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# Rain Deposition of Pesticides in Coastal Waters of the South Atlantic Bight

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Concentrations of currently used pesticides were measured in surface waters of the South Atlantic Bight immediately after a major storm event that deposited significant rainfall (200–300 mm) in the coastal region. A plume of freshened water (salinity at least 2‰ lower than surrounding 36.2‰ salinity waters) was detected offshore. A concurrent study determined that the freshened plume was the result of rainfall. Concentrations of atrazine, metolachlor, and trifluralin were enriched inside the freshened plume (by a factor of approximately 2–6) as compared to surface waters outside the plume, providing direct evidence of rain deposition of these pesticides. Calculated rain end-member concentrations were higher than local river end-members. Estimated quantities of pesticides deposited in the freshened plume during the 2–3-day event ranged from 130 to 490 kg of atrazine, from 95 to 120 kg of metolachlor, and from 10 to 27 kg of trifluralin. These values represent approximately 4–10%, 3–5%, and 1–3% of the estimated yearly riverine discharge of atrazine, metolachlor, and trifluralin, respectively. Our results indicate that short-duration rain events may produce major pulses in the pesticide input to surface waters of the coastal ocean. Our estimates suggest that this mechanism may represent an important source of pesticides to the coastal ocean. No other pesticide was detected in offshore samples, and only alachlor and simazine were detected in local estuarine waters of Winyah Bay and Charleston Harbor.

## Introduction

The increased use of agricultural pesticides has meant that the mechanisms and magnitude of pesticide movement after their application continues to be an active area of research. Many of the pesticides introduced to replace organochlorine pesticides, such as triazines and organophosphate pesticides, were designed to break down fairly quickly. However, their higher solubilities in water makes them more mobile in the environment. Studies dealing with the movement of pesticides in water have concentrated on measuring runoff from sites of application and transport to groundwater, streams, and estuaries (1, 2). Studies on pesticide movement into

estuarine systems have shown that in general pesticides will be transported via runoff in the dissolved phase and that most transport occurs within a few weeks of application, depending on local precipitation. Kucklick and Bidleman (1), for example, carried out a study in Winyah Bay, SC, to determine concentrations of agricultural pesticides most heavily used in the region. Levels were highest for atrazine, but simazine, alachlor, and malathion were also detected. Concentrations were seasonal, with the highest levels detected in May, which coincides with early spring application. They estimated that the total annual input of atrazine to the bay was roughly 2% (3.1 t) of the amount applied annually to the watershed. Glotfelty et al. (2) carried out a study in Chesapeake Bay in which they determined that about 2–3% of the atrazine and simazine applied to the Wye River watershed was transported via runoff within 2 weeks of application. Little is known, however, regarding the transport of pesticides to offshore areas either via water mass movement or rain washout.

Rainfall is a significant transport and removal mechanism for some airborne agricultural pesticides. Goolsby et al. (3) carried out a detailed study in the midwestern and northeastern United States in which they concluded that the geographical pattern of pesticide deposition in rain provided evidence for long-range transport for some pesticides (e.g., atrazine and alachlor). Struger and Chan (4) recently reported the levels of atrazine and metolachlor in precipitation from the Canadian region of the Great Lakes Basin and concluded, in part, that there is evidence of long-range airborne transport of these pesticides based on their spatial distribution (e.g., detection in remote islands far removed from areas of use). Nations and Hallberg (5) have suggested that seasonal trends in concentrations of pesticides in precipitation parallel the trends in surface water and groundwater. They also suggested that in nontarget areas (areas remote from sites of application) rain washout may be the principal source of pesticides. Their calculations indicated that the total pesticide load associated with precipitation in Iowa watersheds was less than 1% of that applied to cropland; this is in agreement with the figure of approximately 0.6% estimated for atrazine by Hatfield et al. (6). The impact of rain deposition on pesticide transport to the coastal ocean, however, has not been documented due to the inherent logistical limitations on the collection of precipitation samples in the coastal ocean. This would require the placement of collectors either on moorings or some pristine location such as an undeveloped island. Yet this information is important to determine the significance of this pathway as a source of pesticide input to the coastal ocean, especially in sensitive coastal environments. Some studies, for example, have reported high incidences of disease and mortality in coral reefs in tropical coastal waters where pesticides were present (7).

To determine the significance of rain deposition as a source of pesticides to the coastal ocean, it is necessary to distinguish this pathway from riverine input. Thus it is necessary to be able to track the movement of riverine plumes offshore. One method for achieving this is via the use of Ra isotopes, as described in Moore et al. (8) and Moore and Arnold (9). When river and seawater mix in estuarine areas, Ra isotopes are released into the water column via desorption from particulates. This results in enrichment of Ra isotopes in estuarine waters when they are in contact with sediments. The levels of these isotopes and the activity ratios (ARs) of  $^{228}\text{Ra}/^{226}\text{Ra}$  and  $^{224}\text{Ra}/^{223}\text{Ra}$  measured in estuarine areas provide characteristic riverine signatures (8). These signatures can be used as a sensitive tracer of the aging and mixing of

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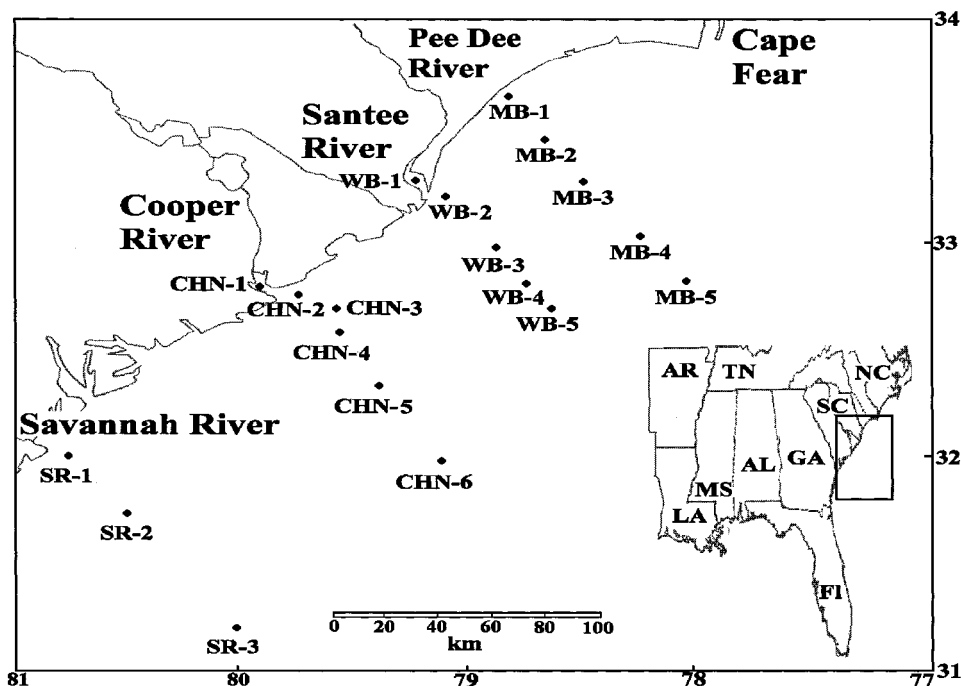


FIGURE 1. Sampling region for cruise of July 7–16, 1994.

waters and of the presence of coastal water in the ocean. As estuarine waters move offshore, the ARs will change because the Ra isotopes decay at different rates (e.g.,  $^{224}\text{Ra}$  has a half-life of 3.6 days while  $^{223}\text{Ra}$  has a half-life of 11 days). Unlike other tracers of surface water that change by evaporation, precipitation, and biological activity, the ARs will change only by radioactive decay or mixing. Ra isotope activities have been coupled with Si concentrations (Si is considered conservative in estuaries (10)) as a means to distinguishing river-derived from rain-derived plumes (8). This method (8) provides an opportunity for estimating the pesticide input associated with rain deposition.

In collaboration with Moore et al. (8), we initiated a study to examine the importance of offshore transport of currently used pesticides in the southeastern coast of the United States. During the course of the study, we sampled surface waters immediately after a major storm event (200–300 mm accumulation) and compared levels of pesticides in waters directly affected by precipitation from the storm event with levels in surface waters less affected or unaffected by the storm event. The goal of this study was to examine the potential of long-distance transport and rain deposition of pesticides to the coastal ocean as a distinct mechanism from input via surface runoff from local sources.

## Experimental Section

**Sampling.** Water samples were collected on July 8–16, 1994, in coastal waters of the South Atlantic Bight (Figure 1). Sampling stations were located along shore-perpendicular transects beginning at Myrtle Beach (MB, July 8–10), Winyah Bay (WB, July 11–13), Charleston Harbor (CHN, July 13–15), and Savannah River (SR, July 16). Water samples for pesticide analysis were collected at 17 offshore stations and inside Charleston Harbor (CHN-1) and Winyah Bay (five stations, mean values represented by WB-1) (Figure 1). Concurrently, samples for Ra isotopes, salinity, and Si analyses were collected for these and many other stations along the transects by Moore et al. (8).

Salinity measurements (8) taken during the cruise indicated the presence of a plume of lower than expected salinity lying offshore that affected the CHN, WB, and MB transects (Figure 2). This offshore freshened plume was determined

to have been the result of rainfall (see Results and Discussion section below and Moore et al. (8)). Temperature and salinity profiles (8) showed that the plume consisted of a continuous, well-mixed layer 5–7 m deep that was at least 2‰ fresher than surrounding surface water. Samples for pesticide analysis were collected from the mixed layer (1–2 m below the surface) to ensure that concentrations of pesticides measured were representative of actual mixed layer concentrations and were not affected by surface microlayer artifacts. Samples were collected on board the RV *Cape Hatteras* by pumping through Teflon-lined tubing into 18-L stainless steel canisters (as in ref 11). Sample volumes ranged from 18 L (near-shore stations) to 76 L (offshore stations). Water samples were then pulled through a 293 mm (1  $\mu\text{m}$  nominal pore size) glass fiber filter (GFF) and then a glass column containing 10 g of XAD-2 resin (11). GFFs were wrapped in aluminum foil and frozen, and the XAD-2 resin was refrigerated until analysis.

**Pesticide Extraction and Analysis.** Pesticides targeted in this study were triazines (atrazine, simazine, cyanazine, and propazine), organophosphate pesticides (malathion, chlorpyrifos, methyl parathion, diazinon, and azinphos-methyl), linuron, carbaryl, carbofuran, trifluralin, metolachlor, and alachlor. These pesticides are used extensively in the southeastern United States.

Pesticides were extracted from GFFs and XAD-2 resin as in Kucklick et al. (11). Hexane extracts were concentrated to 1 mL and separated via column chromatography with Florisil. Florisil chromatography allowed cleanup and separation of pesticides from polycyclic aromatic hydrocarbons, which were also analyzed as part of a different study: A 1 cm i.d. glass column was loaded with 8 g of Florisil (prebaked at 500 °C, deactivated with 200  $\mu\text{L}$  of E-pure water) overlain with approximately 0.5 g of anhydrous sodium sulfate. The column was pre-eluted with 100 mL of 1:1 dichloromethane–hexane, followed by 100 mL of hexane. The sample was loaded on the column and eluted with 100 mL of hexane, then 100 mL of dichloromethane, and finally 100 mL of acetone. Trifluralin and chlorpyrifos were eluted in the dichloromethane fraction; all other pesticides were eluted in the acetone fraction. Some of the acetone fractions from near-shore samples were treated with a Florisil microcolumn cleanup (12) to remove chlo-

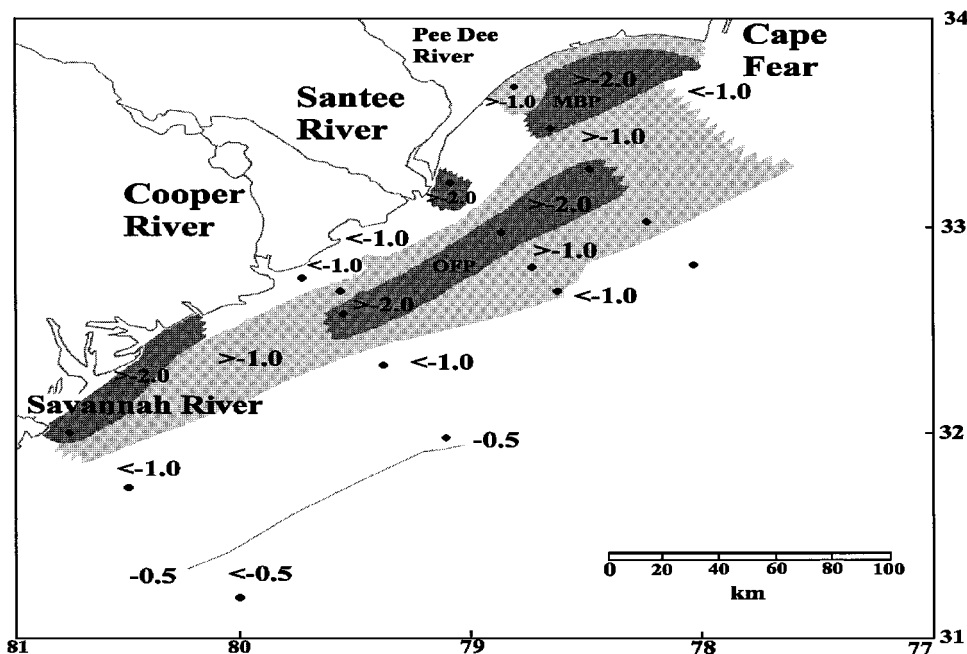


FIGURE 2. Surface distribution of salinity anomaly (measured salinity  $-36.2\text{‰}$ ).

rophyll and other organics that were coeluted along with pesticides (as evidenced by the green color of the eluent). Ethyl acetate eluted pesticides, leaving chlorophyll and other organics on the column.

Acetone and dichloromethane fractions from Florisil chromatography were concentrated to 200  $\mu\text{L}$  and solvent-exchanged into isooctane. Prior to the cruise, we carried out a study in Winyah Bay to determine if mirex and pentachloronitrobenzene (PCNB) were present in surface waters. We did not detect these two pesticides in any of our samples, in agreement with data from Gianessi and Anderson (13, 14), which indicated that they were not used in the region. Consequently, we decided to use mirex and PCNB as internal standards. Previous investigators have used mirex in this region (1). Each sample was spiked to yield a concentration of 10  $\mu\text{g/L}$ . Triazines and organophosphate pesticides were measured by gas chromatography/electron impact mass spectrometry (GC/MS) using a Finnigan 4500 instrument with a 30  $\text{m} \times 0.25 \text{ mm i.d.} \times 0.25 \mu\text{m}$  DB-5 (J & W Scientific Co.) capillary column. Samples were injected at 90  $^{\circ}\text{C}$  splitless. After a 0.1 min hold, the oven was programmed at 10  $^{\circ}\text{C/min}$  to 150  $^{\circ}\text{C}$ , then 5  $^{\circ}\text{C/min}$  to 300  $^{\circ}\text{C}$  with a 15 min hold. Sensitivity was enhanced by operation in the selected ion monitoring mode (SIM). SIM ions targeted were as follows: mirex: 237, 272; PCNB: 265, 295; atrazine: 200, 215; simazine: 186, 201; propazine: 214, 229; cyanazine: 225, 240; carbofuran: 164, 221; methyl parathion: 125, 263; carbaryl: 144, 201; malathion: 173, 285; chlorpyrifos: 314, 351; azinphos-methyl: 132, 160. After GC/MS analysis, samples were diluted to 1 mL, additional mirex and PCNB were added to adjust the concentrations to 10  $\mu\text{g/L}$ , and analysis for trifluralin, linuron, alachlor, and metolachlor was carried out by gas chromatography/electron capture detection (GC/ECD) using a Varian 3700 chromatograph with a 25  $\text{m} \times 0.25 \text{ mm i.d.} \times 0.25 \mu\text{m}$  DB-5 (J & W Scientific Co.) capillary column. Samples were injected at 90  $^{\circ}\text{C}$  splitless (30 s split time). After a 1 min hold, the oven was programmed at 5  $^{\circ}\text{C/min}$  to 300  $^{\circ}\text{C}$  with a 5 min hold. After analysis by GC/ECD, trifluralin was confirmed by GC/MS using ions 248 and 250. Analyses were done in triplicate and concentrations were determined using the internal standards.

**Quality Control for Pesticide Analysis.** Six solvent blanks were measured by adding 500 mL of solvents to clean

volumetric flasks and treating as samples. Ten spikes were measured by adding analytes in acetone to 1 or 2 L of deionized (E-pure) water at concentrations of 100 ng–10  $\mu\text{g/L}$  and treating as samples. Average recoveries for pesticides reported here were as follows: atrazine  $78 \pm 15\%$ , trifluralin  $76 \pm 15\%$ , metolachlor  $82 \pm 16\%$ , alachlor  $78 \pm 12\%$ , and simazine  $80 \pm 15\%$ . Four samples (WB-2, CHN-2, SR-3, and WB-5) were collected with two XAD-2 resin columns in sequence to determine breakthrough values. Results from breakthrough studies were consistent with recovery studies above (approximately 80% recovery for the first column). Concentrations reported in this study were corrected for recoveries.

## Results and Discussion

Figure 1 shows the sampling area and stations in this study. Salinity measurements in the region (which included our sampling stations) indicated an area having a significant salinity anomaly. Figure 2 shows the distribution of salinity anomaly. Values in Figure 2 were calculated relative to offshore salinity (i.e., measured salinity  $-36.2\text{‰}$ ). Figure 2 shows two distinct regions within the sampling area. At the SR transect, the anomalies approach zero moving offshore, as expected with dilution of the riverine signal. Transects starting at CHN, WB, and MB, however, all cross a distinct water mass with salinity anomaly (lower than expected salinity, anomalies  $> -2\text{‰}$ ) lying offshore.

In a concurrent study, Moore et al. (8) investigated this freshened plume to identify the source of freshwater (i.e., rain versus river). Verification of rainwater as the source of the freshening of the plume in question was made by Ra isotope and Si analysis (8). Table 1 summarizes the Ra and Si results, including representative values for the inner shelf and Gulf stream for comparison.

To summarize the arguments of Moore et al. (8) briefly, if one takes the null hypothesis that the freshened plume sampled in this study originated in an estuary and moved offshore with little mixing (as evidenced by the similar salinities between the plume and the estuary mouths), it would contain Ra isotope activities and Si concentrations typical of these estuaries (especially the SR or WB estuaries whose rivers dominate discharge into the SAB). Waters inside the offshore freshened plume, however, were depleted in



TABLE 1. Characteristics of Ra Isotopes and Si in South Atlantic Bight Coastal Waters<sup>a</sup>

water body	salinity (‰)	Si (mM)	<sup>226</sup> Ra (dpm/100 L)	<sup>228</sup> Ra (dpm/100 L)	<sup>223</sup> Ra (dpm/100 L)	<sup>224</sup> Ra (dpm/100 L)	<sup>224</sup> Ra/ <sup>223</sup> Ra AR
estuary mouths	33.4 ± 1.4	7 ± 5	19 ± 3	28 ± 5	3 ± 1	16 ± 6	7 ± 3
inner shelf	35.1 ± 0.6	0–3	17 ± 4	23 ± 8	1.9 ± 0.9	8 ± 4	4.3 ± 1.3
Gulf Stream	36.2 ± 0.1	<0.1	8.9 ± 0.5	5.8 ± 1.3	0.05 ± 0.04	0.01 ± 0.13	<0.5
OFP-MB	33.7	0	14	22	1.4	4.0	1.3
OFP-WB	33.9	0	9	13	0.35	0.45	1.2 ± 0.1
OFP-CHN	33.8	0	11	17	0.65	0.5	<1.0

<sup>a</sup> From Table 1; OFP = offshore freshened plume.

<sup>226</sup>Ra, <sup>228</sup>Ra, and Si and had significantly lower <sup>224</sup>Ra/<sup>223</sup>Ra ARs as compared with estuary mouth values. The low Ra activities and Si concentrations measured inside the plume suggested that the plume did not have a riverine origin when compared with estuarine values.

Depletion of Ra isotopes in the freshened plume is expected when one realizes that rainwater does not contain Ra. Therefore, all the Ra in the plume samples is from dilution of shelf waters by rain. Using as an example shelf water values for <sup>226</sup>Ra (17 dpm/100 L) and multiplying by salinity ratios, the results below are obtained, showing that the plume is indeed depleted in <sup>226</sup>Ra:

	calculated	found (Table 1)
CHN-4	17 × (33.7/35.1) = 16.3	11
WB-3	17 × (33.9/35.1) = 16.4	9
MB-3	17 × (33.7/35.1) = 16.3	14

A second argument by Moore et al. (8) supporting their hypothesis that the offshore freshened plume was not a detached estuarine plume was provided by the observed rate of decay of the plume. If the plume represented a detached estuarine plume, it had to have traveled 30–40 km offshore and several hundred kilometers along shore without significant mixing with surrounding waters and lost half of its initial <sup>226</sup>Ra activity by radioactive decay and all of its Si via biochemical removal (Table 1). Based on the change in <sup>224</sup>Ra/<sup>223</sup>Ra ARs, Moore et al. (8) calculated that the age of the offshore freshened plume was 10–12 days if it had originated in the Savannah River and 13–16 days if it had originated in Winyah Bay (8). However, during the sampling period, the plume was observed to dissipate in 3–6 days. It is unlikely that the plume would move several hundred kilometers and remain essentially intact for about 2 weeks and then dissipate in 3–6 days. Therefore, their conclusion was that the offshore freshened plume was the result of rainfall (8).

On June 30, 1994, a tropical depression formed near 22° N, 85° W. This tropical depression moved westward through the Caribbean, and on July 1 part of this large and disorganized depression organized into Tropical Storm Alberto, which made landfall in Florida, reaching peak intensity on July 3 (15–17). Tropical Storm Alberto moved north and weakened into a depression on July 4. This tropical depression affected the southeastern United States, causing heavy rainfall between July 4 and 7 (15–17). The heaviest rainfall (620 mm) occurred in Americus, GA (17).

Some of the original tropical depression, however, did not organize into Tropical Storm Alberto. Instead, a large cloud mass moved north along the Atlantic Coast of Florida and became a stationary front over the South Carolina coastal region (17). This stationary front resulted in heavy rainfall off the coast of South Carolina, as indicated by images from the Special Sensor Microwave Imager (8). Estimates of total rainfall were 200–300 mm for July 1–4, with higher amounts likely in localized areas (8). This rainfall was responsible for

TABLE 2. Pesticide Concentrations (ng/L)<sup>a</sup>

station	latitude	longitude	salinity (‰)	atrazine	trifluralin	metolachlor
SR-1	31.977°	80.740°	33.9	12.6	3.3	16.7
SR-2	31.716°	80.496°	35.6	5	2.1	10.9
SR-3	31.183°	80.011°	36.2	1	0.1	BD
CHN-1 <sup>b</sup>	32.735°	79.891°	21.4	18.8 (36) <sup>c</sup>	1.1 (3) <sup>c</sup>	17.2 (38) <sup>c</sup>
CHN-2	32.695°	79.765°	33.8	12.3	1	11
CHN-3	32.662°	79.586°	34.9	6.5	0.8	8.9
CHN-4	32.558°	79.596°	33.8	32.3 (502) <sup>d</sup>	1.3 (18) <sup>d</sup>	14.4 (269) <sup>d</sup>
CHN-5	32.339°	79.404°	35.6	6.1	0.7	1
CHN-6	31.973°	79.124°	35.7	5.9	0.1	BD
WB-1 <sup>b</sup>	33.253°	79.208°	16.8	117.0 (222) <sup>c</sup>	2.7 (5) <sup>c</sup>	33.0 (59) <sup>c</sup>
WB-2	33.210°	79.114°	34.6	6	0.3	11.8
WB-3	32.989°	78.889°	33.9	25.1 (839) <sup>d</sup>	1.7 (51) <sup>d</sup>	16.8 (552) <sup>d</sup>
WB-4	32.824°	78.751°	34.7	4.6	1.1	7.9
WB-5	32.770°	78.617°	34.8	4.4	BD	BD
MB-1	33.669°	78.859°	35.2	5.4	BD	13.6
MB-2	33.482°	78.677°	35.8	6	BD	15.6
MB-3	33.293°	78.511°	33.7	12.9	0.5	21.8
MB-4	33.015°	78.234°	35.2	2.1	BD	9.2
MB-5	32.818°	78.058°	36.1	BD	BD	BD

<sup>a</sup> Concentrations are the mean of triplicate analysis and have been adjusted for analytical recoveries. <sup>b</sup> Estuarine stations inside WB and CHN used to estimate river end-members (WB-1 represents mean values of five stations). <sup>c</sup> Values in parentheses represent river end-members extrapolated using these estuarine stations as representative of riverine input. <sup>d</sup> Values in parentheses represent extrapolated rain end-members necessary to yield surface water concentrations at these stations.

the offshore freshened plume detected in our study between July 7 and July 16.

Table 2 shows concentrations of pesticides (dissolved + particulate) measured in this study. Results indicate an area of enrichment associated with the offshore freshened plume. Along the SR transect, where there were no offshore salinity anomalies (Figure 2), all pesticides showed a steady decrease in concentration with increasing distance from the river mouth, indicating dilution of riverborne pesticides with surrounding seawater (Table 2). During the sampling period, heavy runoff in Georgia due to the intense rainfall from Tropical Storm Alberto led to a high flow of the SR. However, this did not lead to any freshened plume offshore (8). Stations CHN-4, WB-3, and MB-3 showed enrichment of atrazine, trifluralin, and metolachlor (Table 2, stations shown in bold lettering, and Figure 3a–c). Stations CHN-4, WB-3, and MB-3 all lie within the freshened plume attributed to precipitation based on salinity, Si, and Ra concentrations (8). Enrichment associated with the plume exceeds near-shore levels (Figure 3a–c).

We believe that the pesticide enrichment seen in this study was due to rain scavenging and deposition of pesticides during the storm event off the coast of South Carolina described previously. The presence of atrazine, trifluralin, and metolachlor in air and precipitation has been well

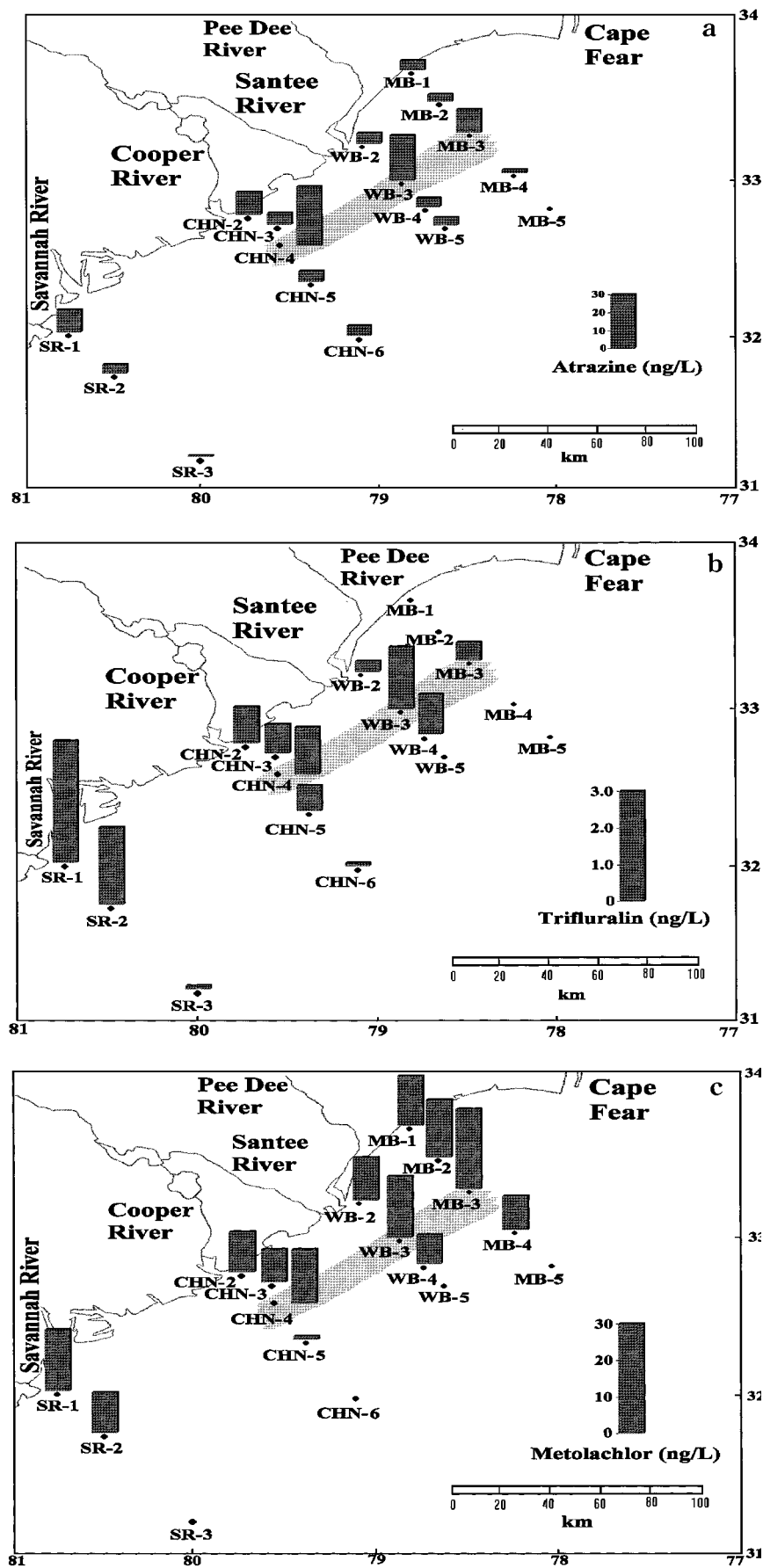


FIGURE 3. (a) Concentrations of atrazine (ng/L) at offshore sampling stations. (b) Concentrations of trifluralin (ng/L) at offshore sampling stations. (c) Concentrations of metolachlor (ng/L) at offshore sampling stations.

documented, especially in areas of high usage (3, 5, 6, 18). Atrazine, trifluralin, and metolachlor are three of the most heavily used pesticides in the southeastern United States (13, 14). Since application of these pesticides occurs during early spring, their presence in air during the time of our sampling is most likely due to volatilization or dust transport rather than spray drift.

Concentrations of trifluralin in the freshened plume were considerably lower than atrazine and metolachlor (Table 2). This may simply reflect the differences in quantities of the three pesticides used in the region (which translates to different quantities in air available for washout). Data (13, 14, 19) indicate that in the southeastern United States the quantities of pesticides used are highest for atrazine and lowest for trifluralin. For example, in Florida, where the air mass responsible for the rain event made landfall, approximately 688 t of atrazine, 57 t of metolachlor, and 21 t of trifluralin were used in 1992 (14). The differences in physicochemical properties of the pesticides may also contribute to differences in observed concentrations. Atrazine has a vapor pressure approximately 1–2 orders of magnitude lower than metolachlor and 2–3 orders of magnitude lower than trifluralin (3, 20, 21). Studies have shown that pesticides with very high vapor pressures tend to volatilize from soil in large pulses immediately after application while those with lower vapor pressures volatilize more slowly and over longer periods of time (22). Taylor, for example, determined that approximately 90% of all trifluralin volatilized from soil within 2–3 days of application (22). Consequently, of the three, atrazine has the longest residence time in soil while trifluralin has the lowest. As a result, atrazine tends to be found in air and precipitation essentially year-round while trifluralin tends to be found mostly during months of application (3–5). Since our sampling occurred in July and application times in the region occur from late April to early May, there should be little trifluralin remaining from application. The concentrations measured inside the freshened plume are in the order atrazine > metolachlor > trifluralin, as would be expected from the residence times in soil and seasonal occurrence in air/precipitation (3, 4, 22).

Figure 2 indicates the presence of a second offshore freshened plume off Myrtle Beach (MBP). This plume was determined to also be the result of rainfall (8). Due to sampling limitations, we only obtained one sample at the edge of this plume (MB-2) that showed slight enrichment of atrazine and metolachlor. Consequently, we drew no firm conclusion on deposition in this plume.

To compare the importance of rain deposition with riverine discharge into waters of the South Atlantic Bight, we calculated the concentrations in rain (rain end-members) necessary to produce the surface water pesticide concentrations measured at CHN-4 and WB-3 using salinity as a conservative tracer and surrounding water pesticide concentrations as a baseline. These values were compared with river end-members calculated similarly using concentrations measured at one station inside Charleston Harbor (CHN-1) and five stations inside Winyah Bay (mean results represented by WB-1) as representative of riverine discharges at each transect. End-members were calculated by extrapolating (at 95% confidence) the slope of a  $\Delta[\text{pesticides}]/\Delta[\text{salinity}]$  graph from ambient levels and using the above stations to zero salinity (10). These calculations assume that pesticides behave conservatively in the time scale of the mixing of the fresh and seawater end-members. We realize that due to the small number of samples the error associated with these calculations is high. However, as noted below, our results using this method are consistent with precipitation concentrations measured by previous investigators.

End-members for atrazine, metolachlor, and trifluralin calculated in the above manner are shown in parentheses

in Table 2. Rain end-members for atrazine (500–830 ng/L) and metolachlor (270–550 ng/L) are similar to rainwater concentrations reported for the midwestern and northeastern United States (atrazine typically 200–900 ng/L and metolachlor <50–650 ng/L), for Iowa (mean of 700 ng/L for atrazine and 200 ng/L for metolachlor), and for the Canadian section of the Great Lakes Basin (<100–800 ng/L for atrazine and ca. 50–1150 ng/L for metolachlor) (3, 4, 6). Rain end-member concentrations were consistently higher than river end-member concentrations (Table 2). This suggests that rain events may represent an important input mechanism for pesticides from distant sources to coastal waters, especially since rain deposition represents direct input into the coastal ocean, bypassing the estuarine trap that affects riverine input from local sources. As some pollutants are discharged via rivers into estuaries, the residence time of waters inside these systems may be long enough to permit chemical and biological degradation of some pesticides, while others may be removed through processes such as air–water exchange or sedimentation via adsorption to particulates. These mechanisms do not affect rain deposition.

As a further indicator of the importance of rain deposition, we calculated the amount of pesticides deposited in the freshened water plume. Temperature and salinity measurements in depth profiles and Ra isotope data indicated that the plume was a continuous, well-mixed water mass, so the concentrations measured at the three stations within (located at both ends and the middle of the plume) are representative of the concentration range for this mixed surface plume. We estimated the volume of the water lens using surface area (160 km  $\times$  20 km) and an average lens depth of 6 m from water column salinity and temperature data (8) and multiplied by the average of the concentrations measured at the three stations inside the plume (corrected for background levels) to obtain total mass of pesticides deposited. Results for atrazine were approximately 130–490 kg, for metolachlor they were 95–120 kg, and for trifluralin they were 10–27 kg over a 2–3-day period. These are clearly rough estimates, but they provide values to compare with estimates of riverine discharges in the area. Using calculated river end-members (Table 2) and a total regional river input of  $7 \times 10^{10}$  L/day (23), yearly discharge into the region would be approximately 920–5600 kg of atrazine, 970–6000 kg of metolachlor, and 80–1175 kg of trifluralin. These estimates are consistent with previous estimates by Kucklick and Bidleman (1), who estimated a yearly discharge 3.1 t of atrazine into Winyah Bay, whose watershed receives 80–85% of the total pesticides applied in our study region (19). In addition, Smith et al. (24) reported that 0.3–2% of the atrazine applied annually to small Piedmont watersheds was lost in stormwater. This range is typical of watersheds in other areas (2). Assuming that 0.3–2% loss via runoff is typical for all three pesticides in all watersheds in South Carolina, that most of the runoff is discharged into estuaries, and using data from Gianessi and Anderson (13), total yearly discharge into South Carolina estuaries would be approximately 585–3800 kg of atrazine, 325–2200 kg of metolachlor, and 150–1000 kg of trifluralin, which fall in the range of our estimates. Based on the upper limit of our river discharge estimates, the masses of pesticides deposited in 2–3 days by the rain event represent approximately 4–10%, 3–5%, and 1–3% of the yearly riverine discharge of atrazine, metolachlor, and trifluralin, respectively. These are significant quantities of pesticides deposited in the coastal ocean in a very short time. These results indicate that rain events such as the one detailed in this study may be the source of major pulses of pesticides originating from distant sites to surface waters of the coastal ocean.

Alachlor and simazine were the only other pesticides measured above detection limits (<0.1 ng/L). Alachlor was detected inside Winyah Bay at two of the five stations (not

shown in Figure 1) at concentrations of 40 and 36 ng/L and inside Charleston Harbor (CHN-1) at 1.5 ng/L. Simazine was detected inside Winyah Bay at four of the five stations at a mean concentration of  $15 \pm 6.8$  ng/L. In 1992, 163 t of alachlor (which was the second most heavily used pesticide in South Carolina) and 56 t of simazine were applied in South Carolina (13). Alachlor is also soluble and simazine is fairly soluble in water, so surface runoff from local application, especially in the Winyah Bay watershed, probably accounts for their presence inside Winyah Bay and Charleston Harbor. Previous studies have detected both alachlor and simazine in estuarine areas (2). Alachlor and simazine were not detected offshore however. Alachlor and simazine may be degraded more quickly as compared with the pesticides detected offshore in this study (3). Our results suggest that rain deposition of these two pesticides is low with respect to runoff, at least during the time of sampling.

Most other pesticides targeted in this study were used in smaller quantities in South Carolina than the ones noted above (13, 19). All other pesticides, excluding carbofuran, adsorb more strongly than atrazine and metolachlor to particulates (21). This combination of lower application and stronger adsorption to particulates may explain the absence of these pesticides both in surface runoff and in rainwater. In addition, some pesticides may not be detectable due to degradation (e.g., chlorpyrifos, azinphos-methyl, and methyl parathion).

Our results provide direct evidence of significant input of pesticides to surface waters of the coastal ocean. Our results also indicate that precipitation may be an important nonlocal source of some pesticides to the coastal ocean in the South Atlantic Bight and needs to be included in pesticide input budgets in coastal regions. This is distinct from local sources that affect the coastal ocean mainly via surface runoff. This mechanism may be very important in sensitive offshore environments, such as tropical coral reefs (7). Disease and mortality in coral reefs has been documented in waters in which pesticides were detected (7). Tropical areas often combine heavy and year-round pesticide usage, higher temperatures (which can lead to increased volatilization of pesticides), and long rainy seasons (25). Consequently, there is the potential for events such as the one documented in this study depositing considerable quantities of pesticides in sensitive coastal areas. We recognize that this was an unusually intense rain event, but our results do point out the need to include the impact of rain events when investigating sources of pollutant input to the coastal ocean.

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## Literature Cited

- (1) Kucklick, J. R.; Bidleman, T. F. *Mar. Environ. Res.* **1994**, *37*, 63–78.

- (2) Glotfelty, D. E.; Taylor, A. W.; Isensee, A. R.; Jersey, J.; Glenn, J. *J. Environ. Qual.* **1984**, *13*, 115–121.
- (3) Goolsby, D. A.; Thurman, E. M.; Pomes, M. I.; Mayer, M.; Battaglin, W. A. *Environ. Sci. Technol.* **1997**, *31*, 1325–1333.
- (4) Struger, J.; Chan, C. H. Occurrence and transport of herbicides in precipitation from the Canadian section of the Great Lakes Basin. Presented at the 17th Annual SETAC Meeting, Washington, DC, November 17–21, 1996.
- (5) Nations, B. K.; Hallberg, G. R. *J. Environ. Qual.* **1992**, *21*, 486–492.
- (6) Hatfield, J. L.; Wesley, C. K.; Prueger, J. H.; Pfeiffer, R. L. *J. Environ. Qual.* **1996**, *25*, 259–264.
- (7) Glynn, P. W.; Howard, L. S.; Corcoran, E.; Freay, A. D. *Mar. Pollut. Bull.* **1984**, *15*, 370–374.
- (8) Moore, W. S.; Kjerfve, B.; Todd, J. F. *J. Geophys. Res.* **1998**, *103*, 7709–7717.
- (9) Moore, W. S.; Arnold, R. *J. Geophys. Res.* **1996**, *101*, 1321–1329.
- (10) Boyle, E. A.; Collier, R.; Dengler, A. T.; Edmond, J. M.; Ng, A. C.; Stallard, R. F. *Geochim. Cosmochim. Acta* **1974**, *38*, 1719–1728.
- (11) Kucklick, J. R.; Harvey, H. R.; Ostrom, P. H.; Ostrom, N. E.; Baker, J. E. *Environ. Toxicol. Chem.* **1996**, *15*, 1388–1400.
- (12) Hinckley, D. A.; Bidleman, T. F. *Environ. Sci. Technol.* **1989**, *23*, 995–1000.
- (13) Gianessi, L. P.; Anderson, J. E. *Pesticide use in South Carolina Crop Production*; National Center for Food and Agricultural Policy: Washington, DC, 1995.
- (14) Gianessi, L. P.; Anderson, J. E. *Pesticide use in Florida Crop Production*; National Center for Food and Agricultural Policy: Washington, DC, 1995.
- (15) Hale, H. T. The independence day flood of 1994. In *USGS Yearbook, fiscal year 1994*; USGS: Denver, CO, 1995.
- (16) Hippe, D. J.; Wangsness, D. J.; Frick, E. A.; Garrett, J. W. *Water quality of the Apalachicola-Chattahoochee-Flint and Ocmulgee river basins related to flooding from tropical storm Alberto; pesticides in urban and agricultural watersheds; and nitrate and pesticides in groundwater, Georgia, Alabama, and Florida*; USGS Water-Resources Investigations Report 94-4183; USGS: Denver, CO, 1994.
- (17) Korotky, J.; Michael, J.; Williford, C. E. Tropical storm Alberto: A WSR-88-D radar review. *Preprints, 14th Conference on Weather Analysis and Forecasting*; American Meteorological Society: Dallas, TX, 1995; pp 559–564.
- (18) Richards, R. P.; Kramer, J. W.; Baker, D. B.; Krieger, K. A. *Nature* **1987**, *327*, 129–131.
- (19) Pait, A. S.; DeSouza, A. E.; Farrow, D. R. G. *Agricultural pesticide use in coastal areas: A national summary*; National Oceanic and Atmospheric Administration: Rockville, MD, 1992.
- (20) ARS Pesticide Properties Database (U.S. Department of Agriculture); available on the Internet at <http://www.arsusda.gov>.
- (21) EXTNET (Extension Toxicology Network); available on the Internet at <http://ace.orst.edu/info/extoxnet>.
- (22) Taylor, A. W. *J. Air Pollut. Control Assoc.* **1978**, *28*, 922–927.
- (23) Moore, W. S. *Nature* **1996**, *380*, 612–614.
- (24) Smith, C. N.; Bailey, G. W.; Leonard, R. A.; Langdale, G. W. *Transport of agricultural chemicals from small upland piedmont watersheds*; Report to the U.S. Environmental Protection Agency; EPA-600/3-78-056; U.S. EPA: Athens, GA, 1978.
- (25) Lacher, T. E., Jr.; Goldstein, M. I. *Environ. Toxicol. Chem.* **1997**, *16*, 100–111.

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