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Melanie Mobley

Georgia College & State University

Lance Cramer

Georgia College & State University

Daniel Brooks

Georgia College & State University

Catrena Higginbotham Ph.D

Georgia College & State University

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“MIDDLE GEORGIA WATERS:” CHEMICAL ANALYSIS BY GC&SU
UNDERGRADUATES

Melanie Mobely

Lance Cramer

Daniel Brooks

Catrena Higginbotham, Ph.D

Catrena Higginbotham, Ph.D

Faculty Sponsor

Abstract

Every living organism on Earth depends on water, many of which must consume liters of fresh water daily [1]. Unfortunately, a readily available source of clean, fresh water is diminishing. Over the years, the fresh water supply has been polluted by biological and chemical sources. The nutrient levels and pesticide chemical contamination of several water locations in the Middle Georgia area were analyzed and monitored by chemistry majors at GC&SU over the past two years.

1. Introduction

Ground water, which is found underground and in aquifers, is used as a supply of drinking water by almost half of North America and one-third of Great Britain [1]. Once considered an untainted source of drinking water because of its filtration through soil compared to surface fresh water found in lakes and rivers, the ground water has been contaminated by chemicals for many decades [1]. In rural areas, the source of contamination stems from organic pesticides leaching from surface water into the pores of soil particles, and hence, contaminating the ground water as it is filtered by the soil.

A pesticide is defined as any substance or mixture of substances intended to prevent, destroy, or repel any pest or intended for use as a plant regulator, defoliant, or desiccant, according to the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) [2]. Major classes of pesticides include the organochlorines or chlorinated hydrocarbons, organophosphates, carbamates, thiocarbamates, substituted acid amines, phenoxy acids, triazines, substituted ureas, dinitroanilines, bypyridiums, benzoic acids, synthetic pyrethins or pyrethroids, aliphatic hydrocarbons, organometallic complexes, and inorganic pesticides [3]. Environmental fate and transport of pesti-

cides is dependent in part upon their physical and chemical properties and the degradation processes for these compounds [4]. Some of the physical and chemical properties that pertain to water contamination include soil-sorption coefficient, solubility in water, vapor pressure, octanol-water partitioning coefficient, acid/base ionization equilibrium constants, and field half-life.

Pesticides that are relatively persistent in the soil have the greatest tendency to be leached to ground water [6]. The physical and chemical properties that are associated with increased pesticide-leaching potential are high solubility in water; low vapor pressure; and long field half life. The pesticides that have the greatest leaching potentials generally have water solubilities greater than 30 mg/L and field half lives greater than 21 days [5]. Climatic factors, agricultural practices, and soil and aquifer properties also influence the transport of chemicals to ground water [4].

Pesticides are transported to streams and rivers through surface runoff by two modes, either (a) in solution: dissolved in runoff water or (b) in suspension: attached to soil particles that are entrained in runoff [7]. Pesticides with considerable transport in surface runoff in solution have high water solubilities, low vapor pressures, and long field half lives. Pesticides with appreciable transport in surface runoff in suspension have low vapor pressures and long field half lives but low water solubilities. The transport of pesticides in surface runoff to streams and rivers is strongly influenced by climatic factors, soil properties, agricultural practices, and topographic relief [4].

2. Experimental

In this research, we report on the monitoring of nutrient levels, pH, and temperature using on sight testing kits for various streams, rivers, and lakes in the middle Georgia area (Table 1, Locations). Also we compare two methods (a) liquid-liquid extraction, and (b) headspacing extraction for sample preparation for chemical analysis using gas chromatography/mass spectrometry (GC/MS). These two methods are commonly used for pesticide analysis of water samples using GC/MS. This research project was divided into teams, and each team was assigned different locations and counties. The results for Team 1 (Locations 4-9 and 13) are reported within this paper.

Table 1 – Location Number, Location, and County

Number	Location & County
1	Tobosofkee Creek (Bibb County)
2	Commission Creek (Jones County)
3	Lake Sinclair (Baldwin County)
4	Lake Oconee (Putnam County)
5	Lake Sinclair (Hancock County)
6	Lake Laurel (Champion Creek) Milledgeville, GA (Baldwin County)
7	Oconee River (Baldwin County)
8	North Lake, Sandersville, GA (Washington County)
9	Lake Sinclair (Power Plant), Milledgeville, GA (Baldwin County)
10	Lake Sinclair - Villamar Dock (Baldwin County)
11	River Bridge (Baldwin County)
12	Little Fishing Creek (Baldwin County)
13	Fishing Creek (Baldwin County)
14	Buffalo Creek (Washington County)
15	College Station Creek (Baldwin County)
16	Potato Creek (Baldwin County)
17	Tobler Creek (Baldwin County)
18	Lake Tchukalaho (Washington County)
19	Walden Woods Pond (Washington County)
20	Rum Creek (Jones County)
21	Murder Creek (Baldwin County)
22	Town Creek (Baldwin County)

2.1 Materials

Reagents are as follows: methylene chloride (Aldrich), iso-octane (Aldrich), methanol (Aldrich, reagent grade), ammonia salicylate reagent powder (Hach), ammonia cyanurate reagent powder (Hach), DPD Free Chlorine reagent powder (Hach), DPD Total Chlorine reagent powder (Hach), PhosVer 3 Phosphate Reagent Powder (Hach), NitraVer 5 Nitrate Reagent (Hach), and ultra high purity Helium (Specialty Gases).

2.2 Sample Collection

All water samples were collected according to EPA Method 525.4 [8]. The samples were collected mid stream in amber glass bottles that were placed under water and filled. All samples were refrigerated and chemical analysis via GC/MS was conducted within seven days after collection.

2.3 Sample Preparation

Two methods of sample preparation were used for a comparison study to find the easier, more reliable, and cost effective way of conducting chemical analysis.

2.3.1 Liquid-liquid Extraction

The procedure for liquid-liquid extraction was followed according to EPA Method 3510C [8]. This method describes a procedure for isolating organic compounds from aqueous samples. The extraction works by exchanging the analytes (pesticides) from the aqueous sample to an organic solvent (iso-octane). The liquid sample is then injected into the GC.

2.3.2 Headspace Extraction

The headspace extraction conditions were as follows: a sample of water was placed in a headspace vial, incubated for the appropriate time and temperature according to EPA Method 8260B [8]. A headspace sample was collected in a gas tight syringe and injected into the GC.

2.4 Instrumentation: Kits

Hach's self-contained Surface Waters Test Kit includes all necessary reagents and apparatus for performing seven critical water quality determinations, which is ideal for field testing. The kit includes a durable polypropylene carrying case designed to keep chemistries and apparatus neat and well-organized [9].

All colorimetric tests included with the kit are based on proven Hach procedures. Tests for ammonia, chlorine and phosphorus are performed with Hach's unique color disc comparators, which feature a continuous-gradient color wheel for fast, accurate results [9]. Also included in the kit is the battery powered Pocket Pal pH Tester and a Fahrenheit scale Pocket Thermometer for quick, on-the-spot pH and temperature determinations [9].

2.5 Instrumentation: GC/MS

The experimental conditions for the GC/MS are summarized in Table 2.

Table 2 – GC/MS Conditions

GC Column	DB-WAX, 60 meters
GC	Varian 3600, spitless injection 32°C for 5 minutes, ramp to 225° Celcius at 5°C/Celcius/min
Carrier Gas	Helium, 1.0 mL/min
MS	Varian Saturn 2000, ion trap
Internal Standard	d-8 toluene

An unknown analyte was identified by comparison of two parameters: (1) the sample mass spectrum with a standard reference spectrum that is part of the NIST spectral library and (2) the retention time of the unknown component with retention times of standard target compounds.

The concentration of each identified component was measured by relating the mass spectral response of the quantitation ion produced by the target compound to the response of the quantitation ion produced by an internal standard. An internal standard (a pure analyte added to a sample, extract, or standard solution in known amounts and used to measure the relative responses of other method analytes and surrogates that are components of the same solution) was used to quantify the analyte signal.

Response factors for analyses were calculated as follows [10]:

$$RF = A_x Q_{is} / A_{is} Q_x$$

Where: A_x and A_{is} are integrated areas of the quantitation ions for the analyte and internal standard, respectively Q_x and Q_{is} are quantities in nanograms or concentration units injected for analyte and internal standard, respectively.

3. Results and Discussion

3.1 pH and Temperature

The pH and water temperature (Figure 1 and 2, respectively) were measured over the past two years for locations 4 – 9, and 13. The pH remained around 7.0 (± 0.1) for all locations tested, but the water temperature fluctuated depending on the climate and season. Several measurements were taken over various temperatures throughout the year to determine if the water temperature would cause a change in the other nutrient levels or the pesticide retention in water.

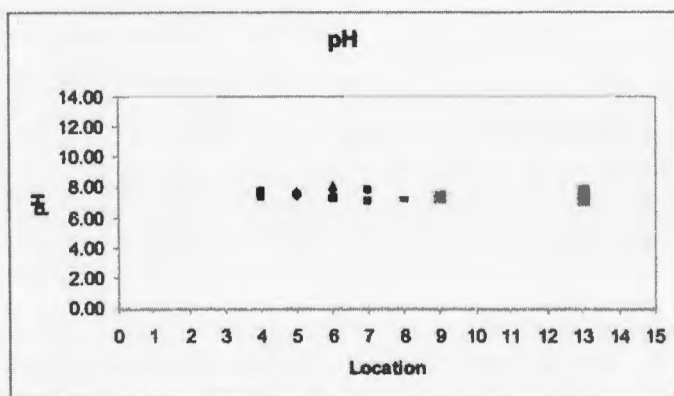


Figure 1 – Data for pH measurements taken over several months.

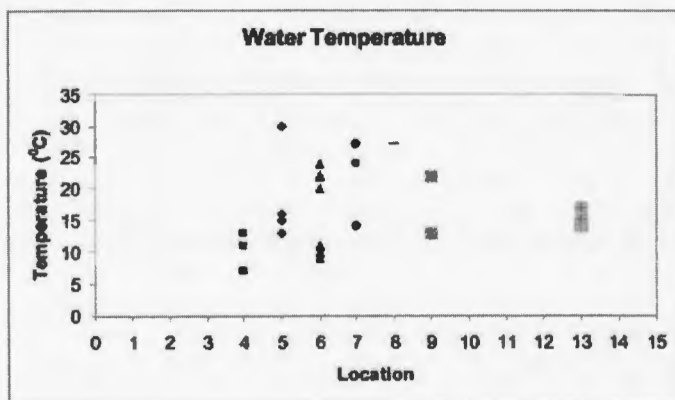


Figure 2 – Data for temperature measurements taken over several months.

3.2 Nutrients

The nutrients that were analyzed using the Hach water testing kits included ammonium nitrogen, nitrate, free chlorine, total chlorine, and phosphate. Figure 3 shows the data for the ammonium nitrogen tests, and over the testing period only two water samples had results greater than $0.000(\pm 0.005)$ mg/L. Locations 5 and 7 showed ammonium nitrogen levels of $0.380 (\pm 0.015)$ mg/L and $0.120 (\pm 0.005)$ mg/L.

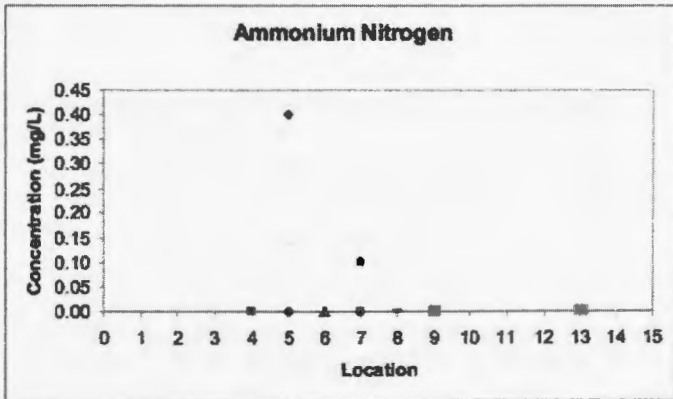


Figure 3 – Ammonium nitrogen data for locations 4-9, and 13.

Similarly to the ammonium nitrogen, the nitrate analysis (Figure 4) only had one sample that had a measurement greater than $0.00 (\pm 0.02)$ mg/L, and that was location 6 with a nitrate level of $0.40 (\pm 0.02)$ mg/L

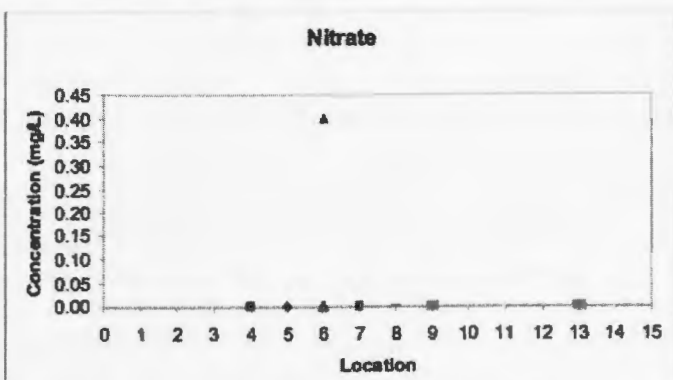


Figure 4 – Nitrate data for locations 4-9, and 13.

The free and total chlorine results fluctuated from 0.00 (± 0.01) mg/L to 0.30 (± 0.01) mg/L, as seen in figures 5 and 6, respectively.

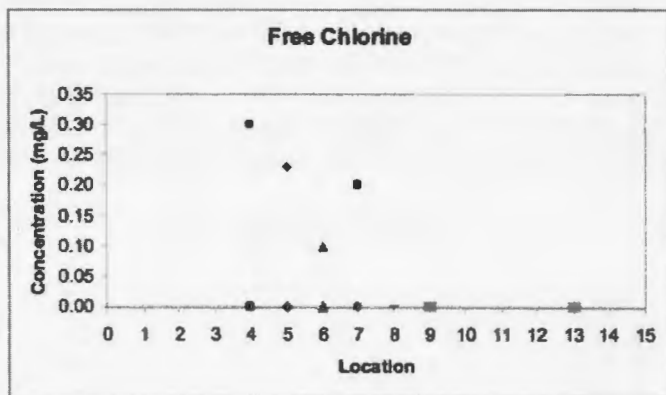


Figure 5 – Free Chlorine data for locations 4-9, and 13.

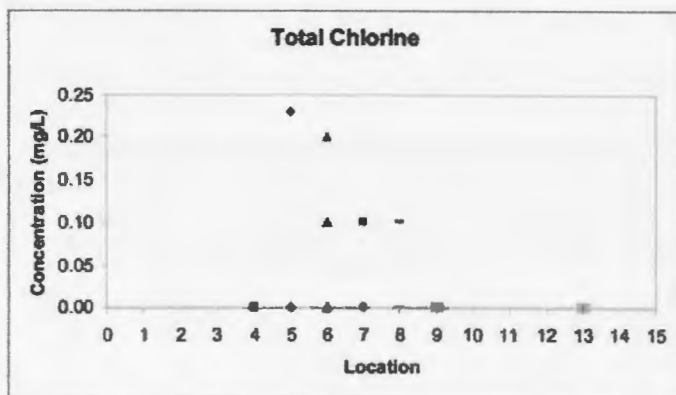


Figure 6 – Total Chlorine data for locations 4-9, and 13.

Location 8 had an unusually high phosphate level at 0.80 (± 0.03) mg/L on one occasion. This location was tested three times that particular day to confirm the measurement, and all 3 readings were the same. The only explanation that we can conclude is on that particular day it was raining, and the testing location was down stream from a home with a large landscaped yard with extremely green grass. The testing location was subject to surface runoff from the fertilizer for the lawn.

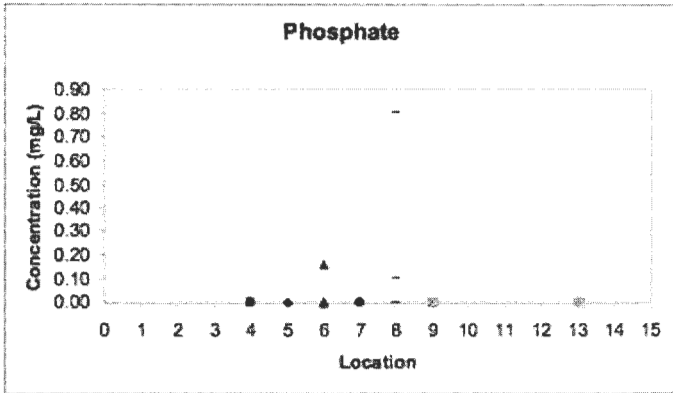


Figure 7 – Phosphate data for locations 4-9, and 13.

3.3 Organic Pesticide Compounds

A sample from each location was extracted via both methods and analyzed by GC/MS. A representative chromatogram for a water sample from location 9, Lake Sinclair (Baldwin County) is presented below. The bulk water sample was divided into two aliquots or testing samples and each aliquot underwent liquid-liquid extraction and headspace extraction (Figure 8 and 9, respectively). The peak with a retention time around 13 minutes is the internal standard, d-8 toluene. In figure 9, the peak around 14 minutes, after the peak for the internal standard, corresponds to some residual water that remained in the extracted sample. No other significant peaks were noticed and no response factors were calculated for the water samples.

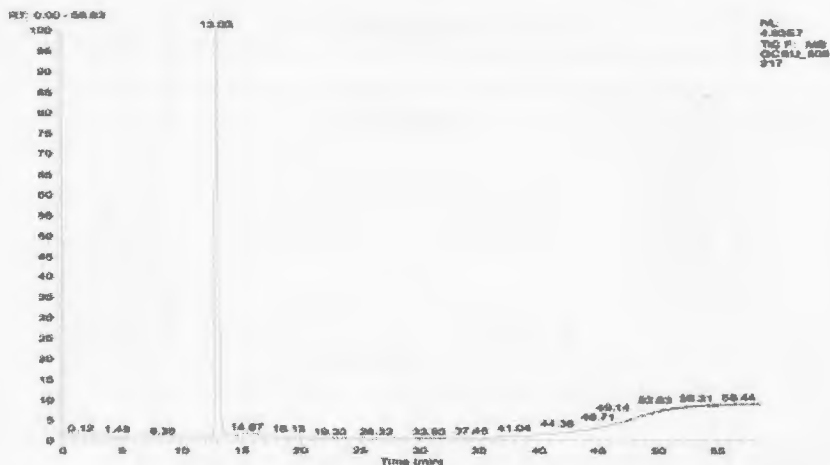


Figure 8 – Chromatogram for location 9 aliquot that underwent liquid-liquid extraction.

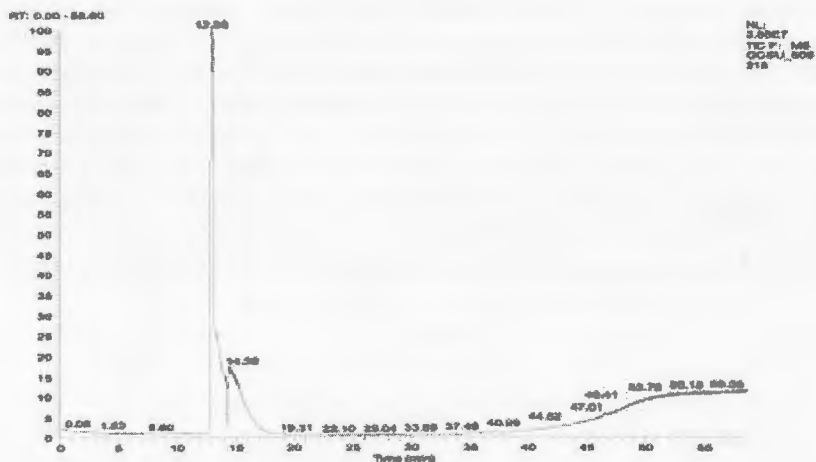


Figure 9 – Chromatogram for location 9 aliquot that underwent headspace extraction.

After conducting the 8 hour liquid-liquid extraction compared to the 9 minute headspace extraction, it was concluded that the headspace method is definitely more time efficient but did not remove all of the

residual water which can cause problems with the manifold of the mass spectrometer. Another method of extraction is currently being used called Solid Phase Micro-Extraction (SPME). The SPME apparatus coupled with the GC/MS will allow for the time efficiency of the headspace extraction but the effectiveness of the liquid-liquid extraction.

4. Conclusions

It has been shown that the nutrients, pH, and temperature can be successfully monitored using the on sight Hach surface water testing kits. With the coupling of SPME and GC/MS, the pesticide analysis along with other organic compounds will continue to be monitored. This research has important implications for the chemical monitoring of middle Georgia surface waters. Research is on-going to incorporate biological aspects to the monitoring process.

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