or 20 days; however, neither amino analogues and other products sensitive to the P-specific detector nor hydrolysis products were detected. It is not clear, in the absence of isotope studies, whether this decrease in the levels of parent molecules was due to their binding by the soil or their conversion to other metabolites.

The degradation of fenitrothion and methyl parathion by hydrolysis in the first experiment (Table I) and by nitro group reduction in a subsequent experiment (Table IV) merits further discussion. The soil used in this study registered a redox potential of +100 mV after 10 days of flooding (at the time of insecticide addition) and −40 mV after 20 days of flooding (Table II). Evidently, significant nitro group reduction of parathion can occur at a potential of around −40 mV as reflected in the considerable accumulation of aminoparathion even at 6 days after application (16 days after flooding) in the first experiment (Table I). Under the same conditions, nitro group reduction of fenitrothion and methyl parathion was negligible. But, the same soil, with further reduction after prolonged flooding for 60–90 days, could effect substantial accumulation of amino analogues of fenitrothion and methyl parathion as it did with parathion (Table IV). Probably, nitro group reduction of dimethyl phosphorothioates occurs at a potential lower than that required for similar conversion in parathion. According to earlier reports, the degradation of fenitrothion in soils proceeds essentially by hydrolysis under nonflooded conditions (Takimoto et al., 1976; Spillner et al., 1979) and by nitro group reduction in predominantly anaerobic flooded soil (Takimoto et al., 1976). This is probably analogous to the hydrolysis of fenitrothion in flooded soil with relatively high potential in the first experiment (Table I) and its nitro group reduction under more reducing conditions (Table IV).

Of the two pathways implicated in the degradation of the organophosphorus insecticides used in this study, hydrolysis can be both chemical and microbiological while nitro group reduction is essentially microbiological. Chemical hydrolysis proceeds fairly rapidly under alkaline

conditions in the order methyl parathion > fenitrothion > parathion (Munnecke, 1976). But, in the enzymatic hydrolysis, parathion was the least persistent when a cell-free suspension from a mixed bacterial culture readily hydrolyzed parathion but not methyl parathion and fenitrothion (Munnecke, 1976). Likewise, the data presented in this study showed that parathion is the least persistent of all three insecticides when the major pathway in their degradation is nitro group reduction. Thus, the relative stability of the selected organophosphorus insecticides is related to the pathway operating and the agents (chemical and/or microbial) involved in their degradation.

ACKNOWLEDGMENT

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Volatilization and Exudation Losses of Three *N*-Methylcarbamate Insecticides Applied Systemically to Rice

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Rice seedlings were treated by a root-soak systemic method or by foliage spray with carbofuran, carbaryl, or aldicarb. Distribution of residues was followed for 10 days in a small glass chamber provided with air flow and illumination for 12 h each day. The plant culture medium, plant parts, outflow vapor trap, and chamber walls were analyzed for parent carbamate. For carbofuran, physical loss of systemically absorbed residue occurred by root exudation (1775 μg or 35.6% of the initial residue in plant tissue) and volatilization (290 μg or 5.8% of the initial residue in plant tissue). Comparable data for carbaryl and aldicarb were 1928 μg (22%) and 2280 μg (14%), respectively, for root exudation and 367 μg (4.2%) and 920 μg (5.6%), respectively, for volatilization. A rapid translocation of all three insecticides to leaves occurred after treatment; residues moved through the leaf tip to the outside leaf surface by guttation and were available for volatilization. The relative importance of steps contributing to volatilization was related to insecticide stability, water solubility, and vapor pressure.

Systemic *N*-methylcarbamate insecticides such as carbofuran have been shown to be effective against a number

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of important rice pests when applied to paddy soil or water (Pathak and Dyck, 1973; International Rice Research Institute, 1975). Treatments which place carbofuran within or near the root zone of the rice plant favor absorption and provide more effective and longer lasting control of foliage feeding insects than that obtained with broadcast applications to the paddy water (Aquino and Pathak, 1976). An

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alternate application method, designed to control rice insects for 2–3 weeks after transplanting, involves soaking seedling roots in aqueous carbofuran solution before transplanting. Seedlings take on a protective complement of insecticide principally in the leaves from this root-soak treatment (Pathak and Dyck, 1973).

Root-zone and root-soak treatments increase the efficiency of relatively expensive insecticides such as carbofuran. The extensive hydrolytic decomposition which may occur in natural paddy waters (Seiber et al., 1978a) is minimized as the bulk of the insecticide resides in the relatively buffered soil zone (Siddaramappa et al., 1978) or in the rice plant itself, in which carbofuran is also relatively stable. Nevertheless, initially high foliage residues of carbofuran (~500 ppm) in seedlings treated by root soak dropped off sharply within 50 days following treatment (to less than 1 ppm) when plants were maintained in the greenhouse and even more rapidly in the field (Seiber et al., 1978b). Too little of the known metabolites of carbofuran were formed during the dissipation period to explain the loss, pointing to the operation of physical loss routes as factors in residue decline. We subsequently reported preliminary evidence that carbofuran was physically lost from root soak treated rice seedlings by root exudation and volatilization (Ferreira and Seiber, 1978) while Siddaramappa and Watanabe (1979) provided further evidence for vapor loss of ^{14}C-labeled carbofuran from rice plants dosed in the culture medium or injected in the root zone with the insecticide.

The present report provides details on the pathways of dissipation for carbamates in rice by contrasting the behavior of systemic and topical (surface) residues. Three chemicals—carbofuran, carbaryl, and aldicarb—were selected to represent a range of physicochemical properties. Loss by physical processes was correlated with the water solubility, volatility, and reactivity of these three insecticides.

MATERIALS AND METHODS

Chemicals. The insecticides were greater than 99% pure and were used as received from their manufacturers: aldicarb [2-methyl-2-(methylthio)propionaldehyde O-(methylcarbamoyl)oxime; Union Carbide, New York, NY], carbaryl (1-naphthyl N-methylcarbamate; Union Carbide), and carbofuran (2,2-dimethyl-2,3-dihydro-7-benzofuranyl N-methylcarbamate; FMC, Middleport, NY). Insecticides employed in plant treatments were as follows: carbaryl as Sevin 4F (Stauffer Chemical Co., New York, NY); carbofuran as Furadan 4F (FMC); aldicarb as a solution of the analytical standard (Union Carbide) in water. Other chemicals were analytical reagent grade and used as received from commercial sources. Solvents were Nanograde, doubly distilled, or equivalent except for acetonitrile which was UV grade (Burdick and Jackson, Muskegon, MI). Other materials included the following: Florisil, 60–100 mesh (Floridin Co., Berkeley Springs, VA); Nuchar-Attaclay, acid washed (Kensington Scientific, Emeryville, CA); silica gel, particle size greater than 0.036 mm (Woelm, ICI Nutritional Biochemicals, Cleveland, OH); Hyflo supercell (Fisher Scientific, Santa Clara, CA); 20–50-mesh Amberlite XAD-4 and XAD-7 resins (Rohm and Haas, Philadelphia, PA), Soxhlet extracted with acetone prior to use.

Laboratory Chamber. A laboratory chamber was assembled by using as the body a Pyrex bell jar 17.5 cm in diameter and 37 cm in height (Figure 1). The base was plywood (50 × 45 × 2.5 cm) covered with heavy duty aluminum foil. A 10 cm diameter air disperser made of 0.6-cm (o.d.) copper tubing previously drilled with 1 mm diameter holes was connected to a charcoal-filtered air
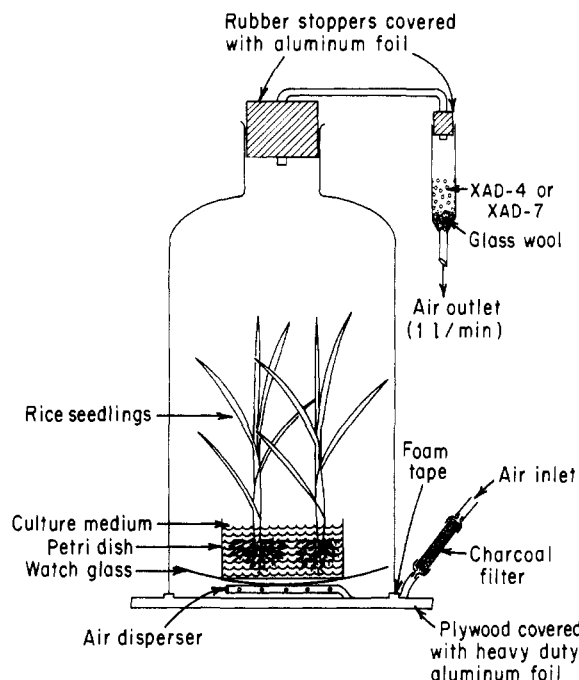

Figure 1. Laboratory chamber for maintaining plant growth.

supply outside the chamber. A 16 cm diameter watch glass was placed over the air disperser to collect water which fell from the leaf tips. The plants were kept in a 9.5 × 5 cm Petri dish supported on the watch glass. The chamber was sealed at the bottom with foam tape. The top was tightly fitted with a No. 13 rubber stopper covered with aluminum foil and connected via a 9-mm (o.d.) glass tube to a vapor trap containing 2 g of XAD-4 (carbaryl and carbofuran) or XAD-7 resin (aldicarb). The temperature was continuously recorded just outside the chamber by a Model 594 Hygro-Thermograph (Bendix Aviation, Baltimore, MD). Fluctuations were generally between 20 °C (night) and 35 °C (day).

The experiment was begun when treated rice seedlings (12–18 days old; Calrose 76 variety) were placed in the Petri dish along with 200 mL of a 9:1 dilution of Hoagland's solution (Hoagland and Arnon, 1950). Air was passed through the chamber at 1 L/min during a 12 h/day illumination cycle provided by two 30-W fluorescent Gro-Lux/F20T8-GRO lamps (Sylvania, Danvers, MA) and two 75-W incandescent Gro and Sho lamps (GE, Cleveland, OH). The chamber was opened briefly at 48-h intervals during which time resin was changed in the vapor trap, the jar walls were washed with acetone, and the volume of the culture medium was adjusted to 200 mL. The experiment was continued for 10 days after which time the plant parts, culture medium, outflow vapor traps, and chamber wall washings were prepared for analysis.

Treatments. For the root-soak treatment a batch of ~100 seedlings was placed in a 9.5 × 5 cm Petri dish containing 400 mL of a dilution corresponding to 500–800 ppm of insecticide in water made by mixing the appropriate amount of Sevin 4F (carbaryl), Furadan 4F (carbofuran), or analytical-grade aldicarb with water. The water dilutions gave partial solutions for carbaryl and carbofuran and a clear solution for aldicarb. The seedlings were soaked for 24 h which included 12 h of illumination. After the soaking, the roots were thoroughly rinsed with a vigorous flow of water to remove the insecticide adhering to root surfaces.

For the foliar spray treatment a batch of ~100 seedlings was inverted in a hood with the roots covered with aluminum foil. The plants were sprayed by using a glass

atomizer sprayer with 500–800 ppm of aqueous dilution of insecticide prepared by mixing the appropriate amount of formulation (carbaryl; carbofuran) or analytical standard (aldicarb) with water as for the root-soak treatments. The plants were sprayed until thoroughly wetted, allowed to dry, and then sprayed again—a process which was repeated until 150 mL of dilution was disbursed.

One-third of the seedlings treated by one of the above procedures was kept for analysis and the remainder was placed in the chamber.

Control plants were treated as described above and then cut 2 cm above the root juncture. The roots and stem stubs were placed in the chamber's Petri dish along with diluted Hoagland's solution such that no foliage was visible above the surface of the solution.

Plant Tissue Analysis. For carbofuran, 2–5 g of leaves, stems, or roots was extracted with 50 mL of acetone in a Waring blender for 5 min and filtered through Whatman No. 1 paper. The procedure was repeated with two 25-mL additional portions of acetone. The combined filtrates were concentrated to 5 mL by using a rotary evaporator and then mixed with 50 mL of coagulating solution (1.25 g of ammonium chloride and 1.0 mL of concentrated phosphoric acid in 1 L of water) and 0.5 g of Hyflo Super Cell. The mixture was agitated, allowed to stand for 1 hr, and then filtered through a sintered glass funnel. The filtrate, including a washing made with 50 mL of additional coagulating solution, was extracted with 30-, 15-, and 15-mL portions of dichloromethane. The extracts were dried (Na_2SO_4) and concentrated to 2 mL. A 1.7 × 30 cm glass column was slurry packed with, first, 5 g of silica gel in dichloromethane, second, 2 g of Nuchar-Attaclay, and, third, 3 g of sodium sulfate. The concentrated extract was added to the column by using a small volume of dichloromethane to complete the transfer and then eluted with 25 mL of dichloromethane, 60 mL of 1:1 ethyl acetate–hexane, and 50 mL of 7:3 ethyl acetate–hexane. The eluates were combined, concentrated just to dryness under nitrogen, and constituted in acetone for analysis by GLC. The average recovery for five fortifications at 8–1000 ppm of carbofuran was 94.7 ± 7.4%.

For carbaryl, the extraction and coagulation steps were as described for carbofuran. Cleanup was done on a 1.7 × 30 cm glass column slurry packed with 5 g of Florisil (previously deactivated with 2% water) in 1:1 dichloromethane–hexane and capped with sodium sulfate. The dichloromethane extract of the coagulation solution was concentrated to near dryness and then placed on the column in 5 mL of 1:1 dichloromethane–hexane. The column was eluted with 25 mL of dichloromethane which was discarded, 100 mL of 15:85 ethyl acetate–hexane, and 50 mL 20:80 ethyl acetate–hexane. The latter two eluates were combined and concentrated just to dryness under nitrogen and then reconstituted in acetone for GLC analysis. The average recovery for five fortifications at 8–1000 ppm of carbaryl was 94.8 ± 4.7%.

For aldicarb the spectrophotometric method of Johnson and Stransberry (1966) was employed with the following modifications. The color reagent was changed from α-naphthylamine (a suspected carcinogen) to *N*-1-naphthylethylenediamine dihydrochloride and, consequently, the wavelength of determination was changed to 550 nm. The average recovery for six fortifications at 5–500 ppm of aldicarb was 88.4 ± 9.5%.

Air, Chamber Walls, and Water Analysis. XAD resins from the traps were extracted by shaking for 1 h with each of three 30-mL portions of acetone. The combined extracts were concentrated and centrifuged if nec-

essary prior to analysis by high-performance LC. Acetone washings of the chamber walls were handled similarly. Water samples were analyzed by high-performance LC directly or following dilution with water.

Water Solubility Determinations. A 16 × 125 mm screw-cap test tube containing 10 mL of deionized water was clamped in a constant-temperature bath. After 1 h of equilibration, 0.5 g of crystalline *N*-methylcarbamate was added. The test tube was kept in the bath for 2 h except that it was removed briefly 3 times and vortexed vigorously for 30 s each time. After the third vortexing the test tube was kept for 30 min in the bath and then centrifuged. The solution was then filtered through a Millipore FH 0.5-μm filter (Millipore Corp., Bedford, MA), and an aliquot of the filtrate was diluted to a known volume with deionized water. Analysis was by high-performance LC.

Vapor Pressure Determinations. Sand (40 g) was coated in a rotary evaporator with 40 mg of *N*-methylcarbamate by slowly evaporating a dilute solution of the carbamate in dichloromethane. The sand was packed into a 28/15 Pyrex ball joint adapter by using glass wool wads to position the sand. Two grams of XAD-4 (carbaryl; carbofuran) or XAD-7 (aldicarb) was similarly placed in a 28/15 Pyrex socket joint adapter. The two adapters were clamped together such that the sand was in the bottom section and covered with aluminum foil to exclude light. A nitrogen flow of 50 mL/min was maintained for several days through the adapters from bottom to top. The assembly was kept in a constant-temperature bath (25 ± 0.1 °C) for the duration of the experiment. Upon termination the XAD-4 or XAD-7 resin and glass adapter from the upper section of the assembly were washed with 20-, 10-, and 10-mL portions of acetone with agitation provided by a gyrorotary shaker. The combined filtrates were concentrated to an appropriate volume for analysis by high-performance LC (carbaryl; carbofuran) or spectrophotometry (aldicarb). Vapor pressure was calculated from the perfect gas law equation assuming gas saturation conditions (Spencer and Cliath, 1969).

Hydrolysis Rate Determination. A 13 × 100 mm glass-stoppered test tube containing 5 mL of a sterilized buffer solution was charged with 50–100 μg of *N*-methylcarbamate from a stock solution in acetone. The solution was vortexed thoroughly and clamped in a constant-temperature bath. Just following mixing a 20-μL aliquot was withdrawn with a syringe for high-performance LC analysis. Additional aliquots were taken at several subsequent intervals. Rate constants and half-lives were determined by standard methods (Aly and El-Dib, 1972).

High-Performance LC Analysis. A high-performance LC system consisting of a 5000-psi pump with pulse dampener (mini Pump, Laboratory Data Control, Riviera Beach, FL), injection valve fitted with 20 μL loop (Rheodyne, Berkeley, CA), a 25-cm μBondapak C_{18} reversed-phase column (Waters Associates, Milford, MA), and a variable-wavelength UV–visible detector (Spectromonitor I, Laboratory Data Control) was used. The mobile phase was 40:60 acetonitrile–water delivered at 1.25 mL/min (1000 psi). The optimum UV wavelength and compound retention times were as follows: aldicarb, 247 nm, 6.0 min; carbofuran, 280 nm, 7.5 min; carbaryl 280 nm, 9.0 min.

GLC Analysis. A Hewlett-Packard Model 5710-A gas chromatograph with FID detectors was equipped with a 1.2 m × 2 mm (i.d.) glass column packed with 3% Apiezon L on 80–100-mesh Chromosorb W HP (Analabs, New Haven, CT). Injector and detector temperatures were 200 and 250 °C, respectively. Nitrogen carrier gas, hydrogen,
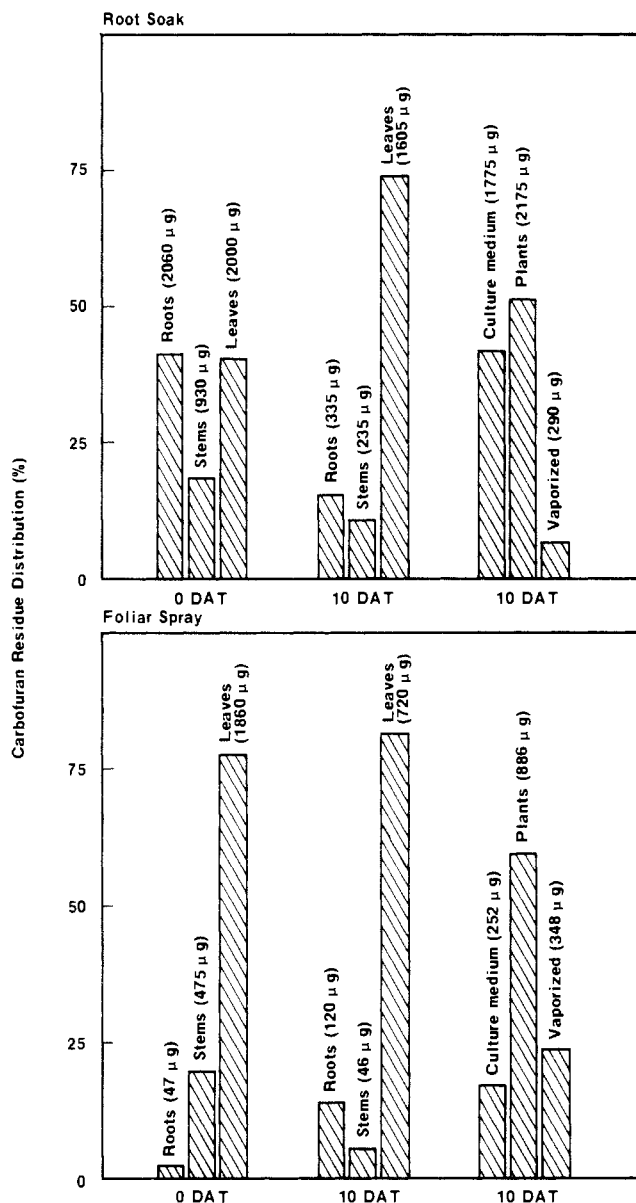
Figure 2. Carbofuran residue distribution in rice plants and chamber components at 0 and 10 days after treatment (DAT) by root soak and foliar spray. Each set of three bars is normalized to 100%.

and air flows were 28, 30, and 240 mL/min, respectively. Column temperatures were 165 °C (carbofuran) or 185 °C (carbaryl).

RESULTS AND DISCUSSION

The essence of our experimental method consisted of administering an N-methylcarbamate insecticide to rice seedlings and then following the distribution of the parent compound within the rice tissue and its exchange to the air and culture medium during a 10-day period in a laboratory chamber. A systemic root-soak treatment and foliar spray application were compared for each chemical.

Results for carbofuran are summarized in Figure 2. The overnight root-soak treatment gave an initial leaf residue of 2000 μg or 1053 ppm. An equivalent amount (2060 μg) was in the roots, and a smaller residue (930 μg) was in the stems. Considering that total biomass was 70, 19, and 11% for the roots, stems, and leaves, respectively, it was clear that residue favored the leaves upon completion of the root-soak treatment. By 10 days after treatment, carbofuran residue in the plant had declined to 44% (2175 μg) of its initial value, and tissue distribution was more pro-

nounced toward the leaves than at the beginning of the experiment. Considering both absolute quantities and relative biomass, the residue of parent carbofuran in the roots and stems after 10 days was quite small.

Of the carbofuran lost from plant tissue during the 10-day period (2815 μg), a major proportion (1775 μg) was in the culture medium. This could include some chemical left on the root surface following soaking although the effort made to remove most of this excess prior to placing the treated plants in the medium would argue against a substantial contribution from this source. Principally, the culture medium residue after 10 days reflects exudation of carbofuran from roots to the medium. We determined that the half-life for hydrolysis of carbofuran at the average pH (7.09) and temperature (30 °C) of the culture medium was 308 h so that potentially up to 39% of the exuded parent carbamate could have hydrolyzed in the 10-day period.

A smaller quantity (290 μg or 6.8% of the initial plant residue) was recovered in the vapor trap and from the chamber walls during the 10-day experiment with whole plants (Figure 2). Control plants, that is, those treated similarly with carbofuran but lacking foliage, liberated insignificant amounts of carbofuran as vapors (18 μg) even though exuded chemical present in the culture medium after 10 days (2000 μg) was comparable to that obtained from treated plants with foliage. This argues against volatilization of significant amounts of carbofuran from the culture medium and points to the foliage as the source of evaporated residue from whole plants.

Foliar application of carbofuran gave initial residues almost exclusively in the stems and leaves (2382 μg; Figure 2). By 10 days after treatment 886 μg or 37.3% of the initial residue remained in the plant, principally in the leaves and roots. Of the residue lost from the plant, 252 μg (10.6% of the initial plant residue) was in the culture medium and 348 μg (14.8%) had evaporated. There was 904 μg (37.9%) unaccounted for, some of which may have been lost by hydrolysis in the culture medium, as noted previously, or by breakdown in the plant tissue.

Similar analyses were carried out for carbaryl (Figure 3) and aldicarb (Figure 4). In both cases systemic application resulted in substantial losses (22% of the initial residue of carbaryl in plant tissue; 14% for aldicarb) to the culture medium by root exudation, while a small quantity (367 μg or 4.2% of the initial residue of carbaryl in plant tissue and 920 μg or 5.6% for aldicarb) had volatilized. Once again, analysis of control plants showed clearly that evaporation had taken place principally from plant foliage surfaces rather than from the culture medium. Overall accountability based on parent material was 51% for carbaryl and 23.9% for aldicarb after 10 days in the chamber. The relatively rapid metabolism of aldicarb by oxidation (Metcalf et al., 1966) was a likely major factor in overall dissipation of this chemical. Hydrolytic reactivities at pH 7 and 30 °C for carbaryl ($t_{1/2}$ = 87 h) and aldicarb ($t_{1/2}$ = 1170 h) would indicate that hydrolysis of the parent compounds in the culture medium was important in the dissipation of carbaryl but not of aldicarb in these chamber experiments.

Results from foliar applications indicated that both carbaryl and aldicarb exited to the culture medium to a greater extent than carbofuran and that carbaryl residues favored the plant's stems relative to the other two insecticides after 10 days. Accountability for parent carbaryl was the lowest among the three chemicals following the 10-day tests with foliar applications, a possible reflection of its greater distribution to the culture medium where it

Losses of N-Methylcarbamate Insecticides

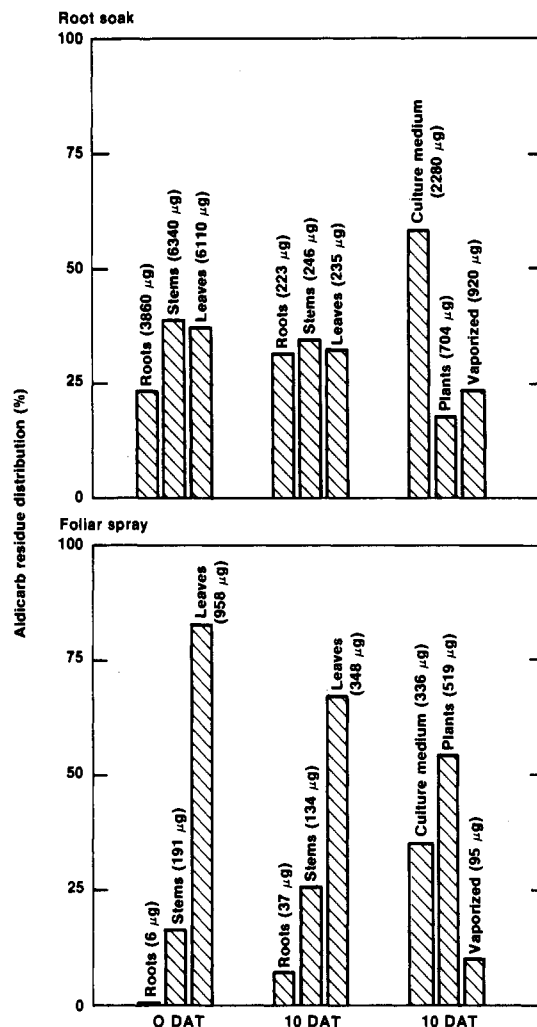J. Agric. Food Chem., Vol. 29, No. 1, 1981   97
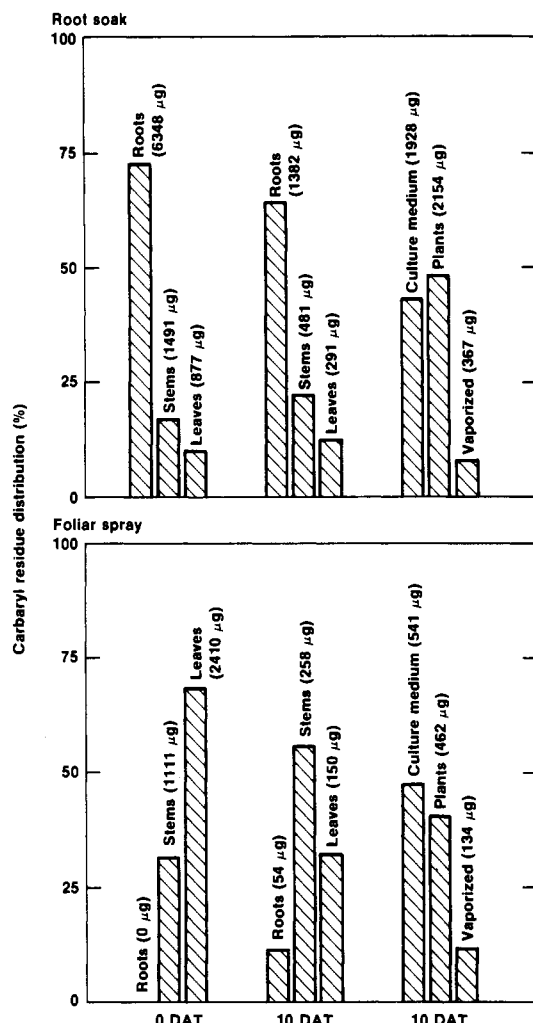
Figure 3. Carbaryl residue distribution in rice plants and chamber components at 0 and 10 days after treatment (DAT) by root soak and foliar spray.

Figure 4. Aldicarb residue distribution in rice plants and chamber components at 0 and 10 days after treatment (DAT) by root soak and foliar spray.

is the least stable of the three chemicals toward hydrolysis. Both carbaryl and aldicarb underwent measurable vaporization but in lesser total quantities than for carbofuran.

The results of the chamber experiments thus pointed to two physical processes as of importance in the elimination of systemic carbamates from rice plants. The major one, root exudation, was predictable considering the extreme concentration gradient which existed from root to culture medium for plants freshly treated by root soaking and by analogy with other organic chemicals known to be lost by this process. Mitchell and Linder (1963), for example, reported on the root exudation of several chemicals, including herbicides, applied to the foliage of plants. Among the classes of compounds known to leak out of roots following systemic treatment are phenylacetic and benzoic acids (Linder et al., 1964), (phenyloxy)acetic acids (Neidermyer and Nalewaja, 1969), and picolinic acid (Reid and Hurtt, 1970; Sharma et al., 1971), many of which could be expected to have solubilities comparable to those of the compounds studied here. The root loss was reported to take place in substantial quantities within 24 h following to the leaves, frequently without alteration of the parent compound.

It was less obvious to us how volatilization losses of systemically applied chemicals could occur from the rice plants. Our results clearly showed that all three carbamates underwent such a loss and that the proportion of each compound lost by this route was comparable to or exceeded evaporative losses from plants treated topically.

We thus examined our experimental data in several ways to help delineate the pathway for the observed volatilization of systemic residues.

Even though the water solubilities of the three test compounds varied considerably, there was practically no difference in the initial amounts of each chemical absorbed by the plants on a part per million basis (Table I). The apparently much greater quantity absorbed for aldicarb (Figure 4) was due to a larger plant size in the aldicarb experiment. Differences appeared in distribution by plant part; the least soluble chemical (carbaryl) was localized principally in the roots after soaking, while the more water soluble chemicals (aldicarb and carbofuran) showed greater initial movement to the leaves. The ratio of chemical in the leaves to that in the roots just after soaking (Table I) was in fact clearly related to water solubility.

Analysis of 2-cm segments of the leaf showed that all three insecticides were concentrated in the tip segment but less so for the least water soluble compound (carbaryl) than for carbofuran and aldicarb (Table I). Once again, the ratio of percent of chemical in the leaf tips to that in a leaf segment 6–8 cm from the tip was related to water solubility. Roughly the same trend was evident in leaf segments analyzed 10 days after dosing.

Carbamates are known to be transported rapidly to leaf tissue following absorption through the roots, a fact which helps explain their effectiveness as pest control agents. BPMC, for example, was concentrated in the apical or subapical part of rice within 24 h after dipping in an
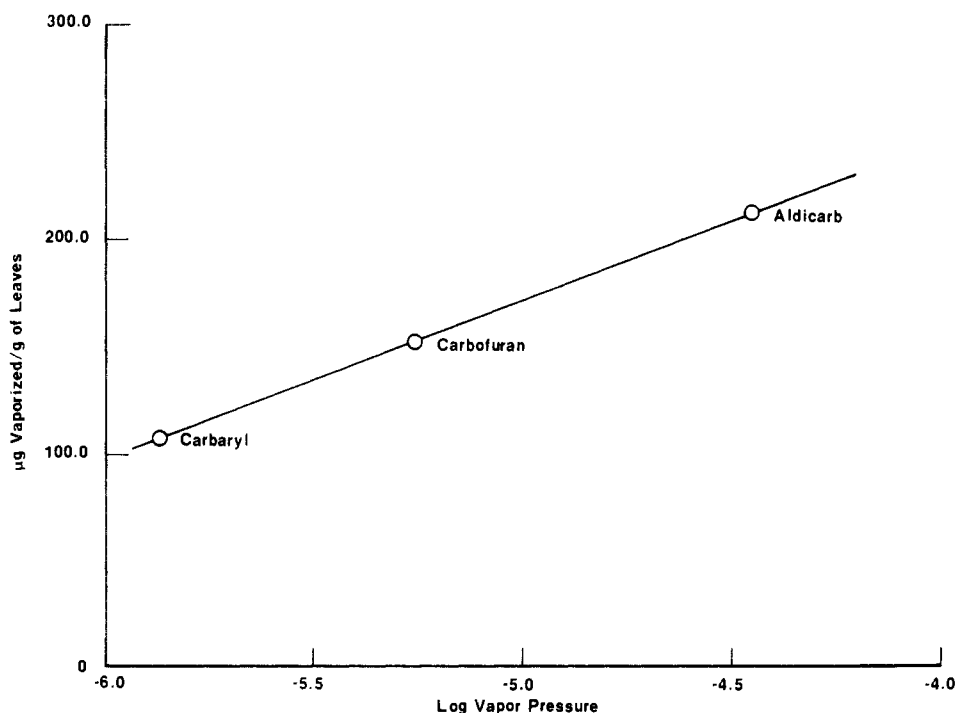
Figure 5. Relationship between quantity of insecticide lost by volatilization (normalized for leaf weights) and vapor pressure.

Table I. Uptake and Distribution of N-Methylcarbamates following Root Soak Treatment

	carbaryl	carbo-furan	aldicarb
water solubility, µg/g	107	257	5730
relative water solubility	0.42	1.00	22.30
amount initially absorbed by plants, µg/g	305	297	328
% in roots (~60)[a]	72.8	41.3	23.7
% in stems (~30)[a]	17.1	18.6	38.9
% in leaves (~10)[a]	10.1	40.1	37.4
% in first 2 cm of leaves (tips)[b]	47.7	54.4	76.7
% in second 2 cm of leaves[b]	20.6	23.8	14.1
% in third 2 cm of leaves[b]	16.0	12.8	5.2
% in fourth 2 cm of leaves[b]	15.7	8.8	4.0
concn in water drops from leaves, µg/mL[c]	50	254	2152
% on outside leaf surface[c]	12.6	8.4	4.7

[a] Determined immediately after treatment (0 DAT). Numbers in parentheses represent percent of tissues in total biomass. [b] Determined immediately after treatment. [c] Determined 1 day after treatment.

aqueous solution (Ogawa et al., 1976). Relative quantities of BPMC in the leaves (Ueji and Kanazawa, 1980) were, however, less than those for the three compounds studied here—consistent with the low water solubility of BPMC. Carbofuran is similarly accumulated in the tip of the rice leaves following absorption from paddy water (Siddaramappa and Watanabe, 1979). Other cereal crops, notably corn (Caro et al., 1973), show an appreciable residue of carbofuran in the leaves at harvest whereas very little remains in the stalks, cobs, or kernals. Residues of the carbamate metabolites of carbofuran, 3-oxo- and 3-hydroxycarbofuran, persist in the corn leaves whereas neither metabolite archieves much significance relative to the parent in rice leaves (Seiber et al., 1978b). Our results and those of others thus indicate that translocation of

systemic carbamates to leaves takes place rapidly, apparently through xylem transport, with the efficiency of movement to the leaf tips a function of the chemical's water solubility.

Analysis of droplets of guttation fluid formed during the first night in the chamber showed quite high concentrations of all three carbamates (Table I). This liquid accumulates at the leaf tips, having been forced out stomate-like pores in the epidermis under high humidity conditions (Kramer, 1969). Guttation fluid has previously been shown to contain a variety of organic compounds and mineral elements (Goatley and Lewis, 1966), and several reports indicate that the composition is a function of salts and fertilizers in the soil (Kramer, 1969). Our analyses showed that the concentration of parent carbamates remarkably paralleled the water solubility of the three test chemicals (Table I). The combined results—highest leaf concentrations in the leaf tips and near saturation in the guttation fluid—indicated that guttation is the major means for movement of systemic carbamates from inside to the outside surface of rice leaves. Some exchange through stomata located along the length of the leaves is likely also but is of apparently less importance than guttation when climatic conditions promote the latter's occurrence.

Evaporation of water from the guttation fluid left a deposit of carbamates on the leaf tip surface. This was shown by analysis of a rapid rinse of leaf surface with carbon tetrachloride immediately following the 24-h initial root-soak treatment (Table I). Of the total leaf residue, 8.4, 12.6, and 4.7% were on the outside surface for carbofuran, carbaryl, and aldicarb, respectively. A similar analysis carried out for carbofuran-treated plants at 4 and 8 days after treatment showed a decrease in surface residue with time, to 5.6 and 2.3%, respectively, of the total leaf residue.

The total amount of insecticide lost by volatilization during the 10-day experiment was normalized for leaf weight, giving 152.6, 107.9, and 213.0 µg/g for carbofuran, carbaryl, and aldicarb, respectively (Table II). A plot of these figures against the logarithm of vapor pressure yielded a linear relationship (Figure 5). Comparing this relationship with the percents of residue on the outside

Table II. Vapor Pressure and Volatilization Losses of N-Methylcarbamates during 10-day Chamber Experiment

	carbaryl	carbofuran	aldicarb
vapor pressure, mmHg	1.36×10^{-6}	4.85×10^{-6}	3.47×10^{-5}
relative vapor pressure	0.28	1.00	7.15
amount vaporized, μg	367	290	920
% vaporized[a]	4.2	5.8	5.7
amount vaporized per gram of leaf tissue, μg/g[b]	152.6	107.9	213.0

[a] Relative to total amount in plants at 0 DAT.   [b] Relative to total leaf tissue at 0 DAT.

surface (Table I), which was roughly inversely related to vapor pressure, it appears that the most volatile compound (aldicarb) underwent the highest rate of evaporation and left behind the smallest surface residue. Carbaryl, the least volatile of the three, became relatively more concentrated on the surface. Thus, while movement to the outside leaf surface occurred significantly for all three compounds, evaporation was a limiting step governing transfer to the air. A comparable situation occurs in soil when movement to the surface (e.g., by the wick effect or diffusion) is rapid and yet vaporization is slow because of a chemical's low vapor pressure (Hartley, 1969). In such a case, buildup of residue on the soil surface may occur.

There was no comparably simple correlation of volatilization loss with physical properties for the three insecticides when applied by foliar spray to rice plants. This may be partly due to uneven distribution in the surface deposits (Taylor, 1978) or to differences in penetration of insecticide into leaf tissue. For both foliar spray and root-soak treatments, however, a trend was noted in that relatively more of the vaporized residue survived to entrapment on the XAD resin than was recovered from condensate on the bell jar walls as the vapor pressure of the chemical increased.

Summarizing our findings, evidence was provided that systemically absorbed carbamate insecticides move within and exit from rice plants in accord with their physicochemical properties. The three test compounds were absorbed rapidly and in high concentrations from root-soak solutions. Upward movement, apparently by xylem transport, was also rapid, the extent of movement to the stems and leaves being a function of water solubility. Foliage residues moved principally to the leaf tips and in significant amounts to the outside leaf surface in the guttation fluid. Some movement to the outside surface through stomata along the length of the leaves probably occurred also but apparently to a lesser extent than by guttation. Evaporation of water from guttation fluid left a residue of each compound on the outside surface of leaf tips, from which evaporation occurred at a rate dependent on vapor pressure when climatic conditions were held constant. Competing loss routes are by root exudation, a major process for all three chemicals under the conditions of our experiments, and metabolism, which was apparently most pronounced for aldicarb. Although not examined here, we can surmise that leaf surface residues could also be physically removed by washing-off processes which might accompany rainfall or overhead irrigation in a field situation.

While only a 4.2–5.8% of the initial systemic plant residue was lost by evaporation in these tests, the results indicate that considerably more residue was potentially available for loss by this route. Assessment of residue loss by evaporation when plants are exposed to the atmosphere for longer periods of time, particularly under outdoor climatic conditions, will require further testing in the field.

A mechanism thus exists by which rice plants may transfer soil deposits of N-methylcarbamate insecticides of appreciable water solubility and vapor pressure to the surrounding air. This mechanism should be considered along with metabolic transformation and root exudation as of potential importance to the overall dissipation of systemically absorbed pesticides in plants.

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