

Appendix to:

EFSA (European Food Safety Authority), 2017. Conclusion on the peer review of the pesticide risk assessment of the active substance terbuthylazine. EFSA Journal 2017;15(6):4868, 58 pp. doi:10.2903/j.efsa.2017.4868

© European Food Safety Authority, 2017

Appendix A – List of end points for the active substance and the representative formulation

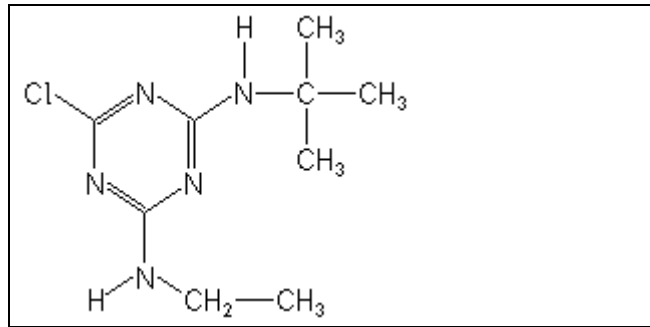
Identity, Physical and Chemical Properties, Details of Uses, Further Information

Active substance (ISO Common Name) ‡	Terbuthylazine (ISO 1750)
Function (<i>e.g.</i> fungicide)	Herbicide
Rapporteur Member State	United Kingdom (UK)

Identity (Annex IIA, point 1)

Chemical name (IUPAC) ‡	<i>N</i> ² - <i>tert</i> -butyl-6-chloro- <i>N</i> ⁴ -ethyl-1,3,5-triazine-2,4-diamine	
Chemical name (CA) ‡	6-chloro- <i>N</i> -(1,1-dimethylethyl)- <i>N</i> ⁷ -ethyl-1,3,5-triazine-2,4-diamine	
CIPAC No ‡	234	
CAS No ‡	5915-41-3	
EC No (EINECS or ELINCS) ‡	227-637-9	
FAO Specification (including year of publication) ‡	Yes (1993) terbuthylazine content not less than 930 g/kg. (234/TC/S (1991))	
Minimum purity of the active substance as manufactured ‡	Syngenta	960 g/kg
	Oxon	980 g/kg
Identity of relevant impurities (of toxicological, ecotoxicological and/or environmental concern) in the active substance as manufactured	Propazine (SYN)	10 g/kg
	Atrazine (Oxon)	1 g/kg
	Simazine (SYN)	30 g/kg
	Simazine (Oxon)	5 g/kg
Molecular formula ‡	C ₉ H ₁₆ ClN ₅	
Molecular mass ‡	229.7 g/mol	

Structural formula ‡



Physical and chemical properties (Annex IIA, point 2)

Melting point (state purity) ‡	Syngenta: 175.5°C (99.4%) Oxon: 175.7°C (99.6%)
Boiling point (state purity) ‡	Syngenta: decomposition observed at 224°C (99.4%) Oxon: decomposition after melting (99.6%)
Temperature of decomposition (state purity)	Syngenta: 224°C (99.4%) Oxon: 230°C (99.6%)
Appearance (state purity) ‡	Syngenta: White crystalline powder (99.4%) Oxon: White powder (99.6%)
Vapour pressure (state temperature, state purity) ‡	Syngenta: 9.0×10^{-5} Pa at 25 °C (99.4%) Oxon: 1.52×10^{-4} Pa at 22 °C (>99%.)
Henry's law constant ‡	Syngenta: 2.3×10^{-3} Pa m ³ mol ⁻¹ Oxon: 4.18×10^{-3} Pa m ³ mol ⁻¹
Solubility in water (state temperature, state purity and pH) ‡	Syngenta: 9.0 mg/L at 25 °C (pH 7.4) (99.4%) Oxon: 6.6 mg/L at 20 °C (pH 4-10) (>99%)
Solubility in organic solvents ‡ (state temperature, state purity)	Syngenta: at 25°C in g/L (96.8%) hexane 0.41 toluene 9.8 dichloromethane 51 methanol 18 octanol 12 acetone 41 ethyl acetate 35 Oxon: at 20°C in g/L (99.5%) hexane 0.275 toluene 7.17 dichloromethane 62.7 methanol 14.9 acetone 32.8 ethyl acetate 30.5
Surface tension ‡ (state concentration and temperature, state purity)	Syngenta: 71.8 mN/m at 20 °C (90 % saturated solution)(96.5%) Oxon: 70.9 mN/m at 20 °C (90 % saturated solution)(96.8%)
Partition co-efficient ‡ (state temperature, pH and purity)	Syngenta: $\log P_{O/W} = 3.4$ at 25 °C (not pH dependant (99.4%) Oxon: $\log P_{O/W} = 3.41$ at 20 °C (not pH dependant (99.5%)
Dissociation constant (state purity) ‡	Syngenta: $pK_{a1} = 1.95$ (99.4%) Oxon: $pK_{a1} = 1.84$ (99.5%)

UV/VIS absorption (max.) incl. ϵ ‡
(state purity, pH)

Syngenta: solution:		
Solution	λ (nm)	ϵ (l/mol cm)
neutral	222	38538
	263	3444
acidic	223	30103
	263	4468
basic	223	37426
	263	3395
No absorption maximum observed between 290 and 750 nm in neutral and basic solution and between 310 nm and 750 nm in acidic solution.		
Oxon: solution:		
Solution	λ (nm)	ϵ (l/mol cm)
neutral	222	38696
	262	3291
acidic	222	29424
basic	222	38191
	262	3241
Flammability ‡ (state purity)		
Syngenta: Not highly flammable (96.8%)		
Oxon: Not highly flammable (96.5%)		
Not classified.		
Explosive properties ‡ (state purity)		
Syngenta: Not explosive (96.8%)		
Oxon: Not explosive (96.5%)		
Oxidising properties ‡ (state purity)		
Syngenta: Not oxidising (96.8%)		
Oxon: Not oxidising (96.5%)		

Summary of representative uses evaluated

a) Syngenta - Tradename: [GARDO[®] GOLD[®]]

Active Ingredients: [Terbuthylazine and S-metolachlor]

Crop and/or situation (a)	Member State or Country	Product name	F G or I (b)	Pests or Group of pests controlled (c)	Formulation		Application				Application rate per treatment			PHI (days) (l)	Remarks: (m)
					Type (d-f)	Conc. of as (i)	method kind (f-h)	growth stage & season (j)	number min-max (k)	interval between applications (min)	kg as/hL min-max	water L/ha min-max	kg as/ha min-- max		
Maize	N.EU.	GARDO [®] GOLD [®]	F	Dicot and monocot weeds	SE	187.5 g/L Terbuthylazine 312.5 g/L S-metolachlor	Tractor - mounted sprayer	pre- emergence - 8 leaf	1	Not applicable	0.15-0.375 Terbuthylazine 0.25-0.614 S-metolachlor	200 500	Max. 0.75 Terbuthylazine Max. 1.228 S- metolachlor	Not appli- cable	[1] [2] [3] [4] [5]
Maize	S.EU.	GARDO [®] GOLD [®]	F	Dicot and monocot weeds	SE	187.5 g/L Terbuthylazine 312.5 g/L S- metolachlor	Tractor - mounted sprayer	pre- emergence - 8 leaf	1	Not applicable	0.168-0.422 Terbuthylazine 0.28-0.71 S- metolachlor	200 500	Max. 0.844 Terbuthylazine Max. 1.415 S- metolachlor	Not appli- cable	[1] [2] [3] [4] [5]

b) Oxon - Tradename: [Terbuthylazine 500 g/L SC]

Active Ingredients: [Terbuthylazine]

Crop and/or situation (a)	Member State or Country	Product name	F G or I (b)	Pests or Group of pests controlled (c)	Preparation		Application				Application rate per treatment (for explanation see the text in front of this section)			PHI (days) (m)	Remarks
					Type (d-f)	Conc. of as (i)	method kind (f-h)	growth stage & season (j)	number min-max (k)	interval between applications (min)	kg as/hL min-max (l)	Water L/ha min-max	kg as/ha min-max (l)		
Maize	France (N) Germany (N) The Netherlands (N)	Terbuthylazine 500 g/L SC	F	Annual and perennial broad leaved weeds	SC	500 g/l	Spray	Pre-emergence Early post emergence (12-16)	1	-	0.15-0.5	200-500	0.75-0.844	n.r	[1] [3] [4] [5]
	France(S) Italy (S) Spain S)														[1] [3] [4] [5]
Sorghum	Italy (S) Spain (S)	Terbuthylazine 500 g/L SC	F	Annual and perennial broad leaved weeds	SC	500 g/l	Spray	Pre-emergence Early post emergence (14)	1	-	0.2-0.5	200-500	0.844	n.r.	[1] [3] [4] [5]

- [1] A critical area of concern is identified because a high long-term risk and a high risk from secondary poisoning were indicated for mammals in section 5 of EFSA (2011).
- [2] A high long-term risk to earthworms was indicated in the risk assessment for the representative uses of the formulation 'Gardo® Gold®' according to EFSA (2011)..
- [3] Critical areas of concern were identified for groundwater contamination of metabolites (MT1, MT13 and MT14) for which the groundwater relevance was indicated due to intakes of infants being calculated to be above the ADI and because a herbicidally relevant metabolite (MT1) occurs in groundwater, both over a wide range of geoclimatic conditions.
- [4] For the metabolites LM2, LM3, LM4, LM5 and LM6 the groundwater relevance assessment could not be finalised.
- [5] A high long-term risk to birds was indicated according to EFSA (2011)..

<p>(a) For crops, the EU and Codex classifications (both) should be taken into account; where relevant, the use situation should be described (e.g. fumigation of a structure)</p> <p>(b) Outdoor or field use (F), greenhouse application (G) or indoor application (I)</p> <p>(c) e.g. biting and suckling insects, soil born insects, foliar fungi, weeds</p> <p>(d) e.g. wettable powder (WP), emulsifiable concentrate (EC), granule (GR)</p> <p>(e) GCPF Codes - GIFAP Technical Monograph No 2, 1989</p> <p>(f) All abbreviations used must be explained</p> <p>(g) Method, e.g. high volume spraying, low volume spraying, spreading, dusting, drench</p> <p>(h) Kind, e.g. overall, broadcast, aerial spraying, row, individual plant, between the plant- type of equipment used must be indicated</p>	<p>(i) g/kg or g/L.</p> <p>(j) Growth stage at last treatment (BBCH Monograph, Growth Stages of Plants, 1997, Blackwell, ISBN 3-8263-3152-4), including where relevant, information on season at time of application</p> <p>(k) Indicate the minimum and maximum number of application possible under practical conditions of use</p> <p>(l) The values should be given in g or kg whatever gives the more manageable number (e.g. 200 kg/ha instead of 200 000 g/ha or 12.5 g/ha instead of 0.0125 kg/ha)</p> <p>(m) PHI - minimum pre-harvest interval n.r.= not relevant, the pre-harvest interval is covered by the growing period remaining between the envisaged application and harvest</p>
---	--

Methods of Analysis

Analytical methods for the active substance (Annex IIA, point 4.1)

Technical as (analytical technique)	Syngenta: Method AW52/3. GC-FID and internal calibration with prometryn Oxon: HPLC-UV at 220nm and external calibration
Impurities in technical as (analytical technique)	Syngenta: Relevant impurities: GC-FID and internal calibration with prometryn Oxon: GC-FID and internal calibration with 0.02% solution dibutylphthalate in acetone
Plant protection product (analytical technique)	Syngenta: Method AF-1301/3. Reverse phase HPLC-UV at 210nm and external calibration Oxon: Method MAN/024/01. Reverse phase HPLC-UV at 254nm and external calibration

Analytical methods for residues (Annex IIA, point 4.2)

Residue definitions for monitoring purposes

Food of plant origin	Terbuthylazine (MT0)
Food of animal origin	Not necessary for the representative uses.
Soil	Terbuthylazine (MT0) plus desethyl-terbuthylazine (MT1) plus hydroxyl-terbuthylazine (MT13)
Water surface	Terbuthylazine (MT0) plus desethyl-terbuthylazine (MT1) plus hydroxyl-terbuthylazine (MT13)
drinking/ground	Terbuthylazine (MT0), desethyl-terbuthylazine (MT1), hydroxy-terbuthylazine (MT13), desethyl-hydroxy-terbuthylazine (MT14). Open regarding LM2, LM3, LM4, LM5 and LM6
Air	Terbuthylazine

Monitoring/Enforcement methods

Food/feed of plant origin (analytical technique and LOQ for methods for monitoring purposes)	Syngenta: DFG S19. GC-NPD with LOQ of 0.02 mg/kg in grain (acceptable ILV). Terbuthylazine only Oxon: Published method. GC-NPD with LOQ of 0.02 mg/kg in grain. Terbuthylazine only
Food/feed of animal origin (analytical technique and LOQ for methods for monitoring purposes)	Not required

Soil (analytical technique and LOQ)

Syngenta: REM 148.05 GC-MS confirmation with target m/z of 214 and 3 qualifier ions (m/z 216, 229 and 173). LOQ was 0.02 mg/kg.

REM 148.11. HPLC-MS/MS parent ion m/z = 230 and daughter ion m/z was 174. MT1 m/z was 202 and daughter m/z 146. MT13 m/z was 212 and daughter m/z was 156. MT14 m/z was 184 and daughter m/z was 128. LOQ was 0.01 mg/kg for each.

Oxon: HPLC-MS/MS parent ion m/z = 230 and daughter ion m/z was 174. MT1 m/z was 202 and daughter m/z 146. MT13 m/z was 212 and daughter m/z was 156. LOQ was 0.01 mg/kg for each

Water (analytical technique and LOQ)

Syngenta: RAM 426/01 (validated in river, ground and drinking water). Reverse phase HPLC-MS/MS. Parent ion m/z = 230 and daughter ion m/z was 174. MT1 m/z was 202 and daughter m/z 146. MT13 m/z was 212 and daughter m/z was 156. MT14 m/z was 184 and daughter m/z was 128. LOQ was 0.1 $\mu\text{g/l}$ for each.

Oxon: Reverse phase HPLC-MS/MS (validated in surface and drinking water). . Parent ion m/z = 230 and daughter ion m/z was 174. MT1 m/z was 202 and daughter m/z 146. MT13 m/z was 212 and daughter m/z was 156. LOQ was 0.05 $\mu\text{g/l}$ for each.

Air (analytical technique and LOQ)

Syngenta: GC-NPD with confirmation by GC-MS with target m/z 214 and qualifier ions m/z 216, 229 and 173. LOQ was $1\mu\text{g/m}^3$.

Oxon: GC-NPD with LOQ of $1\mu\text{g/m}^3$.

Body fluids and tissues (analytical technique and LOQ)

Syngenta: No data submitted or required.

Oxon: No data submitted or required.

Classification and proposed labelling with regard to physical and chemical data (Annex IIA, point 10)

Active substance

RMS/peer review proposal

None

Impact on Human and Animal Health

Absorption, distribution, excretion and metabolism (toxicokinetics) (Annex IIA, point 5.1)

Toxicologically relevant compounds ‡
(animals and plants)

Terbuthylazine

Toxicologically relevant compounds ‡
(environment)

Terbuthylazine and desethyl-metabolite (MT1), MT13,
MT14, LM1,
Data gap regarding LM2, LM3, LM4, LM5, LM6

Other toxicological studies (Annex IIA, point 5.8)

Mechanism studies ‡

None submitted

Studies performed on metabolites or impurities ‡

MT14

Acute oral LD₅₀ (rats) : > 2000 mg/kg bw.
90-day dietary rats: NOAEL and LOAEL of 10.3 and 45.7 mg/kg bw/day, based on increased mortality and water consumption, changes in haematology, clinical chemistry and urinalysis parameters and increased kidney weight, renal (histo)pathology secondary to chronic renal failure.

Mutagenicity in bacterial cells: negative.

Clastogenicity in CHO (Chinese Hamster Ovary) cells: negative.

Mouse Lymphoma assay: negative

MT13

Acute oral LD₅₀ (rats) : > 2000 mg/kg bw.
90-day dietary rats: NOAEL and LOAEL of 3.4 and 10.3 mg/kg bw/day based on changes in haematology and clinical chemistry parameters.

Mutagenicity in bacterial cells: negative

Mouse lymphoma assay in L5178Y cells: negative

Clastogenicity in cultured human lymphocytes: negative

MT20

Acute oral LD₅₀ (rats) : > 5500 mg/kg bw

90-day dietary rats:

M: NOAEL and LOAEL of 16.7 and 34.1 mg/kg bw/day, based on decreased bodyweight, changes in clinical chemistry and urinalysis parameters and organ weight effects

F: NOAEL and LOAEL of 0.7 and 7.6 mg/kg bw/day, based on altered oestrus cycle length and prolonged oestrus and/or dioestrus

Mutagenicity in bacterial cells: negative

Mouse micronucleus assay: negative

MT1	<p>Acute oral LD₅₀ (rats) : 236 mg/kg bw Acute oral LD₅₀ (rats) : 300-500 mg/kg bw Mutagenicity in bacterial cells: negative Second Mutagenicity in bacterial cells: negative <i>In Vitro</i> Cytogenetic Assay in Human Lymphocytes: negative Gene Mutation Assay: weakly positive Mouse micronucleus assay: negative <i>in vivo</i> unscheduled DNA synthesis: negative 90-day rat study Reduced bodyweight gain Total WBC (white blood cells) reduced no NOAEL</p>
LM1	<p>Mutagenicity in bacterial cells: negative Mammalian cell Gene Mutation Assay: negative <i>In Vitro</i> Chromosome Aberration: negative</p>
LM2	<p>Mutagenicity in bacterial cells: negative Mammalian cell Gene Mutation Assay: negative <i>In vitro</i> Chromosome Aberration: negative</p>
LM3	<p>Mutagenicity in bacterial cells: negative Mammalian cell Gene Mutation Assay: negative <i>In vitro</i> Chromosome Aberration: negative</p>
LM4	<p>Mutagenicity in bacterial cells: negative Mammalian cell Gene Mutation Assay: negative <i>In vitro</i> Chromosome Aberration: negative</p>
LM5	<p>Mutagenicity in bacterial cells: negative Mammalian cell Gene Mutation Assay: negative <i>In vitro</i> Chromosome Aberration: negative</p>
LM6	<p>Mutagenicity in bacterial cells: negative Gene Mutation Assay: weakly positive <i>In Vitro</i> Chromosome Aberration: negative Mouse micronucleus assay: negative</p>

Summary (Annex IIA, point 5.10)

	Value (mg/kg bw (per day))	Study	Uncertainty factor
ADI ‡	0.004	dog, 1-year & rat, 2-year	100
AOEL ‡	0.0032	dog, 1-year	Overall 126* (100 + 79 %*)
ARfD ‡	0.008	rabbit developmental study	100

*correction for oral absorption (79 %)

Metabolites MT1, MT13, MT14

ADI ‡

0.004	dog, 1-year & rat, 2-year	100
0.008	rabbit developmental study	100

ARfD ‡

Classification and proposed labelling with regard to toxicological data (Annex IIA, point 10)

Substance :

Terbuthylazine

Harmonised classification according to Regulation (EC) No 1272/2008 and its Adaptations to Technical Process [Table 3.1 of Annex VI of Regulation (EC) No 1272/2008 as amended]¹ :

No current Annex VI entry.
RAC opinion (June 2015):
Acute Tox.4 - H302 “Harmful if swallowed”
STOT-RE-2 – H373 May cause damage to organs through prolonged or repeated exposure.

Peer review proposal² for harmonised classification according to Regulation (EC) No 1272/2008:

Acute Tox.4 - H302 Harmful if swallowed
STOT-RE-2 – H373 May cause damage to organs through prolonged or repeated exposure.

¹ Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006. OJ L 353, 31.12.2008, 1-1355.

² It should be noted that harmonised classification and labelling is formally proposed and decided in accordance with Regulation (EC) No 1272/2008.

Consumer risk assessment (Annex IIA, point 6.9, Annex IIIA, point 8.8)

ADI	0.004 mg/kg bw/day
TMDI (% ADI) according to WHO European diet	
IEDI (% ADI) according to EFSA PRIMo rev2 model	Highest IEDI: 21.6 % ADI (WHO cluster B) considering as a worst case, the STMRs of 0.06 mg/kg (total residues) in maize, sorghum and in rotational oilseed crops, root crops, and cereals (rice, wheat/ rye, oat/ barley)
NEDI (% ADI) according to national diets (to be specified)	Population groups (EFSA PRIMo) with profile similar to consumer group defaults for drinking water assessment (WHO, 2011) Adult: 12.6 % ADI (IE); Toddler: 9.1% ADI (FR 1-1.5 yrs, 10.6 kg) Infant: 9.0% ADI (UK; 0.5-1 yr, 8.7 kg)
Factors included in IEDI and NEDI	
ARfD	0.008 mg/kg bw
IESTI (% ARfD) according to EFSA PRIMo rev2 model	Highest IESTI: 63% ARfD (Carrot as rotational crop, HR 0.08 mg/kg)
NESTI (% ARfD) according to national (to be specified)	
Factors included in IESTI and NESTI	

Additional contribution to the consumer intakes through drinking water resulting from groundwater metabolite(s)

	Concentration [µg/L] ³	Intakes via drinking water					
		[mg/kg bw per day]			[% ADI]		
		Adult	Toddler	Infant	Adult	Toddler	Infant
M13	26.15	0.000872	0.002615	0.003922	21.8	65.4	98.1
M1	0.13	0.000004	0.000013	0.000019	0.10	0.31	0.47
M14	2.41	0.000080	0.000241	0.000362	2.0	6.0	9.0
Sum	26.15	0.000956	0.002869	0.004303	23.9	71.7	107.6

³ parent equivalents

Route of degradation (aerobic) in soil (Annex IIA, point 7.1.1.1) – SYN and OXON

Mineralisation after 100 days ‡	0.4 – 10.35 % after 112 - 120 d at 20 °C, [¹⁴ C-triazine ring]-label (n ⁴ = 17) 0.29 % after 118 d at 10 °C, [¹⁴ C-triazine ring]-label (n= 1; SYN only)
Non-extractable residues after 100 days ‡	17.3 – 30.8 % after 112 - 120 d at 20 °C, [¹⁴ C-triazine ring]-label (n= 17) 9.31 % after 118 d at 10 °C, , [¹⁴ C-triazine ring]-label (n= 1; SYN only)
Metabolites requiring further consideration ‡ - name and/or code, % of applied (range and maximum)	Max values from studies: desethyl-terbuthylazine (MT1) – 3.0 – 25.1 % at 56 - 210 d at 20 °C (n= 17) 14.6 % at 118 d at 10 °C (n=1; SYN only) hydroxy-terbuthylazine (MT13) – 4.2 – 34.5 % at 90 - 311 d at 20 °C (n= 17) 1.4 % at 98 d at 10 °C (n= 1; SYN only) [¹⁴ C-triazine ring]-label

Route of degradation in soil - Supplemental studies (Annex IIA, point 7.1.1.2) – SYN and OXON

Anaerobic degradation ‡	
Mineralisation after 100 days	≤ 0.1 % after 100 - 118 d, [¹⁴ C-triazine ring]-label (n= 2)
Non-extractable residues after 100 days	30.1 – 39.43 % after 100 - 118 d, [¹⁴ C-triazine ring]-label (n= 2)
Metabolites that may require further consideration for risk assessment - name and/or code, % of applied (range and maximum)	Max values from studies: desethyl-terbuthylazine (MT1) – 0.3 – 4.5 % at 30 - 56 d (n= 2) hydroxy-terbuthylazine (MT13) – 1.0 – 8.16 % at 91 - 100 d (n= 2) [¹⁴ C-triazine ring]-label
Soil photolysis ‡	
Metabolites that may require further consideration for risk assessment - name and/or code, % of applied (range and maximum)	DT50 in light exposed samples = 52 d; DT50 in dark control = 117 d (DT50 via photolysis only = 93.6 d; SYN) DT50 in light exposed samples = 28.2 d; DT50 in dark control = 126.6 d (DT50 via photolysis only = 36.3 d; OXON) Max values from studies (irradiated value

⁴ n corresponds to the number of soils.

minus non-irradiated value):

Desethyl-terbuthylazine (MT1) – 3.6 % at 31 d exposure 12 hours irradiated at 550 W.m²/ 12 hours dark (n= 1; SYN)

12.59 % at 15 d – exposure 700 W.m² continuous (n= 1; OXON).

Hydroxy-terbuthylazine (MT13) – 5.49 % at 15 d – exposure 700 W.m² continuous (n= 1; OXON)

Rate of degradation in soil (Annex IIA, point 7.1.1.2, Annex IIIA, point 9.1.1) – SYN and OXON

Laboratory studies ‡

Terbuthylazine	Aerobic conditions							
	Soil name and classification	% OM	pH (KCl or CaCl ₂)	temp. °C / soil moisture for study (% w/w)	Soil moisture at pF 2 (% w/w)	DT _{50, actual} (d)	DT _{50, ref} 20 °C pF2 (d)	Min chi ² error (%)
Gartenacker Sandy Loam	3.79	7.25	20 °C / 26.73 %	48.92	78.7	51.6	1.7	SFO
Pappelacker Loamy Sand	1.9	7.6	20 °C / 15.8 %	29.3	93.1	60.4	2.9	SFO
Weide Sandy Loam	2.24	7.5	20 °C / 18.96 %	36.6	65.0	41.0	2.5	SFO
Speyer 2.2 Loamy Sand	3.91	6.1	20 °C / 19.2 %	12.1	167	167	2.1	SFO
Borstel Loamy Sand	2.59	5.8	20 °C / 10.88 %	14 ^b	143	120	1.0	SFO
Lorsch Sandy Clay Loam	3.1	5.3	20 °C / 19.92 %	22 ^b	110	103	1.4	SFO
Gartenacker Silt Loam 1.57 kg/ha	3.59	7.32	20 °C / 29.17 %	48.61	77.0	53.9	4.4	SFO
Gartenacker Silt Loam 0.15 kg/ha	3.59	7.32	20 °C / 29.17 %	48.61	59.7	41.8	4.9	SFO
Collombey Sand	2.29	7.7	20 °C / 16.8 %	25.31	80.0	60.0	5.9	SFO
Les Evouettes Silt Loam	2.41	6.1	20 °C / 22.12 %	40.21	58.4	38.2	7.7	SFO
Speyer 2.2 Loamy Sand	4.4	6.0	20 °C / 16.16 %	21.21	122	101	2.2	SFO
Speyer 2.3 Sandy Loam	1.28	6.6	20 °C / 12.56 %	18.61	112	85.2	2.4	SFO
Les Evouettes Loam	6.4	6.8	20 °C / 35.85 %	47.8	69.7	57.0	4.3	SFO
Speyer 2.2 Loamy Sand	3.95	6.18	20 °C / 17.72 %	14 ^b	136	138	5.6	SFO
Sisseln Sandy Loam	2.71	7.16	20 °C / 20.96 %	19 ^b	83.7	83.7	4.1	SFO
Collombey Loamy Sand	2.02	7.45	20 °C / 16.12 %	14 ^b	73.6	73.6	4.2	SFO
Diegten Clay Loam	2.74	6.9	20 °C / 20.76 %	28 ^b	117	94.9	1.9	SFO
Geometric mean^a					91.1	72.0	-	-
Median					88.4	75.1	-	-

- (a) Geometric mean for replicate soil values calculated first (excluding the two Les Evouettes soils that were considered to be substantially different from each other due to contrasting organic matter contents e.g. 2.41 and 6.4% organic matter)
- (b) FOCUS default moisture content based on soil texture
Note that the t-test result was >99% for every soil

Desethyl- terbuthylazine (MT1)	Aerobic conditions (where metabolite applied as starting material)							
	Soil name and classification	% OM	pH (KCl or CaCl ₂)	temp. °C / soil moisture for study (% w/w)	Soil moisture at pF 2 (% w/w)	DT _{50, actual} (d)	DT _{50, ref} 20 °C pF2 (d)	Min chi ² error (%)
Borstel – Loamy Sand	2.63	5.79	20 °C / 10.9 %	14 ^a	83.9	70.3	1.9	SFO
Gartenacker* - Loam	3.20	7.28	20 °C / 26.7 %	25 ^a	61.8	61.8	3.1	SFO
Lorsch – Sandy Clay Loam	3.16	5.25	20 °C / 19.9 %	22 ^a	40.7	38.0	3.3	SFO
Speyer 2.3 – Sandy Loam	2.1	6.4	20 °C / 15.6 %	19 ^a	61.8	53.8	6.7	SFO
Speyer 2.1 – Sand	1.07	5.9	20 °C / 12.4 %	12 ^a	45.2	45.2	4.9	SFO
Speyer 2.2 – Loamy Sand	4.00	5.6	20 °C / 19.2 %	14 ^a	50.7	50.7	4.1	SFO
Westmaas – Silt Loam	2.41	7.4	20 °C / 15.6 %	26 ^a	93.8	65.6	6.0	SFO
Geometric mean					60.0	54.0	-	-
Median					61.8	53.8	-	-

* NB. Significant volatiles observed for Gartenacker soil

^a FOCUS default moisture content based on soil texture

^b t-test result was >99% for every soil

Desethyl- terbuthylazine (MT1)	Aerobic conditions (where metabolite formed from parent terbuthylazine during the study)								
	Soil name and classification	% OM	pH (KCl or CaCl ₂)	temp. °C / soil moisture for study (% w/w)	Soil moisture at pF 2 (% w/w)	DT _{50, actual} (d)	Form. frac. (ffm)	DT _{50, ref} 20 °C pF2 (d)	Min chi ² error (%)
Gartenacker Sandy Loam	3.79	7.25	20 °C / 26.73 %	48.92	66.0	0.606	43.2	5.8	SFO
Pappelacker Loamy Sand	1.9	7.6	20 °C / 15.8 %	29.3	105.7	0.591	68.6	6.2	SFO
Weide Sandy Loam	2.24	7.5	20 °C / 18.96 %	36.6	87.4	0.536	55.2	4.6	SFO
Borstel Loamy Sand	2.59	5.8	20 °C / 10.88 %	14 ^b	53.8	0.357	45.1	2.3	SFO
Gartenacker Silt Loam 1.57 kg/ha	3.59	7.32	20 °C / 29.17 %	48.61	112.8	0.430	78.9	11.3	SFO
Gartenacker Silt Loam 0.15 kg/ha	3.59	7.32	20 °C / 29.17 %	48.61	42.9	0.575	30.0	9.3	SFO
Collombey Sand	2.29	7.7	20 °C / 16.8 %	25.31	26.9	0.498	20.2	18.1	SFO
Les Evouettes Silt Loam	2.41	6.1	20 °C / 22.12 %	40.21	21.7	0.594	14.3	13.7	SFO
Speyer 2.3 Sandy Loam	1.28	6.6	20 °C / 12.56 %	18.61	91.6	0.346	69.6	11.7	SFO
Sisseln Sandy Loam	2.71	7.16	20 °C / 20.96 %	19 ^b	76.6	0.536	76.6	6.0	SFO
Collombey Loamy Sand	2.02	7.45	20 °C / 16.12 %	14 ^b	60.4	0.580	60.4	3.5	SFO
Diegten Clay Loam	2.74	6.9	20 °C / 20.76 %	28 ^b	63.5	0.323	51.5	7.7	SFO
Arithmetic mean^a					-	0.484	-	-	-
Geometric mean^a					61.8	-	46.9	-	-
Median^a					68.4	0.536	51.5	-	-

(a) Average formation fraction and geometric mean DT₅₀ for replicate soil values calculated first

(b) FOCUS default moisture content based on soil texture

Note that the t-test result was >99% for all soils except Collombey (>95%), Les Evouettes (>98%) and Speyer 2.3 (>92%)

Hydroxy-terbuthylazine (MT13)		Aerobic conditions (where metabolite applied as starting material)						
Soil type	% OM	pH (K Cl)	temp. °C / soil moisture for study (% w/w)	Soil moisture at pF 2 (% w/w)	DT _{50, actual} (d)	DT _{50, ref} 20 °C pF2 (d)	Min chi ² error (%)	Method of calc.
Borstel – Loamy Sand	2.6	5.8	20 °C / 10.88 %	14 ^a	207	173	4.7	SFO
Gartenacker – Loam	2.8	7.6	20 °C / 25.08 %	25 ^a	298	298	2.2	SFO
Vetroz – Silt Loam	3.1	7.7	20 °C / 23.56 %	26 ^a	281	278	2.9	SFO
Cranfield 115 – Clay Loam	2.9	7.4	20 °C / 22.1 %	30.4 ^c	>1000	>1000	3.3	SFO
Cranfield 164 – Silt Loam	5.2	6.5	20 °C / 29.12 %	41.2 ^c	>1000	>1000	3.7	SFO
Cranfield 243 – Sandy Loam	1.9	4.3	20 °C / 20.44 %	22.7 ^a	645	600	1.7	SFO
Geometric mean					473^b	453^b	-	-

^a FOCUS default moisture content based on soil texture

^b the geometric mean was calculated assuming a default DT₅₀ of 1000 d for Cranfield 115 and Cranfield 164 soils

^c measured pF2.5 value was above the FOCUS default pF2 and the measured pF2.5 was used as a worst-case assessment.

Hydroxy-terbuthylazine (MT13)	Aerobic conditions (where metabolite formed from parent terbuthylazine during the study)					
	Soil type	% OM	pH (KCl or CaCl ₂)	Visual inspection	Form. frac. (ffm)	Min chi ² error (%)
Gartenacker Sandy Loam (Out)	3.79	7.25	Acceptable	0.076	10.1	SFO using a fixed DT ₅₀ of 473 d
Pappelacker Loamy Sand	1.9	7.6	Acceptable	0.065	27.7	SFO using a fixed DT ₅₀ of 473 d
Weide Sandy Loam	2.24	7.5	Acceptable	0.057	28.5	SFO using a fixed DT ₅₀ of 473 d
Speyer 2.2 Loamy Sand ^a	3.91	6.1	Acceptable	0.302	25.9	SFO using a fixed DT ₅₀ of 473 d
Borstel Loamy Sand	2.59	5.8	Very good	0.212	2.7	SFO using a fixed DT ₅₀ of 473 d
Lorsch Sandy Clay Loam	3.1	5.3	Very good	0.367	6.3	SFO using a fixed DT ₅₀ of 473 d
Gartenacker Silt Loam 2.6 kg/ha ^a	3.59	7.32	Acceptable	0.06	16.1	SFO using a fixed DT ₅₀ of 473 d
Gartenacker Silt Loam 0.25 kg/ha ^a	3.59	7.32	Acceptable	0.07	22.4	SFO using a fixed DT ₅₀ of 473 d
Collombey Sand ^a	2.29	7.7	Acceptable	0.287	18.7	SFO using a fixed DT ₅₀ of 473 d
Les Evouettes Silt Loam	2.41	6.1	Good	0.363	10.8	SFO using a fixed DT ₅₀ of 473 d
Speyer 2.2 Loamy Sand ^a	4.4	6.0	Good	0.362	12.8	SFO using a fixed DT ₅₀ of 473 d
Speyer 2.3 Sandy Loam	1.28	6.6	Acceptable	0.238	27.6	SFO using a fixed DT ₅₀ of 473 d
Speyer 2.2 Loamy Sand ^a	3.95	6.18	Reasonable	0.474	20	SFO using a fixed DT ₅₀ of 473 d
Sisseln Sandy Loam	2.71	7.16	Acceptable	0.14	13.4	SFO using a fixed DT ₅₀ of 473 d
Collombey Loamy Sand ^a	2.02	7.45	Good	0.106	13.5	SFO using a fixed DT ₅₀ of 473 d
Diegten Clay Loam	2.74	6.9	Very good	0.191	3.3	SFO using a fixed DT ₅₀ of 473 d
Arithmetic mean^a				0.207	-	-
Median^a				0.196	-	-

(Out) = Outlier excluded.

^a Average for replicate soil values calculated first [Gartenacker 0.069; Speyer 2.2 0.379; Collombey 0.196]. Note the actual value selected for modelling purposes included additional information from the field dissipation studies.

Desethyl hydroxy-terbuthylazine (MT14)	Aerobic conditions (where metabolite applied as starting material)							
	Soil type	% OM	pH (KCl)	temp. °C / soil moisture for study (% w/w)	Soil moisture at pF 2 (% w/w)	DT _{50, actual} (d)	DT _{50, ref} 20 °C pF2 (d)	Min chi ² error (%) ^b
Borstel – Loamy Sand	2.6	5.8	20 °C / 10.88 %	14 ^a	135	113	7.7	SFO

Desethyl hydroxy-terbuthylazine (MT14)		Aerobic conditions (where metabolite applied as starting material)						
Soil type	% OM	pH (KCl)	temp. °C / soil moisture for study (% w/w)	Soil moisture at pF 2 (% w/w)	DT _{50, actual} (d)	DT _{50, ref} 20 °C pF2 (d)	Min chi ² error (%) ^b	Method of calc.
Gartenacker – Loam	2.8	7.6	20 °C / 25.08 %	25 ^a	50.1	50.1	5.3	SFO
Lorsch – sandy clay loam	3.1	5.3	20 °C / 19.92 %	22 ^a	377	351	5.1	SFO
Vetroz – Silt Loam	3.1	7.7	20 °C / 23.56 %	26 ^a	69.7	65.1	4.0	SFO
Geometric mean					115	107	-	-

^a FOCUS default moisture content based on soil texture

^b t-test result was >99% for every soil except Lorsch where it was >97%

Desethyl hydroxy-terbuthylazine (MT14)		Aerobic conditions (where metabolite formed from parent desethyl-terbuthylazine during the study)				
Soil type	% OM	pH (KCl)	Visual inspection	Form. frac. (ffm)	Min chi ² error (%)	Method of calc.
Borstel – Loamy Sand	2.6	5.8	Very good	0.203	2.7	SFO using a fixed DT ₅₀ of 135 d
Gartenacker – Loam	2.8	7.6	Very good	0.179	9.1	SFO using a fixed DT ₅₀ of 50.1 d
Lorsch – sandy clay loam	3.1	5.3	Very good	0.458	3.5	SFO using a fixed DT ₅₀ of 377 d
Arithmetic mean				0.280	-	-

All studies performed at 20°C

LM1 (MT24)		Aerobic conditions (where metabolite was applied as parent)						
Soil type	% OM	pH (water)	temp. °C / soil moisture for study (% w/w)	Soil moisture at pF 2 (% w/w)	DT _{50, actual} (d)	DT _{50, ref} 20 °C pF2 (d)	Min chi ² error (%)	Method of calc.
Gartenacker – Loam	1.96	7.5	20 °C / pF2	35.3	0.41	0.41	4.1 (p=5.3E-009)	SFO
18 Acres	2.88	7	20 °C / pF2	29.8	0.48	0.48	10.1 (p=1.5E-006)	SFO
Vetroz – Silt Loam	2.36	7.6	20 °C / pF2	26.4	0.33	0.33	24.2 (p=2.8E-004)	SFO
Geometric mean					0.4	0.4	-	-

LM2 (MT28)		Aerobic conditions (where metabolite was applied as parent)						
Soil type	% OM	pH (water)	temp. °C / soil moisture for study (% w/w)	Soil moisture at pF 2 (% w/w)	DT _{50, actual} (d)	DT _{50, ref} 20 °C pF2 (d)	Min chi ² error (%)	Method of calc.
Gartenacker – Loam	3.1	7.5	20 °C / pF2	35.3	19.1	19.1	8.8 (p=1.9E-009)	SFO
18 Acres	3.4	6.5	20 °C / pF2	29.8	11.5	11.5	7.9 (2.2E-008)	SFO
Vetroz – Silt Loam	3.9	7.8	20 °C / pF2	26.4	20.5	20.5	6.3 (p=3.1E-011)	SFO
Geometric mean					16.5	16.5	-	-

LM3		Aerobic conditions (where metabolite was applied as parent)						
Soil type	% OM	pH (water)	temp. °C / soil moisture for study (% w/w)	Soil moisture at pF 2 (% w/w)	DT _{50, actual} (d)	DT _{50, ref} 20 °C pF2 (d)	Min chi ² error (%)	Method of calc.
Gartenacker – Loam	3.1	7.5	20 °C / pF2	35.3	7.3	7.3	7.2 (3.4E-009)	SFO
18 Acres	3.4	6.5	20 °C / pF2	29.8	38.7	38.7	13.2 (1.3E-006)	SFO
Vetroz – Silt Loam	3.9	7.8	20 °C / pF2	26.4	6.5	6.5	5.1 (1.6E-010)	SFO
Geometric mean					12.2	12.2	-	-

LM4		Aerobic conditions (where metabolite was applied as parent)						
Soil type	% OM	pH (water)	temp. °C / soil moisture for study (% w/w)	Soil moisture at pF 2 (% w/w)	DT _{50, actual} (d)	DT _{50, ref} 20 °C pF2 (d)	Min chi ² error (%)	Method of calc.
Gartenacker – Loam	3.1	7.5	20 °C / pF2	35.3	49.9	49.9	2.5 (1.1E-013)	SFO
18 Acres	3.4	6.5	20 °C / pF2	29.8	65.2	65.2	6.8 (2.0E-008)	SFO
Vetroz – Silt Loam	3.9	7.8	20 °C / pF2	26.4	47.4	47.4	3.1 (1.7E-012)	SFO
Geometric mean					53.6	53.6	-	-

LM5 (MT23)		Aerobic conditions (where metabolite was applied as parent)						
Soil type	% OM	pH (water)	temp. °C / soil moisture for study (% w/w)	Soil moisture at pF 2 (% w/w)	DT _{50, actual} (d)	DT _{50, ref} 20 °C pF2 (d)	Min chi ² error (%)	Method of calc.
Gartenacker – Loam	3.0	7.5	20 °C / pF2	35.3	40.2	40.2	2.9 (7.6E-012)	SFO

LM5 (MT23)		Aerobic conditions (where metabolite was applied as parent)						
Soil type	% OM	pH (water)	temp. °C / soil moisture for study (% w/w)	Soil moisture at pF 2 (% w/w)	DT _{50, actual} (d)	DT _{50, ref} 20 °C pF2 (d)	Min chi ² error (%)	Method of calc.
18 Acres	4.7	6.5	20 °C / pF2	29.8	70.6	70.6	5.9 (1.4E-008)	SFO
Vetroz – Silt Loam	4.1	8.0	20 °C / pF2	26.4	36.5	36.5	7.1 (4.2E-009)	SFO
Geometric mean					47.0	47.0	-	-

LM5		Aerobic conditions (where metabolite was formed from parent desethyl-hydroxy terbuthylazine)							
Soil type	% OM	pH (KCl)	temp. °C / soil moisture for study (% w/w)	Soil moisture at pF 2 (% w/w)	DT _{50, actual} (d)	DT _{50, ref} 20 °C pF2 (d)	Formation fraction	Min chi ² error (%)	Method of calc.
Gartenacker – Loam	2.8	7.6	20 °C / 25.08 %	25 ^a	119	119	0.491	4.72 (p = 0.0812 ^b)	SFO
Vetroz – Silt Loam	3.1	7.7	20 °C / 23.56 %	26 ^a	146	136	0.440	3.00 (p = 0.1570 ^b)	SFO
Geometric mean					132	128	0.466 (arithmetic mean)	-	-

^a FOCUS default moisture content based on soil texture

^b due to the high degree of uncertainty associated with the LM5 DT50 values derived from this study the modelling endpoint has been taken from the LM 5 dosed studies only (i.e. geometric mean of 47.0 d).

LM6		Aerobic conditions (where metabolite was applied as parent)						
Soil type	% OM	pH (water)	temp. °C / soil moisture for study (% w/w)	Soil moisture at pF 2 (% w/w)	DT _{50, actual} (d)	DT _{50, ref} 20 °C pF2 (d)	Min chi ² error (%)	Method of calc.
Gartenacker – Loam	3.0	7.5	20 °C / pF2	35.3	211	211	3.3 (2.5E-007)	SFO
18 Acres	4.7	6.5	20 °C / pF2	29.8	390	390	2.1 (2.2E-006)	SFO
Vetroz – Silt Loam	4.1	8.0	20 °C / pF2	26.4	171	171	2.6 (1.7E-009)	SFO
Geometric mean					241	241	-	-

Field studies ‡

Terbuthylazine	Aerobic conditions								
Soil type (indicate if bare or cropped soil was used).	Location (country or USA state).	% OM	pH	Depth (cm)	DT _{50, ref} 20 °C pF2 (d)	DT _{90, ref} 20 °C pF2 (d)	Min chi ² error (%)	t-test (%)	Method of calc. ^a
Loam – Bare soil	St Aubin, Switzerland	3.1	7.2	0 – 10	17.4	58	5.2	> 99%	SFO
Silt loam – Bare soil	Eschwege, Germany	4.0	6.2	0 – 20	16.9	56.1	16.7	> 99%	SFO
Silt loam – Bare soil	Goch, Germany	6.4	6.25	0 – 20	28.8	95.8	8.2	> 99%	SFO
Silty clay loam – Bare soil	Keeken, Germany	7.6	6.1	0 – 20	24.3	80.9	17.7	> 99%	SFO
Silt loam – Bare soil	Pleidsheim, Germany	2.1	6	0 – 20	15.4	51.1	19.2	> 99%	SFO
Loamy sand – Bare soil	Lorsch Helming, Germany	1.4	5.25	0 – 20	6.43	21.4	21	> 99%	SFO
Loamy sand – Bare soil	Weeze Wemb, Germany	3.8	6.2	0 – 20	11.1	36.8	17.7	> 99%	SFO
Clay loam – Bare soil	Grisolles, Southern France	1.62	7.3	0 – 30	52.5	175	13.2	> 99%	SFO
Silt loam – Bare soil	Molinella, Italy ^d	1.31	7.6	0 - 30	149	497	12.9	> 99%	SFO
Silt loam – Bare soil	St Firmin, France (North) (1.0) ^c	1.6	8.4	0 – 10	24.8	82.3	8.7	> 99%	SFO
Silt loam – Bare soil	St Firmin, France (North) (1.5) ^c	1.6	8.4	0 – 10	21.2	70.5	9.5	> 99%	SFO
Sand – Bare soil	Nevoy, France (North) (1.0) ^c	1.0	8.6	0 – 10	12.5	41.5	8.8	> 99%	SFO
Sand – Bare soil	Nevoy, France (North) (1.5) ^c	1.0	8.6	0 – 10	19.4	64.4	6.5	> 99%	SFO
Silt loam – Bare soil	Charny, France (North) (1.0) ^c	1.0	5.9	0 – 10	12.5	41.5	8.8	> 99%	SFO
Silt loam – Bare soil	Charny, France (North) (1.0) ^c	1.0	5.9	0 – 10	17.6	58.5	9.4	> 99%	SFO
Silty sand – Bare soil	Ports sur Vienne, France (North) (1.0) ^c	1.9	6.6	0 – 10	13.9	46.3	4.9	> 99%	SFO
Silty sand – Bare soil	Ports sur Vienne, France (North) (1.5) ^c	1.9	6.6	0 – 10	27.9	92.8	13.7	> 99%	SFO
Sandy silt loam – Bare soil	Eraclea, Italy (1.0) ^b	3.4	7.6	0 – 10	67.7	225	39.6	>81%	SFO
Sandy silt loam – Bare soil	Eraclea, Italy (1.0) ^b	3.4	7.6	0 – 10	9.51	31.6	20.2	>98%	SFO
Clay – Bare soil	Emilia, Italy ^c	3.3	7.5	0 – 10	32.6	1.8	7	> 99%	SFO
Clay – Bare soil	Emilia Italy ^c	3.3	7.5	0 – 10	31.8	1.6	5.3	> 99%	SFO
Soft clayey sand – Bare soil	Hilgermissen, Germany ^e	1.5	5.9	0 – 10	33.5	111	11.8	> 99%	SFO
Clayey sand – Bare soil	Leutzke, Germany	2.9	5.5	0 – 10	9.72	32.3	25.7	> 99%	SFO

Field studies ‡

Terbuthylazine	Aerobic conditions								
Soil type (indicate if bare or cropped soil was used).	Location (country or USA state).	% OM	pH	Depth (cm)	DT _{50, ref} 20 °C pF2 (d)	DT _{90, ref} 20 °C pF2 (d)	Min chi ² error (%)	t-test (%)	Method of calc. ^a
Geometric mean ^c					21.8	72.6	-	-	-
Median ^c					20.0	66.5	-	-	-

NK – not known

^a soils were normalised for temperature assuming a Q10 of 2.58 using a time step normalisation procedure. Soil moisture content was assumed to be at pF2 and not corrected for.

^b Excluded from statistical evaluations due to poor fits

^c Geometric mean of replicate trials calculated first; median based on n = 16

^d The un-normalised SFO DT50 at the Molinella field site (SEU) was 149.9 d (chi2 error level = 12.8%, acceptable visual fit)

^d The un-normalised SFO DT50 at the Hilgermissen field site (NEU) was 46.6 d (chi2 error level = 17.2%, acceptable visual fit up to approximate DT90)

Field studies

Desethyl terbuthylazine	Aerobic conditions (where metabolite formed from parent terbuthylazine during the study)									
	Soil type (indicate if bare or cropped soil was used).	Location (country or USA state).	% OM	pH	DT _{50, ref} 20 °C pF2 (d)	DT _{90, ref} 20 °C pF2 (d)	Form. frac. (ffm)	Min chi ² error (%)	t-test (%)	Method of calc. ^d
Loam – Bare soil	St Aubin, Switzerland	3.1	7.2	16.6	55.3	0.292	17.6	>99%	SFO	
Silt loam – Bare soil	Pleidsheim, Germany	2.1	6	31	103	0.112	17	>76%	SFO	
Loamy sand – Bare soil	Lorsch Helming, Germany	1.4	5.25	2.13	7.08	0.256	22.1	>68%	SFO	
Clay loam – Bare soil	Grisolles, Southern France	1.62	7.3	51	169	0.767	15.6	>99%	SFO	
Silt loam – Bare soil	Molinella, Italy	1.31	7.6	208	693	0.513	6.6	>77%	SFO	
Silt loam – Bare soil	St Firmin, France (North) (1.0)	1.6	8.4	15.5	51.6	0.829	18.1	>99%	SFO	
Silt loam – Bare soil	St Firmin, France (North) (1.5)	1.6	8.4	19	63.2	0.445	3.1	>96%	SFO	
Silt loam – Bare soil	Charny, France (North) (1.0)	1.0	5.9	47.3	157	0.306	5.8	>97%	SFO	
Silt loam – Bare soil	Charny, France (North) (1.5)	1.0	5.9	69.9	231	0.258	11.4	>97%	SFO	
Soft clayey sand – Bare soil	Hilgermissen, Germany	1.5	5.9	23.4	77.8	0.695	8	>99%	SFO	
Arithmetic mean^{a,b}					-	-	0.444	-	-	-
Geometric mean^{a,c}					26.8	89.2	-	-	-	-
Median^{a,c}					27.2	90.4	-			

^a only valid datasets considered

^b arithmetic mean of replicate soils calculated first

^c geometric mean of replicate soils calculated first

^d soils were normalised for temperature assuming a Q10 of 2.58 using a time step normalisation procedure. Soil moisture content was assumed to be at pF2 and not corrected for.

NB the applicant proposed a geometric mean of 29.6 d based on a marginally different set of soils considered acceptable

Field studies

Hydroxy-terbuthylazine		Aerobic conditions (where metabolite formed from parent terbuthylazine during the study)					
Soil type (indicate if bare or cropped soil was used).	Location (country or USA state).	% OM	pH	Visual inspection	Form. frac. (ffm)	Min chi ² error (%)	Method of calc.
Clay loam – Bare soil	Grisolles, Southern France	1.62	7.3	Acceptable	0.068	12.1	SFO using a fixed DT ₅₀ of 453 d
Silt loam – Bare soil	Molinella, Italy	1.31	7.6	Reasonable	0.122	14.5	SFO using a fixed DT ₅₀ of 453 d
Loam – Bare soil	St Aubin, Switzerland	3.1	7.2	Reasonable	0.079	24.2	SFO using a fixed DT ₅₀ of 453 d
Silt loam – Bare soil	St Firmin, France (North) (1.5)	1.6	8.4	Good	0.056	11.3	SFO using a fixed DT ₅₀ of 453 d
Sand – Bare soil	Nevoy, France (North) (1.0)	1.0	8.6	Acceptable	0.163	20.1	SFO using a fixed DT ₅₀ of 453 d
Sand – Bare soil	Nevoy, France (North) (1.5)	1.0	8.6	Good	0.431	15.4	SFO using a fixed DT ₅₀ of 453 d
Silty sand – Bare soil	Ports sur Vienne, France (North) (1.5)	1.9	6.6	Reasonable	0.198	20.9	SFO using a fixed DT ₅₀ of 453 d
Soft clayey sand – Bare soil	Hilgermissen, Germany	1.5	5.9	Acceptable	0.154	32.4	SFO using a fixed DT ₅₀ of 453 d
Arithmetic mean^{a, b}					0.139	-	-
Median^a					0.122	-	-

^aarithmetic mean of replicate soils calculated first

^b arithmetic mean of replicate soils calculated first

Note the actual formation fraction proposed for modelling was derived from combined lab and field datasets and was calculated to be 0.197

pH dependence ‡
(yes / no) (if yes type of dependence)

Soil accumulation and plateau concentration ‡

Possible weak negative correlation between degradation of terbuthylazine and soil pH based on laboratory studies ($r^2 = 0.3485$). No correlation observed based on field dissipation studies.

No evidence of accumulation of terbuthylazine, desethyl-terbuthylazine, hydroxy-terbuthylazine or desethyl-hydroxy-terbuthylazine after repeated applications at 7 locations in Northern Italy.

Laboratory studies ‡

Terbuthylazine	Anaerobic conditions						
Soil type	OM %	pH	t. °C / % MWHC	DT ₅₀ / DT ₉₀ (d)	DT ₅₀ (d) 20 °C pF2/10kPa	St. (r ²)	Method of calculation
Gartenacker – Sandy loam - SYN	3.79	7.25	20 oC / flooded soil	108.3 / 359.9	N/A	0.981	SFO
Speyer 2.3 – Sandy Loam - SYN	2.07	6.3	20 oC / flooded soil	131 / 436	N/A	0.966	SFO
Geometric mean				119.1			

Soil adsorption/desorption (Annex IIA, point 7.1.2)

Terbuthylazine ‡								
Soil Type	OC %	Soil pH	Kd (mL/g)	Koc (mL/g)	Kf (mL/g)	Kfoc (mL/g)	1/n	
Speyer 2.2 Loamy Sand – OXON	2.29	6.0	N/A	N/A	5.34	233	0.98	
Les Evouettes Sandy Loam – OXON	1.20	5.9	N/A	N/A	2.95	246	0.90	
Sisseln Sandy Loam – OXON	1.57	7.1	N/A	N/A	2.37	151	0.93	
Vetroz Silt Loam - OXON	4.1	7.3	N/A	N/A	8.18	200	0.90	
Pappelacker Loamy Sand – SYN	1.1	7.6	N/A	N/A	2.10	191	0.92	
Lorsch Sandy Clay Loam – SYN	1.8	5.3	N/A	N/A	5.86	318	0.94	
Gartenacker Loam – SYN	2.0	7.1	N/A	N/A	3.74	187	0.88	
Vetroz Silt Loam - SYN	4.7	7.2	N/A	N/A	10.49	223	0.97	
Borstel Loamy Sand – SYN*	1.48	6.1	N/A	N/A	4.93	333	0.91	
Arithmetic mean						5.1	231	0.93
pH dependence, Yes or No			Possible weak negative correlation between sorption and soil pH (r ² = 0.5456)					

NR = not recorded

Desethyl-terbuthylazine (MT1) ‡							
Soil Type	OC %	Soil pH	Kd (mL/g)	Koc (mL/g)	Kf (mL/g)	Kfoc (mL/g)	1/n
Collombey Loamy Sand - SYN	0.80	7.3	N/A	N/A	0.594	74.0	0.85
Les Evouettes Silt Loam – SYN	2.40	7.2	N/A	N/A	1.43	59.0	0.86
Vetroz Silt Loam - SYN	4.70	7.2	N/A	N/A	3.29	70.0	0.91
Speyer 2.1 Sand – OXON	0.6	5.9	N/A	N/A	0.43	67.2	0.95
Speyer 2.2 Loamy Sand – OXON	2.3	5.6	N/A	N/A	1.9	81.7	0.91
Beek Silt Loam – OXON	0.6	6.6	N/A	N/A	0.28	43.8	0.94
Marknesse Silt Loam - OXON	1.3	7.5	N/A	N/A	1.24	96.9	0.92
Lorsch Sandy Clay Loam - SYN	1.84	5.25	N/A	N/A	1.56	85.0	0.94
Borstel Loamy Sand – SYN	1.48	6.1	N/A	N/A	1.80	122	0.77
Arithmetic mean					1.39^a	77.7^a	0.89
pH dependence (yes or no)				No			

^a arithmetic mean based on all data

Hydroxy-terbuthylazine (MT13) ‡							
Soil Type	OC %	Soil pH	Kd (mL/g)	Koc (mL/g)	Kf (mL/g)	Kfoc (mL/g)	1/n
Cranfield 115 Clay Loam – OXON	1.7	7.9	N/A	N/A	3.51	208.6	0.82
Cranfield 164 Silt Loam – OXON	3.0	7.1	N/A	N/A	5.94	196.9	0.8
Cranfield 243 Sandy Loam - OXON	1.1	5.4	N/A	N/A	2.14	193.1	0.85
Borstel Sandy Loam - SYN	1.3	5.0	N/A	N/A	3.64	279.7	0.87
Collombey Loamy Sand - SYN	0.80	7.3	N/A	N/A	1.19	149	0.91
Les Evouettes Silt Loam - SYN	2.40	7.2	N/A	N/A	2.49	104	0.79
Vetroz Silt Loam - SYN	4.70	7.2	N/A	N/A	8.36	178	1.31
Arithmetic mean					3.90	187	0.91
pH dependence (yes or no)				No			

Desethyl-hydroxy-terbuthylazine (MT14) ‡							
Soil Type	OC %	Soil pH (CaCl ₂)	Kd (mL/g)	Koc (mL/g)	Kf (mL/g)	Kfoc (mL/g)	1/n
Borstel Loamy Sand	1.3	5.0	1.8	136	1.44	111	0.93
Lorsch Sandy Clay Loam	1.8	5.3	3.8	211	3.39	188	0.97
Gartenacker Loam/Silt Loam	2.0	7.1	1.2	59	1.10	55	0.98
Vetroz Silt Loam	4.7	7.2	2.8	60	2.67	57	0.98
Wisborough- Silty Clay Loam	3.44	5.02	4.40	375	3.36	98	0.8892

18 Acres - Sandy Clay Loam	1.95	5.27	4.79	242	3.34	171	0.9166
Kochi - Loam	1.17	5.65	8.26	213	2.98	254	0.8991
Bosket - Loam ^a	0.58	5.68	3.97	158	5.83	1010	0.9572
Ushiku - Sandy Clay Loam	1.98	5.99	6.98	1208	2.83	143	0.8674
Tsukuba - Loam	3.87	6.49	5.23	152	5.07	131	0.8881
Pappelacker - Sandy Loam	2.76	7.06	0.78	28	0.61	22	0.9220
Champaign - Silty Clay	2.52	7.34	4.62	236	2.50	99	0.8787
Median (all data, n=12)					2.91	121	0.92
pH dependence (yes or no)					No		

Terbutryn (MT26) ‡							
Soil Type	OC %	Soil pH (KCl)	Kd (mL/g)	Koc (mL/g)	Kf (mL/g)	Kfoc (mL/g)	1/n
Pappelacker - Sandy Loam	1.1	7.6	N/A	N/A	4.3	392	1.01
Speyer 2.1 - sand	0.6	7.4	N/A	N/A	3.7	605	1.06
Gartenacker Loam/Silt Loam	2.1	7.3	N/A	N/A	10.5	504	1.39
Vetroz Silt Loam	4.7	7.2	N/A	N/A	25.1	533	1.01
Illarsaz – silt loam	19.8	6.7	N/A	N/A	109.9	555	1.02
Arithmetic mean					13	518	1.04
pH dependence (yes or no)				No evidence from narrow pH range studied			

LM1							
Soil Type	OC %	Soil pH (CaCl ₂)	Kd (mL/g)	Koc (mL/g)	Kf (mL/g)	Kfoc (mL/g)	1/n
Gartenacker Silt Loam	2.95	7.1	0.507	30	0.51	30.2	1.03
18 Acres Clay Loam	4.34	7.2	0.853	34	0.82	32.7	0.98
Vetroz Loam	4.09	7.6	0.832	35	0.87	36.6	1.05
Arithmetic mean					0.73	33.2	1.02
pH dependence (yes or no)				No evidence from narrow pH range studied			

LM2							
Soil Type	OC %	Soil pH (CaCl ₂)	Kd (mL/g)	Koc (mL/g)	Kf (mL/g)	Kfoc (mL/g)	1/n
Gartenacker Silt Loam	2.95	7.1	0.16	8.7	0.16	9	1.07
18 Acres Clay Loam	4.74	6.1	0.35	13.7	0.35	13	0.93
Vetroz Loam	4.09	7.6	0.15	6.1	0.15	6	1.1

Arithmetic mean	0.22	9.4	1.03
pH dependence (yes or no)	Yes - slight trend relating increasing Kfoc with decreasing pH. However given the low sorption the mean was considered appropriate for modelling.		

LM3							
Soil Type	OC %	Soil pH (CaCl ₂)	Kd (mL/g)	Koc (mL/g)	Kf (mL/g)	Kfoc (mL/g)	1/n
Gartenacker Silt Loam	2.95	7.1	0.083	4.8	0.071	4.2	0.85
18 Acres Clay Loam	4.74	6.1	0.101	3.7	0.091	3.3	0.9
Vetroz Loam	4.09	7.6	0.098	4.1	0.087	3.7	0.87
Arithmetic mean					0.083	3.7	0.87
pH dependence (yes or no)			No evidence from narrow pH range studied				

LM4							
Soil Type	OC %	Soil pH (CaCl ₂)	Kd (mL/g)	Koc (mL/g)	Kf (mL/g)	Kfoc (mL/g)	1/n
Gartenacker Silt Loam	2.95	7.1	0.103	6	0.097	4.9	0.81
18 Acres Clay Loam	4.74	6.1	0.474	17.2	0.463	15.4	0.91
Vetroz Loam	4.09	7.6	0.108	4.5	0.096	3.8	0.84
Arithmetic mean					0.22	8.0	0.85
pH dependence (yes or no)			Yes - trend relating increasing Kfoc with decreasing pH. However given the low sorption the mean was considered appropriate for modelling.				

LM5							
Soil Type	OC %	Soil pH (CaCl ₂)	Kd (mL/g)	Koc (mL/g)	Kf (mL/g)	Kfoc (mL/g)	1/n
Gartenacker Silt Loam	2.95	7.1	0.414	24	0.32	19	0.87
18 Acres Clay Loam	4.74	6.1	0.549	20	0.39	14	0.88
Vetroz Loam	4.09	7.6	0.486	21	0.31	13	0.83
Arithmetic mean					0.34	15.3	0.86
pH dependence (yes or no)			No evidence from narrow pH range studied				

LM6							
Soil Type	OC %	Soil pH (CaCl ₂)	Kd (mL/g)	Koc (mL/g)	Kf (mL/g)	Kfoc (mL/g)	1/n
Gartenacker Silt Loam	2.95	7.1	0.282	16	0.23	13	0.92
18 Acres Clay Loam	4.74	6.2	0.485	18	0.4	14	0.93
Vetroz Loam	4.09	7.6	0.43	18	0.31	13	0.89
Arithmetic mean					0.38	13.3	0.91
pH dependence (yes or no)				No evidence from narrow pH range studied			

Mobility in soil (Annex IIA, point 7.1.3, Annex IIIA, point 9.1.2) – SYN and OXON

Column leaching ‡ (SYN)

Elution (mm): 200 mm
Time period (d): 2 d
Leachate: < 0.01 - 0.04 % total residues/radioactivity in leachate
82.45 - 90.14 % active substance and 0.46 - 1.49 % extractable metabolites in soil.
45.48 – 87.37 % total residues/radioactivity retained in top 2 cm

Lysimeter/ field leaching studies ‡ (SYN)

Summary of metabolite codes:-

MT1 = GS26379
 MT13 = GS23158
 MT14 = GS28620
 MT19 = GS17792
 MT20 = GS28273
 MT22 = G28279
 LM1 = MT24 = G35713
 LM2 = MT28 = CSAA036479
 LM3 = SM9 = CSCD692760
 LM4 = CSAA404949
 LM5 = MT23 = SM12 = GS16984
 LM6 = SM6 = CSCD648241

Location: Schmallenberg/Grafschaft, Germany
Study type (e.g.lysimeter, field): lysimeter (x2)
Soil properties (0 – 30 cm): Borstel Sandy Loam, pH = 5.7, OC= 1.5 % , MWHC = not stated (FC = 20 – 34 % by volume)
Dates of application : 28/05/1990
Crop : maize followed by the rotational crops winter wheat and winter barley.
Number of applications: 1 application to maize in first year only
Duration: 2 years,
Application rate: 700 - 790 g/ha
Average annual rainfall (mm): 863 mm
Average annual leachate volume (mm): 418.3 mm
% radioactivity in leachate (maximum/year): 1.45 – 1.48 % AR
Annual average maximum concentrations (e.g. 1 st or 2 nd yr, Lysimeter 38 or 44): < 0.02 µg/L terbuthylazine,

	<p>< 0.02 µg/L desethyl-terbuthylazine, 0.03 µg/L hydroxy-terbuthylazine. 0.03 µg/L G 28273 (MT20) 0.05 µg/L GS 17792 (MT19) < 0.02 µg/L G 28279 (MT22), G 28260 (MT14) 1.96 µg/L Unidentified radioactivity Bi-annual average concentrations (e.g. 1st and 2nd yr, Lysimeter 38 and 44): < 0.02 µg/L terbuthylazine, < 0.02 µg/L desethyl-terbuthylazine, 0.02 µg/L hydroxy-terbuthylazine. 0.02 µg/L G 28273 (MT20) 0.03 µg/L GS 17792 (MT19) < 0.02 µg/L G 28279 (MT22), G 28260 (MT14) 1.21 µg/L Unidentified radioactivity Amount of radioactivity in the soils at the end of the study = 65.6 – 75.2 % AR; consisting of: 5.9 – 6.4 % AR as terbuthylazine, 1.2 – 1.5 % AR as desethyl-terbuthylazine, 0.2 – 0.5 % AR as hydroxy-terbuthylazine, < LOD – 0.2 % AR as G 28279 (MT22), 0.1 – 0.2 % AR as GS 28260 (MT14)</p>
Lysimeter/ field leaching studies ‡ (SYN)	<p>Location: Itingen, Switzerland Study type (e.g.lysimeter, field): lysimeter Soil properties (0 – 30 cm): Neustadt Sand, pH = 6.1, OC= 1.05, MWHC = 34.5 % Dates of application : May 1992 Crop : maize followed by two rotations of winter wheat Interception estimated: 25 % (based on standard crop interception values and growth stage of maize at time of application) Number of applications: 1 application to maize in first year only Duration: Application rate: 891 g/ha Average annual rainfall (mm): 1090 mm Average annual leachate volume (mm): 413.2 mm % radioactivity in leachate (maximum/year): 2.34 % AR Structural assignments for the parent and</p>

metabolites in the leachate were determined based on analysis during the original study coupled with additional information from further more recent accurate mass structural elucidation work. Parent and desethyl terbuthylazine were identified in the original study. Two further metabolites were plausibly assigned to LM3 and LM6 based on the additional mass spectral elucidation work. Assignment of other peaks was less certain based on matching relative retention times since matching HPLC conditions between this study and later definitive studies were not available. Quantitative concentrations are also uncertain due to the presence of multiple components in single peaks.

Annual average concentrations ($\mu\text{g/l}$ parent equivalents)

Lysimeter 27:

< 0.05 $\mu\text{g/L}$ terbuthylazine (1st year); < 0.05 $\mu\text{g/L}$ terbuthylazine (2nd year); < 0.05 $\mu\text{g/L}$ terbuthylazine (mean of 1st and 2nd year)

< 0.05 $\mu\text{g/L}$ desethylterbuthylazine (1st year); < 0.05 $\mu\text{g/L}$ desethylterbuthylazine (2nd year); < 0.05 $\mu\text{g/L}$ desethylterbuthylazine (mean of 1st and 2nd year)

0.12 $\mu\text{g/L}$ LM1* (1st year); 0.33 $\mu\text{g/L}$ LM1* (2nd year); 0.25 $\mu\text{g/L}$ LM1* (mean of 1st and 2nd year)

0.17 $\mu\text{g/L}$ LM2* (1st year); 0.17 $\mu\text{g/L}$ LM2* (2nd year); 0.17 $\mu\text{g/L}$ LM2* (mean of 1st and 2nd year)

0.43 $\mu\text{g/L}$ LM3 (1st year); 1.09 $\mu\text{g/L}$ LM3 (2nd year); 0.84 $\mu\text{g/L}$ LM3 (mean of 1st and 2nd year)

0.36 $\mu\text{g/L}$ LM5* (1st year); 0.70 $\mu\text{g/L}$ LM5* (2nd year); 0.57 $\mu\text{g/L}$ LM5* (mean of 1st and 2nd year)

0.07 $\mu\text{g/L}$ MT14 and LM4* (1st year); 0.11 $\mu\text{g/L}$ MT14 and LM4* (2nd year); 0.09 $\mu\text{g/L}$ MT14 and LM4* (mean of 1st and 2nd year)

0.05 $\mu\text{g/L}$ LM6 (1st year); 0.50 $\mu\text{g/L}$ LM6 (2nd year); 0.33 $\mu\text{g/L}$ LM6 (mean of 1st and 2nd year)

0.25 $\mu\text{g/L}$ LM7* (1st year); 0.05 $\mu\text{g/L}$ LM7* (2nd year); 0.12 $\mu\text{g/L}$ LM7* (mean of 1st and 2nd year)

*= structures tentatively assigned to peaks

Lysimeter/ field leaching studies ‡
(OXON)

Additional unidentified radioactivity (sum of smaller peaks) 0.11 µg/L (1st year); 0.29µg/l (2nd year); 0.22µg/l (mean of 1st and 2nd year)

Amount of radioactivity in the soils at the end of the study = 67.7 % AR; consisting of (0 – 18 cm depth only)

0.92 % AR as parent

0.92 % AR as desethyl-terbuthylazine,

11.97 % AR as hydroxy-terbuthylazine,

1.52 % as desethyl-hydroxy-terbuthylazine,

6.29 % unidentified

Location: Itingen, Switzerland

Study type (e.g.lysimeter, field): lysimeter (x2)

Soil properties (0 – 30 cm): Neustadt Sand, pH = 6.1, OC= 1.05, MWHC = 34.5 %

Dates of application : 18/05/93

Crop : maize, followed by two rotations of winter wheat

Number of applications: 1 application to maize in first year only.

Duration: 2 years

Application rate: 905 g/ha/lysimeter 7; 929 g/ha/lysimeter 9 (application in first year only)

Average annual rainfall (mm): 1090 mm

Average annual leachate volume (mm): 485.6 mm

% radioactivity in leachate (maximum/year): 1.60 - 1.70 % AR

Annual average concentrations (e.g. 1st and 2nd yr, Lysimeter 7 and 9):

not detected – terbuthylazine, desethyl terbuthylazine, hydroxy terbuthylazine

0.04/0.06µg/l LM1 (lysimeter 7/9, 1st year);

0.12/0.15µg/l LM1 (lysimeter 7/9, 2nd year)

0.04/0.03µg/l LM2 (lysimeter 7/9, 1st year);

0.10/0.10µg/l LM2 (lysimeter 7/9, 2nd year)

0.26/0.31µg/l LM3 (lysimeter 7/9, 1st year);

0.85/0.83µg/l LM3 (lysimeter 7/9, 2nd year)

0.38/0.40µg/l LM4 (lysimeter 7/9, 1st year);

0.14/0.18µg/l LM4 (lysimeter 7/9, 2nd year)

0.10/0.08µg/l LM5 (lysimeter 7/9, 1st year);

0.71/0.62µg/l LM5 (lysimeter 7/9, 2nd year)

0.03/0.01µg/l LM6 (lysimeter 7/9, 1st year);

0.53/0.40µg/l LM6 (lysimeter 7/9, 2nd year)

Lysimeter/ field leaching studies †
(OXON)

0.08/0.08µg/l LM7 (lysimeter 7/9, 1st year);
0.06/0.03µg/l LM7 (lysimeter 7/9, 2nd year)

Amount of radioactivity in the soils at the end of the study = 76.20 - 80.62 %AR; consisting of (0 – 38 cm depth only – max values)

6.4 % AR as terbuthylazine

1.0 % AR as desethyl-terbuthylazine,

53.8 % AR as hydroxy-terbuthylazine,

30 - 52 % AR unextracted radioactivity

Location: Itingen, Switzerland

Study type (e.g.lysimeter, field): lysimeter (x2)

Soil properties (0 – 30 cm): Neustadt Sandy loam, pH = 6.18, OC= 1.43, MWHC = 45.35 %

Dates of application : 10/05/05

Crop : bare soil followed by plot being split and one of the following crops being sown: radish, spinach, wheat

Interception estimated: 0 % (based on application to bare soil)

Annual rainfall during first year May 2005 to April 2006 (mm): 798.5 mm

Number of applications: 1 application to bare soil

Duration: 1 year

Application rate: 972 g/ha (Lysimeter 4); 980 g/ha (Lysimeter 6)

Average annual leachate volume (mm): 731 mm

% radioactivity in leachate (maximum/year): 1.60 - 1.70 % AR

Annual average concentrations (e.g. 1st yr, Lysimeter 4 or 6):

not detected – terbuthylazine, desethyl terbuthylazine, hydroxy terbuthylazine

0.03/0.02µg/l LM1 (lysimeter 4/6, 1st year);

0.07/0.08µg/l LM2 (lysimeter 4/6, 1st year);

0.24/0.23µg/l LM3 (lysimeter 4/6, 1st year);

0.11/0.21µg/l LM4 (lysimeter 4/6, 1st year);

0.68/0.78µg/l LM5 (lysimeter 4/6, 1st year);

0.18/0.19µg/l LM6 (lysimeter 4/6, 1st year);

0.08/0.08µg/l LM7 (lysimeter 4/6, 1st year);

All concentrations are in µg metabolite/l.

Amount of radioactivity in the soils at the end of the study = not reported

Lysimeter/ field leaching studies ‡ (SYN)

Location: Lorsch, Hessen, Germany
 Study type (e.g.lysimeter, field): Field leaching study
 Soil properties (0 – 30 cm): sandy loam, pH = 5.2 – 6.3, OC= 2.3 – 2.6, MWHC = not reported
 Dates of application : 1990, 1992, 1994 – 1997, 1999 - 2000
 Crop : maize in application years.
 Interception estimated: 25 % (based on standard crop interception values and growth stage of maize at time of application)
 Number of applications: 8 applications, maximum of 1 per year
 Duration: 11 years
 Application rate: 735 g/ha in 1990; 750 g/ha in all other application years
 Average annual rainfall (mm): 587 mm (NB. data from 1993, 1995 and 1998 not reported)
 Average annual leachate volume (mm): Not applicable
 % radioactivity in leachate (maximum/year): Not applicable.
 Frequency of detections, detections above >0.1µg/l and maximum conc.:

 Terbuthylazine: 1 detection out of 418 samples; 0% (~0 samples) >0.1µg/l; maximum concentration = 0.09µg/l.
 Desethyl terbuthylazine: 0 detections out of 419 samples;
 Desethyl hydroxyterbuthylazine: 17 detections out of 51 samples; 24% (~12 samples) >0.1µg/l; maximum concentration = 0.41µg/l.
 2-hydroxy terbuthylazine: 10 detections out of 51 samples, 0%(0 samples) >0.1µg/l; maximum concentration = 0.08µg/l.

 Individual annual maximum concentrations (e.g. 1st, 2nd, 3rd yr):
 < 0.05 µg/L terbuthylazine
 < 0.05 µg/L desethyl-terbuthylazine,
 0.06 µg/L 2-hydroxy-terbuthylazine
 0.25 µg/L desethylhydroxy-terbuthylazine

Individual annual average concentrations (e.g. 1st, 2nd, 3rd yr):

< 0.05 µg/L terbuthylazine

< 0.05 µg/L desethyl-terbuthylazine,

< 0.05 µg/L 2-hydroxy-terbuthylazine

< 0.05 - 0.12 µg/L desethylhydroxy-terbuthylazine

Amount of radioactivity in the soils at the end of the study = not reported

Note that 2-hydroxy terbuthylazine was only analysed for in 1999-2000 and 2000-2001.

Desethylhydroxy terbuthylazine was only analysed for in 1997-1998, 1999-2000 and 2000-2001.

Location: 10 sites in 5 regions (Emilia Romagna, Friuli Venezia – Giulia, Lombardia, Piemonte, Veneto) in Northern Italy

Study type (e.g.lysimeter, field): field leaching study

Soil properties: texture class – 5 sandy loams, 3 loams , 1 sandy clay and 1 clay loam; pH = 4.9 7.7; OC= 0.9 – 3.6%; MWHC = not reported

Groundwater depth: 0.12 to 7.1m below ground surface

Dates of application : 2005 to 2007

Crop : maize

Irrigation: sprinkler, basin , border or no irrigation

Interception estimated: 0 % (applications made shortly after seeding maize)

Number and rate of applications: between 2005 and 2007, 7 sites had 3 annual applications of 856 g terbuthylazine/ha. The remaining 3 sites had either 2 or 1 annual application.

Duration: bi-monthly sampling for 3 years (17 sampling events)

Average annual rainfall (mm): Reported to be below the overall average for the period 2000-2007 but supplemented by irrigation at 9 out of 10 sites.

Frequency of detections, detection >0.1µg/l and maximum conc. (excluding basin irrigated sites, n=8):

Terbuthylazine: 62 detections out of 395 samples; 3% (~13 samples) >0.1µg/l;

maximum concentration = 3.20 µg/l.

Desethyl terbuthylazine: 125 detections out of 395 samples; 5% (~21 samples) >0.1 µg/l; maximum concentration = 3.18 µg/l. Excluding results from the V2 site after April 2007 when contamination may have occurred, the peak monitored concentration was 1.984 µg/l and actual concentrations >0.1 µg/l were observed in 17 out of 384 samples (4.4 %).

Desethyl hydroxyterbuthylazine: 57 detections out of 144 samples; 29% (~42 samples) >0.1 µg/l; maximum concentration = 2.65 µg/l.

2-hydroxy terbuthylazine: 2 detections out of 144 samples, 0% (0 samples) >0.1 µg/l; maximum concentration = 0.05 µg/l.

LM5: 11 detections out of 21 samples; 29% (~6 samples) > 0.1 µg/l; maximum concentration = 0.68 µg/l.

LM6: 9 detections out of 21 samples; 38% (~8 samples) >0.1 µg/l; maximum concentration = 1.58 µg/l.

Annual average concentrations:

0.03 – 0.58 µg/L terbuthylazine (basin irrigation)

<0.01 – 0.07 µg/L terbuthylazine (sprinkler or border irrigation)

0.07 – 0.73 µg/L desethyl terbuthylazine (basin irrigation)

<0.01 – 0.22 µg/L desethyl terbuthylazine (sprinkler or border irrigation)

< 0.05 – 0.05 µg/L (single sample) 2-hydroxy terbuthylazine (analysed for 2007 only)

0.04 – 0.37 µg/L desethyl hydroxy-terbuthylazine (analysed for the 2007 season only)

<0.05 – 0.48 µg/L GS16984 (LM5) (analysed for the 2007 season only)

<0.05 – 1.3 µg/L CSCD648241 (LM6) (analysed for the 2007 season only)

Additional monitoring between 2009-2010 at 7 sites across 4 regions (Emilia Romagna, Lombardy, Veneto and Friuli-Venezia-Giulia) to measure residues of LM2, 3, 4, 5 and 6.

LM2 maximum concentration = 0.26µg/l
 LM3 maximum concentration = 0.29µg/l
 LM4 maximum concentration = 0.50µg/l
 LM5 maximum concentration = 0.50µg/l
 LM6 maximum concentration = 1.4µg/l

Annual average concentrations in downstream clusters:

LM2 <0.05 - 0.11µg/l
 LM3 <0.05 - 0.14µg/l
 LM4 <0.05 - 0.13µg/l
 LM5 <0.05 - 0.27µg/l
 LM6 <0.05 - 0.53µg/l

Note that as high concentrations were also found in the upstream monitoring wells (all substances), parts of residues found in downstream monitoring wells are likely to derive from previous usage following several years of commercial application in the upstream areas.

Route and rate of degradation in water (Annex IIA, point 7.2.1) – SYN and OXON

Hydrolytic degradation of terbuthylazine and metabolites > 10 % ‡

SYN - pH 5: 73 d at 25 °C (1st order)
 Hydroxy-terbuthylazine: 16 % AR (50 d)
 OXON - pH 4: > 1 year at 20 °C (1st order, extrapolated beyond study duration)

pH 7: SYN - 205 d at 25 °C (1st order)
 OXON - No significant degradation at 50 °C after 5 days

pH 9: SYN - 194 d at 25 °C (1st order)
 OXON - No significant degradation at 50 °C after 5 days

Photolytic degradation of terbuthylazine and metabolites above 10 % ‡	<p>SYN - Xenon arc lamp (wavelengths filtered < 290 nm), 12 hours light/12 hours dark for 10 days. Light equivalent to 13.4 days of midsummer sunlight at 30/40° N.</p> <p>DT₅₀: No significant degradation</p> <p>OXON - Xenon arc lamp (wavelengths filtered < 290 nm) for 30 days. 1 day equivalent to 1.64 days of summer sunlight at 40° N.</p> <p>DT₅₀: 14.1 d under the test conditions; equivalent to 29.5 d in natural sunlight at 40° N in the summer.</p> <p>hydroxy-terbuthylazine: 38.9 % AR (30 d) desethyl-terbuthylazine: 11.4 % AR (30 d)</p>
Quantum yield of direct phototransformation in water at Σ > 290 nm	3 x 10 ⁻⁶ mol · Einstein ⁻¹
Readily biodegradable ‡ (yes/no) (OXON and SYN)	No
Hydrolytic degradation of desethyl-terbuthylazine (MT1) and metabolites > 10 % ‡ (SYN)	<p>pH 4: 135.9 d at 25 °C (1st order) desethyl-2-hydroxy-terbuthylazine: 11.5 % AR (30 d)</p> <p>pH 5: No significant degradation at 50 °C after 5 days</p>
	<p>pH 7: No significant degradation at 50 °C after 5 days</p>
	<p>pH 9: No significant degradation at 50 °C after 5 days</p>
Photolytic degradation of desethyl-terbuthylazine (MT1) and metabolites above 10 % ‡	<p>SYN - Xenon arc lamp (wavelengths filtered < 290 nm) for 15 days. Light equivalent to 13, 15 and 23 days of summer sunlight at 30 and 50 °N on a 12 h light: 12 dark basis at pH 5, 7 and 9 respectively.</p> <p>DT₅₀: No significant degradation</p>
Quantum yield of direct phototransformation in water at Σ > 290 nm	A valid molar absorption coefficient could not be calculated because of very little or no absorption occurring over the wavelength range 290 – 800 nm.
Readily biodegradable ‡ (yes/no)	No data submitted, substance considered to be not ready biodegradable.

Hydrolytic degradation of hydroxy-terbuthylazine (MT13) and metabolites > 10 % ‡ (SYN)

pH 4: No significant degradation at 50 °C after 5 days

pH 7: No significant degradation at 50 °C after 5 days

pH 9: No significant degradation at 50 °C after 5 days

Photolytic degradation of hydroxy-terbuthylazine (MT13) and metabolites above 10 % ‡

Not performed

Quantum yield of direct phototransformation in water at $\Sigma > 290$ nm

A valid molar absorption coefficient could not be calculated because of very little or no absorption occurring over the wavelength range 290 – 800 nm.

Readily biodegradable ‡ (yes/no)

No. Not readily biodegradable

PEC (surface water) and PEC sediment (Annex IIIA, point 9.2.3)

As a result of the confirmatory information assessment, quantified predictions of LM2, LM3, LM4, LM5 and LM6 in groundwater above 0.1µg/l are available. The UK RMS therefore considers that LM2, LM3, LM4, LM5 and LM6 could be added to residue definition for surface water and sediment (by default). Endpoints for use in the surface water assessment are proposed as follows:-

LM2

DT₅₀: 16.5dK_{FOC}: 9.4 L/kg, $1/n = 1.03$

LM3

DT₅₀: 12.2dK_{FOC}: 3.7 L/kg, $1/n = 0.87$

LM4

DT₅₀: 53.6dK_{FOC}: 8.0 L/kg, $1/n = 0.85$

LM5

DT₅₀: 47.0dK_{FOC}: 15.3 L/kg, $1/n = 0.86$

LM6

DT₅₀: 241dK_{FOC}: 13.3 L/kg, $1/n = 0.91$

In the absence of information on peak occurrence in soil and degradation rates in water, it is proposed that for the purposes of a simple, conservative assessment, peak occurrence in soil is set at 100% and water/sediment DT50 values set to 1000 d. These values may be refined if necessary.

PEC (ground water) (Annex IIIA, point 9.2.1)

Method of calculation and type of study
(e.g. modelling, field leaching, lysimeter)

For FOCUS gw modelling, values used –
Modelling using FOCUS model(s), with appropriate FOCUSgw scenarios, according to FOCUS guidance.

Model(s) used: PEARL 4.4.4 and PELMO 4.4.3

Scenarios (list of names): Châteaudun (C), Hamburg (H), Kremsmünster (K), Okehampton (N), Piacenza (P), Porto (O), Sevilla (S), Thiva (T)

Q10 = 2.58

Crop: maize

Terbuthylazine:

DT₅₀: 20.0 d (normalised median of field studies).

K_{FOC}: worst case assessment using lowest K_{foc} value of 151 L/kg and associated ¹/_n of 0.93 to reflect possible pH dependence:-

Metabolites:

Desethyl-terbuthylazine:

DT₅₀: 26.8 d (geomean of field studies).

K_{FOC}: 77.7 L/kg, ¹/_n= 0.89 (mean values).

Formation fraction: 0.44 from parent

Hydroxy-terbuthylazine:

DT₅₀: 453 d (geomean of lab studies)

K_{FOC}: 187 L/kg, ¹/_n= 0.91 (mean values).

Formation fraction: 0.17 from parent (Applicant) and 0.197 (RMS)

Desethylhydroxy-terbuthylazine:

DT₅₀: 107 d (geomean of lab studies).

K_{FOC}: 121 L/kg, ¹/_n= 0.92 (median values,

Applicant) or 111 L/kg, ¹/_n= 0.92 (median values excluding results from the Bosket loam soil, RMS)

Formation fraction: 0.28 (from desethyl-terbuthylazine)

LM1

DT₅₀: 0.4d

K_{FOC}: 33.2 L/kg, ¹/_n= 1.02

Formation fraction: 0.59 (from LM5)

LM2

DT₅₀: 16.5d

K_{FOC}: 9.4 L/kg, ¹/_n= 1.03

Application rate

<p>Formation fraction: 1 (from LM4)</p> <p>LM3 DT_{50}: 12.2d K_{FOC}: 3.7 L/kg, $1/n = 0.87$ Formation fraction: 1 (from LM2)</p> <p>LM4 DT_{50}: 53.6d K_{FOC}: 8.0 L/kg, $1/n = 0.85$ Formation fraction: 0.08 (from parent terbuthylazine)</p> <p>LM5 DT_{50}: 47.0d K_{FOC}: 15.3 L/kg, $1/n = 0.86$ Formation fraction: 0.47 (from MT14)</p> <p>LM6 DT_{50}: 241d K_{FOC}: 13.3 L/kg, $1/n = 0.91$ Formation fraction: 0.41 (from LM5)</p>
<p>Application rate: 750 g/ha Northern Europe 850 g/ha Southern Europe</p> <p>No. of applications: 1</p> <p>Time of application (month or season): 1 day before crop emergence</p>

PEC(gw) - FOCUS modelling results (80th percentile annual average concentration at 1m)

FOCUS-PEARL PEC_{GW} values for Terbuthylazine (using minimum measured K_{foc} = 151 ml/g; K_{fom} = 87.6 ml/g) and three metabolites, following application to Maize at 750 g/ha (RMS simulations)

Scenario	PEC _{GW} at 1 m Soil Depth (µg/l)			
	Terbuthylazine	2-Hydroxy-terbuthylazine (GS23158) ¹	Desethyl-terbuthylazine (GS26379)	Desethyl-hydroxy-terbuthylazine (GS28620) ²
Châteaudun	<0.001	15.0	0.061	2.17
Hamburg	0.005	18.3	0.28	3.44
Kremsmünster	0.002	12.8	0.186	2.29
Okehampton	0.007	13.3	0.316	2.89
Piacenza	0.003	15.4	0.163	2.25
Porto	<0.001	7.63	0.047	1.25
Sevilla	<0.001	4.19	<0.001	0.188
Thiva	<0.001	21.0	0.009	1.66

¹: 2-hydroxy terbuthylazine DT₅₀ = 453 d, formation fraction = 0.197

²: desethyl-hydroxy terbuthylazine K_{foc} = 111 ml/g; K_{fom} = 64.4 ml/g (median of 11 values)

FOCUS-PEARL PEC_{GW} values for Terbuthylazine (using minimum measured K_{foc} = 151 ml/g; K_{fom} = 87.6 ml/g) and three metabolites, following application to Maize at 850 g/ha (RMS simulations)

Scenario	PEC _{GW} at 1 m Soil Depth (µg/l)			
	Terbuthylazine	2-Hydroxy-terbuthylazine (GS23158) ¹	Desethyl-terbuthylazine (GS26379)	Desethyl-hydroxy-terbuthylazine (GS28620) ²
Châteaudun	< 0.001	17.2	0.075	2.51
Hamburg	0.006	20.9	0.336	3.97
Kremsmünster	0.002	14.7	0.225	2.65
Okehampton	0.008	15.2	0.4	3.33
Piacenza	0.003	17.7	0.2	2.6
Porto	<0.001	8.69	0.058	1.44
Sevilla	<0.001	4.88	<0.001	0.223
Thiva	<0.001	24.1	0.011	1.93

¹: 2-hydroxy terbuthylazine DT₅₀ = 453 d, formation fraction = 0.197

²: desethyl-hydroxy terbuthylazine K_{foc} = 111 ml/g; K_{fom} = 64.4 ml/g (median of 11 values)

FOCUS-PEARL PEC_{GW} values for Terbuthylazine six lysimeter metabolites LM1-LM6 (using minimum measured K_{foc} = 151 ml/g; K_{fom} = 87.6 ml/g) following application to Maize at 750 g/ha (RMS simulations)

Scenario	PEC _{GW} at 1 m Soil Depth (µg/L)					
	LM1	LM2	LM3	LM4	LM5	LM6
Châteaudun	0.01	2.57	2.1	5.82	2.55	3.97
Hamburg	0.014	4.59	3.4	10.4	4.02	4.72
Kremsmünster	0.009	2.26	1.74	5.37	2.37	2.78
Okehampton	0.009	2.26	1.64	5.43	2.37	1.8
Piacenza	0.008	1.46	1.88	4.14	2.28	4.54
Porto	0.006	1.23	0.93	2.66	1.43	1.67
Sevilla	0.003	0.64	0.54	1.07	0.728	3.71
Thiva	0.009	2.13	1.88	4.78	2.39	8.0

FOCUS-PEARL PEC_{GW} values for Terbuthylazine six lysimeter metabolites LM1-LM6 (using minimum measured K_{foc} = 151 ml/g; K_{fom} = 87.6 ml/g) following application to Maize at 850 g/ha (RMS simulations)

Scenario	PEC _{GW} at 1 m Soil Depth (µg/L)					
	LM1	LM2	LM3	LM4	LM5	LM6
Châteaudun	0.011	2.93	2.39	6.68	2.92	4.49
Hamburg	0.016	5.19	3.86	12	4.62	5.32
Kremsmünster	0.01	2.56	1.97	6.14	2.71	3.13
Okehampton	0.01	2.56	1.86	6.21	2.7	2.02
Piacenza	0.009	2.13	1.66	4.78	2.61	5.14
Porto	0.007	1.39	1.06	3.05	1.65	1.88
Sevilla	0.003	0.727	0.619	1.23	0.838	4.21
Thiva	0.01	2.43	2.15	5.49	2.76	9.06

Residues requiring further assessment

Environmental occurring metabolite requiring further assessment by other disciplines (toxicology and ecotoxicology) or for which a groundwater exposure assessment is triggered.

Soil: terbuthylazine, desethyl-terbuthylazine, hydroxy-terbuthylazine
 Surface Water: terbuthylazine, desethyl-terbuthylazine, hydroxy-terbuthylazine (MT13), desethyl-hydroxy terbuthylazine and terbutryn (MT26)
 Sediment: terbuthylazine, desethyl-terbuthylazine, hydroxy-terbuthylazine (MT13), desethyl-hydroxy terbuthylazine and terbutryn (MT26)
 Groundwater: terbuthylazine, desethyl-terbuthylazine, hydroxy-terbuthylazine (MT13) and desethyl-hydroxy-terbuthylazine, LM1, LM2, LM3, LM4, LM5 and LM6
 Air: terbuthylazine

The above is the original residue definition for environmentally occurring metabolites requiring further assessment by other disciplines. As a result of the confirmatory information assessment, quantified predictions of LM2, LM3, LM4, LM5 and LM6 in groundwater above 0.1 µg/l are available. The UK RMS therefore considers that LM2, LM3, LM4, LM5 and LM6 could be added to residue definition for surface water and sediment (by default).

Monitoring data, if available (Annex IIA, point 7.4) - SYN

Soil (indicate location and type of study)

Surface water (indicate location and type of study)

a) Two sites in Germany susceptible to run-off and adjacent to streams in typical maize growing areas were selected. Upstream and downstream points of streams were monitored for terbuthylazine and desethyl-terbuthylazine (MT1) from May to August in 1999 and 2000 following terbuthylazine application to maize in adjacent field. Samples were taken every hour and combined into weekly samples. Samples also taken after heavy rainfall events. Neither analyte detected at 'Ramholz' site at concentrations > 0.05 µg/L (LOQ). Max weekly concentrations at the 'Kemading' site were 0.28 and 0.08 µg/L for terbuthylazine and desethyl-terbuthylazine (MT1) respectively. Max concentrations in event samples were 0.87 µg/L and 0.20 µg/L. Concentrations similar at upstream and downstream sample sites indicate residues arose from applications in upstream catchment.

Ground water (indicate location and type of study)

b) Two sites in Germany adjacent to brooks were selected each with 10 m vegetated filter strip. Formulations were applied to maize between growth stages BBCH 13 and 16 in 1999 and 2000, and brook surface water samples at the upstream and downstream field edges were taken from one week before application (early May) until early September. Streams were sampled hourly and combined into weekly samples. Samples were also taken after heavy rainfall events. At the ‘Adenstadt’ site neither terbuthylazine nor desethyl-terbuthylazine (MT1) were observed at concentrations > LOQ (0.05 µg/L). Only once, in the first week following application was terbuthylazine detected at the ‘Süplingen’ site at a max concentration of 0.07 µg/L in a weekly sample. Desethyl-terbuthylazine (MT1) was not detected above the LOQ.

a) Full sample details not provided. 27103 sample data from Germany for the occurrence of terbuthylazine in groundwater. 328 detections of terbuthylazine were observed with 41 > (0.15% of the total analyses) displaying residues in excess of 0.1 µg/L. The Applicant states that none of these exceedences were due to the correct GAP for approved uses being applied.

b) Full sample details not provided. Groundwater samples from more than 1000 intakes from 15 municipalities in counties around Denmark in 1990 – 2001 were analysed for residues of plant protection products and their degradation products. The mean depth to the top of the groundwater sample was 24 - 25 m with a mean intake length of 3.5 m. In addition to the groundwater survey, the report also contained information on the analyses of water samples taken from a group of “other borings” which are not used to extract groundwater for drinking purposes. 1016 intakes were analysed for terbuthylazine (the number of analyses was 4086). There were 17 (1.7 %) intakes with detections of terbuthylazine, however, none of them contained concentrations ≥ 0.1 µg/L. With regard to the group “other borings”, 1156 and 311 borings were analysed for terbuthylazine and desethyl-terbuthylazine (MT1) respectively with 1492 and 527 individual analyses respectively. Terbuthylazine and desethyl-terbuthylazine (MT1) were found in 18 (1.6 %) and 14 (4.5 %) borings, with 3 (0.3 %) and 4 (1.3 %) of these findings being detected at concentrations ≥ 0.1 µg/L.

c) Danish government monitoring programme selected two sites (Jyndevad and Silstrup) in Denmark to assess the leaching potential of pesticides including terbuthylazine. Applications were made to maize in May 2001 at Jyndevad and in May/June 2002 at Silstrup. Soil pore waters and groundwaters were analysed monthly for terbuthylazine and desethyl-terbuthylazine, additionally at Silstrup hydroxy-terbuthylazine, hydroxy-desethyl-

terbuthylazine (MT1) and atrazine-desisopropyl-2-hydroxy (MT22) were also monitored for from February 2003.

At Jyndevad, terbuthylazine was not detected in either the soil pore water or the groundwater at concentrations $> 0.01 \mu\text{g/L}$ in the two year monitoring period. Desethyl-terbuthylazine (MT1) was detected in pore water at 1 m depth in all but three of the monthly samples between October 2001 (five months after application) and May 2003 at concentrations of $0.020 - 0.056 \mu\text{g/L}$, however it was not detected in pore waters at 2 m and was only detected once in any of the downstream groundwater monitoring wells.

At Silstrup terbuthylazine residues in well water at 1.5-2.5 m depth ranged from $0.013-0.124 \mu\text{g/L}$ over the year with one sample containing $> 0.1 \mu\text{g/L}$. Residues of desethyl-ranged from $0.046-0.143 \mu\text{g/L}$ over the year with two samples containing $> 0.1 \mu\text{g/L}$. Residues from deeper screens were always $< 0.08 \mu\text{g/L}$ for both terbuthylazine and desethyl-terbuthylazine. Of the remaining metabolites hydroxy-terbuthylazine (MT13) was not detected in the well water. Hydroxy-desethyl-terbuthylazine (MT1) was only detected once in the well water at a depth of 1.5 – 2.5 m at a concentration of $0.016 \mu\text{g/L}$. Atrazine-desisopropyl-2-hydroxy (MT22) was detected three times in the well at 1.5 – 2.5 m depth at concentrations around $0.01 \mu\text{g/L}$. It was also detected once at a depth of 3.5 – 4.5 m at a concentration of $0.047 \mu\text{g/L}$.

d) Targeted groundwater monitoring studies were conducted in Germany in areas of documented use of terbuthylazine containing products. Typical maize regions were investigated i.e. Schleswig-Holstein, Mecklenburg-West Pomerania, Muenster-Emsland (stretching from the federal state North Rhine-Westfalia to Lower Saxony), Rottal (Bavaria) and the Upper Rhine Valley (stretching from the federal state Baden-Wuerttemberg to Hesse). Groundwater was collected from monitoring screen typically situated 5 m below ground surface. Confirmed usage of terbuthylazine containing products in upstream areas ($2.5 \times 2.5\text{km}$ or 625 ha) was determined via farmer surveys and interviews over three years (2002 – 2004). Results for each site represent the sum over this period as follows:- Wanderup 277 ha, Alt-Bennebek 497ha, Breiholz-Ost 198 ha, Hagen-Suedost 61 ha, Luettow 57 ha, Torgelow 225 ha, Lelkendorf 72 ha, Warnow 60 ha, Pinnow 288ha, Tabeckendorf 114 ha, Postmuenster 92 ha, Hammersbach 102 ha, Kirchham-Pfaffenhof 336 ha, Simbach-Stoelln 137 ha, Biblis 82 ha, Lorsch 56 ha, Rheinhausen-Oberhausen 198 ha, Breisach-Weingenossenschaft 240 ha, Grezhausen 69 ha, Rehderfeld 154 ha, Flechum 114 ha, Dalumer Moor 174 ha, Bexten 139 ha, Große-Luettke 103 ha, and Veltrup

202 ha. The overall mean hectareage treated was reported to be 120 ha across all sites and only those sites that received at least 50 ha of treatment were included in the final 25 sites monitored. The groundwater table was mostly less than 5 meters below ground surface and a wide range of soil properties was covered by the selected regions. No residues of terbuthylazine and desethyl-terbuthylazine were detected in any of the ground water monitoring samples analysed. Small residues of GS 28620 (MT14) and GS 23158 (MT13) were found in water samples taken from ground water monitoring wells at two locations. The residues of GS 28620 (MT14) occurred in May-July 2003 and ranged from 0.05-0.06 µg/l. The residues of GS 23158 (MT13) were detectable but not quantifiable (i.e. < 0.05 but > 0.02 µg/l). In addition, the lysimeters metabolites LM3, LM5 and LM6 were detected at 19 of the 25 locations, confirming the linkage to terbuthylazine treated areas in the catchment. Residues of the metabolite CSCD648241 (LM6) in 29 samples from 25 individual sampling points were determined to be between < 0.05 µg/l and 0.66 µg/l. Residues of the metabolite GS16984 (MT23, LM5) in 29 samples from 25 individual sampling points, were determined to be between < 0.05 µg/l and 0.98 µg/l. The metabolite CSCD692760 (LM3) was detected at 19 (10 above the LOQ and 9 below the LOQ) of the 25 locations. Quantifiable residues ranged from 0.06-0.69 µg/l.

e) In 1997, a monitoring study was carried out in four maize cultivated areas in the plain of the river Po in Italy to evaluate the degree of contamination of the groundwater table. No residues of terbuthylazine were detected above 0.1 µg/l in the 1997 study. A follow-up study was conducted in 2006 in the same areas identified in the previous monitoring study. The majority of superficial wells sampled were over 20 m deep, with deep wells often greater than 50m. In these follow-up studies 8 out of approximately 100 wells were found to contain residues of terbuthylazine or its metabolites desethyl-terbuthylazine and hydroxy-terbuthylazine above 0.1 µg/l. However the average age of the wells was over 30 years and characterised by degraded materials, rust, holes or cracks etc and as a whole, the 90th percentile terbuthylazine and metabolite residues were all <0.05 µg/l on the basis of this monitoring

f) A retrospective monitoring study was conducted in four regions of Portugal from 1999 to 2007. As a retrospective study, only limited details on the history of pesticide use in the upstream areas was available. However throughout the eight year duration of the study, 773 water samples were taken and analysed for terbuthylazine and desethyl-terbuthylazine from 68 different sampling sites, generating a total of 1546 data points. Sampling sites covered a relatively wide variety of sales history, cropping density, depth to groundwater

and nitrate concentration (this last parameter used as general indicator for the vulnerability of an aquifer to agricultural practices). Although terbuthylazine has not been in widespread use in two of the monitored regions, it has been extensively used in vineyards in the Oeste and the Douro valley at a rate of 490 g/ha (1400 g/ha in row). Neither terbuthylazine nor desethyl-terbuthylazine residues exceeded 0.05 µg/l at the 90th percentile of the population. Overall the RMS considered that the additional data from the Portuguese monitoring programs did provide useful information. However it should be noted that the monitoring is only of partial relevance in the regions where prior use of terbuthylazine is known to be extensive, and also taking into account that the use covers applications to vineyards rather than the extensive use on maize as investigated in the German and Italian studies. Taking these caveats into account, the RMS considers that the data should be viewed as providing supporting information alongside the monitoring data from other regions, as well as taking into account the results of the standard first tier FOCUS groundwater exposure assessments.

g) Retrospective monitoring studies were conducted in 3 regions of Spain covering use of terbuthylazine on olive crops in Andalucia (2000 to 2003), use on maize and citrus crops in South Eastern Spain (2000 to 2001) and use on maize and vineyards in Northern Spain (2000-2001). As retrospective studies, only limited details on the history of pesticide use in the upstream areas was available. In addition in many cases, the relatively large distance between the discharge point and the upland aquifer made it difficult to relate monitored residues back to a specific product use pattern. However throughout each study sampling sites were selected using local knowledge of cropping density, regional product sales data, hydrogeological information and information pertaining to the integrity of the respective sampling sites. In three regions the 90th percentile concentration was less than 0.1 µg/l for both terbuthylazine and metabolite desethyl-terbuthylazine (the only metabolite monitored for). However it should be noted that methods of analysis were unvalidated and the LOQ was only reported to be 0.1µg/l in the studies conducted in South Eastern Spain. In Andalucia, following extensive use of terbuthylazine on olive crops, the 90th percentile concentration of terbuthylazine was 0.14 µg/l. However the majority of detections in this region came from springs discharging groundwater into lagoons, troughs or drainage canals that were not protected from direct contamination. Overall the RMS considered that the additional data from the Spanish monitoring programs did provide limited useful information. However it should be noted that the monitoring is only of partial relevance in the regions where prior use of terbuthylazine is known to be extensive, and also taking into account that the monitoring covers areas where terbuthylazine may be applied to olive crops, citrus and vineyards in addition to use on maize in two of the three

regions investigated. In addition, the sampling of groundwater from springs discharging to surface water bodies meant that the influence of direct contamination (rather than conventional leaching) could not be excluded. Taking these caveats into account, the RMS considers that the data should be viewed as providing limited supporting information only alongside the monitoring data from other regions, as well as taking into account the results of the standard first tier FOCUS groundwater exposure assessments.

Air (indicate location and type of study)

None

Points pertinent to the classification and proposed labelling with regard to fate and behaviour data

Candidate for chronic (long term) aquatic hazard

Toxicity data for aquatic species (most sensitive species of each group) (Annex IIA, point 8.2, Annex IIIA, point 10.2)

Group	Test substance	Time-scale (Test type)	End point	Toxicity ¹ (mg/L)
Laboratory tests ‡				
Fish				
<i>Oncorhynchus mykiss</i>	a.s.	96 hr (static)	Mortality, _{nom} LC ₅₀	2.2 mg a.s./L (SYN)
<i>Oncorhynchus mykiss</i>	a.s.	90 d (flow-through)	Early life cycle _{mm} NOEC	0.09 mg a.s./L (SYN)
<i>Oncorhynchus mykiss</i>	Preparation: 'Gardo Gold' (A-9476 C)	96 hr (static)	Mortality, _{mm} LC ₅₀	8.32 mg formulation/ L (1.58 mg a.s./L) (SYN)
<i>Oncorhynchus mykiss</i>	Preparation: 'Terbuthylazine 500 g/L SC'	96 hr (static)	Mortality, _{mm} LC ₅₀	12 mg formulation/ L (6.6 mg a.s./L) (OXON)
<i>Oncorhynchus mykiss</i>	Metabolite MT1 (GS 26379, desethyl- terbuthylazine)	96 hr (static)	Mortality, _{nom} LC ₅₀	18 mg/L (SYN)
<i>Oncorhynchus mykiss</i>	Metabolite MT13 (GS 23158, 2- hydroxy- terbuthylazine)	96 hr (static)	Mortality, _{mm} LC ₅₀	>2.5 mg/L (SYN)
<i>Oncorhynchus mykiss</i>	Metabolite MT26 (GS 14260, terbutryn)	96 hr (static)	Mortality, _{mm} LC ₅₀	1.1 mg/L (SYN)
Aquatic invertebrate				
<i>Daphnia magna</i>	a.s.	48 h	Mortality, EC ₅₀	No definitive endpoint available ²

Group	Test substance	Time-scale (Test type)	End point	Toxicity ¹ (mg/L)
<i>Daphnia magna</i>	a.s.	21 d (semi-static)	Reproduction, _{nom} NOEC	0.019 mg a.s./L (SYN)
<i>Daphnia magna</i>	Preparation: 'Gardo Gold' (A-9476 C)	48 h (static)	Mortality, EC ₅₀	No definitive endpoint available ³
<i>Daphnia magna</i>	Preparation: 'Terbuthylazine e 500 g/L SC'	48 h (static)	Mortality, EC ₅₀	No definitive endpoint available ³
<i>Daphnia magna</i>	Metabolite MT1 (GS 26379, desethyl- terbuthylazine)	48 h (static)	Mortality, _{nom} EC ₅₀	42 mg/L (SYN)
<i>Daphnia magna</i>	Metabolite MT13 (GS 23158, 2- hydroxy- terbuthylazine)	48 h (static)	Mortality, _{nom} EC ₅₀	>2.8 mg/L (SYN)
Sediment dwelling organisms				
<i>Chironomus riparius</i>	a.s.	27 d (static)	_{nom} NOEC (water phase)	0.5 mg a.s./L (SYN)
<i>Chironomus riparius</i>	Metabolite MT13 (GS 23158, 2- hydroxy- terbuthylazine)	28 d (static)	_{nom} NOEC (sediment phase)	400 mg/kg (sediment) (SYN)
<i>Chironomus riparius</i>	Metabolite MT26 (GS 14260, terbutryn)	28 d (static)	_{nom} NOEC (sediment phase)	16 mg/kg (sediment)
Algae				
Blue green algae (<i>Microcystis aeruginosa</i>)	a.s.	72 h (static)	Biomass: _{mm} E _b C ₅₀	0.016 mg a.s./L (OXON)
			Growth rate: _{mm} E _r C ₅₀	0.102 mg a.s./L (OXON)

Group	Test substance	Time-scale (Test type)	End point	Toxicity ¹ (mg/L)
<i>Pseudokirchneriella subcapitata</i>	a.s.	72 h (static)	Biomass: mmE_bC_{50}	0.012 mg a.s./L (OXON)
			Growth rate: mmE_rC_{50}	0.028 mg a.s./L (OXON)
<i>Desmodesmus subspicatus</i>	Preparation: 'Gardo Gold' (A-9476 C)	72 h (static)	Biomass: $nomE_bC_{50}$	0.108 mg formulation/ L (0.0205 mg a.s./L) (SYN)
			Growth rate: $nomE_rC_{50}$	0.211 mg formulation/ L (0.0401 mg a.s./L) (SYN)
<i>Pseudokirchneriella subcapitata</i>	Preparation: 'Terbuthylazine 500 g/L SC'	72 h (static)	Biomass: mmE_bC_{50}	0.039 mg formulation/ L (0.021 mg a.s./L) (OXON)
			Growth rate: mmE_rC_{50}	0.073 mg formulation/ L (0.040 mg a.s./L) (OXON)
<i>Selenastrum capricornutum</i>	Metabolite MT1 (GS 26379, desethyl- terbuthylazine)	72 h (static)	Biomass: mmE_bC_{50}	0.14 mg/L (SYN)
			Growth rate: mmE_rC_{50}	0.38 mg/L (SYN)
<i>Desmodesmus subspicatus</i>	Metabolite MT13 (GS 23158) 2- hydroxy- terbuthylazine)	72 h (static)	Biomass: $nomE_bC_{50}$	>3.96 mg/L (OXON)
<i>Selenastrum capricornutum</i>			Growth rate: mmE_rC_{50}	>3.8 mg/L (SYN)
<i>Pseudokirchneriella subcapitata</i>	Metabolite MT26(GS 14260) terbutryn)	72 h (static)	Biomass: mmE_bC_{50}	0.0017 mg/L (SYN)
			Growth rate: mmE_rC_{50}	0.0036 mg/L (SYN)

Group	Test substance	Time-scale (Test type)	End point	Toxicity ¹ (mg/L)
<i>Pseudokirchneriella subcapitata</i>	Metabolite LM3	72h (static)	Growth rate: ${}_{\text{nom}}E_rC_{50}$	80
			Yield: ${}_{\text{nom}}E_yC_{50}$	39
			Biomass: ${}_{\text{nom}}E_bC_{50}$	39
<i>Pseudokirchneriella subcapitata</i>	Metabolite LM5	72h (static)	Growth rate: ${}_{\text{nom}}E_rC_{50}$	>100
			Yield: ${}_{\text{nom}}E_yC_{50}$	>100
			Biomass: ${}_{\text{nom}}E_bC_{50}$	>100
<i>Pseudokirchneriella subcapitata</i>	Metabolite LM6	72h (static)	Growth rate: ${}_{\text{nom}}E_rC_{50}$	>100
			Yield: ${}_{\text{nom}}E_yC_{50}$	>100
			Biomass: ${}_{\text{nom}}E_bC_{50}$	>100
Higher aquatic plants				
<i>Lemna gibba</i>	a.s.	14 d (static)	Fronnd number: ${}_{\text{nom}}E_{\text{fn}}C_{50}$	0.0128 mg a.s./L (OXON)
			Growth rate: ${}_{\text{nom}}E_rC_{50}$	0.412 mg a.s./L (OXON)
			Biomass: ${}_{\text{nom}}E_bC_{50}$	0.0133 mg a.s./L (OXON)
<i>Lemna gibba</i>	Metabolite MT26 (GS 14260, terbutryn)	14 d (static)	Fronnd density: ${}_{\text{mm}}E_{C_{50}}$	0.025
<i>Myriophyllum aquaticum</i>	Metabolite MT26 (GS 14260, terbutryn)	14 d (static)	Root fresh weight: ${}_{\text{nom}}E_{C_{50}}$	2.0 mg/kg (sediment)
Microcosm or mesocosm tests				
Higher tier data are available, but insufficient information is currently available to derive an endpoint.				

¹ nominal (${}_{\text{nom}}$) or mean measured concentrations (${}_{\text{mm}}$).

$E_{\text{fn}}C_{50}$: effect concentration on frond number

In the case of preparations indicate whether end points are presented as units of preparation or a.s.

² As discussed in Section B.9.2.4.3.1 of the DAR no definitive acute toxicity endpoint was derived from the submitted aquatic invertebrate studies as neither of the submitted studies used a suitable method to determine the amount of terbuthylazine in solution. However, the studies were considered to be of adequate quality to clearly demonstrate that terbuthylazine is of less toxicity to aquatic invertebrates than other aquatic species and therefore the risk assessment for fish is deemed to cover the aquatic invertebrate risk assessment.

³ As discussed in Section B.9.2.4.5 of the DAR no definitive toxicity endpoint for aquatic invertebrates was determined for either of the submitted aquatic invertebrate studies. However, as for the a.s. both studies were considered suitable to clearly demonstrate the formulations are of less toxicity to aquatic invertebrates than other aquatic species and therefore the risk assessment for fish is deemed to cover the aquatic invertebrate risk assessment.

Groundwater

Metabolite TERs for aquatic organisms when groundwater becomes surface water calculated for the Piacenza scenario, assuming a 0.844 kg a.s./ha application of terbuthylazine in Southern Europe. Metabolites LM3 and LM5 calculated from the Hamburg scenario with an application rate of 850 g/ha. Metabolite LM6 calculated from the Thiva scenario with an application rate of 850 g/ha.

Time scale	Organism	Toxicity endpoint µg/L	Diluted ground water PEC µg/L ²	TER	Annex VI trigger value	
MT1 (desethyl-terbuthylazine)						
Acute	Fish	LC ₅₀	18000	0.1429	125962	100
Acute	Aquatic invertebrate	EC ₅₀	42000	0.1429	293912	100
	Algae	E _b C ₅₀	140	0.1429	980	10
MT13 (2-hydroxy-terbuthylazine)						
Acute	Fish	LC ₅₀	>2500	1.283	>1949	100
Acute	Aquatic invertebrate	EC ₅₀	>2800	1.283	>2182	100
	Algae	E _r C ₅₀	>3800	1.283	>2962	10
MT14 (desethyl-hydroxy-terbuthylazine, GS 28620)						
Acute	Fish	LC ₅₀	15000 ¹	0.3627	41356	100
Acute	Aquatic invertebrate	EC ₅₀	15000 ¹	0.3627	41356	100
	Algae	E _b C ₅₀	15000 ¹	0.3627	41356	10
LM3						
	Algae	E _b C ₅₀	39000	3.88	100515	10
LM5						
	Algae	E _b C ₅₀	100000	4.62	216450	10
LM6						
	Algae	E _b C ₅₀	100000	9.24	108225	10

¹ The study authors proposed the acute fish and *Daphnia magna* L/EC₅₀ for MT14 was >100 mg/L and the EC₅₀ to algae to be 30.7 mg/L. However, these values are greater than the water solubility of MT14 (18 mg/L) and therefore the Rapporteur has reservations in accepting quantified toxicity endpoints. The water solubility of MT14 is 18 mg/L and therefore to assume the saturation level (the amount of MT14 in solution under the conditions of the study) of 15 mg

a.s./L is not unreasonable. Assuming the acute fish LC_{50} , acute *Daphnia magna* EC_{50} and the algae EC_{50} are 15 mg/L a TER of 2617.3 is calculated which clearly demonstrates that metabolite MT14 does not pose a high risk to fish, aquatic invertebrates and algae

Ecotoxicologically relevant compounds (consider parent and all relevant metabolites requiring further assessment from the fate section)

Compartment	
soil	Terbuthylazine
water	Terbuthylazine, metabolite MT26 (terbutryn), desethyl terbuthylazine,
sediment	Terbuthylazine
groundwater	None

Classification and proposed labelling with regard to ecotoxicological data (Annex IIA, point 10 and Annex IIIA, point 12.3)

Active substance

No current Annex VI entry. RAC opinion (June 2015): Aquatic Acute 1 (H400) with an M-factor of 10 Aquatic Chronic 1 (H410) with an M-factor of 10.
