ANNEX B

Clothianidin

ADDENDUM
Report on potentially harmful or unacceptable effects
(August 2012)

(B.8 Environmental fate and behaviour & B.9 Ecotoxicology)

Rapporteur Member State: Belgium

TABLE OF CONTENT

A. Introduction

The active substance Clothianidin was included in Annex I of Council Directive 91/414/EEC on 1 August 2006 by entry into force of Commission Directive 2006/41/EC of 7 July 2006.

On 12 October 2011, Sumitomo Chemical Agro Europe S.A.S (who was the sole data submitter supporting Annex I inclusion of clothianidin), supported by Bayer CropScience, notified the RMS Belgium according to Article 56 of Regulation 1107/2009 that following the generation of a new time dependant sorption study performed by Bayer CropScience, a new metabolite (TZFA) has been observed > 5% in one of the 4 tested soils, and that another already identified metabolite (TZMU) previously observed at levels < 5% reached the level of 10.6% in the same soil.

These results were notified according to Article 56 of Regulation 1107/2009 without the groundwater risk assessment for metabolites as at that time the degradation and adsorption studies were not finalised.

On 13 March 2012, Sumitomo Chemical Agro Europe S.A.S together with Bayer CropScience submitted to RMS Belgium six new studies addressing the groundwater risk assessment for the metabolites TZFA and TZMU.

In the following, RMS assesses these new studies and the corresponding risk assessment.

B. Evaluation and risk assessment

B.8 Environmental fate and behaviour

B.8.1.1 Route of degradation (Annex IIA 7.1.1.1)

B.8.1.1.1 Aerobic degradation in soil (Annex IIA 7.1.1.1.1)

Background

During the performance of a new study (5.1.2.e WOO , 2011) to further investigate the time dependant sorption behaviour of clothianidin in soil, Bayer CropScience identified some differences to the previously described route of degradation of clothianidin in aerobic soil. As result, the following significant findings were noted:

- Identification of a new soil metabolite TZFA (N-[(2-chloro-1,3-thiazol-5-yl)methyl]-N'-methylimidoformamide) at amounts of up to 6.7% in one soil at day 35 and decreasing to the end of the study. The maximum in the three other soils was <3%.
- Increase in the amount of TZMU (1-(2-chloro-1,3-thiazol-5-ylmethyl)-3-methyl-urea) formed, the maximum amount of TZMU increased to 10.6% on day 9 of the study in one soil. Maximum in the other soils was 5.9%. In the previous studies TZMU was detected at a maximum of < 5%.

The results and the assessment by RMS of this new study are reported below.

Report:	5.1.2.e WOO (2011): [Guanidine-^{14}C] Clothianidin: Time dependent Sorption from Four European Field Dissipation Soils. Report No. MEF-10/563. SCC. Study Number M-131 1911-7, 11 April 2011.
Guidelines:	OECD guideline 106, Adsorption/desorption, 2001 (in parts) OECD guideline 307, Aerobic and Anaerobic Transformation in Soil, 2002 (in parts)
GLP:	Yes

<u>Materials and methods:</u>

Test substance:

[Guanidine-^{14}C] Clothianidin (radiochem purity >98%); site of radiolabel see* in Figure B.8.1.1.1-1.

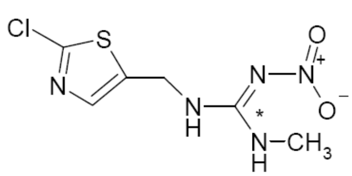


Figure B.8.1.1.1-1: [Guanidine-^{14}C] Clothianidin

Soils:

Table B.8.1.1.1-1: Characteristics of the soils

Parameter	**Results/Units**			
Soil / Batch ID	**Hoefchen am Hohenseh plot 4011 (20090903)**	**Wellesbourne (20090918)**	**Mas du Coq (20090831)**	**Vilobi d'Onyar (20090918)**
Soil Taxonomic Classification (USDA)	(N/A)	(N/A)	(N/A)	(N/A)
Soil Series	(N/A)	(N/A)	(N/A)	(N/A)
Texture Class[A]	Silt Loam	Sandy Loam	Clay Loam	Sandy Loam
Sand[A] Silt[A] Clay[A]	22% 54% 24%	72% 12% 16%	20% 50% 30%	54% 32% 14%
pH in water: in $CaCl_2$: in KCl:	5.9 5.7 5.2	6.3 6.1 5.7	7.7 7.7 7.5	6.2 6.1 5.6
Organic Matter[B]	1.9%	1.4%	1.4%	1.4%
Organic Carbon[C]	1.1%	0.8%	0.8%	0.8%
Initial & Final Soil Biomass or Microbial Activity [mg microbial C /kg dry wt]	341	176	129	290
Cation Exchange Capacity (CEC)	12.2 meq/ 100 g	9.3 meq/ 100 g	11.2 meq/ 100 g	8.0 meq/ 100 g
Water Holding Capacity at 0.33 bar	16.3%	7.9%	17.7%	11.1%
WHCmax (g H_2O/ 100 g soil dry wt)	55.1 g	38.9 g	39.9 g	33.5 g
Bulk Density (disturbed)	1.1 g/mL	1.31 g/mL	1.19 g/mL	1.33 g/mL

[A]) According to USDA classification
[B]) Calculated: Organic matter = organic carbon * 1.724
[C]) Determination method: Combustion

Experimental design:

The time-dependent sorption of [Guanidine-^{14}C] Clothianidin was studied in four soils as reported in Table B.8.1.1.1-1 for 120 days under aerobic conditions in the dark at 20°C and about 55% WHCmax. Clothianidin was applied at a rate of 20 µ a.s./100 g dry soil, equivalent to approx. 150 g a.s/ha assuming a soil density of 1.5 g/cm³ and a soil depth of 5 cm. The study was based in principle on OECD Guideline 307 and for respective sorption parts on OECD Guideline 106.
The test system consisted of biometer-type flasks with traps for the collection of CO_2 and volatile organic compounds. The soil samples were incubated as replicates. In order to determine the sorption behavior, the treated soils were shaken with 0.01 M $CaCl_2$ solution for 24h. The suspensions were centrifuged and the supernatants were analysed separately. Then, the soil samples were extracted four times at ambient temperature with 80 mL

acetonitrile/water (50/50, v/v, ambient extracts). With respect to the fast formation of non-extractable residues, the extraction was repeated once at an elevated temperature in microwave (aggressive extracts). The $CaCl_2$-exctracts as well as the ambient and aggressive organic extracts were analyzed by LSC and radio-HPLC. Identification of the transformation products was achieved by LC-MS/MS experiments and/or Co-chromatography. TLC analysis of selected samples was used to confirm the results.

With regard to the pesticide use history of the sites where the soils were sampled, there is no information for the sites Hoefchen am Hoshenseh and Vilobi d'Onyar. For sites Wellesbourne and Mas du Coq, no use of pesticide was done for at least 3 years.

Findings:

The results of the recovery and distribution of the compounds are reported in Table B.8.1.1.1-2 to Table B.8.1.1.1-5.

Table B.8.1.1.1-2: recovery of radioactivity and distribution of the active substance and metabolites after application of [Guanidine-^{14}C] Clothianidin in soil Hoefchen am Hohenseh, 2 replicates

		DAT											
Compound		**0**	**1**	**3**	**9**	**21**	**28**	**35**	**49**	**63**	**77**	**98**	**120**
Clothianidin	Mean	96.9	86.0	77.8	51.1	36.9	36.6	30.9	29.4	26.9	26.9	22.2	21.5
	SD	±0.6	±0.6	±0.6	±0.0	±1.3	±1.1	±1.1	±0.1	±0.6	±0.6	±0.2	±1.1
TZNG	Mean	n.d.	n.d.	0.0	0.1	0.5	0.5	0.6	0.8	0.8	1.0	1.0	1.1
	SD			±0.0	±0.1	±0.0	±0.0	±0.1	±0.1	±0.1	±0.0	±0.1	±0.0
MNG	Mean	n.d.	0.5	1.3	2.5	3.1	3.6	4.7	4.8	4.8	5.6	4.5	6.4
	SD		±0.1	±0.2	±0.1	±0.0	±0.0	±0.1	±0.4	±0.3	±0.3	±0.7	±0.0
TZMU	Mean	0.5	2.3	6.2	10.6	6.9	5.4	4.2	2.9	2.2	2.1	1.4	1.2
	SD	±0.0	±0.0	±0.3	±0.0	±0.4	±0.0	±0.1	±0.1	±0.3	±0.0	±0.0	±0.0
TMG	Mean	n.d.	0.1	0.3	0.6	0.6	0.8	0.8	0.7	0.6	0.8	0.6	0.5
	SD		±0.1	±0.0	±0.0	±0.0	±0.0	±0.1	±0.2	±0.0	±0.1	±0.1	±0.1
NTG	Mean	n.d.	0.1	<LOQ	0.0	0.2	0.2	0.8	0.6	1.5	1.5	2.8	2.2
	SD		±0.0		±0.0	±0.0	±0.0	±0.0	±0.1	±0.1	±0.2	±0.6	±0.1
TZFA	Mean	n.d.	0.8	1.8	4.2	5.3	4.9	6.7	4.3	5.0	4.0	4.6	3.8
	SD		±0.0	±0.0	±0.5	±0.0	±0.8	±0.1	±0.6	±0.5	±0.1	±0.3	±0.1
Unidentified	Mean	1.6	2.2	1.8	2.4	1.9	1.7	1.3	1.7	1.5	0.8	1.4	1.1
radioactivity	SD	±0.4	±0.1	±0.1	±0.2	±0.6	±0.1	±0.0	±0.3	±0.3	±0.0	±0.3	±0.1
Total	Mean	99.0	92.0	89.2	71.4	55.2	53.8	49.8	45.2	43.4	42.7	38.4	37.7
extractable res.	SD	±0.9	±0.2	±1.0	±0.9	±0.4	±0.4	±1.0	±0.5	±0.8	±0.7	±0.0	±0.7
$^{14}CO_2$	Mean	n.a.	0.2	0.8	4.4	13.1	15.5	18.3	21.5	23.7	25.5	28.2	29.3
	SD		±0.0	±0.0	±0.1	±0.3	±0.4	±0.1	±0.1	±0.1	±0.1	±0.1	±0.1
Volatile	Mean	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2
organics	SD												±0.2
Non-extractable	Mean	3.0	6.1	9.6	22.5	29.6	29.6	29.8	30.0	30.8	31.5	30.7	30.8
residues	SD	±0.1	±0.3	±0.5	±0.1	±0.8	±0.1	±0.4	±0.0	±0.1	±0.4	±0.3	±0.1
Total %	Mean	101.9	98.3	99.6	98.2	98.0	98.9	98.0	96.7	97.9	99.8	97.3	97.9
recovery	SD	±1.0	±0.1	±0.5	±0.8	±0.1	±0.1	±0.5	±0.3	±0.8	±1.2	±0.2	±0.2

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

Table B.8.1.1.1-3: recovery of radioactivity and distribution of the active substance and metabolites after application of [Guanidine-^{14}C] Clothianidin in soil Wellesbourne, 2 replicates

Compound	Replicate No.	DAT 0	1	3	9	21	28	35	49	63	77	98	120
Clothianidin	Mean	99.8	91.7	88.6	75.8	64.5	64.7	61.6	58.5	53.8	53.2	48.4	46.2
	SD	±0.7	±0.3	±0.8	±0.3	±1.5	±0.4	±0.0	±0.2	±1.3	±0.1	±0.4	±0.2
TZNG	Mean	n.d.	0.0	0.0	0.2	1.1	1.7	2.0	2.1	2.3	2.7	2.9	3.0
	SD		±0.0	±0.0	±0.1	±0.1	±0.0	±0.0	±0.1	±0.0	±0.1	±0.1	±0.3
MNG	Mean	n.d.	0.6	0.8	2.2	4.0	3.9	4.7	5.7	5.4	6.8	5.6	6.4
	SD		±0.2	±0.1	±0.0	±0.3	±0.3	±0.0	±0.2	±0.1	±0.4	±0.5	±0.2
TZMU	Mean	n.d.	0.9	3.0	5.9	5.1	3.0	2.5	2.1	1.7	1.5	1.0	1.0
	SD		±0.0	±0.3	±0.2	±0.9	±0.3	±0.0	±0.0	±0.1	±0.0	±0.0	±0.1
TMG	Mean	n.d.	0.0	0.1	0.1	0.2	0.3	0.3	0.1	0.1	n.d.	0.2	0.1
	SD		±0.0	±0.1	±0.1	±0.0	±0.0	±0.0	±0.1	±0.1		±0.1	±0.0
NTG	Mean	n.d.	n.d.	0.1	0.1	0.1	0.3	0.6	1.2	1.7	1.4	2.5	3.1
	SD			±0.1	±0.1	±0.0	±0.2	±0.0	±0.2	±0.2	±0.1	±0.1	±0.4
TZFA	Mean	n.d.	n.d.	0.4	1.9	2.8	2.1	2.7	2.0	2.6	1.9	1.9	1.5
	SD			±0.3	±0.0	±0.4	±0.3	±0.2	±0.2	±0.2	±0.1	±0.2	±0.2
Unidentified	Mean	2.3	1.6	1.5	1.1	1.5	0.5	1.0	0.4	1.3	0.7	1.3	0.5
radioactivity	SD	±0.3	±0.2	±0.6	±0.0	±0.0	±0.2	±0.2	±0.1	±0.2	±0.3	±0.2	±0.1
Total	Mean	102.0	94.8	94.5	87.4	79.4	76.5	75.5	72.1	68.9	68.4	63.8	61.8
extractable res.	SD	±0.4	±0.3	±1.1	±0.1	±0.0	±0.9	±0.0	±0.8	±1.0	±0.1	±0.3	±0.1
$^{14}CO_2$	Mean	n.a.	0.2	0.3	2.0	5.9	7.3	8.2	10.6	12.3	13.1	14.8	16.2
	SD		±0.0	±0.0	±0.0	±0.1	±0.1	±0.0	±0.2	±0.0	±0.2	±0.2	±0.2
Volatile	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
organics	SD												
Non-extractable	Mean	2.2	3.5	4.7	10.8	14.6	15.5	16.0	17.0	18.8	19.4	19.9	20.2
residues	SD	±0.1	±0.2	±0.2	±0.0	±0.2	±0.4	±0.2	±0.2	±0.0	±0.1	±0.1	±0.1
Total %	Mean	104.2	98.4	99.6	100.2	99.9	99.3	99.7	99.8	100.0	100.8	98.5	98.2
recovery	SD	±0.3	±0.4	±1.2	±0.1	±0.3	±0.6	±0.2	±0.9	±1.0	±0.2	±0.3	±0.1

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

Table B.8.1.1.1-4: recovery of radioactivity and distribution of the active substance and metabolites after application of [Guanidine-^{14}C] Clothianidin in soil Mas Du Coq, 2 replicates

		DAT											
Compound		0	1	3	9	21	28	35	49	63	77	98	120
Clothianidin	Mean	99.2	94.4	91.0	87.8	80.6	77.6	75.8	72.6	70.2	70.1	63.4	60.8
	SD	±0.3	±0.4	±0.8	±0.6	±1.2	±0.5	±0.2	±0.8	±0.6	±0.7	±0.7	±0.5
TZNG	Mean	n.d.	n.d.	n.d.	0.1	0.7	1.0	0.9	1.3	1.6	1.8	2.0	2.1
	SD				±0.0	±0.1	±0.0	±0.0	±0.2	±0.1	±0.2	±0.2	±0.1
MNG	Mean	n.d.	0.4	0.3	0.9	2.2	2.5	3.5	4.0	2.9	5.2	3.9	5.3
	SD		±0.1	±0.3	±0.0	±0.1	±0.4	±0.1	±0.0	±0.0	±0.7	±0.5	±0.2
TZMU	Mean	n.d.	0.8	1.8	2.2	1.8	1.8	1.8	1.7	1.6	1.5	1.5	1.2
	SD		±0.2	±0.0	±0.2	±0.2	±0.0	±0.0	±0.0	±0.1	±0.1	±0.2	±0.2
TMG	Mean	n.d.	n.d.	0.0	0.0	0.1	0.0	0.2	0.1	0.2	0.1	0.3	0.2
	SD			±0.0	±0.0	±0.1	±0.0	±0.1	±0.1	±0.2	±0.1	±0.0	±0.1
NTG	Mean	n.d.	0.2	0.1	0.1	n.d.	0.2	0.2	0.2	2.1	0.2	2.1	0.9
	SD		±0.2	±0.1	±0.1		±0.2	±0.2	±0.2	±0.0	±0.1	±0.2	±0.0
TZFA	Mean	n.d.	n.d.	0.1	0.7	0.4	0.4	0.6	0.2	0.1	n.d.	0.3	0.0
	SD			±0.1	±0.1	±0.1	±0.0	±0.1	±0.0	±0.1		±0.1	±0.0
Unidentified	Mean	1.8	1.6	1.8	1.2	1.0	1.4	1.3	1.3	0.9	1.2	0.8	0.8
radioactivity	SD	±0.2	±0.5	±0.2	±0.2	±0.2	±0.4	±0.5	±0.4	±0.4	±0.3	±0.0	±0.0
Total	Mean	101.0	97.3	95.0	93.2	86.8	84.8	84.2	81.6	79.5	80.1	74.2	71.2
extractable res.	SD	±0.5	±1.4	±0.2	±0.5	±0.5	±0.5	±0.5	±0.1	±0.1	±1.2	±0.2	±0.2
$^{14}CO_2$	Mean	n.a.	0.1	0.2	0.7	2.0	3.0	3.5	4.8	5.8	6.8	8.3	9.4
	SD		±0.0	±0.0	±0.0	±0.1	±0.1	±0.0	±0.0	±0.0	±0.0	±0.1	±0.2
Volatile	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
organics	SD												
Non-extractable	Mean	2.4	2.9	4.2	6.4	9.7	10.2	11.2	12.2	13.9	15.5	16.5	18.1
residues	SD	±0.2	±0.1	±0.1	±0.0	±0.0	±0.1	±0.0	±0.0	±0.1	±0.0	±0.0	±0.1
Total %	Mean	103.4	100.3	99.4	100.3	98.5	98.1	99.0	98.6	99.2	102.4	99.1	98.7
recovery	SD	±0.7	±1.5	±0.1	±0.5	±0.6	±0.5	±0.5	±0.0	±0.1	±1.2	±0.5	±0.1

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

Table B.8.1.1.1-5: recovery of radioactivity and distribution of the active substance and metabolites after application of [Guanidine-^{14}C] Clothianidin in soil Vilobi d'Onyar, 2 replicates

		DAT											
Compound		0	1	3	9	21	28	35	49	63	77	98	120
Clothianidin	Mean	99.1	93.5	89.3	81.7	71.1	70.3	67.9	64.0	61.5	59.5	53.5	51.6
	SD	±0.9	±0.6	±1.5	±0.7	±0.1	±0.1	±0.7	±0.4	±0.1	±0.7	±0.1	±0.5
TZNG	Mean	n.d.	0.0	n.d.	0.2	0.7	0.9	1.1	1.7	1.5	1.9	1.7	1.9
	SD		±0.0		±0.0	±0.1	±0.1	±0.1	±0.2	±0.1	±0.0	±0.0	±0.2
MNG	Mean	n.d.	0.2	0.6	1.5	2.4	3.0	3.6	4.0	2.9	4.3	4.5	3.8
	SD		±0.1	±0.0	±0.1	±0.1	±0.1	±0.4	±0.1	±0.3	±0.0	±0.1	±0.1
TZMU	Mean	0.1	0.7	2.5	4.5	2.9	2.4	2.1	2.0	1.7	1.5	1.2	1.1
	SD	±0.1	±0.0	±0.5	±0.2	±0.2	±0.1	±0.2	±0.1	±0.3	±0.1	±0.0	±0.1
TMG	Mean	n.d.	n.d.	0.1	0.1	0.2	0.2	0.3	0.3	0.4	<LOQ	0.1	0.2
	SD			±0.1	±0.1	±0.0	±0.1	±0.0	±0.1	±0.1		±0.0	±0.1
NTG	Mean	n.d.	n.d.	0.1	0.0	0.1	0.4	0.9	1.3	3.2	2.1	2.8	3.5
	SD			±0.1	±0.0	±0.1	±0.1	±0.2	±0.1	±0.2	±0.1	±0.1	±0.1
TZFA	Mean	n.d.	n.d.	0.3	1.1	1.0	1.2	1.0	1.3	1.2	0.7	1.2	0.9
	SD			±0.1	±0.2	±0.1	±0.1	±0.0	±0.2	±0.1	±0.0	±0.1	±0.1
Unidentified	Mean	1.6	2.1	1.5	1.5	0.8	1.5	0.6	0.5	0.6	1.5	0.4	0.7
radioactivity	SD	±0.2	±0.1	±0.4	±0.1	±0.1	±0.1	±0.0	±0.1	±0.2	±0.3	±0.1	±0.2
Total	Mean	100.9	96.5	94.3	90.7	79.1	79.8	77.5	75.1	72.9	71.4	65.4	63.6
extractable res.	SD	±1.2	±0.6	±0.5	±0.3	±0.0	±0.5	±0.3	±0.2	±0.3	±0.3	±0.2	±0.6
$^{14}CO_2$	Mean	n.a.	0.2	0.3	1.7	5.1	6.6	7.9	9.9	11.4	12.9	14.7	15.9
	SD		±0.0	±0.0	±0.0	±0.1	±0.0	±0.0	±0.2	±0.1	±0.1	±0.1	±0.3
Volatile	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
organics	SD												
Non-extractable	Mean	2.3	3.2	5.3	8.8	13.8	13.5	14.3	15.1	16.3	17.7	19.1	19.8
residues	SD	±0.4	±0.1	±0.3	±0.3	±0.3	±0.2	±0.2	±0.3	±0.0	±0.1	±0.3	±0.2
Total %	Mean	103.1	99.9	100.0	101.2	98.0	100.0	99.7	100.1	100.6	101.9	99.2	99.3
recovery	SD	±0.8	±0.7	±0.2	±0.0	±0.2	±0.7	±0.6	±0.1	±0.4	±0.1	±0.5	±0.7

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

The proposed metabolic pathway in soil under aerobic conditions is shown in Figure B.8.1.1.1-2.

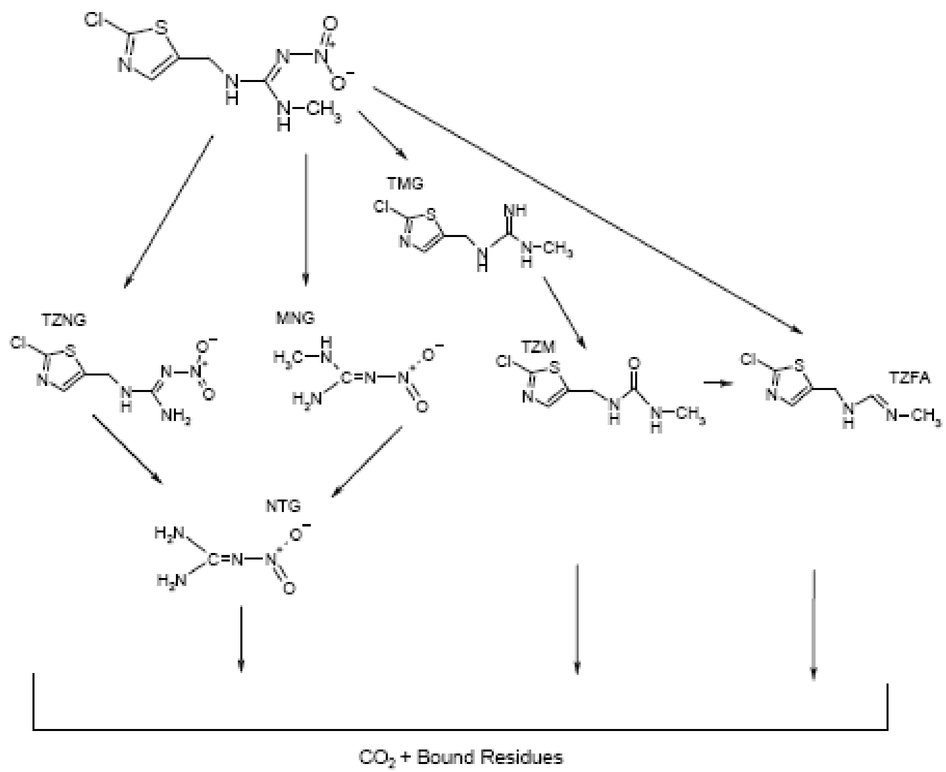


Figure B.8.1.1.1-2: proposed metabolic pathway of clothianidin in soil under aerobic conditions

Note: metabolite TZM should be read metabolite TZMU

Conclusion:

The material balances ranged from 96.7% up to 104.2%. Only the results of the aerobic degradation step are reported. The results show that a new soil metabolite TZFA (N-[(2-chloro-1,3-thiazol-5-yl)methyl]-N'-methylimidoformamide) was identified at amounts of up to 6.7% in one soil, and that the already known TZMU metabolite increased to 10.6% in one soil instead of maximum of < 5% in the previous studies performed for the Annex I inclusion of the active substance to the directive 91/414/EEC. The study is acceptable.

Report:	5.1 2 e WOO (2011): BCS-CQ88479 (Clothianidin-TZFA) Degradation Rate in Three Soils Incubated Under Aerobic Conditions, Report No. 105 01 023, SCC Report No. THM-0063
Guidelines:	Council Directive 91/414/EEC; Annex II, 7.1.1.1.1 & 7.1.1.2.1 OECD guideline 307, Aerobic and Anaerobic Transformation in Soil, 2002
GLP:	Yes

This study aims to investigate the rate of degradation of the new soil metabolite TZFA in three soils.

<u>Materials and methods:</u>

Test substance:

N-({[(2-chloro-1,3-thiazol-5-yl)methyl]amino}methylene)methanaminium chloride, also named TZFA (purity 92%) ; see Figure B.8.1.1.1-3

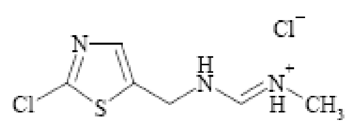


Figure B.8.1.1.1-3: test item

Soils:

Table B.8.1.1.1-6: Characteristics of the soils

	Soils		
Parameter	Wurmwiese (soil I)	Hoefchen am Hohenseh (soil II)	Dollendorf II (soil III)
Texture class (USDA)	Loam	Silt loam	Clay loam
Sand (%)	51	25	35
Silt (%)	33	59	35
Clay (%)	16	16	30
pH in water	5.2	6.6	7.2
pH in CaCl2	4.9	6.4	7.1
pH in KCl	4.5	6.1	6.8
Organic Matter	3.1	4.1	7.2
Organic Carbon	1.8	2.3	4.2
Initial Soil Biomass (mg microbial C/kg dry wt)	436	687	2309
Final Soil Biomass (mg microbial C/kg dry wt)	913	1110	1155
CEC	10.3	14	17
WHCmax (g water at 100 g DM)	54.8	63	83
Bulk density (disturbed)	1.13	1.1	0.99

Experimental design:

The rate of degradation of the test item TZFA was investigated in three soils as reported in Table B.8.1.1.1-6, for 120 days under aerobic conditions in the dark at 20°C and about 55% WHCmax. Prior to treatment, the soils were pre-incubated at those conditions for 10 days. The soils were collected from different agricultural areas where no pesticide treatments occurred during the last five years. TZFA was applied at a rate of 10 µ a.s./100 g dry soil, equivalent to approx. 100 g/ha in the field. The test system consisted of all-glass metabolism flasks in open gas-flow systems, where samples were ventilated with moistened air. The soil samples were incubated as replicates. Samples were removed for analysis at different times as indicated in Table B.8.1.1.1-7. The soil samples were extracted three times successively with acetonitrile/0.5 M aqueous acetic acid (4:1 v/v) followed by LC-MS/MS analysis of the combined extracts for determination of residues of TZFA. The efficiency of the analytical method for determination of TZFA in the presence of soil matrix was confirmed at each sampling interval by concurrent recoveries, i.e. the fortification of incubated, but untreated soil samples at different concentrations ranging from 8 µ test item/kg soil (8% of initial) to 90 µ/kg (90% of initial). Furthermore, blank extracts were generated consisting of untreated soil that was extracted and the extracts processed like treated samples. The test item TZFA was added at a defined concentration to the extracts and analysed by LC/MS. Stability test showed that the test item in extracts is stable for at least four months of storage under frozen conditions.

<u>Findings:</u>

While concurrent recoveries of fortified samples were in the acceptable range for most sampling intervals (from 72% to 107% for soil I, from 74% to 96% for soil II, and from 71% to 89% for soil III), lower ones were observed at days 28 and 60 for soil I, at days 60 and 120 for soil II, and at days 28, 60 and 120 for soil III. Analysis was repeated to result in confirmation of lower recoveries at those sampling intervals. The results of all sampling intervals were therefore corrected by concurrent recoveries from fortified samples generated the same day.

Recoveries of fortified extracts were stated to be between 85.5% and 111.8%.

All soils showed significant microbial activity throughout the study. The LOQ of the test item corresponded to the lowest point in the calibration curve (i.e. 0.0005 µg/mL).

Table B.8.1.1.1-7: degradation of TZFA in the different soils – values given in percent of the applied amount

Time (days)	Wurmwiese (soil I)	Hoefchen am Hohenseh (soil II)	Dollendorf II (soil III)
0	99.5	102.2	104.6
0	100.5	97.8	95.4
3	91.9	88.9	94.5
3	96.1	85.5	88.7
7	86.4	72.8	71.7
7	84.1	71.2	71.8
14	76.8	62.2	66.7
14	76.3	63.8	58.6
28	68.3	45.6	23.9
28	63.9	46.5	24.1
60	53.5	18.9	6.3
60	56.8	18.1	4.6
91	38.1	14.3	2.4
91	44.2	16.1	2.6
120	31.9	10.6	1.6
120	32.1	10.4	1.2

Additionally, the author of the study carried out a kinetic analysis according to FOCUS (2006). The details of the kinetic evaluation for metabolite TZFA are reported in Appendix E.1. SFO fits visually and statistically acceptable. SFO DT50 and DT90 are reported in Table B.8.1.1.1-8 for the three tested soils.

Table B.8.1.1.1-8: Statistical summary of degradation data of SFO fit for metabolite TZFA

Soils	***M0***	***k***	***Prob > t****	***SFO DT50***	***SFO DT90***	***χ^2 error***
Wurmwiese	93.7	0.0095	2 e^{-16}	73.3	243.7	4.8
Hoefchen am Hosenseh	93.6	0.0254	2.3e^{-9}	27.3	90.8	7.2
Dolledendorf II	102.2	0.0445	3.1e^{-10}	15.6	51.8	6.9

* In order to assess the fitted degradation rates as statistically acceptable, Prob > t (i.e the p-value) should be < 0.05

5.1 2.e WOO (2012a) re-assessed the kinetic parameters of the soil Hoefchen am Hosenseh (see section B.8.6.1 for the assessment of this study). For this soil, the overall goodness of fit for SFO would be sufficient. However, for the last two sampling times, the residues are underestimated. Therefore SFO was considered not acceptable. The DFOP fit improved the goodness of fit substantially and also the later residues were much better represented. Therefore DFOP was selected as appropriate model for groundwater modelling purposes.

<u>Conclusion:</u>

The rate of degradation of the metabolite TZFA was investigated in three different soils under aerobic conditions in the dark at 20°C. TZFA was degraded in soils Wurmwiese, Hoefchen am Hosenseh and Dolledendorf II with SFO DT_{50} of 73.3, 27.3 and 15.6 days, respectively. With regard to the soil Hoefchen am Hosenseh, using the DT_{50} of the slowest phase of the

DFOP kinetic, the DT_{50} becomes 34.4 days. Therefore, the geomean SFO DT_{50} becomes 34.0 days (n=3). The study is acceptable.

B.8.2 Adsorption, desorption and mobility in soil (Annex IIA 7.1.2 and 7.1.3 ; Annex IIIA 9.1.2)

B.8.2.1 Adsorption and desorption of the active substance and relevant metabolites (Annex IIA 7.1.2)

Report:	5.1.2.e WOO (2011) [Imidoformamide-^{14}C] BCS-CQ88479: Adsorption/desorption in five different soils, AgroScience GmbH Report No. AS157
Guidelines:	EC, Commission Directive 95/36/EC Amending Council Directive 91/414/EEC (Annexes II + III, Fate and Behavior in the Environment) July 14, 1995 OECD Guideline for Testing of Chemicals, No 106 “Adsorption/Desorption”, Jan. 21, 2000 US EPA, Fate, Transport and Transformation Test Guidelines OPPTS 835.1220 Sediment and Soil Adsorption/Desorption Isotherm Canada Pest Management Regulatory Agency (PMRA), Environmental Chemistry and Fate, Guidelines for Registration of Pesticides in Canada, 1987
GLP:	Yes

This study aims to investigate the adsorption/desorption characteristics of the new soil metabolite TZFA in five soils.

<u>Materials and methods:</u>

Test substance:

^{14}C-labelled N-({[(2-chloro-1,3-thiazol-5-yl)methyl]amino}methylene)methanaminium chloride, also named TZFA (chemical and radiochemical purity > 98% by HPLC) ; specific activity 4.08 MBq/mg ; site of radiolabel see* in Figure B.8.2.1-1

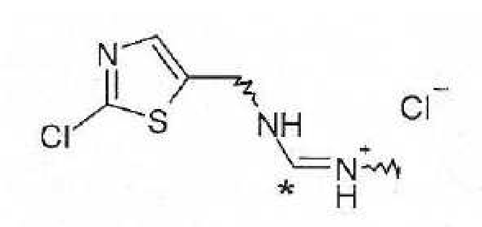


Figure B.8.2.1-1: test item

Soils:

The study included three soils sampled from European field sites (Germany) and two soils sampled from Northern American field sites (USA) see Table B.8.2.1-1.

Table B.8.2.1-1: Characteristics of the soils

	Soils				
Parameter	Wurmwiese, Germany (soil I)	Hoefchen am Hohenseh, Germany (soil II)	Dollendorf II, Germany (soil III)	Guadalupe, USA (soil IV)	Springfield, USA (soil V)
Texture class (USDA)	Loam	Silt loam	Clay loam	Sandy loam	Silt loam
Sand (%)	51	27	31	56	12.7
Silt (%)	28	54	38	32.6	60.8
Clay (%)	21	19	31	11.4	26.5
pH in water	5.5	6.8	7.4	6.8	7.2
pH in CaCl2	5.3	6.6	7.3	6.7	6.6
Organic Matter	3.03	4.17	8.14	1.1	2.9
Organic Carbon	1.76	2.42	4.72	0.7	1.7
CEC (meq/100 g soil)	10.8	13.9	21.9	16.1	16.1

Experimental design:

The adsorption/desorption characteristics of the TZFA metabolite were studied in five soils as reported in Table B.8.2.1-1, in batch equilibrium experiments. The adsorption phase of the study was carried out using pre-equilibrated air-dried soil with radiolabelled TZFA at nominal concentrations of 1.0, 0.3, 0.1, 0.03 and 0.01 mg/L, in the dark at 20°C for 24 hours. The equilibrium solution used was 0.01 M aqueous $CaCl_2$ solution with a soil to solution ratio of 1:10 for all soils (preliminary test were carried out with soil to solution ratio of 1:1, 1:2 and 1:10). 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, except for the highest concentration (1.0 mg/L), where three desorption cycles were performed. The aqueous supernatant after adsorption and desorption was separated by centrifugation and analysed by LSC. Soil extraction was carried out with ACN. Radioactivity remaining in the soil was quantified after combustion in a sample oxidiser. Samples without soil were used as control in preliminary test and did not show adsorption to the vessels or degradation. HPLC analysis of supernatants and soil extracts taken after 24, 48, 72, 96 and 120 hours in preliminary test, showed that the test item was stable in all soils.

Findings:

The parental Mass Balance after 24h, showed that 92.8-97.9% of applied radiolabeled TZFA could be recovered in the different soils.

The mass balance of the soils was determined by LSC of the supernatants after adsorption and desorption and by combustion of the remaining soils. The overall material balance for all concentrations for individual replicates was in the range of 94.3-96.9%, 92.3-95.5%, 78.2-93.9%, 93.7-96.2%, and 92.0-94.6% of the applied radioactivity in soils Wurmwiese, Hoefchen am Hohenseh, Dollendorf II, Guadalupe, Springfield, respectively.

In the definitive adsorption test 30.5-47.7%, 42.0-58.3%, 52.0-70.1%, 37.3-51.9%, and 69.7-81.7% of the applied test material was adsorbed in soils Wurmwiese, Hoefchen am Hohenseh, Dollendorf II, Guadalupe, Springfield, respectively. The calculated adsorption constants $K_F^{(ads)}$ of the Freundlich isotherms for the five test soils ranged from 4.5 mL/g to 20.7 mL/g. The corresponding organic carbon normalised adsorption coefficients $K_{F,OC}^{(ads)}$ ranged from 212 to 1216. The Freundlich exponents 1/n were in the range of 0.8546 to 0.8829.

At the end of one adsorption and one desorption phase, 34.3-45.3%, 26.8-37.9%, 18.0-32.1%, 27.2-38.0%, and 10.9-19.8% of the initially adsorbed amount were desorbed in soils Wurmwiese, Höfchen am Hohenseh, Dollendorf II, Guadalupe, Springfield, respectively. The desorption $K_F^{(des)}$ ranged from 7.3 to 28.3. The $K_{F,OC}^{(des)}$ ranged from 282.0 to 1661.8. The mean desorption $K_{F,OC}^{(des)}$ was therefore 1.5 times higher than those obtained for adsorption phase.

The Table B.8.2.1-2 summarizes the key soil properties and results of the study.

Table B.8.2.1-2: soil properties and adsorption characteristics of TZFA for the five tested soils

	Soils				
Parameter	Wurmwiese, Germany (soil I)	Hoefchen am Hohenseh, Germany (soil II)	Dollendorf II, Germany (soil III)	Guadalupe, USA (soil IV)	Springfield, USA (soil V)
Soil type (USDA)	Loam	Silt loam	Clay loam	Sandy loam	Silt loam
pH (0.01 M $CaCl_2$)	5.3	6.6	7.3	6.7	6.6
Organic carbon (%)	1.76	2.42	4.72	0.7	1.7
$K_F^{(ads)}$ (mL/g)	4.5	7.0	10.0	5.8	20.7
1/n	0.8719	0.8780	0.8546	0.8829	0.8730
$K_{F,OC}^{(ads)}$ (mL/g)	255.5	288.8	212.1	826.8	1216.3

Conclusion:

The adsorption/desorption characteristics of the TZFA metabolite were studied in five soils (three European soils and two Northern American soils). The $K_{F,OC}^{(ads)}$ ranged from 212.1 to 1216.3, with an arithmetic mean value of 559.9 mL/g. The $K_{F,OC}^{(des)}$ ranged from 282 to 1662. The study is acceptable.

B.8.6 Predicted Environmental Concentrations in surface water and in groundwater (PECsw, PECgw) (Annex IIIA 9.2.1, 9.2.3)

B.8.6.1 Predicted Environmental Concentrations in groundwater (PECgw) (Annex IIIA 9.2.1)

Report:	5.1.2.e WOO (2012a) Kinetic Evaluation of the Aerobic Metabolism of Clothianidin (TI 435), MNG, TZNG, TZMU, TZFA and NTG in Soil for Modelling Purposes Bayer CropScience Report No. MEF-11/1043
Guidelines:	FOCUS (2005) Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration – Report of the FOCUS Working Group on Degradation Kinetics. EC Document Reference Sanco/10058/2005 version 1.0
GLP:	Not applicable

The study aims to evaluate kinetically the aerobic degradation of clothianidin and its metabolites based on the laboratory study by 5.1.2.e WOO (2011). The degradation of TZFA in soils where TZFA was applied as test item in the study by 5.1.2.e WOO 2011) is also kinetically evaluated.

<u>Materials and methods:</u>

The aerobic degradation and Clothianidin and its soil metabolites MNG, TZNG, TZMU, TZFA and NTG was kinetically evaluated based on the laboratory study by 5.1.2.e WOO (2011) carried out on four soils conducted at a temperature of 20°C, and a soil moisture of 55% of the WHCmax. Additionnaly, the degradation of TZFA was kinetically evaluated from the separate study by Völkel (2011) where TZFA was applied as test item.

The kinetic evaluation was performed following the recommendations of FOCUS (2005) to derive degradation parameters for environmental fate modelling.

<u>*Data pre-processing of the data obtained in the study by Stupp and Unold (2011)*</u>

Before performing the kinetic evaluation, the data were pre-processed as follows. Single measured data were taken into account as reported (replicates). For all residues used for the kinetic evaluation, the following procedure was applied. Any non-detect (n.d.) directly before or after a value ≠ n.d. was set to 0.5 LOD (limit of detection). A LOD of 0.1 % applied radioactivity (AR) was adopted following 5.1.2.e WOO (2011). The limit of quantification (LOQ) was given as 0.3 % AR. Typically, values between LOD and LOQ were reported as analysed and used directly for the kinetic evaluation. Values reported as < LOQ were set to 0.5 × (LOD + LOQ). For metabolites of the compound incubated, the day zero value (days after treatment DAT = 0) was set to zero if the next value ≠ n.d. Additionally, the original experimental day zero value of the metabolite was added to the day zero value of the parent. The reason for this modification is that exactly at the time of application only parent can occur. The remaining n.d. values were excluded from the analysis.

Kinetic analysis

For the kinetic evaluation of the data, a compartment model was developed based on the results of the study by 5.1.2.e WOO (2011), see Figure B.8.6.1-1.

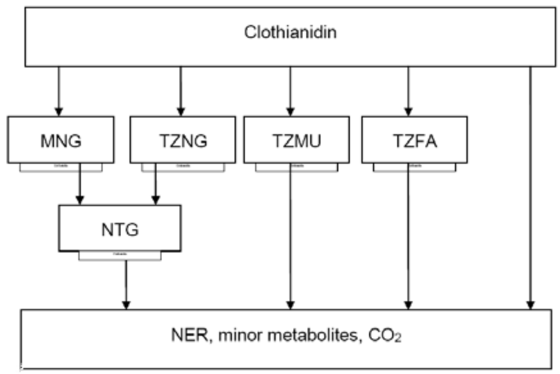


Figure B.8.6.1-1: Compartment model used for the kinetic analysis (based on the results of the study by 5.1.2.e WOO (2011))

The initial amount of the parent was fitted and the initial amount of the metabolites was set to 0 as recommended. All data belonging to one compound were equally weighted employing an iteratively reweighted least squares (IRLS) method (Gao et al., 2011).

First the parent was fitted to SFO. If the SFO fit was not acceptable, the DFOP model was tested as biphasic model. The FOMC model was not considered because the final residues were greater than 10% of the initial residues for all soils. For metabolites, only the SFO model was considered.

The goodness of fit was assessed by visual inspection and an error criterion based on the chi-square significance test ($\alpha = 0.05$). Significance of the parameters was tested using the single-slided T-test.

Findings:

Clothianidin

For clothianidin, a bi-phasic pattern of the degradation was observed for all four soils. The kinetic paramaters are reported in Appendix E.2.1. DFOP model was selected as appropriate model for clothianidin for all soils. Optimised degradation parameters of clothianidin in the soils studied by 5.1.2.e WOO (2011) are reported in the Table B.8.6.1-1. The fitted curves are presented in Appendix E.2.2.

Table B.8.6.1-1: optimised degradation parameters of clothianidin in the soils studied by 5.1.2.e WOO 2011)

Soil	Model	k_1 (1/days)	k_2 (1/days)	g	$DT50_1$ (days)	$DT50_2$ (days)
Hoefchen am Hohenseh	DFOP	0.1631	0.0070	0.554	4.2	99.1
Wellesbourne	DFOP	0.0932	0.0040	0.261	7.4	174.9
Mas du Coq	DFOP	0.3843	0.0035	0.080	1.8	196.7
Vilobi d'Onyar	DFOP	0.1324	0.0038	0.192	5.2	182.9
Geometric mean					4.1	158
Arithmetic mean				0.272		

MNG metabolite

The residues of MNG are relatively low in general (up to 6.8% AR). Therefore, the Chi² errors are relatively high (see Appendix E.2.1) although the absolute errors are small. Thus the 15% Chi² error criterion is not seen as crucial for MNG and the other metabolites as for the parent fits.

Table B.8.6.1-2: optimised degradation parameters of MNG in the soils studied by 5.1.2.e WOO (2011)

Soil	Model	DT50 (days)	$f_{clothianidin\_to\_MNG}$
Hoefchen am Hohenseh	SFO	n.a.	n.a.
Wellesbourne	SFO	138.5	0.174
Mas du Coq	SFO	178.2	0.174
Vilobi d'Onyar	SFO	77.9	0.154
Geometric mean		124.3	
Arithmetic mean			0.167

TZNG metabolite

The residues of TZNG are very low in general (up to 3% AR). Therefore, the Chi² errors are relatively high (see Appendix E.2.1) although the absolute errors are well below 1% AR in general. Though the fits for three of the four soils would be visually acceptable none can be accepted due to non-significance of the degradation rate. In all four soils, the behavior of the TZNG residues is similar. They are steadily increasing until the end of the study at day 120. Thus the potential degradation can not be identified from the data. Consequently, the statistical test qualifies the degradation as not significantly different from zero. The degradation parameters derived from a separate study with TZNG 5.1.2.e WOO 2000) are therefore used for the groundwater modeling purposes.

TZMU metabolite

The residues of TZMU reach up to 10.6% AR. The Chi² errors are all below 15% (see Appendix E.2.1) indicating a high goodness of fit. The residuals are well below 1% AR in general. In all four soils the behaviour of the TZMU residues is similar. After an immediate initial increase the residues peak around day 9. Then a phase with clear decline down to 1-2 % AR follows.

Table B.8.6.1-3: optimised degradation parameters of TZMU in the soils studied by 5.1.2.e WOO (2011)

Soil	Model	DT50 (days)	$f_{clothianidin\_to\_TZMU}$
Hoefchen am Hohenseh	SFO	11.4	0.316
Wellesbourne	SFO	6.9	0.544
Mas du Coq	SFO	12.9	0.301
Vilobi d'Onyar	SFO	8.1	0.416
Geometric mean		9.5	
Arithmetic mean			0.394

TZFA metabolite

The residues of TZFA are relatively low in general (up to 6.7% AR) similar to MNG. For three of the four soils, the Chi² errors are low (see Appendix E.2.1) indicating a high goodness of fit. This is due to very small absolute errors.

Table B.8.6.1-4: optimised degradation parameters of TZFA in the soils studied by 5.1.2.e WOO (2011)

Soil	Model	DT50 (days)	$f_{clothianidin\_to\_TZFA}$
Hoefchen am Hohenseh	SFO	90.9	0.103
Wellesbourne	SFO	40.1	0.115
Mas du Coq	SFO	n.a.	n.a.
Vilobi d'Onyar	SFO	44.8	0.059
Geometric mean		54.7	
Arithmetic mean			0.092

Kinetic parameters derived from the study by 5.1.2.e WOO (2011) where TZFA was applied as test item are presented in Table B.8.6.1-5. Kinetic parameters and fitted curves are presented in Appendix E.1.

Table B.8.6.1-5: optimised degradation parameters of TZFA derived from study by 5.1.2.e WOO (2011)

Soil	Model	DT50 (days)	g	$DT50_1$	$DT50_2$
Wurmwiese	SFO	73.3	-	-	-
Hoefchen am Hohenseh	DFOP	34.4[a]	0.206	3.4	34.4
Dollendorf II	SFO	15.6	-	-	-
Geometric mean		34.0	-	-	-

[a] Slow phase DT50 of DFOP

RMS note:

In its original application, the Notifier supported a DT_{50} of 34.0 days for modeling purposes, which was determined from the metabolite study. The Notifier considered that normally the DT_{50} derived from a metabolite study are superior because the residues are higher and degradation parameters are more reliably identified (degradation not superimposed by simultaneous formation). During the assessment period, RMS was however of the opinion that, as the parent study gave valid DT_{50} and in order to have a larger set of data, the DT_{50} from the parent study have to be pooled together with the DT_{50} of the metabolite study in order to derive the geomean DT_{50} value to be used for modeling purpose. Afterwards, the

Notifier calculated the geomean of 43.1 days at 20°C and experimental moisture and 43.0 days at 20°C and 100% FC (n=6). These geomean DT_{50} values were used in the following together with the mean ff of 0.092 for modeling purposes. Additionally, the Notifier performed a statistical test according to "*Guidance for evaluating laboratory and field dissipations studies to obtain DegT50 values of plant protection products in soil*" of EFSA (2010) to determine if the DT_{50}'s of TZFA from the metabolite study are statistically different from the DT_{50}'s obtained with the study where clothianidin was applied as parent. The statistical test result was that the DT_{50} obtained from the parent study are not statistically different from the DT_{50} obtained in the metabolite degradation study.

NTG metabolite

The residues of NTG are very low in general (up to 3.5% AR). Therefore the Chi² errors are relatively high (see Appendix E.2.1) although the absolute errors are well below 0.5% AR in general. Though the fits for two of the four soils would be visually acceptable and with sufficient goodness of fit none can be accepted due to no-significance of degradation rate.

Conclusion:

The aerobic degradation of Clothianidin and its soil metabolites MNG, TZNG, TZMU, TZFA and NTG was kinetically evaluated based on a laboratory study (5.1.2.e WOO, 2011), conducted on four soils at a temperature of 20°C and soil moisture of 55% WHCmax. Additionally, the degradation of TZFA was kinetically evaluated from a separate study where TZFA was incubated as test substance. The kinetic evaluation followed the recommendations of FOCUS (2005) and considered modeling endpoints. DFOP was chosen as appropriate kinetic model for the parent clothianidin, resulting in DT_{50}'s of the slow phase of 99, 175, 197 and 183 days, respectively for the soils Hoefschen am Hosenseh, Wellesbourne, Mas du Coq and Vilobi d'Onyar. For TZFA, the degradation was additionally evaluated from the study by 5.1 2 e WOO (2011) where TZFA was applied directly. The DT_{50} from the parent study and the metabolite study were pooled together, resulting in a normalized geomean DT_{50} value of 43.0 days at 20°C and 100% FC (n=6). This geomean DT_{50} value of 43.0 days has to be used together with the mean formation fraction of 0.092 for modeling purposes to predict the concentrations of TZFA in groundwater. For TZMU metabolite, a geomean DT_{50} value of 9.5 days has to be used together with the mean formation fraction of 0.394 for modeling purposes to predict the concentrations of TZFA in groundwater. The study is acceptable.

Report:	5.1.2.e WOO (2012) CTD PECgw EU: Predicted Environmental Concentrations in Groundwater Recharge Based on Model FOCUS PEARL – Use in sugarbeets and maize in Europe Bayer CropScience Report No. MEF-11/1045
Guidelines:	Not reported
GLP:	Not applicable

The study aims to estimate the groundwater concentrations of clothianidin and its soil metabolites TZFA and TZMU, using FOCUS PEARL 4.4.4 and the long term sorption properties of the active substance clothianidin.

Materials and methods:

Predicted environmental concentrations of the active substance clothianidin and its metabolites MNG, TZNG, NTG, TZMU and TZFA in groundwater recharge (PECgw) were calculated for the use in sugarbeets and maize as seed treatment in EU, using the simulation model FOCUS PEARL 4.4.4. PECgw were evaluated as the 80th percentile of the mean annual leachate concentration at 1 m soil depth. Model parameters and scenarios consisting of weather, soil, and crop data were used as proposed by FOCUS (2009).

The use in sugarbeets and maize as seed treatment is described in Table B.8.6.1-6. Parameters used in the simulation are given in Table B.8.6.1-7.

Table B.8.6.1-6: Application data of clothianidin according to the use pattern in EU

Individual crop	FOCUS crop	Rate (kg a.s./ha)	Plant interception (%)	Application date and method	Amount reaching soil (kg a.s./ha)
Sugarbeets	Sugarbeets	1x0.078	0	Planting – incorporation at 3 cm – every 3rd year	1x0.078
Maize	Maize	1x0.05	0	Planting – incorporation at 3 cm – every year	1x0.050

Table B.8.6.1-7: FOCUS modeling input parameters for clothianidin and its soil metabolites

Parameters	**Values**	**Justification**
Clothianidin		
MM	249.7	-
Water solubility (mg/L) 20°C	327	Review Report January 2005
Vapor pressure (Pa) (20°C)	3.8E-11	Review Report January 2005
DT_{50} (days)	95	Geomean field DT50 value (Hammel and Kahl, 2009a) ; n=8
k_d (days^{-1})	0.0313	Arithmetic mean (Hammel and Bingemann, 2004a) ; n=2
f_{ne}	0.6	Arithmetic mean (Hammel and Bingemann, 2004a) ; n=2
Koc / Kom	160 / 92.8	Arithmetic mean from the Review Report January

Parameters	**Values**	**Justification**
		2005 ; n=5
Freundlich exponent	0.83	Arithmetic mean from the Review Report January 2005 ; n=5
Fraction formed	-	-
Plant uptake	0	Field DT_{50}
Q_{10}	2.58	PPR Panel (2007)
TZNG soil metabolite		
MM	236	-
Water solubility (mg/L) 20°C	19950	EPIWIN
Vapor pressure (Pa) (20°C)	0.000535	EPIWIN
DT_{50} (days)	61.7	Geomean lab DT_{50} from study by Hein (2000) normalised at 20°C and 100% FC ; n=3
Koc / Kom	275.4 / 159.7	Arithmetic mean from the Review Report January 2005 n=5
Freundlich exponent	0.82	Arithmetic mean from the Review Report January 2005 ; n=5
Fraction formed	0.34	Arithmetic mean (Schad, 2002) ; n=3
Plant uptake	0.5	Schriever et al. (2012)
Q_{10}	2.58	PPR Panel (2007)
MNG soil metabolite		
MM	118.1	
Water solubility (mg/L) 20°C	1000000	EPIWIN
Vapor pressure (Pa) (20°C)	0.001	EPIWIN
DT_{50} (days)	66.4	Geomean lab DT_{50} from study by Dorn (2000) normalised at 20°C and 100% FC ; n=3
Koc / Kom	20.5 / 11.9	Arithmetic mean from the Review Report January 2005 ; n=5
Freundlich exponent	0.91	Arithmetic mean from the Review Report January 2005 ; n=5
Fraction formed	0.51	Arithmetic mean (Schad, 2002) ; n=3
Plant uptake	0.5	Schriever et al. (2012)
Q_{10}	2.58	PPR Panel (2007)
TZFA soil metabolite		
MM	226.1	
Water solubility (mg/L) 20°C	1000	Worst-case assumption
Vapor pressure (Pa) (20°C)	1E-20	Worst-case assumption
DT_{50} (days)	43	Geomean lab DT_{50} normalised to 20°C and 100% FC from the study by Stupp and Unold (2011) and the study by Völkel (2011) ; n=6
Koc / Kom	559.9 / 324.8	Arithmetic mean value from 5 soils (3 Germany, 2 USA) (Möndel, 2011) ; n=5
Freundlich exponent	0.872	Arithmetic mean value from 5 soils (3 Germany, 2 USA) (Möndel, 2011) ; n=5
Fraction formed	0.092	Arithmetic mean value (Hammel, 2012a) ; n=3
Plant uptake	0.5	Schriever et al. (2012)
Q_{10}	2.58	PPR Panel (2007)
TZMU soil metabolite		

Parameters	Values	Justification
MM	205.7	
Water solubility (mg/L) 20°C	1000	Worst-case assumption
Vapor pressure (Pa) (20°C)	1E-20	Worst-case assumption
DT_{50} (days)	9.1	Geomean lab DT_{50} value normalised to 20°C and 100% FC estimated from the study where the parent was applied as test substance (Hammel, 2012a) ; n=4
Koc / Kom	61.8 / 35.8	Arithmetic mean from the Review Report January 2005 ; n=5
Freundlich exponent	0.877	Arithmetic mean from the Review Report January 2005 ; n=5
Fraction formed	0.394	Arithmetic mean value (Hammel, 2012a) ; n=4
Plant uptake	0.5	Schriever et al. (2012)
Q_{10}	2.58	PPR Panel (2007)
NTG soil metabolite		
MM	205.7	
Water solubility (mg/L) 20°C	10000	EPIWIN
Vapor pressure (Pa) (20°C)	19.6	EPIWIN
DT_{50} (days)	52.7	Geomean lab DT_{50} from study by Fliege (2004) normalised at 20°C and 100% FC ; n=3
Koc / Kom	16.0 / 9.3	Arithmetic mean from the Review Report January 2005 ; n=3
Freundlich exponent	0.877	Arithmetic mean from the Review Report January 2005
Fraction formed	1 TZNG -> NTG 1 MNG -> NTG	Worst-case assumption
Plant uptake	0.5	Schriever et al. (2012)
Q_{10}	2.58	PPR Panel (2007)

Degradation of clothianidin and its soil metabolites

The characterization of the degradation of clothianidin in soil was based on field dissipation studies of 5.1.2.e WOO (2000a), 5.1.2.e WOO (2000b) and 5.1.2.e WOO (2000c). Three of the eight field trials were conducted in France, two in Germany, two in UK and one in Spain. The data from these studies were used by 5.1.2.e WOO (2009a) to derive first order half-life values for clothianidin which are shown in Table B.8.6.1-8. This evaluation considered the normalization of degradation with respect to soil moisture and temperature on daily basis. According to FOCUS (2000) a temperature of 20°C and 100% field capacity (FC) were chosen as reference values. The effect of photolysis was separated from that of degradation by utilizing the Hockey stick model, and appropriate first order degradation half-lives (DT_{50}) for clothianidin were derived from the slow phase degradation rate.

Table B.8.6.1-8: daily temperature and moisture normalized degradation half-life values (DT50) of clothianidin, derived from slow phase degradation rate of the hockey stick model (data issued from the study by 5.1.2.e WOO , 2009a)

Site	Trial number	DT_{50} at 20°C and 100% FC (days)
Terrebonica, Spain	R814016	161.2
Elm Farm Development, UK	R811222	198.0
Elm Farm Development, UK	R813982	277.3
Guiseniers, France	R813990	128.4
Guiseniers, France	R814008	138.6
St. Etienne du Gres, France	R811249	203.9
Bursheid, Germany	R811214	78.8
Monheim, Germany	R813974	119.5
Geometric mean		153.1

The evaluation of the field dissipation data with respect to kinetic sorption was performed by 5.1.2.e WOO (2009b). Using the kinetic sorption model, it is assumed that only the compound in the equilibrium domain is accessible for degradation. For the kinetic sorption model, the equilibrium degradation rates (k_t) shown in Table B.8.6.1-9 were obtained. For the eight trials, a geometric mean value of k_t = 0.0073 days^{-1} (corresponding to a DT_{50} of 95 days) was determined. The k_t values are generally higher than standard or bulk degradation rates. For the trials considered here, 5.1.2.e WOO (2009a) determined a geometric mean value of $k_{standard}$ = 0.0045 days^{-1} (corresponding to a DT50 of 153.1 days). This difference is due to the definition of the kinetic sorption model, where no degradation occurs in the non-equilibrium domain. Thus, the overall degradation is not only determined by the degradation rate constant k_t but equally by the kinetic sorption rate constant k_d by which the supply to the equilibrium domain is limited. Therefore, the k_t values are to be used exclusively in combination with the kinetic sorption model.

Table B.8.6.1-9: Standard first order rate constants $k_{standard}$ and k_t values (20°C and 100% FC) of clothianidin (data issued from the study by 5.1.2.e WOO , 2009b)

Trial	**$k_{standard}$ (days^{-1})***	**k_t (days^{-1})**
R814016, Terrebonica, Spain	0.0043	0.0069
R811222, Elm Farm Development, UK	0.0035	0.0056
R813982, Elm Farm Development, UK	0.0025	0.0040
R813990, Guiseniers, France	0.0054	0.0091
R814008, Guiseniers, France	0.0050	0.0077
R811249, St. Etienne du Gres, France	0.0034	0.0056
R811214, Bursheid, Germany	0.0088	0.0144

Trial	**$k_{standard}$ (days^{-1})***	**k_t (days^{-1})**
R813974, Monheim, Germany	0.0058	0.0095
Geometric mean	0.0045	0.0073

*derived from the slow phase degradation rate of the Hockey stick model

The geometric mean k_t = 0.0073 days^{-1} with the corresponding DT_{50} of 95 days was used for the calculations with the simulation model PEARL which includes kinetic sorption. A Q_{10} value of 2.58 as recommended by EFSA (2007) was used. RMS notes that the DT_{50} of 95 days is quite similar to the DT_{50} used in the study by Hammel and Bingemann (2004a) to estimate PECgw with FOCUS PEARL for the Annex I inclusion, and which is described in Addendum to DAR May 2005 (*i.e.* a DT_{50} of 100 days was used for clothianidin in combination with the k_d value of 0.0313 days^{-1} and the f_{ne} value of 0.6).

With regard to the soil metabolites, laboratory DT_{50} values were standardized according to the recommendations of FOCUS (2000). The geomean DT_{50} at 20°c and 100% FC are reported in Table B.8.6.1-7.

Adsorption properties of clothianidin and its soil metabolites

The agreed equilibrium adsorption properties of clothianidin and its soil metabolites MNG, TZNG, TZMU, TNG are available in the List of Endpoints of the Review Report SANCO/10533/05 January 2005. These values are reported in Table B.8.6.1-7 as input parameters in the simulations of PECgw. As equilibrium adsorption properties of TZFA were tested by 5.1.2.e WOO (2011) in five soils, the arithmetic mean value is also reported in Table B.8.6.1-7.

Kinetic sorption of clothianidin

The time-dependent sorption of clothianidin was studied by 5.1.2 e WOO (2001) using batch equilibrium experiments in two soils from Germany. The results of this study were used in the PECgw study by 5.1.2.e WOO (2004a) described in Addendum to DAR May 2005. The kinetic sorption parameters are shown in Table B.8.6.1-10. The arithmetic mean values k_d = 0.0313 days^{-1} and f_{ne} = 0.6 are used in the simulations. These values indicate that the kinetically controlled "sorption capacity" is about 60% of the instantaneous "sorption capacity" and that the characteristic time (calculated as "pseudo half-life") for the transfer between equilibrium and non-equilibrium domain is about 22 days.

Table B.8.6.1-10: Parameters of the kinetic sorption model for the soils AIII and AXXa (5.1.2.e WOO 2004a)

Soil	k_d (days^{-1})	f_{ne}
AIII	0.0241	0.660
AXXa	0.0385	0.541
Mean	0.0313	0.600

Plant uptake factor (PUF)

For clothianidin, a plant uptake factor of 0 was used. For the metabolites, a plant uptake factor of 0.5 was used. The justification for the use of this value is derived from the generic background paper by Schriever et al. (2012) describing briefly the results of a generic plant uptake study. In this study the PUF for a large number of compounds (n = 18) was determined in hydroponic test system. The compounds tested cover a wide range of lipophilicity, i.e. logKow values, which are considered the main driver for the PUF. The plant uptake was investigated for three major crops (oil seed rape, wheat and tomatoes). The experimental results showed that the mean measured PUF assumes a value of 1 which indicates that the test compounds are taken up passively via the mass flux of the water consumed by the plants. The standard deviation of the measured PUF is approximately 0.25 from which it can be derived that the large majority of the values is greater than 0.5. Therefore it is concluded by the Notifier that the default PUF of 0.5 proposed by FOCUS (2009) is a conservative default value of the plant uptake factor implemented in the leaching models.

Findings:

Table B.8.6.1-11 to Table B.8.6.1-12 show PECgw values for sugarbeets (1 x 78 g as/ha, 0% interception, every 3rd year) and for maize (1 x 50 g as/ha, 0% interception, every year).

Table B.8.6.1-11: PECgw of clothianidin and its soil metabolites at application rate of 1 x 78 g as/ha as seed treatment in sugarbeets using FOCUS PEARL model (µg/L)

Scénario	PECgw Clothianidin	PECgw MNG	PECgw TZNG	PECgw NTG	PECgw TZMU	PECgw TZFA
Chateaudun	0.005	0.406	<0.001	0.520	<0.001	<0.001
Hamburg	0.004	0.532	<0.001	0.691	<0.001	<0.001
Jokioinen	<0.001	0.436	<0.001	0.609	<0.001	<0.001
Kremsmunster	0.001	0.361	<0.001	0.488	<0.001	<0.001
Okehampton	0.004	0.382	<0.001	0.468	<0.001	<0.001
Piacenza	0.003	0.302	<0.001	0.399	<0.001	<0.001
Porto	<0.001	0.272	<0.001	0.367	<0.001	<0.001
Sevilla	<0.001	0.153	<0.001	0.252	<0.001	<0.001
Thiva	<0.001	0.266	<0.001	0.456	<0.001	<0.001

Table B.8.6.1-12: PECgw of clothianidin and its soil metabolites at application rate of 1 x 50 g as/ha as seed treatment in maize using FOCUS PEARL model (µg/L)

Scénario	PECgw Clothianidin	PECgw MNG	PECgw TZNG	PECgw NTG	PECgw TZMU	PECgw TZFA
Chateaudun	0.001	0.714	<0.001	0.993	<0.001	<0.001
Hamburg	0.017	1.065	0.002	1.406	0.002	<0.001
Kremsmunster	0.006	0.732	<0.001	0.985	<0.001	<0.001
Okehampton	0.021	0.790	0.002	0.955	0.003	<0.001
Piacenza	0.013	0.621	0.001	0.871	0.002	<0.001
Porto	0.002	0.446	<0.001	0.592	<0.001	<0.001
Sevilla	<0.001	0.289	<0.001	0.485	<0.001	<0.001
Thiva	<0.001	0.482	<0.001	0.795	<0.001	<0.001

Conclusion

In order to estimate the concentrations of clothianidin and its soil metabolites in groundwater recharge, the Notifier used the simulation model FOCUS PEARL 4.4.4 taking into account the long term sorption properties of the active substance. This approach was presented in the Addendum to DAR May 2005, where PECgw were calculated by 5.1.2.e WOO (2004a) with a geomean field DT_{50} of 100 days for clothianidin, in combination with the kinetic sorption parameters k_d = 0.0313 $days^{-1}$ and f_{ne} = 0.6. In the current study, the Notifier used a geomean DT_{50} value of 95 days, which is quite similar to the DT_{50} of 100 days reported in the Addendum May 2005, in combination with the same k_d and f_{ne} values.

With regard to the plant uptake factor of 0.5 used by the Notifier to simulate the concentrations of metabolites in groundwater, only a background paper was submitted to support this 0.5 value. As RMS hadn't access to the raw data, RMS asked the Notifier to replicate the simulations by setting the plant uptake factor at 0 as recommended by FOCUS. The new simulations were performed in the study by 5.1 2.e WOO (2012b) described below, and as expected, the plant uptake factor has no significant impact on PECgw of TZMU and TZFA.

Simultaneously, the Notifier also simulated the groundwater concentrations of the already known metabolites of clothianidin (*ie.* MNG, TZNG and NTG metabolites). For the current simulations, the Notifier used the same main input parameters as used in the last peer reviewed addendum of May 2005. However, RMS would like just to point out that the normalisation procedure followed to derive the DT_{50} of the already known metabolites is not in agreement with the FOCUS recommendations. The Notifier didn't use the actual measured moisture at WHCmax as reference moisture contents, but erroneously used the default values given in Table 2.2 of the guidance document FOCUS (2000). According to the FOCUS recommendations, the normalised DT_{50}'s at 20°C and pF2 should be 67.9, 76.6 and 82.3 days respectively for NTG, TZNG and MNG, instead of 52.7, 61.7 and 66.4 days. Anyway, as the simulations of these metabolites is reported only for completeness and as the DT_{50}'s used in the current study are in accordance with those used for the Annex I inclusion, RMS considers that no further action is required for the metabolites MNG, TZNG and NTG.

The study is acceptable.

Report:	5.1.2.e WOO (2012b) Clothianidin (TI-435) and its Metabolites : PECgw FOCUS PEARL EUR (PUF metabolites 0) – Use in sugarbeets and maize in Europe Bayer CropScience Report No. EnSa-12-0395
Guidelines:	Not reported
GLP:	Not applicable

Materials and methods:

The study aims to estimate the groundwater concentrations of clothianidin and its soil metabolites TZFA and TZMU using FOCUS PEARL 4.4.4 and the long term sorption properties of the active substance. The input parameters and the GAP in sugarbeets and maize used in the simulations are the same as those used in the study by 5.1.2.e WOO (2012). Only the plant uptake factor changed, which was set to 0 instead of 0.5 as recommended by FOCUS in absence of experimental data.

Findings:

Table B.8.6.1-13 to Table B.8.6.1-14 show PECgw values for sugarbeets (1 x 78 g as/ha, 0% interception, every 3rd year) and for maize (1 x 50 g as/ha, 0% interception, every year).

Table B.8.6.1-13: PECgw of clothianidin and its soil metabolites at application rate of 1 x 78 g as/ha as seed treatment in sugarbeets using FOCUS PEARL model (µg/L)

Scénario	PECgw Clothianidin	PECgw MNG	PECgw TZNG	PECgw NTG	PECgw TZMU	PECgw TZFA
Chateaudun	0.005	0.598	<0.001	0.785	<0.001	<0.001
Hamburg	0.004	0.736	<0.001	1.012	<0.001	<0.001
Jokioinen	<0.001	0.576	<0.001	0.854	<0.001	<0.001
Kremsmunster	0.001	0.473	<0.001	0.683	<0.001	<0.001
Okehampton	0.004	0.452	<0.001	0.570	<0.001	<0.001
Piacenza	0.003	0.385	<0.001	0.585	<0.001	<0.001
Porto	<0.001	0.330	<0.001	0.472	<0.001	<0.001
Sevilla	<0.001	0.209	<0.001	0.368	<0.001	<0.001
Thiva	<0.001	0.559	<0.001	0.992	<0.001	<0.001

Table B.8.6.1-14: PECgw of clothianidin and its soil metabolites at application rate of 1 x 50 g as/ha as seed treatment in maize using FOCUS PEARL model (µg/L)

Scénario	PECgw Clothianidin	PECgw MNG	PECgw TZNG	PECgw NTG	PECgw TZMU	PECgw TZFA
Chateaudun	0.001	0.949	<0.001	1.426	<0.001	<0.001
Hamburg	0.017	1.544	0.002	2.201	0.002	<0.001
Kremsmunster	0.006	0.926	<0.001	1.283	<0.001	<0.001
Okehampton	0.021	0.978	0.002	1.200	0.003	<0.001
Piacenza	0.013	0.893	0.001	1.403	0.002	<0.001
Porto	0.002	0.545	<0.001	0.791	<0.001	<0.001
Sevilla	<0.001	0.393	<0.001	0.708	<0.001	<0.001
Thiva	<0.001	0.901	<0.001	1.506	<0.001	<0.001

Conclusion

The notifier used the correct input data to simulate the concentrations of TZMU and TZFA in groundwater. For clothianidin, the notifier used similar input parameter as those used for the Annex I inclusion in the DAR and its addenda. PECgw of TZMU and TZFA are predicted to be less than 0.1 µg/L. The study is acceptable.

Report:	5.1.2.e WOO (2012a) Predicted Environmental Concentrations (PEC) of TZFA and TZMU by the application of SANTANA (Clothianidin) in groundwater using the FOCUS groundwater scenario Sumitomo Chemical Report No. MT-120730-1
Guidelines:	FOCUS (2000) FOCUS groundwater scenarios in the EU pesticide registration process. Report of the FOCUS groundwater scenarios workgroup. EC Document Reference Sanco/321/2000 version 1.0
GLP:	Not applicable

The study aims to estimate the groundwater concentrations of the soil metabolites TZFA and TZMU, using FOCUS PEARL 4.4.4 and the kinetic sorption properties of clothianidin.

Materials and methods:

The groundwater leaching assessment was conducted with FOCUS PEARL 4.4.4 for clothianidin and its soil metabolites TZFA and TZMU. The GAP of the product SANTANA (a clothianidin 0.7% granular formulation) on maize as listed in Table B.8.6.1-15 was used as realistic conditions of use. The properties of clothianidin and its soil metabolites TZFA and TZMU used in the simulation are summarized in Table B.8.6.1-16. Essentially, the properties of the compounds are the same or similar to those used in the study by 5.1.2.e WOO (2012b).

Table B.8.6.1-15: The GAP of the product SANTANA (0.7% G)

Crop and/ or situation	Pest or group of pests controlled	F G or I	Application method	Growth stage (BBCH) & season	No.	Interval (days)	Application rate per treatment Kg as/ha
Maize	*Wireworms*	F	In furrow application	BBCH 00	1	-	0.05
Maize	*Diabrotica*	F	In furrow application	BBCH 00	1	-	0.08
Sweet Maize	*Wireworms*	F	In furrow application	BBCH 00	1	-	0.05
Sweet Maize	*Diabrotica*	F	In furrow application	BBCH 00	1	-	0.08
Sorghum	*Wireworms*	F	In furrow application	BBCH 00	1	-	0.05
Sorghum	*Diabrotica*	F	In furrow application	BBCH 00	1	-	0.08

F, G, I= Field, glasshouse, indoor

In accordance with the GAP, the application parameters for the simulation were as follows:

FOCUS crop:	Maize
Application rate:	1 x 0.05 kg a.s./ha or 1 x 0.08 kg a.s./ha
Application timing:	15 days before emergence
Crop interception:	0%
Soil treatment depth:	3 cm (soil incorporation)
Application frequency:	every year

Table B.8.6.1-16: FOCUS modeling input parameters for clothianidin, TZFA and TZMU

Parameters	Values	Justification
Clothianidin		
MM	249.7	-
Water solubility (mg/L) 20°C	327	Review Report January 2005
Vapor pressure (Pa) (20°C)	3.8E-11	Review Report January 2005
DT_{50} (days)	95	Geomean field DT50 value (Hammel and Kahl, 2009a) ; n=8
k_d ($days^{-1}$)	0.0313	Arithmetic mean (Hammel and Bingemann, 2004a) ; n=2
f_{ne}	0.6	Arithmetic mean (Hammel and Bingemann, 2004a) ; n=2
Koc / Kom	160 / 92.8	Arithmetic mean from the Review Report January 2005 ; n=5
Freundlich exponent	0.83	Arithmetic mean from the Review Report January 2005 ; n=5
Fraction formed	-	-
Plant uptake	0	Field DT_{50}
Q_{10}	2.58	PPR Panel (2007)
TZFA soil metabolite		
MM	226.13	
Water solubility (mg/L) 20°C	10000	Worst-case assumption
Vapor pressure (Pa) (20°C)	1E-19	Worst-case assumption
DT_{50} (days)	43.1	Geomean lab DT50 normalised to 20°C and 100% FC from the study by Stupp and Unold (2011) and the study by Völkel (2011) ; n=6
Koc / Kom	559.9 / 324.8	Arithmetic mean value from 5 soils (3 Germany, 2 USA) (Möndel, 2011) ; n=5
Freundlich exponent	0.872	Arithmetic mean value from 5 soils (3 Germany, 2 USA) (Möndel, 2011) ; n=5
Fraction formed	0.092	Arithmetic mean value (Hammel, 2012a) ; n=3
Plant uptake	0	Worst-case assumption
Q_{10}	2.58	PPR Panel (2007)
TZMU soil metabolite		
MM	205.66	
Water solubility (mg/L) 20°C	10000	Worst-case assumption
Vapor pressure (Pa) (20°C)	1E-19	Worst-case assumption
DT_{50} (days)	9.5	Geomean DT50 value estimated from the study where the parent was applied as test substance and kinetically evaluated by Hammel (2012a)

Koc / Kom	61.8 / 35.8	Arithmetic mean from the Review Report January 2005
Freundlich exponent	0.877	Arithmetic mean from the Review Report January 2005
Fraction formed	0.394	Arithmetic mean value (5.1.2.e WOO 2012a) ; n=4
Plant uptake	0	Worst-case assumption
Q_{10}	2.58	PPR Panel (2007)

Findings:

Table B.8.6.1-17 and Table B.8.6.1-18 show PECgw values for 50 g as/ha and 80 g as/ha. The PECgw were all below 0.1 µg/L for TZFA and TZMU.

Table B.8.6.1-17: The results at a single application rate of 50 g as/ha using FOCUS PEARL model (µg/L)

	50 g as/ha		
Scénario	PECgw clothianidin	PECgw TZFA	PECgw TZMU
Chateaudun	0.001235	0.000017	0.000204
Hamburg	0.016287	0.000205	0.001997
Kremsmunster	0.006202	0.000066	0.000839
Okehampton	0.020702	0.000235	0.002766
Piacenza	0.012577	0.000176	0.001725
Porto	0.001648	0.000020	0.000352
Sevilla	0.000000	0.000000	0.000000
Thiva	0.000109	0.000002	0.000030

Table B.8.6.1-18: The results at a single application rate of 80 g as/ha using FOCUS PEARL model (µg/L)

	50 g as/ha		
Scénario	PECgw clothianidin	PECgw TZFA	PECgw TZMU
Chateaudun	0.005764	0.000071	0.000829
Hamburg	0.047745	0.000605	0.005475
Kremsmunster	0.020287	0.000239	0.002641
Okehampton	0.055659	0.000625	0.007069
Piacenza	0.037232	0.000494	0.004502
Porto	0.005977	0.000071	0.001107
Sevilla	0.000000	0.000000	0.000001
Thiva	0.000848	0.000010	0.000165

Conclusion

In order to estimate the concentrations of the soil metabolites TZMA and TZFU in groundwater recharge, the Notifier used the simulation models FOCUS PEARL 4.4.4 for a realistic GAP in maize and sorghum. The compound properties used as input data in the simulations are the same or similar to those used by 5.1 2.e WOO (2012b). PECgw of TZMU and TZFA are predicted to be less than 0.1 µg/L. The study is acceptable.

Report:	5.1.2.e WOO (2012b) Predicted Environmental Concentrations (PEC) of TZFA and TZMU by the application of Dantop (Clothianidin) in groundwater using the FOCUS groundwater scenario Sumitomo Chemical Report No. MT-120730-2
Guidelines:	FOCUS (2000) FOCUS groundwater scenarios in the EU pesticide registration process. Report of the FOCUS groundwater scenarios workgroup. EC Document Reference Sanco/321/2000 version 1.0
GLP:	Not applicable

Materials and methods:

The study aims to estimate the groundwater concentrations of clothianidin and its soil metabolites TZFA and TZMU, using FOCUS PEARL 4.4.4 and the long term sorption properties of the active substance. The properties of the compounds used as input parameters in the simulations are the same as those used in the study by 5.1.2.e WOO (2012a) (see Table B.8.6.1-16).

The GAP of the product DANTOP (a clothianidin 50WG product) on apple/pear and potato as listed in Table B.8.6.1-19 was used as realistic conditions of use.

Table B.8.6.1-19: The GAP of the product DANTOP (50 WG)

Crop and/ or situation	Pest or group of pests controlled	F G or I	Application method	Growth stage (BBCH) & season	No.	Interval (days)	Application rate per treatment Kg as/ha	PHI
Apple/pear	*Aphids*	F	Foliar application	BBCH 69-72	1	-	0.150	21
Apple/pear	*Aphids*	F	Foliar application	BBCH 69-72	2	10	0.075	14
Potato	*Aphids*	F	Foliar application	BBCH 11-91	2	10-14	0.075	14

F, G, I= Field, glasshouse, indoor

In accordance with the GAP, the application parameters for the simulation were as follows:

FOCUS crop: Apple
Application rate: 1 x 0.150 kg a.s./ha
Application timing: June 1
Crop interception: 65%
Application frequency: every year

FOCUS crop: Apple
Application rate: 2 x 0.075 kg a.s./ha
Application timing: June 1 and 11
Crop interception: 65%

Application frequency: every year

FOCUS crop: Potato
Application rate: 2 x 0.075 kg a.s./ha
Application timing: April 10 and 20
Crop interception: 15%
Application frequency: every year

Findings:

Table B.8.6.1-20 to Table B.8.6.1-21 show PECgw values for Apples (1 x 150 g as/ha and 2 x 75 g as/ha) and Potato (2 x 75 g as/ha). The PECgw were all below 0.1 µg/L for TZFA and TZMU.

Table B.8.6.1-20: The results at application rate of 1 x 150 g as/ha and 2 x 75 g as/ha in apples using FOCUS PEARL model (µg/L)

	1 x 150 g as/ha		
Scénario	PECgw Clothianidin	PECgw TZFA	PECgw TZMU
Chateaudun	0.013035	0.000157	0.001585
Hamburg	0.040450	0.000516	0.004364
Jokioinen	0.000000	0.000000	0.000005
Kremsmunster	0.011220	0.000122	0.001513
Okehampton	0.020615	0.000243	0.002686
Piacenza	0.015532	0.000221	0.002050
Porto	0.004340	0.000052	0.000810
Sevilla	0.005161	0.000063	0.000802
Thiva	0.011708	0.000148	0.001480

	2 x 75 g as/ha		
Scénario	PECgw Clothianidin	PECgw TZFA	PECgw TZMU
Chateaudun	0.012972	0.000158	0.001583
Hamburg	0.040872	0.000521	0.004408
Jokioinen	0.000000	0.000000	0.000005
Kremsmunster	0.011282	0.000123	0.001530
Okehampton	0.020747	0.000243	0.002690
Piacenza	0.015519	0.000225	0.002052
Porto	0.004353	0.000052	0.000811
Sevilla	0.004723	0.000058	0.000738
Thiva	0.010889	0.000138	0.001385

Table B.8.6.1-21: The results at a single application rate of 2 x 75 g as/ha in potatoes using FOCUS PEARL model (µg/L)

	2 x 75 g as/ha		
Scénario	PECgw Clothianidin	PECgw TZFA	PECgw TZMU
Chateaudun	0.006564	0.000084	0.000902
Hamburg	0.079459	0.000957	0.008923
Jokioinen	0.000000	0.000000	0.000026
Kremsmunster	0.038853	0.000450	0.004702
Okehampton	0.090654	0.000991	0.010982
Piacenza	0.059199	0.000809	0.007531
Porto	0.010665	0.000117	0.001843

Sevilla	0.000001	0.000000	0.000001
Thiva	0.006564	0.000084	0.000902

Conclusion

In order to estimate the concentrations of the soil metabolites TZMA and TZFU in groundwater recharge, the Notifier used the simulation models FOCUS PEARL 4.4.4 for a realistic GAP as foliar application in apple and potato. The compound properties used as input data in the simulations are the same as those used by 5.1.2.e WOO (2012a). PECgw of TZMU and TZFA are predicted to be less than 0.1 µg/L. The study is acceptable.

B9. Ecotoxicology

B9.1 Surface water risk assessment TZMU

The soil metabolite TZMU occurs at a level higher than 10% (10.6%). Since the trigger value of 10% is exceeded, a surface water risk assessment is therefore required. The notifier was requested to submit a justification why surface water risk assessment was not performed.
In response to this question, the notifier has submitted the following statement:

"*The toxicity of TZMU to the Chironomus riparius is > 100 mg/L (DAR). The value for chlothianidin is 0.029 mg/L therefore the metabolite is > 3400 times less toxic. The surface water risk assessment is covered by that of the parent.*"

RMS agrees with this statement. The study on *Chironomus riparius* with the metabolite TZMU indicates that the toxicity of this metabolite is much lower compared with the active substance. No further testing on aquatic organisms with this metabolite is required.

B9.2 Soil risk assessment TZMU

The notifier provided no specific ecotoxicity test on the soil metabolite TZMU. In order to be sure that the ecotoxicity tests on soil organisms carried out with clothianidin are sufficient to cover the ecotoxicity of the metabolite TZMU, the notifier was requested to give evidence that this metabolite TZMU occurred at level exceeding 10% during the performance of the ecotoxicity tests with clothianidin.
In response to this question, the notifier has submitted the following statement:

"There is currently no data on soil ecotox values available for the soil metabolite TZMU. However a weight of evidence approach can be followed considering the available information for all other metabolites of clothianidin and all organisms which demonstrate that the metabolites are all significantly less toxic than the parent and therefore are not of concern and the risk assessment is covered by the parent. This is presented more in detail below:

- *General toxicity profile of clothianidin and its metabolites:*
  Acute toxicity studies with the arthropod species Chironomus riparius and Apis mellifera are available for clothianidin and its metabolites TZNG, MNG and TZMU (table 1). Both MNG and TZMU were not toxic to Chironomus riparius and Apis mellifera. Their toxicity is more than 3448-fold lower to Chironomus riparius and more than 45200-fold lower to Apis mellifera, compared to chlothianidin.

Table B9.2-1: *Toxicity of clothianidin and its metabolites TZNG, MNG, and TZMU to the arthropod species Chironomus riparius and Apis mellifera*

	Chironomus riparius	*Reference*	*Acute oral bee toxicity LD50 (µg/bee)*	*Reference*
Clothianidin	*0.029*	*Clothianidin DAR*	*0.0025 (0.00379)*	*Schmitzer, 2008#* *(Clothianidin*

				DAR)
TZNG	*0.433*	*Clothianidin DAR*	*3.9*	*Clothianidin DAR*
MNG	*>100*	*Clothianidin DAR*	*>153*	*Clothianidin DAR*
TZMU	*>100*	*Clothianidin DAR*	*>113*	*Clothianidin DAR*

 # an additional study has been performed since AI inclusion due to guideline change; this resulted in a lower endpoint which is included in this table.

- *Collembola risk assessment:*
  Reproduction tests with Folsomia candida are available for clothianidin and the metabolites TZNG and MNG. Similar to the results on Chironomus riparius and Apis mellifera the toxicity to Folsomia candida declines in the order clothianidin > TZNG>MNG (table 2).
  A reproduction study with Folsomia candida is not available for the metabolite TZMU. However, this metabolite should be seen as being not critical in the soil risk assessment. Considering (1) the similar toxicity profile of clothianidin and the metabolites for the different arthropods species (Chironomus riparius, Apis mellifera and Folsomia candida) and (2) the overall low toxicity of TZMU to Apis mellifera and Chironomus riparius, a high toxicity of TZMU to Folsomia candida is not to be expected.
  Taking a PECsoil-value of 0.0091 mg/kg for TZMU into account (application rate of 1 x 78 g as/ha is sugar beet and 10.6% occurrence in soil) a potential risk of TZMU would be indicated if the toxicity to Folsomia candida is by factor 21978 higher than the toxicity of MNG (potentially critical NOEC = 0.0455 mg/kg). This is considered to be highly unlikely.

***Table B9.2-2**: Toxicity of clothianidin and its metabolites TZNG and MNG to the soil arthropod Folsomia candida*

	NOEC	*Reference*
Clothianidin	*0.32*	*Clothianidin DAR*
TZNG	*1*	*Clothianidin DAR*
MNG	*>1000*	*Clothianidin DAR*

- *Earthworm risk assessment:*
  Acute earthworm toxicity tests are available for Clothianidin and the metabolites TZNG and MNG (table 3). Similar to the arthropod species Apis mellifera,

Chironomus riparius and Folsomia candida the toxicity to the earthworm Eisenia fetida declines in the order Clothianidin > TZNG > MNG (table 3).
Taking a PECsoil-value of 0.0091 mg/kg for TZMU into account a potential risk would be indicated for if the acute toxicity of TZMU to Eisenia fetida is by factor 10989 higher than the toxicity of MNG (potential critical LC50 = 0.091 mg/kg). This is considered to be highly unlikely and the risk for earthworms can be considered to be negligible.

***Table B9.2-3**: Acute toxicity of clothianidin and its metabolites TZNG and MNG to the earthworm Eisenia fetida*

	Earthworm acute toxicity test LC50 (mg/kg)	*Reference*
Clothianidin	*13.21*	*Clothianidin DAR*
TZNG	*970*	*Clothianidin DAR*
MNG	*>1000*	*Clothianidin DAR*

“

RMS considers the statement of the notifier as acceptable. The risk of TZMU for soil organisms can be considered to be negligible. No further testing is required.
The following additional remarks can be made:

- The notifier made a theoretical risk assessment for TZMU and *Folsomia candida* and earthworm considering a PEC-soil of 0.0091 mg/kg (based on application as seed treatment in sugar beet). For the use in potato a higher PECsoil of maximum 0.0148 mg TZMU/kg soil is expected. However considering this higher PECsoil a very high margin of safety still remains.
- In addition to the argumentation of the notifier, it can be noted that an earthworm field study with a 50% WDG formulation is available in the original DAR where observations are made up to twelve months after application. Since the metabolite TZMU occurs at maximum 10,6% in soil within 9 days, this earthworm field study is considered to cover possible effects of the metabolite TZMU on earthworms.

C. Overall conclusions

In 2011, Sumitomo as Notifier of Clothianidin, supported by Bayer CropScience, reported the finding of a new metabolite (TZFA) and increased amounts of a second metabolite (TZMU) during a soil study performed with Clothianidin technical as potential adverse effects according to Article 56 of Regulation 1107/2009.

After finalization of the groundwater risk assessment, the both companies submitted their dossier to the RMS Belgium. This Addendum presents the RMS conclusion about the potential adverse effects of the metabolites TZFA and TZMU.

The PECgw for the metabolites TZFA and TZMU do not exceed the trigger of 0.1 µg/L, the metabolites therefore do not pose a concern for groundwater.

From an ecotoxicological point of view, only TZMU occurred at more than 10% in soil, which is the threshold to perform an ecotoxicological risk assessment. The risk of TZMU for aquatic and soil organisms can be considered to be negligible.

In conclusion, based on the dossier submitted by Sumitomo and Bayer CropScience, no potential adverse effects are expected resulting from the finding of the new metabolite (TZFA) and the increasing amount of the already known metabolite (TZMU). Therefore, no change of the approval for the active substance Clothianidin is necessary.

D. List of references relied upon

Environmental fate and behaviour

Annex Point/ Reference Number	Author(s)	Year	Title Source (where different from the Company), Company, Report Number, GLP or GEP status (where relevant), Published or not	Data Protection claimed (Y/N)	Owner
IIA 7.1.1.1	5.1.2.e WOO ; 5.1.2.e WOO	2011	[Guanidine-^{14}C] Clothianidin: Time dependent Sorption from Four European Field Dissipation Soils. Bayer CropScience Report No. MEF-10/563. Study Number M-131 1911-7 Date: 11/04/2011. GLP/GEP (Y/N): Y Published (Y/N): N	Y	Bayer CropScience
IIA 7.1.1.2.1/01	5.1.2.e WOO	2011	BCS-CQ88479 (Clothianidin-TZFA) Degradation Rate in Three Soils Incubated Under Aerobic Conditions Innovative Environmental Services Ltd, Witteswil, Switzerland Report No.: 105 01 023 Study Number THM-0063 Date: 21/12/2011 GLP/GEP (Y/N): Y Published (Y/N): N	Y	Bayer CropScience
IIA 7.1.1.2.1/02	5.1.2.e WOO	2012a	Kinetic Evaluation of the Aerobic Metabolism of Clothianidin (TI 435), MNG, TZNG, TZMU, TZFA and NTG in Soil for Modelling Purposes Bayer CropScience Report No.: MEF-11/1043 Study Number - Date: 18/01/2012 GLP/GEP (Y/N): N Published (Y/N): N	Y	Bayer CropScience
IIA 7.1.2	5.1.2.e WOO	2011	[Imidoformamide-^{14}C] BCS-CQ88479: Adsorption/desorption in five different soils Rheinland-Pfalz Agroscience GmbH, Neustadt, Germany Report No.: AS157 Study Number - Date: 21/04/2011 GLP/GEP (Y/N): Y Published (Y/N): N	Y	Bayer CropScience
IIIA 9.2.1/01	5.1.2.e WOO 5.1.2 e WOO	2012	CTD PECgw EU: Predicted Environmental Concentrations in Groundwater Recharge Based on Model FOCUS PEARL – Use in sugarbeets and maize in Europe Bayer CropScience Report No.: MEF-11/1045 Study Number - Date: 25/07/2012 GLP/GEP (Y/N): N Published (Y/N): N	Y	Bayer CropScience

Annex Point/ Reference Number	**Author(s)**	**Year**	**Title** **Source (where different from the Company), Company, Report Number,** **GLP or GEP status (where relevant),** **Published or not**	**Data Protection claimed (Y/N)**	**Owner**
IIIA 9.2.1/02	5.1.2.e WOO	2012b	Clothianidin (TI-435) and its Metabolites : PECgw FOCUS PEARL EUR(PUF metabolites 0) – Use in sugarbeets and maize in Europe Bayer CropScience Report No.: EnSa-12-0395 Study Number - Date: 25/07/2012 GLP/GEP (Y/N): N Published (Y/N): N	Y	Bayer CropScience
IIIA 9.2.1/03	5.1.2.e WOO	2012a	Predicted Environmental Concentrations (PEC) of TZFA and TZMU by the application of SANTANA (Clothianidin) in groundwater using the FOCUS groundwater scenario Sumitomo Report No.: MT-120730-1 Study Number - Date: 30/07/2012 GLP/GEP (Y/N): N Published (Y/N): N	Y	Sumitomo
IIIA 9.2.1/04	5.1.2.e WOO	2012b	Predicted Environmental Concentrations (PEC) of TZFA and TZMU by the application of Dantop (Clothianidin) in groundwater using the FOCUS groundwater scenario Sumitomo Report No.: MT-120730-2 Study Number - Date: 30/07/2012 GLP/GEP (Y/N): N Published (Y/N): N	Y	Sumitomo

E. Appendix

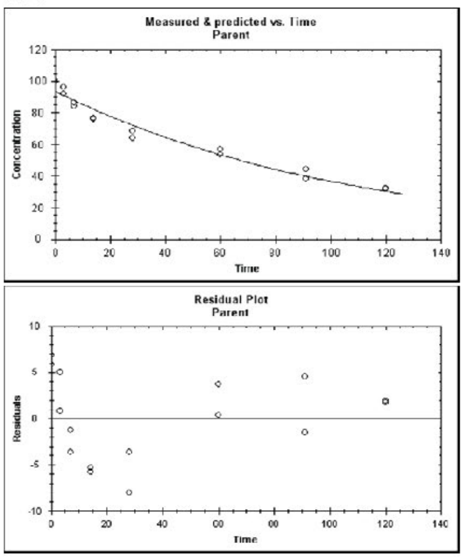
E.1 Details of the kinetic evaluation for TZFA (5.1.2 e WOO 2011)

E.1.1. Results of the kinetic evaluation for clothianidin-TZFA in soil I (Wurmwiese)

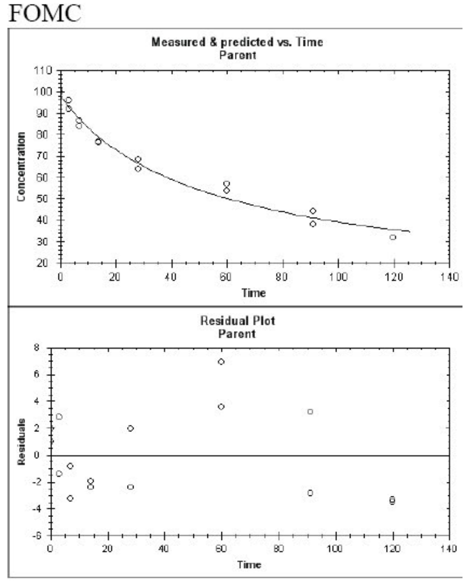
Statistical summary of degradation data and fitted curves

Model	M_0	Parameter	Prob > t[a)]	DT_{50}	DT_{90}	χ^2-error
SFO	93.7	k= 0.0095	2.0 e^{-16}	73.3	243.7	4.8
FOMC	98.5	α = 0.72 β = 38.24		61.8	896.3	3.1
DFOP	100.6	k_1 = 1.35 e^{-01} k_2 = 7.60 e^{-03} g = 1.78 e^{-01}	0.0037 3.8 e^{-09} 5.6 e^{-05}	65.5	277.3	1.6

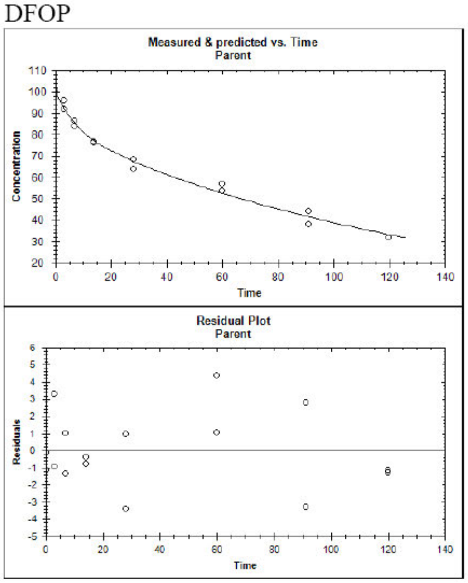
SFO



FOMC



DFOP

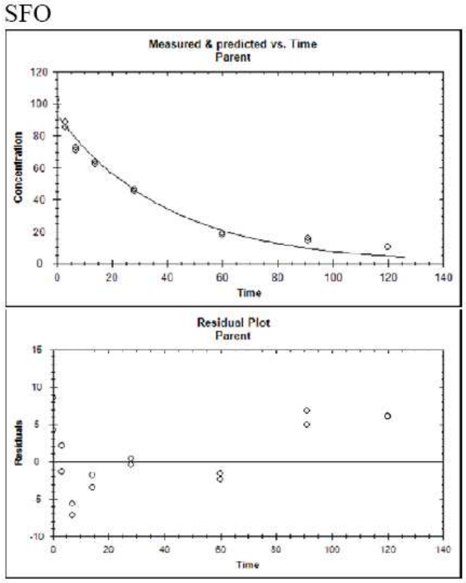


E.1.2. Results of the kinetic evaluation for clothianidin-TZFA in soil II (Hoefchen am Hosenseh)

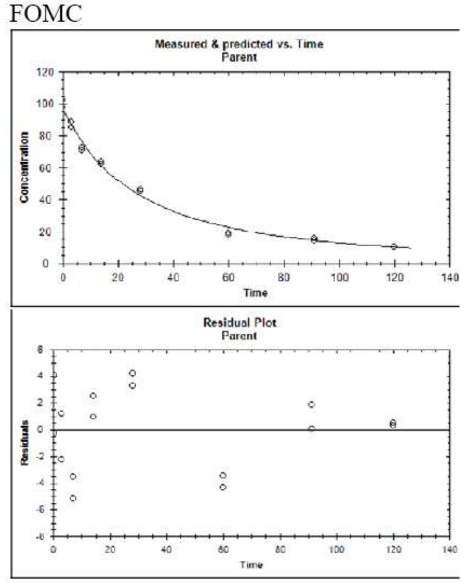
Statistical summary of degradation data and fitted curves

Model	M_0	Parameter	Prob > t[a)]	DT_{50}	DT_{90}	χ^2-error
SFO	93.6	k= 0.0254	$2.3\ e^{-09}$	27.3	90.8	7.2
FOMC	98.1	α = 1.77 β = 46.10		22.1	123.0	4.3
DFOP	100.2	k_1 = 0.206 k_2 = 0.0202 g = 0.206	0.049 $1.9\ e^{-07}$ 0.0036	23.1	102.8	4.4

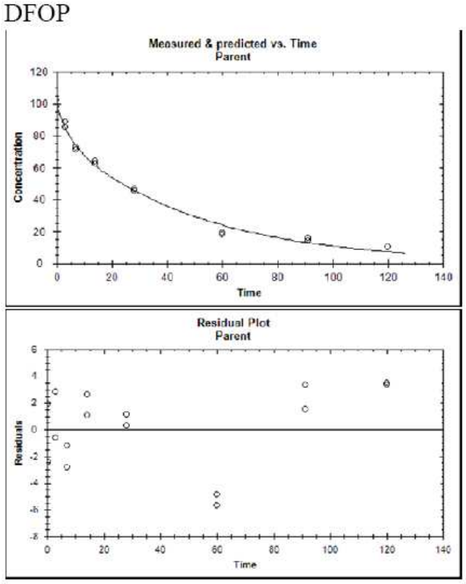
SFO



FOMC



DFOP



E.1.3. Results of the kinetic evaluation for clothianidin-TZFA in soil III (Dollendorf II)

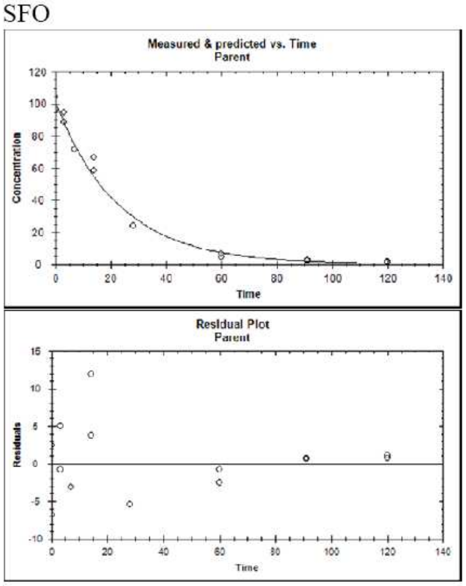
Statistical summary of degradation data and fitted curves

Model	M_0	Parameter	Prob > t[a)]	DT_{50}	DT_{90}	χ^2-error
SFO	102.2	k= 4.45 e^{-02}	3.1 e^{-10}	15.6	51.8	6.9
FOMC	102.2	α = 5.26 e^{02} β = 1.18 e^{04}		15.6	51.8	7.1
DFOP	102.2	k_1 = 4.45 e^{-02} k_2 = 4.45 e^{-02} g = 7.60 e^{-01}	7.3 e^{-05} NA NA	15.6	51.8	7.3

NA: not acceptable

Note: for both FOMC parameters α and β, since they are shape parameters rather than degradation parameters, the confidence interval should not include zero. In this case, for both parameters, the confidence interval included zero.

SFO



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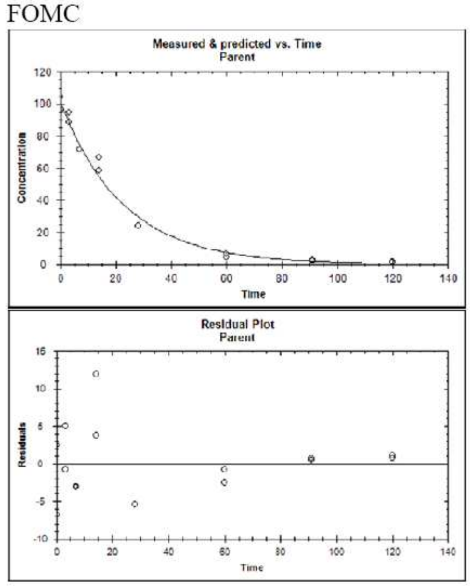
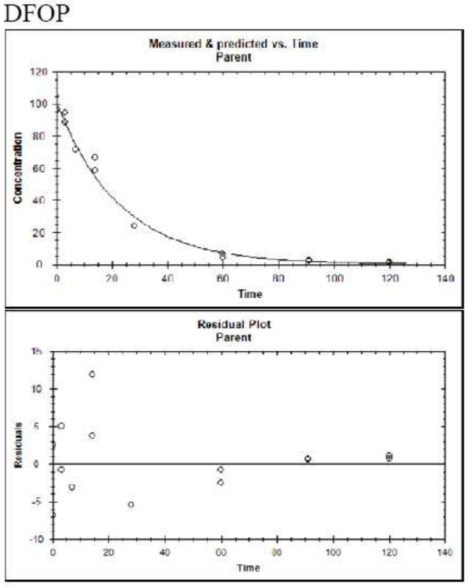


DFOP



E.2 Details of the kinetic evaluation for clothianidin and its metabolites (5.1.2.e WOO 2012a)

E.2.1 Kinetic parameters

Table E.2.1-1: Scaled error chi², visual assessment (VA) and significance of degradation rate (T-prob) for clothianidin and the soils studied by Stupp and Unold (2011). Kinetic evaluations accepted in bold

Soil	Model	Chi² (%)	VA*	T-prob
Hoefchen am Hohenseh	SFO	27.3	--	<0.001
Wellesbourne	SFO	17.6	--	<0.001
Mas du Coq	SFO	4.4	--	<0.001
Vilobi d'Onyar	SFO	7.1	--	<0.001
Hoefchen am Hohenseh	**DFOP**	**4.0**	**+**	**<0.001[a]/<0.001[b]**
Wellesbourne	**DFOP**	**3.0**	**+**	**<0.001[a]/<0.001[b]**
Mas du Coq	**DFOP**	**2.4**	**+**	**<0.001[a]/<0.001[b]**
Vilobi d'Onyar	**DFOP**	**1.7**	**+**	**<0.001[a]/<0.001[b]**

*Visual assessment : + good, -- not acceptable, [a]k1, [b]k2

Table E.2.1-2: Scaled error chi², visual assessment (VA) and significance of degradation rate (T-prob) for MNG and the soils studied by Stupp and Unold (2011). Kinetic evaluations accepted in bold.

Soil	Model	Chi² (%)	VA*	T-prob
Hoefchen am Hohenseh	SFO	23.2	--	<0.001
Wellesbourne	**SFO**	**11.3**	**+**	**<0.001**
Mas du Coq	**SFO**	**20.1**	**°**	**0.017**
Vilobi d'Onyar	**SFO**	**17.0**	**°**	**<0.001**

*Visual assessment : + good,   acceptable, -- not acceptable, [a]k1, [b]k2

Table E.2.1-3: Scaled error chi², visual assessment (VA) and significance of degradation rate (T-prob) for TZNG and the soils studied by Stupp and Unold (2011). Kinetic evaluations accepted in bold.

Soil	Model	Chi² (%)	VA*	T-prob
Hoefchen am Hohenseh	SFO	24.9	--	0.500
Wellesbourne	SFO	15.7	°	0.500
Mas du Coq	SFO	13.6	+	0.500
Vilobi d'Onyar	SFO	19.3	°	0.500

*Visual assessment : + good,   acceptable, -- not acceptable, [a]k1, [b]k2

Table E.2.1-4: Scaled error chi², visual assessment (VA) and significance of degradation rate (T-prob) for TZMU and the soils studied by Stupp and Unold (2011). Kinetic evaluations accepted in bold.

Soil	Model	Chi² (%)	VA*	T-prob
Hoefchen am Hohenseh	**SFO**	**10.1**	**+**	**< 0.001**
Wellesbourne	**SFO**	**12.0**	**+**	**< 0.001**
Mas du Coq	**SFO**	**4.9**	**+**	**< 0.001**
Vilobi d'Onyar	**SFO**	**13.4**	**+**	**< 0.001**

*Visual assessment : + good,   acceptable, -- not acceptable, [a]k1, [b]k2

Table E.2.1-5: Scaled error chi², visual assessment (VA) and significance of degradation rate (T-prob) for TZFA and the soils studied by Stupp and Unold (2011). Kinetic evaluations accepted in bold.

Soil	Model	Chi² (%)	VA*	T-prob
Hoefchen am Hohenseh	**SFO**	**11.6**	**+**	**<0.001**
Wellesbourne	**SFO**	**12.1**	**+**	**<0.001**
Mas du Coq	SFO	49.4	--	0.001

Vilobi d'Onyar	**SFO**	**16.1**	**°**	**<0.001**

*Visual assessment : + good,   acceptable, -- not acceptable, [a]k1, [b]k2

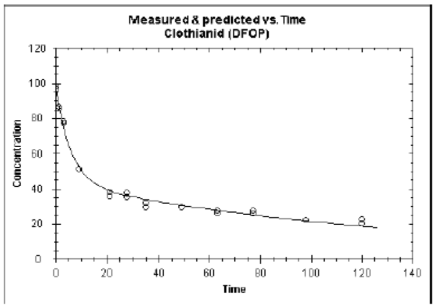
Table E.2.1-6: Scaled error chi², visual assessment (VA) and significance of degradation rate (T-prob) for NTG and the soils studied by Stupp and Unold (2011). Kinetic evaluations accepted in bold.

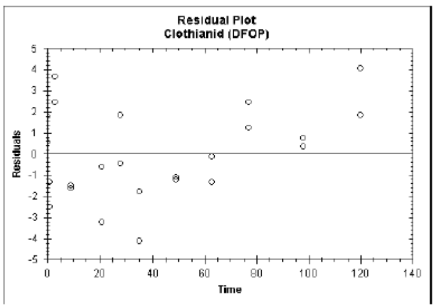
Soil	Model	Chi² (%)	VA*	T-prob
Hoefchen am Hohenseh	SFO	27.9	+	0.500
Wellesbourne	SFO	14.4	+	0.500
Mas du Coq	SFO	89.8	--	0.500
Vilobi d'Onyar	SFO	28.4	°	0.500

*Visual assessment : + good,   acceptable, -- not acceptable, [a]k1, [b]k2

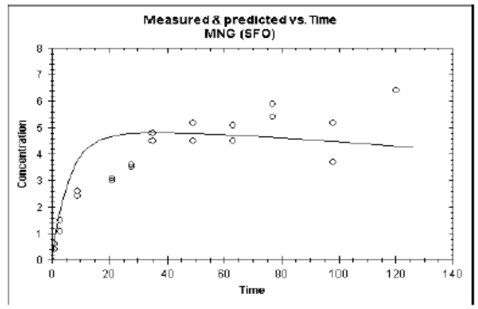
E.2.2 fitted curves for the soil Hoefchen am Hosenseh (DFOP kinetic for clothianidin and SFO kinetic for its metabolites)

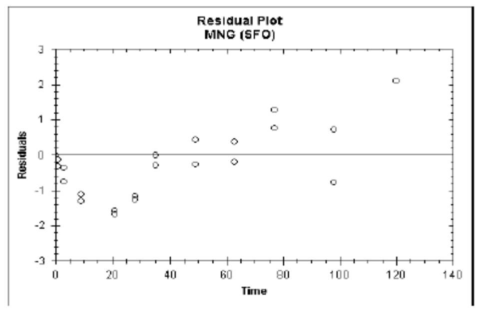
Graphs clothianidin



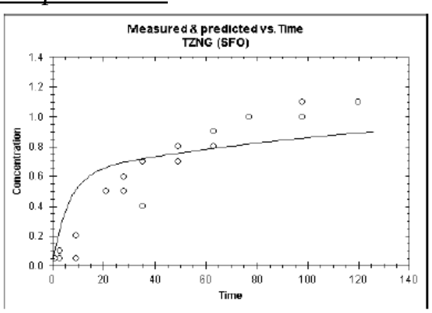


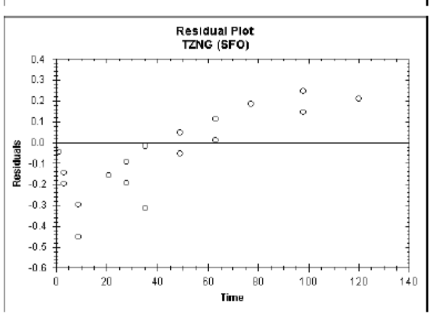
Graphs MNG



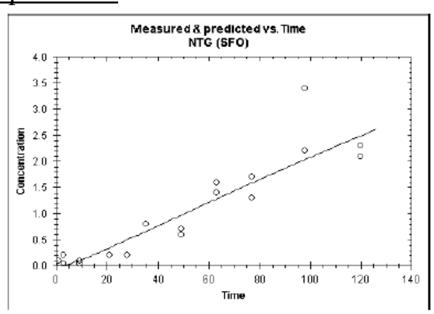


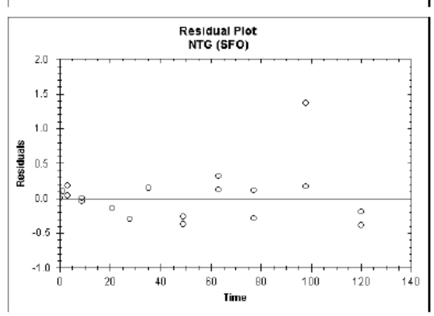
Graphs TZNG

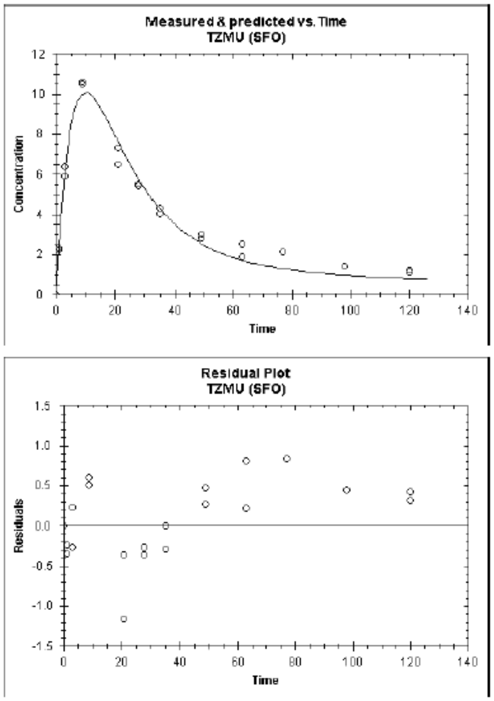
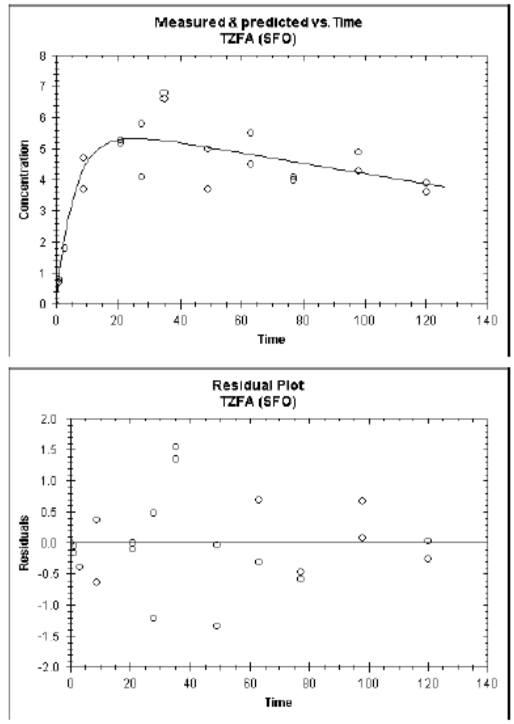




Graphs NTG

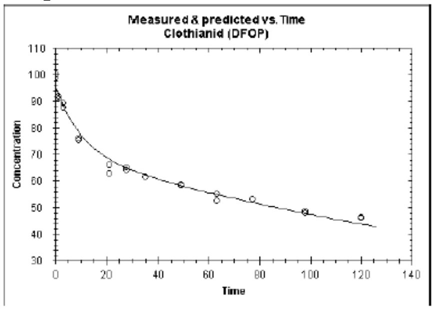


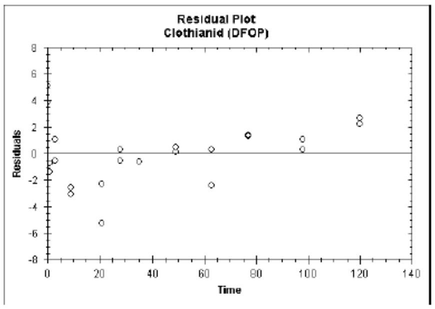


Graphs TZMU	*Graphs TZFA*
	

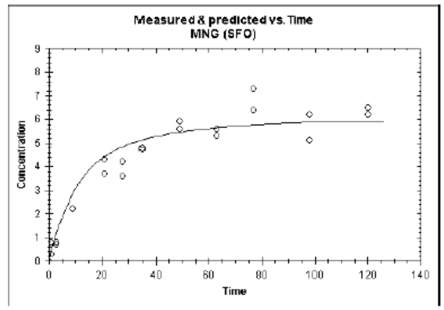
E.2.3 fitted curves for the soil Wellesbourne (DFOP kinetic for clothianidin and SFO kinetic for its metabolites)

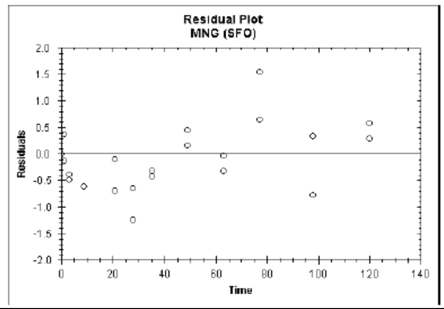
Graphs clothianidin



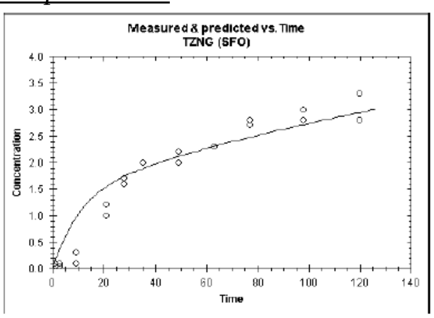


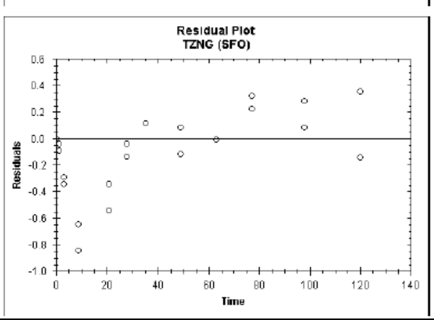
Graphs MNG



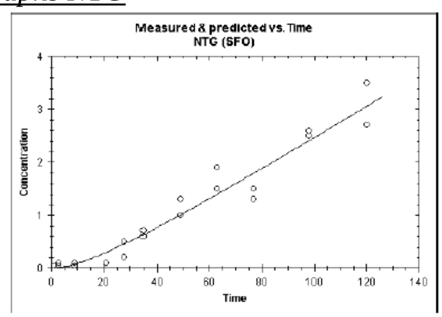


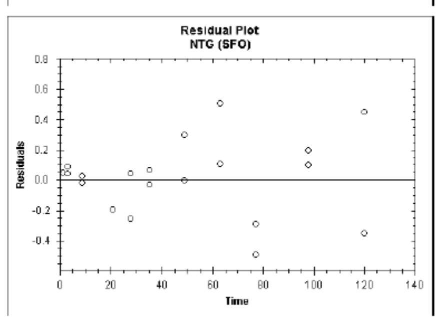
Graphs TZNG

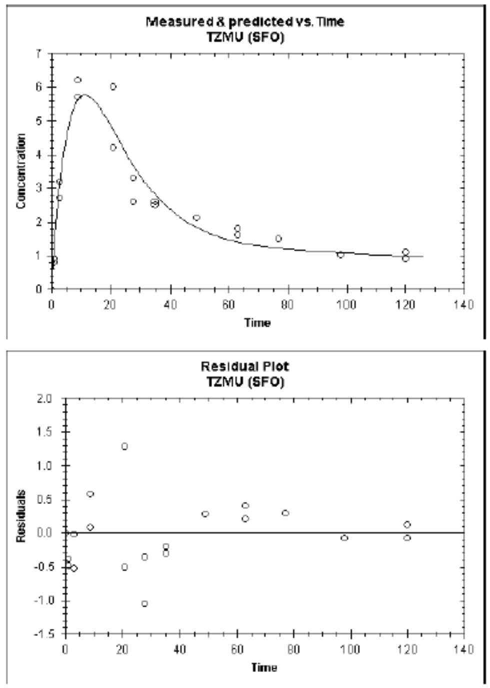
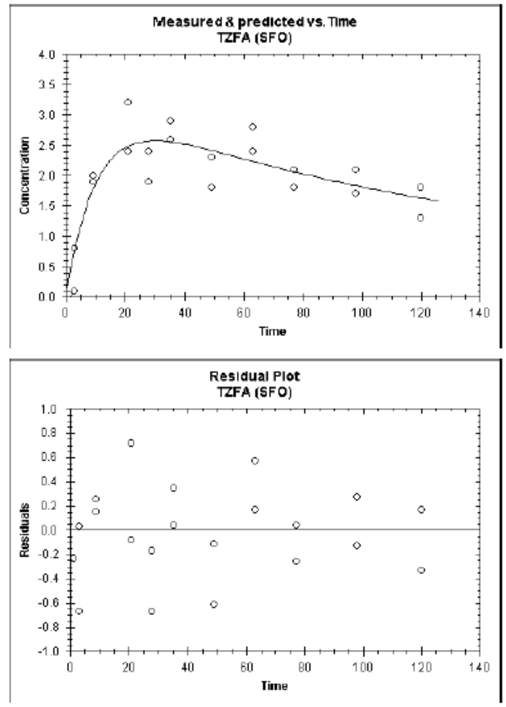




Graphs NTG

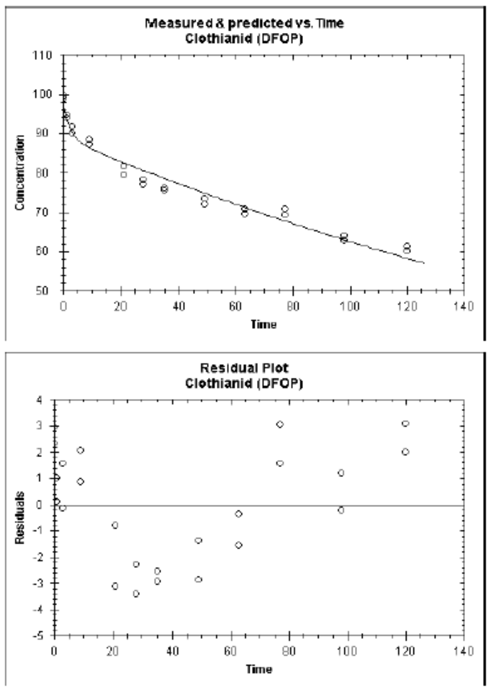




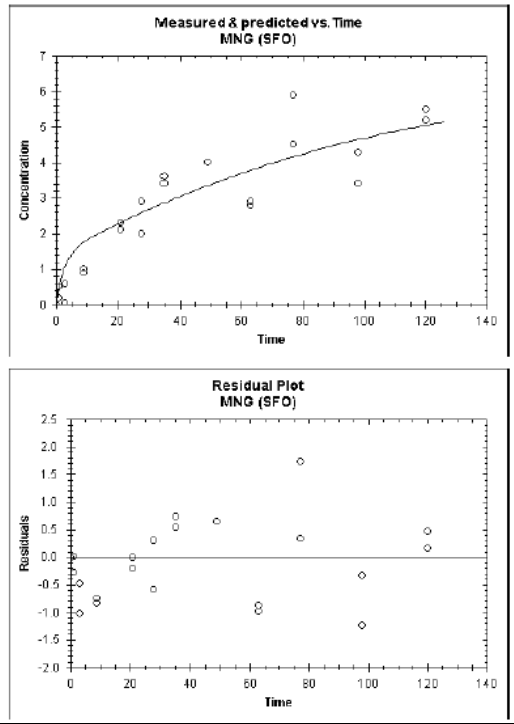
Graphs TZMU	*Graphs TZFA*
	

<u>E.2.4 fitted curves for the soil Mas du Coq (DFOP kinetic for clothianidin and SFO kinetic for its metabolites)</u>

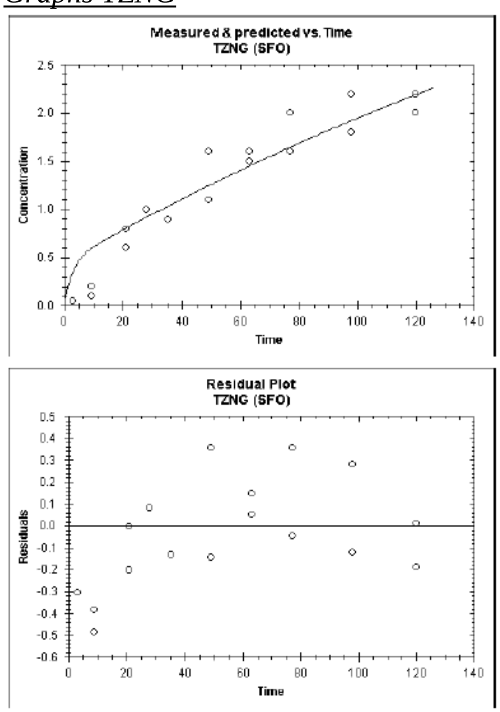
<u>Graphs clothianidin</u>



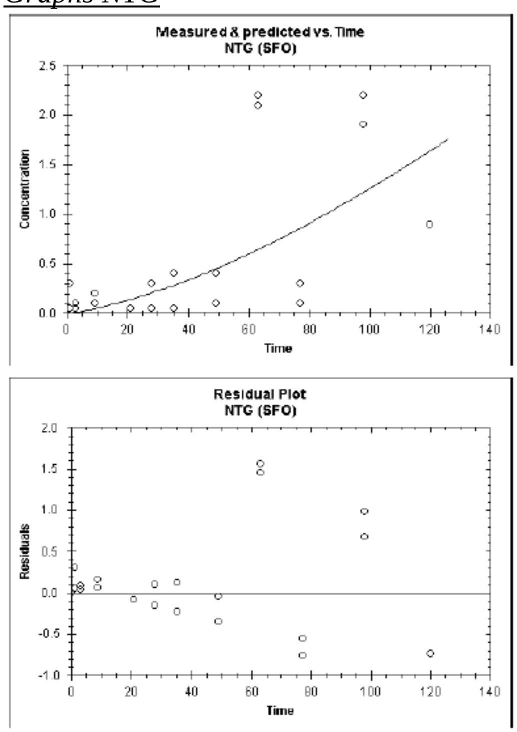
<u>Graphs MNG</u>

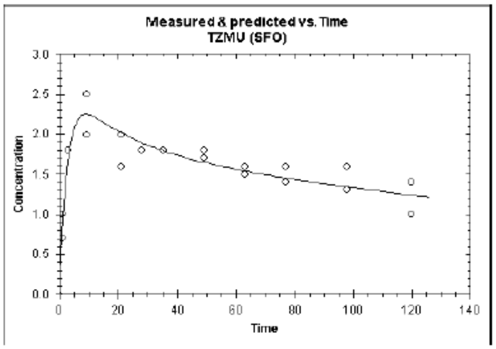
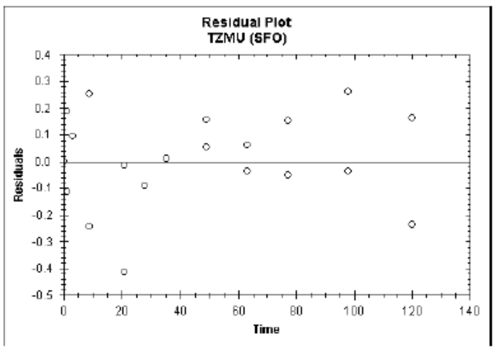
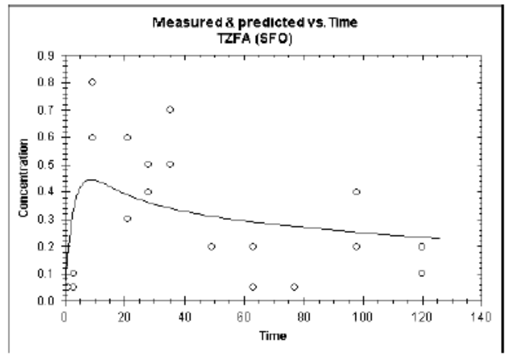
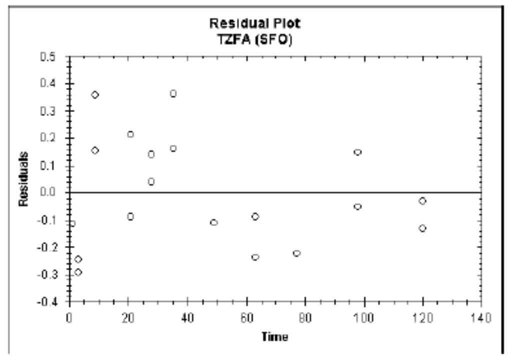


<u>Graphs TZNG</u>



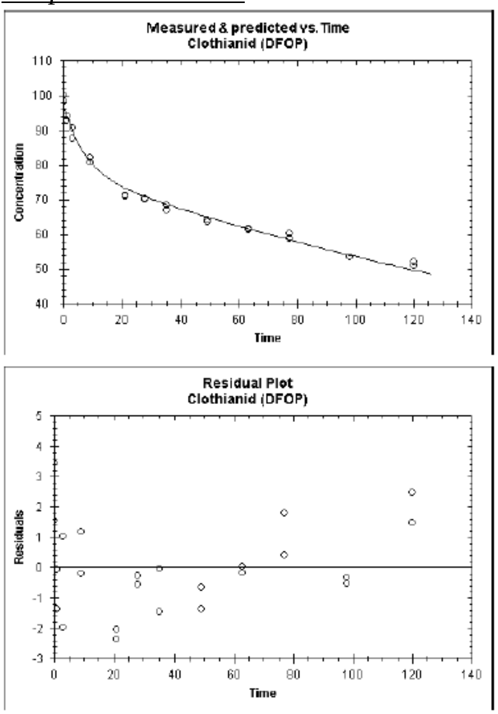
<u>Graphs NTG</u>



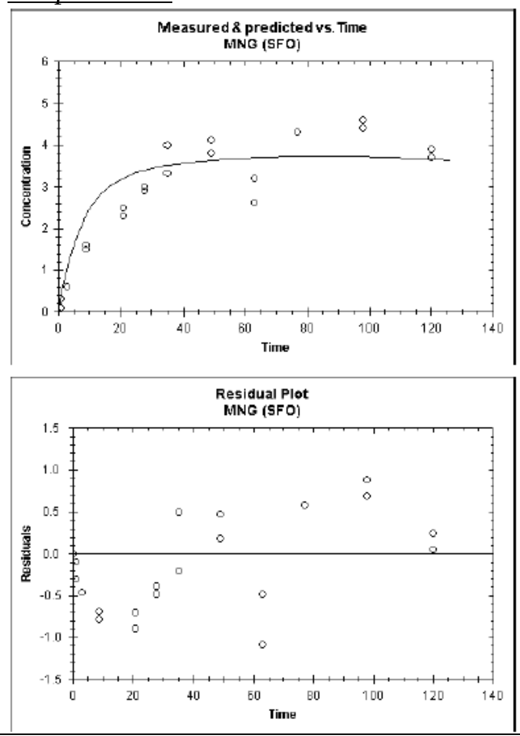
<u>Graphs TZMU</u>	*<u>Graphs TZFA</u>*
	

E.2.5 fitted curves for the soil Vilobi d'Onyar (DFOP kinetic for clothianidin and SFO kinetic for its metabolites)

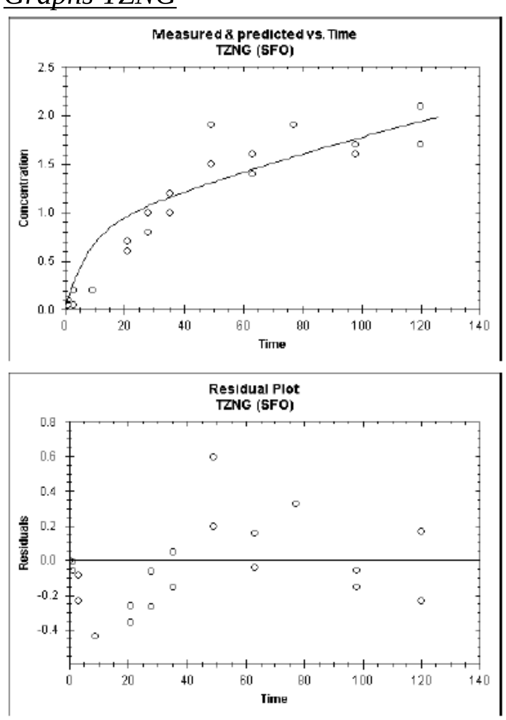
Graphs clothianidin



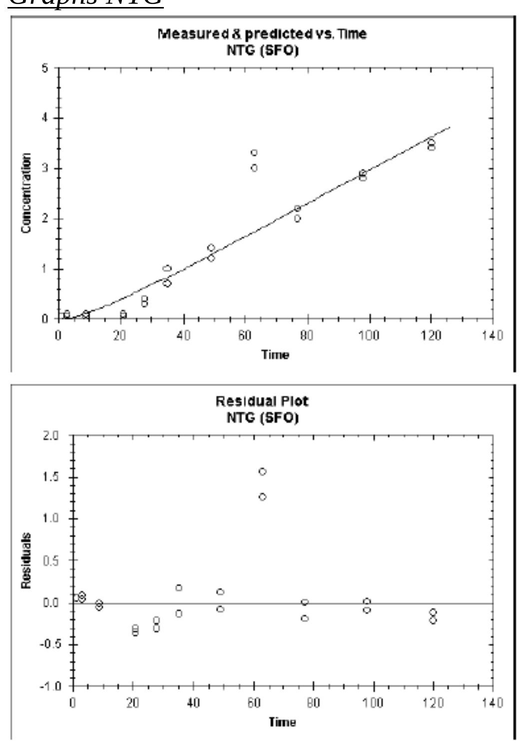
Graphs MNG



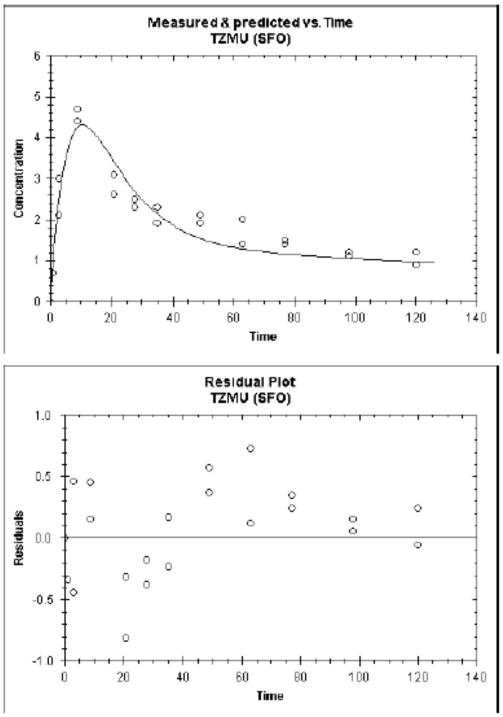
Graphs TZNG



Graphs NTG



Graphs TZMU



Graphs TZFA