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Inter-Method Comparison of US EPA Analytical Methods 507 and 508.1 to Test for Atrazine in Kentucky Drinking Water

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INTER-METHOD COMPARISON OF US EPA ANALYTICAL METHODS 507 AND 508.1 TO TEST FOR ATRAZINE IN KENTUCKY DRINKING WATER

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Jonathan Suhl

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INTER-METHOD COMPARISON OF EPA ANALYTICAL METHODS 507 AND 508.1 TO TEST FOR ATRAZINE IN KENTUCKY DRINKING WATER

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Jonathan Suhl August 2012 79 pages

Directed by: Dr. Vijay Golla, Dr. Boubakari Ibrahimou, Dr. Emmanuel Iyiegbuniwe, and Dr. Ritchie Taylor

Department of Public Health Western Kentucky University

This study examined United States Environmental Protection Agency (US EPA) methods 507 and 508.1; analytical methods used to test drinking water for Atrazine. Additionally, this study examines the seasonal variation of Atrazine in Kentucky drinking water. Atrazine is a triazine herbicide used to control and inhibit the growth of broad leaf and grassy weeds. Atrazine's ability to be transported to community drinking water supplies makes it a significant public health issue, as it has been linked to myriad negative health endpoints ranging from endocrine disruption to various forms of cancer, including stomach and ovarian cancer. To date, there is little research examining the current methods used to test for Atrazine and its seasonal variation in drinking water. Drinking water samples previously collected by the Kentucky Division of Water and the Kentucky Geological Survey from 117 of 120 counties throughout the state from January 2000 to December 2008 were used for this study. To examine inter-method comparison between methods 507 and 508.1, samples were subjected to the Mann-Whitney U test. Median values of methods 507 and 508.1 were found to be similar (p=0.7421). To examine seasonal variation, data from each year from 2000 to 2008, as well as the entire 2000-2008 period, were analyzed using the Kruskal-Wallis One Way Analysis of Variance. Years 2000, 2002, 2003, 2004, 2007, and 2008 as well as the full 2000-2008 span were found to have significantly different Atrazine concentrations from season to season. Years 2001, 2005, and 2006 were not found to have significantly different concentrations from season to season. The 2000-2008 span was then subjected to the Seasonal Kendal Test for Trend, which determined a significant ($p=0.000092$) decreasing linear trend of -7.6×10^{-6} mg/L/year of Atrazine in Kentucky. Similar decreasing linear trends were seen throughout the five regions in the state during this time period as well. This study further expands on knowledge of the occurrence and persistence of Atrazine in the environment. Comparative analysis of US EPA analytical methods and the seasonal variation of Atrazine in drinking water provide a background for future research.

Chapter 1

Introduction

There are an estimated seven billion people in the world today, of which, nearly 1 billion do not have sufficient food and over 1 billion lack access to safe drinking water (Food and Agricultural Organization, 2010; World Health Organization, 2010). With the world's population expected to grow to over 10 billion people by the year 2100, the demand for food and potable water is greater than ever (World Health Organization, 2010). The ever increasing world population in conjunction with the ever increasing demand for increased crop yield to feed the population has led to the increased use of pesticides throughout the world; since 1945 worldwide pesticide production has doubled every 10 years (Dich et al, 1997). Additionally, demand for ethanol has increased in recent years, contributing to the increased use of pesticides. In the United States alone, ethanol production increased by more than 1 billion gallons between 2005 and 2006, and its demand is expected to increase in coming years (Westcott, 2007) This increased pesticide use has led to an increased potential for environmental contamination, especially fresh water contamination. Contamination of fresh water supplies is of considerable concern due to the limited nature of fresh water throughout the world; roughly 3% of water on earth is fresh water (United States Geological Survey, 2012). The contamination of the physical environment leads to another problem, the potential for the negative impaction of human health. Chronic human health effects of many commonly used pesticides are largely unknown and under researched, though research is beginning to link many pesticides to myriad illnesses and diseases ranging from reproductive effects to cancer. The potential health effects of pesticides are of growing concern worldwide, and especially in the United States.

Atrazine is one of the most commonly used pesticides in the United States today and is a restricted use, triazine herbicide used to control and inhibit the growth of broad leaf and grassy weeds in the production of corn, sorghum, sugar cane and numerous other crops. First developed in the late 1950s, its use has increased steadily over the years, with 74 million pounds used in 1997 and nearly 80 million pounds used in 2007 (Kiely, Donaldson & Grube, 2004; Grube, Donaldson, Kiely & Wu, 2011). Widespread use has led to near environmental ubiquity in the United States. The primary concerns regarding Atrazine include its mobility and potential to contaminate ground and surface fresh water sources, both of which are used as drinking water supplies (Porter, Jaeger, & Carlson, 1999). Today, it is one of the most frequently detected agricultural chemicals found in drinking water samples (Benotti et al, 2009). With ingestion being one of the major routes of exposure for Atrazine and its largely unknown potential to cause illness and disease in humans, the contamination of drinking water supplies with Atrazine poses a significant risk to public health.

Atrazine poses a potential threat to human health, therefore it is regulated by the United States Environmental Protection Agency's (US EPA) Safe Drinking Water Act (SDWA). The SDWA established a Maximum Contaminant Level (MCL) of 3 parts per billion (ppb), or 0.003 mg/L, for Atrazine (Agency for Toxic Substances and Disease Registry, 2003). Furthermore, the SDWA requires that every public water system must test for Atrazine and maintain an average level at or below the 3 ppb MCL. Currently, under 40 CFR 141.24, the US EPA has approved six separate analytical methods for the testing and detection of Atrazine in public water supplies, these methods include five US EPA methods, 505, 507, 508.1, 525.2, and 551.1, and one private company method, Syngenta AG-625. Five of the methods employ gas chromatography, while the Syngenta AG-625 is an immunoassay (United States Environmental Protection Agency, 2011). Three of the US EPA methods, 507, 508.1, and 525.2, as well as US EPA method 8270C, are commonly used for drinking water analysis in Kentucky public water systems. Method 8270C is not listed in 40 CFR 141.24 or its appendices, but is commonly used in Resource Conservation and Recovery Act compliance analysis (Massachusetts Department of Environmental Protection, n.d.). Though the US EPA has approved six analytical methods, there has been little to no published research concerning the similarity of the results obtained using each method.

From an environmental health standpoint, Atrazine poses a substantial risk. To date, Atrazine has been linked to numerous environmental problems. Of note is its link with endocrine disruption in amphibians; its estrogenic effects have resulted in hermaphroditism and chemical castration, amongst other problems, in frogs at levels well below the US EPA mandated MCL (Hayes et al, 2010). Furthermore, it has been deemed an embryotoxin in rodents (Villanueva et al, 2005). The effects of Atrazine on humans are not well documented and are not as conclusive as in animal studies. However, studies have linked Atrazine's numerous health effects, including, but not limited to, endocrine disruption, reproductive effects, cardiovascular difficulty and potential carcinogenicity. The environmental effects and the potential human health effects of Atrazine have led to great concern worldwide, resulting in a complete ban in the European Union and heavy use restrictions in the United States (Sass & Colangelo, 2006).

Research Objectives

The primary aim of this study is to compare two analytical methods currently used to test drinking water for Atrazine contamination. These two methods are US EPA methods 507 and 508.1, used by the Kentucky Department of Environmental Protection Division of Water and the Kentucky Geological Survey, in the analysis of Atrazine in drinking water samples. The data collected also allows for the research of seasonal variations of Atrazine in Kentucky drinking water from 2000 to 2008, in addition to the study of inter-method comparisons. This should ultimately lead to a better understanding of the persistence and availability of Atrazine in the environment, aid in future development of effective exposure assessment methodologies, and gain insight into the reliability of analytical methods used for Atrazine testing.

The objectives of this study are twofold:

1) To determine inter-method comparison between US EPA analytical methods 507 and 508.1 used to test Kentucky drinking water samples for Atrazine from 2000 to 2008.
2) To assess seasonal variations of Atrazine in Kentucky drinking water to study the persistence of Atrazine over time.

This leads to the primary research question: Does the use of US EPA analytical methods 507 and 508.1 to assess Atrazine in drinking water produce similar results?

Chapter 2

Background/Literature Review

Physical and Chemical Properties

The chemical name of Atrazine, as defined by the International Union of Pure and Applied Chemistry (IUPAC), is 1-Chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine (molecular formula $C_8H_{14}ClN_5$) and the molecular weight is 215.69 (Agency for Toxic Substances and Disease Registry, 2003). In its pure state, Atrazine is an odorless and colorless, organic, crystalline powder, with a melting point between 173 and 175 degrees Celsius, a vapor pressure of 2.89×10^{-7} mmHG and a density of 1.23 g/cm^3 (Agency for Toxic Substances and Disease Registry, 2003). Commercially, Atrazine is typically around 95% pure (World Health Organization, 1996), though it need only be 92% pure according to the Food and Agricultural Organization (Food and Agricultural Organization, 1975). Though temperature dependent, Atrazine is soluble in numerous organic solvents including: acetone, ethanol, toluene, methanol and ethyl acetate. Additionally, it is not very soluble in water, with a solubility of roughly 30 mg/L (Agency for Toxic Substances and Disease Registry, 2003).

Atrazine Production and Use

Atrazine is produced using numerous registered trade names, including: Aatrex, Aatram, Atratol, and Gesaprim (Agency for Toxic Substances and Disease Registry, 2003). Atrazine is most commonly used in the agricultural field as both a pre and post-emergence herbicide to control and inhibit the growth of a variety of both broadleaf and grassy weeds in crop production (Agency for Toxic Substances and Disease Registry, 2003). It is the second most commonly used herbicide in the United States, with 74 to 80 million pounds used in the United States in 2001 (Kiely, Donaldson & Grube, 2004) and similar amounts used in subsequent years (Grube, Donaldson, Kiely & Wu, 2011). It is used most heavily in the large corn production states in the Midwestern United States of Illinois, Iowa, Nebraska, and Indiana (Solomon et al, 1995).

Atrazine is classified by the US EPA as a toxicity class III pesticide, meaning it is considered to be only slightly toxic (Agency for Toxic Substances and Disease Registry, 2003). For the aforementioned reason, as well as its potential for environmental contamination, Atrazine has been designated a restricted use pesticide by the US EPA, implying that its purchase and use is limited to certified applicators or under the direct supervision of a certified applicator (United States Environmental Protection Agency, 2011).

In plants, Atrazine acts as an inhibitor of photosynthesis; more specifically, it is a photosystem II electron transport inhibitor (Stryer, 1995). In this process, Atrazine reduces the flow of electrons found in water to NADPH2+, an enzyme critical for the completion of the photosynthetic process. This then leads to an accumulation of electrons on the chlorophyll cells, resulting in excessive oxidation reactions, and ultimately plant death (Stryer, 1995).

Environmental Fate and Toxicity

The use of Atrazine as an agricultural herbicide results in its direct release into the environment, making it a potential soil, air and water contaminant.

In soil, Atrazine is expected to have moderate to high mobility, with a half-life of up to 385 days, depending on soil and degradation type (Hazardous Substances Data Bank, 2012). Its lengthy half-life is of concern, as it enables Atrazine to persist in soil for more than a year. The persistence and degradation of Atrazine in soil is due to multiple factors including soil type, pH, temperature and moisture content. Atrazine degrades in soil by microbial and chemical activities, hydrolysis and photolysis. The long half-life and mobility in soil is believed to enhance its potential to contaminate both ground and surface water sources (Agency for Toxic Substances and Disease Registry, 2003).

In water, Atrazine is expected to adsorb to suspended sediment, but is not expected to volatilize from the water's surface (Hazardous Substances Data Bank, 2012). Therefore, Atrazine breaks down in water by chemical degradation, hydrolysis and photolysis, and microbial degradation, though it has been found to be reasonably resistant to microbes. In basic or acidic water, Atrazine hydrolyzes quickly, but is thought to be stable in neutral pH water. The half-life of Atrazine in water is dependent on multiple factors including water temperature and pH Agency for Toxic Substances and Disease Registry, 2003), but has been determined to be 96 days in natural groundwater (Hazardous Substances Data Bank, 2012).

In air, Atrazine exists in vapor and particulate phases. In the vapor phase, Atrazine degrades through two methods, atmospheric hydroxyl radicals or photolysis. In the particulate phase, Atrazine is removed via wet and/or dry deposition (Agency for Toxic Substances and Disease Registry, 2003).

Atrazine is considered to have relatively low toxicity, and is classified by the US EPA as class 3, but due to its environmental fate, as well as its application methods, human exposure may occur through numerous routes, including ingestion, the primary route, dermal absorption and inhalation (Agency for Toxic Substances and Disease Registry, 2003).

In humans, Atrazine is readily absorbed in the gastrointestinal tract, with 66% of the ingested dose excreted in urine. Approximately 14% of the ingested dose of Atrazine is retained in tissue, typically persisting in erythrocytes, liver, spleen and kidney with a whole body elimination half-life of 31.3 hours (World Health Organization, 1996; California Environmental Protection Agency, 2008). Laboratory studies on rats have determined the oral median lethal dose (LD_{50}) to be 3090 mg/kg body weight (Zimdahl, 1993). Absorption of Atrazine through the skin is limited (World Health Organization, 1996). In humans, Atrazine is rapidly secreted through feces and urine (Hazardous Substances Data Bank, 2012).

Environmental and Health Effects

The effects of Atrazine on the environment, specifically animals, are well documented. Studies on rodents and rabbits have shown Atrazine to have embryotoxic effects, though no teratogenic or developmental effects have been observed (Villanueva et al, 2005; International Agency for Research on Cancer, 1999). Other effects seen in rodents include muscular weakness, reduced respiratory rate, and central nervous system lesions (International Agency for Research on Cancer, 1999). Myriad effects have also been observed in amphibians. Studies on amphibians have shown Atrazine to be an endocrine disrupting compound (EDC), leading to hermaphroditism, retardation of gonadal development and chemical castration (Hayes et al, 2010). These studies have shown Atrazine to have estrogenic effects, causing the induction of aromatase, the enzyme responsible for the conversion of androgen to estrogen, leading to the feminization of males (Hayes, 2004). The induction of aromatase has been demonstrated in numerous other animals in addition to amphibians. Furthermore, Atrazine has demonstrated carcinogenicity in animals. Atrazine has been linked to mammary tumors, adenocarcinomas, and carcinosarcomas in rats (International Agency for Research on Cancer, 1999).

While the effects of Atrazine on animals are well documented, the effects on humans are still not well understood. Acute exposure at levels substantially greater than the MCL may result in effects ranging from nausea and dizziness to coma, gastric failure and renal failure (Agency for Toxic Substances and Disease Registry, 2003). Atrazine has also been linked to numerous other health effects. A number of studies have linked ingestion of drinking water contaminated with Atrazine to small-for-gestational-age status and preterm delivery (Villanueva et al, 2005). A study by Munger et al (1997) also found that Atrazine increased the risk of intrauterine growth retardation.

The potential for carcinogenicity in humans is still unknown. However, it is classified as an IARC Class 3 carcinogen, meaning “the agent is not classifiable as to its carcinogenicity to humans” (International Agency for Research on Cancer, 1999). Though classified as only a Class 3 carcinogen, multiple studies have linked Atrazine to various forms of cancer. Bingham et al (2001) found an increased risk of ovarian tumors in Italian women exposed to Atrazine contaminated drinking water. Furthermore, Atrazine was also found to increase the risk of stomach cancer (Van Leeuwen, 1999). Significant research is currently being conducted due to the uncertainty surrounding Atrazine's carcinogenicity, in spite of its class 3 rating.

Regulations and Guidelines

Atrazine is covered under the Safe Drinking Water Act (SDWA), which was enacted by the US EPA in 1974 to ensure safe drinking water in public water systems. The SDWA requires the US EPA, under 40 CFR 141.24, to develop National Primary Drinking Water Regulations (NPDWR) for contaminants that pose a risk to human health. NPDWRs include both Maximum Contaminant Levels (MCLs), which are enforceable standards, as well as Maximum Contaminant Level Goals (MCLGs), which are non-enforceable guidelines. The MCLG for Atrazine is 3 ppb, with the MCL set at the same level. NPDWRs also determined the appropriate analytical methods for the detection and quantification of each of the regulated contaminants (United States Environmental Protection Agency, 2012). Additionally, acceptable treatment technologies were also developed. The most commonly used methods to treat for Atrazine in public drinking water systems include adsorption methods (granular activated charcoal and powdered activated charcoal), and reverse osmosis (Committee to Advise on Reassessment and Transition, 2000). Granulated activated charcoal has been found to be the best available technology for the removal of Atrazine from drinking water (Golla, 2003).

Analytical methods

The US EPA has approved 6 different analytical methods to test for Atrazine in drinking water under 40 CFR 141.24. These methods include US EPA method 505, US EPA method 507, US EPA method 508.1, US EPA method 525.2, US EPA method 551.1 and Syngenta Ag-625. Four of these methods (US EPA method 505, 507, 508.1, and 525.2) are commonly used in Kentucky. Additionally, US EPA method SW846-8270C is commonly used for the detection of Atrazine in Kentucky, though not formally approved by the US EPA.

US EPA method 505 ("Analysis of Organohalide Pesticides and Commercial Polychlorinated Biphenyl (PCB) Products in Water by Microextraction and Gas Chromatography") is a gas chromatographic analytical method for detection of 25 unique compounds in treated water. In this method sample analyte is extracted by adding hexane and vigorous shaking, and then allowed to separate. The extracted sample is then injected into a fused-silica capillary column gas chromatographic system. Analytes are then identified by comparison of their retention time to reference retention times of a gas chromatograph. In this method, Atrazine has a retention time of 11.2 minutes (Munch, 1995).

US EPA method 507 ("Determination of Nitrogen and Phosphorus-Containing Pesticides in Water by Gas Chromatography with a Nitrogen-Phosphorus Detector") is a gas chromatographic analytical method. It has the capability of detecting 46 unique compounds, and was first approved for use in 1995. In this method, the sample is extracted with methylene chloride. The methylene chloride is then isolated, dried and concentrated using a Kuderna-Danish (K-D) apparatus during solvent exchange process to methyl tert-butyl ether, MTBE, followed by separation and measurement of analytes of interest by Capillary Column Gas Chromatography with a nitrogen phosphorus detector. Analytes are then identified by comparison of their retention time to reference retention times of a gas chromatograph. Using this method, Atrazine has a retention time between 31.77 and 32.12 minutes (Munch, 1995).

Like 507, US EPA method 508.1 ("Determination of Chlorinated Pesticides, Herbicides and Organohalides by Liquid-Solid Extraction and Electron Capture Gas Chromatography") is a gas chromatographic, liquid-solid extraction analytical method with the capability to determine concentrations of 45 unique compounds; it was first approved for use in 1995. In this method, sample water is passed through a preconditioned disk containing a solid inorganic matrix coated with organic phase C18 allowing for extraction of analytes (liquid-solid extraction). Analytes are then eluted from the disk and concentrated via evaporation. Following evaporation, analytes are then separated and measured in a fused silica capillary column of a gas chromatograph/electron capture detector system. Finally, analytes are identified by comparison of their retention time to reference retention times of a gas chromatograph. In this method, Atrazine has a retention time of 18.23 minutes (Munch, 1995).

US EPA method 525.5 (" Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry") is another gas chromatographic, liquid-solid extraction analytical method with the capability to determine concentrations of at least 118 unique compounds; it was first approved for use in 1995. In this method, sample water is passed through a preconditioned disk containing a solid inorganic matrix coated with organic phase C_{18} allowing for extraction of analytes (liquid-solid extraction). Analytes are then eluted from the disk and concentrated via evaporation. Following evaporation, analytes are separated and measured in a fused silica capillary column of a gas chromatography/ mass spectrometry system. Analytes are then identified by comparison of their retention time to reference retention times of a gas chromatograph, as well as a comparison of the mass spectrum to a reference spectrum. In this method, Atrazine has a retention time between 9.38 minutes and 10.49 minutes (Munch, 1995).

US EPA method SW846-8270C ("Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)") is an analytical method which has been approved for use in sampling and analysis in compliance with the Resource Conservation and Recovery Act (RCRA). Like the aforementioned methods, it is a gas chromatographic method, which is used to determine concentrations of numerous semivolatile organic compounds in solid waste, soil, air or water. Pursuant to the method, sample first undergoes extraction by either a liquid-liquid extraction or solid-phase extraction process. The extraction is then concentrated and dried using a Kuderna-Danish (K-D) apparatus (United States Environmental Protection Agency, 2007). The dried, concentrated extraction is then injected into a Gas Chromatograph mass spectrometry system, with a narrow-bore fused-silica capillary column. Analytes are identified through comparison of the mass spectra with the electron impact spectra of a known standard; quantitation is achieved through the comparison of response of the ion of interest to an internal standard using a five point calibration curve (United States Environmental Protection Agency, 1996).

There are numerous similarities between each of the aforementioned methods. The key similarity between each of the methods is that they are each a gas chromatographic method, utilizing a narrow bore fused silica capillary column. It should be noted that gas chromatographic methods are the preferred methods in Atrazine detection in drinking water. Methods 508.1 and 525.2 both share the same liquid-solid extraction, isolation and concentration process, including the same materials and reagents used. Additionally, both methods 525.2 and 8270C utilize the same gas chromatography system/mass spectrometry system. The calculation for concentration is the same for methods 507, 508.1 and 525.2.

There are also numerous differences between each of the methods. Each method yields a unique retention time for Atrazine due to the differences in detectors and columns used in the various systems. Furthermore, method 507 utilizes a unique extraction, isolation and concentration method as well as a unique detector in the gas chromatography system, a nitrogen-phosphorus detector. Additionally, method 508.1 utilizes a unique detector in the gas chromatography system, an electron capture system.

Chapter 3

Methodology

Drinking water Atrazine concentrations were monitored in 117 of the 120 counties in Kentucky from 1991 to 2008. Multiple US EPA analytical methods were used in the analysis of drinking water samples for Atrazine during this time period. Statistical and environmental modeling was used to study the drinking water Atrazine concentrations in order to observe season distribution and inter-method variability of Atrazine in Kentucky water. The primary emphasis of this design is the assessment of the comparability of results obtained using US EPA analytical methods 507 and 508.1 to test drinking water for Atrazine.

The research hypotheses of this study are as follows:

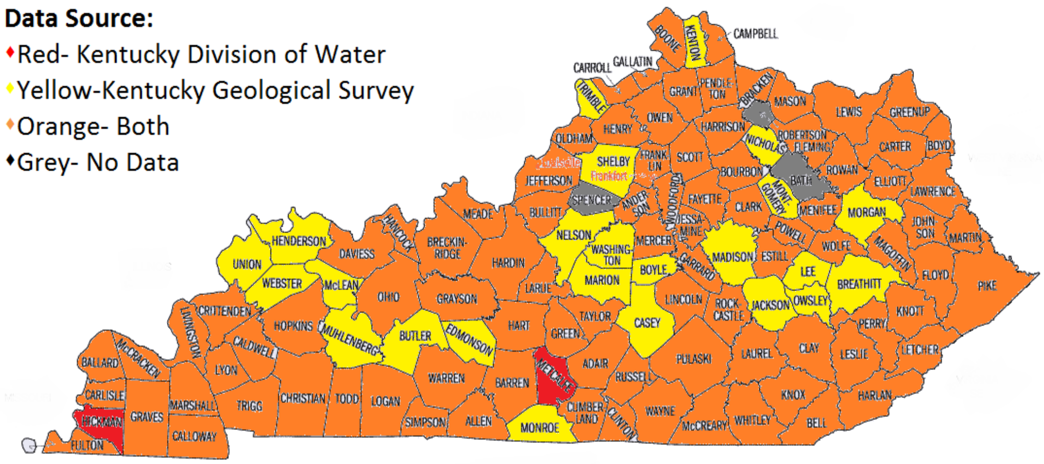
Null Hypothesis: There is no difference between US EPA analytical methods 507 and 508.1 used for the determination of Atrazine concentrations in Kentucky drinking water between the years 2000 and 2008.

Alternative Hypothesis: The use of US EPA analytical methods 507 and 508.1 used for the determination of Atrazine concentrations in Kentucky drinking water between the years 2000 and 2008.

Sample Collection and Analysis-

Secondary data sets were obtained from two sources, the Kentucky Department for Environmental Protection's Division of Water and the Kentucky Geological Survey, a research group within the University of Kentucky-Lexington. Samples were collected between 1991 and 2008 using multiple methods, including approved US EPA analytical methods 505, 507,508.1, 525.2, as well as method SW846-8270C. Additionally, some samples were analyzed using the ELISA (enzyme-linked immunosorbent assay) method, a biochemistry assay us to detect substances in liquid samples (Van Emon & Chuang, 2006). Samples were taken from 117 of the total 120 counties in the state of Kentucky (Figure 1).

Figure 1. Counties in Kentucky Sampled for the Occurrence of Atrazine in Drinking Water

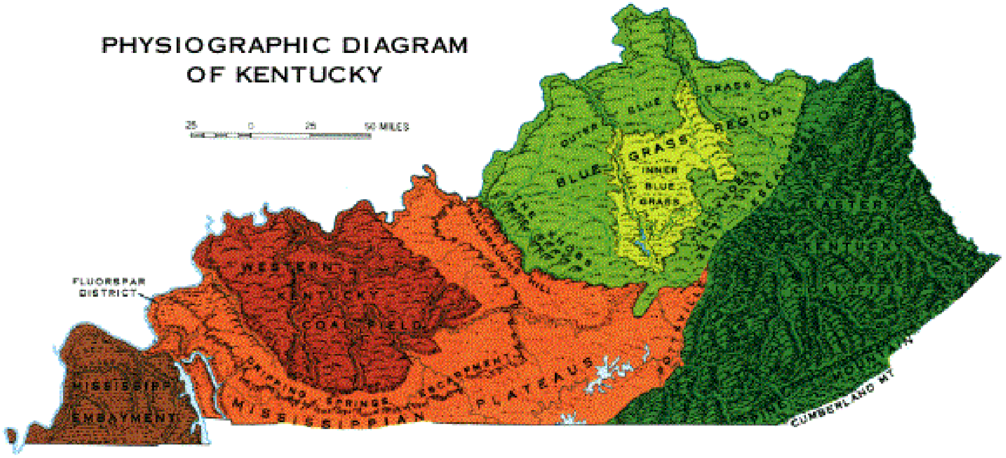


United States Census Bureau, http://quickfacts.census.gov/qfd/img/counties/stout21.gif

The two data sets had a common starting date of January, 2000. Common data collected for each sample included: analyte name, water supply identification number, sample date, county, limit of detection (LOD), Atrazine result (in µg/L or mg/L), and analytical method used. All results in µg/L were converted to mg/L. A total of 11,218 samples were collected between 1991 and 2008 by the two sources. For the inter-method comparison of methods 507 and 508.1, data sets were merged using the variables: analyte name, sample date starting in year 2000, county, result (in mg/L), method ID (505, 507, 508.1, 525.2, or 8270C). Only data points that contained a response for each of the above listed variables were included in the analysis for inter-method comparison for analytical methods 507 and 508.1. This resulted in 66 sample pairs for statistical analysis. Data were first tested for normality. This analysis was completed using SAS v 9.2 statistical software (SAS Institute, Inc., Cary, NC) with the univariate normality testing function, more specifically, the Kolmogorov-Smirnov goodness-of-fit test. This test was utilized to compare the distributions of methods 507 and 508.1 to a specified, normal, distribution. In this analysis, the null hypothesis that the sample distributions are normally distributed is tested. Upon completion of normality testing, the inter-method comparison data was subjected to the Mann-Whitney U test; this test is considered to be the non-parametric analog of the two-sample t-test. This test allows for the determination of statistical differences between the two methods, or more specifically the determination of whether the two independent samples originate from the same distribution, with a null hypothesis that the samples represent populations with similar median values (Sheskin, 2000). For this test, data pairs for the two methods are considered to be independent, as the resultant concentration of one method does not affect the result of the other.

For the assessment of the seasonal variation component of this study, data points were merged using the same criteria as the inter-method comparison, with the exception that data points with unlisted and non-505, 507,508.1, 525.2 and 8270C methods were included, and only data points that did not include sample date, county, or result were removed. Of the 11,218 samples collected, 4,129 samples were retained for statistical analysis. Seasonal data for each year and the entire 2000-2008 span were first tested for normality using SAS v. 9.2 statistical software with the univariate normality testing function and the Kolmogorov-Smirnov (KS) goodness-of-fit test. As stated in a previous section, this test was utilized to compare the distribution of values in each season to a specified, normal distribution. In this analysis, the null hypothesis that the sample distributions come from a normal distribution is tested. This testing would also aid in the determination of subsequent analytical methods. Data was then statistically analyzed using the Kruskal-Wallis One Way Analysis of Variance test using SAS v 9.2 statistical software (SAS Institute, Inc., Cary, NC). This test allowed for studying any statistically significant differences between the median concentrations of Atrazine in each of the four seasons; the null hypothesis of these tests is that the samples represent populations with similar median values (Sheskin, 2000). This was followed by the Seasonal Kendall Test for Trend using S-Plus v. 6.2 (Insightful, Corp, Seattle, WA), a test which would determine a positive or negative linear trend in the data. The Seasonal Kendall Test for Trend would be applied each of the five regions of Kentucky: Mississipian Plateaus, Bluegrass, Jackson Purchase, Eastern Coal Field, and Western Coal Field. A graphical representation of these regions is illustrated in Figure 2. The use of these methods allowed for the determination of differences in concentration between the different seasons, as well as the determination of a positive or negative linear trend of Atrazine over time throughout the state.

Figure 2. Graphical Representation of Kentucky Regions



Kentucky Atlas and Gazetteer, http://www.uky.edu/KentuckyAtlas/kentucky-physiographic.gif

In accordance with US EPA guidelines, Atrazine methodology calls for 4 quarterly samples to be taken for Atrazine in drinking water (United States Environmental Protection Agency, 2012). The use of quarterly sampling is taken into account for the statistical analysis of seasonal variation; in this study, a quarter is defined as a season. For the seasonal variation component of this study, samples were divided quarterly according to seasonal dates. The first day of each season for the years 2000 to 2008 and is shown in Table 1.

Table 1. Quarterly Sampling Strategy by Seasonal Date

Season	2000	2001	20002	2003	2004	2005	2006	2007	2008
Spring	3/20	3/20	3/20	3/21	3/20	3/20	3/20	3/21	3/20
Summer	6/21	6/21	6/21	6/21	6/21	6/21	6/21	6/21	6/20
Fall	9/22	9/22	9/23	9/23	9/22	9/22	9/23	9/23	9/22
Winter	12/21	12/21	12/22	12/22	12/21	12/21	12/22	12/22	12/21

If multiple samples were collected in a county within a single season/sampling period, a mean value was determined. All county values were then averaged to produce a mean value for the entire state of Kentucky (these values are shown in Tables 8 through 12). Median values were also determined. These seasonal averages were then graphed and analyzed in order to test for differences between seasons.

Chapter 4

Results

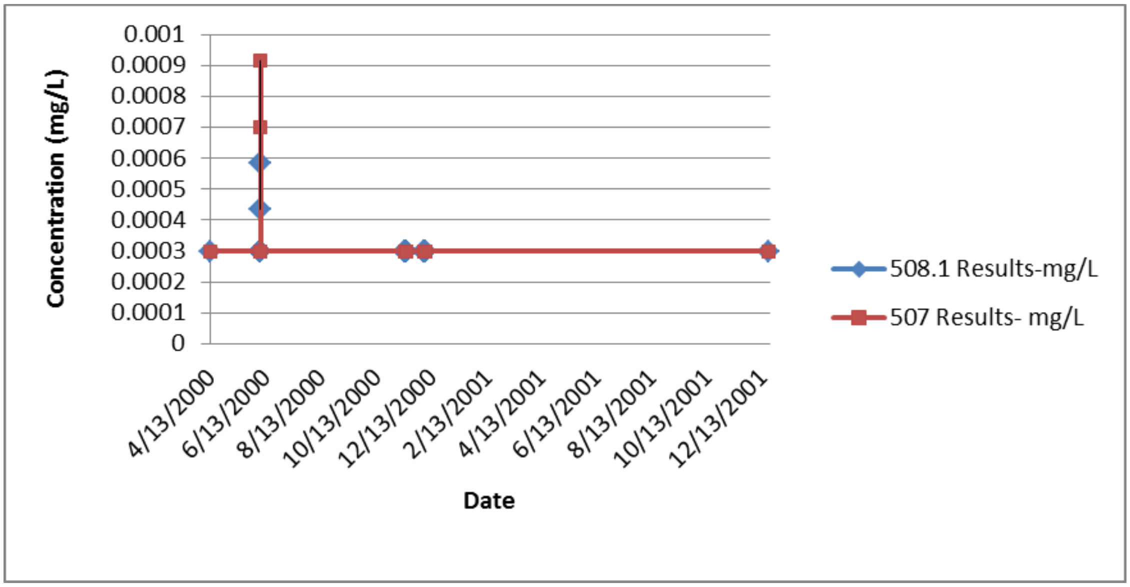
Inter-method Comparison

The frequency of use of each method from 2000 to 2008 is documented in Table 2. This table shows the overall use of each method during the selected sampling period in terms of the total number of samples in which they were used. Method 8270C was the most commonly used method during the study period with 54% of samples analyzed using this method, methods 525.2 and 507 made up 34% of the analyzed samples, and the remainder using methods 505, 508.1, and others. Data points taken within the same county on the same day using both US EPA methods 507 and 508.1 are shown in Table 7. These data points were used in the inter-method comparison analysis. A total of 66 sample pairs were used. A graphical analysis of these samples, in terms of sample result as a function of time, is also presented in Figure 3 for preliminary determination of the adequacy of statistical methods to compare the methods' medians and distribution.

Table 2. Analytical Method Usage by Total Number of Samples

Method	Sample Use (% of Samples)
505	1(0.0003)
507	527(17.68)
508.1	77(2.58)
525.2	497(16.68)
8270C	1611(54.06)
Other (Gas Chromatographic, Organochlorine Pesticide)	267(8.96)

Figure 3. US EPA Methods 507 and 508.1 Sample Results as a Function of Time



Statistical Analysis of Inter-method Comparison

Inter-method comparison data for the 2000 to 2008 sampling period was first tested for normality. This testing would allow for determination of the use of non-parametric or parametric statistical methods for method comparison. The results of this analysis can be seen graphically in Table 3. Data was then subjected to the Mann-Whitney U test. The results for this test are shown in Table 5.

Table 3. Descriptive Statistics of Inter-method Comparison Data

Method	N	Mean (mg/L)	Standard Deviation (mg/L)	Median (mg/L)	D	P-Value
507 & 508.1	66	0.00032	0.000097	0.0003	0.53	<0.01
507	33	0.00031	0.000126	0.0003	0.54	<0.01
508	33	0.00033	0.000054	0.0003	0.53	<0.01

As shown in Table 3, the 66 total samples (33 of 507 and 33 of 508.1) yield a mean of 0.00032 mg/L (±0.00097 mg/L). Method 507 had a mean concentration of 0.00033 mg/L (±0.00013 mg/L) and a median concentration of 0.0003 mg/L. Method 508.1 had a mean concentration of 0.00031 mg/L (±0.000054 mg/L) and a median concentration of 0.0003 mg/L. Kolmogorov-Smirnov normality testing resulted in a D-statistic of 0.53 ($p<0.01$), 0.54 ($p<0.01$), and 0.53 ($p<0.01$), for both methods, 507 and 508.1, respectively, meaning that the data is non-normally distributed.

Table 4. Wilcoxon Scores (Rank Sums) for Average Classified by US EPA Method

Method	N	Sum of Scores	Expected Under H_0	Std Dev Under H_0	Mean Score
508.1	33	1103.50	1105.50	32.25	33.44
507	33	1107.50	1105.50	32.25	33.56

*Average scores were used for ties

Table 5. Results of Mann-Whitney U. Test for Inter-method Comparison

Methods	S-Value	P-Value
507 & 508.1	1103.5	0.7421

*1 degree of freedom used

Ranks sum means scores of 507 and 508.1 were found to be 33.56 and 33.44, respectively. Mann-Whitney U. test resulted in an S-statistic of 1103.5 (p=0.7421). This result suggests that the two methods tested yielded similar median Atrazine concentrations. Furthermore, the results indicate that there is no statistically significant difference seen between the Atrazine concentrations obtained by both US EPA analytical methods.

Seasonal Variation

The mean concentration of Atrazine by season from 2000 to 2008 for counties throughout Kentucky can be seen in Tables 10-14. The overall Kentucky Atrazine trend by mean and median for each year can be seen graphically in Figures 4 through 13.

Figure 4. 2000 Kentucky Atrazine Trend

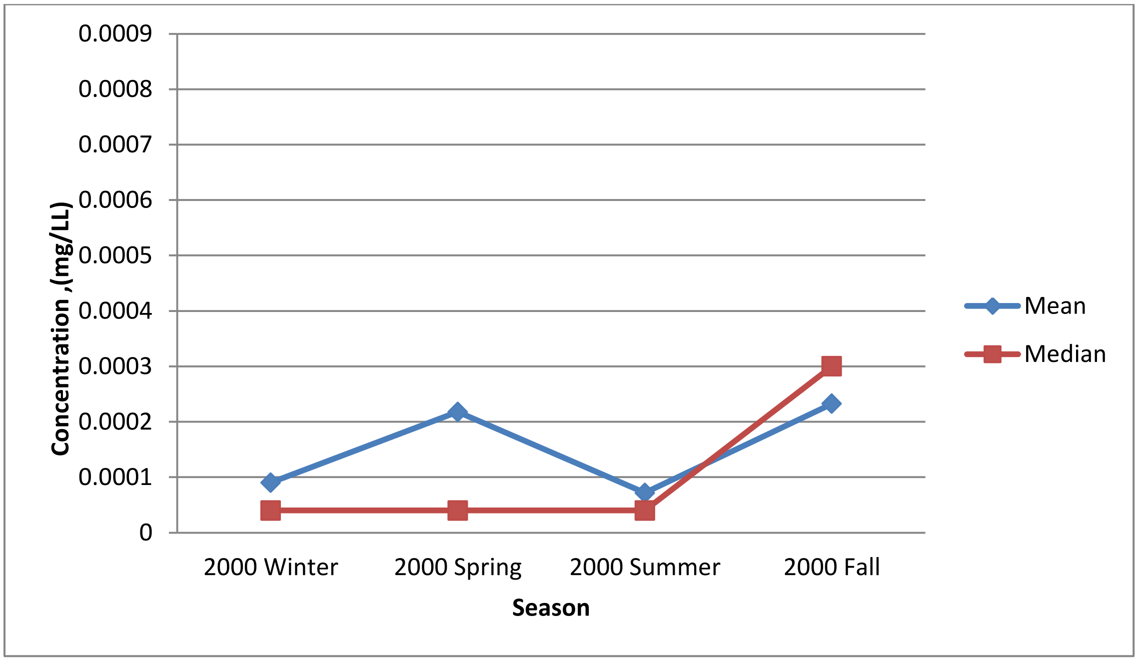


Figure 5. 2001 Kentucky Atrazine Trend

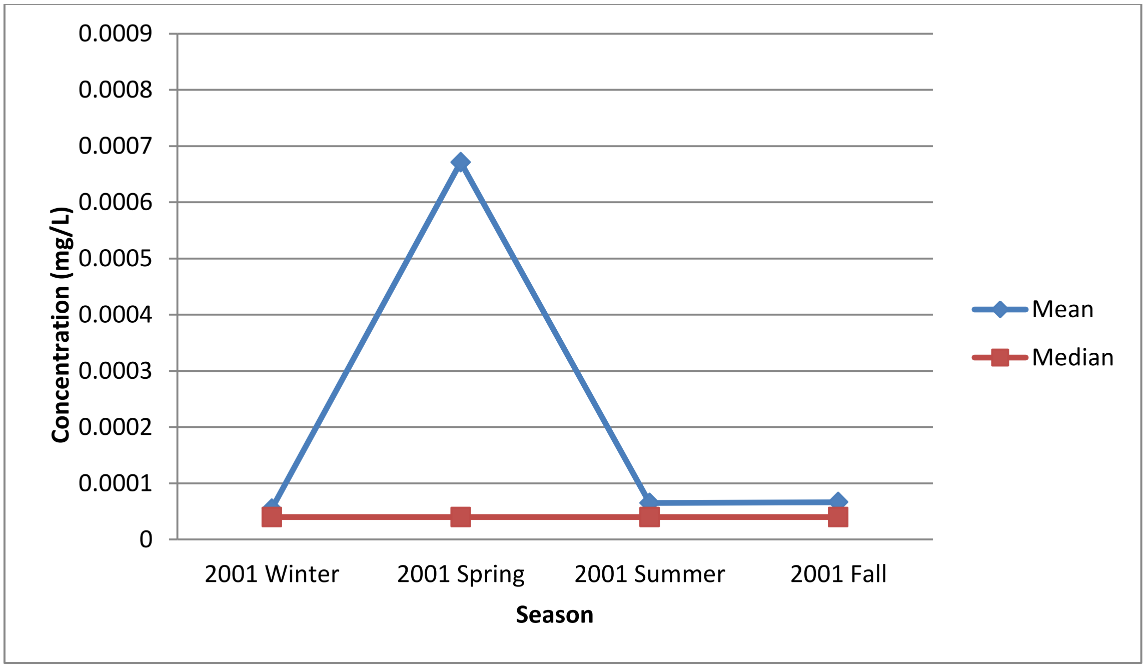


Figure 6. 2002 Kentucky Atrazine Trend

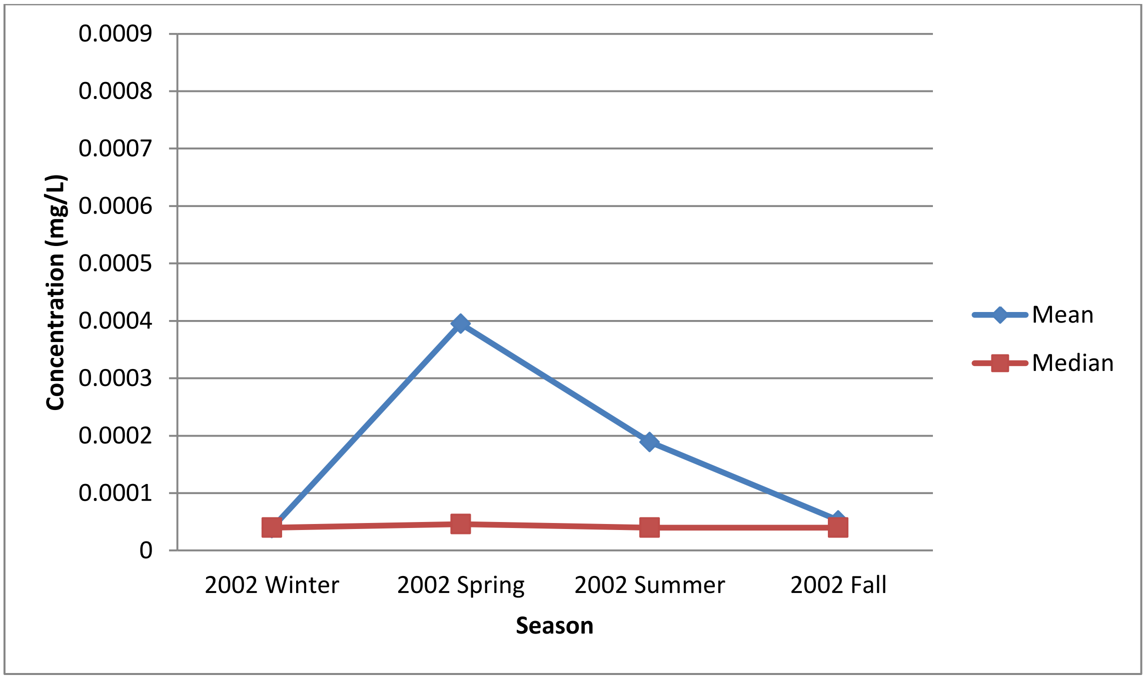


Figure 7. 2003 Kentucky Atrazine Trend

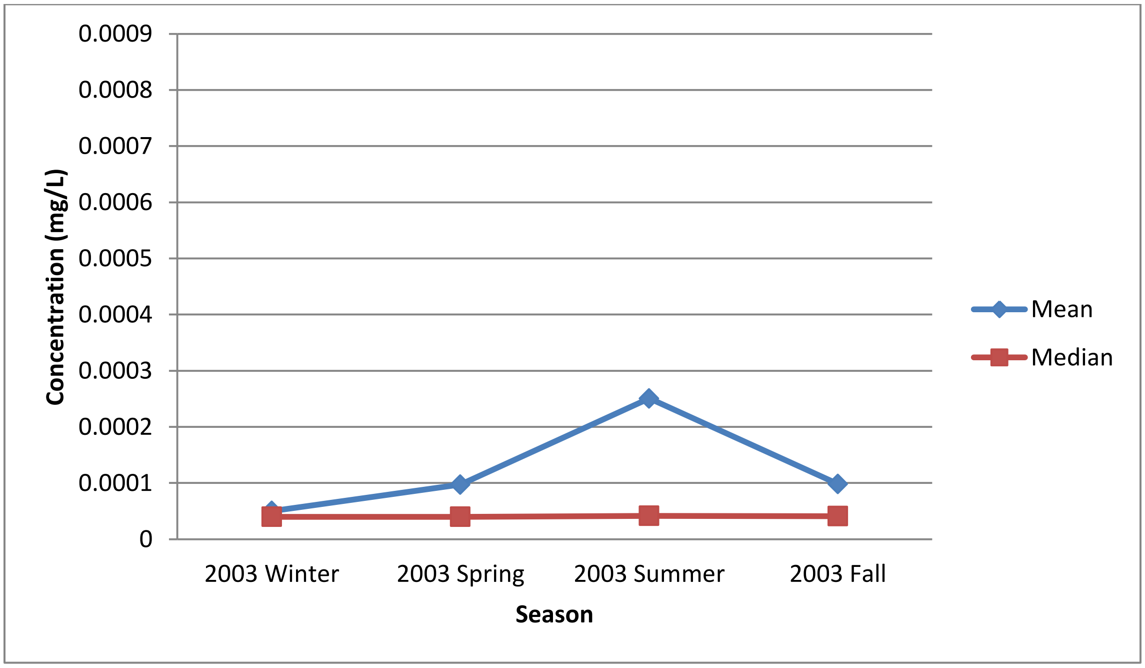


Figure 8. 2004 Kentucky Atrazine Trend

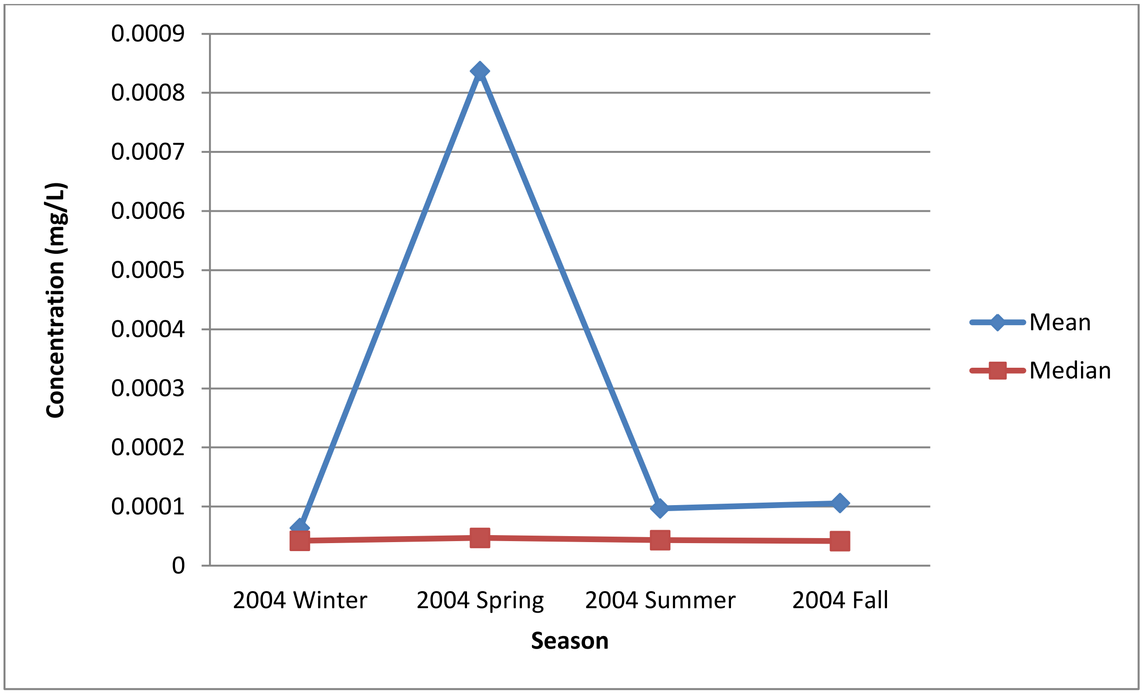


Figure 9. 2005 Kentucky Atrazine Trend

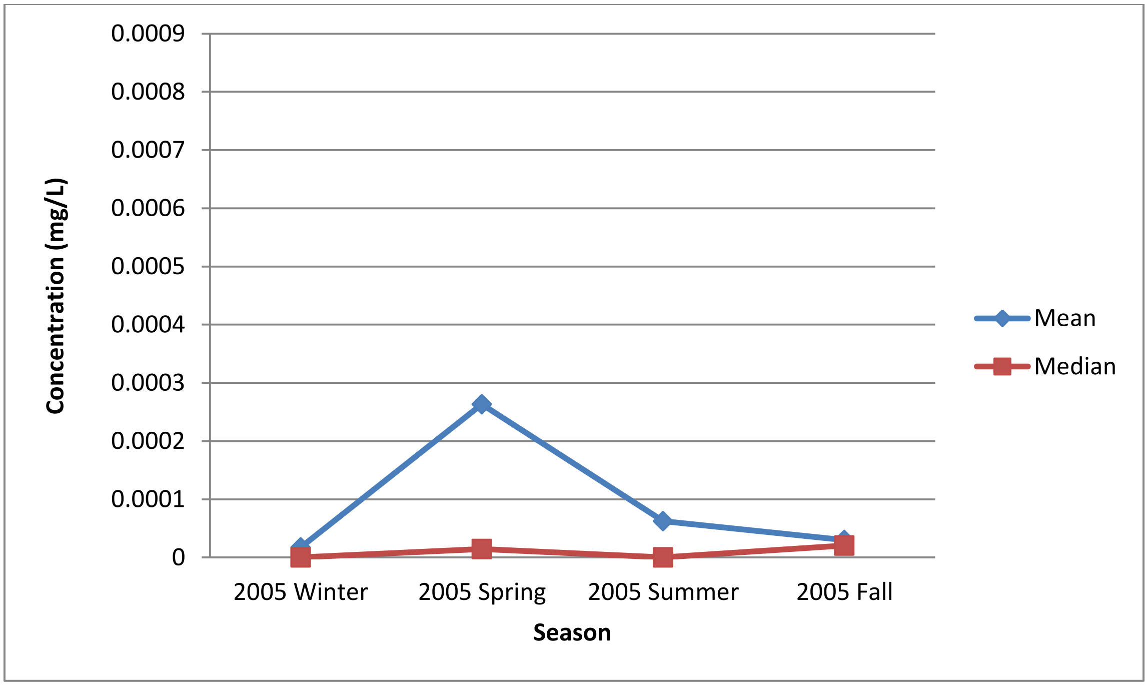


Figure 10. 2006 Kentucky Atrazine Trend

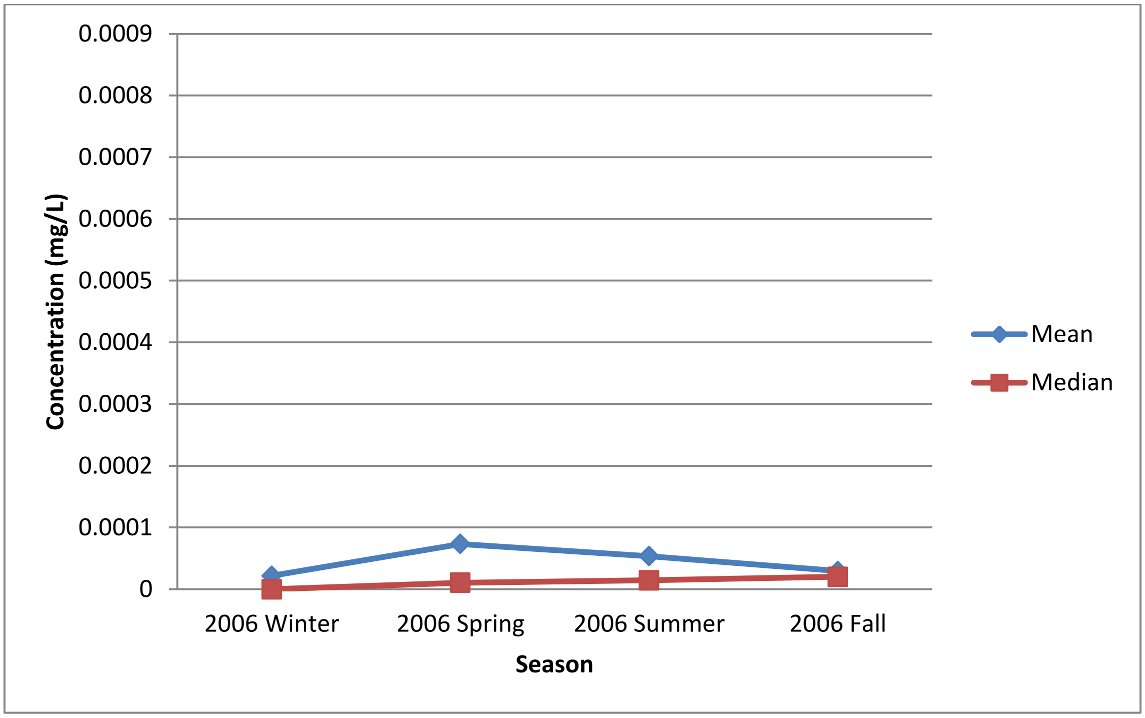


Figure 11. 2007 Kentucky Atrazine Trend

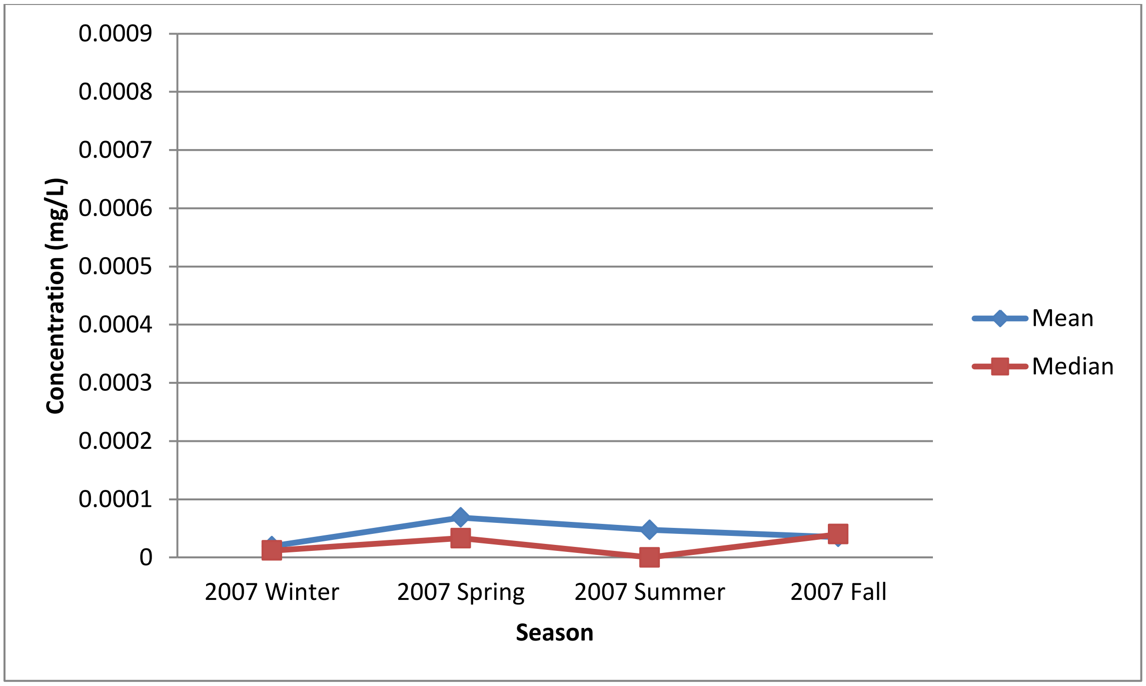


Figure 12. 2008 Kentucky Atrazine Trend

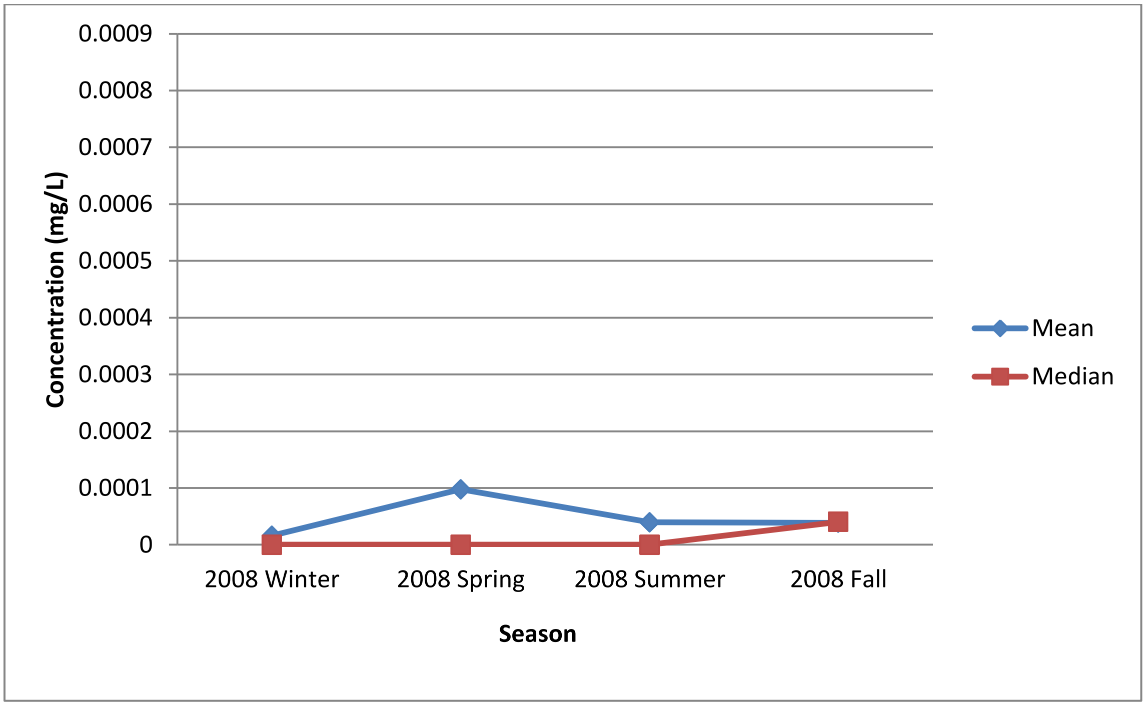
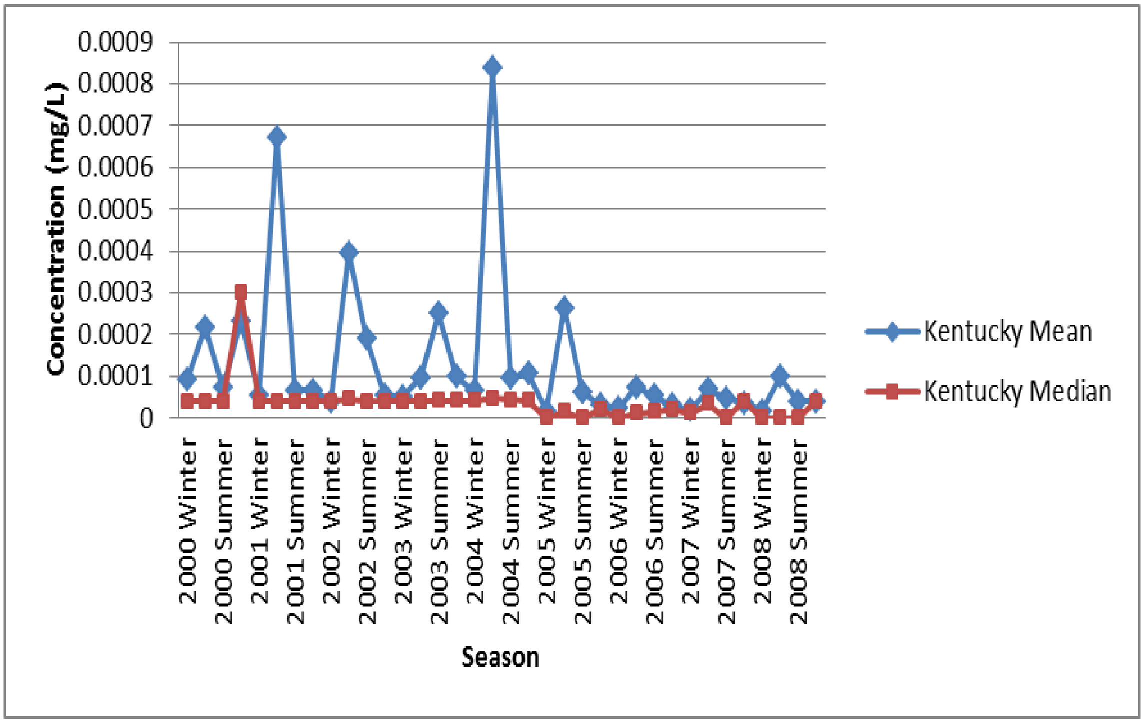


Figure 13. 2000-2008 Kentucky Atrazine Trend



Statistical Analysis of Seasonal Variation

Seasonal data was first subjected to normality testing. The results of these analyses can be seen in Table 6.

Table 6. Descriptive Statistics for Years 2000 to 2008 and 2000-2008 Span

Year	N	Mean (mg/L)	Standard Deviation (mg/L)	Median (mg/L)	D	P-Value
2000	180	0.000146	0.000274	0.00004	0.34	<0.01
2001	217	0.000219	0.00204	0.00004	0.46	<0.01
2002	200	0.000186	0.000427	0.00004	0.39	<0.01
2003	195	0.000129	0.000359	0.00004	0.40	<0.01
2004	143	0.000239	0.000905	0.00004	0.40	<0.01
2005	260	0.0000995	0.00051	0.0	0.42	<0.01
2006	289	0.000046	0.00014	0.00001	0.37	<0.01
2007	248	0.000043	0.000011	0.00002	0.35	<0.01
2008	257	0.000050	0.000143	0.0	0.36	<0.01
2000-2008	1989	0.000117	0.000772	0.00004	0.44	<0.01

Yearly mean values ranged from 0.000043 mg/L (±0.000011 mg/L) and 0.000995 mg/L (± 0.00051 mg/L). Median values ranged from 0.0 mg/L to 0.00004 mg/L. Upon completion of normality testing, each year, and the entire 2000 to 2008 span was subjected to the non-parametric test, the Kruskal-Wallis one-way analysis of variance by rank test using SAS v. 9.2 statistical software. The results of these tests are summarized in Table 7. Rank sums for the Kruskall-Wallis tests can be seen in Table 13.

Table 7. Results of Kruskal-Wallis One Way Analysis of Variance by Rank for Years 2000 to 2008 and the 2000-2008 Span.

Year	Chi- Square Value	P-Value
2000	24.36	<0.0001*
2001	2.52	0.472
2002	35.95	<0.0001*
2003	45.50	<0.0001*
2004	9.17	0.0272*
2005	4.871	0.182
2006	3.603	0.308
2007	8.7398	0.033*
2008	16.5134	0.0009*
2000-2008	35.9417	<0.0001*

*Each test used 3 degrees of freedom
* (*) denotes significant results

Seven of the 10 tested periods yielded p-values of less than 0.05, while years 2001, 2005, and 2006 had p-values greater than 0.05. H-statistics ranged from 2.5 to 35.94. These results suggest that in years 2000, 2002, 2003, 2004, 2007, 2008, and the entire 2000-2008 period, there were significant differences in median Atrazine concentrations between the seasons, and that Atrazine in drinking water varied in concentration throughout the year.

Finally, each of the five regions and the entire state were subjected to the Seasonal Kendall Test for Trend using the environmental module in S-Plus v. 6.2 statistical software for the entire 2000-2008 period. This test would determine whether or not there was a significant positive or negative linear trend in the data; with a null hypothesis that all values of tau are equal to zero, or there is no positive or linear trend, and an alternative hypothesis that all tau values are not equal to zero (Millard, 2002). The results of this test can be seen in Table 8.

Table 8. Seasonal Kendall Test for Trend for Mean Atrazine Concentration in Kentucky Drinking Water by Region from 2000-2008

Region	**Slope (mg/L/year)**	**Test Statistics (P-Value)**
Jackson Purchase	-7.16×10^{-6}	Z (Trend)= -2.90 (0.0038) Chi- Square (Het)= 2.97 (0.40)
Western Coal Field	-8.94×10^{-6}	Z (Trend)= -1.98 (0.047) Chi- Square (Het)= 1.85 (0.60)
Bluegrass	-5.31×10^{-6}	Z (Trend)= -3.70 (0.00021) Chi- Square (Het)= 0.26 (0.97)
Eastern Coal Field	-4.31×10^{-6}	Z (Trend)= -3.45 (0.00055) Chi- Square (Het)= 0.94 (0.94)
Mississippian Plateaus (Pennyrile)	-1.03×10^{-5}	Z (Trend)= -3.18 (0.0015) Chi- Square (Het)= 1.34 (0.72)
Entire State	-7.6×10^{-6}	Z (Trend)= -3.91 (0.000092) Chi- Square (Het)= 0.739 (0.864)

The Seasonal Kendall test yielded an estimated annual trend of $-7.6\text{x}10^{-6}$mg/L/year (p=.000092) for the entire state during the 2000-2008 period. Additionally, there were no differences in this trend seen between seasons (p=0.864). Similar decreasing linear trends were seen throughout the five regions in the state during this time period as well. The greatest decrease was seen in the Mississippian Plateaus region in Southern Kentucky, which was determined to have a $-1.03\text{x}10^{-5}$ mg/L/year (p=0.0015) trend. Therefore, during the entire sampling time period of 2000 to 2008, there was an overall, constant decrease in the amount of Atrazine in Kentucky drinking water.

Chapter 5

Discussion

Inter-method Comparison

Even though US EPA methods 507 and 508.1 are not the most widely used analytical methods in Kentucky (17.68% and 2.58% of samples, respectively), they allowed for inter-method comparison, with 33 data pairs, while the other methods did not yield more than 1 data pair for the sampling period. The concentration of each data point is similar for 31 of the 33 drinking water samples, with an average Atrazine concentration being 0.0003 mg/L. The pairs differed at two points, both occurring on 6/7/2000, where method 508.1 had concentrations of 0.000586 mg/L (0.586 ppb) and 0.000436 mg/L (0.436 ppb) and method 507 had concentrations 0.000916 mg/L (0.916 ppb) and 0.0007 mg/L (0.7 ppb). Overall, method 508.1 had a mean value of 0.000313 mg/L (0.313 ppb) and median 0.0003 mg/L (0.3 ppb), while method 507 had a mean value of 0.000331 mg/L (0.331 ppb) and median 0.0003 mg/L (0.3 ppb). The inter-method comparison data was first subjected to the Kolmogorov-Smirnov goodness-of-fit test; the null hypothesis of this test is the distribution of the data is normal, a p value of less than 0.05 is considered significant. According to the Kolmogorov-Smirnov goodness-of-fit, the data has a D statistic of 0.53 and a p value less than 0.05 ($p < 0.01$). The Mann-Whitney U test was then administered. The null hypothesis of this test is that US EPA analytical methods 507 and 508.1 represent populations with similar median values, and thus, represent similar results; a p value of less than 0.05 is considered significant. The result of this test yielded statistically non-significant results ($p=.7421$), meaning the null hypothesis should be accepted, indicating that the median values of the distributions for methods 507 and 508.1 are similar. Hence, the null hypothesis is accepted, stating there is no difference between US EPA analytical methods 507 and 508.1 for Atrazine concentrations in drinking water samples collected between 2000 and 2008

According to the data presented in Figure 2 and the descriptive statistics of the analysis conducted, all but two data points are the same, and the variation between these points is minute. The US EPA's approval of multiple methods for the analysis of Atrazine in drinking water would indicate that similar results are to be expected. The results that the use of US EPA methods 507 and 508.1 yield similar results are encouraging, considering that multiple methods are used throughout the state, and likely throughout the entire United States. The results also validate that the use of US EPA multiple methods, specifically 507 and 508.1, provide comparable results to test for public exposure to Atrazine through drinking water.

Seasonal Variation

Each of the seasonal data sets was first subjected to the Kolmogorov-Smirnov goodness-of-fit test; the null hypothesis of this test is that the distribution of the data is normal. A p-value of less than 0.05 is considered significant. According to the Kolmogorov-Smirnov goodness-of-fit test, none of the years from 2000 to 2008 were normally distributed, with each p-value less than 0.05 ($p<0.01$), thus the null hypothesis should be rejected in each case. The D-statistic for years 2000 to 2008 and the 2000 to 2008 span were: .34, .46, .39, .40, .40, .42, .37, .35, .36, and .44, respectively, indicating skewed distributions.

The non-normal distribution of each year led to the use of the non-parametric Kruskal-Wallis one-way analysis of variance by rank test to determine the differences between the median values of each season. Each year was divided by season, prior to the administration of the Kruskal-Wallis test. The null hypothesis for each of these tests is that the each of the four seasons represent populations with like median values, and thus, represent similar results; a p-value of less than 0.05 is considered to be significant. The results of this test yielded mixed results. Years 2000 ($p<.0001$), 2002 ($p<.001$), 2003 ($p<.0001$), 2004 ($p=.02$), 2007 ($p=.033$) and 2008 ($p=.0009$) yielded statistically significant results, meaning that the null hypothesis should be rejected for these years, and the Atrazine concentrations in drinking water samples between seasons for these years are not similar. Years 2001 ($p=.47$), 2005 ($p=.18$), and 2006 ($p=.31$) yielded non-statistically significant results, meaning that the null hypothesis should not be rejected for these years, and the Atrazine concentrations in drinking water samples for each season for these years are similar. The span from year 2000 to 2008 yield statistically significant results ($p<.0001$), meaning that the null hypothesis for this span of years should be rejected, thus the median values of the distributions from season to season are dissimilar.

The 2000 to 2008 series was then subjected to the Seasonal Kendall Test for Trend. As previously stated, the null hypothesis for this test is that all values of tau equal zero, and thus, there is no positive or negative linear trend; a p-value of less than 0.05 is considered to be significant. The test yielded an estimated annual trend of $-7.6\text{x}10^{-6}$ mg/L/year, meaning there is an annual decrease in the concentration of Atrazine in Kentucky drinking water with time. This trend was found to be statistically significant ($p=.000092$, $[-1.64\text{x}10^{-5}, -4.06\text{x}10^{-6}]$). The chi-square test for heterogeneity, which tested for differences in trend for different seasons, yielded non-statistically significant results (p=.74), meaning that there is no evidence of different amounts of trend within the different seasons.

These results indicate that, for the most part, individuals in the state of Kentucky are not being exposed to unhealthy levels of Atrazine. While no statewide mean or median value exceed the MCL of 0.003 mg/L (only five counties exceeded the MCL at some point during the study period), both the graphical and statistical analysis results suggest that there are differences in concentrations of Atrazine in Kentucky drinking water from season to season, though the magnitude of these differences is not explored in this paper. While these results may suggest issues with the methodology currently in place to test drinking water for Atrazine, it shows that an overwhelming portion of the state is not currently exposed to unhealthy levels of Atrazine through drinking water. Furthermore, it may suggest that the current control technologies in place are adequately removing Atrazine from drinking water to levels at, or below, the US EPA MCL, and potentially lowering the overall level from year to year. Though the levels of Atrazine are being maintained at levels deemed to be safe by the US EPA, there is still fluctuation throughout the year, rather than maintaining a stationary concentration. In the future, this fluctuation could lead to over-exposure of Atrazine, should there be increased usage in coming years.

Relationship of Results to Atrazine Sampling Methodology and Public Exposure

The aforementioned results suggest that while the current US EPA analytical methods for testing drinking water for Atrazine may be adequate, as methods 507 and

508.1 yield similar results and that Atrazine in drinking water is being maintained at levels below the US EPA MCL. It also suggests that the sampling strategy of using 4 quarterly samples may lead to unrepresentative concentrations for an entire year. Differences in concentrations for different seasons may lead to a truly unrepresentative average value for the entire year, as single samples per season could yield gross over or underestimations of Atrazine levels in drinking water. For instance, because there is no set sampling date, one could strategically sample on four dates throughout the year, such as the first day of the spring quarter when levels would be expected to be at their lowest, to yield resultant levels well below the US EPA MCL. Further, this potential for underestimation of Atrazine concentration due to variation could lead to public exposure to Atrazine at levels greater than the US EPA MCL and a truly unrepresentative average. Therefore, while the current methodology for testing and controlling Atrazine in drinking water may be both convenient and provide numerous options for drinking water facilities and potentially maintain drinking water levels to at or below the MCL, it may lead to resultant annual Atrazine concentrations that are unrepresentative of the true levels seen throughout the year. Increasing the number of necessary samples in peak usage seasons could lead to a better representation of public exposure to Atrazine in drinking water and lead to methods to better control and maintain lower, stationary levels.

Study Limitations

There were numerous limitations to this study. The first of these limitations was the secondary nature of the data set. The use of secondary data sets did not allow for the development of the sampling methodology and strategy to be designed by the researcher. The use of secondary data sets resulted in limited data for the inter-method comparison analysis, leading the comparison of only two of the US EPA analytical methods approved for SDWA analysis. Additionally, it allowed for only a limited number (66) samples to be analyzed, which could affect the statistical power of this portion of the study. The secondary data set also did not supply information for every county in the state of Kentucky, nor did it supply samples for each season of each year for any county within the state. Additionally, the methods used in SDWA analysis are very advanced analytical methods, and there is potential for operator error in the analysis of the collected drinking water samples. Finally, the statistical techniques used to assess seasonal variation are not the most ideal methods; statistical modeling techniques may provide more thorough results about the seasonality of Atrazine in drinking water.

Chapter 6

Conclusion

In this study, US EPA methods 507 and 508.1 analytical methods used to test drinking water for Atrazine and the seasonal variation of Atrazine in Kentucky drinking water were examined. Secondary data sets of drinking water samples collected by the Kentucky Division of Water and the Kentucky Geological Survey from 117 of 120 counties throughout Kentucky from January 2000 to December 2008 were studied. The Kruskal-Wallis One Way Analysis of Variance was used to examine the similarity of results obtained by US EPA method 507 and 508.1. Median values of methods 507 and 508.1 were found to be similar (p=0.9505). The Kruskal-Wallis One Way Analysis of Variance test was again used to examine seasonal variation of Atrazine for each year from 2000 to 2008, as well as the entire 2000-2008 period,. Years 2000, 2002, 2003, 2004, 2007, and 2008 as well as the full 2000-2008 span were found to have significantly different Atrazine concentrations from season to season. Years 2001, 2005, and 2006 were not found to have significantly different concentrations from season to season. The 2000-2008 span was then subjected to the Seasonal Kendal Test for Trend, which determined a significant (p=0.000092) decreasing linear trend of -7.6×10^{-6} mg/L/year of Atrazine in Kentucky.

The results of this study may lead to a better understanding about the persistence and variation of Atrazine in Kentucky drinking water. Though not the intent of this study, it has also shown that the entire state mean concentration of Atrazine in drinking water has not exceeded the US EPA MCL of 0.003 mg/L. As previously stated, there were numerous limitations to this study that could, ultimately, affect the results, specifically the secondary nature of the data and the lack of control of sampling methodology and frequency of the researcher. Though these limitations were present in the study, this study expands the current knowledge about Atrazine. While it expands on the current knowledge, it also points to numerous areas of need in future research and policy.

There are myriad areas which could be explored that could lead to a better understanding of Atrazine's persistence in the environment, as well as allow for better regulations, analytical methods and policies for the control of Atrazine. While there are numerous methods for the control of Atrazine in drinking water, these methods do not maintain Atrazine at a stationary level throughout the year, as this study suggests. For this reason, there is potential for overexposure of Atrazine through drinking water should there be spikes in Atrazine use. Future research into new, more effective control technologies beyond the use of granulated activated charcoal which could maintain stationary levels would be ideal. Additionally, further research into the variation between seasons of Atrazine in drinking water is necessary, ideally using more advanced statistical techniques, such as time series analysis or other statistical modeling techniques, which would allow for a greater understanding of the magnitude of effects which seasons play on Atrazine in drinking water. This research could have far reaching implications, as it could ultimately affect the sampling methodology used to test for Atrazine in drinking. This study has shown that the differences in concentrations of Atrazine between seasons may lead to unrepresentative exposure to the public. Additionally, there should be further examination of the other analytical methods which were not included in the inter-method comparison portion of this study to determine if they, too, yield comparable results. Finally, additional factors, such as meteorological and other environmental factors, and their effect on Atrazine concentrations in drinking water should also be examined.

While there are numerous limitations to this study, it serves as a starting point for future research into the analysis of the current US EPA methodology for testing drinking water for Atrazine and its persistence in the environment. It illustrates the need for future research in numerous areas including the current methodology used to test for Atrazine in drinking water, as well as how the environment affects Atrazine. Specifically, though, this study illustrates the potential need for changes in the sampling methodology used today, as it poses potential for underestimation of Atrazine in drinking water, which could ultimately affect the public's exposure. Ultimately, this study serves as a basis for the future research into both the seasonal variation of Atrazine in drinking water and the analytical methods used to test drinking water for Atrazine.

Appendix A.

Table 9. US EPA Analytical Methods 507 and 508.1 Sample Results

Date	County	508.1 Results (mg/L)	507 Results (mg/L)
4/13/2000	Woodford	0.0003	0.0003
6/7/2000	Breckinridge	0.0003	0.0003
6/7/2000	Breckinridge	0.0003	0.0003
6/7/2000	Carroll	0.0003	0.0003
6/7/2000	Gallatin	0.0003	0.0003
6/7/2000	Hardin	0.0003	0.0003
6/7/2000	Hardin	0.000586	0.000916
6/7/2000	Jefferson	0.0003	0.0003
6/7/2000	Meade	0.000436	0.0007
6/7/2000	Meade	0.0003	0.0003
11/13/2000	Laurel	0.0003	0.0003
11/13/2000	Laurel	0.0003	0.0003
11/13/2000	Mccreary	0.0003	0.0003
11/13/2000	Whitley	0.0003	0.0003
11/14/2000	Adair	0.0003	0.0003
11/14/2000	Clinton	0.0003	0.0003
11/14/2000	Clinton	0.0003	0.0003
11/14/2000	Cumberland	0.0003	0.0003
11/14/2000	Metcalfe	0.0003	0.0003
11/14/2000	Wayne	0.0003	0.0003
11/14/2000	Wayne	0.0003	0.0003
11/15/2000	Pulaski	0.0003	0.0003
11/15/2000	Pulaski	0.0003	0.0003
11/15/2000	Rockcastle	0.0003	0.0003
12/5/2000	Calloway	0.0003	0.0003
12/5/2000	Calloway	0.0003	0.0003
12/5/2000	Fulton	0.0003	0.0003
12/5/2000	Hickman	0.0003	0.0003
12/6/2000	Calloway	0.0003	0.0003
12/6/2000	Christian	0.0003	0.0003
12/6/2000	Lyon	0.0003	0.0003
12/6/2000	Lyon	0.0003	0.0003
12/20/2001	Pendleton	0.0003	0.0003
Mean		0.00031	0.00033

Standard Deviation	0.000054	0.00013
Median	0.0003	0.0003

Appendix B

Table 10. Seasonal Atrazine Averages by County for Year 2000

County	2000 winter	2000 spring	2000 summer	2000 fall
Adair			0.00004	0.0003
Allen			0.00035	
Anderson	0.00004	0.00004	0.00004	0.00004
Ballard		0.00004	0.00004	
Barren			0.0001	
Bell		0.00004	0.00004	
Boone	0.00004			
Bourbon	0.00004	0.00004	0.00004	
Boyd				
Boyle	0.000085			
Bracken	0.00004	0.00004		
Breathitt				
Breckinridge	0.00004	0.0003	0.00004	
Bullitt				
Butler				
Caldwell		0.0003	0.000058	
Calloway		0.00004	0.00014	0.0003
Campbell	0.00004			
Carlisle		0.00004		
Carroll	0.00004	0.0003		
Carter				
Casey	0.00004			
Christian		0.00066	0.00015	0.0003
Clark				
Clay		0.00004	0.00004	
Clinton			0.00004	0.0003
Crittenden		0.00004	0.00004	
Cumberland			0.00004	0.0003
Daviess		0.00004	0.00004	
Edmonson	0.00004			
Elliott				
Estill		0.00004	0.00004	
Fayette	0.00004	0.00004	0.00004	
Fleming	0.00004		0.00004	
Floyd		0.00004		
Franklin	0.00004	0.00004	0.00004	
Fulton		0.00004	0.00004	0.0003
Gallatin		0.0003		0.00004
Garrard	0.00004		0.00004	
Grant				
Graves		0.00004	0.00004	
Grayson	0.00004	0.00004	0.00019	

Green				
Greenup		0.00004	0.00004	
Hancock			0.00004	
Hardin	0.00004	0.00016	0.0001	0.0001
Harlan			0.00004	
Harrison	0.00004			
Hart				
Henderson		0.0015	0.0003	0.0004
Henry				
Hickman		0.00004	0.00004	0.0003
Hopkins		0.00004		
Jackson				
Jefferson	0.00004	0.00014	0.00003	
Jessamine				
Johnson				0.00004
Kenton				
Knott		0.00004		0.00004
Knox				
Larue		0.00007	0.00005	
Laurel			0.00004	0.0003
Lawrence				
Lee				
Leslie				
Letcher		0.00004		0.00004
Lewis	0.00004	0.00004	0.00004	0.00004
Lincoln	0.00008		0.00004	
Livingston		0.00004	0.00004	
Logan	0.00171	0.00072	0.00026	0.0016
Lyon			0.000045	0.0003
Madison				
Magoffin		0.00004		
Marion	0.00004			
Marshall			0.00004	
Martin				
Mason		0.00004	0.00004	0.00004
McCracken		0.0012		
Mccreary			0.00004	0.0003
McLean		0.00127	0.00004	
Meade	0.00004	0.00043		
Menifee		0.00004	0.00004	
Mercer	0.00004	0.00004	0.00004	0.00004
Metcalfe			0.000035	0.0003
Monroe				
Montgomery	0.00004			
Morgan	0.00004			
Muhlenberg				
Nelson	0.00004		0.0004	
Nicholas				

Ohio		0.00004	0.00004	
Oldham	0.00005	0.00005		
Owen	0.00004		0.00004	
Owsley				
Pendleton				
Perry		0.00004	0.00004	0.00004
Pike	0.00004			
Powell		0.00004	0.00004	0.00004
Pulaski		0.00004	0.00016	0.0003
Rockcastle		0.00004	0.00004	0.00014
Rowan	0.00004	0.00004	0.00004	
Russell				0.00004
Scott	0.00004	0.000037	0.00004	
Shelby	0.00004			
Simpson				
Taylor			0.0001	
Todd		0.0011	0.00006	
Trigg		0.00086	0.00006	
Trimble				
Union				
Warren		0.00084	0.00011	0.0001
Washington	0.00004			
Wayne				0.0003
Webster				
Whitley		0.00004	0.00004	0.0003
Wolfe			0.00004	
Woodford	0.000037	0.00013	0.00004	
Total Mean	9.03429E-05	0.000217907	7.17705E-05	0.0002327
Total Median	0.00004	0.00004	0.00004	0.0003

Table 11. Seasonal Atrazine Averages by County for Year 2001

County	2001 winter	2001 spring	2001 summer	2001 fall
Adair	0.00004	0.00004	0.00004	0.00004
Allen	0.00004	0.00013	0.000013	0.0001
Anderson	0.00004		0.00004	0.00004
Ballard		0.00004		0.00004
Barren			0.00004	0.00004
Bell	0.00004	0.00016	0.00022	0.00004
Boone				
Bourbon				
Boyd		0.03		
Boyle				
Bracken	0.00004		0.00004	0.00004
Breathitt				
Breckinridge		0.00004	0.00016	0.00004
Bullitt				
Butler		0.0032		
Caldwell	0.000035	0.000025	0.00004	0.00004
Calloway	0.00015	0.00013	0.00004	0.00004
Campbell				
Carlisle		0.00016		0.00004
Carroll	0.00004		0.00004	0.00004
Carter				
Casey			0.00004	0.00004
Christian	0.00012	0.00026	0.0001	0.00004
Clark				
Clay		0.00004	0.00004	0.00004
Clinton	0.00004	0.00004		
Crittenden	0.00004	0.00004	0.00004	0.00006
Cumberland	0.00004	0.00004		
Daviess			0.00004	0.00004
Edmonson			0.00004	0.00004
Elliott				
Estill	0.00004	0.00004		0.00004
Fayette	0.00004	0.00004	0.00004	0.00004
Fleming				0.00004
Floyd		0.00004		
Franklin				
Fulton	0.00004	0.00004	0.00004	
Gallatin	0.00004		0.00004	0.00004
Garrard	0.00004	0.00004	0.00004	0.00004
Grant				
Graves	0.00004	0.00004	0.00004	
Grayson		0.00004	0.00023	0.00017
Green			0.00008	0.00004
Greenup	0.00004		0.00004	

Hancock			0.00004	0.00004
Hardin	0.000037	0.00011	0.00013	0.00004
Harlan	0.00004	0.00004		0.00004
Harrison				
Hart		0.00004	0.00004	0.00004
Henderson	0.0001	0.0002	0.00035	0.00012
Henry	0.00004	0.00004	0.00004	
Hickman	0.00004	0.00004		
Hopkins		0.00004	0.00004	0.00004
Jackson				
Jefferson	0.00004	0.00012	0.00004	
Jessamine				
Johnson				
Kenton				
Knott		0.00004		0.00004
Knox				
Larue	0.0002	0.00004	0.00004	0.00019
Laurel	0.00004	0.00004		
Lawrence				
Lee				
Leslie				
Letcher		0.00004		
Lewis	0.00004		0.00004	0.00004
Lincoln	0.00004	0.00005	0.00005	0.000057
Livingston	0.00004	0.00004	0.00004	0.00004
Logan	0.00013	0.0004	0.00014	0.0007
Lyon	0.00003	0.00004		
Madison				
Magoffin				0.00004
Marion				
Marshall		0.00004	0.00004	
Martin				
Mason			0.00004	0.00004
McCracken				
Mccreary	0.00004	0.00004		
McLean			0.00004	0.00004
Meade			0.00004	
Menifee				
Mercer	0.00004		0.00004	0.00004
Metcalfe	0.00004	0.00009	0.00004	0.00004
Monroe				
Montgomery				
Morgan				
Muhlenberg				
Nelson	0.00002	0.00004	0.00004	0.00004
Nicholas				
Ohio		0.00004	0.00004	0.00004
Oldham	0.0001	0.000045	0.00021	0.00004

Owen				
Owsley				
Pendleton				0.0003
Perry		0.00004	0.00004	0.00004
Pike				
Powell	0.00004	0.00004	0.00004	0.00004
Pulaski	0.00005	0.00014	0.00004	0.00005
Rockcastle	0.00004	0.00004	0.00004	0.00004
Rowan	0.00004	0.00004	0.00004	0.00004
Russell		0.00004		
Scott	0.00004		0.00004	0.00004
Shelby				
Simpson			0.00004	0.00004
Taylor				
Todd	0.00017	0.00028	0.00022	0.00013
Trigg	0.00005	0.00004	0.00004	0.00004
Trimble				
Union				
Warren	0.00005	0.00058	0.00005	0.000064
Washington				
Wayne	0.00005	0.00003		
Webster				
Whitley	0.00004	0.00004	0.00004	0.00004
Wolfe				
Woodford		0.00004	0.00004	
Total Mean	5.47234E-05	0.00067125	6.51404E-05	6.633E-05
Total Median	0.00004	0.00004	0.00004	0.00004

Table 12. Seasonal Atrazine Averages by County for Year 2002

County	2002 winter	2002 spring	2002 summer	2002 fall
Adair	0.00004	0.000047		
Allen	0.00004	0.000043	0.000113	0.000076
Anderson		0.00004	0.00004	0.00004
Ballard			0.00004	
Barren	0.00004	0.000074		
Bell	0.00004	0.00004	0.00004	0.00004
Boone				
Bourbon				
Boyd				0.00004
Boyle				
Bracken	0.00004		0.00004	
Breathitt				
Breckinridge	0.00004	0.00279	0.000163	0.000192
Bullitt				
Butler				
Caldwell	0.000046	0.00032	0.000054	
Calloway	0.00004	0.00004	0.00004	
Campbell				
Carlisle			0.00004	
Carroll	0.00004		0.00004	
Carter				0.00004
Casey	0.00004	0.000065		
Christian		0.0013		0.000094
Clark				
Clay	0.00004	0.00004	0.00004	0.00004
Clinton				
Crittenden	0.00004	0.00004	0.000063	
Cumberland				
Daviess	0.00004	0.00004		
Edmonson	0.00004	0.000046	0.0015	
Elliott				0.00004
Estill		0.00004	0.000117	0.000033
Fayette		0.00004	0.000047	0.00004
Fleming				
Floyd		0.00004		0.00004
Franklin		0.00004	0.00004	0.00004
Fulton		0.00004	0.00004	
Gallatin	0.00004		0.00004	
Garrard		0.00004	0.00004	0.00004
Grant				
Graves	0.00004	0.00004	0.00004	
Grayson	0.00004	0.00056	0.00004	0.00004
Green	0.00004	0.00004		
Greenup	0.00004		0.00004	0.00004
Hancock	0.00004	0.00004		

Hardin	0.00004	0.000427	0.0005365	0.000038
Harlan				
Harrison				
Hart	0.00004	0.0002	0.00004	0.00004
Henderson	0.000051	0.00039	0.0009	0.0003
Henry	0.00004	0.00004		0.000088
Hickman			0.00004	
Hopkins		0.00003	0.00004	
Jackson				
Jefferson	0.00002	0.0001	0.00025	0.00004
Jessamine	0	0		0
Johnson				0.00004
Kenton				
Knott				0.00004
Knox				0
Larue	0.000034	0.002	0.00049	0.000024
Laurel	0			
Lawrence				0.00004
Lee				
Leslie				
Letcher	0.00004	0.00004		0.00004
Lewis	0.00004	0.00004	0.00004	0.00004
Lincoln		0.000056	0.000075	0.000021
Livingston	0.000004	0.00004	0.00004	
Logan	0.000065	0.00044	0.00025	0.000089
Lyon				
Madison				
Magoffin				
Marion				
Marshall				
Martin				0.00004
Mason	0.00004		0.00004	
McCracken		0.0012	0.00004	
Mccreary				
McLean	0.00004	0.00004		
Meade		0.0011		
Menifee				
Mercer		0.000184	0.000063	0.00004
Metcalfe	0.00004	0.00004	0.0004	0.00004
Monroe				
Montgomery				
Morgan				
Muhlenberg		0.0015		
Nelson	0.00004	0.00135	0.00053	0.00004
Nicholas				
Ohio	0.00004	0.002	0.00004	
Oldham	0.00004	0.000072	0.0001	0.000035
Owen				

Owsley				
Pendleton				
Perry		0.00004	0.00004	0.00004
Pike			0.00004	0.00004
Powell		0.00004	0.00004	0.00004
Pulaski		0.000049	0.000054	0.000022
Rockcastle		0.00004	0.00004	0.0000375
Rowan	0.00004	0.00004	0.00004	0.00004
Russell				
Scott		0.001	0.000068	0.00004
Shelby		0.0026	0.0017	
Simpson	0.00006	0.00053		
Taylor		0.00043		
Todd		0.0011	0.00094	0.00012
Trigg	0.0000645	0.0002	0.000082	
Trimble				
Union				
Warren	0.00004	0.000055	0.000173	0.00009
Washington				
Wayne				
Webster				
Whitley	0.00004	0.00004	0.00004	0.00004
Wolfe				
Woodford				
Total Mean	3.87093E-05	0.000394881	0.00018901	5.2598E-05
Total Median	0.00004	0.000046	0.00004	0.00004

Table 13. Seasonal Atrazine Averages by County for Year 2003

County	2003 winter	2003 spring	2003 summer	2003 fall
Adair				
Allen		0.0000315	0.000059	0.000421
Anderson	0.00004	0.00004	0.0000412	0.0000412
Ballard	0.00004		0.00004	
Barren				
Bell	0.00004	0.00004		0.0000408
Boone				
Bourbon				
Boyd		0.00004	0.00004	0.0000406
Boyle				
Bracken		0.00004		
Breathitt				
Breckinridge		0.00004		0.0000412
Bullitt				
Butler				
Caldwell	0.000043	0.00019	0.0000696	0.000057
Calloway	0.00053	0.00004		0.0000408
Campbell				
Carlisle	0.00004		0.0000215	
Carroll	0.00004		0.000041	
Carter	0.00004	0.00004	0.00015	0.000039
Casey				
Christian		0.00044	0.000132	
Clark				
Clay	0.00004	0.00004	0.0000404	0.0000421
Clinton				
Crittenden	0.00004	0.00004		0.0000408
Cumberland				
Daviess				
Edmonson				
Elliott	0.00004	0.00004	0.0000417	
Estill	0.00004	0.000021	0.0000426	0.0000404
Fayette	0.00003	0.00004	0.00004	0.0000268
Fleming				
Floyd	0.00004	0.00004	0.000041	
Franklin	0.00004	0.00004	0.0000323	0.0000351
Fulton		0.00004		0.0000408
Gallatin	0.00004		0.0000417	
Garrard	0.00004	0.00004	0.000063	
Grant				
Graves		0.00004		0.00004
Grayson	0.00004	0.00004	0.00078	0.000258
Green				
Greenup		0.00004	0.00004	0.000041
Hancock				

Hardin	0.00004	0.00003	0.00028832	0.000042
Harlan		0		
Harrison				
Hart	0.00004	0.00004	0.0000426	0.0000412
Henderson			0.00025	0.0001
Henry	0.000036	0.0000314	0.000325	0.0000984
Hickman	0.00004		0.0000222	
Hopkins				
Jackson				
Jefferson	0.00004	0.00004	0.0000713	0.000034
Jessamine				
Johnson	0.00004	0.000032	0.000041	
Kenton				
Knott	0.00004	0.0000267	0.0000417	
Knox	0	0		
Larue	0.0000255	0.0000367	0.00047	0.000035
Laurel		0		
Lawrence	0.00004	0.00004	0.000041	
Lee				
Leslie				
Letcher	0	0.00002		0.0000412
Lewis		0.000033	0.000041	0.0000413
Lincoln	0.000049	0.000057	0.0000421	
Livingston	0.00004	0.00004	0.0000404	0.0000404
Logan		0.00125	0.00021	0.00015
Lyon				
Madison				
Magoffin				
Marion				
Marshall				
Martin	0.00004	0.00004	0.000041	
Mason		0.00004		0.0000408
McCracken				
Mccreary				
McLean			0.0025	
Meade		0.00004	0.0011	
Menifee				
Mercer	0.00004	0.000024	0.0000408	0.0000266
Metcalfe		0.000034	0.0000617	0.0000406
Monroe				
Montgomery				
Morgan				
Muhlenberg				
Nelson		0.000078		
Nicholas				
Ohio	0.00004		0.0000408	
Oldham	0.00004	0.000043	0.0000408	0.0000295
Owen				

Owsley				
Pendleton				
Perry	0.00004	0.00004	0.0000449	0.0000412
Pike	0.000085	0.00004	0.000041	0.00148
Powell	0.00004	0.00004	0.0000421	0.0000421
Pulaski	0.0000285	0.0000425	0.0000412	
Rockcastle	0.00004	0.00004	0.0000421	0.0000404
Rowan		0.00004	0.0000404	0.0000435
Russell				
Scott	0.00004	0.00004	0.00004	0.0000234
Shelby		0.00075	0.00216	
Simpson				
Taylor			0.003	
Todd		0.000524	0.000056	0.00016
Trigg	0.000046	0.00037	0.000094	0.0000722
Trimble				
Union				
Warren		0.000193	0.000127	0.000098
Washington				
Wayne				
Webster				
Whitley	0.00004	0.00004	0.00004	0.0000404
Wolfe				
Woodford				0.0000417
Total Mean	5.00698E-05	9.71544E-05	0.000250517	9.83452E-05
Total Median	0.00004	0.00004	0.0000417	0.0000411

Table 14. Seasonal Atrazine Averages by County for Year 2004

County	2004 winter	2004 spring	2004 summer	2004 fall
Adair		0.001		
Allen	0.000149	0.0000912	0.0000946	0.0000421
Anderson	0.0000412		0.000421	0.0000415
Ballard	0		0.000404	0.0000417
Barren				
Bell	0.0000408			0.0000417
Boone				
Bourbon		0.0000408		
Boyd				
Boyle				
Bracken				
Breathitt				
Breckinridge		0.00011	0.000143	0.000307
Bullitt				
Butler				
Caldwell	0.000047		0.00005	
Calloway				
Campbell				
Carlisle			0.0000426	
Carroll	0.000043			
Carter				
Casey				
Christian	0.000079	0.0094	0.000173	0.00039
Clark				
Clay	0.0000408			
Clinton				
Crittenden	0.0000404		0.0000417	
Cumberland	0.00005			
Daviess				
Edmonson				
Elliott		0.0000408		
Estill	0.0000408	0.0000419	0.0000413	0.0000041
Fayette	0.000042	0.0000432	0.0000415	0.0000418
Fleming				
Floyd				0.000043
Franklin	0.0000404		0.0000412	0.0000408
Fulton	0.0000412			
Gallatin	0.0000421			
Garrard	0.0000417		0.0000421	0.00004125
Grant	0.00005			
Graves	0.0000417			
Grayson	0.0000408	0.000566	0.000693	0.0003434
Green				
Greenup		0.0000408		0.0000412
Hancock				

Hardin	0.000042	0.00089	0.000046	0.000041
Harlan				
Harrison				
Hart	0.0000426	0.0000417	0.0000417	
Henderson	0.0002	0.0027		0.0001
Henry				
Hickman			0.0000412	
Hopkins			0	0
Jackson				
Jefferson	0.0000426	0.0000512	0.0000399	0.0000417
Jessamine	0.000043	0.00005		0.0000412
Johnson				
Kenton	0.0001	0	0	0
Knott				
Knox				
Larue	0.0000404	0.000354	0.0000629	0.0000417
Laurel				
Lawrence				
Lee				
Leslie				
Letcher	0.0000411	0.0000408		0.0000408
Lewis				0.0000417
Lincoln			0.0000762	0.0000379
Livingston	0.0000404		0.0000408	
Logan	0.000157	0.00286	0.0000769	0.00054
Lyon				
Madison				
Magoffin				
Marion				
Marshall			0.0000421	
Martin	0.00004215			
Mason		0.0000204		0.0000408
McCracken				
Mccreary				
McLean				
Meade		0.0018		
Menifee				
Mercer			0.0000426	0.00003235
Metcalfe	0.0000421	0.000047	0.0000417	0.0000417
Monroe				
Montgomery				
Morgan				
Muhlenberg				
Nelson				
Nicholas				
Ohio	0.0000404			
Oldham	0.0000426			
Owen				

Owsley				
Pendleton				
Perry	0.0000408	0.0000408		0.0000444
Pike				
Powell		0.0000421	0.0000417	0.0000417
Pulaski	0.0000618		0.0000503	0.0000418
Rockcastle	0.00004125	0.00004165	0.000042	0.0000422
Rowan	0.0000417			0.0000417
Russell				
Scott	0.00004258	0.0000462	0.00006	0.00004008
Shelby				
Simpson				
Taylor				
Todd	0.000115	0.0035	0.000174	0.000114
Trigg	0.00032		0.0000469	
Trimble				
Union				
Warren	0.000152	0.00032	0.0000538	0.0000408
Washington				
Wayne				
Webster				0.001
Whitley	0.0000408			
Wolfe				
Woodford	0.000053	0.0000454	0.000044	0.00004262
Total Mean	6.36553E-05	0.000836757	9.68735E-05	0.000105668
Total Median	0.0000421	0.000047	0.0000433	0.0000417

Table 15. Seasonal Atrazine Averages by County for Year 2005

County	2005 winter	2005 spring	2005 summer	2005 fall
Adair	0		0	0
Allen	0.0000737		0	0
Anderson	0.0000152	0.0000408	0	
Ballard			0	0.0000404
Barren	0	0		0
Bell	0	0.0000274	0	0.0000204
Boone	0	0	0.0000204	0
Bourbon	0	0		0
Boyd			0	
Boyle	0	0	0	
Bracken				
Breathitt		0		0
Breckinridge	0.0000437		0	
Bullitt	0		0.0000339	
Butler	0	0	0	0
Caldwell	0.0000279		0	
Calloway	0.0000421	0.00019		0.000228
Campbell				
Carlisle	0			
Carroll	0		0.0000284	
Carter	0	0		
Casey		0	0	0
Christian	0.00005894	0.000794	0.0000302	0.0000767
Clark	0	0.0000571		
Clay		0.00004		0.0000209
Clinton		0	0	0
Crittenden	0.0000408	0	0	0
Cumberland				
Daviess		0	0	
Edmonson			0	0
Elliott				
Estill	0.0000419		0.0000834	
Fayette	0.0000313	0.0000274		0.0000408
Fleming		0	0	0
Floyd				0
Franklin	0	0.0000204	0	0.0000408
Fulton	0.0000421	0		
Gallatin			0.0000834	0
Garrard		0.0000145		0.0000204
Grant		0		0
Graves	0.0000213	0.0000446	0	0.0000605
Grayson	0	0.000735	0.000205	0.0000206
Green	0		0	
Greenup	0.0000417	0.00004		
Hancock			0.000086	

Hardin	0	0.000041	0.000045	0.000052
Harlan	0.000044	0	0	0.0000408
Harrison		0		
Hart		0.0000435	0.0000417	
Henderson	0	0.00055	0.00055	0.0001
Henry	0		0	
Hickman		0		0.0000412
Hopkins	0.0000246	0	0.0000136	0.0000213
Jackson			0	
Jefferson	0.0000729	0.0000136	0.000138	0
Jessamine	0.0000228	0.000026	0	0
Johnson		0.0000408		
Kenton				
Knott		0		
Knox			0	
Larue	0	0.0000435	0.000729	0.0000732
Laurel		0	0	
Lawrence				0.0000426
Lee		0		
Leslie		0		0
Letcher	0.00004		0	0.0000317
Lewis		0.00004		
Lincoln	0	0.0000484		
Livingston	0.0000206	0	0	0.0000404
Logan	0.0000604	0.000895	0.000138	0.000168
Lyon		0.0000275	0	
Madison	0	0	0	
Magoffin				
Marion				
Marshall		0.0000204		0.0000204
Martin				
Mason	0	0	0.0000408	
McCracken	0	0.003	0	0
Mccreary	0	0		
McLean	0	0.0067	0	
Meade	0		0	
Menifee		0.00000435	0.0000888	0
Mercer		0.0000209		
Metcalfe	0.0000426		0.0000408	
Monroe				
Montgomery				
Morgan				
Muhlenberg	0	0		
Nelson	0	0	0	
Nicholas	0		0	
Ohio	0	0	0.0000136	
Oldham	0		0.0000166	
Owen	0	0		

Owsley	0			0
Pendleton				
Perry		0.0000204	0	0.0000198
Pike		0	0	0.0000276
Powell	0.0000404		0.0000842	
Pulaski	0	0.0000292	0	0.0000444
Rockcastle	0.0000276	0.00002175	0.00005	
Rowan		0.0000444		
Russell	0		0	
Scott	0.00003318	0.0000428		0.0000408
Shelby	0	0	0.00146	
Simpson	0	0.000531		0.0000532
Taylor	0		0.00012	
Todd	0.0000765	0.00147		0.000092
Trigg	0.0000524	0	0	0
Trimble	0		0	
Union	0	0.0028	0	
Warren	0.0000945		0.0000475	0.0000224
Washington				
Wayne				0.0000213
Webster	0	0.0004		
Whitley	0	0.00002175		
Wolfe			0.0000435	
Woodford	0.0000416	0.0000139	0	
Total Mean	1.70249E-05	0.000263074	6.22324E-05	2.9855E-05
Total Median	0	0.0000142	0	0.0000204

Table 16. Seasonal Atrazine Averages by County for Year 2006

County	2006 winter	2006 spring	2006 summer	2006 fall
Adair	0	0	0.0001308	0
Allen				
Anderson			0.0000404	
Ballard	0	0.0000209	0	
Barren	0	0	0	0
Bell		0.0000136	0	0.00002
Boone	0		0	
Bourbon				
Boyd	0			
Boyle	0	0	0	0
Bracken	0.0000408	0	0	
Breathitt		0		
Breckinridge	0		0.0000426	
Bullitt				
Butler	0	0.00029	0.00024	0
Caldwell		0.0000412		0.0000601
Calloway	0.0000206		0.0000213	0
Campbell				
Carlisle		0		
Carroll				0.00004
Carter		0	0	
Casey	0			
Christian	0.000041	0.00005769	0.0000422	0.000295
Clark		0		0
Clay		0.0000204	0	0.00004
Clinton	0			
Crittenden	0	0.0000408	0	0.00002
Cumberland	0		0	
Daviess				
Edmonson			0.00015	
Elliott		0	0	
Estill	0.0000417	0.0000204	0.0000272	0.0000422
Fayette	0.0000404	0.000042	0.0000421	0.0000418
Fleming	0		0	0
Floyd	0.0000202	0	0.0000204	
Franklin	0.0000202	0.0000408	0.00002	0.0000291
Fulton	0		0.0000208	
Gallatin	0	0	0	0.00004
Garrard	0.0000408	0.0000417	0.00004	0.0000412
Grant	0	0		0
Graves		0	0.0000145	0
Grayson	0.0000142	0.000139	0.0000404	0.0000327
Green	0		0	
Greenup		0	0.0000104	
Hancock	0.0000455	0.0000416	0.0000137	0.0000135

Hardin	0.0000254	0.001086	0.000048	0.0000581
Harlan	0.0000404	0.0000816	0.0000153	0.00004
Harrison	0		0	
Hart	0.0000424	0.000138	0.000068	0.0000517
Henderson	0	0.00000667	0.00005	0
Henry				
Hickman			0.00005	
Hopkins	0	0.0000102	0.0000102	0.00004
Jackson				
Jefferson	0.0000419	0.00002165	0.0000846	0.0000409
Jessamine			0.00002	0
Johnson	0.0000204		0.0000213	0.00004
Kenton				
Knott		0	0.00002	
Knox	0	0		
Larue	0.0000326	0.00157	0.000149	0.000066
Laurel	0	0	0	
Lawrence	0.0000427	0	0	
Lee	0			
Leslie				
Letcher	0.0000412	0	0	
Lewis	0.0000408	0.0000247	0.0000145	
Lincoln	0.0000169	0.0000408	0.0000533	
Livingston	0	0.0000204	0.00002	0.00002
Logan	0.000435	0.000115	0.000967	0.0000777
Lyon		0		
Madison		0	0	0
Magoffin		0	0	
Marion				0
Marshall	0.0000426	0.0000145	0	0
Martin		0	0	
Mason		0	0	
McCracken	0	0	0.00023	0
Mccreary				
McLean	0		0.00035	0
Meade				0
Menifee	0.0000222	0.0000215	0.0000204	0.0000202
Mercer	0.0000419	0	0.000043	
Metcalfe				
Monroe	0		0	
Montgomery		0	0	
Morgan		0	0	
Muhlenberg		0	0	
Nelson	0	0	0	0
Nicholas				
Ohio			0.00031	0.00004
Oldham				0.0000426
Owen	0	0	0	0

Owsley	0			
Pendleton		0		
Perry	0.0000408	0.0000311	0.0000213	0.0000413
Pike	0	0.0000206	0.0000306	
Powell	0.000044	0.0000206	0.0000204	0.0000406
Pulaski	0.0000417	0.0000241	0	0.00001
Rockcastle	0.0000426	0.000426	0.0000412	0.00002
Rowan	0	0	0	0.0000404
Russell				
Scott	0	0.0000224	0.00004	0.00004
Shelby	0	0	0	0
Simpson	0.0000161	0.000011		0.000055
Taylor			0	
Todd	0.0000565	0.0001445		0.0000962
Trigg	0	0.0000272	0	0.0000648
Trimble				
Union	0	0.000255	0.00027	0
Warren		0.000415	0.000107	0.0000774
Washington	0		0	
Wayne	0.000088	0.000027		0.0000385
Webster	0		0.00041	0
Whitley	0	0	0.00001	0
Wolfe			0	0
Woodford	0	0.0000312	0.0000352	0.0000275
Total Mean	2.17113E-05	7.32001E-05	5.35795E-05	2.9582E-05
Total Median	0	0.0000106	0.0000145	0.0000202

Table 17. Seasonal Atrazine Averages by County for Year 2007

County	2007 winter	2007 spring	2007 summer	2007 fall
Adair		0	0	
Allen				0
Anderson				
Ballard			0.0000204	0
Barren	0	0	0.000029	0
Bell		0.0000434	0	0.000004
Boone	0	0	0	0
Bourbon				
Boyd	0		0	
Boyle	0	0	0	0
Bracken				
Breathitt	0			
Breckinridge	0.0000412	0.0000444	0.0000204	0
Bullitt	0			
Butler	0	0.00028	0	0
Caldwell		0.000146		0.0000847
Calloway			0	0.0000416
Campbell		0		
Carlisle		0.00002		
Carroll				
Carter				
Casey				
Christian	0.000066	0.000168	0.0000615	0.000101
Clark				
Clay		0.00004		0.00004
Clinton	0	0		
Crittenden	0	0.0000615	0	0.0000404
Cumberland	0	0	0	
Daviess	0.0000408			
Edmonson	0			0
Elliott				
Estill	0.00004	0.000025	0.0000204	0.00004
Fayette	0.0000436	0.000041		0.0000527
Fleming		0	0.0000536	
Floyd	0	0.0000342	0.0000326	0.000041
Franklin	0.00002	0.000023	0	0.0000267
Fulton	0		0	0.0000425
Gallatin		0	0	0
Garrard	0.0000424	0.0000412		0.0000406
Grant	0		0	0
Graves		0	0	0.0000213
Grayson	0.0000309	0.000161	0.00079	0.0000137
Green	0		0	
Greenup	0.0000408			
Hancock	0.0000206	0.00004	0.0000416	0.0000418

Hardin	0.0000405	0	0.000046	0.000052
Harlan	0.00002	0.000032	0	0.00004
Harrison	0		0	
Hart	0.0000486	0.0000419	0.0000412	0.00004
Henderson	0	0.0003	0.00015	0
Henry				
Hickman		0.0000434		
Hopkins	0.0000404	0.0000426	0.0000404	0.0000416
Jackson				
Jefferson	0.0000202	0.0000297	0.0000306	0.00003135
Jessamine				0
Johnson	0.00004108	0.00004	0.0000426	0.0000426
Kenton				0
Knott	0.0000408	0.0000426	0.0000426	0.00004
Knox	0.0000416		0.00004	
Larue	0.0000444	0	0.000268	0.000193
Laurel				
Lawrence		0.0000434		0.0000426
Lee	0			
Leslie		0.0000408		
Letcher	0	0.0000402	0.0000337	0.0000408
Lewis	0.0000422			
Lincoln	0.00000352	0.0000634		
Livingston	0	0.0000217	0	0.0000203
Logan	0.0000348	0.0000467	0.000446	0.000154
Lyon		0		
Madison		0	0	0
Magoffin				
Marion			0	0
Marshall		0	0	
Martin				
Mason	0.0000434			
McCracken	0	0.000021	0.0000202	
Mccreary				
McLean	0	0.0013	0	0
Meade	0.0000405	0.00004		
Menifee	0.0000408	0.0000434	0.0000412	0.0000426
Mercer				
Metcalfe				
Monroe				
Montgomery		0	0	
Morgan				
Muhlenberg		0.00056	0	0
Nelson		0		
Nicholas				
Ohio	0	0	0.00005	0.000067
Oldham				
Owen				0.0000434

Owsley				
Pendleton	0	0		
Perry				
Pike		0.0000422	0.0000402	0.0000396
Powell	0.00004	0.0000204	0.0000202	
Pulaski	0	0.0000201	0	0.0000309
Rockcastle	0.0000202	0.00004	0.0000412	0.0000423
Rowan	0	0	0	
Russell				
Scott	0.0000416	0.00002		0.0000529
Shelby			0	
Simpson	0	0.0000412	0.000187	0.0000412
Taylor			0	
Todd		0.0000565	0.000147	0.000103
Trigg		0.000327		0.000033
Trimble				
Union	0	0	0	
Warren	0.0000677	0.00006245	0.0000256	0.0000852
Washington	0		0	
Wayne		0.0000202	0.000108	0.0000425
Webster				
Whitley	0.0000213	0	0	0.00004
Wolfe		0.00004		
Woodford	0.0000304	0	0	0
Total Mean	1.91717E-05	6.84051E-05	4.72774E-05	3.50664E-05
Total Median	0.00001176	0.0000331	0	0.00004

Table 18. Seasonal Atrazine Averages by County for Year 2008

County	2008 winter	2008 spring	2008 summer	2008 Fall
Adair	0	0	0	
Allen	0		0	
Anderson	0		0	
Ballard		0	0	
Barren				
Bell		0		
Boone	0	0		
Bourbon		0	0	0
Boyd				
Boyle	0	0	0	
Bracken				
Breathitt		0		
Breckinridge		0	0	
Bullitt			0	
Butler	0	0.0000195	0.000115	
Caldwell	0	0.00133	0	
Calloway	0		0.00002	0.00005
Campbell		0		
Carlisle	0			0.0000412
Carroll	0	0.00004	0	
Carter				
Casey			0	
Christian	0.0000937	0.00044		0.0000674
Clark	0	0		
Clay				
Clinton	0	0		
Crittenden	0	0.0000471	0	0
Cumberland	0	0	0	
Daviess		0		
Edmonson	0	0		
Elliott				
Estill	0.00004	0.0000208	0	0.00004
Fayette	0	0.0000411	0.0000227	
Fleming	0.0000416	0.0000404	0.0000426	
Floyd	0.0000413	0		
Franklin	0.00002	0.0000423	0.0000332	0.00004
Fulton	0		0	
Gallatin	0	0.0000202	0	
Garrard	0			
Grant	0		0	
Graves		0	0	0.0000412
Grayson	0	0.000465	0.000327	
Green	0	0.00004	0	
Greenup	0.0000416	0	0.0000211	
Hancock		0.0000202	0.0000408	0.0000444

Hardin	0	0.000069	0.000064	
Harlan	0	0.00001	0	
Harrison	0.00004		0	
Hart	0.0000422	0.000041	0.0000417	0.00004
Henderson	0	0.000277	0	
Henry	0		0	
Hickman				0.0000416
Hopkins	0.0000416	0		0.0000133
Jackson		0	0	
Jefferson	0	0.0000135	0.0000365	0.0000985
Jessamine		0		
Johnson	0.0000426	0.0000404	0.0000404	
Kenton	0	0	0	
Knott			0	
Knox	0	0	0	
Larue	0	0	0.00038	
Laurel	0	0	0.0000213	
Lawrence	0.0000426	0.0000434		
Lee	0		0.0000211	
Leslie		0		
Letcher	0.00003105	0	0	
Lewis	0.0000416		0.0000408	
Lincoln	0			
Livingston	0		0.000258	0
Logan	0.0000981	0.000282	0.0000958	0.000103
Lyon		0.00021	0	
Madison	0	0	0	0
Magoffin	0.0000411		0	
Marion			0	
Marshall		0	0	
Martin				
Mason	0.0000206	0.00068	0.0000434	
McCracken		0.000154	0.000135	
Mccreary	0	0	0	
McLean	0	0.00083	0	
Meade	0		0	
Menifee				
Mercer		0	0	
Metcalfe				
Monroe				
Montgomery		0	0	
Morgan				
Muhlenberg	0	0.000365	0	
Nelson				
Nicholas		0	0	
Ohio	0.0000135	0.000048	0.000648	
Oldham	0		0	
Owen	0		0	

Owsley		0	0	
Pendleton		0	0	
Perry	0.0000213		0	
Pike	0.0000394	0.000041	0	
Powell	0.000043	0.0000422		0.0000404
Pulaski	0.0000211	0.0000253	0	
Rockcastle	0.0000411	0.0000142	0	0.0000404
Rowan	0	0	0	
Russell		0	0	
Scott	0.0000267	0.0000633	0.0000491	0.000047
Shelby	0	0	0.00032	
Simpson	0.000051	0.000123	0.000224	
Taylor			0	
Todd	0.000108	0.000924	0.000261	
Trigg		0.000282		
Trimble	0		0	
Union	0	0.00007	0	
Warren	0.0000942		0	0.0000639
Washington	0		0	
Wayne		0.0000436	0.0000694	0
Webster	0	0.000255	0	
Whitley		0	0	
Wolfe			0	
Woodford	0	0	0	
Total Mean	1.59318E-05	9.75779E-05	3.96694E-05	3.8681E-05
Total Median	0	0	0	0.0000404

Appendix C.

Table 19. Wilcoxon Scores (Rank Sums) for Variable Average Classified by Variable Season

		Wilcoxon Scores (Rank Sums) for Variable Average Classified by Variable Season				
Year	**Season**	**N**	**Sum of Scores**	**Expected Under H_0**	**Std Dev Under H_0**	**Mean Score**
2000	Winter	35	2476.50	3167.50	234.29	70.76
	Spring	54	5099.50	4887.00	271.28	94.44
	Summer	61	5059.00	5520.50	280.20	82.93
	Fall	30	3655.00	2715.00	220.62	121.83
2001	Winter	47	4832.50	5123.00	296.72	102.82
	Spring	56	6572.00	6104.00	315.19	117.36
	Summer	57	6155.00	6213.00	317.01	107.98
	Fall	57	6093.50	6213.00	317.01	106.90
2002	Winter	43	3225.00	4321.50	300.73	75.00
	Spring	59	7309.00	5929.50	333.83	123.88
	Summer	52	6004.00	5226.00	321.09	115.46
	Fall	46	3562.00	4623.00	308.06	77.43
2003	Winter	43	3034.00	4214.00	318.71	70.56
	Spring	57	4250.00	5586.00	349.63	74.56
	Summer	53	7018.00	5194.00	341.99	132.42
	Fall	42	4808.00	4116.00	316.01	114.48
2004	Winter	43	2855.00	3096.00	226.80	66.40
	Spring	29	2542.00	2088.00	198.87	87.66
	Summer	34	2687.50	2448.00	210.55	79.04
	Fall	37	2211.50	2664.00	216.60	59.77
2005	Winter	69	8250.50	9004.50	492.77	119.57
	Spring	72	10101.00	9396.00	499.40	140.29
	Summer	68	8414.00	8874.00	490.47	123.74
	Fall	51	7164.50	6655.50	443.16	140.48
2006	Winter	71	9317.50	10295.00	579.38	131.23
	Spring	74	10645.50	10730.00	587.59	143.86
	Summer	83	12441.00	12035.0	609.13	149.89
	Fall	61	9501.00	8845.00	549.38	155.75
2007	Winter	60	6560.00	7470.00	466.59	109.33
	Spring	68	9259.00	8466.00	486.03	136.16
	Summer	62	7031.50	7719.0	471.77	113.41
	Fall	58	8025.50	7221.00	461.18	138.37
2008	Winter	74	8687.00	9546.00	481.76	117.39
	Spring	77	10943.50	9933.00	487.38	142.12

	Summer	85	9932.50	10965.00	500.56	116.85
	Fall	21	3590.00	2709.00	291.44	170.95
2000-2008	Winter	485	424064.00	482575.00	10796.64	874.36
	Spring	546	568754.50	543270.00	11220.79	1041.67
	Summer	555	549549.50	552225.00	11277.56	990.18
	Fall	403	736687.00	400985	10106.43	1083.59

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