40 to 8.59 mg/L in the high dose sterile and from 5.42 to 8.25 mg/L in the low dose experiment. Corresponding values for pH were 8.03 to 8.35, 8.03 to 8.34 and 7.82 to 8.32 respectively. Similar values were observed in the untreated control samples ranging from 6.28 to 8.13 mg/L for oxygen concentration and from 7.99 to 8.47 with for the pH values. The results demonstrated that the test item had no significant effects on the physico-chemical parameters of the test system.

Within 7 days of incubation, the amount of benzoic acid decreased rapidly from initially 93.3 to 0% under formation of 55.0% radioactive carbon dioxide. As more than 90% of benzoic acid degraded within 7 days, the test water could be considered as microbial active.

The main results of study are summarized by Table 7.2.2.2- 2. Total mean recoveries were 103.9 ± 1.7% of applied radioactivity (AR) for the high dose, 105.9 ± 3.6% AR for the high dose sterile and 102.0 ± 1.6% AR for the low dose experiments.

Immediately after treatment (time 0), mean values of 103.6%, 108.0% and 101.0% of AR were measured in the water phases of the high dose, high dose sterile and low dose systems, respectively. After 62 days of incubation, the amount of radioactivity in the respective systems represented mean values between 101.2% and 105.3% of AR for the high dose, 100.3% and 110.6% of AR for the high dose sterile and 101.0% and 102.9% of AR for the low dose systems. Correspondingly, radioactive carbon dioxide did not exceed 0.3% of AR in the high dose, 0.1% of AR in the sterile and 0.9% of AR in the low dose systems throughout the study. Volatile products other than $^{14}CO_2$ did not exceed 0.1% of AR during the entire incubation period.

Table 7.2.2.2- 2: Pattern of degradation and formation of metabolites after treating water by Thiacloprid (values expressed as % of AR; mean of duplicates)

Compound	Incubation time						
	0	**3**	**7**	**14**	**28**	**40**	**62**
High dose experiment							
[^{14}C]Thiacloprid (YRC 2894)	103.6	104.8	105.3	101.1	89.7	94.1	73.6
YRC 2984-amide (M02)	-	-	-	-	14.4	10.3	30.0
$^{14}CO_2$	n.p.	<0.1	<0.1	<0.1	0.1	0.1	0.2
Other volatiles	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Total	103.6	104.9	105.3	101.2	104.2	104.5	103.7
High dose experiment, sterile							
[^{14}C]Thiacloprid (YRC 2894)	108.0	108.4	107.1	100.2	103.2	103.4	110.5
YRC 2984-amide (M02)	-	-	-	-	-	-	-
$^{14}CO_2$	n.p.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Other volatiles	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Total	108.0	108.5	107.2	100.3	103.2	103.5	110.6
Low dose experiment							
[^{14}C]Thiacloprid (YRC 2894)	101.0	102.9	101.9	101.0	89.3	68.1	59.4
YRC 2984-amide (M02)	-	-	-	-	12.9	34.0	42.8
$^{14}CO_2$	n.p.	<0.1	<0.1	<0.1	<0.1	<0.1	0.7
Other volatiles	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Total	101.0	102.9	101.9	101.1	102.2	102.2	102.9

-: Not detected; n.p.: Not performed
High dose experiment: 100% of applied test item corresponded to 9.726 µg/test flask (97 µg/L water).
Low dose experiment: 100% of applied test item corresponded to 0.988 µg/test flask (10 µg/L water).

No degradation of Thiacloprid was observed in the high dose sterile system. The reference substance benzoic acid degraded completely from initially 93.3 to 0% of AR within 7 days of incubation indicating high microbial activity in the test water.

At the first sampling interval (time 0), the test item represented 103.6 and 101.0% of AR in the high dose and low dose systems respectively, declining to 73.6% of AR in the high dose and 59.4% of AR in the low dose systems within 62 days of incubation. The concentration of Thiacloprid decreased very slowly in all systems during a first study period of approx. 14 days (a typical kind of lag phase of biodegradation). Then, between day 14 and 28, biodegradation in the viable test systems started. Subsequently, the replicates of i.e. the low dose intervals showed a higher variation with respect to test item degradation. The development of biota might have been inhomogeneous in the individual flasks. However, the pattern of degradation was found to be the same.
Besides the test item and radioactive carbon dioxide, just one metabolite was observed, which was identified by co-chromatography using HPLC and TLC as YRC 2894-amide (M02, AE1303043). It was first detected after 28 days of incubation and represented 14.4 and 12.9% of AR in the high and low dose systems respectively. After 62 days, the amount of M02 rose to 30.0 and 42.8% of AR in the high and low dose systems respectively.

The calculated half-life (DT_{50}) and DT_{90} values for [^{14}C]-Thiacloprid in the different systems, based on single first-order (SFO) kinetics, are presented in the table below.

Table 7.2.2.2- 3: Kinetics of biodegradation of Thiacloprid in water

Test System	Kinetic model	[14C]Thiacloprid			
		DT_{50} (d)	DT_{90} (d)	r^2	ε %
High dose	SFO	117.9	391.8	0.777	3.9
High dose sterile*	SFO	2.6E+12	8.8E+12	0.003	2.5
Low dose	SFO	57.7	191.7	0.553	3.9

* a visually acceptable fit was obtained by SFO, although the statistical evaluation showed statistically invalid results due to no degradation of the test item under sterile conditions. As the test item did not degrade significantly, SFO was chosen as kinetic model.

In conclusion, Thiacloprid, regardless of its concentration, degraded slowly in natural surface water systems with a lag phase of approx. 14 days. Thereafter, degradation started and was faster in the low dose than in the high dose test. Since the concentration of Thiacloprid remained stable in the sterile systems, its degradation in surface water can be attributed to microbial activity. However, prior to starting biodegradation, a biological matrix (bio-film, etc.) has to be formed in the test flasks.

CA 7.2.2.3 Water/sediment study

The behaviour of Thiacloprid and its residues in the water/sediment system was evaluated during the Annex I inclusion (compare EU Monograph, Annex B8), and was accepted by the European Commission (SANCO/4347/2000 – Final; 13 May 2004). The following study by [redacted], K. included in the Baseline Dossier was regarded as relevant, the study by [redacted], R. included in the Baseline Dossier was regarded as not relevant during the Annex I inclusion.

Author(s)	Year	Document No.
[redacted], K.	1997	M-001248-01-1
[redacted], R.	1998	M-001432-01-1

Summary of study performed by [redacted], K.; 1997

The metabolism and degradation of [14C]-Thiacloprid was investigated in two laboratory water/sediment test systems incubated at a temperature of 20 ± 1 °C in darkness over a maximum period of 100 days.
The following results and respective conclusions were reported in Appendix II (End Points and Related Information) on page 14 of above mentioned SANCO document:

DT_{50} water: DT_{50} whole system: DT_{90} water: DT_{90} whole system: Distribution in water / sediment systems (active substance):	6-11 days 21-35 days (1st order, r^2=0.98-0.98, n=2) 11-27 days 35-92 days (1st order, r^2=0.97-0.99, n=2) Maximum of 10-50%AR in sediment after 1-3 days.
Distribution in water / sediment systems (metabolites):	Water: M02 max of 17-62%AR after 35 days M30 represented 5.3-9.5% AR at the end of the study (100 days) with no evidence that concentrations had peaked. Sediment: M02 max of 7-36%AR after 35-62 days.
Accumulation in water and/or sediment:	None

Summary of study performed by [redacted], R.; 1998

The anaerobic water/sediment study conducted according to EPA guidelines (Pesticide Assessment Guidelines, Subdivision N, Series 162-3) showed no degradation of Thiacloprid under strictly anaerobic incubation conditions.

No additional experimental studies are submitted within this Supplemental Dossier for the Thiacloprid renewal of approval. However, a kinetics evaluation of the degradation behaviour of Thiacloprid and its major metabolite M02 in the aerobic water/sediment system was performed according to FOCUS kinetics (2006) to derive kinetic parameters suitable for modelling purpose and environmental risk assessment. This report is summarized as follows.

Report:	**KCA 7.2.2.3 /03; [redacted], L.; 2010**
Title:	Kinetic Evaluation of Aerobic Aquatic Metabolism of Thiacloprid and its Metabolite in the Water-Sediment System.
Report No:	MEF-10/252
Document No:	M-368441-01-1
Guidelines:	FOCUS (2006): Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration. Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference Sanco/10058/2005 version 2
GLP:	No (modelling calculation)

EXECUTIVE SUMMARY

The aquatic degradation and dissipation behaviour of the insecticide Thiacloprid (YRC 2894) and its major metabolite in water, YRC 2894-amide (M02) has been investigated in a laboratory aquatic metabolism study in two water-sediment systems ([redacted], K.; 1997). The data from this study were evaluated here in order to derive values of the kinetic parameters to be used for predictions of environmental concentrations of the substances.

The measured data were taken into account as reported (individual true replicates). All experimental data sets and all single data points were weighted equally (weighting factor 1). The original report does not provide the information of values below the limit of detection/quantification (LOD/LOQ). Pre-processing of the experimental data with respect to LOD and LOQ was, therefore, not carried out. All experimental residue values used for the kinetic evaluation are summarised in the Appendix 9.1 of report. Up to 51% of the applied Thiacloprid was found in the sediment over the course of the water-sediment study.

The degradation pathway of Thiacloprid in aquatic systems can be represented by the following simple scheme:

$$\text{Thiacloprid (P)} \rightarrow \text{YRC 2894-amide (M)} \rightarrow CO_2\text{, NER}$$

In the case of degradation in the total system, the parameters for Thiacloprid and YRC 2894-amide were fitted simultaneously. For water dissipation, separate fits starting at the respective maximum values (decline fits) were used instead. The pathway can be mathematically described as a set of differential equations (depending on the type of the kinetic model used) which have to be numerically solved using an appropriate algorithm.

The results of the evaluation for Thiacloprid and its metabolite YRC 2894-amide (M02) are given in Table 7.2.2.3- 1. At the level P-I and M-I as defined by FOCUS (2006), total system degradation rates could be derived for both parent substance and metabolite. Dissipation rates in water and sediment phases were obtained only for the parent substance due to the insufficient number of data points available for the evaluation of the metabolite.

Analysis of the individual degradation rates in water and sediment according to FOCUS (2006) levels P-II and M-II was attempted. No statistically significant modelling endpoint values could be extracted due to almost absolute correlation of the resulting degradation rates.

Table 7.2.2.3- 1: Summary of DT_{50} values obtained for Thiacloprid and YRC 2894-amide (M02)

System	DT_{50} [days]					
	Thiacloprid			YRC 2894-amide (M02)		
	Water dissipation	Sediment dissipation	Total system	Water dissipation	Sediment dissipation	Total system
[redacted]	5.1	16.4	20.0	n.d.	n.d.	67.8
[redacted]	10.8	32.7	12.4	n.d.	n.d.	145.2
Geomean	*	*	15.8	#	#	99.2

In conclusion, for Thiacloprid, the geometric mean total system degradation DT_{50} of 15.8 days is proposed to be used for both water and sediment phases (see for * in Table 7.2.2.3- 1). At Step 3 level, the degradation in sediment can be described by using the default value of 1000 days. The use of the geometric mean follows the recommendation given in the FOCUS guidance document on degradation kinetics (FOCUS 2006).

In conclusion, for YRC 2894-amide (M02), the geometric mean total system degradation DT_{50} of 99.2 days is proposed to be used for both water and sediment phases (see for # in Table 7.2.2.3- 1). At Step3 level, the degradation in sediment can be described by using the default value of 1000 days. The use of the geometric mean follows the recommendation given in the FOCUS guidance document on degradation kinetics (FOCUS 2006). The maximum amount of 69% of radioactivity found in the total system of [redacted] (day 35) is proposed to be used in the calculations at Step1,2 level and for the prediction of aquatic formation of the metabolite at Step3 level.

CA 7.2.2.4 Irradiated water/sediment study

The behaviour and some biological effects of Thiacloprid and its residues (i.e. of M02) in water/sediment systems kept under outdoor conditions (outdoor microcosms, i.e. including sunlight) were evaluated during the Annex I inclusion (compare EU Monograph, Annex B8), and was accepted by the European Commission (SANCO/4347/2000 – Final; 13 May 2004). The following study by [redacted], F. 1997, included in the Baseline Dossier was regarded as relevant:

Author(s)	Year	Document No.
[redacted], F.	1997	M-001191-01-1

Summary of study performed by [redacted], F.; 1997

In 9 outdoor microcosm ponds in Germany (11-26 °C, pH 8-10, silty sand sediment 1.1 % OC), YRC 2894 SC 480 was applied twice at 14 day intervals to the water surface. The analytical data showed that after application 79-95% of the total amount applied was detected in the water, confirming the nominal target concentrations were largely achieved. YRC 2894 dissipated from the water phase with a first order DT_{50} of approx. 31 days (r^2 = 0.82 to 1.0). YRC 2894 reached its peak concentration in sediment 28 days after a second application at up to 141 % of the nominal initial water concentration (the sum of 2 applications). Concentrations then declined in sediment with a first order DT_{50} of 62 days (r^2 = 0.82, only 4 data points available). Concentrations of the metabolite M02 in the sediment were first detected 14 days after the second application, these continued to increase to the end of the

experiment (98 days) where they represented 62-89% of the nominal initial water concentration (the sum of 2 applications, note the molecular weight of M02 is 1.02 times that of YRC 2894). No analysis (in either water or sediment) was carried out for the metabolite M30. No water phase analysis for M02 was carried out.

No new studies are submitted within this Supplemental Dossier for the Thiacloprid renewal of approval.

CA 7.2.3 Degradation in the saturated zone

The degradation in the saturated zone was not studied since Thiacloprid is not expected to reach the saturated zone after its use according to good agricultural practices. No additional studies are submitted within Supplemental Dossier for the Thiacloprid renewal of approval.

CA 7.3 Fate and behaviour in air

Fate and behaviour of Thiacloprid in the air was evaluated during the Annex I inclusion (compare EU Monograph, Annex B8), and was accepted by the European Commission (SANCO/4347/2000 – Final; 13 May 2004). The following two studies by [redacted], J.; 1996, and [redacted], K.; 1997, included in the Baseline Dossier were regarded as relevant for the evaluation of a potential entry into the air. The study by [redacted], E.; 1995, belongs to next Section CA 7.3.1.

Author(s)	Year	Document No.
[redacted], J. *	1996	M-000646-01-1
[redacted], K.	1997	M-000681-01-1

*: This information is filed in the phys.-chem. section, also.

EU Conclusions of studies by [redacted], J.; 1996, [redacted], K.; 1997, and [redacted], E.; 1995

Sufficient information has been submitted regarding the fate and behaviour of YRC 2894 in air to show that volatilisation is not expected to be significant.

It was concluded that Thiacloprid has a low vapour pressure (extrapolated with 3 x 10^{-10} Pa at 20 °C) and a low Henry's Law Constant (calculated with 5 x 10^{-10} Pa m^3 mol^{-1} at 20°C), indicating a low volatility of the active substance from aqueous solutions, soil and water.

Volatilisation from soil and plant surfaces was studied under field conditions in three independent trials of 24 hour duration after spray application of [methylene-^{14}C]-YRC 2894, formulated as SC 480. The three experiments contrasted in that no loss of radioactivity was noted for the first trial. The average measured loss of radioactivity for the two remaining trials was 26% (average of 15% when considering the three trials). The measured volatilisation rate from soil (12% of intercepted radioactivity) was slightly lower than that from plants (15% of intercepted radioactivity). However, it should be noted that such values were resulting from indirect measurements of remaining residues, not from direct measurements of the gaseous phase.

A theoretical Atkinson calculation of the potential for photo-oxidation of YRC 2894 led to a short DT_{50} value in the lower atmosphere of 1.5 hours.

According to before-mentioned results, a significant entry of Thiacloprid residues into the air, accumulation or long-range transport in the air and subsequent contamination of the environment by wet or dry deposition are not to be expected.

CA 7.3.1 Route and rate of degradation in air

Route and rate of degradation of degradation of Thiacloprid in air was evaluated during the Annex I inclusion (compare EU Monograph Annex B8), and was accepted by the European Commission (SANCO/4347/2000 – Final; 13 May 2004). The following study included in the Baseline Dossier was regarded as relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted], E.	1995	M-000641-01-1

Summary of study by [redacted], E.; 1995

A theoretical Atkinson calculation of the potential for photo-oxidation of YRC 2894 led to a quite short DT_{50} value in the lower atmosphere of 1.5 hours. Therefore accumulation or long-range transport in the air and subsequent contamination of the environment by wet or dry deposition are not to be expected.

No new studies are submitted within Supplemental Dossier for the Thiacloprid renewal of approval.

CA 7.3.2 Transport via air

According to the before mentioned properties long-range transport of Thiacloprid residues in the air and a subsequent contamination by wet or dry deposition are not to be expected.

No new studies are submitted within Supplemental Dossier for the Thiacloprid renewal of approval.

CA 7.3.3 Local and global effects

Local and global effects of Thiacloprid are not to be considered since the half-life of its residues in air is << 2 days (see section CA 7.3.1).

No new studies are submitted within Supplemental Dossier for the Thiacloprid renewal of approval.

CA 7.4 Definition of the residue

CA 7.4.1 Definition of the residue for risk assessment

The proposed residue definitions relevant for exposure assessments, which can be used as basis for risk assessments in each compartment, are the following:

Compartment	Residue Definition
Soil	Thiacloprid (YRC 2894) YRC 2894-amide, M02 YRC 2894-des-cyano, M29 YRC 2894-sulfonic acid, M30
Groundwater	Thiacloprid (YRC 2894) YRC 2894-amide, M02 YRC 2894-des-cyano, M29 YRC 2894-sulfonic acid, M30 YRC 2894-sulfonic acid amide, M34 YRC 2894-thiadiazine, M46
Surface water	Thiacloprid (YRC 2894) YRC 2894-amide, M02 YRC 2894-des-cyano, M29 YRC 2894-sulfonic acid, M30
Sediment	Thiacloprid (YRC 2894)
Air	Thiacloprid (YRC 2894)

CA 7.4.2 Definition of the residue for monitoring

For the compartments soil, groundwater, surface water, sediment and air the proposed residue definition for monitoring is Thiacloprid (YRC 2894).

CA 7.5 Monitoring data

No monitoring data of Thiacloprid (YRC 2894) were evaluated during the Annex I inclusion (compare EU Monograph Annex B8, and SANCO/4347/2000 – Final; 13 May 2004).

No respective monitoring data in published literature were to be considered for Thiacloprid in soil, ground/drinking water, sediment and air, and no new studies were performed with respect to monitoring of soil, surface water, ground/drinking water, sediment and air.

The following article found in published literature with respect to surface water was regarded relevant for inclusion and evaluation in the Baseline Dossier. It well confirmed the knowledge about fate and behaviour of Thiacloprid in the aquatic environment: If detected at all, the observed concentrations of Thiacloprid in surface water are expected to be very low.

Aquatic Compartment:

Report:	**KCA 7.5 /01; [redacted], D.; [redacted], W.; [redacted], J.; 2009**
Title:	Pesticide residues in surface water samples collected in area of intensive agricultural practice of the Wielkopolska province (2006-2007).
Source:	Proc. ECOpole, Volume 3, Issue 2, Page 445-449, Publication Year 2009
Document No:	M-460937-01-2
Guidelines:	None
GLP:	No, published study
Literature review classification:	b) supplementary information (EFSA Journal 2011; 9(2):2092)

EXECUTIVE SUMMARY

Samples of surface waters of intensively exploited arable lands in Wielkopolska province of Poland were collected in 2006 and 2007. Totally, 55 samples (30 and 25 in 2006 and 2007, resp.) from lakes (15 and 10 in 2006 and 2007, resp.), rivers (9 and 9 in 2006 and 2007, resp.) and ponds (6 and 6 in 2006 and 2007, resp.) were collected. The studies included 42 herbicides (and their metabolites), insecticides and fungicides popularly used in plants protection.

All selected pesticides were extracted from water samples by means of solid phase extraction (SPE, carbon black) followed by reverse phase ultra performance liquid chromatography with quadrupole mass detection (RP-UPLC-MS/MS). Of all samples, 43 (78.2%) were contaminated with residues of plant protection products used in intensive plant production.

Contamination with atrazine (60.0%), atrazine-desethyl (56.4%), carbendazim (45.4%), simazine (36.4%), atrazine-deisopropyl (34.5%), isoproturon (29.1%), and ethofumesate (21.8%) of the samples were mostly detected. Totally, twenty nine of forty two studied pesticides were found however, concentrations of their residues were very low, usually. The limit of quantification was between 0.01 to 0.05 µg/L.

The highest concentration was quantified for the triazine metabolite atrazine-desethyl (0.55 µg/L, pond, May 2007). All the pond water samples were contaminated by pesticide residues and the highest concentration was found in these samples.

In the river water samples pesticide residues were detected only occasionally and on the very low level (0.01 to 0.04 µg/L).

Findings (of Thiacloprid)

Thiacloprid was detected in pond water just at the LOD of 0.01 µg/L, thus below the limit of quantification. The number of detects was not given in the article.

Conclusion:

If detected at all, the observed concentrations of Thiacloprid in surface water (pond and river water) of a pesticide use area of Poland were very low.