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# Avermectin $B_{1a}$ Metabolism in Celery: A Residue Study

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Radioactivity equivalent to less than 4% of the total avermectin $B_{1a}$ applied to mature and immature celery as a mixture of unlabeled and [$^{14}$C]- or [$^{3}$H]avermectin $B_{1a}$ remained in harvested plants. The half-lives of radiolabeled avermectin $B_{1a}$ residues as measured by the dissipation of total $^{3}$H radioactivity from celery parts ranged from 5.2 to 12.9 days in celery treated at 0.01 and 0.10 lb of AI/acre. The percentage of total radioactivity in celery parts readily extractable with acetone (range of 57.8-97.1%) generally decreased with increasing postharvest intervals. High-performance liquid chromatography of acetone extracts of celery leaves and stalks produced four discernible peaks of radioactivity, designated as polar metabolites, moderately polar metabolites, avermectin $B_{1a}$, and the $\Delta^{8,9}$ isomer of avermectin $B_{1a}$. The percentage of acetone extract radioactivity represented by polar metabolites generally increased with increasing postharvest intervals.

Abamectin (MK-0936) is a macrocyclic lactone pesticide that has been under investigation as an acaricide/nematicide/insecticide in citrus, orchard, and field crops (Price, 1983; Schuster and Everett, 1983; Wright, 1984; Reed et al., 1985; Burts, 1985). It is being developed as a miticide/insecticide to control imported red fire ants and several phytophagus pests on horticultural and agronomic crops. The use of this compound to control the leaf miner (*Liriomyza sp.*) in celery is currently proposed, and the results of this study present data relevant to such use. Avermectin $B_{1a}$ (AVM-$B_{1a}$) is the major component of abamectin (MK-0936). The specific objectives of the present study were (1) to determine the dissipation rate of this major component from radiolabeled AVM-$B_{1a}$-treated immature and mature celery plants and (2) to examine the metabolism of AVM-$B_{1a}$ by immature and mature celery plants grown in pots under field conditions after multiple applications.

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## MATERIALS AND METHODS

**Formulations and Chemicals.** Radiolabeled and nonradiolabeled avermectin $B_{1a}$ (AVM-$B_{1a}$; molecular weight 872) and emulsifiable concentrate formulation (EC) were supplied by Merck Sharp & Dohme Research Laboratories.

[$^3$H]Avermectin $B_{1a}$ ([$^3$H]AVM-$B_{1a}$) (>99+% radiochemical purity, specific activity 1.64 mCi/mg), in which the $^3$H label was located at the C5 position, was added to unlabeled AVM-$B_{1a}$ to give two stock solutions, one containing 1.8 g of total AVM-$B_{1a}$/L of EC (300 $\mu$Ci of $^3$H/mL of EC) and the other 18.0 g of total AVM-$B_{1a}$/L of EC (300 $\mu$Ci of $^3$H/mL of EC).

[$^{14}$C]Avermectin $B_{1a}$ ([$^{14}$C]AVM-$B_{1a}$; >99+% radiochemical purity, specific activity 16.3 $\mu$Ci/mg), in which the $^{14}$C label was located at the C3, C7, C11, C13, or C23 position, was added to unlabeled AVM-$B_{1a}$ to give a stock solution of 2.7 g of total AVM-$B_{1a}$/L of EC (24.4 $\mu$Ci/mL of EC).

A standard of the $\Delta^{8,9}$ isomer of AVM-$B_{1a}$ was also supplied by Merck Sharp & Dohme Research Laboratories. Carbo-Sorb for $^{14}$C absorption during oxidative combustion and Permafluor V scintillation solution for $^{14}$C counting following combustion were obtained from Packard Instruments. Biofluor scintillation solution used for $^3$H counting following combustion was obtained from New England Nuclear. Acetone (HPLC grade) and methanol (HPLC grade) were obtained from Fisher Scientific Co.

**Materials and Design.** Celery seedlings (approximately 6 in. tall) were acquired from a commercial seed bed facility and transplanted in 5-gal pots (with drain holes) filled with Lauderhill muck soil (organic carbon content 38.3%). This is the type of soil in which celery is normally grown. All pots were placed on a plastic film ground cover within a fenced area at the Central Florida Research and Education Center of the University of Florida at Sanford. From the time of transplantation to the time of the last harvest, plants were fertilized three times with soluble plant food and treated four times with Bravo fungicide. On one occasion, plastic film was placed around the celery plants to provide protection from near-freezing temperatures. On the following day all plants were moved into a wooden shelter for less than 24 h to prevent damage anticipated from predicted freezing temperatures.

The study involved the application of radiolabeled AVM-$B_{1a}$ to 66 immature (treatment beginning 3 weeks following transplantation) and 78 mature (treatment beginning 5 weeks following transplantation) celery plants. [$^3$H]AVM-$B_{1a}$ was applied weekly to 60 immature plants for 4 weeks and to 72 mature plants weekly for 10 weeks. [$^{14}$C]AVM-$B_{1a}$ was applied to six immature plants and to six mature plants according to the same schedule.

**[$^3$H]- and [$^{14}$C]AVM-$B_{1a}$ Treatment.** Thirty of the 60 immature plants and 36 of the 72 mature plants were treated with [$^3$H]AVM-$B_{1a}$ at a rate of 0.01 lb of active ingredient (AI)/acre (24 $\mu$Ci and 144 $\mu$g/plant per application). The remaining 30 immature and 36 mature plants were treated with [$^3$H]AVM-$B_{1a}$ at a rate of 0.10 lb of AI/acre (24 $\mu$Ci and 1.44 mg/plant per application). Two formulated [$^3$H]AVM-$B_{1a}$ solutions containing 1.8 and 18.0 g of AI/L of EC (corresponding to the 0.01 and 0.10 rates, respectively) were diluted 1:75 with water immediately before application. Six-milliliter portions of these diluted solutions were applied to the foliar portion of each plant with a plastic syringe fitted with a 23-gauge needle. The application rate of the diluted solutions was equivalent to 49.5 gal/acre.

Twelve plants (six immature and six mature) were treated with [$^{14}$C]AVM-$B_{1a}$ at a rate of 0.015 lb of AI/acre (1.9 $\mu$Ci and 216 $\mu$g/plant per application). The formulated [$^{14}$C]AVM-$B_{1a}$solution contained 2.7 g of AI/L of EC, which was diluted 1:75 with water immediately before application. The application rate of the diluted solution was equivalent to 49.9 gal/acre. The method of application was identical with that described for the [$^3$H]AVM-$B_{1a}$ application. Applications of [$^3$H]- and [$^{14}$C]AVM-$B_{1a}$ to immature plants occurred from Jan 6 to Jan 25, 1984, and to mature plants from Jan 18 to March 21, 1984.

Twelve celery plants served as controls. These plants were transplanted at the same time as the experimental plants and were grown in the same fenced area under the same conditions as the experimental plants but were not treated with avermectin $B_{1a}$ (labeled or unlabeled) or EC. Three of these plants were harvested randomly on April 12, 1984, the sixth and last harvest date for mature celery plants. Harvest procedures were identical with those described below for experimental crops.

**Harvesting of Celery and Soil Sampling.** *[$^3$H]AVM-$B_{1a}$-Treated Celery.* Two groups of three plants each were harvested randomly from the immature celery crop immediately after the treatment solution was dry (5–7.5 h following the final application, zero time) and 1, 2, 4, and 6 weeks after the fourth and last [$^3$H]AVM-$B_{1a}$ application. The postharvest intervals (PHIs) for mature plants, two groups of three plants each, were zero time (5–7.5 h) and 1, 3, 7, 15, and 22 days after the tenth and last [$^3$H]AVM-$B_{1a}$ application. The leaves of all three plants within each group were harvested first and packaged together in double-plastic bags. The stalks of the same plants were similarly harvested and packaged together. All samples were frozen at −20 °C until analysis.

*[$^{14}$C]AVM-$B_{1a}$-Treated Celery.* Three plants were harvested randomly from the immature celery crop immediately after the treatment solution was dry (5–7.5 h, zero time) and 2 weeks after the fourth and last application of [$^{14}$C]AVM-$B_{1a}$. The PHIs for mature plants were 5–7.5 h (zero time) and 1 week after the tenth and last application of [$^{14}$C]AVM-$B_{1a}$. The harvest procedure was identical with that used for the [$^3$H]AVM-$B_{1a}$-treated crops except that plants parts from each plant were packaged separately.

*Soil Sampling.* At each harvesting time, soil samples (3 in. × 1 in.; top, middle, and bottom layers) were taken from each pot by a stainless steel auger. The top soil layers from each of three pots in each [$^3$H]AVM-$B_{1a}$ treatment group were packaged together in double-plastic bags. This same procedure was followed for middle and bottom soil samples taken from three pots within the same group. Soil samples from [$^{14}$C]AVM-$B_{1a}$-treated plants were packaged separately for each plant harvested and were later combined by layer for analysis. All samples were frozen until analysis.

**Analytical Methods.** For each harvest date, two groups of celery plants treated with [$^3$H]AVM-$B_{1a}$ at 0.01 lb of AI/acre and one group of celery plants treated with [$^3$H]AVM-$B_{1a}$ at 0.10 lb of AI/acre were analyzed for total and acetone-extractable [$^3$H]AVM-$B_{1a}$ and possible $^3$H-labeled metabolites of this compound. Measured radioactivity was expressed in terms of AVM-$B_{1a}$ equivalents following conversion of disintegrations per minute (dpm) values to milligrams of AVM-$B_{1a}$ using the specific activity of initial radiolabeled material in the calculation.

**Extraction and Oxidative Combustion of Radiolabeled Compounds.** Frozen celery leaves and stalks from each group of [$^3$H]AVM-$B_{1a}$-treated plants or from single plants treated with [$^{14}$C]AVM-$B_{1a}$ were weighed and then allowed to thaw at room temperature. The celery parts were then cut into pieces (~1 in. long) with scissors or a knife. Acetone (HPLC grade) was added to the chopped leaves or stalks (milliliters of acetone added = at least 2× the weight in grams of frozen plant material), and the resultant mixture was blended (Brinkman Polytron) to homogeneity. The weight of the resultant mixture was determined, and an aliquot representing ~10% by weight was removed to be further extracted with acetone. The remaining blended material was returned to frozen storage, and the aliquoted sample was again blended with acetone and filtered. The resultant mat was extracted three to six more times with 50–500 mL of acetone for each extraction. The number of extractions for each sample was determined empirically for each sample as that required to remove sufficient radioactivity such that one additional extraction removed <1% of the radioactivity removed in all prior extracts. The mat was allowed to air-dry and was then weighed. The volume of the combined acetone filtrates was recorded and concentrated when necessary by rotary evaporation to a final volume of not less than 32 mL.

The $^3$H content of the acetone filtrate was determined by oxidative combustion of 1 mL of filtrate (Tri-Carb sample oxidizer, Model B306, Packard Instrument Co., Inc.) that was evaporated to dryness before combustion on a Combusto-Pad held by a Combusto-Cone (Packard Instruments). The $^3$H content

of the mat was determined by combusting 35–100 mg of air-dried mat in a Combusto-Cone.

Recovery studies of [$^3$H]AVM-$B_{1a}$ and [$^{14}$C]AVM-$B_{1a}$ applied to commercially obtained celery stalks and leaves were conducted to determine the loss of radioactivity that occurred during the analytical procedures. A 200-μL portion of the AVM-$B_{1a}$ solution used for field application to celery at the 0.01 lb/acre rate was used to fortify commercially obtained celery plants. The extraction and combustion analyses were then conducted as described above.

**Combustion of Soil Samples.** Before analysis, soil from each sample layer was mixed thoroughly while still in the storage bag. Clumps of compacted soil, when present, were crushed in the bag with a mallet and mixed well with the remaining soil in the sample. Forceps were used to removed any root parts inadvertently included in the soil sample. Each soil sample was weighed and dried for 24 h in a hood at 50 °C under an infrared heat lamp. After reweighing, 200 mg was combusted as described above.

**High-Performance Liquid Chromatography (HPLC) of Acetone Extracts of Celery.** Aliquots (1–120 mL) of the concentrated acetone filtrate were evaporated to dryness (under a stream of $N_2$, by lyophilization, or refrigerated evaporation) and reconstituted with 85% MeOH/$H_2O$ (1.0–3.0 mL). The particular aliquot volume was selected to provide at least 1800 dpm in the sample injected onto the HPLC (Altex Model 110A pumps). Portions of 100–200 μL of the reconstituted filtrates were injected onto an Alltech $C_{18}$ column (250 × 4.6 mm, 5 μm) with 85% MeOH/$H_2O$ as the mobile phase to elute the first 33 fractions and 100% MeOH for the remaining fractions. The flow rate was 1 mL/min, and 0.5-mL fractions were collected in a Gilson microfractionator (Model FC-100). The effluent was monitored continuously by UV spectrophotometry at 254 nm, and the elution positions of radiolabeled AVM-$B_{1a}$ and the $\Delta^{8,9}$ isomer were confirmed by coelution of these peaks and corresponding unlabeled standards of these two compounds. The eluted fractions from this second chromatographic run were collected in the same tubes used to collect the corresponding fractions from the first chromatographic run. Of the resultant combined fractions, 1 mL was counted in a Searle Analytic 92 liquid scintillation system using Aquasol-2 (New England Nuclear) as the scintillation solution. Internal standard quench corrections were used to account for any quenching.

The radioactivity collected in fractions 7–40 represented four distinguishable components designated as polar metabolites, moderately polar metabolites, AVM-$B_{1a}$, and the $\Delta^{8,9}$ isomer of AVM-$B_{1a}$ (Figure 1). When the percent of the total filtrate represented by each of these components was calculated, the radioactivity present in each of the radiochromatographic peaks was divided by the total radioactivity injected onto the chromatographic column as determined by oxidative combustion.

## RESULTS

The average recoveries of $^3$H- and $^{14}$C-labeled AVM-$B_{1a}$ applied to commercially obtained celery were 102.2% (range 99.4–105.0%, $N$ = 3) and 87.1% (range 84.7–90.3%, $N$ = 3), respectively. More than 96.8% of the [$^3$H]AVM-$B_{1a}$ radioactivity and 97.1% of the [$^{14}$C]AVM-$B_{1a}$ radioactivity in stock solutions stored under refrigeration for 2 years were found in HPLC fractions that coeluted with freshly prepared unlabeled AVM-$B_{1a}$ standard. This demonstrates that during 2 years of storage AVM-$B_{1a}$ remained relatively stable.

The celery parts examined in this study contained radioactivity equivalent to no more than 4% of the total AVM-$B_{1a}$ applied to these parts (Table I). Comparison of radiolabeled residue concentrations (expressed as AVM-$B_{1a}$ equivalents) in plant parts treated with [$^3$H]AVM-$B_{1a}$ with those in plant parts treated with [$^{14}$C]AVM-$B_{1a}$ at the same PHI generally reflected the difference in the total amount of AVM-$B_{1a}$ applied. That is, [$^{14}$C]AVM-$B_{1a}$-treated plant parts (0.015 lb of AI/acre) contained higher radiolabeled residue concentrations than plant parts

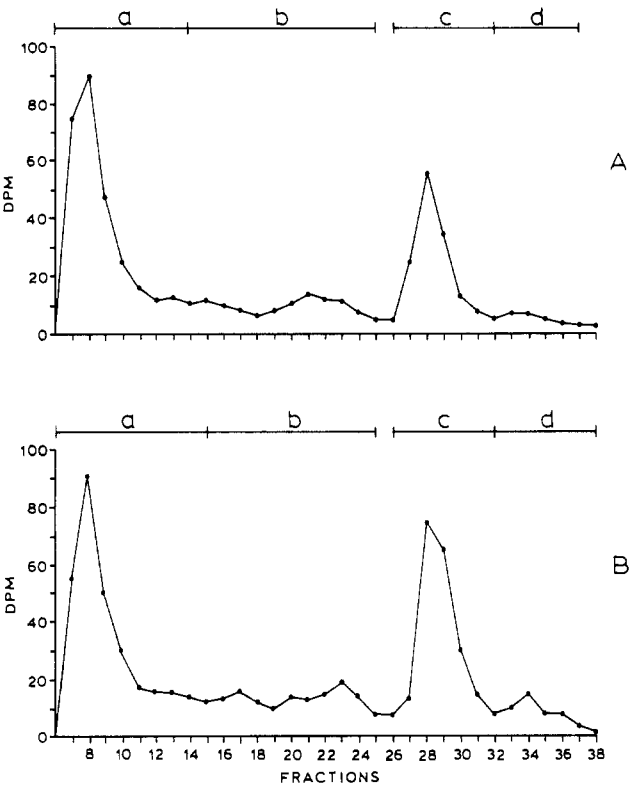


**Figure 1.** Radiochromatograms of acetone extracts of leaves (A) and stalks (B) of an immature celery plant harvested 14 days after treatment with [$^3$H]AVM-$B_{1a}$ at 0.10 lb of AI/acre. Pooled fractions were designated as (a) polar metabolites, (b) moderately polar metabolites, (c) avermectin $B_{1a}$, and (d) $\Delta^{8,9}$ metabolite.

treated with [$^3$H]AVM-$B_{1a}$ at the 0.01 lb of AI/acre rate but lower residue concentrations than those treated at 0.10 lb of AI/acre (Table I).

Under all treatment conditions for all plants, celery leaves contained greater total amounts and concentrations of radiolabeled AVM-$B_{1a}$ material than did their corresponding stalks (Table II). Leaves of immature celery plants treated four times with [$^3$H]AVM-$B_{1a}$ at both application rates contained from 2.8 to 5.01 times the concentration of radiolabeled residues present in their corresponding stalks, while leaves of mature celery plants treated 10 times with [$^3$H]AVM-$B_{1a}$ at both rates contained from 4.76 to 12.6 times the concentrations of radiolabeled residues present in their corresponding stalks. Similarly, leaves of immature and mature plants treated 4 and 10 times, respectively, with [$^{14}$C]AVM-$B_{1a}$ at 0.015 lb of AI/acre contained from 3.65 to 8.25 and from 9.85 to 14.0 times, respectively, the concentrations of radiolabeled residues present in the corresponding stalks (Table II).

The dissipation of radiolabeled AVM-$B_{1a}$ residues from immature celery leaves and stalks is illustrated in Figures 2 and 3, respectively, and that from mature celery leaves and stalks in Figures 4 and 5, respectively. Assuming a first-order decay of radiolabeled residues, the equation $t_{1/2} = 0.693/k$ ($-k$ = slope; $\ln [A] = \ln[A]_0 - kt$) was used to calculate the half-life of the slower, second phase of decay of [$^3$H]avermectin $B_{1a}$ and total [$^3$H]AVM-$B_{1a}$ residues in each plant part for each growth state (immature and mature; Table III). Zero-time values were not included in these calculations because of an initial rapid decline from zero time to the next harvest time in two groups (stalks and leaves of mature plants treated with [$^3$H]AVM-$B_{1a}$ at 0.01 lb of AI/acre). In the present study,

**Table I. Radiolabeled Residues in Celery following Application of [$^3$H]- and [$^{14}$C]Avermectin $B_{1a}$**

| day[a] | % applied | [$^3$H]AVM-$B_{1a}$ at 0.01 lb/acre,[b] μg/kg (AVM-$B_{1a}$ equiv, mean of two groups) | % applied | [$^3$H]AVM-$B_{1a}$ at 0.10 lb/acre,[c] μg/kg (AVM-$B_{1a}$ equiv, one group) | % applied | [$^{14}$C]AVM-$B_{1a}$ at 0.015 lb/acre,[d] μg/kg (AVM-$B_{1a}$ equiv, mean of two plants) |
|---|---|---|---|---|---|---|
| | | | | Immature Plants | | |
| | | | | Leaves | | |
| 0 | 1.33 | 2740 | 1.36 | 26800 | 1.67 | 9570 |
| 7 | 0.46 | 544 | 0.41 | 7830 | | |
| 14 | 0.35 | 200 | 0.31 | 2690 | 0.52 | 519 |
| 29 | 0.21 | 25.7 | 0.19 | 286 | | |
| 43 | 0.20 | 11.5 | 0.21 | 96.7 | | |
| | | | | Stalks | | |
| 0 | 0.31 | 550 | 0.29 | 6440 | 0.19 | 1160 |
| 7 | 0.10 | 135 | 0.08 | 2260 | | |
| 14 | 0.09 | 60.6 | 0.06 | 851 | 0.08 | 142 |
| 29 | 0.07 | 6.90 | 0.04 | 57.1 | | |
| 43 | 0.14 | 4.10 | 0.08 | 21.6 | | |
| | | | | Mature Plants | | |
| | | | | Leaves | | |
| 0 | 1.86 | 196 | 2.56 | 2140 | 3.66 | 514 |
| 1 | 1.55 | 135 | 2.29 | 2170 | | |
| 3 | 1.85 | 127 | 1.84 | 1650 | | |
| 7 | 1.58 | 95.6 | 1.38 | 1134 | 1.50 | 197 |
| 15 | 1.18 | 61.4 | 0.75 | 554 | | |
| 22 | 0.79 | 45.4 | 0.74 | 458 | | |
| | | | | Stalks | | |
| 0 | 0.56 | 28.9 | 1.03 | 400 | 0.55 | 36.6 |
| 1 | 0.42 | 16.2 | 0.69 | 331 | | |
| 3 | 0.52 | 13.3 | 0.51 | 204 | | |
| 7 | 0.34 | 8.30 | 0.74 | 238 | 0.30 | 20.0 |
| 15 | 0.28 | 5.24 | 0.17 | 43.8 | | |
| 22 | 0.24 | 4.50 | 0.24 | 50.9 | | |

[a] Postharvest interval [b] Total avermectin $B_{1a}$ applied to three immature plants (one group) 1.728 mg; total avermectin $B_{1a}$ applied to three mature plants (one group) 4.320 mg. [c] Total avermectin $B_{1a}$ applied to three immature plants (one group) 17.28 mg; total avermectin $B_{1a}$ applied to three mature plants (one group) 43.2 mg. [d] Total avermectin $B_{1a}$ applied to one immature plant 0.864 mg; total avermectin $B_{1a}$ applied to one mature plant 2.16 mg.

**Table II. Ratio of Radiolabeled Residues of Avermectin $B_{1a}$ in Celery Leaves/Stalks**

| postharvest interval | treatment[a] [$^3$H]AVM-$B_{1a}$ 0.01 lb/acre | [$^3$H]AVM-$B_{1a}$ 0.10 lb/acre | [$^{14}$C]AVM-$B_{1a}$ 0.015 lb/acre |
|---|---|---|---|
| | Immature Plants | | |
| 0 | 4.96 | 4.16 | 8.25 |
| 7 | 4.03 | 3.46 | |
| 14 | 3.30 | 3.16 | 3.65 |
| 29 | 3.72 | 5.01 | |
| 43 | 2.80 | 4.48 | |
| | Mature Plants | | |
| 0 | 6.78 | 5.35 | 14.0 |
| 1 | 8.33 | 6.56 | |
| 3 | 9.55 | 8.09 | |
| 7 | 11.5 | 4.76 | 9.85 |
| 15 | 11.8 | 12.6 | |
| 22 | 10.1 | 9.00 | |

[a] Ratios calculated from data presented in Table I.

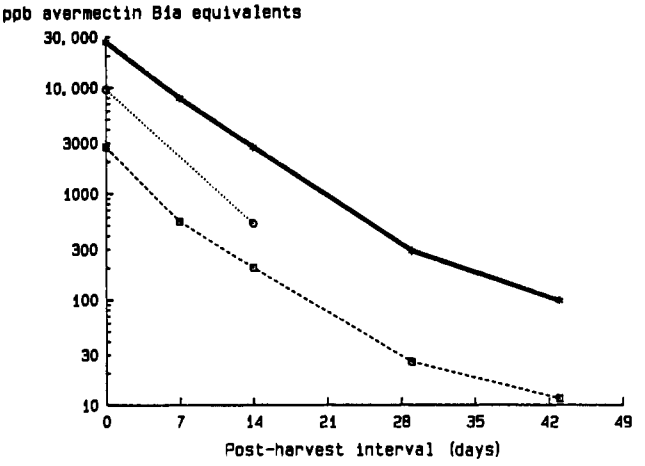


**Figure 2.** Radiolabeled residues remaining in leaves of avermectin $B_{1a}$ treated immature celery. Key: (—) 0.10 lb/acre $^3$H, one group; (O···O) 0.015 lb/acre $^{14}$C, mean of two plants; (□- -□) 0.01 lb/acre $^3$H, mean of two groups.

the half-lives of $^3$H-labeled AVM-$B_{1a}$ in leaves and stalks of both immature and mature celery plants treated at 0.10 lb of AI/acre were very similar (range 4.6–5.8 days). The half-life range of $^3$H-labeled AVM-$B_{1a}$ in leaves and stalks of plants treated at the 0.01 lb of AI/acre was 5.6–9.0 days. The half-lives calculated for total radiolabeled [$^3$H]AVM-$B_{1a}$ residues range from 5.2 to 9.2 days and 6.3 to 12.9 days in leaves and stalks of plants treated at 0.10 and 0.01 lb of AI/acre, respectively. While the half-lives of total radiolabeled residues were consistently longer in mature plants than in immature plants under both treatments, the significance of these differences could not be tested due to the small number of plant groups examined (two at each PHI sampling at the 0.01 rate and one at each PHI sampling at the 0.10 rate).

Half-lives of [$^{14}$C]AVM-$B_{1a}$ were not calculated due to the small number of data points that could be used to generate a dissipation curve. However, the initial slope of the dissipation curve for [$^{14}$C]AVM-$B_{1a}$-treated plants is not markedly different from those of [$^3$H]AVM-$B_{1a}$-treated plants (Figures 2–5), which suggests a similar half-life for [$^{14}$C]AVM-$B_{1a}$.

**Acetone-Extractable Radioactivity.** The percentage of total radioactivity and total equivalents of AVM-$B_{1a}$ extractable from celery leaves and stalks decreased

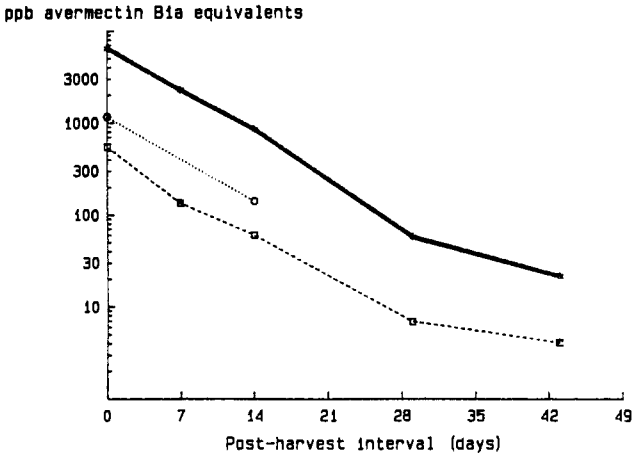


**Figure 3.** Radiolabeled residues remaining in stalks of avermectin $B_{1a}$ treated immature celery. Key: (—) 0.10 lb/acre $^3H$, one group; (O···O) 0.015 lb/acre $^{14}C$, mean of two plants; (□- -□) 0.01 lb/acre $^3H$, mean of two groups.

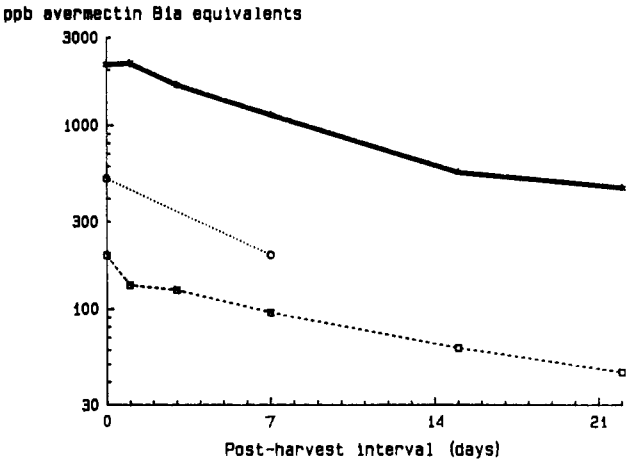


**Figure 4.** Radiolabeled residues remaining in leaves of avermectin $B_{1a}$ treated mature celery. Key: (—) 0.10 lb/acre $^3H$, one group; (O···O) 0.015 lb/acre $^{14}C$, mean of two plants; (□--□) 0.01 lb/acre $^3H$, mean of two groups.

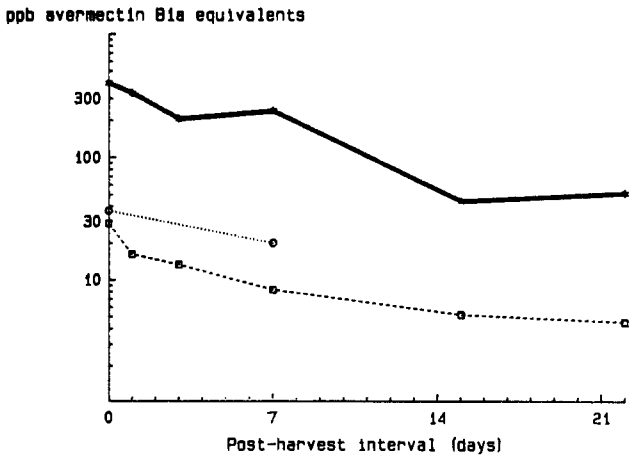


**Figure 5.** Radiolabeled residues remaining in stalks of avermectin $B_{1a}$ treated mature celery. Key: (—) 0.10 lb/acre $^3H$, one group; (O···O) 0.015 lb/acre $^{14}C$, mean of two plants; (□- -□) 0.01 lb/acre $^3H$, mean of two groups.

with increasing PHI under most AVM-$B_{1a}$ treatments (Table IV). The percentages of acetone-extractable radioactivity were generally greater in stalks than in the corresponding leaves of all plants under all AVM-$B_{1a}$ treatments.

The results of high-performance liquid chromatographic studies of acetone extracts of celery parts are presented in Table V. The percentage of radioactivity in the acetone extracts represented by polar metabolites in all plant parts under all conditions of AVM-$B_{1a}$ application generally increased with increasing PHI. An exception to this trend was found in stalks of immature celery treated with [$^3H$]AVM-$B_{1a}$ at both application rates. In these stalks there was an early increase in the percentage of polar as well as moderately polar metabolites present at PHI's of 7 or 14 days followed by a decline. This was the reciprocal of the pattern of the percentage of AVM-$B_{1a}$ present in these samples over this same period.

When measured from the first harvest date, the increase in the percentage of polar metabolites present was consistently greater in immature than in mature plants. Polar metabolites represented a greater percentage of the total components present in leaves than that present in their corresponding stalks at PHI's greater than zero under all AVM-$B_{1a}$ treatments. In direct contrast to the pattern of polar metabolites, the relative percentage of radiolabeled AVM-$B_{1a}$ in acetone extracts of [$^3H$]AVM-$B_{1a}$-treated plants generally decreased with increasing PHI with the exception of immature celery stalks under both treatments. The pattern in these stalks was an initial decrease in the percentage of AVM-$B_{1a}$ followed by an increase. This biphasic trend was the converse of that observed for polar metabolites in these stalks during the same harvest period. As was the case for polar metabolites, the magnitude of the decreasing trend in the percentage of AVM-$B_{1a}$ in all groups other than immature stalks was consistently greater in immature than in mature plants when measured from the first harvest date. Also in direct contrast to the pattern of polar metabolites in acetone extracts of [$^3H$]AVM-$B_{1a}$-treated plants, stalks of all mature plants and immature plants treated at the 0.10 lb/acre rate contained a greater proportion of AVM-$B_{1a}$ than did their corresponding leaves (Table V).

The pattern of the percentage composition represented by moderately polar metabolites and the $\Delta^{8,9}$ isomer of AVM-$B_{1a}$ was generally irregular during harvest periods for all groups (Table V). Stalks of mature plants treated at 0.01 lb/acre contained a greater proportion of moderately polar metabolites and the $\Delta^{8,9}$ isomer of AVM-$B_{1a}$ than did their corresponding leaves. However, a similar relationship was not consistently present in immature plants nor in plants treated at the 0.10 lb of AI/acre rate.

Increasing the application rate of [$^3H$]AVM-$B_{1a}$ by 10-fold did not produce a marked or consistent change in the pattern of metabolites in acetone-extract filtrates of harvested celery plants. Also, the metabolic patterns and relative proportions of metabolites of [$^{14}C$]AVM-$B_{1a}$ were not substantially different from those observed in plants treated with [$^3H$]AVM-$B_{1a}$. The single exception to this statement was the finding of almost equivalent percent-

**Table III. Half-Life[a] (Days) of [$^3H$]Avermectin $B_{1a}$ and Total $^3H$-Labeled Residues in Celery Leaves and Stalks Treated with [$^3H$]Avermectin $B_{1a}$**

| | [$^3H$]AVM-$B_{1a}$[b] | | total [$^3H$]AVM-$B_{1a}$ residues | |
|---|---|---|---|---|
| | 0.01 lb/acre | 0.10 lb/acre | 0.01 lb/acre | 0.10 lb/acre |
| | | Immature Plants | | |
| leaves | 5.6 | 5.1 | 6.3 | 5.6 |
| stalks | 8.4 | 4.6 | 6.8 | 5.2 |
| | | Mature Plants | | |
| leaves | 7.9 | 5.8 | 12.9 | 9.2 |
| stalks | 9.0 | 5.3 | 11.2 | 7.1 |

[a] Half-life calculated from $t_{1/2} = 0.693/k$; $\ln [A] = \ln [A]^0 - kt$. [b] Calculated from acetone-extractable radioactivity and subsequent HPLC separation of extracted components.

**Table IV. Acetone-Extractable Radioactivity[a] in Celery Plants**

| postharvest interval | total radioactivity found in celery parts, % [extractable + unextractable (MAT)] | | | | | |
|---|---|---|---|---|---|---|
| | leaves | | | stalks | | |
| | [$^3$H]AVM-$B_{1a}$, 0.01 lb/acre | [$^3$H]AVM-$B_{1a}$, 0.10 lb/acre | [$^{14}$C]AVM-$B_{1a}$, 0.015 lb/acre | [$^3$H]AVM-$B_{1a}$, 0.01 lb/acre | [$^3$H]AVM-$B_{1a}$, 0.10 lb/acre | [$^{14}$C]AVM-$B_{1a}$, 0.015 lb/acre |
| | | | Immature Plants | | | |
| 0 | 95.8 | 96.6 | 97.1 | 97.0 | 95.2 | 96.0 |
| 7 | 80.6 | 78.3 | | 83.3 | 78.9 | |
| 14 | 71.4 | 68.2 | 69.9 | 82.1 | 74.0 | 74.2 |
| 29 | 73.1 | 63.6 | | 75.4 | 73.6 | |
| 43 | 68.9 | 65.6 | | 83.5 | 83.1 | |
| | | | Mature Plants | | | |
| 0 | 70.9 | 75.3 | 73.7 | 79.8 | 85.1 | 75.5 |
| 1 | 69.6 | 77.0 | | 78.7 | 92.0 | |
| 3 | 66.9 | 76.4 | | 79.0 | 78.0 | |
| 7 | 66.4 | 64.2 | 57.8 | 70.9 | 81.3 | 67.0 |
| 15 | 62.7 | 68.6 | | 71.8 | 83.7 | |
| 22 | 57.9 | 66.4 | | 69.1 | 77.5 | |

[a] Values for [$^3$H]avermectin $B_{1a}$ treated plants (0.01 rate) represent the mean of values for two groups (three plants/group). Values for [$^3$H]avermectin $B_{1a}$ treated plants (0.10 rate) represent the value from one group (three plants/group). Values for [$^{14}$C]avermectin $B_{1a}$ treated plants represent the mean of values for two plants.

**Table V. Metabolism of Avermectin $B_{1a}$ and Its Metabolites in Acetone Extracts of Celery**

| days after first applicn | postharvest interval | [$^3$H]AVM-$B_{1a}$ (0.01 lb/acre) (mean value from 2 gps, 3 plants/gp) | | | | [$^3$H]AVM-$B_{1a}$ (0.10 lb/acre) (single group, 3 plants/gp) | | | | [$^{14}$C]AVM-$B_{1a}$ 0.015 lb/acre) (mean value from 2 plants) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | % polar metabolites | % moderately polar metabolites | % $B_{1a}$ | % $\Delta^{8,9}$ isomer | % polar metabolites | % moderately polar metabolites | % $B_{1a}$ | % $\Delta^{8,9}$ isomer | % polar metabolites | % moderately polar metabolites | % $B_{1a}$ | % $\Delta^{8,9}$ isomer |
| | | | | | | Immature | | | | | | | |
| | | | | | | Leaves | | | | | | | |
| 19 | 0 | 4.3 | 16.5 | 73.4 | 5.3 | 3.3 | 14.1 | 74.9 | 7.7 | 4.7 | 19.2 | 65.3 | 10.8 |
| 26 | 7 | 54.5 | 19.9 | 21.2 | 4.4 | 50.3 | 22.3 | 22.8 | 4.5 | | | | |
| 33 | 14 | 53.1 | 22.8 | 18.7 | 5.3 | 50.0 | 19.8 | 25.6 | 4.6 | 62.0 | 17.0 | 15.8 | 5.2 |
| 48 | 29 | 66.2 | 18.2 | 14.3 | 1.4 | 69.8 | 13.0 | 14.5 | 2.6 | | | | |
| 62 | 43 | 68.4 | 14.8 | 15.8 | 1.1 | 61.3 | 12.2 | 20.5 | 5.9 | | | | |
| | | | | | | Stalks | | | | | | | |
| 19 | 0 | 4.8 | 22.8 | 67.7 | 4.6 | 3.3 | 15.3 | 80.7 | 0.7 | 5.6 | 28.5 | 54.8 | 11.2 |
| 26 | 7 | 42.3 | 27.2 | 27.0 | 3.6 | 36.0 | 32.1 | 28.2 | 3.6 | | | | |
| 33 | 14 | 33.4 | 22.3 | 37.1 | 4.6 | 43.4 | 19.7 | 30.7 | 6.2 | 50.9 | 14.9 | 29.2 | 5.0 |
| 48 | 29 | 34.6 | 19.6 | 43.3 | 2.6 | 33.4 | 21.0 | 37.5 | 8.1 | | | | |
| 62 | 43 | 22.7 | 20.3 | 56.1 | 1.0 | 30.4 | 24.9 | 38.6 | 6.1 | | | | |
| | | | | | | Mature | | | | | | | |
| | | | | | | Leaves | | | | | | | |
| 75 | 0 | 61.0 | 19.7 | 15.2 | 4.0 | 42.2 | 19.8 | 33.0 | 5.0 | 33.8 | 22.5 | 38.6 | 5.2 |
| 76 | 1 | 63.4 | 19.0 | 14.5 | 3.1 | 46.2 | 23.7 | 23.9 | 6.2 | | | | |
| 78 | 3 | 67.3 | 17.4 | 12.7 | 2.6 | 65.1 | 19.4 | 11.5 | 4.0 | | | | |
| 82 | 7 | 68.3 | 16.7 | 11.4 | 2.7 | 63.7 | 18.8 | 14.8 | 2.7 | 71.6 | 16.2 | 9.8 | 2.1 |
| 90 | 15 | 72.3 | 14.5 | 10.6 | 1.9 | 66.7 | 19.5 | 9.9 | 3.9 | | | | |
| 97 | 22 | 80.1 | 11.5 | 7.5 | 1.0 | 71.7 | 17.7 | 8.3 | 2.1 | | | | |
| | | | | | | Stalks | | | | | | | |
| 75 | 0 | 36.2 | 17.9 | 36.3 | 4.7 | 22.3 | 18.5 | 56.6 | 2.7 | 43.0 | 18.3 | 31.6 | 7.1 |
| 76 | 1 | 41.3 | 25.2 | 30.3 | 3.3 | 26.0 | 17.0 | 55.6 | 1.3 | | | | |
| 78 | 3 | 35.3 | 24.8 | 36.4 | 3.3 | 34.2 | 18.9 | 43.7 | 3.3 | | | | |
| 82 | 7 | 42.5 | 20.7 | 32.4 | 4.1 | 31.4 | 19.2 | 44.0 | 5.4 | 66.7 | 12.2 | 17.2 | 3.5 |
| 90 | 15 | 48.1 | 20.6 | 26.4 | 4.2 | 39.9 | 21.8 | 31.4 | 6.9 | | | | |
| 97 | 22 | 51.5 | 15.4 | 28.3 | 4.8 | 48.3 | 14.1 | 29.6 | 8.1 | | | | |

ages of polar metabolites and AVM-$B_{1a}$ in mature leaves treated with [$^{14}$C]AVM-$B_{1a}$ at the zero PHI.

The results of the analysis of the soil in which the celery was grown show that much of the radioactivity applied to the plants was found in the soil at the times of harvest (Table VI). The probable source of this radioactivity is runoff of radiolabeled AVM-$B_{1a}$ that occurred during application or following rainfall events. This runoff was readily observable at the time of application and was greater during AVM-$B_{1a}$ applications to immature plants than during application to mature plants that had larger foliar surface areas. The measured radioactivity in the soil layers analyzed reflects the effects of at least three independently covarying factors: the amount of applied AVM dripping from the plant onto the soil, the distance of the sampling site from the sprayed plant, and the depth of the soil sample. Consequently, the uppermost soil layer does not always contain the greatest amount of radioactivity.

## DISCUSSION

The results of the present study document the profiles of radiolabeled AVM-$B_{1a}$ and its breakdown products in celery plants treated at three different rates.

Table VI. $^{3}H$ and $^{14}C$ Radioactivity in Muck Soils (ppb)

| days after last applicn | | [$^{3}H$]AVM (0.01 lb/acre) (mean, 2 gps) | [$^{3}H$]AVM (0.10 lb/acre) (gp 1) | [$^{14}C$]AVM (0.015 lb/acre) (mean, 2 plants) |
|---|---|---|---|---|
| | | Immature Celery | | |
| 0 | top | 228 | 2920 | 1650 |
| | middle | 116 | 2110 | 664 |
| | bottom | 121 | 4220 | 370 |
| 7 | top | 888 | 3860 | |
| | middle | 433 | 1820 | |
| | bottom | 439 | 4690 | |
| 14 | top | 362 | 9810 | 592 |
| | middle | 176 | 4980 | 361 |
| | bottom | 213 | 3750 | 467 |
| 29 | top | 130 | 3260 | |
| | middle | 79 | 1120 | |
| | bottom | 38 | 932 | |
| 43 | top | 190 | 3010 | |
| | middle | 142 | 2100 | |
| | bottom | 131 | 2020 | |
| | | Mature Celery | | |
| 0 | top | 284 | 5850 | 847 |
| | middle | 100 | 1700 | 273 |
| | bottom | 105 | 1460 | 787 |
| 1 | top | 336 | 2680 | |
| | middle | 247 | 2950 | |
| | bottom | 162 | 842 | |
| 3 | top | 236 | 1570 | |
| | middle | 228 | 1040 | |
| | bottom | 293 | 542 | |
| 7 | top | 288 | 2330 | 175 |
| | middle | 208 | 1060 | 109 |
| | bottom | 56 | 541 | 159 |
| 15 | top | 66 | 1260 | |
| | middle | 45 | 389 | |
| | bottom | 44 | 445 | |
| 22 | top | 52 | 663 | |
| | middle | 37 | 2800 | |
| | bottom | 660 | 292 | |

Although less than 4% of the applied radioactivity remained in the plants, this residual AVM-$B_{1a}$, together with its breakdown products, was sufficient to permit the study of the pattern of AVM-$B_{1a}$ metabolites in immature and mature plants harvested at various PHIs.

The maximum recovery of applied radioactivity in the present study (<4.0%) is substantially lower than the maximum recovery of $^{3}H$ radioactivity from leaves of cotton seedlings treated with [$^{3}H$]AVM (100% at zero time; Bull et al., 1984). This discrepancy in the results of the two studies is probably attributable, in part, to the difference in the volume in which the initial AVM was applied (150 μL in the Bull et al. study and 6.0 mL in the present study) and the subsequent runoff loss of most of the applied AVM in the present study as reflected by the radioactivity found in the soils. Other factors contributing to the low recoveries of leaf and stalk radioactivity in the present study in celery samples taken after zero time were rainfall events and possibly volatilization of radiolabeled fragments following photodecomposition of the molecule (Bull et al., 1984).

It is important to note that, as a result of the preferential application of AVM-$B_{1a}$ to the leaves of celery plants in this study, concentrations of the parent compound and its breakdown products were higher in the leaves than in the stalks of these plants (Tables I and II). This effect is emphasized in mature plants treated 10 times with radiolabeled AVM-$B_{1a}$ (leaf/stalk ratios of radioactivity of 4.76–14.0) when compared to immature plants that were treated only 4 times (leaf/stalk ratios of radioactivity of 2.80–8.25). The greater amount of AVM-$B_{1a}$ applied to leaves than to stalks may have been the basis of some of the metabolic patterns observed in this study (see below).

The half-lives of the total $^{14}C$ radioactive residues and [$^{14}C$]AVM-$B_{1a}$ in the present study, 5.2–12.9 and 4.6–9.0 days, respectively, are shorter than those calculated in a similar manner (disregarding the initial disappearance from zero time to the first PHI) and reported in studies of citrus (56–98 and 20–38 days, respectively; Maynard et al., 1989a). The shorter half-lives in the present study are probably due, in part, to losses produced by precipitation, a factor controlled by a fiberglass roof in the Maynard et al. (1989a) study. The phenomenon of a slower degradation rate (longer half-life) of AVM-$B_{1a}$ at lower application rates has also been observed on the surface of oranges (Maynard et al., 1989a).

The decrease in the percentage of acetone-extractable total radioactivity with increasing PHI under most AVM-$B_{1a}$ treatments indicates a disappearance of the parent compound relative to acetone-unextractable components. This phenomenon has been observed also in the rind of citrus fruits (Maynard et al., 1989a). This may have occurred via metabolism and/or by photodegradation of AVM-$B_{1a}$. The non-acetone-extractable radioactivity remaining in the celery may reflect the incorporation of small molecular weight degradation products of AVM-$B_{1a}$ into the natural products of the plant as has been observed in both cotton plants and oranges (Maynard et al., 1989a,b). AVM-$B_{1a}$ has also been shown to rapidly photodegrade in water and on a number of surfaces including soil, citrus fruit, leaves, and glass (Ku et al., 1983; Maynard et al., 1989a,b). Either or both of these mechanisms may have been operative in reducing the relative amount of the parent compound present in harvested plants over the time period of this study.

The finding of generally greater percentages of acetone-extractable radioactivity in stalks than in the corresponding leaves of all plants under all AVM-$B_{1a}$ treatments suggests that there exists in leaves as compared to stalks a relatively more active metabolism of AVM-$B_{1a}$ to compounds not readily extractable with acetone. This may be due to an intrinsic difference in the metabolic activity of the two plant parts or to the greater amounts of AVM-$B_{1a}$ applied to the leaves than to the stalks at each application time. Also likely is a more rapid photodegradation of the parent compound on leaves than on stalks due to the greater exposure of leaves to sunlight.

The existence of a more active metabolism and/or a more rapid breakdown of AVM-$B_{1a}$ in leaves than in stalks is also suggested by the pattern of metabolites isolated by HPLC of the acetone extracts of celery parts (Table V). The general metabolite pattern observed in acetone extracts of immature and mature plants under all treatments was one of greater percentages of polar metabolites and smaller percentages of the parent compound in leaves than in their corresponding stalks at all PHIs. This pattern was apparently not affected by a 10-fold difference in application rate from 0.01 to 0.10 lb of AI/acre.

**Registry No.** Avermectin $B_{1a}$, 65195-55-3.

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# Atrazine in Organic Soil: Chemical Speciation during Heterogeneous Catalysis†

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Two Brönsted acid catalysts are known to cause the hydrolysis of atrazine. They are $H^+$ and un-ionized carboxyl groups, both of which can exist in organic soils. When hydroxyatrazine is the only reaction product, there are four chemical species. These are the reactant and product in both free and sorbed states. A typical heterogeneous kinetics experiment would monitor only one or two of these. An HPLC technique has now been demonstrated however, which monitors five chemical species during the course of heterogeneous catalysis experiments. These are solution-phase reactant and product, reversibly sorbed reactant and product, and material balance loss. A 2-week experiment can produce equilibrium and rate constants for sorption and the reaction rate constant. These are relevant to the persistence and movement of atrazine in soils. The constants are consistent with those previously found for a humic acid.

The prediction and management of pesticide behavior in soils require several types of physical and chemical information. These include the kinetics and equilibria of sorption, the kinetics of chemical reactions, and chemical speciation. The sorption parameters are related to pesticide movement in soils, and reaction rate constants are related directly to their persistence. For soils with high organic matter content, the types, amounts, and chemical reactivity of organic chemical functional groups will also have to be known. The quantitative functional group information is necessary for the use of exact chemical stoichiometry.

Atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine] is a widely used selective herbicide for the control of annual grasses and broad-leaved weeds. When it is applied to a soil containing high levels of organic matter, the important phenomena might include reversible sorption of atrazine, catalyzed hydrolysis of the atrazine, reversible desorption of hydroxyatrazine reaction product, and a material balance loss. If the chemical reaction in a heterogeneous catalysis system yields only one reaction product, then a complete description of the system would require four chemical analyses. The amounts of reactant and product would have to be measured in both the free and sorbed states. The monitoring of all four variables throughout a kinetics experiment has usually not been practical. Frequently only the product in the free state is measured. In such cases, important information is lost. In our earlier work we demonstrated an indirect calculation technique by which it was possible to obtain some of the required information (Gamble and Khan, 1988). However, to get better insight into the foregoing processes, direct experimental measurements are preferable.

According to Mill (1980), a widely held opinion is that laboratory tests are the key to effective assessment of environmental hazards. He states that well-designed laboratory tests will provide the necessary kinetics and equilibrium constants at a fraction of the cost of field tests. Chemical stoichiometry must be taken into account to establish quantitative relationships. Some authors have recognized (Freeman and Cheung, 1981; Karickhoff, 1984; Perdue and Wolfe, 1983) the importance of soil organic matter fractions (such as humic acid, acidic functional groups) to sorption and hydrolysis. This implies that they should be measured and accounted for in the interpretive calculations. This applies to hydrolysis, believed to be very important in chemical decomposition of pesticides in soils (Macalady and Wolfe, 1984; Perdue and Wolfe, 1982). In addition, Karickhoff and Morris (1985) have stated monitoring both physical phases is useful. At the level of general strategy, Wolfe (1980) has advised

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