Total Residue Analysis of Amitraz [1,5-Bis(2,4-dimethylphenyl)-3-methyl-1,3,5-triazapenta-1,4-diene] Residues in Fruit and Soil Samples by Electron Capture Gas Chromatography

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A total residue method for the analysis of amitraz [1,5-bis(2,4-dimethylphenyl)-3-methyl-1,3,5-triazapenta-1,4-diene] residues in various crops and soil has been developed. The method consists of a base hydrolysis of amitraz and its metabolites to 2,4-dimethylaniline, a steam distillation/continuous extraction, an acid/base partition cleanup, and derivatization to the heptafluorobutyranilide for quantitation by electron capture gas chromatography. The method is sensitive to levels of 0.05 ppm of amitraz and has a nominal recovery of 77 ± 10% in the 0.05–1.0-ppm range over eight types of samples including pears, apples, citrus fruits, cottonseeds, and soil. The analysis of variance of the recoveries in pears and soils reflected a highly significant linear trend.

Amitraz [1,5-bis(2,4-dimethylphenyl)-3-methyl-1,3,5-triazapenta-1,4-diene], I (Figure 1), is a member of the formamidine family of pesticides of which chlordimeform, II, is perhaps the most familiar. Amitraz has exceptional miticidal activity toward mites of pears, apples, and citrus fruits (Harrison et al., 1972; Knowles and Roulston, 1973; Weighton and Osborne, 1973; Chang and Knowles, 1977; Giles et al., 1979; Collyer, 1980; Leeper and Reissig, 1980) and is currently marketed in the United States as BAAM EC and BAAM WP (Baam is a registered tradmark of The Upjohn Co., Kalamazoo, MI) for the treatment of pear psylla insects and pear rust mites. It also has exceptional acaricidal activity against demodectic and sarcoptic mange mites in the dog (Folz et al., 1978, 1983, 1984; Bussieras, 1979; Shirk, 1983) and is marketed as Mitaban LC (Mitaban is a registered trademark of The Upjohn Co., Kalamazoo, MI) for these indications.

The metabolism of amitraz in the various fruit crops has been fully elucidated, and >95% of the residue left on the crop and soil samples can be accounted for as compounds I, III, and IV (Lewis, 1972; Somerville and Nichelson, 1972; Somerville, 1983). Compounds III and IV likely arise from I by a simple hydrolysis process. Oxidative processes then metabolize these residues to VI and VII, compounds likely to be of much less toxicological concern. The simple 2,4-dimethylaniline (DMA), V, has never been found as a significant residue in either plant or animal dosing studies (Knowles and Benezet, 1981; Somerville, 1983; Hornish, 1983; Knowles and Gayen, 1983).

Residue analysis procedures for amitraz and the hydrolytic metabolites III and IV in apples and pears have been worked out (Staten et al., 1973; Staten and Thornton, 1975), but the methods for each compound are slightly different and require separate gas chromatographic columns and conditions. A residue method based on the degradative hydrolysis of I, III, and IV to V was therefore developed to quantitate these residues as an indication of "total" amitraz residue levels. Such a degradative approach has been applied to chlordimeform (II) residues in various crops and soils (Geissbuhler et al., 1971) and consisted of an acid hydrolysis of II to VIII followed by a base hydrolysis to IX with simultaneous steam distillation/continuous extraction into isooctane using an appratus designed by Bleidner et al. (1954) and modified by Heizler (Geissbuhler et al., 1971).

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During the development of a like procedure for amitraz residues, the acid hydrolysis step was found to be unnecessary. The amitraz method was thus shortened to a base hydrolysis/steam distillation, using the Bleidner/Heizler continuous extraction apparatus. The generated DMA (V) was derivatized to the heptafluorobutyranilide, X, for EC-GC quantitation. Some crop samples, especially citrus and cottonseeds, required additional cleanup because of various endogenous substances in unexposed blank samples that gave EC-GC peaks near the retention time of X. Cleanup was readily accomplished at the DMA stage before derivatization, and this cleanup step was incorporated into the analysis of all samples.

EXPERIMENTAL SECTION

Apparatus. The distillation/continuous extraction head was Heizler's modified Bleidner apparatus as described by Geissbuhler et al. (1971). The gas chromatograph was a Tracor Model MT-220 equipped with a Ni-63 electron capture detector and operated at RF mode, 56 V, 230-μs pulse rate, and 6-μs pulse width and heated to 265 °C. The column was 180 cm × 3 mm borosilicate glass packed with 3% OV-17 on 100–120-mesh Gas-Chrom Q, heated to 109 °C. The injection port temperature was 165 °C. The carrier and purge gas was nitrogen at 30 mL/min and 0.3 rotometer setting, respectively. The autoinjector was a Hewlett-Packard Model 7671A automatic sampler, set for a cycle time of 40 min.

Chemicals and Reagents. 2,2,4-Trimethylpentane (isooctane) was distilled in glass from Burdick and Jackson Laboratories, Muskegon, MI. Sodium hydroxide was a 50% aqueous solution from Mallinckrodt Chemical Works, Paris, KY. Antifoam A (dimethylpolysiloxane and silica) was food grade obtained from Dow Corning, Midland, MI. Heptafluorobutyric anhydride (HFBA) reagent was obtained from Pierce Chemical Co., Rockford, IL. The amitraz analytical reference standard was lot no. 11905-VLR-85, The Upjohn Company, Kalamazoo, MI. The HFBA–DMA derivative analytical reference standard was lot no. JLN-XI-41, a crystalline solid, mp 52–53 °C, indefinitely stable at 4 °C (The Upjohn Company, Kalamazoo, MI).

Sample Preparation. *Soil.* The bulk soil sample was spread in a thin layer on heavy brown wrapping paper in a laboratory hood and allowed to air-dry overnight. The air-dried soil was passed through a No. 8 U.S. standard sieve, and the screened-out extraneous materials were discarded. The screened soil was placed in a V-mixer for 30 min and then passed through a riffler 8–10 times.

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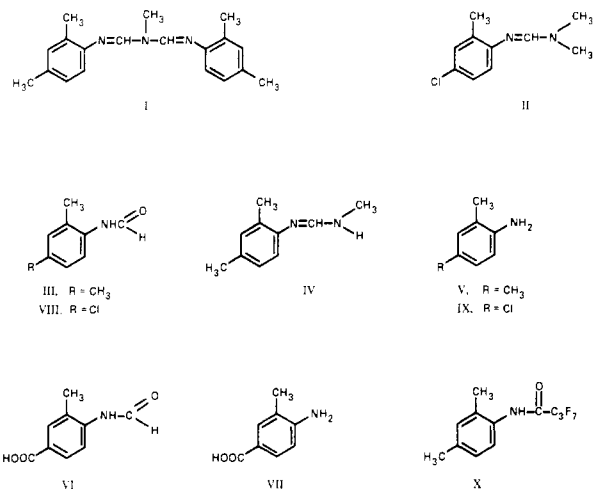

Figure 1. Compounds in the amitraz and chlordimeform series.

Subsamples of 50 g each were taken for analysis.

Fruit. Whole fruit, thawed if frozen, was twice passed through a Hobart TG215 multimixer fitted with a $^1/_4$ in. hole faceplate. Subsamples of 50 g each were taken for analysis.

Cottonseeds. The cottonseeds were processed through a cotton gin and ground in a Wiley Mill fitted with a No. 2 sieve.

Hydrolysis, Steam Distillation, and Continuous Extraction. A 50-g sample of the soil or crop was placed in a 1-L round-bottom one-neck flask followed by 200 mL of deionized water, 20 mL of 50% NaOH, 5–10 drops of Antifoam A, and 5–10 boiling chips. The flask was swirled vigorously several times and attached to the lower arm of the Bleidner/Heizler apparatus. Teflon sleeves were used at all ground glass joints. Approximately 85 mL of isooctane and 5–10 3-mm glass boiling beads (Glassballs No. 3000, Seargent-Welch) were placed in a 250-mL round-bottom one-neck flask, and this was attached to the upper arm of the apparatus. A 3–5-mL volume of water was added to the apparatus through the top to partially fill the separation chamber, followed by 3–5 mL of isooctane. This precaution aided the correct flow of distillates to the appropriate sides; otherwise, a backward flow of isooctane to the water side would occasionally occur. A 350-mm Friedrich condenser was then attached to the top of the apparatus. Heating mantles were placed under each flask and the rates of reflux adjusted to nearly equal rates as judged by the flow of the immiscible solvent globules into the separation chamber. If the isooctane rate was too rapid, a backward flow of isooctane to the water pot occurred with subsequent loss of sample. The distillation/extraction process was continued for 2–3 h.

Sample Cleanup. The isooctane in the 250-mL flask was quantitatively transferred to a 100-mL volumetric flask followed by three 2–3-mL flask rinses and the volume adjusted to the 100-mL mark. A 2.0-mL aliquot was transferred by pipet to a 15-mL screw-cap centrifuge tube and extracted 3 times with 1.0-mL aliquots of 0.1 N HCl. The aqueous acid extracts were combined in a fresh tube, made basic with 1.0 mL of 1 N NaOH, and extracted 3 times with 3-L aliquots of fresh isooctane. Vigorous mixing of the two phases for at least 1 min in all extraction steps was necessary to ensure good recoveries. The isooctane extracts were combined in a 10.0-mL volumetric flask, and the volume was adjusted to the mark. Note that there has been a 5-fold dilution.

Derivatization. A 4.0-mL aliquot of the above extract was placed in a 15-mL screw-cap vial or tube and treated with 10–20 μL of HFBA reagent at 50 °C for 1 h. On cooling, the solution was washed with 4 mL of saturated $NaHCO_3$. A 1–2-mL aliquot of the derivatized sample was placed in the autosampler vials and a 2-μL sample injected onto the GC. If the initially observed concentration was greater than 10 ppb relative to amitraz (see below), dilutions were made to achieve a concentration in the 1–10-ppb range.

GC Standards. A stock solution of the HFBA derivative of DMA at a concentration of 216 μg/mL in isooctane was prepared by dissolving 21.6 mg of crystalline derivative in 100.0 mL of isooctane in a 100-mL volumetric flask. This is equivalent to 100 ppm of amitraz (two molecules of DMA are generated from each molecule of amitraz). An intermediate stock solution of the derivative with a concentration of 216 ppb (100 ppb of amitraz) in isooctane was prepared by diluting 100 μL to 100 mL. The standard curve solutions for GC analysis were then prepared by diluting 100, 80, 60, 40, 20, and 10 μL of the intermediate stock solution to 1.0 mL with isooctane in 1.0-mL volumetric tubes. The standard curve concentrations were thus 10, 8, 6, 4, 2, and 1 ppb, respectively, in equivalents of amitraz. A 2-μL injection of each generated a standard curve in the linear range of the EC detector.

Recovery Study. With each set of samples, usually four samples per set, a blank control and a fortified control were also run. The fortified control was prepared by spiking a 50-g blank control with 1.0 mL of amitraz in isooctane at either 2.5, 5.0, 10.0, 25.0, or 50.0 μg/mL, which gave a fortification level of 0.05, 0.10, 0.20, 0.50, or 1.0 ppm, respectively.

Calculation. A standard curve of the instrument response was generated from the analytical standards by plotting peak height (Y) vs. amount on column (X) and the curve evaluated by linear regression analysis. The amount of amitraz derived from the sample was determined from the standard curve and the final residue concentration of amitraz equivalents in the 50-g sample calculated by the equation

$$\text{ppm of amitraz} = \frac{(\text{pg on column})(\text{dilution factor})(100\ \text{mL})}{(2\ \mu\text{L})(50\ \text{g})} \frac{10^3\ \mu\text{L}}{\text{mL}} \frac{1\ \mu\text{g}}{10^3\ \text{pg}} \quad (1)$$

RESULTS AND DISCUSSION

The total residue method for amitraz residues was initially developed for apples, pears, and soils. The original method consisted of a base hydrolysis of amitraz and the hydrolytic metabolites III and IV to 2,4-dimethylaniline (DMA), steam distillation/continuous extraction of DMA into isooctane, and HFBA derivatization of DMA for EC-GC quantitation. In order to optimize the sensitivity of the method, the HFBA–DMA derivative, structure X in Figure 1, gave excellent electron capture sensitivity: on-column sample sizes as low as 2 pg were readily detected. Since these first applications, the method has been applied to various citrus crops, strawberries, cottonseeds, and their byproducts. In addition, methods for amitraz in swine tissue and cows milk have also been developed since amitraz has excellent ectoparasite activity against mites and ticks of these species. However, these methods are beyond the scope of this paper.

Many of the various crops, especially citrus and cotton seeds, generate many components that interfere with the DMA derivatized peak in the gas chromatogram. A cleanup step was therefore incorporated and was based on the premise that the coextractives with DMA were perhaps different in their acid/base properties. The isooctane

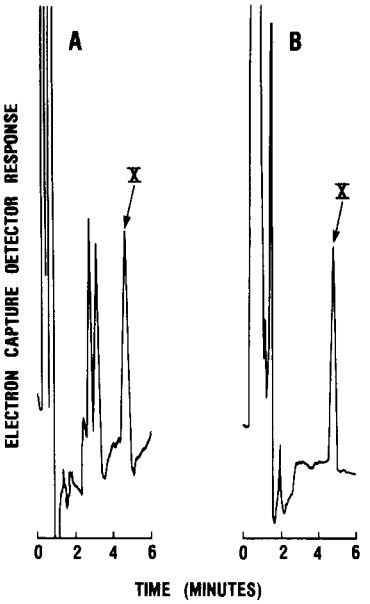

Figure 2. Gas chromatograms of orange samples fortified with amitraz at 1.0 ppm. Curve A was obtained from the crude isooctane extract with no acid/base cleanup and curve B from the same sample but after the cleanup step.

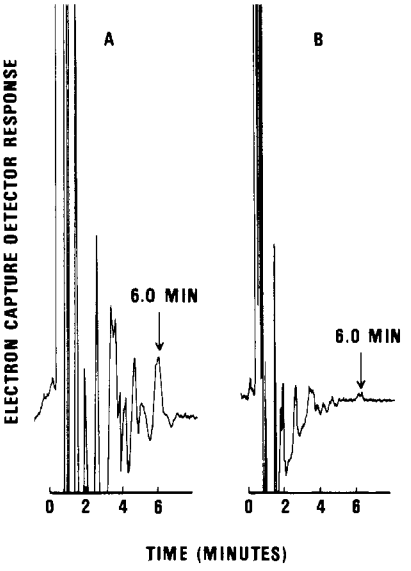

Figure 3. Gas chromatograms of a control orange sample, nontreated or nonfortified with amitraz. Curve A was obtained from the crude isooctane extract with no acid/base cleanup and curve B from the same sample but after the cleanup step with no dilution of the final solution.

solution of DMA was extracted with dilute hydrochloric acid, to water solubilize DMA as its hydrochloride salt. The salt was then converted back to the free DMA with base and reextracted into fresh isooctane. Parts A and B of Figure 2 show typical chromatograms of an orange sample spiked with amitraz and analyzed with and without this cleanup step. This step introduced no more than a 5–10% loss when carefully executed. The effect of this cleanup step is best illustrated in parts A and B of Figure 3 where control samples were analyzed before and after this step. The key substep is the reextraction of free DMA into isooctane. Vigorous mixing and contact times of >1 min are critical.

The sensitivity of the method, or limit of quantitation (LOQ), can be established by the model defined by the ACS Subcommittee on Environmental Analytical Chemistry (MacDougall and Crummett, 1980) or IUPAC (IUPAC, Chemical Division, 1978) and further examined by long and Winefordner (1983). The model is based on first establishing a good instrument calibration through a series of standards of known concentration and second measuring the detection levels and variability of a number of field blanks (samples of the crop that presumably contain no analyte residues). The first task to establish the LOQ was to calibrate the gas chromatograph and define the linear response range. For the Tracor MT-220 GC used throughout this study, a range of the HFBA–DMA derivative from 2 to 20 pg on the column at the settings noted gave excellent results. Typical linear regression analyses data are presented in Table I. Each set of data is comprised of 15 standard curves generated over a 1–2-month period. The correlation coefficient in both cases is >0.990. The intercept is essentially zero (<0.5 mm). The analysis of variance (ANOVA) of each set clearly shows a highly significant linear trend [regression (probability > F) <0.05]. Therefore, the linearity of the instrument response in the 2–20-pg range was well-defined.

The second task in the model evaluation was to examine field blank samples and establish the base-line noise. The data for three soils and three crops are presented in Table II. The criteria outlined by the ACS guidelines (Mac-

Table I. Linear Regression Analysis of the EC-GC Response to (Heptafluorobutyryl)-2,4-dimethylanilide Standards

Data Set 1[a]			
X,[b] ppb	Y,[c] mm	SD of Y	coeff of var
1.0	13.1	1.6	0.122
2.0	25.9	1.9	0.073
4.0	52.5	2.8	0.053
6.0	79.4	4.6	0.058
8.0	106.8	6.2	0.058
10.0	131.5	7.5	0.057

slope = 13.256
Y intercept = −0.286
corr. coeff = 0.994
ANOVA[d] regression probability > F = 0.000
ANOVA[d] lack of fit probability > F = 0.867

Data Set 2[a]			
X[b], ppb	Y[c], mm	SD of Y	coeff of var
1.0	13.3	1.1	0.083
2.0	26.0	2.1	0.081
4.0	52.2	2.8	0.054
6.0	78.2	3.3	0.042
8.0	108.1	5.1	0.047
10.0	131.3	5.6	0.043

slope = 13.273
Y intercept = −0.379
corr coeff = 0.996
ANOVA[d] regression probability > F = 0.000
ANOVA[d] lack of fit probability > F = 0.075

[a] Data collected over a 1–2-month period. [b] Concentration of substrate in parts per billion. [c] Mean value of 15 measurements, peak height, in millimeters. [d] Analysis of variance.

Table II. Amitraz Total Residue Method—Limit of Detection and Limit of Quantitation

crop	no. of blanks	concn, ppm			
		X_B	S_B	LOD[d]	LOQ[e]
soil 1[a]	23	0.00223	0.00291	0.011	0.031
soil 2[b]	11	0.05073	0.00857	0.076	0.136
soil 3[c]	18	0.00556	0.00414	0.018	0.047
pears	22	0.00504	0.00492	0.020	0.054
cottonseed	10	0.00564	0.00312	0.015	0.037
oranges	15	0.00513	0.00296	0.014	0.035

[a] California clay loam. [b] Oregon sandy clay loam. [c] Michigan sandy clay. [d] LOD = $X_B + 3S_B$. [e] LOQ = $X_B + 10S_B$.

Table III. Linear Regression Analysis of Recovery Data for Pears and Soil Fortified with Amitraz

crop	no. of determinations	X added, ppm	X found, ppm
pears	3	0.05	0.037
	12	0.10	0.077
	12	0.20	0.151
	12	0.50	0.388
	12	1.00	0.768

slope = 0.7704
99% CL on slope = 0.731–0.810
y intercept = −0.00068
corr coeff = 0.9910
ANOVA[a] regression probability > F = 0.000
ANOVA[a] lack of fit probability > F = 0.976

crop	no. of determinations	X added	X found
soil	7	0.05	0.038
	15	0.10	0.078
	15	0.20	0.153
	15	0.50	0.391
	15	1.00	0.784

slope = 0.7860
99% CL on slope = 0.747–0.825
y intercept = −0.00204
corr coeff = 0.9888
ANOVA[a] regression probability > F = 0.000
ANOVA[a] lack of fit probability > F = 0.996

[a] Analysis of variance.

Dougall and Crummett, 1980) require a minimum of seven sample measurements and define the limit of quantitation (LOQ) as

$$\mathrm{LOQ} = X_B + 10S_B \quad (2)$$

where X_B = the mean blank concentration and S_B = the standard deviation of the blanks. The LOQ for five of the items in Table II is 0.03–0.05. Therefore, a value of 0.05 ppm was established as the sensitivity of the method. The exception to the data in Table II are the soil 2 samples from Oregon. The relatively high mean background (0.05 ppm) in these samples was probably due to the widespread use of amitraz in the area where the samples were obtained. The more virgin soils from California and Michigan reflect a 10-fold lower level of background values. Clearly, since the LOQ is directly dependent on the levels of background noise and the standard deviation of this noise, the importance of obtaining true uncontaminated blank samples cannot be overemphasized.

The recovery data for 51 assays of blank pear samples and for 67 assays of blank soil samples, fortified with amitraz at levels ranging from 0.05 to 1.0 ppm, were examined by linear regression analysis of ppm added (x) vs. ppm found (y). The data are presented in Table III. These results indicate a highly significant linear trend over the ranges studied, as indicated by the correlation coefficients of 0.9910 and 0.9888, respectively, and the significant regression (probability > F = 0.000) in both cases. The intercept values suggest a very slight negative bias. Recall that the instrument response was also biased slightly negative. The overall recovery for the pears as 77.0 (slope = 0.7704) with a range of 73.1–81.0% at the 99% confidence level. The overall recovery for the soil was 78.6% with a range of 74.7–82.5% at the 99% confidence level.

Recovery studies conducted over the years, 1976 to present, in many crops have reflected consistent mean recoveries of 75% or more in the 0.05–1.0-ppm range of amitraz concentration as seen in Table IV. Over the course of hundreds of analyses, the variability of the recovery ranged from 8 to 14%. The mean recovery over the entire data set, 558 samples, was 77.5 ± 9.9%. Close examination of the method has shown that the primary source of error occurs in the acid/base partition cleanup step as previously indicated. Moreover, once the isooctane distillate of DMA is obtained, the cleanup and derivatization should be carried out within several hours or by the next day since losses occur, probably by oxidative degradation of the DMA. A time study of the decline was carried out, and the data are presented in Table V. These data were generated from pear samples. The half-lives at ambient temperature (22–23 °C) were 12.7 days for the 1.0-ppm samples and 7.1 days for the 0.2-ppm samples. The loss is thus about 5% per day. Another critical step was found to be the continuous extraction. As indicated by Geissbuhler in the chlordimeform method (Geissbuhler, 1971), a careful adjustment of the flow rates of the condensates into the separation chamber of the apparatus is crucial for optimum results.

The residue method requires approximately 8 h from the time the hydrolysis is set up until the derivatized DMA extracts are ready for EC-GC analysis. With sufficient equipment, one analyst can process 6–12 samples per day.

Table IV. Recovery Data from Various Crops

crop	fortifn level, ppm	no. of assays	mean recovery %	SD, %
pears	0.05–1.0	118	78.3	±9.8
apples	0.05–1.0	47	74.4	±7.9
oranges	0.05–1.0	66	77.3	±8.3
grapefruit	0.1–0.5	9	85.8	±13.7
lemons	0.1–1.0	18	79.2	±9.7
strawberries	0.5–1.0	9	76.3	±9.0
cottonseed	0.05–1.0	30	77.9	±9.5
soil	0.05–1.0	261	77.2	±10.6
total		558	77.5	±9.9

Table V. Stability of the Isooctane Solution of DMA Derived from Spiked Pear Samples

time, days	concn of amitraz found,[a] ppm: 1.0-ppm samples	0.20-ppm samples
0	0.81	0.14
1	0.76	0.15
2	0.73	0.09
5	0.60	0.11
7	0.56	0.07
First-Order Rate Model: log c vs. Time		
slope	−0.02358	−0.04266
y intercept	0.803	0.141
k_{el}	−0.0543	−0.0983
$t_{1/2}$, days	12.7	7.1
corr coeff	−0.8442	−0.7118
ANOVA regression probability > F	0.000	0.003
ANOVA lack of fit probability > F	0.969	0.025

[a] Determined in triplicate from three samples of each.

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Kinetics and Mechanism of Alkaline and Acidic Hydrolysis of Aldicarb

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The hydrolysis of aldicarb, 2-methyl-2-(methylthio)propanal *O*-[(methylamino)carbonyl]oxime, was investigated over the pD (pH) region 3.0–8.6 by using pulse Fourier transform nuclear magnetic resonance (FT NMR). At pH values above 7.0, a base-catalyzed carbamate decomposition via methyl isocyanate is observed. The principal products are the oxime of 2-methyl-2(methylthio)propanol, dimethylurea, methylamine, and carbon dioxide. At pH values below 5.0 an unusual acid-catalyzed reaction leading principally to 2-methyl-2(methylthio)propionitrile and methylamine was found. In the intervening and environmentally significant acidity regions, both schemes were obtained. Minor products in both reactions include those from the small amount of anti isomer as well as other reaction paths for the syn isomer. These results indicate that at the pH and temperature of the Long Island aquifer aldicarb is likely to remain a contaminant for many years.

Recently, aldicarb, 2-methyl-2-(methylthio)propanal *O*-[(methylamino)carbonyl)]oxime (I), has been found

$$CH_3SC(CH_3)_2CH{=}NOC(O)NHCH_3$$

I

contaminating the aquifers in New York (Guerrera, 1981). The contamination was initially considered unique to the Long Island geography. However, other areas of the country, such as Arizona, Maine, Virginia, and Wisconsin, have also experienced groundwater contamination from aldicarb (Cohen et al., 1984). A most recent occurrence has been in Florida where the pesticide was used to control orange crop pests (Cohen et al., 1984).

Since introduction in 1965 (Weiden et al., 1965), this carbamate pesticide has been widely used for protection of commercial crops, such as cotton, potatoes, peanuts, sugar beets, corn, sweet potatoes, and many others, from attack by mites, nematodes, and other pests (Richey et al., 1977). Aldicarb has a high degree of contact toxicity to a variety of insects and a remarkable systemic potency. Most conveniently, it is planted with the crops in the spring and absorbed into the plants as they grow, thus providing nearly seasonal protection from these insects.

Many laboratory and field studies have been performed to determine aldicarb degradation in soils and crops, and these are valuably summarized (Maitlen and Powell, 1982). Of primary interest to this work, the pathways involve oxidation to aldicarb sulfoxide and sulfone and hydrolysis to aldicarb oxime, aldicarb sulfoxide oxime, and aldicarb sulfane oxime. These pathways are apparently less important in some soils. When aldicarb was used on Long Island, NY, where the water table is high, the pesticide was found to make a rapid migration into the Upper Glacial Aquifer (Guerrera, 1981).

This discovery of aquifer contamination by aldicarb, which led to a ban on its usage on Long Island, underscores the need to learn the fate of this pesticide after it has entered the underground waters. Once in the aquifer some of the degradative pathways available in surface soils, such as photolysis by sunlight, are no longer available, and some such as biolysis by soil microbes are less likely. The major degradative process remaining is hydrolysis and is likely without oxidative pathways. In actual fact, whereas aldicarb is rapidly oxidized in many environments (Maitlen and Powell, 1982), analyses of some Long Island well waters show predominance of the unoxidized sulfide form (Eadon, 1984).

In the Long Island aquifer this must take place at a pH of approximately 5.5 and a temperature of about 11 °C. Even for chemicals as widely used as aldicarb, little has been reported about its fate and persistence in natural water systems. Long-term hydrolysis of aldicarb leads to significant decay at pH 8.5 and 15 °C in 186 days (Hansen

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