UPTAKE OF ALDICARB AND ITS TOXIC DEGRADATION PRODUCTS IN WATERMELONS

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ABSTRACT

Temik aldicarb was applied to watermelon vines by two methods of treatment; (1) A side dressing of Temik 15 G granules by shank incorporation to ca 4 in below the bed surface at rates of 1, 2, and 4 lb a.i./acre and (2) addition of irrigation water containing 0.02, 0.1, and 0.5 ppm dissolved aldicarb to the furrows. The treatments were made to fairly well developed vines on Sept 3 and 4, 1985, at the UC Davis Field Station. Samples of melons, bed soil, furrow irrigation water, and leaves were taken at 3 intervals (Sept 13, Sept 20, and Oct 16) after treatment. Analysis was conducted for parent aldicarb and for the sulfoxide and sulfone oxidation products by gas chromatography of prepared extracts. The results showed residues (primarily as the sulfoxide) in melons fruit ranging from 0.01 - 0.13 ppm from the incorporation treatments. Residues in soil from the incorporation treatments ranged up to 0.43 ppm for sulfoxide plus sulfone. Residues in water were not detectable (minimum detection limit 0.01 ppm) for the soil incorporation treatments, while leaves gave combined sulfoxide-sulfone residues ranging to above 1 ppm. These results indicate that soil incorporation of Temik granules produced measureable aldicarb-related residues in melon vines and fruit. Treatment of melon vines with aldicarb dissolved in irrigation water did not lead to measureable residues in soil, water, melons or (with a few exceptions considered to be anomalies) in melon leaves.

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OBJECTIVES

1. Determine the concentration of aldicarb and its toxic degradation products in watermelons and watermelon vine leaves resulting from treatment by side dressing with Temik granules at 3 rates of application and by introduction of aldicarb dissolved in irrigation water.

2. Follow the concentration of residue in melons, leaves, soil, and irrigation water at 3 intervals following treatment.

PROJECT PARTICIPANTS

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METHODS AND MATERIALS

LOCATION OF FIELD EXPERIMENTS. Watermelon beds were located at the vegetable crops field area near the airport at UC Davis.

The watermelon beds (5 ft on center by 210 ft in length) were laid out by Sid Lucero, Field Superintendent for vegetable crops at UCD (Table 1). The soil type was a Reiff loam (Huntington, 1981; see attachment). The area was fertilized with 200 lbs/acre ammonium phosphate (16:20:0) before planting. Blue ribbon variety melons were planted on May 9th, 1985 and then side dressed with ammonium sulfate approximately 4 weeks after planting. Watering was done by furrow irrigation for 12 to 24 hours every 7 to 10 days, depending on the soil moisture.

LAYOUT. Twenty ft by 5 ft plots (Table 2 and figure 1) were staked out with a 15 ft buffer zone between plots. The plot boundaries ran from the middle of one furrow to the middle of the next. Background soil, foliage and melons were sampled on Sept 2. Outstretched vines were laid back towards the center of the plants so they would not interfere with the application of Temik.

SOIL APPLICATION. Aldicarb granular formulation (Temik 15G, 15% a.i.) was applied at 1, 2, and 4 lb a.i./acre by shanking in a preweighed amount that was diluted with 500 ml of blank granules. The aldicarb and blank granules were rolled for one hour to insure a homogenous mixture. The mixture was applied with a tractor that was equipped with a calibrated shank and was preset to a depth of four inches below the surface. Application was done on the morning of Sept 3.

TABLE 1. SCHEDULE OF FIELD ACTIVITIES.

DATE	ACTIVITY
5/85	Pre-plant fertilizer added (200 lbs/acre ammonium phosphate 16:20:0)
5/9/85	Blue Ribbon watermelons planted
6/9/85	Melons side dressed with 500 lbs/acre ammonium sulfate (21:0:0)
9/2/85	Background soil, leaf and melon samples taken.
9/3/85	Soil treatments shanked in. Barriers around plots installed. Irrigation begun at 5 pm.
9/4/85	Water added to inside barriers. Water treatments applied. Irrigation terminated at 10 am. Water samples taken on outside of barriers (all plots) and inside of barrier plots 1-3.
9/13/85	Plots divided into thirds. Soil, leaf, water (outside of barriers) and melons sampled.
9/20/85	Soil, leaf, water (outside of barriers) and melons sampled.
10/16/85	Soil, leaf, and melons sampled.

TABLE 2. PLOT TREATMENT AND AMOUNT OF TEMIK ALDICARB APPLIED.

PLOT NUMBER	APPLICATION TYPE	TREATMENT RATE (a.i.)[a]	MATERIAL APPLIED[b] a.i.	Formulation
1	SHANK	1.0	1.04	6.93
2	SHANK	2.0	2.08	13.8
3	SHANK	4.0	4.18	27.9
4	CONTROL	---	----	----
5	WATER	0.5	107	713
6	WATER	0.02	4.25	28.3
7	CONTROL	---	----	----
8	WATER	0.1	21.3	142

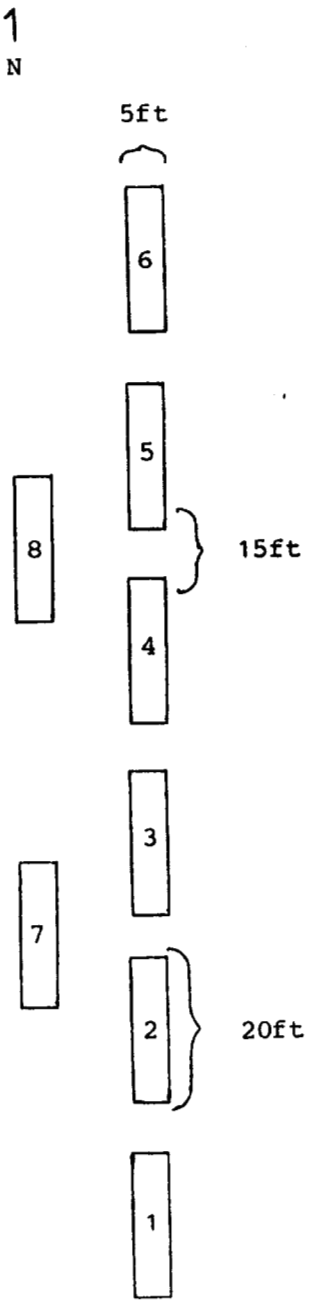
[a] For shank application units are pounds/acre; water units are p.p.m.

[b] Units = grams for shank; units = milligrams for water.

Figure 1.

Plot Layout

Plot	Type	Applied at
1	Side dress	1 lb/acre
2	Side dress	2 lb/acre
3	Side dress	3 lb/acre
4	Control	---
5	Water	0.5 ppm
6	Water	0.02 ppm
7	Control	---
8	Water	0.1 ppm



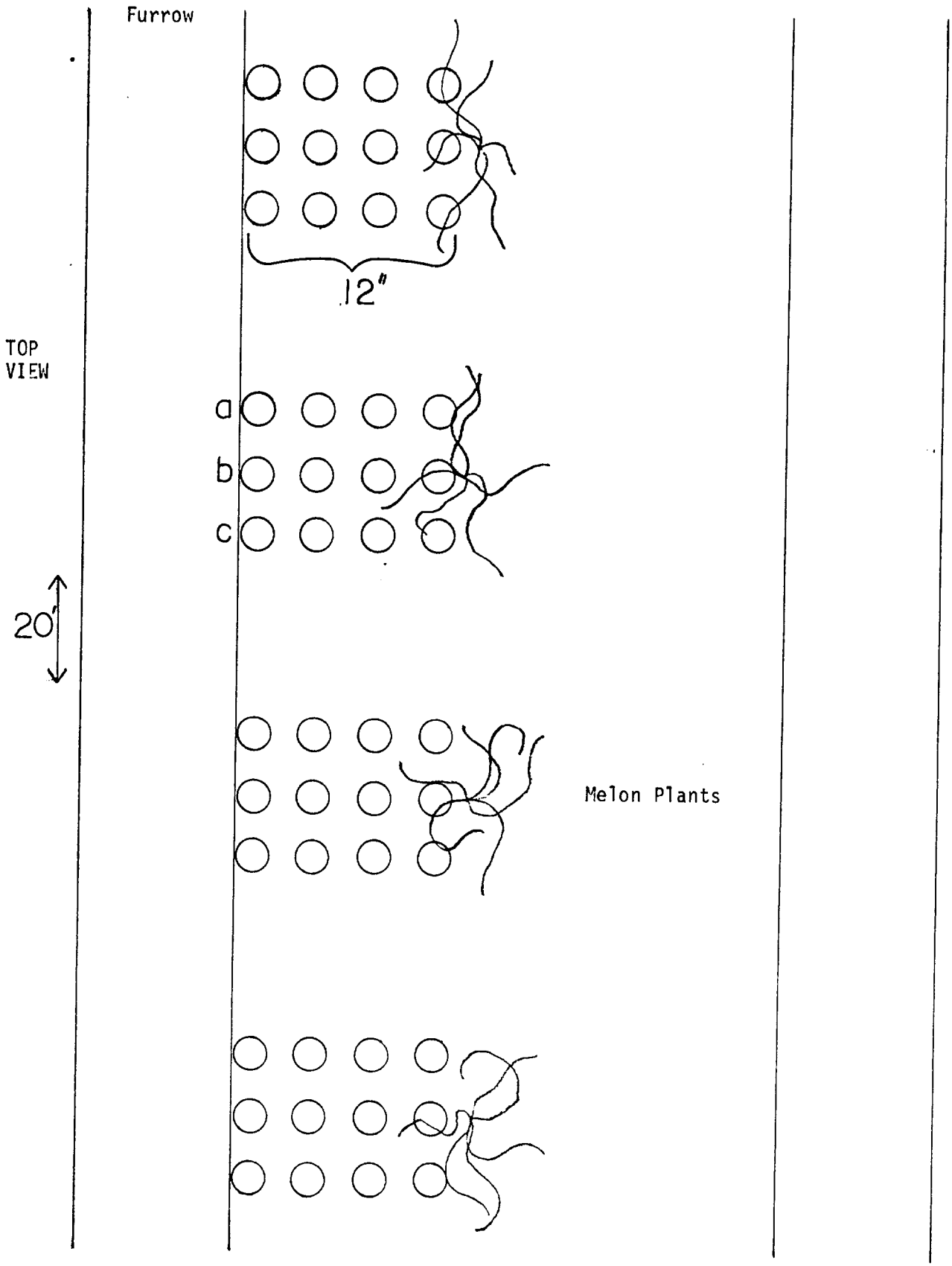
Ten inch aluminum sheet metal flashing was buried six inches deep around the perimeter of each plot to act as a barrier to prevent exchange of irrigation water in the treated plots from ground flow of irrigation water. The barrier was placed so that one half of the furrow on each side was included in the plot; irrigation of plants in the buffer zones was not impaired. The top of each barrier was bent at a 90 degree angle to ensure no injury to plant vines resting on its sharp edges.

WATER APPLICATION. Aldicarb granular formulation (Temik 15 G, 15% a.i.) was applied at 0.02, 0.1 and 0.5 ppm active ingredient in the following manner. Preweighed formulation was added to 500 ml of tap water and mixed for 2.5 hours. Twenty gallons of irrigation water was added to furrows inside of the barriers. The aldicarb solutions were added in a uniform manner via a small watering can to the standing water in the furrows on both sides of the plot. It should be noted that all melons were irrigated for 12 hours before aldicarb was added to the water application plots, so that the treated irrigation water did not immediately penetrate into the soil.

SOIL SAMPLING. Three replicates were taken at each treatment. Each replicate consisted of four 1-in diameter by 6-in deep cores taken at the end of the furrow and in towards the center of the plant (Figure 2). The sampling was repeated at four points along the plot with ca 4 ft between sampling points. Thus a rep consisted of sixteen 1-in by 6-in cores. Reps were only taken from the side where the aldicarb had been shanked in. It could not be determined that any cores were taken directly in the shank line, because the latter was no longer visible during soil sampling.

Figure 2.

Soil Sampling Schematic



FOLIAGE SAMPLING. Three replicates were taken for each treatment. Each rep. consisted of leaves that were from the 7th knuckle from the end of the vine, or one leaf from either side of the 7th knuckle. Ten to 15 leaves made up each rep.

WATER SAMPLING. Irrigation water (500 ml) was collected in canning jars from furrows outside of the barriers (3 reps/plot). Water was also collected from inside the barriers on Sept 4 for the 1, 2 and 4 lbs/acre soil treatments, and on the outside of the barrier on Sept 13 and 20 for all treatments.

MELON SAMPLING. Nine melons were sampled for background on Sept 2. Plots were then marked and partitioned into thirds for inventory and sampling purposes. One melon from each third was sampled at every post-treatment sampling period. Thus there were three melons sampled per plot. Melons were inspected before sampling to insure that they were still connected to the vine with a viable stem.

TREATMENT OF SAMPLES AT THE LABORATORY. Soil and foliage samples were stored at -20°C. Watermelons were cored with a 1-in by 30-in copper tube that was sharpened at one end. Four cores, along the long axis, were taken from each melon. The rinds were removed from the cores which were then cut up into 1-in segments according to CDFA protocol (attached), mixed, and then stored in canning jars at -20°C. Water samples were stored at 4°C. All lids on storage containers contained either aluminum foil or Teflon liners in the lids.

WATER ANALYSIS. Irrigation water (50 ml) was partitioned four times for 2 min each in a 250 ml separatory funnel with 50 ml aliquots of methylene

chloride and 10 grams of sodium chloride. The organic layers were combined, dried over anhydrous sodium sulfate and evaporated to ca 2 ml using a roto-evaporator and a 300 ml round bottom flask. Samples were quantitatively transferred to graduated centrifuge tubes and then concentrated to 0.5 ml with a gentle stream of dry nitrogen.

MELON ANALYSIS. The CDFA procedure for melons (see attachment) was used except that the samples were analyzed by gas chromatography instead of HPLC. The procedure was as follows:

Melons (50 gm) were blended for 3 min with 100 ml of acetonitrile using a Tissuemizer. Extracts were filtered through sharkskin filter paper into 125 ml Erlenmeyer flasks equipped with 24/40 ground glass stoppers. The flasks were shaken for 2 min, after the addition of 15 gm of sodium chloride. Layers were allowed to separate (ca 30 min). 50 ml (25 gm of melon equivalents) of the organic layer was pipetted into a 250 ml beaker. The solvent was evaporated to dryness with a gentle stream of dry nitrogen. Acetone was used to transfer the sample to a graduated centrifuge tube and the solvent was again evaporated to dryness. Acetone (1 ml) was added to the tube and then the tube was vortexed and centrifuged. The solvent was transferred to a second tube. The acetone addition, vortexing, centrifugation and transfer steps were repeated twice more. The volume of the second tube was reduced to 0.5 ml by concentration under nitrogen.

SOIL ANALYSIS. Soil samples were air dried at ca 22°C on aluminum foil for about 10 hr. Soil (50 g) was extracted with 100 ml of a 1:1 (v/v) acetone:water solution. The extract was swirled for 30 min then vacuum filtered through glass fiber filters. The extract (50 ml, representing 25 g)

was transferred to 250 ml separatory funnels and 5 gm of sodium chloride was added to each funnel. The extracts were partitioned with 4 X 10 ml of chloroform. The chloroform was evaporated to dryness, the samples were quantitatively transferred with 5 ml of ethyl acetate, and the final volumes adjusted for analysis.

GAS CHROMATOGRAPHY. Aldicarb, sulfone and sulfoxide was analyzed as the corresponding nitriles (Figure 3). The instrument used was a Hewlett Packard 5710A gas chromatograph with a nitrogen-phosphorus detector. The column was a 30 m X 0.31 mm DB-1 WCOT fused silica capillary with a 0.25 micron film thickness. Flows for helium, air and hydrogen gases were 1.5, 50, and 3 ml/min respectively. The split ratio was approximately 59:1. Temperatures for injector, column and detector were 250, 70 and 250°C, respectively.

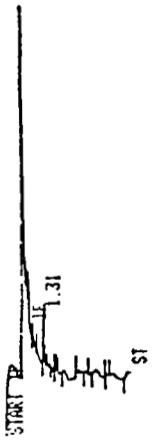
NOTE: Interferences prevented the analysis for the parent compound in melons using this procedure.

RECOVERY EXPERIMENTS. Irrigation water from the irrigation pipe outlet was spiked at 0.05 ppm level and stirred for one hour. 50 ml of the spiked water was analyzed using the procedure for water analysis. Melons (50 g) were spiked at 0.1 ppm (six samples) and analyzed using the procedure for melons. Soil (50 g) was spiked at 0.1 ppm and analyzed using the soil procedure. See Table 3 for results.

MINIMUM LEVEL OF DETECTION: 0.01 ppm was estimated for all matrices based upon chromatograms of background samples and standards.

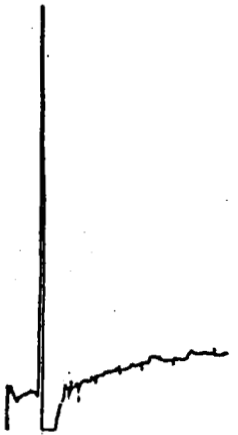
Figure 3.

Gas Chromatograms of Soil, Water and Melon controls and controls spiked with 0.1 ppm Aldicarb, Sulfoxide, and Sulfone, and of a Leaf control and control spiked with 1.0 ppm



Control leaves
chart speed 1.0 cm/min

Control Soil
chart speed 1.0 cm/min



Control Water
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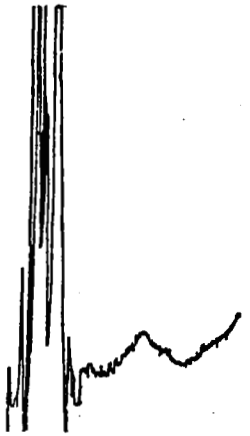
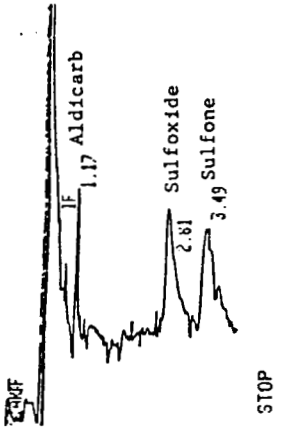
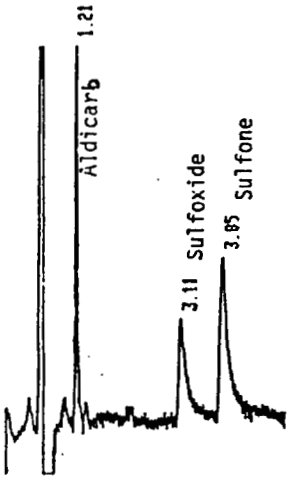


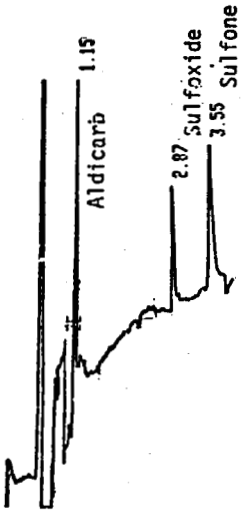
Control Melons
chart speed 0.5 cm/min



Leaf spike 1.0 ppm
chart speed 0.5 cm/min



Soil Spike 0.1 ppm



Water Spike 0.1 ppm

Melon Spike 0.1 ppm

TABLE 3. SPIKING LEVELS AND PER CENT RECOVERIES

	ALDICARB			SULFOXIDE			SULFONE		
	level	avg	s.d.	level	avg	s.d.	level	avg	s.d.
WATER	0.05	71	7.8	0.05	67	9.7	0.05	91	8.9
SOIL	0.1	62	6.1	0.1	70	10.1	0.1	80	11.0
MELONS	0.1	--[a]		0.1	75	7.0	0.1	93	2.4
LEAVES	0.5	43	18.4	0.5	55	2.7	0.5	67	3.1

[a] Interferences, therefore, none reported.

RESULTS

MELONS. The analytical results for melon tissue are in Table 4. At a treatment rate of 1 lb a.i./acre, sulfoxide residues ranged from not detectable (MDL = 0.01 ppm) to 0.01 ppm. At 2 lb a.i./acre, sulfoxide residue averaged 0.05 ppm (9/13/85), 0.03 ppm (9/20/85), and 0.03 ppm (10/16/85). At 4 lb a.i./acre, sulfoxide residue averaged were 0.01 ppm (9/13/85), 0.06 ppm (9/20/85), and 0.05 ppm (10/16/85). The trend was toward higher residues as the treatment rate increased, but with substantial scatter in the values for individual sampling dates and treatments. Sulfoxide residues were much more pronounced than sulfone residues in all positive samples; the highest residue of all samples was 0.13 ppm sulfoxide. Aldicarb parent could not be determined because of analytical interferences; data in the literature indicate that aldicarb parent should be at best a minor residue in melon fruits under systemic treatment conditions. Control melons were free of sulfoxide and sulfone residue (i.e. <0.01 ppm). Melons from all plots treated with aldicarb in the irrigation water were also free of residue (<0.01 ppm).

WATER. No detectable residues of aldicarb, sulfoxide, or sulfone were observed (MDL = 0.01 ppm) in any water samples collected from the furrows adjacent to any of the treatments. This included water taken on Sept 4 from inside the metal barrier used to confine water in any given plot, even with water sampled from the highest soil treatment plot (4 lb a.i./acre) the day after treatment (9/3/85). Calculated concentrations of aldicarb in water used to treat the water-run plots were confirmed by analysis of aliquots of the treatment water.

SOIL. The analytical results for soil core samples are in Table 5. For the 9/13/85 sampling, no parent aldicarb was detected in any of the plots (MDL = 0.01 ppm). Sulfoxide/sulfone residue averages were 0.01/0.02 ppm (1 lb a.i./acre), 0.05/0.06 ppm (2 lb a.i./acre), and 0.09/0.13 ppm (4 lb a.i./acre). On this sampling date, there was a trend toward higher soil residues with increasing rates of treatment, and for sulfoxide and sulfone residues to be approximately equal. The results for the 9/19/85 and 10/16/85 soil samples did not follow these trends; there was neither a dose-related residue magnitude trend nor an approximately equal sulfoxide/sulfone residue. Also, the 10/16/86 sampling showed parent aldicarb in 7 of 9 soil samples, ranging to 0.12 ppm, where it was virtually absent in the 9/13/85 and 9/19/85 samplings -- a phenomenon which could reflect reduction of sulfoxide/sulfone by soil microorganisms. There was no detectable aldicarb-related residue in any soil background, control, or water treatment plots (MDL = 0.01 ppm for each chemical moiety).

LEAVES. The analytical results for melon leaves are in Table 6. For the 9/13/85 sampling, parent aldicarb was detectable (0.01 ppm) in just one of the samples. Sulfoxide was the dominant residue, with sulfoxide/sulfone results averaging 0.75/0.15 (1 lb a.i./acre), 0.73/0.28 ppm (2 lb a.i./acre), and 0.82/0.13 ppm (4 lb a.i./acre). There was thus no trend toward an increase in leaf residue with increasing treatment rate in this sampling. The 9/20/85 and 10/15/85 were generally lower for sulfoxide than the earlier sampling, indicating a dissipation with time of sulfoxide residues and a higher proportion of sulfone as the time to sampling increased. Generally, except for the anomaly noted above for one 9/13/85 sample and the appearance of 0.34 ppm of parent aldicarb in one 9/20/85 sample, the leaf results confirmed that

TABLE 4. ALDICARB SULFOXIDE RESIDUES (PPM) IN WATERMELONS[a,b]

DATE	PLOT ONE (1 LB/ACRE) S	M	N	PLOT TWO (2 LB/ACRE) S	M	N	PLOT 3 (4 LB/ACRE) S	M	N
9/13/85	<0.01	<0.01	<0.01	0.04	0.09	0.03	0.01	0.01	0.01
9/20/85	<0.01	0.01	0.01	0.02	0.04	0.03	0.04	0.13	<0.01
10/16/85	<0.01	<0.01	<0.01	0.04	0.02	0.02	0.05	0.06	0.03

S: = south; M = middle; N = north

[a] Sulfone residues: 0.02, 0.01, 0.01 PLOT 3 10/16. Sulfone residues were not detected in any other melon samples (MDL = 0.01 ppm).

[b] There were no detectable levels of aldicarb, sulfoxide or sulfone in any of the water application or control plots (plots 4-8) (MDL = 0.01 ppm).

TABLE 5. ALDICARB, SULFOXIDE, AND SULFONE RESIDUES (PPM) IN SOIL.

	ALDICARB Rep A	B	C	SULFOXIDE Rep A	B	C	SULFONE Rep A	B	C
9/2/85	NONE DETECTED IN ANY PLOTS								
9/13/85									
PLOT 1	<0.01	<0.01	<0.01	0.02	<0.01	0.01	0.04	<0.01	0.02
PLOT 2	<0.01	<0.01	<0.01	0.11	0.02	0.02	0.10	0.04	0.04
PLOT 3	<0.01	<0.01	<0.01	0.19	0.03	0.03	0.24	0.06	0.08
PLOTS 4-8 NO ALDICARB, SULFOXIDE OR SULFONE DETECTED (MDL = 0.01 ppm)									
9/19/85									
PLOT 1	<0.01	0.01	<0.01	0.18	0.18	0.04	0.05	0.04	0.06
PLOT 2	<0.01	<0.01	<0.01	0.02	0.17	<0.01	0.02	0.07	0.02
PLOT 3	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01
PLOTS 4-8 NO ALDICARB, SULFOXIDE OR SULFONE DETECTED (MDL = 0.01 ppm)									
10/16/85									
PLOT 1	0.02	<0.01	<0.01	0.04	0.01	0.01	0.06	0.04	0.03
PLOT 2	0.03	0.02	0.03	0.04	0.01	0.01	0.06	0.03	0.03
PLOT 3	0.12	0.05	0.01	0.01	<0.01	<0.01	0.05	0.03	0.02
PLOTS 4-8 NO ALDICARB, SULFOXIDE OR SULFONE DETECTED (MDL = 0.01 ppm)									

aldicarb and/or sulfoxide/sulfone was systemically taken up and transported to leaf tissue, where the residue was primarily the sulfoxide and sulfone metabolites. The leaf residues were substantially higher than melon residues as expected, perhaps because the flow of xylem (which presumably contains the residue) is predominately to the leaves for moisture transpiration.

There was no residue detected in the control leaves, or those from water treatment plots with a few exceptions. Sulfone appeared in a few water treatment plots (although it was <0.01 in most), indicating either sample contamination, or anomalous field behaviour of treatment chemical.

DISCUSSION.

GENERAL. It was recognized at the outset of the experiment that there were several inadequacies and/or uncertainties in the design. First, the time of treatment and subsequent sampling were quite late in the growing season (September) where as the normal period for growing melons in the Central Valley is April - August. At the time of treatment the melon vines were quite large (average vine length 5-10 ft) and some melons were up to 20 cm in length, although all were still far from ripe. For 2 of the weeks after treatment, cool, cloudy weather predominated slowing melon growth and thus presumably minimizing water and nutrient movement through the vines to the melons. The weather was thus not conducive to optimal melon development. Second, the treatments were selected by guess, both in terms of rates of application and the methods of application. Soil incorporation rates and treatment method were done in approximate accord with label directions for Temik 15 G on potatoes. Water treatment rates were selected by estimating the maximum tail water residue contents which might occur in the irrigation tail water; the estimate was based on analysis conducted by CDFA (Don Weaver) of

TABLE 6. ALDICARB, SULFOXIDE, AND SULFONE RESIDUES (PPM) IN MELON LEAVES.

	ALDICARB			SULFOXIDE			SULFONE		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
9/13/85									
PLOT 1	<0.01	<0.01	<0.01	0.26	1.32	0.66	<0.01	<0.01	<0.01
PLOT 2	<0.01	<0.01	<0.01	0.15	0.58	1.46	0.22	<0.01	0.21
PLOT 3	<0.01	<0.01	<0.01	0.30	0.70	1.46	0.22	0.36	0.27
PLOT 6	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.36	<0.01
PLOT 8	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.20	<0.01	<0.01
PLOTS 4, 5, 7 ALL BELOW DETECTABLE LEVELS.									
9/20/85									
PLOT 1	<0.01	<0.01	<0.01	<0.01	0.15	0.15	<0.01	0.22	<0.01
PLOT 2	<0.01	<0.01	<0.01	0.28	0.20	0.33	0.46	0.30	0.27
PLOT 3	0.34	<0.01	<0.01	0.84	1.16	0.61	0.30	0.21	<0.01
PLOT 5	<0.01	<0.01	0.03	<0.01	<0.01	<0.01	<0.01	1.24	0.22
PLOT 8	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.28	<0.01
PLOTS 4, 6, 7 ALL BELOW DETECTABLE LEVELS.									
10/15/85									
PLOT 1	<0.01	<0.01	<0.01	0.36	0.24	<0.01	1.01	0.50	<0.01
PLOT 2	<0.01	<0.01	<0.01	<0.01	0.01	0.06	0.19	0.21	0.23
PLOT 3	<0.01	<0.01	<0.01	0.02	0.01	0.26	0.20	0.20	0.28
PLOTS 4-8 ALL BELOW DETECTABLE LEVELS.									

water exiting a potato field treated by soil incorporation with Temik 15 G granules. Third, the available field size precluded replication of individual plots. The results must be interpreted with these points in mind.

MELONS. The results showed clearly that watermelons contain residues of aldicarb (as the sulfoxide) when the soil is treated with Temik 15 G by incorporation. The samples which gave positive values (primarily from the 2 and 4 lb a.i./acre rates) ranged from 0.01 to 0.13 ppm. Sulfone residues were much less than sulfoxide residues in all positive samples.

The results also indicate that treatment of melon plots with aldicarb in the irrigation water at rates of 0.02, 0.1, and 0.5 ppm was insufficient to produce measureable residues in the melons.

The magnitude of the melon residues from the soil incorporation plots was approximately 1/10th those alleged to have been present in commercial watermelons from the July 4, 1985, episode in California. The lower residue values could have been due to the timing, rate, and method of application in the experimental plots as well as the lateness of the season. It is not possible to speculate on which one of these factors was dominant in this regard.

WATER. The failure to detect aldicarb-related residues in irrigation water sampled after treatment was somewhat surprising. We can only speculate that aldicarb from both types of treatments moved into the soil to sufficient depths to prevent significant exchange with water in the irrigation furrows. This is in agreement with the high solubility of aldicarb (5730 ppm), and its known tendency to leach through irrigated soil.

SOIL. The soil residues were lower than expected. Calculation shows that 1 lb/acre of active ingredient uniformly incorporated in the top 10 cm of soil would give an average residue of 0.76 ppm. The highest residues in our core samples from the 1 lb/acre treatment was 0.43 ppm for combined sulfoxide plus sulfone while most samples showed a combined residue much less than 0.43 ppm. This was in spite of taking the cores from near the shank zone, although it was not possible to determine whether any core sample actually penetrated the shank zone. Residue penetration to below the depth of coring with the downward water flow (see p 20; see also results in J. Agric. Food Chem. 1986, 34:717-720) and breakdown of soil residues are possible explanations for the generally low soil residues from the incorporation treatments.

Failure to detect aldicarb-related residues in the soil from plots treated via irrigation water is less surprising. Calculation shows that at the highest water rate (0.5 ppm) the residue in the top foot of soil should be 0.07 ppm if it were uniformly distributed and no breakdown occured. At the 0.02 and 0.1 ppm water rates, residue should be near or below detection limits. Considering that the water additions were made in the furrows (rather than to that part of soil subjected to core sampling) and that some breakdown should occur in the soil, the non-detectable soil residues following this type of treatment are not unexpected.

LEAVES. Leaves showed the highest residues among the sample types analyzed, ranging to above 1 ppm combined sulfoxide/sulfone residue in many samples. These results confirm that the plants were taking up aldicarb residue and transporting them along the stems, presumably in the plants' xylem solution.

CONCLUSIONS

Even though the experimental design was not optimal in terms of replication and seasonal timing, several conclusions can be made.

1. When Temik was soil incorporated, at the rates studied, as a side dressing to fairly well developed melon plants, aldicarb-related residue was absorbed from the soil and transported to the aerial parts of the plant.

2. Residues were detected in melon flesh from the plants grown in the soil incorporation plots. Although the magnitude of residues observed in this study was relatively small (0.01 - 0.1 ppm), increasing the rate of application, changing the placement of applied material, and timing the treatment to a time of year when melons would be expected to grow vigorously could all influence residue magnitude in a given melon.

3. The principal soil, melon, and leaf residue observed was sulfoxide, with lesser amounts of sulfone, and still lesser amounts of aldicarb.

4. Treatment of melons plots with aldicarb dissolved in irrigation water did not, under conditions of our tests, lead to measureable residues in melons, soil, or (with a few exceptions) in melon leaves.

ACKNOWLEDGEMENTS

Financial assistance for this work was provided by the California Department of Food and Agriculture under a contract with the University of California.

Table 12. Continued. — PHYSICAL AND CHEMICAL SOIL ANALYSES —

Soil Series Reiff — Location W 1/2, Sec. 20, T. 8 N., R2E — Date Sampled 8/7/80

Sample No. 80-CA-113-18 — MDB&M — Date Reported 12/29/80

Lab No. 1483 — County Yolo — Analyst CM, AS, WRA

HORIZON SYMBOL	DEPTH (cm) From	DEPTH (cm) To	% GRAVEL [1]	PARTICLE SIZE DISTRIBUTION [2] % Sand (mm.) VCS 2.0mm to 1.0mm	CS 1.0mm to 0.5mm	MS 0.5mm to 0.25mm	FS 0.25mm to 0.10mm	VFS 0.10mm to 0.05mm	TOTAL 2.0mm to 0.05mm	% Silt 50µ - 2µ	% Clay [3] <2µ	% Clay [3] <1µ	TEXTURE Lab.	Bulk Density g/cc. [4]	MOISTURE RETENTION DATA [5] % Moisture Retained Air Dry	1/3 Atm.	15 Atms.	% Available Moisture 1/3 to 15 Atms.	% Moisture at Saturation
Ap1	0	23	0.3	0.6	1.0	2.6	17.9	21.9	44.0	39.3	16.7	14.2	1	1.6	3.3	22.3	12.2	10.1	41.6
Ap2	23	40	0.7	0.1	0.7	2.5	21.7	23.3	48.3	35.5	16.2	13.1	1	1.6	3.2	20.9	11.0	9.9	36.5
C1	40	83	0.0	0.2	0.2	1.2	19.8	27.6	49.0	38.1	12.9	10.6	1	1.5	3.3	20.5	10.6	9.9	37.1
C2	83	103	0.0	0.1	0.2	1.0	24.1	24.6	50.0	36.0	14.0	11.6	1	1.4	3.3	19.8	10.5	9.3	35.6
IIC3	103	130	0.0	0.0	0.3	1.4	32.6	29.3	63.6	25.6	10.8	9.3	fsl	1.4	3.1	16.3	9.1	7.2	34.3
IIC4	130	138	0.0	0.1	0.7	4.0	42.3	24.7	71.8	19.9	8.3	7.1	fsl	---	2.8	13.7	9.6	4.1	33.8
IIC5	138	158	0.0	0.0	0.9	5.0	33.2	26.0	65.1	24.5	10.4	8.4	fsl	1.4	2.9	15.0	8.5	6.5	33.3
IIIC6	158	184	0.0	0.0	0.4	1.3	18.3	30.1	50.1	37.4	12.5	10.6	1	1.4	3.4	19.2	10.3	8.9	36.1
IVC7	184	205	0.0	0.1	0.7	6.1	38.2	24.9	70.0	20.7	9.3	8.2	fsl	1.4	2.8	14.1	8.0	6.1	32.4

HORIZON SYMBOL	pH Glass electrode (Saturated paste)	% Carbonates	ppm Phosphorus [6] in the soil	Fe as $\%Fe_2O_3$ [10]	EXCHANGEABLE CATIONS (me./100 grams soil) [7] Ca *	Mg *	Na	K	Cation Exchange Capacity (me/100 grams soil) [8]	% Base Saturation	ORGANIC MATTER % Organic Carbon	% Organic Nitrogen	C/N	WATER SOLUBLE CATIONS (me./liter) [9] Ca	Mg	Na	K	EC x 10^3 mmhos/cm
Ap1	6.7	–	11.3	–	10.2	10.4	0.2	0.5	21.7	98.2	1.11	0.104	11	3.4	5.6	1.0	0.3	0.7
Ap2	6.9	–	3.4	–	9.0	10.1	0.2	0.3	22.7	86.3	0.61	0.062	10	1.2	2.2	1.0	0.1	0.4
C1	7.0	–	25.3	–	8.4	10.7	0.2	0.5	22.8	86.8	0.50	0.048	8	0.8	1.4	0.8	0.1	0.2
C2	7.1	–	28.7	–	9.0	10.2	0.3	0.3	23.8	83.2	0.45	0.043	10	0.8	1.2	1.1	0.1	0.2
IIC3	7.3	0.0	24.5	–	7.7	10.4	0.2	0.2	20.1	92.0	0.24	0.026	9	1.0	1.0	1.1	0.0	0.2
IIC4	7.5	0.0	19.6	–	5.2	9.1	0.2	0.1	18.0	81.1	0.20	0.023	9	1.2	1.4	1.2	0.1	0.3
IIC5	7.6	0.0	21.9	–	8.3	9.9	0.2	0.1	19.0	97.4	0.22	0.026	8	1.2	3.0	1.8	0.1	0.4
IIIC6	7.7	0.1	14.7	–	9.0	11.0	0.3	0.2	22.2	92.3	0.27	0.032	9	1.2	1.4	1.5	0.1	0.3
IVC7	7.8	0.1	20.5	–	5.2	9.4	0.4	0.1	17.0	88.8	0.22	0.025	9	0.8	1.6	1.5	0.1	0.3

Analyses by Soil Morphology Laboratory University of California Davis

1 BY WEIGHT OF FIELD SAMPLE
2 BY WEIGHT OF SOIL <2MM
3 PIPETTE METHOD
4 DENSITY OF AIR DRY CLOD
5 MOISTURE ON OVEN DRY BASIS
6 SODIUM BICARBONATE EXTRACTABLE
7 IN AMMONIUM ACETATE pH 7.0
8 BARIUM SATURATED
9 SOLUTION EXTRACTED FROM SATURATED PASTE
10 CBD METHOD

REMARKS: *Ca & Mg by $BaCl_2$ • TEA extraction

PHYSICAL AND CHEMICAL SOIL ANALYSES —

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Original Date: 8/26/85
Supercedes: NEW
Current Date: 8/26/85
Method #: 110

ALDICARB RESIDUES IN WATERMELON

SCOPE:
This method has been developed and used for the rapid analysis of aldicarb sulfoxide, aldicarb sulfone, and aldicarb in watermelons

PRINCIPLE:
The aldicarb and metabolites are extracted from the watermelon tissue with acetonitrile. The acetonitrile is then separated from the water by shaking out with salt. The acetonitrile extract is then run directly by post column reaction techniques on HPLC or concentrated and run by gas chromatography.

REAGENTS AND EQUIPMENT:

1. Acetonitrile, HPLC grade
2. Sodium Chloride - crystal, reagent, A.C.S.
3. Methanol, HPLC grade
4. Acetone, pesticide grade
5. Water, HPLC quality, filtered.
6. High Speed Blender, Sorval or equivalent. Explosion proof with 1 pint capacity jars and blender heads.
7. Graduated glass mixing cylinders with ground glass stoppers, 100 ml capacity.
8. Funnels, 60 degree short stem. 3 or 4 inch diameter.
9. Sharkskin filter paper to fit funnels in item 8.
10. Vials, automatic liquid sampler vials and seals or appropriate 1- 2 ml vial for holding sample for chromatography.
11. Bottles, 2 ounce brown bottles with teflon or foil lined lid.
12. Assorted pipets and other volumetric glassware for measuring and dispensing reagents as required.
13. Reverse phase HPLC with post column reaction system for fluorescence detection.
14. Gas chromatograph equipped with Hall detector in sulfur mode, FPD detector in the sulfur mode, or a nitrogen detector as third choice.

ANALYSIS:

1. Sample watermelons by using a coring device to take cores on the long axis of the melon from end to end. Cut the rind off of the cores and discard. Dice the cores and take a representative sample from the diced fruit. As an alternative cut a wedge from the melon along the long axis. Cut the fruit off of the rind and dice and mix. Use the composited fruit for the sample.

2. Weigh 50 grams of edible portion of the watermelon into a pint mason jar. Add 100 ml of HPLC grade acetonitrile and blend on a high speed blender, such as Sorval, for three minutes.

3. Add about 15 grams of sodium chloride to a glass mixing cylinder.

4. Pour the homogenized extract through a funnel containing sharkskin filter paper until about 100 ml of extract is collected in the mixing cylinder.

5. Stopper and shake the mixing cylinder vigorously for at least one minute. Let the cylinders settle for about 10 minutes or centrifuge to separate the acetonitrile and water phases.

6. The acetonitrile layer (upper) is used for the analytical determination.

HPLC DETERMINATION:

1. Depending of the sensitivity of the HPLC system a portion of the acetonitrile extract may be filtered through a 0.45 micron LC filter and injected directly into the HPLC.

2. If more cleanup is required a 25 ml portion of the acetonitrile extract may be passed through a C18 Waters SEP Pack and evaporated down to the desired concentration (1 or 2 ml). The concentrated extract is the filtered through the 0.45 micron LC filter and injected into the HPLC.

3. If further cleanup is still required pass a 25ml aliquot of the acetonitrile extract through the C18 SEP Pack. Evaporate the acetonitrile just to dryness. Redissolve the residue in 5-10 ml of methylene chloride and pass it through a Waters Florisil SEP Pack. Discard the eluate. Wash the SEP PAck with 5 ml of 50% acetone in diethyl ether and discard eluate. Wash with an additional 2 ml of the 50% mixture and discard. Elute the aldicarb sulfoxide from the SEP Pack with 5ml of methanol. Concentrate the methanol to 1.0 ml and inject into the HPLC.

   NOTE: In step #3 above, the aldicarb sulfone is not quantitatively recovered under these elution conditions. Further investigation would be required to elute both the aldicarb sulfoxide and sulfone for this determination.

NOTE: Some investigators feel that better recovery is obtained by exchanging the solvent from acetoneitrile to methanol prior the running on the HPLC.

GAS CHROMATOGRAPHIC DETERMINATION:

1. Take a 25 ml aliquot of the acetonitrile extract. Evaporate just to dryness in a 100 or 150 ml beaker using a steam bath and gently flowing air. Remove from steam bath and immediately add 1 or 2 ml of acetone to cool and dissolve the residue. Quantitatively transfer with portions of acetone to a graduated 15 ml test tube. Evaporate the combined acetone washings to 1.0 ml final volume. Transfer into an autosampler vial and cap.

2. If a nitrogen detector is to be used for the determination, add one or two mls of acetone just as the beaker goes dry on the steam bath and evaporate just to dryness. Repeat once more to eliminate traces of acetonitrile. Then proceed as in step 1 above.

3. Inject from 1 to 8 microliters as required for sensitivity. This method will determine the sulfoxide and the sulfone. The parent aldicarb is not readily chromatographed and (according to R. Romine of Union Carbide) is not expected to be present in the sample.

EQUIPMENT CONDITIONS:

HPLC CONDITIONS:

Perkin Elmer Series 4 HPLC with ISS-100 automatic sampler and column oven, or equivalent. Post column derivatization system and fluorescence detector as described by Krause, Muth, or Ting, or equivalent.

Column:

A. Sepralyte cyclohexyl (CH), 5 micron, 4.6mm i.d. x 25 cm (Analytichem International).
B. Ultrasphere ODS, 5 micron, 4.6mm x 15cm (Beckman).

Flow conditions:

For aldicarb sulfoxide and sulfone use:
1.5ml/min of 18% acetonitrile / 82% water.

For parent aldicarb and metabolites a gradient run is required.
1.5ml/min
7 minutes @ 15% Acetonitrile / 85% water
7 minute gradient to 50% acetonitrile / 50% water
5 minutes @ 50% acetonitrile / 50% water
7 minutes equilibrium @ 15% acetonitrile / 85% water

Oven Temperature = 35 degrees C.

Injection Volume = 20 microliters or greater.

GC CONDITIONS:

The gas chromatographic technique uses a pyrolysis reaction in the injector to fragment the aldicarb molecules to components which may be chromatographed without peracetic acid oxidation of the sample.

Gas chromatograph equipped with 530 micron injector and detector adapters (or capillary inlet/outlet equipped). Detectors used include Sulfur Hall, Sulfur FPD, and nitrogen specific detectors.

Injector Temperature = 250 to 270 degrees C. The injector should be lightly packed with glass wool to aid the pyrolysis reaction. If a packed column is used the packing should not extend into the injector heat zone.

Column:
50% Phenylmethyl 530 micron x 10 meter fused silica column at 95 to 100 degrees C and 30 ml/min of Helium carrier gas.

Detectors:
Run per manufacturer supplied instructions. On Sulfur Hall detector a furnace temperature of 820 degrees C is used an about 30 ml/min. of reactant air. Hall scrubbers and solvent modules from Craven Laboratories were used in the project.

CALCULATION:
Report data in ppm.

DISCUSSION:
This method is for the rapid determination of the aldicarb metabolites in watermelon. It may be extended to other crops dependent on coextractive interferences. The peracetic acid oxidation method from the Pesticide Analytical Manual (FDA) can be used for further confirmation if required. Recoveries from this method average about 80%.

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