Appendix C: Environmental Fate Date

Myclobutanil

Selected environmental fate and transport properties for myclobutanil are summarized in Appendix C. Table 1.

Appendix C. Table 1. Selected Fate and Transport data for Myclobutanil.

Parameter	Input Value and Unit	Source
Molecular Weight	288.8 g/ mol	DP Barcode D289700 (6/25/03)
Vapor Pressure @25 ºC	1.49×10^{-06} mm Hg	
Henry's Law Constant @25 ºC	3.25×10^{-09} atm m^3/mol	Calculated
Solubility in Water (pH 7, 20°C)	142 mg/L	DP Barcode D289700 (6/25/03)
161-1 Hydrolysis at pH 5,7, and 9	Stable	MRID 00141679
161-2 Aqueous Photolysis (T½)	Stable	MRID # 40641501, 40319801, 40528801
161-3 Soil Photolysis	143 days	Acc# 266121, 214084 (D197478)
163-1 Partition Coefficient, K_{ads} [a]	1.46, 2.39, 4.44, 7.08, 9.77 mL/g	MRID# 00141602
162-1 Aerobic Soil Metabolism (T½)[b]	198, 224 days	MRID# 00164561
162-3 Anaerobic Soil Metabolism	Assume Stable, No appreciable degradation in 62 days	DP Barcode D289700 (6/25/03) 00141680
162-3 Anaerobic Aquatic Metabolism	No Data Submitted	No data
162-4 Aerobic Aquatic Metabolism	No Data Submitted	No data
164-1 Terrestrial Field Dissipation	92 to 292 days	MRID # 00164563

[a] Kocs are presented in Appendix B, Table 3.

[b] (T½) – Myclobutanil decline does not follow first-order kinetics, therefore the decay rate is not truly a half-life. Estimate of DT_{50} or half-life is dependant upon method used to determine value.

Model input parameters were estimated from the fate and transport properties given Appendix C, Table 1 and the other default values are prepared or selected as recommended by EFED Input Guidance document (USEPA, 2002). The models currently used by EFED, assume that the degradation follow first order kinetics, and therefore require an estimate of the half-life. Myclobutanil degradation, however, is best described using a hockey stick degradation pattern. This type of degradation pattern cannot be modeled using first-order kinetics.

The previously reported half-lives for myclobutanil cite a range of between 61 and 71 days (D289700), which described the decline reasonably well for the first 90 days of the

study, but grossly overestimates the remaining decline. The method used to estimate these half-lives was not stated, but it appears that only the first 90 (or less) days of a 367 day study were used. EFED reevaluated the data and re-estimated the decline rate constants utilizing all the data for myclobutanil and myclobutanil plus 1,2,4-triazole (see discussion in Appendix C, Tables 2 and 3).

The linear regression of the log-normal transformed myclobutanil radioactivity provided the best estimate of the measured residues (as percent of applied radioactivity) versus time (e.g., 29 to 33% myclobutanil) remaining at 367 days (Appendix C, Tables 2 and 3). The study was not conducted long enough to observe a DT_{75} or DT_{90}. The 90-percent upper bound of the mean (n=2) aerobic soil metabolism half-life for myclobutanil was estimated to be 251 days. Additionally, the models currently used by EFED were not developed for a persistent chemical where accumulation might occur.

The aerobic aquatic metabolism half-life was assumed to be twice that of the aerobic soil metabolism half-life estimated as a model input (USEPA, 2002).

Re-estimation of "half-life"

The method used to determine the aerobic soil metabolism (MRID 164561) half-lives reported in earlier DERs could not be replicated. The pattern of decline appears to fit the common degradation pattern termed the "hockey stick". An analysis of degradation kinetics was conducted to derive the best description of the measured decline curves in aerobic soil metabolism studies. The entire data set (0 to 367 days) and a portion of the data (0 to 90 days) were analyzed using linear regression of the ln-transformed data and non-linear regression of the untransformed data.

The following equations and assumptions were made (based upon draft guidance being developed by the Fate Tech Team, Eckel, 1/2007.

Eq 1. $dC/dt = -kC^n$

if n=1, then $\ln(C_0/C) = -kt$ (first order equation)

if $n \neq 1$ then

Eq. 2. $(1/(n-1))*((1/C^{n-1}) - (1/C_0^{n-1})) = -kt$

C =((n-1)*k*t + (1/co^(n-1)))^(-1/(n-1)); co = Co/100

The both rings of myclobutanil, triazole and chlorophenyl rings were labeled [^{14}C], thus, the decline (of radioactivity) of myclobutanil was measured by each ring. The formation and decline of 1,2,4-triazole could also be tracked with the triazole ring.

Assuming first-order kinetics (eq. 1) a half-life ($T_{½}$) was calculated using linear regression on the ln-transformed concentration versus time (time = 0 to 90 days or time = 0 to 367) and a DT_{50} was calculated using non-liner regression (the Levenberg-Marquardt least squares method for curve fitting) of concentration versus time (time = 0 to 90 days or time = 0 to 367). The decay rate (k, or slope) and R^2 are summarized in Appendix C, Table 2.

The second equation (Eq 2.) results from using all the data (0 to 367 days) data points, fit the data (Levenberg-Marquardt least squares), but it was not a first order.

Appendix C Table 2. Summary of regression method, time, decay rate, coefficient of determination (R^2), intercept, and reaction order.

Parent (myclobutanil)					
Regression		Time (days)	k	R^2	n
Linear	lnc = lnCo exp (-kt)	90	0.0096[a] 0.0077[b]	0.99 0.97	1 1
Linear		367	0.0035 0.0031	0.81 0.82	1 1
Nonlinear	C=CoExp(-kt)	90	0.10 0.0091	0.99 0.95	1 1
		367	0.0067 0.0058	0.83 0.77	1 1
Nonlinear-N[st] order	C[c]	367	0.01676	0.98	n = 2.929 co = 1.012
Myclobutanil + 1,2,4-triazole					
Regression	lnc = lnCo exp (-kt)	Time (days)			
Linear		90	0.0058[a]	0.96	1
Linear		367	0.0022	0.85	1
Nonlinear	C=CoExp(-kt)	90	0.0069	0.92	1
Nonlinear		367	0.0037	0.68	1
Nonlinear-N[st] order	C[c]	367	0.01434	0.978	n = 4.789 co = 0.978

[a] Triazole ring labeled will include 1,2,4-triazole.

[b] Chlorophenyl ring label.(1,2,4-triazole not label)

[c] C =((n-1)*k*t + (1/co^(n-1)))^(-1/(n-1)); co = Co/100

Appendix C, Table 3 summarizes the distribution of measured radioactivity, and the estimated half-life or DT_{50}, DT_{75}, and 367 days (end of study). The rate constant (k /day) and coefficient of determination (R^2) is also shown. From a statistical stand point (the linear and nonlinear methods) were significant (slopes) and the R^2 were fair to good, and therefore, acceptable. But in reality the linear or nonlinear methods did not fit the data very well. Either the method fit the data well at times less than 90 days, but not at longer times, or it fit the data at both ends, but not in the middle. The non-linear, n-order curve fitting equation (eq. 2) fit the data also exactly. Unfortunately, it is not a first-order equation.

In summary, neither the first-order linear regression nor nonlinear regression (curve fitting) gives totally satisfactory results. When only part of the data is used the initial

decline can be fit quite well, but the later data is underestimated. Using all the data, over estimated the half-life (or DT_{50}), but under estimated the DT_{70} or DT_{90}. The first-order linear regression (transform data), using all the data, was the only method that gave a reasonable estimate of the residue remaining at the end of the study (367). Neither DT_{75} or DT_{90} were reached in the study, the residues remaining at day 367 was used to evaluate the results. This was selected because it was the most conservative as it fit the data best at both the beginning and end of the study. This would result in a conservative estimate of myclobutanil concentrations in water.

Appendix C, Table 3. Summary of half-lives, DT50, DT75, DT90, and decay rate of myclobutanil and myclobutanil + 1,2,4 triazole estimated by linear and non-linear regression.

	Half-life or DT50	DT75	DT90	% Radioactivity at 367 days	Rate constant	Coefficient of Determination
PARENT ONLY	50% decline	75% decline	90% decline			
Triazole Label Position	Time (days)				$Days^{-1}$	R^2
Observed Myclobutanil	75	>365	>365	29		
Liner Regression (t <100 days)	72.2	144	239	3.0	0.0096	0.99
Linear Regression (all)	**198.0**	**396**	**657**	**27.9**	**0.0035**	**0.81**
Nonlinear 1st order (t <100 days)	69.3	138	230	2.6	0.010	0.99
Nonlinear 1st order	103.5	206	343	8.7	0.0067	0.83
Nonlinear nst order	87.6	400	2600	26.7	0.0167	0.98
Observed Chlorophenyl Label	90	>365	>365	33		
Liner Regression (t <100 days)	90	180	299	6.0	0.0077	0.97
Linear Regression (all)	**224**	**447**	**742**	**32.3**	**0.0031**	**0.82**
Nonlinear 1st order (t<100 days)	76	152	253	3.6	0.0091	0.95
Nonlinear 1st order	113	237	354	11.6	0.0059	0.77
Nonlinear nst order	103	630	>1000	31.2	0.0164	0.98
PARENT + DEGRADATE						
Observed Myclobutanil + 1,2,4 triazole	220	>365	>365	42		
Liner Regression (t <100 days)	119.5	239	397	12.0	0.0058	0.96
Linear Regression (all)	315.1	630	1047	44.8	0.0022	0.85
Nonlinear 1st order (t<100 days)	100.5	201	334	8.1	0.0069	0.92
Nonlinear 1st order	186.3	372	619	25.9	0.0037	0.68
Nonlinear nst order	235.2			44.85	0.0144	0.98

Adsorption/Desorption Data Summary

Analysis of the sorption data (Appendix C, Tables 4) indicate sorption is not significantly correlated with organic matter (carbon) (EAB# 6087. 03/05/86). Therefore, lowest non-sand Freundlich K_{ads} was used to estimate the EDWCs for myclobutanil (USEPA, 2002). The desorption values for myclobutanil are also summarized in Appendix C, Table 4.

Appendix C, Table 4 Textural class, Organic Matter, Freundlich K_{ads}, Koc, and Desorption for Myclobutanil (MRID # 141682).

Myclobutanil					
MRID #141602	Texture Class	OM%	K_{ads} mL/g	Koc[1] $ml/g_{soil\ carbon}$	K_{des}
	Clay	0.44	2.39	936	0.588
	Sand	0.95	1.46	265	0.468
	Silty loam	2.05	7.08	595	4.178
	Sandy loam	2.9	9.77	581	4.082
	Clay loam	3.42	4.44	224	1.186

[1]Koc = (K_d/(%OM/1.724)) * 100 where K_{ads} is assumed to equal to K_d and OC% = OM%/1.724

The sorption and desorption data for 1,2,4-triazole are summarized in Appendix C, Table 5

Appendix C, Table 5 Textural class, Organic Matter, Freundlich K_{ads}, Koc, and Desorption for 1,2,4-triazole (MRID # 40891501)

1,2,4-Triazole					
MRID # 408915-01	Texture Class	OM%	K_{ads} mL/g	Koc[1] $ml/g_{soil\ carbon}$	K_{des}
	Sand	0.2	0.234	202	0.61
	Silty clay loam	1.2	0.722	104	0.82
	Silty clay	1.2	0.833	120	2.13
	Sandy loam	1.4	0.719	89	1.14
	Clay loam	3.0	0.748	43	1.07

[1]Koc = (K_d/(%OM/1.724)) * 100 where K_{ads} is assumed to equal to K_d and OC% = OM%/1.724

The fate and transport values used for modeling myclobutanil and myclobutanil plus 1,2,4-triazole concentrations for aquatic exposure assessments are summarized in Appendix C. Table 5.

Appendix C. Table 5. Input parameters for the Models used in Myclobutanil and Myclobutanil plus 1,2,4-triazole Water Exposure Assessment		
Input	**Value**	**Rationale**
Vapor Pressure @25 ºC	1.49 x 10^{-06} mm Hg	
Molecular weight	288.8 g/mol	
Henry's Law Constant @25 ºC	3.25 x 10^{-09} atm m^3/mol	
Incorporation depth	0	USEPA, 2002
Hydrolysis	0 (stable)	USEPA, 2002
Aquatic Photodegradation	0 (stable)	USEPA, 2002
Solubility	142.0 mg/L	USEPA, 2002
Aerobic Soil Metabolism Myclobutanil	251 days	= Upper 90th bound on mean
Aerobic Soil Metabolism Myclobutanil +1,2,4-triazole	315 days	= Upper 90th bound on mean
Aerobic Aquatic Metabolism Myclobutanil	*Estimated as* 502 days	= 2 x ASM per USEPA, 2002
Aerobic Aquatic Metabolism Myclobutanil + 1,2,4-triazole	*Estimated as* 630 days	= 2 x ASM per USEPA, 2002
Anaerobic Aquatic Metabolism	0 Stable	= Assumed stable to be conservative
Mobility (Freundlich K_{ads}) Myclobutanil	2.39 mL/g	GENEEC, PRZM/EXAMS = Lowest non-sand value
Mobility (Koc) Myclobutanil	224	For SCI-GROW1 = Lowest Koc
Mobility (Freundlich K_{ads}) 1,2,4-triazole	0.722	= Lowest non-sand value
Mobility (Koc) 1,2,4-triazole	43	= Lowest Koc
Aerial Spray Drift Ground Spray Drift Granular	0.05 (fraction) 0.01 (fraction) 0.0 (fraction)	USEPA, 2002
Application Efficiency (APPEFF) Aerial Spray Ground Spray Granular	 0.95 (fraction) 0.99 (fraction) 1.00 (fraction)	USEPA, 2002
Wetted In	No	Label

[1] SCI-GROW input specifies a Koc rather than K_{ads} as an input value.

1,2,4-Triazole

Additional environmental fate data has been submitted to the Agency in support of the Reregistration and Registration Actions for Triazole-derivative Fungicide Compounds; 1,2,4-triazole (PC Code: 600074), triazole alanine (PC Code: 600011) and triazole acetic acid (PC Code 60082) are also considered (D320682). The half-lives of 1,2,4-triazole ranged from 22.2 to 375 days.

Appendix C. Table 5. Environmental Fate and Chemistry Input Parameters for 1,2,4-Triazole

Parameters	Input Value and Unit	Source of Info/Reference
Soil Partition Coefficient (K_f)[1]	0.72	MRID 40891501 (GLN 163-1)
Molecular Weight	69.07 g/mole	MRID 45574104
Solubility (pH 7, 20 ^oC) [2]	7,000,000 mg/l	MRID 45574104 (GLN 63-7)
Vapor Pressure at 20 ^oC	1.65 x 10^{-3} mm Hg	MRID 45574104 (GLN 63-9)
Henry's Law Constant at 20 ^oC	1.97 x 10^{-10} atm·m^3/mol	MRID 45574104 (GLN 63-8)
Aerobic Soil Metabolism $T_{1/2}$	250 days[3] 107 days[4]	MRIDs: 45284032, 45297203, and 45284027 MRIDs: 45284032 and 45284027 (GLN 162-1)
Aqueous Photolysis (pH 5) $T_{1/2}$	stable	MRID 45284026 (GLN 161-2)
Hydrolysis $T_{1/2}$ (pH7)	161 days	MRID 43241019 (GLN 161-1)
Aerobic aquatic metabolism half-life	500 days[5] 214 days[6]	assumed 2 x aerobic soil metabolism half-life input value because the compound is stable to hydrolysis and no aerobic aquatic metabolism data are available (Guidance for Selecting Input Parameters in Modeling the Environmental Fate and Transport of Pesticides; Feb 2, 2002)
Anaerobic aquatic metabolism half-life[7]	504 days	assumed 2 x anaerobic soil metabolism half-life multiplied by three ($T_{1/2}$ = days, MRID 45930701) because no anaerobic aquatic metabolism data are available and the compound is stable to hydrolysis (Guidance for Selecting Input Parameters in Modeling the Environmental Fate and Transport of Pesticides; Feb 2, 2002)

[1] – The lowest non-sand Kf value was used.
[2] – The water solubility was multiplied by 10.
[3] – Upper 90 percentile confidence bound of the mean metabolism half-life from all half-lives available ($t_{1/2}$ (6)= 26.5; 46.7; 22.2; 343, 375; and 155 days) was used.
[4] – Upper 90 percentile confidence bound of the mean metabolism half-life and from all but the highest concentration half-lives ($t_{1/2}$ (4)= 26.5; 46.7; 22.2; and 155 days) was used.
[5] – Aerobic soil metabolism half-life input x 2 = 250 * 2 = 500 days
[6] – Aerobic soil metabolism half-life input x 2 = 107 * 2 = 214 days
[7] – Only one anaerobic soil metabolism half-life was available (84 days, MRID 45930701)