Environmental Chemistry

PESTICIDES IN MISSISSIPPI AIR AND RAIN: A COMPARISON BETWEEN 1995 AND 2007

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Abstract: A variety of current-use pesticides were determined in weekly composite air and rain samples collected during the 1995 and 2007 growing seasons in the Mississippi Delta (MS, USA) agricultural region. Similar sampling and analytical methods allowed for direct comparison of results. Decreased overall pesticide use in 2007 relative to 1995 generally resulted in decreased detection frequencies in air and rain; observed concentration ranges were similar between years, however, even though the 1995 sampling site was 500 m from active fields whereas the 2007 sampling site was within 3 m of a field. Mean concentrations of detections were sometimes greater in 2007 than in 1995, but the median values were often lower. Seven compounds in 1995 and 5 in 2007 were detected in ≥50% of both air and rain samples. Atrazine, metolachlor, and propanil were detected in ≥50% of the air and rain samples in both years. Glyphosate and its degradation product, aminomethyl-phosphonic acid (AMPA), were detected in ≥75% of air and rain samples in 2007 but were not measured in 1995. The 1995 seasonal wet depositional flux was dominated by methyl parathion (88%) and was >4.5 times the 2007 flux. Total herbicide flux in 2007 was slightly greater than in 1995 and was dominated by glyphosate. Malathion, methyl parathion, and degradation products made up most of the 2007 nonherbicide flux. *Environ Toxicol Chem* 2014;9999:1–11. © 2014 SETAC

Keywords: Pesticides   Air   Rain   Deposition flux

INTRODUCTION

The atmosphere is an important component of the hydrologic cycle that facilitates the widespread movement of pesticides throughout the environment. Pesticides can become airborne through volatilization and wind erosion of particles both during and after their application [1–3]. Volatilization from treated areas is a continuous process and can be a major dissipative route for many pesticides [4–6]. Airborne pesticides can be carried by wind and deposited in unintended areas by dry (gas and particle) and wet (rain and snow) deposition. Rainfall efficiently cleans the atmosphere of suspended particulate matter to which pesticides might be sorbed, and gas-phase pesticides can partition directly into a falling raindrop [7]. 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 [8–10]. Atmospheric deposition of pesticides is most likely to affect the water quality in rivers and streams during runoff events when precipitation and direct surface runoff are oftentimes the major sources of stream flow.

The timing of application, amount applied, and coverage area of each pesticide, as well as the proximity of pesticide applications to the sampling site, all play major roles in whether a pesticide is present in air or rain samples and at what concentration. The results of many studies on pesticide occurrence in the environment show that generally those pesticides detected most frequently and at the highest concentrations are also those that are the most heavily used [11]. Locally high pesticide concentrations in rain and air are very seasonal, are often correlated to local use,

and usually occur during the spring and summer months [12,13]. The physical and chemical properties of each pesticide also play an important role in determining whether a pesticide becomes airborne, whether it then exists primarily in the gaseous or particle phase, and how efficiently rainfall removes it from the atmosphere [14,15].

The occurrence of organochlorine compounds, such as polychlorinated biphenyls, DDT, and others, has been documented in the atmosphere since the 1960s [16–18]. The occurrence of other pesticide classes, such as the triazine, chloroacetanilide, chlorophenoxy acid, and organophosphorus pesticides, has been documented in the United States and Canada as well [14,15,19,20]. In one of the most spatially comprehensive studies of the occurrence of selected pesticides in rain in the United States, Goolsby et al. [21] found that several triazine and chloroacetanilide herbicides were present in rainfall throughout the midwestern and northeastern United States during late spring and summer in 1990 and 1991. The estimated deposition flux for atrazine and alachlor ranged from more than $240\,\mu g/m^2/yr$ in some areas of the Midwest to less than $10\,\mu g/m^2/yr$ for the New England states. Interestingly, estimates of depositional mass for alachlor, atrazine, and metolachlor from rainfall in the Midwest represent less than 1% of the amounts applied for each of these compounds [21–23].

The present study was conducted in northwestern Mississippi (USA) near the Mississippi River within the alluvial plain area referred to as the Delta (Figure 1). The Delta is an agriculturally intensive area that includes more than 80% of the harvested acreage in Mississippi (E. Young, US Department of Agriculture National Agricultural Statistics Service, Little Rock, AR, USA, personal communication) and where a broad variety of pesticides are used. From 1995 to 2007, agriculture underwent many dramatic changes that potentially affected the occurrence of pesticides in the environment. The amount of land used for agricultural production in the Delta did not change much
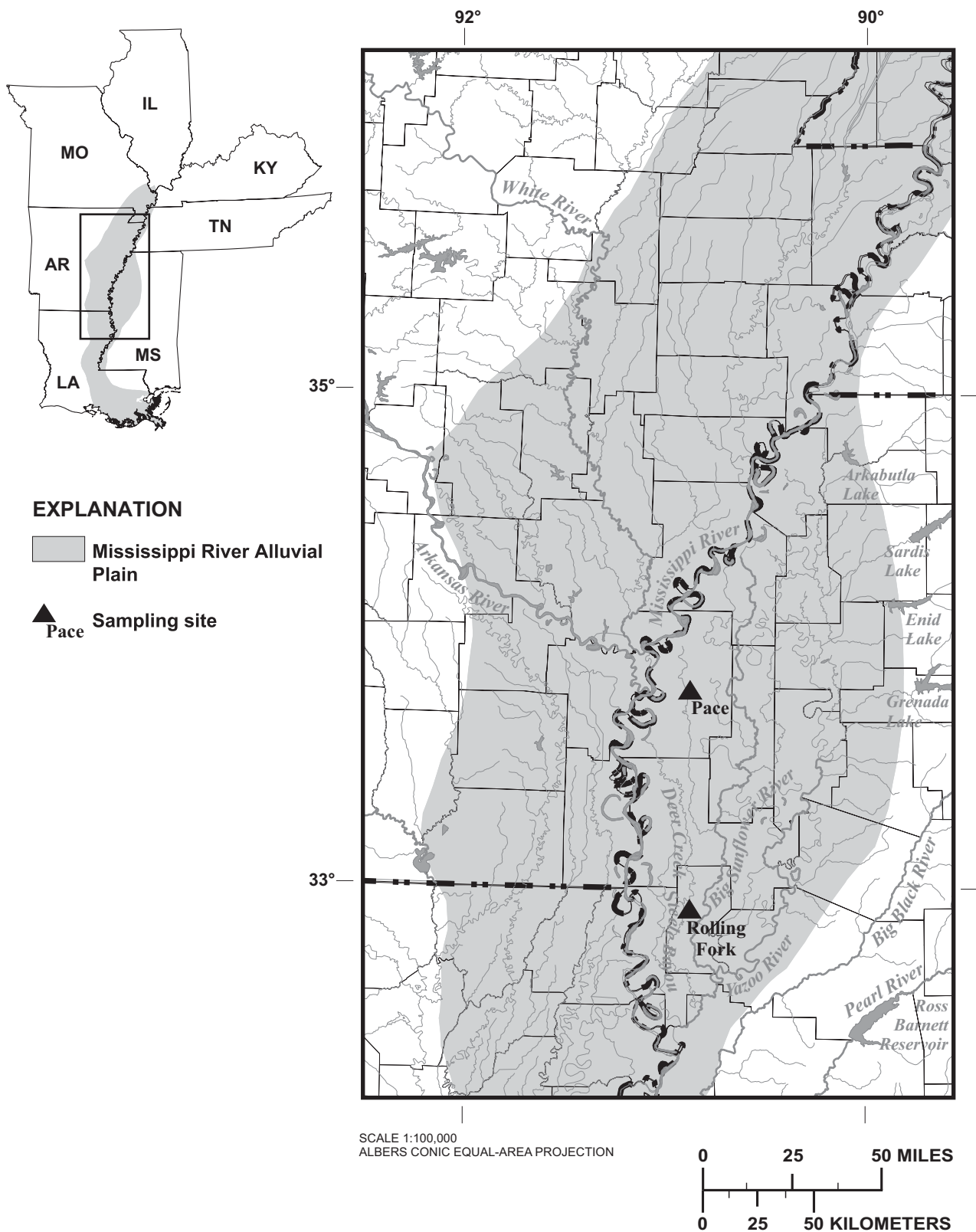

Figure 1. Map showing the sampling locations in the Mississippi Delta agricultural region, USA. The 1995 site was located near the city of Rolling Fork, Mississippi, and the 2007 site was located approximately 100 km north near the city of Pace, Mississippi. [Color figure can be viewed in the online issue which is available at wileyonlinelibrary.com]

between the 2 yr. The same crop types were grown, but the proportions of some crops changed. For example, corn acreage increased from 1.21 million ha in 1995 to 3.76 million ha in 2007, whereas cotton decreased from 5.91 million ha to 2.67

million ha during the same time period (http://quickstats.nass. usda.gov/results/658C3944-93EB-344A-AF98-11D723DEB2CE). Also over this time period, new developments in pest management changed how some pests, both weeds and insects, were

controlled. Voluntary and regulatory decisions resulted in some pesticides being removed from the US market; for example, cyanazine was cancelled in December 1999 (http://www.epa.gov/pesticides/reregistration/status_page_c.htm), molinate was voluntarily phased out by 2009 (http://www.epa.gov/fedrgstr/EPA-PEST/2008/July/Day-30/p17475.htm), and new pesticides, such as the insecticide fipronil, were introduced or more broadly applied.

The largest single change has been the development and introduction of genetically modified crops, particularly corn, cotton, and soybeans. These crops were introduced in the mid-1990s with genetic modifications that made them resistant to specific herbicides or that imparted insecticidal properties within the plant itself, or both. Two of the more common modifications are resistance to glyphosate, which allows this herbicide to be applied directly to the crop for weed control throughout the growing season without harming the crop itself, and incorporation into the plant DNA of gene codes that cause the expression of *Bacillus thuringiensis* (B_t) protein toxins for controlling certain types of insects [24]. Widespread use of these genetically modified crops has caused major changes in the amount and type of pesticides applied to the landscape. Many herbicides previously vital to weed control in the Delta have been replaced by glyphosate [25]. In addition, the use of insecticides, including methyl parathion, in the Delta region has declined because of the increased use of genetically modified crops incorporating B_t insect control, particularly cotton and corn. These changes in pest control, and the resultant potential effects on the environment, may be similar in other areas of the country where genetically modified crops are grown.

The present study documents the occurrence, concentration, and depositional amounts of pesticides in air and rain during the 1995 and 2007 growing seasons in the Mississippi Delta. These data are compared with changes in cropping patterns, chemical use, sampling site location, and proximity to fields, to help understand pesticide movement in the atmosphere.

METHODS

Weekly composite air and rainfall samples were collected during the growing season (March through September) in 1995 and 2007. The sampling sites were located in the Delta area of the lower Mississippi River watershed in west-central Mississippi (Figure 1). The 1995 sampling site was located at the center of a catfish farm pond complex near the town of Rolling Fork, Mississippi, and was approximately 500 m from the nearest agricultural fields [26]. This site was selected to minimize the influence of pesticide applications on nearby cotton, corn, alfalfa, and soybean fields. The 2007 sampling site was located near Pace, Mississippi, approximately 100 km north of the 1995 site and within approximately 3 m of a soybean field in an area surrounded by both soybean and rice fields [27,28]. Detailed descriptions of the methods used to collect the weekly composite air (operationally defined gas and particle phases) and wet-only precipitation samples are given in Foreman et al. [29] and Majewski et al. [30], respectively.

Air and rain sampling for glyphosate and its degradation product aminomethyl-phosphonic acid (AMPA) occurred in 2007 only. The same sampling methods were used for glyphosate as for the other pesticides, but a separate air sampling unit was used because the glyphosate compounds required a different analytical method than the multiresidue one used for the other pesticides and degradation products.

Most rain samples were composites of several precipitation events that occurred during the 7-d sampling periods. If more than 1 L of rainwater was collected during a sampling period, the total volume was recorded, and a 1-L subsample was taken for analysis. The composite rain samples were collected in refrigerated glass carboys. To ensure reasonable analytical results, at least 75 mL of rainfall were required as a minimum sample size. This volume or greater was collected for all samples during both studies. The total amount of rainfall during the sample collection period was recorded by a rain gauge at each site, and the amount of rain from each event ranged from a trace amount to several centimeters (Figure 2). The weekly integrated rainfall samples were collected over the same total period as the air samples. The mass of pesticide deposited by rain for the week (a weekly flux) was calculated by multiplying the concentration ($\mu g/m^3$) by the rainfall amount (m), resulting in a mass/m^2 value. Weekly fluxes were summed to yield a cumulative, seasonal deposition flux.

The analytical methods used in 1995 and 2007 were very similar overall, but there were a few differences, primarily in the number of target analytes and in the applied reporting levels (see below). In 1995, the methods determined 47 analytes (Supplemental Data, Table S1) including 4 degradation products. The 2007 methods determined 76 analytes including 21 degradation products (Supplemental Data, Table S1). A total of 35 of the 1995 analytes were analyzed by the 2007 method; but of the 3 1995 degradation products, only 2-chloro-4-isopropylamino-6-amino-*s*-triazine (CIAT) was analyzed in 2007.

The air samples were analyzed using research methods [29,31] adapted from the multiresidue pesticides in water method [32,33] applied to the rain samples. Air sample components were individually extracted in a Soxhlet apparatus, and resultant extracts were passed through Florisil (1995) or C18 (2007) solid-phase extraction (SPE) columns. Rain samples were passed through C18 SPE columns, and the pesticides were eluted using isopropanol (1995) or ethyl acetate (2007).

Air and rain sample extracts were analyzed by gas chromatography/mass spectrometry (GC/MS) using selected-ion monitoring with overall identical operational parameters between years. For 1995, applied rain reporting levels were set equivalent to the method detection limits (MDLs) estimated using the US Environmental Protection Agency (USEPA) MDL procedure for the applied water method [32]. For 2007, rain reporting levels were set to twice the long-term MDLs, a value typically greater than the USEPA MDL [34]. Indeed, applied reporting levels in 2007 were at least twice those for 1995 (Supplemental Data, Table S1), and likely better reflect true reporting levels for the 1995 rain samples. Air method reporting levels were estimated based on an 850 m^3 average air volume and using twice the corresponding water methods' MDLs [34], or were determined from instrumental detection levels with consideration of method performance. Air and rain values below the MDLs and reporting levels were reported as estimated concentrations as described in Childress et al. [34] and were used in data evaluations. Glyphosate and AMPA in air and rain samples were derivatized and analyzed by online SPE coupled to liquid chromatography/mass spectrometry [27].

Total (gas + particle) air concentrations are discussed except where noted. Although separate gas- and particle-phase air concentrations were determined in both years, an in-depth analysis of the observed gas–particle partitioning is beyond the scope of the present study. The mean concentrations and percentages of detection for each phase are presented in Supplemental Data, Tables S2 and S3. Mean air and rain values
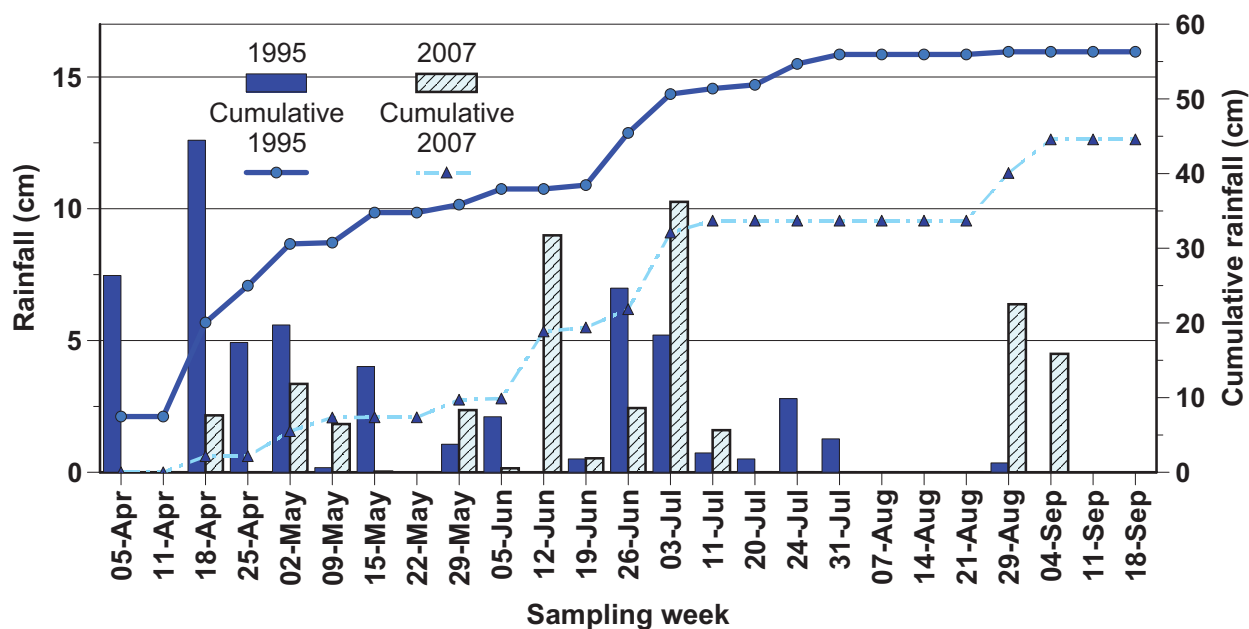
Figure 2. Weekly and cumulative amount of rainfall from April through mid-September at the 1995 and 2007 sampling sites. [Color figure can be viewed in the online issue which is available at wileyonlinelibrary.com]

represent detections only, whereas the median values include the nondetections.

Mississippi statewide pesticide use for 1995 and 2007 was estimated with proprietary and US Department of Agriculture National Agriculture Statistics Service (USDA NASS) data (http://www.pestmanagement.info/nass/) using a method developed by Thelin and Stone [35]. Local pesticide use within a 20-km radius around each sampling site was also estimated from the statewide use data, application rates, and mapped agricultural land within the 20-km radius area, in a manner similar to Nakagaki and Wolock [36]. The local-use estimates were examined to see whether they would provide a better correlation than the statewide estimates between use and the observed occurrences, concentrations, and deposition fluxes of the detected pesticides.

RESULTS

Rainfall patterns in 1995 and 2007

Figure 2 shows the weekly rainfall amounts and cumulative deposition from April through mid-September for both 1995 and 2007. Approximately 20% more rain fell in 1995 than in 2007. In 1995, the frequency and amounts of rainfall were both greater in the early months (April and May) of the growing season when preplant/pre-emergence herbicides were applied. In 2007, most of the rainfall events occurred in June after most of the herbicide had been applied. Accordingly, detection frequencies, concentrations, and deposition amounts for most herbicides might be expected to be greater in 1995 than in 2007.

Sampling rainfall does not offer the continuous data record of atmospheric pesticide burden that air sampling does, but it does provide a direct measure of the atmospheric occurrence of a pesticide and the amount redeposited back to the earth's surface, including to unintended areas. Sampling rainfall also provides insight into the contribution of wet deposition to pesticide loads observed in runoff and surface waters.

Summary of 1995 observations

In 1995, 32 compounds were detected in the air or the rain (Supplemental Data, Table S2). Of these, 20 were common to

both matrices (Figure 3A). Six were only detected in rain (alachlor, prometon, simazine, linuron, terbacil, and parathion), and 5 others were only detected in air (4,4′-dichlorodiphenyldichloroethylene [DDE], α-hexachlorocyclohexane [αHCH], γ-HCH [lindane], metribuzin, and butylate). Eleven compounds were detected in 50% or more of all the rain or air samples collected in 1995 (Supplemental Data, Table S2). Seven of these (atrazine, metolachlor, molinate, methyl parathion, propanil, pendimethalin, and trifluralin) were detected in both air and rain at ≥50% frequency. The atrazine (and propazine) degradation product CIAT (often called deethylatrazine) was detected in 71% of the air samples but in only 38% of the rain samples. 2-Chloro-6-ethylamino-4-amino-*s*-triazine (CEAT), a degradation product of atrazine, cyanazine, simazine, and terbuthylazine (often called deisopropylatrazine), was detected in 38% of air samples but was not analyzed in rain samples because of poor SPE collection efficiency.

In 100% of the gas-phase and 52% of the particle-phase air samples, DDE was detected, but it was not found in any rain sample. The mean DDE concentration $(0.62 \, ng/m^3)$ was approximately 7 times greater than in ambient air samples from Louisiana (USA) and Texas (USA), but less than samples taken 40 cm above the soil from those states and Alabama (USA) [37]. The occurrence of DDE was indicative of volatilization losses from past use of DDT. Nineteen of the 28 detected parent compounds were reportedly used in Mississippi, and 4 others that were not detected had reported use. Nine pesticides had no reported use but were detected in the air, the rain, or both (Supplemental Data, Table S2).

Summary of 2007 observations

In 2007, 37 compounds were detected in the air or rain samples (Supplemental Data, Table S3). As was the case in 1995, 20 of these were present in both air and rain (Figure 3B). Four compounds were detected only in rain (the oxygen analog of methyl parathion, acetochlor, dichlorvos, and prometryn), and 13 compounds were detected only in air. Fourteen compounds were detected in 50% or more of the samples, but only 5 of these (atrazine, glyphosate, AMPA, metolachlor/*S*-metolachlor, and
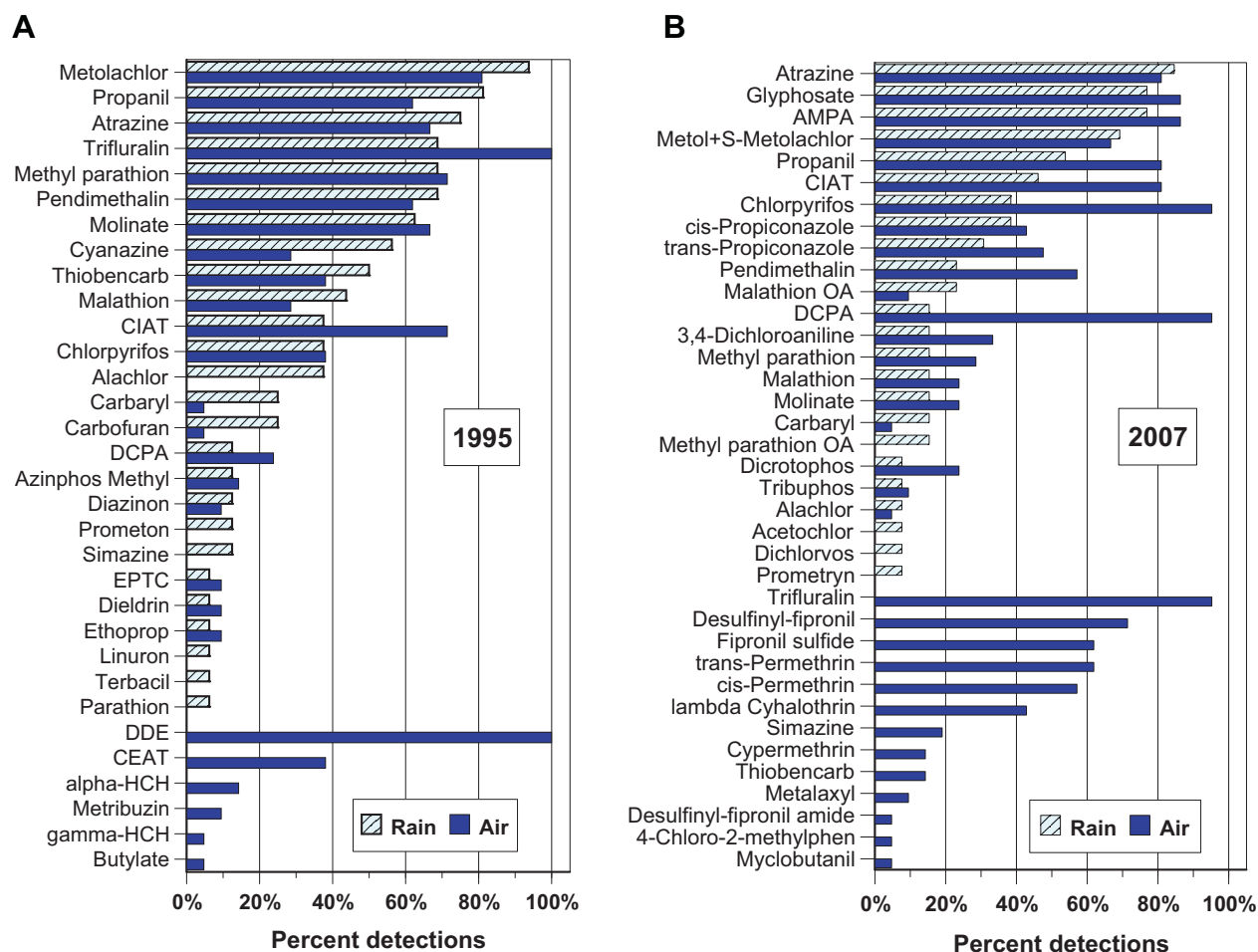
Figure 3. Detection frequencies for compounds detected in air or rain in 1995 (**A**) and 2007 (**B**). CIAT = 2-chloro-4-isopropylamino-6-amino-s-triazine; DCPA = dimethyl tetrachloroterephthalate; EPTC = S-ethyl dipropylthiocarbamate; DDE = 4,4'-dichlorodiphenyldichloroethylene; CEAT = 2-Chloro-6-ethylamino-4-amino-s-triazine; HCH = hexachlorocyclohexane; AMPA = aminomethyl-phosphonic acid; OA = oxygen analog. [Color figure can be viewed in the online issue which is available at wileyonlinelibrary.com]

propanil) were detected in 50% or more of the rain samples (Supplemental Data, Table S3). Of the 27 parent pesticides detected, 19 had reported statewide use, and 4 others that were analyzed for had reported use but were not detected. Seven had no reported use but were detected in the air, rain, or both (Supplemental Data, Table S3). Cyanazine, which was detected in 29% of air and 56% of rain samples in 1995, was not detected in any 2007 air or rain samples, a clear reflection of its use cancelation in 1999. Molinate was also detected in both air and rain in 2007 even though its voluntary phase-out began 4 yr earlier. These detections were possibly the result of unreported use of stored molinate reserves.

Six compounds (CEAT, DDE, α-HCH, γ-HCH, linuron, and parathion) were not analyzed for in 2007 because of programmatic changes to the GC/MS target analyte list. A variety of compounds (10 insecticides, 4 herbicides, and 5 fungicides) were added to the 2007 analyses, including the herbicide glyphosate and 1 of its major degradation products (AMPA), the insecticides fipronil and dicrotophos, and the fungicide isomers *cis*- and *trans*-propiconazole. Glyphosate was the predominant new herbicide detected in both air (86%) and rain (77%); *cis*- and *trans*-propiconazole were detected between 30% and 50% in both air and rain. Use of many of these compounds either began or increased dramatically between collection years primarily because of the increased planting of

genetically modified crops or in response to the detection of soybean rust that began in 2005.

DISCUSSION

Seasonal patterns

Pesticide compounds were detected in both air and rain beginning in April 1995 and 2007, coinciding with the planting season. The sampling in 2007, however, started approximately 2 wk later than in 1995 for both matrices.

Herbicides. Herbicides in air and rain were detected primarily in May of both years at nearly equivalent concentrations. Concentrations for many herbicides peaked around mid-May and then declined. By July, concentrations were generally very low or not detectable. Figure 4A and B shows the weekly concentrations in air for 4 of the most frequently detected herbicides (atrazine, metolachlor, pendimethalin, and propanil) in relation to the sum of the other herbicides detected in 1995 and 2007, respectively. Figure 4B includes glyphosate, which was not analyzed in 1995. These 4 (or 5) herbicides were detected in more than 50% of the air samples.

In 1995, the "Other herbicides" category dominated the concentrations for most air samples, with 3 herbicides contributing to the weekly totals most frequently and with the highest concentrations. Trifluralin was detected in every sample,
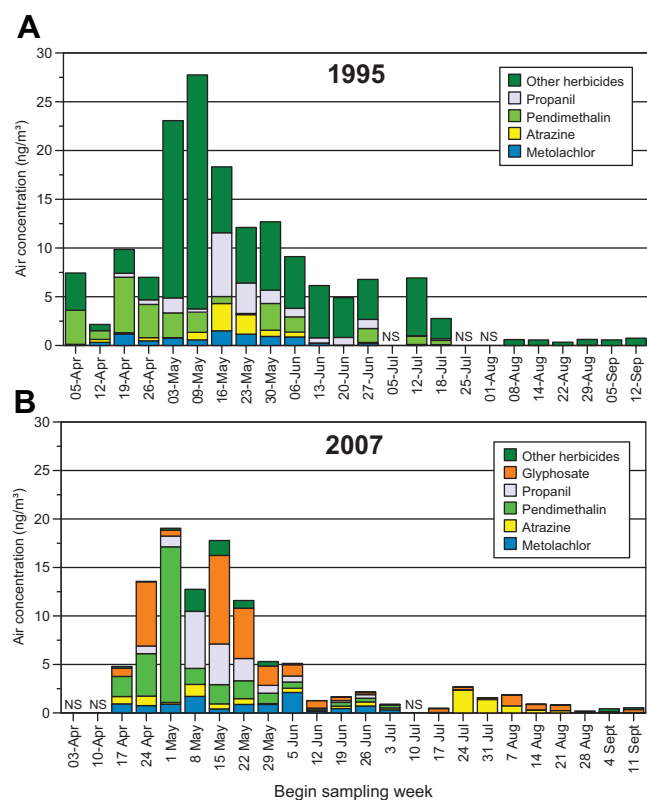
A

B

Figure 4. Weekly air concentrations for select herbicides in 1995 (**A**) and 2007 (**B**). Glyphosate determined in 2007 only. NS = no sample taken.

with median and mean concentrations of detection of 0.81 ng/m^3 and 1.69 ng/m^3, respectively. Molinate (67%; 0.31 ng/m^3 and 1.14 ng/m^3 median and mean, respectively) and thiobencarb (38%; nondetection and 5.91 ng/m^3 median and mean, respectively), both rice herbicides, accounted for much of the rest.

In 2007, the "Other herbicides" category made only minimal contributions to the total weekly observed air concentrations (Figure 4B). Trifluralin was again detected in nearly every sample (95%), but its median and mean concentrations were approximately 20 times less than in 1995 (Supplemental Data, Tables S2 and S3), similar to the nearly 20-fold decrease in reported use within 20 km of the sampling site. No molinate use was reported in 2007, yet it was detected in 24% of the air samples with a mean concentration only slightly less than in 1995. Conversely, thiobencarb use within 20 km of the sampling site was approximately 4 times higher than in 1995, yet the detection frequency (14%) and mean concentration (0.26 ng/m^3) were both much lower than in 2007. The fact that molinate concentrations in 2007 were not substantially different than in 1995 was likely because the 2007 site was near more rice fields than the 1995 site.

Pendimethalin and propanil were detected in nearly every air sample from April through June in both 1995 and 2007 and were usually present at concentrations greater than other compounds detected during the same period. Both herbicides are used on rice, but pendimethalin is also used on field corn, potatoes, cotton, soybeans, tobacco, peanuts, and sunflowers. For pendimethalin, changes in detection frequencies (62%–57%) and mean concentrations (2.00–2.58 ng/m^3) between 1995 and 2007 were not substantial, even though 2007 estimates of statewide and local use were 27 times and 8 times lower, respectively, than in 1995 (Supplemental Data, Tables S2 and S3). In contrast, the propanil detection frequency increased from

57% to 81%, and the mean concentration decreased from 1.36 ng/m^3 to 0.97 ng/m^3. While the reported statewide use decreased by two-thirds, the local use decreased by only 12% (Supplemental Data, Tables S2 and S3). The increased propanil detection frequency is most likely because the 2007 site was nearer to more rice fields than the 1995 site.

Metolachlor detections decreased from 81% in 1995 to 67% in 2007, but the mean concentration increased more than 3 times, from 0.20 ng/m^3 to 0.74 ng/m^3, even though estimated statewide and local use decreased by approximately 30% and more than 75%, respectively. In 1995, the metolachlor formulation contained racemic metolachlor (50% *S*- and *R*-metolachlor enantiomers). Beginning in 1998, use of a new formulation, called *S*-metolachlor, that contained 88% of the more herbicidally active *S*-enantiomer and 12% *R*-enantiomer began displacing use of racemic metolachlor, with the goal of reducing overall metolachlor application rates by 35% (http://www.thecre.com/quality/20020305_SyngentaLet2CRE_reCedar.html). In 2007, applications of racemic and *S*-metolachlor formulations occurred (2007 use and detections shown as Metol + *S*-Metolachlor in Supplemental Data, Table S3). Preferential use of *S*-metolachlor in 2007 might account for a portion of the reduced use of Metol + *S*-Metolachlor compared with 1995. There are no substantial differences in the physical/chemical properties (same vapor pressures, water solubilities, and soil partition coefficients [http://www.epa.gov/opp00001/chem_search/cleared_reviews/csr_PC-108801_28-Feb-02_234.pdf]) between the *R*- and *S*-enantiomers to explain the 67% detection frequency relative to reduced use in 2007. Instead, closer proximity of the 2007 sampling site to application sites might explain both the detection frequency and the higher mean air concentration relative to 1995.

Atrazine use increased substantially statewide from 1995 to 2007 because corn production increased by more than 3-fold, and glyphosate use also increased because genetically modified crops were introduced. While local glyphosate use increased proportionally to statewide use in 2007, local atrazine use decreased by more than 36%. This discrepancy might be the result of the manner in which local use was estimated—as a percentage of statewide use and agricultural acreage within the 20-km radius of the sampling site. It also may be the result of adoption of best management practices that included lower applications rates, the use of different formulations, or a change in weed control protocols for corn with the addition of glyphosate. The change in sampling location also may have contributed to the discrepancy because the distribution of crops receiving atrazine applications may have changed. The 2007 atrazine weekly air concentration pattern was markedly different from the 1995 pattern (Supplemental Data, Figure S1A and B). The first maximum 2007 concentration (1.24 ng/m^3) occurred 1 wk before the higher 1995 maximum (2.80 ng/m^3), but planting was also 3 wk earlier in 2007. The 2007 weekly concentrations over time, however, did not drop off after mid-May as they did in 1995. In late July, there was a 5-wk period during which the air concentrations were very similar in level and pattern to what was observed during the normal application period in May 1995, with a secondary, late-season maximum concentration of 2.36 ng/m^3. There are no known reasons for atrazine applications this late in the growing season. It is possible that these late-season detections resulted from the entrainment of atrazine-bound soil or pulverized plant tissue particles into the lower atmosphere during the harvesting process [38]. Because nearly all of the measured concentration was associated with the gas phase (Supplemental Data, Table S3 and Figure S1B), a likely

source would be the volatilization of atrazine residues on the disturbed soil and pulverized plant tissue during the harvesting process. This late-season atrazine air concentration pattern has not been reported previously.

The 2007 weekly air concentration pattern for glyphosate (Figure 4B) was similar to those of other commonly detected herbicides in both 1995 and 2007 in that the highest concentrations occurred in April and May. However, there were detectable concentrations of glyphosate over the entire growing season, which is consistent with how glyphosate is used on genetically modified crops, including for postemergent weed control throughout the growing season.

Nine herbicides were detected in 50% or more of the rain samples in 1995, and only 3 of these (atrazine, metolachlor, and propanil) were detected in 50% or more of the 2007 rain samples, along with glyphosate (Supplemental Data, Tables S2 and S3). Detection patterns in rain were similar to those seen in corresponding air samples during both years for the more frequently detected herbicides, with the highest concentrations and most frequent rain detections occurring in April and May (Supplemental Data, Figure S2A–C). Both years also had very similar concentration ranges in rain even though detection frequencies and statewide and local use were generally lower in 2007.

Several compounds with no reported use in Mississippi were detected in air, rain, or both in 1995 or 2007. One is the herbicide dimethyl tetrachloroterephthalate (DCPA), which was detected in air (24% in 1995; 95% in 2007) and rain ($\leq$15% both years) at very low concentrations (Supplemental Data, Tables S2 and S3). The combination of low or no use, variable detection frequencies, and very low concentrations might be an indicator of regional and long-range transport of pesticides into the study area, as observed by others for DCPA [39,40]. The presence of DCPA in most air samples in 2007, coupled with very low concentrations, might also be a result of nonagricultural uses or use on low-acreage specialty crops within the sampling area.

Insecticides. Insecticides generally are not applied prophylactically like the pre-emergence herbicides, but are used as needed to combat specific insect infestations. Insecticide application rates and the overall mass used during a growing season are often considerably less than for most herbicides [11] (Supplemental Data, Tables S2 and S3).

The greatest insecticide air concentrations (Figure 5) during both years occurred later in the growing season than herbicides (Figure 4). Figure 5A shows 1995 weekly air concentrations for the 3 most frequently detected insecticides, and the sum of the other insecticides that were only detected once or twice in air. Methyl parathion was the most frequently detected (71%) insecticide in 1995, and it had the highest air concentrations of any compound during both study years, with a mean concentration of 14.2 ng/m^3. It was heavily used (160 000 kg), primarily on cotton [41] in Mississippi. By 2007, methyl parathion's reported statewide use dropped nearly 20-fold to 7900 kg, and as a result its detection frequency decreased to 29%. The methyl parathion concentrations (Figure 5B) were also considerably lower except during the week of 4 September, which had the greatest measured concentration (25.4 ng/m^3) of any detected compound in 2007 and exceeded all but 2 of the 1995 air concentrations. Excluding this value, the 2007 mean concentration of detections was 0.47 ng/m^3. Most weekly methyl parathion air concentrations were similar to ambient concentrations for California (USA) sites, and the timing of peak concentrations compares well with that previously observed for studies in Stoneville, MS in the 1970s, although our maximum
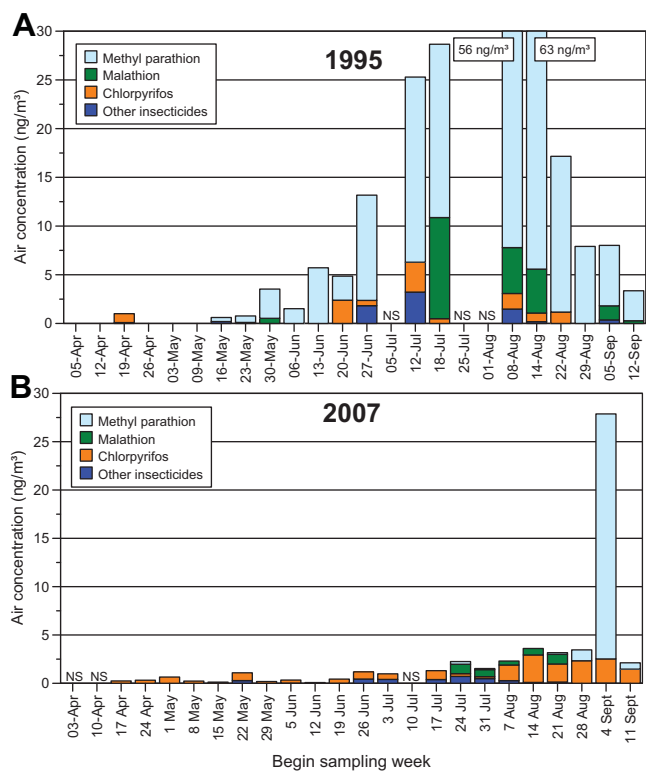

Figure 5. Weekly air concentrations for select insecticides in 1995 (**A**) and 2007 (**B**). NS = no sample taken.

concentrations were 2 times to 100 times less (data summarized in California Environmental Protection Agency [42]). Parathion (ethyl) had the highest reported use of all of the targeted insecticides, but was not detected in air and was only detected once in rain. This is consistent with a short atmospheric lifetime [43]. The parathion oxygen analog degradation product was not measured in the present study.

Chlorpyrifos was the second most frequently detected (38%) insecticide in 1995 air, with a mean concentration of 1.38 ng/m^3. Malathion was detected less frequently (29%) than chlorpyrifos, but its statewide and local uses were greater (Supplemental Data, Table S2), as was its mean concentration (3.64 ng/m^3), with some of the weekly values being similar in magnitude to those of methyl parathion. In 2007, the reported statewide uses for chlorpyrifos and malathion were considerably less than in 1995, with both having no estimated local use. In fact, the reported statewide chlorpyrifos use dropped from over 19 000 kg in 1995 to 2 kg in 2007, yet the detection frequency in air increased to 95%, and its mean air concentration was only slightly less than in 1995. The mean concentration from mid-June to mid-September was 1.23 ng/m^3, nearly equal to that observed during the same time period in 1995. This indicates that the 2007 chlorpyrifos atmospheric burden was likely from a combination of local and regional sources [44]. The apparent discrepancy between the reported 2007 chlorpyrifos use and detection frequency also could be the result of the way that the use was estimated. Thelin and Stone [35] report that both low and high statewide use values were based on harvested crop acreage and were estimated when data were unavailable. The low and high use estimates generally agreed well with other published values for selected pesticides, crops, and years, but not for some compounds. Chlorpyrifos is one compound for which the low estimate of 2 kg (the value reported by the USDA NASS) was very different from the high estimate of >14 000 kg. This illustrates the uncertainty

associated with comparing detection frequencies and observed concentrations with reported use data.

In 2007, the "Other insecticides" category was mainly comprised of 4 pyrethroid insecticides and dicrotophos. Both *cis-* and *trans-*permethrin detections were nearly 60%, with mean concentrations of approximately 0.05 ng/m^3 each. Permethrin, however, had essentially no reported statewide or local use. Of the pyrethroid insecticides, λ-cyhalothrin had the highest reported statewide use (8237 kg) and was detected in 43% of the samples, with a mean concentration of only 0.07 ng/m^3. These low concentrations are consistent with how insecticides in general, and pyrethroid insecticides specifically, are applied with rates on the order of grams per hectare instead of kilograms per hectare used with some herbicides. They are also reflective of the low volatility of pyrethroid insecticides. Dicrotophos and acephate (not measured) were the 2 primary insecticides used on cotton in 2007 that displaced methyl parathion use (http://quickstats.nass.usda.gov/results/D33D31E3-1111-31A9-ADA2-5C075AC0C56F; [45]). The detection frequency of dicrotophos in air (24%) was similar to that of malathion, but its mean concentration was approximately one-third less (0.23 ng/m^3), even though its statewide and local uses were at least 4 times greater than malathion.

The insecticide fipronil was not detected in air, but 2 of its degradation products, fipronil sulfide (62%) and desulfinyl fipronil (71%), were frequently detected at low levels (<0.012 ng/m^3; Supplemental Data, Table S3). Neither fipronil nor any targeted degradation products were detected in rain.

Concentrations in rain generally paralleled their counterparts in air for the most frequently detected insecticides (Supplemental Data, Figure S3A–C). Methyl parathion was detected in 69% of the rain samples (comparable to air). It was detected almost continuously from mid-May through July 1995. It had a high mean concentration (3.04 μg/L) because of 2 very high sample concentrations (Supplemental Data, Figure S3A). The highest concentration in rain (22.9 μg/L; ~7 cm of rainfall), which occurred in late June, did not correspond with the highest air concentrations, which occurred in August. However, the lack of rain over nearly the entire month of August (Figure 2) may have contributed to the high air concentration. Washout and rainout are very efficient mechanisms for removing airborne pesticide residues [14], and greater time between rainfall events leads to greater potential for more pesticides to become airborne through application drift or volatilization or to be sorbed to soil particles entrained into the lower atmosphere by wind. In 2007, methyl parathion was detected only twice in rain, in late August and early September, at concentrations similar to those in 1995. All the other insecticides were detected in less than 40% of the 2007 rain samples. Malathion (Supplemental Data, Figure S3B) was also detected in only 2 samples in 2007, with nearly the same mean concentration as methyl parathion (0.71 μg/L and 0.75 μg/L, respectively). This is consistent with the decrease in reported use. Although the rain detection frequencies of chlorpyrifos (38%) were the same in both years, its 2007 mean concentration (0.005 μg/L) was approximately 3 times less than in 1995 (0.017 μg/L). The 4 pyrethroid insecticides and dicrotophos were not detected in any rain sample.

Seasonal deposition by rain

Detection frequencies and concentrations indicate how often a pesticide occurred in rain and what the potential exposure might be to nontarget organisms, but the significance of these occurrences and concentrations also depends on the actual mass deposited by rainfall. The total seasonal rain deposition or flux

(μg/m^2) for each pesticide and degradation product is given in Supplemental Data, Tables S2 and S3.

The total pesticide flux in 1995 (1981 μg/m^2) was 4.5 times greater than in 2007 (437 μg/m^2). Pesticide deposition was dominated by methyl parathion, which comprised 88% of the total pesticide flux (Figure 6). Herbicides contributed only 11% (210 μg/m^2) of the total pesticide flux in 1995. Nearly all (>98%) the methyl parathion deposition came from only 2 rain events and may have been a result of drift from nearby applications. Calculating an adjusted flux that does not include these 2 outlying values may provide a more realistic assessment of ambient conditions and better show the deposition contributions of the other pesticides.

Under this adjustment, the total insecticide deposition decreases to 64 μg/m^2, 23% of the total deposition. The adjusted methyl parathion contribution (30 μg/m^2) still contributes nearly one-half of the total insecticide deposition. The herbicide contribution to the adjusted total deposition increases to 76%, with propanil and atrazine contributing over one-half (51%) of the total herbicide flux. Pendimethalin, metolachlor, and molinate together account for 33% of the total adjusted herbicide flux, with 11 others contributing the remaining 16%. Carbofuran, which was detected in only one-quarter of the rain samples, accounted for 25% of the adjusted insecticide flux, while chlorpyrifos and malathion accounted for 10%. Although detected only twice, azinphos methyl accounted for 6.5% of the adjusted total insecticide flux, nearly the same as the more commonly detected malathion. The remaining 4 detected insecticides accounted for 5.7% of the adjusted total insecticide flux.

In 2007, herbicides contributed 235 μg/m^2 (54%) to the total pesticide deposition flux, a slight flux increase from 1995. Glyphosate accounted for 55% of the total herbicide flux, which was not surprising considering that more than 2 million kg were applied statewide in 2007, 3 times that of atrazine and approximately one-third of the total reported applications for the other measured herbicides. The same 5 herbicides (propanil, atrazine, metolachlor, pendimethalin, and molinate) that contributed most to the overall herbicide flux in 1995 also contributed the most in 2007. Glyphosate was the exception because it was not analyzed for in 1995. It was likely present in some of the 1995 air and rain samples, but probably at lower concentrations than seen in 2007. Based on the 1995 reported use of glyphosate (147 000 kg statewide and 4751 kg within
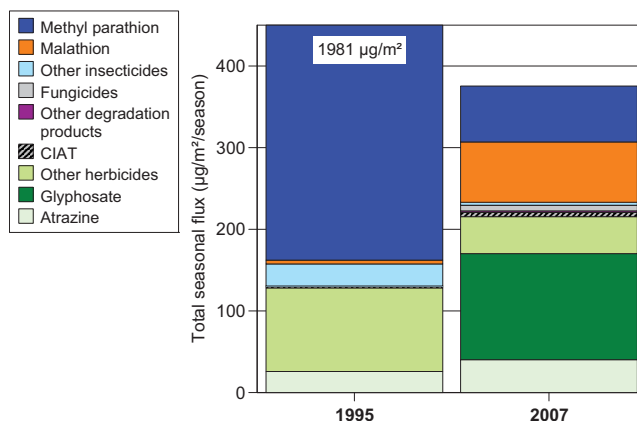

Figure 6. Total seasonal deposition for the detected pesticides and degradation products in 1995 and 2007. CIAT = 2-chloro-4-isopropylamino-6-amino-*s*-triazine.

20 km), and the ratio of the 2007 use-to-flux amount, glyphosate could have added an estimated 3% ($\sim$7 μg/m^2) to the 1995 total herbicide flux.

The introduction of glyphosate-resistant crops resulted in several significant changes in agriculture as well as in herbicide use. In some respects, it has simplified weed management, with glyphosate applications on glyphosate-resistant soybeans almost completely replacing the use of other herbicides [25]. In addition, because glyphosate has minimal, if any, residual herbicide activity, some growers delay applications until several weeks after planting instead of the usual preplant or pre-emergence weed control [25], with the goal of reducing herbicide application costs and eliminating or reducing multiple applications. With the reliance on glyphosate for weed control in glyphosate-resistant crops, some weeds have evolved resistance to glyphosate [24,46,47], and there is now a need to diversify and rotate applications using herbicides with different modes of action [48].

In 2007, the atrazine flux increased by 36% relative to 1995, consistent with its statewide increased use (although the estimated local use of atrazine decreased from 1995 to 2007). The propanil flux was approximately one-quarter of the 1995 value, also consistent with its decreased statewide use. Eleven other herbicides were detected in 2007, but their total flux was less than one-half of that in 1995, with metolachlor, molinate, and pendimethalin contributing 95% of the other herbicides flux.

Insecticides contributed 33% (146 μg/m^2) to the 2007 total pesticide flux. Methyl parathion (47%) and malathion (51%) dominated the insecticide portion, but all of their contributions (and almost one-half of the chlorpyrifos flux) came from just 2 large rainfall events in late August and early September that constituted nearly 25% of the total April–September rainfall (Supplemental Data, Figure S3A–C). Chlorpyrifos, which was detected predominantly in the gas phase in nearly every 2007 air sample, was only detected in 5 rain samples and contributed less than 1% to the total insecticide flux. The low occurrence of chlorpyrifos in rain is not unexpected because its Henry's law constant is approximately 50 times and 500 times greater than that of methyl parathion and malathion, respectively [14]. Other insecticides like carbaryl, dichlorvos, and dicrotophos contributed only 2% to the 2007 total insecticide flux. Fungicides were analyzed only in 2007 and accounted for less than 2% of the total seasonal pesticide flux, all of it from *cis-* and *trans-*propiconazole.

In 1995, 3 degradation products (CIAT, DDE, and α-HCH) were analyzed; but only CIAT was detected in rain, and it accounted for <1% of the total pesticide flux. The most commonly detected degradation products in 2007 were AMPA; CIAT; 3,4-dichloroaniline (a propanil degradation product); the oxygen analogs of chlorpyrifos, malathion, and methyl parathion; and 2 degradation products of fipronil—fipronil sulfide and desulfinyl fipronil. The most frequently detected degradation product in both air (86%) and rain (77%) in 2007 was AMPA, and it had the highest flux relative to the parent pesticide (AMPA flux was $\sim$20% of glyphosate flux). Both malathion oxygen analog and methyl parathion oxygen analog were detected in less than 25% of the rain samples, with fluxes approximately 10% of the parent compounds (Supplemental Data, Table S3). In 46% of the rain samples, CIAT was detected, and its seasonal flux was approximately 13% of its presumed parent, atrazine. Although propanil was detected in more than 50% of the rain samples, its degradation product, 3,4-dichloroaniline, was detected in only 2 samples and contributed approximately 0.5% to the total seasonal flux.

Reasons for observed differences between years. The 1995 sampling site was somewhat removed from active fields, so the concentrations in air and rain would have reflected a well-mixed atmosphere and would have been more indicative of regional concentrations. Nevertheless, the methyl parathion concentrations in both rain and air were the highest measured for any compound during both years. These very high values indicate that use in the surrounding area was high, that off-site drift was excessive, and that it rained shortly after nearby applications. The concentrations of the other detected insecticides and herbicides in 1995 were variable, but none were present in the very high concentrations measured for methyl parathion.

The 2007 sampling site location, adjacent to an active soybean field, may explain why the metolachlor detection frequencies and concentrations in both air and rain were similar to those in 1995 even though the reported use decreased by nearly one-half. The atrazine concentrations were consistent and comparable to those in 1995 even though the use increased nearly 3-fold. These results are indicative of a regional source. The 2007 methyl parathion concentrations were generally much lower than in 1995, but there was 1 relatively high air and rain concentration in early September that may have been from applications near the sampling site. It also may have been from regional transport, as methyl parathion is extensively used on cotton, but there was no cotton grown in the immediate area of the sampling site. The extremely elevated concentrations and flux of methyl parathion in 1995 suggest a substantial local source.

The occurrence of pesticides in rain depends on rainfall. The timing and amount of rain, relative to application, is an important determinant for what, how much, and when a pesticide is detected. Pesticide detection frequencies in rainfall are a function of the number of rainfall events that occur during the study period. The number of rainfall events can either increase or decrease the detection frequency. As an example, if only a few rainfall events occur during the sampling period, but all of them occur during the peak application time, then the detection frequencies could be very high. Conversely, if many rainfall events occur outside application periods, then the detection frequencies could be very low.

Low detection frequencies do not necessarily mean that the resulting concentrations or deposition amounts are insignificant. The last 2 rain events of the 2007 season occurred in August and September and accounted for nearly 25% of the total seasonal rainfall amount. These 2 rain events contributed nearly one-half of the seasonal deposition for chlorpyrifos and all of the deposition for malathion and methyl parathion (Supplemental Data, Figure S3A–C). These results show that 1 or 2 high concentrations in sizable rainfall events can add significantly to the seasonal total depositional loads.

A wide variety of pesticides and their degradation products were detected in both air and rain, and many of the same compounds were detected in both 1995 and 2007. Atrazine, metolachlor, and propanil were the most frequently detected pesticides in both air and rain during both years. The most noticeable change from 1995 to 2007 was the decrease in the annual amounts of pesticides used, with the exception of glyphosate, atrazine, and a few others with minor use. The decrease in overall use generally resulted in decreased detection frequencies in air and rain, but those pesticides with the highest use generally were detected most frequently. The relationship between use and detection frequency was not a simple one, however, and the decrease in detections was generally not proportional to the decrease in use. In some cases, as with

propanil and chlorpyrifos, detections actually increased with a supposed substantial decrease in use. In addition, some pesticides, like DCPA, were detected yet had no reported use while others had reported use but were not detected. Local use estimates helped explain some of these variations, but as with statewide use, they did not consistently explain the variations.

The most compelling explanations for differences in pesticide occurrence and concentration in air and rain from 1995 to 2007 are changes in use that include regulatory restrictions and replacement by other or newer compounds; changes in sampling site location, with different cropping patterns surrounding the site; and variability in the timing, intensity, and amount of rainfall. It is more likely, however, that the observed differences occurred as a result of a combination of these factors. Although detection frequencies and the seasonal median concentrations were lower in 2007, it was difficult to ascertain whether pesticides came from local, regional, or long-range transport. To better understand the ecological and human health implications of the wide variety of pesticides detected in the air and rain, more detailed information on pesticide use is needed, along with more extensive air and rain sampling networks.

SUPPLEMENTAL DATA

Tables S1–S3. (40 KB XLS)
Figures S1–S3. (490 KB PDF)

Disclaimer—Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the US Government.

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