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ORIGINAL RESEARCH

Assessing the Nitrogen and Phosphorus Loading in the Alabama (USA) River Basin Using PLOAD Model

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Abstract: Pollutant loadings in two watersheds, Mulberry and Catoma were assessed using the pollutant loading (PLOAD) model and model results were compared with those obtained from field sampling followed by laboratory analysis. The PLOAD model was used to determine water pollutants including total nitrogen (TN), total phosphorus (TP), orthophosphate (PO_4^{3-}), nitrite (NO_2^-) and nitrate (NO_3^-) in two watersheds, Mulberry and Catoma that are part of the Alabama River Basin. Results revealed that both Mulberry and Catoma watersheds had TN and TP values that exceeded the US Environmental Protection Agency (EPA) limits set for rivers and streams. The TN and TP values were in the range of hypertrophic for lakes, and eutrophic for rivers. The PLOAD model results were in agreement with analytical results. We conclude that PLOAD is a valid model for determining pollutant loading in watersheds and provides a relatively faster and cheaper method of assessing impairment of watershed bodies compared to conventional methods.

Keywords: PLOAD, non-point source (NPS) pollution, watersheds, nitrogen, phosphorous

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Introduction

According to the Alabama Department of Environmental Management (ADEM), about 18 percent of all surface water in the contiguous US flows through Alabama.[1] Approximately 1/6th of Alabama's surface area is inundated by various water bodies such as ponds, rivers, streams, reservoirs, and wetlands. Surface waters in Alabama cover approximately 500 square miles, including 47,072 linear miles of perennial streams and rivers. Nationally, Alabama ranks first in miles of navigable water, second in power generation water use, seventh in miles of perennial streams, tenth in industrial and mining water withdrawals, fourteenth in acres of lakes, reservoirs, ponds and total freshwater withdrawals, and twenty-fourth in acres of wetlands.[1] The Alabama River Basin faces a significant threat of pollution emanating from human activities, including both point sources and non-point sources (NPS). NPS pollution is difficult to manage and control due to its complicated generation and formation mechanism[2]. Hence, many studies have been conducted focusing on NPS pollution and management.[2–7] Runoff from agricultural land is one of the major sources of NPS pollution and often contributes the greatest pollution load to a watershed.[2,4,8–12] NPS is the nation's largest source of water quality problems, and has been suggested as the reason why approximately 40 percent of rivers, lakes, and estuaries are not able to meet their designated water quality criteria for fishing or swimming.[13] NPS pollution is the number one contributor to water quality degradation of Alabama and it accounts for two-thirds of the water quality impairments in streams and lakes.[14] Agriculture ranks first among NPS pollution of rivers, streams, lakes, ponds, and reservoirs in the United States.[15] Crop and animal production contributes excess nutrients in surface water due to fertilizer run-off and bacteriological contamination from animals raised in confined areas.[16] The major negative outcome of excess nutrients is eutrophication, caused by excess of nitrogen and phosphorus, promoting algal bloom.[17,18] Eutrophication causes problems such as altered water taste and odor, low dissolved oxygen, abnormal fish and other aquatic life problems, disruption of the normal functioning of the ecosystem, and hindering of recreation, fishing, hunting, and aesthetic enjoyment.[1,19] Eutrophication in many surface waters may stimulate harmful species, such as the zebra mussel in the Great Lakes.[20,21] The loading of streams with nutrients in the Alabama and the Mississippi rivers have resulted in hypoxia and dead zones in estuaries of the Gulf of Mexico and have thus led to a significant decline in its commercial productivity. Because of such serious effects, unchecked nutrient fluxes in the environment may lead to impacts on quality of life in the US.[22]

Eutrophic ecosystems can be described using terms referring to their supplies of growth-limiting nutrients (Table 1).Waters having relatively large supplies of nutrients are termed eutrophic (well nourished), and those having poor nutrient supplies are termed oligotrophic (poorly nourished). Waters having intermediate nutrient supplies are termed mesotrophic.[23,24]

The type and severity of surface water contamination often is directly related to land use types. Contaminants related to land use types include nitrogen, bacteria, salts, pesticides, and volatile organic compounds. There are three main categories of land use types (LUTs) including development, agriculture, and forestry. Each of these LUTs influences water quality in a unique manner.[25] Therefore, understanding the characteristics of each type of land use allows policy makers, land use planners, hydrologists, and water quality specialists to be more accurate when predicting water contamination. Urbanization increases impervious surface, which is linked to a decrease in surrounding water quality following the removal of vegetation cover that may lead to soil erosion, sedimentation and increased

Table 1. Trophic classification of lakes and streams based on total nitrogen and total phosphorous.[23,24]

Trophic state	TN (mg L^{-1})	TP (mg L^{-1})
Lakes		
Oligotrophic	<0.35	<0.01
Mesotrophic	0.35–0.65	0.01–0.03
Eutrophic	0.65–1.20	0.03–0.10
Hypertrophic	>1.20	>0.10
Streams		
Oligotrophic	<0.70	<0.025
Mesotrophic	0.70–1.50	0.025–0.075
Eutrophic	>1.50	>0.075

Notes: The terms oligotrophic, mesotrophic, and eutrophic correspond to systems receiving low, intermediate, and high inputs of nutrients. Hypertrophic is the term used for systems receiving greatly excessive nutrient inputs.
Abbreviations: TN, total nitrogen; TP, total phosphorus.

runoff.[26] Impervious surface as a result of urbanization is linked to increases in the amount of pollutants delivered to nearby streams. In some cases, the pollutants are generated by the impervious surface itself, such as polynuclear aromatic hydrocarbons (PAHs) from asphalt sealant or copper running off of roofing tiles.[27] In other cases, this link is due to the impervious surface preventing infiltration of water, bypassing systems which may naturally remove pollutants.[28] As the amount of impervious surface in an area increases, so does its detrimental effects. Agricultural land use is associated with increased nutrients coming from fertilizer and sediment runoff from exposed land surface after tillage. Some agricultural practices such as row-cropping and continuous grazing often lead to decreased vegetation cover, increased erosion and associated pollutant transport.[27] Agricultural land used close to streams can lead to stream bank erosion and affect the ability of future vegetation to buffer out pollutants.[29] Contrary to the previous two land use categories, which are often associated with declining water quality, forestry is generally associated with improved water quality by offering mechanisms for water cleaning and stabilization with riparian forests.[27]

In order to maintain the quality and quantity of surface water and control eutrophication, it is important to promote clean water initiatives for surface water at the state and local level. According to the Clean Water Act (CWA), states are required to set specific criteria for possible pollutants of its surface waters that are similar to the drinking water standards set by the federal government. Alabama does not have specific nutrient criteria set for possible pollutants like nitrogen or phosphorus. An assessment of 463,111 acres of lakes and reservoirs in Alabama carried out by ADEM revealed that 9 percent of surface water resources did not support their designated use classification and 25 percent partially supported their use classification.[30] It is important to determine the level of nutrient loading and develop rapid assessment tools and procedures for these loadings as a first step to developing better management practices.

There are various models that have been used to study pollutants in watersheds. The hydrologic simulation program for FORmula TRANslation FORTRAN (HSPF) is a comprehensive, conceptual, dynamic watershed scale model that simulates NPS hydrology and water quality, combines it with point source contributions, and performs flow and water quality routing in the watershed reaches.[31] The soil and water assessment tool (SWAT), developed at the USDA-ARS, is a physically based, distributed parameter continuous simulation model that runs on daily time step.[32] It is a long-term simulation model capable of predicting sediment, nutrient, and pesticide yields from agricultural watersheds. SWAT has been used to predict, over long periods of time, the impact of land management practices on water, sediment, and agricultural chemical loads in large complex watersheds with varying soils, land use, and management conditions.

HSPF and SWAT have been used to model the hydrology of the 2150 square mile Iroquois River watershed located in central Illinois and to model daily output flow, sediment, and nutrients measured at five stream sites of the Upper North Bosque River watershed located in central Texas.[31,33] In both studies calibration and validation results from both HSPF and SWAT showed that the models generally predict daily, and average monthly and annual stream flows that are close to respective observed stream flows. However, the average daily flow, sediment, and nutrient loading simulated by SWAT were reported to be closer to measured values, with SWAT generally appearing to be a better predictor of nutrient loading during both the calibration and verification periods.[31]

QUAL2E is a steady state water quality and eutrophication model that allows fate and transport modeling for point and NPS loadings. QUAL2E is used where users are concerned with a dissolved oxygen (DO) endpoint in an effluent dominated system where one can justify the use of flow steady state assumptions.[34] QUAL2E model was used in the Kao-Ping River Basin in Taiwan where it successfully predicted concentrations of biochemical oxygen demand, dissolved oxygen, total phosphate-phosphorus, and ammonia-nitrogen for the entire river system.[35] QUAL2E showed that full compliance could not be accomplished with the practices that were in place and that water transfer in the upstream area further increased negative impacts on the water quality in the wet season.[35]

The PLOAD (pollutant loading) model, developed by Cornell, Howland, Hayes, Merryfield and Hill (CH_2M-HILL) company, is a simple, screening level model that can provide estimates of nonpoint source pollutant loading on an annual average basis.[36,37] The model allows for an evaluation of the relative magnitude of change in pollutant loading associated with various future scenarios. In addition, results can be used to target management measures to those areas with the highest existing and/or future pollutant loading.

The objectives of this study were to: (i) assess the loadings of nitrogen and phosphorus in two watersheds, Mulberry and Catoma, that are part of Alabama River Basin using PLOAD model and (ii) compare the results of the PLOAD model with laboratory analytical results.

Methodology

Study area and the sampling point locations

The study area covered two watersheds, Mulberry and Catoma, located in the Alabama River Basin, southeast of the United States (US). Mulberry watershed is located mostly inside Chilton and Autauga Counties of Alabama and is more rural compared to the Catoma watershed. It is made up of eight sub-watersheds called Buck, Coon, Little Mulberry, Lower Little Mulberry, Lower Mulberry, Middle Mulberry, Upper Little Mulberry and Upper Mulberry (Fig. 1). Catoma watershed is located entirely inside Montgomery County, which is in the south-central part of the Alabama in the northern part of the Coastal Plain. It is made up of nine sub-watersheds called Antioch Branch, Baldwin Slough, Baskin, Caney, Little Catoma, Miller Pond,

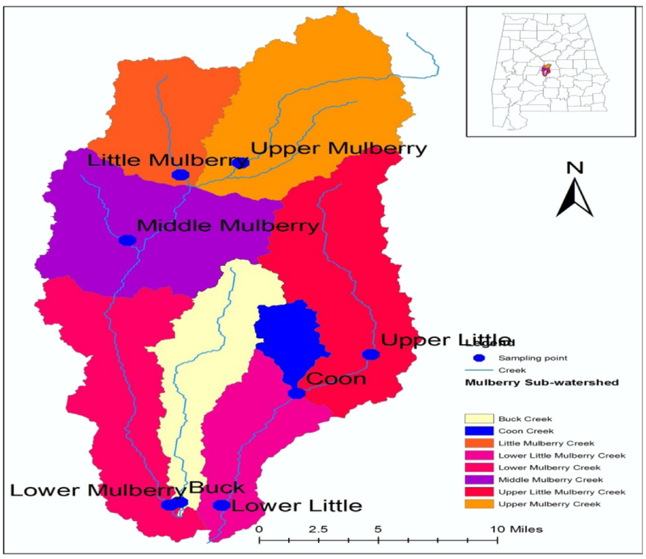

Figure 1. Sampling points for Mulberry watershed.

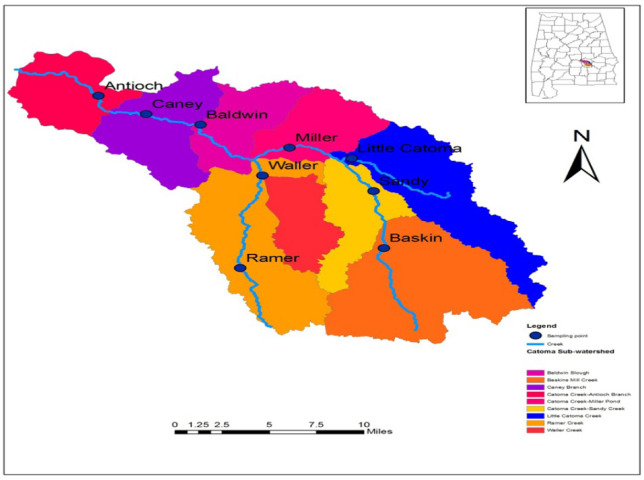

Figure 2. Sampling points for Catoma watershed.

Ramer, Sandy and Waller (Fig. 2). Figures 1 and 2 show the sampling points within Mulberry and Catoma watersheds, respectively.

Agriculture makes up about 50 percent of the major land use in the Catoma watershed (Table 2). About 25 percent of the land is used for field crops or pasture. Most of the acreage is in large farms, ranging up to several thousand acres in size.

About 35 percent of the woodland in the Catoma watershed is owned by corporations or individuals that have holdings of more than 1,000 acres.[39] Among the sub-watersheds, Miller, Baldwin and Caney have agriculture as the dominant land use compared to the Antioch Branch, Ramer, Waller, Sandy, Little Catoma and Baskin that have both agriculture and forest as dominant land use types. Although agriculture is a dominant land use, the cultivated acreage in Montgomery County where Catoma is located has decreased in recent years due to industrial growth in the city of Montgomery. Unlike the Catoma water-

Table 2. Land use in Catoma and Mulberry watersheds.[38]

Land use	Catoma watershed	Mulberry watershed
Urban or built-up land	8%	1%
Agriculture land	50%	20%
Range land	1%	10%
Forest land	35%	63%
Water	3%	1%
Wet land	2%	2%
Barren land	1%	3%
Total	100%	100%

shed, the Mulberry watershed is mainly forested, with about 63% forest cover and 20% agricultural land. In Upper, Middle, Upper Little, and Lower Little Mulberry and Coon sub-watersheds, forestry is the dominant land use type. However, in Little and Lower Mulberry and Buck sub-watersheds, both forestry and agricultural lands are equally dominant. Most of the agricultural land is used for field crops or pasture. Corn, cotton, and peaches are the principal crops. Beef cattle, hogs, and dairy cattle are the principal kinds of livestock.

PLOAD model

The PLOAD model, which was developed by CH_2M-HILL, is a simplified, GIS-based model used to calculate the pollutant loads for watersheds (Fig. 3).[34]

PLOAD model estimates NPS pollution on an annual average basis, for any user-specified pollutant. Watershed boundary and land-use GIS data coverages are required, where the watersheds define the areas for which the pollutant loads are calculated. Watershed boundaries are delineated using the United States Geological Survey (USGS) Digital Elevation Model (DEM) data files. Pollutant loading rate, impervious factor, and BMP efficiency information (if BMPs are modeled) are compiled in tabular files for use in the PLOAD application. The pollutant loading tables consist of the event mean concentration (EMC) and the export coefficient. The EMC and export coefficient tables contain pollutant rates for urban and rural land use types, respectively. The user may use PLOAD to estimate pollutant loads for any pollutant if EMCs or export coefficients are available. PLOAD calculates pollutant loads using one of two methods: (i) export coefficient method, that requires data on watershed boundaries, land use coverage, export coefficient, BMP efficiency and point source pollutant data, and (ii) simple method, that is based on event mean concentration (EMC) produced from a specific land use. The required data for the simple method include watershed boundaries, land use coverage, annual precipitation, event mean concentration (EMC), and land use imperviousness

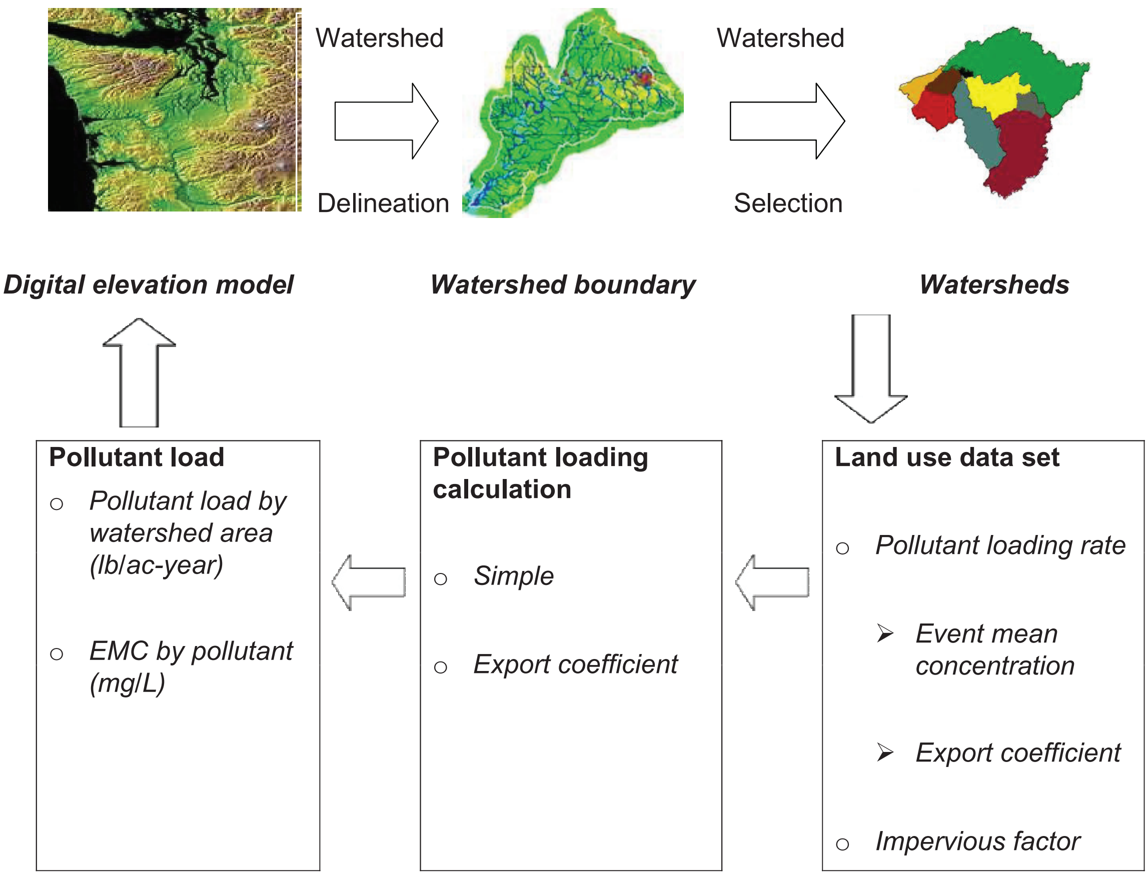

Figure 3. Schematic of the PLOAD model.[40]

data. If desired, the BMP efficiency data and point source pollutant data may be included. In the export coefficient method, only an export coefficient table and area of land use type are needed to calculate the pollutant loadings. However, due to unavailability of export coefficient data in many parts of the US, the method has limited use. This contrasts with the simple method where the required input parameters are readily available. Hence, the simple method was selected for this study. The boundaries for Mulberry and Catoma watersheds were delineated automatically by selecting the relevant watersheds from the USA map available at the Environmental Protection Agency (EPA) Better Assessment Science Integrating point and Non-point Sources (BASINS) system.[41] Hydrologic information in BASINS is arranged in hydrologic unit identified by a unique Hydrologic Unit Code (HUC) ranging from 2 to 12 digits (even numbers) based on the levels of classification in the hydrologic unit system (Table 3).

BASINS 4.0 has up to an 8-digit HUC Sub-basin. Therefore, in order to get to the subwatershed level, a 12-digit HUC was necessary. This was obtained from Alabama Cooperation Extension System (ACES) and imported to BASINS 4.0.[41] Relevant land use type, annual precipitation, event mean concentration (EMC) data, land use, impervious data and the ratio of storms producing runoff were imported into PLOAD and NO_2^-/NO_3^-, PO_4^{3-}, TN and TP outputs were generated. The PLOAD output results were compared with those obtained from field sampling followed by laboratory analysis.

Field data collection and analysis

Triplicate water samples were collected from each of the sub-watersheds, in Mulberry (Fig. 1) and Catoma (Fig. 2), using 125 mL Nalgene® bottles. At each sampling point three water samples were collected at an approximately one- to two-foot depth from the water surface. The samples were composited, placed in Nalgene® bottles, labeled, stored in ice and then transported to the Water Quality Laboratory at Tuskegee University for analysis. Analysis was done for total nitrogen (TN) and total phosphorus (TP) using a modification of peroxodisulfate oxidation method.[42] Twenty grams of $K_2S_2O_8$ and 3.0 g of NaOH were dissolved in 1 L of water to create an oxidizing solution. Five milliliters (5 mL) of the oxidizing solution was added to 5 mL of each water sample in a 10 mL test tube. The test tube was immediately capped and autoclaved at 120 °C for 30 minutes. After oxidation, the solutions were cooled to room temperature. The solutions were then analyzed for Nitrate-(NO_3^-) using the cadmium reduction method and orthophosphates (PO_4^{3-}) by the ascorbic acid reduction method and spectrophotometer (Model No. HACH DR/4000) used to determine the concentration.[43] A sample cell was filled with 10 mL of sample and the contents of one Phos Ver 3® phosphate powder pillow was added to the cell (the prepared sample). The cell was then shaken to mix and then left for two minutes for reaction to take place. A blank cell was prepared and placed into the cell holder to calibrate the spectrophotometer. The readings were done at wavelength 890 nm for orthophosphate, TP and 408 nm for TN. Statistical analysis was done using the mixed models methodology as implemented in PROC MIXED of PC SAS Version 9.2 to analyze the level of pollutant loadings.[45] These included the Total nitrogen (TN), total phosphorus (TP), orthophosphate (PO_4^{3-}), nitrite (NO_2^-) and nitrate (NO_3^-) in two watersheds, Mulberry and Catoma that are part of the Alabama River Basin. Where variables showed significant differences, multiple comparison procedures were completed using the "simulation" option with LS means of PROC

Table 3. Hydrologic Unit Code (HUC) description.[34]

Code	Level	Official name	Number of units in US	General description
HUC-2	1	Region	21	Major land areas
HUC-4	2	Subregion	222	Subregions
HUC-6	3	Basin	352	Accounting unit
HUC-8	4	Subbasin	2,149	Cataloging unit
HUC-10	5	Watershed	22,000	Drainage basin
HUC-12	6	Sub-watershed	160,000	Subdivisions of the drainage basin

MIXED. Pearson correlations for the PLOAD versus laboratory data was performed using PROC CORR in SAS Version 9.2.[44]

Results and Discussion

PLOAD model results

The event mean concentration of total nitrogen (TN) determined using the PLOAD model in Mulberry watershed (Fig. 4) ranged from 1.18 mg L^{-1} in Lower, Upper Little and Lower Little Mulberry sub-watersheds, to 1.21 mg L^{-1} in Little Mulberry and Buck sub-watersheds. The average TN event mean concentration for the entire watershed was 1.19 mg L^{-1}. The TN loading ranged from 0.65 kg ha^{-1} in Coon and Buck sub-watersheds to 0.72 kg ha^{-1} in Little Mulberry sub-watersheds. The TN loading per year ranged from 2,301 kg yr^{-1} in Coon sub-watershed to 15,189 kg yr^{-1} in Upper Mulberry sub-watershed. The TN loading per year for Mulberry watershed was 83, 289 kg yr^{-1}.

For Mulberry watershed, the event mean concentrations for total phosphorus (TP) ranged from 0.12 mg L^{-1} in Buck sub-watershed to 0.13 mg L^{-1} in the Upper Little and Lower Mulberry sub-watersheds (Fig. 5). The average TP event mean concentration in the Mulberry watershed was 0.125 mg L^{-1}. The TP loading per acre in Mulberry watershed ranged from 0.129 to 0.147 kg ha^{-1}. The highest TP loading per acre was found in Little Mulberry sub-watershed (0.147 kg ha^{-1}) while the lowest loading of 0.129 kg ha^{-1} was found in Coon sub-watershed. The highest TP loading of 1,758 kg yr^{-1} was found in Upper Little sub-watershed, while the lowest loading was found in Coon sub-watershed (226 kg yr^{-1}). The total loading of TP in Mulberry watershed was 9,299 kg yr^{-1}.

The results of TN concentrations determined by the PLOAD model in Catoma watershed are shown (Fig. 6). Total Nitrogen concentration in Catoma ranged from 1.13 mg L^{-1} in Little Catoma sub-watershed to 1.56 mg L^{-1} in Baldwin Slough sub-watershed. The average TN concentration in the Catoma watershed was 1.29 mg L^{-1}. The loading per acre in Catoma watershed ranged from 0.73 kg ha^{-1} in Waller sub-watershed to 3.36 kg ha^{-1} in Caney Branch and Baldwin sub-watershed. The TN loading per year for Catoma watershed ranged from 4,242 kg yr^{-1} in Waller sub-watershed to 40,718 kg yr^{-1} in Caney Branch sub-watershed. The total TN loading per year in the Catoma watershed was 136,097 kg yr^{-1}.

The results of TP concentration determined using the PLOAD model for Catoma watershed are shown (Fig. 7). TP ranged from 0.200 mg L^{-1} to 0.283 mg L^{-1}. The average TP event mean concentration in the Catoma watershed was 0.221 mg L^{-1}. The TP loading per acre ranged from 0.127 kg ha^{-1} in Baskin Mill sub-watershed to 0.791 kg ha^{-1} in Caney sub-watershed. The mean TP loading was 0.297 kg ha^{-1}. The TP

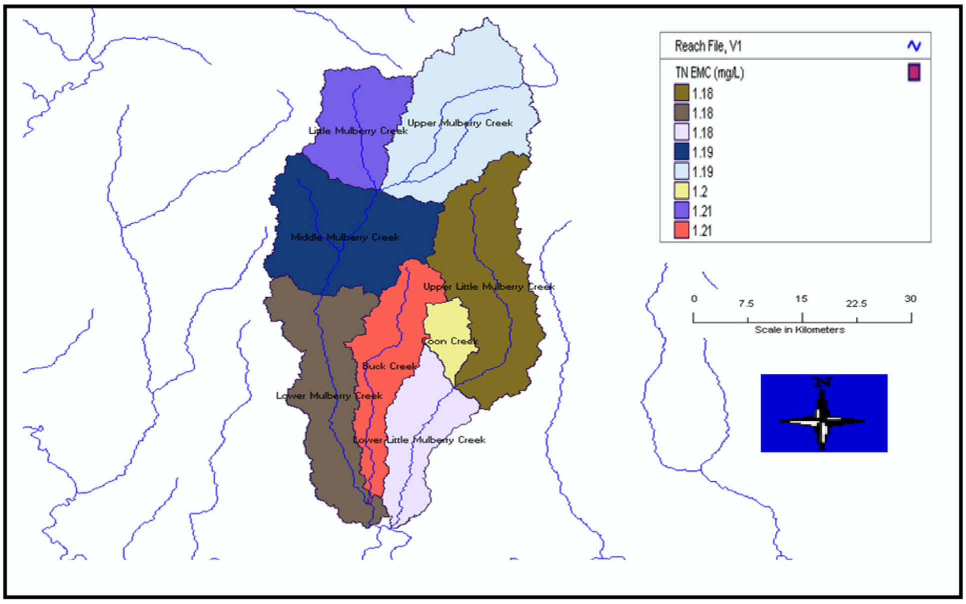

Figure 4. The PLOAD model TN concentration (mg L^{-1}) for Mulberry watershed.

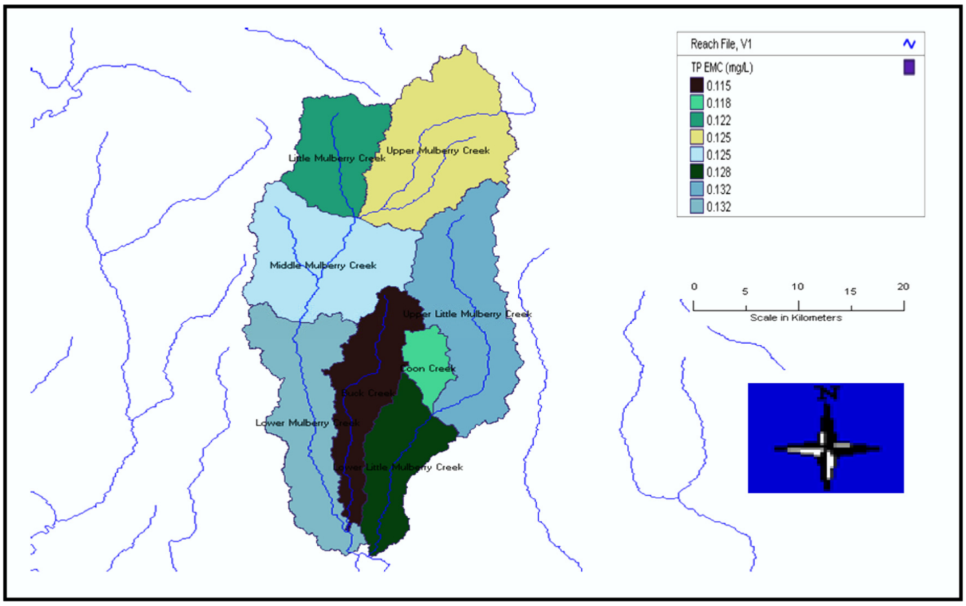

Figure 5. The PLOAD TP concentration (mg L^{-1}) for Mulberry watershed.

loading per year ranged from 740 kg yr^{-1} in Waller sub-watershed to 8,059 kg yr^{-1} in Caney Branch sub-watershed. The total TP loading in Catoma watershed was 24,885 kg yr^{-1}.

Laboratory data results

The laboratory results for total nitrogen (TN), total phosphorus (TP), orthophosphate (PO_4^{3-}), nitrite (NO_2^-) and nitrate (NO_3^-) in two watersheds, Mulberry and Catoma are shown in Table 4.

The highest concentration of TN was found in Little Mulberry sub-watershed and Buck sub-watershed, while the lowest concentration was found in Middle Mulberry and Lower Little Mulberry sub-watersheds. The TN value measured in all of the Mulberry sub-watersheds exceeded the EPA recommendation maximum value of 0.69 mg L^{-1} for rivers and streams. The laboratory results for NO_2^-/NO_3^- in the Mulberry watershed ranged from 0.55 mg L^{-1} in Upper Mulberry, Middle Mulberry, Buck and Coon sub-watersheds to 0.6 mg L^{-1} in Little Mulberry, Upper Little and Lower Little Mulberry sub-watersheds. The laboratory results for TP for the Catoma watershed showed that the highest concentration was found in Baldwin-Slough sub-watershed, while the lowest concentration was found in Waller sub-watershed. The highest concentration of PO_4^{3-} was found in Caney, while the lowest concentration was found in Miller, Ramer, Waller, Sandy and Baskin sub-watersheds. Although no significant ($P < 0.05$) differences in PO_4^{3-} values were observed between the sub-watersheds, the trends of PO_4^{3-} concentration for samples collected from the watershed and analyzed in the laboratory and the values determined using the PLOAD model were similar.

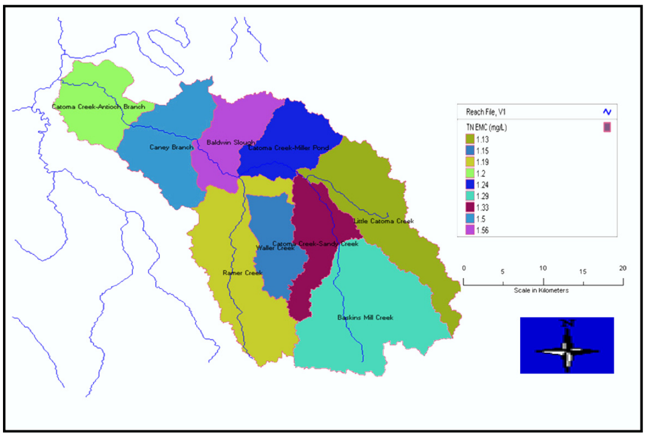

Figure 6. The PLOAD model TN concentration (mg L^{-1}) for Catoma watershed.

The laboratory results for TN for the Catoma watershed showed that the highest concentration was in Miller Pond sub-watershed. Ramer, Little Catoma, Baskin and Sandy sub-watersheds had moderate values, while the lowest concentration was in the Antioch Branch and Waller sub-watersheds. The TN values of Antioch Branch sub-watershed showed highly significantly lower TN values ($P < 0.05$) than

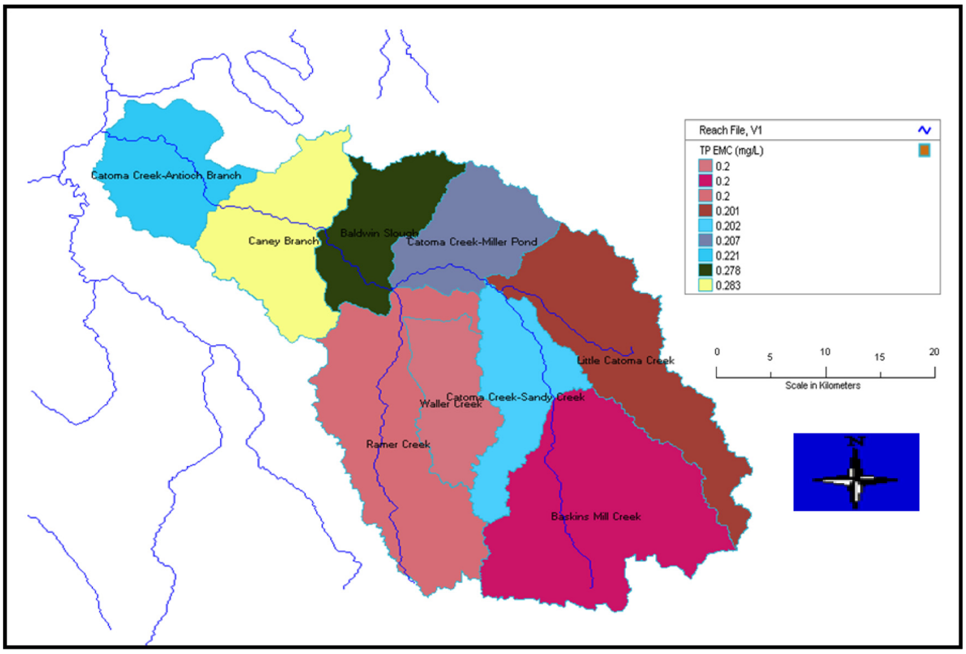

Figure 7. The PLOAD model TP concentration (mg L^{-1}) for Catoma watershed.

all other sub-watersheds except for Ramer, Waller, and Little Catoma sub-watersheds. On the other hand, Miller Pond sub-watershed showed highly significantly higher TN values ($P < 0.05$) than all the other sub-watersheds, except Caney and Baldwin Slough sub-watersheds. The NO_2^-/NO_3^- concentrations in the Catoma watersheds ranged from of 0.5 mg L^{-1} in Ramer and Waller sub-watersheds to 0.70 mg L^{-1} in Little Catoma sub-watershed. In Catoma watershed, the only significant ($P < 0.05$) differences in NO_2^-/NO_3^- values were observed between Antioch Branch and Little Catoma sub-watersheds, Ramer and Little Catoma sub-watersheds, and Waller and Little Catoma sub-watersheds.

The TN revealed no significant ($P < 0.05$) differences among the Mulberry sub-watersheds except between Little Mulberry and Middle Mulberry sub-watersheds, between Little Mulberry and Lower Little Mulberry sub-watersheds, between Middle Mulberry and Buck sub-watersheds and between Buck and Lower

Table 4. Laboratory results of pollutants in Mulberry and Catoma watershed.

Sub-watershed	*Mulberry watershed				**Catoma watershed			
	NO_2/NO_3 (mg L^{-1})	PO_4^{3-} (mg L^{-1})	TN (mg L^{-1})	TP (mg L^{-1})	NO_2/NO_3 (mg L^{-1})	PO_4^{3-} (mg L^{-1})	TN (mg L^{-1})	TP (mg L^{-1})
1	0.60	0.12	1.40	0.39	0.55	0.20	1.30	0.43
2	0.55	0.11	1.30	0.32	0.60	0.22	1.60	0.35
3	0.55	0.11	1.20	0.35	0.60	0.21	1.60	0.48
4	0.60	0.13	1.30	0.38	0.60	0.20	1.70	0.38
5	0.55	0.11	1.40	0.30	0.50	0.20	1.40	0.34
6	0.60	0.12	1.30	0.35	0.50	0.20	1.30	0.26
7	0.55	0.12	1.30	0.26	0.60	0.20	1.50	0.32
8	0.60	0.12	1.20	0.38	0.70	0.21	1.40	0.32
9	–	–	–	–	0.60	0.20	1.50	0.28
Average	0.57	0.12	1.30	0.34	0.58	0.20	1.50	0.35

Notes: *Mulberry watershed: 1 = Little Mulberry, 2 = Upper Mulberry, 3 = Middle Mulberry, 4 = Lower Mulberry, 5 = Buck, 6 = Upper Little, 7 = Coon, 8 = Lower little Mulberry; **Catoma watershed: 1 = Antioch Branch, 2 = Caney, 3 = Baldwin Slough, 4 = Miller Pond, 5 = Ramer, 6 = Waller, 7 = Sandy, 8 = Little Catoma, 9 = Baskin.

Table 5. Least Significance Mean (LSM) of TP for Mulberry watershed.

Sub-watershed	1	2	3	4	5	6	7	8	LSM of TP
1		<0.01	<0.05	>0.05	<0.001	<0.05	<0.001	>0.05	0.39
2	<0.01		>0.05	<0.01	>0.05	>0.05	<0.01	<0.01	0.32
3	<0.05	>0.05		>0.05	<0.05	>0.05	<0.001	>0.05	0.35
4	>0.05	<0.01	>0.05		<0.001	>0.05	<0.001	>0.05	0.38
5	<0.001	>0.05	<0.05	<0.001		<0.05	<0.05	<0.001	0.30
6	<0.05	>0.05	>0.05	>0.05	<0.05		<0.001	>0.05	0.35
7	<0.001	<0.01	<0.001	<0.001	<0.05	<0.001		<0.001	0.26
8	>0.05	<0.01	>0.05	>0.05	<0.001	>0.05	<0.001		0.38

Notes: ***Significant ($P < 0.001$); **Significant ($P < 0.01$); *Significant ($P < 0.05$); NS = Non significant. 1 = Little Mulberry, 2 = Upper Mulberry, 3 = Middle Mulberry, 4 = Lower Mulberry, 5 = Buck, 6 = Upper Little Mulberry, 7 = Coon, 8 = Lower Little Mulberry.

Little Mulberry sub-watersheds. Little Mulberry and Buck sub-watersheds were observed to have the highest TN concentration (1.4 mg L^{-1}; data not shown).

The TP values for Little Mulberry sub-watershed was significantly ($P < 0.05$) higher than all the other sub-watersheds except Lower Mulberry and Lower Little Mulberry sub-watersheds (Table 5).

The TP in the Coon sub-watershed was significantly ($P < 0.05$) lower than all the other sub-watersheds. With the exception of Little Mulberry and Buck sub-watersheds, no significant differences were observed between Upper Little Mulberry and other sub-watersheds. The variation in TP among the sub-watersheds in Mulberry was higher than that observed for TN. The trends of TP concentration for samples collected from the watershed and analyzed in the laboratory were similar to results estimated using the PLOAD model. The TP concentration in Coon sub-watershed was 0.26 mg L^{-1} while the value obtained using the PLOAD model was 0.12 mg L^{-1}. In the Upper Mulberry sub-watershed, the measured TP concentration was 0.32 mg L^{-1} while 0.13 mg L^{-1} was estimated using the PLOAD model.

The TN values of Antioch Branch sub-watershed showed highly significantly lower TN values ($P < 0.05$) than all other sub-watersheds except for Ramer, Waller, and Little Catoma sub-watersheds. On the other hand, Miller Pond sub-watershed showed highly significantly higher TN values ($P < 0.05$) than all the other sub-watersheds, except Caney and Baldwin Slough sub-watersheds (Table 6).

The Antioch Branch sub-watershed showed significantly higher TP values ($P < 0.001$) than most sub-watersheds, but significantly lower values ($P < 0.001$) than Baldwin Slough sub-watershed (Table 7).

The Baskin sub-watershed on the other hand showed significantly lower TP values ($P < 0.01$)

Table 6. Least Significant Mean (LSM) of TN for Catoma watershed.

Sub-watershed	1	2	3	4	5	6	7	8	9	LSM of TN
1		<0.01	<0.01	<0.001	>0.05	>0.05	<0.05	>0.05	<0.05	1.30
2	<0.01		>0.05	>0.05	<0.05	<0.01	>0.05	<0.05	>0.05	1.60
3	<0.01	>0.05		>0.05	<0.05	<0.01	>0.05	<0.05	>0.05	1.60
4	<0.001	>0.05	>0.05		<0.01	<0.001	<0.05	<0.01	<0.05	1.70
5	>0.05	<0.05	<0.05	<0.01		>0.05	>0.05	>0.05	>0.05	1.40
6	>0.05	<0.01	<0.01	<0.001	>0.05		<0.05	>0.05	<0.05	1.30
7	<0.05	>0.05	>0.05	<0.05	>0.05	<0.05		>0.05	>0.05	1.50
8	>0.05	<0.05	<0.05	<0.01	>0.05	>0.05	>0.05		>0.05	1.40
9	<0.05	>0.05	>0.05	<0.05	>0.05	<0.05	>0.05	>0.05		1.50

Notes: ***Significant ($P < 0.001$); **significant ($P < 0.01$); *significant ($P < 0.05$); NS = Non significant. [a]1 = Antioch Branch, 2 = Caney, 3 = Baldwin slough, 4 = Millor Pond, 5 = Ramer, 6 = Waller, 7 = Sandy, 8 = Little Catoma, 9 = Baskin.

Table 7. Least Significant Mean (LSM) of TP for Catoma watershed.

Sub-watershed	1	2	3	4	5	6	7	8	9	LSM of TP
1		<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.43
2	<0.001		<0.001	<0.01	>0.05	<0.0001	<0.05	<0.05	<0.0001	0.35
3	<0.001	<0.001		<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.48
4	<0.001	<0.01	<0.001		<0.001	<0.001	<0.001	<0.001	<0.001	0.38
5	<0.001	>0.05	<0.001	<0.001		<0.001	>0.05	>0.05	<0.001	0.34
6	<0.001	<0.001	<0.001	<0.001	<0.001		<0.001	<0.001	<0.01	0.25
7	<0.001	<0.01	<0.001	<0.001	>0.05	<0.0001		>0.05	<0.01	0.32
8	<0.001	<0.01	<0.001	<0.001	>0.05	<0.0001	>0.05		<0.01	0.32
9	<0.001	<0.001	<0.001	<0.001	<0.0001	<0.01	<0.01	<0.01		0.28

Notes: ***Significant ($P < 0.001$); **significant ($P < 0.01$); *significant ($P < 0.05$); NS = Non significant. 1 = Antioch Branch, 2 = Caney, 3 = Baldwin slough, 4 = Millor Pond, 5 = Ramer, 6 = Waller, 7 = Sandy, 8 = Little Catoma, 9 = Baskin.

than most of other sub-watersheds with the exception of Ramer and Sandy sub-watersheds. It showed significantly higher TP values ($P < 0.001$) than Waller sub-watershed. In Caney, Baldwin and Miller sub-watersheds, the nitrogen and phosphorus concentrations observed were considerably higher than other sub-watersheds. This may be explained by the agricultural land use and addition by point sources from the adjacent urban area.

The PLOAD versus laboratory results for TN, NO_2/NO_3 and PO_4^{3-} were very comparable for both Mulberry and Catoma watersheds (Table 8).

For TP, it is apparent that the PLOAD model yielded results that were relatively lower than those of laboratory analyses. The TP range was 0.12–0.13 mg L^{-1} for PLOAD compared to 0.26–0.39 mg L^{-1} from laboratory analyses for Mulberry watershed. For Catoma watershed the TP range was 0.22–0.28 mg L^{-1} and 0.26–0.48 mg L^{-1}, respectively, for PLOAD and laboratory analyses.

The results revealed that both Mulberry and Catoma watersheds had TN and TP values that exceeded the US EPA limits of 0.69 mg L^{-1} for TN and 0.04 mg L^{-1} for TP set for rivers and streams Comparatively, Catoma was found to be more impaired than Mulberry watershed, suggesting the impact of land use types. Also, for both watersheds, the trophic levels for TN and TP would be classified as hypertrophic for lakes based eutrophic for streams, while the TN and TP would be classified as ranging from mesotrophic to eutrophic for Mulberry watershed (see Table 1).

The PLOAD and laboratory results were compared using a Pearson's correlation. The parameters compared were the TN, TP, PO_4^- and NO_2/NO_3 concentrations. The PLOAD and laboratory data showed a high correlation which was highly significant for TN, TP, and PO_4^{3-}, but not for NO_2/NO_3 in both watersheds and PO_4^{3-} in the Mulberry watershed. The results for the the Pearson correlation between PLOAD and laboratory data for TN in Mulberry watershed (Fig. 8) showed a highly significant positive correlation ($P < 0.01$; r = 0.92). Similarly, the TP values for the Mulberry watershed showed a significant positive correlation ($P < 0.05$; r = 0.83) (Fig. 9).

Table 8. PLOAD versus laboratory data for Mulberry watershed and Catoma watershed.

	Mulberry watershed		Catoma watershed		EPA limits
	PLOAD	Laboratory	PLOAD	Laboratory	
TN	1.18–1.21	1.20–1.40	1.13–1.56	1.30–1.70	0.69
TP	0.12–0.13	0.26–0.39	0.22–0.28	0.26–0.48	0.04
NO_2/NO_3	0.50	0.55–0.60	0.50–0.57	0.50–0.70	–
PO_4^{3-}	0.10	0.11–0.13	0.10–0.11	0.20–0.22	–

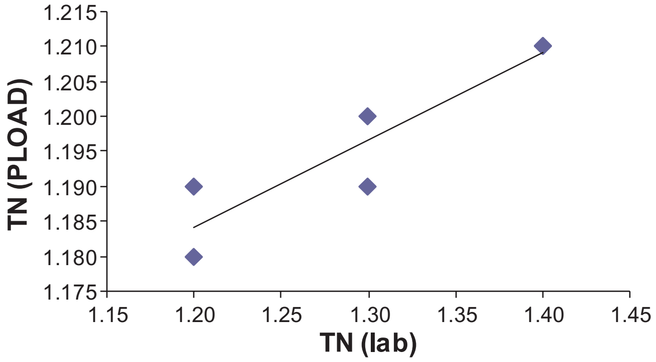

Figure 8. Pearson correlation between PLOAD and laboratory TN data in Mulberry Creek watershed.

The results from this study suggest that PLOAD models TP and TN loadings relatively well and can be useful in determining possible impairment of river bodies. This finding may help speed up identifying possible impairment quicker than the present procedures.

Conclusion

This study was conducted to determine whether nitrogen and phosphorus loadings in Mulberry watershed and Catoma watersheds in the Alabama River Basin could be fairly well predicted using the PLOAD model and to determining the nitrogen and phosphorus respective watersheds. We selected two adjacent watersheds, one that was listed as impaired according to the Alabama State 303 (d), 2008 list (Catoma) and the other (Mulberry) which was considered unimpaired. The PLOAD outputs (NO_2^-/NO_3^-, PO_4^{3-}, TN and TP) were determined using and laboratory analyses. Water samples were collected from eight sub-watersheds of Mulberry watershed and nine sub-watersheds of Catoma watershed with three replicates per sampling location. Each replicate was a composite (mixture) of three subsamples. Each of the replicates was analyzed for NO_2^-/NO_3^-, PO_4^{3-}, TN and TP and compared to the PLOAD outputs. Both watersheds were found to be impaired with respect to TN and TP as both exceeded the EPA recommendation standards of 0.69 mg L^{-1} for TN and 0.04 mg L^{-1} for TP in river and stream. Comparatively, the Catoma Watershed exhibited a higher loading than the Mulberry Watershed. The differences in the nutrient loadings might be attributed to the differences in land use types for the two watersheds. Agriculture is the major land use in the Catoma watershed, whereas Mulberry watershed is mainly forested, with about 63% forest cover and 20% agricultural land. The results from the study suggest that PLOAD models TP and TN loadings fairly well and can be useful in determining possible impairment of river bodies. This finding may help speed up the identification of possible impairment quicker than present commonly-used procedures.

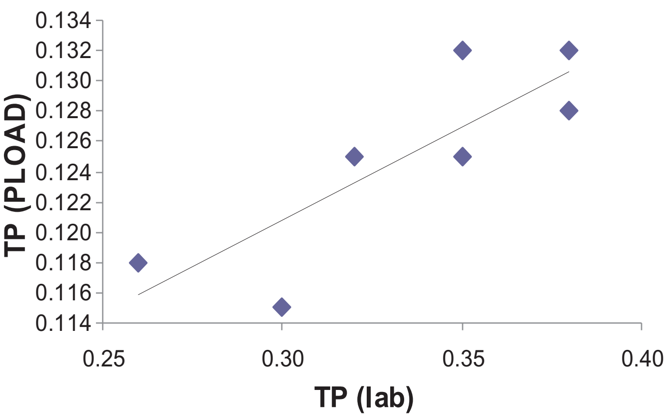

Figure 9. Pearson correlation between laboratory and PLOAD TP data in Mulberry Creek watershed.

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Competing Interests

Author(s) disclose no potential conflicts of interest.

Author Contributions

Conceived and designed the experiments: DG, LG, RA. Analyzed the data: DG, LG. Wrote the first draft of the manuscript: DG. Contributed to the writing of the manuscript: DG, LG, RA. Agree with manuscript results and conclusions: DG, LG, RA. Jointly developed the structure and arguments for the paper: DG, LG, RA. Made critical revisions and approved final version: LG. All authors reviewed and approved of the final manuscript.

Disclosures and Ethics

As a requirement of publication author(s) have provided to the publisher signed confirmation of compliance with legal and ethical obligations including but not limited to the following: authorship and contributorship, conflicts of interest, privacy and confidentiality and (where applicable) protection of human and animal research subjects. The authors have read and confirmed their agreement with the ICMJE authorship and conflict of interest criteria. The authors have also confirmed that this article is unique and not under consideration or published in any other publication, and that they have permission from rights holders to reproduce any copyrighted material. Any disclosures are made in this section. The external blind peer reviewers report no conflicts of interest.

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