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DATA EVALUATION RECORD

STUDY 4

CHEM 057701 Malathion §161-4

FORMULATION--00--ACTIVE INGREDIENT

STUDY MRID 40969301
Miller, G., B. R. Smith, and J. D. Geddes. 1988. Vapor phase photolysis of malathion. Laboratory Report No. PD-M 25-60. Unpublished study performed by the Department of Biochemistry, University of Nevada, Reno, NV, and submitted by the Malathion Reregistration Task Force.

DIRECT REVIEW TIME = 10

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CONCLUSIONS:

Degradation - Photodegradation in Air

1. This study cannot be used to fulfill data requirements.
2. Malathion contained in new Tedlar bags did not degrade during 8 hours of irradiation with sunlight, and <10% was lost during 4 days of irradiation.

The portion of the study using Tedlar bags is scientifically sound, but does not meet Subdivision N guidelines for the following reasons:

1. Environmental conditions (sunlight and temperature) were not adequately described.

2. The experiment was terminated before a half-life could be established.
 3. Data were not provided for the dark controls.
 4. There was no material balance for the sunlight-irradiated samples.
3. The portion of the study using borosilicate glass bottles is unacceptable for the following reason:
- the photodegradation of malathion appeared to be catalyzed by the glass in which the samples were contained.
4. Since malathion reacted with the glass containers, invalidating that portion of the study, and since the portion of the study using non-reactive Tedlar bags was terminated before the half-life of malathion in vapor was established, the problems with this study probably cannot be solved by the submission of additional data. A new study probably should be submitted.

METHODOLOGY:

Tedlar air bags: In order to determine the adsorption of malathion to Tedlar air sampling bags, air (20 L) at 22-28° C was filtered through a Sep-Pak cartridge and was introduced into 100-L Tedlar bags. Aliquots (25 uL) of [¹⁴C]malathion (radiochemical purity not provided; specific activity 0.1 uC/uL, American Cyanamid) dissolved in toluene, at 0.893 mg/mL, were injected directly into a gas vaporizing chamber set at 150° C; the malathion vapor was added to the sampling bags through a teflon stopcock. Additional air (30 L) was pumped through the chamber into the bags and the bags were equilibrated for 20 minutes at 22-25° C (conditions not further specified). After equilibration, the gas was removed from the bags by suction through a Sep-Pak cartridge. The Sep-Pak cartridges and bags were rinsed three times with acetone. The rinsates from the bags were concentrated by evaporation (Kuderna Danish concentrator) and all rinsates were analyzed by LSC.

To study photolysis of malathion vapor inside the Tedlar bags, malathion was dissolved in acetone at 10.4 mg/mL, and aliquots (25 uL) were added to six 100-L Tedlar bags as previously described. One bag was covered with black polyethylene sheeting and aluminum foil to serve as a dark control. After equilibration (time and conditions not specified), the bags were exposed to "midday sunlight" for 0, 1, 2, 4, 7, and 8 hours (conditions not further specified); a similar experiment was sampled after 0 and 4 days of irradiation. These experiments were also conducted using an unlabeled malathion/acetone solution. All bags and Sep-Pak cartridges were extracted (method not specified) and the extracts were analyzed using GC with nitrogen-phosphorous (NP) detection or HPLC.

Borosilicate glass flasks: In order to determine the absorption of malathion to the flask walls, an aliquot (3 uL) of the unlabeled malathion/acetone solution was placed in three round bottom borosilicate glass flasks. The acetone was allowed to evaporate and the flask sealed with an aluminum-covered stopper. The flask was vented through a Sep-Pak cartridge inserted into the stopper, and the flask was equilibrated for 1 hour (conditions not specified). The flask was rinsed three times with acetone, and the combined rinsates were concentrated under a nitrogen stream and placed in "cold storage" (conditions not specified) until analysis by GC using NP detection.

To determine the malathion concentration in the vapor phase, four flasks were prepared as described above and treated with an aliquot (15 uL) of the [¹⁴C]malathion/toluene solution. After a 1-hour equilibration period at room temperature (25 C°; conditions not further specified), air (6 L) was passed through the flask by withdrawing this volume of gas from each bottle through a Sep-Pak cartridge. The Sep-Pak cartridges and all flasks were rinsed three times with acetone; the combined rinsates were concentrated to dryness under a nitrogen stream. The residues were redissolved in scintillation cocktail and the samples were analyzed by LSC.

In order to determine the photolysis of malathion vapor in the flasks, aliquots (3 uL) of the unlabeled malathion/acetone solution (10.4 mg/mL) were added to seven flasks. The flasks were prepared as previously described, and one flask was covered with aluminum foil to serve as a dark control. The flasks were exposed to sunlight for 0, 0.5, 1, 2, 4, and 7 hours (conditions not further specified) during September, 1988. Flasks and gas traps were rinsed with acetone as previously described and analyzed using GC with NP detection. Additionally, aliquots (15 uL) of the [¹⁴C]malathion in toluene solution (0.893 mg/mL) were added to seven flasks. The flasks were prepared as previously described; the flasks were exposed to sunlight for 0, 0.5, 1, 2, 4, and 7 hours (conditions not further specified). The flasks and traps were rinsed with acetone as previously described; the rinsates were placed in "cold storage" until analysis by reverse-phase HPLC (C-18 column) eluted with a gradient of acetonitrile:water. Radiolabeled compounds were detected using radioactive flow detection.

DATA SUMMARY:

The vapor pressure of malathion was reported to be 4×10^{-5} mm Hg at 30° C or 5.3 mPa at 30° C.

Malathion, contained in Tedlar bags that had not been used previously, did not degrade during 8 hours of exposure to sunlight (Figure 5a). Less than 10% of the malathion in the bags degraded during 4 days of

irradiation (Figure 5b). Material balances were not provided for the sunlight-irradiated samples. No data were provided for the dark controls.

Malathion, contained within borosilicate glass flasks, degraded in sunlight with observed half-lives of 1 to 1.5 hours (Figure 1).

Malaoxon

and one unidentified degradate were detected in the irradiated samples, but were not quantified. Material balances were 90-105% of the applied radioactivity. In the dark controls, "recoveries" were 88% and 96% (it was unclear whether this referred to undegraded malathion or to material balance).

Adsorption experiments demonstrated that the majority ($\geq 99\%$) of the malathion in both the bottles and bags had adsorbed to the walls of the sample containers and that $< 1\%$ remained in the vapor phase. The study authors concluded that malathion was photooxidized on the borosilicate glass, and in fact, was photochemically stable in the vapor phase.

REVIEWER'S COMMENTS:

1. Environmental conditions were not adequately described. It was only stated that the bottles and bags were exposed to natural sunlight; the intensity of the sunlight, the location of the test site, the time of year (the bottle experiment was done in September), and the atmospheric conditions were not reported. Also, the air temperatures for the experiments conducted outdoors were not reported.
2. The experiments using the Tedlar bags were terminated prior to establishing the half-life of malathion; after 4 days of irradiation, approximately 90% of the malathion remained undegraded. Subdivision N guidelines state that the study should be conducted for 30 days or until the half-life of the parent is established.
3. Data on the material balances and the dark controls for the sunlight-irradiated bags of malathion were not reported. In all cases, the results of the studies were vague and reported only in graph form. No tabular data were presented for review. All numbers cited in this review came from the text of the study. Although duplicate samples were analyzed, it was not possible to assess variation from the information provided.
4. The description of methodology for these experiments was incomplete and poorly written. The "equilibration" conditions were not adequately described: the light conditions were not reported, and in some cases, the equilibration time was not reported. The extraction methods were not adequately described. The "cold storage" conditions were not adequately described: it is not clear if the rinsates were refrigerated or stored in the freezer.

5. In the portion of the experiment using borosilicate glass containers, although significant degradation occurred, degradates were not quantified. Malaoxon was identified as the major degradate; one degradate was described as "unknown".
6. Several Tedlar bag experiments were performed that utilized previously used Tedlar bags, or included trifluralin and diazinon with malathion in the bags as "in situ actinometers to measure light intensity". One bag was covered with black polyethylene sheeting and aluminum foil to serve as a dark control. In both instances, degradation of malathion was observed. Malathion did not degrade when irradiated alone in new Tedlar bags. The study author stated that "Tedlar" is a low sorptive polymer which should not interact with organic compounds, but that previous use may have resulted in contamination of the bags with photosensitizing compounds. The study author also suggested that trifluralin and diazinon residues may have interacted with the malathion and have contributed to the apparent photolysis.
7. The study author suggested that the acetone used for the rinsing of all flasks, bags, and cartridges may have accelerated malathion degradation.

MALATHION

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Pages 6 through 11 are not included.

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