

ABSTRACT

McCARTHY, ANNETTE M. Fate and Distribution of Current-Use Pesticides in the Albemarle-Pamlico Estuarine System of North Carolina. (Under the direction of Dr. Damian Shea and Dr. W. Gregory Cope).

Estuaries are complex ecosystems that are composed of a number of sensitive and inter-dependent environments. An abundance of nutrients combine with the dynamic conditions to create some of the most productive environments on the planet. Almost 85% of the commercially harvested fish in the United States depend on estuaries and the surrounding coastal waters at some stage in their life history. Many estuarine drainage basins contain large quantities of agricultural acreage. Over 29 million pounds of active ingredient of pesticides are applied in coastal drainage basins in the United States each year. Studies have shown that the overall condition of the nation's estuaries is fair, while benthic condition is poor. Seventy five percent of estuarine sediments are contaminated with pesticides. Concentrations of pesticides in 30% of the estuaries exceed the levels that are known to result in ecological effects at least 10% of the time. There have been few comprehensive pesticide studies in estuaries to date. The Albemarle-Pamlico (A-P) Drainage Basin of North Carolina forms the second largest estuarine system in the United States and supports heavy agricultural production with high pesticide use. I evaluated measurement and modeling strategies to assess exposure in the A-P

drainage basin. Atrazine and metolachlor were the most frequently detected pesticides in water samples that were collected in the A-P drainage basin in 2000 and 2001. Concentrations of these compounds exceeded both human health and aquatic life criteria in 2000. No toxicity thresholds were exceeded in samples collected in 2001. Due to the expense associated with field sampling and pesticide analysis alternative methods for estimating pesticide exposure have been developed, including fate models. The Exposure Analysis Modeling System (EXAMS) was modified to model the fate of pesticides, specifically atrazine and metolachlor, in a small tidal estuary of the larger A-P estuarine system. Based on the estimate that 10% of the total amount of atrazine and metolachlor applied in the Bath Creek drainage basin would enter the estuary the EXAMS steady state model predicts concentrations of both atrazine and metolachlor that fall between the mean and maximum values that were measured in Bath Creek in 2002. Concentrations of pesticides in the A-P drainage basin, both measured and modeled, are significantly less than acute toxicity thresholds for even the most sensitive aquatic species. Due to the short lived nature of these compounds it is unlikely that organisms in the region would experience adverse health effects due to exposure to the existing concentrations.

FATE AND DISTRIBUTION OF CURRENT-USE PESTICIDES
IN THE ALBEMARLE-PAMLICO ESTUARINE SYSTEM OF
NORTH CAROLINA

by
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Biography

A New Yorker to the core Annette Marie McCarthy was born on September 11, 1974 in New York City. The third of four children born to James and Annette C. McCarthy she grew up in Mamaroneck, NY. Her early education took place mainly in Catholic schools: Holy Trinity Grammar School, Resurrection Grammar School and the Academy of the Resurrection High School. The planned closing of the Academy forced a change of schools. In 1992, she graduated at the top of her class from Rye Neck Union Free High School.

Polluted beaches and clean-up attempts at local parks and streams created a lasting interest in environmental issues. In September of 1992 Annette entered Southampton College a part of Long Island University as an Environmental Science major with a Biology concentration. As part of a required internship in her junior year Annette worked in the Department of Toxicology at North Carolina State University. She returned to school in the fall and graduated magna cum laude in the spring of 1996.

Annette started graduate school at the University of Texas Medical Branch in August 1996. In June 1997 she transferred to North Carolina State University, to what was then known as the Department of Toxicology. She studied the fate of current-use pesticides in the aquatic environment under the guidance of Dr. Damian Shea and Dr. Greg Cope. She earned her doctoral degree from the renamed Department of Environmental and Molecular Toxicology in December 2002.

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INTRODUCTION

By definition, an estuary is the area where a river meets the sea. The freshwater and sediment input from the river and the tidal action of the sea provide a transition zone between the freshwater of the river and the saline environment of the sea (EPA, 2001). Comprised of brackish water, estuaries are dynamic environments that experience constant fluctuations in salinity, water depth, temperature and wind (Gale, 1989). They process both organic and inorganic material and sustain complex physical and biological habitats (Clark, 1993). Estuaries serve as repositories for transported sediments and as catchment basins for flood waters (Clark, 1993). An abundance of nutrients combine with these dynamic physical conditions to create some of the most productive environments on the planet.

The shallow, nearshore areas of an estuary provide shelter and food for a number of species of fish, shrimp and crabs during their early life stages (Gale, 1989). The economy of the surrounding areas is often dependent upon the fishing industry. Almost 85% of the commercially harvested fish in the United States depend on estuaries and the surrounding coastal waters at some stage in their life history (EPA, 2001).

Environmental conditions of the estuary during early life stages can be crucial to the survival of an organism. The quality of estuarine waters can be greatly influenced by human activities. Development of the land within a drainage basin can alter the rate of sedimentation, the freshwater flow, the nutrient load to an estuary and the contaminant input.

The amount of freshwater that enters an estuary and the rate at which it enters is one of the most important factors influencing salinity (Gale, 1989). As forests are cleared to make room for agricultural, residential or industrial development, the flow of freshwater to an estuary will increase, resulting in a decrease in salinity, changes in tidal-flow patterns and the loss of habitat (Gale, 1998). This increased flow is especially important following large rainfalls when the freshwater load will rapidly reach the head of the estuaries, often entering in the vulnerable nursery habitat areas, and causing rapid changes in salinity to which the organisms may be unable to survive. Human development may also decrease freshwater flow through the creation of flood control measures such as dams. The decreased water flow may result in the loss of spawning territory in upper areas, and an increase in the salinity of the region as freshwater input is reduced (Gale, 1989).

The impact of increased nutrient loads to an estuary can often be seen in the form of algal blooms. The increased nutrients frequently come from water that drains off of agricultural land that has been treated with fertilizers. Other sources of nutrients to estuaries are point source discharges from industries or municipal sewage plants, improperly maintained septic systems, and coastal forestry activities (Gale, 1989). Algal blooms can greatly reduce the dissolved oxygen that is available to estuarine organisms, resulting in massive die-offs of many species (Gale, 1989).

The same factors that alter the physical aspects of the estuary can also increase the contaminant load that the estuary receives. The increased sediment load may contain heavy metals or sorbed contaminants. Low salinity, high turbidity

estuaries are capable of removing a substantial portion of the freshwater inputs of dissolved trace metals in the upper estuary (Uncles, 1987). It is theorized that the removal of the metals is due to rapid uptake of the compounds onto suspended sediment (Morris, 1986). However, this sediment may also act as a source of trace metals further down the estuary (Uncles, 1987).

Human development also results in both point and non-point source release of contaminants into the watershed. The release of pollutants into the air and surface waters, even large distances upstream of an estuary, have the potential to negatively impact these waters. The importance that each of these contaminant sources plays in an estuary will depend upon the individual drainage basin. For example, a drainage basin that is comprised mainly of agricultural lands is more likely to be negatively impacted by non-point source pollution from agricultural runoff than it will be from industrial or municipal point source discharges.

Many estuarine drainage basins contain large quantities of agricultural land. Nationally the predominant crops in estuarine regions are corn, hay, soybean and wheat, although the acreage and importance of the crops varies on a regional scale (Pait, 1989). Soybean and corn are the more dominant crops in the southeast while citrus and sugarcane dominate in the estuarine drainage basins of Florida (Pait, 1989). In the northeastern United States and along the Gulf of Mexico soybean are again the dominant crop, although sorghum dominates along the southern Texas coast (Pait, 1989). Hay, cranberries and peas are the most prevalent crops in

Oregon and Washington. Further south on the West Coast alfalfa, barley and corn are more prevalent.

An area of heavy pesticide use is seen from Delaware Bay, DE to Winyah Bay, SC where agriculture accounts for an average 28% of the total land use in the drainage basins. The heaviest pesticide applications occur in the Chesapeake Bay in Maryland and the Albemarle-Pamlico Sounds in North Carolina (Pait, 1989; Pait, 1992). Pesticide use is further increased because some of the most pesticide intensive crops, such as soybean and corn, are the dominant crops in this region. A study of 35 of the most commonly used pesticides in the US showed that soybean and corn receive over 55% of the total amount of pesticide applied (Pait, 1992). Over 800 million pounds of active ingredient are applied in the United States annually (Pait, 1989). This is almost double the amount that was applied in 1987, 430 million pounds (Pait, 1992). Pait's study showed that over 29.4 million pounds of the 35 compounds studied were applied in the nation's coastal watersheds in 1987 (1992). While 35 pesticides were analyzed, it has been estimated that there are 600 active ingredients marketed in the 45,000 to 50,000 pesticide formulations that are available indicating that the actual pesticide application rate in coastal watersheds is greater than the 29.4 million pounds suggested (Wilkinson, 1987; Moore, 1987).

The per-acre application rates of pesticides are dependent upon crop acreage, type of crop and size of the drainage basin. The estuaries along the Gulf of Mexico and the estuaries along the South Atlantic coast applied the largest

quantities of pesticides in 1987; 10.1 and 9.8 million pounds, respectively. The region along the Gulf of Mexico has roughly three and a half times more cropland than the South Atlantic yet has a lower per-acre application rate due to the fact that large quantities of the agricultural land in the region is devoted to hay and pastures which do not receive large quantities of pesticides (Pait, 1992).

The timing of pesticide application and exposure in estuaries is important in determining the impact that the compound will have on the ecosystem. Agricultural pesticide applications coincide with the growing period of commercial crops. This period differs based on the climatic conditions but is usually between March and October (Pait, 1992). This coincides with major growth and reproductive periods of many estuarine species which may be at risk of exposure during sensitive stages of their life history.

From 1990 to 1997, the United States Environmental Protection Agency (EPA) assessed the condition of American estuaries (EPA, 2001). They found that while there was sufficient information to assess the northeastern, southeastern and Gulf of Mexico estuaries there was insufficient evidence to do full assessments of the estuaries on the West Coast and in the Great Lakes. No information was available to assess any of the estuarine systems in Alaska, Hawaii or any island territory. The goal of their study was to rank the estuaries on the basis of seven parameters: water clarity, dissolved oxygen, loss of coastal wetland, eutrophic condition, sediment contamination, benthic condition and accumulation of contaminants in fish tissue. It was concluded that 56 percent of the estuaries in the

United States were in good condition, the best of the three possible rankings. The remaining 44 percent were characterized as being impaired for either human or aquatic life. The parameters that were the most adversely impacted were coastal wetland loss, eutrophic condition and benthic condition. The least impacted indicators were water clarity and dissolved oxygen.

The condition of sediment in the nation's estuaries is poor. Seventy five percent of US estuarine sediment is enriched with pesticides (EPA, 2001). An additional 40% are enriched with metals and 45% with PCBs (EPA, 2001). Twenty nine percent of the surface sediments have concentrations of pesticides that fall between the effects range medium (ERM) and the effects range low (ERL), with 1% exceeding the ERM defined as the concentration of a contaminant that will result in ecological effects 50% of the time. The ERL will result in effects approximately 10% of the time (EPA, 2001). Ten to 23% of estuarine sediments had concentrations of PAH and PCBs, or metals, that fell between the ERL and ERM (EPA, 2001).

The benthic communities of the nation's estuaries are in fair to poor condition. Twenty two percent, primarily along the eastern seaboard and the coast of the Gulf of Mexico, have estuarine communities that have been rated poor (EPA, 2001). This appears to be the result of sediment contamination, hypoxic conditions, habitat degradation and eutrophication. Contaminated sediment is found in 62% of these estuaries (EPA, 2001).

Despite this obvious problem, there have been relatively few studies conducted to look at the extent of pesticide contamination within the nation's

estuaries. The majority of the studies that have been conducted focused on organochlorine pesticides and not those that are currently applied.

The Hudson-Raritan Estuary has been heavily impacted by anthropogenic activities that include chemical contamination from runoff, wastewater treatment facilities, illegal dumping and accidental spills, as well as such processes as dredging and residential development (Wolfe, 1996). There are also elevated levels of trace metals, DDT, dioxins, polychlorinated biphenyls and polycyclic aromatic hydrocarbons (Hauge, 1994; Wolfe, 1996). Concentrations of many of these contaminants are among the highest nationally and regularly exceed known toxicity thresholds (Wolfe, 1996).

Sediment toxicity tests were conducted from samples collected throughout the Hudson-Raritan Estuary in 1991 (Wolfe, 1996). Tests were performed using the amphipod, *Ampelisca abdita*, the bivalve, *Mulinia lateralis*, and the bacterium, *Photobacterium phosphoreum*. Of the 117 sediment samples that were analyzed, 54 were significantly toxic to amphipods, 47 to bacteria and 23 to bivalves. Analysis of the sediment suggested that with the possible exception of mercury, metals were not responsible for the observed toxicity. Among all contaminants, toxicity was more strongly correlated with polycyclic aromatic hydrocarbons (Wolfe, 1996). The study did not look at any current-use pesticides. However, analysis of compounds such as lindane, aldrin, heptachlor epoxide, endrin and mirex found concentrations that were at or below limits of detection (Wolfe, 1996).

The Newark Bay watershed in New Jersey is a portion of the Hudson-Raritan estuary that is influenced by a high-density urban area. High levels of toxic chemicals have been reported in the water and sediments of numerous harbors due to wastes from a wide variety of urban, industrial and riverine sources (Crawford, 1995). Excessive loadings of total suspended solids, organic matter, nitrogen, ammonia and pathogens are associated with wastewater discharge. Elevated concentrations of heavy metals have been found in the sediments of the bay and its tributaries. Concentrations of organochlorine pesticides, the only pesticides that were analyzed, ranged from 20 to 310 ppb in sediment (Crawford, 1995).

A study conducted in the Biloxi Bay-Mississippi Sound Estuary looked at chlorinated hydrocarbon insecticides in sediment samples from 37 sites (Walker, 1976). Analysis of these samples by electron capture gas-liquid chromatography detected no concentrations that exceeded the detection limit of one part per billion.

Padilla Bay in Washington is part of the larger Puget Sound estuary. Intensively managed agricultural areas to the east of the Bay pose a potential threat to ecosystem. In 1987 and 1988, water and sediment samples were collected in the eastern reaches of the bay as well as in the sloughs that drain the agricultural land (Mayer, 1990). There were two sampling periods each year, one proceeding pesticide application and one after pesticide applications were completed. Samples were analyzed for the 14 pesticides that are known to be applied in the region by gas chromatography-electron capture detector. No pesticides were detected in the samples that were collected prior to pesticide application in either year. Only two

were detected in the samples that were collected after pesticide application, dicamba and 2,4-D (Mayer, 1990). The levels of these compounds were not toxicologically relevant and no adverse effects are anticipated.

Sediment cores were collected from the Savannah River Estuary in Georgia to reconstruct the history of contaminant input into the estuary (Alexander, 1999). The cores were analyzed by gas chromatography-electron capture detector for a variety of inorganic and organic contaminants. The major pesticides that were found included DDT and its isomers. Concentrations peaked in 1967 which corresponds with peak use of the compound (Alexander, 1999). Low concentrations of lindane and alpha-chlordane were detected in the samples. The concentrations of all other chlorinated pesticides were below the detection limit (Alexander, 1999).

A similar study was conducted in the St. Lucie Estuary in Florida. This study focused solely on polychlorinated biphenyls and DDT and its isomers (Wang, 1979). Parent DDT was not found in any of the samples.

As described previously Winyah Bay in South Carolina is the lower edge of an area of intensive pesticide use. In 1990, an experiment was conducted to look at atrazine levels in the estuary (Kucklick, 1994). Water samples were collected at ebb tide at a water depth of 0.5 meters. Atrazine was extracted from whole water samples and quantified using gas chromatography-electron impact mass spectrometry. Atrazine was detected in all samples located downstream from the river regardless of season (Kucklick, 1994). Concentrations exhibited a seasonality with the highest concentrations being detected in May (610 ng/L) and the lowest

concentrations in December (7 ng/L) (Kucklick, 1994). This follows the application of the compound. A pre-emergent herbicide, atrazine, is typically applied in March and April in South Carolina (Pait, 1992).

Chesapeake Bay is the largest estuarine system in the United States and has the highest pesticide application rate of any American estuary (Pait, 1989; Pait, 1992). The US Geological Survey (USGS) analyzed all available pesticide data for the region of the estuary known as the Potomac River Basin (Zappia, 1992). Of the 41 pesticides that were analyzed 13 had concentrations at or above the detection limit in surface water samples. These compounds include 2,4-D, atrazine, aldrin, chlordane, DDT, dieldrin, endrin, lindane, prometon, Prometryn and simazine. Nineteen pesticides, including aldrin, chlordane, DDT, diazinon, dieldrin, endosulfan, endrin, ethion, heptachlor, heptachlor epoxide, lindane, parathion and toxaphene were found in bottom material samples.

The Sacramento-San Joaquin delta and the San Francisco Bay comprise what is known as the San Francisco Bay-Estuary. Over 500,000 pounds of herbicides are applied annually in the delta with an additional 5 million pounds being applied upstream (Kuivila, 1999). Water samples were collected in the delta from May through November 1997 and analyzed for herbicide concentrations in two studies to determine if herbicide exposure were inhibiting photosynthesis and impairing phytoplankton primary productivity (Kuivila, 1999; Edmunds; 1999). Thirteen herbicides were detected in one or more of the samples with diuron (2.1 µg/L), metolachlor (1.1 µg/L) and diethatyl-ethyl (1.0 µg/L) were present in the

highest concentrations (Kuivila, 1999). It was determined that there was no correlation between the peak herbicide concentrations and any reduction of phytoplankton primary productivity (Edmunds, 1999; Kuivila, 1999). Studies have also shown pulses of diazinon, methidathion and chlorpyrifos in the estuary following rain events in January and February (Kuivila, 1995). Peak concentrations of 1.1 µg/L of diazinon, 0.59 µg/L of methidathion and 0.042 µg/L of chlorpyrifos were measured (Kuivila, 1995).

In 1995, pesticides associated with suspended sediments entering the San Francisco Bay during the “first flush”-runoff from the first major storm of the water year- were analyzed (Bergamaschi, 1999). Of the 19 pesticides analyzed an average of 10 were found in each of the 15 samples collected. Most of the samples contained chlordane, chlorpyrifos, dacthal, DDD, DDE, DDT, molinate, oxyfluorfen, pebulate and thiobencarb. DDT and its metabolites were the most abundant with concentrations ranging from 5.1 to 11.1 ng/g (Bergamaschi, 1999).

Organochlorine, organophosphate and carbamate pesticides have been detected in water samples in the Pajaro River estuarine system in California (Hunt, 1999). This includes concentrations of diazinon, toxaphene and DDT that exceed toxicity thresholds for resident aquatic species. With the exception of carbaryl, all pesticides detected in the estuary were found at higher concentrations in the surrounding sloughs and agricultural ditches. This corresponds with the toxicity identification evaluations (TIEs) which showed the greatest toxicity in samples collected in the agricultural ditches.

The Albemarle-Pamlico (A-P) Drainage Basin of North Carolina forms the second largest estuarine system in the United States. The A-P system is one of the most extensively fished areas on the Atlantic coast with an annual commercial catch that exceeded \$65 million in 1999 (NCDENR, 2001). Tourism in the region brings in an additional \$1 billion annually. The A-P drainage basin also supports heavy agricultural production with high pesticide use. In 1999, the region contained approximately 2.5 million acres of farmland with a crop value of over \$1.5 billion (NCDA, 2001). An estimated 6 million pounds of active ingredient of pesticide were applied to agricultural fields that year.

Few studies have evaluated pesticide contamination in this region. Those that have been performed focused mainly on the A-P region known as the inner coastal plain (Woodside, 2001). The pesticide detection rates in the coastal plain were among the highest nationally, although pesticide concentrations were generally below the drinking water standards (Spruill, 1998; Skrobialowski, 1996).

This work was designed to evaluate measurement and modeling strategies to assess contaminant exposure and apply these methods to the A-P estuarine system. The potential hazard of high pesticide use raises questions about the impact of pesticide use on the North Carolina coastal ecosystems. One species of commercial interest, the blue crab (*Callinectes sapidus*), has been identified as having particularly high risk. In the past decade, local soft-crab shedding operations have reported high crab mortality in soft-shell shedding systems that often coincides with nearby pesticide application. In at least one case, filtering the source water with

charcoal dramatically reduced crab mortality, suggesting that something in the water that is removed by charcoal (e.g., pesticides) and was the primary cause of mortality, not the ambient conditions of temperature, salinity, or ammonia. Shedding is a highly stressful period for crabs. The additional stress of exposure to pesticides has been implicated as a possible cause for the high mortality in shedding operations and may also be impacting natural crab populations and other fisheries in North Carolina. Despite these observations, there has been little research into the extent of pesticide contamination in the region. This study was intended to synthesize pesticide use data in coastal North Carolina, measure pesticide exposures in the region, and determine whether pesticide exposure is likely to have an adverse effect on the ecosystem and soft-crab survival.

Pesticide use estimates are commonly employed to determine which pesticides pose a risk to a specific environment. The major limitation of this procedure is the lack of accurate reporting of pesticide use. While several states have implemented laws requiring the reporting of pesticide sales or use, there are no federal laws that deal with this issue. The state of North Carolina amended its laws governing pesticides in 2001 to require dealers to maintain records of all sales of restricted use pesticides but these amendments do not require mandatory reporting of the data. The lack of adequate pesticide use reporting means that alternative methods had to be developed to estimate pesticide-use on a regional scale (Thelin, 2000)

The primary objective of this project was to characterize pesticide exposure in surface water and sediment in the region of the A-P Drainage Basin that is classified as the outer coastal plain. Pesticide application in the A-P drainage basin begins in early March with pre-emergent herbicides and continues through early fall. Pesticide levels in both water and sediment are expected to be elevated at this time of year and coincides with the reproductive periods of many of the organisms that reside in the estuary. Thus, any assessment of biological effect needs to consider sub-lethal reproductive and developmental effects.

My objectives were to:

1. Evaluate methods for estimating pesticide use
2. Estimate exposure to current-use pesticides and historical chlorinated pesticides in surface water and sediment in the A-P estuarine system by taking actual measurements.
3. Assess the potential hazard of pesticides to blue crabs and other ecosystem components.
4. Assess the feasibility of using passive sampling devices to monitor current-use pesticides in the water column

5. Modify or develop a fate model for predicting current-use pesticides in estuaries.

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CHAPTER 1

ESTIMATING PESTICIDE USE RATES: COMPARISON OF REPORTED AGRICULTURAL STATISTICS TO SURVEY DATA

Abstract:

Pesticide use estimates to determine which pesticides pose a risk to a specific environment is a common practice. The major limitation of this procedure is the lack of accurate reporting of pesticide use. The lack of data availability made it necessary to establish a method to estimate pesticide use. The established method requires information on county crop acreage, statewide pesticide use-coefficients for the pesticide application rates, and the percent of acres treated.

An assessment of pesticide use in Beaufort and Hyde Counties in the North Carolina outer coastal plain was performed. We estimated the amount of pesticides applied in the two counties using the established method and using crop acreage estimates from the agricultural extension agents in the counties. Decreases of total pesticide were 40% and 20%, respectively when extension agent estimates were used in place of the crop acreage from the prior year and the statewide use coefficients. Thus, surveying the county agricultural extension agents can provide much more accurate pre-production estimates, the crop acreage for the current growing season as predicted by the county extension agent, yet even this can lead to overestimates or underestimates of crop acreage of as much as 30%.

The results from the comparison of methods for estimating pesticide use in North Carolina coastal counties above led us to investigate how differences in use estimates relate to measured concentrations or frequency of detection in surface waters, using measurements performed in a watershed in Mississippi. Unlike North Carolina, the pre-production and post-production crop acreage surveys in

Mississippi (of the county extension agents and farmers) yielded the same estimates. There was a good correlation was seen between the pesticide use estimates and the frequency of detected pesticides in surface water when the pesticides were divided into 2 groups based on half-life. The method of pesticide use estimation has only a small influence on the correlation between frequency of detection and estimated pesticide use. A better correlation was observed between the longer-lived pesticides using the extension agent estimates with a nearly identical fit for the short-lived pesticides.

Introduction:

Statistics from the U.S. Census Bureau's Census of Agriculture show that there are nearly one billion acres of farmland in the United States [1] and that nearly one billion pounds of pesticides are applied annually in an effort to control insects, weeds, fungus and other pests and diseases that reduce the crop yield [2]. Pesticide use in California and Florida accounts for 27 percent of the annual pesticide usage in the United States [3]. Overall, annual pesticide usage increased by over 90 million pounds between 1992 and 1997 [3]. The increase is attributable to changes in governmental policies, pest management and other farming practices, pest populations, and economics. The largest single increase in pesticide use, 48 million pounds of total pesticide, was the result of a reduction in prices that growers received for processed oranges. This caused farmers to switch to less expensive, horticultural oil-based products that required higher active-ingredient application

rates in the 1990s [3]. Other factors that have resulted in higher U.S. pesticide use are the expansion of the Boll Weevil Eradication Program for cotton, reduced tillage production practices to prevent soil erosion and more virulent strains of the potato late blight fungus [3].

Underlying these long-term national and regional scale pesticide use patterns and changes is substantial variability and trends in pesticide use at more local spatial and temporal scales. Crop acreage within a small watershed can easily change by factors of 2 or 3 between years, and pesticide application rates can change even more. Thus, order of magnitude changes in pesticide application rates can occur within a watershed over as little as one year, yet this information may not be captured by national, state-wide, or even county-wide crop acreage and pesticide use databases.

Given the large volume of pesticides used in the US and concern over their potentially harmful effects on non-target organisms, it is important that we be able to estimate pesticide use to help determine whether any pesticides pose an unacceptable risk to human or ecosystem health. National and even most statewide pesticide use estimates are insufficient for predicting more localized health risks. It is not known whether countywide pesticide use estimates provide sufficient resolution and accuracy for risk estimation to a county. Clearly, the major limitation to estimating pesticide use and risk is the lack of accurate and timely reporting of pesticide use at local spatial scales.

There are several federal programs and state laws that produce pesticide use surveys. Two of the most well established federal programs are the US Census Bureau's Census of Agriculture, and the US Department of Agriculture's National Agricultural and Statistical Service. Every five years, beginning in 1982, the Census of Agriculture conducts surveys of all farms in the United States that have sold over \$1000 worth of agricultural products during the census year [3]. Data collected include such factors as crop acreage, quantities harvested, value of products sold, and land use. On a national level the information is used to evaluate agricultural programs and administer farm programs. On a state or local level the information can be used to develop policies on land use, water use and irrigation. The Census non-disclosure rule prohibits it from publishing data related to an individual farm. As a result, no data are presented for counties that have 3 or fewer farms producing a specific crop.

The National Agricultural and Statistical Service (NASS) conducts annual surveys of pesticide use for the major crops. NASS estimates acreage and production of selected crops and the chemical use on major crops at the county level. Data collected include acres that are planted and harvested, quantity harvested, acreage grown and treated with a chemical, as well as the amount applied, method of application and the timing of application [4].

There is no federal law requiring the reporting of either the sale or use of pesticides. Regulations have been established on a state-by-state basis. One of the first states to require reporting of pesticide use was California. The state's

Environmental Protection Agency's Department of Pesticide Regulation collects state-wide information annually on the amount of individual pesticides used on crops, based on location [5]. Several other states, including New York and Oregon, have established similar laws. In October 2001, North Carolina joined states such as Vermont and New Hampshire in requiring that dealers maintain records of all sales of restricted use pesticides, but these states do not require mandatory reporting of the data.

The lack of adequate pesticide use reporting means that alternative methods must be developed to estimate pesticide use at watershed, county, state or national scales. In 2000, Thelin and Gianessi developed a method to calculate the pesticide use on a county-wide scale [5]. The method uses the crop acreage within the county and state-wide pesticide use coefficients representing both state-wide average application rates and fraction of crop acreage that was treated with the pesticide [5]. These coefficients were developed for 208 active ingredients or pesticides, 86 crops and 48 states (excluding Alaska and Hawaii). The pesticide-use coefficients were calculated by the National Center for Food and Agricultural Policy on the basis of the results from over 130 surveys and reports. The coefficients apply only to the application of a pesticide to cropland. They do not include commercial treatment of seeds, use in greenhouses, or non-agricultural uses of pesticides, such as highway rights-of-way or home uses.

Previous studies have found a positive correlation between pesticide use estimates and the frequency of pesticide detection in ground water, and between

pesticide-use estimates and environmental concentrations in surface waters [7, 8]. The frequency of detection of herbicides in groundwater was generally lower in areas of lower pesticide use. While the frequency of detection was greater in areas of higher pesticide use, so was the variability suggesting that high use is a necessary condition for the frequency of detection. However, other factors are also responsible for the environmental concentrations [6]. In surface water samples, there was a positive correlation between pesticide use of the 14 most commonly used pesticides in the region and the average concentration of these pesticides in the water column [7]. The relationship was stronger with the triazine herbicides than with acetanilide compounds, probably due to the faster degradation of the acetanilides in water [7].

Estimates of pesticide use may also be obtained through either individual county agricultural extension agents or from direct surveys of farmers, although this process is more time consuming. We calculated the pesticide use for two counties, Beaufort and Hyde, in eastern North Carolina (NC), and a small watershed in Yazoo County, Mississippi (MS) using the method developed by the USDA [5]. We then compared these estimates to those obtained through surveys of county agricultural extension agents in North Carolina and Mississippi, and farmers in Mississippi only.

Materials and Method:

Pesticide usage was calculated using the method of Thelin and Gianessi [5] from state-level pesticide use rates and the most recent county-level harvested crop acreage (1999):

$$\text{Lbs Applied} = \sum (\text{Crop acreage} * \text{AI per acre} * \% \text{ of acres treated})$$

where AI is active ingredient. Crop acreage was obtained from the North Carolina and Mississippi Departments of Agriculture. Additional estimates of pesticide use were made by surveying the county agricultural extension agents (in NC and MS) and farmers (MS only), incorporating *actual* crop acreage and pesticide use.

Study Areas:

The Albemarle-Pamlico Estuarine System (APES) of North Carolina forms the second largest estuarine system in the United States, draining over 81,000 km² of land in North Carolina and Virginia. The APES region supports heavy agricultural activity (i.e., 30% of land use) with production of soybean and cotton and associated pesticide use [3]. In 1999, the region contained approximately 2.5 million acres of farmland with a crop value of over \$1.5 billion dollars [8]. An estimated 6 million pounds of active ingredient of pesticide were applied to agricultural fields that year. The typical period of pesticide application in the APES drainage basin is from March through September. In addition, the APES is one of the most extensively fished

areas on the Atlantic coast with an annual commercial catch that exceeded \$65 million in 1999 [9]. Beaufort and Hyde counties in North Carolina are located on the western side of the Pamlico Sound. Agriculture is one of the primary sources of income in these counties, with cotton, corn and soybean being the most abundantly grown crops. The second study area was near the Panther Swamp National Wildlife Refuge in Yazoo County, MS with nearly 60% of the surrounding land in the watershed used for row crop production. Cotton is the dominant crop, with smaller amounts of corn and soybean. This study area was restricted to a sub-watershed within Yazoo County where individual farmers agreed to provide anonymous crop acreage and pesticide use data.

Results and Discussion:

There was no predictable trend or bias in the discrepancy between calculated and actual (extension agent/farmer survey) values. The differences between the calculated and actual pesticide usage varied greatly depending on both the pesticide and the area (Figures 2, 3, and 4). This includes a total difference in pesticide application predicted for the counties by as much as 40%, as well as differences in the application of individual pesticides.

North Carolina Study Area

There were 192,515 acres of cropland in Beaufort County and 106,550 acres in Hyde County in 1998 [8]. The main crops in these counties are corn, cotton,

soybean and wheat, as well as tobacco in Beaufort County. Based on these values and the method designed by Thelin and Gianessi [5], it was estimated that approximately 714,000 pounds of active ingredient of pesticide was applied in Beaufort County and 232,000 pounds in Hyde County in 1999. Using the crop acreage estimates from agricultural extension agents in these counties, we estimated that the amount applied would be 425,000 pounds in Beaufort County and 190,000 pounds in Hyde County, a decrease of 40 and 20 percent, respectively (Figure 1).

The difference in the two estimated values was due primarily to changes in crop acreage between 1998 and 1999 and, secondarily, to changes in the application rates of the pesticides between state-wide averages and extension agent estimates. Pre-production estimates from the extension agents predicted a decrease in corn acreage in Beaufort County from 55,600 acres in 1998 to 46,000 acres in 1999 (17% decline) (Table 1). A 15 percent decrease was expected in wheat acreage and cotton acreage was expected to more than double from 10,200 acres to 23,800 acres from 1998 to 1999. Data collected at the end of the growing season showed the expected decrease in wheat as well as the expected increase in cotton, although the increase turned out to be slightly less than double the previous year (19,000 acres). Contrary to predictions made by the county extension agents, there was a 20 percent increase in corn acreage (Table 1).

In Hyde County, North Carolina, cotton acreage was expected to increase from 11,000 acres in 1998 to 20,000 acres in 1999. This increase in cotton acreage

was expected to decrease the planted acres of corn and soybean from 1998 to 1999 (Table 1). No changes were predicted for any other crop in the county. A significant increase in cotton acreage (67%), as well as decreases in corn (23%) and soybean (32%), was observed in 1999. There was also a 50% decrease in the acreage of wheat. Sorghum, which was not grown in the region in 1998, accounted for 1150 acres in 1999.

These data illustrate the potential problems when extrapolating crop acreage from previous years to future years. Surveying the county agricultural extension agents can provide much more accurate pre-production estimates, though even this can lead to overestimates or underestimates of as much as 30% (e.g., corn in Beaufort County). The doubling of crop acreage in a county between two years is not a common occurrence, and in this case was driven by economic factors. A review of historical reported crop acreage in these two counties and throughout NC indicates that much smaller changes (e.g., less than 25%) are more typical for major crops.

Differences were also observed between the statewide pesticide application rates and the percentage of the acres treated with a compound and the estimates of use provided by the county extension agents. For example, in the 1990s the fraction of acres treated with glyphosate, trade name Roundup, greatly increased in Beaufort County and is now applied to as much as 75% of the cotton acreage and 50% of the corn acreage. Using statewide pesticide use-coefficients, it was estimated that 10,000 pounds of active ingredient of glyphosate would be applied in Beaufort

County in 1999. The actual use rates for this compound increased that value to over 60,000 pounds (Figure 2). A similar decrease is observed with alachlor and aldicarb, with a decrease of at least 85% from the values calculated. In Hyde County, 95% of the cotton seed and 65% of the soybean seed that were planted are Roundup™ ready. This seed has been altered to increase the plant's resistance to glyphosate, increasing the utility of the herbicide. The increased use of Roundup™ ready seed has altered the herbicide use in the region by increasing the amount of glyphosate that is applied which has resulted in a decrease in the use of pre-emergent herbicides such as alachlor. The changes in the type of seed used has dramatically altered the estimated use rates for alachlor and glyphosate, but the changes in pesticide use would not be reflected in agricultural statistics (using the method of Thelin and Gianessi [5]) for several more years. Thus, order of magnitude changes in pesticide use rates are possible between years when significant changes occur in pest management practices or pesticide registration and regulation, but there is a lag time up to several years before this information is reflected in the agricultural statistical database.

Another potential problem when estimating the amount of pesticide applied is the use of statewide pesticide-use coefficients for a given crop when local soil conditions might require alternative pesticides. For example, compounds such as metolachlor, pendimethalin, and trifluralin are not used very often in North Carolina coastal counties such as Beaufort and Hyde, because the high organic content of the soil makes these compounds less effective and therefore economically

undesirable (Figures 2 and 3). This discrepancy in pesticide use is most apparent for metolachlor and pendimethalin use in Hyde County, where neither pesticide was used in 1999 (Figure 3). In Beaufort County (Figure 2), metolachlor was more widely used than in Hyde County but there were certain corn and soybean farms in Beaufort County that did not use metolachlor. Thus, even countywide estimates from extension agent or farmer surveys may not accurately represent pesticide application on smaller spatial scales.

Mississippi Study Area

The results from the comparison of pesticide use estimates between 1998 and 1999 in North Carolina coastal counties led us to investigate how differences in use estimates relate to measured concentrations or frequency of detection in surface waters. We lacked the resources necessary to collect and analyze a sufficient number of water samples in coastal North Carolina to make this comparison; however, a study recently completed in our laboratory from samples collected in Mississippi did provide a spatially and temporally robust data set on which to perform this analysis of the relationship between pesticide use and frequency of detection [11]. By focusing on an intensively sampled watershed near the Yazoo National Wildlife Refuge, we obtained pesticide use estimates from county and statewide statistics [12], as well from one agricultural county extension agents and four farmers in 1999. The extension agent and farmers were surveyed to discover

which crops they grew, the crop acreages and the pounds of active ingredient of pesticides that they applied.

Unlike the North Carolina case described above, the pre-production and post-production crop acreage surveys in Mississippi (from county extension agent and farmers) yielded similar estimates. A comparison of the two estimation methods is shown in Figure 4. There is generally much better agreement (within 12%) within this region compared to the NC counties, due to much smaller changes in crop production and pesticide application rates compared to the prior year. The largest differences between the pesticide use estimated using the Thelin and Gianessi method [5] and the estimate based on the data provided by the extension agents and farmers were the reduction in use of alachlor (and, thus, estimates of its degradation product 2,6-diethylaniline), cyanazine, molinate, and propanil. Decreases in the latter two pesticides were due to a substantial reduction in rice production. The reduction in alachlor use was similar to that seen in North Carolina.

Barbash et al. [6] reported a positive correlation between pesticide use and frequency of detection of pesticides in groundwater, while Crawford [7] found a similar relationship between pesticide use and mean concentrations in surface waters. Though one might expect these relationships to exist, they often are not apparent due to complicating factors of transport, dilution, and degradation. These fate processes would have a greater influence on concentration than detection frequency. Thus, we plotted detection frequency as a function of pesticide use for state-reported estimates and extension agent estimates (Figures 5 and 6,

respectively). To account for the influence of degradation on the relationship between pesticide use and frequency of detection, the pesticides were segregated into those with short (< 10 day) half-lives and those with longer (> 10 day) half-lives. Although this time frame is arbitrary, it did coincide with the frequency of sampling (7-10 days) over the growing season within the watershed. The regression results (Figures 5 and 6) changed very little if the cutoff was moved to higher half-lives ($r^2=0.6298$ and 0.5975 for >12 days and <12 days respectively) or to as low as 7-8 days ($r^2=0.6482$ and 0.6119 for >7 days and <7 days respectively), but when all the data were included together a much poorer fit ($r^2=0.3222$) was obtained. Both plots clearly show a good relationship ($r^2=0.6429$ to 0.8093) and the stratified data sets indicate the expected increased detection frequency with the longer-lived pesticides (Figures 5 and 6). The method of pesticide use estimation has only a small influence on the fit, with a better relationship ($r^2=0.8093$) for longer-lived pesticides using the extension agent estimates and a nearly identical fit for the short-lived pesticides. Four of the pesticides with the greatest change in estimated use are apparent in Figure 5. Alachlor, its degradation product 2,6-diethylaniline and cyanazine all have half-lives greater than 10 days, and their use was overestimated using the state-reported statistics (Figure 4). In addition, they fell farthest below the regression line (Figure 5). Using the revised extension agent estimates for use, all three of these pesticides fall much closer to the regression line and the relationship is improved (Figure 6). Using revised use estimates for molinate and other short-lived pesticides has little influence on the overall regression statistics.

There are a number of factors that influence pesticide use estimates in a county. They include crop acreage, environmental parameters such as soil type, and the type of seeds used. The calculations used in this study can only be used in 48 lower states in the United States. Pesticide use-coefficients were not calculated for either Alaska or Hawaii.

Crop Acreage:

A number of factors influence what crops will be grown in a county in any given year. These include environmental factors such as temperature, rainfall and soil content, as well as economic factors that influence the price for which the crop can ultimately be sold. Countywide crop acreage is typically reported on an annual basis at the end of the growing season. Therefore, the data that are available to the public never reflects the current growing season. As crop acreage varies, so too will the total amount of a pesticide applied to a given crop. The fluctuations in crop acreage from year to year can result in over or under estimations of pesticide use in the region. County extension agent estimates of crop acreage for a given growing season has the potential to reduce the error in the estimate, but large discrepancies may still be observed as evidenced with corn acreage in Beaufort County. Using the 1998 values obtained from the North Carolina Department of Agriculture and Consumer Services caused us to underestimate the total amount of pesticides applied to corn in the region. The expected acreage obtained from the county extension agent in Beaufort County, North Carolina served to only further increase

the error in crop acreage by further reducing the overall crop acreage when the corn acreage actually increased by 11,600 acres between 1998 and 1999. For the majority of other crops in both NC counties, the county extension agents' estimates reduced the difference between the 1998 crop acreage and the acreage that was reported at the end of the 1999 growing season.

National or statewide estimates of pesticide use may not be affected by changes in crop acreage or use rates as much as local or county estimates. However, there have been no systematic estimates of pesticide use based on United States Department of Agriculture and state data. Because calculated values are based on statewide averages, we would expect less of a difference between calculated and actual pesticide usage on a state level.

Pesticide Use-Coefficients:

Pesticide use-coefficients representing pesticide application rates and the percent of acres treated with a pesticide are based on statewide averages and represent the general trend in use over a 4-year period, not a single year. As a result, there can be significant differences between these statewide averages and the way a pesticide is actually applied in a given county. A number of factors influence these management practices, including the pretreatment of seeds, the organic carbon content of the soil, the availability of new pesticides, or the removal of pesticides from the market. Moreover, economic factors often play a substantial role in the decisions made.

The outer coastal plain of North Carolina, where Beaufort and Hyde Counties are located, contains soil that is rich in organic carbon. As a result, compounds such as pendimethalin and trifluralin, which are both used on 45% of the cotton acres in the state, are applied infrequently, if at all, in this region. Pesticide use-coefficients estimated that over 30,000 pounds of active ingredient of pendimethalin and 17,000 pounds of trifluralin would be applied in the region. The ineffectiveness of these and other compounds in the region has forced farmers to replace the compound with another. Mepiquat chloride and glyphosate are two compounds in this region that are used on a larger portion of the acreage than the statewide average.

Genetically altered seed can alter pesticide use in a region. Roundup™ ready cotton and soybean in Beaufort County have played a large role in the decrease in alachlor use in the county, because farmers are no longer required to apply large amounts of pre-emergent herbicides. The pretreated seeds have also served increase glyphosate use because the seeds will typically be treated with two applications of this compound. Studies have shown that the number of pesticide applications decrease with the use of Roundup™ ready soybean [10]. Roundup™ ready varieties have simplified weed control programs, by requiring the use of only a single herbicide instead of the three or more active ingredients that had been applied previously [10].

Pesticide-use coefficients were originally determined in 1992 for 208 active ingredients and pesticides [5]. These values do not exist for newer compounds that have arrived on the market since that time. These new products are frequently used

in place of older compounds. Therefore, the use of some pesticides will be overestimated while others are not calculated.

The Census of Agriculture:

In an effort to protect individual farmers, the Census of Agriculture has a rule that prohibits the publishing of any data for a crop when there are three or fewer farms that produce the crop in a county. As a result, pesticide use calculations can underestimate the pesticide use in a region. The potential magnitude of this error depends on the size of the farms in question. The discrepancy between the actual amount of pesticide applied and the amount calculated by the Thelin and Gianessi method [5] will increase as the farm, and the total number of acres in question, increase.

Disease:

In the mid-1990s a more virulent form of the potato late blight fungus appeared. In an effort to prevent huge losses in potato production, the use of fungicides increased by 37% [3]. The pesticide use-coefficients do not take into account these types of changes in pesticide use and estimates of pesticide use on potatoes in the affected regions would have greatly underestimated overall fungicide use.

Agricultural and non-agricultural use of pesticides:

Pesticides are applied for a variety of purposes. These include agricultural uses such as direct application to crop acreage, pre-treatment of seeds, treatment of livestock, and non-agricultural uses including application to rangeland, forest land, highway right-of-ways, turf, use in greenhouses and a variety of home uses [5]. The pesticide use-coefficients have been calculated to reflect only those pesticides that are applied to crop acreage. Currently, few data exist on the non-agricultural use of pesticides. This lack of data makes it likely that the estimated pesticide use in a county is actually an underestimation of the total amount that is applied to a region. Until more data becomes available for non-agricultural uses, it is not possible to correct overall estimates.

The absence of non-agricultural pesticide use rates, as well as the variability in use that is associated with disease, regional differences and the constantly increasing number of pesticides on the market limits the utility of pesticide-use estimates. The values that are predicted provide a potentially useful survey of the pesticides used in the region. However, it is important that the user recognize the limitations of the method in terms of predicting actual values.

One of the biggest problems in acquiring accurate estimates of pesticide use is the lack of standard reporting requirements such as a comprehensive federal law mandating the reporting of both pesticide sales and use. A law similar to the ones that have been passed in states such as California and New York could greatly reduce the error in pesticide use estimates.

Acknowledgements:

We thank Gaylon Ambrose and Mac Gibbs of the North Carolina Cooperative Extension Service for their assistance with estimating pesticide use in Beaufort and Hyde Counties of North Carolina.

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Figure captions

Figure 1. Comparison of total countywide pesticide use rates estimated using method of Thelin and Gianessi [5] with state-reported application coefficients and crop acreage (black bar) and using data from extension agent surveys (shaded bar).

Figure 2. Comparison of Beaufort County pesticide use rates estimated using method of Thelin and Gianessi [5] using state-reported application coefficients and crop acreage (black bar) and using data from extension agent surveys (shaded bar).

Figure 3. Comparison of Hyde County pesticide use rates estimated using method of Thelin and Gianessi [5] with state-reported application coefficients and crop acreage (black bar) and using data from extension agent surveys (shaded bar).

Figure 4. Comparison of pesticide use rates in Yazoo, MS watershed estimated using method of Thelin and Gianessi [5] with state-reported application coefficients and crop acreage (black bar) and using data from extension agent surveys (shaded bar).

Figure 5. Frequency of detection (% of sites in Yazoo, MS watershed) as a function of pesticide use estimating with state-reported application coefficients and crop acreage. Data are segregated into pesticides with half-lives greater than 10 days (open diamond) and less than 10 days (filled diamond).

Figure 6. Frequency of detection (% of sites in Yazoo, MS watershed) as a function of pesticide use using extension agent and farmer estimates of crop acreage and pesticide use. Data are segregated into pesticides with half-lives greater than 10 days (open diamond) and less than 10 days (filled diamond).

Table 1. Comparison of crop acreage estimates and reported values in Beaufort and Hyde Counties, NC

	<u>Beaufort County</u>			<u>Hyde County</u>		
	Reported	Pre-Production Estimate	Reported	Reported	Pre-Production Estimate	Reported
	1998	1999	1999	1998	1999	1999
Corn	55600	46000	67000	31000	<31000	24000
Cotton	10200	23800	19000	11000	20000	18400
Hay	500	500	500	300	300	300
Peanuts	290	265	245	0	0	0
Potatoes	410	0	200	250	250	230
Soybeans	70000	70000	67000	40000	<40000	27000
Tobacco	4165	2970	3550	0	0	0
Wheat	51000	44000	43000	24000	24000	11900

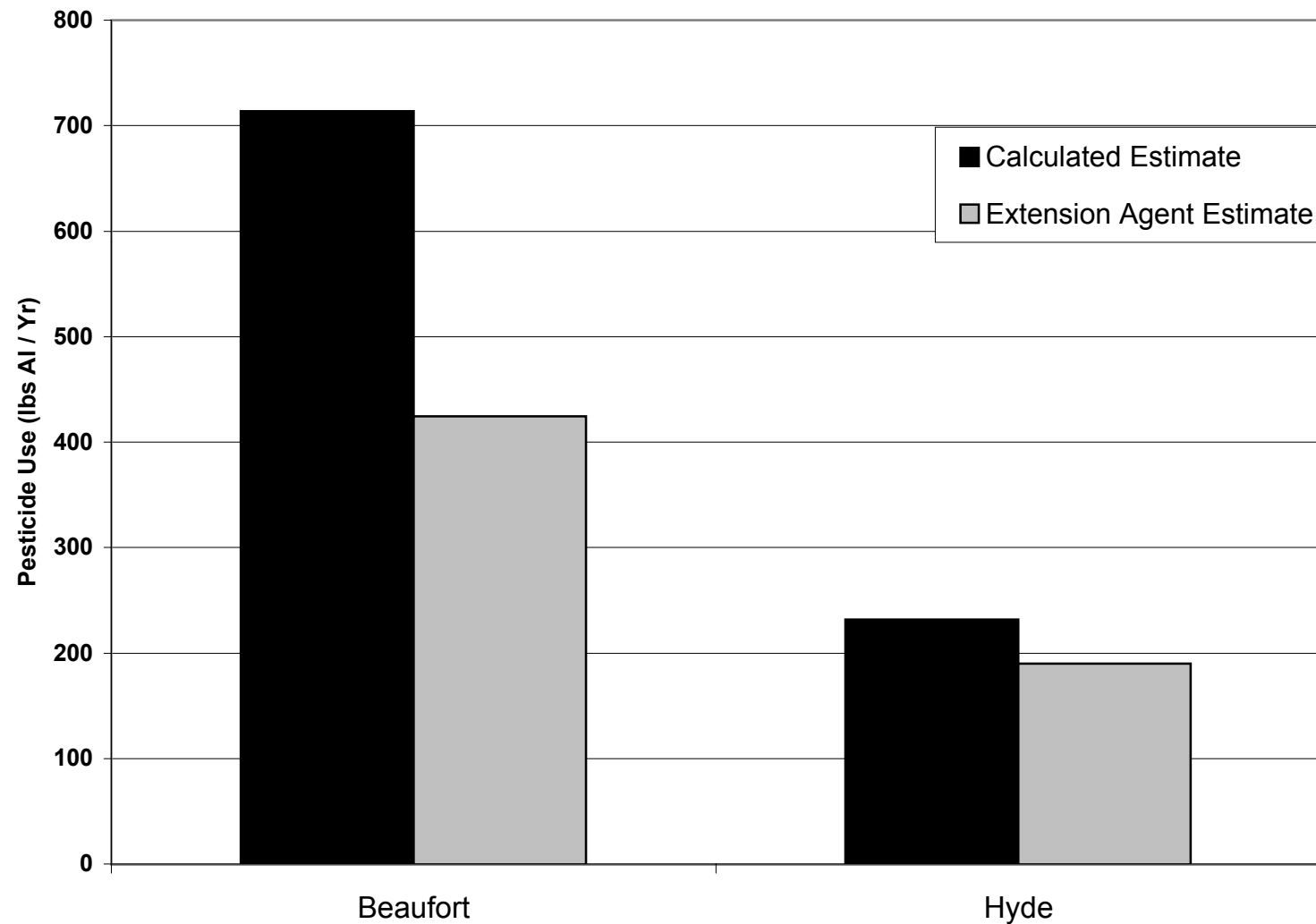


Figure 1. Comparison of total county-wide pesticide use rates estimated using method of Thelin and Gianessi [5] with state-reported application coefficients and crop acreage (black bar) and using data from extension agent surveys (shaded bar).

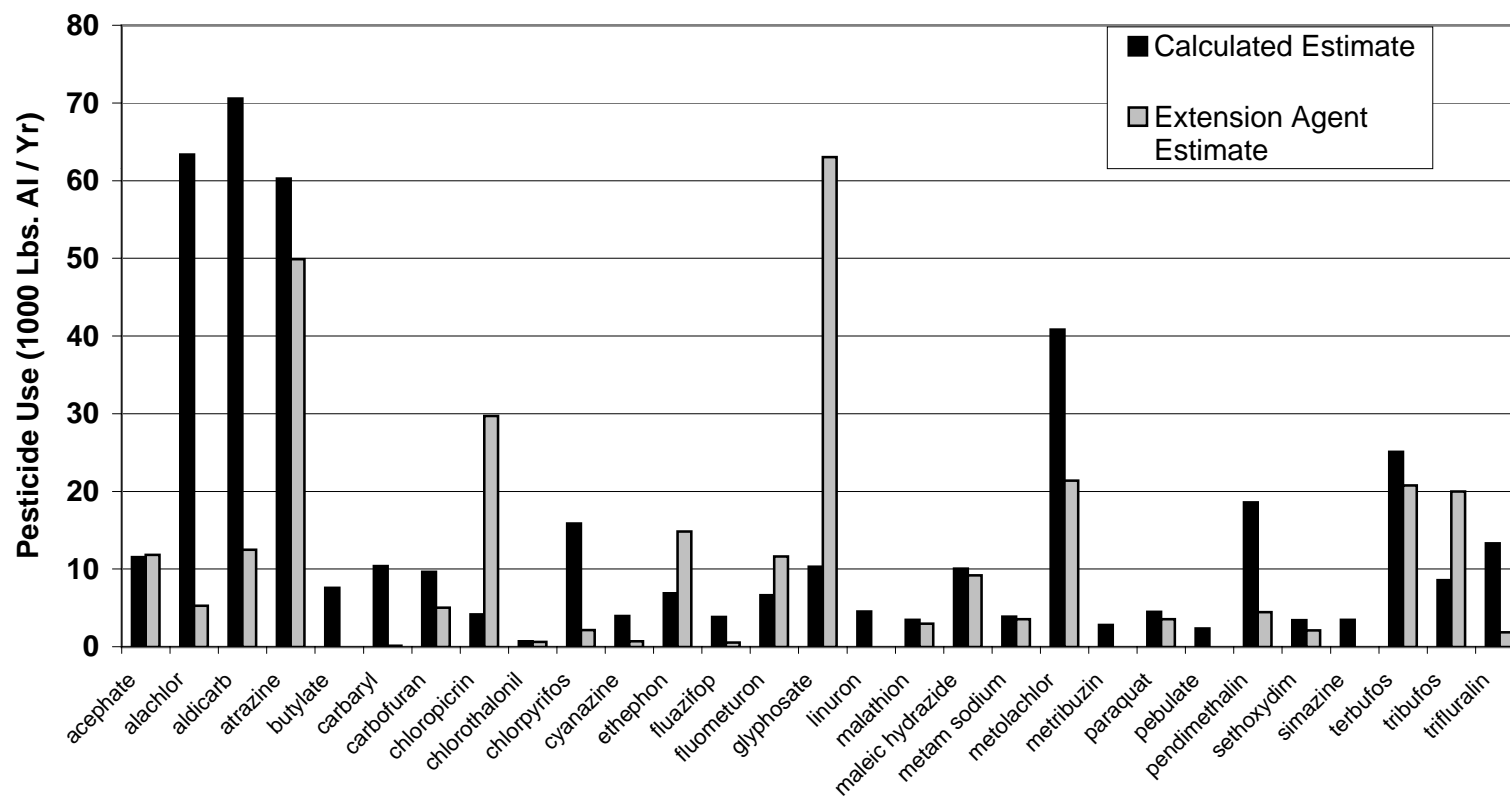


Figure 2. Comparison of Beaufort County pesticide use rates estimates using method of Thelin and Gianessi [5] using state-reported application coefficients and crop acreage and using data from extension survey results.

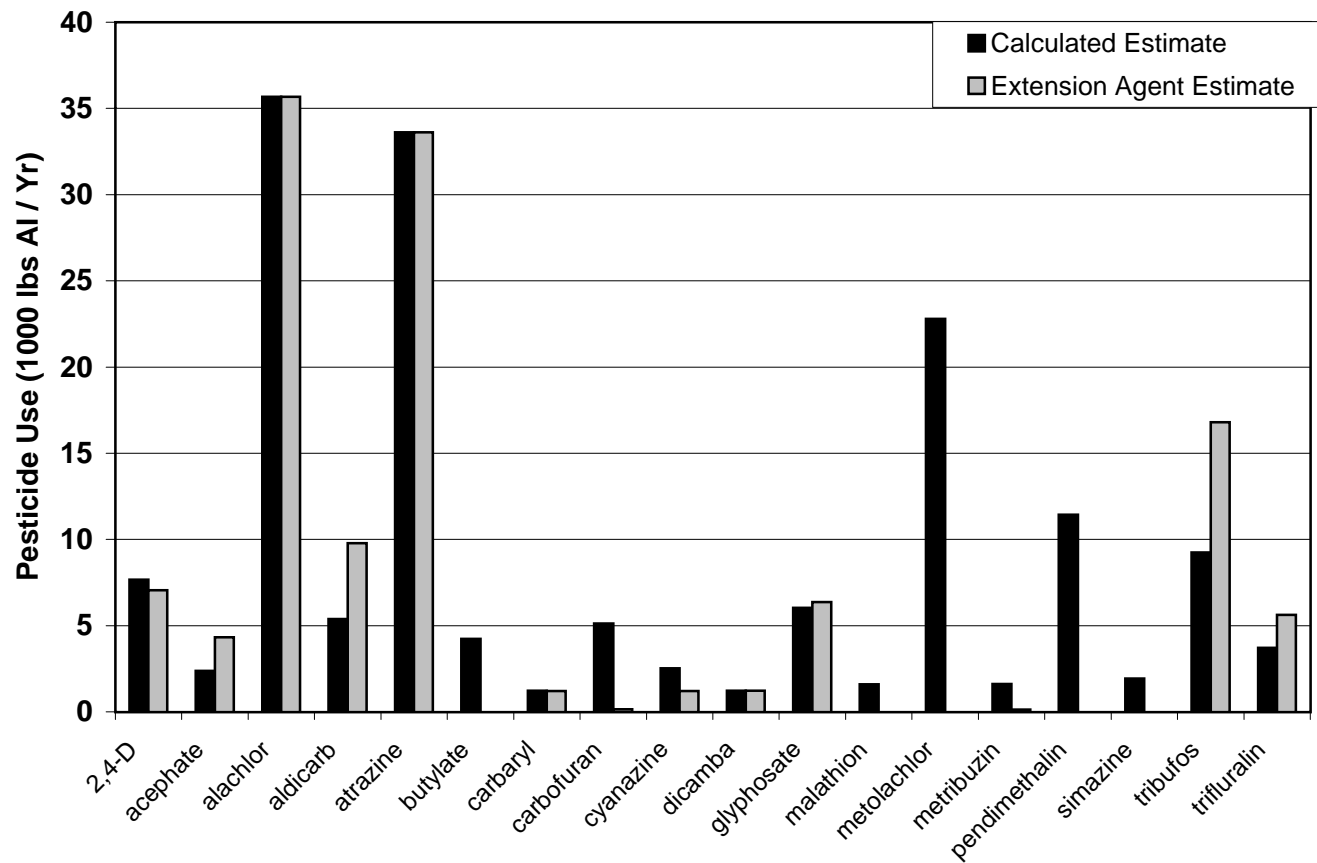


Figure 3. Comparison of Hyde County pesticide use rates estimated using method of Thelin and Gianessi [5] with state-reported application coefficients and crop acreage (black bar) and using data from extension agent surveys (shaded bar).

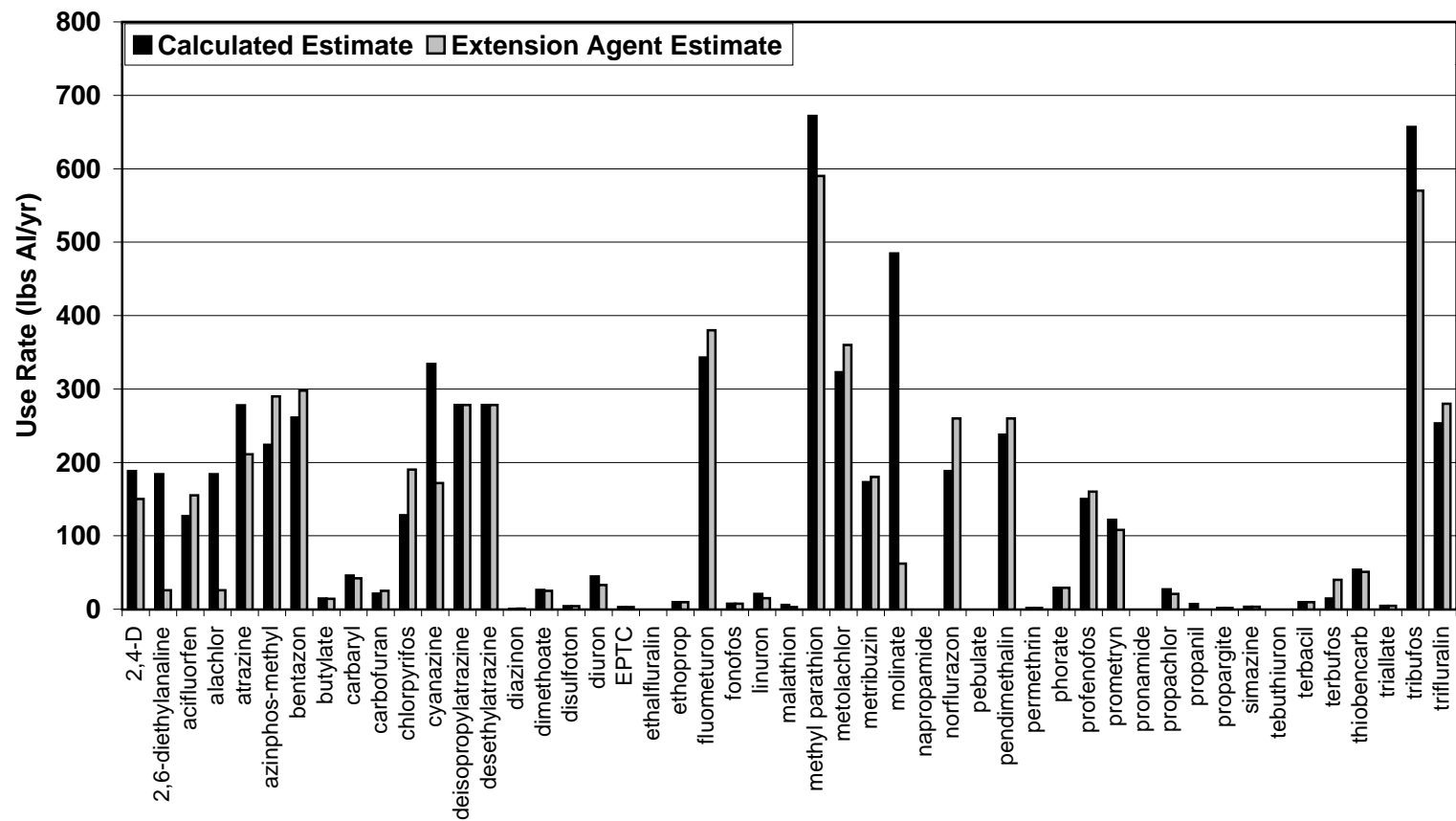


Figure 4-Comparison of pesticide use rates in Yazoo, MS watershed estimated using method of Thelin and Gianessi with state-reported application coefficients and crop acreage and using data from extension agent surveys

Figure 5. Frequency of detection (% of sties in Yazoo, MS watershed) as a function of pesticide use estimating with state-reported application coefficients and crop acreage. Data are segregated into pesticides with half-lives greater than 10 days (open diamond) and less than 10 days (filled diamond).

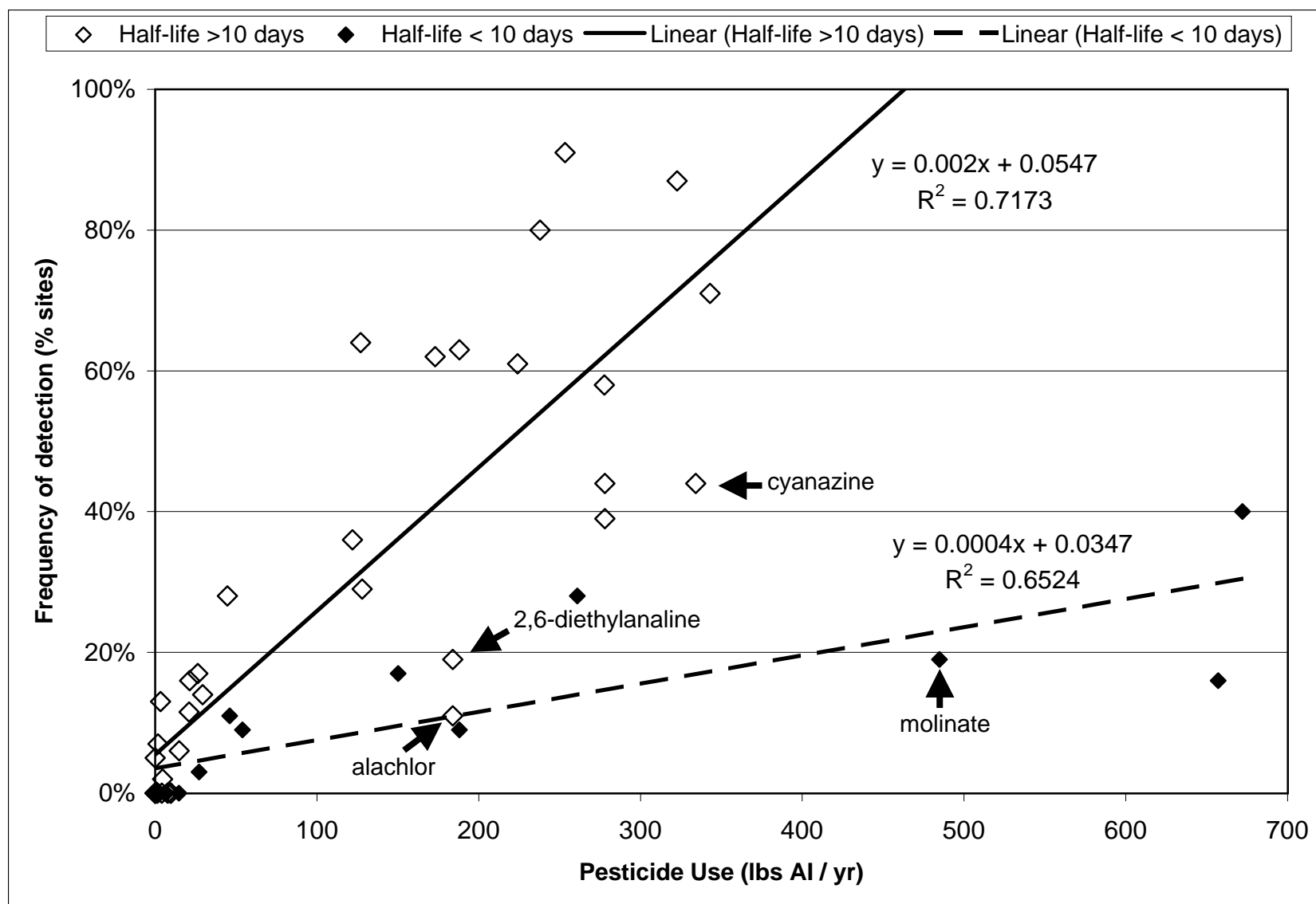
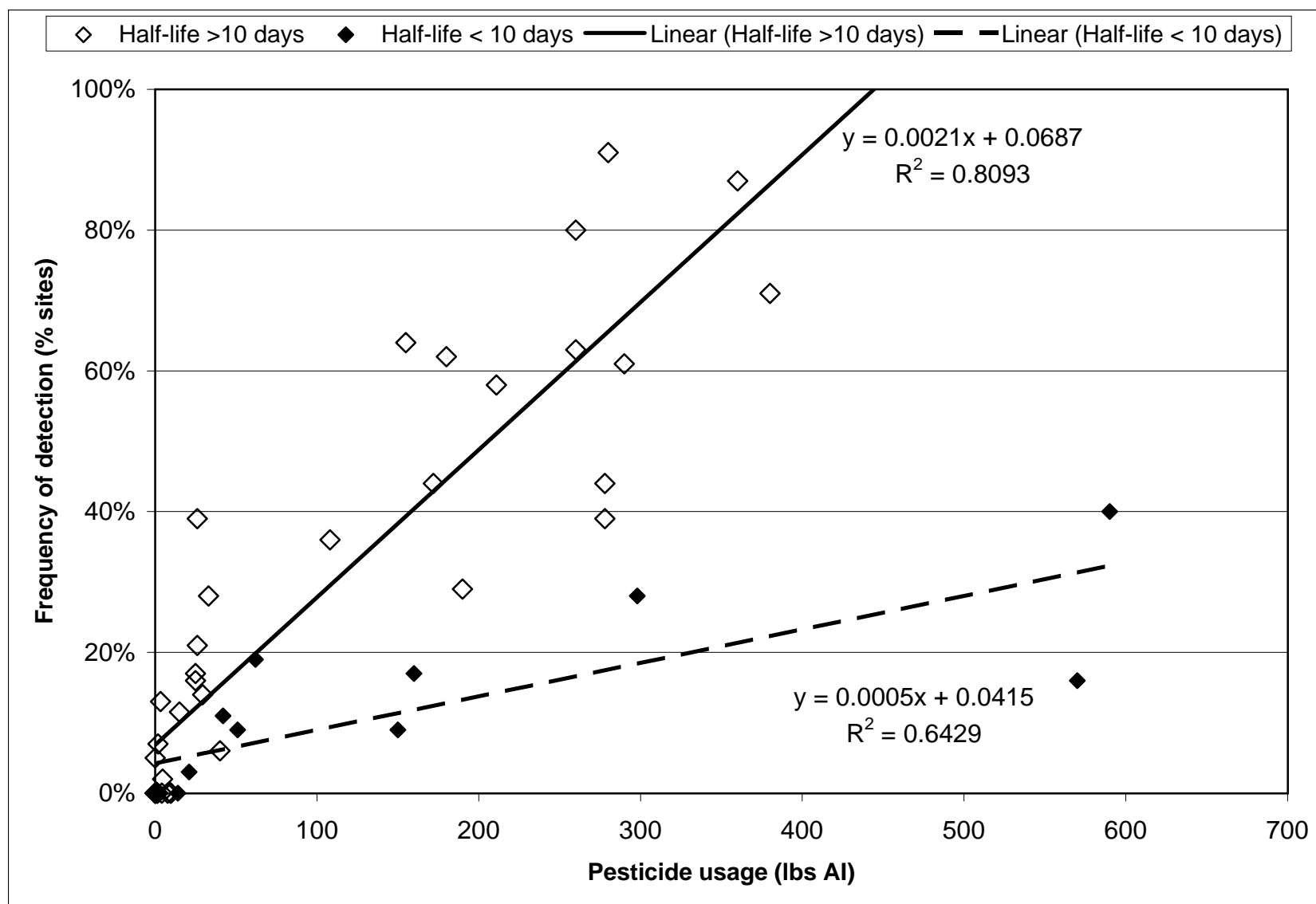


Figure 6. Frequency of detection (% of sites in Yazoo, MS watershed) as a function of pesticide use using extension agent and farmer estimates of crop acreage and pesticide use. Data are segregated into pesticides with half-lives greater than 10 days (open diamond) and less than 10 days (filled diamond).



CHAPTER 2

PESTICIDE CONTAMINATION IN SURFACE WATERS OF THE ALBEMARLE-PAMLICO SOUND, NC; 2000-2001

Abstract:

The biological productivity of Albemarle-Pamlico (A-P) Sound, the second largest estuarine system in the United States, has declined substantially over the past 30 years. The National Oceanic and Atmospheric Administration published a hazard-based risk assessment for pesticides in 1992, which concluded that the outer coastal plain of North Carolina had the greatest risk of adverse ecological effects in the US, based on hazard-normalized pesticide application rates. However, this risk has not been empirically evaluated through field measurements. Despite heavy pesticide use in the region, few studies have been performed to evaluate the extent of pesticide contamination in the region.

Surface water grab samples were collected in 2000 between May and July and in 2001 between April and October. Samples were collected throughout the A-P Sound in 2000. Concentrations of alachlor, atrazine and metolachlor in the surface water samples exceeded U.S. lifetime drinking water standards. Concentrations of atrazine and metolachlor were also found to exceed aquatic life criteria. Timing is important for the measurement of pesticide exposure, as pre- and post-emergent herbicides display very different temporal exposure patterns. So in 2001, the sampling scheme was redesigned. The Tar-Pamlico River located in the Albemarle-Pamlico Estuarine System (APES) was sampled once every two weeks during the 2001 agricultural production season. The highest concentrations of pre-emergent herbicides; atrazine, simazine and metolachlor, peaked in May and June. Prometryn, a post-emergent herbicide was not detected in any sample. Neither the

safe drinking water nor the aquatic life criteria were exceeded in any samples collected in 2001.

Introduction:

The creation of synthetic pesticides has altered modern agricultural practices, increasing crop productivity and the profit margin of the farmers. The widespread use of these pesticides has resulted in their detection in numerous water bodies (Kolpin *et al.*, 1998; Gilliom *et al.*, 1999). Over 50% of the surface water and shallow groundwater in the United States, in both agricultural and urban areas, has some pesticide contamination (Kolpin *et al.*, 1998; Gilliom *et al.*, 1999). The most frequently detected pesticides are atrazine and its metabolite desethylatrazine, simazine, metolachlor and prometon (Kolpin *et al.*, 1998; Gilliom *et al.*, 1999).

While many estuarine drainage basins contain large amounts of agricultural land, few studies have looked at the extent of pesticide contamination in these regions. Chesapeake Bay, the largest estuarine system in the United States, and the San Francisco Bay-Estuary are the two most well characterized estuaries in the United States in terms of pesticide contamination. The Chesapeake Bay watershed has the highest pesticide application rate of any American estuary (Pait, 1989; Pait, 1992). The US Geological Survey (USGS) analyzed all available pesticide data for the Potomac River Basin of Chesapeake Bay (Zappia, 1992). Of the 41 pesticides that were analyzed, 13 had concentrations at or above the detection limit in surface water samples.

Over 500,000 pounds of herbicides are applied annually in the delta of the San Francisco Bay-Estuary, with an additional 5 million pounds being applied upstream (Kuivila, 1999). In 1997, 13 herbicides were detected in surface water samples. Diuron (peak concentration=2,141 ng/L), metolachlor (1,107 ng/L) and diethatyl-ethyl (1,041 ng/L) were present in the highest concentrations (Kuivila, 1999). Suspended sediments entering the San Francisco Bay during the “first flush”-runoff from the first major fall storm of the year were analyzed, most of the samples contained chlordane, chlorpyrifos, dacthal, DDD, DDE, DDT, molinate, oxyfluorfen, pebulate and thiobencarb (Bergamaschi, 1999).

In 1992, the National Oceanic and Atmospheric Administration (NOAA) published a report of agricultural use in coastal areas of the United States (Pait, 1992). The report concluded that the APES region in North Carolina was the estuarine drainage area at the greatest risk from pesticide exposure in the U.S. However, no actual measurements of pesticide concentrations in the region were performed to verify this conclusion. Few studies have evaluated pesticide contamination in this region. Those that have been performed focused mainly on the APES region that is known as the Inner Coastal Plain (Woodside, 2001), where alachlor, atrazine, metolachlor and prometon were the most commonly detected pesticides found in surface waters (Spruill, 1998; Skrobialowski, 1996). The pesticide detection rates in the coastal plain of North Carolina were among the highest nationally, although pesticide concentrations were generally below the

drinking water standards. The only compound with concentrations that exceeded the safe drinking water standard was alachlor (>2 mg/L) (Spruill, 1998).

Agriculture is one of the primary land uses in the outer coastal plain of North Carolina, accounting for roughly 30% of the land use in the region (Woodside, 1996). The primary crops include soybean and cotton. In 1999, the region contained approximately 2.5 million acres of farmland with a crop value of over \$1.5 billion dollars (NCDA&CS, 2001). Heavy agricultural production requires the use of a large amount of pesticides for the control of weeds, insects and fungi. An estimated 6 million pounds of active ingredient of pesticide were applied to agricultural fields in the Albemarle-Pamlico Estuarine System (APES) in 1999 (Chapter 1).

Previous studies have found that metolachlor, atrazine and alachlor are among the most frequently detected pesticides in the upper reaches of the Tar River, North Carolina (Woodside, 2001; Spruill, 1998). These three compounds are also the most commonly used herbicides in the region (Chapter 1). The Tar River is part of the larger Tar-Pamlico River Basin. The Tar and Pamlico Rivers are one river, which makes the Tar-Pamlico River basin the fourth largest river basin in North Carolina. The region known as the Tar River is the upstream freshwater portion of the river that extends north and west of the town of Washington, North Carolina. The section of the river that flows south and east of Washington is the estuarine portion of the river known as the Pamlico River (NCDEM, 1994). Agriculture is the predominant form of land use covering 34% of the available land. Few samples

have been collected from estuarine portions of the drainage system known as the outer coastal plain.

For compounds such as alachlor and metolachlor, the highest concentrations in streams were reported during the months of June and July, with an increase in concentrations beginning as early as March or April (Spruill, 1998). This initial increase in concentration coincides with early application of the alachlor and metolachlor. Pesticides are applied in this region primarily between the months of March and September. These application periods coincide with the major growth and reproductive periods of many aquatic organisms. Menhaden (*Brevoortia tyrannus*), an important forage and commercial species, reproduce throughout the spring and summer months and larvae and juvenile fish may be exposed to pesticides at any point during this time period. The molting period of the blue crab (*Callinectes sapidus*), one of the most commercially valuable species in the region, begins in April and continues through the spring months. This organism increases in body size by approximately one-third with each successive molt. Mating of crabs also occurs during this time period while the female is in the last soft-shell stage immediately following her final molt to maturity.

The fishery and tourism industries have a large positive economic impact on the region. The Albemarle and Pamlico Sounds of North Carolina form the second largest estuarine system in the United States, draining over 81,000 km² of land in North Carolina and Virginia. It is one of the most extensively fished areas on the Atlantic coast with an annual commercial catch that exceeded \$65 million in 1999

(NCDMF, 2001). Tourism in the region brings in an additional \$1 billion annually (NCDMF, 2001).

The relatively high pesticide use and associated potential hazard in North Carolina raises questions about the potential impact of pesticides on the NC coastal ecosystem. There is a concern among local fisherman that one species of commercial interest, the blue crab, may be at risk. In the past decade, local soft-crab shedding operations have reported high mortality that often coincides with nearby pesticide application (Robert Hines, personal communication). A reduction in mortality was sometimes obtained by filtering the source water with charcoal, suggesting that something in the water that is removed by charcoal (e.g., pesticides) was the primary cause of mortality and not the ambient conditions of temperature, salinity, or ammonia (Robert Hines, personal communication). Despite these observations, there has been little research into the extent of pesticide contamination in the region.

In addition to the reported blue crab mortality, there have been a number of incidents involving either lesions on the skin of fish or large scale fish kills, primarily involving menhaden. Studies have attributed these incidents to either low dissolved oxygen conditions or to the presence of the dinoflagellate species, *Pfiesteria piscicida* (CAAE, 2002). The timing of these die-offs, primarily in mid to late summer, suggests that pesticide contamination may also be a causative agent. This study was intended to measure pesticide residues in surface waters of coastal North Carolina, and determine whether pesticide concentrations are likely to have an

adverse effect on soft-shell crab survival and other biological components of the ecosystem.

Materials and Methods:

Sample Collection:

Surface water samples were collected from 27 sites within the APES region between May and July 2000 by the North Carolina Department of Environment and Natural Resources (DENR) (Figure 1). A single sample was collected from the middle of the river at each of the sites. Samples were collected in teflon-lined amber jars and stored on ice. Samples were also collected from the drainage ditches of a farm located in Beaufort County, NC. These samples were collected approximately once every two weeks from March through October.

Based on the data from the samples collected in 2000, the sampling design was modified in 2001. Ten sampling sites in the Tar-Pamlico River were selected for 2001. The section of the river that was chosen is located entirely in North Carolina. It runs through urban, suburban and rural areas before reaching the Pamlico Sound. The town of Washington, NC marks the delineation between the freshwater Tar River and the brackish Pamlico River. The four sites in the Tar River, at the towns of Louisburg, Rocky Mount, Tarboro and Greenville, as well as the site in Washington were chosen because they are USGS continuous monitoring sites. The site in Swan Quarter was chosen due to its proximity to a large number of blue crab shedding operations. Samples at these six sites were collected from the river banks. The four

remaining sites, sites 6-9, in the Pamlico River were established monitoring sites of the North Carolina Department of Environment and Natural Resources (NCDENR). Surface water grab samples were collected on a biweekly basis from 5 May through 19 September for the sites in Louisburg, Tarboro, Greenville, Washington and Swan Quarter. Samples were collected from 5 May through 7 August in Rocky Mount but construction at the sampling site caused sampling to be terminated at that time. The four sites sampled by NCDENR were sampled from 19 April through 18 September on a biweekly basis. Each of the samples from these sites represented a composite of 2 to 3 samples collected in a cross section of the river. A 250-mL aliquot of water was collected at each site and combined into a single sample.

Sample Extraction and Analysis:

A total of 37 pesticides and 3 metabolites were analyzed in this study (Table 1). These compounds were chosen based on their estimated use in the region (Chapter 1), toxicity, whether the compounds had previously been detected in water samples from the region, and the ability to analyze all of the compounds in a single extraction.

Solid phase extraction with Empore C-18 Extraction disks (3M-Company, 47-mm diameter) was used to extract all water samples, with the exception of the samples collected in the farm drainage ditches in 2000. Those samples were extracted with mixed-mode extraction cartridges to recover certain metabolites. Sample volumes were measured and spiked with surrogate internal standard

(diazinon d_{10}) prior to extraction. Samples were pre-filtered with glass microfiber filters (Whatman, GF/B, 1 μ m pore size) and nylon filters (Osmonics Inc, 0.45 μ m pore size) to remove particulates. C-18 Empore Extraction disks were conditioned using ethyl acetate and methanol. Samples were extracted using the Empore C₁₈ extraction method described by Mueller et al. (2000). Extracts were concentrated under N₂ gas. Samples were analyzed by GC-MS with the method described by Zuagg et al. (1995), which was modified to include additional pesticides of interest (Table 1). Thirty-two pesticides were analyzed for each year, 3 metabolites were analyzed in 2000 and 2 metabolites were analyzed for in 2001.

Results:

Of the 35 pesticides and metabolites analyzed in 2000, a total of 13 were detected in the water samples (Table 1). Atrazine (70% of samples), alachlor (85%), metolachlor (100%) and simazine (78%) were the most commonly detected pesticides in this region in 2000 (Figure 2). The highest concentrations of these compounds were detected in the Tar River (Figure 3). With the exception of simazine, these compounds have historically been shown to be the most frequently detected pesticides in the region, as well as being the most commonly applied herbicides (NCDEM, 1994). Concentrations of atrazine, chlorpyrifos and metolachlor were found to exceed the aquatic life criteria (AQLC- see definition in appendix) (1800 ng/L for atrazine, 3.5 ng/L for chlorpyrifos, 7800 ng/L for metolachlor) (USGS, 1999). Alachlor, atrazine and metolachlor were found to

exceed the safe drinking water criteria (2000 ng/ L for alachlor, 3000 ng/ L for atrazine, 70000 ng/ L for metolachlor) (USGS, 1999). These drinking water criteria were presented for comparative purposes only because these surface waters are not used as a drinking water source. It should be noted that these values, for both aquatic life criteria and safe drinking water criteria, are unavailable for many of the other compounds analyzed and detected.

Samples collected from the Beaufort county farm showed that atrazine, a pre-emergent herbicide used on corn, exhibited expected peak concentrations following application in spring (Figure 4). Desethylatrazine, the main atrazine metabolite, shows a similar pattern (Figure 4). Cyanazine, a post-emergent herbicide used on both corn and cotton, and cyanazine-amide, the main cyanazine metabolite, peaked later in the season (Figure 4). Desisopropylatrazine is a metabolite of both atrazine and cyanazine. It follows atrazine with a slight lag period and then increases again following the cyanazine pattern, thus peaking twice during the growing season.

Thirty-four pesticides and metabolites were analyzed in samples collected from the Tar-Pamlico River in 2001 and 18 were detected. As seen in 2000, atrazine (in 38% of samples), metolachlor (72%) and simazine (27%) were the most commonly detected pesticides in the region (Figure 2). Alachlor was detected in only 2 of the 103 samples analyzed. Prometryn was found in 24% of the samples but was not detected in any sample collected earlier than mid-July. The mean pesticide concentrations measured in 2001 were lower than those measured in 2000

(Figure 5). Aquatic life criteria and safe drinking water criteria were not exceeded for any compound in 2001.

Even though atrazine is a pre-emergent herbicide commonly used on corn, this triazine herbicide can be used for season long weed control. In the Tar-Pamlico River Basin, the heaviest applications of atrazine occur in May and June, with the greatest usage being in Beaufort County where corn is one of the primary crops (Chapter 1). Atrazine concentrations were detected in samples beginning in early May 2001 (Figure 6a) and concentrations remained elevated through June, and then began a slow decline. The highest concentrations of atrazine were detected in the estuarine region of Beaufort County (sites 5 to 9).

Belonging to the same class of pesticides as atrazine, simazine is a selective pre-emergent herbicide that is commonly used for weed control in corn. It is not one of the more commonly applied agricultural herbicides in the region (Chapter 1). Yet it is often found in measurable concentrations in water samples in this region (Figure 6b). Simazine is licensed for nonspecific control of weeds in industrial areas and at higher application rates than in agricultural fields. Coefficients of use have never been calculated for non-agricultural use of pesticides. Therefore, it is not possible to estimate how much simazine is applied for non-agricultural purposes each year. As seen with atrazine, the highest concentrations of simazine were detected in Beaufort County (Figure 6b). Samples collected in mid-April contained the highest concentration of simazine detected in 2001. Concentrations decreased over the

course of the spring and summer and no simazine was detected later than early August.

Prometryn, another triazine herbicide that is used for post-emergent control of broadleaf weeds in cotton fields, was not detected in any sample prior to mid-July maximum concentrations were detected in late July 2001 (Figure 6c).

Metolachlor is a pre-emergent chloracetanilide herbicide commonly used on crops such as corn, cotton, sorghum and is applied most heavily in Beaufort and Edgecombe counties of North Carolina. The heaviest application of metolachlor occurs in May and June (Pait, 1992). The highest concentration of metolachlor was detected at Washington, North Carolina, although the highest mean concentration was detected upstream at site 4 (Figure 6d). Metolachlor concentrations peaked in mid-June and persisted at low levels throughout the growing season (Figure 6d). The pesticide concentrations of metolachlor, as well as the triazine herbicides, degrade rapidly in the ecosystem. No cumulative effects are expected to be seen between the growing seasons.

There has been concern among local fisherman that fish kills in the Albemarle-Pamlico drainage basin may be attributable, at least in part, to pesticide exposure. A comparison of peak pesticide concentrations and fish kills in 2001 was performed. In 2001, there were eighteen fish kills in the lower Tar-Pamlico River Basin (Figures 7-9) (NCDWQ, 2001; USGS, 2002). The primary species affected was menhaden. Eight of these events occurred after September 19, the final day of field sampling. The major period of pesticide application had already ended and

pesticide concentrations were declining (Figure 6). Nine of the remaining ten die-offs occurred in a six week period from July 3 to August 13. The concentrations of the pre-emergent herbicides had peaked two weeks earlier and were in decline. Concentrations of the post-emergent herbicide prometryn peak during this period in time when the maximum concentration measured was 57 ng/L, considerably less than the concentration shown to cause acute toxicity (EPA, 1987). Low dissolved oxygen levels and algal blooms were believed to be the primary causative factors leading to the fish kills (NCDWQ, 2001).

Discussion:

Studies have shown that the pesticide detection rates in the APES as well as the pesticide use rates in the region are among the highest in U.S. coastal drainage basin. However, pesticide concentrations, as measured in the study, do not indicate that pesticides are likely to be having an adverse effect on the ecological health of the ecosystem.

While many of the compounds detected were the same in both 2000 and 2001, the concentrations were noticeably different. The concentrations measured in 2001 are less than those measured in 2000 for a number of the compounds detected. Among the most frequently detected compounds; alachlor, atrazine, metolachlor, and simazine, the mean concentrations were at least 20 times higher in 2000 than in 2001. Similar decreases were observed in samples analyzed from the region in the early 1990s compared to the samples collected as part of this study

(Figure 5) (Spruill, 1998; Woodside, 1996, Woodside, 2001). Atrazine and metolachlor concentrations typically peak in North Carolina between May and June (Spruill, 1998), which is consistent with our results where atrazine levels remained elevated from early May through June in 2001 and from March through May in 2000, and metolachlor peaking in mid-June. Atrazine and metolachlor have been, and continue to be, the most commonly detected compounds in the Tar-Pamlico River Basin (Figure 3) (Woodside, 2001). Alachlor is among the most commonly detected compounds, as well as being one of the compounds with the highest mean concentrations in the Tar-Pamlico River Basin (Spruill, 1998, Woodside, 2001). The data from 2000 supported these observations. However, alachlor concentrations decreased significantly in 2001. This decrease in 2001 coincided with a decrease in alachlor use in the region due to an increase in the use of Roundup™ [Mac Gibbs, NC Cooperative Extension Service, Hyde County Center, personal communication]. I expect that alachlor will be detected less frequently in the future as farmers switch to Roundup™ ready seed.

From January through early June 2001, eastern North Carolina, including much of the Tar-Pamlico drainage basin, experienced conditions that ranged from abnormally dry to a moderate drought as designated by the US Drought Monitor. By the end of the year, the town of Washington in Beaufort County had received 13.6 inches less rain than the mean annual precipitation, and 12.2 inches less than 2000. By the end of May, Washington had already received over 5 inches less rain than a normal year, including 2000. The drought was less severe to the west. Heavy

rainfall in the city of Rocky Mount in March 2001 had rainfall totals falling only 0.7 inches below the mean precipitation expected between January and May. Dry conditions from July until December would bring the total annual rainfall to 5.2 inches below the average annual precipitation. Abnormally high amounts of precipitation, 7.81 inches, were recorded in Washington in June of 2001. The majority of this rain, 5.6 inches, fell in a four day period from 13 June to 16 June. The samples that were collected on 13 June 2001 were collected prior to the start of the rain event and therefore missed any increase in concentration that would have been expected as a result of the run-off. As seen in Figure 6 concentrations of the most frequently detected pesticides decrease rapidly. A substantial decrease in pesticide concentration is likely to have occurred in the two week interval between the start of the rain event and the following sampling date.

Non-point source run-off is one way that pesticides are transported into a water body. The dry conditions experienced in 2001 during the period of peak applications of many of the pre-emergent herbicides most likely contributed to the reduced concentrations that were observed in the Tar-Pamlico drainage basin during the 2001 growing season.

Information on the toxicity of current-use pesticides, both acute and chronic, to estuarine species is limited. LC_{50} values for compounds such as alachlor (35 mg/L) and metolachlor (25 mg/L) have been determined for *Daphnia* (Table 2) (Kamrin, 1997; Jarvinen, 1999). These values are over 100 times greater than the maximum concentrations measured in this study. To my knowledge, there are no

LC₅₀ values in estuarine species available for atrazine, prometryn or simazine. However, LC₅₀ studies have been conducted with non-estuarine aquatic species. The concentrations required to cause acute toxicity in these species are at least 100 times greater than the mean concentrations measured in the APES in either 2000 or 2001. Therefore, it is unlikely that the estuarine species that reside in this region are exposed to concentrations would have a deleterious effect on their short-term survival.

Water quality guidelines (AQLC) have been established to protect aquatic species from toxic effects due to chronic exposure to pesticides (Table 2) (CCREM, 1987). In 2000, the concentrations of atrazine, chlorpyrifos and metolachlor exceeded the AQLC in certain samples (Figure 3). The samples collected in 2001 showed that these concentrations did not persist for long periods of time, thus, reducing the probability of chronic toxicity to the exposed organisms. The pesticide concentrations that were measured in 2001 were at least an order of magnitude less than the AQLC values.

The lack of toxicity data for current-use pesticides and estuarine species makes it difficult to assess the ecological impact of these pesticides in estuaries. In 2001, the majority of the fish kills that occurred in the Tar-Pamlico River Basin involved menhaden. Currently no studies have been conducted to determine either the acute or chronic toxicity of pesticides on this species. In addition, it can be expected that species in the environment will be exposed to a number of chemicals at any given time. Synergistic or additive effects of current-use pesticides are not

currently known for the majority of the compounds that are available. Based on existing measures of acute toxicity in freshwater species as well as chronic toxicity indicators, such as aquatic life criteria and safe drinking water criteria, I determined that the concentrations of pesticides in the APES were unlikely to result in any adverse effects. In order to further test this conclusion the peak pesticide concentrations that were measured in the Tar-Pamlico River Basin in 2001 were compared to information on fish kills that occurred in the river. The majority of fish kills that were observed in the region occurred at least one month after peak pesticide concentrations were observed. Therefore, I concluded that current-use pesticides are most likely not the cause of the lethal effects seen on the species in the region.

If pesticides were responsible for the fish kills that are regularly observed in this region, it would be expected that more die-offs would be observed in the months of May and June, when many of the pesticides applied have reached their peak concentrations. While prometryn concentrations peak during the six-week period from July to August, the concentrations were too low to cause acute toxicity.

Acknowledgments

We would like to thank Larry Ausley, Garcy Ward and the Pamlico River Response Team of the North Carolina Department of Environment and Natural Resources for their assistance. This project was partially funded by North Carolina Sea Grant and the North Carolina Department of Environmental and Natural Resources.

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Figure captions

Figure 1. Sampling sites in the Albemarle-Pamlico Drainage Basin; 2000-2001

Figure 2. The frequency of detection of pesticides in the Albemarle-Pamlico drainage basin.

Figure 3. Surface water samples collected in 2000 from the Pamlico Sound drainage basin, NC.

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Figure 7. Minimum dissolved oxygen levels in the Pamlico River at Washington, NC in 2001 in relation to peak concentrations of metolachlor and fish kill events.

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Figure 9. Minimum dissolved oxygen levels in the Pamlico River near the Pungo River, NC in 2001 in relation to peak concentrations of metolachlor and fish kill events.

Table 1- Pesticides measured in the Albemarle-Pamlico Estuarine System; 2000-2001 (ng/L)

Pesticide	Detected By	Mean Conc. 2000	Std Dev. 2000	Mean Conc. 2001	Std. Dev. 2001.00	Lowest LC ₅₀ (ng/L)	AQLC (ng/L)
Herbicides							
alachlor	B	489.17	1248.94	bdl	na	1800000	
atrazine	B	1754.36	6973.07	13.21	21.59	4300000	1800
benfluralin	B	11.44	14.36	bdl	na		
butylate	N	bdl	na	0.59	0.75	4200000	
cyanazine	B	10.31	13.16	bdl	na	7500000	2000
dacthal (DCPA)	U	bdl	na	0.52	0.16		
EPTC	N	bdl	na	na	na	19000000	
ethalfuralin	N	bdl	na	bdl	na		
flumetralin	ND	na	na	bdl	na	30000000	
linuron	N	bdl	na	na	na	1600000	7000
metolachlor	B	2857.20	13670.70	46.53	77.33	2000000	7800
metribuzin	B	24.72	71.95	9.70	49.84	4500000	1000
mollinate	B	bdl	na	bdl	na	300000	
napropamide	N	12.25	19.80	bdl	na	9000000	
pebulate	B	bdl	na	bdl	na	7400000	
pendimethalin	N	10.50	19.80	bdl	na	138000	
prometon	B	76.07	76.07	0.86	2.18		
prometryn	U	na	na	7.66	12.28	2500000	
simazine	B	89.86	163.67	5.22	10.14	100000	10000
tebuthiuron	N	bdl	na	0.60	0.58	87000000	1600
tribufos	U	na	na	0.72	1.81		
trifluralin	N	bdl	na	3.06	16.00	11000	200
Herbicide Metabolites							
2,6-diethylaniline	B	73.67	193.00	0.53	0.19		
deethylatrazine	B	95.08	284.37	na	na		
desisopropylatrazine	U	na	na	2.34	5.47		
Fungicides							
chlorothalonil	U	bdl	na	0.65	0.75	250000	180
Insecticides							
carbaryl	B	14.25	14.25	0.93	3.64	1300000	200
carbofuran	N	bdl	na	bdl	na	380000	1800
chlorpyrifos	B	5.14	0.83	bdl	na	2600	3.5
diazinon	N	bdl	na	1.73	4.92	52000	
dimethoate	ND	bdl	na	na	na	20000000	6200
disulfoton	N	bdl	na	0.88	3.21	38000	
ethoprop	N	bdl	na	bdl	na	2100000	
fenamiphos	ND	na	na	bdl	na	110000	
fonofos	N	bdl	na	bdl	na	45000	
malathion	N	bdl	na	na	na	1000000	
methyl parathion	U	bdl	na	bdl	na	1900000	
permethrin	B	bdl	na	1.23	3.01	1800	
phorate	N	bdl	na	na	na	110	
terbufos	N	bdl	na	bdl	na	200	

bdl=below detection limit, na= not available, N=NAWQA, U=NCSU, B=Both
H= Herbicide, I= Insecticide, F= Fungicide, d-H= Herbicide metabolite
AQLC= Aquatic Life Criteria (CCREM, 1987)

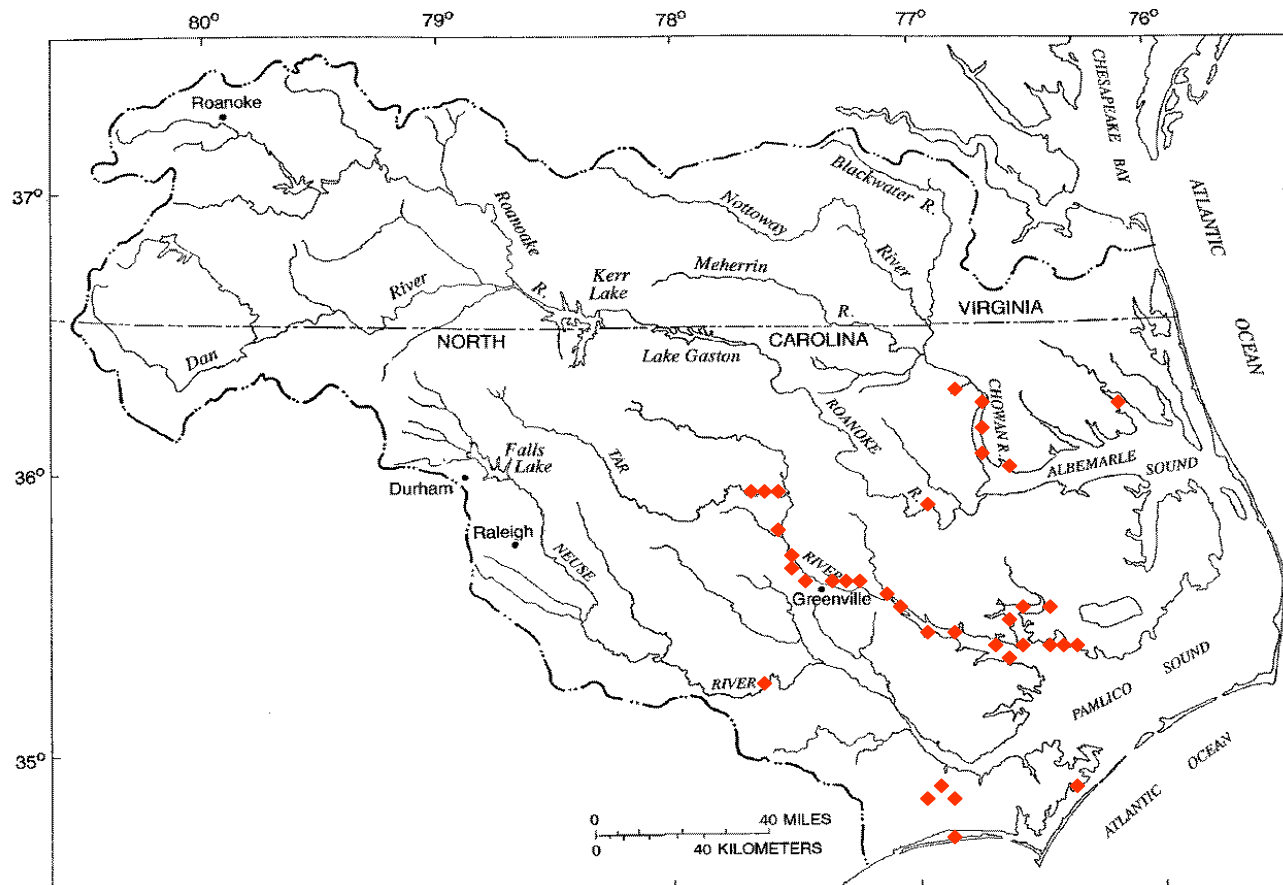


Figure 1- Sampling sites in the Albemarle-Pamlico Drainage Basin; 2000-2001. Study sites in the Tar-Pamlico River Basin in 2001 were 1) Louisburg, 2) Rocky Mount, 3) Tarboro, 4) Greenville, 5) Washington, 6) Whichard's Beach, 7) Blount's Bay, 8) Southeast of Blount's Bay, 9) Mouth of the Pungo River, 10) Swanquarter

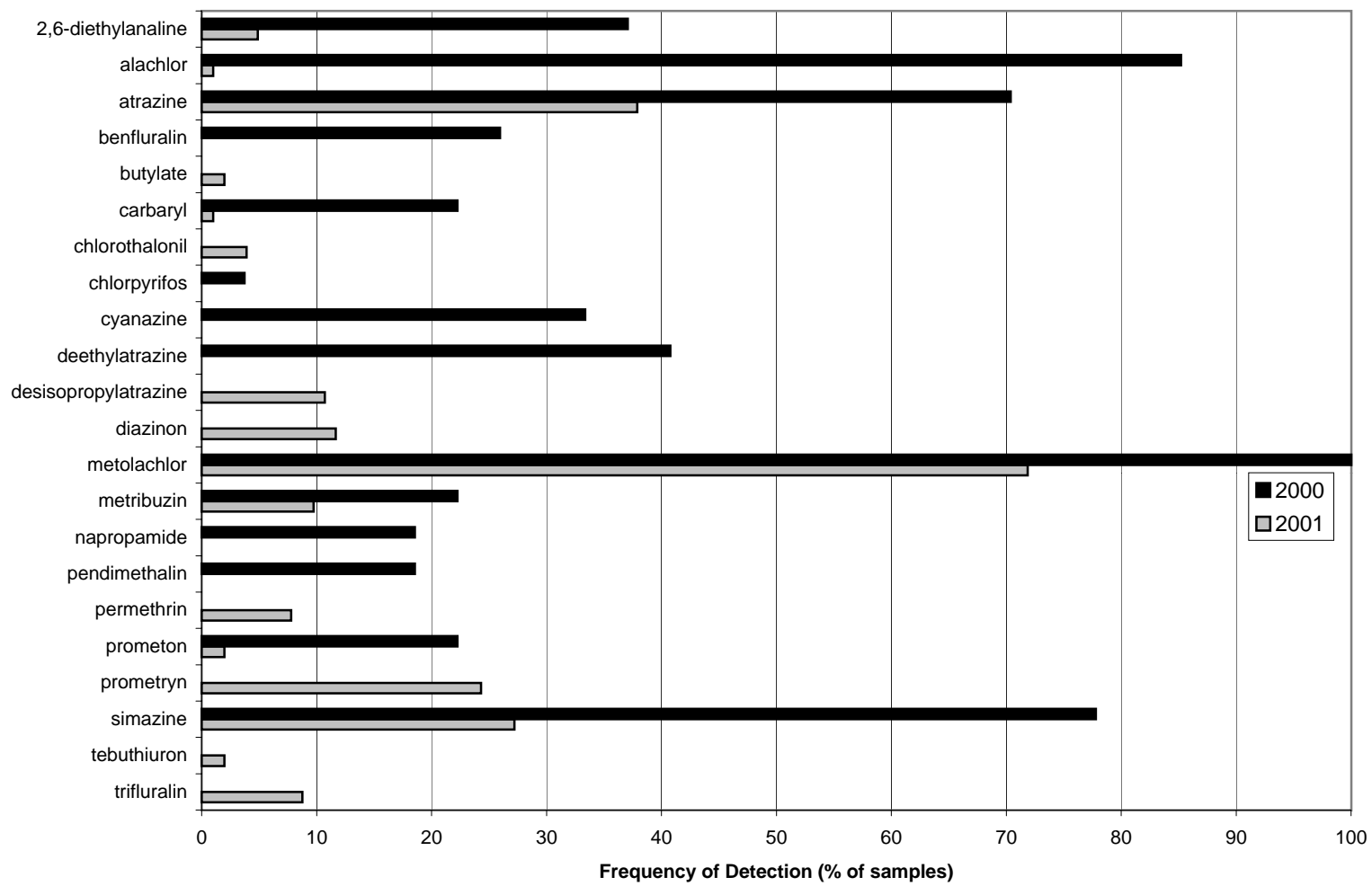


Figure 2- The frequency of detection of pesticides in the Albemarle-Pamlico drainage basin

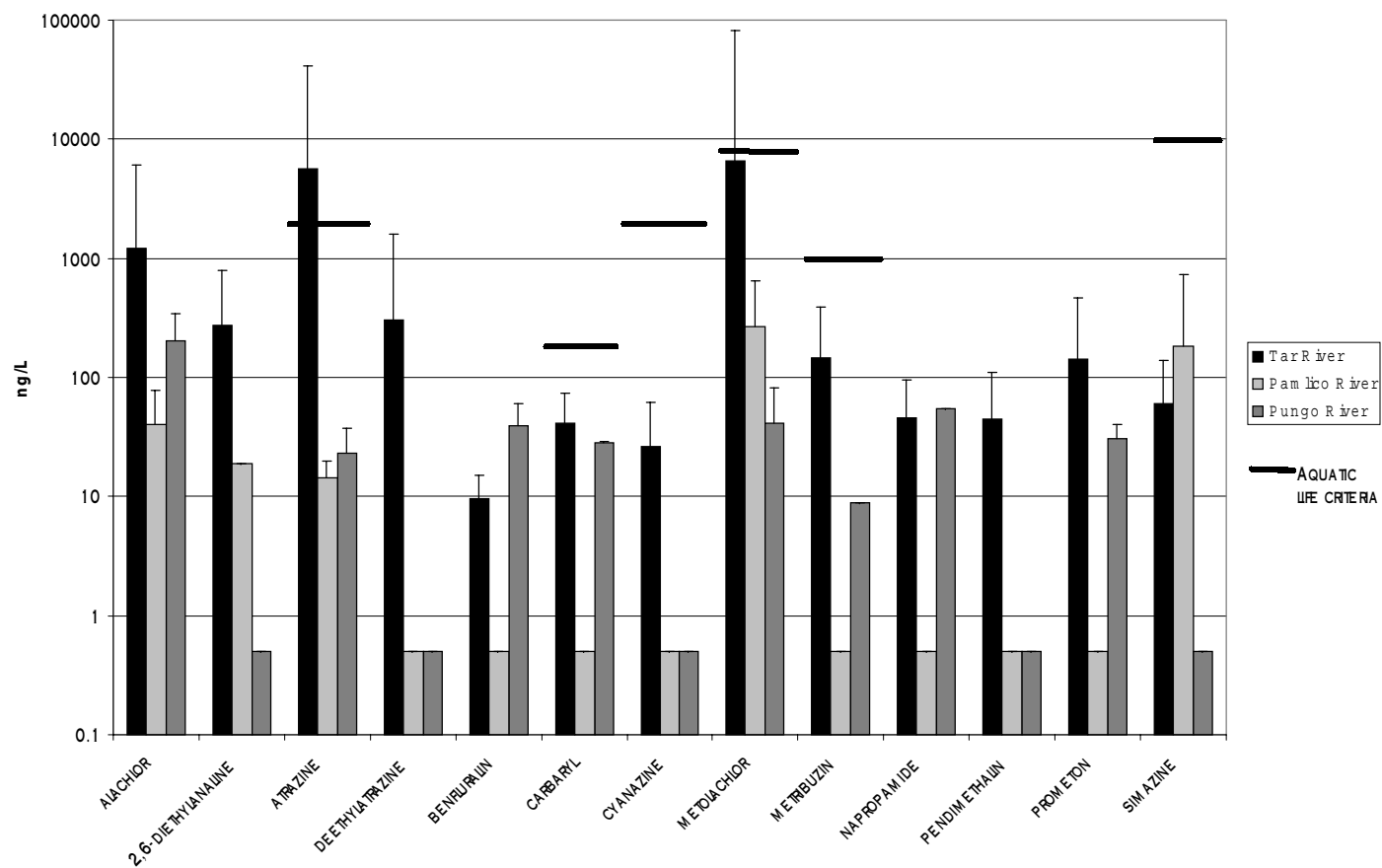


Figure 3- Surface water samples collected in 2000 from the Pamlico Sound drainage basin, NC.
 (Mean concentration represented by solid bars, maximum concentration detected represented by vertical lines)

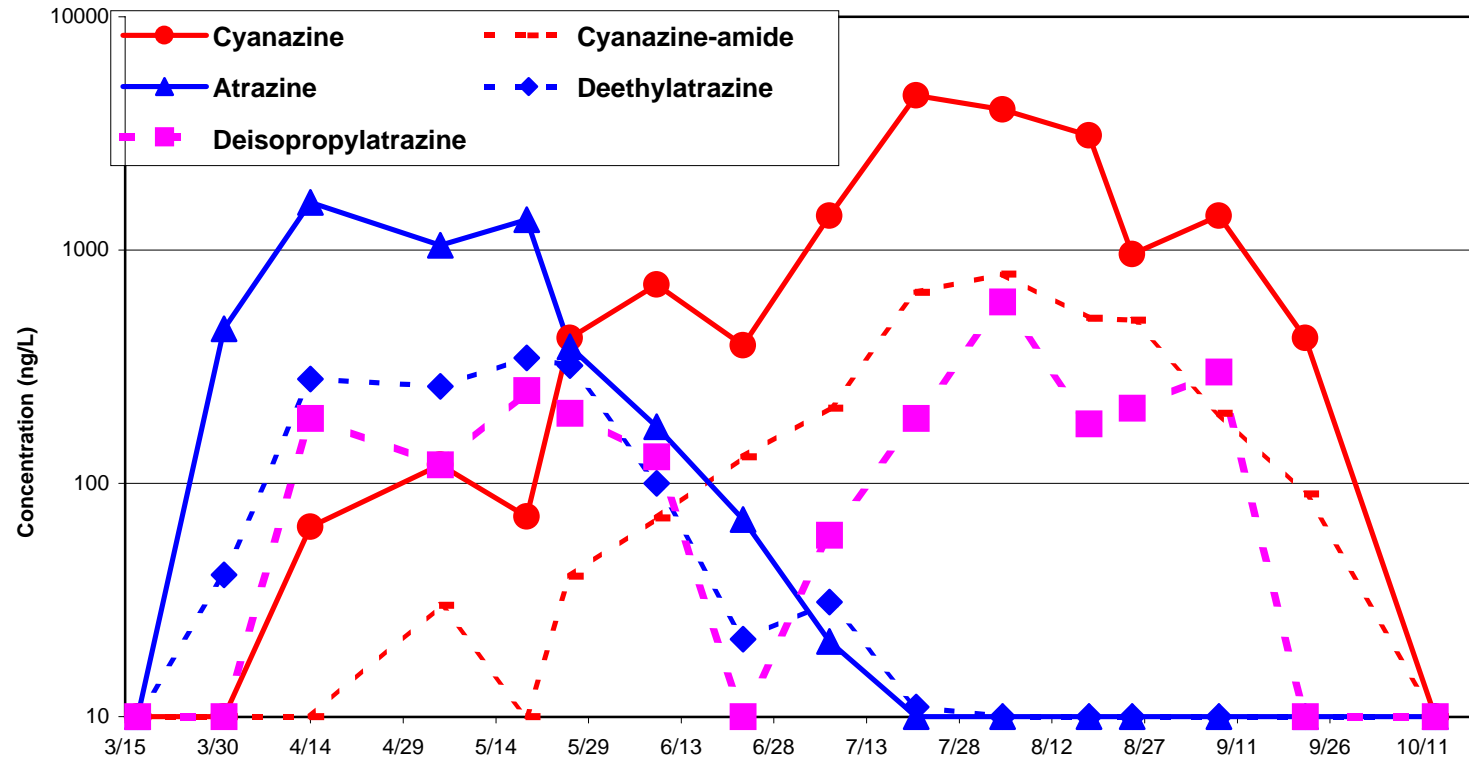


Figure 4- Pesticide concentrations measured in samples of water collected near a cotton farm in eastern NC during the 2000 growing season.

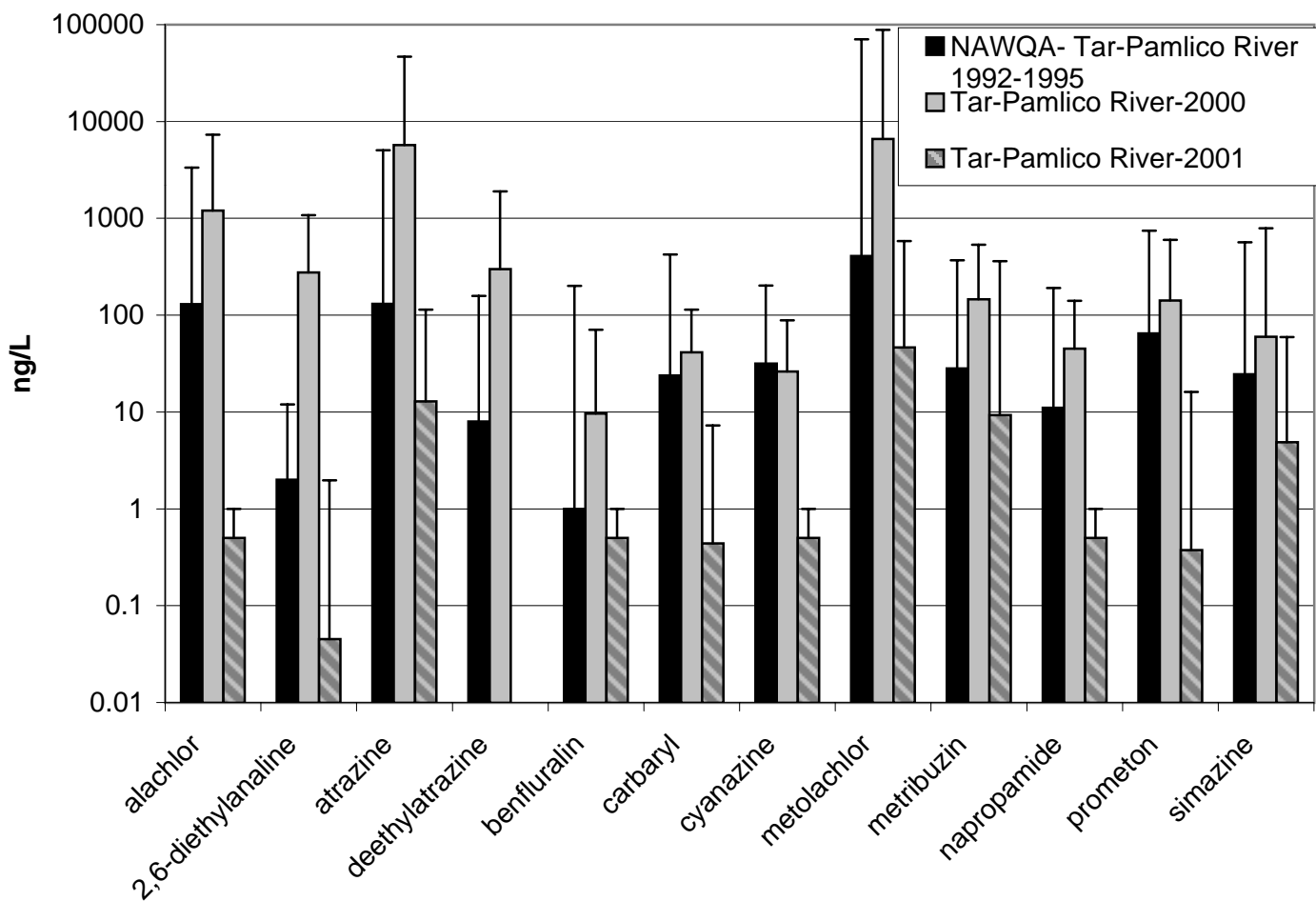


Figure 5 - The mean and maximum pesticide concentrations of the most commonly detected pesticides in the Tar-Pamlico River Basin for the period 1992-1995, 2000 and 2001. Note decreased concentrations in 2001.

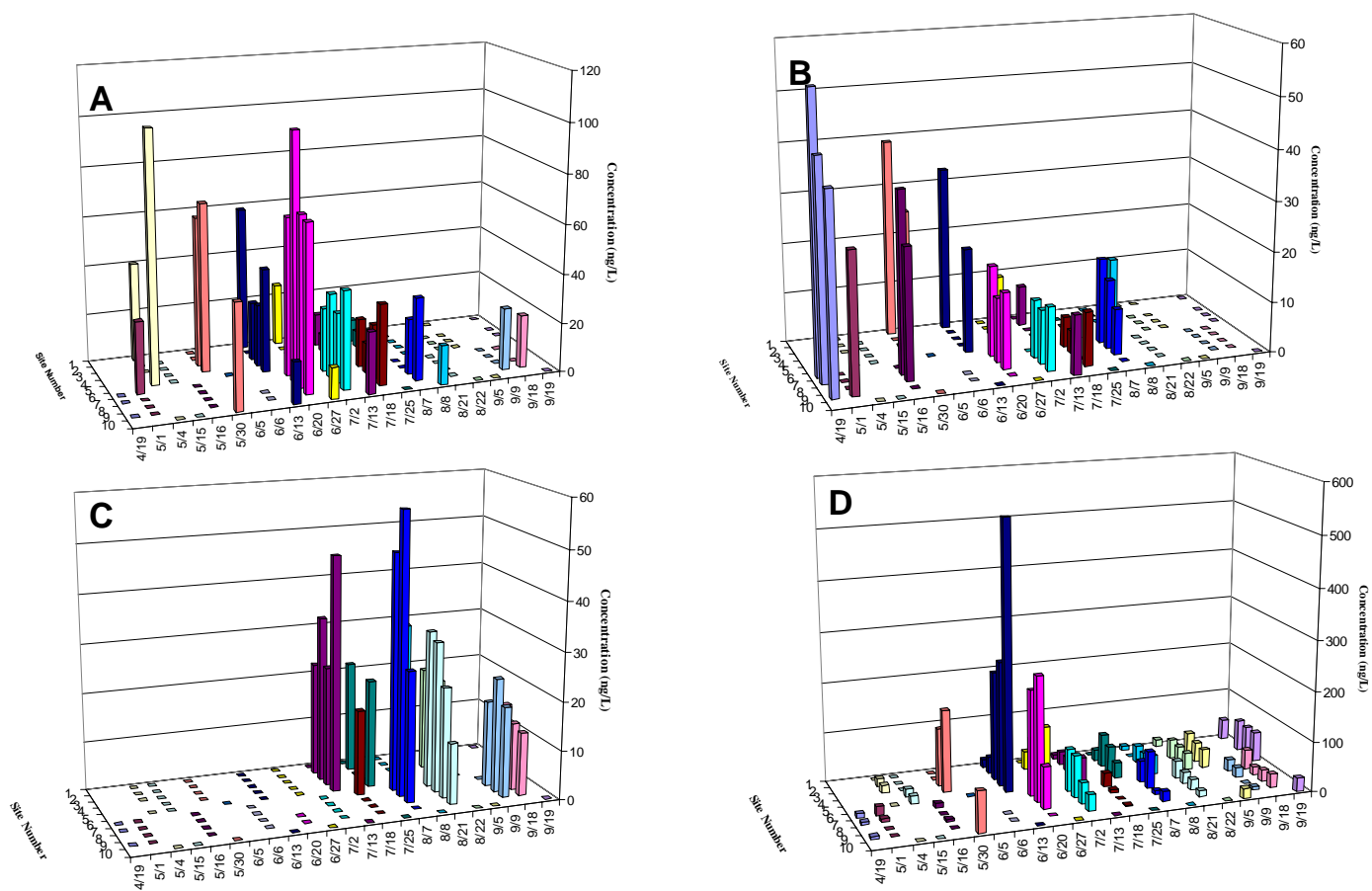


Figure 6- Concentrations (ng/L) of Atrazine (A), Simazine (B), Prometryn (C), and Metolachlor (D) showing differing concentration profiles that reflect the period of pesticide application. (Squares indicate date site was sampled)

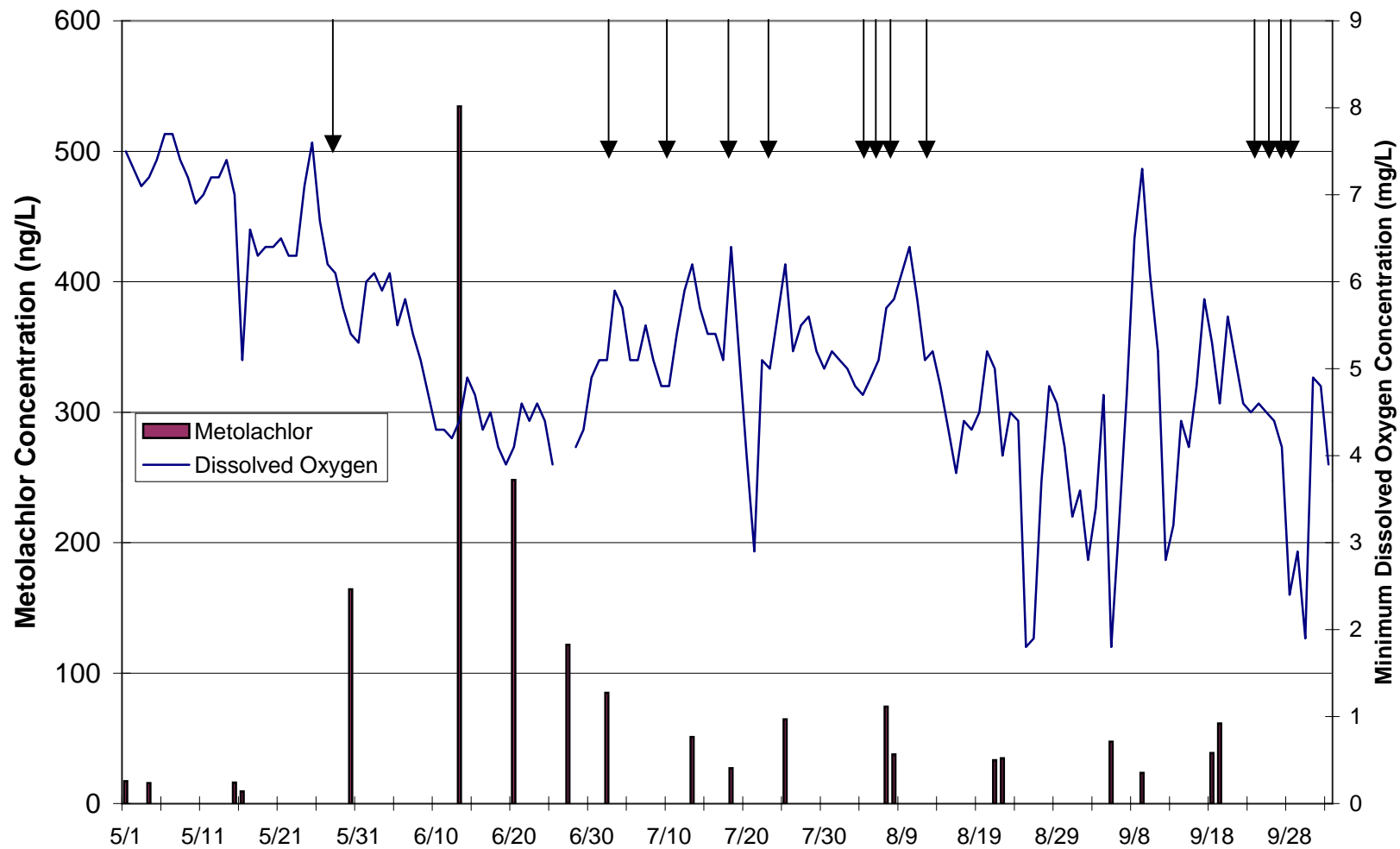


Figure 7- Minimum dissolved oxygen levels in the Pamlico River at Washington, NC in 2001 in relation to peak concentrations of metolachlor and fish kill events.

(Arrows denote fish kills)

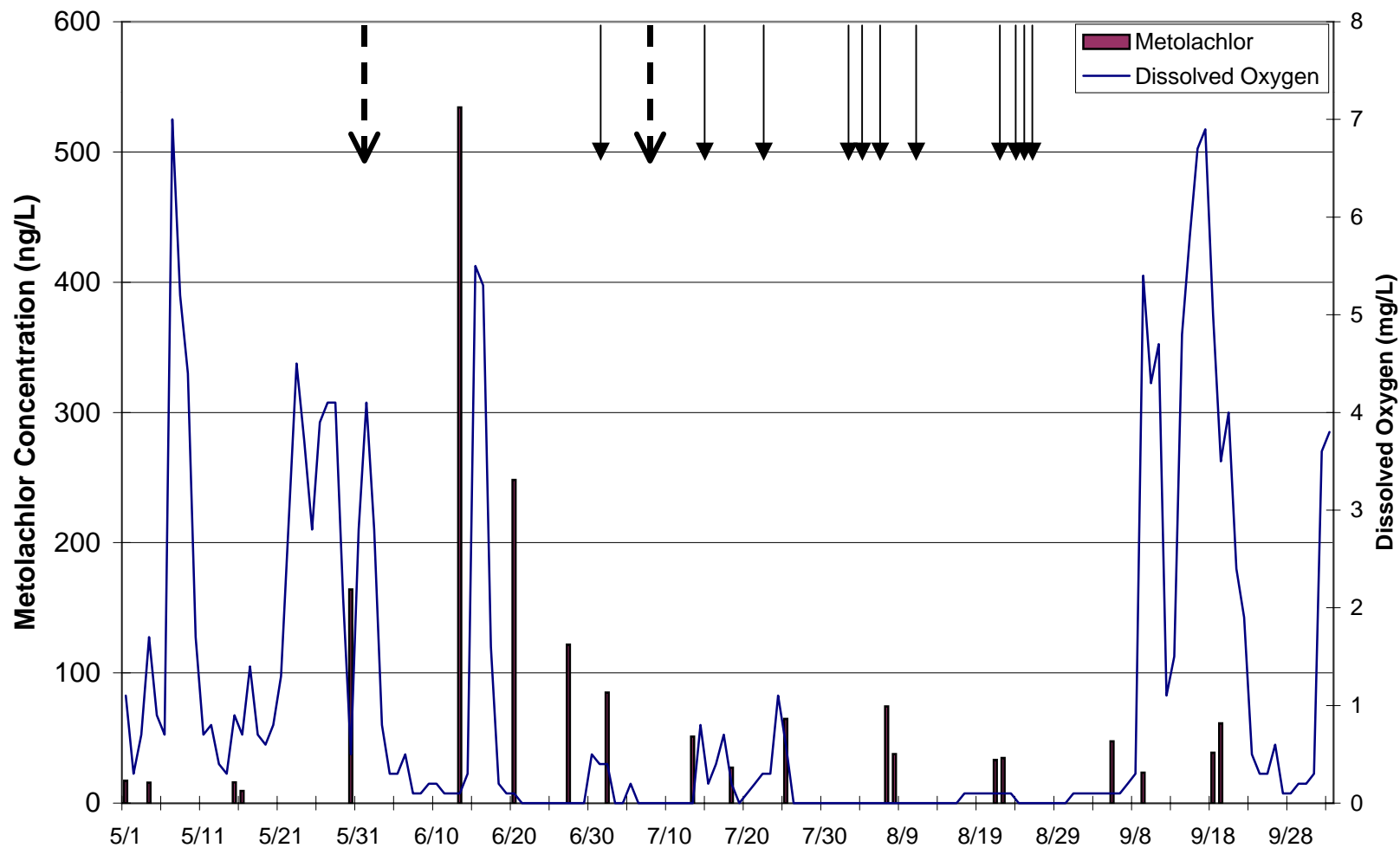


Figure 8- Minimum dissolved oxygen levels in the Pamlico River near Bath Creek in 2001 in relation to peak concentrations of metolachlor and fish kill events.

(Arrows denote fish kills, dotted arrows are fish kills in the area surrounding Bath Creek)

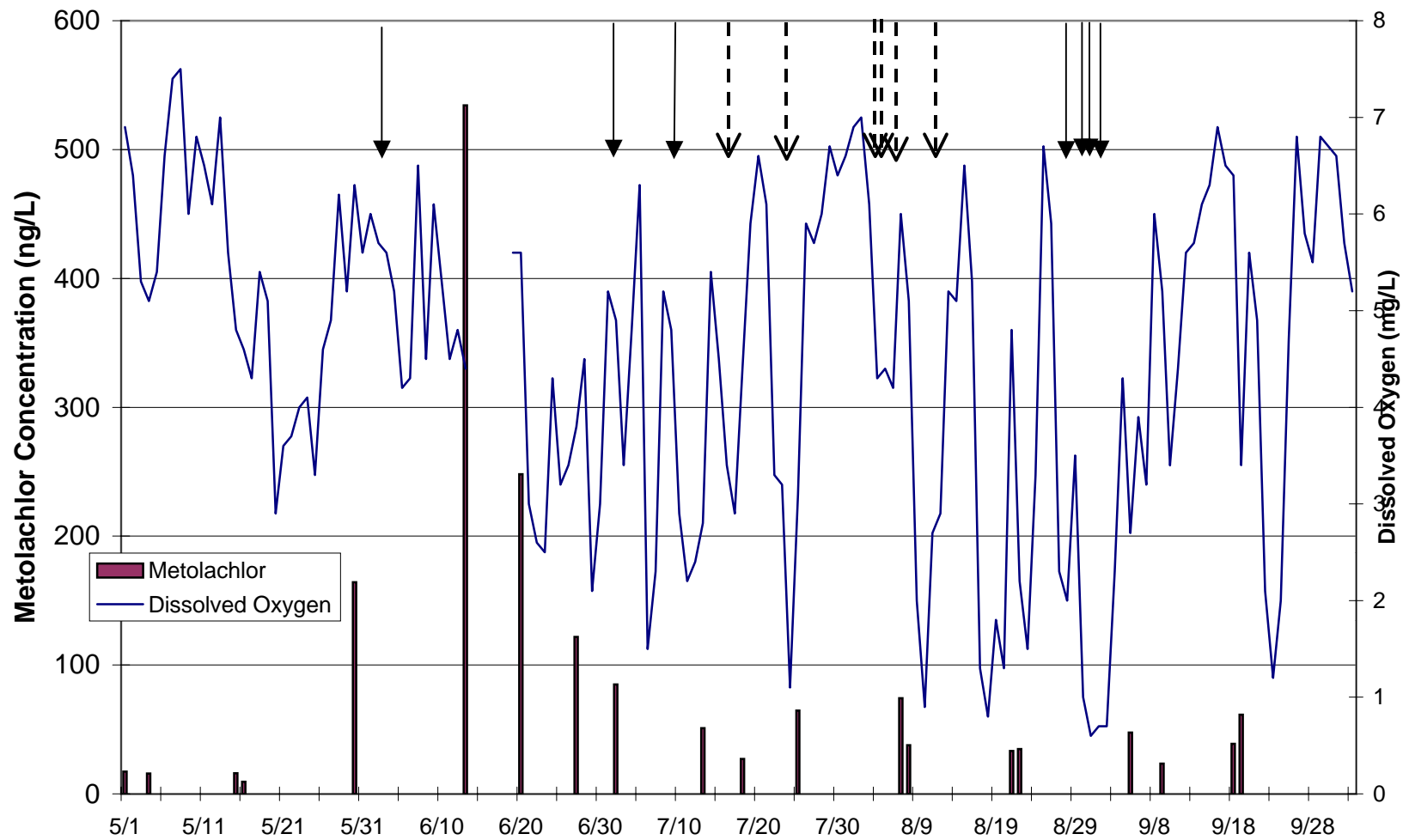


Figure 9- Minimum dissolved oxygen levels in the Pamlico River near the Pungo River in 2001 in relation to peak concentrations of metolachlor and fish kill events.

(Arrows denote fish kills, dotted arrows denote fish kills in or near the Pungo River)

CHAPTER 3

MODELING PESTICIDE FATE IN A SMALL TIDAL ESTUARY USING EXAMS

AND THE FUGACITY-BASED MULTI-MEDIA FATE MODEL CHEMCAN

Abstract:

The Exposure Analysis Modeling System (EXAMS), a pesticide fate model developed by the U.S. Environmental Protection Agency, was modified to model the fate of the herbicides atrazine and metolachlor in a small tidal estuary (Bath Creek) in North Carolina. The modifications simulated the changes in the estuary that occur during the tidal cycle. Two models were created using EXAMS, a steady state model and a tidally driven model. The EXAMS steady state model was compared to the multimedia fugacity-based model ChemCan. The models were validated with measured empirical measures of atrazine and metolachlor concentrations in the estuary. The most accurate prediction of the atrazine and metolachlor concentrations in Bath Creek (115 ng/L and 187 ng/L respectively) were provided by the assumption that 10 percent of the pesticide that is applied in the drainage basin would be transported into the creek using the EXAMS steady state model. The predicted concentrations fell between the mean and maximum concentrations of the pesticides that have been measured in Bath Creek. ChemCan predicted atrazine concentrations between the mean and maximum concentrations that were measured in Bath Creek. However, the ChemCan models underpredicted the metolachlor concentrations. In the EXAMS tidal model, atrazine reaches equilibrium within the system in approximately 120 hours. Model simulations were terminated at 264 hours, before metolachlor achieved equilibrium. Concentrations of atrazine and metolachlor that have been measured in Bath Creek following a rain event were closely predicted by the EXAMS tidal model.

Introduction:

Traditional methods of determining pesticide exposure to the environment require extensive sampling that are costly and time intensive. In an attempt to more rapidly screen for areas that may be subject to environmental contamination, numerous pesticide fate models have been developed. A detailed description of many of these contaminant fate models is given in the appendix.

The Groundwater Loading Effects of Agricultural Management Systems (GLEAMS) model and the Pesticide Root Zone Model (PRZM) are two of the most commonly used pesticide fate models. GLEAMS predicts runoff, percolation and soil and chemical losses of a nutrient or pesticide at the edge of a field and from the root zone (Shirmohammadi, 1994; Rekolainen, 2000). The major limitation to GLEAMS is that it can overpredict water concentrations if it is used to model an entire watershed instead of a field. PRZM is a field scale model that was designed to simulate pesticide transport and transformation down through the root zone (Smith, 1991). PRZM was designed to be a one-dimensional model and was not designed to look at lateral movement of a chemical (Trevisan, 2000).

HSPF, or Hydrological Simulation Program FORTRAN, was developed to simulate the runoff and transportation of pesticides and nutrients from both urban and agricultural watersheds (Laroche, 1996). The major disadvantage with this model is that it has a tendency to overestimate the concentration of a compound in the watershed. The degree of this overestimation is dependent on both the pesticide and the watershed in question (Laroche, 1996).

The vast amount of data required for these models to accurately predict pesticide concentrations in a watershed make them costly to run. The need therefore exists for simpler, less expensive models capable of predicting pesticide concentrations within watersheds, within an order-of-magnitude, particularly for estuaries, which have been largely ignored in the development of contaminant fate models.

Numerous estuarine hydrologic and mixing models have been designed, to predict the fate of nutrients or metals in a system or to model parameters such as salinity and dissolved oxygen. Few have been designed to model the fate of pesticides in the estuaries. Most of these hydrologic models are very complex and are designed for a single estuarine system. Models such as the nitrogen loading model (NLM) and the estuarine loading model (ELM) were designed to predict at the fate of nutrients in estuaries in general, whereas the Cape Cod Commission model (CCC) and the Buzzard Bay Project model (BBP) were both created to predict the fate of nitrogen in specific estuaries in Massachusetts (Eichner, 1992; Costa, 1999; Valiela, 1997; Valiela, 2002a, Valiela, 2002b).

The Chesapeake Bay estuary model package (CBEMP) simulates dissolved oxygen processes that are dependent on temperature, wind mixing, water current advection, and chemical and biological processes (Wang, 2001). The Chesapeake Bay is a well-characterized estuary and data for such variables are readily available for this system. This type of detailed information is not available for a large proportion of the smaller estuaries in the United States. Moreover, it is impossible to

design a comparable model to the CBEMP for these systems without extensive sampling and the cost of sampling is often prohibitive. Simpler models, requiring less environmental data, are needed to predict order-of-magnitude concentrations of pesticides and other contaminants in these estuaries.

The United States Environmental Protection Agency (EPA) has historically used the standard agricultural field / farm pond scenario to represent pesticide concentrations, not only in the agricultural pond itself, but also concentrations in small upland streams and small estuaries. The standard EPA method consists of a two-step process. This process is conducted by linking the Pesticide Root Zone Model (PRZM), which simulates the leaching of pesticides from an agricultural field into groundwater, to the Exposure Analysis Modeling System (EXAMS) for a standard agricultural field or farm pond. Studies of upper-level concentrations measured in small upland streams show that procedure is reasonable for these environments (Laurence Libelo, USEPA, Personal Communication). This process has not been validated for estuaries due to the limited availability of contamination data.

Few data exist on pesticide concentrations in estuarine environments located near agricultural areas, but constant stream inflow, wind and tidally-influenced hydrodynamics, as well as complex estuarine chemistry, make these environments significantly different from fresh surface water bodies. Estuaries are brackish water environments that can experience fluctuations in salinity as a result of tides or increased freshwater input from precipitation.

Publications describing simulation of pesticide fate and transport in estuaries are limited (Kolset, 1998; Siewicki, 1997). Most of the pesticide models are used to simulate transport at the field scale — movement of pesticides from the application site to ground water or to adjacent surface waters. There have been a few applications to estuaries of models that were designed primarily for freshwater systems, including the EXAMS model, but these applications required several simplifying assumptions (Kolset, 1998; Siewicki, 1997).

EXAMS is an interactive modeling system, designed by the EPA, that can be used to conduct rapid evaluations and error analyses of the probable aquatic fate of synthetic organic chemicals (Burns, 2000). The model combines chemical loadings, transport, and transformation into a set of differential equations using conservation of mass as an accounting principle. The model can account for the interaction between the aquatic environment, the properties of the chemical of interest, and environmental loading characteristics to predict the exposure, persistence and fate of synthetic chemicals in aquatic systems (Siewicki, 1997).

Another alternative to predict the fate and behavior of a compound in the environment are multimedia fugacity based models (Mackay, 1979, Mackay, 1981; Mackay, 1985). (Fugacity is a measure of the ability of a substance to escape from one phase to another.) Fugacity-based models are commonly used to predict the fate of chemicals, including pesticides, in the environment. The fate of a chemical in the environment is controlled by the physico-chemical properties of the compound and environmental parameters such as organic carbon content, that influence

chemical partitioning (Larson, 1997). Fugacity-based models are often used as an preliminary, inexpensive method of evaluating the fate of a compound in the environment. ChemCan is one such model, a steady state model that can be used to predict the fate of pesticides, polycyclic aromatic hydrocarbons and other organic compounds.

Unlike the EXAMS model, many fugacity-based models, including ChemCan, include all components of an ecosystem: air, sediment, soil and water. Each of these components is viewed as a single compartment. Without modification, it is not possible to subdivide the compartments of many of these models. Newer models, such as EcoFate, have addressed this issue (Gobas, 1998). The subdivision of the compartments allows for greater spatial resolution, which is especially useful when modeling large systems where environmental conditions can vary spatially.

Siewicki (1997) applied the EXAMS model to a segment of Murrells Inlet in South Carolina to model the fate of PAHs in the system. Because EXAMS was formulated to simulate the steady (time invariant) flow of water, sediment, and plankton, assumptions were required to apply the model to a dynamic estuary. These assumptions included an average water depth based on mid-tide water level, steady flow, an estimated and constant dispersion coefficient, and an average resuspension rate of bottom sediments. The model predicted sediment concentrations of PAHs that were within 30% of those measured in the inlet.

Kolset and Heiberg (1988) used EXAMS and the fugacity model FEQUM, which is an extended version of the fugacity model developed by Mackay and others

(Mackay, 1979; Mackay, 1981; Mackay, 1985) to simulate fate and transport of kraft mill effluent in a coastal bay in Sweden. Among other things, FEQUM differs from EXAMS in that it includes a somewhat more flexible description of the flow field, with advective flows beginning or terminating in any of the system compartments. Kolset and Heiberg (1988) used water flow rates (assumed to be steady) between compartments as the primary calibration parameter (i.e., flows were adjusted to achieve the best agreement between simulations and measurements).

Sato and Schnoor (1991) used three chemical fate models—SALSA (HydroQual, 1981), EXAMS, and TOXIC (Schnoor and McAvoy, 1981) to simulate the fate of dieldrin in a flood control reservoir in Iowa. Reservoirs are analogous to estuaries in some ways in that (1) density stratification plays a key role in both transport and biogeochemical processes, and (2) flows are unsteady. Sato and Schnoor (1991) divided the study reservoir into 5 water compartments, with the riverine portion of the reservoir represented by one compartment and the lacustrine portion of the reservoir represented by two layers. Average annual flow, suspended sediment, and dieldrin loading rates were provided as reservoir inflows. The models predicted concentrations of dieldrin within the water column that fell within the standard deviation of the concentrations that had been measured in the reservoir.

An estuarine pesticide fate and transport model should have the capability to simulate the unsteady flow processes associated with time variable inflows, tides, and wind. Moreover, longitudinal and vertical salinity gradients govern transport and mixing processes and, because of spatial and temporal variations in ionic strength,

may play a role in some chemical transformations. Because of the size of some estuarine systems, lateral heterogeneities should not be ignored.

The purpose of the study was to modify the existing EXAMS program to develop a model that was suitable for predicting pesticide concentrations in the estuarine environment. In addition, the concentrations predicted in the aqueous environment by the EXAMS model would be compared to a fugacity-based model that required less data to determine which type of model was more appropriate for predicting pesticide concentration in the estuarine environment.

Methods:

Site Description

The area chosen for pesticide modeling was Bath Creek, a small tidal estuary, 4.2 km² in size, that is located in Beaufort County, NC, in the Tar-Pamlico River Basin. From 1992 to 1994, it was part of the U.S. Environmental Protection Agency's Environmental Modeling and Assessment Program (EMAP) study of the Carolinian Province (Balthis, 1998). This study measured many of the parameters necessary for the development of an EXAMS model (Table 1). The western edge of the county marks the beginning of the estuarine portion of the river basin often referred to as the Pamlico River, with Bath Creek located in the northern segment. The county is bisected by the Pamlico River. The primary cause of water turnover in Bath Creek is tidal surge (J. Bales, US Geological Survey, Raleigh, NC, personal communication). There is minimal freshwater input into the creek from agricultural

drainage ditches. Pesticide can enter the system through non-point source run-off or groundwater seepage or associated with stream flow. The tidal range in Bath Creek is approximately 0.3 meters. This means that almost one-ninth of the water in the system is replaced with each tidal cycle. Based on this information, it was estimated that the flushing time of water in the system was approximately nine days. Deployment of surface drogues in the bay confirmed an average residence time of 3.2 days, with shorter residence times near the mouth of the bay and longer residence times (up to 7 days) in more stagnant areas near the head of the bay (D. Shea, North Carolina State University, Raleigh, NC, personal communication).

Agriculture accounts for approximately 29% of the total land use in the county and covers more than 155,000 acres (NCDA, 2002). Beaufort County is the number one producer of corn in the state of North Carolina. The primary crop in the region, with 40% of the total agricultural acreage, is soybean (NCDA, 2002). Other important crops include cotton and wheat.

The most commonly applied pesticides in this region include the herbicides atrazine and metolachlor, which are also among the most frequently detected pesticides in the waters of the Tar-Pamlico River Basin (Woodside, 2001; Chapter 2) (Figure 1). Estimates of pesticide use for the county have shown that over 2700 pounds of active ingredient of atrazine and 1900 pounds of active ingredient of metolachlor are applied annually in the region (Table 2). The chemical parameters used to define these herbicides are shown in Table 2.

Steady state model

The first stage of the project involved the development of a steady state model for the Bath Creek system (Figure 2). This four-compartment model included two benthic compartments, and two water compartments, littoral and epilimnion. Tidal input was ignored in this model. The primary water input influencing residence time in this model was stream flow into the littoral zone, which was used to simulate the three-day residence time of water in the system.

For atrazine and metolachlor, one of the primary mechanisms of chemical input into a water body would be through non-point source run-off into either the water body in question or the tributaries. For the purposes of this model, I assumed that the pesticides entered Bath Creek directly in the form of a non-point source load since there is no data regarding the concentrations of the pesticides in groundwater or precipitation.

The non-point source load of chemical was entered in two different ways. The worst-case scenario assumed that 100 percent of the pesticide that was applied in the Bath Creek drainage basin would enter the system as run-off. For a more realistic chemical input, I assumed that either 3 or 10 percent of the atrazine and metolachlor that were applied in the basin would enter Bath Creek. Studies have shown the 10% input to be a realistic input of pesticide input following a rain event (D. Shea, NC State University, Raleigh, NC, personal communication). The minimum pesticide input observed within a week of a rain event was 2% (D. Shea, NC State University, Raleigh, NC, personal communication).

Previous studies have measured the concentrations of atrazine and metolachlor throughout the Tar-Pamlico River Basin (Woodside, 1996; Woodside, 2001; Spruill, 1998; Skrobialowski, 1996) (Figure 3) (Chapter 2). I augmented this earlier work with measurements of pesticides within Bath Creek itself. These data are presented to provide a comparison to the concentrations predicted by the steady state EXAMS model and the fugacity-based ChemCan model (Table 3).

Tidal model (EXAMS)

The steady state model previously described does not take into account the influence of tides on the movement of water or chemicals in the system. A second model was developed to address this issue. A five-compartment model was developed to be run in mode 2 of the EXAMS program, with a hypolimnion beneath the epilimnion (Figure 4). The hypolimnion was added to allow for the necessary water flow that would be associated with an incoming tide. It can also be used to show the role of water column stratification in estuarine systems. The depth of the epilimnion was assumed to be twice that of the hypolimnion at all times. Tides were simulated by changing the area, depth and volume of the water in the system on an hourly basis, using mode 2 of the EXAMS program (Figure 5). During ebb tide, water enters the system as stream flow into the littoral compartment and chemical input remains as non-point source load. However, the rate of flow is decreased when compared to the steady state model to provide a more realistic depiction of water movement in the system. Few measurements of stream flow have been

conducted in Bath Creek, with recent measurements yielding a total flow range of approximately 20 – 50 ft³/ sec during normal late spring and summer flow periods (D. Shea, North Carolina State University, Raleigh, NC, personal communication). Prior to these measurements, it was necessary to estimate the stream flow into the littoral zone using measurements of stream flow in Durham Creek, a similar watershed which is located across the Pamlico River from Bath Creek. In the absence of actual measurements in Bath Creek, it was assumed that the average annual stream flow into Durham Creek, 35.8 ft³/ sec and was the same flow rate that would be seen in Bath Creek (Jerad Bales, US Geological Survey, Raleigh, NC, personal communication). Given the similarity of this value with the range measured in Bath Creek, we continued to use the value of 35.8 ft³/ sec for subsequent modeling. It was assumed that the depth of the water decreased at a steady rate during ebb tide, at the rate of 0.05 meters per hour resulting in a 0.3 meter change in depth from high tide to low tide. The area of the littoral zone is reduced during the period of ebb tide. It was assumed that the depth of the littoral zone would increase at a steady rate from 0 meter at the shoreline to a maximum depth of 1.4 meters at the interface with the epilimnion. It was calculated that a $1.65 \times 10^5 \text{ m}^2$ change in surface area would be associated with every 0.05 meter change in depth.

For the 6 hours of flood tide, an additional chemical and water input were added to the model. During these hours, water enters the system through both the littoral zone and the hypolimnion. The stream flow into the littoral zone is not changed. The source of water entering the hypolimnion during flood tide is the

Pamlico River. The stream flow was calculated by dividing the total change in water volume during the tidal cycle by the six hour period. It is assumed that the flow rate remains constant over these 6 hours. Measurements have shown that atrazine and metolachlor are frequently detected in the Pamlico River during the growing season. The mean concentration of atrazine (35.6 ng/L) and metolachlor (30.7 ng/L) were calculated for the 2001 sampling site that was located in closest proximity to Bath Creek (Chapter 2). Concentrations were converted into a kg/hr input rate. This input was used as a stream load that enters the hypolimnion and cycles through the epilimnion before exiting the system. It is assumed that the pesticide load entering the hypolimnion during flood tide is carried in from an upstream source to the Pamlico River. The pesticide that has previously exited the system is considered lost. The water movement in the Pamlico River makes this a valid assumption.

Fugacity-based model (ChemCan)

The ChemCan model includes air, sediment, soil and water compartments. Without modifications, the fugacity-based model does not allow for a subdivision of the water compartments. Atrazine and metolachlor input are modeled as a direct application to the soil. The chemical may then be transported into the other compartments. In order to most closely mimic the environmental conditions in the EXAMS model, the ChemCan environment was designed to be 99 percent water, the maximum allowed by the program. This overestimates the amount of the herbicide that will make its way into the water body by neglecting the processes of

soil sorption, uptake into plants and degradation. Therefore, a second set of model simulations were performed with an environment that was composed of 75 percent water. The creek is viewed as a single compartment that is homogeneously mixed. The average depth of the system was 2.3 m; the same depth used for the epilimnion in the steady state model. The model does not explicitly take into account stream flows. However, residence time of water in the system was included among the model parameters.

Results:

Steady State Model

When the assumption that 100 percent of the atrazine that was applied in the Bath Creek drainage basin is transported into Bath Creek was used, the EXAMS model predicted a peak concentration of 1146 ng/L. This exceeds the peak concentrations of atrazine that have been measured in the Pamlico River and Bath Creek by at least a factor of four (Table 3). At steady state 3.67 kilograms of atrazine would be found in the system. The peak concentration that is predicted by the model when it is assumed that only a fraction, 10 percent, of the total atrazine applied enters Bath Creek predicted a concentration in the system (115 ng/L) that fell between the mean and maximum concentrations that were measured in Bath Creek (68 to 270 ng/L).

Assuming a 100 percent input of pesticide applied in the drainage basin into Bath Creek resulted in a predicted concentration of metolachlor of 1874 ng/L. This

is more than twice the peak concentration measured in Bath Creek. A total of 25.4 kilograms are predicted to be in the system during steady state. The more realistic assumption, that 3 percent of the compound is transported into Bath Creek, under predicted the peak concentration measured in the Pamlico River by an order of magnitude. The most accurate prediction of the metolachlor concentration in Bath Creek was provided by the assumption that ten percent of the pesticide that is applied in the drainage basin would be transported into the creek. The predicted concentration, 187 ng/L, is between the mean and maximum metolachlor concentrations that were measured in Bath Creek.

EXAMS Tidal Model

The constantly changing volume of the tidal model causes the peak concentration of both atrazine and metolachlor to change with time (Figures 5 and 6). The differences in the concentrations seen during the tidal cycle are affected by the tidal range. As the tidal range increases, for example from 0.3 meters to 1 meter, the amplitude of the peak will increase. This is attributed to the change in volume, a larger tidal range results in a lower water volume in the system at low tide than would be exhibited with a shallow tidal range.

The model was validated using surface water concentrations of atrazine and metolachlor that were measured in Bath Creek in July 2002 following a rain event on 10 July. Chemical input into the tidal model was assumed to be ten percent of the total amount of pesticide applied to the Bath Creek drainage basin. The model

predicted concentrations of atrazine and metolachlor that are representative of the concentrations that were measured in the head waters of Bath Creek with atrazine concentrations approaching equilibrium in the model (Figure 7). The predicted EXAMS concentrations are representative of the concentration that is likely to be found in the littoral compartment. The head waters of Bath Creek are the most representative of this compartment. The concentration of atrazine in the head waters of Bath Creek peaked sooner than the model predicted. This is attributable to the pulsed nature of the chemical input following the rain event. The model assumed a continuous non-point source input of the chemical. When the chemical input into the model was decreased to zero to reflect the environmental conditions, a decrease in the total mass of the chemical was observed (Figure 8). Similar results were seen with metolachlor although the decrease in the total mass of the compound occurred at a slower rate due to the longer half life of the compound.

ChemCan

The fugacity-based ChemCan model predicted steady-state mean water concentrations close to those of the EXAMS model (Table 3). For atrazine, the ChemCan predictions fell between the EXAMS predictions using 3 and 10 % input. For metolachlor, the ChemCan predictions were slightly below the EXAMS predictions using 3% input. The majority of both atrazine and metolachlor, 99.7 and 99.9 percent, respectively, is predicted to be in the soil regardless of the percent water that comprises the environment. The remainder is transported into the water,

with negligible partitioning into either the sediment or the air. The peak pesticide concentrations that were predicted for the water were higher than the peak concentrations that EXAMS predicted based on a similar pesticide input into the water. The variations in pesticide concentration that are seen between the two environments are the result of very slight differences in the fraction of a percent of the pesticide that is transported into the water. The ChemCan model predictions for atrazine were between the mean and maximum concentrations measured in Bath Creek, but under-predicted metolachlor concentrations by a factor of 4 or more. However, overall the ChemCan predictions are well within an order of magnitude of both the EXAMS predictions and measured concentrations.

Discussion:

A number of the environmental parameters that are required by the EXAMS modeling system are important in predicting accurate environmental concentrations of pesticides. Tidal range can influence the concentrations seen during the tidal cycle. As the tidal range increases, for example from 0.3 meters to 1 meter, the predicted concentration of the pesticide will increase. This is attributed to the change in volume. A larger tidal range results in a smaller water volume in the system at low tide than would be exhibited with a shallow tidal range.

The primary degradation pathway of the compounds that are being modeled will influence which environmental parameters will be most influential in predicting accurate environmental concentrations. For example, an accurate measure of cloud

cover would be important for a compound that degrades by photolysis. Likewise, the benthic bacteria or bacterioplankton populations will influence the loss of chemicals that degrade as a result of aerobic metabolism. The depth of the benthic compartments or the organic carbon content of benthic compartments will influence the fate of compounds that have higher log K_{ow} values.

EXAMS calculates the half-lives of pesticides by using rate constants. In order to obtain an accurate estimate of the environmental pesticide concentration an accurate rate constant is needed for the primary mechanism of action. Loss of the chemical through minor degradation pathways can generally be ignored if the half-life of the compound in the model is representative of the overall chemical half-life.

The fugacity-based ChemCan model can best be compared to the steady state EXAMS model. Neither has a mechanism that allows for changing water flow or chemical loads with time. Both models fail to allow for the temporary nature of the input from a contaminated river that occurs during flood tide. The EXAMS tidal model most accurately depicts the tidally-driven hydrodynamics that are associated with estuaries. The tidal model was modified to simulate the chemical movement into an estuary that is associated with the tides, as well as the changing volume and area, although it is impossible to fully describe the complex estuarine hydrodynamics.

There is relatively little discrepancy between the two models based on the accuracy of the predicted concentration of the atrazine and the actual environmental concentrations. Both the steady state EXAMS model, based on a ten percent input

from the drainage basin, and the ChemCan model predicted concentrations of atrazine that reflected the concentrations measured in the water body. The EXAMS steady state model, based on the same ten percent input, provides the most accurate estimate of the peak concentrations of metolachlor in the region.

Pesticide input into a system is generally episodic in nature with peak inputs corresponding to the pesticide application period. The tidal model provides the user with the ability to determine how changes in the incoming chemical load, both increases and decreases, affect the peak concentrations of the chemical in the water column. In addition to a change in the total kilograms in the system, that is dependent on the chemical input, the tidal model provides information on how the changing water volume, associated with the tidal cycle, will affect the concentration of the pesticide.

Conclusion:

Estuaries are important breeding and nursery habitats for a large number of both estuarine and marine species. These organisms are often found in the shallow waters along the edge of the estuary. Chemical input into this region, along with shallower water, can result in higher concentrations of contaminants being located in these regions. EXAMS allows for the modeling of these environments as separate compartments than the deeper reaches of the estuary. Peak water concentrations are predicted for each of the water compartments that are modeled. The fugacity-

based model predicts a single peak concentration in the water but fails to predict the concentration in the more vulnerable shoreline areas of the estuary.

The capacity of the EXAMS model to be subdivided into numerous compartments within the same water body enables the user to design a model environment that is as complex as required to accurately depict variation within the water body or complex hydrodynamics in the region. It also presents the user with a clear picture of the areas within a water body that a compound is most likely to accumulate, or to focus on specific regions that may be of particular interest. The capability of the EXAMS models to predict environmental concentration in sensitive areas provides a distinct advantage over the simpler fugacity-based models, such as ChemCan, which view the aqueous portion of the ecosystem as a single homogeneous compartment.

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Figure captions

Figure 1. Frequency of Detection of Atrazine and Metolachlor in the Tar-Pamlico River Basin

Figure 2. Diagram of Bath Creek, NC steady state EXAMS model

Figure 3. Sampling sites in the Albemarle-Pamlico Drainage Basin; 2000-2001

Figure 4. Diagram of Bath Creek, NC tidal EXAMS model at both ebb and flood tide

Figure 5. Peak atrazine concentrations vary with tidal cycle in Bath Creek tidal model

Figure 6. The peak concentration of metolachlor varies with tidal volume in the Bath Creek tidal model

Figure 7. Concentrations of atrazine and metolachlor predicted by the EXAMS tidal model were similar to those seen in Bath Creek following a rain event in July 2002.

Figure 8. Atrazine and metolachlor accumulation and depuration in Bath Creek tidal model

Table 1- Environmental Parameters used to Define Bath Creek, NC Fate Models at High Tide

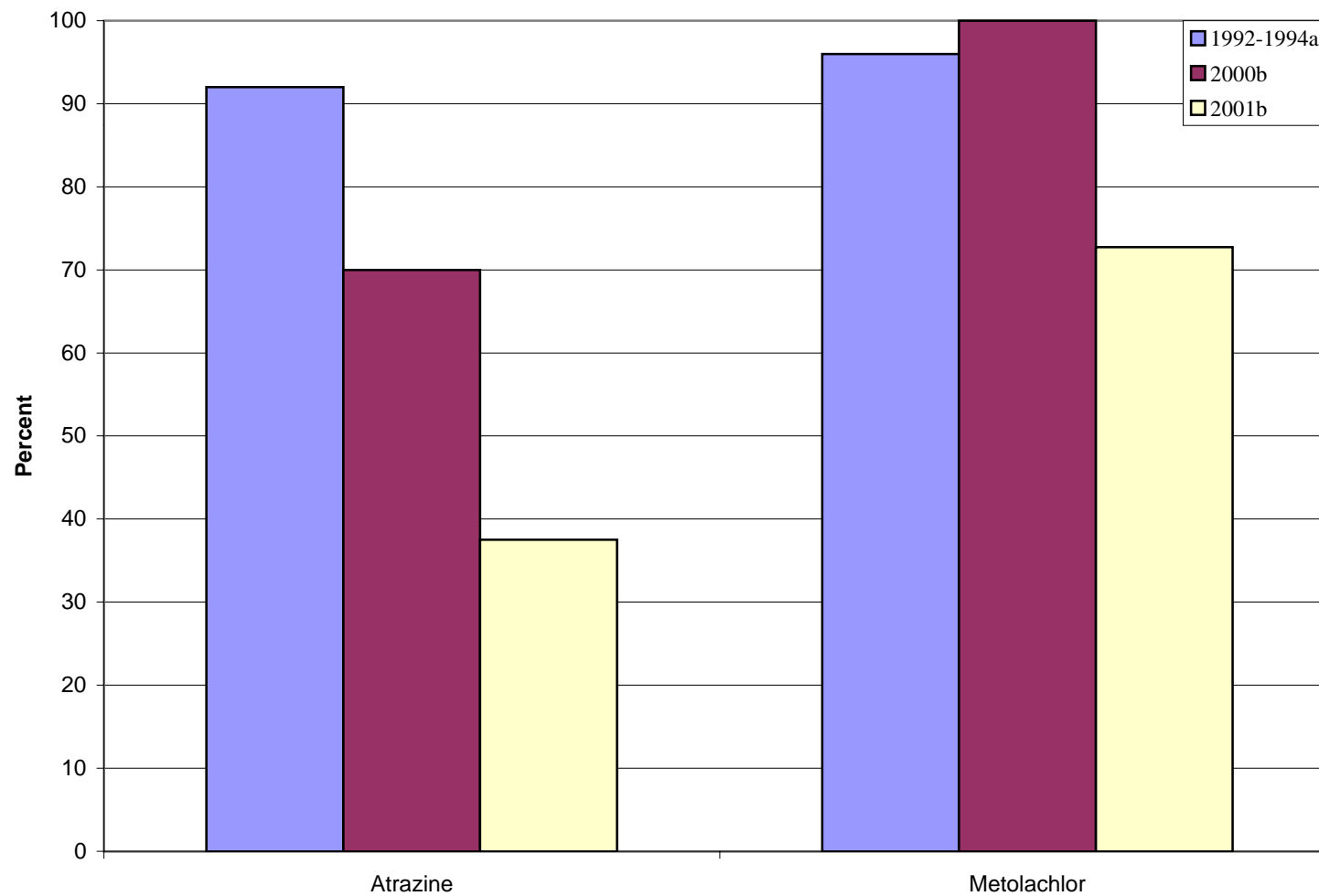
	EXAMS	ChemCan
Air Mass Type	Rural	NA
Area (m ²)	4.20E+06	4.20E+06
Average Water Temperature (Celcius)	9.4	NA
Elevation (m)	3	NA
Fraction Organic Carbon	0.045	0.045
Latitude	35.27	NA
Length (m)	5250	NA
Longitude	76.49	NA
Percent Water	NA	99
pH	8.4	NA
Rainfall (mm/month)	106	NA
Residence Time of Water (days)	NA	3
Sediment Depth (cm)	2	2
Volume (m ³)	8.53E+06	NA
Water Depth (m)	1.4 to 2.3	2.3
Width (m)	800	NA
Wind Speed (m/sec)	4.84	NA

Table 2- Chemical Parameters for Bath Creek Model

	Atrazine	Metolachlor
Hydrolysis	3.89E-02	
Sediment partitioning	22.13	5.31E+01
Aerobic metabolism	2.24E-12	50
Henry's law constant	2.84E-09	2.30E-08
Vapor pressure	3.00E-07	3.15E-05
Photolysis	4.00E-07	
Molecular weight	2.16E+02	2.84E+02
Melting point	1.74E+02	2.50E+01
Kow	5.62E+02	2.82E+03
Koc	2.31E+02	2.81E+02
Water solubility	3.00E+01	5.30E+02
Annual Usage (LBS AI)	2710	1987

Table 3- Atrazine and Metolachlor Concentrations in Bath Creek: Predicted vs. Measured in 2000 (ng/ L)

	Atrazine		Metolachlor	
Predicted	Steady State Prediction		Steady State Prediction	
EXAMS 100% Input	1146		1874	
EXAMS 10% Input	115		187	
EXAMS 3% Input	34		56	
Chem Can 99% water	74		30	
Chem Can 75% water	97		40	
Measured	Mean	Maximum	Mean	Maximum
Bath Creek 2002	68	270	144	805
Pamlico River 2000	10	30	200	600
Pungo River 2000	40	80	40	80
Tar River 2000	100	400	30	140



**Figure 1- Frequency of Detection of Atrazine and Metolachlor in the Tar-Pamlico River Basin
(^aWoodside, 2000, ^bMcCarthy)**

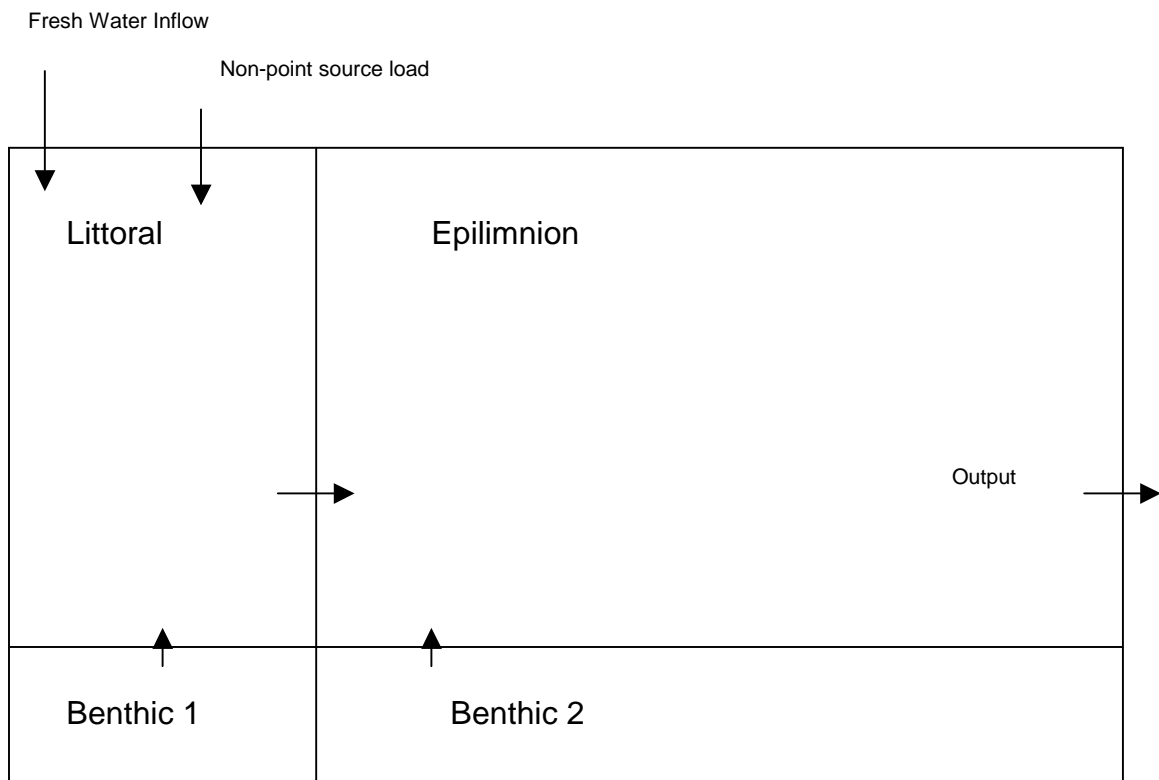


Figure 2- Diagram of Bath Creek, NC steady state EXAMS model
(Arrows denote water movement unless otherwise specified)

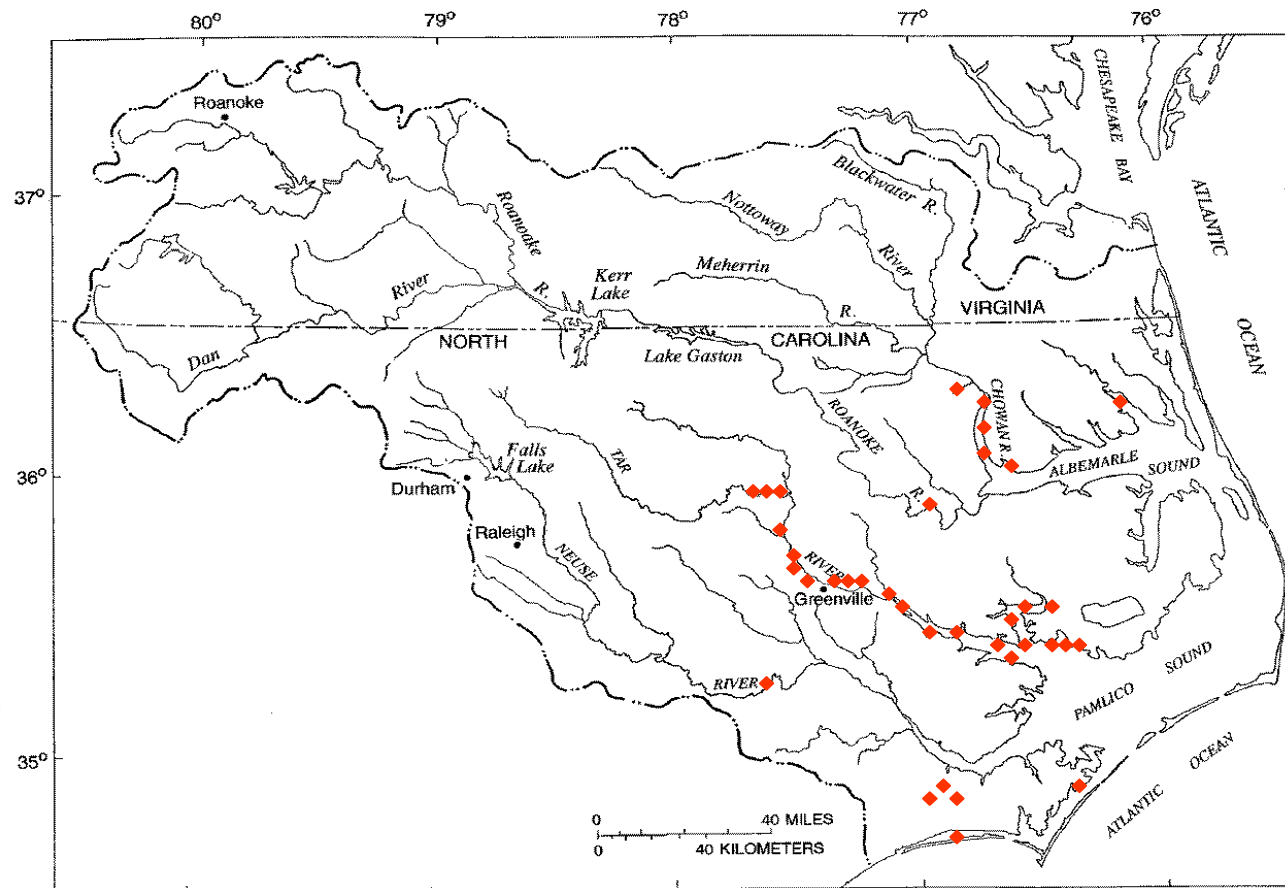
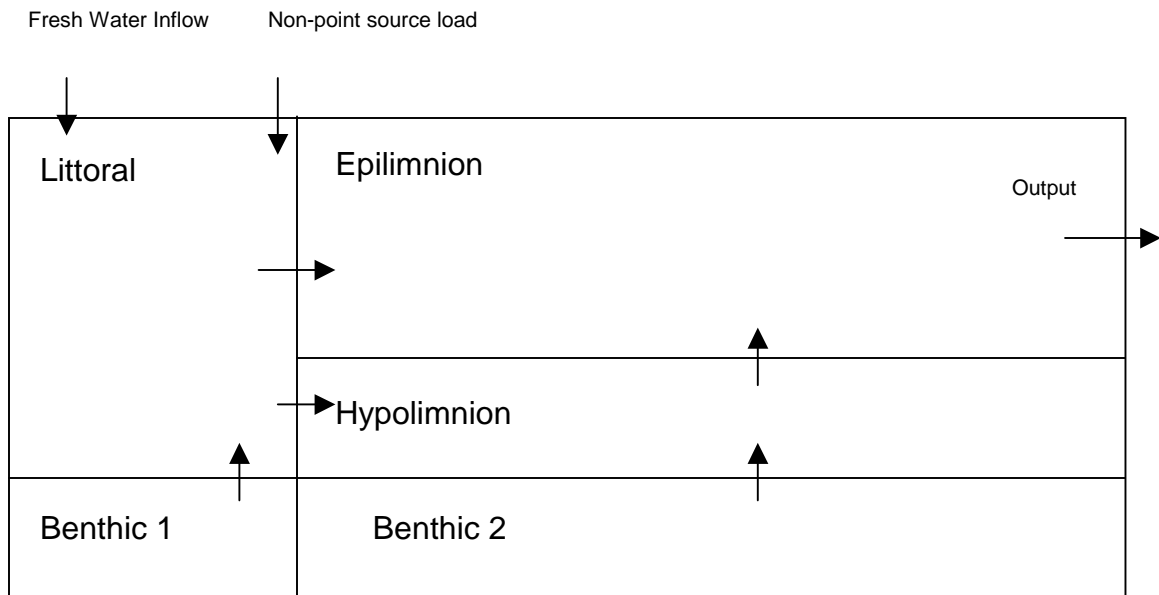


Figure 3- North Carolina State University sampling sites in the Albemarle-Pamlico Sound: 2000-2001

Ebb Tide



Flood Tide

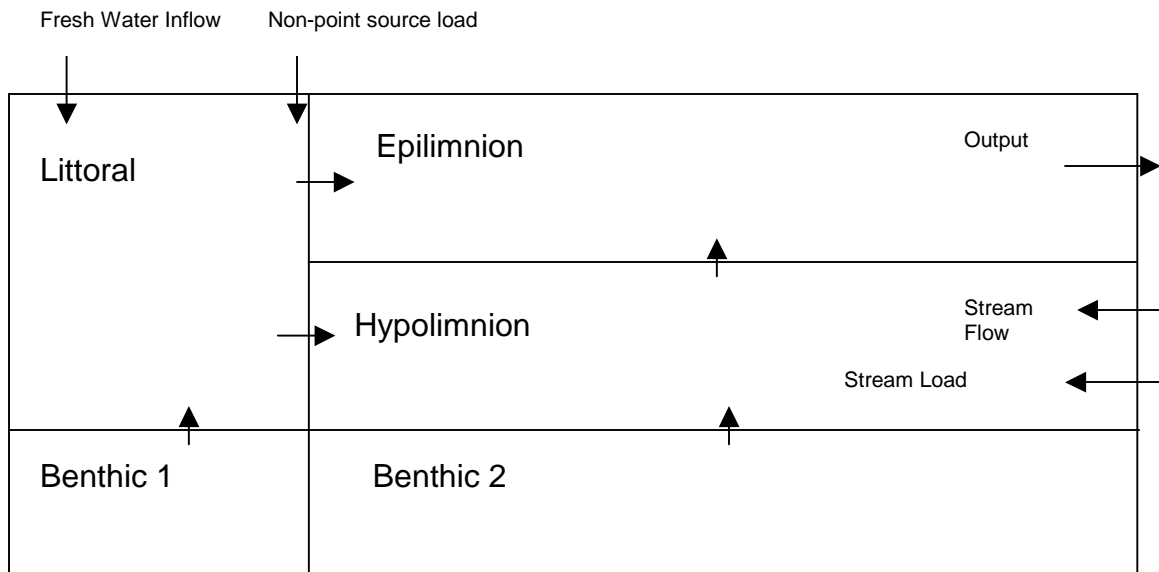


Figure 4- Diagram of Bath Creek, NC tidal EXAMS model at both ebb and flood tide (Arrows denote water movement unless otherwise specified)

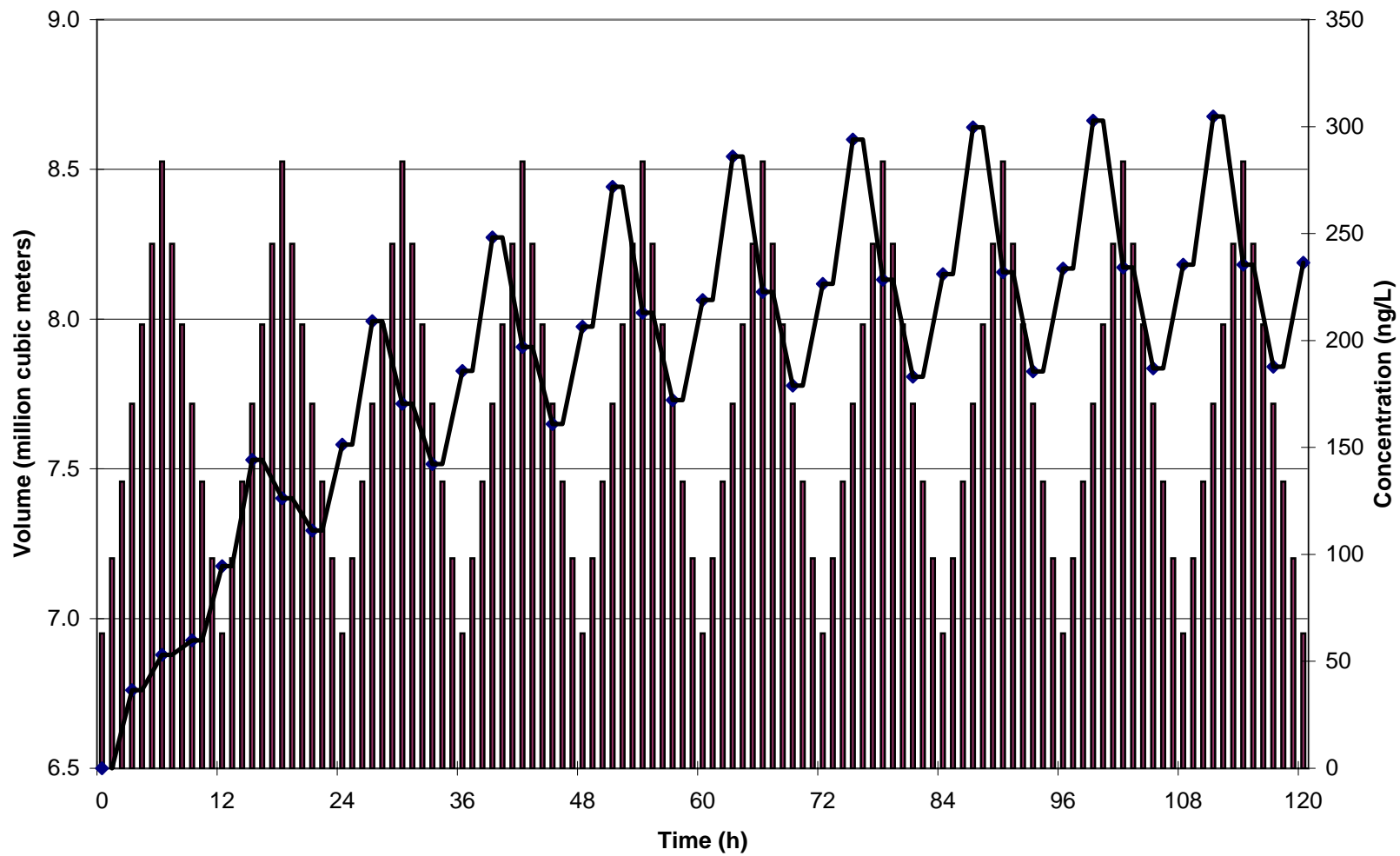


Figure 5- Peak atrazine concentrations vary with tidal cycle in Bath Creek tidal model

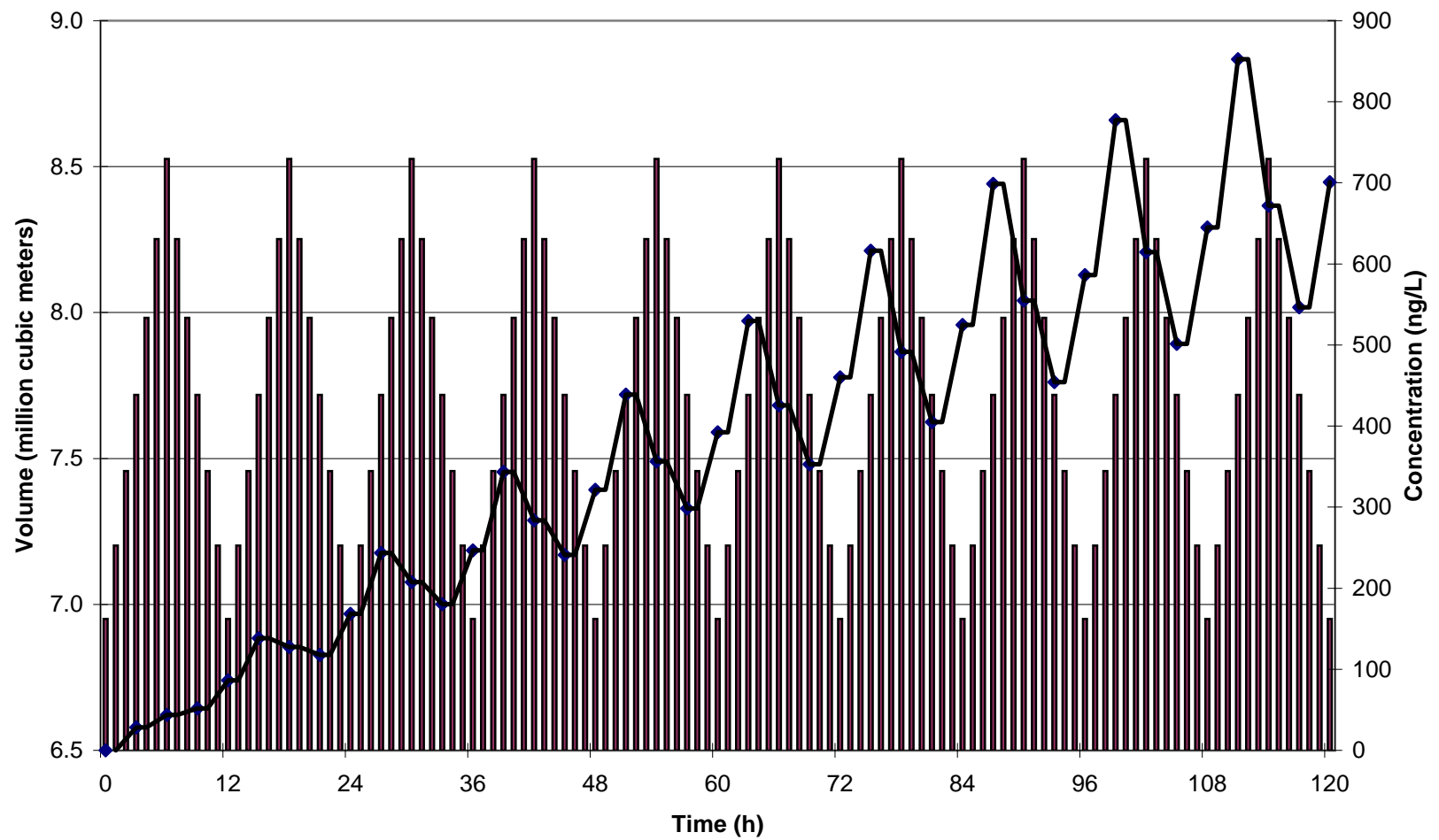


Figure 6- The peak concentration of metolachlor varies with tidal volume in the Bath Creek tidal model

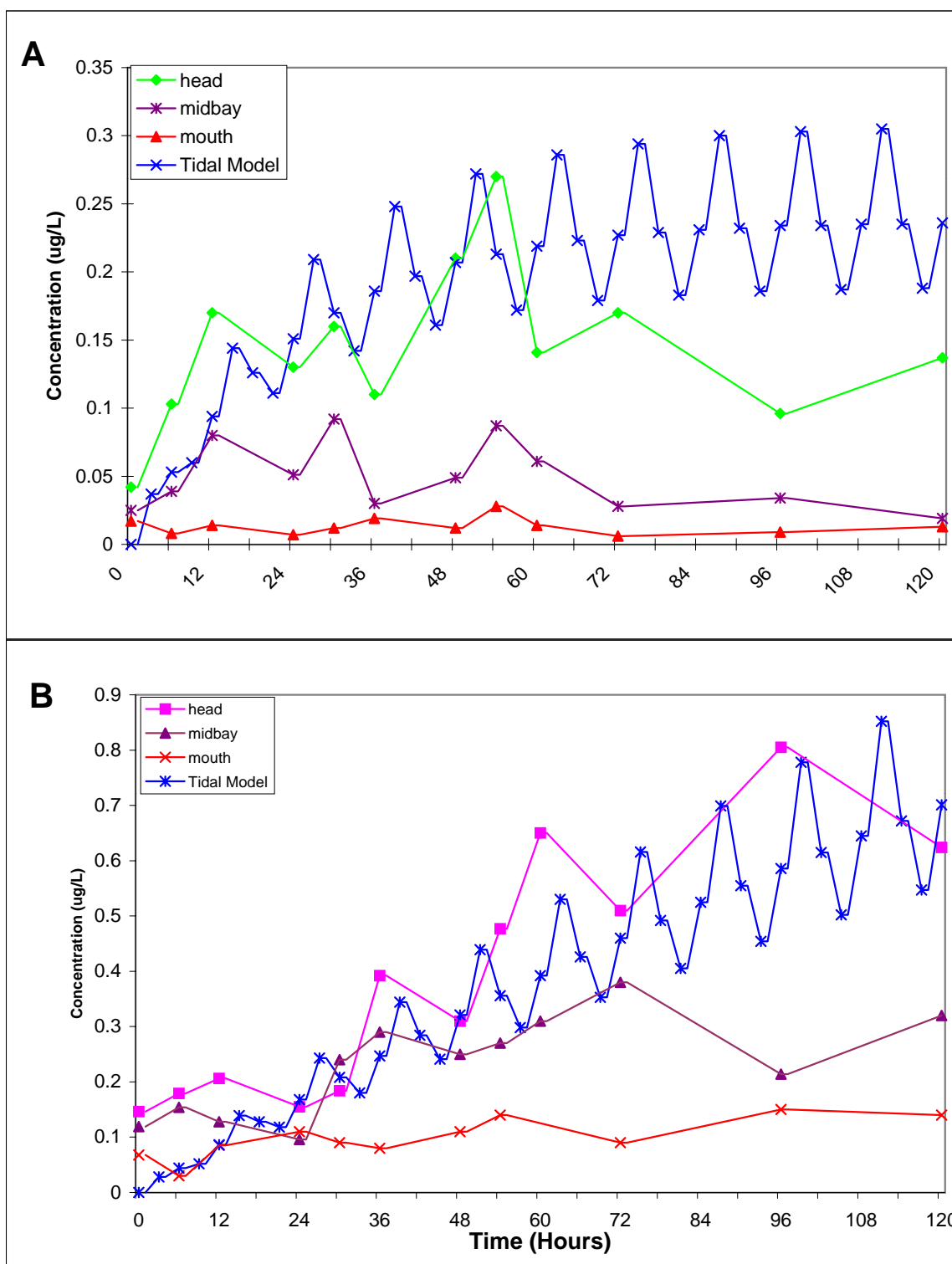


Figure 7- Concentrations of atrazine (A) and metolachlor (B) predicted by the EXAMS tidal model were similar to those seen in Bath Creek following a rain event in July 2002

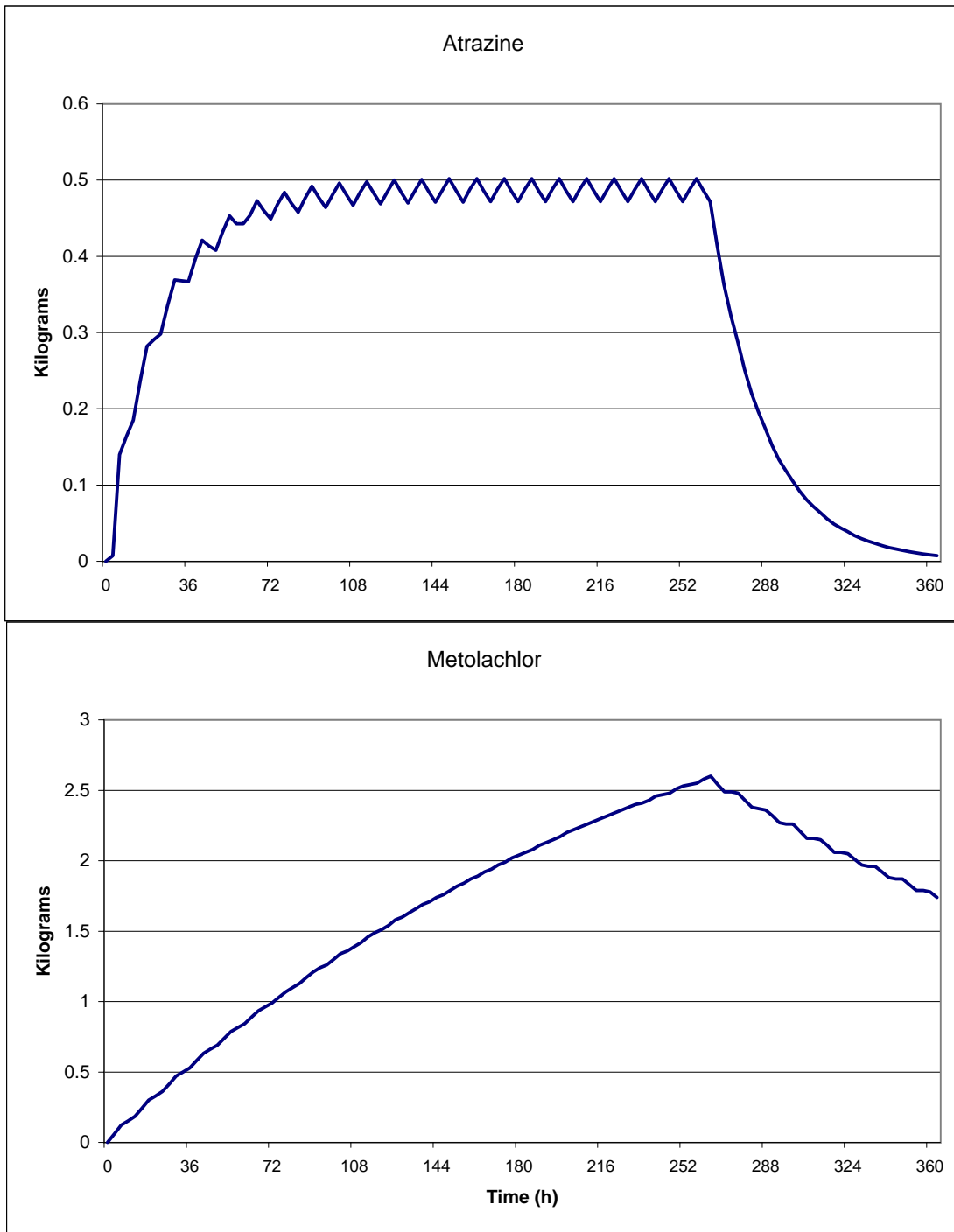


Figure 8- Atrazine and Metolachlor Accumulation and Depuration in Bath Creek Tidal Model

CHAPTER 4
UPTAKE AND ELIMINATION OF CURRENT-USE PESTICIDES
INTO SEMI-PERMEABLE MEMBRANE DEVICES

Abstract:

Uptake rates into a semi-permeable membrane device (SPMD) have been characterized for many compounds with high $\log K_{ow}$ values, typically greater than 4.5. However, few data exist for sampling rates of current-use pesticides with $\log K_{ow}$ values < 4.5 . We determined the elimination rate constants for 49 current use pesticides and metabolites, with $\log K_{ow}$ values ranging from -0.46 to 6.39 . This information was used to assess whether SPMDs would adequately accumulate these compounds in the field. SPMDs were spiked with analytical standards of each of the pesticides and sampled over a period of 60 days with triplicate samples being removed at each time interval. Booij et al. [1] found a linear relationship between $\log k_e$ and $\log K_{ow}$, with a slope of -0.42 for compounds with a $\log K_{ow}$ between 4.2 and 8.1 . Our data set for lower K_{ow} compounds provided a similar relationship (slope = -0.49 , $R^2=0.69$). Using these elimination rate constants, along with degradation rate constants in triolein, we estimate that 26 of the 49 compounds remain in the linear uptake phase for over 3 weeks, another 5 pesticides for approximately 2 weeks, and another 6 for 1 week. For compounds such as alachlor, azinphos methyl and disulfoton, deployment of the device would result in a loss of the compound through degradation. A standard deployment period of approximately 4 weeks is acceptable for compounds such as pendimethalin, chlorpyrifos and tribufos. Twelve of the compounds tested would not accumulate in a linear fashion over 1 week due to rapid elimination rates and short half-lives; these include atrazine, bentazon, carbaryl and 2,4-D.

Introduction

Semi-permeable membrane devices (SPMDs) are passive, *in-situ* samplers for non-ionic, hydrophobic organic compounds, that work through the process of passive partitioning of a compound from the water into the device [1, 3]. This process mimics the mechanism by which hydrophobic compounds bioconcentrate in organisms in the aquatic ecosystem [2,3,4]. SPMDs can be used as surrogates of sentinel species to monitor the concentration of a compound in the surrounding environment. The devices are commonly made of low-density polyethylene tubing that contain a neutral lipid, typically triolein [2]. SPMDs concentrate only the portion of the compound that is freely dissolved in the water and thus bioavailable. In this way, they mimic the passive uptake of compounds across the biological membranes of organisms. The compounds move into the SPMD through transient pores, approximately 10 Å in size [7].

The most common use of SPMDs requires them to be calibrated by measuring uptake (or exchange) rate constants for the device under controlled conditions and then estimating the freely dissolved contaminant concentration in the field using the following equation:

$$C_{W, fd} = C_{SPMD} / k_e t \quad (1)$$

where $C_{W, fd}$ is the concentration of the chemical freely dissolved in water (ng/L), C_{SPMD} is the concentration of the chemical in the SPMD (ng/L), k_e is the first-order exchange (uptake) rate constant ($L\ g^{-1}\ d^{-1}$), and t is the time period the SPMD is deployed (d) [1].

The uptake rates for many highly hydrophobic compounds with a $\log K_{OW}$ greater than 4.5, such as PAHs, PCBs and chlorinated pesticides, have been well characterized [1,3,5,8]. However, little data exist for current use pesticides – compounds that generally have much lower $\log K_{OW}$ values. Compounds with low $\log K_{OW}$ values would be expected to reach steady state more quickly than more hydrophobic compounds, perhaps too quickly for practical use with SPMDs. Rapid exchange will not provide a time-integrated measurement. Booij [1] established a relationship between $\log k_e$ and $\log K_{OW}$ for compounds with $\log K_{OW}$'s between 4.2 and 8.1. The slope of the line was found to be -0.42 and remained constant for different classes of compounds, flow rates and SPMD sizes, whereas the y-intercept varied with exposure conditions. No data exist to confirm if this relationship between $\log k_e$ and $\log K_{OW}$ remains the same at the lower end of the $\log K_{OW}$ range and few uptake rate data exist at all for current use pesticides.

The objective of this study was to determine the elimination rates of 49 current use pesticides and metabolites with a $\log K_{OW}$ range of -0.46 to 6.39 and evaluate the utility of SPMDs for sampling these compounds.

Materials and Methods

SPMD Construction

SPMDs were constructed of 2.5-cm wide, 30- μ m thick layflat polyethylene tubing (Brentwood Plastics, Brentwood, MO) and triolein (99%) (Sigma Chemical Company, St. Louis, MO). The tubing was cut into 20 cm long pieces, which were

pre-extracted overnight in hexane. Tubing was dried and one end of the tubing was sealed with a heat sealer. Then 0.1g triolein, spiked with 100 ng/g of a pesticide mixture (Table 1), was placed into the SPMD in a thin layer and the other end was then sealed. The final length of the sealed portion of the SPMD was 10 cm. Additional heat seals were placed at each end to form loops used to attach the SPMDs within the test chamber.

Flow-through experiment

54 SPMDs were placed in a wire cage and submerged in a 19 L aquarium. Water was maintained at a temperature of $26^{\circ}\text{C} \pm 2^{\circ}\text{C}$, and was exchanged at a rate of $98\text{ L/hr} \pm 1\text{L}$. A copper-based algicide was added to the system once a week to prevent biofouling. All water in the system was tap water that had been filtered with a 10 inch filter cartridge containing a $1\text{-}\mu\text{M}$ particle size filter and two activated carbon filter cartridges, each containing 100g of carbon (Aquatic Ecosystems Triple Filter Kit, Apopka, FL).

Time integrated sampling took place on days 0, 0.25, 0.5, 1, 1.5, 2, 3, 4, 5, 7, 10, 14, 21, 30, 45 and 60. At each time point 3 SPMDs and 500 mL of water were removed. The ends of the SPMDs were cut off and discarded. The remaining 10 cm length was cut into 1 cm long pieces and placed in Teflon tubes containing 15 mL of methylene chloride (DCM). The samples were placed on a shaker table for 24 hours. The solvent was then decanted and the tube was rinsed with an additional 10 mL of DCM, which was combined with the initial solvent fraction. Extracts were

concentrated to 1 mL, filtered using Whatman UniPrep Syringeless Filters PTFE (0.45 µm pore size) and were fractionated by gel permeation chromatography. The extracts were then analyzed by GC/MS (Agilent 6800 GC with a 5973 MS detector) in the selected ion monitoring mode following the method of Zuagg et al. [9].

Results and Discussion

The flow rate of water through the system was maintained at a rate that was sufficient to prevent the accumulation of pesticides or metabolites in the system. Analysis of the water samples collected during the course of the experiment did not find detectable concentrations of any of the compounds.

The elimination of pesticides from the SPMDs are shown in Figure 1. Compounds such as bentazon and propanil were eliminated quickly from SPMDs with the curves showing a rapid decline to the method detection limit in less than 14 days. Compounds that were eliminated more slowly, such as pebulate and trifluralin, tended to exhibit more variability between the replicates.

Elimination rate constants (k_e) were calculated for each of the 49 current use pesticides tested. The constants were calculated using the equation:

$$N(t)=N^0 \exp(-k_e t) \quad (2)$$

where N is the average amount of the compound in the SPMD for the 3 replicates, t is time in days and N^0 is the known amount of pesticide added to the SPMD [1]. The values of k_e ranged from 9.8×10^{-3} for trialate to 1.84 for bentazon (Table 1). Based on the information obtained from the elimination curves (Figure 1) half-lives of the

compounds in the SPMDs were determined to be between 0.46 and 242 days. Selected relevant properties of the pesticides involved in this study are listed in Table 1. Molecular dimensions, and log K_{ow} values that were otherwise not available, were calculated with the computer program Molecular Modeling Pro (WindowChem).

The relationship between log k_e and log K_{ow} was determined (Figure 2) for the current use pesticides analyzed in this study and the chlorinated hydrocarbons and PAHs from the 1998 study by Booij et al.[1]. This linear relationship had a slope of -0.49 . Up to 15 compounds were found to be eliminated either substantially faster or substantially slower than this relationship would predict (labeled in Figure 2). Log K_{ow} values, half lives in sediment and water, molecular weight and molecular dimensions were reviewed to determine if any of these factors affected the elimination rates. Compounds that were eliminated more rapidly than the regression predicted had some of the shortest half lives in water and soil. Degradation of the compounds may be affecting the apparent elimination rate. To investigate this further, we measured the loss of each compound in triolein that was placed in a vial and left for 60 days on a bench top water bath at $25^{\circ}\text{C} \pm 1^{\circ}\text{C}$. Any loss in the absence of flowing water would presumably be due to degradation, though the rate would not necessarily represent the degradation loss rate in our initial elimination experiments. Elimination curves similar to those in Figure 1 were obtained and triolein half-lives were calculated (Table 1). For the nine pesticides identified in Figure 2 as having faster elimination rates than expected, each had a triolein half-life

that was close to the overall apparent SPMD elimination half-life. Thus, it appears that degradation in the triolein may be controlling the loss of these nine compounds in the SPMD, rather than diffusion into the water.

Previous studies have shown that molecular dimensions of greater than about 10 Å can sterically hinder the movement of PAHs through the SPMD membrane. Most of the PAHs fall below the regression line in Figure 2. Our analysis showed no clear relationship between molecular dimensions of current use pesticides and membrane permeability because 45 of the compounds tested, including those that were eliminated more rapidly than expected, had at least one dimension greater than 10 Å (Table 1). Similar problems with transport through the membrane are associated with compounds with a molecular weight of greater than 600 or a log K_{ow} of greater than 6 (Petty, 2000). The compounds tested all had molecular weights less than 375. Only thiobencarb had a log K_{ow} value greater than 6. Because it was eliminated more rapidly than expected, the log K_{ow} value did not appear to be affecting transport through the membrane.

Environmental factors such as temperature, biofouling, and flow rate have also been shown to affect SPMD sampling rates [5, 6]. Biofouling was prevented in the experiment through the addition of an algicide to the experimental chamber. Under field conditions a decrease in the apparent uptake rate would be expected due to reduced surface area available for transport that is associated with biofouling. The experiment was conducted under only a single set of temperature and flow conditions, so the k_e values calculated in this study may require adjustment for use

under different conditions. An increase in the temperature of the system would result in an increase in the sampling rate. An increase in the flow rate, and an increase in turbulence will thin the aqueous boundary layer and result in an increase in the sampling rate of the SPMD [5]. The aqueous boundary layer controls uptake of the compounds when the $\log K_{ow}$ is greater than about 4.4; otherwise uptake is controlled by membrane transfer [5]. Of the 49 compounds, 7 have $\log K_{ow}$ values greater than 4.4; and include chlorpyrifos, pendimethalin, propargite, terbufos, thiobencarb, tribufos and trifluralin. For these compounds, a change in the flow rate would affect the uptake rates. All of these factors can be compensated for by using permeability reference compounds (PRCs), standards that are added to the SPMD prior to deployment and then used to normalize uptake rates (Luellen and Shea, 2002). We did not investigate the use of PRCs for the current use pesticides, but there is no reason that the same or similar set of PRCs used by Luellen and Shea (2002) could not be used here.

The concentration of a compound in an SPMD can be used to calculate the aqueous contaminant concentration. This is done while the compound is in a linear uptake phase before equilibrium can be attained. This is generally a period of time less than the overall half life in the SPMD [4]. Therefore, the deployment period of the SPMD will be determined by the half life of the compound in the SPMD. The calculated SPMD half lives for the compounds tested ranged from 0.38 to 428 days. There are practical limitations with the deployment of SPMDs. When deployed less than about 5-7 days, there can be problems with high variability between replicates,

non-zero intercepts in the uptake curve, and low residue values. Deployments longer than about 30 days can result in heavy biofouling of the SPMD and a decrease in the uptake rate. Thus, we suggest maximum deployment times in Table 1 that represent a practical limit of field application. SPMDs seem to be a viable means of measuring the majority of current use pesticides with deployment times of 1-2 weeks.

Conclusion

SPMDs are not a viable sampling alternative for compounds with a half life in the SPMD of less than about 7 days. This includes 13 of the compounds tested; 2,4-D, atrazine, bentazon, carbaryl, cyanazine, dimethoate, EPTC, metribuzin, molinate, napropamide, propachlor, propanil and simazine. For the remaining 36 compounds, SPMDs appear to offer excellent potential as time-integrated samplers over deployment periods of 1 to 2 weeks.

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Figure captions

Figure 1. The release of 48 pesticides from SPMDs was measured over a period of 60 days under flow-through conditions. Exchange rates and half-lives of the compounds in the device were calculated (Table 1). For each time point and the average of three replicates was used to calculate the exchange rate constants.

Figure 2. The relationship between $\log K_{ow}$ and $\log k_e$ for polycyclic aromatic hydrocarbons (squares) and chlorinated hydrocarbons (triangles) with $\log K_{ow}$ values ranging from 4.2 to 8.1 and $\log k_e$ values ranging from -1.65 to 4.88, has previously been defined as a linear relationship with a slope of -0.42. When these data were analyzed with current use pesticides (circles) with $\log K_{ow}$ values ranging from -0.46 to 6.39 the slope of the line changes to -0.49. Based on this relationship the compounds atrazine (5), butylate (10), carbaryl (11), EPTC (19), molinate (29), napropamide (30), propanil (39), propargite (41) and thiobencarb (46) were eliminated from the SPMDs at a faster rate than would be expected. Likewise, ethoprop (21), linuron (24), metribuzin (28) and terbufos (44) and the metabolites desethylatrazine (6) and desisopropylatrazine (7) were eliminated slower than the relationship would predict.

Table 1. Forty nine current use pesticides were spiked into triolein filled SPMDs. SPMDs were placed in a flow through chamber for a period of 60 days with samples being removed in triplicate at various time points. Elimination rate constants and half-lives in the SPMDs were calculated for each of the compounds.

Pesticide	k_e	$t_{1/2}$ in SPMDs (days)	$\log K_{ow}$	$t_{1/2}$ in water (days)	$t_{1/2}$ in soil (days)	Molecular Weight (daltons)	length* (Å)	width* (Å)	depth* (Å)	Max. Length of SPMD Deployment (days)	Elimination curve r^2
Defoliant											
tribufos	0.0062	137.10	5.87*	n/a	10	298.52	15.20	11.89	8.02	>30	0.43
Herbicides											
2,4-D	0.1400	6.07	2.81	7	16	221.04	13.10	7.99	4.12	6	0.95
acifluorfen	0.1040	8.17	1.18	28	59	361.70	12.02	13.67	5.11	8	0.94
alachlor	0.0392	21.68	3.52	23	15	269.77	9.62	9.46	6.40	21	0.88
atrazine	0.2470	3.44	2.75	5	60	215.69	9.10	12.45	5.38	3	0.96
bentazon	1.8400	0.46	-0.46	2	14	240.28	9.83	9.61	6.72	0.5	0.96
butylate	0.1040	8.17	4.15	2	13	217.38	10.12	11.41	6.64	8	0.93
cyanazine	0.1870	4.55	2.22	14	14	240.70	10.41	12.41	6.64	4	0.96
diuron	0.0427	19.91	2.68	7	90	233.10	10.02	11.25	4.12	19	0.89
EPTC	0.2350	3.62	3.20	2	7	189.32	11.41	9.32	4.13	3	0.96
ethalfuralin	0.0074	114.40	3.99*	n/a	60	333.27	10.77	11.95	5.12	>30	0.38
fluometuron	0.0329	25.84	2.30	365	85	232.29	10.02	11.79	5.12	25	0.89
linuron	0.0132	64.39	3.20	172	60	249.11	13.25	7.61	4.12	>30	0.59
metolachlor	0.0151	56.29	3.13	140	40	283.80	12.30	8.90	5.39	>30	0.73
metribuzin	0.2380	3.57	1.60	7	60	214.29	9.62	11.64	6.64	3	0.96
mollinate	0.1230	6.91	2.88	4	21	187.30	12.27	6.85	4.42	6	0.96
napropamide	0.2300	3.70	3.36	1	70	271.36	12.67	9.99	6.75	3	0.97
norflurazon	0.0456	18.64	2.00	14	90	303.67	11.52	9.94	8.60	18	0.92
pebulate	0.0065	130.77	3.80	11	14	203.35	11.39	13.27	4.13	>30	0.48
pendimethalin	0.0016	524.69	5.18	14	40	281.31	9.47	12.41	5.39	>30	0.08
prometryn	0.0210	40.48	3.34	45	45	241.37	12.32	10.11	5.39	>30	0.85
pronamide	0.0143	59.44	3.20	90	60	256.13	9.75	12.66	7.63	>30	0.74
propachlor	0.1510	5.63	2.18	12	7	211.69	10.41	10.08	5.38	5	0.96
propanil	0.5690	1.49	2.29	2	2	218.08	8.41	12.57	4.12	1	0.98
simazine	0.1290	6.59	2.18	32	75	201.70	12.31	9.97	4.13	6	0.96
tebuthiuron	0.0602	14.12	1.79	60	400	228.31	10.36	11.32	6.64	14	0.92
terbacil	0.0581	14.63	1.89	30	120	216.70	9.02	10.00	6.64	14	0.93
thiobencarb	0.1120	7.59	6.39*	5	5	257.78	15.30	10.39	4.13	7	0.95
triallate	0.0098	87.09	4.29	100	82	304.66	9.68	12.27	6.65	>30	0.58
trifluralin	0.0051	167.65	5.07	5	60	335.50	10.69	13.14	5.12	>30	0.34
Herbicide Metabolites											
2,6-diethylaniline	0.0312	27.24	2.30	15	15	149.24	9.10	10.08	4.14	27	0.82
desethylatrazine	0.0349	24.36	0.20*	n/a	n/a	187.63	10.49	9.93	5.84	24	0.82
deisopropylatrazine	0.0298	28.52	0.68*	n/a	n/a	173.60	8.41	11.33	4.12	28	0.76
3,4-dichloroaniline	0.0194	43.81	1.99*	n/a	n/a	162.02	7.03	8.86	3.54	>30	0.86
Insecticides											
azinphos methyl	0.0235	36.17	2.75	8	20	317.33	14.88	8.81	7.59	>30	0.76
carbaryl	0.3000	2.83	2.36	10	10	201.23	11.28	9.35	4.12	2	0.96
carbofuran	0.0676	12.57	2.32	21	45	221.25	11.19	9.30	6.52	12	0.88
chlorpyrifos	0.0033	259.15	4.96	45	60	350.62	11.67	10.76	6.69	>30	0.18
diazinon	0.0076	111.55	3.70	40	40	304.35	13.86	10.56	7.93	>30	0.43
dimethoate	0.1550	5.48	0.75	20	10	229.28	11.65	8.79	6.68	5	0.98
disulfoton	0.0230	36.96	4.02	10	30	274.40	13.85	12.50	7.93	>30	0.82
ethoprop	0.0117	72.65	3.59	5	25	242.34	9.42	9.03	9.48	>30	0.57
fonofos	0.0084	100.71	3.90	10	40	246.32	12.32	9.77	6.89	>30	0.56
malathion	0.0755	11.26	2.89	7	2	330.36	14.00	11.35	8.67	11	0.96
methyl parathion	0.0242	35.12	3.50	8	5	263.21	11.80	8.47	6.75	>30	0.79
phorate	0.0126	67.46	3.92	7	60	260.38	11.65	9.93	9.26	>30	0.73
profenofos	0.0066	128.01	5.00	10	8	371.94	11.54	11.31	9.47	>30	0.44
propargite	0.0035	242.17	4.50	7	56	350.48	11.46	11.31	9.26	>30	0.21
terbufos	0.0065	130.17	4.48	7	30	288.43	11.65	9.93	9.26	>30	0.46

n/a=not available, *=values calculated using molecular modeling pro
half-lives in water and sediment estimated from literature

Figure 1. The release of 48 pesticides from SPMDs was measured over a period of 60 days under flow-through conditions. Exchange rates and half-lives of the compounds in the device were calculated (Table 1). For each time point and the average of three replicates was used to calculate the exchange rate constants.

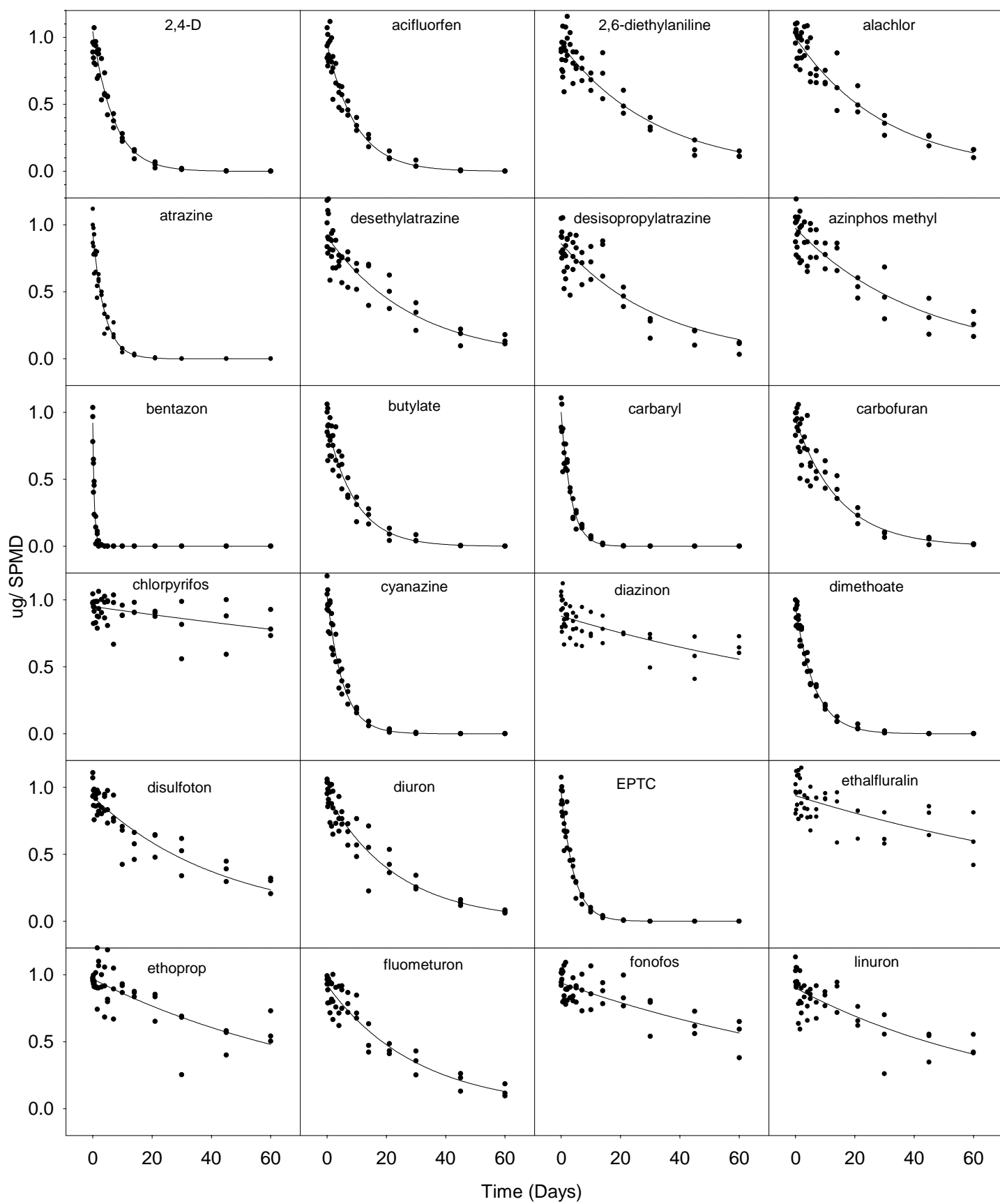


Figure 1

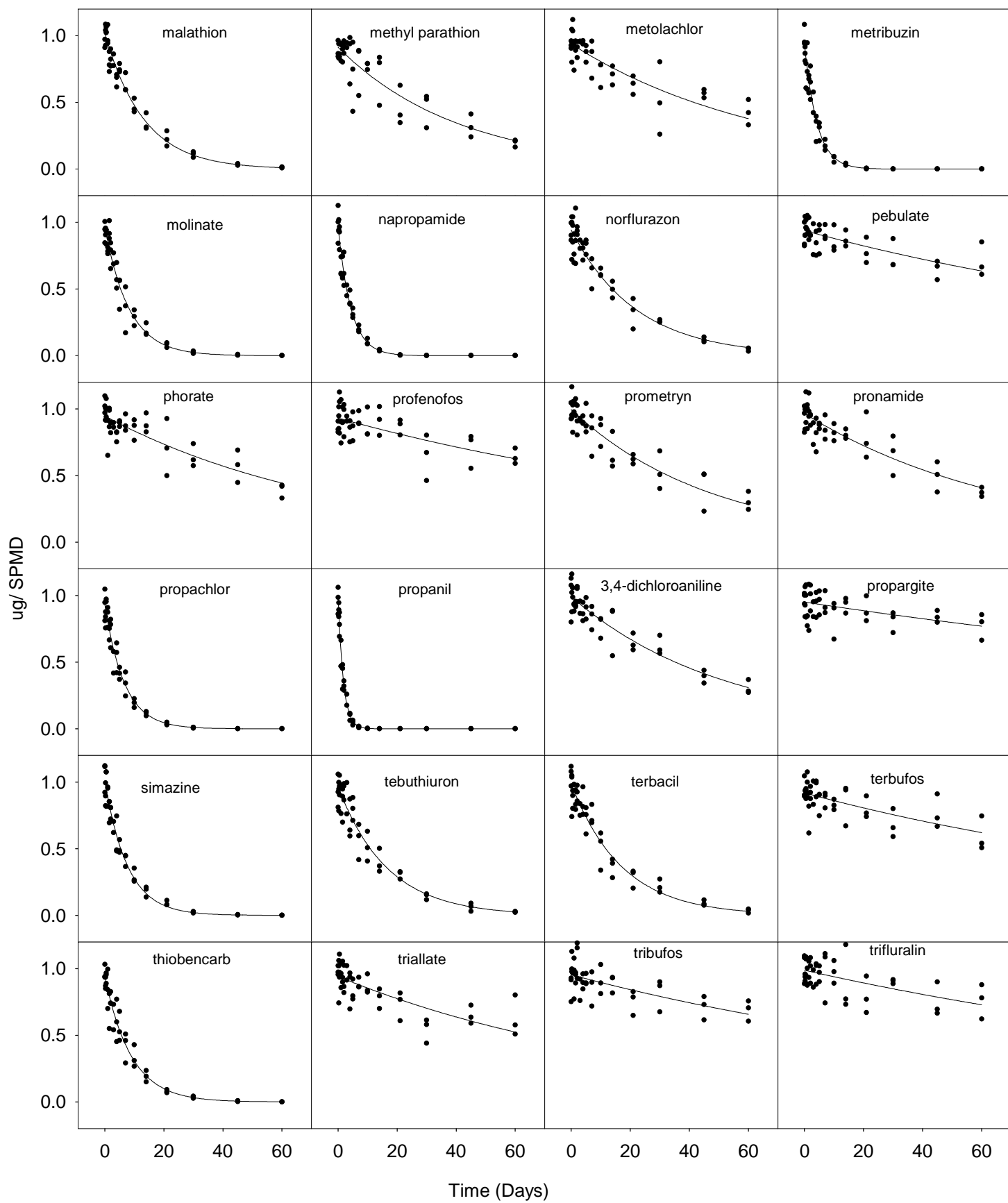


Figure 1

Figure 2. The relationship between $\log K_{ow}$ and $\log k_e$, for polycyclic aromatic hydrocarbons (squares) and chlorinated hydrocarbons (triangles) with $\log K_{ow}$ values ranging from 4.2 to 8.1 and $\log k_e$ values ranging from -1.65 to 4.88, has previously been defined as a linear relationship with a slope of -0.42. When these data were analyzed with current use pesticides (circles) with $\log K_{ow}$ values ranging from -0.46 to 6.39 the slope of the line changes to -0.49. Based on this relationship the compounds atrazine (5), butylate (10), carbaryl (11), EPTC (19), molinate (29), napropamide (30), propanil (39), propargite (41) and thiobencarb (46) were eliminated from the SPMDs at a faster rate than would be expected. Likewise, ethoprop (21), linuron (24), metribuzin (28) and terbufos (44) and the metabolites desethylatrazine (6) and desisopropylatrazine (7) were eliminated slower than the relationship would predict.

APPENDIX

Canadian Aquatic Life Criteria

The Canadian Aquatic Life Criteria (ALC) were designed to protect 100% of the aquatic species 100% of the time. This designation was based on toxicological data for the most sensitive Canadian species and includes all components of the aquatic ecosystem (algae, invertebrates, fish, etc). If toxicological information is not available for all components than interim ALC are set. The ALC by definition is the long-term no effect concentration and is the total concentration in unfiltered samples. It can be calculated in one of two ways. When lowest observed effect level (LOEL) data is available, the equation used is:

$$\text{ALC} = \text{most sensitive LOEL} * 0.1 \text{ (safety factor)}$$

When only acute toxicity studies have been performed, the ALC is calculated using the following:

$$\text{ALC} = \text{most sensitive LC}_{50} \text{ or EC}_{50} * \text{acute/ chronic ratio or an acceptable application factor.}$$

To determine the most sensitive species value a minimum data set must analyzed. This includes studies on the toxicity of the compound to fish, invertebrates and plants. These studies include a minimum of 3 studies on 3 or more freshwater species in North America, including at least one cold water and warm water species and at least 2 chronic studies, at least 2 chronic tests on invertebrate species including 2 or more invertebrates from different classes and at least one North American plankton species, and at least one study of a freshwater vascular plant or algal species found in North America.

(Source- CCREM. 1987. A protocol for the derivation of water quality guidelines for the protection of aquatic life. Available at: http://www.ec.gc.ca/ceqg-rcqe/English/Pdf/water_protocol-aquatic_life.pdf)

SUMMARY OF MODELS

GLEAMS- Groundwater Loading Effects of Agricultural Management Systems

What is GLEAMS

GLEAMS is a modified version of the model CREAMS (Chemicals Runoff and Erosion from Agricultural Management Systems). CREAMS is a non-point source, capacity model for predicting sediment, nutrient and pesticide losses with surface runoff for agricultural management systems. GLEAMS adds components to simulate movement of water and chemicals within the crop root zone (9). Later versions of GLEAMS were also modified to also simulate the generation and degradation of pesticide metabolites (1). It contains pesticide and nutrient components that allow the simulation of 10 pesticides and metabolites at a time. It is a management oriented, field scale model for evaluating the relative impacts of agricultural practices on surface and groundwater quality (1, 6). It predicts runoff, percolation and soil and chemical losses at the edge of the field and from the root zone. Field scale models are usually representative of homogeneous single soil and crop applications. They are less likely to be capable of managing multiple land uses in a single situation (4).

GLEAMS allows the user to specify the frequency of model output and changes in input over the simulation periods. The model simulates output in two ways; on a daily time step and through long-term simulations of up to 50 years (5). The model was designed for relative predictions and comparative analysis. It is

most useful when simulating long-term effects of the interactions between pesticide properties, soil characteristics, management and climate (5).

Surface water runoff

GLEAMS estimates surface water runoff in the model region using the Soil Conservation Service (SCS) curve number runoff model. The SCS model is driven by daily rainfall, with modifications that relate runoff curve number to daily soil water content in the root zone (2). Surface runoff and erosion can be routed overland, in channels and through impoundments (9).

The amount of pesticide transported via surface runoff is calculated from edge-of-field water runoff volumes, empirical extraction coefficients and sediment concentrations by assuming a linear equilibrium adsorption isotherm and constant mixing depths (10 mm) at the surface (2, 8).

Pesticides and the model

There are four types of pesticide application methods allowed for in the model- surface application, incorporation (mixed into the topsoil), injection and chemigation (6). The model assumes that only non-ionic pesticides are used and that adsorption occurs only onto organic carbon (6). The model assumes that sorption is a reversible, linear, equilibrium process with degradation processes obeying first-order kinetics (11). The most important parameter is the degradation rate or degradation half-life, which is usually allowed to vary with depth, soil water

content and temperature (11). Plant uptake is assumed to be passive and proportional to the transpiration rate and the pesticide concentration (11).

Pesticide loss is predicted in three ways; dissolved in runoff, attached to eroded sediment and leached out of the root zone (18).

Erosion and the soil profile

Erosion is predicted using the Onstad and Foster modifications to the Universal Soil Loss Equation (USLE) (9). The vadose zone is not considered between the root zone and the water table. The root zone may be described by up to 5 soil horizons with varying properties. The crop zone can be divided into 3 to 12 computational layers. The surface layer has a thickness of 10 mm and other layers have a maximum thickness of 100-150 mm depending on their location in the soil profile. Lower levels may be thicker than 150 mm to meet the limit of 12 layers (9). Strong correlations have been seen between the pesticide concentration in runoff and the concentration in the top 10 mm of soil (9). Pesticide transport within the root zone is by advection. No dispersive flux components are included. Volatilization is not considered as a separate process (9). The model allows for different degradation rates of a compound on foliage and within the soil (9). There are three sensitive parameters in the erosion component of the GLEAMS model; the contour/management practice factor (PFACT), the soil loss ratio (CFACT) and Manning's coefficient for surface roughness (NFACT). Slight changes in any of these

parameters can result in large differences in the amount of sediment lost from the plots. The same changes have minimal impact on runoff (7).

GLEAMS has been modified to include crack flow by considering shrinkage characteristics of the soil (i.e. the interaction between water content and soil volume). However, it does not consider lateral sub-surface flow or sub-surface drainage systems (3).

Evapotranspiration

GLEAMS calculates evapotranspiration (ET) using the Priestly-Taylor model (10). This model calculates potential ET using daily air temperature and soil radiation. Actual ET can be calculated using soil evaporation and crop transpiration (10).

Previous uses of GLEAMS

Previous work has shown that GLEAMS can be used in a cascade format and can be linked with GIS systems. Integrating GIS and water quality models allows for a quick assessment of “what if” scenarios. The cascade format implies that the models are not run simultaneously. Rather the upland model would be run first and then the downslope model. Outputs from the upland model would be used as inputs for the downslope model. Cascading does not provide the best feedback alternatives but is the most logical approach with two complex system models that are not designed to function as one model. Project design included creating model

input parameter template tables in spreadsheet form. The GIS system was used to determine and assemble the model's input parameters when possible. Otherwise the information was added manually into the table that already contained the GIS-obtained information. Since GLEAMS assumes that the soil is homogenous the GIS system was used to calculate the dominant soil in the region. Finally a subroutine was developed to input the output from the upstream model into the downslope model (4).

Previous work has shown that GLEAMS will over predict water concentrations when it is used to model an entire watershed. Significant adsorption, deposition, infiltration of runoff water and chemical degradation occur as a pesticide travels from the edge of the field to the watershed outlet that the model is not equipped to account for (18). In addition, environmental conditions such as saturated soils and preferential flow will cause discrepancies between the predicted concentrations and the observed concentrations (6).

PRZM- Pesticide Root Zone Model

What is PRZM

PRZM is a field scale, hydrology and transport model, designed for management purposes. It is a continuous simulation model that is capable of simulating water and chemical fluxes over many years of historical or synthetic daily water records (9). PRZM is a modeling system that predicts pesticide transport and transformation down through the root zone. It is a capacity model that simulates the

vertical one-dimensional movement of pesticides and nitrogen in the unsaturated zone within and below the root zone. The more recent versions of the model PRZM2 and PRZM3 link 2 models- PRZM and VADOFT to predict pesticide transport and transformation down through the crop root and unsaturated zones (website). These models combine 2 first-order processes with different rate constants in order to model pesticide transformation (13).

The model contains hydrologic and chemical transport components that simulate erosion, runoff, plant uptake, leaching, decay, foliar washoff and volatilization (website). Pesticide transport and fate processes such as advection, dispersion, molecular diffusion and soil sorption are included (website).

PRZM can simulate multiple applications of one pesticide each year for many years where there is a continuous climate record available (9). Temporal variations in leaching and runoff can be predicted (9).

Surface water runoff

PRZM estimates surface water runoff using the SCS curve number runoff model. PRZM relates the daily runoff curve number to soil moisture limits in the surface zone (top 0.3 m) (2). The amount of pesticide that is transported via surface runoff is calculated from edge-of-field water runoff volumes, empirical extraction coefficients and sediment concentrations by assuming linear equilibrium adsorption isotherms and constant mixing depths at the surface (2). This is the same method used in the GLEAMS model.

Erosion and the soil profile

Erosion is simulated using Williams and Berndt's modification of the USLE for daily time steps (9). The model can simulate the entire vadose zone from soil surface to groundwater. The vadose zone can be characterized by several layers of varying properties. The user is allowed to select the number of compartments to be modeled. For the sake of calculations the vadose zone must be divided into compartments of equal depth (9). The number of compartments needs to be selected carefully. Too many will increase the simulation time while too few will increase the numerical errors in the solution of the equations used in the model (9). The suggested compartment depth to avoid problems is less than 50 mm (9). Percolation through the compartments is based on the water holding capacity of the soil (9).

Pesticides and the model

Pesticide processes represented in the model include advective and dispersive flux, sorption, degradation in soil and on plant foliage, and plant uptake (9). Volatilization and transport in the vapor phase are not considered (9). Pesticide transport is described using a convection-dispersion equation (12). Only the downward movement of water is modeled. Diffusive movement of pesticides due to soil-water gradients are ignored (12). Pesticide degradation is described using first-order kinetics (12). This does not depend on temperature or moisture content (12). The pesticide degradation rates specified for soil and foliar pesticide residues may

differ (9). The degradation rate within the soil may also be varied by soil layer (9). Pesticide sorption is modeled as a linear function that is a reversible, equilibrium process (11, 12). Plant uptake is assumed to be passive and proportional to the transpiration rate and the pesticide concentration (11). A concentration stream factor is incorporated to account for selective uptake (11).

Limitations

PRZM does not simulate subsurface lateral flow, macropore flow, by-pass flow or drainage (12).

Sensitive parameters in the model have been identified. They include the degradation constant, the sorption coefficient, Henry constant, thickness of the compartments in the horizon, hydrodynamic dispersion coefficient, bulk density, and initial soil moisture content (12). A difference is seen in model results with different users for parameters whose values are open to subjectivity based on experience and knowledge of the user (12).

HSPF- Hydrological Simulation Program FORTRAN

HSPF simulates runoff and transport of sediment, pesticides and nutrient transport from urban and agricultural watersheds. The model allows for detailed simulations of stream hydraulics, water quality processes, pesticide and nutrient behaviors in soils and lakes and sediment contamination (14). The model has a

tendency to overestimate the concentrations of a compound. The degree of that overestimation depends on the pesticide and the watershed being modeled (14).

HSPF is composed of 3 application models and 6 utility models. The application models simulate pervious land segments in agricultural areas with homogeneous hydrologic and climate conditions (PERLND), impervious land segments where little or no infiltration occurs (IMPLND) and physical and chemical processes that occur in the reach of an open channel or a completely mixed lake (RCHRES) (14). Each application module requires input data such as climatic data, topographical maps, aerial photographs, land-use maps and pesticide application data (14). Weather data may include precipitation, potential ET, air temperature, wind velocity and global radiation (14). The pesticide application utility module simulates pesticide behavior by including processes of degradation, adsorption/desorption and transport (14). Pesticides move with water flow, by association with sediment or under crystalline form (14).

EXAMS- Exposure Analysis Modeling System

EXAMS is an interactive modeling system that can conduct rapid evaluations and error analyses of the probable aquatic fate of synthetic organic chemicals (website). The model combines chemical loadings, transport and transformation into a set of differential equations using the law of conservation of mass as an accounting principle (website). EXAMS is suitable for estuarine systems (15). It accounts for the interaction between the aquatic environment, the properties of the

chemical of interest and environmental loading characteristics in order to predict the exposure, persistence and fate of synthetic chemicals in the aquatic systems (15). EXAMS assumes a completely mixed system, which is generally applicable to a region where dispersive transport is a predominant mechanism over advective transport. The model requires the number of active organisms in the water column and sediment beds in order to evaluate the biolysis rate (16). In order to look at pesticide transformations it uses pseudo first-order rate constants (16). It requires a significant amount of chemical and environmental data as inputs (16).

DEGAS-WS- Dow AgroSciences Exposure Geographical Assessment System- Watershed (17)

DEGAS-WS combines georeferenced data (soil, crop, weather) and management and mitigation strategies with deterministic models such as PRZM, GLEAMS and EXAMS to estimate edge-of-field experimental exposure concentrations in various environmental matrices (soil, pore water, surface water). It also adds water quality estimates for streams and tributaries found within the defined watershed boundaries. The model is capable of simulating pesticide leaching, surface runoff, and water quality in streams and tributaries resulting from agricultural usage of pesticides. DEGAS-WS is capable of simulating appropriate management practices in a robust watershed modeling system. It is written in a generic form to simulate any agriculturally dominant watershed within the US if appropriate input data are available.

PESTFADE- Pesticide Fate and Dynamics in the Environment

PESTFADE simulates the effects of runoff, leaching, sorption, degradation and volatilization on the fate and transport of a chemical in an agricultural system (19). The model is composed of 2 major programs, 3 subprograms and 5 subroutines that integrate water flow, runoff, erosion, heat flow and solute transport (19, 20). It is intended to describe the movement of water and solutes in unsaturated homogeneous soil (19).

The model assumes that water and solute flow is one-dimensional, the soil is homogeneous, the chemical is non-ionic, there is no loss of the chemical through photolysis during application and the metabolites do not move with depth and time (20).

There are 6 features to the model; the treatment of unsaturated water flow is based on the numerical solution of the Richard's equation, application of a chemical to farmlands occurs under conventional drainage or controlled drainage in arid, semi-arid and humid regions, considers the effect of soil macropores on water and pesticide movement, includes new methods to describe pesticide adsorption/desorption through non-equilibrium adsorption, incorporates chemical and microbial degradation mechanisms and considers the effects of different agricultural practices such as conventional tillage and no tillage on pesticide fate and transport (19).

PESTLA- Pesticide Leaching and Accumulation

PESTLA calculates pesticide leaching. It is very sensitive to sorption and transformation parameters (21). If those values are estimated the uncertainty in calculated amounts will be high for any meaningful model tests (21). PESTLA is composed of 3 submodels; water flow, soil temperature and pesticide behavior (22). The water flow submodel assumes a uniform potential rate of water extraction by plant roots over the whole rooting depth (21). Water flow is assumed to be one-dimensional, vertical and transient in saturated/ unsaturated systems (22). Soil temperature simulations assume a heat conductivity and heat capacity that are functions of the volume fraction of water in the soil (22). Temperature at the soil surface is assumed to be equal to the daily average of the air temperature (22). Pesticide transport in the model system is described by the convection/ dispersion equation (21). It assumes that sorption in the soil is always at equilibrium (21).

ADAPT- Agricultural Drainage and Pesticide Transport (23)

ADAPT incorporates the effects of water table management practices on water quality. There are three components to the model; hydrology, erosion and pesticide transport. ADAPT integrates the models GLEAMS and DRAINMOD. It is an extension of GLEAMS daily simulation model with a capability to account for subsurface drainage and subirrigation from DRAINMOD. Pesticide portioning and degradation are calculated each day. ADAPT requires weather data, soil data,

drainage system parameters and pesticide parameters as inputs. The model predicts concentrations on pesticides in both soil and groundwater.

WAVE (25)

WAVE is a pesticide leaching model that considers a mechanistic description of one-dimensional water, solute and heat transport. Pesticide sorption and transformation are simulated using linear isotherms and first order degradation submodels. The model was created to describe pesticide fate in rigid mineral soils. Processes that affect pesticide fate and transport are poorly represented within the model.

SIMULAT (24)

SIMULAT is a one-dimensional model that calculates the transport and transformation of biodegradable substances, such as nitrogen, sulfur and pesticides, in the unsaturated/ saturated zone of the soil. It is a one-dimensional model consisting of submodels to calculate macropore flow, infiltration, runoff, ET, plant growth, interception and heat flux in the soil. Either potential or actual ET may be used. Pesticide sorption is considered using an equilibrium or kinetic based linear isotherm. The model can simulate the fate of metabolites but does not consider volatilization or plant uptake. The model was designed to predict the fate of pesticides in soil.

VARLEACH (26)

VARLEACH is a simple leaching model that incorporates subroutines to allow for the effects of temperature and soil moisture on degradation rates in soil. The model allows adsorption/ desorption rates to vary with residence time of the pesticide in the soil. Originally the model was designed to simulate mobility and persistence of pre-emergent applications of herbicides in the top layers of the soil (0-15 cm). The model does not include pesticide volatilization, crop growth or crop removal of water. It also does not have erosion or runoff subroutines.

RZWQM- Root Zone Water Quality Model (27)

RZWQM is a process based simulation model of an agricultural system. It integrates the physical, chemical and biological processes that simulate the fate and transport of water, nutrients and pesticides in the soil-plant-atmosphere environment and the effects of agricultural management practices on soil water and solute movement that may cause surface and groundwater quality problems. Pesticide processes that are considered include transformation and metabolism of a pesticide in different compartments in the environment. Pesticide degradation in the soil matrix follows first order dissipation equations.

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PESTICIDE USAGE

Table 1- Estimated pesticide usage in Beaufort county, NC in 1999

CROP	PESTICIDE	Trade Name	ACRES	% ACRES TREATED	APPLICATION RATE	AMOUNT APPLIED*
corn	2,4-D	2,4-D, Weedone, Crossbc	46000	18	0.49 Lbs. AI/ A/YR	4057.2
corn	alachlor	Lasso, Partner	46000	39	1.71 Lbs. AI/ A/YR	30677.4
corn	ametryn	Evik	46000	18	0.79 Lbs. AI/ A/YR	6541.2
corn	atrazine	Aatrex, Purge	46000	78	1.39 Lbs. AI/ A/YR	49873.2
corn	butylate	Sutan +	46000	0	3.41 Lbs. AI/ A/YR	0
corn	carbofuran	Furadan	46000	10	1 Lbs. AI/ A/YR	4600
corn	chlorpyrifos	Dursban, Lorsban, Weedr	46000	0	0.96 Lbs. AI/ A/YR	0
corn	cyanazine	Bladex, Extrazine, Cycle	46000	0	2 Lbs. AI/ A/YR	0
corn	dicamba	Banvel, Clarity	46000	15	0.2 Lbs. AI/ A/YR	1380
corn	glyphosate	Roundup, Rodeo, Accord	46000	50	0.4 Lbs. AI/ A/YR	9200
corn	metolachlor	Derby, Bicep, Turbo	46000	30	1.55 Lbs. AI/ A/YR	21390
corn	nicosulfuron	Accent	46000	16	0.03 Lbs. AI/ A/YR	220.8
corn	paraquat	Cyclone, Prelude, Surefire	46000	7	0.56 Lbs. AI/ A/YR	1803.2
corn	primisulfuron	Beacon	46000	0	0.03 Lbs. AI/ A/YR	0
corn	simazine	Printrex, Simazat	46000	0	1.25 Lbs. AI/ A/YR	0
corn	terbufos	Counter	46000	41	1.1 Lbs. AI/ A/YR	20746
cotton	acephate	Orthene	23800	40	0.54 Lbs. AI/ A/YR	5140.8
cotton	aldicarb	Temik	23800	94	0.52 Lbs. AI/ A/YR	11633.44
cotton	bifenthrin	Brigade, Capture 2	23800	1	0.05 Lbs. AI/ A/YR	11.9
cotton	cyanazine	Bladex, Extrazine, Cycle	23800	10	0.3 Lbs. AI/ A/YR	714
cotton	cyfluthrin	Aztec, Baythroid	23800	10	0.1 Lbs. AI/ A/YR	238
cotton	cypermethrin	Ammo, Cynoff	23800	15	0.17 Lbs. AI/ A/YR	606.9
cotton	dicofol	Kelthane	23800	1	2.16 Lbs. AI/ A/YR	514.08
cotton	dicrotophos	Bidrin, Chiles Go Better	23800	1	0.12 Lbs. AI/ A/YR	28.56
cotton	dimethipin	Harvade	23800	5	0.31 Lbs. AI/ A/YR	368.9
cotton	dimethoate	Cygon	23800	1	0.1 Lbs. AI/ A/YR	23.8
cotton	disulfoton	Di-Syston, Root-X, Stand	23800	2	0.8 Lbs. AI/ A/YR	380.8
cotton	dsma	DSMA Liquid	23800	15	1.5 Lbs. AI/ A/YR	5355
cotton	esfenvalerate	Asana XL, Fury	23800	6	0.11 Lbs. AI/ A/YR	157.08
cotton	ethephon	Ethrel, Florel, Prep	23800	40	1.5 Lbs. AI/ A/YR	14280
cotton	etridiazole	Terrazole	23800	5	0.25 Lbs. AI/ A/YR	297.5
cotton	fenamiphos	Nemacur	23800	0	1 Lbs. AI/ A/YR	0
cotton	fluazifop	Fusilade DX, Ornamec	23800	5	0.16 Lbs. AI/ A/YR	190.4
cotton	fluometuron	Cotoran, Meturon	23800	75	0.65 Lbs. AI/ A/YR	11602.5
cotton	glyphosate	Roundup, Rodeo, Accord	23800	75	0.75 Lbs. AI/ A/YR	13387.5
cotton	lambdacyhalothrin	Commodore, Karate	23800	54	0.07 Lbs. AI/ A/YR	899.64
cotton	mepiquat chloride	Pix	23800	90	0.03 Lbs. AI/ A/YR	642.6
cotton	metalaxyl	Ridomil, Subdue, Apron	23800	0	0.14 Lbs. AI/ A/YR	0

Table 1 continued

cotton	methamazole		23800	0	0.33 Lbs. AI/ A/YR	0
cotton	metolachlor	Derby, Bicep, Turbo	23800	0	0.5 Lbs. AI/ A/YR	0
cotton	msma	Bueno 6	23800	40	1 Lbs. AI/ A/YR	9520
cotton	norflurazon	Zorial, Solicam, Predict	23800	0	1.1 Lbs. AI/ A/YR	0
cotton	oxyfluorfen	Goal	23800	0	0.12 Lbs. AI/ A/YR	0
cotton	paraquat	Cyclone, Prelude, Surefire	23800	0	0.63 Lbs. AI/ A/YR	0
cotton	pcnb	Terrachlor, Turfcide, Terra	23800	8	0.8 Lbs. AI/ A/YR	1523.2
cotton	pendimethalin	Prowl, Stomp, Squadron	23800	5	0.75 Lbs. AI/ A/YR	892.5
cotton	phorate	Thimet, Rampart, Milo Ba	23800	7	0.8 Lbs. AI/ A/YR	1332.8
cotton	profenfos	Curacon	23800	0	0.25 Lbs. AI/ A/YR	0
cotton	sethoxydim	Poast, Poast Plus, Vantage	23800	0	0.3 Lbs. AI/ A/YR	0
cotton	thidiazuron	Dropp	23800	50	0.07 Lbs. AI/ A/YR	833
cotton	thiodicarb	Larvin	23800	1	0.25 Lbs. AI/ A/YR	59.5
cotton	tralomethrin	Scout, Striker	23800	8	0.06 Lbs. AI/ A/YR	114.24
cotton	tribufos	DEF	23800	75	1.12 Lbs. AI/ A/YR	19992
cotton	trifluralin	Treflan, Trilin, Tri-4	23800	0	0.75 Lbs. AI/ A/YR	0
hay	2,4-D	2,4-D, Weedone, Crossbc	500	10	0.5 Lbs. AI/ A/YR	25
hay	carbaryl	Sevin	500	5	1 Lbs. AI/ A/YR	25
hay	dicamba	Banvel, Clarity	500	3	0.15 Lbs. AI/ A/YR	2.25
hay	methomyl	Lannate, Lannabait	500	0	0.45 Lbs. AI/ A/YR	0
oats	2,4-D	2,4-D, Weedone, Crossbc	800	15	0.5 Lbs. AI/ A/YR	60
oats	carbaryl	Sevin	800	5	1 Lbs. AI/ A/YR	40
oats	dicamba	Banvel, Clarity	800	1	0.12 Lbs. AI/ A/YR	0.96
oats	malathion	Cythion	800	15	0.095 Lbs. AI/ A/YR	11.4
oats	methomyl	Lannate, Lannabait	800	0	0.45 Lbs. AI/ A/YR	0
peanuts	2,4-DB	Weedone	265	59	0.22 Lbs. AI/ A/YR	34.397
peanuts	acephate	Orthene	265	8	0.5 Lbs. AI/ A/YR	10.6
peanuts	acifluorfen	Blazer	265	75	0.38 Lbs. AI/ A/YR	75.525
peanuts	alachlor	Lasso, Partner	265	1	4 Lbs. AI/ A/YR	10.6
peanuts	aldicarb	Temik	265	68	1 Lbs. AI/ A/YR	180.2
peanuts	benefin	Balan	265	0	1.5 Lbs. AI/ A/YR	0
peanuts	bentazon	Basagran	265	60	0.75 Lbs. AI/ A/YR	119.25
peanuts	carbaryl	Sevin	265	20	1.25 Lbs. AI/ A/YR	66.25
peanuts	carboxin	Vitavax	265	3	1.12 Lbs. AI/ A/YR	8.904
peanuts	chlorothalonil	Bravo	265	94	2.47 Lbs. AI/ A/YR	615.277
peanuts	chlorthrifos	Dursban, Lorsban, Weedr	265	56	2 Lbs. AI/ A/YR	296.8
peanuts	copper		265	1	2.15 Lbs. AI/ A/YR	5.6975
peanuts	disulfoton	Di-Syston, Root-X, Stand	265	6	1 Lbs. AI/ A/YR	15.9
peanuts	esfenvalerate	Asana XL, Fury	265	12	0.03 Lbs. AI/ A/YR	0.954

Table 1 continued

peanuts	ethalfuralin	Sonalan	265	45	0.75 Lbs. AI/ A/YR	89.4375
peanuts	ethoprop	Mocap	265	10	2 Lbs. AI/ A/YR	53
peanuts	fenoxaprop	Acclaim, Bugle, Whip	265	1	0.15 Lbs. AI/ A/YR	0.3975
peanuts	fonofos	Dyfonate	265	10	2 Lbs. AI/ A/YR	53
peanuts	imazethapyr	Pursuit	265	15	0.06 Lbs. AI/ A/YR	2.385
peanuts	iprodione	Rovral	265	19	0.4 Lbs. AI/ A/YR	20.14
peanuts	malathion	Cythion	265	1	1 Lbs. AI/ A/YR	2.65
peanuts	metam sodium		265	42	31.8 Lbs. AI/ A/YR	3539.34
peanuts	methomyl	Lannate, Lannabait	265	14	0.4 Lbs. AI/ A/YR	14.84
peanuts	metolachlor	Derby, Bicep, Turbo	265	0	2.5 Lbs. AI/ A/YR	0
peanuts	paraquat	Cyclone, Prelude, Surefire	265	16	0.12 Lbs. AI/ A/YR	5.088
peanuts	pcnb	Terrachlor, Turfcide, Terra	265	2	5 Lbs. AI/ A/YR	26.5
peanuts	pendimethalin	Prowl, Stomp, Squadron	265	5	1 Lbs. AI/ A/YR	13.25
peanuts	phorate	Thimet, Rampart, Milo Ba	265	15	1.11 Lbs. AI/ A/YR	44.1225
peanuts	propargite	Comite	265	4	1.6 Lbs. AI/ A/YR	16.96
peanuts	pyridate	Tough	265	3	0.93 Lbs. AI/ A/YR	7.3935
peanuts	sethoxydim	Poast, Poast Plus, Vantage	265	8	0.28 Lbs. AI/ A/YR	5.936
peanuts	sulfur		265	1	3 Lbs. AI/ A/YR	7.95
peanuts	thiophanate methyl	Topsin	265	1	1.5 Lbs. AI/ A/YR	3.975
peanuts	vernolate	Vernam	265	32	2.19 Lbs. AI/ A/YR	185.712
potatoes	azinphos-methyl	Guthion, DuTox	0	62	0.75 Lbs. AI/ A/YR	0
potatoes	carbofuran	Sevin	0	7	0.75 Lbs. AI/ A/YR	0
potatoes	carbofuran	Furadan	0	83	0.75 Lbs. AI/ A/YR	0
potatoes	chlorothalonil	Bravo	0	8	1.25 Lbs. AI/ A/YR	0
potatoes	disulfoton	Di-Syston, Root-X, Stand	0	3	2.5 Lbs. AI/ A/YR	0
potatoes	esfenvalerate	Asana XL, Fury	0	30	0.05 Lbs. AI/ A/YR	0
potatoes	fenvalerate	Asana XL, Fury	0	31	0.1 Lbs. AI/ A/YR	0
potatoes	linuron	Lorex, Linex, Linuron	0	7	1.5 Lbs. AI/ A/YR	0
potatoes	maleic hydrazide	Royal Slo-Gro	0	14	2.23 Lbs. AI/ A/YR	0
potatoes	mancozeb	Dikar, zyban	0	37	1.5 Lbs. AI/ A/YR	0
potatoes	maneb	Dithane, manex	0	12	1 Lbs. AI/ A/YR	0
potatoes	metalaxyl	Ridomil, Subdue, Apron	0	6	1.75 Lbs. AI/ A/YR	0
potatoes	methamidophos	Monitor	0	14	1 Lbs. AI/ A/YR	0
potatoes	metolachlor	Derby, Bicep, Turbo	0	11	2 Lbs. AI/ A/YR	0
potatoes	metribuzin	Lexone, Sencor	0	100	0.5 Lbs. AI/ A/YR	0
potatoes	oxamyl	Vydate	0	7	0.75 Lbs. AI/ A/YR	0
potatoes	permethrin	Pounce, Ambush, Ketokil	0	83	0.1 Lbs. AI/ A/YR	0
potatoes	phorate	Thimet, Rampart, Milo Ba	0	70	2.5 Lbs. AI/ A/YR	0
potatoes	sethoxydim	Poast, Poast Plus, Vantage	0	7	0.2 Lbs. AI/ A/YR	0

Table 1 continued

soybeans	2,4-D	2,4-D, Weedone, Crossbc	70000	0	0.5 Lbs. AI/ A/YR	0
soybeans	2,4-DB	Weedone	70000	10	0.03 Lbs. AI/ A/YR	210
soybeans	acifluorfen	Blazer	70000	15	0.24 Lbs. AI/ A/YR	2520
soybeans	alachlor	Lasso, Partner	70000	5	1.5 Lbs. AI/ A/YR	5250
soybeans	bentazon	Basagran	70000	7	0.43 Lbs. AI/ A/YR	2107
soybeans	chlorimuron	Classic	70000	15	0.02 Lbs. AI/ A/YR	210
soybeans	clomazone	Command	70000	0	0.66 Lbs. AI/ A/YR	0
soybeans	fenoxaprop	Acclaim, Bugle, Whip	70000	0	0.1 Lbs. AI/ A/YR	0
soybeans	fluazifop	Fusilade DX, Ornamec	70000	2	0.25 Lbs. AI/ A/YR	350
soybeans	fomesafen	Typhoon	70000	0	0.16 Lbs. AI/ A/YR	0
soybeans	glyphosate	Roundup, Rodeo, Accord	70000	75	0.77 Lbs. AI/ A/YR	40425
soybeans	imazaquin	Scepter, Image	70000	8	0.1 Lbs. AI/ A/YR	560
soybeans	imazethapyr	Pursuit	70000	7	0.06 Lbs. AI/ A/YR	294
soybeans	linuron	Lorex, Linex, Linuron	70000	0	0.64 Lbs. AI/ A/YR	0
soybeans	metolachlor	Derby, Bicep, Turbo	70000	0	1.97 Lbs. AI/ A/YR	0
soybeans	metribuzin	Lexone, Sencor	70000	0	0.31 Lbs. AI/ A/YR	0
soybeans	paraquat	Cyclone, Prelude, Surefire	70000	5	0.5 Lbs. AI/ A/YR	1750
soybeans	pendimethalin	Prowl, Stomp, Squadron	70000	5	0.69 Lbs. AI/ A/YR	2415
soybeans	quizalofop	Assure II	70000	5	0.06 Lbs. AI/ A/YR	210
soybeans	sethoxydim	Poast, Poast Plus, Vantaq	70000	15	0.2 Lbs. AI/ A/YR	2100
soybeans	thiodicarb	Larvin	70000	0	0.69 Lbs. AI/ A/YR	0
soybeans	tralomethrin	Scout, Striker	70000	0	0.02 Lbs. AI/ A/YR	0
soybeans	trifluralin	Treflan, Trilin, Tri-4	70000	3	0.88 Lbs. AI/ A/YR	1848
tobacco	1,3-D		2970	20	70 Lbs. AI/ A/YR	41580
tobacco	acephate	Orthene	2970	100	2.24 Lbs. AI/ A/YR	6652.8
tobacco	aldicarb	Temik	2970	10	2.25 Lbs. AI/ A/YR	668.25
tobacco	BT		2970	13	0 Lbs. AI/ A/YR	0
tobacco	carbofuran	Sevin	2970	2	1.2 Lbs. AI/ A/YR	71.28
tobacco	carbofuran	Furadan	2970	2	6 Lbs. AI/ A/YR	356.4
tobacco	chloropicrin	Telone	2970	20	50 Lbs. AI/ A/YR	29700
tobacco	chlorypyrifos	Dursban, Lorsban, Weedr	2970	25	2.5 Lbs. AI/ A/YR	1856.25
tobacco	diazinon	Spectracide	2970	6	2.5 Lbs. AI/ A/YR	445.5
tobacco	diphenamid	Dymid	2970	6	2 Lbs. AI/ A/YR	356.4
tobacco	disulfoton	Di-Syston, Root-X, Stand	2970	4	4 Lbs. AI/ A/YR	475.2
tobacco	ethephon	Ethrel, Florel, Prep	2970	15	1.2 Lbs. AI/ A/YR	534.6
tobacco	ethoprop	Mocap	2970	25	2 Lbs. AI/ A/YR	1485
tobacco	fenamiphos	Nemacur	2970	15	1 Lbs. AI/ A/YR	445.5
tobacco	fonofos	Dyfonate	2970	2	1.5 Lbs. AI/ A/YR	89.1
tobacco	isopropalin	Paarlan	2970	0	1 Lbs. AI/ A/YR	0

Table 1 continued

tobacco	malathion	Cythion	2970	1	1.2 Lbs. AI/ A/YR	35.64
tobacco	maleic hydrazide	Royal Slo-Gro	2970	100	3.1 Lbs. AI/ A/YR	9207
tobacco	metalaxyl	Ridomil, Subdue, Apron	2970	50	0.5 Lbs. AI/ A/YR	742.5
tobacco	methomyl	Lannate, Lannabait	2970	14	0.6 Lbs. AI/ A/YR	249.48
tobacco	methyl bromide		2970	2	426 Lbs. AI/ A/YR	25304.4
tobacco	napropamide	Devrinol	2970	15	1 Lbs. AI/ A/YR	445.5
tobacco	pebulate	Tillam	2970	0	4 Lbs. AI/ A/YR	0
tobacco	pendimethalin	Prowl, Stomp, Squadron	2970	50	0.75 Lbs. AI/ A/YR	1113.75
wheat	2,4-D	2,4-D, Weedone, Crossbc	44000	36	0.5 Lbs. AI/ A/YR	7920
wheat	bromoxynil	Buctril	44000	1	0.75 Lbs. AI/ A/YR	330
wheat	chlorimuron	Sevin	44000	5	1 Lbs. AI/ A/YR	2200
wheat	dicamba	Banvel, Clarity	44000	10	0.12 Lbs. AI/ A/YR	528
wheat	diclofop	Hoelon, Illoxan, Brestan	44000	5	0.75 Lbs. AI/ A/YR	1650
wheat	dimethoate	Cygon	44000	2	0.5 Lbs. AI/ A/YR	440
wheat	disulfoton	Di-Syston, Root-X, Stand	44000	1	1 Lbs. AI/ A/YR	440
wheat	malathion	Cythion	44000	7	0.95 Lbs. AI/ A/YR	2926
wheat	methomyl	Lannate, Lannabait	44000	0	0.45 Lbs. AI/ A/YR	0
wheat	propiconazole	Banner, Tilt, Orbit	44000	2	0.11 Lbs. AI/ A/YR	96.8
wheat	triadimefon	Bayleton, Strike	44000	1	0.1 Lbs. AI/ A/YR	44
wheat		Harmony Extra	44000	20		

Table 2- Estimated pesticide usage in Hyde County, NC in 1999

CROP	PESTICIDE	Trade Name	ACRES	% ACRES TREATED	APPLICATION RATE	AMOUNT APPLIED*
corn	2,4-D	2,4-D, Weedone, Crossbow	31000	18	0.49 Lbs. AI/ A/YR	2734.2
corn	alachlor	Lasso, Partner	31000	39	1.71 Lbs. AI/ A/YR	20673.9
corn	ametryn	Evik	31000	18	0.79 Lbs. AI/ A/YR	4408.2
corn	atrazine	Aatrex, Purge	31000	78	1.39 Lbs. AI/ A/YR	33610.2
corn	butylate	Sutan +	31000	4	3.41 Lbs. AI/ A/YR	4228.4
corn	carbofuran	Furadan	31000	16	1 Lbs. AI/ A/YR	4960
corn	chlorpyrifos	Dursban, Lorsban, Weedmaster	31000	17	0.96 Lbs. AI/ A/YR	5059.2
corn	cyanazine	Bladex, Extrazine, Cycle	31000	3	2 Lbs. AI/ A/YR	1860
corn	dicamba	Banvel, Clarity	31000	15	0.2 Lbs. AI/ A/YR	930
corn	glyphosate	Roundup, Rodeo, Accord	31000	18	0.4 Lbs. AI/ A/YR	2232
corn	metolachlor	Derby, Bicep, Turbo	31000	32	1.55 Lbs. AI/ A/YR	15376
corn	nicosulfuron	Accent	31000	16	0.03 Lbs. AI/ A/YR	148.8
corn	paraquat	Cyclone, Prelude, Surefire	31000	7	0.56 Lbs. AI/ A/YR	1215.2
corn	primisulfuron	Beacon	31000	2	0.03 Lbs. AI/ A/YR	18.6
corn	simazine	Printrex, Simazat	31000	5	1.25 Lbs. AI/ A/YR	1937.5
corn	terbufos	Counter	31000	41	1.1 Lbs. AI/ A/YR	13981
cotton	acephate	Orthene	20000	40	0.54 Lbs. AI/ A/YR	4320
cotton	aldicarb	Temik	20000	94	0.52 Lbs. AI/ A/YR	9776
cotton	bifenthrin	Brigade, Capture 2	20000	1	0.05 Lbs. AI/ A/YR	10
cotton	cyanazine	Bladex, Extrazine, Cycle	20000	20	0.3 Lbs. AI/ A/YR	1200
cotton	cyfluthrin	Aztec, Baythroid	20000	12	0.1 Lbs. AI/ A/YR	240
cotton	cypermethrin	Ammo, Cynoff	20000	20	0.17 Lbs. AI/ A/YR	680
cotton	dicofol	Kelthane	20000	1	Lbs. AI/ A/YR	0
cotton	dicrotophos	Bidrin, Chiles Go Better	20000	1	0.12 Lbs. AI/ A/YR	24
cotton	dimethipin	Harvade	20000	10	0.31 Lbs. AI/ A/YR	620
cotton	dimethoate	Cygon	20000	1	0.1 Lbs. AI/ A/YR	20
cotton	disulfoton	Di-Syston, Root-X, Stand Aid	20000	2	0.8 Lbs. AI/ A/YR	320
cotton	dsma	DSMA Liquid	20000	15	1.5 Lbs. AI/ A/YR	4500
cotton	esfenvalerate	Asana XL, Fury	20000	6	0.11 Lbs. AI/ A/YR	132
cotton	ethephon	Ethrel, Florel, Prep	20000	40	1.5 Lbs. AI/ A/YR	12000
cotton	etridiazole	Terrazole	20000	5	0.25 Lbs. AI/ A/YR	250
cotton	fenamiphos	Nemacur	20000	1	1 Lbs. AI/ A/YR	200
cotton	fluazifop	Fusilade DX, Ornamec	20000	20	0.16 Lbs. AI/ A/YR	640
cotton	fluometuron	Cotoran, Meturon	20000	100	0.65 Lbs. AI/ A/YR	13000
cotton	glyphosate	Roundup, Rodeo, Accord	20000	5	0.75 Lbs. AI/ A/YR	750
cotton	lambdacyhalothrin	Commodore, Karate	20000	54	0.07 Lbs. AI/ A/YR	756
cotton	mepiquat chloride	Pix	20000	50	0.03 Lbs. AI/ A/YR	300
cotton	metalaxyl	Ridomil, Subdue, Apron	20000	13	0.14 Lbs. AI/ A/YR	364

Table 2 continued

cotton	methamazole		20000	25	0.33 Lbs. AI/ A/YR	1650
cotton	metolachlor	Derby, Bicep, Turbo	20000	5	0.5 Lbs. AI/ A/YR	500
cotton	msma	Bueno 6	20000	40	1 Lbs. AI/ A/YR	8000
cotton	norflurazon	Zorial, Solicam, Predict	20000	25	1.1 Lbs. AI/ A/YR	5500
cotton	oxyfluorofen	Goal	20000	1	0.12 Lbs. AI/ A/YR	24
cotton	paraquat	Cyclone, Prelude, Surefire	20000	3	0.63 Lbs. AI/ A/YR	378
cotton	pcnb	Terrachlor, Turfcide, Terra-coat	20000	18	0.8 Lbs. AI/ A/YR	2880
cotton	pendimethalin	Prowl, Stomp, Squadron	20000	45	0.75 Lbs. AI/ A/YR	6750
cotton	phorate	Thimet, Rampart, Milo Bait	20000	7	0.8 Lbs. AI/ A/YR	1120
cotton	profenfos	Curacon	20000	3	0.25 Lbs. AI/ A/YR	150
cotton	sethoxydim	Poast, Poast Plus, Vantage	20000	20	0.3 Lbs. AI/ A/YR	1200
cotton	thidiazuron	Dropp	20000	50	0.07 Lbs. AI/ A/YR	700
cotton	thiodicarb	Larvin	20000	1	0.25 Lbs. AI/ A/YR	50
cotton	tralomethrin	Scout, Striker	20000	8	0.06 Lbs. AI/ A/YR	96
cotton	tribufos	DEF	20000	75	1.12 Lbs. AI/ A/YR	16800
cotton	trifluralin	Treflan, Trilin, Tri-4	20000	45	0.75 Lbs. AI/ A/YR	6750
hay	2,4-D	2,4-D, Weedone, Crossbow	300	10	0.5 Lbs. AI/ A/YR	15
hay	carbaryl	Sevin	300	5	1 Lbs. AI/ A/YR	15
hay	dicamba	Banvel, Clarity	300	3	0.15 Lbs. AI/ A/YR	1.35
hay	methomyl	Lannate, Lannabait	300	5	0.45 Lbs. AI/ A/YR	6.75
potatoes	azinphos-methyl	Guthion, DuTox	250	62	0.75 Lbs. AI/ A/YR	116.25
potatoes	carbaryl	Sevin	250	7	0.75 Lbs. AI/ A/YR	13.125
potatoes	carbofuran	Furadan	250	83	0.75 Lbs. AI/ A/YR	155.625
potatoes	chlorothalonil	Bravo	250	8	1.25 Lbs. AI/ A/YR	25
potatoes	disulfoton	Di-Syston, Root-X, Stand Aid	250	3	2.5 Lbs. AI/ A/YR	18.75
potatoes	esfenvalerate	Asana XL, Fury	250	30	0.05 Lbs. AI/ A/YR	3.75
potatoes	fenvalerate	Asana XL, Fury	250	31	0.1 Lbs. AI/ A/YR	7.75
potatoes	linuron	Lorex, Linex, Linuron	250	7	1.5 Lbs. AI/ A/YR	26.25
potatoes	maleic hydrazide	Royal Slo-Gro	250	14	2.23 Lbs. AI/ A/YR	78.05
potatoes	mancozeb	Dikar, zyban	250	37	1.5 Lbs. AI/ A/YR	138.75
potatoes	maneb	Dithane, manex	250	12	1 Lbs. AI/ A/YR	30
potatoes	metalaxyl	Ridomil, Subdue, Apron	250	6	1.75 Lbs. AI/ A/YR	26.25
potatoes	methamidophos	Monitor	250	14	1 Lbs. AI/ A/YR	35
potatoes	metolachlor	Derby, Bicep, Turbo	250	11	2 Lbs. AI/ A/YR	55
potatoes	metribuzin	Lexone, Sencor	250	100	0.5 Lbs. AI/ A/YR	125
potatoes	oxamyl	Vydate	250	7	0.75 Lbs. AI/ A/YR	13.125
potatoes	permethrin	Pounce, Ambush, Ketokil	250	83	0.1 Lbs. AI/ A/YR	20.75
potatoes	phorate	Thimet, Rampart, Milo Bait	250	70	2.5 Lbs. AI/ A/YR	437.5
potatoes	sethoxydim	Poast, Poast Plus, Vantage	250	7	0.2 Lbs. AI/ A/YR	3.5

Table 2 continued

soybeans	2,4-D	2,4-D, Weedone, Crossbow	40000	3	0.5 Lbs. AI/ A/YR	600
soybeans	2,4-DB	Weedone	40000	15	0.03 Lbs. AI/ A/YR	180
soybeans	acifluorfen	Blazer	40000	15	0.24 Lbs. AI/ A/YR	1440
soybeans	alachlor	Lasso, Partner	40000	25	1.5 Lbs. AI/ A/YR	15000
soybeans	bentazon	Basagran	40000	7	0.43 Lbs. AI/ A/YR	1204
soybeans	chlorimuron	Classic	40000	31	0.02 Lbs. AI/ A/YR	248
soybeans	clomazone	Command	40000	1	0.66 Lbs. AI/ A/YR	264
soybeans	fenoxaprop	Acclaim, Bugle, Whip	40000	20	0.1 Lbs. AI/ A/YR	800
soybeans	fluazifop	Fusilade DX, Ornamec	40000	20	0.25 Lbs. AI/ A/YR	2000
soybeans	fomesafen	Typhoon	40000	6	0.16 Lbs. AI/ A/YR	384
soybeans	glyphosate	Roundup, Rodeo, Accord	40000	11	0.77 Lbs. AI/ A/YR	3388
soybeans	imazaquin	Scepter, Image	40000	27	0.1 Lbs. AI/ A/YR	1080
soybeans	imazethapyr	Pursuit	40000	7	0.06 Lbs. AI/ A/YR	168
soybeans	linuron	Lorex, Linex, Linuron	40000	10	0.64 Lbs. AI/ A/YR	2560
soybeans	metolachlor	Derby, Bicep, Turbo	40000	9	1.97 Lbs. AI/ A/YR	7092
soybeans	metribuzin	Lexone, Sencor	40000	12	0.31 Lbs. AI/ A/YR	1488
soybeans	paraquat	Cyclone, Prelude, Surefire	40000	6	0.5 Lbs. AI/ A/YR	1200
soybeans	pendimethalin	Prowl, Stomp, Squadron	40000	28	0.69 Lbs. AI/ A/YR	7728
soybeans	quizalofop	Assure II	40000	3	0.06 Lbs. AI/ A/YR	72
soybeans	sethoxydim	Poast, Poast Plus, Vantage	40000	20	0.2 Lbs. AI/ A/YR	1600
soybeans	thiodicarb	Larvin	40000	7	0.69 Lbs. AI/ A/YR	1932
soybeans	tralomethrin	Scout, Striker	40000	6	0.02 Lbs. AI/ A/YR	48
soybeans	trifluralin	Treflan, Trilin, Tri-4	40000	16	0.88 Lbs. AI/ A/YR	5632
wheat	2,4-D	2,4-D, Weedone, Crossbow	24000	36	0.5 Lbs. AI/ A/YR	4320
wheat	bromoxynil	Buctril	24000	1	0.75 Lbs. AI/ A/YR	180
wheat	carbaryl	Sevin	24000	5	1 Lbs. AI/ A/YR	1200
wheat	dicamba	Banvel, Clarity	24000	10	0.12 Lbs. AI/ A/YR	288
wheat	diclofop	Hoelon, Illoxan, Brestan	24000	5	0.75 Lbs. AI/ A/YR	900
wheat	dimethoate	Cygon	24000	2	0.5 Lbs. AI/ A/YR	240
wheat	disulfoton	Di-Syston, Root-X, Stand Aid	24000	1	1 Lbs. AI/ A/YR	240
wheat	malathion	Cythion	24000	7	0.95 Lbs. AI/ A/YR	1596
wheat	methomyl	Lannate, Lannabait	24000	5	0.45 Lbs. AI/ A/YR	540
wheat	propiconazole	Banner, Tilt, Orbit	24000	2	0.11 Lbs. AI/ A/YR	52.8
wheat	triadimefon	Bayleton, Strike	24000	1	0.1 Lbs. AI/ A/YR	24

Table 3- Comparison of calculated pesticide use and actual pesticide use (Total 1000 Lbs. AI/YR)

PESTICIDE	Beaufort County		Hyde County	
	Extension Agent	Calculated	Extension Agent	Calculated
2,4-D			7.05	7.67
acephate	11.54	11.80	4.32	2.38
alachlor	63.34	5.26	35.67	35.67
aldicarb	70.59	12.48	9.78	5.38
atrazine	60.28	49.87	33.61	33.61
butylate	7.58	0.00	0.00	4.23
carbaryl	10.39	0.13	1.20	1.23
carbofuran	9.65	5.03	0.16	5.12
chloropicrin	4.17	29.70		
chlorothalonil	0.71	0.62		
chlorpyrifos	15.85	2.15		
cyanazine	3.95	0.71	1.20	2.52
dicamba			1.22	1.22
ethephon	6.87	14.81		
fluazifop	3.83	0.54		
fluometuron	6.63	11.60		
glyphosate	10.31	63.01	6.37	6.03
linuron	4.52	0.00		
malathion	3.46	2.98	0.00	1.60
maleic hydrazide	10.07	9.21		
metam sodium	3.87	3.54		
metolachlor	40.84	21.39	0.00	22.80
metribuzin	2.81	0.00	0.13	1.61
paraquat	4.48	3.56		
pebulate	2.33	0.00		
pendimethalin	18.59	4.43	0.00	11.44
sethoxydim	3.42	2.11		
simazine	3.48	0.00	0.00	1.94
terbufos	25.08	20.75		
tribufos	8.57	19.99	16.80	9.24
trifluralin	13.30	1.85	5.63	3.71
Total AI/ YR	430.51	297.53	123.13	157.39

Table 4- Crop acreage in the Albemarle-Pamlico Estuarine System in 1999

	Barley	Corn	Cotton	Hay	Oats	Peanuts	Potatoes	Sorghum	Soybeans	Tobacco	Wheat
Beaufort		43000	19000	500	1700	245	200		67000	3550	43000
Bertie		17500	33300	200		16480			16300	2260	3700
Camden		14800	1700				2900		20000		11500
Cartaret		21000	4900	200			490	250	20000	530	4100
Chowan		4000	19500	200		5405	250	500	7000	200	2200
Craven		12000	18000	1200		35			19000	3585	4500
Currituck		12000	1100	200		85	950		16000		9000
Dare								250	2100		400
Edgecombe		11000	44000	2400	420	12335	1900	300	24000	5135	5000
Gates		5000	20700	800		6225			10200	95	2300
Greene		96000	17000	2300	250	75	600		27000	5540	8800
Hertford		9300	18200	600		10705			7400	1350	800
Hyde		24000	18400	300			230	1150	27000		11900
Jones		7000	22400	1400					13000	2350	6200
Martin		6000	42400	1100		13330			10500	3510	2200
Pamlico		10400	4400	300			2400		21000	385	9700
Pasquotank		18500	4500			130	4200	2600	41000		24800
Perquimans		15000	20300	400	200	2910	200		29000		12500
Pitt		16000	37500	3400	650	4380			46000	11180	17800
Tyrell		25500	3500	200	600	90	2200		32000		17700
Washington		26000	10800	1200		2505	2500	200	43000	300	2100
Totals	0	394000	361600	16900	3820	74935	19020	5250	498500	39970	200200

Crop Acreage for the Year 1999- printed from the ncagr.com website December 2000

MEASURED PESTICIDE CONCENTRATIONS

Table 5- Pesticide concentrations measured in samples collected from the Albemarle-Pamlico Estuarine System in 2000

Sample ID	Edgecombe County		0517TR1	0517TR2	0606TR1	0606TR2	0615TR1	0615TR2	0705TR3	0705TR4
	Total Lbs. Pesticide Applied		520	504	540	531	535	518	534	499
Volume (mL)			5/17/2000	5/17/2000	6/6/2000	6/6/2000	6/15/2000	3/15/2000/	7/5/2000	7/5/2000
Collection Date			Downstream from Princeville	Hwy 64 Bypass	P003	P004	P001	P002	P003	P004
Station			Tar River	Tar River	Tar River	Tar River	Tar River	Tar River	Tar River	Tar River
Water Body										
alachlor	16919.3		0.29	0.104	0.033	0.018	0.035	0.016	0.008	0.006
2,6-diethylaniline			0.041	0.02	nd	nd	0.01	0.008	nd	nd
atrazine	12124.2		0.35	0.17	0.11	0.08	0.21	0.06	nd	nd
deethylatrazine			0.098	0.025	0.06	0.1	0.006	0.019	nd	nd
benfluralin			nd	nd	nd	nd	nd	nd	nd	nd
butylate	1500.4		nd	nd	nd	nd	nd	nd	nd	nd
carbaryl	3697.74		nd	nd	nd	nd	nd	nd	nd	nd
carbofuran	3558.95		nd	nd	nd	nd	nd	nd	nd	nd
chlorothalonil	28829.403		nd	nd	nd	nd	nd	nd	nd	nd
chlorpyrifos	23584.65		nd	nd	nd	nd	nd	nd	nd	0.01
cyanazine	3300		nd	nd	nd	nd	0.048	0.029	0.01	nd
dacthal			nd	nd	nd	nd	nd	nd	nd	nd
diazinon	770.25		nd	nd	nd	nd	nd	nd	nd	nd
dimethoate	94		nd	nd	nd	nd	nd	nd	nd	nd
disulfoton	2458.2		nd	nd	nd	nd	nd	nd	nd	nd
EPTC			nd	nd	nd	nd	nd	nd	nd	nd
ethalfuralin	4163.0625		nd	nd	nd	nd	nd	nd	nd	nd
ethoprop	4418.3		nd	nd	nd	nd	nd	nd	nd	nd
fonofos	2621.05		nd	nd	nd	nd	nd	nd	nd	nd
linuron	1735.5		nd	nd	nd	nd	nd	nd	nd	nd
malathion	523.455		nd	nd	nd	nd	nd	nd	nd	nd
methyl parathion			nd	nd	nd	nd	nd	nd	nd	nd
metolachlor	32882.95		0.14	0.061	0.007	0.015	0.015	0.011	0.019	0.007
metribuzin	1842.8		nd	nd	nd	nd	nd	nd	nd	nd
molinate			nd	nd	nd	nd	nd	nd	nd	nd
napropamide	1129.7		nd	nd	nd	nd	nd	nd	nd	nd
pebulate	2875.6		nd	nd	nd	nd	nd	nd	nd	nd
pendimethalin	23879.425		nd	nd	nd	nd	nd	nd	nd	nd
permethrin	157.7		nd	nd	nd	nd	nd	nd	nd	nd
prometon			nd	nd	nd	nd	nd	nd	nd	nd
phorate			nd	nd	nd	nd	nd	nd	nd	nd
simazine	687.5		0.082	0.009	0.041	0.03	0.078	0.13	0.065	0.055
tebuthiuron			nd	nd	nd	nd	nd	nd	nd	nd
terbufos	4961		nd	nd	nd	nd	nd	nd	nd	nd
trifluralin	18229.2		nd	nd	nd	nd	nd	nd	nd	nd

Table 5 (continued)

Pitt County

Total Lbs. Pesticide Applied	0705TR1	0705TR2	0607PR1	0607PR3	0607PR4	0607PR5	0607PR6	0607PR7
	500	501	508	479	508	490	531	523
	7/5/2000	7/5/2000	6/6/2000	6/6/2000	6/6/2000	6/6/2000	6/6/2000	6/6/2000
	P006	P005	0865000N	0982500N	Channel Marker 9	Core Point Marker #5	Hwy 17- Washington	06500000 P0007
	Tar River	Tar River	Pamlico River	Pamlico River	Pamlico River	Pamlico River	Pamlico River	Pamlico River
18492.24	nd	nd	0.026	0.059	nd	0.026	0.012	nd
	nd	nd	0.019	nd	nd	nd	nd	nd
1734.72	nd	nd	0.02	0.011	0.019	0.008	nd	nd
	nd	nd	nd	nd	nd	nd	nd	nd
	nd	nd	nd	nd	nd	nd	nd	nd
218.24	nd	nd	nd	nd	nd	nd	nd	nd
2455.82	nd	nd	nd	nd	nd	nd	nd	nd
1597.6	nd	nd	nd	nd	nd	nd	nd	nd
10169.484	nd	nd	nd	nd	nd	nd	nd	nd
22495.72	nd	nd	nd	nd	nd	nd	nd	nd
2346	0.034	0.016	nd	nd	nd	nd	nd	nd
	nd	nd	nd	nd	nd	nd	nd	nd
1677	nd	nd	nd	nd	nd	nd	nd	nd
215.5	nd	nd	nd	nd	nd	nd	nd	nd
2829.6	nd	nd	nd	nd	nd	nd	nd	nd
	nd	nd	nd	nd	nd	nd	nd	nd
1478.25	nd	nd	nd	nd	nd	nd	nd	nd
5124.4	nd	nd	nd	nd	nd	nd	nd	nd
1211.4	nd	nd	nd	nd	nd	nd	nd	nd
2944	nd	nd	nd	nd	nd	nd	nd	nd
1370.9225	nd	nd	nd	nd	nd	nd	nd	nd
	nd	nd	nd	nd	nd	nd	nd	nd
17551.9	0.012	0.011	0.64	0.41	0.016	0.035	0.48	0.027
1711.2	nd	nd	nd	nd	nd	nd	nd	nd
	nd	nd	nd	nd	nd	nd	nd	nd
2459.6	nd	nd	nd	nd	nd	nd	nd	nd
6260.8	nd	nd	nd	nd	nd	nd	nd	nd
26611.95	nd	nd	nd	nd	nd	nd	nd	nd
0	nd	nd	nd	nd	nd	nd	nd	nd
	nd	nd	nd	nd	nd	nd	nd	nd
2829.27	nd	nd	nd	nd	nd	nd	nd	nd
100	0.041	0.14	0.08	0.11	0.045	0.09	0.73	0.065
	nd	nd						
721.6	nd	nd						
19133.05	nd	nd						

Table 5 (continued)

Beaufort County						
Total Lbs. Pesticide Applied		0607PR1	0607PR2	0607PR3	0607PR4	0607PR5
		508	532	479	508	490
		6/6/2000	6/6/2000	6/6/2000	6/6/2000	6/6/2000
		0865000N	0768000 Marker 16 P008	0982500N	07870000 Channel Marker 9	08498000- Core Point Marker #5
		Pamlico River	Pamlico River	Pamlico River	Pamlico River	Pamlico River
63341.24	0.026		0.077	0.059	nd	0.026
	0.019		nd	nd	nd	nd
60281.5	0.02		nd	0.011	0.019	0.008
	nd		nd	nd	nd	nd
	nd		nd	nd	nd	nd
7583.84	nd		nd	nd	nd	nd
10392.825	nd		nd	nd	nd	nd
9651.025	nd		nd	nd	nd	nd
714.322	nd		nd	nd	nd	nd
15854.47	nd		nd	nd	nd	nd
3948	nd		nd	nd	nd	nd
	nd		nd	nd	nd	nd
624.75	nd		nd	nd	nd	nd
520.2	nd		nd	nd	nd	nd
1387.75	nd		nd	nd	nd	nd
	nd		nd	nd	nd	nd
97.875	nd		nd	nd	nd	nd
1640.7	nd		nd	nd	nd	nd
182.95	nd		nd	nd	nd	nd
4523.05	nd		nd	nd	nd	nd
3455.78	nd		nd	nd	nd	nd
	nd		nd	nd	nd	nd
40841.3	0.64		0.27	0.41	0.016	0.035
2809	nd		nd	nd	nd	nd
	nd		nd	nd	nd	nd
916.3	nd		nd	nd	nd	nd
2332.4	nd		nd	nd	nd	nd
18586.375	nd		nd	nd	nd	nd
34.03	nd		nd	nd	nd	nd
	nd		nd	nd	nd	nd
1336.985	nd		nd	nd	nd	nd
3475	0.08		0.17	0.11	0.045	0.09
25075.6						
13298.5						

Table 5 (continued)

0607PR6 531 6/6/2000 0765000 Hwy 17- Washington Pamlico River	0628PU1 529 6/28/2000 0976300W Pungo River	0628PU2 538 6/28/2000 CM 23 near ICW Pungo River	0628PU3 499 6/28/2000 0976600C Pungo River	0628PU4 535 6/28/2000 09764000 Pungo River	Hertford County	
					Total Lbs. Pesticide	06XXAC1 512 6/XX/2000 P200 Ahoskie Creek
0.012	0.24	0.16	0.065	0.34	9405.37	0.032
nd	nd	nd	nd	nd		nd
nd	0.037	0.014	nd	0.019	10083.06	0.071
nd	nd	nd	nd	nd		nd
nd	0.061	0.03	nd	0.026		0.019
nd	nd	nd	nd	nd	1268.52	nd
nd	0.028	0.029	nd	nd	2778.65	0.012
nd	nd	nd	nd	nd	1650	nd
nd	nd	nd	nd	nd	24854.869	nd
nd	nd	nd	nd	nd	15599.86	nd
nd	nd	nd	nd	nd	1650	nd
nd	nd	nd	nd	nd		nd
nd	nd	nd	nd	nd	202.5	nd
nd	nd	nd	nd	nd	26.2	nd
nd	nd	nd	nd	nd	1157.5	nd
nd	nd	nd	nd	nd		nd
nd	nd	nd	nd	nd	3612.9375	nd
nd	nd	nd	nd	nd	2654	nd
nd	nd	nd	nd	nd	2181.5	nd
nd	nd	nd	nd	nd	473.6	nd
nd	nd	nd	nd	nd	176.45	nd
nd	nd	nd	nd	nd		nd
0.48	0.081	0.018	0.026	0.042	25113.57	0.27
nd	nd	0.009	nd	nd	275.28	nd
nd	nd	nd	nd	nd		nd
nd	nd	0.055	nd	nd	297	nd
nd	nd	nd	nd	nd	756	nd
nd	nd	nd	nd	nd	10219.43	nd
nd	nd	nd	nd	nd	0	nd
nd	nd	0.04	0.021	nd		nd
nd	nd	nd	nd	nd	2801.5825	nd
0.73	nd	nd	nd	nd	581.25	nd
	nd	nd	nd	nd	321.15	nd
	nd	nd	nd	nd	4194.3	nd
	nd	nd	nd	nd	7184.42	nd

Table 5 (continued)

Hyde County					County Unknown				
Total Lbs. Pesticide Applied	0628PU1	0628PU2	0628PU3	0628PU4	0505TRT1	0505TRT2	0505TRT3	0505TRT4	0505TRT5
	529	538	499	535	989	995	972	990	990
	6/28/2000	6/28/2000	6/28/2000	6/28/2000	5/5/2000	5/5/2000	5/5/2000	5/5/2000	5/5/2000
	0976300W	CM 23 near ICW	0976600C	09764000					
	Pungo River	Pungo River	Pungo River	Pungo River	Tar River	Tar River	Tar River	Tar River	Tar River
35673.9	0.24	0.16	0.065	0.34	6.1	2.4	4	0.91	1.7
	nd	nd	nd	nd	0.8	0.55	0.69	0.12	0.25
33610.2	0.037	0.014	nd	0.019	41	6.5	3.1	2.7	8.5
	nd	nd	nd	nd	1.6	0.49	0.5	0.18	0.22
	0.061	0.03	nd	0.026	0.015	0.008	nd	0.006	nd
4228.4	nd	nd	nd	nd	nd	nd	nd	nd	nd
1228.13	0.028	0.029	nd	nd	0.073	0.043	0.008	nd	nd
5115.63	nd	nd	nd	nd	nd	nd	nd	nd	nd
25	nd	nd	nd	nd	nd	nd	nd	nd	nd
5059.2	nd	nd	nd	nd	nd	nd	nd	nd	nd
2520	nd	nd	nd	nd	0.062	0.025	0.008	nd	0.004
	nd	nd	nd	nd	nd	nd	nd	nd	nd
	nd	nd	nd	nd	nd	nd	nd	nd	nd
251	nd	nd	nd	nd	nd	nd	nd	nd	nd
434.75	nd	nd	nd	nd	nd	nd	nd	nd	nd
	nd	nd	nd	nd	nd	nd	nd	nd	nd
	nd	nd	nd	nd	nd	nd	nd	nd	nd
	nd	nd	nd	nd	nd	nd	nd	nd	nd
2586.25	nd	nd	nd	nd	nd	nd	nd	nd	nd
1596	nd	nd	nd	nd	nd	nd	nd	nd	nd
	nd	nd	nd	nd	nd	nd	nd	nd	nd
22798	0.081	0.018	0.026	0.042	82	9.4	3.9	2.1	1.1
1613	nd	0.009	nd	nd	0.39	0.21	0.045	0.06	0.022
	nd	nd	nd	nd	nd	nd	nd	nd	nd
	nd	0.055	nd	nd	0.095	0.052	0.02	nd	0.014
	nd	nd	nd	nd	nd	nd	nd	nd	nd
11440.5	nd	nd	nd	nd	0.11	0.06	0.028	0.005	0.02
20.75	nd	nd	nd	nd	nd	nd	nd	nd	nd
	nd	0.04	0.021	nd	0.46	0.064	0.031	0.01	nd
1053.5	nd	nd	nd	nd	nd	nd	nd	nd	nd
1937.5	nd	nd	nd	nd	0.091	0.044	0.008	0.026	nd
	nd	nd	nd	nd	nd	nd	nd	nd	nd
13981	nd	nd	nd	nd	nd	nd	nd	nd	nd
3712.5	nd	nd	nd	nd	nd	nd	nd	nd	nd

Table 6- Mean and maximum values measured in the Albemarle-Pamlico Estuarine System in 2000

	Usage (lbs A.I.)	NAWQA		Tar River Tributary		Tar River - Main Stem	
		Mean	Maximum	Mean	Maximum	Mean	Maximum
alachlor	206031	0.130181	3.2	3.022	6.1	0.051	0.29
2,6-diethylaniline		0.002	0.01	0.482	0.8	0.009	0.041
atrazine	178568	0.131214	4.9	12.36	41	0.098	0.35
deethylatrazine		0.008	0.15	0.598	1.6	0.031	0.1
benfluralin		0.001	0.2	0.0062	0.015	0.001	0.001
carbaryl	9017	0.023906	0.401	0.0252	0.073	0.001	0.001
cyanazine	15960	0.031719	0.171	0.02	0.062	0.014	0.048
metolachlor	80587	0.408	70	19.7	82	0.030	0.14
metribuzin	59079	0.028097	0.34	0.1454	0.39	0.001	0.001
napropamide	20585	0.01105	0.18	0.0364	0.095	0.001	0.001
prometon		0.065	0.68	0.1132	0.46	0.001	0.001
simazine	12967	0.024474	0.54	0.034	0.091	0.067	0.14

Table 6- (continued)

	Pamlico River		Pungo River		Ahoskie
	Mean	Maximum	Mean	Maximum	
alachlor	0.028857143	0.077	0.20125	0.34	0.032
2,6-diethylaniline	0.003571429	0.019	0.001	0.001	0.001
atrazine	0.008714286	0.02	0.01775	0.037	0.071
deethylatrazine	0.001	0.001	0.001	0.001	0.001
benfluralin	0.001	0.001	0.0295	0.061	0.019
carbaryl	0.001	0.001	0.01475	0.029	0.012
cyanazine	0.001	0.001	0.001	0.001	0.001
metolachlor	0.268285714	0.64	0.04175	0.081	0.27
metribuzin	0.001	0.001	0.003	0.009	0.001
napropamide	0.001	0.001	0.0145	0.055	0.001
prometon	0.001	0.001	0.01575	0.04	0.001
simazine	0.184285714	0.73	0.001	0.001	0.001

Table 7. Concentrations of current-use pesticides in water collected at Whichard's Beach and Choco Bay, NC - 2001 (ng/ L)

	C1-0419 19-Apr-01	C1-0501 1-May-01	C1-0516 16-May-01	C1-0620 20-Jun-01	C1-0702 2-Jul-01	C1-0718 18-Jul-01	C1-0807 7-Aug-01	C1-0821 21-Aug-01	C1-0904 4-Sep-01	C1-0918 18-Sep-01
<u>Herbicides</u>										
2,6-diethylani	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
alachlor	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
atrazine	bdl	29	bdl	64	26	20	bdl	bdl	bdl	bdl
benfluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
butylate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
cyanazine	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
dacthal	bdl	bdl	bdl	bdl	bdl	bdl	bdl	2	bdl	bdl
desisopropyl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	21	19
ethalfluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
metolachlor	8	17	9	209	85	27	42	33	23	39
metribuzin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
mollinate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
napropamide	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
pebulate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
pendimethalin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
prometon	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
prometryne	bdl	bdl	bdl	bdl	bdl	17	48	32	bdl	bdl
simazine	55	bdl	bdl	18	bdl	6	17	bdl	bdl	bdl
tebuthiuron	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
trifluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	1
<u>Insecticides</u>										
carbaryl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Carbofuran	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
chlorpyrifos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
diazinon	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
disulfoton	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
ethoprop	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
flumetralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
fonofos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
methyl parath	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
permethrin	bdl	bdl	bdl	bdl	bdl	bdl	8	12	bdl	5
terbufos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Others</u>										
chlorothalonil	3	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
fenamiphos (l	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
tribufos (defo	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Surrogate Recoveries (%)</u>										
diazinon d10	52.28	52.16	49.48	56.63	43.83	50.40	51.37	75.29	54.11	50.01

bdl: below detection limit (1 ng/ L)

Table 8. Concentrations of current-use pesticides in water collected at Broad Creek and Blounts Bay, NC- 2001 (ng/ L)

	C2-0419 19-Apr-01	C2-0501 1-May-01	C2-0516 16-May-01	C2-0620 20-Jun-01	C2-0702 2-Jul-01	C2-0718 18-Jul-01	C2-0807 7-Aug-01	C2-0821 21-Aug-01	C2-0904 4-Sep-01	C2-0918 18-Sep-01
<u>Herbicides</u>										
2,6-diethylaniline	bdl	bdl	bdl	bdl	2	bdl	bdl	bdl	bdl	bdl
alachlor	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
atrazine	bdl	bdl	bdl	100	34	12	bdl	bdl	bdl	bdl
benfluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
butylate	bdl	bdl	bdl	bdl	bdl	3	bdl	bdl	bdl	bdl
cyanazine	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
dacthal	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
desisopropylatrazine	bdl	bdl	bdl	bdl	bdl	bdl	bdl	21	15	17
ethalfluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
metolachlor	5	7	bdl	248	84	7	74	23	19	17
metribuzin	bdl	bdl	bdl	bdl	bdl	bdl	8	bdl	bdl	bdl
molinate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
napropamide	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
pebulate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
pendimethalin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
prometon	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
prometryne	bdl	bdl	bdl	bdl	bdl	bdl	57	31	17	17
simazine	43	bdl	36	13	12	5	14	bdl	bdl	bdl
tebuthiuron	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
trifluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	2	bdl
<u>Insecticides</u>										
carbaryl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Carbofuran	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
chlorpyrifos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
diazinon	bdl	bdl	bdl	bdl	bdl	bdl	16	18	bdl	bdl
disulfoton	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
ethoprop	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
flumetralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
fonofos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
methyl parathion	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
permethrin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
terbufos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Others</u>										
chlorothalonil (fungicide)	1	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
fenamiphos (nematocide)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
tribufos (defoliant)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Surogate Recoveries (%)</u>										
diazinon d10	42.72	34.92	49.07	59.90	40.76	23.89	50.54	57.03	60.63	51.37

bdl: below detection limit (1 ng/ L)

Table 9. Concentrations of current-use pesticides in water collected southeast of Bayview, NC-2001 (ng/ L)

	C3-0501 1-May-01	C3-0516 16-May-01	C3-0606 6-Jun-01	C3-0620 20-Jun-01	C3-0702 2-Jul-01	C3-0718 18-Jul-01	C3-0807 7-Aug-01	C3-0821 21-Aug-01	C3-0904 4-Sep-01	C3-0918 18-Sep-01
<u>Herbicides</u>										
2,6-diethylaniline	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
alachlor	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
atrazine	bdl	bdl	bdl	69	29	22	23	bdl	bdl	bdl
benfluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
butylate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
cyanazine	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
dacthal	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
desisopropylatrazine	bdl	bdl	bdl	bdl	bdl	bdl	bdl	15	bdl	bdl
ethalfluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
metolachlor	bdl	5	bdl	84	43	bdl	8	22	bdl	23
metribuzin	16	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
molinate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
napropamide	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
pebulate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
pendimethalin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
prometon	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
prometryne	bdl	bdl	bdl	bdl	bdl	bdl	27	23	23	14
simazine	bdl	26	bdl	15	11	bdl	9	bdl	bdl	bdl
tebuthiuron	bdl	4	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
trifluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	5	bdl
<u>Insecticides</u>										
carbaryl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Carbofuran	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
chlorpyrifos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
diazinon	17	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
disulfoton	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
ethoprop	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
flumetralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
fonofos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
methyl parathion	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
permethrin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
terbufos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Others</u>										
chlorothalonil (fungicide)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
fenamiphos (nematocide)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
tribufos (defoliant)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Surogate Recoveries (%)</u>										
diazinon d10	45.85	46.58	45.57	60.17	43.53	71.66	60.77	52.49	45.85	41.52

bdl: below detection limit (1 ng/ L)

Table 10. Concentrations of current-use pesticides in water collected near Pamlico Beach, NC-2001 (ng/ L)

	C4-0419 19-Apr-01	C4-0501 1-May-01	C4-0516 16-May-01	C4-0606 6-Jun-01	C4-0620 20-Jun-01	C4-0702 2-Jul-01	C4-0718 18-Jul-01	C4-0807 7-Aug-01	C4-0821 21-Aug-01	C4-0904 4-Sep-01	C4-0918 18-Sep-01
<u>Herbicides</u>											
2,6-diethylaniline	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
alachlor	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
atrazine	bdl	bdl	bdl	bdl	68	40	33	34	bdl	25	21
benfluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
butylate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
cyanazine	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
dacthal	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
desisopropylatrazine	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	8	bdl	bdl
ethalfluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
metolachlor	6	bdl	bdl	bdl	bdl	32	2	19	11	5	27
metribuzin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
molinate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
napropamide	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
pebulate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
pendimethalin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
prometon	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
prometryne	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	12	19	13
simazine	39	28	bdl	bdl	bdl	13	11	bdl	bdl	bdl	bdl
tebuthiuron	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
trifluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	39	4
<u>Insecticides</u>											
carbaryl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Carbofuran	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
chlorpyrifos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
diazinon	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
disulfoton	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
ethoprop	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
flumetralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
fonofos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
methyl parathion	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
permethrin	bdl	bdl	bdl	bdl	4	bdl	bdl	bdl	bdl	bdl	bdl
terbufos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Others</u>											
chlorothalonil (fungicide)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
fenamiphos (nematocide)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
tribufos (defoliant)	16	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Surogate Recoveries (%)</u>											
diazinon d10	44.95	41.74	47.32	47.71	58.20	50.64	49.40	61.09	46.99	46.98	48.44

bdl: below detection limit (1 ng/ L)

Table 11. Concentrations of current-use pesticides in water collected at Louisburg, NC-2001 (ng/ L)

	LO-0504 4-May-01	LO-0515 15-May-01	LO-0530 30-May-01	LO-0613 13-Jun-01	LO-0627 27-Jun-01	LO-0713 13-Jul-01	LO-0725 25-Jul-01	LO-0808 8-Aug-01	LO-0822 22-Aug-01	LO-0905 5-Sep-01	LO-0919 19-Sep-01
<u>Herbicides</u>											
2,6-diethylaniline	bdl	bdl	bdl	bdl	4	bdl	bdl	bdl	bdl	bdl	bdl
alachlor	bdl	bdl	bdl	14	bdl	bdl	bdl	bdl	bdl	bdl	bdl
atrazine	40	bdl	bdl	58	25	bdl	bdl	bdl	bdl	bdl	bdl
benfluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
butylate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
cyanazine	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
dacthal	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
desisopropylatrazine	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
ethalfluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
metolachlor	bdl	bdl	bdl	16	bdl	8	bdl	10	15	bdl	41
metribuzin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
molinat	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
napropamide	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
pebulate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
pendimethalin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
prometon	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
prometryne	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
simazine	bdl	bdl	39	33	bdl	bdl	bdl	bdl	bdl	bdl	bdl
tebuthiuron	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
trifluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	2
<u>Insecticides</u>											
carbaryl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Carbofuran	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
chlorpyrifos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
diazinon	bdl	9	bdl	bdl	15	bdl	bdl	bdl	11	bdl	bdl
disulfoton	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
ethoprop	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
flumetralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
fonofos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
methyl parathion	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
permethrin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	7	bdl	bdl
terbufos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Others</u>											
chlorothalonil (fungicide)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
fenamiphos (nematocide)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
tribufos (defoliant)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Surogate Recoveries (%)</u>											
diazinon d10	41.91	41.04	31.11	52.04	46.29	50.92	39.62	37.63	48.98	50.49	73.34

bdl: below detection limit (1 ng/ L)

Table 12. Concentrations of current-use pesticides in water collected at Rocky Mount, NC-2001 (ng/ L)

	WM-0504 4-May-01	WM-0515 15-May-01	WM-0530 30-May-01	WM-0613 13-Jun-01	WM-0627 27-Jun-01	WM-0713 13-Jul-01	WM-0725 25-Jul-01	WM-0808 8-Aug-01
<u>Herbicides</u>								
2,6-diethylaniline	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
alachlor	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
atrazine	bdl	bdl	bdl	bdl	bdl	13	9	bdl
benfluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
butylate	bdl	bdl	7	bdl	bdl	bdl	bdl	bdl
cyanazine	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
dacthal	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
desisopropylatrazine	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
ethalfluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
metolachlor	16	bdl	bdl	34	36	26	22	bdl
metribuzin	bdl	235	19	9	bdl	bdl	8	bdl
molinate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
napropamide	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
pebulate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
pendimethalin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
prometon	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
prometryne	bdl	bdl	bdl	bdl	bdl	23	22	bdl
simazine	bdl	bdl	bdl	bdl	bdl	8	bdl	bdl
tebuthiuron	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
trifluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Insecticides</u>								
carbaryl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Carbofuran	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
chlorpyrifos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
diazinon	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
disulfoton	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
ethoprop	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
flumetralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
fonofos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
methyl parathion	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
permethrin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	4
terbufos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Others</u>								
chlorothalonil (fungicide)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
fenamiphos (nematocide)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
tribufos (defoliant)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Surogate Recoveries (%)</u>								
diazinon d10	48.35	37.58	40.12	56.84	69.22	48.91	48.32	44.47

bdl: below detection limit (1 ng/ L)

Table 13. Concentrations of current-use pesticides in water collected at Tarboro, NC- 2001 (ng/ L)

	TA-0504 4-May-01	TA-0515 15-May-01	TA-0530 30-May-01	TA-0613 13-Jun-01	TA-0627 27-Jun-01	TA-0713 13-Jul-01	TA-0725 25-Jul-01	TA-0808 8-Aug-01	TA-0822 22-Aug-01	TA-0905 5-Sep-01	TA-0919 19-Sep-01
<u>Herbicides</u>											
2,6-diethylaniline	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
alachlor	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
atrazine	bdl	bdl	61	24	bdl	7	7	bdl	bdl	bdl	bdl
benfluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
butylate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
cyanazine	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
dacthal	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
desisopropylatrazine	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	11	bdl
ethalfluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
metolachlor	15	0	116	217	73	27	65	33	37	47	61
metribuzin	bdl	5	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
mollinate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
napropamide	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
pebulate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
pendimethalin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
prometon	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
prometryne	bdl	bdl	bdl	bdl	bdl	34	bdl	bdl	21	bdl	bdl
simazine	bdl	bdl	bdl	bdl	13	bdl	bdl	bdl	bdl	bdl	bdl
tebuthiuron	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
trifluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Insecticides</u>											
carbaryl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Carbofuran	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
chlorpyrifos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
diazinon	13	bdl	9	bdl	bdl	bdl	31	bdl	bdl	bdl	bdl
disulfoton	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
ethoprop	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
flumetralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
fonofos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
methyl parathion	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
permethrin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	21	bdl	bdl	bdl
terbufos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Others</u>											
chlorothalonil (fungicide)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	5	bdl	bdl
fenamiphos (nematocide)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
tribufos (defoliant)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Surogate Recoveries (%)</u>											
diazinon d10	54.32	41.68	55.54	48.85	62.72	49.44	62.52	30.29	44.46	52.24	66.93

bdl: below detection limit (1 ng/ L)

Table 14. Concentrations of curent-use pesticides in water collected at Greenville, NC-2001 (ng/ L)

	GR-0515 15-May-01	GR-0530 30-May-01	GR-0613 13-Jun-01	GR-0627 27-Jun-01	GR-0713 13-Jul-01	GR-0725 25-Jul-01	GR-0808 8-Aug-01	GR-0822 22-Aug-01	GR-0905 5-Sep-01	GR-0919 19-Sep-01
<u>Herbicides</u>										
2,6-diethylaniline	bdl	bdl	bdl	bdl	1	bdl	bdl	bdl	bdl	bdl
alachlor	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
atrazine	bdl	69	25	bdl	8	bdl	bdl	bdl	bdl	bdl
benfluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
butylate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
cyanazine	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
dacthal	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
desisopropylatrazine	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	19
ethalfluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
metolachlor	16	164	248	93	33	52	31	35	40	59
metribuzin	bdl	bdl	bdl	bdl	11	bdl	bdl	bdl	bdl	bdl
mollinate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
napropamide	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
pebulate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
pendimethalin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
prometon	bdl	bdl	bdl	bdl	bdl	11	bdl	bdl	bdl	bdl
prometryne	bdl	bdl	bdl	bdl	24	bdl	26	18	bdl	bdl
simazine	bdl	28	bdl	13	bdl	bdl	bdl	bdl	bdl	bdl
tebuthiuron	bdl	bdl	bdl	4	bdl	bdl	bdl	bdl	bdl	bdl
trifluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	5
<u>Insecticides</u>										
carbaryl	bdl	bdl	bdl	31	bdl	bdl	bdl	bdl	bdl	bdl
Carbofuran	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
chlorpyrifos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
diazinon	bdl	bdl	bdl	bdl	bdl	bdl	21	bdl	bdl	bdl
disulfoton	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
ethoprop	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
flumetralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
fonofos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
methyl parathion	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
permethrin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
terbufos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Others</u>										
chlorothalonil (fungicide)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	4	bdl	bdl
fenamiphos (nematocide)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
tribufos (defoliant)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Surogate Recoveries (%)</u>										
diazinon d10	44.71	51.79	40.19	55.21	51.10	48.25	40.65	47.65	51.65	65.04

bdl: below detection limit (1 ng/ L)

Table 15. Concentrations of current-use pesticides in water collected at Washington, NC -2001 (ng/ L)

	WA-0504 4-May-01	WA-0515 15-May-01	WA-0605 5-Jun-01	WA-0613 13-Jun-01	WA-0627 27-Jun-01	WA-0713 13-Jul-01	WA-0725 25-Jul-01	WA-0808 8-Aug-01	WA-0822 22-Aug-01	WA-0905 5-Sep-01	WA-0919 19-Sep-01
<u>Herbicides</u>											
2,6-diethylaniline	bdl	bdl	bdl	bdl	bdl	bdl	bdl	2	bdl	bdl	bdl
alachlor	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
atrazine	101	bdl	bdl	42	21	18	12	bdl	bdl	bdl	bdl
benfluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
butylate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
cyanazine	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
dacthal	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
desisopropylatrazine	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	17	25
ethalfluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
metolachlor	bdl	16	bdl	534	122	51	32	38	33	37	59
metribuzin	353	bdl	bdl	bdl	bdl	bdl	bdl	bdl	3	bdl	bdl
mollinate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
napropamide	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
pebulate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
pendimethalin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
prometon	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	16	bdl
prometryne	bdl	bdl	bdl	bdl	bdl	48	22	33	21	bdl	bdl
simazine	bdl	bdl	bdl	21	bdl	bdl	bdl	15	bdl	bdl	bdl
tebuthiuron	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
trifluralin	bdl	bdl	130	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Insecticides</u>											
carbaryl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Carbofuran	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
chlorpyrifos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
diazinon	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
disulfoton	bdl	bdl	bdl	bdl	bdl	bdl	bdl	28	bdl	bdl	bdl
ethoprop	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
flumetralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
fonofos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
methyl parathion	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
permethrin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
terbufos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Others</u>											
chlorothalonil (fungicide)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
fenamiphos (nematocide)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
tribufos (defoliant)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Surogate Recoveries (%)</u>											
diazinon d10	46.57	50.86	66.18	50.94	49.18	47.78	50.51	45.92	39.28	45.86	64.55

bdl: below detection limit (1 ng/ L)

Table 16. Concentrations of current-use pesticides in water collected at Swanquarter, NC-2001 (ng/ L)

	SQ-0504 4-May-01	SQ-0515 15-May-01	SQ-0530 30-May-01	SQ-0613 13-Jun-01	SQ-0627 27-Jun-01	SQ-0713 13-Jul-01	SQ-0725 25-Jul-01	SQ-0808 8-Aug-01	SQ-0822 22-Aug-01	SQ-0905 5-Sep-01	SQ-0919 19-Sep-01
<u>Herbicides</u>											
2,6-diethylaniline	bdl	bdl	bdl	bdl	6	bdl	bdl	bdl	bdl	bdl	bdl
alachlor	bdl	bdl	5	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
atrazine	bdl	bdl	43	17	13	25	bdl	16	bdl	bdl	bdl
benfluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
butylate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
cyanazine	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
dacthal	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
desisopropylatrazine	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
ethalfluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
metolachlor	bdl	bdl	81	bdl	bdl	bdl	bdl	bdl	bdl	20	27
metribuzin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
molinate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
napropamide	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
pebulate	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
pendimethalin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
prometon	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
prometryne	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
simazine	bdl	bdl	bdl	bdl	bdl	12	bdl	bdl	bdl	bdl	bdl
tebuthiuron	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
trifluralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	4	bdl
<u>Insecticides</u>											
carbaryl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Carbofuran	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
chlorpyrifos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
diazinon	bdl	10	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	23
disulfoton	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
ethoprop	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
flumetralin	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
fonofos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
methyl parathion	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
permethrin	bdl	bdl	bdl	bdl	bdl	7	bdl	bdl	bdl	bdl	bdl
terbufos	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Others</u>											
chlorothalonil (fungicide)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
fenamiphos (nematocide)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
tribufos (defoliant)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
<u>Surogate Recoveries (%)</u>											
diazinon d10	45.10	45.12	29.41	49.65	47.04	44.04	45.04	43.65	63.45	61.69	57.47

bdl: below detection limit (1 ng/ L)

MODEL PARAMETERS

Table 17- Site Description for Bath Creek, NC EXAMS Model

Air Mass Type	Rural
Area (m ²)	4200000
Atmospheric turbidity	2
Elevation (m)	3
Latitude	35.27
Length (m)	5250
Longitude	76.49
O ₂ Exchange Constant (cm/hr)	0
Oxidant Radicals (moles/L)	1.00E-09
Rainfall (mm/month)	106
Reducing Agents (moles/L)	0
Volume (m ³)	1764000
Width (m)	800

Table 18- Monthly data used in Bath Creek models

Month	Ozone (cm NTP)	Wind Speed (m/sec)
January	0.3013	5.32
February	0.3155	5.28
March	0.3174	5.32
April	0.3068	5.23
May	0.3027	4.78
June	0.286	4.34
July	0.273	4.47
August	0.2673	4.25
September	0.2676	4.65
October	0.2694	4.83
November	0.2713	4.78
December	0.2853	4.87
Yearly Average	0.2866	4.84

Table 19- Environmental parameters used for Bath Creek models

	Area (m ²)	Depth (m)	Dissolved O ₂ (mg/L)	DOC (mg/L)	Fraction organic C	pH	pOH	Temperature (Celcius)	Volume (m ³)	Width (m)
<i>Steady state model</i>										
Littoral	1260000	1.4	7.4	2	0.045	8.4	5.6	9.6	1764000	240
Benthic 1	1260000	0.2	5	2	0.045	8.4	5.6	9.2	126000	240
Epilimnion	2940000	2.3	7.4	2	0.045	8.4	5.6	9.6	6762000	560
Benthic 2	2940000	0.2	5	2	0.045	8.4	5.6	9.2	294000	560
<i>Tidal model- high tide</i>										
Littoral	1.26E+06	1.4	7.4	2	0.045	8.4	5.6	9.6	1.76E+06	240
Benthic 1	1.26E+06	0.2	5	2	0.045	8.4	5.6	9.2	2.52E+04	240
Epilimnion	2.94E+06	1.54	7.4	2	0.045	8.4	5.6	9.6	4.53E+06	560
Hypolimnion	2.94E+06	0.76	7.4	2	0.045	8.4	5.6	9.2	2.23E+06	560
Benthic 2	2.94E+06	0.2	5	2	0.045	8.4	5.6	9.2	2.94E+05	560
<i>Tidal model- low tide</i>										
Littoral	3.60E+05	0.4	7.4	2	0.045	8.4	5.6	9.6	1.44E+05	69
Benthic 1	3.60E+05	0.2	5	2	0.045	8.4	5.6	9.2	7.20E+03	69
Epilimnion	2.94E+06	0.87	7.4	2	0.045	8.4	5.6	9.6	2.56E+06	560
Hypolimnion	2.94E+06	0.43	7.4	2	0.045	8.4	5.6	9.2	1.26E+06	560
Benthic 2	2.94E+06	0.2	5	2	0.045	8.4	5.6	9.2	2.94E+05	560

Table 20- Default values used for Bath Creek models

	Non-Point Sediment Load (kg/hr)	Seepage Flows (m3/hr)	Stream-Borne Sediment (kg/hr)	Suspended Sediment (mg/L)	% H2O- Bottom Sediment
<u><i>Steady state model</i></u>					
Littoral	4	NA	0.6	30	NA
Benthic 1	NA	0.4833	NA	NA	137
Epilimnion	0	NA	0	30	NA
Benthic 2	NA	0.4833	NA	NA	137
<u><i>Tidal model</i></u>					
Littoral	4	NA	0.6	30	NA
Benthic 1	NA	0.4833	NA	NA	137
Epilimnion	0	NA	0	30	NA
Hypolimnion	0	NA	0	30	NA
Benthic 2	NA	0.4833	NA	NA	137

Table 21- Chemical parameters for Bath Creek models

	Atrazine	Metolachlor
Hydrolysis	3.89E-02	
Sediment partitioning	22.13	5.31E+01
Aerobic metabolism	2.24E-12	50
Henry's law constant	2.84E-09	2.30E-08
Vapor pressure	3.00E-07	3.15E-05
Photolysis	4.00E-07	
Molecular weight	2.16E+02	2.84E+02
Melting point	1.74E+02	2.50E+01
Kow	5.62E+02	2.82E+03
Koc	2.31E+02	2.81E+02
Water solubility	3.00E+01	5.30E+02
Annual Usage (LBS AI)	2710	1987

Table 22- Advection of water in Bath Creek models

Advected From:	Advected To:	Fraction Advected
<u><i>Steady state model</i></u>		
Littoral	Epilimnion	1
Benthic 1	Littoral	1
Epilimnion	Out of System	1
Benthic 2	Epilimnion	1
<u><i>Tidal model</i></u>		
Littoral	Epilimnion	0.67
Littoral	Hypolimnion	0.33
Benthic 1	Littoral	1
Hypolimnion	Epilimnion	1
Benthic 2	Hypolimnion	1
Epilimnion	Out of System	1

Table 23- Dispersion of water in Bath Creek models

Dispersion From:	Dispersion To:	Characteristic Length (m)	Cross Sectional Area (m²)	Dispersion Coefficient
<u><i>Steady state model</i></u>				
Littoral	Benthic 1	1.025	1.00E+04	1.00E-03
Epilimnion	Benthic 2	0.275	300	1.00E-03
<u><i>Tidal model</i></u>				
Littoral	Epilimnion	1.76E+03	816	0.2
Hypolimnion	Epilimnion	0.65	2.94E+06	0.2
Littoral	Hypolimnion	1.46E+03	441	0.2
Epilimnion	Out of System	1.57E+03	816	0.2

Table 24-Changes in volume, depth and area in Bath Creek tidal model

Time Hours	Littoral			Benthic 1		Epilimnion		Hypolimnion		Bath Creek Total Vol m ³
	Area m ²	Depth m	Volume m ³	Area m ²	Volume m ³	Depth m	Volume m ³	Depth m	Volume m ³	
0	3.60E+05	0.4	1.44E+05	3.60E+05	7.20E+03	0.87	2.56E+06	0.43	1.26E+06	3.96E+06
1	4.35E+05	0.4833	2.10E+05	4.35E+05	8.70E+03	0.9222	2.71E+06	0.4611	1.36E+06	4.28E+06
2	5.10E+05	0.5666	2.89E+05	5.10E+05	1.02E+04	0.9777	2.87E+06	0.4889	1.44E+06	4.60E+06
3	5.85E+05	0.6499	3.80E+05	5.85E+05	1.17E+04	1.0333	3.04E+06	0.5166	1.52E+06	4.94E+06
4	6.60E+05	0.7332	4.84E+05	6.60E+05	1.32E+04	1.0888	3.20E+06	0.5444	1.60E+06	5.28E+06
5	7.35E+05	0.816	6.00E+05	7.35E+05	1.47E+04	1.1443	3.36E+06	0.5722	1.68E+06	5.64E+06
6	8.10E+05	0.8988	7.29E+05	8.10E+05	1.62E+04	1.1999	3.53E+06	0.5999	1.76E+06	6.02E+06
7	8.85E+05	0.9831	8.70E+05	8.85E+05	1.77E+04	1.2554	3.69E+06	0.6277	1.84E+06	6.40E+06
8	9.60E+05	1.0664	1.02E+06	9.60E+05	1.92E+04	1.3109	3.85E+06	0.6555	1.93E+06	6.80E+06
9	1.04E+06	1.1497	1.19E+06	1.04E+06	2.07E+04	1.3665	4.02E+06	0.6832	2.01E+06	7.22E+06
10	1.11E+06	1.233	1.37E+06	1.11E+06	2.22E+04	1.422	4.18E+06	0.711	2.09E+06	7.64E+06
11	1.19E+06	1.3163	1.56E+06	1.19E+06	2.37E+04	1.4775	4.34E+06	0.7388	2.12E+06	8.02E+06
12	1.26E+06	1.4	1.76E+06	1.26E+06	2.52E+04	1.54	4.53E+06	0.76	2.23E+06	8.52E+06
13	1.19E+06	1.36163	1.56E+06	1.19E+06	2.37E+04	1.4775	4.34E+06	0.7388	2.12E+06	8.02E+06
14	1.11E+06	1.233	1.37E+06	1.11E+06	2.22E+04	1.422	4.18E+06	0.711	2.09E+06	7.64E+06
15	1.04E+06	1.1497	1.19E+06	1.04E+06	2.07E+04	1.3665	4.02E+06	0.6832	2.01E+06	7.22E+06
16	9.60E+05	1.0664	1.02E+06	9.60E+05	1.92E+04	1.3109	3.85E+06	0.6555	1.93E+06	6.80E+06
17	8.85E+05	0.9831	8.70E+05	8.85E+05	1.77E+04	1.2554	3.69E+06	0.6277	1.84E+06	6.40E+06
18	8.10E+05	0.8988	7.29E+05	8.10E+05	1.62E+04	1.1999	3.53E+06	0.5999	1.76E+06	6.02E+06
19	7.35E+05	0.816	6.00E+05	7.35E+05	1.47E+04	1.1443	3.36E+06	0.5722	1.68E+06	5.64E+06
20	6.60E+05	0.7332	4.84E+05	6.60E+05	1.32E+04	1.0888	3.20E+06	0.5444	1.60E+06	5.28E+06
21	5.58E+05	0.6499	3.80E+05	5.58E+05	1.17E+04	1.0333	3.04E+06	0.5166	1.52E+06	4.94E+06
22	5.10E+05	0.5666	2.89E+05	5.10E+05	1.02E+04	0.9777	2.87E+06	0.4889	1.44E+06	4.60E+06
23	4.35E+05	0.4833	2.10E+05	4.35E+05	8.70E+03	0.9222	2.71E+06	0.4611	1.36E+06	4.28E+06
24	3.60E+05	0.4	1.44E+05	3.60E+05	7.20E+03	0.87	2.56E+06	0.43	1.26E+06	3.96E+06

Table 25- Atrazine and metolachlor concentrations in Bath Creek:
 Predicted by models vs. field measurements in 2000 (ug/ L)

Predicted	Atrazine		Metolachlor	
	Mean	Maximum	Mean	Maximum
EXAMS 100% Input	NA	0.612	NA	0.636
EXAMS 2% Input	NA	NA	NA	0.0127
EXAMS 3% Input	NA	0.018	NA	NA
Chem Can	NA	0.758	NA	0.0775
Measured				
Pamlico River	0.01	0.03	0.2	0.6
Pungo River	0.04	0.08	0.04	0.08
Tar River	0.1	0.4	0.03	0.14
Tar River Tributaries	10	80	20	100

SPMD Parameters

Table 26- Chemical parameters for current-use pesticides used in semi-permeable membrane devices

Pesticide	K _o	t _{1/2} (days)	Molecular Weight	length	width	depth	log K _{ow}	water t _{1/2} (d)	soil t _{1/2} (d)	(mg/L) Solubility	(ug/L) log K _{oc}	LC50 (lowest)	AQLC*	NAWQA > ALC
2,4-D	0.14	6.07	221.04	13.0977	7.9932	4.1228	2.81	7	16	796000	1.6	900	4	
atrazine	0.25	3.44	215.69	9.0958	12.4474	5.3845	2.75	5	60	33	2	4300	1.8	0.38
butylate	0.10	8.17	217.38	10.121	11.4138	6.6375	4.15	2	13	44	2.60206	4200		
carbaryl	0.30	2.83	201.23	11.2754	9.3516	4.1214	2.36	10	10	100	2.3	1300	0.2	
EPTC	0.24	3.62	189.32	11.4109	9.3193	4.1278	3.2	2	7	375	2.3	19000		
molinate	0.12	6.91	187.3	12.2699	6.8548	4.4221	2.88	4	21	880	2.28	300		
napropamide	0.23	3.70	271.36	12.6712	9.9864	6.7535	3.36	1	70	74	2.8451	9000		
propanil	0.57	1.49	218.08	8.4145	12.5679	4.1227	2.29	2	2	225	2.17	140		
thiobencarb	0.11	7.59	257.7832	15.2962	10.3903	4.1269	6.39	5	5	28	2.95			
ethoprop	0.01	72.65	242.34	9.4204	9.031	9.4781	3.59	5	25	750	2	2100		
linuron	0.01	64.39	249.11	13.2509	7.607	4.1236	3.2	172	60	75	2.60206	1600	7	
profenofos	0.01	128.01	371.935	11.5369	11.3138	9.4742	5	10	8	28	3.30103	80		
terbufos	0.01	130.17	288.43	11.6498	9.9316	9.263	4.48	7	30	5	2.69897	0.2		
acifluorfen	0.10	8.17	361.7	12.0247	13.6734	5.1086	1.18	28	59	250000		31000		
alachlor	0.04	21.68	269.77	9.6187	9.4608	6.3991	3.52	23	15	240	2.47	1800		
2,6-diethylaniline	0.03	27.24	149.24	9.0967	10.0757	4.1426	2.3	15	15	1000				
desethylatrazine	0.03	24.36	145.48				n/a	n/a	n/a					
deisopropylatrazine	0.03	28.52					n/a	n/a	n/a					
azinphos methyl	0.02	36.17	317.33	14.8798	8.8112	7.5875	2.75	8	20	29	3	0.1	0.01	0.31
bentazon	1.84	0.46	240.28	9.833	9.6124	6.7223	-0.46	2	14	500	3.82	190000		
carbofuran	0.07	12.57	221.25	11.194	9.3023	6.522	2.32	21	45	351	2	380	1.75	
chlorpyrifos	0.00	259.15	350.62	11.665	10.7592	6.6908	4.96	45	60	2	3.78319	2.6	0.041	0.3
cyanazine	0.19	4.55	240.7	10.406	12.405	6.6438	2.22	14	14	170	2.27875	7500	2	0.18
diazinon	0.01	111.55	304.35	13.8622	10.5635	7.9338	3.7	40	40	60	3	52	0.08	0.25
dimethoate	0.16	5.48	229.28	11.6546	8.7885	6.6786	0.75	20	10	25000	0.96	20000		
disulfoton	0.02	36.96	274.4	13.852	12.4967	7.9318	4.02	10	30	25	2.77815	38		
diuron	0.04	19.91	233.1	10.0228	11.249	4.1246	2.68	7	90	42	2.58	5600		
ethalfuralin	0.01	114.40	333.27	10.7709	11.946	5.117	3.99	n/a	60	0.3	3.60206			
fluometuron	0.03	25.84	232.29	10.0228	11.7934	5.117	2.3	365	85	80	1.8	30000		
fonofos	0.01	100.71	246.32	12.3163	9.7728	6.8905	3.9	10	40	13	2.93952	45		
malathion	0.08	11.26	330.36	13.9961	11.3512	8.6749	2.89	7	2	141	2.61	1000	0.1	0.18
methyl parathion	0.02	35.12	263.21	11.799	8.4727	6.7507	3.5	8	5	60	3.71	1900		
metolachlor	0.02	56.29	283.8	12.302	8.8991	5.3856	3.13	140	40	530	2.30103	2000	7.8	
metribuzin	0.24	3.57	214.29	9.6199	11.644	6.6438	1.6	7	60	1220	1.77815	4500	1	
norflurazon	0.05	18.64	303.67	11.5201	9.9404	8.5996	2	14	90	28	2	200000		
pebulate	0.01	130.77	203.35	11.3882	13.2706	4.1288	3.8	11	14	60	2.63347	7400	0.0045	
pendimethalin	0.00	524.69	281.31	9.468	12.4053	5.3866	5.18	14	40	0.3	2.93	138		
phorate	0.01	67.46	260.38	11.6462	9.925	9.263	3.92	7	60	50	3	0.11		
prometryn	0.02	40.48	241.37	12.3182	10.1102	5.389	3.34	45	45	48	2.6	2500		
pronamide	0.01	59.44	256.13	9.7485	12.6578	7.6266	3.2	90	60	15	2.9	5600		
propachlor	0.15	5.63	211.69	10.4065	10.0815	5.3844	2.18	12	7	613	2.1	170		
3,4-dichloroaniline	0.02	43.81	162.02	7.0289	8.8644	3.543	1.99	n/a	n/a					
propargite	0.00	242.17	350.48	11.4569	11.3139	9.2646	4.5	7	56	0.5	3.60206			
simazine	0.13	6.59	201.7	12.3074	9.9718	4.127	2.18	32	75	6.2	2.14	100	10	
tebuthiuron	0.06	14.12	228.31	10.359	11.3242	6.6438	1.79	60	400	2500	1.9	87000	1.6	
terbacil	0.06	14.63	216.7	9.0165	9.9981	6.6437	1.89	30	120	710	1.74	46200		
triallate	0.01	87.09	304.66	9.6829	12.2743	6.646	4.29	100	82	4	3.38	1200	0.24	
tribufos	0.01	137.10	298.5171	15.203	11.8855	8.0241	5.87	n/a	10	2.3	3.69897			
trifluralin	0.01	167.65	335.5	10.6943	13.1403	5.117	5.07	5	60	4	3.90309	11	0.2	