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Surface water pesticide contamination in the Upper Terrebonne Basin of Louisiana

John S. Walther
Louisiana State University and Agricultural and Mechanical College, jwalth1@lsu.edu

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SURFACE WATER PESTICIDE CONTAMINATION IN THE UPPER TERREBONNE BASIN OF LOUISIANA

A Thesis

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By
John S. Walther
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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Triazine herbicides are the most heavily used pesticides in the United States. Atrazine and Simazine are the primary triazine herbicides used for broadleaf weed control in the production of corn, sugarcane, and sorghum. Recent monitoring studies of surface waters in the Upper Terrebonne Basin of Louisiana indicate elevated amounts of triazines are running off fields and entering drinking water supplies. Atrazine has been classified as a possible carcinogen by the United States Environmental Protection Agency. Recent epidemiological studies have revealed increases in breast cancer and pre-term births following exposure to triazines at levels detected in drinking water. Non-point source pollution is a major problem affecting the water quality in the United States. Agriculture contributes a large percentage of non-point source water pollution, with sediment, pesticides and animal waste transported into waterways with surface runoff. Recent amendments to the Clean Water Act require that States identify impaired waters and develop Total Maximum Daily Load Budgets for these waters. Best Management Practices have been advocated as a method to reduce non-point pollution to meet these new regulations. Data were collected in the Upper Terrebonne Basin of Louisiana before and after the farmers were advised to follow Best Management Practices to reduce Atrazine runoff . Samples of finished and raw water were collected from Iberville Water District Three and analyzed for atrazine concentration by the Louisiana Department of Agriculture and Forestry. Atrazine concentration data were evaluated using Dynamic Linear Models, with stream flow from Bayou Grosse Tete as a regressor. This analysis revealed that stream flow has a significant influence and accounts for most of the change in atrazine concentrations at the Iberville water facility. The trend in acreage of crops planted in the UTB had a decrease in the number of crop acres that could utilize Atrazine. The sale of Atrazine in the UTB also increased for the years at the beginning and end of this study. From the results of the time series analysis, it appears that Best Management Practices had less effect than stream flow on Atrazine concentrations at Iberville Water District Three.

INTRODUCTION

The Upper Terrebonne Basin, located in Point Coupe, Iberville, and West Baton Rouge Parishes, forms the surface watershed for the Iberville Water District Number Three treatment facility in Plaquemine, Louisiana. The geographic location of this basin is an important factor to consider in its management. (Figure 1) Bounded by the leveed Mississippi River to the east and by the Atchafalaya riverbanks to the north and west, all surface water discharged originates from rainfall runoff from within the basin. Three main tributaries drain the basin; Bayou Grosse Tete, Bayou Choctaw, and Bayou Plaquemine. These streams connect to the Intracoastal Waterway. Iberville Parish Water District Number Three draws water from the Intracoastal Water Way approximately one-half mile south of the confluence of Bayou Plaquemine for treatment and distribution to users in the water district.

Land use in the Upper Terrebonne Basin is dominated by agricultural crop production of corn, sugarcane, cotton, and soybeans. atrazine is a cost-effective herbicide used in the production of corn, sorghum, and sugarcane. atrazine is susceptible to runoff and leaching because of its high solubility. Current agricultural practices include pre-plant application in early spring and post plant application in midsummer. Heavy rainfall events typically occur in the months of March and April with the passage of frontal weather systems.

A drinking water monitoring project initiated in 1995 by Louisiana Department of Agriculture and Forestry (LDAF) and Ciba Geigy revealed atrazine herbicide levels above the Safe Drinking Water Act maximum contaminant level (MCL) at the Iberville Water District Number Three treatment facility. Surface water contaminated by runoff from corn and sugarcane farms in the closed upper terrebonne basin upstream of the water treatment facility was the suspected cause. Elevated atrazine levels have prompted the water treatment facility to adopt activated carbon treatment, the current Best Available Technology consisting of to lower atrazine concentrations in excess of MCLs.

A cooperative panel representing regulatory agencies, university extension researchers, and the Iberville Water District Number Three was formed to monitor, evaluate, and encourage the use of best management practices by sugarcane and corn farmers to reduce contaminant runoff or face restrictions on the use of atrazine. The program is ongoing and has the goal of reduction in atrazine levels in the raw water at Iberville Water District Number Three treatment plant (Louisiana Department of Agriculture and Forestry 1998).

The consequence of MCL excedence, as mandated by the Safe Water Drinking Act, include non-point source control and additional treatment by water users. Non-point source controls could include restrictions or bans on the use of atrazine, which is an important crop production tool. Additional treatment of raw water causes economic impact to the water works and a economic cost to the customers of Iberville Water District Number Three.

Non-point source pollution is a major problem affecting water quality in the United States (Goolsby and Pereira 1995). Agriculture contributes a large percentage of non point source pollution nationwide comprised of sediment, pesticide, and animal waste transported into waterways with surface runoff (Goolsby and Pereira 1995). Methods of agricultural production may need to be improved to limit the impact of non-point source pollution on water quality.

The presence of pesticides in surface water has become a concern for water treatment utilities since, they are required to test quarterly for several agricultural pesticides under the Safe Drinking Water Act. The Maximum Contaminant Level of some common agricultural pesticides has been exceeded in several watersheds across the country, causing additional treat drinking water or other reductions the contaminant level (Ribaudo and Bouzaher 1994).

Recent amendments to the Clean Water Act require States to identify waters not meeting state water quality standards and establish pollution budgets, called Total Maximum Daily Loads (TMDL's). Action taken by the U.S. Environmental Protection Agency on October 18, 2001 establishes April 30, 2003 as the effective date by which States must list waters not meeting quality standards and complete Total Maximum Daily Load Programs. A TMDL is a pollution budget for a specific water body stating the maximum amount of contaminants that can be released without causing water to be impaired for drinking, fishing and swimming. Point and non point source controls are to be implemented to meet the newly established TMDLs (Federal Resister: 2001). The States face the problem of controlling non point source pollution from agricultural producers that previously were not regulated on this issue.

Best Management Practices are the suggested method for reducing non point source pollution. These practices are readily available, but will the target participants adopt BMP's? Best Management Practices have traditionally addressed maximizing production or profits, however they can be designed to reduce water contamination and maintain sustainable agricultural production.

Five years of atrazine water concentration data from Iberville Water District Number Three and selected UTB stream sites will be studied with time series analysis models. Analysis of the modeled data will be utilized to observe the mean concentrations, trends in the concentrations, and influential factors of the concentrations for the study period. Bayesian time series analysis will be used in this study due to their flexibility in comparing components, ability to estimate component distributions, and evolving parameters that demonstrate changes in component relationships.

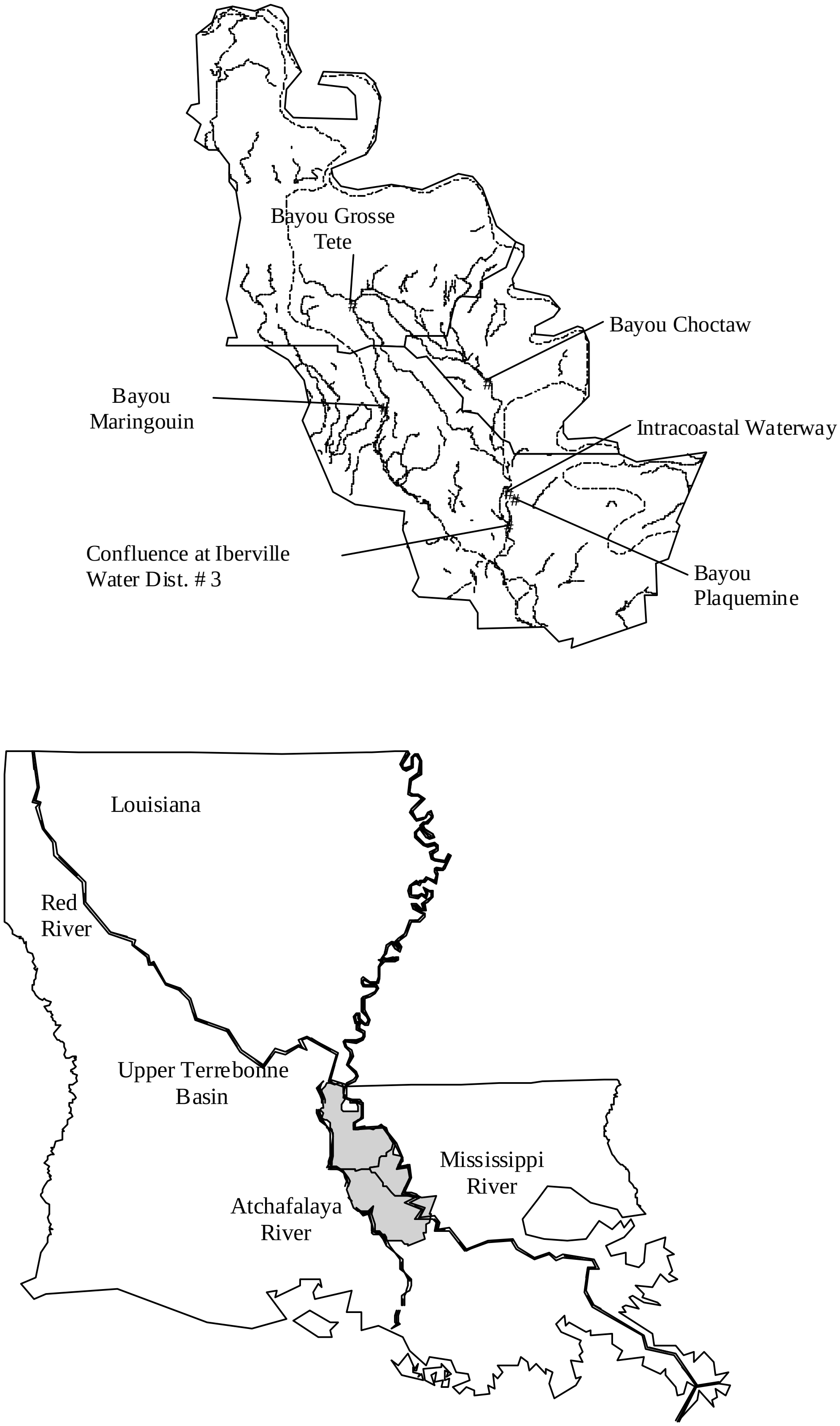


Figure 1. Overview of the Upper Terrebonne Basin of Louisiana

LITERATURE REVIEW

Properties Exposures, and Toxic Effects of Triazines

Triazine Properties

The Geigy Chemical Company of Basel, Switzerland developed atrazine herbicide in 1952. Atrazine was patented in Switzerland in 1958, and registered for commercial use in the United States in 1959. (Solomon et al. 1996.) There are two major triazine herbicides used in crop production; atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) and simazine (2-chloro-4, 6-bis-etylamino-s-triazine) (Gianessi L. P. 1998).

Triazines are selective pre-emergent broadleaf (dicot) herbicides that produce a reversible inhibition of photosynthesis while causing little or no injury to corn, sorghum, or sugarcane (Solomon et al 1996). Triazines are the primary herbicide used in the production of corn and sorghum, and sugarcane with annual sales in the United States, of 80-90- million pounds in 1992 (Tierney et al. 1998). Triazines can be applied to cropland pre-planting, pre-emergent, or post-planting, making it a flexible herbicide for agricultural users. Secondary uses of triazines include industrial, right of way, and landscaping applications.

Triazines are very cost efficient herbicides for the agricultural producer and are used on approximately two thirds of the U. S. corn and sugarcane acreage, 90 percent of the sugarcane acreage and 67 percent of the sorghum acreage annually. Atrazine is the primary triazine used in crop production and simazine is most widely used in tree fruit, nut orchards, and vineyards (Gianessi L. P. 1998). Uncontrolled weeds can lower the yield of crops through competition for sunlight, nutrients, and moisture. The use of residual herbicides such as triazines produce a long period of weed control at reduced cost in comparison to other methods (Ribaudo and Bouzaher 1994).

Exposure to Triazine Pesticide

The most significant route of exposure for humans and animals to triazine herbicides is through drinking water contamination. Atrazine has a low vapor pressure, a low Henry's constant and volatilization from surfaces and water is negligible (Solomon et al. 1996). The moderate water solubility and small partition coefficients favor movement of atrazine in the dissolved state from treated soils into surface or subsurface waters (Solomon et al 1996). Triazines do not readily enter the body via dermal exposure, with the actual amount absorbed being one percent (Lunchick et al. 1998).

Triazines have been detected in the surface and ground waters in several use states. Detection of triazines in surface water follows a pattern of major peaks in agricultural field applications associated with spring planting. Studies by Ciba Giegy, conducted from January 1993 through December 1995, indicate the presence of atrazine and simazine in both surface and ground water sources of community water supplies. (Tierney et al. 1998) Other water quality monitoring studies have found atrazine 10 to 20 times more frequently than the next most detectable pesticide (Ribaudo et al. 1994).

The physio-chemical properties of triazines make them especially susceptible to leaching and surface runoff, especially during heavy rains. Triazines have a large potential for movement into a solution and only a moderate potential for soil sorption. These properties have resulted in the contamination of surface and ground waters. Agricultural cropland in the United States is heavily concentrated in the areas drained by the Mississippi River. From April 1991 through May 1992, approximately 365,700 kilograms of atrazine and its metabolites were transported into the Gulf of Mexico by the Mississippi River (Goolsby and Pereira 1995).

Toxic Properties of Triazine Pesticides

The metabolism of atrazine and simazine in the rat has been studied extensively. In a recent study with Sprauge-Dawley rats (Wu et al.1998) documents rapid absorption from the gastrointestinal system into blood circulation with, maximum whole blood concentration in two hours. The highest levels of triazine were found in the kidney, liver and red blood cells. Other tissue residues were low and there was no evidence of accumulation. The major degradation pathway for atrazine in rats is N-dealkylation, producing monodealkylated chloro-s-triazine. The routes of excretion are through bile, urine, and feces, with urine as the major route (Wu et al.1998).

The effects of 2-chloro-s-triazines on hepatic microsomal cytochrome P450 enzymes in rats have been reported (Haniola et al.1998). Cytochrome P450 enzymes are important catalyst in the degradation of toxins in the liver. Rats were treated intraperitoneally with Atrazine and Simazine to observe P450 activity. Testosterone 2 alpha-hydrolase (T2AH) in the rat associated with P450 CYP2C11 decreased after doses of atrazine and simazine. Oestradiol 2-hydroxylase (ED2H) activity was also decreased by both triazines tested. Simazine has been shown to induce P450 CYP 2C11 and CYP4A1/2 protein expression. These herbicides change the P450 isoforms in the rat liver, and these changes relate to the toxicity of triazines (Haniola et al. 1998).

A recent study of the identity of Phase 1 enzymes formed in human liver microsomes found a significant correlation between P450 CYP1A2 and the metabolism of triazines. Flavin containing monooxygenases (FMOs) were also evaluated for sulfoxidation reactions with thiomethyl triazine derivatives and exhibited no significant activities. Cytochrome P450

CYP1A2 is likely to be responsible for the majority if hepatic Phase-1 metabolism of triazines and its derivates in humans (Lang et al. 1997).

The toxicological properties of atrazine and its degradation products have been studied in mammals and aquatic organisms following the discovery of surface water contamination in many usage areas. Atrazine is rated as moderately toxic with a mammalian LD 50 of 3.0 grams per kilogram. The target organs for atrazine include skin, eyes, mucous membranes, respiratory systems, kidneys and liver. Chronic exposure to atrazine is currently an issue of importance due to the contamination of drinking water supplies by agricultural application sources. Atrazine has been shown to cause increased mammary tumors in female Sprague-Dawley rats in long term feeding studies. Atrazine has been reported to be more toxic than any of its degradation products formed in water. The final degradation product of atrazine, Cyanuric acid is less than half as toxic as the parent compound with a LD50 of 7.7 grams per kilogram (Pugh, K. C., 1994).

Epidemiological Studies of Triazine

Atrazine has been classified as a possible carcinogen by the United States Environmental Protection Agency. Recent research has demonstrated that triazines cause chromosomal damage to Chinese Hamster ovary cells when exposed to U.S. E.P.A. drinking water maximum contaminant level (MCL) of three parts per billion (Teats et al. 1998). Combinations of the most prevalent triazine herbicides (atrazine, simazine, and cyanazine), were also tested on CHO cells to determine synergy. No synergy was observed with combinations of the triazines. Chromosome damage was equal to or less than atrazine or simazine alone. These findings are significant because all three triazines are found in water supplies, with atrazine the most prevalent. Pesticides at low contamination levels have not been thoroughly studied. A potential human risk may be associated with herbicide contamination of drinking water supplies. If chromosomal damage is occurring in animal cell cultures, it could be possible these low levels also affect human chromosomes (Teats et al.1998).

A study of triazine exposure and breast cancer incidence by the University of Kentucky, College of Medicine examined exposure levels and breast cancer risk (Kettles et al. 1997). All 120 Kentucky counties were examined for triazine exposure from corn acreage, groundwater and surface water sample data. The counties were divided into three groups of low, medium and high exposure levels. Surface water detection of triazines, for both low and high exposure counties, was associated with an increased incidence of breast cancer. Contamination of groundwater showed less consistent results than that of surface water. The study concluded that the association between triazine and cancer is most apparent with drinking water contamination and less apparent with corn planting acres.

In a study of reproductive outcomes of farm couples in the Ontario Farm Family Health Study (Swift et al. 1997), data were collected concerning farm activities, reproductive experiences, and chemical exposure. Pre-term delivery was not strongly associated with farm chemical activities. Exposure to atrazine, glyphosate, organophosphates and other yard chemicals was associated with pre-term birth at an odds ratio of 2:1 (Swift et al. 1997).

While contamination of drinking water supplies by runoff from agricultural production has been detected with significant frequency in the United States (Fawcett et al 1992), the health risk's associated with the toxicity of pesticides found in drinking water has only recently been evaluated. Triazines are a frequently occurring pesticide contaminant in drinking water supplies. Triazines are not reported to be acutely toxic at the levels detected in drinking water supplies. The possible carcinogenic potential and deleterious reproductive effects reported at sub-lethal doses of triazines in animals and humans raises concern. Future research on the safety of exposure to triazines from drinking water is warranted as current literature is limited.

Best Management Practices to Reduce Pesticides in Surface Waters

Scope of Agricultural Non-Point Sources

Atrazine is one of the triazine herbicides with a water solubility (at 22ºC) of 70 milligrams per liter. It is relatively stable in the aquatic environment and degrades in soil by photolysis and microbial action. Studies show that herbicides with solubility similar to atrazine are transported in the dissolved phase (Solomon et al 1996). The amount of atrazine transported is a function of atrazine concentration and flow rate of water in the stream. Because atrazine is applied to farmland at or before spring planting and transported in spring and summer runoff there is a large seasonal variability in concentrations in surface waters. Higher levels of atrazine occur concurrently with periods of high stream flow and usually are highest immediately after application. Extreme inter annual variation in concentration can occur as a direct result of hydrologic events. A very wet year followed by a dry year will show large differences in the atrazine load carried by the stream (Pope et al 1997).

Triazine herbicides have the potential to leach into ground and surface water. Monitoring studies in the Midwest have shown widespread detection of herbicides in ground and surface waters. Thurman et al. (1991) assessed the levels of herbicide runoff in surface waters of the Midwestern states and identified several factors important to management decisions. This transport of herbicide occurs as pulses in response to late spring and early summer rainfall. Several herbicides, including atrazine, exceeded Safe Drinking Water Act maximum contaminant levels. Large loads of herbicides were flushed from crop land and transported in surface water systems in pulses in response to spring and summer rainfall events. Continuous monitoring for atrazine at one site showed that the MCL is exceeded after rainfall events. Persistence of herbicides in the waterways was also observed. Atrazine was detected in pre-plant and harvest samples, indicating that some parent herbicides as well as degradation products stay in the soil and water from year to year.

Intense use of pesticides in modern agriculture is cause for concern in the Mississippi River basin, where eighteen million people depend on surface water sources for drinking water (Goolsby et al. 1995). More than forty pesticides were detected in water samples from the Mississippi River or from the mouths of large rivers that flow into the Mississippi. Most of the transport of pesticides during this study occurred in May and June. For a period of several weeks during May through July concentrations of three herbicides (including atrazine), exceeded the maximum concentration levels mandated by the Safe Drinking Water Act. Goolsby et al.(1995) found a correlation between the solubility of a pesticide and the transport phase where it can be found, dissolved in water or adsorbed to sediment particles. Both phases originate from non-point sources that transported pollutants to surface waters.

Management Practices and Effects on Surface Water Contamination

Management practices to control soil loss have long been accepted practice in agriculture; soil conservation was recognized as vital for sustainable agriculture. In the twenty first century, agriculture will face challenges to survive in an economy of stationary commodity prices and rising production costs. Increased yields through scientific management are the most logical solution to economic viability in agriculture. The use of crop protection chemicals is vital to maintain production and the loss of some or all of these products due to environmental and health impacts are a real possibility. Management plans to reduce pesticide runoff into surface and ground water will become a new and challenging part of agriculture.

Management practices that reduce pesticides in surface water can be categorized into two broad groups; 1) product selection and efficient use, and 2) land, crop, and pesticide management. Fawcett et al.(1992) reviewed best management practice research and field studies that examine conservation tillage systems, filter strips, grass waterways, and other best management practices and found that all conservation practices reduced atrazine movement from the treated field, with no till practices as the most effective and ridge till planting the second most effective. Herbicide loss was also greatly reduced by the use of filter strips and grass waterways to slow and reduce runoff. This review also found that herbicide runoff was reduced by soil incorporation when crop production is not on highly erodible soils. These conservation practices also have the benefit of decreasing sediment transport into waterways.

Limiting the amount of pesticide applied to the minimum acceptable rate for adequate crop protection will proportionally reduce the contamination in runoff (Bengston et al. 1997). The authors compare the costs and benefits of banning a specific herbicide, limiting the use to post planting and a targeted ban to achieve surface water standards. Evidence from water monitoring indicates that the problem of herbicides, including atrazine, exceeding standards in drinking water treatment plants water is not widespread. It may be a more efficient policy to target only those areas where controls are necessary and offer farmers flexibility in pesticide management practices. This report demonstrated a problem with a chemical specific control strategy and increased use of another herbicide. Best management plans must consider both the target chemical and its substitutes.

Pesticides that are surface applied (not mixed with the soil,) are more susceptible to runoff. Incorporation of soil applied, herbicides, (mixing with the soil) can reduce runoff. This may be used as a management practice in combination with emerged weed control.

Timing of pesticide application can also affect pesticide run-off and losses are greatest when heavy rains follow application (Thurman et al. 1991). Applications to wet soils when heavy rain is likely should be avoided. While timing of heavy rain events cannot be precisely predicted, runoff risk for specific areas can be estimated from historical runoff data.

Analysis of data from other watersheds with similar pesticide runoff problems can be a useful tool to direct sampling protocol and basin management decisions. Small scale studies and demonstrations would help tailor management decisions to the individual watershed and basin.

Implementation of Best Management Practices

Bennett (1994) examined case studies prior to the mandate of TMDLs. In Wisconsin, a non-point source abatement grant program was started in 1978 in response to the realization that a large part of the state's economy is related to the recreational use of its water resource. In this program, the state paid for the cost of an electric fence to keep cows two hundred and fifty feet from creeks. Approximately thirty percent of the farmers participated while the rest continued to allow cows access to the streams. Recently, Wisconsin's Non-point Source and Soil and Water Resource programs, based on best management practices, changed the practices on thirteen hundred farms reducing sediment, pesticide and nutrient transport. This study demonstrated that some farmers could be persuaded to change practices and become more environmentally friendly.

Based on observations by Ohlmer et al. (1998), the farmer's decision process can be divided into four phases; problem detection, problem definition, analysis and choice, and implementation. Four sub processes are also identified by this study; searching and paying attention, planning, evaluating and choosing, and checking the choice. Farmers also prefer to continually update their evaluation in a qualitative manner, with a small test and incremental implementation, then focusing on compensation rather than post implemental evaluation. These results indicate that farmers are comfortable making changes that are understandable, proven or likely to be successful, and rewarded by compensation. This decision process is key to designing programs to change years of traditional practice (Ohlmer et.al.1998).

Providing incentives to encourage watershed protection by changing production methods has been studied (Farrell, 1996). Farmers in upstate New York in 1990 undertook practices to protect the quality of the city's drinking water. The New York Department of Environmental Protection proposed rules and regulations for the protection of the New York City water supply. The regulations would have placed restrictions on the farms in the Catskill/Delaware watersheds by not allowing their animals or storm water runoff to enter watercourses. Debate on the proposed rules led to the Department of Agriculture and Markets to act as a facilitator between farmers and city officials. The farmers wanted a locally managed, voluntary program that would be funded by the city. Whole farm planning/best management practices were developed to be individually fitted to farms to eliminate the release of contaminants at their sources, reduce runoff and prevent contaminants from entering watercourses. The city agreed to fund this project with forty million dollars, an average of seventy-five thousand per farm, for pollution control improvements. This New

York program could serve as a model for cooperation between urban and rural communities on water quality issues.

Surface Water Standards and Treatment Technology

Weekly sampling results of raw and treated water samples collected at Iberville Water District Number Three treatment facility by Louisiana Department of Agriculture revealed samples with atrazine in excess of single sample EPA Maximum Contaminant Levels of three parts per billion (LDAF 1998). The Safe Drinking Water Act requires additional treatment to lower atrazine below MCL'S using Best Available Technology (BAT). Currently BAT for pesticide removal designated by the EPA is granulated activated carbon.

Granulated activated carbon (GAC) has been shown to reduce atrazine to below detection limits. This treatment involves capital investment in new equipment (replacement of filter bed) but offers other benefits in removal of taste, and odor, and provides continuous control. This may be the best choice for plants experiencing routine exceedence of MCL's for atrazine. Powered activated carbon is another treatment option that may be considered. This system injects the PAC during water treatment and does not require the large capital investment of GAC. The low cost and ability to treat only when needed makes this system feasible for water suppliers facing seasonal herbicide problems (Thurman et al. 1991).

Ribaudo and Bouzaher (1994) reported that eleven public water supplies in the Midwest could need additional treatment to meet the atrazine MCL. The initial cost for additional treatment systems for these eleven suppliers a total of 8.3 million dollars annually. Additional costs to operate and maintain these systems were estimated to be 180 thousand dollars per year. These water systems supply 36 thousand people. Per-capita cost for GAC treatment would be 229 dollars per year. Using PAC treatment as needed instead of GAC could reduce treatment cost.

The literature on non point source pollution addresses issues important to the current debate over surface water contamination. Surface water runoff from agricultural operations has added a major burden to the streams and rivers of North America. Special concern for compliance with the Safe Drinking Water Act has focused on the previously unregulated non point source pollution produced by agriculture. The Mississippi River basin carries large loads of herbicides flushed from farm fields by rainfall (Goolsby and Pereira 1995). These factors have led to new regulations on water quality that will affect future agricultural production methods by mandatory or voluntary means. A workable system of best management practices have been proposed researched, and analyzed over the last decade (Ribaudo and Bouzaher 1994).

Previous research has focused on soil and water conservation as vital components for sustainable agriculture. Management practices that reduce pesticides (herbicides) and nutrient contamination in surface waters are currently a top priority in environmental compliance. Research specific to contaminant runoff has demonstrated that cost efficient methods are possible with small changes in current practices. Current research illustrates that traditional conservation practices are effective in reducing contaminant movement (Fawcett et.al.1992). The reduction of pesticide inputs to levels that maintain yields is also a viable option for pollution reduction as part of best management practices (Bengston et.al.1997).

Agricultural researchers are currently developing these combinations of practices for specific crops, areas, and environmental risks to meet the new challenges of water quality protection.

The method of implementation of new farming practices to reduce water contamination is now the question at hand. Mandatory methods used to regulate point source pollution may be difficult to adapt to non point source pollution. The common pool nature of watersheds would make individual monitoring of farms very difficult. Agricultural production practices are highly adaptive to individual decisions and management skills. The voluntary adoption of best management practices to improve water quality by agricultural producers currently appears to be a logical solution to non point source pollution.

Research indicates that a farmer’s decision making process follows logical phases from problem detection to implementation and involves their planning and evaluation. The end result of the farmer’s decision making process is directed to making changes that are understandable and lead to success rewarded by compensation (Ohlmer et.al. 1998). The economics of a modern agriculture focus a producer’s decisions toward maintenance of a sustainable cash flow. The use of incentives to help farmers convert to environmentally friendly practices has increased participation in case studies. Funding by parties who are dependent on the watershed for drinking water could be an approach to water quality compliance (Farrell, 1996).

METHODS

Sample Data

In February 1995, the Louisiana Department of Agriculture and Forestry (LDAF) began a voluntary Atrazine Water Monitoring Program in association with Ciba Geigy Crop Protection. The purpose of this atrazine monitoring was to gather data for Ciba's re-registration requirements as mandated by a 1994 Environmental Protection Agency notice of initiation of special review.(E.P.A. 1994) The Ciba / LDAF Atrazine Monitoring Program included water treatment facilities located in Jefferson, Lafourche, and Iberville Parishes. Samples of finished and raw water were collected on predetermined dates and submitted to Ciba Geigy's laboratory for analysis of triazine compounds. In 1995 and 1996, LDAF collected duplicate samples on a quarterly basis and analyzed these samples at the Louisiana State University Agricultural Chemistry Laboratory. Beginning in 1997, LDAF collected duplicate weekly samples at the Iberville Water District #3 treatment facility, analyzed by LDAF-LSU Agricultural Chemistry Lab and Ciba. The samples collected for LDAF were analyzed for atrazine concentration by gas chromatography (EPA method 507). The samples submitted to Syngenta (formerly Ciba Geigy) were analyzed by immuno- assay method and are not used in this paper.

The LDAF and the Louisiana Department of Environmental Quality initiated a joint sampling program of the surface waters of the Upper Terrebonne Basin (UTB) in 1998. This UTB sampling was a result of initial LDAF sampling that revealed atrazine levels well in excedence of the Safe Drinking Water Act MCL of 3 parts per million at Iberville Water District #3. Sampling occurred weekly during the traditional atrazine use period of March, April, and May. Sampling frequency for the winter months was biweekly and monthly when Atrazine is traditionally not applied.

Surface water samples were collected in major and minor streams at 30 sites by LDEQ in 1998. In 1999, LDEQ collected surface water samples from 8 sites in the basin. In 2000 LDAF collected surface samples from 8 sites and in 2001, 6 sites were sampled in the Upper Terrebonne Basin. Samples. These sites in these years were analysed by the Louisiana State University Agricultural Chemistry Laboratory (EPA Method 507). Table 1 provides a summary of all atrazine monitoring used in the present study.

Data were analyzed for six stream locations within the Upper Terrebonne Basin to determine spatial variation in atrazine concentrations for the period of 1998 through 2001. The locations studied were Station 1 on Bayou Grosse Tete, Station 17 on Bayou Choctaw, Station 24 on the Intracoastal Waterway, Station 25 on Bayou Plaquemine, Station 28 at intake of Iberville Water Facility, and Station 35 on Bayou Maringouin. Rainfall data for New Roads, Port Allen, Brusly, Plaquemine, and Port Barre were assigned to each stream station by proximity using ArcView Geographical Information System. (Table 1) (Figure 1)

Environmental data for the period of atrazine Monitoring were obtained from several agencies with monitoring sites in and near the UTB. The United States Geological Survey maintains a stream flow data station at Bayou Grosse Tete at Rosedale Louisiana (D07381440), with flow measurements reported as mean daily discharge in cubic feet per second. Daily streamflow data were obtained from Bayou Grosse Tete, Rosedale stream flow station in located approximately in the center of the UTB drainage area via the USGS website (www.la.waterdata.usgs.gov) for the period. Daily rainfall data were obtained from the Southern Regional Climate Center, Louisiana Office of State Climatology. Rainfall (inches) from stations in New Roads, Port Allen, Brusly, and Plaquemine. The R and D Research Farm located west of the basin in Port Barre collected rainfall data that were reported by the Louisiana AgriClimatic Information System.

Crop acreage data were obtained from the Louisiana Summary of Agriculture and Natural Resources, published by Louisiana State Agricultural Center. Annual accounting of the acreage of agricultural commodities is reported in this summary. The major agronomic crops of the Upper Terrebonne Basin include sugarcane, corn, soybeans, and cotton. The acreage of major crops planted in the UTB was compared for the years 1997–2001 (Figure 3).

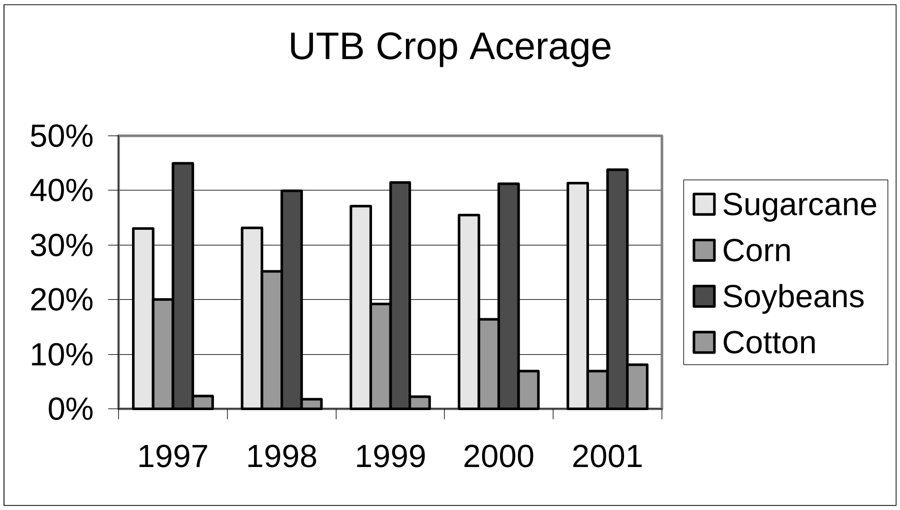
Data Analysis

The LDAF sample data were sorted and merged with daily stream flow and rainfall data. The Iberville Water District Number Three raw and finished water data (response) were merged with the stream flow data (regressor). The Upper Terrebonne Basin stream site atrazine concentration data were merged with streamflow and rainfall data. Atrazine concentrations were transformed to the $\log_{10}$ scale. A value of .009 was added to the weekly rainfall sums before transforming to a $\log_{10}$ scale. The .009 was added to the weekly rainfall to avoid creation of missing values by the $\log_{10}$ transformation. All regression variables were then standardized to have a zero mean before further analysis.

Finished water atrazine concentration, raw water atrazine concentration and UTB stream atrazine concentration data were analyzed using Bayesian Analysis Time

Table1. UTB Surface Water Monitoring History (LDEQ 1998) (LDAF 2001)

UTB Surface Water Monitoring			Sample	Year	
Location	Site Number	1998	1999	2000	2001
Bayou Grosse Tete at Hwy 77 and Hwy 190	1	**X**	**X**	**X**	**X**
Bayou Fordoche at Hwy 77 and Hwy 190	2	**X**			
Bayou Tommy at Hwy 190 in Lovinia	3	**X**			
Bayou Sterling at Hwy 1 and Hwy 190	4	**X**			
Bayou Cholpe at Hwy 1 and Hyw 190	5	**X**			
Drainage Canal at Hwy1 and Hwy 190	6	**X**			
Bayou Poydras at Hwy 143 and Hwy 190	7	**X**			
Drainage Canal at Hwy 190 and Erwinville	8	**X**			
Bayou Stumpy at Hwy 383 and Hwy 190	9	**X**			
Drainage Ditch at Hwy 383 and Hwy 190	10	**X**			
Unnamed Canal at Hwy 383 and Hwy 190	11	**X**			
Bayou Chalpin at Hwy 76 and Hwy 383	12	**X**			
Unnamed Canal at Hwy 76 in Rosedale	13	**X**			
Bayou Grosse Tete at Hwy 76 in Rosedale	14	**X**			
Bayou Maringouin at Hwy 76 and Hwy 3000	15	**X**			
Bayou Maringouin at Hwy 76 and Hwy 77	16	**X**			
Bayou Choctaw at I-10, 12 mi. east of B.R.	17	**X**	**X**	**X**	**X**
Johnson Canal at Bayou Choctaw	19	**X**			
Unnamed Canal at Intra Coastal Waterway	20	**X**			
Bayou BourbeauX at northwest of Hwy 1148	22	**X**			
Wilbert Canal at Hwy 1148	23	**X**			
Intra Coastal Waterway at Hwy 77	24	**X**	**X**	**X**	**X**
Bayou Plaquemine at Hyw 3066	25	**X**	**X**	**X**	**X**
Intra Coastal Waterway at Port Allen	26	**X**			
Portage Canal at Hwy1 in New Roads	27	**X**			
Intake at Iberville Water District Three	28	**X**	**X**	**X**	**X**
Borrow Ditch south of I-10	29	**X**			
Portage Canal at Hwy 78	30	**X**			
Light House Canal at Hwy 1 at False River	31	**X**			
Grand River at Intra Coastal Waterway	32	**X**			
Unnamed Ditch at I-10 east of Rosedale eXit	33		**X**	**X**	
Bayou Grosse Tete at Hwy 77 at Maringouin	34		**X**	**X**	
Bayou Maringouin at I-10	35		**X**	**X**	**X**



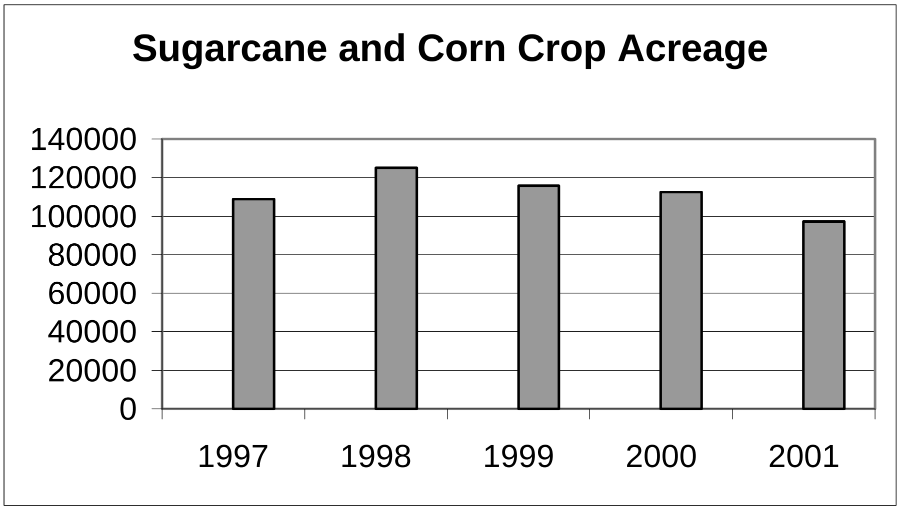


Figure 2: Upper Terrebonne Basin Crop Acreage and Distributions (LSU Ag Center 2001)

Series, Dynamic Linear Models to identify and estimate models providing the best predictive performance, as measured by cumulative log likelihood. Bayesian Dynamic

Linear Models were fit and selected for the Upper Terrebonne Basin stream data with the same methods utilized with the Finished and Raw water data. (Pole et al 1994).

Table 2. Atrazine Sales in the Upper Terrebonne Basin (LDAF 2001)

Upper Terrebonne Basin Atrazine Sales Survey	1997	2001
RUP Pesticide Dealer	Atrazine LBS. A.I.	Atrazine LBS. A.I.
Farmers Feed Mill (New Roads/Maringouin)	37,836	45,547
Feed Service Inc. (New Roads)	21,282	27,000
Helena Chemical (New Roads)	36,460	58,725
Tri-State Delta (UAP Midsouth) (New Roads)	74,433	54,446
White Castle Fertilizer Coop.* (White Castle)	25,928	33,059
Total	195,939	218,797
Percent Increase / 1997	11.67%	

* Includes some sales to producers below the Iberville Water Distict #3 intake.

Time series data consist of observations collected sequentially over time. Order is irrelevant to a standard (static) regression model, however it is crucial to a time series model. Actions at some time have consequences and effects that are experienced at some other time. Dynamic linear models allow parameter values to change as time passes. Additional information in sequential time increases the knowledge of this system. The passage of time imparts a loss in the value of the knowledge gained by the model. Allowance for variable parameter values is made in a dynamic model, allowing changes in the relationships between variables (Pole et.al.1994).

Model specifications investigated included both a constant or linear trend for the response variable, atrazine. Next a seasonal component (first harmonic) with a period of

52 weeks was added to the trend models. A stream flow regressor was added to the models. The stream flow volumes were transformed into $\log_{10}$ scale and standardized to have a mean of zero for this analysis. The last components evaluated in these models were discount rates associated with the trend variable. The information aging process is modeled by the DLM by adding uncertainty with the passage of time. Informational loss is expressed in terms of increased uncertainty. The discounting process is a way to think about the information aging effect and is independent of the scale of the observation. Useful discounts are not much less than 0.8, smaller discounts lead to models that make predictions based on only the 2 or 3 most recent observations. (Pole et.al. 1994)

Model selection is based on forecast performance; BATS provides the cumulative log likelihood for each model tested. The Bayes factor is a ratio of the log likelihood of two competing models and priors for each model will cancel if they are the same. The fit of models presented are in terms of $\log_{10}$ likelihoods, with a difference in $\log_{10}$ likelihood of 1 (-1) between competing model specifications considered evidence for (against), and a difference of 10 (-10) is considered strong evidence for (against), the competing model. (Jeffreys, 1961)

Next, the selected DLM's, were used for a retrospective analysis. Combining information from later observations with the earlier observations produces smoothed estimate of model parameters, of the analysis reducing uncertainty (Pole et.al. 1994). The smoothed atrazine concentration level, when combined with the smoothed regression effect produces a plot of fitted values for $\log_{10}$ atrazine concentration. BATS also estimates a 90% credible interval about the parameter estimates and retrospective fit, representing both observation and model parameter uncertainty.

RESULTS

Iberville Water District Number Three

The model selected for the finished water $\log_{10}$ atrazine concentration data consisted of a constant trend with a discount rate of .85 and a $\log_{10}$ streamflow regressor. The finished water $\log_{10}$ atrazine model had a log likelihood difference greater than 10 indicating strong evidence for the selected model (compared to the simple trend model). The selected raw water $\log_{10}$ atrazine model has a constant trend and a streamflow regressor and a log likelihood difference was greater that 10 compared to the simple trend model (Table 3). The finished water data responded to a smaller discount (less memory) in the trend component, possibly indicating more variability in the trend due to periodic attempts to treat with activated carbon.

Fitted values for finished Water at Iberville Water District Three Facility exceed the 3ppb MCL for atrazine in the first quarter of 1997, the first quarter of 1998, and the first quarter of 2001. Raw water fitted values followed the same pattern as finished water, exceeding the MCL in 1997, 1998, and 2001. The standard filtration and periodic activated carbon treatment appear to have had little effect on the concentration of atrazine at the Iberville Water District Three Facility. When overlaid, the fitted retrospective values of finished and raw water models indicate similar concentrations. The stream flow effects appear to be proportional to the fitted values in both finished and raw $\log_{10}$ atrazine level as expected. Stream flow is the transport mechanism for atrazine to reach the water treatment facility after rain events. The fitted values for atrazine concentration are near the 3ppb MCL from beginning to end of the time series (Figure 4).

Table 3. Summary of the model selection process using cumulative log likelihood for finished and raw water. Response variable is atrazine concentration ($\log_{10}$ ppb), streamflow regressor is streamflow (standardized,$\log_{10}$ cfs). **Bold is selection.**

Model Parameters:	**Finished Water**	**Raw Water**
Constant trend	-107.88	-81.583
Linear trend	-106.66	-86.521
Constant trend, one harmonic cycle	-102.29	-82.901
Constant trend, streamflow regressor	-85.094	**-66.294**
Constant trend, .85 discount streamflow regressor	**-83.197**	-66.288
Constant trend, .80 discount streamflow regressor	-82.298	-66.087

The regression coefficients of DLM's are not constant through time, they are influenced by a system variance that changes with time. Changes in the regressor coefficients indicate variations in the underlying process of the streamflow versus atrazine concentration relationship over time. The stream flow coefficients for the raw water model are positive and tend to be constant over time (Figure 5).

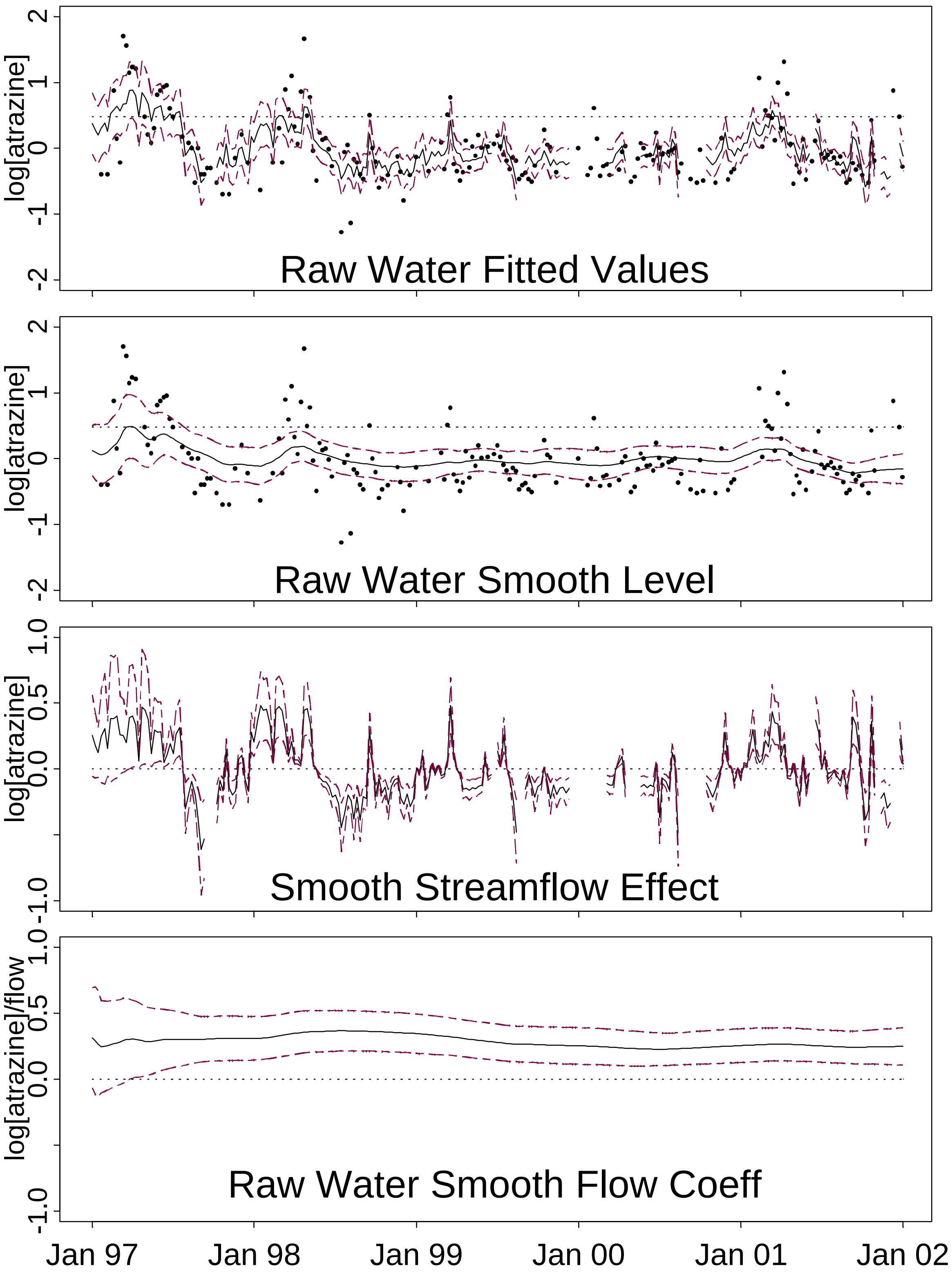


Figure 3. Log$_{10}$ Raw Water Model, dotted line in the fitted and level view is 3ppb atrazine MCL, dashed line is 95% and 5% credible interval.

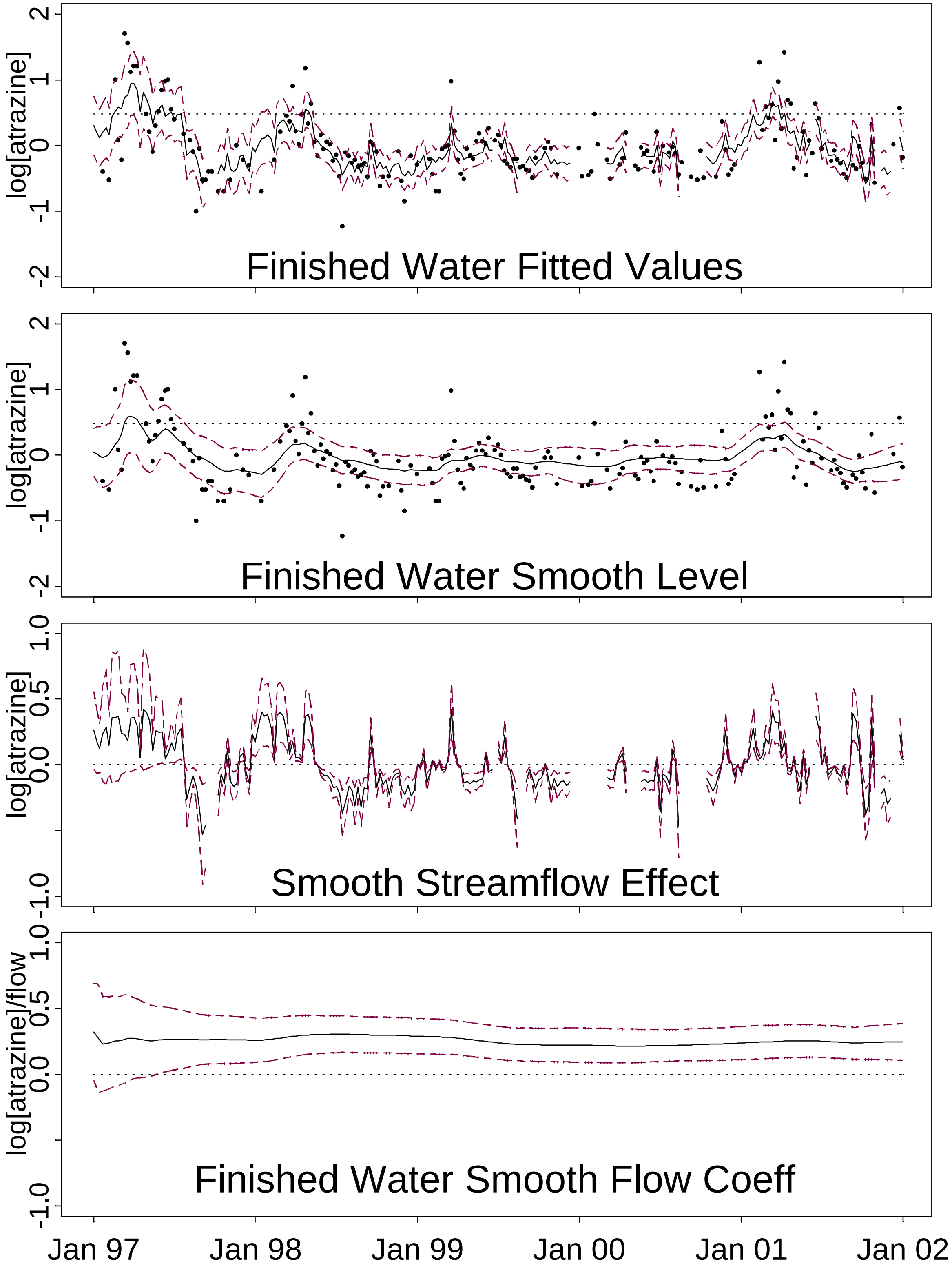


Figure 4. Log_{10} Finished Water Model, dotted line in the fitted and level views is 3ppb atrazine MCL, dashed line is 95% and 5% credible interval.

Forecast levels of $\log_{10}$ atrazine concentration may also be estimated by the DLM. Extending the time frame of the model into the future and setting a level of stream flow produces a forecast atrazine level. The probability of exceeding the 3ppb level can be calculated from the forecast distribution. This information could be used to determine the timing of additional treatment of water with activated carbon to meet the SDWA 3ppb MCL for atrazine (Figure 4).

The summary of crop acreage and distribution (Figure 3) in the UTB indicate an increase of crop acreage from 1997 to 1998 then a decreasing trend to 2001. The distribution of major crop acreage in the UTB begins in 1997 with 55% in corn and sugarcane and ends with 48% in corn and sugarcane. Overall the acreage of crops that can utilize atrazine has decreased by 12 percent for the time series. Conversely the amount of atrazine sold in the UTB (Table 2) has increased by 12 percent from 1997 to 2001. The amount of atrazine sold in 2001 was 218,797 pounds of active ingredient, compared to 93836 acres planted to corn and sugarcane. The rate of atrazine used in the UTB in 2001 would be 2.3 pounds of A.I. per acre of corn and sugarcane planted and within labeled rate of application.

Upper Terrebonne Basin Stream Sites

DLM's were fit to atrazine data from six sites located on the major streams that provide the water source for Iberville Water District Number Three (Table 4). The retrospective (smooth) $\log_{10}$ atrazine fitted values from the six sites can be compared to evaluate differences in concentrations from these sub-basins.

At Site 1, $\log_{10}$ atrazine concentration data, the model selected consisted of a constant trend with a discount rate of .90 and a $\log_{10}$ streamflow regressor. The Site 17 $\log_{10}$ atrazine model had a constant trend with a discount rate of .80 and a $\log_{10}$ streamflow regressor.

Model selection for Sites 24, 25, and 28 models selected have constant trends with .90 discount rates and a $\log_{10}$ streamflow regressor. The Site 35 selected model had a constant trend with a discount rate of .80 and a log10 streamflow regressor. All of the selected models with a constant trend and a streamflow regressor and had a log likelihood difference was greater that 10 compared to the simple trend model (Table 4), indicating strong evidence in favor of addition of the streamflow regressor.

Site 1 and Site 17 fitted values stayed near the 3ppb threshold, both sites exceeding 3ppb in the spring of 1998, 2000, and 2001 (Fig. 6,7). Sites 24 and 25 mean fitted values for the time series that were below the 3ppb SDWA MCL with the exception of spring 1998.(Fig.8,9) Site 28 is at the confluence of the UTB stream system at the Iberville Water District Number Three intake. Site 28 has fitted values very similar to the raw water data staying near the 3ppb limit (Fig10). Site 35 displayed the largest mean fitted values the basin with periods above the 3ppb MCL in 1999, 2000,and 2001.(Fig.11)

Fitted values of $\log_{10}$ atrazine followed similar patterns to the smooth levels but were slightly higher in scale. The fitted values also demonstrate the relationship of stream flow on concentration as proportionately correlated in a constant trend. Once again stream flow is the transport mechanism for atrazine concentration in the surface waters of the UTB.

The regression coefficients from the stream models can illustrate changes in the system that causes atrazine concentrations in the UTB waters. The stream flow coefficients for the six UTB stream sites are positive and slightly decline over the time series. This may indicate that some change in the system is causing stream flow to have less effect of atrazine concentration.

Table 4. Summary of model selection process using cumulative log likelihoods for stream sites. Response variable is atrazine concentration (log$_{10}$ ppb), rainfall regressor is weekly rainfall plus .009 (log$_{10}$ inches), streamflow regressor is streamflow (log$_{10}$cf/s), **Bold is selection.**

Model Parameters:	Site1	Site17	Site24	Site25	Site28	Site35
Constant trend	-81.593	-65.006	-43.377	-26.432	-39.474	-66.120
Linear trend	-86.521	-63.160	-46.178	-26.869	-43.799	-65.462
Constant trend, one harmonic cycle	-82.901	-54.820	-51.831	-23.376	-46.067	-64.656
Constant trend, rainfall regressor	-84.160	-67.770	-44.017	-27.038	-39.098	-67.639
Constant trend, lagged rainfall regressor	-83.450	-67.379	-44.296	-25.632	-40.600	-64.690
Constant trend, streamflow regressor	**-72.239**	-54.457	**-34.365**	**-13.384**	**-29.750**	-63.467
Constant trend, .85 disc streamflow regressor	-71.927	-51.605	-34.541	-13.281	-29.994	-61.555
Constant trend, .80 disc streamflow regressor	-71.580	**-49.508**	-35.019	-13.241	-30.209	**-60.133**
Constant trend, one harmonic cycle streamflow regressor		-57.730		-24.800		-64.855
Constant trend,.85 disc one harmonic cycle streamflow regressor		-52.750		-18.234		-67.956

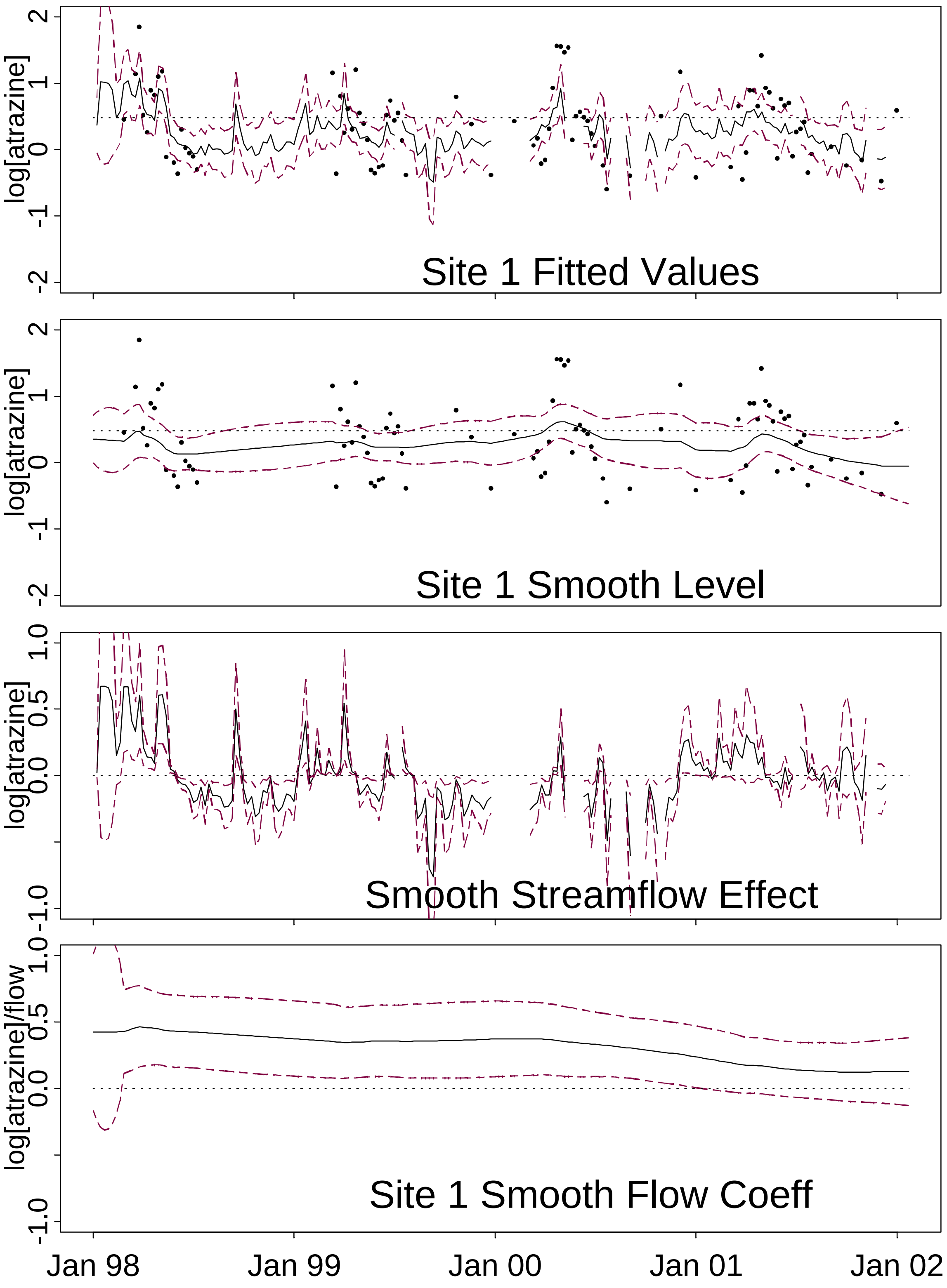


Figure 5. Log$_{10}$ Site 1 Model, dotted line in the fitted and level views is 3ppb atrazine MCL, dashed line is 95% and 5% credible interval.

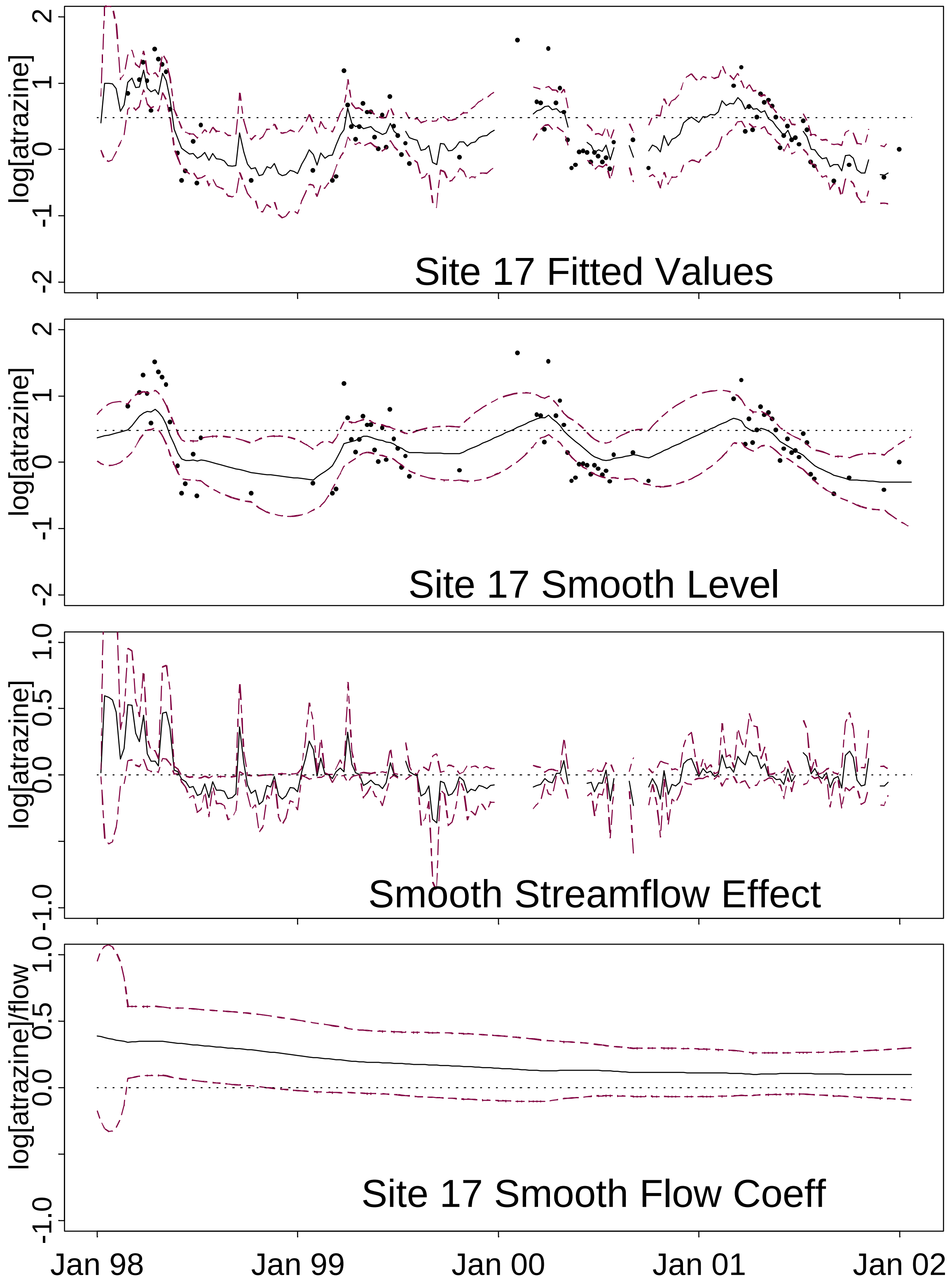


Figure 6. Log_{10} Site 17 Model, dotted line in the fitted and level views is 3ppb atrazine MCL, dashed line is 95% and 5% credible interval.

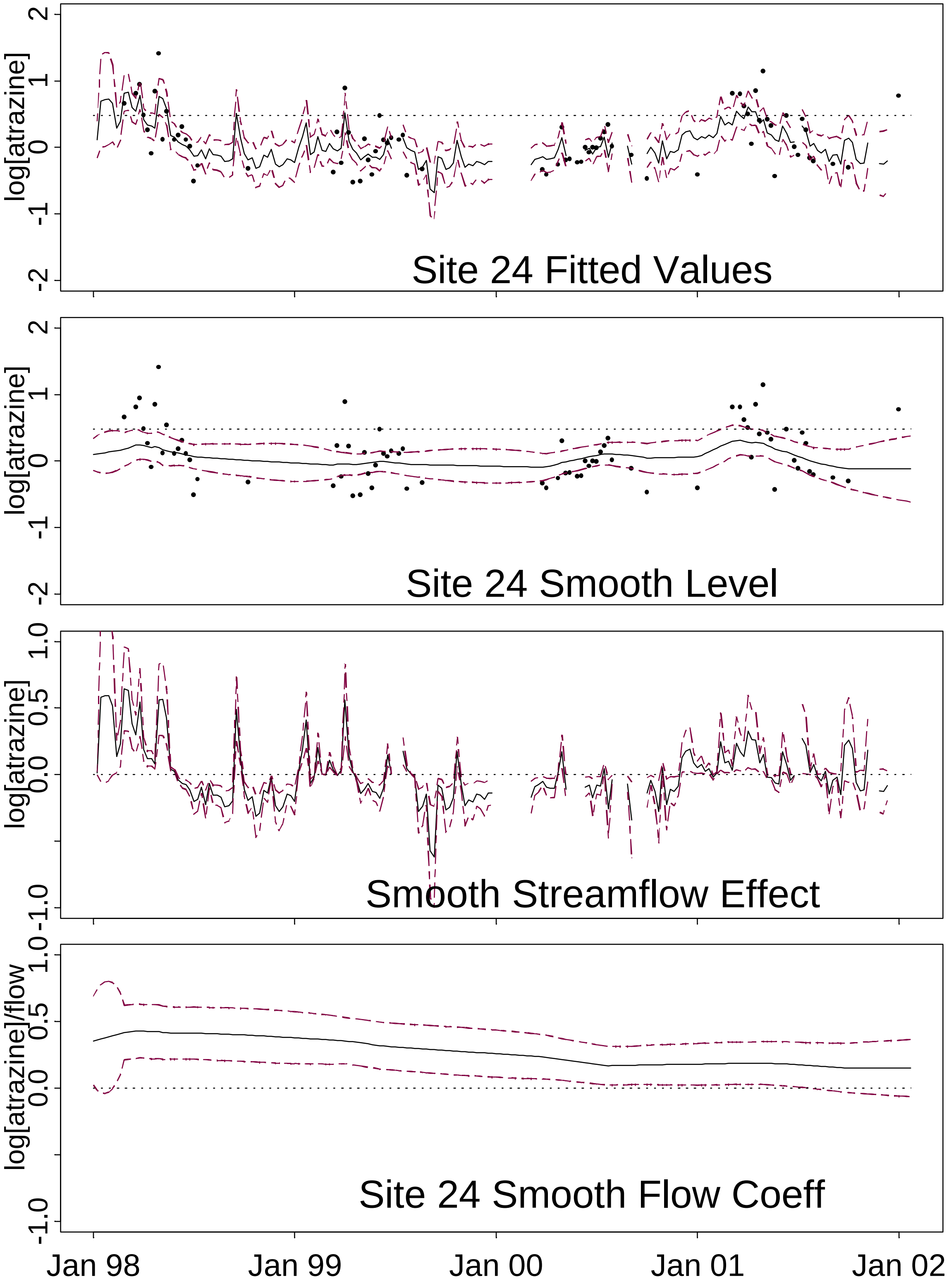


Figure 7. Log$_{10}$ Site 24 Model, dotted line in the fitted and level views is 3ppb atrazine MCL, dashed line is 95% and 5% credible interval.

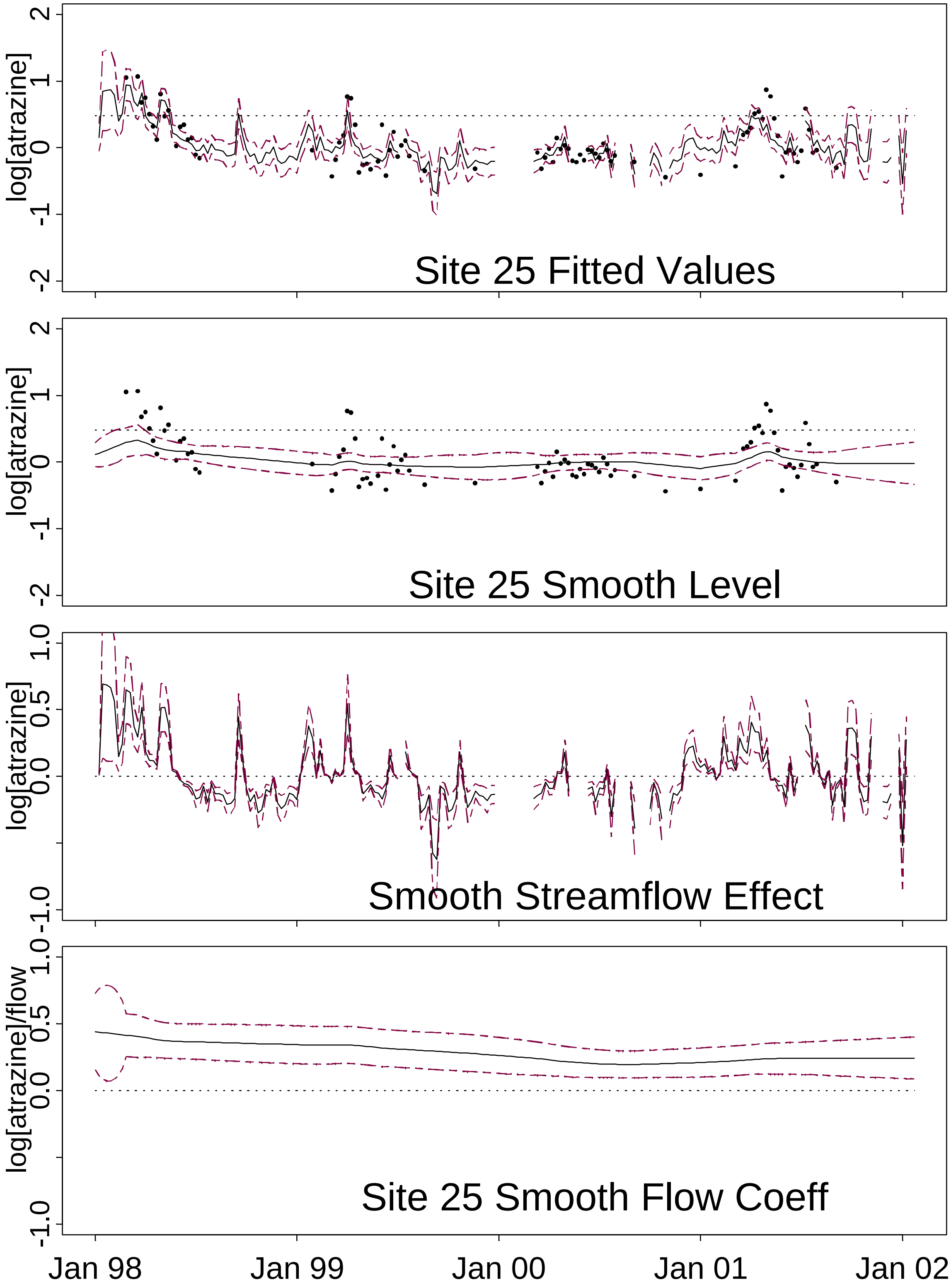


Figure 8. Log$_{10}$ Site 25 Model, dotted line in the fitted and level views is 3ppb atrazine MCL, Dashed line is 95% and 5% credible interval.

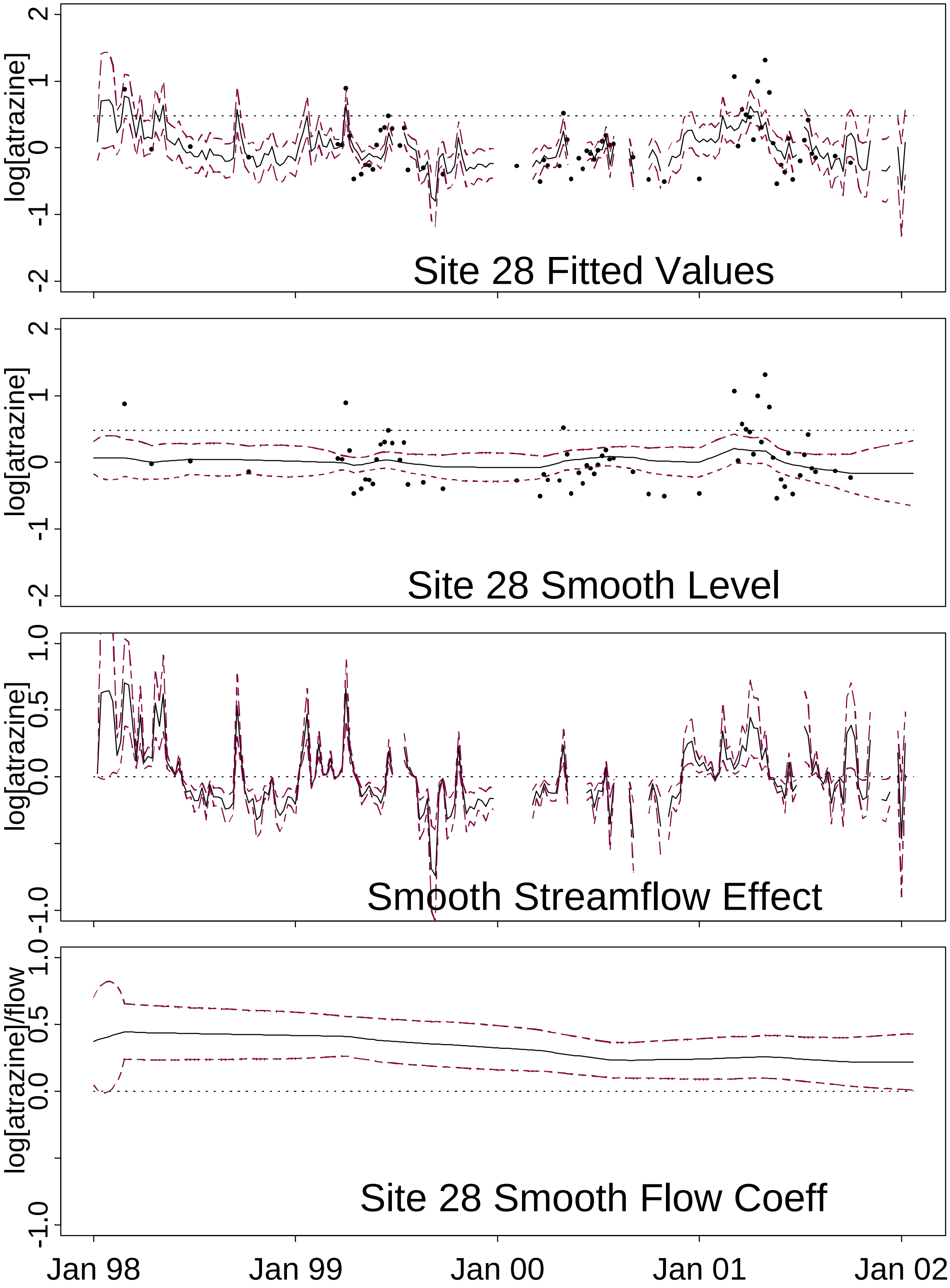


Figure 9. Log_{10} Site 28 Model, dotted line in the fitted and level views is 3ppb atrazine MCL, dashed line is 95% and 5% credible interval.

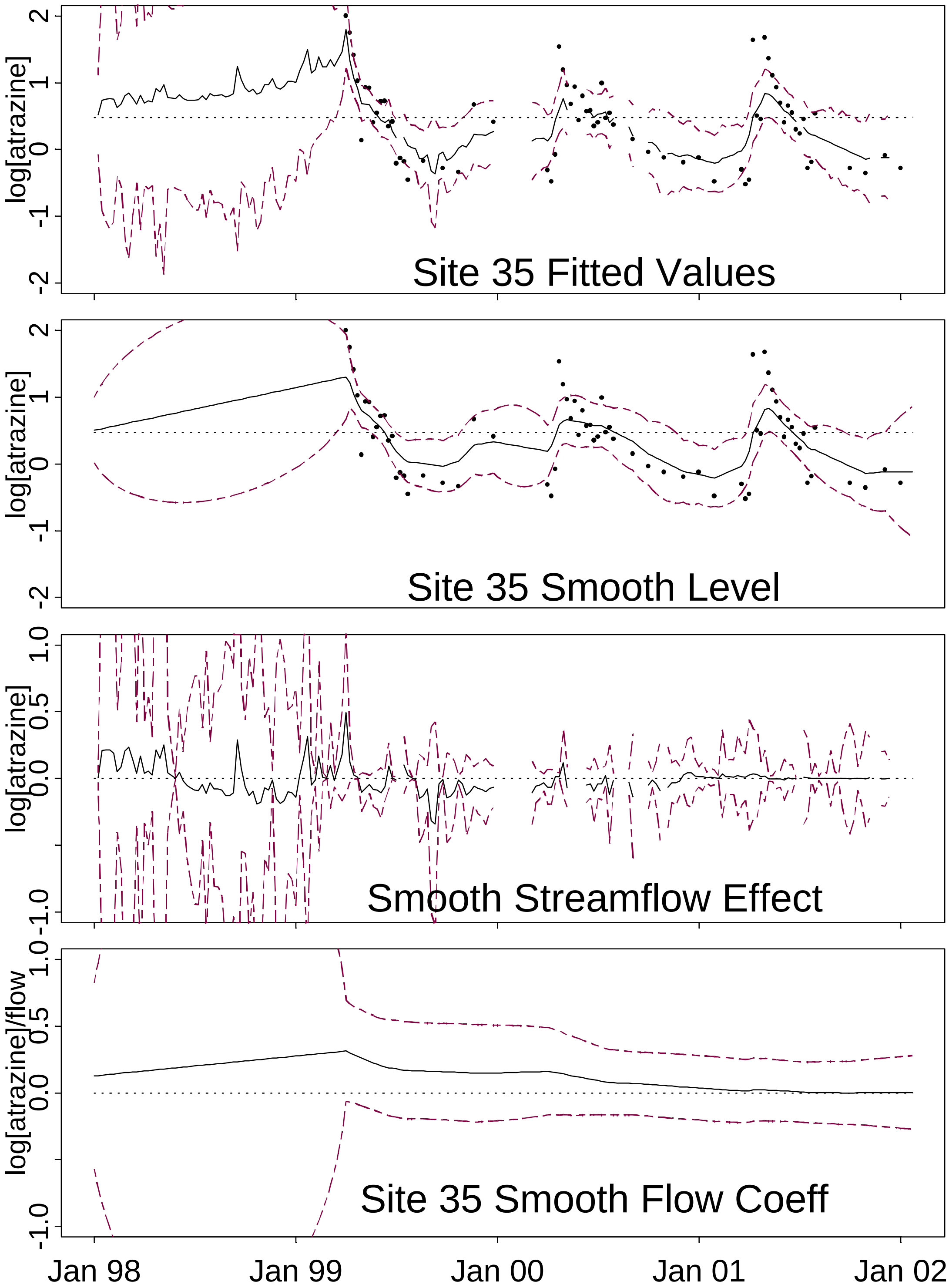


Figure 10. Log_{10} Site 35 Model, dotted line in the fitted and level views is 3ppb atrazine MCL, dashed line is 95% and 5% credible interval.

DISCUSSION

The Louisiana Department of Agriculture and Forestry has been involved in the monitoring of atrazine concentrations in the waters of the Upper Terrebonne Basin since 1995. This monitoring began as a study initiated by the manufacturer of atrazine, Syngenta Crop Protection. Samples of surface water from the UTB, along with finished and raw water from Iberville Water District Number Three will be collected for the foreseeable future, as the controversy over health and environmental effects of Atrazine are debated. The use of the Dynamic Linear Model as presented in this study is an approach to evaluate existing knowledge of Atrazine concentrations in the UTB.

Streamflow of the tributaries within the closed geography of the UTB is the transport mechanism for atrazine to reach the Iberville Water District Number Three treatment facility. Evaluation of the model components available in this study verified the relationship between streamflow and atrazine concentration. The regression coefficient estimates of streamflow on concentration offer an indication of slight changes in this relationship, as the DLM allows parameter estimates to evolve through time based on prior and current information (Lamon et.al. 1998). The flexibility in model parameters is useful when the time series is evaluated for changes.

The goal of LDAF and Louisiana State University Ag Center has been to reduce atrazine concentrations in the UTB. The levels of atrazine in the streams of the UTB and the water received by and treated by Iberville Water District Number Three have changed, but the analysis indicates this is due to changes in streamflow for the period of 1997 to 2001. The trend in the regression coefficient estimates of the raw water from Iberville Water District Number Three indicates little change in the relationship of concentration and streamflow though time. These changes are slight between the years 1998 and 1999, but almost zero from 1998 to 2001. The relationship of streamflow as a predictor of atrazine concentration is evidence in support of runoff as a source of atrazine to the streams.

Best management practices to reduce atrazine concentrations in the waters of the UTB have been promoted since February 1998 by the LSU Ag Center. The practices suggested included methods to limit runoff following applications, reduced application rates, and alternative herbicide selection. Surveys in the UTB indicate that more atrazine has been sold for use on fewer crop acres at the end of the time series, without a significant increase in water concentrations. Perhaps farmers are now more cautious with the application of atrazine and the increased usage has not caused concentrations to increase, or the timing of applications with respect to streamflow has changed.

The models developed in this study could be useful for management of activated carbon treatment for Atrazine mitigation at Iberville Water District Number Three. Model forcasts distributions may be made using streamflow, and odds of MCL exceedence calculated with these models. Treatment could be initiated when odds exceeded “acceptable” limits, to be determined based on treatment cost balanced against health effects.

Future issues facing the atrazine users and drinking water consumers will be driven by several environmental statutes and decisions from regulatory agencies. On January 31, 2003 the United States Environmental Protection Agency, Office of Prevention, Pesticides, and Toxic Substances released an “Interim Reregistration Eligibility Decision for Atrazine” (IRED)(U.S.EPA, 2003). The Agency’s decision on the individual chemical atrazine included the health mitigation of dietary drinking water. The IRED identified community water systems (CWS) of concern that have exceeded 12.5 ppb for at least one 90 day period since

1993. The Iberville Water District Number Three is one of the thirty-four CWS of concern identified by the IRED. Beginning in January 2004 the registrants of atrazine are required to begin intensive monitoring and written mitigation plans for eight of the CWS's of concern including Iberville Water District Number Three. The mitigation plan will describe measures to be implemented and a strategy for communication with growers and quarterly progress reports. A 37.5 ppb atrazine concentration (as a ninty-day average) has been set as a trigger for banning the use of atrazine in an intensively monitored watershed.

The Safe Drinking Water Act (SDWA) is still in force for the Iberville Water District Number Three. The maximum contaminant level of 3 ppb for atrazine is a threshold for watershed controls including the ban of atrazine. Future regulations for non-point source pollution control, Clean Water Act section 319, include the Total Maximum Daily Load of atrazine. The TMDL for atrazine will be yet another compliance issue in the Upper Terrebonne Basin.

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APPENDIX

Iberville Water District Number Three data, raw and finished water 1997-2001. Atrazine concentration in ppb. Bayou Grosse Tete at Rosedale streamflow in cubic feet per second.

Week	Finished	Raw	Flow
1	NA	NA	265
2	NA	NA	164
3	NA	NA	122
4	0.4	0.4	426
5	NA	NA	693
6	0.3	0.4	169
7	NA	NA	1170
8	10	7.5	1070
9	1.2	1.4	1190
10	0.6	0.6	342
11	50	50	300
12	36	36	192
13	13	14	790
14	16	17	864
15	16	16	518
16	NA	NA	66
17	NA	NA	1660
18	3	3	1470
19	1.6	1.6	848
20	0.8	1.2	105
21	2	2	425
22	3.3	6.5	364
23	7	7.5	371
24	9.5	8.5	61
25	10	9	96
26	3.5	4	177
27	2.5	3	102
28	NA	NA	305
29	NA	NA	445
30	1.5	1.5	47
31	NA	NA	4.3
32	1.2	1.2	9.6
33	0.8	1	20
34	0.1	0.3	9.1
35	0.9	1	2.5
36	0.3	0.4	0.4
37	0.3	0.4	0.75
38	0.4	0.5	NA

Week	Finished	Raw	Flow
39	0.4	0.5	1.8
40	NA	NA	NA
41	0.2	0.3	5.7
42	NA	NA	22
43	0.2	0.2	12
44	NA	NA	123
45	0.3	0.2	14
46	NA	NA	9.6
47	1	0.7	12
48	NA	NA	73
49	0.6	1.6	90
50	NA	NA	24
51	0.5	0.6	12
52	NA	NA	325
53	NA	NA	186
54	NA	NA	624
55	0.2	0.23	1490
56	NA	NA	1090
57	NA	NA	1140
58	NA	NA	460
59	0.6	0.6	58
60	NA	NA	1010
61	1.6	2	1140
62	NA	0.6	883
63	2.8	7.8	327
64	2.3	3.9	79
65	8	12.5	165
66	1.64	2.1	65
67	1.03	1.16	65
68	3	7.17	52
69	15.12	46.16	720
70	2.15	3.1	767
71	4.32	5.93	358
72	1.14	0.92	48
73	0.69	0.32	39
74	1.45	1.71	27
75	0.88	1.34	23
76	1.14	1.42	22
77	1.04	0.96	18
78	0.58	0.53	11
79	0.72	NA	12
80	0.34	NA	7.8
81	0.059	0.053	2.6
82	0.78	0.87	4.8
83	0.69	1.12	12

Week	Finished	Raw	Flow
84	0.54	0.073	9.2
85	0.6	0.68	3.8
86	0.47	0.6	11
87	0.5	0.4	3.6
88	0.54	0.34	11
89	0.33	NA	10
90	1.14	3.14	271
91	1.02	1	51
92	0.8	0.62	11
93	0.24	0.25	26
94	0.33	0.34	13
95	NA	NA	17
96	0.34	0.39	7.4
97	NA	NA	18
98	NA	NA	24
99	0.81	0.74	26
100	0.29	0.44	9.5
101	0.14	0.16	7.2
102	NA	NA	12
103	0.69	0.39	6.4
104	NA	NA	8.9
105	0.51	0.73	43
106	NA	NA	33
107	NA	NA	81
108	NA	NA	14
109	0.62	0.45	25
110	0.37	NA	54
111	0.2	NA	33
112	0.2	NA	51
113	0.88	1.22	29
114	0.96	0.48	32
115	0.99	3.23	59
116	9.53	5.88	1280
117	1.62	0.57	83
118	0.6	0.45	40
119	0.37	0.32	33
120	0.31	0.43	13
121	0.9	1.3	14
122	0.7	0.51	12
123	0.62	1.05	14
124	1.17	0.77	13
125	1.53	1.57	15
126	1.16	1.02	16
127	1.04	NA	83
128	1.82	1.05	26

Week	Finished	Raw	Flow
129	NA	NA	29
130	1.19	1.16	NA
131	1.44	1.56	127
132	0.99	1.05	47
133	0.58	0.8	365
134	0.52	0.65	40
135	0.46	0.48	26
136	0.62	0.72	5.3
137	0.62	0.64	0.68
138	0.46	0.34	NA
139	0.48	0.39	NA
140	0.42	0.42	11
141	0.41	0.34	29
142	0.32	0.31	15
143	0.64	0.54	6.4
144	NA	NA	13
145	NA	NA	15
146	0.91	1.9	45
147	1.13	1.13	17
148	0.91	1.03	5.6
149	NA	NA	14
150	0.36	0.43	7.4
151	NA	NA	11
152	NA	NA	12
153	NA	NA	8.2
154	NA	NA	11
155	NA	NA	NA
156	NA	NA	NA
157	0.91	1	NA
158	0.34	NA	NA
159	NA	NA	NA
160	0.35	0.39	9.8
161	0.4	0.5	NA
162	3.02	4.06	NA
163	1.03	1.4	NA
164	NA	0.38	8.2
165	NA	0.53	NA
166	0.6	0.56	15
167	0.31	0.39	13
168	NA	NA	13
169	NA	NA	41
170	0.51	0.47	67
171	0.63	0.88	106
172	1.58	1.07	10
173	NA	NA	NA

Week	Finished	Raw	Flow
174	NA	0.31	NA
175	0.49	0.37	NA
176	0.43	0.69	NA
177	0.93	1.19	11
178	0.76	0.99	13
179	0.83	0.77	10
180	0.56	0.79	12
181	0.4	0.66	11
182	1.61	1.72	63
183	NA	1.02	1
184	0.98	0.8	20
185	NA	NA	16
186	0.78	0.88	8.4
187	0.94	0.93	145
188	0.75	0.99	64
189	0.36	0.43	0.34
190	0.55	0.58	NA
191	NA	NA	NA
192	NA	NA	9.2
193	0.33	0.34	NA
194	NA	NA	14
195	0.3	0.3	NA
196	0.83	0.95	25
197	0.32	0.32	NA
198	NA	NA	15
199	NA	NA	9.2
200	NA	NA	5.6
201	0.33	0.3	9.8
202	NA	NA	23
203	2.3	1.41	50
204	0.86	NA	553
205	0.36	0.33	57
206	0.43	0.43	45
207	0.51	0.48	17
208	NA	NA	43
209	NA	NA	24
210	NA	NA	55
211	NA	NA	50
212	NA	NA	200
213	NA	NA	582
214	NA	NA	100
215	18.3	11.6	64
216	1.71	1.06	80
217	3.87	3.73	268
218	2.62	3.12	181

Week	Finished	Raw	Flow
219	4.12	2.86	1830
220	1.2	1.32	858
221	9.37	9.89	803
222	1.79	2.01	97
223	25.88	20.63	211
224	4.87	6.68	27
225	4.33	1.17	26
226	0.45	0.29	60
227	0.66	0.55	17
228	NA	0.43	6.9
229	1.61	1.37	84
230	0.35	0.33	11
231	1.18	NA	31
232	0.76	0.63	NA
233	4.3	1.29	1190
234	2.59	2.59	498
235	0.9	0.81	41
236	NA	0.71	98
237	NA	0.79	21
238	0.58	0.88	26
239	0.84	0.72	37
240	0.61	0.58	23
241	0.53	0.74	18
242	0.37	0.44	37
243	0.32	0.3	9.7
244	NA	0.33	43
245	0.5	0.59	1780
246	0.44	0.47	1060
247	0.97	0.54	155
248	0.54	0.39	11
249	0.31	NA	1.1
250	NA	0.3	2.2
251	2.06	2.66	1240
252	0.27	0.65	12
253	NA	NA	NA
254	NA	NA	5.2
255	NA	NA	7.5
256	NA	NA	2.6
257	NA	NA	3.7
258	1.03	7.5	NA
259	NA	NA	NA
260	3.7	3	344
261	0.66	0.52	59

Upper Terrebonne Basin data, stream sites 1998-2001. Atrazine concentration in ppb. Bayou Grosse Tete at Rosedale streamflow in cubic feet per second.

Week	Site1	Site17	Site24	Site25	Site28	Site35	Flow
1	NA	NA	NA	NA	NA	NA	NA
2	NA	NA	NA	NA	NA	NA	36
3	NA	NA	NA	NA	NA	NA	1240
4	NA	NA	NA	NA	NA	NA	1230
5	NA	NA	NA	NA	NA	NA	1150
6	NA	NA	NA	NA	NA	NA	688
7	NA	NA	NA	NA	NA	NA	73
8	NA	NA	NA	NA	NA	NA	123
9	2.82	6.94	4.57	11.22	7.5	NA	1180
10	NA	NA	NA	NA	NA	NA	1090
11	NA	NA	NA	NA	NA	NA	267
12	13.7	11.1	6.5	11.5	NA	NA	170
13	69.2	20.6	8.82	4.7	NA	NA	630
14	3.25	10.8	3.05	5.58	NA	NA	93
15	1.81	3.85	1.83	3.15	NA	NA	65
16	7.78	32.18	0.81	2.06	0.94	NA	65
17	6.62	22.78	7	1.32	NA	NA	52
18	12.52	18.92	25.63	6.4	NA	NA	720
19	14.97	14.75	1.31	2.93	NA	NA	767
20	0.77	4.01	3.46	3.6	NA	NA	358
21	NA	NA	NA	NA	NA	NA	42
22	0.63	0.88	1.3	1.05	NA	NA	39
23	0.43	0.34	1.53	2.03	NA	NA	27
24	1.99	0.47	2.03	2.21	NA	NA	23
25	1.06	NA	1.3	1.32	NA	NA	22
26	0.88	1.32	1.04	1.38	1.03	NA	18
27	0.78	0.31	0.31	0.78	NA	NA	11
28	0.5	2.31	0.53	0.69	NA	NA	12
29	NA	NA	NA	NA	NA	NA	20
30	NA	NA	NA	NA	NA	NA	9.5
31	NA	NA	NA	NA	NA	NA	23
32	NA	NA	NA	NA	NA	NA	14
33	NA	NA	NA	NA	NA	NA	14
34	NA	NA	NA	NA	NA	NA	13
35	NA	NA	NA	NA	NA	NA	8.5
36	NA	NA	NA	NA	NA	NA	8.9
37	NA	NA	NA	NA	NA	NA	11
38	NA	NA	NA	NA	NA	NA	560
39	NA	NA	NA	NA	NA	NA	68
40	NA	NA	NA	NA	NA	NA	18
41	NA	0.34	0.48	NA	0.72	NA	9.4
42	NA	NA	NA	NA	NA	NA	13

Week	Site1	Site17	Site24	Site25	Site28	Site35	Flow
43	NA	NA	NA	NA	NA	NA	5.4
44	NA	NA	NA	NA	NA	NA	6.3
45	NA	NA	NA	NA	NA	NA	17
46	NA	NA	NA	NA	NA	NA	15
47	NA	NA	NA	NA	NA	NA	30
48	NA	NA	NA	NA	NA	NA	8.4
49	NA	NA	NA	NA	NA	NA	6.4
50	NA	NA	NA	NA	NA	NA	7.9
51	NA	NA	NA	NA	NA	NA	14
52	NA	NA	NA	NA	NA	NA	13
53	NA	NA	NA	NA	NA	NA	10
54	NA	NA	NA	NA	NA	NA	41
55	NA	NA	NA	NA	NA	NA	111
56	NA	NA	NA	NA	NA	NA	416
57	NA	0.48	NA	0.92	NA	NA	22
58	NA	NA	NA	NA	NA	NA	30
59	NA	NA	NA	NA	NA	NA	122
60	NA	NA	NA	NA	NA	NA	35
61	NA	NA	NA	NA	NA	NA	33
62	NA	0.34	NA	0.37	NA	NA	68
63	14.28	0.39	0.42	0.66	NA	NA	43
64	0.43	NA	1.7	1.19	1.13	NA	32
65	6.39	15.27	0.58	1.51	1.1	NA	42
66	1.77	4.66	7.72	5.77	7.78 1	1.27	1250
67	4.09	2.18	1.66	5.48	1.5	56	83
68	2.01	1.42	0.3	2.21	0.34	25.97	40
69	15.8	2.2	NA	0.42	NA	10.63	35
70	3.5	4.88	0.31	0.55	0.4	1.37	13
71	2.43	3.63	1.34	0.57	0.55	8.53	16
72	1.38	3.65	0.64	0.47	0.54	8.44	21
73	0.49	1.53	0.39	NA	0.47	2.53	14
74	0.44	1.01	0.87	0.62	1.09	3.53	13
75	0.54	3.25	3.01	2.21	1.83	5.25	9.4
76	0.57	1.08	1.29	0.38	1.99	5.34	16
77	3.3	6.23	1.16	0.91	3	2.23	100
78	5.43	2.24	1.4	1.71	1.93	2.61	35
79	2.74	1.61	NA	0.73	NA	0.62	29
80	3.51	0.83	1.3	1.07	1.07	0.74	-27
81	1.37	1.23	1.53	1.27	1.97	0.66	127
82	0.41	0.61	0.38	0.74	0.46	0.35	47
83	NA	NA	NA	NA	NA	NA	35
84	NA	NA	NA	NA	NA	NA	30
85	NA	NA	NA	NA	NA	NA	4
86	NA	NA	0.47	0.45	0.5	0.67	5.4
87	NA	NA	NA	NA	NA	NA	11

Week	Site1	Site17	Site24	Site25	Site28	Site35	Flow
88	NA	NA	NA	NA	NA	NA	0.37
89	NA	NA	NA	NA	NA	NA	0.25
90	NA	NA	NA	NA	NA	NA	18
91	NA	NA	NA	NA	0.4	0.52	15
92	NA	NA	NA	NA	NA	NA	3.9
93	NA	NA	NA	NA	NA	NA	4.5
94	NA	NA	NA	NA	NA	NA	8.2
95	6.16	0.75	NA	NA	NA	0.46	27
96	NA	NA	NA	NA	NA	NA	18
97	NA	NA	NA	NA	NA	NA	4.8
98	NA	NA	NA	NA	NA	NA	6.9
99	2.41	NA	NA	0.48	NA	4.71	13
100	NA	NA	NA	NA	NA	NA	9.9
101	NA	NA	NA	NA	NA	NA	9
102	NA	NA	NA	NA	NA	NA	6.8
103	NA	NA	NA	NA	NA	NA	10
104	0.41	NA	NA	NA	NA	2.58	12
105	NA	NA	NA	NA	NA	NA	NA
106	NA	NA	NA	NA	NA	NA	NA
107	NA	NA	NA	NA	NA	NA	10
108	NA	NA	NA	NA	NA	NA	NA
109	NA	NA	NA	NA	NA	NA	5.8
110	2.65	44	NA	NA	0.53	NA	NA
111	NA	NA	NA	NA	NA	NA	NA
112	NA	NA	NA	NA	NA	NA	NA
113	NA	NA	NA	NA	NA	NA	NA
114	NA	NA	NA	NA	NA	NA	6.6
115	1.15	5.18	NA	0.84	NA	NA	8.2
116	1.47	4.96	NA	0.48	0.31	NA	9.5
117	0.61	1.99	0.46	0.71	0.66	NA	21
118	0.69	32.7	0.39	0.96	0.54	0.49	13
119	2.03	NA	NA	0.6	NA	0.33	13
120	8.44	5	NA	1.4	NA	0.84	41
121	35.86	8.38	0.55	0.95	0.53	34.44	40
122	35.23	3.64	1.99	1.07	3.29	15.55	213
123	29	1.38	0.65	0.96	1.32	9.24	10
124	34.3	0.52	0.67	0.63	0.34	4.79	NA
125	1.4	0.58	NA	0.6	NA	8.72	NA
126	3.15	0.92	0.59	0.78	0.69	2.72	NA
127	3.67	0.95	0.6	0.65	0.48	6.31	NA
128	3.04	0.9	0.99	0.93	0.9	3.72	11
129	2.68	0.65	0.84	0.89	0.81	3.84	13
130	1.73	0.9	0.99	0.81	0.67	2.25	3.7
131	1.13	0.79	0.98	0.7	0.91	2.55	12
132	NA	0.64	1.36	1.15	1.24	9.89	85

Week	Site1	Site17	Site24	Site25	Site28	Site35	Flow
133	0.57	0.74	1.7	0.92	1.51	2.97	63
134	0.25	0.51	2.19	0.62	1.1	3.52	1
135	NA	1.28	1.04	0.75	1.14	2.37	9.4
136	NA	NA	NA	NA	NA	NA	-1
137	NA	NA	NA	NA	NA	NA	-10
138	NA	NA	NA	NA	NA	NA	-3.6
139	NA	NA	NA	NA	NA	NA	13
140	0.4	1.38	0.77	0.61	0.72	1.42	0.34
141	NA	NA	NA	NA	NA	NA	-5.1
142	NA	NA	NA	NA	NA	NA	11
143	NA	NA	NA	NA	NA	NA	-7.8
144	NA	0.52	0.34	NA	0.33	0.92	2
145	NA	NA	NA	NA	NA	NA	19
146	NA	NA	NA	NA	NA	NA	6.4
147	NA	NA	NA	NA	NA	NA	0.89
148	3.17	NA	NA	0.36	0.31	0.75	-1.6
149	NA	NA	NA	NA	NA	NA	1.8
150	NA	NA	NA	NA	NA	NA	8
151	NA	NA	NA	NA	NA	NA	6.5
152	NA	NA	NA	NA	NA	NA	11
153	14.7	NA	NA	NA	NA	0.64	113
154	NA	NA	NA	NA	NA	NA	331
155	NA	NA	NA	NA	NA	NA	400
156	NA	NA	NA	NA	NA	NA	105
157	0.38	NA	0.39	0.39	0.34	0.75	67
158	NA	NA	NA	NA	NA	NA	88
159	NA	NA	NA	NA	NA	NA	47
160	NA	NA	NA	NA	NA	NA	61
161	NA	NA	NA	NA	NA	0.33	26
162	NA	NA	NA	NA	NA	NA	39
163	NA	NA	NA	NA	NA	NA	746
164	NA	NA	NA	NA	NA	NA	101
165	NA	NA	NA	NA	NA	NA	115
166	0.54	9.04	6.43	0.52	11.6	NA	52
167	NA	NA	NA	NA	1.06	NA	606
168	4.5	17.22	6.41	1.56	3.73	0.5	268
169	0.35	1.86	4.16	1.7	3.12	0.3	181
170	0.89	4.44	3.16	1.97	2.86	0.35	1830
171	7.73	1.96	1.13	3.21	1.32	43.64	858
172	7.78	3.07	7.07	3.48	9.89	3.2	803
173	4.51	6.86	2.54	2.7	2.01	2.86	97
174	25.9	5.12	13.89	7.36	20.63	47.6	211
175	8.41	5.55	2.64	5.84	6.68	23.17	27
176	7.19	4.51	2.1	2.72	1.17	12.94	26
177	4.14	3.04	0.37	1.49	0.29	8.56	16

Week	Site1	Site17	Site24	Site25	Site28	Site35	Flow
178	0.73	1.05	NA	0.37	0.55	4.95	17
179	5.75	1.59	NA	0.84	0.43	2.53	6.9
180	4.59	2.22	2.99	0.91	1.37	4.52	84
181	5.02	1.38	NA	0.81	0.33	3.56	11
182	0.79	1.48	1.02	0.6	NA	2	31
183	1.83	1.19	0.77	0.9	0.63	1.73	-3
184	2.04	2.68	2.65	3.82	1.29	2.86	1190
185	2.59	1.96	1.83	1.84	2.59	0.52	629
186	0.45	0.65	0.69	0.84	0.81	0.65	41
187	0.85	0.56	0.62	0.92	0.71	3.49	98
188	NA	NA	NA	NA	NA	NA	28
189	NA	NA	NA	NA	NA	NA	18
190	NA	NA	NA	NA	NA	NA	47
191	NA	NA	NA	NA	NA	NA	4.2
192	1.1	0.33	0.56	0.5	0.74	NA	18
193	NA	NA	NA	NA	NA	NA	26
194	NA	NA	NA	NA	NA	NA	3.7
195	NA	NA	NA	NA	NA	NA	942
196	0.57	0.58	0.5	NA	0.59	0.52	1780
197	NA	NA	NA	NA	NA	NA	667
198	NA	NA	NA	NA	NA	NA	14
199	NA	NA	NA	NA	NA	NA	5.3
200	0.69	NA	NA	NA	NA	0.44	1.1
201	NA	NA	NA	NA	NA	NA	542
202	NA	NA	NA	NA	NA	NA	NA
203	NA	NA	NA	NA	NA	NA	NA
204	NA	NA	NA	NA	NA	NA	5.3
205	0.33	0.38	NA	NA	NA	0.82	5.2
206	NA	NA	NA	NA	NA	NA	9.6
207	NA	NA	NA	NA	NA	NA	-1.2
208	NA	NA	NA	NA	NA	NA	206
209	3.88	1	5.95	NA	NA	0.52	NA
210	NA	NA	NA	NA	NA	NA	434
211	NA	NA	NA	NA	NA	NA	NA
212	NA	NA	NA	NA	NA	NA	308

VITA

John Stanley Walther was born on December 7, 1956, in Houma, Louisiana. He graduated from Vandebilt Catholic High School in Houma on May 1974.

From 1974 to1978 he attended Louisiana State University where he received the degree of Bachelor of Science in Animal Science. While attending school in 1978 he began work at Prentice Oil and Gas Company in Houma. He continued to work for Prentice as Farm Manager until 1983.

From 1983 until 1992 he and his wife owned and operated a farming operation located in Terrebonne and Lafourche parishes producing soybeans, wheat, grain sorghum, and cattle.

He was married to Carolyn Hyland Brown of New Orleans, Louisiana on August 27, 1983 in New Orleans.

After retiring from farming in 1992 he began work as an Environmental Specialist at the Louisiana Department of Agriculture and Forestry as is currently an Environmental Specialist Supervisor. In 1999 he entered the graduate program at Louisiana State University and is a candidate for a Masters of Science in Environmental Sciences.