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Levels of Arsenical Species in Cotton After Field Application of a Cacodylic Acid Defoliant

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Organo-arsenical compounds are used as defoliants and weed control agents in cotton production in various parts of the United States. Cacodylic acid (dimethylarsinic acid) is a registered defoliant and is used primarily to aid in mechanical harvesting of irrigated cotton in the West. However, the fate of arsenic compounds on plants, after application has not been extensively studied.

Several authors (WOOLSON 1983, ISENSEE et al. 1973, BRAMAN & FOREBACK 1973) have detected degradation of cacodylic acid (CA) and methanearsonic acid (MAA) to dimethyl- and trimethylarsines in soil or grass/soil systems.

BRAMAN & FOREBACK (1973) studied the evolution of alkylarsines on grass plots treated with water containing CA and MAA. They found production of both dimethyl- and trimethylarsine but not methylarsine. Avenues of soil breakdown of CA were studied by WOOLSON & KEARNEY (1973) & WOOLSON (1977a). Two aerobic mechanisms of breakdown were identified, C-As bond cleavage to yield arsenate and reduction to a volatile organoarsenical, while only the reduction process was identified for anaerobic systems.

Degradation of MAA in soils has been studied and several methods of inactivation noted (HILTBOLD et al. 1974, COX and ALEXANDER 1973, HILTBOLD 1975, SANDBERG & ALLEN 1975). Transformations of MAA to CA and CA to MAA in soil are summarized by WOOLSON (1977b).

Degradation and transformation of CA in plant species have not been well studied. SACHS & MICHAEL (1971) examined metabolism of CA in Black Valentine bean and found what appeared to be unchanged CA in extracts of leaf and root tissue. No arsenite or MAA was found.

Degradation of MAA in plants has been more extensively studied. Many authors report complexation of the As in plants into organic molecules (SACHS & MICHAEL 1971, DOMIR et al. 1976, WOOLSON et al. 1976). Transformation of MAA to CA has been reported as one possible method of breakdown and detoxification although differences between resistant and susceptible species exist.

This project was an attempt to identify degradation pathways and quantitate rates of transformation of CA applied as a defoliant to cotton.

METHODS AND MATERIALS

A John Deere Hi Cycle sprayer applied 3 pints of cacodylic acid defoliant formulation (Bolls-Eye, Table 1) in 35 gallons to each acre in two separate fields in Dos Pasos, Calif. Test 1 was planted in Acala SJ-2 cotton and Test 2 in Acala SJ-4. Application was made when about 50% of the bolls were open. Random boll samples were gathered before application and at 2, 4, and 8 days afterwards. An additional sample was obtained about 25 days after application and after the cotton had been picked the first time.

TABLE 1. Analysis of Herbicide BOLLS-EYE[1].

	%
Cacodylic Acid and Sodium Cacodylate (as CA)	24.81
MSMA	3.99
Combined As (as CA) from CA + MSMA	28.21
As (III) (inorganic)	0.2
As (V) (inorganic)	0.69
Sodium Chloride	7.23
Sodium Sulfate	0.8
Surfactant	1.7
Ethylene Glycol	5.0

[1] As reported by Crystal Chemical Co., 1980. Trade mark of Crystal Chemical Co. Average of six batches.

Three replicate samples were taken at each site. The samples were stored at -5°C until analyzed. Results from each field were analyzed separately since field conditions and cotton varieties were not identical. In Test 1, 0.4 inch of rain fell on day 7, while in Test 2, the same amount fell on day 5.

Cotton seed was ginned and analyzed in order to determine if there was active transport of As to the seed after spraying. Lint was removed from the seed with H_2SO_4.

Total As for duplicate lint and seed samples was determined by graphite furnace atomic absorption spectroscopy (GFAA) after digestion of a subsample by $HNO_3/H_2SO_4/HClO_4$ techniques (WOOLSON et al. 1971).

A modification of the technique described by SACHS et al. (1971) [using (1:1/v:v) MeOH and 2M NH_4OH] was used to extract the arsenicals from the lint for analysis. Analysis was by high performance liquid chromatography (HPLC) using GFAA as the detector (WOOLSON & AHARONSON 1980). This technique effectively separates and quantitates levels of CA, MAA, arsenate and arsenite with detection limits of about 5 ng. Duplicate analyses were averaged in order to arrive at a final value for each species in each sample.

Statistically significant differences in the levels of each arsenical species were determined by Analysis of Variance Procedure (ANOVA) (STEELE & TORRIE 1960) and Duncan's New Multiple Range Test (DUNCAN 1955) ($p<0.05$). Correlation coefficients between levels of each As species were determined.

RESULTS AND DISCUSSION

Though the absolute levels differed in the two tests (Table 2), in most cases the statistically significant trends identified were similar. The levels of total As in the lint decrease over time dropping significantly between 4 and 8 days after application. Levels dropped nearly to background (pre-application) at 25 days (after first picking).

TABLE 2. Total and speciated arsenic residues in cotton lint following defoliation with cacodylic acid.

		As found in lint ug As/g				
Test	Time[1]	By digestion		By digestion		
(days)		(Total As)	CA	MAA	Arsenate	Total
I	PA	3.0a[2]	0.03a	0.06a	0.88a	0.97
	2	32.5b	35.7b	3.45c	0.88a	40.0
	4	37.9b	34.0b	2.70b	1.67b	38.4
	8	12.1a	15.9a	1.82b	1.41a	19.2
	AFP	4.8a	4.0a	0.40a	1.06a	5.5
II	PA	2.1a	0.02a	0.33a	0.81a	1.2
	2	86.9b	72.7b	9.13b	3.03b	84.9
	4	76.5b	57.7b	8.48b	1.78a	68.0
	8	16.1a	20.9a	1.52a	0.89a	23.3
	AFP	3.6a	0.3a	0.02a	1.13a	1.4

[1] PA = preapplication; AFP = After first picking.

[2] Means within each column and each test followed by the same letter are not significantly different using ANOVA and Duncan's Multiple Range Test ($P<0.05$).

Cacodylic acid, MAA and arsenate were detected in the lint in both tests. There is about a 4% (ca. 12% of the organoarsenical actually applied) contamination of Bolls-Eye with MAA prior to spray (Table 1). No arsenite or other forms were noted.

Cacodylic acid in cotton lint (Table 2) exhibited a decreasing trend over the study period with significant differences being noted between 4 and 8 days after application. Levels after picking were not significantly different from that prior to application or 8 days after application. Mean levels found at days 2 and 4 were not significantly different from each other but were significantly higher than all others. Both Tests 1 and 2 show similar results.

Methanearsonic acid in cotton lint (Table 2) followed a similar decreasing trend. In Test 1, the MAA level found 2 days after spraying was significantly different from all other means. The levels found at 4 and 8 days were significantly less than at day 2. Pre-application and post first-pick levels of MAA were not different from one another, but significantly different from all other means.

Arsenate levels in lint (Table 2) showed no significant change from baseline throughout Test 1. In Test 2, arsenate levels were found to be significantly higher only 2 days after spraying and returned to near baseline levels at 4 days. In both Test 1 and Test 2 (Table 3), high positive correlations were found for CA and MAA in cotton lint. Similar results were found for the correlation between arsenate and CA as well as arsenate and MAA in Test 2.

This indicates that all compounds were at their respective peaks simultaneously in lint. Results of Test 2 for correlations with arsenate did not bear the same high positive coefficients. However, arsenate levels were not significantly above background in Test 1 (Table 2).

TABLE 3. Correlation Coefficients (Value) Of Speciated Arsenical Forms In Cotton Lint From Two Fields In Dos Pasos, California.

Time	Test I	Test II
Cacodylic acid - Methanearsonic acid	.898	.973
Cacodylic acid - Arsenate	.393	.823
Methanearsonic acid - Arsenate	.294	.789

Total As, CA, MAA, and arsenate (Tables 2 & 4) peak immediately after spraying and decline over time. In all cases the levels found are not significantly above the pre-application background level at 8 days. In most cases, background level is reached within 4 days for all three forms.

Cotton seed total As (Table 4) levels were low, nearly at detection limit (0.2 ug As/g seed) and exhibited no significant differences. This suggests there was no detectable transport or translocation of CA within the plant after spraying. Residues are higher, even for the controls, than those reported for MSMA in cottonseed by BAKER et al. (1969)(0.05 ppm As) or EHMAN (1966)(0.4 ppm As). Differences in sample digestion techniques or growing conditions may account for the observed differences in residue levels. Differences between the 2 tests were not significant.

TABLE 4. Mean Total As In Cotton Seed After Field Application Of Cacodylic Acid[1].

Time	Test I	Test II
	Total As ug/g cotton seed	
Pre-application	0.77	<0.1
2 Days	0.37	0.52
4 Days	1.24	0.77
8 Days	0.73	0.39
After first picking	0.70	0.11

[1] Crystal Chemical Co., 1980; trade mark (Bolls-Eye).
[2] No values were different using ANOVA and Duncan's Multiple Range Test ($p<0.05$).

The results of the correlation analyses lead one to the conclusion that levels of both MAA and arsenate are not significantly affected by the breakdown of CA. In fact, it seems that levels of MAA and arsenate peak and decline over the same time frame as does CA. It is likely therefore, that their presence is from the application of the original herbicide solution and not degradation products of CA. This conclusion is in agreement and supported by the data in Table 1 showing levels of MAA and arsenate in Bolls Eye of 3.97% and 0.69%, respectively. The apparent reduction in residues with time may have been due to dilution since the open bolls were not tagged prior to spraying. A second possibility is loss of volatile alkyl arsines from the lint. A more complete picture of the fate of organo-arsenicals in the field can be obtained with air sampling and tagging open bolls at the time of application for later sampling and analysis.

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