COMPARISON OF SOIL PHOTOLYSIS IN DRY AND MOIST SOIL LAYERS

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INTRODUCTION

The original guideline for soil photolysis was part of the Procedures for Assessing Environmental Fate and Ecotoxicology of Pesticides from the 1995 SETAC publication. An OECD guideline for the Phototransformation of Chemicals on Soil Surfaces was introduced as a draft document in 2002, but has never actually been implemented.

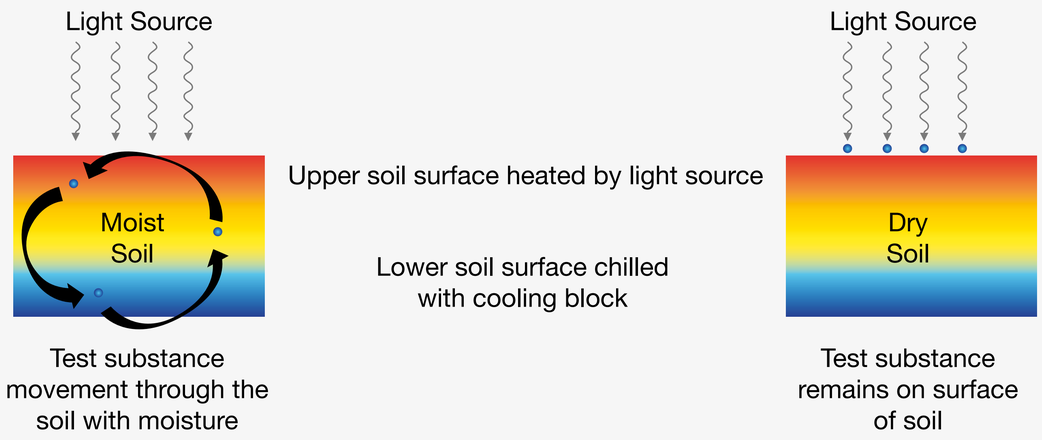
The original SETAC guideline was based on photolysis on dry soil layers only, but the OECD draft document states that testing can be done using dry or moistened soil surfaces, and in recent years there has been a general trend towards conducting studies under moist conditions.

We thought it would be interesting to compare the results of soil photolysis tests performed in both conditions to see if there are any trends and what (if any) conclusions may be formed.

SOIL PHOTOLYSIS

Substances may be transformed on soil by microbial, chemical or photochemical processes. Regulatory tests (e.g. OECD 307) are performed in the dark to specifically exclude photolysis products; however transformation by light can be a significant pathway for degradation under field conditions.

Photolysis reactions are caused by light waves imparting energy into chemicals, and this can give chemical bonds the impetus to break, stretch or reform in ways they would not otherwise have the ability to do. This can produce unique degradates that would not be formed in other regulatory tests in the dark



STUDY DESIGN

- Thin layers of soil treated with test substance and irradiated by simulated sunlight under laboratory conditions.
- After appropriate time intervals, soil thin layers extracted and analysed.
- Non-irradiated dark controls kept under identical conditions to distinguish between photochemical and other reactions.
- Volatile products collected and analysed.

STUDY SPECIFICS

- Soil – Preferably a silt loam or clay loam
- Soil layer thickness – *ca* 2 mm
- Temperature – 20 ± 2°C
- Moist soil layers maintained at a soil moisture equivalent to *ca* 75% field capacity.
- Light source – Xenon lamp with similar spectrum to summer sunlight over 290 to 800 nm
- Light intensity – Recorded between 300 and 400 nm

STUDY OBJECTIVES

- To investigate the formation of unique phototransformation products
- To investigate the rate of degradation of test substance on soil under light, and determine if photolysis is a significant depletion mechanism
- To establish a mass balance for the test

RESULTS

			Dry Soil Layers		Moist Soil Layers		Compound A and Compound B show degradation to the same degradates under both dry and moist conditions but have differing degradation rates.
			Irradiated	Dark	Irradiated	Dark	
Compound A	% AR as Degradates	Degradate A1 (hydrolysis product)	5	ND	20	25	• The hydrolysis product A1 was formed in greater amounts in the moist soil where there was more water for reaction. The amount observed in the dark controls indicates that this was primarily a chemical rather than photochemical reaction.
		Degradate A2 (nitrite reduction product of A1)	4	ND	7	ND	• The reduction of A1 to A2 was not detected in the dark at all showing that this was a photolysis reaction, and occurred at a similar rate in both dry and moist soil.
		Carbon Dioxide	3	ND	7	2	
	DT-50 (Days)		86	No degradation	13	17	• The rate of degradation for moist soil layers can be corrected for chemical degradation by subtracting the rate constant for dark degradation from the rate constant for light degradation. This revised rate constant can then be input into the calculations for DT-50 to give the half-life for photolytic degradation only.
	DT-50 Corrected (Days)		86	-	24	-	• Overall, even after correcting for the degradation observed in the dark controls, the rate of degradation was faster in moist soil.
Compound B	% AR as Degradates	Degradate B1 (reduction product)	1.5	0.8	1.3	0.8	
		Degradate B2 (not identified)	2.4	0.9	1	0.7	
		Carbon Dioxide	0.9	ND	0.3	0.1	
	DT-50 (Days)		154	No degradation	361	No degradation	• For Compound B the amount of degradation products formed between dry and moist soil layers was similar but despite the low amount of degradation, the rate was faster in dry soils than in moist soils.
							Compound C and Compound D are examples where differing products were formed in dry and moist soil layers.
Compound C	% AR as Degradates	Degradate C1 (reduction product)	11.1	ND	1.9	ND	• Compound C had faster degradation in moist soil than dry soil. C1 was a significant degradate in dry soil, but was present at less than 2% in moist soil.
		Degradate C2 (hydrolysis product of C1)	3.1	ND	2.4	ND	• C2 was formed in approximately equal amounts in both dry and moist conditions.
		Degradate C3 (not identified)	ND	ND	4.3	ND	• Degradates C3 and C4 were not identified but were each only detected in one soil condition.
		Degradate C4 (not identified)	2.5	ND	ND	ND	
		Carbon Dioxide	1	ND	0.5	0.3	
	DT-50 (Days)		151	No degradation	89	No degradation	
Compound D	% AR as Degradates	Degradate D1 (hydrolysis product)	15	0.1	25.3	8.2	• Degradate D1 was formed in greater amounts in moist soil. It was also observed in the moist soil dark controls, indicating there was a chemical reaction occurring and not just photolysis. In fact, the amount formed in dry soil (15% AR) plus the amount formed in the moist soil dark controls (8% AR) corresponded well with the amount in the irradiated moist soil (25% AR).
		Degradate D2 (hydrolysis and oxidation product of D1)	ND	ND	9.6	1.1	• Degradate D2 appears to be the result of a mostly photochemical reaction that requires the presence of water, as it was not observed in dry soil layers.
		Degradate D3 (hydrolysis and oxidation product)	ND	ND	5.7	4.7	• Degradate D3 was the result of a chemical reaction observed only in moist soil layers, and was present in equal amounts in both irradiated samples and dark controls.
		Degradate D4 (ring-opening and reduction product)	4.8	0.7	ND	ND	• Degradate D4 was only observed in dry soil layers. This degradate was a unique photolysis product formed by ring opening and reduction.
		Degradate D5 (not identified)	7.3	0.4	0.5	ND	• Degradates D5 and D6 were also only detected in dry soil layers, but were ultimately not identified.
		Degradate D6 (not identified)	5.3	0.5	0.8	0.3	
		Carbon Dioxide	3.8	ND	20.1	11.1	• For Compound D, significantly more carbon dioxide was recovered from moist soil layers (in both irradiated and dark conditions).
	DT-50 (Days)		57	No degradation	25	43	• The rate of degradation, after correction for the degradation observed in the dark controls, was the same in both soil conditions (57 days versus 58 days), but the degradation products formed were very different.
	DT-50 Corrected (Days)		57	-	58	-	

CONCLUSION

- Non-irradiated dark controls can provide a correction factor for the rate of degradation.
- Sometimes dry soil layers degrade faster than moist soil layers but generally either moist soil is faster or there is little difference between dry and moist soil layers.
- There can be different degradation products observed in dry and moist soil layers.
- The rate and route of degradation is very dependent on the compound being tested.
- Analysis of both dry and moist soil layers is recommended.

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