

ANNEX B

Active substance: Bensulfuron methyl

B.8: Environmental fate and behaviour

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

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Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Fate and behaviour in soil (Annex IIA 7.1)

B.8.1.1 Route and rate of degradation in soil (Annex IIA 7.1.1; Annex IIIA 9.1.1)

B.8.1.1.1 Route of degradation (Annex IIA 7.1.1)

B.8.1.1.1.1 Aerobic degradation in soil (Annex IIA 7.1.1.1.1)

1) *Route of degradation of bensulfuron methyl in aerobic soil. Anderson, J.J., Swain, R.S., 2002*

Cross reference IIA, 7.1.1.1.1.01

Guidelines:

SETAC – Procedures for Assessing Environmental Fate and Ecotoxicity of Pesticides. OECD Guidelines for the Testing of Chemicals: Aerobic and Anaerobic Transformation in Soil (Draft Document, October 1999)

GLP:

Yes

The study is acceptable

Materials and Methods:

The metabolism of bensulfuron methyl in fresh soil was investigated using compound uniformly labeled in the phenyl ring (DuPont CPC Isotope Inventory No. 320; specific activity: 57.5 $\mu\text{Ci}/\text{mg}$; radiochemical purity: > 95%) and labeled at the 2-position of the pyrimidine ring (DuPont CPC Isotope Inventory No. 319; specific activity: 53.1 $\mu\text{Ci}/\text{mg}$; radiochemical purity: > 95%). The study was conducted in loamy sand soil (Table B.8.1) from Pavia, Italy, for 122 days under aerobic conditions in the dark at $20 \pm 1^\circ\text{C}$ and 50% of the 0 bar moisture holding capacity.

Table B.8.1: Soil characteristics

Characteristic ^a	Soil
Soil Name or Designation	Pavia
Origin Location	Pavia, Italy
pH (water)	5.2
pH (0.01 M CaCl_2)	4.6
% Sand (2000 - 50 μm)	78.4
% Silt (<50 - 2 μm)	14.8
% Clay (<2 μm)	6.8
Texture ^b	Loamy sand
Organic matter (%)	0.8
Organic carbon (%) ^c	0.5
Cation exchange capacity	2.59
Maximum water-holding capacity at 0 bar (%)	16.7
Microbial biomass – Initial (mg microbial C/100 g soil)	4.92
Microbial biomass – Final (mg microbial C/100 g soil)	3.25

^a Soil characterisation analyses were performed at Harris Laboratories, Lincoln, NE. Soil fumigation was performed at Springborn Laboratories, Wareham, MA.

^b U.S.D.A. soil classification system

^c % organic carbon = % organic matter * 0.58

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Italy	May 2006	Bensulfuron methyl

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Both [phenyl(U)-¹⁴C]- and [pyrimidine-2-¹⁴C]bensulfuron methyl were applied at a rate of 0.2 mg/kg soil (dry weight soil) equivalent to approximately 0.55 kg/ha (0.49 lb/acre; applied radioactivity, AR). Separate vessels were treated at a rate of 11 mg/kg for the sole purpose of metabolite identification. The test system consisted of 50-mL centrifuge tubes each containing 10 g of soil contained within a larger flow through vessel (modified dessicator). Aerobic conditions were maintained by passing a steady stream of humidified air through the larger vessel, then through caustic containing traps to collect ¹⁴CO₂ or other volatile, acidic metabolites. Samples were analysed (0.2 mg/kg treatment rate) at 0, 3, 7, 14, 21, 31, 45, 60, 95, and 122 days after application. High dose flasks were analysed after 32 and 118 days ([phenyl(U)-¹⁴C]bensulfuron methyl), and 66 and 118 days ([pyrimidine-2-¹⁴C]bensulfuron methyl) incubation. Soil samples were extracted with 0.1 M (NH₄)₂CO₃/acetone (9/1, v/v) and extracts analysed by LSA, reversed phase HPLC, and by LC/MS/MS.

Findings:

All results are summarised in Table B.8.2 and Table B.8.3.

Material balance: Average recovery of applied radioactivity over all replicates was >95% AR. Volatile radioactivity accounted for 4.16 and 5.32% AR after 122 days of incubation, respectively, for the [phenyl(U)-¹⁴C]bensulfuron methyl and [pyrimidine-2-¹⁴C]bensulfuron methyl treated soils. Unextractable radioactivity reached a maximum of 24.9% AR on Day 95 in the [¹⁴C-phenyl(U)]bensulfuron methyl treated soil, and a maximum of 29.1% AR at 122 days in the [pyrimidine-2-¹⁴C]bensulfuron methyl treated soil. Extractable radioactivity was maximum on Day 0 (accounting for 99.3 and 102.5% AR for the [pyrimidine-2-¹⁴C]bensulfuron methyl and [phenyl(U)-¹⁴C]bensulfuron methyl treated soils, respectively) and decreased to 65.4 and 61.6% AR at Day 122 in the [pyrimidine-2-¹⁴C]bensulfuron methyl and [phenyl(U)-¹⁴C]bensulfuron methyl treated soils, respectively.

Principal degradation products: In the [pyrimidine-2-¹⁴C]bensulfuron methyl treated soil IN-R9419 reached a maximum of 24.5%AR at day 45, IN-F7880 3.3%AR at day 31 and IN-J0290 21.0%AR at day 122. In the [phenyl(U)-¹⁴C]bensulfuron methyl treated soil IN-R9419 reached a maximum of 27.7%AR and IN-F7880 of 4.3%AR at day 31, IN-N5297 6.8%AR and IN-B6895 1.77%AR at day 122, IN-68991 3.8%AR at day 60 and IN-D1R84 18.20%AR at day 122.

Known minor products observed were IN-B6895 (<2%AR) and IN-68991 (<4%AR). Other minor products were present at no greater than 3.28% AR. The sum of total detectable but unidentified radioactivity in extracts (contained in multiple components) ranged from 2.61 to 6.35% AR in the [phenyl(U)-¹⁴C]bensulfuron methyl treated soil, and from 3.72 to 8.98% AR in the [pyrimidine-2-¹⁴C]bensulfuron methyl treated soil. Extractable radioactivity decreased from 99.3%AR at day 0 to 65.4%AR at day 122, in the [pyrimidine-2-¹⁴C]bensulfuron methyl treated soils, and from 102.5%AR at day 0 to 61.6%AR at day 122 in the [phenyl(U)-¹⁴C]bensulfuron methyl.

At study termination, evolved ¹⁴CO₂ accounted for 14.2 and 5.32%AR in the [phenyl(U)-¹⁴C]- and [pyrimidine-2-¹⁴C]bensulfuron methyl treated systems, respectively. No organic volatiles were collected, nor quantified. However the material balance indicated that such degradates were insignificant.

Non-extractable residues (NER): The amount of NERs generally increased during the study reaching a maximum of 29.1% AR in the [pyrimidine-2-¹⁴C]bensulfuron methyl treated soil at Day 122 and a maximum of 24.9% AR in the [phenyl(U)-¹⁴C]bensulfuron methyl treated soil at Day 95.

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Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.2: Percent distribution of radiolabeled components in aerobic soils after application of [pyrimidine-2-¹⁴C]bensulfuron methyl (DPX-F5384)

Time (days)	% of Applied Radioactivity									
	0	3	7	14	21	31	45	60	95	122
DPX-F5384	90.32	84.63	79.81	64.48	53.65	43.07	31.55	23.68	18.14	12.47
IN-R9419	1.40	2.90	4.38	10.43	12.59	17.39	24.53	21.58	16.54	18.76
IN-F7880	0.33	0.34	1.00	2.22	2.82	3.30	3.22	3.05	2.54	1.53
IN-J0290	0.58	0.54	1.11	2.30	5.79	10.29	9.92	13.89	19.91	20.97
Unidentified Radioactivity ≥Ld	6.26	5.21	3.72	6.07	6.66	5.37	6.45	8.98	6.01	4.44
Unidentified Radioactivity ≥Lc ≥Ld	0.41	0.52	4.33	3.84	3.67	2.92	4.00	3.35	2.92	2.83
Extracted	99.30	94.12	94.34	89.33	88.89	81.58	79.01	76.87	69.73	65.42
¹⁴ CO ₂	ND	<0.06	0.08	0.30	0.65	1.35	2.26	3.07	4.51	5.32
Volatile Organics	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Unextracted	1.23	4.62	4.98	8.67	10.46	13.06	17.90	19.82	25.70	29.11
Total	100.53	98.75	99.40	98.30	100.00	95.98	99.17	99.77	99.94	99.85

Lc = critical limit = radioactivity that is differentiable from background but is not reliably detected; Lc for HPLC analyses was 0.07% AR or 0.0002 µg/g.

Ld = detection limit = radioactivity that is reliably detected; the Ld for HPLC analyses was 0.16% AR or 0.0003 µg/g.

ND = not determined. Volatile organic components were not trapped in this study.

Table B.8.3: Percent distribution of radiolabeled components in aerobic soils after application of [phenyl(U)-¹⁴C]bensulfuron methyl (DPX-F5384)

Time (days)	% of Applied Radioactivity									
	0	3	7	14	21	31	45	60	95	122
DPX-F5384	92.6	81.15	73.23	48.58	38.25	23.49	19.01	18.96	10.13	8.82
IN-R9419	1.54	4.02	9.88	17.32	19.00	27.74	26.85	19.89	16.33	16.51
IN-F7880	0.46	0.40	1.47	3.52	4.24	4.30	2.92	2.20	1.91	2.76
IN-N5297	0.39	2.70	3.96	4.27	4.47	4.06	4.17	5.98	6.06	6.83
IN-B6895	0.47	0.33	<0.16	0.79	<0.16	0.34	0.65	0.60	1.40	1.77
IN-68991	0.50	0.33	0.98	1.00	0.94	1.92	3.42	3.81	2.38	2.88
IN-D1R84	0.25	0.31	<0.16	1.84	2.06	3.29	4.48	7.28	14.46	18.20
Unidentified Radioactivity ≥Ld	5.50	3.26	2.61	5.19	5.79	3.53	3.72	4.38	6.35	3.31
Unidentified Radioactivity ≥Lc ≥Ld	0.23	0.32	2.40	2.19	1.85	1.99	2.15	1.56	2.34	3.35
Extracted	102.53	92.82	94.53	84.68	76.59	70.67	67.36	64.65	58.97	61.55
¹⁴ CO ₂	ND	0.14	0.46	2.04	4.42	6.68	8.98	10.74	12.96	14.16
Volatile organics	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Unextracted	1.01	5.38	5.96	11.13	14.60	18.72	21.20	21.07	24.92	22.84
Total	103.55	98.34	100.95	97.85	95.61	96.08	97.54	96.45	96.85	98.55

Lc = critical limit = radioactivity that is differentiable from background but is not reliably detected; Lc for HPLC analyses was 0.07% AR or 0.0002 µg/g.

Ld = detection limit = radioactivity that is reliably detected; the Ld for HPLC analyses was 0.16% AR or 0.0003 µg/g.

ND = not determined. Volatile organic components were not trapped in this study.

Degradation pathway: The proposed degradation pathway is summarised in Figure B.8.1. This proposed metabolic pathway for bensulfuron methyl in soil involves de-esterification of the methyl ester to form IN-R9419, followed by hydrolysis of the sulfonylurea bridge of IN-R9419 to form IN-D1R84 and IN-J0290 as major soil degradates. Minor pathways included O-demethylation of the pyrimidine amine to form IN-F7880 and hydrolysis of the sulfonylurea linkage of bensulfuron methyl to yield IN-J0290 and IN-N5297. Next, IN-N5297 cyclises to form IN-B6895. IN-B6895 formation is believed to be an artefact of the considerably more basic soil extraction conditions used in previous studies.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

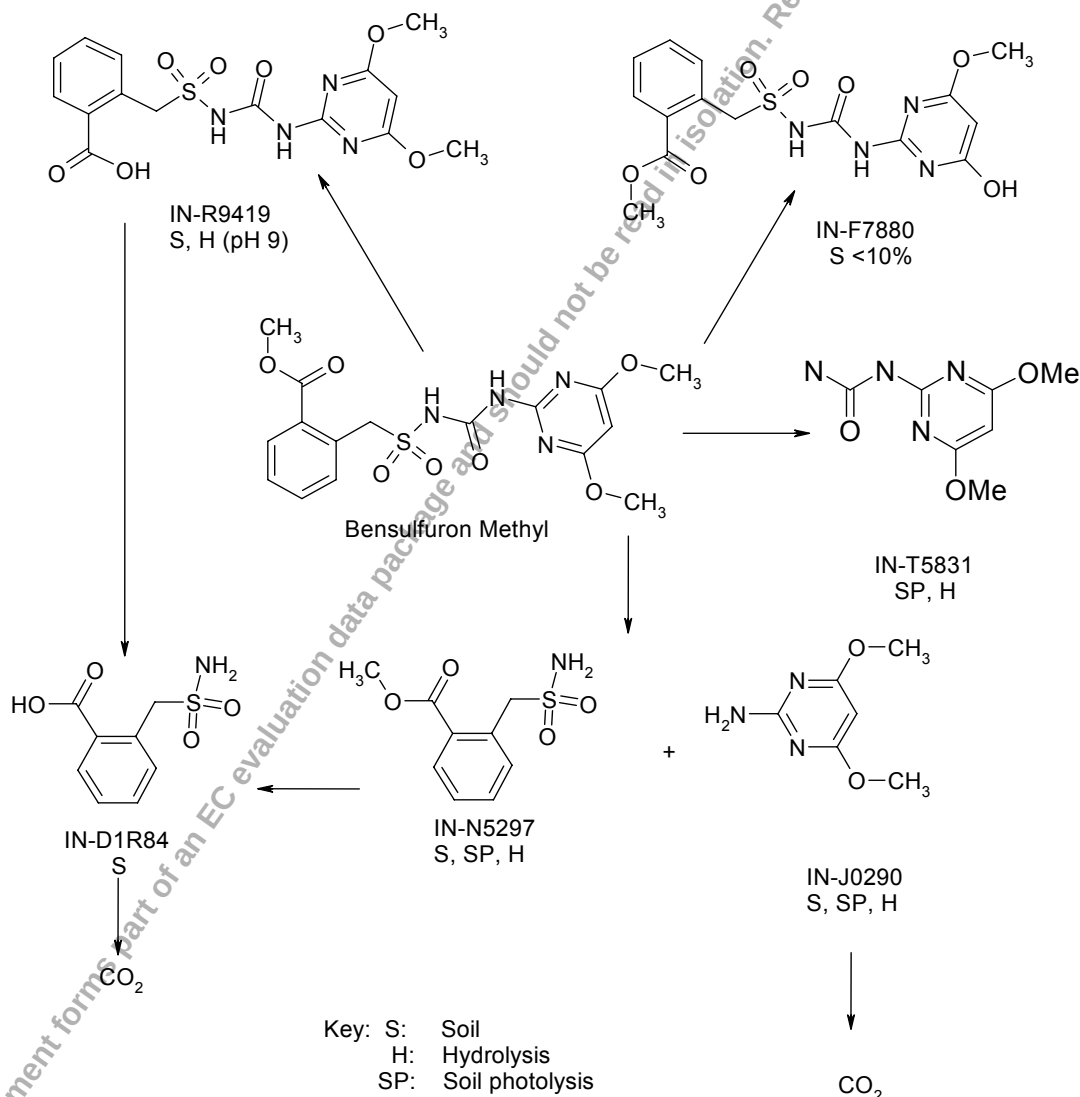
Environmental fate and behaviour

Conclusion:

Degradation of [^{14}C]bensulfuron methyl was rapid; besides $^{14}\text{CO}_2$, IN-R9419, IN-J0290, and IN-D1R84 were the only degradation products found at levels greater than 10% of the applied radioactivity. Degradates present between 5-10% AR were IN-N5297 and IN-F7880. IN-B6895 was identified as a minor degradate less than 2%. The formation of $^{14}\text{CO}_2$, which accompanied the disappearance of bensulfuron methyl, IN-R9419, and the formation (and decline) of the other degradates was indicative that soil microbes played a significant part in the ultimate mineralisation of bensulfuron methyl. In other soil degradation studies, no $^{14}\text{CO}_2$ was observed to form from [^{14}C]bensulfuron methyl if soils were sterilised prior to treatment (Friedman, 1984; Yordy, 1987).

The results obtained in this study indicate that bensulfuron methyl should readily degrade in a microbially viable soil, with eventual mineralisation to CO_2 .

Figure B.8.1: Proposed degradation pathway of bensulfuron methyl in soil



2) *Aerobic soil metabolism of ^{14}C -DPX-F5384. Friedman, P.L., 1984*

Cross reference IIA 7.1.1.1.1/02, IIA 7.1.1.2.1/05

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Guidelines:

U.S. Environmental Protection Agency – “Pesticide Assessment Guidelines, Subdivision N—Chemistry: Environmental Fate” (EPA 540/9-82-021)

GLP:

No

The study is acceptable

Materials and Methods:

Two radiolabeled forms of bensulfuron methyl were used: [^{14}C -2-Pyrimidine]bensulfuron methyl (radiochemical purity >99%) and [^{14}C -phenyl-]bensulfuron methyl (radiochemical purity >99%). The behaviour of bensulfuron methyl (DPX-F5384) was studied in non-sterile and sterile Flanagan and Keyport silt loam soils (characteristics are reported in Table B.8.4) under aerobic laboratory conditions.

Table B.8.4: Soil characteristics

Characteristic	Soil	
Soil Name or Designation	Flanagan	Keyport
Origin Location	Rochelle, IL	Newark, DE
pH	5.6	6.7
% Sand (2000 - 50 μm)	13	0
% Silt (<50 - 2 μm)	71	87
% Clay (<2 μm)	16	13
Texture ^a	Silt Loam	Silt Loam
Organic matter (%)	4.2	1.7
Organic Carbon (%) ^b	2.4	0.99
Cation exchange capacity (meq/100 g)	22.0	8.7

^a U.S.D.A. soil classification system

^b % organic carbon = % organic matter * 0.55

Test vessels containing fresh silt loam soil (equivalent to 50-g oven dried soil) were treated with aqueous bensulfuron methyl solutions at rates of 0.59 ppm (1 mL of 29.3 ppm phenyl label), 0.49 ppm (7 mL of 3.5 ppm pyrimidine label) and 0.05 ppm (0.06 mL of 44.0 ppm phenyl label). Assuming a soil depth of 5 cm and a bulk density of 1.5 g/cm³, the resulting application rate was of 442, 368 and 38 g a.i./ha. Soil samples were incubated under aerobic conditions up to one year in the dark at approximately 25°C at a soil moisture content of 70% of moisture holding capacity. Provisions were made to trap radiolabeled $^{14}\text{CO}_2$. Microbial viability was confirmed at 0, 11, and 32 weeks by soil treatment with ^{14}C -cellulose. In non-sterile tests eight sampling times were established for [Phenyl- ^{14}C]bensulfuron methyl (week 0, 1, 2, 4, 8, 17, 35 and 52) and four for [Pyrimidine-2- ^{14}C]bensulfuron methyl (week 0, 17, 35 and 52). In sterile tests the samples were analysed at week 4, 26 and 52 for phenyl label and at week 17, 35 and 52 for pyrimidine label.

Each soil sample was extracted three times with methylene chloride/methanol/1 M ammonium carbonate (200 mL of 4/3/1, v/v/v). Combined filtrates were concentrated, the pH adjusted to 4 with glacial acetic acid, and the resultant solutions extracted with methylene chloride. After the initial extraction, soil samples were subsequently refluxed for 1 hour with acetone/1 M ammonium carbonate (3/1, v/v). For each sample, all aliquots were analysed by liquid scintillation counting (LSC) to determine total extractable radioactivity. Extracted soil samples were combusted to determine levels of non-extractable residues.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Findings:

All results are reported in Table B.8.5 and Table B.8.6.

Table B.8.5: Percent distribution of radiolabeled components in Keyport aerobic soil after application of ¹⁴C-bensulfuron methyl (DPX-F5384)

% of Applied Radioactivity									
Sampling Point (weeks)	Extractable	DPX-F5384	IN-N5297	IN-B6895	IN-J0290	Polars	¹⁴ CO ₂	Non-Extractable Residue	Total ^a
Phenyl Label (0.59 ppm)									
0 NS	97	93	0	0	ND	2	0	2	99
1 NS	83	67	6	2	ND	0	0	9	92
2 NS	95	55	6	2	ND	3	1	10	106
4 NS	87	61	9	2	ND	6	6	8	101
8 NS	63	36	21	2	ND	3	14	18	95
17 NS	44	28	6	1	ND	3	27	19	90
35 NS	28	16	4	0	ND	4	38	19	85
52 NS	24	7	3	5	ND	4	42	17	83
4 S	92	68	12	2	ND	0	0	7	99
26 S	91	50	22	9	ND	3	0	2	93
52 S	92	35	23	10	ND	17	1	5	98
Phenyl Label (0.05 ppm)									
0 NS	63	63	0	0	ND	2	0	0	63
1 NS	76	69	0	0	ND	0	0	7	83
2 NS	82	60	0	2	ND	0	3	11	96
4 NS	73	64	0	2	ND	3	8	8	89
8 NS	92	83	3	0	ND	5	16	17	125
17 NS	69	46	7	2	ND	5	29	29	127
35 NS	38	16	5	1	ND	7	39	19	96
52 NS	27	8	0	5	ND	4	44	19	90
4 S	101	68	12	1	ND	2	0	11	112
26 S	80	48	16	4	ND	6	0	5	85
52 S	89	35	31	2	ND	13	1	4	94
Pyrimidine Label (0.49 ppm)									
0 NS	97	84	ND	ND	4	0	0	0	97
17 NS	62	36	ND	ND	7	8	25	24	111
35 NS	40	16	ND	ND	6	7	35	24	99
52 NS	27	13	ND	ND	9	5	38	16	81
17 S	54	43	ND	ND	9	1	0	11	65
35 S	47	25	ND	ND	9	3	1	27	75
52 S	34	17	ND	ND	7	3	1	21	56

ND = Not determined

NS = Non-sterile

S = Sterile

^a Total includes extractable, ¹⁴CO₂, and non-extractable residue.

Material balance: Material balance for the [¹⁴C-phenyl] label applied at 0.59 ppm to nonsterile soils ranged from 82 to 122% of applied radioactivity (AR), while for sterile soil it ranged from 93 to 103% AR. Material balance for the [¹⁴C-pyrimidine] label applied at 0.49 ppm to nonsterile soils ranged from 81 to 123%AR and to sterile soil ranged from 56 to 96%AR. The lowest mass balance occur after 35 weeks, while for the first period of the experiment, mass balance is acceptable. Material balance for the [¹⁴C-phenyl] label applied at 0.05 ppm to non-sterilised soil samples ranged from 63-127% and to sterile soil from 85-112%. The experiments performed with 0.05 ppm a.s present a very low mass balance since the beginning of the study; therefore they are considered not acceptable.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.6: Percent distribution of radiolabeled components in Flanagan aerobic soil after application of ^{14}C -bensulfuron methyl (DPX-F5384)

% of Applied Radioactivity									
Sampling Point (weeks)	Extractable	DPX-F5384	IN-N5297	IN-B6895	IN-J0290	Polars	$^{14}\text{CO}_2$	Non-Extractable Residue	Total ^a
Phenyl Label (0.59 ppm)									
0 NS	90	84	0	0	ND	2	0	7	97
1 NS	116	94	6	2	ND	1	0	6	122
2 NS	91	72	11	2	ND	3	0	6	97
4 NS	87	57	15	3	ND	2	2	7	96
8 NS	79	48	9	4	ND	6	7	13	99
17 NS	58	25	15	5	ND	3	19	13	90
35 NS	37	12	9	0	ND	4	32	13	82
52 NS	35	9	13	3	ND	4	38	13	86
4 S	97	72	12	2	ND	1	0	4	101
26 S	94	46	40	3	ND	1	0	5	99
52 S	97	6	72	7	ND	4	1	5	103
Phenyl Label (0.05 ppm)									
0 NS	66	66	0	0	ND	2	0	2	68
1 NS	64	56	2	0	ND	1	0	5	69
2 NS	69	62	0	0	ND	1	1	10	80
4 NS	70	53	10	0	ND	3	2	8	80
8 NS	81	48	12	2	ND	3	7	10	98
17 NS	59	34	11	5	ND	0	15	11	85
35 NS	49	16	4	2	ND	4	24	11	84
52 NS	37	10	6	1	ND	5	29	12	78
4 S	87	65	12	4	ND	0	0	5	92
26 S	81	29	38	7	ND	4	0	4	85
52 S	86	21	53	2	ND	1	0	4	90
Pyrimidine Label (0.49 ppm)									
0 NS	122	97	ND	ND	5	7	0	1	123
17 NS	80	47	ND	ND	26	2	2	13	95
35 NS	80	21	ND	ND	46	2	4	15	99
52 NS	82	10	ND	ND	29	2	5	20	107
17 S	79	39	ND	ND	34	1	0	11	90
35 S	74	23	ND	ND	48	2	0	20	94
52 S	72	17	ND	ND	42	2	0	24	96

ND = Not determined

NS = Non-sterile

S = Sterile

^a Total includes extractable, $^{14}\text{CO}_2$, and non-extractable residue.

Principal degradation products: Carbon dioxide (CO_2), IN-N5297 (sulfonamide), and IN-J0290 (pyrimidine amine) were identified as the principal degradation products in non-sterile soil. Polar compounds were also detected (<8% AR) in non-sterile soil. $^{14}\text{CO}_2$ increased to a maximum of 44 (Keyport soil) and 38% (Flanagan soil) AR at 52 weeks. In non-sterile soils, the amount of bensulfuron methyl declined to approximately 7- 13% of applied radioactivity at week 52. In sterile soils, the amount of bensulfuron methyl declined to approximately 6-35% of applied radioactivity at week 52. $^{14}\text{CO}_2$ levels in sterile soils were insignificant while levels of IN-N5297 and IN-J0290 were higher than in the non-sterile soils.

Non-extractable residues (NER): The amount of NERs increased with time and reached a maximum of 29 (17 weeks) and 24% (17-35 weeks) of the applied radioactivity in the Keyport soil samples with the phenyl and

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pyrimidine labels, respectively. NERs increased with time and reached a maximum of 13 (8-52 weeks) and 24% (52 weeks) of the applied radioactivity in the Flanagan soil samples in the phenyl and pyrimidine labels, respectively. The identity of the non-extractable residues was not further investigated.

Degradation pathway: The degradation pathway of bensulfuron methyl is shown in Figure B.8.1. Degradation of bensulfuron methyl in aerobic soil proceeds through a combination of biotic and abiotic process, as can be seen by comparing the route of degradation in sterile and non-sterile soils. The most significant degradation pathway was mineralisation by microorganisms to form CO₂ and non-extractable soil residues. Also, cleavage of the sulfonylurea bridge occurred to yield IN-J0290 (pyrimidine amine) and IN-N5297 (sulfonamide). The proportion of IN-N5297 and IN-J0290 was higher in sterile soils, showing that the sulfonylurea bridge hydrolysis occurs *via* biotic or abiotic processes. Lower amounts of non-extractable soil residues (NER) were found in the sterile soils, showing that microorganisms contribute to the formation of NER.

Conclusion:

Bensulfuron methyl degraded in soil under aerobic conditions. Mineralisation to form CO₂ and cleavage of the sulfonylurea bridge are the major degradation pathways in non-sterile soil. Only studies performed with about 0.5 ppm bensulfuron are acceptable. It has to be stated that the dose is about 10 times the supported GAP. RMS believe that this value can be acceptable for the clarification of the route of degradation of the substance.

3) *Aerobic soil metabolism of DPX-F5384. Yordy, J.R., 1987*

Cross reference IIA 7.1.1.1.1/03, 7.1.1.2.1/10

Guidelines:

Not specified

GLP:

Yes

The study is acceptable only in part

Materials and Methods:

Two radiolabeled forms of bensulfuron methyl were used: [pyrimidine-2-¹⁴C]bensulfuron methyl (Ag Prod Dept File No #194, radiochemical purity 98.1%) and [phenyl-¹⁴C]bensulfuron methyl (Ag Prod Dept File No #199, radiochemical purity 96.5%). The rate and pattern of metabolism of bensulfuron methyl (DPX-F5384) was studied in three rice paddy soils under aerobic laboratory conditions. Soil characteristics are reported in Table B.8.7.

Biometer flasks containing non-sterile and sterile rice paddy soil (equivalent to 50 g oven dried soil) were treated with aqueous bensulfuron methyl solutions at a rate of 0.1 ppm (79.9 µL of 62.6 ppm phenyl label or 97.3 µL of 51.4 ppm pyrimidine label). Assuming a soil depth of 5 cm and a bulk density of 1.5 g/cm³, the equivalent rate of application is 0.08 kg a.i./ha. High dose flasks (1.9 mL of non-radioactive DPX-F5384 stock solution and 79.9 µL or 97.3 µL of phenyl label or pyrimidine label respectively) with a DPX-F5384 concentration of 10 µg/g (10 ppm, 7.5 kg a.i./ha) were set to enable isolation of sufficient amount of radiolabeled metabolites.

Sterile soils were autoclaved before treatment for one hour on each of three consecutive days. Soil samples were incubated under aerobic conditions up to one year in the dark at 25±3°C at a soil moisture content of 70% of

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moisture holding capacity. Provisions were made to trap radiolabeled $^{14}\text{CO}_2$. Microbial mineralisation was measured in soils treated with ^{14}C -cellulose.

Table B.8.7: Soil characteristics

Characteristic	Soil		
Soil Name or Designation	Nagano	Tochigi	California
Origin Location	Japan	Japan	U.S.A.
pH	5.2	6.1	6.5
% Sand (2000 - 50 μm)	57.0	29.0	25
% Silt (<50 - 2 μm)	30.0	38.0	63
% Clay (<2 μm)	13.0	33.0	12
Texture ^a	Sandy Loam	Clay Loam	Silt Loam
Organic matter (%)	2.1	7.4	1.9
Organic carbon (%) ^b	1.2	4.3	1.1
Cation exchange capacity (meq/100 g)	16.5	12.3	17.5

^a U.S.D.A. soil classification system

^b %organic carbon = % organic matter x 0.58

Soil samples were extracted overnight with 50 mL 0.1 M ammonium carbonate. After centrifugation, the soil pellets were subsequently extracted with methanol/methylene chloride/2 M ammonium carbonate (4/3/1, v/v/v) and acetone. All extracts were combined, concentrated, and re-suspended in 0.1 M ammonium carbonate. After the initial extraction, soil samples were subsequently refluxed with acetone/0.1 M ammonium carbonate (3/1, v/v). The reflux extracts were concentrated and re-suspended in acetone. For each sample, all aliquots were analysed by liquid scintillation counting (LSC) to determine total extractable radioactivity. Extracted soil samples were combusted to determine levels of non-extractable residues. Degradation products were positively identified in concentrated extracts by chromatography (TLC or HPLC) with reference standards. The presence of $^{14}\text{CO}_2$ was confirmed by barium carbonate precipitation.

Findings:

Material balance: The Japanese soil results have not a good mass balance. California soil has a better mass balance even if not the one required by current guidelines. In general, material balance (Table B.8.8 to Table B.8.10) for the [^{14}C -phenyl] label applied to non-sterile soil ranged from 68.6 to 111.6%AR and, for sterile soils, from 84.1 to 104.7%AR. Material balance for the [^{14}C -pyrimidine] label applied to non-sterile and sterile soils ranged from 70.5 to 107.5%AR and from 70.5 to 125.7%AR respectively.

Principal degradation products: Bensulfuron methyl degraded rapidly in non-sterile soils under aerobic conditions (Table B.8.11 to Table B.8.13), declining to 52% or less of applied radioactivity (AR) after 4 weeks and to 7%AR or less after 52 weeks. Carbon dioxide (CO_2), IN-N5297 (sulfonamide), IN-J0290 (pyrimidine amine), and IN-B6895 (homosaccharin) were identified as the principal degradation products. In all three soils tested, IN-B6895 was observed to form in higher amounts in the sterile soil than in the non-sterile soil. The cyclisation of IN-N5297 to form IN-B6895 in the alkaline environment was well documented (Sabadie, J., 1996; cross reference 7.2.1.1/02). Therefore, the formation of IN-B6895 is believed to be an artefact of the considerably more basic soil extraction conditions used in this study. Polar compounds and unidentified degradates were also detected. They were identified as 0.03-0.08, 0.5-0.6 and 0.73 migration distance relative to DPX-F5384. The polar compound with 0.03-0.08 migration distance reached a maximum of 14%AR at week 4 in non autoclaved soils and of 27%AR at week 30 in

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autoclaved soils. The unknown compound with 0.5-0.6 migration distance accounted for less than 20%AR (week 4) in non-sterile soils and for less than 29%AR (week 20) in sterile soil. The unknown metabolite with 0.73 migration distance was found only in Tochigi soil and accounted less than 3%AR, except for week 45 with the phenyl labelled soil (7%AR). $^{14}\text{CO}_2$ increased to a maximum of 40.1 (phenyl label) and 21.6% (pyrimidine label) AR at 52 weeks. In sterile soils, $^{14}\text{CO}_2$ levels were insignificant while levels of sulfonamide and homosaccharin were higher than in the non-sterile soils. *Non-extractable residues (NER)*: The amount of NERs in the non-sterile soils reached a maximum of 30.3 (28 weeks) and 37.7% (19 weeks) of the applied radioactivity with the phenyl and pyrimidine labels, respectively. Levels of NERs were generally lower in the sterile soils. The identity of the non-extractable residues was not further investigated.

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

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Table B.8.8: Percent distribution of radioactivity in aerobic California soil after application of ^{14}C -bensulfuron methyl (DPX-F5384)

% of Applied Radioactivity						
Sampling Point (weeks)	Extracted	Extracted by Reflux	Total Extracted	Non-Extractable Residue	$^{14}\text{CO}_2$	Total
Phenyl Label (Non-sterile)						
0	87.1	2.2	89.3	7.9	0.0	97.2
1	87.0	2.8	89.8	9.4	1.4	100.6
2	86.9	3.5	90.4	11.6	2.5	104.4
4	75.2	14.7	89.9	12.1	4.6	106.5
8	63.8	2.6	66.4	22.5	7.2	96.0
14	50.1	4.4	54.5	21.1	11.7	87.3
19	67.2	6.2	73.4	22.9	15.2	111.6
28	50.4	3.2	53.6	24.1	20.8	98.4
36	42.6	9.0	51.6	20.0	25.8	97.4
45	40.7	7.6	48.3	15.5	33.0	96.8
52	30.6	7.3	37.9	16.8	36.4	91.1
Phenyl Label (Sterile)						
0	95.7	4.0	99.7	5.0	0.0	104.7
10	79.6	5.7	85.3	6.9	0.1	92.4
20	82.7	2.6	85.3	7.1	0.2	92.6
30	85.6	5.0	90.6	6.3	0.2	97.1
40	80.4	3.1	83.5	6.0	0.3	89.8
52	75.0	4.5	79.5	4.6	0.0	84.1
Pyrimidine Label (Non-sterile)						
0	86.0	2.5	88.5	8.9	0.0	97.4
1	74.3	3.8	78.1	6.9	0.1	85.0
2	78.3	3.5	81.8	14.1	0.2	96.4
4	73.6	17.3	90.9	14.9	0.9	106.7
8	57.4	7.3	64.7	22.0	2.0	88.6
14	49.1	3.4	52.5	27.6	4.4	84.4
19	46.3	3.4	49.7	33.9	6.5	90.1
28	39.5	6.5	46.0	33.2	10.1	89.2
36	40.3	6.4	46.7	33.4	12.7	92.8
45	37.3	7.7	45.0	32.1	16.0	93.1
52	33.1	4.8	37.9	34.3	17.3	89.5
Pyrimidine Label (Sterile)						
0	95.0	6.5	101.5	11.9	0.0	113.4
10	60.6	7.8	68.4	5.9	0.0	74.4
20	56.3	4.6	60.9	9.9	0.0	70.9
30	62.0	7.1	69.1	10.3	0.0	79.3
40	64.9	4.0	68.9	14.5	0.0	83.4
52	52.9	5.1	58.0	14.0	0.0	72.0

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Table B.8.9: Percent distribution of radioactivity in aerobic Nagano soil after application of ^{14}C -bensulfuron methyl (DPX-F5384)

% of Applied Radioactivity						
Sampling Point (weeks)	Extracted	Extracted by Reflux	Total Extracted	Non-Extractable Residue	$^{14}\text{CO}_2$	Total
Phenyl Label (Non-sterile)						
0	85.5	3.6	89.1	12.1	0.0	101.2
1	59.7	3.3	63.0	10.4	1.8	75.1
2	79.7	3.8	83.5	11.3	3.6	98.5
4	67.2	9.7	76.9	16.5	8.1	101.4
8	53.4	3.6	57.0	20.6	13.7	91.3
14	36.6	3.7	40.3	23.8	21.7	85.8
19	39.4	3.3	42.7	28.4	26.2	97.2
28	33.5	3.8	37.3	30.3	31.8	99.4
36	28.8	6.2	35.0	22.3	35.1	92.4
45	23.4	10.4	33.8	15.0	38.7	87.5
52	20.6	10.3	30.9	17.9	40.1	88.9
Phenyl Label (Sterile)						
0	89.8	5.3	95.1	3.1	0.0	98.2
10	79.5	7.3	86.8	3.2	0.1	90.1
20	87.3	2.8	90.1	5.3	0.1	95.5
30	86.9	7.2	94.1	4.9	0.2	99.2
40	82.9	3.3	86.2	5.1	0.2	91.5
52	82.5	5.7	88.2	5.4	0.0	93.6
Pyrimidine Label (Non-sterile)						
0	91.5	5.6	97.1	10.5	0.0	107.5
1	83.1	2.0	85.1	13.3	0.2	98.6
2	82.5	4.2	86.7	11.3	0.7	98.7
4	68.7	10.6	79.3	12.1	2.2	93.6
8	61.4	6.8	68.2	16.7	4.3	89.2
14	50.6	2.7	53.3	18.0	7.8	79.0
19	41.1	3.4	44.5	21.8	10.2	76.4
28	40.1	6.7	46.8	24.2	13.2	84.2
36	44.4	6.1	50.5	21.0	14.7	86.2
45	42.2	17.3	59.5	16.3	16.5	92.2
52	35.9	6.6	42.5	18.8	17.1	78.4
Pyrimidine Label (Sterile)						
0	89.1	2.0	91.1	9.2	0.0	100.2
10	73.6	9.7	83.3	3.4	0.0	86.7
20	68.2	4.4	72.6	6.1	0.0	78.7
30	78.4	10.0	88.4	5.0	0.0	93.4
40	71.0	3.5	74.5	5.8	0.0	80.2
52	61.2	2.8	64.0	6.5	0.0	70.5

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Table B.8.10: Percent distribution of radioactivity in aerobic Tochigi soil after application of ^{14}C -bensulfuron methyl (DPX-F5384)

% of Applied Radioactivity						
Sampling Point (weeks)	Extracted	Extracted by Reflux	Total Extracted	Non-Extractable Residue	$^{14}\text{CO}_2$	Total
Phenyl Label (Non-sterile)						
0	73.2	6.7	79.9	12.9	0.0	92.8
1	44.2	5.0	49.2	18.9	0.7	68.6
2	71.1	6.5	77.6	14.0	1.1	92.7
4	60.9	13.3	74.2	11.1	2.0	87.3
8	56.0	6.7	62.7	24.1	3.3	90.0
14	55.0	5.0	60.0	25.0	6.0	91.0
19	46.6	6.4	53.0	27.8	8.3	89.1
28	49.8	8.0	57.8	22.7	12.3	92.8
36	51.1	13.0	64.1	12.0	15.6	91.6
45	49.8	16.6	66.4	9.1	19.8	95.2
52	36.1	13.6	49.7	12.4	21.6	83.8
Phenyl Label (Sterile)						
0	91.7	3.1	94.8	1.8	0.0	96.8
10	64.0	9.2	73.2	19.7	0.0	92.9
20	59.7	8.0	67.7	28.0	0.0	95.7
30	59.1	22.5	81.6	10.9	0.0	92.5
40	59.6	19.8	79.4	10.7	0.0	90.0
52	56.5	28.1	84.6	5.8	0.0	90.4
Pyrimidine Label (Non-sterile)						
0	69.5	4.1	73.6	17.2	0.0	90.8
1	56.7	5.3	62.0	13.9	0.0	76.0
2	63.3	7.5	70.8	15.8	0.2	86.9
4	54.2	15.7	69.9	11.9	0.9	82.7
8	41.2	6.9	48.1	25.4	2.7	76.2
14	33.3	10.4	43.7	37.2	6.9	87.8
19	32.8	7.7	40.5	37.7	10.4	88.5
28	31.2	10.7	41.9	35.7	15.2	92.8
36	30.8	11.5	42.3	35.4	18.0	95.6
45	25.8	16.0	41.8	23.9	20.7	86.4
52	20.8	12.4	33.2	30.3	21.6	85.1
Pyrimidine Label (Sterile)						
0	87.3	2.5	89.8	3.3	0.0	93.1
10	59.5	11.4	70.9	21.7	0.0	92.6
20	48.0	9.3	57.3	31.3	0.0	88.7
30	90.3	19.6	109.9	15.8	0.0	125.7
40	43.1	18.4	61.5	21.4	0.0	82.9
52	39.8	22.6	62.4	20.5	0.0	82.8

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Environmental fate and behaviour

Table B.8.11: Percent distribution of radiolabeled components in aerobic California soil after application of ¹⁴C-bensulfuron methyl (DPX-F5384)

% of applied Radioactivity ^a						
Sampling point (weeks)	DPX-F5384	Polars ^b	IN-B6895 (Homosaccharin)	Other (UK1) ^c	IN-N5297 (Sulfonamide)	IN-J0290 (Pyrimidine amine)
Phenyl label (non-sterile)						
0	86	2	0	0	0	--
1	66	12	0	0	5	--
2	62	4	10	0	0	--
4	41	9	5	20	0	--
8	31	0	10	18	0	--
14	18	6	13	14	0	--
19	23	5	30	9	2	--
28	9	6	35	0	0	--
36	10	2	17	15	2	--
45	16	0	2	18	4	--
52	6	4	13	4	2	--
Phenyl label (sterile)						
0	96	0	0	0	0	--
10	26	15	37	0	1	--
20	19	6	28	29	0	--
30	17	3	38	27	1	--
40	8	6	65	0	0	--
52	7	0	23	0	32	--
Pyrimidine Label (Non-sterile)						
0	86	0	--	--	--	0
1	66	4	--	--	--	0
2	59	6	--	--	--	8
4	44	14	--	--	--	11
8	46	3	--	--	--	7
14	34	8	--	--	--	7
19	38	5	--	--	--	7
28	25	0	--	--	--	12
36	29	0	--	--	--	12
45	9	0	--	--	--	8
52	5	0	--	--	--	5
Pyrimidine Label (Sterile)						
0	95	0	--	--	--	0
10	36	18	--	--	--	7
20	36	13	--	--	--	7
30	39	0	--	--	--	23
40	23	12	--	--	--	19
52	10	6	--	--	--	8

^a Presented in report as ppb DPX-F5384 equivalents. Since the application rate was 100 ppb, the values in the report are equivalent to percent-applied radioactivity.

^b Identified in report as 0.03-0.08 migration distance relative to DPX-F5384.

^c UK1: unknown product1, identified in report as 0.5-0.6 migration distance relative to DPX-F5384

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Table B.8.12: Percent distribution of radiolabeled components in aerobic Nagano soil after application of ¹⁴C-bensulfuron methyl (DPX-F5384)

% of Applied Radioactivity ^a						
Sampling Point (weeks)	DPX-F5384	Polars ^b	IN-B6895 (Homosaccharin)	Other (UK1) ^c	IN-N5297 (Sulfonamide)	IN-J0290 (Pyrimidine amine)
Phenyl Label (Non-sterile)						
0	79	0	0	0	0	--
1	52	0	0	0	0	--
2	52	8	0	6	0	--
4	37	11	13	5	1	--
8	32	6	16	0	0	--
14	18	4	6	4	2	--
19	16	6	6	8	1	--
28	8	6	8	8	2	--
36	8	5	8	7	1	--
45	5	3	5	7	3	--
52	5	4	3	4	3	--
Phenyl Label (Sterile)						
0	90	0	0	0	0	--
10	38	5	32	0	1	--
20	34	8	44	0	0	--
30	21	3	63	0	2	--
40	11	5	65	0	2	--
52	11	0	20	0	38	--
Pyrimidine Label (Non-sterile)						
0	86	5	--	--	--	0
1	83	0	--	--	--	0
2	61	0	--	--	--	0
4	41	13	--	--	--	6
8	40	10	--	--	--	10
14	35	10	--	--	--	6
19	24	0	--	--	--	10
28	13	10	--	--	--	17
36	22	0	--	--	--	18
45	6	0	--	--	--	12
52	0	4	--	--	--	8
Pyrimidine Label (Sterile)						
0	89	0	--	--	--	0
10	53	13	--	--	--	8
20	52	9	--	--	--	7
30	47	0	--	--	--	31
40	35	0	--	--	--	21
52	18	0	--	--	--	13

^a Presented in report as ppb DPX-F5384 equivalents. Since the application rate was 100 ppb, the values in the report are equivalent to percent-applied radioactivity.

^b Identified in report as 0.03-0.08 migration distance relative to DPX-F5384.

^c UK1: unknown product1, identified in report as 0.5-0.6 migration distance relative to DPX-F5384

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Table B.8.13: Percent distribution of radiolabeled components in aerobic Tochigi soil after application of ¹⁴C-bensulfuron methyl (DPX-F5384)

% of Applied Radioactivity ^a							
Sampling Point (weeks)	DPX-F5384	Polars ^b	IN-B6895 (Homosaccharin)	Other		IN-N5297 (Sulfonamide)	IN-J0290 (Pyrimidine amine)
				UK1 ^c	UK2 ^d		
Phenyl Label (Non-sterile)							
0	67	0	0	0	0	0	--
1	31	0	0	0	0	10	--
2	53	0	0	0	0	0	--
4	40	14	12	4	0	2	--
8	29	0	23	2	1	4	--
14	19	5	28	2	0	3	--
19	15	4	18	9	0	2	--
28	10	0	0	13	0	25	--
36	12	0	22	7	3	11	--
45	4	0	23	0	7	5	--
52	7	3	20	0	1	3	--
Phenyl Label (Sterile)							
0	92	0	0	0	--	0	--
10	32	7	24	0	--	0	--
20	26	3	32	1	--	1	--
30	21	0	21	0	--	27	--
40	10	3	53	4	--	2	--
52	7	0	9	0	--	40	--
Pyrimidine Label (Non-sterile)							
0	69	0	--	--	0	--	0
1	38	0	--	--	0	--	2
2	54	0	--	--	0	--	4
4	52	0	--	--	1	--	8
8	36	0	--	--	0	--	5
14	29	3	--	--	0	--	5
19	28	0	--	--	0	--	7
28	18	0	--	--	3	--	8
36	23	0	--	--	2	--	7
45	10	0	--	--	0	--	7
52	3	2	--	--	3	--	2
Pyrimidine Label (Sterile)							
0	87	0	--	--	--	--	0
10	47	8	--	--	--	--	5
20	38	4	--	--	--	--	7
30	55	27	--	--	--	--	14
40	32	0	--	--	--	--	14
52	12	0	--	--	--	--	14

^aPresented in report as ppb DPX-F5384 equivalents. Since the application rate was 100 ppb, the values in the report are equivalent to percent-applied radioactivity.

^bIdentified in report as 0.03-0.08 migration distance relative to DPX-F5384.

^cUK1: unknown product1 identified in report as 0.5-0.6 migration distance relative to DPX-F5384.

^dUK2: unknown product2 identified in report as 0.73 migration distance relative to DPX-F5384.

Degradation pathway: The degradation pathway of bensulfuron methyl is shown in Figure B.8.1. The most significant degradation pathway was mineralisation by microorganisms to form CO₂ and non-extractable soil residues. Also, cleavage of the sulfonylurea bridge occurred to yield IN-J0290 (pyrimidine amine) and IN-N5297 (sulfonamide).

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Conclusion:

Bensulfuron methyl degraded moderately in soil under aerobic conditions. IN-N5297 (sulfonamide), IN-J0290 (pyrimidine amine), non-extractable residues, and carbon dioxide are the principal degradation products in non-sterile soil under aerobic conditions. Microbes are capable of, but not essential for, the initial bensulfuron methyl breakdown. The studies confirm the degradation previously presented. It have to be underlined that a poor mass balance characterises this study.

B.8.1.1.2 Anaerobic degradation (Annex IIA 7.1.1.2)

- 4) *Anaerobic aquatic metabolism of [pyrimidine-2-¹⁴C]DPX-F5384 and [phenyl(U)-¹⁴C]DPX-F5384 in Firebaugh, California, rice paddy sediment. Cadwgan, G. E., Ryan, T.W. 1986*

Cross reference IIA 7.1.1.2./01, IIA 7.1.1.2./03

Guidelines:

USEPA 162-3 (1982)

GLP:

No, GLP was not required at the time this study was conducted. However the work was done in the spirit of GLP.

The study is acceptable

Material and Methods:

Two radiolabeled forms of bensulfuron methyl were used: [phenyl(U)-¹⁴C]bensulfuron methyl (specific activity 29.8 µCi/mg; radiochemical purity >99%) and [pyrimidine-2-¹⁴C]bensulfuron methyl (specific activity 16.6 µCi/mg; radiochemical purity >99%). Approximately 0.25 mg of each radiolabel was dissolved in 25 mL acetone/water.

The rate and pattern of metabolism of bensulfuron methyl (DPX-F5384) was studied in nonsterilised and sterilised aquatic rice paddy soil systems (Table B.8.14) under laboratory anaerobic conditions.

Table B.8.14 Characteristics of the sediment/water system

Characteristic	System
Location/Source	Firebaugh, California, U.S.A.
<i>Sediment</i>	
pH	6.5
% Sand (2000 - 50 µm)	25.0
% Silt (<50 - 2 µm)	63.0
% Clay (<2 µm)	12.0
Texture ^a	Silt Loam
Organic matter (%)	1.9
Organic carbon (%) ^b	1.1
Cation exchange capacity (meq/100 g)	17.5
<i>Water</i>	
pH	7.0

^a U.S.D.A. soil classification system

^b % organic carbon = % organic matter × 0.58

Paddy sediment (~2 kg), covered with 3 kg deionised distilled water, was incubated under nitrogen in darkness at 25°C. After 30 days, 75 g wet paddy sediment, equivalent to 48 g dry weight, and 150 mL water were transferred to

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

250 mL plastic bottles. Sterilised systems were autoclaved at 100°C for 1 hour on three consecutive days. Systems were treated with 0.54 mL 0.0091 mg/mL [phenyl(U)-¹⁴C] or 0.62 mL 0.0074 mg/mL [pyrimidine-2-¹⁴C]bensulfuron methyl stock solutions for a nominal rate of 0.1 ppm (0.099 ppm [phenyl(U)-¹⁴C]; 0.092 ppm [pyrimidine-2-¹⁴C]) based upon the dry weight of the sediment. This rate corresponds approximately to an application rate of 75 g/ha. Test vessels were flushed with nitrogen, tightly capped, and incubated for an additional 53 weeks (nonsterilised) or 36 weeks (sterilised) at 25°C. No attempts were made to trap volatiles.

Water was separated from the soil by filtration and aliquots were analysed by liquid scintillation counting (LSC). Sediment samples were extracted at least four times with 100 mL methylene chloride:methanol:2 M ammonium carbonate (4:3:1; v:v:v). After 4 weeks, samples were also extracted two times by refluxing with 200 mL acetone: 0.1 M ammonium carbonate (9:1, v:v). Nonsterilised 36- and 53-week sediment samples were also refluxed with 0.1 M aqueous NaOH. Extracts were combined and aliquots were analysed by LSC to determine total extractable radioactivity. Extracted soil samples were combusted to determine levels of NER residues. Samples were concentrated, purified on C18 Bond Elut columns, and analysed by TLC. Degradation products were identified by co-chromatography using authentic standards by TLC.

Findings:

Results are reported from Table B.8.15 to Table B.8.18

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.15: Percent distribution of applied radioactivity and mass balance in anaerobic aquatic systems treated with 0.1 ppm bensulfuron methyl (DPX-F5384)

Week	% of Applied Radioactivity			
	Water	Sediment Extractable	Non-Extractable Residues	Total Recovered
Pyrimidine-2- ¹⁴ C (Non-sterile)				
0	70.3	24.0	2.0	96.3
2	39.2	44.6	14.6	98.4
4	28.8	70.6	5.6	105.0
8	22.5	55.1	9.5	87.1
16	21.5	44.9	23.5	89.9
25	21.9	61.8	24.0	107.7
36	10.4	74.5	7.1	92.0
53	10.1	51.7	7.2	69.0
Pyrimidine-2- ¹⁴ C (Sterile)				
0 ^a	70.3	24.0	2.0	96.3
2	42.5	51.4	8.8	102.7
16	25.8	57.6	11.5	94.9
36	17.7	66.9	15.7	100.3
Phenyl(U)- ¹⁴ C (Non-sterile)				
0	74.4	24.6	2.2	101.2
2	40.5	50.6	10.7	101.8
4	30.6	62.9	6.1	99.6
8	28.9	53.8	9.5	92.2
16	21.5	30.8	25.3	77.6
25	8.0	52.2	17.2	77.4
36	10.1	44.0	6.1	60.2
53	6.0	37.5	5.4	48.9
Phenyl(U)- ¹⁴ C (Sterile)				
0 ^a	74.4	24.6	2.2	101.2
2	52.9	40.4	11.9	105.2
16	61.1	35.2	7.0	103.3
36	59.3	32.4	9.4	101.1

^a Week 0 is the same as non-sterilised Week 0 sample.

Mass balance: Material balance (Table B.8.15) for nonsterilised systems treated with the [¹⁴C-phenyl] label ranged from 101.2% of AR at Week 0 to 48.9% of AR at Week 53. Material balance for nonsterilised systems treated with the [¹⁴C-pyrimidine] label ranged from 96.3% at Week 0 to 69.0% at Week 53. Material balance for sterilised systems was greater than 94%.

Distribution between water and sediment: For both labels, there was a movement of radioactivity from the water to the sediment (Table B.8.15). By the end of the study (53 weeks), radioactivity associated with the water fell to approximately 10% or less.

Non-extractable residues: Radioactivity associated with the sediment became more difficult to extract over time so 36- and 53-week sediments were refluxed with 0.1 M NaOH. Non-extractable residues (NER) in 36- and 53-week sediments accounted for a maximum of 7.2% of the applied radioactivity in both labels (Table B.8.15).

Principal degradation products: Bensulfuron methyl degraded more quickly in non-sterile compared to sterile anaerobic aquatic systems (Table B.8.16 to Table B.8.18).

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.16: Percent distribution of applied radioactivity in the water phase of anaerobic aquatic systems treated with 0.1 ppm bensulfuron methyl (DPX-F5384)

Week	% Applied Radioactivity						
	DPX-F5384	IN-J0290	IN-W8956 ^d	IN-R9419	Polars ^a	Others ^b	
Pyrimidine-2- ¹⁴ C (Non-sterile)							
0	67.7	<0.1	<0.1	<0.1	<0.1	2.6	
2	35.0	1.9	<0.1	<0.1	<0.1	2.3	
4	28.1	0.5	<0.1	0.1	<0.1	0.1	
8	21.1	0.9	<0.1	0.2	<0.1	0.3	
16	1.8	0.3	<0.1	0.8	18.1	0.5	
36	2.2	0.9	<0.1	0.8	2.7	3.9	
53	2.1	0.7	0.5	1.6	5.2	0.1	
Pyrimidine-2- ¹⁴ C (Sterile)							
0 ^c	67.7	<0.1	<0.1	<0.1	<0.1	2.6	
2	33.5	6.2	<0.1	2.3	<0.1	0.6	
16	13.9	4.3	1.0	0.5	5.9	0.2	
36	9.0	6.8	<0.1	<0.1	1.2	0.7	
Phenyl(U)- ¹⁴ C (Non-sterile)							
0	74.3	<0.1	<0.1	<0.1	<0.1	<0.1	0.1
2	38.4	1.6	<0.1	<0.1	<0.1	<0.1	0.4
4	23.9	3.9	<0.1	1.0	<0.1	<0.1	1.8
8	15.4	9.9	1.3	1.4	0.9	<0.1	<0.1
16	3.2	3.3	2.5	2.0	3.3	6.7	0.2
36	0.7	6.5	0.1	<0.1	2.8	<0.1	<0.1
53	0.6	0.2	<0.1	0.6	2.0	2.5	<0.1
Phenyl(U)- ¹⁴ C (Sterile)							
0 ^c	74.3	<0.1	<0.1	<0.1	<0.1	<0.1	0.1
2	41.6	8.3	<0.1	<0.1	<0.1	<0.1	3.0
16	10.4	7.4	9.7	3.0	7.3	22.2	1.2
36	6.2	22.7	11.4	0.8	14.8	3.5	0.1

^a Includes origin material and other minor (<10% applied radioactivity) polar unknowns.

^b Includes background radioactivity in chromatograms.

^c Sterilised Week 0 is the same as non-sterilised Week 0.

^d IN-W8956 is Methyl 2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]methyl]-4-hydroxybenzoate

In non-sterile soils, the amount of bensulfuron methyl declined to approximately 16-22% applied radioactivity at week 53. In sterile soils, the amount of bensulfuron methyl declined to approximately 36-66% of applied radioactivity at week 53.

The major degradation products (>10% AR) in the non-sterilised water and sediment were IN-N5297 (sulfonamide) produced from the phenyl label, IN-J0290 (pyrimidine amine) produced from the pyrimidine label, and IN-R9419 produced from both phenyl and pyrimidine labels. A bridge-intact IN-W8956 was detected in the non-sterile system and reached a maximum of 4.9 % AR at week 8 and decreased to less than 0.1% AR at the end of the study (week 53) in Pyrimidine and Phenyl labels respectively. In sterile system, IN-W8956 reached a maximum of 11.4% AR at Week 36. IN-B6895 (homosaccharin) also reached a maximum of 14.8% in the sterile total system at Week 36. IN-B6895 formation is believed to be an artefact of the considerably more basic soil extraction conditions used in this study.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.17: Percent distribution of applied radioactivity in the sediment phase of anaerobic aquatic systems treated with 0.1 ppm bensulfuron methyl (DPX-F5384)

Week	% Applied Radioactivity						
	DPX-F5384	IN-J0290	IN-W8956 ^d	IN-R9419	Polars ^a	Others ^b	
Pyrimidine-2- ¹⁴ C (Non-sterile)							
0	23.9	<0.1	<0.1	<0.1	<0.1	0.2	
2	36.5	3.7	1.4	<0.1	<0.1	3.1	
4	46.0	7.6	2.1	10.2	0.1	4.5	
8	35.3	5.2	2.5	2.8	1.7	7.6	
16	29.1	5.9	3.2	1.7	3.5	1.6	
25	39.7	18.2	0.4	2.0	0.4	1.0	
36	32.7	4.6	2.3	3.2	26.4 ^c	5.5	
53	19.4	7.8	<0.1	<0.1	23.0 ^c	1.5	
Pyrimidine-2- ¹⁴ C (Sterile)							
0 ^d	23.9	<0.1	<0.1	<0.1	<0.1	0.2	
2	43.0	4.8	<0.1	<0.1	<0.1	3.6	
16	49.5	7.8	<0.1	<0.1	<0.1	0.4	
36	57.4	6.9	<0.1	<0.1	<0.1	2.5	
Phenyl(U)- ¹⁴ C (Non-sterile)							
0	24.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.4
2	47.7	0.8	<0.1	<0.1	<0.1	<0.1	2.1
4	53.1	2.6	1.7	<0.1	2.2	<0.1	3.3
8	36.7	6.0	3.6	2.1	3.2	0.1	2.1
16	23.6	2.1	2.0	1.6	1.6	<0.1	<0.1
25	29.8	8.5	2.7	3.3	2.6	1.4	4.1
36	16.0	4.2	<0.1	14.7	<0.1	5.7	3.2
53	15.5	3.3	<0.1	<0.1	<0.1	18.1 ^c	0.6
Phenyl(U)- ¹⁴ C (Sterile)							
0 ^d	24.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.4
2	28.9	5.2	<0.1	<0.1	<0.1	<0.1	6.2
16	33.1	<0.1	<0.1	0.9	<0.1	<0.1	1.1
36	29.4	<0.1	<0.1	<0.1	<0.1	<0.1	3.0

^a Includes origin material and other minor (<10% applied radioactivity) polar unknowns.

^b Includes background radioactivity in chromatograms.

^c Includes radioactivity in NaOH reflux extract

^d Sterilised Week 0 is the same as non-sterilised Week 0.

^d IN-W8956 is Methyl 2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]methyl]-4-hydroxybenzoate

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.18: Percent distribution of applied radioactivity in the total anaerobic aquatic systems treated with 0.1 ppm bensulfuron methyl (DPX-F5384)

Week	% Applied Radioactivity						
	DPX-F5384	IN-J0290	IN-W8956 ^d	IN-R9419	Polars ^a	Others ^b	
Pyrimidine-2- ¹⁴ C (Non-sterile)							
0	91.6	<0.1	<0.1	<0.1	<0.1	2.8	
2	71.5	5.6	1.4	<0.1	<0.1	5.4	
4	74.1	8.1	2.1	10.3	0.1	4.6	
8	56.4	6.1	2.5	3.0	1.7	7.9	
16	30.9	6.2	3.2	2.5	21.6	2.1	
25	39.7	18.2	0.4	2.0	0.4	1.0	
36	34.9	5.5	2.3	4.0	29.1	9.4	
53	21.5	8.5	0.5	1.6	28.2	1.6	
Pyrimidine-2- ¹⁴ C (Sterile)							
0 ^c	91.6	<0.1	<0.1	<0.1	<0.1	2.8	
2	76.5	11.0	<0.1	2.3	<0.1	4.2	
16	63.4	12.1	1.0	0.5	5.9	0.6	
36	66.4	13.7	<0.1	<0.1	1.2	3.2	
Phenyl(U)- ¹⁴ C (Non-sterile)							
0	98.4	<0.1	<0.1	<0.1	<0.1	<0.1	0.5
2	86.1	2.4	<0.1	<0.1	<0.1	<0.1	2.5
4	77.0	6.5	1.7	1.0	2.2	<0.1	5.1
8	52.1	15.9	4.9	3.5	4.1	0.1	2.1
16	26.8	5.4	4.5	3.6	4.9	6.7	0.2
25	29.8	8.5	2.7	3.3	2.6	1.4	4.1
36	16.7	10.7	0.1	14.7	2.8	5.7	3.2
53	16.1	3.5	<0.1	0.6	2.0	20.6	0.6
Phenyl(U)- ¹⁴ C (Sterile)							
0 ^c	98.4	<0.1	<0.1	<0.1	<0.1	<0.1	0.5
2	70.6	13.5	<0.1	<0.1	<0.1	<0.1	9.2
16	43.5	7.4	9.7	3.9	7.3	22.2	2.3
36	35.5	22.7	11.4	0.8	14.8	3.5	3.1

^a Includes origin material and other minor (<10% applied radioactivity) polar unknowns.

^b Includes background radioactivity in chromatograms.

^c Sterilised Week 0 is the same as nonsterilised Week 0.

^d IN-W8956 is Methyl 2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]methyl]-4-hydroxybenzoate

Degradation pathway: The proposed degradation pathway is summarised in Figure B.8.1. Under anaerobic conditions, bensulfuron methyl degrades mainly *via* hydrolysis of the sulfonylurea bridge to form IN-N5297 and IN-J0290. An alternative pathway involves ester hydrolysis of bensulfuron methyl to form IN-R9419.

Conclusion:

In anaerobic aquatic systems treated with ¹⁴C-bensulfuron methyl, most of the radiolabel partitioned into the sediment. IN-N5297 (sulfonamide), IN-J0290 (pyrimidine amine), and IN-R9419 were the major degradation products.

B.8.1.1.1.3 Soil photolysis (Annex IIA 7.1.1.1.2)

5 Photodegradation of [phenyl(U)-¹⁴C]DPX-F5384 and [pyrimidine-2-¹⁴C]DPX-F5384 on soil. Scott, M.T., 1986

Cross reference IIA 7.1.1.1.2./02

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Guidelines:

USEPA 161-3 (1982)

GLP:

No

*The study is acceptable*Materials and Methods:

Two radiolabeled forms of bensulfuron methyl were used: labeled with carbon-14 in the [phenyl(U)-¹⁴C] ring (radiochemical purity >98%) and labeled with carbon-14 in the [pyrimidine-2-¹⁴C] ring (radiochemical purity >99%). The photodegradation of bensulfuron methyl was studied under simulated sunlight in fresh non-sterile Flanagan silt loam soil from Rochelle, Illinois (Table B.8.19).

Table B.8.19: Soil characteristics

Characteristic	Flanagan
Origin Location	Rochelle, Illinois
pH	5.8
% Sand (2000 - 50 µm) ^a	4
% Silt (<50 - 2 µm) ^a	70
% Clay (<2 µm) ^a	26
Texture ¹	Silt loam
Organic matter (%)	3.0
Cation exchange capacity ^b	24.4

^a USDA Classification system^b Meq/100g, 1N, pH 7.0, NH₄AcO

The thin soil layers (~1 mm thickness, 16.5 cm²), previously air dried at ambient temperature, were treated with bensulfuron methyl dissolved in acetonitrile (400 µL per sample each of a 28.8 µL/mL acetonitrile solution of the phenyl label and 29.1 µL/mL acetonitrile solution of the pyrimidine label). This is equivalent to an application rate of 70 g a.i./ha. The thin soil layers were placed on microscope slides contained within watertight, ventilated Lucite™[®] boxes with individual heat exchangers and 1/8-inch thick Pyrex[®] glass. The boxes containing non-irradiated samples were shielded from light by aluminium foil. Test vessels were exposed to a xenon arc lamp (Model Suntest, Hanau) light source operated continuously for 15 days. Total radiation in the UV region (300-384 nm) was 56.4 W/m² and in UV-vis regions (300-800 nm) was 836 W/m². The temperature of the soil thin layers was maintained at approximately 25°C by a thermostatically controlled circulating water bath. Provisions were made for trapping radiolabeled CO₂ or other labeled volatile compounds. Treated irradiated and dark control samples were taken at each sampling interval.

Soil thin layers were extracted three times with 25 mL of methanol:2.0 M ammonium carbonate (3:1, v/v) with aliquots analysed by liquid scintillation counting (LSC) for total radioactivity after each extraction. The extracts were combined, the volume reduced by concentration and aliquots analysed by TLC. Degradation products were identified by co-chromatography using authentic analytical standards. Confirmation of the identity of more polar photolysis products was obtained by two additional methods of TLC co-chromatography using different one-dimensional and two-dimensional mobile phase analysis. Subsamples of extracted soils were combusted to determine levels of non-extractable residues.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Aliquots of the volatile trap solutions were analysed by LSC for total radioactivity. Confirmation that all radiolabeled material in solution was $^{14}\text{CO}_2$ was obtained by barium carbonate precipitation.

The rate of degradation of bensulfuron methyl in irradiated and non-irradiated samples was calculated by linear regression using the combined data for each radiolabeled form of test material.

Findings:

Material balance: Recovery generally ranged from 91 to 119% for the phenyl label and 100 to 110% for the pyrimidine label (Table B.8.20).

Table B.8.20: Composition of radioactivity from irradiated and control soils treated with ^{14}C -bensulfuron methyl (DPX-F5384)

		% of Applied Radioactivity					
	Time (Days)	DPX-F5384 ^a	IN-N5297 (Sulfonamide) ^a	IN-B6895 (Homosaccharin) ^b	Others ^c	Unextracted ^d	Total Recovered ^e
[Phenyl(^{14}C)] Label							
Irradiated	0	93.8	0.3	ND	5.7	0.2	119.1
	1	88.9	2.7	ND	7.4	1.0	101.5
	2	85.1	1.6	3.2	8.8	1.3	100.8
	5	79.3	3.5	3.8	11.6	1.8	95.9
	9	69.9	8.3	5.3	14.1	2.4	98.8
	15	67.7	4.8	5.3	19.9	2.3	90.9
Non-irradiated	5	92.9	2.2	2.7	1.7	0.5	104.5
	9	92.3	2.5	2.4	2.2	0.6	107.0
	15	87.0	4.8	4.2	3.1	0.9	108.4
	Time (Days)	DPX-F5384 ^a	IN-T5831 (Pyrimidine urea) ^a	IN-J0290 (Pyrimidine amine) ^a	Others ^c	Unextracted ^d	Total Recovered ^e
[Pyrimidine-2- ^{14}C] Label							
Irradiated	0	90.4	1.3	ND	8.0	0.3	100.3
	1	88.0	3.6	0.5	7.0	0.9	109.7
	2	85.5	5.2	1.1	6.9	1.3	107.7
	5	73.7	6.5	2.1	16.1	1.6	108.7
	9	65.0	7.6	3.2	22.9	1.3	105.6
	15	57.5	11.9	1.8	27.1	1.7	105.8
Non-irradiated	5	94.6	0.8	1.3	2.9	0.4	97.0
	9	93.9	0.8	1.6	3.3	0.4	104.3
	15	90.9	1.0	2.5	4.8	0.8	111.3

^a Analysed by TLC using MMAII (methylene chloride:methanol:ammonium hydroxide, 165:30:5)

^b Analysed by TLC using MMAII (methylene chloride:methanol:ammonium hydroxide, 140:55:3)

^c IN-R9419 (Free acid), IN-F7880, and other minor unidentified radiolabeled compounds.

^d From combustion of dried, extracted soil

^e The total recovery expressed as a percentage of the theoretical applied radioactivity in each sample

ND - None detected

Principal degradation products: The only major degradation product formed from the phenyl label was IN-N5297 (sulfonamide) accounting for up to 8.3% of applied radioactivity in the irradiated samples, and up to 4.8% of applied radioactivity in the non-irradiated samples. In addition, other minor radiolabeled compounds, each comprising <5% of the applied radioactivity after 15 days continuous exposure were IN-R9419, the free acid analog of DPX-F5384, IN-F7880, the O-demethylated analog of DPX-F5384, and minor unidentified radiolabeled compounds. Further work to characterise the minor unidentified residues was not performed due to the large number of minor photoproduct comprising approximately 20% of the applied radioactivity. Two-dimensional TLC was used to confirm the presence

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

of the IN-R9419 and IN-F7880 degradates. No single photoproduct accounted for more than 10% of applied radioactivity after 15 days continuous exposure.

Major radiolabeled degradation product for the pyrimidine label was IN-T5831 (pyrimidinyl urea), accounting for up to 11.9% of applied radioactivity in the irradiated samples, and up to 1.0 and 2.5% of the applied radioactivity, respectively, in the non-irradiated samples. The IN-R9419 and IN-F7880 degradates, and other minor unidentified radiolabeled compounds each accounted for less than 10% of applied radioactivity after 15 days continuous exposure. $^{14}\text{CO}_2$ and other volatiles were not significant in either label and were below the limit of detection.

Non-extractable residue: Non-extractable residues were low and accounted for less than 3% of the applied radioactivity from both labels under irradiated as well as dark conditions.

DT₅₀ value for bensulfuron methyl: Under the conditions of this study (continuous irradiation, dry soil) bensulfuron methyl degraded with a calculated DT₅₀ of 32 and 22 days for the phenyl and pyrimidine radiolabels, respectively. The DT₅₀ for the dark controls were 156 and 170 days for the phenyl and pyrimidine labels, respectively. The determination coefficient (r^2) was not provided. Values are reported in Table B.8.21.

Table B.8.21 DT₅₀ values and rate constants for bensulfuron methyl (DPX-F5384)

Radiolabel	Sample	half-life (days) ^a	k (day ⁻¹) ^b	Method of Calculation
Phenyl	Irradiated	32.2	-0.0215	First-order
	Non-irradiated	156	-0.00445 ^c	First-order
Pyrimidine	Irradiated	21.9	-0.0317	First-order
	Non-irradiated	170	-0.00408 ^c	First-order

^a Half-life = $0.693 \div k$ derived from kinetic expression below (in footnote b)

^b k was determined from the linear least squares best fitting line to the first order kinetic equation:

$\ln(\% \text{DPX-F5384})_t - kt + \ln(\% \text{DPX-F5384})_0 = 0$ where t = time in days.

^c Used values for Days 5, 9, and 15.

Degradation pathway: The primary degradation pathway for irradiated bensulfuron methyl involved the formation of pyrimidine urea (IN-T5831), which was observed as a major product (11.9%). An alternative pathway involves the cleavage of sulfonylurea bridge of bensulfuron methyl to form IN-J0290 and IN-N5297 (<10%). All of these major and minor products were also observed in the dark control therefore irradiation did not appear to be required for their formation.

Conclusion:

Photolysis of bensulfuron methyl resulted in an estimated half-life of 22-32 days with continuous irradiation or 44-64 days for a 12-hour photoperiod indicating accelerated degradation in simulated sunlight compared to aerobic soil metabolism (4-20 weeks). The major degradation products were IN-N5297 (sulfonamide) in the phenyl labeled study, IN-T5831 (pyrimidinyl urea) in the pyrimidine labeled study.

B.8.1.1.1.4 Further information on the active substance

- 6) *Bensulfuron methyl: Mixed culture microbial degradation. Brusa, T., F.Ferrari. 1997.*

Cross reference IIA 7.1.1.2.1./02

Guidelines:

Not applicable

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

GLP:

No

The study is a published paper. It can be considered as supplementary information

Materials and methods:

Ten mixed microbial cultures previously shown to degrade bensulfuron methyl were inoculated and maintained under methanogenic conditions. Degradation of 16-18 ppm of bensulfuron methyl was compared between mixed cultures, sterilised mixed cultures, and buffer. Filtered culture broth was analysed by HPLC with UV detection. The ability of the cultures to maintain degradative activity was evaluated for 7-8 months.

Findings:

Mixed cultures incubated under methanogenic conditions were able to degrade bensulfuron methyl. Abiotic degradation was about 30% of the total degradation. A gradual reduction of methanogenic microbes coincided with diminishing degradative activity.

Conclusion:

Bensulfuron methyl can be degraded by mixed microbial cultures under methanogenic conditions.

B.8.1.2 Rate of degradation in soil (Annex IIA 7.1.1.1.2; Annex IIIA 9.1.1)

B.8.1.2.1 Aerobic degradation of the active substance

7) *Route of degradation of bensulfuron methyl in aerobic soil. Anderson, J.J., Swain, R.S., 2002*

Cross reference IIA 7.1.1.2.1/01

Guidelines:

SETAC – Procedures for Assessing Environmental Fate and Ecotoxicity of Pesticides. OECD Guidelines for the Testing of Chemicals: Aerobic and Anaerobic Transformation in Soil (Draft Document, October 1999)

GLP:

Yes

The study is acceptable

Material and methods:

A full description of the study can be found in §B.8.1.1.1. DT₅₀ and DT₉₀ values for bensulfuron methyl, IN-R9419 and IN-F7880, were calculated using first-order kinetic modelling of parent and each metabolite in series, using the %AR, from both labelled forms of bensulfuron methyl, of each analyte versus time. The software used was ModelManager, version 1.1. For determination of the degradation kinetics of IN-R9419 and IN-F7880, each metabolite was assumed to form independently from bensulfuron methyl

Results:

Results are reported in Table B.8.22. The average DT₅₀ and DT₉₀, for the active substance, are 25 and 84 days, respectively. The DT₅₀ and DT₉₀ values for IN-R9419 were 54 and 181 days, respectively. The DT₅₀ and DT₉₀ values for IN-F7880 were 31 and 101 days, respectively. All fits are acceptable

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Table B.8.22: DT₅₀ and DT₉₀ values for bensulfuron methyl and degradation products in aerobic soil

Analyte	DT ₅₀ (days)	DT ₉₀ (days)	r ²	Method of calculation ^a
¹⁴ C-bensulfuron methyl	25.1	83.5	≥0.957	Non-linear simple first order
IN-R9419	54.4	181	≥0.957	Non-linear SFO parent and one metabolite in series, simultaneous fit
IN-F7880	30.5	101	≥0.957	Non-linear SFO parent and one metabolite in series, simultaneous fit

Conclusions:

The average DT₅₀ and DT₉₀, for the active substance, are 25 and 84 days, while for IN-R9419 were 54 and 181 days and for IN-F7880 were 31 and 101 days, respectively.

8) *Calculated half-lives of bensulfuron methyl in environmental fate studies. A. Van-Nguyen, 2004.*

Cross reference IIA 7.0/01

Guidelines:

Not applicable

GLP:

Not applicable

The study is acceptable

Material and methods:

The software program, ModelManager[®], Version 1.1 (Cherwell Scientific Limited, 1999), was used to calculate the first order rate constants and DT₅₀ values of bensulfuron methyl in various laboratory environmental fate studies.

The types of environmental studies conducted were the aerobic soil metabolism (Friedman P.L., 1984; Cross reference IIA 7.1.1.1.1/02 and Yordy, J.R., 1987, cross reference IIA 7.1.1.1.1/03), the anaerobic soil metabolism (Cadwgan, G. E., 1986, cross reference IIA 7.1.1.1.2/01) and the aerobic aquatic metabolism (Hunt O.R., 1986; cross reference IIA 7.2.1.3.2/01). Calculation for the different laboratory experiment are described in the proper paragraph. Here below only the aerobic soil study is considered.

The aerobic soil metabolism of bensulfuron methyl degradation under laboratory conditions was studied in US soils (Flanagan, Keyport silt loam, and California) and two Japan soils (Nagano and Tochigi) conditions. All soils were incubated in the dark at 25°C for up to one year.

Results:

Results from the regression analyses are reported in Table B.8.23 and Table B.8.24.

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Table B.8.23: DT₅₀ and DT₉₀ mean values for bensulfuron methyl (DPX-F5384) in non-sterile aerobic soils (Friedman P.L., 1984; cross reference IIA 7.1.1.1.1./02)

SoilName/ Origin	Texture	pH	Soil Moisture	Incubation T (°C)	DT ₅₀ (days)	DT ₉₀ (days)	r ²	Method of calculation
Flanagan, Rochelle, IL	Silt Loam	5.6	70% WHC	25	89	294	0.978	Non-linear SFO
Keyport, Newark, DE	Silt Loam	6.7	70% WHC	25	89	294	0.941	Non-linear SFO

DT₅₀ and DT₉₀ values were calculated using the high concentrations (0.59 ppm and 0.49 ppm for phenyl and pyrimidine labels, respectively). For the Friedman study, (1984 cross reference IIA 7.1.1.1.1./02), just the highest concentrations were used (0.59 ppm and 0.49 ppm). DT₅₀ and DT₉₀ values were calculated for pyrimidine label and phenyl label separately and then mean values were calculated. It has to be underlined that some of the data used are characterised by a quite poor mass balances, especially the ones at the end of the study; moreover, the applied dose corresponds to 6-7 times the highest supported dose.

For the Yordy study (1987, cross reference IIA 7.1.1.1.1./03), DT₅₀ and DT₉₀ values were calculated considering in the same regression data from pyrimidine label and phenyl label experiments. It has to be underlined that the Japanese soil results have not a good mass balance; California soil has a better mass balance even if not the one required by current guidelines. The results of regression analysis are reported in Table B.8.24.

Table B.8.24: DT₅₀ and DT₉₀ values for bensulfuron methyl (DPX-F5384) in non-sterile aerobic soils (Yordy, J.R., 1987, cross reference IIA 7.1.1.1.1./03)

Soil Name/ Origin	Texture	pH	Soil Moisture	Incubation T (°C)	DT ₅₀ (days)	DT ₉₀ (days)	r ²	Method of calculation
California, USA	Silt Loam	6.5	70% WHC	25	90	297	0.840	Non-linear SFO
Nagano, Japan	Sandy Loam	5.2	70% WHC	25	65	214	0.875	Non-linear SFO
Tochigi, Japan	Clay Loam	6.1	70% WHC	25	102	339	0.809	Non-linear SFO

Regression analysis was performed also on results for degradation in sterile soil. Results are reported in Table B.8.25. Also in this case mass balance is quite poor.

Table B.8.25: DT₅₀ and DT₉₀ values for bensulfuron methyl (DPX-F5384) in sterile aerobic soils (Yordy, J.R., 1987, cross reference IIA 7.1.1.1.1./03)

Soil Name/ Origin	Texture	pH	Soil Moisture	Incubation T (°C)	DT ₅₀ (days)	DT ₉₀ (days)	r ²	Method of calculation
California, USA	Silt Loam	6.5	70% WHC	25	83	277	0.840	Non-linear SFO
Nagano, Japan	Sandy Loam	5.2	70% WHC	25	139	464	0.875	Non-linear SFO
Tochigi, Japan	Clay Loam	6.1	70% WHC	25	123	407	0.809	Non-linear SFO

Conclusions

The kinetics of bensulfuron methyl were calculated with ModelManager in order to standardize these calculations. The calculated DT₅₀ values for bensulfuron methyl in aerobic soils ranged from 65 to 102 days for the non-sterile soils and from 83 to 139 days for sterile soils. The calculated DT₉₀ values for bensulfuron methyl in non-sterile and

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sterile soils ranged from 214 to 339 days and 277 to 464 days, respectively. A poor mass balance characterises the of the five soils considered. A quite high dose application characterises the remaining two soils.

B.8.1.2.2 Anaerobic degradation of the active substance

8) *Calculated half-lives of bensulfuron methyl in environmental fate studies. A. Van-Nguyen, 2004.*

Cross reference IIA 7.0/01

Guidelines:

Not applicable

GLP:

Not applicable

The study is acceptable

Material and methods:

The software program, ModelManager^o, Version 1.1 (Cherwell Scientific Limited, 1999), was used to calculate the first order rate constants and DT₅₀ values of bensulfuron methyl in various laboratory environmental fate studies.

The types of environmental studies conducted were the aerobic soil metabolism (Friedman P.L., 1984; Cross reference IIA 7.1.1.1.1/02 and Yordy, J.R., 1987, cross reference IIA 7.1.1.1.1/03), the anaerobic soil metabolism (Cadwgan, G. E., 1986, cross reference IIA 7.1.1.2/01) and the aerobic aquatic metabolism (Hunt O.R., 1986; cross reference IIA 7.2.1.3.2/01). Calculation for the different laboratory experiment are described in the proper paragraph. Here below only the anaerobic soil study is considered.

The anaerobic soil metabolism of bensulfuron methyl was studied in California soil. Soil was incubated in the dark at 25°C for up to one year.

Results:

Degradation of bensulfuron methyl occurred slowly under anaerobic conditions. The average DT₅₀ in the total system was 118 days for non-sterile systems (Table B.8.26) and 366 days for sterile systems (Table B.8.27).

Table B.8.26: DT₅₀ and DT₉₀ values for bensulfuron methyl (DPX-F5384) in anaerobic non-sterile aquatic systems

Compartment	DT ₅₀ (days)	DT ₉₀ (days)	r ²	Method of calculation
Total System (Phenyl label)	83	275	0.946	Non-linear SFO
Total System (Pyrimidine label)	153	509	0.852	Non-linear SFO

Table B.8.27: DT₅₀ and DT₉₀ values for bensulfuron methyl (DPX-F5384) in anaerobic sterile aquatic systems

Compartment	DT ₅₀ (days)	DT ₉₀ (days)	r ²	Method of calculation
Total System (Phenyl label)	150	498	0.841	Non-linear SFO
Total System (Pyrimidine label)	583	1939	0.568	Non-linear SFO

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Conclusions

The calculated DT₅₀ values for bensulfuron methyl in anaerobic conditions the non-sterile total system ranged from 83 to 153 days and 150 to 583 days for sterile systems. The calculated DT₉₀ values for non-sterile systems ranged from 275 to 509 days and were higher than 498 days for sterile systems.

B.8.1.2.3 Aerobic degradation of the major metabolites

9) *Degradation rates of IN-F7880 in four soils. Crowe, A., 2002*

Cross reference IIA 7.1.1.2.1./04

Guidelines:

SETAC – Europe: Procedures for Assessing Environmental Fate and Ecotoxicity of Pesticides (March 1995); OECD Guidelines for the Testing of Chemicals: Aerobic and Anaerobic Transformation in Soil, Draft Document (1999)

GLP:

Yes

The study is acceptable

Material and Methods:

IN-F7880, methyl 2-[[[(4-hydroxy-6-methoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]methyl]benzoate (Batch No. F7880-3, purity 95%), was used. The rate of degradation of IN-F7880 was determined under laboratory conditions in four field-fresh agricultural soils (Table B.8.28) at 20±2°C.

Table B.8.28: Characteristics of test soils

Characteristic	Soil			
Soil Name or Designation	Nambsheim	Pavia	Speyer 2.2	Vercelli
Origin	France	Italy	Germany	Italy
pH (in water)	8.1	5.8	5.9	6.2
% Sand (2000 – 50 µm)	60.8	72.8	80.8	24.8
% Silt (<50 – 2 µm)	33.2	22.8	15.2	60.8
% Clay (<2 µm)	6.0	4.4	4.0	14.4
Texture ^a	sandy loam	sandy loam	loamy sand	silt loam
Organic carbon (%) ^b	1.0	0.6	2.1	1.2
Cation exchange capacity (meq/100g)	5.3	4.3	8.4	9.7
Maximum water-holding capacity (%)	39.0	25.0	42.9	51.2
Bulk density (g/cm ³)	1.20	1.25	1.23	1.11
Microbial biomass - Initial (mg microbial C/kg soil)	532	137	433	287
Microbial biomass - Final (mg microbial C/kg soil)	520	127	394	177

^a USDA soil classification system; ^b organic carbon = organic matter/1.724

IN-F7880 was dissolved in acetonitrile at a nominal concentration of 50 µg/mL and 200 µL was applied to 50-g dry weight of soil to give a nominal soil concentration of 0.2 mg/kg. This concentration corresponds to an application rate of 150 g/ha assuming a soil depth of 5 cm and a bulk density of 1.5 g/cm³. Soil samples were incubated under aerobic conditions in darkness at a soil moisture content of 50% of maximum water holding capacity for up to 30 days (Nambsheim soil), 90 days (Pavia soil), or 120 days (Speyer 2.2 and Vercelli soils). For each group, duplicate soil

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samples e extracted with 0.1 M ammonium carbonate/acetone (9/1 by volume). Soil extracts were analysed by LC-MS-MS for IN-F7880. The first-order rate constants and DT₅₀ and DT₉₀ values for IN-F7880 in each of the soils were calculated with ModelManager (version 1.1).

Findings

The total percentage of IN-F7880 in soil declined over time in all four soils. IN-F7880 decreased in Nambsheim soil from a level of 0.16 ppm at time zero (T₀) to less than the LOQ (0.01 ppm) after 30 days, in Pavia soil from a level of 0.17 ppm at T₀ to 0.017 ppm (9.7% of applied) after 90 days, in Speyer 2.2 soil from a level of 0.17 ppm at T₀ to less than (0.01 ppm) after 120 days, and in Vercelli soil from a level of 0.16 ppm at T₀ to 0.016 ppm (9.7% of applied) after 120 days (Table B.8.29).

Table B.8.29: Percent remaining of IN-F7880 after application to aerobic soils

Days	% IN-F7880 Remaining (Average of Replicates)			
	Nambsheim	Pavia	Speyer 2.2	Vercelli
0	100	100	100	100
3	55.0	70.6	58.5	71.9
7	32.2	73.5	35.6	71.9
14	10.6	52.6	22.6	52.8
30	<LOQ	24.1	13.5	24.7
45	nd	20.6	17.6	20.9
59	nd	15.9	10.3	19.1
90	nd	9.7	10.3	12.5
120	nd	nd	<LOQ	9.7

nd: Not determined, below LOQ

DT₅₀ values for IN-F7880 were determined for all four soils. DT₅₀ values, across all soils, assuming non-linear first-order regression, ranged from 4 to 20 days (Table B.8.30). DT₉₀ values ranged from 14 to 67 days.

Table B.8.30: DT₅₀ and DT₉₀ values for IN-F7880 in aerobic soil

Soil Name	Texture	pH	First-Order Rate Constant (day ⁻¹)	DT ₅₀ (days)	DT ₉₀ (days)	r ²	Method of Calculation
Nambsheim	Sandy loam	8.1	0.171	4.1	13.5	0.994	Non-linear SFO
Pavia	Sandy loam	5.8	0.037	18.8	62.4	0.957	Non-linear SFO
Speyer 2.2	Loamy sand	5.9	0.125	5.6	18.4	0.890	Non-linear SFO
Vercelli	Silt loam	6.2	0.034	20.2	67.1	0.947	Non-linear SFO

Conclusion:

IN-F7880 rapidly degraded in the four soils analysed with DT₅₀ values ranging from 4 to 20 days and DT₉₀ values ranging from 14 to 67 days.

10) *Degradation rates of [¹⁴C]IN-N5297 in four soils. Shaw, D., 2002a*

Cross reference IIA 7.1.1.2.1./06

Guidelines:

Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, SETAC (1995); OECD Guidelines for the Testing of Chemicals: Aerobic and Anaerobic Transformation in Soil, Draft Document (October 1999)

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Environmental fate and behaviour

GLP:

Yes

*The study is acceptable*Material and Methods:

IN-N5297, radiolabeled as [phenyl-¹⁴C]methyl 2-[[amino)sulfonyl]methyl]benzoate (Batch No. HOTC 568; radiochemical purity >95%), was used. The rate of degradation of IN-N5297 was determined under laboratory conditions in four field-fresh agricultural soils (Table B.8.31) at 20±2°C. The soils were allowed to acclimatise into an air flow through system, in darkness, at 50% of their maximum water holding capacity, for two weeks prior to test substance application.

Table B.8.31: Characteristics of test soils

Characteristic	Soil			
	Nambsheim	Pavia	Speyer 2.2	Vercelli
Soil Name or Designation	France	Italy	Germany	Italy
Origin	France	Italy	Germany	Italy
pH (in water)	8.0	5.5	6.7	6.1
% Sand (2000 - 50 µm)	57.2	82.0	73.2	22.0
% Silt (<50 - 2 µm)	30.0	10.4	20.0	64.4
% Clay (<2 µm)	12.8	7.6	6.8	13.6
Texture ^a	sandy loam	loamy sand	sandy loam	silt loam
Organic carbon (%) ^b	0.8	0.3	2.5	1.0
Cation exchange capacity	5.54	5.01	9.09	9.66
Maximum water-holding capacity (%)	35.0	31.7	47.8	56.7
Microbial biomass - Initial (mg microbial C/kg soil)	167	59	468	101
Microbial biomass - Final (mg microbial C/kg soil)	141	22	564	69

^a USDA soil classification system^b organic carbon = organic matter/1.724

IN-N5297 was dissolved in acetonitrile/water (1:3 by volume) at a nominal concentration of 5 µg/mL and 1.00 mL was applied to 50-g dry weight of soil to give a nominal soil concentration of 0.1 mg/kg, corresponding to IN-N5297 application rate of 75 g/ha, assuming soil depth of 5 cm and bulk density of 1.5g/cm³. Soil samples were incubated under aerobic conditions in darkness at a soil moisture content of 50% of maximum water holding capacity. Duplicate soil samples were taken for analysis after test substance application (zero-time) and after 3, 7, 14, 30, 45, 62 days and (Pavia, Nambsheim and Vercelli soils only) 90 and 120 days. Soil samples were extracted with acetone and in some cases additionally with 0.1 M ammonium carbonate/acetone (9/1 by volume). Soil extracts were analysed by HPLC for IN-N5297. Radiolabelled volatile degradates, including CO₂, and unextractable ¹⁴C were also quantified. The first-order rate constants and DT₅₀ and DT₉₀ values for IN-N5297 in each of the soils were calculated.

Findings:

The average mass balance (Table B.8.32) was in the range of 88.7% and 108.5% of applied radioactivity in all soil groups. Non-extracted radioactivity increased from less than 1 - 3% AR at zero-time to up to 48.1% AR in Speyer 2.2 soil (after 7 days), 24.9% AR in Pavia soil (after 45 days), 52.9% AR in Nambsheim soil (after 14 days), and 42.4% AR in Vercelli soil (after 90 days). Similarly, volatile radioactivity increased to 65.0% AR in Speyer 2.2 soil after 62 days, and to 28.9% AR, 55.1 % AR and 30.7% AR in Pavia, Nambsheim and Vercelli soils respectively after

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120 days. Almost all of the volatile radioactivity produced by the incubated samples was trapped in potassium hydroxide solution. This radioactivity was shown to be exclusively associated with $^{14}\text{CO}_2$ by precipitation of the insoluble barium [^{14}C]carbonate. Small amounts of radioactivity were trapped in ethyl digol (maximum 0.4% AR).

Table B.8.32: Percent distribution of applied radioactivity and mass balance in aerobic soils after application of ^{14}C -IN-N5297

Days	% of Applied Radioactivity			
	Extracted	Non-extracted	Volatiles	Total Recovered
Speyer 2.2 soil				
0	101.7	1.7	nd	103.3
3	62.7	31.9	3.9	98.5
7	38.9	48.1	10.6	97.6
14	26.7	37.6	30.6	94.9
30	7.7	26.1	54.9	88.7
45	6.3	28.7	63.2	98.1
62	4.7	23.9	65.0	93.6
Pavia soil				
0	104.6	<0.9	nd	104.6
3	95.0	2.9	1.3	99.2
7	87.6	11.2	5.7	104.5
14	69.1	11.2	15.1	95.4
30	63.5	10.1	27.4	100.9
45	56.9	24.9	26.7	108.5
62	54.7	20.9	27.6	103.1
90	49.5	23.8	28.5	101.8
120	46.0	23.4	28.9	98.3
Nambesheim Soil				
0	102.5	1.3	nd	103.8
3	78.8	20.4	1.5	100.7
7	55.1	37.9	3.8	96.8
14	36.4	52.9	9.1	98.3
30	26.3	36.0	29.5	91.8
45	21.9	40.8	36.2	98.9
62	14.9	39.9	38.4	93.2
90	8.6	35.9	47.3	91.8
120 ^a	4.8	30.6	55.1	90.5
Vercelli Soil				
0	100.9	3.0	nd	103.8
3	89.6	13.0	1.5	104.0
7	79.3	18.2	5.0	102.5
14	64.7	17.1	10.6	92.4
30 ^a	51.5	24.3	16.6	92.4
45	48.8	34.0	19.1	101.9
62	44.0	32.3	22.2	98.5
90	31.1	42.4	26.7	100.1
120	27.0	39.3	30.7	96.9

^a Values are from one replication
nd: Not determined

IN-N5297 declined in Speyer 2.2 soil from 92.9% AR at zero-time to 1.6% AR after 62 days, in Pavia soil from 101.7% AR at zero-time to 27.6% AR after 120 days, in Nambesheim soil from 101.0% AR at zero-time to 0.5% AR after 120 days and in Vercelli soil from 98.1 % AR at zero-time to 20.1 % AR after 120 days. Percent applied radiolabel of IN-N5297 after application to aerobic soils are reported in Table B.8.33.

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Table B.8.33: Percent applied radiolabel of IN-N5297 after application to aerobic soils

Days	% Applied Radioactivity			
	Speyer 2.2	Pavia	Nambsheim	Vercelli
0	92.9	101.7	101.0	98.1
3	55.5	85.0	69.6	87.0
7	24.7	83.7	48.3	77.5
14	9.2	68.7	24.2	62.5
30	3.2	57.2	8.5	48.5
45	1.7	48.8	4.6	42.8
62	1.6	47.8	2.3	38.9
90	^a	39.4	0.8	24.1
120	^a	27.6	0.5	20.1

^a No samples were taken beyond 62 days

In aerobic soil, dissipation of IN-N5297 proceeded largely via incorporation into the soil organic fraction (bound residue) and formation of CO₂. Dissipation was satisfactorily described by first-order kinetics, with r^2 values in all groups higher than 0.92. The DT₅₀ values across all soils ranged from 4 to 63 days (Table B.8.34). DT₉₀ values ranged from 13 to 208 days.

Table B.8.34: DT₅₀ and DT₉₀ values for IN-N5297 in aerobic soil

Soil Name	Texture	pH	First-Order Rate Constant (day ⁻¹)	DT ₅₀ (days)	DT ₉₀ (days)	r ²	Method of Calculation
Nambsheim	Sandy loam	8.0	0.101	7	23	0.995	Non-linear SFO
Pavia	Sandy loam	5.5	0.0111	63	208	0.924	Non-linear SFO
Speyer 2.2	Loamy sand	6.7	0.178	4	13	0.997	Non-linear SFO
Vercelli	Silt loam	6.2	0.0155	45	148	0.951	Non-linear SFO

Conclusion:

The rate of degradation of IN-N5297 was studied in four aerobic soils at 20°C. Dissipation of IN-N5297 proceeded largely via incorporation into the soil organic fraction (bound residue) and formation of CO₂. Degradation rates varied considerably between soil types and DT₅₀ values ranged from 4 to 63 days while DT₉₀ values ranged from 13 to 208 days.

11) Degradation rates of [¹⁴C]IN-J0290 in four soils. Shaw, D., 2002b.

Cross reference IIA 7.1.1.2.1/07

Guidelines:

Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, SETAC (1995); OECD Guidelines for the Testing of Chemicals: Aerobic and Anaerobic Transformation in Soil, Draft Document (October 1999)

GLP:

Yes

The study is acceptable

Material and Methods:

IN-J0290, radiolabeled as [pyrimidine-2-¹⁴C]2-amino-4,6-dimethoxypyrimidine (Batch No. HOTC#318, radiochemical purity >95%), was used. The rate of degradation of IN-J0290 was determined under laboratory

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

conditions in four field-fresh agricultural soils (Table B.8.35) at 20±2°C.

Table B.8.35: Characteristics of test soils

Characteristic	Soil			
Soil Name or Designation	Nambsheim	Pavia	Speyer 2.2	Vercelli
Origin	France	Italy	Germany	Italy
pH (in water)	8.0	5.5	6.7	6.1
% Sand (2000 - 50 µm)	57.2	82.0	73.2	22.0
% Silt (<50 - 2 µm)	30.0	10.4	20.0	64.4
% Clay (<2 µm)	12.8	7.6	6.8	13.6
Texture ^a	sandy loam	loamy sand	sandy loam	silt loam
Organic carbon (%) ^b	0.8	0.3	2.5	1.0
Cation exchange capacity	5.54	5.01	9.09	9.66
Maximum water-holding capacity (%)	35.0	31.7	47.8	56.7
Microbial biomass - Initial (mg microbial C/kg soil)	231	51	482	174
Microbial biomass - Final (mg microbial C/kg soil)	158	32	572	89

^a USDA soil classification system

^b organic carbon = organic matter/1.724

The soils were allowed to acclimatise into an air flow through system, in darkness, at 50% of their maximum water holding capacity, for two weeks prior to test substance application. IN-J0290 was dissolved in acetonitrile/water (1:3 by volume) at a nominal concentration of 5 µg/mL and 0.95 mL was applied to 50-g dry weight of soil to give a nominal soil concentration of 0.1 g/kg, corresponding to IN-J0290 application rate of 75 g assuming soil depth of 5 cm and bulk density of 1.5 g/cm³. Soil samples were incubated moisture content of 50% of maximum water holding capacity. Duplicate soil samples were taken for analysis after test substance application (zero-time) and after 3, 7, 14, 30, 45, 62 days and (Pavia, Nambsheim and Vercelli soils only) 90 and 120 days. Soil samples were extracted with acetone and 0.1 M ammonium carbonate/acetone (9/1 by volume). Soil extracts were analysed by HPLC and TLC (zero-time samples only), to quantify IN-J0290. Radiolabelled volatile degradates, including CO₂, and unextractable ¹⁴C were also quantified. The first-order rate constants and DT₅₀ and DT₉₀ values for IN-J0290 in each of the soils were calculated using non-linear first-order regression with the computer software ModelManager (version 1.1).

Findings:

The average material balance was between 87% and 109% of applied radioactivity at all sampling intervals in all soil groups. The extractability of radioactivity declined with time in all four soils, from essentially all of the applied radioactivity (97-100% AR) at zero-time to 6.2% AR in Speyer 2.2 soil after 62 days, and to 26.1, 11.5, and 14.1% AR in Pavia, Nambsheim, and Vercelli soils, respectively, after 120 days. These declines were matched by increases in non-extracted and volatile radioactivity. Labeled carbon dioxide was produced from each soil (60.8% AR after 62 days in Speyer 2.2 soil, 27.2-53.4% AR after 120 days in the other soils). Total organic volatiles ranged from a minimum of 0.4% AR (after 3 days in Nambsheim soil) to a maximum of 61.3%, 29.8%, 53.5% and 27.2% AR for Speyer 2.2, Pavia, Nambsheim and Vercelli soil respectively. The extractable fraction contained primarily unmetabolised IN-J0290. Minor metabolites of IN-J0290 were observed in all soils.

Non-extracted radioactivity increased from 1-5% AR at zero-time to up to 45.2% AR in Speyer 2.2 soil (after 14 days), 39.6% AR in Pavia soil (after 30 days), 33.1% AR in Nambsheim soil (after 30 days), and 53.8% AR in Vercelli soil (after 90 and 120 days) (Table B.8.36).

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Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.36: Percent distribution of applied radioactivity and mass balance in aerobic soils after application of ^{14}C -IN-J0290

Week	% of Applied Radioactivity				
	Extracted	Non-extracted	Total Volatiles (including CO ₂)	CO ₂	Total Recovered
Speyer 2.2 soil					
0	100.1	1.9	nd	0	102.0
3	58.0	35.5	15.4	7.7	108.9
7	32.3	36.0	34.8	17.4	103.1
14	12.3	45.2	50.0	24.9	107.5
30	7.1	27.2	55.7	27.7	90.0
45	6.4	31.4	57.3	28.5	95.1
62	6.2	31.9	61.3	60.8	99.4
Pavia soil					
0	98.3	4.9	nd	0	103.2
3	86.7	9.0	0.9	0.9	96.6
7	68.1	22.7	3.7	3.7	94.4
14	55.4	31.3	7.3	6.8	94.0
30	38.7	39.6	15.7	15.2	93.9
45	31.3	34.2	25.2	25.2	90.6
62	29.5	35.1	26.8	26.8	91.4
90	29.6	34.6	28.5	28.5	92.7
120	26.1	34.6	29.8	29.8	90.5
Nambesheim Soil					
0	100.2	1.4	nd	0	101.5
3	85.6	8.7	0.4	0.4	94.6
7	71.3	10.0	13.0	6.4	94.3
14	48.8	27.0	25.3	12.5	101.1
30	30.9	33.1	38.9	19.3	102.9
45	25.0	22.4	43.2	21.6	90.5
62	21.2	23.3	47.5	23.7	92.0
90	15.6	22.5	50.8	25.4	88.9
120	11.5	22.6	53.5	53.4	87.6
Vercelli Soil					
0	96.6	3.6	nd	0	100.2
3	71.9	24.7	3.7	3.7	100.3
7	57.8	30.8	8.6	8.4	97.1
14	40.3	33.9	16.2	16.0	90.4
30	21.3	51.6	21.2	21.1	94.0
45	24.5	49.2	23.1	11.5	96.7
62	23.3	52.3	24.5	24.5	100.0
90	19.3	53.8	26.1	26.1	99.2
120	14.1	53.8	27.2	27.2	95.1

nd: Not determined

IN-J0290 declined in Speyer 2.2 soil from 94.8% AR at zero-time to 2.2% AR after 62 days, in Pavia soil from 96.4% AR at zero-time to 16.3% AR after 120 days, in Nambesheim soil from 92.9% AR at zero-time to 7.6% AR after 120 days and in Vercelli soil from 94.8% AR at zero-time to 10.1 % AR after 120 days. Percent applied radiolabel of IN-J0290 after application to aerobic soils are reported in Table B.8.37.

In aerobic soil, dissipation of IN-J0290 proceeded largely via incorporation into the soil organic fraction (bound residue) and formation of CO₂.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.37: Percent applied radiolabel of IN-J0290 after application to aerobic soils

Days	% Applied Radioactivity			
	Speyer 2.2	Pavia	Nambsheim	Vercelli
0	94.8	96.4	92.9	94.8
3	46.2	78.4	68.2	64.9
7	19.5	60.3	60.9	48.6
14	7.5	39.6	39.3	32.3
30	2.7	24.7	25.2	17.7
45	3.1	19.0	19.9	18.5
62	2.2	18.8	17.0	17.9
90	^a	18.2	11.1	13.4
120	^a	16.3	7.6	10.1

^a No samples were taken beyond 62 days

Dissipation was satisfactorily described by first-order kinetics, with r^2 values in all groups higher than 0.86. The DT_{50} values across all soils ranged from 3 to 19 days while DT_{90} values ranged from 10 to 63 days. Details are reported in Table B.8.38.

Table B.8.38: DT_{50} and DT_{90} values for IN-J0290 in aerobic soil

Soil Name	Texture	pH	First-Order Rate Constant (day^{-1})	DT_{50} (days)	DT_{90} (days)	r^2	Method of Calculation
Nambsheim	Sandy loam	8.0	0.0369	19	63	0.936	Non-linear SFO
Pavia	Sandy loam	5.5	0.0382	18	60	0.880	Non-linear SFO
Speyer 2.2	Loamy sand	6.7	0.226	3	10	0.995	Non-linear SFO
Vercelli	Silt loam	6.1	0.0550	13	42	0.864	Non-linear SFO

Conclusion:

The rate of degradation of IN-J0290 was studied in four aerobic soils at 20°C. Dissipation of IN-J0290 proceeded largely *via* incorporation into the soil organic fraction (bound residue) and formation of CO_2 . Degradation rates varied between soil types and DT_{50} values were between 3 and 19 days (mean value: 13 days). DT_{90} values ranged from 10 to 63 days.

12) Degradation rates of [^{14}C]IN-R9419 in four soils. Shaw, D., 2002c.

Cross reference IIA 7.1.12.1./08

Guidelines:

Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, SETAC (1995); OECD Guidelines for the Testing of Chemicals: Aerobic and Anaerobic Transformation in Soil, Draft Document (October 1999)

GLP:

Yes

The study is acceptable

Material and Methods:

IN-R9419 (benzoic acid, 2-((((4,6-dimethoxypyrimidin-2-yl)aminocarbonyl))-aminosulfonylmethyl))-, specific activity 59.5 $\mu\text{Ci}/\text{mg}$, purity higher than 95% was used. The rate of degradation of radiolabeled IN-R9419 was examined in four soils (Table B.8.39) under laboratory aerobic conditions. After a one-week incubation into the air

Rapporteur Member State	Month and year	Active Substance (Name)
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Environmental fate and behaviour

flow-through system, the test soils were treated with ^{14}C -IN-R9419 at a concentration of 0.1 mg/kg soil, corresponding to an application rate of IN-R9419 of 0.75 g/ha assuming a soil depth of 5 cm and considering a bulk density value of 1.5 cm³/g. The test soil were then incubated in darkness at 20°C with a soil moisture of 50% of maximum water holding capacity for up to 121 days. The samples were incubated under aerobic conditions in groups of dishes of soil in flow-through systems with traps for the collection of CO₂ and volatile organic compound. Samples were analysed at approximately 0, 3, 7, 14, 30, 44, 62, and 90 days (Nambenheim and Speyer 2.2 soils) and also 121 days (Pavia and Vercelli soils) from treatment.

Table B.8.39: Characteristics of test soil

Characteristic	Nambenheim	Pavia	Speyer 2.2	Vercelli
DuPont Soil Number	2001-029	2001-027	2001-030	2001-028
pH (in water)	8.1	5.8	5.9	6.2
pH (in 0.01 M CaCl ₂)	7.5	5.7	5.5	6.5
Phosphorus (Bray) (mg/kg)	2	153	30	24
Phosphorus (Olsen) (mg/kg)	15	56	10	22
Total Nitrogen (mg/kg)	1012	736	2062	1614
Organic Matter (Ashing)	1.4	0.9	3.2	2.2
Organic Matter (Walkley-Black)	1.7	1.0	3.7	2.0
Organic Carbon (%) ^a	1.0	0.6	2.1	1.2
CEC (meq/100 g)	5.3	4.3	8.4	9.7
Bulk Density (g/cm ³)	1.20	1.25	1.23	1.11
Field Moisture Capacity at 0 bar	39.0	25.0	42.9	51.2
Field Moisture Capacity at 0.1 bar	22.9	24.1	21.2	37.4
Field Moisture Capacity at 0.33 bar	18.7	12.8	18.1	34.8
Field Moisture Capacity at 15 bar	5.4	4.9	7.8	11.8
Sand (%)	60.8	72.8	80.8	24.8
Silt (%)	33.2	22.8	15.2	60.8
Clay (%)	6.0	4.4	4.0	14.4
Texture ^b	Sandy loam	Sandy loam	Loamy sand	Silt loam
Microbial biomass – Initial (mg microbial C/kg soil)	371	42	239	126
Microbial biomass – Final (mg microbial C/kg soil)	526	165	456	386

^a Organic carbon = organic matter (Walkley Black) ÷ 1.724

^b USDA classification

Soil samples were extracted with a mixture of acetone and 0.1 M ammonium carbonate solution (1:9, by volume). Extractable IN-R9419 was separated and quantified by reversed phase HPLC. Identification of IN-R9419 was performed by reversed phase HPLC and normal phase TLC. For HPLC the limit of detection was 3.0% of applied radioactivity. Unextractable ^{14}C -residues were also quantified.

The DT₅₀ values are obtained assuming first-order kinetics for calculation of predicted environmental concentrations. Degradation rates and DT₅₀ and DT₉₀ values were determined using the computer software ModelManager (version 1.1, Cherwell Scientific Ltd, Oxford, UK).

Findings:

The test conditions outlined in the study protocol and amendments were maintained throughout the study. The mean values of the mass balance, for both replicates, ranged from 80.6% to 104.4% of applied radioactivity, while the material balance for individual replicates ranged from 75.9% to 106.0% AR. Volatile radioactivity (all CO₂) accounted for up to 43.8, 35.0, 54.0, and 37.8% AR in Nambenheim, Pavia, Speyer 2.2, and Vercelli soils, respectively at the last

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Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

sampling times (Table B.8.40). Non-extractable residues accounted for up to 33.6, 28.1, 26.7, and 37.1% AR in Nambshheim, Pavia, Speyer 2.2, and Vercelli soils, respectively at day 90, 121, 62 and 121 respectively.

Table B.8.40: Percent distribution of applied radioactivity and mass balance in aerobic soils after application of ^{14}C -IN-R9419

Week	% of Applied Radioactivity			
	Extracted	Non-extracted	Volatiles (CO ₂)	Total Recovered
Speyer 2.2 soil				
0	100.8	nd	nd	100.8
3	88.1	3.2	2.0	93.3
7	76.4	8.9	11.0	96.2
14	36.9	24.1	29.7	90.7
30	24.0	25.3	44.2	93.5
44	14.2	25.6	48.6	88.4
62	9.1	26.7	51.2	87.0
90	7.5	23.0	54.0	84.5
Pavia soil				
0	102.2	nd	nd	102.1
3	91.1	1.8	1.3	94.1
7	87.1	4.3	5.6	97.1
14	68.2	10.1	16.2	94.5
30	55.2	12.0	26.2	93.4
44	50.4	16.0	28.2	94.6
62	44.9	16.2	29.8	90.9
90	31.9	25.3	32.1	89.4
121	31.8	28.1	35.0	94.9
Nambshheim Soil				
0	104.4	nd	nd	104.4
3	91.7	1.5	2.6	95.8
7	91.9	2.9	5.3	100.1
14	86.8	3.6	7.3	97.7
30	56.7	16.3	23.0	98.0
44	31.2	25.4	31.4	88.0
62	16.5	25.1	39.1	80.6
90	11.3	33.6	43.8	88.7
Vercelli Soil				
0	103.9	nd	nd	103.8
3	88.9	4.3	3.4	96.5
7	71.1	12.5	11.3	94.9
14	51.1	21.9	22.5	95.5
30	45.2	22.1	26.9	94.2
44	33.9	34.1	28.3	96.3
62	32.9	32.0	31.3	96.2
90	27.4	33.8	34.4	95.6
121	19.5	37.1	37.8	94.4

nd: not determined

IN-R9419 declined in Nambshheim soil from 101.8% AR at zero-time to 2.0% AR after 90 days, in Pavia soil from 99.1% AR at zero-time to 13.5% AR after 121 days, in Speyer 2.2 soil from 98.6% AR at zero-time to 2.5% AR after 90 days and in Vercelli soil from 101.1% AR at zero-time to 12.3% AR after 121 days (Table B.8.41).

DT₅₀ values for IN-R9419 were calculated using non-linear first-order regression, for all four soils. The DT₅₀ values across all soils, ranged from 8 to 29 days and (Table B.8.42). DT₉₀ values ranged from 27 to 95 days.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.41: Percent applied radiolabel of IN-R9419 after application to aerobic soils

Days	% Applied Radiolabel			
	Speyer 2.2	Pavia	Nambsheim	Vercelli
0	98.6	99.1	101.8	101.1
3	83.1	86.3	84.3	83.1
7	65.8	76.6	83.6	61.5
14	19.1	52.0	78.4	37.3
30	10.2	39.1	37.3	30.3
44	4.1	32.3	12.9	22.6
62	3.1	26.8	3.9	22.2
90	2.5	14.8	2.0	17.3
121	nd	13.5	nd	12.3

nd: not determined

Table B.8.42: IN-R9419 dissipation kinetics

Soil	First Order Rate Constant (Day ⁻¹)	DT ₅₀ (Days)	DT ₉₀ (Days)	r ²	Method of Calculation
Nambsheim	0.0355	20	65	0.960	Non-linear simple first order
Pavia	0.02413	29	95	0.950	Non-linear simple first order
Speyer 2.2	0.0853	8	27	0.975	Non-linear simple first order
Vercelli	0.03553	20	65	0.877	Non-linear simple first order

Conclusion:

between soil types and DT₅₀ values were between 8 and 29 days. Degradation of IN-R9419 proceeded largely *via* incorporation into the soil organic fraction (non-extractable residues) and mineralisation to CO₂. Degradation rates varied between soil types and DT₅₀ values were between 8 and 29 days (mean value: 19 days). DT₉₀ values ranged from 27 to 95 days.

13) Degradation rates of [¹⁴C]IN-D1R84 in four soils. Shaw, D., 2002d.

Cross reference IIA 7.1.1.2.1./09

Guidelines:

Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides, SETAC (1995); OECD Guidelines for the Testing of Chemicals: Aerobic and Anaerobic Transformation in Soil, Draft Document (October 1999)

GLP:

Yes

The study is acceptable

Material and Methods:

¹⁴C-IN-D1R84 (2-[(aminosulfonyl)methyl]benzoic acid), specific activity 56.8 µCi/g, purity: >95% was used. The rate of degradation of radiolabeled IN-D1R84 was examined in four soils (Table B.8.43) under laboratory aerobic conditions. The test soils were treated ¹⁴C-IN-D1R84 at a concentration of 0.1 mg/kg soil, corresponding to an application rate of IN-D1R84 of 0.75 g/ha assuming a soil depth of 5 cm and considering a bulk density value of 1.5 cm³/g. The test soil were then incubated in darkness at 20°C with a soil moisture of 50% of maximum water holding

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

capacity for up to 121 days. The samples were incubated under aerobic conditions in groups of dishes of soil in flow-through systems with traps for the collection of CO₂ and volatile organic compound. Samples were analysed at approximately 0, 3, 7, 14, 30, and 44 days (Nambshiem and Speyer 2.2 soils) and also 62, 90, and 121 days (Pavia and Vercelli soils) of incubation.

Table B.8.43: Characteristics of test soil

Characteristic	Nambshiem	Pavia	Speyer 2.2	Vercelli
DuPont Soil Number	2001-029	2001-027	2001-030	2001-028
pH (in water)	8.1	5.8	5.9	6.2
pH (in 0.01 M CaCl ₂)	7.5	5.7	5.5	6.5
Phosphorus (Bray) (mg/kg)	2	153	30	24
Phosphorus (Olsen) (mg/kg)	15	56	10	22
Total Nitrogen (mg/kg)	1012	736	2062	1614
Organic Matter (Ashing)	1.4	0.9	3.2	2.2
Organic Matter (Walkley-Black)	1.7	1.0	3.7	2.0
Organic Carbon (%) ^a	1.0	0.6	2.1	1.2
CEC (meq/100 g)	5.3	4.31	8.4	9.71
Bulk Density (g/cm ³)	1.20	1.25	1.23	1.11
Field Moisture Capacity at 0 bar	39.0	25.0	42.9	51.2
Field Moisture Capacity at 0.1 bar	22.9	24.1	21.2	37.4
Field Moisture Capacity at 0.33 bar	18.7	12.8	18.1	34.8
Field Moisture Capacity at 15 bar	5.4	4.9	7.8	11.8
Sand (%)	60.8	72.8	80.8	24.8
Silt (%)	33.2	22.8	15.2	60.8
Clay (%)	6.0	4.4	4.0	14.4
Texture	Sandy loam	Sandy loam	Loamy sand	Silt loam
Microbial biomass – Initial (mg microbial C/kg soil)	368	68	233	160
Microbial biomass – Final (mg microbial C/kg soil)	466	156	321	331

^a Organic carbon = organic matter (Walkley Black) × 1.724

Soil samples were extracted with a mixture of acetone and 0.1 M ammonium carbonate solution (1:9, by volume). Extractable IN-D1R84 was separated and quantified by reversed phase HPLC. Identification of IN-D1R84 was performed by reversed phase HPLC and normal phase TLC. Unextractable ¹⁴C-residues were also quantified.

Radioactivity was measured by liquid scintillation counting (LSC).

Degradation rates and DT₅₀ and DT₉₀ values were determined using computer software ModelManager (version 1.1, Cherwell Scientific Ltd.). Simple first-order kinetics were assumed, using the equation:

Findings:

The test conditions outlined in the study protocol and amendments were maintained throughout the study. Material balance was 95.2 ± 5.7% (range = 84.4 to 118.0%) of the applied amount (Table B.8.44). Volatile radioactivity (virtually all CO₂; maximum 0.1% AR in ethyl digol) accounted for up to 51.3, 56.9, 63.2, and 59.4% AR in Nambshiem, Pavia, Speyer 2.2, and Vercelli soils, respectively.

Non-extractable residues accounted for up to 24.7% AR, 26.8% AR after 44 days in Speyer 2.2 and Nambshiem soils; 27.2% AR, 32.0% AR after 121 days in Pavia and Vercelli soils, respectively (Table B.8.44).

IN-D1R84 declined in Nambshiem soil from 98.7% AR at zero-time to 5.7% AR after 44 days, in Pavia soil from 100.0% AR at zero-time to 6.2% AR after 121 days, in Speyer 2.2 soil from 99.4% AR at zero-time to 0.8% AR after 44 days and in Vercelli soil from 101.7% AR at zero-time to 1.6% AR after 121 days (Table B.8.45).

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.44: Percent distribution of applied radioactivity and mass balance in aerobic soils after application of ^{14}C -IN-D1R84

Week	% of Applied Radioactivity			
	Extracted	Non-extracted	Volatiles (CO ₂)	Total Recovered
Speyer 2.2 soil				
0	101.4	0	nd	101.4
3	68.6	8.0	18.5	95.1
7	22.8	25.2	41.7	89.6
14	7.9	25.2	57.0	90.1
30	4.9	25.3	60.4	91.6
44	3.5	24.7	63.1	91.5
Pavia soil				
0	101.5	0	nd	100.5
3	95.3	2.2	2.1	99.6
7	90.4	8.0	9.8	108.2
14	51.8	13.8	25.4	91.0
30	38.0	15.4	37.9	91.3
44	29.5	17.3	45.4	92.2
62	20.9	23.2	49.4	93.4
90	26.2	21.1	53.6	101.0
121	9.8	27.2	56.9	93.9
Nambshheim Soil				
0	101.8	0	nd	101.8
3	89.0	2.8	4.1	95.9
7	80.8	6.8	12.4	100.0
14	56.0	10.5	26.1	92.6
30	11.9	23.8	49.1	84.9
44	10.8	26.8	51.3	88.9
Vercelli Soil				
0	103.7	0	nd	103.7
3	89.9	3.4	2.8	96.0
7	77.4	10.2	8.2	95.8
14	67.1	13.4	12.9	93.4
30	67.0	14.1	16.1	97.2
44	25.1	25.9	43.3	94.3
62	20.7	23.7	50.0	94.4
90	10.7	26.2	56.0	92.9
121	3.2	32.0	59.4	94.7

nd: not determined

Table B.8.45: Percent applied radiolabel of IN-D1R84 after application to aerobic soils

Days	% Applied Radioactivity			
	Speyer 2.2	Pavia	Nambshheim	Vercelli
0	99.4	100.0	98.7	101.7
3	67.9	92.6	88.2	89.4
7	9.7	80.7	72.0	64.7
14	2.6	39.5	42.7	48.6
30	1.3	23.4	5.4	41.4
44	0.8	22.1	5.7	16.9
62	nd	18.5	nd	11.3
90	nd	15.4	nd	7.7
121	nd	6.2	nd	1.6

nd: not determined

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

DT₅₀ values for IN-D1R84 were measured in 4 soils. The DT₅₀ values across all soils ranged from 3 to 19 days with a mean value of 12.5 days (Table B.8.46). DT₉₀ values ranged from 11 to 62 days.

Table B.8.46: IN-D1R84 dissipation kinetics

Soil	First Order Rate Constant (Day ⁻¹)	DT ₅₀ (Days)	DT ₉₀ (Days)	r ²	Method of Calculation
Nambsheim	0.06525	11	35	0.981	Non-linear simple first order
Pavia	0.04191	17	55	0.934	Non-linear simple first order
Speyer 2.2	0.21662	3	11	0.958	Non-linear simple first order
Vercelli	0.03735	19	62	0.970	Non-linear simple first order

Conclusion:

The rate of degradation of IN-D1 R84 was studied in four aerobic soils at 20°C. Dissipation of IN-D1R84 proceeded largely *via* incorporation into the soil organic fraction (non-extractable residues) and mineralisation to CO₂. Degradation rates varied between soil types and DT₅₀ values were between 3 and 19 days (mean value 12.5 days). DT₉₀ values ranged from 11 to 62 days.

B.8.1.3 Field studies (Annex IIA 7.1.1.2.2; Annex IIIA 9.1.1.2)

B.8.1.3.1 Soil dissipation studies (Annex IIA 7.1.1.2.2; Annex IIIA 9.1.1.2)

- 14) *Field dissipation of bensulfuron methyl and metsulfuron methyl from a representative rice field following treatment of three consecutive years with Sigma 60 DF herbicide in Italy. Bonacini, F., Zenide, D., Gasser, F., Leka, A., 1998.*

Cross reference IIA 7.1.1.2.2./01

- 15) *Field dissipation of bensulfuron methyl and metsulfuron methyl from a representative rice field following treatment of three consecutive years with Sigma 60 DF herbicide in Italy, Seasons 1994-1996, and magnitude of residues in rice grains. Bonacini, F., Zenide, D., Gasser, F., Leka, A., 1999. Amendment no.1.*

Cross reference IIA 7.1.1.2.2./02

Guidelines:

OECD/GD(92) 37— Environmental Monograph N°50-Paris 1992 - Protocol

GLP:

Yes

The study is acceptable

Material and methods:

A field soil dissipation study of bensulfuron methyl and metsulfuron methyl was conducted at three locations in northern Italy Ceretto Lomellina, Villarboit, and Rosate, which are typical for the rice grown in this country. The product was applied to rice paddies in a single application over each of three years (1994, 1995, and 1996).

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

The characterisations of the field soil at each site can be found in Table B.8.47. Each field site contained two plots, one treated and one untreated. The treated plots varied in size from 5741 to 17422 m².

Table B.8.47: Characteristics of test soil

Characteristic	Test Site		
	Ceretto Lomellina, Italy	Villarboit, Italy	Rosate, Italy
pH	6.2	5.7	6.2
% Sand (2000 – 50 µm)	77.76	27.27	51.85
% Silt (<50 - 2 µm)	18.14	59.93	36.64
% Clay (<2 µm)	4.1	12.81	11.51
Texture	Sandy	Silt Loam	Sandy loam
Organic matter (%)	1.3	2.1	1.5
Cation exchange capacity (meq/100 g)	6.2	8.0	10.8

Bensulfuron methyl was applied to each treated plot as DPX-JM206 60WG, a formulated product containing 58% of the active ingredient bensulfuron methyl, 2% of the active ingredient metsulfuron methyl, and 40% of inert ingredients, at application rates ranging from 46.2 to 63.5 g active ingredients/ha. At each site on each of three subsequent years, the test substance was applied to the water-flooded soil of the designated rice paddy at the end of tillering rice growth stage. Description of test site is reported in Table B.8.48.

Table B.8.48: Description of test site

Test Site	Cropping Scenario	Target Application Rate (g a.s./ha)	Date of Application	Air Temperature Range/Average Temperature (°C) ^a	Cumulative Rainfall (mm) ^a
Ceretto Lomellina, Italy	Overall spray in flooded soil	60	July 1994	16.9 (min) 26.8 (max)	238.4
	Overall spray in flooded soil	60	July 1995	12.9 (min) 22.8 (max)	386.8
	Overall spray in flooded soil	60	July 1996	13.3 (min) 23.8 (max)	404.4
Villarboit, Italy	Overall spray in flooded soil	60	July 1994	16.9 (min) 27.2 (max)	423.8
	Overall spray in flooded soil	60	July 1995	15.8 (min) 25.9 (max)	381
	Overall spray in flooded soil	60	July 1996	14.1 (min) 23.9 (max)	442.2
Rosate, Italy	Overall spray in flooded soil	60	July 1994	15.1 (min) 25.4 (max)	202.4
	Overall spray in flooded soil	60	July 1995	14.0 (min) 25.4 (max)	142.3
	Overall spray in flooded soil	60	July 1996	14.0 (min) 24.0 (max)	282.8

^a Minimum and maximum of monthly averages over the sampling period.

From both treated and control plots, samples were collected for “closed water,” “running water,” soil, and rice grain. Samples were collected from both treated and control plots of “closed water” at approximately -1 hour (1 hour before the treatment), 3 hours, 2, and 5 days after treatment (DALA) and of “running water” at approximately 5, 10, and 15 DALA. Paddy soil samples were taken from the 0-10, 10-30, and 30-50 cm depth at approximately -1 day (1 day before the treatment), 3 hour, 2, 5, 10, 70, and 100 DALA. All samples were taken in triplicate. Rice grains were sampled in 1995 and 1996 at harvest.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Where water was present, three replicate samples of either “closed” or “running” paddy water were taken at each interval. At the approximately 5 DALA interval both “closed” and “running” water was sampled. Each replicate consisted of approximately 1 L stored in glass bottles (in 1994) or into polypropylene plastic bottles (in 1995 and 1996). The sampling of the water from the closed paddy was made with a beaker until about 1 L was sampled in triplicate. For “running” water, 1L samples were collected from the exit of the paddy field at 15 minute intervals forming three replicates within 45 minutes.

At each sampling interval, five soil cores were removed from each of three subplots in both the treated and control plots. Fifteen cores total were taken from the three treated subplots and fifteen cores total were taken from the three untreated subplot. The three treated subplot cores were held as replicates while the three control subplot cores were combined into a single replicate. Soil cores were taken to a depth of 30 cm at all sampling events using a mechanical carrot system with application of parafilm to prevent contamination from the liquid phase (water). The samples were frozen immediately. The cores were segmented in three depths, *i.e.*, 0-10 cm, 10-20 cm, and 20-30 cm segments, in the laboratories of Piacenza University where each segment of each replicate was mixed and homogenised prior to shipment to the analytical laboratory.

Regarding sample preparation prior to analysis, the bottles containing the water samples were transferred from the freezer at $\leq -18^{\circ}\text{C}$ to a refrigerator at $+4^{\circ}\text{C}$. The next morning the bottles were agitated manually for homogenisation and a 200 mL aliquot taken for extraction and chemical analysis. The samples were filtered and adjusted to pH 3.0 to 3.5 with dilute phosphoric acid prior to extraction with one portion of 100 mL of toluene followed by an additional two extractions of 50 mL of toluene each. From this point on, both water and soil samples followed the same procedure. That is, the combined toluene extracts were then back-extracted with one portion of 100 mL of 1 mM ammonium hydroxide followed by an additional two extractions of 50 mL of 1 mM ammonium hydroxide. The combined aqueous extracts were then adjusted to pH 3.0 to 3.5 with dilute phosphoric acid. The samples were charged to C18 solid phase extraction cartridges (C18 SPE Isolute™). After a water wash, the analytes were eluted with a portion of ethyl acetate acidified with glacial acetic acid. After evaporating to dryness, the residues were redissolved in ethyl acetate and charged to a silica solid phase extraction cartridge (Silica SPE Isolute™). After a hexane:ethyl acetate (80:20) rinse, the analytes were eluted with ethyl acetate acidified with glacial acetic acid that was evaporated to dryness and reconstituted with mobile phase prior to chromatographic analysis.

For soil samples a portion (5 to 10 grams) was taken for the determination of soil moisture by oven drying at 105°C until a constant weight was obtained. All residues found in the soil samples have been corrected for soil moisture. An additional portion (50 grams) of the homogenised soil material was removed for chemical analysis. This portion was extracted twice with 100 mL of 100 mM ammonium carbonate solution by rigorous shaking on a wrist-action shaker followed by centrifugation and decanting. A 100 mL aliquot of the combined extracts was adjusted to pH 3.0 to 3.5 using dilute phosphoric acid and extracted with one portion of 50 mL of toluene followed by an additional two extractions of 25 mL of toluene each. From this point, the same procedure was used for as for the water samples.

All sample solutions were analysed by normal phase HPLC with photoconductivity detection. The Limits of Quantitation (LOQ) for bensulfuron methyl as determined by recovery studies conducted on fortified controls in soil, water and rice grain were determined to be 1, 0.5, and 20 ppb respectively for most analyses. Soil analyses from year 3 were fortified at the 5 and 10 ppb levels. The Limits of Detection (LOD) in soil, water, and rice grain were reported to be 1, 0.1, and 20 ppb respectively.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Degradation rates were determined for the data using a linear regression of a first-order kinetic equation. Data modelled for bensulfuron methyl degradation in soil was based on the average of the three replicates for the 0-15 cm depth at the Ceretto Lomellina site and reported in $\mu\text{g a.i./kg}$ soil and water kinetics modelling was based on average of 3 replicate samples.

Findings:

Dissipation of bensulfuron methyl in water: The nominal application rate of bensulfuron methyl ranged from 44.7 to 61.4 g a.i./ha under regular field conditions or 59.6 to 81.9 $\mu\text{g a.i./kg}$ of soil assuming a typical soil density of 1.5 g/cm^3 and 5 cm of depth. However, as the applications were made to water-flooded paddies, much of the active ingredient remained in the water phase. This is reflected in the results of the water analyses that range on Day 0 from 54.4 to 10.1 $\mu\text{g a.i./L}$ (Table B.8.49 to Table B.8.51). Dissipation was rapid during the time the water was held in the paddies and continued at approximately same rate when the water was released. All values presented are the average of three replicates. For calculation of plot averages, residue results <LOD were assigned a value of 0.05 $\mu\text{g/L}$ when at least one of the three replicates had a residue concentration above the LOD. All time points (Closed and Running) were used in the kinetic analysis.

Table B.8.49: Average concentration of bensulfuron methyl in water ($\mu\text{g/L}$; Ceretto Lomellina)

Days after Application	Closed	Running
1994		
3 hours	54.4	NA ^a
2	4.3	NA
6	0.3	2.8
10	NA	0.3
15	NA	0.3
1995		
3 hours	37.3	NA
2	27.1	NA
5	0.4	1.8
9	NA	0.5
15	NA	<LOD
1996		
3 hours	37.0	NA
2	16.5	NA
5	2.2	12.3
9	NA	0.3
15	NA	2.0

^a Not Applicable (samples were either not collected, Day 0, or not analysed)

LOQ = Limit of Quantitation = 0.5 $\mu\text{g/L}$; LOD = Limit of Detection = 0.1 $\mu\text{g/L}$

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.50: Average concentration of bensulfuron methyl in water (µg/L; Villarboit)

Days after Application	Closed	Running
1994		
-1	0.1	NA ^a
3 hours	46.5	NA
2	26.6	NA
5	11.6	13.7
15	NA	2.6
1995		
0	20.7	NA
2	13.2	NA
6	4.4	9.9
9	NA	2.2
15	NA	0.4
1996		
0	32.5	NA
2	28.7	NA
6	11.7	6.13
9	NA	2.0
15	NA	2.5

^a Not Applicable (samples were either not collected, Day 0, or not analysed)

LOQ = Limit of Quantitation = 0.5 µg/L; LOD = Limit of Detection = 0.1 µg/L

Table B.8.51: Average concentration of bensulfuron methyl in water (µg/L; Rosate)

Days after Application	Closed	Running
1994		
3 hours	10.1	NA ^a
2	15.9	NA
6	15.9	4.5
10	NA	11.5
15	NA	1.3
1995		
3 hours	24.1	NA
2	19.0	NA
6	11.0	9.33
9	NA	8.97
1996		
3 hours	37.4	NA
2	14.9	NA
5	10.5	16.0
9	NA	8.33
14	NA	5.57

^a Not Applicable (samples were either not collected, Day 0, or not analysed)

LOQ = Limit of Quantitation = 0.5 µg/L LOD = Limit of Detection = 0.1 µg/L

Dissipation of bensulfuron methyl in soil. The concentration of bensulfuron methyl in soil was very low (below 5.0 µg/kg) and decrease with the DALA. When bensulfuron methyl was found in the soil, the residues were usually in the 0-15 cm layer (Table B.8.52 and Table B.8.54). All values presented are the average of three replicates except where otherwise noted. For calculation of plot averages, residue results reported as <LOD were assigned a value of 0.5 µg/kg when at least one of the three replicates had a residue concentration above the LOD.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.52: Average concentration of bensulfuron methyl in each soil horizon (µg/kg; Ceretto Lomellina)

Days after Application	0-15 cm	15-30 cm	30-50 cm
1994			
3 hours	1.9	<LOD	<LOD ^a
2	1.7	<LOD	NA ^b
6	1.0	<LOD	<LOD
10	1.2	<LOD	NA
15	<LOD	NA	NA
60	<LOD	<LOD	NA
96	NA	NA	<LOD
1995			
3 hours	3.4	0.9	1.4
2	1.2	0.9	NA
6	1.6	0.7	<LOD
9	<LOD	<LOD	NA
15	<LOD	<LOD	<LOD
71	NA	NA	<LOD
110	<LOD	<LOD	<LOD
1996			
3 hours	1.9	0.7	0.8
2	2.0	0.8	NA
5	1.7	1.1	<LOD
9	0.8	<LOD	NA
15	0.5	<LOD	<LOD
60	NA	NA	<LOD
91	<LOD	<LOD	<LOD

^a Based on one replicate^b Not Applicable (samples were either not collected, Day 0, or not analysed)

LOQ = Limit of Quantitation = 1 µg/kg; LOD = Limit of Detection = 1 µg/kg

Table B.8.53: Average concentration of bensulfuron methyl in each soil horizon (µg/kg; Villarboit)

Days after Application	0-15 cm	15-30 cm	30-50 cm
1994			
3 hours	2.75	<LOD	<LOD
2	2.7	<LOD	NA ^a
5	2.3	<LOD	<LOD
9	1.7	<LOD	NA
15	1.4	<LOD	<LOD
60	NA	NA	<LOD
96	NA	NA	<LOD
1995			
3 hours	<LOD	<LOD	<LOD
2	0.7	0.7	NA
6	3.3	<LOD	<LOD
9	<LOD	<LOD	NA
77	NA	NA	<LOD
108	<LOD	<LOD	1.2
1996			
3 hours	<LOD	<LOD	<LOD
2	0.8	<LOD	NA
6	1.4	<LOD	<LOD
9	3.0	<LOD	NA
15	<LOD	<LOD	<LOD
63	NA	NA	<LOD
101	<LOD	<LOD	<LOD

^a Not Applicable (samples were either not collected, Day 0, or not analysed)

LOQ = Limit of Quantitation = 1 µg/kg; LOD = Limit of Detection = 1 µg/kg

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.54: Average concentration of bensulfuron methyl in each soil horizon expressed in µg/kg soil (Rosate)

Days after Application	0-15 cm	15-30 cm	30-50 cm
1994			
-1	<LOD	<LOD	<LOD
3 hours	<LOD	<LOD	<LOD
2	0.7	1.1	NA
6	1.3	<LOD	<LOD
10	0.7	<LOD	NA
15	<LOD	<LOD	<LOD
1995			
-1	<LOD	<LOD	<LOD
3 hours	<LOD	<LOD	<LOD
2	<LOD	<LOD	NA ^a
6	<LOD	<LOD	1.3
9	<LOD	<LOD	NA
71	NA	NA	0.7
99	<LOD	<LOD	<LOD
1996			
-2	<LOD	<LOD	<LOD
3 hours	<LOD	<LOD	<LOD
2	<LOD	<LOD	NA ^a
5	1.2	<LOD	<LOD
9	<LOD	<LOD	NA
61	NA	NA	<LOD
112	<LOD	<LOD	<LOD

^a Not Applicable (samples were either not collected, Day 0, or not analysed)

LOQ = Limit of Quantitation = 1 µg/kg; LOD = Limit of Detection = 1 µg/kg

The actual results of soil analysis showed concentrations ranging from 3.4 µg a.i./kg of soil to <LOD immediately after application. In all cases, the concentrations dropped to less than the LOD prior to the next year's application. Further, in most cases the concentrations had dropped below the LOD on or before Day 15 with the exception of year one at the Villarboit site that samples were either not taken or not analysed.

Movement of residues in to the lower soil cores: Bensulfuron methyl was generally not detected below the 30-50 cm, with the exception of Day 0 samples at the Ceretto Lomellina site in years 2 and 3 (Table B.8.52). As these were Day 0 samples, the movement appears to be caused by the sampling procedure rather than by leaching. Another case was Rosate 1995, where bensulfuron was detected at a maximum average value of 1.3 µg/kg. Bensulfuron methyl was occasionally found in the 15-30 cm horizon at levels barely above the LOD at intervals less than 6 days from application.

DT₅₀ and DT₉₀ values for bensulfuron methyl. In the original report, some mistakes occurred in reporting water concentrations for calculation of DT₅₀ and DT₉₀. In those cases, RMS corrected the value and recalculated DT₅₀ and DT₉₀ consequently. This fact occurred for Ceretto Lomellina soil, in year 1996 and Ceretto Lomellina water, in year 1995. Moreover, RMS calculated soil DT₅₀ for Villarboit, in 1994, as residue values were considered enough to derive DT₅₀ value. RMS agrees with notifier that for Villarboit (1995, 1996) and Rosate sites (all three years), the bensulfuron methyl residues in soil were less than 1 ppb at almost all sampling times therefore the declined curves could not be calculated. All DT₅₀ and DT₉₀ values are reported in Table B.8.55.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.55: DT₅₀ and DT₉₀ values for bensulfuron methyl in field soil and water

Soil properties		Statistical Evaluation					
Site/Year	Test System	% OM	pH	DT ₅₀ (days)	DT ₉₀ (days)	r ²	Method of Calculation
Field Soil							
Ceretto Lomellina/1994	Soil	1.3	6.2	12	39	0.937	Pseudo First-Order Regr.
Ceretto Lomellina/1995	Soil	1.3	6.2	4	14	0.843	Pseudo First-Order Regr.
Ceretto Lomellina/1996	Soil	1.3	6.2	7	23	0.963	Pseudo First-Order Regr.
Villarboit/1994	Soil	2.1	5.7	14	48	0.983	Pseudo First-Order Regr.
Field Water							
Ceretto Lomellina/1994	Water	ND ^a	7.5 – 8.3	2	7	0.834	Pseudo First-Order Regr.
Ceretto Lomellina/1995	Water	ND	8.2 - 8.9	1.5	5	0.947	Pseudo First-Order Regr.
Ceretto Lomellina/1996	Water	ND	7.5 - 8.2	3	10	0.709	Pseudo First-Order Regr.
Villarboit/1994	Water	ND	7.6 - 8.6	4	12	0.985	Pseudo First-Order Regr.
Villarboit/1995	Water	ND	7.3 - 7.9	3	10	0.927	Pseudo First-Order Regr.
Villarboit/1996	Water	ND	7.3 - 8.5	3	11	0.892	Pseudo First-Order Regr.
Rosate/1994	Water	ND	8.5 - 8.6	5	18	0.721	Pseudo First-Order Regr.
Rosate/1995	Water	ND	7.3 - 8.7	5	18	0.973	Pseudo First-Order Regr.
Rosate/1996	Water	ND	6.9 - 7.8	6	19	0.908	Pseudo First-Order Regr.

^a determined

The average DT₅₀ and DT₉₀ values for bensulfuron methyl derived by the soil samples at the Ceretto Lomellina site were 8 and 28 days, respectively. Considering also the DT₅₀ derived at Villarboit site in 1994, the average DT₅₀ and DT₉₀ values for bensulfuron methyl in soil field are 9.3 days and 31 days. The DT₅₀ values for bensulfuron methyl in the water samples were 2, 3, and 5 days for Ceretto Lomellina, Villarboit, and Rosate, respectively. The DT₉₀ values in water were 7, 11, and 18 days for Ceretto Lomellina, Villarboit, and Rosate, respectively. The overall average DT₅₀ and DT₉₀ values for bensulfuron methyl in water field are 3.6 days and 12 days.

Conclusion:

Bensulfuron methyl degraded rapidly in soil (DT₅₀ ranged from 4-14 days) and water (DT₅₀ ranged 2-5 days). Low level of bensulfuron methyl was detected in few soil samples at the 0-15 cm depth (<5 µg kg⁻¹ after 5 days) and was not detectable 60 days after application. Average bensulfuron methyl residues observed in the 15-30 cm layer were just above the quantitation limit (0.1 µg kg⁻¹) and reached a maximum concentration of 0.26 µg kg⁻¹ after 2 days and decreased to undetectable levels 10 days after the treatment. Bensulfuron methyl degrades rapidly in the field and shows little potential for accumulation as evidenced by a DT₉₀ ranging from 14 days to 48 days.

B.8.1.3.2 Soil residue studies - soil accumulation studies (Annex IIA 7.1.1.2.2; Annex IIIA 9.1.1.2)

B.8.1.3.2.1 Soil residue studies

Soil residue studies are not required since the DT₅₀ value for bensulfuron methyl in the field is typically less than one third of the interval between application and harvest (e.g. rice: PHI=60 days). The DT_{50field} values ranged from 4 days to 14 days. Soil cores removed from the treated field at the end of study (60 days after application) showed no detectable level of bensulfuron methyl. In addition, soil residue concentration at planting of succeeding crops can be

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

reliably estimated from the field soil dissipation studies conducted with bensulfuron methyl. Sampling times used in these studies covered most scenarios for succeeding crop planting intervals.

B.8.1.3.2.2 Soil accumulation studies

Soil accumulation studies were not conducted since the $DT_{90\text{field}}$ value was less than one year. The $DT_{90\text{field}}$ values ranged from 14 days to 48 days.

B.8.2 Adsorption, desorption and mobility in soil (Annex IIA 7.1.2 and IIA 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)

- 16) *Adsorption and desorption of bensulfuron methyl on Italian paddy field soils. Cavanna, S., Garatti, E., Rastelli, E., Molinari, G.P., 1998*

Cross reference IIA 7.1.2./05

Guidelines:

Not applicable – published

GLP:

No

The study is acceptable as supporting documentation

Material and Methods:

Methyl-2-[[[(4,6-dimethoxy-pyrimidin-2-yl)aminocarbonyl]-aminosulfonyl]methyl] benzoate, purity 99.4% was used. The adsorption and desorption processes of bensulfuron methyl on three Italian paddy field soils (Table B.8.56) was studied.

Table B.8.56: Characteristics of test soils

Characteristic	Soil		
Soil Name or Designation	Vercelli	Pavia	Milano
Origin Location	Italy	Italy	Italy
pH (in water)	5.7	6.2	6.2
% Sand (2000–50 µm)	27.27	77.77	51.85
% Silt (<50–2 µm)	59.93	18.14	36.64
% Clay (<2 µm)	12.81	4.10	11.50
Texture ^a	Silt loam	Sandy loam	Loamy Sand
Organic matter (%) ^b	2.1	1.3	1.5
Cation exchange capacity (mEq/100 g)	8.0	6.2	10.8

^a USDA soil classification system

^b organic carbon = organic matter/1.72

Bensulfuron methyl solutions were prepared in aqueous 0.01 M CaCl₂ (pH 5) at four different concentrations: 3.31 (saturated solution), 2.38, 1.37, and 0.45 µg/mL. Soil samples for all soil types were then desorbed twice with fresh calcium chloride solutions for 24 hours each time. Aqueous solutions and soil extracts were analysed by HPLC to determine the actual concentrations of bensulfuron methyl in soil extracts and solutions during the equilibration

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

phases. Time to equilibration of bensulfuron methyl between soil and solution was judged to be ~20 minutes for the Vercelli soil (silt loam) and 30 minutes for the Pavia and Milano soils (sandy loam and loamy sand).

2 g of soil were weighed in a 10 ml glass test-tube. Then 5 ml of CaCl_2 0.01 M solution containing test substance were added. The test tube was shaken by vortex to improve the contact between solid and liquid phase and quieted until the sampling of liquid phase for HPLC analysis. The test tube was centrifuged (at 1800 g for 3 min) and 1 ml of liquid phase was drawn for analysis. Subsequently the liquid phase was put in contact with soil again. The samplings were carried out as follows: 5, 10, 15, 20, 25, 30, 45, 60, 124 minutes and 24, 48 and 72 hours after soil-liquid phase contact. Three repetitions were carried out for each level of active ingredient concentration and for each soil type. An adsorption test with standard solutions but without soil, was carried out in order to evaluate substance stability

Findings:

The adsorption parameters for bensulfuron methyl on the three soil types are summarised in Table B.8.57. The adsorption process in Vercelli soil came to a pseudo equilibrium condition after 20 minutes with an adsorption rate of nearly 75% of the initial quantity present in liquid phase. The pseudo equilibrium was reached after 30 minutes in Pavia soil (adsorption 47-55%) and in Milano soil (adsorption 61-67%). For all tests, with the exclusion of Vercelli and Milano soils at the lowest concentration of $0.45 \mu\text{g mL}^{-1}$, the increase of the adsorbed fraction measured after 120 minutes was not statistically significant. The adsorption rate increased to 100% after 24 hours for the lowest concentration of silt-loam and loamy sand soils.

Table B.8.57: Summary of the averaged sorption coefficients for each soil treated with bensulfuron methyl

Soil	Texture	Organic carbon (%)	r^2	$1/n$	K_f	K_{foc}
Vercelli	Silt loam	1.22	0.993	1.07	8.4	684
Pavia	Sandy loam	0.76	0.987	1.08	2.8	364
Milano	Loamy sand	0.87	0.990	1.06	4.8	552

Bensulfuron methyl adsorption was proved to be dependent on soil type. The highest adsorption level was reached in the Vercelli soil ($K_f = 8.35$), an intermediate adsorption was found in the Milano soil ($K_f = 4.81$) and the lowest level of adsorption in the Pavia soil ($K_f = 2.75$). The K_{oc} values were 684, 552, and 364, respectively, for Vercelli, Milano, and Pavia soils. There was correlation between adsorption and soil organic carbon content.

Bensulfuron methyl desorption in three soils is shown in Table B.8.58. The total amount of desorbed bensulfuron methyl was 21% in the Vercelli soil, 40% in the Pavia soil, and 47% in the Milano soil. The desorption coefficients, calculated by linear regression, were low and not significantly different for the three soil types. The ratios between the calculated desorption and adsorption constants were 0.21, 0.30, and 0.56, respectively, for the Vercelli, Milano, and Pavia soils. Soil extractions with acetone after three desorption steps with CaCl_2 recovered a large quantity of bensulfuron methyl in the Vercelli soil (about 44% of the remaining amount before extraction), a moderate quantity in the Pavia soil (22%), and a variable quantity (24 to 40%) in the Milano soil. Therefore, mass balance showed the un-recovered bensulfuron methyl was 44, 47, and 36%, respectively, for the Vercelli, Pavia, and Milano soils.

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Table B.8.58: Summary of the averaged desorption coefficients for each soil treated with bensulfuron methyl

Soil	Texture	Organic carbon (%)	r^2	1/n	K_f	K_{foc}
Vercelli	Silt loam	1.22	0.978	0.99	1.75	143
Pavia	Sandy loam	0.76	0.981	1.01	1.54	202
Milano	Loamy sand	0.87	0.962	0.88	1.43	164

Conclusion:

The adsorption of bensulfuron methyl is a very fast process. Equilibrium is reached in the first 20 minutes in siltloam soil, and in 30 minutes in the other two soils. The average of the adsorbed fraction from watery solutions with initial concentration ranging between 0.45 and 3.3 µg/mL, were as follows: 3.6 µg/g for silt-loam soil, 3 µg/g for loamy-sand soil and 2.5 µg/g for sandy-loam soil. K_{oc} values have shown that bensulfuron methyl desorption mainly involves the clay mineral fraction. Bensulfuron methyl moderately adsorbed to soil. The Freundlich coefficient varies from 1.75 to 1.43. The average K_{foc} value was 533. The average 1/n value was 1.07. Sorption was partially reversible with moderate desorption.

- 17) *Batch equilibrium (adsorption/desorption) and soil thin-layer chromatography studies with ^{14}C -DPX-F5384. Priester, T.M., 1984.*

Cross reference IIA 7.1.2./07

Guidelines:

USEPA 540/9-82-021

GLP:

No

The study is acceptable

Material and Methods:

[Phenyl(^{14}C)] and [Pyrimidine-2- ^{14}C] DPX-F5384 (methyl-2-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]-carbonyl]amino]sulfonyl[methyl]benzoate, specific activity 15 µCi/mg and 16.57 µCi/mg respectively, purity > 99% for both compounds were used.

The chemical standards used for comparison were [2- ^{14}C]terbacil (5-chloro-3-(1,1-dimethylethyl)-6-methyl-2,4(1*H*, 3*H*)-pyrimidinedione] for its hydrophilic properties and [carbonyl- ^{14}C]diuron (N'-(3,4-dichlorophenyl)-N,N-dimethylurea] for its hydrophobic properties. The sorption behaviour of ^{14}C -bensulfuron methyl on four soils was studied. Soil characteristics are reported in Table B.8.59.

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Environmental fate and behaviour

Table B.8.59: Characteristics of test soils

Characteristic	Soil			
Soil Name or Designation	Cecil	Flanagan	Keyport	Woodstown
Origin Location	Raleigh, NC	Rochelle, IL	Newark, DE	Dover, DE
pH (in water)	6.5	5.4	5.2	6.6
% Sand (2000 - 50 µm)	61	2	12	60
% Silt (<50 - 2 µm)	21	81	83	33
% Clay (<2 µm)	18	17	5	7
Texture ^a	Sandy loam	Silt loam	Silt loam	Sandy loam
Organic matter (%)	2.1	4.3	7.5	1.1
Organic carbon (%) ^b	1.2	2.5	4.4	0.6
Cation exchange capacity (mEq/100 g)	6.6	21.1	15.5	5.3

^a USDA soil classification system^b organic carbon = organic matter/1.724

Initial bensulfuron methyl solution concentrations in the range 0.2-6.0 µg/mL in 0.01 N aqueous calcium sulfate (CaSO₄) were studied. For the adsorption phase, the four soil types and solutions were equilibrated for 24 hours at 25°C in the dark using a soil-to-solution ratio of 1:1. Soil samples at the highest concentration for all soil types were then desorbed six times with fresh calcium sulfate solutions for 24 hours each time.

Aqueous solutions containing radioactivity were acidified to pH 3.2 and extracted three times with methylene chloride at a 1:1 v/v ratio. Radioactivity remaining in the aqueous fraction (5-26% of the total) was considered to be polar metabolites. Extracts were detected and analysed by TLC to determine the actual concentrations of bensulfuron methyl in soil extracts and solutions during the equilibration phases.

Soil Thin Layer Studies: the mobility of carbon-14 labeled bensulfuron methyl was studied on each soil type by soil thin layer chromatography.

Each soil sample was applied to glass plates and treated with 1 µg/mL [pyrimidine-2-¹⁴C] bensulfuron methyl, [2-¹⁴C] terbacil, and [carbonyl-¹⁴C] diuron. The lower 0.5 cm of the plate was submerged in water and the water allowed to ascend to a height of 10 cm. The plates were air dried for 24 hours and exposed to X-ray film and analysed after two weeks.

Findings:

The Freundlich adsorption parameters for bensulfuron methyl on the four soil types are summarised in Table B.8.60.

Table B.8.60: Summary of the adsorption coefficients for each soil treated with ¹⁴C-DPX-F5384

Soil	Texture	Organic carbon (%)	K _f (mL/g)	K _{fom} (mL/g)	K _{foc} (mL/g)	1/n
Cecil	Sandy loam	1.2	2.5	120	205	0.89
Woodstown	Sandy loam	0.6	1.4	130	219	0.88
Keyport	Silt loam	4.4	12	160	276	0.97
Flanagan	Silt loam	2.5	14	330	561	0.93

There was a fair correlation of K_f with percent organic matter for bensulfuron methyl. Bensulfuron methyl was weakly adsorbed to the two sandy loam soils (K_f=1.4 to 2.5 mL/g) but was strongly adsorbed to the Flanagan silt loam (K_a=14 mL/g) and Keyport silt loam (K_a=12 mL/g) which have 4.3 and 7.5% organic matter, respectively. The K_{om} values for the Cecil sandy loam (120 mL/g), Woodstown sandy loam (130 mL/g), and Keyport silt loam (160 mL/g) were in reasonably good agreement. The high value on Flanagan silt loam (330 mL/g) and the moderate correlation coefficient suggest that other variables may also be important in the adsorption of bensulfuron methyl.

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Desorption parameters and concentration of bensulfuron methyl in aqueous solution and on soil after each of the two desorption phases are shown in Table B.8.61 and Table B.8.62.

Table B.8.61: Summary of the desorption coefficients for each soil treated with ^{14}C -DPX-F5384

Soil	Texture	Organic matter (%) ^a	K_d (mL/g) ^b	$K_{d,om}$ (mL/g) ^c	1/n
Cecil	Sandy loam	2.1	3.3 (3.3)	160	0.30
Woodstown	Sandy loam	1.1	2.4 (2.4)	220	0.26
Keyport	Silt loam	7.5	ND ^d	ND	ND
Flanagan	Silt loam	4.3	6.4 (6.3)	150	0.18

^a The correlation coefficient for % organic matter vs. K_d was 1.0 for bensulfuron methyl; the corresponding correlation coefficient for % organic matter vs. $1/n_d$ was -0.80.

^b Freundlich desorption distribution coefficient. Values in parenthesis calculated from K_a values using Hornsby equation.

^c Coefficient of desorption per unit organic matter

^d Radioactivity adsorbed to Keyport soil is poorly desorbed: accurate value for $K_{d,om}$ and $1/n_d$ could not be determined.

In general, the K_d values of bensulfuron methyl are about equal to those of diuron on the silt loam soils but are intermediate between terbacil and diuron on sandy loam soils. The consistency of the K_{om} values and inverse relationship of $1/n$ values with percent organic matter indicate that the desorption properties of bensulfuron methyl are directly, but not strongly related to the soils organic matter content. The low $1/n$ values (<0.3) indicate that the adsorbed bensulfuron methyl is only gradually desorbed.

Table B.8.62: Degradation of bensulfuron methyl (DPX-F5384) on test soils

Compound	Rf		% of recovered radioactivity		% of recovered radioactivity in aqueous phase after the final desorption			
	NP ^a	RP ^b	Initial	No Soil 1 Week Incubation	Cecil Sandy loam	Woodstown Sandy loam	Flanagan Silt loam	Keyport Silt loam
DPX-F5384	0.56	0.86	87	72	77	79	27	8
IN-N5297	0.74	0.86	6	18	13	10	58	44
IN-B6895	0.30	0.39	ND	ND	ND	ND	ND	2
IN-R9419	0.12	0.39	ND	ND	ND	ND	ND	11
IN-F7880	0.56	0.63	ND	ND	ND	ND	ND	6
Polars ^c	-	-	5	7	7	6	12	26

^a NP = Normal phase TLC

^b RP = Reverse phase TLC

^c Radioactivity not extracted from the acidified aqueous phase with methylene chloride.

Analyses of the aqueous extracts from the final desorption equilibration (Table B.8.62) indicates bensulfuron methyl degrades to IN-N5297 (sulfonamide) and polar compounds on the sandy loam and Flanagan silt loam. On Keyport silt loam, bensulfuron methyl degrades to polar compounds, IN-N5297, IN-R9419, IN-F7880, and IN-B6895 (homosaccharin). Bensulfuron methyl degraded extensively in the Flanagan and Keyport silt loams (73 to 92%, respectively), but did not degrade any more rapidly over Cecil and Woodstown sandy loams than in water that has incubated without soil (23, 21, and 28%, respectively).

The percent of bensulfuron methyl extracted from the aqueous phase of the last desorption day is inversely proportional to the percent organics found in the desorbed soil.

Soil Thin Layer Studies: The TLC R_f values are listed in Table B.8.63. These data characterise bensulfuron methyl as a Class I (immobile) compound on the silt loam, Class 2 (low mobility) compound on Cecil sandy loam, and Class 3

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(intermediate mobility) compound on Woodstown sandy loam. The mobility as measured by soil TLC R_f values, is inversely proportional to the percent organic matter content of the soil in the range from 1-4%.

Table B.8.63: Soil thin-layer chromatography R_f values of bensulfuron methyl on four soils

Soil	R_f Value
Cecil Sandy loam	0.30
Woodstown Sandy loam	0.45
Keyport Silt loam	0.05
Flanagan Silt loam	0.059

Conclusion:

Adsorption, desorption, and soil thin-layer chromatography studies with radiolabeled bensulfuron methyl were conducted on four soils. The mobility of bensulfuron methyl varied from immobile (Class I) on silt loam soil, low mobility (Class 2) on Cecil sandy loam, and intermediate mobility (Class 3) on Woodstown sandy loam as determined by soil thin-layer chromatography. The R_f values were inversely proportional to the percent organic content of soil.

The K_f values from the adsorption study were proportional to the percent organic matter content of the soil. Bensulfuron methyl was weakly adsorbed to the sandy loam soils ($K_f = 1.4$ - 2.5 mL/g) but was strongly adsorbed to the Flanagan silt loam ($K_f = 14$ mL/g) and Keyport silt loam ($K_f = 12$ mL/g) which have a higher organic matter, respectively. The experimental $1/n$ values (<0.3) were low, indicating little tendency to desorb once adsorption has occurred. The average K_{foc} was 315 mL/g and the average of $1/n$ value was 0.92.

Analysis of the aqueous desorption extracts indicate bensulfuron methyl degrades to IN-N5297 (sulfonamide) and polar compounds on the sandy loam soils and Flanagan silt loam soil. Bensulfuron methyl degrades to IN-N2597, IN-R9419, IN-F7880, IN-B6895, and polar compounds on Keyport silt loam soil. The formation of some of the degradation products appeared to be artefacts of the acidic extraction method used in this study (pH <4). The percent of bensulfuron methyl extracted from the aqueous phase of the desorbed samples inversely correlates to the percent organics found in the desorbed soil.

In Table B.8.64 is reported a summary of the Freundlich equation parameters for the bensulfuron methyl adsorption isotherms, as derived by previous study.

Table B.8.64 Summary of the Freundlich equation parameters for the bensulfuron methyl adsorption isotherms

Soil	Texture	Organic carbon (%)	$1/n$	K_f	K_{fom}	K_{foc}
Vercelli, Italy	Silt loam	1.22	1.07	8.4	-	684
Pavia, Italy	Sandy loam	0.76	1.08	2.8	-	364
Milano, Italy	Loamy sand	0.87	1.06	4.8	-	552
Cecil, U.S.A	Sandy loam	1.2	0.89	2.5	120	205
Woodstown, U.S.A	Sandy loam	0.6	0.88	1.4	130	219
Keyport, U.S.A	Silt loam	4.4	0.97	12	160	276
Flanagan, U.S.A	Silt loam	2.5	0.93	14	330	561

Rapporteur Member State	Month and year	Active Substance (Name)
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Environmental fate and behaviour

18) *Adsorption/desorption of [¹⁴C]IN-N5297 in five soils. Aikens, P.J., 2001a.*

Cross reference IIA 7.1.2./01

Guidelines:

OECD Method 106 (January 2000), US EPA Pesticide Assessment Guidelines Subdivision N 163-1

GLP:

Yes

The study is acceptable

Material and Methods:

¹⁴C-IN-N5297 (Methyl-2-[[[(amino)sulfonyl]methyl]benzoate), specific activity 53.3 µCi/mg and IN-N5297 Technical Metabolite (purity: >95%, 99.9%) were used.

The soil sorption behaviour of ¹⁴C-IN-N5297 on five soils (Table B.8.65) was studied. Initial IN-N5297 solution concentrations in the range 0.01-1.0 µg/mL in 0.01 M aqueous calcium chloride were studied.

Adsorption and desorption experiments were conducted in 55 mL borosilicate glass vessels (150 × 29 mm o.d.) with ground glass stoppers. The vessels were shaken at a constant rate on an orbital shaker. The shaker was kept in darkness in a controlled temperature incubator at 20 - 22°C.

After pre-equilibration, the soil slurries were treated with their respective application solutions (1 mL) to achieve nominal concentrations of the test substance of 1, 0.5, 0.1, 0.05 and 0.01 µg/mL. The blank samples were treated with 1 mL of aqueous calcium chloride solution (0.01 M).

Table B.8.65: Characteristics of test soils

Characteristic	Soil				
Soil Name or Designation	Speyer 2.2	Pavia	Drummer	Nambsheim	Vercelli
Origin Location	Germany	Italy	USA	France	Italy
pH (in water)	6.4	5.2	5.5	7.8	5.8
% Sand (2000 - 50 µm)	69.2	78.4	16.8	57.2	20.4
% Silt (<50 - 2 µm)	24.8	14.8	54.4	32.8	62.8
% Clay (<2 µm)	6.0	6.8	28.8	10.0	16.8
Texture ^a	Loamy sand	Loamy sand	Silt loam	Sandy loam	Silt loam
Organic carbon (%) ^b	2.1	0.5	3.1	0.7	1.2
Cation exchange capacity (mEq/100 g)	10.67	2.59	34.05	6.48	8.45

^a USDA soil classification system

^b organic carbon = organic matter/1.72

For the a main adsorption/desorption experiment, for each soil type 13 pre-weighed tubes were prepared. The five soil types and solutions were equilibrated for 24 hours at 20°C in the dark using a soil-to-solution ratio of 1:2 for three of the soil types, a ratio of 1 : 10 for the Drummer soil type and 1 : 1 for the Nambsheim soil type. Soil samples at the highest concentration for all soil types were then desorbed twice with fresh calcium chloride solutions for 8 hours each time. Aqueous solutions and soil extracts were analysed by TLC to determine the actual concentrations of IN-N5297 in soil extracts and solutions during the equilibration phases. Radioactivity was measured by LSC.

Findings:

TLC analysis of soil extracts and aqueous solution showed that over the incubation period (72 hours: one 24-hour adsorption phase followed by two 24-hour desorption phases), low amounts of degradation of IN-N5297 were

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observed in aqueous solution but the radioactivity in soil extracts contained significant proportions of degradation products. IN-N5297 represented 26.1–81.4% sample radioactivity in these soil extracts. Recoveries of radioactivity from samples set aside for the determination of the material balance upon completion of adsorption were in the range 96.4 - 105.2% of the amount applied. The adsorption parameters for IN-N5297 on the five soil types are summarised in Table B.8.66. There was correlation between adsorption (K_d) and organic carbon content of the soil.

Table B.8.66: Summary of the averaged sorption coefficients for each soil treated with ^{14}C -IN-N5297

Soil	Texture	% OC	K_d (mL/g) ^a	K_{om} (mL/g) ^a	K_{oc} (mL/g) ^a
Speyer 2.2	Loamy sand	2.1	0.48	13	23
Pavia	Loamy sand	0.5	0.09	11	18
Drummer	Silt loam	3.1	3.86	73	125
Nambsheim	Sandy loam	0.7	0.17	15	25
Vercelli	Silt loam	1.2	0.54	27	45

^a mean values

The Freundlich adsorption isotherms obtained from a linear regression using the log-transformed equilibrium concentrations showed good linearity (Table B.8.67). The slopes of the Freundlich isotherms ($1/n$) were in the range of 0.91 to 0.94. The Freundlich adsorption constants (K_F) ranged from 0.0737 to 2.84 mL/g, indicating IN-N5297 was poorly adsorbed to soils tested. K_{Foc} values ranged from 15 to 92 mL/g.

Table B.8.67: Summary of Freundlich equation parameters for the IN-N5297 adsorption

Soil	Texture	% OC	K_f (mL/g)	$1/n$	r^2	K_{fom} (mL/g)	K_{foc} (mL/g)
Speyer 2.2	Loamy sand	2.1	0.398	0.94	1.0	11	19
Pavia	Loamy sand	0.5	0.0737	0.92	1.0	9	15
Drummer	Silt loam	3.1	2.84	0.91	1.0	54	92
Nambsheim	Sandy loam	0.7	0.140	0.92	1.0	12	20
Vercelli	Silt loam	1.2	0.434	0.93	0.99	22	36

Desorption parameters for IN-N5297 and the concentrations of IN-N5297 are shown in Table B.8.68. The mean total desorbed (D_T) ranged from 20-35% of that adsorbed in the four soil types that produced representative values.

Table B.8.68: Percent ^{14}C -IN-N5297 desorbed

Soil	Texture	% OC	1 st desorption (D_1) ^a	2 nd desorption (D_2) ^a	Total desorbed (D_T) ^a
Speyer 2.2	Loamy sand	2.1	17	12	29
Pavia	Loamy sand	0.5	6	NA ^b	NA
Drummer	Silt loam	3.1	19	14	33
Nambsheim	Silt loam	0.7	26	10	35
Vercelli	Silt loam	1.2	7	13	20

^a mean % of adsorbed IN-N5297 that was desorbed

^b Not applicable, negative desorption noted

Conclusion:

The adsorption/desorption behaviour of IN-N5297 was studied in five soils. IN-N5297 is weakly adsorbed to soil. The average linear K_{oc} and Freundlich K_{foc} values were 47.2 and 36 mL/g, respectively. The average Freundlich $1/n$ value was 0.92. The adsorbed IN-N5297 was moderately desorbed.

Rapporteur Member State	Month and year	Active Substance (Name)
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19) Adsorption/desorption of [^{14}C]IN-J0290 in five soils. Aikens, P.J., 2001b.

Cross reference IIA 7.1.2./02

Guidelines:

OECD Method 106 (January 2000) and US EPA Pesticide Assessment Guidelines Subdivision N 163-1.

GLP:

Yes

The study is acceptable

Material and Methods:

^{14}C -IN-J0290 Metabolite (specific activity 141.8 $\mu\text{Ci}/\text{mg}$), IN-J0290 Technical Metabolite (2-Amino-4,6-dimethoxyprimidine), purity: >95%, 99.6% respectively were used

The sorption behaviour of ^{14}C -IN-J0290 on five soils (Table B.8.69) was studied. Initial IN-J0290 solution concentrations in the range 0.01-1.0 $\mu\text{g}/\text{mL}$ in 0.01 M aqueous calcium chloride were studied.

Adsorption and desorption experiments were conducted in 55 mL borosilicate glass vessels (150 $\times$ 29 mm o.d.) with ground glass stoppers. The vessels were shaken at a constant rate on an orbital shaker. The shaker was kept in darkness in a controlled temperature incubator at 20 - 22°C.

Table B.8.69: Characteristics of test soils

Characteristic	Soil				
Soil Name or Designation	Speyer 2.2	Pavia	Drummer	Nambsheim	Vercelli
Origin Location	Germany	Italy	USA	France	Italy
pH (in water)	6.4	5.2	5.5	7.8	5.8
% Sand (2000 - 50 μm)	69.2	78.4	16.8	57.2	20.4
% Silt (<50 - 2 μm)	24.8	14.8	54.4	32.8	62.8
% Clay (<2 μm)	6.0	6.8	28.8	10.0	16.8
Texture ^a	Loamy sand	Loamy sand	Silt loam	Sandy loam	Silt loam
Organic carbon (%) ^b	2.1	0.5	3.1	0.7	1.2
Cation exchange capacity (mEq/100 g)	10.67	2.59	34.05	6.48	8.45

^a USDA soil classification system

^b Organic carbon = organic matter/1.72

After pre-equilibration, the soil slurries were treated with their respective application solutions (1 mL) to achieve nominal concentrations of the test substance of 1, 0.5, 0.1, 0.05 and 0.01 $\mu\text{g}/\text{mL}$. The blank samples were treated with 1 mL of aqueous calcium chloride solution (0.01 M).

For the a main adsorption/desorption experiment, for each soil type 13 pre-weighed tubes were prepared. The five soil types and solutions were equilibrated for 24 hours at 20°C in the dark using a soil-to-solution ratio of 1:2 (for Drummer soil a 1:20 ratio was used). Soil samples at the highest concentration for all soil types were then desorbed twice with fresh calcium chloride solutions for 24 hours each time.

Aqueous solutions and soil extracts were analysed by TLC to determine the actual concentrations of IN- J0290 in soil extracts and solutions during the equilibration phases. Radioactivity was measured by LSC.

Findings:

TLC analysis of soil extracts and aqueous solution showed that over the incubation period (72 hours: one 24-hour adsorption phase followed by two 24-hour desorption phases), low amounts (<11% applied radioactivity) of

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degradation of IN-J0290 were observed. Recoveries of radioactivity from samples set aside for the determination of the material balance upon completion of adsorption were in the range 99.5 - 101.7% of the amount applied.

The adsorption parameters for IN-J0290 on the five soil types are summarised in (Table B.8.70). There was no clear linear correlation between adsorption and soil characteristics.

Table B.8.70: Summary of the averaged sorption coefficients for each soil treated with ^{14}C -IN-J0290

Soil	Texture	% OC	K_d (mL/g) ^a	K_{om} (mL/g) ^a	K_{oc} (mL/g) ^a
Speyer 2.2	Loamy sand	2.1	2.01	56	96
Pavia	Loamy sand	0.5	4.76	595	952
Drummer	Silt loam	3.1	212	4006	6849
Nambsheim	Silt loam	0.7	1.71	143	245
Vercelli	Silt loam	1.2	4.69	235	391

^a mean values

The Freundlich adsorption isotherms obtained from a linear regression using the log-transformed equilibrium concentrations showed good linearity (Table B.8.71). The slopes of the Freundlich isotherms ($1/n$) were in the range of 0.71 to 0.85. The Freundlich adsorption constants (K_F) ranged from 0.9 to 45.3 mL/g and K_{foc} values ranged from 58 to 1460 mL/g.

Table B.8.71: Summary of Freundlich equation parameters for the IN-J0290 adsorption

Soil	Texture	% OC	K_F (mL/g)	$1/n$	r^2	K_{fom} (mL/g)	K_{foc} (mL/g)
Speyer 2.2	Loamy sand	2.1	1.22	0.85	1.0	33.9	58.1
Pavia	Loamy sand	0.5	2.26	0.81	1.0	283	452
Drummer	Silt loam	3.1	45.3	0.71	0.99	855	1460
Nambsheim	Silt loam	0.7	0.859	0.79	1.0	71.6	123
Vercelli	Silt loam	1.2	2.35	0.82	1.0	118	196

Desorption parameters for IN-J0290 and the concentrations of IN-J0290 in aqueous solution and on soil after each of the two desorption phases are shown in Table B.8.72. The percentage of test substance desorbed after the first and second desorption (D_1 and D_2) was moderate and similar between each desorption phase. The total IN-J0290 desorbed (D_T) ranged from 21-47% of that absorbed in the five soil types tested (Table B.8.72).

Table B.8.72: Percent ^{14}C -IN-J0290 desorbed

Soil	Texture	% Organic Carbon	1 st desorption (D_1) ^a	2 nd desorption (D_2) ^a	Total desorbed (D_T) ^a
Speyer 2.2	Loamy sand	2.1	18	10	27
Pavia	Loamy sand	0.5	16	12	28
Drummer	Silt loam	3.1	13	9	21
Nambsheim	Silt loam	0.7	32	16	47
Vercelli	Silt loam	1.2	15	10	25

^a mean % of adsorbed N5297 that was desorbed

Conclusion:

The adsorption/desorption behaviour of IN- J0290 was studied in five soils. IN-J0290 moderately to strongly adsorbed to soil. The average linear K_{oc} and Freundlich K_{foc} values were 1707 and 458 mL/g, respectively. The average Freundlich $1/n$ value was 0.80. The adsorbed IN-J0290 was moderately desorbed.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

20) *Adsorption/Desorption of [¹⁴C]IN-R9419 in five soils. Aikens, P.J., 2002c.*

Cross reference IIA, 7.1.2./03

Guidelines:

OECD Method 106 (January 2000) and US EPA Pesticide Assessment Guidelines Subdivision N 163-1.

GLP:

Yes

The study is acceptable

Material and Methods:

¹⁴C-IN-R9419 (specific activity 59.5 µCi/mg) and IN-R9419 (2-((((4,6-dimethoxypyrimidin-2-yl)amino carbonyl))-aminosulfonylmethyl)) -benzoic acid), purity higher than 95%, were used. The sorption behaviour of ¹⁴C-IN-R9419 on five soils (Table B.8.73) was studied. Initial IN-R9419 solution concentrations in the range 0.01-1.0 µg/mL in 0.01 M aqueous calcium chloride were studied. Adsorption and desorption experiments were conducted in 55 mL borosilicate glass vessels (150 × 29 mm o.d.) with ground glass stoppers. The vessels were shaken at a constant rate on an orbital shaker. The shaker was kept in darkness in a controlled temperature incubator at 20 - 22°C.

Table B.8.73: Characteristics of test soils

Characteristic	Soil				
Soil Name or Designation	Speyer 2.2	Pavia	Drummer	Nambsheim	Vercelli
Origin Location	Germany	Italy	USA	France	Italy
pH (in water)	5.9	5.8	5.6	8.1	6.1
% Sand (2000 - 50 µm)	80.8	72.8	25.2	60.8	22.0
% Silt (<50 - 2 µm)	15.2	22.8	48.0	33.2	64.4
% Clay (<2 µm)	4.0	4.4	26.8	6.0	13.6
Texture ^a	Loamy sand	Sandy loam	Clay loam	Sandy loam	Silt loam
Organic carbon (%) ^b	2.2	0.6	3.0	1.0	1.0
Cation exchange capacity (mEq/100 g)	8.40	4.30	34.52	5.30	9.66

^a USDA soil classification system

^b organic carbon = organic matter/1.72

After pre-equilibration, the soil slurries were treated with their respective application solutions (1 mL) to achieve nominal concentrations of the test substance of 1, 0.5, 0.1, 0.05 and 0.01 µg/mL. The blank samples were treated with 1 mL of aqueous calcium chloride solution (0.01 M).

For the a main adsorption/desorption experiment, for each soil type 13 pre-weighed tubes were prepared. For the adsorption phase, the five soil types and solutions were equilibrated for 8 hours at 20°C in the dark using a soil-to-solution ratio of 1:2 for three of the soil types, a ratio of 1:10 for the Drummer soil type and 1:1 for the Nambsheim soil type. Soil samples at the highest concentration for all soil types were then desorbed twice with fresh calcium chloride solutions for 8 hours each time.

Aqueous solutions and soil extracts were analysed by HPLC to determine the actual concentrations of IN-R9419 in soil extracts and solutions during the equilibration phases.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Findings:

Recoveries of radioactivity from samples set aside for the determination of the material balance upon completion of adsorption were in the range 90.4 - 92.5% of the amount applied. The adsorption parameters for IN-R9419 on the five soil types are summarised in Table B.8.74.

Table B.8.74: Summary of the averaged sorption coefficients for each soil treated with ¹⁴C-IN-R9419

Soil	Texture	% Organic Carbon	K _d (mL/g) ^a	K _{om} (mL/g) ^a	K _{oc} (mL/g) ^a
Speyer 2.2	Loamy sand	2.2	2.49	67	113
Pavia	Sandy loam	0.6	2.04	204	341
Drummer	Clay loam	3.0	25.86	497	862
Nambsheim	Sandy loam	1.0	0.33	20	33
Vercelli	Silt loam	1.0	2.65	147	265

^amean values

The Freundlich adsorption isotherms obtained from a linear regression using the log-transformed equilibrium concentrations showed good linearity (Table B.8.75). The slopes of the Freundlich isotherms (1/n) were in the range of 0.89-0.93. The Freundlich adsorption constants (K_F) ranged from 0.277 to 17.4 mL/g and K_{Foc} values ranged from 27.7 to 580 mL/g. Adsorption constants normalised for soil organic carbon content (K_{foc}) did not correlate well, suggesting that factors other than soil organic carbon content may contribute to the extent of IN-R9419 adsorption.

Table B.8.75: Summary of Freundlich equation parameters for the ¹⁴C-IN-R9419 adsorption

Soil	Texture	% Organic Carbon	K _F (mL/g)	1/n	r ²	K _{fom} (mL/g)	K _{foc} (mL/g)
Speyer 2.2	Loamy sand	2.2	1.86	0.91	0.9981	50.3	84.5
Pavia	Sandy loam	0.6	1.49	0.89	0.9993	149	248
Drummer	Clay loam	3.0	17.4	0.89	0.9991	335	580
Nambsheim	Sandy loam	1.0	0.28	0.93	0.9969	16.3	27.7
Vercelli	Silt loam	1.0	1.87	0.89	0.9991	104	187

Desorption parameters for IN-R9419 and the concentrations of IN-R9419 in aqueous solution and on soil after each of the two desorption phases are shown in Table B.8.76. The percentage of test substance desorbed after the first and second desorption (D₁ and D₂) was moderate and similar between each desorption phase. The total IN-R9419 desorbed (D_T) ranged from 29-40% of that absorbed in the soil types tested. Negative desorption was noted for one replicate for the Nambsheim soil type which affected the mean values for that soil.

Table B.8.76: Percent ¹⁴C-IN- R9419 desorbed

Soil	Texture	% Organic Carbon	1 st desorption (D ₁) ^a	2 nd desorption (D ₂) ^a	Total desorbed (D _T) ^a
Speyer 2.2	Loamy sand	2.2	19	16	34
Pavia	Loamy sand	0.6	25	16	40
Drummer	Silt loam	3.0	18	11	29
Nambsheim	Silt loam	1.0	23 ^a	17 ^a	40 ^b
Vercelli	Silt loam	1.0	24	16	40

^amean % of adsorbed N5297 that was desorbed

^bNambsheim values are based on one replicate. The second replicate gave negative desorption.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Conclusion:

The adsorption/desorption behaviour of IN-R9419 was studied in five soils. IN-R9419 is moderately adsorbed to soil. The average linear K_{oc} and Freundlich K_{foc} values were 323 and 225 mL/g, respectively. The average Freundlich $1/n$ value was 0.90. The adsorbed IN-R9419 was moderately desorbed.

21) *Adsorption/Desorption of [^{14}C]IN-D1R84 in five soils. Aikens, P.J., 2002d.*

Cross reference IIA, 7.1.2./04

Guidelines:

Directive 91/414/EEC, OECD Method 106 (January 2000) and US EPA Pesticide Assessment Guidelines Subdivision N 163-1.

GLP:

Yes

The study is acceptable

Material and Methods:

^{14}C -IN-D1R84 Metabolite (2-[aminosulfonyl)methyl]benzoic acid) specific activity 56.8 $\mu Ci/mg$, purity: >95% was used. The sorption behaviour of ^{14}C -IN-D1R84 on five soils (Table B.8.77) was studied. Adsorption and desorption experiments were conducted in 55 mL borosilicate glass vessels (150 $\times$ 29 mm o.d.) with ground glass stoppers. The vessels were shaken at a constant rate on an orbital shaker. The shaker was kept in darkness in a controlled temperature incubator at 20 - 22°C.

Table B.8.77: Characteristics of test soils

Characteristic	Soil				
Soil Name or Designation	Speyer 2.2	Pavia	Drummer	Nambsheim	Vercelli
Origin Location	Germany	Italy	USA	France	Italy
pH (in water)	5.9	5.8	5.6	8.1	6.1
% Sand (2000 - 50 μm)	80.8	72.8	25.2	60.8	22.0
% Silt (<50 - 2 μm)	15.2	22.8	48.0	33.2	64.4
% Clay (<2 μm)	4.0	4.4	26.8	6.0	13.6
Texture ^a	Loamy sand	Sandy loam	Clay loam	Sandy loam	Silt loam
Organic carbon (%) ^b	2.2	0.6	3.0	1.0	1.0
Cation exchange capacity (mEq/100 g)	8.40	4.30	34.52	5.30	9.66

^a USDA soil classification system

^b organic carbon = organic matter/1.72

After pre-equilibration, the soil slurries were treated with their respective application solutions (1 mL) to achieve nominal concentrations of the test substance of 1, 0.5, 0.1, 0.05 and 0.01 $\mu g/mL$. The blank samples were treated with 1 mL of aqueous calcium chloride solution (0.01 M).

For the a main adsorption/desorption experiment, for each soil type 13 pre-weighed tubes were prepared. The five soil types and solutions were equilibrated for 24 hours at 20°C in the dark using a soil-to-solution ratio of 1:1. Soil samples at the highest concentration for all soil types were then desorbed twice with fresh calcium chloride solutions for 24 hours each time.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Aqueous solutions and soil extracts were analysed by TLC to determine the actual concentrations of IN-D1R84 in soil extracts and solutions during the equilibration phases. Radioactivity was measured by LSC

Findings:

Recoveries of radioactivity from samples set aside for the determination of the material balance upon completion of adsorption were in the range 96.4 - 105.2% of the amount applied.

The adsorption parameters for IN-D1R84 on the five soil types are summarised in Table B.8.78. Examination of K_d values for each soil type showed greatest adsorption at the lowest concentrations tested.

Table B.8.78: Summary of the averaged sorption coefficients for each soil treated with ^{14}C -IN-D1R84

Soil	Texture	% OC	K_d (mL/g) ^a	K_{om} (mL/g) ^a	K_{oc} (mL/g) ^a
Speyer 2.2	Loamy sand	2.2	0.30	8	14
Pavia	Sandy loam	0.6	0.19	19	32
Drummer	Clay loam	3.0	0.47	9	16
Nambsheim	Sandy loam	1.0	0.09	5	9
Vercelli	Silt loam	1.0	0.19	10	19

^a mean values

The Freundlich adsorption isotherms obtained from a linear regression using the log-transformed equilibrium concentrations showed good linearity (Table B.8.79). The slopes of the Freundlich isotherms ($1/n$) were in the range of 0.84-0.45 suggesting non-linearity of adsorption over the concentration range tested. The $1/n$ value for Nambsheim should be treated with caution as very little of the test substance adsorbed to this soil type. Adsorption constants normalised for soil organic content (K_{Foc}) appear reasonably consistent, suggesting that soil organic carbon content was a significant factor in determining the extent of IN-D1R84. The Freundlich adsorption constants (K_F) ranged from 0.0173 to 0.231 mL/g, indicating IN-D1R84 was poorly adsorbed to soils tested. K_{Foc} values ranged from 2 to 21 mL/g.

Table B.8.79: Summary of Freundlich equation parameters for the ^{14}C -IN-D1R84 adsorption

Soil	Texture	% OC	K_f (mL/g)	$1/n$	r^2	K_{fom} (mL/g)	K_{foc} (mL/g)
Speyer 2.2	Loamy sand	2.2	0.133	0.71	0.9992	4	6
Pavia	Sandy loam	0.6	0.123	0.84	0.9942	12	21
Drummer	Clay loam	3.0	0.231	0.76	0.9953	4	8
Nambsheim	Sandy loam	1.0	0.0173	0.45	0.8898	1	2
Vercelli	Silt loam	1.0	0.103	0.77	0.9985	6	10

Desorption parameters for IN-D1R84 and the concentrations of IN-D1R84 in aqueous solution and on soil after each of the two desorption phases are shown in Table B.8.80. As a consequence of the weak adsorption of IN-D1R84 to soil, the desorption parameters should be treated with caution as small variations in concentrations of the test substance measured in aqueous solution may have significant impact on the desorption parameters. Mean desorption totals of 17 and 52% were calculated for Drummer and Pavia soils, respectively (Table B.8.78).

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.80: Percent ¹⁴C-IN-D1R84 desorbed

Soil	Texture	% Organic Carbon	1 st desorption (D ₁) ^a	2 nd desorption (D ₂) ^a	Total desorbed (D _T) ^a
Speyer 2.2	Loamy sand	2.2	NA ^b	NA	NA
Pavia	Loamy sand	0.6	42	11	52
Drummer	Silt loam	3.0	13	4	17
Nambsheim	Silt loam	1.0	NA	NA	NA
Vercelli	Silt loam	1.0	NA	NA	NA

^a mean % of adsorbed IN-N5297 that was desorbed.^b Not applicable, negative desorption notedConclusion:

The adsorption/desorption behaviour of IN-N5297 was studied in five soils. IN-N5297 was weakly adsorbed to all five soils tested. The average linear K_{oc} and Freundlich K_{foc} values were 18 and 9.4 mL/g, respectively. The average Freundlich 1/n value was 0.71. The adsorbed IN-D1R84 was moderately desorbed with mean desorption totals (D_T) of 17 and 52% for Drummer and Pavia soils.

22) *Adsorption/Desorption of IN-F7880 in five soils. Crowe, A., 2002.*

Cross reference IIA, 7.1.2./06

Guidelines:

OECD Method 106 (January 2000); US EPA Guideline Subdivision N, 163-1 (October 1982)

GLP:

Yes

The study is acceptable

Material and Methods:

IN-F7880, methyl 2-[[[(4-hydroxy-6-methoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]methyl]benzoate (Batch No. F7880-3, purity 95%), was used. The adsorption/desorption characteristics of IN-F7880 were investigated on five soils (Table B.8.81). Soils were pre-equilibrated with 0.01 M calcium chloride prior to adsorption.

Table B.8.81: Characteristics of test soils

Characteristic	Soil				
Soil Name or Designation	Nambsheim	Pavia	Speyer 2.2	Vercelli	Drummer
Origin	France	Italy	Germany	Italy	USA
pH (in water)	8.0 or 8.1	5.8	5.9	6.2	5.6
% Sand (>2000 - 50 µm)	57.2 or 60.8	72.8	80.8	24.8	25.2
% Silt (<50 - 2 µm)	30.0 or 33.2	22.8	15.2	60.8	48.0
% Clay (<2 µm)	12.8 or 6.0	4.4	4.0	14.4	26.8
Texture ^a	sandy loam	sandy loam	loamy sand	silt loam	clay loam
Organic carbon (%) ^b	1.0	0.6	2.2	1.2	3.0
Cation exchange capacity (meq/100g)	5.5/5.3	4.3	8.4	9.7	34.5

^a USDA soil classification system^b organic carbon = organic matter/1.724

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Initial solution concentrations of 0.01, 0.05, 0.1, 0.5, and 1.0 µg IN-F7880/mL were prepared in 0.01 M aqueous calcium chloride. Testing was conducted in duplicate with soil:solution ratios of 1:1 or 1:10 for Drummer soil (10 g dry weight of soil:10 mL or 2 g dry weight of soil:20 mL). The soil:solution mixtures were equilibrated for 72 hours at 20±2°C in the dark. Two 72-hour desorption cycles were conducted on the 1 µg/mL samples after the 72-hour adsorption cycle. Desorption was accomplished by completely removing the supernatant (after centrifugation) and replacing it with an equivalent volume of fresh 0.01 M calcium chloride solution. Adsorption isotherm data were analysed using the log form of the Freundlich equation: $\log x/m = 1/n * \log C_e + \log K_F$. Linear distribution coefficients (K_d) were calculated from the mean ratios of x/m to C_e calculated at each concentration level.

The supernatants and soil extracts were analysed by LC-MS-MS.

Findings:

The linear adsorption coefficients for IN-F7880 are listed in Table B.8.82. The K_d values ranged from 0.7 to 13.5 mL/g and K_{oc} values ranged from 95 to 449 mL/g (average = 212 mL/g).

Table B.8.82: Summary of the averaged linear soil adsorption coefficients for IN-F7880 on a range of soils

Soil Origin	Soil Type ^a	pH	Organic carbon ^b %	K_d mL/g	K_{oc} mL/g	K_{om} mL/g
Nambsheim, France	Sandy loam	8.1	1.0	2.2	222	130
Pavia, Italy	Sandy loam	5.8	0.6	0.7	108	65
Speyer, Germany	Loamy sand	5.9	2.1	2.1	95	57
Vercelli, Italy	Silt loam	6.2	1.2	2.2	187	112
Drummer, USA	Clay loam	5.6	3.0	13.5	449	259

^a USDA soil classification system

^b organic carbon = organic matter/1.72

The Freundlich adsorption isotherms obtained from a linear regression using the log-transformed equilibrium concentrations showed good linearity (Table B.8.83). The Freundlich adsorption constant, K_F , ranged from 0.5-14.2 mL/g with K_{Foc} values ranging from 75-472 mL/g (average = 206 mL/g). The $1/n$ values ranges from 0.90 to 1.14 (average = 1.00). K_d and K_{Foc} values generally correlate with the organic carbon content of the soils.

Desorption of IN-F7880: IN-F7880 adsorbed to the Drummer soil was moderately desorbed. IN-F7880 adsorbed to the Speyer 2.2, Pavia, and Vercelli soils were slightly desorbed. IN-F7880 adsorbed to the Nambsheim soil was not desorbed (Table B.8.83).

Table B.8.83: Summary of the Freundlich equation parameters for the adsorption isotherms and desorption intervals of IN-F7880 on a range of soils

Soil Origin	Soil Type ^a	pH	% OC	K_F mL/g	K_{Foc} mL/g	1/n	r^2	% total desorbed	K_{des}^c mL/g
Nambsheim, France	Sandy loam	8.1	1.0	1.6	161	0.92	0.970	NA ^d	NA
Pavia, Italy	Sandy loam	5.8	0.6	0.5	75	0.90	0.951	9.5	9.7
Speyer, Germany	Loamy sand	5.9	2.1	3.1	140	1.14	0.953	10.2	8.8
Vercelli, Italy	Silt loam	6.2	1.2	2.2	181	1.01	0.964	3.6	26.7
Drummer, USA	Clay loam	5.6	3.0	14.2	472	1.05	0.944	40.2	14.9

^a USDA soil classification system

^b organic carbon = organic matter/1.72

^c apparent desorption constant

^d not applicable, could not be calculated as no desorption was measured

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Conclusion:

IN-F7880 is weakly to moderately adsorbed to soil. The average linear K_{oc} and Freundlich K_{foc} values were 212 and 206 mL/g, respectively. The average Freundlich $1/n$ value was 1.00. The adsorbed IN-F7880 was not readily desorbed from the test soils, except for the Drummer soil where it was moderately desorbed.

B.8.2.2 Column leaching studies with the active substance and relevant metabolites (Annex IIA 7.1.3.1; Annex IIIA 9.1.2.1)

Column leaching studies with bensulfuron methyl were conducted but not included since reliable adsorption coefficient values of bensulfuron methyl and its degradates have been obtained in adsorption/desorption studies conducted under § 8.2.1 of this document.

B.8.2.3 Aged residue column leaching (Annex IIA 7.1.3.2; Annex IIIA 9.1.2.1)

Column leaching studies with bensulfuron methyl were conducted but not included since reliable absorption coefficient values of bensulfuron methyl and its degradates have been obtained in adsorption/desorption studies conducted under § 8.2.1 of this document.

B.8.2.4 Lysimeter and field leaching studies (Annex IIA 7.1.3.3; Annex IIIA 9.1.2.2)

A lysimeter study was not conducted with bensulfuron methyl. Data from the adsorption/desorption studies, field dissipation studies, and PEC_{gw} modelling using Med-Rice scenarios were considered sufficient, by notifier, to assess the mobility of bensulfuron methyl and its major soil degradation products IN-J0290, IN-D1R84, IN-F7880, IN-N5297, and IN-R9419. RMS agreed that there is no need for conducting lysimeter studies or field leaching studies with this active substance.

B.8.3 Summary of Behaviour in Soil and Predicted Environmental Concentration in Soil (PECs) (Annex IIIA 9.1.3)

The aerobic route of degradation of bensulfuron methyl has been presented for three studies using 6 different soils. The proposed degradation pathway of bensulfuron methyl in soils is shown in Figure B.8.1. The main metabolic pathway involves ester hydrolysis of bensulfuron methyl to form IN-R9419, which in turn can undergo sulfonylurea bridge hydrolysis to form IN-D1R84 and IN-J0290. These metabolites are subsequently mineralised to carbon dioxide. An alternative pathway involves sulfonylurea bridge hydrolysis of bensulfuron methyl itself to form IN-N5297 and again, IN-J0290. IN-N5297 could in turn undergo ester hydrolysis to form IN-D1R84. Another minor pathway involves O-demethylation of bensulfuron methyl to form IN-F7880, and hydrolysis of the sulfonylurea linkage of bensulfuron methyl to yield IN-J0290 and IN-N5297. IN-B6895 was a significant metabolite in older aerobic and anaerobic metabolism studies with bensulfuron methyl but a minor degradate in the most current aerobic study (DuPont-4325). IN-B6895 formation (from IN-N5297) is believed to be an artefact of the considerably more basic soil extraction conditions used in previous studies. The cyclisation of IN-N5297 to form IN-B6895 in basic condition is well documented in studies presented in this document.

The effect of soil photolysis was investigated in one study using one soil. The rate of degradation of bensulfuron methyl was faster in the irradiated samples as compared to non-irradiated samples, indicating that photolysis is also a significant degradation mechanism for bensulfuron methyl. In the irradiated samples, IN-T5831 (pyrimidine urea)

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

was observed as a major product at level of up to 11.9% of applied radioactivity at the end of the 15-day study. This product was also observed in the natural water photolysis study (§ 8.4.12 of this document) but not observed in any of the aerobic or anaerobic soil degradation studies. This indicates that formation of IN-T5831 is predominantly photo-catalysed product. Minor common metabolites IN-J0290, IN-N5297, and IN-B6895 were also observed (<8.3%) from the cleavage of sulfonylurea bridge of bensulfuron methyl.

Under anaerobic conditions, bensulfuron methyl degrades mainly *via* hydrolysis of the sulfonylurea bridge to form IN-N5297 and IN-J0290. An alternative pathway involves ester hydrolysis of bensulfuron methyl to form IN-R9419. Based on analysis of the aerobic soil metabolism studies, four metabolites in soil are considered major metabolites (>10% applied radiolabel in one test sample or ≥5% applied radioactivity in two or more test samples or plateau not reached at the end of the study jet): IN-R9419, IN-D1R84, IN-N5297 and IN-J0290.

To summarise, the following reactions are believed to be involved in bensulfuron methyl degradation in soils:

- Hydrolysis of bensulfuron methyl to form IN-J0290 and IN-N5297
- De-esterification of the methyl ester to form IN-R9419
- Hydrolysis of the sulfonylurea bridge of IN-R9419 to form IN-D1R84 and IN-J0290
- O-demethylation of the pyrimidine amine of bensulfuron methyl to form IN-F7880
- Photolysis of the bensulfuron methyl to form IN-T5831
- Further mineralisation to CO₂ and formation of non-extractable residues (NER)

The rate of degradation of bensulfuron methyl has been presented for three laboratory studies using six different soils (1 Italy soil, 3 U.S. soils, and 2 Japanese soils). The soils covered a range of soil textures and soil pH (5.2-6.5). Bensulfuron methyl degrades in soils with DT₅₀ values ranging from 25 to 102 days.

The DT₅₀ and DT₉₀ values resulted from the laboratory studies on bensulfuron methyl are reported in Table B.8.84. For the Friedman study, (1984 cross reference IIA 7.1.1.1.1/02), just the highest concentrations were used (0.59 ppm and 0.49 ppm). DT₅₀ and DT₉₀ values calculated for Flanagan and Keyport soils, are characterised by data with a quite poor mass balances, especially the ones at the end of the study; moreover, the dose applied for the study corresponds to 6-7 times the highest supported dose.

The Japanese soil DT₅₀ derived from data with quite a bad mass balance; California soil has data with a better mass balance even if not the one required by current guidelines. Just the Pavia soil DT₅₀ is derived from high quality data.

Table B.8.84: Summary of DT₅₀ and DT₉₀ values for bensulfuron methyl in aerobic soils

Soil Name/ Origin	Texture	pH	Soil Moisture	Incubation T (°C)	DT ₅₀ (days)	DT ₉₀ (days)	r ²	Method of calculation
Pavia, Italy	Loamy sand	5.2	50% of 0 bar	20	25	84	>0.957	Non-Linear SFO
Flanagan, US	Silt loam	5.6	70% WHC	25	89	294	0.978	Non-Linear SFO
Keyport, US	Silt loam	6.7	70% WHC	25	89	294	0.941	Non-Linear SFO
Nagano, Japan	Sandy loam	5.2	70% WHC	25	65	214	0.875	Non-Linear SFO
Tochigi, Japan	Clay loam	6.1	70% WHC	25	102	339	0.809	Non-Linear SFO
California, USA	Silt loam	6.5	70% WHC	25	90	297	0.840	Non-Linear SFO

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Radiolabel laboratory studies show that the aerobic degradation of bensulfuron methyl results in the formation of carbon dioxide (up to 42%), non-extractable residue (up to 38%), and degradation products IN-J0290, IN-F7880, IN-N5297, IN-R9419, and IN-D1R84. The rates of degradation of soil degradation products of bensulfuron methyl have been determined in aerobic laboratory soil studies using four European soils with soil pH ranging from 5.8 to 8.1. The average DT_{50} values, from laboratory studies, were 11, 16, 30, 13, and 13 days for IN-R9419, IN-F7880, IN-N5297, IN-J0290, and IN-D1R84, respectively. Soil pH did not affect the rate of degradation of bensulfuron methyl degradation products in these studies.

The DT_{50} and DT_{90} values resulted from the laboratory studies on bensulfuron methyl metabolites are reported in Table B.8.85.

Bensulfuron methyl degrades under anaerobic condition with an average DT_{50} value of 118 days. Photolysis of bensulfuron methyl resulted in an estimated half-life of 22-32 days with continuous irradiation equivalent to 44-64 days for a 12-hour photo period.

The field dissipation study of bensulfuron methyl was also determined at three locations in Northern Italy, which are typical for the rice producing areas. Bensulfuron methyl was applied to rice paddies in a single application as DPX-JM206 60WG, a formulated product containing 58% of the active ingredient bensulfuron methyl, 2% of the active ingredient metsulfuron methyl, and 40% of inert ingredients over each of three years (1994, 1995, and 1996). Bensulfuron methyl degrades rapidly in the field where DT_{50} values ranged from 4-14 days. Bensulfuron methyl shows little potential for accumulation as evidenced by a DT_{90} ranging from 14 days to 48 days.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.85: Summary of DT₅₀ and DT₉₀ values for IN-R9419, IN-F7880, IN-N5297, IN-J0290, and IN-D1R84 in aerobic soils

Soil Name/ Origin	Texture	pH	Soil Moisture	Incubation Temperature (°C)	DT ₅₀ (days)	DT ₉₀ (days)	r ²	Method of calculation
IN-R9419								
Pavia, Italy	Loamy sand	5.2	50% of 0 bar	20	54.4	181	>0.957	SFO parent/ metabolite
Namsheim, France	Sandy loam	8.1	50% of WHC	20	20	65	0.960	Non-linear SFO
Pavia, Italy	Sandy loam	5.8	50% of WHC	20	29	95	0.950	Non-linear SFO
Speyer 2.2, Germany	Loamy sand	5.9	50% of WHC	20	8	27	0.975	Non-linear SFO
Vercelli, Italy	Silt loam	6.2	50% of WHC	20	20	65	0.877	Non-linear SFO
IN-F7880								
Pavia, Italy	Loamy sand	5.2	50% of 0 bar	20	30.5	101	>0.957	SFO parent/ metabolite
Namsheim, France	Sandy loam	8.1	50% of WHC	20	4.1	13.5	0.994	Non-linear SFO
Pavia, Italy	Sandy loam	5.8	50% of WHC	20	18.8	62.4	0.957	Non-linear SFO
Speyer 2.2, Germany	Loamy sand	5.9	50% of WHC	20	5.6	18.4	0.890	Non-linear SFO
Vercelli, Italy	Silt loam	6.2	50% of WHC	20	20.2	67.1	0.947	Non-linear SFO
IN-N5297								
Namsheim, France	Sandy loam	8.0	50% of WHC	20	7	23	0.995	Non-linear SFO
Pavia, Italy	Sandy loam	5.5	50% of WHC	20	63	208	0.924	Non-linear SFO
Speyer 2.2, Germany	Loamy sand	6.7	50% of WHC	20	4	13	0.997	Non-linear SFO
Vercelli, Italy	Silt loam	6.1	50% of WHC	20	45	148	0.951	Non-linear SFO
IN-J0290								
Namsheim, France	Sandy loam	8.0	50% of WHC	20	19	63	0.936	Non-linear SFO
Pavia, Italy	Sandy loam	5.5	50% of WHC	20	18	60	0.880	Non-linear SFO
Speyer 2.2, Germany	Loamy sand	6.7	50% of WHC	20	3	10	0.995	Non-linear SFO
Vercelli, Italy	Silt loam	6.1	50% of WHC	20	13	42	0.864	Non-linear SFO
IN-D1R84								
Namsheim, France	Sandy loam	8.0	50% of WHC	20	11	35	0.981	Non-linear SFO
Pavia, Italy	Sandy loam	5.5	50% of WHC	20	17	55	0.934	Non-linear SFO
Speyer 2.2, Germany	Loamy sand	6.7	50% of WHC	20	3	11	0.958	Non-linear SFO
Vercelli, Italy	Silt loam	6.1	50% of WHC	20	19	62	0.970	Non-linear SFO

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Bensulfuron methyl was moderately adsorbed to soils from the US and Italy with an organic carbon content ranging from 0.6 to 4.4% and pH values ranging from 5.2 to 6.6. The Freundlich constants (K_f) values ranged from 1.4 to 14 and K_{foc} values ranged from 205 to 684. The average K_{foc} was 315 mL/g and the average of $1/n$ value was 0.92.

The adsorption/desorption behaviour of the degradation products IN-J0290, IN-D1R84, IN-F7880, IN-N5297, and IN-R9419 were studied. The adsorption/desorption behaviour of IN-J0290 was studied in five soils with organic carbon content ranging from 0.5% to 3.1% and pH values from 5.2 to 7.8. IN-J0290 was moderately sorbed in these soils with the K_f values ranged from 0.9 to 45.3 mL/g and the K_{foc} ranged from 58-1460 for an average of 458 mL/g. Mean K_d , K_{oc} , and K_{om} values calculated from the concentrations in aqueous solution and adsorbed to soil at adsorption equilibrium reflects the variable adsorption on IN-J0290. IN-J0290 that was absorbed was moderately desorbed. The average Freundlich $1/n$ value of IN-J0290 was 0.80. IN-R9419 sorption was studied in five soils and found to be also moderately sorbed in these soils with organic carbon content ranging from 0.6 to 3.0% and pH values from 5.8 to 8.1. The K_f values ranged from 0.3 to 17.4 and K_{foc} values ranged from 28 to 580. The average K_{foc} was 225 mL/g. K_{foc} values calculated from the Freundlich adsorption constants for the five soil types ranged widely, suggesting that factors other than organic carbon content of the soil may have influenced the adsorption of IN-R9419. Mean K_d , K_{oc} , and K_{om} values calculated from the concentrations in aqueous solution and adsorbed to soil at adsorption equilibrium reflect the variable adsorption of IN-R9419. IN-R9419 that was absorbed was moderately desorbed. The average Freundlich $1/n$ value of IN-R9419 was 0.90. IN-D1R84 sorption was studied in 5 soils with organic carbon content ranging from 0.6% to 3.0% and pH values from 5.8 to 8.1. IN-D1R84 was weakly adsorbed with K_{foc} values ranging from 2 to 21 for an average value of 9 mL/g. K_f values ranged from 0.02 to 0.2 mL/g. The average Freundlich $1/n$ value of IN-D1R84 was 0.71. IN-N5297 was weakly to moderately sorbed to the five soil with organic carbon content ranging from 0.5-3.1% and pH values from 5.2-7.8. K_{foc} values ranged from 15 to 92 and the average K_{foc} was 36 mL/g with adsorption tended to correlate with the organic carbon content of the soil. K_f values ranged from 0.07 to 2.8 mL/g. The average Freundlich $1/n$ value of IN-N5297 was 0.92. The adsorption of IN-F7880 was studied in five soils and found to be moderately adsorbed to soils. The soils have organic carbon content ranging from 0.6% to 3.0% and pH values from 5.6 to 8.1. The K_f values ranging from 0.5-14.2 mL/g and K_{foc} values ranged from 75 to 472 mL/g. The average K_{foc} was 206 mL/g. The average Freundlich $1/n$ value of IN-F7880 was 1.0.

B.8.3.1 Estimation of expected concentrations in soil

- 23) *Predicted Environmental Concentrations of Bensulfuron Methyl and Metabolites in Soil, Ground Water, Surface Water, Sediment, and Air Following Application to Rice in the EU. Warren, R.L., 2004.*

Cross reference IIIA 9.1.3/01, IIIA 9.2.1/01, IIIA 9.2.3/01

- 24) *Predicted Environmental Concentrations of Bensulfuron Methyl and Metabolites in Soil, Ground Water, Surface Water, Sediment, and Air Following Application to Rice in the EU. Revision No. 1, Warren, R.L., 2006.*

Cross reference not provided.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Guidelines:

Not applicable - calculations.

GLP:

No.

The study is acceptable

Material and methods:

The Tier 1 predicted environmental concentrations of bensulfuron methyl and metabolites IN-J0290, IN-DAT97, IN-F7880, IN-R9419, IN-N5297, IN-D1R84, and IN-T5831 were determined for soil (PEC_{soil}) using the equations and guidance provided by the Med-Rice working group (Med-Rice, 2003). Higher tier paddy simulations using RICEWQ version 1.64 were also conducted for bensulfuron methyl.

For the Tier 1 assessment, a single application of 60 g a.s./ha to flooded rice was simulated per proposed Good Agricultural Practices (GAP). Foliar interception was conservatively assumed not to occur (100% reaching the flooded paddy surface). Partitioning from paddy water to paddy soil was treated as an instantaneous, irreversible process. The amount of partitioning was determined by the compound distribution coefficient ($K_{FOC} \times$ fraction organic carbon of soil), the depth of the paddy water (10 cm), depth of paddy soil active in the sorption process (5 cm), and the paddy soil bulk density (1.5 g/cm^3). Since separate degradation values in water and sediment were not available, the longest total system degradation DT_{50} values were selected to represent degradation in both water and sediment phases per Med-Rice (2003) and FOCUS (2001) guidance. Total system DT_{50} values were available for bensulfuron methyl, IN-J0290, IN-DAT97, IN-F7880, IN-R9419, and IN-N5297 from Lentz (2001). Alternatively, the geometric mean DT_{50} from the aerobic soil degradation study was selected as for IN-D1R84, where the geometric mean aerobic soil DT_{50} was used. The average Freundlich sorption values (K_{FOC}) were selected since they were lower (more conservative) than the average linear K_{OC} values in each case. No sorption information was available for IN-DAT97, therefore a K_{FOC} value of 9 mL/g (lowest value observed for any metabolite) was assumed. Sorption, water/sediment, and aerobic soil data were not available for IN-T5831, therefore a K_{FOC} value of 9 mL/g (lowest observed for any metabolite) and DT_{50} of 21.1 days (same as for IN-J0290, a structurally similar metabolite) were used. In Table B.8.86 is reported a listing of K_{FOC} , first-order DT_{50} , and application rates used for the Tier 1 PEC_{soil} calculations; while some of the key input variables used in RICEWQ are listed in Table B.8.87.

Table B.8.86: Inputs used in Med-Rice Tier 1 PEC calculations for bensulfuron methyl and metabolites

Compound	Molecular weight (g/mol)	Maximum formed in any efate study (%)	Foliar interception ^a (%)	Equivalent application rate ^c (g/ha)	K_{FOC} (mL/g)	Total system water sediment DT_{50} ^a (days)
bensulfuron methyl	410.41	100	0	60.0	315	59
IN-F7880	396.38	9.7	0	5.62	206	79.1
IN-R9419	396.38	27.7	0	16.1	225	6.9
IN-D1R84 ^b	215.23	18.2	0	5.72	9	10.2
IN-J0290	155.16	46.0	0	10.4	458	21.1
IN-N5297	229.26	31.7	0	10.6	36	30.8
IN-T5831 ^f	198.18	13.7	0	3.96	9	21.1
IN-DAT97	320.28	9.9	0	4.64	9	37.8

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.87: Selected RICEWQ inputs and simulation information

Parameter	Value used	Source/rationale
Simulation		
• RICEWQ model version	1.64	Williams, et al. 1999
• simulation duration (years)	20	Duration to match the FOCUS daily weather files
Bensulfuron methyl parameters		
• application rate (g a.s./ha)	60	GAP
• number of applications per year	1	GAP
• KOC (mL/g)	315	Priester, 1985
• water solubility (mg/L)	67	Bonacini et al., 1998
• paddy water DT ₅₀ (days)	4	Bonacini et al., 1998
• paddy soil DT ₅₀ (days)	12	Moore, 1994
• foliar DT ₅₀ (days)	10	Default FOCUS value (FOCUS, 2001)
• foliar interception fraction (BBCH 20)	0.5	Bonacini et al., 1998; Linders et al., 2000
• foliar wash off rate per cm precipitation	0.5	Default FOCUS value (FOCUS, 2001)
Agronomic activity timing (days relative to sowing)		
• initial paddy flood	-16	Generalised representative agronomic practice timing derived from information given in section 2 of the Med-Rice (2003) guidance and input from a local EU expert (Ettore Capri, personal communications).
• rice sowing	0	
• first drain after flood to promote pegging	2	
• resume irrigation after pegging	8	
• rice seedling emergence	9	
• bensulfuron application (BBCH 20)	30	
• drain paddy after bensulfuron application	36	
• resume irrigation	43	
• maximum crop canopy development	50	
• stop irrigation prior to final drain	85	
• final drain	90	Representative timing of bensulfuron methyl application taken from the GAP.
• harvest	100	
Hydrologic parameters		
• surface area of paddy (ha)	2	Med-Rice, 2003 – page 16 and 22
• maximum paddy drainage rate (cm/d)	2.5	Conservative professional judgment
• irrigation rate (cm/d)	2.592	Med-Rice, 2003 – in range of values on page 42
• depth of paddy outlet (cm)	20	Conservative assumption for overflow
• initial depth of paddy (cm)	0	Depth on 01-January of each simulation year
• Seepage rate in paddy (cm/d)	0.1	Med-Rice, 2003 – rate for the clay scenario
• depth at which irrigation will begin (cm)	5	Assumed typical practice for the region
• depth at which irrigation will cease (cm)	10	Water level per Med-Rice, 2003 – page 43
Paddy soil parameters		
• depth of active soil layer (cm)	5	Med-Rice, 2003 – page 53
• soil bulk density (g/cm ³)	1.50	Med-Rice, 2003 – page 84
• organic matter (% wt/wt)	3.0	Med-Rice, 2003 – page 43
• field capacity (cm/cm)	0.42	Rawls & Brackensiek (1985) for Med-Rice clay soil
• wilting point (cm/cm)	0.23	Rawls & Brackensiek (1985) for Med-Rice clay soil
• soil moisture (cm/cm)	0.42	Field capacity
• mixing depth for partitioning to soil (cm)	0.1	Professional judgment
• suspended sediment concentration (mg/L)	45	Capri et al., 2002 not used
• burial velocity (m/day)	0	
Crop Parameters		
• maximum crop coverage fraction	0.98	Professional judgment
• harvest flag	-2	straw disposal, residues removed with straw

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Tier 1 PEC_{soil} values for metabolites were calculated with the dose rate determined using the maximum percentage formed in any environmental fate study and the molecular weight conversion. The maximum single replicate percent observed in any environmental fate study (water/sediment, aerobic soil metabolism/degradation, soil photolysis, etc.) was conservatively selected for the Tier 1 screen. The actual and time-weighted average PEC_{soil} values over time were calculated using standard first-order expressions provided in the Med-Rice (2003) guidance document. Higher tier paddy simulations were conducted for bensulfuron methyl using RICEWQ. The goal of the higher tier simulation was to provide a more realistic assessment based on refined environmental process descriptions and on typical product use. Therefore, a 60 g a.s./ha post emergence broadcast application to flooded rice at tillering (BBCH20, mid point of the GAP) was simulated. Foliar interception was assumed to be 50% as recommended from the literature, which is consistent with foliar interception estimates from field studies conducted with bensulfuron methyl in Italy. Partitioning from paddy water to paddy soil in RICEWQ is based on sorption directly to paddy soil as well as partitioning to and settling (or resuspension) of suspended soil particles. The degree of chemical movement between paddy water and soil is driven by diffusion gradients. Partitioning (based on K_d) is reversible and non-instantaneous.

Results:

Estimation of Predicted Environmental Concentration Values in soil (PEC_{soil}). The Tier 1 actual and time-weighted average PEC_{soil} values for bensulfuron methyl and metabolites from the Med-Rice clay and sand scenarios are given in Table B.8.88 and Table B.8.89. Table B.8.90 contains a summary of the maximum daily PEC_{soil} values for bensulfuron methyl from each RICEWQ simulation year.

Table B.8.88: Clay scenario Tier 1 PEC_{soil} values ($\mu\text{g/kg}$ dry weight) for bensulfuron methyl and degradates determined using the methods given in Med-Rice (2003). Water depth: 10 cm

Compound	Actual or TWA PEC ($\mu\text{g/kg}$)	Days after application										
		0	1	2	4	7	14	21	28	42	50	100
bensulfuron methyl	Actual	64.7	64.0	63.3	61.8	59.6	54.9	50.6	46.6	39.5	36.0	20.0
	TWA	--	64.4	64.0	63.2	62.2	59.7	57.4	55.2	51.1	49.0	38.1
IN-F7880	Actual	5.51	5.46	5.42	5.32	5.18	4.88	4.58	4.31	3.81	3.56	2.29
	TWA	--	5.49	5.46	5.42	5.35	5.19	5.03	4.89	4.61	4.46	3.67
IN-R9419	Actual	16.1	14.6	13.2	10.8	7.99	3.96	1.96	0.970	0.238	0.106	0.0007
	TWA	--	15.4	14.6	13.3	11.6	8.67	6.73	5.40	3.77	3.19	1.61
IN-D1R84	Actual	0.826	0.772	0.721	0.630	0.514	0.319	0.198	0.123	0.0476	0.0276	0.0009
	TWA	--	0.799	0.773	0.724	0.658	0.533	0.440	0.370	0.273	0.235	0.122
IN-J0290	Actual	11.9	11.6	11.2	10.5	9.48	7.54	5.99	4.76	3.00	2.31	0.447
	TWA	--	11.7	11.6	11.2	10.7	9.57	8.62	7.80	6.47	5.86	3.50
IN-N5297	Actual	4.62	4.52	4.42	4.22	3.95	3.37	2.88	2.46	1.80	1.50	0.487
	TWA	--	4.57	4.52	4.42	4.28	3.96	3.68	3.43	2.99	2.77	1.84
IN-T5831	Actual	0.572	0.554	0.536	0.502	0.454	0.361	0.287	0.228	0.144	0.111	0.0214
	TWA	--	0.563	0.554	0.536	0.511	0.458	0.413	0.374	0.310	0.281	0.168
IN-DAT97	Actual	0.670	0.658	0.646	0.623	0.590	0.518	0.456	0.401	0.310	0.268	0.107
	TWA	--	0.664	0.658	0.646	0.629	0.591	0.556	0.524	0.467	0.439	0.307

For presentation purposes, PEC values were rounded to three significant figures or to a maximum of four decimal places.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.89: Sand scenario Tier 1 PEC_{soil} values (µg/kg dry weight) for bensulfuron methyl and degradates determined using the methods given in Med-Rice (2003). Water depth: 10 cm

Compound	Actual or TWA (µg/kg)	Days after application										
		0	1	2	4	7	14	21	28	42	50	100
bensulfuron methyl	Actual	54.4	53.7	53.1	51.9	50.1	46.2	42.5	39.2	33.2	30.2	16.8
	TWA	--	54.1	53.8	53.2	52.2	50.2	48.2	46.4	42.9	41.1	32.0
IN-F7880	Actual	4.36	4.32	4.28	4.21	4.10	3.86	3.63	3.41	3.02	2.81	1.81
	TWA	--	4.34	4.32	4.28	4.23	4.10	3.98	3.86	3.65	3.53	2.90
IN-R9419	Actual	12.9	11.7	10.6	8.66	6.41	3.17	1.57	0.777	0.190	0.0852	0.0006
	TWA	--	12.3	11.7	10.6	9.30	6.95	5.39	4.32	3.02	2.56	1.29
IN-D1R84	Actual	0.437	0.408	0.381	0.333	0.271	0.169	0.105	0.0651	0.0252	0.0146	0.0005
	TWA	--	0.422	0.408	0.382	0.348	0.282	0.233	0.195	0.144	0.124	0.0642
IN-J0290	Actual	10.5	10.1	9.81	9.19	8.32	6.61	5.26	4.18	2.64	2.03	0.392
	TWA	--	10.3	10.1	9.82	9.36	8.40	7.57	6.85	5.68	5.14	3.07
IN-N5297	Actual	2.76	2.70	2.64	2.52	2.36	2.02	1.72	1.47	1.07	0.897	0.291
	TWA	--	2.73	2.70	2.64	2.56	2.37	2.20	2.05	1.79	1.66	1.10
IN-T5831	Actual	0.302	0.293	0.283	0.265	0.240	0.191	0.152	0.121	0.0761	0.0585	0.0113
	TWA	--	0.298	0.293	0.283	0.270	0.242	0.218	0.198	0.164	0.148	0.0886
IN-DAT97	Actual	0.354	0.348	0.342	0.329	0.312	0.274	0.241	0.212	0.164	0.142	0.0566
	TWA	--	0.351	0.348	0.342	0.335	0.312	0.294	0.277	0.247	0.232	0.162

For presentation purposes, PEC values were rounded to three significant figures or to a maximum of four decimal places.

Table B.8.90: Higher tier maximum daily PEC_{soil} values (µg/kg dry weight) for bensulfuron methyl from RICEWQ

Summary for individual meteorological scenarios							
Meteorological scenario	Number of simulation years	maximum daily PEC _{sed} (µg/kg dry weight) ^a					
		Minimum	25 th %	Average	Median	75 th %	Maximum
France	200	10.1	13.0	15.0	14.2	16.8	22.6
Greece	200	10.7	12.8	13.8	13.0	14.0	20.9
Italy	200	7.89	13.2	15.3	15.1	16.8	25.7
Portugal	200	6.84	12.8	15.0	14.9	17.1	22.5
Spain	200	10.1	11.9	13.7	12.6	15.0	25.7
Overall summary – data from all meteorological scenarios combined							
Meteorological scenario	Number of simulation years	maximum daily PEC _{sed} (µg/kg dry weight)					
		Minimum	25 th %	Average	Median	75 th %	Maximum
France, Greece, Italy, Portugal, and Spain data combined	1000	6.84	12.6	14.5	13.8	16.3	25.7

^a The maximum daily PEC_{sed} value in each simulation year was selected. All simulations were 20 years. Since one treated paddy was evaluated from each of 10 management blocks, the total number of simulation years of PEC data was 20 × 10 = 200 for each meteorological scenario and 200 × 5 = 1000 in aggregate.

As the supported GAP indicate also the application on saturated land (1 cm water), RMS believe that this situation can be a worst case scenario for PEC_{soil}. Therefore, RMS recalculated PEC_{soil} using the methods given in MED-RICE (2003), considering the same input data as reported in Table B.8.86, and considering a water level in field of 1 cm. Results for bensulfuron methyl and major metabolites are reported in Table B.8.91

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.91: TIER 1: PEC_{soil} values determined using the methods given in MED-RICE (2003). Water depth: 1 cm

Compound	Clay scenrio	Sand scenrio
	PEC_{soil} $\mu\text{g/kg}$	PEC_{soil} $\mu\text{g/kg}$
Bensulfuron methyl	78.2	76.0
IN-F7880	7.23	6.99
IN-R9419	20.8	20.1
IN-D1R84	4.18	2.88
IN-J0290	13.6	13.4
IN-N5297	11.7	10.0
IN-T5831	2.90	2.00
IN-DAT97	3.39	2.34

Conclusions:

The Tier 1 predicted environmental concentrations of bensulfuron methyl and metabolites IN-J0290, IN-DAT97, IN-F7880, IN-R9419, IN-N5297, IN-D1R84, and IN-T5831 were determined for soil (PEC_{soil}) using the equations and guidance provided by the Med-Rice working group (Med-Rice, 2003). Higher tier paddy simulations using RICEWQ version 1.64 were also conducted for bensulfuron methyl. Highest value for bensulfuron in soil is 78.8 $\mu\text{g/kg}$ in clay scenario, tier 1, as recalculated by RMS considering a water level of 1 cm.

B.8.4 Fate and behaviour in water (Annex IIA 7.2.1; Annex IIIA 9.2)

B.8.4.1 Hydrolysis rate of active substance, relevant metabolites, degradation and reaction products (Annex IIA 7.2.1.1)

25) *Bensulfuron methyl: Hydrolysis in buffer solutions of pH 4, 7, and 9. Hatzenbeler, C.L., 2002.*

Cross reference IIA 7.2.1.1./01

Guidelines:

USEPA 161-1 (1982); Directive 91/414/EEC; SETAC – Europe Procedures for Assessing Environmental Fate and Ecotoxicity of Pesticides, Part 1.1; OECD Section 1, Method 111

GLP:

Yes

The study is acceptable

Material and Methods:

Two radiolabeled forms of bensulfuron methyl were used: [Phenyl(U)- ^{14}C]-[HOTC 320; radiochemical purity $\geq 95\%$] and [Pyrimidine-2- ^{14}C] (HOTC 319; radiochemical purity $\geq 95\%$). The rate and route of hydrolysis of bensulfuron methyl (methyl 2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]methyl]benzoate), was determined in darkness in sterile pH 4, 7, and 9 buffered aqueous solutions. Buffered solutions were treated with bensulfuron methyl at a nominal concentration of 1.0 $\mu\text{g/mL}$ and were incubated for 30 days at $25 \pm 1^\circ\text{C}$ in the dark. At selected intervals, aqueous test solutions were analysed by high-performance liquid chromatography with radiochemical flow detection (HPLC-RAD) to determine the distribution of radioactivity.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Findings:

The material balance of radioactivity throughout the study for each buffer system was within the range of 95.8-106.8% of the applied radioactivity or AR (Table B.8.92 to Table B.8.94). No traps for volatiles were employed.

Degradation products: The hydrolysis products of bensulfuron methyl appear to be similar at pH 4 and pH 7. The main degradation products were pyrimidine amine (IN-J0290) and sulfonamide (IN-N5297) formed through the hydrolytic cleavage of the sulfonylurea bridge. IN-R9419 was the major degradation product at pH 9, generated by de-esterification. Pyrimidine amine (IN-J0290) in the [pyrimidine-2-¹⁴C] bensulfuron methyl and homosaccharin (IN-B6895) in the [phenyl-¹⁴C]bensulfuron methyl were also observed in pH 9 buffer test solution.

Degradation of major breakdown product(s): The only major degradate found in the pH 4 samples treated with [pyrimidinyl-2-¹⁴C] bensulfuron methyl was pyrimidine amine (IN-J0290) which ranged from 2.7% AR at Day 0 to 98.3% AR at Day 30. The only major degradate found in the samples treated with [phenyl(U)-¹⁴C]bensulfuron methyl was IN-N5297, which ranged from 2.0% AR at Day 0 to 98.6% AR at Day 30 (Table B.8.92).

Minor hydrolytic products pyrimidine amine (IN-J0290, <0.6% AR at Day 30) and pyrimidine urea (IN-T5831, <2% AR at Day 30) were found in pH 7 buffered samples treated with [pyrimidinyl-2-¹⁴C] bensulfuron methyl. Minor hydrolytic products sulfonamide (IN-N6297, <4% AR at Day 30) and homosaccharin (IN-B6895, <1% AR at Day 30) were found in the samples treated with [phenyl(U)-¹⁴C]bensulfuron methyl (Table B.8.93).

The only major metabolite found in the pH 9 buffered samples treated with [pyrimidinyl-2-¹⁴C] bensulfuron methyl or [phenyl(U)-¹⁴C]bensulfuron methyl was IN-R9419, which ranged from <0.1% AR at Day 0 to approximately 15% AR at Day 30. Minor hydrolytic products which each accounted for less than 2.5% AR were pyrimidine amine (IN-J0290) in the [pyrimidinyl-2-¹⁴C] test samples and IN-B6895 in the [phenyl(U)-¹⁴C]label test samples (Table B.8.94).

Table B.8.92: Distribution and mass balance of radioactivity in pH 4 buffer samples treated with bensulfuron methyl (DPX-F5384)

Sampling Day	Pyrimidinyl-2- ¹⁴ C			
	DPX-F5384 %AR (µg/mL)	IN-J0290 %AR (µg/mL)	Others %AR (µg/mL)	Total ^a %AR (µg/mL)
0	95.7 (0.94)	2.7 (0.03)	1.6 (0.02)	100.0 (0.98)
2	74.9 (0.73)	22.7 (0.22)	2.4 (0.02)	100.0 (0.98)
4	57.0 (0.56)	38.8 (0.38)	ND (ND)	95.8 (0.87)
6	49.5 (0.49)	52.5 (0.51)	ND (ND)	102.0 (1.00)
10	30.3 (0.30)	71.8 (0.70)	ND (ND)	102.1 (1.00)
21	10.3 (0.10)	91.8 (0.90)	ND (ND)	102.1 (1.00)
30	2.7 (0.03)	98.3 (0.96)	ND (ND)	101.0 (0.99)
	Phenyl(U)- ¹⁴ C			
	DPX-F5384 %AR (µg/mL)	IN-N5297 %AR (µg/mL)	Others %AR (µg/mL)	Total ^a %AR (µg/mL)
0	97.6 (1.01)	2.0 (0.02)	0.4 (<0.01)	100.0 (1.03)
2	76.6 (0.79)	22.2 (0.23)	1.2 (0.01)	100.0 (1.03)
4	59.0 (0.61)	40.4 (0.42)	ND (ND)	99.4 (0.95)
6	48.7 (0.50)	52.3 (0.54)	ND (ND)	101.0 (1.04)
10	29.4 (0.30)	72.5 (0.75)	ND (ND)	101.9 (1.05)
21	8.2 (0.08)	94.7 (0.98)	ND (ND)	102.9 (1.06)
30	3.3 (0.03)	98.6 (1.02)	ND (ND)	101.9 (1.05)

^a Recovery of administered radioactivity as determined by LSC analyses (based on Day-0 analyses).

%AR = Percent of applied radioactivity

ND = Not detected

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.93: Distribution and mass balance of radioactivity in pH 7 buffer samples treated with bensulfuron methyl (DPX-F5384)

Sampling Day	Pyrimidinyl-2- ¹⁴ C				
	DPX-F5384 %AR (µg/mL)	IN-T5831 %AR (µg/mL)	IN-J0290 %AR (µg/mL)	Others %AR (µg/mL)	Total ^a %AR (µg/mL)
0	96.1 (0.99)	ND (ND)	0.9 (0.01)	3.0 (0.03)	100.0 (1.03)
7	103.8 (1.07)	ND (ND)	2.5 (0.03)	0.5 (0.01)	106.8 (1.10)
14	92.1 (0.95)	1.5 (0.02)	2.7 (0.03)	1.8 (0.02)	98.1 (1.01)
21	94.2 (0.97)	0.9 (0.01)	4.1 (0.04)	0.8 (0.01)	100.0 (1.03)
30	90.8 (0.94)	0.8 (0.01)	5.3 (0.05)	2.1 (0.02)	99.0 (1.02)
	Phenyl(U)- ¹⁴ C				
	DPX-F5384 %AR (µg/mL)	IN-N5297 %AR (µg/mL)	IN-B6895 %AR (µg/mL)	Others %AR (µg/mL)	Total ^a %AR (µg/mL)
0	97.3 (1.07)	1.2 (0.01)	ND (ND)	1.5 (0.02)	100.0 (1.10)
2	98.0 (1.08)	1.1 (0.01)	ND (ND)	ND (ND)	99.1 (1.09)
4	94.5 (1.04)	2.9 (0.03)	ND (ND)	1.7 (0.02)	99.1 (1.09)
21	94.4 (1.04)	3.6 (0.04)	0.7 (0.01)	1.3 (0.01)	100.0 (1.10)
30	95.5 (1.05)	3.7 (0.04)	0.8 (0.01)	ND (ND)	100.0 (1.10)

^a Recovery of administered radioactivity as determined by LSC analyses (based on Day-0 analyses).

%AR = Percent of applied radioactivity

ND = Not detected

Table B.8.94: Distribution and mass balance of radioactivity in pH 9 buffer samples treated with bensulfuron methyl (DPX-F5384)

Sampling Day	Pyrimidinyl-2- ¹⁴ C				
	DPX-F5384 %AR (µg/mL)	IN-R9419 %AR (µg/mL)	IN-J0290 %AR (µg/mL)	Others %AR (µg/mL)	Total ^a %AR (µg/mL)
0	96.0 (0.95)	0.5 (<0.01)	1.4 (0.01)	2.1 (0.02)	100.0 (0.99)
7	92.9 (0.92)	4.6 (0.05)	2.1 (0.02)	1.3 (0.01)	100.9 (1.00)
14	89.9 (0.89)	6.7 (0.07)	1.4 (0.01)	2.0 (0.02)	100.0 (0.99)
21	86.2 (0.85)	11.0 (0.11)	1.9 (0.02)	1.9 (0.02)	101.0 (1.00)
30	82.9 (0.82)	15.0 (0.15)	1.6 (0.02)	2.4 (0.02)	101.9 (1.01)
	Phenyl(U)- ¹⁴ C				
	DPX-F5384 %AR (µg/mL)	IN-R9419 %AR (µg/mL)	IN-B6895 %AR (µg/mL)	Others %AR (µg/mL)	Total ^a %AR (µg/mL)
0	97.1 (1.09)	ND (ND)	0.7 (0.02)	2.5 (0.02)	100.3 (1.12)
2	96.2 (1.08)	3.0 (0.03)	1.7 (0.02)	ND (ND)	100.9 (1.13)
4	90.7 (1.02)	7.0 (0.08)	2.3 (0.03)	ND (ND)	100.0 (1.12)
21	89.3 (1.00)	10.1 (0.11)	1.5 (0.02)	ND (ND)	100.9 (1.13)
30	84.3 (0.94)	14.6 (0.16)	1.0 (0.01)	ND (ND)	99.9 (1.13)

^a Recovery of administered radioactivity as determined by LSC analyses (based on Day-0 analyses).

%AR = Percent of applied radioactivity

ND = Not detected

DT₅₀ values for Bensulfuron methyl: Bensulfuron methyl degraded rapidly at pH 4 and slowly at pH 9. Bensulfuron was hydrolytically stable at pH 7. The half-lives of bensulfuron methyl at pH 4 and 9 were 6.1 days and 141 days, respectively (Table B.8.95). This suggests that hydrolysis is a major degradative mechanism in acidic environments.

Degradation pathway: The main degradation pathway was the hydrolytic cleavage of sulfonylurea bridge to form IN-J0290 and IN-N5297. At pH 9, bensulfuron methyl slowly hydrolyses to IN-J0290 and IN-N5297, which cyclises to IN-B6895 (homosaccharin).

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.95: Half-lives and rate constants for bensulfuron methyl (DPX-F5384)

pH	Half-life ($t_{1/2}$)	Rate Constant (days^{-1})	Method of Calculation	r^2
4	6.1	0.1143	First-order	0.9967
7	Stable over 30-day test period			
9	141	0.0049	First-order	0.9395

Conclusion:

Bensulfuron methyl degraded rapidly at pH 4, and was hydrolytically stable at pH 7. Bensulfuron methyl degraded slowly at pH 9. The half-lives of bensulfuron methyl at pH 4 and 9 were 6 days and 141 days, respectively.

The major hydrolysis products were pyrimidine amine (IN-J0920) and sulfonamide (IN-N5297) at pH 4 and pH 7, and IN-R9419 at pH 9. Bensulfuron methyl slowly hydrolyses to pyrimidine amine (IN-J0290) and sulfonamide (IN-N5297), which cyclises to homosaccharin (IN-B6895) in the pH 9 buffer solution. Pyrimidine urea (IN-T5831) was detected in a trace quantity in only the pH 7 buffer solutions. Based on the results of this study, hydrolysis will be a major dissipation route of bensulfuron methyl in acidic environments.

26) *Alcoholysis and chemical hydrolysis of bensulfuron methyl*. Sabadie, J., 1996.

Cross reference IIA 7.2.1.1./02

Guidelines:

Not applicable – publication

GLP:

Not specified

The study is acceptable as additional information

Material and Methods:

DPX-F5384 Technical was used (purity: not specified). The alcoholysis and hydrolysis of the herbicide bensulfuron methyl was studied in unsterilised aqueous solutions buffered at pH values 5 to 11. Solutions containing bensulfuron methyl technical were prepared at nominal concentrations of 50 mg/L for pH 7 to 11. Nominal concentrations of 5 and 20 mg/L were prepared for pH 5 and 6 samples, respectively. Hydrolysis experiments were conducted at 30 and 50°C and extracted by stirring for 30 minutes with a chloroform and acetic acid mixture (3 + 0.1 mL). Alcoholysis samples were evaporated to dryness under vacuum and stirred for 30 minutes with a water/chloroform/acetic acid mixture (2 + 3 + 0.1 mL). Chloroform solution analysis was performed with normal phase high performance liquid chromatography and UV detection.

Findings:

Hydrolysis and alcoholysis rates of bensulfuron methyl: The alcoholysis and hydrolysis rates of bensulfuron methyl followed first-order kinetics. Alcoholysis rate constants of bensulfuron methyl ranged from 0.11 to 0.15 day⁻¹ at 30°C. The rate of hydrolysis reached a minimum at pH 8 and increased under alkaline conditions. Increasing the temperature to 50°C increased the degradation rates.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

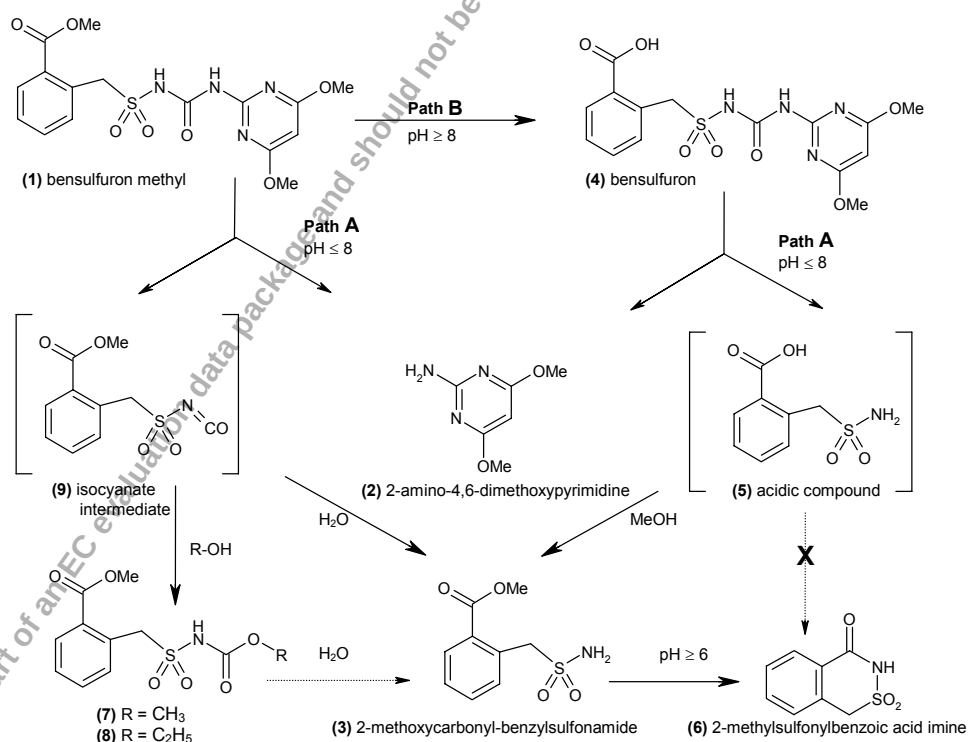
Degradation products: Bensulfuron methyl undergoes alcoholysis (in methyl or ethyl alcohol) and hydrolysis at 30 or 50°C (see Figure B.8.2). The major degradation products were IN-J0290 (pyrimidine amine), carbamate, and benzylsulfonamide (IN-N5297). IN-N5297 was easily cyclised at pH >6 to form IN-B6895.

Chemical hydrolysis pathway: Depending on the pH value, the chemical hydrolysis pathway of bensulfuron methyl involves two different highly pH-dependent degradation pathways. Path A implicates hydrolysis of the sulfonylurea bridge of the herbicide molecule to form stable IN-J0290 (pyrimidinamine) and IN-N5297 (benzylsulfonamide) that becomes cyclised if the conditions are $\geq$ pH 6. Path B involves hydrolysis of the carbomethoxy substituent of the aromatic ring (see Figure B.8.2). In neutral or acidic solutions (pH <8) hydrolysis of bensulfuron methyl *via* path A was the only mechanism detected. Conversely the proportion of path B was always greater in an alkaline solution and increased with pH. At pH 8, path A and B are equivalent and activity was at a minimum.

Conclusion:

The pH governs the hydrolysis pathway of bensulfuron methyl. Only the cleavage of the urea function of the molecule was observed in neutral or aqueous acid solutions. The reaction products are IN-J0290 (pyrimidinamine) that is stable, and IN-N5297, which is easily cyclised to form IN-B6895 (homosaccharin) at pH $\geq$ 6.

Figure B.8.2: Proposed pathway of alcoholysis and chemical hydrolysis of bensulfuron methyl



Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

B.8.4.2 Direct phototransformation of active substance, relevant metabolites, degradation and reactions products in water (Annex IIA 7.2.1.2)

27) *Photodegradation of [phenyl (U)-¹⁴C]DPX-F5384 and [pyrimidine-2-¹⁴C]DPX-F5384 in water (conducted in sunlight). Horne, P., 1987.*

Cross reference IIA 7.2.1.2./01

Guidelines:

USEPA 161-2

GLP:

No

The study is acceptable

Material and Methods:

Two radiolabeled forms of bensulfuron methyl were used: (1) [Phenyl(U)-¹⁴C] (radiochemical purity ≥95%) and (2) [Pyrimidine-2-¹⁴C] (radiochemical purity ≥95%). The photolytic stability of bensulfuron methyl was studied in aqueous solutions (10mM acetate, phosphate and boate buffes) at pH values of 5, 7, and 9 for the [phenyl(U)-¹⁴C] label and pH 9 for the [pyrimidine-2-¹⁴C] label. Solutions containing ¹⁴C-DPX-F5384 were prepared at nominal concentrations of 10 mg/L and were exposed to continuous direct sunlight (global radiation 285-2800 nm) for up to 30 days (midday summer sunlight at a latitude of 39°40'N and longitude 75°36'W, Wilmington, Delaware, USA), under sterile conditions, at 25±1°C by circulating water from a thermostatically controlled water bath. Dark controls were also prepared and maintained at 25±1°C. No volatiler adiolabeled degradation products were expected in this study, therefore caustic traps were not included in the experimental set-up. Approximately 5-mL aliquots of each irradiated and nonirradiated solution were removed for analysis on Days 0, 3, 7, 14, 21, and 30, for all solutions except the pH 5 ones. Those were sampled on Days 0, 1, 3, 6, 14, 21, and 30.

Reversed phase HPLC with radiochemical and UV detection and thin-layer chromatography analysis using a linear analyser and fluorescence quenching was used to analyse radiolabeled and non-radiolabeled samples.

Findings:

Recovery generally ranged from 93.7 to 108.9% as reported in Table B.8.96.

Identification of degradation products was not conducted as none reached 10% of the applied material after 30 days exposure. [Phenyl (U)-¹⁴C]DPX-F5384 and [pyrimidine-2-¹⁴C]DPX-F5384 were relatively stable throughout the study with 86.4 and 90% remaining intact after 30 days exposure in pH 9 buffer solution, respectively. In the non-irradiated control, approximately 90% of the test substance remained after the same period in both phenyl and pyrimidine samples (Table B.8.97). Two minor degradation products were observed in both the irradiated and non-irradiated samples indicating that these relatively polar degradates were a result of hydrolysis rather than photolysis. Under non-irradiated conditions both [phenyl (U)-¹⁴C] and [pyrimidine-2-¹⁴C] samples showed insignificant hydrolytic degradation at pH 9, the most hydrolytically stable pH. The degradation rate of the non-irradiated [phenyl (U)-¹⁴C] samples at pH 7 was similar to that at pH 9. At pH 5, degradation occurs rapidly in the dark and the primary product was IN-N5297 (sulfonamide).

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.96: Material balance of ^{14}C -DPX-F5384 (bensulfuron methyl) in sterile buffers

Phenyl(U)- ^{14}C	Irradiated % Applied Radioactivity			Non-irradiated % Applied Radioactivity		
	pH 5	pH 7	pH 9	pH 5	pH 7	pH 9
Sampling Interval						
0	100.0	100.0	100.0	100.0	100.0	100.0
1	103.7	-	-	103.5	-	-
3	93.7	99.7	99.8	96.0	97.2	98.3
6	106.3	-	-	106.5	-	-
7	-	97.4	100.3	-	97.9	97.6
14	105.9	101.4	105.9	104.2	99.9	98.5
21	108.9	104.3	101.5	107.4	100.4	100.3
30	108.5	99.8	100.7	107.7	98.5	100.7
Pyrimidine-2- ^{14}C	Irradiated % Applied Radioactivity			Non-irradiated % Applied Radioactivity		
	pH 9			pH 9		
Sampling Interval						
0	100.0			100.0		
1	-			-		
3	96.2			94.3		
6	-			-		
7	101.1			96.5		
14	101.4			95.7		
21	102.8			97.5		
30	99.5			95.5		

Table B.8.97: Photochemical degradation of ^{14}C -DPX-F5384 (bensulfuron methyl) in sterile buffers

Sampling Time (days)	% of Applied Radioactivity			
	DPX-F5384	Compound 1	Compound 2	Other
Phenyl(U)- ^{14}C : Irradiated – pH 9				
0	94.0	0.6	3.5	1.9
3	92.8	0.8	1.8	4.6
7	98.7	1.6	3.8	1.9
14	91.3	2.6	4.2	1.9
21	86.4	4.6	6.5	2.5
30	86.4	3.6	5.7	4.3
Phenyl(U)- ^{14}C : Non-irradiated – pH 9				
0	94.0	0.6	3.5	1.9
3	92.3	1.7	3.8	2.2
7	92.2	1.3	4.2	2.3
14	92.6	2.3	2.5	2.6
21	88.4	4.3	3.9	3.4
30	90.6	4.1	3.3	2.0
Pyrimidine-2- ^{14}C : Irradiated – pH 9				
0	95.6	0.2	0.5	3.7
3	93.7	0.6	1.3	4.4
7	93.2	0.5	1.5	4.8
14	92.7	1.4	1.5	4.4
21	87.6	3.1	2.7	6.6
30	89.6	3.5	2.7	4.2
Pyrimidine-2- ^{14}C : Non-irradiated – pH 9				
0	95.5	0.2	0.5	3.8
3	93.6	0.6	1.6	4.2
7	92.8	0.6	2.1	4.5
14	93.3	2.3	2.5	1.9
21	89.8	3.2	1.2	5.8
30	89.7	3.4	1.4	5.5

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

DT₅₀ values for bensulfuron methyl: The calculated half lives for the [phenyl (U)-¹⁴C] label were 13, 251, and 223 days for the pH 5, 7, and 9 buffered samples, respectively, and >1000, 505, and 405 days for the hydrolytically corrected samples (dark control) at pH 5, 7, and 9, respectively. The calculated half-life for the [pyrimidine-2-¹⁴C] label was 286 days for the pH 9 buffered samples and >1000 days for the hydrolytically corrected samples (dark control). All values are reported in Table B.8.98.

Table B.8.98: DT₅₀ values and rate constants for ¹⁴C-DPX-F5384 (bensulfuron methyl)

Radiolabel	pH	Half-life (days)	Corrected ^a half-life (days)	k (days)	Method of Calculation
Phenyl(U)- ¹⁴ C	5	13	>1000	-0.053958	Linear first-order
	7	251	505	-0.002765	
	9	223	405	-0.003104	
Pyrimidine-2- ¹⁴ C	9	286	>1000	-0.002421	Linear first-order

^a Corrected half-life = photolysis - hydrolysis

Conclusion:

The degradation of bensulfuron methyl in aqueous solution exposed to natural sunlight is dependent on the pH of the solution with half-lives ranging from 13 days at pH 5 to greater than 200 days at pH 9. However, when observed degradation rates are corrected for the hydrolysis component, the photolysis component is insignificant (half life greater than 400 days) and independent of pH in the range of 5-9. These results are consistent with the UV absorption spectrum of bensulfuron methyl that showed little or no absorption in the region above 290 nm. Sunlight reaching the earth's surface only contains significant radiation above 290 nm, therefore little or no direct photolysis of bensulfuron methyl is expected. At pH 9, the most hydrolytically stable pH, bensulfuron methyl degraded slowly and none of the degradation products were greater than 10% of the applied radioactivity. At pH 5, degradation occurs primarily by hydrolysis and the primary product obtained from [phenyl(U)-¹⁴C]DPX-F5384 was IN-N5297 (sulfonamide).

28) Photodegradation of [¹⁴C] bensulfuron methyl in natural water by simulated sunlight. Lentz, N.R., 2003.

Cross reference IIA 7.2.1.2./02

Guidelines:

Japan JMAFF (Japanese guideline 12 Nohsan No. 8147)

GLP:

Yes

The study is acceptable

Material and Methods:

Two radiolabeled forms of bensulfuron methyl, DPX-F5384, were used: labeled with carbon-14 in the pyrimidinyl ring (DuPont Isotope Inventory Number 319; radiochemical purity >95%) and labeled with carbon-14 in the phenyl ring (DuPont Isotope Inventory Number 320; radiochemical purity >95%).

The photolytic stability of bensulfuron methyl was studied in two natural waters and sterile pH 7 aqueous buffer solution. Physicochemical characteristics of the natural waters are reported in Table B.8.99.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.99 Physicochemical Characteristics of the Natural Waters

Analysis	Results	
	Ten-Mile Creek Water	Cavrini Farm Pond Water
pH	8.1	7.5
Sodium (ppm)	227	31
Calcium (ppm)	136	28
Magnesium (ppm)	45	15
Hardness (mg eq CaCO ₃ /L)	528	132
Conductivity (mmhos/cm)	1.87	0.45
Sodium Absorption Rate (SAR)	4.31	1.16
Total Dissolved Solids (ppm)	1168	256
Total Suspended Solids (ppm)	6	14
Total Phosphorus (ppm)	0.3	0.6
Phosphate Phosphorus (ppm)	0.3	0.5
Turbidity (NTU)	0.88	7.55
Sulfate Sulfur (ppm)	147	57
Nitrate-Nitrogen (ppm)	0.2	Na
Total Nitrogen (ppm)	28	23.3
Chloride (ppm)	420	27
Total Organic Carbon (ppm)	11.0	10.1
Alkalinity (mg CaCO ₃ /L)	185	91

Na=not analysed

Solutions containing bensulfuron methyl were prepared at nominal concentrations of 1 mg/L and were continuously irradiated for 15 days using a xenon arc simulated sunlight source (intensity equal to midday summer sunlight at a latitude of 52°N; equivalent to 28 days of sunlight) at 25°C under sterile conditions. Dark controls were also prepared and maintained at 25°C. No volatile traps were used for the irradiated test samples and non-irradiated test control samples. A subsample (3 mL) for each radiolabel for the Ten-Mile Creek natural water and sterile pH 7 buffer were taken immediately after the test solutions was placed in the reaction vessels and at 2, 4, 7, 10, 12 and 15 days for the irradiated and control samples. A subsample (3 mL) for each radiolabel for the Cavrini Farm pond natural water was taken immediately after the test solutions was placed in the reaction vessels and at 0.33, 1, 2, 3, 7, 10 and 15 days for the irradiated and control samples. Sterility was determined on Day-0 samples and from the final sample of each of the irradiated and dark control natural water and sterile pH 7 buffer test systems.

At each sampling interval 3-mL of the test solutions were subsampled from the irradiated and dark control samples. Triplicate 250-μL aliquots of the test solutions for the irradiated and dark control samples were assayed by LSC at each sampling interval to determine the total radioactivity. An aliquot (250 μL, approximately 30,000 dpm) from each sample was then analyzed by HPLC. Tentative identification of metabolites was made by co-injection of authentic reference standards with the photolysis samples. The degradation rate of parent material expressed as percent of radioactivity in the buffer solution as bensulfuron methyl was estimated from fitting the data according to first-order equation

Findings:

Material balance: Recovery ranged from 95.0 to 105.8% (Table B.8.101 to Table B.8.103)

Quantum yield for bensulfuron methyl: The calculated quantum yield for bensulfuron methyl was 0.00003.

Degradation products: Photolytic degradation products that were detected in both water systems including IN-J0290, IN-D1R84, IN-B6895, IN-N5297, IN-T5831, IN-F7880, IN-R9419, and IN-YY142. The major degradation product that was detected at >10% was IN-T5831. IN-YY142 (phenyl glyoxylic acid) was also detected at 7.2% applied

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

radioactivity in the natural water and 14.7% of applied radioactivity in sterile pH 7 buffer. The amount of bensulfuron methyl in the irradiated samples (Ten-Mile Creek natural water) decreased slowly from 95.7% AR on Day 0 to 85.6% AR by Day 15 for the samples treated with [phenyl(U)-¹⁴C]bensulfuron methyl and from 93.4% AR on Day 0 to 85.1 % AR by Day 15 for the samples treated with [pyrimidinyl-2-¹⁴C]bensulfuron methyl (Table B.8.101). The amount of bensulfuron methyl in the irradiated samples (sterile buffer) decreased slowly from 97.5% AR on Day 0 to 63.6% AR at Day 15 for the samples treated with [phenyl(U)-¹⁴C]bensulfuron methyl and from 97.4% AR on Day 0 to 72.1 % AR at Day 15 for the samples treated with [pyrimidinyl-2-¹⁴C]bensulfuron methyl. Degradate IN-YY142 was observed in the Day 15 sample at a maximum of 14.7% in the samples treated with [phenyl(U)-¹⁴C]bensulfuron methyl. A 13-min peak was observed in the Day 15 sample at approximately 4% AR in the samples treated with [pyrimidinyl-2-¹⁴C]bensulfuron methyl. Analysis by (-)ESI LC/MS identified the 13-min peak as having a m/z 278, however the structure of the 13-min peak was not determined (Table B.8.102).

The amount of bensulfuron methyl in the dark control sterile pH 7 buffer samples was 97.0% AR on Day 0 and 95.4% AR at Day 15 for the sample treated with [phenyl(U)-¹⁴C]bensulfuron methyl and 95.5% AR on Day 0 and 95.3% AR at Day 15 for the sample treated with [pyrimidinyl-2-¹⁴C]bensulfuron methyl (Table B.8.103).

The amount of bensulfuron methyl in the irradiated samples (in Cavrini Farm Pond Natural Water) decreased quickly from 99.2% AR on Day 0 to 46.6% AR by Day 15 for the samples treated with [phenyl(U)-¹⁴C]bensulfuron methyl and from 96.5% AR on Day 0 to 23.6% AR by Day 15 for the samples treated with [pyrimidinyl-2-¹⁴C]bensulfuron methyl (Table 3 and Table 4). Degradate IN-YY142 was observed in the Day 15 sample at a maximum of 7.2% in the samples treated with [phenyl(U)-¹⁴C]bensulfuron methyl. A 14-min peak was observed in the Day 15 sample at a maximum of 11.0 and 4.1 % AR in the samples treated with [phenyl(U)-¹⁴C] and [pyrimidinyl-2-¹⁴C]bensulfuron methyl, respectively. A 15-min peak was observed in the Day 15 samples at a maximum of 6.5 and 10.5% AR in the samples treated with [phenyl(U)-¹⁴C] and [pyrimidinyl-2-¹⁴C]bensulfuron methyl, respectively (Table B.8.100).

Table B.8.100: Distribution and mass balance of radioactivity in irradiated Cavrini Farm Pond natural water samples. Phenyl(U)-¹⁴C and [pyrimidinyl-2-¹⁴C]bensulfuron methyl (DPX-F5384)

<i>[phenyl(U)-¹⁴C]bensulfuron methyl</i>		Days Post-Treatment							
		0	0.33	1	2	3	7	10	15
DPX-F5384	%AR	99.2	95.5	91.4	86.5	81.2	70.0	58.5	46.6
	µg/mL	0.96	0.93	0.89	0.84	0.79	0.68	0.57	0.45
Others ^b	%AR	4.9	9.7	12.7	17.6	21.9	34.1	44.6	54.4
Total % Recovery ^a in the Aqueous	%AR	104.1	105.2	104.1	104.1	103.1	104.1	103.1	101.0
<i>[pyrimidinyl-2-¹⁴C]</i>		0	0.33	1	2	3	7	10	15
DPX-F5384	%AR	96.5	97.1	81.7	80.3	68.4	46.2	38.3	23.6
	µg/mL	1.09	1.10	0.92	0.91	0.77	0.52	0.43	0.27
Others ^b	%AR	4.4	6.4	21.0	23.2	35.1	55.6	63.5	78.2
Total % Recovery ^a in the Aqueous	%AR	100.9	103.5	102.7	103.5	103.5	101.8	101.8	101.8

%AR = Percent of applied radioactivity (dosing solution = 0.97 µg/ML for [phenyl(U)-¹⁴C] and 1.13 µg/mL for [pyrimidinyl-2-¹⁴C])

^a Recovery of administered radioactivity as determined by LSC analyses of the dosing solution.

^b Others = all components not identified as bensulfuron methyl. Non-radiolabeled reference standards IN-J0290, IN-D1R84, IN-B6895, IN-N5297, IN-T5831, IN-F7880, and IN-R9419 were co-injected with all samples analysed by HPLC. A component at R_f=14-min was present at Day 15 at 11.0% and had a molecular weight of 314 as determined by (-)ESILC/MS. All other individual ¹⁴C components detected by HPLC were less than 10% of the applied radioactivity.

The amount of bensulfuron methyl in the irradiated samples (Ten-Mile Creek natural water) decreased slowly from 95.7% AR on Day 0 to 85.6% AR by Day 15 for the samples treated with [phenyl(U)-¹⁴C]bensulfuron methyl and

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

from 93.4% AR on Day 0 to 85.1 % AR by Day 15 for the samples treated with [pyrimidinyl-2-¹⁴C]bensulfuron methyl (Table B.8.101). The amount of bensulfuron methyl in the irradiated samples (sterile buffer) decreased slowly from 97.5% AR on Day 0 to 63.6% AR at Day 15 for the samples treated with [phenyl(U)-¹⁴C]bensulfuron methyl and from 97.4% AR on Day 0 to 72.1 % AR at Day 15 for the samples treated with [pyrimidinyl-2-¹⁴C]bensulfuron methyl. Degradate IN-YY142 was observed in the Day 15 sample at a maximum of 14.7% in the samples treated with [phenyl(U)-¹⁴C]bensulfuron methyl. A 13-min peak was observed in the Day 15 sample at approximately 4% AR in the samples treated with [pyrimidinyl-2-¹⁴C]bensulfuron methyl. Analysis by (-)ESI LC/MS identified the 13-min peak as having a m/z 278, however the structure of the 13-min peak was not determined (Table B.8.101).

Table B.8.101: Distribution and mass balance of radioactivity in irradiated Ten-Mile Creek natural water samples. Phenyl(U)-¹⁴C and [pyrimidinyl-2-¹⁴C]bensulfuron methyl (DPX-F5384)

<i>[phenyl(U)-¹⁴C] bensulfuron methyl</i>		Days Post Treatment						
		0	2	4	7	10	12	15
DPX-F5384	%AR	95.7	93.8	94.4	89.0	86.4	84.8	85.6
	µg/mL	0.96	0.94	0.96	0.90	0.87	0.86	0.91
Others ^b	%AR	3.3	5.2	6.6	11.0	13.6	16.2	19.4
Total % Recovery ^a in the Aqueous	%AR	99.0	99.1	101.0	100.0	100.0	101.0	105.0
<i>[pyrimidinyl-2-¹⁴C]</i>		0	2	4	7	10	12	15
DPX-F5384	%AR	93.4	93.9	89.5	88.7	86.2	86.7	85.1
	µg/mL	0.95	0.98	0.90	0.92	0.91	0.94	0.94
Others ^b	%AR	4.7	6.1	7.6	11.3	14.8	17.1	20.7
Total % Recovery ^a in the Aqueous	%AR	98.1	100.0	97.0	100.0	101.0	103.8	105.8

%AR Percent of applied radioactivity (dosing solution = 1.01 µg/mL for [phenyl(U)-¹⁴C] and 1.03 µg/mL for [pyrimidinyl-2-¹⁴C])

^a Recovery of administered radioactivity as determined by LSC analyses of the dosing solution.

^b Others = all components not identified as bensulfuron methyl. Non-radiolabeled reference standards IN-J0290, IN-D1R84, IN-B6895, IN-N5297, IN-T5831, IN-F7880 and IN-R9419 were co-injected with all samples analysed by HPLC. Individual ¹⁴C components detected by HPLC were less than 10% of the applied radioactivity.

Table B.8.102: Distribution and mass balance of radioactivity in irradiated sterile pH 7 buffer samples. Phenyl(U)-¹⁴C and [pyrimidinyl-2-¹⁴C]bensulfuron methyl (DPX-F5384)

<i>[phenyl(U)-¹⁴C]bensulfuron methyl</i>		Days Post Treatment						
		0	2	4	7	10	12	15
DPX-F5384	%AR	97.5	91.2	88.7	79.6	73.8	68.0	63.6
	µg/mL	0.98	0.91	0.90	0.80	0.73	0.65	0.63
Others ^b	%AR	2.5	7.8	11.3	19.4	24.2	27.0	34.4
Total % Recovery ^a in the Aqueous	%AR	100.0	99.0	100.0	99.0	98.0	95.0	98.0
<i>[pyrimidinyl-2-¹⁴C]</i>		0	2	4	7	10	12	15
DPX-F5384	%AR	97.4	94.8	92.1	83.9	81.5	82.5	72.1
	µg/mL	1.01	1.01	0.96	0.85	0.84	0.87	0.71
Others ^b	%AR	3.6	9.1	8.9	14.2	18.5	20.4	23.0
Total % Recovery ^a in the Aqueous	%AR	101.0	103.9	101.0	98.1	100.0	102.9	95.1

%AR = Percent of applied radioactivity (dosing solution = 0.97 µg/mL for [phenyl(U)-¹⁴C] and 1.13 µg/mL for [pyrimidinyl-2-¹⁴C])

^a Recovery of administered radioactivity as determined by LSC analyses of the dosing solution.

^b Others = all components not identified as bensulfuron methyl. Non-radiolabeled reference standards IN-J0290, IN-D1R84, IN-B6895, IN-N5297, IN-T5831, IN-F7880, IN-R9419, and IN-YY142 were co-injected with samples analysed by HPLC. One component identified as reference standard IN-YY142 was detected in the HPLC analysis at 10.6-14.7% of the applied radioactivity at Days 10-14. All other individual ¹⁴C components detected by HPLC were less than 10% of the applied radioactivity.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

The amount of bensulfuron methyl in the irradiated samples of sterile buffer 7, decreased slowly from 97.5% AR on Day 0 to 63.6% AR at Day 15 for the samples treated with [phenyl(U)-¹⁴C]bensulfuron methyl and from 97.4% AR on Day 0 to 72.1 % AR at Day 15 for the samples treated with [pyrimidinyl-2-¹⁴C]bensulfuron methyl. Degradate IN-YY142 was observed in the Day 15 sample at a maximum of 14.7% in the samples treated with phenyl bensulfuron methyl. A 13-min peak was observed in the Day 15 sample at approximately 4% AR in the samples treated with pyrimidinyl bensulfuron methyl. Analysis by (-)ESI LC/MS identified the 13-min peak as having a m/z 278, however the structure of the 13-min peak was not determined (

Table B.8.102).

The amount of bensulfuron methyl in the dark control sterile pH 7 buffer samples was 97.0% AR on Day 0 and 95.4% AR at Day 15 for the sample treated with [phenyl(U)-¹⁴C]bensulfuron methyl and 95.5% AR on Day 0 and 95.3% AR at Day 15 for the sample treated with [pyrimidinyl-2-¹⁴C]bensulfuron methyl (Table B.8.103).

Table B.8.103: Distribution and mass balance of radioactivity in dark control sterile pH 7 buffer samples treated with [phenyl(U)-¹⁴C] and [pyrimidinyl-2-¹⁴C]bensulfuron methyl (DPX-F5384)

<i>[phenyl(U)-¹⁴C] bensulfuron methyl</i>		Days Post Treatment						
		0	2	4	7	10	12	15
DPX-F5384	%AR	97.0	97.5	95.3	94.1	96.5	95.2	95.4
	µg/mL	0.95	0.96	0.92	0.90	0.95	0.93	0.93
Others ^b	%AR	3.0	2.5	3.7	3.9	3.5	4.8	4.6
Total % Recovery ^a in the Aqueous	%AR	100.0	100.0	99.0	98.1	100.0	100.0	100.0
<i>[pyrimidinyl-2-¹⁴C]</i>		0	2	4	7	10	12	15
DPX-F5384	%AR	95.5	95.1	95.5	93.5	93.7	95.7	95.3
	µg/mL	0.97	0.97	0.96	0.94	0.96	0.98	0.98
Others ^b	%AR	4.5	4.9	3.5	4.5	6.3	4.3	5.7
Total % Recovery ^a in the Aqueous	%AR	100.0	100.0	99.0	98.0	100.0	100.0	100.9

%AR = Percent of applied radioactivity (dosing solution = 0.98 µg/mL)

^aRecovery of administered radioactivity as determined by LSC analyses of the dosing solution.

^bOthers = all components not identified as bensulfuron methyl. Nonradiolabeled reference standards IN-J0290, IN-D1R84, IN-B6895, IN-N5297, IN-T5831, IN-F7880, and IN-R9419 were coinjected with all samples analysed by HPLC. Individual ¹⁴C components detected by HPLC were less than 5% of the applied radioactivity.

DT₅₀ value for bensulfuron methyl: Degradation kinetics were determined for irradiated and dark control samples of bensulfuron methyl in two natural waters and sterile pH 7 buffer. The first-order rate constants and half-life for bensulfuron methyl are summarised in Table B.8.104.

Table B.8.104: DT₅₀ values and rate constants for bensulfuron methyl (DPX-F5384)

Sample	Analyte	half-life (days)	k (day ⁻¹)	Method of Calculation (r ²)	Quantum Yield
Irradiated	Cavrini Farm Pond Water pH=7.5	10	0.0712	First-order linear (0.8246)	Not determined
	Ten-Mile Creek Natural Water pH=8.1	89	0.0078	First-order linear (0.8766)	Not determined
	Sterile Buffer pH=7	29	0.0237	First-order linear (0.8489)	0.00003
Non-irradiated	DPX-F5384 Sterile Buffer pH=7	Stable	–	–	Not determined

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Conclusion:

The photolysis half-life of bensulfuron methyl in Cavrini Farm was 10 days as compared to 29 days in sterile pH 7 buffer. The increase in the rate of degradation of bensulfuron methyl in Cavrini Farm is primarily due to indirect photolysis of bensulfuron-methyl. In the Ten-Mile Creek natural water system, the photolysis half-life was 89 days. The longer half-life of bensulfuron methyl in the Ten-Mile Creek natural water test system compared to the pH 7 buffer test system is most likely a result of the high dissolved organic carbon (DOC) of the Ten-Mile Creek water. The high DOC concentration of the water not only reduced the light intensity (25% reduction), but may also be responsible for scavenging of free radicals from the test system. The major degradation product that formed in the irradiated natural water system >10% was IN-T5831. Based on the results of this study, indirect photolysis may contribute significantly to elimination of bensulfuron methyl from the environment and direct photolysis will be a minor route of elimination. The quantum efficiency of bensulfuron methyl was calculated to be 0.00003.

B.8.4.3 Ready biodegradability of the active substance (Annex IIA 7.2.1.3.1)

29) *Bensulfuron methyl (DPX-F5384): Assessment of ready biodegradability by modified Sturm test. Barnes, S.P., 2002.*

Cross reference IIA, 7.2.1.3.1./01

Guidelines:

Directive 92/69/EEC Procedure C.4-C and OECD 301B.

GLP:

Yes

The study is acceptable

Material and Methods:

A sample of activated sludge was collected from Oakley, Suffolk, UK, sewage treatment works, which treats predominantly domestic waste. It was aerated in the laboratory for approximately four hours and aliquots (25 mL) of a homogenised sample were filtered through dried (approximately 105°C) and pre-weighed filter papers. The filters were dried for at least one hour (approximately 105°C), allowed to cool, and re-weighed. The solids level in the sludge was determined and then an appropriate volume was used to inoculate control and test vessels to give final suspended solids concentrations of 30 mg/L. The test substance bensulfuron methyl (batch: F5384-258, purity: 97.9%) was added to test vessels containing the freshly collected activated sludge micro-organism bacteria as a stock solution containing 30 mg/L to give nominal concentrations of 10 mg carbon[C]/L. Two control vessels contained inoculated mineral salts medium alone and one contained inoculated mineral salts medium plus the reference substance sodium benzoate (10 mg C/L). An additional mixture containing sodium benzoate (10 mg C/L) and bensulfuron methyl (10 mg C/L) was established in order to assess the potential inhibitory effects of the test substance on the activity of the microbial inoculum. The test vessels were incubated at temperatures nominally in the range of 20 to 24°C for 29 days with aeration. The CO₂ produced by each culture was trapped the residual barium hydroxide determined at intervals by titration.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Findings:

Percent of biodegradation of control and reference mixtures: Sodium benzoate degraded by 61% after 5 days and 91% after 29 days in the absence of bensulfuron methyl, and by 72% after 7 days in its presence, which confirmed that bensulfuron methyl was not inhibitory to the activity of the microbial inoculum (Table B.8.105). Cumulative levels of CO₂ production in the controls after 29 days (74.8 and 65.5 mg CO₂) were typical for this type of test and inoculum source and were within the acceptable range for this assay system. These results confirm that the inoculum was viable and that the test was valid.

Table B.8.105 Cumulative CO₂ production by the controls, blank-corrected cumulative CO₂ production and degradation as a percentage of TCO₂ in reference and test mixtures

Day	Cumulative control CO ₂		Sodium benzoate (10 mg C/L)		Sodium benzoate in bensulfuron methyl + sodium benzoate mixture both at 10 mg C/L		Bensulfuron methyl (10 mg C/L)				
							Culture 1		Culture 2		Mean
	CO ₂ (mg)		CO ₂ (mg)	% TCO ₂	CO ₂ (mg)	% TCO ₂	CO ₂ (mg)	% TCO ₂	CO ₂ (mg)	% TCO ₂	% TCO ₂
2	7.2	7.2	20.9	19	18.7	17	0.0	0	1.1	1	0
3	13.8	12.7	44.0	40	42.1	38	1.1	1	1.6	1	1
5	23.1	19.3	67.4	61	64.6	59	1.9	2	3.6	3	2
7	29.2	24.2	82.2	75	79.2	72	2.5	2	4.7	4	3
9	37.4	31.4	88.3	80	-	-	2.5	2	4.7	4	3
12	43.5	37.4	94.3	86	-	-	2.5	2	5.8	5	4
16	50.6	42.9	98.5	89	-	-	3.9	3	6.6	6	5
21	59.4	51.7	100.7	91	-	-	4.4	4	8.8	8	6
28	67.7	59.4	100.7	91	-	-	4.4	4	9.1	8	6
29	74.8	65.5	100.7	91	-	-	4.4	4	9.1	8	6

Percent of biodegradation of bensulfuron methyl: Cumulative CO₂ production by mixtures containing bensulfuron methyl had achieved, at most, 8% of the theoretical value (TCO₂, 110.1 mg CO₂) by the end of test on Day 29.

Conclusion:

The biodegradation of sodium benzoate in the presence of the test substance, bensulfuron methyl, was monitored in order to assess whether any inhibitory effects were exerted on the activity of the microbial inoculum. None were observed. Substances are considered to be readily biodegradable in this test if CO₂ production is equal to or greater than 60% of the theoretical value within ten days of achieving the 10% level. Bensulfuron methyl cannot, therefore, be considered to be readily degradable.

B.8.4.4 Water/sediment study (Annex IIA 7.2.1.3.2)

- 30) *Aerobic aquatic metabolism of [phenyl(U)-¹⁴C] DPX-F5384 and [pyrimidine-2-¹⁴C] DPX-F5384. Hunt, O.R., 1986.*

Cross reference IIA, 7.2.1.3.2./01

Guidelines:

USEPA 162-4 (1982)

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

GLP:

No, GLP was not required at the time this study was conducted.

The study is acceptable

Material and Methods:

Two radiolabeled forms of bensulfuron methyl were used: [Phenyl(U)-¹⁴C]bensulfuron methyl (Batch No. HOTC 199; radiochemical purity >99%), and [Pyrimidine-2-¹⁴C]bensulfuron methyl (Batch No. HOTC 194; radiochemical purity >99%). The rate and pattern of metabolism of bensulfuron methyl (DPX-F5384) was studied in three different aquatic soil systems under laboratory aerobic conditions. Three soils were used throughout the study. The soils were Nagano, Japan; Tochigi, Japan; and California, USA (Table B.8.106).

Table B.8.106: Soil characteristics

Characteristic	Soil		
Soil Name or Designation	Nagano	Tochigi	California
Origin Location	Japan	Japan	U.S.A.
pH	6.7	5.5	6.5
% Sand (2000 - 50 µm)	35.0	22.0	25.0
% Silt (<50 - 2 µm)	57.0	53.0	63.0
% Clay (<2 µm)	8.0	8.0	12.0
Texture ^a	Silt Loam	Silt Loam	Silt Loam
Organic matter (%)	12.6	2.3	1.9
Organic carbon (%) ^b	7.3	1.3	1.1
Cation exchange capacity (meq/100 g)	55.0	21.9	17.5

^a U.S.D.A. soil classification system

^b %organic carbon = % organic matter x 0.58

For each soil type, 75 g (50 g dry weight) of soil was weighed into each of ten 500 mL erlenmeyer flasks. Deionized water was added to each flask to a depth of approximately 1 cm above the soil layer. The flasks were stoppered with rubber stoppers and placed in a shaking water bath, under aerobic conditions at approximately 25°C. After 14 days, each flask was treated at a nominal rate of 0.1 ppm by adding acetone stock solution (35 µL of 4.5 mg/25 mL for [Phenyl(U)-¹⁴C] DPX-F5384 or 50 µL of 2.5 mg/25 mL [Pyrimidine-2-¹⁴C]DPX-F5384). Test vessels were aerated four times daily and incubated for an additional 30 days at approximately 25°C. One flask from each soil was monitored for ¹⁴CO₂ with a 2 M sodium hydroxide trap. One flask was removed from each "soil type" aerobic system at 0, 1, 2, 5, 7, 14, 21 and 30 days post-treatment. Sodium hydroxide in the traps was changed and analyzed by LSC at the same intervals. Additionally, one of the control samples was taken randomly at 0, 1, 2, 5, 7 and 14 days.

Water from the soil samples was decanted, adjusted to pH 4, partitioned with methylene chloride and the methylene chloride analysed by HPLC. Soil samples were extracted four times with methylene chloride:methanol:2 M ammonium carbonate (100 mL of 3:4:1; v:v:v) and two times by refluxing with acetone: 2 M ammonium carbonate 100 mL (3:1, v:v). Extracts were combined and aliquots were analysed by liquid scintillation counting (LSC) to determine total extractable radioactivity. Samples were concentrated using a rotary evaporator, adjusted to pH 4, partitioned with methylene chloride, and analysed by HPLC. Degradation products were identified by co-chromatography using authentic standards by HPLC. Extracted soil samples were combusted to determine levels of NER residues.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Findings:

Mass balance: Material balance for the [^{14}C -phenyl] label ranged from 98% to 101%. Material balance for the [^{14}C -pyrimidine] label ranged from 99.4 to 100.2% (Table B.8.107 and Table B.8.108).

Distribution between water and sediment: Most of the dose was immediately associated with the sediment. The amount of radioactivity associated with the sediment remained constant throughout the study.

Non-extractable residues: Non-extractable residues (NER) were low and accounted for a less than 5% of the applied radioactivity in both labels.

Principal degradation products: Bensulfuron methyl degraded under aerobic aquatic conditions declining to 66.8-76.0% and 60.6-71.3% AR after 30 days in the pyridine and pyrimidine labels, respectively. IN-N5297 (sulfonamide), IN-J0290 (pyrimidine amine), and IN-F7880 were identified as the major degradation products (<10%). An uncommon aquatic degradation product IN-N8989 was also detected and peaked to 11.5% at 7 days but quickly declined to 0.5% after 14 days in California soil system. The formation of IN-N8989 was not significant (<1.7% AR) in the [^{14}C -pyrimidine] label, suggesting that this was a transient product. The formation of $^{14}\text{CO}_2$ was negligible in either label.

Table B.8.107: Percent distribution of applied radioactivity and mass balance in the total aerobic aquatic systems treated with [phenyl(^{14}C)]bensulfuron methyl (DPX-F5384)

Day	% of Applied Radioactivity					
	Volatiles Recovered in 2 M NaOH	Water	Sediment Extractable by MMA ^a	Sediment Extractable by AA ^b	Non-Extractable Residues	Total Recovered ^c
California Silt Loam						
0	--	5.9	92.1	2.6	0.5	101.1
1	0.7	5.1	85.4	8.0	0.7	99.9
2	0.7	5.6	83.4	9.1	0.9	99.7
5	1.2	6.7	88.2	2.3	1.7	100.1
7	1.2	7.6	80.5	8.8	2.0	100.1
14	2.7	6.9	83.2	5.0	2.5	100.3
21	2.7	10.2	82.1	6.1	2.9	104.0
30	2.9	6.2	64.0	22.0	2.9	98.0
Nagano Silt Loam						
0	--	3.8	93.4	2.1	0.7	100.0
1	0.3	5.9	87.2	5.1	1.5	100.0
2	0.4	5.3	86.8	5.7	1.8	100.0
5	0.9	6.3	88.5	2.3	2.1	100.1
7	0.9	8.4	83.6	4.3	2.7	99.9
14	1.2	6.1	82.1	6.4	4.2	100.0
21	1.4	6.4	80.5	7.8	4.7	100.8
30	1.5	8.0	78.2	11.8	1.3	100.8
Tochigi Silt Loam						
0	--	20.0	76.3	3.4	0.2	99.9
1	0.5	3.5	84.5	10.9	0.6	100.0
2	0.6	1.5	86.7	10.2	1.0	100.0
5	0.8	1.3	93.9	3.0	1.1	100.1
7	0.8	1.2	83.5	13.4	1.1	100.0
14	0.9	1.2	85.8	10.6	1.5	100.0
21	1.0	1.2	89.7	6.4	1.7	100.0
30	1.8	2.5	81.8	14.4	0.1	100.6

^a Methylene chloride:methanol:2 M ammonium carbonate (3:4:1; v:v:v)

^b Acetone:2 M ammonium carbonate 100 mL (3:1, v:v)

^c Includes volatiles, water, MMA extracts, AA extracts, and non-extractable residues.

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Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.108: Percent distribution of applied radioactivity and mass balance in the total aerobic aquatic systems treated with [pyrimidine-2-¹⁴C]bensulfuron methyl (DPX-F5384)

Day	% of Applied Radioactivity					
	Volatiles Recovered in 2 M NaOH	Water	Sediment Extractable by MMA ^a	Sediment Extractable by AA ^b	Non-Extractable Residues	Total Recovered ^c
California Silt Loam						
0	--	6.9	75.6	16.8	0.7	100.0
1	0.2	4.3	82.2	12.2	0.6	99.5
4	0.9	8.3	64.5	22.5	4.0	100.2
7	0.9	10.1	82.5	5.5	1.9	100.9
14	2.0	4.0	85.0	7.1	1.9	100.0
21	2.3	5.3	74.1	14.4	3.9	100.0
30	2.6	2.5	85.8	6.6	2.5	100.0
Nagano Silt Loam						
0	--	3.3	79.8	16.1	0.8	100.0
1	0.1	3.6	83.1	12.9	0.3	100.0
4	0.9	2.0	77.6	15.4	4.3	100.2
7	0.9	3.0	87.6	7.2	1.2	99.9
14	1.2	2.5	85.9	8.7	1.7	100.0
21	1.6	2.0	81.6	12.4	2.3	99.9
30	2.9	6.7	84.8	3.7	1.9	100.0
Tochigi Silt Loam						
0	--	1.2	80.0	18.1	0.1	99.4
1	0.1	1.4	80.9	17.2	0.4	100.0
4	0.5	1.3	77.3	19.0	1.9	100.0
7	0.5	1.5	78.7	18.0	1.3	100.0
14	0.8	0.7	84.2	13.0	1.3	100.0
21	0.9	1.1	79.5	16.4	2.0	99.9
30	2.0	0.9	79.7	14.2	3.3	100.1

^a Methylene chloride:methanol:2 M ammonium carbonate (3:4:1; v:v:v)

^b Acetone:2 M ammonium carbonate 100 mL (3:1, v:v)

^c Includes volatiles, water, MMA extracts, AA extracts, and nonextractable residues.

Distribution of Radioactivity in [Phenyl(U)-¹⁴C]DPX-F5384 treated Systems. Data for radioactivity as [phenyl(U)-¹⁴C]DPX-F5384 and metabolites are summarized in Table B.8.109. DPX-F5384 degraded to a group of metabolites which include sulfonamide, homosaccharin, HPY-DPX-F5384 and ODM-DPX-F5384. The two principal metabolites are sulfonamide and HPY-DPX-F5384. After 30 days, more than half of the treatment was recovered as intact DPX-F5384. Degradation of [phenyl(U)-¹⁴C]DPX-F5384 is relatively similar for all three soils. Half-lives, are estimated to be on the order of 2 months.

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Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.109: Percent distribution of applied radioactivity in the total aerobic aquatic systems treated with [phenyl(U)-¹⁴C]bensulfuron methyl (DPX-F5384)

Day	% Applied Radioactivity				
	DPX-F5384	IN-N5297	IN-B6895	IN-F7880	IN-N8989
California Silt Loam					
0	96.5	1.4	1.2	N.D.	0.9
1	86.4	1.6	N.D.	0.1	7.0
2	86.1	1.6	2.6	2.0	1.1
5	87.9	3.1	N.D.	N.D.	N.D.
7	69.8	1.7	0.1	0.1	11.5
14	78.7	8.7	1.2	N.D.	0.5
21	71.7	9.6	1.0	0.5	0.5
30	66.8	15.0	1.2	0.4	0.3
Nagano Silt Loam					
0	94.0	1.5	1.8	N.D.	1.2
1	90.8	1.1	0.6	0.7	1.6
2	88.8	0.9	1.4	1.4	0.9
5	85.5	2.3	N.D.	N.D.	N.D.
7	81.8	6.4	0.1	0.2	N.D.
14	79.2	6.0	0.9	N.D.	0.5
21	68.2	13.4	0.8	N.D.	0.5
Tochigi					
0	95.1	3.3	0.9	N.D.	1.4
1	90.4	1.8	N.D.	0.8	2.7
2	86.9	2.0	1.3	1.9	2.1
5	85.8	2.4	N.D.	0.5	0.8
7	87.6	4.2	N.D.	N.D.	N.D.
14	85.7	3.8	1.0	N.D.	1.0
21	76.0	9.5	0.9	0.7	1.0

N.D. = None detected (<0.5%)

Distribution of Radioactivity in [Pyrimidine-2-¹⁴C]DPX-F5384 treated systems. Data for radioactivity as [pyrimidine-2-¹⁴C]DPX-F5384 and metabolites are summarized in Table B.8.110. This data indicates DPX-F5384 degraded to pyrimidine amine, an unknown, HPY-DPX-F5384 and ODM-DPX-F5384. HPY-DPX-F5384 and ODM-DPX-F5384 were generally detected at 5% of the applied radioactivity or less. Pyrimidine amine, the major metabolite, was present at less than 10% of the applied radioactivity. DPX-F5384 accounted for greater than 60% of the radioactivity in the system at the end of the sampling period.

Degradation of [pyrimidine-2-¹⁴C]DPX-F5384, as in [phenyl(U)-¹⁴C] DPX-F5384 treated systems, is similar for all three soils. The first half-lives are estimated to be on the order of 2 months.

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Environmental fate and behaviour

Table B.8.110: Percent distribution of applied radioactivity in the total aerobic aquatic systems treated with [pyrimidine-2-¹⁴C] bensulfuron methyl (DPX-F5384)

Day	% Applied Radioactivity				
	DPX-F5384	Unknown	IN-J0290	IN-F7880	IN-N8989
California Silt Loam					
0	94.8	0.8	3.4	N.D.	N.D.
1	95.4	N.D.	N.D.	N.D.	0.5
4	84.8	1.8	5.8	N.D.	N.D.
7	82.3	0.5	4.3	0.5	1.1
14	78.4	0.7	6.4	1.1	1.7
21	71.6	3.2	6.3	2.1	0.7
30	71.3	N.D.	6.2	3.8	0.7
Nagano Silt Loam					
0	95.3	1.6	1.0	N.D.	N.D.
1	97.9	0.5	0.8	N.D.	1.2
4	84.1	3.0	5.1	N.D.	1.0
7	84.3	1.3	2.4	N.D.	0.6
14	80.9	N.D.	4.4	2.7	6.7
21	73.1	0.6	4.6	1.2	0.6
30	60.6	0.5	7.6	2.3	0.8
Tochigi Silt Loam					
0	90.1	1.0	1.6	N.D.	N.D.
1	95.0	N.D.	1.8	N.D.	0.6
4	89.7	2.0	6.5	0.5	1.2
7	83.6	2.0	5.1	0.8	1.2
14	77.0	N.D.	4.0	0.6	N.D.
21	77.3	0.6	5.2	1.2	1.0
30	63.1	0.8	6.6	1.8	1.4

N.D. = None detected (<0.5%)

Conclusion:

Bensulfuron methyl dissipated in all three aerobic aquatic systems. In aerobic aquatic systems treated with DPX-F5384 most of the material is adsorbed into the sediment. DPX-F5384 is degraded with a first half-life of approximately 2 months in this system. IN-N5297 and IN-J0290 were the major degradation products under aerobic aquatic conditions. Volatile metabolites accounted for less than 3% of applied radioactivity.

8) *Calculated half-lives of bensulfuron methyl in environmental fate studies. A. Van- Nguyen, 2004.*

Cross reference IIA 7.0/01

Guidelines:

Not applicable

GLP:

Not applicable

The study is acceptable

Material and methods:

The software program, ModelManager^o, Version 1.1 (Cherwell Scientific Limited, 1999), was used to calculate the first order rate constants and DT₅₀ values of bensulfuron methyl in various laboratory environmental fate studies.

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The types of environmental studies conducted were the aerobic soil metabolism (Friedman P.L., 1984; Cross reference IIA 7.1.1.1.1./02 and Yordy, J.R., 1987, cross reference IIA 7.1.1.1.1./03), the anaerobic soil metabolism (Cadwgan, G. E., 1986, cross reference IIA 7.1.1.1.2./01) and the aerobic aquatic metabolism (Hunt O.R., 1986; cross reference IIA 7.2.1.3.2./01). Calculation for the different laboratory experiment are described in the proper paragraph. Here below only the aerobic aquatic metabolism.

The DT₅₀ and DT₉₀ values of bensulfuron methyl were calculated from data obtained in the aerobic metabolism study performed with bensulfuron methyl, as described in the previous study.

Results:

The averaged DT₅₀ values of bensulfuron methyl were 66, 50, and 87 days for California, Nagano, and Tochigi soil systems, respectively. The respective averaged DT₉₀ values were 220, 167, and 289 days (Table B.8.111).

Table B.8.111: DT₅₀ and DT₉₀ values for bensulfuron methyl (DPX-F5384) in the total aerobic aquatic systems

Soil Name/ Origin	Texture	pH	Incubation T (°C)	DT ₅₀	DT ₉₀	r ²	Method of calculation
California, USA	Silt Loam	6.5	25	66	220	0.677-0.878	Non-linear SFO
Nagano, Japan	Silt Loam	6.7	25	50	167	0.928-0.958	Non-linear SFO
Tochigi, Japan	Silt Loam	5.5	25	87	289	0.746-0.897	Non-linear SFO

Conclusion:

The DT₅₀ and DT₉₀ values of bensulfuron methyl were calculated from data obtained in the aerobic metabolism study. The averaged DT₅₀ values of bensulfuron methyl were 66, 50, and 87 days for California, Nagano, and Tochigi soil systems, respectively. The respective averaged DT₉₀ values were 220, 167, and 289 days

31) *Aerobic aquatic metabolism of bensulfuron methyl in two water/sediment systems. Lentz, N.R., 2001.*

Cross reference IIA 7.2.1.3.2./02

Guidelines:

SETAC Guidelines Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides (March 1995), OECD Guidelines for the Testing of Chemicals: Aerobic and Anaerobic Transformation in Aquatic Sediment, Draft Document (December 1999)

GLP:

Yes

The study is acceptable

Material and Methods:

Two radiolabeled forms of bensulfuron methyl were used: [pyrimidine-2-¹⁴C]bensulfuron methyl (HOTC 319; radiochemical purity ≥95%); and [phenyl(U)-¹⁴C]bensulfuron methyl (HOTC 320; radiochemical purity ≥95%). Degradation of bensulfuron methyl was studied in two different water/sediment systems (Table B.8.112). The study was conducted in a flow-through test apparatus purged with pre-moistened air that was incubated in the dark at 20±2°C. The experimental system comprised test vessels containing fresh sediment (approximately 35 g dry weight

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basis) covered with 115 g associated water for a sediment to water ratio of approximately 1:3 (w/w). The water sediment systems were acclimatised for approximately one week prior to dosing. After the acclimatisation period, water layers were treated with ^{14}C bensulfuron methyl (21 μg in 121 μL acetonitrile/water (1/4, v/v) at nominal concentrations of 0.2 $\mu\text{g/mL}$ water.

Table B.8.112: Characteristics of the water/sediment systems

System:	System 1	System 2
<i>Water</i>		
Location/Source	Irrigation water Pavia, Italy	Irrigation water Vercelli, Italy
pH	7.4	7.7
Hardness (mg eq CaCO_3/L)	45	57
Total Phosphorus (ppm)	7.3	2.2
Total Nitrogen (ppm)	20.9	26.1
Total Organic Carbon Initiation (ppm)	1.0	1.3
Total Organic Carbon Termination (ppm)	15.1	29.9
<i>Sediment</i>		
System:	System 1	System 2
Location/Source	Pavia, Italy	Vercelli, Italy
pH (Water)	5.2	5.8
pH (0.01 M CaCl_2)	4.6	5.4
Initial % Organic Carbon (Day 0)	ND ^a	ND
Final % Organic Carbon (end of study)	0.5	1.4
Cation Exchange Capacity (meq/100 g)	2.59	8.45
% Sand	78.4	20.4
% Silt	14.8	62.8
% Clay	6.8	16.8
Texture ^b	Loamy sand	Silt Loam
Initial Microbial biomass	3.41	14.0
Microbial biomass at Day 100	4.93	14.0
Final Microbial biomass	6.57	13.2

^a Not determined

^b Texture USDA

^c Microbial Biomass (mg C/100 g sediment)

Samples were removed from the two systems 0, 3, 7, 14, 21, 30, 40, 50, 70, 100, and 130 days after application. Volatiles, including $^{14}\text{CO}_2$, were collected during the study. The presence of $^{14}\text{CO}_2$ in the NaOH traps was verified by the precipitation with BaCl_2 . Designated microbial biomass samples were analysed at the start, at Day 100 and at termination of the study. Redox potential, dissolved oxygen content, and pH of the water phase along with the sediment phase redox and pH were measured.

Following separation of the water and sediment phases by centrifugation, the total radioactivity of the water phase was determined in triplicate by LSC (liquid scintillation counting). The water layer was concentrated to dryness using a rotary evaporator. Approximately 2 mL of ACN:H₂O (75:25) was added to dissolve the residue. The concentrated aqueous fraction was then analysed by HPLC with radiochemical detection. Degradation products were identified by mass spectrometry and by co-chromatography using authentic standards by HPLC.

Sediments were extracted three times with 100 mL 0.1 M ammonium carbonate:acetone (9:1, v:v) using a wrist action shaker for 30 minutes. The samples were centrifuged to precipitate solids and the extracts decanted. The extracts were combined and the radioactivity quantified by LSC. The combined extracts were concentrated using a rotary evaporator and 2 mL of acetonitrile:H₂O (75:25) added to dissolve the residue. The concentrated extract

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fraction was then analysed by HPLC with radiochemical detection. Remaining extracted sediment residues were air-dried, homogenised, and weighed. Triplicate aliquots were analysed for radioactivity by combustion followed by liquid scintillation counting. Bound residues were characterised by fractionation of the Day 100 post extraction solid samples of each sediment into humin, humic acid, and fulvic acid fractions.

Degradation kinetics of the parent compound bensulfuron methyl in a water/sediment system has been modelled using Model Manager, Version 1.1 (Cherwell Scientific Limited, 1999). DT_{50} and DT_{90} values of bensulfuron methyl (parent) in the total system, the water phase, and the sediment/soil phase were determined from single first-order kinetic modeling of parent using the %AR (from both labeled forms of bensulfuron methyl) versus time in each phase.

Findings:

Mass balance: Overall recovery in Pavia test system for the ^{14}C -pyrimidine label ranged from 86.9 to 99.4% of the applied radiolabel, while for the ^{14}C -phenyl label, overall recovery ranged from 90.8 to 102.4% applied radiolabel. Overall recovery in Vercelli test system for the ^{14}C -pyrimidine label ranged from 95.6 to 100.5% of the applied radiolabel, while for the ^{14}C -phenyl label, overall recovery ranged from 94.8 to 100.0% applied radiolabel (Table B.8.113 - Table B.8.114).

Distribution between water and sediment: The distribution of radioactivity between water and sediment was similar in both test systems. For both labels, there was a movement of radioactivity from the water to the sediment (Table B.8.113). By the end of the study, radioactivity associated with the water accounted for between 11.1 and 33.7% AR. Radioactivity in the sediment phase (extractable and non-extractable residues) by the end of the study accounted for between 32.4 and 67.1% AR.

Water. Radioactivity in the water phase of each label for the Pavia sediment decreased slowly throughout the course of the study (Table B.8.114). Radioactivity in the [pyrimidine-2- ^{14}C]bensulfuron methyl treated water decreased from 95.1 % AR at Day 0 to 11.1 % AR at day 130. Samples treated with [phenyl(U)- ^{14}C]bensulfuron methyl showed a similar decline from 99.3% AR at day 0 to 33.7% AR at day 130. The amount of radioactivity in the water phase of each label for the Vercelli sediment decreased slowly throughout the course of the study. Radioactivity in the pyrimidine bensulfuron methyl treated water decreased from 98.8% AR at day 0 to 15.4% AR at day 130. The phenyl bensulfuron methyl showed a similar decline from 97.8% AR at day 0 to 21.5% AR at day 130.

Sediment. Extractable ^{14}C -residues ranged from 15.4 to 39.3% AR over the course of the study for the Pavia sediment. Sediment extractable radioactivity in the [pyrimidine-2- ^{14}C]bensulfuron methyl treated system increased from 15.4% AR at day 3 to 39.3% AR at day 130. Sediment extractable radioactivity in the [phenyl(U)- ^{14}C]bensulfuron methyl treated system increased from 18.2% AR at day 3 to a maximum of 32.4% AR at day 40 and decreased to 19.6% at day 130. The amount of [^{14}C]bensulfuron methyl in the sediment extract for each label increased slowly over 30 days and then decreased for the remainder of the study. The amount of [pyrimidine-2- ^{14}C]bensulfuron methyl in the extract increased from 14.69% AR at day 3 to a maximum of 29.93% AR at day 30 and then decreased to 7.27% AR at day 130. The [phenyl(U)- ^{14}C]bensulfuron methyl in the extract also increased from 17.77% AR at day 3 to a maximum of 27.43% AR at day 30 and then decreased to 7.49% AR at day 130.

Sediment extractable ^{14}C -residues ranged from 21.8 to 50.4% AR over the course of the study for the Vercelli treated sediment. The radioactivity in the sediment extract of the [pyrimidine-2- ^{14}C]bensulfuron methyl treated system increased from 22.3% AR at day 3 to a maximum of 50.4% AR at day 30 and then decreased to 24.4% AR at day 130. Sediment extractable radioactivity in the [phenyl(U)- ^{14}C]bensulfuron methyl treated extract increased from

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21.8% AR at day 3 to a maximum of 47.2% AR at day 50 and decreased to 26.4% at day 130. The amount of [¹⁴C]bensulfuron methyl in the sediment extract for each label increased slowly over 21 to 30 days and then decreased for the remainder of the study. The amount of [pyrimidine-2-¹⁴C]bensulfuron methyl in the extract increased from 21.63% AR at day 3 to a maximum of 44.62% AR at day 30 and then decreased to 18.19% AR at day 130. The [phenyl(U)-¹⁴C]bensulfuron methyl in the extract also increased from 21.39% AR at day 3 to a maximum of 41.64% AR at day 21 and then decreased to 17.98% AR at day 130 and decreased to 26.4% at day 130.

Principal degradation products: ¹⁴CO₂ was a significant degradation product from both labels accounting for a maximum of 26.1 and 16.6% AR in the Pavia and Vercelli test systems, respectively (Table B.8.113).

The major degradation products in the water phase were IN-N5297 and IN-J0290. IN-N5297 formed steadily and reached a maximum of 27.3% AR in the Pavia test system on Day 130. IN-J0290 reached a maximum level of 10.06% after 70 days of incubation before declining to 1.34% AR by Day 130. IN-DAT97, IN-F7880, IN-D1R84, and IN-R9419 were all minor metabolites in the water phase, each accounting for <10% AR (Table B.8.114).

The identified transformation products detected in the Pavia sediment system treated with bensulfuron methyl were IN-J0290, IN-D1R84, IN-N5297, IN-DAT97, IN-F7880 and IN-R9419. IN-J0290 was detected in the sediment treated with pyrimidine bensulfuron methyl and had a maximum concentration of 0.040 µg/mL (19.69% AR) observed on day 130 of incubation. IN-DAT97 was also detected in the sediment treated with pyrimidine bensulfuron methyl and had a maximum concentration of 0.020 µg/mL (9.86% AR) observed on day 50 and declined to a nondetectable level by day 130. IN-N5297 was detected in the Pavia sediment treated with phenyl bensulfuron methyl and had a maximum concentration of 0.064 µg/mL (31.73% AR) observed on day 130. IN-F7880 was detected in the sediment treated with pyrimidine and phenyl bensulfuron methyl and had a maximum concentration respectively of 0.019 µg/mL (9.71 and 9.51 % AR) on day 40 and day 70. IN-F7880 declined to approximately 3% AR by day 130 for both of the labeled test materials. IN-R9419 was detected in the sediment treated with pyrimidine and phenyl bensulfuron methyl and had a maximum concentration of respectively 0.012 µg/mL (6.15 % AR) and 0.011 µg/mL (5.80% AR) on day 30. IN-R9419 declined to below 2% AR by day 130. The total unidentified radioactivity (up to 6 components, none greater than 3 %AR) for the pyrimidine treated Pavia sediment reached a maximum of 15.95% AR at Day 130. The total unidentified radioactivity for the phenyl bensulfuron methyl treated Pavia sediment reached a maximum of 6.73% AR on day 100 and declined to 5.23% AR at day 130 (Table B.8.116).

The transformation products detected in the Vercelli sediment system treated with bensulfuron methyl were IN-J0290, IN-D1R84, IN-N5297, IN-DAT97, IN-F7880 and IN-R9419. IN-J0290 was detected in the sediment treated with [pyrimidine-2-¹⁴C]bensulfuron methyl and had a maximum concentration of 0.016 µg/mL (8.19% AR) at day 40 and declined to less than 1 % AR at study termination (day 130). IN-DAT97 was detected in the sediment treated with both labeled test materials and had a maximum concentration of 0.007 µg/mL (3.59% AR) and 0.001 µg/mL (0.47% AR) observed on day 50 and day 70, for the pyrimidine and phenyl bensulfuron methyl, respectively. Degradate IN-DAT97 declined to less than 1.5% AR by day 130. IN-N5297 was detected in the Pavia sediment treated with phenyl bensulfuron methyl and had a maximum concentration of 0.033 µg/mL (16.13% AR) observed on day 50 and declined to 3.72% AR at day 130. IN-F7880 was detected in the sediment treated with both labels and had a maximum concentration of 0.009 µg/mL (4.49% AR) and 0.011 µg/mL (5.34% AR) on day 70 for the pyrimidine and with phenyl treated sediments, respectively. IN-F7880 declined to below 4% AR by day 130 for both of the labeled test materials. IN-R9419 was detected in the sediment treated with both labels and at a maximum concentration of 0.007 µg/mL (3.69 and 3.64% AR) on day 21 for the pyrimidine and phenyl treated sediments,

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respectively. IN-R9419 declined to below 1 % AR by day 130. reached a maximum of 11.61 % AR at day 130. The total unidentified radioactivity for the phenyl treated Vercelli sediment reached a maximum of 7.29% AR (comprised of up to 6 components, none greater than 3 %AR) on day 70 and declined slightly to 5.58% AR at day 130.

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

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Table B.8.113: Percent distribution of applied radioactivity and mass balance in water/sediment systems treated with bensulfuron methyl (DPX-F5384)

Day	% of Applied Radioactivity					
	Volatile Organics	CO ₂	Surface Water	Sediment Extractable	Non-Extractable Residues	Total Recovered
<i>Pyrimidine (Pavia Test System)</i>						
0	NA	NA	95.1	NA	NA	95.1
3	ND	ND	76.6	15.4	1.0	93.0
7	NA	0.1	74.8	20.5	1.8	97.2
14	NA	0.17	73.0	23.6	2.6	99.4
21	NA	0.31	59.2	32.1	2.0	93.6
30	NA	0.8	51.2	38.5	6.3	96.8
40	NA	2.5	49.4	34.2	9.4	95.5
50	ND	4.7	42.2	36.5	11.1	94.5
70	NA	10.0	31.3	31.7	18.4	91.4
100	NA	14.6	16.6	34.2	25.4	90.8
130	ND	16.7	11.1	39.3	19.8	86.9
<i>Pyrimidine (Vercelli Test System)</i>						
0	NA	NA	98.8	NA	NA	98.8
3	NA	0.04	69.3	22.3	4.0	95.6
7	NA	0.1	62.3	32.9	4.7	100.0
14	NA	0.13	40.5	47.1	8.9	96.6
21	NA	0.25	42.3	44.3	12.3	99.2
30	NA	0.63	23.6	50.4	21.4	96.0
40	NA	5.04	23.4	47.6	23.6	99.6
50	0.01	5.83	21.6	47.8	23.2	98.4
70	NA	8.23	25.9	39.6	26.8	100.5
100	NA	12.07	19.9	28.1	37.5	97.6
130	ND	16.6	15.4	24.4	42.7	99.1
<i>Phenyl (Pavia Test System)</i>						
0	NA	NA	99.3	NA	NA	99.3
3	NA	0.2	78.1	18.2	1.3	97.8
7	NA	0.4	75.5	19.5	1.8	97.2
14	NA	1.1	75.4	20.5	2.5	99.5
21	NA	2.1	57.7	30.4	5.5	95.7
30	NA	3.8	62.5	31.0	5.1	102.4
40	NA	4.5	48.3	32.4	9.1	94.3
50	0.01	8.4	39.8	31.6	12.1	91.9
70	NA	15.5	39.7	24.5	13.3	93.0
100	NA	22.5	34.6	19.8	13.9	90.8
130	0.01	26.10	33.7	19.6	12.8	92.2
<i>Phenyl (Vercelli Test System)</i>						
0	NA	NA	97.8	NA	NA	97.8
3	NA	0.2	71.8	21.8	5.4	99.2
7	NA	0.3	56.8	35.5	6.1	98.7
14	NA	0.63	51.4	39.1	7.4	98.5
21	NA	0.96	39.9	45.9	12.5	99.3
30	NA	1.77	33.6	45.3	19.3	100.0
40	NA	3.18	27.0	44.5	22.0	96.7
50	ND	4.86	24.1	47.2	22.0	98.2
70	NA	7.56	26.9	37.0	26.2	97.7
100	NA	11.74	23.2	30.6	30.9	96.4
130	ND	14.9	21.5	26.4	32.0	94.8

NA = Not analysed
ND = Not detected

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.114: Percent distribution of applied radioactivity in the water phase of the systems treated with ^{14}C -bensulfuron methyl (DPX-F5384)

Day	% of Applied Radioactivity						
	DPX-F5384	IN-J0290	IN-DAT97	IN-F7880	IN-R9419	Unknown ^a	
Pyrimidine (Pavia Test System)							
0	89.28	4.14	ND ^b	ND	0.47	1.21	
3	73.31	1.00	0.34	0.21	1.33	0.41	
7	70.77	0.76	0.61	0.42	1.67	0.57	
14	63.66	1.17	1.64	1.56	2.35	2.62	
21	46.72	3.07	1.40	2.20	3.34	1.49	
30	31.12	7.81	1.38	4.60	4.14	2.15	
40	20.18	8.54	5.73	9.04	2.17	3.74	
50	14.18	8.32	8.44	6.18	0.82	4.26	
70	4.28	10.06	6.59	4.93	0.24	5.20	
100	0.76	3.54	1.65	3.13	0.23	7.29	
130	0.30	1.34	ND	1.25	ND	8.21	
Pyrimidine (Vercelli Test System)							
0	92.04	5.10	ND	ND	ND	1.66	
3	66.64	0.60	0.29	0.20	0.97	0.60	
7	59.86	0.46	0.35	0.21	1.06	0.36	
14	36.48	1.20	0.34	0.29	1.70	0.49	
21	38.17	0.52	0.25	0.35	2.22	0.79	
30	16.60	3.44	0.41	0.74	1.71	0.70	
40	13.18	3.53	3.03	1.73	0.28	1.65	
50	11.24	3.65	2.72	2.09	ND	1.90	
70	12.67	2.10	2.72	2.87	ND	5.54	
100	8.68	2.00	1.59	1.97	ND	5.66	
130	5.07	0.92	1.25	1.86	ND	6.30	
	DPX-F5384	IN-D1R84	IN-N5297	IN-DAT97	IN-F7880	IN-R9419	Unknown
Phenyl (Pavia Test System)							
0	94.63	ND	4.67	ND	ND	ND	ND
3	75.35	ND	1.46	ND	0.25	0.75	0.29
7	71.20	ND	1.31	ND	0.42	1.64	0.93
14	67.78	ND	1.58	ND	1.24	2.01	2.79
21	48.04	ND	3.47	ND	2.64	1.58	1.97
30	45.81	ND	4.96	ND	3.77	4.58	3.38
40	20.02	ND	17.72	1.18	4.97	1.53	2.88
50	7.43	ND	24.23	1.38	4.14	0.31	2.31
70	4.79	ND	25.82	0.96	5.42	0.29	2.42
100	1.47	ND	25.30	ND	4.07	0.25	3.51
130	0.37	1.62	27.30	ND	1.52	ND	2.89
Phenyl (Vercelli Test System)							
0	92.34	ND	5.46	ND	ND	ND	ND
3	70.13	ND	0.80	ND	0.29	0.58	ND
7	53.45	ND	0.53	ND	0.41	1.01	1.40
14	47.70	ND	0.53	ND	0.26	1.78	1.13
21	34.82	ND	1.45	ND	0.69	1.97	0.97
30	24.77	ND	2.53	ND	0.90	2.12	3.28
40	13.84	0.99	9.30	0.35	1.60	0.42	0.50
50	10.43	0.54	10.28	0.46	1.26	0.12	1.01
70	12.91	2.85	7.29	0.47	2.31	ND	1.07
100	9.36	5.59	3.67	ND	2.28	ND	2.30
130	6.88	7.31	2.24	ND	2.52	ND	2.55

^a Unknown radioactivity composed of up to 6 peaks, none of which exceeded 3% AR at any time.

^b ND = Not detected

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.115: Percent distribution of applied radioactivity in the sediment phase of test systems treated with ^{14}C -bensulfuron methyl (DPX-F5384)

Day	% of Applied Radioactivity						
	DPX-F5384	IN-J0290	IN-DAT97	IN-F7880	IN-R9419	Unknown ^a	
Pyrimidine (Pavia Test System)							
0	NA	NA	NA	NA	NA	NA	
3	14.69	0.23	0.12	ND	0.36	ND	
7	19.34	0.15	0.09	0.19	0.56	0.17	
14	19.66	0.54	0.90	0.87	1.2	0.43	
21	24.33	0.16	0.61	4.11	1.26	1.63	
30	29.93	2.95	0.58	1.47	2.01	1.56	
40	23.28	3.75	0.56	0.67	0.30	5.64	
50	24.92	6.20	1.42	1.42	1.10	1.44	
70	14.84	8.37	1.05	1.17	1.24	5.03	
100	10.53	13.3	1.86	2.34	1.43	4.74	
130	7.27	18.35	ND	1.81	1.89	9.98	
Pyrimidine (Vercelli Test System)							
0	NA	NA	NA	NA	NA	NA	
3	21.63	0.26	ND	ND	0.19	0.22	
7	30.88	0.55	ND	0.18	0.55	0.74	
14	43.10	0.85	0.52	ND	1.79	0.84	
21	39.18	0.64	0.50	1.10	1.47	1.41	
30	44.62	3.09	0.65	0.53	1.52	ND	
40	38.06	4.66	0.56	1.18	0.52	2.62	
50	39.45	3.57	ND	1.20	ND	3.58	
70	30.48	3.37	ND	1.62	ND	4.13	
100	21.10	1.73	0.89	1.16	ND	3.22	
130	18.19	ND	ND	ND	0.90	5.31	
	DPX-F5384	IN-D1R84	IN-N5297	IN-DAT97	IN-F7880	IN-R9419	Unknown
Phenyl (Pavia Test System)							
0	NA	NA	NA	NA	NA	NA	NA
3	17.77	ND	0.28	ND	ND	0.15	ND
7	17.99	ND	0.28	ND	ND	0.57	0.66
14	17.86	ND	0.49	ND	0.70	0.94	0.51
21	24.87	ND	0.50	ND	2.33	1.20	1.50
30	27.43	ND	0.68	ND	1.00	1.22	0.67
40	25.86	ND	3.32	ND	0.40	ND	2.82
50	22.27	ND	3.70	ND	1.02	0.21	4.40
70	13.61	1.71	2.03	ND	4.09	0.43	2.63
100	10.12	ND	3.90	ND	1.21	1.35	3.22
130	7.49	2.55	4.33	ND	1.20	1.59	2.34
Phenyl (Vercelli Test System)							
0	NA	NA	NA	NA	NA	NA	NA
3	21.39	ND	0.24	ND	ND	0.17	ND
7	33.79	ND	0.40	ND	0.10	0.43	0.78
14	36.28	ND	0.59	ND	0.39	1.13	0.71
21	41.64	ND	0.67	ND	0.79	1.67	1.13
30	38.73	ND	1.75	ND	0.71	1.46	2.65
40	36.12	ND	3.19	ND	0.51	0.22	4.46
50	36.06	1.23	5.85	ND	1.17	0.75	2.14
70	27.75	ND	ND	ND	3.03	ND	6.22
100	23.47	ND	2.85	ND	0.95	0.37	2.96
130	17.98	2.64	1.48	ND	1.27	ND	3.03

^a Unknown radioactivity composed of up to 6 peaks, none of which exceeded 3% AR at any time.

NA = Not analysed; ND = Not detected

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.116: Percent distribution of applied radioactivity in the total test systems treated with ^{14}C -bensulfuron methyl (DPX-F5384)

Day	% of Applied Radioactivity						
	DPX-F5384	IN-J0290	IN-DAT97	IN-F7880	IN-R9419	Unknown ^a	
Pyrimidine (Pavia Test System)							
0	89.28	4.14	ND	ND	0.47	1.21	
3	88.00	1.23	0.46	0.21	1.69	0.41	
7	90.11	0.91	0.70	0.61	2.23	0.74	
14	83.32	1.71	2.54	2.43	3.55	3.05	
21	71.05	3.23	2.01	6.31	4.60	3.12	
30	61.05	10.76	1.96	6.07	6.15	3.71	
40	43.46	12.29	6.29	9.71	2.47	9.38	
50	39.10	14.52	9.86	7.60	0.92	5.70	
70	19.12	18.43	7.64	6.10	1.48	10.23	
100	11.29	16.84	3.51	5.47	1.66	12.03	
130	7.57	19.69	ND	3.06	1.89	18.19	
Pyrimidine (Vercelli Test System)							
0	92.04	5.10	ND	ND	ND	1.66	
3	88.27	0.86	0.29	0.20	1.16	0.82	
7	90.74	1.01	0.35	0.39	1.61	1.1	
14	79.58	2.05	0.86	0.29	3.49	1.33	
21	77.35	1.16	0.75	1.45	3.69	2.20	
30	61.22	6.53	1.06	1.27	3.23	0.7	
40	51.24	8.19	3.59	2.91	0.80	4.27	
50	50.69	7.22	2.72	3.29	ND	5.48	
70	43.15	5.47	2.72	4.49	ND	9.67	
100	29.78	3.73	2.48	3.13	ND	8.88	
130	23.26	0.92	1.25	1.86	0.90	11.61	
	DPX-F5384	IN-D1R84	IN-N5297	IN-DAT97	IN-F7880	IN-R9419	Unknown
Phenyl (Pavia Test System)							
0	94.63	ND	4.67	ND	ND	ND	ND
3	93.12	ND	1.74	ND	0.25	0.90	0.29
7	89.19	ND	1.59	ND	0.42	2.21	1.59
14	85.64	ND	2.07	ND	1.94	2.95	3.30
21	72.91	ND	3.97	ND	4.97	2.78	3.47
30	73.24	ND	5.64	ND	4.77	5.80	4.05
40	45.88	ND	21.04	1.18	5.37	1.53	5.70
50	29.70	ND	27.93	1.38	5.16	0.52	6.71
70	18.40	1.71	27.85	0.96	9.51	0.72	5.05
100	11.59	ND	29.20	ND	5.28	1.60	6.73
130	7.86	4.17	31.73	ND	2.72	1.59	5.23
Phenyl (Vercelli Test System)							
0	92.34	ND	5.46	ND	ND	ND	ND
3	91.52	ND	1.04	ND	0.29	0.75	ND
7	87.24	ND	0.93	ND	0.51	1.44	2.18
14	83.98	ND	1.12	ND	0.65	2.91	1.84
21	76.46	ND	2.12	ND	1.48	3.64	2.10
30	63.50	ND	4.28	ND	1.61	3.58	5.93
40	49.96	0.99	12.49	0.35	2.11	0.64	4.96
50	46.49	1.77	16.13	0.46	2.43	0.87	3.15
70	40.66	2.85	7.29	0.47	5.34	ND	7.29
100	32.83	5.59	6.52	ND	3.23	0.37	5.26
130	24.86	9.95	3.72	ND	3.79	ND	5.58

^a Unknown radioactivity composed of up to 6 peaks, none of which exceeded 3% AR at any time.
ND = Not detected

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Environmental fate and behaviour

Non-extractable residues: The radioactivity associated with the Pavia sediment was more readily extracted than that associated with the Vercelli sediment. In the Vercelli test system, 42.7 and 32.0% AR for the pyrimidine and phenyl labels, respectively, was non-extractable at the end of the study; whereas in the Pavia test system, 19.8 and 12.8% AR for the pyrimidine and phenyl labels, respectively, was not extractable (Table B.8.113). The post-extracted solid (PES) from Day 100 sediment was fractionated by alkaline hydrolysis to the fulvic acid, humic acid, and humin fractions (Table B.8.17).

Table B.8.117: Distribution of Day 100 unextractable components in soil organic matter

System	Soil Fraction	% of Radiolabel	
		Pyrimidine	Phenyl
Pavia	Fulvic acid	13.7	6.0
	Humic acid	6.3	3.4
	Humin	2.9	1.3
Vercelli	Fulvic acid	15.3	15.4
	Humic acid	8.7	7.1
	Humin	11.9	8.4

DT₅₀ and DT₉₀ values of bensulfuron methyl: Degradation kinetics were determined for bensulfuron methyl and its degradation products IN-J0290, IN-N5297, IN-DAT97, IN-F7880 and IN-R9419. For determination of the degradation kinetics each metabolite was assumed to form independently from bensulfuron methyl. The calculated DT₅₀ values of bensulfuron methyl in the water phase ranged from 16-21 days, in the sediment phase between 47-82 days, and in the whole test system between 37-59 days respectively (Table B.8.118 and Table B.8.119). The calculated DT₉₀ values in the water phase were between 52-69 days, in the sediment phase between 157-273 days, and for the total test system between 122-195 days.

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Environmental fate and behaviour

Table B.8.118: DT₅₀ and DT₉₀ values for bensulfuron methyl (DPX-F5384) and degradation products in Pavia test systems

Compound	DT ₅₀ (days)	DT ₉₀ (days)	r ²	Method of calculation
Pavia Test System				
Bensulfuron methyl				
Water	21	69	0.971	Non-Linear First-Order Regression
Sediment	47	157	0.964	Non-Linear First-Order Regression
Whole System	37	122	0.959	Non-Linear First-Order Regression
IN-J0290				
Water	55.3	184	0.986	Non-Linear First-Order Regression
Sediment	ND	ND		
Whole System	ND	ND		
IN-DAT97				
Water	54.3	180	0.988	Non-Linear First-Order Regression
Sediment	ND	ND		
Whole System	34.6	115	0.986	Non-Linear First-Order Regression
IN-F7880				
Water	60.6	201	0.981	Non-Linear First-Order Regression
Sediment	ND	ND		
Whole System	39.2	115	0.982	Non-Linear First-Order Regression
IN-R9419				
Water	9.1	30.1	0.982	Non-Linear First-Order Regression
Sediment	ND	ND		
Whole System	6.9	22.9	0.982	Non-Linear First-Order Regression

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Table B.8.119: DT₅₀ and DT₉₀ values for bensulfuron methyl (DPX-F5384) and degradation products in Vercelli test system

Compound	DT ₅₀ (days)	DT ₉₀ (days)	r ²	Method of calculation
Vercelli Test System				
Bensulfuron methyl				
Water	16	52	0.953	Non-Linear First-Order Regression
Sediment	82	273	0.967	Non-Linear First-Order Regression
Whole System	59	195	0.974	Non-Linear First-Order Regression
IN-J0290				
Water	76.4	254	0.968	Non-Linear First-Order Regression
Sediment	ND	ND		
Whole System	21.1	70.2	0.992	Non-Linear First-Order Regression
IN-N5297				
Water	106	353	0.966	Non-Linear First-Order Regression
Sediment	ND	ND		
Whole System	30.8	102	0.987	Non-Linear First-Order Regression
IN-DAT97				
Water	394	NM	0.970	Non-Linear First-Order Regression
Sediment	ND	ND		
Whole System	37.8	126	0.995	Non-Linear First-Order Regression
IN-F7880				
Water	NM	NM	0.972	Non-Linear First-Order Regression
Sediment	ND	ND		
Whole System	79.1	263	0.994	Non-Linear First-Order Regression
IN-R9419				
Water	7.0	23.2	0.972	Non-Linear First-Order Regression
Sediment	ND	ND		
Whole System	3.5	11.6	0.994	Non-Linear First-Order Regression

ND= Not determined; NM = Not meaningful

DT₅₀ and DT₉₀ values of metabolites: The calculated DT₅₀ values for IN-J0290 in the water phase ranged from 55-76 days and the DT₅₀ in the Vercelli whole test system was 21 days. The calculated DT₅₀ values for IN-DAT97 in the water phase ranged from 54-394 days, while in the whole test system values ranged from 35-38 days. The calculated DT₅₀ value for IN-F7880 in the Pavia water phase was 61 days, while in the whole test system DT₅₀ values ranged from 39-79 days. The calculated DT₅₀ values for IN-R9419 in the water phase ranged from 7-9 days, while in the whole test system values ranged from 3.5-7 days. The calculated DT₅₀ values for IN-N5297 in the Vercelli water phase and whole test system were 106 and 31 days, respectively (Table B.8.118 and Table B.8.119).

Degradation pathway: The proposed degradation pathway is presented in Figure B.8.3. Bensulfuron methyl degraded primarily through the cleavage of the sulfonylurea bridge forming IN-J0290 and IN-N5297. IN-N5297 could in turn undergo ester hydrolysis form IN-D1R84. A minor pathway involves O-demethylation of bensulfuron methyl to form IN-7880. These degradation products were further mineralised to ¹⁴CO₂ and non-extractable residues.

Conclusion:

Bensulfuron methyl dissipates rapidly in both the Pavia and Vercelli water sediment systems, with DT₅₀ values in the water phase of 21 and 16 days, respectively, and DT₉₀ values of 69 and 52 days, respectively. In the sediment phase, bensulfuron methyl had DT₅₀ values of 47 and 82 days and DT₉₀ values of 157 and 273 days in the Pavia and Vercelli test systems, respectively. The DT₅₀ and DT₉₀ values for bensulfuron methyl in Pavia and Vercelli total test systems were 37 and 122 days and 59 and 195 days, respectively. The major degradation pathway of bensulfuron methyl in water sediment systems involves formation of IN-J0290 and IN-N5297. Mineralisation to ¹⁴CO₂ accounted

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for 16.7 to 26.1% AR for pyrimidine and phenyl labels, respectively. IN-DAT97, IN-F7880, IN-D1R84, IN-N5297, and IN-R9419 were all minor metabolites, each accounting for <10% AR.

- 32) *Photodegradation of bensulfuron methyl in a simulated paddy system. Van-Nguyen, A., Theilacker, W. M., 2003.*

Cross reference II, 7.2.1.3.2./03

Guidelines:

No

GLP:

Yes

The study is acceptable

Material and Methods:

One radiolabeled form of bensulfuron methyl was used: [phenyl(U)-¹⁴C]bensulfuron methyl (DuPont SMS #3000320; radiochemical purity >95%). Photodegradation of [¹⁴C]bensulfuron methyl was determined in two natural simulated rice paddy systems (Table B.8.120).

Table B.8.120: Characteristics of the water/sediment systems

System:	System 1	System 2
Location/Source	Irrigation water Cavrini, Italy	Irrigation water Lonoke, Arkansas
WATER		
pH	7.5	7.0
Sodium (ppm)	31	nd
Calcium (ppm)	28	41
Magnesium (ppm)	15	11
Total Organic Carbon (ppm)	10.1	7.7
Total Nitrogen (ppm)	23.3	nd
NO ₃ -N (ppm)	nd	0.1
Phosphate Phosphorus (ppm)	0.5	<0.1
Hardness (mg equivalent CaCO ₃ L ⁻¹) (ppm)	132	149
Total Dissolved Solids (ppm)	256	nd
SEDIMENT		
% Sand	39	67
% Silt	34	22
% Clay	27	11
Texture (USDA)	Loam	Sandy Loam
pH (1:1 soil/water ratio)	8.3	6.9
% Organic Carbon (OM x 0.58)	1.0	0.8
% Total Nitrogen	0.100	nd
Olsen Phosphorus	9	nd
Cation Exchange Capacity (meq/100g)	15.9	6.4
% Moisture (1/3 Bar)	29.7	nd

nd: not determined

Test vessels containing each of the natural water and sediment and a pH 7 buffer were treated with bensulfuron methyl at 0.1 µg bensulfuron methyl per g of water (0.1 mg/L). Non-irradiated water/sediment vessels (dark) and

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irradiated pH 7 buffer solutions were used as controls. Test vessels were incubated outdoor under natural sunlight for up to 26 days. The test vessels were setup in a flow-through system with traps for $^{14}\text{CO}_2$ evolved during the study and maintained between 22-33°C.

The experimental system comprised water-jacketed test vessels with quartz lids containing 2.0 to 2.5 cm height of sediment with an approximately 5-cm layer (approximately 250 mL) of water. A vacuum pump was placed after the $^{14}\text{CO}_2$ volatile traps to ensure a steady flow of air through the system. The water/sediment systems were acclimatised for approximately one week prior to dosing. After the acclimatisation period, water layers were treated with ^{14}C -bensulfuron methyl (0.1 µg bensulfuron methyl g⁻¹ of water based on 250 mL of water).

Samples were removed from the two systems 0, 1, 2, 3, 5, 6, 14, and 26 days after application. Dark control and buffer control samples were removed at 7, 14, and 26 days after application. The presence of $^{14}\text{CO}_2$ in the NaOH traps was determined by LSA of triplicate 1 mL aliquots. Designated microbial biomass samples were analysed at the start, at Day 100 and at termination of the study. Redox potential, dissolved oxygen content, and pH of the water phase along with the sediment phase redox and pH were measured.

Following separation of the water and sediment phases by centrifugation, the total radioactivity of the water phase was determined in triplicate by LSC (liquid scintillation counting). The water phase was then analysed by HPLC using LC-ARC™ (Liquid Chromatography - Accurate Radioisotope Counting) system to determine the amount of ^{14}C -bensulfuron methyl in the sample.

Sediments were extracted three times with 1/9 (v/v) mixture of acetone and 0.1 M ammonium carbonate in reagent water using a wrist action shaker for 30 minutes. The samples were centrifuged to precipitate solids and the extracts decanted. The extracts were combined and the radioactivity quantified by LSC. The combined extracts were concentrated using a Turbo-Vap® to a volume of about 1–2mL. The concentrated extract fraction was transferred and diluted to 10 mL with 80/20 acetonitrile/water. Solids from the concentrated extracts were removed by centrifugation, the supernatant removed and analysed by LSA and HPLC with LC-ARC™.

Remaining extracted sediment residues were air-dried, homogenised, and weighed. Sediment residues were homogenised by grinding with ceramic balls and triplicate aliquots were analysed for radioactivity by combustion followed by liquid scintillation counting. The degradation kinetics were determined for irradiated and dark control samples of bensulfuron methyl in two water/sediment systems and pH 7 buffer. The percent of AR of phenyl radiolabeled form at each time point was plotted and the DT₅₀ and DT₉₀ values were calculated for both both the total water-sediment systems and the water phase and the buffer. Degradation rates were determined for the reported data using a nonlinear regression of conventional first-order kinetic equations. The software program used for this fitting procedure was ModelManager®, Version 1.1 (Cherwell Scientific Limited, Oxford, UK, 1999).

Findings:

Mass balance: Distribution of the total radioactivity of the two water-sediment systems into various fractions (water/sediment phase and non-extractable residues) for each sampling interval are reported in Table B.8.121 to Table B.8.123. Overall recovery in the Cavrini test system ranged from 92.0 to 97.4% of the applied radioactivity. The overall recovery in the Lonoke test system ranged from 87.8 to 98.2% of the applied radioactivity. The overall recovery in the pH 7 buffer test system ranged from 96.9 to 100.0%.

Non-extractable residues: In the Cavrini test system, 33.1 and 16.2% AR of the irradiated and non-irradiated samples, respectively, was non-extractable at the end of the study. In the Lonoke test system, 31.5 and 17.0% AR of

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the irradiated and non-irradiated samples, respectively, was non-extractable at the end of the study (Table B.8.121 to Table B.8.123).

Table B.8.121: Mass balance in Cavrini, Italy rice/paddy system treated with bensulfuron methyl

Time (days)	Percent of Applied ¹⁴ C Radioactivity (Irradiated)				
	Water Phase	Volatiles	Sediment Associated		Total
		KOH Trap (Cumulative)	Extractable	Non-Extractable	
0	91.6	nd	3.4	nd	95.1
1	85.1	nd	11.1	1.2	97.4
2	79.1	0.1	13.8	2.5	95.5
3	71.8	0.1	18.5	3.4	93.8
5	67.6	0.2	21.9	5.8	95.3
7	63.9	0.2	24.2	7.5	95.9
14	52.1	0.3	28.1	16.5	97.0
26	37.5	1.2	20.2	33.1	92.0
	Percent of Applied ¹⁴ C Radioactivity (Non-Irradiated)				
	Water Phase	Volatiles	Sediment Associated		Total
		KOH Trap (Cumulative)	Extractable	Non-Extractable	
0	91.6	nd	3.4	nd	95.1
7	62.0	0.6	28.7	4.9	96.2
14	47.5	1.9	38.2	6.2	93.8
26	42.7	4.3	29.6	16.2	92.8

nd: not detected

Table B.8.122: Mass balance in Lonoke Farm, Arkansas rice/paddy system treated with bensulfuron methyl

Time (days)	Percent of Applied ¹⁴ C Radioactivity (Irradiated)				
	Water Phase	Volatiles	Sediment Associated		Total
		KOH Trap (Cumulative)	Extractable	Non-Extractable	
0	90.1	nd	4.1	nd	94.2
1	84.5	nd	11.6	2.0	98.2
2	75.2	nd	16.8	3.3	95.4
3	69.9	0.1	17.7	4.0	91.7
5	63.1	0.1	19.3	5.3	87.8
7	66.3	0.1	22.8	5.5	94.7
14	52.1	0.8	26.7	13.3	92.9
26	34.4	2.0	24.4	31.5	92.2
	Percent of Applied ¹⁴ C Radioactivity (Non-Irradiated)				
	Water Phase	Volatiles	Sediment Associated		Total
		KOH Trap (Cumulative)	Extractable	Non-Extractable	
0	90.1	nd	4.1	nd	94.2
7	64.4	0.4	25.1	6.7	96.6
14	60.7	0.9	28.8	6.0	96.4
26	45.6	2.3	32.0	17.0	96.9

nd: not detected

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Table B.8.123: Mass balance in pH 7 buffer rice/paddy system treated with bensulfuron methyl

Time (days)	Percent of Applied ¹⁴ C-Radioactivity		
	Water Phase	Volatiles	Total
		KOH Trap (Cumulative)	
0	97.9	nd	97.9
7	99.8	0.2	100.0
14	97.2	1.0	98.2
26	94.7	2.2	96.9

nd: not detected

Distribution between water and sediment: The distribution of radioactivity between water and sediment was similar in both test systems. For both labels, there was slight movement of radioactivity from the water to the sediment. By the end of the study, radioactivity associated with the water accounted for between 11.7 and 31.5% AR. Radioactivity in the sediment phase by the end of the study accounted for between 10.2 and 24.2% AR (Table B.8.124, Table B.8.125).

Table B.8.124: Distribution of bensulfuron methyl (DPX-F5384) between water and sediment: Cavrini, Italy

Time (days)	Percent of Applied Radioactivity (Irradiated)			Percent of Applied Radioactivity (Non-Irradiated)		
	DPX-F5384 Water	DPX-F5384 Sediment	Total system DPX-F5384	DPX-F5384 Water	DPX-F5384 Sediment	Total system DPX-F5384
0	87.1	nd	87.1	87.1	nd	87.1
1	76.3	12.0	88.3	-	-	-
2	69.5	11.7	81.2	-	-	-
3	59.7	15.0	74.7	-	-	-
5	51.4	18.0	69.4	-	-	-
7	46.0	15.2	61.2	55.0	27.0	82
14	23.2	16.6	39.8	37.5	31.4	68.9
26	12.9	10.2	23.1	31.5	23.2	54.7

nd: not detected

Table B.8.125: Distribution of bensulfuron methyl (DPX-F5384) between water and sediment: Lonoke, Arkansas

Time (days)	Percent of Applied Radioactivity (Irradiated)			Percent of Applied Radioactivity (Non-Irradiated)		
	DPX-F5384 Water	DPX-F5384 Sediment	Total system DPX-F5384	DPX-F5384 Water	DPX-F5384 Sediment	Total system DPX-F5384
0	88.6	nd	88.6	88.6	nd	88.6
1	76.6	nd	76.6	-	-	-
2	55.1	12.0	67.1	-	-	-
3	53.3	13.2	66.5	-	-	-
5	46.4	13.4	59.8	-	-	-
7	38.3	15.1	53.4	60.7	23.0	83.7
14	25.8	16.8	42.6	48.2	22.4	70.6
26	11.7	14.5	26.2	29	24.2	53.2

nd: not detected

Principal degradation products: In the irradiated system of Carvini Test System (Table B.8.126, Table B.8.127), the amount of bensulfuron methyl in the water decreased from 87.1% AR at Day 0 to 12.9% at Day 26. Bensulfuron methyl dissipated rapidly in the water phase with the metabolite IN-R9419 detected at greater than 10% AR. Several

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Italy	May 2006	Bensulfuron methyl

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other minor degradation products were also observed, but at levels <10% AR. For the dark control samples, the amount of bensulfuron methyl in the water decreased from 87.1% AR at Day 0 to 31.5% at Day 26. In contrast to the irradiated samples, bensulfuron methyl degraded at a slower rate with several other degradation products observed, but not exceeding 10% AR.

Extractable ¹⁴C-residues in the sediment ranged from 3.4 to 28.1% and 3.4 to 38.2% AR over the course of the study for the irradiated and non-irradiated samples, respectively. The majority of radioactivity detected was bensulfuron methyl, which reached a maximum of 18 and 31.4% AR for irradiated and non-irradiated systems, respectively. Minor degradation products were detected but none exceeded 10% AR.

Table B.8.126: Distribution of the applied radioactivity in the water phase of Cavrini, Italy simulated pond system

Time (days)	Percent of Applied Radioactivity (Irradiated)								
	DPX-F5384	IN-68991	IN-D1R84	IN-YY142	IN-B6895	IN-N5297	IN-F7880	IN-R9419	Others ^a
0	87.1	nd	nd	nd	1.8	nd	0.9	1.9	nd
1	76.3	nd	nd	1.3	2.8	nd	1.6	3.1	nd
2	69.5	nd	nd	2.3	2.9	nd	nd	4.4	nd
3	59.7	nd	nd	2.9	3.2	nd	nd	5.9	nd
5	51.4	nd	nd	3.6	3.5	nd	nd	9.0	nd
7	46.0	nd	nd	3.9	3.8	nd	nd	10.1	nd
14	23.2	1.1	nd	4.0	nd	nd	2.3	13.4	8.1
26	12.9	nd	3.7	2.6	nd	nd	1.9	10.2	6.2
Time (days)	Percent of Applied Radioactivity (Non-Irradiated)								
	DPX-F5384	IN-68991	IN-D1R84	IN-YY142	IN-B6895	IN-N5297	IN-F7880	IN-R9419	Others ^a
0	87.1	nd	nd	nd	1.8	nd	0.9	1.9	nd
7	55.0	nd	nd	nd	0.0	1.9	1.5	3.6	nd
14	37.5	nd	nd	nd	1.7	1.5	4.3	2.6	nd
26	31.5	nd	nd	nd	2.8	1.9	6.5	nd	nd

^a Unknown peaks at different elution time intervals

nd: not detected

Table B.8.127: Distribution of the applied radioactivity in the sediment phase of Cavrini, Italy simulated pond system

Time (days)	Percent of Applied Radioactivity (Irradiated)								
	DPX-F5384	IN-68991	IN-D1R84	IN-YY142	IN-B6895	IN-N5297	IN-F7880	IN-R9419	Others ^b
0 ^a	nd	nd	nd	nd	nd	nd	nd	nd	nd
1	12.0	nd	nd	nd	nd	nd	nd	nd	0.9
2	11.7	nd	nd	nd	nd	nd	nd	nd	1.9
3	15.0	nd	nd	nd	nd	nd	nd	0.2	2.0
5	18.0	nd	nd	0.7	nd	nd	nd	0.4	4.0
7	15.2	nd	nd	0.5	nd	nd	0.3	0.5	5.4
14	16.6	nd	nd	1.8	nd	nd	0.9	0.5	8.4
26	10.2	nd	1.8	1.9	nd	nd	1.8	1.0	3.5
Time (days)	Percent of Applied Radioactivity (Non-Irradiated)								
	DPX-F5384	IN-68991	IN-D1R84	IN-YY142	IN-B6895	IN-N5297	IN-F7880	IN-R9419	Others ^b
0 ^a	nd	nd	nd	nd	nd	nd	nd	nd	nd
7	27.0	nd	nd	nd	nd	nd	nd	nd	1.6
14	31.4	nd	0.9	nd	nd	0.7	0.4	0.6	4.2
26	23.2	nd	nd	0.5	nd	nd	3.4	1.1	1.5

^a Day 0 sample was not analysed due to low level of radioactivity (<3.4% AR)

^b Unknown peaks at different elution time intervals

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Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

In the irradiated system of Lonoke Test System (Table B.8.128, Table B.8.129), the amount of bensulfuron methyl in the water decreased from 88.6% AR at Day 0 to 11.7% at Day 26. Bensulfuron methyl degraded rapidly in the water phase with the metabolite, IN-R9419, detected at greater than 10% AR and declined at 26 days. Several other degradation products were also observed, but not exceeding 5% AR. In the dark control samples, the amount of bensulfuron methyl in the water decreased from 88.6% AR at Day 0 to 29.0% at Day 26. In contrast to the irradiated samples, bensulfuron methyl degraded at a slower rate with the metabolite, IN-F7880 detected and increased to 11.4% at 26 days. Several other degradation products were also observed but at levels <3% AR.

Table B.8.128: Distribution of the applied radioactivity in the water phase of Lonoke, Arkansas simulated pond system

Time (days)	Percent of Applied Radioactivity (Irradiated)								
	DPX-F5384	IN-68991	IN-D1R84	IN-YY142	IN-B6895	IN-N5297	IN-F7880	IN-R9419	Others ^a
0	88.6	nd	nd	nd	1.5	nd	nd	nd	nd
1	76.6	nd	nd	nd	1.9	nd	nd	6.0	nd
2	55.1	0.7	nd	2.6	3.5	1.4	1.4	9.3	1.3
3	53.3	nd	nd	2.1	3.0	1.4	nd	10.1	nd
5	46.4	nd	nd	3.1	nd	1.1	nd	9.1	3.4
7	38.3	1.8	nd	6.1	nd	1.0	2.3	11.8	5.0
14	25.8	1.2	nd	5.2	1.1	nd	nd	11.0	7.9
26	11.7	1.8	nd	4.7	nd	nd	2.2	5.9	8.0
Time (days)	Percent of Applied Radioactivity (Non-Irradiated)								
	DPX-F5384	IN-68991	IN-D1R84	IN-YY142	IN-B6895	IN-N5297	IN-F7880	IN-R9419	Others ^a
0	88.6	nd	nd	nd	1.5	nd	nd	nd	nd
7	60.7	nd	nd	nd	nd	1.5	2.2	nd	nd
14	48.2	nd	nd	nd	2.2	nd	7.6	2.6	nd
26	29.0	nd	nd	nd	1.4	nd	11.4	nd	3.8

^a Unknown peaks at different elution time intervals

nd: not detected

Table B.8.129: Distribution of the applied radioactivity in the sediment phase of Lonoke, Arkansas simulated pond system

Time (days)	Percent of Applied Radioactivity (Irradiated)								
	DPX-F5384	IN-68991	IN-D1R84	IN-YY142	IN-B6895	IN-N5297	IN-F7880	IN-R9419	Others ^b
0 ^a	nd	nd	nd	nd	nd	nd	nd	nd	nd
1	nd	nd	nd	nd	nd	nd	nd	nd	2.0
2	12.0	0.1	0.1	0.1	nd	nd	0.1	0.2	2.6
3	13.2	0.3	nd	0.2	nd	nd	0.1	0.3	3.6
5	13.4	0.3	0.2	0.3	nd	0.2	0.3	0.3	4.4
7	15.1	0.2	0.9	0.3	nd	0.2	0.3	0.3	5.4
14	16.8	nd	nd	1.0	1.5	nd	1.2	0.6	5.6
26	14.5	nd	nd	1.4	nd	nd	0.5	0.8	7.1
Time (days)	Percent of Applied Radioactivity (Non-Irradiated)								
	DPX-F5384	IN-68991	IN-D1R84	IN-YY142	IN-B6895	IN-N5297	IN-F7880	IN-R9419	Others ^b
0 ^a	nd	nd	nd	nd	nd	nd	nd	nd	nd
7	23.0	nd	nd	nd	nd	nd	2.1	nd	nd
14	22.4	nd	nd	nd	nd	1.8	1.5	nd	3.2
26	24.2	nd	nd	nd	nd	nd	1.6	1.1	5.1

^a Day-0 sample was not analysed due to low level of radioactivity (<4.1%)

^b Unknown peaks at different elution time intervals

nd: not detected

Extractable ¹⁴C-residues ranged from 4.1 to 26.7% and 4.1 to 32% AR over the course of the study for the irradiated and non-irradiated samples, respectively. The majority amount of radioactivity detected was bensulfuron methyl,

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which reached a maximum of 16.8 to 24.2% AR for irradiated and non-irradiated systems, respectively. Degradation products were detected but in negligible amounts.

The amount of bensulfuron methyl in the irradiated samples of pH 7 buffer system (Table B.8.130) decreased slowly from 95.5% on Day 0 to 71.9% at Day 26.

Table B.8.130: Distribution of the applied radioactivity in the pH 7 buffer system

Time (days)	Percent of Applied Radioactivity (Irradiated)								
	DPX-F5384	IN-68991	IN-D1R84	IN-YY142	IN-B6895	IN-N5297	IN-F7880	IN-R9419	Others ^a
0	95.5	nd	nd	nd	nd	2.4	nd	nd	nd
7	92.8	nd	nd	2.5	nd	4.6	nd	nd	nd
14	80.3	nd	nd	3.5	2.1	6.0	3.4	nd	2.0
26	71.9	1.5	nd	7.1	3.4	7.2	2.7	nd	0.9

^a Unknown peaks at different elution time intervals

nd: not detected

DT₅₀ and DT₉₀ values of bensulfuron methyl: The calculated DT₅₀ values of bensulfuron methyl in the irradiated water phase were 7.7 days in the Cavrini system, 6.7 days in the Lonoke system, and 50.3 days in the pH 7 system. The calculated DT₉₀ values in the water system ranged from 25.6 days in the Cavrini system, 22.4 days in the Lonoke system, and 167 days in the pH 7 system. All results are reported in Table B.8.131.

Table B.8.131: DT₅₀ and DT₉₀ values for bensulfuron methyl (DPX-F5384) in simulated pond test systems

Test System	DT ₅₀ (days)	DT ₉₀ (days)	r ²	Method of calculation
Carvini, Italy				
Irradiated Water	7.7	25.6	0.987	Non-Linear First-Order Regression
Non-Irradiated Water	14.3	47.5	0.937	
Irradiated Total System	12.7	42.2	0.993	
Non-Irradiated Total System	33.1	110.0	0.936	
Lonoke, Arkansas				
Irradiated Water	6.7	22.4	0.930	Non-Linear First-Order Regression
Non-Irradiated Water	15.8	52.6	0.991	
Irradiated Total System	14.2	47.3	0.944	
Non-Irradiated Total System	35.9	119	0.963	
pH 7 Buffer				
Irradiated Water	50.3	167	0.937	Non-Linear First-Order Regression

Conclusion:

In this high tier study that represented the real field condition for rice paddy system, bensulfuron methyl dissipated rapidly from the two aqueous phases by natural sunlight, with an average DT₅₀ value for bensulfuron methyl in the water phase of 7.2 days as compared to 50 days in the pH 7 buffer system. The major degradation was IN-R9419, detected at greater than 10% AR. The most significant dissipation mechanisms for bensulfuron methyl in rice paddies appear to be indirect photolysis of bensulfuron methyl from the aqueous phases and partitioning of bensulfuron methyl in the paddy sediment.

B.8.4.5 Degradation in the saturated zone of active substance, metabolites, degradation and reaction products (Annex IIA 7.2.1.4)

Bensulfuron methyl and its degradation products do not show significant leaching potential by reason of intended

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Environmental fate and behaviour

mode of use. Therefore, no study were provided to address this topic.

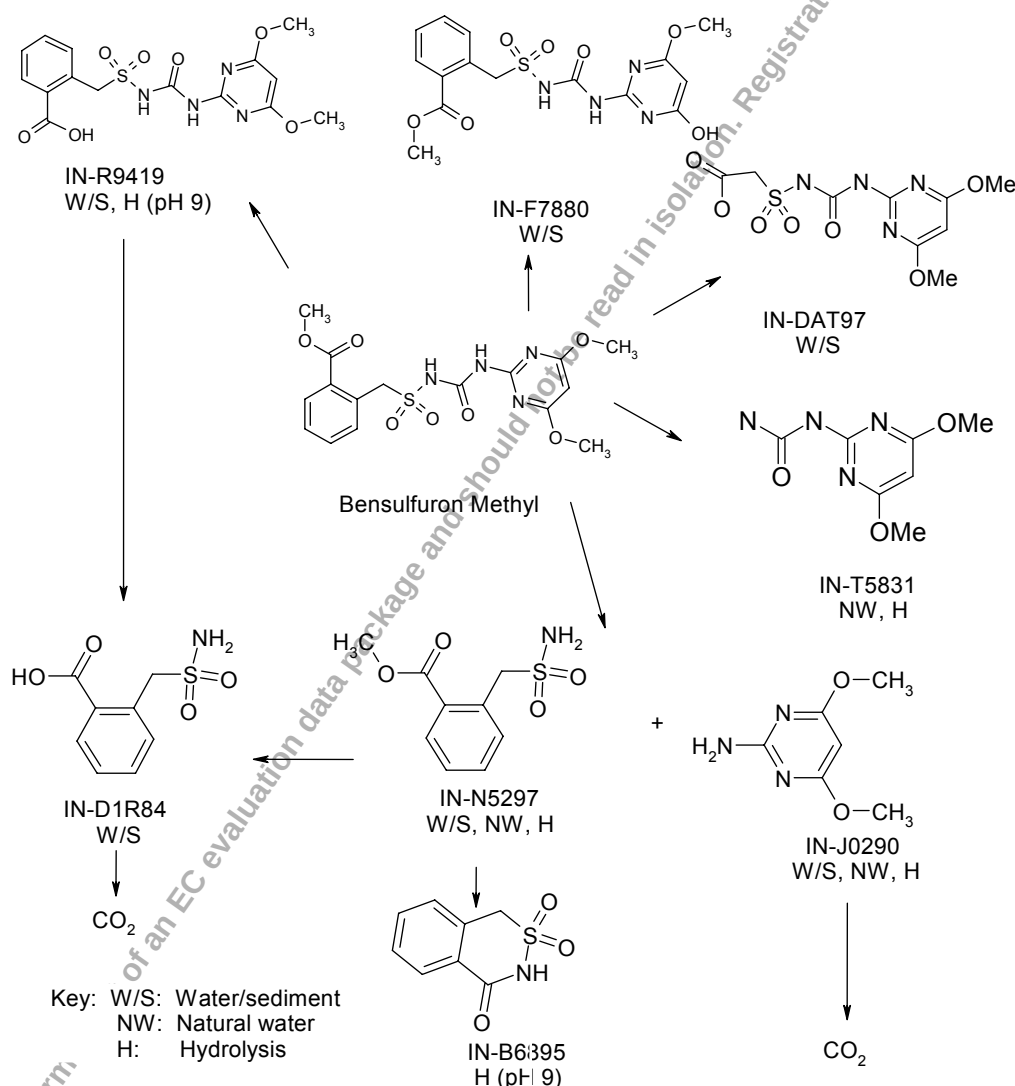
B.8.5 Impact on water treatment procedures (Annex IIIA, 9.2.2)

Studies on the impact on water treatment procedures have not been submitted.

B.8.6 Summary of Behaviour in Water and Predicted Environmental Concentrations in surface water and in ground water (PEC_{sw}, PEC_{gw}) (Annex IIIA 9.2.1, 9.2.3)

The proposed degradation pathway of bensulfuron methyl in aquatic systems is presented in Figure B.8.3.

Figure B.8.3: Proposed degradation pathways of bensulfuron methyl in the aquatic systems



Hydrolytic degradation of bensulfuron methyl in aqueous buffer solutions was determined at pH 4, 7, and 9. Bensulfuron methyl hydrolysed rapidly at pH 4. Hydrolysis is a significant degradation process for bensulfuron methyl under acidic conditions, but hydrolysis is much less significant under neutral or basic conditions. The hydrolysis of the sulfonyleurea bridge of bensulfuron methyl produces IN-J0290 and IN-N5297. IN-N5297 cyclises to form homosaccharin (IN-B6895). At pH 9, de-esterification of bensulfuron methyl occurs to form IN-R9419. The

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DT₅₀ for bensulfuron methyl for hydrolysis at pH 4 and 9 was 6 and 141 days, respectively. Bensulfuron methyl was stable at pH 7.0.

The aqueous photodegradation of bensulfuron methyl was investigated at pH 5, 7, and 9. The degradation of bensulfuron methyl in aqueous solution exposed to natural sunlight is dependent on the pH of the solution with half-lives ranging from 13 days at pH 5 to greater than 200 days at pH 9. However, when observed degradation rates are corrected for the hydrolysis component, the photolysis component is insignificant (half-life greater than 400 days) and independent of pH in the range of 5-9. These results are consistent with the UV absorption spectrum of bensulfuron methyl that showed little or no absorption in the region above 290 nm. The quantum efficiency of bensulfuron methyl was calculated to be 0.00003. Since sunlight reaching the earth's surface only contains significant radiation above 290 nm, little or no direct photolysis of bensulfuron methyl is expected.

The photolytic stability of bensulfuron methyl was studied in two natural waters and sterile pH 7 aqueous buffer solutions. The test systems were continuously irradiated for 15 days using a xenon arc simulated sunlight source (intensity equal to midday summer sunlight at a latitude of 52°N; equivalent to 28 days of sunlight) at 25°C under sterile conditions. The photolysis half-life of bensulfuron methyl in Cavrini Farm was 10 days as compared to 29 days in sterile pH 7 buffer, which suggests that the increase in the rate of degradation of bensulfuron methyl in Cavrini Farm is primarily due to indirect photolysis of bensulfuron methyl. In the Ten-Mile Creek natural water system, the photolysis half-life was 89 days. The longer half-life of bensulfuron methyl in the Ten-Mile Creek natural water test system compared to the pH 7 buffer test system is most likely a result of the high dissolved organic carbon (DOC) of the Ten-Mile Creek water. The high DOC concentration of the water not only reduced the light intensity (25% reduction), but may also be responsible for scavenging of free radicals from the test system. The major degradation product that formed in the irradiated natural water system >10% was IN-T5831. Based on the results of this study, indirect photolysis may contribute significantly to elimination of bensulfuron methyl from the environment and direct photolysis will be a minor route of elimination.

Photodegradation of bensulfuron methyl in a simulated paddy system was also studied in two water/sediment systems collected from Cavrini, Italy and Lonoke, Kansas, U.S.A. In this high tier study, which represented the real field situation of the rice paddy system, bensulfuron methyl dissipated rapidly in the water phase of Cavrini system with the metabolite IN-R9419 detected at greater than 10% AR. Several other minor degradation products were also observed, but at levels <10% AR. For the dark control samples, bensulfuron methyl degraded at a slower rate with several other degradation products observed, but none exceeding 10% AR. The amount of bensulfuron methyl in the water decreased from 87.1% AR at Day 0 to 31.5% at Day 26. In the Lonoke water/sediment system, bensulfuron methyl degraded rapidly in the water phase with the metabolite, IN-R9419, detected at greater than 10% AR and declined at 26 days. Several other degradation products were also observed, but none exceeding 5% AR. In the dark control samples, the amount of bensulfuron methyl in the water decreased from 88.6% AR at Day 0 to 29.0% at Day 26. In contrast to the irradiated samples, bensulfuron methyl degraded at a slower rate with the metabolite, IN-F7880 detected and increased to 11.4% in water phase at 26 days. Several other degradation products were also observed but at levels <3% AR. The calculated DT₅₀ values of bensulfuron methyl in the water phase ranged from 7.7 days in the Cavrini system, 6.7 days in the Lonoke system, and 50.3 days in the pH 7 system. The calculated DT₉₀ values in the water system ranged from 25.6 days in the Cavrini system, 22.4 days in the Lonoke system, and 167 days in the pH 7 system.

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Environmental fate and behaviour

The rate and route of degradation of bensulfuron methyl was studied in two Italy water/sediment systems. Bensulfuron methyl degrades rapidly in both the Pavia and Vercelli water sediment systems with DT₅₀ values in the water phase of 21 and 16 days, respectively. In the sediment phase, bensulfuron methyl, had DT₅₀ values of 47 and 82 in the Pavia and Vercelli test systems, respectively. The DT₅₀ values for bensulfuron methyl in Pavia and Vercelli total test systems were 37 and 122 days, respectively. The major degradation products in water phase were IN-J0290 and IN-N5297, which exceeded 10%. IN-J0290 exceeded 10% in the sediment of the Pavia test system and non-extractable residues exceeded in both test systems. Mineralisation to ¹⁴CO₂ accounted for 16.7 to 26.1% AR for pyrimidine and phenyl labels, respectively. Other minor degradation products that formed below 10% in the total phase were IN-R9419, IN-F7880, IN-DAT97, and IN-D1R84. The DT₅₀ values of IN-DAT97, IN-F7880, and IN-R9419 in the total phase of Pavia test system were 35, 39, and 7 days, respectively. The DT₅₀ values of IN-J0290, IN-DAT97, IN-F7880, IN-N5297, and IN-R9419 in the total phase of Vercelli test system were 21, 31, 38, 79, and 4 days, respectively.

The rate of degradation of bensulfuron methyl was also studied in two Japan and one US water/sediment system. Bensulfuron methyl degraded under aerobic aquatic conditions. IN-N5297 (sulfonamide), IN-J0290 (pyrimidine amine), and IN-F7880 were identified as the major degradation products (<10%). The averaged DT₅₀ values of bensulfuron methyl were 66, 50, and 87 days for California, Nagano, and Tochigi soil systems, respectively. The respective averaged DT₉₀ values were 220, 167, and 289 days. An uncommon aquatic degradation product IN-N8989 was also detected and peaked to 11.5% at 7 days in the [¹⁴C-phenyl] label but quickly declined to 0.5% after 14 days in California soil system. The formation of IN-N8989 was not significant (<1.7% AR) in the [¹⁴C-pyrimidine] label, suggesting that this was a transient product. The formation of ¹⁴CO₂ was negligible in either label.

B.8.6.1 Estimation of concentrations in groundwater (IIIA 9.2.1)

- 23) *Predicted Environmental Concentrations of Bensulfuron Methyl and Metabolites in Soil, Ground water, Surface water, Sediment, and Air Following Application to Rice in the EU. Warren, R.L., 2004.*

Cross reference IIIA 9.1.3/01, IIIA 9.2.1/01, IIIA 9.2.3/01

- 24) *Predicted Environmental Concentrations of Bensulfuron Methyl and Metabolites in Soil, Ground water, Surface water, Sediment, and Air Following Application to Rice in the EU. Revision No. 1, Warren, R.L., 2006.*

Cross reference not provided

Guidelines:

Not applicable - calculations.

GLP:

Not applicable - calculations.

The study is acceptable

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Material and methods

Modelling approach. Annual average PEC_{gw} values were calculated for bensulfuron methyl and metabolites IN-J0290, IN-DAT97, IN-F7880, IN-R9419, IN-N5297, IN-D1R84, and IN-T5831 based on the procedures described in Med-Rice (2003), with some modification. The calculation procedure was modified after a mass balance accounting error was noted in the equations used to calculate PEC_{gw} . When following the Med-Rice equations explicitly, the mass of compound leached could be higher than the amount applied. This is due to the fact that when calculating PEC_{pw} there is no accounting for the dilution effect from inflowing water to replace water lost by infiltration. Not accounting for this dilution leads to over estimation of the amount bensulfuron methyl remaining in the infiltrating paddy water on which PEC_{gw} is based.

To account for the inflowing water dilution effect (mass loss to infiltration), the infiltration rates for the clay scenario (1 mm/d) and the sand scenario (10 mm/d) were converted to rate constants (0.01 and 0.1 d⁻¹, respectively). These rate constants were added to equations 4, 5, 8, and 10 given in section 5.3 of Med-Rice (2003). In this way the “dissipation” of compound in paddy water due to dilution is accounted for in the same manner as already done for paddy outflow when the paddy is open.

Assumptions and input parameters used in groundwater modelling. A single application of 60 g a.s./ha to flooded rice was simulated per proposed Good Agricultural Practices (GAP). Foliar interception was conservatively assumed not to occur (100% reaching the flooded paddy surface). Where available, the longest total system first-order DT_{50} values from the water/sediment study were used to represent degradation in paddy water and paddy soil. Alternatively, the geometric mean DT_{50} from the aerobic soil degradation study was selected. The average K_{FOC} was used to represent sorption. PEC_{gw} values for metabolites were calculated in the same manner as for bensulfuron methyl, but with the dose rate determined using the maximum percentage formed in any environmental fate study and the molecular weight conversion. In Table B.8.86 for a listing of K_{FOC} , first-order DT_{50} , and application rates used in the PEC_{gw} calculations of bensulfuron methyl and associated metabolites.

As the supported GAP suggest the possible application in saturated land (1 cm water), RMS recalculated annual average PEC_{gw} for this peculiar type of application with the same modified version of tier 1 Med-Rice used by notifier.

Results:

The annual average PEC_{gw} values for bensulfuron methyl and its major degradation products are given in Table B.8.132.

Table B.8.132: PEC_{gw} values determined using a modification of the procedures given in Med-Rice (2003)

Compound	Annual average PEC_{gw} (µg/L) ^{a,b}		
	Clay scenario (10 and 1 cm water)	Sand scenario (10 cm water)	Sand scenario (1 cm water)
bensulfuron methyl	0.0000	0.0391	0.0356
IN-F7880	0.0000	0.0149	0.0154
IN-R9419	0.0000	0.0000	0.0000
IN-D1R84	0.0000	0.0126	0.0629
IN-J0290	0.0000	0.0000	0.0000
IN-N5297	0.0000	0.0633	0.1545
IN-T5831	0.0000	0.0275	0.126
IN-DAT97	0.0003 (0.0007 with 1 cm water)	0.0524	0.229

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

No problem for leaching are identified for bensulfuron methyl and major metabolites in the clay scenario with both types of application. For the sand scenario, the typical application on flooded soil (10 cm) does not show a significant risk for groundwater. On the other hand, application on saturated land might present some leaching concerns for the major metabolites IN-N5297 and for the minor metabolites IN-T5831 and IN-DAT97. This concern should be addressed by those MS, where the application on saturated land is a common practice in areas characterised by sand scenarios for rice crop.

Conclusions:

The annual average PEC_{gw} values for bensulfuron methyl and its major degradation products have been addressed using a modified version of tier 1 Med-Rice. No problem for leaching are identified for bensulfuron methyl and major metabolites in the clay scenario with both types of application. For the sand scenario, the typical application on flooded soil (10 cm) does not show a significant risk for groundwater. On the other hand, application on saturated land might present some leaching concern for the major metabolites IN-N5297, and for the minor metabolites IN-T5831 and IN-DAT97. This concern should be addressed by those MS, where the application on saturated land is a common practice in areas characterised by sand scenarios for rice crop.

B.8.6.2 Estimation of concentrations in surface water and sediment (IIIA 9.2.3)

- 23) *Predicted Environmental Concentrations of Bensulfuron Methyl and Metabolites in Soil, Ground water, Surface water, Sediment, and Air Following Application to Rice in the EU. Warren, R.L., 2004.*

Cross reference IIIA 9.1.3/01, IIIA 9.2.1/01, IIIA 9.2.3/01

- 24) *Predicted Environmental Concentrations of Bensulfuron Methyl and Metabolites in Soil, Ground water, Surface water, Sediment, and Air Following Application to Rice in the EU. Revision No. 1, Warren, R.L., 2006.*

Cross reference not provided

Guidelines:

Not applicable - calculations.

GLP:

No.

The study is acceptable

Material and methods:

Modelling approach

Tier 1 Med-Rice. PEC_{sw} and PEC_{sed} values were calculated for bensulfuron methyl and metabolites IN-J0290, IN-DAT97, IN-F7880, IN-R9419, IN-N5297, IN-D1R84, and IN-T5831 using the procedures described in Med-Rice (2003). The initial paddy water concentration PEC_{pw} was calculated assuming the maximum application rate (60 g a.s./ha), a paddy water depth of 10 cm, and following instantaneous, irreversible sorption to paddy soil as described for PEC_{soil} . Foliar interception was conservatively assumed to be zero for the Tier 1 calculations.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

PEC_{sw} is defined as the PEC in water of a static ditch receiving surface water drainage directly from a treated paddy. PEC_{sed} is defined as the sediment in this ditch with an organic carbon content of 1.6%, bulk density of 1.5 g/cm³, and active sorption depth of 5 cm. Applied compounds may reach the ditch by spray drift (assumed 2.77% for a ground spray broadcast application) and by movement with the drainage water coming from the treated paddy. Partitioning of the drift component between ditch water and sediment was defined as an instantaneous, irreversible process. The contribution of drift and drainage were summed to give the initial PEC_{sw} and PEC_{sed}. Metabolite PEC values were calculated in the same manner as for bensulfuron methyl, but with the dose rate determined using the maximum percentage formed in any environmental fate study and the molecular weight conversion.

Where available, the longest total system first-order DT₅₀ values from the water/sediment study were used to represent degradation in paddy water. Alternatively, the geometric mean DT₅₀ from the aerobic soil degradation study was selected. The average K_{FOC} was used to represent sorption.

See Table B.8.86 for a listing of K_{FOC}, first-order DT₅₀, and application rates used in the Tier 1 calculations.

Higher Tier RICEWQ/RIVWQ Simulations. PEC values were determined for bensulfuron methyl using RICEWQ version 1.64 for the paddy (PEC_{pw}) and RIVWQ version 2.02 for ditches, canals, and the river (PEC_{sw} and PEC_{sed}). The linked model system was conceptualised as a small, intensively cropped watershed of 2000 ha, which was divided into 10 management blocks of 200 ha each. Each paddy was 2 ha in size. Paddies drained to ditches, canals, and then a river. The timing of key agronomic activities, such as flooding, drainage, and bensulfuron methyl application were identical for each management block in relation to the date of rice sowing. The date of sowing was randomly varied among the blocks between 24-April and 14-May, typical timing for bensulfuron methyl applications to rice. Randomly varying the date of rice sowing and related management activities in the 2000 ha watershed increased the realism of the simulations through the interaction of variable agronomic timing with variable daily weather. Daily meteorological inputs from Roujan, France; Thiva, Greece; Piacenza, Italy; Porto, Portugal; and Sevilla, Spain were imposed on the watershed for a simulation period of 20 years each. These long term daily weather files, representative of the major European rice production areas, were used to assess the impact of variable weather patterns on the PEC values.

A single post emergence application of bensulfuron methyl was simulated to occur 30 days post sowing (representative of BBCH 20, tillering) in each year with 50% foliar interception. Foliar interception was assumed to be 50% as recommended from the literature, which is consistent with foliar interception estimates from field studies conducted with bensulfuron methyl in Italy. 25% of the watershed (50 ha per management block, 500 ha total) was treated, which is assumed to be a realistic upper limit based on the typical usage of bensulfuron methyl and a watershed of this size. Twenty five, 2-ha paddies (50 ha total) receiving treatment were randomly selected for one of the 200 ha management blocks. This randomization pattern was then repeated for the other nine management blocks. Soil and hydrology of the model system were based on information from the Med-Rice guidance document (clay scenario), field notes and photos from European rice fields, and discussions with local rice experts. A summary of the key inputs are given in Table B.8.87 for RICEWQ and Table B.8.133 for RIVWQ.

PEC_{sw} and PEC_{sed} in receiving ditches, canals, and the river were generated using RIVWQ. One ditch node and one canal node in each management block was assessed for each meteorological scenario. The nodes “sampled” for PEC output were selected to coincide with logical points that might be sampled in a real watershed, such as the outflow from a treated paddy into a ditch, the outflow from a ditch into a canal, and the outflow from a canal into the river. Daily PEC values for the one river node at the exit of the watershed were also evaluated. This node was exposed to

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

simulated drainage from all 2000 ha of rice paddies in the watershed. In this way the effect of variable agronomic timing (over the 10 management blocks) and variable weather patterns (over the five meteorological scenarios) could be evaluated.

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.133: RIVWQ input parameters and simulation information

Parameter	Value used	Source/rationale
Simulation		
• RIVWQ model version	2.02	Williams, et al. 1999b
• simulation duration (years)	20	Duration to match the FOCUS daily weather files
Bensulfuron methyl parameters		
• initial concentration in water (mg/L)	0	not used
• initial concentration in sediment	0	not used
• K_{OC} (mL/g)	315	Priester, 1985
• water solubility (mg/L)	67	Moore, 1994
• ditch/canal/river water DT_{50} (days)	7	Van-Nguyen & Theilacker, 2003; Anselmetti et al. 1999
• ditch/canal/river sediment DT_{50} (days)	118	Cadwgan and Ryan, 1986
• volatilization coefficient (m/d)	0	not used
• Application drift into ditches adjacent to treated paddies (%)	2.77	FOCUS, 2001; Med-Rice, 2003 – page 59
Aquatic/sediment parameters		
• settling velocity (m/day)	2.0	Calculated for fine grained particles (Guy, 1977)
• mixing velocity (diffusion) (m/day)	0.01	Within range of 0 to 0.1 m/day (Arnold et al. 1991)
• suspended sediment concentration (mg/L)	45	Capri et al., 2002
• mixing depth for sediment partitioning (cm)	0.08	Professional judgment
• depth of active sediment layer (cm)	5	Med-Rice, 2003 – page 53
• porosity of bed sediment (cm^3/cm^3)	0.43	Calculated from bulk density (Arnold et al., 1991)
• sediment bulk density (g/cm^3)	1.50	Med-Rice, 2003 – page 84
Ditch parameters		
• Top width (m)	1.0	Field notes & photos ^a ; Spain, Portugal, France maps
• Length between ditch nodes (m)	100.0	Paddy width
• Base depth (m)	0.5	Field notes and photos ^a
• QC coefficient in stage-flow rating curve for depth	4.16	Calculated for 0.01 m/s velocity and 0.5 m base depth
• QD exponent in stage-flow rating curve for depth	0.40	Average exponent value (Knighton, 1984)
• Longitudinal dispersion (m^2/s)	0.01	Fischer et al., 1979
• Muskingum-K coefficient	10000	Calculated by dividing the length by velocity of 0.01 m/s
• Muskingum-X coefficient	0.20	Typically 0.1 to 0.3
Canal parameters		
• Top width (m)	2.0	Field notes & photos ^a ; Spain, Portugal, France maps
• Length between canal nodes (m)	200.0	Paddy length
• Base depth (m)	1.0	Med-Rice, 2003 – page 53; Field notes and photos ^a
• QC coefficient in stage-flow rating curve for depth	3.08	Calculated for 0.03 m/s velocity and 1.0 m base depth
• QD exponent in stage-flow rating curve for depth	0.40	Average exponent value (Knighton, 1984)
• Longitudinal dispersion (m^2/s)	5.0	Fischer et al., 1979
• Muskingum-K coefficient	6666.7	Calculated by dividing the length by velocity of 0.03 m/s
• Muskingum-X coefficient	0.20	Typically 0.1 to 0.3
River parameters		
• Top width (m)	25	Spain, Portugal, France maps
• Length between river nodes (m)	10000	Paddy block length
• Depth (m)	2.0	Med-Rice, 2003 – page 42
• QC coefficient in stage-flow rating curve for depth	1.05	Calculated for 0.1 m/s velocity and 2.0 m base depth
• QD exponent in stage-flow rating curve for depth	0.40	Average exponent value (Knighton, 1984)
• Longitudinal dispersion (m^2/s)	5.0	Fischer et al., 1979
• Base flow (m^3/s)	5.0	Calculated based on a 0.1 m/s velocity
• Muskingum-K coefficient	10000	Calculated by dividing the length by velocity of 0.1 m/s
• Muskingum-X coefficient	0.20	Typically 0.1 to 0.3

^a Field notes and photos from Waterborne Environmental, Incorporated.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Results:

The Tier 1 paddy water (PEC_{pw}), ditch water (PEC_{sw}), and ditch sediment (PEC_{sed}) values for bensulfuron methyl and its degradates are given in Table B.8.134 to Table B.8.139.

Table B.8.134: Clay scenario Tier 1 PEC_{pw} values ($\mu\text{g/L}$) for bensulfuron methyl and degradates in the paddy determined using the methods given in Med-Rice (2003)

Chemical	Actual or TWA ($\mu\text{g/L}$)	Days after application										
		0	1	2	4	7	14	21	28	42	50	100
bensulfuron methyl	Actual	11.4	11.3	11.2	10.9	10.5	9.69	8.92	8.22	6.97	6.35	3.53
	TWA	--	11.4	11.3	11.2	11.0	10.5	10.1	9.73	9.02	8.64	6.72
IN-F7880	Actual	1.49	1.47	1.46	1.44	1.40	1.31	1.24	1.16	1.03	0.959	0.619
	TWA	--	1.48	1.47	1.46	1.44	1.40	1.36	1.32	1.24	1.20	0.990
IN-R9419	Actual	3.99	3.61	3.26	2.67	1.97	0.977	0.484	0.239	0.0587	0.0263	0.0002
	TWA	--	3.79	3.61	3.28	2.86	2.14	1.66	1.33	0.931	0.789	0.397
IN-D1R84	Actual	5.10	4.77	4.45	3.87	3.17	1.97	1.22	0.761	0.294	0.171	0.0057
	TWA	--	4.93	4.77	4.46	4.06	3.29	2.72	2.28	1.68	1.45	0.750
IN-J0290	Actual	1.45	1.40	1.36	1.27	1.15	0.914	0.726	0.577	0.364	0.280	0.0542
	TWA	--	1.42	1.40	1.36	1.29	1.16	1.05	0.947	0.785	0.711	0.424
IN-N5297	Actual	7.13	6.97	6.82	6.52	6.09	5.21	4.45	3.80	2.77	2.32	0.752
	TWA	--	7.05	6.98	6.82	6.60	6.12	5.68	5.29	4.61	4.28	2.84
IN-T5831	Actual	3.53	3.42	3.31	3.10	2.81	2.30	1.77	1.41	0.889	0.683	0.132
	TWA	--	3.47	3.42	3.31	3.15	2.83	2.55	2.31	1.92	1.73	1.03
IN-DAT97	Actual	4.13	4.06	3.99	3.84	3.64	3.20	2.82	2.48	1.92	1.65	0.661
	TWA	--	4.10	4.06	3.99	3.88	3.65	3.43	3.24	2.88	2.71	1.90

For presentation purposes, PEC values were rounded to three significant figures or to a maximum of four decimal places.

Table B.8.135: Sand scenario Tier 1 PEC_{pw} values ($\mu\text{g/L}$) for bensulfuron methyl and degradates in the paddy determined using the methods given in Med-Rice (2003)

Chemical	Actual or TWA ($\mu\text{g/L}$)	Days after application										
		0	1	2	4	7	14	21	28	42	50	100
bensulfuron methyl	Actual	19.2	19.0	18.7	18.3	17.7	16.3	15.0	13.8	11.7	10.7	5.9
	TWA	--	19.1	19.0	18.7	18.4	17.7	17.0	16.4	15.1	14.5	11.3
IN-F7880	Actual	2.35	2.33	2.31	2.27	2.21	2.08	1.96	1.84	1.63	1.52	0.979
	TWA	--	2.34	2.33	2.31	2.28	2.21	2.15	2.08	1.97	1.90	1.56
IN-R9419	Actual	6.39	5.78	5.23	4.28	3.16	1.57	0.775	0.383	0.0940	0.0421	0.0003
	TWA	--	6.08	5.79	5.26	4.59	3.43	2.66	2.14	1.49	1.26	0.636
IN-D1R84	Actual	5.39	5.04	4.71	4.11	3.35	2.08	1.29	0.804	0.311	0.180	0.0060
	TWA	--	5.21	5.04	4.72	4.29	3.48	2.87	2.41	1.78	1.53	0.793
IN-J0290	Actual	2.54	2.46	2.38	2.23	2.02	1.60	1.28	1.01	0.640	0.492	0.0952
	TWA	--	2.50	2.46	2.38	2.27	2.04	1.84	1.66	1.38	1.25	0.745
IN-N5297	Actual	8.53	8.34	8.15	7.79	7.28	6.22	5.32	4.54	3.31	2.77	0.898
	TWA	--	8.43	8.34	8.16	7.89	7.31	6.80	6.33	5.52	5.12	3.39
IN-T5831	Actual	3.73	3.61	3.50	3.27	2.97	2.36	1.87	1.49	0.940	0.722	0.140
	TWA	--	3.67	3.61	3.50	3.34	2.99	2.70	2.44	2.02	1.83	1.09
IN-DAT97	Actual	4.37	4.29	4.22	4.06	3.85	3.38	2.98	2.62	2.02	1.75	0.699
	TWA	--	4.33	4.30	4.22	4.11	3.86	3.63	3.42	3.05	2.86	2.00

For presentation purposes, PEC values were rounded to three significant figures or to a maximum of four decimal places.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Maximum bensulfuron methyl concentrations in paddy water (PEC_{PW}) ranged from 11.4 to 19.2 $\mu\text{g/L}$ on application day following instantaneous partitioning with the paddy soil. Metabolite $PECP_W$ ranged from 1.45 $\mu\text{g/L}$ for IN-J0290 to 8.53 $\mu\text{g/L}$ for IN-N5297. In all cases the highest initial paddy water concentrations were observed in the sand scenario, which is defined to have half the soil organic carbon of the clay scenario (0.9% versus 1.8%), resulting in less partitioning to paddy soil and more remaining in the water column.

Table B.8.136: Clay scenario Tier 1 PEC_{sw} values ($\mu\text{g/L}$) for bensulfuron methyl and degradates in the receiving ditch determined using the methods given in Med-Rice (2003)

Chemical	Actual or TWA ($\mu\text{g/L}$)	Days after application										
		0	1	2	4	7	14	21	28	42	50	100
bensulfuron methyl	Actual	1.08	1.07	1.06	1.03	0.997	0.918	0.846	0.779	0.661	0.602	0.334
	TWA	--	1.08	1.07	1.06	1.04	0.998	0.959	0.923	0.854	0.819	0.637
IN-F7880	Actual	0.140	0.139	0.138	0.135	0.132	0.124	0.117	0.110	0.0970	0.0905	0.0584
	TWA	--	0.140	0.139	0.138	0.136	0.132	0.128	0.124	0.117	0.114	0.0934
IN-R9419	Actual	0.239	0.216	0.195	0.160	0.118	0.0585	0.0290	0.0143	0.0035	0.0016	0.0000
	TWA	--	0.227	0.216	0.197	0.171	0.128	0.0994	0.0798	0.0557	0.0472	0.0238
IN-D1R84	Actual	0.340	0.318	0.297	0.259	0.211	0.131	0.0817	0.0507	0.0196	0.0114	0.0004
	TWA	--	0.329	0.318	0.298	0.271	0.220	0.181	0.152	0.112	0.0968	0.0500
IN-J0290	Actual	0.126	0.122	0.118	0.111	0.100	0.0796	0.0632	0.0502	0.0317	0.0244	0.0047
	TWA	--	0.124	0.122	0.118	0.113	0.101	0.0910	0.0824	0.0684	0.0619	0.0369
IN-N5297	Actual	0.602	0.589	0.576	0.551	0.514	0.440	0.376	0.321	0.234	0.196	0.0635
	TWA	--	0.596	0.589	0.576	0.557	0.517	0.480	0.447	0.390	0.362	0.239
IN-T5831	Actual	0.281	0.272	0.263	0.246	0.223	0.177	0.141	0.112	0.0706	0.0543	0.0105
	TWA	--	0.276	0.272	0.263	0.251	0.225	0.203	0.184	0.152	0.138	0.0823
IN-DAT97	Actual	0.354	0.347	0.341	0.329	0.311	0.274	0.241	0.212	0.164	0.141	0.0565
	TWA	--	0.351	0.347	0.341	0.332	0.312	0.294	0.277	0.247	0.232	0.162

For presentation purposes, PEC values were rounded to three significant figures or to a maximum of four decimal places.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.137: Sand scenario Tier 1 PEC_{sw} values (µg/L) for bensulfuron methyl and degradates in the receiving ditch determined using the methods given in Med-Rice (2003)

Chemical	Actual or TWA (µg/L)	Days after application										
		0	1	2	4	7	14	21	28	42	50	100
bensulfuron methyl	Actual	1.75	1.73	1.71	1.67	1.61	1.48	1.37	1.26	1.07	0.972	0.540
	TWA	--	1.74	1.73	1.71	1.68	1.61	1.55	1.49	1.38	1.32	1.03
IN-F7880	Actual	0.215	0.214	0.212	0.208	0.203	0.191	0.179	0.169	0.149	0.139	0.897
	TWA	--	0.214	0.214	0.212	0.209	0.203	0.197	0.191	0.180	0.174	0.144
IN-R9419	Actual	0.371	0.336	0.303	0.248	0.184	0.0909	0.0450	0.0223	0.0055	0.0024	0.0000
	TWA	--	0.353	0.336	0.306	0.266	0.199	0.154	0.124	0.0866	0.0734	0.0369
IN-D1R84	Actual	0.359	0.336	0.314	0.274	0.223	0.139	0.0862	0.0536	0.0207	0.0120	0.0004
	TWA	--	0.347	0.336	0.314	0.286	0.232	0.191	0.161	0.119	0.102	0.0528
IN-J0290	Actual	0.210	0.204	0.197	0.185	0.167	0.133	0.106	0.0839	0.0530	0.0407	0.0079
	TWA	--	0.207	0.204	0.197	0.188	0.169	0.152	0.138	0.114	0.103	0.0617
IN-N5297	Actual	0.716	0.700	0.684	0.654	0.611	0.522	0.446	0.381	0.278	0.232	0.0754
	TWA	--	0.708	0.700	0.684	0.662	0.614	0.570	0.531	0.463	0.430	0.284
IN-T5831	Actual	0.296	0.287	0.278	0.260	0.236	0.187	0.149	0.118	0.0746	0.0573	0.0111
	TWA	--	0.292	0.287	0.278	0.265	0.238	0.214	0.194	0.161	0.146	0.0868
IN-DAT97	Actual	0.373	0.367	0.360	0.347	0.328	0.289	0.254	0.223	0.173	0.149	0.0597
	TWA	--	0.370	0.367	0.360	0.350	0.329	0.310	0.292	0.260	0.244	0.171

For presentation purposes, PEC values were rounded to three significant figures or to a maximum of four decimal places.

In the receiving ditch, PEC_{sw} values for bensulfuron methyl and metabolites were highest in the sand scenario. Since more of the compounds were in the water phase in the sand scenario paddy, more reached the receiving ditch during paddy drainage following the five-day holding time. Bensulfuron methyl PEC_{sw} ranged from 1.08 to 1.75 µg/L. Metabolite PECsW ranged from 0.126 µg/L for IN-J0290 to 0.716 µg/L for IN-N5297.

Table B.8.138: Clay scenario Tier 1 PEC_{sed} values (µg/kg dry weight) for bensulfuron methyl and degradates in the receiving ditch determined using the methods given in Med-Rice (2003)

Chemical	Actual or TWA (µg/kg)	Days after application										
		0	1	2	4	7	14	21	28	42	50	100
bensulfuron methyl	Actual	4.51	4.46	4.41	4.31	4.16	3.83	3.53	3.25	2.76	2.51	1.39
	TWA	--	4.49	4.46	4.41	4.33	4.16	4.00	3.85	3.56	3.41	2.65
IN-F7880	Actual	0.415	0.412	0.408	0.401	0.391	0.367	0.346	0.325	0.288	0.268	0.173
	TWA	--	0.414	0.412	0.408	0.403	0.391	0.379	0.368	0.348	0.336	0.277
IN-R9419	Actual	0.761	0.688	0.622	0.509	0.376	0.186	0.0922	0.0457	0.0112	0.0050	0.0000
	TWA	--	0.724	0.689	0.626	0.546	0.408	0.317	0.254	0.178	0.150	0.0757
IN-D1R84	Actual	0.0533	0.0498	0.0466	0.0406	0.0331	0.0206	0.0128	0.0080	0.0031	0.0018	0.0001
	TWA	--	0.0516	0.0499	0.0467	0.0424	0.0344	0.0284	0.0238	0.0176	0.0152	0.0078
IN-J0290	Actual	0.697	0.674	0.652	0.611	0.554	0.440	0.349	0.278	0.175	0.135	0.0261
	TWA	--	0.685	0.674	0.653	0.622	0.558	0.503	0.455	0.378	0.342	0.204
IN-N5297	Actual	0.366	0.358	0.350	0.335	0.313	0.267	0.228	0.195	0.142	0.119	0.0386
	TWA	--	0.362	0.358	0.350	0.339	0.314	0.292	0.272	0.237	0.220	0.146
IN-T5831	Actual	0.0440	0.0426	0.0412	0.0386	0.0350	0.0278	0.0221	0.0175	0.0111	0.0085	0.0016
	TWA	--	0.0433	0.0426	0.0412	0.0393	0.0353	0.0318	0.0288	0.0239	0.0216	0.0129
IN-DAT97	Actual	0.0554	0.0544	0.0535	0.0515	0.0488	0.0429	0.0377	0.0332	0.0257	0.0222	0.0089
	TWA	--	0.0549	0.0544	0.0535	0.0520	0.0489	0.0460	0.0434	0.0387	0.0363	0.0254

For presentation purposes, PEC values were rounded to three significant figures or to a maximum of four decimal places.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.139: Sand scenario Tier 1 PEC_{sed} values (µg/kg dry weight) for bensulfuron methyl and degradates determined in the receiving ditch using the methods given in Med-Rice (2003)

Chemical	Actual or TWA (µg/kg)	Days after application										
		0	1	2	4	7	14	21	28	42	50	100
bensulfuron methyl	Actual	7.19	7.11	7.02	6.86	6.62	6.10	5.62	5.18	4.39	4.00	2.22
	TWA	--	7.15	7.11	7.02	6.90	6.63	6.37	6.13	5.68	5.44	4.23
IN-F7880	Actual	0.634	0.628	0.623	0.612	0.596	0.561	0.528	0.496	0.439	0.409	0.264
	TWA	--	0.631	0.628	0.623	0.615	0.597	0.579	0.562	0.531	0.513	0.422
IN-R9419	Actual	1.17	1.06	0.960	0.785	0.581	0.287	0.142	0.0704	0.0173	0.0077	0.0001
	TWA	--	1.12	1.06	0.966	0.842	0.630	0.489	0.392	0.274	0.232	0.117
IN-D1R84	Actual	0.0563	0.0526	0.0491	0.0429	0.0350	0.0217	0.0135	0.0084	0.0032	0.0019	0.0001
	TWA	--	0.0544	0.0526	0.0493	0.0448	0.0363	0.0300	0.0252	0.0186	0.0160	0.0083
IN-J0290	Actual	1.14	1.10	1.06	0.996	0.902	0.717	0.570	0.453	0.286	0.220	0.0425
	TWA	--	1.12	1.10	1.06	1.01	0.910	0.820	0.742	0.616	0.558	0.333
IN-N5297	Actual	0.435	0.426	0.416	0.398	0.372	0.318	0.271	0.232	0.169	0.141	0.0459
	TWA	--	0.430	0.426	0.416	0.403	0.373	0.347	0.323	0.282	0.261	0.173
IN-T5831	Actual	0.0465	0.0450	0.0435	0.0407	0.0369	0.0293	0.0233	0.0185	0.0117	0.0090	0.0017
	TWA	--	0.0457	0.0450	0.0435	0.0415	0.0372	0.0336	0.0304	0.0252	0.0228	0.0136
IN-DAT97	Actual	0.0585	0.0575	0.0564	0.0544	0.0515	0.0453	0.0398	0.0350	0.0271	0.0234	0.0094
	TWA	--	0.0580	0.0575	0.0564	0.0549	0.0516	0.0486	0.0458	0.0408	0.0383	0.0268

For presentation purposes, PEC values were rounded to three significant figures or to a maximum of four decimal places.

The higher amount reaching the receiving ditch from the sand scenario paddy further resulted in higher PEC_{sed} values compared to the clay scenario. PEC_{sed} values ranged from 4.51 µg/kg to 7.19 µg/kg for bensulfuron methyl. Metabolite PEC_{sed} ranged from 0.0440 µg/kg for IN-T5831 to 1.17 µg/kg for IN-R9419.

The higher tier daily PEC output values were summarized in two ways.

First way. The maximum daily PEC_{sw} and PEC_{sed} values were taken from each simulation year (20 years per scenario) for each sample point (10 for paddies, ditches, and canals; 1 for the river) for each meteorological scenario (5 scenarios). This resulted in 20 to 200 daily maximum values per meteorological scenario and 100 to 1000 daily maximum values aggregated across all scenarios. The minimum, 25th percentile, average, median, 75th percentile, and maximum of these maximum values were calculated to conservatively assess PEC magnitude in paddies, ditches, canals, and the river. These values are given in Table B.8.140 and Table B.8.141.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.140: RICEWQ/RIVWQ PEC_{sw} summary statistics for treated paddies, ditches, canals, and the river for bensulfuron methyl

Summary for individual meteorological scenarios								
Meteorological scenario	Water body	Number of simulation years	Maximum daily PEC _{sw} (µg/L)					
			Minimum	25 th %	Average	Median	75 th %	Maximum
France	paddy	200	15.2	27.5	33.8	32.5	37.8	148
	ditch	200	2.00	2.98	4.44	4.16	5.55	16.3
	canal	200	0.664	1.00	1.48	1.40	1.88	3.30
	river	20	0.170	0.242	0.350	0.358	0.424	0.625
Greece	paddy	200	23.3	29.1	33.4	32.3	36.4	78.6
	ditch	200	1.97	2.25	3.22	2.88	3.70	8.40
	canal	200	0.635	0.755	1.06	0.924	1.23	2.41
	river	20	0.152	0.185	0.231	0.217	0.237	0.434
Italy	paddy	200	13.7	25.7	34.9	30.4	36.0	223
	ditch	200	1.98	3.63	5.29	4.99	6.19	26.3
	canal	200	0.636	1.21	1.76	1.78	2.14	3.61
	river	20	0.224	0.400	0.540	0.456	0.639	1.13
Portugal	paddy	200	12.2	25.1	33.7	30.3	36.2	256
	ditch	200	2.02	3.51	4.60	4.34	5.66	9.24
	canal	200	0.656	1.16	1.58	1.53	1.96	3.05
	river	20	0.160	0.336	0.393	0.383	0.451	0.655
Spain	paddy	200	21.1	29.5	34.7	34.3	38.7	59.6
	ditch	200	1.97	2.58	3.55	3.25	3.99	8.23
	canal	200	0.657	0.868	1.20	1.06	1.31	3.18
	river	20	0.177	0.194	0.313	0.225	0.411	0.812
Overall summary – data from all meteorological scenarios combined								
Meteorological scenario	Water body	Number of simulation years	Maximum daily PEC _{sw} (µg/L)					
			Minimum	25 th %	Average	Median	75 th %	Maximum
France, Greece, Italy, Portugal, and Spain data combined	paddy	1000	12.2	27.5	34.0	32.2	37.2	256
	ditch	1000	1.97	2.85	4.22	3.77	5.36	26.3
	canal	1000	0.635	0.949	1.42	1.25	1.84	3.61
	river	100	0.152	0.221	0.365	0.338	0.437	1.13

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Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.141: RICEWQ/RIVWQ PEC_{sed} summary statistics for treated paddies, ditches, canals, and the river for bensulfuron methyl

Summary for individual meteorological scenarios								
Meteorological scenario	Water body	Number of simulation years	Maximum daily PEC _{sw} (µg/kg)					
			Minimum	25 th %	Average	Median	75 th %	Maximum
France	paddy	200	10.1	13.0	15.0	14.2	16.8	22.6
	ditch	200	1.23	1.74	2.83	2.36	3.24	21.9
	canal	200	0.483	0.843	1.25	1.16	1.59	2.92
	river	20	0.484	0.589	0.789	0.751	0.982	1.16
Greece	paddy	200	10.7	12.8	13.8	13.0	14.0	20.9
	ditch	200	1.15	1.36	1.84	1.54	1.92	9.37
	canal	200	0.445	0.675	0.831	0.775	0.943	2.44
	river	20	0.401	0.441	0.520	0.491	0.558	0.789
Italy	paddy	200	7.89	13.2	15.3	15.1	16.8	25.7
	ditch	200	1.21	2.11	3.30	3.03	3.59	33.3
	canal	200	0.518	1.17	1.57	1.58	1.99	3.32
	river	20	0.571	0.823	1.00	1.05	1.19	1.42
Portugal	paddy	200	6.84	12.8	15.0	14.9	17.1	22.5
	ditch	200	1.19	2.02	2.96	2.88	3.53	12.8
	canal	200	0.512	1.08	1.43	1.41	1.72	2.62
	river	20	0.457	0.793	0.916	0.912	1.05	1.32
Spain	paddy	200	10.1	11.9	13.7	12.6	15.0	25.7
	ditch	200	1.20	1.47	2.06	1.76	2.19	12.0
	canal	200	0.474	0.738	0.968	0.848	1.04	2.42
	river	20	0.449	0.487	0.618	0.520	0.715	1.06
Overall summary – data from all meteorological scenarios combined								
Meteorological scenario	Water body	Number of simulation years	maximum daily PEC _{sw} (µg/kg)					
			Minimum	25 th %	Average	Median	75 th %	Maximum
France, Greece, Italy, Portugal, and Spain data combined	paddy	1000	6.84	12.6	14.5	13.8	16.3	25.7
	ditch	1000	1.15	1.58	2.60	2.12	3.18	33.3
	canal	1000	0.445	0.784	1.21	1.06	1.58	3.32
	river	100	0.401	0.520	0.768	0.718	0.974	1.42

Based on data combined across all meteorological scenarios and simulation years (100 to 1000), the average maximum bensulfuron methyl PEC_{sw} was 34.0 µg/L in paddies, 4.22 µg/L in ditches, 1.42 µg/L in canals, and 0.365 µg/L in the river. The average maximum bensulfuron methyl PEC_{sed} was 14.5 µg/kg in paddies, 2.60 µg/kg in ditches, 1.21 µg/kg in canals, and 0.768 µg/kg in the river.

The presence of bensulfuron methyl in the ditches, canals, and the river was predicted to be of a transient nature. Levels increased primarily as a result of paddy drainage and then quickly decreased due to the combined effect of chemical (e.g. degradation and sorption) and physical (e.g. hydrodynamic dispersion and dilution) processes.

In the higher tier RICEWQ/RIVWQ simulations for bensulfuron methyl, the effect of moving water was also considered. Initial concentrations in paddy water and ditch water are higher than in the Med-Rice tier 1 calculations, but this was primarily due to the different way that partitioning between the water and solid phases was handled. Depending on the location in the watershed system (paddy, ditch, canal, or river), the actual number of days that bensulfuron methyl was present at concentrations of interest was related to rainfall inputs, paddy drainage practices, the DT₅₀ in surface water and sediment, partitioning, and the hydrology of the water body

Second way. In order to support refinement of the higher tier aquatic risk assessment, 14-day time weighted average (TWA) PEC_{sw} and PEC_{sed} values for bensulfuron methyl were calculated. All 14-d TWA values in each

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Italy	May 2006	Bensulfuron methyl

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simulation year ($365 - 13 = 352$ values, 353 for leap years) were calculated for each “sampling” point in the RICEWQ/RIVWQ watershed. There were 10 sampling points for treated paddies, ditches, and canals and one sampling point for the river at the exit of the watershed. The 90th percentile of these 14-d TWA values was calculated for each of the 20 simulation years. The 50th percentile of the 90th percentile values was then calculated to obtain a conservative 14-d TWA value for use in aquatic risk assessment. The method of taking the 50th percentile of the 90th percentile values in higher tier assessments has been supported in recent discussions within the EUFRAM Maths group (John Green, personal communication, 2006). Distribution of 90th percentile 14-day TWA PEC_{sw} values for bensulfuron methyl in treated paddies, ditches, canals and rivers are reported in Table B.8.142 to Table B.8.145.

Table B.8.142 Distribution of 90th percentile 14-day TWA PEC_{sw} values for bensulfuron methyl in treated paddies

90 th percentile 14-day TWA PEC _{sw} values (µg/L) calculated for each simulation year of each meteorological scenario ^a					
Year	France	Greece	Italy	Portugal	Spain
1	0.126	0.070	0.160	0.044	0.022
2	0.188	0.053	0.141	0.273	0.021
3	0.161	0.089	0.048	0.201	0.023
4	0.390	0.283	0.042	0.039	0.056
5	0.138	0.023	0.146	0.274	0.076
6	0.195	0.024	0.037	0.193	0.020
7	0.414	0.026	0.070	0.219	0.055
8	0.211	0.022	0.433	0.214	0.065
9	0.398	0.022	0.293	0.065	0.052
10	0.056	0.022	0.060	0.373	0.102
11	0.174	0.059	0.187	0.103	0.036
12	0.058	0.022	0.074	0.108	0.020
13	0.119	0.072	0.202	0.032	0.069
14	0.307	0.021	0.195	0.222	0.185
15	0.083	0.034	0.325	0.089	0.021
16	0.116	0.021	0.065	0.139	0.127
17	0.079	0.021	0.145	0.099	0.045
18	0.111	0.044	0.092	0.269	0.021
19	0.157	0.112	0.501	0.088	0.038
20	0.385	0.026	0.038	0.336	0.106
Distribution of the 90 th percentile 14-day TWA values (µg/L) for each individual meteorological scenario					
	France	Greece	Italy	Portugal	Spain
N =	20	20	20	20	20
50 th % =	0.159	0.026	0.143	0.166	0.048
80 th % =	0.323	0.071	0.220	0.270	0.081
90 th % =	0.391	0.091	0.335	0.280	0.108
95 th % =	0.399	0.120	0.436	0.338	0.130
99 th % =	0.411	0.250	0.488	0.366	0.174
99.9 th % =	0.414	0.280	0.500	0.372	0.184
Distribution of the 90 th percentile 14-day TWA values (µg/L) for all meteorological scenarios combined					
N = 100					
50 th % = 0.088					
80 th % = 0.201					
90 th % = 0.295					
95 th % = 0.385					
99 th % = 0.433					
99.9 th % = 0.494					

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

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Table B.8.143 Distribution of 90th percentile 14-day TWA PEC_{sw} values for bensulfuron methyl in ditches

90th percentile 14-day TWA PECSW values (µg/L) calculated for each simulation year of each meteorological scenario					
Meteorological scenario					
Year	France	Greece	Italy	Portugal	Spain
1	0.039	0.026	0.036	0.050	0.031
2	0.022	0.040	0.034	0.030	0.023
3	0.046	0.045	0.037	0.058	0.022
4	0.030	0.026	0.025	0.034	0.032
5	0.027	0.024	0.028	0.037	0.026
6	0.040	0.035	0.036	0.047	0.020
7	0.028	0.021	0.049	0.037	0.032
8	0.041	0.020	0.046	0.019	0.022
9	0.031	0.018	0.028	0.049	0.032
10	0.032	0.023	0.043	0.036	0.045
11	0.042	0.025	0.033	0.037	0.022
12	0.038	0.033	0.047	0.041	0.029
13	0.072	0.028	0.080	0.038	0.036
14	0.035	0.023	0.032	0.033	0.021
15	0.024	0.030	0.030	0.035	0.022
16	0.032	0.019	0.034	0.046	0.046
17	0.036	0.018	0.034	0.033	0.029
18	0.049	0.026	0.045	0.021	0.020
19	0.023	0.029	0.028	0.037	0.026
20	0.037	0.021	0.039	0.035	0.030

Distribution of the 90th percentile 14-day TWA values (µg/L) for each individual meteorological scenario					
Meteorological scenario					
	France	Greece	Italy	Portugal	Spain
N=	20	20	20	20	20
50 th % =	0.035	0.025	0.035	0.037	0.028
80 th % =	0.041	0.030	0.045	0.047	0.032
90 th % =	0.046	0.036	0.047	0.049	0.037
95 th % =	0.051	0.040	0.050	0.050	0.045
99 th % =	0.067	0.044	0.074	0.057	0.046
99.9 th % =	0.071	0.045	0.079	0.058	0.046

Distribution of the 90th percentile 14-day TWA values (µg/L) for all meteorological scenarios combined	
N = 100	
50th% = 0.032	
80th% = 0.040	
90th% = 0.046	
95th% = 0.049	
99th% = 0.072	
99.9th% = 0.079	

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

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Table B.8.144 Distribution of 90th percentile 14-day TWA PEC_{sw} values for bensulfuron methyl in canals

90th percentile 14-day TWA PEC_{sw} values (µg/L) calculated for each simulation year of each meteorological scenario					
Year	France	Greece	Italy	Portugal	Spain
1	0.009	0.006	0.008	0.014	0.005
2	0.004	0.006	0.009	0.008	0.004
3	0.010	0.011	0.006	0.010	0.004
4	0.006	0.005	0.009	0.009	0.009
5	0.005	0.004	0.006	0.009	0.005
6	0.009	0.006	0.013	0.009	0.004
7	0.004	0.006	0.013	0.006	0.007
8	0.007	0.004	0.016	0.003	0.004
9	0.006	0.003	0.005	0.010	0.006
10	0.007	0.004	0.013	0.008	0.009
11	0.009	0.004	0.007	0.007	0.005
12	0.008	0.005	0.010	0.008	0.005
13	0.011	0.005	0.016	0.007	0.005
14	0.006	0.004	0.006	0.009	0.004
15	0.004	0.006	0.010	0.006	0.004
16	0.009	0.003	0.008	0.011	0.014
17	0.008	0.003	0.008	0.006	0.006
18	0.017	0.004	0.009	0.005	0.004
19	0.004	0.005	0.007	0.008	0.005
20	0.008	0.006	0.012	0.006	0.006

Distribution of the 90th percentile 14-day TWA values (µg/L) for each individual meteorological scenario					
	France	Greece	Italy	Portugal	Spain
N=	20	20	20	20	20
50 th %=	0.007	0.005	0.009	0.008	0.005
80 th %=	0.009	0.006	0.013	0.009	0.006
90 th %=	0.010	0.006	0.014	0.010	0.009
95 th %=	0.011	0.006	0.016	0.011	0.009
99 th %=	0.016	0.010	0.016	0.014	0.013
99.9 th %=	0.017	0.011	0.016	0.014	0.014

Distribution of the 90th percentile 14-day TWA values (µg/L) for all meteorological scenarios combined	
N =	100
50 th % =	0.006
80 th % =	0.009
90 th % =	0.011
95 th % =	0.013
99 th % =	0.016
99.9 th % =	0.017

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

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Table B.8.145 Distribution of 90th percentile 14-day TWA PEC_{sw} values for bensulfuron methyl in the river

90 th percentile 14-day TWA PEC _{sw} values (µg/L) calculated for each simulation year of each meteorological scenario					
Year	France	Greece	Italy	Portugal	Spain
1	0.002	0.003	0.004	0.018	0.004
2	0.003	0.001	0.008	0.015	0.001
3	0.008	0.005	0.004	0.013	0.003
4	0.002	0.004	0.017	0.014	0.013
5	0.003	0.003	0.003	0.013	0.007
6	0.002	0.003	0.025	0.007	0.001
7	0.003	0.003	0.014	0.002	0.009
8	0.002	0.003	0.038	0.002	0.002
9	0.008	0.003	0.001	0.009	0.004
10	0.003	0.003	0.016	0.009	0.003
11	0.011	0.003	0.006	0.002	0.003
12	0.006	0.001	0.004	0.008	0.002
13	0.004	0.004	0.015	0.003	0.001
14	0.002	0.003	0.003	0.010	0.002
15	0.004	0.002	0.016	0.003	0.003
16	0.010	0.003	0.002	0.014	0.019
17	0.004	0.003	0.012	0.001	0.009
18	0.043	0.003	0.003	0.010	0.003
19	0.006	0.005	0.010	0.008	0.001
20	0.008	0.003	0.019	0.006	0.004

Distribution of the 90 th percentile 14-day TWA values (µg/L) for each individual meteorological scenario					
	France	Greece	Italy	Portugal	Spain
N=	20	20	20	20	20
50 th %=	0.004	0.003	0.009	0.008	0.003
80 th %=	0.008	0.004	0.016	0.013	0.007
90 th %=	0.010	0.004	0.020	0.015	0.010
95 th %=	0.012	0.005	0.026	0.015	0.013
99 th %=	0.037	0.005	0.035	0.017	0.018
99.9 th %=	0.042	0.005	0.037	0.017	0.019

Distribution of the 90 th percentile 14-day TWA values (µg/L) for all meteorological scenarios combined					
N = 100					
50th% = 0.004					
80th% = 0.010					
90th% = 0.015					
95th% = 0.018					
99th% = 0.038					
99.9th% = 0.042					

The 90th percentile 14-day TWA PEC_{sw} values for bensulfuron methyl in treated paddies had a 50th percentile ranging from 0.026 µg/L for the Greek meteorological scenario to 0.166 µg/L for the Portuguese meteorological scenario. The overall 50th percentile 14-d TWA value, calculated from the 90th percentile values from all five meteorological scenarios, was 0.088 µg/L.

The 90th percentile 14-day TWA PEC_{sw} values for bensulfuron methyl in ditches had a 50th percentile ranging from 0.025 µg/L for the Greek meteorological scenario to 0.037 µg/L for the Portuguese meteorological scenario. The overall 50th percentile 14-d TWA value, calculated from all five meteorological scenarios, was 0.032 µg/L.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

The 90th percentile 14-day TWA PEC_{sw} values for bensulfuron methyl in canals had a 50th percentile ranging from 0.005 µg/L for the Spanish and Greek meteorological scenarios to 0.008 µg/L for the Portuguese meteorological scenario. The overall 50th percentile 14-d TWA, values calculated from all five meteorological scenarios, was 0.006 µg/L.

The 90th percentile 14-day TWA PEC_{sw} values for bensulfuron methyl in the river had a 50th percentile ranging from 0.003 µg/L for the Spanish and Greek meteorological scenarios to 0.009 µg/L for the Italian meteorological scenario. The overall 50th percentile 14-d TWA value, calculated from all five meteorological scenarios, was 0.004 µg/L.

Distribution of 90th percentile 14-day TWA PEC_{sed} values for bensulfuron methyl in treated paddies, ditches, canals and rivers are reported in Table B.8.146 to Table B.8.149.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.146 Distribution of 90th percentile 14-day TWA PEC_{sed} values for bensulfuron methyl in treated paddies

90th percentile 14-day TWA PEC_{sw} values (µg/kg) calculated for each simulation year of each meteorological scenarioa					
Year	France	Greece	Italy	Portugal	Spain
1	4.205	3.165	4.291	4.414	3.120
2	3.229	3.373	4.352	4.493	3.127
3	4.146	3.063	3.694	4.394	2.954
4	4.175	3.663	3.780	2.851	4.685
5	3.447	3.220	4.521	3.621	3.372
6	4.475	3.419	3.656	2.886	2.796
7	4.116	3.063	4.050	3.767	4.019
8	4.740	3.064	4.295	3.522	2.955
9	3.919	3.033	3.202	4.139	3.810
10	3.177	3.049	4.192	4.597	4.204
11	4.295	3.039	4.950	2.945	2.836
12	3.793	3.164	4.300	4.184	2.783
13	4.517	3.342	4.088	3.634	2.920
14	4.458	3.043	3.746	4.687	3.195
15	3.457	4.154	4.510	3.670	2.987
16	4.136	2.981	2.902	4.464	4.155
17	4.053	2.992	4.591	4.120	3.943
18	4.235	3.328	4.445	4.366	2.945
19	3.585	3.369	4.022	4.645	2.762
20	4.649	3.060	3.677	4.414	3.981

Distribution of the 90th percentile 14-day TWA values (µg/kg) for each individual meteorological scenario					
	France	Greece	Italy	Portugal	Spain
N =	20	20	20	20	20
50 th % =	4.141	3.114	4.140	4.161	3.124
80 th % =	4.461	3.369	4.458	4.470	3.989
90 th % =	4.531	3.443	4.528	4.602	4.160
95 th % =	4.654	3.688	4.609	4.647	4.228
99 th % =	4.723	4.061	4.882	4.679	4.594
99.9 th % =	4.738	4.145	4.943	4.686	4.676

Distribution of the 90th percentile 14-day TWA values (µg/kg) for all meteorological scenarios combined	
N = 100	
50th% = 3.756	
80th% = 4.355	
90th% = 4.511	
95th% = 4.645	
99th% = 4.742	
99.9th% = 4.929	

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.147 Distribution of 90th percentile 14-day TWA PEC_{sed} values for bensulfuron methyl in ditches

90th percentile 14-day TWA PEC_{sw} values (µg/kg) calculated for each simulation year of each meteorological scenario					
Year	France	Greece	Italy	Portugal	Spain
1	2.135	0.946	2.198	2.701	1.394
2	1.120	0.946	1.797	1.362	1.149
3	2.323	0.948	1.957	2.698	1.126
4	1.472	0.951	2.211	1.910	1.912
5	1.355	0.960	1.463	1.792	1.272
6	1.982	1.028	2.050	1.632	1.030
7	1.267	1.100	2.502	1.699	1.579
8	2.222	1.113	1.912	1.023	1.088
9	1.287	1.116	1.371	2.646	1.501
10	1.863	1.138	2.446	1.752	1.976
11	1.737	1.162	1.858	1.910	1.117
12	1.730	1.195	2.367	2.520	1.251
13	3.273	1.199	3.411	1.948	1.504
14	1.765	1.231	1.416	1.909	1.044
15	1.170	1.321	1.609	1.824	1.070
16	1.664	1.346	1.817	2.447	2.104
17	1.856	1.437	2.187	1.717	1.190
18	2.552	1.532	2.605	1.192	1.088
19	1.103	1.575	1.226	2.153	1.204
20	1.676	1.687	2.541	1.704	1.453

Distribution of the 90th percentile 14-day TWA values (µg/kg) for each individual meteorological scenario					
	France	Greece	Italy	Portugal	Spain
N =	20	20	20	20	20
50 th % =	1.733	1.150	2.004	1.866	1.227
80 th % =	2.153	1.364	2.457	2.461	1.519
90 th % =	2.346	1.537	2.547	2.651	1.919
95 th % =	2.588	1.580	2.645	2.698	1.982
99 th % =	3.136	1.665	3.258	2.701	2.079
99.9 th % =	3.260	1.684	3.395	2.701	2.101

Distribution of the 90th percentile 14-day TWA values (µg/kg) for all meteorological scenarios combined					
N = 100					
50 th % = 1.594					
80 th % = 2.110					
90 th % = 2.452					
95 th % = 2.607					
99 th % = 3.275					
99.9 th % = 3.397					

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.148 Distribution of 90th percentile 14-day TWA PEC_{sed} values for bensulfuron methyl in canals

90th percentile 14-day TWA PEC_{sw} values (µg/kg) calculated for each simulation year of each meteorological scenario					
Year	France	Greece	Italy	Portugal	Spain
1	1.051	0.502	1.104	1.171	0.603
2	0.499	0.680	0.880	0.617	0.519
3	1.132	0.446	0.951	0.982	0.524
4	0.693	0.533	1.195	1.012	0.947
5	0.587	0.513	0.745	0.835	0.577
6	0.825	0.658	1.139	0.720	0.469
7	0.591	0.397	1.236	0.755	0.681
8	0.992	0.473	0.752	0.463	0.466
9	0.510	0.415	0.623	1.277	0.681
10	0.949	0.469	1.243	0.797	0.894
11	0.657	0.559	0.920	0.897	0.478
12	0.657	0.706	1.107	1.242	0.490
13	1.152	0.584	1.118	0.924	0.524
14	0.791	0.477	0.553	1.041	0.455
15	0.520	0.707	0.736	0.921	0.445
16	0.831	0.399	0.962	1.012	0.934
17	0.886	0.413	1.048	0.873	0.539
18	1.195	0.480	1.152	0.526	0.514
19	0.479	0.557	0.551	1.058	0.500
20	0.665	0.396	1.376	0.786	0.697
Distribution of the 90th percentile 14-day TWA values (µg/kg) for each individual meteorological scenario					
	France	Greece	Italy	Portugal	Spain
N=	20	20	20	20	20
50 th %=	0.742	0.491	1.005	0.909	0.524
80 th %=	1.004	0.599	1.161	1.045	0.685
90 th %=	1.134	0.683	1.237	1.178	0.898
95 th %=	1.154	0.706	1.250	1.244	0.935
99 th %=	1.187	0.707	1.351	1.270	0.944
99.9 th %=	1.194	0.707	1.373	1.276	0.946
Distribution of the 90th percentile 14-day TWA values (µg/kg) for all meteorological scenarios combined					
N = 100					
50th% = 0.695					
80th% = 1.012					
90th% = 1.140					
95th% = 1.197					
99th% = 1.278					
99.9th% = 1.366					

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.149 Distribution of 90th percentile 14-day TWA PEC_{sed} values for bensulfuron methyl in the river

90th percentile 14-day TWA PEC_{sw} values (µg/kg) calculated for each simulation year of each meteorological scenario					
Year	France	Greece	Italy	Portugal	Spain
1	0.681	0.317	0.735	0.780	0.383
2	0.319	0.436	0.585	0.414	0.321
3	0.739	0.285	0.611	0.621	0.336
4	0.453	0.339	0.805	0.676	0.663
5	0.379	0.324	0.523	0.541	0.351
6	0.524	0.419	0.773	0.475	0.306
7	0.391	0.260	0.784	0.474	0.441
8	0.646	0.301	0.453	0.295	0.299
9	0.320	0.277	0.406	0.838	0.483
10	0.633	0.310	0.791	0.529	0.574
11	0.434	0.368	0.613	0.600	0.311
12	0.448	0.474	0.722	0.834	0.309
13	0.699	0.374	0.687	0.598	0.334
14	0.503	0.295	0.373	0.678	0.302
15	0.352	0.488	0.501	0.615	0.286
16	0.558	0.268	0.636	0.694	0.628
17	0.559	0.274	0.727	0.593	0.382
18	0.790	0.314	0.764	0.360	0.337
19	0.315	0.350	0.364	0.696	0.317
20	0.414	0.259	0.929	0.534	0.498
Distribution of the 90th percentile 14-day TWA values (µg/kg) for each individual meteorological scenario					
	France	Greece	Italy	Portugal	Spain
N=	20	20	20	20	20
50 th % =	0.478	0.316	0.662	0.599	0.336
80 th % =	0.653	0.383	0.775	0.694	0.486
90 th % =	0.703	0.439	0.793	0.785	0.580
95 th % =	0.741	0.474	0.811	0.834	0.630
99 th % =	0.780	0.486	0.905	0.837	0.656
99.9 th % =	0.789	0.488	0.926	0.838	0.662
Distribution of the 90th percentile 14-day TWA values (µg/kg) for all meteorological scenarios combined					
N = 100					
50th% = 0.463					
80th% = 0.676					
90th% = 0.741					
95th% = 0.790					
99th% = 0.839					
99.9th% = 0.920					

The higher tier PEC_{sed} values were summarized using the same method as described above for PEC_{sw}. The 50th percentile of the 90th percentile 14-d TWA PEC_{sed} values, from all meteorological scenarios together, was 3.76 µg/kg for treated paddies, 1.59 µg/kg for ditches, 0.695 µg/kg for canals, and 0.463 µg/kg for the river.

Based on the Tier 1 Med-Rice calculations (instantaneous, irreversible sorption), the degree of partitioning is directly related to the compound K_{OC} and the organic carbon content of the soil/sediment. Therefore, partitioning was shown to be a more significant process for those compounds with higher sorption values such as bensulfuron methyl and IN-J0290. In the higher tier RICEWQ/RIVWQ modelling for bensulfuron methyl, sorption was reversible and based on concentration gradients. This more realistic process description indicated that partitioning of bensulfuron methyl to soil and sediment was important, but not to the same degree as indicated by the Tier 1 calculations. Simulation results

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

suggest that dissipation of bensulfuron methyl from the aquatic environments associated with rice production would be due to both degradation and to partitioning, in addition to the physical processes of dispersion and dilution.

Conclusions:

Given the defined differences in soil organic carbon between the Tier 1 sand and clay scenarios, and the way sorption is calculated (instantaneous, irreversible partitioning), the bensulfuron methyl and metabolite PEC_{pw} values in the sand scenario were higher than in the clay scenario. The higher PEC_{pw} values of the sand scenario resulted in higher associated PEC_{sw} values since more chemical remained in the paddy water that drained to the receiving ditch. Higher tier simulations with a linked RICEWQ/RIVWQ model system gave bensulfuron methyl PEC_{sw} values in simulated paddies and a river body that were of a similar magnitude and duration to observed values from paddy and river monitoring.

The overall 50th percentile 14-d TWA value in treated paddies, calculated from the 90th percentile values from all five meteorological scenarios, was 0.088 µg/L. The overall 50th percentile 14-d TWA value in ditches, calculated from all five meteorological scenarios, was 0.032 µg/L. The overall 50th percentile 14-d TWA values in canals, calculated from all five meteorological scenarios, was 0.006 µg/L. The overall 50th percentile 14-d TWA value in the river, calculated from all five meteorological scenarios, was 0.004 µg/L.

The 50th percentile of the 90th percentile 14-d TWA PEC_{sed} values, from all meteorological scenarios together, was 3.76 µg/kg for treated paddies, 1.59 µg/kg for ditches, 0.695 µg/kg for canals, and 0.463 µg/kg for the river.

B.8.7 Fate and behaviour in air (Annex IIA 7.2.2; Annex IIIA 9.3)

B.8.7.1 Rate and route of degradation in air (Annex IIA 7.2.2)

33) *Photochemical oxidative degradation of bensulfuron methyl. Schmuckler, M.E., 2002.*

Cross reference IIA, 7.2.2./01

Guidelines:

OECD Photochemical Oxidative Degradation in the Environment (1087a, 1988a), USEPA 796.3900 (1992)

GLP:

Not required

The study is acceptable

Material and methods:

Hydrogen abstraction, reaction with nitrogen, and addition to the aromatic rings is predicted to contribute to the overall photochemical degradation pathway. The method of Atkinson was used to calculate the second-order rate constant and associated half life for the reaction of bensulfuron methyl in the gas phase in the troposphere. This calculation is an estimate of the photochemical oxidative degradation (indirect phototransformation) of bensulfuron methyl. Estimates of the rate of photochemical oxidative degradation for bensulfuron methyl were obtained using The Syracuse Research Corporation (SRC) Atmospheric Oxidation Program (version 1.83).

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Findings:

The overall OH rate constant is $210.1620 \times 10^{-12} \text{ cm}^3/\text{molecule}\cdot\text{sec}$. The half-life of bensulfuron methyl for reaction with average daily air concentrations of hydroxyl radicals (12-hr day, 1.5×10^6 OH radicals per cm^3) is 0.611 hours. The vapour pressure of bensulfuron methyl has been measured at 2.8×10^{-12} Pa at 20°C. The Henry's law constant for bensulfuron methyl has been measured at $2 \times 10^{-11} \text{ Pa}\cdot\text{m}^3/\text{mol}$, which is significantly lower than the Henry's law constant for water ($3 \times 10^{-2} \text{ Pa}\cdot\text{m}^3/\text{mol}$). Bensulfuron methyl can be considered to be non-volatile.

Conclusion:

The overall OH rate constant is $210.1620 \times 10^{-12} \text{ cm}^3/\text{molecule}\cdot\text{sec}$. The half-life of bensulfuron methyl for reaction with average daily air concentrations of hydroxyl radicals (12-hr day, 1.5×10^6 OH radicals per cm^3) is 0.611 hours. Bensulfuron methyl can be considered to be non-volatile.

B.8.8 Summary of behaviour in air and predicted environmental concentrations in air (PEC_a) (Annex IIIA 9.3)

The vapour pressure of bensulfuron methyl has been measured at 2.8×10^{-12} Pa at 20°C. The Henry's law constant for bensulfuron methyl has been measured at $2 \times 10^{-11} \text{ Pa}\cdot\text{m}^3/\text{mol}$, which is significantly lower than the Henry's law constant for water ($3 \times 10^{-2} \text{ Pa}\cdot\text{m}^3/\text{mol}$). The overall OH rate constant is $210.1620 \times 10^{-12} \text{ cm}^3/\text{molecule}\cdot\text{sec}$. The half-life of bensulfuron methyl for reaction with average daily air concentrations of hydroxyl radicals (12-hr day, 1.5×10^6 OH radicals per cm^3) is 0.611 hours. Oxadiazon would not be expected to be found in any significant concentration in air.

- 23) *Predicted Environmental Concentrations of Bensulfuron Methyl and Metabolites in Soil, Ground water, Surface water, Sediment, and Air Following Application to Rice in the EU. Warren, R.L., 2004.*

Cross reference IIIA 9.1.3/01, IIIA 9.2.1/01, IIIA 9.2.3/01

- 24) *Predicted Environmental Concentrations of Bensulfuron Methyl and Metabolites in Soil, Ground water, Surface water, Sediment, and Air Following Application to Rice in the EU. Revision No. 1, Warren, R.L., 2006.*

Cross reference not provided

Guidelines:

Not applicable - calculations.

GLP:

No.

The study is acceptable

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Material and methods:

Currently, no models have been recommended for the estimation of the predicted environmental concentrations of chemicals in air. In the absence of a recommended model, volatilization losses and predicted concentrations in air adjacent to treated fields were empirically estimated using the method described in Thomas (1995).

Step 1

Soil surface volatilization estimation using the "Dow method" (Thomas, 1995):

$$k_v = 4.4 \times 10^7 \left(\frac{v_p}{K_{oc} \times S} \right)$$

where:

k_v = rate constant for volatilization, day⁻¹

v_p = vapor pressure of chemical in air, mm Hg

K_{oc} = organic carbon partition coefficient, mL/g

S = water solubility, mg/L

Step 2

Estimate of initial daily loss from a treated field:

$$loss = (1 - \exp(-k_v)) \times 100$$

where:

$loss$ = percent of applied compound volatilised from soil surface within 24 hours after application

k_v = rate constant for volatilisation, day⁻¹

The water solubility of bensulfuron methyl ranges from 2.1 mg/L at pH 5 to 3100 mg/L at pH 9, the average soil sorption coefficient is 315 mL/g, and the vapour pressure is 2.8×10^{-12} Pa at 25°C. Based on the lowest water solubility value and the equations above it can be predicted that $1.4 \times 10^{-7}\%$ of applied bensulfuron methyl would be lost from a treated field into the air within 24 hours. Assuming a uniformly mixed stagnate layer of air to a height of 1 m over a treated field, the PEC_{air} in this layer would be negligible following application (8.4×10^{-6} µg/m³).

In order to calculate a PEC_{air} value for bensulfuron methyl, the amount lost from the soil surface in 24 hours was assumed to be uniformly distributed in a stagnant layer of air to a height of 1 m over a treated soil surface.

Results:

Based on the lowest water solubility value (2.1 mg/L at pH 5) and the equations above it can be predicted that $1.4 \times 10^{-7}\%$ ($\ll 0.01\%$) of applied bensulfuron methyl from a 60 g/ha application would be lost from a treated field into the air within 24 hours. Assuming a uniformly mixed stagnate layer of air to a height of 1 m over a treated field, the PEC_{air} in this layer would be negligible following application (8.4×10^{-6} µg/m³).

Conclusions:

Volatilization is an insignificant dissipation mechanism for bensulfuron methyl ($\ll 0.001\%$) lost from treated fields within 24 hours) resulting in negligible PEC_{air} .

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

B.8.9 Definition of the residue

Soil. The major soil degradation products of bensulfuron methyl are IN-J0290, IN-N5297, IN-D1R84, and IN-R9419. Mineralisation to carbon dioxide is contributed significantly to the degradation of bensulfuron methyl in soil (up to 40% applied radiolabel).

Water and sediment. In water/sediment studies, IN-J0290, IN-R9419, and IN-N5297 were the major degradation products in the water phase and IN-J0290 was the only major metabolite in sediment (other than non-extractable residues).

Groundwater. In case of application in saturated land (sand scenarios), major metabolites IN-N5297, and the minor metabolites IN-T5831 and IN-DAT97 are the residue of concern.

Air. No residues are expected

B.8.10 Monitoring data

34) *Monitoring of surface and groundwaters in Italy in the district of East and West Sesia to evaluate contamination by bensulfuron methyl and metsulfuron methyl following the application of Sigma. Years 1 and 2 of 4 – 1997-1998. Peter, J., 1999.*

Cross reference IIA 7.4./03

Guidelines:

None stated

GLP:

Yes, except field application phase

The study is acceptable

Materials and methods:

Sigma® 60 DF is a commercial rice herbicide containing the active ingredients 58% bensulfuron methyl and 2% metsulfuron methyl. Sigma® 60 DF was applied both in 1997 and in 1998 at a rate of 0.1 kg/ha. Normal practice in rice-growing areas is to keep treated chambers closed 5-7 days after application. Six surface water locations in rice-growing regions, four in the East Sesia and two in the West Sesia, were monitored for bensulfuron methyl and metsulfuron methyl. The selected surface water locations represent principal ditches and permanent waterways that receive drainage from rice paddies.

Surface Water Sampling. Sampling points were selected at places where the capacities of the waterways could also be estimated, or calculated with a good approximation. Surface waters were sampled according to the schedule reported in the table below.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.150 Surface water sampling date

Year	1	2
Date	05-Jun-1997	2-Jun-1998
	16-Jun-1997	15-Jun-1998
	15-Jul-1997	15-Jul-1998
	18-Aug-1997	18-Aug-1998
	15-Sep-1997	15-Sep-1998

In accordance with the planned sampling procedure, locations with direct discharge at a distance of less than 500 meters were avoided. The capacities of the waterways monitored ranges from 7 m³/sec for the Lucca channel to 360 m³/sec for the Sesia River at Palestro (maximum capacity measures on 6/2/1998). The principal ditches have an average capacity of about 20-30 m³/sec during May. Duplicate 2.5 L samples were taken and analysed for pH and bensulfuron methyl. Meteorological conditions and appearance of the water were recorded.

Groundwater Sampling. Groundwater was sampled using 6 piezometers adjacent to a 1.5-ha rice paddy treated with Sigma[®] and about 20 meters from the channel that supplies irrigations water for the paddy. The length of the piezometers ranged from 2 to 19 meters. Each 2.5 inch diameter steel tube was perforated along the last 30 cm in order capture water only at the desire depth. Before each sampling, a volume of water equal to or greater than the piezometer was purged with a manual pump. Water samples (two samples of 2.5 liters) were sent for pH and bensulfuron methyl analysis immediately after collection.

Groundwater was sampled according to the schedule reported in the table below.

Table B.8.151 Groundwater sampling date

	Year 1 – Date	Year2 - Date
Sample No. 1	29-May-1997	26-May-1998
Sample No. 2	16-Jun-1997 (10 days after application)	15-Jun-1998
Sample No. 3	26-Jun-1997	24-Jun-1998
Sample No. 4	15-Jul-1997	15-Jul-1998
Sample No. 5	15-Sep-1997	15-Sep-1998
Sample No. 6	15-Dec-1997	16-Dec-1998
Sample No. 7	16-Mar-1998	15-Mar-1999

Soil samples. Soil samples were collected at the piezometer site. Samples were taken every 0.5 meters for the first 5 meters and every meter for the next 15 meters. Soil was also collected from the rice paddy. The texture of each sample was determined.

Analytical method: Bensulfuron methyl residues were extracted from the water by passing samples, adjusted to pH 2, through a reverse phase C18 filter. The residues were eluted with ethyl acetate. Water samples were analysed by LC-MS with an LOD of 0.01 µg/L. Recovery of 101±3% validated the method.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Findings:

Soil characterisation: The texture of each sample was determined in collaboration with the DIFCA of the University of Milan. The characteristics of soil samples are reported in Table B.8.152.

Table B.8.152 Characteristics of soil samples

Sample	Classification ^a	Sample	Classification ^a
<i>Rice field</i>	<i>Plain sand</i>	<i>Rice field</i>	<i>Plain sand</i>
from 0.5 to 1m	Plain silt	From 9.0 to 10.0m	Coarse sand
from 1.0 to 1.5m	Plain sand	From 10.0 to 11.0m	Fine skeleton
From 1.5 to 2.0m	Plain sand	From 11.0 to 12.0m	Very coarse sand
From 2.0 to 2.5m	Plain sand	From 12.0 to 13.0m	Coarse sand
From 2.5 to 3.0m	Plain sand	From 13.0 to 14.0m	Fine skeleton
From 3.0 to 4.0m	Plain sand	From 14.0 to 15.0m	Medium sand
From 4.0 to 4.5m	Plain silt	From 15.0 to 16.0m	Medium sand
From 4.5 to 5.0m	Plain sand	From 16.0 to 17.0m	Medium sand
From 5.0 to 6.0m	Fine skeleton	From 17.0 to 18.0m	Medium sand
From 6.0 to 7.0m	Very coarse sand	From 18.0 to 19.0m	Medium sand
From 7.0 to 8.0m	Fine skeleton	From 19.0 to 20.0m	Medium fine sand
From 8.0 to 9.0m	Fine skeleton		

^a The classification is as follows: Fine skeleton: 8-2 mm; Coarse sand: 2-0.2 mm; Fine sand: 0.2-0.05 mm; Coarse silt: 0.05-0.02 mm; Fine silt: 0.02-0.002 mm; Clay: <0.002 mm;

The texture was finer in the top 5 meters and became coarser at greater depth. The texture of the surface layer was determined to be 23.95% sand, 25.70% coarse silt, 35.50% fine silt, and 14.85% clay.

Surface water and groundwater analyses: During 1997, 116 surface and 145 groundwater samples were collected. During 1998, 120 surface and 132 groundwater samples were collected. The pH of surface water samples ranged from 6.8-8.0 while the pH of groundwater samples ranged from 6.85-8.28. No detections of bensulfuron methyl were found in surface water or groundwater in 1997. During 1998, bensulfuron methyl was found on June 2 at average concentrations ranging from 0.16 to 0.31 µg/L (Table B.8.153 Table B.8.153).

Table B.8.153: Summary of all water samples with detectable bensulfuron methyl residues

Surface Water				
Waterway	Sample Date	Sample No.	pH	Bensulfuron methyl (µg/L)
Sesia Palestro	02-Jun-1998	0289W-3534	6.93	0.15
Sesia Palestro	02-Jun-1998	0289W-3535	6.92	0.17
Bona	02-Jun-1998	0297W-3538	7.11	0.3
Bona	02-Jun-1998	0297W-3538	7.14	0.28
Marcova	02-Jun-1998	0301W-3540	7.34	0.3
Marcova	02-Jun-1998	0302W-3541	7.37	0.32
Agogna	02-Jun-1998	0305W-3542	7.01	0.17
Agogna	02-Jun-1998	0306W-3543	6.95	0.2
Busca	02-Jun-1998	0309W-3544	7.14	0.21
Busca	02-Jun-1998	0310W-3545	7.11	0.22
Groundwater				
Piezometer No./ Depth	Sample Date	Sample No.	pH	Bensulfuron methyl (µg/L)
1/2 m	24-Jun-1998	0457W-4225	6.89	0.03

The detections followed intense rainfall (29 mm) on 28 May 1998 that compelled growers to open irrigation chambers early. Part of the bensulfuron methyl still in the irrigation systems was probably flushed into the drainage

Rapporteur Member State	Month and year	Active Substance (Name)
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Environmental fate and behaviour

waterways. No detections were found subsequently. Bensulfuron methyl was detected in a single groundwater sample at 0.03 µg/L at a depth of 2 meters.

Meteorological data collected for the years 1997–1998 was used to assess evaporation/transpiration and water movement in the water system of the region. Monitoring results support the conclusion that under worst-case conditions, bensulfuron methyl would degrade before reaching groundwater. The presence of bensulfuron methyl in surface water is limited to the period of application (~30 days) and is influenced by precipitation and/or regulation in the irrigation chambers.

This study was requested by Italian authorities in order to get the registration renewal of IN-JM206 52WG and IN-JM206 60WG products. The study was conducted for 2 of the initially scheduled 4 years, since the Health Minister agreed to stop the study due to the results showing that the concentration was always well below 0.01 µg/L.

Conclusion:

Monitoring results suggest that bensulfuron methyl, applied to rice paddies, would have a negligible effect on water systems and will generally be found in surface and groundwater at concentrations below 0.01 µg/L.

- 35) *Monitoring of the surface and stratum waters of the rice-growing area of Northwest Italy. Anselmetti, M.P., Vietti, L., Greppi, M., and Silvestri, S., 1998.*

Cross reference IIA, 7.4./01

Guidelines:

None stated, published report

GLP:

Not specified

The study is acceptable as additional information

Materials and methods:

A study area located in Northwest Italy was monitored to ensure no permanent impact on the environment. In this study, the movement of herbicides used in rice growing was monitored in the irrigation waters, surface-drainage waters, and groundwater. The study area chose covered an area of 693 km², which is sufficiently large to represent the entire rice-growing region and represents about 37% of the total Italian rice area. The northern boundary of the rice growing area is the Cavour Canal and the southern boundary is the river Po. The eastern boundary is the river Sesia, which receives most of the water that flows out of the rice production area. The western boundary is the river Dora Baltea, which is the source of most of the irrigation water used in the rice production of the study area. These hydrological boundaries permit an estimation of the water quantity entering the monitoring area. The water outflows from the study are estimated from the flow rate of the two main outlets, the stream Roggia Bona and the stream Roggia Marcova.

The rice growing area is fairly uniform in soil texture and has a high water holding capacity. The evaluation of herbicides in the unconfined groundwater was made by analysing samples taken from six piezometers and shallow wells in the region of Vercelli. The piezometers were located near the Tenuta Aramino of Asigliano. The shallow wells were selected statistically from all the shallow wells located especially south of Vercelli. The confined aquifer is important because all drinking water wells draw water from this aquifer. Water from the confined aquifer is tested

Rapporteur Member State	Month and year	Active Substance (Name)
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biennially for the presence of pesticides. Estimates of the maximum quantities of the active agents used in 1998 in the Vercellese area is summarised in Table B.8.154.

Table B.8.154: Estimated tonnage of the active agents used in 1998

Active Agent	Tonnage	Active Agent	Tonnage
Bensulfuron methyl	1.47	Molinate	150
Bentazone	0.81	Oxadiazon	16.4
Dimepiperate	3.5	Propanil	383
Diemethenamide	20	Pretilachlor	46
Cinosulfuron	1.2	Quinclorac	2.64
2,4 D	1	Terbuthylazine	15
Dalpon	400	Thiobencarb	7.5
MCPA	7.5	Tiocabazil	7.0
MCPP	1	Triclopyr	0.5

Because mixtures of active agents are a common practice, estimation of the area covered by each product application is difficult. Residues of all active agents listed in Table B.8.154 have been studied except for dalapon, which is unstable in an aqueous environment. The method of analysis used is based on the concentration of the active agents at a suitable pH on a solid matrix formed by an active phase of octadecyl and successive elutions with ethyl acetate. Estimates of the hydrological balance were made for 1997-1998 based on the evaluation of all water flows entering and leaving the area. This determination was made based on assumptions of precipitation, the difference between surface runoff entering and leaving the system, the difference between underground runoff entering and leaving the system, evaporation, transpiration, and volume stored by the system. Data on incoming surface quantities and average daily flow amounts were provided by the AIOS (the Associazione Irrigazione Ovest Sesia, or the West Sessia Irrigation Association). The data provided the sum of quantities measured in the three main contributing channels: the Depretis Canal, the Naviglio d'Ivrea Canal, and the Lucca Canal after the diversion of the Cavour Canal. The total volume used during the 1997 and 1998 irrigation seasons was 1087 and 934.9 Mm³, respectively. Rain gauges were distributed throughout the region to evaluate the net rainfall.

The evapotranspiration (ET) for the entire study area was calculated using the Hargreaves formula. The total ET volume for the study area was obtained by the sum of the products of the ET for all cultivated and non-cultivated areas. Each study area was subdivided into parcels and each parcel subdivided. In order to permit comparison between different years, a reference point was established based on cultivated areas in an average year. Data from the last 15 years found that 75% of the total area was for rice production and 12% was used mainly for corn and soybean production. The ET volume was calculated only for rice, corn and soybean crops. During the irrigation season, infiltration ranged between 11 mm/day in April to 6 mm/day in September. Corn and soybean water infiltration was neglected due to the small amount of irrigation used on these crops as well as their limited acreage.

Findings:

Surface water: The surface water in the study area is affected most by the presence of herbicides during May and June when treatments are made. The main sources of irrigation water generally do not contain any herbicides or pesticides. The concentrations and the average flow rates of herbicides present in the river Sesia at Palestro are reported in Table B.8.155. Corresponding values for the Roggia Marcova are presented in Table B.8.156. The herbicide data are given as concentrations in µg/L and as daily quantities of grams/day.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

The environmental fate of the two sulfonylureas is different. Bensulfuron methyl cannot be detected above the limit of detection 30 days after the maximum concentration was observed.

Unconfined aquifer: The unconfined aquifer evaluation of the environmental persistence of herbicides is very important in understanding their potential to enter into and remain in the unconfined aquifer. In general, the longer herbicides persist in the environment, the greater the possibility of contamination of the aquifer. Environmental characteristics for bensulfuron methyl and cinosulfuron, based on the literature, are given in Table B.8.157. Both herbicides are used at almost identical use rates and have comparable average half lives in water and soil. The greatest difference between the two compounds is their coefficients of distribution (K_{oc}). Cinosulfuron has greater potential mobility ($K_{oc} = 20$) while the potential mobility of bensulfuron methyl is lower ($K_{oc} = 684$). This difference in adsorption is the likely reason cinosulfuron was detected and bensulfuron methyl was not.

Confined aquifer: The confined aquifer in the rice growing area from which most of the wells used for drinking water receive water, was free of herbicide contamination. Geological investigations have shown that all the wells were drawing water from the semi-confined aquifer. Other wells with depths greater than 120 meters have been drilled at Asigliano and Terranova. These wells draw water only from the confined aquifer. The Vercelli well constructed protection to prevent water from entering from the semi-confined aquifer.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.155: Concentration and average flow rate of some herbicides in the Sesia river at Palestro

Date		16 Apr	22 Apr	30 Apr	8 May	15 May	22 May	29 May	2 June	11 June	18 June	24 June	3 July	18 Sept	22 Oct
Discharge	m ³ /s	55	53	84	127	48	32	179	315	133	60	11	11	126	97
Molinate	µg/L	0.09	0.10	0.09	0.15	0.15	0.10	0.20	0.16	0.71	0.35	0.21	0.20	-	-
Bensulfuron met.	µg/L	-	-	-	0.20	0.10	0.12	0.15	0.16	0.26	-	-	-	-	-
Cinosulfuron	µg/L	-	-	-	0.12	0.10	0.14	0.10	0.14	0.25	0.18	0.02	0.05	-	-
Dimethenamide	µg/L	0.08	0.07	0.04	0.02	-	-	-	-	-	-	-	-	-	-
Oxadiazon	µg/L	0.22	0.30	0.15	0.26	0.12	0.15	-	-	0.08	0.09	0.09	0.04	-	-
Bentazone	µg/L	0.06	0.03	0.02	0.04	0.04	0.01	0.03	0.03	0.03	0.08	0.08	0.10	0.02	0.06
Pretilachlor	µg/L	0.90	0.50	-	-	-	-	-	-	-	-	-	-	-	-
Propanil	µg/L	-	-	-	-	-	-	-	-	0.38	0.18	-	-	-	-
MCPA	µg/L	-	-	-	0.07	-	-	-	0.08	0.15	-	0.15	0.10	-	-
Mecoprp	µg/L	-	-	-	-	-	-	-	0.03	0.10	-	-	-	-	-
Exazinone	µg/L	-	-	-	0.11	0.05	0.08	0.03	0.04	0.08	0.06	0.04	-	-	-
Terbutilazina	µg/L	0.06	0.03	0.03	0.08	0.04	0.02	0.06	0.02	0.07	0.04	0.04	0.02	-	-
Date		16 Apr	22 Apr	30 Apr	8 May	15 May	22 May	29 May	2 June	11 June	18 June	24 June	3 July	18 Sept	22 Oct
Discharge	m ³ /s	55	53	84	127	48	32	179	315	133	60	11	11	126	97
Molinate	g/d	428	454	653	1647	624	279	3093	4355	8172	1811	202	194	0	0
Bensulfuron met	g/d	0	0	0	2195	416	335	2320	4355	2992	0	0	0	0	0
Cinosulfuron	g/d	0	0	0	1320	397	484	1547	3810	2722	871	19	48	0	0
Dimethenamide	g/d	380	318	289	217	0	0	0	0	0	0	0	0	0	0
Oxadiazon	g/d	1045	1363	1088	2854	499	418	0	0	921	466	86	39	0	0
Bentazone	g/d	285	109	145	434	164	279	461	816	346	414	77	97	218	504
Pretilachlor	g/d	4277	2272	0	0	0	0	0	0	0	0	0	0	0	0
Propanil	g/d	0	0	0	0	0	0	0	0	4372	933	0	0	0	0
MCPA	g/d	0	0	0	768	0	0	0	2177	1726	0	144	140	0	0
Mecoprp	g/d	0	0	0	0	0	0	0	816	115	0	0	0	0	0
Hexazinone	g/d	0	0	0	1208	207	223	464	1089	921	310	38	0	0	0
Terbutilazina	g/d	285	134	218	878	88	55	928	544	805	207	39	19	0	0

- = not detected (below 0.01 µg/L)

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.156: Average flow rates of some herbicides present in the Roggia Marcova (g/d)

Date	16 Apr	22 Apr	5 May	13 May	20 May	27 May	2 June	10 June	16 June	29 June	1 July	10 July	13 July	21 July	5 Aug	10 Aug	20 Aug
Discharge m ³ /s	4	2	14	1	4	19	11	3	3	1	3	1	1	1	22	9	11
Atrazina	0	20	95	3	0	0	0	8	8	0	0	1	1	3	0	0	0
Dimepiperate	0	0	581	13	52	0	0	0	0	0	0	0	0	0	0	0	0
Dimethenamide	0	31	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
Hexazinone	0	17	254	0	10	49	0	8	10	0	13	3	2	4	57	0	45
Molinate	0	35	956	19	214	1330	1869	303	122	9	22	3	0	2	0	0	9
Oxadiazon	0	17	714	18	10	460	0	0	39	5	15	6	3	8	209	0	64
Pretilachlor	0	259	302	0	166	0	608	75	0	0	0	0	0	0	0	0	0
Propanil	0	0	641	0	0	0	245	0	67	0	0	0	0	0	0	0	0
Terbuthylazine	0	0	109	0	24	0	0	13	10	0	0	1	0	3	0	0	0
Thiobencarb	0	69	121	46	0	0	0	0	0	0	0	0	0	0	0	0	0
Tiocarbazil	0	0	484	10	41	0	0	0	0	0	0	0	0	0	0	0	0
Bensulfuron met.	0	0	0	41	0	460	327	83	54	0	13	1	0	0	0	0	0
Bentazone	9	22	302	4	52	295	54	26	10	9	15	0	1	2	285	140	127
Cinosulfuron	0	0	218	34	35	640	490	130	83	17	43	9	3	10	0	0	0
MCPA	0	0	581	48	59	115	363	130	52	13	39	0	0	0	0	0	0
Mecoprop	0	0	0	1	28	0	118	78	13	4	17	0	0	0	0	0	0
Triclopyr	0	0	0	6	7	0	0	52	0	0	0	0	0	0	0	0	0

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Table B.8.157: Environmental characteristics of bensulfuron methyl and cinosulfuron

Active agent	Dosage used (g/ha)	K _{oc} ^c	DT ₅₀ soil (days)	DT ₅₀ water (days)
Bensulfuron methyl ^a	60	684	24	5
Cinosulfuron ^b	50	20	20	3

^a S. Cavanna et al. 1998^b The Pesticide Manual, 11th ed.^c C.R. Leake and E.W. Gatzweiler 1995Conclusion:

An attempt has been made to evaluate the environmental fate of the main herbicides used in rice production. This study area consisted of a dynamic system with continuous interchange of water, waterways, rice paddies, and the unconfined groundwater. Estimates of all volumes exchanged during rice production were made. For most herbicides, the impact on surface water is closely related to the application period and the quantity used. The impact of herbicides on surface aquifers is also a function of the quantity of herbicides used and the characteristics of the various herbicides. Bensulfuron methyl was determined to have the same solubility as cinosulfuron, but is less mobile in soil and is degraded before reaching the unconfined aquifer.

- 36) *Summary of surface water monitoring data for bensulfuron methyl in Italy. Barefoot, A.C., Whitehead, C.F., 2004.*

Cross reference IIA 7.4./02

Guidelines:

Not applicable – position paper

GLP:

No

The study is acceptable

Material and methods:

Two surface water-monitoring studies were made to evaluate the environmental fate of bensulfuron methyl following use of Sigma^o herbicide used during rice production in Italy. The selected surface water sampling locations represent main irrigation channels and permanent waterways that receive drainage from rice paddies surrounding Vercelli, Italy. The study collected water samples from six locations within the rice-growing districts of the East and West Sesia Irrigation Boards. Surface water samples were taken throughout the irrigation seasons of 1997 and 1998, and the water flow capacities (in m³/sec) were estimated on each sampling date. The capacities of the monitored waterways ranged from 7 m³/sec for the Lucca channel to 360 m³/sec for the Sesia River at Palestro (maximum capacity measures on 6/2/1998). The principal ditches have an average capacity of about 20-30 m³/sec during May. Data were also recorded on the air and water temperature, meteorological conditions, and appearance of the water (clear or muddy). All the samples were collected in duplicate and the water samples were analysed by the A.R.P.A. (Agenzia Regionale per la Protezione Ambientale = Regional Agency for Environmental Protection) Laboratory in Vercelli in accordance with the analytic method (VC.T2.M002 R01 “Research and determination of sulfonylurea in

Rapporteur Member State	Month and year	Active Substance (Name)
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Environmental fate and behaviour

bodies of water” and subsequent revisions) based on extraction and analysis by LC/MS with an limit of determination (LOD) of 0.01 µg/L. The pH of each sample was also determined.

Moreover, DuPont undertook a monitoring study in collaboration with the Institute of Agricultural Hydraulics and the Vercelli Regional Board for Environmental Protection. During the same time period, the University of Milan Institute of Agricultural Hydraulics and the Vercelli Regional Environmental Agency carried out a separate monitoring study at the same sites. The results of the water monitoring study are documented in ABOVE (cross reference II7.4./01 and IIA 7.4./03. Additional monitoring results were available through the courtesy of the M. Greppi, the principal investigator at the Institute of Agricultural Hydraulics. This position paper summarises the results from all sources so that the complete data set is readily available.

Findings:

Water samples were collected from the six locations between June 5 and September 16, 1997, and again between April 16 and October 22, 1998. The concentration of bensulfuron methyl did not exceed the LOD (0.01 µg/L) for any samples collected in 1997. During 1998, the second season of monitoring, bensulfuron methyl was found at detectable levels on several occasions. Data have been collected from three references discussing the two studies in 1998 and are reported in Table B.8.158.

In 1998, the concentration of bensulfuron methyl in the drainage water at five locations reached a maximum value in May or early June and declined to <0.01 µg/L by mid-July. Bensulfuron methyl was not detected above the LOD at the sixth location, Cavo Lucca. The maximum concentration of bensulfuron methyl at any location was 0.68 µg/L, measured on May 13 in Roggia Marcova. The location nearest Roggia Marcova is Roggia Bona, which had a similar flow rate and comparable bensulfuron methyl concentrations at each sampling date. In the Sesia, which is the largest waterway sampled, the bensulfuron methyl concentration never exceeded 0.26 µg/L.

Abundant rainfall during bensulfuron methyl application can cause the premature release of paddy water containing bensulfuron methyl as excess water spills into drainage canals. Daily weather data for the years 1997 and 1998, obtained from a weather station located in Vercelli (central to the monitoring area), indicates that more rain fell in 1998 than in 1997 during the critical bensulfuron methyl application months of April, May, and June.

Comparing the rainfall in Vercelli to the 20-year (1974-1993) weather record for the nearby city of Piacenza, Italy (from FOCUS; 2000) establishes a statistical profile for the two years. In 1997, the cumulative rainfall in Vercelli during April, May, and June (190.9 mm) was equivalent to the 30th percentile of the 20-year weather file. In 1998, the cumulative rainfall in Vercelli during April, May, and June (318.5 mm) was equivalent to the 82nd percentile of the 20-year weather file.

Rapporteur Member State	Month and year	Active Substance (Name)
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Environmental fate and behaviour

Table B.8.158: Surface water monitoring results from 1998 for bensulfuron methyl in east and west Sesia, Italy

Date	Location (µg/L)					
	Sesia	Marcova	Bona	Agogna	Busca	Lucca
16-APR	< 0.01 ^a	< 0.01 ^c	- ^e	-	-	-
22-APR	< 0.01 ^a	< 0.01 ^c	-	-	-	-
30-APR	< 0.01 ^a	-	-	-	-	-
5-MAY	-	< 0.01 ^c	< 0.01 ^c	-	-	-
8-MAY	0.20 ^a	-	-	-	-	-
13-MAY	-	0.68 ^c	0.50 ^c	-	-	-
15-MAY	0.10 ^a	-	-	-	-	-
20-MAY	-	< 0.01 ^c	< 0.01 ^c	-	-	-
22-MAY	0.12 ^a	-	-	-	-	-
27-MAY	-	0.28 ^c	0.40 ^c	-	-	-
29-MAY	0.15 ^a	-	-	-	-	-
2-JUN	0.16 ^{a,b}	0.31 ^b	0.30 ^{b,c}	0.19 ^b	0.22 ^b	< 0.01 ^b
2-JUN	-	0.36 ^c	-	-	-	-
10-JUN	-	0.32 ^c	0.19 ^c	-	-	-
11-JUN	0.26 ^a	-	nd	-	nd	-
15-JUN	< 0.01 ^b	< 0.01 ^b	< 0.01 ^b	-	-	-
16-JUN	-	0.21 ^c	0.06 ^c	-	-	-
18-JUN	< 0.01 ^a	-	-	-	-	-
24-JUN	< 0.01 ^a	-	-	-	nd	-
29-JUN	-	< 0.01 ^c	< 0.01 ^c	< 0.01 ^b	< 0.01 ^b	< 0.01 ^b
1-JUL	-	0.05 ^d	-	-	-	-
3-JUL	< 0.01 ^a	-	-	-	-	-
10-JUL	-	0.012 ^d	-	-	-	-
13-JUL	-	< 0.01 ^d	-	-	-	-
15-JUL	< 0.01 ^b	< 0.01 ^b	< 0.01 ^b	< 0.01 ^b	< 0.01 ^b	< 0.01 ^b
21-JUL	-	< 0.01 ^d	-	-	-	-
5-AUG	-	< 0.01 ^d	-	-	-	-
10-AUG	-	< 0.01 ^d	-	-	-	-
18-AUG	< 0.01 ^b	< 0.01 ^b	< 0.01 ^b	< 0.01 ^b	< 0.01 ^b	< 0.01 ^b
20-AUG	-	< 0.01 ^d	-	-	-	-
15-SEP	< 0.01 ^b	< 0.01 ^b	< 0.01 ^b	< 0.01 ^b	< 0.01 ^b	< 0.01 ^b
18-SEP	< 0.01 ^a	-	-	-	-	-
22-OCT	< 0.01 ^a	-	-	-	-	-

^a Values from Anselmetti, Vietti, Greppi, and Silvestri (1999).

^b Values from Peter (1999)

^c Values from a personal communication with Greppi (2003).

^d Calculated from the daily loading and discharge data presented in Anselmetti.

^e Not determined; no samples taken

Conclusion:

Monitoring results provide a clearer picture of bensulfuron methyl discharge from Italy's rice-growing region during the 1998 season. The mid-May measurements of bensulfuron methyl in the Marcova and Bona, which are both low volume streams, detected the highest bensulfuron methyl concentrations (0.68 and 0.50 µg/L, respectively) observed at any time or location during the study. Bensulfuron methyl concentrations were below detectable levels both 7 days before and 5 days after those samples were taken. By mid-July, bensulfuron methyl concentrations were below the detection limits at each of the sampling locations. Monitoring results from these two studies support the conclusion that bensulfuron methyl does not pose a significant threat of persistent contamination in the waterways of the monitored area.

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

B.8.11 Reference s relied on

Annex No., EU Data Requirement No., Reference No.	Author(s)	Year	Title Source Company Report No. GLP or GEP Status (where relevant) Published or not	EU Data Protection Claimed (Y/N)	Owner
IIA 7.1.1.1.1 IIA7.1.1.1.1./01	Anderson, J.J., Swain, R.S.	2002	Route of degradation of bensulfuron methyl in aerobic soil DuPont Stine-Haskell Research Center DuPont-4325 GLP: Yes Published: No	Y	DuPont
IIA 7.1.1.1.1 IIA7.1.1.1.1./02 IIA, 7.1.1.2.1./05	Friedman, P.L.	1984	Aerobic soil metabolism of ¹⁴ C-DPX-F5384 DuPont Experimental Station AMR 216-84 GLP: No Published: No	N	DuPont
IIA 7.1.1.1.1 IIA7.1.1.1.1./03 IIA 7.1.1.1.2; IIIA 9.1.1 IIA7.1.1.2.1./10	Yordy, J.R.	1987	Aerobic soil metabolism of DPX-F5384 DuPont Stine-Haskell Research Center AMR 782-87 GLP: Yes Published: No	N	DuPont
IIA 7.1.1.1.2 IIA7.1.1.1.2./0 IIA 7.1.1.1.2; IIIA 9.1.1 IIA7.1.1.2.1./03 I	Cadwgan, G.E., Ryan, T.W.	1986	Anaerobic aquatic metabolism of [Pyrimidine -2- ¹⁴ C] DPX-F5384 and [Phenyl(U)- ¹⁴ C] DPX-H6573 in water DuPont Experimental Station AMR 606-86 GLP: Yes Published: No	N	DuPont
IIA 7.1.1.1.2 IIA7.1.1.1.2./02	Scott, M.T.	1986	Photodegradation of [Phenyl(U)- ¹⁴ C] DPX-F5384 and [Pyrimidine-2- ¹⁴ C] DPX-F5384 on soil DuPont Experimental Station AMR 512-86 GLP: No Published: No	N	DuPont
IIA 7.1.1.1.2; IIIA 9.1.1 IIA7.1.1.2.1./01	Anderson, J.J., Swain, R.S.	2002	Route of degradation of bensulfuron methyl in aerobic soil DuPont Stine-Haskell Research Center DuPont-4325 GLP: Yes Published: No	Y	DuPont
IIA 7.1.1.1.1 IIA7.1.1.2.1./02	Brusa, T., Ferrari, F.	1997	Bensulfuron methyl: Mixed culture microbial degradation maintenance Microbiol. Res., Volume 152, pages 137-141 Not applicable – Publication GLP: No Published: Yes	N	Authors
IIA 7.1.1.1.2; IIIA 9.1.1 IIA 7.0/01	A. Van- Nguyen	2004	Calculated half-lives of bensulfuron methyl in environmental fate studies DuPont -Stine-Haskell Research Center DuPont-14410 Not applicable – Calculation GLP: No	Y	Owner

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Annex No., EU Data Requirement No., Reference No.	Author(s)	Year	Title Source Company Report No. GLP or GEP Status (where relevant) Published or not	EU Data Protection Claimed (Y/N)	Owner
IIA 7.1.1.1.2; IIIA 9.1.1 IIA7.1.1.2.1./04	Crowe, A.	2002	Degradation rate of IN-F7880 in four soils Huntingdon Life Sciences, Ltd. DuPont-7177 GLP: Yes Published: No	Y	DuPont
IIA 7.1.1.1.2; IIIA 9.1.1 IIA7.1.1.2.1./06	Shaw, D.	2002a	Degradation rates of [¹⁴ C]IN-N5297 in four soils Huntingdon Life Sciences, Ltd. DuPont-5265 GLP: Yes Published: No	Y	DuPont
IIA 7.1.1.1.2; IIIA 9.1.1 IIA7.1.1.2.1./07	Shaw, D.	2002b	Degradation rates of [¹⁴ C]IN-J0290 in four soils Huntingdon Life Sciences, Ltd. DuPont-5266 GLP: Yes Published: No	Y	DuPont
IIA 7.1.1.1.2; IIIA 9.1.1 IIA7.1.1.2.1./08	Shaw, D.	2002c	Degradation rates of [¹⁴ C]IN-R9419 in four soils Huntingdon Life Sciences, Ltd. DuPont-6245 GLP: Yes Published: No	Y	DuPont
IIA 7.1.1.1.2; IIIA 9.1.1 IIA7.1.1.2.1./09	Shaw, D.	2002d	Degradation rates of [¹⁴ C]IN-D1R84 in four soils Huntingdon Life Sciences, Ltd. DuPont-6247 GLP: Yes Published: No	Y	DuPont
IIA 7.1.1.2.2; IIIA 9.1.1.2 IIA7.1.1.2.2./01	Bonacini, F., Zenide, D., Gasser, F., Leka, A.	1998	Field dissipation of bensulfuron methyl and metsulfuron methyl from a representative rice field following treatment of three consecutive years with Sigma 60 DF herbicide in Italy (seasons 1994 – 1996) Battelle Europe-Geneva Research Centres AMR 4162-96 GLP: Yes Published: No	N	DuPont
IIA 7.1.1.2.2; IIIA 9.1.1.2 IIA7.1.1.2.2./02	Bonacini, F., Zenide, D., Gasser, F., Leka, A.	1999	Field dissipation of bensulfuron methyl and metsulfuron methyl from a representative rice field following treatment of three consecutive years with Sigma 60 DF herbicide in Italy seasons 1994-1996, and magnitude of residue in rice grains Battelle Europe - Geneva Research Centres AMR 4162-96, Amendment No. 1 GLP: Yes Published: No	Y	DuPont

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Annex No., EU Data Requirement No., Reference No.	Author(s)	Year	Title Source Company Report No. GLP or GEP Status (where relevant) Published or not	EU Data Protection Claimed (Y/N)	Owner
IIA 7.1.2 IIA 7.1.2./01	Aikens, P.J.	2001a	[¹⁴ C]IN-N5297: Adsorption/Desorption in five soils Huntingdon Life Sciences, Ltd. DuPont-5263 GLP: Yes Published: No	Y	DuPont
IIA 7.1.2 IIA 7.1.2./02	Aikens, P.J.	2001b	[¹⁴ C]IN-J0290: Adsorption/Desorption in five soils Huntingdon Life Sciences, Ltd. DuPont-5264 GLP: Yes Published: No	Y	DuPont
IIA 7.1.2 IIA 7.1.2./03	Aikens, P.J.	2002a	Adsorption/Desorption of [¹⁴ C]IN-R9419 in five soils Huntingdon Life Sciences, Ltd. DuPont-6246 GLP: Yes Published: No	Y	DuPont
IIA 7.1.2 IIA 7.1.2./04	Aikens, P.J.	2002b	Adsorption/Desorption of [¹⁴ C]IN-DIR84 in five soils Huntingdon Life Sciences, Ltd. DuPont-6248 GLP: Yes Published: No	Y	DuPont
IIA 7.1.2 IIA 7.1.2./05	Cavanna, S., Garatti, E., Rastelle, E., Molinari, G.P.	1998	Adsorption and desorption of bensulfuron methyl on Italian paddy field soils Chemosphere, Volume 37(8), pages 1547-1555 Not applicable – Publication GLP: No Published: Yes	N	DuPont
IIA 7.1.2 IIA 7.1.2./06	Crowe, A.	2002	Adsorption/Desorption of IN-F7880 in five soils Huntingdon Life Sciences, Ltd. DuPont-7178 GLP: Yes Published: No	Y	DuPont
IIA 7.1.2 IIA 7.1.2./07	Priester, T.M.	1985	Batch equilibrium (adsorption/desorption) and soil thin-layer chromatography studies with ¹⁴ C-DPX-F5384 DuPont Experimental Station AMR 254-84 GLP: No Published: No	N	DuPont
IIA 7.2.1.1 IIA 7.2.1.1./01	Hatzenbeler, C.J.	2002	Bensulfuron methyl: Hydrolysis in buffer solutions of pH 4, 7, and 9 Ricerca, LLC DuPont-4499 GLP: Yes Published: No	Y	DuPont

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Annex No., EU Data Requirement No., Reference No.	Author(s)	Year	Title Source Company Report No. GLP or GEP Status (where relevant) Published or not	EU Data Protection Claimed (Y/N)	Owner
IIA 7.2.1.1 IIA 7.2.1.1./02	Sabadie, J.	1996	Alcoholysis and chemical hydrolysis of bensulfuron methyl Weed Research, Volume 36, pages 441-448 Not applicable – Publication GLP: No Published: Yes	N	Author
IIA 7.2.1.2 IIA 7.2.1.2./01	Horne, P.	1987	Photodegradation of [Phenyl(U)- ¹⁴ C] DPX-F5384 and [Pyrimidine-2- ¹⁴ C] DPX-F5384 in water (conducted in sunlight) DuPont Experimental Station AMR 899-87 GLP: No Published: No	N	DuPont
IIA 7.2.1.2 IIA 7.2.1.2./02	Lentz, N.R.	2003	Photodegradation of [¹⁴ C] bensulfuron methyl in natural water by simulated sunlight Ricerca, LLC DuPont-8697 GLP: Yes Published: No	Y	DuPont
IIA 7.2.1.3.1 IIA 7.2.1.3.1./01	Barnes, S.P.	2002	Bensulfuron methyl (DPX-F5384): Assessment of ready biodegradability by modified sturm test Huntingdon Research Centre (UK) DuPont-9781 GLP: Yes Published: No	Y	DuPont
IIA 7.2.1.3.2 IIA 7.2.1.3.2./01	Hunt, O.R.	1986	Aerobic aquatic metabolism of [Phenyl(U)- ¹⁴ C] DPX-F5384 and [Pyrimidine-2- ¹⁴ C] DPX-F5384 DuPont Experimental Station AMR 475-86 GLP: Yes Published: No	N	DuPont
IIA 7.2.1.3.2 IIA 7.2.1.3.2./02	Lentz, N.R.	2001	Aerobic aquatic metabolism of bensulfuron methyl in two water/sediment systems Ricerca, LLC DuPont-4362 GLP: Yes Published: No	Y	DuPont
IIA 7.2.1.3.2 IIA 7.2.1.3.2./02	Van-Nguyen, A., Theilacker, W.M.	2003	Photodegradation of bensulfuron methyl in a simulated paddy system DuPont Stine-Haskell Research Center DuPont-11110 GLP: Yes Published: No	Y	DuPont

Rapporteur Member State	Month and year	Active Substance (Name)
Italy	May 2006	Bensulfuron methyl

Environmental fate and behaviour

Annex No., EU Data Requirement No., Reference No.	Author(s)	Year	Title Source Company Report No. GLP or GEP Status (where relevant) Published or not	EU Data Protection Claimed (Y/N)	Owner
IIA 7.2.2 IIA 7.2.2./01	Schmuckler, M.E.	2000	Photochemical oxidative degradation of bensulfuron methyl DuPont Stine-Haskell Research Center DuPont-4662 GLP: Not required Published: No	Y	DuPont
IIIA 9.2.3 IIA 7.4./01	Anselmetti, M.P., Vietti, L., Greppi, M., Silvestri S.	1998	Monitoring of the surface and stratum waters of the rice-growing area of northwest Italy XI Symposium, Pesticide Chemistry, pages 211-222 Not applicable – Publication GLP: No Published: Yes	N	DuPont
IIIA 9.2.3 IIA 7.4./02	Barefoot, A.C., Whitehead, C.F.	2004	Summary of surface water monitoring data for bensulfuron methyl in Italy DuPont Stine-Haskell Research Center DuPont-15347 GLP: Not applicable – position paper Published: No	Y	DuPont
IIIA 9.2.1 IIIA 9.2.3 IIA 7.4./03	Peter, J.	1997	Surface and ground water monitoring study in Italy, east and west Sesia area, to access contamination of bensulfuron methyl and metsulfuron methyl following annual application of Sigma Battelle Europe - Geneva Research Centres AMR 4618-97 GLP: Yes, except field application phase Published: No	N	DuPont
IIIA 9.1.3 IIA 9.1.3./01	Warren, R.	2004	Predicted Environmental Concentrations of Bensulfuron Methyl and Metabolites in Soil, Ground Water, Surface Water, Sediment, and Air Following Application to Rice in the EU DuPont Stine-Haskell Research Center DuPont-12165 GLP: No Published: No	Y	DuPont
IIIA 9.1.3 cross reference not provided IIIA 9.2.1 IIIA 9.2.1./01 IIIA 9.2.3 IIIA 9.2.3./01	Warren, R.	2006	Predicted Environmental Concentrations of Bensulfuron Methyl and Metabolites in Soil, Ground Water, Surface Water, Sediment, and Air Following Application to Rice in the EU. Revision 1 DuPont Stine-Haskell Research Center DuPont-12165 GLP: No Published: No	Y	DuPont