Pesticides in the atmosphere of the Mississippi River Valley, Part I — Rain

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ABSTRACT

Weekly composite rainfall samples were collected in three paired urban and agricultural regions of the midwestern United States and along the Mississippi River during April - September 1995. The paired sampling sites were located Mississippi, Iowa, and Minnesota. A background site, removed from dense urban and agriculture areas, is located near Lake Superior in Michigan. Herbicides were the predominant type of pesticide detected at every site. Each sample was analyzed for 47 compounds and 23 of 26 herbicides, 13 of 18 insecticides, and 3 of 3 related transformation products were detected in one or more sample from each paired site. The detection frequency of herbicides and insecticides were nearly equivalent at the paired Iowa and Minnesota sites. In Mississippi, herbicides were detected more frequently at the agricultural site and insecticides were detected more frequently at the urban site. The highest total wet depositional amounts (µg pesticide/m² per season) occurred at the agricultural sites in Mississippi (1,980 µg/m²) and Iowa (490 µg/m²) and at the urban site in Iowa (696 µg/m²). Herbicides accounted for the majority of the wet depositional loading at the Iowa and Minnesota sites, but methyl parathion (1,740 µg/m²) was the dominant compound contributing to the total loading at the agricultural site in Mississippi. Atrazine, CIAT (a transformation product of atrazine) and dacthal were detected most frequently (76, 53, and 53 percent, respectively) at the background site indicating their propensity for long-range atmospheric transport.

INTRODUCTION

More than 500 million kg (kilograms) of pesticides are used each year in the United States to control many different types of weeds, insects, and other pests in a wide variety of agricultural and urban settings (Aspelin, 1994). The highest density of agricultural activity and harvested cropland in the United States is in the upper Midwest and along the lower Mississippi River. A wide variety of herbicides and insecticides are used on many of the diverse crops grown in this region. Although increased pesticide use has resulted in increased crop production, concerns about the potential adverse effects of pesticides and pesticide transformation products on the environment and human health have grown steadily.

A wide variety of pesticides have been detected in the atmosphere throughout the world (Grover, and others, in press; Majewski and Capel, 1995). Pesticides become airborne through volatilization and wind erosion of particles both during and 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 pesticide can be carried by wind and deposited in unintended areas by dry (gas and particle) and wet (fog and precipitation by rain and snow) depositional processes. These deposited residues can revolatilize, re-enter the atmosphere, 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, this deposition and revolatilization process can continue for decades.

A six-month study was conducted that was designed to characterize the atmospheric occurrence, temporal patterns, transport, and deposition of a variety of pesticides used 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 occurrence and detection frequency of a wide variety of herbicides, insecticides, and selected transformation products in the various 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. The results of the study in relation to the precipitation data are reported in this paper.

Sampling Sites

Each monitoring site was chosen to be within or near an existing NAWQA (U.S. Geological Survey National Water Quality Assessment program) study unit. The urban and suburban sampling sites (Figure 1) for this study were located at Jackson, Miss. (Mississippi Embayment NAWQA study unit), Iowa City, Iowa (Eastern Iowa Basins NAWQA study unit), and Minneapolis, Minn. (Upper Mississippi River Basin NAWQA study unit). The agricultural sampling sites were located near Rolling Fork, Miss. (sampler located ca. 0.5 km [kilometer] from cotton field), at the Cedar Rapids, Iowa, airport (sampler located *ca*. 15 m [meters] from corn field), and at the U.S. Department of Agriculture's MSEA (Management Systems Evaluation Area) near Princeton, Minn., (sampler located *ca*. 300 m from MSEA fields). A background site removed from large urban and agriculture areas was located at Eagle Harbor, Mich. This site is part of the IADN (Integrated Atmospheric Deposition Network) for Lake Superior.

Sampling began during the first week of April and continued through September, 1995. The precipitation samples were collected using a modified automatic wet-dry precipitation collector. Modifications to the collector included replacing the plastic collection bucket with a 31-cm (centimeter) diameter, Teflon coated, metal funnel connected by Teflon tubing to a 3-L (liter) glass carboy inside a small refrigeration unit located beneath the deposition collector. Teflon sheeting also lined the cover of the collector, which was placed over the funnel during dry periods. Each sample was a composite of the precipitation events that occurred during a one-week period. If more than one liter of liquid was collected during a sampling period, the total volume was recorded and a 1-L sub-sample was taken for analysis. If less than 75 ml (milliliter) of rainwater was collected at the end of the 1-week sampling period, it was left in the container and the sampling period was extended for another week. If at the end of a 2-week period there was not sufficient rainwater for an appropriate extraction, the liquid was discarded, the carboy cleaned, and a new collection period was begun.

Each sample was extracted using C-18 solid-phase extraction followed by selected ion GC/MS (gas chromatographic/mass spectometric) analysis for 47 herbicides, insecticides, and selected transformation products (Zaugg, and others, 1995). The concentration of each pesticide compound in

microgram per liter (µg/L) was divided by the actual rainfall amount in cm (centimeter) to obtain the total depositional flux (µg/m² [microgram per square meter] per sample and per growing season). This was done to facilitate the comparison between each sampling period and sampling site.

Results and Discussion

An average of 18 samples were collected at each location — 16 at each of the Mississippi sites, 18 at Iowa City, Iowa, 20 at Cedar Rapids, Iowa, 20 at Minneapolis, Minn., 17 at Princeton, Minn., and 17 at Eagle Harbor, Mich. Six herbicides (alachlor, atrazine, CIAT [2-chloro-4-isopropylamino-6-amino-*s*-triazine, a transformation product of atrazine], cyanazine, dacthal, and metolachlor) were detected at every site in at least one sample. Six other herbicides (acetochlor, EPTC, pendimethalin, prometon, simazine and trifluralin) were detected at six of the seven sites in at least one sample. Herbicides were the predominant type of pesticide detected at every site. Of the pesticides analyzed for, 23 of 26 herbicides, 13 of 18 insecticides, and 3 of 3 transformation products were detected.

The general trend in pesticide occurrence and detection frequency in rain samples at the three paired sampling sites was that nearly every pesticide detected at the agricultural site was also detected at the urban site. The exception was at the Mississippi sites where herbicide detection frequencies were dominate in the agricultural samples and insecticide detection frequencies were dominate in the urban samples (Figure 2 A). The same nine herbicides and CIAT were detected at every urban and agricultural site (Figure 2). The most frequently detected classes of herbicides were the triazines (atrazine, CIAT, and cyanazine) and chloroacetanilides (acetochlor, alachlor, metolachlor, and propachlor). Both the triazine and chloroacetanilide herbicides are used extensively in the production of corn, soybeans, sorghum, and to a lesser extent, cotton. Their state-wide use in Iowa and Minnesota range from 1 to 4 million kg each annually with an order of magnitude less used in Mississippi (Gianessi and Anderson, 1995). In Mississippi, the rice herbicides molinate, propanil, and thiobencarb were among the most frequently detected pesticides at both the agricultural and the urban sites.

Atrazine, CIAT, and dacthal were the most frequently detected compounds (76, 53, and 53 percent, respectively) at Eagle Harbor, Mich., the background site. These findings indicate that of the 47 pesticides analyzed for in this study, these three are relatively stable in the atmosphere and are subject to at least regional-atmospheric transport. Atmospheric transport and deposition often are the major or only input mechanisms for the movement of these types of pesticides into remote, pristine environments.

Five insecticides (carbaryl, carbofuran, chlorpyrifos, diazinon, and parathion) were frequently detected at most of the paired sites. Many of the insecticides were detected at comparable frequencies at both the agricultural and the urban sampling locations, but the depositional amounts at the agricultural sites generally were higher with the exception of malathion, carbaryl, diazinon, and chlorpyrifos. These four compounds are used extensively in the urban environment (Whitmore, and others, 1992) and the elevated detection frequencies and depositional amounts are, most likely, an indication of urban use. Methyl parathion was detected primarily at the two Mississippi sites. The detections were continual from mid-May at Rolling Fork and from mid-June at Jackson to the end of the study. There is no legal urban use for methyl parathion, but it was detected nearly as often at the urban site as the agricultural site. This compound was recently implicated in an illegal housing fumigation operation in Mississippi and other souther states (Hileman, 1996; Hileman, 1997) and this may be a possible

urban source.

The largest total amount of pesticide deposition (µg/m² per season) occurred at the agricultural sites in Mississippi and Iowa and the urban site in Iowa (fig. 3). Herbicides were the most significant type of pesticide contributing to the depositional loading by precipitation in Iowa, Minnesota, and, with the exception of methyl parathion at Rolling Forks, Mississippi. Methyl parathion (1,740 µg/m²) which is used primarily in the production of cotton, but also to a lesser extent on corn, rice, and soybeans, was the single greatest contributor to the wet depositional loading at Rolling Fork. In addition, metolachlor (81.3 µg/m²) used on used on corn and soybeans, propanil (25.8 µg/m²) used on used on rice, atrazine (25.6 µg/m²) used on used on corn, trifluralin (22.1 µg/m²) and pendimethalin (20.4 µg/m²) used on used on corn, cotton, sorghum, and soybean, and molinate (12.2 µg/m²) used on used on rice, were the other significant contributors to the wet depositional loading at the Rolling Fork site. The occurrence of atrazine is a result of the increasing corn production in the Mississippi delta region (Mississippi Cooperative Extension Service, 1995; U.S. Department of Agriculture, 1996).

The first widespread application in the United States of the new corn herbicide acetochlor occurred in 1994. It was used on an estimated 7 percent of the total corn acreage using 1994 data compiled for 10 major crop producing states. For 1995, acetochlor was used on about 20 percent of the corn acreage (U.S. Department of Agriculture, 1996). Acetochlor was detected in rain samples at each site in Iowa and Minnesota from the initiation of sampling during April - July, 1995. The greatest concentration and detection frequency occurred during periods of extensive herbicide application in late April and throughout May. Lack of acetochlor detections in samples collected in Mississippi and at Eagle Harbor suggests that the atmospheric transport and deposition of this compound is limited to the local- and, at most, a regional-scale. The observations for acetochlor were comparable to those observed for alachlor in this study and were similar to those previously reported for alachlor (Glotfelty, and others, 1990; Goolsby, and others, 1997). Acetochlor accounted for more than 35 percent of the total pesticide flux (500–700 µg/m²) for the 1995 growing season at the Iowa sites (fig. 3).

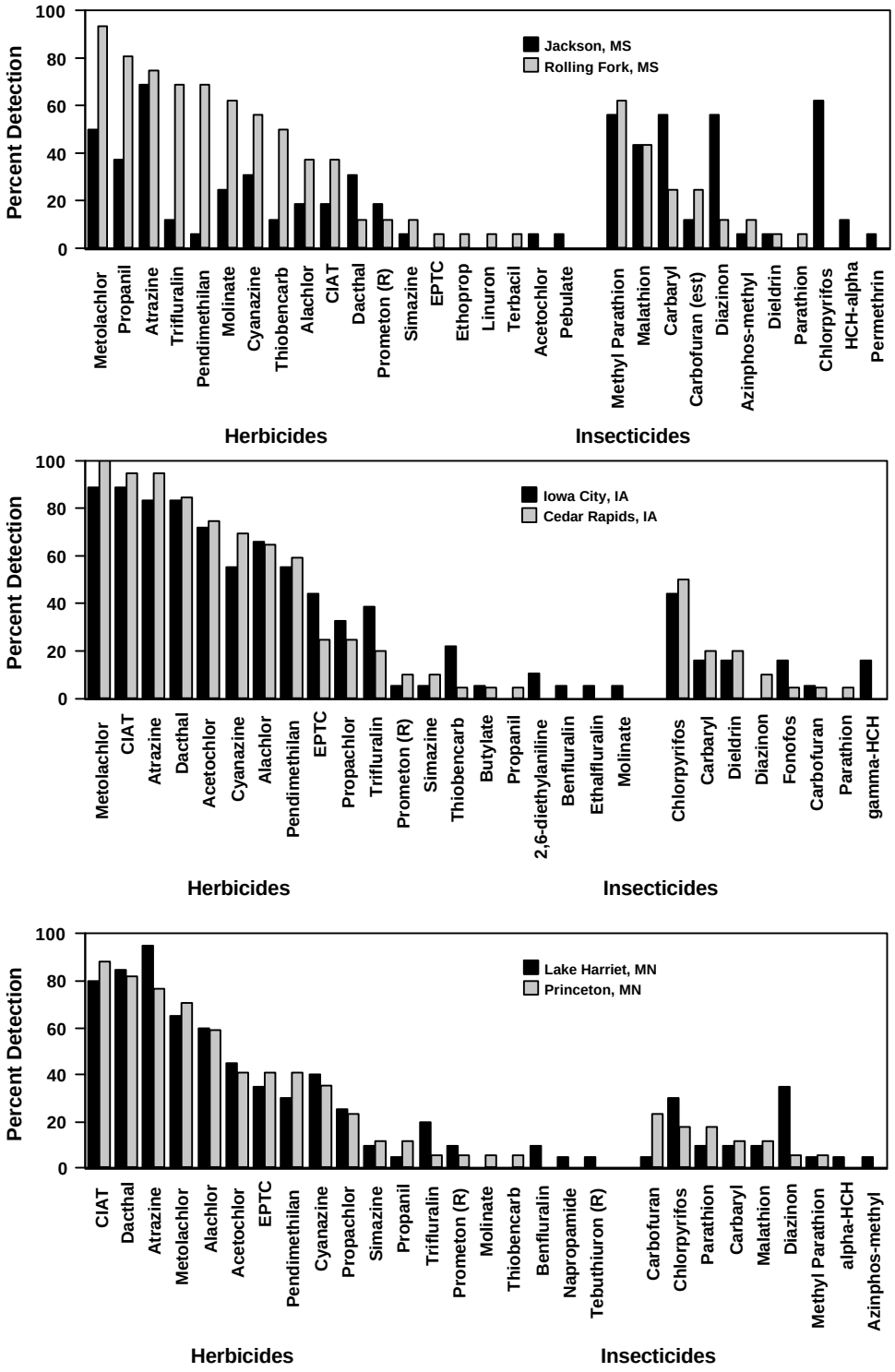

Figure 2. The frequency of detection (%) for each pesticide detected in rain at the A) Mississippi sites, B) Iowa sites, and C) Minnesota sites.

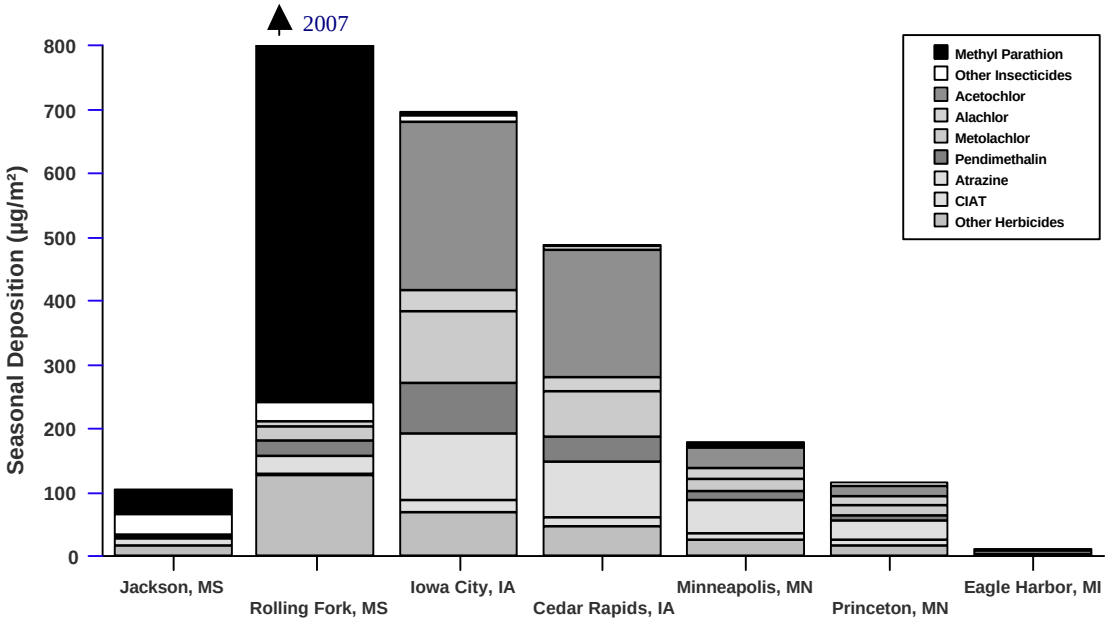

Figure 3. Total deposition by rain for those pesticides detected at the sample collection locations from April through mid-September, 1995.

Figure 1. Sampling locations: urban (Jackson, Iowa City, Minneapolis), agricultural (Rolling Fork, Cedar Rapids, Princeton), and background (Eagle Harbor) sites.

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