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Water Quality, Modeling, And Land Use Investigations In The Upper Pearl River Basin Of East-Central Mississippi

Mary Love Mortimer Tagert

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WATER QUALITY, MODELING, AND LAND USE INVESTIGATIONS

IN THE UPPER PEARL RIVER BASIN

OF EAST-CENTRAL MISSISSIPPI

By

Mary Love Mortimer Tagert

A Dissertation
Submitted to the faculty of
Mississippi State University
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Candidate for Degree of Doctor of Philosophy

Little historical water quality data is available for the Upper Pearl River

Basin (UPRB), yet there are UPRB waters listed as impaired. Objectives of this

research were to measure pesticide and sediment concentrations in UPRB

surface waters and validate the Annualized Agricultural Nonpoint-Source

(AnnAGNPS) runoff model with the measured data for a portion of the UPRB. An

additional objective was to quantify effects of land use changes on UPRB surface

waters from 1987 to 2002 using AnnAGNPS.

Of the fifteen compounds analyzed, hexazinone was most frequently

detected, in 94% of samples, followed by metolachlor, tebuthiuron, and atrazine.

Metribuzin was detected in only 6% of samples. Total dissolved solids (TDS)

concentrations were highest at Carthage, which drains the largest area of three

sites sampled for TDS. Most samples measured below Environmental Protection

Agency (EPA) standards for pesticides and TDS in drinking water and also below levels toxic to aquatic organisms.

For eight of twelve months analyzed between October 2001 and January 2003, average monthly sediment loadings for measured and AnnAGNPS-simulated data differed no more than 109%, resulting in an R^2 value of 0.328. A comparison of measured and simulated atrazine and metolachlor loadings by event resulted in R^2 values of 0.095 and 0.062, respectively. Most daily atrazine and metolachlor loadings for measured and predicted data were very low. On May 18, 2003, AnnAGNPS predicted a metolachlor loading of 80 mg, while measured data showed a loading of 5.6 mg. Measured data showed an earlier spike on January 20, 2003 that was not mirrored by the model. Atrazine comparisons followed the same trend, except measured loadings did not spike until February 22, 2003.

The 2002 AnnAGNPS simulation resulted in 15% more average annual runoff than the 1987 simulation, although both simulations had the same precipitation. The 2002 simulation also had higher values for sediment and organic carbon loading. Nitrogen loading was the only runoff or pollutant loading category that was less for 2002 than for 1987. Urban land cover contributed more runoff and pollutant loadings from 1987 to 2002, while traditional row crop agriculture had less of an impact on pollutant loadings.

DEDICATION

I dedicate this research first and foremost to my loving husband, Mike Tagert, and to our growing family. You have always listened to me and responded with the best advice, and you have always supported me in all of my educational and career aspirations since we first met over six years ago. You have truly been my partner and other half, always encouraging me and wanting the best for me. Thanks for your unconditional love and support. I love you more than anything and am eternally grateful that God allowed our paths to cross. I could not have completed this research or degree program without your constant support and encouragement, and I look forward to sharing a lifetime of fun, relaxing weekends (sigh) with you.

I also dedicate this research to my parents, Rodney and Ethlyn Mortimer, who have always wanted me to have the best education available and have always encouraged me to challenge myself. Thanks to them, I have been afforded many educational opportunities for which others only wish. Daddy, now you and Mama can finally answer, "Yes, she's done" when people ask if your daughter is *STILL* in school! Thanks also to my brother Kent for your support. Last but certainly not least, I would like to thank my grandparents – Carl and Frances Brown and Lagrone and Ellen Mortimer – mostly for just being such a large part of my life but also for your support. Through all the basketball games,

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INTRODUCTION

Water quality has long been a concern to government officials, as well as to the general public. Over the past few decades, existing regulations have been more extensively enforced, and new regulations have been established to improve the quality of the nation's surface, ground, and drinking waters. The nation's first water quality standards became federal law with the passage of the Water Quality Act (WQA) of 1965, which set federal standards for interstate waters but did not set effluent limitations (Public Law No. 89-23). Congress significantly amended and superceded the WQA with passage of the Clean Water Act (CWA) in 1972 (33 U.S.C. §§ 1251 et seq.). The CWA of 1972 extended water quality standards to intrastate waters and required states to undertake a continuing planning process to coordinate pollution control efforts (CWA §§ 303(b) and 303(d); Houck, 1999).

There were parts of the CWA that were immediately enforced upon passage of the bill. National Pollution Discharge Elimination System (NPDES) permits were required to be completed for entities emitting point sources of pollution or wastewater into a body of water, and these NPDES permits were issued by individual state environmental agencies (CWA § 1311(a); Chen et al., 1999). NPDES permits are still in effect today. When Congress passed the

CWA, point-sources of pollution were of more concern than nonpoint-sources,

partially because they were the most obvious sources of pollution and also

because they could be fairly easily monitored and regulated. Examples of some

point-source discharges are those pollutants discharged, often continuously, from

factories or municipal sewage systems (Federal Register, July 13, 2000).

However, when the CWA was passed, nonpoint-sources of pollution in general

and, specifically, CWA § 303(d) did not receive much attention from the

Environmental Protection Agency (EPA) or state environmental agencies.

Examples of nonpoint-sources of pollution are runoff from land in agricultural

production, stormwater runoff, and urban runoff (Federal Register, July 13,

2000). Nonpoint-source runoff loads are difficult to monitor and make the waste

load allocation process complicated (Haith, 2003).

CWA § 303(d) requires state agencies to identify sections of rivers and

streams that cannot meet minimum water quality standards with the control of

point-sources alone (Christman, 1999). Once these WQLS are put on a state's

list of impaired surface waters, the state is required to establish the maximum

pollutant load, including point- and nonpoint-source pollutants, that can enter a

body of water and allow that body of water to still meet minimum water quality

standards (Chen et al., 1999). This combined maximum allowable pollution load,

which also has a margin of safety (MOS), is called the Total Maximum Daily Load

(TMDL) for a body of water (Schwer, 2000).

From its inception in 1972 until the late 1990's, state agencies did not

enforce § 303(d) of the CWA that includes TMDL regulations, and the EPA

allowed state agencies to mostly ignore this part of the CWA (Sears, 1998). Only

in the past several years, when the EPA and state environmental agencies were

sued by environmental groups, have they been more stringently enforcing the

CWA, requiring that state environmental agencies submit lists of impaired

surface waters and begin the initial process of establishing TMDLs for those

impaired waters (Pelley, 1998; Adler, 1998; Kreuzer, 2001). The EPA is now

requiring states to submit more comprehensive lists of impaired waters, with lists

being submitted every even-numbered year (Federal Register, July 13, 2000).

Also, the new rule requires that waters remain on the list until water quality

standards are met, calls for more public input in the TMDL process, and sets

goals of attaining water quality standards within 10-15 years (Bergeson, 2001).

The enforcement of §303(d) of the CWA has shifted the nation's clean water

program from focusing mainly on technology-based pollution control for point-

sources to now being centered on water quality-based controls for nonpoint-

sources, which requires watershed level management.

By necessity, the TMDL implementation procedure is a combined effort of

local stakeholders, scientists, and regulatory agencies (Maguire, 2003). The

implementation of TMDLs will include participation from federal, state, and local

agencies, with state environmental agencies shouldering a majority of the

responsibility (Harris et al., 1995). State environmental agencies are having

great difficulty meeting the financial demands of implementing TMDLs. Agencies

argue that they do not have the resources to go through the costly and time-

consuming procedure of establishing TMDLs (Pelley, 1998). Also, since water

quality programs are now applied to entire watersheds, there is a large focus on the effects of land use and land management practices on water quality (Jones et al., 2000). This large-scale watershed approach contributes, in part, to the high cost of establishing TMDLs. Environmental agencies are particularly concerned with agricultural nonpoint-source runoff, but agricultural producers are unlikely to voluntarily establish BMPs with no financial assistance from the federal or state government. Programs such as the United States Department of Agriculture's (USDA) Environmental Quality Incentives Program (EQIP) of 1996 and Conservation Reserve Program (CRP) provide financial compensation to producers who voluntarily establish BMPs or other conservation measures on lands in priority watersheds, making these USDA programs a great fit with the EPA's TMDL program (Ogg and Keith, 2002).

   After the establishment of new conservation practices in watersheds, state environmental agencies must evaluate their effectiveness by monitoring load reductions in nearby surface waters. These agencies must also collect other data as they establish TMDLs. Water quality determinations for surface waters have traditionally been made by taking actual water samples and transporting them back to the laboratory for analysis. This sampling method is still suitable for some projects. However, traditional water sampling is becoming increasingly difficult to use, due to financial and time constraints, for the process of establishing TMDLs in a watershed. The financial burden and time constraints under which state environmental agencies are operating have thus led them to search for new and alternative solutions to intensive manual sampling and seek

help from entities such as land-grant universities in understanding and implementing the latest technologies for combating specific types of nonpoint-source pollution, especially agricultural nonpoint-source runoff (Harris et al., 1995).

One of the newest emerging technologies in water quality modeling and hydrology is remote sensing. Remote sensing has improved the accuracy of inputs used in water quality models by evaluating important parameters that affect water quality. Examples of such parameters include the determination of land use and land characteristics, as well as changes in vegetation (Rio and Lozano-Garcia, 2000; Thenkabail et al., 2000). Previously, research had focused more on the classification of land cover, and little was known regarding the impacts of remote sensing on water quality research. In the past ten to fifteen years, however, interest in remote sensing applications for determining water quality has greatly increased.

As a result of improved spatial, spectral, and temporal resolutions for remotely sensed imagery, certain water quality parameters can be determined from remote sensing images because they have a direct effect on the optical properties of water (Herut et al., 1999). Research in 1987 showed the capability of Landsat Multispectral Scanner (Landsat MSS) data to estimate suspended sediment concentrations in surface waters when the concentration was greater than 50 mg/L, although it was unable to distinguish the reflectance of chlorophyll at high concentrations of suspended sediments due to the poor resolution of the images (Ritchie et al., 1987; Ritchie et al., 1990). More recently, suspended

sediment concentrations have been estimated by hyperspectral Compact Airborne Spectrographic Imager (CASI) data and used to verify results of hydrodynamic models (Jorgensen and Edelvang, 2000). Tolk et al. (2000) have also studied how bottom brightness affects the reflectance of surface waters under different suspended sediment concentrations. Although remote sensing can also be used to determine surface concentrations of chlorophyll in water, high levels of suspended sediments and dissolved organic matter in turbid waters can hide the characteristic reflectance signature of chlorophyll (Keiner and Yan, 1998). Other water quality parameters that do not have a direct impact on the optical properties of water can be determined by correlating them with parameters that do affect the water's reflectance characteristics. For example, phosphorus levels in water can be estimated from their correlation with the chlorophyll-a concentrations in water, and the spatial distribution of potentially toxic particulate metals may be determined by their correlation with suspended particulate matter (Herut et al., 1999).

Remote sensing provides a cost-effective means of ascertaining the different types of land cover or vegetation in watersheds that cover large geographic areas for use in modeling nonpoint-source runoff (Lunetta et al., 2004). Remote sensing, in combination with geographic information systems (GIS), can reduce the time needed to derive inputs to water quality models and can also increase the accuracy of estimating watershed conditions (Bhuyan et al., 2002). Remote sensing can be used to determine land cover over small areas such as a field or farm and even look at variations in a single type of

vegetation, such as a particular crop species (Flores and Martinez, 2000).

However, remote sensing applications would be applied to an entire watershed

basin for land cover classification as inputs to nonpoint-source water quality

models. GIS is commonly used to manipulate remotely sensed imagery and

digital elevation model (DEM) data to derive land cover maps, slope information,

and other inputs for watershed models (Basnyat et al., 2000; Lee et al., 1990).

GIS is helpful in storing and manipulating large amounts of land use data as well

as water quality data once these values are determined from the remote sensing

imagery (Mattikalli and Richards, 1996; Swalm et al., 2000).

When using remote sensing to classify land cover or determine other

environmental factors that may be inputs to water quality models, it is important

to find correlations or similarities between variables in the remotely sensed

images and variables describing the land cover or environment (Andrefouet and

Claereboudt, 2000). When remote sensing images are analyzed for land use

information, each pixel is classified into a certain land use category based on the

spectral and statistical characteristics of that pixel, and sometimes these

categories are merged during the analysis procedure (Martinez-Casasnovas,

2000). Many studies have been performed to observe the relationship between

remotely sensed data and on-site water quality measurements. One group of

researchers went a step further to move remote sensing applications to a more

practical level of forecasting water quality parameters in real-time (Yang et al.,

1999).

Remote sensing is an asset to water quality monitoring because it can be used to monitor several parameters of large bodies of water without traditional manual water sampling (Islam et al., 2003). Remote sensing images can be used to monitor and predict migrations of phytoplankton in coastal waters and, as a result, determine chlorophyll-a concentrations as well as the Secchi disc depth of the water (Allee and Johnson, 1999). Remote sensing applications have also been explored for water management, such as assessing the factors that affect crop irrigation (Bastiaanssen et al., 2000). Although such research is valuable to predicting water quality, the recent trend using remotely sensed data to determine and verify inputs for water quality models and increase the accuracy of such models has had more of a direct and immediate impact on the development and evaluation of TMDLs.

Water quality models have become an important tool used by agencies assigned the task of implementing TMDLs (Bowen and Hieronymus, 2003; Wool et al., 2003; Santhi et al., 2001). Water quality models are valuable because they can be used to predict water quality as a function of loads and components of the hydrologic cycle. Models ultimately help form a decision support system (DSS) for making TMDL prescriptions (Chapra, 2003). There are a wide variety of models available for different applications. Some models are tailored for smaller watersheds and some for larger watersheds. There are single-event models, continuous simulation models, and both simple and complex models (Bingner, 1996). There is even a model, the USDA's Riparian Ecosystem Management Model (REMM), which predicts the buffering capability of riparian

zones (Lowrance et al., 2000). Modeling is a more efficient means of evaluating water quality than performing intense manual water sampling throughout a watershed. However, models should be compared to experimental water quality data, and these actual data should be used to validate the model for different scenarios. The efficiency models provide in evaluating water quality is why the EPA's Office of Water developed the Better Assessment Science Integrating Point and Nonpoint Sources (BASINS) model primarily for TMDL development in watersheds (Whittemore and Beebe, 2000).

Recent developments have been made to the BASINS model, including the integration of the USDA's Soil and Water Assessment Tool (SWAT) (Di Luzio et al., 2002). More water quality models being used today, including the EPA's BASINS model, are incorporating GIS and/or remotely sensed imagery. GIS can manipulate large amounts of water quality data as well as tie this data to a geographic location within a watershed.

Researchers in the area of water quality modeling have had difficulty estimating some of the input variables for the models, and have turned to remote sensing for help in obtaining and/or verifying some of these inputs (Schultz, 1988). In light of new concerns about nonpoint-source pollution and the establishment of TMDLs, much recent work in remote sensing has focused on improving land cover classification systems and determining other environmental inputs, such as soil moisture, to water quality models that estimate runoff (Blumberg et al., 2000).

Soil moisture is a common input to water quality models, and it is a parameter that is difficult to measure, in part because it can be so variable over an area of land. Soil properties are important in determining the movement of pollutants contained in runoff water, and the USDA-Natural Resource Conservation Service (NRCS) soil survey databases (SSURGO or STATSGO), when combined with other parameters, are valuable in predicting nonpoint-source runoff (Macur et al., 2000). Soil moisture, specifically antecedent soil moisture, is an important variable in water quality models because it plays a role in interactions and processes between the soil, vegetation, and the atmosphere. Soil moisture is important in determining evaporation, rainfall partitioning between surface runoff and infiltration, and infiltration from the soil surface to underground aquifers, just to name a few.

Studies such as the one by Quesney et al. (2000) have been performed to test different methods of using remotely sensed data to estimate the soil moisture throughout a watershed. Quesney et al. were able to accurately determine soil moisture using Earth Resource Satellite Synthetic Aperture Radar (ERS/SAR), except during the months of May and June, when the vegetative cover was too dense to obtain reliable soil information. These scientists studied land cover types for which the SAR signal is mainly sensitive to soil water content variations and for which the effects of vegetation and soil roughness could be estimated and removed.

Land cover classification is another factor that is equally important with respect to input variables for water quality models. The type of vegetation or

land cover over an area has a large impact on surface water runoff and therefore the water quality of surface waters. Much of the recent research in the water quality area (from remote sensing to more traditional water quality studies) has tried to determine the linkages between land use and surface water quality (McFarland and Hauck, 1999; Narumalani et al., 1997; Scribner et al., 2000).

Land use practices can affect water quality in various ways, first and foremost by greatly impacting the water hydrology of the area. The hydrology of an area, in turn, influences the sediment load that goes into nearby surface waters as well as the load of chemicals in runoff. Different types of land cover or land usage can also affect the retention of sediments, nutrients, and pesticides, and can in some cases aid the transformation of nutrients and pesticides (Basnyat et al., 1999; Blanchard and Lerch, 2000).

Differentiating between various types of land cover is important in calculating amounts of nonpoint-source runoff because topography, land management factors, and vegetation type are some of the more important input variables in water quality models (Bingner, 1990). Different types of buffers such as riparian zones along streams and rivers and vegetative filter strips bordering agricultural fields and golf courses are examples of land cover classifications than can improve water quality by filtering runoff containing sediments, pesticides, and nutrients (Basnyat et al., 2000; Cole et al., 1997; Tingle et al., 1998; Webster and Shaw, 1996). Other land use or land management factors affecting nonpoint-source runoff are conservation tillage, percentage of a watershed that is cropped, location of cropped areas, and the pesticides applied

to the vegetation (Battaglin and Goolsby, 1999; Blanchard and Lerch, 2000; Uri, 1997).

Great strides have been made in recent years in the fields of remote sensing and water quality modeling, both separately and in combination. Scientists have discovered how remotely sensed imagery can improve inputs to water quality models so that the models can more accurately predict water quality parameters and aid in formulating TMDLs. As the remote sensing arena continues to progress and provide imagery with better spatial, spectral, and temporal resolution, remote sensing applications for monitoring water quality parameters should increase and become even more diverse than they are today (Ritchie et al., 2003). Remote sensing has the possibility to revolutionize the way we study water quality by improving efficiency, monitoring large areas simultaneously, and increasing the accuracy of water quality predictions.

There are still areas of research that need to be explored with regard to the integration of remote sensing, GIS, and water quality modeling. This research seeks to address some of those areas. The overall goals of this research are to evaluate the use of the USDA's Annualized Agricultural Nonpoint Source (AnnAGNPS) runoff model for establishing TMDLs for selected pesticides and to evaluate changes in land use in the Upper Pearl River Basin, using remote sensing and GIS in combination with the AnnAGNPS model. There are not a plethora of models that are capable of modeling the runoff and transport of a variety of pesticides. The AnnAGNPS runoff model was selected for this research because it utilizes a fairly comprehensive database of pesticides and

can model the movement of a variety of pesticides. Additional pesticides can also be added to the AnnAGNPS databases. Furthermore, the study area has had some row crop production in recent years, and the AnnAGNPS model is designed primarily for agricultural watersheds (Pantone and Young, 1996).

The Upper Pearl River Basin was chosen for several reasons as the study area to validate the AnnAGNPS model with manual water sampling data. The Mississippi Department of Environmental Quality (MDEQ) has recently been in the process of establishing TMDLs for segments of the Upper Pearl River and its tributaries, and there are several stream segments in the Upper Pearl River Basin that have been on Mississippi's 303(d) list for the past few years. However, there is limited historical water quality available for this area. In addition, the Upper Pearl River (HUC 0318001) drains into the Ross Barnett Reservoir, which is located in HUC 0318002. The Ross Barnett Reservoir is a 13,200-ha surface water impoundment that serves as the primary source of drinking water for Mississippi's capital city, Jackson (Ballweber et al., 2000). Thus, the area that drains into the Ross Barnett Reservoir is an important area with respect to water quality.

Chapter Two presents results from pesticide and sediment samples that are used to validate the AnnAGNPS model to portions of the Upper Pearl River Basin. Chapter Three compares the AnnAGNPS model predictions for sediment and pesticide runoff to the field data for selected portions of the Upper Pearl River Basin, and Chapter Four shows how changes in land use affect the AnnAGNPS model predictions. In Chapters Three and Four, remotely sensed

images are used to derive land use maps for input to the model, and the land

use, DEM, and soils data are all processed within a GIS.

LITERATURE CITED

Adler, R.W. 1998. New TMDL litigation leaves many unanswered questions. Rivers 6:269-274.

Allee, R.J. and J.E. Johnson. 1999. Use of satellite imagery to estimate surface chlorophyll a and Secchi disc depth of Bull Shoals Reservoir, Arkansas, USA. Int. J. Remote Sens. 20:1057-1072.

Andrefouet, S. and M. Claereboudt. 2000. Objective class definitions using correlation of similarities between remotely sensed and environmental data. Int. J. Remote Sens. 21:1925-1930.

Ballweber, J.A., D. Parisi, and J.R. Steil. 2000. Riparian management's role within a basin-scale management partnership. Pages 463-468 In Proc. AWRA's Summer Specialty Conference on Riparian Ecology and Management in Multi-Land Use Watersheds. Middleburg, VA:AWRA.

Basnyat, P., L.D. Teeter, K.M. Flynn, and B.G. Lockaby. 1999. Relationships between landscape characteristics and nonpoint source pollution inputs to coastal estuaries. Environ. Manage. 23:539-549.

Basnyat, P., L.D. Teeter, B.G. Lockaby, and K.M. Flynn. 2000. Land use characteristics and water quality: A methodology for valuing of forested buffers. Environ. Manage. 26:153-161.

Basnyat, P., L.D. Teeter, B.G. Lockaby, and K.M. Flynn. 2000. The use of remote sensing and GIS in watershed level analyses of non-point source pollution problems. For. Ecol. Manage. 128:65-73.

Bastiaanssen, W.G.M., D.J. Molden, I.W. Makin. 2000. Remote sensing for irrigated agriculture: Examples from research and possible applications. Agric. Water Manage. 46:137-155.

Battaglin, W.A. and D.A. Goolsby. 1999. Are shifts in herbicide use reflected in concentration changes in midwestern rivers? Environ. Sci. Technol. 33:2917-2925.

Bergeson, L.L. 2001. One hot issue: TMDL litigation. Pollut. Eng. 33:17-18.

Bhuyan, S.J., L.J. Marzen, J.K. Koelliker, J.A. Harrington, Jr., and P.L. Barnes. 2002. Assessment of runoff and sediment yield using remote sensing, GIS, and AGNPS. J. Soil and Water Conserv. 57:351-363.

Bingner, R.L. 1990. Comparison of the components used in several sediment yield models. Trans. ASAE 33:1229-1238.

Bingner, R.L. 1996. Runoff simulated from Goodwin Creek watershed using SWAT. Trans. ASAE 39:85-90.

Blanchard, P.E. and R.N. Lerch. 2000. Watershed vulnerability to losses of agricultural chemicals: Interactions of chemistry, hydrology, and land-use. Environ. Sci. Technol. 34:3315-3322.

Blumberg, D.G., V. Freilikher, I.V. Lyalko, L.D. Vulfson, A.L. Kotlyar, V.N. Shevchenko, and A.D. Ryabokonenko. 2000. Soil moisture (water-content) assessment by an airborne scatterometer: The Chernobyl disaster area and the Negev Desert. Remote Sens. Environ. 71:309-319.

Bowen, J.D. and J.W. Hieronymus. 2003. A CE-QUAL-W2 model of Neuse Estuary for total maximum daily load development. J. Water Resour. Plan. Manage. 129:283-294.

Chapra, S.C. 2003. Engineering water quality models and TMDLs. J. Water Resour. Plan. Manage. 129:247-256.

Chen, C.W., J. Herr, L. Ziemelis, R.A. Goldstein, and L. Olmsted. 1999. Decision support system for total maximum daily load. J. Environ. Eng. July:653-659.

Christman, J.N. 1999. Total maximum daily loads (TMDLs). Environ. Regul. Permitting. 8:5-38.

Cole, J.T., J.H. Baird, N.T. Basta, R.L. Huhnke, D.E. Storm, G.V. Johnson, M.E. Payton, M.D. Smolen, D.L. Martin, and J.C. Cole. 1997. Influence of buffers on pesticide and nutrient runoff from bermudagrass turf. J. Environ. Qual. 26:1589-1598.

Di Luzio, M., R. Srinivasan, and J.G. Arnold. 2002. Integration of watershed tools and SWAT model into BASINS. J. Am. Water Resour. Assoc. 38:1127-1141.

Federal Register. 2000. Environmental Protection Agency: Revisions to the water quality planning and management regulation and revisions to the national pollutant discharge elimination system program in support of revisions to

the water quality planning and management regulation; final rules. July 13. 65:43586-43670.

Flores, L.A. and L.I. Martinez. 2000. Land cover estimation in small areas using ground survey and remote sensing. Remote Sens. Environ. 74:240-248.

Haith, D.A. 2003. Systems analysis, TMDLs and watershed approach. J. Water Resour. Plan. Manage. 129:257-260.

Harris, B.L., T.L. Nipp, D.K. Waggoner, and A. Weber. 1995. Agricultural water quality program policy considerations. J. Environ. Qual. 24:405-411.

Herut, B., G. Tibor, Y.Z. Yacobi, and N. Kress. 1999. Synoptic measurements of chlorophyll-a and suspended particulate matter in a transitional zone from polluted to clean seawater utilizing airborne remote sensing and ground measurements, Haifa Bay (SE Mediterranean). Marine Pollut. Bull. 38:762-772.

Houck, O.A. 1999. Chapter 2: The history and evolution of §303 in The Clean Water Act TMDL Program: Law, Policy, and Implementation. Washington, D.C.: Environmental Law Institute.

Islam, M.A., J. Gao, W. Ahmad, D. Neil, and P. Bell. 2003. Image calibration to like-values in mapping shallow water quality from multitemporal data. Photogramm. Eng. Remote Sensing 69:567-575.

Jones, R., J. McNitt, and G. Keith. 2000. Implications for the future: A strategic look at policies for polluted runoff. Water Resour. Impact 2:7-9.

Jorgensen, P.V. and K. Edelvang. 2000. CASI data utilized for mapping suspended matter concentrations in sediment plumes and verification of 2-D hydrodynamic modelling. Int. J. Remote Sens. 21:2247-2258.

Keiner, L.E. and X. Yan. 1998. A neural network model for estimating sea surface chlorophyll and sediments from thematic mapper imagery. Remote Sens. Environ. 66:153-165.

Kreuzer, H. 2001. Enforcement in the early 21st century. Pollut. Eng. 33:14-19.

Lee, M.T., J. Kao, and Y. Ke. 1990. Integration of GIS, remote sensing, and digital elevation data for a hydrologic model. Hydraulic Engineering: Proceedings of the 1990 National Conference. Chang, H. H. and Hill, J. C., Eds. 1:427-432.

Lowrance, R., L.S. Altier, R.G. Williams, S.P. Inamdar, J.M. Sheridan, D.D. Bosch, R.K. Hubbard, and D.L. Thomas. 2000. REMM: The riparian ecosystem management model. J. of Soil and Water Conserv. 55:27-34.

Lunetta, R.S., D.M. Johnson, J.G. Lyon, and J. Crotwell. 2004. Impacts of temporal frequency on land-cover change detection monitoring. Remote Sens. Environ. 89:444-454.

Macur, R.E., H.M. Gaber, J.M. Wraith, and W.P. Inskeep. 2000. Predicting solute transport using mapping-unit data: Model simulations versus observed data at four field sites. J. Environ. Qual. 29:1939-1946.

Maguire, L.A. 2003. Interplay of science and stakeholder values in Neuse River total maximum daily load process. J. Water Resour. Plan. Manage. 129:261-270.

Martinez-Casasnovas, J.A. 2000. A cartographic and database approach for land cover / use mapping and generalization from remotely sensed data. Int. J. Remote Sens. 21:1825-1842.

Mattikalli, N.M. and K.S. Richards. 1996. Estimation of surface water quality changes in response to land use change: Application of the export coefficient model using remote sensing and geographical information system. J. Environ. Manage. 48:263-282.

McFarland, A.M.S. and L.M. Hauck. 1999. Relating agricultural land uses to in-stream stormwater quality. J. Environ. Qual. 28:836-844.

Narumalani, S., Y. Zhou, and J.R. Jensen. 1997. Application of remote sensing and geographic information systems to the delineation and analysis of riparian buffer zones. Aquat. Bot. 58:393-409.

Ogg, C.W. and G.A. Keith. 2002. New federal support for priority watershed management needs. J. Am. Water Resour. Assoc. 38:577-586.

Pantone, D.J. and R.A. Young. 1996. AGNPS: A software program for assessing nonpoint source pesticide pollution. HortTechnology 6:344-350.

Pelley, J. 1998. The challenge of watershed cleanup. Environ. Sci.Technol./News Aug. 1:364A-365A.

Quesney, A., S.L. Hegarat-Mascle, O. Taconet, D. Vidal-Madjar, J.P. Wigneron, C. Loumagne, and M. Normand. 2000. Estimation of watershed soil moisture index from ERS/SAR data. Remote Sens. Environ. 72:290-303.

Rio, J.N.R. and D.F. Lozano-Garcia. 2000. Spatial filtering of radar data (RADARSAT) for wetlands (brackish marshes) classification. Remote Sens. Environ. 73:143-151.

Ritchie, J.C., C.M. Cooper, and F.R. Schiebe. 1990. The relationship of MSS and TM digital data with suspended sediments, chlorophyll, and temperature in Moon Lake, Mississippi. Remote Sens. Environ. 33:137-148.

Ritchie, J.C., C.M. Cooper, and J. Yongqing. 1987. Using landsat multispectral scanner data to estimate suspended sediments in Moon Lake, Mississippi. Remote Sens. Environ. 23:65-81.

Ritchie, J.C., P.V. Zimba, and J.H. Everitt. 2003. Remote sensing techniques to assess water quality. Photogramm. Eng. Remote Sensing 69:695-704.

Santhi, C., J.G. Arnold, J.R. Williams, L.M. Hauck, and W.A. Dugas. Application of a watershed model to evaluate management effects on point and nonpoint source pollution. Trans. ASAE 44:1559-1570.

Schultz, G.A. 1988. Remote sensing in hydrology. J. Hydrol. 100:239-265.

Schwer, D. 2000. The TMDL program – an industry perspective. Ind. Wastewater 8:17-19.

Scribner, E.A., W.A. Battaglin, D.A. Goolsby, and E.M. Thurman. 2000. Changes in herbicide concentrations in Midwestern streams in relation to changes in use, 1989-1998. Sci. Total Environ. 248:255-263.

Sears, E.B. 1998. Rebirth of EPA's TMDL program. Environ. Regul. Permitting 8:85-94.

Swalm, C., J.T. Gunter, V. Miller, D.G. Hodges, J.L. Regens, J. Bollinger, and W. George. 2000. GIS blossoms on the mighty Mississippi. Geo Info Systems April:30-34.

Thenkabail, P.S., R.B. Smith, and E. De Pauw. 2000. Hyperspectral vegetation indices and their relationships with agricultural crop characteristics. Remote Sens. Environ. 71:158-182.

Tingle, C.H., D.R. Shaw, M. Boyette, and G.P. Murphy. 1998. Metolachlor and metribuzin losses in runoff as affected by width of vegetative filter strips. Weed Sci. 46:475-479.

Tolk, B.L., L. Han, and D.C. Rundquist. 2000. The impact of bottom brightness on spectral reflectance of suspended sediments. Int. J. Remote Sens. 21:2259-2268.

Uri, N.D. 1997. Link between conservation tillage and factor inputs. Int. J. Environ. Stud. 53:43-73.

Webster, E.P. and D.R. Shaw. 1996. Impact of vegetative filter strips on herbicide loss in runoff from soybean (Glycine max). Weed Sci. 44:662-671.

Whittemore, R.C. and J. Beebe. 2000. EPA's BASINS model: Good science or serendipitous modeling? J. Am. Water Resour. Assoc. 36:493-499.

Wool, T.A., S.R. Davie, and H.N. Rodriquez. 2003. Development of three-dimensional hydrodynamic and water quality models to support total maximum daily load decision process for the Neuse River Estuary, North Carolina. J. Water Resour. Plan. Manage. 129:295-306.

Yang, M., C.J. Merry, and R.M. Sykes. 1999. Integration of water quality modeling, remote sensing, and GIS. J. Am. Water Resour. Assoc. 35:253-263.

CHAPTER II

WATER QUALITY SURVEY OF MISSISSIPPI'S

UPPER PEARL RIVER: 2001-2003

ABSTRACT

To assess the current level of impairment by pesticides and siltation in the

Upper Pearl River Basin (UPRB), grab samples were collected at seven United

States Geological Survey (USGS) gauged locations within the watershed.

Depth-integrated water samples were also collected at three sites to be analyzed

for total dissolved solids (TDS). Samples for pesticide analysis were collected

weekly from May through August 2002, and monthly thereafter through May

2003. Samples for TDS analysis were collected from September 2001 through

January 2003. Pesticide samples were extracted via Solid Phase Extraction

(SPE) and analyzed for fifteen different pesticides using a multi-residue method:

triclopyr, 2,4-D, tebuthiuron, simazine, atrazine, metribuzin, alachlor, metolachlor,

cyanazine, norflurazon, hexazinone, pendimethalin, diuron, fluometuron, and

dichlorodiphenyltrichloroethane (DDT) insecticide degradation product p,p'-DDE.

TDS samples were analyzed using a gravimetric method.

Of the fifteen pesticides analyzed, hexazinone was the most frequently

detected compound, with 171 out of a possible 181 detections, followed by

metolachlor, tebuthiuron, and atrazine. Metribuzin was the least detected

compound of the analyzed compounds, with 11 detections out of a potential 181 detections. TDS concentrations were highest at the Carthage site, which drains the largest area of the three sites that were sampled for TDS. Most samples measured well below Environmental Protection Agency (EPA) standards for pesticides and TDS in drinking water and also well below levels that might be toxic to aquatic organisms.

INTRODUCTION

Over the past several years, the EPA has begun enforcing §303(d) of the Clean Water Act (CWA) , which includes Total Maximum Daily Loads (TMDLs). Nonpoint-source (NPS) pollution, especially pesticide and sediment runoff, has gained much attention. Many studies have shown pesticide detections in surface waters. As new pesticides were developed and thus were increasingly used by farmers from the 1960's to the current time, detections of pesticides in surface waters have been consistently linked to agricultural production (Smith et al. 1993; Coupe et al. 1998; Wauchope 1978). Quite often, however, levels of detected pesticides are extremely low (Senseman et al. 1997; Zimmerman et al. 2000). Nevertheless, agricultural pesticides have been detected in the Mississippi River and its tributaries, in surface waters of the Midwestern United States and of California, as well as in agricultural areas of other countries (Tanabe et al. 2001; Domagalski 1996; Pereira and Hostettler 1993; Battaglin et al. 2003; Dabrowski et al., 2002).

Although row crop agricultural production is a large contributor to NPS runoff, there are various other sources as well. Pesticides enter surface waters through surface transport mechanisms, and significant amounts of pesticides can be transported by surface water runoff if the runoff volume is fairly large and occurs soon after the pesticide application (Wauchope, 1978). However, the occurrence of intense rainfall shortly after a pesticide application is not a frequent event. The aforementioned scenario is more likely to happen on golf courses due to frequent application of pesticides to golf course fairways (Ma et al., 1999). Various pesticides have been detected in surface waters on or near golf courses, making golf courses a likely source for pesticide inputs to surface waters (Cohen et al., 1999).

Urban areas can also be significant contributors of some pesticides such as diazinon. Crawford (2001) monitored the occurrence and transport of certain pesticides in an Indiana river basin and found that concentrations of diazinon were higher in an urban drainage area than in two agricultural drainage areas. One possible route of pesticide input to surface waters in urban areas can occur when misapplication occurs on impervious areas such as sidewalks, streets, or driveways (Walston et al., 2001).

Although urban areas and residential landscapes contribute pesticide runoff to streams, modification of planting practices and planting covers in residential landscapes can alter soil chemical properties, microbial activity, pesticide degradation, and thus the runoff potential of selected herbicides (Gan et al., 2003). The establishment of low maintenance landscapes and native

plants can also reduce chemical inputs needed to maintain an attractive residential landscape, and reduced chemical inputs would potentially decrease the amount of pesticides in runoff (Hipp et al., 1993).

Certain herbicides are also used in forest site preparation and to release small pine trees, making silviculture sites additional potential sources for herbicide inputs to surface waters (Neary, 1985). Triclopyr and hexazinone, two herbicides commonly used in silviculture practices, have been detected in plants located off-site of the application area (Ando et al., 2003). Forestry practices, such as the creation of skid trails, can contribute to increased runoff and soil erosion (Hartanto, et al., 2003).

Other potential sources for pesticides in surface waters include runoff from roofs, vineyards, and containerized plant production nurseries (Bucheli et al., 1998; Louchart et al., 2001). For more water soluble herbicides, up to 15% of the applied herbicide can be lost in the first irrigation event after an application to containerized plants (Riley, 2003).

As there are a variety of sources that contribute to nonpoint-source pesticide runoff, there are also a variety of factors that control the movement and fate of compounds in the environment, and more specifically in surface water runoff. The environmental fate of pesticides is controlled by four main factors: the physical and chemical properties of the individual compound, soil characteristics, climate, and also agronomic management practices (Hapeman et al., 2003; Larson et al., 1995; Leonard, 1990). All but the first category could also apply to sediment runoff.

There are several physical and chemical properties that primarily control the behavior of a pesticide in the environment: acid dissociation constant (pK_a), aqueous solubility (S_W), vapor pressure (P_{VP}), air-water partition coefficient (K_H or Henry's Law), and soil-water distribution coefficient (K_D). When the soil-water distribution coefficient is normalized for soil organic matter content, it is referred to as K_{OC}. As an example of how a pesticide's properties can greatly affect its environmental fate, pesticides that have a high K_D or K_{OC} and are strongly adsorbed to soil particles are more likely to be transported off the field with soil erosion (Agassi et al., 1995). A pesticide's sorption properties are likely its most important properties, determining the pesticide's primary and secondary routes of transport through the environment. The adsorption of weakly basic and weakly acidic organic compounds that have a pK_a can be affected by the pH of the soil (Koskinen and Harper, 1990). A pesticide that has a high K_D and low P_{VP} will remain sorbed to soil particles, and a pesticide that has a low K_D and high P_{VP} will be more likely to dissipate through volatilization (Himel et al., 1990). Compounds with low K_D values and high S_W are more likely to be dissolved in water and thus leach or runoff into surface waters.

Soil properties or characteristics that influence the movement of pesticides through the environment include organic matter content, texture, slope, and moisture content. In one study by Truman et al. (2001), runoff and erosion losses for bare soil conditions increased as slope length increased, but total runoff and maximum runoff and erosion for each rainfall event were similar. Soil

characteristics also affect the amount of sediment present in runoff (Shirazi et al., 2001; Steegen et al., 2001).

The amount of pesticides and sediment in surface water runoff is also governed by climatic factors such as rainfall amount, duration, and timing, in combination with antecedent soil moisture (Leu et al., 2004). Rainfall intensity is also important, as an increase in rainfall intensity causes an increase in runoff initiation (Müller et al., 2004). Herbicides have also been detected in rainfall, showing that herbicide volatization into the atmosphere can result in the deposition of herbicides in areas where no herbicide application has been made. Goolsby showed a higher ratio of deethylatrazine to atrazine in rainfall, suggesting that atrazine might have undergone atmospheric degradation (1997).

Agronomic practices play a major role in determining the concentration of pesticides and sediment in surface water runoff. Various types of conservation tillage have been successful in reducing pesticide runoff from agricultural fields. Conservation tillage systems can stabilize soil, slow and reduce runoff, and therefore increase water infiltration and reduce erosion and pesticide runoff (Felsot et al., 1990). In one study, tillage showed no significant effect on surface runoff, but ridge tillage reduced concentrations of sediment in runoff when compared to moldboard plowing (Zhao et al., 2001). It is important for conservation tillage systems to be implemented based on site conditions, as pesticide runoff can be equal or greater in conservation tillage systems than in conventional systems if heavy rains occur soon after herbicide application, or if infiltration is limited due to poor drainage and impervious soils (Fawcett et al.,

1994). Herbicide runoff and the concentration of herbicides in runoff can be reduced by other means, such as using a banded rather than a broadcast application (Hansen et al., 2001). The rate of herbicide application also has a large effect on herbicide concentrations in runoff (Baker and Mickelson, 1994).

In addition to conservation tillage, the incorporation of other best management practices (BMPs) is another way to reduce runoff volumes and velocities and therefore sediment and pesticide runoff amounts. Residue management systems can protect against soil erosion, conserve soil moisture, and inhibit weed emergence (Locke and Bryson, 1997). Grassed waterways adjacent to and within fields have shown great promise for decreasing both sediment and pesticide runoff from agricultural areas (Fiener and Auerswald, 2003).

Studies have been performed in the highly agricultural Mississippi Delta to measure pesticide concentrations in surface and ground water, soil sediment, and aquatic animals (Ford and Hill, 1991). However, there is very little, if any, historical pesticide or sediment data available for the UPRB, located in east-central Mississippi (Figure 2.1).

Nationwide litigation over the past decade has forced the EPA and state primacy agencies to address the CWA's TMDL provisions. The TMDL process requires state environmental agencies to submit a biannual CWA §303(d) list of impaired waterbodies to EPA, while later preparing and submitting a TMDL for each impaired waterbody. The TMDL must address both point and NPS contaminants. Mississippi's 2004 §303(d) list showed 19 impaired waters (13

monitored and 6 evaluated) in HUC 03180001, with the following impairments:

12 biological and 4 each for nutrient, pathogen, organic enrichment, pesticide,

and sediment (MDEQ, 2004). Evaluated stream segments are those for which

there was no monitoring data available, and they were based mostly on land-

based anecdotal information and initially placed on the state's 1996 CWA

§303(d) list. In Mississippi, pesticides have been frequently listed as an

"evaluated" NPS of contamination based on past land use patterns, with no

regular monitoring data to support the listing. The UPRB was selected as a

study area to monitor selected pesticide and total dissolved solids (TDS) levels in

nearby surface waters because of its unique water quality and public health

issues. The Pearl River feeds into the Ross Barnett Reservoir, which is the

drinking water supply for Jackson, Mississippi. However, due to changes in land

use/land cover (LULC) in the UPRB, such as the decrease in cropland, waters

that were once impaired by pesticides and siltation may not currently be

impaired.

The main objectives of this study were two-fold. The first objective was to

determine the presence and concentration of selected pesticides in portions of

the UPRB, in particular in segments of the Upper Pearl River and in segments of

the Yockanookany River and Tuscolameta Creek, which are both tributaries of

the Pearl River. The second objective was to determine the concentration of

TDS at selected sites along the Upper Pearl River. Samples were analyzed for

TDS because siltation was the leading cause of impairment in the UPRB on the

MDEQ's 1998 303(d) list (MDEQ, 1999).

MATERIALS AND METHODS

Pesticide Selection Criteria

Compounds were selected for analysis based on several factors.

Samples were analyzed for p,p'-DDE (a metabolite of DDT) due to regulatory

concern over the presence of persistent, organic pollutants in Mississippi's

surface waters. Samples were analyzed for hexazinone and triclopyr because of

the silviculture acreage in the study area, since these compounds are commonly

used in site preparation and release of young pine trees. The remaining

compounds were studied because a literature review showed that they have

been detected in surface and/or ground water samples in various countries and

in agricultural production areas in the Mississippi River Delta (Buttle, 1990; David

et al., 2003; Field et al., 2003; Kalkhoff, et al., 2003; Kolpin et al., 1998; Nelson

and Jones, 1994; Selim, 2003; Senseman et al., 1997; Verstraeten, et al., 1999).

Atrazine, simazine, and metolachor have even been detected in finished water of

community water supplies (Coupe and Blomquist, 2004). Finally, the selected

compounds were analyzed because of their physical and chemical

characteristics. Characteristics that most affect the runoff potential of a pesticide

are its soil half-life, soil sorption coefficient, and water solubility (Table 2.1).

Pesticide Analysis

Grab samples were taken weekly from seven USGS gauged sites in the

UPRB from May 2002 through August 2002 and then monthly thereafter through

May 2003 (Figure 2.2). Four liters of water were retrieved at each site – 2 liters

for extraction and 2 liters to be stored as a duplicate sample. Four 1-L amber bottles were strapped to a metal rack and lowered below the water surface in the approximate center of flow at each site (Senseman et al, 1997). Samples were immediately placed on ice for transport and stored at approximately 4±1 °C until extraction. When each sample was taken, the stage height of the river, time of sample retrieval, and temperature of the sample were recorded.

Burnside was the first site to be sampled on each sampling trip, so it was designated as the fortification site where four extra liters of water were sampled and fortified. A 2-mL aliquot of a methanol solution with the fifteen pesticides to be analyzed was added to each liter. The final concentration of all compounds in a 2-L sample was approximately 20 µg/L, except diuron and fluometuron, which were at concentrations of approximately 50 µg/L. Freshly spiked samples were also prepared in the lab and extracted with each sample set for quality control. Table 2.2 shows the pesticides analyzed with their method of detection.

Before extraction, each surface water sample and fortified sample was labeled, and the sample number and other pertinent information were recorded. Each sample set consisted of twelve samples – seven actual surface water samples, one high lab spike, one low lab spike, one field spike, one deionized (DI) water blank, and a glassware wash. The latter was not extracted but condensed, processed, and analyzed like the other samples. At least one spike was extracted per run on the six-unit filtration apparatus so that there was always at least one spike per five samples filtered. All glassware used in each extraction procedure (filter reservoirs, graduated test tubes, and collection vials) was

thoroughly rinsed in ethyl acetate (EtAc). The rinsate was set aside and later

analyzed as the glassware wash sample. The rinsate was evaporated on the

Rotovap[1] until it was condensed enough to fit in a graduated test tube,

evaporated with nitrogen, and processed in accordance with the other samples.

The extraction procedure used was a modified version of EPA Method

525.2, which allows for either solid phase extraction (SPE) or liquid-liquid

extraction (Eichelberger at al., 1988). For this research, the SPE method was

used with the Bakerbond Speedisks$^®$ and J. T. Baker Speedisk$^®$ Expanded

Extraction Station[2]. The SPE disks were Bakerbond Speedisks™ C_{18} with a

50mm diameter and 1mm bed height. The disks were placed onto the extraction

station, and 1-L glass reservoirs were placed snugly on top of the disks. The

manifold was set up so that liquid flowed through the disks and into several large

Erlenmeyer flasks connected in sequence with plastic tubing. The flasks were

then connected to a solvent trap, which was connected to a vacuum source.

Surface water samples and DI water used for lab spikes and the lab blank

were placed in the lab prior to extraction so that they could slowly reach room

temperature. With all samples at room temperature, more accurate pH readings

could be taken during the extraction procedure. Sample preparation began by

removing 10 mL of sample water from each 1-L sample bottle to allow room for

MeOH to be added and mixed with the sample. Next, 5 mL MeOH was added

per liter of water to each sample to aid in sample homogenation. Immediately

prior to extraction, drops of 11.6 M hydrochloric acid (HCl) were added to each

liter of water to adjust the sample pH between 2.0 and 2.5 (Mueller et al., 2001).

The Beckman Φ295 pH meter[3] was calibrated before each use with the 1.68 and 4.0 pH standards, and the pH for each 1-L sample was recorded.

Next, high and low lab spikes were prepared by fortifying DI water with a stock solution that contained all pesticides at a concentration of approximately 1000 µg/L, except diuron and fluometuron, which were at a concentration of approximately 2500 µg/L. The stock solution was added to the high and low lab spikes, respectively, in 10- and 1-mL aliquots. The final concentration of all compounds in a 2-L sample of water was approximately 5 µg/L for the high spike and 0.5 µg/L for the low spike, except for diuron and fluometuron, which were at concentrations of approximately 12.5 µg/L and 1.25µg/L, respectively, for the high and low fortified samples. Diuron and fluometuron were at higher concentrations due to the method of analysis by a Hewlett-Packard 1100 Series High Performance Liquid Chromatography – Photo Diode Array (HPLC-PDA)[4].

After sample preparation was complete, each disk was washed with 5 mL of a 1:1 mixture of EtAc and methylene chloride (MeCl$_2$) to wash off any impurities. The disks were then pre-wetted with 5 mL methanol (MeOH), which soaked the disk for one minute. A vacuum was then applied, drawing most but not all of the MeOH through the disk. A thin layer of MeOH was left on the disk surface, which was not allowed to go dry after this point in the procedure. The disk was next rinsed with 5 mL DI water by adding the water to the methanol-soaked disk. A vacuum was applied, drawing the MeOH and most of the DI water through the disk but leaving a thin layer of DI water on the disk surface.

Next, samples were poured through the reservoirs, slowly applying a vacuum so the flow rate did not exceed 200 mL/minute. Each sample bottle was vigorously rinsed with approximately 30 mL of DI water to dislodge any sediment particles from the wall of the bottle. The disks were then dried by maintaining a vacuum for approximately ten minutes. The disk and reservoir, remaining intact, were removed from the extraction station. The collection chamber and vial were inserted into the extraction station, and the disk and reservoir were placed on top of the collection chamber. The reservoirs were rinsed with 5 mL EtAc. Half of the EtAc was drawn through the disk, the vacuum was released, and the solvent was allowed to soak the disk for one minute before the remaining solvent was drawn through the disk. This same procedure was repeated with 5 mL of $MeCl_2$. The filtration reservoirs were then rinsed with two 3-mL portions of 1:1 $EtAc:MeCl_2$, and the solvent was slowly drawn through the disks.

The collection vials were removed from the extraction manifold, and five to seven grams of anhydrous sodium sulfate were poured into the vials to absorb any water present in the eluates. The eluates were then poured into a graduated test tube and placed under a gentle stream of nitrogen in a sand bath at approximately 40°C. The vials and sodium sulfate were rinsed with two 3-mL portions of 1:1 $EtAc:MeCl_2$, and the rinsate was placed in the graduated test tubes to be concentrated. Samples were concentrated to approximately 2.5 mL and carefully brought to a final volume of 3.0 mL with ethyl acetate. One mL was placed in a vial for analysis by Gas Chromatography – Mass Selective Detector (GC-MSD)[5], and one mL was pipeted into another vial for derivatization at a later

time. The remaining mL of extract was placed back under a gentle stream of nitrogen, blown down to dryness at approximately 40°C, and brought back up in one mL of MeOH. The extract in MeOH was filtered through 0.2- µm syringe filters[6] using 3-mL syringes and placed in a vial for analysis by HPLC-PDA.

For the in-vial derivatization procedure, calibration standards for 2,4-D and triclopyr were made in duplicate at the following concentrations using a 2500 ppb stock solution and derivatized along with each set: 50, 100, 250, 500, 1000, 2000, and 4000 ppb. The one mL of extract was blown to near dryness under a gentle stream of nitrogen at 40°C. A ring of concentrated eluates remained around the bottom, outer edge of the vial, but no standing liquid was in the vial. Next, 50 µL of the derivatization reagent[7] boron trifluoride-methanol, 14% solution, was added to each vial for derivatization, and vial caps were replaced. The vials were placed in an 60°C oven for one hour. Vials were then uncapped, and 450 µL of saturated sodium chloride (NaCl) solution was added to each vial, followed by 700 µL of hexane. The vials were recapped and vigorously vortexed for one minute. All samples were stored at approximately -15 C° until analysis.

The field and lab fortified samples were included in the extraction procedure to provide quality assurance for compound recoveries (Table 2.3). The targeted range for average recoveries of field and lab fortified samples was 70% - 120%, with a relative standard deviation (RSD) of approximately 15% or less. If recoveries fell too far outside this range, samples were re-extracted. Recoveries for tebuthiuron and metribuzin were consistently low, but the RSD of recoveries was also low. Field spikes for p,p'-DDE and pendimethalin had lower

recoveries and a slightly higher RSD, most likely because both compounds are often highly adsorbed to soil particles. Field spikes contained organic matter and suspended solids, unlike fortified lab samples.

Extracts in MeOH were analyzed on an Agilent 1100 HPLC-PDA. An injection volume of 100 µL was used for all samples. Additionally, an Alltech C-18 reverse-phase column (150 mm X 4.6 mm) was employed, with a column temperature of 40°C. A gradient mobile phase of acetonitrile:water (20:80v/v) was applied at a flow rate of 0.500 mL/min, and absorbance was measured at 245 nm. Table 2.2 lists average retention times for diuron and fluometuron, and Figure 2.3 shows an example chromatogram for both compounds.

Extracts in EtAc:MeCl$_2$ were analyzed on a Hewlett Packard Model 6890 GC with a Model 5973 MSD, using a 2 µL injection volume. GC-MSD separation was performed using a 5% phenyl methyl siloxane column (30 m x 250 µm) with a nominal film thickness of 0.25 µm. Helium was the carrier gas at an average velocity of 37 cm/sec and initial pressure of 10.5 psi, and the maximum column temperature was 325°C. Table 2.2 lists average retention times for all compounds, and Figures 2.4 and 2.5 show example chromatograms for non-derivatized and derivatized compounds, respectively, analyzed on the GC-MSD. An example calibration curve for diuron can be seen in Figure 2.6, with example calibration curves for all other analyzed compounds shown in Appendix A.

Total Dissolved Solids Analysis

Samples were taken for TDS analysis at three USGS gauged sites in the UPRB from September 2001 through January 2003. Samples were taken following substantial rainfall events in the watershed. The USGS website that displays real-time data taken at the sites was monitored for flow, and sampling was targeted for peak flow during a rainfall event. However, during the summer months, when rainfall was infrequent and river levels were extremely low, routine sampling was performed bi-monthly.

Since the TDS concentration of samples was determined gravimetrically, empty sample bottles were weighed before a sampling run to determine the tare weight of each bottle. Lids were removed from the pint-sized glass bottles before obtaining the tare weight. The tare weight was written on the bottle, along with a sample number, and this information was recorded. Samples were taken with a US DH-48 depth-integrating suspended sediment sampler[8] during times of low flow, usually during the summer months when the river was wadable, and with a US DH-59 depth integrating suspended hand line sampler[8] when the river could not be waded. The date, sample site, water temperature, gauge height, and time were recorded for each sample, and duplicate samples were taken at each site. Once at the lab, samples were placed in a walk-in cooler and stored at approximately 4±1 °C until analysis, in order to prevent evaporation of the water.

A modified version of the USGS method for fluvial sediment analysis was adapted and used for this study (Sholar and Shreve, 1998). At the time of analysis, lids were again removed from the sample bottles, and the weight of the

bottle, water, and dissolved solids mixture therein were recorded. Samples were analyzed via the filtration method of analysis, using 60-mL Buchner funnels[9] with a 44 mm fritted disc. The neck of the funnel was inserted through a rubber stopper, and the stopper and funnel were placed in the top of a heavy-wall filter flask. A vacuum was created, pulling water through the funnel and into the flask.

Once the funnel and stopper were snugly fitted in the flask, DI water was filtered through the funnel to remove any remaining filter fibers in the fritted disc. Next, DI water was poured into the funnel, a 42.5 mm Whatman #934-AH glass fiber filter[10] was centered in the funnel and suspended on the water, and a vacuum was applied. DI water was filtered through the funnel once more to seat the filter and remove any loose filter fibers. Once the filters were properly seated on the funnels, the funnels were labeled with a corresponding sample number. The funnels were then placed in a wire rack and oven dried for four hours at approximately 103°C (Matthes et al., 1991). After being dried, the funnels were left in the wire racks and cooled in a desiccator cabinet for three hours. Latex gloves were worn while handling the dried funnels to prevent contamination with moisture, dirt, or oil. Once cooled, each funnel was weighed to the nearest 0.0001 g on an analytical balance, and this tare weight was recorded. Finally, the water and dissolved solids mixture was poured from the sample bottle through the funnel, and a vacuum was applied. Once the sample bottle was emptied, it was thoroughly rinsed with DI water, and the rinsate was poured into the funnel. Sample bottles were checked to ensure that no particles remained in the bottle. Once all samples were filtered, the funnels were placed in a wire rack

and oven dried for four hours at approximately 103°C. The funnels remained in

the wire racks and were removed from the oven to cool in a desiccator cabinet

for three hours. At this time, each funnel was weighed to the nearest 0.0001 g,

and the weight of the dissolved solids, funnel, and filter was recorded. The

weight of the dissolved solids was determined by subtracting the tare weight of

the funnel and filter from the weight of the dissolved solids, funnel, and filter. The

dissolved solids concentration, in mg/L, was calculated for each sample:

$$\frac{\text{Weight of dissolved solids} \times 10^6}{\text{Weight of water-dissolved solids mixture}}$$

RESULTS AND DISCUSSION

<u>Pesticide Analysis</u>

The level of quantification (LOQ) for all pesticides was 0.1 ng/mL. Only

detections that were at or above the LOQ are reported. The PROC

UNIVARIATE procedure in SAS statistical software was used to determine the

quartiles for detections $\geq$ the LOQ for each compound (Table 2.4) (SAS, 2005).

Most detections were at low levels. There was one sample, collected at the

Burnside site on May 16, 2002, which had unusually high concentrations

detected, representing the highest concentration detected for all compounds but

hexazinone.

Compounds were also summarized by the number of detections for each

compound at each site and the total number of detections at each site (Table

2.5). Burnside was the site with the highest number of detections, at 154 out of a

possible 390 detections for all compounds, and Walnut Grove was the site with the lowest number of detections, at 112 detections. All sites were sampled 26 times for 15 compounds, except the Ofahoma site, which was sampled 25 times for a possible 375 detections.

Although detections for most compounds were fairly frequent, they were at levels that rarely exceeded EPA Lifetime Health Advisory Levels (LHAL), which is one of the most stringent water quality criteria for drinking water. Table 2.6 summarizes the total number of detections for each compound and the number of detections per compound that exceeded the LHAL.

There were 905 total detections out of a potential 2,715 detections for all compounds over all sites and sampling dates. There were only three detections that were above the LHAL established by the EPA. The LHAL, as stated by the EPA, is "the concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects for a lifetime of exposure" (EPA 2002). The LHAL is based on the effects of a compound on a 70-kg adult drinking two liters of water every day (EPA, 2004).

The lack of pesticide detections above the LHAL is indicative of the low percentage of cropped land in the UPRB and the physical and chemical properties of pesticides being used today. Since the original listing of waters in the late 1980's and early 1990's, there has been a decline in cropped land in the UPRB. Furthermore, today's pesticides are much more environmentally friendly than those used in the past. Most notably, compounds have shorter half-lives. Of the 15 compounds analyzed, tebuthiuron has the longest half-life, at 12-15

months, with the degradation time depending on yearly rainfall and soil organic

matter content (Vencill, 2002). Half-lives of other compounds analyzed are much

shorter than a year. This is a vast improvement over the persistence of older

compounds such as DDT, whose half-life, along with its degradation products,

can be as long as 15 years (Boul et al., 1994; Howard et al., 1991).

Although pesticide detections were frequent, the detections generally

occurred at levels well below the LHAL set by the EPA. These findings agree

with results from studies in other areas of the Southeast (Coupe et al., 1998;

Senseman et al., 1997). Most pesticide concentrations were also well below

levels that would pose a toxicity hazard to aquatic organisms (Morgan and

Brunson, 2002).

<u>Total Dissolved Solids Analysis</u>

The PROC UNIVARIATE procedure in SAS statistical software was also

used to determine quartiles for TDS concentrations (SAS, 2005). Quartiles of

TDS concentrations for Burnside, Edinburg, and Carthage, the three sites that

were also sampled for TDS in addition to pesticides, are shown in Table 2.7. The

relationship of instantaneous water discharge to sediment concentration can be

found in Figure 2.7, Figure 2.8, and Figure 2.9 for Burnside, Carthage, and

Edinburg, respectively. The sediment concentration in the water should peak just

before the discharge peaks, and this trend can be observed, for the most part, in

these results. Although rainfall events were targeted for sampling, more frequent

sampling would have been desirable. However, due to the physical and time

limitations of remaining on site during a multi-day rainfall event, fewer samples were collected for some events, resulting in lower correlations between sediment concentration and water discharge for particular rainfall events. In addition, correlations were not as good during the summer months, possibly due to extremely low discharge levels that might have been out of reach for the continuous-sampling equipment.

Although Carthage had higher overall TDS concentrations than Burnside or Edinburg, this was likely due to the sandier soils and higher water velocities prevalent at this particular sampling site rather than non-point source agricultural runoff. Furthermore, most TDS concentrations for Carthage remained well below the 500 mg/L criteria established by the EPA for TDS (EPA, 2004). Care must be used in interpreting water quality data, as local disturbances (e.g. channelization or streambank erosion) near sampling points may misrepresent overall water quality in the larger watershed.

Based on the results of this UPRB water quality survey, selected UPRB waters on Mississippi's 2004 303(d) list, the most recent list that has been approved by the EPA, should be reevaluated and possibly removed from the list. Segments of the Pearl River, the Yockanookany River, and Tuscolameta Creek which were tested in this study appear to be meeting their designated uses, according to the results presented in this study. In the least, it is apparent that more water sampling data is needed to either remove waters from the state's 303(d) list or establish TMDLs for these waters.

SOURCES OF MATERIALS

[1]The Meyer N-Evap Model 111, Organomation Assn. Inc., Box 159, S. Berlin, MA 01549.

[2]J.T. Baker Speedisks and J.T. Baker Speedisk Extraction Station, Mallinckrodt Baker, Inc., 222 Red School Lane, Phillipsburg, NJ 08865.

[3]Beckman Φ295 pH/Temp./mV/ISE meter, Beckman Coulter, Inc. 4300 North Harbor Boulevard, P.O. Box 3100, Fullerton, CA 92834-3100.

[4]Hewlett-Packard 1100 Series HPLC-PDA, 2850 Centerville Rd., Wilmington, DE 19808.

[5]Hewlett-Packard Model 6890 GC and Model 5973 MSD, Hewlett-Packard Co., Boxwood Commerce Center, 300 Century Blvd., Wilmington, DE 19808.

[6]Acrodisc 13mm syringe filter with 0.2µm nylon membrane, Pall Gelman Sciences, 600 South Wagner Rd., Ann Arbor, MI 48103-9019.

[7]Derivatization agent, Sigma Chemical Company, P.O. Box 14508, St. Louis, MO 63178.

[8]USGS Hydrologic Instrumentation Facility, Building 2101, Stennis Space Center, MS 39529.

[9]Pyrex® 60-mL capacity, 40-60 µm porosity Buchner funnels, Corning® No. 36060, Corning Incorporated Life Sciences, 45 Nagog Park, Acton, MA 01720.

[10]Whatman 42.5 mm #934-AH glass fiber filters, Whatman Inc., Clifton, NJ 07014.

LITERATURE CITED

Agassi, M., J. Letey, W.J. Farmer, and P. Clark. 1995. Soil erosion contribution to pesticide transport by furrow irrigation. J. Environ. Qual. 24: 892-895.

Ando, C., R. Segawa, C. Gana, L. Li, J. Walters, R. Sava, T. Barry, K.S. Goh, P. Lee, D. Tran, J. White, and J. Hsu. 2003. Dissipation and offsite movement of forestry herbicides in plants of imporptance to Native Americans in California national forests. Bull. Environ. Contam. Toxicol. 71: 354-361.

Baker, J.L. and S.K. Mickelson. 1994. Application technology and best management practices for minimizing herbicide runoff. Weed Technol. 8: 862-869.

Battaglin, W.A., E.M. Thurman, S.J. Kalkhoff, and S.D. Porter. 2003. Herbicides and transformation products in surface waters of the Midwestern United States. J. Am. Water Resour. Assoc. August: 743-756.

Biggar, J.W. and R.L. Riggs. 1974. Apparent solubility of organochlorine insecticides in water at various temperatures. Hilgardia. 42: 383-391.

Bucheli, T.D., S.R. Müller, A. Voegelin, and R.P. Schwarzenbach. 1998. Bituminous roof sealing membranes as major sources of the herbicide (R,S)-Mecoprop in roof runoff waters: Potential contamination of groundwater and surface waters. Environ. Sci. Technol. 32: 3465-3471.

Buttle, J.M. 1990. Metolachlor transport in surface runoff. J. Environ. Qual. 19: 531-538.

Cohen, S., A. Svrjcek, T. Durborow, and N.L. Barnes. 1999. Water quality impacts by golf courses. J. Environ. Qual. 28:798-809.

Coupe, R.H. and J.D. Blomquist. 2004. Water-soluble pesticides in finished water of community water supplies. J. Am. Water Works Assoc. 96:10.

Coupe, R.H., E.M. Thurman, and L.R. Zimmerman. 1998. Relation of usage to the occurrence of cotton and rice herbicides in three streams of the Mississippi Delta. Environ. Sci. Technol. 32: 3673-3680.

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Crawford, C.G. 2001. Factors affecting pesticide occurrence and transport in a large midwestern river basin. J. Am. Water Resour. Assoc. 37: 1-15.

Dabrowski, J.M., S.K.C. Peall, A.J. Reinecke, M. Liess, and R. Schulz. 2002. Runoff-related pesticide input into the Lourens River, South Africa: Basic data for exposure assessment and risk mitigation at the catchment scale. Water, Air, and Soil Pollut. 135: 265-283.

David, M.B., L.E. Gentry, K.M. Starks, and R.A. Cooke. 2003. Stream transport of herbicides and metabolites in a tile-drained, agricultural watershed. J. Environ. Qual. 32:1790-1801.

Domagalski, J. 1996. Occurrence of dicofol in the San Joaquin River, California. Bull. Environ. Contam. Toxicol. 57:284-291.

Eichelberger, J.W., Behymer, T.D., and Budde, W.L. 1988. Determination of organic compounds in drinking water by liquid-solid extraction and capillary column gas chromatography/mass spectrometry: Method 525, Edition 2.1. U.S. Environ. Protect. Agency: Cincinnati, OH.

EPA. 2004. 2004 Edition of the Drinking Water Standards and Health Advisories. EPA 822-R-04-005. U. S. Environ. Protect. Agency, Office of Water: Washington, D.C.

Fawcett, R.S., B.R. Christensen, and D.P. Tierney. 1994. The impact of conservation tillage on pesticide runoff into surface water: A review and analysis. J. Soil Water Conserv. 49:126-135.

Field, J.A., R.L. Reed, T.E. Sawyer, S.M. Griffith, and P.J. Wigington, Jr. 2003. Diuron occurrence and distribution in soil and surface and ground water associated with grass seed production. J. Environ. Qual. 32:171-179.

Fiener, P. and K. Auerswald. 2003. Effectiveness of grassed waterways in reducing runoff and sediment delivery from agricultural watersheds. J. Environ. Qual. 32:927-936.

Felsot, A.S., J.K. Mitchell, and A.L. Kenimer. 1990. Assessment of management practices for reducing pesticide runoff from sloping cropland in Illinois. J. Environ. Qual. 19:539-545.

Ford, W.M. and E.P. Hill. 1991. Organochlorine pesticides in soil sediments and aquatic animals in the Upper Steele Bayou Watershed of Mississippi. Arch. Envir. Contam. Toxicol. 20:161-167.

Gan, J., Y. Zhu, C. Wilen, D. Pittenger, and D. Crowley. 2003. Effect of planting covers on herbicide persistence in landscape soils. Environ. Sci. Technol. 37:2775-2779.

Hansen, N.C., J.F. Moncrief, S.C. Gupta, P.D. Capel, and A.E. Olness. 2001. Herbicide banding and tillage system interactions on runoff losses of alachlor and cyanazine. J. Environ. Qual. 30:2120-2126.

Hapeman, C.J., L.L. McConnell, C.P. Rice, A.M. Sadeghi, W.F. Schmidt, G.W. McCarty, J.L. Starr, P.J. Rice, J.T. Angier, and J.A. Harmon-Fetcho. 2003. Current United States Department of Agriculture – Agriculture Research Service research on understanding agrochemical fate and transport to prevent and mitigate adverse environmental impacts. Pest Manag. Sci. 59:681-690.

Hartanto, H., R. Prabhu, A.S.E. Widayat, and C. Asdak. 2003. Factors affecting runoff and soil erosion: Plot-level soil loss monitoring for assessing sustainability of forest management. For. Ecol. Manage. 180:361-374.

Himel, C.M., H. Loats, and G.W. Bailey. 1990. Pesticide sources to the soil and principles of spray physics. *In* Pesticides in the Soil Environment: Processes, impacts, and modeling. Cheng, H. H., ed. SSSA:Madison, WI. pp. 7-50.

Hipp, B., S. Alexander, and T. Knowles. 1993. Use of resource-efficient plants to reduce nitrogen, phosphorus, and pesticide runoff in residential and commercial landscapes. Water Sci. Technol. 28:205-213.

Howard, P.H., R.S. Boethling, W.F. Jarvis, W.M. Meylan, and E.M. Michalenko. 1991. Handbook of environmental degradation rates. H.T. Printup, ed. Lewis Publishers:Chelsea, MI. pp. 121-123.

Kalkhoff, S.J., K.E. Lee, S.D. Porter, P.J. Terrio, and E.M. Thurman. 2003. Herbicides and herbicide degradation products in upper Midwest agricultural streams during August base-flow conditions. J. Environ. Qual. 32:1025-1035.

Kolpin, D.W., J.E. Barbash, and R.J. Gilliom. 1998. Occurrence of pesticides in shallow groundwater of the United States: Initial results from the national water-quality assessment program. Environ. Sci. Technol. 32:558-566.

Koskinen, W.C. and S.S. Harper. 1990. The retention process: Mechanisms. *In* Pesticides in the Soil Environment: Processes, impacts, and modeling. Cheng, H. H., ed. SSSA:Madison, WI. pp. 51-77.

Larson, S.J., P.D. Capel, and D.A. Goolsby. 1995. Relations between pesticide use and riverine flux in the Mississippi River Basin. Chemosphere 31: 3305-3321.

Leonard, R.A. 1990. Movement of pesticides into surface waters. *In* Pesticides in the Soil Environment: Processes,impacts, and modeling. Cheng, H.H., ed. SSSA:Madison, WI. pp. 303-349.

Leu, C., H. Sincer, C. Stamm, S.R. Müller, and R.P. Schwarzenbach. 2004. Simultaneous assessment of sources, processes, and factors influencing herbicide losses to surface waters in a small agricultural catchment. Environ. Sci. Technol. 38:3827-3834.

Locke, M.A. and C.T. Bryson. 1997. Herbicide-soil interactions in reduced tillage and plant residue management systems. Weed Sci. 45:307-320.

Louchart, X., M. Voltz, P. Andrieux, and R. Moussa. 2001. Herbicide transport to surface waters at field and watershed scales in a Mediterranean vineyard area. J. Environ. Qual. 30:982-991.

Ma, Q.L., A.E. Smith, J.E. Hook, R.E. Smith, and D.C. Bridges. 1999. Water runoff and pesticide transport from a golf course fairway: Observations vs. Opus model simulations. J. Environ. Qual. 28:1463-1473.

Matthes, W.J., C.J. Sholar, and J.R. George. 1991. Quality-assurance plan for the analysis of fluvial sediment: U.S. Geological Survey Open-File Report 91-467, pp. 1-31.

MDEQ. 1999. State of Mississippi 1998 List of Waterbodies. Miss. Dept. Environ. Qual.:Jackson, MS.

MDEQ. 2004. Mississippi 2004 section 303(d) list of impaired water bodies. MDEQ, Surface Water Division of the Office of Pollution Control:Jackson, MS. pp. 96-126.

Morgan, E.R. and M.W. Brunson. 2002. Toxicities of agricultural pesticides to selected aquatic organisms. Southern Regional Aquaculture Center. Publication No. 4600. pp. 1-26.

Mueller, T.C., S.A. Senseman, K.H. Carson, and A.S. Sciumbato. 2001. Stability and recovery of triazine and chloroacetamide herbicides from pH adjusted water samples by using Empore solid-phase extraction disks and gas chromatography with ion trap mass spectrometry. J. AOAC Int. 84:1070-1073.

Müller, K., M. Trolove, T.K. James, and A. Rahman. 2004. Herbicide loss in runoff: Effects of herbicide properties, slope, and rainfall intensity. Aust. J. Soil Res. 42:17-27.

Neary, D.G. 1985. Fate of pesticides in Florida's forests: An overview of potential impacts on water quality. *In* Proceedings of the Soil and Crop Science Society of Florida. 44:18-24

Nelson, H. and R.D. Jones. 1994. Potential regulatory problems associated with atrazine, cyanazine, and alachlor in surfacewater source drinking water. Weed Technol. 8:852-861.

Pereira, W.E. and F.D. Hostettler. 1993. Nonpoint source contamination of the Mississippi River and its tributaries by herbicides. Environ. Sci. Technol. 27:1542-1552.

Riley, M.B. 2003. Herbicide losses in runoff of containerized plant production nurseries. HortTechnology 13:16-22.

Sabljic, A. 1984. Predictions of the nature and strength of soil sorption of organic pollutants by molecular topology. J. Agric. Food Chem. 32:243-246.

SAS. 2005. SAS Institute, Inc., SAS Campus Dr., Cary, NC, 27513 USA.

Selim, H.M. 2003. Retention and runoff losses of atrazine and metribuzin in soil. J. Environ. Qual. 32:1058-1071.

Senseman, S.A., T.L. Lavy, and T.C. Daniel. 1997. Monitoring groundwater for pesticides at selected mixing/loading sites in Arkansas. Environ. Sci. Technol. 31:283-288.

Senseman, S.A., T.L. Lavy, J.D. Mattice, E.E. Gbur, and B.W. Skulman. 1997. Trace level pesticide detections in Arkansas surface waters. Environ. Sci. Technol. 31:395-401.

Shirazi, M.A., L. Boersma, C.B. Johnson, and P.K. Haggerty. 2001. Predicting physical and chemical water properties from relationships with watershed soil characteristics. J. Environ. Qual. 30:112-120.

Sholar, C.A. and E.A. Shreve. 1998. Quality-assurance plan for the analysis of fluvial sediment by the Northeastern Region, Kentucky District Sediment Laboratory: U. S. Geological Survey Open-File Report 98-384, pp. 1-20.

Smith, S.J., A.N. Sharpley, and L.R. Ahuja. 1993. Agricultural chemical discharge in surface water runoff. J. Environ. Qual. 22:474-480.

Steegen. A., G. Govers, I. Takken, J. Nachtergaele, J. Poesen, and R. Merckx. 2001. Factors controlling sediment and phosphorus export from two Belgian agricultural catchments. J. Environ. Qual. 30:1249-1258.

Tanabe, A., H. Mitobe, K. Kawata, A. Yasuhara, and T. Shibamoto. 2001. Seasonal and spatial studies on pesticide residues in surface waters of the Shinano River in Japan. J. Agric. Food Chem. 49:3847-3852.

Truman, C.C., R.D. Wauchope, H.R. Sumner, J.G. Davis, G.J. Gascho, J.E. Hook, L.D. Chandler, and A.W. Johnson. 2001. Slope length effects on runoff and sediment delivery. J. Soil Water Conserv. 56:249-256.

USA EPA Registration Eligibility Decision (RED). Triclopyr October 1998. EPA 738-R-98-011.

Vencill, W.K., Ed. 2002. Herbicide Handbook, 8th Edition. Weed Sci. Soc. Am.: Lawrence, KS.

Verstraeten, I.M., J.D. Carr, G.V. Steele, E.M. Thurman, K.C. Bastian, and D.F. Dormedy. 1999. Surface water-ground water interaction: Herbicide transport into municipal collector wells. J. Environ. Qual. 28:1396-1405.

Walston, A.T., R.C. Williamson, and J.C. Stier. 2001. Pesticide runoff: How does turf contribute? Turfgrass Trends. 10:1-6.

Wauchope, R.D. 1978. The pesticide content of surface water draining from agricultural fields – a review. J. Environ. Qual. 7:459-472.

Wauchope, R.D., T.M. Buttler, A.G. Hornsby, P.W.M. Augustijn-Beckers, and J.P. Burt. 1992. The SCS/CES pesticide properties database for environmental decision-making. Rev. Environ. Contam. Toxicol. 123:1-164.

Zhao, S.L., S.C. Gupta, D.R. Huggins, and J.F. Moncrief. 2001. Tillage and nutrient source effects on surface and subsurface water quality at corn planting. J. Environ. Qual. 30:998-1008.

Zimmerman, L.R., E.M. Thurman, and K.C. Bastian. 2000. Detection of persistent organic pollutants in the Mississippi Delta using semipermeable membrane devices. Sci. Total Environ. 248:169-179.

Table 2.1. Characteristics of compounds analyzed [a].

Pesticide	pK$_a$	Soil Half-Life (d)	Soil Sorption (Koc)	Water Solubility (mg/L)
alachlor	none	21 avg.	124 avg.	200 at 20°C
atrazine	1.7 at 21°C	60 [b]	100 avg. [b]	33 at 22°C and pH=7
cyanazine	5.1	14 avg. [b]	190 avg. [b]	160 at 23°C
diuron	none	90 avg. [b]	480 [b]	42 at 25°C
2,4-D	2.8 [b]	10 avg. [b]	20 avg. acid [b]	900 at 25°C
p,p'-DDE	none	2-15.6 years [c]	50,100 [d]	0.12 at 25°C [e]
fluometuron	none	85 [b]	100 avg. [b]	110 at 22°C
hexazinone	not available	90 [b]	54 avg. [b]	33,000 at 25°C
metolachlor	none	90 [b]	200 [b]	488 at 20°C
metribuzin	not available	30-60	60 avg. (estimated) [b]	1,100 at 20°C
norflurazon	none	45-180, depending on OM and clay content	700 avg. [b]	28 at 25°C
pendimethalin	none	44	17,200 avg.	0.275 at 25°C
simazine	1.62	60 avg. [b]	130 avg. [b]	6.2 at 22°C
tebuthiuron	none	365-455	80 avg. [b]	0.00257 at 20°C
triclopyr	2.68	30 avg.	20 for triethylamine salt [f]	430 at 25°C

[a] Vencill, 2002. [b] Wauchope et al., 1992. [c] Howard et al., 1991. [d] Sabljic, 1984. [e] Biggar and Riggs, 1974. [f] USA EPA Registration Eligibility Decision (RED), 1998.

Table 2.2. List of compounds with their primary detection methods and average retention times.

COMPOUND	PRIMARY METHOD OF DETECTION	RETENTION TIME (mins.)
tebuthiuron	GC-MSD	14.68
fluometuron	HPLC-PDA	15.04
diuron	HPLC-PDA	16.00
2,4-D	GC-MSD (derivatized)	17.12
triclopyr	GC-MSD (derivatized)	18.34
simazine	GC-MSD	19.16
atrazine	GC-MSD	19.23
metribuzin	GC-MSD	21.47
alachlor	GC-MSD	21.99
metolachlor	GC-MSD	23.15
cyanazine	GC-MSD	23.32
pendimethalin	GC-MSD	24.37
p,p'-DDE	GC-MSD	26.23
norflurazon	GC-MSD	28.58
hexazinone	GC-MSD	29.01

Table 2.3. Average spike recoveries and standard deviations of recoveries for each compound (n = 26).

HERBICIDE	Field Spike	High Spike	Low Spike
	Recovery (%)		
2,4 D	68.0 $\pm$ 28.1	61.8 $\pm$ 31.0	86.0 $\pm$ 36.8
triclopyr	75.6 $\pm$ 29.2	66.0 $\pm$ 26.3	88.9 $\pm$ 36.0
diuron	78.2 $\pm$ 16.4	76.1 $\pm$ 10.8	80.4 $\pm$ 18.2
fluometuron	83.5 $\pm$ 17.7	84.2 $\pm$ 12.5	89.1 $\pm$ 20.1
hexazinone	89.7 $\pm$ 24.5	84.3 $\pm$ 17.9	120.5 $\pm$ 17.0
tebuthiuron	44.5 $\pm$ 9.2	68.7 $\pm$ 19.9	98.5 $\pm$ 11.0
alachlor	82.4 $\pm$ 20.2	83.6 $\pm$ 14.7	111.4 $\pm$ 16.1
atrazine	84.3 $\pm$ 19.9	84.2 $\pm$ 16.0	108.0 $\pm$ 16.7
cyanazine	80.1 $\pm$ 32.2	89.5 $\pm$ 31.9	121.0 $\pm$ 23.7
p,p'-dde	43.7 $\pm$ 15.6	78.3 $\pm$ 13.5	73.6 $\pm$ 18.8
metolachlor	84.6 $\pm$ 20.0	84.3 $\pm$ 14.5	115.3 $\pm$ 16.8
metribuzin	39.6 $\pm$ 13.1	60.2 $\pm$ 9.6	84.6 $\pm$ 12.2
norflurazon	91.4 $\pm$ 26.7	88.4 $\pm$ 20.7	128.2 $\pm$ 18.3
pendimethalin	30.8 $\pm$ 24.9	84.9 $\pm$ 12.3	107.3 $\pm$ 15.9
simazine	80.1 $\pm$ 18.5	81.0 $\pm$ 15.6	106.2 $\pm$ 15.6

Table 2.4. Detections ≥ level of quantification (0.1 µg/L), in quartiles, for each
pesticide*.

HERBICIDE	QUARTILES (Concentration, µg/L)				
	MINIMUM	LOWER	MEDIAN	UPPER	MAXIMUM
2,4 D	0.10	0.12	0.17	0.25	14.40
triclopyr	0.10	0.14	0.20	0.23	13.18
diuron	0.16	0.24	0.27	0.51	25.46
fluometuron	0.23	0.97	1.07	1.18	27.93
tebuthiuron	0.12	0.18	0.21	0.25	0.48
alachlor	0.10	0.12	0.16	0.21	9.49
atrazine	0.10	0.13	0.15	0.16	6.60
cyanazine	0.11	0.15	0.20	0.24	4.82
p,p'-dde	0.10	0.11	0.12	0.14	2.57
hexazinone	0.10	0.21	0.27	0.36	3.54
metolachlor	0.10	0.14	0.17	0.19	9.89
metribuzin	0.13	0.21	0.24	0.25	2.19
norflurazon	0.10	0.23	0.28	0.32	11.06
pendimethalin	0.22	0.25	0.29	0.33	7.03
simazine	0.11	0.14	0.15	0.18	6.29

*Quartiles are as follows: minimum = minimum concentration; lower = concentration > than 25%
of concentrations detected; median = concentration > than 50% of the concentrations detected;
upper = concentration > than 75% of the concentrations detected; maximum = maximum
concentration detected. NA = LHAL not available. UR = LHAL under review by the EPA.

Table 2.5. Number of detections for each compound by site and total detections by site.

HERBICIDE	BURNSIDE	CARTHAGE	EDINBURG	LENA	KOSCIUSKO	OFAHOMA	WALNUT GROVE
2,4 D	6	8	12	9	12	6	6
triclopyr	2	1	2	2	7	1	3
diuron	17	6	1	0	4	2	0
fluometuron	2	13	0	0	0	1	0
tebuthiuron	16	15	17	18	3	2	15
alachlor	9	3	4	5	6	7	5
atrazine	16	10	15	13	13	13	5
cyanazine	12	8	13	7	12	9	10
p,p'-dde	7	7	6	8	4	4	5
hexazinone	17	26	25	26	26	25	26
metolachlor	20	18	21	22	19	20	18
metribuzin	3	1	0	1	3	1	2
norflurazon	13	11	11	10	12	13	8
pendimethalin	5	1	2	0	1	1	3
simazine	9	2	7	5	9	11	6
TOTAL DETECTS FOR EACH SITE	154	130	136	126	131	116	112

Table 2.6. Total detections for each compound, LHAL, and detections that exceeded the LHAL.

HERBICIDE	TOTAL DETECTS FOR EACH COMPOUND	LHAL (ppb)	NO. OF DETECTS ≥LHAL
2,4 D	59	70	0
triclopyr	18	NA	NA
diuron	30	10	1
fluometuron	16	90	0
tebuthiuron	86	500	0
alachlor	39	NA	NA
atrazine	85	UR*	NA
cyanazine	71	1	1
p,p'-dde	41	NA	NA
hexazinone	171	400	0
metolachlor	138	100	0
metribuzin	11	200	0
norflurazon	78	NA	NA
pendimethalin	13	NA	NA
simazine	49	4	1
TOTAL DETECTS FOR ALL SITES	905		3

Table 2.7. Quartiles of TDS concentrations for each site sampled.*

SAMPLING SITE	QUARTILES (mg/L)				
	MINIMUM	LOWER	MEDIAN	UPPER	MAXIMUM
Burnside	0	8.69	12.55	18.9	133.79
Edinburg	0.1	0.14	0.2	0.23	13.18
Carthage	3.09	12.48	20.03	28.64	613.73

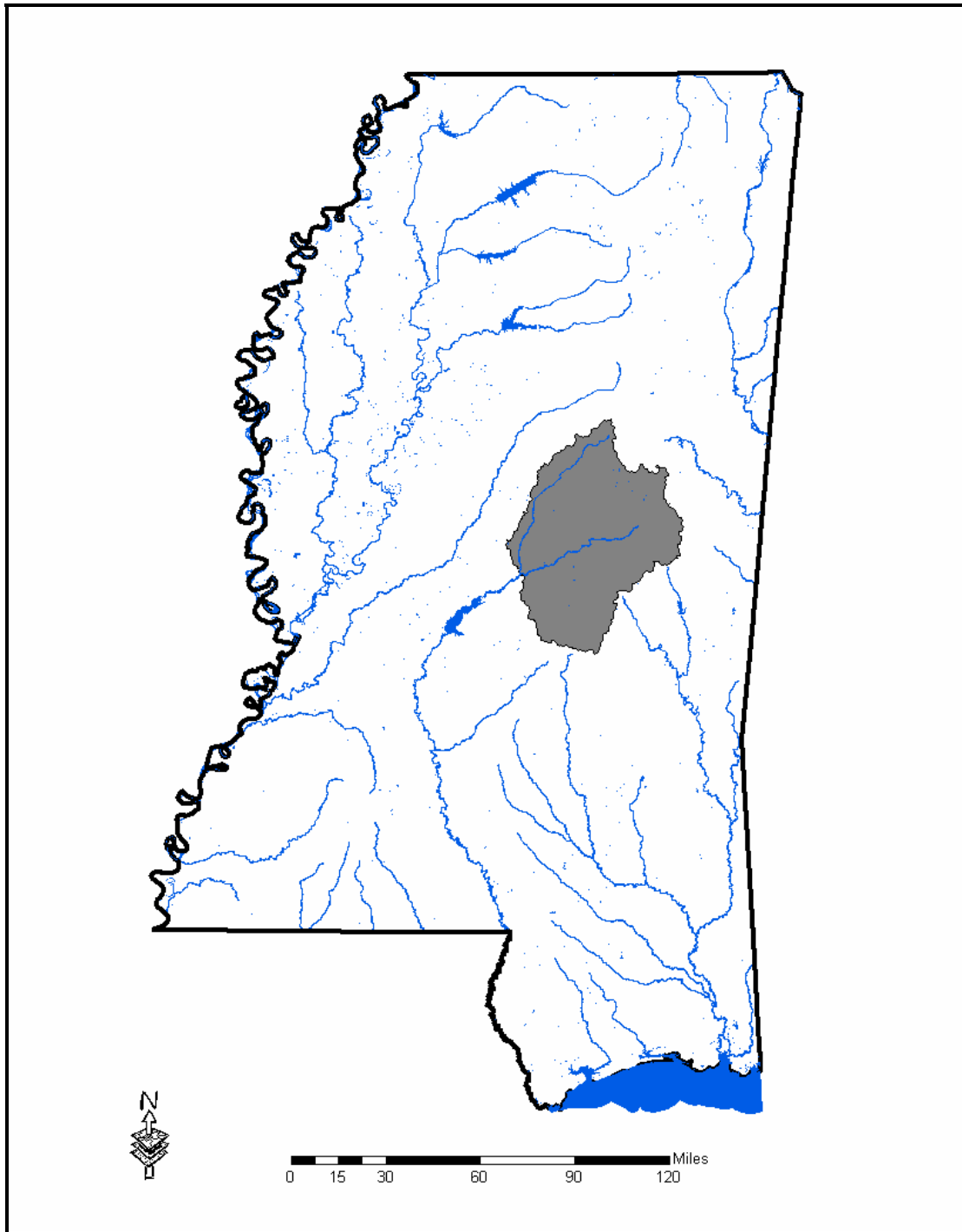*See Table 2.4 for a definition of quartiles.

Figure 2.1 Location of the Upper Pearl River Basin in East-Central Mississippi.

Figure 2.2. Sampling locations within the UPRB.
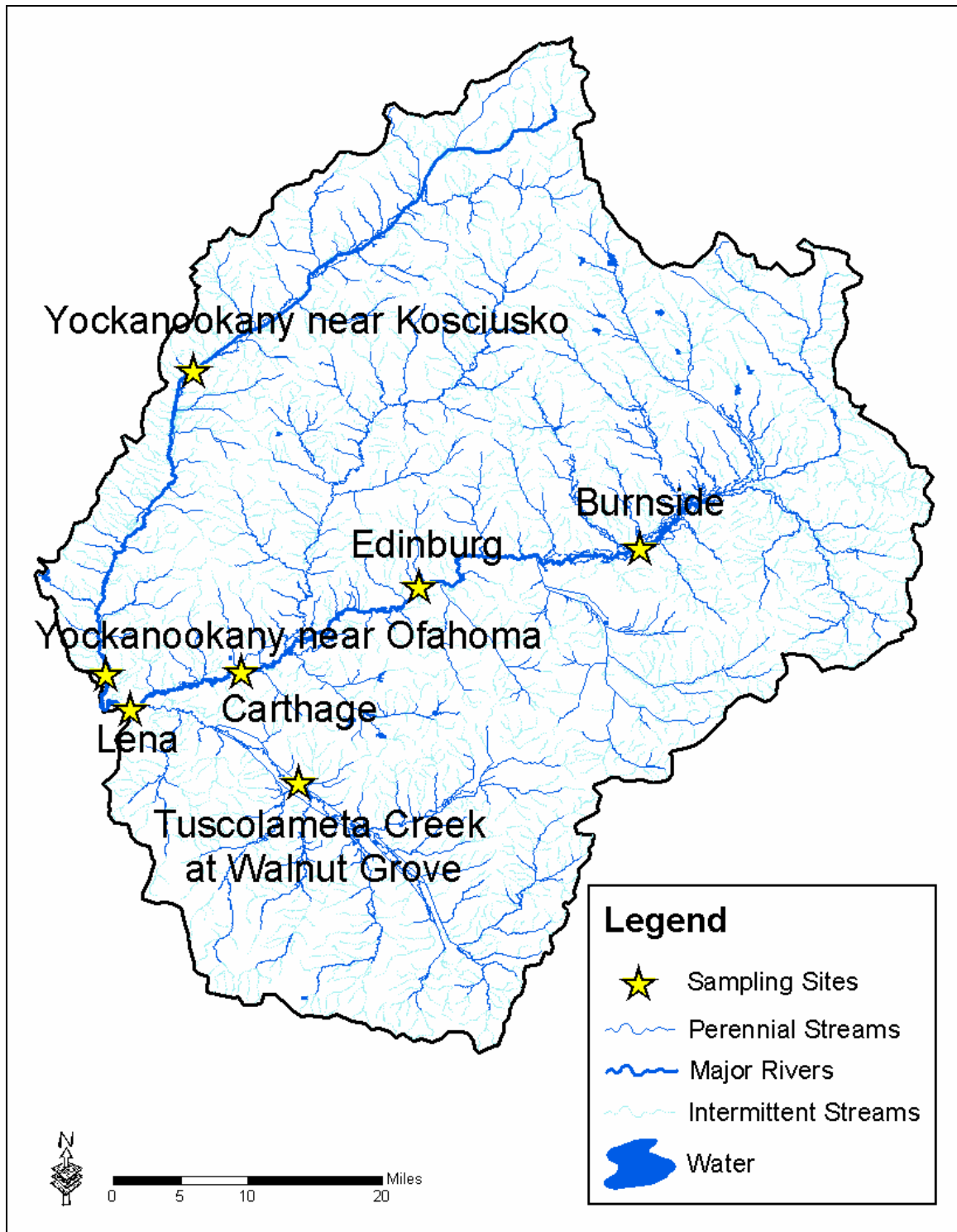
Figure 2.3 Example chromatogram for diuron and fluometuron from field spike (1:10 dilution of sample 8709) sampled on 1/20/03, extracted on 7/26/03, and analyzed on 8/22/03.
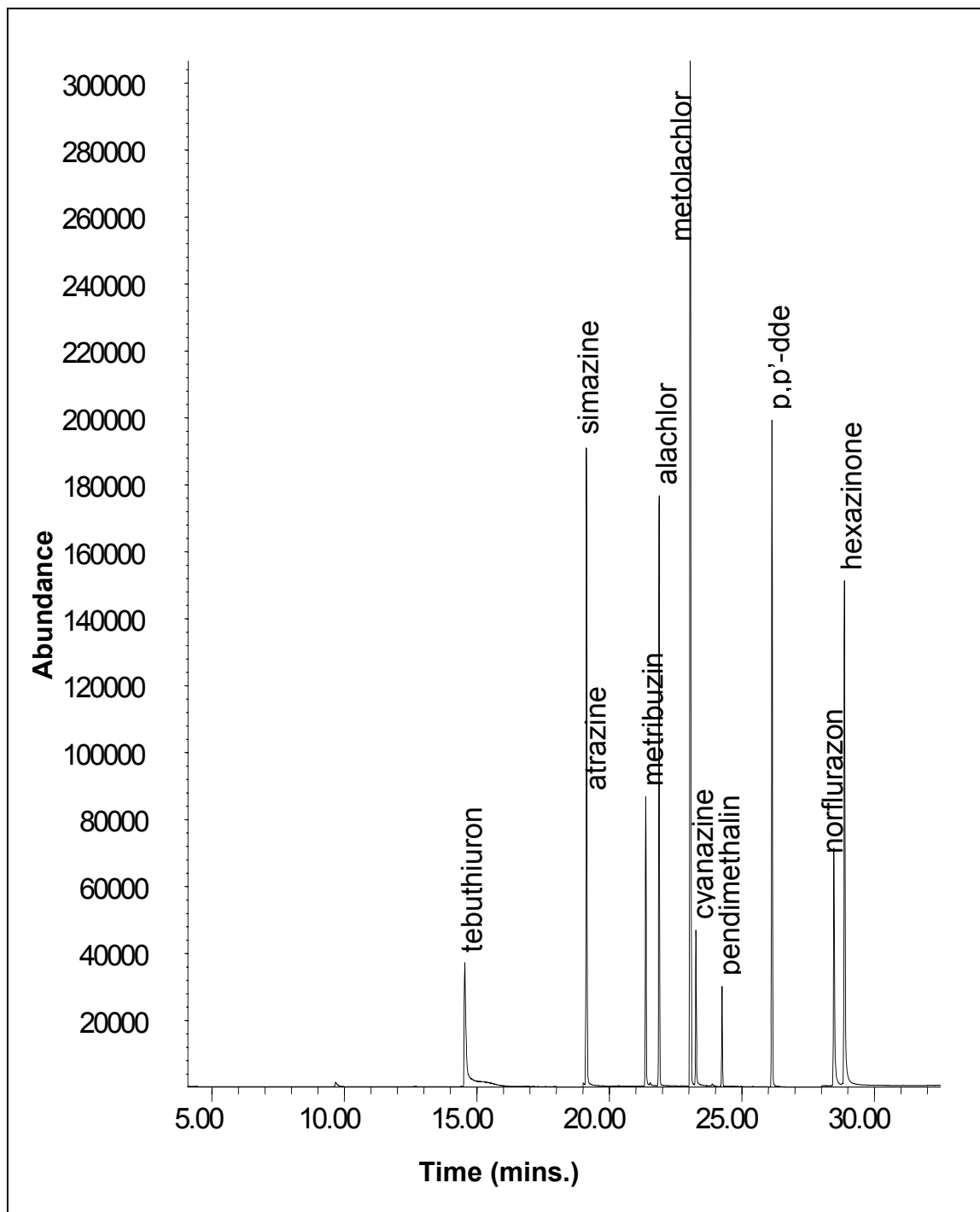
Figure 2.4. Example chromatogram from field spike (1:10 dilution of sample 8709) sampled on 1/20/03, extracted on 7/26/03, and analyzed on 12/3/03 for all non-derivatized compounds analyzed on the GCMS.
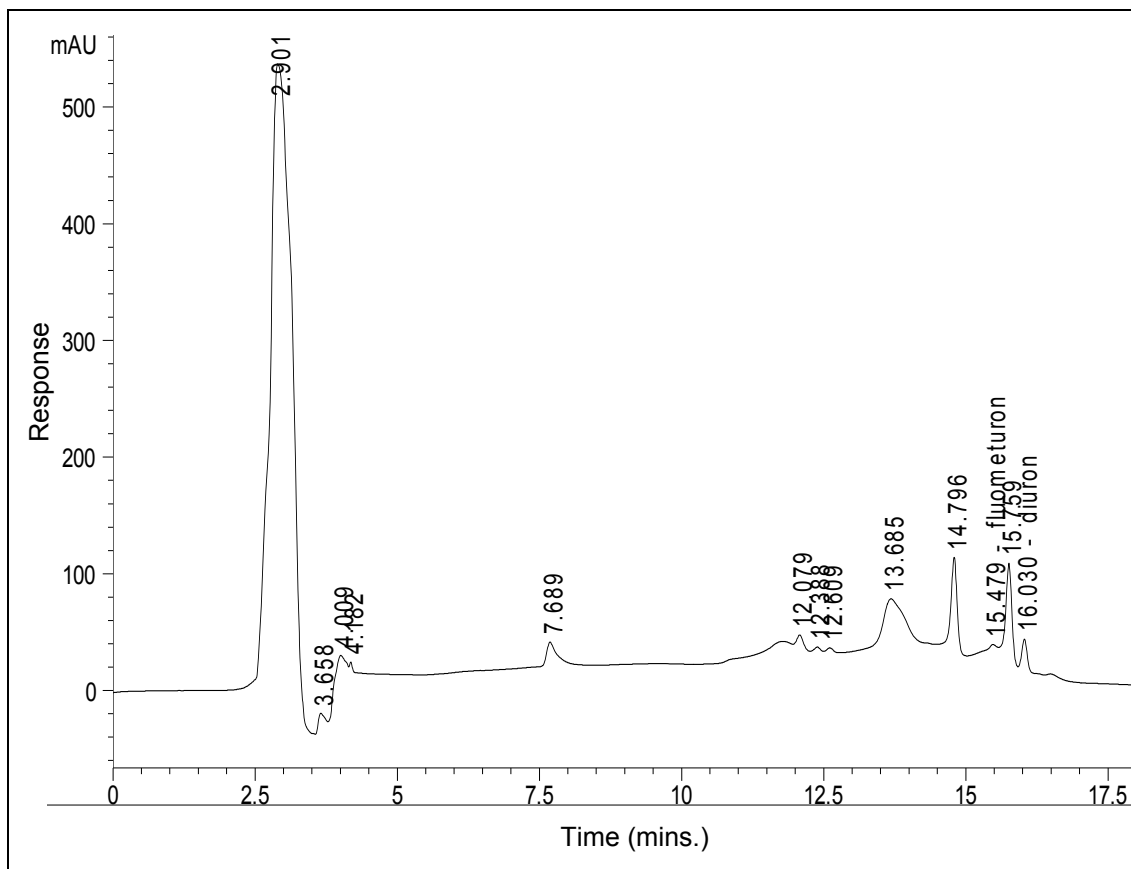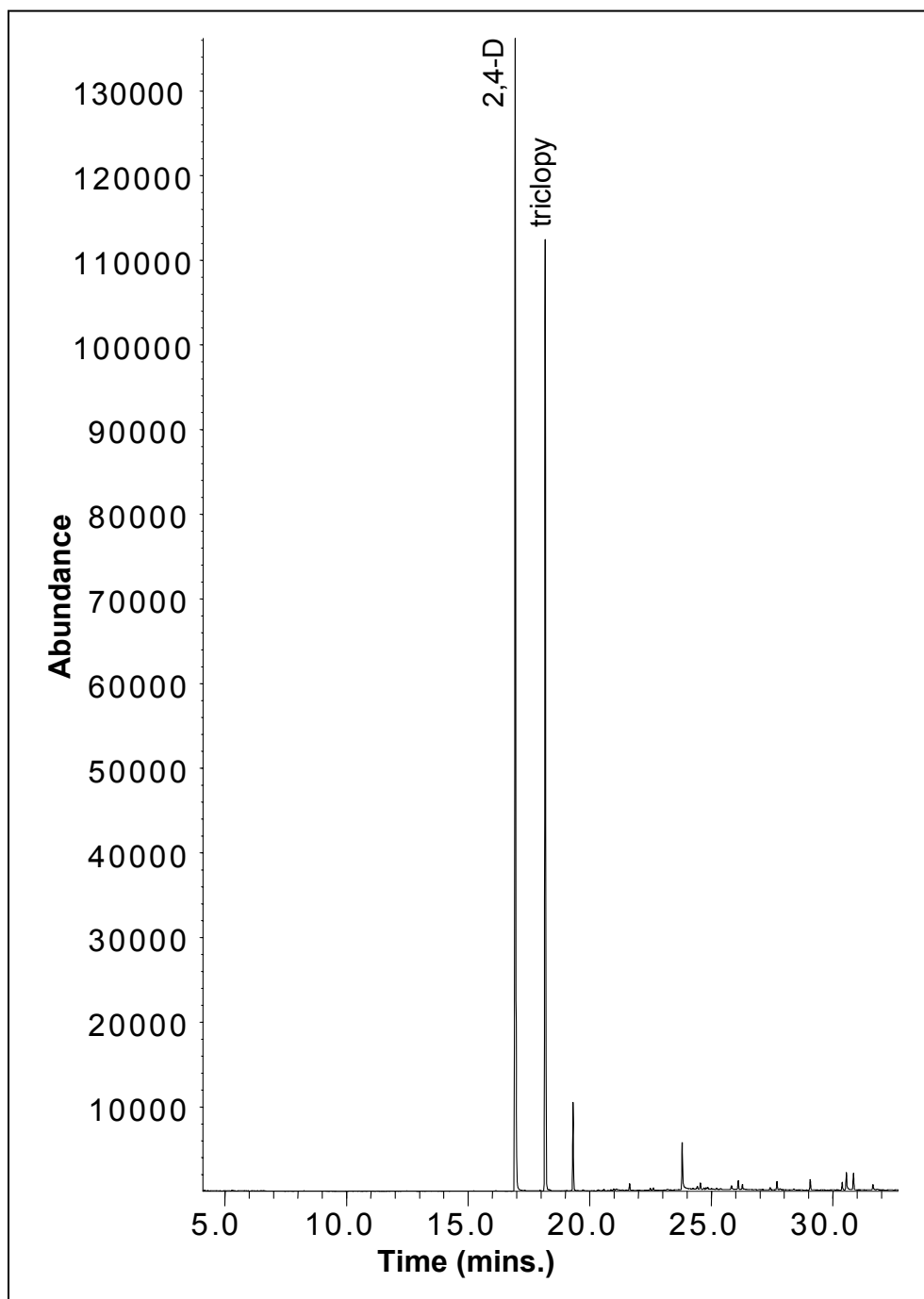
Figure 2.5. Example chromatogram for 2,4-D and triclopyr from field spike (1:10 dilution of sample 8709) sampled on 1/20/03, extracted on 7/26/03, and analyzed on 12/28/03.

Example Calibration Curve for Diuron

$$y = 0.0306x - 0.3791$$
$$R^2 = 0.9998$$

Response — Concentration (ppb)

Figure 2.6. Example calibration curve for diuron.

Figure 2.7. Relation of instantaneous water discharge to sediment concentration for the Burnside site on the Pearl River, MS.

Figure 2.8. Relation of instantaneous water discharge to sediment concentration for the Carthage site on the Pearl River, MS.

Figure 2.9. Relation of instantaneous water discharge to sediment concentration for the Edinburg site on the Pearl River, MS.

CHAPTER III

VALIDATION OF AnnAGNPS MODEL PREDICTIONS FOR SEDIMENT AND

PESTICIDE RUNOFF IN THE UPPER PEARL RIVER BASIN

ABSTRACT

Watershed models provide a cost-effective and efficient means of
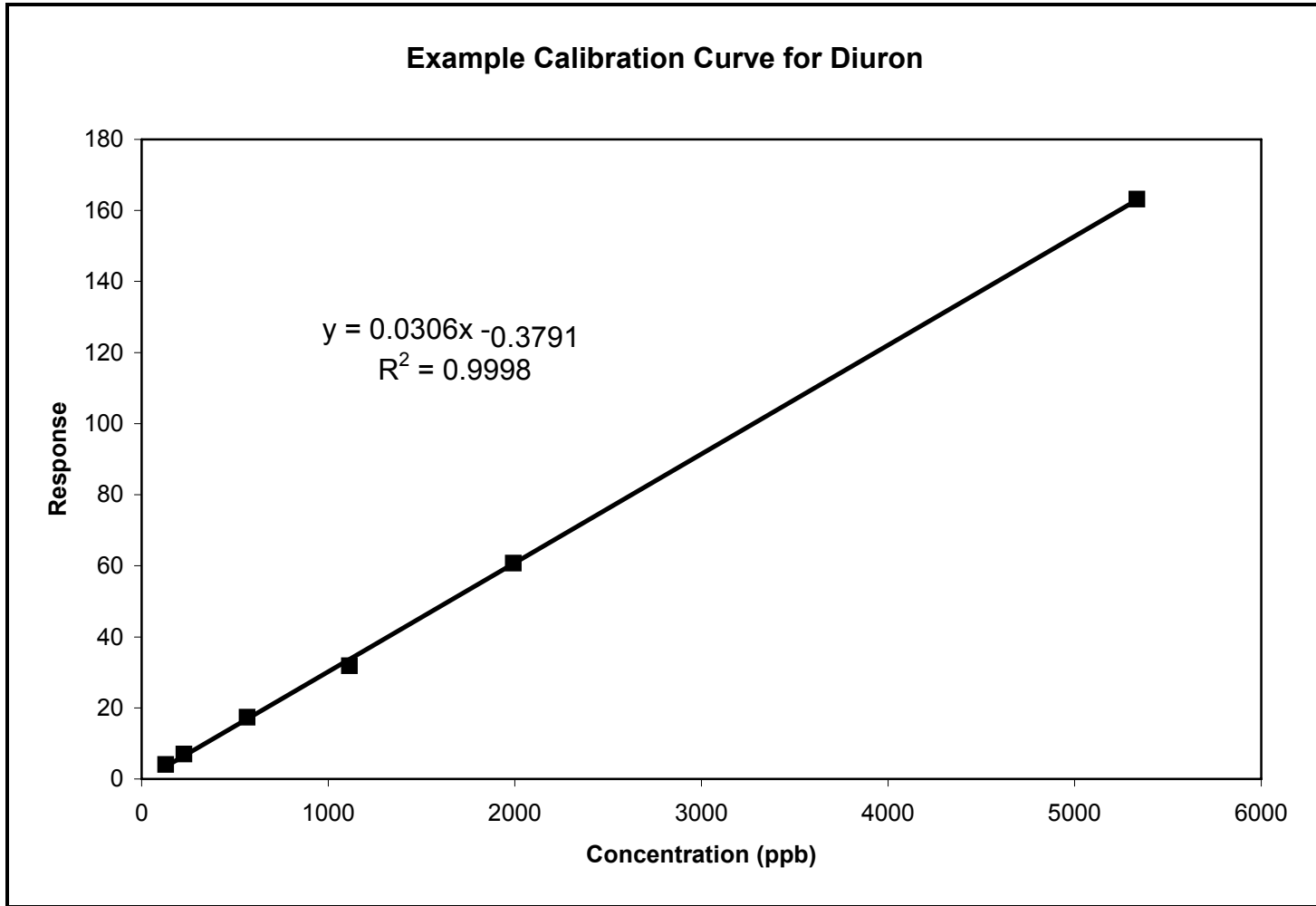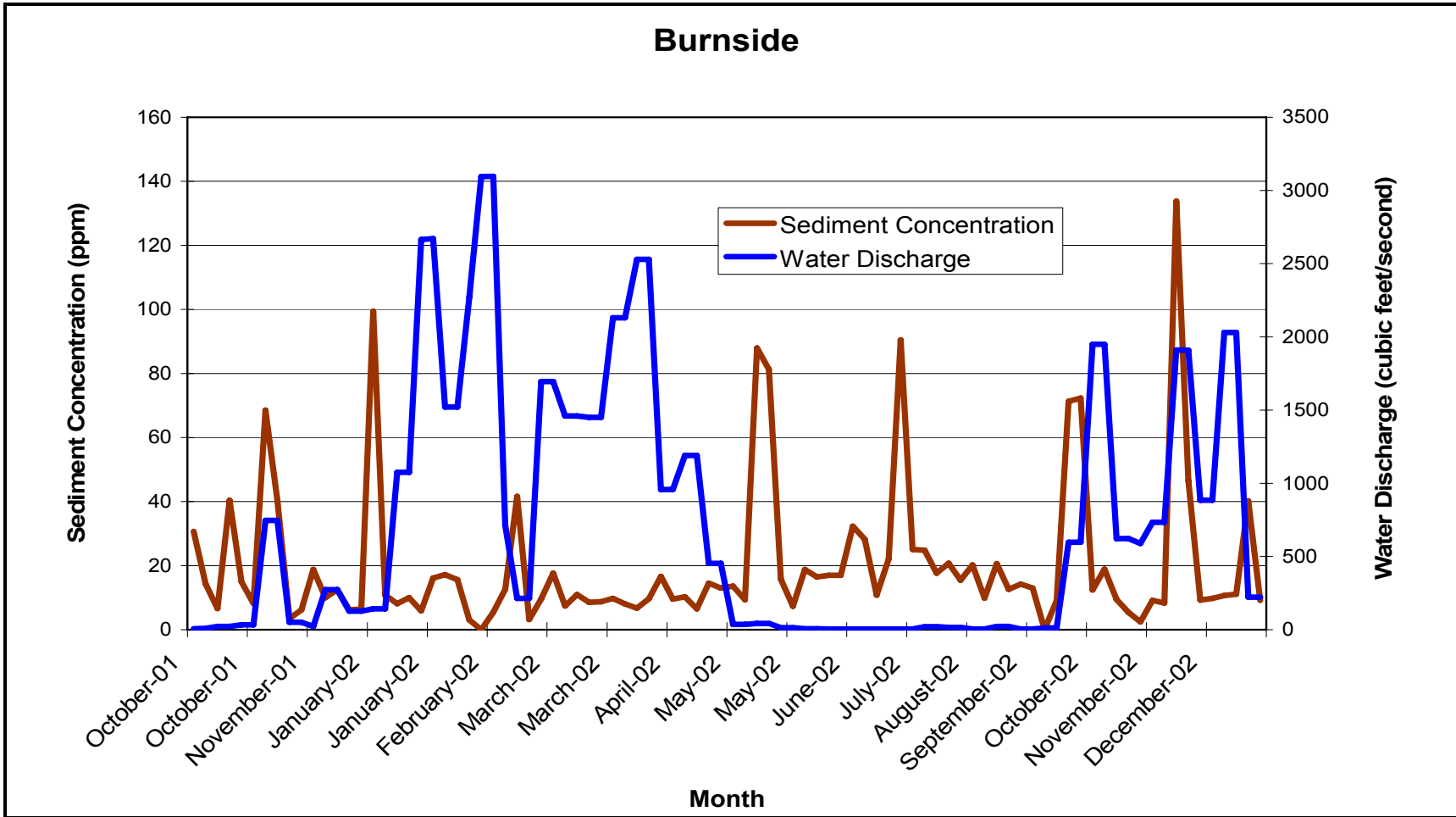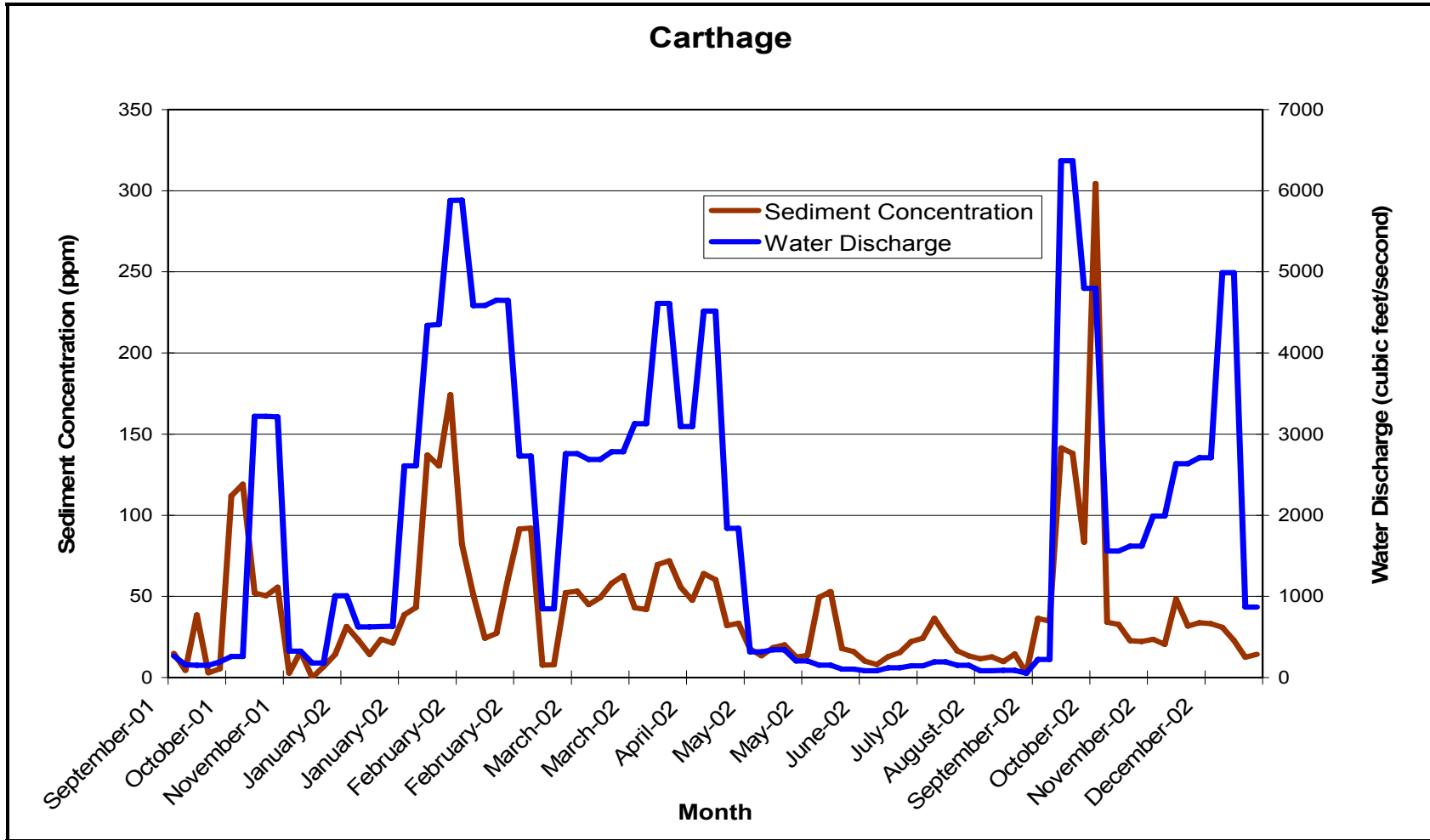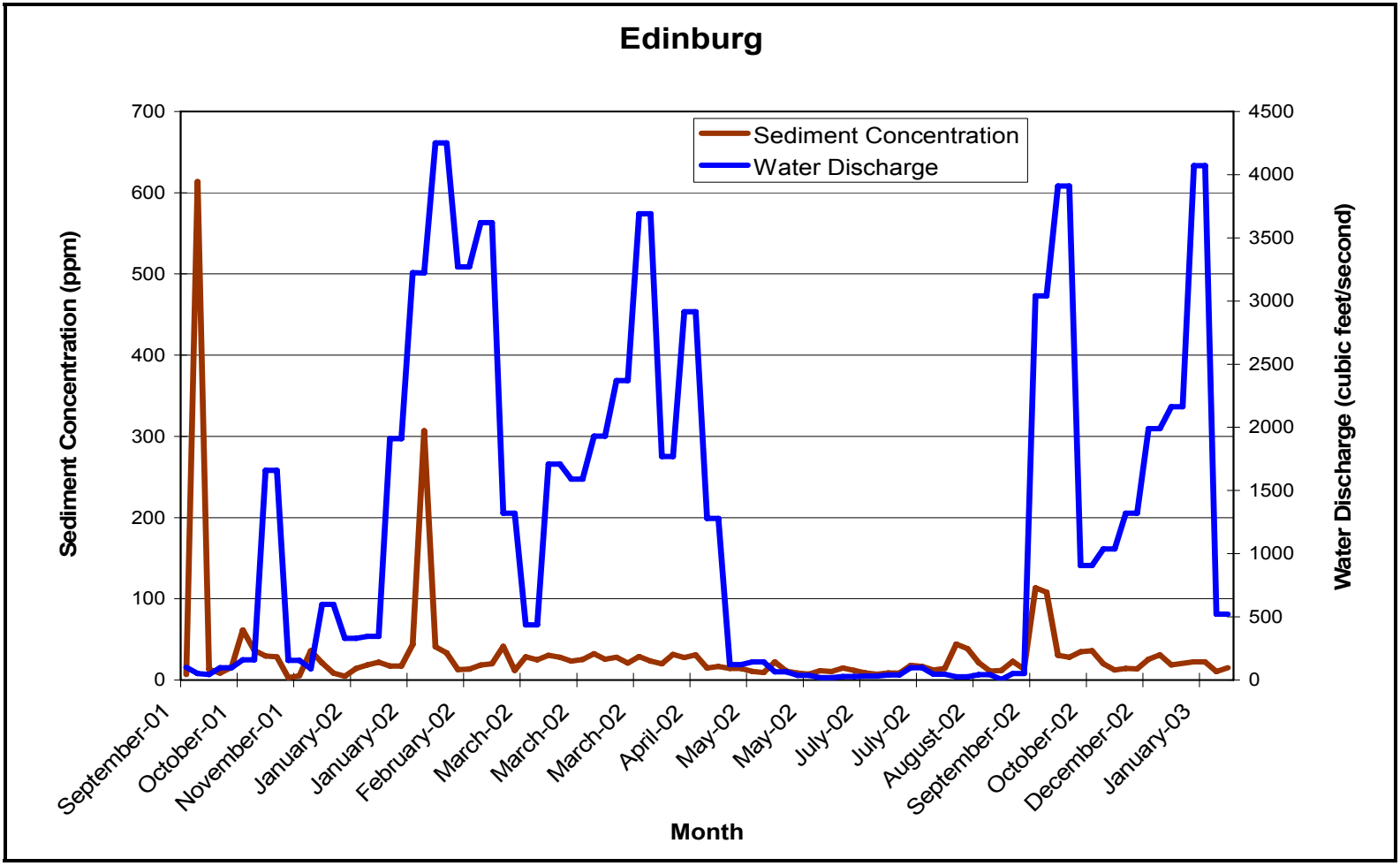
estimating the pollutant loadings entering surface waters, especially when

combined with traditional water quality sampling and analyses. The objective of

this study was to validate sediment and selected pesticide loading predictions of

the Annualized Agricultural Non-Point Source (AnnAGNPS) pollutant loading

model with traditional on-site water quality measurements for a portion of the

Upper Pearl River Basin (UPRB). In particular, loading comparisons were made

for sediment and the pesticides metolachlor and atrazine, which are commonly

used for weed control in corn production. Average monthly sediment loadings for

both the model and the measured data were compared. The AnnAGNPS model

predictions showed considerably higher total sediment loadings than the

measured data for January, March, and September of 2002, but measured

loadings were 1080% higher than the model loadings in December 2002. For the

other eight months between October 2001 and January 2003, average monthly

loadings differed no more than 3094 Mg/month, or 109%. Daily pesticide

loadings for both the model and the measured data were compared only

for the days on which manual sampling was performed. Both measured and

simulated data for atrazine were below 1.7 mg per eleven of thirteen dates

analyzed. For metolachlor, measured and simulated data were below 4 mg per

ten of thirteen dates analyzed. On May 18, 2003, AnnAGNPS predicted a daily

metolachlor loading of 80 mg, while measured data showed a loading of 5.6 mg

for that day. Measured data showed an earlier initial spike on January 20, 2003

that was not mirrored by the model. Atrazine comparisons followed the same

trend, except the measured atrazine loadings did not spike until the February 22,

2003 sampling date. Earlier planting dates for corn likely resulted in the earlier

peaks for the measured data. However, most daily pesticide loadings for both

measured results and AnnAGNPS predictions were very low. Increased manual

sampling intensity for both sediment and pesticide analysis might have improved

the comparison results.

INTRODUCTION

As concern over nonpoint-source pollution has increased in recent years,

so have the various types of models used to predict runoff and movement of

various types of pollutants. Traditional sampling methods for water quality

monitoring are time-consuming and expensive, and it is difficult to sample over

large geographical areas. Water quality modeling, especially when combined

with remote sensing and geographic information systems (GIS) software,

provides a more efficient means of forecasting water quality and is also easier to

repeat over time (Yang et al., 1999).

There are a variety of models, from urban growth models that simulate future development scenarios and their corresponding hydrology to pollutant runoff models that predict pesticide, sediment, and nutrient runoff (Arthur-Hartranft et al., 2003; Haan et al., 1993; Line et al., 1997). Examples of pollutant loading models include the Soil and Water Assessment Tool (SWAT), the Water Erosion Prediction Project (WEPP), the Environmental Protection Agency's (EPA) Better Assessment Science Integrating Point and Nonpoint Sources (BASINS) model, and various United States Department of Agriculture (USDA) models (Arnold et al., 1993; Bingner et al., 1992; Bingner et al., 1997; EPA, 2001; Laflen et al., 1991; Wauchope et al., 2003).

The USDA's AnnAGNPS suite of models was chosen for this study for a variety of reasons, the first of which is that the model has an integrated GIS interface that can process large amounts of spatially distributed watershed data needed for model inputs. For example, a GIS interface can process remotely sensed images, which can be used to determine the land use/land cover (LU/LC) management for an area, a common input to most water quality models (Jain and Kothyari, 2000). Even with older single-event versions of the model called AGNPS, integration of a GIS helped to characterize nonpoint sources of pollution at a landscape level by allowing a user to create model input layers and data files, control model simulations, and maneuver model outputs for display (Tim and Jolly, 1994; Liao and Tim, 1997). Incorporating a GIS interface with AGNPS 5.0 significantly improved the efficiency of the modeling process (He et al., 2001). Specialized GIS interfaces, such as altered versions of the Geographic

Resources Analysis Support System (GRASS), have also been integrated with event-based versions of the model, such as AGNPS 3.65 (Goran et al., 1983; He et al., 1993; Srinivasan et al., 1994).

Although AGNPS is not the only model with an integrated GIS interface, the AGNPS model also has other desirable capabilities (Srinivasan and Arnold, 1994). AGNPS was developed as a watershed event model and has been extensively evaluated and validated throughout the United States and internationally (Bhuyan et al., 2002; Choi and Blood, 1999; Grunwald and Norton, 1999; Grunwald and Norton, 2000; Mankin et al., 1999; Mitchell et al., 1993; Perrone and Madramootoo, 1997; Perrone and Madramootoo, 1999; Summer et al., 1990). Studies have been performed to assess the accuracy of AGNPS model simulations. Haan et al. (1998) found that the model produces stable and replicable predictions. Another study, however, found that with AGNPS and other water quality models, large uncertainties in estimated model parameters can occur if spatial variations in the input rainfall are not considered (Chaubey et al., 1999). Problems such as this are often difficult to avoid when few rainfall gauges are present in a watershed and other data sources are unavailable.

Parson et al. (1998) studied the risk of making decisions based on AGNPS simulations. Results showed that, as input variation increases, so does the risk of choosing a best management practice (BMP) that does not significantly decrease nonpoint source runoff loads. Also, water-based outputs such as soluble nutrients and runoff volume had lower decision risk values than sediment-based outputs.

More recently, AnnAGNPS was developed as an enhanced continuous version of the original AGNPS single event model (Bingner and Theurer, 2001a; 2001b). AnnAGNPS, a physically-based model, was chosen for this study because it is a much-improved version of its event-based predecessor and has not yet been validated as extensively. In this paper, the new continuous version of the model will be referred to as AnnAGNPS, which still includes some data preparation components from AGNPS (Yuan et al., 2002). AnnAGNPS, however, has more advanced features than AGNPS, including a pollutant loading model that predicts loadings for sediment, nutrients, and pesticides on a daily basis.

AnnAGNPS was designed for predominantly agricultural watersheds and was developed jointly by the USDA's Agricultural Research Service (ARS) and Natural Resources Conservation Service (NRCS) (Wauchope et al., 2003). The model includes a comprehensive pesticide database that allows the prediction of pesticide loadings in surface waters. Multiple sources and formats are available for data layers used to populate the model, and these data layers can be obtained in many different spatial, temporal, and spectral resolutions (Gesch et al., 2002; Ram et al., 2000; Steiner et al., 1999; Weng, 2001). AnnAGNPS can be used to assess the downstream effects of agricultural management practices at different watershed scales, which helps agricultural producers understand the source of pollutants associated with risk management, such as Total Maximum Daily Load (TMDL) implementation (Alonso and Bingner, 2000).

There have often been questions about the accuracy or certainty of models and their predictions, especially when used to establish TMDLs (Cotter et al., 2003; Osidele et. al, 2003). Although the single-event AGNPS has been fairly extensively validated, there is still a need to validate AnnAGNPS, the new continuous version of the model, for diverse watersheds and various loadings throughout the United States (Yuan et al., 2001). Thus, the objective of this study is to validate the estimation of sediment and pesticide runoff by the AnnAGNPS pollutant loading model for a portion of the UPRB. This objective will be accomplished by comparing the estimations of the AnnAGNPS model with traditional manual sampling data for sediment, atrazine, and metolachlor nonpoint source runoff.

MATERIALS AND METHODS

Watershed Description

The UPRB (HUC 03180001) contains portions of the following Mississippi counties: Attala, Kemper, Neshoba, Leake, Winston, Choctaw, Madison, Newton, and Scott. The area consists mostly of gently rolling hills and is the headwater area of the Pearl River. The UPRB is an important watershed because it drains into the Ross Barnett Reservoir, which is the largest of Mississippi's three surface water impoundments used for drinking water. The Ross Barnett Reservoir is approximately 13,200 ha in size and constitutes the primary source of drinking water for Mississippi's capital city, Jackson (Ballweber et al., 2000).

The UPRB contains eight USGS gauges located along both the main stem and tributaries of the Pearl River. The Burnside gauge, located in the headwater region of the Pearl River, was selected as the watershed outlet for the AnnAGNPS simulation outlined in this study. Burnside was selected as the outlet because it drained the smallest area of any gauged site in the study area. Water quality samples for pesticide and sediment analyses were collected at the Burnside location for model validation. The USGS (2005) cites the drainage area for the Burnside gauge as 1,300 km^2, but the drainage area delineated by the model totals 131,500 hectares, or 1315 km^2. Grab samples for pesticide analysis were taken weekly from May 2002 through August 2002 and then monthly thereafter through May 2003, and sediment samples were taken from September 2001 through January 2003. Sediment samples were taken as a single vertical sample with a US DH-48 depth-integrating suspended sediment sampler[1] during times of low flow, usually during the summer months when the river was wadable, and with a US DH-59 depth integrating suspended hand line sampler[1] when the river could not be waded. Timing of the sediment sampling differed from pesticide sampling in that sediment sampling was targeted around substantial rainfall events in the watershed. The USGS has a website that displays real-time data taken at gauged locations. This website was monitored for flow, and sampling was targeted for peak flow during a rainfall event. However, during the summer months when rainfall was infrequent and river levels were extremely low, routine sediment sampling was performed bi-monthly.

Pre-processing of Geospatial Data

Versions 3.42 and 3.51 of the AnnAGNPS ArcView interface were used

for this study. The following text gives a summary of model input sources as well

as the pre-processing steps that were performed on these geospatial data. See

Appendix B for more detailed information on processing steps that were

performed on input data layers.

The DEMs[2], at a horizontal resolution of 10 m and vertical resolution of

approximately 1.5 m, were downloaded for each county present in the UPRB.

For the watershed size modeled, the mosaiced 10-m DEM contained too many

rows and columns for the model to process, so the DEM was resampled to a 20-

m pixel size.

The 2002 land use information was obtained from Mississippi's 2002

cropland data layer[3], which contains LU/LC broken into eleven classes. The

cropland data layer contains a mosaic of georeferenced Landsat 5 – Thematic

Mapper (TM) and Landsat 7 – Enhanced Thematic Mapper (ETM) scenes on

which a supervised classification has been performed. The AnnAGNPS ArcView

interface requires that the LU/LC information be in a shapefile format, therefore

the LU/LC file was converted from a raster format to a shapefile.

Digital soils data originated from the State Soil Geographic (STATSGO)

database[4], and all geospatial input layers were clipped to the estimated

watershed boundary, leaving an appropriate buffer. All relevant climate stations[5]

in the watershed were identified. The station name, location, and identification

number were used to create a point shapefile of the stations, and Thiessen

polygons were created from the shapefile for these stations (Louisville, Gholson, and Philadelphia) (Fig. 3.1).

Preparation of Input Files

The AnnAGNPS ArcView interface was used to prepare input files for the Input Editor. The Input Editor then produced one AnnAGNPS input file that was used, in combination with the climate files, by the pollutant loading module. See Appendix C for more detailed information on the preparation of input files.

Values for the Critical Source Area (CSA) and Minimum Source Channel Length (MSCL) were set at 50 hectares and 100 meters, respectively. The CSA and MSCL values determine the hydrographic segmentation of the watershed by controlling the characteristics and topology of the stream channel network and sub-catchments generated by the TopAGNPS module. The user controls the size of the sub-watersheds, or CSA, allowing increased resolution of input data layers in more heterogeneous areas of the watershed. Reducing the AnnAGNPS cell size, especially in heterogeneous areas of the watershed, can increase the accuracy of model results, but time and labor requirements of the model are also increased (Young et al., 1989). These two factors were balanced accordingly to optimize data preparation criteria. Figure 3.2 shows the DEM-based watershed delineation and channel network, with the user-defined watershed outlet placed as close as possible to the USGS gauge site at Burnside. Figure 3.3 illustrates the sub-watershed delineation and connectivity between the sub-watersheds and the generated channel network. Additionally, Figure 3.4 shows a comparison of

the generated channel network and the USGS National Hydrography Dataset (NHD) stream network.

The sub-watershed cells were intersected with the soils data, using the field 'MUID' as the soil identifier in the overlay. The STATSGO soils database contains soil associations, but AnnAGNPS requires that a dominant soil type, along with its characteristics, be selected for each generalized soil association. The Map Unit Use File (MUUF) program, using the Map Unit Identification (MUID) number in the STATSGO database, retrieved the desired soil characteristics information from the NRCS Soils5 database (Baumer et al., 1994). Another program, the MUUF converter, transformed the retrieved MUUF data to a format that is compatible with the AnnAGNPS model (Bingner, 2004). The original STATSGO soils layer for the delineated watershed and the STATSGO soil type assigned to each sub-watershed cell can be seen in Figures 3.5 and 3.6, respectively.

The sub-watershed cells were also intersected with the LU/LC layer. The original LU/LC layer can be seen in Figure 3.7. During the overlay process, the model assigned a LU/LC class to each sub-watershed cell, which is based on the dominant LU/LC class within that cell. The AnnAGNPS ArcView Interface was employed to determine how well the LU/LC information from the original file was reflected in the sub-watershed LU/LC designations, by calculating the percentage of each LU/LC class in both the original LU/LC layer and in the sub-watershed file and comparing the two. See Appendix D for a more detailed description of the previously mentioned LU/LC analyses.

The heterogeneity of the agricultural LU/LC classes resulted in some classes not being assigned to any sub-watershed cells. These classes were underrepresented because they were not the dominant LU/LC class within many, or any, sub-watersheds. The detailed hydrographic description performed on the watershed still did not reflect the patchy nature of the agricultural LU/LC classes. Thus, the LU/LC classes assigned to sub-watershed cells were later adjusted in the Input Editor to better reflect the class percentages in the original LU/LC layer.

The Thiessen polygons previously created for the climate stations were intersected with the sub-watershed cells, assigning a climate station identification (CSID) number to each sub-watershed (Figure 3.8). Creating synthetic weather information with GEM (Generation of weather Elements for Multiple applications) was the final step to be performed in the ArcView interface, before moving to the Input Editor. Even though actual precipitation data was obtained from National Oceanic and Atmospheric Administration (NOAA) agencies, other variables must be obtained based on historical records. Actual precipitation data were available for the Gholson, Louisville, and Philadelphia sites, and daily maximum and minimum temperature data were also available for the Louisville station. Historical estimates were used for daily maximum and minimum temperatures for the other two sites, as well as for daily dew point temperature, sky cover, and wind speed and direction for all sites. Even when actual precipitation data are available, there are often gaps in the data due to equipment malfunctions and other problems, so it can be helpful to supplement actual data with synthetically generated data. Since the Meridian climate station was the nearest station to the

UPRB, the GEM program used historical data from the Meridian station to generate synthetic climate information. Climate files could be imported into the Input Editor for manual edits as needed. Appendix E gives more detailed information on processing climate files.

Finally, the soils, topographic, and LU/LC data were imported into the AnnAGNPS Input Editor to help create the required AnnAGNPS input file needed to run the pollutant loading model. Other AnnAGNPS data sections that must be defined by the user include crop or non-crop land use type, runoff curve numbers, residue cover, input and output units, simulation period, desired output files, and more. More detailed management information, such as planting, tillage, pesticide, fertilizer, and irrigation information must be described for crop land use classes. Version 3.51 of the Input Editor and AnnAGNPS Pollutant Loading module was used for this study. The AnnAGNPS Pollutant Loading module was set to run for two initialization years before beginning the simulation period, which was October 1, 2001 through June 30, 2003.

Once the cell and reach data were imported into the Input Editor, the LU/LC class designations for the sub-watershed cells could be adjusted to more accurately reflect the total LU/LC areas in the original LU/LC layer. Table 3.1 shows a comparison of the LU/LC class percentages in the original LU/LC layer, model delineated LU/LC layer, and final adjusted layer. The final LU/LC designation for the sub-watershed cells is illustrated in Figure 3.9. Operational management information was also outlined for each sub-watershed, including data regarding typical pesticide applications and harvesting schedules, where

applicable. Management information was described based on recommendations

by Mississippi State University Extension Service specialists and their associated

publications (Anonymous, 2005).

<center>Sediment Analysis</center>

AnnAGNPS-predicted sediment loadings were compared to measured

data for the watershed outlet at Burnside. Since AnnAGNPS pollutant loading

predictions are based primarily on storm runoff, the model does not account for a

stream's base flow. However, since the Burnside outlet is in the headwaters of

the Pearl River Basin, base flow at the site was minimal and thus not excluded

from measured loadings.

First, a flow weighted concentration was calculated for each monthly time

period so that extra weight was not given to flows occurring on sampling dates

(Hem, 1985). Each sample concentration value (mg/L) was multiplied by the

stream discharge (cfs) applicable to that sample. The duplicate samples for each

sampling date were averaged. For each month, these concentrations

[(mg/L)(cfs)] were summed and divided by the sum of the discharges (cfs),

resulting in a flow- or discharge-weighted concentration (mg/L) for each monthly

time period. The flow-weighted concentration (mg/L) for each month was then

multiplied by the mean monthly flow (ft^3/month) after converting units, resulting in

the average sediment loading for each month in mg/month (USGS, 2005). Since

the AnnAGNPS model produces sediment loading predictions in Mg, measured

data were converted to these units for comparison. When comparing measured

data to the AnnAGNPS model predictions, only dates for which measured data were available were compared. For example, if the model showed sediment runoff on a date for which there were no measured data available, this date was not included in the monthly summed sediment load. Dates with modeled data and no measured data occurred due to limitations in the sampling regime. Taking this into consideration, the sediment loads were summed by month for both the measured data and model predictions.

Pesticide Analysis

Metolachlor and atrazine loadings were also predicted by the AnnAGNPS model and compared to measured data for the Burnside outlet. AnnAGNPS predicts loadings for both the dissolved and attached portions of each pesticide, and references to modeled pesticide loadings in this study are for the combined dissolved and attached portions of each compound. Pesticide sampling, although performed for a longer period of time than sediment sampling, was not sampled as frequently as sediment. Thus, the pesticide data were analyzed somewhat differently than the sediment data. For both metolachlor and atrazine, each sample concentration value (ng/mL) was multiplied by the instantaneous stream discharge (cfs) applicable to that sample after converting units, resulting in the pesticide loading at the time of sampling (in units ng/s). Although duplicate samples were retrieved for pesticide analysis quality assurance, no duplicate samples were included in these results. The instantaneous sampled loadings were then converted to mg/second for comparison with the AnnAGNPS

simulated data. Since the AnnAGNPS model produced pesticide loading predictions in kg, these loading units were converted to mg for comparison with the measured data. Comparisons were made in mg due to the low measured and modeled loadings.

RESULTS AND DISCUSSION

Sediment

Sediment sampling ran from October 2001 through January 2003 at the Burnside outlet location. There were 26 dates during this period that had both sampling data and data predicted by the AnnAGNPS model. There were three months – November 2001, June 2002, and November 2002 – that did not have any coinciding sampled and modeled data. Of the 26 dates for which measured and predicted data were available, there was not enough rainfall for the AnnAGNPS model to produce any runoff for seven of those dates. For the remaining 19 dates during the sampling period, AnnAGNPS predicted a total suspended sediment loading of 59,920 Mg at the Burnside outlet, with a particle-size distribution of 38% clay, 60% silt, and 2% sand.

For the twelve months represented in Figure 3.10, predicted sediment loading overestimated measured data for seven months and underestimated measured data for five months. For eight of the twelve months, there were no differences larger than 3,094 Mg, or 109%, and differences were usually much less. For the four months with differences greater than 3,094 Mg, predicted results were more than measured data for three months and less than measured

data for the remaining month. Figure 3.11 shows a comparison of measured and predicted sediment loading by month, with an R^2 value of 0.3279. Yuan et al. compared observed and predicted sediment loading by event for the Deep Hollow watershed in the Mississippi Delta, resulting in an R^2 value of 0.5 (2001). The Deep Hollow watershed was much smaller (82 ha) and had more events available for comparison than the watershed modeled in this study.

Although no impoundments were observed that might have affected the results of either the measured data or the AnnAGNPS predictions, there are other reasons as to why the predicted results overestimated measured sediment data for certain months. First, increased manual sampling intensity might have improved the results. On March 11, 2002, the Gholson station recorded 49.5 mm of rainfall, and on March 12, 2002, the Louisville and Philadelphia stations recorded 34.0 mm and 26.9 mm, respectively (Figures 3.12, 3.13, and 3.14). However, the first sampling event for that month did not occur until March 16. The largest discrepancy between the measured data and modeled data occurred in September 2002. On September 26, Gholson, Louisville, and Philadelphia recorded rainfall amounts of 130 mm, 114 mm, and 113 mm, respectively. September 23 and 27 were the only corresponding sampling events for the month of September 2002. Stream sediment concentrations commonly peak just before the water discharge hydrograph peaks (Guy, 1973). It is likely that the sediment had already peaked before the September 27 sampling date, so while the manual sampling missed the sediment peak, it was captured by AnnAGNPS.

Additionally, even though the focus of these analyses is on event data and not average annual results, a better understanding of the watershed processes can be gained by looking at the average annual sediment loading (Figure 3.15). The average annual sediment loading for each sub-watershed shows that many of the higher sediment-producing sub-watersheds are located near the outlet, meaning there will be a shorter travel time for sediment from these sub-watersheds to reach the outlet. A shorter travel time could cause water and sediment runoff to peak sooner and makes the timing of sampling more critical. The higher sediment-producing sub-watersheds near the outlet are likely a result of the soil type in those sub-watersheds, combined with the fact that runoff and loadings in the upper part of the watershed are routed downstream. In future studies, comparisons might be improved if the sampling duration is shortened and sampling intensity is increased, while at the same time trying to better target rainfall events.

<u>Metolachlor and Atrazine</u>

Pesticide sampling occurred weekly from May through August 2002 and monthly from September 2002 through May 2003. Again, when comparing measured data to the AnnAGNPS model predictions, only dates which had both measured data and AnnAGNPS-predicted pesticide runoff were compared, even though AnnAGNPS simulated pesticide runoff on other days when no sampling occurred. Taking this into consideration, the pesticide loads for 13 dates which

had both measured data and AnnAGNPS-simulated runoff were compared for both atrazine and metolachlor in Figures 3.16 and 3.17, respectively.

In the management section of the AnnAGNPS Input Editor, an application of metolachlor and atrazine was scheduled for reduced-till corn on May 15 at the labeled rate. The AnnAGNPS predictions for both atrazine and metolachlor runoff remained extremely low from May 30, 2002 through April 17, 2003 for the events that were analyzed, and then spiked on May 18, 2003. The spike was most likely the May 15 timing of the pesticide application, in combination with a recorded May 18, 2003 rainfall of 23.4 mm, 30.0 mm, and 36.8 mm, respectively, at the Louisville, Gholson, and Philadelphia climate stations.

The measured data for both metolachlor and atrazine remained extremely low for analyzed sampling dates between May 30 and December 20, 2002, except for a slight rise on October 27, 2002. Metolachlor peaked on January 20, 2003, while atrazine peaked on February 22, 2003, the next sampling date. Metolachlor then steadily increased from March 9 through May 18, 2003, and atrazine concentrations were higher on May 18, 2003, as well. It is probable that measured results were showing increased peaks before the AnnAGNPS peaks on May 18 due to progressively earlier planting dates. The AnnAGNPS management schedule had a planting date of April 1 for reduced-till corn, but the actual planting dates in the watershed could have been earlier if weather conditions were favorable.

A comparison of measured and simulated atrazine loading by event is shown in Figure 3.18, with an R^2 value of only 0.0954. Figure 3.19 shows a

comparison of measured and simulated metolachlor loading by event, with an R^2 value of 0.0616. Despite the poor R^2 values, both measured and simulated data for atrazine were below 1.7 mg for eleven of thirteen dates analyzed. For metolachlor, measured and simulated data were below 4 mg for ten of thirteen dates that were analyzed. Perhaps the biggest discrepancy was that AnnAGNPS missed the initial peak for atrazine on February 22, 2003 and for metolachlor on January 20, 2003. However, the AnnAGNPS pesticide predictions were based, in part, on user-defined management information. As mentioned earlier, actual planting dates were apparently earlier than those defined in AnnAGNPS. Unfortunately, there are no previous AGNPS or AnnAGNPS pesticide validation studies available to compare with the pesticide loading results presented in this study.

The same suggestions mentioned earlier regarding the increase in sampling intensity for sediment also hold true for pesticide sampling. In addition, pesticide sampling could have been better targeted around rainfall events. If a rainfall event is not large enough for the AnnAGNPS model to produce runoff, the model will also not produce any pesticide runoff. Several pesticide sampling dates during the summer months were on days with no rain occurring just prior to or on the day of sampling. Thus, there was no runoff simulated by AnnAGNPS on these dates. Even with the low sampling intensity, metolachlor and atrazine showed roughly similar patterns for the measured data and more so with the AnnAGNPS predictions. This similar pattern is not surprising since these two

compounds are often applied to corn in combination or at close timing

sequences.

A limiting factor in this study was the low sampling intensity. AnnAGNPS

predicts loadings at daily time intervals, and these daily values were compared to

instantaneous sediment and pesticide samples. Comparisons could have been

improved if manual samples were collected on a continuous basis. Although

continuous sediment and pesticide sampling was not possible in this study,

Figure 3.20 shows how continuously monitored stream discharge data may vary

from AnnAGNPS-predicted daily water loading estimates. AnnAGNPS predicts

daily water, sediment, and pesticide loadings that may differ considerably from

instantaneous sample data or continuously monitored stream discharge data.

This study demonstrates that although AnnAGNPS can predict loadings

on an event basis, the model may be better suited for predicting long-term annual

loadings for sediment and pesticide runoff. This is due in part to the fact that

some parameters associated with the model are based on long-term estimates.

Also, the sampling period should have been adequate, but there were a limited

number of sampling dates that coincided with dates for which AnnAGNPS

predicted runoff. With so few dates for comparison of measured and predicted

loadings, it is not surprising that regression analysis showed poor results. More

detailed and site-specific management information for the watershed would have

been helpful and likely improved the results, but it was difficult to obtain detailed

management information for a 131,497-ha watershed. Other recommendations

for the model include having measurement units shown on all output files and

including pesticide loadings in the 'AnnAGNPS_TXT_Gaging_Station_Data.txt'

output file and the Version 2 event output.

SOURCES OF MATERIALS

[1] USGS Hydrologic Instrumentation Facility, Building 2101, Stennis Space Center, MS 39529.

[2] Mississippi Automated Resource Information System's website: http://www.maris.state.ms.us

[3] United States Department of Agriculture – National Agricultural Statistics Service (USDA-NASS)

[4] USDA Natural Resources Conservation Service (NRCS)

[5] National Oceanic and Atmospheric Administration's (NOAA) National Weather Service (NWS) office in Jackson, MS and the Southern Regional Climate Center (SRCC) in Baton Rouge, LA

LITERATURE CITED

Alonso, C.V. and R.L. Bingner. 2000. Goodwin Creek experimental watershed: A unique field laboratory. J. Hydraul. Eng. 126:174-177.

Anonymous. 2005. Weed control guidelines for Mississippi. Publication 1532, Mississippi State University Extension Service. 197 pp.

Arnold, J.G., P.M. Allen, and G. Bernhardt. 1993. A comprehensive surface-groundwater flow model. J. Hydrol. 142(1/4):47-69.

Arthur-Hartranft, S.T., T.N. Carlson, and K.C. Clarke. 2003. Satellite and ground-based microclimate and hydrologic analyses coupled with a regional urban growth model. Remote Sens. Environ. 86:385-400.

Ballweber, J.A., D. Parisi, and J.R. Steil. 2000. Riparian management's role within a basin-scale management partnership. Pages 463-468 In Proc. AWRA's Summer Specialty Conference on Riparian Ecology and Management in Multi-Land Use Watersheds. Middleburg, VA:AWRA.

Baumer, O., P. Kenyon, and J. Bettis. 1994. Prediction of soil properties. Map Unit Use Files (MUUF). User's manual version 2.14. Nat. Resour. Conserv. Serv., Wetland Sci. Inst., Laurel, MD.

Bhuyan, S.J., L.J. Marzen, J.K. Koelliker, J.A. Harrington Jr., and P.L. Barnes. 2002. Assessment of runoff and sediment yield using remote sensing, GIS, and AGNPS. J. Soil Water Conserv. 57:351-364.

Bingner, R.L., C.K. Mutchler, and C.E. Murphree. 1992. Predictive capabilities of erosion models for different storm sizes. Trans. ASAE 35:505-513.

Bingner, R.L., J. Garbrecht, J.G. Arnold, and R. Srinivasan. 1997. Effect of watershed subdivision on simulation runoff and fine sediment yield. Trans. ASAE 40:1329-1335.

Bingner, R.L. 2004. Personal communication. Oxford, MS, 11 August 2004.

Bingner, R.L. and F.D. Theurer. 2001a. AGNPS 98: A Suite of water quality models for watershed use. *In* Proceedings of the Sedimentation:

Monitoring, Modeling, and Managing, 7th Federal Interagency Sedimentation Conference, Reno, NV, 25-29 March 2001. p. VII-1-VII-8. 2001.

Bingner, R.L. and F.D. Theurer. 2001a. AGNPS 98: A Suite of water quality models for watershed use. _In_ Proceedings of the Sedimentation: Monitoring, Modeling, and Managing, 7th Federal Interagency Sedimentation Conference, Reno, NV, 25-29 March 2001. p. VII-1-VII-8. 2001.

Bingner, R.L. and F.D. Theurer. 2001b. AnnAGNPS: Estimating sediment yield by particle size for sheet & rill erosion. _In_ Proceedings of the Sedimentation: Monitoring, Modeling, and Managing, 7th Federal Interagency Sedimentation Conference, Reno, NV, 25-29 March 2001. p. I-1-I-7. 2001.

Chaubey, I., C.T. Haan, S. Grunwald, and J.M. Salisbury. 1999. Uncertainty in the model parameters due to spatial variability of rainfall. J. Hydrol. 220:48-61.

Choi, K.S. and E. Blood. Modeling developed coastal watersheds with the agricultural non-point source model. J. Am. Water Resour. Assoc. 35:233-244.

Cotter, A.S., I. Chaubey, T.A. Costello, T.S. Soerens, and M.A. Nelson. 2003. Water quality model output uncertainty as affected by spatial resolution of input data. J. Am. Water Resour. Assoc. 39:977-986.

Gesch, D., M. Oimoen, S. Greenlee, C. Nelson, M. Steuck, and D. Tyler. 2002. The national elevation dataset. Photogramm. Eng. Remote Sensing 68:5-11.

Goran, W.D., W.E. Dvorak, L. Van Warren, and R.D. Webster. 1983. Fort Hood Geographic Information System: Pilot system development and user instructions. Technical Report N-154. Champaign, IL:USA Construction Engineering Research Laboratory.

Grunwald, S. and L.D. Norton. 1999. An AGNPS-based runoff and sediment yield model for two small watersheds in Germany. Trans. ASAE 42:1723-1731.

Grunwald, S. and L.D. Norton. 2000. Calibration and validation of a non-point source pollution model. Agric. Water Manage. 45:17-39.

Guy, H. P. 1973. Fluvial sediment concepts. Techniques of Water-Resources Investigations of the United States Geological Survey. Book 3, Chapter C1. Washington, D.C.:U.S. Government Printing Office. p. 22.

Haan, C.T., D.L. Nofziger, and M. Gregory. 1993. An agricultural chemical evaluation and management system. J. Agric. Eng. Res. 56:301-312.

Haan, C.T., D.E. Storm, T. Al-Issa, S. Prabhu, G.J. Sabbagh, and D.. Edwards. 1998. Effect of parameter distributions on uncertainty analysis of hydrologic models. Trans. ASAE 41:65-70.

He, C., J.F. Riggs, and Y. Kang. 1993. Integration of geographic information systems and a computer model to evaluate impacts of agricultural runoff on water quality. Water Resour. Bull. 29:891-900.

He, C., C. Shi, C. Yang, and B.P. Agosti. 2001. A windows-based GIS-AGNPS interface. J. Am. Water Resour. Assoc. 37:395-406.

Hem, J.D. 1985. Study and interpretation of the chemical characteristics of natural water, 3rd ed. USGS Water-Supply Paper 2254, p. 168.

Jain, M.K. and U.C. Kothyari. 2000. Estimation of soil erosion and sediment yield using GIS. Hydrol. Sci. J. 45:771-786.

Laflen, J.M., L.J. Lane, and G.R. Foster. 1991. WEPP, A new generation of erosion prediction technology. J. Soil Water Conserv. 46:34-38.

Liao, H. and U.S. Tim. 1997. An interactive modeling environment for non-point source pollution control. J. Am. Water Resour. Assoc. 33:591-603.

Line, D.E., S.W. Coffey, and D.L. Osmond. 1997. Watershedss Grass-AGNPS model tool. Trans. ASAE 40:971-975.

Mankin, K.R., J.K. Koelliker, and P.K. Kalita. 1999. Watershed and lake water quality assessment: An integrated modeling approach. J. Am. Water Resour. Assoc. 35:1069-1080.

Mitchell, J.K., B.A. Engel, R. Srinivasan, and S.S.Y. Wang. 1993. Validation of AGNPS for small watersheds using an integrated AGNPS/GIS system. Water Resour. Bull. 29:833-842.

Osidele, O.O., W. Zeng, and M.B. Beck. 2003. Coping with uncertainty: A case study in sediment transport and nutrient load analysis. J. Water Resour. Plan. Manage. 129:345-355.

Parson, S.C., J.M. Hamlett, P.D. Robillard, and M.A. Foster. 1998. Determining the decision-making risk from AGNPS simulations. Trans. ASAE 41:1679-1688.

Perrone, J. and C.A. Madramootoo. 1997. Use of AGNPS for watershed modeling in Quebec. Trans. ASAE 40:1349-1354.

Perrone, J. and C.A. Madramootoo. 1999. Sediment yield prediction using AGNPS. J. Soil Water Conserv. 54:415-418.

Ram, S.V. Khatri, Y. Hwang, and S.R. Yool. 2000. Semantic modeling and decision support in hydrology. Photogramm. Eng. Remote Sensing 66:1229-1239.

Steiner, M., J.A. Smith, S.J. Burgess, C.V. Alonso, and R.W. Darden. 1999. Effect of bias adjustment and rain gauge data quality control on radar rainfall estimation. Water Resour. Res. 35:2487-2503.

Srinivasan, R. and J.G. Arnold. 1994. Integration of a basin-scale water quality model with GIS. Water Resour. Bull. 30:453-462.

Srinivasan, R., B.A. Engel, J.R. Wright, J.G. Lee, and D.D. Jones. 1994. The impact of GIS-derived topographic attributes on the simulation of erosion using AGNPS. Appl. Eng. Agric. 10:561-566.

Summer, R.M., C.V. Alonso, and R.A. Young. 1990. Modeling linked watershed and lake processes for water quality management decisions. J. Environ. Qual. 19:421-427.

Tim, U.S., and R. Jolly. 1994. Evaluating agricultural nonpoint-source pollution using integrated geographic information systems and hydrologic/water quality model. J. Environ. Qual. 23:25-35.

USGS. 2005. http://waterdata.usgs.gov/ms/nwis/.

Wauchope, R.D., L.R. Ahuja, J.G. Arnold, R. Bingner, R. Lowrance, M.T. van Genuchten, and L.D. Adams. 2003. Software for pest-management science: Computer models and databases from the United States Department of Agriculture – Agricultural Research Service. Pest Manag. Sci. 59:691-698.

Weng, Q. 2001. Modeling urban growth effects on surface runoff with the integration of remote sensing and GIS. Environ. Manage. 28:737-748.

Yuan, Y., R.L. Bingner, and R.A. Rebich. 2001. Evaluation of AnnAGNPS on Mississippi Delta MSEA watersheds. Trans. ASAE 44:1183-1190.

Yuan, Y., S.M. Dabney, and R.L. Bingner. 2002. Cost effectiveness of agricultural BMPs for sediment reduction in the Mississippi Delta. J. Soil Water Conserv. 57:259-267.

Yang, M., C.J. Merry, and R.M. Sykes. 1999. Integration of water quality modeling, remote sensing, and GIS. J. Am. Water Resour. Assoc. 35:253-263.

Young, R.A., C.A. Onstad, D.D. Bosch, and W.P. Anderson. 1989. AGNPS: A nonpoint-source pollution model for evaluating agricultural watersheds. J. Soil Water Conserv. 44:168-173.

Table. 3.1. Land use percentages (%) for the delineated Burnside watershed.

Land Use Class	Percentage of Total Area (%) in Original LULC Layer	Percentage of Total Area (%) as Determined by AnnAGNPS	Percentage of Total Area (%) Used in Final Adjusted LULC Layer
Pasture	61.79	64.15	63.04
Woods	35.39	35.72	35.57
Water	0.86	0.07	0.07
Other Small Grains and Hay	0.68	0.01	0.66
Corn	0.35	0	0.32
Urban	0.29	0.04	0.28
Water and/or Clouds	0.23	0.01	0
Fallow	0.13	0	0
Clouds	0.10	0	0
Cotton	0.07	0.01	0.07
Soybeans	0.07	0	0
Christmas Tree Farms	0.03	0	0
Aquaculture	0.01	0	0

Figure 3.1. Thiessen polygons for climate stations from which historical data were obtained.
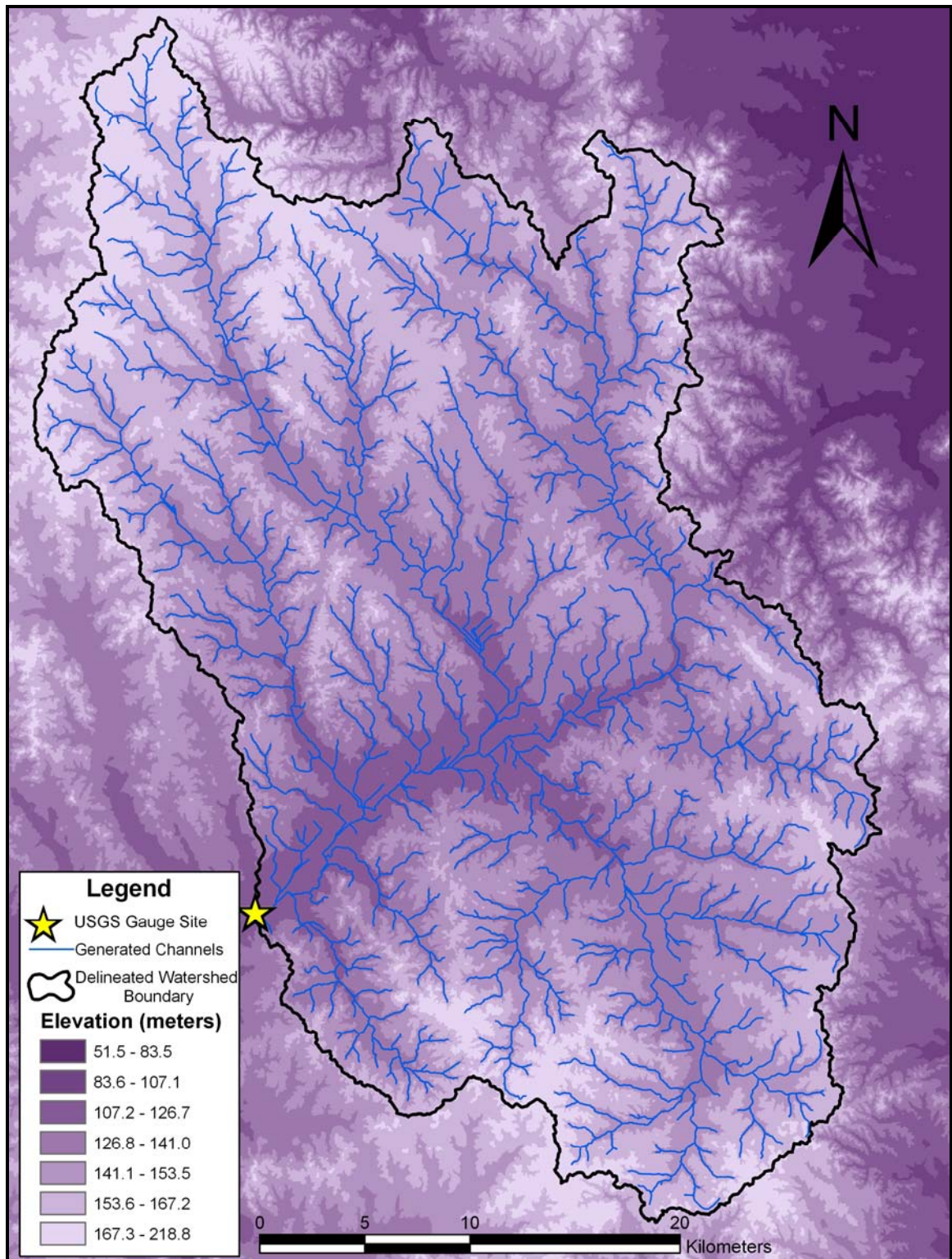
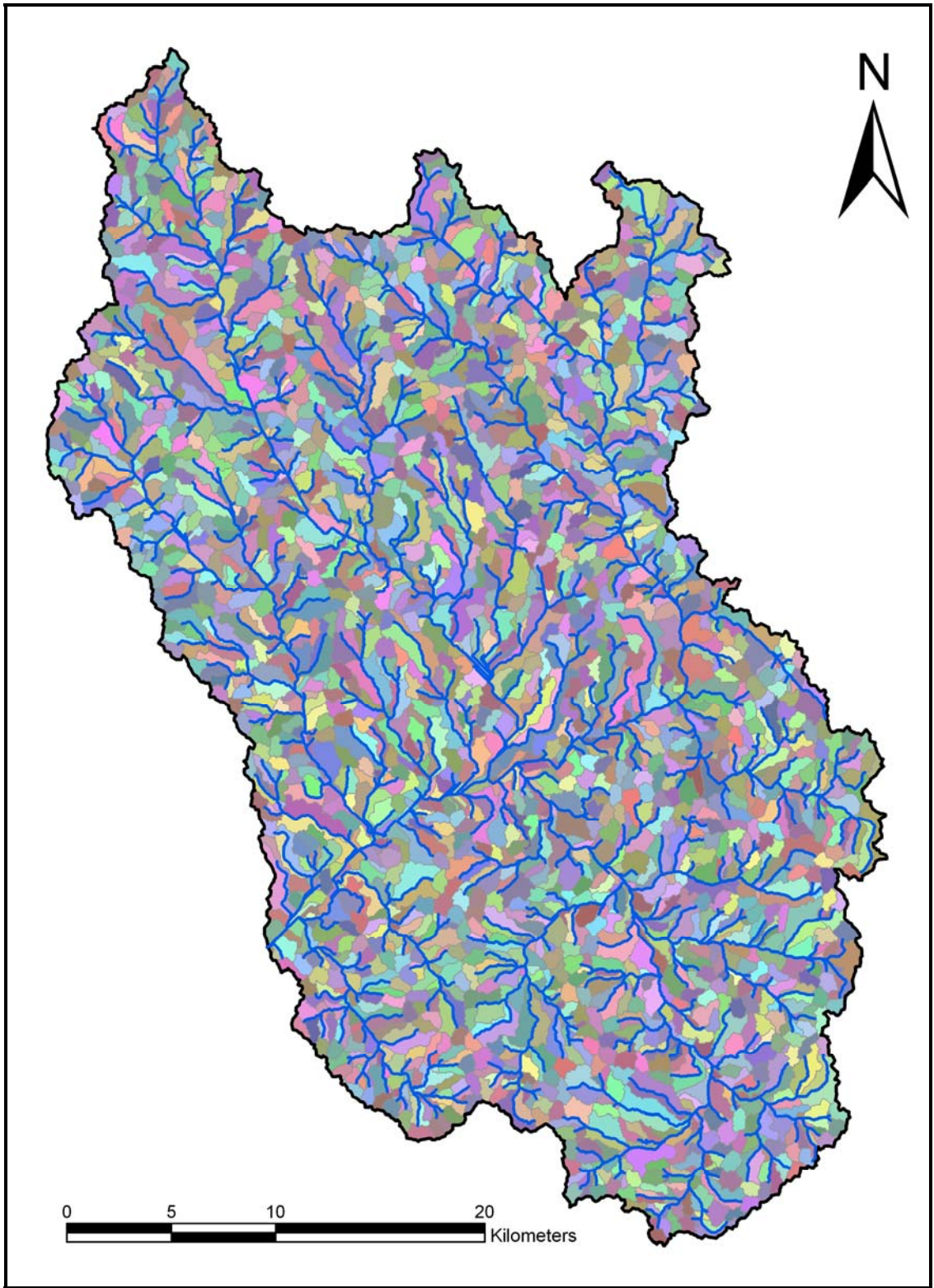Figure 3.2. Delineated watershed boundary for Burnside outlet with generated channel network.

Figure 3.3. Sub-watershed delineation with generated channel network.
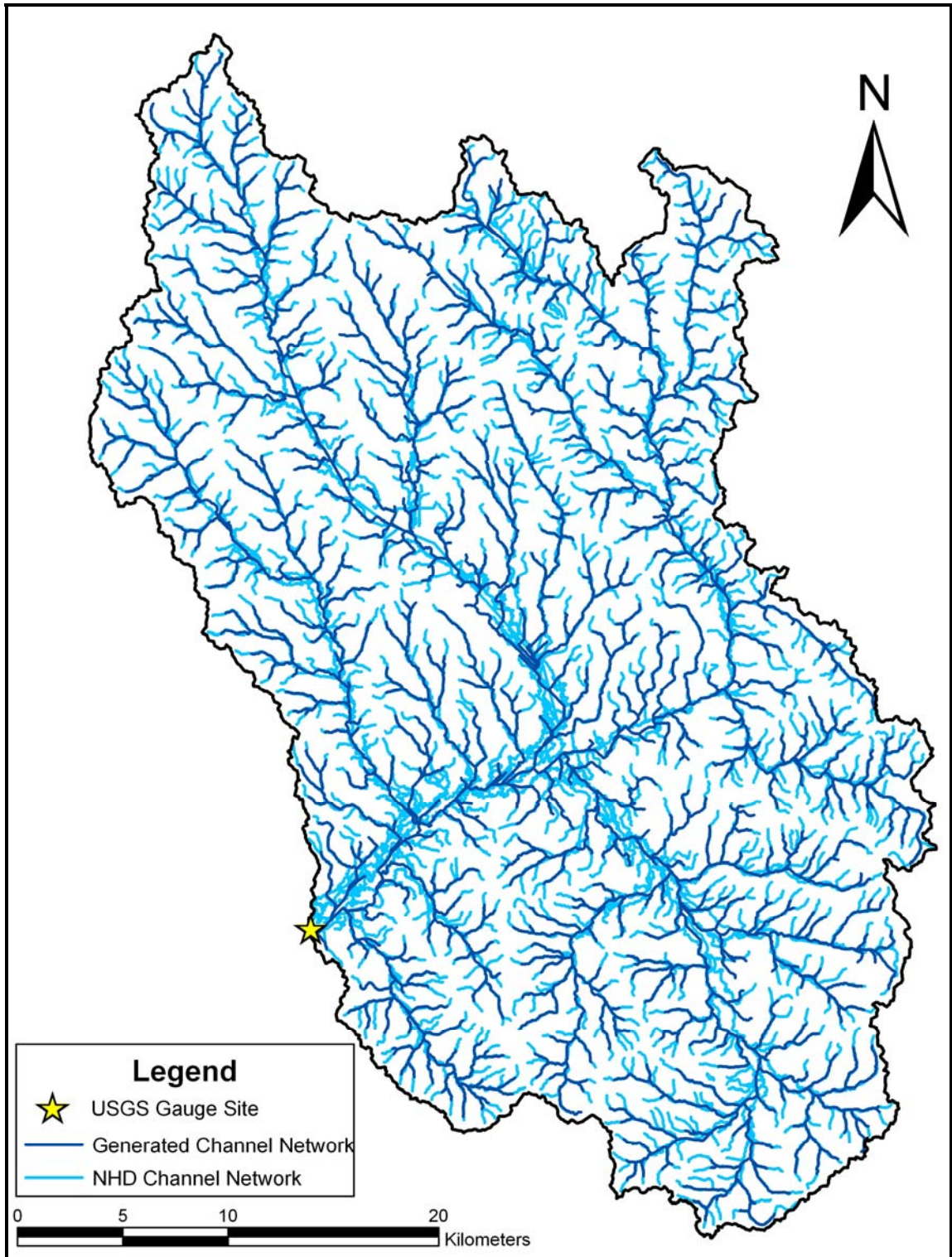
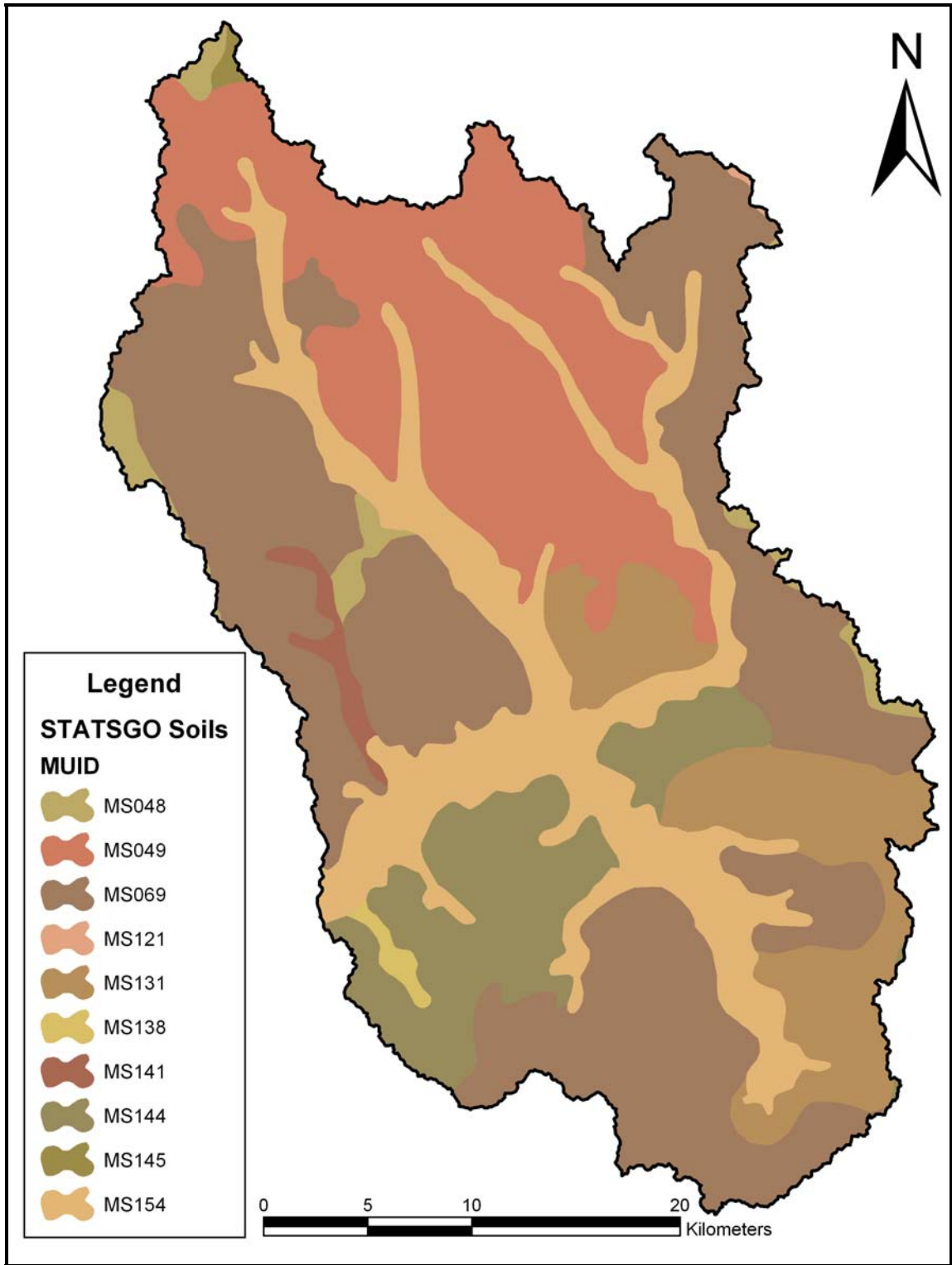Figure 3.4. Generated channel network as compared to the USGS NHD channel network.

Figure 3.5. STATSGO soil types throughout the delineated watershed.
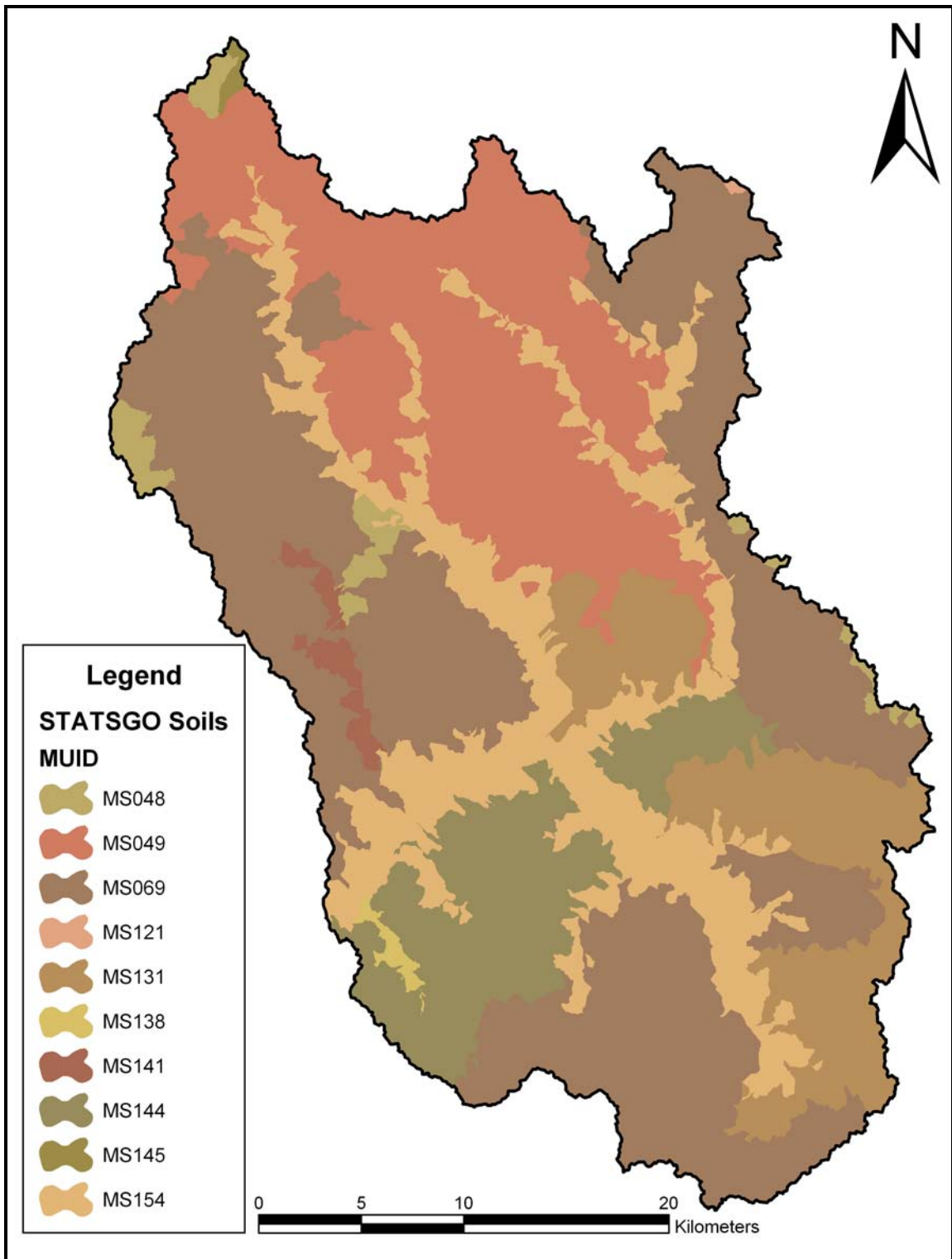
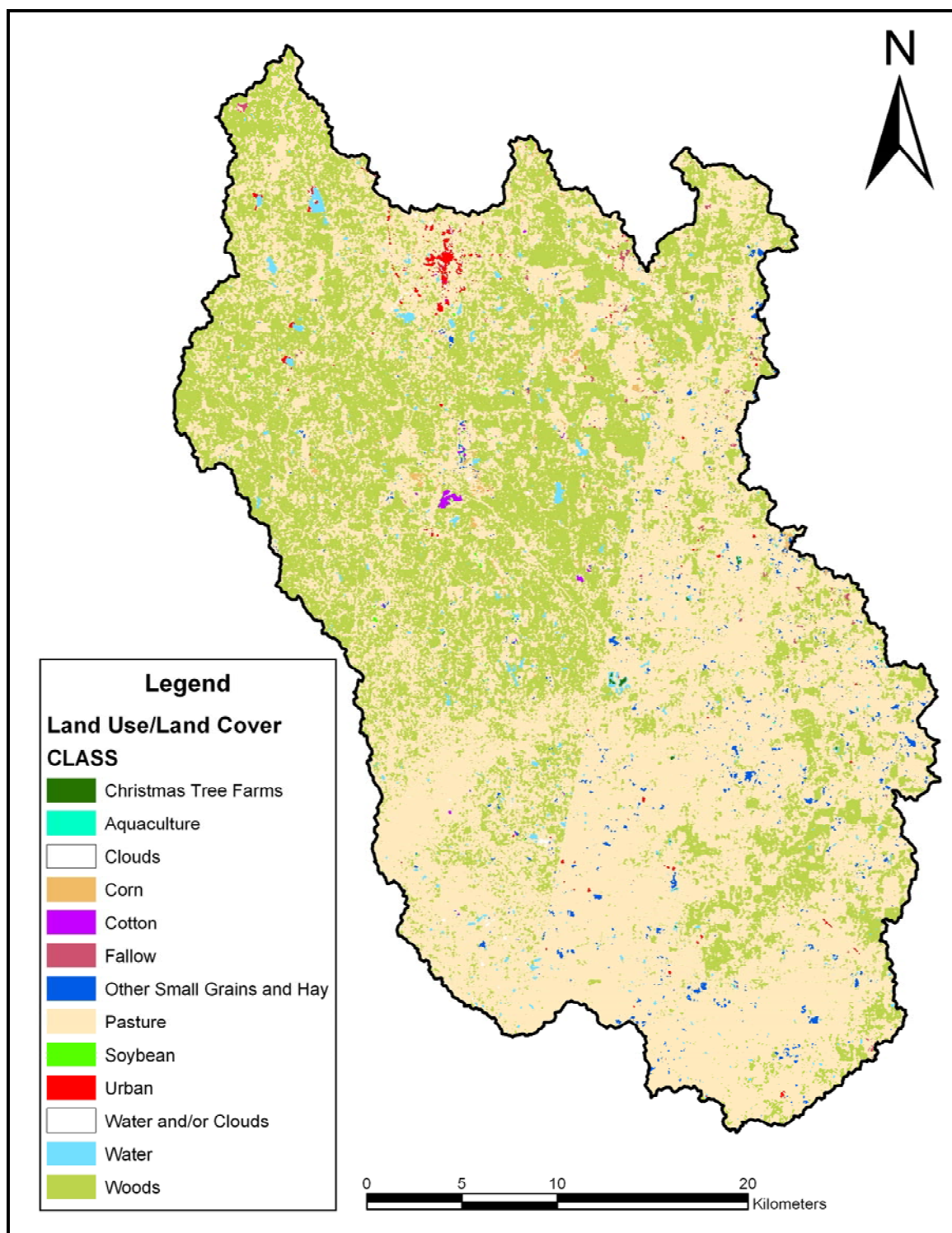Figure 3.6. STATSGO soil types as assigned to sub-watershed cells.

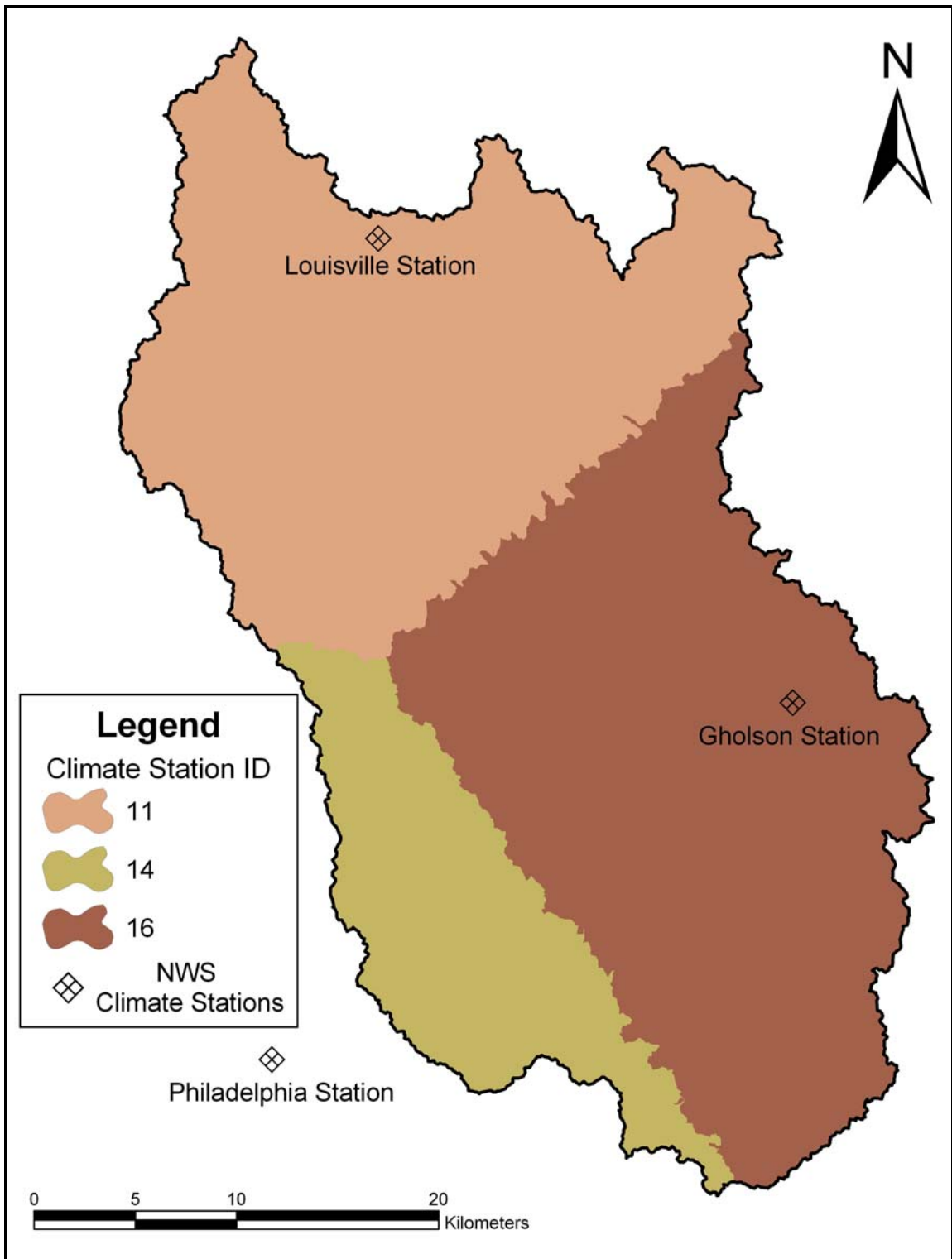Figure 3.7. Original NASS 2002 cropland data LULC layer.

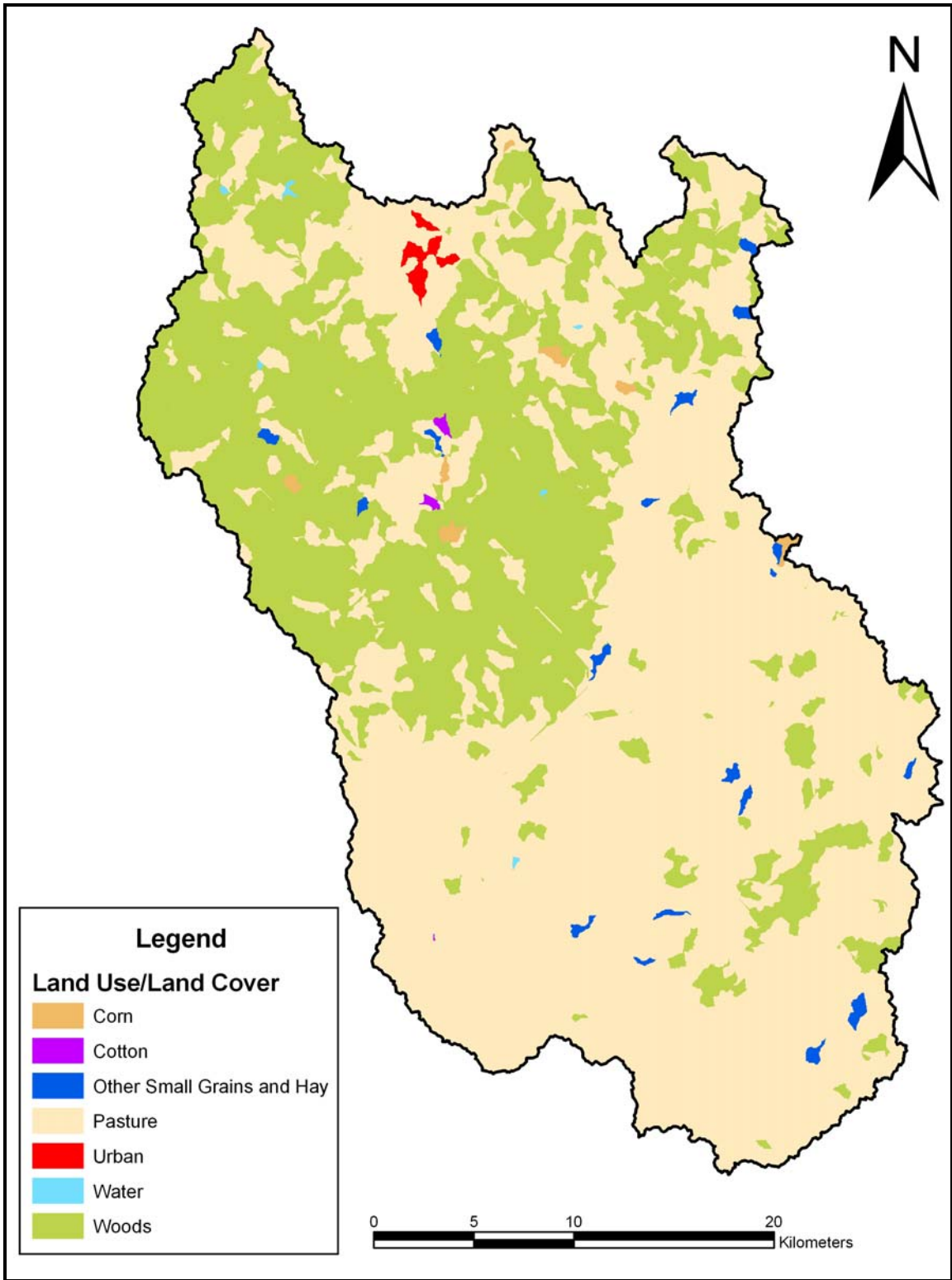Figure 3.8. Thiessen polygons as assigned to sub-watershed cells.

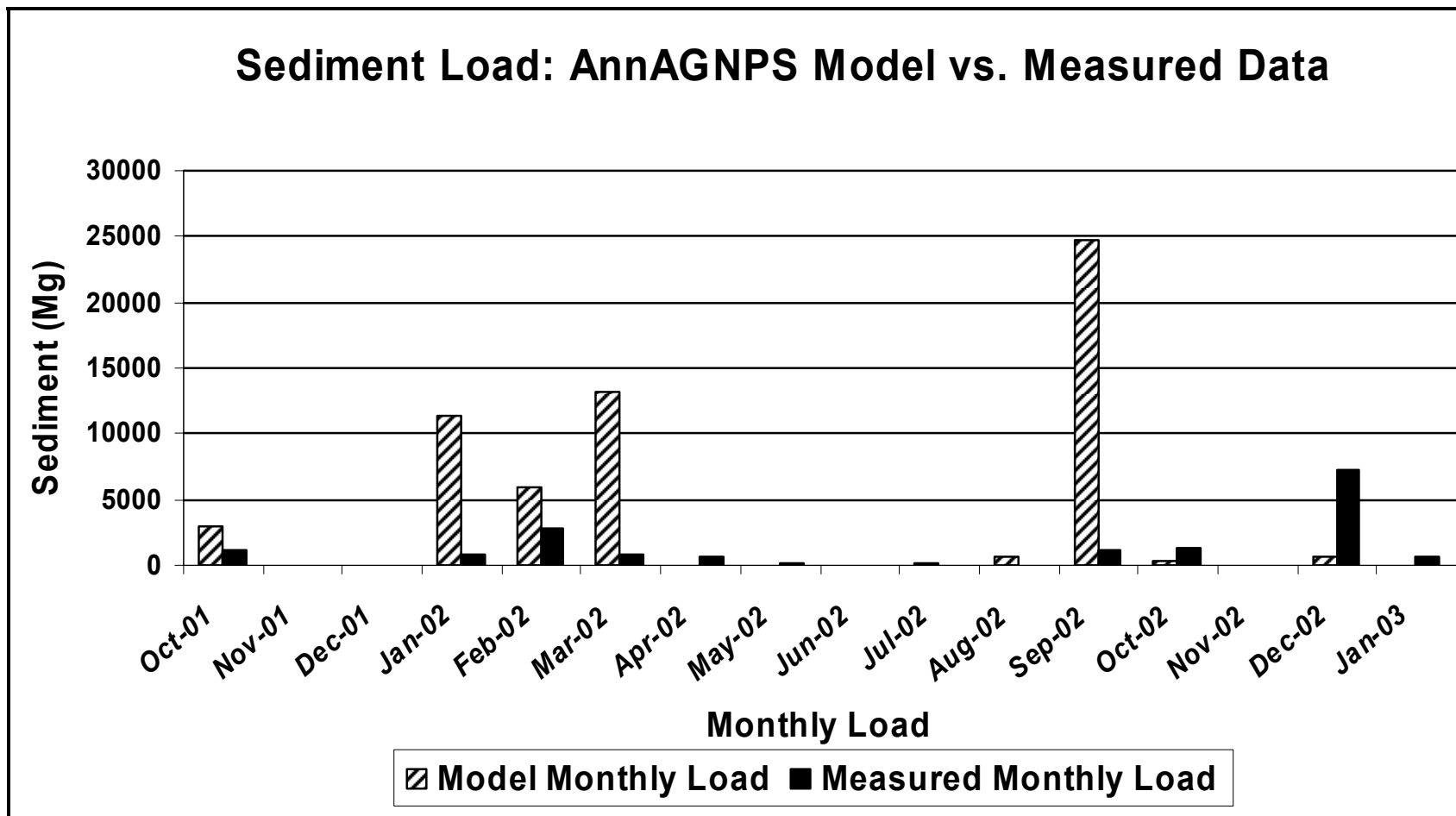Figure 3.9. LU/LC classes as assigned to sub-watershed cells.

Figure 3.10. AnnAGNPS-predicted monthly sediment loadings as compared to measured data.
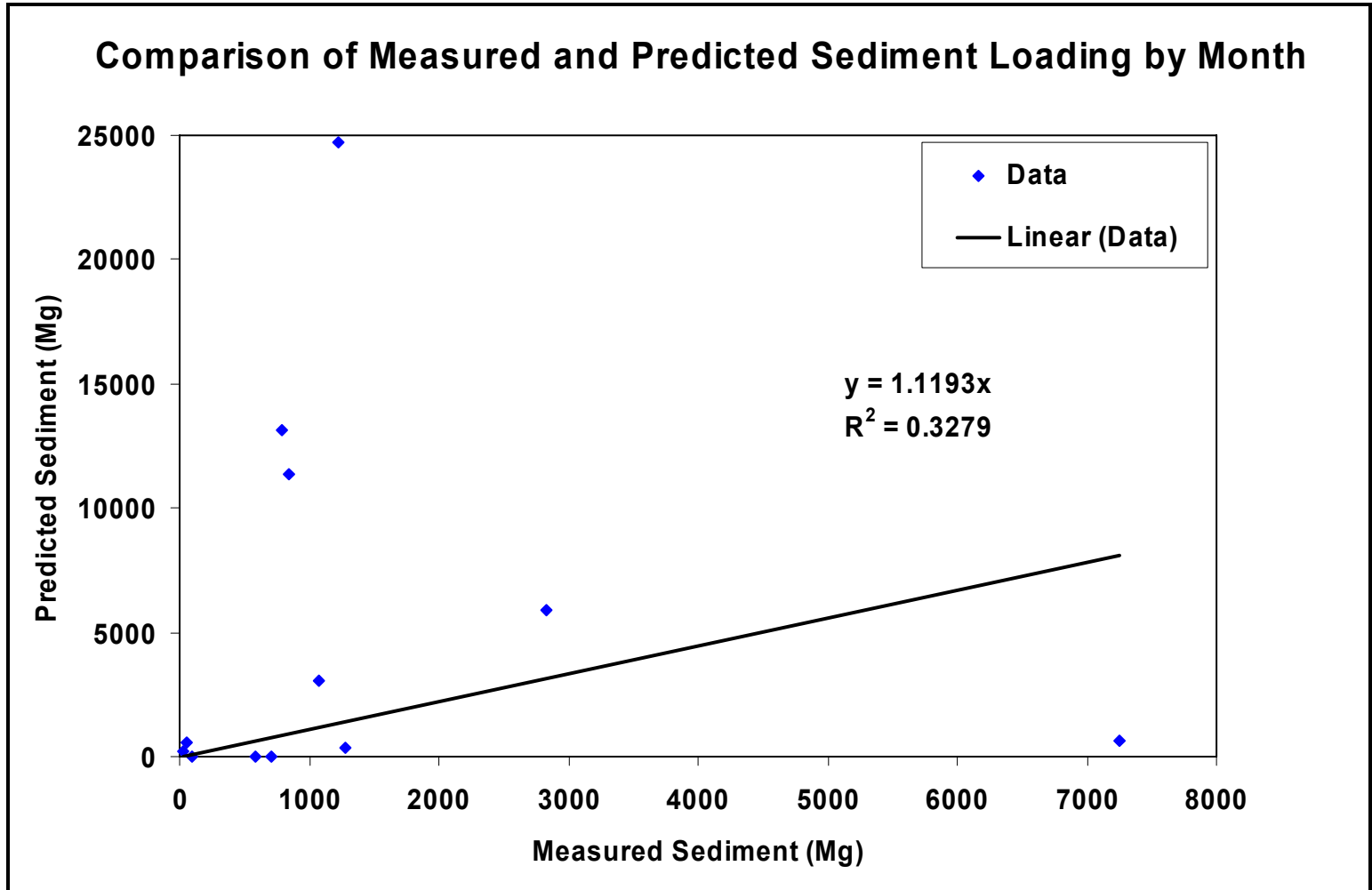
Figure 3.11. Comparison of measured and predicted sediment loading by month.
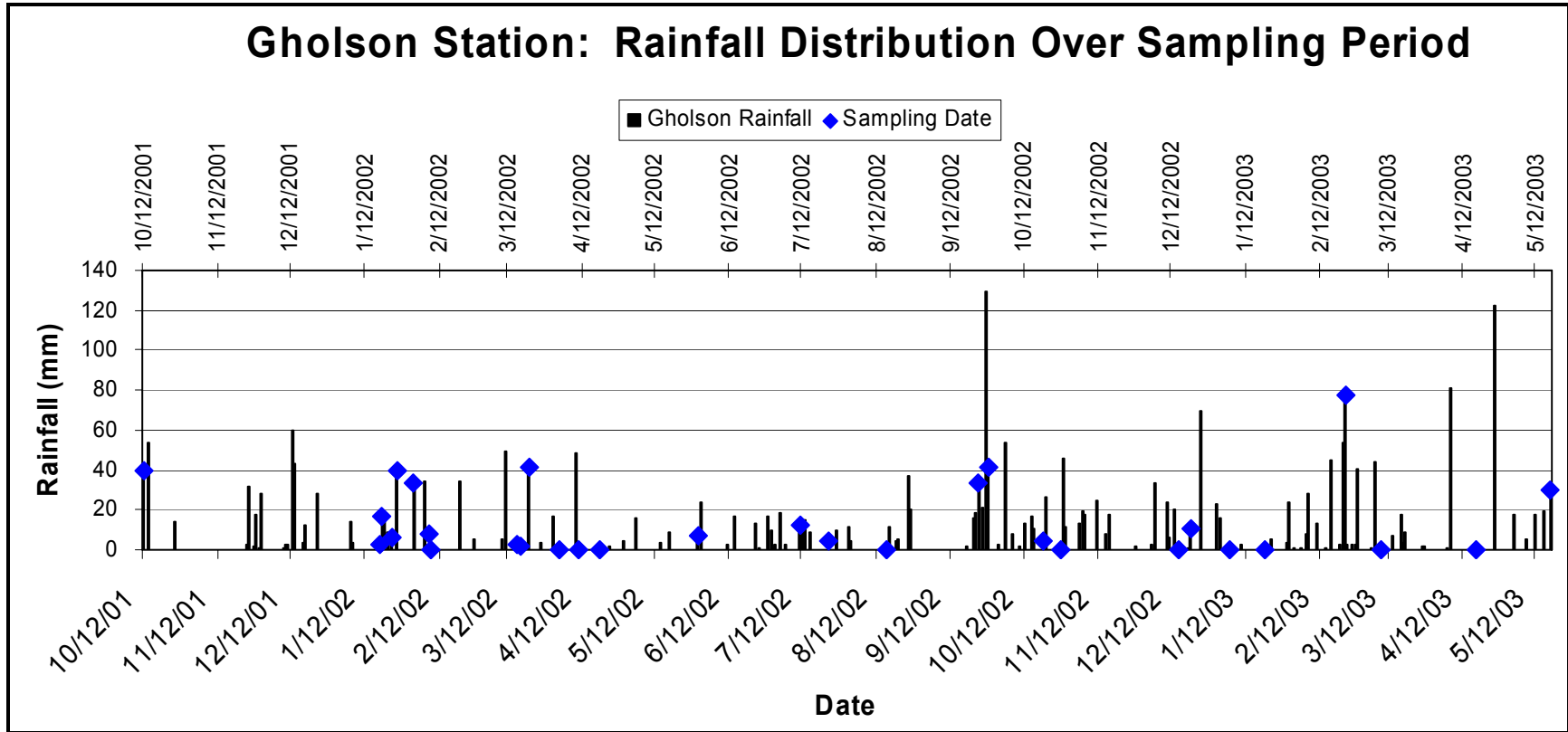
Figure 3.12. Rainfall distribution over the sampling period is shown for the Gholson climate station.
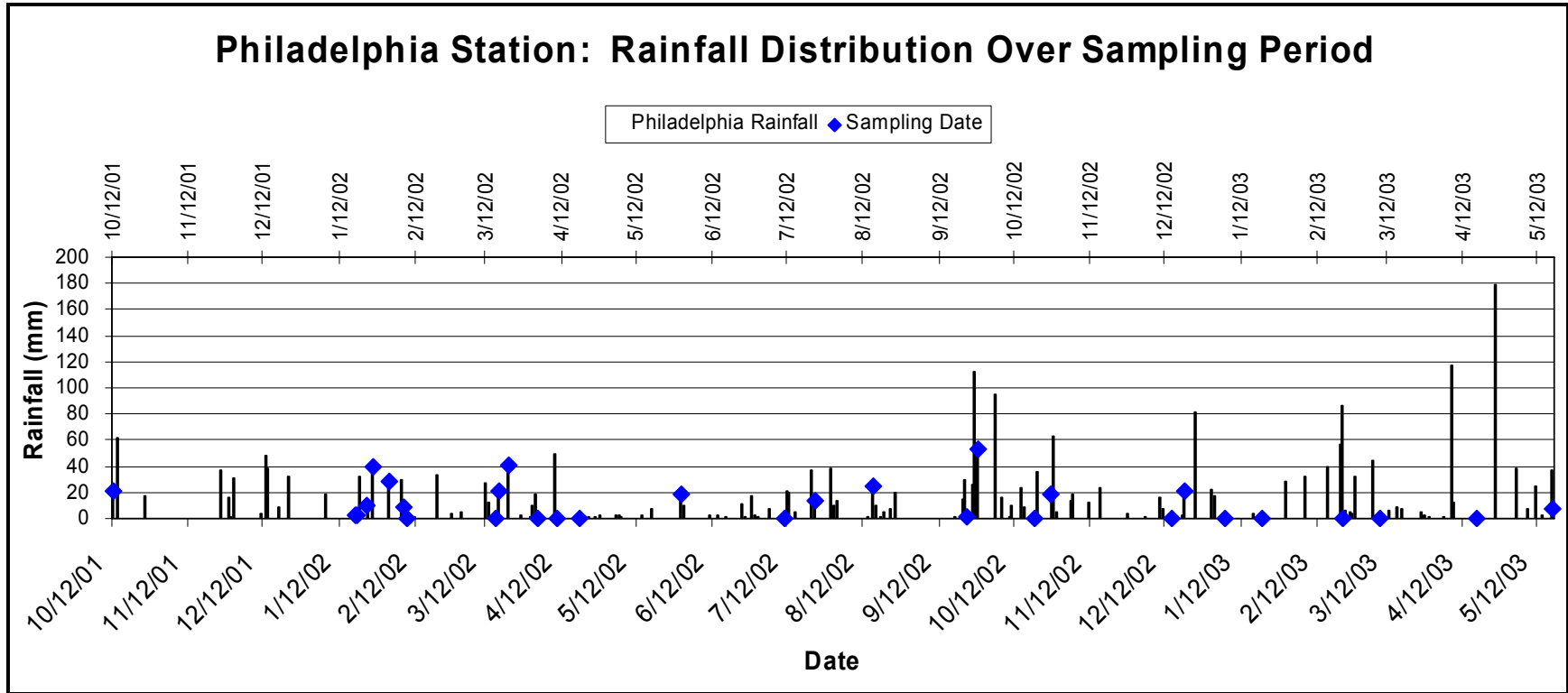
Figure 3.13. Rainfall distribution over the sampling period is shown for the Philadelphia climate station.
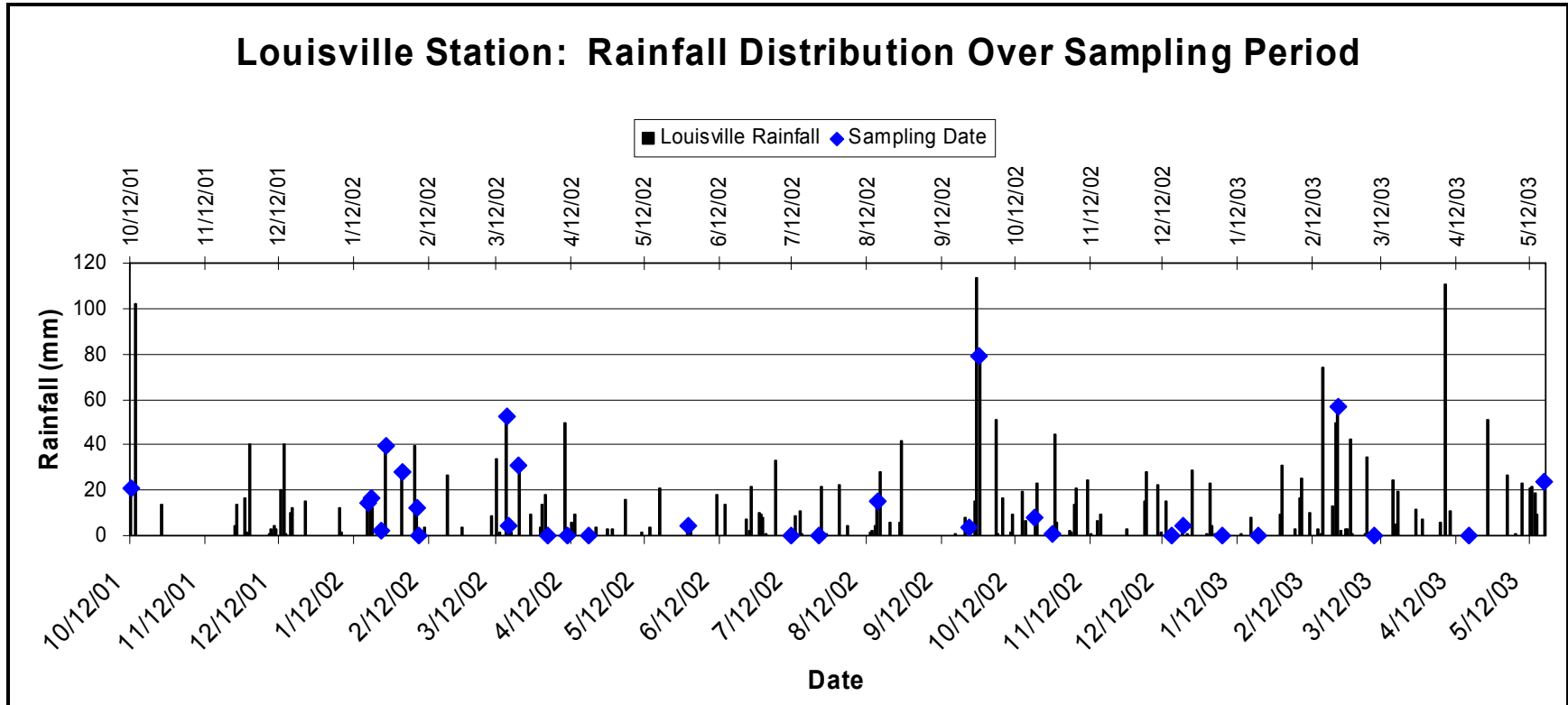
Figure 3.14. Rainfall distribution over the sampling period is shown for the Louisville climate station.
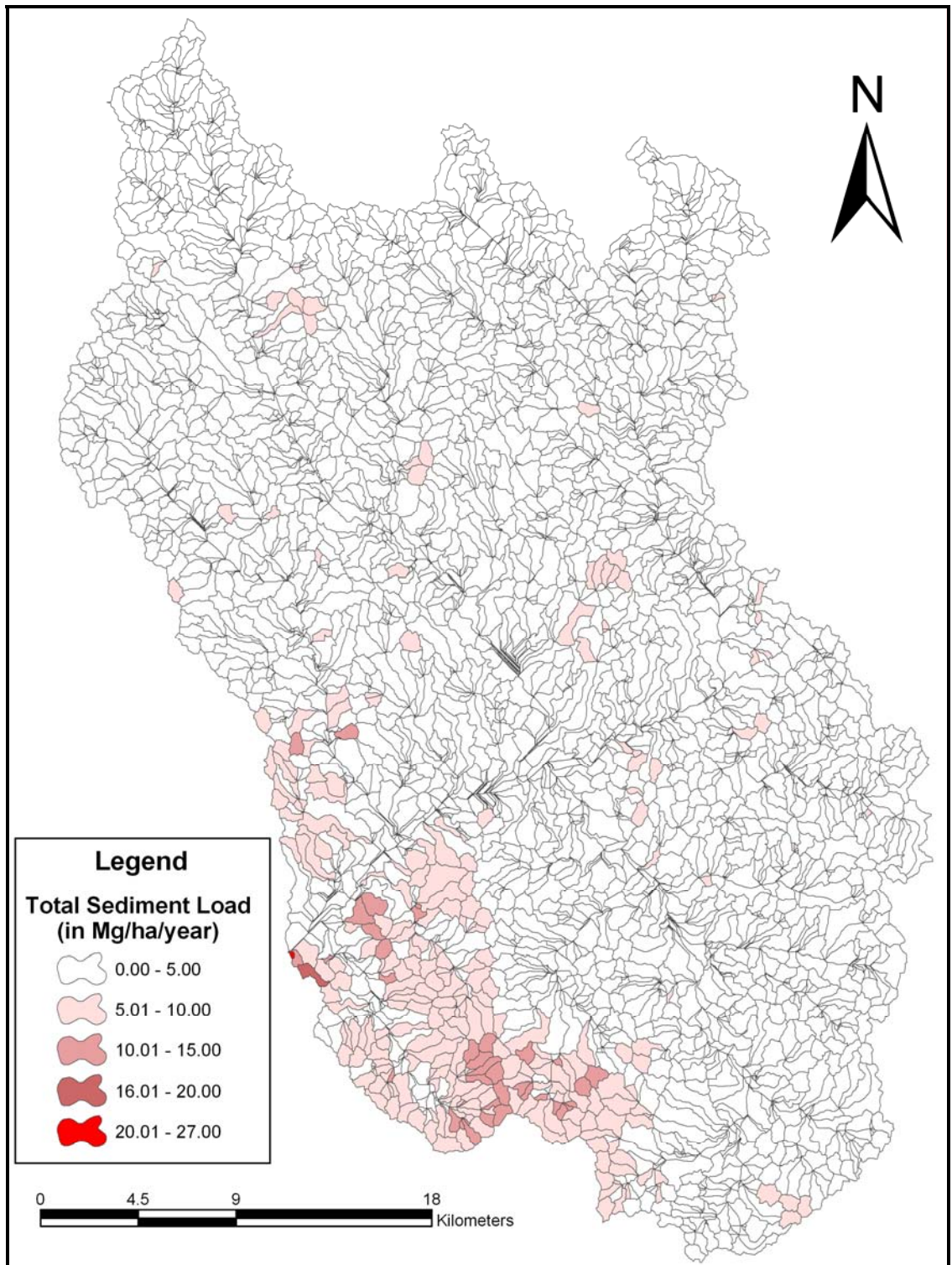
Figure 3.15. Average annual total sediment load (Mg/ha/yr) for each sub-watershed.
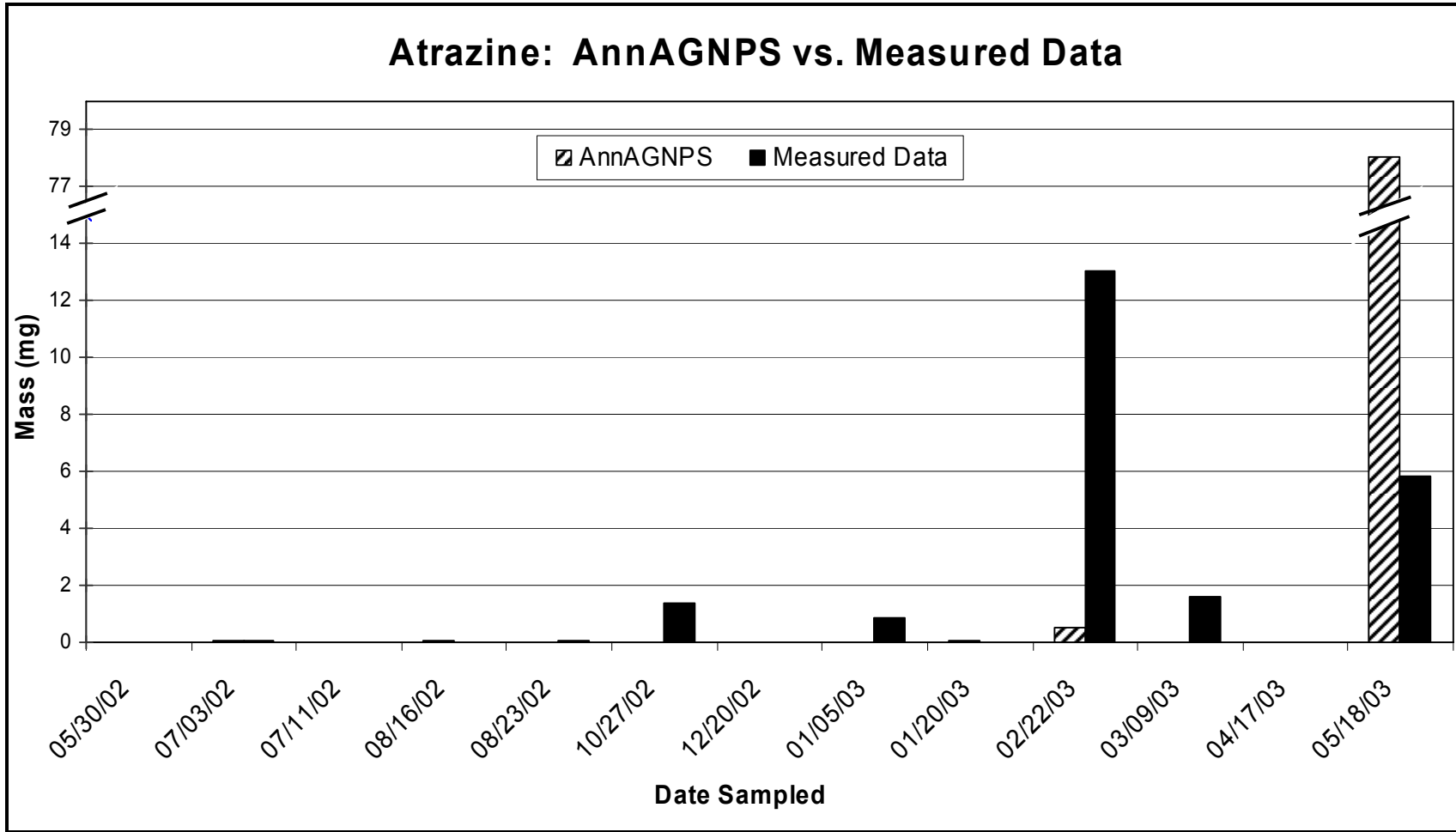
Figure 3.16. Atrazine loading at Burnside outlet: AnnAGNPS predictions versus measured data.
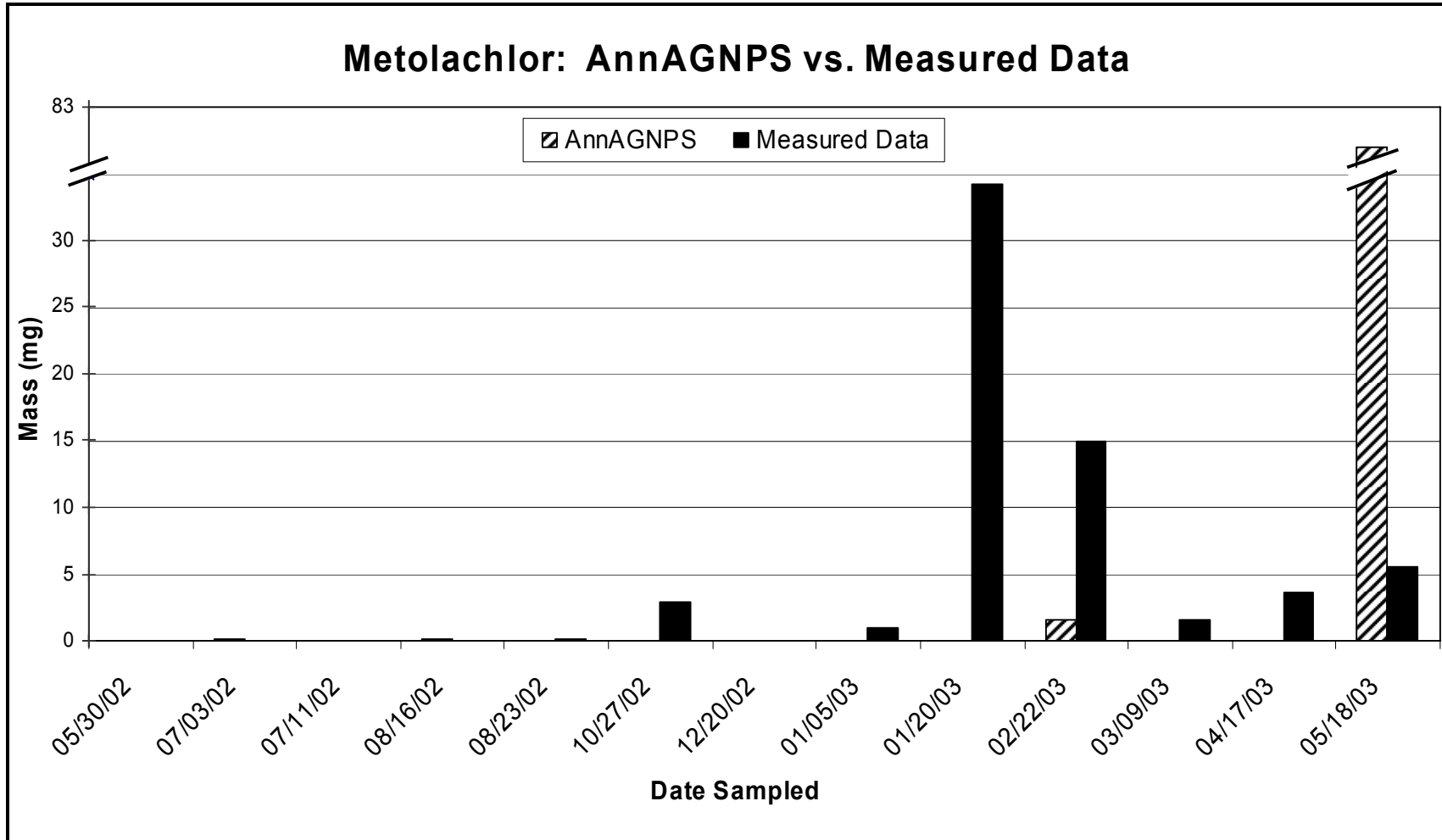
Figure 3.17. Metolachlor loading at Burnside outlet: AnnAGNPS predictions versus measured data.
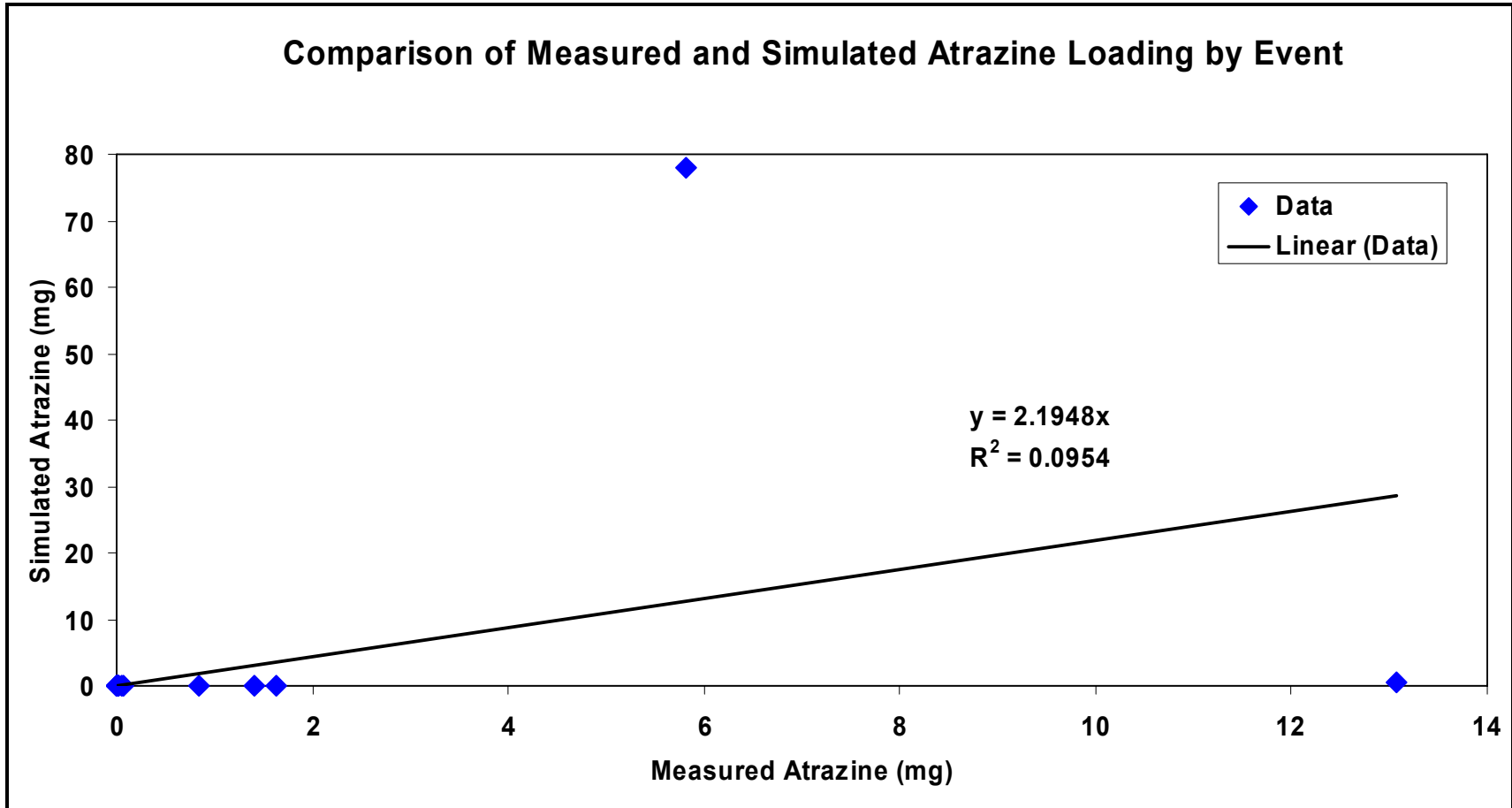
Figure 3.18. Comparison of measured and simulated atrazine loading by event.
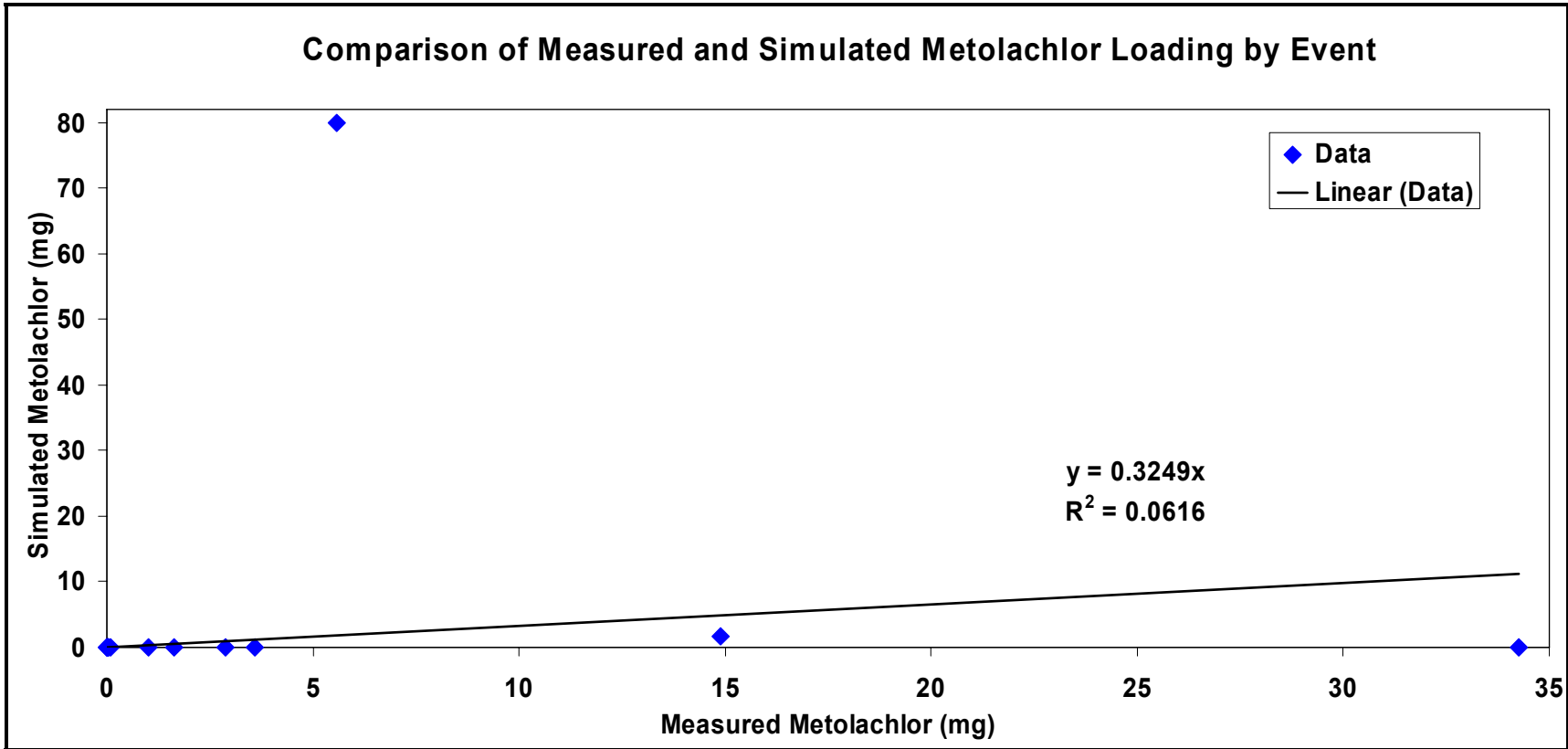
Figure 3.19. Comparison of measured and simulated metolachlor loading by event.
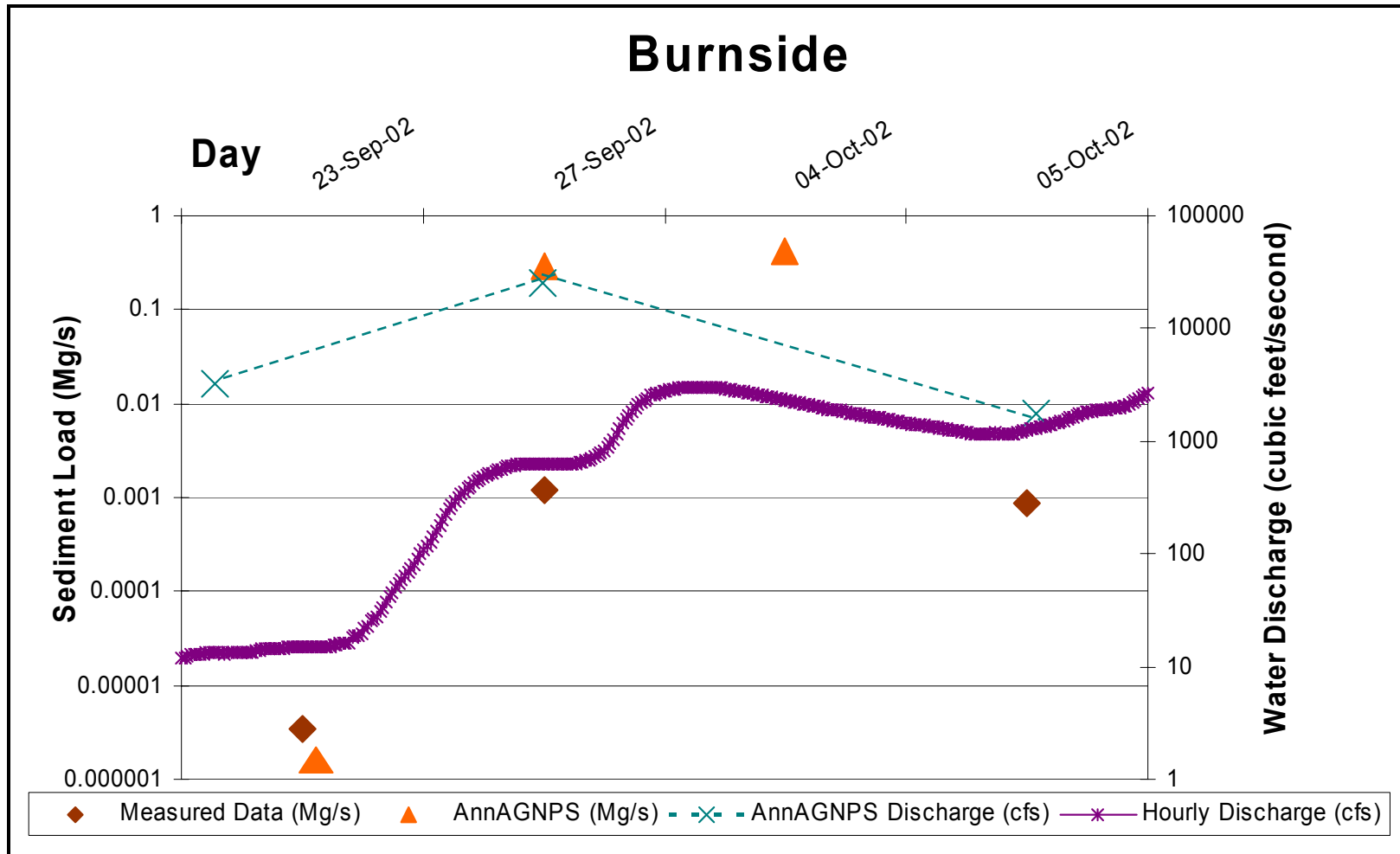
Figure 3.20. Daily AnnAGNPS sediment and discharge loadings converted to instantaneous values and plotted with continuous stream discharge and instantaneous sediment data for the Burnside outlet.

CHAPTER IV

EVALUATING EFFECTS OF LAND USE CHANGES ON SURFACE

WATERS IN THE UPPER PEARL RIVER BASIN

USING THE AnnAGNPS RUNOFF MODEL

ABSTRACT

Watershed models are an efficient means of estimating water runoff and

pollutant loadings entering surface waters. Watershed models are also useful in

analyzing the effects of land use and land use changes on nearby surface

waters. This study was designed to compare runoff and pollutant loading

predictions of the Annualized Agricultural Non-Point Source (AnnAGNPS)

pollutant loading model with 1987 and 2002 land use datasets. The simulation

with 2002 land cover resulted in 15% more average annual water runoff than did

the simulation with 1987 land cover, although both simulations had similar

average annual precipitation. The AnnAGNPS simulation with 2002 land cover

data also had significantly higher values for average annual sediment and

organic carbon loading. This can be explained by the decrease in forested

acreage in the watershed from 1987 to 2002. Average annual nitrogen loading

was the only runoff or pollutant loading category that was less for the 2002 land

cover simulation than for the 1987 land cover simulation. Additionally, the urban

land cover class was a more dominant contributor to water runoff and pollutant

loadings from 1987 to 2002, while traditional row crop agriculture had less of an impact on runoff and pollutant loadings.

INTRODUCTION

Landscapes are both complex and diverse, making it difficult to measure the effects of land use/land cover (LU/LC) and LU/LC management on surface water quality. The link between LU/LC and water quality is an important concept, because the local connections between land use and surface water quality have cumulative effects within an area, its watershed, and ultimately the receiving coastal waters (Turner and Rabalais, 2003). An area's LU/LC can potentially have a large impact – either positively or negatively – on the surrounding environment and, especially the quality of nearby surface waters. For instance, different agronomic tillage practices can result in different amounts of water runoff, peak runoff rates, and nutrient losses (Andraski et al., 2003; Yu et al., 2000). Studies have also shown that pesticide concentrations in surface waters often reflect estimated annual use rates for pesticides and also agricultural and other land use patterns (Gilliom et al., 1999; Harman-Fetcho et al., 1999).

Different land uses and, more specifically different crops, require varying pesticide and nutrient inputs. For example, hay and forage crops have a much lower use of applied nitrogen than do seed crops (Hellkamp et al., 2000). As a result of these varying inputs and management practices, land use information can be used to derive typical edge-of-field concentrations for pesticide runoff, determine which compounds are applied at rates that might be toxic to aquatic

fauna, and reduce pesticide analyses in regional sampling schemes (Wilcock, 1993). In one study, non-urban watersheds had higher variation of herbicide concentrations in streams than did urban watersheds, showing that land use patterns were important to most herbicides surveyed (Qian and Anderson, 1999). Land use also influences the mineralization of atrazine and the sorption of compounds such as deisopropylatrazine (DIA), atrazine, and prometryn (Aelion and Cresci, 1999; Oliver et al., 2003).

Agricultural land is not the only land use type that may yield potentially harmful runoff. Of particular interest to some are the environmental impacts of urbanization (Ha et al., 2003; Pijanowski et al., 2002; Walker et al, 1999). Even though the use of chlordane-containing products has been illegal in the United States since 1988, residual concentrations can still be detected in soils of previously applied areas and at much higher levels around residential foundations treated for termites than for residential lawns or agricultural areas treated for insects (Mattina et al., 1999). Drapper et al. (2000) found that characteristics such as highway exit lanes or road areas with rapid deceleration can result in increased concentrations of copper, lead, and zinc in runoff. However, different land use scenarios can be simulated with water quality models to help predict which scenarios will result in minimal environmental impacts, thus helping policy-makers develop better land management strategies for the future (Im et al., 2003).

As governments invest more money in conservation programs, there is an increasing desire to measure the effects of these conservation programs to

determine if they are having the desired effect on the environment (Oñate et al., 2000). Various studies have attempted to quantify the effects of particular LU/LC types and the environmental effects of implementing best management practices (BMPs). Initial results of a long-term study on the effects of converting row crops to short rotation woody crops showed a trend of higher soil erosion from cotton [*Gossypium hirsutum* L.] fields than from areas planted in cottonwood [*Populus deltoides* Bartr.] trees and also higher runoff and nitrate leaching from fertilized corn than from unfertilized sycamore [*Platanus occidentalis* L.] or sweetgum [*Liquidambar styraciflua* L.] trees (Joslin and Schoenholtz, 1997). The higher soil erosion from watersheds planted in cotton is possibly to due higher cultivation frequencies in cotton fields versus areas planted in cottonwood trees. More differences in runoff quality and quantify are expected after the establishment phase for trees has passed. There is also substantial evidence to suggest that the implementation of BMPs in North Carolina's Long Creek Watershed has reduced phosphorus and bacteria levels in the creek (Line, 2002).

Better prediction methods are needed to more accurately determine the impact of LU/LC and LU/LC changes on water quality (Hapeman et al., 2002). Individual sampling events cannot adequately characterize the interactions between land use and stream chemistry, and comprehensive sampling regimes are costly and time-consuming (Wayland et al., 2003). Remote sensing is one technology that has been in existence for quite some time but has only gradually emerged as an effective means of determining LU/LC and its effects on water quality. Remote sensing applications can also be used to directly monitor water

quality parameters such as turbidity and chlorophyll (Dekker et al., 1991; Koponen et al., 2002; Zhang, et al., 2003). Thermal bands, such as Band 6 of Landsat 7 – Enhanced Thematic Mapper (ETM) data, can be used to measure water temperatures (Schott et al., 2001). However, only those water quality parameters that have a direct effect on the optical properties of water can be measured directly by remote sensing (Brando and Dekker, 2003; Bukata et al., 2001; Forget et al., 2001). Therefore, pesticide and nutrient concentrations cannot be directly measured by remote sensing applications.

Many scientists have used remote sensing applications to indirectly estimate and model pesticide and nutrient concentrations in surface water because remotely sensed imagery can quantify LU/LC, and relationships can then be established between LU/LC and surface water quality parameters (Atkinson et al., 2001; Johnson and Ebert, 2000; Lattin et al., 2004). Remote sensing has also been used to identify environmental impact indicators through LU/LC delineation, as well as through derived vegetation indices, such as the normalized difference vegetation index (NDVI) (Griffith, 2002; Griffith et al., 2002; Jain and Goel, 2002; Santo and Sánchez, 2002). In hydrologic modeling applications, remotely sensed imagery is frequently used in combination with geographic information systems (GIS) to effectively establish correlations between land use and stream water quality parameters (Tong and Chen 2002).

There have been many advances in the field of remote sensing in recent years, including the commercial availability of high-resolution satellite imagery from the IKONOS and Quickbird satellites (Sawaya et al., 2003). Higher

resolution imagery can result in better classification accuracies, more so with

simple vegetation cover classes that have low spectral variation than with areas

high in species diversity (Treitz et al., 1992). IKONOS imagery has even been

used, in combination with ground truth data, to verify conservation tillage

practices (Viña et al., 2003). However, since commercially available, high-

resolution imagery has only been obtainable in the past 2-5 years, depending on

the source, it is impossible to use it as a sole data source for long-term land use

change studies (Morain, 2002).

Historical imagery is often available for an area, allowing scientists to

evaluate the changes in land use over longer periods of time (Miller, 1999;

Wayland et al., 2002). Remote sensing and GIS have been increasingly used in

land use change studies and have proven to be an efficient and effective means

of analyzing the direction, rate, and spatial pattern of land use changes (Weng,

2002; Yang et al., 2003). Landsat satellite data are commonly used for change

detection studies and other earth resource studies because the Landsat series of

earth-observing satellites has resulted in a large global imagery archive over time

(Arvidson et al., 2001; Frazier and Page, 2000; Miller et al., 2002; Neville et al.,

2000). Landsat data can be classified using different methods, with some

resulting in better classification accuracies (Foody, 2001; Watson and Wilcock,

2001). Accuracy can also be improved by combining two data sources or using

scenes taken on multiple dates, but atmospheric corrections are sometimes

needed to place multi-temporal imagery on the same radiometric scale (de

Colstoun et al., 2003; Song et al., 2001; Töyrä et al., 2001).

Mississippi's 2004 Clean Water Act (CWA) § 303(d) list showed 19 impaired waters (13 monitored and 6 evaluated) in the Upper Pearl River Basin (UPRB) (HUC 03180001), with the following impairments: 12 biological and 4 each for nutrient, pathogen, organic enrichment, pesticide, and sediment (MDEQ, 2004a). The Mississippi Department of Environmental Quality (MDEQ) develops Mississippi's CWA § 303(d) lists, as well as a Total Maximum Daily Load (TMDL) for each impaired water on the list. Evaluated stream segments are those for which there was no monitoring data available, and they were initially placed on the state's 1996 CWA § 303(d) list primarily due to land-based anecdotal information. Unable to determine the validity of many evaluated listings, MDEQ performed an extensive Mississippi Benthic Index of Stream Quality (M-BISQ) monitoring effort in preparation for the state's 2002 CWA § 303(d) list, but there are numerous evaluated waters remaining on Mississippi's 2004 list of impaired waters. The M-BISQ monitoring data do not suggest the cause of biological impairment, such as a particular pollutant, due to a lack of comprehensive monitoring data for many waters on the state's impaired list. The objectives of this study are 1) to use AnnAGNPS to quantify the effects of land use changes from 1987 to 2002 in a portion of the UPRB and 2) to provide more data on the surface water quality in the UPRB which may help prioritize waters on Mississippi's § 303(d) list or develop and validate TMDLs.

MATERIALS AND METHODS

Landsat was the remote sensing data source chosen for this LU/LC change analysis study because of its historical archive and affordability. The AnnAGNPS pollutant loading model was chosen as the hydrologic model to be applied in this study for several reasons (Bingner and Theurer, 2001a; Bingner and Theurer, 2001b). Older, single-event versions of AnnAGNPS, called AGNPS, have previously been used to assess management alternatives in agricultural watersheds by identifying appropriate BMPs for a particular watershed (Mostaghimi et al., 1997). Also, AnnAGNPS has an integrated GIS that can manipulate remotely sensed imagery, and the model can simulate nutrient, sediment, and pesticide runoff in agricultural watersheds.

Watershed Description

The UPRB (HUC 03180001) contains portions of nine counties in east-central Mississippi. The UPRB consists mostly of gently rolling hills and is the headwater region of the Pearl River, which ultimately drains into the Gulf of Mexico and forms the most eastern segment of the Mississippi-Louisiana boundary. The UPRB is important because it drains into the Ross Barnett Reservoir, which is the primary source of drinking water for Mississippi's capital city, Jackson (Ballweber et al., 2000).

Pre-processing of Geospatial Data

The Burnside location is the uppermost United States Geological Survey (USGS) gauged location along the main stem of the Pearl River and was

selected as the outlet location to be modeled by AnnAGNPS. The USGS (2005)

cites the area drained at the Burnside gauge location as being 1,300 km^2, but the

drainage area delineated by the model totals 131,500 hectares (325,000 acres),

or 1315 km^2.

Versions 3.42 and 3.51 of the AnnAGNPS ArcView interface were used

for this study. The following text gives a summary of model input sources as well

as the pre-processing steps that were performed on these geospatial data. See

Appendix B for more detailed information on processing steps that were

performed on input data layers.

The digital elevation models (DEMs)[1], at a horizontal resolution of 10 m

and vertical resolution of approximately 1.5 m, were downloaded for each county

present in the UPRB. For the watershed size modeled, the mosaiced 10-m DEM

contained too many rows and columns (over 10,000 pixels) for the model to

process, so the DEM was resampled to a 20-m pixel size.

The 2002 land use information was obtained from Mississippi's 2002

cropland data layer[2], which contains LU/LC described by eleven classes. The

cropland data layer contains a mosaic of georeferenced Landsat 5 – Thematic

Mapper (TM) and Landsat 7 – Enhanced Thematic Mapper (ETM) scenes on

which a supervised classification has been performed. The AnnAGNPS ArcView

interface requires that the LU/LC information be in a shapefile format, therefore

the LU/LC file was converted from a raster format to a shapefile.

The cropland data layer does not exist for Mississippi prior to 1999, so an

orthorectified Landsat 5 – TM image[3] acquired on August 21, 1987 was used for

the1987 LU/LC dataset. A supervised classification was performed using ground truth information from county USDA Farm Service Agency (FSA) offices. Ground truth fields were identified for corn [*Zea mays* L.], cotton, and soybean [*Glycine max* (L.) Merr.], and the image was classified using the following categories: cotton, corn, soybean, woods, fallow, and water.

Digital soils data were obtained from the State Soil Geographic (STATSGO) database[4], and all geospatial input layers were clipped to the estimated watershed boundary, leaving an appropriate buffer. The watershed was estimated with using the AnnAGNPS ArcView interface. The closest climate station that was contained within GEM (Generation of weather Elements for Multiple applications) was at Meridian, MS; GEM used data from this station to generate historically-based synthetic climate data for the watershed.

<u>Preparation of Input Files</u>

The AnnAGNPS ArcView interface was used to prepare input files for the Input Editor. The Input Editor then produced one AnnAGNPS input file that was used, in combination with the climate file, by the pollutant loading module. See Appendix C for more detailed information on the preparation of input files.

Data preparation steps for both the 1987 and 2002 simulations were completed in the AnnAGNPS ArcView interface. Values for the Critical Source Area (CSA) and Minimum Source Channel Length (MSCL) were set at 50 hectares and 100 meters, respectively. The CSA and MSCL values determine the hydrographic segmentation of the watershed by controlling the characteristics

and topology of the stream channel network and sub-catchments generated by the TopAGNPS module. Figure 4.1 illustrates the sub-watershed delineation and connectivity between the sub-watersheds and the generated channel network.

The sub-watershed cells were intersected with the soils data, using the field 'MUID' as the soil identifier in the overlay. The STATSGO soils database contains soil associations, but AnnAGNPS requires that a dominant soil type, along with its characteristics, be selected for each generalized soil association. The Map Unit Use File (MUUF) program, using the Map Unit Identification (MUID) number in the STATSGO database, retrieved the desired soil characteristics information from the NRCS Soils5 database (Baumer et al., 1994). Another program, the MUUF converter, transformed the retrieved MUUF data to a format that is compatible with the AnnAGNPS model (Bingner, 2004).

The sub-watershed cells were also intersected with the LU/LC layer. The overlay was performed with the 2002 cropland data layer and, in a second run of the model, with the 1987 land use dataset. See Figures 4.2 and 4.3 for the original 1987 and 2002 LU/LC layers, respectively. During the overlay process, the model assigned a LU/LC class to each sub-watershed cell, which is based on the dominant LU/LC class within that sub-watershed cell. The AnnAGNPS ArcView Interface was employed to determine how well the LU/LC information from the original file was reflected in the sub-watershed LU/LC designations, by calculating the percentage of each LU/LC class in both the original LU/LC layer and in the sub-watershed file. The two were then compared. See Appendix D for a more detailed description of the previously mentioned LU/LC analyses.

The heterogeneity of some LU/LC classes, especially urban and agricultural classes, caused these classes to be underrepresented in the sub-watershed file. These particular classes were assigned to fewer sub-watershed cells because they were not the dominant LU/LC class within many sub-watersheds. The detailed hydrographic description performed on the watershed still did not reflect the patchy nature of the agricultural and urban LU/LC classes. Thus, the LU/LC classes assigned to sub-watershed cells were later adjusted using the Input Editor to more accurately reflect the class percentages in the original LU/LC layer.

The final step to be performed in the ArcView interface was the creation of synthetic weather information using the synthetic weather generator, GEM. Since the Meridian climate station was the nearest station to the UPR watershed that was contained within the GEM climate station database, the GEM program used historical data from the Meridian station to generate synthetic climate information for daily precipitation, maximum and minimum temperatures, and solar radiation. A monthly climate file with Meridian monthly dew point, sky cover, and wind speed was also created with data obtained from the *Climatic Atlas of the United States* (United States Department of Commerce, 1968). Once the climate files were created and in their final format, the files were imported into the Input Editor. Appendix E gives more detailed information on processing climate files.

For each run of the model, the soils, topographic, and LU/LC data were imported into the AnnAGNPS Input Editor to help create the required AnnAGNPS

input file needed to run the pollutant loading model. Other AnnAGNPS data

sections that must be defined by the user include crop or non-crop land use type,

runoff curve numbers, residue cover, input and output units, simulation period,

desired output files, and more. More detailed management information, such as

planting, tillage, pesticide, fertilizer, and irrigation information must be described

for crop land use classes. Version 3.51 of the Input Editor and the AnnAGNPS

pollutant loading module were used for this study. The AnnAGNPS pollutant

loading module was set to run for two initialization years and ten simulation

years.

Once the cell and reach data were imported into the Input Editor, the

LU/LC class designations for the sub-watershed cells could be adjusted to more

accurately reflect the total LU/LC areas in the original LU/LC layer. Tables 4.1

and 4.2 show a comparison of the LU/LC class percentages in the original LU/LC

layer, model delineated LU/LC layer, and final adjusted layer. The LU/LC

designation for the sub-watershed cells is illustrated in Figures 4.4 and 4.5 for the

1987 and 2002 land cover layers, respectively. Operational management

information was also outlined for the watershed, including data regarding typical

pesticide applications and management schedules, where applicable

(Anonymous, 1987; Anonymous, 2005).

The average annual results for both runs of the AnnAGNPS pollutant

loading model were compared using Fisher's protected LSD (least significant

difference) with a probability value of alpha equals 0.05 (SAS, 2005). The

average annual output tables for the 1987 and 2002 results were joined with the

sub-watershed tables, which contain the final LU/LC information, and analyzed.

These tables were joined in the AnnAGNPS ArcView interface, using a common

attribute and creating one file containing the attributes of both files. With land

use as the class, means were separated for water runoff and several pollutants,

using Fisher's protected LSD with a probability value of alpha equals 0.05. The

number of replications varied for each LU/LC class for each year, as they were

based on the number of sub-watersheds assigned to each LU/LC class.

RESULTS AND DISCUSSION

When comparing the AnnAGNPS pollutant loading simulation with 1987

LU/LC to the simulation with 2002 LU/LC, the 2002 LU/LC resulted in 15% more

average annual runoff than did the 1987 LU/LC, although both simulations had

the same average annual precipitation (Table 4.3). The AnnAGNPS pollutant

loading model predicts pesticide output on an event basis. However, it does not

produce average annual pesticide yield and loadings, thus these data were not

included.

A more detailed look at runoff and pollutant loadings for both 1987 and

2002 LU/LC for each year of the ten-year simulation period can be seen in

Tables 4.4 and 4.5. Where applicable, t-groupings were also included in these

tables by the mean for each year. Although outputs varied for each year, with

variation based primarily on the yearly precipitation and the timing of precipitation

events with management operations, outputs for sediment (Mg/ha) and organic

carbon loading (kg/ha) were significantly higher with the 2002 LU/LC data than

with the 1987 LU/LC data. Since all other model inputs, including precipitation, were constant for both simulations, results indicate that the change in LU/LC did have an effect on the AnnAGNPS predictions for sediment and organic carbon loadings in the UPRB.

The average annual sediment loadings produced by AnnAGNPS for both 1987 and 2002, when compared to Total Maximum Daily Loads (TMDLs) set by the MDEQ, are within an acceptable range. The sediment TMDL for the Fannegusha Creek Watershed, which is south of the study area in the Pearl River Basin, lists an acceptable range of $1.55x10^3$ to $9.42x10^3$ Mg/ha/day, or 0.57 to 3.44 Mg/ha/year, and sediment loadings predicted by AnnAGNPS for 1987 and 2002 fall within this range (MDEQ, 2004b). Although Mississippi does not currently have numeric water quality standards for acceptable nutrient concentrations, MDEQ has estimated a phosphorus TMDL for Oakahay Creek at 24.99 to 39.28 kg/day, or 9,122 to 14,338 kg/year (MDEQ, 2005). The phosphorus loadings predicted by AnnAGNPS for both 1987 and 2002 fell well below this range. There are no nutrient TMDLs in any part of the Pearl River Basin, but Oakahay Creek is located in the Pascagoula River Basin near the Pearl River Basin. The MDEQ uses phosphorus as the nutrient of concern when developing nutrient TMDLs.

Although there have been no other studies to date applying AnnAGNPS in the Pearl River Basin, several studies have been performed to validate the single event version of the model, called AGNPS, in other areas of the United States and internationally (Choi and Blood, 1999; Mankin et al., 1999; Mitchell et al.,

1993; Perrone and Madramootoo, 1997; Perrone and Madramootoo, 1999).

Overall, these studies found AGNPS to be adequate in predicting runoff and

pollutants, but the outputs of the model often depended on the ability to capture

the spatial variation of important watershed characteristics. AnnAGNPS is the

continuous version of the single event AGNPS that includes many enhancements

but retains some important features from AGNPS. Since few studies have been

performed to validate the continuous version of the model, there is still a great

need to validate AnnAGNPS on a variety of watersheds throughout the country

(Yuan et al., 2001; Yuan et al., 2002).

This study would possibly have had better AnnAGNPS predictions had

spatially variable historical climate data been applied, but historical data were not

available for 1987. Furthermore, since the goal of this study was to evaluate the

effects of LU/LC changes over time, it was thought that both simulations should

have the same climatic inputs so that the only variable input was the LU/LC layer.

The generally higher rates for water runoff and pollutant loadings for the

2002 simulation can be explained by the apparent decrease in forested acreage

from 1987 to 2002 (Tables 4.1 and 4.2). In general, forested areas have lower

water runoff rates than all other types of land cover. These results were

somewhat surprising, as reduced runoff rates were expected for 2002 because

much cropped acreage had been taken out of production as a result of federal

incentive programs encouraging environmental conservation. There was a

decrease in cropped areas within the watershed from 1987 to 2002, which also

coincided with a considerable increase in pastureland in the watershed (Tables

4.1 and 4.2). Cropped land was apparently converted to pastureland more so than silviculture as a result of federal incentive programs such as the NRCS Conservation Reserve Program (CRP). Thus, the probable benefits from reduced cropped land in 2002, as compared to 1987, were offset by the simultaneous decrease in forested acreage during this same time period.

For the AnnAGNPS simulation with 1987 land use, the following number of sub-watershed cells were present: 3,865 for woods, 723 for fallow, 713 for pasture, 244 for corn, 178 for soybean, 122 for urban, and 98 for cotton. Urban land cover had a higher water loading than did any other aforementioned land cover, while woods had the least (Fig. 4.6). For peak discharge, soybean had the highest rate, followed by cotton, and woods had the lowest rate (Fig. 4.7). For sediment, phosphorus, organic carbon, and nitrogen loading, the cotton land cover class had higher runoff rates than any other land cover class (Figs. 4.8, 4.9, 4.10, and 4.11). Even with a reduced tillage management scheme, the cotton land cover class still had high runoff rates. Although this is not surprising, a rainfall event might have occurred in conjunction with a cotton tillage event, whereas there might not have been any rainfall in conjunction with soybean or corn tillage events, depending on the management schedule for each crop. Urban and woods land cover classes had the lowest sediment and organic carbon loading, while woods had the lowest phosphorus and nitrogen loading (Figs. 4.8, 4.9, 4.10, and 4.11). Again, it was expected that the woods land cover class would have lower nutrient rates than the other land cover classes.

Urban areas are being recognized for their increasing contribution to nonpoint source runoff. However, AnnAGNPS is a runoff model that is geared towards agricultural watersheds. As such, the model is established so that the user can define a management schedule for cropped lands, citing the various operations performed for each crop throughout the year. Unless non-crop land use classes are defined as a crop, a management schedule cannot be applied to those land use classes. In this study, urban areas were defined as a non-crop land use class. Thus, if there was much activity – tillage, pesticide, or fertilizer applications – on urban lands in the UPRB, the nonpoint source contributions from urban areas might be underestimated by AnnAGNPS.

For the AnnAGNPS simulation with 2002 land use, sub-watershed cell numbers by class were as follows: 3,904 for pasture, 1,971 for woods, 30 for other small grains and hay, 20 for corn, 8 for urban, and 7 for cotton. With the 2002 land cover input, the urban land cover had the highest water loading, peak discharge, and the highest phosphorus loading (Figs. 4.12, 4.13, and 4.15). The urban and other small grains and hay land cover classes had higher nitrogen loading than the other land cover classes, while woods had the lowest nitrogen loading and the lowest water loading (Figs. 4.12 and 4.17). Urban and woods had the lowest organic carbon loading, and cotton had the lowest phosphorus loading (Figs. 4.15 and 4.16). The woods land cover class had lower sediment loading than all other land cover classes except the urban class (Fig. 4.14). Additionally, cotton had the lowest peak discharge, although it was only

significantly less than the urban and other small grains and hay land cover

classes (Fig. 4.13).

For the 2002 results, there was 12.83% less land in agricultural production

than in 1987, and there was more urban land cover than soybean and cotton

land cover. In AnnAGNPS, urban land cover is assigned higher runoff curve

numbers by the user, so it is expected that urban areas would have higher runoff

rates for water, nitrogen, and phosphorous due to large areas of impervious

surfaces. However, the urban land cover class did have lower rates for organic

carbon and sediment loadings, probably because there are low amounts of

vegetation and soil associated with urban areas.

It is also helpful to see the percent change over time from 1987 to 2002 for

water, sediment, and nutrient loadings (Tables 4.6 and 4.7). Perhaps the biggest

change was an overall reduction in loadings from cotton from 1987 to 2002.

Also, there was so little soybean production in the watershed in 2002 that this

LU/LC class was not assigned to a single sub-watershed, nor was the fallow

LU/LC class. The other small grains and hay ('othsmgrhay') LU/LC class was not

used in the 1987 LU/LC layer.

In summary, the urban land cover class was a more dominant contributor

to water runoff and pollutant loadings from 1987 to 2002, while traditional row

crop agriculture had less of an impact on runoff and pollutant loadings. Also, the

2002 LU/LC resulted in higher sediment and organic carbon loadings than did the

1987 LU/LC. For future studies, similar datasets that have been classified in the

same manner would likely improve results. For example, the percentage of

urban land cover in the delineated watershed actually decreased from 1987 to 2002, according to the classified images that were employed in this study. However, it is unlikely that the amount of urban land cover actually decreased during this time period. The USDA's cropland data layer, which was used for the 2002 dataset, is very accurate and specific for cropped land, but lacks detail for other land cover layers. As can be seen in Figure 4.3, the cropland data layer did not identify road networks. Also, the land use dataset for 1987 was acquired in August, so there might have been some confusion between the corn and urban land cover classes. Unfortunately, the cropland data layer was not available until 1999, which necessitated the purchase and classification of a Landsat 5 TM image for the 1987 dataset, using historically-available ground truth information. Furthermore, when doing supervised classifications, it is obviously easier to collect ground truth information, historical or current, over smaller areas. Recommended improvements to the AnnAGNPS model include simplifying or automating the extraction of data from the STATSGO soils database, including pesticide loading in the average annual and event output files, and making it easier to assign management activities to urban and forested areas. Given the available data and the size of the watershed modeled, the results presented in this study capture the main effects of land cover changes in the UPRB from 1987 to 2002.

SOURCES OF MATERIALS

[1] Mississippi Automated Resource Information System's website:
http://www.maris.state.ms.us

[2] United States Department of Agriculture – National Agricultural Statistics
Service (USDA-NASS)

[3] USGS Earth Resources and Observation (EROS) Data Center

[4] USDA Natural Resources Conservation Service (NRCS)

LITERATURE CITED

Aelion, C.M. and D.C. Cresci. 1999. Impact of land use on microbial transformations of atrazine. J. Environ. Qual. 28:683-691.

Anonymous. 1987. 1987 weed control guidelines for Mississippi. Publication 1532, Mississippi State University Extension Service. 225 pp.

Anonymous. 2005. Weed control guidelines for Mississippi. Publication 1532, Mississippi State University Extension Service. 197 pp.

Arvidson, T., J. Gasch, and S.N. Goward. 2001. Landsat 7's long-term acquisition plan – an innovative approach to building a global imagery archive. Remote Sens. Environ. 78:13-26.

Atkinson, S.F., W.T. Waller, and T.J. Crooks. 2001. Assessing atrazine pollution potential to a drinking water reservoir using remote sensing and geographic information system modeling. Aquat. Ecosys. Health Manage. Soc. 4:327-338.

Baumer, O., P. Kenyon, and J. Bettis. 1994. Prediction of soil properties. Map Unit Use Files (MUUF). User's manual version 2.14. Nat. Resour. Conserv. Serv., Wetland Sci. Inst., Laurel, MD.

Ballweber, J.A., D. Parisi, and J.R. Steil. 2000. Riparian management's role within basin-scale management partnership. Pages 463-468 In Proc. AWRA's Summer Specialty Conference on Riparian Ecology and Management in Multi-Land Use Watersheds. Middleburg, VA:AWRA.

Bingner, R.L. 2004. Personal communication. Oxford, MS, 11 August 2004.

Bingner, R.L. and F.D. Theurer. 2001a. AGNPS 98: A suite of water quality models for watershed use. *In* Proceedings of the Sedimentation: Monitoring, Modeling, and Managing, 7th Federal Interagency Sedimentation Conference, Reno, NV, 25-29 March 2001. p. VII-1–VII-8. 2001.

Bingner, R.L. and F.D. Theurer. 2001b. AnnAGNPS: Estimating sediment yield by particle size for sheet & rill erosion. *In* Proceedings of the Sedimentation: Monitoring, Modeling, and Managing, 7th Federal Interagency Sedimentation Conference, Reno, NV, 25-29 March 2001. p. I-1–I-7. 2001.

Brando, V.E. and A.G. Dekker. 2003. Satellite hyperspectral remote sensing for estimating estuarine and coastal water quality. IEEE Trans. Geosci. Remote Sens. 1:1378-1387.

Bukata, R.P., D.V. Pozdnyakov, J.H. Jerome, and F.J. Tanis. 2001. Validation of a radiometric color model applicable to optically complex water bodies. Remote Sens. Environ. 77:165-172.

Choi, K.S. and E. Blood. Modeling developed coastal watersheds with the agricultural non-point source model. J. Am. Water Resour. Assoc. 35:233-244.

De Colstoun, E.C.B., M.H. Story, C. Thompson, K. Commisso, T.G. Smith, and J.R.Irons. 2003. National park vegetation mapping using multitemporal Landsat 7 data and a decision tree classifier. Remote Sens. Environ. 85: 316-327.

Dekker, A.G., T.J. Malthus, and E. Seyhan. 1991. Quantitative modeling of inland water quality for high-resolution MSS systems. IEEE Trans. Geosci. Remote Sens. 29:89-95.

Drapper, D., R. Tomlinson, and P. Williams. 2000. Pollutant concentrations in road runoff: Southeast Queensland case study. J. Environ. Eng. 126:313-320.

EPA. 2001. Better assessment science integrating point and nonpoint sources (BASINS), Version 3.0, User's Manual. EPA-823-B-01-001. Office of Water, EPA:Washington, DC.

Foody, G. 2001. Problems in evaluating thematic maps derived from imagery: Accuracy of image classifications. Geomatics Info. Mag. Int. 15:41-43.

Forget, P., P. Broche, and J. Naudin. 2001. Reflectance sensitivity to solid suspended sediment stratification in coastal water and inversion: A case study. Remote Sens. Environ. 77:92-103.

Frazier, P.S. and K.J. Page. 2000. Water body detection and delineation with Landsat TM data. Photogramm. Eng. Remote Sensing 66:1461-1467.

Gillion, R.J., J.E. Barbash, D.W. Kolpin, and S.J. Larson. 1999. Testing water quality for pesticide pollution. Environ. Sci. Technol. 33:164A-169A.

Griffith, J.A. 2002. Geographic techniques and recent applications of remote sensing to landscape-water quality studies. Water, Air, and Soil Pollut. 138:181-197.

Griffith, J.A., E.A. Martinko, J.L. Whistler, and K.P. Price. 2002. Interrelationships among landscapes, NDVI, and stream water quality in the U.S. Central Plains. Ecol. Appl. 12:1702-1718.

Ha, S.R., S.Y. Park, and D.H. Park. 2003. Estimation of urban runoff and water quality using remote sensing and artificial intelligence. Water Sci. Technol. 47:319-325.

Harman-Fetcho, J.A., L.L. McConnell, and J.E. Baker. 1999. Agricultural pesticides in the Patuxent River, a tributary of the Chesapeake Bay. J. Environ. Qual. 28:928-938.

Hellkamp, A.S., J.M. Bay, C.L. Campbell, K.N. Easterling, D.A. Fiscus, G.R. Hess, B.F. McQuaid, M.J. Munster, G.L. Olson, S.L. Peck, S.R. Shafer, K. Sidik, and M.B. Tooley. 2000. Assessment of the condition of agricultural lands in six Mid-Atlantic states. J. Environ. Qual. 29:795-804.

Hapeman, C.J., C.P. Dionigi, P.V. Zimba, and L.L. McConnell. 2002. Agrochemical and nutrient impacts on estuaries and other aquatic systems. J. Agric. Food Chem. 50:4382-4384.

Im, S., K.M. Brannan, and S. Mostaghimi. 2003. Simulating hydrologic and water quality impacts in an urbanizing watershed. J. Am. Water Resour. Assoc. 39:1465-1479.

Jain, S.K. and M.K. Goel. 2002. Assessing the vulnerability to soil erosion of the Ukai Dam catchments using remote sensing and GIS. Hydrol. Sci. J. 47:31-40.

Johnson, A.K.L. and S.P. Ebert. 2000. Quantifying inputs of pesticides to the Great Barrier Reef Marine Park – A case study in the Herbert River Catchment of north-east Queensland. Mar. Pollut. Bull. 41:302-309.

Joslin, J.D. and S.H. Schoenholtz. 1997. Measuring the environmental effects of converting cropland to short-rotation woody crops: A research approach. Biomass and Bioenergy 13:301-311.

Koponen, S., J. Pulliainen, K. Kallio, and M. Hallikainen. 2002. Lake water quality classification with airborne hyperspectral spectrometer and simulated MERIS data. Remote Sens. Environ. 79:51-59.

Lattin, P.D., P.J. Wigington, Jr., T.J. Moser, B.E. Peniston, D.R. Lindeman, and D.R. Oetter. 2004. Influence of remote sensing imagery source on quantification of riparian land cover/land use. J. Am. Water Resour. Assoc. 40:215-227.

Line, D.E. 2002. Changes in land use/management and water quality in the Long Creek Watershed. J. Am. Water Resour. Assoc. 38:1691-1701.

Mankin, K.R., J.K. Koelliker, and P.K. Kalita. 1999. Watershed and lake water quality assessment: An integrated modeling approach. J. Am. Water Resour. Assoc. 35:1069-1080.

Mattina, M.J.I., W. Iannucci-Berger, L. Dykas, and J. Pardus. 1999. Impact of long-term weathering, mobility, and land use on chlordane residues in soil. Environ. Sci. Technol. 33:2425-2431.

MDEQ. 2004a. Mississippi 2004 section 303(d) list of impaired water bodies. MDEQ, Surface Water Division of the Office of Pollution Control:Jackson, MS. pp. 96-126.

MDEQ. 2004b. Total maximum daily load Fannegusha Creek Watershed including Red Cane Creek and Hurricane Creek for biological impairment due to sediment. MDEQ, Office of Pollution Control TMDL/WLA Branch:Jackson, MS. 27 pp.

MDEQ. 2005. Phase 1 total maximum daily load for biological impairment due to organic enrichment/low DO and nutrients Oakahay Creek Pascagoula River Basin Smith County, Mississippi. MDEQ, Office of Pollution Control TMDL/WLA Branch:Jackson, MS. 39 pp.

Miller, M.E. 1999. Use of historic aerial photography to study vegetation change in the Negrito Creek Watershed, southwestern New Mexico. Southwest. Nat. 44:121-137.

Miller, S.N., W.G. Kepner, M.H. Mehaffey, M. Hernandez, R.C. Miller, D.C. Goodrich, K.K. Devonald, D.T. Heggem, and W.P. Miller. Integrating landscape assessment and hydrologic modeling for land cover change analysis. J. Am. Water Resour. Assoc. 38:915-929.

Mitchell, J.K., B.A. Engel, R. Srinivasan, and S.S.Y. Wang. 1993. Validation of AGNPS for small watersheds using an integrated AGNPS/GIS system. Water Resour. Bull. 29:833-842.

Morain, S. 2002. Industry News. Photogramm. Eng. Remote Sensing 68:131-132.

Mostaghimi, S., S.W. Park, R.A. Cooke, and S.Y. Wang. 1997. Assessment of management alternatives on a small agricultural watershed. Water Res. 31:1867-1878.

Neville, P., R.I. Coward, R.P. Watson, M. Inglis, and S. Morain. 2000. The application of TM imagery and GIS data in the assessment of arid lands water and land resources in West Texas. Photogramm. Eng. Remote Sensing 66:1373-1379.

Oliver, D.P., R.S. Kookana, R.B. Salama, and R. Correll. 2003. Land use effects on sorption of pesticides and their metabolites in sandy soils. II. Atrazine and two metabolites, deethylatrazine and deisopropylatrazine, and prometryne. Aust. J. Soil Res. 41:861-874.

Oñate, J.J., E. Andersen, B. Peco, and J. Primdahl. 2000. Agri-environmental schemes and the European agricultural landscapes: The role of indicators as valuing tools for evaluation. Landsc. Ecol. 15:271-280.

Perrone, J. and C.A. Madramootoo. 1997. Use of AGNPS for watershed modeling in Quebec. Trans. ASAE 40:1349-1354.

Perrone, J. and C.A. Madramootoo. 1999. Sediment yield prediction using AGNPS. J. Soil Water Conserv. 54:415-418.

Pijanowski, B.C., B. Shellito, S. Pithadia, and K. Alexandridis. 2002. Forecasting and assessing the impact of urban sprawl in coastal watersheds along eastern Lake Michigan. Lakes Reservoirs: Res. Manage. 7:271-285.

Qian, S.S. and C.W. Anderson. 1999. Exploring factors controlling the variability of pesticide concentrations in the Willamette River Basin using tree-based models. Environ. Sci. Technol. 33:3332-3340.

SAS. 2005. SAS Institute, Inc., SAS Campus Dr., Cary, NC, 27513 USA.

Santo, E.L. and L.E. Sánchez. 2002. GIS applied to determine environmental impact indicators made by sand mining in a floodplain in southeastern Brazil. Environ. Geol. 41:628-637.

Schott, J.R., J.A. Barsi, B.L. Nordgren, N.G. Raqueño, and D. de Alwis. 2001. Calibration of Landsat thermal data and application to water resource studies. Remote Sens. Environ. 78:108-117.

Song, C., C.E. Woodcock, K.C. Seto, M.P. Lenney, and S.A. Macomber. 2001. Classification and change detection using Landsat TM data: When and how to correct atmospheric effects? Remote Sens. Environ. 75:230-244.

Tong, S.T.Y. and W. Chen. 2002. Modeling the relationship between land use and surface water quality. J. Environ. Manage. 66:377-393.

Töyrä, J., A. Pietroniro, and L.W. Martz. 2001. Multisensor hydrologic assessment of a freshwater wetland. Remote Sens. Environ. 75:162-173.

Treitz, P.M., P.J. Howarth, R.C. Stuffling, and P. Smith. 1992. Application of detailed ground information to vegetation mapping with high spatial resolution digital imagery. Remote Sens. Environ. 42:65-82.

Turner, R.E. and N.N. Rabalais. 2003. Linking landscape and water quality in the Mississippi River Basin for 200 years. BioScience 53:563-572.

United States Department of Commerce, Environmental Science Services Administration, Environmental Data Service. 1968. Climatic atlas of the United States. United States Government Printing Office: Washington, D.C.

United States Geological Survey. 2005. http://waterdata.usgs.gov/ms/nwis/.

Viña, A., A.J. Peters, and L. Ji. 2003. Use of multispectral Ikonos imagery for discriminating between conventional and conservation agricultural tillage practices. Photogramm. Eng. Remote Sensing 69:537-544.

Walker, W.J., R.P. McNutt, and C.K. Maslanka. 1999. The potential contribution of urban runoff to surface sediments of the Passaic River: Sources and chemical characteristics. Chemosphere 38:363-377.

Watson, N. and D. Wilcock. 2001. Preclassification as an aid to the improvement of thematic and spatial accuracy in land cover maps derived from satellite imagery. Remote Sens. Environ. 75:267-278.

Wayland, K.G., D.W. Hyndman, D. Boutt, B.C. Pijanowski, and D.T. Long. 2002. Modelling the impact of historical land uses on surface-water quality using groundwater flow and solute-transport models. Lakes Reservoirs: Res. Manage. 7:189-199.

Wayland, K.G., D.T. Long, D.W. Hyndman, B.C. Pijanowski, S.M. Woodhams, and S.K. Haack. 2003. Identifying relationships between baseflow geochemistry and land use with synoptic sampling and R-mode factor analysis. J. Environ. Qual. 32:180-190.

Weng, Q. 2002. Land use change analysis in the Zhujiang Delta of China using satellite remote sensing, GIS and stochastic modeling. J. Environ. Manage. 64:273-284.

Wilcock, R.J. 1993. Application of land-use data and screening tests for evaluating pesticide runoff toxicity in surface waters. Environ. Manage. 17:365-371.

Yang, L., G. Xian, J.M. Klaver, and B. Deal. 2003. Urban land-cover change detection through sub-pixel imperviousness mapping using remotely sensed data. Photogramm. Eng. Remote Sensing 69:1003-1010.

Yuan, Y., R.L. Bingner, and R.A. Rebich. 2001. Evaluation of AnnAGNPS on Mississippi Delta MSEA watersheds. Trans. ASAE 44:1183-1190.

Yuan, Y., S.M. Dabney, and R.L. Bingner. 2002. Cost effectiveness of agricultural BMPs for sediment reduction in the Mississippi Delta. J. Soil Water Conserv. 57:259-267.

Zhang, Y., J.T. Pulliainen, S.S. Koponen, and M.T. Hallikainen. 2003. Water quality retrievals from combined Landsat TM data and ERS-2 SAR data in the Gulf of Finland. IEEE Trans. Geosci. Remote Sens. 41:622-629.

Table 4.1. 1987 land use percentages (%) for the delineated Burnside watershed.

1987 Land Use Class	Percentage of Total Area (%) in Original LULC Layer	Percentage of Total Area (%) as Determined by AnnAGNPS	Percentage of Total Area (%) Used in Final Adjusted LULC Layer
Woods	49.08	71.60	66.22
Pasture	13.46	8.24	10.51
Fallow	12.98	14.7	13.88
Urban	10.17	1.14	1.62
Corn	9.35	2.95	3.21
Soybean	2.56	1.02	2.39
Cotton	2.13	0.19	2.01
Water	0.27	0.17	0.17

Table. 4.2. 2002 land use percentages (%) for the delineated Burnside watershed.

2002 Land Use Class	Percentage of Total Area (%) in Original LULC Layer	Percentage of Total Area (%) as Determined by AnnAGNPS	Percentage of Total Area (%) Used in Final Adjusted LULC Layer
Pasture	61.79	64.15	63.04
Woods	35.39	35.72	35.57
Water	0.86	0.07	0.07
Other Small Grains and Hay	0.68	0.01	0.66
Corn	0.35	0	0.32
Urban	0.29	0.04	0.28
Water and/or Clouds	0.23	0.01	0
Fallow	0.13	0	0
Clouds	0.10	0	0
Cotton	0.07	0.01	0.07
Soybeans	0.07	0	0
Christmas Tree Farms	0.03	0	0
Aquaculture	0.01	0	0

Table 4.3 Comparison of AnnAGNPS average annual output with 1987 and 2002 land use.

Variable	1987 Land Use	2002 Land Use
Area	131,497.34 ha	131,497.34 ha
Runoff	348.479 mm/yr	399.587 mm/yr
Watershed Erosion[a]	3.676	6.308
Sediment Loading[a]	1.1096	1.9116
Clay	0.4374	0.8024
Silt	0.6539	1.0738
Sand	0.0183	0.0353
Nitrogen Loading[b]	0.051	0.041
Attached	0.043	0.038
Dissolved	0.008	0.003
Organic Carbon Loading[b] (attached)	13.607	22.239
Phosphorus Loading[b]	1.855	2.188
Attached	0.229	0.405
Dissolved	1.627	1.783

[a] Units for watershed erosion and sediment loading are Mg/ha/year.

[b] Units for nitrogen, organic carbon, and phosphorus loading are kg/ha/year.

Table 4.4. Precipitation, peak discharge, and runoff with t-groupings for 1987 and 2002.

Simulation Year	1987 and 2002 Precipitation (mm)	Peak Discharge (cms)		Runoff (mm)	
		1987	2002	1987	2002
1	1674.1	4658.7	5253.1	511.7	577.0
2	1477.0	2689.5	3175.3	296.0	349.2
3	1082.8	1593.1	1873.5	175.2	206.3
4	1218.2	1908.4	2248.9	210.1	247.6
5	1665.2	4244.8	4783.2	466.7	525.5
6	1607.8	3637.8	4176.3	400.0	459.0
7	1641.3	4124.5	4655.5	453.6	512.3
8	1801.9	4866.1	5491.1	535.1	604.0
9	1093.0	1269.9	1564.8	139.9	172.2
10	1421.1	2752.9	3180.4	302.9	350.0
Mean	1468.2	3174.6 (a)	3640.2 (a)	349.1 (a)	400.3 (a)
Standard Deviation	244.2	1243.8	1358.1	136.6	149.2

Table 4.5. Sediment, nitrogen, phosphorus, and organic carbon loading with t-groupings for 1987 and 2002.

Simulation Year	Sediment Loading (Mg/ha)		Nitrogen Loading (kg/ha)		Phosphorus Loading (kg/ha)		Organic Carbon Loading (kg/ha)	
	1987	2002	1987	2002	1987	2002	1987	2002
1	1.74	2.98	0.049	0.061	1.89	2.26	19.87	34.81
2	0.97	1.75	0.037	0.041	1.55	1.83	12.69	22.76
3	0.59	1.02	0.031	0.027	1.04	1.30	8.52	14.22
4	0.59	1.06	0.030	0.026	1.30	1.54	8.11	13.97
5	1.41	2.45	0.059	0.050	1.89	2.27	16.43	27.04
6	1.10	1.82	0.058	0.038	1.84	2.11	13.82	20.99
7	1.61	2.74	0.076	0.056	1.75	2.07	18.74	29.52
8	1.66	2.78	0.083	0.053	2.06	2.41	19.16	29.49
9	0.42	0.79	0.031	0.022	1.09	1.31	6.22	10.30
10	1.00	1.74	0.061	0.035	1.56	1.79	12.52	19.28
Mean	1.11 (b)	1.91 (a)	0.051 (a)	0.041 (a)	1.60 (a)	1.89 (a)	13.61 (b)	22.24 (a)
Standard Deviation	0.46	0.76	0.018	0.013	0.33	0.38	4.66	7.57

Table 4.6. Water and sediment loading by LU/LC class for 1987 and 2002 with percent change over time.

Water Loading (mm/year)				Peak Discharge (cms)				Sediment Loading (Mg/ha/year)			
LU/LC Class	1987	2002	Percent Change	LU/LC Class	1987	2002	Percent Change	LU/LC Class	1987	2002	Percent Change
cotton	581.1	620.8	6.8	urban	17.1	39.7	131.9	cotton	4.2	1.3	-69.8
woods	275.7	271.2	-1.6	cotton	23.2	9.2	-60.2	pasture	2.0	2.3	14.3
corn	573.6	564.4	-1.6	corn	14.2	18.4	29.0	urban	0.4	0.3	-14.2
pasture	480.5	476.9	-0.8	pasture	17.9	17.0	-4.7	woods	0.0	0.0	-6.5
urban	704.7	708.3	0.5	woods	10.2	10.6	3.5	corn	3.5	3.4	-3.6
soybean	576.0	n/a	n/a	soybean	27.5	n/a	n/a	soybean	3.4	n/a	n/a
fallow	468.6	n/a	n/a	fallow	17.0	n/a	n/a	fallow	2.9	n/a	n/a
othsmgrhay	n/a	543.5	n/a	othsmgrhay	n/a	20.6	n/a	othsmgrhay	n/a	2.9	n/a

Note: othsmgrhay = other small grains and hay; n/a = not applicable

Table 4.7. Phosphorus, organic carbon, and nitrogen loading by LU/LC class for 1987 and 2002 with percent change over time.

Phosphorus Loading (kg/ha/year)				Organic Carbon Loading (kg/ha/year)				Nitrogen Loading (kg/ha/year)			
LU/LC Class	1987	2002	Percent Change	LU/LC Class	1987	2002	Percent Change	LU/LC Class	1987	2002	Percent Change
cotton	2.9	0.2	-93.4	cotton	90.2	33.6	-62.8	cotton	0.7	0.2	-73.7
urban	2.4	3.4	38.9	urban	3.9	2.5	-35.8	urban	0.3	0.4	32.9
woods	1.3	1.4	13.9	pasture	19.8	26.9	35.7	woods	0.0	0.0	8.8
pasture	2.4	2.1	-12.2	woods	0.1	0.0	-9.8	pasture	0.0	0.0	8.0
corn	1.7	1.9	8.7	corn	40.7	39.4	-3.3	corn	0.2	0.2	1.2
soybean	1.8	n/a	n/a	soybean	62.4	n/a	n/a	soybean	0.3	n/a	n/a
fallow	2.3	n/a	n/a	fallow	34.5	n/a	n/a	fallow	0.1	n/a	n/a
othsmgrhay	n/a	1.7	n/a	othsmgrhay	n/a	51.1	n/a	othsmgrhay	n/a	0.4	n/a

Note: othsmgrhay = other small grains and hay; n/a = not applicable
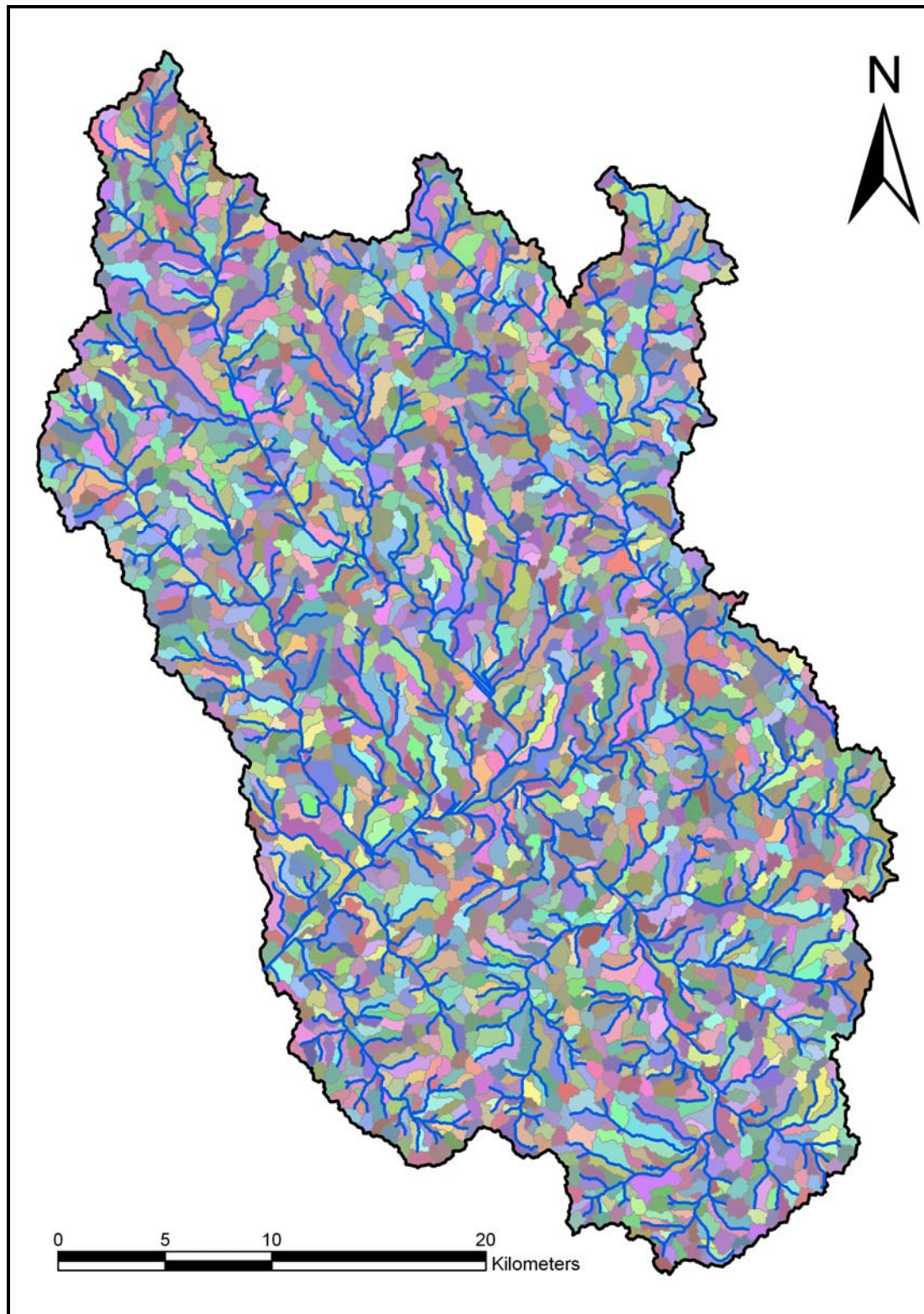
Figure 4.1. Connectivity between generated channel network and sub-watersheds.
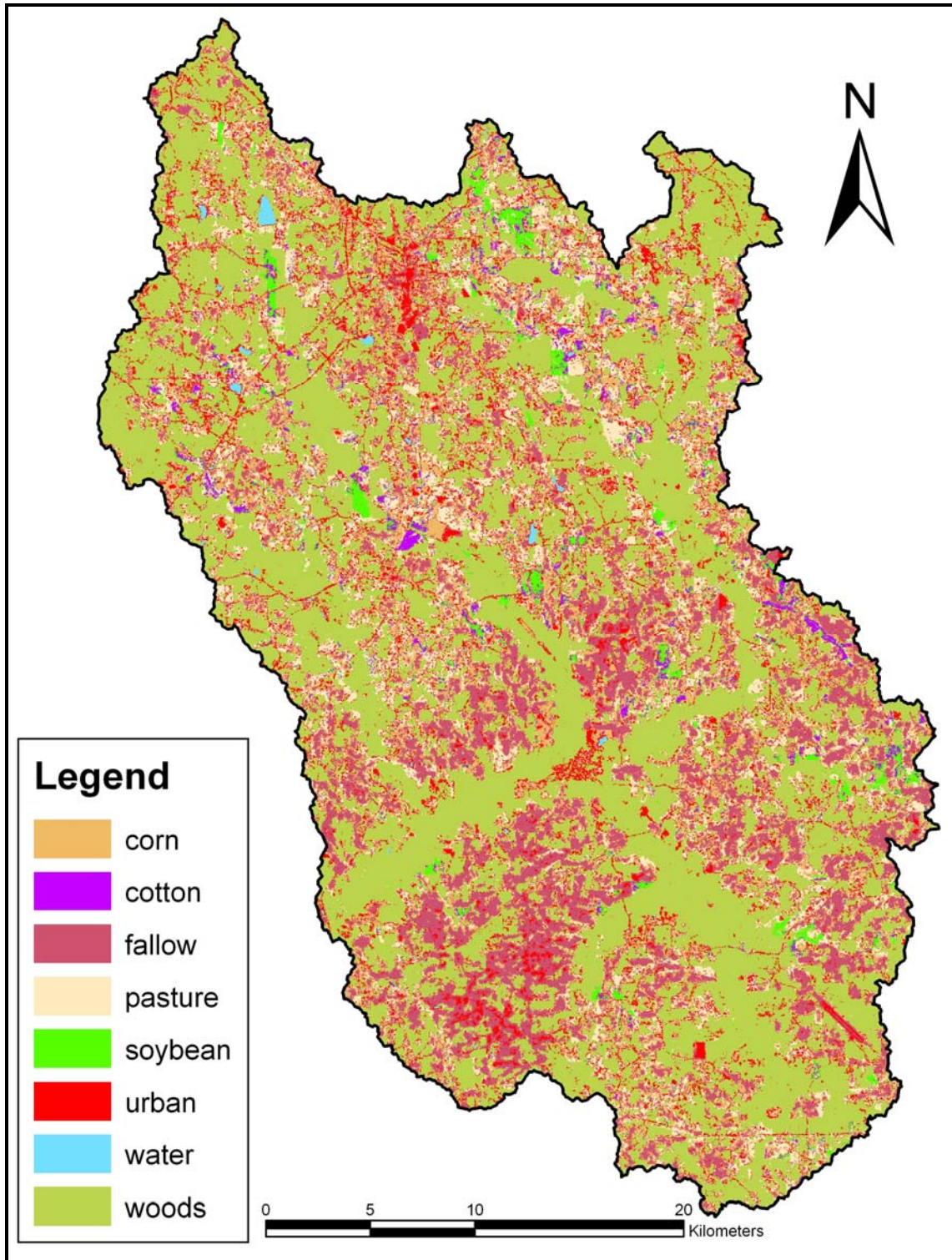
Figure 4.2. Original 1987 LU/LC layer with supervised classification.

Legend

Land Use/Land Cover

CLASS

- Christmas Tree Farms
- Aquaculture
- Clouds
- Corn
- Cotton
- Fallow
- Other Small Grains and Hay
- Pasture
- Soybean
- Urban
- Water and/or Clouds
- Water
- Woods
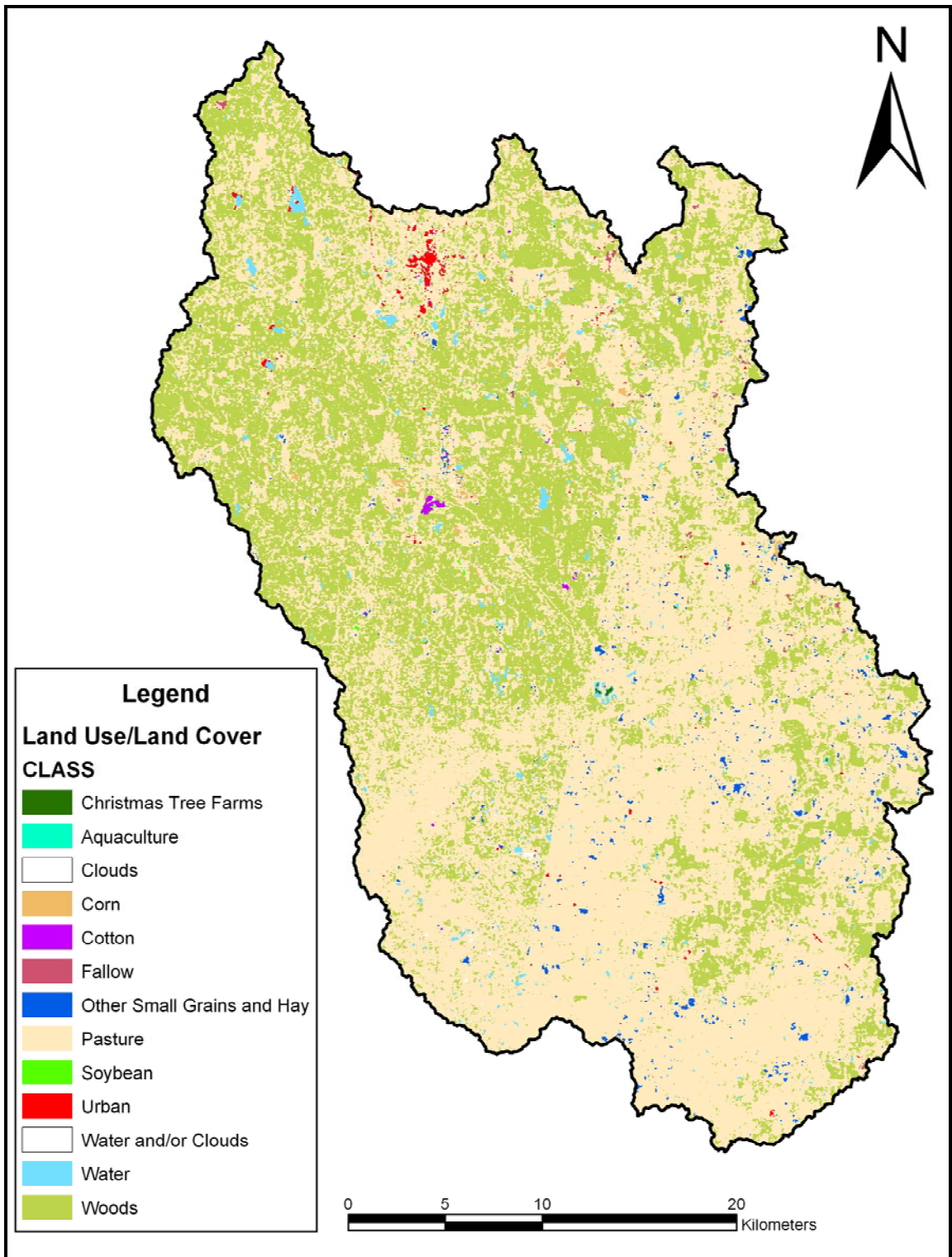
Figure 4.3. Original NASS 2002 cropland data LU/LC layer.
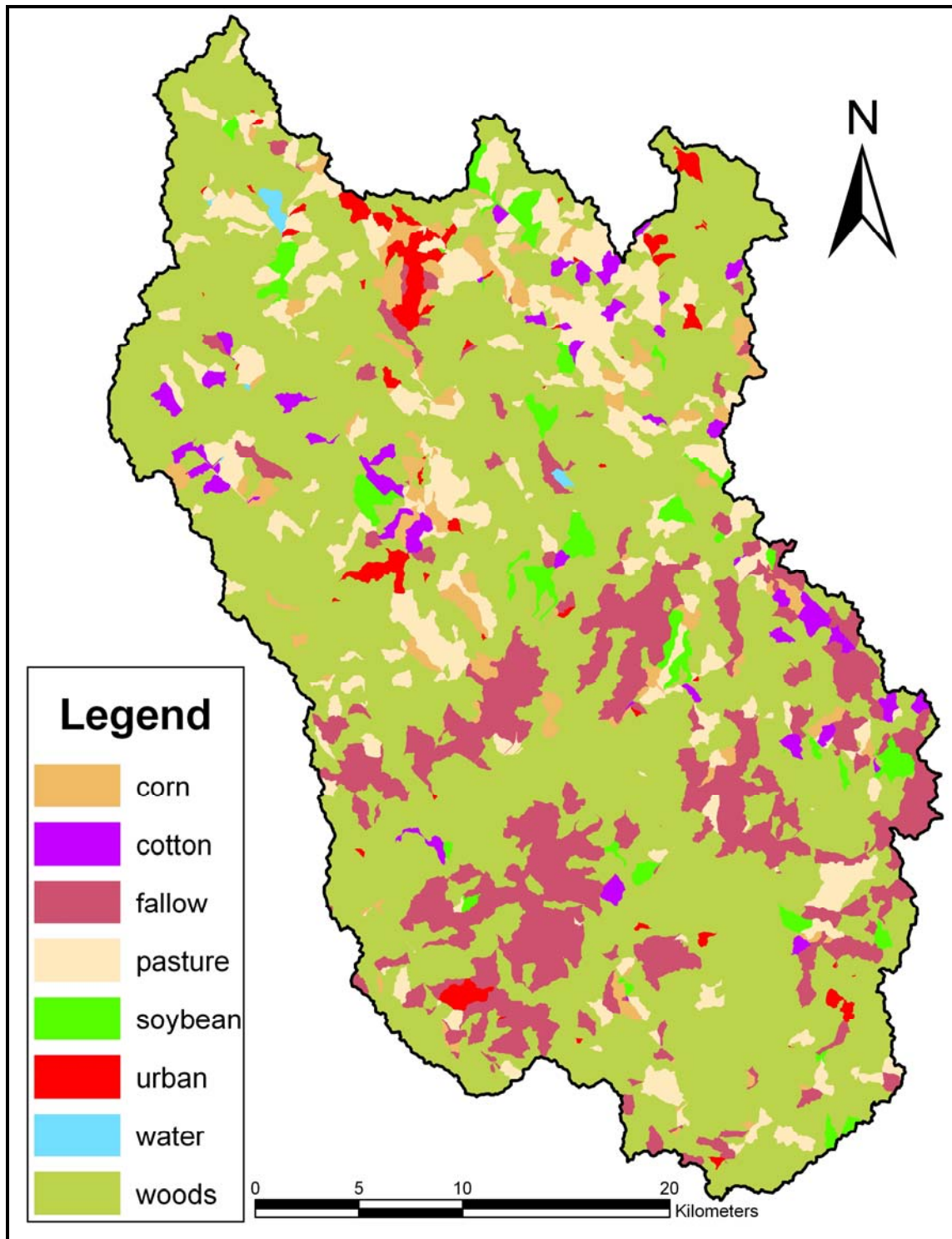
Figure 4.4. 1987 LU/LC classes as assigned to AnnAGNPS-delineated sub-watershed cells.
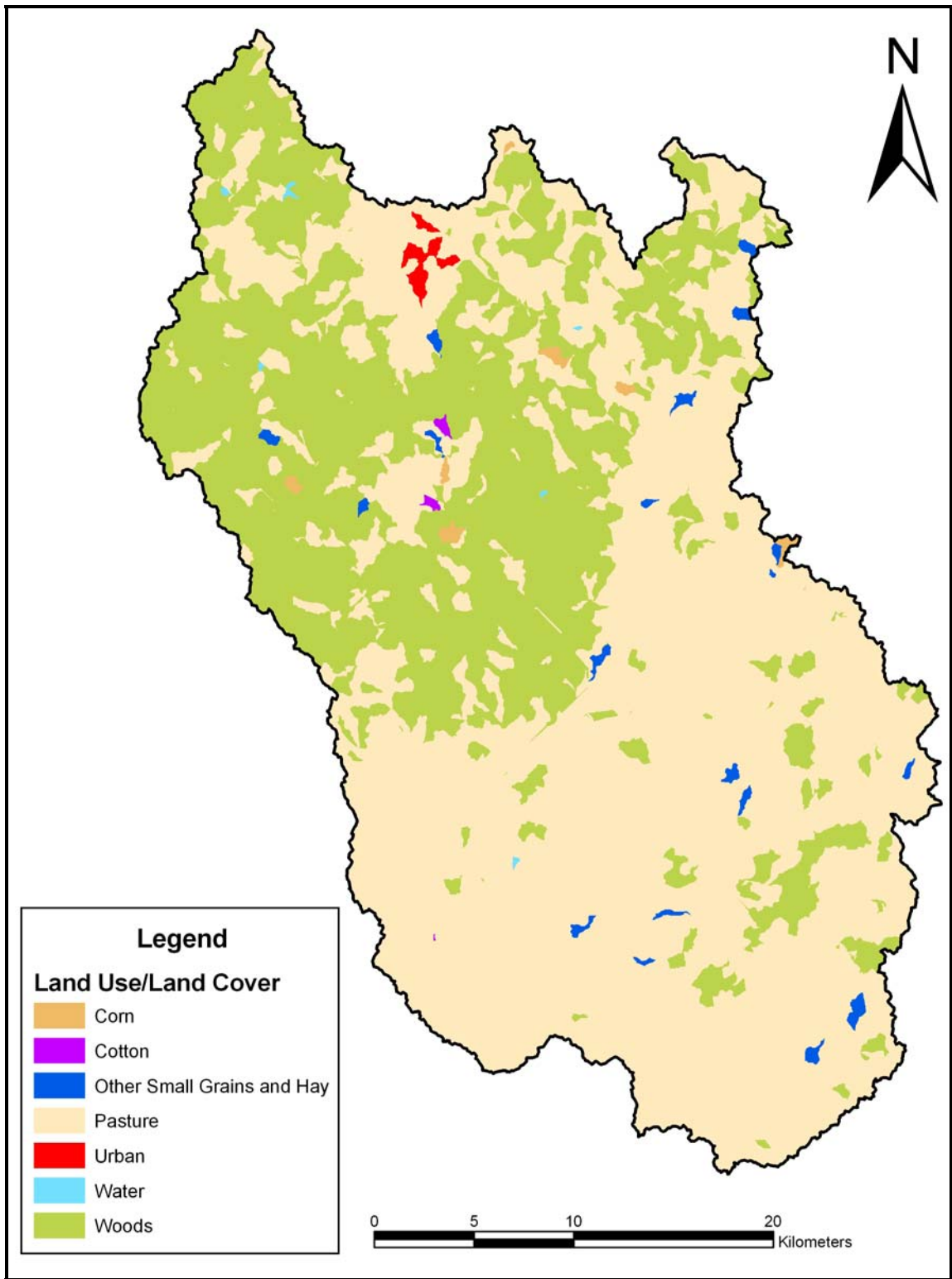
Figure 4.5. 2002 LU/LC classes as assigned to AnnAGNPS-delineated sub-watershed cells.
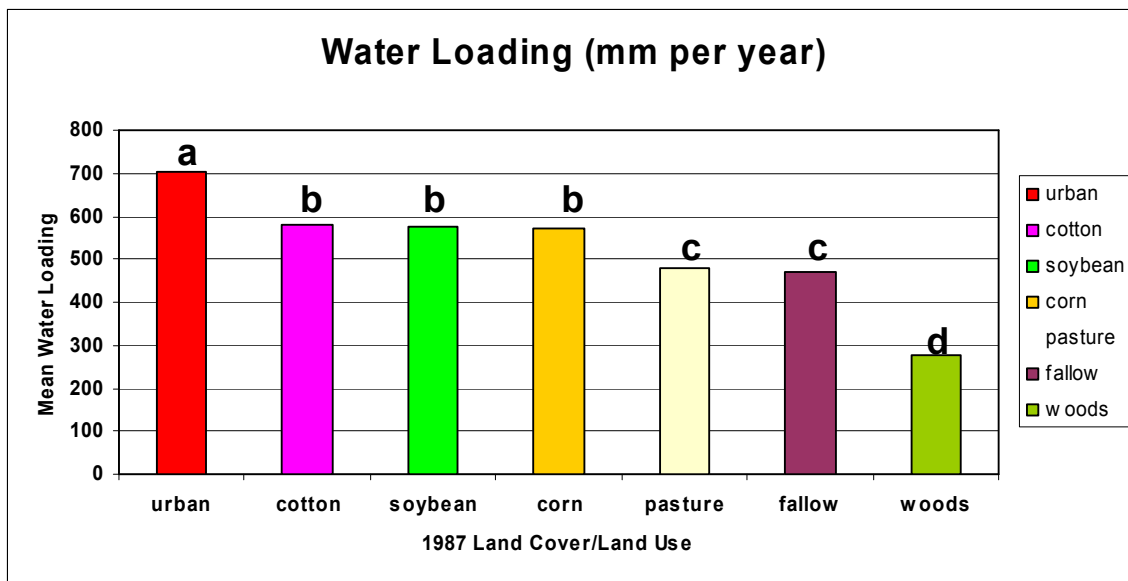
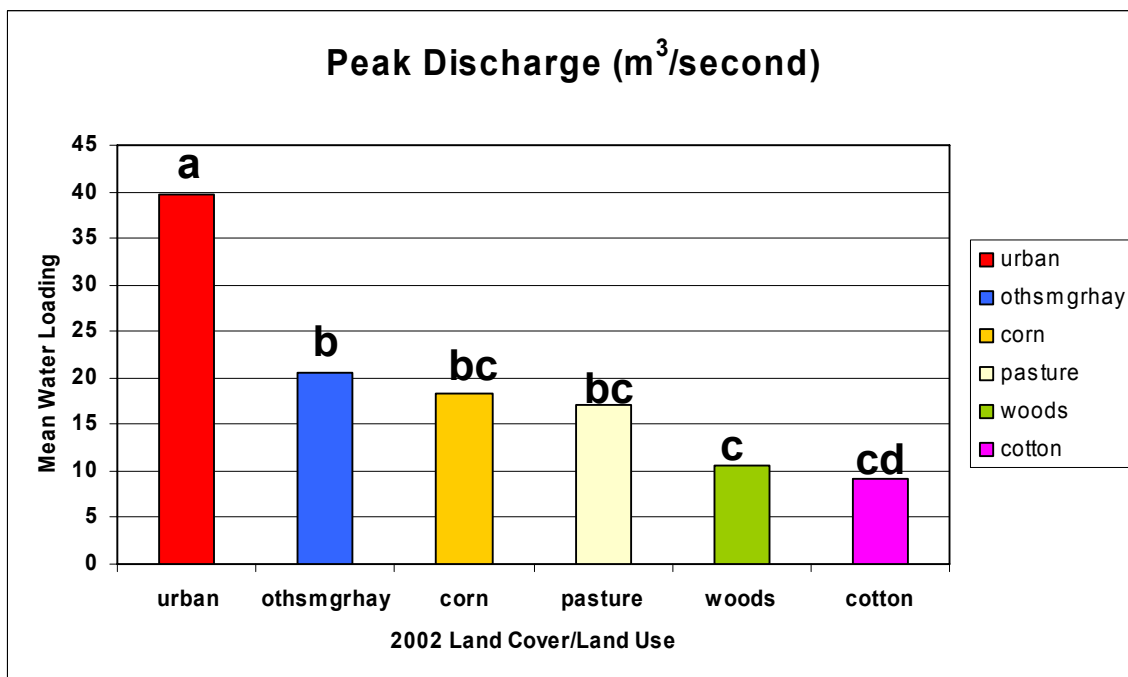Figure 4.6. AnnAGNPS predicted water loading (mm/year) with 1987 LU/LC.
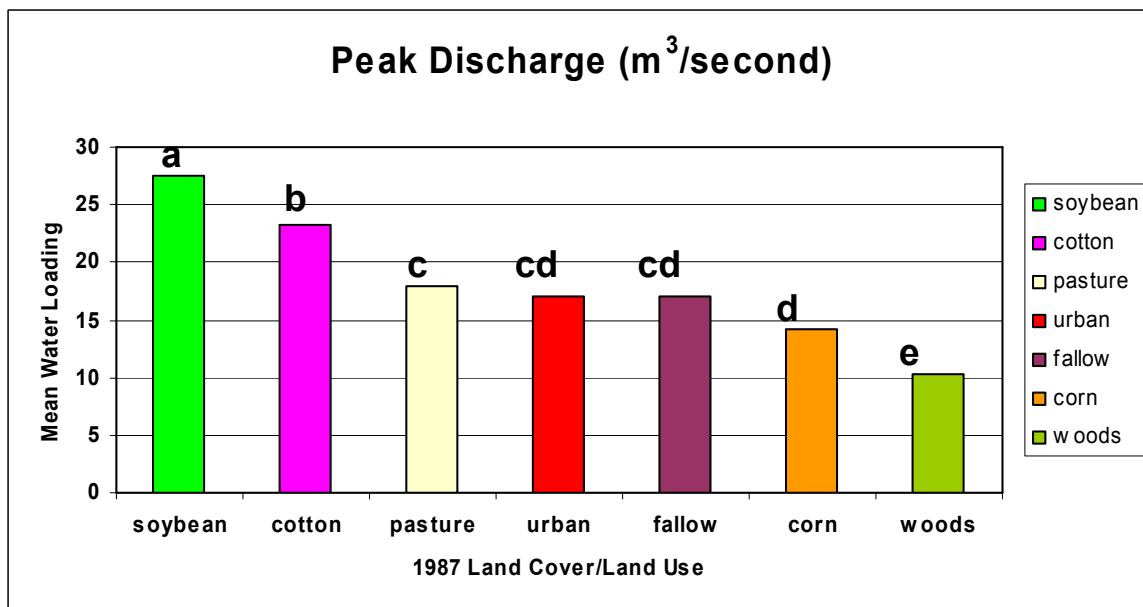
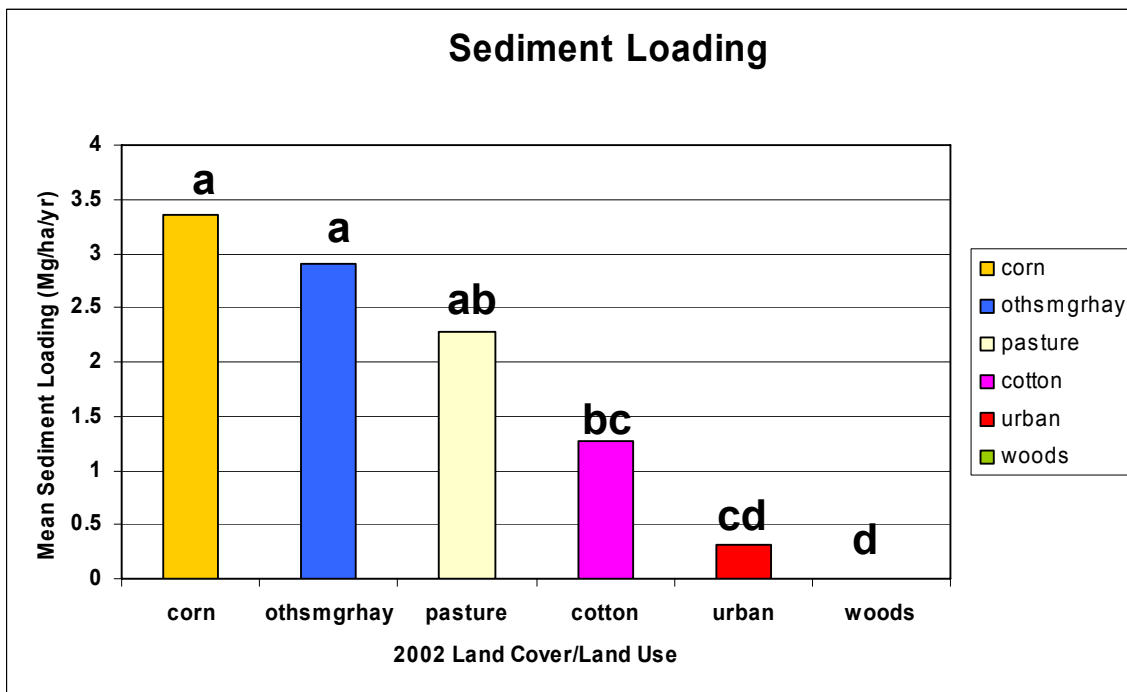Figure 4.7. AnnAGNPS predicted water loading (cms) with 1987 LU/LC.
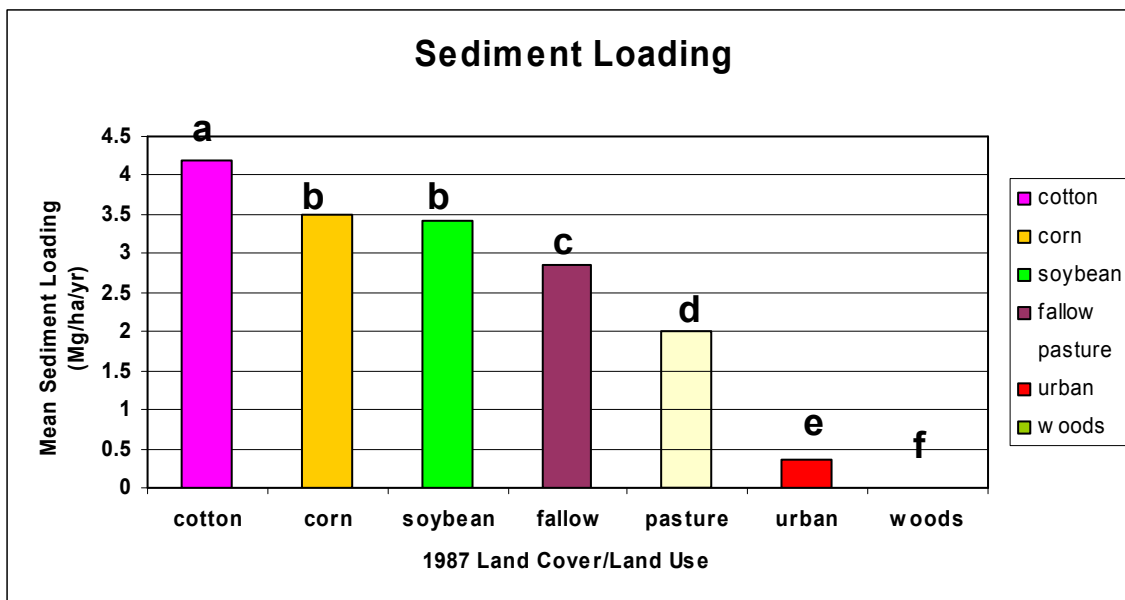
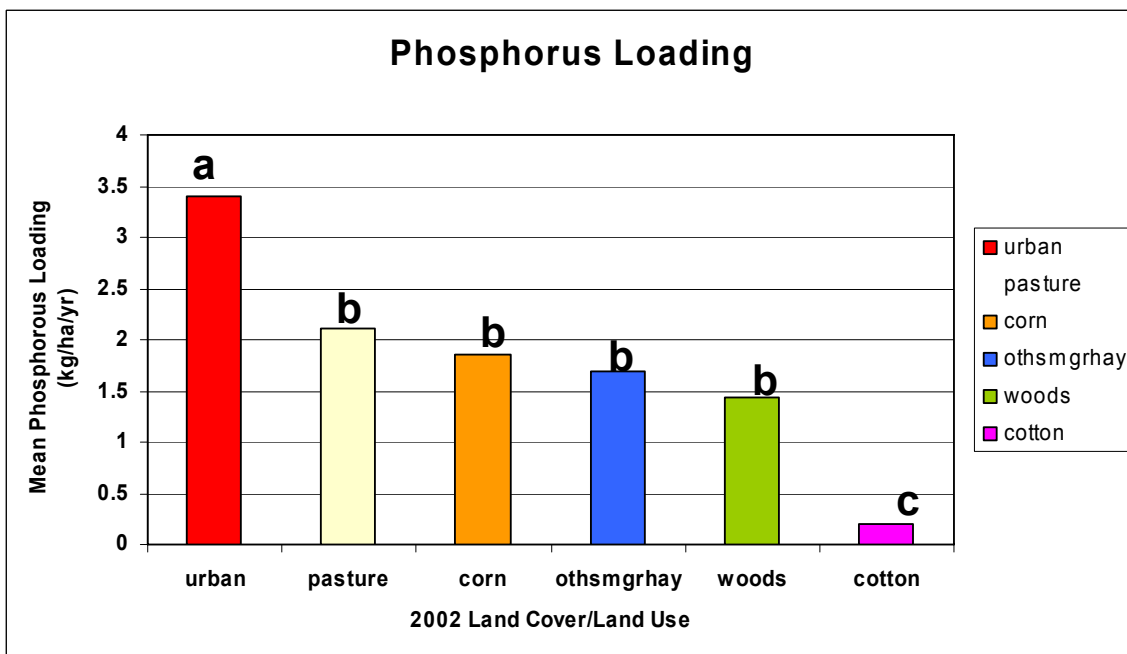Figure 4.8. AnnAGNPS predicted sediment loading with 1987 LU/LC.
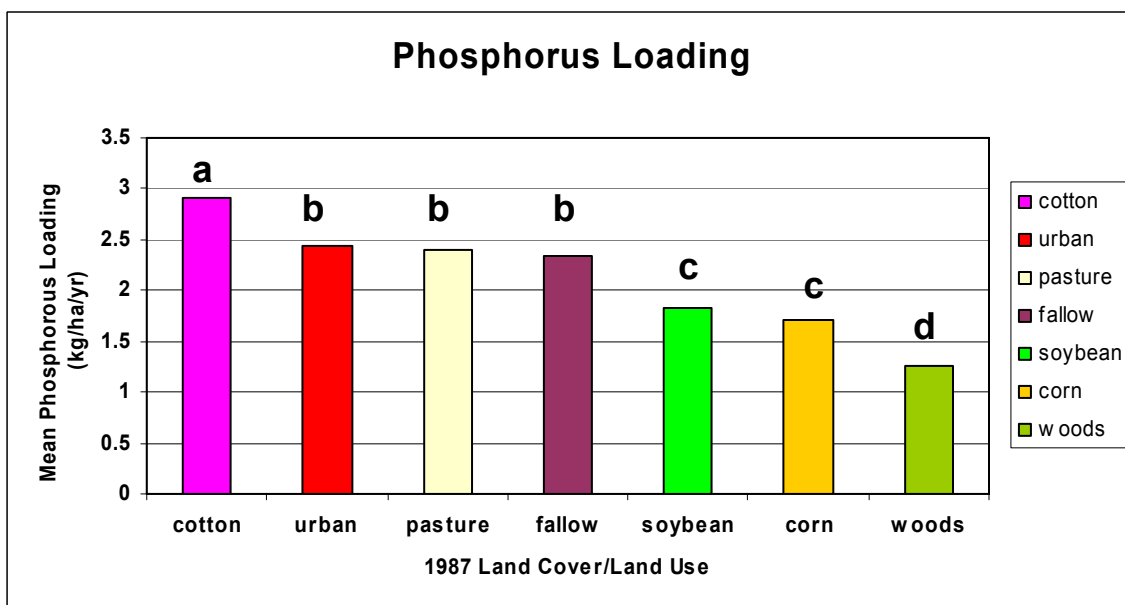
Figure 4.9. AnnAGNPS predicted phosphorus loading with 1987 LU/LC.
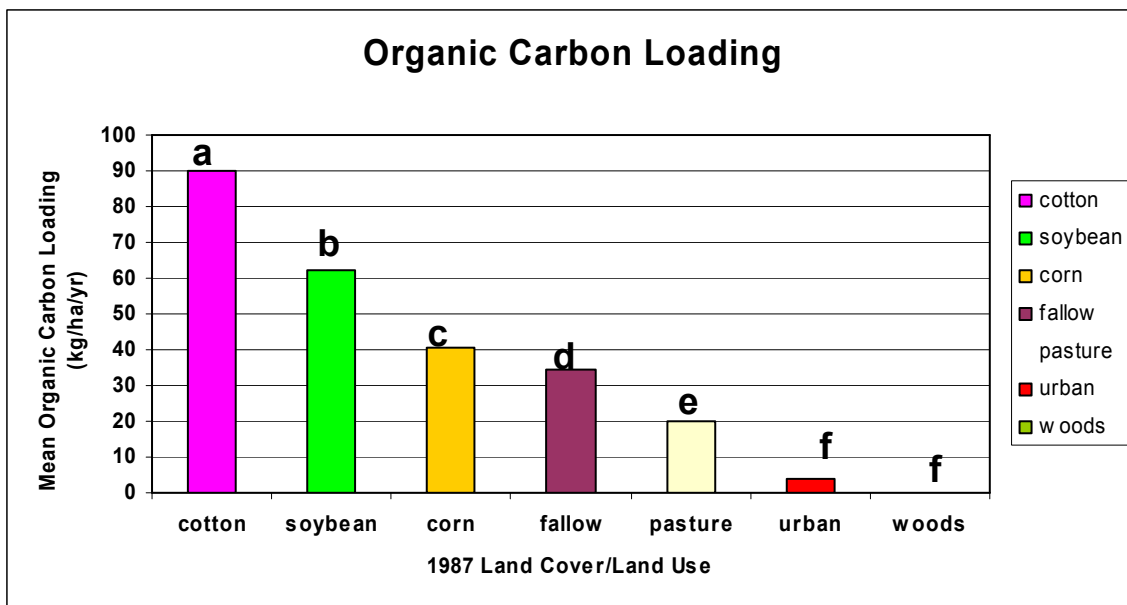
Figure 4.10. AnnAGNPS predicted organic carbon loading with 1987 LU/LC.
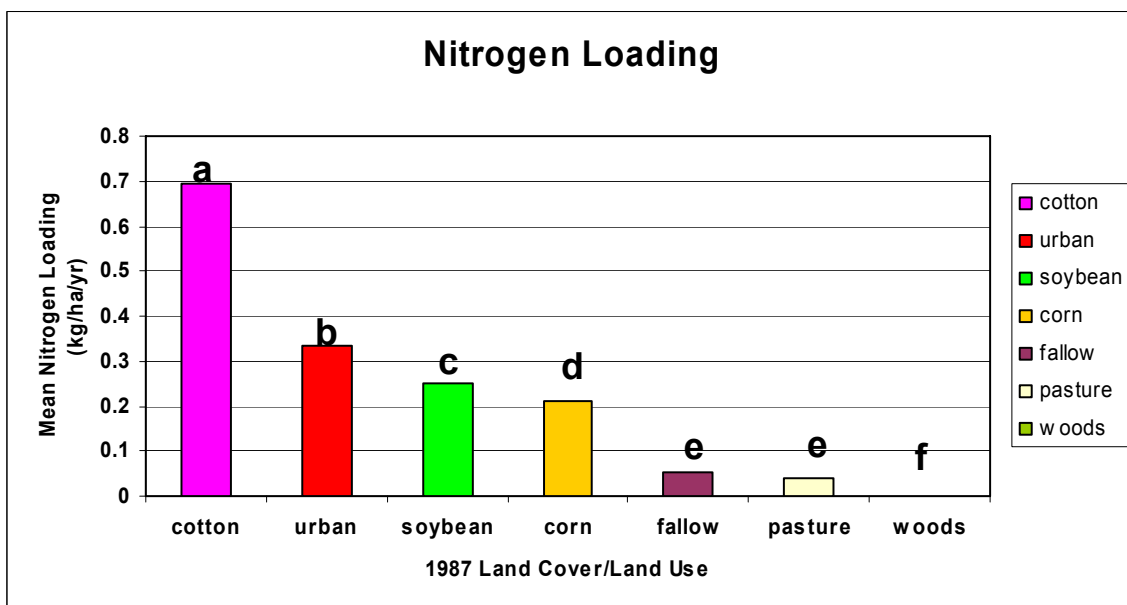
Figure 4.11. AnnAGNPS predicted nitrogen carbon loading with 1987 LU/LC.
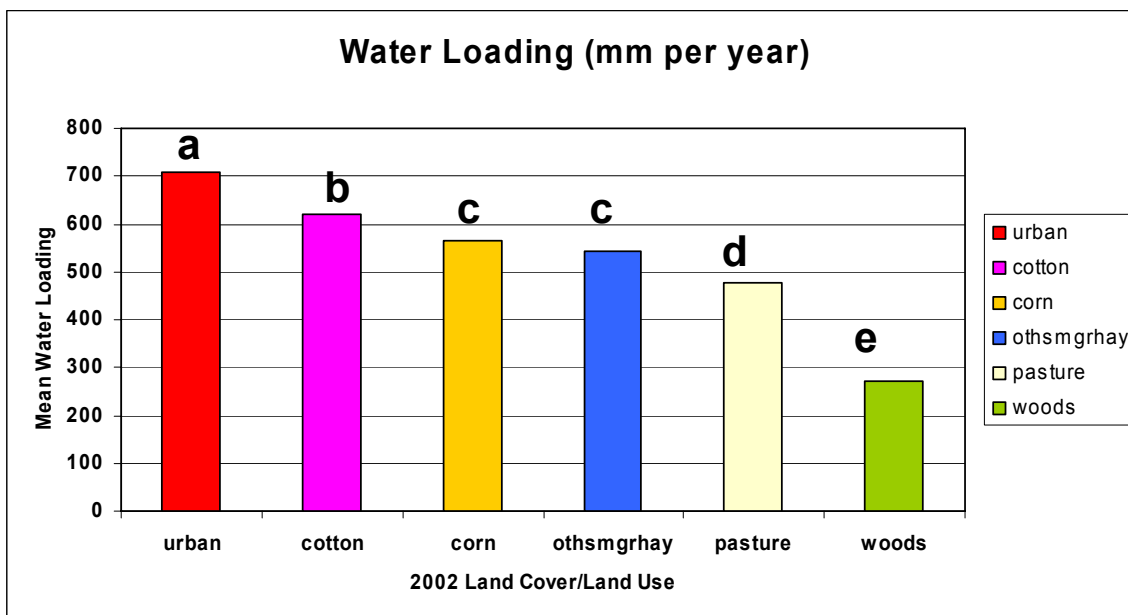
Figure 4.12. AnnAGNPS predicted water loading (mm/year) with 2002 LU/LC.

Figure 4.13. AnnAGNPS predicted water loading (cms) with 2002 LU/LC.

Figure 4.14. AnnAGNPS predicted sediment loading with 2002 LU/LC.

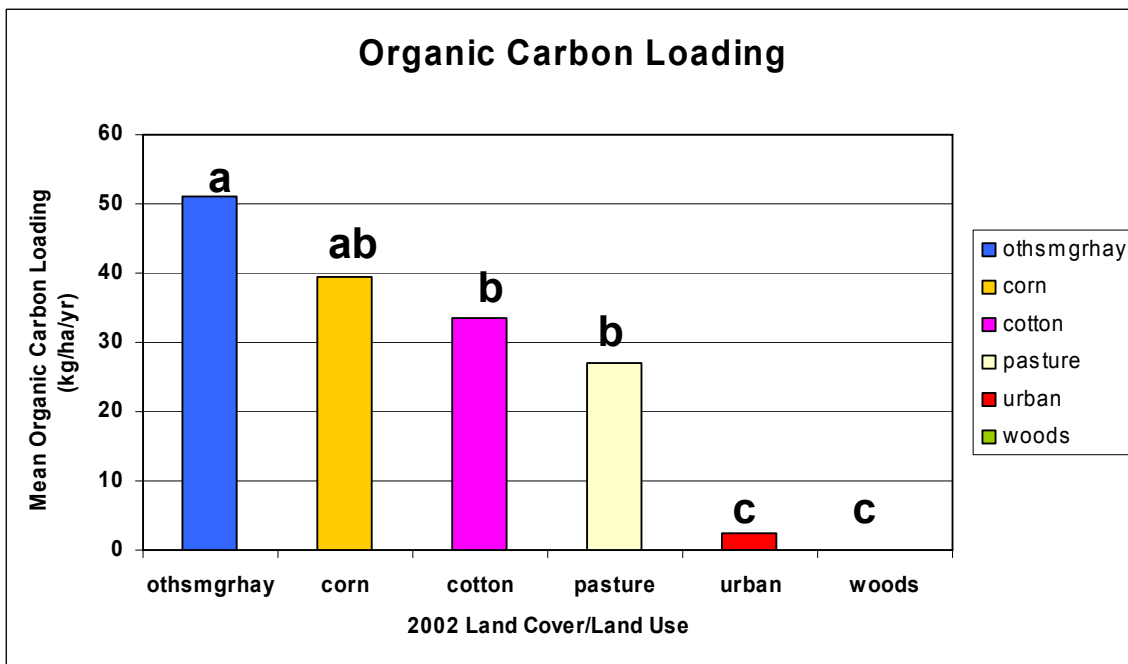Figure 4.15. AnnAGNPS predicted phosphorus loading with 2002 LU/LC.

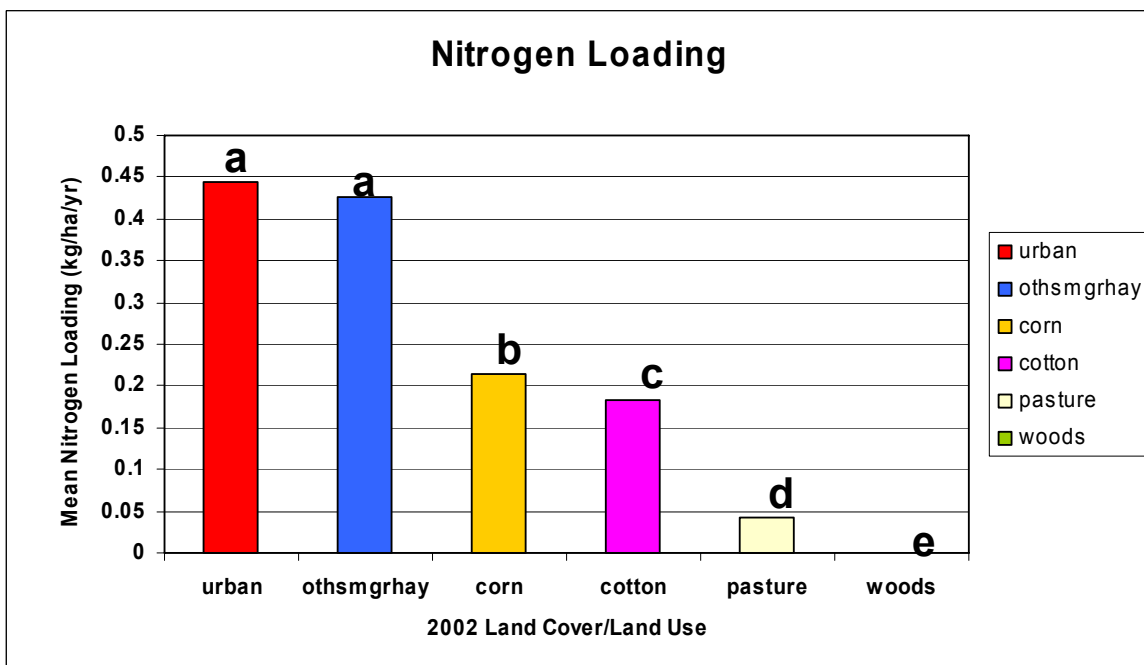Figure 4.16. AnnAGNPS predicted organic carbon loading with 2002 LU/LC.

Figure 4.17. AnnAGNPS predicted nitrogen loading with 2002 LU/LC.

CHAPTER V

RECOMMENDATIONS FOR FUTURE RESEARCH

Based on the objectives addressed and conclusions reached in previous chapters, several suggestions can be made for future research. There were various difficulties encountered in meeting the objectives set forth in previous chapters, and these difficulties have offered useful lessons and resulted in recommendations for continued studies on these topics.

The measured data in Chapter II was used to assess the water quality status of surface waters in the Upper Pearl River Basin (UPRB) and to validate the Annualized Agricultural Nonpoint-Source (AnnAGNPS) runoff model. For the purpose of assessing water quality in the UPRB, sampling for fifteen different pesticides and total dissolved solids (TDS) was necessary to obtain a more complete picture of the health of surface waters in the UPRB.

However, for the purpose of de-listing waters on Mississippi's Clean Water Act (CWA) §303(d) list that are classified as impaired due to pesticides, more legacy pesticides should have been sampled. Throughout the course of this research, it was discovered that the listing of many stream segments by the Mississippi Department of Environmental Quality (MDEQ) as pesticide-impaired was a result of chronic contamination by legacy pesticides such as dichlorodiphenyltrichloroethane (DDT) and toxaphene. For future efforts to

assess waters listed as pesticide-impaired, sampling should better target these legacy pesticides, although they would have been difficult to model since they are no longer being used.

Many difficulties were encountered during the AnnAGNPS validation study in Chapter III. The AnnAGNPS runoff model produces loadings in daily time intervals throughout a rainfall event. However, when using actual climate data for validation studies, weather stations do not necessarily collect data from 12:00 am to 12:00 am. In reality, data collection may overlap from one calendar day to the next. This could lead to AnnAGNPS-produced loadings the day before or the day after precipitation actually occurred, causing more difficulty when comparing modeled loadings to measured loadings.

In Chapter III, the measured data were collected at discrete time intervals. The United States Geological Society has a website that shows real-time stream heights and flow. This website was monitored to time sediment sampling around the peak flow resulting from a rainfall event. Since sediment loading typically peaks just before the flow peaks, sampling was targeted for the first half of the hydrograph, although samples were attempted throughout an event. Limitations such as driving distance to the sampling site and class schedules sometimes hampered the timing of sample collection.

Also, pesticide sampling was not necessarily targeted during rainfall events. The majority of pesticide samples were taken during summer months, when rainfall was less frequent. Results might have been improved if pesticide

sampling had been targeted during rainfall events. At the least, it might have resulted in more events available for comparison, since comparisons were only made for dates which had both measured and modeled data, and AnnAGNPS does not produce loadings unless there is sufficient precipitation to cause runoff.

In future studies of this type, comparisons between measured and modeled data can be attempted differently. Rather than limiting comparisons to days which have both modeled and measured data, comparisons could be improved by analyzing monthly averages for all days within a month which have modeled runoff and monthly averages for all days within a month that have measured data. Changing the comparisons in such a way would help address two issues, the first of which is the earlier problem mentioned with 'daily' climate data that may overlap two actual days. The second issue that would be improved is that of comparing discretely sampled measured data with daily modeled loadings.

The most accurate way to compare measured data with modeled data of any kind would include measured data that was continuously sampled during a rainfall event. However, it is often difficult and expensive to install monitoring equipment with capabilities of obtaining continuous samples. Another option for a model validation study could be better selection of the watershed outlet so that it is more easily accessible. For example, in Chapter III a shorter driving distance to the outlet sample site would not have allowed continuous sampling, but it

would have likely resulted in increased sampling frequency and possibly better timing of sample collection.

For a validation study, analysis of a smaller watershed would also make it easier to obtain more detailed management information for the drainage area. In Chapter III, the measured data showed that metolachlor and atrazine applications were made much sooner than initially assumed. In future studies of this manner, management information will be better defined based on measured data. If the validation watershed is small enough, detailed management information may even be obtained from individual property owners. This would be helpful since actual management practices may differ, for various reasons, from those recommended by extension service agents and other agricultural professionals.

After the AnnAGNPS validation study in Chapter III, Chapter IV applied AnnAGNPS to quantify the effects of land use changes on surface waters in the UPRB from 1987 to 2002. Although AnnAGNPS performed adequately, a model's outputs are only as good as its inputs, and one or more of the inputs used in Chapter IV could be improved. Most notably, the remote sensing inputs could be improved to better capture land cover in 2002. For Chapters III and IV, the Cropland Data Layer (CDL), produced by the National Agricultural Statistics Service, was used to represent UPRB land cover in 2002. This dataset was selected because the primary interest in both chapters was the contribution of nonpoint-source runoff to UPRB surface waters from agricultural lands, and the

CDL gives accurate and detailed information on agricultural land cover classes. However, this dataset does a poor job of accurately capturing non-agricultural land cover classes.

Thus, even though the agricultural land cover classes were the primary interest, their effects on surface waters were overshadowed by the inadequate representation of the non-agricultural land cover classes. For example, Chapter IV showed that nonpoint-source inputs from agricultural land cover classes decreased from 1987 to 2002, but sediment and organic carbon loading increased, most likely as a result of the apparent decrease in forested acreage during this time period. Future studies might be improved by exploring combinations of remotely sensed datasets, such as using two data layers to represent one year or fusing two datasets. In Chapter IV, results might have been better by simply obtaining the 2002 land cover data in the same fashion as the 1987 data layer. In this manner, the two land cover datasets would be classified and analyzed in a like manner, which is important in a land use change study.

Several opportunities for future research have come from the difficulties encountered in previous chapters. In Chapter II, due to driving distance to the sampling sites and the frequency at which TDS samples were to be collected, only three sites were sampled for TDS, while all seven UPRB gauged sites were sampled for pesticides. There were gauged sites downstream of channelized reaches on Pearl River tributaries which were not sampled for TDS. It would be

interesting to perform a study that would compare TDS data downstream of channelized reaches to TDS data collected along unaltered reaches.

A priority for subsequent research is performing other validation studies using AnnAGNPS. The single event version of the model, called the Agricultural Nonpoint-Source (AGNPS) runoff model, has been fairly extensively validated for diverse geographic regions. Although there are ongoing AnnAGNPS validation studies, there are very few published studies to date, and the continuous version of the model has not been as extensively validated as the older single-even version.

If adequate funding could be identified, the ideal validation study would include continuous monitoring equipment established to collect measured data. The study could be performed on a small to medium drainage area, targeting one or more streams on the state's Clean Water Act (CWA) §303(d) list. The study could alternatively be geared towards helping establish a Total Maximum Daily Load (TMDL). In future validation studies, comparisons of measured and AnnAGNPS-predicted data would be made differently, based on the aforementioned lessons learned from the comparisons made in Chapter III.

An UPRB land use change study with improved land cover inputs would also be useful. It would be interesting to perform a sensitivity analysis to see how improved remotely sensed land cover inputs, such as fused datasets, affected AnnAGNPS-predicted loadings as compared to the land use inputs in Chapter IV. A sensitivity analysis on remotely sensed land cover inputs

investigating the effects of different spatial resolutions on AnnAGNPS predictions

might also be helpful. Additional land use change studies could analyze the

effects of land use changes on surface waters in other areas of the basin,

possibly looking at different time periods or focusing on different land cover

classes, such as the effects of increasing urbanization.

Another appropriate sensitivity analysis might include looking into the

effects of channelization in certain areas of the UPRB. Portions of Tuscolameta

Creek and the Yockanookany River, both tributaries of the Pearl River, have

been channelized. In this sensitivity analysis, the digital elevation model (DEM)

inputs would vary before and after the channelization process.

Finally, there are more general ideas for future research topics.

Throughout the previous studies included in this dissertation, a need was

observed for watershed runoff models that can accurately predict pesticide

loadings. Future work might include working with AnnAGNPS developers to

strengthen the pesticide loading component of the model. Additional ideas for

future research involve investigations using other watershed runoff models, such

as the Hydrological Simulation Program – Fortran (HSPF) or the Soil and Water

Assessment Tool (SWAT), for example, as well as developing customized

applications for existing models such as these. Many conclusions can be

reached from the studies performed in previous chapters, but just as many

recommendations, if not more, can be made for future work that is needed.
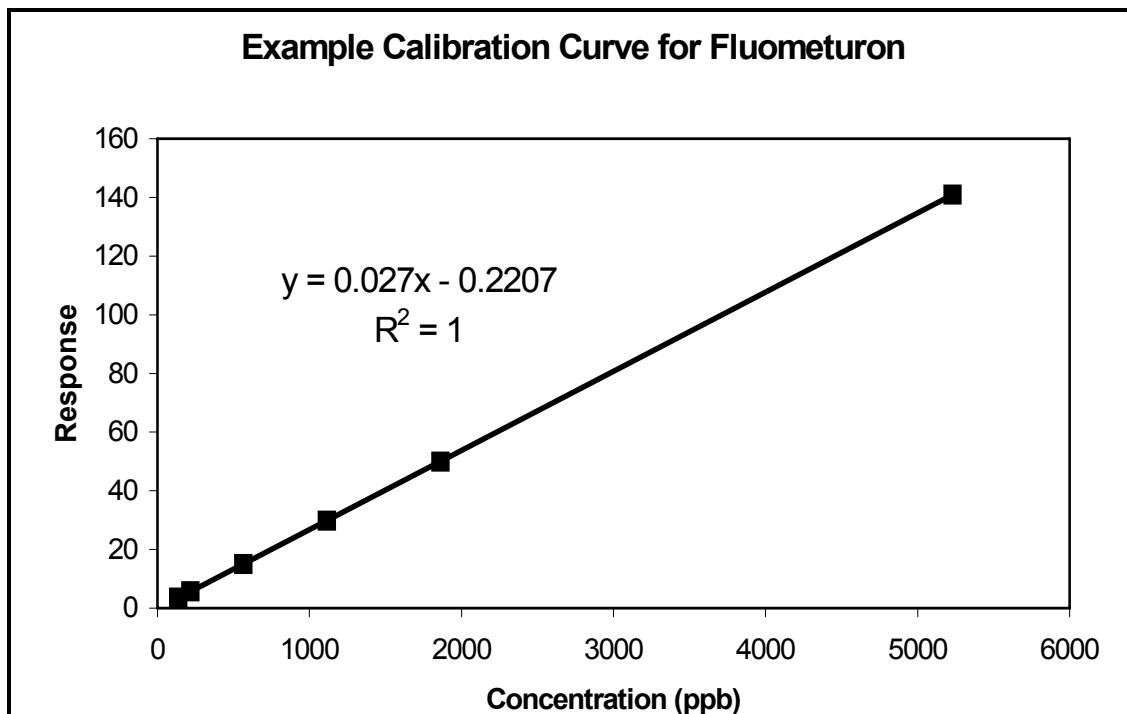
APPENDIX A

EXAMPLE CALIBRATION CURVES

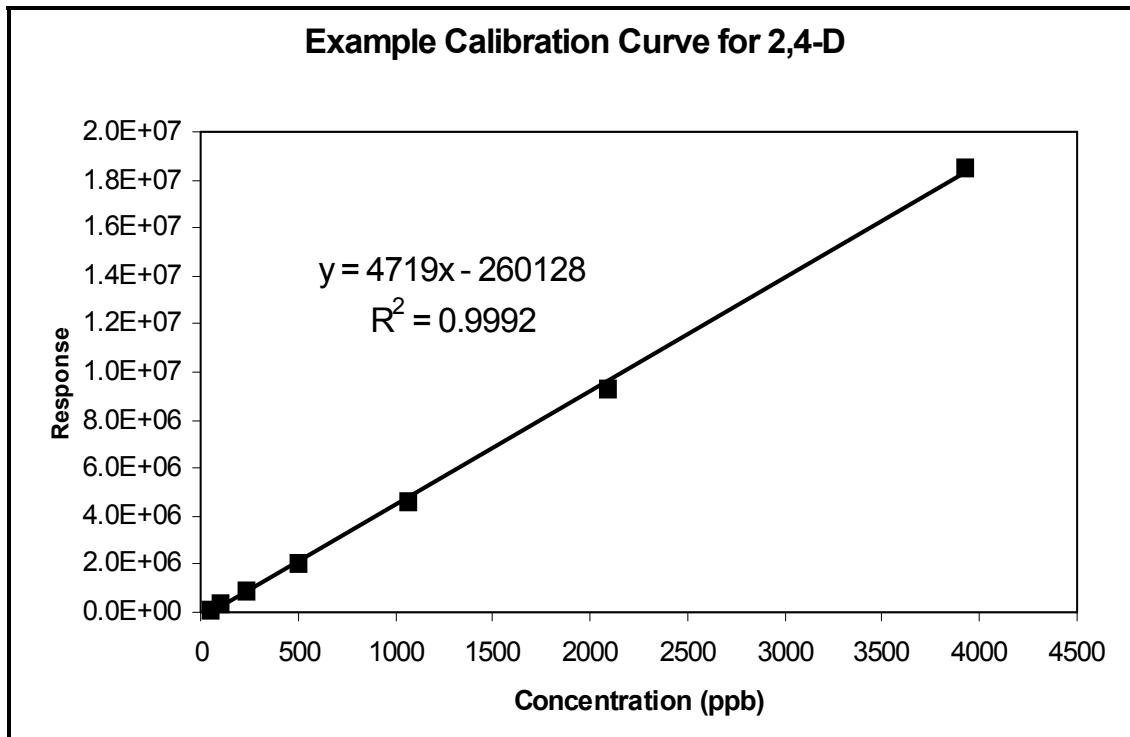Figure A.1. Example calibration curve for fluometuron.
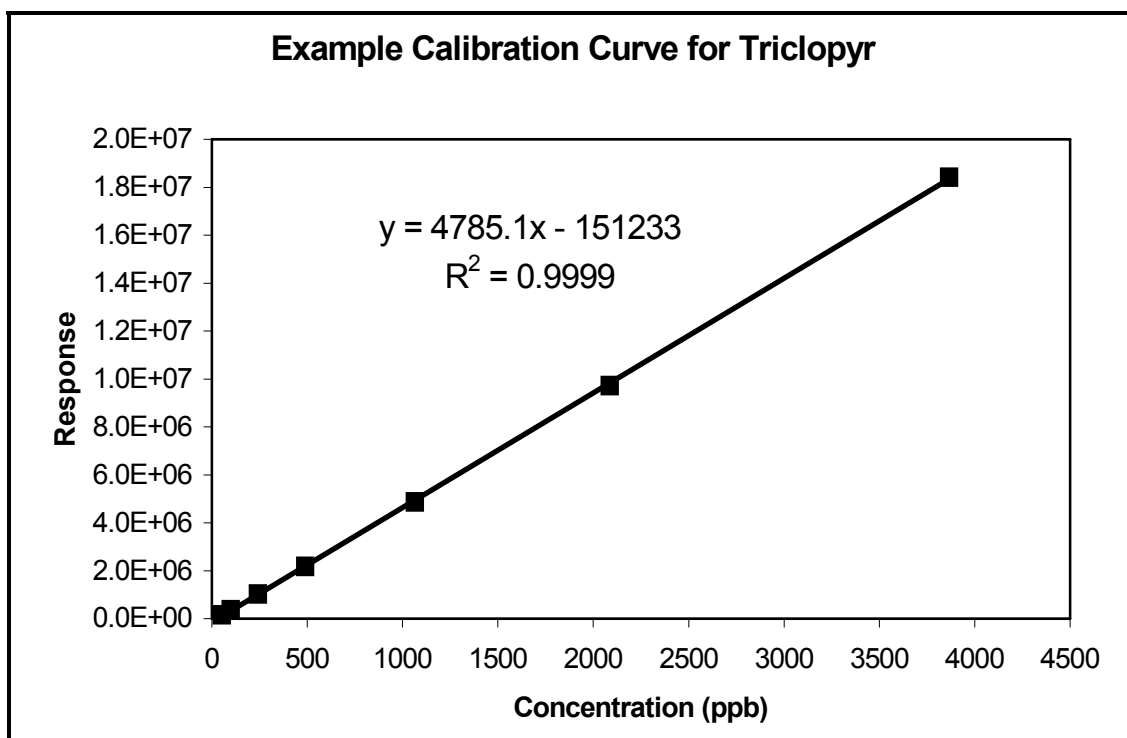

Figure A.2. Example calibration curve for 2,4-D.
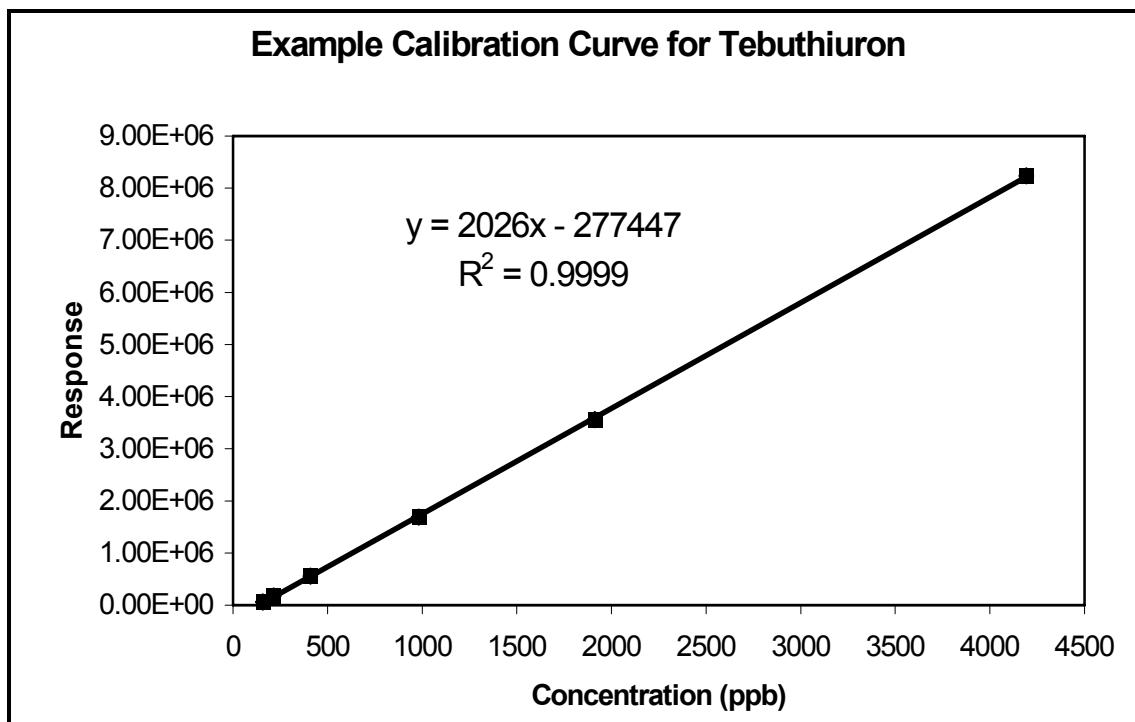
Figure A.3. Example calibration curve for triclopyr.

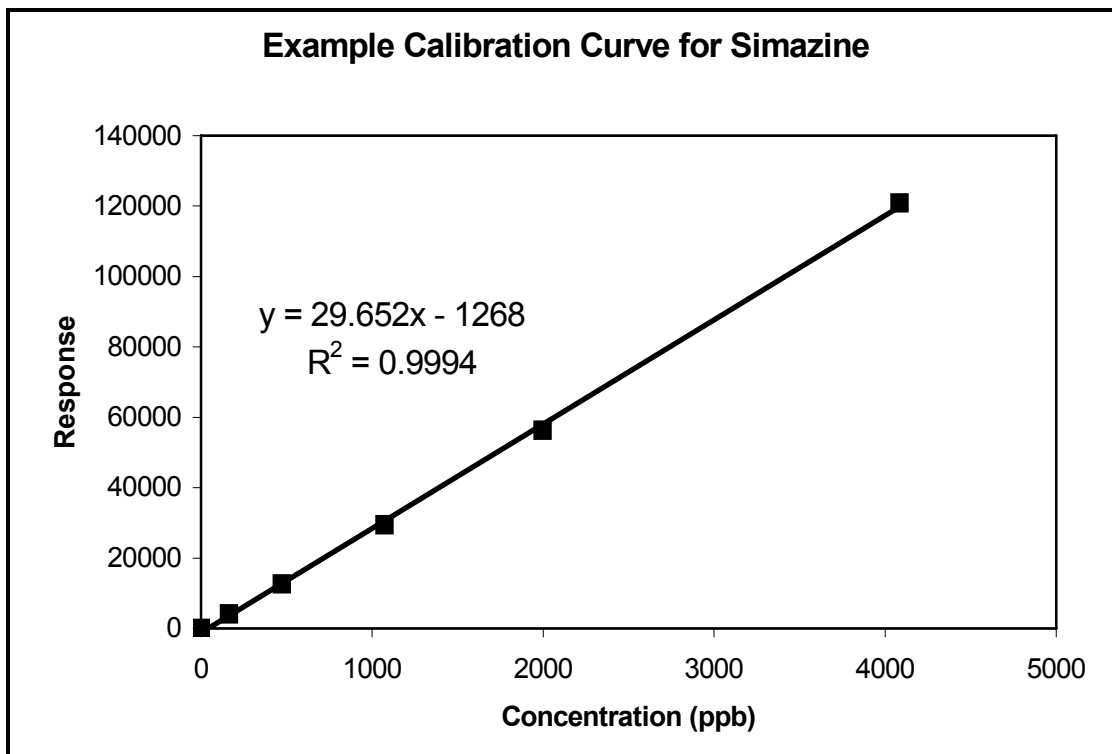Figure A.4. Example calibration curve for tebuthiuron.

Example Calibration Curve for Simazine

$y = 29.652x - 1268$

$R^2 = 0.9994$

Figure A.5. Example calibration curve for simazine.

Example Calibration Curve for Atrazine
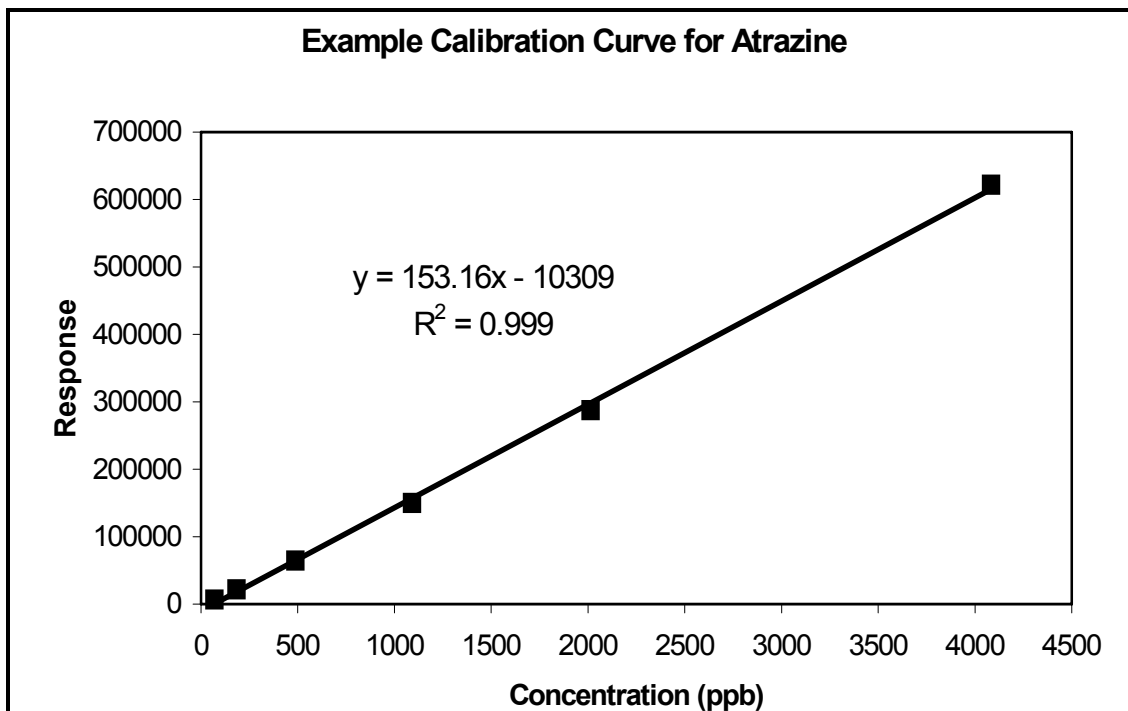
$y = 153.16x - 10309$

$R^2 = 0.999$

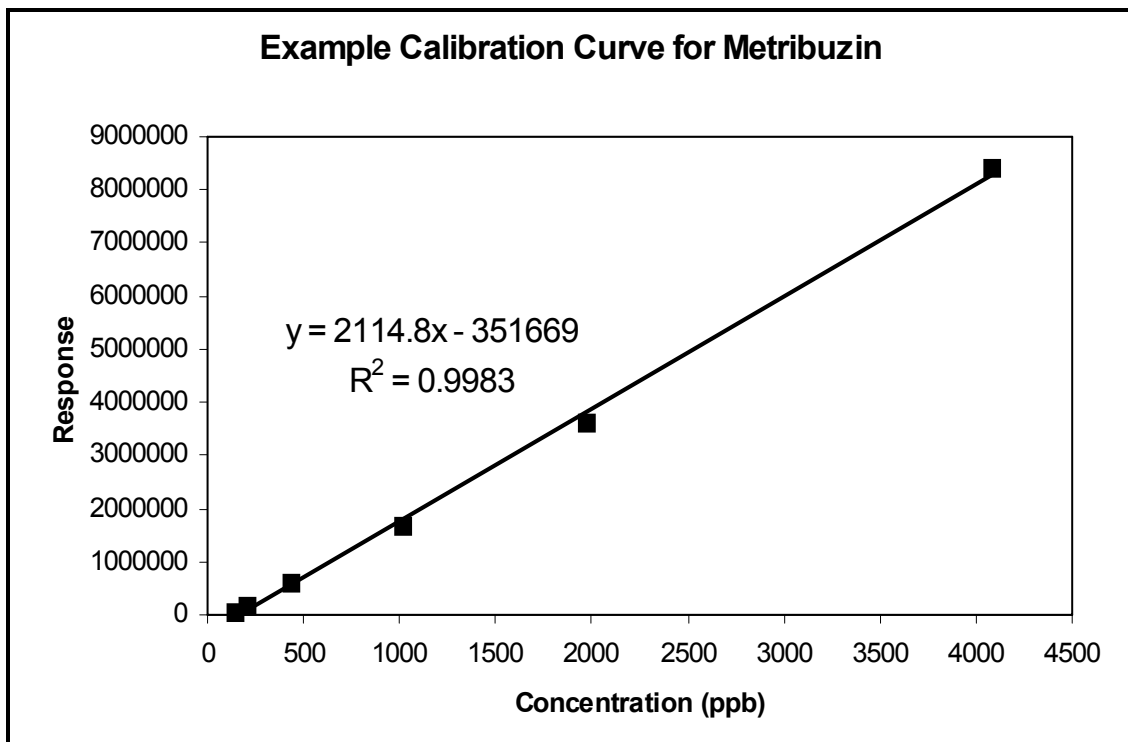Figure A.6. Example calibration curve for atrazine.

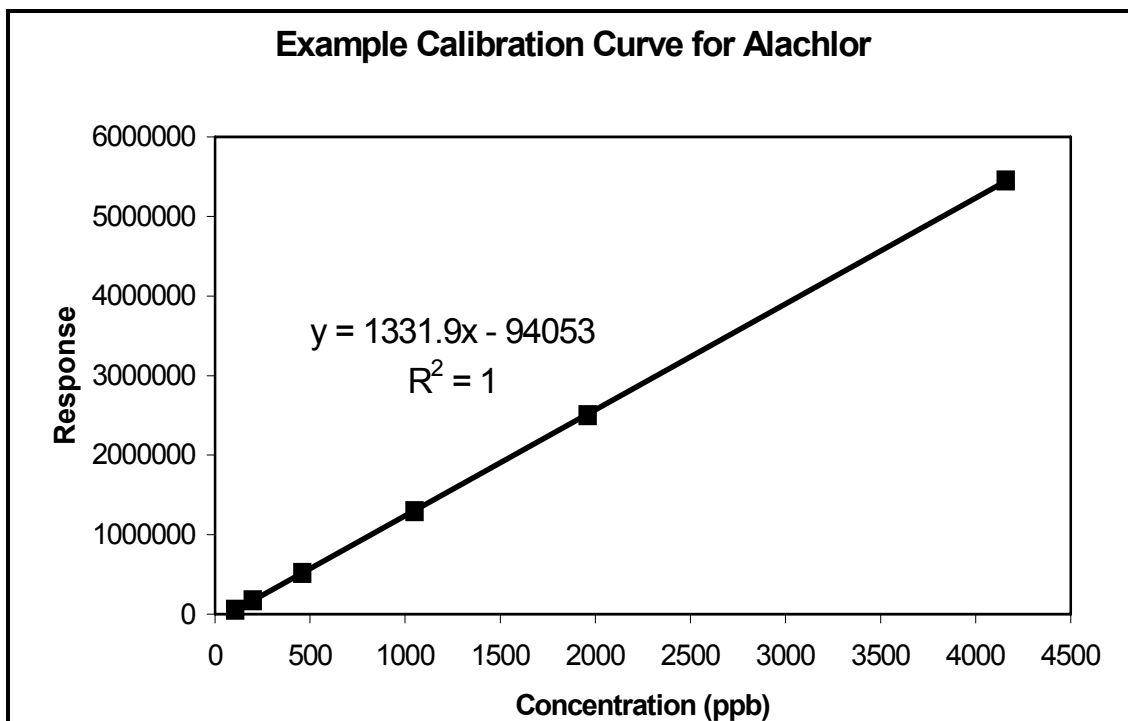Figure A.7. Example calibration curve for metribuzin.

Figure A.8. Example calibration curve for alachlor.
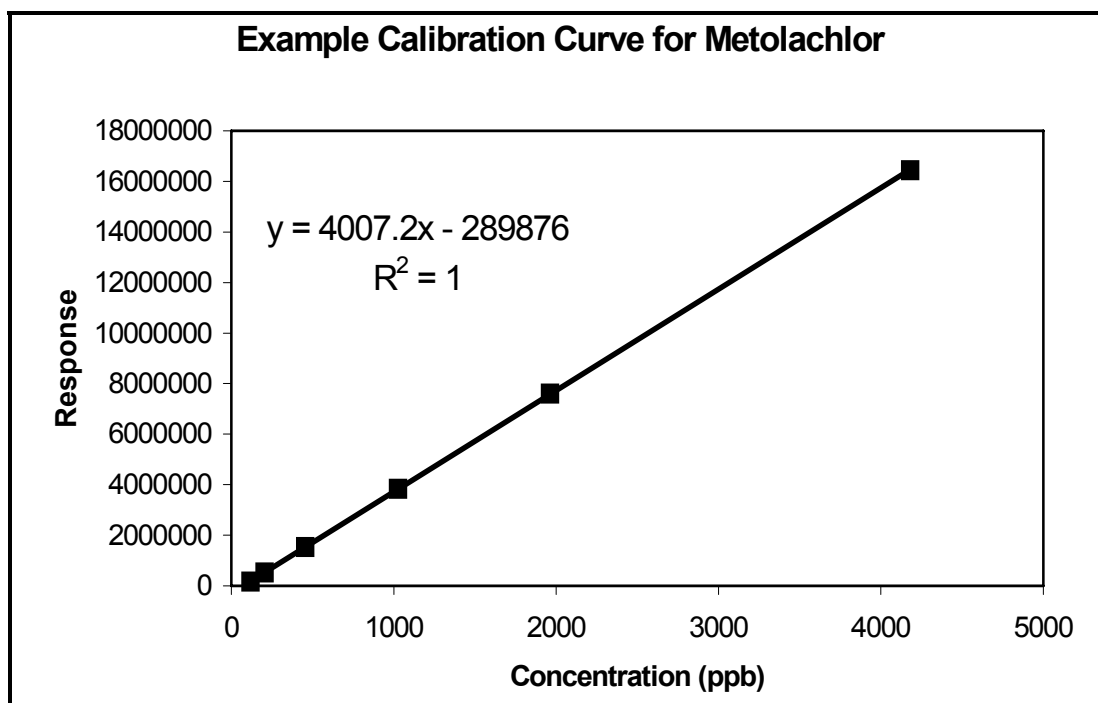
Figure A.9. Example calibration curve for metolachlor.
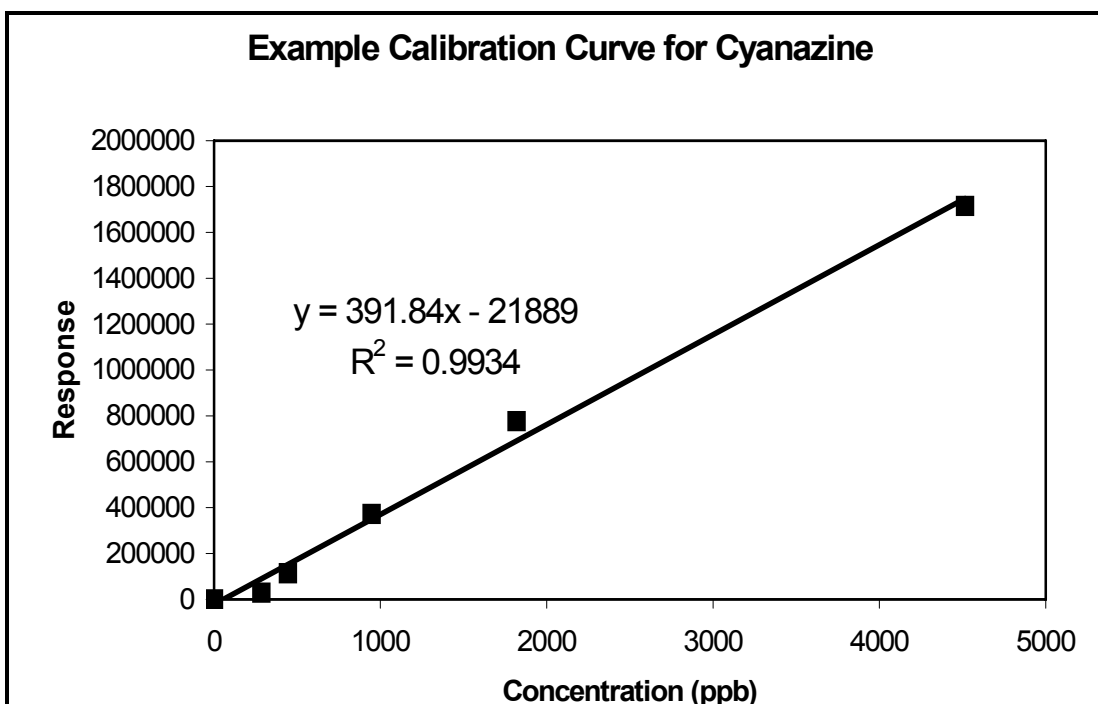

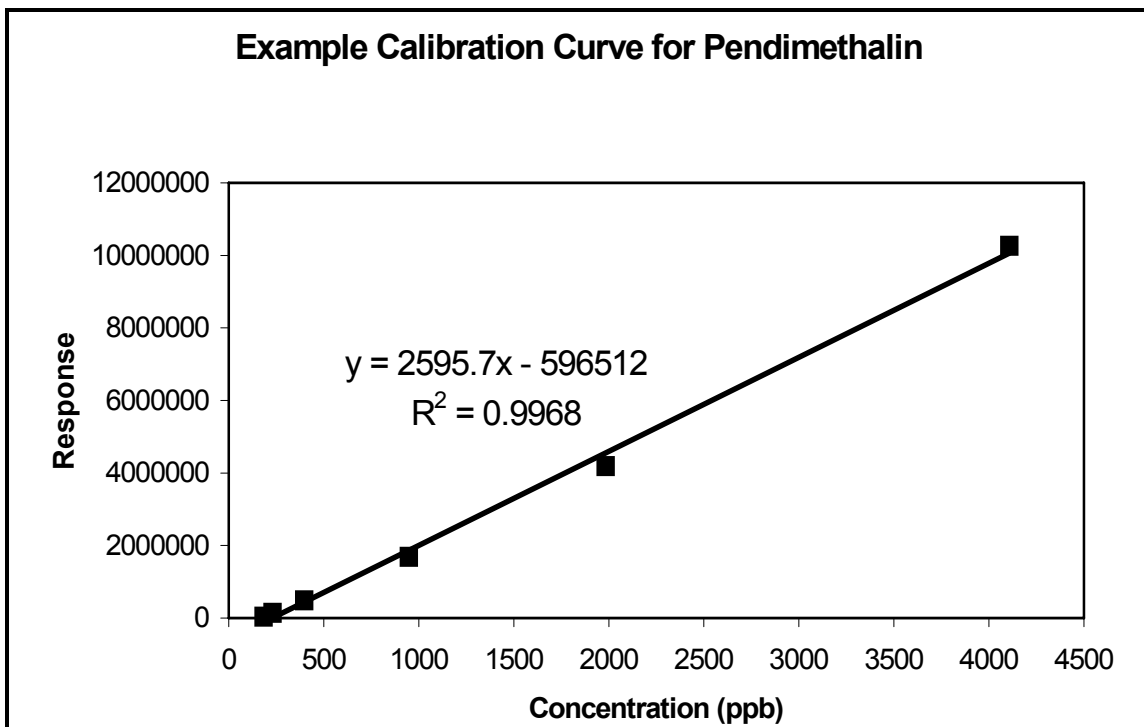Figure A.10. Example calibration curve for cyanazine.

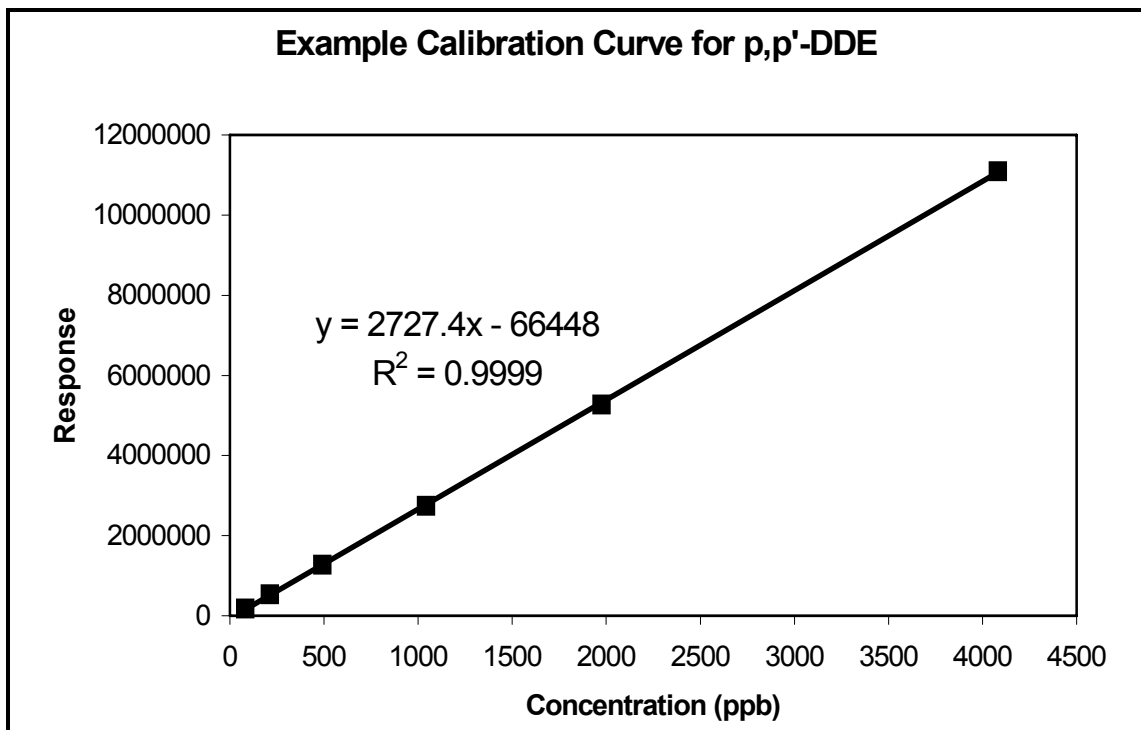Figure A.11. Example calibration curve for pendimethalin.

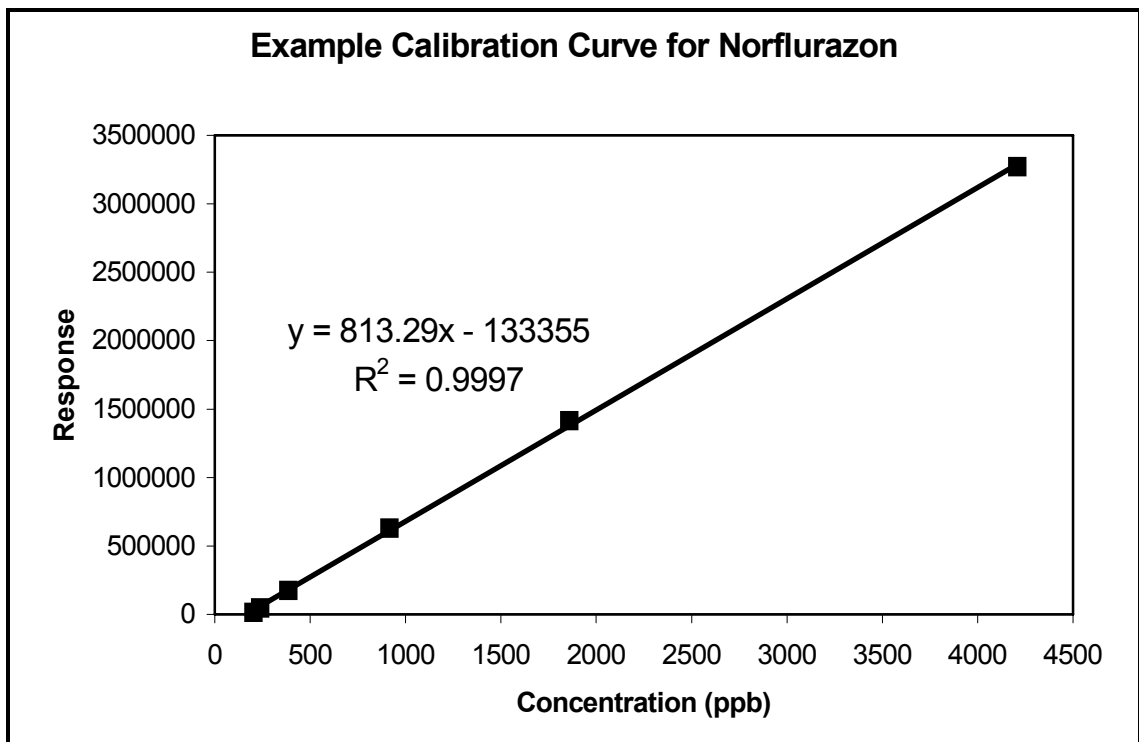Figure A.12. Example calibration curve for p,p'-DDE.

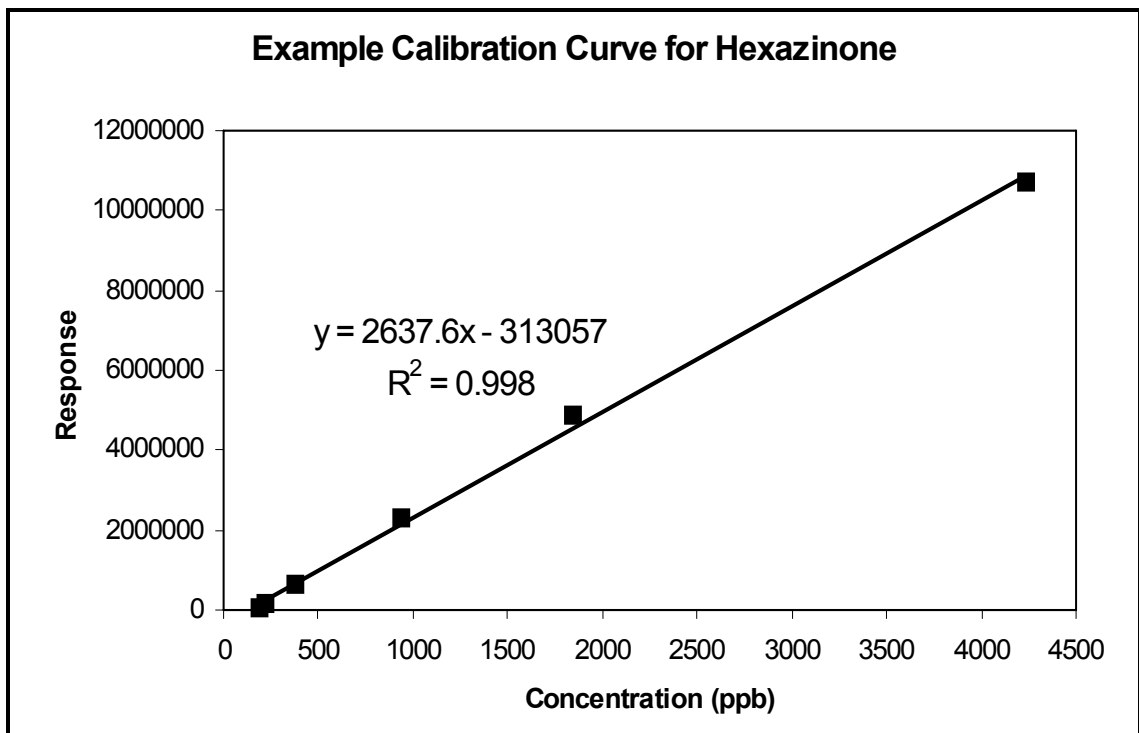Figure A.13. Example calibration curve for norflurazon.

Figure A.14. Example calibration curve for hexazinone.

APPENDIX B

PRE-PROCESSING OF GEOSPATIAL DATA

The DEMs were downloaded from the Mississippi Automated Resource Information System's (MARIS) website for each county present in the Upper Pearl River Basin (UPRB). MARIS created tagged vector contours at a scale of 1:24,000 from USGS mylar separates and then used these contour files to produce the DEMs at a 10-m horizontal resolution. The DEMs were downloaded from the MARIS website as zipped .e00 files. Once downloaded, the files were unzipped and converted from .e00 interchange files to grid files.

The individual grid files for each county were opened in the AnnAGNPS ArcView interface. Versions 3.42 and 3.51 of the ArcView interface were used for this study. The *DEM Utilities* pull-down menu in the ArcView interface was used to mosaic the county grids and eliminate any 'no data' values that might have occurred during the mosaic process. These 'no data' areas often appear as slivers between the merged grids and must be corrected by assigning the 'no data' pixels an average value taken from the surrounding pixels. For the size watershed that was modeled, the 10-m DEMs contained too many rows and columns for the model to process. The solution was to re-sample the DEM to a 20-m pixel size using a freeware ArcView extension called Grid Utilitys v1.1. Finally, both the horizontal and vertical units of the DEM must be in metric units. The vertical elevation units of the DEM were checked using digital raster graphics (DRGs), or scanned USGS 1:24,000 topographic maps. The elevation units were in feet, so the Leica Geosystems[©] ERDAS Imagine[®] software package was used to convert the elevation units from feet to meters. In ERDAS Imagine[®], the *Image Interpreter* toolbar pull-down menu was selected, followed by the

'Topographic Analysis' option. The selection of the 'Topographic Analysis' button opens another pull-down menu with many functions. The 'DEM Height Converter' function was chosen to convert the DEM elevation units from feet to meters.

Land use/land cover (LULC) information was obtained from the United States Department of Agriculture's National Agricultural Statistics Service (USDA-NASS) 2002 cropland data layer product. The USDA-NASS cropland data layer can be obtained on a cd-rom, which can only be ordered through the NASS website (http://www.nass.usda.gov/research/Cropland/SARS1a.htm). NASS personnel performed a supervised classification on georeferenced Landsat 5 – TM and Landsat 7 – ETM scenes. The scenes were then mosaiced together for the state. The Landsat mosaic is at a scale of 1:100,000 and has a spatial resolution of 30 m^2. The cropland data layer for 2002 contains LULC broken into eleven separate classes for the state. The LULC layer was obtained from the NASS cd-rom in ERDAS Imagine .img file format. The LULC .img file was then subset for the UPRB in ERDAS Imagine, creating another .img file that contained only the subset area of interest.

The AnnAGNPS ArcView interface requires that the LULC information be in a shapefile format, so the .img subset file must be converted to a shapefile. If the original LULC raster file is not in the desired geographical projection, the user can wait and re-project the final shapefile rather than re-projecting the image file. First, however, a 'Neighborhood Functions' process was performed on the image subset in ERDAS Imagine, using a 3x3 kernel and majority function. This

process can be found by clicking on the *Interpreter* button and then selecting 'GIS Analysis.' The Neighborhood Functions process has a smoothing effect on the classified image subset by eliminating island pixels, or pixels of one class that are completely surrounded by pixels of another class. Eliminating island pixels prevents single-pixel island polygons and speeds the model processing.

Next, the smoothed image subset was converted to a polygon shapefile in ArcGIS using the *raster to feature* option of the Spatial Analyst extension. The *value* field in the image file, which represents the LULC classification, was used to populate the *gridcode* field in the new shapefile. Finally, the resultant LULC shapefile was re-projected, if needed, and added to the AnnAGNPS ArcView interface. A dissolve process was also performed on the LULC shapefile to combine any adjacent polygons. The dissolve process resulted in multipart features being created, where a single feature containing discontiguous elements was represented in the attribute table as one record. For example, there were multiple unconnected forestry polygons scattered throughout the watershed; but all of these polygons were collectively represented by one record in the attribute table, rather than having multiple, individual records for each of these polygons. The attributes of the newly dissolved shapefile were updated to reflect the new combined size of each LULC class.

Soils data were obtained through the USDA Natural Resources Conservation Service (NRCS) State Soil Geographic (STATSGO) database. STATSGO data for Mississippi were obtained in GIS coverage format, along with documentation and a user guide, from the following NRCS website:

http://www.ncgc.nrcs.usda.gov/products/datasets/statsgo/data/ms.html. With the

exception of Alaska, all STATSGO data are at a scale of 1:250,000. The USDA-

NRCS is currently working to complete the Soil Survey Geographic (SSURGO)

database for selected counties and areas throughout the United States and its

territories. At scales ranging from 1:12,000 to 1:63,360, the SSURGO database

is the finest level of digital soil mapping produced by the NRCS, duplicating

original soil survey maps. Unfortunately, SSURGO data has not been completed

for most counties in the UPRB, so the STATSGO soils database was used for

the soils GIS input for AnnAGNPS model simulations.

Since STATSGO is a national database, the data were compiled by NRCS

in an Albers Equal Area projection. After downloading the Mississippi STATSGO

data in an ESRI GIS coverage format, the coverage was converted to a

shapefile, and the shapefile was then re-projected to a specialized Mississippi

Transverse Mercator (MSTM) projection. Similar to the LULC data layer, the

soils shapefile for the state was subset to the UPRB area of interest and then

added to the AnnAGNPS ArcView interface.

It is important to note that the geospatial input layers were subset, or

clipped, only to simplify and speed processing steps during input file preparation

and model execution. When these statewide or regional geospatial layers were

subset, an adequate buffer outside the supposed, estimated watershed boundary

was included in the subset to help eliminate errors if the outlet was moved and

another watershed delineation became necessary.

All relevant climate stations in the drainage area were identified in consultation with the National Oceanic and Atmospheric Administration's (NOAA) National Weather Service (NWS) office in Jackson, MS and the Southern Regional Climate Center (SRCC), located in Baton Rouge, LA. The latitude and longitude for climate stations located in the UPR watershed were obtained in degrees, minutes, and seconds and converted to decimal degrees. The climate station name, location in decimal degrees, and identification number were then used to create a point shapefile of the climate stations. The climate station identification number (CSID), a field in the shapefile, must be a character field entered as a number within the range of 0-99.

A Thiessen polygon extension was added to the ArcView interface. The relevant climate stations in the drainage area (Louisville, Gholson, and Philadelphia) were selected and highlighted, and Thiessen polygons were created using these points. The CSID was selected as the point field for the polygon identification link. The user was then asked to select a polygon as the boundary for the new Thiessen polygons and name the new Thiessen polygon layer. Since the Gholson station fell just outside the probable watershed drainage area, it was necessary to define the Thiessen polygon boundary as a polygon whose perimeter encompasses all of the climate station locations to be used in the model run.

APPENDIX C

PREPARATION OF AnnAGNPS INPUT FILES

The AnnAGNPS ArcView interface was used to prepare input files for the Input Editor. The Input Editor then produced one AnnAGNPS input file that was used, in combination with the climate files, by the pollutant loading module. The pre-processed geospatial data layers were added to the AnnAGNPS ArcView interface, and themes were assigned for the following data layers: fields (LU/LC), soils, DEM, subwatersheds, and climate stations. If a Thiessen polygon layer was created, it was assigned to the climate station theme. The DEM was clipped to the approximate drainage area, and a point shapefile with sampling locations was added to the view to aid in interactively selecting a watershed outlet, completing Steps 1 and 2 in the ArcView interface. The watershed outlet was interactively defined as row 2436 and column 595, based on the point feature that showed the sampling location.

After the watershed outlet was selected, Step 3 converted GIS files into the ASCII format needed for the TopAGNPS module. A full TopAGNPS run was applied, and the user-defined values for the Critical Source Area (CSA) and Minimum Source Channel Length (MSCL) were set at 50 hectares and 100 meters, respectively. The CSA and MSCL values determine the hydrographic segmentation of the watershed by controlling the characteristics and topology of the stream channel network and sub-catchments generated by the TopAGNPS module.

Step 4 then executed TopAGNPS, which created amorphous AnnAGNPS cells, or sub-watersheds, that follow the terrain. These cells were created from the DEM and contain necessary hydrologic and hydraulic parameters. During

Step 4, the raster cell that defines the drainage outlet was redefined as row 2460 and column 596.

Step 5 followed with the execution of AgFlow, which created amorphous grids with stream reach characteristics and cell data. These stream reach characteristics include stream network, length, elevation, and slope and cell data describing the drainage area, elevation, aspect, slope, and receiving stream reach for that cell.

Step 6 then imported selected DEM-based TopAGNPS files into the ArcView interface, and the directory for the dataset was defined. Figure 4.1 illustrates the sub-watershed delineation and connectivity between the sub-watersheds and the generated channel network.

Continuing through the procedures in the AnnAGNPS ArcView interface, Step 7 intersected the sub-watershed cells with the soils data, using the field 'MUID' as the soil identifier in the overlay. The STATSGO soils database contains soil associations, but AnnAGNPS requires that a dominant soil type, along with its characteristics, be selected for each generalized soil association. The Map Unit Use File (MUUF) program, using the Map Unit Identification (MUID) number in the STATSGO database, retrieved the desired soil characteristics information from the NRCS Soils5 database (Baumer et al., 1994). Another program, the MUUF converter, transformed the retrieved MUUF data to a format that is compatible with the AnnAGNPS model (Bingner, 2004).

Next, Step 8 intersected the sub-watershed cells with the field data, or LU/LC layer, using the LU/LC attribute field 'Class' as the field identifier in the

overlay. The overlay was performed with the 2002 cropland data layer and, in a

second run of the model, with the 1987 land use dataset. See Figures 4.2 and

4.4 for the original 1987 and 2002 LULC layers, respectively. During the overlay

process, the model assigned a LU/LC class to each sub-watershed cell, which is

based on the dominant LU/LC class within that sub-watershed cell. The

AnnAGNPS ArcView Interface was employed to determine how well the LU/LC

information from the original file was reflected in the sub-watershed LU/LC

designations, by calculating the percentage of each LU/LC class in both the

original LU/LC layer and in the sub-watershed file. The two were then compared.

The heterogeneity of some LU/LC classes, especially urban and

agricultural classes, caused these classes to be underrepresented in the sub-

watershed file. These particular classes were assigned to fewer sub-watershed

cells because they were not the dominant LU/LC class within many sub-

watersheds. A detailed hydrographic description was performed on the

watershed, but it still did not reflect the patchy nature of the agricultural and

urban LU/LC classes. Thus, the LU/LC classes assigned to sub-watershed cells

were later adjusted using the Input Editor, to more accurately reflect the class

percentages in the original LU/LC layer. Step 9 followed and extracted the cell

and reach information from the ArcView interface in a format that could be

imported into the Input Editor.

The creation of synthetic weather information was the final step to be

performed in the ArcView interface, before moving to the Input Editor. A monthly

climate file (MonClim.inp) was created for use with the synthetic weather

generator, GEM (Generation of weather Elements for Multiple applications). This monthly climate file contained monthly averages, based on historical data, for dew point, percent sky cover, and wind speed for a given climate station. Although there were no climate stations that were both located within the delineated watershed and available in GEM, the Meridian station was located just east of the watershed. Since this was the nearest station to the UPR watershed, the GEM program used historical data from the Meridian climate station to generate synthetic climate information for daily precipitation, maximum and minimum temperatures, and solar radiation. Once the climate files were created and in their final format, the files could be imported into the Input Editor for manual edits as needed. See Appendix E for more detailed information on processing climate files.

For each run of the model, the soils, topographic, and LU/LC data were imported into the AnnAGNPS Input Editor to create the required AnnAGNPS input file that was needed to run the pollutant loading model. Version 3.51 of the Input Editor and the AnnAGNPS Pollutant Loading module were used for this study. The Input Editor provided an interface for the user to make a detailed characterization of the watershed. The Input Editor also allowed the user to select the desired output files and enter information about the model simulation period. The AnnAGNPS Pollutant Loading module was set to run for two initialization years and ten simulation years.

Once the cell and reach data were imported into the Input Editor, the LU/LC class designations for the sub-watershed cells could be adjusted to more

accurately reflect the total LU/LC areas in the original LU/LC layer. Tables 4.1

and 4.2 show a comparison of the LU/LC class percentages in the original LU/LC

layer, model delineated LU/LC layer, and final adjusted layer. The LU/LC

designation for the sub-watershed cells is illustrated in Figures 4.3 and 4.5 for the

1987 and 2002 land cover layers, respectively.

The Input Editor contained numerous variables that may be used to

describe a watershed. One of these variables is the Soil Conservation Service

(SCS) curve number (CN). Curve numbers are a convenient way to describe the

potential maximum retention of a surface, after runoff begins. The CN will vary

by storm for a given soil type and is dependent on many factors, such as

antecedent soil moisture. The CN is important in accurately predicting runoff and

sediment yields, so the appropriate CN was assigned to each LU/LC type, taking

into consideration the growth stage of any vegetative cover. Operational

management information was also outlined for each sub-watershed, based on

the Revised Universal Soil Loss Equation (RUSLE) guidelines. Information

regarding typical pesticide applications and harvesting schedules was described

as well, where applicable (Anonymous, 1987; Anonymous, 2005).

APPENDIX D

LAND USE/LAND COVER ANALYSES

In the ArcView Interface, the *Analysis* tab was selected from the Toolbar menu, and the 'Tabulate Areas' function was used to first calculate the percentage of each LULC class in the original LULCL layer, based on the total LULC distribution within the delineated watershed boundary. The original LULC layer was selected as the 'Row Theme,' and the LULC class was selected as the 'Row Field.' The boundary grid file, which contains the delineated watershed boundary, was used as the 'Column Theme,' and the attribute field named Value (from the boundary grid file) was used as the 'Column Field.'

It is now important to see how well the LULC information from the original file is reflected in the subwatershed LULC designations. The LULC information that the Pollutant Loading portion of the model will actually use is contained within the file named subwat.shp. The 'Tabulate Areas' procedure was again used to determine the percentage of each LULC class, this time based on the total LULC distribution as assigned by AGNPS to the subwatershed cells. The file subwat.shp was selected as the 'Row Theme,' and the LULC class (called 'Field_id' in the file subwat.shp) was assigned to the 'Row Field.'   After calculating the percentage of each LULC class in both the original LULC layer and in the subwatershed file, the two layers could then be compared.

LULC class designations for the subwatershed cells were adjusted to more accurately reflect the class percentages in the original LULC layer, once the cell and reach data were imported into the Input Editor. To view these manual changes, the subwatershed cell information was exported from the Input Editor as a comma separated values file (*.dbf), and the *.dbf file was joined to

the file subwat.shp in the ArcView interface. The manual changes could be

visualized, and the 'Tabulate Areas' function was performed once again, using

the same subwat.shp file as the 'Row Theme' and the new revised LULC class

column as the 'Row Field.'

APPENDIX E

WEATHER DATA

Chapter 3

Actual climate data obtained from NOAA was received in a comma

separated value file format. These data files, as well as the synthetically

generated climate file, were opened in a Microsoft® Excel spreadsheet. The

desired spreadsheet columns in the NOAA dataset (daily precipitation and, when

available, maximum and minimum temperatures) were copied and pasted into

the synthetic data file to replace the GEM-generated data. Once the generated

data columns were replaced with actual historical data, the file was exported from

the spreadsheet format as a fixed width text file. These text files were renamed

following the DayClim_XX.inp nomenclature and placed in the 6_Editor_Datasets

folder with a *.inp file extension. Copies of all climate files were also placed in

the folder 5_Weather_Datasets.

Chapters 3 and 4

The monthly climate file (MonClim.inp) contained historical monthly

averages for dew point, sky cover, and wind speed for the Meridian location; and

the GEM program used historical data, also from the Meridian climate station, to

generate daily precipitation, maximum and minimum temperatures, dew point

temperature, sky cover, and wind speed and direction. GEM creates a

temporary daily climate file (~dayclim.tmp) that resides in the *~agedit* folder. It is

helpful to have GEM create this file, as it saves time in formatting the daily

climate input file correctly if you are using historical data.