MONITORING PESTICIDES IN THE SOIL, GROUNDWATER, AND SUBMARINE GROUNDWATER DISCHARGE OF THE CHESAPEAKE BAY AREA

by

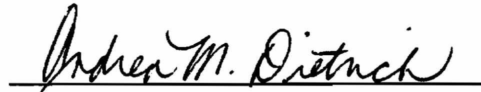
Douglas Linden Schicho

Thesis submitted to the Faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

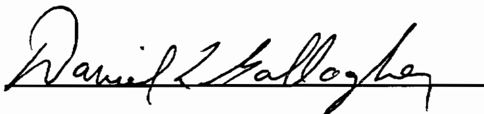
MASTER OF SCIENCE

in

Environmental Engineering



A.M. Dietrich, Chair



D.L. Gallagher

G.M. Simmons Jr.

August, 1993

Blacksburg, Virginia

c.2

LD
5655
V855
1993
S342
c.2

MONITORING PESTICIDES IN THE SOIL, GROUNDWATER, AND SUBMARINE GROUNDWATER DISCHARGE OF THE CHESAPEAKE BAY AREA

by

Douglas Linden Schicho

Committee Chairperson: Dr. Andrea M. Dietrich

(ABSTRACT)

The first objective of this research was to determine if pesticides were leaching into the shallow groundwater beneath agricultural sites, and if so, to determine a correlation between soil and groundwater pesticide concentrations. The second was to examine the correlation between pesticide concentrations measured by gas chromatography with electron capture detector (GC/ECD) and an immunoassay method developed by OHMICRON Corporation. Samples from four agricultural and one reference (undeveloped) site were analyzed for pesticides over an 11 month period from April, 1992 to February, 1993. One-hundred and nineteen separate groundwater samples were analyzed for: alachlor, atrazine, carbofuran, cyanazine, and metolachlor. Pesticide analysis of groundwater and seepage meter water was carried out by immunoassay and by solid phase extraction (SPE) with octadecyl bonded extraction disks followed by GC/ECD. Fifty-five soil and sediment samples were Soxhlet extracted followed by gas

chromatography/mass spectrometry (GC/MS). Pesticides were detected in 13.4% groundwater samples by GC/ECD with only one detection being greater than 1 ppb. The immunoassay method detected pesticides in 32% of the groundwater samples with the majority of these detections also being below 1 ppb. Alachlor and/or metolachlor were detected in 44% of the soil samples at concentrations ranging from 7 ppb to 485 ppb. The study concluded that the majority of the target pesticides were being adsorbed by the soil and only limited amounts, less than 1 ppb, were being transported to the groundwater. It was also concluded that the immunoassay had lower limits of detection, but may yield some false positive results.

DEDICATION

This work is dedicated to Bernadette. Without her help and support it would not have been completed. She never failed me and deserves more credit than I for its completion.

Acknowledgements

The author would like to thank the Pesticide Control Board of the Virginia Department of Agriculture and Consumer Services and the Trustees of the Edna Bailey Sussman fund for their generous funding of this project.

The author would like to thank Drs. Dietrich and Gallagher for the countless times their assistance was given. The support and help of Drs. Simmons and Reay with site selection and field technique was greatly appreciated and made this project feasible.

Marilyn Grender and Julie Petruska's advice and technical assistance kept the laboratory analysis from getting out of hand.

The author would like to thank all of the faculty and students in the environmental engineering laboratory for their knowledge and companionship. A special thanks to Tom for his partnership and hard work.

Finally, my family was with me for every step and offered unyielding support.

Table of Contents

I. INTRODUCTION..1

II. LITERATURE REVIEW..................................4

A. INTRODUCTION..4

B. PESTICIDE PROPERTIES................................4

B.1. Properties of Alachlor............................4

B.2. " " Atrazine......................................5

B.3. " " Carbofuran....................................5

B.4. " " Cyanazine.....................................6

B.5. " " Metolachlor...................................6

C. PESTICIDE APPLICATION IN THE CHESAPEAKE BAY AREA..8

D. EXTRACTION OF PESTICIDES FROM WATER................8

D.1. Liquid-Liquid Extraction..........................8

D.2. Solid Phase Extraction...........................10

D.2.A. Cartridges......................................10

D.2.B. Extraction Disks................................11

E. EXTRACTION OF PESTICIDES FROM SOIL................12

E.1. Methods used to Extract Target Pesticides from Soil.................................13

F. METHODS OF DETECTING PESTICIDES...................15

F.1. Gas Chromatography/Mass Spectrometry......15

F.2. Gas Chromatography/Electron Capture Detection................................16

F.3. Immunoassay.......................................17

G. FATE AND TRANSPORT OF PESTICIDES IN THE ENVIRONMENT....................................19

G.1. Pesticide Adsorption to Soil..............19

G.2. Pesticide Degradation......................20

G.2.A. Alachlor............................21

G.2.B. Atrazine............................23

G.2.C. Carbofuran..........................24

G.2.D. Cyanazine...........................25

G.2.E. Metolachlor.........................25

G.3. Groundwater Contamination by Pesticides...25

G.4. Surface Water Contamination by Pesticides.27

III. METHODS AND MATERIALS...............................29

A. GENERAL...29

B. RESEARCH CHEMICALS..............................29

B.1. Pesticides, Chemical Standards, and Solvents..............................29

B.2. Stock Solution Preparation................30

C. LABORATORY GLASSWARE PROCEDURES.................31

C.1. Glassware.................................31

C.2. Cleaning Procedures.......................31

D. FIELD SAMPLING PROCEDURES.......................32

D.1. Site Selection............................32

D.2. Sampling Equipment........................34

D.3. Sampling Procedure and Preservation.......36

D.3.A. Well Samples........................36

D.3.B. Seepage Meters....................36
D.3.C. Soil and Sediment Samples..........37
E. LABORATORY ANALYSIS...............................39
E.1. Extraction of Water Samples...............39
E.2. Extraction of Soil and Sediment Samples...41
E.3. Gas Chromatography........................43
E.3.A. GC/FID AND GC/ECD..................43
E.3.B. Gas Chromatography/Mass Spectrometry....................46
E.4. Immunological Assay.......................53
F. QUALITY ASSURANCE AND QUALITY CONTROL............56
F.1. Instrument's performance..................56
F.2. Check Standards...........................56
F.3. Fortified Samples (matrix spikes).........56
F.4. Lowest Detectible Quantity................58
F.5. Method Detection Limits...................60
F.6. Duplicates................................62
F.7. Blanks....................................64
F.8. Recoveries of Surrogates..................64
G. STATISTICAL ANALYSES.............................65
IV. RESULTS AND DISCUSSION..............................66
A. SOIL CONCENTRATIONS..............................67
A.1. Pesticide Application Data and Persistence...........................70
A.2. Other Organic Compounds Detected in

Soil/Sediment.............................82

B. COMPARISON OF GROUNDWATER CONCENTRATIONS TO SOIL CONCENTRATIONS..................................82

B.1. Alachlor..............................84

B.2. Atrazine..............................86

B.3. Carbofuran............................86

B.4. Cyanazine.............................95

B.5. Metolachlor...........................95

C. SOIL-WATER EQUILIBRIA.............................96

D. WATER CONCENTRATIONS.............................99

D.1. Groundwater Samples.......................99

D.2. Seepage Meter Water Samples..............100

E. BIOMAGNIFICATION

F. COMPARISON OF GC/ECD AND IMMUNOASSAY METHODS....106

F.1. Graphical Comparison.....................106

F.2. False Positive Detection.................121

F.3. Statistical Comparison...................125

F.4. Cost Comparison..........................127

F.5. Laboratory Time Comparison...........................134

V. SUMMARY AND CONCLUSIONS 135

VI. RECOMMENDATIONS.....................................138

VI. LITERATURE CITED....................................139

VII. APPENDICES 146

A. GC/ECD and Immunoassay Concentrations organized by

month....................................146

B. Raw data used in Figures........................156

C. Complete List of Soil Samples Taken............167

D. Mass Spectra and Chromatograms.................169

E. List of all GC/ECD Samples.....................177

F. Chronology.......................................211

List of Figures

Figure 1. Immunoassay Schematic......................54

Figure 2. Metolachlor Concentration in Soil.........67

Figure 3. Comparison of Alachlor Soil and Groundwater Concentrations................68

Figure 4. Metolachlor Concentration verses Time.....81

Figure 5. Average Detected Alachlor Concentration in Groundwater Measured by Immunoassay.......85

Figure 6. Average Detected Atrazine Concentration in Groundwater Measured by GC/ECD............87

Figure 7. Average Detected Atrazine Concentration in Groundwater Measured by Immunoassay.......88

Figure 8. Average Detected Cyanazine Concentration in Groundwater by GC/ECD.....................89

Figure 9. Average Detected Metolachlor Concentration in Groundwater Measured by GC/ECD............55

Figure 10. Average Detected Metolachlor Concentration in Groundwater measured by Immunoassay.......94

Figure 11. Typical Seepage Meter Chromatogram Using GC/ECD.................................101

Figure 12. Comparison of Alachlor Concentrations Determined by GC/ECD and Immunoassay.....108

Figure 13. Comparison of Atrazine Concentrations Determined by GC/ECD and Immunoassay.....109

Figure 14. Comparison of Carbofuran Concentrations

Determined by GC/ECD and Immunoassay.....110

Figure 15. Comparison of Cyanazine Concentrations Determined by GC/ECD and Immunoassay.....111

Figure 16. Comparison of Metolachlor Concentrations Determined by GC/ECD and Immunoassay.....112

Figure 17. Comparison of Fortified Alachlor concentrations to Concentrations Measured by GC/ECD and Immunoassay...................114

Figure 18. Comparison of Fortified Atrazine Concentrations to Concentrations Measured by GC/ECD and Immunoassay...................115

Figure 19. Comparison of Fortified Carbofuran Concentrations to Concentrations Measured by GC/ECD and Immunoassay...................116

Figure 20. Comparison of Fortified Cyanazine Concentrations to Concentrations Measured by GC/ECD and Immunoassay...................117

Figure 21. Comparison of Fortified Metolachlor Concentrations to Concentrations Measured by GC/ECD and Immunoassay...................118

Figure 22. Number of Detections by GC/ECD and Immunoassay in Fortified Solutions.......122

Figure D.1. Mass Spectra of Pesticides and Internal Standards. A: Acenapthene d_{10}; B: 4-Chlorobiphenyl; C: Carbofuran...........170

Figure D.2. Mass Spectra of Pesticides and Internal Standards. D: Atrazine; E: Phenanthrene d_{10}; F: Alachlor..........................171

Figure D.3. Mass Spectra of Pesticides. G: Metolachlor; H: Cyanazine..............................172

Figure D.4. Representative GC/MS Total Ion Chromatograms. A: Sample BVF 12/5/92; B: Sample CHF 10/11/92; C: Sample EVF 12/5/92.........173

Figure D.5. Representative GC/MS Total Ion Chromatograms. D: Site 4 Sample WFF 12/6/92; E: Site 3 Sediment EVOS 12/5/92; F: 5 mg/L Standard (Cal 1)....................................174

Figure D.6. Mass Spectra of Tentatively Identified Non-Target Organic Compounds Extracted from Soil or Sediment. A: 2,4-Bis(1,1-dimethylethyl)-phenol; B: Fluoranthene; C: Methylantrhacene or Methylphenanthrene....175

Figure D.7. Mass Spectra of Tentatively Identified Non-Target Organic Compounds Extracted from Soil or Sediment. D: Methylanthrancene or Methylphenanthrene: E: Benzothiazole; F: (E)-3-Eicosnene..........................176

List of Tables

Table 1. Properties of Studied Pesticides..............7

Table 2. Organic Carbon Coefficient and Range of Half-Lives..................................22

Table 3. Months Soil and Sediment Samples Were Taken...38

Table 4. Retention Times for Pesticides and Internal Standards.....................................47

Table 5. Quantitation Ions..............................50

Table 6. Mass Spectrum Response Factors................51

Table 7. Pesticide Concentrations Measured in Check Standards.....................................57

Table 8. Soil and Sediment Fortification Concentrations............................59

Table 9. Limits of Detection...........................61

Table 10. Fortification and Recovery Concentrations for Soil Analysis.......................................63

Table 11. Pesticide Concentrations Measured in Soil Samples................................69

Table 12. Percent Volatile Solids and Percent Moisture for Soil and Sediment Samples....................71

Table 13. Pesticide Application Data...................74

Table 14. Non-Target organic Compounds Tentatively Identified in Soil and Sediment Samples.......83

Table 15. Pesticides Detected in Groundwater by GC/ECD..90

Table 16. Pesticides Detected in Groundwater by Immunoassay....................................91
Table 17. Predicted Metolachlor Concentration in Soil-Water....................................98
Table 18. Summary of Pesticide Detections in Seepage Water by GC/ECD....................................103
Table 19. Summary of Pesticide Detections in Seepage Meter Water by Immunoassay..........................104
Table 20. Regression Data for Concentration Comparison Graphs.......................................113
Table 21. Regression Results for Fortified Concentration verses Measured Concentration Graphs..........120
Table 22. False Positive Detection of Pesticides in Reagent water Samples Which Contained No Pesticides.......................................123
Table 23. Statistical Comparison Data...................126
Table 24. Cost and Amounts Used per Sample of Consumable Supplies.......................................128
Table 25. Purchase Cost of Durable Equipment............130
Table 26. Cost of Analysis per Sample Batch.............132
Table A.1. May Samples...............................147
Table A.2. June Samples..............................148
Table A.3 July Samples..............................149
Table A.4. August Samples............................150
Table A.5. October Samples...........................151

Table A.6. November Samples....................152
Table A.7. December Samples....................153
Table A.8. January Samples....................154
Table A.9. February Samples....................155
Table B.1. Figure 2 Data....................157
Table B.2. Figure 3 Data....................158
Table B.3. Figure 4 Data....................159
Table B.4. Figure 5 Data....................160
Table B.5. Figure 6 Data....................161
Table B.6. Figure 7 Data....................162
Table B.7. Figure 8 Data....................163
Table B.8. Figure 9 Data....................164
Table B.9. Figure 10 Data....................165
Table.B.10. Figure 22 Data....................166
Table C.1. Soil Samples....................168
Table E.1. April Samples....................178
Table E.2. May Samples....................181
Table E.3. June Samples....................184
Table E.4. July Samples....................187
Table E.5. August Samples....................190
Table E.6. October Samples....................193
Table E.7. November Samples....................197
Table E.8. December Samples....................201
Table E.9. January Samples....................204

Table E.10. February Samples..........................207

Table F.1 Chronology..............................212

I. INTRODUCTION

Farming has changed drastically in the last several decades. Crop yields and farm size have both increased dramatically. The two main causes for these advances have been the increased use of mechanized farm machinery and pesticides. The term pesticide includes two main categories, insecticides and herbicides. Insecticides are used in the control of insects, arachnids, and nematodes which consume or cause disease in crops. Herbicides are used to control grasses, fungi, and molds which interfere in the production of crops. Pesticides have increased world crop production enormously, but also have generated some cause for concern regarding their use.

Historically the main threats to surface water and groundwater were contamination from salts, organic matter, or other naturally occurring material. The last thirty years has seen anthropogenic contaminants become the foremost threat to water resources. The discovery of the problems caused by the persistence and environmental effects of compounds such as polychloronated biphenyls (PCBs) and DDT increased the interest and activity in the field of environmental analysis. Study of the fate and transport of pesticides on agricultural sites was a natural extension of this interest. The effort to determine the

extent and ability of pesticides to enter the groundwater was greatly increased by the discovery of aldicarb in the groundwater of an agricultural area of Long Island in 1979 (Bushway, *et al.*, 1992). The knowledge that groundwater was being contaminated by pesticides and the increasing information on the potential hazards of human exposure to pesticides increased public demand for greater knowledge of groundwater contamination.

This desire for pesticide data has greatly increased the number of samples which have been analyzed world-wide. The great number of samples analyzed has initiated a need for a faster, simpler, and more cost effective analytical method for pesticide analysis than the traditional methods of gas chromatography and high pressure liquid chromatography. Immunological methods were originally developed for detecting the presence of infectious disease and for measuring the levels of hormones in body fluids but within the last fifteen years immunoassays have emerged as an alternative to the traditional environmental analytical methods.

Many studies have been undertaken to determine what soil types and which pesticides have a propensity for groundwater contamination (Holden, *et al.*, 1992; Pionke, *et al.*, 1988; Walker and Zimdahl, 1981). The results of these studies seem to indicate that movement of pesticides can be

very site dependent. This study was initiated with three main objectives:

1. To determine if alachlor, atrazine, carbofuran, cyanazine, or metolachlor are being transported to the groundwater beneath agricultural sites

2. Examine the relationship between measured soil and groundwater concentrations

3. Determine the correlation between measurement of pesticides by GC/ECD and an immunoassay technique

II. Literature Review

A. Introduction

This study tested the groundwater, soil, sediment, and submarine groundwater discharge (SGWD) of the Chesapeake Bay area for the presence of five pesticides; alachlor, atrazine, carbofuran, cyanazine, and metolachlor.

B. Pesticide Properties

The properties and background history of each pesticide in this study are given in the following section.

B.1. Properties of Alachlor

Alachlor (2-Chloro-2'6'-diethyl-N-(methoxymethyl)-acetanilide) was patented by the Monsanto Corporation in 1967 for use as a herbicide for the control of grasses and broadleaf weeds in corn, dry beans, peanuts, and soybean crops. The water solubility of alachlor is 242 ppm at 25°C. Alachlor is soluble in most polar organic solvents (eg. ethyl acetate, methanol and acetone). Alachlor has an oral toxicity in 50% of test rats (LD_{50}) of 1800 mg/kg (Meister, *et al.*, 1992), an EPA maximum contaminate level (MCL) of 2 ppb in drinking water with a maximum contaminant level goal (MCLG) of 0 ppb (Bushway, et al., 1992 citing U.S. EPA, 1989). Alachlor is also known as Chimiclor and Lasso and is in the chloracetanilide family of herbicides (Meister, *et al.*, 1992).

B.2. Properties of Atrazine

Atrazine (2-Chloro-4-ethylamino-6-isopropylamino-s triazine) was patented by Ciba-Geigy in 1960 for use as a selective herbicide for season-long weed control in corn and sorghum crops (Meister, *et al.*, 1992). At higher application rates atrazine can be used as a non-selective herbicide in non-planted areas (Clark, *et al.*, 1991). Atrazine has a water solubility of 33 ppm at 25°C and was the least water soluble pesticide in this study. It is soluble in polar and moderately polar organic solvents (eg. chloroform, diethyl ether, acetone, and methanol). Atrazine has an LD_{50} of 1780 mg/kg in rats (Meister, *et al.*, 1992), and an EPA MCL of 3 ppb in drinking water (Bushway, *et al.*, 1992). Atrazine is also known as Malermais, Gesaprim, and Zeaphos and is in the triazine family of herbicides (Meister, *et al.*, 1992).

B.3. Properties of Carbofuran

Carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranol methylcarbamate) was patented by the Bayer corporation in 1964 for use as an insecticide, miticide, and nematicide in corn, alfalfa, rice, cotton, vegetables, grapes, peanuts, potatoes, grains, and soybeans (Meister, *et al.*, 1992). With a aqueous solubility of 700 ppm (Gustafson, 1989), carbofuran is the most water soluble pesticide in the study and it is soluble in non-polar organic solvents such as

dichloromethane. It has an LD_{50} of 11 mg/kg in rats making it the most acutely toxic pesticide in the study (Meister, *et al.*, 1992). Carbofuran has a proposed MCLG of 40 ppb (Bushway, *et al.*, 1992 citing U.S. EPA, 1989). Other names for carbofuran are Bay and Curaterr. Carbofuran is in the carbamate class of insecticides (Meister, *et al.*, 1992).

B.4. Properties of Cyanazine

Cyanazine (2-[[4-chloro-6-(ethylamino)-s-triazine-2-yl]amino]-2-methylpropionitrile) was patented by Degussa in 1968 for use as a preemergence or postemergance herbicide for use on corn, potatoes and fallow cropland in the control of broadleaf weeds. The water solubility of cyanazine is 171 ppm (Gustafson, 1989) and it is soluble in polar and moderately polar organic solvents. Cyanazine exhibits an LD_{50} of 288 mg/kg in rats. Cyanazine, also known as Bladex, is in the triazine family of herbicides (Meister, *et al.*, 1992).

B.5. Properties of Metolachlor

Metolachlor (2-Chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide) was patented in 1973 by Ciba-Geigy for use as a preemergence herbicide on corn, soybeans, peanuts, grain, sorghum, potatoes, pod crops, cotton, and safflower. It has a water solubility of 530 ppm at 20°C and is miscible in most organic solvents. The oral LD_{50} of metolachlor in rats is 2780 mg/kg and by this

Table 1.
Properties of Pesticides in this Study

Pesticide	LD_{50} in Rats (mg/kg)	Solubility in Water[a] (ppm)
Alachlor	1800	242
Atrazine	1780	33
Carbofuran	11	700
Cyanazine	288	171
Metolachlor	2780	530[b]

Data from: Gustafson, 1989; Jury, *et al.*,1987; Meister, *et al.*, 1992
a: solubilities at 25°C unless noted
b: solubility at 20°C

measure metolachlor is the least acutely toxic pesticide in this study. Metolachlor, like alachlor, is a member of the chloracetanilide family of herbicides and is also known as Dual (Meister, *et al.*, 1992).

C. Pesticide Application in the Chesapeake Bay Area

Common crops in the Chesapeake Bay area are soybeans, corn, barley, and wheat. A herbicide is necessary to control grasses in corn and soybeans. All four herbicides in this study are used for that purpose and carbofuran could be used as an insecticide on a variety of crops including the four commonly planted crops listed above (Meister, *et al.*, 1992). All five of the pesticides targeted in this study are commonly utilized in the Chesapeake Bay area (Hubbard, 1993 citing Hohlt, 1993).

D. Extraction of Pesticides from Water

This section will concentrate on pesticide extraction methods which are relevant to the five target pesticides in this study.

D.1. Liquid-Liquid Extraction

Liquid-liquid extraction (LLE) of neutral pesticides from water with hexanes was the method of choice for many pesticides several years ago. In this method, 50 mL of hexanes was added to one liter of sample in a separatory funnel and shaken for two minutes. The solvent layers were allowed to separate, the hexanes were decanted and passed

through a drying agent to remove the small amount of dissolved water. This was repeated three times. The nearly 150 mLs of solvent were then reduced to less than 1 mL in a Kuderna-Danish (K-D) concentrator and analyzed by gas chromatography (Blumberg, 1988). Liquid-liquid extraction has been proven over a number of years to have good extraction recoveries.

However, there are many drawbacks to LLE. The principle disadvantage is the large amount of solvent which is consumed. The extraction itself requires the use of 150 mLs of hexanes. In addition, the final rinse given to all the glassware which will come into contact with the sample is also done with hexanes. In the author's experience this would bring the total solvent volume consumed per sample to over 200 mL. The consumption of large volumes of solvent has negative repercussions for the economics of the project, the health of the laboratory personnel, and the environment. The EPA has made solvent minimization a priority for these reasons.

Liquid-liquid extraction also requires a relatively large supply of glassware. Two liter separatory funnels, Kuderna-Danish concentrators with two sets of three-ball snyder columns, and funnels for drying the solvent after extraction are all necessary. The extractions are labor intensive requiring the constant attention of a technician

for the entire procedure which takes approximately three hours.

D.2. Solid Phase Extraction

Solid phase extraction (SPE) of organic compounds from water is another extraction technique for environmental analysis. Solid phase extraction allows for sample sizes as large as LLE with a smaller amount of solvent and glassware required. Solid phase extraction techniques involve passing the water sample through a stationary solid medium. This solid contains a substance onto which the organic compounds will preferentially adsorb. There are a variety of solid matrices and adsorbing materials. The use of different adsorbing materials, such as forms of activated carbon or various ionic resins can allow the extraction of compounds with widely varying chemical characteristics (Di Corcia and Marchetti, 1992; Basta and Olness, 1992). The most widely used combination of solid matrixes and adsorbents is tetrafluoro-polyethene (TFPE) and either octyl or octadecyl bonded porous silica. The average recoveries for SPE in pesticide extractions are often very good (eg. greater than 85%)(Junk and Richard, 1988). The two main types of TFPE extraction apparatuses are cartridges and disks.

D.2.A Cartridges

One technique for SPE uses cartridges containing the

silica impregnated TFPE inside a casing which resembles a 1-10 ml plastic syringe. The plastic casings are known to be a source of phalate contamination and the small physical size of the cartridges causes some difficulties. A solvent reservoir is needed to avoid frequent transfer of water into the cartridge. Environmental samples which contain suspended solid material may often clog the cartridge causing extraction times to extend to several hours. Even samples without suspended solid materials may take 2-3 hours at the recommended flow rates (Krout-Vass and Thoma, 1991). The cartridge extraction methodology is not as labor intensive as LLE but can take just as long, or longer. However, the solvent usage is reduced by greater than 90% and the amount of glassware is also drastically reduced cutting costs and preparation time. Typical extraction recoveries were 90%, 95%, 77%, and 99% for alachlor, atrazine, carbofuran, and cyanazine (Nash, 1990).

D.2.B. Extraction Disks

The most recent EPA method for the determination of organic compounds in drinking water, Method 525.1, specifies the use of SPE disks such as those sold by Empore^{tm}. This method specifically lists alachlor and atrazine as analytes amenable to the technique. The disks are 47 mm in diameter and 0.5 mm thick composed of 10% PTFE and 90% octadecyl bonded silica. The disks are placed in an extraction

apparatus which can hold 300 mL of water at a time. The extraction disks have a much higher surface area than the cartridges, thereby reducing sample clogging. A one liter sample can be extracted in a much shorter period of time than either LLE or cartridges (30 minutes at recommended flow rates). The extraction efficiencies are similar to that of the cartridges (Kraut-Vass and Thoma, 1991). Eichelberger, et al., (1991) listed a recovery of 78% for 2-chlorobiphenyl an internal standard specified in EPA method 525.1. The amount of glassware required for disk extractions is comparable to the cartridge method and therefore much less than the required glassware for LLE.

E. Extraction of Pesticides from Soil

Pesticides can be extracted from soil in several ways. In many instances, extraction methods are optimized for the extraction of a single pesticide. The two main categories of extraction from soil are leaching methods and shaking methods. Examples of leaching methods are column extraction and soxhlet extraction. Examples of shaking methods are sonication, stirring, and shakers. All of the above soil extraction methods require similar amounts of time and solvents. Historically, shaking extraction was the method of choice for triazine and acetanilide herbicides. However, McGlamery, *et al.* (1967) found soxhlet extraction to be 15% more efficient than shaking for extracting atrazine from

soil while using the same solvent system.

The solubilities of the target analytes should not be the only factors considered when choosing a soil extraction solvent system. The solvent in which the pesticide is most soluble is not always the solvent which will exhibit the highest extraction efficiency (Huang and Pignatello, 1990). The adsorbed pesticide may be so strongly bound to a soil constituent that unless that portion of the soil is extracted, as well the pesticide, recovery will be poor.

E.1. Methods Used to Extract Target Pesticides from Soil

Dunigan and McIntosh (1971) found that unless soil compounds resembling polysaccharide were extracted along with atrazine the recoveries were low. In light of this finding, they recommended a polar solvent system (eg. ethanol and water) for the extraction of atrazine even though atrazine is more soluble in solvents with medium polarity (eg. methylene chloride and benzene). The difficulty with using a polar extraction solvent system is that lengthy cleanup procedures are often required due to all of the organic material being co-extracted from the soil (Basta and Olness, 1992).

Basta and Olness (1992) extracted alachlor, carbofuran, and atrazine simultaneously with hot water and then employed ion exchange resin to remove the pesticides from the water

with a custom made resin extracting rod. The resin extraction separated the pesticides with less solvent usage than a traditional liquid-liquid separation and or column clean-up. However, no one resin extracted each of these pesticides well. Using three separate resins the maximum absorptions were 26%, 95%, and 100% for alachlor, atrazine, and carbofuran respectively. The pesticides were then removed from the resin with methanol and analyzed by gas chromatography with a nitrogen-phosphorous detector.

McGlamery *et al.* (1967) found that soxhlet extraction with polar solvents such as acetone and methanol could remove atrazine from soil with recoveries of 87% and 84% respectively. These extractions were followed by solvent partitioning and in some cases an alumina column to clean the samples before spectrophotometric analysis.

Carbofuran residues were removed from soil by stirring soil samples with methanol-water (2:1,v/v). The carbofuran was then derivitized to the corresponding phenol (2,3-Dihydro-2-2-dimethyl-7-hydroxybenzofuran) before analysis by liquid chromatography (Nelsen and Cook, 1979).

In a 1992 study of pesticide transport in the Virginia coastal plain, acetone-hexane (1:1, v/v) was used to extract atrazine and metolachlor from soil in a column leaching method (Heatwole, *et al.*, 1992). Average recovery values from laboratory fortified samples were 73% and 80.5% for

atrazine and metolachlor respectively. Further clean-up was necessary before analysis by GC/ECD.

Acetone-hexane (1:1,v/v) was also the solvent system of choice for the extraction of atrazine, lindane, pentachlorophenol, and diazinon from soil in a California study. The soil was extracted by sonication and was analyzed by GC/MS without further sample clean-up (Lopez-Avila, *et al.*, 1985).

Clearly there are many ways of extracting pesticides from soil and preparing them for analysis. There is a trade off between high extraction efficiency and fewer sample manipulations. The extraction procedures which yield the greatest extraction efficiency almost always require further sample cleaning. Extraction methodologies using acetone-hexane (1:1, v/v) have been used in the past with good extraction efficiency and minimal necessary cleanup.

F. Methods of Detecting Pesticides

There are a variety of pesticide detection methods. Capillary gas chromatography is one of the most common analytical tools for environmental analysis. It can effect separations of chemical components to ease their quantification and identification by many different detectors.

F.1. Gas Chromatography/Mass Spectrometry

Gas Chromatography/Mass Spectrometry (GC/MS) is an

invaluable tool for the identification of environmental contaminants. The confirmatory step of mass spectrum detection provides nearly unambiguous data. The instrumental limits of detection for GC/MS vary widely depending upon the type of mass spectrometric detector. The lowest limits of detection encountered during this literature review, were in recent study using SPE and GC/MS. The detection limits were 0.05 ppb for alachlor, atrazine, and metolachlor and 0.2 ppb for cyanazine (Thurman, *et al.*, 1992).

F.2. Gas Chromatography/Electron Capture Detection

Gas chromatography with electron capture detection (GC/ECD) is also an invaluable tool in environmental analysis. The disadvantage of GC/ECD when compared to GC/MS is that there is no confirmatory mass spectrum. The possibility of false positive detection is therefore higher. Co-extractants from environmental samples can make pesticides appear to be present when they are not (Boshoff, 1979). However, steps can be taken to reduce this possibility. A second column or detector can be used to verify the initial result (Krill and Sonzogni, 1986). The detection limits for GC/ECD are dependent upon the chemical composition of the analyte. Compounds which are halogenated elicit a greater response than non-halogenated analytes and therefore have the lowest limits of detection on the ECD.

F.3. Immunoassay

After years of success in medical fields, immunological assays are receiving wide use as a screening technique in the field of environmental analysis due to the ease, speed, and cost effectiveness of the procedure. The first practical immunoassay techniques began in the late 1960s when enzyme labelling became feasible. The techniques were first used to identify substances such as hormones in body fluids. Later the use of immunoassays spread to identifying chemical compounds, such as drugs, in body fluids. The use of immunoassays in environmental samples is relatively recent. In immunoassays the sample solution can be analyzed without extraction. Immunological assays utilize antibodies which have been made specifically for a target analyte and which are bound to a solid support. A target analyte bound to an active enzyme is also necessary. A solution containing the specialized antibody is treated with the target analyte and the target analyte bound to an active enzyme. These two molecules compete to react with the specialized antibody. The solution is removed and the antibody bound to the solid phase which has reacted with the target compound and the target compound enzyme conjugate remains. A chromogen which will produce color upon reaction with the target compound-enzyme conjugate is added. The color is then measured spectrophotometrically and the analyte is quantified based

upon the color intensity. The more intense the color the smaller the concentration of target compound in the sample.

This analytical method has no means of confirming its result. There have been reports of problems with false positive detection due to non-target compounds reacting with the antibody. Cross reactivity is often seen between compounds with similar chemical structure. Cross-reactivity between alachlor and a soil metabolite of alachlor was reported in a 1993 study. This caused the reporting of false positive detection of alachlor in 103 out of 136 samples which had tested positive for alachlor by immunoassay in well water (Baker, *et al.*, 1993). A group of triazine herbicides; atrazine, ametryn, prometryn, propazine, prometon, simazine, and terbutryn; were all shown to cross react in an enzyme-linked immunosorbant assay (ELISA) (Thurman, *et al.*, 1992). A metolachlor immunoassay was shown to cross-react with three other chloracetanilide compounds alachlor, metalaxyl, and metalaxyl (Hall, *et al.*, 1992).

The detection limits of immunoassay techniques are generally good. An atrazine LOD of 0.05 ppb was reported by Thurman *et al.* (1992). An immunoassay for metolachlor developed by Hall *et al.* (1992) reported an LOD of 2 ppb. A study using Enviroguard^{tm} immunoassay kits reported LODs of 0.1 ppb for alachlor, atrazine, and carbofuran (Bushway, *et*

al., 1992). The OHMICRON Corporation (1993) reports Minimum Detectible Quantities, which are analogous to limits of detection, of 0.05 ppb, 0.04 ppb, 0.06 ppb, 0.04 ppb, and 0.06 for alachlor, atrazine, carbofuran, cyanazine, and metolachlor respectively.

G. Fate and Transport of Pesticides in the Environment

The main processes determining the fate of pesticides in the soil are adsorption, biological and chemical transformations, and transport. The composition of the soil and the chemical structure of the pesticide will help to determine how strongly it is bound to the soil surface and how rapidly it degrades. Transport can include movement into plants, surface water, groundwater, or the atmosphere.

G.1. Pesticide Adsorption to Soil

Soil adsorption is a reversible interaction between soil components and chemical functionalities on the pesticide molecules. Adsorption of a pesticide to the soil is of primary importance in determining the pesticides fate and transport. The strength of this attraction is a determining factor in the length of time a pesticide remains active in the soil and the likelihood of it moving and causing contamination. A weakly adsorbed pesticide may wash off-site, leach, or be lost to the atmosphere, whereas a strongly adsorbed pesticide may not degrade within the desired time frame. "The success of atrazine application is

being hindered by its erratic performance and the carryover of its residues to affect plants in some soil types and not in others." (Huang, *et al.*, 1984).

Soil properties which affect adsorption are clay content, moisture, surface area, percent organic matter, cation exchange capacity, and pH (Saltzman and Yaron, 1986). Due to the complex nature of soil chemistry, the mechanisms of adsorption are not fully understood. However, soil organic content is often the largest factor in adsorption strength.

Even with the still unknown soil pesticide interactions on a molecular level a good adsorption model can be based upon the organic carbon partition coefficient K_{oc} (Jury, *et al.*, 1987). The Freundlich isotherm is frequently used as a model of soil pesticide associations (Heatwole, et al., 1992). The K_{oc} values for the pesticides in this are listed in Table 2. Carbofuran has the lowest K_{oc} value; this along with its high water solubility (see Table 1) would point to a propensity for leaching into the groundwater. Surprisingly this has not been seen in environmental surveys. The values of K_{oc} for the rest of the target pesticides are all similar with metolachlor having the highest value.

G.2. Pesticide Degradation

The pathways by which pesticides degrade are of primary

importance in determining their usefulness and their potential for contaminating the environment. Pesticides which degrade too quickly will not provide adequate protection to the fields for the entire crop cycle. Long-lived pesticides can inhibit crop growth in the next planting and have an increased pollution potential. The amount of time a pesticide remains intact in a field is communicated by a half-life value. The half-lives for the pesticides in this study are shown in Table 2.

Most pesticides undergo both biological and chemical degradation through multiple degradation pathways. Soil is an ideal medium for many degradation reactions. Degradation in soil is dependent upon several factors including soil moisture content, percent organic carbon, soil pH, temperature, clay content, and depth. Some of the degradation pathways for the pesticides in this study are discussed below.

G.2.A. Alachlor

Sharp (1988) found that degradation by both photolysis and hydrolysis were of little importance for alachlor. However, metabolic by-products of alachlor were found in plant tissue as quickly as two days after application. Plant metabolic processes alter the molecular structure of these herbicides in many ways. Sharp reported eleven plant

Table 2.
Organic Carbon Partition Coefficients and Range of Half-Lives for Target Pesticides

Pesticide	Organic Carbon Partition Coefficients, K_{oc} (m^3/kg)	Range of Half-Lives, $t_{½}$ (days)
Alachlor	0.12	12-50
Atrazine	0.16	20-480
Carbofuran	0.028	30-45
Cyanazine	0.168	14-85
Metolachlor	0.181	20-1303

* Data from: Bouchard, *et al.*, 1982; Gustafson, 1989; Jury, *et al.*, 1987 Loague, *et al.*, 1989; Spalding, *et al.*, 1989; Shirmohammadi, *et al.*, 1989; Thurman, *et al.*, 1992; Walker and Zimdahl, 1981

derived metabolic products of alachlor.

The pathway which accounts for the largest amount of alachlor degradation is microbial metabolism (Sharp, 1988). A population of acclimated microorganisms can consume alachlor rapidly. One type of fungus (*Paecilomyces* sp.) consumed 60% of alachlor present within 7 days. Microbial degradation, like plant metabolism, forms a complex mixture of products (Sharp, 1988).

The fact that the degradation pathways of alachlor produce a wide variety of end-products makes the detection of metabolites very difficult. In this review of the literature only one study reported finding an alachlor soil metabolite (Baker, *et al.*, 1993).

G.2.B. Atrazine

Unlike the other pesticides in this study, the degradation products of atrazine are now being monitored with greater frequency (Thurman, *et al.*, 1992; Miles, 1992). The three major atrazine degradation products are hydroxyatrazine, deethylatrazine, and deisopropylatrazine.

Atrazine can be hydrolyzed by high pH solutions or photolyzed by UV light in water to form hydroxyatrazine (Pape and Zabik, 1970). This degradation product has been isolated from sterilized soil indicating that its formation is not biologically driven. Conditions which were shown to enhance this reaction in soil were; increasing temperature,

increasing moisture, and increasing organic matter (Esser, *et al.*, 1975).

Deethylatrazine and diisopropyl atrazine are known to be formed through biological atrazine degradation (Esser, *et al.*, 1975). A 1992 study of atrazine and its metabolites in surface water found deethylatrazine in concentrations ranging from 0.05 ppb to 4.4 ppb, deisopropylatrazine in concentrations ranging from 0.05 ppb to 3.2 ppb, and atrazine in concentration ranging from 0.28 ppb to 108 ppb (Thurman, *et al.*, 1992). These degradation products are clearly formed in appreciable amounts and are capable of environmental contamination.

G.2.C. Carbofuran

The most well known degradation reaction for carbofuran is chemical hydrolysis under alkaline conditions. This reaction is responsible for carbofuran degradation in soil (Saltzman and Yaron, 1986). This same reaction is often utilized in the laboratory for the purpose of forming a derivative of carbofuran before HPLC analysis (see Lit. Review, Section E.1).

A radio-labeling study by Kaufman and Edwards (1986) showed that the carbonyl group of carbofuran undergoes attack by microbes. In the same study the rate of carbofuran disappearance was decreased by the addition of antibiotics to the soil confirming the role microbes play in

degrading carbofuran.

G.2.D. Cyanazine

The degradation of cyanazine and other s-triazine compounds proceeds much like the degradation of atrazine. The same two major reactions, hydrolysis and dealkylation, which affect atrazine also affect cyanazine (Esser, *et al.*, 1975).

G.2.E. Metolachlor

Like alachlor, metolachlor does not undergo major degradation through chemical pathways. The half-life through aqueous hydrolysis alone was calculated to be 200 days in a laboratory study by LeBaron, *et al.*, (1988). Photo-degradation is also considered to be of no great importance under field conditions.

Degradation of metolachlor by plant metabolism is similar to alachlor degradation in plants. A number of complex products have been isolated but, as with alachlor, the greatest amount of degradation is thought to be carried out by microorganisms which also yield a large number of complex products. Metolachlor is readily degraded in aerobic and anaerobic soil environments (LeBaron, *et al.*, 1988).

G.3. Groundwater Contamination by Pesticides

The five pesticides in this study have all been detected in groundwater with atrazine being detected most

often (Clark, *et al.*, 1991; Frank, *et al.*, 1987; Krill and Sonzogni, 1986; LeGrand, *et al.*, 1991; Pionke, *et al.*, 1988; Spalding, *et al.*, 1980). Following are summarized results of groundwater monitoring studies.

In a study of twenty possible pollutants with known use in an aquifer recharge area, only atrazine and simazine were found in low levels (eg. 0.05-0.31 ppb) in drinking water wells (Clark, *et al.*,1991). The authors stated that the triazine herbicides were found with greater frequency then the agricultural usage would lead one to believe.

In a French study which monitored 38 pesticides in the groundwater beneath active agricultural sites, atrazine was detected most frequently and at the greatest concentrations, 0.06-0.23 ppb (LeGrand, *et al.*, 1991).

A Canadian study of 91 farm wells, all of which were used for drinking water for families and/or livestock, revealed that eight of the wells were contaminated with 0.1-4.7 ppb of atrazine. Another well had levels of alachlor, atrazine, and metolachlor at concentrations between 42 ppb and 128 ppb. These were thought to be the result of a spill on the well site. Of the 91 farms, 25 reported the use of alachlor, 68 reported the use of atrazine, and 39 the use of metolachlor (Frank, *et al.*, 1987).

A Nebraska study of atrazine and alachlor concentrations in 14 wells from shallow aquifers beneath

farmland detected 0.06-3.12 ppb of atrazine in the fourteen wells; alachlor was detected in two wells at concentrations of 0.18-0.71 ppb (Spalding, *et al.*, 1980). This study found no relationship between soil texture and ability of the pesticide to migrate vertically through the soil. However, it did not report on or investigate soil composition when making this conclusion.

A Wisconsin screening of groundwater for volatile organic chemicals and pesticides found atrazine in 12 of 208 community wells carbofuran in 1 of the 208 wells sampled. No concentrations were reported in this study (Krill and Sonzogni, 1986).

A Pennsylvania study of 21 farm wells found atrazine levels of 0.013 to 1.1 ppb in 14 wells. Cyanazine was found in two wells at trace levels (Pionke and Glotfelty, 1989).

G.4. Surface Water Contamination by Pesticides

When agricultural land is adjacent to surface water, movement of applied pesticides into the marine environment is a concern. Pesticides can enter surrounding surface water through drift during application, deposition during rainfall, and runoff during storm event. Recently it has been shown that contaminants have been transported from unconfined coastal aquifers to aquatic systems through submarine groundwater discharge (SGWD). Water in unconfined coastal aquifers generally flows toward surface water due to

elevated hydraulic heads in the upland regions. (Hubbard, 1993; Lee, *et al.*, 1977; Lee, 1980; Sayles and Jenkins, 1982; Simmons, 1989; Simmons *et al.*, 1991; Reay and Gallagher, 1991).

The sample data used in this thesis was also used in conjunction with the Department of Biology, Virginia Polytechnic Institute and State University in a study of submarine groundwater discharge of nutrients. Concurrently the SGWD of pesticides was studied by a masters student in the department of Environmental Engineering.

Hubbard (1993), Reay and Gallagher (1990), Simmons (1989), and Simmons, *et al.* (1992) found that nutrients were in fact being transported off-site by SGWD at the four agricultural sites studied during this project. They found that nitrogen containing nutrients and nitrate in particular were being transported off-site by the advective mechanisms described in the above references. The transport of the alachlor, atrazine, carbofuran, cyanazine, and metolachlor was found to be minor with few detections and pesticide concentrations less than 1 ppb. These studies concluded that, although nutrients were being transported off-site, if pesticides were being transported off-site by SGWD they were not at a great enough concentration to be detected by the methods utilized.

III. Methods & Materials

A. General

Water samples were taken from five sites on the eastern and western shores of the Chesapeake Bay. Soil and sediment samples were taken from four of these sites. Water samples were treated in accordance with the Environmental Protection Agency (EPA) Method 525.1 unless noted. Soil and sediment samples were treated in accordance with EPA method 3540 unless noted.

B. Research Chemicals

B.1. Pesticides, Chemical Standards, and Solvents

All pesticides and chemical standards were purchased 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) acetanilide), 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-methylpropionitrile), 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 preparation of most of the chemical standards was pesticide or Optima^{tm} grade methylene chloride (dichloromethane) CAS # 75-09-2. Pesticide grade methanol CAS # 67-56-1, hexanes and acetone CAS # 67-64-1 were also used. Anhydrous sodium sulfate CAS was used as a drying agent. All of the solvents, boiling chips, Shark skin filter paper (order # 17010), and sodium sulfate were bought from Fisher Chemical Corporation (Raleigh, NC). Milli-Q water from a Milli-Q ion exchange system, Milli-Q Corporation (Milford, MA), was used for all reagent blanks.

B.2. Stock Solution Preparation

All pesticide and chemical stock standards were prepared 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. Solutions of 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 solutions, 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 spiking solution were added to the spiked samples.

C. Laboratory Glassware Procedures

C.1. Glassware

For extraction of water samples, a three piece, all glass, vacuum filter was used (Kontos, Vineland, 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).

The extraction of soils was performed with a soxhlet extraction apparatus (45/50 24/40 Kimax, USA) used with a 250 ml boiling flask and a cool water condenser.

C.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. The teflon bags used to collect seepage water were rinsed with distilled deionized water

three times before each use. The plexiglass tubes were washed with soap and water and rinsed with distilled, deionized water.

D. Field Sampling Procedures

D.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 monitoring (Dr. George Simmons Jr., Biology Department). 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 is 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 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 displayed vertical hydraulic conductivities of 14.0 cm/hr. Mean tidal range was 0.6 meters with summer salinities on the order of

30 ppth.

Agricultural site 2. This site is located on the southern shore of the Rappahannock River in Middlesex County. The winter 1991 crop consisted of winter wheat with soybeans planted in spring 1992. The surface soils have been classified as a Slagle silt loam which demonstrate moderate permeabilities (1.5 to 5.1 cm/hr)(Newhouse, *et al.*, 1985a). The water table was located approximately 4.0 meters below the soil surface. Surficial 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.

Agricultural site 3. This site is located on Cherrystone Inlet in Northampton County. Winter 1991 crop consisted of winter wheat with soybeans planted in spring 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.

Agricultural site 4. This site is located on the southern shore of the Piankatank River in Glouchester County. The surfical soils have been classified as a mix of Psamments-Hamludults complex and Ochlockonee Variant complex which demonstrate permeabilities varying from 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 near shore 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.

Wetlands Site 1. This site is located on Magothy Bay in Northampton County. The site is 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.

D.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. The middle well at Wetlands site 1

tapped the second, confined aquifer. All wells extended 2 to 3 feet below the water table. Site 2 had the deepest wells, approximately 20 feet, and site 4 had the shallowest at about 4 feet. The wells were lined with 2 inch 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 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 groundwater seeping into the Chesapeake Bay. Seepage meters were one ended cylinders 76 cm. in diameter and 15 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 rubber stopper and a Nalgene® tube, approximately 15 cm. in length.

D.3. Sampling Procedure and Preservation

D.3.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 quickly enough for the full number 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. Extractions were always completed within one week of the samples being taken.

D.3.B. Seepage Meter Samples

At low tide, four seepage meters and collection bags were placed,at each site, far enough off-shore so that they were completely under water. The seepage meters were placed in approximately the same area each time. Occasionally they would have to be placed nearer or farther from shore depending upon the tidal conditions. The meters were imbedded into the sediments to within an inch of the

top of the meter. 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, as it was mostly sea water that had been trapped in the head space of the meter. The collection bags were then replaced. At low tide the collection bags were removed and the seepage meter samples were taken directly from the teflon sampling bags. The bags had a 3.75 L capacity, but they were never completely full. All the water in the collection bags at low tide was retained for analysis. The seepage meter samples were also stored in 1 L amber borosilicate bottles with teflon lids on ice in coolers until returned to the laboratories at Virginia Tech. At Virginia Tech, they were stored at 4°C until extracted.

D.3.C. Soil and Sediment Samples

The four agricultural sites sampled for the target pesticides were sampled in both the off-shore sediments in the area where the seepage meters were positioned and in the field. The soil samples were taken from the same position in the field each time sampled. For a summary of soil and sediment collections during this study, see Table 3. The soil samples were collected in plexiglass tubes (i.d. 7.5 cm, length approx. 30 cm) which were open on both ends. The tubes were forced into the soil as far as possible,

Table 3.
Months Soil and Sediment Samples Were Collected

Month	Site 1		Site 2		Site 3		Site 4	
	Soil	Sediment	Soil	Sediment	Soil	Sediment	Soil	Sediment
June	yes	yes	yes	yes	yes	yes	yes	yes
July	yes	yes	no	no	yes	yes	yes	yes
August	no	no	no	no	no	no	no	no
September	no	no	no	no	no	no	no	no
October	yes	yes	yes	yes	yes	yes	yes	yes
November	yes	yes	yes	yes	yes	yes	yes	yes
December	yes	yes	no	no	yes	yes	yes	yes
January	yes	no	no	no	yes	no	yes	yes
February	yes	yes	yes	no	yes	yes	yes	yes

approximately 15-20 cm. The upper end was capped with a rubber stopper and the tube was then pulled out and the lower end capped. Sediment samples were taken in the same manner except the tubes were entirely filled with sediment. After both ends had been tightly capped the tubes were stored on ice in coolers until returning to Virginia Tech.

E. Laboratory Analyses

E.1. Extraction of Water Samples

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 chromatographic retention 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). Acenapthene and Phenanthrene were added at 5 ppb for the April samples and 2 ppb for all months while 4-chlorobiphenyl was added at 10 ppb.

Solid phase extraction was performed 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) which was seated on top of the Empore disk to trap the particulates and prevented them from clogging the Empore disk.

After assembly, the Empore disk was preconditioned by adding 5 mL of methylene chloride and drawing it through in the following manner. Roughly half of the solvent was drawn through the disk, then allowed to soak for approximately one minute. Then the solvent was nearly all drawn through leaving a meniscus on the top. Five mL of methanol was drawn through in the same manner, again leaving a covering of 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 caused the performance to become erratic and unreproducible.

After the disk was preconditioned, the 1 liter sample was drawn through the apparatus. As stated earlier the sample had been treated with surrogates and 5 ml of methanol and mixed well before extraction. The 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 allowed 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. Half of the solvent was drawn through at a time in the same procedure used in conditioning the disk, except the disk was allowed to dry between each 5 mL 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. To remove any residual water, the 15 mL of methylene chloride eluant were passed through a funnel containing a few grams of anhydrous sodium sulfate, which had been previously rinsed with $MeCl_2$. The eluant was evaporated down to 1 mL under a cool nitrogen gas stream, then stored at 4°C until analyzed on the GC.

E.2. Extraction of Soil and Sediment Samples

The soil/sediment samples were analyzed according to EPA method 3540. Large materials such as twigs and rocks were removed from the sample prior to extraction. Approximately 10 g of wet soil/sediment was combined with an equal mass of sodium sulfate, made into an intimate mixture, and spiked with 4-chlorobiphenyl as an internal standard. The soil was taken directly from the plexiglass soil core tube from a depth of approximately 5 cm. This depth would be expected to have a higher pesticide level then samples taken at depths greater then 15 cm (Heatwole, *et al.*, 1992). The mixture was then folded into two sheets of 24 cm shark skin filter paper. The filter paper containing the

soil/sediment was then placed in a soxhlet apparatus and extracted for 18 hrs with an azeotrope of 1:1 acetone/hexane. The soxhlet rinse cycle was approximately one rinse every 10 minutes. The sample extracts were then dried with Na_2SO_4 and concentrated to 1 mL using a Kuderna-Danish (K-D) concentrator. A solvent exchange was performed in the K-D concentrator by adding 50 mLs of hexane. The 1 mL extracts were stored in 4 mL amber vials with teflon lined screw caps at 4°C until the time of analysis.

The percentage moisture was determined by placing 2 to 5 g of wet sample in an aluminum pan and drying at 105°C overnight. Due to a limited number of plexiglass soil tubes some soil and sediment samples had to be transferred to glass bottles after pesticide analysis, but before percent moisture analysis. In the glass bottle, the gravity-water drained from the sediment, so the percent moisture was not an indication of sediment porosity. After percent moisture analysis, the sample was then placed in a muffle furnace at 550°C for twenty minutes to determine volatile loss in grams per gram of soil/sediment. The pesticide concentrations for the soil/sediment samples were calculated based upon dry weight of the sample using the following equation:

$$\%\ moisture = \frac{g\ of\ sample\ wet - g\ of\ sample\ dry}{g\ of\ sample\ wet} * 100$$

$$\text{dry weight g} = \frac{\text{wet weight} * (100 - \%\ \text{moisture})}{100}$$

$$\text{volatile loss per g soil} = \frac{\text{dry weight} - \text{weight @ } 550^{\circ}C}{\text{dry weight}}$$

E.3. 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. On January 5, 1992 an auto-sampler 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 auto-sampler for injection. Selected samples were injected on a Hewlett-Packard Gas Chromatograph model # 5890 series II; connected to a Hewlett-Packard Mass Spectrometric Detector (MS) model # 5970 with a Hewlett-Packard data station model # 5970. The data station model # 5970 was replaced in December of 1992 so all samples that were run after December were analyzed on the HP G1034C data station. The details of each instrument are as follows.

E.3.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 for May and June, 1992 were analyzed using the FID. However, since all the pesticides except carbofuran were chlorinated, analysis using the ECD was instituted in June, 1992. This provided better sensitivity, but metolachlor (which was monitored after July, 1992) 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), which, although it did separate metolachlor and cyanazine, caused the carbofuran and metolachlor peaks to co-elute. Metolachlor co-eluted with a different target analyte on both columns. Therefore to reliably detect metolachlor the water samples were run on both columns for August 1992 to February 1993. A peak at the metolachlor, cyanazine retention time on the DB-5 column could be positively identified through the use of the chromatogram generated by the DB-210 column. Starting in August, 1992 the ECD was used with both the DB-5 and DB-210 columns for detection and quantification of the five pesticides.

Carbofuran, because it contains no halogens, was the most poorly detected pesticide by the ECD detector. The MDL of carbofuran, 1.5 ppb, was three times higher then the second highest, metolachlor, 0.50 ppb. The carbofuran chromatographic peaks were often broad and usually not very

uniform. Many times this caused the carbofuran peak to be lost in the background noise, or integrated improperly. At times a sample fortified to 1 ppb or 2 ppb was reported as not detected and at other times it was reported to have a concentration ten times the actual fortified concentration.

The temperature program for the FID analysis using the DB-5 column was to 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 which equalled a flow rate of 2 mL/min. Approximately 3 μL of each sample were injected. This temperature program is altered slightly from method 525.1. The final ramp continues to 320°C. This was omitted because all of the target analytes were eluted from the column upon reaching 280°C.

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 pesticides diluted from either

column within 19 minutes (see Table 4). The helium linear velocity was 35 cm/sec and the nitrogen make up gas flow was 70 mL/min for both columns. These temperature programs differed from method 525.1. The complex temperature ramps specified in EPA Method 525.1 were not necessary due to the small number of analytes included in this study as compared to the EPA method.

The GC/ECD, calibration curves were generated from 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. Samples in which pesticides were detected were also analyzed by the GC/MS.

Four different standard curves were generated throughout the term of the project. The first curve was made in June. The second was made in October after a heated high capacity gas purification column (Supelco, Belafonte Park, PA) was installed to purify the nitrogen make-up gas to the ECD detector. A third calibration curve was made in November after a second purification column was added to the helium carrier gas. Finally the last curve was made after the installation of the autosampler in January, 1993.

E.3.B. Gas Chromatography/Mass Spectrometry

A DB-5 30 m x 0.25 mm capillary column with a film thickness of 0.25 μm (J&W Scientific, Rancho Cordova, CA) was used for the pesticide analysis. A multi-ramp

Table 4.
Retention times for Pesticides and Internal Standards (GC/ECD)

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

temperature program as specified in EPA Method 525.1 was used for separation of the compounds. Approximately 3 μL 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. As with the GC/FID the continuation of the last temperature ramp to 320°C was not necessary to elute the target analytes so the ramp was stopped at 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.

The Mass Spectrometer (MS) was a quadrupole 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 on line library of spectra in the data station (Wiley-NBS database). For the GC/MS the autotune program was run at the start of every days 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.

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 listed in Table 5 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:

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

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 internal standard (mg/L)

Table 5.
Quantitation Ions of Pesticides and Internal Standards

PESTICIDE	QUANTITATION ION (m/z)
Alachlor	160 *
Atrazine	200 *
Carbofuran	164
Cyanazine	225
Metolachlor	162
INTERNAL STANDARD	QUANTITATION ION (m/z)
Phenanthrene d_{10}	188 *
4-Chlorobiphenyl	152

* - quantitation ion specified in EPA method 525.1

Table 6.
Mass Spectrum Response Factors with Respect to 4-Chlorobiphenyl

PESTICIDE	RESPONSE FACTOR
Alachlor	0.634
Atrazine	0.709
Carbofuran	0.451
Cyanazine	0.119
Metolachlor	1.860

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

$$Concentration\,(ppb) = \frac{A_x Q_{is}}{A_{is} RFV}$$

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 sensitivity was not as high as the GC/ECD for the five pesticides and was only used to test for possible confirmation of pesticides detected by the GC/FID and GC/ECD.

Soil samples were expected to have higher levels of pesticides and were found to have greater matrix interferences. The pesticides in soil samples were quantified through response factors using 4-chlorobiphenyl as an internal standard. This internal standard was chosen for its compatibility with the GC/ECD. Concentrations were calculated in μg/g with the following equation:

$$Concentration\ (ppm) = \frac{A_x\, Q_{is}}{A_{is}\, RF\, dW_s}$$

A_x = Area of characteristic ion for measured compound

Q_{is} = Total quantity of internal standard added to sample

RF = response factor

dW_s = dry weight of sample

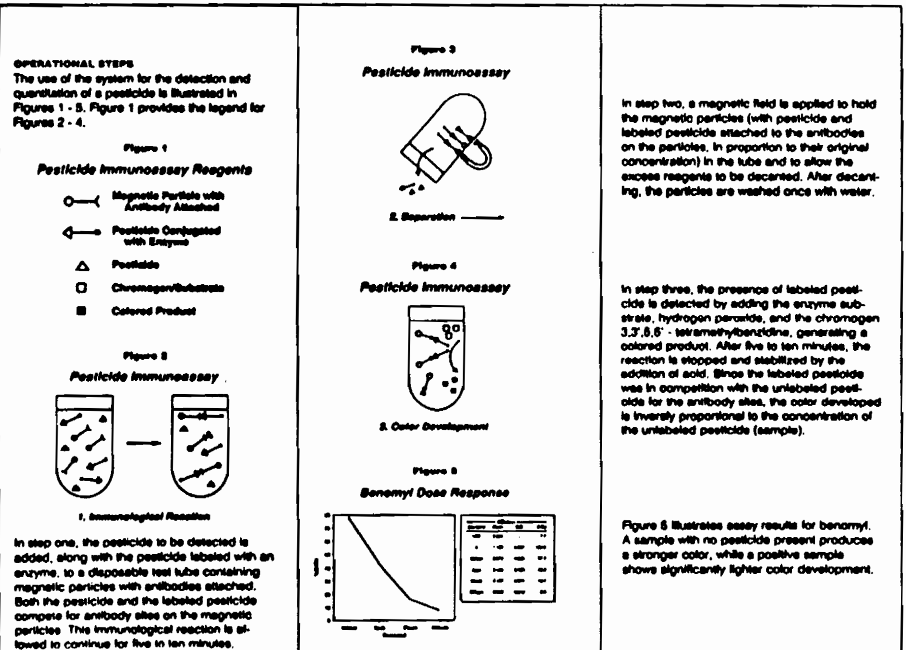
E.4. Immunological Assay

Pesticide immunoassays utilize a combination of an antibody selective for a pesticide, an enzyme and a chromogen which produces color when it reacts with the enzyme. Immunoassays take advantage of high reaction selectivity of antibodies and high reaction efficiency of enzymes to create a powerful analytical methodology.

The Rapid Pesticide Immuno Detection Assays (RaPID) developed by the OHMICRON Corporation utilize an antibody specialized for a particular pesticide. This antibody will react preferentially with this pesticide and not with any others. The antibody is bound to a magnetic particle to ease its removal from solution. The second requirement is a molecule consisting of the pesticide of interest bound to an enzyme conjugate. The third requirement is a chromogen/substrate which will react with the enzyme on the pesticide enzyme conjugate to produce a colored end-product.

RaPID Assays®

(Rapid Pesticide Immune Detection Assays)



OPERATIONAL STEPS

The use of the system for the detection and quantitation of a pesticide is illustrated in Figures 1 - 5. Figure 1 provides the legend for Figures 2 - 4.

In step one, the pesticide to be detected is added, along with the pesticide labeled with an enzyme, to a disposable test tube containing magnetic particles with antibodies attached. Both the pesticide and the labeled pesticide compete for antibody sites on the magnetic particles. This immunological reaction is allowed to continue for five to ten minutes.

In step two, a magnetic field is applied to hold the magnetic particles (with pesticide and labeled pesticide attached to the antibodies on the particles, in proportion to their original concentration) in the tube and to allow the excess reagents to be decanted. After decanting, the particles are washed once with water.

In step three, the presence of labeled pesticide is detected by adding the enzyme substrate, hydrogen peroxide, and the chromogen 3,3',5,5' - tetramethylbenzidine, generating a colored product. After five to ten minutes, the reaction is stopped and stabilized by the addition of acid. Since the labeled pesticide was in competition with the unlabeled pesticide for the antibody sites, the color developed is inversely proportional to the concentration of the unlabeled pesticide (sample).

Figure 5 illustrates assay results for benomyl. A sample with no pesticide present produces a stronger color, while a positive sample shows significantly lighter color development.

FIGURE 1. Schematic Representation of the Immunoassay Mechanism

The specific antibody, the pesticide-enzyme conjugate and the chromogen substrate are provided with the immunoassay kit along with stopping solution and disposable test tubes. A schematic of the immunoassay is shown in Figure 1.

The first step in the analysis is mixing the sample solution (200 μL) with a solution containing the pesticide enzyme conjugate. This solution is then added to a slurry of the magnetic particles with the antibody attached. The solid phase in the RaPID assays has the advantage of being slurried in solution, thus increasing contact with the sample solution and decreasing reaction time. In this first step the pesticide bound with the enzyme conjugate and the pesticide from the sample solution compete to react with the antibody. The second step is to remove the antibodies from solution through the use of a magnetic tray after a specified reaction time (i.e. carbofuran is 20 minutes). Some of the antibodies would have reacted with the pesticide-enzyme conjugate and if there was pesticide present in the environmental sample then it also would have reacted with some of the antibodies. In step three the chromogen/substrate was added and allowed to react with the pesticide-enzyme conjugate for twenty minutes. A stopping solution was then added and the color read.

The color was only formed by pesticide enzyme conjugate which had been removed from the solution by the antibody

bound to the magnetic particle. The amount of pesticide enzyme conjugate remaining was inversely proportional to the amount of pesticide which was in the environmental sample Therefore, a greater color intensity indicates a smaller concentration of pesticide in the environmental sample.

F. Quality Assurance and Quality Control

F.1. Instrument's Performance

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 15% of the predicted value based on the calibration curve, then no samples were analyzed until the instrument was demonstrated to be operating properly.

F.2. Check Standards

An independent analytical chemist not associated with the project prepared check standards that were analyzed to determine any experimental bias (Table 7).

F.3. Fortified Samples (Matrix Spikes)

Fortified samples were prepared for water, soil and sediment samples. For every twenty water samples a lab fortified blank was analyzed. It was made of Milli-Q reagent water with internal standards and the pesticides. The internal standards were at 2 ppb, while the pesticides were added at 0.25, 0.5, 1, 2, or 5 ppb. Additionally, matrix spikes were made from quadruplicate field samples. Two matrix spikes

Table 7.
Pesticide Concentrations Measured in Check Standards

Pesticide	Concentration, (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

were made from each site from April to September, 1992 and four from each site after September. They were originally fortified to 2 ppb and 5 ppb, but as detection limits improved, the fortification concentrations were lowered to 0.25, 0.5, 1, and 2 ppb. There were then four matrix spikes made for each site, one at each fortification concentration. There was one spiking solution which contained alachlor, atrazine, cyanazine, and metolachlor. Another contained alachlor, atrazine, carbofuran, and cyanazine. The former was used to fortify water to 0.25 ppb and 0.5 ppb. The latter at 1 ppb and 2 ppb. This was done because carbofuran and metolachlor co-eluted on the DB-210 column and could not both be quantified in the same sample. Metolachlor had a lower LOD so it was chosen for the less concentrated spiked samples.

Matrix spikes were made for soil/sediment samples. Five soil samples and one sediment sample were spiked throughout the project.

F.4. Lowest Detectable Quantity

The lowest detectable quantity (LDQ) was determined by analyzing the calibration standards prepared at concentrations of 0.01. 0.05, 0.10, 0.25, 0.5, 1, 2, 5, and 10 mg/L. All nine calibration standards were analyzed, with the LDQ recorded for each pesticide. Table 9 lists the LDQ's for each pesticide on each instrument. The LDQ

Table 8.
Instrument Lowest Detectable Quantities of Pesticides

Pesticide	GC/MS (ppm)	GC/FID (ppm)	GC/ECD (ppm)
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: The LDQ did not include the extraction concentration factor of 1000, which would make the sample concentration in ppb.

measured the response of the various instruments to the directly introduced pesticides. There was no extraction step involved so the concentration factor of approximately 1000 was already incorporated into this value. Water samples were concentrated from a 1000 mL starting volume to a 1 mL extract volume. So, the instrumental LDQs should be approximately 1000 times higher than the detection limit in an actual pesticide. The LDQs shown in Table 9 clearly indicate that GC/ECD was the most sensitive method for the five target pesticides.

F.5. Method Detection Limits

The Method Detection Limits (MDL's) represented detection limits that incorporated all the steps of the method; extraction, concentration, and GC analysis. The MDLs were calculated for the seepage and groundwater through the quantification of fortified samples. The standard deviation of the concentrations was calculated for samples fortified to the same level. The MDL was calculated by multiplying the t-statistic at the 99% confidence value and the standard deviation of the calculated concentrations added to the instrumental background noise which was assumed to be zero.

Because the GC/ECD was the main method for quantifying pesticides in water, the MDLs were only calculated for GC/ECD.

Table 9.
Limits of Detection

Pesticide	GC/ECD MDL (ppb)	Immunoassay MDC (ppb)[a]
Alachlor	0.36	0.05
Atrazine	0.33	0.04
Carbofuran	1.50	0.06
Cyanazine	0.32	0.04
Metolachlor	0.50	0.06

a - Data from OHMICRON Corporation

The fortification concentration which was used in calculating the MDL was chosen for each pesticide based upon its response to the ECD detector. Lower fortification concentrations were used for the pesticides which demonstrated a stronger response. The fortification concentration chosen was the lowest concentration at which the pesticide was always detected.

A fortification and recovery experiment was performed for the soil samples by separating one soil sample into four portions of the approximately the same weight. The portions were fortified with the same amount of pesticide spiking solution and extracted using EPA method 3540 as previously described. The percent recovery and standard deviation were then calculated for each pesticide, these data are reported in Table 10.

F.6. Duplicates

Duplicate samples were taken from at least one well each trip. This was done to assess the variability of the sampling and analytical techniques. Duplicates were taken from one well at each site from April to September. From October to February duplicates were taken from all three wells. In addition, enough water was taken to perform matrix spikes at two different levels per site from April to September and at four different levels per site from September to February.

Table 10.
Fortification and Recovery Concentrations for Soil Analysis

Pesticide	Fortification Level (ppb)	Measured Concentration (ppb)	Mean Percent Recovery ±s.d.
Alachlor	1187	1035	85.3±9.65
	1105	1020	
	1163	805	
	1186	1104	
Atrazine	1187	924	81.3±11.4
	1105	1021	
	1163	746	
	1186	1076	
Cyanazine	1187	1313	123.5±32.45
	1105	1700	
	1163	879	
	1186	1811	
Metolachlor	1187	1009	83.0±9.49
	1105	1007	
	1163	784	
	1186	1053	

a - based on dry weight
b - s.d.=standard deviation

F.7. Blanks

For every group of twenty water samples, one lab blank, one equipment blank, and one travel blank were analyzed. All blanks were made with Milli-Q reagent water. The lab blank was designed to evaluate if laboratory procedures were adding contaminants to the samples. The equipment blank evaluated if the pump and tubing was contaminating the sample. Finally, the travel blank assessed if the sample was contaminated while it was being transported.

Laboratory blanks were made for soil/sediment samples to determine if samples or extracts were becoming contaminated from laboratory sources. Blanks were made from sodium sulfate, the drying agent added to soil samples, wrapped in shark skin filter paper, a tear resistant paper, which was extracted in the same way as the soil/sediment samples.

F.8. Recoveries of Surrogates

As internal standards acenapthene d_{10} and phenanthrene d_{10} were added to all water samples throughout the project. 4-chlorobiphenyl was add to all water samples from August 1992 to February 1993. A standard curve was developed based upon multiple injections of 4-chlorobiphenyl standard solutions an four different concentrations. A curve was developed employing least squares regression. Percent recovery of 4-chlorobiphenyl was calculated with this curve

by dividing calculated concentrations by concentration assuming 100% recovery.

G. Statistical Analyses

Linear regression was carried out using Borland's Quattro Pro, version 4.0, or Lotus Freelance Graphics, version 4.0. Systat, version 5.0, was used for the calculation of the Spearman Correlation Coefficients and the performance of the Wilcoxon Signed Rank Test.

IV. RESULTS AND DISCUSSION

A. Soil Concentrations

Soil and sediment samples were taken from the four agricultural sites on seven occasions during the nine month period between June, 1992 and February, 1993. Throughout the course of the study 55 soil and sediment samples were collected, 6 of which were at a depth of greater than 5 cm, the remaining 49 samples were taken near the surface at a depth of approximately 5 cm. For a pesticide to be reported as positively detected in a soil or sediment sample, the two major ions in the compounds mass spectrum must have been present at the proper chromatographic retention time, soil samples were analyzed only by GC/MS. Mass spectra for the pesticides and internal standards used in this study are found in Appendix D.

Target analytes were found in soil samples from all four of the agricultural sites. Thirty-two soil samples were tested in all, fourteen were positive for the presence of pesticides. Alachlor was found only in samples from site 1, while metolachlor was found in soil samples from all four agricultural sites (Figures 2 and 3). The measured soil concentrations of alachlor ranged from a low of 145 ppb to a high of 485 ppb. Measured concentrations of metolachlor ranged from a low of 7 ppb to a high of 110 ppb. Atrazine, carbofuran, and cyanazine were not detected in any soil

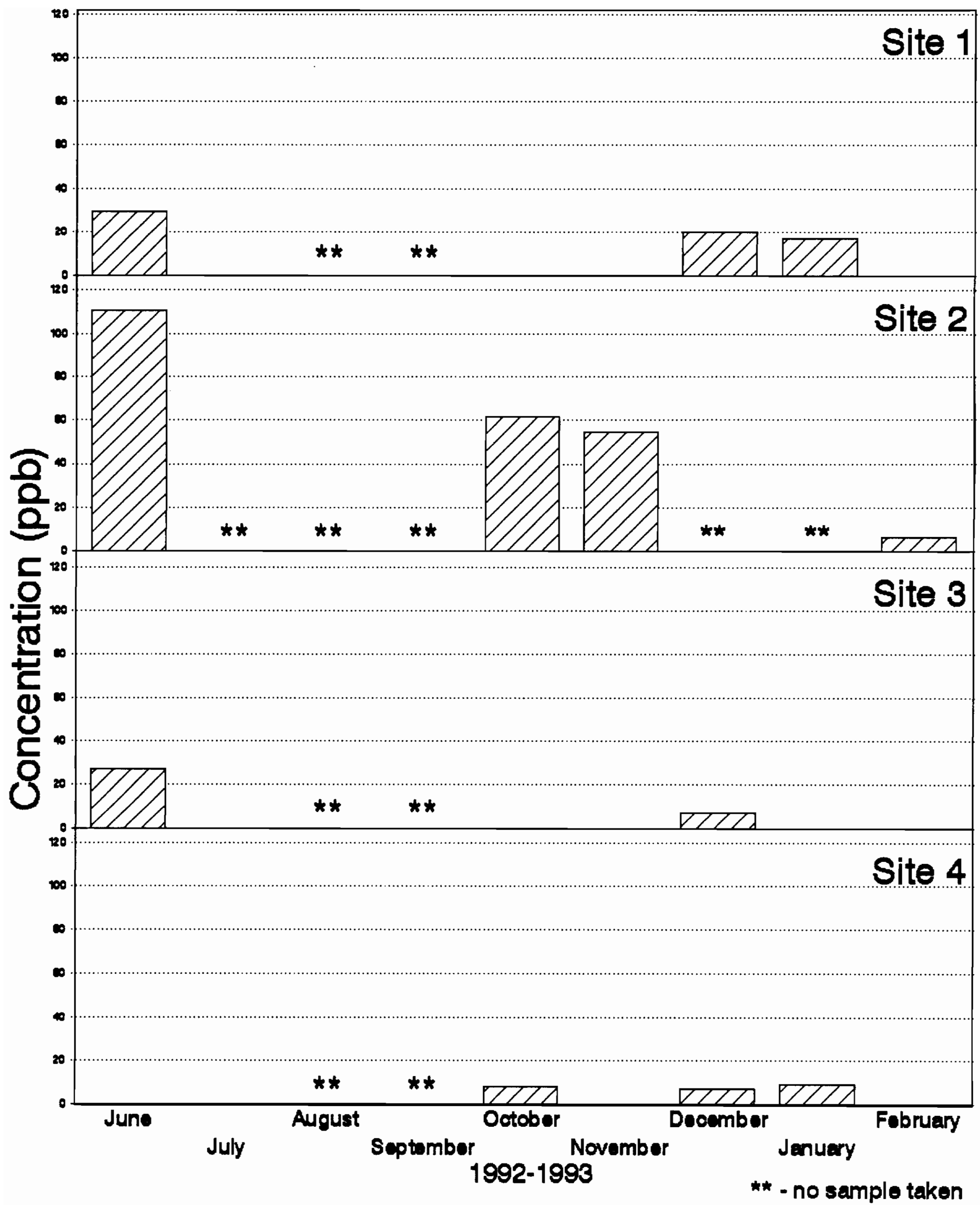


Figure 2. Metolachlor Concentration (ppb) in Soil
Samples from the Four Agricultural Sites.
Metolachlor was detected using GC/MS.

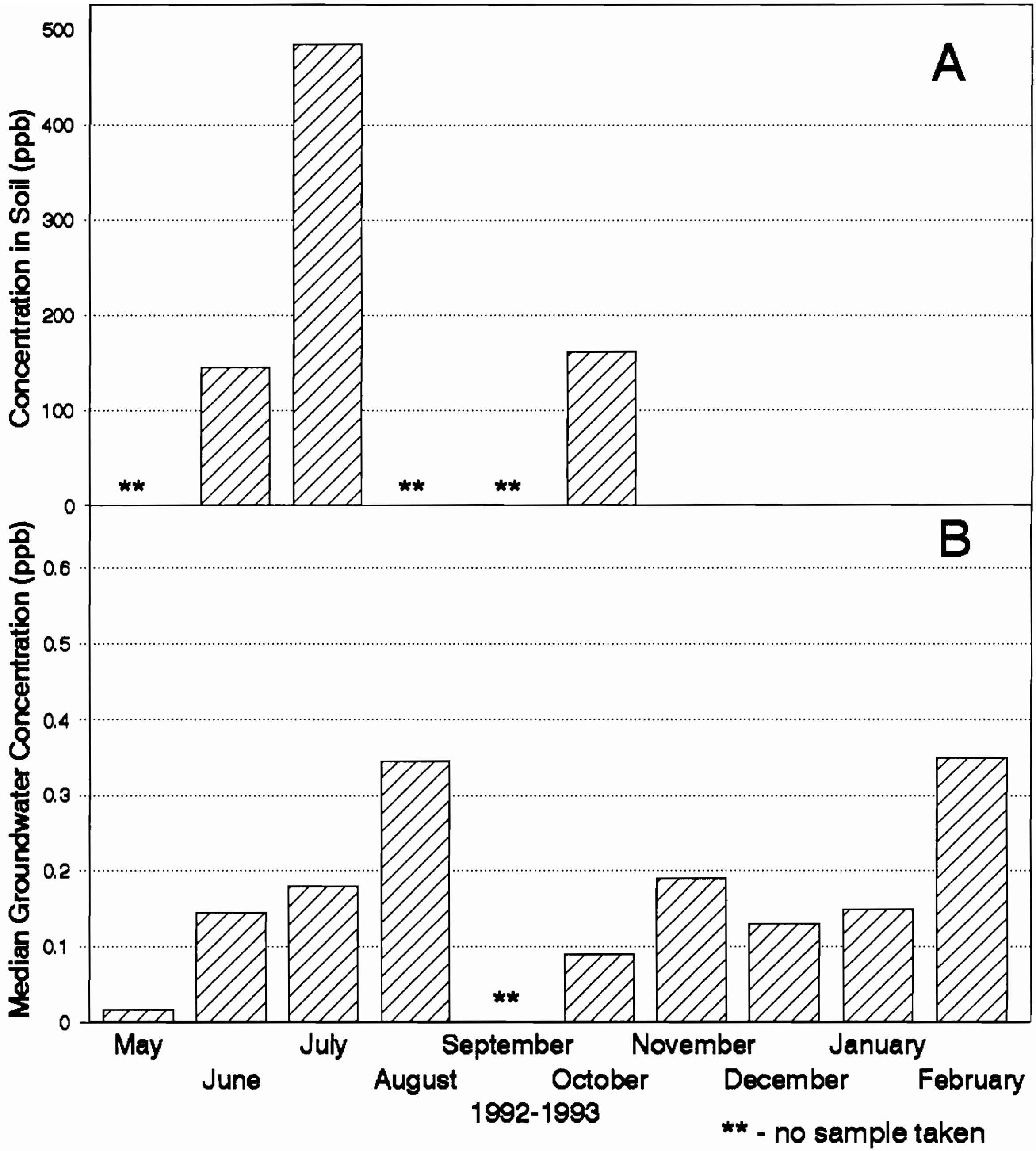


Figure 3. A - Concentration of Alachlor in Soil Samples from Site 1 by GC/MS. B - Median Concentration of Alachlor in Ground-Water Samples from Site 1 by Immunoassay.

Table 11.
Pesticide Concentrations (μg/kg or ppb) Measured in Soil Samples

Sample	Alachlor	Atrazine	Carbofuran	Cyanazine	Metolachlor
SITE 1					
BVF 6/18/92	145	nd	nd	nd	26
BVF 7/17/92	484	nd	nd	nd	nd
BVF 10/10/92	162	nd	nd	nd	nd
BVF 12/5/92	nd	nd	nd	nd	20
BVF 1/10/93	nd	nd	nd	nd	17
SITE 2					
CHF 6/19/92	nd	nd	nd	nd	111
CHF 10/11/92	nd	nd	nd	nd	61
CHF 11/15/92	nd	nd	nd	nd	55
CHF 2/13/93	nd	nd	nd	nd	7
SITE 3					
EVF 6/18/92	nd	nd	nd	nd	27
EVF 12/5/92	nd	nd	nd	nd	7
SITE 4					
WFF 10/11/92	nd	nd	nd	nd	8
WFF 12/6/92	nd	nd	nd	nd	7
WFF 1/11/93	nd	nd	nd	nd	9

samples. None of the twenty-one off-shore sediment samples were found to contain measurable amounts of the target pesticides. None of the six soil samples taken from depths greater than 5 cm were found to contain measurable amounts of the target pesticides.

Data for percent moisture and percent volatile solids (a measure of percent organic matter) for all soil and sediment samples are presented in Table 12.

A.1. Pesticide Application Data and Persistence

Limited pesticide and fertilizer application data were available for two of the four agricultural study sites, site 2 and site 3. These application data were obtained from the farmers in response to inquiries made by Dr. William Reay. The following section compares measured pesticide concentrations in soil to known application data. These data are presented in Table 13.

The application data for site 2 included the time period from spring of 1991 to the summer of 1992. Both metolachlor and atrazine were applied to site 2 in the spring of 1991. These were the only pesticides targeted in our study with a known application date. The first sampling of the soil at site 2 occurred approximately 14 months after known application of atrazine and metolachlor.

The metolachlor application data for site 2 correlates relatively well to measured pesticide concentrations in the

Table 12.
Percent Volatile Solids and Percent Moisture for Soil and Sediment Samples

Sample	Sample Type	% Moisture	% Volatile Solids
SITE 1			
BVF 6/18/92	soil	9.32	2.89
BVF 7/17/92	soil	5.51	2.50
BVF 10/10/92	soil	10.48	16.13
BVF 11/14/92	soil	12.75	10.48
BVF 12/5/92	soil	13.82	2.42
BVF 1/10/93	soil	26.31	10.19
BVF 2/12/93	soil	10.55	2.54
BVOS 6/18/92	sediment	17.35	1.16
BVOS 7/17/92	sediment	27.21	1.57
BVOS 10/11/92	sediment	23.15	2.35
BVOS 11/14/92	sediment	23.01	2.01
BVOS 12/5/92	sediment	21.28	1.39
BVOS 2/12/93	sediment	15.60	0.78
SITE 2			
CHF 6/19/92	soil	21.39	3.28
CHF 10/11/92	soil	15.14	12.00
CHF 11/15/92	soil	16.59	8.20
CHF 2/13/93	soil	14.84	6.12
CHOS 6/19/92	sediment	21.39	3.28
CHOS 10/11/92	sediment	15.14	12.00
CHOS 11/15/92	sediment	16.59	8.20

Table 12. continued

Sample	Sample Type	% Moisture	% Volatile Solids
SITE 3			
EVF 6/18/92	soil	8.94	2.67
EVLot#1 7/18/92	soil[a]	15.24	0.24
EV3ft#2 7/18/92	soil[a]	9.34	1.50
EV3ft#3 7/18/92	soil[a]	7.26	1.28
EV4ft1 7/18/92	soil[a]	7.36	1.26
EVLot3 7/18/92	soil[a]	11.66	0.47
EVWT#2 7/18/92	soil[a]	14.44	0.14
EVSurf1 7/18/92	soil	3.94	2.26
EVSurf2 7/18/92	soil[b]	2.39	1.94
EVSurf3 7/18/92	soil[b]	6.11	1.90
EVF 10/10/92	soil	18.17	6.37
EVF 11/14/92	soil	15.62	9.40
EVF 12/5/92	soil	19.51	7.51
EVF 1/10/93	soil	16.64	5.27
EVF 2/12/93	soil	9.52	8.05
EVOS 6/18/92	sediment	16.07	0.46
EVOS 7/18/92	sediment	21.55	1.24
EVOS 10/10/92	sediment	21.98	1.53
EVOS 11/14/92	sediment	21.91	0.68
EVOS 12/5/92	sediment	23.28	7.15
EVOS 2/12/93	sediment	17.89	0.95

a - Soil sample taken from a depth greater than 5 cm.
b - Duplicate of EVSurf1

Table 12. continued

Sample	Sample Type	% Moisture	% Volatile Solids
SITE 4			
WFF 6/18/92	soil	16.55	3.23
WFF 7/18/92	soil	9.82	1.55
WFF 10/11/92	soil	20.42	2.08
WFF 11/15/92	soil	11.36	10.09
WFF 12/6/92	soil	9.84	8.49
WFF 1/10/93	soil	14.19	1.89
WFF 2/13/93	soil	18.00	7.87
WFOS 6/19/92	sediment	29.87	1.18
WFOS 7/18/92	sediment	23.10	1.27
WFOS 10/11/92	sediment	32.06	6.50
WFOS 11/15/92	sediment	21.59	6.26
WFOS 12/6/92	sediment	20.92	8.96
WFOS 1/10/93	sediment	21.98	1.21
WFOS 2/13/93	sediment	34.02	8.88

Table 13.
Pesticide Application Data

Date	Pesticide Applied
Site 2	
spring 1991	Atrazine and Metolachlor (Dual)
summer 1992	Granoxome and Linuron (Lorox)
Site 3	
prior to 3/92	Metolachlor (Dual)
4/24/92	Trilin
6/26/92	Storm
3/10/93	Harmony Extra

soil, with metolachlor detected in every sample taken at site 2. The concentration of metolachlor appears to have decreased in the soil over time from June, 1992 to February, 1993 (Figure 2).

Atrazine was not detected in the soil samples collected from site 2. Because atrazine was known to be applied but was not detected, an attempt was made to detect known atrazine degradation products in the soil. Total ion chromatograms from GC/MS analysis of site 2 soil samples were examined for the three major ions in the mass spectra of hydroxyatrazine, deethylatrazine, and deisopropylatrazine. None of the atrazine degradation products were detected in the soil. Possible reasons that these products were not detected include the higher instrumental limit of detection by GC/MS for atrazine, and the extraction solvents utilized in this study (Thurman, *et al.*, 1992) The extraction of the five pesticides required that a general extraction scheme be adopted, and an acetone/hexane azeotrope was used as a non-polar solvent mixture for this purpose. For extraction of atrazine and its more polar degradation products a more polar solvent system would be preferred. The use of hot methanol in a batch process was shown to be effective for the extraction of atrazine (Huang and Pignatello, 1990).

Detailed data for site 3 were available for the time

period from March 24, 1992 to March 10, 1993. A list of previously applied pesticides and fertilizers, without application dates, was also supplied for site 3. The pesticide application data indicated that metolachlor was applied to site 3 at some time prior to March, 1992. The exact time of application is unknown. None of the target pesticides were applied to site 3 after March, 1992.

These data for site 3 correlated fairly well with pesticide concentrations measured in the soil. Metolachlor was the only target analyte both applied and detected; the detected concentrations were low, which would be expected over one year after application. This suggested that the herbicide leached from the soil or was degraded by chemical and biological means.

The detection of metolachlor at site 2 was unexpected because 14 months had passed since application of the herbicide. Metolachlor generally has a shorter half-life than atrazine so it was unexpected that metolachlor was detected and atrazine was not. Although both metolachlor and atrazine were applied at site 2 at the same time and only one was detected, it is difficult to draw firm conclusions about their degradation rates in soil without exact knowledge of the amount applied. Nonetheless, the literature provides insights into factors affecting the relative rates of degradation of these two pesticides.

The degradation pathways for the acetanilide herbicides (e.g. alachlor and metolachlor) include degradation in plants, degradation by animals, photodegradation, and degradation by microorganisms. However, the majority of breakdown of alachlor and metolachlor in soil is thought to be mediated by microorganisms. The degradation pathways are complex and yield many different products. Sharp (1988), citing multiple alachlor laboratory studies identified five metabolic products from fungus, five metabolic products from photodegradation, and many more from plant degradation. Very similar metabolic by-products were isolated in metolachlor degradation experiments. These degradation products are difficult to isolate in environmental samples because there are so many end products, each at only a fraction of the original pesticide concentration.

A laboratory study by Walker and Zimdahl (1981), which examined the relative persistence of linuron, atrazine, and metolachlor in soil, may give some insight into the degradation of pesticides at site 2. Metolachlor and atrazine showed different trends with regard to the percent organic carbon found in the soil. Metolachlor exhibited a greater persistence with increasing organic carbon, whereas atrazine was the opposite. Metolachlor showed half-lives of 15 and 22 days in two soils with percent organic carbon values of 1.1% and 2.6%; atrazine had half-lives of 27 and

15 days, respectively. The percent organic carbon levels in soil samples from site 2 were greater than 3.3%. The organic carbon levels may have been high enough to allow metolachlor to be more persistent than atrazine.

The half-lives of atrazine and metolachlor showed the expected trends with regard to temperature and moisture. Increased moisture and temperature resulted in shorter half-lives for both of the pesticides (Walker and Zimdahl, 1981). Soil moisture and temperature are principal factors affecting degradation rates due to the major effect they have on microbial activity. In soil, 90% of the degradation of acetanilide herbicides is carried out by microbial activity (Zimdahl and Clark, 1982 citing Weed Science Society of America, 1979). There can be major variations in the persistence of these herbicides in different microbial environments. A percent moisture change from 17.3% to 2.5% caused the metolachlor half-life to go from 19 to 1303 days while atrazine went from 22-480 days (Walker and Zimdahl, 1981). A temperature drop from 25° C to 5° C caused the half-life of metolachlor to increase from 35 to 135 days and atrazine from 28 to 133 days (Walker and Zimdahl, 1981).

In a temperate zone such as the Chesapeake Bay area the temperature, moisture, and therefore the microbial activity, in the first few centimeters of soil will vary widely throughout the year. This is particularly the case for

surface soils, such as the soil samples used in this study. The percent moisture varied from 2.6% to 21.4% for the four sites in this study, which is a similar range to that investigated by Walker and Zimdahl (1981). Because atrazine degradation is less influenced by moisture, then atrazine likely continued to degrade while the degradation of metolachlor was slower and more dependent on moisture content.

The percent organic carbon probably had the greatest effect on the relative persistence of metolachlor and atrazine at this site. The other variables, moisture and temperature, both perturbed the atrazine and metolachlor half-lives in the same direction. Therefore these variables did not have the same ability to affect the relative persistence of these herbicides as percent organic carbon.

The fact that atrazine was not detected at site 2, fourteen months after application, is consistent with the data presented by Heatwole *et al*. (1992). In that study 272 days (9 months) after 1.68 kg/ha application, the mean atrazine level in the first 1-15 cm of surface soil was 92 ppb. A rough estimate of the time site 2 was first sampled after atrazine application is 450 days, which should have been sufficient time for atrazine levels to degrade below the detection limits of the methodology used in this study.

The level of metolachlor detected (eg. 7-111 ppb) was

surprising when compared to other research. Heatwole et al. (1992) found that metolachlor levels were down to 10 ppb 272 days after application of 2.24 kg/ha. This result seems to point to a long metolachlor half-life at this site.

In an effort to further explain the metolachlor levels at site 2 a plot of concentration verses time was made (see Figure 4). Based upon these limited data, the trend appeared linear, suggesting a possible zero order disappearance with a half-life of 130 days. Based upon this half-life and 14 months since the last metolachlor application, a starting concentration of approximately 290 ppb was calculated. Heatwole, *et al.* determined a mean metolachlor concentration of 243 ppb 3 days after application of 2.24 kg/ha of metolachlor to a study site. The calculated starting concentration, 290 ppb, is within the error estimate calculated by Heatwole, *et al.* for the measured mean, 243 ppb. Based upon this evidence the half-life estimate of 130 days was a reasonable one.

Alachlor was found in high concentrations, 145 to 484 ppb in site 1 soil samples during June, July, and October, 1993. Alachlor was not detected after October. These three months were the first months in which samples were collected. These measured concentrations would indicate application of alachlor in the spring of 1992 for pre-emergence use on the soybeans grown in 1992. That alachlor

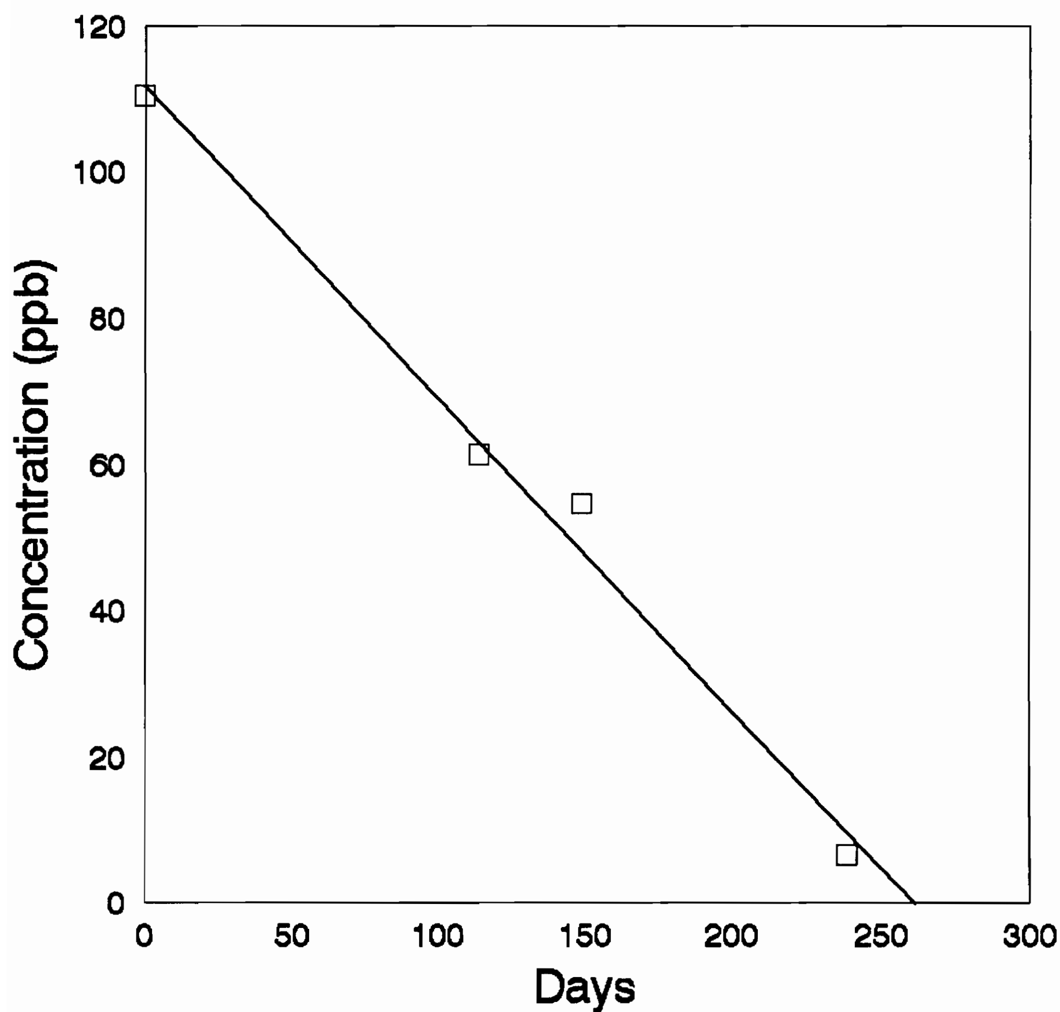


Figure 4. Metolachlor Concentration (ppb) Versus Time (days) at Site 2. (Day 0 = 6/19/92 and Day 239 = 2/13/93)
Note: Raw Data presented in Appendix B, Table B.3.

persisted through the summer months and then could not be detected in late fall, 1992 is consistent with the known use and relatively short half-life for alachlor of 10 days (Jury, *et al.*, 1987).

A.2. Other Organic Compounds Detected in Soil/Sediment

During the course of the soil and sediment analyses mass spectra of chromatographic peaks other than those of the target pesticides were examined and interpreted. Six compounds were tentatively identified (Table 14). At site 3 a compound tentatively identified as methyl-anthracene or methyl-phenanthrene was found in both the sediment (Spectrum C) and the soil spectrum (Spectrum D). Many analytes with mass spectra similar to spectrum E (Appendix D), tentatively identified as eicosene, were observed in the soil and sediment samples. These compounds contain long alkyl chains, greater than C_{18}, and were similar to compounds produced by algae (Rashash, 1992). Algae are a possible source of these compounds which were present in nearly all the soil and sediment chromatograms.

B. Comparison of Groundwater Concentrations to Soil Concentrations

There were few groundwater samples in which pesticides were detected during this study. Out of 119 separate groundwater samples, only 16 samples had pesticide concentrations above the limits of detection according to

Table 14.
Non-Target Organic Compounds Tentatively[b] Identified in Soil and Sediment Samples

Organic Compounds in Soil and Sediment Samples			
Mass Spectrum[a]	Sample	Matrix	Compound
A	CHF 10/11/92	Soil	2,4-bis(1,1-dimethylethyl)-phenol
B	WFF 1/11/92	Soil	fluoranthene
C	EVF 2/12/93	Soil	methyl-anthracene or methyl-phenanthrene
D	EVOS 2/12/93	Sediment	methyl anthracene or methyl-phenanthrene
E	BVF 12/5/92	Soil	benzothiazole
F	EVL#3 7/18/92	Soil	(E)-3-eicosene

a - Mass spectra are presented in Appendix D

b - Tentative identification based on matching sample spectra to library spectrum and reporting matches with greater than 70% agreement.

GC/ECD analysis, three samples contained more than one pesticide. To produce a more complete data set, the GC/ECD data were combined with the data from the immunoassay analysis to generate a more coherent picture of the contamination of the groundwater under the agricultural sites. These data are presented in the Appendix A in Tables A.1. through A.9. This section discusses pesticides in groundwater using this combined data set.

B.1. Alachlor

Alachlor was detected by immunoassay in the groundwater for every month that samples were obtained from site 1. In four of these months it was detected at all three wells sampled at site 1. The detected groundwater concentrations ranged from 0.07 ppb to 4.46 ppb. These results are in agreement with the soil data which indicated application of alachlor in the spring of 1992. Alachlor was detected by GC/ECD at site 1 in February at a concentration of 0.05 ppb. Alachlor was not detected in any other month by GC/ECD even though the concentrations indicated by immunoassay were well above the LOD for GC/ECD. A cause for this could have been the cross reactivity of an alachlor degradation product with the reactive agent in the alachlor immunoassay. In a study of 136 environmental samples that tested positive above 0.2 ppb for alachlor in an immunoassay, GC/MS analysis confirmed the presence of alachlor in only 33 of these 136 samples

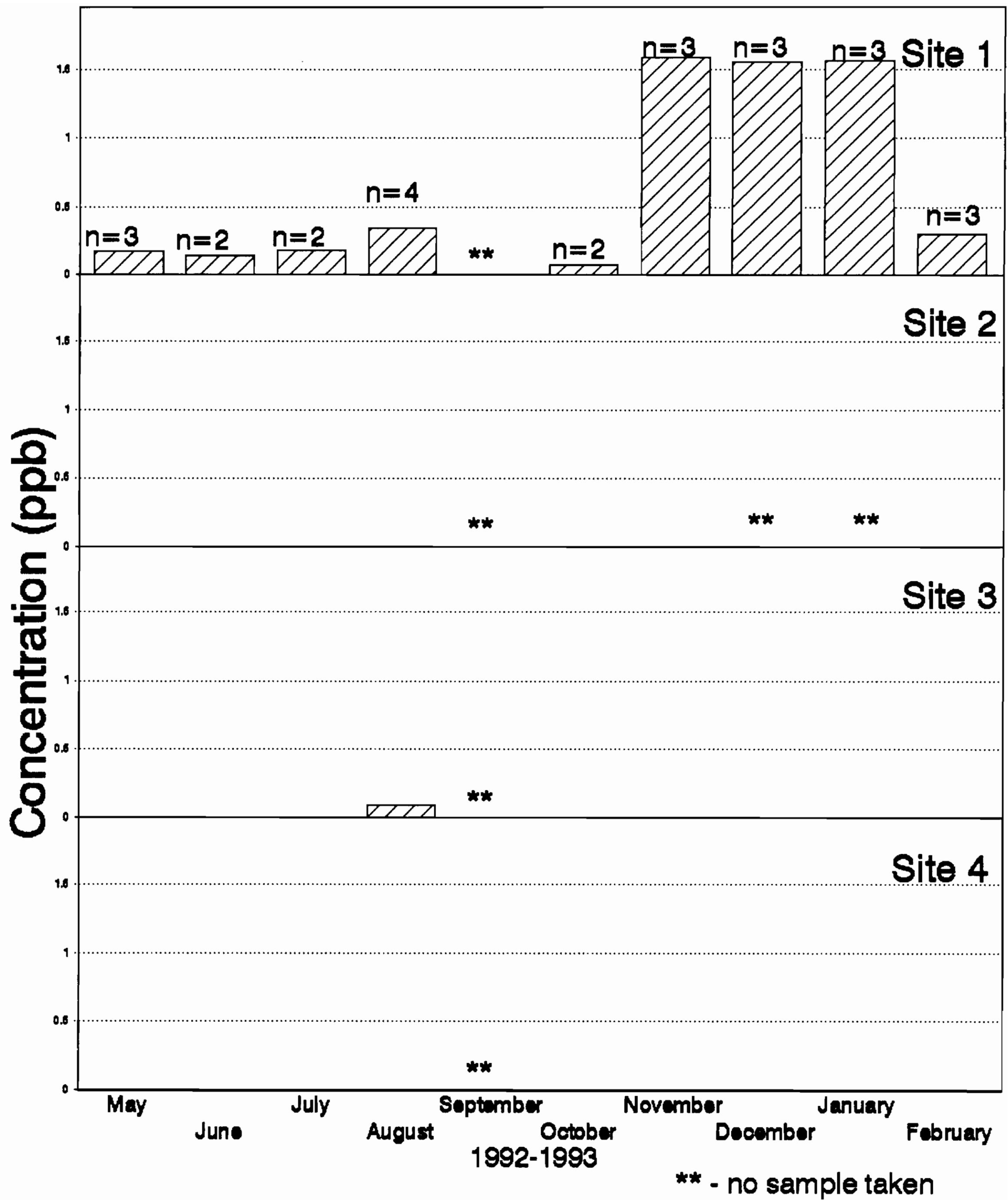


Figure 5. Average Detected Alachlor Concentration in Groundwater; Alachlor Detected by Immunoassay. (number of samples was, n=1 unless noted)

(Baker, *et al.*, 1993). The immunoassay-determined concentrations in the thirty-three water samples confirmed to contain alachlor were consistently higher than the levels predicted by GC/MS. Thirty of the false positive detections were then tested by HPLC for an ethanesulfone soil metabolite of alachlor, 2-{(2,6-diethyl-phenyl) (methoxymethyl)amino}-2-oxoethanesulfonate, known to interfere with the assay; twenty-four of these samples were positive for the ethanesulfone metabolite. This interpretation suggests that alachlor could be degrading rapidly at site 1 so only the soil metabolite is being detected (Baker, *et al.*, 1993).

B.2. Atrazine

The atrazine concentrations exhibited no clear trends and would seem to indicate that atrazine was at three out of four sites at low levels, close to the detection limits (Figure 6). Atrazine was detected a total of twelve times with low ppb concentrations ranging from 1.5 ppb at site 2 to 0.05 ppb at site 4. These low groundwater levels indicate that atrazine was not applied to the field sites during or immediately preceding the sampling period, which is in agreement with the application data.

B.3. Carbofuran

Carbofuran was not detected in the groundwater by GC at any time during the study. This is in agreement with the

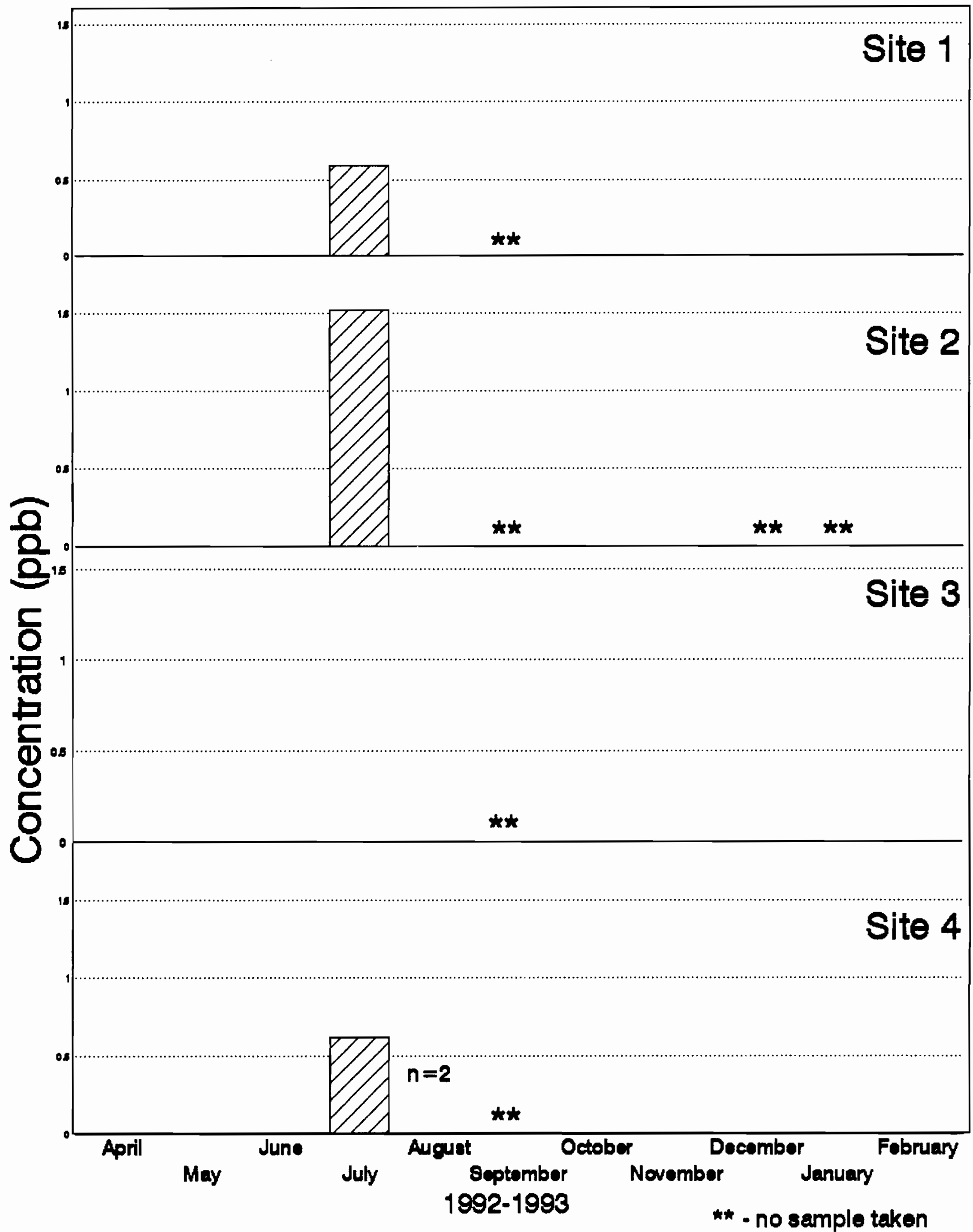


Figure 6. Average Detected Atrazine Concentration in Groundwater; Atrazine Detected by GC/ECD. (number of samples was, n=1 unless noted)

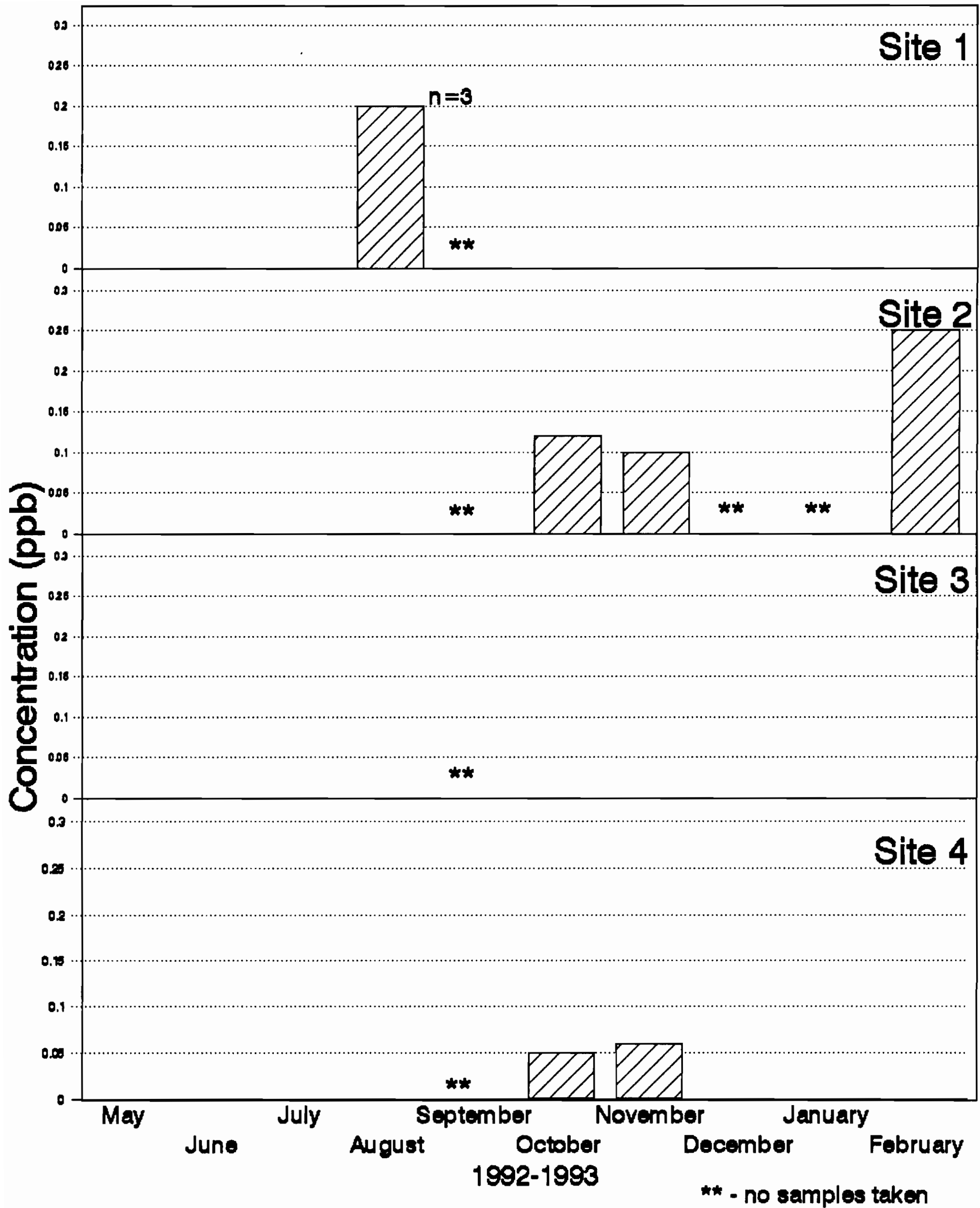


Figure 7. Average Detected Atrazine Concentration in Groundwater; Atrazine Detected by Immunoassay (number of samples was, n=1 unless noted)

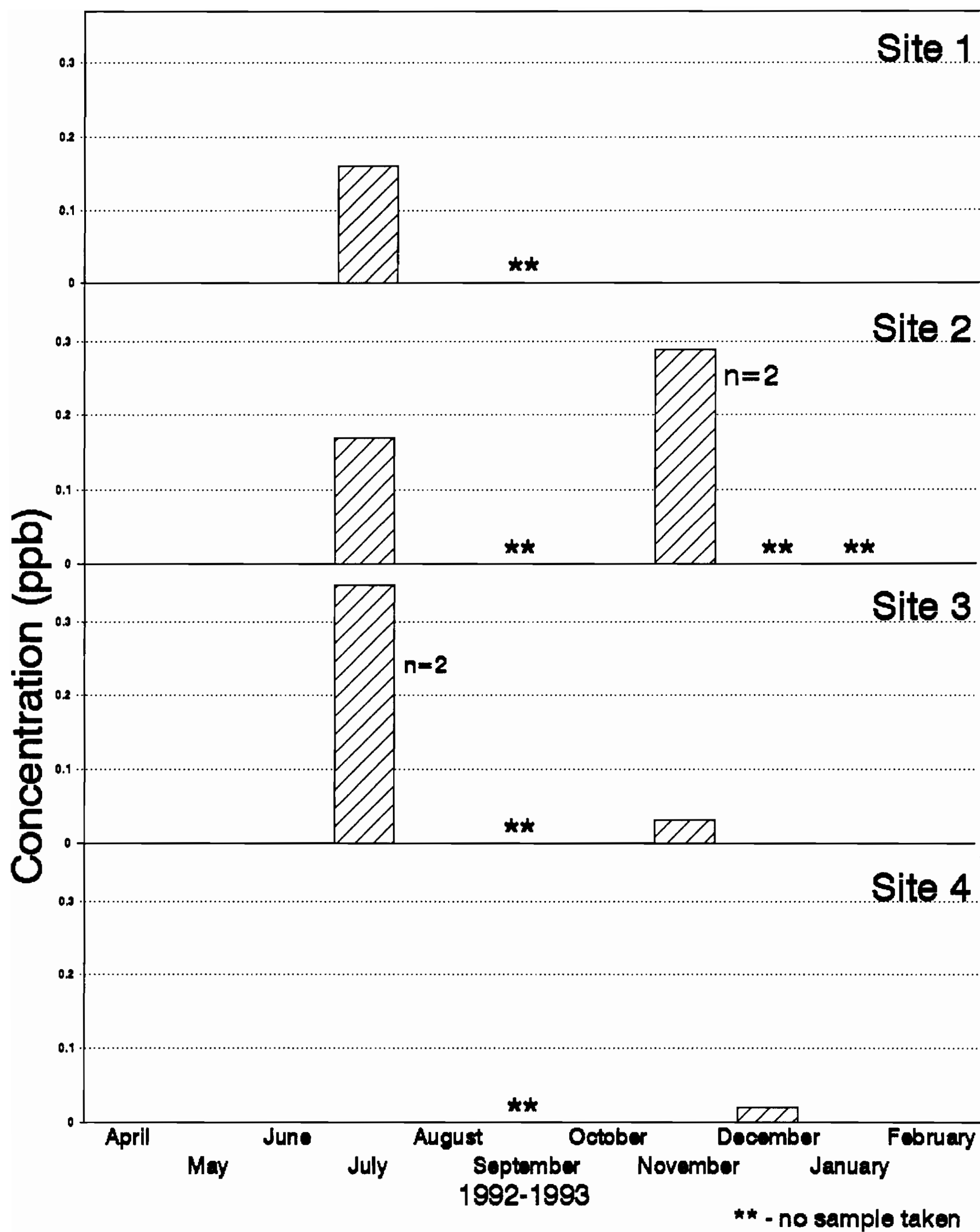


Figure 8. Average Detected Cyanazine Concentration in Groundwater; Cyanazine Detected by GC/ECD. (number of samples was, n=1 unless noted)

Table 15.
Pesticides Detected in Groundwater by GC/ECD

Month	GC/ECD ID	Site	Concentration, ppb				
			Ala	Atr	Car	Cya	Met
June	WF1 #1[a]	4	0.66	nd	nd	nd	nd
July	BV1 #1	1	nd	0.59	nd	0.16*	nd
	CH2 #1	2	nd	1.52	nd	0.17*	nd
	EV2 #1	3	nd	nd	nd	0.16*	nd
	EVF/R #1	3	nd	nd	nd	0.53	nd
	WF2 #1	4	nd	0.60	nd	nd	nd
	WF1 #1	4	nd	0.63	nd	nd	nd
Aug	BV2 #2	1	nd	nd	nd	nd	0.07*
	CH3 #1	4	nd	nd	nd	nd	0.33
	WFSW #1	2	nd	nd	nd	nd	0.07*
Nov	BVCW #2	1	nd	nd	nd	nd	a
	CH2	2	nd	nd	nd	0.02*	nd
	CH5 #1	2	nd	nd	nd	0.55	nd
	EV2 #1	3	nd	nd	nd	0.03*	nd
Dec	WFSW	4	nd	nd	nd	0.02*	nd
Feb	BV2 #1	1	0.05*	nd	nd	nd	0.04*

Abbreviations: nd=not detected, Ala=alachlor, Atr=atrazine, Car=carbofuran, Cya=cyanazine, Met=metolachlor
a - metolachlor was detected by GC/MS but not by GC/ECD

Table 16.
Summary of Pesticides Detected in Groundwater by Immunoassay

Month	Site	GC/ECD ID	Imm. ID	Concentration (ppb)				
				Ala	Atr	Car	Cya	Met
May	1	BV1#1	19a	0.23[a]	nd	nd	nd	nd
	1	BV2#1	18a	0.10[a]	nd	nd	nd	nd
	1	BVCW#3	22a	nd	nd	nd	0.06	nd
	2	CHNew#1	20a	nd	nd	0.10	nd	nd
	2	CH2	24a	nd	nd	nd	nd	0.33
June	1	BV1	7b	0.19	nd	nd	nd	nd
	1	BV2	15b	0.10	nd	nd	nd	nd
July	1	BV1	23c	0.27	nd	nd	nd	0.05
	1	BV2	6c	0.09	nd	nd	nd	nd
August	1	BV2	1d	0.61	0.13	nd	nd	nd
	1	Hopper	2d	0.06	nd	nd	nd	nd
	1	BVCW	17d	0.07	0.12	nd	nd	nd
	1	BVCF1	8d	0.64	0.36	nd	nd	nd
	3	EVF/R	5d	0.09	nd	nd	nd	nd
October	1	BVCW	21e	0.10	nd	nd	nd	nd
	1	BV2	22e	0.09	nd	0.07	nd	nd

Abbreviations: nd=not detected, Imm=immunoassay,
Ala=alachlor, Atr=atrazine, Car=carbofuran,
Cya=cyanazine, Met=metolachlor
a - alachlor also detected in duplicate

Table 16. continued

Month	Site	GC/ECD ID	Imm. ID	Concentration (ppb)				
				Ala	Atr	Car	Cya	Met
October	2	CH2	29e	nd	0.12	nd	nd	nd
	4	WF2	30e	nd	0.05	nd	nd	nd
November	1	BVCW	48f	4.46	nd	nd	nd	nd
	1	BV1	44f	0.19	nd	nd	nd	nd
	1	BV2	11f	0.12	nd	nd	nd	nd
	2	AACH2	6f	nd	0.10	nd	nd	nd
	4	WF1	47f	nd	0.06	nd	nd	nd
December	1	BV1	8g	0.12	nd	nd	nd	nd
	1	BV2	9g	0.18	nd	nd	nd	nd
	1	BVCW	16g	4.42	nd	nd	nd	nd
January	1	BV1	20h	0.15	nd	nd	nd	nd
	1	BV2	12h	0.15	nd	nd	nd	nd
	1	BVCW	26h	1.22	nd	nd	nd	nd
February	1	BV1	8i	0.16	nd	nd	nd	0.10
	1	BV2	4i	0.19	nd	nd	nd	nd
	1	BVCW	36i	0.54	nd	nd	nd	nd
	2	CH2	14i	nd	0.25	nd	nd	nd

Abbreviations: nd=not detected, Imm=immunoassay, Ala=alachlor, Atr=atrazine, Car=carbofuran, Cya=cyanazine, Met=metolachlor.

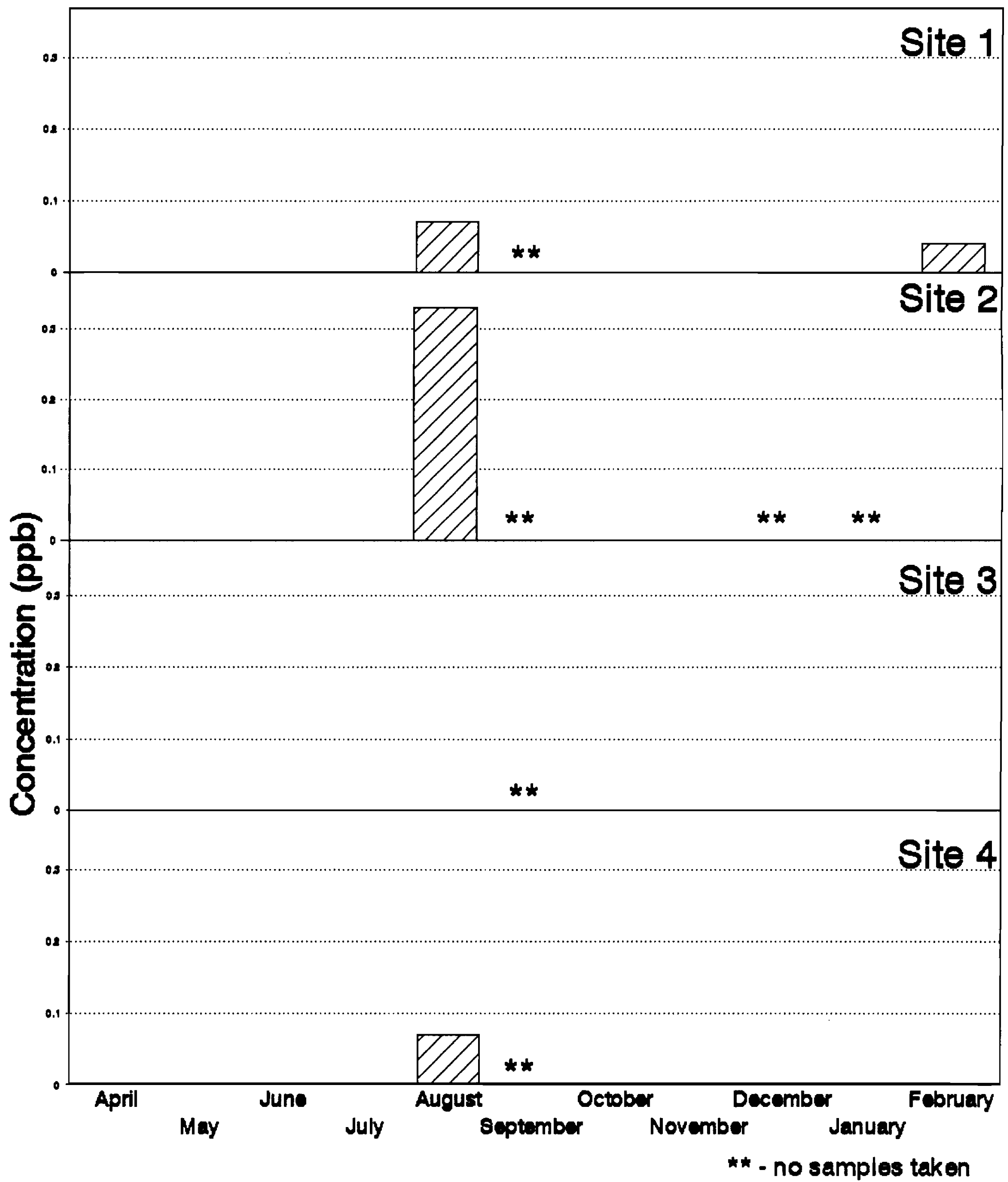


Figure 9. Average Detected Metolachlor Concentration in Groundwater; Metolachlor Detected by GC/ECD. (number of samples was, n=1 unless noted)

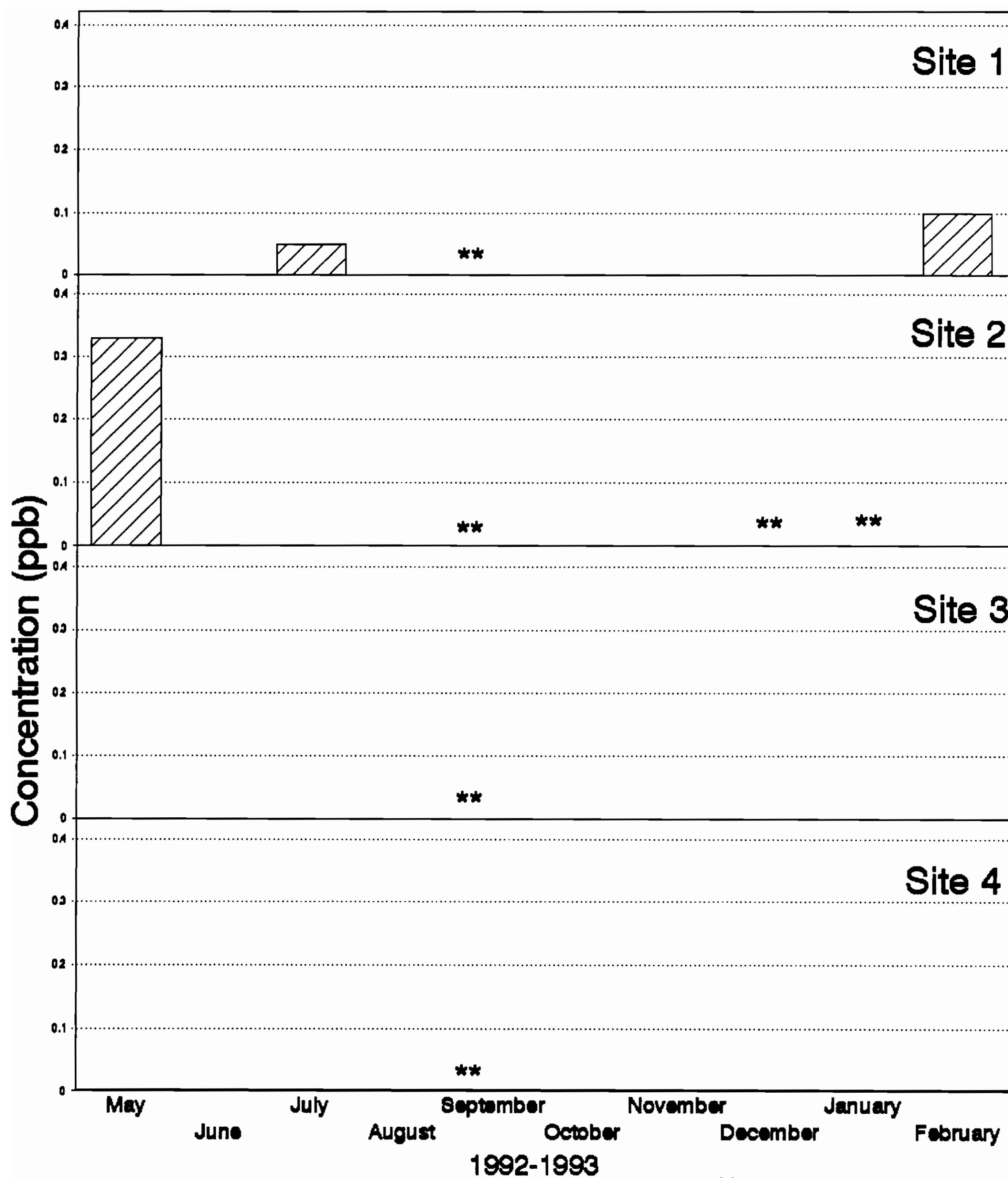


Figure 10. Average Detected Metolachlor Concentration in Groundwater; Metolachlor Detected by Immunoassay. (number of samples was, n=1 unless noted)

soil and available application data . The immunoassay detected carbofuran only twice at concentrations of 0.07 ppb and 0.1 ppb.

B.4. Cyanazine

Cyanazine was detected eight times in the groundwater by GC/ECD at concentrations ranging from 0.55 ppb to 0.02 ppb. Cyanazine was only detected in one groundwater sample by Immunoassay at 0.06 ppb. Detection of cyanazine is not in agreement with soil results or the application data which indicated no use of cyanazine at two sites within many months of this study. The GC/ECD detections showed no pattern and may indicate past application or false positive detection.

B.5. Metolachlor

Metolachlor was detected in groundwater at all four sites at concentrations ranging from 0.33 ppb at site 2 to 0.05 ppb at site 1. The detection of metolachlor in the groundwater at these four sites is in concordance with the detection of metolachlor in the soil at all four sites.

At site 2, low levels of metolachlor were found in the groundwater during May and August. The range of concentrations was 0.1 ppb to 0.33 ppb. The concentration in an August groundwater sample was the highest concentration of metolachlor detected in a groundwater sample and was one of two positive results which had a

sufficient concentration to be detected by GC/MS. These detections were in accordance with the soil data. The concentrations of metolachlor found in the soil samples taken from site 2 were the highest found at any site.

Metolachlor was found in the groundwater at site 1 in July, August, and February. The range of concentrations found was from 0.05 ppb to 0.1 ppb. This range of groundwater detections is reasonable given the range of metolachlor concentrations found in the soil at site 1.

C. Soil Water Equilibria

The pesticide concentrations measured in the groundwater are likely to be related to those measured in the soil by a relationship similar to the Freundlich isotherm. For most pesticides the exponent (n) is in the range 0.7 to 1 so a linear simplification gives a good approximation (Heatwole, *et al.*, 1992 citing Rao and Davidson, 1980).

$$S = K_D C^n$$

S = soil concentration (μg/kg)

K_D = equilibrium constant (21.6 L/Kg)

C = water concentration (μg/L)

n = constant between 0 and 1 dependent upon the solute

The equilibrium constant K_D for metolachlor was

calculated from the partition coefficient K_{oc}= 0.18 m^3/kg reported by Jury (1987). The concentration of a pesticide in soil-water can then be predicted from pesticide concentrations measured in the soil. The soil and water concentration data obtained in this study were not ideally suited for comparison because the matrixes were not in direct contact with one another. The soil was taken from a depth of 5 cm which was substantially above the water table at all the agricultural sites. However, a rough idea of the pesticide concentration on soil in the saturated zone and concentration in water in the vadose zone can be obtained from this linear model.

The predicted concentrations in Table 17 appear to be reasonable. The pesticide concentration on soil will become smaller with depth as predicted with the linear Freundlich approximation. Soil-water at the surface will have much higher concentration then water in the saturated zone. The predicted concentration of metolachlor in the soil below water table the is less than the measured soil concentration at the surface and the predicted concentration of soil-water at the surface is greater than the measured water concentration. Therefore based upon the Freundlich isotherm the two measured concentrations are correct relative to one another.

Table 17.
Predicted Metolachlor Concentrations in Soil-Water and Soil in the Saturated Zone in October for Site 2[a]

Matrix	Concentration (ppb)	
	Measured	Predicted[b]
Soil	61	7.13
Water	0.33	2.84

a - Calculated based on $S = K_D C^n$, where a value of n = 1 was assumed for the exponent
b - The predicted soil concentration is based upon the measured water concentration. The predicted water concentration is based upon the measured soil concentration

D. Water Concentrations

D.1. Groundwater Samples

In this research, 119 individual groundwater samples were investigated for the presence of five target pesticides by GC/ECD. Thus there were 595 chances to detect any of the five pesticides in groundwater by GC/ECD. The GC/ECD method had 19 pesticide detections, which corresponded to 3.2% detection for the pesticides in groundwater (i.e., 19/595). The same five pesticides were monitored in 101 groundwater samples by immunoassay, for a total of 505 chances to detect pesticides. The immunoassay method detected one of the five pesticides 40 times in these 101 groundwater samples (7.9 percent, or 40/505). There was only one case in which the same pesticide was detected in a groundwater sample by both immunoassay and GC/ECD. This detection was for alachlor which was measured in the February BV1 sample at 0.05 ppb by GC/ECD and at 0.16 ppb by immunoassay. The majority of the concentrations measured by GC/ECD were above the limits of detection for the immunoassay method, and therefore, the immunoassay should have also detected pesticides in the sample. Most notable was the site 2 August CH3#1 sample which was confirmed to contain metolachlor at 0.33 ppb by GC/MS, but reported as not detected by the immunoassay. Two explanations for the lack of agreement between GC/ECD and immunoassay were detection of false positives by GC/ECD or

detection of false negatives by the immunoassay. GC/ECD false positive detection was always a concern due to the complexity of the chromatogram (Figure 11) and the lack of a confirmatory procedure. Both false positive detection by immunoassay and false negative detection by GC/ECD probably contributed to the discrepancies between the two methods.

The GC/ECD method did not detect 39 of the 40 pesticide detections that were measured by immunoassay. The majority of the groundwater concentrations reported by the immunoassay were below the LOD for the GC/ECD technique. The exceptions were in the August sample BV1 which contained atrazine at 0.36 ppb and 6 detections for alachlor at concentrations of 0.61, 0.64, 4.46, 4.42, 1.22, and 0.54 ppb all these samples were taken from site 1. A probable explanation for the alachlor detections was given previously in Results Section B.1. which cited the presence of a soil metabolite which responded to the immunoassay method but not the GC/ECD method.

D.2. Seepage Meter Water Samples

There were 53 distinct seepage meter samples analyzed by both GC/ECD and immunoassay. Seven times an insufficient sample volume was obtained for GC/ECD analysis, but enough sample was available for the immunoassay, so it was performed. Therefore, a total of 60 samples were analyzed

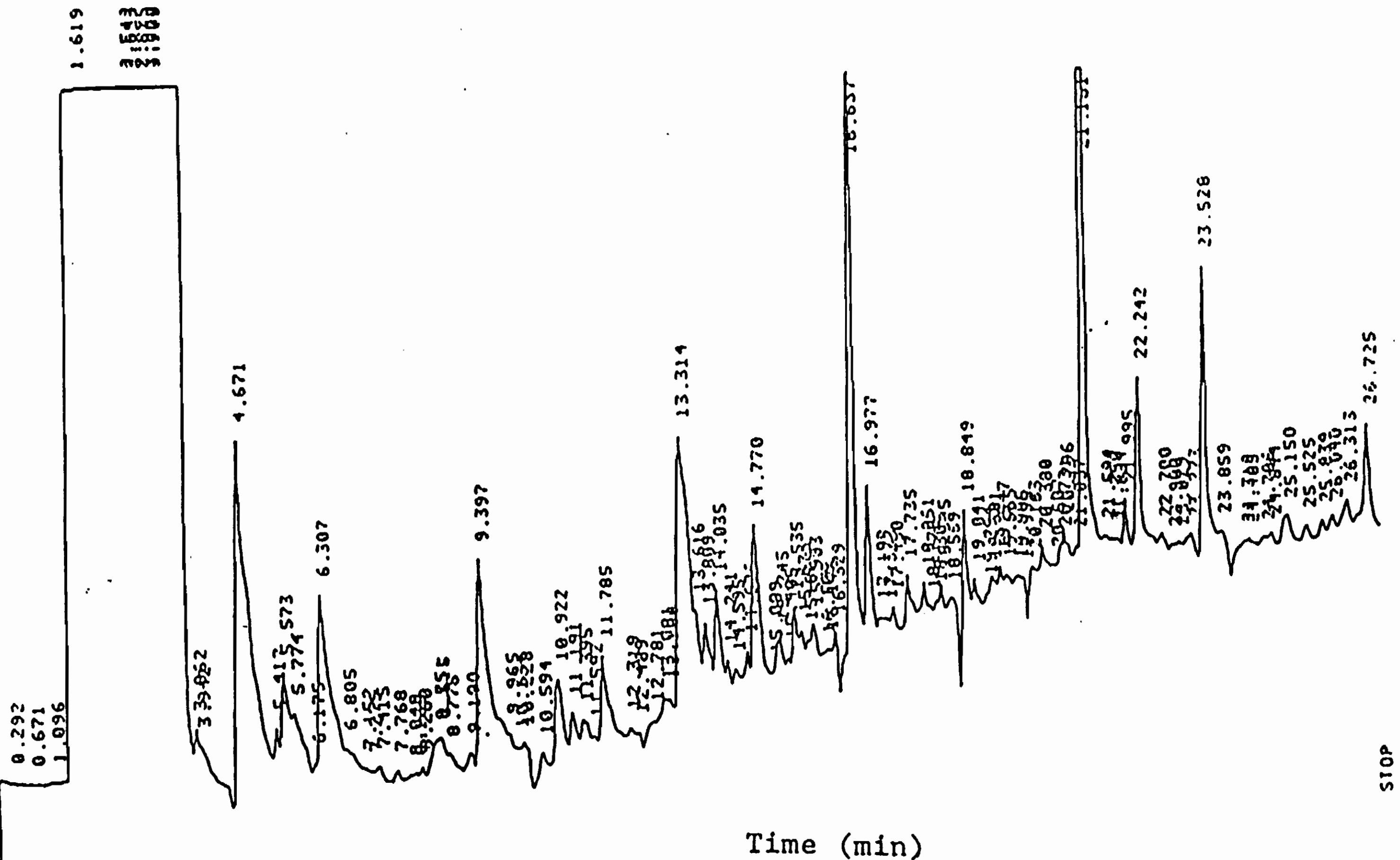


Figure 11. Typical seepage meter water sample chromatogram using GC/ECD. The sample was BVSM 1&3 combined. No pesticides were detected

by immunoassay and 53 by GC/ECD. Two of the 53 samples tested by GC/ECD were found to be positive for metolachlor; 14 of the samples tested by immunoassay were found to contain pesticides. Six of these samples contained more than one pesticide, so there were a total of 23 detections by immunoassay. The majority of the detected concentrations (18 of 23) by immunoassay were below the LOD of the GC/ECD method. A major difficulty in detecting pesticides in seepage meter samples by the GC/ECD method was caused by the large amount of chromatographical material present in the seepage meter samples (Figure 11). This chromatographic material provided a matrix interference at many retention times. The presence of so many chromatographic peaks increased the possibility that an interfering peak occurred at the retention time of a target pesticide, also increasing the possibility of false positive detection.

E. Biomagnification

It appeared that generally very small levels (e.g., << 1 ppb) of pesticides were being transported off site through groundwater discharge. However, this should not be the only criterion examined when assessing the impact to the Chesapeake Bay ecosystem. Sub-part per billion levels of a persistent contaminant with a propensity for biomagnification would be detrimental.

The half-lives of the five pesticides studied were on

Table 18.
Summary of Pesticide Detections in Seepage Water by GC/ECD

Month	Site	GC/ECD ID	Concentration (ppb)				
			Ala	Atr	Car	Cya	Met
October	2	CHSM1-4	nd	nd	nd	nd	0.04*
February	2	CHSM2	nd	nd	nd	nd	0.32

Abbreviations: Ala=alachlor, Atr=atrazine, Car=carbofuran, Cya.=cyanazine, Met=metolachlor, and nd=not detected
* - below limit of detection

Table 19.
Summary of Pesticide Detections in Seepage Water Samples by Immunoassay

Month	Site	GC/ECD ID	Imm. ID	Concentration (ppb)				
				Ala	Atr	Car	Cya	Met
July	2	CHSM1	27c	nd	nd	nd	0.05	nd
	2	CHSM4	24c	nd	0.07	nd	nd	nd
August	1	BVSM1	13d	0.11	0.14	nd	nd	nd
	2	CHSM1	14d	0.09	0.47	nd	nd	nd
	2	CHSM3	9d	0.19	0.05	0.06	nd	nd
	4	WFSM2	15d	0.06	0.24	nd	nd	nd
	4	WFSM3	10d	0.28	0.51	nd	0.09	nd
	4	WFSM4	6d	0.21	0.36	nd	0.06	nd
October	2	CHSM1	9e	nd	0.08	nd	nd	nd
	2	CHSM2	12e	nd	0.11	nd	nd	nd
	2	CHSM3	20e	nd	0.14	nd	nd	nd
	2	CHSM4	18e	nd	0.10	nd	nd	nd
November	1	BVSM4	46f	nd	0.05	nd	nd	nd
December	4	WFSM2	19g	nd	0.07	nd	nd	nd

Abbreviations: Imm=immunoassay, Ala=alachlor, Atr=atrazine, Car=carbofuran, Cya=cyanazine, Met=metolachlor, and nd=not detected

average less then six months, which is much less than chemicals which are known to biomagnify such as DDT and PCBs. The half-lives for these compounds were often estimated at many years and under some conditions no measurable degradation of PCBs occurs (Bopp, *et al.*, 1981).

Kenaga and Goring (1980) reviewed biomagnification studies on different species of fish in a simulated flowing water ecosystem. The biomagnification was assessed through the calculation of a Bioconcentration Factor (BCF). This factor was a measure of the partitioning of the chemicals into the tissue of the fish. Metolachlor was not included in the Kenaga and Goring study but BCFs were calculated for the rest of the pesticides in this study. Alachlor, carbofuran, and cyanazine were all found to have bioconcentration factors of zero. This indicated that either the compound decomposed during the experiment or was completely metabolized by the test organism. Atrazine was found to have a BCF of 11, more than three orders of magnitude less than DDT and Arochlor 1254 a PCB which had BCFs of 84,500 and 12,150 respectively.

The study also found a significant linear correlation between K_{oc} and BCF. The K_{oc} value reported in the literature was 0.18 m^3/Kg for metolachlor and 0.16 m^3/kg for atrazine (Table 2). Therefore an estimate of the BCF for metolachlor would put its concentration several orders of

magnitude less than compounds which were known to biomagnify.

F. Comparison of GC/ECD and Immunoassay Methods

F.1. Graphical Comparison

Due to the relatively small number of groundwater and seepage water samples which tested positive for the target pesticides, it was necessary to use the data from fortified and reagent water samples in addition to seepage and groundwater sample results for a statistical comparison. Data from 206 samples obtained between August, 1992 and February, 1993 were used in the following comparisons. These 206 samples were blanks, groundwater, seepage water, and fortified samples that were simultaneously analyzed by GC/ECD and immunoassay. There were 82 fortified samples in this set of 206 samples. Thirty-nine of the 82 samples were fortified to concentrations of 0.25 ppb and 0.5 ppb; samples fortified at these concentration generally contained metolachlor and not carbofuran. Forty-one of the 82 samples were fortified to concentrations of 1, 2 or 4 ppb these samples generally contained carbofuran and not metolachlor. Samples were fortified in this manner because carbofuran and metolachlor co-eluted on the DB-210 column. Data from May, June, and July were not used in this comparison because of the initial difficulty in finding a GC method which could successfully identify and measure of all

five target analytes.

The 206 data points were graphed with the immunoassay concentrations plotted against the GC/ECD concentrations (Figures 12 to 16). These figures present the complete 206 point data set for each pesticide; for samples in which a pesticide was not detected, the concentration was designated as 0 ppb for graphical purposes.

The slope of the line calculated through linear regression was less then the ideal value of one in 3 out of 5 cases (i.e. atrazine, carbofuran, and cyanazine). The y-intercept was greater then the ideal value of 0 for every pesticide. This was due in part to the number of detections reported by the immunoassay at low concentrations that were not detected by the GC/ECD. This was expected in light of the lower LOD of the immunoassay.

The greatest concurrence between measured concentration by the two methods was for alachlor and metolachlor. The two sets of carbofuran concentrations appeared visually to have the worst agreement. The GC/ECD method had a very high LOD for carbofuran, 1.5 ppb, which resulted in a large number of possible false negative results. This can be seen on Figure 14 by the large number of points on the y-Axis.

Figures 17 through 21 were generated to assess the accuracy with which the two methods determined concentrations in fortified solutions only. The regression

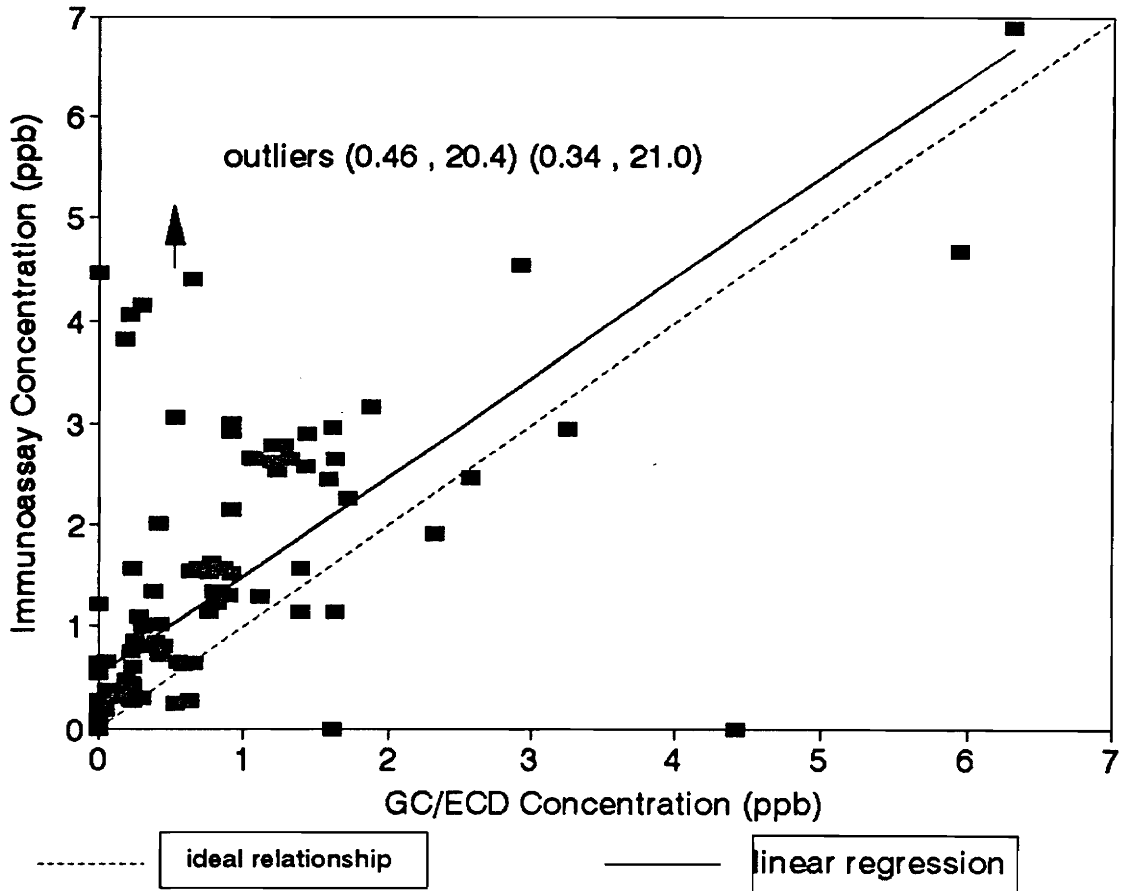


Figure 12. Comparison of alachlor concentrations determined by GC/ECD and immunoassay in groundwater, seepage meter and reagent water samples to which alachlor was added. Alachlor was added to these samples in the concentration range from 0.25 - 4.0 µg/L (ppb). The data were from samples obtained between August, 1992 and February, 1993.

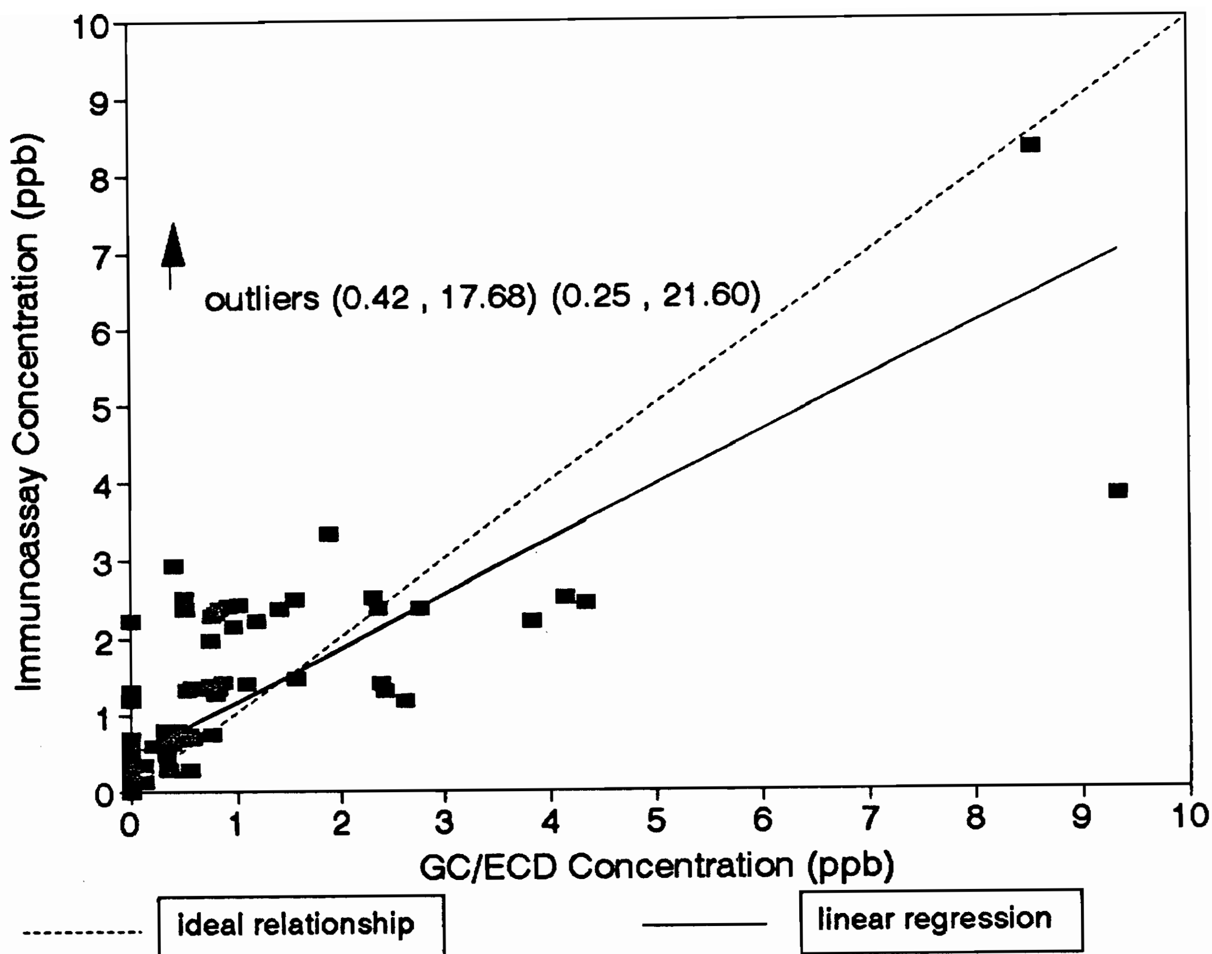


Figure 13. Comparison of atrazine concentrations determined by GC/ECD and immunoassay in groundwater, seepage meter and reagent water samples to which atrazine was added. Atrazine was added to these samples in the concentration range from 0.25 - 4.0 μg/L (ppb). The data were from samples obtained between August, 1992 and February, 1993.

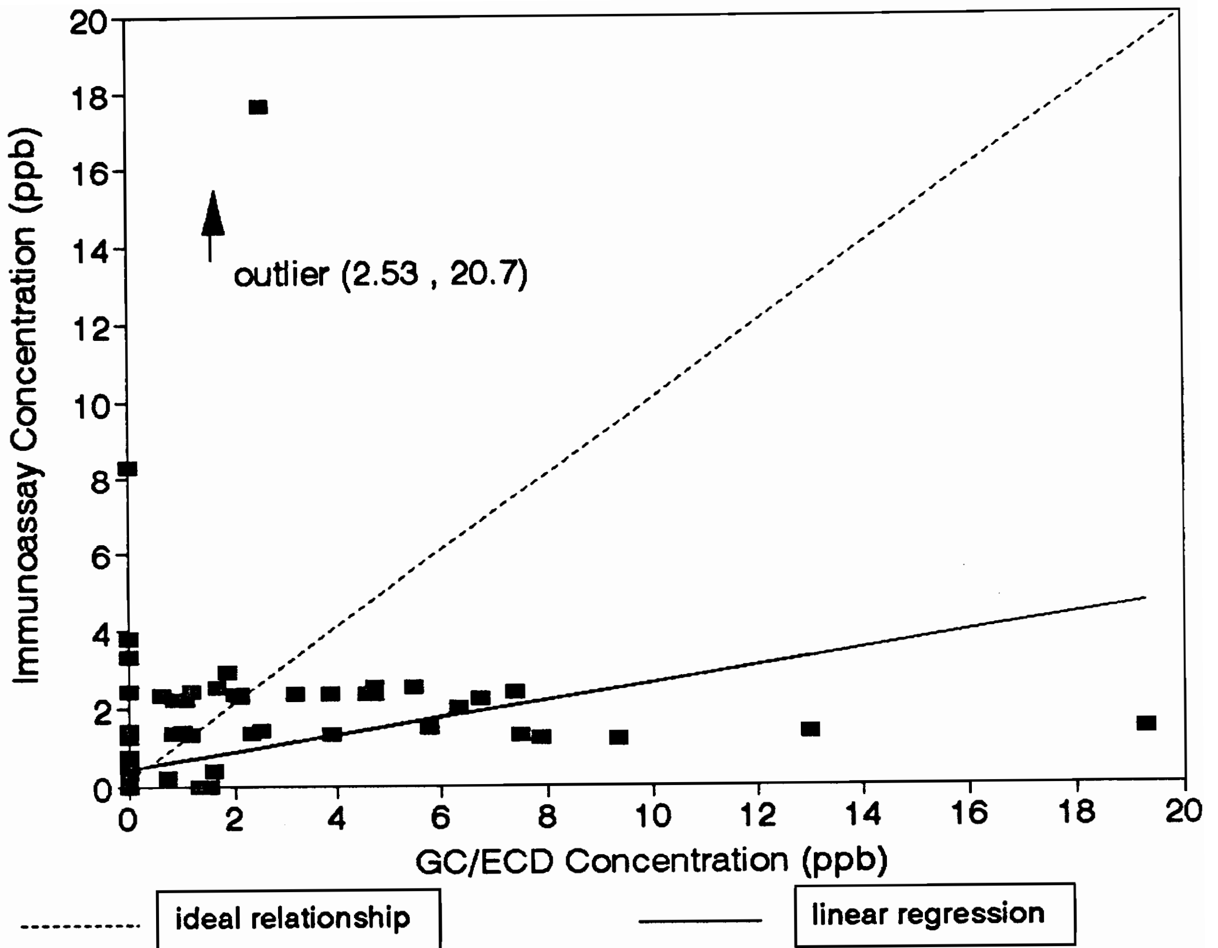


Figure 14. Comparison of carbofuran concentrations determined by GC/ECD and immunoassay in groundwater, seepage meter and reagent water samples to which carbofuran was added. Carbofuran was added to these samples in the concentration range from 0.25 - 4.0 µg/L (ppb). The data were from samples obtained between August, 1992 and February, 1993.

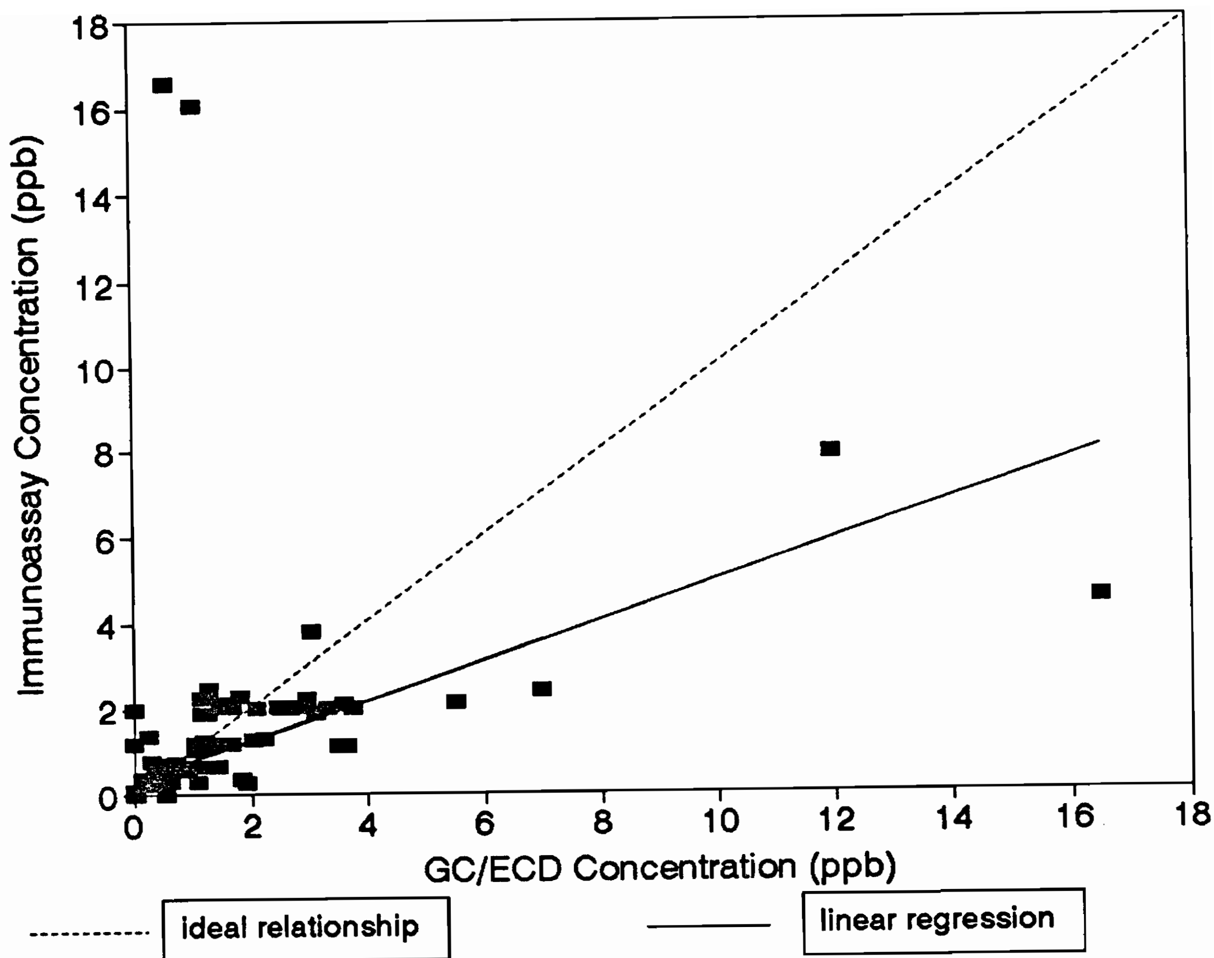


Figure 15. Comparison of cyanazine concentrations determined by GC/ECD and immunoassay in groundwater, seepage meter and reagent water samples to which cyanazine was added. Cyanazine was added to these samples in the concentration range from 0.25 - 4.0 µg/L (ppb). The data were from samples obtained between August, 1992 and February, 1993.

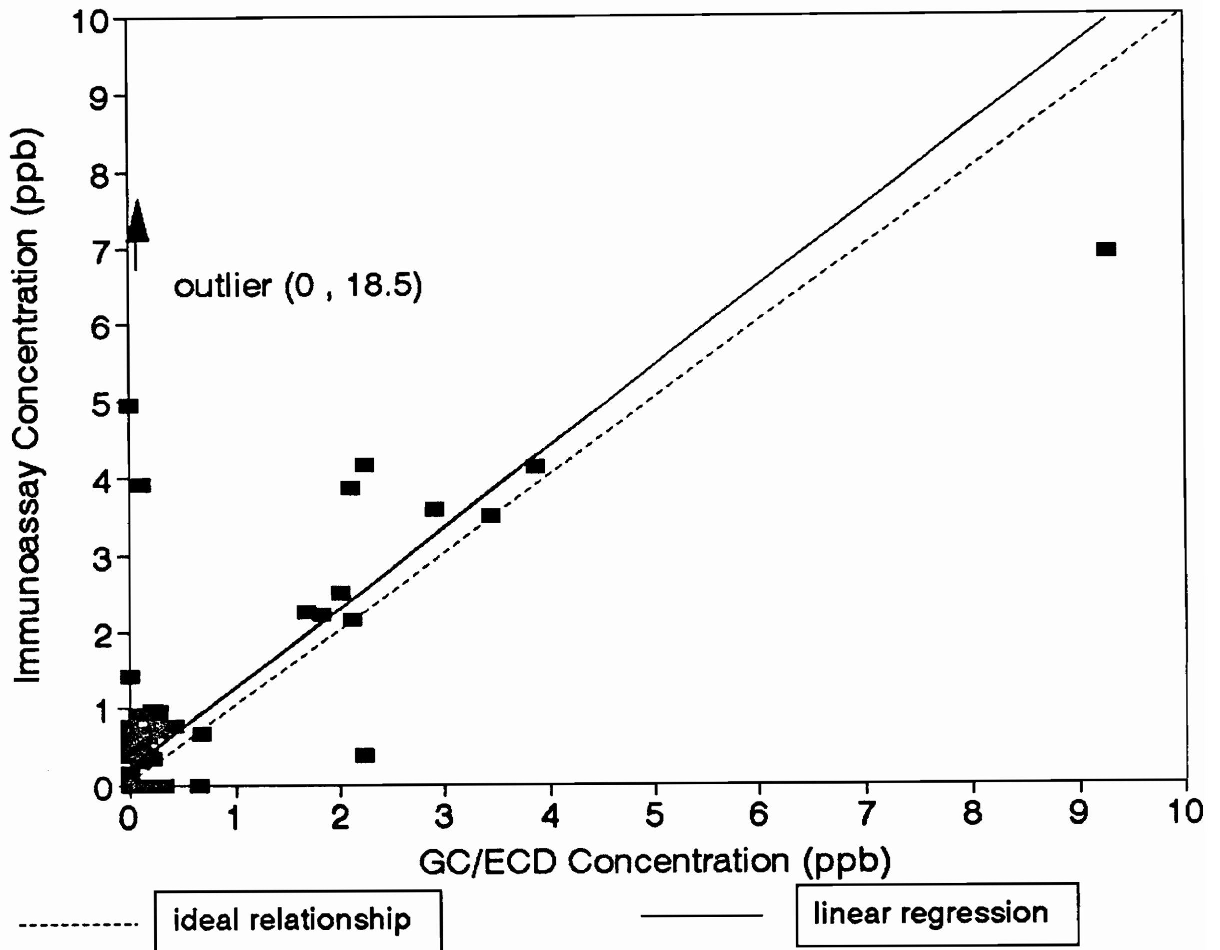
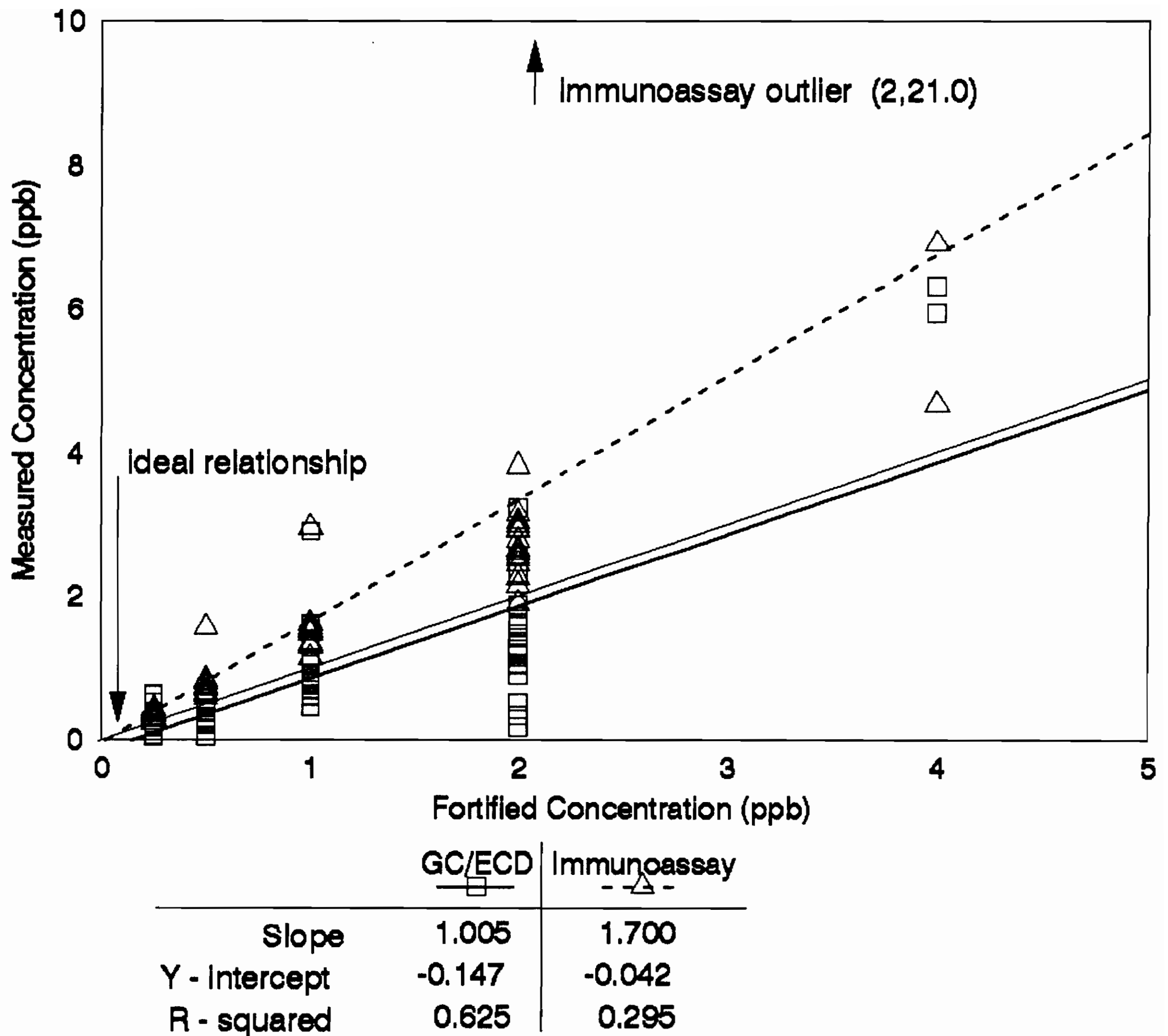


Figure 16. Comparison of metolachlor concentrations determined by GC/ECD and immunoassay in groundwater, seepage meter and reagent water samples to which metolachlor was added. Metolachlor was added to these samples in the concentration range from 0.25 - 4.0 μg/L (ppb). The data were from samples obtained between August, 1992 and February, 1993.

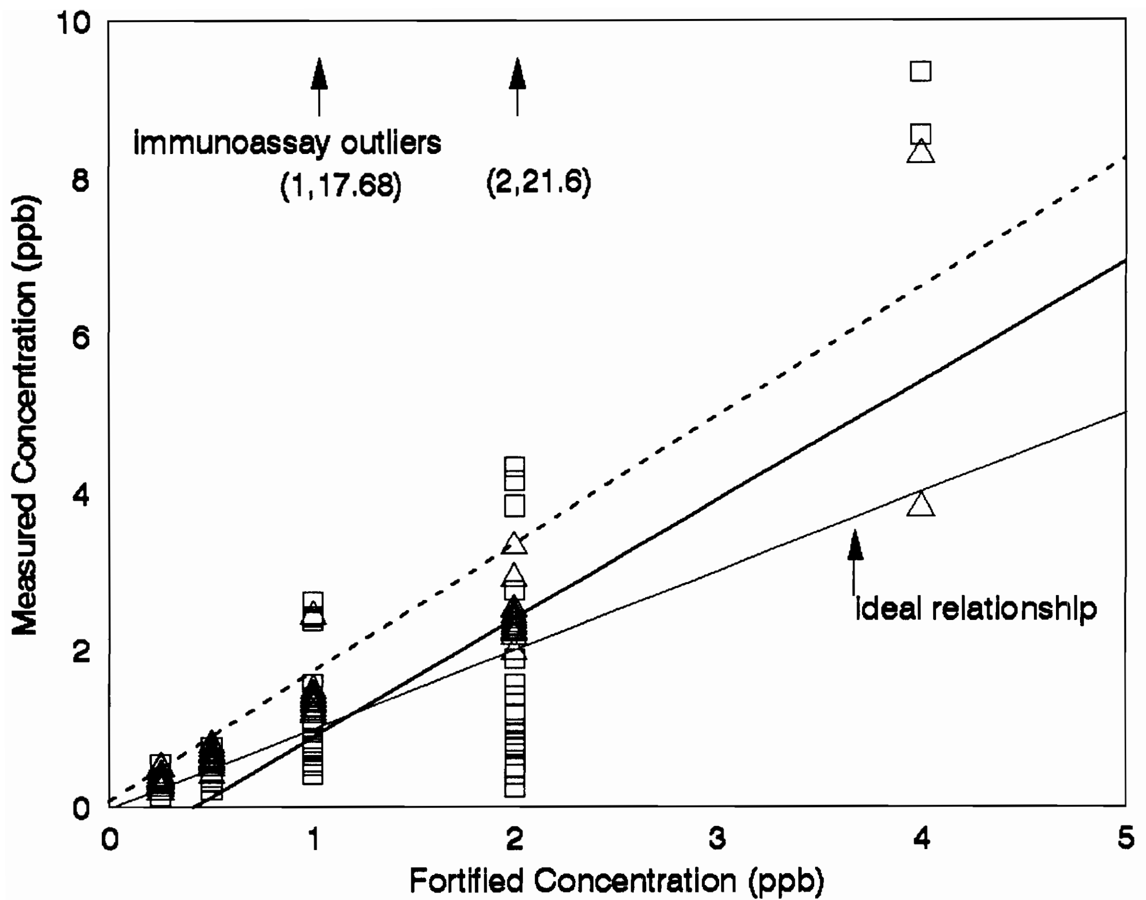
Table 20.
Regression Data for Comparison of Concentrations Measured by Both Immunoassay and GC/ECD

	Slope	Y-intercept	R-squared
Alachlor	0.98	0.52	0.13
Atrazine	0.70	0.47	0.13
Carbofuran	0.22	0.45	0.052
Cyanazine	0.46	0.33	0.19
Metolachlor	1.04	0.22	0.29



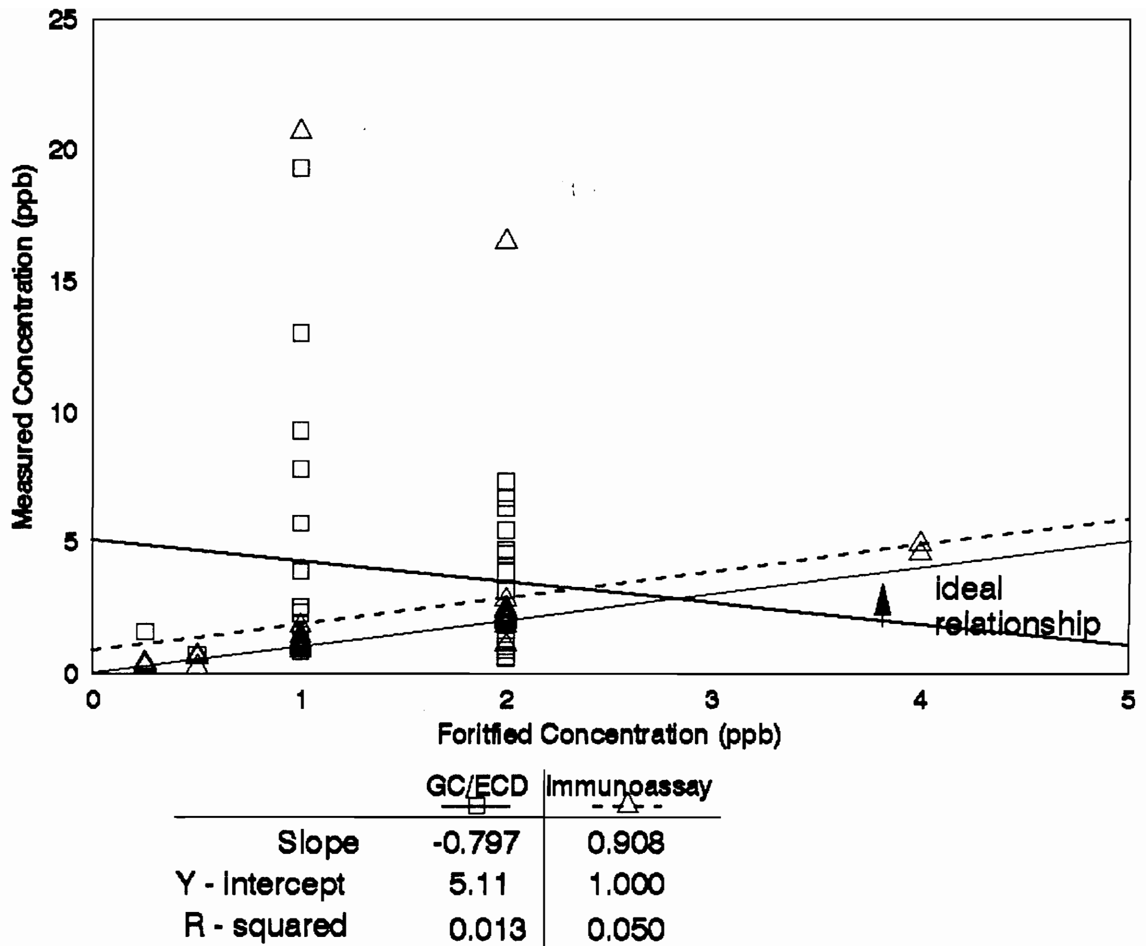
	GC/ECD	Immunoassay
Slope	1.005	1.700
Y - Intercept	-0.147	-0.042
R - squared	0.625	0.295

Figure 17. Comparison of fortified alachlor concentrations versus concentrations measured by GC/ECD and immunoassay in groundwater, seepage, and reagent water samples. Alachlor was added to these samples in the concentration range from 0.25 - 4.0 micrograms/liter (ppb). The data were from samples obtained between August, 1992 and February, 1993. Groundwater samples whose unspiked duplicate tested positive for alachlor were omitted.



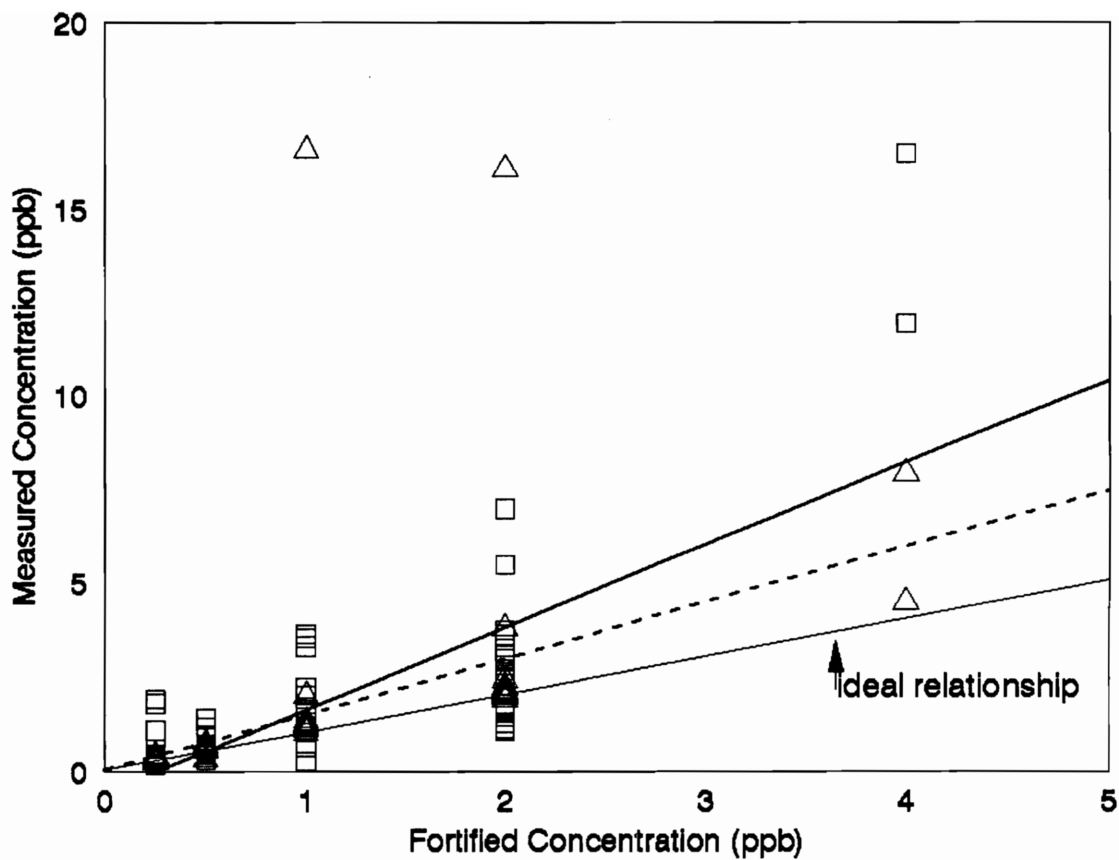
	GC/ECD	Immunoassay
Slope	1.511	1.634
Y - Intercept	-0.634	0.084
R - squared	0.510	0.193

Figure 18. Comparison of fortified atrazine concentrations and measured concentrations by GC/ECD and Immunoassay in groundwater, seepage water, and reagent water. Atrazine was added to these samples in the concentration range from 0.25 - 4.0 micrograms/liter (ppb). The data were from samples obtained between August 1992 and February 1993. Samples which tested negative for atrazine were omitted. Fortified groundwater and seepage water samples which had non-fortified duplicate samples which tested positive for atrazine were also omitted.



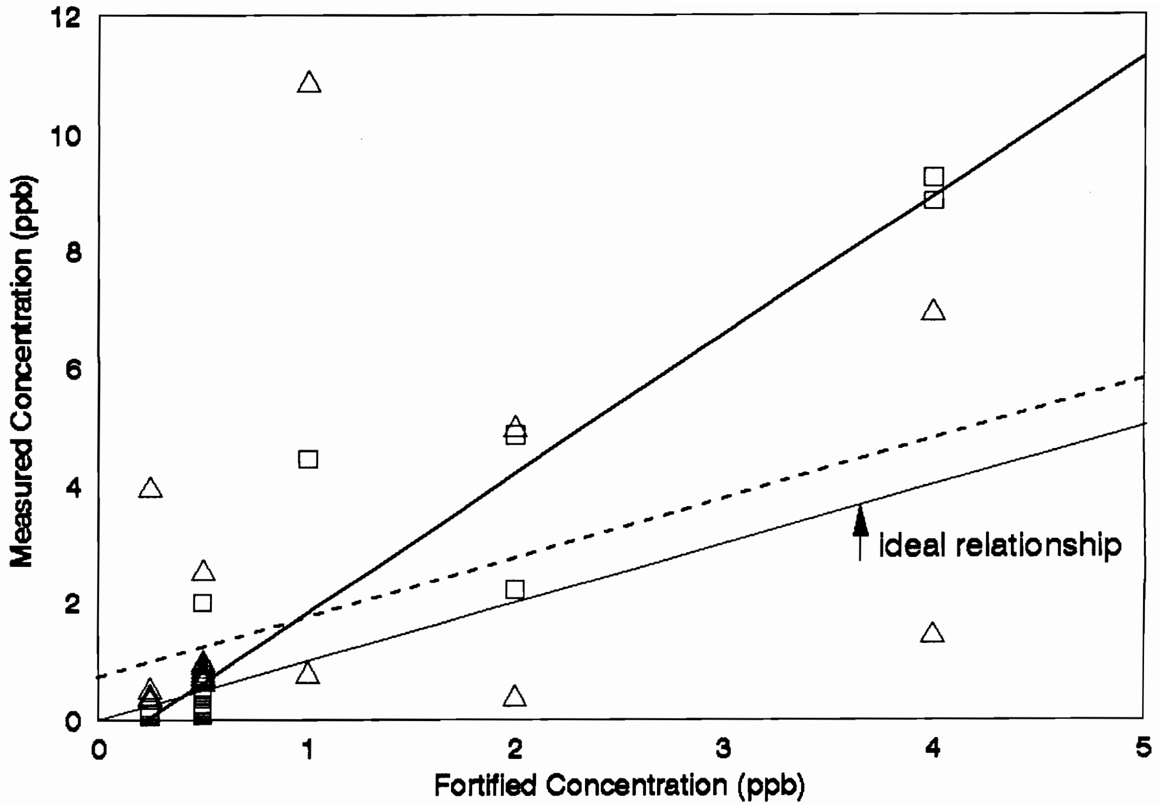
	GC/ECD	Immunoassay
Slope	-0.797	0.908
Y - Intercept	5.11	1.000
R - squared	0.013	0.050

Figure 19. Comparison of carbofuran concentrations determined by GC/ECD and immunoassay in groundwater, seepage water and reagent water samples to which carbofuran was added. Carbofuran was added to these samples in the concentration range from 0.25 - 4.0 micrograms/liter (ppb). The data were from samples obtained between August, 1992 and February,1993. Carbofuran was not detected in the groundwater or seepage meter water duplicate corresponding to any of these matrix spikes.



	GC/ECD	Immunoassay
Slope	2.196	1.483
Y - Intercept	-0.550	0.061
R - squared	0.585	0.225

Figure 20. Comparison of fortified cyanazine concentrations versus measured concentration determined by GC/ECD and immunoassay in groundwater, seepage meter and reagent water to which cyanazine was added. Cyanazine was added to these samples in the concentration range from 0.25 - 4.0 micrograms/liter (ppb). The data were from samples obtained between August 1992 and February 1993. Samples which tested negative for cyanazine were omitted. Fortified cyanazine concentrations in samples which had non-fortified duplicate samples which tested positive for cyanzine were also omitted.



	GC/ECD	Immunoassay
Slope	2.370	1.012
Y - intercept	-0.548	0.749
R - squared	0.912	0.184

Figure 21. Comparison of fortified metolachlor concentrations versus concentrations measured by GC/ECD and immunoassay in groundwater, seepage water and regent water to which metolachlor was added. Metolachlor was added to these samples in the concentration range from 0.25 - 4.0 micrograms/liter (ppb). The data were from samples obtained in August, 1992, January and February, 1993 Fortified samples in which the duplicate groundwater sample tested positive were omitted.

values are presented in Table 21. The results of this comparison were mixed. The regression slope was used as an indicator of accuracy within the fortification range used in this study. The regression slopes calculated from the GC/ECD data were closer to the ideal slope of one for alachlor and atrazine. The slopes calculated with the immunoassay data were closer to the ideal slope of one for carbofuran, cyanazine, and metolachlor.

The calculated y-intercept was used as an indication of accuracy in measuring the smaller concentrations (0.25 and 0.50 ppb) in fortified samples. The y-intercept was closer to zero in the immunoassay data sets for every pesticide with the exception of metolachlor. For the GC/ECD data, four of the five y-intercepts were highly negative (y-intercept>-0.15). This indicates that the GC/ECD method had poor accuracy at low concentrations (approximately<1 ppb). The only negative y-intercept in the immunoassay was for the pesticide alachlor, and the y intercept was only slightly negative with a value of -0.04.

The precision of the data was assessed by a comparison of the regression R-squared values. All R-squared values were somewhat low. The GC/ECD value for metolachlor was 0.92 but all others were below 0.63. The GC/ECD precision was greater than that of the immunoassay for atrazine, alachlor, metolachlor, and cyanazine. The difficulty in

Table 21.
Linear Regression Results for Comparison of Concentrations Measured by Immunoassay and GC/ECD in Fortified Samples to Known Fortification Concentrations

Pesticide	Slope		y - Intercept		R^2	
	GC/ECD	Imm.	GC/ECD	Imm.	GC/ECD	Imm.
Alachlor	1.00	0.70	-0.15	-0.04	0.63	0.30
Atrazine	1.51	1.63	-0.63	0.08	0.51	0.19
Carbofuran	-0.80	0.91	5.11	1.00	0.01	0.05
Cyanazine	2.20	1.48	-0.55	0.06	0.59	0.23
Metolachlor	2.37	1.01	-0.55	0.75	0.91	0.18

Abbreviation: Imm.=immunoassay
Note: These data are also presented in Figures 17 to 21.

calculating the concentration of carbofuran in water samples by GC/ECD was again shown in Figure 19 and by the very low R-squared value of 0.01. The concentration values calculated by the GC/ECD for carbofuran were erratic, in some instances, an order of magnitude greater than fortified concentrations. Carbofuran was the only non-chlorinated pesticide in the study; consequently, the GC/ECD detector did not respond strongly to it. Chromatographic peaks were sometimes obscured by the background noise hindering proper integration.

The ability of the two methods to detect pesticides which had been added to the samples is compared in Figure 22. The immunoassay detected each added pesticide 100% of the time. The GC/ECD analysis detected alachlor 100% of the time but, failed to detect carbofuran 24.3% of the time, atrazine 32.9% of the time, cyanazine 2.4% of the time, and metolachlor 13.5% of the time. The immunoassay technique was equal to or far superior at detecting the five pesticides over the concentration range chosen for this study (e.g., 0.25-4 ppb).

F.2. False Positive Detection

The immunoassay detected atrazine in several reagent water samples to which no pesticides had been added (Table 22). These detections suggest that the immunoassay can report false positive results. Throughout the study period,

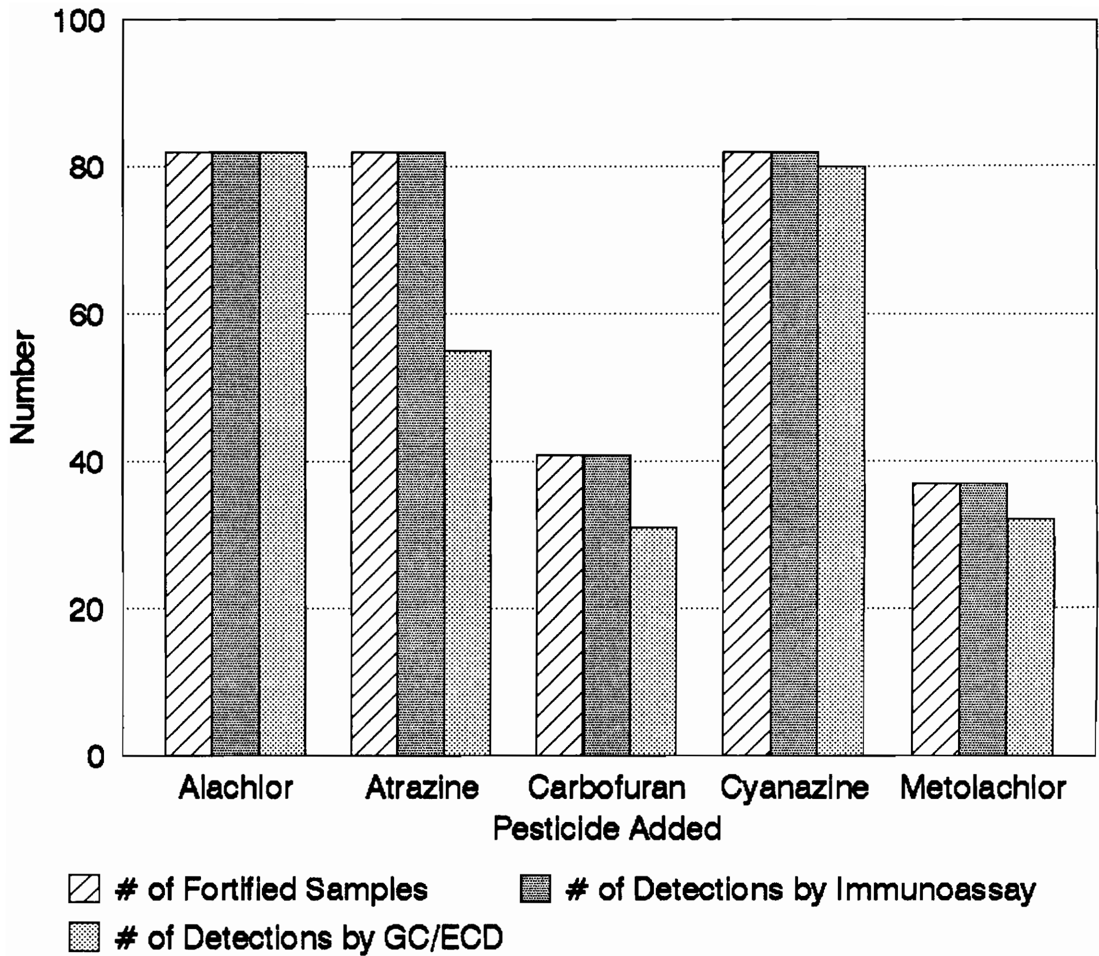


Figure 22. Comparison of the ability of the immunoassay and GC/ECD to detect pesticides which have been added to groundwater, seepage meter water and reagent water. The data were from samples obtained between August, 1992 and February, 1993.

Table 22.
False Positive Detection of Pesticides in Reagent Water Samples Which Contained No Pesticides

Pesticide	Number of Reagent Water Samples	Number and Concentration Range of Detections	
		GC/ECD	Immunoassay
Alachlor	22	n=0	n=0
Atrazine	22	n=0	n=4 (0.05 to 0.07 ppb)
Carbofuran	22	n=0	n=0
Cyanazine	22	n=0	n=0
Metolachlor	22	n=0	n=0

22 reagent water samples, lab blanks, travel blanks, and equipment blanks were analyzed by the immunoassay method. The atrazine immunoassay returned several suspicious positive results, four of which were low atrazine levels near the detection limits (e.g. 0.05 ppb to 0.07 ppb) in travel and equipment blank samples. The low levels of atrazine, both 0.07 ppb, reported in two equipment blanks could have been either the result of environmental contamination of the sampling equipment or detection of a false positive. The unexpected result of low levels of atrazine reported in two travel blanks by the immunoassay was more difficult to explain.

A metolachlor concentration was determined in 25 samples fortified with alachlor but not metolachlor during the study. Two of these samples were laboratory fortified blanks, and therefore there was no possibility of metolachlor from environmental sources. In these fortified blanks the metolachlor concentrations were well below the fortified concentration of alachlor (e.g., two samples fortified with alachlor to 2 ppb had measured concentrations of 0.46 ppb and 0.11 ppb of metolachlor). These results are in agreement with the cross reactivity percentage of 23% reported in the literature (Hall, *et al.*, 1992).

None of the five pesticides were detected by GC/ECD in any QA/QC blanks (e.g., reagent water blanks, travel blanks,

equipment blanks) by GC/ECD.

F.3. Statistical Comparison

Two statistical comparisons were performed with the complete data sets of 206 samples. The Wilcoxon Signed Rank Test and the Spearman Correlation were both performed for the five pairs of data sets corresponding to the five pesticides.

The Wilcoxon Signed Rank Test is the non-parametric analogue to the paired sample t-test. This statistical test assumes that the underlying distribution is symmetric but not necessarily normally distributed. The Wilcoxon Signed Rank Test tested the null hypothesis that the data set generated from GC/ECD determination of the concentration of a specific pesticide was the same as the data set generated from the determination of that pesticide concentration by immunoassay. The alpha (α) values which were calculated (Table 23) were the probability of a type I error, or the probability of making an error in rejecting the null hypothesis when it was true.

The greater the α value the more alike were the GC/ECD and immunoassay derived data sets. If an alpha value of 0.05 was used as a test, then carbofuran and cyanazine are not significantly different. The Wilcoxon test indicated that the other three pairs of data were different. The most similar pairs were the concentrations of carbofuran

Table 23.
Statistical Comparisons of Pesticide Concentration Determined by GC/ECD and Immunoassay[a]

Pesticide	Spearman Correlation Coefficient R^2	Wilcoxon Signed Rank Test Results Alpha α (probability of a type I error)
Alachlor	0.855	<0.001
Atrazine	0.758	<0.001
Carbofuran	0.706	0.11
Cyanazine	0.929	0.052
Metolachlor	0.606	<0.001

a - 206 samples representing groundwater, reagent water and seepage water , both fortified and unfortified; were used in this analysis

determined by the immunoassay and GC/ECD methods. The probability of a type I error was 11%. If the sample concentration sets were deemed dissimilar then there was only an 11% chance of an error being made.

The Spearman rank correlation coefficients were also calculated for the five pairs of pesticide data. This test also assumes no underlying distribution and uses ranking in analyzing the data. This statistical test indicated a fairly high degree of correlation between the two data sets for all the pesticides based on relative ranks. The correlation coefficients R^2 were all statistically significantly different from zero with p values < 0.001.

These two statistical analyses indicate that the five data sets are statistically different but highly correlated. The trends in the paired data sets are the same but the individual pairs of data are different to a significant degree.

F.4. Cost Comparison of GC/ECD and Immunoassay Methods

This cost comparison summarizes the capitol and variable costs involved for performing analysis of the five target pesticides in 1993 by GC/ECD and immunoassay. It applies to purchased equipment and supplies. No labor costs or allowances for equipment upkeep were calculated.

Table 24 lists the amounts of consumable supplies and chemicals needed per sample when analyzed by the GC/ECD

Table 24.
Costs of Supplies and Amounts of Supplies Consumed for Analysis of 5 Pesticides per Sample During Extraction and GC/ECD Analysis

Item	Amount or Number Consumed Per Sample	Cost and Typical Purchase Volume
Methylene Chloride (pesticide grade)[b]	26 mLs	$ 54.85/4 L
Methanol (pesticide grade)[b]	10 mLs	$ 39.95/4 L
Empore[tm] Disks[d]	1	$ 130.00/20
Amber Vials (4 mL)[a]	1	$ 46.20/144
Amber Vials (40 mL)[a]	1	$ 46.20/72
Glass Fiber Filters[a]	1	$ 16.01/100
Filter Paper[a]	1	$ 3.50/100
Helium Carrier Gas[c]	0.003[e]	$ 82.73/tank
Nitrogen Make-Up Gas[c]	0.005[e]	$ 83.40/tank
Disposable Pipets (9 in. glass)[a]	2	$ 37.00/720
Sodium Sulfate[a]	5 gm	$ 21.00/500 gm

Data from:
a - Fisher, 1993
b - Baxter, 1992
c - Grender, 1993
d - Varian, 1992
e - fraction of tank

method. Some of these amounts were based upon estimates made by the author during extraction and sample analysis. The greatest expense on a per sample basis was the solid phase extraction disk for which the amount consumed is known exactly. Therefore a slight error in estimating the cost or amount of an item such as carrier gas would not substantially change the outcome of the cost comparison. The list of durable equipment consists of materials which a functioning laboratory would need to carry out the immunoassay and GC/ECD methods. A functioning laboratory was assumed to contain basic equipment, such as non-specialized glassware, vacuum pumps, purified water systems, and fume hoods. The costs of durable equipment are summarized in Table 26. The GC/ECD method had an initial capitol expenditure of $ 16,030 which was nearly three times that of the immunoassay, $ 5,275.

The variable cost was derived using an eighteen samples per batch. The number of samples, eighteen, was based upon full consumption of a thirty test immunoassay kit. The immunoassay manufacturer recommends that for each batch of samples, a three point standard curve be analyzed in duplicate and that the standard curve also include data from a manufacture supplied blank. In addition to these eight standard EPA QA/QC procedures recommend that a check sample, travel blank, equipment blank, and two fortified field

Table 25.
Purchase Cost of Durable Equipment Required for the Analysis of the Five Target Pesticides

GC/ECD		IMMUNOASSAY[a]	
Durable Equipment	Cost	Durable Equipment	Cost
Gas Chromatograph (HP 5890a)[b]	$ 6,490	RPAI Photometric Analyzer	$ 3,985
Electron Capture Detector (ECD)[b]	$ 3,250	Sample Tube Rack (60 position)	$ 450
HP Capillary Injection Port[b]	$ 1,670	Pipet Repeater	$ 350
Integrator (HP 3396)[b]	$ 2,395	Tri-Volume Pipet	$ 280
Hamilton 10 µL syringes (pack of six)[c]	$ 99	Vortex Mixer	$ 210
SPE Disk Glass Funnel Support (five Sets)[d]	$ 566		
High Capacity Gas Purifiers (two)[e]	$ 790		
DB-5 Capillary Column[d]	$ 380		
DB-210 Capillary Column[d]	$ 390		
Total	$16,030	Total	$ 5,275

Data from: a - OHMICRON, 1993
b - Hewlett Packard, 1993
c - Fisher, 1993
d - Baxter, 1992

samples should be analyzed with each batch of field samples. No laboratory reagent water blank is needed because the three point standard curve includes a manufacturer-supplied standard containing no pesticides. Therefore, the total number of pesticide standards and QA/QC samples is twelve per batch, for the immunoassay procedure. After accounting for the standards and QA/QC blanks there is enough material for eighteen distinct water samples. The summary of variable costs for the immunoassay and GC/ECD methods are included in Table 26.

The variable costs for the GC/ECD method were based upon the analysis of eighteen samples, a travel blank, an equipment blank, a laboratory fortified blank, a laboratory reagent water blank, and two fortified samples bringing the total to twenty-four. For EPA Method 525.1, the standards are prepared for direct injection into the GC without solid phase extraction. The variable cost of the GC/ECD method was more than 75% less than that of the immunoassay.

The number of samples needed for the two methods to break-even in terms of cost of analyzing these five pesticides was calculated based upon batches of eighteen samples and ignoring the cost of preparing standard curves for the GC/ECD method. The extra cost of the durable purchases needed for the GC/ECD method would be compensated for by its lower supply cost after the analysis of 281

Table 26.
Cost of Consumable Supplies Needed to Analyze Five Pesticides in each of Eighteen Distinct Water Samples by GC/ECD and Immunoassay

GC/ECD		IMMUNOASSAY[a]	
Consumable Supplies[b]	Cost per Eighteen Water Samples plus 6 QA/QC Samples[c]	Consumable Supplies	Cost per Eighteen Water Samples and 5 QA/QC Samples[d]
Methylene Chloride	$ 8.56	Rapid Assay Alachlor Kit	$ 175.00
Methanol	$ 2.40	Rapid Assay Atrazine Kit	$ 175.00
Empore[tm] Extraction Disks	$ 156.00	Rapid Assay Carbofuran Kit	$ 175.00
Filter Paper	$ 0.84	Rapid Assay Cyanazine Kit	$ 190.00
Disposable Pipets	$ 2.47	Rapid Assay Metolachlor Kit	$ 190.00
Amber 4 and 40 mL Vials	$ 23.10		
Helium and Nitrogen Gas	$ 15.84		
Sodium Sulfate	$ 5.04		
Glass Fiber Filter	$ 3.84		
Total	$ 218.09	Total	$ 905.00

a-OHMICRON, 1992; b-prices from Baxter, 1992 and Fisher, 1993; c-GC/ECD requires that a laboratory blank be analyzed; this same blank is part of the standard curve for the immunoassay method; d-the immunoassay kits contain sufficient materials to analyze 30 samples. The manufacturer recommends analysis of a 3 point curve in duplicate in addition to 18 water samples and 5 QA/QC samples.

samples, a study more than twice the size of this one.

The number of pesticides analyzed has a large effect on a cost analysis such as this one. The immunoassay has the disadvantage of needing a different kit for each analysis. For the analysis of a single pesticide, the immunoassay variable cost would be similar to GC/ECD. Since the GC/ECD method can determine concentrations of one or many pesticides with little change in variable cost it has the advantage in studies focusing on multiple target compounds. The only change in cost due to adding additional pesticides would result from purchasing standards, which has been ignored in this cost comparison. The cost of carrying out the immunoassay analysis will increase linearly as more pesticides are measured, because a separate kit must be purchased for each pesticide analysis.

GC/ECD is a good method in general for halogenated pesticides, but it is not a good method for non-halogenated pesticides and a separate analysis would be needed. All pesticides are not equally recovered or possess the same LOD for SPE with GC/ECD analysis, so optimizing extraction or gas chromatography for one target pesticide may hinder extraction recovery or analysis of another.

F.5. Laboratory Time Comparison

Immunoassays require approximately two hours per assay. For a study of five pesticides with one RPIA analyzer and

one magnetic tube rack it would require about 10 hours to generate a measured concentration for all five pesticides in eighteen samples plus QA/QC samples. The GC/ECD method would require sixteen hours of extraction and concentration time for an equivalent batch (e.g. 18 samples plus 6 QA/QC samples). After extraction it would take an analyst another 25 hours to complete the GC/ECD analysis. Clearly the immunoassay technique has the advantage of speed, a four to one advantage. Another advantage is the skill level required to perform the immunoassay. The equipment required for the immunoassay is easy to use and the laboratory manipulations require less skill then the GC/ECD manipulations. After the color is measured by the spectrophotometer the concentration is printed out directly. The chromatograms still have to be read and the measured areas recorded before area can be calculated.

V. SUMMARY AND CONCLUSIONS

The presence of alachlor, atrazine, carbofuran, cyanazine, and metolachlor in surface soil samples (e.g., top 10 cm), sediment, groundwater and seepage water from four agricultural sites and one non-agricultural wetlands site in the Chesapeake Bay area was investigated by two methods: 1)a solid phase extraction method based on EPA method 525 followed by GC/ECD detection; and 2) an immunoassay method.

1. Alachlor, atrazine, cyanazine, and metolachlor were detected in groundwater samples, with alachlor and atrazine detected most frequently (e.g., approximately 22% of the samples for alachlor and 10% of the samples for atrazine). The detected concentrations were generally below 1 ppb.
2. Alachlor and metolachlor were found in 14 out of 32 surface soil samples with concentrations ranging from 7 to 485 ppb. Detection of these acetanilide pesticides was consistent with known pesticide application data for the agricultural sites and detection of these pesticides in groundwater.
3. Atrazine, carbofuran, and cyanazine were not detected in any soil samples. Because available pesticide application data indicated that atrazine had been

applied to one agricultural site and this pesticide was detected in several groundwater samples at sub-ppb levels, soil degradation and/or groundwater transport of atrazine must be occurring to remove it from the soil column. Although cyanazine and carbofuran were occasionally detected in groundwater at sub ppb levels, neither pesticide could be detected in the soil.

4. The relationship between measured concentrations of pesticides in soil and concentrations in groundwater seems to be that for alachlor and metolachlor the soil adsorbs the pesticide where it degrades. Small amounts of both of these pesticides do leave the soil since the adsorption is reversible but for alachlor and metolachlor and soil-types in this study it appears that adsorption and degradation were the pervasive mechanism of pesticide disappearance.

5. Two analytical methods, e.g., GC/ECD and Immunoassay, were compared for their abilities to determine pesticide concentrations in groundwater and fortified water samples. Both methods had their advantages and disadvantages. Although the data generated by the two methods was statistically different, in three out of five cases the high degree of correlation indicated that both methods were valid means for determining pesticide concentrations. In general the immunoassay

method performed better for measuring low concentrations of the target pesticides, but for alachlor, atrazine, cyanazine, and metolachlor the GC/ECD method showed better precision.

6. The immunoassay method reported false positive detections for atrazine in several reagent water blank samples; the concentrations measured were near the reported limit of detection of 0.05 ppb. The immunoassay method falsely detected metolachlor in several reagent water blanks and laboratory fortified samples to which alachlor, but not metolachlor, had been added.

7. The non-detection of pesticides in the groundwater from wetlands site one (a non-agricultural site) and ambient saline water from all sites indicated that any pesticide detections at the agricultural sites were likely a result of agricultural activity and not background contamination.

8. Transport of pesticides was not a major concern in the agricultural areas studied. The transported concentrations were low (e.g., << 1 ppb). For alachlor and metolachlor chemical/biological degradation appeared to be the prevalent means of removal.

RECOMMENDATIONS

1. Routine and regular monitoring of the groundwater seepage into the Chesapeake Bay does not appear warranted at this time. However, occasional groundwater monitoring would be prudent, and, if pesticides are consistently found above allowable levels, groundwater seepage monitoring would be indicated.
2. The immunoassay method would be a good quantitative screening procedure to determine if pesticides, or possibly pesticide degradation products, were present in water samples.

VII. LITERATURE CITED

Baker, D.B., Bushway, R.J., Adams, S.A., Macomber, C., "Immunoassay Screens for Alachlor in Rural Wells: False Positives and an Alachlor Soil Metabolite." *Environmental Science and Technology, 27*, 562-564(1993)

Barron, M.G., "Bioconcentration." *Environmental Science and Technology, 24(11),* 1612-1618(1990)

Basta, N.T., Olness, A., "Determination of Alachlor, Atrazine, and Metribuzin in Soil by Resin Extraction." *Journal of Environmental Quality, 21,* 497-502(1992)

Baxter Incorporated, *Scientific Products, Baxter*, McGaw Park, IL., pp.2430(1991)

Blumberg, R., *Liquid-Liquid Extraction*, Academic Press, San Diego, CA., 5-57(1988)

Bopp, R.F., Simpson, H.J., Olsen, C.R., Kostyk, N., "Polychloronated Biphenyls in Sediments of the Tidal Hudson River, New York." *Environmental Science and Technology, 15(2),* 210-216(1981)

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

Boshoff, P.R., Hopkins, B.J., "Performance of a Solute Switched Electron Capture Detector for Pesticides." *Journal of Chromatographic Science, 17*, 588-594(1979)

Brooks, M.W., Tessier, D., Soderstrom, D., Jenkins, J., Clark, J.M., "A Rapid Method for the Simultaneous Analysis of Chlorpyrifos, Isofenphos, Carbaryl, Iprodione, and Triadimefon in Groundwater by Solid-Phase Extraction." *Journal of Chromatographic Science, 28*, 487-491(1990)

Burkhard, N., Guth, J.A., "Chemical Hydrolysis of 2-Chloro-4,6-bis(alkylamino)-1,3,5-triazine Herbicides and Their Breakdown in Soil Under the Influence of Adsorption." *Pesticide Science, 12*, 45-52(1981)

Bushway, R.J., Hurst, H.L., Perkins, L.B., Tian, L., Guiberteau Cananillas, C., Young, B.E.S., Ferguson, B.S., Jennings, H.S., "Atrazine, Alachlor, and Carbofuran Contamination of Well Water in Central

Maine." *Bulletin of Environmental Contamination and Toxicology, 49,* 1-9(1992)

Clark, L., Gomme, J., Hennings, S., "Study of Pesticides in Waters from a Chalk Catchment, Cambridgeshire." *Pesticide Science, 32*, 15-33(1991)

Damla, B., Gael, D., Boavot, V., "Use of Extraction Disks for Trace Enrichment of Various Pesticides from River Water and Simulated Seawater Samples Followed by Liquid Chromatography-Rapid Scanning UV-Visible and Thermospray-Mass Spectrometry Detection." *Environmental Science and Technology, 27*, 271-277(1993)

Di Corcia, A., Marchetti, M., "Method Development for Monitoring Pesticides in Environmental Waters: Liquid-Solid Extraction Followed by Liquid Chromatography." *Environmental Science and Technology, 26*, 66-74(1992)

Dunigan. E.P., McIntosh, T.H., "Atrazine Soil Organic Matter Interactions." *Weed Science, 19(3)*, 279-282(1971)

Eichelberger, J.W., Behymer, T.D., Budde, W.L., *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, 323-360(1991)

Esser, E.O., Dupuis, G., Ebert, E., Marco, G. and Vogel, C. "s-Triazines." in *Herbicides: Chemistry, Degradation and Mode of Action, 1*, 2nd ed., eds., P.C. Kearney, P.C., Kaufman, D.D., Marcel Dekker, Inc., New York, NY., 129-189(1975)

Fisher Scientific, *The Fisher Catalog 93/94,* Pittsburgh, PA., pp.1745(1993)

Frank, R., Ripley, B.D., Braun, H.E., Clegg, S., Johnston, R., O'Neill, T.J., "Survey of Farm Wells for Pesticides Residues, Southern Ontario, Canada, 1981-1982, 1984." *Archives of Environmental Contamination and Toxicology, 16,* 1-8(1987)

Grender, M., Personal Communication, July, (1993)

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

Gustafson, D.I., "Field Calibration of Surface: A Model of Agricultural Chemicals in Surface Waters." *Journal of Environmental Science and Health, B, 25,* 665-687(1990)

Hall, J.C., Wilson, L.K., Chapman, R.A., "An Immunoassay for Metolachlor Detection in River Water and Soil." *Journal of Environmental Science and Health, B, 27,* 523-544(1992)

Heatwole, C.D., Zacharias, S., Mostaghimi, S., Dillaha, T.A., Young, R.W., "Fate and Transport of Pesticides in a Virginia Coastal Plain Soil." *Virginia Polytechnic Institute and State University-Virginia Water Resources Research Center-Bulletin, 175,* 1-166(1992)

Hewlett-Packard, Customer Information Telephone Line, Valley Forge, Pennsylvania, July, (1993)

Hohlt, H., Professor for the Agricultural Extension Laboratory, at Virginia Polytechnic Institute and State University, Personal Communication. May, 1993

Holden, L.R., Graham, J.A., Wittmore, R.W., Alexander, J.W., Pratt, R.W., Liddle, S.K., Piper, L.L., "Results of the National Alachlor Well Water Survey." *Environmental Science and Technology, 26,* 935-943(1992)

Huang, L.Q., Pignatello, J.J., "Improved Extraction of Atrazine and Metolachlor in Field Soil Samples." *Journal of the Association of Official Analytical Chemists, 73(3)*, 443-446(1990)

Huang, P.M., Grover, R., McKercher, R.B., "Components and Particle Size Fraction Involved in Atrazine Adsorption by Soils." *Soil Science, 138,* 20-24(1984)

Hubbard, T.W., *Monitoring Pesticides in the Groundwater and Submarine Groundwater Discharge of the Eastern Shore of Virginia*. Master's Thesis, Civil Engineering Department, Virginia Polytechnic Institute and State University. July, 1993

Junk, G.A., Richard, J.J., "Organics in Water: Solid Phase Extraction on a Small Scale." *Analytical Chemistry, 60,* 451-454(1988)

Jury, W.A., Spencer, W.F., Farmer, W.J., "Behavior Assessment Model for Trace Organics in Soil: IV. Review of Experimental Evidence." *Journal of*

Environmental Quality, 13, 580-586(1984)

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

Kaufman, D.D., Edwards, D.F., "Pesticide/Microbe Interaction Effects on Persistence of Pesticides in Soil." in *Pesticides in Soil*, eds. Saltzman, S., Yaron, B., Van Nostrand Reinhold Company Inc., New York, NY., 240-246(1986)

Kenaga, E.E., Goring, C.A.I., "Relationship Between Water Solubility, Soil Sorption, Octanol-Water Partitioning, and Concentration of Chemicals in Biota." *Aquatic Toxicology, ASTM STP 707,* eds. Eaton, J.G., Parrish, P.R., Hendriks, A.C., American Society for the Testing of Materials, 78-115(1980)

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

Krill, R.M., Sonozogni, W.C., "Chemical Monitoring of Wisconsin's Groundwater." *Journal of the American Water Works Association, 78(9),* 70-75(1986)

LeBaron, H.M., McFarland, J.E., Simoneaux, B.J., Ebert, E. "Metolachlor" in *Herbicides: Chemistry, Degradation and Mode of Action, 3,* eds., Kearney, P.C., Kaufman, D.D., Marcel Dekker, Inc., New York, NY, 336-384(1988)

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

Loague, K., Yost, R.S., Green, R.E., Liang, T.C., "Uncertainty in a Pesticide Leaching Assessment for Hawaii" *Journal of Contaminate Hydrology, 4,* 139-161(1989)

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

Lee, D.R., Cherry, J.A., Pickens, J.F., "Groundwater

Transport of a Salt Tracer Through a Sandy Lakebed." *Limnology and Oceanography, 25,* 45-61(1980)

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

Lopez-Avila, G., Hirata, P., Kraska, S., Flanagan, M., Taylor, J.H. Jr., Hern, S., "Determination of Atrazine, Lindane, Pentachlorophenol, and Diazinon in Water and Soil By Isotope Dilution Gas Chromatography/Mass Spectrometry." *Analytical Chemistry, 57,* 2797-2810(1985)

McGlamery, M.D., Slife, F.W., Butler, H., "Extraction and Determination of Atrazine from Soil." *Weeds, 15,* 35-38(1967)

Meister, R.T., Sine, C., Naegely, S.K., Fisher, N., Vlahovski, F., Weil, E.D., Rigo, W.A. Jr., Puskas, M.J., Pierce, T., *Farm Chemicals Handbook.* Meister Publishing Company. Willoughby, OH. pp. 507(1992)

Miles, C.J., "Determination of National Survey of Pesticides Analytes in Groundwater by Liquid Chromatography with Post-column Reaction Detection." *Journal of Chromatography, 592*, 283-290(1992)

Munch, D.J., Frebis, C.P., "Analyte Stability Studies Conducted During the National Pesticide Survey." *Environmental Science and Technology, 26*, 921-925(1992)

Nash, R.G., "Solid-Phase Extraction of Carbofuran, Atrazine, Simazine, Alachlor, and Cyanazine from Shallow Well Water." *Journal of the Association of Official Analytical Chemists, 73,* 438-442(1990)

Nelsen, T.R., Cook, R.F., "A High Pressure Liquid Chromatographic Method for the Determination of Carbofuran Residues in Soil and Water." *Journal of Agriculture and Food Chemistry, 27(6)*, 1186-1189(1979)

Newhouse, M.E., Cobb, P.R., Baldwin, L.F., McCloy, D.V., *Soil Survey of Middlesex County, Virginia.* U.S. Department of Agriculture and Virginia Polytechnic Institute and State University, (1985a)

Newhouse, M.E., Cobb, P.R., Barnes, W.S., McCloy, D.V., *Soil Survey of Glouchester County, Virginia.* U.S. Department

of Agriculture and Virginia Polytechnic Institute and State University, (1985b)

OHMICRON Corporation, *Price Schedule*, Newtown, PA., (1993)

Pape, B.E., Zabik, M.J., "Photochemistry of Selected 2-Chloro- and 2-Methylthio-4,6-di(Alkylamino)-s-Triazine Herbicides." *Journal of Agricultural and Food Chemistry, 18,* 202-207(1970)

Pionke, H.B., Glotfelty, D.E., Lucas, A.D., Urban, J.B., "Pesticide Contamination of Groundwaters in the Mahantango Creek Watershed." *Journal of Environmental Quality, 17(1)*, 76-84(1988)

Pionke, H.B., Glotfelty, D.E., "Nature and Extent of Groundwater Contamination By Pesticides in an Agricultural Watershed." *Water Research, 23(8),* 1031-1037(1989)

Rashash, D., personal communication, December, (1992)

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

Saltzman, S., Yaron, B., (Editors) *Pesticides in Soil*. Van Nostrand Reinhold Company. New York, NY. 379 pp., (1986)

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

Senseman, S.A., Lavy, T.L., Mattice, J.D., Myers, B.M., Skulman, B.W., "Stability of Various Pesticides on Membranous Solid-Phase Extraction Media." *Environmental Science and Technology, 27,* 516-519(1993)

Sharp, D.B. "Alachlor" in *Herbicides: Chemistry, Degradation and Mode of Action, 3,* eds., Kearney, P.C., Kaufman, D.D., Marcel Dekker, Inc., New York, NY, 302-335(1988)

Shirmohammadi, A., Magette, W.L., Brinsfield, R.V., Staver,

K. "Ground Water Loading of Pesticides in the Atlantic Coastal Plain." *Ground Water Monitoring Review, 9*, 141-148(1989)

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

Simmons, G.M., Miles, E., Reay, W., Gallagher, D., "Submarine Groundwater Discharge Quality in Relation to Land Use Patterns in the Southern Chesapeake Bay." Proceedings on the 1st International Conference on Groundwater Ecology, Stanford, J.A., Simons, J.J. (eds.), American Water Resources Association, 341-350(1992)

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

Spalding, R.F., Junk, G.A., Richard, J.J., "Pesticides in Ground Water Beneath Irrigated Farmland in Nebraska, August, 1978 ." *Pesticides Monitoring Journal, 14(2)*, 70-73(1980)

Supelco, Inc., *Chromatography Product Catalog*, Belefonte Park, PA., pp.440(1991)

Thurman, E.M., Goolsby, D.A., Meyer, M.T., Mills, M.S., Pomes, M.L., Kolpin, D.W., "A Reconnaissance Study of Herbicides and Their Metabolites in Surface Water of the Midwestern United States Using Immunoassay and Gas Chromatography/Mass Spectrometry." *Environmental Science and Technology, 26*, 2440-2447(1992)

Walker, A., Zimdahl, R.L., "Simulation of the Persistence of Atrazine, Linuron and Metolachlor in Soil at Different Sites in the USA. *Weed Research, 21*, 255-265(1981)

Varian Incorporated, Customer Service Telephone Line, July, (1993)

Zimdahl, R.L., Clark, S.K., "Degradation of Three Acetanilide Herbicides in Soil." *Weed Science, 30*, 545-548(1982).

APPENDIX A.

Pesticide Concentrations Determined in Water Samples by GC/ECD and Immunoassay

Table A.1. GC/ECD and Immunoassay Results for the Month of May

MAY SAMPLING			ATRAZINE ppb		CYANAZINE ppb		ALACHLOR ppb		METOLACHLOR ppb		CARBOFURAN ppb	
Virginia Tech ID	Ohmicron ID	Spike Level	VT	OHM	VT	OHM	VT	OHM	VT	OHM	VT	OHM
WFAmbTo	1a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CHAmbTo	2a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BVAmbTo	3a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EVAmbTo	4a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
LFB #2	5a	2 ppb	0.53	1.19	nd	1.21	0.8	1.28	N/A	0.46	0.91*	1.18
Equip Blank #2	6a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Equip Blank #1	7a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BVSM3#2	8a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BVSM1	9a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BVSM2	10a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BVSM3	11a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BVSM4	12a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BVCW#2	13a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fd Blank	14a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BV2#2	15a		nd	nd	nd	nd	nd	0.15	nd	nd	nd	nd
Lab Blank#1	16a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BV1#2	17a		nd	nd	nd	nd	nd	0.18	nd	nd	nd	nd
BV2#1	18a		nd	nd	nd	nd	nd	0.1	nd	nd	nd	nd
BV1#1	19a		nd	nd	nd	nd	nd	0.23	nd	nd	nd	nd
CHNew #1	20a		nd	nd	nd	nd	nd	nd	nd	nd	nd	0.1
BVCW#1	21a	2 ppb	0.66	1.48	nd	0.16	1.06	2.66	N/A	0.1	1.67	2.61
BVCW#3	22a		nd	nd	nd	0.06	nd	nd	nd	nd	nd	nd
EV2#1	23a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CH2	24a		nd	nd	nd	nd	nd	nd	nd	0.33	nd	nd
WFSM 1-4	25a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EVF/R #1	26a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EV2#2	27a	2 ppb	0.37	2.13	nd	0.16	0.76	2.65	N/A	N/A	1.09*	2.66
EV2#3	28a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EV1#1	29a	2 ppb	nd	1.26	nd	0.11	1.28	2.31	N/A	N/A	0.51	2.49
EV1#2	30a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EVF/R #2	31a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EV1#3	32a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CHSM 3	33a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EVSM 1&4	34a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CHSM#4	35a	10 ppb	4.75	8.5	4.55	0.3	5.64	9.5	N/A	0.16	11.1	13.63
EVSM2	36a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WF#1	37a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WFSW	38a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CH5	39a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CHNew#1	40a		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

NOTES: nd:not detected, N/A:not added, I/S:insufficient sample, *below MDL (method detection limit), S/L:sample lost

Five additional blank samples, duplicate samples or spiked samples not listed here were analyzed by GC/ECD

Table A.2. GC/ECD and Immunoassay Results for the Month of June

JUNE SAMPLING			ATRAZINE ppb		CYANAZINE ppb		ALACHLOR ppb		METOLACHLOR ppb		CARBOFURAN ppb	
Virginia Tech ID	Ohmicron ID	Spike Level	VT	OHM	VT	OHM	VT	OHM	VT	OHM	VT	OHM
EVF/R	1b		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EV2	2b		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BVCW	3b		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CHNew	4b		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WFSW#4	5b		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WFSW#3	6b		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BV1	7b		nd	nd	nd	nd	nd	0.19	nd	nd	nd	nd
WF1#1	8b		nd	nd	nd	nd	0.66	nd	nd	nd	nd	nd
BVSM1	9b		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WF2#2	10b		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CHSM2	11b		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CH2	12b		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WF2#1	13b		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EV1	14b		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BV2	15b		nd	nd	nd	nd	nd	0.1	nd	nd	nd	nd
BVSM4	16b		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WF1#2	17b		nd	nd	nd	nd	0.57	nd	nd	nd	nd	nd

NOTES: nd:not detected, N/A:not added, I/S:insufficient sample, *:below MDL (method detection limit), S/L:sample lost

Thirty-One additional blank samples, duplicate samples or spiked samples not listed here were analyzed by GC/ECD

Table A.3. GC/ECD and Immunoassay Results for the Month of July

JULY SAMPLING			ATRAZINE ppb		CYANAZINE ppb		ALACHLOR ppb		METOLACHLOR ppb		CARBOFURAN ppb		
Virginia Tech ID	Ohmicron ID	Spike Level	VT	OHM	VT	OHM	VT	OHM	VT	OHM	VT	OHM	Notes
EV1#4	1c	4 ppb	1.01	4.9	2.53	7.1	3.22	6.6	N/A	0.06	nd	6.76	some VT extract spilled
EV1#3	2c	2 ppb	3.58	9.4	1.99	12	3.51	11.5	N/A	0.16	nd	9.88	
WF1#4	3c	4 ppb	3.79	14.5	3.17	15.6	4.59	19.4	N/A	0.16	nd	11.92	
WF1#3	4c	2 ppb	1.88	3.69	1.7	5.7	3.22	5.8	N/A	0.06	nd	3.65	
WF1	5c		0.63	nd	nd	nd	nd	nd	nd	nd	nd	nd	
BV2	6c		nd	nd	nd	nd	nd	0.09	nd	nd	nd	nd	
EV1	7c		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	
LB#3	8c		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	
BV2#3	9c	2 ppb	0.39	4.3	0.14*	7.4	4.6	7.8	N/A	0.07	0.85*	6.36	
CH5#3	10c	2 ppb	2.15	4.1	1.21	8.9	2.35	7.2	N/A	0.11	2.75	5.64	
EVF/R	11c		nd	nd	0.53	nd	nd	nd	nd	nd	nd	nd	
WFSW	12c		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	
LFB#1	13c	2 ppb	1.06	4.1	1.7	9.3	2.84	8.3	N/A	0.17	nd	6.72	see attached note
BV2#4	14c	4 ppb	5.11	11.3	3.64	15.4	4.98	14.6	N/A	0.17	0.85*	10.16	
LB#2	15c		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	
FB#1	16c	2 ppb	2.77	4.63	2.55	6.5	3.98	5.4	N/A	N/A	nd	3.05	see attached note
CH5#4	17c	4 ppb	3	10.4	2.68	14.4	3.93	14.2	N/A	0.18	3.6	9.64	
EV2	18c		nd	nd	0.16*	nd	nd	nd	nd	nd	nd	nd	
CH5	19c		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	
CH2	20c		1.52	nd	0.17*	nd	nd	nd	nd	nd	nd	nd	
WF2	21c		0.6	nd	nd	nd	nd	nd	nd	nd	nd	nd	
WFSM2	22c		I/S	nd	I/S	nd	I/S	nd	I/S	nd	I/S	nd	
BV1	23c		0.59	nd	0.16*	nd	nd	0.27	nd	0.05	nd	nd	
CHSM4	24c		nd	0.07	nd	nd	nd	nd	nd	nd	nd	nd	
WFSM1	22c		I/S	nd	I/S	nd	I/S	nd	I/S	nd	I/S	nd	
CHNew	26c		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	
CHSM1	27c		nd	nd	nd	0.05	nd	nd	nd	nd	nd	nd	
BVCW	28c		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	

NOTES: nd:not detected, N/A:not added, I/S:insufficient sample, *below MDL (method detection limit), S/L:sample lost

Twenty-Seven additional blank samples, duplicate samples or spiked samples not listed here were analyzed by GC/ECD

Table A.4. GC/ECD and Immunoassay Results for the Month of August

AUGUST SAMPLING			ATRAZINE ppb		CYANAZINE ppb		ALACHLOR ppb		METOLACHLOR ppb		CARBOFURAN ppb	
Virginia Tech ID	Ohmicron ID	Spike Level	VT	OHM	VT	OHM	VT	OHM	VT	OHM	VT	OHM
BV2	1d		nd	0.13	nd	nd	nd	0.61	0.07*	nd	nd	nd
Hopper	2d		nd	nd	nd	nd	nd	0.06	nd	nd	nd	nd
WF1#4	3d	4 ppb	9.34	3.8	16.5	4.5	5.94	4.67	9.26	6.92	nd	4.94
EV1	4d		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EVF/R	5d		nd	nd	nd	nd	nd	0.09	nd	nd	nd	nd
WFSM4	6d		nd	0.36	nd	0.06	nd	0.21	nd	nd	nd	nd
EV2	7d		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BVCF1	8d		nd	0.36	nd	nd	nd	0.64	nd	nd	nd	nd
CHSM3	9d		nd	0.5	nd	0.06	nd	0.19	nd	nd	nd	nd
WFSM3	10d		nd	0.51	nd	0.09	nd	0.28	nd	nd	nd	nd
EB	11d		nd	0.07	nd	nd	nd	nd	nd	nd	nd	nd
CH3	12d		nd	nd	nd	nd	nd	nd	0.33*	nd	nd	nd
BVSM1	13d		nd	0.14	nd	nd	nd	0.11	nd	nd	nd	nd
CHSM1	14d		nd	0.47	nd	nd	nd	0.09	nd	nd	nd	nd
WFSM2	15d		nd	0.24	nd	nd	nd	0.06	nd	nd	nd	nd
LFB#3	16d	4 ppb	8.55	8.3	11.96	7.9	6.31	6.9	8.85	1.42	nd	4.56
BVCW	17d		nd	0.12	nd	nd	nd	0.07	nd	nd	nd	nd
CH5	18d		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CH2#1	19d		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
LFB#1	20d	2 ppb	1.89	3.32	3.08	3.8	0.18*	3.83	2.23	0.37	nd	2.5
WFSW	21d		nd	nd	nd	nd	nd	nd	0.07*	nd	nd	nd
WF1	22d		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WF1#2	23d	2 ppb	4.33	2.45	6.98	2.43	3.25	2.95	4.84	4.94	nd	2.8
NOLABEL	24d		S/L	0.11	S/L	nd	S/L	nd	S/L	nd	S/L	nd

NOTES: nd:not detected, N/A:not added, I/S:insufficient sample, *:below MDL (method detection limit), S/L:sample lost

Twenty-Five additional blank samples, duplicate samples or spiked samples not listed here were analyzed by GC/ECD

Table A.5. GC/ECD and Immunoassay Results for the Month of October

OCTOBER SAMPLING			ATRAZINE ppb		CYANAZINE ppb		ALACHLOR ppb		METOLACHLOR ppb		CARBOFURAN ppb	
Virginia Tech ID	Ohmicron ID	Spike Level	VT	OHM	VT	OHM	VT	OHM	VT	OHM	VT	OHM
CH5	1•		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EV2#4	2•	1 ppb	2.61	1.18	3.54	1.13	1.62	1.15	N/A	N/A	9.33	1.05
BVSM3	3•		I/S	nd	I/S	nd	I/S	nd	I/S	nd	I/S	nd
BV1#4	4•	2 ppb	3.83	2.22	1.28	1.92	2.57	2.46	N/A	N/A	6.72	2
WFSM1&2	5•		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CH3#4	6•	1 ppb	nd	1.26	3.65	1.13	1.39	1.15	N/A	N/A	nd	1.1
WF1#3	7•	0.5 ppb	nd	0.66	0.97	0.66	0.58	0.63	N/A	N/A	nd	0.62
WF1#4	8•	2 ppb	2.35	2.37	3.63	2.14	1.72	2.27	N/A	N/A	4.57	2.09
CHSM1	9•		nd	0.08	nd	nd	nd	nd	0.04*	nd	nd	nd
EV2	10•		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WF1	11•		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CHSM2	12•		nd	0.11	nd	nd	nd	nd	0.04*	nd	nd	nd
LB#1	13•		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BVSM2	14•		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CH3	15•		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WFSM1	16•		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EV1#4	17•	1 ppb	1.56	1.48	2.23	1.3	1.11	1.3	N/A	N/A	5.76	1.32
CHSM4	18•		nd	0.1	nd	nd	nd	nd	0.04*	nd	nd	nd
EVSM1	19•		I/S	nd	I/S	nd	I/S	nd	I/S	nd	I/S	nd
CHSM3	20•		nd	0.14	nd	nd	nd	nd	0.04*	nd	nd	nd
BVCW	21•		nd	nd	nd	nd	nd	0.1	nd	nd	nd	nd
BV2	22•		nd	nd	nd	nd	nd	0.09	nd	nd	nd	0.07
BVSM4	23•		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EVFR	24•		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EVSM2	25•		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BVSM4#1	26•	2 ppb	2.77	2.37	1.69	2.06	0.91	2.16	N/A	N/A	3.87	2.16
ST3	27•		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BVCW#3	28•	1 ppb	2.42	1.31	1.55	1.19	0.8	1.34	N/A	N/A	3.9	1.28
CH2	29•		nd	0.12	nd	nd	nd	nd	nd	nd	nd	nd
WF2	30•		nd	0.05	nd	nd	nd	nd	nd	nd	nd	nd
EVSM3	31•		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BV1#3	32•	0.5 ppb	0.76	0.75	1.43	0.65	0.25*	0.85	N/A	N/A	nd	0.71
EV1	33•		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WFSW	34•		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EVSM1#1	35•	0.25 ppb	nd	0.35	1.82	0.35	0.62	0.28	N/A	N/A	nd	0.37
CH3#1	36•	0.25 ppb	nd	0.4	1.1	0.31	0.53	0.25	N/A	N/A	nd	0.42
WFSM3	37•		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EVSM4	38•		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CH5#2	39•	2 ppb	4.15	2.52	5.5	2.17	2.32	1.91	N/A	N/A	5.49	2.36

NOTES: nd:not detected, N/A:not added, I/S:insufficient sample, *:below MDL (method detection limit), S/L:sample lost

Twenty additional blank samples, duplicate samples or spiked samples not listed here were analyzed by GC/ECD

Table A.8. GC/ECD and Immunoassay Results for the Month of November

NOVEMBER SAMPLING			ATRAZINE ppb		CYANAZINE ppb		ALACHLOR ppb		METOLACHLOR ppb		CARBOFURAN ppb	
Virginia Tech ID	Ohmicron ID	Spike Level	VT	OHM	VT	OHM	VT	OHM	VT	OHM	VT	OHM
CHS	1f		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EV2	2f		nd	nd	0.03*	nd	nd	nd	nd	nd	nd	nd
CHS	3f		nd	nd	0.55	nd	nd	nd	nd	nd	nd	nd
WFSM1	4f		I/S	nd	I/S	nd	I/S	nd	I/S	nd	I/S	nd
EVF/R	5f		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
AACH2	6f		nd	0.1	0.02*	nd	nd	nd	nd	nd	nd	nd
WF2	7f		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BVSM2	8f		I/S	nd	I/S	nd	I/S	nd	I/S	nd	I/S	nd
WFSW	9f		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EV1	10f		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BV2	11f		nd	nd	nd	nd	nd	0.12	nd	nd	nd	nd
EVSM2	12f		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
ST1	13f		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
TB#2	14f		nd	0.08	nd	nd	nd	nd	nd	nd	nd	nd
WF1#3	15f	0.25 ppb	nd	0.27	0.41	0.24	0.22*	0.43	2.11	2.17	N/A	N/A
WF2#4	16f	0.5 ppb	nd	0.59	0.43	0.57	0.25*	0.8	2.1	3.88	N/A	N/A
BVCW#3	17f	0.25 ppb	nd	0.24	1.93	0.28	0.85	4.4	2.91	3.58	N/A	N/A
WF2#2	18f		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EV2#4	19f	0.25 ppb	nd	0.24	0.28	0.24	0.23*	0.41	1.88	2.25	N/A	N/A
WF2#1	20f		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EVFR#3	21f	0.5 ppb	nd	0.5	0.9	0.54	0.45	0.8	3.88	4.14	N/A	N/A
LFB#2	22f	0.5 ppb	nd	0.8	0.52	0.82	0.28*	0.8	N/A	N/A	0.72	0.24
BVSM3#2	23f	2 ppb	0.78	2.29	1.58	2.08	0.53	3.08	N/A	N/A	2.11	2.12
BV1#3	24f	0.5 ppb	nd	0.54	0.72	0.58	0.42	1.01	3.44	3.5	N/A	N/A
WF1#4	25f	1 ppb	nd	1.2	1.22	1.23	0.78	1.82	N/A	0.13	7.88	0.94
WF2#3	26f	2 ppb	1.19	2.24	2.71	2.03	1.42	2.57	N/A	N/A	0.15*	2
LFB#1	27f	0.25 ppb	nd	0.2	0.47	0.27	0.23*	0.28	0.02*	nd	N/A	N/A
TB#1	28f		nd	0.05	nd	nd	nd	nd	nd	nd	nd	nd
CHS#4	29f	0.25 ppb	nd	0.24	0.48	0.28	0.20*	0.38	1.82	2.23	N/A	N/A
CHS#3	30f	1 ppb	nd	1.3	1.2	1.24	0.78	1.53	N/A	N/A	1.17*	1.11
EVF/R#4	31f	2 ppb	nd	2.23	2.51	2.03	1.27	2.8	N/A	N/A	0.89	2.04
LFB#3	32f	2 ppb	0.98	2.18	3.14	1.91	1.82	2.88	9.78	18.5	N/A	N/A
BV1#4	33f	0.5 ppb	nd	0.57	0.55	0.55	0.31*	0.99	2.24	4.17	N/A	N/A
EV2#3	34f	1 ppb	nd	1.3	1.22	1.18	0.89	1.57	N/A	N/A	1.52	1.01
EB#2	35f		nd	0.07	nd	nd	nd	nd	nd	nd	nd	nd
BVSM	36f		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BV1#1	37f	2 ppb	1.55	2.5	3.78	2.05	1.88	3.18	N/A	N/A	1.87	2.05
EVSM3	38f		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EB#1	39f		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BV1#2	40f	1 ppb	1.02	2.43	3.32	2.04	1.81	2.97	N/A	N/A	1.19*	1.82
BVCW#4	41f	1 ppb	0.75	1.39	1.87	1.19	0.92	4.54	N/A	N/A	1.01*	0.94
WFSM3	42f		I/S	nd	I/S	nd	I/S	nd	I/S	nd	I/S	nd
EVSM1	43f		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BV1	44f		S/L	nd	S/L	nd	S/L	0.19	S/L	nd	S/L	nd
EVSM4	45f		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BVSM4	46f		nd	0.05	nd	nd	nd	nd	nd	nd	nd	nd
WF1	47f		nd	0.08	nd	nd	nd	nd	nd	nd	nd	nd
BVCW	48f		nd	nd	nd	nd	nd	4.48	nd	nd	nd	nd

NOTES: nd:not detected, N/A:not added, I/S:insufficient sample, *:below MDL (method detection limit), S/L:sample lost

Thirteen additional blank samples, duplicate samples or spiked samples not listed here were analyzed by GC/ECD

Table A.7. GC/ECD and Immunoassay Results for the Month of December

DECEMBER SAMPLING			ATRAZINE ppb		CYANAZINE ppb		ALACHLOR ppb		METOLACHLOR ppb		CARBOFURAN ppb	
Virginia Tech ID	Ohmicron ID	Spike Level	VT	OHM	VT	OHM	VT	OHM	VT	OHM	VT	OHM
WFAmbTo	1g		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EVF/R	2g		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BVCW#3	3g	0.25 ppb	nd	0.51	0.6	0.42	0.21*	4.06	0.12*	3.92	N/A	N/A
EVF/R#2	4g	2 ppb	0.84	2.38	2.82	2.07	1.19	2.62	N/A	0.1	2	2.07
EV1	5g		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EV2	6g		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EVSM2	7g		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BV1	8g		nd	nd	nd	nd	nd	0.12	nd	nd	nd	nd
BV2	9g		nd	nd	nd	nd	nd	0.18	nd	nd	nd	nd
LB#2	10g		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WF1	11g		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
LFB#2	12g	1 ppb	0.53	1.32	1.44	1.2	0.63	1.54	4.44	10.84	N/A	N/A
WF2	13g		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WF2#1	14g	2 ppb	0.25*	21.6	1.1	16.1	0.34	21	N/A	0.58	0.61*	16.5
WFSM3	15g		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BVCW	16g		nd	nd	nd	nd	nd	4.42	nd	nd	nd	nd
EB#1	17g		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EVSM1	18g		I/S	nd	I/S	nd	I/S	nd	I/S	nd	I/S	nd
WFSM2	19g		I/S	0.07	I/S	nd	I/S	nd	I/S	nd	I/S	nd
LB#1	20g		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BV1#2	21g	1 ppb	0.58	1.36	2.04	1.28	0.86	1.56	N/A	0.1	0.85*	1.47
LFB#1	22g	0.25 ppb	nd	0.41	0.33	0.35	0.2	0.35	N/A	N/A	1.6	0.27
BVCW#1	23g	0.5 ppb	nd	0.41	0.63	0.3	0.29*	4.14	2.01	2.52	N/A	N/A
WFSW	24g		nd	nd	0.02*	nd	nd	nd	nd	nd	nd	nd
BV1#1	25g	2 ppb	1.41	2.37	2.98	2.24	1.43	2.91	N/A	0.11	2.1	2.24

NOTES: nd:not detected, N/A:not added, I/S:insufficient sample, *below MDL (method detection limit), S/L:sample lost

Sixteen additional blank samples, duplicate samples or spiked samples not listed here were analyzed by GC/ECD

Table A.8. GC/ECD and Immunoassay Results for the Month of January

JANUARY SAMPLING			ATRAZINE ppb		CYANAZINE ppb		ALACHLOR ppb		METOLACHLOR ppb		CARBOFURAN ppb	
Virginia Tech ID	Ohmicron ID	Spike Level	VT	OHM	VT	OHM	VT	OHM	VT	OHM	VT	OHM
WF1#3	1h	1 ppb	0.71	1.34	1.04	1.04	0.76	1.15	N/A	N/A	2.33	1.15
BVCW#2	2h	0.25 ppb	0.35*	0.29	0.34	0.33	0.23*	1.57	0.1*	0.49	N/A	N/A
BV1#3	3h	0.25 ppb	0.37	0.28	0.39	0.31	0.19*	0.37	0.18*	0.39	N/A	N/A
BV1#1	4h	1 ppb	0.42	17.68	0.64	16.6	0.46	20.4	N/A	0.76	2.53	20.7
WFSM4#3	5h	2 ppb	0.8	2.33	2.1	2.04	1.31	2.65	N/A	N/A	0.63*	2.19
EVF/R	6h		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WF1#4	7h	2 ppb	2.3	2.52	2.46	2.08	1.58	2.45	N/A	N/A	4.72	2.27
WF1	8h		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WFSM4	9h		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EVF/R#4	10h	2 ppb	0.42	2.92	1.48	2.17	1.05	2.67	N/A	0.16	1.88	2.42
EV2#1	11h	0.25 ppb	0.34*	0.48	0.35	0.35	0.21*	0.29	0.09*	0.49	N/A	N/A
BV2	12h		nd	nd	nd	nd	nd	0.15	nd	nd	nd	nd
EV1	13h		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BVCW#4	14h	0.5 ppb	0.44	0.79	0.73	0.59	0.41	2.01	0.25*	0.85	N/A	N/A
EB	15h		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WFSM1	16h		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BV1#4	17h	2 ppb	0.75	1.97	1.81	2.28	1.2	2.79	N/A	0.14	6.33	1.83
EV2#3	18h	0.5 ppb	0.22*	0.58	0.67	0.64	0.41	0.73	0.27*	0.73	N/A	N/A
EV2	19h		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
BV1	20h		nd	nd	nd	nd	nd	0.15	nd	nd	nd	nd
WFSM3	21h		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WF2#4	22h	0.5 ppb	nd	0.68	0.64	0.61	0.41	0.75	nd	0.7	N/A	N/A
TB#1	23h		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WF2#3	24h	0.25 ppb	0.14*	0.34	0.32*	0.27	0.19*	0.38	0.09*	0.31	N/A	N/A
LFB#1	25h	1 ppb	S/L	1.17	S/L	1.16	S/L	1.48	S/L	N/A	S/L	0.85
BVCW	26h		nd	nd	nd	nd	nd	1.22	nd	nd	nd	nd
WFSM2	27h		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
LFB#2	28h	0.5 ppb	0.39	0.62	0.66	0.62	0.42	0.72	0.28*	0.7	N/A	N/A
WF2	29h		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WFSW	30h		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

NOTES: nd=not detected, N/A=not added, I/S=insufficient sample, *below MDL (method detection limit), S/L=sample lost

Fourteen additional blank samples, duplicate samples or spiked samples not listed here were analyzed by GC/ECD

Table A.9. GC/ECD and Immunoassay Results for the Month of February

FEBRUARY SAMPLING			ATRAZINE ppb		CYANAZINE ppb		ALACHLOR ppb		METOLACHLOR ppb		CARBOFURAN ppb	
Virginia Tech ID	Ohmicron ID	Spike Level	VT	OHM	VT	OHM	VT	OHM	VT	OHM	VT	OHM
CHSM2	1I		nd	nd	nd	nd	nd	nd	0.32	nd	nd	nd
IV1#4	2I	0.5 ppb	0.34*	0.88	0.58	0.7	0.4	0.84	0.28*	0.93	N/A	N/A
CHS	3I		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
IV2	4I		nd	nd	nd	nd	0.05*	0.19	0.04*	nd	nd	nd
IVSM4	5I		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CV1	6I		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WFSM1	7I		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
IV1	8I		nd	nd	nd	nd	nd	0.18	nd	0.1	nd	nd
LB #2	9I		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
LB #3	10I		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CHS#4	11I	0.25 ppb	nd	0.33	0.34	0.35	0.22*	0.37	0.08*	0.49	N/A	N/A
WFSM2	12I		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WFSM3	13I		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CH2	14I		nd	0.25	nd	nd	nd	nd	nd	nd	nd	nd
IVCW#4	15I	0.5 ppb	nd	0.7	0.5	0.72	0.38	1.34	0.22*	0.95	N/A	N/A
IVSM4#3	16I	1 ppb	0.83	1.34	0.28*	1.38	1.39	1.57	N/A	0.05	13	1.04
CHS#3	17I	0.25 ppb	nd	0.38	0.19*	0.38	0.08*	0.38	nd	0.49	N/A	N/A
IVSM1#4	18I	2 ppb	0.5	2.51	1.18	2.28	0.91	3	N/A	0.11	4.71	2.07
LFB #2	19I	0.5 ppb	0.58	0.73	0.73	0.74	0.54	0.88	0.43*	0.77	N/A	N/A
LFB #4	20I	2 ppb	0.92	2.41	1.29	2.28	1.07	2.85	N/A	0.11	7.43	1.1
WFSM4	21I		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
IVSM3	22I		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CHS#1	23I	0.5 ppb	0.32*	0.7	0.31*	0.78	0.22*	0.75	0.08*	0.91	N/A	N/A
LB #1	24I		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
LFB#1	25I	0.25 ppb	0.55	0.28	0.44	0.31	0.30*	0.3	0.22*	0.35	N/A	N/A
CV2#4	26I	2 ppb	0.52	2.38	nd	1.99	1.22	2.53	N/A	N/A	3.17	2.09
IVSM3#1	27I	0.5 ppb	0.58	0.89	1.19	0.85	0.88	0.85	0.88	0.88	N/A	N/A
TB	28I		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WF1#3	29I	0.5 ppb	0.33*	0.79	0.48	0.84	0.08*	0.88	0.18*	0.83	N/A	N/A
CV2	30I		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WF1#4	31I	0.25 ppb	nd	0.38	0.23*	0.33	0.08*	0.32	nd	0.37	N/A	N/A
CHS	32I		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WF1	33I		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WFSW	34I		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CV2#3	35I	1 ppb	0.88	1.43	1.04	1.2	0.83	1.34	N/A	N/A	2.52	1.13
IVCW	36I		nd	nd	nd	nd	nd	0.54	nd	nd	nd	nd
CVF/R	37I		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
IVCW#3	38I	0.25 ppb	nd	0.5	0.38	0.43	0.27*	1.09	0.12*	0.5	N/A	N/A
IVSM1	39I		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
EB#2	40I		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
CV1#4	41I	0.25 ppb	nd	0.34	0.18*	0.35	0.07*	0.31	0.09*	0.38	N/A	N/A
WF2#3	42I	1 ppb	1.09	1.41	1.31	1.13	0.89	1.31	N/A	0.05	19.3	1.19
CHSM3	43I		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
WF2	44I		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
IV1#3	45I	0.25 ppb	nd	0.38	0.28*	0.31	0.19*	0.47	0.08*	0.42	N/A	N/A
CV1#3	46I	0.5 ppb	0.45	0.87	0.47	0.81	0.23*	0.59	0.11*	0.87	N/A	N/A
IVSM1#4	47I	2 ppb	0.5	2.38	1.18	1.91	0.91	2.93	N/A	0.09	4.71	2.13
CHSM1	48I		I/S	nd	I/S	nd	I/S	nd	I/S	nd	I/S	nd
IVSM1#3	49I	1 ppb	2.38	1.42	nd	1.18	0.81	1.52	N/A	N/A	nd	1.03
CHSM4	50I		nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
IVSM2	51I		I/S	nd	I/S	nd	I/S	nd	I/S	nd	I/S	nd
LFB#3	52I	1 ppb	0.8	1.27	1.12	1.11	0.81	1.23	N/A	N/A	7.53	1.02

NOTES: nd=not detected, N/A=not added, I/S=insufficient sample, *=below MDL (method detection limit), S/L=sample lost

Twenty additional blank samples, duplicate samples or spiked samples not listed here were analyzed by GC/ECD

APPENDIX B.

Raw Data used in the Construction of Certain Figures

Table B.1.
Concentrations of Metolachlor Measured in Soil (ppb) (data also presented in Figure 2)

Month	Soil Conc Site 1	Soil Conc Site 2	Soil Conc Site 3	Soil Conc Site 4
June	29.5	110.5	26.9	nd
July	nd	ns	nd	nd
August	ns	ns	ns	ns
September	ns	ns	ns	ns
October	nd	61.4	nd	8.3
November	nd	54.7	nd	nd
December	19.8	ns	7.4	7.1
January	nd	ns	nd	8.7
February	nd	6.7	nd	nd

Abbreviation: nd=not detected, ns=not sampled, conc=concentration

Table B.2.
Raw Data Used in the Comparison of Alachlor Concentrations found in Soil Samples by GC/MS and Alachlor Concentrations Measured in Groundwater Samples by Immunoassay at Site 1 (data also presented in Figure 3)

Month	Soil Concentrations of Alachlor (ppb)	Median Groundwater Concentration (ppb)
May	nd	0.0165
June	145.2	0.145
July	484.7	0.18
August	ns	0.345
September	ns	ns
October	162	0.09
November	nd	0.19
December	nd	0.13
January	nd	0.15
February	nd	0.35

Abbreviation: nd=not detected, ns=not sampled

Table B.3.
Concentration of Metolachlor Measured at Site 2 in Soil and the Number of Days Since the First Sample was Collected (data also presented in Figure 4)

Time Since First Sample Collected (days)	Soil Concentration of Metolachlor (ppb)
0	110.5
114	61.4
149	54.7
239	6.7

Table B.4.
Average Detected Alachlor Concentrations Measured by Immunoassay in Groundwater (data also presented in Figure 5)

Month	Site 1	Site 2	Site 3	Site 4
May	0.17, n=3	nd	nd	nd
June	0.15, n=2	nd	nd	nd
July	0.18, n=2	nd	nd	nd
August	0.35, n=4	nd	0.09	nd
September	ns	ns	ns	ns
October	0.08, n=2	nd	nd	nd
November	1.59, n=3	nd	nd	nd
December	1.56, n=3	ns	nd	nd
January	1.57, n=3	ns	nd	nd
February	0.3, n=3	nd	nd	nd

Abbreviations: nd=not detected, ns=not sampled
number of samples, n=1, unless noted

Table B.5.
Average Detected Atrazine Concentration (ppb) in Groundwater Measured by GC/ECD (data also presented in Figure 6)

Month	Site 1	Site 2	Site 3	Site 4
April	nd	nd	nd	nd
May	nd	nd	nd	nd
June	nd	nd	nd	nd
July	0.59	1.52	nd	0.62
August	nd	nd	nd	nd
September	ns	ns	ns	ns
October	nd	nd	nd	nd
November	nd	nd	nd	nd
December	nd	ns	nd	nd
January	nd	ns	nd	nd
February	nd	nd	nd	nd

Abbreviations: nd=not detected, ns=not sampled
number of samples, n=1, unless noted

Table B.6.
Average Detected Atrazine Concentration (ppb) in Groundwater Measured by Immunoassay (data also presented in Figure 7)

Month	Site 1	Site 2	Site 3	Site 4
May	nd	nd	nd	nd
June	nd	nd	nd	nd
July	nd	nd	nd	nd
August	0.2, n=3	nd	nd	nd
September	ns	ns	ns	ns
October	nd	0.12	nd	0.05
November	nd	0.1	nd	0.06
December	nd	nd	nd	nd
January	nd	nd	nd	nd
February	nd	0.25	nd	nd

Abbreviations: nd=not detected, ns=not sampled
number of samples, n=1 unless noted

Table B.7.
Average Detected Cyanazine Concentration (ppb) in Groundwater Measured by GC/ECD (data also presented in Figure 8)

Month	Site 1	Site 2	Site 3	Site 4
April	nd	nd	nd	nd
May	nd	nd	nd	nd
June	nd	nd	nd	nd
July	0.16	0.17	0.35, n=2	nd
August	nd	nd	nd	nd
September	ns	ns	ns	ns
October	nd	nd	nd	nd
November	nd	0.29, n=2	0.03	nd
December	nd	ns	nd	0.02
January	nd	ns	nd	nd
February	nd	nd	nd	nd

Abbreviations: nd=not detected, ns=not sampled
number of samples, n=1 unless noted

Table B.8.
Average Detected Metolachlor Concentration in Groundwater measured by GC/ECD (data also presented in Figure 9)

Month	Site 1	Site 2	Site 3	Site 4
April	nd	nd	nd	nd
May	nd	nd	nd	nd
June	nd	nd	nd	nd
July	nd	nd	nd	nd
August	0.07	0.33	nd	0.07
September	ns	ns	ns	ns
October	nd	nd	nd	nd
November	nd	nd	nd	nd
December	nd	ns	nd	nd
January	nd	ns	nd	nd
February	nd	nd	nd	nd

Abbreviations: nd=not detected, ns=not sampled
number of samples, n=1 unless noted

Table B.9.
Average Detected Metolachlor Concentration in Groundwater; Measured by Immunoassay (data also presented in Figure 10)

Month	Site 1	Site 2	Site 3	Site 4
May	nd	0.33	nd	nd
June	nd	nd	nd	nd
July	0.05	nd	nd	nd
August	nd	nd	nd	nd
September	ns	ns	ns	ns
October	nd	nd	nd	nd
November	nd	nd	nd	nd
December	nd	ns	nd	nd
January	nd	ns	nd	nd
February	0.1	nd	nd	nd

Abbreviations: nd=not detected, ns=not sampled
number of samples, n=1, unless noted

Table B.10.
Number of Fortified Samples Analyzed between August, 1992 and February, 1993 and Number of positive Results Returned by Immunoassay and GC/ECD (data also presented in Figure 22)

Pesticide	Number of Fortified Samples	Number of Immunoassay Detections	Number of GC/ECD Detections
Alachlor	82	82	82
Atrazine	82	82	55
Carbofuran	41	41	31
Cyanazine	82	82	80
Metolachlor	37	37	32

Appendix C.
Complete List of Soil Samples

Table C.1. Concentration of Pesticides in Soil Samples (Complete list of soil samples taken)

Sample	Sample Type	Spike Level	Carbofuran	Atrazine	Alachlor	Metolachlor	Cyanazine
CHF 6/19	SOIL		nd	nd	nd	110.5	nd
EVF 6/18	SOIL		nd	nd	nd	26.9	nd
WFF 6/19	SOIL		nd	nd	nd	nd	nd
BVF 6/18	SOIL		nd	nd	145.2	25.5	nd
CHOS 6/19	SEDIMENT		nd	nd	nd	nd	nd
EVOS 6/18	SEDIMENT		nd	nd	nd	nd	nd
BVOS 6/18	SEDIMENT		nd	nd	nd	nd	nd
WFOS 6/19	SEDIMENT		nd	nd	nd	nd	nd
WFF 7/18	SOIL		nd	nd	nd	nd	nd
BVF 7/17	SOIL		nd	nd	484.7	nd	nd
WFOS 7/19	SEDIMENT		nd	nd	nd	nd	nd
BVOS 7/18	SEDIMENT		nd	nd	nd	nd	nd
EVSurf3 7/18**	SOIL		nd	nd	nd	nd	nd
EVSurf1 7/18	SOIL		nd	nd	nd	nd	nd
EVOS 7/18	SEDIMENT		nd	nd	nd	nd	nd
EV3ft#2 7/18	SOIL b		nd	nd	nd	nd	nd
EVLot#1 6' 7/18	SOIL b		nd	nd	nd	nd	nd
EVLot#3 7/18	SOIL b		nd	nd	nd	nd	nd
EV 4FT1 7/18	SOIL b		nd	nd	nd	nd	nd
EV WT#2 7/18	SOIL b		nd	nd	nd	nd	nd
EVSurf2 7/18**	SOIL		nd	nd	nd	nd	nd
EV 3ft3 7/18	SOIL b		nd	nd	nd	nd	nd
BVF 10/10	SOIL		nd	nd	162	nd	nd
BVF 10/10	MATRIX SPIKE	2050 ppb	5692.5	2706	3456	223.6	2456
WFF 10/11	SOIL		nd	nd	nd	8.3	nd
CHF 10/11	SOIL		nd	nd	nd	61.4	nd
EVF 10/10	SOIL		nd	nd	nd	nd	nd
LB 10/21	LAB BLANK		nd	nd	nd	nd	nd
BVOS 10/10	SEDIMENT		nd	nd	nd	nd	nd
WFOS 10/11	SEDIMENT		nd	nd	nd	nd	nd
EVOS 10/10	SEDIMENT		nd	nd	nd	nd	nd
CHOS 10/11	SEDIMENT		nd	nd	nd	nd	nd
BVF 11/14	SOIL		nd	nd	nd	nd	nd
EVF 11/14	SOIL		nd	nd	nd	nd	nd
CHF 11/15	SOIL		nd	nd	nd	54.7	nd
WFF 11/15	SOIL		nd	nd	nd	nd	nd
WFOS 11/15	SEDIMENT		nd	nd	nd	nd	nd
CHOS 11/15	SEDIMENT		nd	nd	nd	nd	nd
EVOS 11/14	SEDIMENT		nd	nd	nd	nd	nd
BVOS 11/14	SEDIMENT		nd	nd	nd	nd	nd
EVF 12/5	SOIL		nd	nd	nd	7.4	nd
BVF 12/5	SOIL		nd	nd	nd	nd	nd
WFF 12/6	SOIL		nd	nd	nd	7.1	nd
EVOS 12/5	SEDIMENT		nd	nd	nd	nd	nd
BVOS 12/5	SEDIMENT		nd	nd	nd	nd	nd
WFOS 12/6	SEDIMENT		nd	nd	nd	nd	nd
WFOS 12/6	MATRIX SPIKE	1170 ppb	nd	5433	1502	84971	2796
WFF 1/11	SOIL		nd	nd	nd	8.7	nd
BVF 1/10	SOIL		nd	nd	nd	17.2	nd
EVF 1/10	SOIL		nd	nd	nd	nd	nd
WFOS 1/11	SEDIMENT		nd	nd	nd	nd	nd
EVF 1/10 #4	REP. MAT. SPIKE	1187 ppb	nd	924	1035	1009	1313
EVF 1/10 #3	REP. MAT. SPIKE	1105 ppb	nd	1021	1020	1007	1700
EVF 1/10 #2	REP. MAT. SPIKE	1163 ppb	nd	746	805	784	879
EVF 1/10 #1	REP. MAT. SPIKE	1186 ppb	nd	1076	1104	1053	1811
BVF 2/12	SOIL		nd	nd	nd	nd	nd
EVF 2/12	SOIL		nd	nd	nd	nd	nd
CHF 2/13	SOIL		nd	nd	nd	6.7	nd
WFF 2/13	SOIL		nd	nd	nd	nd	nd
EVOS 2/12	SEDIMENT		nd	nd	nd	nd	nd
BVOS 2/12	SEDIMENT		nd	nd	nd	nd	nd
WFOS 2/13	SEDIMENT		nd	nd	nd	nd	nd

** – Duplicate of EVSurf1

b – collected froma depth of greater than 10 cm.

Appendix D.

Chromatograms and Mass Spectra

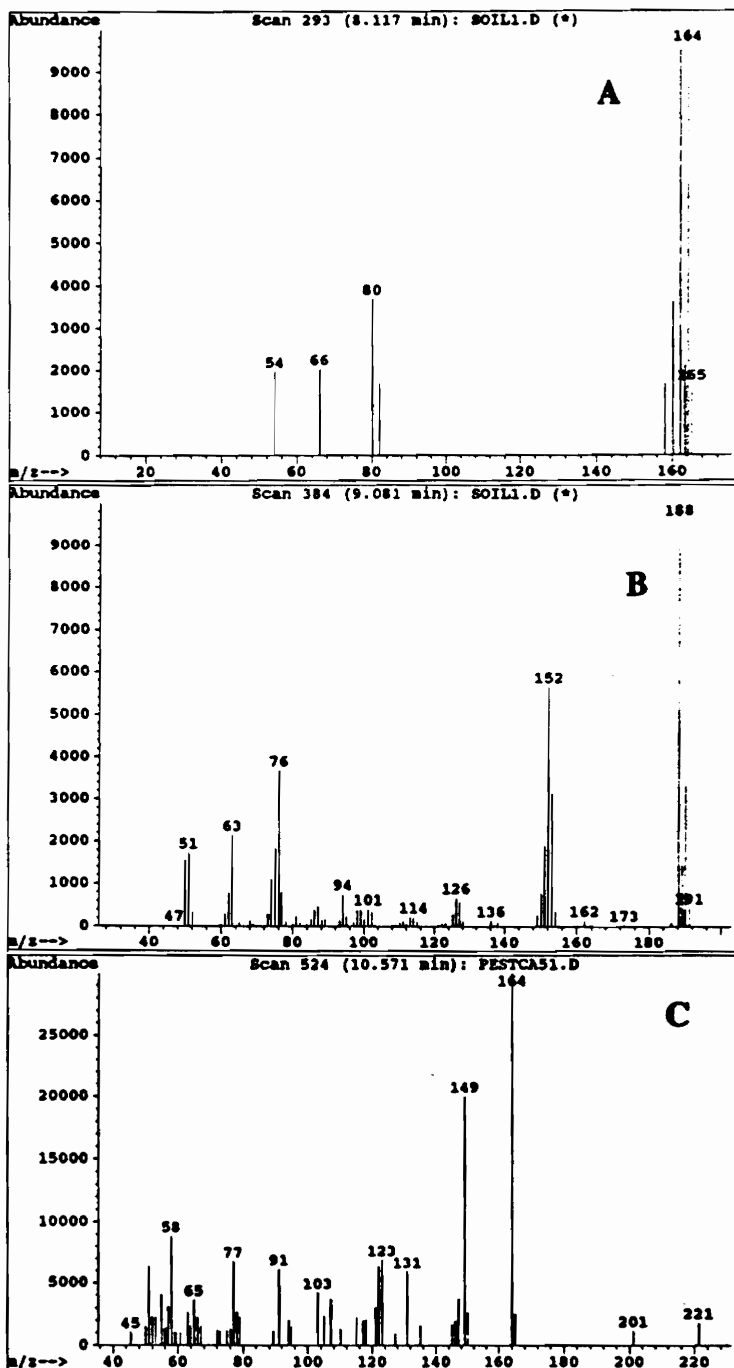


Figure D.1. Mass spectra of pesticides and internal standards in this study. (A: acenapthene d_{10}, B: 4-chlorobiphenyl, C: carbofuran).

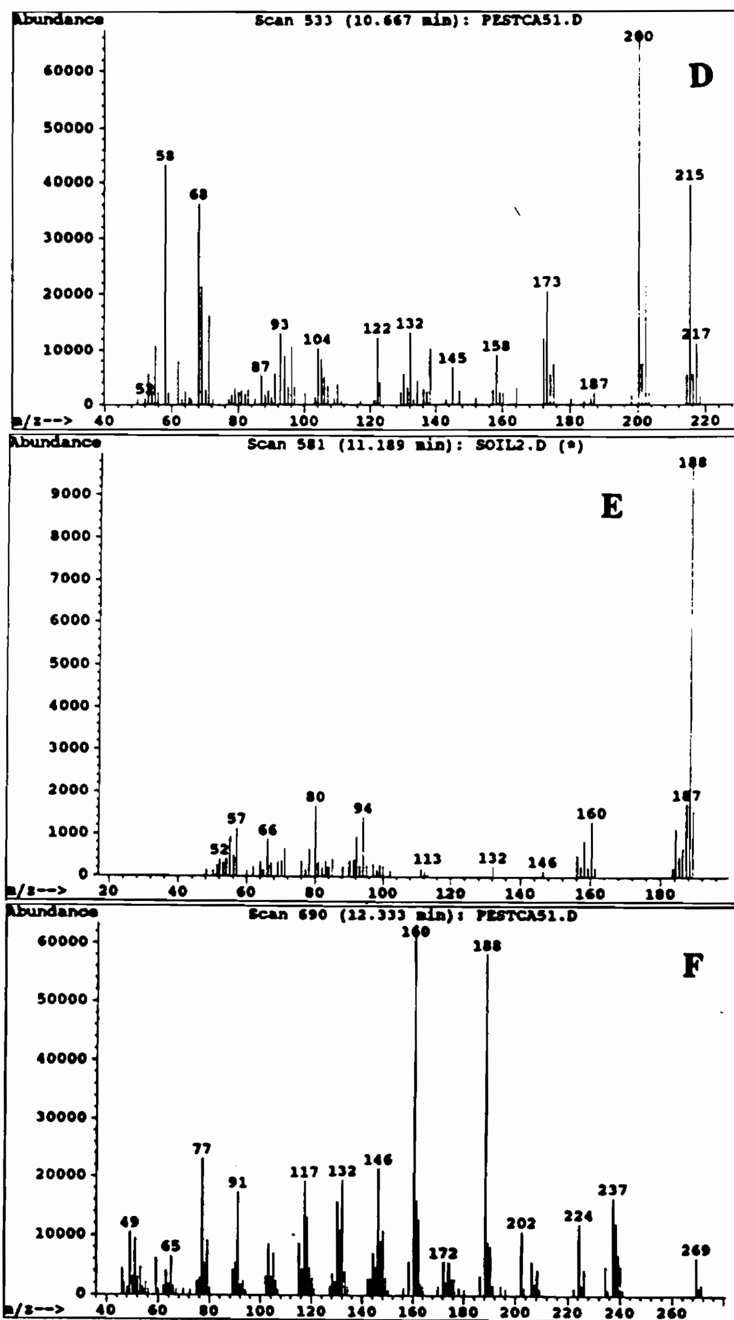


Figure D.2. Mass spectra of pesticides and internal standards in this study. (D: atrazine, E: phenanthrene d_{10}, F: alachlor).

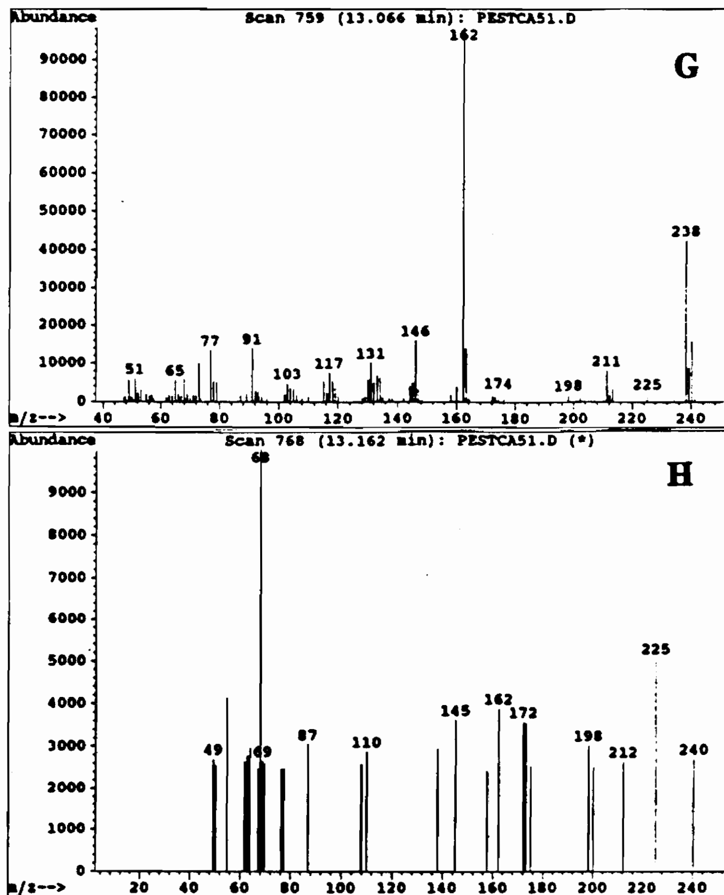


Figure D.3. Mass spectra of pesticides and internal standards in this study. (G: metolachlor, H: cyanazine).

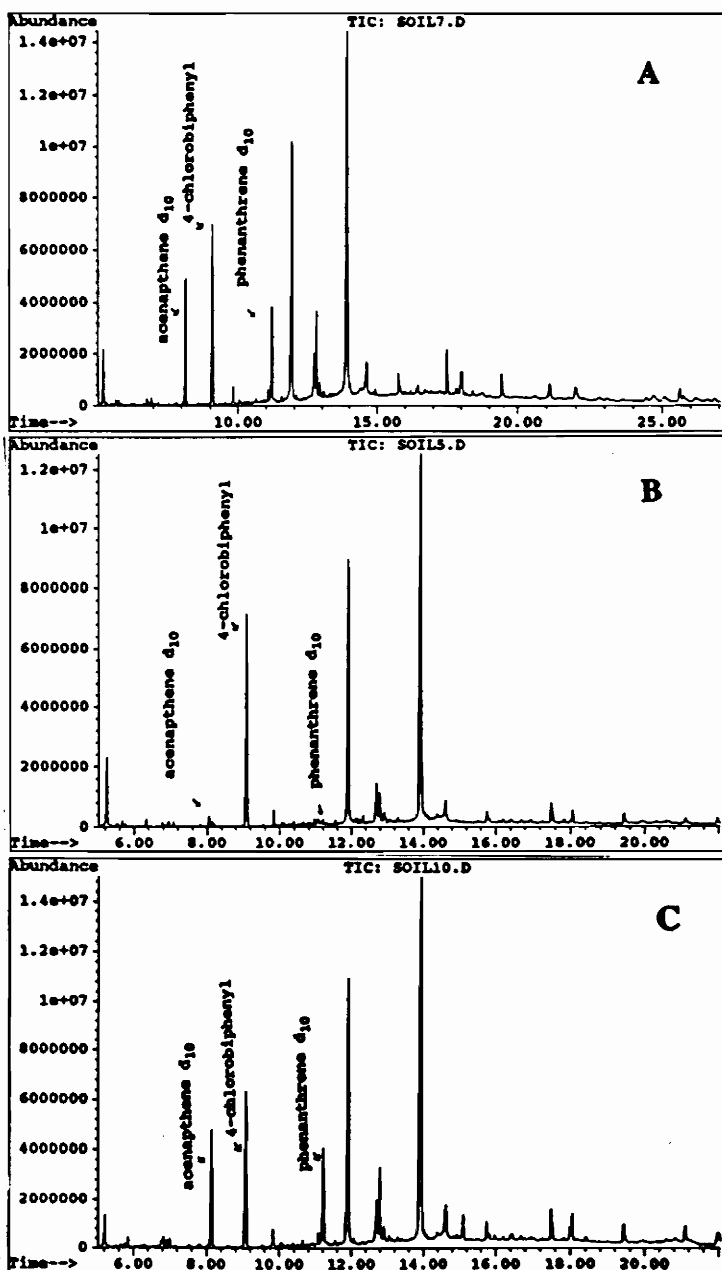


Figure D.4. Representative total ion chromatograms of soil and sediment extracts. [A: BVF 12/5, B: CHF 10/11 (note-acenapthene d_{10} and phenanthrene d_{10} added in smaller amount in October then in December, C: EVF 12/5].

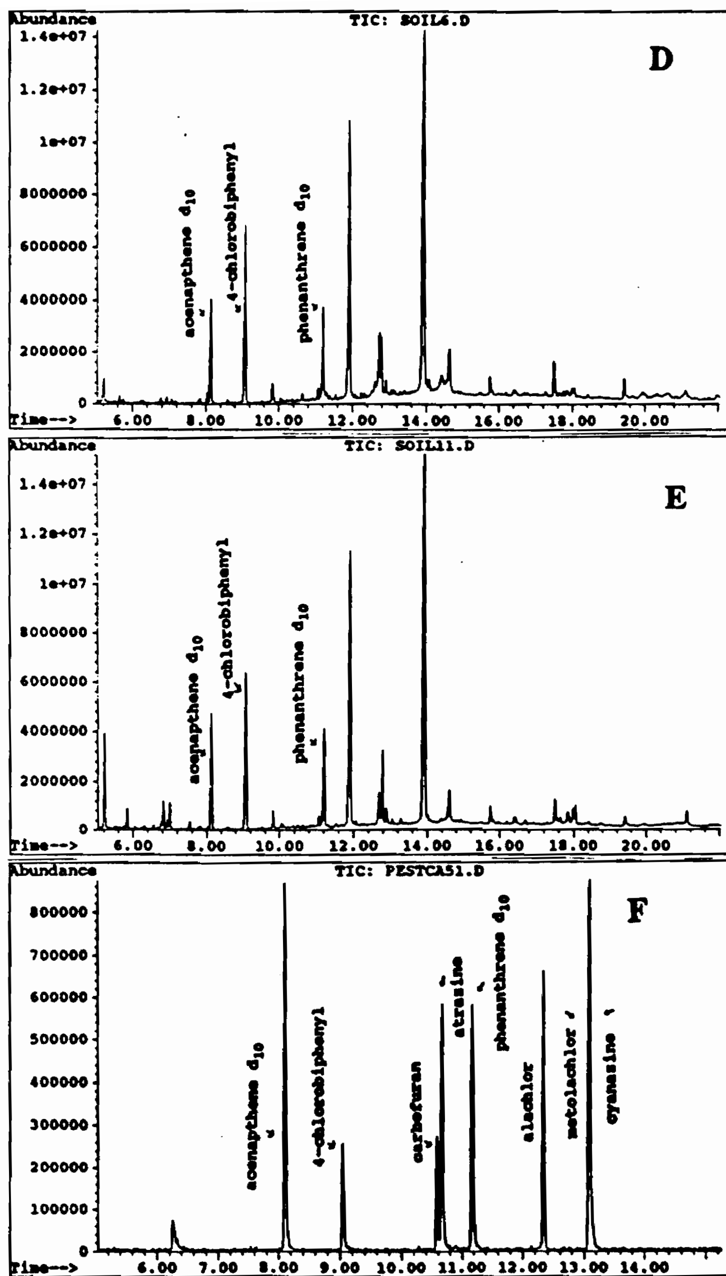


Figure D.5. Representative total ion chromatograms of a soil and sediment extract and a calibration solution. [D: Site 4(WFF 12/6), E: Site 3 sediment(EVOS 12/5), F: calibration solution 1 (5 μg/mL)].

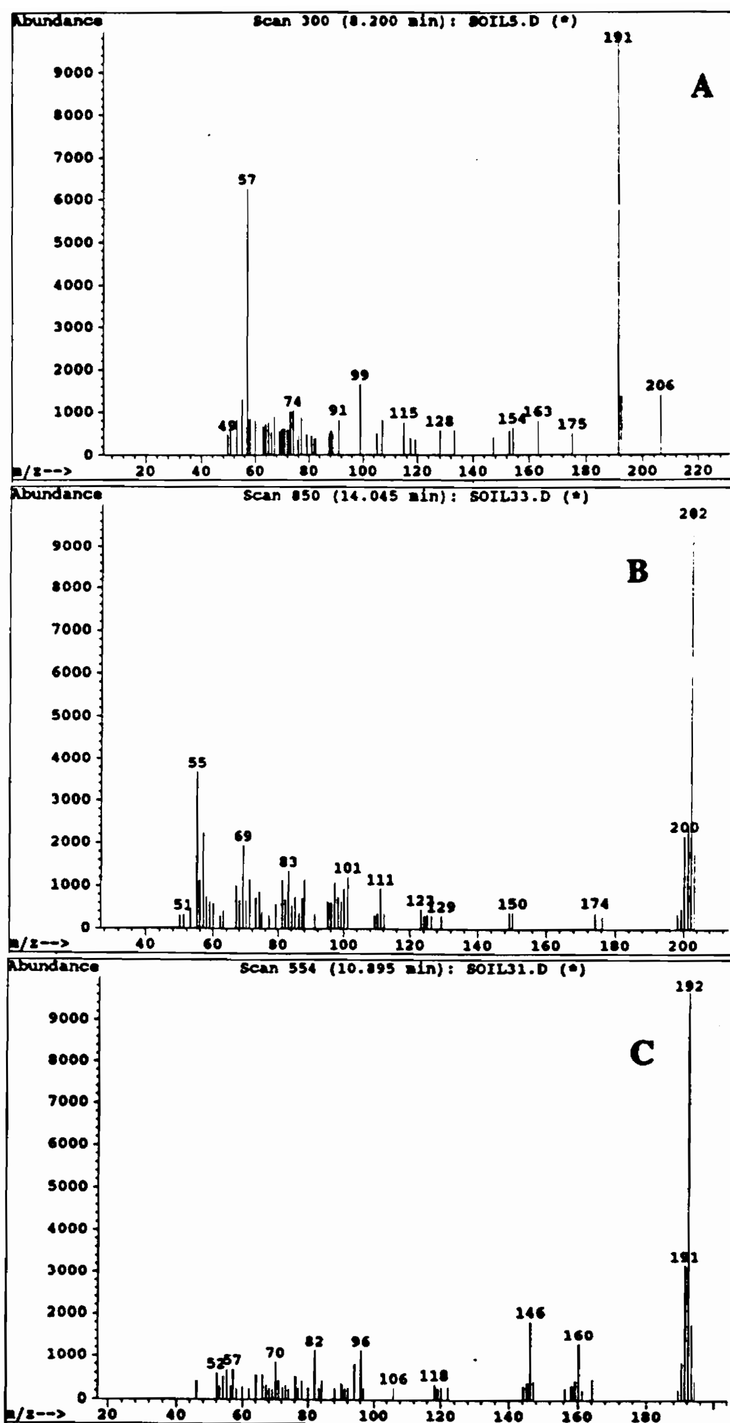


Figure D.6. Mass spectra of tentatively identified non-target organic compounds extracted from soil or sediment. (A: 2,4-bis(1,1-dimethylethyl)-Phenol, B: Flouranthene, C: methyl-anthracene or methyl-phenanthrene).

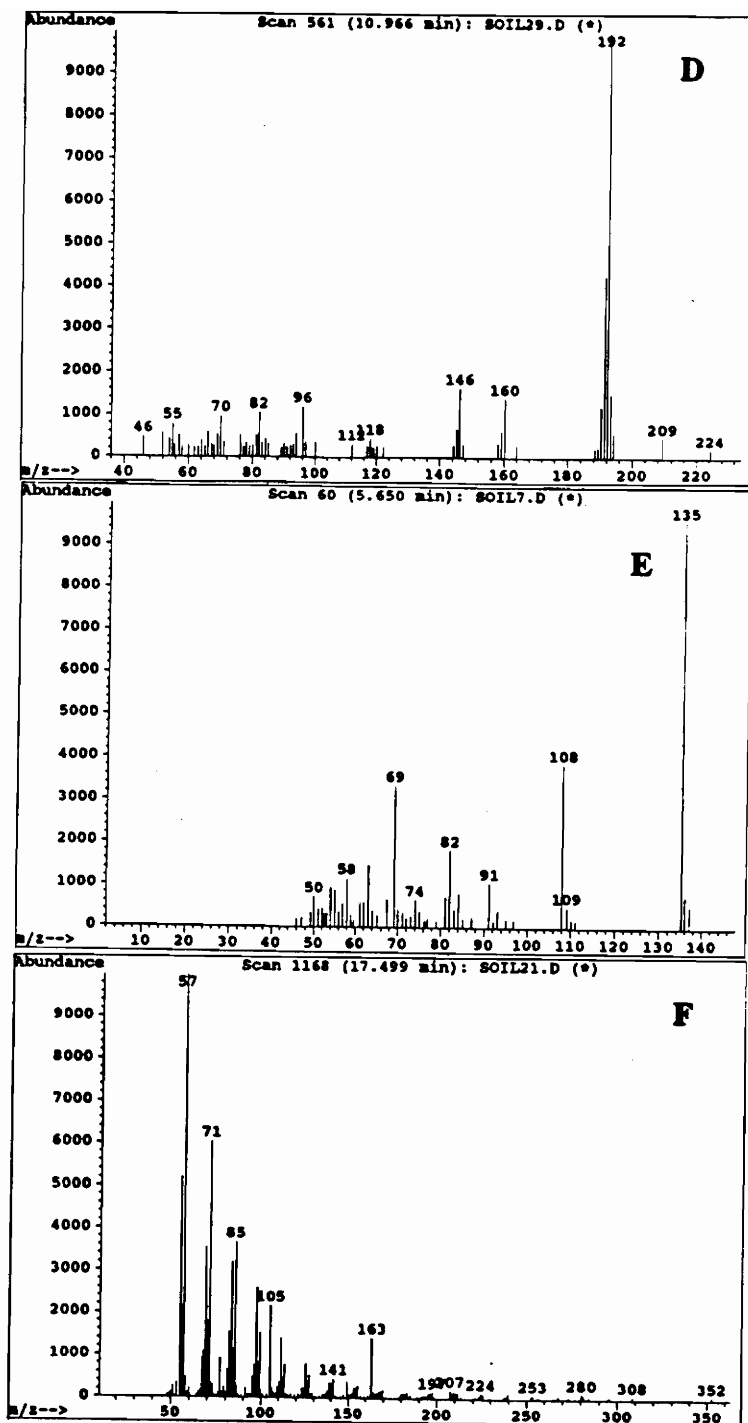


Figure D.7. Mass spectra of tentatively identified non-target organic compounds extracted from soil or sediment. (D: methyl anthracene or methyl-phenanthrene, E: Benzothiazole, F: (E)-3-Eicosene).

Appendix E

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 E.1.
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 E.1. continued

Name	Type	Comments	Volume	Measured Conc. ($\mu g/L$)			
				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 E.1. 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 E.2.
May Samples

Name	Type	Comments	Volume	Measured Conc. ($\mu g/L$)			
				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 E.2. continued

Name	Type	Comments	Volume	Measured Conc. ($\mu g/L$)			
				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 E.2. 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	<u>0.80</u>	0.91*	ND

Table E.3.
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 E.3. Continued

Name	Type	Comments	Volume	Measured Conc. ($\mu g/L$)			
				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 E.3. Continued

Name	Type	Comments	Volume	Measured Conc. ($\mu g/L$)			
				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 E.4.
July Samples

Name	Type	Comments	Volume	Measured Conc. ($\mu g/L$)			
				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 E.4. Continued

Name	Type	Comments	Volume	Measured Conc. ($\mu g/L$)			
				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 E.4. Continued

Name	Type	Comments	Volume	Measured Conc. ($\mu g/L$)			
				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 E.5.
August Samples

Name	Type	Comments	Volume	(%) Res	Measured Conc. ($\mu g/L$)				
					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 E.5. Continued

Name	Type	Comments	Volume	(%) Res	Measured Conc. ($\mu g/L$)				
					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 E.5. 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 E.6.
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 E.6. 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 E.6. Continued

Name	Type	Comments	Volume	(%) Resp	Measured Conc. ($\mu g/L$)				
					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 E.6. Continued

Name	Type	Comments	Volume	(%) Resp	Measured Conc. ($\mu g/L$)				
					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 E.7.
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 E.7. 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 E.7. Continued

Name	Type	Comments	Volume	(%) Resp	Measured Conc. ($\mu g/L$)				
					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 E.7. 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 E.8.
December Samples

Name	Type	Comments	Volume	(%) Resp	Measured Conc. ($\mu g/L$)				
					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 E.8. 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 E.8. Continued

Name	Type	Comments	Volume	(%) Resp	Measured Conc. ($\mu g/L$)				
					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 E.9.
January Samples

Name	Type	Comments	Volume	(%) Resp	Measured Conc. ($\mu g/L$)				
					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 E.9. Continued

Name	Type	Comments	Volume	(%) Resp	Measured Conc. ($\mu g/L$)				
					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 E.9. 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 E.10.
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 E.10. Continued

Name	Type	Comments	Volume	(%) Resp	Measured Conc. ($\mu g/L$)				
					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 E.10. Continued

Name	Type	Comments	Volume	(%) Resp	Measured Conc. ($\mu g/L$)				
					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 E.10. 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 F

Chronology

The dates of all the important procedures performed in the study are listed in table F.1.

Table F.1.
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 F.1. 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 F.1. 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

VITA

Douglas Linden Schicho was born on January 17, 1966 in Orange, New Jersey, of Richard and Alice Schicho. Doug received his B.S. in Chemistry from the University of Vermont in the spring of 1988. He worked as an assistant scientist in the field of new drug discovery for Pfizer Inc. before attending VPI&SU. He completed his M.S. in Environmental Engineering in the summer of 1993.