**Monitoring Pesticides in the Groundwater and Submarine Groundwater Discharge of the Eastern Shore of Virginia.**

by

Thomas W. Hubbard

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Daniel L. Gallagher, Chair

George M. Simmons Jr.

Andrea M. Dietrich

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MONITORING PESTICIDES IN THE GROUNDWATER AND THE SUBMARINE GROUNDWATER DISCHARGE OF THE EASTERN SHORE OF VIRGINIA

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Committee Chairman: Daniel L. Gallagher

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(ABSTRACT)

The purpose of the research was to determine if pesticides were being transported from the place of application by the shallow groundwater and discharged into the Chesapeake Bay and Atlantic Ocean, and quantify the pesticides if they were transported. One reference (undeveloped) and four agricultural sites were tested over a 11 month period from April 1992 to February 1993. Over 500 groundwater samples were analyzed from both shallow wells and seepage meters placed in the Chesapeake Bay and Magothy Bay. The samples were analyzed in accordance to EPA Method 525.1 by solid phase extraction with octadecyl bonded disks followed by gas chromatography. The samples were examined for 5 of the most commonly used pesticides: atrazine, alachlor, carbofuran, cyanazine, and metolachlor. Pesticides were detected in only 16 samples. All the detections were at low concentrations, with only one being over 1 μg/L. The study concluded that if pesticides were being transported by the groundwater, they were below a μg/L (ppb).

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# I. Introduction

Since prehistoric times humans have cultivated crops for a steady food source. With the advent of man-made compounds and intensive farming techniques, crop yields have steadily improved. One of the reasons for the improvement was the widespread use of pesticides. Pesticides are divided into two main categories; insecticides and herbicides. Insecticides are used to kill a wide variety of insects and nematodes. Herbicides are used against grasses, molds, and fungi that attack or compete with the crop.

Gradually, people realized that pesticides could effect humans as well. The discovery of DDT's bioaccumulation and long half-life in the environment led to a greater public concern and awareness. Testing by the EPA showed that two of the pesticides in this study, alachlor and atrazine, are possible carcinogens. The maximum contaminate levels (MCL) in drinking water set by the EPA were 3 μg/L for atrazine and 2 μg/L for alachlor. The long term affect of many pesticides on humans is not well known.

Studies have confirmed that some groundwater sources have been contaminated by synthetic organic compounds, including pesticides (Domagaski and Dubrovsky, 1992; Holden, *et al.*, 1992; Krill and Sonzogni, 1986; Leonard, *et al.*, 1988; Pionke and Glotfelty, 1989).

Recently, researchers have demonstrated that submarine

groundwater discharge (SGWD), which is the discharge of groundwater below the surface of a body of water, such as an ocean, accounts for a much larger fraction of the hydrological cycle than previously thought (Simmons, *et al.*, 1992). This raised the question of whether pesticides were being transported by SGWD into bays and oceans. In response, this study was undertaken with two main objectives:

1. To determine if pesticides were being transported by the groundwater from the fields they were applied and into the Chesapeake Bay and Magothy Bay.

2. To quantify the amount pesticide transport, if any occurred.

The study also analyzed soil samples, and an independent laboratory, Ohmicron Corporation, analyzed duplicates of most of the samples. The soil samples were included to determine if there was a correlation between the soil and groundwater concentrations of pesticides, while the Ohmicron samples were used help confirm if any pesticides were in the water samples.

## II. Literature Review

### A. Introduction

The study tested the groundwater and SGWD of the Eastern Shore of Virginia for five pesticides; atrazine, alachlor, carbofuran, cyanazine, and metolachlor. The pesticides were selected by the following criteria: they were commonly used on the eastern shore of Virginia (Hohlt, 1993); they were highly susceptible to leaching into the groundwater, and they had been detected in other groundwater studies in the United States.

### B. Submarine Groundwater Discharge

In general, unconfined coastal aquifers are characterized by flow in the direction of adjacent surface waters. These flow patterns are in response to elevated hydraulic heads within upland regions. The advective movement of groundwater into aquatic systems is termed submarine groundwater discharge (SGWD). As fresh groundwater moves into nearshore coastal environments, flow paths are sharply deflected upwards by salinity density gradients. Consequently, most unconfined groundwater discharge occurs immediately adjacent to the land-water interface and represents a mixture of fresh groundwater and interstitial seawater (Bear, 1979).

A consideration of SGWD as a contaminant transport mechanism is relatively recent. Traditional methods to estimate solute flux across the sediment-water interface only

considered diffusion and assumed advective transport mechanisms to be negligible. However, evidence now suggests that advective transport mechanisms of solutes are significant in lake, estuarine, and marine sediments (Lee, 1977: Lee, *et al.*, 1980: Sayles and Jenkins, 1982; Zimmermann, *et al.*, 1985; Cornett, *et al.*, 1989; Simmons, 1989; Reay and Gallagher, 1991; Simmons, *et al.*, 1991). Groundwater discharge has been implicated in nitrogen enrichment of coastal systems (Sewell, 1982; Johannes and Hearn, 1985; Lee and Olsen, 1985; Valiela, *et al.*, 1990). Although significant effort has been invested in studying surface and groundwater quality in the Chesapeake Bay watershed, it has only been recently that research has focused on the significance of groundwater discharge to the Bay system (Simmons, 1989; Libelo, *et al.*, 1991). Research has also shown that transport of fertilizer-related nutrients by SGWD significantly influence water column nutrient concentrations in Virginia's coastal waters (Reay, *et al.*, 1992).

### C. History of the Pesticides

Each pesticide's history and properties are given in the following sections (also see Table 1).

#### 1. Alachlor

Monsanto patented alachlor (2-chloro-2',6'-diethyl-N-(methoxymethyl) acetamide) in 1967. It has an acute lethal dose in 50% of the test animals ($LD_{50}$) of 1200 mg/kg of body

weight (Windhole, 1983). Alachlor is classified as a herbicide, and used to control grasses and broadleaf weeds in corn, soybeans, and peanuts (Holden, *et al.*, 1992). Its solubility in water is 203 mg/L (Gustafson, 1989).

2. Atrazine

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) was patented by Giegy in 1960. Its $LD_{50}$ is 1750 mg/kg (Windhole, 1983). The water solubility of atrazine is listed as 52 mg/L (Gustafson, 1989). Atrazine is applied as a pre- and post-emergence herbicide. It is one of the most commonly used pesticides in the United States, being applied to corn and soybean fields to control grasses. Heatwole, citing Pait, estimated that approximately 0.65 million Kg of atrazine were applied in the Chesapeake Bay drainage area in 1988 (Heatwole, *et al.*, 1992).

3. Carbofuran

Carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranol methylcarbamate) is a insecticide/nematicide patented by Bayer in 1964. It is used on a wide variety of crops to control insect infestations. Carbofuran was the only highly toxic pesticide in the study with an $LD_{50}$ of 3 mg/kg (Windhole, 1983). It has a water solubility of 700 mg/L (Gustafson, 1989).

4. Cyanazine

Degussa patented cyanazine (2-[[4-chloro-6-(ethylamino)-

Table 1
Studied Pesticides' Properties

| Pesticide | $LD_{50}$, mg/kg | Solubility, mg/L | $K_{ow}$ |
|---|---|---|---|
| Alachlor | 1200 | 203 | 2.78 |
| Atrazine | 1750 | 52 | 2.45 |
| Carbofuran | 3 | 700 | 2.44 |
| Cyanazine | 182 | 171 | 2.24 |
| Metolachlor | 2780 | 530 | 2.81 |

* Data from: Domagalski and Dubrovsky, 1992; Gustafson, 1989; Windhole, 1983

S-triazin-2-yl]amino]-2-methylpropanenitirile) in 1968. The listed $LD_{50}$ for cyanazine is 182 mg/kg (Windhole, 1983). The solubility in water of cyanazine is 171 mg/L (Gustafson, 1989). Cyanazine is a herbicide, and is used to kill grasses in corn, soybean, and sorghum (Squillace and Thurman, 1992).

5. Metolachlor

Metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methyethyl)acetamide) was patented in 1973 by Ciba-Giegy. It was the least toxic of the pesticides studied with a $LD_{50}$ of 2780 mg/kg (Windhole, 1983). Metolachlor is classified as a herbicide, and mainly used to control grasses in corn and soybeans (Bouchard, *et al.*, 1982). Its water solubility is 530 mg/L (Gustafson, 1989).

## C. Pesticide Transport and Breakdown

All five of the pesticides in the study have been detected in the groundwater of the United States (Domagaski and Dubrovsky, 1992; Holden, *et al.*, 1992; Krill and Sonzogni, 1986; Leonard, *et al.*, 1988; Pionke and Glotfelty, 1989). Atrazine was the most commonly found pesticide in all the cited studies. This was unexpected, since most pesticide transport models predict that carbofuran, with its higher solubility and lower $K_{oc}$ would be found in higher concentrations than atrazine (Donigian and Carsel, 1987; Jury, *et al.*, 1987; Shirmohammadi, *et al.*, 1989).

1. Pesticides detected in groundwater studies

The following groundwater studies were conducted with one or more of the pesticides in this project. It should be noted that all the studies were looking at high risk areas with shallow water tables and very permeable soils.

In a study of artificially recharged groundwater in Nebraska, Exner (1990) found that the shallow, unconfined aquifer was contaminated with atrazine, alachlor, metolachlor, and cyanazine. Atrazine was found in almost all the samples from 0.3 to 8.8 ppb, while the other 3 pesticides were found in about half the samples at concentrations from 0.1 to 0.9 ppb. Atrazine was also found in the deeper regional aquifer, at concentrations from 0.1 to 2.5 ppb.

Also in Nebraska, a study of 41 wells in a shallow, river influenced aquifer found atrazine in all 108 samples (Wehtje, *et al.*, 1983). The concentrations ranged from 0.01 to 8.29 µg/L, with an average of 0.38 µg/L. Nitrate and atrazine appear to be linked with the highest concentrations of nitrate and atrazine occurring in the same wells.

A third Nebraska study with over 2200 well samples found 13.5% of the samples contained atrazine. The contamination was at very low concentrations with a median of 0.38 µg/L. Alachlor, cyanazine, and metolachlor were also detected in 0.77, 0.57, and 0.50% of the samples, respectively. Like atrazine, the median concentration were very low with

cyanazine being the highest at 0.10 µg/L (Spalding, *et al.*, 1989).

Testing the discharge of Big Spring, a large groundwater spring in Iowa, Libra, *et al.* (1987) said, "Atrazine is the most widely used herbicide in the basin, and it is the dominant pesticide found in the groundwater." Atrazine was detected at an average concentration of 0.2 µg/L in the base flow of the spring. During discharge events, atrazine, alachlor, cyanazine, and metolachlor were detected at concentrations of 5.1, 0.6, 1.2, and 0.6 µg/L, respectively. Alachlor and cyanazine were also intermittently found in the base flow.

A Wisconsin survey of 349 wells found all five pesticides. Metolachlor was detected in 27% of the samples. Atrazine, alachlor, cyanazine, and carbofuran were also found in 14, 12, 7, and 3% of the samples, respectively (Holden, 1986).

A later Wisconsin study of 358 wells found pesticides in only 7% of the samples. The most commonly detected pesticide was atrazine, which was found in 3% of the samples. Alachlor, metolachlor, and carbofuran were all detected once in separate samples (Krill and Sonzogni, 1986).

However, an Arkansas study of 119 wells found only 1 sample with pesticides detected. Alachlor, cyanazine, and metolachlor were detected at 5.5, 5.8, and 6.9 µg/L. Since

the pesticides were not detected in previous or subsequent samples, the sample was concluded to be a spill or laboratory error (Cavalier, *et al.*, 1989)

In a Kansas study of 103 wells, atrazine was detected in 4 wells, and alachlor was detected in 1 well. The highest concentrations were 40 µg/L for atrazine and 1.8 µg/L for alachlor (Steichen, *et al.*, 1988).

Pionke, *et al.*(1989) found atrazine in 70% of the wells tested in a Pennsylvania study. The concentrations ranged from 0.013 to 1.11 µg/L. He also found the following correlation between pesticide detection and nitrate and chloride concentrations.

> The probability of atrazine being found above the minimum detection limit was high when $NO_3$-N and Cl concentrations were above 4.0 and 3.0 mg/L, respectively. Also, generally the higher these concentrations, the higher the atrazine concentration.

Holden, *et al.* (1992) also found a link between the nitrate level and the probability of finding a pesticide in the sample. In the national alachlor well water survey, sponsored by Monsanto, over 1400 wells were sampled for pesticides. Atrazine, alachlor, cyanazine, and metolachlor were detected in 12, 0.8, 0.3, and 1% of the samples, respectively. Almost all the pesticide concentrations were at low levels with only 0.22% of the concentrations being over 1 µg/L.

An upstate New York study of 73 wells and 129 samples found pesticides in 6 samples. Atrazine was detected twice, at 1 and 3 µg/L. Also, a carbofuran metabolite, 3-hydroxy carbofuran, was detected in 2 samples at 2 and 3 µg/L (Walker and Porter, 1990). In the project, metabolites were not considered, only the actual pesticides.

A shallow groundwater study in the Coastal Plains geological region of Georgia, atrazine movement through the soil was tested. Atrazine was detected in the groundwater two months after application, with the highest concentration, 52 µg/L, occurring 150 days after application. Smith, *et al.* (1990) stated that "Up to 5% of the applied atrazine was calculated to be present within the saturated zone 187 days after application."

In another study of pesticide movement in the Coastal Plains soil in Georgia, atrazine and other pesticides were applied to test plots for a three year period. Atrazine was detected in the second and third year's groundwater samples at depths up to 2.4 meters below the ground's surface (Leonard, *et al.*, 1988). This indicated that atrazine had a months long lag in transport from the surface to the groundwater, and even though its reported half life was as low as 20 days, detectable amounts remained in the soil for over a year.

2. Pesticides detected in SGWD

Since contamination of SGWD was a new field of study,

there were few references about it. However, in a study of Big Spring in Iowa, it was estimated that the baseflow concentration of atrazine was 0.2 μg/L in the groundwater seepage (Libra, *et al.*, 1987). Also, in a study of the pesticides in the Cedar River in Minnesota and Iowa, Squillace and Thurman (1992) said,

> A minimal estimate of atrazine transported by the groundwater flow component of the river discharge past the Bertram sampling site is 800 kg/year (April 1984 through March 1985), which is ~6% of the total atrazine transported.

3. Half lives of the pesticides

The half life of a pesticide in the soil or groundwater depended on many factors including temperature, organic content, soil moisture, clay content, and depth. Increasing any of the factors except depth decreased the half life of the pesticide. Increasing depth increased the half life of the pesticide (Bouchard, *et al.*, 1982; Weber and Peter, 1982). For atrazine the half life was listed as between 20 and 140 days (Loague, *et al.*, 1990; Thurman, *et al.*, 1992). Alachlor's half life was reported in a range from 14 to 50 days (Gustafson ,1989; Spalding, *et al.*, 1989; Thurman, *et al.*, 1992). The range of half lives listed for carbofuran was 30 to 45 days (Spalding, *et al.*, 1979; Shirmohammadi, *et al.*, 1989). Cyanazine had a half life range from 14 to 85 days (Gustafson, 1989; Thurman, *et al.*, 1992). The range for metolachlor's half life was 20 to 180 days (Spalding, *et al.*,

Table 2
Pesticide Half Live Ranges

| Pesticide | Range of Half Lives, days |
|---|---|
| Alachlor | 12-50 |
| Atrazine | 20-140 |
| Carbofuran | 30-45 |
| Cyanazine | 14-85 |
| Metolachlor | 20-180 |

* Data from : Loague, *et al.*, 1989; Thurman, *et al.*, 1992; Gustafson, 1989; Spalding, *et al.*, 1979; Spalding, *et al.*, 1989; Shirmohammadi, *et al.*, 1989; Bouchard, *et al.*, 1982.

1979; Bouchard, *et al.*, 1982) (See Table 2).

### D. Pesticide Detection Methods

#### 1. Liquid-liquid extraction

Liquid-liquid extraction (LLE), was commonly used to separate analytes with polarities different from their original solvent into a new solvent. For water samples a nonpolar solvent like methylene chloride or hexene was added to the sample. The added solvent could not be miscible with water. This caused two separate phases to form, and nonpolar compounds would migrate into the added solvent (Blumberg, 1988). Liquid-liquid extraction was generally done as follows. The sample was poured into a separatory flask and a small amount of the nonpolar solvent was added (approximately 50 mL for a 1 L sample). The flask was shaken vigorously allow the analytes to contact the solvent. The flask was then set down and time was given for the solvents to separate. The nonpolar solvent was decanted into another container. This process was repeated twice, and all of the nonpolar solvent was collected, then evaporated down to the required volume.

While LLE works well at extracting most nonpolar compounds from water, it uses a relatively large amount of solvents. This was a concern because most nonpolar solvents are either known (benzene) or suspected (methylene chloride) carcinogens. Occasionally, an emulsion would form at the interface between the two solvents, making the removal of the

second solvent difficult or impossible. Also, the shaking procedure often caused lost samples due to spills and dropping of the flask.

2. Solid phase extraction

In Solid Phase Extraction (SPE) the sample is drawn through a porous matrix by a vacuum. The matrix was made of tetrafluoro-polyethene (TFPE) fibril holding either otcyl or octadecyl bonded silica. Nonpolar compounds were attracted and adsorbed to the hydrocarbon chains on the silica in the matrix. After the water sample was passed through the matrix, the nonpolar solvent was drawn through the matrix. The compounds were desorbed from the hydrocarbon chains and dissolved into the solvent. For a 1 L sample, approximately 30 mL of solvent was required, while LLE would need about 5 or 6 times more solvent for the same sample.

a. Cartridges

With Method 525.1,"Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry", the EPA switched from LLE to SPE for most pesticides and poly-aromatic hydrocarbons (Eichelberger, *et al.*, 1991). The original technique used small plastic cartridges, similar to the body of a syringe, to hold the TFPE/bonded silica matrix. The cartridges only held approximately 10 mL of the sample, so multiple transfers of the sample or a cartridge reservoir was required. The

plastics in the cartridge could interfere or contaminate the sample being extracted (Junk, *et al.*, 1988). Also, the small surface area of the cartridges lead to frequent clogging and long extraction times, 2-3 hours at the recommended flow rate (Kraut-Vass and Thoma, 1991).

b. Disks

An alternative to the cartridges, Empore$^{tm}$ extraction disks were designed to decrease the extraction time and the probability of clogging. The Empore$^{tm}$ extraction disks were 47 mm diameter and 0.5 mm thick. They were 90% octadecyl-bonded silica (octyl-bonded was also available) and 10% PFTE by weight (Figure 1). Hagen said, "The SPE disk can be considered to be a large-diameter, short-length extraction column." (Hagen, *et al.*, 1990) At the recommended flow rate, a 1 L sample was extracted in about 30 minutes. Although the overall flow rate increased, the specific discharge (flow/area) in the disk was about the same as it was in the cartridge. In a comparison of the cartridges vs. the disks, Kraut-Vass and Thoma (1991) said, "Despite the short contact time, the general performance of the disk compared well with that of the extraction cartridge." Finally, since the disk was made entirely of PFTE and bonded silica the risk of contamination or interference with the sample was reduced.

**E. Limits of Detection**

There was a wide range in the limit of detection (LOD) of

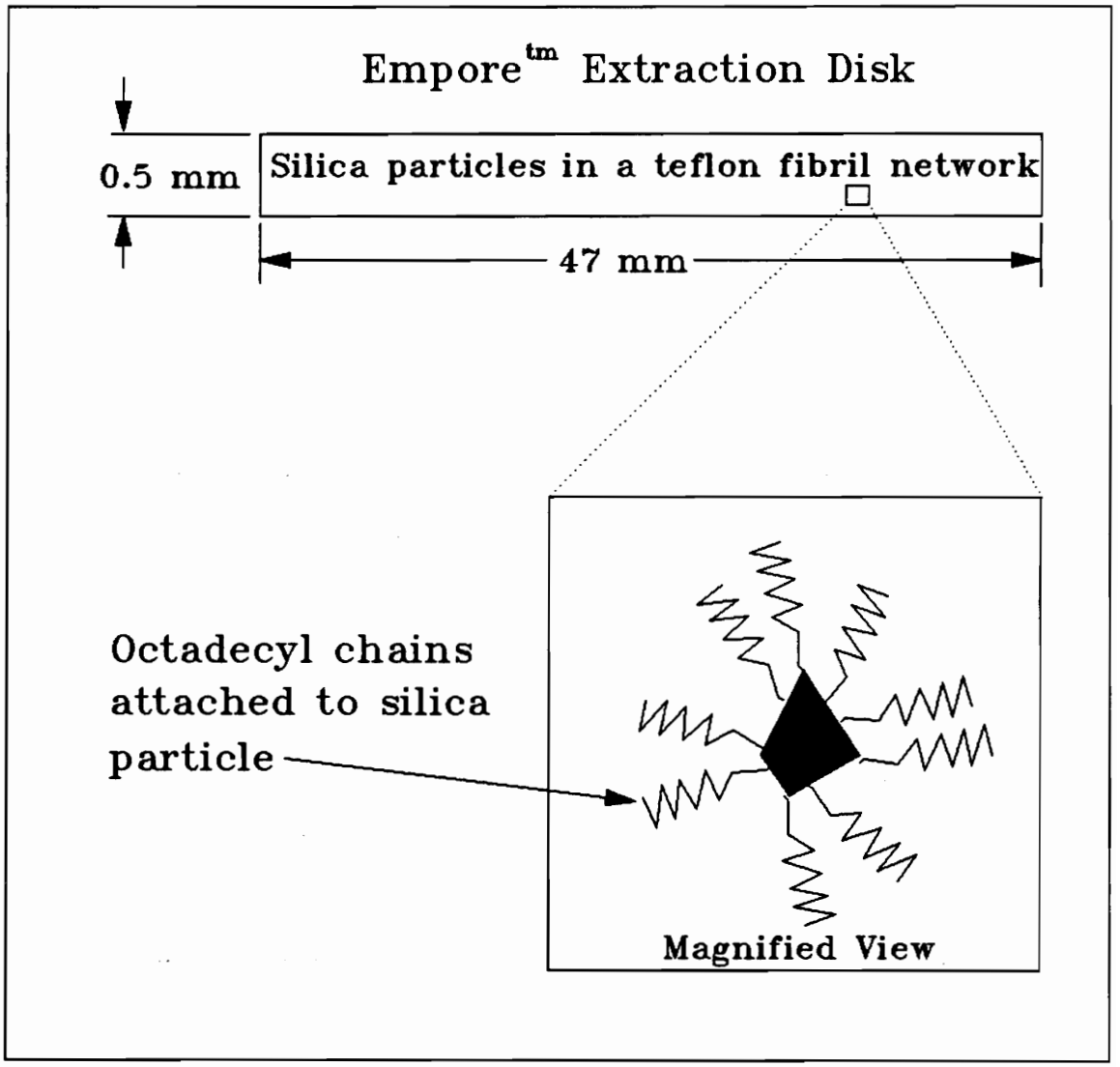



Figure 1
Diagram of Solid Phase Extraction Disk

the pesticides reported in the literature. The lowest reported LODs were: 0.01 µg/L for atrazine (Spalding, *et al.*, 1989; Wehtji, *et al.* 1983), 0.03 µg/L for alachlor, and metolachlor (Holden, *et al.*, 1992), 0.05 µg/L for cyanazine (Exner, 1990), and 0.05 µg/L for carbofuran (Legrand, *et al.*, 1991). The highest LODs reported were: 1.2 µg/L for atrazine (Steichen, *et al.*, 1988), 1 µg/L for alachlor, metolachlor, and cyanazine (Krill and Sonzogni, 1986; Walker and Porter, 1990), and 5 µg/L for carbofuran (Walker and Porter, 1990) (See Table 3). Interestingly all the highest LOD's were in studies using LLE.

**F. Efficiencies of Recovery**

Since SPE with the Empore$^{tm}$ disks is newly approved by the EPA, few literature sources are available. However three sources were found:

In a test of 43 organic compounds, the percent recovery varied from 18% to 519% with an average of 103% (Kraut-Vass and Thoma, 1991). In a test of phthalates in tap water, Hagen, *et al.* (1990) found percent recoveries from 82 to 117%. Finally, EPA Method 525.1 listed the recovery of 2-chlorobiphenyl at 78% at 0.2 µg/L (Eichelberger, *et al.*, 1991).

For the study 4-chlorobiphenyl was used as a surrogate at 10 µg/L with an average recovery of 74%, which was within the range found in the literature, and only 4% different from the

listed value for 2-chlorobiphenyl by the EPA.

Table 3
Range of LOD's in the Literature

| Pesticide | LOD range, in µg/L |
|---|---|
| Alachlor | 0.03-1 |
| Atrazine | 0.01-1.2 |
| Carbofuran | 0.05-5 |
| Cyanazine | 0.05-1 |
| Metolachlor | 0.03-1 |

* Data from: Spalding, *et al.*, 1989; Wehtji, *et al.*, 1983; Holden, *et al.*, 1992; Exner, 1990; Legrand, *et al.*, 1991; Krill and Sonzogi, 1986; Walker and Porter, 1990.

## III. Methods & Materials

### A. Research Chemicals

#### 1. Pesticides, Chemical Standards, and Solvents

All pesticides and chemical standards were bought from Chemical Services, Incorporated, West Chester, PA. The pesticides used in the study were: atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine), CAS # 1912-24-9, alachlor (2-chloro-2',6'-diethyl-N-(methoxymethyl) acetamide), trade name Lasso, CAS # 15972-60-8, carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranol methylcarbamate), trade name Furadan, CAS # 1563-66-2, cyanazine (2-[[4-chloro-6-(ethylamino)-S-triazin-2-yl]amino]-2-methylpropanenitirile), trade name Bladex, CAS # 21725-46-2, and metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide), trade name Dual, CAS # 51218-45-2.

The internal standards were 4-chlorobiphenyl, and the two deuterated compounds acenaphthene-$d_{10}$, and phenanthrene-$d_{10}$, CAS # 1517-22-2.

The main solvent used for extraction and for the preparation of most of the chemical standards was pesticide and Optima$^{tm}$ grade methylene chloride (dichloromethane) CAS # 75-09-2. Pesticide grade methanol CAS # 67-56-1, and acetone CAS # 67-64-1 were also used. Anhydrous Sodium Sulfate CAS # 7757-82-6 was used as a drying agent. All of the solvents and the sodium sulfate were bought from Fisher Chemical

Corporation (Raleigh, NC).

2. Stock Solution Preparation

All pesticide and chemical stock standards were made in 2 mL volumetric flasks at a concentration of 5 mg/mL, and then stored in 4 Ml amber vials with teflon lined lids at 4° C. The alachlor stock standard was made in acetone, but all the other standard solutions were prepared in methylene chloride. Solutions of lower concentrations were made by injecting the necessary number of μL of stock standard into a 2 mL volumetric flask and then diluting to 2 mL with methylene chloride. Calibration standards were made for quantitative analysis of samples; these solutions were prepared at 0.01, 0.05, 0.1, 0.25, 0.5, 1, 2, 5, and 10 mg/L. Spiking solution, for adding to the matrix/spike duplicates and reagent blanks, were prepared from the stock solutions at a concentration of 50 μg/mL. Varying volumes of this solution were added to the spiked samples to create the proper concentration.

**B. Laboratory Glassware Procedures**

1. Glassware

For extraction, a three piece, all glass, vacuum filter was used (Kontos, Vinland, NJ). The extract was stored in 40 mL amber, borosilicate glass vials with teflon lined tops (Scientific Specialties, Randallstown, NJ), until blown down, when they were stored in 4 mL amber, borosilicate glass vials with teflon lined tops, (Scientific Specialties, Randallstown,

NJ).

2. Cleaning Procedures

The 1 liter sampling jars were washed with soap and water, then rinsed three times with distilled, deionized water. All extraction equipment was washed and rinsed three times with distilled, deionized water between samples. The 40 and 4 mL vials were rinsed three times with methylene chloride before each use.

**C. Field Sampling Procedures**

1. Site Selection

Five sites were sampled on Virginia's coastal plains, with three on the eastern shore of Virginia. Four of the sites are working farms with the fifth being an undeveloped marsh. The sites were chosen because the watershed characteristics were conducive to possible groundwater contamination, and the sites were already being used by another Virginia Tech researcher for nutrient transport studies (Dr. George Simmons Jr., Biology Department). A map of all the sites is included (Figure 2). The sites were sampled every 4 to 6 weeks except for the marsh which was sampled every 2 or 3 months. The sites are described below:

*Agricultural site 1*

This site was located on the Phillips Creek which drains into the Hog Island Bay in Northampton County. The surfical soils have been classified as Bojac sandy loam which

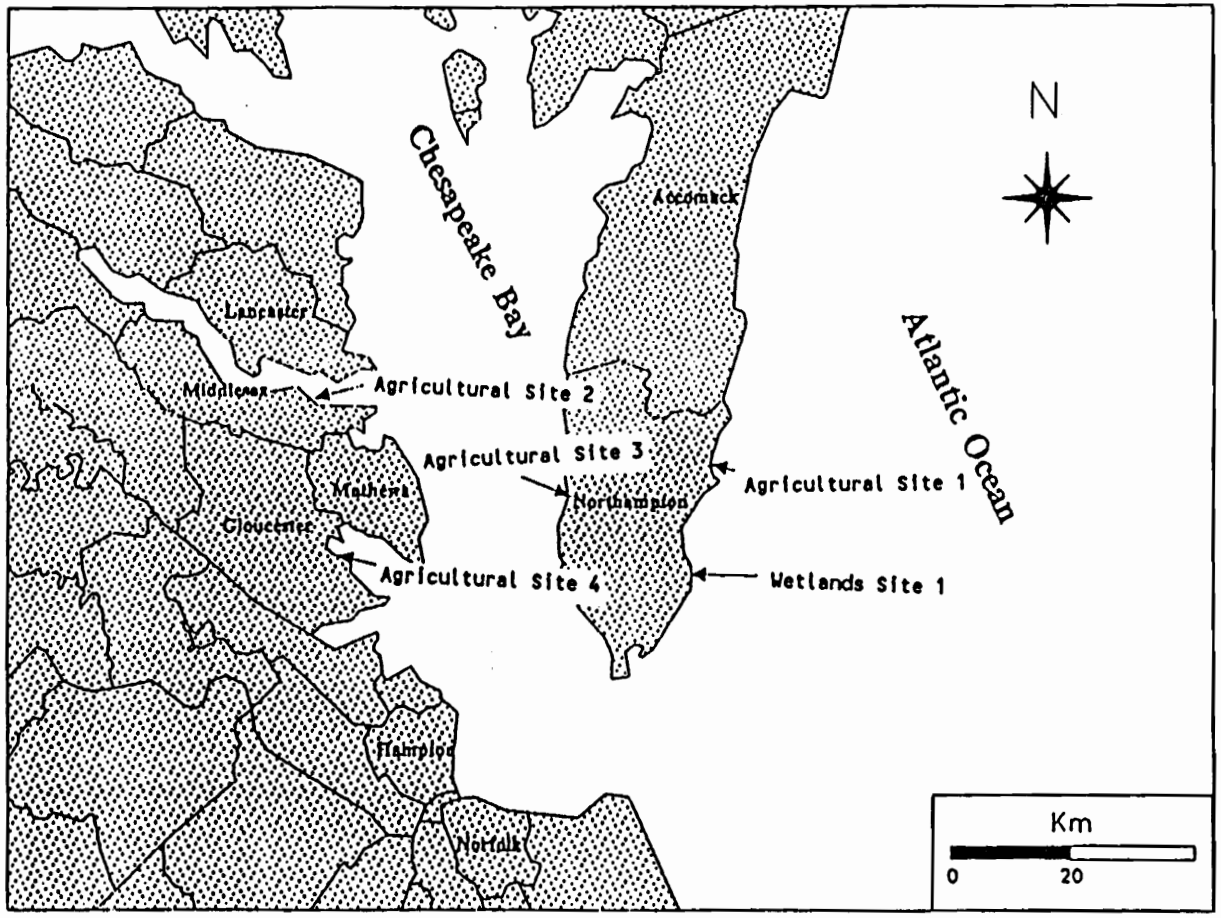



Figure 2
Map of All Sampling Sites

demonstrates very rapid permeabilities (5.0 to 50.0 cm/hr). The water table was located approximately 1.0 meters below the soils surface. Surfical nearshore sediments were sandy and display vertical hydraulic conductivities of 14.0 cm/hr. Mean tidal range was 0.6 meters with summer salinities on the order of 30 ppth. Sampled well locations were shown in Figure 3.

*Agricultural site 2*

This site was located on the southern shore of the Rappahannock River in Middlesex County. The spring 1991 crop was corn with atrazine and metolachlor applied for weed control. The winter 1991 crop consisted of winter wheat with soybeans planted in spring 1992. The surface soils have been classified as Slagle silt loam which demonstrates moderate permeabilities (1.5 to 5.1 cm/hr)(Newhouse *et al.*, 1985a). The water table was located approximately 4.0 meters below the soils surface. Surfical near shore sediments were sandy underlain by a thin clay lens. Vertical hydraulic conductivities were on the order of 0.6 cm/hr. Mean tidal range was approximately 0.5 meters with summer salinities on the order of 13 ppth. The approximate location of the sampled wells was shown in Figure 4.

*Agricultural site 3*

This site was located on Cherrystone Inlet in Northampton County. Winter 1991 crop consisted of winter wheat with soybeans planted in spring 1992. In the

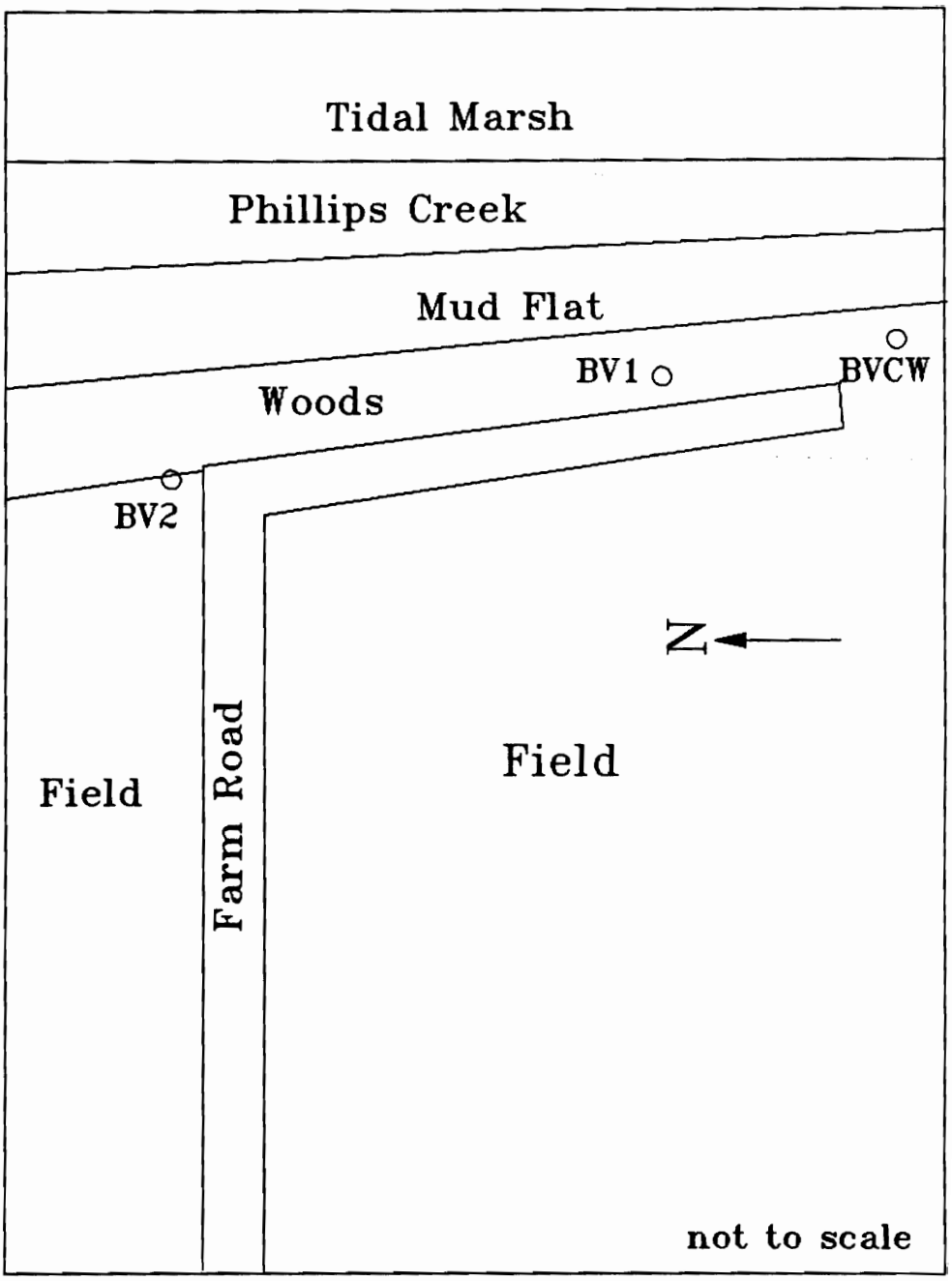



Figure 3
Wells at Agricultural Site 1

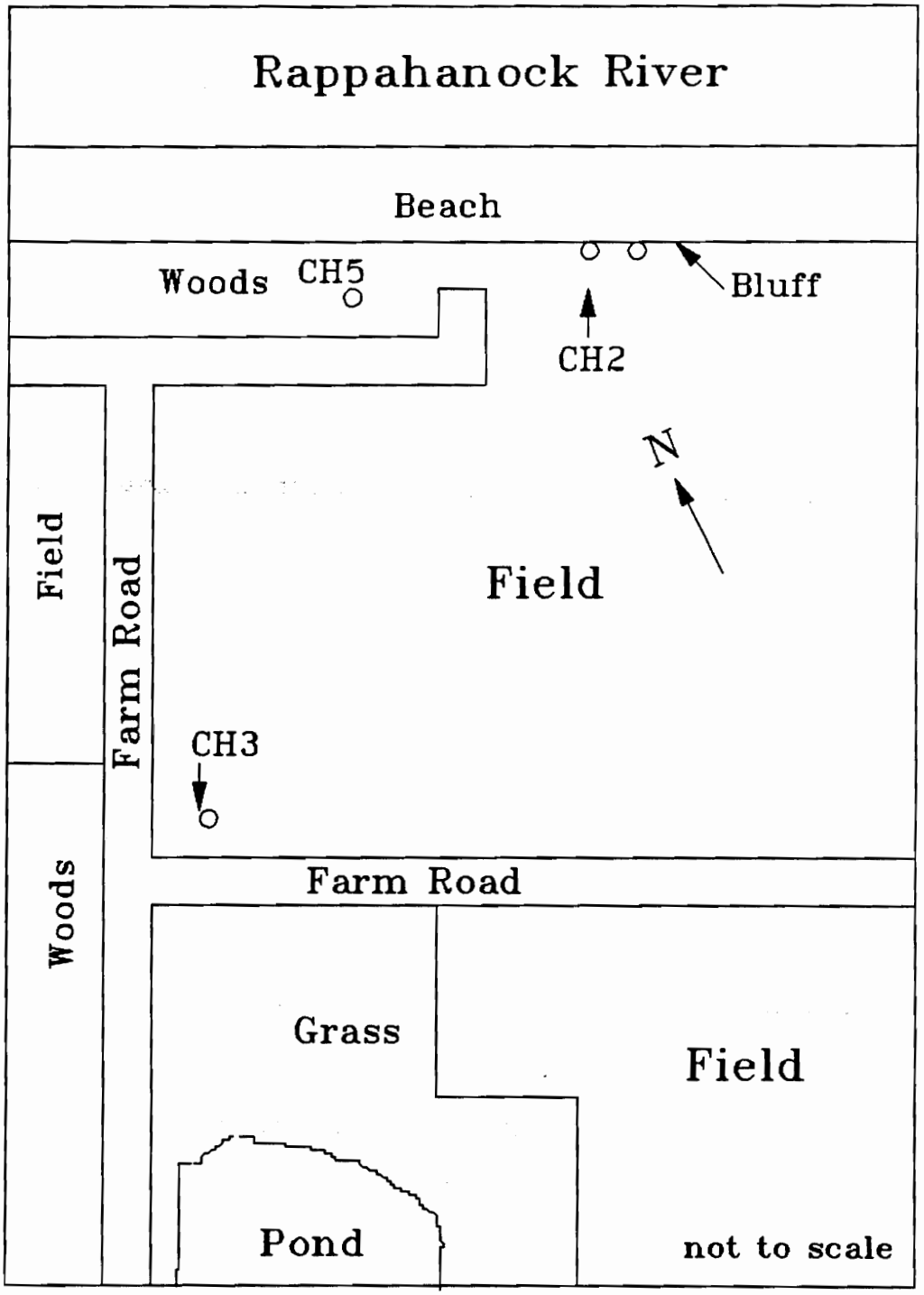



Figure 4

Wells at Agricultural Site 2

fall of 1992 barley was planted. None of the pesticides monitored by the study were applied in 1991 or 1992. The surfical soils have been classified as Bojac fine and Munden sandy loams which demonstrate moderately rapid (5 to 15 cm/hr) and rapid (15 to 120 cm/hr) permeabilities (Cobb and Smith, 1989). The water table was located approximately 2 meters below the soils surface. Surfical nearshore sediments were sandy with vertical hydraulic conductivities on the order of 16.1 cm/hr. Mean tidal range was 0.7 meters with summer salinities on the order of 20 ppth. The approximate location of the sampled wells was included in Figure 5.

*Agricultural site 4*

This site was located on the southern shore of the Piankatank River in Gloucester County. The surfical soils have been classified as a mix of Psamments-Hamludults complex and Ochlockonee Variant complex which demonstrate permeabilities varying form moderately slow (0.5 to 1.5 cm/hr) to rapid (15.2 to 50.8 cm/hr),(Newhouse *et al.*, 1985b). The water table was located approximately 1.0 meters below the soils surface. Surfical nearshore sediments were sandy with vertical hydraulic conductivities on the order of 0.9 cm/hr. Mean tidal range was 0.4 meters with summer salinities on the order of 11 ppth. Figure 6 contained the approximate well locations.

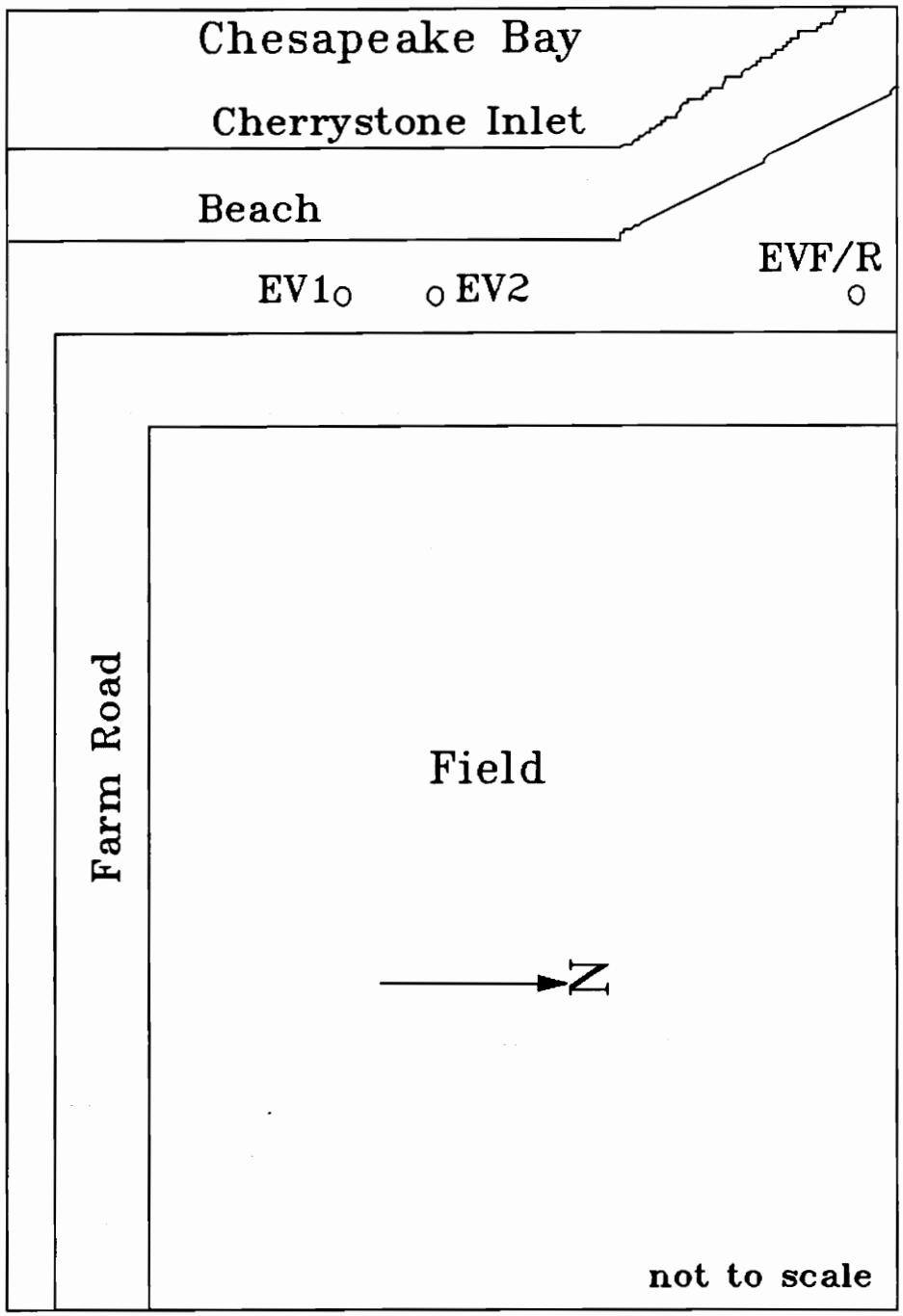



Figure 5
Wells at Agricultural Site 3

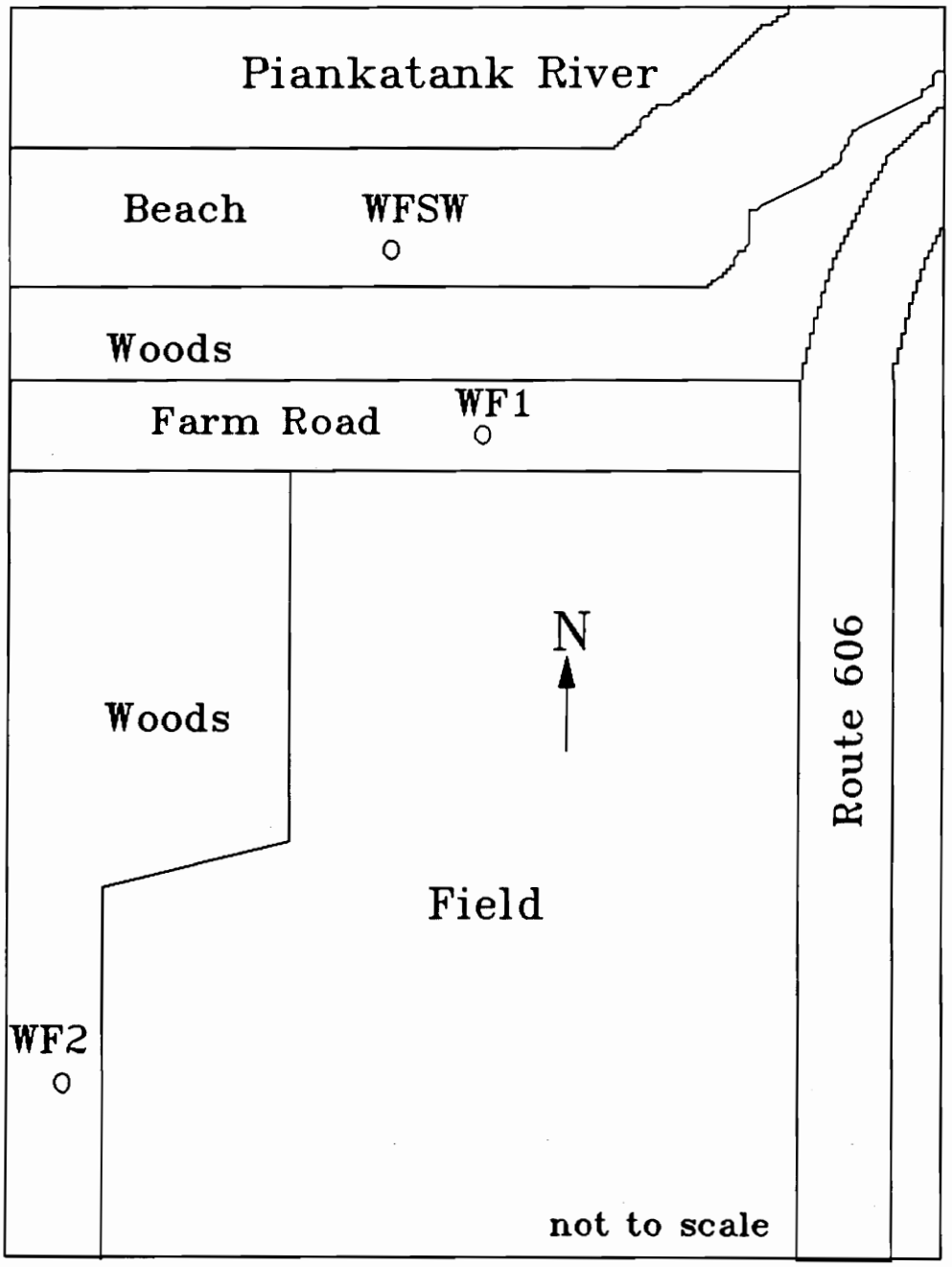



Figure 6
Wells at Agricultural Site 4

*Wetlands site 1*

This site was located on Magothy Bay in Norhtampton County. The site was adjacent to 300 meters of salt marsh followed by 300 meters of mesic forest before reaching an upland agricultural field. Surfical soils have been classified as Chincoteague silt loam. Mean tidal range was 0.9 meters with summer salinities on the order of 32 ppth. This site served as a natural background site, and had no agricultural activity. Figure 7 showed the estimated locations of the sampled wells.

2. Sampling Equipment

All wells were water jet drilled by or under the directions of Dr. William Reay. All the wells, except the middle well at wetlands site 1, penetrated only the top, unconfined aquifer. All wells extended approximately 1 meter below the water table. The bottom meter of the wells was screened to allow groundwater entrance. The wells were packed with pea gravel for approximately 1.5 meters from the bottom of the well. The middle well at wetlands site 1 tapped the second, confined aquifer. Agricultural site 2 had the deepest wells, approximately 6 meters, and site 4 had the shallowest at about 1.3 meters. The wells were lined with 5 cm diameter polyvinylchloride (PVC) casing and well screen.

The wells were pumped at 1 liter per minute with a Geotech Geopump 2 battery powered peristaltic pump with a 50

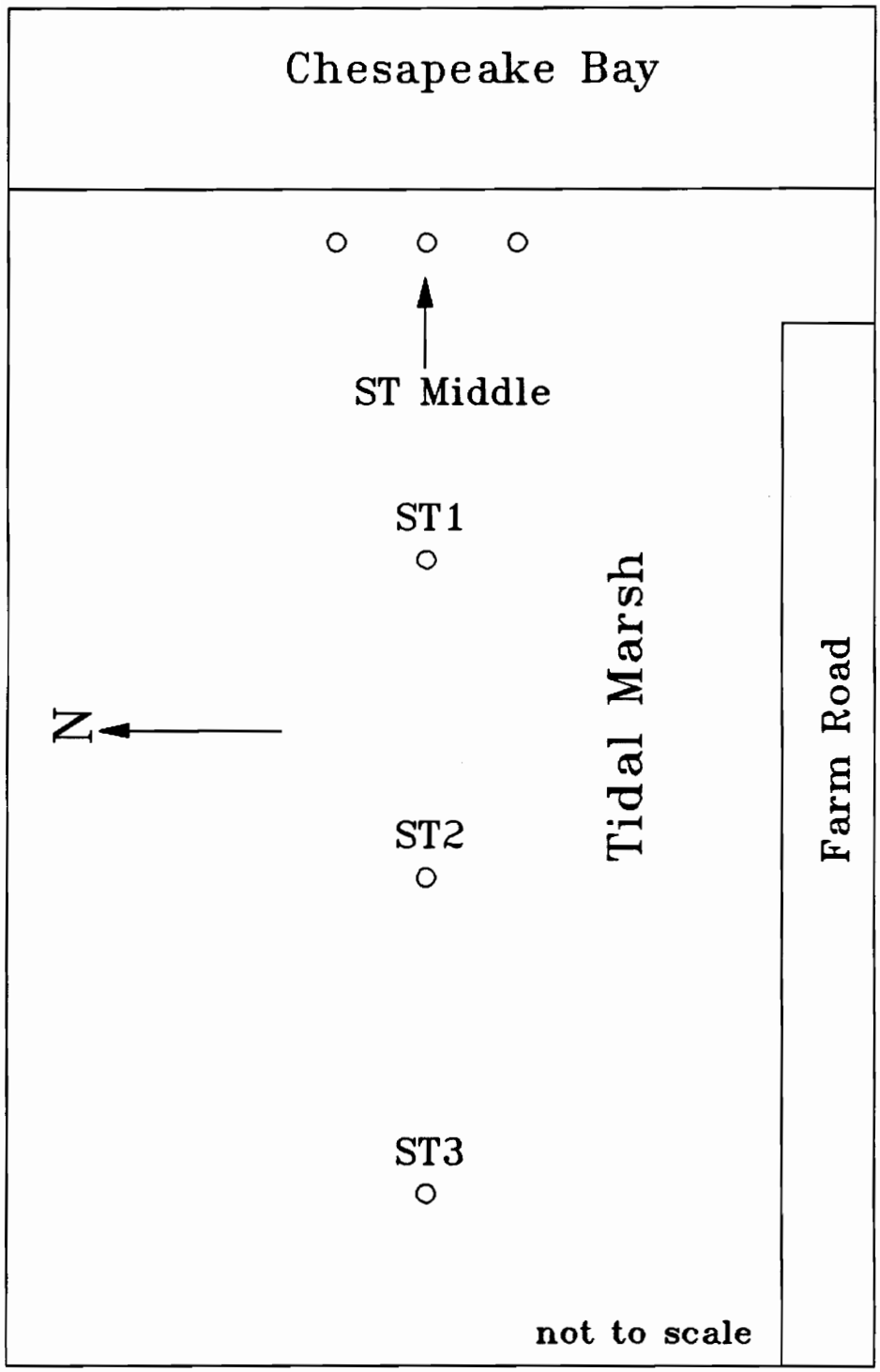



Figure 7
Wells at Wetland Site 1

cm piece of three-sixteenths inch inside diameter Nalgene™ tubing in the pump head. To lift the water from the well to the pump, three-sixteenths inch inside diameter teflon tubing was used. The samples were collected directly from the end of the pump and collected in 1 liter, amber borosilicate glass jars with teflon lined lids.

Seepage meters were used to collect the ground water seeping into the Chesapeake Bay. Seepage meters were one ended cylinders .75 meters in diameter and 20 cm deep. The top, enclosed end of the cylinder, had a hole drilled into it for attachment of a teflon bag to collect the seepage. The seepage meters were made of Nalgene® and plexiglass with a silicone sealant. The seepage bags were teflon gas sampling bags having a 3.75 liter volume (Fisher, Raleigh, NC). Seepage bags were connected to the seepage meters by a nalgene tube and a rubber stopper.

3. Sampling Procedure and Preservation

a. Well Samples

The well water samples were taken after approximately 5 well volumes had been pumped out of the well. The sample was taken directly from the end of the pump. Three wells at each site were sampled each 4 to 6 weeks. Originally, duplicate samples were taken from two wells and quadruplicate samples from the third well. Starting in September, 1992, two wells had quadruplicate samples taken,and the remaining well had

duplicate samples taken. Occasionally, one of the wells would not recharge enough for the full amount of samples to be taken from the site. The samples were stored on ice in coolers until returned to the laboratories at Virginia Tech, where they were stored in refrigerators at 4° C until extraction. Samples for the nutrient study and Ohmicron's immunoassay procedure were taken at the same time as the study's samples.

b. Seepage Meter Samples

At low tide, four seepage meters were placed far enough offshore that they were completely under water. The meters were imbedded into the sediments with the closed end up to within an inch of the top of the meter (Figure 8). This was done to minimize the amount of sea water trapped in the headspace between the sediment and the top of the meter. At high tide, the bags were removed and the volume of the seepage water was measured. This water was discarded, for it was mostly sea water that had been trapped in the head space of the meter. Then the collection bags were replaced. At the next low tide the collection bags were removed and the seepage meter samples were taken directly from the teflon sampling bag. The bags were 3.75 L, but they were rarely full. All the water in the collection bags at low tide was retained for analysis. See Table 4 for a complete listing of actual volumes for seepage meter samples. The seepage meter samples were also stored on ice in coolers until returned to the

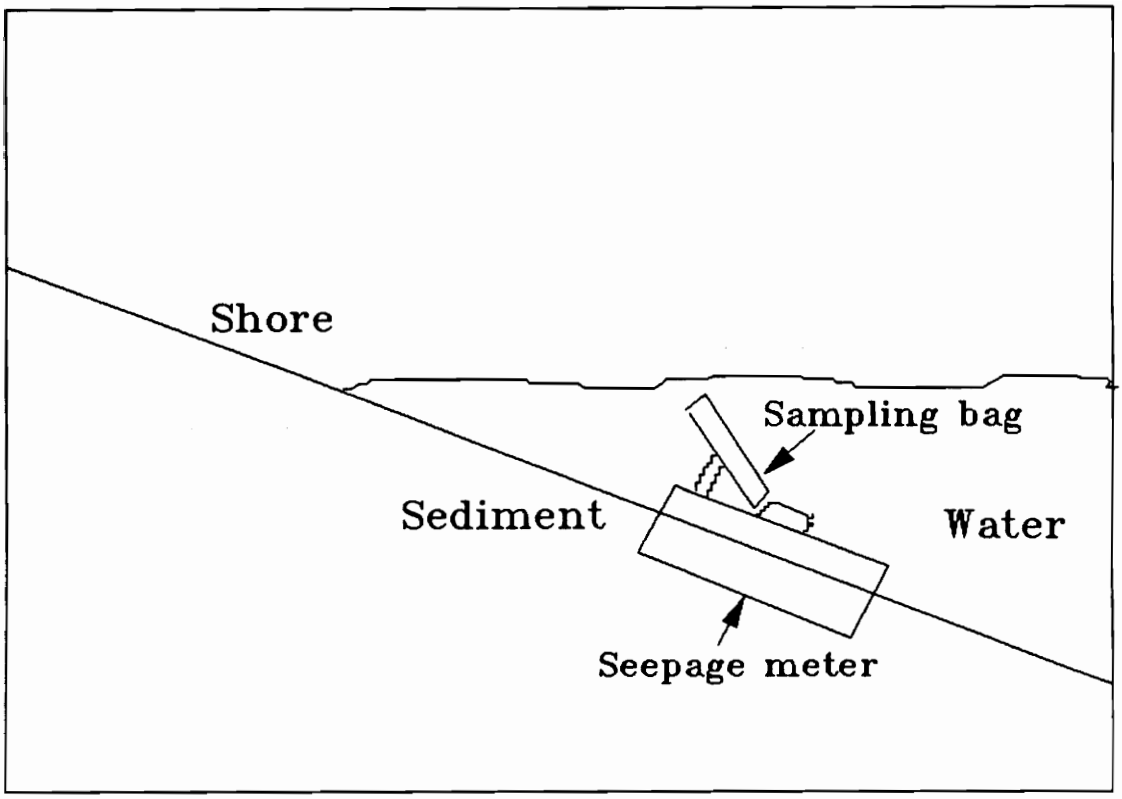



Figure 8
Typical Seepage Meter Placement

Table 4
Seepage Meter Sample Volumes (mL)

| Site | SM[a] | Month | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | May | June | July | Aug | Oct | Nov | Dec | Jan | Feb |
| EV[b] | 1 | 700 | 1300 | 700 | 1300 | 2200 | 200 | | | 200 |
| | 2 | 1200 | 900 | 600 | 1000 | 2300 | 500 | 1300 | | 150 |
| | 3 | | 1300 | | 1300 | 1300 | 600 | | | |
| | 4 | 500 | 700 | | 1100 | 2300 | 1300 | | | |
| CH[c] | 1 | | | 1300 | 1300 | 300 | | CLOSED for Hunting Season | | 290 |
| | 2 | | 1300 | 1300 | | 700 | | | | 480 |
| | 3 | 1300 | 1100 | | 1300 | 1300 | | | | 1280 |
| | 4 | | | 1300 | | 300 | | | | 2280 |
| BV[d] | 1 | 1300 | 2900 | | 400 | | 700 | | | 3600 |
| | 2 | 1300 | | 800 | 100 | 1300 | | | | 580 |
| | 3 | 2300 | 1100 | | 300 | | 3500 | | | 4300 |
| | 4 | 1300 | 1300 | | 700 | 2300 | 2300 | | | 4700 |
| WF[e] | 1 | | | | | 1500 | | | 1100 | 880 |
| | 2 | | | | 500 | 900 | | 1300 | 1700 | 1250 |
| | 3 | | 1300 | | 1300 | 1300 | | | 1700 | 1480 |
| | 4 | | 1300 | | 800 | | | | 3500 | 1580 |
| ST[f] | 1 | | | 1300 | | | | | | |
| | 2 | | | 1300 | | | | | | |
| | 3 | | | 1000 | | | | | | |
| | 4 | | | 1300 | | | | | | |
| | 5 | | | 1300 | | | | | | |
| | 6 | | | 1300 | | | | | | |

a SM was Seepage Meter number
b EV was Agricultural Site 3
c CH was Agricultural Site 2
d BV was Agricultural Site 1
e WF was Agricultural Site 4
f ST was Wetlands Site #1

goose grass

laboratories at Virginia Tech. At Virginia Tech, they were stored at 4°C until extracted. Samples for Dr. Simmons' nutrient study and Ohmicron's testing were taken directly from the collection bags.

**D. Laboratory Analyses**

1. Extraction

All samples were spiked with surrogates of deuterated acenaphthene and phenanthrene. Chrysene-$d_{10}$ was tried in May but discontinued due to its much longer detention time than the pesticides of interest. Starting in September, 1992, 4-chlorobiphenyl was added to all the samples as a surrogate for detection on the electron capture detector (ECD). The deuterated surrogates were added at 5 µg/L for the April samples and 2 µg/L for all others, while the 4-chlorobiphenyl was added at 10 µg/L.

Solid phase extraction was done with 47 mm Empore$^{tm}$ extraction disks (Varian, Harbor City, CA) in an all glass filtering apparatus (Kontos, Vineland, NJ). The apparatus consists of a funnel; a vacuum armed, fritted glass filter, and a 2 L flask. The Empore disk was placed between the funnel and the fritted glass filter. Due to the turbidity of some of the samples, all the extractions used a 1 micrometer non-bonded glass fiber filter (Fisher Scientific, Raleigh, NC) seated on top of the Empore disk to trap the particulates and prevented them from clogging the Empore disk (Figure 9).

After assembly, the Empore disk was preconditioned by drawing 5 mL of methylene chloride through the disk, leaving a meniscus of liquid on the top. Five mL of methanol was then drawn through, again leaving a little liquid on top of the filter. Finally, 5 mL of reagent water was drawn through, leaving a layer of water on top. The disk was not allowed to dry, as this causes the performance to become erratic and unreproducible.

After preconditioning, the 1 liter sample was drawn through the apparatus. Flow rate varied depending on the turbidity of the sample, but averaged 30 mL per minute. When the entire sample had passed through the disk (approximately 30 to 60 minutes), the disk was allow to dry for 5 minutes with the vacuum attached to reduced the amount of water trapped in the disk. The 2 L flask was replaced by a smaller flask containing a 40 mL test tube. Three 5 mL volumes of methylene chloride were passed through the disk into the test tube, with the disk allowed to dry between each volume. The first two volumes were also used to rinse the sample bottle before being poured into the apparatus. The final rinse was pipetted around the rim of the funnel of the apparatus. The 15 mL of methylene chloride eluant were passed through a funnel with a few grams of anhydrous sodium sulfate to absorb and remove any residual water. The eluant was evaporated down to approximately 1 mL under a cool nitrogen gas stream, then

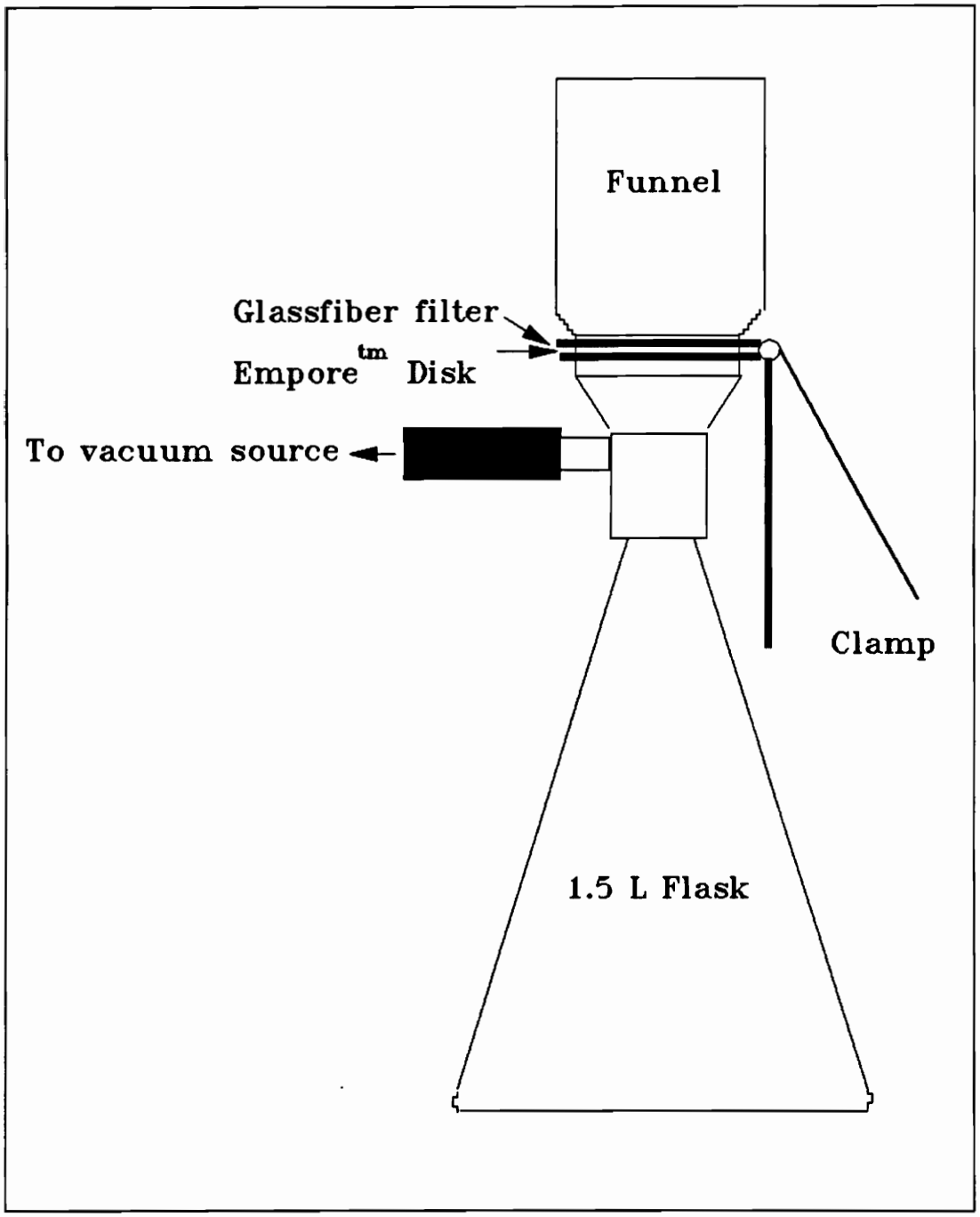



Figure 9

Extraction Apparatus

stored at 4° C until analyzed on the GC.

2. Gas Chromatography

All samples were injected on a Hewlett-Packard Gas Chromatograph model # 5890, with a Hewlett-Packard model # 3396 series II Integrator. Both a Flame Ionization Detector (FID) and a Electron Capture Detector (ECD), with $Ni^{63}$, were used. Selected samples were injected on a Hewlett-Packard Gas Chromatograph model # 5890 series II; connected to a Hewlett-Packard Mass Spectrum Detector (MS) model # 5970 with a Hewlett-Packard data station model # 5970. The details of each instrument were described as follows.

a. GC/FID and GC/ECD

Originally, the FID was used with a 30 m x 0.25 mm x 0.25 μm DB-5 capillary column. The FID proved to be more sensitive than the GC/MS, so all samples from May and June 1992 were analyzed using the FID. However, since all the pesticides except carbofuran were chlorinated, the ECD was more sensitive than the FID for most of the pesticides. All samples from June 1992 to February 1993 were injected on the ECD. The ECD provided better sensitivity, but metolachlor (which was monitored after the July 1992 samples) and cyanazine co-eluted on the DB-5 column. To resolve the compounds, a different column was employed, the 30m x 0.25mm x 0.25 μm DB-210 (J&W Scientific, Rancho Cordova, CA). Although it did separate metolachlor and cyanazine, the DB-210 caused the carbofuran

and metolachlor peaks to co-elute, so the DB-5 column was also used to analyze the samples. From October, 1992 on, the ECD was used with both the DB-5 and DB-210 columns (Table 5).

The temperature program for the FID analysis was to start and hold for one minute at 45°C, then 42.5°C/min to 130°C, then 7°C/min to 180°C, and finally 12°C/min to 280°C with a final time of 3 minutes at 280°C. The injection port was at 250°C and the detector was at 300°C. The helium linear velocity was 35 cm/sec or 2 mL/min. Approximately 3 μL of each sample were injected.

For the ECD with the DB-5 column, the temperature program used was: start and hold for 1 minute at 75°C, then ramp at 10°C/min to 275°C and hold for two minutes. The injector port was at 250°C and the ECD was at 300°C. With the DB-210 column, the program was: start and hold for 1 minute at 140°C, then ramp at 5°C/min to 240°C, with a final time of 2.5 minutes at 240°C. The injector port and the detector were at 250°C. The helium linear velocity was 35 cm/sec and the nitrogen make up gas flow was 70 mL/min for both columns.

For the GC/ECD, calibration curves were made by multiple injections (4 or 5) of the 0.1, 0.5, 0.75, 1, 2, and 5 mg/L calibration standards. A calibration curve was calculated using least squares regression. A single calibration standard, usually the 2 mg/L, was injected at the beginning of each work day and after every eight hours of analysis. If the

calibration standard was not within 1 standard deviation of the predicted value based on the calibration curve, then no samples were analyzed until the instrument was demonstrated to be operating properly. The chromatograph of a typical standard was included as Figure 10. Samples in which pesticides were detected were also analyzed by the GC/MS.

On January 5, 1992 an autosampler was installed on the GC/ECD. Some of the December samples and all of the January and February samples analyzed on the GC/ECD used the autosampler for injection.

b. GC/MS

A DB-5 30 m x 0.25 mm capillary column with a film thickness of 0.25 $\mu$m (J&W Scientific, Rancho Cordova, CA) was used for the pesticide analysis. A multi-ramp temperature program as specified in EPA Method 525.1 was used for separation of the compounds. Approximately 3 $\mu$L of a sample was injected each analysis.

The temperature program was as follows: the initial oven temperature was 45°C held for one minute followed by a ramp of 28.3°C / minute to 130°C immediately followed by a ramp of 12°C / minute to 180°C which was in turn followed by a 7°C / minute ramp to a temperature of 240°C and finally a 12°C ramp to 280°C. The injection temperature was 220°C and the transfer line was held at 250°C. The carrier gas was helium with a linear velocity of 33 cm/sec.

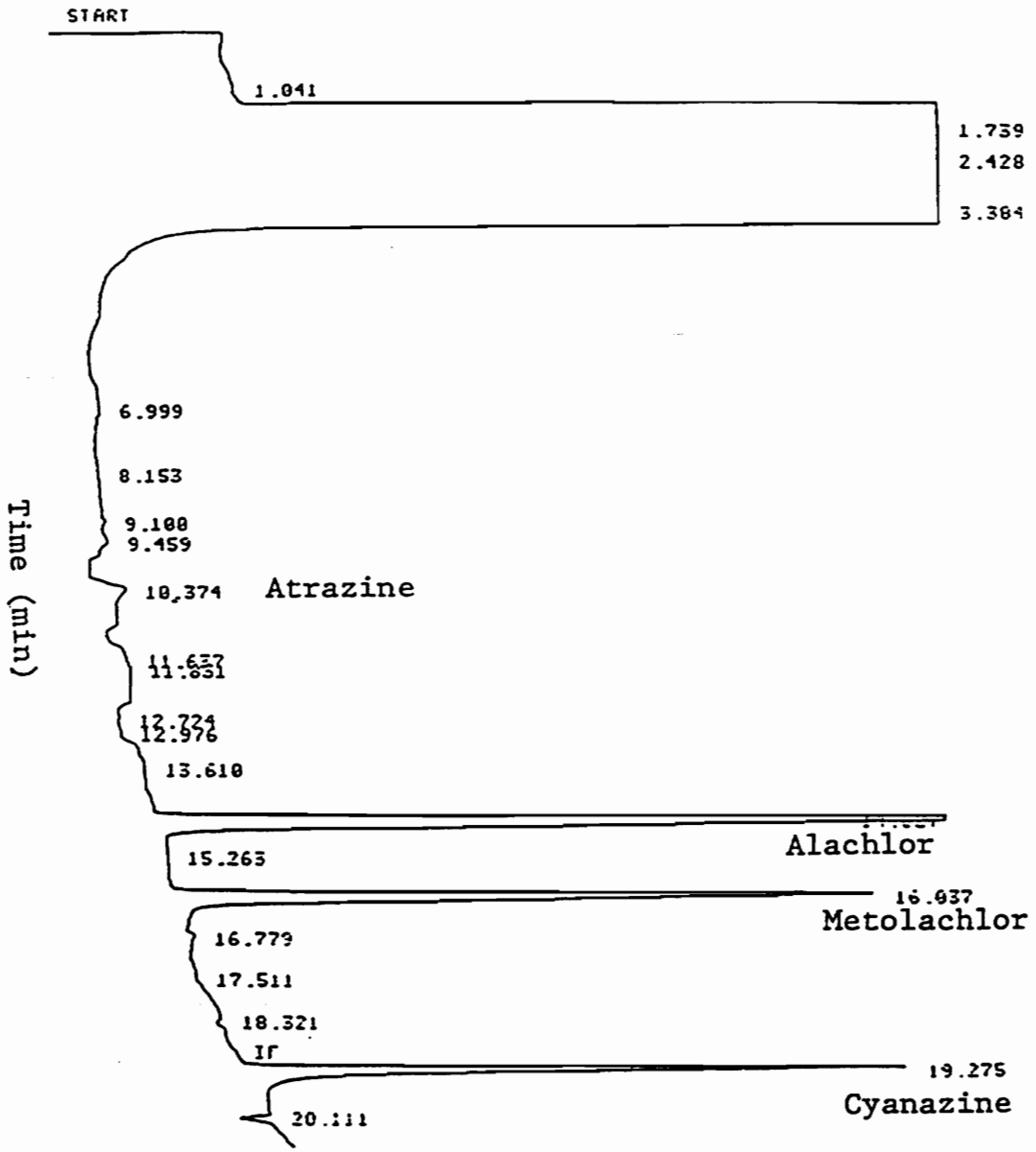



Figure 10

Chromatogram of a 0.5 g/L Calibration Standard Using the GC/ECD

The Mass Spectrometer (MS) was a quadropole model with 70 electron volt electron impact ionization. A mass range from 50 to 450 m/z was scanned. The scanning rate was 1.1 scans per second. Compounds were identified by retention time and comparison to the online library of spectra in the data station (Wiley-NBS database). For the GC/MS the autotune program was run at the start of every day's run and after eight hours work. The autotune used perfluorotributylamine (PFTBA) as a test substance. The autotune was checked by injecting decafluorotriphenyl phosphine (DFTPP) and checking the relative strength of its ions against the guidelines stated in EPA Method 525.1. A pesticide calibration standard was also injected to evaluate and compare retention times, mass spectra, and response factor (Figure 11). The retention times of the surrogates and pesticides were listed in Table 5.

The pesticide concentration in an individual sample was calculated from the response factors generated from the internal standards (acenaphthene-$d_{10}$, and phenanthrene-$d_{10}$). The quantification ions specified in EPA Method 525.1 were used to generate response factors and to calculate pesticide concentrations. These response factors were calculated by injecting standard pesticide solutions at 0.75, 1, 2, and 5 mg/L with a constant internal standards concentration of 2 mg/L. The standard response factor equation was used, which is as follows:

Table 5
Pesticide Retention Times using the GC/ECD

| DB-5 | Retention time (min) | DB-210 | Retention time (min) |
|---|---|---|---|
| 4-Chloro-biphenyl | 12.00 | 4-Chloro-biphenyl | 5.80 |
| Carbofuran | 14.77 | Carbofuran | 15.36 |
| Atrazine | 14.88 | Atrazine | 9.56 |
| Alachlor | 16.73 | Alachlor | 13.74 |
| Metolachlor | 17.50 | Metolachlor | 15.22 |
| Cyanazine | 17.53 | Cyanazine | 18.45 |

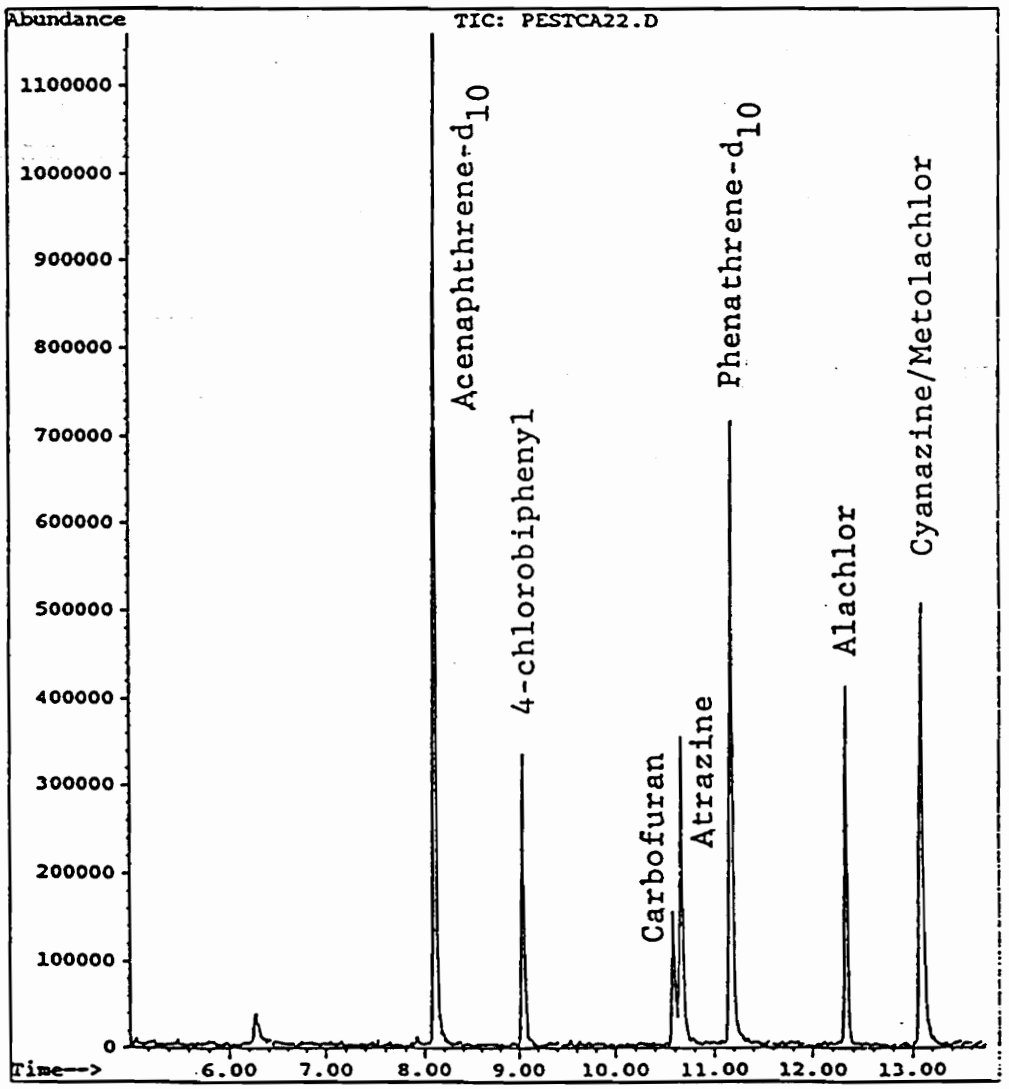



Figure 11

Chromatogram of a 5 µg/L Calibration Standard Using the GC/MS

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

RF = Response Factor

$A_x$ = Area of the quantitation ion for the compound being measured

$A_{is}$ = Area of the quantitation ion for the specific internal standard

$C_x$ = Concentration of the compound being measured (mg/L)

$C_{is}$ = Concentration of the specific internal standard (mg/L)

Measured concentration were calculated in micrograms per liter (ppb).

$$Concentration(ppb) = \frac{A_x * Q_{is}}{A_{is} * RF * V}$$

$A_x$ = Area of characteristic ion for compound being measured

$Q_{is}$ = Total quantity of internal standard added to water sample (micrograms)

V = Volume of original water sample.

The GC/MS had poor sensitivity for the five pesticides and was

only used to test for possible confirmation of pesticides detected by the GC/FID and GC/ECD.

**E. Quality Assurance and Quality Control**

1. Instrument's Performance

An independent analytical chemist not associated with the project prepared 6 check samples in July 1992 that were analyzed to determine any experimental bias. The samples were extracted and injected on the GC/MS. The regression values were generally close to the actual concentration. Carbofuran's values contained the largest errors. The values are listed in Table 6.

2. Method Detection Limits

All the calibration standards were analyzed, with the instrument Lowest Detectable Quantity (LDQ) for each pesticide recorded. Table 7 listed the LDQ's for the pesticides on each instrument. The instrument Limit of Detection (LOD) was calculated after making the calibration curve for each instrument. The LOD's were determined by multiplying the standard deviation of the a calibration standard on the instrument by the t-test value at a 99% confidence level plus the background noise of the GC. The Method Detection Limits (MDLs) were calculated from the spiked matrix samples the same way as LODs, except the standard deviation of the spiked samples was used (See tables 8&9). In the project, the LODs for the pesticides was

Table 6
Pesticide Concentrations in the Check Standards

| Pesticide | Concentration, µg/L (ppb) | |
|---|---|---|
| | Actual | Measured |
| Alachlor | 1.0 | ND |
| | 1.0 | 1.2 |
| | 2.5 | 3.2 |
| | 2.5 | 2.3 |
| | 6.0 | 6.0 |
| | 6.0 | 6.0 |
| Atrazine | 1.0 | 0.5 |
| | 1.0 | 1.5 |
| | 2.5 | 2.8 |
| | 2.5 | 2.2 |
| | 6.0 | 4.5 |
| | 6.0 | 5.5 |
| Carbofuran | 1.0 | 0.5 |
| | 1.0 | 1.3 |
| | 2.5 | 2.1 |
| | 2.5 | 1.8 |
| | 6.0 | 4.0 |
| | 6.0 | 3.0 |

Table 7
Instrument Lowest Detectable Quantities of Pesticides
(in mg/L)

| | GC/MS | GC/FID | GC/ECD |
|---|---|---|---|
| Atrazine | 1 | 1 | 1 |
| Alachlor | 0.75 | 0.75 | 0.01 |
| Carbofuran | 2 | 1 | 1 |
| Cyanazine | 2 | 1 | 0.01 |
| Metolachlor | 0.5 | 0.5 | 0.01 |

* Note that the LDQ did not include the extraction concentration factor of 1000, which would make the sample concentration in µg/L

Table 8
Instrumental Limits of Detection of the Pesticides
(mg/L)

| Pesticide | GC/MS | GC/FID | GC/ECD |
|---|---|---|---|
| Atrazine | 1.09 | 3.5 | 0.59 |
| Alachlor | 2.5 | 3.9 | 0.099 |
| Carbofuran | 1.0 | 3.8 | 2.6 |
| Cyanazine | 1.9 | 5.9 | 0.025 |
| Metolachlor | 0.3 | N/A* | 0.061 |

* The GC/FID was not used to determine metolachlor
* Note that the LDQ did not include the extraction concentration factor of 1000, which would make the sample concentration in µg/L

Table 9
Method Detection Limits[a] of the Pesticides
(μg/L)

| Pesticide | GC/MS[b] | GC/ECD[c] | Immunoassay (MDC)[d] |
|---|---|---|---|
| Atrazine | 0.64 | 0.36 | 0.05 |
| Alachlor | 0.88 | 0.33 | 0.04 |
| Carbofuran | 1.6 | 1.5 | 0.06 |
| Cyanazine | 1.9 | 0.32 | 0.04 |
| Metolachlor | N/A* | 0.50 | 0.06 |

* GC/MS and GC/FID were not used to determine metolachlor

a The MDLs were determined by multiplying the standard deviation of an added concentration of a pesticide (see below) by the t-test value at the 99% confidence level.

b The added concentration used for the GC/MS was 2 mg/L, except for cyanazine. 5 mg/L was used for it.

c The added concentrations used for the GC/ECD were 0.25 mg/L for alachlor and cyanazine, 0.5 mg/L for atrazine and metolachlor, and 2 mg/L for carbofuran.

d Data from OHMICRON Corporation

within the range of the LODs found in the literature, except for the LODs using the GC/FID. However the GC/FID was only used for two months, May and June 1992.

Ohmicron's immunoassay procedure listed a Minimum Detectable Concentration (MDC), which is a measure of the minimum pesticide concentration necessary to yield a response in the immunoassay. Since the immunoassay method measures pesticides directly in the water sample without prior concentration, the MDCs are comparable to the solid phase extraction/GC MDLs.

3. Duplicates

Duplicate samples were taken from all wells each trip. This was done to assess the variability of the sampling analysis techniques, and for safety in case a sample was lost accidentally. Also, one well from each site from April to September, and two wells from each site after September had quadruplicates samples taken for spikes.

4. Blanks

For every group of twenty samples, one lab blank, one equipment blank, and one travel blank were analyzed. All blanks were made with Milli-Q reagent water. No blank sample ever had a detectable amount of a pesticide. The lab blank was to ensure that the analysis itself was not adding contaminates to the samples. The equipment blank was to ensure that the pump and tubing were not contaminating the

sample. Finally, the travel blank ensured that the samples were not contaminated during transportation.

5. Fortified Samples (Spiked Samples)

A spike was a sample that had pesticides added before it was extracted. For every twenty samples a lab fortified spike was analyzed. It was made of Milli-Q reagent water with internal standards and the pesticides. Additionally, matrix spikes were made from quadruplicate field samples. Two matrix spikes were made from each site's samples from April to September, 1992 and four from each site's samples after September. The internal standards were at 5 μg/L and the pesticides were added at 5 and 20 μg/L for the April samples. After April, the internal standards were added at 2 μg/L while the pesticides were added at 0.25, 0.5, 1, 2, and 5 μg/L. The pesticides were added at the same concentration in a sample, i. e. 0.25 μg/L, but at different concentrations for different samples. Graphical correlation of the spikes is included in Appendix G.

6. Recoveries of Surrogates

Initially phenanthrene-$d_{10}$ and acenaphthrene-$d_{10}$ were used as surrogates at 5 μg/L in April 1992, and 2 μg/L afterwards. However, they did not produce good peaks on the GC/ECD. Starting in August 1992, 4-chlorobiphenyl was added to all samples at 10 μg/L. The recovery rate for it is listed for every sample from August to February 1993 in Appendix A. The

overall recovery rate for 4-chlorobiphenyl was 74%. By month, the recovery rate was 39%, 62%, 68%, 65%, 120%, and 90% for August, October, November, December, January, and February respectively. A standard curve was developed based upon multiple injections of 4-chlorobiphenyl standard solutions at four different concentrations. A curve was developed using least squares regression. Percent recovery was calculated with this curve by dividing the calculated 4-chlorobiphenyl concentration by the added concentration, 10 μg/L, assuming 100% recovery.

### G. Statistical Analyses

All statistical analysis was done using Borland's Quattro Pro version 4.0. The coefficients of the regressions performed were included in Appendix C.

## IV. Results and Discussion

### A. Seepage Rates

The average seepage rate for all the samples was 0.63 L/($m^2$*hr). Individual seepage rates for each site were shown in Figure 12. Note that the seepage rates listed were the gross movement of water through the sediment. From salinity studies, only 35% of the water was estimated to be fresh water, with the other 65% being seawater that had migrated into the sediment (Simmons, *et al.*, 1992).

The seepage rates varied with each sample, but the average discharges over the study period were 0.96, 0.74, 0.59, and 0.40 L/($m^2$*hr) for Agricultural Sites 1, 2, 3, and 4, respectively. The two sites with the highest discharge, agricultural sites 1 and 2, also had soils with the most clay and silt. Both site's soil contained layers or pockets of sandier soils in between the clayey soils. This might have caused the seepage to be funneled into the sandier areas of soil, which would have increased the discharge rate.

The lowest or close to the lowest discharges for all sites were in November and December of 1992. The highest discharge was in February 1993 for two sites, 1 and 4, July 1992 for agricultural site 2, and October 1992 for site 3. The discharge appeared to follow the seasonal rainfall variations, with high flows in late spring of 1992 and late winter of 1993, and low discharges in the summer and late fall

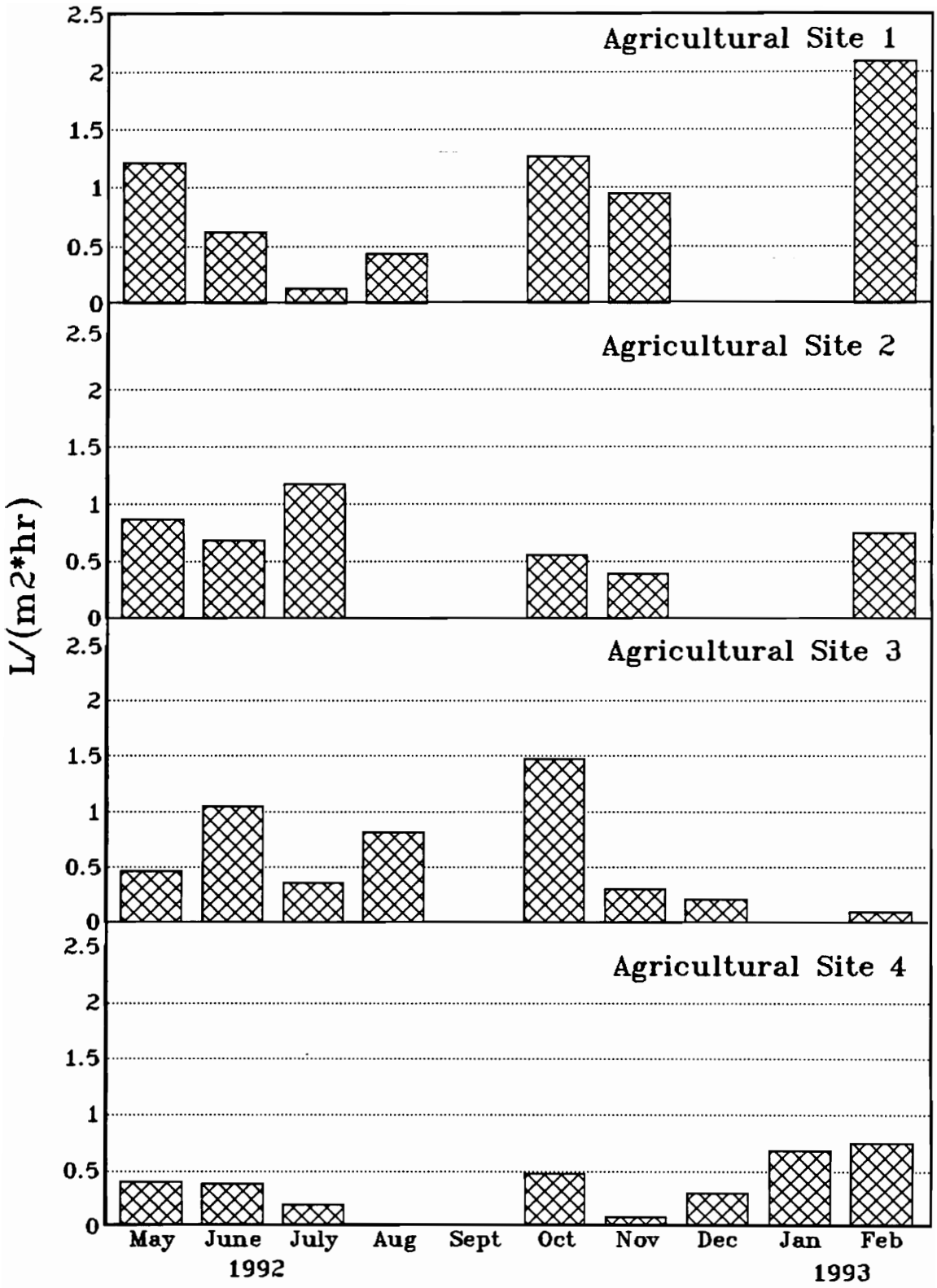



Figure 12
Seepage Rates by Site

of 1992. It rained the day before and the first day of the October 1992 sampling trip, which probably increased the discharges.

Although all the seepage rates seemed small, the total area which groundwater seepage occurred is millions of square meters. It has been estimated that the total groundwater inflow into the Chesapeake Bay was approximately equal to a major tributary, such as the James River, and 30% of the nitrogen flux in the Chesapeake Bay occurred by the submarine groundwater discharge's nutrient content (Reay and Simmons, 1992).

**B. Nutrient Concentrations/Fluxes**

Since the study was done in cooperation with Dr. Simmons' groundwater and seepage water nutrient flux study, samples for the nutrient study were taken at the same time as the samples from the pesticide study. From the nutrient sample analyses, nutrients, especially nitrate, are present at high levels in the agricultural sites' groundwater, and seepage water samples often had high levels of nutrient transport. Several researchers have linked high nitrate concentrations with an increase probability of pesticide contamination (Spalding, *et al.*, 1979; Spalding, *et al.*, 1989; Domagalski and Dubrovsky, 1992; and Leonard, *et al.*, 1988). The entire nutrient sample data was listed in Appendix D.

1. Upland well nutrient concentration

A typical chromatogram of an upland well sample is included as Figure 13. The average nitrate concentration for all the upland well nutrient samples was 14.25 mg/L as N. The average nitrate concentration in the groundwater over the period of the study was 15.04, 14.32, 15.18, and 12.37 mg/L as N for agricultural sites 1, 2, 3, and 4 respectively (Figure 14). The EPA's maximum contaminate level (MCL) for nitrate is 10 mg/L as N. Therefore, the average nitrate concentration in the groundwater over the study period at all the agricultural sites was over the EPA's MCL. This indicated that the fertilizers applied to the fields were percolating into the groundwater. The survey from agricultural site 2 showed that fertilizer was applied in the fall of 1991 and spring of 1992. However, the nitrate concentrations are fairly steady in the samples varying form 13.09 to 16.60 mg/L as N. The survey from agricultural site 3 listed fertilizer applied on October 24, 1992 and March 10, 1993. The March application was after the study period ended, but the October 1992 sample was at the same level as the August 1992 sample. Apparently the nitrate traveled slowly down into the aquifer at a relatively constant rate.

Three other nutrients were studied in the groundwater samples: ammonia, nitrite, and phosphate. The ammonia concentrations were always at least two orders of magnitude below the nitrate levels. The ammonia concentrations ranged

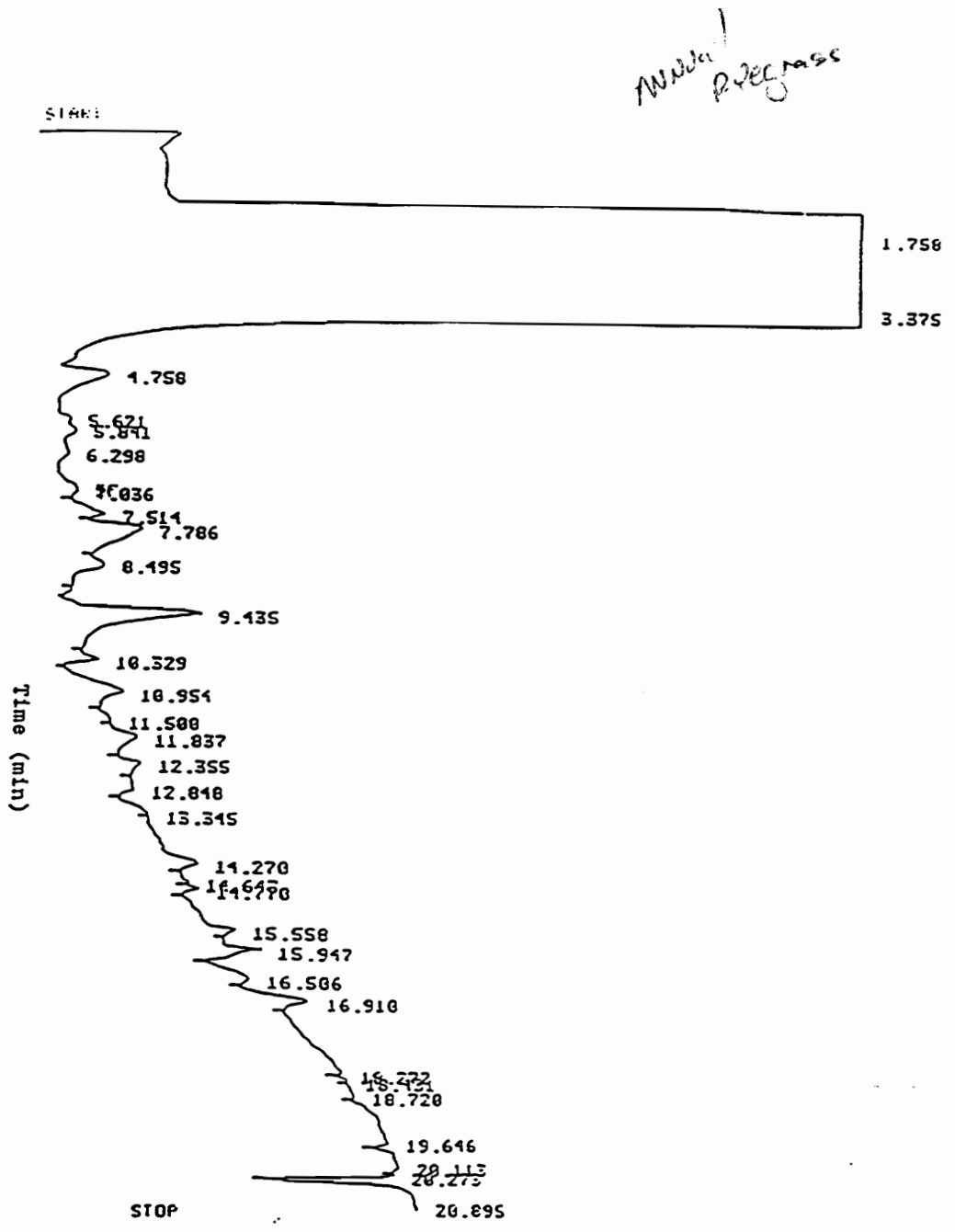



Figure 13

Typical Upland Well Chromatogram Using the GC/ECD (attn 2)

This chromatogram from WF2 #2 (No pesticides detected)

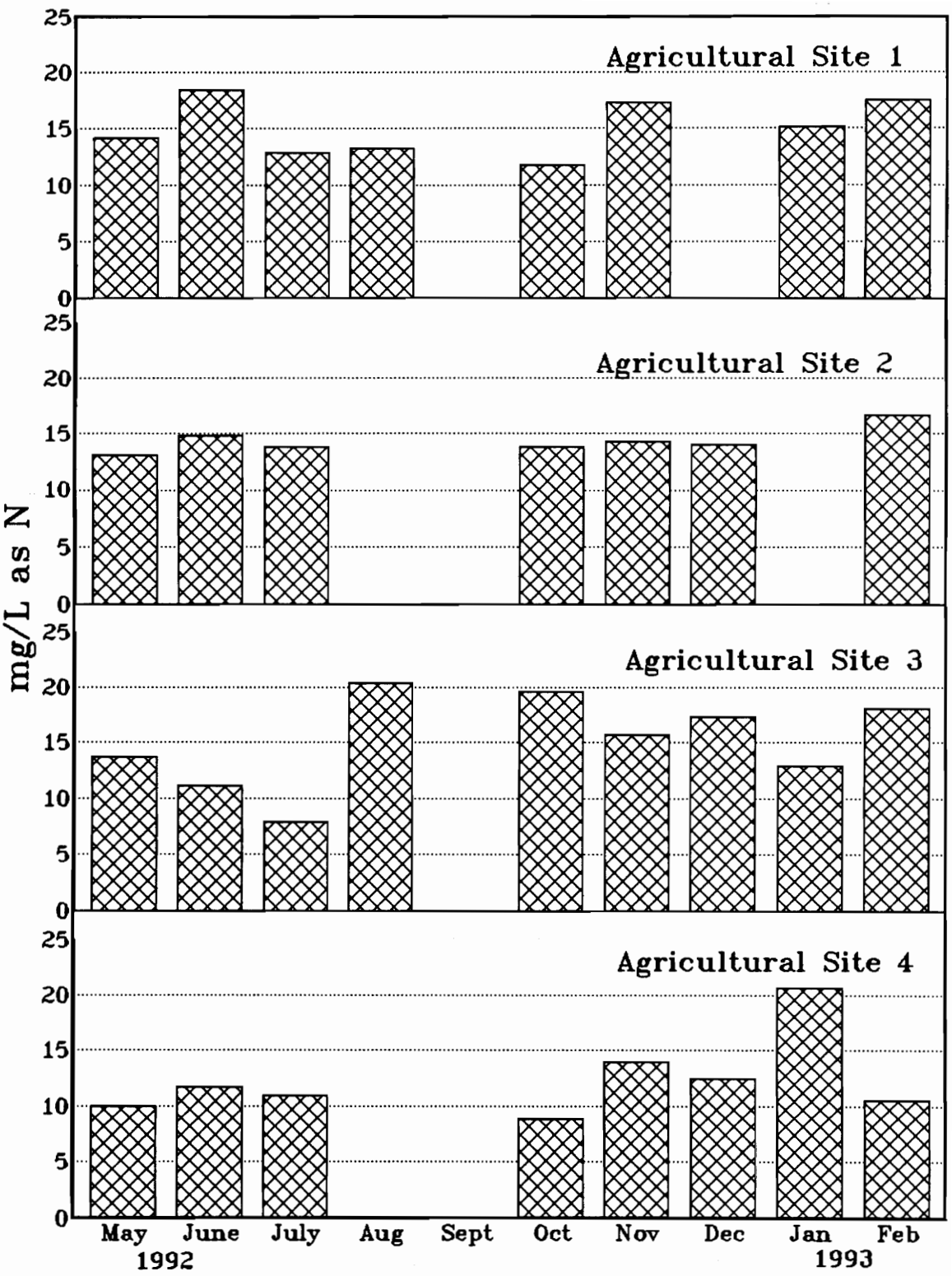



Figure 14
Upland Well Nitrate Concentration

from 0.01 to 0.14 mg/L as N, with the highest ammonia concentration only 1.0% of the average nitrate level. The nitrite concentrations were similarly low compared to the nitrate ones. Nitrite values varied from below detection to 0.12 mg/L as N, which was again less than 1% of the average nitrate concentration. Average phosphate concentration for all the samples was 0.017 mg/L. The phosphate concentrations ranged from <0.001 to 0.093 mg/L. By site, the average phosphate concentrations were 0.011, 0.007, 0.032, and 0.011 mg/L for agricultural sites 1, 2, 3, and 4 respectively.

2. Seepage meter nitrate concentrations

The nitrate concentration in the seepage water was measured directly from the sample, Therefore, the concentrations were diluted by the seawater which entered the seepage meters. The seepage meter samples averaged 35% freshwater, but varied from <0.1 to >99% freshwater. The average nitrate concentration for all the seepage meter samples was 0.73 mg/L as N. The average nitrate concentrations at each site were: 1.50 mg/L as N at site 1, 0.41 mg/L as N at site 2, 0.59 mg/L as N at site 3, and 0.43 mg/L as N at agricultural site 4. Sites 1 and 3, showed larger than average concentrations in October and November 1992. The October 1992 sample at site 3, measured at 3.09 mg/L as N, was an order of magnitude greater than an other sample taken at the site. The highest nitrate concentration

was in a sample from agricultural site 1, with a 4.05 mg/L as N concentration in November 1992. Except site 3, all the sites also a high nitrate concentration in the February 1993 seepage meter samples (Figure 15).

The high nitrate concentration and nitrate flux in the October 1992 submarine groundwater discharge sample from site 3 correlated well with the upland groundwater sample. All three were the highest taken at the site during the study, which indicated that the nitrate was being transported from the field into Chesapeake Bay. However, a comparison of the all the upland well vs. the seepage meter nitrate concentrations had a poor correlation with an $R^2 = 0.188$ (Figure 16).

3. Sediment nutrient fluxes

The nutrient fluxes were calculated by comparing the nutrient's concentration in the ambient seawater to its concentration in the sampling bag. The seepage meter was assumed to contain 6 L of seawater in its headspace when inserted into the sediment. The volume of the seepage bag plus 6 L was multiplied by the nitrate concentration in the bag to yield the mass of nitrate in the sample. The mass present at the installation of the seepage meter was calculated has 6 L times the ambient nutrient concentration. The difference, the sample mass minus the ambient mass, was divided by the product of the area of the seepage meter, 0.25

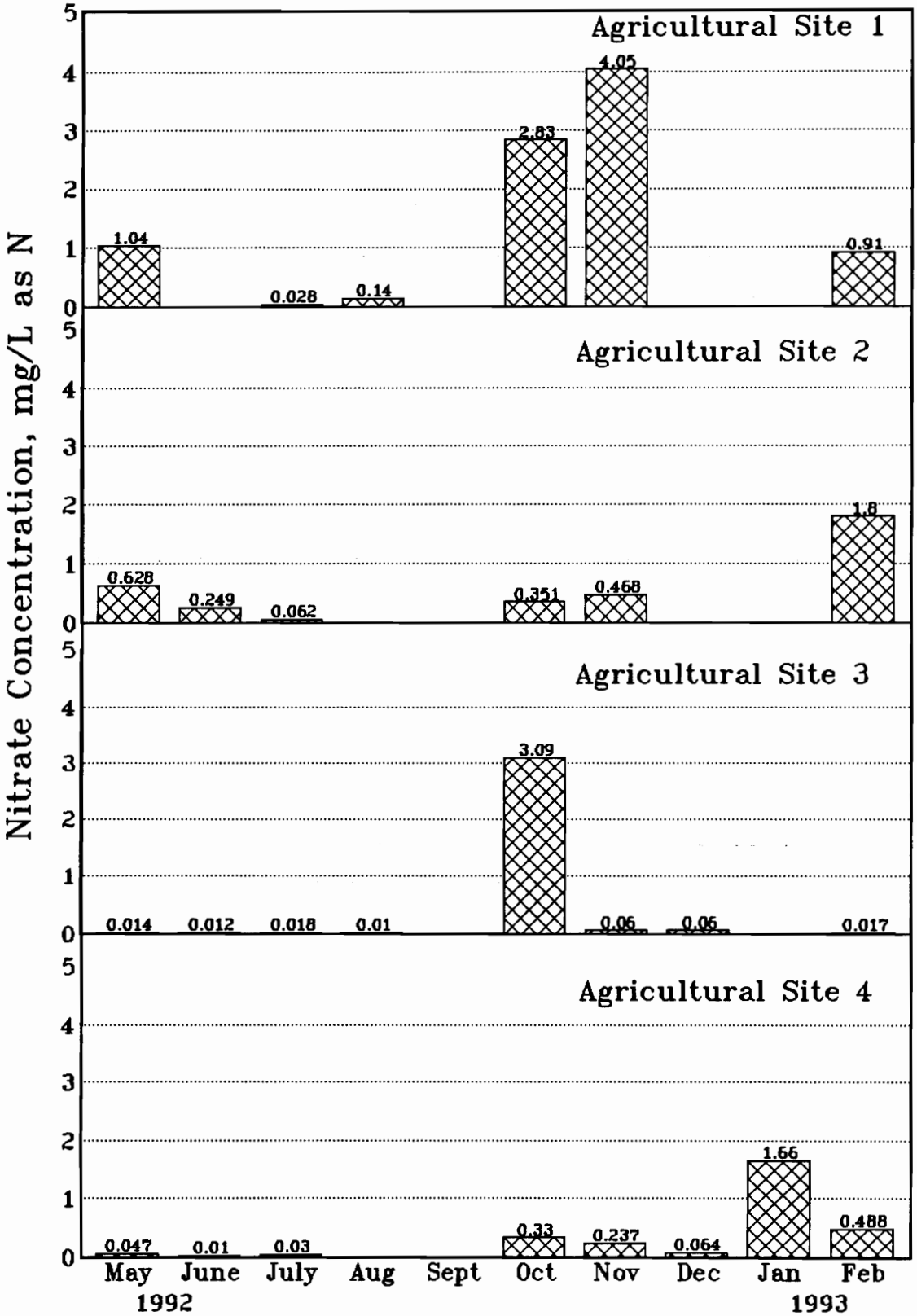



Figure 15
Seepage Meter Nitrate Concentration

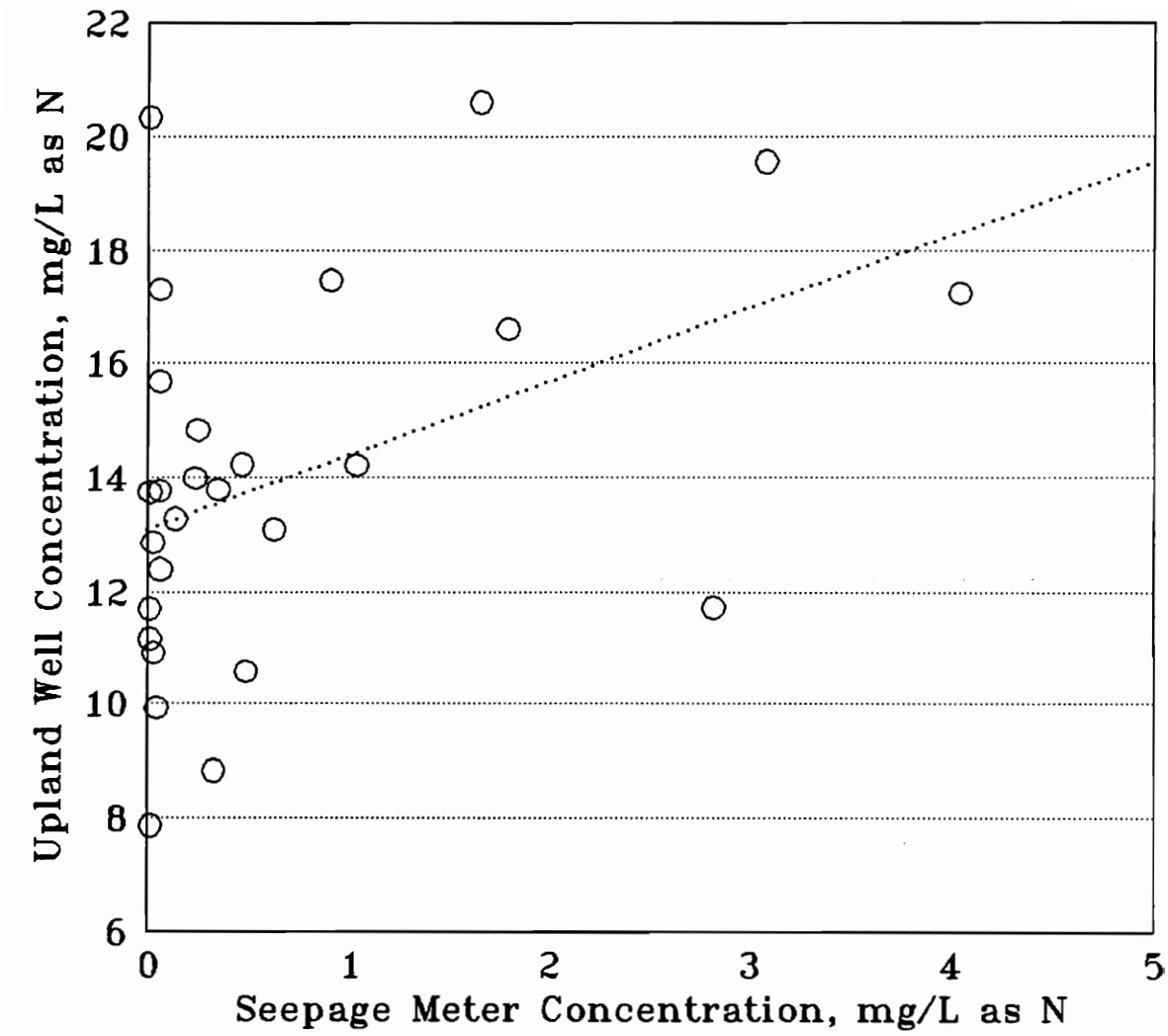



Figure 16

Seepage Meter Nitrate Concentration

vs.

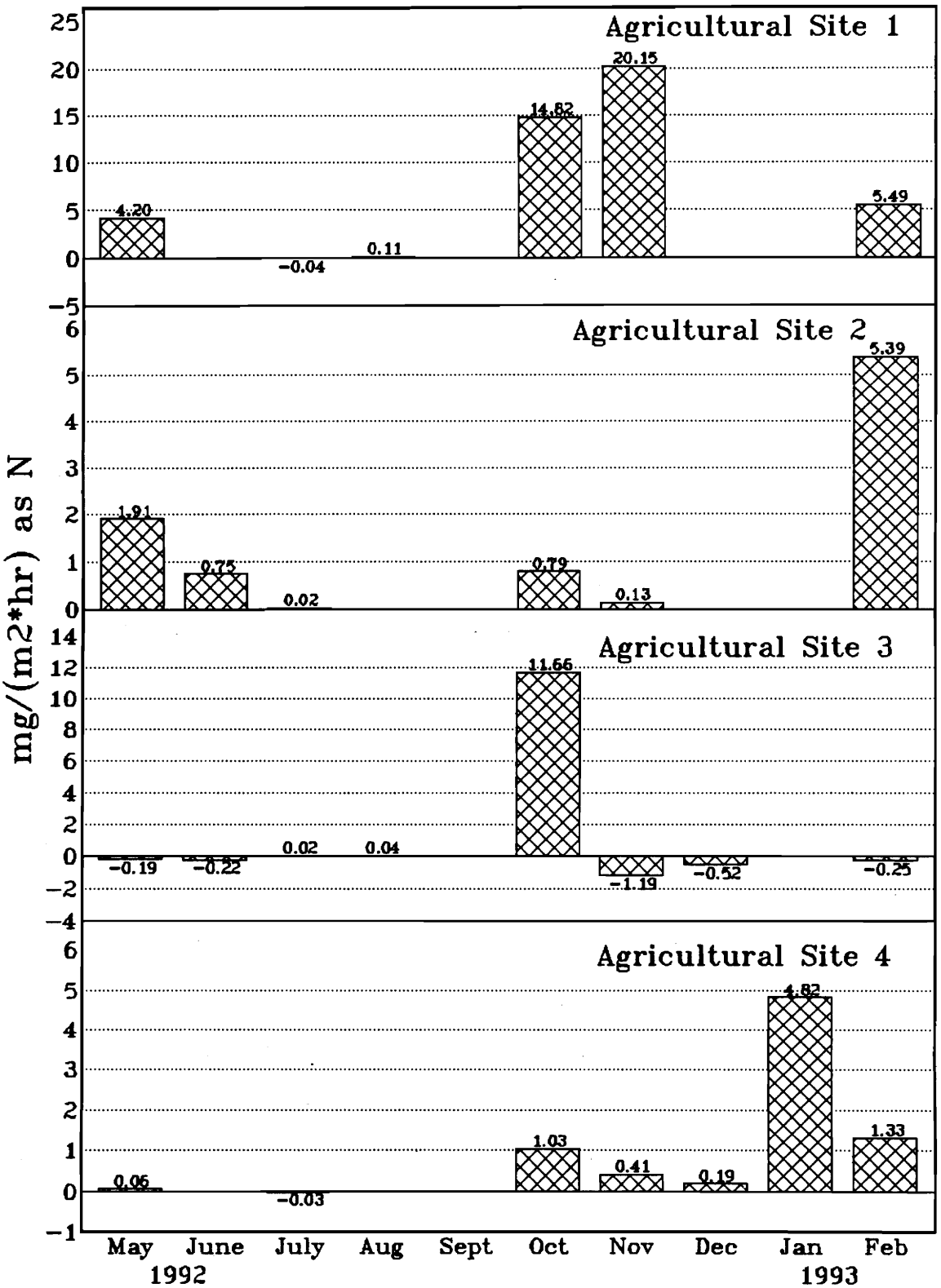
Upland Well Nitrate Concentration

$m^2$, and multiplied by the time between installation and removal of the bag to determine the flux.

The seepage meter nitrate fluxes varied widely from 20.15 mg/($m^2$*hr), November 1992 at agricultural site 1, to several negative values, most at site 3 (Figure 17). The October 1992 samples from all the sites showed a high nitrate flux in the submarine groundwater discharge.

By plotting the sediment nitrate flux vs. the freshwater discharge rate and using linear regression to find the best fit line, the slope can be calculated. The slope of the regression line equals the nitrate concentration of the freshwater entering the seepage meter, which is the SGWD (Figure 18). Assuming the nitrate is conservative, the SGWD nitrate concentration is the same as the upland well nitrate concentration. The accuracy of the graphs was directly related to their coefficient of determination, $R^2$. The graph of agricultural site 3 had the highest $R^2$ at 0.96, and its slope, 15.5 mg/L, was the closest to the actual average upland well concentration of 15.18 mg/L. Site 3 had the worst $R^2$ value at 0.24, and its slope was only a forth of the actual upland well concentration (Table 10).

The sediment contained many types of bacteria and algae, which could consume and produce ammonia, nitrate, and phosphate. The average ammonia concentration in the seepage meter samples was 0.27 mg/L as N, which was approximately an




# Figure 17
## Sediment Nitrate Flux
**Note the Y-axis are not to the same scale**

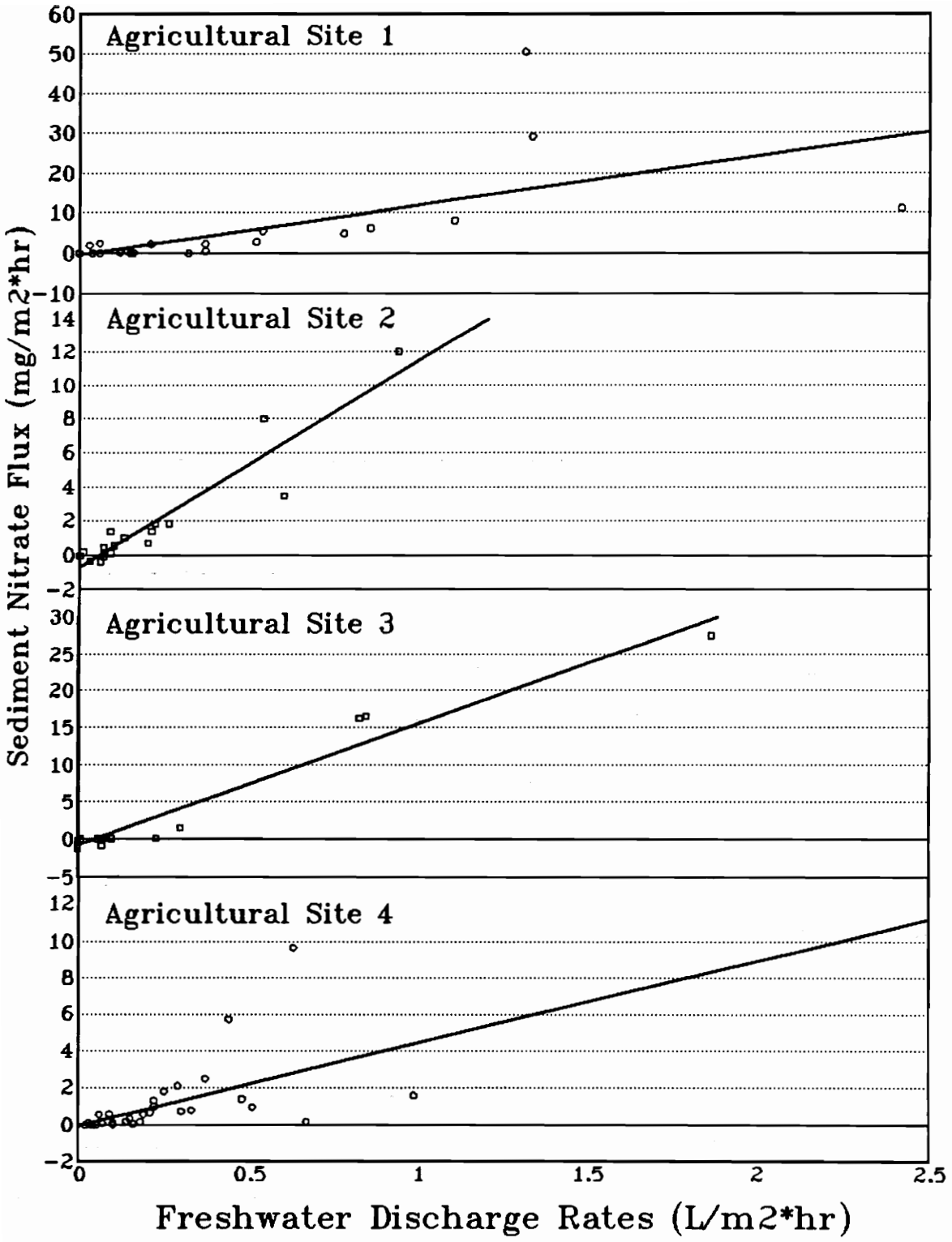



Figure 18

Sediment Nitrate Flux vs. Freshwater Discharge Rate

Table 10

Groundwater Nitrate Concentrations

| Site # | $R^2$ | Regression Slope, mg/L | Ave. Upland Nitrate concentration, mg/L |
|---|---|---|---|
| 1 | 0.40 | 12.0 | 15.04 |
| 2 | 0.89 | 11.5 | 14.32 |
| 3 | 0.96 | 15.5 | 15.18 |
| 4 | 0.24 | 4.3 | 12.37 |

order of magnitude higher than the ammonia concentrations in the upland groundwater samples. Agricultural site 4 had the highest average ammonia concentration in the seepage meter samples at 0.85 mg/L as N, and it also had the lowest nitrate concentrations in seepage meter samples. Dr. Simmons showed that nitrification and denitrification occurred in some of the sediments at the study sites (Simmons, *et al.*, 1992), which caused reduced or negative values in the seepage nutrient flux.

### C. Pesticides

For a pesticide to be reported as positively detected, the pesticide must have been detected above the instrumental LOD at the correct detention time using the GC/ECD on both the DB-5 and the DB-210 columns, and/or positively identified by GC/MS analysis. Due to the high LOD on the GC/MS, only two samples were positively identified as having a pesticide by GC/MS analysis. The two samples were the August CH3 #1 sample at site 2 for metolachlor, and the November BVCW #2 at agricultural site 1, also for metolachlor.

Of the over 500 samples analyzed on the GC, only 20 could be considered to have positive detection of a pesticide. Of these, 9 were quantified, with the other 11 being below the MDL (See Table 11).

The most common pesticide detected was cyanazine with 8. Metolachlor was next with 6; atrazine was detected 4 times,

Table 11
Summary of Pesticide Detections in Groundwater by GC Analysis

| Month | Virginia Tech ID | Site # | Pesticide Conc., µg/L | | | | |
|---|---|---|---|---|---|---|---|
| | | | Atr | Ala | Carb | Cyan | Met |
| June | WF1 #1[a] | 4 | | 0.66 | | | |
| July | EV2 #1 | 3 | | | | 0.16* | |
| | EVF/R #1 | 3 | | | | 0.53 | |
| | BV1 #1 | 1 | 0.59 | | | 0.16* | |
| | WF1 #1 | 4 | 0.63 | | | | |
| | WF2 #1 | 4 | 0.60 | | | | |
| | CH2 #1 | 2 | 1.52 | | | 0.17* | |
| Aug | BV2 #2 | 1 | | | | | 0.07* |
| | WFSW #1 | 4 | | | | | 0.07* |
| | CH3 #1 | 2 | | | | | 0.33 |
| Oct | CHSM 1-4 combined | 2 | | | | | 0.04* |
| Nov | BVCW #2 | 1 | | | | | [b] |
| | CH2 | 2 | | | | 0.02* | |
| | CH5 #1 | 2 | | | | 0.55 | |
| | EV2 #1 | 3 | | | | 0.03* | |
| Dec | WFSW | 4 | | | | 0.02* | |
| Feb | BV1 #1 | 1 | | 0.05* | | | 0.04* |
| | CHSM 2 | 2 | | | | | 0.32 |

* Below Method Detection Limit
a alachlor was also detected in a duplicate at 0.57 µg/L
b metolachlor was identified using the GC/MS, below the LOD

and alachlor was found twice. Carbofuran was not detected in any sample. This could be because it was not applied during the period of the study (not all of the surveys have been returned), or because of its high LOD on all the analytical instruments.

1. Upland well concentrations

Agricultural site 2 had the highest number of samples with pesticides detected with 7. Agricultural sites 1, and 4 had pesticides detected in 5 samples, and site 3 had pesticides detected in 3 samples.

Although agricultural site 1 did not return the survey, it had the highest number of pesticides detected in the soil samples. Alachlor was identified in 4 of the samples, June, July, October, and December 1992 at 145, 484, 162, and 19.8 µg/kg respectively (Schicho, 1993). The site also had 4 pesticides detected in the groundwater samples. Metolachlor was detected, below the MDL, in the August and November 1992 samples. In the July 1992 BV1 #1 sample, Atrazine was detected at 0.59 µg/L, and cyanazine was detected below the MDL.

According to the returned survey, agricultural site 2 had atrazine and metolachlor applied in the summer of 1991. Atrazine was detected in the groundwater in July, 1992, at 1.52 µg/L, but not in any of the soil samples taken by Schicho (1993). He did find metolachlor in the June and October 1992,

and February 1993 soil samples, and metolachlor was detected in the groundwater in August 1992 and February 1993, below the MDL. Also, cyanazine was detected in the groundwater at 0.17 µg/L in July 1992, even though it was not listed as being applied. Agricultural site 2 also had anoxic groundwater for much of the study, which could explain why, even a year after application the two pesticides, atrazine and metolachlor, were still detected. The half-life for atrazine has been estimated between 20 and 140 days, and metolachlor's half-life was estimated at 20 to 90 days (Leonard, *et al.*, 1988; Spalding, *et al.*, 1989; Thurman, *et al.*, 1992), although Bouchard found metolachlor still detectable after 2 years in some soil samples (Bouchard, *et al.*, 1982).

Agricultural site 3's survey stated that they did not apply any of the pesticides which were monitored in the study. However, cyanazine was detected in the groundwater in 3 samples, two in July and one in November of 1992. The July 1992 EVF/R #1 concentration was 0.53 µg/L, but the other two concentrations were below the MDL. Two soil samples from the site contained metolachlor, June at 26.9 µg/kg and December at 7.4 µg/kg, but the concentrations were closed to the LOD for the pesticide.

The survey from agricultural site 4 was not returned. In the groundwater, metolachlor was detected, below the MDL, in the August 1992. Also, alachlor was detected twice in June

1992, at 0.57 µg/L in WF1 #2 and 0.66 µg/L in WF2 #1, and atrazine was detected in WF1 #1 and WF2 #1 at 0.63 and 0.60 µg/L, respectively, in July 1992. Metolachlor was detected in the December and January soils samples at 7.1 and 8.7 µg/kg respectively.

No pesticides were detected in any of the samples for wetlands site 1.

Since cyanazine was not reported as being applied to any of the sites, but was detected in 5 samples, the possibility of false positive detection was a real concern. Cyanazine was eluted at the same time as metolachlor with the DB-5 column. While the DB-210 column eluted cyanazine at a much later time than metolachlor (19.2 vs. 15.9 minutes), it was still possible that the cyanazine "detections" could have been metolachlor with a contaminate on the DB-210 column at the right time, or a contaminate with the same retention time as cyanazine.

2. Seepage meter concentrations

The seepage water samples had only 2 sample with a pesticide detected. Metolachlor was detected, below the MDL, in the October CHSM1-4 combined and the February CHSM 2 samples at site 2. All the other seepage meter samples did not have any pesticides above the LOD. Most of the seepage meter samples were very dirty after extraction, with dozens of GC peaks (Figure 18). The presence of so many compounds could

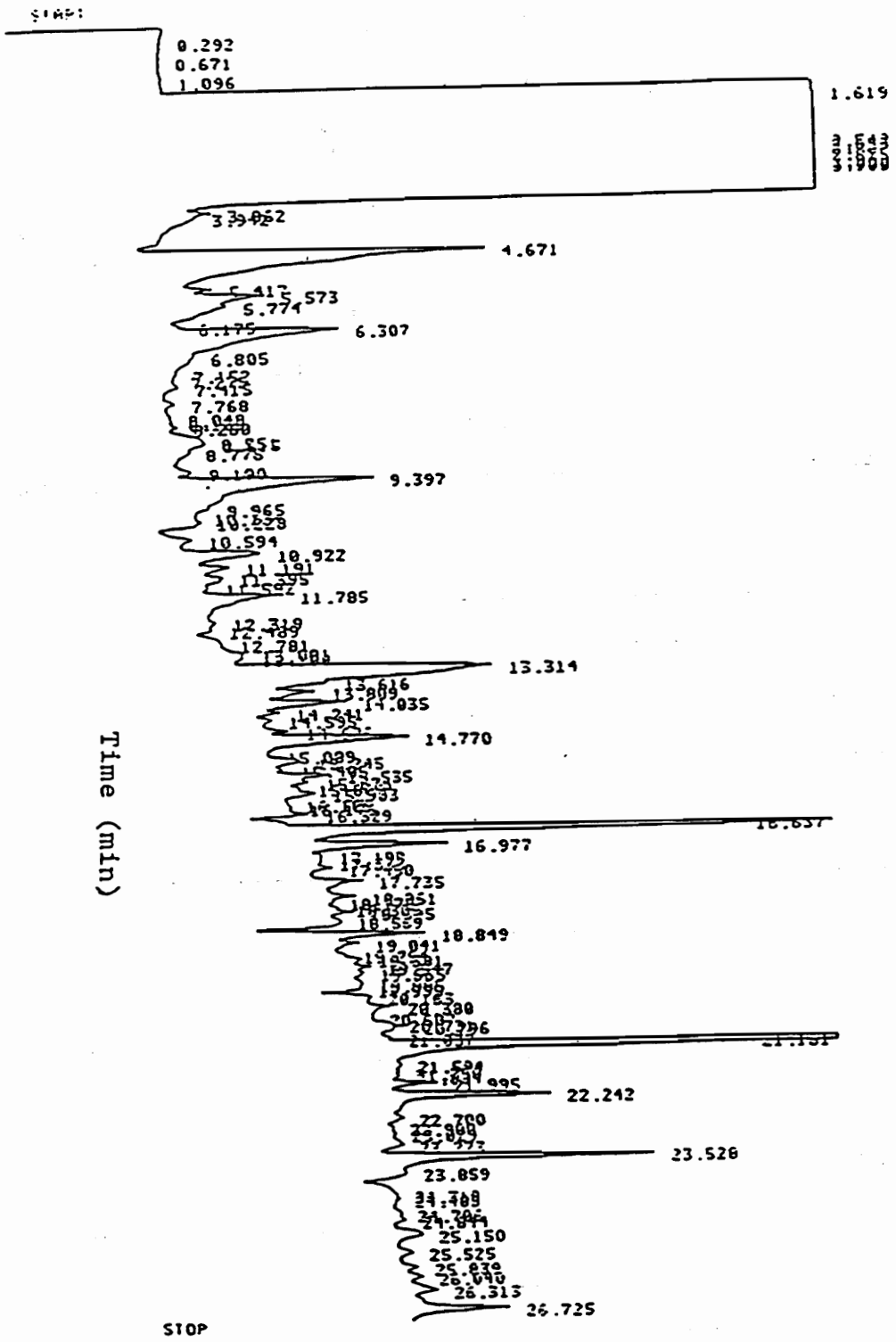



Figure 19

Typical Seepage Meter Chromatogram Using the GC/ECD (atta 2)

This was BVSM 1&3 Combined (No pesticides detected)

have masked the any of the pesticides present. Due to the low number of pesticides detected in the cleaner groundwater samples, however, few, if any, detectable pesticides are expected in the seepage. Also, the soil data supports the theory that most of the pesticides were bound to the soil, rather than migrating into the groundwater. Finally, the seepage samples were only about 35% groundwater, with the rest being infiltrated seawater. This 3:1 dilution ratio may have caused any pesticides present in the seepage water to be below the LOD.

The Ohmicron results listed 20 pesticides detected in the seepage meter samples. However, Ohmicron listed three seepage meter samples with three separate pesticides, atrazine, alachlor, and cyanazine, detected in each sample, and three seepage meter samples each with two pesticides, atrazine and alachlor, detected. All the seepage meter samples with multiple pesticides detected were in August 1992. The only pesticide detected by Ohmicron in all the other seepage meter samples was atrazine.

3. Ohmicron Concentrations

Ohmicron Corporation reported 63 detections of the five pesticides in the study over their LOD in the samples they analyzed (See Table 12). The highest pesticide concentration was 4.46 µg/L in the November 1992 BVCW sample. The only other pesticide detected over 1 µg/L was the January 1993 BVCW

Table 12
Pesticide Detections by Ohmicron Corporation

| Site | Number of times the pesticide was detected | | | | |
|---|---|---|---|---|---|
| | Atr | Ala | Carb | Cyan | Metol |
| Ag. site 1 | 5 | 23 | 0 | 0 | 2 |
| Ag. site 2 | 8 | 2 | 1 | 2 | 1 |
| Ag. site 3 | 0 | 1 | 0 | 0 | 0 |
| Ag. site 4 | 6 | 3 | 0 | 2 | 0 |
| Wet. site 1 | 0 | 0 | 0 | 0 | 0 |

sample at 1.22 μg/L. The samples from agricultural site 1 had 30 of the detections, 23 of them for alachlor, which was also found in 4 soil samples. Site 2 samples were next with 14 detections, then site 4 samples with 11, and finally site 3 samples had only 1 pesticide detected. The complete results were included in Appendix F.

Although none of the blank samples had any pesticides detected using gas chromatography, Ohmicron data stated that two of the equipment blanks and two of the travel blanks contained atrazine. The concentrations reported, 0.05, 0.06, 0.07, and 0.07 μg/L, were well under the LOD for the GC analysis. The equipment blanks could have been contaminated by a pesticide adsorbed to the tubing used to pump the samples out of the wells. The travel blank detections were unexpected. Since the same milli-Q water was used for all the blanks, the laboratory blanks should have had the contaminate too, but not detections were reported for the laboratory blanks.

Most of Ohmicron's reported pesticide detections were below the LOD of the GC analysis. The detections could have been either a low concentration of the pesticides in the groundwater, which has been reported by several researchers (Holden, *et al.*, 1992; Spalding, *et al.*, 1989; Steichen, *et al.*, 1988), or false positives, which have been reported for alachlor and metolachlor using the immunoassay procedure

(Baker, *et al.*, 1993). In the study, the 1 and 2 µg/L laboratory and matrix spikes from October 1992 through February 1993 did not have metolachlor added, yet Ohmicron listed 18 of the spiked samples as having metolachlor present. The GC analysis did not detect any metolachlor in the 1 and 2 µg/L spikes. The immunoassay procedure was significantly faster and easier to perform than the solid phase extraction, but it appeared to general more false positives.

4. Soil sample concentrations

Soil samples were taken at the sites at the same time as the groundwater samples. A master's candidate analyzed them using a soxhlex extraction process with identification on the GC/MS. Mr. Schicho found pesticides in about a fifth of all the soil samples taken. However, half, 14 of 28, of the field soil samples contained a detectable amount of a pesticide, while none of the sediment samples had a detectable pesticide. The largest concentration was 484 µg/kg of Alachlor, in the July 1992 field sample from agricultural site 1 (Schicho, 1993). Complete soil sample data was included in Appendix E.

The field soil samples had a much higher concentration of pesticides than the water samples. The average concentration of all the pesticides detected in the soil samples was approximately 82 µg/kg (Schicho, 1993), The groundwater samples were at much lower concentrations. Only one of the

detections was over 1 ppb, which was July CH2 #1 at 1.5 ppb, with the second highest being 0.63 ppb, July WF2 #1. This suggests that the pesticides in the study were being mostly adsorbed to the soils, and not transported by the groundwater at a concentration above 1 μg/L.

5. Spiking Results

For all spikes, the pesticide recovered with the greatest precision was alachlor, and carbofuran had the most variability. All the spikes' measured values had a large variability, but the values were generally within 50% of the added concentration, except for carbofuran's measured concentration, which was often several times the added value. Since carbofuran was the only non-chlorinated pesticide in the study, it had much poorer resolution on the GC/ECD than the other pesticides. Consequently, carbofuran was not detected in many of the spiked samples. Spiked sample results were also discussed in Appendix G.

**D. Contaminates**

The most common contaminate found was di-ethyl phthalate which was found in most samples, with several other phthalates also observed in many samples. In the summer and early fall of 1992, many samples contained N,N-diethyl toluamide (DEET), which was the active ingredient of the insect repellant Off!™. This was surprising because the insect repellant was never sprayed in the area were the samples were taken, although it

was used at the eastern shore laboratory, and equipment handling was minimized. Petroleum products were detected in several of the samples from agricultural site 4 in the summer of 1992, but later samples contained no detectable oil products. Also, most of the seepage meter samples and several of the groundwater samples contained hexanedioc acid dioctyl ester. A doctoral candidate, who was working with algae, said that hexanedioc acid was a byproduct of some types of algae (Rashash, 1992).

# V. Conclusions

The purpose of the study was to quantify pesticides in the groundwater of the Chesapeake Bay area and determine if pesticides were being transported by the groundwater into the Chesapeake Bay. Solid phase liquid extraction followed by gas chromatography was used to analysis the water samples, and an independent company, Ohmicron Corporation, also analyzed samples using an immunoassay analysis. Pesticides were analyzed in groundwater, SGWD, and soil samples. The study also examined groundwater transport of nutrients from the sites into the Chesapeake Bay.

From the results of this study, the following conclusions were derived:

1. Alachlor, atrazine, carbofuran, cyanazine, and metolachlor were not detected in the groundwater in most (96%) of the samples analyzed by gas chromatography.

2. In all the samples where a pesticide was detected, the concentration of the pesticide was below 1 μg/l, except for one sample.

3. Half of the field soil samples contained a detectable pesticide with an average concentration of 82 μg/kg. It appeared that most of the pesticides were adsorbed to the soils, with a small amount dissolved into the groundwater.

5. The submarine groundwater discharge of the studied

pesticides into the Chesapeake Bay was too dilute to find with the method used.

6. The Ohmicron immunoassay analysis had a lower LOD for the pesticides than solid phase liquid extraction, but appeared to generate more false positive detections.

7. Nutrients, especially nitrate, were being transported by the groundwater into the Chesapeake Bay.

## VI. Literature Cited


Baker, David A., Bushway, Rodney J., Adams, Stephen A., Macomber, Carol (1993) "Immunoassay Screens for Alachlor in Rural Wells: False Positives and an Alachlor Soil Metalbolite" *Environmental Science & Technology,* **27**, 562-564.

Bear, J. (1989) *Hydraulics of Groundwater.* McGraw-Hill Book Company. New York, NY. 569 pp.

Blumberg, Ruth, (1988) *Liquid-Liquid Extraction,* Academic Press, San Diego, CA.

Bouchard, Dermont C., Lavy, Terry L., and Marx, Dave B. (1982) "Fate of Metribuzin, Metolachlor, and Fluometuron in Soil" *Weed Science,* **30,** 629-632.

Cavalier, T. C., Lavy, T. L., and Mattice, J. D. (1989) "Assessing Arkansas Ground Water for Pesticides: Methodology and Findings" *Ground Water Monitoring Review,* **9,** 159-166.

Cornett, R. A., Risto, B. A., and D. R. Lee (1989) "Measuring Groundwater Transport Through Lake Sediments by Advection and Diffusion" *Water Resources Research,* **25,** 1815-1823.

Domagalski, Joseph L., and Dubrovsky, Niel M. (1992) "Pesticide residues in ground water of the San Joaquin Valley, California" *Journal of Hydrology,* **130,** 299-338.

Donigian Jr., Anthony S. and Carsel, Robert F. (1987)

"Modeling the Impact of Conservation Tillage Practices in Pesticide Concentrations in Ground and Surface Waters" *Environmental Toxicology and Chemistry,* **6,** 241-250.

Eichelberger, J. W., Behymer, T. D., and Budde, W. L. (1991) *Method 525.1 Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry,* U.S. Environmental Protection Agency, Cincinnati, Ohio.

Exner, Mary E. (1990) "Pesticide Contamination of Ground Water Artificially Recharged by Farmland Runoff" *Ground Water Monitoring Review.* **10,** 147-159.

Gustafson, D. I. (1989) "Groundwater Ubiquity Score: A Simple Method for Assessing Pesticide Leachability" *Environmental Toxicology and Chemistry.* **8,** 339-357.

Hagen, Donald F., Markell, Craig G., and Schmitt, George A. (1990) "Membrane approach to solid-phase extractions" *Analytica Chimica Acta,* **236,** 157-164.

Heatwole, Conrad D., Zacharias, Sebastian, Mostaghimi, Saied, Dillaha, Theo A., and Young, R. W. (1992) *Fate and Transport of Pesticides in a Virginia Coastal plain Soil.* Virginia Water Resources Research Center, Blacksburg, Va.

Hohlt, Herman, Professor for the Agricultural Extension Laboratory, at VPI & SU. Personal Communication. May 1993.

Holden, Larry R., Graham, Jeffery A., Whitmore, Roy W.,

Alexander, W. Joseph, Pratt, Richard W., Liddle, Susan K., and Piper, Lanny L. (1992) "Results of the National Alachlor Well Water Survey" *Environmental Science & Technology,* **26,** 935-943.

Holden, Patrick W. (1986) *Pesticides and Groundwater Quality: Issues and Problems in Four States*. National Academy Press, Washington, D. C.

Johannes, R. E., and Hearn, C. J. (1985) "The Effect of Submarine Groundwater Discharge on Nutrient and Salinity Regimes in a Coastal Lagoon off Perth, Western Australia" *Estuarine, Coastal and Shelf Science,* **21,** 789-800.

Junk, Gregor A., Avery, Michael J., and Richard, John J. (1988) "Interferences in Solid-Phase Extraction Using C-18 Bonded Porous Silica Cartridges" *Analytical Chemistry,* **60,** 1347-1350.

Jury, William A., Focht, Dennis D., and Farmer, Walter J. (1987) "Evaluation of Pesticide Groundwater Pollution Potential from Standard Indices of Soil-Chemical Adsorption and Biodegradation" *Journal of Environmental Quality,* **16,** 422-428.

Kraut-Vass, Anna and Thoma, Jerry (1991) "Performance of an Extraction Disk in Synthetic Organic Chemical Analysis using Gas Chromatography-Mass Spectrometry" *Journal of Chromatography,* **538,** 233-240.

Krawchuk, Bert P., and Webster, G. R. Barrie (1987) "Movement

of Pesticides to Groundwater in an Irrigated Soil" *Water Pollution Resources Journal, Canada,* **22,** 129-145.

Krill, Robert M. and Sonzogni, William C. (1986) "Chemical Monitoring of Wisconsin's Groundwater" *Journal of AWWA,* 70-75.

Lee, D. R. (1977) "A Device for Measuring Seepage Flux in Lakes and Estuaries" *Linmnology and Oceanography,* **22,** 140-147.

Lee, D. R., Cherry, J. A., and Pickens, J. F. (1980) "Groundwater Transport of a Salt Tracer Through a Sandy Lakebed" *Limnology and Oceanography,* **25,** 45-61.

Lee, V. and Olsen, S. (1985) "Eutrophication and Management Initiatives for the Control of Nutrient Inputs to Rhode Island Coastal Lagoons" *Estuaries,* **8,** 191-202.

Legrand, M. F., Costentin, E., and Bruchet, A. (1991) "Occurance of 38 Pesticides in Various French Surface and Ground Waters" *Environmental Technology,* **12,** 985-996.

Leonard, R. A., Shirmohammadi, A., Johnson, A. W., and Marti, L. R. (1988) "Pesticide Transport in Shallow Groundwater" *Transactions of the ASAE,* **3,** 776-788.

Libelo, L., MacIntyre, W. G., and Johnson, G. H. (1991) "Groundwater Nutrient Discharge to the Chesapeake Bay: Effects of Nearshore Land Use Practices" pp. 613-922. In: *New Perspectives in the Chesapeake Bay System: A Research and Management Partnership.* J. A. Mihursky and A. Chaney

(Editors). Dec 4-6, 1990. Baltimore, MD. Cheaspeake Research Consortium Publication 137.

Libra, Robert D., Hallberg, George R., and Hoyer, Bernard E. (1987) Impacts of Agricultural Chemicals on Ground Water Quality in Iowa, in: *Ground Water Quality and Agricultural Practices*. by Fairchild, Deborah M., Lewis Pub., Chelsea, MI.

Loague, Keith, Green, Richard E., Giambelluca, Thomas W., Liang, Tony C., and Yost, Russel S. (1990) "Impact of Uncertainty in Soil, Climatic, and Chemical Information in a Pesticide Leaching Assessment" *Journal of Contaminate Hydrology,* **5,** 171-194.

Loague, Keith, Yost, Russel S., Green, Richard E., and Liang, Tony C. (1989) "Uncertainty in a Pesticide Leaching Assessment for Hawaii" *Journal of Contaminate Hydrology,* **4,** 139-161.

Newhouse, M. E., Cobb, P. R., Baldwin, L. F., and McCloy, D. V. (1985a) *Soil Survey of Middlesex County, Virginia*. U.S. Dept. of Agriculture and VPI&SU.

Newhouse, M. E., Cobb, P. R., Barnes, W. S., and McCloy, D. V. (1985b) *Soil Survey of Gloucester County, Virginia*. U.S. Dept of Agriculture and VPI&SU.

Pionke, H. B., Glotfelty, D. E., Lucas, A. D., and Urban, J. B. (1988) "Pesticide Contamination of Groundwaters in the Mahantango Creek Watershed." *Journal of Environmental*

*Quality,* **17,** 76-85.

Pionke, H. B., and Glotfelty, D. E. (1989) "Nature and Extent of Groundwater Contamination by Pesticides in an Agricultural Watershed" *Water Research,* **23,** 1031-1037.

Rashash, Diana. Personal Communication. June 1992.

Reay, William G., and Gallagher, Daniel L. (1990) "Advective and Dispersive Transport of Interstitial Solutes on Nearshore Estuarine Environments", *New Perspectives in the Chesapeake Bay System: A Research and Management Partnership,* J. A. Mihursky and A. Chaney (Editors), Chesapeake Research Consortium Publication 137, Baltimore, MD. 651-662.

Reay, William G., and Simmons Jr., George M. (1992) "Ground Water Discharge in Coastal Systems: Implications for the Chesapeake Bay" *Perspectives on the Chesapeake Bay: Advances in Esturaine Sciences,* S. Nelson, P. Elliot, B. Farquhar, and C. McManus (Editors), Chesapeake Research Consortium Publication No. 143, 17-44.

Reay, William G., Gallagher, Daniel L., and Simmons Jr., George M. (1992) "Groundwater Discharge and Its Impact in Surface Water Quality in a Chesapeake Bay Inlet" *Water Resources Bulletin,* **28,** 1121-1134.

Sayles, F. L., and Jenkins, W. J. (1982) "Advection of Pore Fluids through Sediments in the Equatorial East Pacific" *Science,* **217,** 245-248.

Schicho, Douglas. *Evaluating Pesticide Transport from Groundwater to Surface water via Submarine Groundwater Discharge*, Master's Thesis, Civil Engineering Department, Virginia Polytechnic Institute & State University. August 1993.

Senseman, Scott A., Lavy, Terry L., Mattice, John D., Myers, Benjamin M., and Skulman, Briggs W. (1993) "Stability of Various Pesticides on Membranous Solid-Phase Extraction Media" *Environmental Science & Technology,* **27**, 516-519.

Sewell, P. L. (1982) "Urban Groundwater as a Possible Nutrient Source for an Estuarine Benthic Algal Bloom" *Estuarine, Coastal and Shelf Science,* **15**, 569-576.

Shirmohammadi, A., Magette, W. L., Brinsfield, R. B., and Staver, K. (1989) "Ground Water Loading of Pesticides in the Atlantic Coastal Plain" *Ground Water Monitoring Review,* , 141-148.

Simmons Jr., G. M. (1989) "The Chesapeake Bay's Hidden Tributary: Submarine Groundwater Discharge" pp.9-29. In: *Proceeding of Groundwater Issues and Solutions in the Potomac River Basin/Chesapeake Bay Region*. National Water Well Association, Dublin, Ohio.

Simmons Jr., G. M., Miles, E., Reay, W., and Gallagher, D. (1992) "Submarine Groundwater Discharge Quality in Relation to Land Use Patterns in the Southern Chesapeake Bay" *Proceedings of the 1st International Conference on*

*Groundwater Ecology,* Stanford, J. A. and Simons, J. J. (Editors), American Water Resources Ass., 341-350.

Smith, M. C., Thomas, D. L., Bottcher, A. B., and Campbell, K. L. (1990) "Measurement of Pesticide Transport to Shallow Groundwater" *Transactions of the ASAE,* **33,** 1573-1582.

Spalding, R. F., Burbach, M. E., and Exner, M. E. (1989) "Pesticides in Nebraska's Ground Water" *Ground Water Monitoring Review,* **9,** 126-133.

Spalding, R. F., Exner, M. E., Sullivan, J. J., and Lyon, P. A. (1979) "Chemical Seepage from a Tail Water Recovery Pit to Adjacent Ground Water" *J. of Environmental Quality,* **8,** 374-383.

Squillace, Paul J., and Thurman, E. M. (1992) "Herbicide Transport in Rivers: Importance of Hydrology and Geochemistry in Nonpoint-Source Contamination" *Environmental Science & Technology,* **26,** 538-545.

Steichen, James, Koelliker, James, Grosh, Doris, Hieman, Alan, Yearout, Robert, and Robbins, Victor (1988) "Contamination of Farmstead Wells by Pesticides, Volatile Organics, and Inorganic Chemicals in Kansas" *Ground Water Monitoring Review,* **8,** 153-159.

Thurman, Michael E., Goolsby, Donald A., Meyer, Michael T., Mills, Margaret S., Pomes, Michael L., and Kolpin, Dana W. (1992) "A Reconnaissance Study of Herbicides and Their Metabolites in the Surface Water of the Midwestern United

States Using Immunoassay and Gas Chromatography/Mass Spectrometry" *Environmental Science & Technology,* **26,** 2440-2447.

Valiela, J. M., Costa,J., Kenneth, K., Teal, J. M., Howes, B., and Aubrey, D. (1990) "Transport of Groundwater-Borne Nutrients From Watersheds and Their Effect of Coastal Waters" *Biogeochemistry,* **10,** 177-197.

Walker, Mark J. and Porter, Keith S. (1990) "Assessment of Pesticides in Upstate New York Ground Water: Results of a 1985-1987 Sampling Survey" *Ground Water Monitoring Review,* **10,** 116-125.

Weber, Jerome B., and Peter, John (1982) "Adsorption, Bioactivity, and Evaluation of Soil Tests for Alachlor, Acetochlor, and Metolachlor" *Weed Science,* **30,** 14-20.

Wehtje, Glenn R., Spalding, Roy F., Burnside, Orvin C., Lowry, Stephen R., and Leavitt, Robert C. (1983) "Biological Significance and Fate of Atrazine under Aquifer Conditions" *Weed Science,* **31,** 610-618.

Windhole, Martha Ed. (1983) *The Merck Index, 10$^{th}$ Edition,* Merck & Company, Inc. Rahway, NJ.

Zimmermann, C. R., Montgomery, J. R., and Carlson, P. R. (1985) "Variability of Dissolved Reactive Phosphate Flux in Nearshore Estuarine Sediments: Effects of Groundwater Flow" *Estuaries,* **8,** 228-236.

## Appendix A

### List of All Water Samples

Every sample extracted is listed in tables 1A through 10A. The tables corresponded to the month the samples were taken, with Table 1A being April, 1992 and Table 10A being February, 1993. Numbers with an asterix (*) are below the MDL for the pesticide.

Abbreviations

BV, BR: Agricultural site 1

CH: Agricultural site 2

EV: Agricultural site 3

WF, AH: Agricultural site 4

ST: Wetlands site 1

EB: Equipment blank

TB: Travel blank

LB: Laboratory blank

LFB: Laboratory Fortified blank (pesticides added)

(%) Res: The percent response of 4-chlorobiphenyl in the sample after injection on the GC, compared to an injection of an equal amount of the standard of 4-chlorobiphenyl on the GC.

**: The 4-chlorobiphenyl peak was masked, or not present.

ND: Not Detected

N/A: Not applicable, the pesticide was not added to the sample.

Table 1A
April Samples

| Name | Type | Comments | Volume | Measured Conc. (µg/L) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Atr | Ala | Carb | Cyan |
| EV7 #1 | well | Spiked @ 20 ppb | 1 L | 1.24 | 1.77 | 1.88 | 0.41 |
| EV7 #2 | well | Spiked @ 5 ppb | 1 L | 0.17* | 0.25* | 0.34* | ND |
| EV7 #3 | well | | 1 L | ND | ND | ND | ND |
| EV7 Field #4 | well | | 1 L | ND | ND | ND | ND |
| EV1 #1 | well | | 1 L | ND | ND | ND | ND |
| EV1 #2 | well | duplicate of EV1 #1 | 1 L | ND | ND | ND | ND |
| ESGS1 #1 | well | | 1 L | ND | ND | ND | ND |
| ESGS1 #2 | well | duplicate of ESGS1 | 1 L | ND | ND | ND | ND |
| ESGS2 #1 | well | | 1 L | ND | ND | ND | ND |
| ESGS2 #2 | well | duplicate of ESGS2 | 1 L | ND | ND | ND | ND |
| WF #1 | well | Spiked @ 5 ppb | 1 L | 0.27* | 0.33 | 0.56* | ND |
| WF #2 | well | Spiked @ 20 ppb | 1 L | 1.58 | 2.01 | 2.40 | 1.03 |
| WF #3 | well | duplicate of WF #2 | 1 L | ND | ND | ND | ND |
| WF #4 | well | duplicate of WF #2 | 1 L | ND | ND | ND | ND |
| WUP #1 | well | | 1 L | ND | ND | ND | ND |
| WUP #2 | well | duplicate of WUP #1 | 1 L | ND | ND | ND | ND |
| CH2 #1 | well | | 1 L | ND | ND | ND | ND |
| CH2 #2 | well | duplicate of CH2 #1 | 1 L | ND | ND | ND | ND |
| CH2 #3 | well | duplicate of CH2 #1 | 1 L | ND | ND | ND | ND |
| CH2 #4 | well | | 1 L | ND | ND | ND | ND |

Table 1A continued

| Name | Type | Comments | Volume | Measured Conc. (µg/L) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Atr | Ala | Carb | Cyan |
| CH5 #1 | well | | 1 L | ND | ND | ND | ND |
| CH5 #2 | well | duplicate of CH5 #1 | 1 L | ND | ND | ND | ND |
| AH1 #1 | well | | 1 L | ND | ND | ND | ND |
| AH1 #2 | well | duplicate of AH1 #1 | 1 L | ND | ND | ND | ND |
| AH1 #3 | well | Spiked @ 5 ppb | 1 L | ND | 0.25* | 0.07* | 1.03 |
| AH1 #4 | well | Spiked @ 20 ppb | 1 L | 1.65 | 1.91 | 2.59 | 1.21 |
| AH Beach #1 | well | | 1 L | ND | ND | ND | ND |
| AH Beach #2 | well | duplicate of AH Beach #1 | 1 L | ND | ND | ND | ND |
| AH Beach #3 | well | Spiked @ 5 ppb | 1 L | 0.06* | 0.52 | 0.09* | ND |
| AH Beach #4 | well | Spiked @ 20 ppb | 1 L | 0.43 | 1.15 | 1.66 | ND |
| LH Tap #1 | well | | 1 L | ND | ND | ND | ND |
| BR9 #1 | well | | 1 L | ND | ND | ND | ND |
| BR9 #2 | well | duplicate of BR9 #1 | 1 L | ND | ND | ND | ND |
| BR15 #1 | well | | 1 L | ND | ND | ND | ND |
| BR15 #2 | well | duplicate of BR15 #2 | 1 L | ND | ND | ND | ND |
| BR15 #3 | well | Spiked @ 5 ppb | 1 L | 0.07* | 0.44 | 0.41* | ND |
| BR15 #4 | well | Spiked @ 20 ppb | 1 L | 1.08 | 1.90 | 1.88 | ND |
| LB #1 | blank | Reagent water | 1 L | ND | ND | ND | ND |
| TB #1 | blank | Travel blank | 1 L | ND | ND | ND | ND |
| TB #2 | blank | duplicate of TB #1 | 1 L | ND | ND | ND | ND |

Table 1A Continued

| Name | Type | Comments | Volume | Measured Conc. (µg/L) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Atr | Ala | Carb | Cyan |
| EB #1 | blank | equipment blank | 1 L | ND | ND | ND | ND |
| EB #2 | blank | duplicate of EB #1 | 1 L | ND | ND | ND | ND |

Table 2A
May Samples

| Name | Type | Comments | Volume | Measured Conc. (µg/L) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Atr | Ala | Carb | Cyan |
| WF #1 | well | | 1 L | ND | ND | ND | ND |
| WF #2 | well | Spiked @ 2 ppb | 1 L | 0.32* | 0.61 | 0.70* | ND |
| WF #3 | well | duplicate of WF #1 | 1 L | ND | ND | ND | ND |
| WFSW | well | | 1 L | ND | ND | ND | ND |
| WFSM 1-4 | SM | | 1 L | ND | ND | ND | ND |
| WF Amb To | sea | | 1 L | ND | ND | ND | ND |
| CH New #1 | well | | 1 L | ND | ND | ND | ND |
| CH New #2 | well | Spiked @ 2 ppb | 1 L | 0.77 | 1.18 | 1.67 | ND |
| CH New #3 | well | Spiked @ 10 ppb | 1 L | 3.54 | 4.57 | 7.69 | 0.92 |
| CH2 | well | | 1 L | ND | ND | ND | ND |
| CH5 | well | | 1 L | ND | ND | ND | ND |
| CHSM 3 | SM | | 1 L | ND | ND | ND | ND |
| CHSM 4 | SM | Spiked @ 10 ppb | 1 L | 4.75 | 5.64 | 11.1 | 4.55 |
| CH Amb To | sea | | 1 L | ND | ND | ND | ND |
| EV2 #1 | well | | 1 L | ND | ND | ND | ND |
| EV2 #2 | well | Spiked @ 2 ppb | 1 L | 0.37 | 0.76 | 1.09* | ND |
| EV2 #3 | well | duplicate of EV2 #1 | 1 L | ND | ND | ND | ND |
| EV1 #1 | well | Spiked @ 2 ppb | 1 L | ND | 1.28 | 0.51* | ND |
| EV1 #2 | well | | 1 L | ND | ND | ND | ND |
| EV1 #3 | well | duplicate of EV1 #2 | 1 L | ND | ND | ND | ND |

Table 2A continued

| Name | Type | Comments | Volume | Measured Conc. (µg/L) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Atr | Ala | Carb | Cyan |
| EVF/R #1 | well | | 1 L | ND | ND | ND | ND |
| EVF/R #2 | well | duplicate of EVF/R #1 | 1 L | ND | ND | ND | ND |
| EVSM 1&4 | SM | | 800 mL | ND | ND | ND | ND |
| EVSM 2 | SM | | 900 mL | ND | ND | ND | ND |
| EV Amb To | sea | | 1 L | ND | ND | ND | ND |
| BVCW #1 | well | Spiked @ 2 ppb | 1 L | 0.66 | 1.06 | 1.67 | ND |
| BVCW #2 | well | | 1 L | ND | ND | ND | ND |
| BVCW #3 | well | duplicate of BVCW #2 | 1 L | ND | ND | ND | ND |
| BV1 #1 | well | | 1 L | ND | ND | ND | ND |
| BV1 #2 | well | duplicate of BV1 #1 | 1 L | ND | ND | ND | ND |
| BV2 #1 | well | | 1 L | ND | ND | ND | ND |
| BV2 #2 | well | duplicate of BV2 #1 | 1 L | ND | ND | ND | ND |
| BVSM1 | SM | | 1 L | ND | ND | ND | ND |
| BVSM2 | SM | | 1 L | ND | ND | ND | ND |
| BVSM3 #1 | SM | | 1 L | ND | ND | ND | ND |
| BVSM3 #2 | SM | duplicate of BVSM3 #1 | 1 L | ND | ND | ND | ND |
| BVSM3 #3 | SM | duplicate of BVSM3 #1 | 1 L | ND | ND | ND | ND |
| BVSM 4 | SM | | 1 L | ND | ND | ND | ND |
| BV Amb To | sea | | 1 L | ND | ND | ND | ND |
| EB #1 | blank | equipment blank | 1 L | ND | ND | ND | ND |

Table 2A continued

| Name | Type | Comments | Volume | Measured Conc. (µg/L) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Atr | Ala | Carb | Cyan |
| EB #2 | blank | duplicate of EB#1 | 1 L | ND | ND | ND | ND |
| TB #1 | blank | | 1 L | ND | ND | ND | ND |
| TB #2 | blank | duplicate of TB #1 | | | | | |
| LB #1 | blank | Reagent blank | 1 L | ND | ND | ND | ND |
| LFB #2 | blank | Spiked @ 2 ppb | 1 L | 0.53 | 0.80 | 0.91* | ND |

Table 3A
June Samples

| Name | Type | Comments | Volume | Measured Conc. (µg/L) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Atr | Ala | Carb | Cyan |
| EV1 #1 | well | | 1 L | ND | ND | ND | ND |
| EV1 #2 | well | duplicate of EV1 #1 | 1 L | ND | ND | ND | ND |
| EV2 #1 | well | | 1 L | ND | ND | ND | ND |
| EV2 #2 | well | duplicate of EV2 #1 | 1 L | ND | ND | ND | ND |
| EVF/R #1 | well | Spiked @ 5 ppb | 1 L | 1.86 | 3.05 | 2.36 | 1.86 |
| EVF/R #2 | well | | 1 L | ND | ND | ND | ND |
| EVF/R #3 | well | duplicate of EVF/R #2 | 1 L | ND | ND | ND | ND |
| EVF/R #4 | well | Spiked @ 2 ppb | 1 L | ND | 0.71 | 0.60* | 0.34 |
| EVSM 1 | SM | | 1 L | ND | ND | ND | ND |
| EVSM 2&4 combined | SM | | 1 L | ND | ND | ND | ND |
| EVSM 3 | SM | | 1 L | ND | ND | ND | ND |
| EV Amb To | Sea | seawater at site of SM | 1 L | ND | ND | ND | ND |
| BV1 #1 | well | | 1 L | ND | ND | ND | ND |
| BV1 #2 | well | duplicate of BV1 #1 | 1 L | ND | ND | ND | ND |
| BV2 #1 | well | | 1 L | ND | ND | ND | ND |
| BVCW #1 | well | Spiked @ 2 ppb | 1 L | 0.29* | 2.09 | 0.93* | 1.08 |
| BVCW #2 | well | Spiked @ 5 ppb | 1 L | 4.77 | 5.94 | 4.78 | 4.61 |
| BVCW #3 | well | | 1 L | ND | ND | ND | ND |
| BVCW #4 | well | duplicate of BVCW #3 | 1 L | ND | ND | ND | ND |

Table 3A Continued

| Name | Type | Comments | Volume | Measured Conc. (μg/L) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Atr | Ala | Carb | Cyan |
| BVSM 1 #1 | SM | | 1 L | ND | ND | ND | ND |
| BVSM 1 #2 | SM | | 1 L | ND | ND | ND | ND |
| BVSM 1 #3 | SM | | 600 mL | ND | ND | ND | ND |
| BVSM 3 | SM | | 1 L | ND | ND | ND | ND |
| BVSM 4 | SM | Some extract spilled | 1 L | ND | ND | ND | ND |
| BV Amb To | Sea | Seawater at site of SM | 1 L | ND | ND | ND | ND |
| WF1 #1 | well | | 1 L | ND | 0.66 | ND | ND |
| WF1 #2 | well | duplicate of WF1 #1 | 1 L | ND | 0.57 | ND | ND |
| WF2 #1 | well | Spiked @ 2 ppb | 1 L | ND | 0.68 | ND | ND |
| WF2 #2 | well | | 1 L | ND | ND | ND | ND |
| WFSW #1 | well | Spiked @ 5 ppb | 1 L | 2.62 | 4.38 | 2.51 | 2.76 |
| WFSW #2 | well | Spiked @ 2 ppb | 1 L | ND | 1.07 | ND | 0.35 |
| WFSW #3 | well | | 1 L | ND | ND | ND | ND |
| WFSW #4 | well | duplicate of WFSW #3 | 1 L | ND | ND | ND | ND |
| WFSM 3 | SM | | 1 L | ND | ND | ND | ND |
| WFSM 4 | SM | | 1 L | ND | ND | ND | ND |
| CH2 #1 | well | Spiked @ 5 ppb | 1 L | 3.88 | 4.97 | 3.63 | 3.53 |
| CH2 #2 | well | Spiked @ 2 ppb | 1 L | 2.22 | 3.12 | 1.92 | 1.90 |
| CH2 #3 | well | Spiked @ 1 ppb | 1 L | 2.34 | 2.12 | ND | 1.14 |
| CH2 #4 | well | | 1 L | ND | ND | ND | ND |

Table 3A Continued

| Name | Type | Comments | Volume | Measured Conc. (μg/L) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Atr | Ala | Carb | Cyan |
| CH New #1 | well | | 1 L | ND | ND | ND | ND |
| CH New #2 | well | duplicate of CH New #1 | 1 L | ND | ND | ND | ND |
| CHSM 2 | SM | | 1 L | ND | ND | ND | ND |
| CHSM 3 | SM | | 800 mL | ND | ND | ND | ND |
| CH Amb To | Sea | Seawater at site of SM | 1 L | ND | ND | ND | ND |
| TB #1 | blank | Travel blank | 1 L | ND | ND | ND | ND |
| TB #2 | blank | duplicate of TB #1 | 1 L | ND | ND | ND | ND |
| EB #1 | blank | equipment blank | 1 L | ND | ND | ND | ND |
| EB #2 | blank | duplicate of EB #1 | 1 L | ND | ND | ND | ND |

Table 4A
July Samples

| Name | Type | Comments | Volume | Measured Conc. (µg/L) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Atr | Ala | Carb | Cyan |
| EV1 #1 | well | | 1 L | ND | ND | ND | ND |
| EV1 #2 | well | duplicate of EV1 #1 | 1 L | ND | ND | ND | ND |
| EV1 #3 | well | Spiked @ 2 ppb | 1 L | 3.58 | 3.51 | ND | 1.99 |
| EV1 #4 | well | Spiked @ 4 ppb-some of sample spilled | 1 L | 1.01 | 5.22 | ND | 2.53 |
| EV2 #1 | well | | 1 L | ND | ND | ND | 0.16* |
| EV2 #2 | well | duplicate of EV2 #1 | 1 L | ND | ND | ND | ND |
| EVF/R #1 | well | | 900 mL | ND | ND | ND | 0.53 |
| EVSM 1&2 Combined | SM | | 1 L | ND | ND | ND | ND |
| EVSM 2 | SM | | 1 L | ND | ND | ND | ND |
| EV Amb To | Sea | Seawater at site of SM | 1 L | ND | ND | ND | ND |
| BV1 #1 | well | | 1 L | 0.59 | ND | ND | 0.16* |
| BV1 #2 | well | duplicate of BV1 #1 | 1 L | ND | ND | ND | ND |
| BV1 #3 | well | duplicate of BV1 #1 | 1 L | ND | ND | ND | ND |
| BV1 #4 | well | duplicate of BV1 #1 | 1 L | ND | ND | ND | ND |
| BV2 #1 | well | | 1 L | ND | ND | ND | ND |
| BV2 #2 | well | duplicate of BV2 #1 | 1 L | ND | ND | ND | ND |
| BV2 #3 | well | Spiked @ 2 ppb | 1 L | 0.39 | 4.60 | 0.85* | 0.14* |
| BV2 #4 | well | Spiked @ 4 ppb | 1 L | 5.11 | 4.98 | 0.85* | 3.64 |
| BVCW #1 | well | | 1 L | ND | ND | ND | ND |

Table 4A Continued

| Name | Type | Comments | Volume | Measured Conc. (µg/L) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Atr | Ala | Carb | Cyan |
| BVCW #2 | well | duplicate of BVCW #1 | 1 L | ND | ND | ND | ND |
| BV Amb To | Sea | Seawater at site of SM | 1 L | ND | ND | ND | ND |
| WF1 #1 | well | | 1 L | 0.63 | ND | ND | ND |
| WF1 #2 | well | duplicate of WF1 #1 | 1 L | ND | ND | ND | ND |
| WF1 #3 | well | Spiked @ 2 ppb | 1 L | 1.88 | 3.22 | ND | 1.70 |
| WF1 #4 | well | Spiked @ 4 ppb | 1 L | 3.79 | 4.59 | ND | 3.17 |
| WF2 #1 | well | | 1 L | 0.60 | ND | ND | ND |
| WF2 #2 | well | duplicate of WF2 #1 | 1 L | ND | ND | ND | ND |
| WFSW #1 | well | | 1 L | ND | ND | ND | ND |
| WFSW #2 | well | duplicate of WFSW #1 | 1 L | ND | ND | ND | ND |
| WF Amb To | Sea | seawater at site | 1 L | ND | ND | ND | ND |
| CH2 #1 | well | | 1 L | 1.52 | ND | ND | 0.17* |
| CH2 #2 | well | duplicate of CH2 #1 | 1 L | ND | ND | ND | ND |
| CH5 #1 | well | | 1 L | ND | ND | ND | ND |
| CH5 #2 | well | duplicate of CH5 #1 | 1 L | ND | ND | ND | ND |
| CH5 #3 | well | Spiked @ 2 ppb | 1 L | 2.15 | 2.35 | 2.75 | 1.21 |
| CH5 #4 | well | Spiked @ 4 ppb | 1 L | 3.00 | 3.93 | 3.60 | 2.68 |
| CH New | well | | 1 L | ND | ND | ND | ND |
| CHSM 1 | SM | | 1 L | ND | ND | ND | ND |
| CHSM 2 | SM | | 1 L | ND | ND | ND | ND |

Table 4A Continued

| Name | Type | Comments | Volume | Measured Conc. (μg/L) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Atr | Ala | Carb | Cyan |
| CHSM 3 | SM | | 700 mL | ND | ND | ND | ND |
| CHSM 4 | SM | | 1 L | ND | ND | ND | ND |
| CH Amb To | Sea | Seawater at site of SM | 1 L | ND | ND | ND | ND |
| ST Last | well | | 1 L | ND | ND | ND | ND |
| STSM 1 | SM | | 1 L | ND | ND | ND | ND |
| STSM 2 | SM | | 1 L | ND | ND | ND | ND |
| STSM 4 | SM | | 1 L | ND | ND | ND | ND |
| STSM 5 | SM | | 1 L | ND | ND | ND | ND |
| STSM 6 | SM | | 1 L | ND | ND | ND | ND |
| LFB #1 | blank | Spiked @ 2 ppb | 1 L | 1.06 | 2.84 | ND | 1.70 |
| LB #2 | blank | Reagent blank | 1 L | ND | ND | ND | ND |
| LB #3 | blank | duplicate of LB #2 | 1 L | ND | ND | ND | ND |
| TB #1 | blank | Spiked @ 2 ppb | 1 L | 2.77 | 3.98 | ND | 2.55 |
| TB #2 | blank | Travel blank | 1 L | ND | ND | ND | ND |
| EB #1 | blank | Spiked @ 2 ppb | 1 L | 0.37 | 1.08 | 1.70 | 0.38 |
| EB #2 | blank | equipment blank | 1 L | ND | ND | ND | ND |

Table 5A
August Samples

| Name | Type | Comments | Volume | (%) Res | Measured Conc. (µg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Atr | Ala | Carb | Cyan | Met |
| EV1 #1 | well | | 1 L | 49 | ND | ND | ND | ND | ND |
| EV1 #2 | well | duplicate of EV1 #1 | 1 L | 27 | ND | ND | ND | ND | ND |
| EV2 #1 | well | | 1 L | 39 | ND | ND | ND | ND | ND |
| EV2 #2 | well | duplicate of EV2 #1 | 1 L | 66 | ND | ND | ND | ND | ND |
| EV2 #3 | well | Spiked @ 2 ppb | 1 L | 51 | 3.07 | 2.50 | ND | 7.10 | ND |
| EVF/R #1 | well | | 1 L | 22 | ND | ND | ND | ND | ND |
| EVF/R #2 | well | duplicate of EVF/R #1 | 1 L | ** | ND | ND | ND | ND | ND |
| EVSM 1 | SM | | 1 L | 62 | ND | ND | ND | ND | ND |
| EVSM 2 | SM | | 700 mL | 46 | ND | ND | ND | ND | ND |
| EVSM 3 | SM | | 1 L | 41 | ND | ND | ND | ND | ND |
| EVSM 4 | SM | | 800 mL | 28 | ND | ND | ND | ND | ND |
| EV Amb To | Sea | Seawater at site of SM | 1 L | 76 | ND | ND | ND | ND | ND |
| BV1 #1 | well | | 1 L | 36 | ND | ND | ND | ND | ND |
| BV1 #2 | well | duplicate of BV1 #1 | 1 L | 56 | ND | ND | ND | ND | ND |
| BV2 #1 | well | | 1 L | 32 | ND | ND | ND | ND | ND |
| BV2 #2 | well | duplicate of BV2 #1 | 1 L | 55 | ND | ND | ND | ND | 0.07* |
| BVCW #1 | well | | 1 L | 59 | ND | ND | ND | ND | ND |
| BVCW #2 | well | duplicate of BVCW #1 | 1 L | 48 | ND | ND | ND | ND | ND |
| BVCW #3 | well | Spiked @ 2 ppb | 1 L | 52 | 2.74 | 0.36 | 0.14* | 2.74 | N/A |
| BVCW #4 | well | duplicate of BVCW #1 | 1 L | 48 | ND | ND | ND | ND | ND |

Table 5A Continued

| Name | Type | Comments | Volume | (%) Res | Measured Conc. (µg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Atr | Ala | Carb | Cyan | Met |
| BVSM 1-4 combined | SM | | 900 mL | ** | ND | ND | ND | ND | ND |
| BV Amb To | Sea | Seawater at site of SM | 1 L | 25 | ND | ND | ND | ND | ND |
| WF1 #1 | well | | 1 L | 46 | ND | ND | ND | ND | ND |
| WF1 #2 | well | Spiked @ 2 ppb | 1 L | 57 | 4.33 | 3.25 | ND | 6.98 | 4.84 |
| WF1 #3 | well | duplicate of WF1 #1 | 1 L | 47 | ND | ND | ND | ND | ND |
| WF1 #4 | well | Spiked @ 4 ppb | 1 L | 35 | 9.34 | 5.94 | ND | 16.5 | 9.26 |
| WF2 #1 | well | | 1 L | 22 | ND | ND | ND | ND | ND |
| WF2 #2 | well | duplicate of WF2 #1 | 1 L | 1.2 | ND | ND | ND | ND | ND |
| WFSW #1 | well | | 1 L | 39 | ND | ND | ND | ND | 0.07* |
| WFSW #2 | well | duplicate of WFSW #1 | 1 L | 21 | ND | ND | ND | ND | ND |
| WFSM 2&4 Combined | SM | | 1 L | 35 | ND | ND | ND | ND | ND |
| WFSM 3 | SM | | 1 L | 19 | ND | ND | ND | ND | ND |
| CH2 #1 | well | | 1 L | 33 | ND | ND | ND | ND | ND |
| CH2 #2 | well | duplicate of CH2 #1 | 1 L | 47 | ND | ND | ND | ND | ND |
| CH3 #1 | well | | 1 L | 57 | ND | ND | ND | ND | 0.33* |
| CH3 #2 | well | duplicate of CH3 #1 | 1 L | 9.7 | ND | ND | ND | ND | ND |
| CH3 #3 | well | Spiked @ 2 ppb | 1 L | 75 | ND | 7.48 | ND | 6.75 | N/A |
| CH3 #4 | well | Spiked @ 4 ppb | 1 L | 8.5 | ND | 12.7 | ND | 8.10 | N/A |
| CH5 #1 | well | | 1 L | 20 | ND | ND | ND | ND | ND |

Table 5A Continued

| Name | Type | Comments | Volume | (%) Res | Measured Conc. (μg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Atr | Ala | Carb | Cyan | Met |
| CH5 #2 | well | duplicate of CH5 #1 | 1 L | 38 | ND | ND | ND | ND | ND |
| CHSM 1 | SM | | 1 L | 24 | ND | ND | ND | ND | ND |
| CHSM 3 | SM | | 1 L | 50 | ND | ND | ND | ND | ND |
| Hoopers Farm #1 | well | | 1 L | 50 | ND | ND | ND | ND | ND |
| Hoopers Farm #2 | well | duplicate of HF #1 | 1 L | 20 | ND | ND | ND | ND | ND |
| TB | blank | Travel blank | 1 L | 23 | ND | ND | ND | ND | ND |
| EB | blank | equipment blank | 1 L | 119 | ND | ND | ND | ND | ND |
| LFB #1 | blank | Spiked @ 2 ppb | 1 L | 76 | 1.89 | 0.18* | ND | 3.08 | 2.23 |
| LB #2 | blank | Reagent blank | 1 L | 12.1 | ND | ND | ND | ND | ND |
| LFB #3 | blank | Spiked @ 4 ppb | 1 L | 5.5 | 8.55 | 6.31 | ND | 11.96 | 8.85 |

Table 6A
October Samples

| Name | Type | Comments | Volume | (%) Res | Measured Conc. (µg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Atr | Ala | Carb | Cyan | Met |
| EV1 #1 | well | | 1 L | | ND | ND | ND | ND | ND |
| EV1 #2 | well | duplicate of EV1 #1 | 1 L | 54 | ND | ND | ND | ND | ND |
| EV1 #3 | well | Spiked @ 2 ppb | 1 L | 63 | 4.54 | 2.66 | 7.28 | 5.98 | N/A |
| EV1 #4 | well | Spiked @ 1 ppb | 1 L | 35 | 1.56 | 1.11 | 5.76 | 2.23 | N/A |
| EV2 #1 | well | Spiked @ 0.25 ppb | 1 L | 41 | ND | 0.36 | N/A | 1.62 | N/A |
| EV2 #2 | well | | 1 L | | ND | ND | ND | ND | ND |
| EV2 #3 | well | duplicate of EV2 #2 | 1 L | 84 | ND | ND | ND | ND | ND |
| EV2 #4 | well | Spiked @ 1 ppb | 1 L | 119 | 2.61 | 1.62 | 9.33 | 3.54 | N/A |
| EVF/R #1 | well | | 1 L | 89 | ND | ND | ND | ND | ND |
| EVF/R #2 | well | duplicate of EVF/R #1 | 1 L | 37 | ND | ND | ND | ND | ND |
| EVSM 1 #1 | SM | Spiked @ 0.25 ppb | 1 L | 38 | ND | 0.62 | N/A | 1.82 | N/A |
| EVSM1 #2 | SM | Spiked @ 1 ppb | 1 L | 75 | 5.76 | 1.93 | 3.93 | 5.44 | N/A |
| EVSM 2 #1 | SM | | 1 L | 13.3 | ND | ND | ND | ND | ND |
| EVSM 2 #2 | SM | | 1 L | 142 | ND | ND | ND | ND | ND |
| EVSM 3 #1 | SM | | 1 L | 31 | ND | ND | ND | ND | ND |
| EVSM 4 #1 | SM | | 1 L | 32 | ND | ND | ND | ND | ND |
| EVSM 4 #2 | SM | Spiked @ 0.5 ppb | 1 L | 40 | ND | 0.71 | N/A | 2.29 | N/A |
| EV Amb To | Sea | Seawater at site of SM | 1 L | 45 | ND | ND | ND | ND | ND |
| BV1 #1 | well | | 1 L | 36 | ND | ND | ND | ND | ND |
| BV1 #2 | well | duplicate of BV1 #1 | 1 L | 4.1 | ND | ND | ND | ND | ND |

Table 6A Continued

| Name | Type | Comments | Volume | (%) Resp | Measured Conc. (μg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Atr | Ala | Carb | Cyan | Met |
| BV1 #3 | well | Spiked @ 0.5 ppb | 1 L | 15 | 0.76 | 0.25* | N/A | 1.43 | N/A |
| BV1 #4 | well | Spiked @ 2 ppb | 1 L | 65 | 3.83 | 2.57 | 6.72 | 1.28 | N/A |
| BV2 #1 | well | | 1 L | 106 | ND | ND | ND | ND | ND |
| BV2 #2 | well | duplicate of BV2 #1 | 1 L | 47 | ND | ND | ND | ND | ND |
| BVCW #1 | well | | 1 L | 41 | ND | ND | ND | ND | ND |
| BVCW #2 | well | duplicate of BVCW #1 | 1 L | 65 | ND | ND | ND | ND | ND |
| BVCW #3 | well | Spiked @ 1 ppb | 1 L | 26 | 2.42 | 0.80 | 3.90 | 1.55 | N/A |
| BVCW #4 | well | Spiked @ 0.25 ppb | 1 L | 9.1 | ND | 0.18* | N/A | 0.16* | N/A |
| BVSM 2 | SM | | 1 L | 96 | ND | ND | ND | ND | ND |
| BVSM 4 #1 | SM | Spiked @ 2 ppb | 1 L | ** | 2.77 | 0.91 | 3.87 | 1.69 | N/A |
| BVSM 4 #2 | SM | | 1 L | 9.7 | ND | ND | ND | ND | ND |
| BV Amb To | Sea | Seawater at site of SM | 1 L | 56 | ND | ND | ND | ND | ND |
| WF1 #1 | well | | 1 L | 85 | ND | ND | ND | ND | ND |
| WF1 #2 | well | duplicate of WF1 #1 | 1 L | 71 | ND | ND | ND | ND | ND |
| WF1 #3 | well | Spiked @ 0.5 ppb | 1 L | 79.6 | ND | 0.58 | N/A | 0.97 | N/A |
| WF1 #4 | well | Spiked @ 2 ppb | 1 L | 45 | 2.35 | 1.72 | 4.57 | 3.63 | N/A |
| WF2 #1 | well | | 1 L | 56 | ND | ND | ND | ND | ND |
| WF2 #2 | well | duplicate of WF2 #1 | 1 L | 43 | ND | ND | ND | ND | ND |
| WF2 #3 | well | Spiked @ 0.25 ppb | 1 L | 64 | 1.10 | 0.30* | N/A | 2.4 | ND |
| WF2 #4 | well | Spiked @ 1 ppb | 1 L | 75 | 1.60 | 1.10 | ND | 1.90 | N/A |

Table 6A Continued

| Name | Type | Comments | Volume | (%) Resp | Measured Conc. (µg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Atr | Ala | Car | Cyn | Met |
| WFSW #1 | well | | 1 L | 15 | ND | ND | ND | ND | ND |
| WFSW #2 | well | duplicate of WFSW #1 | 1 L | 69 | ND | ND | ND | ND | ND |
| WFSM 1&2 Combined | SM | | 1 L | 38 | ND | ND | ND | ND | ND |
| WFSM 1 | SM | | 1 L | 11 | ND | ND | ND | ND | ND |
| WFSM 3 | SM | | 1 L | 64 | ND | ND | ND | ND | ND |
| WF Amb To | Sea | Seawater at site of SM | 1 L | | ND | ND | ND | ND | ND |
| CH2 #1 | well | | 1 L | 11.5 | ND | ND | ND | ND | ND |
| CH3 #1 | well | Spiked @ 0.25 ppb | 1 L | 81 | ND | 0.53 | N/A | 1.10 | N/A |
| CH3 #2 | well | | 1 L | 21 | ND | ND | ND | ND | ND |
| CH3 #3 | well | duplicate of CH3 #2 | 1 L | 51 | ND | ND | ND | ND | ND |
| CH3 #4 | well | Spiked @ 1 ppb | 1 L | 69 | ND | 1.39 | ND | 3.65 | N/A |
| CH5 | well | | 1 L | 26 | ND | ND | ND | ND | ND |
| CH5 #1 | well | | 1 L | 75 | ND | ND | ND | ND | ND |
| CH5 #2 | well | Spiked @ 2 ppb | 1 L | 52 | 4.15 | 2.32 | 5.49 | 5.50 | N/A |
| CHSM 1-4 Combined | SM | | 1 L | 4.1 | ND | ND | ND | ND | 0.04* |
| CHSM 3 | SM | | 1 L | 2.5 | ND | ND | ND | ND | ND |
| CH Stream | | Stream on Site | 1 L | 88 | ND | ND | ND | ND | ND |
| CH Amb To | Sea | Seawater at site of SM | 1 L | ** | ND | ND | ND | ND | ND |
| ST1 #1 | well | | 1 L | 36 | ND | ND | ND | ND | ND |

Table 6A Continued

| Name | Type | Comments | Volume | (%) Resp | Measured Conc. (µg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Atr | Ala | Carb | Cyan | Met |
| ST3 #1 | well | Spiked @ 0.25 ppb | 1 L | ** | ND | 0.27* | N/A | 0.22* | N/A |
| ST3 #2 | well | | 1 L | 126 | ND | ND | ND | ND | ND |
| ST3 #3 | well | duplicate of ST3 #1 | 1 L | ** | ND | ND | ND | ND | ND |
| ST3 #4 | well | duplicate of ST3 #2 | 1 L | ** | ND | ND | ND | ND | ND |
| EB #1 | blank | equipment blank | 1 L | ** | ND | ND | ND | ND | ND |
| EB #2 | blank | duplicate of EB #1 | 1 L | 33 | ND | ND | ND | ND | ND |
| EB #3 | blank | duplicate of EB #1 | 1 L | 77 | ND | ND | ND | ND | ND |
| TB | blank | Travel blank | 1 L | 33.5 | ND | ND | ND | ND | ND |
| LB #1 | blank | Reagent blank | 1 L | 2.6 | ND | ND | ND | ND | ND |
| LB #2 | blank | duplicate of LB #1 | 1 L | ** | ND | ND | ND | ND | ND |
| LB #3 | blank | duplicate of LB #1 | 1 L | 47 | ND | ND | ND | ND | ND |
| LFB #1 | blank | Spiked @ 0.25 ppb | 1 L | 86 | 1.35 | 0.20* | N/A | 0.98 | N/A |
| LFB #2 | blank | Spiked @ 0.5 ppb | 1 L | 38 | ND | 0.78 | N/A | 1.40 | N/A |
| LFB #3 | blank | Spiked @ 1 ppb | 1 L | 3.3 | 1.40 | 0.96 | 6.77 | 1.52 | N/A |
| LFB #4 | blank | Spiked @ 2 ppb | 1 L | 6 | 4.01 | 0.16* | 5.53 | 3.80 | N/A |

Table 7A
November Samples

| Name | Type | Comments | Volume | (%) Resp | Measured Conc. (µg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Atr | Ala | Car | Cyn | Met |
| EV1 #1 | well | | 1 L | 65 | ND | ND | ND | ND | ND |
| EV1 #2 | well | duplicate of EV1 #1 | 1 L | 80 | ND | ND | ND | ND | ND |
| EV2 #1 | well | | 1 L | 110 | ND | ND | ND | 0.03* | ND |
| EV2 #2 | well | duplicate of EV2 #2 | 1 L | 88 | ND | ND | ND | ND | ND |
| EV2 #3 | well | Spiked @ 1 ppb | 1 L | 9.3 | ND | 0.69 | 1.52 | 1.22 | N/A |
| EV2 #4 | well | Spiked @ 0.25 ppb | 1 L | 108 | ND | 0.23* | N/A | 0.28 | 1.68 |
| EVF/R #1 | well | | 1 L | 66 | ND | ND | ND | ND | ND |
| EVF/R #2 | well | duplicate of EVF/R#1 | 1 L | | ND | ND | ND | ND | ND |
| EVF/R #3 | well | Spiked @ 0.5 ppb | 1 L | 91 | ND | 0.45 | N/A | 0.90 | 3.86 |
| EVF/R #4 | well | Spiked @ 2 ppb | 1 L | 6.5 | ND | 1.27 | 0.89* | 2.51 | N/A |
| EVSM 1-4 Combined | SM | | 1 L | 54 | ND | ND | ND | ND | ND |
| EVSM 4 | SM | | 1 L | 86 | ND | ND | ND | ND | ND |
| BV1 #1 | well | Spiked @ 2 ppb | 1 L | 49 | 1.55 | 1.88 | 1.67 | 3.76 | N/A |
| BV1 #2 | well | Spiked @ 1 ppb | 1 L | 49 | 1.02 | 1.61 | 1.19* | 3.32 | N/A |
| BV1 #3 | well | Spiked @ 0.5 ppb | 1 L | 74 | ND | 0.42 | N/A | 0.72 | 3.44 |
| BV1 #4 | well | Spiked @ 0.5 ppb | 1 L | 99 | ND | 0.31* | N/A | 0.55 | 2.24 |
| BV2 #1 | well | | 1 L | 62 | ND | ND | ND | ND | ND |
| BV2 #2 | well | duplicate of BV2 #1 | 1 L | 79 | ND | ND | ND | ND | ND |
| BVCW #1 | well | | 1 L | 51 | ND | ND | ND | ND | ND |

Table 7A Continued

| Name | Type | Comments | Volume | (%) Resp | Measured Conc. (µg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Atr | Ala | Car | Cyn | Met |
| BVCW #2 | well | duplicate of BVCW #1 | 1 L | 63 | ND | ND | ND | ND | • |
| BVCW #3 | well | Spiked @ 0.25 ppb | 1 L | 78 | ND | 0.65 | N/A | 1.93 | 2.91 |
| BVCW #4 | well | Spiked @ 1 ppb | 1 L | 37 | 0.75 | 0.92 | 1.01* | 1.67 | N/A |
| BVSM 1 | SM | | 400 mL | 36 | ND | ND | ND | ND | ND |
| BVSM 3 #1 | SM | | 1 L | | ND | ND | ND | ND | ND |
| BVSM 3 #2 | SM | Spiked @ 2 ppb | 1 L | 31 | 0.76 | 0.53 | 2.11 | 1.56 | N/A |
| BVSM 3 #3 | SM | duplicate of BVSM 3 #3 | 1 L | 67 | ND | ND | ND | ND | ND |
| BVSM 4 #1 | SM | | 1 L | 11.3 | ND | ND | ND | ND | ND |
| BVSM 4 #2 | SM | duplicate of BVSM 4 #1 | 1 L | | ND | ND | ND | ND | ND |
| WF1 #1 | well | | 1 L | 52 | ND | ND | ND | ND | ND |
| WF1 #2 | well | duplicate | 1 L | 93 | ND | ND | ND | ND | ND |
| WF1 #3 | well | Spiked @ 0.25 ppb | 1 L | 100 | ND | 0.22* | N/A | 0.41 | 2.11 |
| WF1 #4 | well | Spiked @ 1 ppb | 1 L | 67 | ND | 0.78 | 7.88 | 1.22 | N/A |
| WF2 #1 | well | | 1 L | 47 | ND | ND | ND | ND | ND |
| WF2 #2 | well | duplicate of WF2 #1 | 1 L | 26 | ND | ND | ND | ND | ND |
| WF2 #3 | well | Spiked @ 2 ppb | 1 L | 45 | 1.19 | 1.42 | 1.05* | 2.71 | N/A |
| WF2 #4 | well | Spiked @ 0.5 ppb | 1 L | 45 | ND | 0.25* | N/A | 0.43 | 2.10 |
| WFSW #1 | well | | 1 L | 92 | ND | ND | ND | ND | ND |
| WFSW #2 | well | duplicate of WFSW #1 | 1 L | 78 | ND | ND | ND | ND | ND |
| WF Amb To | Sea | Seawater at site of SM | 1 L | 74 | ND | ND | ND | ND | ND |

• Note that Metolachlor's spectrum was detected on the GC/MS below the LDQ

Table 7A Continued

| Name | Type | Comments | Volume | (%) Resp | Measured Conc. (μg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Atr | Ala | Car | Cyn | Met |
| CH2 | well | | 1 L | | ND | ND | ND | 0.02* | ND |
| CH2 #1 | well | duplicate of CH2 | 1 L | 73 | ND | ND | ND | ND | ND |
| CH3 #1 | well | | 1 L | 86 | ND | ND | ND | ND | ND |
| CH3 #2 | well | duplicate of CH3 #1 | 1 L | 102 | ND | ND | ND | ND | ND |
| CH3 #3 | well | Spiked @ 1 ppb | 1 L | ** | ND | 0.76 | 1.17* | 1.20 | N/A |
| CH3 #4 | well | Spiked @ 0.25 ppb | 1 L | | ND | 0.20* | N/A | 0.46 | 1.82 |
| CH5 #1 | well | | 1 L | 85 | ND | ND | ND | 0.55 | ND |
| CH5 #2 | well | duplicate of CH5 #2 | 1 L | 88 | ND | ND | ND | ND | ND |
| CH Amb To | Sea | | 1 L | 38 | ND | ND | ND | ND | ND |
| STI 4 | well | | 1 L | 103 | ND | ND | ND | ND | ND |
| ST Middle | well | | 1 L | 52 | ND | ND | ND | ND | ND |
| ST Middle #1 | well | duplicate of ST Middle | 1 L | 115 | ND | ND | ND | ND | ND |
| EB #1 | blank | equipment blank | 1 L | 93 | ND | ND | ND | ND | ND |
| EB #2 | blank | duplicate of EB #1 | 1 L | 95 | ND | ND | ND | ND | ND |
| TB #1 | blank | Travel blank | 1 L | 43 | ND | ND | ND | ND | ND |
| TB #2 | blank | duplicate of TB #1 | 1 L | 61 | ND | ND | ND | ND | ND |
| LB #1 | blank | Reagent blank | 1 L | | ND | ND | ND | ND | ND |
| LB #2 | blank | duplicate of LB #1 | 1 L | 67 | ND | ND | ND | ND | ND |
| LB #3 | blank | duplicate of LB #1 | 1 L | | ND | ND | ND | ND | ND |
| LFB #1 | blank | Spiked @ 0.25 ppb | 1 L | 83 | ND | 0.23* | N/A | 0.47 | 0.02 |

Table 7A Continued

| Name | Type | Comments | Volume | (%) Resp | Measured Conc. (µg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Atr | Ala | Car | Cyn | Met |
| LFB #2 | blank | Spiked @ 0.5 ppb | 1 L | 16 | ND | 0.28* | 0.72* | 0.52 | N/A |
| LFB #3 | blank | Spiked @ 2 ppb | 1 L | 59 | 0.98 | 1.62 | N/A | 3.14 | 9.76 |

Table 8A
December Samples

| Name | Type | Comments | Volume | (%) Resp | Measured Conc. (µg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Atr | Ala | Car | Cyn | Met |
| EV1 #1 | well | Spiked @ 0.5 ppb | 1 L | 89 | ND | 0.29* | N/A | 0.70 | ND |
| EV1 #2 | well | Spiked @ 0.25 ppb | 1 L | 95 | ND | 0.25* | N/A | 0.48 | 1.42 |
| EV1 #3 | well | | 1 L | 32 | ND | ND | ND | ND | ND |
| EV1 #4 | well | duplicate of EV1 #3 | 1 L | 31 | ND | ND | ND | ND | ND |
| EV2 #1 | well | | 1 L | 67 | ND | ND | ND | ND | ND |
| EV2 #2 | well | duplicate of EV2 #1 | 1 L | 124 | ND | ND | ND | ND | ND |
| EVF/R #1 | well | | 1 L | 76 | ND | ND | ND | ND | ND |
| EVF/R #2 | well | Spiked @ 2 ppb | 1 L | 52 | 0.84 | 1.19 | 2.00 | 2.82 | N/A |
| EVF/R #3 | well | Spiked @ 1 ppb | 1 L | 24 | 0.90 | 1.17 | 2.31 | 2.56 | N/A |
| EVF/R #4 | well | duplicate of EVF/R #3 | 1 L | 18 | ND | ND | ND | ND | ND |
| EVSM 2 | SM | | 500 mL | 27 | ND | ND | ND | ND | ND |
| EV Amb To | Sea | Seawater at site of SM | 1 L | 49 | ND | ND | ND | ND | ND |
| BV1 #1 | well | Spiked @ 2 ppb | 1 L | 37 | 1.41 | 1.43 | 2.10 | 2.98 | N/A |
| BV1 #2 | well | Spiked @ 1 ppb | 1 L | 107 | 0.58 | 0.86 | 0.85* | 2.04 | N/A |
| BV1 #3 | well | | 1 L | 81 | ND | ND | ND | ND | ND |
| BV1 #4 | well | duplicate of BV1 #3 | 1 L | 89 | ND | ND | ND | ND | ND |
| BV2 #1 | well | | 1 L | 90 | ND | ND | ND | ND | ND |
| BV2 #2 | well | duplicate of BV2 #1 | 1 L | 67 | ND | ND | ND | ND | ND |
| BVCW #1 | well | Spiked @ 0.5 ppb | 1 L | 106 | ND | 0.29* | N/A | 0.63 | 2.01 |
| BVCW #2 | well | | 1 L | ** | ND | ND | ND | ND | ND |

Table 8A Continued

| Name | Type | Comments | Volume | (%) Resp | Measured Conc. (μg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Atr | Ala | Car | Cyn | Met |
| BVCW #3 | well | Spiked @ 0.25 ppb | 1 L | 38 | ND | 0.21* | N/A | 0.60 | 0.12* |
| BVCW #4 | well | duplicate of BVCW #2 | 1 L | ** | ND | ND | ND | ND | ND |
| WF1 #1 | well | | 1 L | 113 | ND | ND | ND | ND | ND |
| WF1 #2 | well | duplicate of WF1 #1 | 1 L | 43 | ND | ND | ND | ND | ND |
| WF1 #3 | well | Spiked @ 0.25 ppb | 1 L | 49 | ND | 0.19* | N/A | 0.57 | 1.09 |
| WF1 #4 | well | Spiked @ 0.5 ppb | 1 L | 44 | ND | 0.35 | N/A | 0.57 | 2.27 |
| WF2 #1 | well | Spiked @ 2 ppb | 1 L | 53 | 0.25* | 0.34 | 0.61* | 1.10 | N/A |
| WF2 #2 | well | | 1 L | 21 | ND | ND | ND | ND | ND |
| WF2 #3 | well | Spiked @ 1 ppb | 1 L | 24 | 1.37 | 1.22 | 1.75 | 2.47 | N/A |
| WF2 #4 | well | duplicate of WF2 #3 | 1 L | 44 | ND | ND | ND | ND | ND |
| WFSW #1 | well | | 1 L | 135 | ND | ND | ND | 0.02* | ND |
| WFSW #2 | well | duplicate of WFSW #2 | 1 L | 106 | ND | ND | ND | ND | ND |
| WFSM 3 | SM | | 1 L | ** | ND | ND | ND | ND | ND |
| WF Amb To | Sea | Seawater at site of SM | 1 L | 36 | ND | ND | ND | ND | ND |
| TB | blank | Travel blank | 1 L | 56 | ND | ND | ND | ND | ND |
| EB #1 | blank | equipment blank | 1 L | 16 | ND | ND | ND | ND | ND |
| EB #2 | blank | duplicate of EB #1 | 1 L | 62 | ND | ND | ND | ND | ND |
| LB #1 | blank | Reagent blank | 1 L | 23 | ND | ND | ND | ND | ND |
| LB #2 | blank | duplicate of LB #1 | 1 L | 82 | ND | ND | ND | ND | ND |

Table 8A Continued

| Name | Type | Comments | Volume | (%) Resp | Measured Conc. (µg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Atr | Ala | Car | Cyn | Met |
| LFB #1 | blank | Spiked @ 0.25 ppb | 1 L | 44 | ND | 0.20* | 1.60 | 0.33 | 0.05* |
| LFB #2 | blank | Spiked @ 1 ppb | 1 L | 61 | 0.53 | 0.63 | N/A | 1.44 | 4.44 |

Table 9A
January Samples

| Name | Type | Comments | Volume | (%) Resp | Measured Conc. (μg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Atr | Ala | Car | Cyn | Met |
| EV1 #1 | well | | 1 L | 63 | ND | ND | ND | ND | ND |
| EV1 #2 | well | duplicate of EV1 #1 | 1 L | ** | ND | ND | ND | ND | ND |
| EV2 #1 | well | Spiked @ 0.25 ppb | 1 L | 3.6 | 0.34 | 0.21* | N/A | 0.35 | 0.09* |
| EV2 #2 | well | | 1 L | 4.1 | ND | ND | ND | ND | ND |
| EV2 #3 | well | Spiked @ 0.5 ppb | 1 L | ** | 0.22* | 0.41 | N/A | 0.67 | 0.27* |
| EV2 #4 | well | duplicate of EV2 #3 | 1 L | 3.4 | ND | ND | ND | ND | ND |
| EVF/R #1 | well | | 1 L | 102 | ND | ND | ND | ND | ND |
| EVF/R #2 | well | duplicate of EVF/R #1 | 1 L | ** | ND | ND | ND | ND | ND |
| EVF/R #4 | well | Spiked @ 2 ppb | 1 L | 70 | 0.42 | 1.05 | 1.88 | 1.48 | N/A |
| BV1 #1 | well | Spiked @ 1 ppb | 1 L | 34 | 0.42 | 0.46 | 2.53 | 0.64 | N/A |
| BV1 #2 | well | Spiked @ 2 ppb | 1 L | ** | 0.75 | 1.20 | 6.33 | 1.81 | N/A |
| BV1 #3 | well | | 1 L | ** | ND | ND | ND | ND | ND |
| BV1 #4 | well | Spiked @ 0.25 ppb | 1 L | ** | 0.37 | 0.19* | N/A | 0.39 | 0.18* |
| BV2 #1 | well | | 1 L | 115 | ND | ND | ND | ND | ND |
| BV2 #2 | well | duplicate of BV2 #1 | 1 L | 122 | ND | ND | ND | ND | ND |
| BVCW #1 | well | | 1 L | 104 | ND | ND | ND | ND | ND |
| BVCW #2 | well | Spiked @ 0.25 ppb | 1 L | 36 | 0.35* | 0.23* | N/A | 0.34 | 0.10* |
| BVCW #3 | well | duplicate of BVCW #1 | 1 L | ** | ND | ND | ND | ND | ND |
| BVCW #4 | well | Spiked @ 0.5 ppb | 1 L | ** | 0.44 | 0.41 | N/A | 0.73 | 0.25* |
| WF1 #1 | well | | 1 L | 144 | ND | ND | ND | ND | ND |

Table 9A Continued

| Name | Type | Comments | Volume | (%) Resp | Measured Conc. (µg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Atr | Ala | Car | Cyn | Met |
| WF1 #2 | well | duplicate of WF1 #1 | 1 L | 147 | ND | ND | ND | ND | ND |
| WF1 #3 | well | Spiked @ 1 ppb | 1 L | 125 | 0.71 | 0.76 | 2.33 | 1.04 | N/A |
| WF1 #4 | well | Spiked @ 2 ppb | 1 L | ** | 2.30 | 1.58 | 4.72 | 2.46 | N/A |
| WF2 #1 | well | | 1 L | 116 | ND | ND | ND | ND | ND |
| WF2 #2 | well | duplicate of WF2 #1 | 1 L | 122 | ND | ND | ND | ND | ND |
| WF2 #3 | well | Spiked @ 0.25 ppb | 1 L | ** | 0.14* | 0.19* | N/A | 0.32* | 0.09* |
| WF2 #4 | well | Spiked @ 0.5 ppb | 1 L | 137 | ND | 0.41 | N/A | 0.64 | ND |
| WFSW #1 | well | | 1 L | 11 | ND | ND | ND | ND | ND |
| WFSW #2 | well | duplicate of WFSW #1 | 1 L | 150 | ND | ND | ND | ND | ND |
| WFSM 1 | well | | 800mL | 29 | ND | ND | ND | ND | ND |
| WFSM 2 | SM | | 1 L | 30 | ND | ND | ND | ND | ND |
| WFSM 2&3 Combined | SM | | 800 mL | 71 | ND | ND | ND | ND | ND |
| WFSM 3 | SM | | 1 L | 48 | ND | ND | ND | ND | ND |
| WFSM 4 #1 | SM | | 1 L | ** | ND | ND | ND | ND | ND |
| WFSM 4 #2 | SM | duplicate of WFSM 4 #1 | 1 L | 77 | ND | ND | ND | ND | ND |
| WFSM 4 #3 | SM | Spiked @ 2 ppb | 1 L | 75 | 0.80 | 1.31 | 0.63* | 2.10 | N/A |
| WF Amb To | Sea | Seawater at site of SM | 1 L | 144 | ND | ND | ND | ND | ND |
| TB #1 | blank | Travel blank | 1 L | 103 | ND | ND | ND | ND | ND |
| TB #2 | blank | duplicate of TB #1 | 1 L | ** | ND | ND | ND | ND | ND |
| EB #1 | blank | equipment blank | 1 L | 60 | ND | ND | ND | ND | ND |

Table 9A Continued

| Name | Type | Comments | Volume | (%) Resp | Measured Conc. (µg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Atr | Ala | Car | Cyn | Met |
| EB #2 | blank | duplicate of EB #1 | 1 L | ** | ND | ND | ND | ND | ND |
| LB #1 | blank | Reagent blank | 1 L | ** | ND | ND | ND | ND | ND |
| LB #2 | blank | duplicate of LB #1 | 1 L | ** | ND | ND | ND | ND | ND |
| LFB #2 | blank | Spiked @ 0.5 ppb | 1 L | ** | 0.39 | 0.42 | N/A | 0.66 | 0.28* |

Table 10A
February Samples

| Name | Type | Comments | Volume | (%) Resp | Measured Conc. (µg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Atr | Ala | Car | Cyn | Met |
| EV1 #1 | well | | 1 L | ** | ND | ND | ND | ND | ND |
| EV1 #2 | well | duplicate of EV1 #1 | 1 L | ** | ND | ND | ND | ND | ND |
| EV1 #3 | well | Spiked @ 0.5 ppb | 1 L | 116 | 0.45 | 0.23* | N/A | 0.47 | 0.11* |
| EV1 #4 | well | Spiked @ 0.25 ppb | 1 L | 45 | ND | 0.07* | N/A | 0.16* | 0.09* |
| EV2 #1 | well | | 1 L | ** | ND | ND | ND | ND | ND |
| EV2 #2 | well | duplicate of EV2 #1 | 1 L | 52 | ND | ND | ND | ND | ND |
| EV2 #3 | well | Spiked @ 1 ppb | 1 L | 37 | 0.88 | 0.83 | 2.52 | 1.04 | N/A |
| EV2 #4 | well | Spiked @ 2 ppb | 1 L | 17 | 0.52 | 1.22 | 3.17 | ND | N/A |
| EVF/R #1 | well | | 1 L | ** | ND | ND | ND | ND | ND |
| EVF/R #2 | well | duplicate of EVF/R #1 | 1 L | 130 | ND | ND | ND | ND | ND |
| EV Amb To | Sea | Seawater at site of SM | 1 L | 48 | ND | ND | ND | ND | ND |
| BV1 #1 | well | | 1 L | 142 | ND | ND | ND | ND | ND |
| BV1 #2 | well | duplicate of BV1 #1 | 1 L | 59 | ND | ND | ND | ND | ND |
| BV1 #3 | well | Spiked @ 0.25 ppb | 1 L | 48 | ND | 0.19* | N/A | 0.28* | 0.06* |
| BV1 #4 | well | Spiked @ 0.5 ppb | 1 L | 30 | 0.34* | 0.40 | N/A | 0.58 | 0.28* |
| BV2 #1 | well | | 1 L | 96 | ND | 0.05* | ND | ND | 0.04* |
| BV2 #2 | well | duplicate of BV2 #1 | 1 L | 82 | ND | ND | ND | ND | ND |
| BVCW #1 | well | | 1 L | ** | ND | ND | ND | ND | ND |
| BVCW #3 | well | Spiked @ 0.5 ppb | 1 L | 22 | ND | 0.27* | N/A | 0.38 | 0.12* |
| BVCW #4 | well | Spiked @ 0.5 ppb | 1 L | 73 | ND | 0.38 | N/A | 0.50 | 0.22* |

Table 10A Continued

| Name | Type | Comments | Volume | (%) Resp | Measured Conc. (µg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Atr | Ala | Car | Cyn | Met |
| BVSM 1 #1 | SM | | 1 L | 141 | ND | ND | ND | ND | ND |
| BVSM 1 #2 | SM | duplicate of BVSM 1 #1 | 1 L | ** | ND | ND | ND | ND | ND |
| BVSM 1 #3 | SM | Spiked @ 1 ppb | 1 L | 28 | 2.38 | 0.61 | ND | ND | N/A |
| BVSM 1 #4 | SM | Spiked @ 2 ppb | 1 L | 17 | 0.50 | .91 | 4.71 | 1.16 | N/A |
| BVSM 1&3 Combined | SM | | 1 L | 94 | ND | ND | ND | ND | ND |
| BVSM 3 #1 | SM | Spiked @ 0.5 ppb | 1 L | ** | 0.58 | 0.66 | N/A | 1.19 | 0.68 |
| BVSM 3 #2 | SM | | 1 L | ** | ND | ND | ND | ND | ND |
| BVSM 3 #3 | SM | duplicate of BVSM 3 #1 | 1 L | 40 | ND | ND | ND | ND | ND |
| BVSM 3&4 Combined | SM | | 600 mL | 50 | ND | ND | ND | ND | ND |
| BVSM 4 #1 | SM | | 1 L | | ND | ND | ND | ND | ND |
| BVSM 4 #2 | SM | Spiked @ 0.5 ppb | 1 L | 24 | ND | ND | ND | ND | ND |
| BVSM 4 #3 | SM | Spiked @ 1 ppb | 1 L | 118 | 0.83 | 1.39 | 13.0 | 0.26* | N/A |
| BVSM 4 #4 | SM | duplicate of BVSM 4 #1 | 1 L | | ND | ND | ND | ND | ND |
| BV Amb To | Sea | Seawater at site of SM | 1 L | 31 | ND | ND | ND | ND | ND |
| WF1 #1 | well | | 1 L | 53 | ND | ND | ND | ND | ND |
| WF1 #2 | well | duplicate of WF1 #1 | 1 L | 122 | ND | ND | ND | ND | ND |
| WF1 #3 | well | Spiked @ 0.5 ppb | 1 L | 24 | 0.33* | 0.06* | N/A | 0.48 | 0.18* |
| WF1 #4 | well | Spiked @ 0.25 ppb | 1 L | 51 | ND | 0.08* | N/A | 0.23* | ND |
| WF2 #1 | well | | 1 L | | ND | ND | ND | ND | ND |

Table 10A Continued

| Name | Type | Comments | Volume | (%) Resp | Measured Conc. (μg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Atr | Ala | Car | Cyn | Met |
| WF2 #2 | well | duplicate of WF2 #1 | 1 L | 115 | ND | ND | ND | ND | ND |
| WF2 #3 | well | Spiked @ 1 ppb | 1 L | ** | 1.09 | 0.89 | 19.3 | 1.31 | N/A |
| WFSW #1 | well | | 1 L | 41 | ND | ND | ND | ND | ND |
| WFSW #2 | well | duplicate of WFSW #1 | 1 L | 20 | ND | ND | ND | ND | ND |
| WFSM 1 | SM | | 750 mL | ** | ND | ND | ND | ND | ND |
| WFSM 2 | SM | | 1 L | 58 | ND | ND | ND | ND | ND |
| WFSM 3 | SM | | 1 L | 46 | ND | ND | ND | ND | ND |
| WFSM 3&4 Combined | SM | | 1 L | ** | ND | ND | ND | ND | ND |
| WFSM 4 | SM | | 1 L | 141 | ND | ND | ND | ND | ND |
| WF Amb To | Sea | Seawater at site of SM | 1 L | 68 | ND | ND | ND | ND | ND |
| CH2 #1 | well | | 1 L | 65 | ND | ND | ND | ND | ND |
| CH3 #1 | well | Spiked @ 0.5 ppb | 1 L | 57 | 0.32* | 0.22* | N/A | 0.31* | 0.08* |
| CH3 #2 | well | | 1 L | ** | ND | ND | ND | ND | ND |
| CH3 #3 | well | duplicate of CH3 #2 | 1 L | 102 | ND | ND | ND | ND | ND |
| CH3 #4 | well | Spiked @ 0.25 ppb | 1 L | 107 | ND | 0.22* | N/A | 0.34 | 0.06* |
| CH5 #1 | well | | 1 L | 54 | ND | ND | ND | ND | ND |
| CH5 #2 | well | duplicate of CH5 #1 | 1 L | 83 | ND | ND | ND | ND | ND |
| CH5 #3 | well | Spiked @ 0.25 ppb | 1 L | 72 | ND | 0.06* | N/A | 0.19* | ND |
| CHSM 2 | SM | | 1 L | 18 | ND | ND | ND | ND | 0.32* |

Table 10A Continued

| Name | Type | Comments | Volume | (%) Resp | Measured Conc. (µg/L) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Atr | Ala | Car | Cyn | Met |
| CHSM 3 | SM | | 1 L | 21 | ND | ND | ND | ND | ND |
| CHSM 4 | SM | | 1 L | 52 | ND | ND | ND | ND | ND |
| CH Amb To | Sea | Seawater at site of SM | 1 L | 60 | ND | ND | ND | ND | ND |
| EB #1 | blank | equipment blank | 1 L | 130 | ND | ND | ND | ND | ND |
| EB #2 | blank | duplicate of EB #1 | 1 L | 33 | ND | ND | ND | ND | ND |
| TB | blank | Travel blank | 1 L | 109 | ND | ND | ND | ND | ND |
| LB #1 | blank | laboratory blank | 1 L | 29 | ND | ND | ND | ND | ND |
| LB #2 | blank | duplicate of LB #1 | 1 L | ** | ND | ND | ND | ND | ND |
| LB #3 | blank | duplicate of LB #1 | 1 L | ** | ND | ND | ND | ND | ND |
| LB #4 | blank | duplicate of LB #1 | 1 L | 31 | ND | ND | ND | ND | ND |
| LFB #1 | blank | Spiked @ 0.25 ppb | 1 L | 129 | 0.55 | 0.30* | N/A | 0.44 | 0.22* |
| LFB #2 | blank | Spiked @ 0.5 ppb | 1 L | 105 | 0.56 | 0.54 | N/A | 0.73 | 0.43* |
| LFB #3 | blank | Spiked @ 1 ppb | 1 L | 127 | 0.80 | 0.81 | 7.53 | 1.12 | N/A |
| LFB #4 | blank | Spiked @ 2 ppb | 1 L | 49 | 0.92 | 1.07 | 7.43 | 1.29 | N/A |

# Appendix B

## Chronology

The date of all the important procedures performed in the study are listed in table B1.

Table B1
Chronology of Data Collection

| | |
|---|---|
| April 1992 | |
| 3/28-3/29 | Collected samples |
| 3/30-4/2 | Extracted samples |
| 4/9 | Injected samples into the GC/FID |
| 4/15-4/16 | Injected samples into the GC/MS |
| 4/23 | Injected samples into the GC/MS |
| May 1992 | |
| 5/5-5/8 | Collected samples |
| 5/9-5/11 | Extracted samples |
| 5/18-5/19 | Injected samples into the GC/MS |
| 5/30 | Injected calibration standards into the GC/MS |
| June 1992 | |
| 6/18-6/20 | Collected samples |
| 6/21-6/22 | Extracted samples |
| 6/25-6/27 | Injected samples into the GC/FID |
| 6/30 | Injected samples into the GC/MS |
| 7/2-7/4 | Injected samples into the GC/ECD |
| 7/1 | Extracted check standards |
| 7/1 | Injected calibration standards into the GC/ECD |
| 7/8 | Injected check standards into the GC/MS |
| 8/2 | Injected samples with possible pesticides into the GC/MS |
| July 1992 | |
| 7/18-7/20 | Collected samples |
| 7/21-7/22 | Extracted samples |
| 7/26-7/28 | Injected samples into the GC/ECD |
| 8/10 | Injected samples into the GC/ECD |

Table B1 continued

| | |
|---|---|
| 8/11 | Injected samples into the GC/FID |
| 8/19 | Injected Calibration standard into the GC/MS |
| August 1992 | |
| 8/24-8/26 | Collected samples |
| 8/26-8/27 | Extracted samples |
| 8/30 | Extracted samples |
| 9/2-9/4 | Injected samples into the GC/ECD |
| 9/5 | Injected samples into the GC/MS |
| 9/9 | Injected samples into the GC/MS |
| 9/9 | Injected samples into the GC/ECD with DB-5 column |
| 9/10-9/11 | Injected samples into the GC/ECD with DB-210 column |
| 9/17-9/18 | Injected samples into the GC/ECD with DB-210 column |
| 9/22 | Injected samples into the GC/MS |
| 10/6-10/7 | Injected calibration standards into the GC/ECD with DB-210 column |
| October 1992 | |
| 10/9-10/11 | Collected samples |
| 10/12-10/14 | Extracted samples |
| 10/17 | Injected Calibration standards into the GC/MS |
| 10/25-10/27 | Injected samples into the GC/ECD with DB-5 column |
| 10/28-10/31 | Injected samples into the GC/ECD with DB-210 column |
| 11/5-11/6 | Injected calibration standards into the GC/ECD with DB-210 column |
| 11/9-11/10 | Injected calibration standards into the GC/ECD with DB-210 column |

Table B1 continued

| November 1992 | |
|---|---|
| 11/13-11/15 | Collected samples |
| 11/16-11/18 | Extracted samples |
| 12/1-12/2 | Injected samples into the GC/ECD with DB-210 column |
| December 1992 | |
| 12/4-12/6 | Collected samples |
| 12/7-12/8 | Extracted samples |
| 12/10-12/12 | Injected samples into the GC/ECD with DB-210 column |
| 12/31, 1/3, 1/6 | Injected samples into the GC/ECD with the DB-5 column |
| 1/4 | Autosampler installed on GC/ECD |
| January 1993 | |
| 1/9-1/11 | Collected samples |
| 1/12-1/13 | Extracted samples |
| 1/19-1/20 | Injected samples into the GC/ECD with DB-5 column |
| 1/21-1/22 | Injected calibration standards into the GC/ECD with DB-5 column |
| 1/23-1/24 | Injected calibration standards into the GC/ECD with DB-210 column |
| 1/24-1/25 | Injected samples into the GC/ECD with DB-210 column |
| 1/26-1/27 | Re-injected samples with pesticides detected into the GC/ECD with DB-210 column |
| 1/29-1/30 | Re-injected samples with pesticides detected into the GC/ECD with DB-5 column |
| February 1993 | |
| 2/11-2/14 | Collected samples |
| 2/15-2/16 | Extracted samples |

Table 1B Continued

| | |
|---|---|
| 2/17-2/18 | Injected samples into the GC/ECD with DB-5 column |
| 2/19-2/21 | Injected samples into the GC/ECD with DB-210 column |

## Appendix C

## Statistical Analysis

For the project, only standard statistical tests were performed, including mean, standard deviation, and linear regression. For the instrument limit of detection (LOD) and method detection limit (MDL), the standard deviation of the samples in question was multiplied by the value of the t-test at a 99% confidence level. The LOD and MDL's were given in the methods and materials section under tables 3 and 4. The following tables contain the least squares regression equations for the pesticides, separated by instrument, column, and time.

Table 1C
Regression Output for the GC/MS in June, 1992

| Pesticide | $R^2$ | Regression Output, where x = ng injected on column |
|---|---|---|
| Atrazine | 0.97 | 806853x - 131959 |
| Alachlor | 0.97 | 458920x - 281977 |
| Carbofuran | 0.84 | 586335x - 1357451 |

* Note y predicts pesticide concentration in $\mu g/L$

Table 2C
Regression Output for the GC/MS in Oct., 1992

| Pesticide | $R^2$ | Regression Output, where x = ng injected on column |
|---|---|---|
| Alachlor | 0.96 | 414939x - 741467 |
| Atrazine | 0.91 | 1146072x - 4260664 |
| Carbofuran | 0.85 | 664297x - 3934340 |
| Metolachlor | 0.97 | 1062405 - 1720167 |

* Note y predicts pesticide concentration in $\mu g/L$

Table 3C
Regression Output for GC/FID in June 1992

| Pesticide | $R^2$ | Regression Output, where x = ng injected on column |
|---|---|---|
| Alachlor | 0.55 | 855x - 19.8 |
| Atrazine | 0.63 | 586x - 980 |
| Carbofuran | 0.53 | 1285x - 3982 |
| Cyanazine | 0.42 | 298x - 131 |

* Note y predicts pesticide concentration in μg/L

Table 4C
Regression Output for GC/ECD with DB-5 Column in Aug. 1992

| Pesticide | $R^2$ | Regression Output, where x = ng injected on the column |
|---|---|---|
| Alachlor | 0.70 | 72943x + 144953 |
| Atrazine | 0.97 | 4694x + 7615 |
| Carbofuran | 0.46 | 3520x - 9747 |
| Cyanazine | 0.80 | 58382x -18546 |

* Note y predicts pesticide concentration in $\mu g/L$

Table 5C
Regression Output for GC/ECD with DB-5 column in Jan. 1993

| Pesticide | $R^2$ | Regression Output, where x = ng inject on column |
|---|---|---|
| Alachlor | 0.992 | 465934x + 87653 |
| Atrazine | 0.994 | 59391x - 41172 |
| Carbofuran | 0.97 | 4859x - 9983 |
| Cyanazine/Metolachlor* | 0.88 | 934673x - 624817 |

* Note that cyanazine and metolachlor were not resolved on the DB-5 column.
* Note y predicts pesticide concentration in μg/L

Table 6C
Regression Output for the GC/ECD with DB-210 column in Oct. 1992

| Pesticide | $R^2$ | Regression Output, where x = ng injected on the column |
|---|---|---|
| Alachlor | 0.97 | 205166x + 11270 |
| Atrazine | 0.85 | 6064x - 12837 |
| Cyanazine | 0.86 | 71000x + 43649 |
| Metolachlor | 0.88 | 105340x + 19405 |

* Note y predicts pesticide concentration in $\mu g/L$

Table 7C
Regression Output for the GC/ECD with DB-210 column in Nov. 1992

| Pesticide | $R^2$ | Regression Output, where x = ng injected on column |
|---|---|---|
| Alachlor | 0.992 | 306973x + 19426 |
| Atrazine | 0.81 | 11868x + 20666 |
| Carbofuran | 0.78 | 11099x + 13368 |
| Cyanazine | 0.98 | 118721x + 9292 |
| Metolachlor | 0.97 | 145449x + 43303 |

* Note y predicts pesticide concentration in $\mu g/L$

Table 8C
Regression Output for GC/ECD with DB-210 column in Jan. 1992

| Pesticide | $R^2$ | Regression Output, where x = ng injected on the column |
|---|---|---|
| Alachlor | 0.99 | 734129x + 48699 |
| Atrazine | 0.70 | 33827x + 11668 |
| Cyanazine | 0.94 | 50939x - 96479 |
| Metolachlor | 0.997 | 366665x + 72882 |

* Note y predicts pesticide concentration in µg/L

Table 9C
Response factor Output for the GC/MS in Feb.,1992

| Pesticide | Response Factor for Phenanthrene-$d_{10}$ |
|---|---|
| Alachlor | 0.0946 |
| Atrazine | 0.1236 |
| Carbofuran | 0.0949 |
| Cyanazine | 0.0391 |
| Metolachlor | 0.2564 |

# Appendix D

## Nutrient Data

The seepage meter discharge, nutrient flux in the seepage, and nutrient concentration data were calculated by Dr. William Reay. The upland well data was shown in Table 1D, and the submarine groundwater discharge data was included in Table 2D.

Table 1D
Discharge, Sediment Nutrient Flux, and Nitrate Concentration in the Seepage Water at the Study Sites

| Month | Discharge ($L/m^2*hr$) | Conc.[a] $NO_3^-$ (mg/L as N) | Flux $NO_3^-$ ($mg/m^2*hr$) | Flux $NH_4^+$ ($mg/m^2*hr$) |
|---|---|---|---|---|
| **Agricultural site 1** | | | | |
| May | 1.21 | 1.04 | 4.20 | 0.24 |
| June | 0.62 | | | |
| July | 0.12 | 0.03 | - 0.04 | 0.06 |
| Aug | 0.43 | 0.14 | 0.11 | 0.32 |
| Oct | 1.27 | 2.83 | 14.82 | 0.09 |
| Nov | 0.95 | 4.05 | 20.15 | - 0.02 |
| Feb | 2.09 | 0.91 | 5.49 | 0.21 |
| **Agricultural site 2** | | | | |
| May | 0.87 | 0.63 | 1.91 | 0.05 |
| June | 0.69 | 0.25 | 0.75 | 0.02 |
| July | 1.18 | 0.06 | 0.02 | - 0.02 |
| Oct | 0.56 | 0.35 | 0.79 | 0.03 |
| Nov | 0.23 | 0.47 | 0.13 | 0.02 |
| Feb | 0.76 | 1.80 | 5.39 | 0.03 |
| **Agricultural site 3** | | | | |
| May | 0.46 | 0.01 | - 0.19 | 0.18 |
| June | 1.04 | 0.01 | - 0.22 | 0.05 |
| July | 0.36 | 0.02 | 0.02 | - 0.01 |
| Aug | 0.81 | 0.01 | 0.04 | 1.29 |
| Oct | 1.47 | 3.09 | 11.66 | 0.13 |
| Nov | 0.30 | 0.06 | - 1.19 | 0.11 |
| Dec | 0.21 | 0.06 | - 0.52 | |
| Jan | | | | |
| Feb | 0.10 | 0.02 | - 0.25 | 0.02 |

Table 1D Continued

| Agricultural site 4 | | | | |
|---|---|---|---|---|
| Month | Discharge ($L/m^2*hr$) | Conc.[a] $NO_3^-$ (mg/L as N) | Flux $NO_3^-$ | $NH_4^+$ ($mg/m^2*hr$) |
| May | 0.40 | 0.05 | 0.06 | 0.09 |
| June | 0.38 | 0.01 | | |
| July | 0.19 | 0.03 | - 0.03 | 0.30 |
| Oct | 0.48 | 0.33 | 1.03 | 0.29 |
| Nov | 0.09 | 0.24 | 0.41 | 0.13 |
| Dec | 0.30 | 0.06 | 0.19 | |
| Jan | 0.68 | 1.66 | 4.82 | 0.13 |
| Feb | 0.75 | 0.49 | 1.33 | 0.06 |

a Values are for nitrate concentrations measured in seepage water, which is a combination of groundwater and bay water. Abient nitrate concentrations in the bay water ranged from <0.01 to 1.47 mg/L as N.

Table 2D
Upland Groundwater Nutrient Quality at Study Sites

| Agricultural site 2 | | | |
|---|---|---|---|
| Month | $NO_3^-$, (mg/L as N) | $PO_4^{-3}$, (mg/L) | $NH_4^+$, (mg/L as N) |
| May | 13.09 | 0.005 | 0.04 |
| June | 14.83 | 0.006 | 0.03 |
| July | 13.76 | 0.017 | 0.05 |
| Oct | 13.78 | 0.003 | 0.07 |
| Nov | 14.22 | 0.011 | 0.04 |
| Dec | 13.96 | | |
| Feb | 16.60 | <0.001 | 0.05 |
| Agricultural site 3 | | | |
| May | 13.73 | 0.015 | 0.03 |
| June | 11.17 | 0.027 | 0.05 |
| July | 7.86 | 0.038 | 0.04 |
| Aug | 20.33 | 0.039 | 0.06 |
| Oct | 19.57 | 0.042 | 0.038 |
| Nov | 15.68 | 0.022 | 0.02 |
| Dec | 17.32 | 0.023 | |
| Jan | 12.93 | 0.017 | 0.029 |
| Feb | 18.6 | 0.014 | 0.01 |
| Agricultural site 1 | | | |
| May | 14.21 | | 0.031 |
| June | 18.42 | | 0.038 |
| July | 12.86 | 0.034 | 0.013 |
| Aug | 13.27 | 0.012 | 0.034 |
| Oct | 11.71 | 0.008 | 0.051 |
| Nov | 17.23 | 0.020 | 0.016 |
| Jan | 15.14 | 0.002 | 0.043 |

Table 2D Continued

| Agricultural site 1, continued | | | |
|---|---|---|---|
| Month | $NO_3^-$, (mg/L as N) | $PO_4^{-3}$, (mg/L) | $NH_4^+$, (mg/L as N) |
| Feb | 17.48 | 0.03 | 0.03 |
| Agricultural site 4 | | | |
| May | 9.98 | 0.005 | 0.030 |
| June | 11.71 | 0.004 | 0.05 |
| July | 10.92 | 0.035 | 0.04 |
| Oct | 8.82 | 0.005 | 0.14 |
| Nov | 13.98 | 0.017 | 0.02 |
| Jan | 20.60 | 0.011 | 0.018 |
| Feb | 10.56 | 0.005 | 0.01 |

## Appendix E

## Soil Sample Data

Starting in July 1992, Douglas Schicho, a Master's degree candidate at VPI & SU, took soil samples at all the sites as the water samples were being collected. Samples were taken from the area of the monitored wells and from the near shore sediment at each site. The soil samples were soxhlex extracted and injected on the GC/MS. Table 1E contained the LOD for the pesticides, and the data from the soil samples was included in Table 2E.

Abbreviations

BV: Agricultural site 1

CH: Agricultural site 2

EV: Agricultural site 3

WF: Agricultural site 4

F: Field sample

OS: Off-shore (sediment) sample

Table 1E
Instrument LOD for the Soil Samples, after Schicho

| Pesticide | LOD, in mg/kg (ppm) |
|---|---|
| Atrazine | 1.1 |
| Alachlor | 2.5 |
| Cyanazine | 1.9 |
| Metolachlor | 0.3 |

* Note that LOD did not include the extraction concentration factor

Table 2E
Soil Sample Data, after Schicho (all numbers are in mg/kg)

| Extraction date | Sample | Sample Type | Carb | Atr | Ala | Met | Cyan |
|---|---|---|---|---|---|---|---|
| 7/15/92 | CHF 6/19 | FIELD SAMPLE | nd | nd | nd | 0.1105 | nd |
| 7/14/92 | EVF 6/18 | FIELD SAMPLE | nd | nd | nd | 0.0269 | nd |
| 7/14/92 | BVF 6/18 | FIELD SAMPLE | nd | nd | 0.1452 | 0.0295 | nd |
| 7/14/92 | CHOS 6/19 | SEDIMENT | nd | nd | nd | nd | nd |
| 7/14/92 | EVOS 6/18 | SEDIMENT | nd | nd | nd | nd | nd |
| 7/15/92 | BVOS 6/18 | SEDIMENT | nd | nd | nd | nd | nd |
| 7/15/92 | WFOS 6/19 | SEDIMENT | nd | nd | nd | nd | nd |
| 7/25/92 | WFF 7/18 | FIELD SAMPLE | nd | nd | nd | nd | nd |
| 7/25/92 | BVF 7/17 | FIELD SAMPLE | nd | nd | 0.4842 | nd | nd |
| 7/26/92 | WFOS 7/19 | FIELD SAMPLE | nd | nd | nd | nd | nd |
| 7/25/92 | BVOS 7/18 | SEDIMENT | nd | nd | nd | nd | nd |
| 7/25/92 | EV#3Surf 7/18 | SEDIMENT | nd | nd | nd | nd | nd |
| 7/26/92 | EVSurf1 7/18 | SEDIMENT | nd | nd | nd | nd | nd |
| 7/26/92 | EVOS 7/18 | SEDIMENT | nd | nd | nd | nd | nd |
| 7/26/92 | EV3ft#2 7/18 | SEDIMENT | nd | nd | nd | nd | nd |
| 8/4/92 | EVLot#1 6' 7/18 | FIELD SAMPLE | nd | nd | nd | nd | nd |
| 8/4/92 | EVLot#3 7/18 | FIELD SAMPLE | nd | nd | nd | nd | nd |
| 8/4/92 | EV 4FT1 7/18 | FIELD SAMPLE | nd | nd | nd | nd | nd |

Table 2E Continued

| Extraction date | Sample | Sample Type | Carb | Atr | Ala | Met | Cyan |
|---|---|---|---|---|---|---|---|
| 8/4/92 | EV WT#2 7/18 | FIELD SAMPLE | nd | nd | nd | nd | nd |
| 8/4/92 | EVSurf2 7/18 | SEDIMENT | nd | nd | nd | nd | nd |
| 8/5/92 | EV 3ft3 7/18 | SEDIMENT | nd | nd | nd | nd | nd |
| 10/21/92 | BVF 10/10 | FIELD SAMPLE | nd | nd | 0.162 | nd | nd |
| 10/25/92 | BVF 10/10 | MATRIX SPIKE | 5.693 | 2.706 | 3.456 | 0.2236 | 2.456 |
| 10/21/92 | WFF 10/11 | FIELD SAMPLE | nd | nd | nd | 0.0083 | nd |
| 10/21/92 | CHF 10/11 | FIELD SAMPLE | nd | nd | nd | 0.0614 | nd |
| 10/25/92 | EVF 10/10 | FIELD SAMPLE | nd | nd | nd | nd | nd |
| 10/21/92 | LB 10/21 | LAB BLANK | nd | nd | nd | nd | nd |
| 10/22/92 | BVOS 10/10 | SEDIMENT | nd | nd | nd | nd | nd |
| 10/22/92 | WFOS 10/11 | SEDIMENT | nd | nd | nd | nd | nd |
| 10/25/92 | EVOS 10/10 | SEDIMENT | nd | nd | nd | nd | nd |
| 10/25/92 | CHOS 10/11 | SEDIMENT | nd | nd | nd | nd | nd |
| 11/18/92 | BVF 11/14 | FIELD SAMPLE | nd | nd | nd | nd | nd |
| 11/18/92 | EVF 11/14 | FIELD SAMPLE | nd | nd | nd | nd | nd |
| 11/19/92 | CHF 11/15 | FIELD SAMPLE | nd | nd | nd | 0.0547 | nd |
| 11/19/92 | WFF 11/15 | FIELD SAMPLE | nd | nd | nd | nd | nd |
| 11/19/92 | WFOS 11/15 | SEDIMENT | nd | nd | nd | nd | nd |
| 11/19/92 | CHOS 11/15 | SEDIMENT | nd | nd | nd | nd | nd |

Table 2E Continued

| Extraction date | Sample | Sample Type | Carb | Atra | Alac | Met | Cyan |
|---|---|---|---|---|---|---|---|
| 11/18/92 | EVOS 11/14 | SEDIMENT | nd | nd | nd | nd | nd |
| 11/18/92 | BVOS 11/14 | SEDIMENT | nd | nd | nd | nd | nd |
| 12/8/92 | EVF 12/5 | FIELD SAMPLE | nd | nd | nd | 0.0074 | nd |
| 12/8/92 | BVF 12/5 | FIELD SAMPLE | nd | nd | 0.0198 | nd | nd |
| 12/9/92 | WFF 12/6 | FIELD SAMPLE | nd | nd | nd | 0.0071 | nd |
| 12/8/92 | EVOS 12/5 | SEDIMENT | nd | nd | nd | nd | nd |
| 12/8/92 | BVOS 12/5 | SEDIMENT | nd | nd | nd | nd | nd |
| 12/9/92 | WFOS 12/6 | SEDIMENT | nd | nd | nd | nd | nd |
| 12/9/92 | WFOS 12/6 | MATRIX SPIKE | nd | 5.430 | 1.502 | 8.4971 | 2.7955 |
| 1/12/93 | WFF 1/11 | FIELD SAMPLE | nd | nd | nd | 0.0087 | nd |
| 1/12/93 | BVF 1/10 | FIELD SAMPLE | nd | nd | nd | 0.0172 | nd |
| 1/12/93 | EVF 1/10 | FIELD SAMPLE | nd | nd | nd | nd | nd |
| 1/12/93 | WFOS 1/11 | SEDIMENT | nd | nd | nd | nd | nd |
| 1/25/93 | EVF 1/10 #4 | REP. MAT. SPIKE | nd | 0.9236 | 1.0351 | 1.0095 | 1.3128 |
| 1/25/93 | EVF 1/10 #3 | REP. MAT. SPIKE | nd | 1.0206 | 1.0203 | 1.0071 | 1.7006 |
| 1/25/93 | EVF 1/10 #2 | REP. MAT. SPIKE | nd | 0.7464 | 0.8051 | 0.7844 | 0.8785 |
| 1/25/93 | EVF 1/10 #1 | REP. MAT. SPIKE | nd | 1.0759 | 1.1046 | 1.053 | 1.8114 |
| 2/17/93 | BVF 2/12 | FIELD SAMPLE | nd | nd | nd | nd | nd |
| 2/17/93 | EVF 2/12 | FIELD SAMPLE | nd | nd | nd | nd | nd |

Table 2E Continued

| Extraction date | Sample | Sample Type | Carb | Atra | Ala | Met | Cyan |
|---|---|---|---|---|---|---|---|
| 2/18/93 | CHF 2/13 | FIELD SAMPLE | nd | nd | nd | 0.0067 | nd |
| 2/18/93 | WFF 2/13 | FIELD SAMPLE | nd | nd | nd | nd | nd |
| 2/17/93 | EVOS 2/12 | SEDIMENT | nd | nd | nd | nd | nd |
| 2/17/93 | BVOS 2/12 | SEDIMENT | nd | nd | nd | nd | nd |
| 2/18/93 | WFOS 2/13 | SEDIMENT | nd | nd | nd | nd | nd |

## Appendix F

## Ohmicron Sample Data

Each month from May to February 1992, an independent environmental company, Ohmicron Corporation, received one water sample from each well and seepage meter. Ohmicron used a immunoassay procedure to test the samples for the pesticides included in the study. Table 1F listed the LOD's for the pesticides used in the study. The sampling data was incorporated in tables 2F through 10F.

Abbreviations were:

BV: Agricultural Site 1

CH: Agricultural Site 2

EV: Agricultural Site 3

WF: Agricultural Site 4

ST: Wetlands Site 1

nd: not detected

EB: Equipment blank

LB: Laboratory blank

LFB: Laboratory fortified blank (pesticides added)

TB: Travel blank

Table 1F
Ohmicron Limits of Detection

| Pesticide | Concentration, μg/L |
|---|---|
| Alachlor | 0.05 |
| Atrazine | 0.04 |
| Carbofuran | 0.06 |
| Cyanazine | 0.04 |
| Metolachlor | 0.06 |

* Note that the pesticides' MDLs were not provided, but are assumed to be higher.

Table 2F
May Ohmicron Sample Results

| Virginia Tech ID | Ohmicron ID | Spike Level | Atr | Cyan | Ala | Metol | Carb |
|---|---|---|---|---|---|---|---|
| WFAmbTo | 1a | | nd | nd | nd | nd | nd |
| CHAmbTo | 2a | | nd | nd | nd | nd | nd |
| BVAmbTo | 3a | | nd | nd | nd | nd | nd |
| EVAmbTo | 4a | | nd | nd | nd | nd | nd |
| LFB #2 | 5a | 2 µg/L | 1.19 | 1.21 | 1.28 | 1.18 | 0.46 |
| EB #2 | 6a | | nd | nd | nd | nd | nd |
| EB #1 | 7a | | nd | nd | nd | nd | nd |
| BVSM 3#2 | 8a | | nd | nd | nd | nd | nd |
| BVSM 1 | 9a | | nd | nd | nd | nd | nd |
| BVSM 2 | 10a | | nd | nd | nd | nd | nd |
| BVSM 3 | 11a | | nd | nd | nd | nd | nd |
| BVSM 4 | 12a | | nd | nd | nd | nd | nd |
| BVCW #2 | 13a | | nd | nd | nd | nd | nd |
| Tvl Blank | 14a | | nd | nd | nd | nd | nd |
| BV2 #2 | 15a | | nd | nd | 0.15 | nd | nd |
| Lab Blank #1 | 16a | | nd | nd | nd | nd | nd |
| BV1 #2 | 17a | | nd | nd | 0.18 | nd | nd |
| BV2 #1 | 18a | | nd | nd | 0.1 | nd | nd |
| BV1 #1 | 19a | | nd | nd | 0.23 | nd | nd |
| CHNew #1 | 20a | | nd | nd | nd | 0.1 | nd |
| BVCW #1 | 21a | 2 µg/L | 1.48 | 0.16 | 2.66 | 2.61 | 0.1 |
| BVCW #3 | 22a | | nd | 0.06 | nd | nd | nd |
| EV2 #1 | 23a | | nd | nd | nd | nd | nd |
| CH2 | 24a | | nd | nd | nd | nd | 0.33 |
| WFSM 1-4 | 25a | | nd | nd | nd | nd | nd |
| EVF/R #1 | 26a | | nd | nd | nd | nd | nd |
| EV2 #2 | 27a | 2 µg/L | 2.13 | 0.16 | 2.65 | 2.66 | nd |
| EV2 #3 | 28a | | nd | nd | nd | nd | nd |
| EV1 #1 | 29a | 2 µg/L | 1.26 | 0.11 | 2.31 | 2.49 | nd |

Table 2F Continued

| Virginia Tech ID | Ohmicron ID | Spike Level | Atr | Cyan | Ala | Met | Carb |
|---|---|---|---|---|---|---|---|
| EV1 #2 | 30a | | nd | nd | nd | nd | nd |
| EVF/R #2 | 31a | | nd | nd | nd | nd | nd |
| EV1 #3 | 32a | | nd | nd | nd | nd | nd |
| CHSM 3 | 33a | | nd | nd | nd | nd | nd |
| EVSM 1&4 | 34a | | nd | nd | nd | nd | nd |
| CHSM 4 | 35a | 10 µg/L | 8.5 | 0.3 | 9.5 | 13.6 | 0.16 |
| EVSM 2 | 36a | | nd | nd | nd | nd | nd |
| WF | 37a | | nd | nd | nd | nd | nd |
| WFSW | 38a | | nd | nd | nd | nd | nd |
| CH5 | 39a | | nd | nd | nd | nd | nd |
| CH | 40a | | nd | nd | nd | nd | nd |

Table 3F
June Ohmicron Sample Results

| Virginia Tech ID | Ohmicron ID | Spike Level | Atr | Cyan | Ala | Met | Carb |
|---|---|---|---|---|---|---|---|
| EVF/R | 1b | | nd | nd | nd | nd | nd |
| EV2 | 2b | | nd | nd | nd | nd | nd |
| BVCW | 3b | | nd | nd | nd | nd | nd |
| CHNew | 4b | | nd | nd | nd | nd | nd |
| WFSW #2 | 5b | | nd | nd | nd | nd | nd |
| WFSW #1 | 6b | | nd | nd | nd | nd | nd |
| BV1 | 7b | | nd | nd | 0.19 | nd | nd |
| WF1 #1 | 8b | | nd | nd | nd | nd | nd |
| BVSM 1 | 9b | | nd | nd | nd | nd | nd |
| WF2 #2 | 10b | | nd | nd | nd | nd | nd |
| CHSM 2 | 11b | | nd | nd | nd | nd | nd |
| CH2 | 12b | | nd | nd | nd | nd | nd |
| WF2 #1 | 13b | | nd | nd | nd | nd | nd |
| EV1 | 14b | | nd | nd | nd | nd | nd |
| BV2 | 15b | | nd | nd | 0.1 | nd | nd |
| BVSM 4 | 16b | | nd | nd | nd | nd | nd |
| WF1 #2 | 17b | | nd | nd | nd | nd | nd |

Table 4F
July Ohmicron Sample Results

| Virginia Tech ID | Ohmicron ID | Spike Level | Atr | Cyan | Ala | Met | Carb |
|---|---|---|---|---|---|---|---|
| EV1 #4 | 1c | 4 µg/L | 4.9 | 7.1 | 6.6 | 0.06 | 6.76 |
| EV1 #3 | 2c | 2 µg/L | 9.4 | 12 | 11.5 | 0.16 | 9.88 |
| WF1 #4 | 3c | 4 µg/L | 14.5 | 15.6 | 19.4 | 0.16 | 11.92 |
| WF1 #3 | 4c | 2 µg/L | 3.69 | 5.7 | 5.8 | 0.06 | 3.65 |
| WF1 | 5c | | nd | nd | nd | nd | nd |
| BV2 | 6c | | nd | nd | 0.09 | nd | nd |
| EV1 | 7c | | nd | nd | nd | nd | nd |
| LB #3 | 8c | | nd | nd | nd | nd | nd |
| BV2 #3 | 9c | 2 µg/L | 4.3 | 7.4 | 7.8 | 0.07 | 6.36 |
| CH5 #3 | 10c | 2 µg/L | 4.1 | 8.9 | 7.2 | 0.11 | 5.64 |
| EVF/R | 11c | | nd | nd | nd | nd | nd |
| WFSW | 12c | | nd | nd | nd | nd | nd |
| LFB #1 | 13c | 2 µg/L | nd | nd | nd | nd | nd |
| BV2 #4 | 14c | 4 µg/L | 11.3 | 15.4 | 14.6 | 0.17 | 10.16 |
| LB #2 | 15c | | nd | nd | nd | nd | nd |
| LB #1 | 16c | | nd | nd | nd | nd | nd |
| CH5 #4 | 17c | 4 µg/L | 10.4 | 14.4 | 14.2 | 0.18 | 9.64 |
| EV2 | 18c | | nd | nd | nd | nd | nd |
| CH5 | 19c | | nd | nd | nd | nd | nd |
| CH2 | 20c | | nd | nd | nd | nd | nd |
| WF2 | 21c | | nd | nd | nd | nd | nd |
| WFSM 2 | 22c | | nd | nd | nd | nd | nd |
| BV1 | 23c | | nd | nd | 0.27 | 0.05 | nd |
| CHSM 4 | 24c | | nd | nd | nd | nd | nd |
| WFSM 1 | 25c | | nd | nd | nd | nd | nd |
| CHNew | 26c | | nd | nd | nd | nd | nd |
| CHSM 1 | 27c | | nd | 0.05 | nd | nd | nd |
| BVCW | 28c | | nd | nd | nd | nd | nd |

Table 5F
August Ohmicron Sample Results

| Virginia Tech ID | Ohmicron ID | Spike Level | Atr | Cyan | Ala | Met | Carb |
|---|---|---|---|---|---|---|---|
| BV2 | 1d | | 0.13 | nd | 0.61 | nd | nd |
| Hopper | 2d | | nd | nd | 0.06 | nd | nd |
| WF1 #4 | 3d | 4 µg/L | 3.8 | 4.5 | 4.67 | 6.92 | 4.94 |
| EV1 | 4d | | nd | nd | nd | nd | nd |
| EVF/R | 5d | | nd | nd | 0.09 | nd | nd |
| WFSM 4 | 6d | | 0.36 | 0.06 | 0.21 | nd | nd |
| EV2 | 7d | | nd | nd | nd | nd | nd |
| BVCW #1 | 8d | | 0.36 | nd | 0.64 | nd | nd |
| CHSM 3 | 9d | | 0.5 | 0.06 | 0.19 | nd | nd |
| WFSM 3 | 10d | | 0.51 | 0.09 | 0.28 | nd | nd |
| EB | 11d | | 0.07 | nd | nd | nd | nd |
| CH3 | 12d | | nd | nd | nd | nd | nd |
| BVSM 1 | 13d | | 0.14 | nd | 0.11 | nd | nd |
| CHSM 1 | 14d | | 0.47 | nd | 0.09 | nd | nd |
| WFSM 2 | 15d | | 0.24 | nd | 0.06 | nd | nd |
| LFB #3 | 16d | 4 µg/L | 8.3 | 7.9 | 6.9 | 1.42 | 4.56 |
| BVCW | 17d | | 0.12 | nd | 0.07 | nd | nd |
| CH5 | 18d | | nd | nd | nd | nd | nd |
| CH2 #1 | 19d | | nd | nd | nd | nd | nd |
| LFB #1 | 20d | 2 µg/L | 3.32 | 3.8 | 3.83 | 0.37 | 2.5 |
| WFSW | 21d | | nd | nd | nd | nd | nd |
| WF1 | 22d | | nd | nd | nd | nd | nd |
| WF1 #2 | 23d | 2 µg/L | 2.45 | 2.43 | 2.95 | 4.94 | 2.8 |
| NOLABEL | 24d | | 0.11 | nd | nd | nd | nd |

Table 6F
October Ohmicron Sample Results

| Virginia Tech ID | Ohmicron ID | Spike Level | Atr | Cyan | Ala | Met | Carb |
|---|---|---|---|---|---|---|---|
| CH5 | 1e | | nd | nd | nd | nd | nd |
| EV2 #4 | 2e | 1 µg/L | 1.18 | 1.13 | 1.15 | nd | 1.05 |
| BVSM 3 | 3e | | nd | nd | nd | nd | nd |
| BV1 #4 | 4e | 2 µg/L | 2.22 | 1.92 | 2.46 | N/A | 2.0 |
| WFSM 2 | 5e | | nd | nd | nd | nd | nd |
| CH3 #4 | 6e | 1 µg/L | 1.26 | 1.13 | 1.15 | N/A | 1.1 |
| WF1 #3 | 7e | 0.5 µg/L | 0.66 | 0.66 | 0.63 | nd | 0.62 |
| WF1 #4 | 8e | 2 µg/L | 2.37 | 2.14 | 2.27 | nd | 2.09 |
| CHSM 1 | 9e | | 0.08 | nd | nd | nd | nd |
| EV2 | 10e | | nd | nd | nd | nd | nd |
| WF1 | 11e | | nd | nd | nd | nd | nd |
| CHSM 2 | 12e | | 0.11 | nd | nd | nd | nd |
| LB #1 | 13e | | nd | nd | nd | nd | nd |
| BVSM 2 | 14e | | nd | nd | nd | nd | nd |
| CH3 | 15e | | nd | nd | nd | nd | nd |
| WFSM 1 | 16e | | nd | nd | nd | nd | nd |
| EV1 #4 | 17e | 1 µg/L | 1.48 | 1.3 | 1.3 | N/A | 1.32 |
| CHSM 4 | 18e | | 0.1 | nd | nd | nd | nd |
| EVSM 1 | 19e | | nd | nd | nd | nd | nd |
| CHSM 3 | 20e | | nd | nd | nd | nd | nd |
| BVCW | 21e | | nd | nd | 0.1 | nd | nd |
| BV2 | 22e | | nd | nd | 0.09 | nd | nd |
| BVSM 4 | 23e | | nd | nd | nd | nd | nd |
| EVFR | 24e | | nd | nd | nd | nd | nd |
| EVSM 2 | 25e | | nd | nd | nd | nd | nd |
| BVSM 4 #1 | 26e | 2 µg/L | 2.37 | 2.06 | 2.16 | nd | 2.16 |
| ST3 | 27e | | nd | nd | nd | nd | nd |
| BVCW #3 | 28e | 1 µg/L | 1.31 | 1.19 | 1.34 | nd | 1.28 |

Table 6F Continued

| Virginia Tech ID | Ohmicron ID | Spike Level | Atr | Cyan | Ala | Met | Carb |
|---|---|---|---|---|---|---|---|
| CH2 | 29e | | 0.12 | nd | nd | nd | nd |
| WF2 | 30e | | 0.05 | nd | nd | nd | nd |
| EVSM 3 | 31e | | nd | nd | nd | nd | nd |
| BV1 #3 | 32e | 0.5 µg/L | 0.75 | 0.65 | 0.85 | N/A | 0.71 |
| EV1 | 33e | | nd | nd | nd | nd | nd |
| WFSW | 34e | | nd | nd | nd | nd | nd |
| EVSM 1 #1 | 35e | 0.25 µg/L | 0.35 | 0.35 | 0.28 | nd | 0.37 |
| CH3 #1 | 36e | 0.25 µg/L | 0.4 | 0.31 | 0.25 | nd | 0.42 |
| WFSM 3 | 37e | | nd | nd | nd | nd | nd |
| EVSM 4 | 38e | | nd | nd | nd | nd | nd |
| CH5 #2 | 39e | 2 µg/L | 2.52 | 2.17 | 1.91 | nd | 2.36 |

Table 7F
November Ohmicron Sample Results

| Virginia Tech ID | Ohmicron ID | Spike Level | Atr | Cyan | Ala | Met | Carb |
|---|---|---|---|---|---|---|---|
| CH3 | 1f | | nd | nd | nd | nd | nd |
| EV2 | 2f | | nd | nd | nd | nd | nd |
| CH5 | 3f | | nd | nd | nd | nd | nd |
| WFSM 1 | 4f | | nd | nd | nd | nd | nd |
| EVF/R | 5f | | nd | nd | nd | nd | nd |
| CH2 | 6f | | 0.1 | nd | nd | nd | nd |
| WF2 | 7f | | nd | nd | nd | nd | nd |
| BVSM 2 | 8f | | nd | nd | nd | nd | nd |
| WFSW | 9f | | nd | nd | nd | nd | nd |
| EV1 | 10f | | nd | nd | nd | nd | nd |
| BV2 | 11f | | nd | nd | 0.12 | nd | nd |
| EVSM 2 | 12f | | nd | nd | nd | nd | nd |
| ST1 | 13f | | nd | nd | nd | nd | nd |
| TB #2 | 14f | | 0.06 | nd | nd | nd | nd |
| WF1 #3 | 15f | 0.25 µg/L | 0.27 | 0.24 | 0.43 | 2.17 | nd |
| WF2 #4 | 16f | 0.5 µg/L | 0.59 | 0.57 | 0.8 | 3.86 | nd |
| BVCW #3 | 17f | 0.25 µg/L | 0.24 | 0.26 | 4.4 | 3.58 | nd |
| WF2 #2 | 18f | | nd | nd | nd | nd | nd |
| EV2 #4 | 19f | 0.25 µg/L | 0.24 | 0.24 | 0.41 | 2.25 | nd |
| WF2 #1 | 20f | | nd | nd | nd | nd | nd |
| EVFR #3 | 21f | 0.5 µg/L | 0.5 | 0.54 | 0.8 | 4.14 | nd |
| LFB #2 | 22f | 0.5 µg/L | 0.6 | 0.62 | 0.8 | nd | 0.24 |
| BVSM 3 #2 | 23f | 2 µg/L | 2.29 | 2.06 | 3.06 | nd | 2.12 |
| BV1 #3 | 24f | 0.5 µg/L | 0.54 | 0.56 | 1.01 | 3.5 | nd |
| WF1 #4 | 25f | 1 µg/L | 1.2 | 1.23 | 1.62 | 0.13 | 0.94 |
| WF2 #3 | 26f | 2 µg/L | 2.24 | 2.03 | 2.57 | nd | 2.0 |
| LFB #1 | 27f | 0.25 µg/L | 0.2 | 0.27 | 0.28 | nd | nd |
| TB #1 | 28f | | 0.05 | nd | nd | nd | nd |

Table 7F Continued

| Virginia Tech ID | Ohmicron ID | Spike Level | Atr | Cyan | Ala | Met | Carb |
|---|---|---|---|---|---|---|---|
| CH3 #4 | 29f | 0.25 µg/L | 0.24 | 0.26 | 0.38 | 2.23 | nd |
| CH3 #3 | 30f | 1 µg/L | 1.3 | 1.24 | 1.53 | nd | 1.11 |
| EVF/R #4 | 31f | 2 µg/L | 2.23 | 2.03 | 2.8 | nd | 2.04 |
| LFB #3 | 32f | 2 µg/L | 2.16 | 1.91 | 2.66 | – | – |
| BV1 #4 | 33f | 0.5 µg/L | 0.57 | 0.55 | 0.99 | 4.17 | nd |
| EV2 #3 | 34f | 1 µg/L | 1.3 | 1.16 | 1.57 | nd | nd |
| EB #2 | 35f | | 0.07 | nd | nd | nd | nd |
| BVSM | 36f | | nd | nd | nd | nd | nd |
| BV1 #1 | 37f | 2 µg/L | 2.5 | 2.05 | 3.16 | nd | 2.05 |
| EVSM 3 | 38f | | nd | nd | nd | nd | nd |
| EB #1 | 39f | | nd | nd | nd | nd | nd |
| BV1 #2 | 40f | 1 µg/L | 2.43 | 2.04 | 2.97 | nd | 1.82 |
| BVCW #4 | 41f | 1 µg/L | 1.39 | 1.19 | 4.54 | nd | 0.94 |
| WFSM 3 | 42f | | nd | nd | nd | nd | nd |
| EVSM 1 | 43f | | nd | nd | nd | nd | nd |
| BV1 | 44f | | nd | nd | 0.19 | nd | nd |
| EVSM 4 | 45f | | nd | nd | nd | nd | nd |
| BVSM 4 | 46f | | 0.05 | nd | nd | nd | nd |
| WF1 | 47f | | 0.06 | nd | nd | nd | nd |
| BVCW | 48f | | nd | nd | 4.46 | nd | nd |

– Data missing

Table 8F
December Ohmicron Sample Results

| Virginia Tech ID | Ohmicron ID | Spike Level | Atr | Cyan | Ala | Met | Carb |
|---|---|---|---|---|---|---|---|
| WFAmbTo | 1g | | nd | nd | nd | nd | nd |
| EVF/R | 2g | | nd | nd | nd | nd | nd |
| BVCW #3 | 3g | 0.25 µg/L | 0.51 | 0.42 | 4.06 | 3.92 | nd |
| EVF/R #2 | 4g | 2 µg/L | 2.38 | 2.07 | 2.62 | 0.1 | 2.07 |
| EV1 | 5g | | nd | nd | nd | nd | nd |
| EV2 | 6g | | nd | nd | nd | nd | nd |
| EVSM 2 | 7g | | nd | nd | nd | nd | nd |
| BV1 | 8g | | nd | nd | 0.12 | nd | nd |
| BV2 | 9g | | nd | nd | 0.18 | nd | nd |
| LB #2 | 10g | | nd | nd | nd | nd | nd |
| WF1 | 11g | | nd | nd | nd | nd | nd |
| LFB #2 | 12g | 1 µg/L | 1.32 | 1.2 | 1.54 | 1.84 | nd |
| WF2 | 13g | | nd | nd | nd | nd | nd |
| WF2 #1 | 14g | 2 µg/L | 21.6 | 16.1 | 21 | 0.58 | 16.5 |
| WFSM 3 | 15g | | nd | nd | nd | nd | nd |
| BVCW | 16g | | nd | nd | nd | nd | nd |
| ST2 #1 | 17g | | nd | nd | nd | nd | nd |
| EVSM 1 | 18g | | nd | nd | nd | nd | nd |
| WFSM 2 | 19g | | 0.07 | nd | nd | nd | nd |
| LB #1 | 20g | | nd | nd | nd | nd | nd |
| BV1 #2 | 21g | 1 µg/L | 1.36 | 1.28 | 1.56 | 0.1 | 1.47 |
| LFB #1 | 22g | 0.25 µg/L | 0.41 | 0.35 | 0.35 | nd | 0.27 |
| BVCW #1 | 23g | 0.5 µg/L | 0.41 | 0.3 | 4.14 | 2.52 | nd |
| WFSW | 24g | | nd | nd | nd | nd | nd |
| BV1 #1 | 25g | 2 µg/L | 2.37 | 2.24 | 2.91 | 0.11 | 2.24 |

Table 9F
January Ohmicron Sample Results

| Virginia Tech ID | Ohmicron ID | Spike Level | Atr | Cyan | Ala | Met | Carb |
|---|---|---|---|---|---|---|---|
| WF1 #3 | 1h | 1 µg/L | 1.34 | 1.04 | 1.15 | nd | 1.15 |
| BVCW #2 | 2h | 0.25 µg/L | 0.29 | 0.33 | 1.57 | 0.49 | nd |
| BV1 #3 | 3h | 0.25 µg/L | 0.28 | 0.31 | 0.37 | 0.39 | nd |
| BV1 #1 | 4h | 1 µg/L | 17.7 | 16.6 | 20.4 | 0.76 | – |
| WFSM 4 #3 | 5h | 2 µg/L | 2.33 | 2.04 | 2.65 | nd | 2.19 |
| EVF/R | 6h | | nd | nd | nd | nd | nd |
| WF1 #4 | 7h | 2 µg/L | 2.52 | 2.08 | 2.45 | nd | 2.27 |
| WF1 | 8h | | nd | nd | nd | nd | nd |
| WFSM 4 | 9h | | nd | nd | nd | nd | nd |
| EVF/R #4 | 10h | 2 µg/L | 2.92 | 2.17 | 2.67 | 0.16 | 2.42 |
| EV2 #1 | 11h | 0.25 µg/L | 0.48 | 0.35 | 0.29 | 0.49 | nd |
| BV2 | 12h | | nd | nd | 0.15 | nd | nd |
| EV1 | 13h | | nd | nd | nd | nd | nd |
| BVCW #4 | 14h | 0.5 µg/L | 0.79 | 0.59 | 2.01 | 0.85 | nd |
| EB | 15h | | nd | nd | nd | nd | nd |
| WFSM 1 | 16h | | nd | nd | nd | nd | nd |
| BV1 #4 | 17h | 2 µg/L | 1.97 | 2.26 | 2.79 | 0.14 | 1.83 |
| EV2 #3 | 18h | 0.5 µg/L | 0.58 | 0.64 | 0.73 | 0.73 | nd |
| EV2 | 19h | | nd | nd | nd | nd | nd |
| BV1 | 20h | | nd | nd | 0.15 | nd | nd |
| WFSM 3 | 21h | | nd | nd | nd | nd | nd |
| WF2 #4 | 22h | 0.5 µg/L | 0.68 | 0.61 | 0.75 | 0.7 | nd |
| TB #1 | 23h | | nd | nd | nd | nd | nd |
| WF2 #3 | 24h | 0.25 µg/L | 0.34 | 0.27 | 0.38 | 0.31 | nd |
| LFB #1 | 25h | 1 µg/L | 1.17 | 1.16 | 1.48 | nd | 0.85 |
| BVCW | 26h | | nd | nd | 1.22 | nd | nd |
| WFSM 2 | 27h | | nd | nd | nd | nd | nd |

– Data missing

Table 9F Continued

| Virginia Tech ID | Ohmicron ID | Spike Level | Atr | Cyan | Ala | Met | Carb |
|---|---|---|---|---|---|---|---|
| LFB #2 | 28h | 0.5 µg/L | 0.62 | 0.62 | 0.72 | 0.7 | nd |
| WF2 | 29h | | nd | nd | nd | nd | nd |
| WFSW | 30h | | nd | nd | nd | nd | nd |

Table 10F
February Ohmicron Sample Results

| Virginia Tech ID | Ohmicron ID | Spike Level | Atr | Cyan | Ala | Met | Carb |
|---|---|---|---|---|---|---|---|
| CHSM 2 | 1i | | nd | nd | nd | nd | nd |
| BV1 #4 | 2i | 0.5 µg/L | 0.66 | 0.7 | 0.84 | 0.93 | nd |
| CH5 | 3i | | nd | nd | nd | nd | nd |
| BV2 | 4i | | nd | nd | nd | nd | nd |
| BVSM 4 | 5i | | nd | nd | nd | nd | nd |
| EV1 | 6i | | nd | nd | nd | nd | nd |
| WFSM 1 | 7i | | nd | nd | nd | nd | nd |
| BV1 | 8i | | nd | nd | 0.16 | 0.1 | nd |
| LB #2 | 9i | | nd | nd | nd | nd | nd |
| LB #3 | 10i | | nd | nd | nd | nd | nd |
| CH3 #4 | 11i | 0.25 µg/L | 0.33 | 0.35 | 0.37 | 0.49 | nd |
| WFSM 2 | 12i | | nd | nd | nd | nd | nd |
| WFSM 3 | 13i | | nd | nd | nd | nd | nd |
| CH2 | 14i | | 0.25 | nd | nd | nd | nd |
| BVCW #4 | 15i | 0.5 µg/L | 0.7 | 0.72 | 1.34 | 0.95 | nd |
| BVSM 4 #3 | 16i | 1 µg/L | 1.34 | 1.36 | 1.57 | 0.05 | 1.04 |
| CH5 #3 | 17i | 0.25 µg/L | 0.36 | 0.38 | 0.38 | 0.49 | nd |
| BVSM 4 #4 | 18i | 2 µg/L | 2.51 | 2.26 | 3 | 0.11 | 2.07 |
| LFB #2 | 19i | 0.5 µg/L | 0.75 | 0.74 | 0.66 | 0.77 | nd |
| LFB #4 | 20i | 2 µg/L | 2.41 | 2.48 | 2.65 | 0.11 | 1.1 |
| WFSM 4 | 21i | | nd | nd | nd | nd | nd |
| BVSM 3 | 22i | | nd | nd | nd | nd | nd |
| CH3 #1 | 23i | 0.5 µg/L | 0.7 | 0.76 | 0.75 | 0.91 | nd |
| LB #1 | 24i | | nd | nd | nd | nd | nd |
| LFB #1 | 25i | 0.25 µg/L | 0.28 | 0.31 | 0.3 | 0.3 | nd |
| EV2 #4 | 26i | 2 µg/L | 2.38 | 1.99 | 2.53 | nd | 2.09 |
| BVSM 3 #1 | 27i | 0.5 µg/L | 0.69 | 0.65 | 0.65 | 0.66 | nd |
| LB #4 | 28i | | nd | nd | nd | nd | nd |

Table 10F Continued

| Virginia Tech ID | Ohmicron ID | Spike Level | Atr | Cyan | Ala | Met | Carb |
|---|---|---|---|---|---|---|---|
| WF1 #3 | 29i | 0.5 µg/L | 0.79 | 0.64 | 0.66 | 0.63 | nd |
| EV2 | 30i | | nd | nd | nd | nd | nd |
| WF1 #4 | 31i | 0.25 µg/L | 0.38 | 0.33 | 0.32 | 0.37 | nd |
| CH3 | 32i | | nd | nd | nd | nd | nd |
| WF1 | 33i | | nd | nd | nd | nd | nd |
| WFSW | 34i | | nd | nd | nd | nd | nd |
| EV2 #3 | 35i | 1 µg/L | 1.43 | 1.2 | 1.34 | nd | 1.13 |
| BVCW | 36i | | nd | nd | 0.54 | nd | nd |
| EVF/R | 37i | | nd | nd | nd | nd | nd |
| BVCW #3 | 38i | 0.25 µg/L | 0.5 | 0.43 | 1.09 | 0.5 | nd |
| BVSM 1 | 39i | | nd | nd | nd | nd | nd |
| EB #2 | 40i | | nd | nd | nd | nd | nd |
| EV1 #4 | 41i | 0.25 µg/L | 0.34 | 0.35 | 0.31 | 0.36 | nd |
| WF2 #3 | 42i | 1 µg/L | 1.41 | 1.13 | 1.31 | 0.05 | 1.19 |
| CHSM 3 | 43i | | nd | nd | nd | nd | nd |
| WF2 | 44i | | nd | nd | nd | nd | nd |
| BV1 #3 | 45i | 0.25 µg/L | 0.36 | 0.31 | 0.47 | 0.42 | nd |
| EV1 #3 | 46i | 0.5 µg/L | 0.67 | 0.61 | 0.59 | 0.67 | nd |
| BVSM 1 #4 | 47i | 2 µg/L | 2.38 | 1.91 | 2.9 | 1.09 | 2.13 |
| CHSM 1 | 48i | | nd | nd | nd | nd | nd |
| BVSM 1 #3 | 49i | 1 µg/L | 1.42 | 1.18 | 1.52 | nd | 1.03 |
| CHSM 4 | 50i | | nd | nd | nd | nd | nd |
| BVSM 2 | 51i | | nd | nd | nd | nd | nd |
| LFB #3 | 52i | 1 µg/L | 1.27 | 1.11 | 1.23 | nd | 1.02 |

## Appendix G

## Quality Assurance/Quality Control

To insure proper QA/QC in the study, a laboratory blank, equipment blank, and travel blank were included for every 20 samples. Additionally, a laboratory spike, which was milli-Q water with the pesticides added, was included in every 20 samples. Two matrix spikes were made from each site's samples from April to June 1992, and 4 matrix spikes were made from each site's samples from August 1992, to February 1993. The samples were spiked at 4 and 10 μg/L in April 1992, 2, and 4 μg/L in June through August 1992, and then at 0.25, 0.5, 1, and 2 μg/L for the rest of the study.

Acenaphthrene-$d_{10}$ and Phenanthrene-$d_{10}$ were added as surrogate to all the samples, but they did not produce sharp peaks when the GC/ECD was used, so 4-chlorobiphenyl was added to all samples after July 1992. The overall recovery rate of 4-chlorobiphenyl was 74%. The recovery rate for each sample was listed in Appendix A.

A graphical comparison of the added concentration of the spiked samples vs. the measured concentration was included as Figures 1G through 10G. Figures 1G-5G were Matrix spikes, and 6G-10G were laboratory spikes. The actual regression output for the matrix spikes was listed in table 1G, with table 2G containing the laboratory spikes.

Table 1G
Regression Output for Martix Spikes

| Pesticide | $R^2$ | Regression Output, where x = added conc. in µg/L |
|---|---|---|
| Atrazine | 0.11 | 0.601*x + 0.428 |
| Alachlor | 0.53 | 0.632*x + 0.176 |
| Carbofuran | 0.002 | -0.409*x + 4.78 |
| Cyanazine | 0.34 | 1.077*x + 0.481 |
| Metolachlor | 0.033 | 1.624*x + 0.254 |

* Note that the regreesion output is the pesticide's concentration in µg/L.

Table 2G
Regression Output for Laboratory Spikes

| Pesticide | $R^2$ | Regression output, where x = added conc. in µg/L |
|---|---|---|
| Atrazine | 0.33 | 0.866*x + 0.143 |
| Alachlor | 0.19 | 0.255*x + 0.317 |
| Carbofuran | 0.03 | 0.724*x + 3.81 |
| Cyanazine | 0.74 | 1.30*x + 0.177 |
| Metolachlor | 0.49 | 0.78*x + 0.113 |

* Note that the regreesion output is the pesticide's concentration in µg/L.

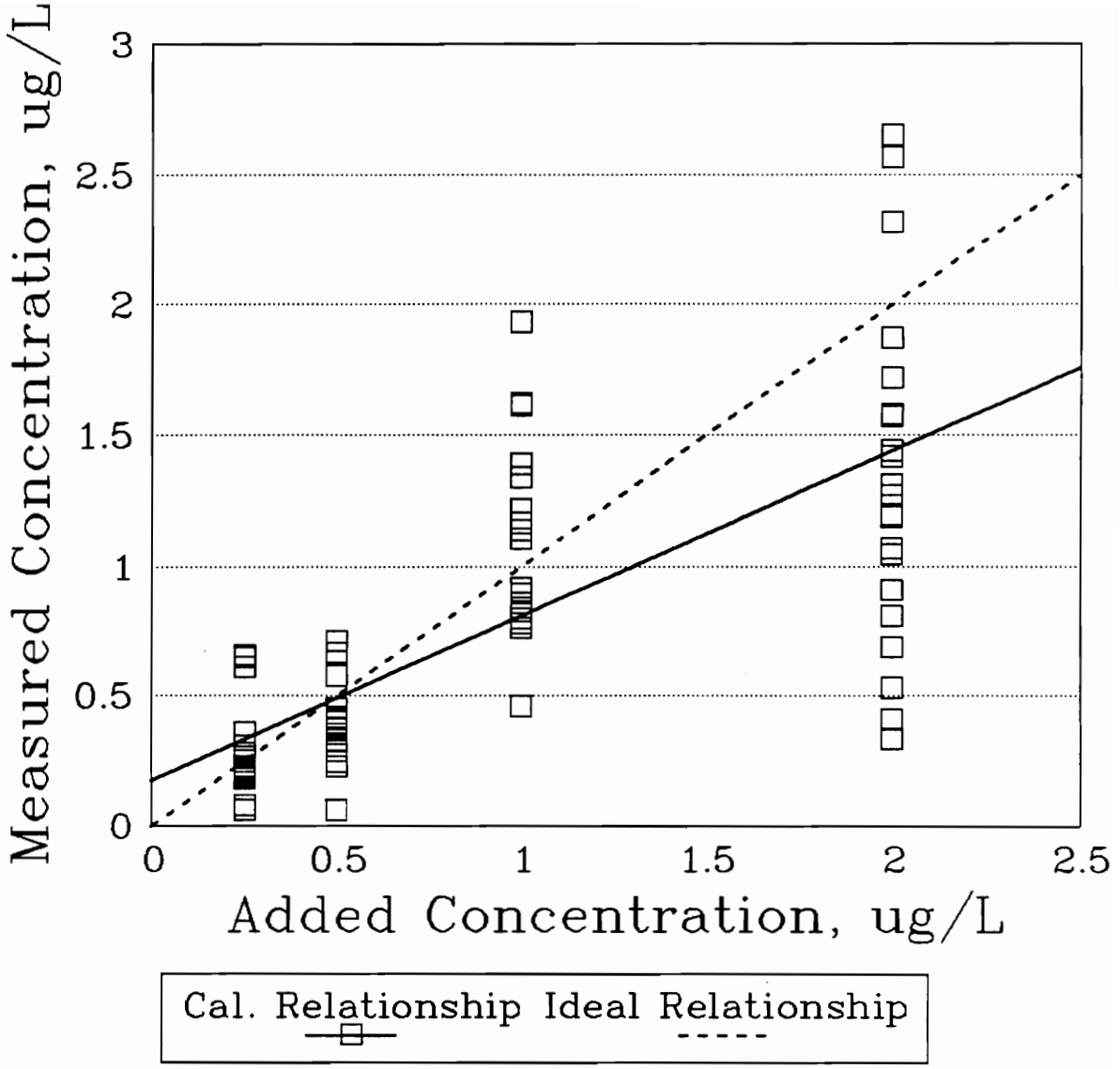



**Figure 1G**

**Measured vs. Added Concentration**

**for Alachlor Matrix Spikes**

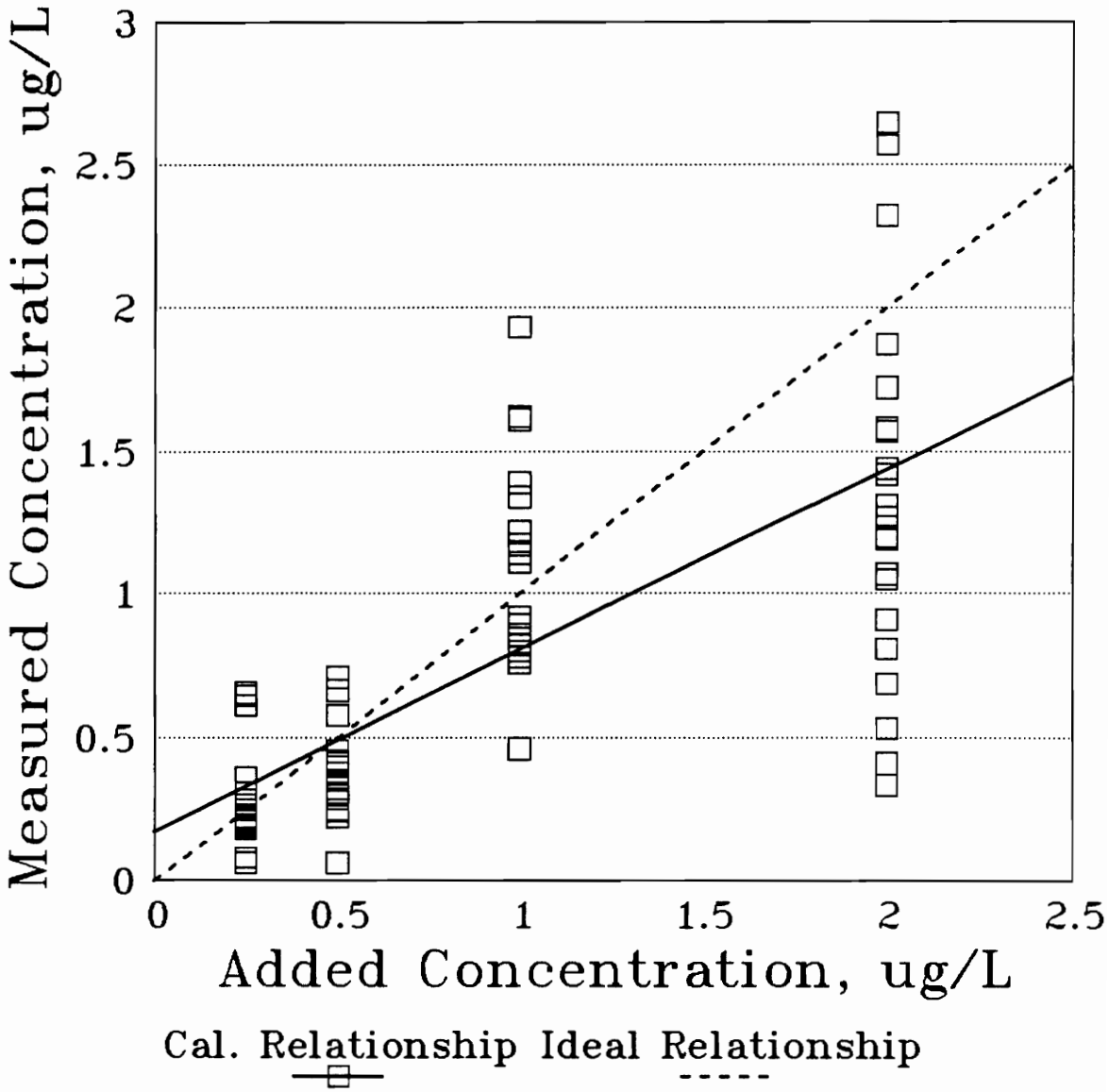



Figure 2G
Measured vs. Added Concentration
for Atrazine Matrix Spikes

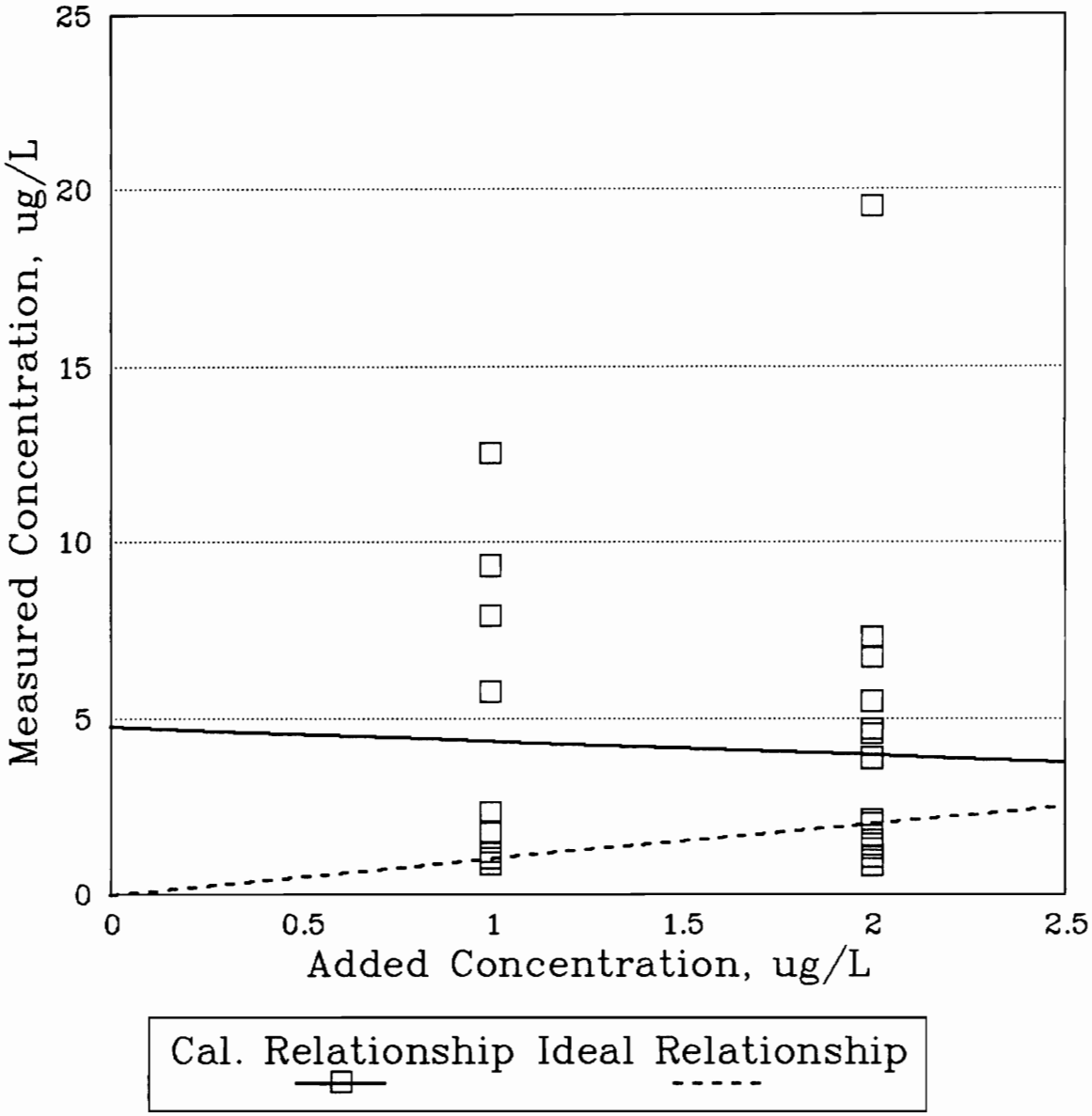



Figure 3G
Measured vs. Added Concentration
for Carbofuran Matrix Spikes

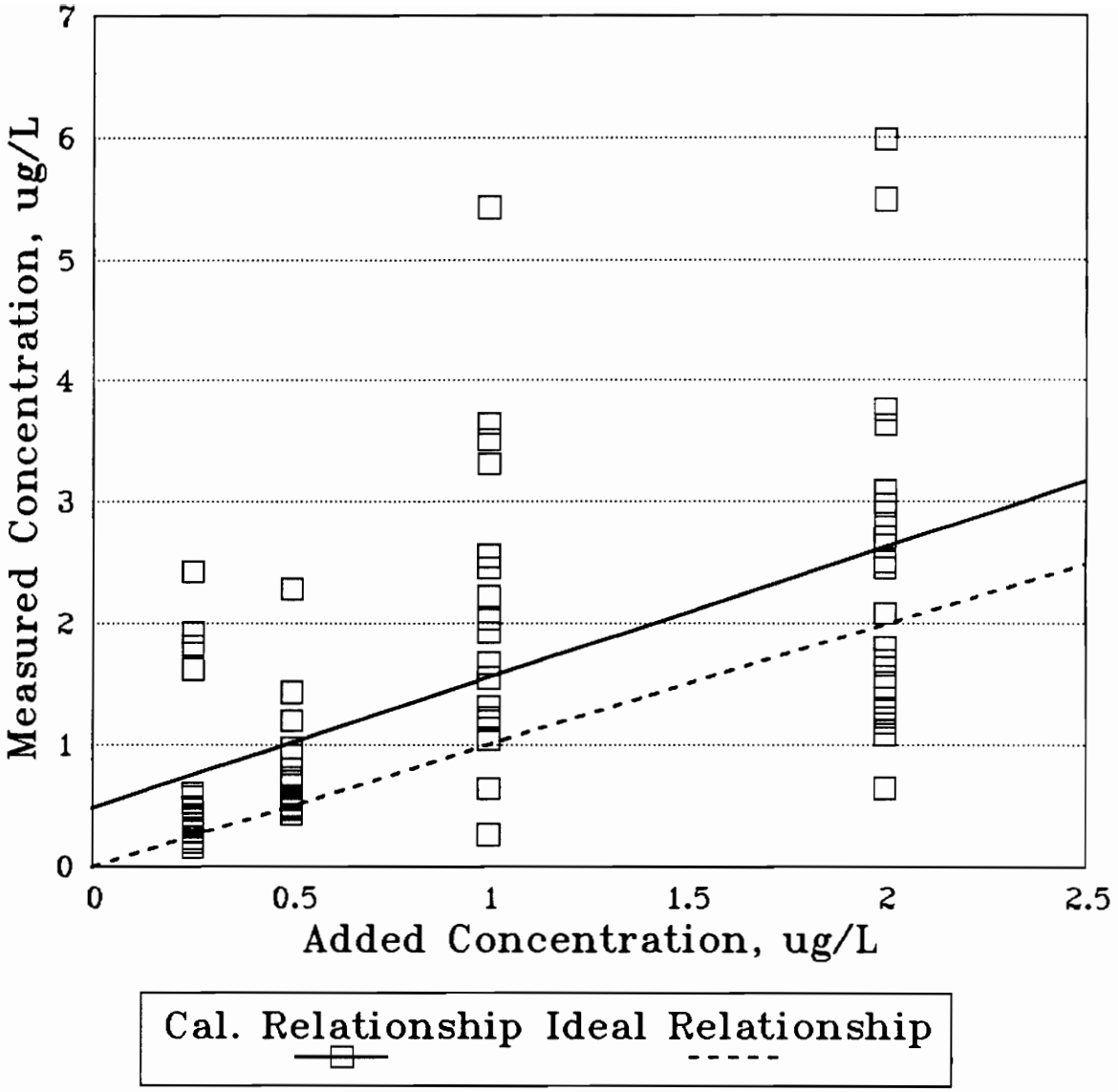



Figure 4G
Measured vs. Added Concentration
For Cyanazine Matrix Spikes

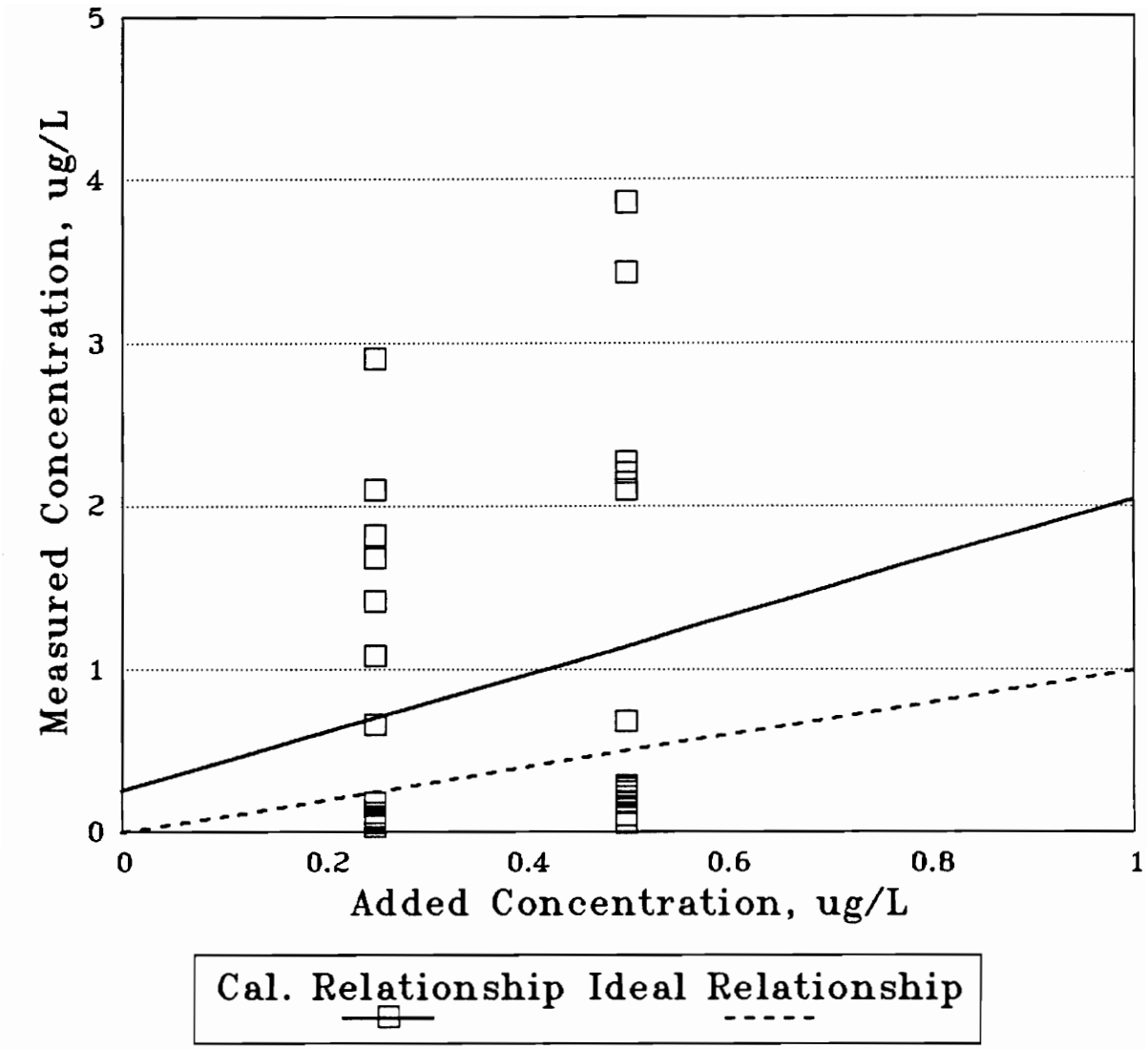



Figure 5G
Measured vs. Added Concentration
For Metolachlor Matrix spikes

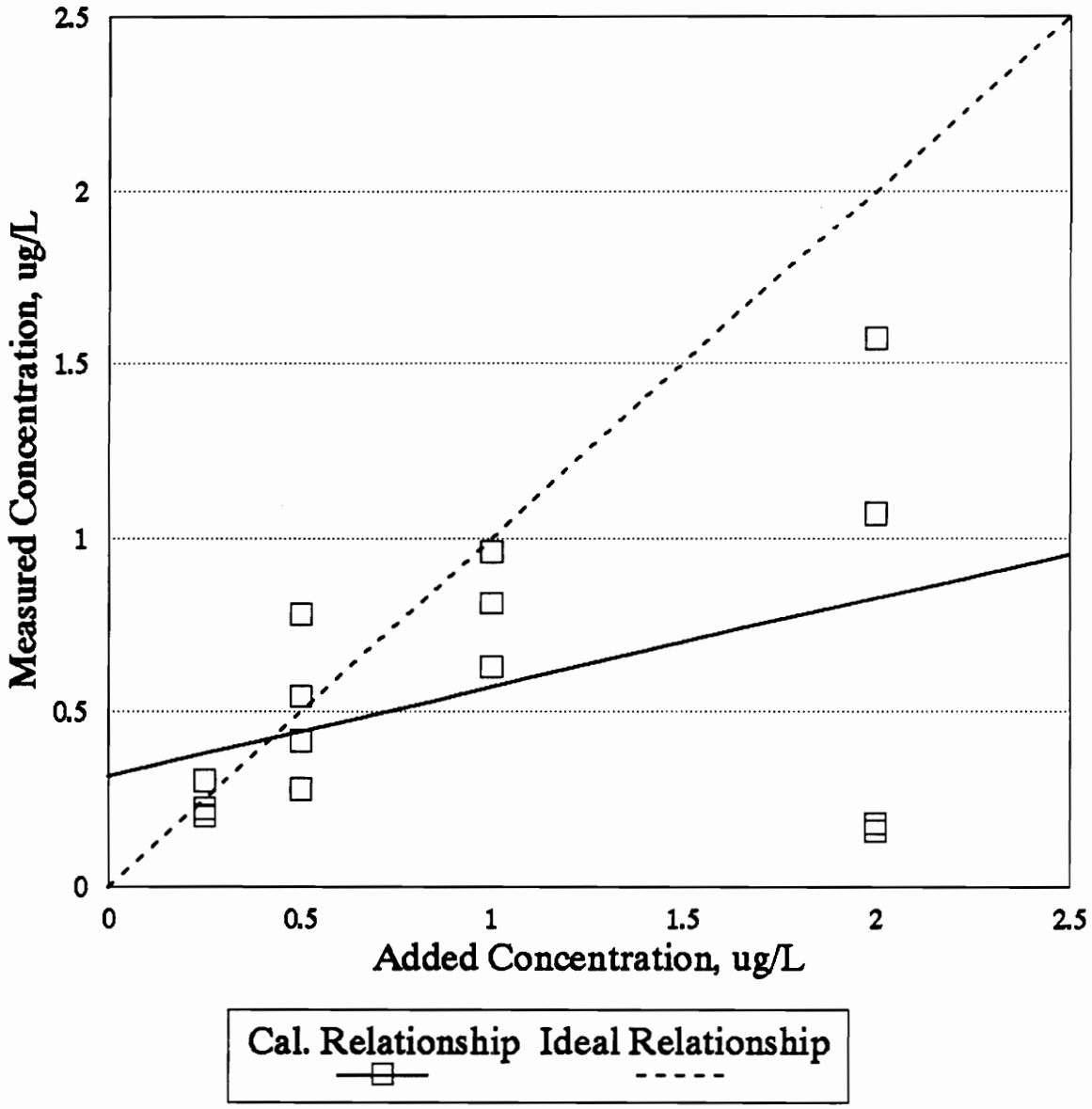



Figure 6G
Measured vs. Added Concentration
For Alachlor Laboratory Spikes

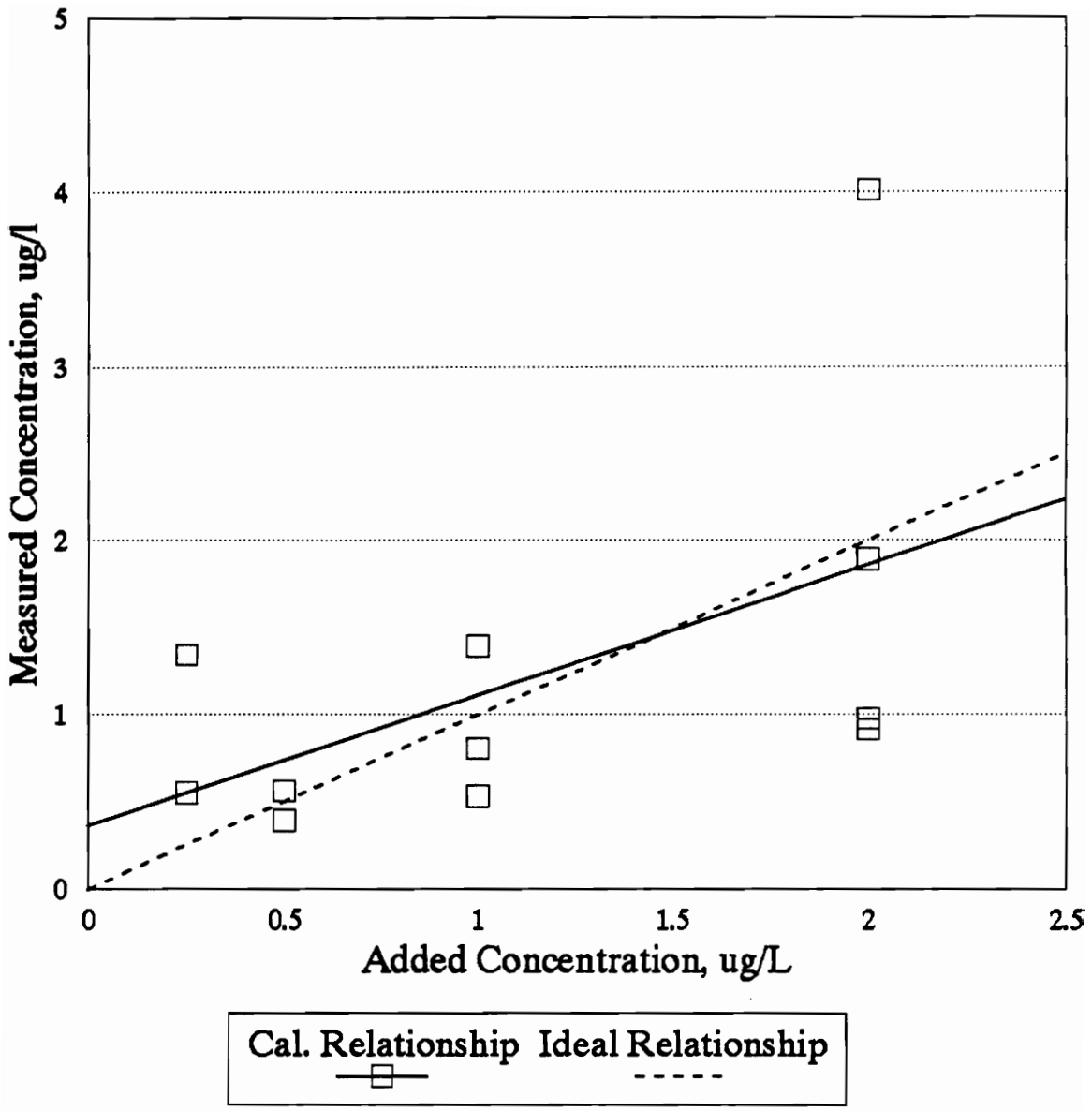



Figure 7G
Measured vs. Added Concentrations
For Atrazine Laboratory Spikes

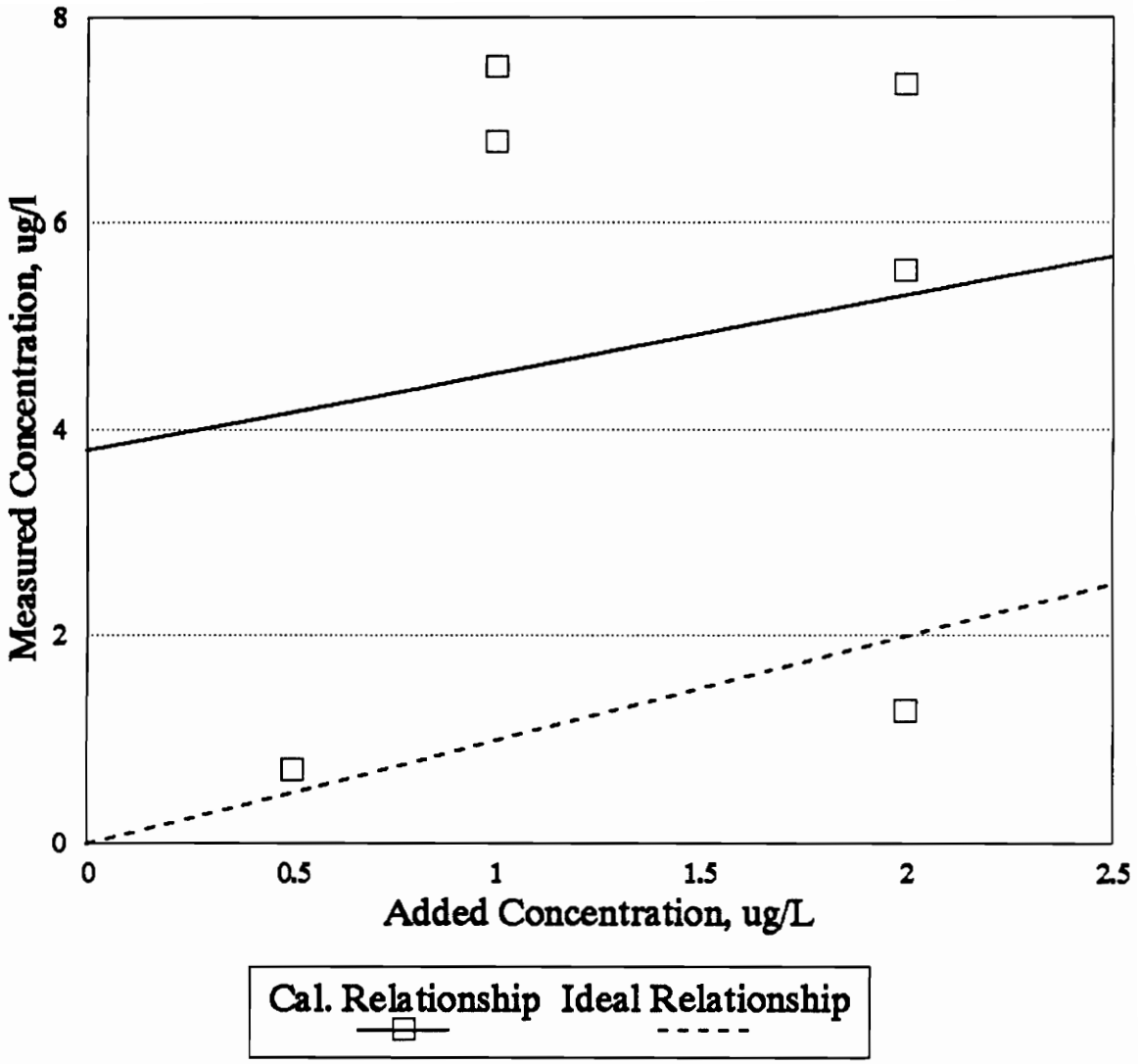



Figure 8G
Measured vs. Added Concentrations
For Carbofuran Laboratory Spikes

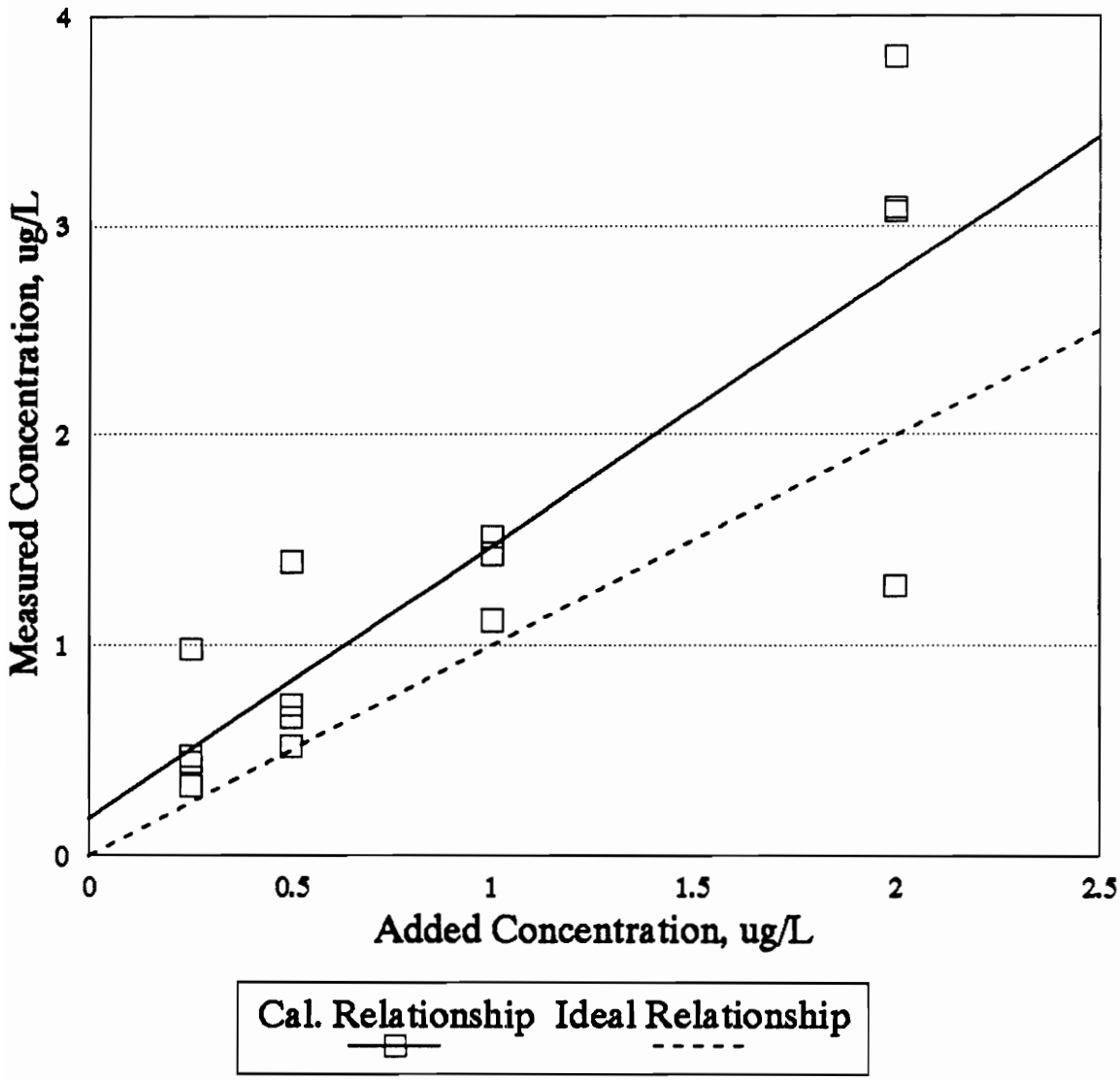



Figure 9G

Measured vs. Added Concentrations
For Cyanazine Laboratory Spikes

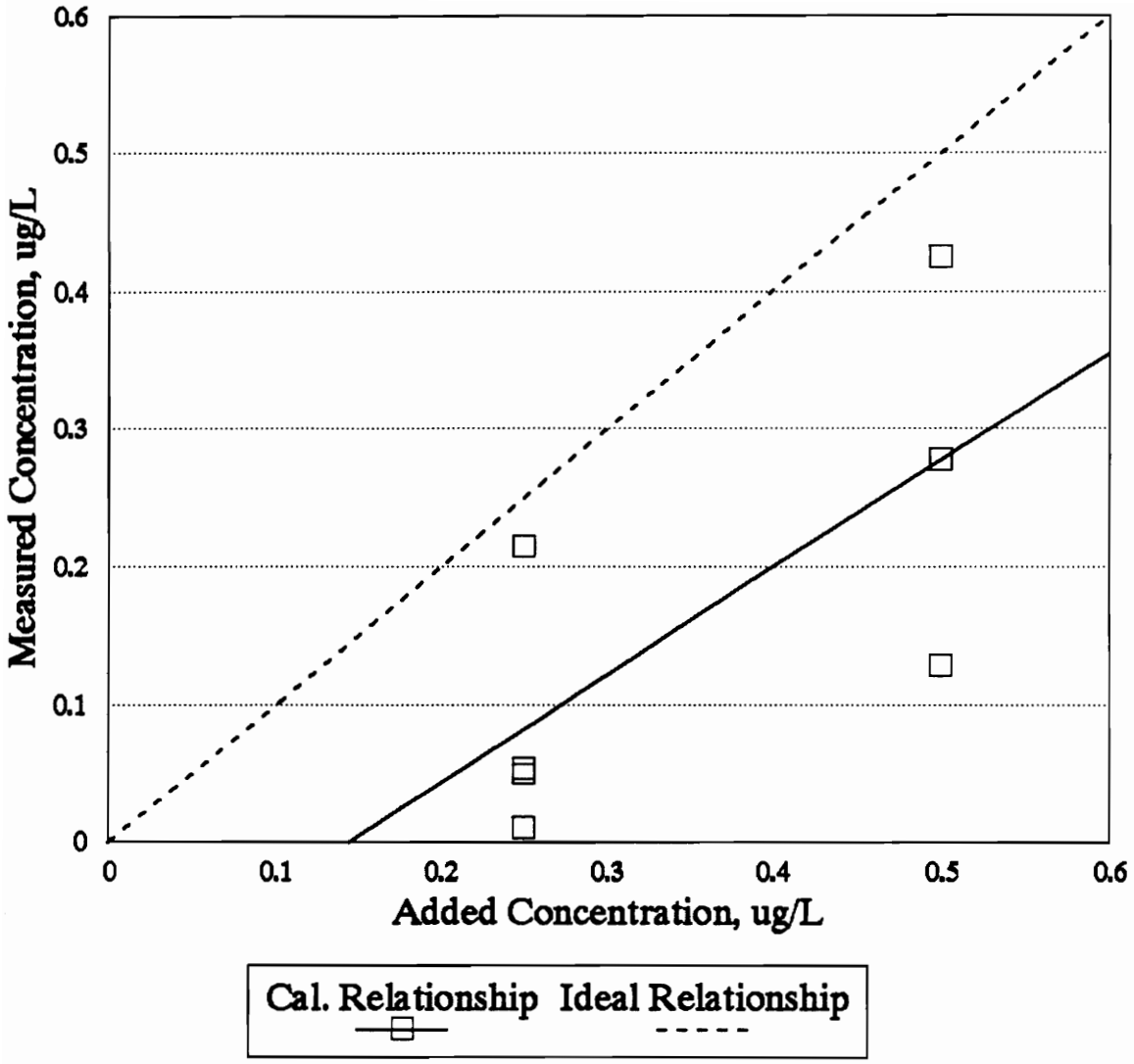



Figure 10G
Measured vs. Added Concentrations
For Metolachlor Laboratory Spikes

## VITA

Thomas W. Hubbard was born on November 8, 1963 in Jacksonville, IL. He graduated *summa cum laude* from Jacksonville High School in 1981, and received a B. S. degree in Civil Engineering, *cum laude* from Bradley University in 1991.