Data Evaluation Report on the aerobic biotransformation of thidiazuron in soil

PMRA Submission Number {.....} EPA MRID Number 46119601

Data Requirement: PMRA Data Code:
EPA DP Barcode: D298740
OECD Data Point:
EPA Guideline: 162-1

Test material:
Common name: Thidiazuron.
Chemical name
IUPAC: 1-Phenyl-3-(1,2,3-thiadiazol-5-yl)urea.
CAS name: N-Phenyl-N'-1,2,3-thiadiazol-5-ylurea.
CAS No: 51707-55-2.
Synonyms: Dropp, AE B049537.
SMILES string: O=C(Nc1ccccc1)Nc1cnns1.

Primary Reviewer: Dana Worcester
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Company Code:
Active Code:
Use Site Category:
EPA PC Code: 120301

CITATION: Allan, J.G. 2003. The kinetics of degradation of [^{14}C-thidiazol]-thidiazuron in three soils at 20°C under laboratory aerobic conditions. Unpublished study performed and submitted by Bayer CropScience, Research Triangle Park, NC. Study Identification: 601AW. Experiment start date August 30, 2001, and completion date June 30, 2003 (p. 7). Final report issued July 2, 2003.

ADMINISTRATIVE CONCLUSIONS

This aerobic soil metabolism study (MRID 46119601) for thidiazuron is classified as *supplemental*. However, because A) the Agency has a previous study (MRID 41950101) conducted with a different radiolabel for thidiazuron (^{14}C uniformly in phenyl ring) that was acceptable for partially satisfying US EPA (EPA) Subdivision N Guideline criteria for an aerobic soil metabolism study (§162-1); B) of the specific chemical nature of thidiazuron; and C) provided the Agency makes reasonable inferences and adjustments to study results, no additional aerobic soil metabolism data are needed at this time.

This study did not technically meet Subdivision N Guideline criteria primarily because the study was: 1) terminated after 160-168-days, which was before the pattern of transformation of parent imazapyr and the pattern of formation and decline of products could be definitively established or before one year had elapsed; 2) conducted at 20 °C, rather than guideline specified 25 °C; 3) conducted at a soil moisture content of 40% of maximum water holding capacity (MWHC), rather than guideline specified 75% of 1/3-bar; and 4) was conducted only with thiadiazol ring-radiolabeled thidiazuron. Nevertheless, with previously submitted data and with the approximations and inferences given in the next section, reasonable conclusions can still be reached. If the submitter disagrees with any inferences the Agency makes or adjustment factors the Agency may use in order to offset study deficiencies, they may chose to submit a new study. Ultimately, whether a more refined aerobic soil metabolism study is needed will be decided after all data related to environmental fate, ecological effects, human health are integrated and risks assessed.

Finally, the submitter should carefully regard reviewer comments made throughout this Data Evaluation Report (DER), particularly those in the Scientific Conclusions Section below and in the Study Deficiencies and Reviewer's Comments Sections of this report. Consideration should be given to their applicability to the acceptability of future study submissions.

SCIENTIFIC CONCLUSIONS

Note: 1) This three-soil study was conducted under the European Union standard experimental conditions for aerobic soil metabolism with a ^{14}C-radiolabel for thidiazuron in the thiadiazol-ring position indicated as follows: [1,2,3-thiadiazol-5-^{14}C]N-phenyl-N'-1,2,3-thiadiazol-5-ylurea (see Attachment 2 for chemical structural formula and position of radiolabel). Conditions were 20 °C and 40% MWHC. The EPA Guideline standard conditions are 25 °C and 75% of 1/3-bar soil suction. In general, these different conditions significantly alter reaction rates and, therefore, half-lives. The EPA condition for soil moisture is typically the lower (dryer), which translates into slower metabolism and longer half-lives; whereas the higher EPA temperature tends to speed reactions and shorten half-lives. Although directionally opposite, these two influences generally do not offset equally. Therefore, it is important to distinguish clearly and to compensate or adjust for differences when reporting standard values, as these may be used for diverse purposes, such as standard inputs to environmental models or for comparisons among compounds in a database. For these reasons, the reviewer has adjusted the study half-lives to EPA standard conditions for soil

moisture by selective use of the Walker equation and for temperature by selective use of the Arrhenius equation, as discussed and referenced in Attaachment 1 of this Data Evaluation Report (DER).

2) Because thidiazuron is relatively long-lived compared to the 160-168-day test periods of this study, half-lives are extrapolations. It is the preferred scientific procedure for study periods to extend for several halving times in order to clearly establish the rates and pattern of parent decline, the identity and characterization of metabolites in sufficient quantify for analysis, and the rates and pattern of formation and decline of metabolites. For compounds that, because of their longevity, cannot meet halving-time criteria in less than one year, then a study lasting only one year is considered sufficient by the EPA. This study did not meet either timing criterion. However, it is reasonable to infer from the data that estimated half-lives for parent are of comparable duration to those that would have been obtained during a longer study period of up to one year, and that the revealed chemical nature of parent and observed products in aerobic soil is adequate for risk assessment purposes at this time.

Kinetics of Thidiazuron Metabolism in Aerobic Soil. Thidiazuron, [1,2,3-thiadiazol-5-^{14}C]N-phenyl-N'-1,2,3-thiadiazol-5-ylurea (radiochemical purity 99%), was long-lived in the three soils tested during study periods lasting for 160-168 days. Test conditions were: aerobic, in the dark, at ***20 ± 1°C***, and at ***soil moisture contents of 40% of maximum water holding capacities (MWHC) for each individual soil***. Material/radioactivity balance was generally excellent for all soils at all sampling intervals. Within observed experimental variation and precision for all sampling intervals and durations of study, the data are consistent with linear, first-order kinetics.

Thidiazuron degraded with the extrapolated linear, first-order kinetic regression half-lives given in Table A below. Column 2 lists the unadjusted experimental half-lives, their regression 95% confidence intervals (C.I.), and regression r-squared values. Column 3 lists the corresponding half-lives after adjustments to the EPA standards for soil moisture (75% of 1/3-bar suction) and temperature (25 °C) (methodologies explained in Attachment 1 of this DER). Although three significant digits are arbitrarily given for tracking calculations and data sets, it is obvious from the confidence limits, which are representative of those of most such conventional guideline studies, that no more than one or two significant decimal digits is/are warranted. Use of the Walker equation and the Arrhenius equation (see Attachment 1 of this DER) also decrease certainty in adjusted half-lives. A comparison of the adjusted and unadjusted half-lives shows that soil moisture differences had the greater influence on the soils from the UK and NC than did the 5 °C temperature difference, since adjusted half-lives are longer; whereas the temperature effect was greater than soil moisture for the Il soil, since the adjusted half-life is shorter. The nature of these differences is discussed in the context of the Walker and the Arrhenius equations in Attachment 1 of this DER.

Table A*

Extrapolated Linear First-Order Regression Half-lives for Thidiazuron at 20 °C and 40% MWHC Versus 25 °C and 75% of 1/3-Bar Soil Suction			
Soil (see Table 3 below for properties)	**Half-Life (days) at 20 °C and 40% MWHC (95% C.I.)**	**Half-Life (days) Adjusted* to 25 °C and 75% of 1/3-Bar**	**Time for 90% Decline (extrapolated) unadjusted / adjusted* (days)**
Sandy Loam (UK)	163 (137-200), $r^2 = 0.95$	**206**	541 / 684
Loamy Sand (NC)	355 (252-599), $r^2 = 0.77$	**436**	1180 / 1450
Silt Loam (IL)	322 (237-500), $r^2 = 0.82$	**253**	1070 / 840

*As discussed in Attachment 1 of this DER, adjustments for soil moisture and temperature are based, respectively, on the Walker equation and the Arrhenius equation.

Note that study periods of 160-168 days are relatively short compared to parent longevity. The study period for the sandy loam soil corresponds to approximately one half-life, while the half-lives in the loamy sand and silt loam soils are extrapolated well beyond the study time. Although data points were irregular for the sandy loam soil at sampling times when concentrations approach half the initial concentration (Table 6a of this DER), visual inspection is consistent with a DT50 that is roughly the same as the first-order half-life. Assuming that degradation continues to follow a first-order model, then 90% of thidiazuron would have degraded in the sandy loam, loamy sand, and silt loam soils, respectively, in 541/684 days (unadjusted/adjusted format), 1180/1450 days, and 1070/840 days. The extrapolated times estimated for 90% decline of parent are in the right-hand column of Table A. Although the extrapolations for 90% decline are extreme, they do clearly indicate the relative persistence of parent.

Metabolic Products. No major (defined as ≥ 10% of applied radioactivity) organic transformation products were isolated or identified in any of the three soils during the 160-168-day test periods. The only *minor* organic transformation product identified was AE F132345 (thiadiazolurea or 1,2,3-thiaiazol-5-ylurea). Within experimental variation, AE F132345 appeared to reach an approximately flat maximum concentration of roughly 6-9% of applied radioactivity in the sandy loam soil (soil in which metabolism was fastest) during the period from approximately 88 days to study end at 168 days (Table 6a of this DER). The broad plateau is evidence that AE F132345 would not form in greater yield, and that it may be a persistent metabolite. Maximum concentrations of AE F132345 in the loamy sand and silt loam soils were roughly 1% and 3%, respectively (Tables 6b and 6c of this DER).

Extracted ^{14}C substances, composed mostly of parent, decreased to approximately 52% in the sandy loam soil at the end of its study (168 days) (Table 6a). In both the loamy sand and silt loam soils,

extracted ^{14}C substances, composed mostly of parent, comprised roughly 70-80% of applied during mid-to-later study periods (Tables 6b and 6c). Extracted substances that were not identified in any soil at any sampling interval comprised no more than roughly 1-6% of applied radioactivity (Tables 6a, 6b, 6c).

Non-extracted ^{14}C material increased to approximately 32% in the sandy loam soil at study end, and increased to roughly 16-25% for both the loamy sand and silt loam soils from around 99 to 160 days (Tables 6a, 6b, 6c).

In the sandy loam soil, $^{14}CO_2$ reached a broad total plateau of 5-12% of applied radioactivity during later study periods (Table 6a). In the loamy sand and silt loam soils, $^{14}CO_2$ totaled around 1-2% and 6-8%, respectively, during later study periods (Tables 6b and 6c). Thus, loss of ^{14}C via $^{14}CO_2$ production (mineralization) from the labeled position appears to be a relatively minor route of transformation. For all three soils, volatile organics totaled ≤0.1% of applied radioactivity.

A possible transformation pathway postulated by the study author was conversion of thidiazuron to AE F132345 (thiadiazolurea) and unidentified simple phenyl compounds via hydrolysis of the urea bridge. These compounds were then posited to degrade to other compounds, which, in turn, would yield bound residues and CO_2. There was, however, insufficient data to support these contentions, and production of additional metabolites through AE F132345 appears to be a minor route of transformation.

EXECUTIVE SUMMARY

The biotransformation of [1,2,3-thiadiazol-5-^{14}C]N-phenyl-N'-1,2,3-thiadiazol-5-ylurea (thidiazuron; radiochemical purity 99%) was studied in three soils (two from the US, one from the UK) for 160-168 days under aerobic conditions in darkness at **20 ± 1°C** and at **soil moisture contents of 40% of maximum water holding capacity**. The three soils were: 1) a *sandy loam soil* (pH 7.2, organic carbon 2.7%) from the UK, 2) a *loamy sand soil* (pH 5.2, organic carbon 1.2%) from North Carolina, and 3) a *silt loam soil* (pH ($CaCl_2$) 5.0, organic carbon 1.6%) from Illinois (see Table 3 of this DER for soil properties). Thidiazuron was applied at a nominal rate of 0.2 mg a.i./kg, which would be equivalent to an EPA field application rate of 0.41 kg/ha (or 0.37 lb/acre), based on a 6-inch incorporation in a typical soil with bulk density of 1.35 g/cm^3 (the rate reported by the study author did not correspond with that used by EPA). This experiment was conducted in accordance with SETAC - Europe Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides (1995) and European Union Commission Directive 95/36/EEC and in compliance with USEPA FIFRA GLP Standards.

The test system consisted of Erlenmeyer-type flasks containing soil (*ca.* 50g) to which the nominal target rate of 10.3 µg/flask of test substance (in acetonitrile solution) was added. The system was incubated in a dark environmental chamber. The flasks were connected to a flow-through volatile trapping system consisting of one ethylene glycol trap and one ethanolamine trap(test apparatus illustrated in Figure 1, p. 41 of study report). Single flasks were collected after 0, 14, 27, 49, 63, 88, 105, 131, 145 and 168 days (sandy loam soil) or after 0, 14, 28, 36, 63, 77, 99, 112, 128, 146 and 160 days loamy sand and silt loam soils) of incubation. Soil samples were extracted with acetonitrile:water with 0.01% glacial acetic acid (4:1, v:v) by shaking at ambient temperatures and by Soxhlet extraction with acetonitrile:water with 0.01% glacial acetic acid (4:1, v:v). Soil extracts, extracted soil and volatile trapping materials were analyzed for total radioactivity using LSC. Extracts were analyzed for [^{14}C]thidiazuron and its transformation products by HPLC and TLC, and identified by comparison to the retention time of reference standards.

Test conditions specified in the study appear to have been maintained throughout the study, however, no records were provided for review.

Overall recoveries of [^{14}C]residues averaged 97.7 ± 3.2% (range 89.9-100.8%) of the applied in the sandy loam soil, 100.0 ± 1.9% (95.3-101.9%) in the loamy sand soil, and 101.8 ± 1.2% (99.9-103.8%) in the silt loam soil. There was no pattern of decline in any of the material balances with time during the study.

In the sandy loam soil, [^{14}C]thidiazuron decreased from 94.2% of the applied at 0 days posttreatment to 57.1% at 105 days and 43.2% at 168 days (study termination). *No major transformation products were isolated.* The only identified minor transformation product, 1,2,3-thiaiazol-5-ylurea (thiadiazolurea, AE F132345), was a maximum of 8.7% of the applied. Extractable [^{14}C]residues decreased from 98.9% of the applied at 0 days posttreatment to 52.2% at

168 days, while nonextractable [^{14}C]residues increased to 32.3% at 168 days. At 168 days posttreatment, $^{14}CO_2$ totaled 12.4% of the applied and volatile organics were ≤0.1%.

In the loamy sand soil, [^{14}C]thidiazuron decreased from 99.2% of the applied at 0 days posttreatment to 68.8% at 160 days (study termination). *No major transformation products were isolated. The only identified minor transformation product, AE F132345*, was a maximum of 1.1% of the applied. Extractable [^{14}C]residues decreased from 99.6% of the applied at 0 days posttreatment to 71-79.3% at 99-160 days, while nonextractable [^{14}C]residues increased to 19.3-24.9% at 99-160 days. At 160 days posttreatment, $^{14}CO_2$ totaled 2.3% of the applied and volatile organics were ≤0.1%.

In the silt loam soil, [^{14}C]thidiazuron decreased from 99.9% of the applied at 0 days posttreatment to 73.4% at 160 days (study termination). *No major transformation products were isolated. The only identified minor transformation product, AE F132345*, was a maximum of 2.7% of the applied. Extractable [^{14}C]residues decreased from 100.9% of the applied at 0 days posttreatment to 69.8-78.5% at 128-160 days, while nonextractable [^{14}C]residues increased to 15.6-22.4% at 128-160 days. At 160 days posttreatment, $^{14}CO_2$ totaled 6.5% of the applied and volatile organics were ≤0.1%.

Based on linear, first-order regression analysis, thidiazuron degraded with *unadjusted* half-lives of 163 days (95% confidence interval 137-200 days, $r^2 = 0.9495$) in the sandy loam soil, 355 days (95% confidence interval 252-599 days, $r^2 = 0.7744$) in the loamy sand soil, and 322 days (95% confidence interval 237-500 days, $r^2 = 0.8176$) in the silt loam soil. These half-lives are relatively short study durations compared to apparent half-lives. Preferably, study periods should extend for several half-lives in order to establish a clear kinetic pattern. The study period for the sandy loam soil corresponds to approximately one half-life, while the half-lives in the loamy sand and silt loam soils are extrapolated well beyond the duration of the studies. We assume that degradation continues to follow a first-order model. Half-life adjustments that the reviewer made for soil moisture and temperature are discussed in the Scientific Conclusions section above and in Attachment 1.

A possible transformation pathway proposed by the study author was conversion of thidiazuron to thiadiazolurea (AE F132345) and unidentified simple phenyl compounds via hydrolysis of the urea bridge. These compounds were then posited to degrade to other compounds, which, in turn, would yield bound residues and CO_2. However, there was insufficient data to support these contentions. Furthermore, production of additional metabolites through AE F132345 appears to be a minor route of transformation, and evolution of CO_2 from the radiolabeled position appeared to reach a broad maximum of 5-12% of applied radioactivity during later study periods in the sandy loam soil (Table 6a of this DER) where transformation was fastest.

Results Synopsis:

Soil type: Sandy loam (UK)
First-order regression half-life at 20 °C and 40% MWHC: 163 days (95% confidence range 137-200 days with $r^2 = 0.9495$)
First-order regression half-life adjusted to 25 °C and 75% of 1/3-bar soil moisture (see Scientific Conclusions section and Attachment 1 for procedures): 206 days
Major transformation products:
CO_2.
Minor identified transformation products:
1,2,3-Thiaiazol-5-ylurea (thiadiazolurea, AE F132345)

Soil type: Loamy sand (US)
First-order regression half-life at 20 °C and 40% MWHC: 355 days (95% confidence range 252-599 days with $r^2 = 0.7744$)
First-order regression half-life adjusted to 25 °C and 75% of 1/3-bar soil moisture (see Scientific Conclusions section and Attachment 1 for procedures): 436 days
Major transformation products:
None.
Minor identified transformation products:
Thiadiazolurea.
CO_2.

Soil type: Silt loam (US)
First-order regression half-life at 20 °C and 40% MWHC: 322 days (95% confidence range 237-500 days, $r^2 = 0.8176$)
First-order regression half-life adjusted to 25 °C and 75% of 1/3-bar soil moisture (see Scientific Conclusions section and Attachment 1 for procedures): 253 days
Major transformation products:
None.
Minor identified transformation products:
Thiadiazolurea.
CO_2.

Study Acceptability: This study is classified as **supplemental**. It has scientifically utility, but does not meet the requirement for an aerobic soil metabolism study because the study was terminated after only 160-168 days, when 43.2-73.4% of the applied thidiazuron remained undegraded.

I. MATERIALS AND METHODS

GUIDELINE FOLLOWED: This study was conducted in accordance with SETAC - Europe Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides (1995) and European Union Commission Directive 95/36/EEC (1995; pp. 17, 30). Significant deviations from the Subdivision N guideline were:

> The study was terminated after 5-6 months, when 43-73% of the applied thidiazuron remained undegraded. This does not affect the validity of the study, but limits utility.

COMPLIANCE: This study was conducted in compliance with USEPA GLP Standards 40 CFR, Part 160 (pp. 3, 17). Signed and dated Data Confidentiality, GLP, Quality Assurance and Certification of Authenticity statements were provided (pp. 2-5).

A. MATERIALS:

1. Test Material: [1,2,3-Thiadiazol-5-^{14}C]thidiazuron (p. 17, Appendix 1, p. 57 of submission).

Chemical Structure: See Attachment 2 of this DER

Description: Solid (p. 23).

Purity: Radiochemical purity: 99% (p. 17).
Batch/Inventory No.: GAR 2026/6 (970).
Analytical purity: Not reported.
Specific activity: 83.8 μCi/mg.
Location of the radiolabel: 3-Carbon linking the thiadiazole ring to the urea moiety.

Storage conditions of test chemicals: Not reported.

Table 1: Physico-chemical properties of thidiazuron.

Parameter	Values	Comments
Molecular weight:	Not reported.	
Water solubility:	Not reported.	
Vapor pressure/volatility (Pa):	Not reported.	
UV absorption:	Not reported.	
pK_a:	Not reported.	
K_{ow}/log K_{ow}:	Not reported.	
Stability of compound at room temperature:	Not reported.	

2. Soil Characteristics:

Table 2: Description of soil collection and storage.

Description	Sandy loam	Loamy sand	Silt loam
Geographic location:	Abington, Cambridge, UK	Pikeville, NC, USA	Carlyle, IL, USA
Pesticide use history at the collection site:	The soils were collected from pasture that had had no pesticide application in the previous five years.		
Collection date:	7/23/01	10/1/01	10/1/01
Collection procedures:	Not reported.		
Sampling depth:	Not reported.		
Storage conditions:	Soils were stored at 6°C within 24 hours of laboratory receipt.		
Storage length:	Approximately 5 weeks.		
Preparation:	The soils were homogenized and sieved (2 mm).		

Data obtained from p. 21, Table 1, p. 31, Table 3, pp. 33-35 of the study report.

Table 3: Properties of the soil.

Property	EFS-117 Sandy loam	EFS-118 Loamy sand	EFS-119 Silt loam
Soil texture:	Sandy loam	Loamy sand	Silt loam
% sand (0.05-2 mm):	71	81	19
% silt (0.002-0.5 mm):	22	10	54
% clay (<0.002 mm):	7	9	17
pH $CaCl_2$: water:	7.2 7.4	5.2 6.1	5.0 5.2
Organic carbon (%):	2.7	1.2	1.6
Organic matter (%):	4.7	2.0	2.8
CEC (meq/100 g):	21.1	5.8	21.7
Moisture content (%) at 1/3 bar: 1/10 bar: 15 bar:	15.8 18.2 11.4	10.5 15.5 4.2	31.2 40.2 16.0
Maximum water holding capacity (%):	63.5	40.6	69
Bulk density (disturbed; g/cm^3):	1.11	1.28	0.94
Soil Taxonomic classification:	Not reported.		
Soil Mapping Unit:	Not reported.		

Data obtained from Table 1, p. 31 of the study report.

B. EXPERIMENTAL CONDITIONS:

1. Preliminary experiments: No preliminary studies were described.

2. Experimental conditions:

Table 4: Study design.

Criteria		Sandy loam	Loamy sand	Silt loam
Duration of the test		168 days.	160 days.	
Soil condition (air dried/fresh):		Fresh.		
Soil (g/replicate)		*ca.* 50 g dry wt equivalent.		
Test concentrations (mg a.i./kg soil and equivalent kg a.i./ha):		0.2 mg a.i./kg dry soil; equivalent to 0.41kg a.i./ha (based on a six-inch soil incorporation).		
Control conditions, if used		Sterile controls were not used.		
No. of Replications:	Controls	Sterile controls were not used.		
	Treatments	Only one sample was collected from each soil at each interval.		
Test apparatus (Type/material/volume):		Erlenmeyer flasks (7 cm top i.d. x 14 cm bottom i.d.) containing treated soil (*ca.* 50 g dry wt equivalent) were sealed with stoppers containing inlet/outlet ports and attached to individual volatile trapping systems. The samples were kept in a dark environmental chamber. The test apparatus is illustrated in Figure 1, p. 41.		
Details of traps for CO_2 and organic volatiles, if any:		Humidified air was continuously drawn (*ca.* 13-32 mL/min) through a flask, then through one tube of ethylene glycol and one tube of ethanolamine.		
If no traps were used, is the system closed/open?		Volatile traps were used.		
Identity and concentration of co-solvent:		Acetonitrile, <1% by volume.		
Test material application:	Vol. of test solution used/treatment:	440 µL/50 g (dry wt) for sandy loam soil. 474 µL/50 g soil (dry wt) for loamy sand and silt loam soils		
	Application method:	Added dropwise using a variable volume positive placement pipette and mixed using a stainless steel spatula.		
	Co-solvent evaporated:	Not reported.		
Any indication of the test material adsorbing to the walls of the test apparatus?		None.		
Microbial biomass of the control (CFU/g)		Sterile controls were not used.		

Criteria		Sandy loam	Loamy sand	Silt loam
Microbial biomass of the treated soil: (mg C/kg)	Initial	422	293.3	170.1
	At 139 or 156 days	290.4 (139 days)	121.2 (156 days)	275.7 (156 days)
Experimental conditions:	Temperature (°C):	20 ± 1°C		
	Moisture content (%):	25%	17.4%	25%
	Moisture maintenance method:	Flasks were weighed and remoistened if necessary.		
	Continuous darkness:	Yes		
Other details, if any:		None.		

Data obtained from pp. 22, 23, Tables 1-3, pp. 31-35, Figure 1, p. 41 of the study report.

3. Aerobic conditions: Humidified air was continuously drawn (*ca.* 13-32 mL/min) through the flasks containing the treated soil (p. 22; Figure 1, p. 41). No determinations such as redox potentials were made to verify that aerobic conditions were maintained in the soil.

4. Supplementary experiments: No supplementary studies were described.

5. Sampling:

Table 5: Sampling details.

Criteria	Sandy loam	Loamy sand	Silt loam
Sampling intervals:	0, 14, 27, 49, 63, 88, 105, 131, 145 and 168 days.	0, 14, 28, 36, 63, 77, 99, 112, 128, 146 and 160 days.	
Sampling method:	Single flasks were collected at each sampling interval.		
Method of collection of CO_2 and volatile organic compounds:	Trapping solutions were collected and replaced "at various intervals".		
Sampling intervals/times for: Sterility check: Moisture content: Redox potential/other:	 Sterile controls were not used. Not specified. Redox potential and other parameters were not measured.		
Sample storage before analysis:	Samples were initially extracted and the extract analyzed by LSC on the day of sampling. Samples were generally Soxhlet extracted within 1 day following sampling after storage at *ca.* 4°C. Dates of sampling, extraction, and analysis are presented in Table 3, pp. 33-35.		
Other observations, if any:	None.		

Data obtained from pp. 23, 25, Table 3, pp. 33-35 of the study report.

C. ANALYTICAL METHODS:

Extraction/clean up/concentration methods: Soil samples were extracted sequentially up to five times with acetonitrile:water with 0.1% glacial acetic acid (4:1, v:v) by mechanical shaking at ambient temperatures for 15 minutes/extraction; extractions continued until <5% of the applied was recovered in the extract (p. 24, Figure 2, p. 42). After each extraction, the samples were centrifuged and the supernatant decanted and analyzed using LSC. The ambient extracts were combined.

The soil pellet was then Soxhlet extracted with acetonitrile:water with 0.1% glacial acetic acid (4:1, v:v) for *ca.* 4 hours; the sample was centrifuged and the supernatant decanted and analyzed using LSC.

The ambient and Soxhlet extracts (analyzed separately) were filtered (200 µm), then concentrated using rotary evaporation and microconcentrated under a stream of nitrogen. Aliquots of the concentrates were analyzed by LSC, HPLC, and TLC as described.

Nonextractable residue determination: The extracted soil was air-dried, homogenized, and ground, and portions were analyzed for total radioactivity by LSC following combustion (p. 24).

Volatile residue determination: Triplicate aliquots (1.0 mL) of the trapping solutions were analyzed for total radioactivity using LSC (p. 23). The identification of [^{14}C]residues in the ethanolamine trapping solution as CO_2 was not confirmed.

Total ^{14}C measurement: Total [^{14}C]residues were determined by summing the concentrations of residues measured in the soil extracts, extracted soil, and volatile trapping solutions (p. 27).

Derivatization method, if used: A derivatization method was not employed.

Identification and quantification of parent compound: Soil extracts were analyzed using reverse-phase HPLC under the following conditions (pp. 19-20):

HPLC Column 1/Mobile Phase 1: Polaris C8 column (250 cm x 4.6 mm, 5 µ) with a gradient mobile phase combining (A) acetonitrile (B) water [percent A:B at 0-12 min., 20:80; 16 min., 25:75; 20 min., 40:60; 25 min., 50:50; 35 min., 70:30];

HPLC Column 2/Mobile Phase 1: Polaris C18 column (250 cm x 4.6 mm, 5 µ) using the same eluants and gradient mobile phase as Mobile Phase 1;

HPLC Column 2/Mobile Phase 2: Polaris C18 column (250 cm x 4.6 mm, 5 µ) with eluants (A) acetonitrile with 0.1% glacial acetic acid (B) water with 0.1% glacial acetic acid but the same A:B gradient;

HPLC Column 2/Mobile Phase 3: Polaris C18 column (250 cm x 4.6 mm, 5 µ), with eluants (A) acetonitrile with 0.1% glacial acetic acid (B) water with 0.1% glacial acetic acid and 0.01M ammonium acetate and a gradient mobile phase of [percent A:B at 0-20 min., 0:100; 25 min., 20:80; 40 min., 40:60; 45 min., 50:50; 55-65 min., 70:30].

In all cases, the analysis was conducted at ambient temperatures with flow rate of 1 mL/minute, and residues were located using UV (254) and radioflow detection. [^{14}C]Thidiazuron was identified by comparison to the retention time of an unlabeled reference standard (p. 19, Rt 26.35 minutes in Gradient 1 and 44.53 in Gradient 2; Appendix 3, pp. 60-61 of submission).

HPLC recoveries were ≥95% of the radioactivity applied to the column (p. 19).

Identification and quantification of transformation products: Transformation products were quantified and identified using the methods described for the parent. The references standards used were thidiazolurea (AE F132345, purity not reported, Rt 3.32 and 19.21 minutes in Gradients 1 and 2, respectively), 3-hydroxy-thidiazuron (AE F147706, purity not reported, Rt 3.52 and 38.49 minutes), and 4-hydroxy-thidiazuron (AE F132346; purity not reported, Rt 9.14 and 36.30 minutes; Appendix 2, p. 58 and Appendix 3, pp. 60-61 of submission).

In order to confirm the identification of thidiazolurea, ambient extracts from the 105- and 145-day sandy loam soil were analyzed using one-dimensional TLC on silica gel plates developed in ethyl acetate with 0.5% glacial acetic acid (p. 21). Following development, radioactive areas on the plate were located and quantified using an AMBIS two-dimensional scanner, and the reference standard was located using UV light (254 nm, Rf = 0.2).

Detection limits (LOD, LOQ) for the parent compound: The LSC Limit of Detection was any concentration greater than background (30 dpm, and the HPLC LOD was 300 dpm (1.6 ng of thidiazuron; p. 25). The LSC Limit of Quantification was twice background (60 dpm); the HPLC LOQ was not provided.

Detection limits (LOD, LOQ) for transformation products: The LOD and LOQs were the same as for the parent.

II. RESULTS AND DISCUSSION:

A. TEST CONDITIONS: It was reported that aerobicity, moisture, temperature and other environmental conditions were maintained during the experiment; no supporting data were provided for review.

B. MATERIAL BALANCE: Overall recoveries of [^{14}C]residues averaged 97.7 ± 3.2% (range 89.9-100.8) of the applied in the sandy loam soil, 100.0 ± 1.9% (95.3-101.9%) in the loamy sand

soil, and 101.8 ± 1.2% (99.9-103.8%) in the silt loam soil (Table 4, pp. 36-38 of submission). There was no decline in the material balances with time in any of the soils.

Table 6a: Biotransformation of [^{14}C]thidiazuron in sandy loam soil, expressed as percentage of applied radioactivity, under aerobic conditions.

Compound	Sampling times (days)									
	0	14	27	49	63	88	105	131	145	168
Thidiazuron	94.2	88.0	76.6	70.6	65.7	57.6	57.1	58.0	47.2	43.2
AE F132345 (Thiadiazolurea)	ND	0.2	1.9	3.3	3.4	6.5	6.4	5.8	8.7	6.7
P1, Rt = 24 min	1.2	0.7	0.6	0.4	0.6	1.3	1.1	0.3	ND	0.1
P2, Rt = 39 min	2.9	1.9	2.7	2.4	2.1	2.5	1.9	1.3	2.8	2.2
Total extractable residues[1]	98.9	91.0	83.0	76.7	71.7	71.3	66.5	65.7	58.7	52.2
Nonextractable residues	1.5	8.8	13.0	19.0	22.2	21.0	23.9	24.7	25.9	32.3
CO_2[2]	NA	1.0	2.0	4.2	2.2	5.0	9.5	6.9	5.3	12.4
Volatile organics	≤0.1									
Total % recovery	100.4	100.8	98.0	99.9	96.1	97.3	99.9	97.3	89.9	96.9

Data obtained from Table 4, p. 36, and Table 5, p. 39 of the study report. Only one sample was collected at each sampling interval.
1 Total extractable was calculated by the reviewer by summing the concentration of residues in the ambient and soxhlet extractions.
2 The identification of CO_2 in the ethanolamine trap was not confirmed.
NA - Not analyzed.
ND - Not detected.

Table 6b: Biotransformation of [^{14}C]thidiazuron in loamy sand soil, expressed as percentage of applied radioactivity, under aerobic conditions.

Compound	Sampling times (days)										
	0	14	28	36	63	77	99	112	128	146	160
Thidiazuron	99.2	82.6	89.5	82.7	80.5	84.4	67.9	74.2	69.3	71.8	68.8
AE F132345 (Thiadiazolurea)	ND	ND	ND	ND	0.6	1.0	0.9	ND	ND	1.1	0.4
P1, Rt = 24 min	0.4	1.3	2.2	0.9	2.7	ND	2.0	3.8	2.8	5.4	6.2
Total extractable residues[1]	99.6	83.9	91.7	83.6	84.0	86.1	71.0	78.0	73.0	79.3	76.5
Nonextractable residues	2.1	14.5	9.4	15.2	14.8	13.4	23.0	20.7	24.9	19.3	22.9
CO_2[2]	NA	0.5	0.8	1.2	0.9	1.5	1.3	0.8	1.2	2.4	2.3
Volatile organics	≤0.1										
Total % recovery	101.7	98.9	101.9	100.0	99.7	101.0	95.3	99.5	99.1	101.0	101.7

Data obtained from Table 4, p. 37, and Table 5, p. 39 of the study report. Only one sample was collected at each sampling interval.
1 Total extractable was calculated by the reviewer by summing the concentration of residues in the ambient and soxhlet extractions.
2 The identification of CO_2 in the ethanolamine trap was not confirmed.
NA - Not analyzed.
ND - Not detected.

Table 6c: Biotransformation of [^{14}C]thiadiazuron in silt loam soil, expressed as percentage of applied radioactivity, under aerobic conditions.

Compound	Sampling times (days)										
	0	14	28	36	63	77	99	112	128	146	160
Thidiazuron	99.9	95.3	88.8	88.8	86.5	86.7	79.9	75.9	64.0	74.0	73.4
AE F132345 (Thiadiazolurea)	0.3	ND	ND	0.8	0.6	0.6	1.5	0.2	2.7	1.7	0.9
P1, Rt = 24 min	ND	0.9	0.6	1.3	2.3	0.3	0.8	2.5	3.0	2.1	2.0
Total extractable residues[1]	100.9	96.2	90.0	91.6	89.3	87.7	82.1	78.6	69.8	78.4	78.5
Nonextractable residues	1.0	6.2	11.8	8.1	9.6	11.6	12.8	16.6	22.4	16.2	15.6
CO_2[2]	NA	0.9	2.0	2.9	2.5	2.5	5.0	6.5	8.2	7.4	6.5
Volatile organics	≤0.1										
Total % recovery	101.9	103.3	103.8	102.6	101.4	101.8	99.9	101.7	100.4	102.0	100.6

Data obtained from Table 4, p. 38, and Table 5, p. 40 of the study report. Only one sample was collected at each sampling interval.
1 Total extractable was calculated by the reviewer by summing the concentration of residues in the ambient and soxhlet extractions.
2 The identification of CO_2 in the ethanolamine trap was not confirmed.
NA - Not analyzed.
ND - Not detected.

C. TRANSFORMATION OF PARENT COMPOUND: In the sandy loam soil, [^{14}C]thidiazuron decreased from 94.2% of the applied at 0 days posttreatment to 57.1% at 105 days and 43.2% at 168 days (study termination; Table 5, p. 39 of submission).

In the loamy sand soil, [^{14}C]thidiazuron decreased from 99.2% of the applied at 0 days posttreatment to 68.8% at 160 days (study termination; Table 5, p. 39 of submission).

In the silt loam soil, [^{14}C]thidiazuron decreased from 99.9% of the applied at 0 days posttreatment to 73.4% at 160 days (study termination; Table 5, p. 40 of submission).

Half-lives were given and discussed in context in the Scientific Conclusions section above and in Attachment 1 of this DER.

TRANSFORMATION PRODUCTS: In the sandy loam soil, no major transformation products were isolated (Table 5, p. 39 of submission). One minor transformation product, 1,2,3-thiaiazol-5-ylurea (thiadiazolurea, AE F132345), was identified at a maximum of 8.7% of the applied. Unidentified HPLC peaks P1 (Rt 24 minutes) and P2 (Rt 39 minutes) were each ≤2.9% of the applied.

In the loamy sand soil, no major transformation products were isolated (Table 5, p. 39 of submission). One minor transformation product, thiadiazolurea, was identified at a maximum of 1.1% of the applied. Unidentified HPLC peak P1 (Rt 24 minutes) was a maximum of 6.2% of the applied.

In the silt loam soil, no major transformation products were isolated (Table 5, p. 40 of submission). One minor transformation product, thiadiazolurea, was identified at a maximum of 2.7% of the applied. Unidentified HPLC peak P1 (Rt 24 minutes) was a maximum of 3.0% of the applied.

NONEXTRACTABLE AND EXTRACTABLE RESIDUES: In the sandy loam soil, extractable [^{14}C]residues decreased from 98.9% of the applied at 0 days posttreatment to 52.2% at 168 days, while nonextractable [^{14}C]residues increased to 32.3% at 168 days (Table 4, p. 36 of submission).

In the loamy sand soil, extractable [^{14}C]residues decreased from 99.6% of the applied at 0 days posttreatment to 71-79.3% at 99-160 days, while nonextractable [^{14}C]residues increased to 19.3-24.9% at 99-160 days (Table 4, p. 37 of submission).

In the silt loam soil, extractable [^{14}C]residues decreased from 100.9% of the applied at 0 days posttreatment to 69.8-78.5% at 128-160 days, while nonextractable [^{14}C]residues increased to 15.6-22.4% at 128-160 days (Table 4, p. 38 of submission).

VOLATILIZATION: $^{14}CO_2$ appeared to reach a broad plateau in the sandy loam soil, comprising approximately 5-12% of the applied during later study periods. At study termination, $^{14}CO_2$

comprised 2.3% of applied in the loamy sand soil, and 6.5% of applied in the silt loam soil (Table 4, pp. 36-38 of submission). Volatile organics totaled ≤0.1% of the applied from each of these soils.

TRANSFORMATION PATHWAY: A transformation pathway postulated by the study author was that thidiazuron degrades to thiadiazolurea (also known as AE F132345 or 1,2,3-thiaiazol-5-ylurea) and unidentified simple phenyl compounds via hydrolysis of the urea bridge (p. 28, Figure 7, p. 53 of submission). These compounds in turn were then thought to degrade to unidentified minor compounds which are incorporated into the organic material and mineralized to CO_2. However, there was insufficient data to support these contentions, and production of additional metabolites through AE F132345 appears to be a minor route of transformation.

D. SUPPLEMENTARY EXPERIMENT-RESULTS: No supplementary studies were described.

III. STUDY DEFICIENCIES: The study was terminated at 160-168 days posttreatment. At this time, 43.2% of the applied thidiazuron remained undegraded in the sandy loam soil, 68.8% remained in the loamy sand soil, and 73.4% in the silt loam soil. Subdivision N Guidelines specify that metabolism studies should extend preferably for several half-lives so that the pattern of decline of the parent and the patterns of formation, identification, and decline of the transformation products are clearly established. However, for compounds that, because of their longevity, cannot meet halving-time criteria in less than one year, then a study lasting only one year is considered sufficient by the EPA. This study did not meet either timing criterion, except marginally for the sandy loam soil.

As a result of the experiments being terminated prematurely, half-lives for thidiazuron are essentially extrapolations beyond the final sampling interval. The accuracy of the half-lives is, therefore, based on the assumption that the pattern of transformation observes first-order kinetics throughout the process. Microbial degradation often follows a curvilinear pattern, with the most rapid decline occurring during the first part of the dissipation process. Therefore, it can not be determined from the data if the pattern of decline continued to follow a first-order model. Also, although it appears from the loamy sand data that AE F132345 (thiadiazolurea) production would not become a major transformation product, longer study periods would be required for verification. The same can be said for $^{14}CO_2$ evolution of more than 5-12% of applied from the radiolabeled position.

IV. REVIEWER'S COMMENTS:

1. During the incubation period, the soil moisture content was maintained at the European standard of 40% of the maximum moisture water holding capacity (MWHC) for each soil (p. 17 of submission). The EPA Subdivision N Guideline standard for soil moisture is 75% of 1/3-bar soil water potential. As a consequence, the sandy loam and loamy sand soils

contained more than twice as much water than specified by Subdivision N and the silt loam soil contained approximately 18% more water than specified, as detailed in Attachment 1 of this DER.

From a soil science standpoint, neither the European nor the EPA measure of soil moisture is a good standard, since it is the energy requirement for abstraction of water from soil that should be controlled and reproduced from lab study to lab study or field condition to field condition. Therefore, for universal utility and for comparison of results in different soils, an agreed upon soil matric potential (soil suction) would be a better standard. Furthermore, since water is so critical to metabolism, metabolism studies at two or more soil moisture potentials would enable a specific functional dependence to be established for each chemical and used to improve environmental modeling capability.

2. Only one sample was collected from each soil at each sampling interval. Replicate sampling is preferred, so that between sample variability can be quantified and outliers identified.

3. The three experiments were not concurrent. The experiment with the sandy loam soil (UK) was conducted from August 30, 2001 to February 14, 2002, and the experiments with the loamy sand and silt loam soils were conducted from November 6, 2001 to April 15, 2002 (Table 3, pp. 33-35 of submission).

4. The identification of [^{14}C]residues in the ethanolamine trapping solution as CO_2 was not confirmed.

5. Although a significant fraction of the applied [^{14}C]residues were not extracted from the soils by the final sampling interval (15.6-32.3%), it is not likely that the use of extraction procedures harsher than those used (Soxhlet extraction) in the study would have been nondestructive.

6. The extracts were reanalyzed after 16 months of storage at approximately -20°C (p. 29; Figure 6, p. 51). The HPLC chromatograms from the two analyses are comparable.

7. Physico-chemical properties such as water solubility, vapor pressure, and UV absorption were not reported.

8. One of the test soils used in the study was from the UK. The soil was fully characterized according to the USDA Soil Textural Classification system, but was not formally compared to soils from the US (Table 1, p. 31 of submission). The physical properties of the soil appear to be typical of US soils.

9. The study author reported that the nominal application rate chosen for this study was based on the maximum field application rate of 196 g a.i./ha (0.196 kg/ha or approximately 0.20 kg/ha) (p. 10 of submission). Although the nominal rate actually used in the study was 0.2 mg a.i./kg

of experimental soil, this concentration is equivalent to a field application rate of 0.41 kg/ha (or 0.37 lb/acre), not 0.196 kg/ha, based on the EPA Environmental Fate and Effects Division standard 6-inch incorporation in a typical soil with bulk density of 1.35 g/cm^3. Therefore, the effective field rate reported by the study author was erroneous by the EPA standard.

10. The final biomass sampling interval is reported as 155 days on page 22 and 156 days in loamy sand and silt loam soils in Table 2 (p. 32 of submission).

11. The figure numbers referenced in the text do not correspond to the actual numbering of the figures. The kinetic degradation values were reported to be in Figures 7, 6, and 8 (p. 26). The kinetic figures are Figures 8, 9, and 10 (pp. 54-56). The DT_{50} and DT_{90} values were reported to be in Figures 10, 11, and 12 (p. 29). The values are in Figures 8, 9, and 10 (pp. 54-56). The transformation pathway was reported to be in Figure 9 (p. 28). The transformation pathway is presented in Figure 7 (p. 53).

V. REFERENCES:

1. U.S. Environmental Protection Agency. 1982. Pesticide Assessment Guidelines, Subdivision N, Chemistry: Environmental Fate, Section 162-1. Aerobic soil metabolism. Office of Pesticide and Toxic Substances, Washington, DC. EPA 540/9-82-021.

2. U.S. Environmental Protection Agency. 1989. FIFRA Accelerated Reregistration, Phase 3 Technical Guidance. Office of the Prevention, Pesticides, and Toxic Substances, Washington, DC. EPA 540/09-90-078.

3. U.S. Environmental Protection Agency. 1993. Pesticide Registration Rejection Rate Analysis - Environmental Fate. Office of the Prevention, Pesticides, and Toxic Substances, Washington, DC. EPA 738-R-93-010.

ATTACHMENT 1

Adjustment of Half-lives for Soil Moisture and Temperature through Use of the Walker Equation and the Arrhenius Equation

Influence of soil moisture on half-lives (reaction rates)--adjustment with the Walker equation. As noted prominently in the main text at the beginning of this Data Evaluation Report (DER), this study was conducted under the European standard for soil moisture of 40% of the maximum water holding capacity (MWHC) for a given soil, whereas the EPA standard is 75% of the water content at 1/3-bar suction. The EPA condition is almost always dryer, and, therefore, less favorable to metabolism. Table B below shows the soil moisture contents under each system for each of the three soils used in this study (based on soil moisture characteristics given in Table 3 of the main text of this DER). [Coincidentally, from a soil science standpoint, neither system provides a good, relative standard (see comment 1 in Reviewer's Comments section in the main text of this DER), but at least experimental conditions are reproducible for a given soil.]

Table B

Comparison of Experimental Soil Moisture Under Two Standards				
Soil (see Table 3 in main text of DER)	**MWHC[1] (%)**	**1/3-Bar[2] (%)**	**European Moisture % (40% of MWHC)**	**EPA Moisture % (75% of 1/3-bar)**
Sandy Loam (UK)	63.5	15.8	0.4 x 63.5 = 25.4	0.75 x 15.8 = 11.9
Loamy Sand (NC)	40.6	10.5	16.2	7.88
Silt Loam (IL)	69	31.2	27.6	23.4

[1]Maximum water holding capacity from Table 3 in main text of DER.
[2]Moisture content at 1/3-bar soil suction (matric potential) from Table 3 in main text of DER.

Note the differences between the soil moisture contents in the two adjacent right-hand columns of Table B above. Under study conditions, the soil from the United Kingdom and the soil from North Carolina contained more than twice as much water than specified by the EPA standard; therefore, half-lives under the EPA standard for these soils would be expected to be dramatically longer. The soil from Illinois contained approximately 18% more; therefore, the half-life should only increase moderately. As can be seen just from these three examples, soil moisture characteristics (matric potential or suction vs. moisture content) can show rather steep changes, and are unique for each soil.

Walker has developed an empirical equation (see, for example, Walker, 1974) that has often been used to quantitatively adjust reaction rates and half-lives of pesticides and nutrients for different soil

moistures in the soil moisture range representative of most agriculture. One form of this equation is:

$t_{1/2} = AM^{-b}$, where $t_{1/2}$ is half-life, M is moisture content, and A and b are constants for each chemical.

Therefore, if half-lives are measured at no fewer than two different experimental soil moistures, then A and b can be determined. Unfortunately, there are currently no regulatory requirements for doing experiments at two or more different moisture contents. However, based on a large number of published aerobic soil metabolism studies for herbicides, it has been determined that b = 0.8 is an appropriate average value for general use (Boesten et al, 1997). Variation in b values for individual pesticides was found to be as great as variation between different pesticides, which indicates that little value is added by measuring b as opposed estimating it, at least under present study guidelines[1]. By using the Walker equation with b = 0.8 and the experimental half-life and water content measured for each soil in this study, "A" for each soil can be calculated. If we reverse the process by using the "A" thus calculated for each soil, then an adjusted half-life can be calculated at different moisture contents, provided extremes of relative wetness or dryness are avoided. Keeping the temperature constant at 20 °C, Table C below gives half-lives resulting from moisture changes alone when the Walker equation is used to adjust from the European Standard of soil moisture to the EPA standard. As is apparent from the table, the effect of differences in soil moisture can be dramatic.

Table C

Half-lives at 40% of MWHC Versus Half-lives Adjusted to 75% of 1/3-Bar Soil Suction (both at 20 °C)		
Soil (see Table 3 in main text of DER)	**Half-Life (95% C.I.) at 40% MWHC (days)**	**Half-Life Adjusted to 75% of 1/3-Bar (days)**
Sandy Loam (UK)	163 (137-200), $r^2 = 0.95$	299
Loamy Sand (NC)	355 (252-599), $r^2 = 0.77$	632
Silt Loam (IL)	322 (237-500), $r^2 = 0.82$	367

[1]Numerous difficulties and potential sources of unnecessary or unquantified variation or error accrue to regulatory guideline studies. For example, in addition to the problem of variation of reaction rates with soil moisture, guidelines require no experimental measure of the effect of temperature, no standard benchmark compounds, benchmark soils, or good measure of microbial activity that would enable meaningful, relative comparisons or normalizations to be made among compounds.

Influence of temperature on half-lives (reaction rates)--adjustment with Arrhenius equation. If conducted at 25 °C (EPA standard) instead of 20 °C (European standard), other things being equal, then rate processes would generally be faster in accordance with the Arrhenius equation, which is based on established thermodynamics and the molecular collision theory of chemical reactions (refer to any physical chemistry or chemical kinetics textbook). A logarithmic form of the Arrhenius equation is:

$\ln (k_2/k_1) = (E_a/R) (1/T_1 - 1/T_2)$, where

> k_1 and k_2 are reaction rate constants at the Kelvin (absolute) temperatures T_1 and T_2, respectively; E_a is the free energy of activation for the reaction; and R is the universal gas law constant.

Thus, if rate constants or half-lives are measured at no fewer than two different experimental temperatures, then the key Arrhenius activation or free energy factor can be determined for a particular compound. This factor can then be used to estimate reaction rates for this compound at other temperatures. Unfortunately, as was the case for soil moisture, there are currently no US EPA regulatory requirements for doing experiments at two or more different temperatures. However, reaction rates for many substances near room temperature (say 10-30 °C) have been observed to roughly double, as a "rule of thumb," for every 10 °C increase in temperature, which is equivalent to reducing a half-life by a factor of two ("halving" the half-life). This observation has lead to a simplified form of the Arrhenius equation known as "Q_{10}" or the "Q_{10} rule," where the dimensionless Q_{10} is defined by the equation:

$Q_{10} = k_2/k_1 =$ reaction rate constant at $(T_1 + 10)$ / reaction rate constant at T_1, where

> T_1 is the reference temperature in *Celsius* (centigrade). [Note carefully that the temperature scale must be Celsius when applying the Q_{10} rule. However, when using the Arrhenius equation in its fundamental form, temperature must be in Kelvins (the thermodynamic or absolute temperature scale).]

Since a first-order half-live is inversely related to the rate constant, then

$Q_{10} = t_1/t_2 =$ half-life at T_1 / half-life at $(T_1 + 10)$.

In a survey of the literature, the European Union has compiled 148 values of experimental activation energies based on the Arrhenius equation for 38 or more herbicides in the temperature range from 10-20 °C (Boesten et al, 1997). Some herbicides, for example, simazine, had many reported values; others, only one. These data yielded an average apparent Arrhenius activation energy for all 148 measurements of 54.0 kJ/mole. From this, the average Q_{10} was directly calculated as 2.20 (verified by this reviewer as 2.18, which is within round-off error based on sensitivity of the logarithmic relationship with activation energy and the number of significant figures reported). The coefficient of variation for all values was about 48%. The upper 90th and

95th percentile values for Q_{10} were approximately 2.8 and 3.1. As was the case for soil moisture and the Walker equation, it is noteworthy that variation in the effects of temperature for individual pesticides was as great as variations between pesticides, which indicates that little information would be gained by measuring the effect of temperature on rate as opposed to estimating it from existing data, at least under presently used study guidelines (see previous footnote). When applying the Q_{10} rule of thumb, it should be remembered that, in accordance with the fundamental Arrhenius equation, even the rough Q_{10} is not constant, but decreases with increasing temperature. Extending the temperature from the original 10-20 °C range to 20-30 °C, the corresponding Q_{10} decreases from approximately 2.2 to 2.1, an unimportant difference *in this temperature range* compared to the variation associated with the rule.

Assuming the Q_{10} rule holds with $Q_{10} = 2.1$, rate constants at 25 and 20 °C are in the proportion $k_{25}/k_{20} = (2.1)^{[(25-20)/10]} = 1.45$. (As an alternative check, direct application of the fundamental Arrhenius equation likewise yields $k_{25}/k_{20} = Q_5 = 1.45$.) Since first-order half-lives are in inverse proportion to rate constants, $t_{25}/t_{20} = 1/1.45$. This is equivalent to a uniform reduction in half-lives by a temperature increase of 5 °C in this temperature range of about 31%. The following Table D shows the effect that raising the temperature from 20 to 25 °C has on half-lives in the present study with soil moisture kept at the constant study level of 40% MWHC for each soil:

Table D

Half-lives at 20 °C Versus Half-lives Adjusted to 25 °C (both at 40% of MWHC)		
Soil (see Table 3 in main text)	**Half-Life (95% C.I.) at 20 °C (days)**	**Half-Life Adjusted to 25 °C (days)**
Sandy Loam (UK)	163 (137-200), $r^2 = 0.95$	112
Loamy Sand (NC)	355 (252-599), $r^2 = 0.77$	245
Silt Loam (IL)	322 (237-500), $r^2 = 0.82$	222

Table A in the main text of this DER shows the combined temperature and soil moisture effects when converting from the European Union standards to the EPA standards. As explained in this attachment and the main DER, the adjusted values are only as reliable as the original study data and the expressed approximations associated with the equations of Walker and Arrhenius.

References for Attachment 1

1. Boesten, J.; Helweg, A.; Businelli, M.; Bergstrom, L.; Schaefer, H.; Delmas, A.; Kloskowski, R.; Walker, A.; Travis, K.; Smeets, L.; Jones, R.; Vanderbroeck, V.; Van Der Linden, A.; Broerse, S.; Klein, M.; Layton, R.; Jacobsen, O-S; and Yon, D.; 29 Feb 1997. *Soil Persistence Models and EU Registration.* (Final report of the work of the Soil Modeling Work group of FOCUS, the FOrum for the Co-ordination of pesticide fate models and their Use. Available at the website: http://europa.eu.int/comm/food/plant/protection/evaluation/guidance/soil_en.pdf

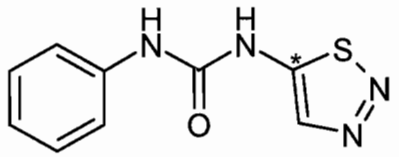
2. Walker, A., 1974. *A Simulation Model for Prediction of Herbicide Persistence.* J. Environ. Quality 3/4, 396-401.

ATTACHMENT 2

Structures of Thidiazuron and the Minor Transformation Product AE F 132345

Thidiazuron (AE B049537; DROPP; SN 49537)

IUPAC name: 1-Phenyl-3-(1,2,3-thiadiazol-5-yl)urea
CAS name: N-Phenyl-N'-1,2,3-thiadiazol-5-ylurea.
CAS No: 51707-55-2 (330-54-1 also found)
SMILES string: O=C(Nc1ccccc1)Nc1cnns1



[1,2,3-Thiadiazol-5-^{14}C]thidiazuron
(*Position of Radiolabel)

Thidiazolurea (AE F132345)

IUPAC name: 1,2,3-Thiadiazol-5-ylurea
CAS name: Not reported.
CAS No: Not reported