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Application of the High-Performance Liquid Chromatography–Flameless Atomic Absorption Method to the Study of Alkyl Arsenical Herbicide Metabolism in Soil

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Arsenite, cacodylic acid (CA), methylarsonic acid (MAA), and arsenate in soil extracts were separated on an anion-exchange high-performance liquid chromatography (HPLC) column and detected on a graphite furnace atomic absorption (GFAA) spectrometer. Laboratory soils were treated with CA and amended with 0, 50, or 100 tons/ha of sewage sludge, manure, or hay. In moist aerobic soils, 80% of the 10 ppm of As applied as CA was degraded within 60 days. Degradation of [^{14}C]CA was followed by the formation of arsenate and small amounts of MAA. ^{14}C and arsenic were lost from the soil in the form of $^{14}CO_2$ and volatile alkylarsines. CA degradation in flooded anaerobic soils was slower with larger amounts of MAA and less $^{14}CO_2$ formed than found in aerobic soils. CA degradation in soils treated with 1000 ppm of $HgCl_2$ or 100 tons/ha sewage sludge was inhibited. In a field experiment, MAA and CA were detected 1.5 years after MAA, CA, or arsenite was applied, but the major product was arsenate. The half-life for field-applied CA or MAA was 20 and 22 days, respectively.

Within the past few years several analytical procedures have been suggested for molecular speciation of methylated and inorganic arsenic residues at sub ppm levels in environmental samples. Recent developments include separation by GLC (Talmi and Bostick, 1975) or cation-exchange resin (Yamamoto, 1975) and detection by highly sensitive detectors such as flameless atomic absorption (AA) (Fitchett et al., 1975; Anderson, 1978) or microwave emission spectroscopy (MES) (Braman et al., 1977). A second approach was the generation of volatile arsines by $NaBH_4$ reduction and direct determination by flameless AA (Chu et al., 1972; Shaikh and Tallman, 1977) or MES. Separation was achieved by stepwise reduction at different solution pHs (Braman and Foreback, 1973) and selective temperature programming after freezing the gases on a solid substrate. Recently Brinckman et al. (1977) suggested HPLC separation coupled with flameless AA for organometallic compounds. Woolson and Aharonson (1980) separated arsenate, arsenite, cacodylic acid (CA), and methylarsonic acid (MAA) by HPLC–flameless AA employing a low-capacity anion-exchange column, with a detection limit of 1–5 ng of As injected onto the column. The procedure is simple, can be completely automated, and enables direct speciation of microquantities without any chemical modification of the compounds.

Arsenate(5+) is the stable oxidized form and can be found in measurable amounts in nearly all aerobic soils (Woolson, 1977a). Under reducing conditions, such as those present in flooded soils, arsenite(3+) might be found. Elevated arsenic levels were detected in agricultural land treated with arsenical pesticides (Woolson et al., 1971).

Methylation of inorganic arsenicals has been shown to occur in nature, and the metabolism in soil probably proceeds through mono- to dimethylarsinic acid and to the volatile gases dimethyl- and trimethylarsines (Hiltbold, 1975; Cox, 1975). GC–MS has been used to speciate methylarsines (Cheng and Focht, 1979). Certain fungi and bacteria were found to transform arsenate, arsenite, CA, and MAA. The rate and direction of transformation in soil will depend upon the type of microorganisms involved and soil conditions (Walsh and Keeney, 1975).

The lack of simple analytical procedures suitable for speciation of arsenic compounds has hampered studies of transformation and fate of these compounds in soil. Results obtained by using a new technique employing HPLC and flameless AA for the organoarsenical herbicides and their metabolites in soil are described in this work.

MATERIALS AND METHODS

[^{14}C]CA and analytical standards of CA (99.8%) and MAA (99.5%) were obtained from the U.S. Environmental Protection Agency, Research Triangle Park, NC. Ana-

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[1]Work was done on sabbatical leave from the Agricultural Research Organization, Volcani Center, Bet-Dagan, Israel.

lytical-grade sodium arsenate and sodium arsenite were purchased.

The HPLC system consists of two A-6000 pumps and a 660 solvent programmer (Waters Associates, Inc.). A 250 × 3 mm i.d. glass low-capacity anion-exchange column (Dionex Co.) was connected via a Teflon flow-through sampling cup to a Perkin-Elmer Model 603 atomic absorption spectrometer, equipped with a HGA-2100 graphite furnace (GFAA), auto sampler, and a printer (Woolson and Aharonson, 1980). Operation conditions were as follows: flow rate, 1.2 mL/min (ca. 300 psi); solvent programmed from 100% H_2O–MeOH (80:20 v/v) to 100% aqueous 0.02 M $(NH_4)_2CO_3$–MeOH (85:15 v/v).

Analytical Procedure. (*a*) *Soil Extraction and Cleanup.* Ten grans of soil was shaken overnight with 50 mL of 2 M NH_4OH and centrifuged (Sorval RC-2), and the soil was shaken 2 more times (5 and 16 h) with 50 mL of 2 M NH_4OH. The extracts were combined and 10 mL of 0.1 M 8-quinolinol sulfate was added. The solution was then passed through a 150 × 20 mm i.d. glass column filled with 100 mm of a carbon–celite (1:1 w/w) mixture and the column washed with an additional 100 mL of H_2O. A vacuum was pulled at the column exit to speed up the flow. The charcoal was Darco S-51 and the Celite, Celite 545 (Fisher Scientific). The extract was concentrated on a rotary evaporator to ca. 1 mL and transferred with a final volume of 10 mL. An aliquot, usually 20 μL, was injected onto the HPLC–GFAA. Additional details on the procedure and recovery results were described elsewhere (Iadevaia et al., 1980). Cochromatography was done with known standards and soil extract.

(*b*) *TLC Cleanup.* Samples that appeared to have less than 0.3 ppm of CA or MAA were concentrated to 2 mL, and 1 mL was placed as a streak on a 500-μm MN 300 cellulose TLC plate. Standards were spotted adjacent to the streak.

After development in ethyl acetate–acetic acid–water (3:2:1 v/v/v), spots were visualized with 1% $AgNO_3$ followed by 0.1% silver diethyldithiocarbamate and exposure to sunlight. The sample was scraped off the cellulose plate at the appropriate R_f (arsenite, 0.36; arsenate, 0.46; MAA, 0.70; CA, 0.83). The dry cellulose was extracted twice with 10 mL of 50% MeOH. Each fraction was centrifuged and concentrated to 2 mL, and 50 μL was injected onto the HPLC–GFAA.

(*c*) *Mass Spectrometric Confirmation.* The soil sample extract was transferred to a 50-mL round-bottom flask and flash evaporated to dryness. Under a nitrogen atmosphere, hydriodic acid (10 mL of 47–51%) was added to the flask, and the resulting solution was stirred continuously for 1 h (Irgolic et al., 1975; Soderquist et al., 1974). The solution was extracted with hexane (4 mL), and the hexane phase evaporated to approximately 0.5 mL under a nitrogen stream. A 1-μL sample of the hexane, which contained the iodoarsines, was injected onto a Finnegan 4000 GC–MS fitted with a 1.8-m 3% dexsil 300 column. Electron impact spectra were obtained at a source block temperature of 200 °C. Data were collected via an Inco data system. Derivatives of standards were run for comparison.

Metabolism of CA in the Soil. *Experiment 1: Laboratory.* Matapeake silt loam soil was air-dried to 10% mositure, sieved to 2 mm, and treated with the equivalent of 50 or 100 tons/ha sewage sludge, dairy manure, or hay according to the procedure described by Doyle et al. (1978). An unamended soil and a sterile control (1000 ppmw of $HgCl_2$) were also included. [^{14}C]Cacodylic acid (6.2 μCi and 10 ppmw of As as CA) was added to all samples and mixed thoroughly by tumbling. After 100-g subsamples were taken, each 250-mL flask received enough water to bring the soil to 77, 82, 93, 125, or 230% of field capacity moisture (34.7%). The flasks were connected in sequence to 0.1 M NaOH and a KI-saturated I_2 scrubber. A vacuum was pulled on the entire system. Incoming air was scrubbed with 0.1 M NaOH to remove CO_2. Samples were taken periodically from the traps and flasks for analysis. The oxidized alkylarsines were detected by the described HPLC–GFAA procedure while $^{14}CO_2$ was detected with a Searle Mark II liquid scintillation counter.

Experiment 2: Field. Eight annual applications of sodium arsenite, cacodylic acid (Phytar 560), and MSMA (Ansar 529) were applied to Matapeake silt loam at 17.9, 22.4, and 11.2 kg of a.i./ha in three replications, respectively. When mixed into the surface 15 cm, each application added 4.6, 5.4, or 2.4 ppm of As, respectively. These rates are double the maximum recommended for each compound. Seven annual applications at 89.5, 112.0, and 56.0 kg of a.i./ha (10 times that recommended) were added to other plots; the last addition of the high rate was made 1 year prior to the start of sampling. The total amount added to the higher treatments was 112, 114, and 70 ppm of As, respectively, in the surface 15 cm of soil.

Soil samples were collected from both rates for each chemical at 1 and 26 weeks after treatment. In addition, the lower rate was also sampled at 2, 5, 8, and 13 weeks after treatment and soil incorporation. Ten random grab samples were taken from each of four replications at each sampling time, dried sufficiently to sieve through a 2-mm screen, and stored at −5 °C until analyzed.

Arsenite Oxidation. Soil extracts from 0, 130, 660, and 1650 mg of soil, were added to 2 M NH_4OH. All solutions were made to 50 mL, and 2 ppm of As as arsenite in 2 M NH_4OH was added. Additional samples consisted of 10 mL of 0.1 M 8-quinolinol sulfate plus soil extract from 660 mg, ferric chloride, and 0.2 M NH_4OH plus soil extract from 660 mg. The solutions were kept at room temperature (24 °C) for 5 weeks. On days 0, 1, 6, 11, and 32 after the start of the experiment, aliquots of 20 μL each were injected onto the HPLC–GFAA. The second replicate was analyzed on days 0, 1, 3, 7, and 11.

RESULTS AND DISCUSSION

The analytical procedure that was developed for speciation of arsenical pesticide residues and their metabolites by HPLC coupled in line to the GFAA (Woolson and Aharonson, 1980) was utilized to study the metabolism of CA in soil. All chemicals and solvents that were used in this work were pretested and selected to prevent matrix interference during quantitation by the GFAA.

Metabolism of CA in the Soil. *Experiment 1: Laboratory.* Speciation by HPLC–GFAA of the arsenical compounds is demonstrated in Figure 1. Each HPLC peak consists of several injections into the GFAA. Each line represents one injection of the automatic sampler into the graphite furnace and is measured as the AA peak area integrated over 8 s of the atomization cycle. The peak area for each compound was proportional to the sum of the individual injections for that peak.

Standards added to untreated soil gave 80 and 90% recovery for MAA and CA, respectively, and 65% for arsenate and arsenite (Iadevaia et al., 1980). At a soil concentration of less than 0.3 ppm of As, an additional cleanup on TLC was needed to remove salts in the soil extract. Recovery was lower by 5–15% when 0.1 ppm of CA or MAA was cleaned up on TLC. Recovery of arsenate at that concentration was not determined since its level in untreated soils is higher than 1.0 ppm. Values were corrected for recovery.

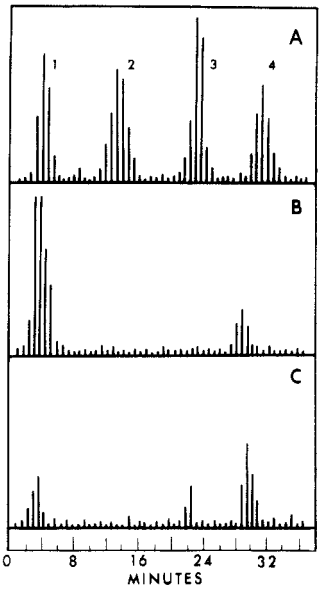

Figure 1. Speciation by HPLC–GFAA of arsenite (1), cacodylic acid (CA) (2), methylarsonic acid (MAA) (3), and arsenate (4). (A) Standard mixture; (B) soil extract 7 days after application of 10 ppm of CA; (C) soil extract 60 days after application. Conditions: 1.2 mL/min; starting solvent, water–methanol (80:20 v/v); final solvent, 100% aqueous 0.02 M ammonium carbonate–methanol (85:15 v/v).

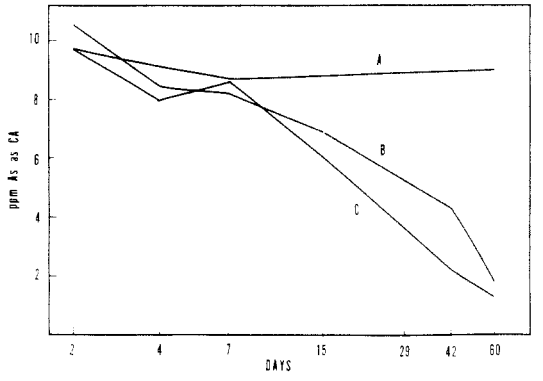

Figure 2. Metabolism of cacodylic acid (CA) in soils that were treated with (A) $HgCl_2$ or 100 tons/ha sludge or (B) 100 tons/ha manure or hay or 50 tons of sludge or (C) untreated.

Cacodylic acid is degraded to two products in soil: (1) volatile di- and trimethylarsine (Woolson, 1977a,b) and (2) arsenate and CO_2 (Woolson and Kearney, 1973). About 80% of the CA was degraded within 60 days (Figure 2). There were no significant differences between soils treated with an equivalent of 100 tons/ha of hay, dairy manure, or 50 tons/ha hay, manure, or sewage sludge. These treatments were therefore averaged and plotted to give a line for treatment with a half-life of 31 days. However, soils treated with an equivalent of 100 tons/ha sewage sludge were toxic, and degradation was inhibited similar to that of the sterile control treated with $HgCl_2$. Cacodylic acid was degraded faster in the untreated soil (i.e., no organic matter added) than in the amended soils. The half-life was only 20 days rather than 31 days. The difference could be attributed to differences in the supply of organic matter and microbial populations.

Water up to 125% of field capacity did not influence the degradation of CA significantly (Table I). However, degradation was slower under flooded conditions, and significant amounts of MAA were found in treated soils after 60 days. Lower amounts of arsenate were also observed under flooded conditions. No moisture effects were observed with the $HgCl_2$ or high-sludge treatments.

Table I. Concentration of Cacodylic Acid (CA) and Two of Its Major Metabolites Extracted from Soil Treated with 10 ppm of As as CA 60 Days after Application

		ppm of As			
treatment	moisture level,[a] %	CA	MAA	arsenate	total As extracted
$HgCl_2$	77-125	9.0	ND[b]	2.2	11.2
	230	8.5	ND	2.1	10.5
sludge 100[c]	77-125	8.2	ND	3.1	11.3
	230	10.4	ND	3.4	13.8
untreated	77-125	1.3	0.8	5.6	7.7
	230	1.6	ND	2.4	4.0
treated[d]	77-125	1.8	0.3	5.1	7.2
	230	4.1	3.6	2.8	10.5

[a] Field capacity = 34.7%. [b] ND = not detected. [c] Treated with 100 tons/ha sewage sludge. [d] Average of soils treated with 50 or 100 tons/ha hay or manure or 50 tons/ha sewage sludge.

Table II. Volatile Metabolites from Soil Treated with 10 ppm of As as [^{14}C]CA

		% of applied	
treatment	moisture level,[a] % of field capacity	alkylarsines	$^{14}CO_2$
$HgCl_2$	77-125	0.5	0.2
	230	0.2	0.2
sludge 100[b]	77-125	0.3	2.3
	230	0.1	0.1
untreated	77-125	0.5	45.2
	230	0.1	23.0
treated[c]	77-125	1.4	26.0
	230	0.6	0.9

[a] Field capacity = 35%. [b] Treated with 100 tons/ha sewage sludge. [c] Average of soils treated with 50 or 100 tons/ha hay or manure or 50 tons/ha sewage sludge.

Moisture and treatment affected the amount of As extracted and recovered from soil. Greater apparent total As losses were observed from the untreated soil under flooded conditions, whereas at lower moisture contents, losses from the treated and untreated soils were similar.

Residues from the low sludge sample were examined by GC–MS. It was confirmed that the observed residues were CA and MAA, determined as the iodo derivatives. The CA was detected as the dimethyliodoarsine (m/z 232). Major fragments were m/z 217 [$(M - CH_3)^+$], 202 [$(M - 2CH_3)^+$], 105 [$(M - I)^+$], 89, and 75. The MAA was detected as the methyldiiodoarsine (m/z 344). Major fragments were m/z 329, [$(M - CH_3)^+$], 217 [$(M - I)^+$], 202, 127, 89, and 75.

Total arsenic found in the soil 60 days after treatment with $HgCl_2$, and sewage sludge was higher than that found in all other soils in which most of the CA was degraded (Figure 2). Part of the CA was transformed and lost from the soil as the volatile alkylarsines after 60 days (Table II). However, the quantities were too small to account for all the missing As. The amounts trapped were not proportional to what was lost. This was probably due to an inefficient trapping procedure.

Degradation under aerobic conditions in treated and untreated samples was very similar when $^{14}CO_2$ was examined. However, under anaerobic conditions, the untreated soil metabolized significant amounts of [^{14}C]CA, whereas the treated soils did not (Table II). Under aerobic conditions, 32% of the CA degraded was trapped as $^{14}CO_2$, whereas under anaerobic conditions very little $^{14}CO_2$ was detected from the treated soil. [^{14}C]Methane would not

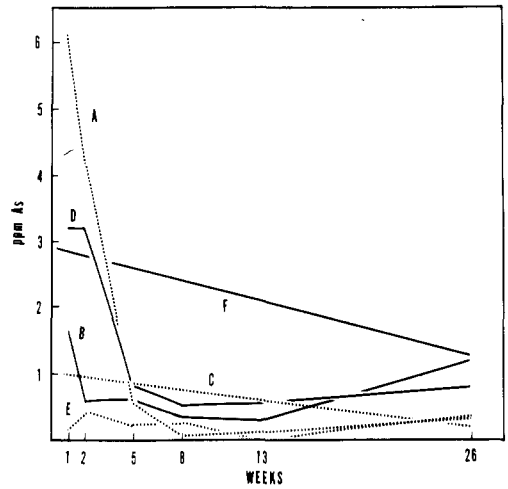

Figure 3. Metabolism of cacodylic acid (CA) in field-treated soils: (A) CA treated; (B) methylarsonic acid (MAA) in CA-treated soil; (C) CA in high CA-treated soil after 1 year; (D) MAA treated; (E) CA in MAA-treated soil; (F) MAA in high MAA treated soil after 1 year.

have been trapped. In untreated soil, 52 and 27% of the degraded [^{14}C]CA was trapped as $^{14}CO_2$ under aerobic and anaerobic conditions, respectively.

The concentrated soil extract solution contained relatively high amounts of salt which caused CA to elute with arsenite. The HPLC peak at 3.5 min (Figure 1B) was found to be CA as confirmed by TLC. On a cellulose plate, arsenite (R_f 0.36) is completely separated from CA (R_f 0.83). Results were in agreement with those obtained from HPLC–GFAA before TLC within ±20%. Only CA was found. Arsenite was not detected in any of the soil samples after extraction.

Experiment 2: Field Samples. Soil samples taken from field plots treated with arsenite, CA, and MAA were analyzed and results summarized in Figure 3. Degradation of CA was followed by some accumulation of MAA. Eight weeks after application, the concentration of MAA in the soil was even slightly higher than the applied CA. In plots treated with MAA, degradation was somewhat slower, but CA, as well as arsenate, was found as a metabolite of MAA. Low levels (<0.5 ppm of As) of MAA and CA were found in soil treated with arsenite. The identity of MAA and CA were confirmed by TLC. The results of this experiment indicate that the metabolism in soil under aerobic conditions will proceed from CA through MAA to arsenate. This is in complete agreement with the results obtained from the laboratory experiment. However, it also appears as if MAA and CA form insoluble compounds which are not immediately subject to degradation. Significant residues of MAA and CA were detected 1 year after their respective applications at a 5-fold higher rate. These residues declined during the 25-week growing period.

The amounts of MAA and CA detected in the extractable form went through a minimum during the 8–13-week (after application) period. By 26 weeks, the extractable levels had increased. This along with the fact that small amounts of MAA and CA were detected from the arsenite treatment indicates a metabolic cycle in which all three forms are present at some level and that these levels change according to environmental conditions. The most important factor is probably moisture which influences metabolic activity and the redox potential of the soil.

Moisture in the field also appears to affect the total amount of extractable As that can be removed from the soil (Figure 4). The extractable levels went through a minimum at 8 weeks after treatment and subsequently

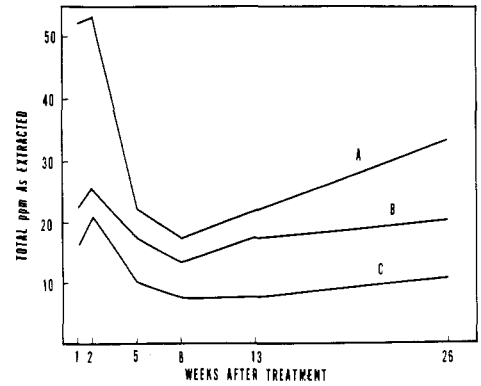

Figure 4. Total arsenic extracted with 2 M NH_4OH after application of (A) cacodylic acid (CA), (B) arsenite, and (C) methylarsonic acid (MAA).

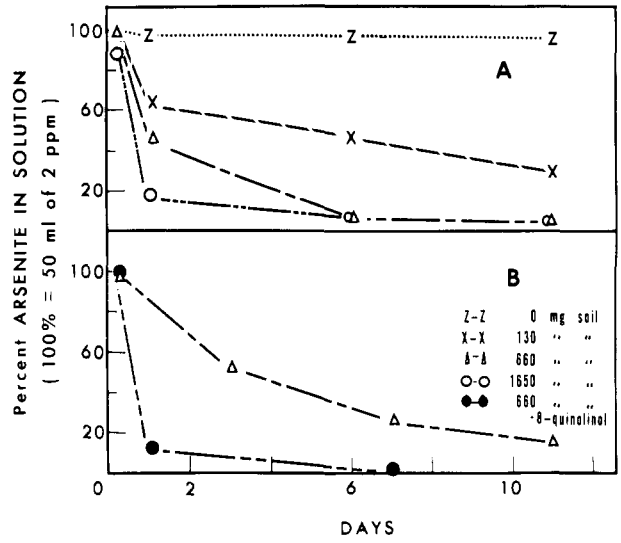

Figure 5. Effect of soil extract concentration in NH_4OH aqueous solutions on the oxidation rate of arsenite to arsenate.

increased. The soil moisture is at a minimum in mid-July to mid-August, the 8–13-week time period. All the added chemicals behaved in a similar manner. This occurred even though the soils were moist for at least 60 h during the extraction process.

The half-life of applied CA (Figure 3) appears to be about 20 days while that of MAA appears to be about 22 days. The value for CA agrees well with that for the untreated soil from the first experiment which had a half-life also of 20 days. The addition of organic matter increased the value to 31 days, although by 60 days, the remaining residue was not significantly different (Figure 2).

Oxidation of Arsenite to Arsenate. Analysis of soil samples that were spiked with arsenite(3+) showed rapid oxidation of arsenite to arsenate (Figure 5). Arsenite was not oxidized in 2 M NH_4OH solution, but when soil extract was added to the solution, rapid oxidation of arsenite was observed. The rate of oxidation was directly related to the concentration of the soil extract. Almost all the oxidized arsenite was recovered by HPLC–GFAA as arsenate. When the concentration of NH_4OH in the solution was lowered to 0.2 M, the rate of oxidation was decreased by a factor of about 2. At concentrations below 0.2 M NH_4OH, adsorption of arsenite on soil interferred with the measurements. 8-Quinolinol sulfate was used as a complexing agent to improve the recovery of the arsenical compounds (Iadevaia et al., 1980) during the cleanup steps. In this experiment, it was found that 8-quinolinol sulfate enhanced considerably the oxidation of arsenite. Even though oxidation of arsenite occurs rapidly in ammoniacal

soil extracts, it is not clear whether oxidation will also occur in the soil. In any case, arsenite will not be found in soil samples as long as ammoniacal solutions are used for soil extraction. Therefore, there is no need to clean up soil extracts on TLC to separate CA from arsenite.

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Ionization and Adsorption-Desorption of Tricyclazole by Soil Organic Matter, Montmorillonite Clay, and Cape Fear Sandy Loam Soil

Jerome B. Weber

Aqueous solutions of tricyclazole (5-methyl-1,2,4-trizolo[3,4-*b*]benzothiazole) were spectrophotometrically titrated to obtain a pK_a of 1.6. The fungicide was adsorbed by Ca-montmorillonite and Cape Fear sandy loam in substantially greater amounts than prometryn [2,4-bis(isopropylamino)-6-(methylthio)-*s*-triazine] and in lesser amounts than prometryn by Ca-organic matter from deionized water. Adsorption isotherms for tricyclazole by the adsorbents were of the S type, C type, and L type, respectively. In 0.01 M buffer solutions at pH 6.0, 4.0, and 2.0, tricyclazole was adsorbed in substantially greater amounts than prometryn by all adsorbents. Adsorption increased greatly as pH decreased. Water effectively desorbed from 17 to 44% of bound tricyclazole from Ca-organic matter and Cape Fear soil but removed only 1-6% from Ca-montmorillonite. Desorption with 0.01 M paraquat(2+) greatly increased displacement of tricyclazole and confirmed the postulated ionic adsorption at low pH levels. Prometryn was more readily desorbed than was tricyclazole. Adsorption mechanisms are postulated and discussed.

Rice blast disease, caused by the fungus *Piricularia oryzae* Cav., is the most serious disease of rice in the world (Parthasarathy and Ou, 1965). The rice blast pathogen infects rice at all stages of growth, and thus the plants must be protected through most of their growth period. Tricyclazole (5-methyl-1,2,4-triazolo[3,4-*b*]benzothiazole) is a new systemic fungicide reported to provide long-term control of rice blast disease when applied as a foliar spray, seed coat treatment, soil drench, or as a transplant bare-root soak treatment (Froyd et al., 1976, 1978). Tricyclazole is readily absorbed by plant roots, translocated to leaves, and provides residual disease control after a single soil or foliar application.

Tricyclazole is a heterocyclic compound which probably has weakly basic properties similar to those of other triazoles and thiazoles (Acheson, 1976). The objectives of this study were to (1) determine the ionization constant of tricyclazole, (2) measure the adsorption of tricyclazole relative to that of the herbicide prometryn [2,4-bis(isopropylamino)-6-(methylthio)-*s*-triazine] by Ca-organic matter, Ca-montmorillonite clay, and a Cape Fear sand loam soil, (3) measure the desorption of tricyclazole from

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