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Airborne Pesticide Residues along the Mississippi River

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The occurrence, concentration, and geographical distribution of agricultural pesticides were determined in air over the Mississippi River from New Orleans, LA, to St. Paul, MN, during the first 10 days of June 1994. Air samples were collected from a research vessel by pulling air through polyurethane foam plugs at about 100 L/min for up to 24 h. Each sample was analyzed for 42 pesticides and 3 pesticide transformation products. Twenty-five compounds—15 herbicides, 7 insecticides, and 3 pesticide transformation products—were detected in one or more samples with concentrations ranging from 0.05 to 80 ng/m^3. Alachlor, chlorpyrifos, diazinon, fonofos, malathion, methyl parathion, metolachlor, metribuzin, pendimethalin, and trifluralin were detected in 80% or more of the samples. The highest concentrations for chlorpyrifos (1.6 ng/m^3), diazinon (0.36 ng/m^3), and malathion (4.6 ng/m^3) all occurred near major metropolitan areas. These samples represent a "snapshot in time", a spatial and temporal integration of which pesticides were present in the air during each sampling period. The occurrence and atmospheric concentrations of the observed pesticides were most closely related to their use on cropland within 40 km of the river.

Introduction

More than 500 million kg of pesticides is 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 (*1*). National agricultural use of herbicides and insecticides on cropland and pasture has grown from 99 million kg of active ingredients (a.i.) in 1964 (*2*), to an estimated 277 million kg a.i. in 1992 (*3*). Although increased pesticide use has resulted in increased crop production and many other benefits, concerns about the potential adverse effects of pesticides and pesticide transformation products on the environment and human health have grown steadily.

The highest density of agricultural activity and harvested cropland in the United States is in the Midwest and along the Mississippi River (Figure 1). A wide variety of herbicides and insecticides are used on many of the diverse crops grown in the Mississippi River Valley region. These pesticides can become airborne through volatilization and wind erosion both during and after the application process. Volatilization is a continuous process and can be a major dissipative route for many pesticides (*4*−*6*). 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 (*7, 8*). 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 occur over decades.

The overall objective of the 1994 research cruise up the Mississippi River was to determine the spatial distribution of concentration and flux for select herbicides, major cations, and nutrients in the Mississippi River, similar to that described by Moody (*9*). The study described here assesses the occurrence, concentration, and geographical distribution of a broad suite of agricultural pesticides in air along the Mississippi River.

Experimental Section

Air Sampling. Air samples were collected from the 17-m research vessel *Acadiana*, which is owned and operated by the Louisiana Universities Marine Consortium, Cocodrie, LA. The R/V *Acadiana* entered the river below New Orleans on June 1 and sailed upstream 24 h per day at 11−14 km h^{-1} stopping only to refuel and lock through navigational dams. The vessel arrived at St. Paul, MN, more than 1700 river miles upstream on June 10, 1994.

Air sampling began just south of New Orleans, LA, at RM (river mile) 88.6. Air was pulled through a primary and a secondary (4.45 cm diameter × 7.62 cm each; average density = 0.043 g m^{-3}) precleaned, PUF (polyurethane foam) plug at a rate of approximately 100 L min^{-1} using a high-volume vacuum pump (Graseby-GMW, Village of Cleves, OH). The flow rates were checked at the beginning and end of each sampling period by briefly attaching a flow meter (Gilmont instruments, model no. 4) to the intake of the cartridge. During each sampling period (approximately 24 h in duration), between 90 and 120 m^3 of air was processed. Samples collected on June 1, 2, and 10 were of reduced volumes (61, 65, and 22 m^3, respectively) due to low flow rates (June 1 and 2) and a shortened sampling period of only 29 RM on June 10. The PUF plugs were held in a Teflon cartridge that was wrapped in aluminum foil to minimize photodegradation of the pesticides and pointed upstream (the direction of travel). Each sample was a whole air sample, that is, no glass fiber prefilter was used to collect particulate matter. The sampling cartridge was mounted off the starboard rear of the pilot's cabin, about 5 m above the water.

At the end of each sampling period, both PUFs were removed from the cartridge, placed in individual clean glass jars, capped with Teflon-lined lids, and refrigerated at 4 °C until they were analyzed. Each sample, except that for June 10, represented approximately 200 RM. During periods of light rain, the sampling cartridge was pointed downward, at approximately 45° from horizontal. If the rain became too intense, the pump was turned off, and the cartridge was covered with aluminum foil until the downpour subsided. The pump also was turned off when locking through navigational dams when other vessels were present.

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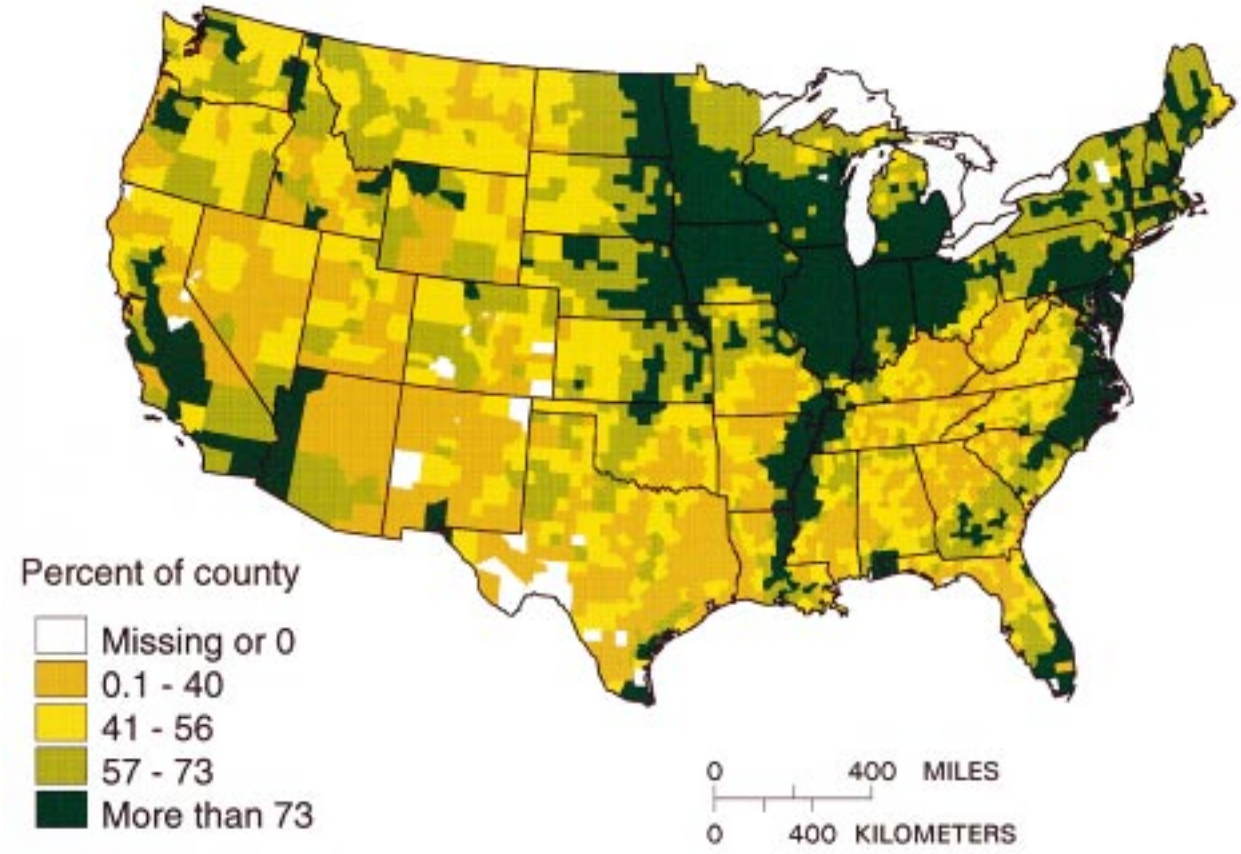

FIGURE 1. Total cropland in the United States for 1992 from refs *3* and *20*.

The weather was typical for the Midwest in June—generally warm days and nights, variable winds, frequent rain showers, and occasional thunderstorms. There were only 2 days (June 6 and 10) when no rain occurred during the 24-h sampling periods. On June 8, the research vessel moved through a cold front, and the average air temperatures dropped 5 °C for 2 days.

Analytical Method. The sample analysis was a modified version of a method developed by the U.S. Geological Survey's National Water Quality Laboratory for analyzing pesticides in water (*10*). Each PUF sample was warmed to room temperature, and 100 μL of a 1 ng/μL solution containing the surrogates diazinon-d_{10}, α-HCH-d_6, and terbuthylazine were added. The samples were then extracted in a Soxhlet apparatus with 250 mL of a hexane:acetone (1:1, v:v) mixture for 20 h. The extract was concentrated to about 3 mL using a Kuderna-Danish apparatus at 85 °C. A total of 100 μL of toluene was added, and the extract was further concentrated to 100 μL under a gentle stream of nitrogen. A 100-μL sample of an internal standard solution in toluene (acenaphthene-d_{10}, phenanthrene-d_{10}, and chrysene-d_{12}) was then added, and the sample was capped and mixed before analysis. Initial analysis of the samples was performed with a Hewlett-Packard model 5971 GC/MS operated in the selected-ion monitoring mode. Each analyte detected was identified using three mass ions (*10*). A more sensitive flame-photometric detector was subsequently used to determine selected organophosphorus compounds. The analytical approach was a multiclass, multiresidue method that included a wide variety of herbicides, insecticides, and several pesticide transformation products (Table 1). Reporting levels were estimated based on a 100 m^3 sample volume. The actual reporting levels for each compound varied somewhat in each sample, however, because of the variable sample volumes. Concentrations reported below the reporting level were estimated.

The pesticide collection efficiency of the PUF for the method was assessed as part of a separate study in 1995 (*11*). A glass fiber prefilter was spiked with about 80 μg of each compound listed in Table 1, the solvent was allowed to evaporate, and 310 m^3 of ambient air at an average temperature of 17 °C was pulled through the prefilter and the two PUFs at 1.17 m^3/min. The prefilter and each PUF were analyzed separately, and the collection efficiency was calculated as (mass on back PUF + mass on front PUF + mass on GFF)/(initial spiked mass on GFF) × 100. Breakthrough from the first PUF to the second PUF was calculated as (mass on back PUF)/(mass on front PUF) × 100.

Results and Discussion

PUF Collection Efficiencies. Collection efficiencies for most compounds were excellent (Table 1). The most volatile compounds (2,6-diethylaniline, butylate, EPTC, and pebulate) had very poor collection efficiencies, exhibiting very short retention times on the PUF. Molinate also exhibited substantial migration into the second PUF, but the overall collection efficiency was good. All other compounds exhibited minimal (<1%) or no migration into the second PUF for the 310 m^3 test volume. The 310 m^3 volume used in the 1995 test was 2.6 times greater than the largest sample volume collected during the cruise (Table 2), and the trapping efficiency for these samples should have been complete for most of the compounds analyzed for.

The collection efficiency of the PUF samples taken over the river was assessed by separate analysis of the front and back PUF plugs for the June 4 and 10 samples. For the June

TABLE 1. Maximum and Median Concentrations, Percent Detections, Reporting Levels, and PUF Collection Efficiencies for Method Pesticides[a]

compound	measured air concn: max (ng/m³)	measured air concn: median (ng/m³)	detections (%)	method reporting level[b] (ng/m³)	collection efficiency: total recovery GFF + 2 PUFs[c] (%)	collection efficiency: PUF breakthrough[d] (%)
Herbicides						
alachlor	8.8	1.5	80	0.10	96	<1
atrazine	2.8	1.1	70	0.05	nq	<1[i]
benfluralin			nd	0.10	87	<1
butylate[e]	0.44	0.00	10	0.10	1.5	100
CIAT[f]	0.50	0.00	60	0.20	95	<1
cyanazine			nd	0.20	32	<1
dacthal (DCPA)	0.33	0.06	60	0.10	101	<1
2,6-diethylaniline[e]	0.40	0.00	20	0.20	3.4	100
EPTC[e]	1.5	0.00	30	0.10	2.6	100
ethalfluralin	0.19	0.00	10	0.20	95	<1
linuron			nd	0.10	74	<1
metolachlor	5.6	1.2	100	0.10	53	<1
metribuzin	6.6	6.0	100	0.20	81	2
molinate[e]	3.1	0.00	40	0.20	75	88
napropamide			nd	0.15	75	<1
pebulate[e]			nd	0.20	15	100
pendimethalin	3.2	1.2	80	0.20	95	<1
prometon			nd	0.90	97	<1
pronamide			nd	0.15	110	<1
propachlor	0.19	0.00	10	0.35	70	<1
propanil	13	0.00	10	0.20	109	<1
simazine			nd	0.25	59	<1
tebuthiuron			nd	0.50	62	<1
terbacil[g]			nd	0.35	5.9	<1
thiobencarb	7.1	0.00	40	0.10	95	<1
tribufos (DEF)[h]	0.04	0.00	10	0.10	ns	ns
trifluralin	80	2.4	90	0.10	91	<1
Insecticides						
carbaryl[g]			nd	0.15	122	<1
carbofuran[g]			nd	0.15	128	<1
chlorpyrifos	1.60	0.29	100	0.20	85	<1
p,*p*′-DDE	1.60	0.00	20	0.30	91	<1
diazinon	0.36	0.08	100	0.10	115	<1
dieldrin	0.64	0.00	10	0.05	112	<1
disulfoton			nd	0.85	54	<1
ethoprop			nd	0.15	86	<1
fonofos	0.67	0.13	100	0.15	113	<1
α-HCH			nd	0.10	nq	<1
γ-HCH			nd	0.20	112	<1
malathion	4.60	0.23	100	0.25	34	<1
methyl parathion	0.85	0.07	80	0.30	120	<1
parathion			nd	0.20	88	<1
cis-permethrin			nd	0.25	85	<1
phorate	0.13	0.00	10	0.10	82	<1
propargite I & II			nd	0.65	12	<1
terbufos			nd	0.65	108	<1

[a] nd, not detected; nq, not quantifiable; ns, not spiked. [b] Estimated reporting level based on 100 m³ volume. [c] Total recovery from 310 m³ PUF collection efficiency test. [d] % breakthrough = (mass back PUF/mass front PUF) × 100, based on PUF collection efficiency test. [e] Concentrations might be biased low due to PUF breakthrough. [f] 6-Amino-2-chloro-isopropylamino-*s*-triazine. [g] Recognized GC performance problems (*10*). [h] Method performance unknown. [i] Atrazine not detected on back PUF.

4 sample (116 m³), migration into the second PUF was 14% for trifluralin and 94% for molinate. These breakthrough results suggest complete collection of trifluralin by the two PUF plugs for this sample but indicate that some loss of molinate was possible. No trifluralin or molinate was detected in the June 10 sample (22 m³) upstream of RM 1772. High molinate and possibly trifluralin values for the other samples, however, may represent minimum concentrations as a result of incomplete collection by the PUF. No other compounds were detected in the back PUF plugs of these two samples.

Recoveries obtained from the 1995 collection efficiency test for other compounds, such as malathion, metolachlor, cyanazine, napronamide, propargite, and terbacil, also were low (<60%, Table 1) but not because of incomplete collection by the PUF or inadequate recoveries during sample preparation steps. For the organophosphorus compounds, it is possible that the oxons were being formed. Aston and Seiber (*12*) observed considerable amounts of chlorpyrifos oxon and methidathion oxon in air samples from Sacramento Valley and the Sierra Nevada Mountains. Transformation of other analytes may have occurred as well.

Overview of Pesticide Detections. Twenty-five of the 45 pesticides and transformation products analyzed for (Table 1) were detected in the air over the Mississippi River during the 10-day cruise. Metolachlor, metribuzin, chlorpyrifos, diazinon, fonofos, and malathion were detected in every sample. Alachlor, methyl parathion, pendimethalin, and trifluralin were detected in 80−90% of the samples. Six compounds were detected in 30−70% of the samples, and

TABLE 2. Sampling Interval, Sample Air Volume, and Air Concentration (ng/m^3) for Herbicides and Insecticides Detected along the Mississippi River[a]

sample day, June 1994	1	2	3	4	5	6	7	8	9	10
start RM	88.5	298	496	677	874	1044	1214	1394	1590	1772
stop RM	280	495	677	851	1043	1214	1393	1590	1771	1801
av air temp (°C)	na	24.8	26.0	25.3	23.6	25.3	23.6	15.11	18.1	25.1
(standard deviation)		(2.0)	(2.7)	(1.8)	(2.5)	(3.3)	(6.6)	(3.7)	(4.3)	(5.1)
air vol (m^3)	61.2	65.4	98.0	116	101	111	90.5	120	111	22.0
alachlor	nd	nd	0.10	2.8	8.8	2.9	1.7	1.8	1.4	0.91
atrazine	nd	1.1	nd	0.83	1.1	2.3	2.8	2.0	2.6	nd
butylate[b]	nd	nd	nd	nd	0.44	nd	nd	nd	nd	nd
CIAT	nd	nd	nd	0.07	0.30	0.50	0.41	0.13	0.14	nd
DCPA	nd	nd	nd	0.33	0.08	0.27	0.08	0.07	0.05	nd
DEF[c]	nd	nd	nd	0.04	nd	nd	nd	nd	nd	nd
2,6-diethylaniline[b]	nd	nd	nd	nd	0.05	nd	nd	nd	nd	0.40
EPTC[b]	nd	nd	nd	nd	nd	nd	nd	0.17	0.12	1.5
ethalfluralin	nd	nd	0.19	nd	nd	nd	nd	nd	nd	nd
metolachlor	2.1	0.58	1.3	5.6	4.5	1.9	0.97	1.1	0.54	0.45
metribuzin	6.6	5.4	2.2	2.2	3.8	11	11	5.3	20	16
molinate[b]	nd	3.1	2.4	0.31	1.29	nd	nd	nd	nd	nd
pendimethalin	1.6	nd	1.6	3.2	2.9	2.1	0.84	0.83	0.71	nd
propachlor	nd	nd	nd	nd	nd	nd	0.19	nd	nd	nd
propanil	nd	nd	13	nd	nd	nd	nd	nd	nd	nd
thiobencarb	nd	nd	7.1	0.48	0.85	0.62	nd	nd	nd	nd
trifluralin	0.75	12	80	78	67	2.8	2.0	0.23	0.90	nd
chlorpyrifos	0.80	0.17	0.12	0.22	0.20	1.6	1.1	0.43	0.18	0.35
p,p′-DDE	nd	nd	1.6	0.40	nd	nd	nd	nd	nd	nd
diazinon	0.36	0.07	0.06	0.11	0.09	0.16	0.05	0.05	0.04	0.19
dieldrin	nd	nd	nd	nd	nd	nd	0.64	nd	nd	nd
fonofos	0.09	0.10	0.04	0.07	0.11	0.18	0.47	0.15	0.59	0.67
malathion	4.6	0.22	0.17	0.54	0.22	0.26	0.15	0.23	0.14	1.0
methyl parathion	nd	0.67	3.4	0.85	0.06	0.08	0.06	nd	0.05	0.24
phorate	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.13

[a] na, not available; nd, not detected; RM, river mile. [b] Concentrations might be biased low due to PUF breakthrough. [c] Method performance unknown.

nine others were detected in at least one sample. The observed concentrations for 2,6-diethylanaline, butylate, and EPTC could only be used as an indication of presence in the air because of the poor PUF collection efficiency for these compounds.

In the 10 states bordering the Mississippi River, 140 different herbicides and insecticides were reportedly used (*3*)—an average of 84 (54 herbicides and 30 insecticides) per state. The 10 most frequently used pesticides in the 10 state area were all herbicides—cyanazine, metolachlor, atrazine, acetochlor, pendimethalin, trifluralin, 2,4-D, alachlor, EPTC, and propanil. Five of the method analytes (benfluralin, dieldrin, prometon, pronamide, and tebuthiuron) had no reported use in the 10-state area and were not detected in any sample. Three analytes were pesticide transformation products and were detected in at least 20% of the samples.

Regional trends were observed for many of the compounds detected. As an example, molinate and thiobencarb, both herbicides used only in rice production, were detected only in the lower river (below RM 1200). Of the states bordering the Mississippi River, only Louisiana, Mississippi, Arkansas, and Missouri grow rice. The heaviest molinate use (kg of active ingredient applied) was reported in Louisiana and Arkansas, and the heaviest thiobencarb use (kg of active ingredient applied) was reported in Arkansas and Missouri (*3*). The observed occurrence and air concentrations of these rice herbicides corresponded reasonably well to their statewide use patterns (Figure 2a) with the highest concentrations occurring between RM 298 and RM 677 (just north of Baton Rouge, LA, at RM 230, to near Helena, AR, at RM 665). The detected air concentrations ranged from 0.31 to 3.06 ng/m^3 for molinate and from 0.48 to 7.14 ng/m^3 for thiobencarb (Figure 2b). In contrast, the herbicide EPTC is used in the production of a variety of crops in six states bordering the Mississippi River (Figure 3a), but primarily on corn, alfalfa, and potatoes in Minnesota, Iowa, Illinois, and Wisconsin (*3*). EPTC detections in air (Figure 3b) did not begin until RM 1394 (0.17 ng/m^3) and were highest near Minneapolis and St. Paul, MN (1.50 ng/m^3). The highest observed EPTC air concentration occurred during the last leg of the cruise, which was also the shortest (29 RM and 22 m^3 of air sampled. This concentration is probably a more accurate representation of the actual EPTC air concentrations in this segment of the river because the lower volume of air processed resulted in no EPTC detected in the second PUF. The relation between regional trends in occurrence, air concentrations, and statewide use were seen for a number of pesticides, including atrazine, chlorpyrifos, fonofos, and methyl parathion.

Herbicide Detections. Herbicides were the dominant pesticide type detected in air during the cruise. Fifteen of 25 herbicides and 2 herbicide transformation products that were analyzed for were detected (Table 2). Metribuzin and metolachlor were detected in every sample, and alachlor, atrazine, pendimethalin, and trifluralin were detected in 70% or more of the samples. Eight other herbicides were detected in 50% or more of the samples. CIAT (6-amino-2-chloro-isopropylamino-*s*-triazine), a possible transformation product of atrazine (*13*), was detected in 60% of the samples at concentrations generally about 10 times less than the corresponding atrazine concentrations. Diethylaniline, a transformation product of alachlor, was found in only 20% of the samples. This low detection frequency was most likely due to the poor collection efficiency of this compound on the PUF.

As noted above, the concentrations of a number of the herbicides detected in air correlated well with their statewide agricultural use. Others did not. One compound that did not correlate well was trifluralin. Trifluralin is used on a wide variety of crops in all states along the Mississippi River as well as in a variety of urban settings as a nonselective

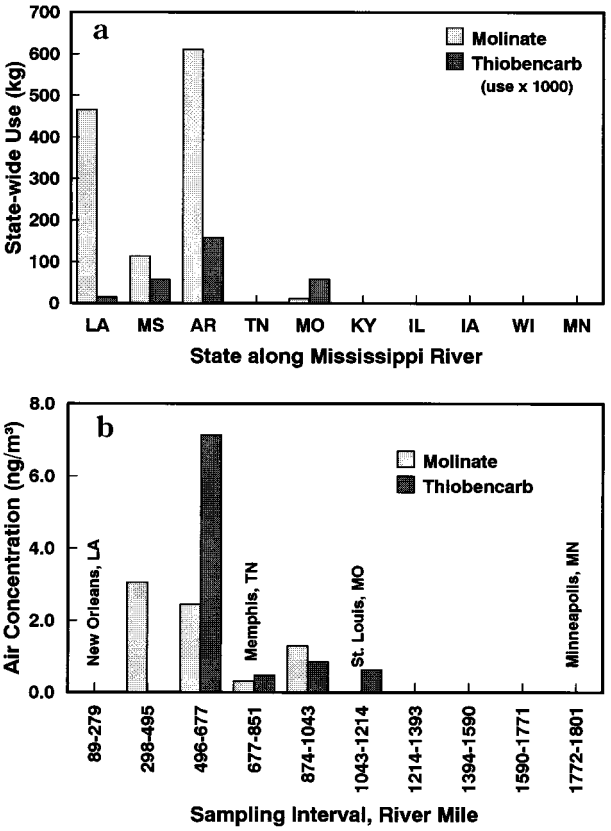

FIGURE 2. (a) 1992 statewide use of molinate and thiobencarb for the 10 states bordering the Mississippi River (*3*), and (b) observed air concentrations per sampling interval along the river.

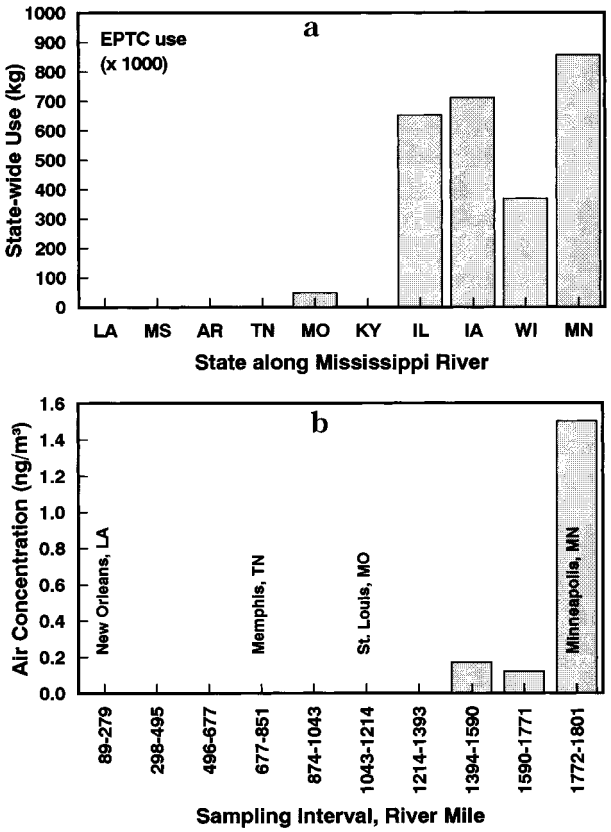

FIGURE 3. (a) 1992 statewide use of EPTC for the 10 states bordering the Mississippi River (*3*), and (b) the observed air concentrations per sampling interval along the river.

herbicide. Its primary agricultural use is on soybeans, cotton, and wheat. Trifluralin is a preplant or pre-emergence herbicide that generally is incorporated 5−7 cm into the soil, but it is also used postemergence in some crops. In cotton production, trifluralin can be applied directly to soil without incorporation between the rows and beneath the emerged plant (*14*). Statewide use of trifluralin varied northward along the river and was highest in Iowa, Minnesota, Arkansas, Illinois, and Mississippi (*3*). The highest measured trifluralin concentrations in air occurred between Greenville, MS (RM 540) and Cairo, IL (RM 960), yet only very low levels were detected north of St. Louis, Mo (RM 1134).

To investigate how pesticide use along the river may be influencing the observed air concentrations, pesticide use per hectare of cropland was compiled within an area of 40 km (25 mi) on either side along the length of the river. We felt that the pesticide use activities within this 40-km zone would be representative of short- to medium-range atmospheric transport of the airborne pesticides. When this compilation was done, a different use pattern emerged. Figure 4 shows trifluralin use on cropland in the 10 states bordering the Mississippi River with a 40-km zone marked on either side of the river. The graph also shows the measured air concentrations for the sampling RM intervals. Trifluralin cropland use by county along the 40-km zone clearly shows that trifluralin is extensively used along the lower portion of the river, which coincided with the highest air concentrations. In the upper river, the highest use areas generally were further inland, and very little trifluralin was measured in the air. The measured trifluralin concentrations in air ranged from 0.23 to 80 ng/m^3 and were generally 1 or more orders of magnitude higher than any other pesticide detected throughout the cruise.

Trifluralin has a very short atmospheric half-life, on the order of minutes depending on the time of year and latitude (*15*, *16*). The high air concentrations measured throughout the lower river suggest that trifluralin was being applied locally. The much lower trifluralin detections in the upper river suggest that the use period was over or that applications were being made further inland, and that the airborne residues were chemically transformed, dispersed, and diluted before reaching the sampling point.

Grover et al. (*17*, *18*) detected the highest trifluralin air concentration (13−63 ng/m^3) during application periods in Melfort, SK, with the lowest concentrations (<20 ng/m^3) occurring after the peak application periods. The trifluralin air concentrations measured during the peak application periods in Melfort, SK, are comparable to those measured along the lower Mississippi River. Hoff et al. (*19*) reported maximum trifluralin concentrations of more than 3.4 ng/m^3 and an average monthly concentration of about 1.3 ng/m^3 in June 1989 at Egbert, ON, a rural area north of Toronto. They did not report if any trifluralin was being used in the area or distances to any potential application areas. The levels measured during the postapplication time periods in Melfort, SK, and during the summer months in Egbert, ON, are comparable to those measured along the upper Mississippi River. Hoff et al. (*19*) suggested that their observed trifluralin air concentrations were a result of long-range transport from western Canada (Saskatchewan) where it is heavily used.

The pesticide use maps presented in this paper are based on pesticide use rates compiled by the National Center for Food and Agricultural Policy (NCFAP) (*3*) from pesticide use information collected by State and Federal agencies over a 4-year period (1990−1993 and 1995) and on crop acreage data obtained from the 1992 Census of Agriculture (*20*). There are three key limitations to this information: (i) State use coefficients represent an average for the entire state and,

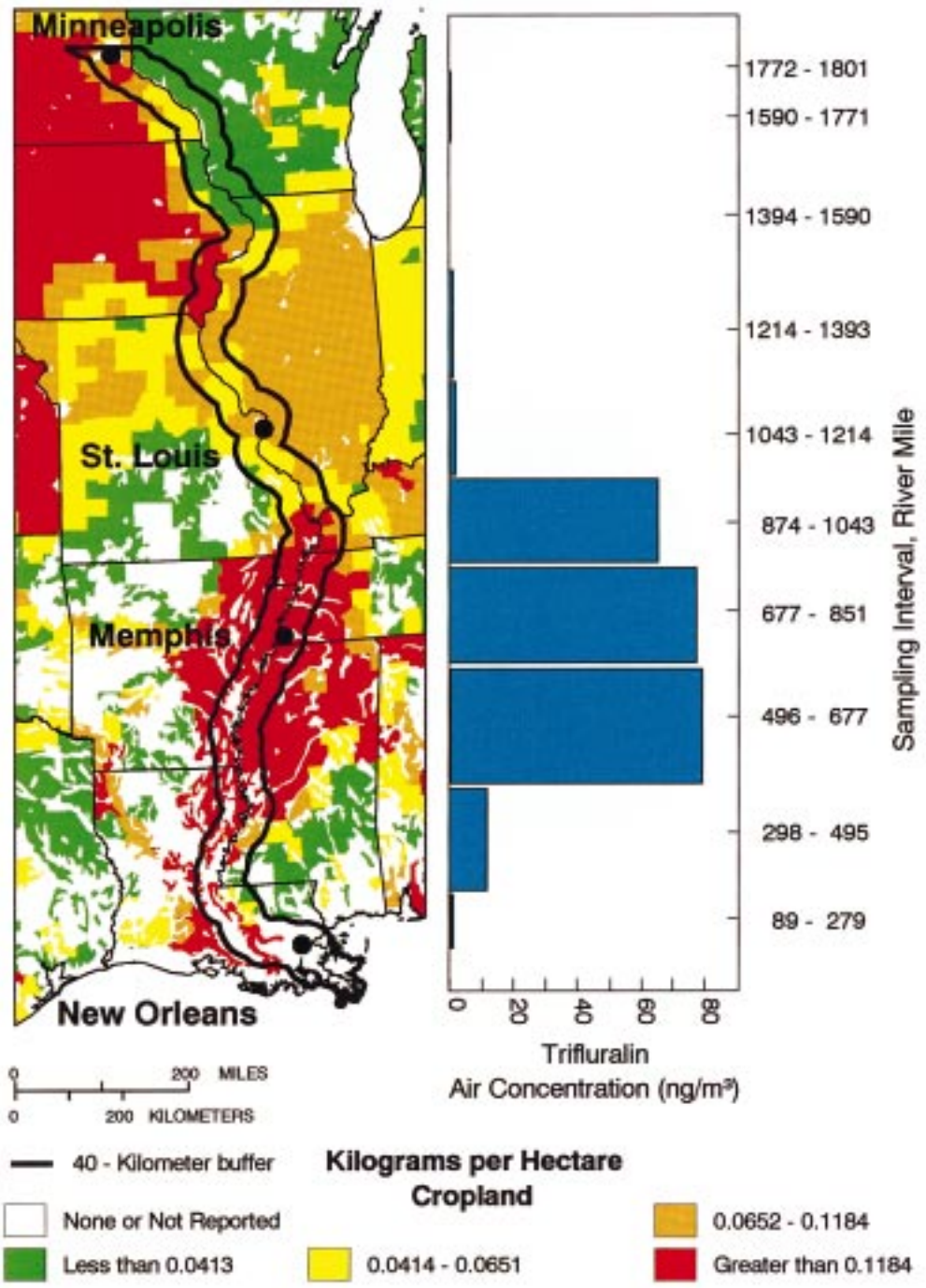

FIGURE 4. 1992 statewide use of trifluralin for the 10 states bordering the Mississippi River (*3, 20*) showing a 40-km zone on both sides of the river, and the observed air concentrations per sampling interval along the river.

consequently, do not reflect the local variability of pesticide management practices found within many states and counties. (ii) The county-level acreage data used to calculate county use are based on the 1992 Census of Agriculture and may not represent all crop acreage because of Census nondisclosure rules that prohibit the Census from publishing information that would disclose the operations of any individual farm. As a result, for counties with fewer than 10 farms reporting acreage for a specific crop, the Census will not publish a county estimate. (iii) Estimates of pesticides applied to pasture represent only the pasture land reported in the Census of Agriculture and no other types of pasture uses (i.e., federally owned land used for pasture or grazing). Despite these limitations, the data provide a useful overview of the regional patterns of pesticide use on the basis of the distribution of crops and the associated intensity of use by compound.

The timing of pesticide applications, relative to the sampling event, plays an important role as to whether a pesticide will be detected in air. The planting season usually begins earlier in the year in the southern part of the United States, but nearly all planting of the major crops (corn, cotton, rice, sorghum, soybeans, spring wheat) along the length of the Mississippi River was completed by June 1, 1994 (*21*). Therefore, much of the preplant herbicide spraying should have been completed prior to our air sampling activity.

The air concentrations of metribuzin, alachlor, and metolachlor did not follow any recognizable use patterns,

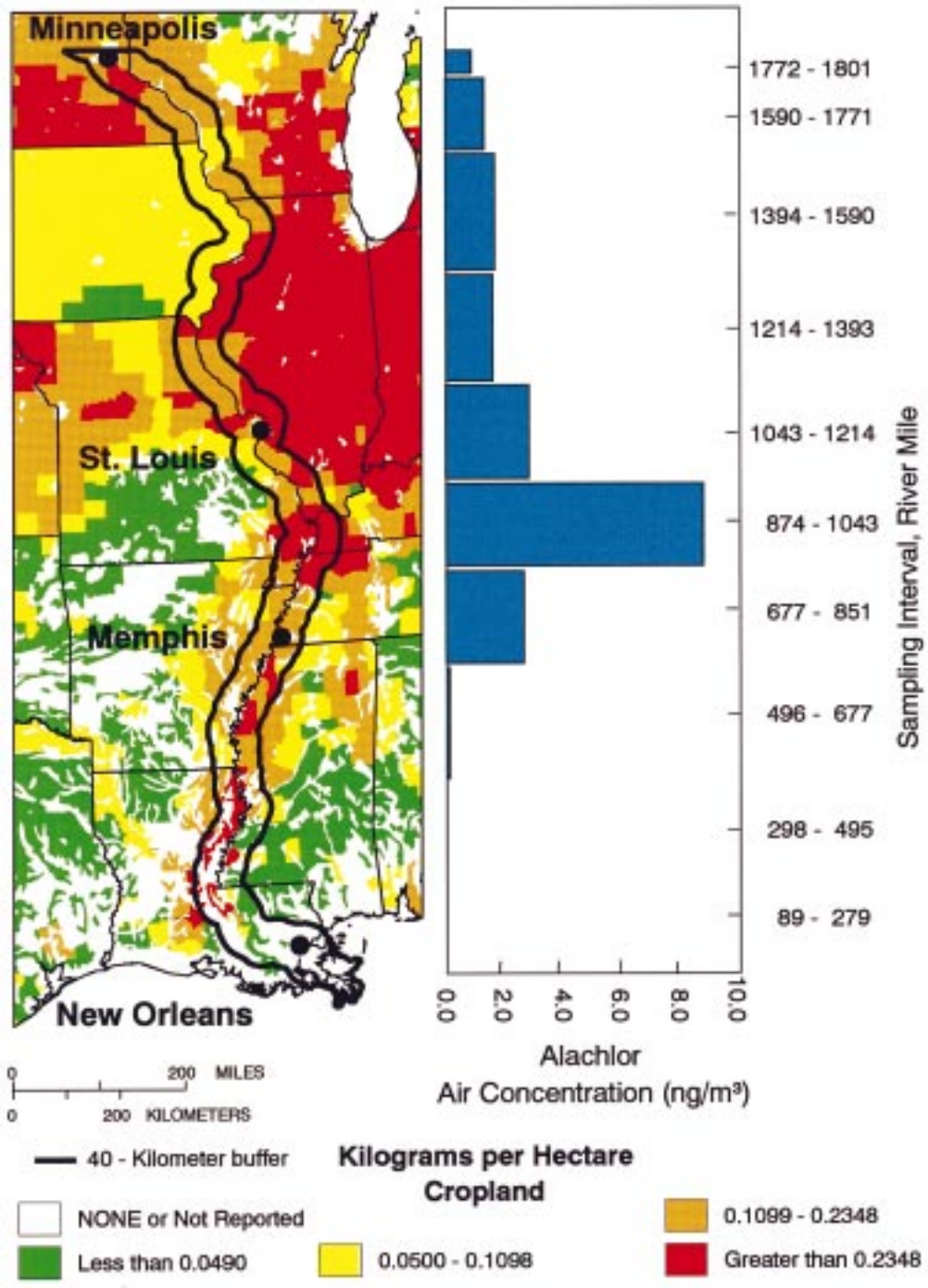

FIGURE 5. 1992 statewide use of alachlor for the 10 states bordering the Mississippi River (*3, 20*) showing a 40-km zone on both sides of the river, and the observed air concentrations per sampling interval along the river.

statewide or by use per hectare of cropland within 40 km of the river. The reported use of metribuzin within 40 km of the river was 5−20 times less than that of alachlor and metolachlor, yet its measured air concentrations were 2.5−5 times greater. The reported near-river use of metribuzin decreased northward, but its measured air concentration increased. Both alachlor and metolachlor use increased northward, while their air concentrations generally decreased. All three of these herbicides are used in a variety of tank mixture combinations and with atrazine on a variety of crops (*22*), yet only atrazine showed any positive correlations between observed air concentrations and statewide use or per hectare of cropland use within 40 km of the river.

The occurrence of metribuzin in air may be partially explained by the active planting of soybeans and its use as a preplant, pre-emergence, as well as a post-emergence herbicide. Soybeans were the only major crop in which active planting was occurring in all states bordering the Mississippi River except Iowa and Wisconsin (*21*).

The majority of alachlor high-use areas are on the east side of the river in Illinois. The highest alachlor air concentration (8.8 ng/m^3), however, occurred between RM 874 and RM 1043 and coincided with high-use areas on both sides of the river (Figure 5). The predominant wind directions for the day preceding and following June 5 were from the east and west, respectively, based on meteorological infor-

mation from the Memphis and St. Louis airports. If the predominant winds were from a westerly direction, in the upper river, we would expect the air concentrations to be lower than if they were from a predominantly easterly direction based on the reported areas of alachlor use. It is, however, difficult to make any conclusions as to the source of the airborne pesticide residues based on wind direction because of the variability of the meteorological data and the lack of spatial coverage.

Both alachlor and metolachlor were detected in Maryland air and rain by Glotfelty et al. (*23*). These two compounds exhibited pronounced, short-lived concentration maxima corresponding to the local planting of corn and conventional till and no-till soybeans. They concluded that both alachlor and metolachlor were very transient in the atmosphere and persisted no longer than 1−2 days. Foreman (*24*) estimated that these two herbicides do not undergo direct photolysis to any great extent and concluded that other atmospheric chemical transformations such as reactions with oxidants, hydroxyl radicals, nitrate radicals, or hydrolysis may be responsible for their sort-lived atmospheric detections.

Atrazine also was detected in Maryland air and rain by Glotfelty et al. (*23*). The highest concentrations occurred during the local planting season, but atrazine also was detected at low concentrations throughout the rest of the year. These findings and those of others (*25*−*27*) suggest that atrazine is a relatively stable compound in the atmosphere with a reasonably long half-life and is capable of being transported considerable distances. Metribuzin may be similar to atrazine with respect to its atmospheric stability, although we found no data in the literature to support this assumption.

Insecticides. The number of insecticides detected in the air during the cruise was considerably less than the number of herbicides. Only 8 of the 18 insecticides analyzed for and 1 transformation product (*p*,*p*′-DDE) were detected. The low number of insecticide detections in air is a reflection of the low number of insecticides used. The top 10 pesticides used in each of the 10 states were all herbicides, with the exception of methyl parathion, which was ranked number one in Louisiana and Mississippi. The application rates for insecticides are generally lower than those for herbicides, and they are also commonly incorporated into the soil.

The measured air concentrations for the detected insecticides generally followed their statewide and cropland area use within 40 km of the river. The highest air concentrations of diazinon (0.36 ng/m^3) and malathion (4.6 ng/m^3) occurred within the first leg of the cruise, between RM 89 and RM 279, as did one of the highest chlorpyrifos (0.80 ng/m^3) concentrations (Figure 6). Agricultural use of each of these insecticides within the 40-km zone was minimal. This section of the river, however, contains two major metropolitan areas—New Orleans and Baton Rouge, LA. With the exception at Minneapolis, MN, where no malathion was detected, both diazinon and malathion had the highest concentrations in those reaches of the river that included a major metropolitan area such as New Orleans, LA, Memphis, TN, St. Louis, MO, or MN, Minnesota (Figure 6). A similar trend was apparent for chlorpyrifos. The measured high air concentrations of diazinon, malathion, and chlorpyrifos may be indicative of their use in the urban environment, as these three insecticides are used extensively in and around urban homes and gardens (*28*) not only along the Mississippi River Basin but throughout the United States.

Methyl parathion, detected in 80% of the samples, is used extensively throughout Mississippi and along the river in Louisiana and Arkansas, primarily on cotton. It has little, if any, legitimate urban use, and the detected concentrations in air followed its use per hectare of cropland within the 40-km zone of the river. Methyl parathion has recently been

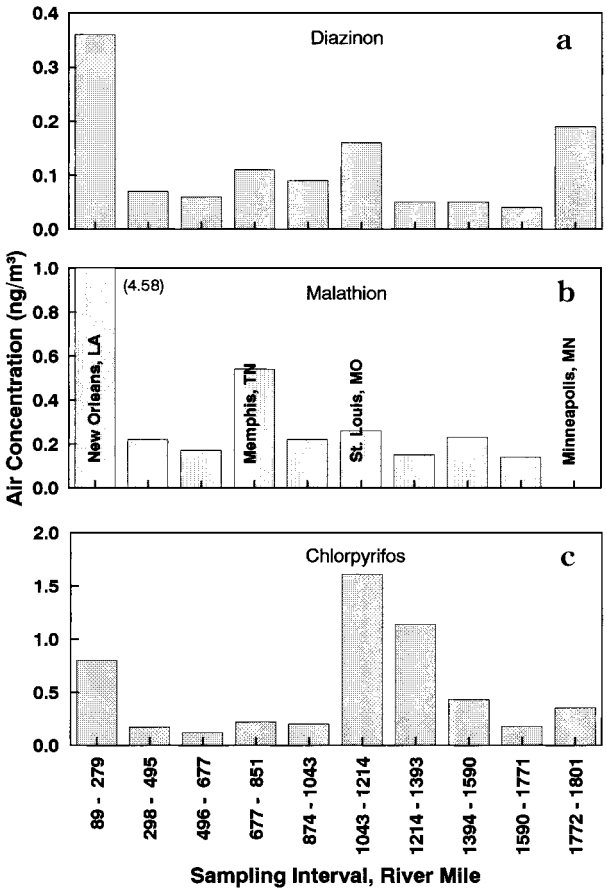

FIGURE 6. Observed air concentrations per sampling interval along the Mississippi River for (a) diazinon, (b) malathion, and (c) chlorpyrifos.

implicated in illegal residential fumigation operations in Mississippi and other states (*29, 30*). This type of nonregulated use also may have contributed to its detection in the air along the river.

The insecticide fonofos was detected in every sample, even in the lower river where no agricultural use was reported for 1992 (Figure 7). Fonofos has no reported urban use, and it is unclear why it was detected in the lower river. Its detection and air concentrations in the upper river did seem to follow its use pattern with the highest concentrations occurring in those areas where its use on cropland within the 40-km zone was the heaviest. The detections in the lower river may reflect the incompleteness of pesticide use data, the nondisclosure rules, or how these data were compiled.

Occurrence Considerations. The occurrence and air concentrations of the pesticides measured in this study represent a snapshot in time. The samples represent both a spatial and a temporal composite of which pesticides were present in the air over the Mississippi River during each sampling period of the 10-day upstream cruise. The vapor pressure of a pesticide will influence its emission rate into the atmosphere. In this study, however, there was no apparent relation between occurrence, observed air concentrations, or application rates and the vapor pressures of the pesticides.

The strongest observed correlation for many of the pesticides detected was between their use on cropland within the 40-km zone of the river and their corresponding air concentration. This relation might have been stronger and included more compounds if the samples had been taken at a stationary location throughout the year. As it was, the

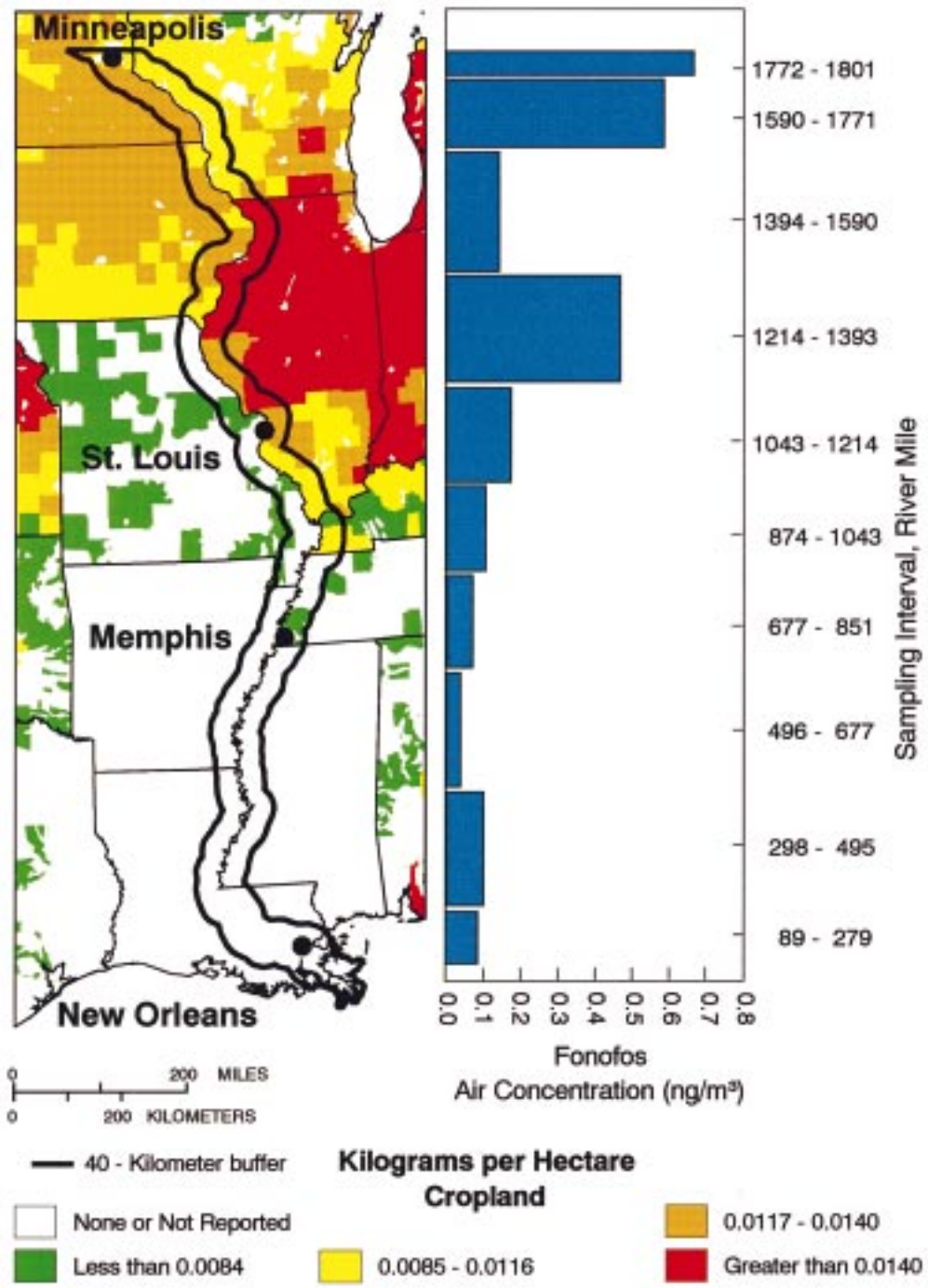

FIGURE 7. 1992 statewide use of fonofos for the 10 states bordering the Mississippi River (*3, 20*) showing a 40-km zone on both sides of the river, and the observed air concentrations per sampling interval along the river.

sampler was moving through different geographic and climatic regions and frequently changing directions with the meandering of the river. Each sample, therefore, reflected an integration of a variety of different cropping patterns and pesticide application activities, rates, and timing.

Many of the reasons why certain pesticides were detected in the air over the Mississippi River also can help explain why other pesticides were not detected: application timing, areal coverage, proximity to the river, analytical detection limits, collection efficiency of the PUF, and inclusion of the compound in the analysis. Variable sample volumes that changed the detection limits were another analytical complication. Those samples that processed a greater volume of air had a greater chance of detecting very low levels of airborne pesticides but are dependent on a favorable collection efficiency of the PUF. Higher sample volumes, however, were usually accompanied by higher background noise contamination that interfered with analyte detection. These contaminants were primarily organic compounds from river barge traffic diesel exhaust and air pollution in general.

Although the number of pesticides detected in air varied, the concentration were generally very low. These findings show that humans as well as forests and other ecosystems are exposed to low concentrations of a variety of herbicides and insecticides in the ambient atmosphere. The occurrence and concentrations usually can be correlated with local use, and high levels of the pesticides in the atmosphere can occur.

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