

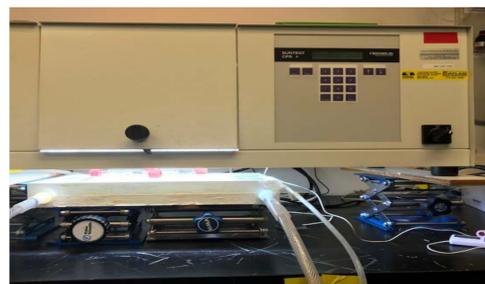
Abstract

The OECD 307 Guideline 'Aerobic and Anaerobic Transformation in Soil' and the EPA Guideline OCSP 835.4100 'Aerobic Soil Metabolism' define the degradation rate of an organic chemical in soil. The tests are conducted in field fresh moist soils at a constant temperature of 20°C under dark conditions. These parameters allow for consistent testing between studies, however these tests do not assess the simultaneous degradation contributed by natural sunlight that can occur in the field for some pesticides that are on the soil surface at least initially.

A soil metabolism study design based on the above guidelines was modified in this experiment by setting up treated soil samples with [¹⁴C]atrazine and exposing them to artificial sunlight for several days prior to introducing the illuminated samples to additional fertile soil. Comparisons of the rate of degradation in the illuminated samples are compared to treated soils incubated solely in the dark. This study design provides an example of higher tiered testing to assess a chemical's persistence.

Methods: Conduct of the Photo-enhanced Soil Metabolism Test

Test Design: Approximately 5 g of Sandy Loam soil (RMN-soil) was weighed into each of 12 cylindrical quartz vessels with PTFE-lined septa the soil. The soils were treated with 52 µg of [¹⁴C]atrazine and the soil moisture was adjusted to pF 2.5 with purified reagent water (PRW). The solvent was allowed to evaporate prior to the addition of PRW. The quartz vessels were placed in a water bath set at 20 ± 2 °C and irradiated using a Suntest unit for approximately 15 days. The irradiated soils were transferred to test vessels containing 45 g of RMN soil and incubated in the dark at 20 ± 2 °C. Another set of dark controls were prepared and incubated in the dark at 20 ± 2 °C. The soils were treated at a final concentration of 1 ppm.



Volatile and CO₂ Trapping solutions: Ethylene glycol used for volatile organics and two 1 N KOH trapping solution used for ¹⁴CO₂.

Aeration: Hydrated air delivered under negative pressure at approximately 1 bubble per second.

Temperature: 20 +/- 2°C

Sampling and Analysis: Duplicate soil samples per soil (irradiated or dark), sacrificed at time zero and on approximately days 15, 29, 46, and 60. Soils were extracted three times with acetonitrile:water (80:20, v:v) at a volume 2.0 times the weight of the soil sample. Extracts were quantified by liquid scintillation counting (LSC) and profiled by high-performance liquid chromatography with radiometric detection (HPLC-RAM). Non-extractable residues (NER) were quantified by combustion followed by LSC.

Kinetics: single, first-order (SFO) kinetics using the computer software CAKE (with the NAFTA option) was used to determine the rate constants.

Soil: The soil characterization of the North Dakota (RMN) Sandy Loam soil is given below.

Soil ID	Soil Type	pH	%Sand	%Silt	%Clay	%OC
RMN	Sandy Loam	6.8	69	18	13	2.6



Sampling Day	Light-exposed soil				
	Ave % Extractables	Ave % NER	% ¹⁴ CO ₂	% VOC	Average % Recovery
0	94.8	2.6	NA	NA	98.4
15	82.3	16.2	0.4	NA	98.5
29	77.8	22.5	0.4	ND	100.7
46	66.7	31.5	0.8	ND	99.0
60	56.2	39.2	1.2	ND	96.6

Sampling Day	Dark Soil				
	Ave % Extractables	Ave % Bound	% ¹⁴ CO ₂	% VOC	Average % Recovery
0	94.8	2.6	NA	NA	97.4
15	87.8	12.8	0.2	ND	100.8
29	76.6	21.6	0.5	ND	98.7
46	71.3	23.4	0.9	ND	95.7
60	64.5	30.4	1.6	ND	96.4

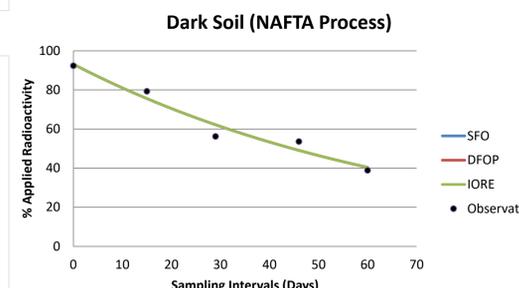
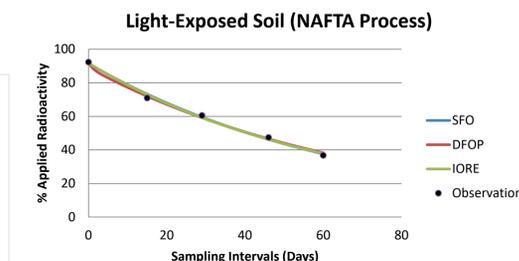
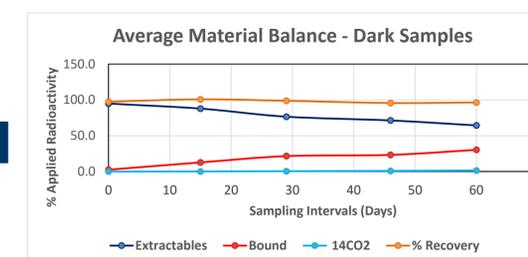
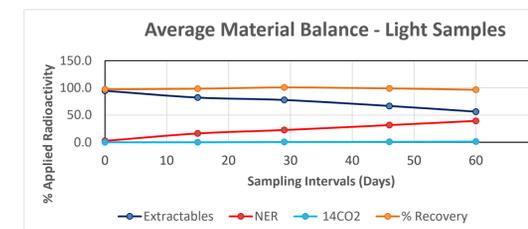
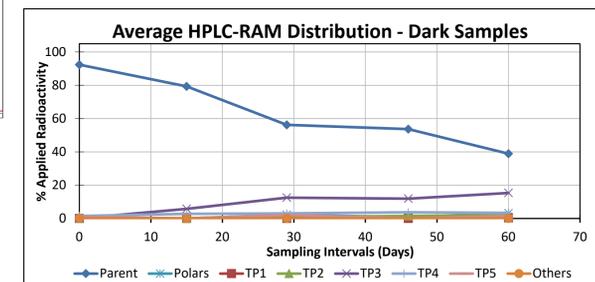
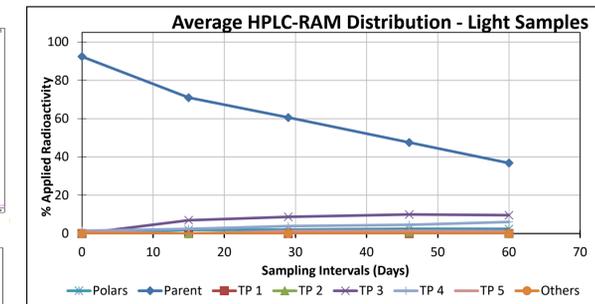
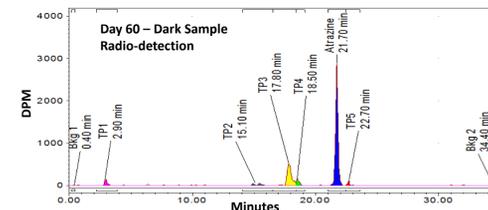
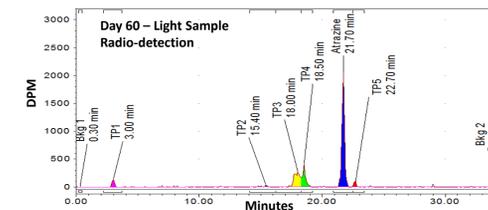
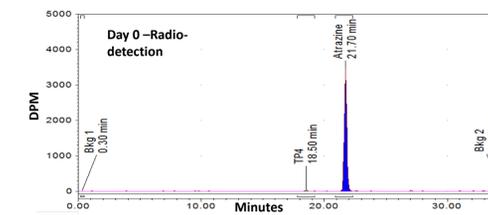
Sampling Day	Light-exposed soil							
	Parent	Polars	TP 1	TP 2	TP 3	TP 4	TP 5	Others
0	92.4	0.0	0.0	0.0	0.0	1.5	0.9	0.0
15	71.0	1.9	0.0	0.0	7.0	2.4	0.0	0.0
29	60.6	2.1	0.0	1.1	8.7	3.9	1.4	0.0
46	47.5	2.5	0.0	0.7	10.0	4.6	1.5	0.0
60	36.8	2.4	0.0	0.0	9.6	6.1	1.2	0.0

Sampling Day	Dark Soil							
	Parent	Polars	TP 1	TP 2	TP 3	TP 4	TP 5	Others
0	92.4	0.0	0.0	0.0	0.0	1.5	0.9	0.0
15	79.3	0.0	0.0	0.0	5.8	2.7	0.0	0.0
29	56.2	2.2	0.0	0.7	12.5	3.0	2.0	0.0
46	53.6	0.7	0.0	1.4	11.9	3.7	0.0	0.0
60	38.9	3.1	0.4	1.9	15.3	3.4	1.5	0.0

Results and Discussion

- Material balance was maintained between 93.6% and 105% applied radioactivity (AR) for both light enhanced soils and dark soils. Average extractability at Day 60 was approximately 56.2% and 64.5% AR, for light and dark sample, respectively. The NER was higher in the light-exposed soil samples compared to the dark samples. The exhaustive extraction of the NER is in progress.
- No organic volatiles were detected in either light-exposed soil or dark soil samples. Less than 2% AR of ¹⁴CO₂ volatile was generated during the 60 days of incubation in both light-exposed soil and dark soil samples.
- Approximately 10% AR of the transformation product, TP3, was observed in light-exposed soil samples after 60 days. TP3 was also found in the dark soil samples during the same period of incubation at nearly 15%. In the light exposed soil sample, the transformation product TP4 was slightly above 5% AR (at 6.1%) after 60 days of incubation whereas the TP4 was less than 5% AR (at 3.7% by Day 46 and declined to 3.4%) in the dark samples. LC/MS results indicate that TP3 could be desethylatrazine and TP4 could be either 2-hydroxyatrazine or deschloro-hydroxy atrazine. Confirmation of the identification of the transformation products is in progress.
- The rate of transformation of [¹⁴C]atrazine was calculated and summarized in the table below:

Condition	DT ₅₀ (days)	DT ₉₀ (days)	χ ²
Light Enhanced	47	155	1.76
Dark	50	165	4.77



Conclusions

- Based on the results of this study, the DT₅₀ for [¹⁴C]atrazine in the light-exposed soil samples are only slightly faster compared to the dark soil sample. The degradation pathway could be slightly different due to the presence of light. The transformation product TP4 (hydroxylated atrazine) was still increasing in the light-exposed soil samples whereas the TP4 production was declining in the dark sample. Further research is ongoing in the identification of the degradation products.
- Results indicate that although half-life of atrazine was only slightly faster in the light samples and photo-degradates were slightly greater in percent of the HPLC-RAM runs, the test design may be useful for pesticides with greater UV-absorbance.

References

OECD 307 and OCSP 835.2410, Testing Guidelines.

Acknowledgments

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