

Pesticides in the Atmosphere of the Mississippi River Valley, Part II – Air

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ABSTRACT

Weekly composite air samples were collected from early April through mid-September 1995 at three paired urban and agricultural sites along the Mississippi River region of the Midwestern United States. The paired sampling sites were located in Mississippi, Iowa, and Minnesota. A background site, removed from dense urban and agricultural areas, was on the shore of Lake Superior in Michigan. Each sample was analyzed for 49 compounds; of these, 21 of 26 herbicides, 13 of 19 insecticides, and 4 of 4 related transformation products were detected during the study, with most pesticides detected in more than one sample. The maximum number of pesticides detected in an air sample was 18; this sample was from the Iowa City urban site in mid-June. Herbicides were the predominant type of pesticide detected at every site. The detection frequencies of most herbicides generally were comparable at the paired Iowa and Minnesota sites. In Mississippi, herbicides generally were detected more frequently at the agricultural site. The insecticides chlorpyrifos, diazinon, and carbaryl, which are used in agricultural and nonagricultural settings, were detected more frequently in urban sites than agricultural sites in Mississippi and Iowa. Methyl parathion was detected in 70 percent of the samples from Rolling Fork, Miss., and at the highest concentration (62 nanograms per cubic meter of air) of any insecticide measured in the study. At the background site, dacthal (100 percent), atrazine (35 percent), cyanazine (22 percent), and the (primarily atrazine) triazine transformation products CIAT (35 percent) and CEAT (17 percent) were detected most frequently, suggesting their potential for long-range atmospheric transport. Estimates of the pesticides' particle and gas distribution provided insight into the primary mechanisms of pesticide transport and deposition.

INTRODUCTION

Of the environmental compartments—air, water, soil, sediment, and biota—the atmosphere represents the largest (for gas-phase contaminants) and most mobile compartment into which a chemical contaminant might be directly released or subsequently move into, undergo transport, and, in some cases, accumulate (Mackay and others, 1997). Pesticides applied in agricultural and nonagricultural settings enter the atmosphere by volatilization and by wind erosion of particles (soil, vegetation, formulation powders) on which the pesticide is sorbed. Pesticide losses to the atmosphere typically are large during application, but losses continue after the application process. Volatilization is a continuous process and can be a major dissipative

route for many pesticides (Glotfelty, 1978; Majewski, 1991; Seiber and Woodrow, 1995).

Once airborne, the scale of transport through the atmosphere will depend on a variety of meteorological conditions and pesticide physical/chemical properties. Atmospheric removal processes include photochemically driven reaction and physical depositional mechanisms. Pesticides that are readily susceptible to photochemical reactions (for example, trifluralin; Woodrow and others, 1978; Mongar and Miller, 1988) have short (minutes to several hours) atmospheric residence times and usually are transported short distances from the source. Pesticides that are less susceptible to these chemical removal processes typically have atmospheric chemical lifetimes of a day or

considerably longer (for example, lindane and DDT; Mackay and others, 1997), and, thus, can be transported greater distances (regional or long-range scales).

The atmospheric transport and fate of a pesticide also depends on whether it exists as a gas, sorbed to atmospheric particles, or both. This particle/gas distribution is largely dependent on the pesticide's vapor pressure. For some pesticides, this distribution changes substantially as atmospheric conditions fluctuate, especially temperature and, to a less extent, concentration and type of airborne particles (Bidleman, 1988). The distance that a pesticide can be carried by wind will depend on this distribution. Pesticides in the gas phase are removed by dissolution into precipitation and surface water, and sorption onto soil and vegetation. Particle-bound pesticides are washed out of the atmosphere by precipitation or removed by dry-particle deposition to surfaces (water, soil, vegetation). These deposited residues can reenter the atmosphere by subsequent volatilization or wind erosion, and be transported and redeposited downwind repeatedly until they are transformed or accumulate, usually in areas with cooler climates (Risebrough, 1990; Wania and Mackay, 1996). This same process also can occur for the products from abiotic or biotic transformations of pesticides. For some persistent compounds (for example, 4,4'-DDT and its primary degradation products 4,4'-DDD and 4,4'-DDE), this deposition and volatilization process can continue for decades and lead to global contaminant distribution.

A variety of pesticides has been detected in the atmosphere throughout the world, but many of these studies have focused on older generation organochlorine insecticides, most of which are banned in many countries (Majewski and Capel, 1995; Grover and others, in press). Several recent studies have focused on current-use pesticides (for example, Baker and others, 1996; Aston and Seiber, 1997; McConnell and others, 1998). Nevertheless, reports of current-use pesticides in precipitation, and, especially, in air remain sparse in comparison to studies in other matrices, in part because of low ambient air concentrations and a lack of regulatory focus on the atmosphere.

To address the lack of information on pesticides in air, the U.S. Geological Survey

(USGS) conducted a 6-month study to characterize the atmospheric presence, temporal patterns, transport, and deposition of a variety of pesticides used in 1995 in agricultural and urban environments in three geographically different regions of the Mississippi River Valley. Weekly composite air (gas and particle phase) and precipitation (rain) samples were collected.

Two principal study objectives were (1) to document the presence and detection frequency of a wide variety of herbicides, insecticides, and selected transformation products in three atmospheric matrices (gas phase, particle phase, and precipitation) at urban and agricultural areas over one growing season, and (2) to compare the types of pesticides detected among three geographically different areas of the Mississippi River Valley region. This region was chosen because the highest density of agricultural activity and harvested cropland in the United States is in the upper Midwest and along the lower Mississippi River (see Majewski and others, 1998, and references therein). A variety of herbicides and insecticides are used on many of the diverse crops grown in this region (U.S. Department of Agriculture, 1996). The Midwestern United States also was the focus of two previous atmospheric-related studies by the USGS (Goolsby and others, 1997; Majewski and others, 1998). Selected air results are reported in this paper. A companion paper describes results for the precipitation samples (Majewski and others, this volume).

EXPERIMENTAL

Field Sampling

Weekly composite air samples were collected from early April through mid-September 1995 at seven locations across the Midwestern United States (fig. 1). Sampling sites at Jackson, Miss. (at Interstate 55 and McDowell Road); Iowa City, Iowa (downtown); and Minneapolis, Minn. (near Lake Harriet) represented urban areas. Sites near Rolling Fork, Miss. [sampler located about 0.5 kilometer (km) from surrounding cotton fields]; at the Cedar Rapids, Iowa, airport [sampler located about 15

meters (m) from corn field]; and at the U.S. Department of Agriculture's Management Systems Evaluation Area (MSEA) near Princeton, Minn. [sampler located 300 m from MSEA fields] represented agricultural areas. The Eagle Harbor, Mich., site is part of the Integrated Atmospheric Deposition Network for Lake Superior (Hillery and others, 1998) and is considered a background site because it is removed from areas of heavy urbanization and agriculture.

Air samples were collected using a conventional high-volume sampler (Graesby-Anderson, Incorporated*) (Thrane and Mikalsen, 1981). The sampler consisted of a 20.3 × 27.9-centimeter (cm) glass-fiber filter (GFF, Whatman, Incorporated EPM2000) to collect airborne particles, followed by two 7.6-cm long by 8.6-cm diameter polyurethane foam (PUF) plugs that were positioned in series to collect gas-phase pesticide. The GFF was precleaned by heat treating for 2 hours (h) at 450 degrees Celsius (°C). The GFF is rated to have 99.999 percent retention efficiency for sodium chloride particles having a mass median diameter of 0.6 microns at a 5 centimeter per second face velocity (Whatman, Incorporated, undated). PUF plugs were precleaned by sequential extraction with water, acetone, and hexane, and vacuum dried.

Samples were collected by drawing air through the GFF and PUF plugs at about 1 cubic meter of air per minute (m³/min) initially for a continuous 4 h each day from 10 a.m. to 2 p.m. By mid-June, sampling times at all sites had been modified to 5 minutes every hour to avoid missing diurnal variations and provide more representative air concentrations (Wallace and Hites, 1996). Typical weeklong air volumes were about 850 m³.

Sample Preparation and Analysis

The custom air method was based in part on the method used for rain samples to facilitate data interpretation. The method used for rain samples

* Use of firm, brand, or trade names in this article is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

was designed to determine multiple classes of pesticides in surface and ground water (Zaugg and others, 1995; Lindley and others, 1996). Briefly, each air sample component (GFF and two PUF plugs) was extracted and analyzed separately to provide estimates of particle/gas distributions and to assess pesticide gas-phase collection efficiency by the PUF plugs. Sample components were extracted with 36.5 percent by volume ethyl acetate in hexane for 16 h using a Soxhlet apparatus. Extracts were dried with sodium sulfate and reduced to 0.5 milliliter (mL) using a Kuderna-Danish concentrator followed by nitrogen gas evaporation.

Extracts were passed through a Pasteur pipet column containing 0.75 gram of fully activated Florisil overlain with 1 cm of powdered sodium sulfate. Pesticides were eluted using 4 mL of ethyl acetate into a test tube containing 0.1 mL of a perdeuterated polycyclic aromatic hydrocarbon internal standard solution. The extract was evaporated to about 150 microliters (μL) using nitrogen gas, transferred to autosampler vial inserts using a 100-μL toluene rinse, and analyzed by gas chromatography with electron-impact mass spectrometry operated in the selected-ion-monitoring mode (GC/MS-SIM) using conditions described in Zaugg and others (1995) and Lindley and others (1996). Extracted PUF plugs were vacuum dried and reused in at least one subsequent sample collection.

Quality Control

Quality-control measures included the addition of surrogate compounds to each sample prior to extraction to monitor laboratory sample preparation and analysis. Field air blanks were obtained at each site on rotation throughout the study and typically consisted of a GFF plus two PUF plugs that were briefly placed in the air sampler to simulate field handling. PUF plugs used for blanks included reused cleaned PUF from previous field samples.

Laboratory spike samples were prepared for each of the 22 sets of analyzed air samples by fortifying 100 nanograms of the 49 compounds onto a PUF plug prior to extraction. In addition to the estimates of gas-phase collection efficiencies for PUF plugs from field samples, three spike

collection-efficiency tests were performed to monitor the migration of pesticides through the two PUF plugs. These tests were carried out by spiking GFFs with the pesticides and drawing ambient air through the sampler at about 1 m³/min under the following volume/average temperature conditions: 310 m³/17 °C, 850 m³/16.1 °C, and 1,730 m³/24.5 °C. Some quality-control results are provided in this paper.

RESULTS AND DISCUSSION

Detection frequencies of pesticides in air samples are dependent on the following:

- Pesticide presence in air during the collection period in either the gas or particle phase, or both, in sufficient concentration to be detected by the GC/MS–SIM method.
- Adequate efficiency by the PUF plugs to collect at least a substantial portion, if not all, of the gas-phase pesticide during the collection period.
- Chemical stability of the pesticide once collected on the GFF or PUF.
- Adequate recovery during the sample preparation and analysis steps.

Butylate, 2,6-diethylaniline, EPTC, and molinate had poor collection efficiency on PUF at the 850 m³ and greater air volumes used in this study. Pebulate and phorate also were poorly collected by the PUF and were not detected in any samples. For these six compounds, detection frequencies might be biased substantially low. Azinphos-methyl, carbaryl, carbofuran, and terbacyl are susceptible to thermal instability during GC/MS–SIM analysis (Zaugg and others, 1995), a condition that can lead to high or low bias during quantitation. Of these, the insecticides were completely collected by the two PUF plugs for the air volumes used in this study. Mean laboratory spike recoveries are provided in table 1 and ranged from 37 ± 28 percent for tebuthiuron (which, along with prometon, were incompletely eluted from the Florisil cartridge) to 140 ± 56 percent for carbaryl, with an overall mean recovery of 92 ± 20 percent for all compounds. Estimates of method reporting levels were provided in Majewski and others (1998), and range from about 0.006 ng/m³ for atrazine to 0.1

ng/m³ for prometon for an 850 m³ air volume. Estimated concentrations below the reporting level were used if all GC/MS–SIM qualifying information were obtained (Zaugg and others, 1995).

For the 25-week study, the following week-long air samples were collected at each site: 24 at Jackson, Miss.; 21 at Rolling Fork, Miss.; 19 at each Iowa site; 22 at Minneapolis, Minn.; and 23 each at Princeton, Minn. and Eagle Harbor, Mich. Equipment or power failures reduced the number of samples to less than 25.

Frequencies of detection in air at paired urban and agricultural sites are shown in figure 2 and are grouped into herbicides and insecticides. The bar graphs are ordered from left to right beginning with the highest number of herbicide or insecticide detections at the agricultural location for each paired site. Detection frequencies at the Eagle Harbor, Mich., background site are shown in figure 3.

Each sample was analyzed for 49 compounds (table 1). Including all sites and samples, 21 of 26 herbicides, 13 of 19 insecticides, and 4 of 4 related transformation products were detected, with most pesticides detected in more than one sample (figs. 2 and 3). The maximum number of pesticides detected was 18 in an air sample taken at the Iowa City urban site from June 13 to 20.

The herbicide trifluralin was the most commonly detected pesticide measured in air samples at six sites, with greater than 80 percent detections at two sites and 100 percent detection at four sites. Nearly all detections of trifluralin were on the PUF sorbent only, indicating nearly exclusive gas-phase transport (table 1). Trifluralin can be applied to more than 40 different crop types (Meister, 1997). Application of this volatile herbicide to multiple crop types likely accounts for its presence in air over the entire 1995 growing season. However, atmospheric transport of trifluralin beyond the local, to at most regional, scale was not evident because it was detected in only one air sample (and no rain samples) from Eagle Harbor (fig. 3). Trifluralin's apparent short atmospheric lifetime also was indicated from its reduced detection frequency in rain samples collected at the other six sites (mean 28 percent; range 5 to 69 percent) (Majewski and others, this

volume). These observations are not unexpected in light of the reported rapid gas-phase and aqueous-suspension direct photolysis and photooxidation reaction rates for trifluralin (Leitis and Crosby, 1974; Woodrow and others, 1978; Mongar and Miller, 1988).

Herbicides applied primarily for corn and soybean production were detected often and in nearly equivalent frequencies at agricultural and urban sites in Iowa and Minnesota. Several of these herbicides (for example, atrazine, metolachlor, pendimethalin) also were commonly observed at the agricultural site in Mississippi.

Acetochlor, metolachlor, atrazine, and the triazine degradation product 2-chloro-4-isopropylamino-6-amino-*s*-triazine (CIAT, a degradation product of atrazine and propazine) were detected in more than 68 percent of the air samples at both Iowa sites. These compounds were detected in the gas- and particle-phase in air samples collected near agricultural fields (including the Iowa City site, which is about 2.5 km from the nearest fields). However, at the Jackson, Minneapolis, and Eagle Harbor sites that are more distant from fields (about 10 km or more), these compounds were predominantly or exclusively detected (if observed at all) on the GFF (the operationally defined particle phase). These findings suggest either preferred sorption of the volatilized herbicide to airborne particles during transport or a selective dissipation (by either chemical or physical processes) of the gas-phase component, or both. The presence of atrazine and cyanazine, and possibly dacthal, CIAT, and 2-chloro-4-ethylamino-6-amino-*s*-triazine (CEAT, a degradation product of atrazine, cyanazine, simazine, and terbuthylazine) at Eagle Harbor (fig. 3) suggests their potential for long-range transport. Atrazine's ability to undergo long-range transport also has been reported by Glotfelty and others (1990), Cromwell and Thurman (1996), Goolsby and others (1997), and Rawn and others (1998).

The herbicide benfluralin was detected in 100 percent of the air samples from Iowa City and Minneapolis (fig. 2). This herbicide is applied preemergent to control annual grasses and broadleaf weeds in, for example, alfalfa and various forage crops (Meister, 1997). However, about twice as much benfluralin reportedly is

used in noncrop settings (Gianessi and Puffer, 1991), primarily on established turf, including golf courses and lawns in urban and suburban locations.

The insecticides chlorpyrifos, diazinon, and carbaryl are applied to a wide variety of agricultural crops. In addition, they are used extensively in nonagricultural settings (Gianessi and Puffer, 1991), which likely accounts for the more frequent detections at the urban sites than agricultural sites in Mississippi and Iowa. For example, all three are used in lawn applications, with chlorpyrifos and diazinon commonly applied to control fire ants. Chlorpyrifos and permethrin are used in termite control, which also might contribute to their higher detection frequency in Jackson than in Rolling Fork. Although applied subterranean, pesticides applied for termite control are lost to indoor and outdoor air (Dearth and Hites, 1991).

Methyl parathion was detected in 70 percent of the samples from Rolling Fork, Miss. It existed almost exclusively in the gas phase and exhibited the highest concentration — 62 nanograms per cubic meter of air (ng/m^3) — of any insecticide measured in the study. Methyl parathion is applied extensively in cotton production and represents the highest-use pesticide applied in Mississippi and Louisiana, with about 1 million kilograms applied in each State in 1995 (U.S. Department of Agriculture, 1996). Because it is designed to control insects on the growing cotton plant, methyl parathion is applied later in the growing season relative to typical herbicide applications, with the earliest low-level detections in air (and rain) in mid-May and increasing to a maximum concentration in air in mid-August (fig. 4). By contrast, rice herbicides, another important category of herbicide applied in the Mississippi delta region, are applied earlier in the growing season, and were detected in air from mid-April ($0.12 \text{ ng}/\text{m}^3$ for 4/18 sample) until early June for thiobencarb (fig. 4) and until mid-July for propanil and molinate. In comparison to thiobencarb, about twice as much molinate and four times as much propanil are used on rice in Mississippi (Coupe and others, 1998a). Molinate and propanil also are suggested more often than thiobencarb for postemergent and midseason applications to rice

(Mississippi Cooperative Extension Service, 1995). A summary of the air and rain concentrations of pesticides detected at the Mississippi sites is provided in Coupe and others (1998b).

The primary aerobic degradation product 4,4'-DDE of the insecticide 4,4'-DDT was observed in 100 percent of air samples from Rolling Fork and Iowa City, and was detected in at least two samples at every other sampling site. Neither DDT nor the anaerobic degradation product 4,4'-DDD were included as compounds in the air and rain methods. Detection of DDE was not unexpected, and higher detection frequencies at the other sampling sites likely would have resulted if the more responsive electron-capture detector had been used. DDE concentrations at Rolling Fork ranged from 0.13 to 1.1 ng/m³ and averaged 0.62 ng/m³. This average is only about 60 percent less than the average measured range (1.4 to 1.8 ng/m³) observed in the region 23 years earlier by Kutz and others (1976). This highly persistent DDT degradation product, which has been classified as a global pollutant because of its detection in remote areas of the earth (Bidleman and others, 1989; Iwata and others, 1993), continues to cycle between the soil and air more than two decades after DDT use was banned in 1972 in the United States.

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Table 1. Mean and standard deviation of recovery for 22 laboratory spike samples, and apparent phase in which the pesticide was detected for air samples collected April to September 1995. Gas phase noted in boldface type when apparent from field results

[±, plus or minus; G, gas phase; **G**, gas phase dominant; P, particle phase; nd, not detected; --, irrelevant]

Herbicides	Mean spike recovery (percent)	Apparent phase distribution		Insecticides	Mean spike recovery (percent)	Apparent phase distribution	
<i>Chloroacetanilides</i>				<i>Organophosphates</i>			
Acetochlor	98 ± 12	G	P	Azinphos-methyl ⁶	76 ± 51	G	P
Alachlor	102 ± 12	G	P	Chlorpyrifos	95 ± 12	G	P
2,6-Diethylaniline ^{1,2}	72 ± 9	G	P	Diazinon	97 ± 12	G	P
Metolachlor	102 ± 11	G	P	Dimethoate	100 ± 33		nd
Propachlor	103 ± 21	G	P	Disulfoton	66 ± 44		nd
<i>Dinitroaniline</i>				Ethoprop ²	91 ± 11	G	P
Benfluralin	66 ± 16	G	P	Fonofos	88 ± 12	G	
Ethalfuralin	76 ± 23		nd	Malathion	107 ± 16	G	P
Trifluralin	71 ± 17	G	P	Methyl parathion	96 ± 19	G	P
<i>Thiocarbamates</i>				Parathion	110 ± 23		nd
Butylate ²	89 ± 14	G	P	Phorate ²	73 ± 23		nd
EPTC ²	90 ± 21	G	P	Terbufos	82 ± 22		nd
Pebulate ²	86 ± 11	G	P	<i>Carbamates</i>			
Triallate	90 ± 13		nd	Carbaryl ⁶	140 ± 56	G	P
Thiobencarb	100 ± 11	G	P	Carbofuran ⁶	135 ± 37	G	P
<i>Triazines</i>				<i>Organochlorines</i>			
Atrazine	97 ± 12	G	P	alpha-HCH	86 ± 17	G	P
CEAT ³	107 ± 8	G	P	Lindane	100 ± 26	G	
CIAT ⁴	107 ± 48	G	P	4,4'-DDE ⁷	82 ± 12	G	P
Cyanazine	112 ± 21	G	P	Dieldrin	80 ± 14	G	
Metribuzin	97 ± 13	G	P	cis-Permethrin	99 ± 19	G	P
Prometon ⁵	53 ± 34		nd	<i>Fungicide</i>			
Simazine	96 ± 11	G	P	Propargite I & II	86 ± 22		nd
<i>Miscellaneous</i>				<i>Surrogates</i>			
Dacthal	99 ± 14	G	P	² H -Diazinon	103 ± 21		--
Linuron	90 ± 32		nd	² H -alpha-HCH	90 ± 12		--
Molinate ²	91 ± 14	G	P	Terbutylazine	94 ± 14		--
Napropamide	93 ± 15		nd				
Pendimethilan	66 ± 19	G	P				
Pronamide	93 ± 12		P				
Propanil	109 ± 19	G	P				
Tebuthiuron ⁵	37 ± 28	G					
Terbacil ⁶	108 ± 27	G					

¹ Alachlor degradation product.

² Gas-phase compound is poorly collected by two PUF plugs at air volumes used in this study.

³ CEAT, 2-chloro-4-ethylamino-6-amino-*s*-triazine, a degradation product of atrazine, cyanazine, simazine, and terbutylazine.

⁴ CIAT, 2-chloro-4-isopropylamino-6-amino-*s*-triazine, a degradation product of atrazine and propazine.

⁵ Variably low recovery during extract preparation.

⁶ Estimated quantitation because of thermal instability during gas chromatography.

⁷ DDT degradation product. DDT not determined in this method.

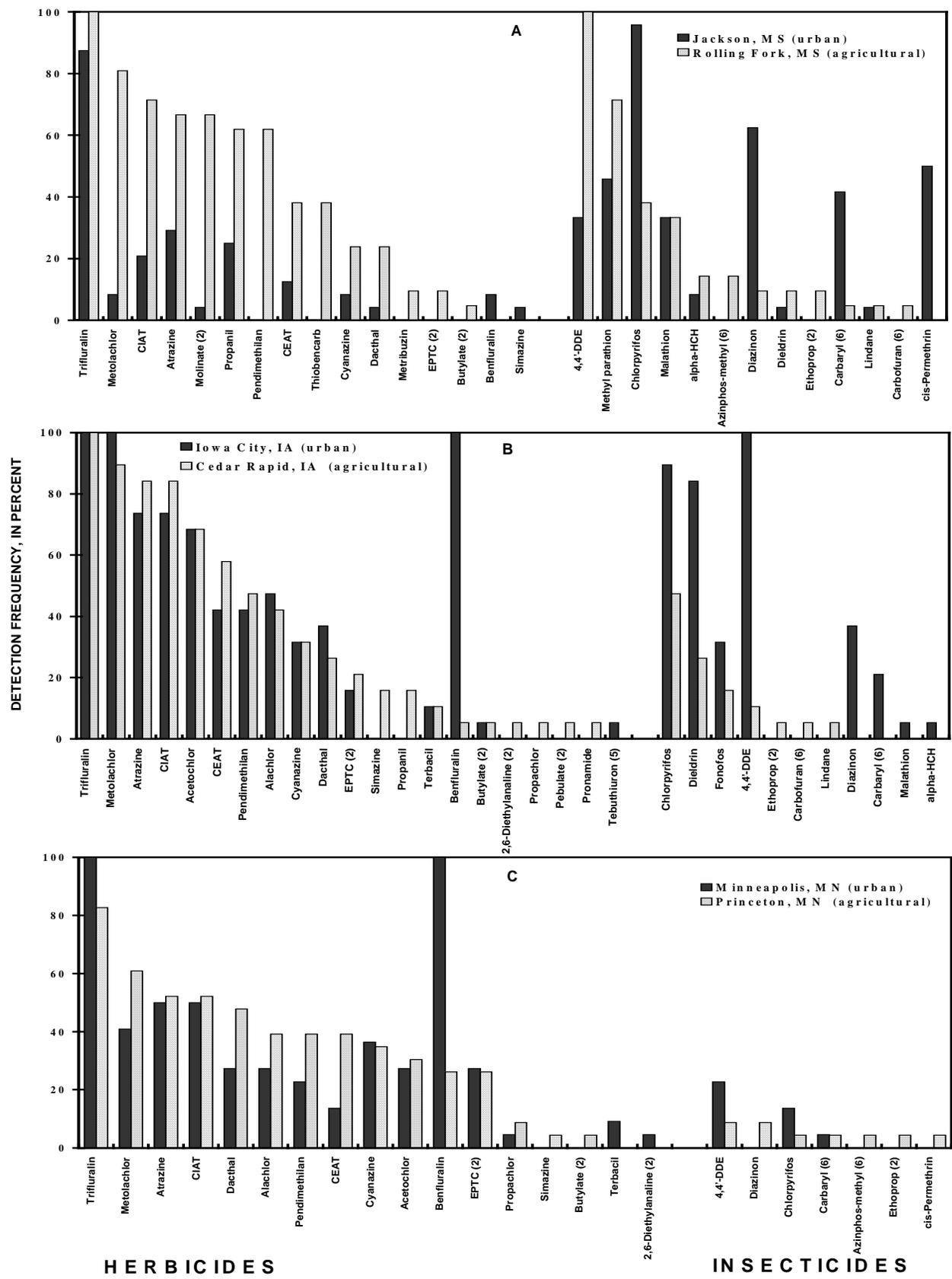


Figure 2. The frequency of detection for herbicides and insecticides in air at the (A) Mississippi, (B) Iowa, and (C) Minnesota sites. Footnotes (2), (5), and (6) are explained in table 1.

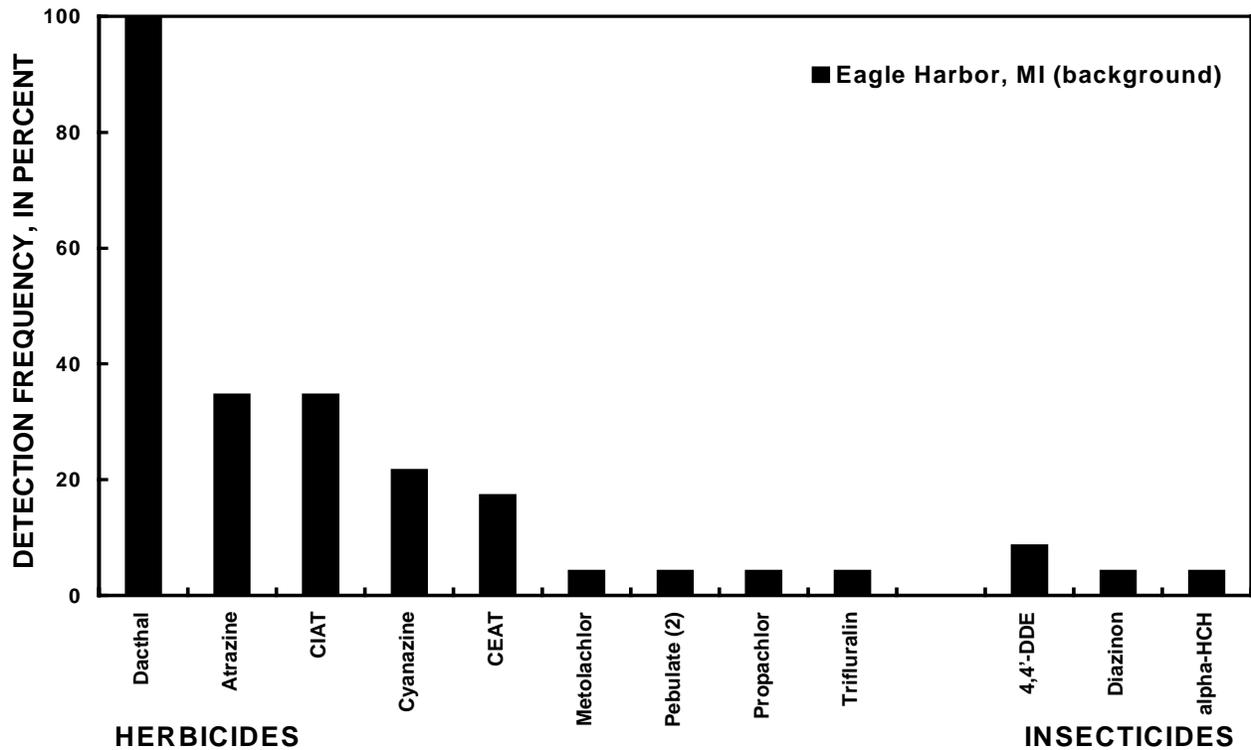


Figure 3. The frequency of detection for herbicides and insecticides in air at Eagle Harbor, Mich. Footnote (2) explained in table 1.

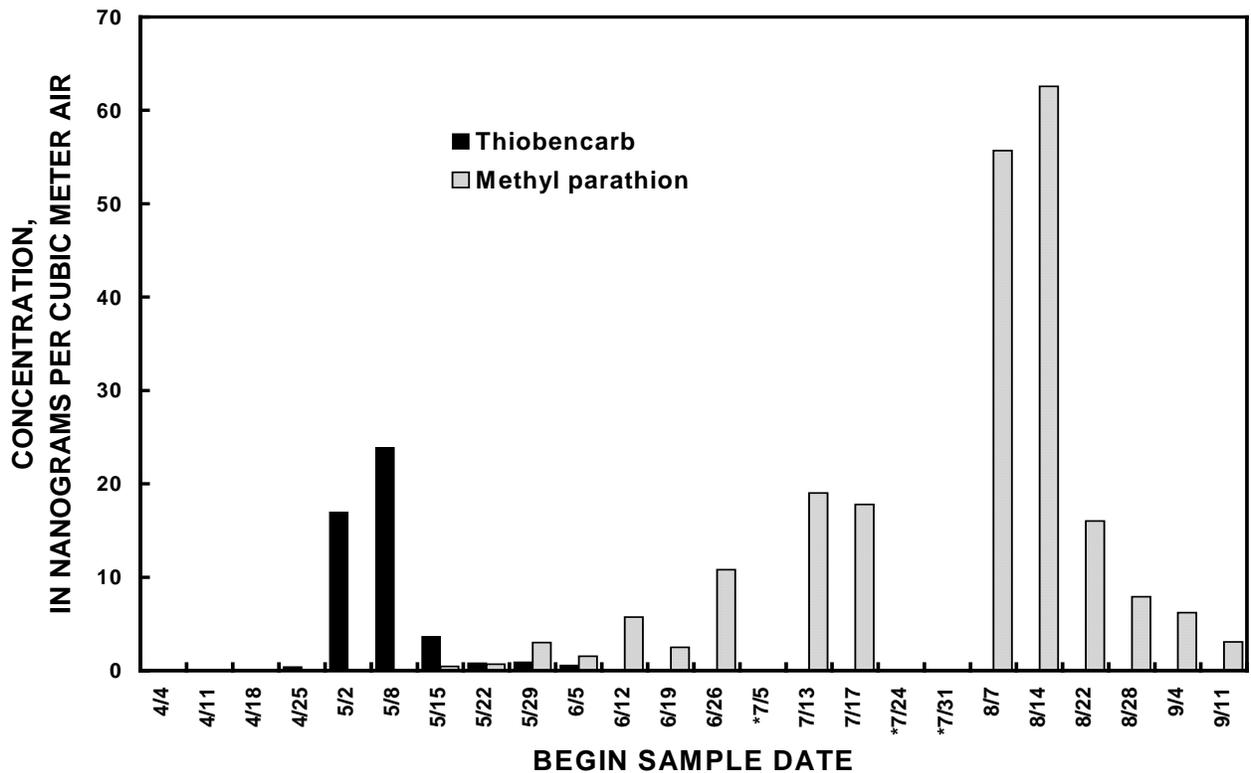


Figure 4. Atmospheric concentration of thiobencarb and methyl parathion at Rolling Fork, Miss., site throughout the study period in 1995. No air sample collected for dates with asterisk.