

Modification of a Laboratory Water Sediment Study using Sunlight to Refine the Estimated Environmental Concentration



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1 Introduction

An agrochemical was observed to degrade rapidly in buffer and natural water in a photolysis screen while degradation in water sediment proceeded slowly. This suggested that photodegradation in the water phase may contribute to reduced persistence of the parent compound in the total system.

An aerobic water sediment study was conducted with the test compound in accordance with regulatory guidelines with incubation in the dark. The irradiated study was conducted similarly but incubated outdoors to permit exposure to natural sunlight where the formation and decline of transformation products and the persistence of the test compound in the total system could be evaluated.

For agrochemicals known to be photolabile, integrating natural sunlight into the guideline-compliant laboratory aerobic water sediment study can provide refinement to the estimated environmental concentration.

2 Materials and Methods

An aerobic water sediment study was conducted in accordance with OPPTS 835.4300 and OECD 308 guidelines. Radiolabeled test compound was selected and a treatment rate chosen to permit the determination of the degradation kinetics and to readily monitor the formation and decline of major transformation products. Samples were collected at 9 intervals over the 100 day incubation period. The test vessels were maintained in flow-through systems with traps to collect CO₂ and non-specific VOCs. Surface waters were separated from sediment at each interval and analyzed directly. Sediment extraction was optimized for the test compound and known transformation products with demonstrated recovery from zero-time samples. Non-extractable residues (NER) occurring at ≥10% of applied radioactivity (% AR) were further assessed per the USEPA EFED guidance (Reference 1). HPLC with radiochemical detection provided resolution and quantification of parent compound from transformation products. High resolution LC-MS analysis confirmed the identity of all major transformation products. The water sediment systems were viable for the study duration as confirmed by microbial biomass determination. Material balance was calculated at each sampling interval.

The irradiated study was conducted similarly except the test vessels were incubated outdoors for 60 days under natural sunlight in optical grade quartz vessels fitted with optical grade quartz lids maintained at 20-25°C. Samples were collected at 8 intervals over the study duration. Appropriate sterile buffer and natural water controls treated with the test compound were incubated and analyzed concurrently.

3 Results and Discussion

Incubation of the test compound in the presence of natural sunlight significantly altered both the route and rate of degradation in the sand and silt test systems when compared to results in the same test systems incubated in the dark.

Route of Degradation

Sand and Silt Systems – Outdoor Incubation

- In general, rapid degradation of the test compound was observed in the water phase beginning at Day 1 with significant photodegradation products and numerous minor degradation products observed.
- By Day 1, ~35-45% of the test compound in the water phase rapidly partitioned into the sediment phase where it continued to degrade more rapidly in the Sand system than in the Silt system over the duration of the study. Similar quantities of photodegradates, biotransformation products and other minor degradation products were observed in both systems over the duration of the study. NERs were significant with ~40-45% bound at the end of the study. Mineralization to CO₂ was low.

Sand and Silt Systems – Dark Incubation

- The test compound in the water phase remained steady from Day 0 to Day 3 at 80-100% AR before declining to about 40% AR at Day 7 then steadily declined over the study duration. Minor hydrolysis products and transformation products similar to aerobic soil metabolism were observed throughout.
- The test compound partitioned slowly into the sediment phase until Day 7 when 50% AR was observed which then degraded slowly in the Sand system and unreliably in the Silt system. Toward the end of the study, the aerobic soil metabolism product was observed as a major product with only minor amounts of hydrolysis product observed. NER and CO₂ accounted for a maximum of 18 and 2% AR, respectively.

- Overall Mass Balance was quantitative for the Sand and Silt systems under both outdoor and dark incubation.

- Exhaustive extractions of bound soil residues >10% AR did not recover a significant amount of additional radioactive residues (<2.2% AR) from any treatment.

Rate of Degradation

- The Sand and Silt systems exposed to natural sunlight significantly faster than systems incubated in the dark in both the water phase and total system.
- The kinetic data for parent in the dark incubated Silt total systems was less reliable ($r^2 = 0.658$) than the sand total system ($r^2 = 0.898$) due to the slow degradation observed in the Silt sediment phase.

System	Incubation conditions	DT ₅₀ (days)	DT ₉₀ (days)	x ² error	r ²	Fit model
Sand	Sunlight	3.01	75.4	3.31	0.994	DFOP
	Dark	113	375	3.48	0.898	SFO
Silt	Sunlight	6.34	301	2.56	0.979	DFOP
	Dark	258	857	3.89	0.658	SFO

TABLE 1: KINETICS DATA FOR PARENT COMPOUND IN THE TOTAL SYSTEM

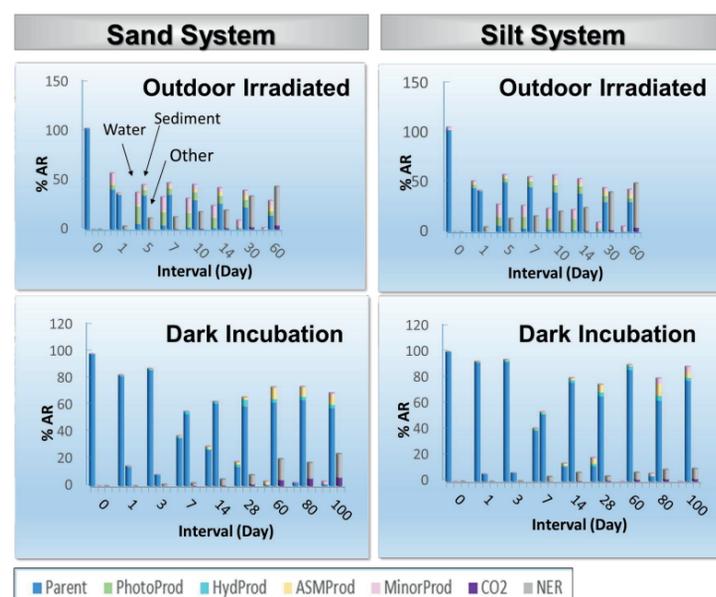


FIGURE 1: DISTRIBUTION OF PARENT AND TRANSFORMATION PRODUCTS

4 Conclusions

- The test compound degraded more rapidly in the irradiated Sand and Silt water sediment systems than in the corresponding dark systems.
- A known photoproduct was observed in both the water and sediment phases of the Sand and Silt systems exposed to natural sunlight.
- The study in natural sunlight can serve as a good indicator that aquatic field (shallow pond or aquatic field dissipation) studies may provide additional refinement of environmental concentrations.

REFERENCE:

- <https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/guidance-addressing-unextracted-pesticide-residues>