Multiresidue Analysis of Cotton Defoliant, Herbicide, and Insecticide Residues in Water by Solid-Phase Extraction and GC−NPD, GC−MS, and HPLC−Diode Array Detection

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A multiresidue procedure was developed for analysis of cotton pesticide and harvest-aid chemicals in water using solid-phase extraction and analysis by GC−NPD, GC−MS, and HPLC−DAD. Target compounds included the defoliants tribufos, dimethipin, thidiazuron; the herbicide diuron; and the insecticide methyl parathion. Three solid-phase extraction (SPE) media, octadecylsilyl (ODS), graphitized carbon black (GCB), and a divinylbenzene-*N*-vinyl pyrollidine copolymer (DVBVP), were evaluated. On GCB and ODS, recoveries varied depending on compound type. Recoveries were quantitative for all compounds on DVBVP, ranging from 87 to 115% in spiked deionized water and surface runoff. The method detection limit was less than 0.1 μg L^{-1}. SPE with DVBVP was applied to post-defoliation samples of surface runoff and tile drainage from a cotton research plot and surface runoff from a commercial field. The research plot was defoliated with a tank mixture of dimethipin and thidiazuron, and the commercial field, with tribufos. Dimethipin was detected (1.9−9.6 μg L^{-1}) in all research plot samples. In the commercial field samples, tribufos concentration ranged from 0.1 to 135 μg L^{-1}. An exponentially decreasing concentration trend was observed with each successive storm event.

Keywords: *Defoliants; cotton; water; solid-phase extraction*

INTRODUCTION

Chemical defoliation and or desiccation of cotton prior to mechanical harvest is a common practice in the United States and in many other cotton-producing countries. Data compiled by the U.S. Department of Agriculture National Agricultural Statistics Service (NASS, 1999) indicate that in crop-year 1998, the most widely used defoliant active ingredients were thidiazuron, a phenyl-urea, and the organo-phosphate, tribufos. The estimated percents of crop area treated with these defoliants were 31% and 29%, respectively. Other active ingredients reportedly used included cyclanilide, dimethipin, sodium chlorate, cacodylic acid, endothall, and paraquat. The estimated total treated acreage with these chemicals was a combined 40%.

Although defoliant chemicals are now widely used on cotton and have been for many years, there are few published studies in which environmental fate and the potential for surface and groundwater contamination were assessed. Among the chemicals in use, tribufos has received the most attention. The U. S. Environmental Protection Agency (USEPA) recently published draft Human Health Effects and Environmental Fate and Effects Risk assessments (USEPA, 1998a; USEPA, 1998b). The most significant finding of the human health assessment was that the compound should be classified as a "likely" carcinogen at high doses. In an ecological context, the USEPA evaluation concluded that chronic risk to freshwater and marine invertebrates was likely under some circumstances. The certainty of this assessment was classified as moderate to high. There has been no such assessment of other defoliants. In some cases, potential adverse health effects are indicated. Dimethipin is a class C (possible) human carcinogen (USEPA, 1997), and its relatively high water solubility and low Koc (Table 1) indicate a significant potential for leaching and groundwater contamination.

It should also be noted that defoliant use typically destroys the plant canopy. This enhances the potential for surface runoff and or leaching during subsequent precipitation events.

To address the need for data which will permit comprehensive human and ecological risk assessments of cotton chemical defoliants, our laboratory has begun a series of investigations to assess potential impacts on surface and groundwater quality. To complete these studies, a sensitive multiresidue procedure was required for the analysis of residues of three cotton defoliant chemicals, tribufos, thidiazuron, and dimethipin, in water. The rationale for the multiresidue approach is that defoliant chemicals are often applied in tank−mix combinations. Thus one or more active ingredients have the potential to occur in water samples following a single defoliation treatment.

Two other compounds, diuron and methyl parathion, were included in the target compound list. The herbicide diuron is used in combination with thidiazuron in a commercial defoliation formulation (AgrEvo,1999) and in certain applications may present a threat to groundwater quality (Field et al., 1997). Methyl parathion is one of the most widely used cotton insecticides. Many concerns have been raised regarding the human and ecological risks of its use (USEPA, 1998c; USEPA, 1998d).

Structures of the five target compounds are shown in Figure 1. Use rates and selected physical−chemical

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Table 1. Selected Physical Chemical Properties and Agricultural Use Rates of the Target Compounds[a]

compound	water solubil. (mg L^{-1})	Koc (ml g^{-1})	vapor press. (kPa)	typ. appl. rate (kg ha^{-1})	est. use on cotton in crop-year 1998 (kg)
dimethipin	3000	3	5.1×10^{-8}	0.4	2.5×10^{4}
thidiazuron	20	110	3.1×10^{-12}	0.1	1.6×10^{5}
tribufos	2.3	5000	2.1×10^{-7}	0.8	1.2×10^{6}
diuron	42	480	9.2×10^{-9}	0.4	4.0×10^{5}
methyl parathion	60	5100	2.0×10^{-6}	1.9	7.9×10^{5}

[a] Water solubility, Koc, and vapor pressure data at 20−25 °C from Hornsby et al., 1996; use rate data from NASS, 1999.

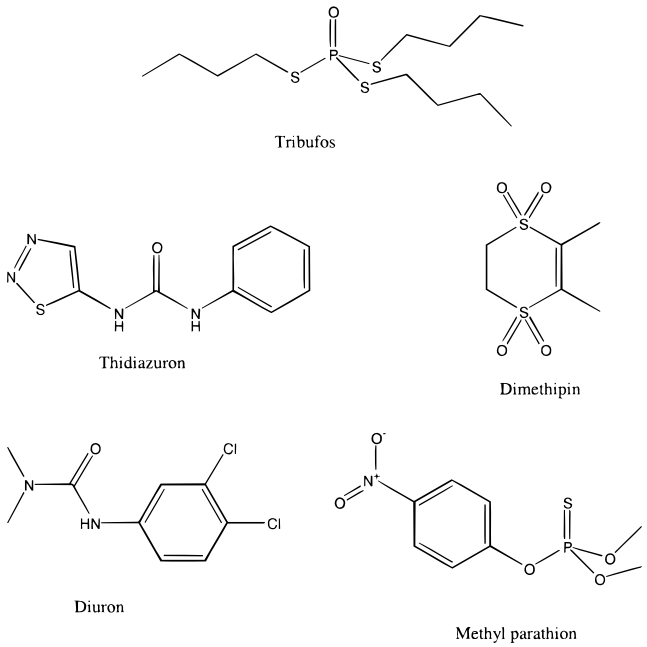

Figure 1. Structures of target compounds.

properties are compiled in Table 1. As indicated, they exhibit a wide range. Typical application rates differ by a factor of 8 and water solubilities and Koc's by more than 1000.

Analytical methods for diuron, tribufos, and methyl parathion have been published. Lehman et al. (1983) described a GC−NPD procedure for tribufos with an estimated detection limit of 0.2 μg L^{-1}. Samples were prepared for analysis by liquid−liquid extraction with dichloromethane. Habig et al. (1987) described a residue method for tribufos in water based on solid-phase extraction (SPE) with Sep-Pak cartridges and GC−NPD. Quantitative recovery at the 1 μg L^{-1} level was reported. Tribufos (merphos) and methyl parathion are also target compounds in USEPA method 8141A. This is a GC−NPD method in which samples are prepared by liquid−liquid extraction with methylene chloride or SPE with octadecylsilyl (ODS)-impregnated filter disks. Reported spike recoveries from water at the 2.0 μg L^{-1} level were tribufos, 79%, and methyl parathion, 46% (USEPA, 1996). Field et al. (1997) described an HPLC−UV procedure for diuron and its metabolites in water. Samples were prepared by SPE with ODS-impregnated filter disks. Quantitative recoveries from surface, ground, and laboratory reagent water spiked at the 10 μg L^{-1} level were reported. Procedures for thidiazuron and dimethipin residue analysis in water were not identified in our literature search nor did we identify any multiresidue procedures for the five compounds targeted in our research.

Work which lead to development of a sensitive, method detection limit (MDL) < 0.1 μg L^{-1}, multiresidue method for tribufos, methyl parathion, dimethipin, diuron, and thidiazuron dissolved in water is described in this publication. The method is based on SPE with a divinylbenzene-*n*-vinylpyrrolidine (DVBVP) copolymer solid phase. Gas chromatography with thermionic nitrogen/phosphorus detection (GC−NPD), GC−mass spectrometry (GC−MS), and HPLC−diode array detection are used to analyze extracts. The suite of target compounds required the use of both GC and HPLC techniques. During GC analysis, the phenyl-urea compounds, diuron and thidiazuron, decompose in the heated GC inlet. Tribufos does not exhibit significant absorption of the wavelength range 200−600 nm and is thus not detectable by photodiode array.

The method was applied to a series of surface runoff and tile drainage samples collected from a cotton research plot after defoliation with a tank mixture of thidiazuron and dimethipin. It was also applied to surface runoff samples collected in a commercial cotton field which had been defoliated with tribufos. Concurrent analysis of quality control samples has indicated that the data were accurate and precise.

MATERIALS AND METHODS

Chemicals. Tribufos, thidiazuron, diuron, methyl parathion, and dimethipin analytical standards which were obtained from Chem Service (West Chester, PA) were used without further purification. Reported purity ranged from 96 to 99%. The internal standard, 2-chlorolepidine (99%), was obtained from Aldrich Chemical Co. (Milwaukee, WI). HPLC-grade methanol and acetonitrile were purchased from Fisher Scientific (Pittsburgh, PA), and pesticide residue analysis-grade methylene chloride was from Burdick and Jackson (Muskegon, MI). Stock standards of the target compounds and 2-chlorolepidine were prepared in methanol. Choice of this internal standard was based on the ability to detect it in GC−NPD, GC−MS, and HPLC−diode array detector (DAD) analyses. When not in use, standards and methanolic stock solutions were stored at −20 °C. Laboratory reagent water for HPLC analysis and sample preparation was prepared using a Continental Type 1 Laboratory Reagent Grade Water System (Continental Water Systems Inc., San Antonio, TX). KCl and sodium dodecyl sulfate were purchased from Fisher Scientific (Pittsburgh, PA).

Solid-Phase Extraction. Four commercially available solid-phase extraction (SPE) cartridges were evaluated for recovery of the target compounds. ODS was the solid phase in two of the cartridges: LC-18, 1 g (Supelco, Belafonte, PA), and EnviroPrep Octadecyl, 500 mg (Burdick and Jackson, Muskegon, MI). The solid phases in the other cartridges were graphitized carbon black (GCB), Envicarb, 500 mg (Supelco, Belafonte, PA); and DVBVP, Oasis HLB, 200 mg (Waters Corporation, Milford, MA). The cartridges were preconditioned, loaded with the water samples, and eluted using a vacuum manifold (Supelco, Belafonte, PA). Preconditioning of the ODS and DVBVP cartridges involved sequential flushing with 5-ml aliquots of reagent water, methanol, methylene chloride, methanol, and reagent water. The GCB cartridges were conditioned by sequential flushing with 5-ml aliquots of 0.016 M KOH in methylene chloride/methanol (60/40), methanol, 2% acetic acid, and reagent water. Cartridges were not allowed

to dry. Samples were applied to the columns by vacuum using Teflon transfer lines at a rate of 20−30 mL min^{-1}. After the entire sample had passed through the cartridges, the vacuum was maintained for an additional 20 min to remove residual water. Cartridges were eluted sequentially with 5-ml aliquots of methanol and methylene chloride.

Extract Concentration and Solvent Exchange. The methanol and methylene chloride eluents were combined and concentrated to 1 mL under a stream of dry high-purity nitrogen. After being spiked with 10 μL of a 0.5 μg μL^{-1} solution of 2-chlorolepidine, extracts were analyzed byGC−NPD and by GC−MS. Each extract was then transferred to a 10-ml glass centrifuge tube, combined with 750 μL of laboratory reagent water, and concentrated to 0.75 mL under a stream of high-purity nitrogen. The volume was adjusted to 1 mL by addition of 250 μL of acetonitrile. This extract was analyzed by HPLC−DAD. The final composition of the extract matched the initial composition of the mobile phase in the gradient HPLC analysis described below.

GC−NPD Analysis. Tribufos and methyl parathion concentration was determined in extracts using a Hewlett-Packard model 6890 gas chromatograph equipped with split−splitless capillary column injector and NPD detector. The column oven was fitted with a 30 m × 0.25 mm HP-5 fused silica capillary column obtained from Hewlett-Packard (Wilmington, DE). The column's methyl-silicone liquid film thickness was 0.25 μm. The helium carrier gas head pressure was maintained at 100 kPa with injection in the splitless model using a model 7073 autosampler. The initial oven temperature of 100 °C was held for 1 min. The temperature was then increased to 260 °C at 25 °C min^{-1} and held for 4 min.

The detector was used with two different "beads": (i) original equipment supplied by Hewlett-Packard (Wilmington, DE) and (ii) TID-2 (black ceramic) supplied by DeTector Technology (Walnut Creek, CA). Nitrogen was the detector makeup gas when the TID-2 bead was used. The TID-2 bead gave superior chromatographic performance. Reduced peak tailing with the TID-2 bead has been attributed to its harder surface. This contributes to reduced organo-phosphorus compound adsorption (Patterson, 1998). A five-point, 0.1, 1.0, 2.5, 5.0, and 10.0 ng μL^{-1}, calibration curve based on the relative response of the target compounds to the internal standard was developed each time a set of samples was analyzed.

GC−MS Analysis. After GC−NPD analysis, extracts were analyzed using a Hewlett-Packard model 5972 GC−MS detector. This was done to confirm the presence of dimethipin, methyl parathion, and tribufos in field samples. The GC column and dimensions, carrier gas type (He) and head pressure, injection temperature and technique, and oven temperature program conditions were all identical to conditions in the GC−NPD analysis. The MSD was tuned for maximum sensitivity prior to each use with software supplied by the instrument manufacturer. Tuning criteria were achieved based on instrument response to perfluorotributylamine (PFTBA).

HPLC−DAD Analysis. After solvent exchange, extracts were analyzed for dimethipin, thidiazuron, diuron, and methyl parathion using a Hewlett-Packard model 1050 HPLC equipped with a DAD. The HPLC column was a Beckman Ultrasphere ODS (5 μm, 4.6 mm by 150 mm) (Alltech, Deerfield, IL). Isocratic (55% acetonitrile/45% water) and gradient separations were performed with a total flow rate of 1 mL min^{-1}. The acetonitrile (A)−water (B) gradient was as follows: initial conditions of A (25%)/B (75%), hold 1 min; increase A linearly to 80% at 5 min; hold solvent composition at A (80%)/B (20%) for 2 min; decrease A linearly to 25% at 9 min; hold the mobile phase composition constant at A (25%)/B (75%) for 2 min. The target compounds, dimethipin, thidiazuron, and diuron, were effectively separated using the isocratic conditions. However, when runoff sample extracts were analyzed, significant disturbance was observed at the beginning of the chromatogram which resulted in elution of dimethipin prior to the detector signal returning to baseline. This made quantitation at low concentrations difficult. A series of gradients were evaluated with the objective of separating the dimethipin from the "solvent" peak. With the gradient described above, the detector signal returned to baseline prior to elution of the dimethipin peak. In addition, the gradient provided minimum peak width and partial separation of the methyl parathion and internal standard peaks. A five-point, 0.1, 1.0, 2.5, 5.0, and 10.0 ng mL−1, external calibration curve was prepared each time a sample set was analyzed. Dimethipin was quantitated by integration of the signal at 220 nm. The signal at 283 nm was used for thidiazuron and at 254 nm for diuron and methyl parathion. These wavelengths represented absorbance maxima. The peak area ratio 254 nm/283 nm for thidiazuron, methyl parathion, and diuron was also determined to provide an index of "peak purity". Ratios obtained with the analytical standards are shown in Table 2. In the gradient HPLC analysis, the internal standard served as a retention time marker.

Table 2. Ratio of Absorbance at 254/283 nm

compound	average[a]	RSD
dimethipin	ND	
thidiazuron	0.30	2.1
tribufos	ND	
diuron	15.7	0.57
methyl parathion	0.70	3.3

[a] Average of five measurements of the concentration range 0.1−10 μg mL^{-1}.

Sample Collection and Analysis. *Set 1*. Surface runoff and lateral subsurface flow, i.e., tile drainage, samples were collected from "Watershed Z", a 0.34-ha research plot, located at the USDA-ARS Southeast Watershed Research Laboratory in Tifton, GA. Plot characteristics are described in detail by Truman et al., 1998. In crop-year 1998, the plot was planted to cotton. It was defoliated with a tank mixture containing dimethipin and thidiazuron on November 25, 1998, and mechanically harvested on December 9, 1998. The following day, the plot was mowed, disced, and harrowed, and a cover crop of wheat was planted. On January 23, 1999, a precipitation event generated surface runoff and lateral subsurface flow. Surface runoff samples were collected with a refrigerated "ISCO" sampler (ISCO, Lincoln, NE). The collector was equipped with glass bottles prepared for field sample collection by soap and water wash, rinsing with distilled water and acetone, and baking overnight at 125 °C in a laboratory oven. The sampler was programmed to withdraw a water sample from a trough in the cement floor of the runoff flume at discrete time intervals, which reflected changes in the shape of the runoff hydrograph. Seven samples were collected during the event. They were removed from the sampler within 24 h of collection, taken directly to the laboratory and placed in refrigerated storage. This storm event and a subsequent event on February 1, 1999, also generated lateral subsurface flow. Grab samples from the field's two tile drain outlets were collected twice daily until flow ceased. Fourteen samples were collected following the first event and 11 after the second event. These samples were collected in 1-L glass bottles and cleaned as described for the autosampler bottles. After collection, sample bottles were sealed with Teflon-lined caps and placed in refrigerated (4 °C) storage in the laboratory. Both surface runoff and lateral subsurface flow samples were prepared for analysis by 0.7-μm glass fiber filter filtration (Fisher Scientific, Pittsburgh, PA) and SPE with DVBVP cartridges.

Set 2. Samples of surface runoff were collected from five surface runoff collectors deployed at the base of the slope a commercial 7-ha cotton field located in Tift County, Georgia. The "dustpan" collectors were constructed of stainless steel and have been described in detail by Sheridan et al. (1996). Below the outlet of each collector, a section of 10.5-cm (i.d.) PVC pipe was placed in a hole excavated with a post-hole digger. A 1-L glass bottle (I−Chem, Newark, DE) was secured in the pipe by inserting a stainless rod through holes drilled in the pipe, 0.5 cm above the top of the bottle. Bottles were covered with 2-mm nylon mesh. The mesh was held in place with an elastic band. The mesh was required to keep large insects from collecting in the bottles prior to storm events. One tenth of the total runoff intercepted by the collectors was routed

Table 3. Percent Recovery of Target Compounds by SPE with ODS and GCB

	ODS (LC-18)		ODS (EnviroPrep)		GCB (Envicarb)	
compound	av[a]	% RSD	av[a]	% RSD	av[a]	% RSD
dimethipin	5.8[b]	18.6	9.7	1.0	69.2	10.2
thidiazuron	82.0	7.1	99.7	1.9	ND[c]	
diuron	70.7	6.0	96.0	7.0	80.1	9.0
methyl parathion	102.2[b]	7.1	89.0	8.3	95.8	14.2
tribufos	97.9[b]	24.5	NA[d]		53	14.5

[a] Average of four replicate samples. [b] Indicates quantitation by GC−MS. [c] ND = not detected. [d] NA = not analyzed.

through the bottles. Within 24 h after each storm event in which runoff was generated, sample bottles were exchanged with clean bottles, sealed with Teflon-lined caps, placed on ice in a plastic cooler and returned to the laboratory for analysis. In the laboratory, samples were placed in refrigerated (4 °C) storage. They were 0.7-μm glass fiber filtered (Fisher Scientific, Pittsburgh, PA) and extracted by SPE with DVBVP cartridges within 72 h of collection. Fifty-two samples following 12 precipitation events were collected from the field from September 1998 to February 1999. The September samples (2) were collected prior to defoliation. All other samples followed defoliation of the entire field with DEF-6 (Bayer Chemical Company, Kansas City, MO). The product active ingredient is tribufos. The estimated application rate was 1 kg ha^{-1}. During 9 out of the 12 runoff events, the sample bottles were overfilled. Thus, runoff generated at the beginning of the storm events was flushed from or diluted in the sample bottles with runoff generated later in the events. The impact on measured concentration values is unknown. Thus, reported values should be considered an indicator of, rather than actual "edge-of-field" concentrations. It should also be noted GFF filtration removed sediment bound chemicals from the samples. The values reported are for the functionally defined "dissolved phase" only.

Quality Control Samples. With sample set 1, a field duplicate of the lateral subsurface flow and a spiked sample of laboratory reagent water were submitted "blind" to the analysts. The dimethipin spiking level was 3.2 μg L^{-1}. In combination with analysis of sample set 2, a matrix spike was analyzed in quadruplicate. The sample was prepared by pooling half of the runoff collected during the first four storm events and spiking at 5 μg L^{-1} with a mixture of the target compounds in methanol.

RESULTS AND DISCUSSION

Method Development. Results of initial experiments with ODS and GCB SPE are summarized in Table 3. Percent recovery varied depending on the compound and sorbent type. Recovery of the more hydrophobic compounds, tribufos, methyl parathion, thidiazuron, and diuron, on ODS was generally high, 70 to 102%. These results are in general agreement with published data for diuron summarized by Field et al. (1997) and for methyl parathion (Zaugg et al., 1995) and tribufos (Habig et al., 1987). ODS is an effective sorbent for relatively nonpolar compounds from water. However, as compound polarity increases, recovery generally decreases (Majors, 1998). The low recovery of dimethipin with both ODS sorbents, 6 to 10%, was consistent with this reported trend.

Much higher recovery of dimethipin, 69%, was obtained by SPE with GCB. Di Corcia and Marchetti (1992) and Di Corcia et al. (1993) have reported on SPE with GCB performance with numerous pesticides including many polar compounds. Recovery was generally high, >90%, and RSD (relative standard deviation) was low, <5.0%. An unanticipated result in our work with GCB SPE was the failure to recover thidiazuron. It was likely degraded or irreversibly absorbed.

Table 4. Effect of KCl and Sodium Dodecyl Sulfate on Percent Recovery by SPE with ODS Solid Phase (LC-18)

	% recovery			
	5% KCl		sodium dodecyl sulfate[a]	
compound	av[b]	% RSD	av[b]	% RSD
dimethipin	9.8	17.2	17.3	9.6
thidiazuron	87.2	16.5	90.9	11.2
diuron	68.8	7.4	84.7	10.0
methyl parathion	42.0	36.4	83.4	11.1
tribufos	NA		NA	

[a] Sodium dodecyl sulfate concentration = 0.0001 M. [b] Average of four replicate samples.

Table 5. Percent Recovery of Target Compounds by SPE with DVBVP Solid Phase

	spike concentration (μg L^{-1})							
	deionized water						surface runoff	
	0.1		1.0		10.0		5.0	
compound	av[a]	% RSD	av[a]	% RSD	av[a]	% RSD	av[a]	% RSD
dimethipin	109	5.6	87.7	2.0	93.2	3.1	101	2.3
thidiazuron	91.5	7.3	95.8	1.7	94.8	2.5	102	7.1
diuron	109	5.7	96.5	5.0	97.2	1.7	104	2.6
tribufos	115	6.3	98	7.7	93.5	2.2	104	2.8
methyl parathion	100	11.0	87	2.1	100	2.8	91.4	3.9

[a] Average of four replicate samples.

In Table 4, data describe recovery of four of the target compounds by SPE with ODS after enrichment of fortified laboratory reagent water with KCl (5% w/w). This was done to evaluate the potential for "salting-out" dimethipin to the hydrophobic ODS surface. Recovery was not substantially increased, indicating little or no "salting out" effect. When sodium dodecyl sulfate (0.0001 M), a wetting agent was added to fortified laboratory reagent water, dimethipin recovery was enhanced (ca. 2×); however, it was still relatively low, < 20%.

Failure to quantitatively recover the target analytes with either ODS or GCB solid phases lead to evaluation of a third, DVBVP. Several SPE products were recently introduced based on this solid phase. The polymer, a balanced ratio of two monomers, the lipophilic divinylbenzene and the hydrophilic *N*-vinylpyrrolidine, was designed for sample preparation for high throughput screening of lipophilic drugs and their polar metabolites (Waters Corp., 1998). Percent recovery of the target compounds by SPE with this sorbent from fortified laboratory reagent water and surface runoff samples are shown in Table 5. In this case, the recovery of each of the compounds was nearly quantitative. Over the concentration range 0.1 to 10 μg L^{-1} in laboratory reagent water, percent recovery was 94−102% with RSDs of 4.8−12%. At the 5 μg L^{-1} level in spiked surface runoff, recoveries were 91−104% with RSDs of 2.7−7.9%.

Figures 2 and 3 provide GC−NPD and HPLC−DAD chromatograms of the spiked runoff. All peaks were symmetric and relatively sharp. The broadest was the dimethipin peak. As indicated above, the HPLC gradient was developed to give minimum dimethipin peak width while providing "baseline" separation from earlier eluting interfering substances. Their highly polar nature, elution before the target compounds, and the fact

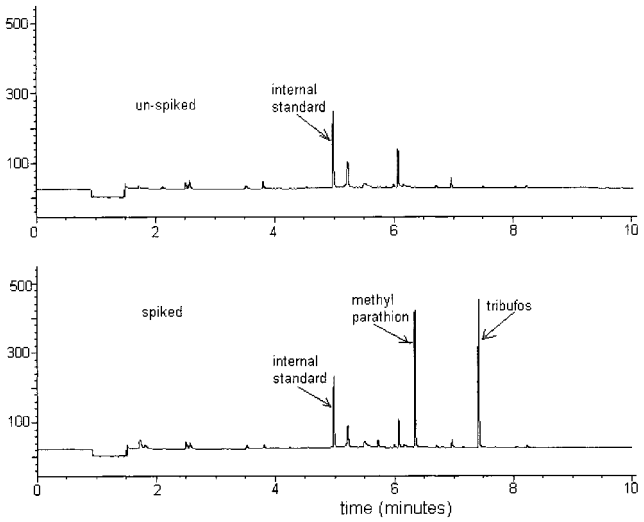

Figure 2. GC−NPD chromatograms of spiked and unspiked surface runoff.

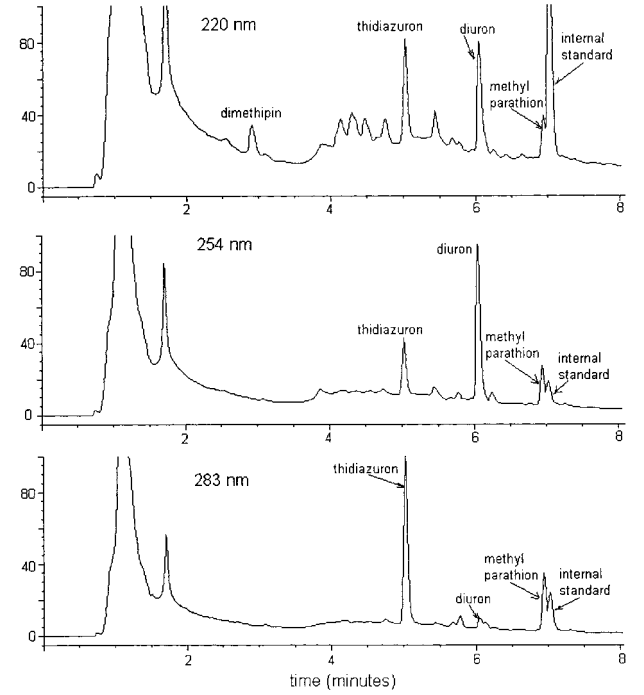

Figure 3. Gradient HPLC−diode array chromatogram of spiked surface runoff.

that absorbance in the UV region was observed suggests they were humic or related materials coextracted from the water.

Attempts were made to quantitate dimethipin in sample extracts by GC−MS. However, chromatographic performance degraded relatively rapidly. Significant tailing was observed after less than 10 injections of runoff extracts. This resulted in higher RSDs for repeat injections of the same extract and reduced sensitivity. It was concluded that HPLC provided more stable chromatographic conditions for dimethipin quantitation.

Overall, these data indicate high precision and accuracy of the SPE with DVBVP. It compared favorably with data reported for other SPE-based multiresidue pesticide analysis procedures (Di Corcia and Marchetti, 1992; Zaugg et al., 1995; Boyd-Boland, 1996). The data

Table 6. Dissolved Dimethipin Concentration in Surface Runoff and Lateral Subsurface Flow

sample type	no. of samples	concn (μg L^{-1}) av	range	% RSD
surface runoff (storm event 1)	7	4.1	2.8 to 4.8	16.4
lateral subsurface flow (storm event 1)	14	4.9	1.9 to 9.6	48.2
lateral subsurface flow (storm event 2)	10	3.9	2.4 to 6.9	45.0

Table 7. Dissolved Tribufos in Surface Runoff

event	concn (μg L^{-1}) av	range	% RSD	no. of samples
1	<0.1	<0.1		2
2[a]	78.7	13−135	73.5	5
3	15.2	4.3−26.1	91	2
4	8.3	0.1−26.6	141	5
5	1.9	0.2−5.6	126	5
6	1.1	0.3−2.6	92	5
7	1.7	0.4−3.8	91	5
8	2.9	0.8−5.5	77	5
9	1.8	0.5−4.5	99	5
10	0.5	0.2−1.2	106	4
11	1.0	0.5−2.4	98	5
12	0.8	0.3−2.1	115	5

[a] Extracted with GCB cartridges.

also indicate an MDL < 0.1 μg L^{-1}. Quantitative recovery, 91.5 to 115%, at this concentration level was observed.

Method Application. The procedure was applied to the analysis of a series of edge-of-field water samples collected from two cotton fields. The first sample set was obtained from a field defoliated with a tank mixture containing dimethipin and thidiazuron. Tribufos was used to defoliate the cotton in the field where the second set of samples was collected.

Summary statistics of the dimethipin concentration in all set 1 water samples are shown in Table 6. This compound was detected in all set 1 surface runoff and lateral subsurface flow samples, whereas thidiazuron was not detected in any of the samples above the nominal MDL, 0.1 μg L^{-1}. Possible explanations include lower thidiazuron application rate, 0.15 kg ha^{-1} versus 0.35 kg ha^{-1} for dimethipin. It is also likely that thidiazuron was degraded more rapidly after application. Hornsby et al. (1996) has reported field half-lives of 10 and 120 days for thidiazuron and dimethipin, respectively.

The set 2 water sample results are summarized in Table 7. Samples collected after the first post-defoliation runoff event had relatively high tribufos levels, 13−135 μg L^{-1} (average 78.7 μg L^{-1}). The concentration decreased exponentially with each succeeding runoff event. Following the 12th and final event samples, the tribufos concentration ranged from 0.8 to 2.1 μg L^{-1} (average 0.8 μg L^{-1}). The tribufos data suggest that biota in surface waters may be negatively impacted by surface runoff from defoliated cotton fields. Published LC50s for the freshwater invertebrate test species, *Daphnia magna*, and for the estuarine species, *Americamysis bahia* are in the 5−12 μg L^{-1} range. The reported no observable effects concentration (NOEC) for *A. bahia* is less than 0.34 μg L^{-1}. However, specific conclusions regarding ecological risk remain uncertain. The manner in which the runoff samples were collected did not permit an estimate of total flow. Thus, loading estimates to surface water were not possible. In addition, the sedi-

ment-bound tribufos concentration was not measured. Since the compound has a relatively high Koc (Table 1), sediment transport is likely to be a significant transport pathway.

Quality control (QC) samples analyzed indicate that the field sample analysis results were accurate and precise. The blind field duplicates yielded dimethipin concentrations in close agreement, 3.0 and 3.1 μg L^{-1}. The nominal dimethipin concentration in the spiked reagent water was 3.2 μg L^{-1}. With the runoff matrix spikes (Table 5), percent recoveries ranged from 91 to 104% and RSDs from 2.7 to 7.2%.

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