PREDICTING SEDIMENT AND NUTRIENT LOADS IN TROPICAL WATERSHEDS IN PUERTO RICO

By

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ABSTRACT

High and resilient sediment and nutrient concentrations in streams are precursors or indicators of stream impairment. According to recent estimates by USEPA (2001), about 40% of the monitored national water supplies do not meet quality standards to support designated uses. A similar situation is observed in Puerto Rico. The 2002 water quality inventory of Puerto Rico reports that 67% of the monitored river miles were impaired (JCA, 2002). In this study water quality parameters were sampled during the 2004-2005 water year in four sub watersheds of the Río Grande de Arecibo watershed, located in the central part of Puerto Rico. The objective of this thesis research was to determine sediment and nutrient loads and to propose mathematical relationships to relate sediment and nutrient loads to physiographic and hydrologic properties of the sub watersheds. Sampled variables included pH, temperature, conductivity, salinity, water velocity, total suspended sediment, chlorophyll-a, total Kjeldahl nitrogen (TKN), total phosphorus (TP) and dissolved phosphorus (DP) loads. Sediment loads and yields from storm events ranged from 3,041 metric tons/event, 32.45 metric tons/km^2 (Río Limón) to 29.99 metric tons/event, 1.69 metric tons/km^2 (Río Jauca). Nutrient concentrations range, from 6.49 to 1.11 mg/L of TKN, 1.82 to 0.05 mg/L of TP and 0.24 to 0.05 mg/L of DP. A method for developing predictive equations of nutrient and sediment loads for tropical sub watersheds is presented in this thesis research. TSS, TKN, TP and DP annual load predictive equations were generated and calibrated using the Partial Least Square regression method in the statistical software MINITAB version 14. The predicted R^2 values for the TSS, TKN, TP and DP annual loads using a 2-component model are 0.74, 0.95, 0.97 and 0.99.

RESUMEN

Altas y persistentes concentraciones de sedimentos y nutrientes en las corrientes de agua son indicadores o precursores de deterioro en las corrientes. De acuerdo a estimados recientes de la Agencia de Protección Ambiental de los Estados Unidos de América (2001), el 40% del agua abastecida a nivel nacional no cumple los requisitos necesarios para respaldar los usos designados. Una situación similar se observa en Puerto Rico. El inventario de calidad de agua de Puerto Rico del 2002, reporto que el 67% de las aguas monitoreadas estaban contaminadas (Junta Calidad Ambiental, 2002). En este estudio diferentes parámetros de calidad de agua fueron examinados durante el año de agua 2004-2005 en cuatro vertientes del Río Grande de Arecibo, localizado en la parte central de Puerto Rico. El objetivo de esta investigación fue determinar las cargas de sedimentos y nutrientes en las vertientes y proponer relaciones matemáticas para determinar la carga anual de estos contaminantes en función de los parámetros fisiográficos y hidrológicos de las vertientes. Las variables observadas fueron pH, temperatura, conductividad, salinidad, velocidad del agua, concentración total de sedimentos suspendidos (TSS), clorofila a, nitrógeno total Kjeldahl (TKN), fósforo total (TP) y fósforo disuelto (DP). La carga y rendimiento de sedimentos para eventos de tormenta varia respectivamente desde 3,040 toneladas métricas por evento, 32.45 toneladas métricas por Km^2 (Río Limón) hasta 29.99 toneladas métricas por evento, 1.69 toneladas métricas por km^2 (Río Jauca). La concentración de nutrientes varia respectivamente desde 6.49 hasta 1.11 mg/L de TKN, 1.82 hasta 0.05 mg\L de TP y 0.24 a 0.05 mg\L de DP. En este trabajo se utilizó el método de regresión de Cuadrados Parciales Mínimos (PLS) para generar ecuaciones de predicción de sedimentos y nutrientes. Se generaron ecuaciones de predicción para carga anual de TSS, TKN, TP y DP, estas ecuaciones fueron evaluadas y calibradas utilizando el método de calibración de PLS en el programa estadístico MINITAB versión 14. Los valores de predicción de R^2 para TSS, TKN, TP, y DP utilizando un modelo de 2-componentes son 0.74, 0.95, 0.97 y 0.99.

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GLOSSARY

- **Dissolved oxygen:** measures the amount of oxygen gas dissolved available in the water column.
- **Dissolved phosphorus:** includes inorganic phosphorus (generally as orthophosphate) organic phosphorus excreted by organism and macro molecular colloidal phosphorus.
- **Hydrologic cycle:** the cyclic transfer of water vapor from the Earth's surface via evapotranspiration into the atmosphere, from the atmosphere via precipitation back to earth, and through runoff into streams, rivers, and lakes, and ultimately into the oceans.
- **Non-point source pollution (NPS):** pollution discharged over a wide land area, not from one specific location.
- **Peak flow:** the maximum instantaneous discharge of a stream or river at a given location, it usually occurs at or near the time of maximum stage.
- **Point-source pollution:** water pollution coming from a single point, such as a sewage-outflow pipe.
- **Pollutants load:** the mass or weight of pollutant which passes a cross-section of the river in a specific amount of time.
- **Rating curve:** a drawn curve showing the relation between gage height and discharge of a stream at a given gagging station.
- **Suspended sediment:** very fine soil particles that remain in suspension in water for a considerable period of time without contact with the bottom.
- **Total Kjeldahl nitrogen:** nitrogen in the form of organic proteins or their decomposition product ammonia, as measured by the Kjeldahl Method.
- **Total phosphorus:** measure of the inorganic and organic form of phosphorus.
- **Watershed:** the land area that drains water to a particular stream, river, or lake.

(USGS Web Water Science Glossary)

LIST OF ABBREVIATIONS

Abbreviation	Explanation
μg/L	micro-grams per liter
μS/cm	micro-Siemens per centimeter
cfs	cubic feet per second
chl a	chlorophyll a
DEM	Digital Elevation Model
DO	dissolved oxygen
DP	dissolved phosphorus
GIS	Geographical Information System
mg	milligram
mg/L	milligrams per liter
N	nitrogen
NRCS	Natural Resources Conservation Service
P	phosphorus
pH	hydrogen potential
ppm	parts per million
ppt	parts per thousand
R^2	coefficient of determination
RGA	Río Grande de Arecibo
TKN	total Kjeldahl nitrogen
TP	total phosphorus
TSS	total suspended solids
USDA	United States Department of Agriculture
USEPA	United States Environment Protection Agency
USGS	United States Geological Survey
UTM	Universal Transverse Mercator

1. INTRODUCTION

Surface water contamination by nonpoint and point sources pollution is a major concern for public and government agencies in the United States and Puerto Rico. Water quality issues are of interest to people because it is an important resource for any community for life support, economic development, recreation facilities, and aesthetic values. Puerto Rico is privileged to have a very well distributed rain pattern throughout the year; however, the lack of adequate urban planning, urban sprawl, increase of impervious areas, and industrial and agricultural sectors are threatening the quality and quantity of water.

Agriculture and urban activities are major sources of phosphorus (P) and nitrogen (N) to aquatic ecosystems. Eutrophication caused by excessive inputs of P and N are the most common impairment of surface water in the United States (USEPA, 1990; Parry, 1998). These nutrients cause diverse problems in aquatic ecosystems such as toxic algal blooms, reduction of oxygen concentrations, fish kills, loss of biodiversity, loss of aquatic plant beds and other problems (Carpenter et al., 1998).

In the United States nonpoint source inputs are the major source of water pollution because they accelerate eutrophication of surface waters in the United States (USEPA, 1996). The eutrophication problem is actually observed in Puerto Rico's streams and lakes. In an island-wide study conducted by the Puerto Rico Environmental Quality Board in 1981 (PR EQB, 1984), Lake Cidra was classified as eutrophic, with total P and total N concentrations ranging from 0.04 to 0.28 mg/L and 0.69 to 0.77 mg/L, respectively.

Martínez (2001) performed a determination of nutrient criteria for lakes and reservoirs of Puerto Rico, a wide variety of water quality parameters were sampled including total Kjeldahl nitrogen (TKN), total phosphorus (TP) and chlorophyll a (chl a). According to the trophic state index approach (TSI) for TP the following reservoirs were ranked in the eutrophic group: Caonillas, Cidra, Curias, Guayabal, Guayo, Guineo, La Plata, Loco, Luchetti, Melania, Dos Bocas and Toa Vaca. The Carraizo reservoir was ranked in the hypertrophic group. Concentrations estimates of TP, TKN, TN and Chl-a were 17.0 μg/L, 0.26 mg/L, 0.36 mg/L and 2.87 μg/L respectively.

The 2002 water quality inventory of Puerto Rico reports that approximately 70% of the river miles being monitored were impaired due to either high sediment loads or bacterial counts (PR EQB, 2002). Rivers are the main transport mechanism of nutrients, especially N and P, to lakes and coastal waters (Castillo et al., 2000).

Nutrient pollution problems may arise from numerous sources including agricultural, urban, rural or industrial land uses and from atmospheric deposition. Residential land use can be an important contributor of nutrients depending on fertilizer use, extent of lawn and status of septic systems. Farmers apply nutrients using different approaches; this means that nutrients entering waterways from agricultural practices (crop land) vary greatly depending on management techniques (irrigation systems, type of fertilizers, soil or foliar application). Typically, streams and other surface waters receive relatively small amounts of nutrients from forest land and relatively large amounts from land uses that involve soil disturbance and application of fertilizers (Maryland Department of Natural Resources, 2004). Agriculture is the nation's leading nonpoint source contributor, responsible for degrading approximately 60% of the impaired river kilometers and 50% of the lakes area of the USA (USEPA, 1997).

The study area is the Río Grande de Arecibo watershed, located in the north central part of Puerto Rico. In the Dos Bocas dam it has a catchment area of 437.13 km^2 and covers parts of the Utuado, Jayuya, Adjuntas, and Ciales municipalities, with an estimated population of 173,721 (U.S. Census Bureau, 2000). There are two reservoirs in the watershed: Lake Dos Bocas and Lake Caonillas that serve as drinking water supplies. The Río Grande de Arecibo watershed has exceptional natural resources value; soils, water, animals and plants which make the area an important ecological zone.

This watershed supplies potable water to the San Juan metropolitan area, delivered by the superaqueduct to approximately 1.6 million of people (PRASA, 1995). The superaqueduct draws water from Dos Bocas and Caonillas reservoirs.

An investigation was undertaken to characterize nutrient and suspended sediment export from four representative sub watersheds of the larger Río Grande de Arecibo basin. These sub watersheds were selected mainly for the existence of an USGS gaging station at the sampling outlet and because they represent major inputs of nutrients and sediments to the Caonillas and Dos Bocas lakes. Some of the stations have been studied by others in the recent years (Díaz-Ramírez, 2004; Sotomayor-Ramírez et al., 2004 and Suárez-Navarez, 2005). Monitoring consisted of sampling runoff water during the 2004-2005 water year from October 1 to September 30, at normal flow conditions and during storm events. Normal flow conditions or grab sampling was done following the USEPA guidelines, while storm event sampling was performed using previously established field equipment set-up, programming and a very close monitoring of precipitation and water storage at four sites. Grab samples were taken during regular biweekly intervals to all sites. Storm events sampling required traveling right after or during the storm event to retrieve samples from the field instruments and prepare and preserve samples for nutrient analysis.

Watershed monitoring data can be used for many purposes, such as to determine sources of impairment, to provide input for management tools such as computer simulation models (e.g. Hydrologic Simulation Program Fortran (HSPF) and Soil and Water Assessment Tool (SWAT)), create nutrient criteria indices, and to support scientifically-based decisions for preserving and improving the quality of a water resource. This research will help in the improvement of water quality in the island and also to better understand the natural and anthropogenic processes that are linked to the pollution of water bodies. This information will be used to document present water quality conditions concerning sediments and nutrients in the Río Grande de Arecibo watershed.

The information generated by this study will improve our understanding of the behavior of tropical watersheds and to determine the primary sources of water pollutants in the area (agriculture, industrial areas or urban areas). This study generated a robust data base that will help to protect the water quality in rivers and streams in Puerto Rico.

This research evaluates sediment and nutrient concentrations trends and proposes empirical relationships between water quality parameters and physiographic/hydrologic properties (drainage area, average slope, max width of the channel, mean elevation above mean sea level, mean annual precipitation and mean annual flow) of the watershed. These relationships can be used to estimate nutrient and sediment loads in other reservoirs of Puerto Rico and help guide the management of important water catchments in tropical areas.

2. OBJECTIVES

The general objective of this thesis project was to determine the load and concentration of sediments and nutrients in the Río Grande de Arecibo watershed.

The specific objectives of this research are:

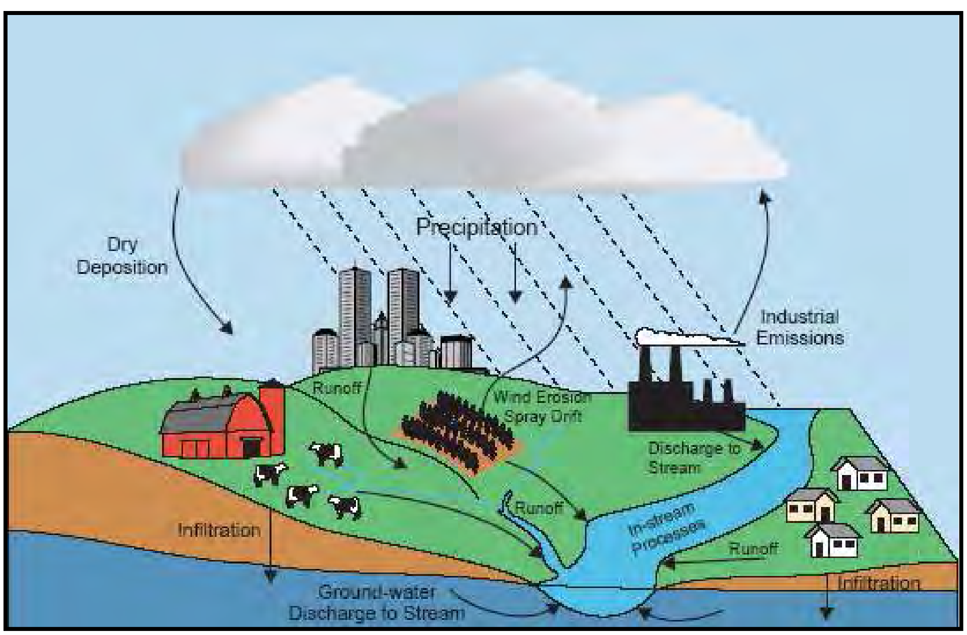
- Quantify N, P and sediment loads (kg/ha) in four selected sub watersheds within the Río Grande de Arecibo.
- Propose mathematical relationships to relate nutrient and sediment loads to physiographic and hydrologic properties of the sub watersheds.

3. LITERATURE REVIEW

3.1 Nutrients

Nitrogen and P are the primary macro-nutrients that enrich streams, lakes and rivers. Phosphorus is the main nutrient controlling productivity and the primary cause of the excess algal biomass in surface waters (Correll, 1998). The directly available forms of N and P are mostly inorganic (NO_3^- and NH_4^+). Total N and total P include soluble fractions, particulate and dissolved organic fractions. Total N and Total P concentrations are used to predict algal biomass in lakes and reservoirs. Nutrient concentrations can differ from stream to stream because of differences in land use, geology, stream flow, point sources and other factors in the drainage basin.

Figure 1 show the nutrient interactions in the hydrological cycle. It show the anthropogenic and natural effects in nutrient transport over the soil surface (erosion processes), ground-water (infiltration) and air (wind erosion).



(Adapted from Delval et al., 1999)

Figure 1. Relationship between nutrients transport and the hydrologic cycle.

Corvera-Gomringer (2005) quantified the concentration and discharges of TKN, TP, DP and TSS during storm events in two sub watersheds: Miraflores (224 ha) and Cerro Gordo (714.7 ha) that are part of the Río Grande de Añasco watershed, Puerto Rico. Average concentration values for total suspended sediments were relatively high 1,552 mg/L for Miraflores and 2,738 mg/L for Cerro Gordo. Average TP concentration values (0.34 mg/L for Cerro Gordo and 0.48 mg/L Miraflores) were found to be over the 0.1 mg/L threshold suggested by the U.S EPA for eutrophication. Differences in TSS, TP, DP and TKN discharges were observed in the two sub watersheds, Cerro Gordo discharges of TSS, TP, DP and TKN (kg/ha) were 4.5, 1.7, 1.5 and 2.3 times higher than those in Miraflores.

Sotomayor-Ramírez et al. (2001) summarized total P concentration, historical trends, and relationships between biological and chemical parameters in eleven rivers of Puerto Rico, during 1989 through 1997. It was found that four rivers had median total P concentration in excess of 0.1 mg/L which is considered a threshold limit for eutrophication. It was found that many surface bodies of Puerto Rico exceed the total P concentration limit proposed by the United States Environmental Protection Agency for rivers (0.1 mg/L) and lakes (0.05 mg/L).

Johnson et al. (1976) performed a study in New York to determine P losses from a watershed with two different land uses; partially agricultural and partially forested. It was determined that 45% of the dissolved phosphorus was from geochemical processes, 35% from point sources, and 20% from diffuse agricultural sources. This research confirmed that there is a close relationship between land use and nutrient loads at watershed scale

Haggard et al. (2003) studied the N and P concentrations and export from the Ozark Plateau catchment in the United States. Ten stream sites were sampled for P and N from 1993 through 1995, 17 times per year within the Beaver Lake Basin in northwest Arkansas, USA. The author concluded that nutrient export in (kg yr^{-1}) increased with basin size, but nutrient yield in (kg km^{-2} yr^{-1}) decreased with basin size. From the ten stream sites sampled the White River has the larger basin size (1,064.08 km^2) and the Richland Creek has the smallest basin size (42.20 km^2). The White River has the higher average export of total P 46.1 Mg yr^{-1} and total N 560 Mg yr^{-1}, and the Richland Creek has the lowest average export of TP 13 Mg yr^{-1} and TN 320 Mg yr^{-1}.

Swank et al. (1994) showed that during base flow conditions, concentrations of constituents in stream water were high and dominated by source area conditions, with generally slight increases observed in a downstream direction for most of the measured chemical, physical, and biological parameters (K^+, Na^+, Ca^{2+}, Mg^{2+}, PO_4^{3-}, SO_4^{2-}, NO_3^-, Cl^-, SiO_2, pH, turbidity, conductivity, temperature, fecal and total coliform bacteria and fecal streptococcus). They also reported that water quality parameters showed steeper, more variable incremental gradients during storm flow conditions than during base flow. Strong, positive relationships were observed between most water quality parameters and landscape variables, particularly those related to cumulative human activities or alteration of the landscape.

In a research developed in the Eastern Iowa basin, a monthly sampling was conducted from 1996 through 1998 for N, P, suspended sediments and organic carbon (United States Geological Service, 2001). Concentrations of N and P varied seasonally and were related to precipitation, runoff, and fertilizers applications. About 22 percent of the samples had nitrate concentrations that exceeded the U.S. Environmental Protection Agency maximum contaminant level of 10 mg/L NO_3 - N for drinking-water regulations. Also, it was found that about 75 percent of the total P concentrations exceeded the U.S. EPA recommended total phosphorus concentration of 0.1 mg/L or less to minimize algal growth.

Dougherty et al. (2003) quantified the non point source discharges from an urbanizing headwater basin in the Occoquan river watershed in Northern Virginia, USA. A discrete weekly or biweekly grab sampling and automated sampling was used for the characterization of storm and non storm events. The authors found that increased discharges and non point source fluxes are most responsive to increased runoff. Seasonal summaries reveal that the majority of total suspended solids flux occurs during winter and spring seasons which have the higher average discharge. The mean annual particulate/dissolved P and N typical values (mg/L) during storm flow were approximately 8.5 times greater than the non-storm flow ratios. In non-urbanizing basin, corresponding P and N storm ratios were on average 5.5 times higher than non-storm ratios.

Ramos-Gines et al. (1997) studied the water balance and quantified of total P and total N loads entering Lake Cidra located at the central part of Puerto Rico with a drainage area of 2,035 ha. The authors found that runoff coefficients for major land use ranged from 0.31 to 0.75 kg/ha-yr. The coefficients were considered to be related primarily to land use characteristics and minimally to geology and soil characteristics in the monitored sub-basins. The total P and total N loads input to Lake Cidra were about 6,530 and 18,700 kilograms per year and the total output were estimated to be 840 and 8,600 kilograms per year, respectively. About 5,700 kilograms of TP per year and about 10,200 kilograms of total N per year were estimated to be retained in the reservoir. Reservoirs are natural traps of sediments and nutrients. Gellis (1993) found the reservoirs trap efficiency for suspended sediment of relatively 74 percent during extreme weather conditions of hurricane Hugo for the Loiza Lake watershed. Soler-López (2001a) reports for the 1990-2000 periods, high reservoirs efficiency values (93%) for Lake Caonillas.

Martínez (2001) performed a determination of nutrient criteria for lakes and reservoirs of Puerto Rico, a wide variety of water quality parameters were sampled including total Kjeldahl nitrogen (TKN), total phosphorus (TP) and chlorophyll a (chl a). According to the trophic state index approach (TSI) for TP the following reservoirs were ranked in the eutrophic group: Caonillas, Cidra, Curias, Guayabal, Guayo, Guineo, La Plata, Loco, Luchetti, Melania, Dos Bocas and Toa Vaca. The Carraizo reservoir was ranked in the hypertrophic group. Concentrations estimates of TP, TKN, TN and Chl-a were 17.0 µg/L, 0.26 mg/L, 0.36 mg/L and 2.87 µg/L respectively. It was found a significance difference in the algal community structures where the TKN/TP ratios were low for example Caonillas and Dos Bocas compared with high TKN/TP ratios for example Guajataca and Patillas. Concerning this study the water quality degradation in Puerto Rico has been increasing in a matter of time.

Sotomayor-Ramírez et al., 2004 performed a characterization and management of nonpoint pollution sources in the Río Grande de Arecibo watershed. A total of five sub watersheds were evaluated as part of this study: Sabana Grande, Jua, Caonillas, Jauca and Saliente, this watersheds were selected based in land use characteristics and hydrologic. A significative correlation between bacteria indicators and nutrient and sediment were found. Mean annual TP and TKN concentrations ranged from 23.2 to 71.5 µg/l and 0.068 to 0.296 mg/L respectively. It was observed greater concentration values of TP and TKN in areas were the animal farm operations or rural community where the principal land use. The TP yields for Jua, Sabana Grande, Caonillas, Jauca and Saliente are 1.67, 1.27, 0.43, 0.28 and 0.67 kg/ha respectively. The TKN yields for Jua, Sabana Grande, Jauca and Saliente are 3.23, 16.60, 1.12 and 2.04 respectively.

3.2 Sediments

One of the principal external dynamic agents of sedimentation is the water as a source of pollutant transport. The detachment of particles in the erosion process occurs through the kinetic energy of raindrop impact, or by the forces generated by the flowing water (Vanoni, 1997). Sediments are detached particles carried by rainwater into streams, lakes, rivers and bays. Sedimentation problems are observed in streams, lakes and other important water bodies used for human consumption and the environment. Some of the problems associated with sediment transport and deposition are: movement of soil particles, loss of soil fertility, reduction of sun light penetration through the water column, reduction in the reservoirs water storage capacity and reduction of dissolved oxygen concentration. Also, sediments can carry concentrations of pollutants that contaminate waterways, including nutrients such as phosphorus and nitrogen which promote eutrophication in surface waters.

Figure 2 shows Lake Dos Bocas that is part of the studied watershed in its natural state. Figure 3 shows the lake after a storm event loaded with sediments. Suspended sediment reduces the light penetration and the DO in the water column. Sediment deposition reduces water storage capacity in reservoirs and lakes.

Figure 2. Lake Dos Bocas at Utuado, Puerto Rico

Figure 3. Lake Dos Bocas after a storm event

In October 1999, Soler-López performed a sedimentation survey of Lake Dos Bocas, Puerto Rico. The sedimentation rate of this lake was about 309,000 m^3 per year for the years from 1942 to 1985. This lake has shown a reduction of 3.27 million cubic meters from 1994 (21.31 million cubic meters) to 1999 (18.04 million cubic meters). Sediment accumulation from 1994 to 1999 ranged from 16.19 to 19.46 millions of cubic meters. The Río Grande de Arecibo branch is the largest contributor of sediments to the lake. The Río Limón branch is the lowest contributor of sediment to Lake Dos Bocas, (Soler-López, 2001a).

In February 2000, Soler-López performed a sedimentation survey of Lake Caonillas, Puerto Rico. The drainage area of the lake at the dam site was 221.42 km^2 and the predominant soil types were Pellejas-Lirios-Ingenio association of the Arecibo area, this association has erosive characteristics such as: deep, steep, excessively drained with a slope raging from 40 to 60 percent and the runoff is very rapid. It was found that the reduction of the lake water storage capacity over time is due to the transport and deposition of suspended sediments in the reservoir bottom. The reduction of 6.98 million cubic meters from 1990 (49.25 million cubic meters) to 2000 (42.27 million cubic meters) represents an overall storage capacity loss of about 11.5 percent by 1990 and 24.1 percent by 2000. The effect of storm events sedimentation on the storage capacity is shown during this period. Two strong hurricanes past thought the island: Hurricane Hortensia 1996 and Hurricane Georges 1998, creating a runoff impact and elevated sediment transport in the area, (Soler-López, 2001b).

Soler-López et al. (2001c) surveyed the principal water supply reservoirs of Puerto Rico. In that study the storage capacity losses for 14 reservoirs range from 12 to 81 percent, with an average of 35 percent. Sediment yields for the reservoirs basins ranged from 483 to 4,102 m^3/km^2 per year. Soler-López showed that sediment accumulation has substantially reduced the storage capacity of the principal water supply reservoirs in Puerto Rico over time. The principal reservoirs are rapidly losing their water storage capacity due to high rates of sediment influx and accumulation. Some of the smaller reservoirs studied are near the end of their useful life. The factors that influence in the capacity loss rates and basin sediment yields in these areas are: rainfall magnitude and frequencies, human impacts, drainage area extension and morphology.

Suárez-Navarez (2005) studied the sediment export coefficient for different sub watersheds and land uses using the Hydrological Simulation Program-Fortran (HSPF). It was found that calculated sediment export coefficient for agricultural lands ranged from 0.12 to 0.55 tons/acre/year, for forest land ranged from 0.003 to 0.019 tons/acre/year, for barren land ranged from 0.33 to 14 tons/acre/year, and for rangeland ranged from 0.009 to 0.022 tons/acre/year. The suspended sediment loads were estimated for Lake Caonillas (9.7 x 10^6 metric tons) and Lake Dos Bocas (15.9 x 10^6 metric tons). The watersheds with the best sediment transport calibration fitting are Río Limón, Río Caonillas and Río Grande de Arecibo below Utuado, with the coefficient of determinations ranging from 0.88 to 0.76.

Díaz-Ramírez (2004) simulated export potential of the Río Caonillas watershed in Puerto Rico. In that study the HSPF computer modeling program was used to evaluate soil erosion and sediment export, with an extended amount of climatologic data (1995-2001) The average mean daily flow for the study period was 2.85 m^3/sec. Díaz-Ramírez (2004) show the effect of extreme hydrologic conditions in sediment transport and simulation processes, hurricanes Hortensia and Georges produced 24 percent and 58.5 percent of the total sediment load (1,348,041 tons) in a three year validation period. High coefficients of determination values were found (0.73) for suspended sediment loads simulation for a five year period (October 1995 to September 2000). Comparing the observed total suspended sediment load (166,289 metric tons) versus the simulated load (170,435 metric tons), the estimated error of the model was 2.49%. It was found that agricultural and barren areas yielded the highest soil losses (54 % and 23 %) of the annual soil erosion during the studied period.

3.3 Land use

Stream water quality monitoring can be used to determine the impacts from different land uses in a watershed to the overall water quality. In watersheds with mixed land uses (agricultural and urban), streams commonly show elevated nutrient concentrations (Spahr and Wynn, 1997). Typically one of the highest sources of nutrient inputs in the watersheds are the agricultural areas, this is due to the application of fertilizers/pesticides and the disturbance of the soil for agricultural production purposes. Agriculture is the principal source of remaining impairments in the nation’s rivers and lakes (Heimlich, 2003). Irrigation practices which can increase the runoff can influence considerably in the water quality. Bevans et al. (1998) related the impact caused by irrigation with an increase in agricultural inputs, such as fertilizers and pesticides in Las Vegas Valley area. He identified urban activities as the primary source of nutrients in the area of study (concentrations of orthophosphate). The lowest source of nutrient was the forest areas, because the soil is well covered and protected. The increasing population in Las Vegas urban area has increases the annual load of total-nitrogen downstream from 680 metric tons in 1974 to 2,177 metric tons in 1988; this represents an increase of 1,496 ton in 14 years. The effect of land use changes in this area is clearly shown in the increase of the total nitrogen loads.

Bolstad and Swank (1997) studied the cumulative impacts of land use on water quality in a southern Appalachian Watershed. The purpose of that study was to observe any changes in water quality, over a range of flow conditions, with concomitant downstream changes in the mix of land use. The variables sampled included pH, electrical conductivity, nutrients, turbidity, temperature, and dissolved oxygen. Linear regression analyses were performed to relate basin and near-stream landscape variables to water quality parameters. It was found that larger downstream changes in water quality variables were observed during storm flow when compared to base flow, suggesting cumulative impacts due to landscape alteration under study conditions were much greater during storm events.

Heathwaite (1993) studied the chemical fractionation of lake sediments to determine the effects of land use change on nutrient loading in a freshwater costal lake (Slapton Ley Lake). Sediment influx to the studied lake increased from less than 2 mm $year^{-1}$ prior to the Second World War to over 10 mm $year^{-1}$. Land use records suggest that the intensification of agriculture and the increase in the area of temporary grass in the 1960s may be the cause of accelerated catchments erosion. In this study, sediment and nutrient export in surface runoff from grazed and ungrazed grassland in the Slapton catchments under a simulated rainfall of 12.5 mm/hr for 4 hr using 0.5 m^2 plots were evaluated. It was found that heavily grazed grassland had higher potential for nutrient and sediment export than ungrazed grassland. Mean total suspended solids were about 32 mg/L, total nitrogen 2.6 mg/L and total phosphorus about 4.7 mg/L in heavily grazed grassland, compared with ungrazed grassland that was total suspended solids 85 mg/L, total N not detectable and total P 0.03 mg/L. It was found that the land use changes in the lake have increase significantly both the quantity of inorganic fertilizers applied to all land uses in the catchment, and the organic nutrient load voided by livestock.

Coulter et al., (2004) studied the water quality in agricultural, urban and mixed land uses watershed at Bluegrass Region of Kentucky. Twenty-six grab samples were taken during a one year period in the watershed. Different parameters were observed: N and P concentration, total suspended solids (TSS), turbidity, pH, temperature and stream flow were measured in this study. It was found that nitrate and orthophosphate concentrations were significantly higher in the agricultural watershed. Total suspended solids, turbidity, temperature and pH were found to be generally higher in the urban and mixed watershed. Fluxes of orthophosphate were found to be greater in the agricultural watershed than in the urban watershed. The highest nitrogen concentration during the study period (5.96 mg/L) was recorded in the agricultural watershed. The mean annual total P concentration was in the agricultural watershed equaled or exceeded (0.03 mg/L).

In October 2003 a watershed characterization was performed for the Lower Charles River watershed, Massachusetts (Maryland Department of Natural Resources, 2004). This watershed has an extended area of 787.90 km^2 and the primary uses were recreation and aquatic life. The dominant land use in the watershed is agriculture (47%). It was found that nutrient concentrations in urban areas were affected by human activities, including the use of fertilizers, the combustion of fossil fuels and the discharge of untreated sewage. Phosphorus concentrations in urban and agricultural areas sampled by USGS National Water-Quality Assessment Program were greater than the U.S EPA guideline (0.1mg/L). Also, results shows that upstream sources contribute most of the N and P loads to the lower Charles River.

3.4 Sediment and nutrient loads

Water quality monitoring for nutrients and sediments requires accurate measurements of stream surface water velocity. For this reason the sampling method, frequency and analysis are some of the principal factors to consider for constituent loads determination. Due to the negative impacts that excess of sediment and nutrient can cause to water bodies (sedimentation and eutrophication) it is important to determinate concentrations, trends and loads of these pollutants and associate them to possible contributors (non-point or point source). Different studies have been conducted for constituent loads determination and evaluation in streams (e.g., Etchells et al., 2005; Huai-en et al., 2003; Sorens and Nelson, 2002; Rice and Izuno, 2001 and Darrell et al., 1998). These studies have been performed to provide a better understanding of constituent loads in streams, such as: monitoring methods, data analysis evaluation and comparison of different mathematical methods to do estimates.

Etchells et al. (2005) quantified the uncertainty of nutrient load estimates. This is based on assumptions about the behavior of pollutant concentration instream during time were data was not collected. To estimate loads from sparse water quality data some estimation techniques must be applied: *interpolation techniques* - where assumptions are made about how concentrations vary in time between samples, *regression or rating curve techniques* - where a relationship is assumed to hold between flow and concentration of a particular time period and the concentration of non sampled periods is inferred from flow data and the *averaging or ration techniques* - where statistics derided from the available concentration samples and flow series are used to estimates loads of longer time spans. Twenty two methods for annual loads calculation were compared; differences between methods were determined and the uncertainty of load estimation demonstrated. A quantification of uncertainty for TP was performed for thirteen drain sites in the years 1993/94, 1998/99 and 2003/04 using daily flow data, it was found that some results were quite reliable but others varied widely. For this reason the appropriated estimation method technique must be selected based on the pollutant behavior and the available data.

Warne et al. (2005) studied the water sediment and nutrient discharges characteristics and their potential influence on coral reef in Puerto Rico. Water discharge data from 29 USGS stream flow gauging stations were analyzed and characterized for suspended sediment and water discharge in Puerto Rico. For each stream studied the mean annual discharge (m^3/sec) and the mean annual runoff (mm) were determined. The estimated mean annual suspended sediment discharge from Puerto Rico to costal waters for the period from October 1990 to September 2000 is as follows: north from 280,000 to 2,300,000 metric tons, east from 51,000 to 180,000 metric tons, south from 1,400,000 to 5,600,000 metric tons, and the west 960 metric tons. These data shows the variation of suspended sediment discharge across the Island. It has been determined that based on drainage basin size, about one half of the sediment discharges through the northern rivers. The effects of sediment and nutrient discharges on the coral reef are better seem in the near shore areas of the north, southwest and west coast, these effects includes the loss of diversity and the reduction of coral abundance.

3.5 Sediment and nutrient loads prediction

The incorporation of monitoring and predicting models to water quality management systems for both surface water and ground water is an excellent way to extrapolate measured water quality parameters in unmonitored areas. Two powerful tools for surface water quality estimates and modeling are computer programs such as the Soil and Water Assessment Tool (SWAT), Hydrological simulation Program – FORTRAN (HSPF), Better Assessment Science Integrating Point and Non Point Sources (BASINS) software (USEPA, 2001; Bicknell et al., 2001) and predictive equations generated with statistical approaches such as Partial Least Square Regression, Multiple Linear Regression and Principal Component Analysis. A recent publication from the USGS (Moving from monitoring to Prediction: The Quality of the Nation's Streams) explains that the successful management of our Nation's water resources requires a combination of monitoring and predictive tools such as models, it is well know the importance of real data inputs during the model calibration and validation processes (Alexander and Smith, 2005).

A statistical examination of water quality conducted in two (Casey Lake and Silver Lake) Iowa lakes reflects significant difference between these two lakes in both 1999 and 2000 as well a significant change in water quality in one of the lakes (Silver Lake). A variety of water quality parameters variables were collected during the research: turbidity, secchi depth, surface temperature, bottom temperature, surface dissolved oxygen, bottom dissolved oxygen, chlorophyll a, total phosphorus, dissolved phosphorus, bacteria and coliform. Statistical analysis demonstrated that Silver Lake P levels increase during summer of 2000, meanwhile they decrease with increasing levels of surface dissolved oxygen and decrease as the water became less clear (Carlson and Ecker, 2002).

Predictive equations for pollutant transport are based on concentrations and loads in surface stream waters. Dodds et al. (1997) developed equations to predict benthic algal biomass as function of TN and TP. Dodds found that the relationships between TP and/or TN and periphytic biomass in streams have low R^2 relatively values. The equations and the R^2 values are as follow:

$$\log(mean\_chl\_a) = 1.091 + \log(TP) * 0.2786 \qquad (R^2 = 0.09)$$

$$\log(mean\_chl\_a) = 0.01173 + \log(TN) * 0.5949 \qquad (R^2 = 0.35)$$

$$\log(\max\_chl\_a) = 1.4995 + \log(TP) * 0.28651 \qquad (R^2 = 0.07)$$

$$\log(\max\_chl\_a) = 0.47022 + \log(TN) * 0.60252 \qquad (R^2 = 0.28)$$

Where seasonal mean maximum benthic chlorophyll are in mg/m^2 and TN and TP are in µg/L.

Roberts and Pelletier (2001) estimated loads of nutrients, bacteria, DO and TSS from seventy-one (71) watersheds using existing and collected data of flow and water quality. Water quality multiple linear regression models were used to evaluate pollutant loads. Specific multiple regression model coefficients were generated for each watershed and for each parameter. The multiple linear regression models generated well R^2 values for prediction purposes: highest values for nitrite plus nitrate (median adjusted $R^2 \sim 0.6$ to 0.7) and the lowest values for fecal coliform and ammonia (median adjusted $R^2 \sim 0.3$). It was determined that the method generated better predictions as function of data quantity (more data better fit). The multiple linear regression equation used for this study is given by the follow equation.

$$\log(c) = b_0 + b_1 \log\left(Q/A\right) + b_2 \log\left(Q/A\right)^2 + b_3 \sin\left(2\prod f_y\right) + b_4 \cos\left(2\prod f_y\right) + b_5 \sin\left(4\prod f\right) + b_6 \cos\left(4\prod f_y\right)$$

Where c is the parameter concentration (mg/L), Q is the discharge (m^3/s), A is the area tributary to the monitored location (km^2), f_y is the year fraction (dimensionless, varies from 0 to 1), and b_i are the best-fit coefficients calculated for each dataset.

Huebner and Douglas (1994) predicted water quality using watershed characteristics. The multiple linear regression method has been performed in order to predict water quality parameters. Two types of multiple linear regressions were evaluated for this study:

- Estimation of water quality parameters (pH, alkalinity, conductivity, nitrate-nitrogen, and water temperature) based on the watershed properties such as area, slope, curve number (CN), hydrologic soil group, time of concentration, and percent of watershed covered by forest, agriculture, or urban area.
- Prediction of ammonia-nitrogen and orthophosphate concentrations using water quality parameters (pH, alkalinity, conductivity, nitrate-nitrogen, and water temperature).

Huebner and Douglas used a multiple linear regression model to generate water quality predictive regression equations. The regression equations were as follows:

$$ph = 8.09 - 4.84Slope - 0.225Agriculture - 1.05 \qquad (R^2 = 0.72)$$

$$Turbidity = -4.05 - 25.3Slope + 2.12Soil\_Type + 4.85Agriculture \qquad (R^2 = 0.94)$$

$$Orthophosphate = 0.0316 + 0.0256NO_3 - N \qquad (R^2 = 0.75)$$

4. OVERVIEW OF THE STUDY AREA

4.1 Location

The area of study is the Río Grande de Arecibo watershed located in the north central part of Puerto Rico, confined within latitudes 18°11' and 18°20' N to the South and North, respectively and longitudes 66°32' and 66°46' W to the East and West, respectively. It has a catchment area of 437.13 km^2 at dam site of Dos Bocas Lake and covers parts of the Utuado, Jayuya, Adjuntas, and Ciales municipalities (Figure 4). The average annual precipitation of the area is 2,235 mm and the average land slope is 36 % (Daly, 2002). Four sub watersheds of the larger Río Grande de Arecibo watershed were selected for the current study (Table 1). Table 2 shows the land use distribution in each of the sub watersheds.

Figure 4. Location of the study area - Río Grande de Arecibo watershed.

Table 1. Physiographic and hydrologic characteristics of the sub watersheds.

Sub watershed	Drainage area at outlet (km^2)	Maximum width of the channel (m)	Average land slope (m/m)	Mean elevation above mean sea level (m)	Mean annual precipitation (mm)	Mean annual flow (m^3/s)
Río Limón	93.71	33.22	0.35	450.85	2554.98	2.67
Río Grande de Arecibo	186.45	41.45	0.35	512.43	1694.68	4.66
Río Caonillas	98.21	25.29	0.38	702.74	1385.06	2.76
Río Jauca	17.74	20.12	0.38	729.76	2088.89	0.52

- Mean annual precipitation and mean annual flow were obtained from the USGS data base for the period of October 1, 2003 to September 31, 2004. Physiographic and hydrologic characteristics were obtained from USGS Water Resources data – Puerto Rico and the U.S. Virgin Islands, 2001.

4.2 Land use

The land use categories in the watershed were developed using Digital Orthophoto Quarter-Quadrangles (DOQQ) color air photography and satellite imagery. This coverage has been modified from previous studies of the University of Puerto Rico at Mayagüez (Suárez-Navarez, 2005; Díaz-Ramírez, 2004). Ground truthing of the land use coverage were performed throughout the course of this research and other investigations being conducted in the same area (Suárez-Navarez, 2005; Díaz-Ramírez, 2004).

Land use information was collected using Global Positioning System (GPS) equipment and transferred to the GIS using Arc GIS software (ESRI, 2004). Six land use types were considered: forest, rangeland, pasture, agriculture, urban and barren land. Rangelands are unmanaged pastures that do not receive inorganic fertilization and are used for cattle grazing. Fertilization comes from animal droppings. Pastures are well managed with inorganic fertilization and or annual manure application. Urban areas include both urban centers and residences along roads that could be delineated in the satellite imagery available at the time.

Delineation of the sub watershed was carried out by other studies within the same study area using the tools in the Watershed Modeling System (WMS, EMS-I) and the suit of Digital Elevation Models (DEM). Topographic data was incorporated within the GIS using USGS 7.5 minutes (1:24,000-scale) Raster Profile Digital Elevation Model (DEM), 08/2001 version. Coordinate projection system used is the Universal Transverse Mercator, Zone 19, distance unit in meters, North American Datum 1927, and Vertical Datum, NGVD 1929. DEM's Resolution are 30 meters by 30 meters in X and Y, and 1 meter in Z. Figure 5 shows the land use distribution in the watershed. Forest and range land are the most abundant land use in the watershed.

Table 2. Land use distribution in the Río Grande de Arecibo watershed.

	Land use (%)					
Sub watershed	Forest	Rangeland	Agriculture	Pasture	Barren	Urban
Río Limón	82.0	8.2	7.6	1.2	0.1	0.9
Río Grande de Arecibo	80.8	9.4	7.0	0.1	0.3	2.4
Río Caonillas	66.2	24.3	5.8	1.8	0.5	1.4
Río Jauca	70.3	23.1	5.6	0.0	0.0	1.0

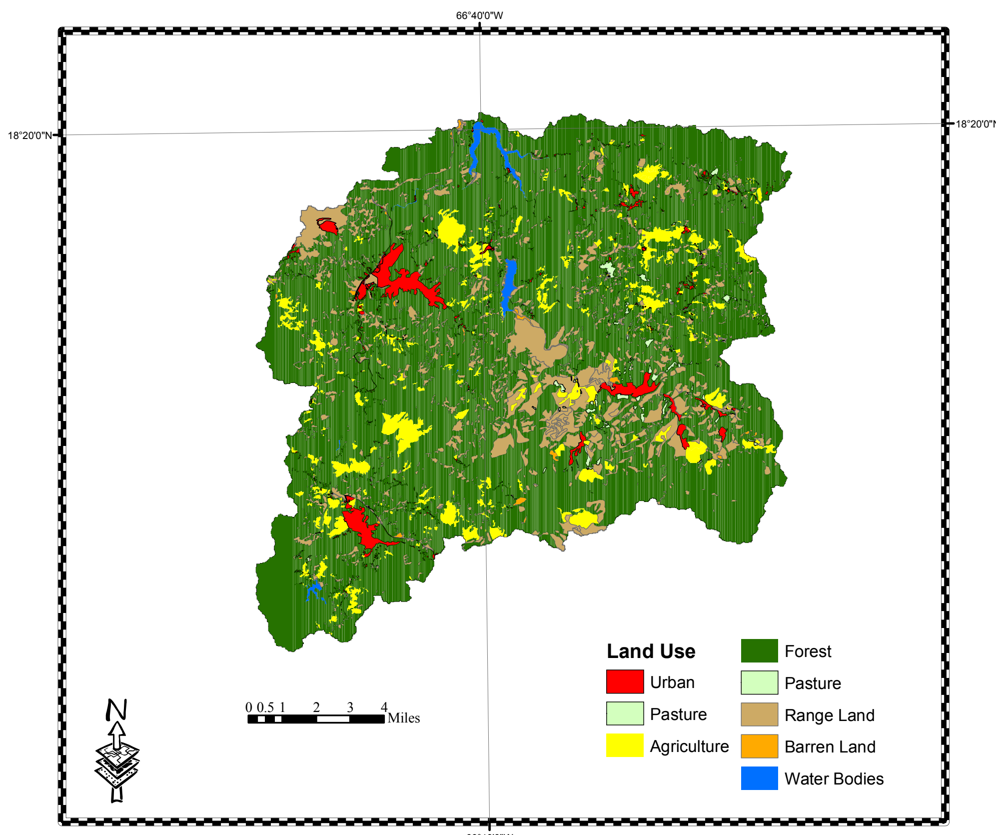


Figure 5. Land use distribution map of the Río Grande de Arecibo watershed.

4.3 Soils

The most common soils series in the Río Grande de Arecibo watershed are the Humatas with 20.5% and the Pellejas with 20.2% of the total area. Humatas soils are deep, very steep and well drained. Pellejas series are deep, very steep and somewhat excessively drained. Both soil series show steep slope (40-60%) and erosion hazard for agriculture purposes (USDA, 1979). Figure 6 shows the thirty-five soil series distribution within the Río Grande de Arecibo watershed (USDA-NRCS, 2001).

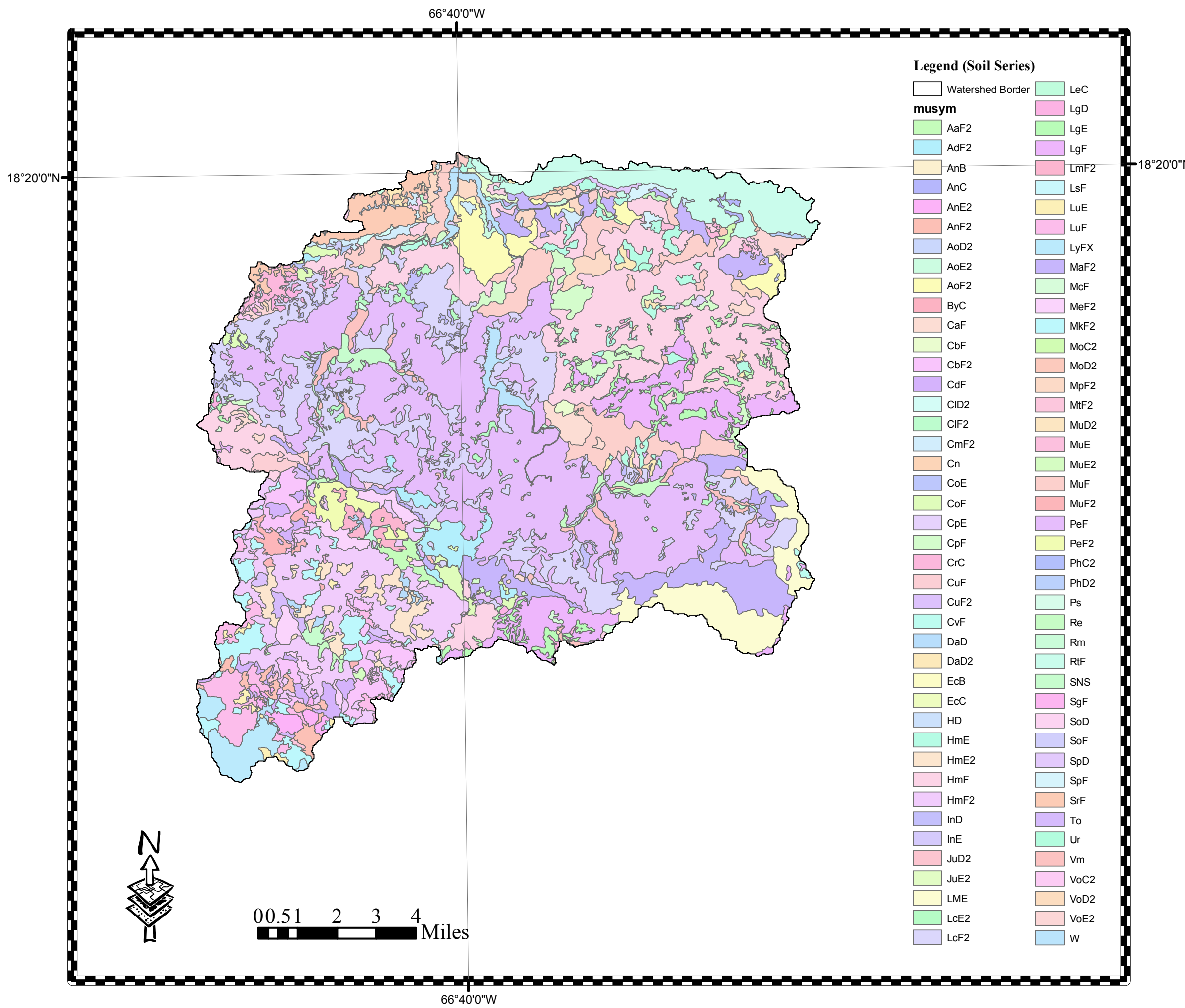


Figure 6. Soil Series distribution of the Río Grande de Arecibo watershed.

Table 3. Taxonomic classification of soils in the Río Grande de Arecibo watershed.

Soil Series	Mapping Units	Taxonomic Classification
Alonso	AoF2	Very-fine parasesquic, isohyperthermic Oxic dystrudepts
Caguabo	CbF2	Loamy, mixed, active, isohyperthermic, shallow Typic Eutrudepts
Consumo	CpF, CuF2	Fine mixed, semiactive, isohyperthermic Typic Haplohumults
Humatas	HmF, HmF2, HmE, HmE2	Very-fine parasesquic, isohyperthermic Typic Haplohumults
Lirios	LcF2	Fine, mixed, subactive, isohyperthermic Typic Hapludults
Los Guineos	LgF, LgE, LuF, LME, LyFx	Very-fine, Kaolinitic, isothermic Humic Haplodox
Maraguez	MaF2	Fine-loamy, mixed, superative, isohyperthermic Typic Eutrudepts
Maricao	MkF2	Fine, mixed, subactive, isohyperthermic Inceptic Hapludults
Mucara	MuF, MuF2	Fine-loamy, mixed, superactive, isohyperthermic Dystric Eutrudepts
Pellejas	PeF, PeF2	Fine-loamy over sandy or sandy-skeletal, mixed, subactive, isohyperthermicTypic Dystrudepts
Viví	Vm	Coarse-loamy over sandy or sandy-skeletal, mixed, subactive, isohyperthermic Fluventic Dystrudepts

♦ Information from Cruz-Rodríguez, 2005.

4.4 Stream flow and climatologic data

Stream flow was monitored in the outlets of the four corresponding sub watersheds. These outlets are constantly monitored by the USGS (stream flow, gage stage and precipitation). For each grab sampling (bi-weekly) the cross section of the channel and the water velocity were collected to calculate the instantaneous flow for each station. Further details of the sampling and storm event sampling are described in the section 5 (Methodology) of this document. Climatologic data were obtained from the USGS stations located in the study area. The USGS stations reported hourly precipitation and flow data for the study period, annual hydrographs are shown in the Appendix A.

Table 4. USGS monitoring stations number and geographical location used in this study.

Sub watershed	USGS Station Number	Location	Monitored Period
Río Limón above Lago Dos Bocas	USGS 50027000	Lat 18°19'32", Lon 66°37'24"	Oct. 1, 2003 - Sep. 31, 2004
Río Grande de Arecibo below Utuado	USGS 50024950	Lat 18°18'07", Lon 66°42'15"	Oct. 1, 2003 - Sep. 31, 2004
Río Caonillas at Paso Palma	USGS 50026025	Lat 18°13'53", Lon 66°38'14"	Oct. 1, 2003 - Sep. 31, 2004
Río Jauca at Paso Palma	USGS 50025850	Lat 18°12'50", Lon 66°38'44"	Oct. 1, 2003 - Sep. 31, 2004

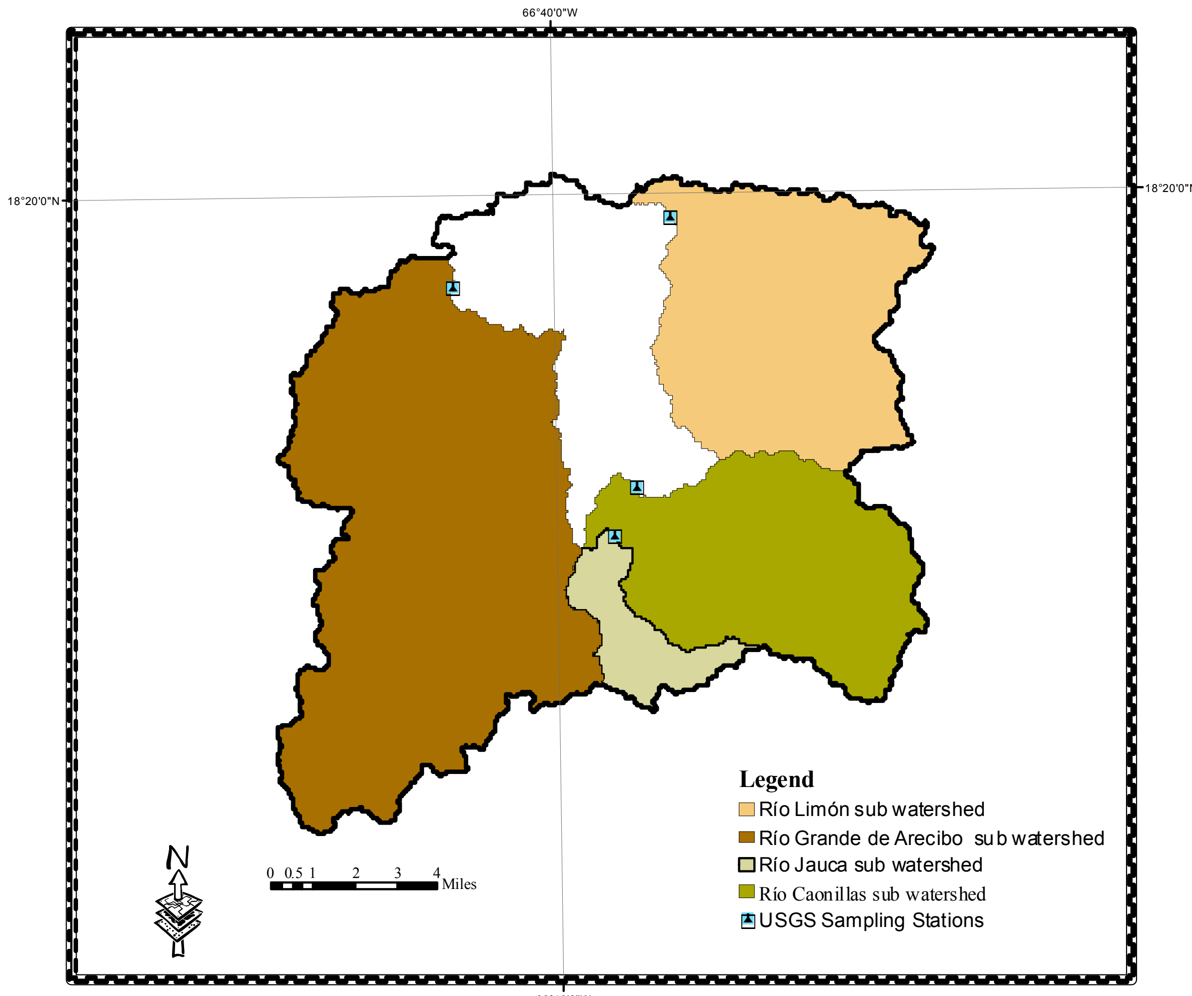


Figure 7. Sub watersheds delineation of the Río Grande de Arecibo watershed.

5. METHODOLOGY

5.1 Physical and chemical characterization

Conductivity, pH, temperature, salinity and dissolved oxygen were measured *in situ* during the study period. For the conductivity, pH, temperature and salinity measurements a calibrated multi-parameter water quality meter (YSI) model 63 was used. For the dissolved oxygen measurements a calibrated multi-parameter water quality meter (YSI) model 59 was used. To estimate the instantaneous flow (Q) a transversal section of the channel and surface water velocity was measured. Surface water velocity was measured with a velocity meter, taking several measurements across the channel length and integrating over the entire cross section (Figure 8). Where L is the length, D is the depth and V is the water velocity.

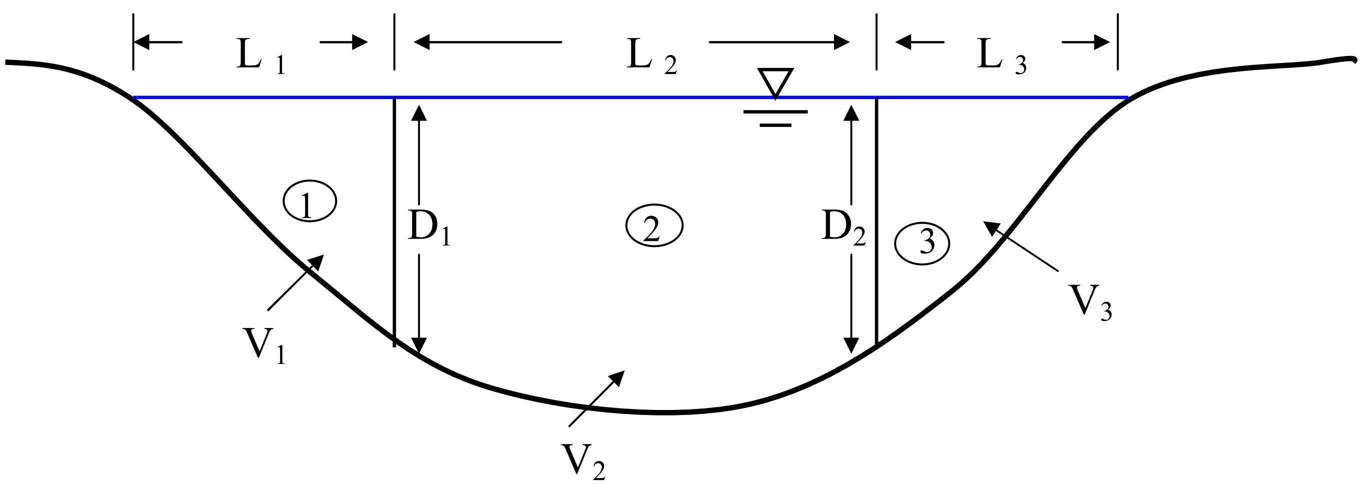


Figure 8. Cross channel section

Where:

L is the length, D is the depth and V is the water velocity.

5.2 Storm events sampling

Storm events were monitored using a combination of flow meter ISCO 4220 and an automatic auto-sampler ISCO 3700 (ISCO, Corp., Lincoln, NE) at the outlet of each sub watershed (Figure 9). The combinations of flow meter and auto-sampler was installed in previous studies (Díaz-Ramírez, 2004; Covera-Gomringer, 2005) and are used to sample the rising and falling limbs of the runoff hydrographs. The auto-samplers were programmed to suction water samples once the stage rises above a pre-established threshold set for each sub watershed typically 15 cm above normal water level.

The ISCO 3700 autosampler is a 24-500 ml bottle sampler array in a chamber canister controlled by a computer interface. The autosampler was programmed to take one water samples (450 ml) every five minutes for the initial five bottles of the runoff hydrograph, afterwards a sample was taken every fifteen minutes until the 20th bottle, and the last four bottles were taken every 60 minutes until the last 24th bottle.

As part of this study a new monitoring station was installed at the Río Jauca sub watershed outlet located in the south central portion of the Río Grande de Arecibo watershed. The other three stations used were previously instrumented to monitor suspended sediments (Díaz-Ramírez, 2004; Covera-Gomringer, 2005).

Discharge for storm events at the outlet location was calculated using the USGS previously developed rating curves for each of the sampling sites (Figure 11, Figure 12, Figure 13 and Figure 14) (USGS Caribbean Area, Puerto Rico Office) Appendix B. A rating curve is a relationship between stage and discharge at a cross section of a river. The cross sections and the channel profiles were surveyed using standard surveying equipment and GPS units (Figure 15, Figure 16, Figure 17 and Figure 18).

A total of 29 storm events were monitored during the 2004-2005 USGS water year and the distribution per sub watershed is as follows: Río Limón 12, Río Grande de Arecibo 2, Río Caonillas 6 and Río Jauca 9 (Table 6).

Table 5. Summary of collected storm events during the 2004-2005 Water Year.

Sub watershed	Collected storms events	Not collected storm events	Total storm events
Río Limón	12	2	14
Río Grande de Arecibo	2	16	18
Río Caonillas	6	5	11
Río Jauca	9	4	13

Figure 9. ISCO - flow meter (4220) and auto sampler (3700).

5.3 Discrete sampling with continuous flow monitoring and time intervals

Figure 10 show concentration distribution through a storm event in which water samples were collected several times (24 times in our case) based on a predetermined time interval (bottles 1-5 each 5 minutes, bottles 6-20 each 15 minutes and bottles 21-24 each 30 minutes) for each volume of water (450 ml). This figure shows that each concentration value is representative of an equal volume of water pumped by the auto sampler during a specific time interval. The instantaneous flow for each of the 24-500 ml bottles was calculated using the USGS rating curves and comparing this versus the measured by the USGS monitoring stations. The concentration in the figure represents the distribution in the smooth curve, the load was calculated selecting the flow rates at appropriates times intervals and used them to calculate the flow volume. The flow volume is represented in the flow rate versus time graph by the colored area. The Appendix F shows the storm events hydrograph for each collected event (flow versus time interval).

The next example show how the calculations were performed to calculate loads per time interval for a storm event (equation 1):

$$Load_{C6} = C_6 * \left[\frac{a+b}{2} * \left(Time_d - Time_c \right) \right] \quad \textbf{(1)}$$

where $time_c$ and $time_d$ are the beginning time interval for collect an individual sample, a and b are the flow rate linked to the time interval describe above, C_6 is the water sample concentration for the bottle number six and $Load_6$ is the (TP, DP, TKN or TSS) load associated with the concentration C_6.

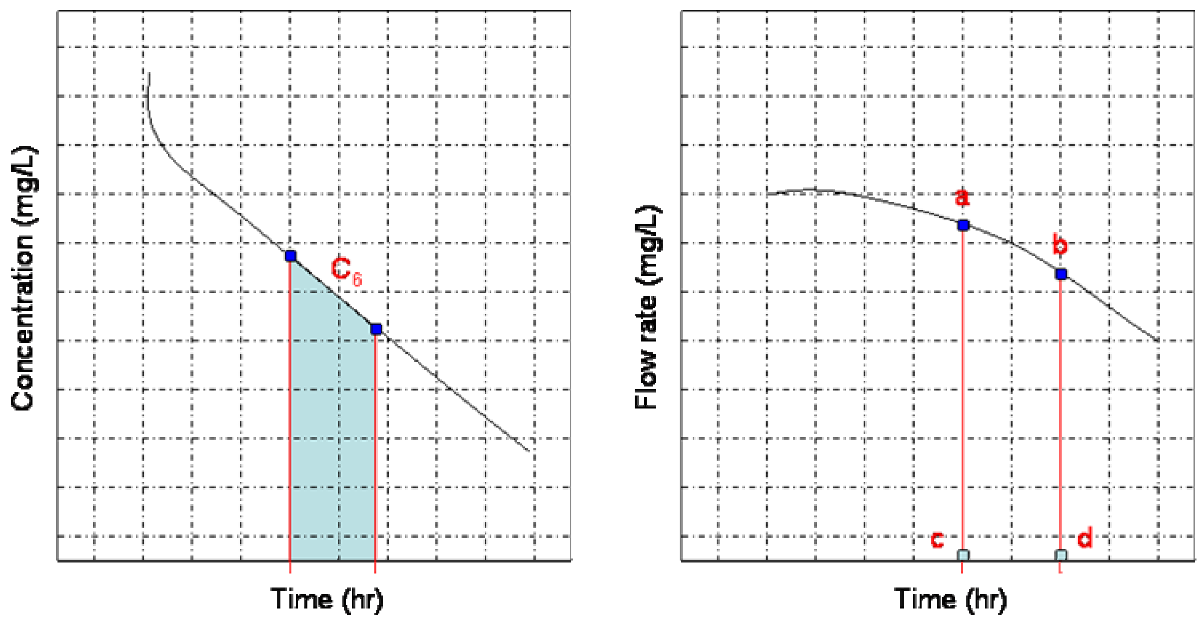


Figure 10. Concentration (TP, DP, TKN or TSS) versus time and flow versus time for predetermined equal flow volumes between time intervals.

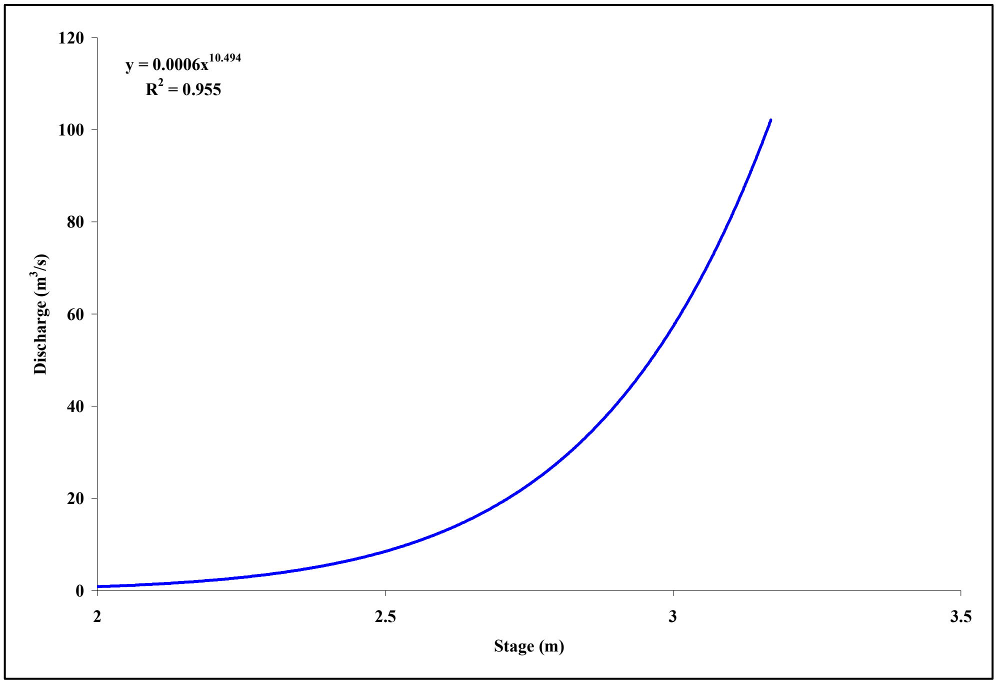


Figure 11. Río Limón USGS rating curve (USGS Caribbean Office).

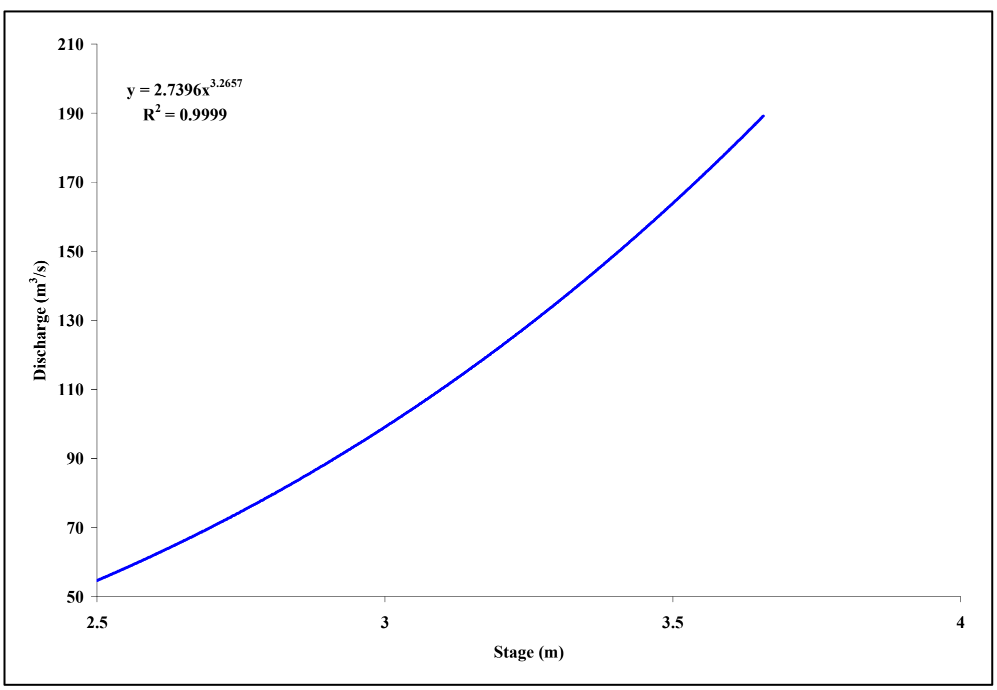


Figure 12. Río Grande de Arecibo USGS rating curve (USGS Caribbean Office).

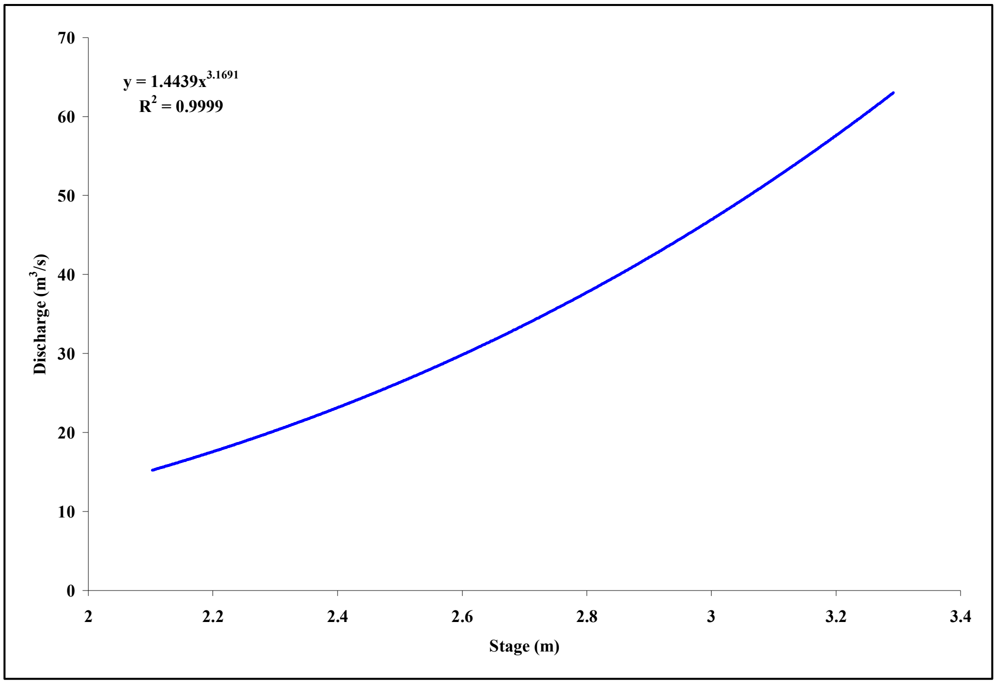


Figure 13. Río Caonillas USGS rating curve (USGS Caribbean Office).

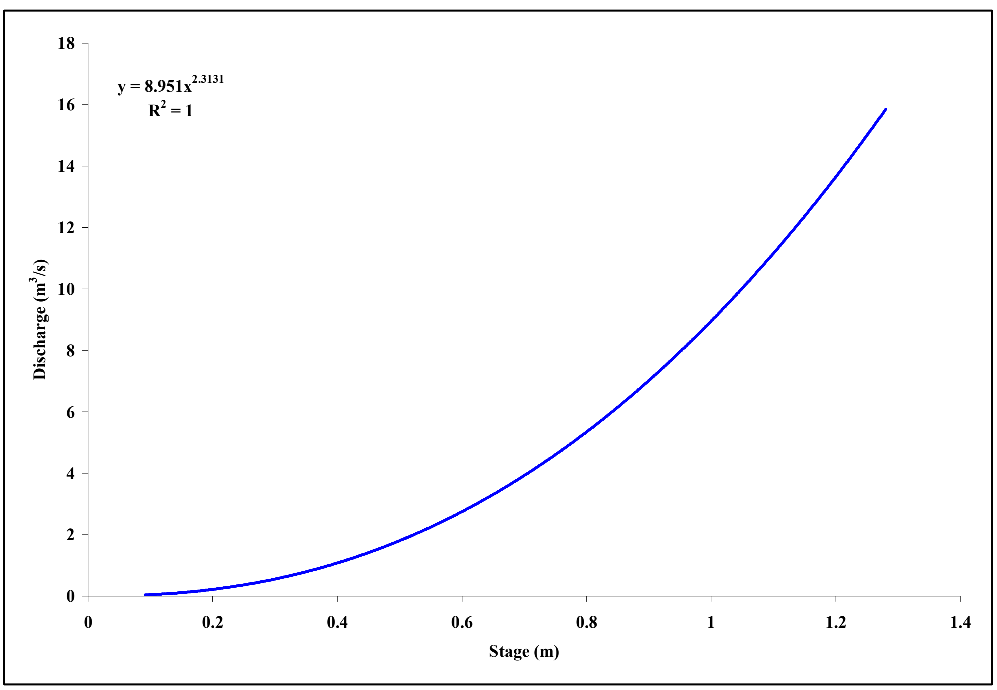


Figure 14. Río Jauca USGS rating curve (USGS Caribbean Office).

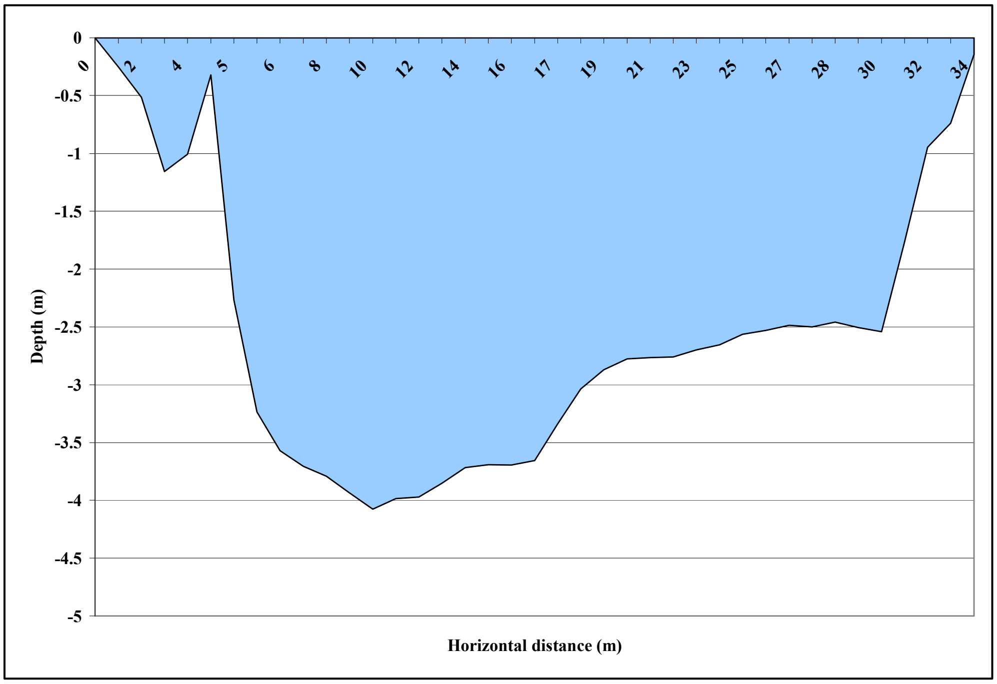


Figure 15. Río Limón cross section at storm sampling site.

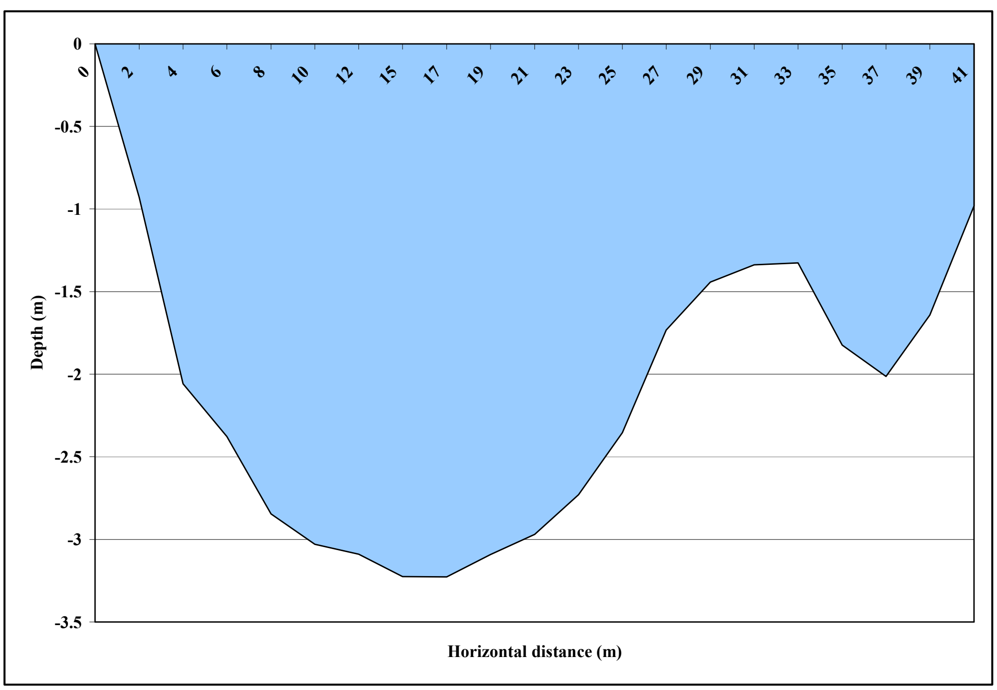


Figure 16. Río Grande de Arecibo cross section at storm sampling site.

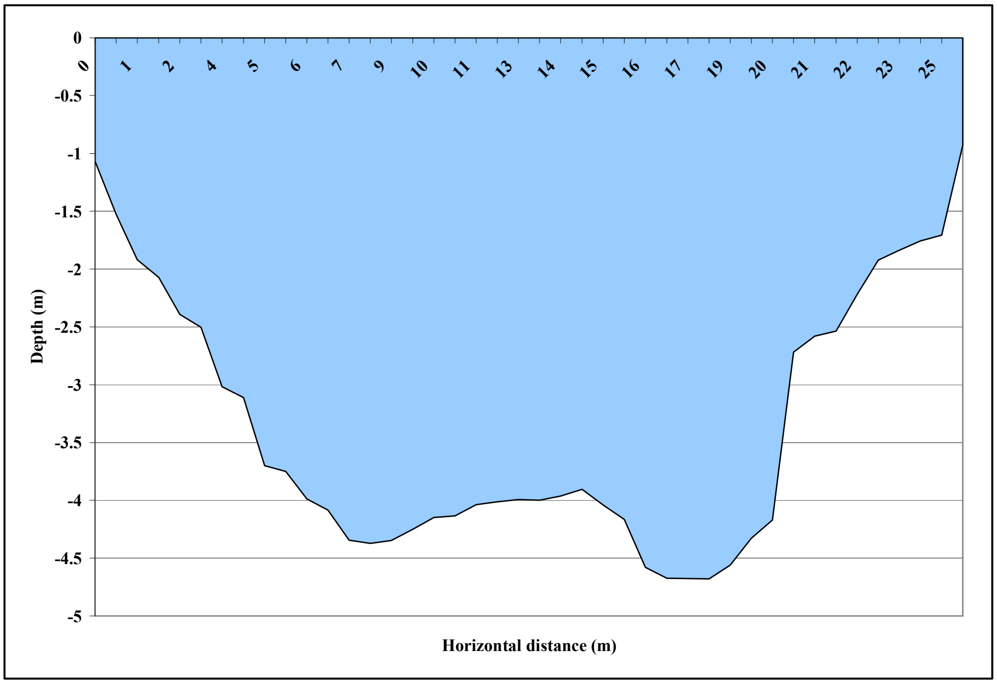


Figure 17. Río Caonillas cross section at storm sampling site.

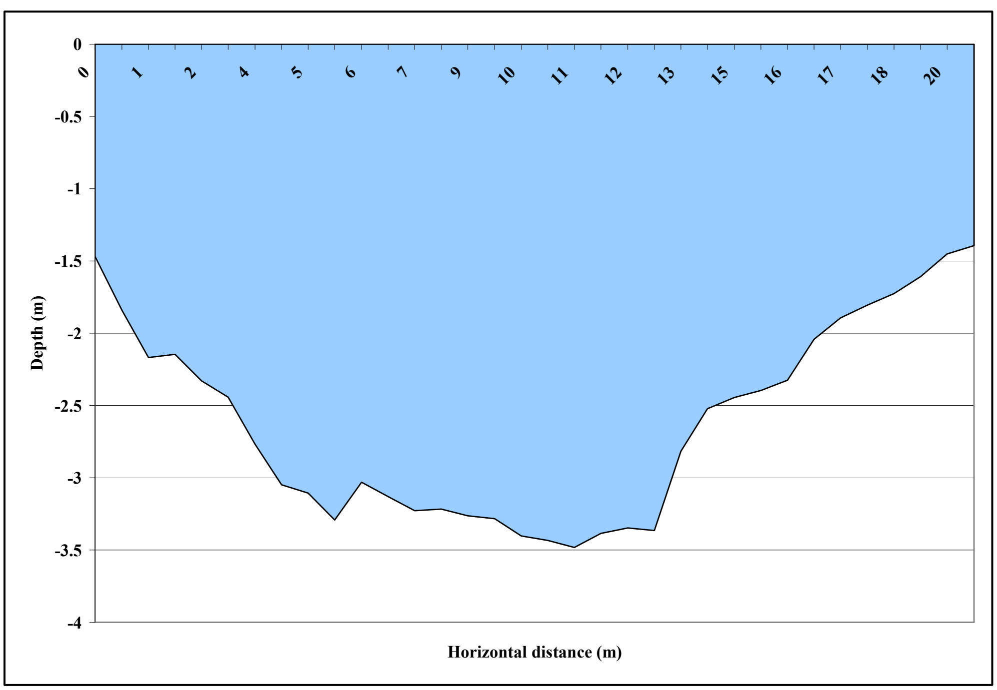


Figure 18. Río Jauca cross section at storm sampling sites.

The collected water sample was split in two fractions: one for suspended sediment analysis and a second for nutrient analysis. Suspended sediments analysis were conducted at the Soil and Water Laboratory of the Agricultural and Biosystem Engineering Department at University of Puerto Rico – Mayagüez, using the (residue, non-filterable) 160.2 method recommended by EPA (USEPA, 1983). For nutrient analysis the samples were frozen and sent to the Chemistry laboratory at the Agricultural Experimental Station – Río Piedras. Total and dissolved P was analyzed by the Persulfate Oxidation Digestion method, EPA 365.2 method (USEPA, 1999). Total Kjeldahl nitrogen (TKN) was analyzed by the Digesting Block method, following the EPA 351.3 method (USEPA, 1999). During storm events; in sufficiently long storm 24-500 ml bottles were taken. Six of those bottles were selected for nutrient analysis according to the storm hydrograph behavior. All 24 bottles were analyzed for suspended sediments.

5.4 Grab sampling

Manual grab samplings were taken biweekly using a subsurface swing sampler (Model 3228, Forestry Suppliers Inc.); all samples were collected using 500 ml polyethylene bottles in the right, center and left of the channel's cross section. Samples were collected for one USGS water year period (October 1, 2004 to September 30, 2005) during low-flow events, following procedures delineated by USGS (Wilde et al., 1998) and others (Haygarth and Edwards, 2000). Nutrient samples were taken using a swing sampler with 1000 ml polyethylene bottles and placed in three 250 ml polyethylene bottles. Suspended sediments were collected using a depth-integrated sampler model US DH-48. This model is used to collect depth integrated suspended sediments samples within 88 mm of the stream bed. The sampler uses a 500 ml polyethylene bottle.

For each grab sample the following physical parameters were measured *in situ*: conductivity, pH, temperature, salinity and dissolved oxygen using a calibrated multi-parameter water quality meter (YSI) model 63 and model 59. Appendix E shows the field data sheet used. These instruments were appropriately calibrated during the study period. Table 6 shows in details the parameters that were measured in the field and laboratory during the study period.

Table 6. Field measurements and laboratory analysis.

Field Measurements	Laboratory Measurements
conductivity	***Particulate:***
pH	total phosphorus
temperature	total Kjeldahl nitrogen
salinity	total suspended sediments
dissolved oxygen	
water velocity	***Dissolved:***
cross section of the channel	total dissolved phosphorous

Discharge (Q) and stage elevation were measured during grab sampling using a velocity meter (Global Water) and cross section of the channel. The instrument was inserted at mid depth of the water column and the average velocity was measured at different points of the cross section, for this purpose the midsection method for surface water flow were used (Gupta, 1995). Stream flow for each of the segments was calculated from the stream cross section area and water velocity. Total stream flow (Q_t; m^3/sec) was the sum of flow at each of the stream segments. This stream flow was to estimate instantaneous loads. The USGS mean daily flow was used to calculate the mean daily load of TP, DP, TKN and TSS for each sub watershed.

$$Q_t = \sum Q_i = \sum_{i=1}^{n} V_i * A_i \qquad \textbf{(2)}$$

Where Q_i is the instantaneous discharge (m^3/s), V_i is the velocity at cross section (m/s) and A_i is the cross section area (m^2) of the channel. The stream flow data was used to calculate the relative loading rates of pollutants.

Stream discharge expressed as mean daily flow (MDF) was classified as base flow or runoff flow following the Green and Haggard (2001) method. Base flow for each sub watershed was determined by series analysis using Log Pearson probability distribution graphs. Appendix G shows the $7Q_{10}$ Log Pearson type III graph with the estimated base flow for each sub watershed. Mean daily flow data series from 1995 to 2003 were used for the Log Pearson type III analysis (Río Limón 1999-2003, Río Grande de Arecibo 1996-2003, Río Caonillas 1995-2003, and Río Jauca 2000-2003). According this method all the grab sampling flows were classified as runoff conditions.

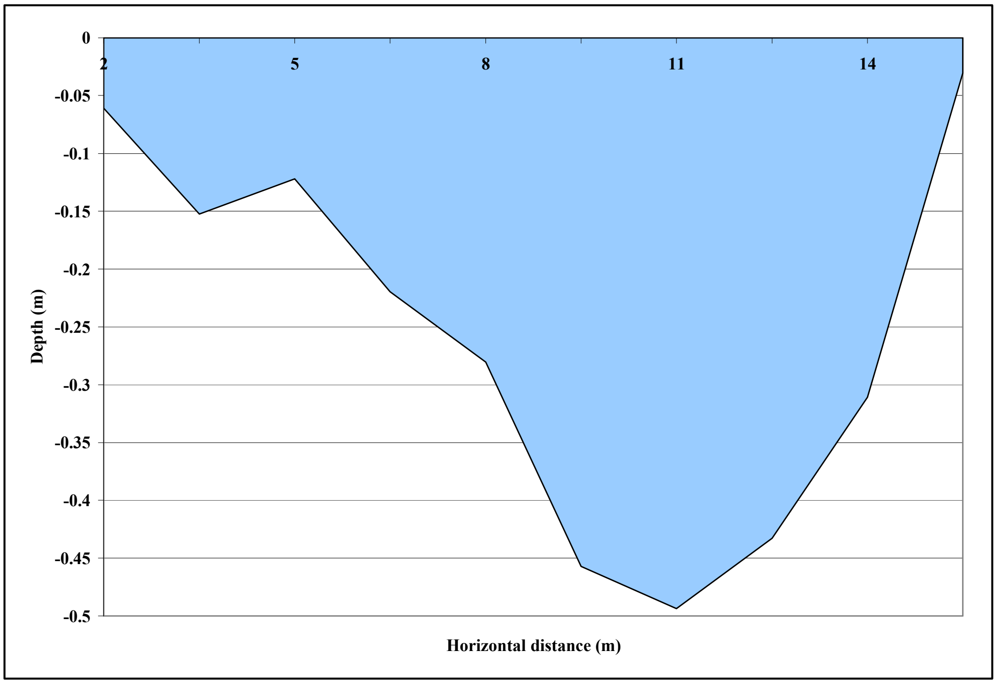


Figure 19. Río Limón cross section at grab sampling site.

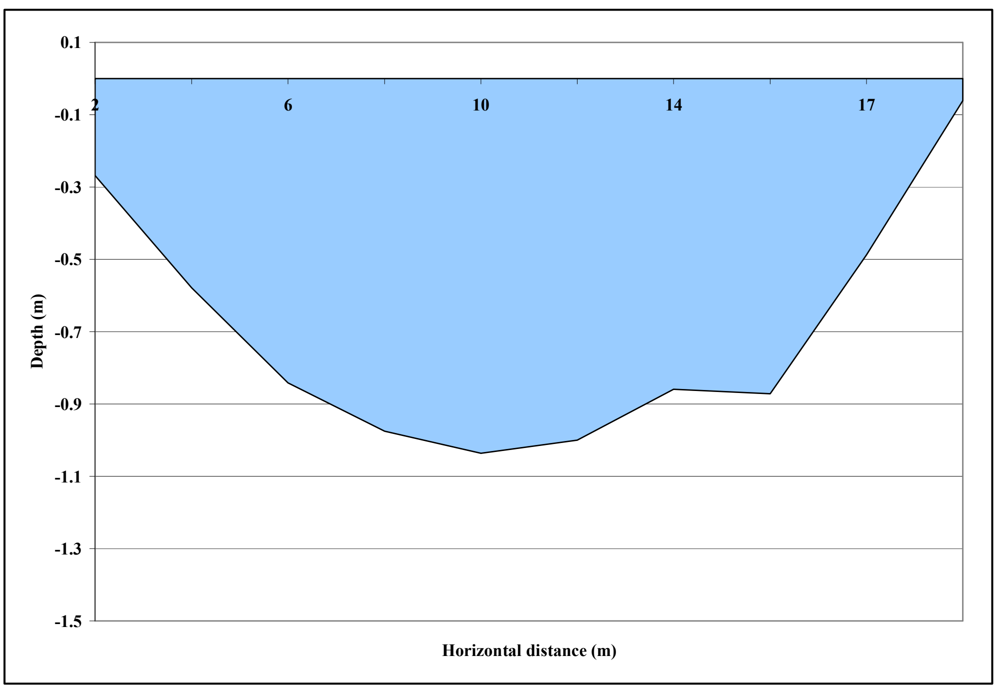


Figure 20. Río Grande de Arecibo cross section at grab sampling site.

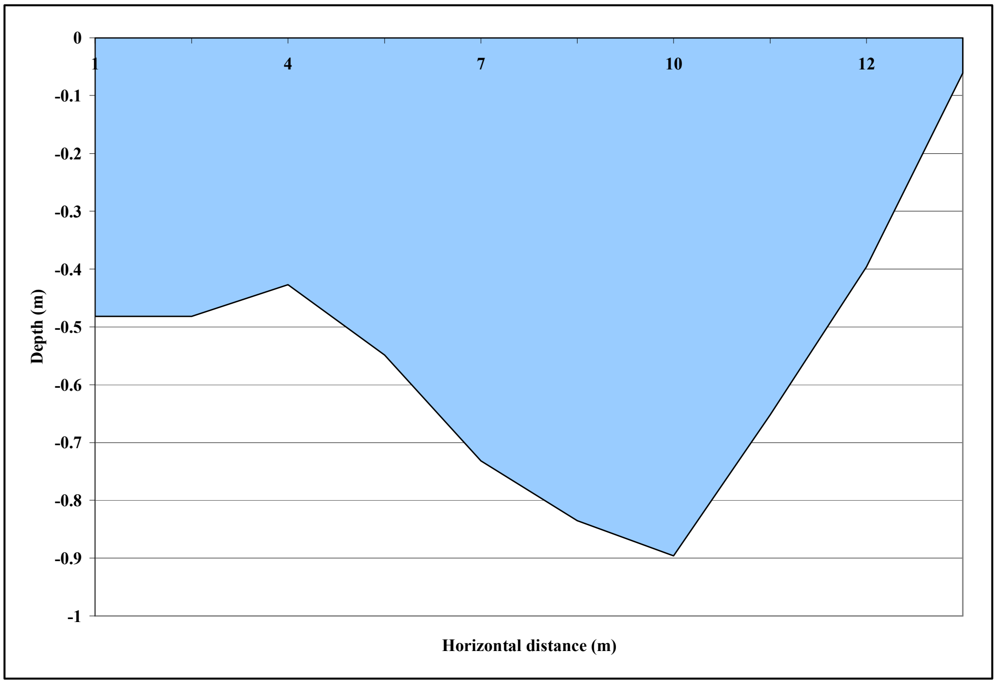


Figure 21. Río Caonillas cross section at grab sampling site.

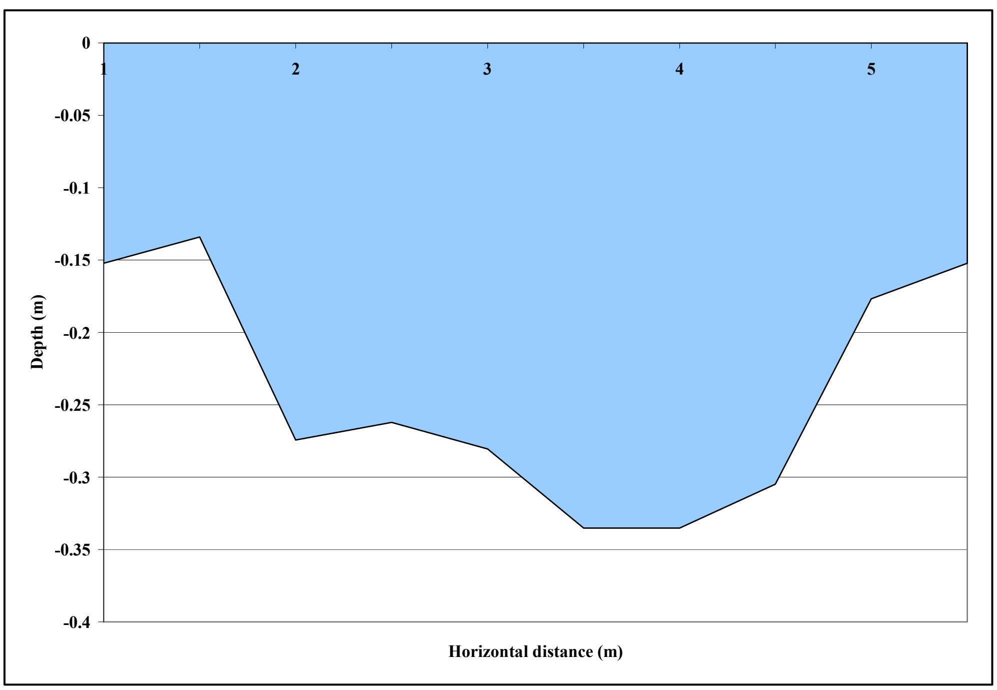


Figure 22. Río Jauca cross section area at grab sampling site.

5.5 Samples handling

Samples for nutrient analysis were placed in 250 ml pre-cleaned polyethylene bottles and frozen until analysis. One sub sample remained unfiltered for total Kjeldahl N and total P and other sample was filtered for dissolved P analysis. Suspended sediments samples were placed in 500 ml pre-cleaned polyethylene bottles and stored in the refrigerator until analysis.

All the collected samples for nutrient were analyzed at the Río Piedras Experimental Station Laboratory for total phosphorus (TP), dissolved phosphorus (DP) and total Kjeldahl nitrogen (TKN). TKN was analyzed using the EPA 351.3 method (U.S. EPA, 1999). The collected samples for suspended sediments were analyzed at the University of Puerto Rico – Mayagüez, using the 160.2 method recommended by EPA (U.S. EPA, 1983). Table 7 shows the EPA methods used in the research.

Table 7. Constituent's analytical methods.

Constituent	Analytical Method
Chlorophyll a (µg/l)	EPA 355.2
Nitrogen, ammonia + organic, total (mg/l as N)	EPA 351.2
Phosphorus, total (mg/l as P)	EPA 445.0
Phosphorus, dissolved (mg/l as P)	EPA 355.2
Sediments, suspended (mg/l)	EPA 160.2

5.6 Estimation of annual loads and yields

Regression analysis between mean daily flow (m^3/sec), nutrient (kg) and sediment (metric tons) loads were developed using collected data for each outlet, to generate annual load regression equations. The regression model was used to predict constituent loads as a function of runoff volume for the study period. Cohn et al. (1995) used the regression method to evaluate the relation between loads and mean daily flow to estimate daily loads of the constituent. Regression approaches provide a relationship between concentration and mean daily flow based on collected samples. The linear relationships developed were used to estimate a representative concentration for days not sampled, using the mean daily flow as input to the linear regression equation. For days were storm events were collected the total storm event load was calculated and substituted for the corresponded day. Not all the storm events were collected during the study period for different reasons such as equipment availability for installation and equipment damage during storm. Storm events not sampled were substituted by the estimated load generated by the regression equations for the corresponded constituent.

The species annual load was calculated as the summation of daily load, expressed by equation 3:

$$DailyLoad_{TP,DP,TKN,TSS} = \int Q_i C_i dt \qquad \textbf{(3)}$$

Where Q_i represents mean daily hydrologic flow (m^3/sec), C_i represents the mean daily species concentrations. Daily load is expressed in kg/day, annual load in kg/year and annual yield is expressed as kg/ha/year.

$$AnnualLoad_{TP,DP,TKN,TSS} = \sum_{i=1}^{365} DailyLoad \qquad \textbf{(4)}$$

$$AnnualYield_{TP,DP,TKN,TSS} = AnnualLoad \div Sub\_watershed\_area \qquad \textbf{(5)}$$

5.7 Statistical approach for annual loads estimation and data validation.

In this research a systematic method was used according with the sampling design and frequency. For each water quality parameter, statistical indicators such as means, medians, minimum values, maximum values, variances, and 95 percent confidence intervals were calculated using the Info-Stat statistical software (InfoStat, 2004) and Minitab 14 (Minitab, 2004). These statistical analyses are an important step in determining if water quality criteria have been exceeded or if water quality was significantly degraded in the study area. In order to calculate the annual loads of TSS and nutrients, linear regression equations (mean daily flow vs. constituent load) were generated and evaluated using the coefficient of determination (R^2), the statistical (P<0.05) value and the normal probability plot of residuals

For each sub watershed a Pearson correlation matrix were generated to observed correlations between TP, DP, TKN, TSS load and mean daily flow. The Fisher Least Significant Difference (LSD) test with 95 percent confidence intervals was used to observe differences between TP, DP, TKN and TSS for each station. All this procedures were performed using the InfoStat statistical software.

5.8 Predictive equations for annual loads

Annual loads were plotted versus six catchment characteristics (drainage area, maximum width of the channel, average land slope, mean elevation above sea level, mean annual precipitation and mean annual flow). A statistical model was developed and fixed to determine possible correlation between predictors and annual loads of sediment (TSS) and nutrient (TKN, TP, and DP). Procedures in the Minitab 14 statistical package such as Partial Least Square regressions method and generalized linear models were used to evaluate possible models to predict annual loads as a function of the most sensitive predictors for each sub watershed studied.

The catchments characteristics were selected based in previous experience of the research group and the simplicity concept (data availability and complexity). All the catchments characteristics were obtained from the literature (USGS, 2001) or measured in the field. This study recognized other more sophisticated methods for selecting predictors. Most of these methods are based in a sensibility analysis (Díaz-Ramírez, 2004; Suárez-Navarez, 2005).

The Partial Least Square regression method is a recent technique that generalizes and combines features from principal components analysis and multiple regressions. It is particularly useful when there is a need to predict a set of dependent variables from a large set of independent variables (predictors). It has been shown that the Partial Least Square regression method have interesting properties for regression and classification, particularly this method can improve the accuracy of unstable predictions and can be used in situations were the dependent variables are smaller than the dependent variables (Helge et al., 2005). The PLS regression approach leads to stable, correct and highly predictive models. The PLS regression is based on linear transitions from a large number of original descriptors to a new variable space based on small number of latent variables. The PLS regression method is an extension of the multiple linear regression model, this method extends the multiple linear regression model without imposing the restrictions employed by discriminants analysis and principal components.

The multiple linear regression method was evaluated to generate predictive equations, but limitations in the number of monitoring stations compared with the number of predictors made the method unsuitable for the current study make the study.

The PLS regression method was performed using Minitab version 14, which includes the PLS model. The input data for the model in order to generate predictive equation was sediment (TSS) and nutrient (TKN, TP, and DP) annual loads and each of the predictors (drainage area, maximum width of the channel, average land slope, average mean sea level elevation, mean annual precipitation, and mean annual flow). The PLS method is a biased regression procedure that relates a set of multiple response variables, and reduces the predictors to a set of uncorrelated components based on the covariance between X and Y, then performs least square regression on these components. It is important to consider the cross validation and prediction in order to evaluate the model performance (Minitab 14, 2004).

A variety of plots were generated in order to evaluate the model prediction data. The loading plot is a scatterplot of the predictors projected onto the first and second component, this plot shows how important the predictors are to fit to the components. The standardized coefficient plot is a projected scatterplot showing the standardized coefficients for each predictor; this plot makes it easier to identify predictors that are more or less significant in the model. The model selection plot is a scatterplot of the R^2 and the predicted R^2 values as a function of the number of components extracted or cross validated; this plot can be used to compare the modeling and predictive power of different model to determinate the appropriate number of components to use in the model. The coefficient plot shows the unstandardized coefficients for each predictor, this was used to compare the sign and magnitude of the coefficients for each predictor. The distance plot shows each observation's distance from the model, this plot also was used to evaluate outliers in the model. The R^2 test was used to evaluate the performance of the generated predictive equations accuracy.

6. RESULTS AND DISCUSSION

6.1 Physical and chemical characterization

A summary of the water physical and chemical characteristics for each sub watershed is shown in Table 8. These parameters were measured during grab sampling (runoff conditions) inside the stream channel in three different locations (right, center and left), in order to acquire a mean measurement of the stream cross section area. A total of 24 grab samples were taken for each sub watershed during the study period from October 1, 2004 to September 30, 2005. Figure 23, Figure 24, Figure 25, and Figure 26 show the range in temperature, pH, conductivity and streamflow, these ranges are generated from a total of 24 grab samples collected during the study period.

Table 8. Summary of water physical and chemical characteristics during grab samples.

Sub Watershed	Temperature (°C)	Conductivity (µS/cm)	pH (standard units)	Dissolved Oxygen (mg/L)	Salinity (ppt)
Río Limón	22.75	175.12	7.69	8.05	0.10
Río Grande de Arecibo	24.16	233.39	8.01	7.33	0.10
Río Caonillas	24.09	167.05	8.19	7.74	0.10
Río Jauca	22.99	146.30	8.03	8.02	0.10

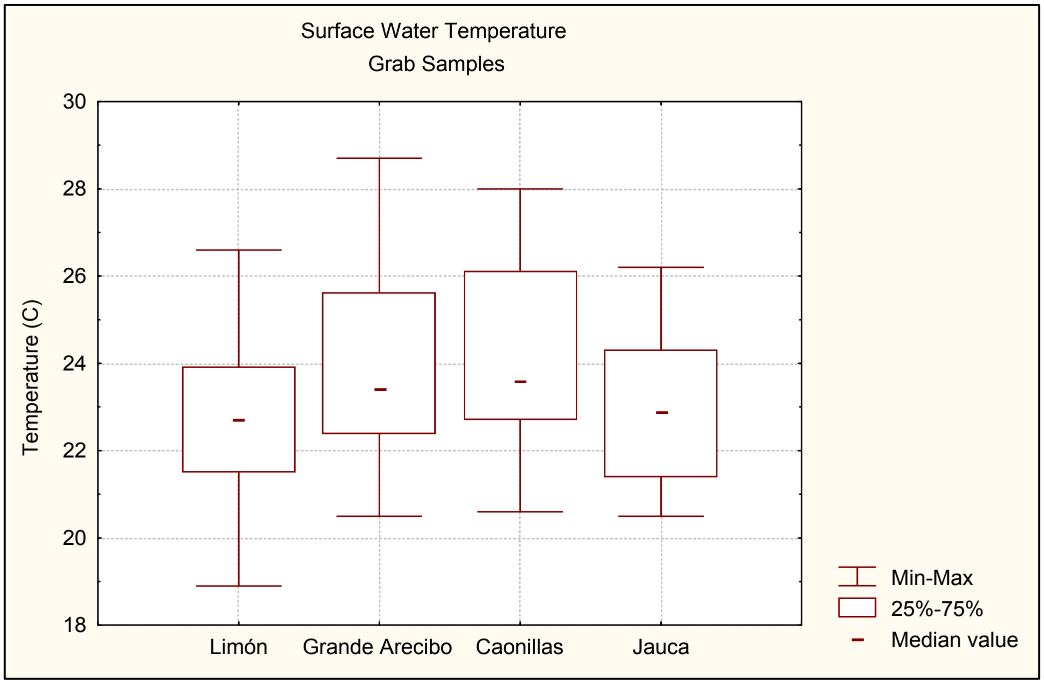


Figure 23. Box plots describing summary statistics of temperature in four sub watersheds in the Río Grande de Arecibo watershed.

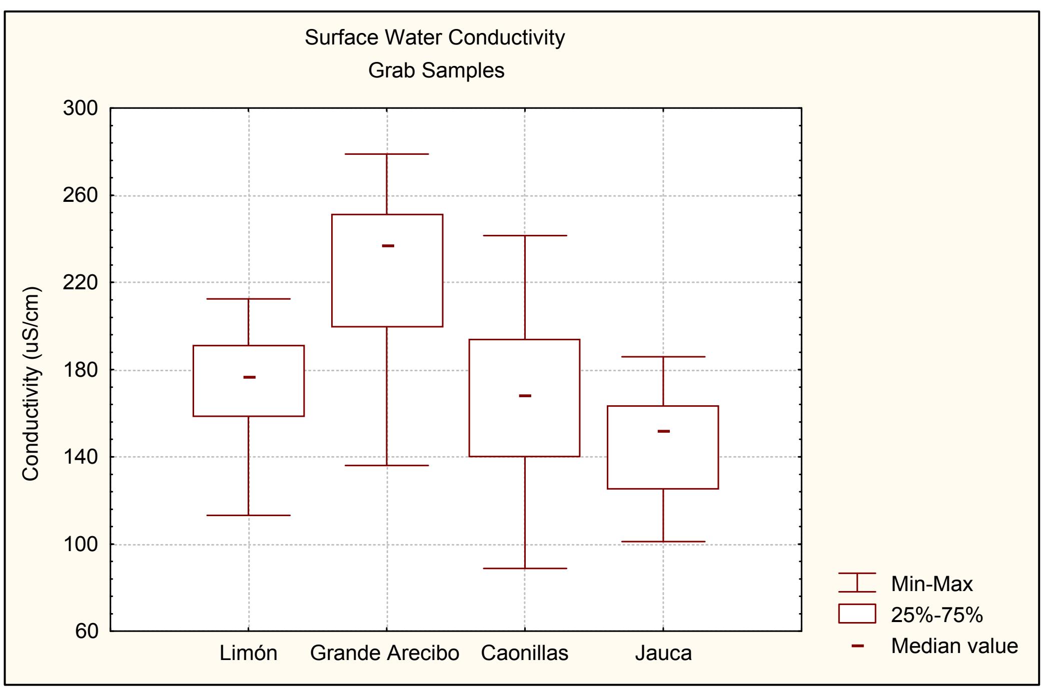


Figure 24. Box plots describing summary statistics of conductivity in four sub watersheds in the Río Grande de Arecibo watershed.

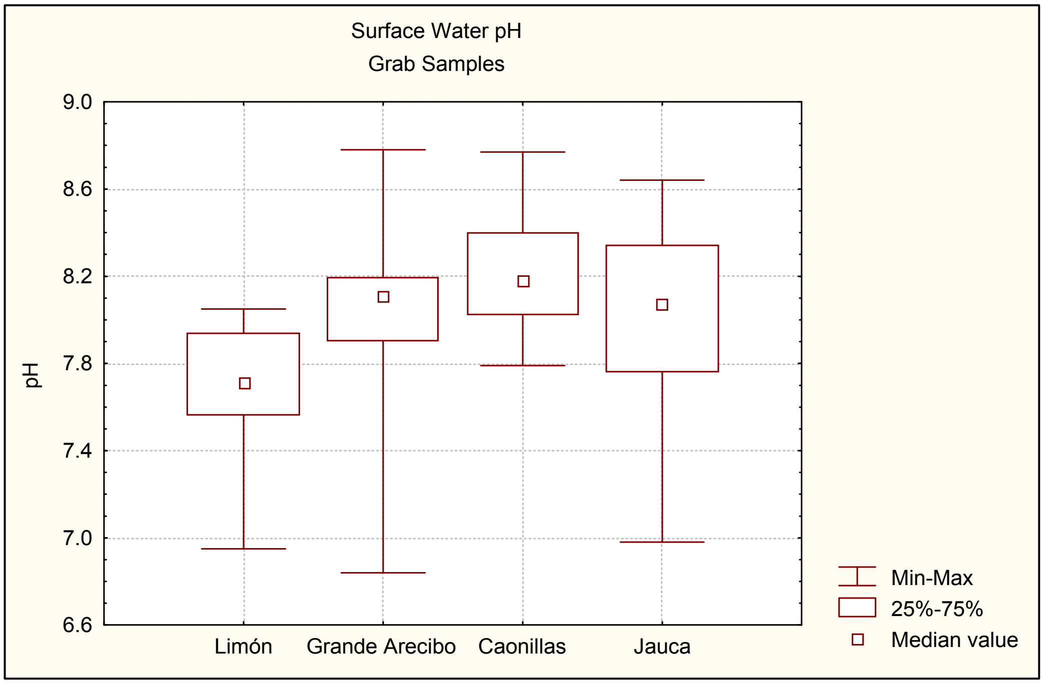


Figure 25. Box plots describing summary statistics of pH in four sub watersheds in the Río Grande de Arecibo watershed.

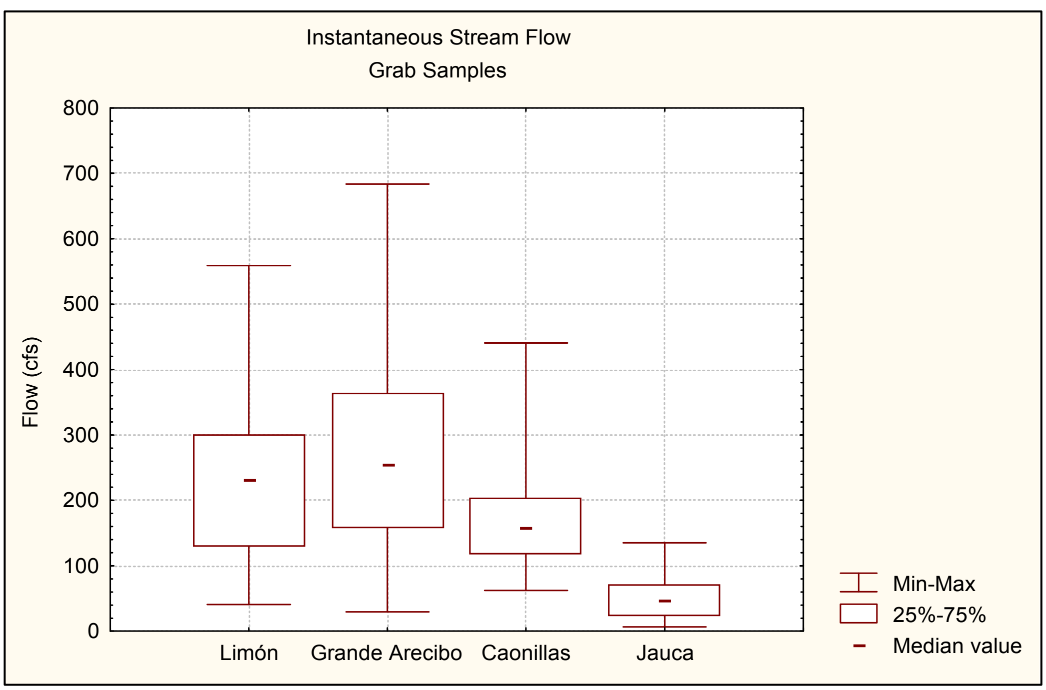


Figure 26. Box plots describing summary statistics of flow in four sub watersheds in the Río Grande de Arecibo watershed.

6.2 Mean monthly distribution of temperature, conductivity and pH.

Figure 27 shows a decrease in temperature from September 2004 to February 2005 and an increase from March to July 2005 (summer). Río Grande de Arecibo shows high values of conductivity compared with the other monitored stations, this could be due to the continuously suspended sediment transport that this watershed has during base flow conditions. The pH values vary from 6.84 to 8.78. Figure 28 and Figure 29 show the mean monthly distribution of water temperature, conductivity and pH in each sub watershed.

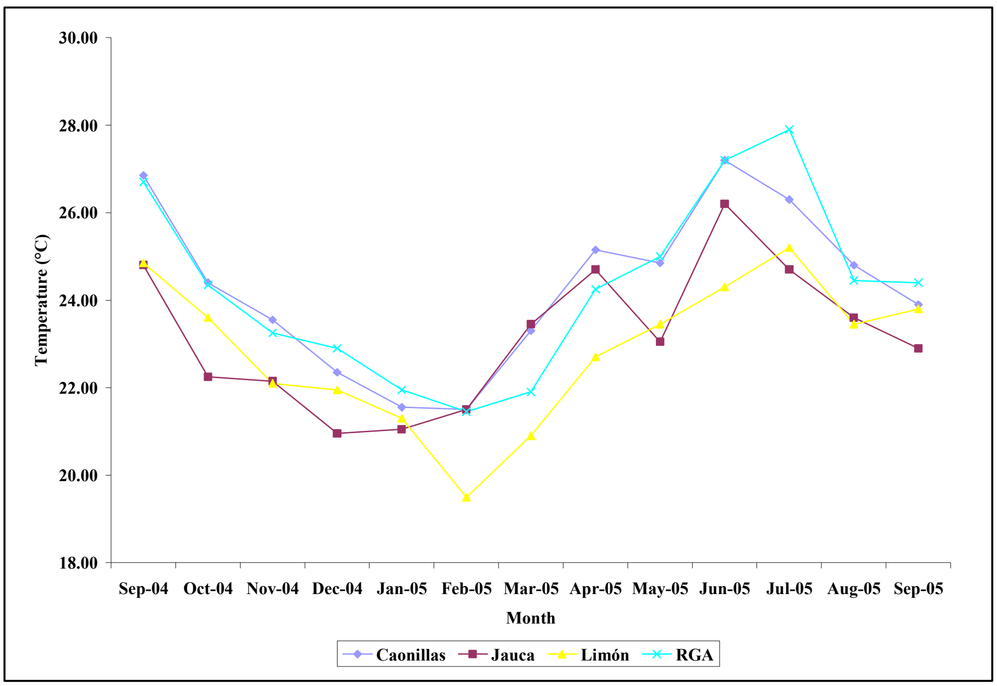


Figure 27. Mean monthly water temperature distribution for four sub watersheds in the Río Grande de Arecibo watershed.

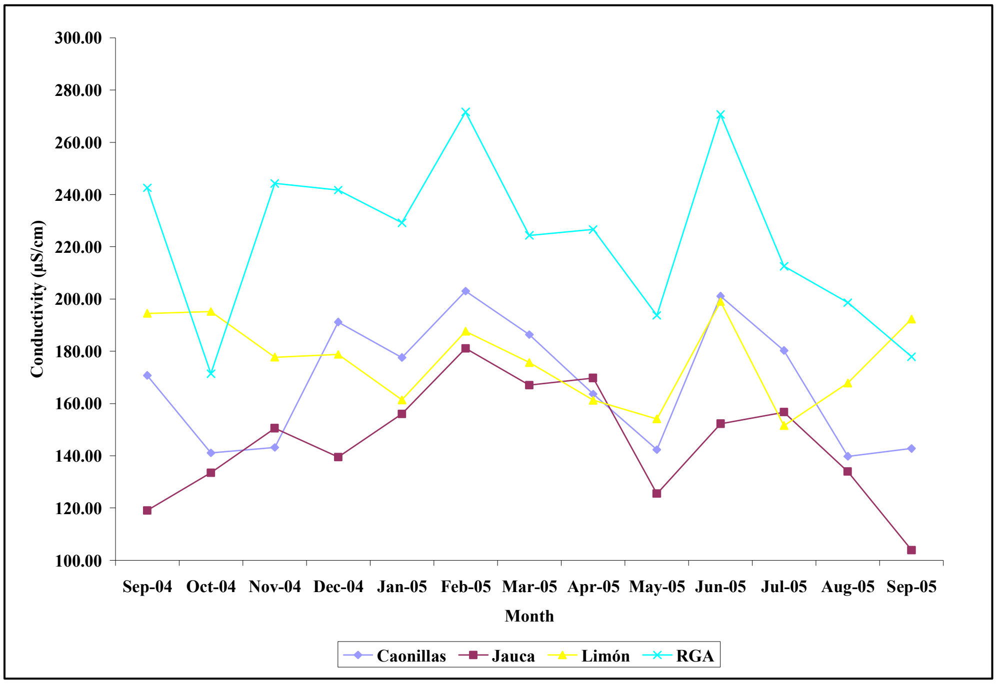


Figure 28. Mean monthly conductivity distribution for four sub watersheds in the Río Grande de Arecibo watershed.

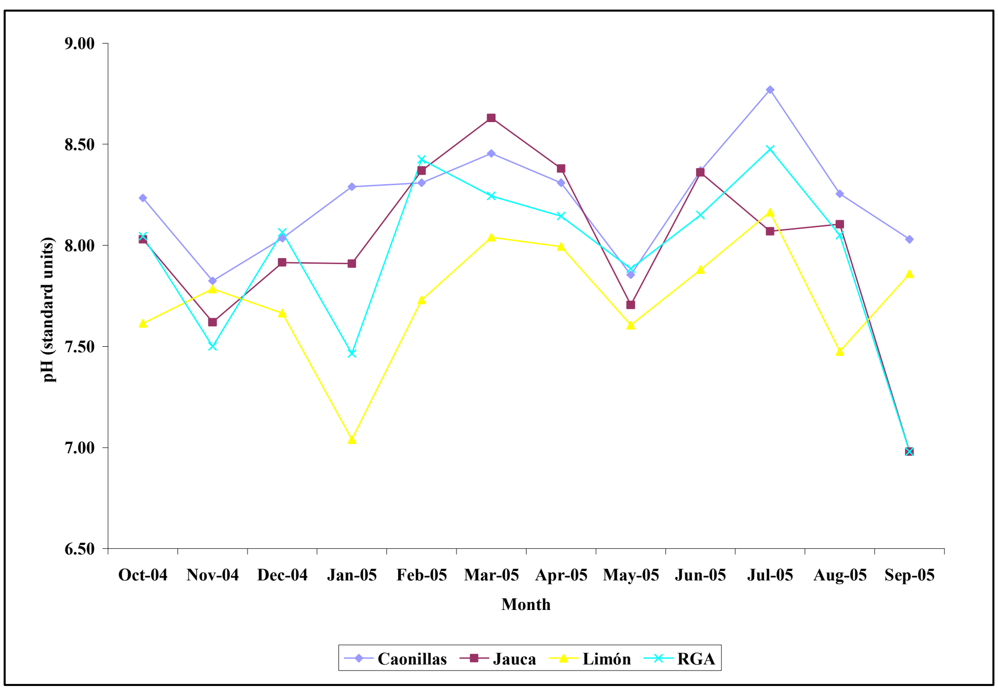


Figure 29. Mean monthly pH distribution for four sub watersheds in the Río Grande de Arecibo watershed.

6.3 Chlorophyll-a, sediment and nutrient concentrations for grab samples.

Table 9 shows chlorophyll-a, nutrient and sediment concentrations for each sub watershed during grab sampling. Tables report the range and median concentration for each of the constituents (chlorophyll-a, TKN, TP, DP, and TSS). The Río Grande de Arecibo watershed had the highest maximum chlorophyll-a concentration (23.94 μg/L). Río Limón has the highest maximum TKN concentration (0.75 mg/L). Río Caonillas has the higher maximum TP and TSS concentrations (0.15 mg/L and 35.0 mg/L). Río Jauca has the highest maximum DP concentration (0.21 mg/L).

The median concentration values of TP for each sub watershed during the grab sampling period was: 0.06 mg/L for Río Limón sub watershed, 0.08 mg/L for Río Grande de Arecibo sub watershed, 0.07 mg/L for Río Caonillas sub watershed and 0.04 mg/L for Río Jauca sub watershed. Comparing these values with the 0.1 mg/L of TP in streams or flowing water suggested by the Environmental Protection Agency (USEPA, 1986) all concentrations were under the water quality criteria. On the other hand, if the fact that all the studied streams are entering to lakes (Lake Dos Bocas and Lake Caonillas) the critical value of 0.05 mg/L for streams entering lakes suggested by USEPA can be applied. In this case 57% of the samples for Río Limón sub watershed, 83% for Río Grande de Arecibo sub watershed, 96% for Río Caonillas sub watershed and 20% for Río Jauca sub watershed exceeded the USEPA standard. Figure 30 to Figure 34 show the range in concentration of Chlorophyll a, TKN, TP, DP and TSS for each sub watershed during grab samples. This figures show the maximum, minimum and average values for this concentrations.

Table 9. Median concentrations of chlorophyll-a, nutrient and sediment for grab samples

Sub Watershed	Chlorophyll-a (μg/l)	Total Kjeldhal Nitrogen (mg/L)	Total Phosphorus (mg/L)	Dissolved Phosphorus (mg/L)	Total Suspended Sediments (mg/L)
Río Limón	3.36	0.12	0.06	0.05	14.17
Río Grande de Arecibo	6.48	0.22	0.08	0.06	22.50
Río Caonillas	5.04	0.13	0.07	0.06	15.00
Río Jauca	3.66	0.07	0.04	0.03	10.00

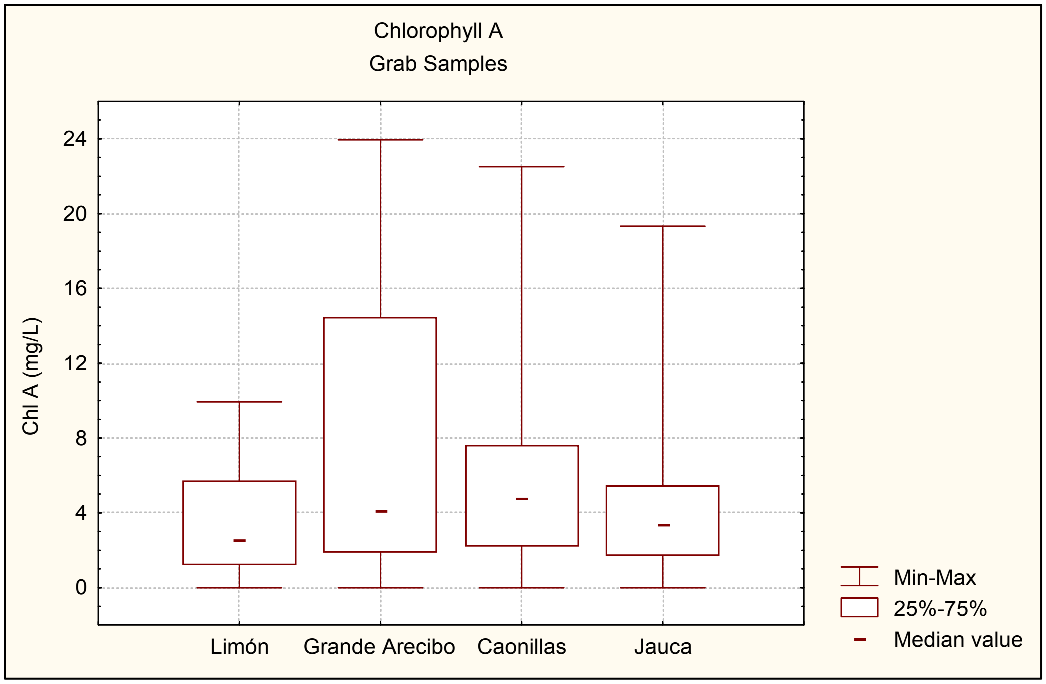


Figure 30. Box plots describing summary statistics of chlorophyll-a concentration in four sub watersheds in the Río Grande de Arecibo watershed.

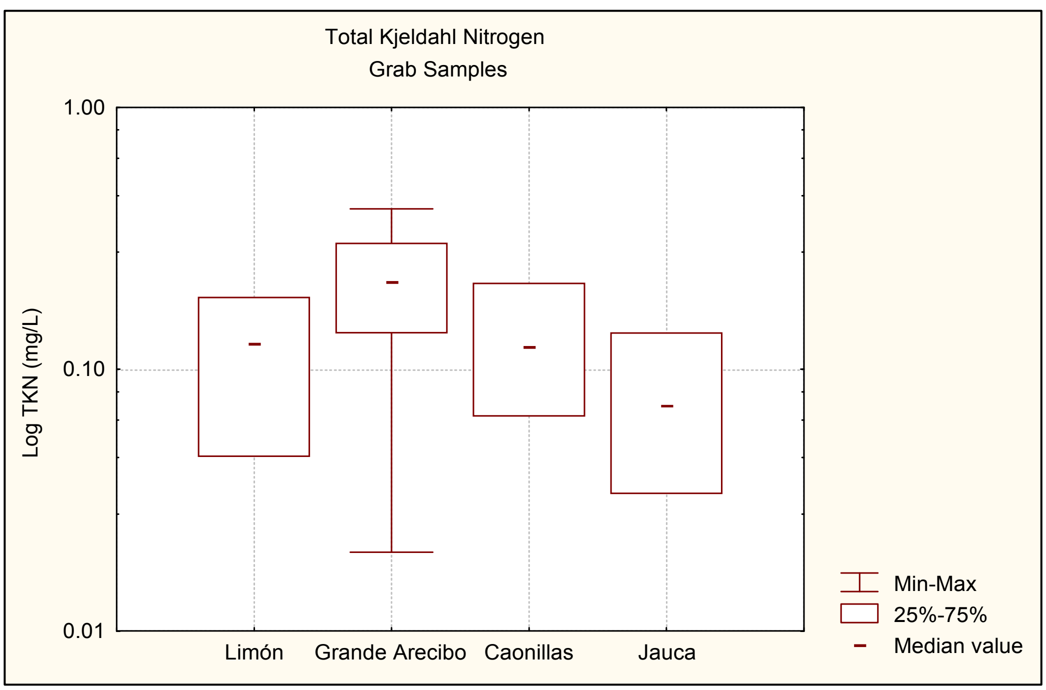


Figure 31. Box plots describing summary statistics of TKN concentration in four sub watersheds in the Río Grande de Arecibo watershed.

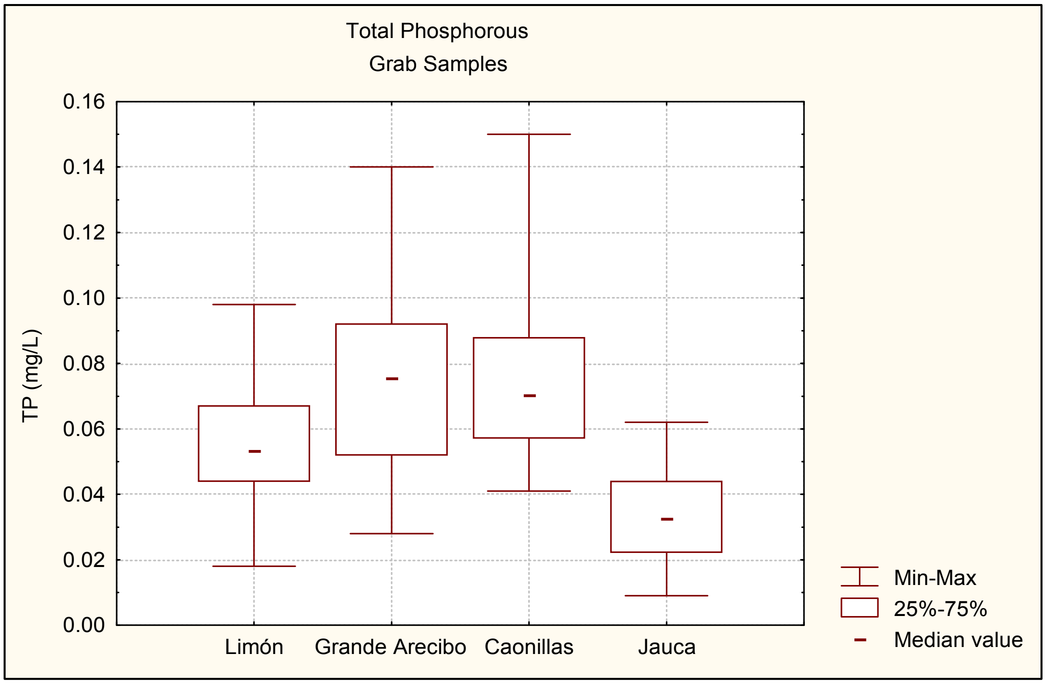


Figure 32. Box plots describing summary statistics of TP concentration in four sub watersheds in the Río Grande de Arecibo watershed.

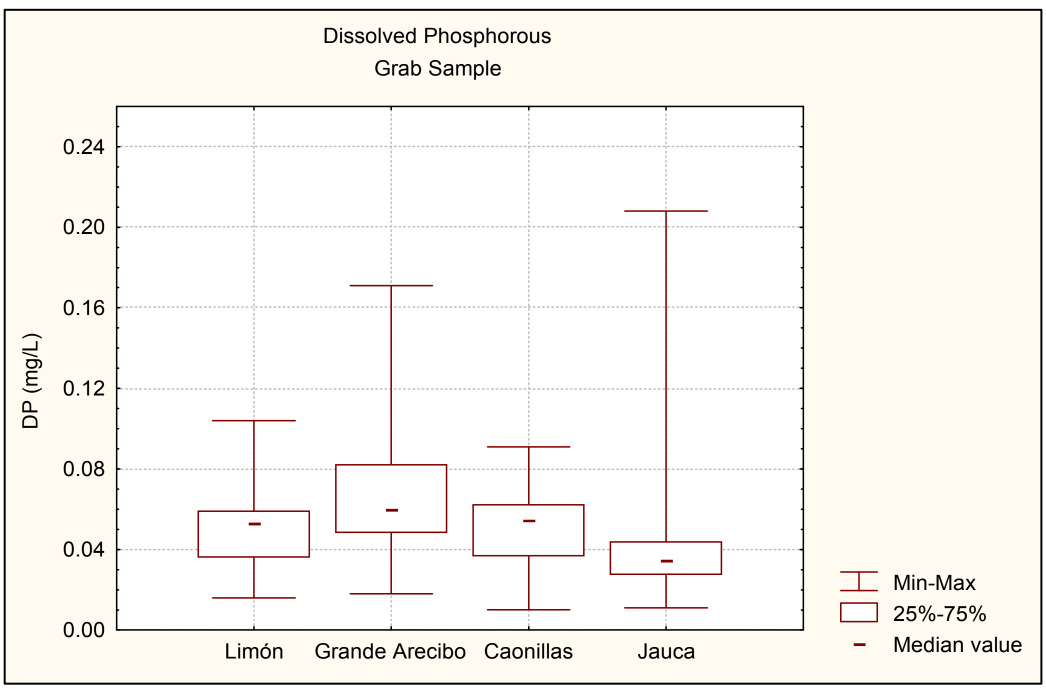


Figure 33. Box plots describing summary statistics of DP concentration in four sub watersheds in the Río Grande de Arecibo watershed.

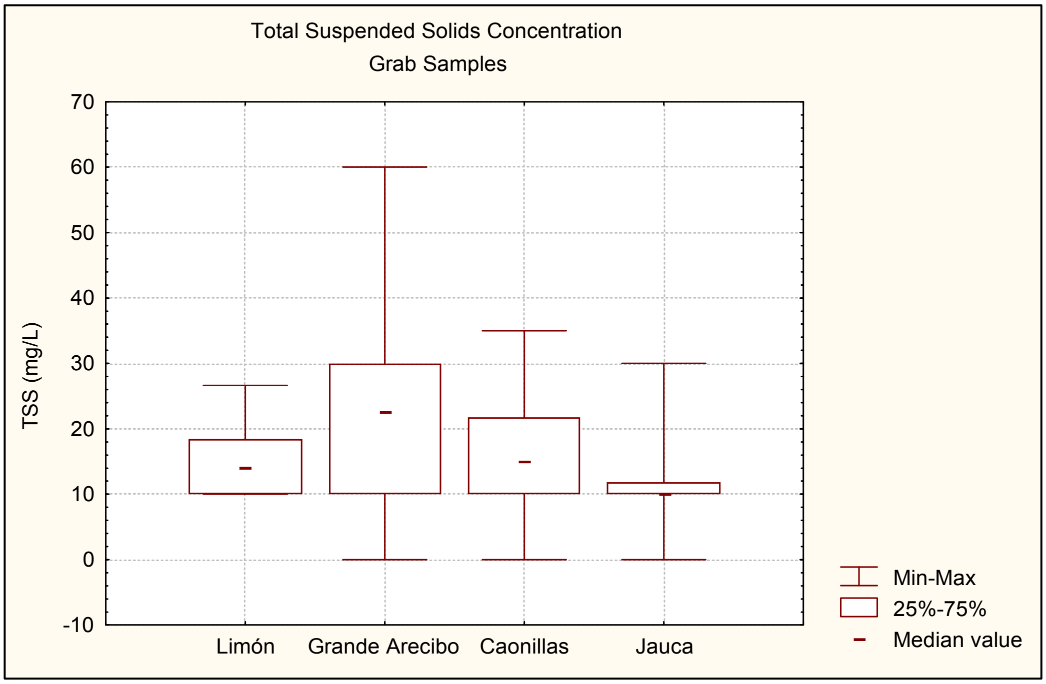


Figure 34. Box plots describing summary statistics of TSS concentration in four sub watersheds in the Río Grande de Arecibo watershed.

6.4 Pearson correlation matrix of chlorophyll-a, TP, DP, TKN, TSS loads and flow

Table 10, Table 11, Table 12 and Table 13 show the Pearson correlations matrix for chlorophyll-a, TP, DP, TKN, TSS and mean daily flow for each of the studied sub watersheds. Chlorophyll-a load show a positive relationship with flow TSS and flow for Río Grande de Arecibo (0.81, 0.64), Río Caonillas (0.71, 0.77) and Río Jauca (0.77, 0.79) sub watersheds. It was observed positive chlorophyll-a relationship in Río Caonillas for TP and DP (0.86, 0.82).

Total phosphorus (TP) load show a high correlation with dissolved phosphorus (DP) for all the sub watersheds, this correlations range from 0.57 (Río Jauca) to 0.93 (Río Caonillas). High correlations values were observed between TP load and mean daily flow, ranging from 0.80 to 0.93. Dissolved phosphorus loads were positively correlated with mean daily flow.

Total Kjeldahl nitrogen load were positively correlated with flow for three of the sub watersheds, Río Grande de Arecibo (0.60), Río Caonillas (0.87) and Río Jauca (0.57). Total suspended sediments (TSS) were found to be positively correlated with the mean daily flow in all four sub watersheds.

Table 10. Río Limón sub watershed correlation matrix

	Chl a	TP	DP	TKN	TSS	Flow
Chl a	1.0000					
TP	0.4750	1.0000				
DP	0.3700	0.9170	1.0000			
TKN	0.0280	0.0460	0.0874	1.0000		
TSS	0.3520	0.5230	0.5991	-0.0303	1.0000	
Flow	0.6380	0.8050	0.7310	-0.1040	0.7739	1.0000

Table 11. Río Grande de Arecibo sub watershed correlation matrix

	Chl a	TP	DP	TKN	TSS	Flow
Chl a	1.0000					
TP	0.2183	1.0000				
DP	0.5257	0.8934	1.0000			
TKN	0.0885	0.8886	0.6805	1.0000		
TSS	0.8143	0.2998	0.6639	0.0057	1.0000	
Flow	0.6414	0.8267	0.9704	0.5969	0.7734	1.0000

Table 12. Río Caonillas sub watershed correlation matrix

	Chl a	TP	DP	TKN	TSS	Flow
Chl a	1.0000					
TP	0.8566	1.0000				
DP	0.8175	0.9300	1.0000			
TKN	0.7001	0.9200	0.8922	1.0000		
TSS	0.7063	0.8216	0.9235	0.7820	1.0000	
Flow	0.7727	0.9300	0.9541	0.8743	0.9259	1.0000

Table 13. Río Jauca sub watershed correlation matrix

	Chl a	TP	DP	TKN	TSS	Flow
Chl a	1.0000					
TP	0.4802	1.0000				
DP	0.1195	0.5737	1.0000			
TKN	0.2289	0.6910	0.3629	1.0000		
TSS	0.7719	0.8206	0.5800	0.4847	1.0000	
Flow	0.7914	0.8820	0.5784	0.5672	0.9708	1.0000

6.5 Mean monthly concentration of chlorophyll-a, sediments and nutrients for grab samples

Figure 35 shows the mean monthly concentration of chlorophyll-a, for the study period. The highest chlorophyll-a concentrations are shown next: (9.48 mg/L) for Río Limón sub watershed during October 2004, (19.17 mg/L) Río Grande de Arecibo sub watershed during February 2005, (15.12 mg/L) Río Caonillas sub watershed during February 2005 and (17.19 mg/L) Río Jauca sub watershed during December 2004.

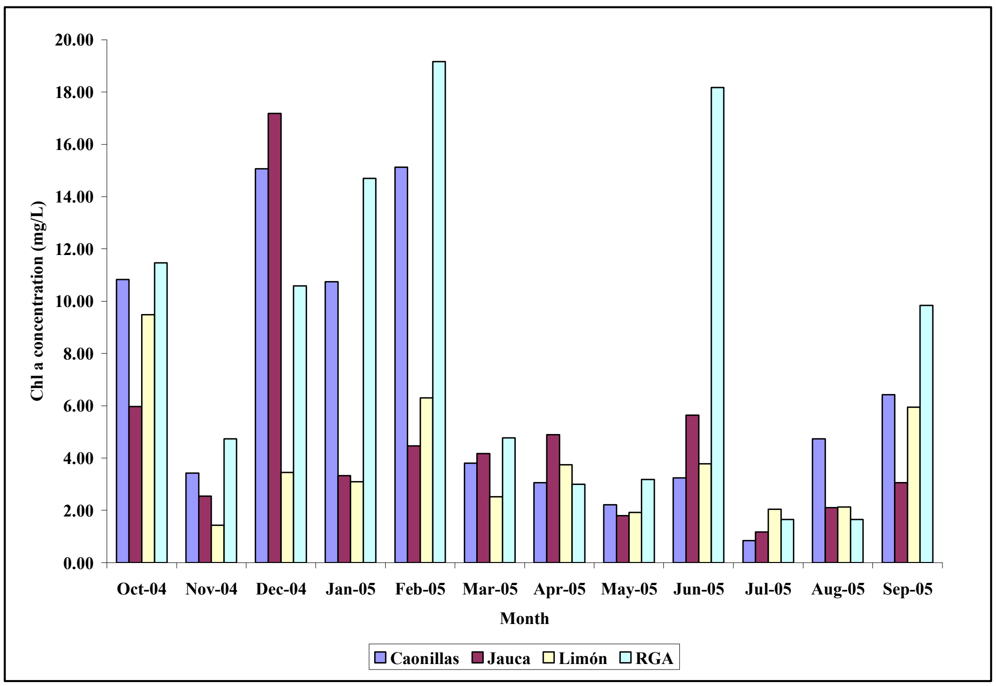


Figure 35. Mean monthly concentration of chlorophyll-a in four sub watersheds in the Río Grande de Arecibo watershed.

Figure 36 shows the mean monthly concentration of TKN, for the study period. The highest mean TKN concentrations are shown next: (0.44 mg/L) for Río Limón sub watershed during March 2005, (0.32 mg/L) Río Grande de Arecibo sub watershed during March 2005, (0.33 mg/L) Río Caonillas sub watershed during September 2004 and (0.24 mg/L) Río Jauca sub watershed during April 2005.

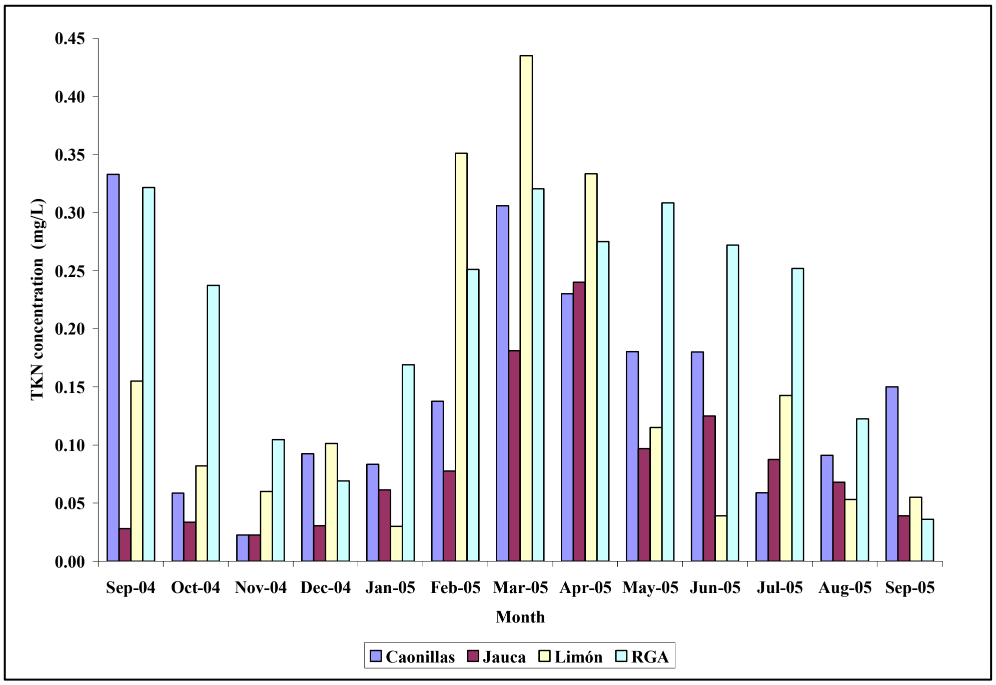


Figure 36. Mean monthly concentration of total Kjeldahl nitrogen in four sub watersheds in the Río Grande de Arecibo watershed.

Figure 37 shows the mean monthly concentration of TP, for the study period. The highest mean TP concentrations are shown next: (0.08 mg/L) for Río Limón sub watershed during May 2005, (0.12 mg/L) Río Grande de Arecibo sub watershed during May 2005, (0.15 mg/L) Río Caonillas sub watershed during September 2005 and (0.06 mg/L) Río Jauca sub watershed during August 2005.

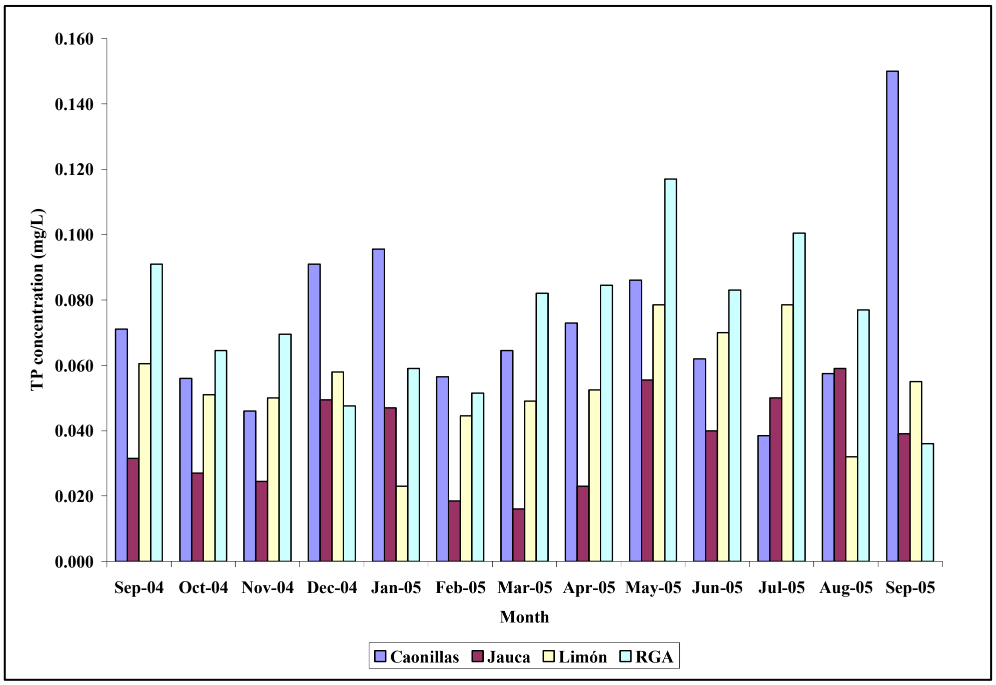


Figure 37. Monthly mean concentration of total phosphorus in four sub watersheds in the Río Grande de Arecibo watershed.

Figure 38 shows the mean monthly concentration of DP, for the study period. The highest mean DP concentrations are shown next: (0.09 mg/L) for Río Limón sub watershed during July 2005, (0.11 mg/L) Río Grande de Arecibo sub watershed during May 2005, (0.07 mg/L) Río Caonillas sub watershed during February 2005 and (0.12 mg/L) Río Jauca sub watershed during May 2005.

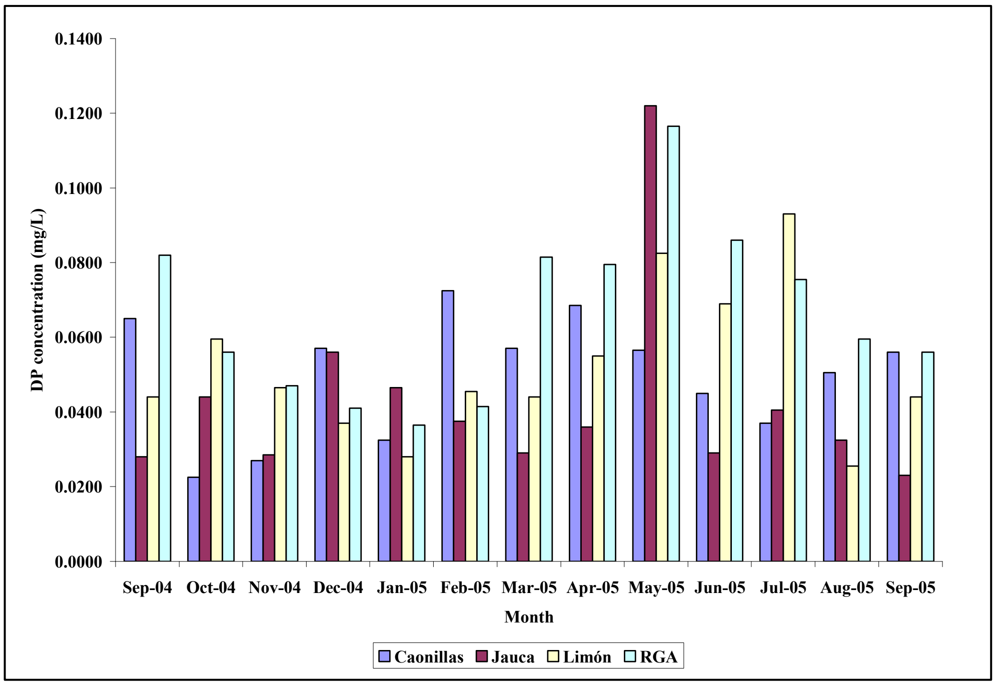


Figure 38. Mean monthly concentration of dissolved phosphorus in four sub watersheds in the Río Grande de Arecibo watershed.

Figure 39 shows the mean monthly concentration of TSS, for the study period. The highest mean TSS concentrations are shown next: (18.30 mg/L) for Río Limón sub watershed during May 2005, (60.00 mg/L) Río Grande de Arecibo sub watershed during September 2005, (30.00 mg/L) Río Caonillas sub watershed during September 2004 and (30.00 mg/L) Río Jauca sub watershed during September 2005.

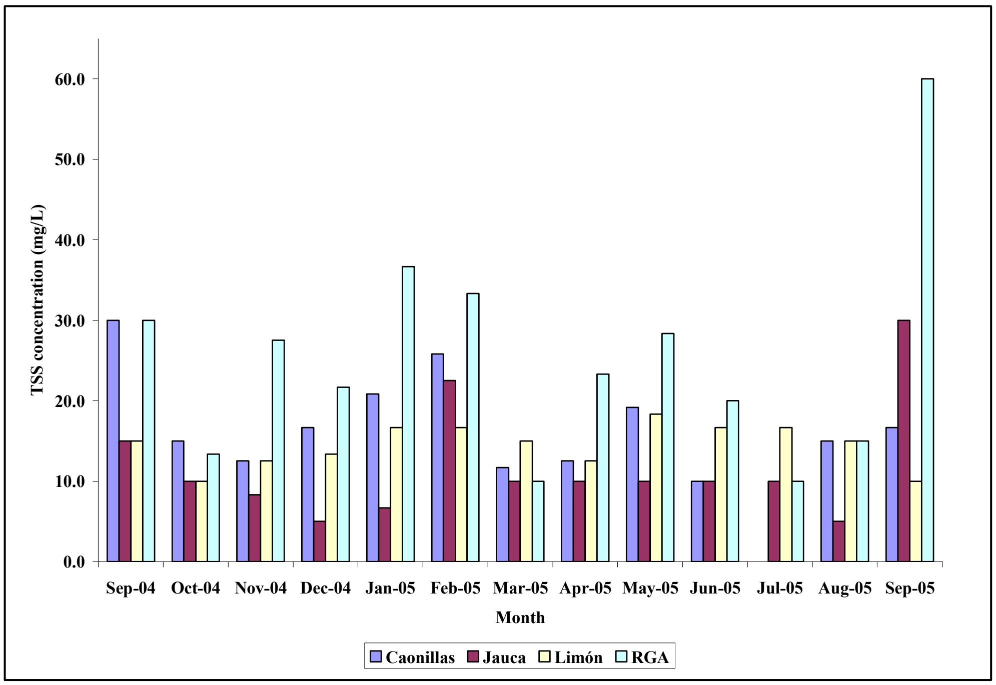


Figure 39. Mean monthly concentration of total suspended sediment in four sub watersheds in the Río Grande de Arecibo watershed.

6.6 Nutrient concentrations during storm events

Table 14, Table 15, Table 16 and Table 17 show chlorophyll-a, nutrient and sediment concentrations for each sub watershed during storm events that took place from October 1, 2004 to September 30, 2005. These tables report the event duration, total storm volume and median concentration values for TKN, TP and DP. A total of seven storm events were collected for Río Limón sub watershed during the research period, nutrient concentration range from: 5.56 mg/L (TKN), 0.99 mg/L (TP) and 0.12 mg/L (DP). Two storm events were collected from Río Grande de Arecibo sub watershed, nutrient concentration range from: 0.08 mg/L (TKN), 0.03 mg/L (TP) and 0.05 mg/L (DP). Four storm events were collected for Río Caonillas sub watershed, nutrient concentration range from: 3.20 mg/L (TKN), 1.75 mg/L (TP) and 0.11 mg/L (DP). A total of five storm events were collected for Río Jauca sub watershed, nutrient concentration range from: 2.45 mg/L (TKN), 1.66 mg/L (TP) and 0.15 mg/L (DP).

Table 14. Summary of nutrient concentrations (Río Limón).

Storm #	Date	Event duration (hours)	Total volume (m^3)	Median Nutrient Concentration TKN (mg/L)	TP (mg/L)	DP (mg/L)
1	12/10/04	2.91	1.71E+05	3.69	0.07	0.01
2	13/10/04	3.66	2.48E+05	6.49	0.24	0.13
3	12/11/04	5.00	1.04E+06	1.11	0.30	0.02
4	14/11/04	5.00	1.06E+06	0.93	0.20	0.03
5	21/11/04	2.91	1.57E+05	2.73	1.06	0.06
6	19/04/05	2.17	6.16E+05	3.28	0.67	0.03
7	09/05/05	1.92	1.30E+05	2.19	0.66	0.02

Table 15. Summary of nutrient concentrations (Río Grande de Arecibo).

Storm #	Date	Event duration (hours)	Total volume (m^3)	Median Nutrient Concentration TKN (mg/L)	TP (mg/L)	DP (mg/L)
1	14/10/04	2.91	3.18E+05	1.20	0.73	0.24
2	11/12/04	4.17	6.47E+05	1.28	0.76	0.19

Table 16. Summary of nutrient concentrations (Río Caonillas).

Storm #	Date	Event duration (hours)	Total volume (m^3)	Median Nutrient Concentration TKN (mg/L)	TP (mg/L)	DP (mg/L)
1	30/10/04	5.17	5.10E+05	3.69	0.07	0.01
2	11/12/04	5.17	7.54E+05	4.56	1.82	0.12
3	19/04/05	1.17	5.52E+04	2.73	1.02	0.07
4	24/05/05	3.92	2.21E+05	1.36	0.19	0.02

Table 17. Summary of nutrient concentrations (Río Jauca).

Storm #	Date	Event duration (hours)	Total volume (m^3)	Median Nutrient Concentration TKN (mg/L)	TP (mg/L)	DP (mg/L)
1	05/10/04	1.92	7.90E+04	2.45	0.05	0.02
2	08/10/04	1.17	3.80E+04	3.88	0.23	0.09
3	10/10/04	1.92	6.93E+04	1.54	0.04	0.01
4	11/12/04	3.17	5.60E+05	1.43	0.22	0.16
5	09/05/05	3.42	2.00E+05	1.85	1.70	0.04

6.7 Total suspended sediment loads during storm events

Twenty nine (29) storm events were monitored for suspended sediment during the 2004-2005 water year. A total of 451 discrete samples were collected from the 29 storm events. On average, 15 bottles were collected for each storm event during the study period. Total event TSS load (metric tons/event) was calculated by integrating over the sedigraph generated by each storm event as shown in Appendix C and Appendix D.

Table 18, Table 19, Table 20 and Table 21 summarize the TSS storm events in the studied watersheds. The maximum storm TSS load (3,047metric tons) obtained during the study period was observed in Río Limón sub watershed on the 12/11/04. The minimum storm TSS load was observed in Río Jauca sub watershed where loads ranged from 30 metric tons on 22/05/05 to 656 metric tons on 09/05/05. The mean total load observed for all the storm events sub watersheds was 768 metric tons.

Table 18. Summary of total suspended sediment loads at Río Limón sub watershed.

		Sediment load (metric tons)		**Event flow (m^3/s)**		
Storm #	Sampling date	Total event load	Mean load	Minimum-maximum	Number of samples	Event duration (hours)
1	11/09/04	1228.35	51.17	6.34-40.66	24	5.00
2	12/09/04	1505.04	62.71	5.18-65.52	24	5.00
3	12/10/04	921.85	57.61	3.57-33.22	15	2.91
4	13/10/04	1013.67	56.31	3.28-55.61	18	3.66
5	12/11/04	3047.35	126.96	20.05-135.24	24	5.00
6	14/11/04	622.70	25.95	38.261-81.55	24	5.00
7	21/11/04	63.92	4.25	8.78-21.97	15	2.91
8	13/01/05	534.99	76.43	14.98-88.77	7	0.91
9	19/01/05	21.75	4.35	13.11-15.97	5	0.42
10	18/04/05	219.85	19.98	5.18-33.44	11	1.92
11	19/04/05	1298.51	108.20	7.16-138.21	12	2.17
12	09/05/05	796.98	72.45	14.36-20.05	11	1.92

Table 19. Summary of total suspended sediment loads at Río Grande de Arecibo sub watershed.

		Sediment load (metric tons)		Event flow (m^3/s)		
Storm #	Sampling date	Total event load	Mean load	Minimum-maximum	Number of samples	Event duration (hours)
1	14/10/04	401.60	25.84	17.61-73.00	15	2.91
2	11/12/04	1233.66	61.68	10.28-77.53	20	4.17

Table 20. Summary of total suspended sediment loads (Río Caonillas).

		Sediment load (metric tons)		Event flow (m^3/s)		
Storm #	Sampling date	Total event load	Mean load	Minimum-maximum	Number of samples	Event duration (hours)
1	30/10/04	1884.08	5.77	10.31-60.99	24	5.17
2	11/12/04	2514.54	104.77	11.13-98.12	24	5.17
3	19/04/05	77.81	9.72	10.31-15.29	8	1.17
4	09/05/05	920.99	65.78	16.45-39.76	14	2.67
5	24/05/05	401.43	21.13	11.58-22.59	19	3.92
6	27/05/05	529.74	22.06	8.98-19.26	24	5.17

Table 21. Summary of total suspended sediment loads (Río Jauca).

		Sediment load (metric tons)		Event flow (m^3/s)		
Storm #	Sampling date	Total event load	Mean load	Minimum-maximum	Number of samples	Event duration (hours)
1	07/09/04	481.44	22.93	1.70-23.50	21	4.42
2	05/10/04	145.28	13.21	9.71-13.99	11	1.92
3	08/10/04	74.95	9.37	5.69-12.20	8	1.17
4	10/10/04	119.40	10.85	3.54-21.07	11	1.92
5	11/12/04	610.26	40.68	46.84-66.54	16	3.17
6	09/05/05	656.80	38.63	5.04-31.40	17	3.42
7	17/05/05	449.90	44.99	19.57-45.56	10	1.67
8	22/05/05	30.05	2.73	2.61-16.19	11	1.92
9	08/10/05	462.70	57.84	51.65-66.54	8	1.17

6.8 Nutrient loads during storm events

For each selected storm event, six 500 ml bottle samples were selected for analysis according to the storm runoff hydrograph. Typically bottles 1, 4, 9, 14, 18 and 24 of a maximum of 24 bottles were selected for nutrient analysis. Bottles 1, 4 and 9 sampled the rising limb of the runoff hydrograph, while bottles 14, 18 and 24 the falling limb. Figure 40 show the typical sampling scheme for nutrients during storm events.

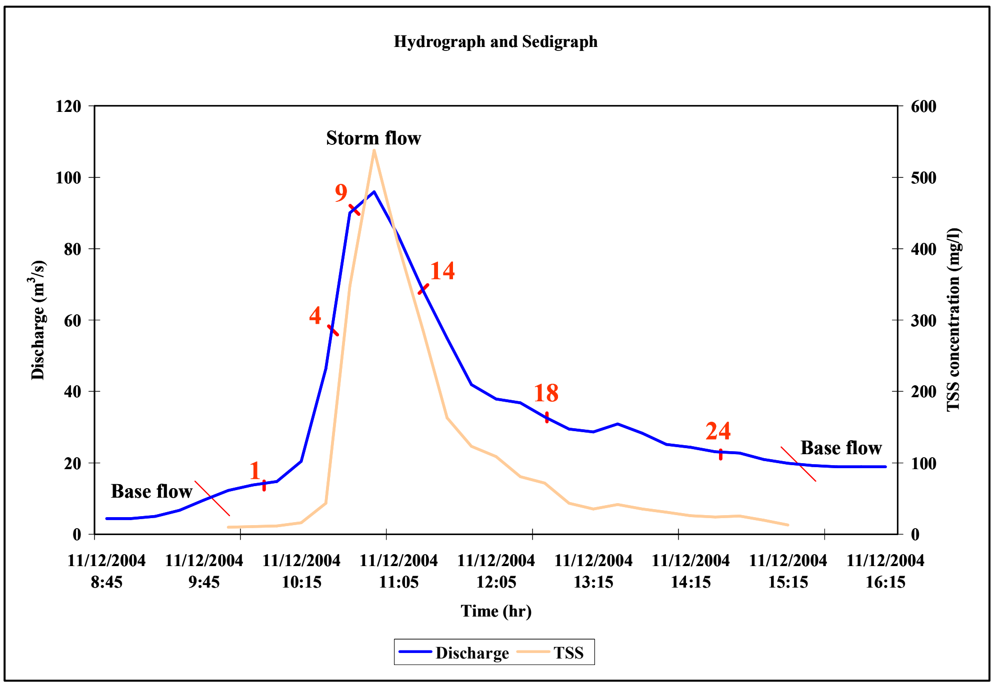


Figure 40. Typical sampling scheme for nutrients during a storm event.

Río Caonillas sub watershed has the highest mean TP load (56.60 kg) and also the highest storm TP load (1357.89 kg) in a storm event occurred on 11/11/2004. Río Grande de Arecibo sub watershed has the highest mean DP load (6.60 kg) and also the highest storms DP load (131.21 kg) during the 11/12/2004. Río Limón sub watershed has the highest mean TKN load (170.87 kg) and Río Caonillas the highest storm TKN load.

Table 22. Storm nutrient loads at Río Limón sub watershed.

		TP load (kg)		DP load (kg)		TKN load (kg)	
Storm #	Sampling date	Total load	Mean	Total load	Mean	Total load	Mean
1	12/10/04	21.55	2.69	2.49	0.17	55.64	3.71
2	13/10/04	113.53	11.95	29.24	1.62	1623.22	170.87
3	12/11/04	337.98	14.08	20.82	0.87	1325.67	55.24
4	14/11/04	263.01	10.99	46.30	1.93	1149.78	47.91
5	21/11/04	165.38	11.03	10.25	0.68	440.23	29.35
6	19/04/05	376.56	31.38	13.58	1.13	1777.37	148.11
7	09/05/05	282.87	25.72	10.85	0.99	280.41	25.49

Table 23. Storm nutrient loads at Río Grande de Arecibo sub watershed.

		TP load (kg)		DP load (kg)		TKN load (kg)	
Storm #	Sampling date	Total load	Mean	Total load	Mean	Total load	Mean
1	14/10/04	233.44	15.60	76.89	5.10	382.63	25.50
2	11/12/04	469.44	23.50	131.21	6.60	788.64	39.40

Table 24. Storm nutrient loads at Río Caonillas sub watershed.

		TP load (kg)		DP load (kg)		TKN load (kg)	
Storm #	Sampling date	Total load	Mean	Total load	Mean	Total load	Mean
1	30/10/04	33.72	1.41	12.93	0.54	1978.55	82.44
2	11/11/04	1357.89	56.60	89.73	3.74	3115.47	129.88
3	19/04/05	57.30	7.16	3.83	0.48	177.87	22.33
4	24/05/05	45.44	2.39	3.71	0.20	311.19	16.38

Table 25. Storm nutrient loads at Río Jauca sub watershed.

		TP load (kg)		DP load (kg)		TKN load (kg)	
Storm #	Sampling date	Total load	Mean	Total load	Mean	Total load	Mean
1	05/10/04	4.15	0.37	1.58	0.14	188.76	17.15
2	08/10/04	7.54	1.00	3.28	0.40	148.95	14.60
3	10/10/04	5.63	0.51	1.10	0.10	89.45	8.14
4	11/12/04	164.67	10.97	84.01	5.60	857.74	57.18
5	09/05/05	309.43	18.20	16.58	0.97	429.17	25.25

6.9 Sediment and nutrient annual loads and yields

Table 26 shows sediment and nutrient annual loads distribution in four sub watershed of the Río Grande de Arecibo watershed, for the 2004-2005 USGS water year. Annual loads were calculated integrating the grab and storm loads for the study period. Load versus flow regression equations and coefficients of determination (R^2) for grab and storm events are shown in the Appendix H, Appendix I, Appendix J, Appendix K. The coefficients of determination generated by the (TP, DP, TKN and TSS) loads versus flow regressions during grab samples were high for all the parameters in the four sub watersheds (R^2 range from 0.51 to 0.94). High correlations were found during storm events for all the parameters (TP, DP, TKN and TSS) in all the sub watersheds, having an exception with Río Grande de Arecibo and Río Jauca sub watersheds where a low coefficient of determination for TP (0.39, 0.42) was observed.

Regression analysis between mean daily flow (m^3/sec), nutrient (kg) and sediment (tons) loads were developed from collected data for each outlet. The regression model was used to predict constituent loads as a function of mean daily flow for the study period.

During storm events the loads generated by these storms were substituted in the days when the storm took place. The estimated annual load includes grabs and loads from events collected. The graphs and mathematical relationships in change in height for storms events were generated using all collected samples in every single storm event. These could be up to 24 plotting points for a single storm event in these plots. The mathematical relationships were not used to estimate loading from storm events. The storm event loading was calculated integrating the hydrographs with the sample and concentration.

Annual loads od TKN range from 3,194 kg (Río Jauca) to 57,236 kg (Río Grande de Arecibo), TP annual loads range from 1,407 kg (Río Jauca) to 17,684 kg (Río Grande de Arecibo), DP annual loads range from 785 kg (Río Jauca) to 12,752 kg (Río Grande de Arecibo) and TSS annual loads range from 2,763.51 metric tons (Río Jauca) to 10,942.27 metric tons (Río Limón). Río Jauca had the lowest annual load (TKN, TP, DP and TSS) compared with the other three sub watersheds. Ramos-Ginés (1997) found an input of 6,530 kg per year of TP and 18,700 kg per year of Total Nitrogen to Lake Cidra (drainage area of 2,150 ha). Comparing the TP load entering to Lake Cidra with the average annual load of TP for the four studied sub watersheds of the Río Grande de Arecibo watershed the delivery of TP in surface waters is an increasing factor.

Seventy one percent of the TSS loads were observed during storm events, where a strong correlation were found between TSS and mean daily flow for each sub watershed during storm and runoff events. The suspended sediment effect goes beyond the reduction in water capacity holding of reservoirs, the mean annual suspended sediment discharge from Puerto Rico into surrounding costal waters is estimated to range from 2.7 to 9.0 million metric tons (Warne et at., 2005), having a potential influence in coral reefs. Nutrient loads were mostly found during runoff events (grab), 71% TKN, 83% TP and 95% DP of the total annual load.

Table 26. Sediment and nutrient annual loads for four sub watersheds of the Río Grande de Arecibo watershed.

	Annual load			
Sub watershed	TKN (kg)	TP (kg)	DP (kg)	TSS (metric tons)
Río Limón	21,718.52	10,805.88	9,074.78	10,942.27
Río Grande de Arecibo	57,235.68	17,683.83	12,751.72	9,364.13
Río Caonillas	19,514.53	11,660.17	6,084.85	7,946.86
Río Jauca	3,193.88	1,406.74	785.30	2,763.51

Table 27 shows the sediment and nutrient annual yields in the four sub watersheds of the Río Grande de Arecibo watershed for the 2004-2005 USGS water year. Río Grande de Arecibo sub watershed has the higher TKN annual yield (3.07 kg/ha/year). Río Caonillas sub watershed has the higher TP annual yield (1.19 kg/ha/year). Río Limón sub watershed has the higher DP annual yield (0.97 kg/ha/year). Río Jauca has the higher TSS annual yield (1.56 metric tons/ha/year).

Table 27. Sediment and nutrient annual yields for four sub watersheds of the Río Grande de Arecibo watershed.

	Annual Yield			
Sub watershed	TKN (kg/ha/year)	TP (kg/ha/year)	DP (kg/ha/year)	TSS (metric tons/ha/year)
Río Limón	2.32	1.15	0.97	1.17
Río Grande de Arecibo	3.07	0.95	0.68	0.50
Río Caonillas	1.99	1.19	0.62	0.81
Río Jauca	1.80	0.79	0.44	1.56

6.10 Fisher least significant difference tests

The Fisher Least Significant Difference (LSD) test was performed to observe differences (95% confidence intervals) between sub watersheds (Río Limón, Río Grande de Arecibo, Río Caonillas and Río Jauca) and Chl a, TP, DP, TKN and TSS concentrations. Significant differences were found between the four sub watersheds and concentrations (Table 28).

There were found no significant difference for Chl a, DP, TKN and TSS in stations 1 and 3 (Río Limón and Río Caonillas). There were found no significant difference for Chl a concentrations for stations 1, 3 and 4. There were found significant difference for TSS concentrations between station number 2 (Río Grande de Arecibo) and other three stations (1, 3 and 4) and also significant difference were observed between stations 3 and 4 (Río Caonillas and Río Jauca). Significant differences in DP concentrations were found between station 2 and 4 (Río Grande de Arecibo and Río Jauca). There were found no significant differences for TP concentrations between stations 2 and 3 (Río Grande de Arecibo and Río Caonillas), but significant difference were observed between stations 1, 3 and 4 (Río Limón, Río Caonillas and Río Jauca). For TKN concentrations no significant difference were observed in stations 1 and 2 (Río Limón and Río Grande de Arecibo).

Table 28. Fisher Least Significant Difference test (p < .05) for Chl a, TP, DP, TKN and TSS concentrations.

Station	Mean Chl a
2	8.32 a (± 1.58)
3	6.99 ab (± 1.35)
4	4.87 b (± 0.99)
1	3.81 b (± 0.59)

Station	Mean TSS
2	24.10 a (± 3.04)
3	16.74 b (± 1.70)
1	14.59 bc (± 0.98)
4	11.04 c (± 1.57)

Station	Mean DP
2	0.07 a (± 0.01)
1	0.05 ab (± 0.005)
3	0.05 ab (± 0.004)
4	0.04 b (± 0.01)

Station	Mean TP
2	0.08 a (± 0.01)
3	0.07 a (± 0.005)
1	0.06 b (± 0.004)
4	0.04 c (± 0.003)

Station	Mean TKN
2	0.22 a (± 0.02)
1	0.17 a (± 0.04)
3	0.15 ab (± 0.02)
4	0.09 b (± 0.01)

- Station number represents: 1- Río Limón, 2- Río Grande de Arecibo, 3- Río Caonillas and 4- Río Jauca.
- Significant differences between stations are denoted by different letters a, b or c (P < 0.05).
- Standard errors values are denoted in parenthesis.

6.11 Relationships between land use sediment and nutrients yields.

The Río Grande de Arecibo watershed is characterized as having a high density of forest land in the area, with this land use being the most abundant in the sub watersheds (Río Limón 82%, Río Grande de Arecibo 81%, Río Caonillas 66% and Río Jauca 70 %). Table 2 shows the land use distribution in the Río Grande de Arecibo watershed. Although urban land is a small fraction in the watershed, visual observation shows that most residences are located near a river or stream, resulting in a direct impact to water quality.

Land uses (Forest, Agriculture and Urban) were plotted versus sediment and nutrient concentrations, loads and yields to determinate trends and relationships between these factors. For this study concentrations and loads were not found related to land use, but a relationship between land use and yields was found in some cases (Figure 41, Figure 42 and Figure 43). It is important to mention that the research sampling sites were selected based on accessibility, and data collection availability (USGS monitoring stations), and not necessary homogeneity of land use in the sub watershed. A positive relationship between forest and DP yield, forest and TKN yield were found in Río Limón and Río Grande de Arecibo sub watersheds. Concerning agricultural land use, Río Limón and Río Grande de Arecibo are the sub watersheds with the highest TP and DP yield, while Río Jauca the highest TSS yield having the lowest agricultural area. Nutrient and sediment export patterns from urban land use are not consistent among the watershed studied. A positive trend of nutrient and sediment exports is seem as a function of agricultural areas in the studied watershed.

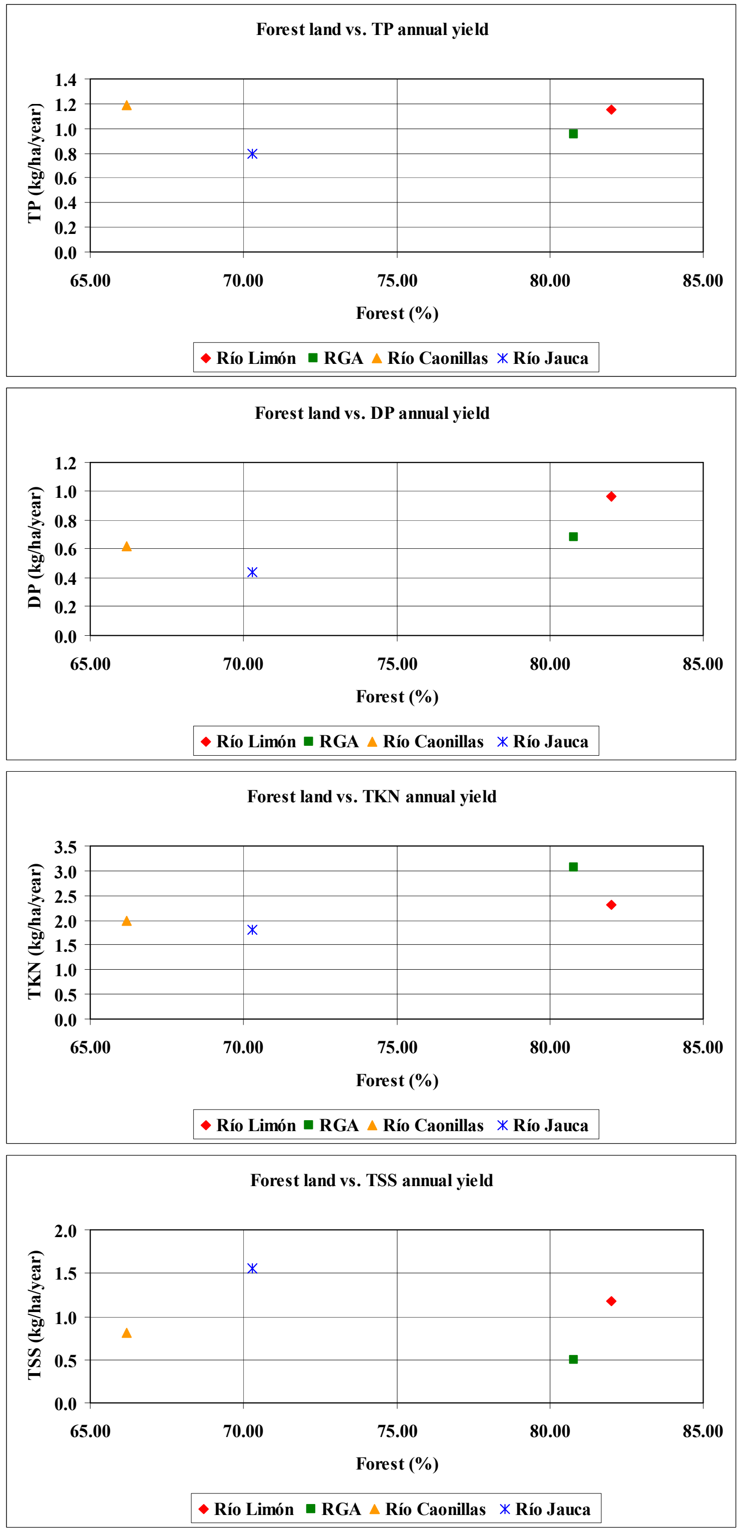


Figure 41. Forest land versus nutrient annual yield

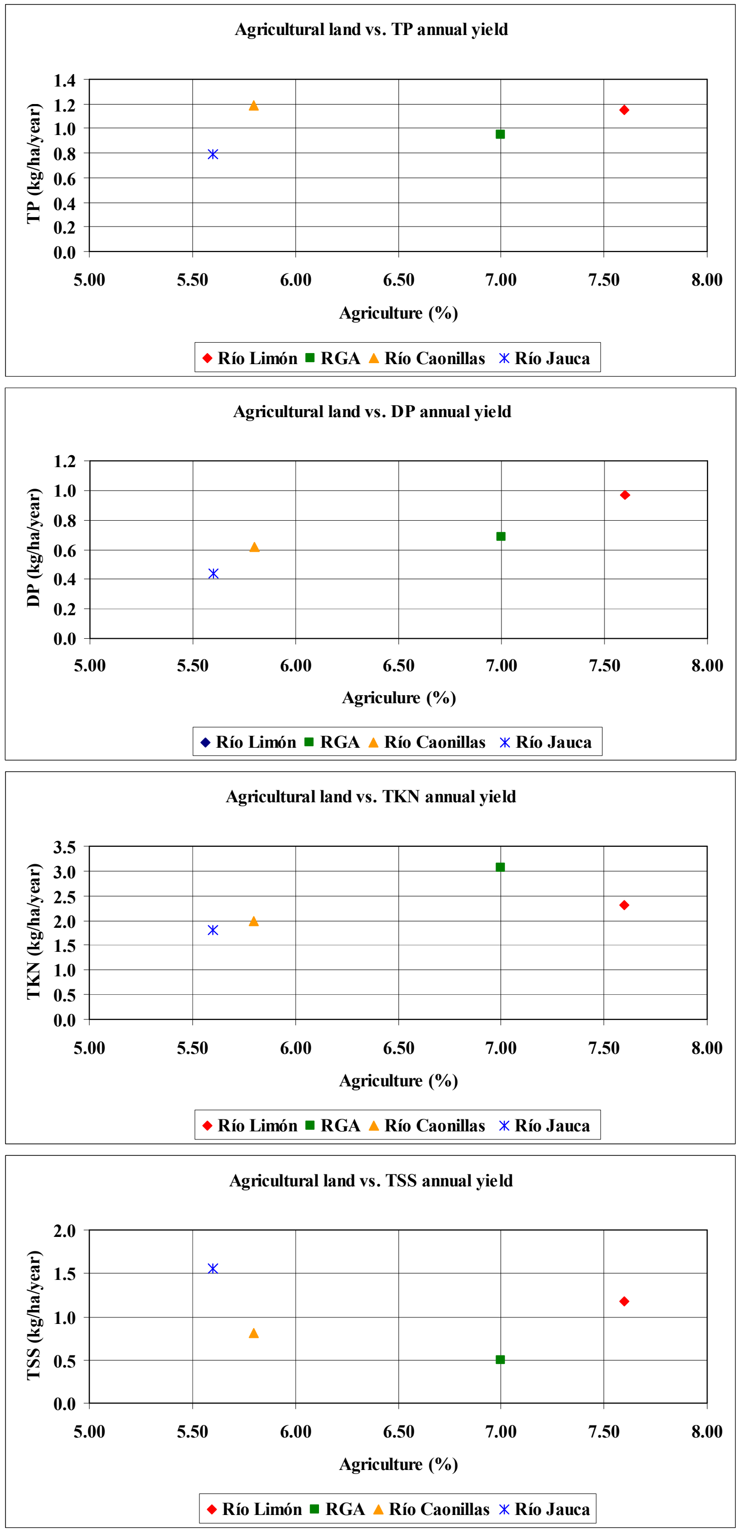


Figure 42. Agricultural land versus yield

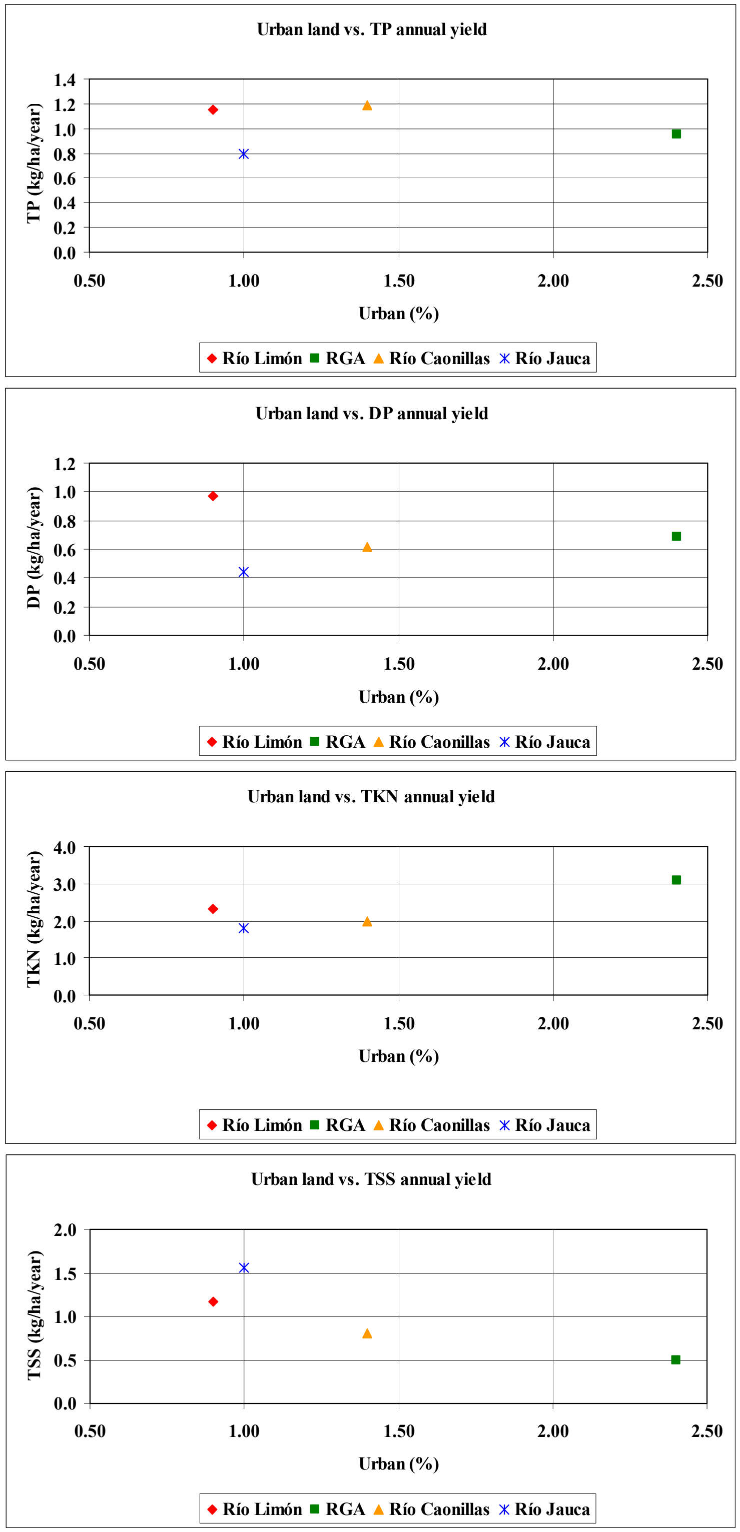


Figure 43. Urban land versus yield

6.12 Predictive equations for sediment and nutrient loads.

The Partial Least Square (PLS) regression method was used to determine the relationship between loads (sediment and nutrient) and watersheds characteristics (physiographic and hydrologic). The PLS regression method is a linear model, relationship between a dependent variable (*Y*) and a set of predictor variables (*X's*). The statistical model fit to data is expressed as follows:

$$\hat{Y} = b_0 + b_1 X_1 + b_2 X_2 + ... + b_n X_n \qquad \textbf{(6)}$$

In this equation b_0 is the independent predictor coefficient for the intercept and b_i values are the regression coefficients (for variables X_1 through X_n) computed from the data. $\hat{Y}$ is the dependent variable that for this study is either the nutrient annual load or the annual sediment load. Dependent variables in this study were the annual nutrient load (TKN, TP and DP) and total suspended sediment (TSS). Independent variables or predictors considered were drainage area, maximum width of the channel, average land slope, mean elevation above mean sea level, mean annual precipitation, and mean annual flow. PLS regression model equations are presented in equations 7, 8, 9 and 10.

Model equations for TSS, TP, DP and TKN annual loads

(7)

Total Suspended Sediment

$$\hat{TSS}_{load} = f(Drainage\_area, Maximum\_width\_of\_the\_channel, Average\_land\_slope,$$
$$Mean\_elevation\_above\_mean\_sea\_level, mean\_annual\_precipitation, Mean\_annual\_flow)$$

(8)

Total Phosphorus

$$\hat{TP}_{load} = f(Drainage\_area, Maximum\_width\_of\_the\_channel, Average\_land\_slope,$$
$$Mean\_elevation\_above\_mean\_sea\_level, mean\_annual\_precipitation, Mean\_annual\_flow)$$

(9)

Dissolved Phosphorus

$$\hat{DP}_{load} = f(Drainage\_area, Maximum\_width\_of\_the\_channel, Average\_land\_slope,$$
$$Mean\_elevation\_above\_mean\_sea\_level, mean\_annual\_precipitation, Mean\_annual\_flow)$$

(10)

Total Kjeldahl Nitrogen

$$\hat{TKN}_{load} = f(Drainage\_area, Maximum\_width\_of\_the\_channel, Average\_land\_slope,$$
$$Mean\_elevation\_above\_mean\_sea\_level, mean\_annual\_precipitation, Mean\_annual\_flow)$$

Where:

Drainage area is in (km^2), maximum width of the channel in (m), average land slope in (m/m), mean elevation above mean sea level in (m), mean annual precipitation (mm) and mean annual flow (m^3/second).

Predictive equations for TSS, TP, DP and TKN annual loads

(11)

Total Suspended Sediment (2 components, R^2 = 0.74)

$$Tss_{load} = 21{,}359.9 + \left[(P_1)(5.3) + (P_2)(20.9) + (P_3)(-31{,}699.5) + (P_4)(-9.8) + (P_5)(0.7) + (P_6)(467.6)\right]$$

(12)

Total Phosphorus (2 components, R^2 = 0.97)

$$TP_{load} = 21{,}649.7 + \left[(P_1)(28.5) + (P_2)(148.5) + (P_3)(-35{,}679.7) + (P_4)(-4.3) + (P_5)(-3.2) + (P_6)(1{,}203.4)\right]$$

(13)

Dissolved Phosphorus (2 components, R^2 = 0.99)

$$DP_{load} = 23{,}636.3 + \left[(P_1)(17.9) + (P_2)(122) + (P_3)(-51{,}233.6) + (P_4)(-6.3) + (P_5)(-0.7) + (P_6)(752.3)\right]$$

(14)

Total Kjeldahl Nitrogen (2 components, R^2 = 0.95)

$$TKN_{load} = 71{,}559 + \left[(P_1)(95) + (P_2)(590) + (P_3)(-161{,}694) + (P_4)(-10) + (P_5)(-9) + (P_6)(3{,}632)\right]$$

Where:

P_1 = drainage area (km^2)

P_2 = maximum width of the channel (m)

P_3 = average land slope (m/m)

P_4 = mean elevation above mean sea level (m)

P_5= mean annual precipitation (mm)

P_6= mean annual flow (m^3/second)

For each constituent (TSS, TKN, TP, and DP) a linear model was generated using the PLS regression method equations 10, 11, 12 and 13. The PLS prediction command in the statistical package Minitab 14 was used to compare real values versus predicted values to validate the predictive equations (Appendix L). To evaluate and calibrate the model, multiple methods were used, for example: analysis of variance, coefficient of determination, regression components, PLS response plot, PLS model selection plot, PLS coefficient plot and PLS loading plot (Appendix M).

Table 29 shows the observed versus predicted annual loads generated by the predictive equations. These values show how the model fit and predict annual loads for the four sub watersheds. The best model fit is seemed for Río Limón and Río Grande de Arecibo, having these sub watersheds the smallest magnitude of error in prediction (TSS 11.3%, TKN 6.5%, DP 2.95% and TP 5%). It has found an underestimation of TKN (observed 3,194 kg versus predicted 311 kg) in the Río Jauca watershed with an error of 90%, and also an overestimate of TP (observed 1,407 kg versus predicted 2,438 kg) with an estimated error of 73% predicted values. These values comparison allow calibrating the model using more factors as dependent or independent variables. Highly precise observations were observed for each constituent (TSS, TKN, TP, DP) as an example the difference between the observed and predicted data for DP in Río Caonillas sub watershed is of 143 kg (observed 6,085 kg versus predicted 5,942 kg) with a 2.3% of error.

Table 29. Observed versus predicted annual loads of TSS, TKN, TP and DP.

Sub watershed	Observed TSS Load (metric tons)	Predicted TSS Load (metric tons)	Observed TKN Load (kg)	Predicted TKN load (kg)	Observed DP Load (kg)	Predicted DP Load (kg)	Observed TP Load (kg)	Predicted TP Load (kg)
Río Limón	10,942	10,129	21,719	25,937	9,075	8,902	10,806	9,925
Río Grande de Arecibo	9,364	10,425	57,236	53,489	12,752	13,129	17,684	18,570
Río Caonillas	7,947	5,892	19,515	25,690	6,085	5,942	11,660	10,688
Río Jauca	2,764	4,427	3,194	311	785	1,343	1,407	2,438

The model selection plots show the calculated response versus the actual response for each of the pollutants (TSS, TKN, TP and DP). The response plot is a scatter plot of the fitted and cross-validated fitted values versus the actual response. The linear patter that these plot show indicates that the model fit data well and accurately predicts the response (Figure 44).

The standardized coefficient plot is a projected scatterplot showing the standardized coefficients for each predictor, this plot makes it easier to identify predictors that are more or less significant in the model (Figure 45). This plot was used to compare the sign and magnitude of the coefficients for each predictor. This plot makes it easier to identify predictors that are not on the same scale.

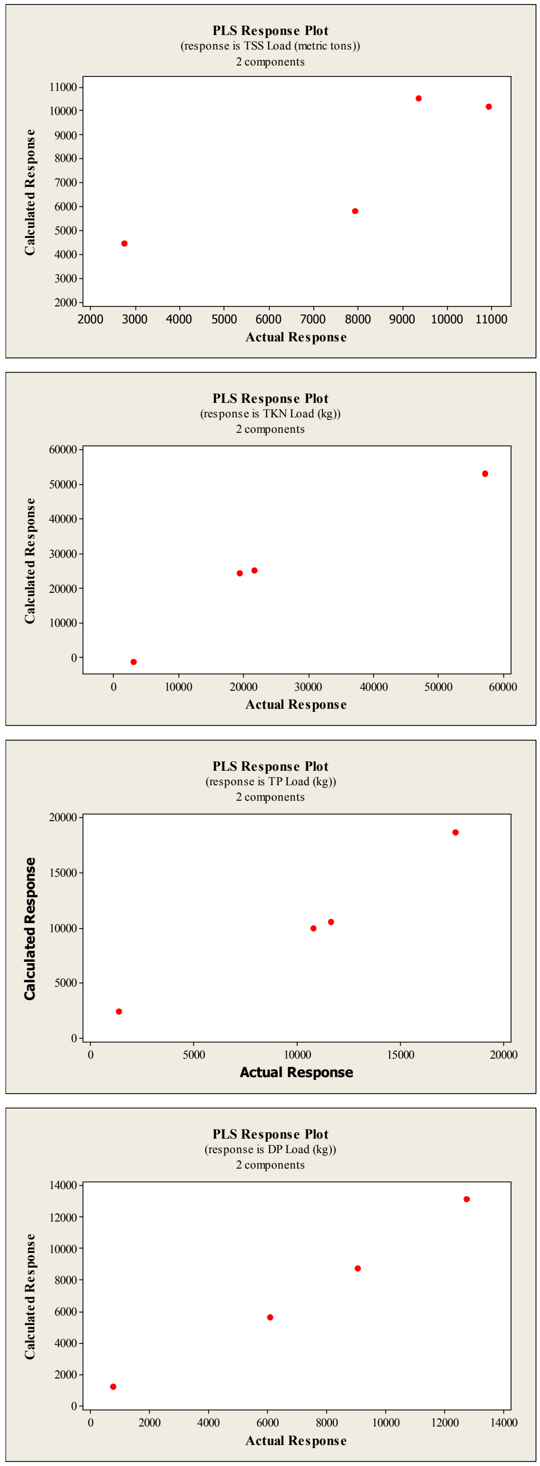


Figure 44. Partial Least Square response plot of the actual versus calculated values.

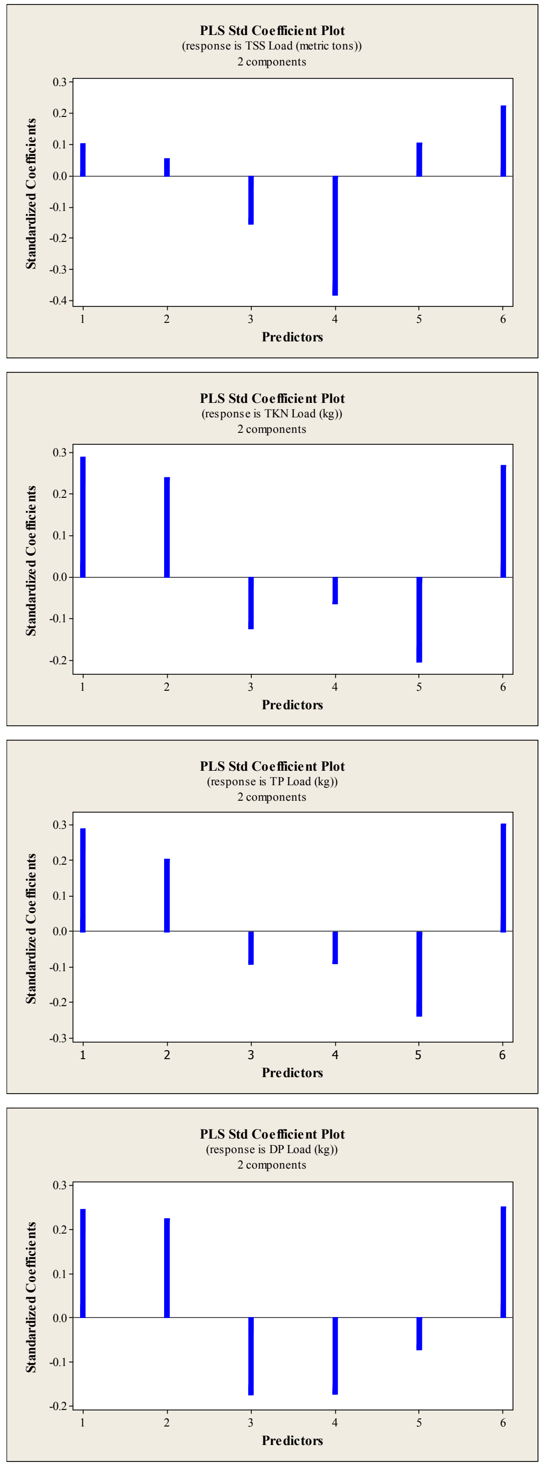


Figure 45. Standardized Partial Least Square coefficient plots for each predictor.

7. MODEL APPLICATIONS AND LIMITATIONS

7.1 Model application for TSS annual load estimation (Example)

In October 1999 Soler-López performed a sedimentation survey of Lake Dos Bocas, Puerto Rico. The sedimentation rate of this lake was about 309,000 m^3 per year (1942 to 1985). Concerning the reduction in water capacity holding of this reservoir is important to quantify the TSS input from Río Limón branch to the lake. Using physiographic and hydrologic properties (drainage area, maximum width of the channel, average land slope, mean elevation above mean sea level, mean annual precipitation, and mean annual flow) of the Río Limón obtained from the U.S. Geological Survey web site (http://pr.water.usgs.gov) and the TSS annual load calculation equation (11). This equation allows the researcher to quantify and compare predicted data versus observed data of TSS.

$$Tss_{load} = 21{,}359.9 + \left[(P_1)(5.3) + (P_2)(20.9) + (P_3)(-31{,}699.5) + (P_4)(-9.8) + (P_5)(0.7) + (P_6)(467.6)\right]$$

Where:

P_1 = drainage area (93.71 km^2)

P_2 = maximum width of the channel (33.22 m)

P_3 = average land slope (0.35 m/m)

P_4 = mean elevation above mean sea level (450.85 m)

P_5= mean annual precipitation (2,554.98 mm)

P_6= mean annual flow (2.67 m^3/second)

$$Tss_{load} = 21{,}359.9 + \left[(93.71)(5.3) + (33.22)(20.9) + (0.35)(-31{,}699.5) + (450.85)(-9.8) + (2{,}554.98)(0.7) + (2.67)(467.6)\right]$$

Predicted load:

$$Tss_{load} = 10{,}129 \ {}^{tons}\!/_{year}$$

Observed load:

$$Tss_{load} = 10{,}942 \ {}^{tons}\!/_{year}$$

7.2 Model limitations

The TSS, TKN, TP and DP annual loads estimation equations were applied for other sub watersheds within the Río Grande de Arecibo watershed and the Río Grande de Añasco watershed. Table 30 shows the sub watersheds physiographic and hydrologic characteristics. It is important to observe that the area of four of the five studied sub watersheds is out of the model range (17.74 to 186.45 km^2), the mean annual flow is also out of the range. It was found that the TSS, TKN, TP and DP equations predicted well for areas ranging from (17.74 to 186.45 km^2) for example Río Saliente (24.73 km^2) were predicted values were similar to observed. The model limitation was observed when the equations were applied for small sub watersheds, for example (Sabana Grande, Miraflores, Jua and Cerro Gordo) were predicted loads were different from observed.

Table 30. Sub watersheds used for model calibration

Sub watershed	Drainage area at outlet (km^2)	Maximum width of the channel (m)	Average land slope (m/m)	Mean elevation above mean sea level (m)	Mean annual precipitation (mm)	Mean annual flow (m^3/s)
Jua	3.28	30.02	0.40	475.00	2036.57	0.22
Sabana Grande	1.52	30.02	0.40	475.00	2036.57	0.10
Saliente	24.73	30.02	0.40	475.00	2084.50	0.67
Miraflores	2.24	12.00	0.32	930.00	2500.00	0.05
Cerro Gordo	7.14	18.00	0.32	930.00	2500.00	0.21

- **Data obtained from the USGS Water resources data and from the Río Grande de Arecibo Final Report, 2004.**

Table 31. Observed versus predicted annual loads of TSS, TKN, TP and DP for model calibration

Sub watershed	Observed TSS Load (metric tons)	Predicted TSS Load (metric tons)	Observed TKN Load (kg)	Predicted TKN load (kg)	Observed DP Load (kg)	Predicted DP Load (kg)	Observed TP Load (kg)	Predicted TP Load (kg)
Jua	-	5,426.00	1,148.00	2,114.18	419.84	2,537.36	464.20	3,692.54
Sabana Grande	-	6,492.00	2,517.68	3,580.33	169.90	2,844.30	293.34	4,183.98
Saliente	-	6,650.54	5,247.90	5,358.74	1,368.93	3,225.65	1,766.97	4,693.00
Miraflores	1,455.00	4,256.73	861.60	5,297.58	29.60	1,077.93	346.00	195.00
Cerro Gordo	20,723.45	4,483.06	6,187.50	710.00	132.40	2,018.00	1,910.40	1,418.00

- **Not observed data is represented with the (-) sign.**

8. CONCLUSIONS

Average monthly nutrient (TKN, TP and DP) concentrations during grab sampling were found to be under the criteria established by the USEPA, Río Limón (0.17, 0.06, and 0.05 mg/L), Río Grande de Arecibo (0.22, 0.08, and 0.07 mg/L), Río Caonillas (0.15, 0.07 and 0.05 mg/L) and Río Jauca (0.09, 0.04 and 0.04 mg/L) during runoff events (grab). Average monthly phosphorus concentrations values during runoff events were under the water quality criteria (0.1 mg/L of P) established by the Environmental Protection Agency (USEPA, 1986).

Average monthly nutrient (TKN, TP and DP) concentrations for Río Limón (2.86, 0.43 and 0.05 mg/L), Río Grande de Arecibo (1.27, 0.74, and 0.22 mg/L), Río Caonillas (3.05, 0.68 and 0.06 mg/L) and Río Jauca (2.04, 0.58 and 0.07 mg/L) during storm events. Average monthly phosphorus concentrations values during storm events were above the water quality criteria (0.1 mg/L of P) established by the Environmental Protection Agency (USEPA, 1986).

Considering the estimated annual loads, it is observed the high potential of pollutant transport of the Río Grande de Arecibo watershed. Concerning that the pollutant loads will be eventually entering to Lake Dos Bocas and Lake Caonillas, pollutant control and reduction practices should be apply in the watershed. Since there is evidence of reduction in this lakes water storage capacity (Soler-López, 2001) during storm events and most of this reduction is due to hurricanes affecting the area (Hurricane Hortense 1996 and Hurricane Georges 1998) implementation of soil erosion and runoff control strategies need to be consider in order to preserve more water storage capacity.

Sediment and nutrient annual loads and yields were calculated for the 2004-2005 USGS-WY. Río Limón sub watershed has the highest total suspended sediment annual load (12,062 tons/year) and Río Jauca has the lowest 3,046 tons/year) Río Grande de Arecibo has the highest TKN, TP, and DP annual load (57,236 kg/year, 17,684 kg/year, and 12,752 kg/year) and Río Jauca has the lowest TKN, TP, and DP annual loads (3,194 kg/year, 1407 kg/year, and 785 kg/year).

A method for developing predictive equations of nutrients and sediment loads for tropical sub watersheds has been presented in this thesis research. Total suspended sediment (TSS), Total Kjeldahl nitrogen (TKN), Total and dissolved phosphorus (TP and DP) annual load predictive equations were generated and calibrated using the Partial Least Square regression method. These predictive equations were evaluated and it was found that estimates of annual loads were similar to observed annual loads. Observed coefficients of determination (R^2) for TSS, TP, DP and TKN are (0.74, 0.97, 0.99 and 0.95). The PLS regression method is a useful and powerful tool to generate predictive equations of annual loads.

It was found a significant correlation between TSS, TP and DP concentrations, which give an idea of how the transport mechanism of these pollutants could be linked to physical or chemical characteristics of the soil particles.

9. RECOMMENDATIONS

- Surface water monitoring is an excellent method to preserve the quality and quantity of water in rivers, streams and lakes. Since sedimentation and eutrophication has been observed in the study area it is recommended that conservation management practices should be applied in the area (buffer strips, animal waste storage facilities, runoff control and nutrient management recommendations).

- It is recommended that nutrient and sediment monitoring stations be set up in homogeneous land use areas to generate reliable nutrient and sediment export coefficients for land use and incorporate these coefficients in simple predictions models like those generated by this study.

- It is recommended that more sub watersheds be included in this analysis to improve the scope of the model as a predictive tool for ungaged watersheds or areas with no nutrient data.

- It is recommended continue to validate the Partial Least Square regression model in other areas of Puerto Rico and elsewhere, and under stream weather conditions (Hurricane conditions).

- The data generated by this study could be used for eutrophication modeling, pollutant transport modeling, nutrient management, nutrient criteria, and mostly for watershed pollution control planning.

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11. APPENDICES

Appendix A. USGS rating curve data (stage versus discharge)

Río Limón

Stream Stage (m)	Rating Discharge (m^3/s)
1.98	0.28
2.01	0.41
2.04	0.61
2.07	0.86
2.10	1.17
2.13	1.53
2.16	1.96
2.19	2.45
2.23	3.00
2.26	3.65
2.29	4.36
2.32	5.13
2.35	6.00
2.38	6.94
2.41	7.96
2.44	9.06
2.47	10.28
2.50	11.58
2.53	12.97
2.56	14.44
2.59	16.06
2.62	17.73
2.65	19.54
2.68	21.44
2.71	23.45
2.74	25.54
2.77	27.78
2.80	30.02
2.83	32.56
2.87	35.11
2.90	37.94
2.93	40.78
2.96	43.61
2.99	46.72
3.02	49.55
3.05	52.10
3.08	55.22
3.11	58.05
3.14	61.16
3.17	64.28

Appendix A. (Continued)

Río Grande de Arecibo

Stream Stage (m)	Rating Discharge (m^3/s)
2.47	52.10
2.50	54.37
2.53	56.63
2.56	59.18
2.59	61.45
2.62	64.00
2.65	66.54
2.68	69.09
2.71	71.64
2.74	74.19
2.77	76.74
2.80	79.57
2.83	82.12
2.87	84.95
2.90	88.07
2.93	91.18
2.96	94.30
2.99	97.69
3.02	101.09
3.05	104.49
3.08	107.89
3.11	111.29
3.14	114.97
3.17	118.36
3.20	122.05
3.23	125.73
3.26	129.69
3.29	133.37
3.32	137.34
3.35	141.30
3.38	145.83
3.41	150.36
3.44	155.18
3.47	159.99
3.51	164.80
3.54	169.90
3.57	175.00
3.60	180.10
3.63	185.19

Appendix A. (Continued)

Río Caonillas

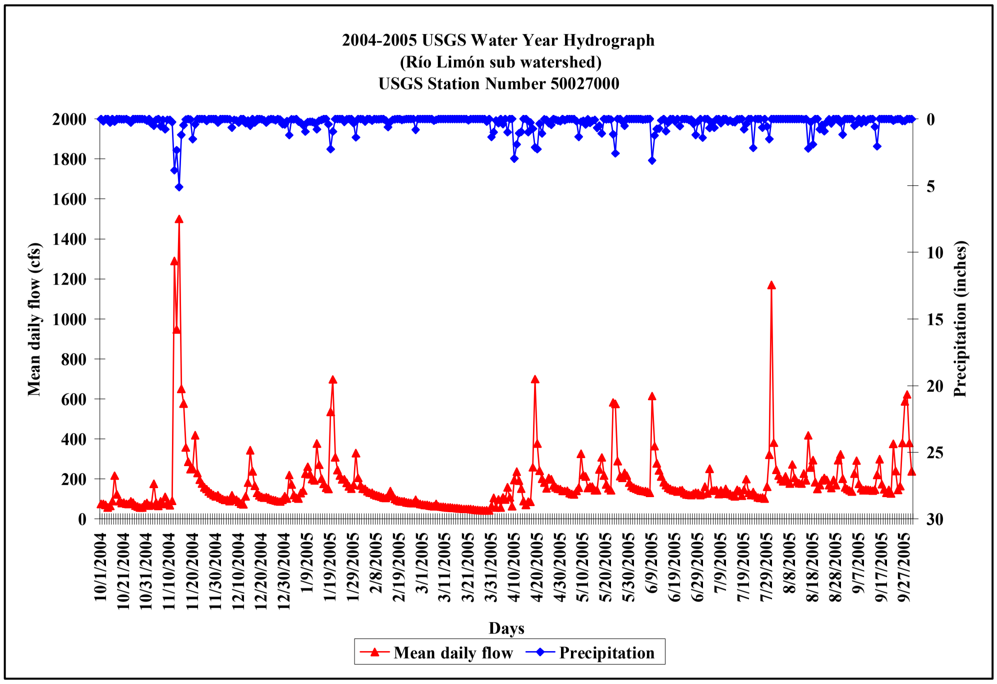
Stream Stage (m)	**Rating Discharge (m^3/s)**
2.10	15.29
2.13	16.01
2.16	16.75
2.19	17.51
2.23	18.29
2.26	19.08
2.29	19.90
2.32	20.73
2.35	21.59
2.38	22.46
2.41	23.36
2.44	24.27
2.47	25.20
2.50	26.15
2.53	27.12
2.56	28.12
2.59	29.22
2.62	30.38
2.65	31.57
2.68	32.79
2.71	34.01
2.74	35.28
2.77	36.59
2.80	37.92
2.83	39.28
2.87	40.66
2.90	42.05
2.93	43.49
2.96	44.97
2.99	46.47
3.02	48.00
3.05	49.58
3.08	51.17
3.11	52.78
3.14	54.42
3.17	56.12
3.20	57.74
3.23	59.38
3.26	61.02
3.29	62.67

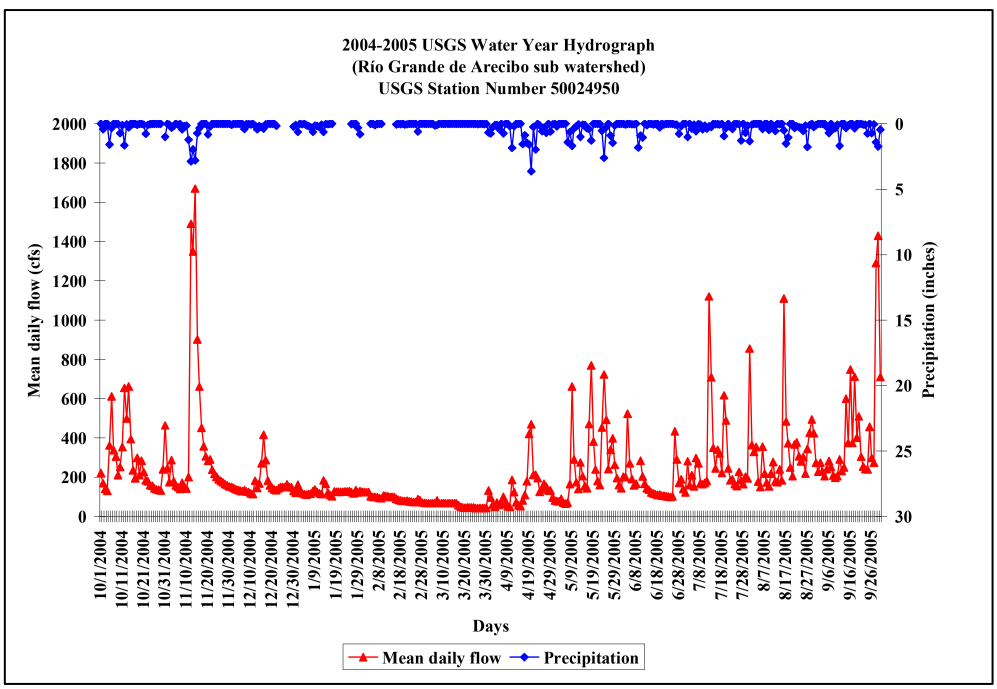
Appendix A. (Continued)

Río Jauca

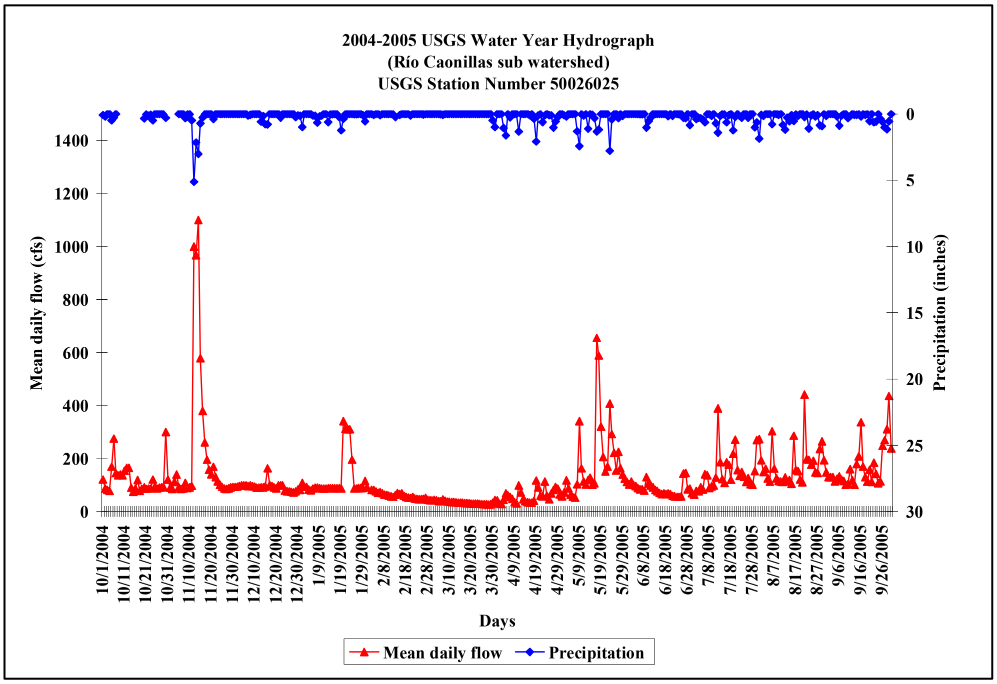
Stream Stage (m)	Rating Discharge (m^3/s)
0.09	0.04
0.12	0.07
0.15	0.12
0.18	0.18
0.21	0.25
0.24	0.34
0.27	0.45
0.30	0.57
0.34	0.71
0.37	0.87
0.40	1.05
0.43	1.25
0.46	1.46
0.49	1.70
0.52	1.96
0.55	2.23
0.58	2.53
0.61	2.85
0.64	3.19
0.67	3.55
0.70	3.94
0.73	4.34
0.76	4.77
0.79	5.23
0.82	5.70
0.85	6.20
0.88	6.73
0.91	7.28
0.94	7.85
0.98	8.45
1.01	9.07
1.04	9.72
1.07	10.40
1.10	11.10
1.13	11.82
1.16	12.58
1.19	13.35
1.22	14.16
1.25	14.98
1.28	15.83

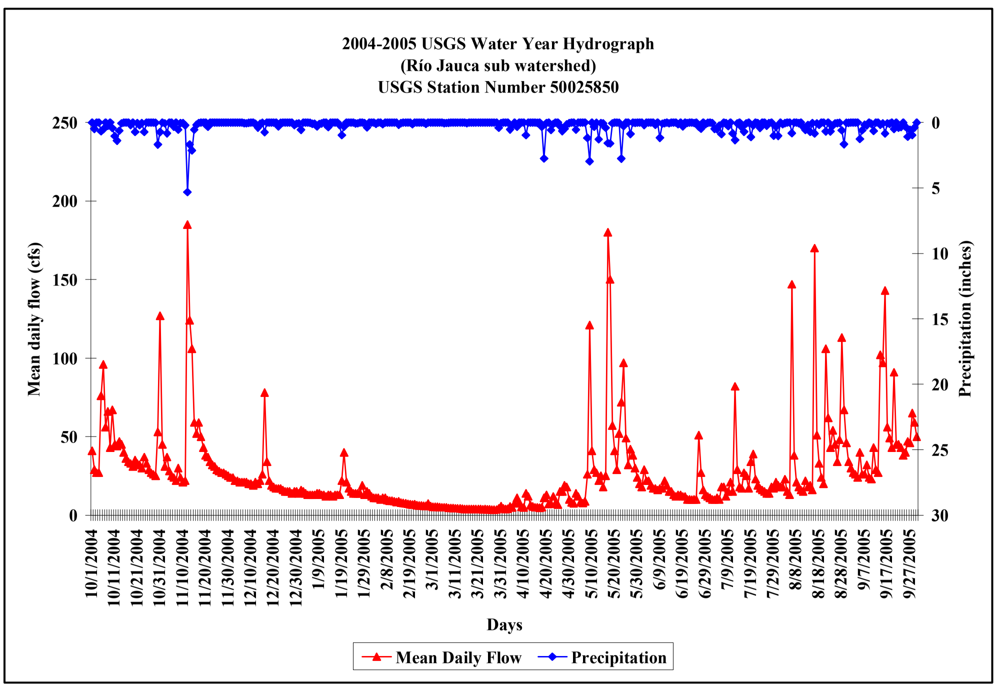
Appendix B. Flow and precipitation hydrograph



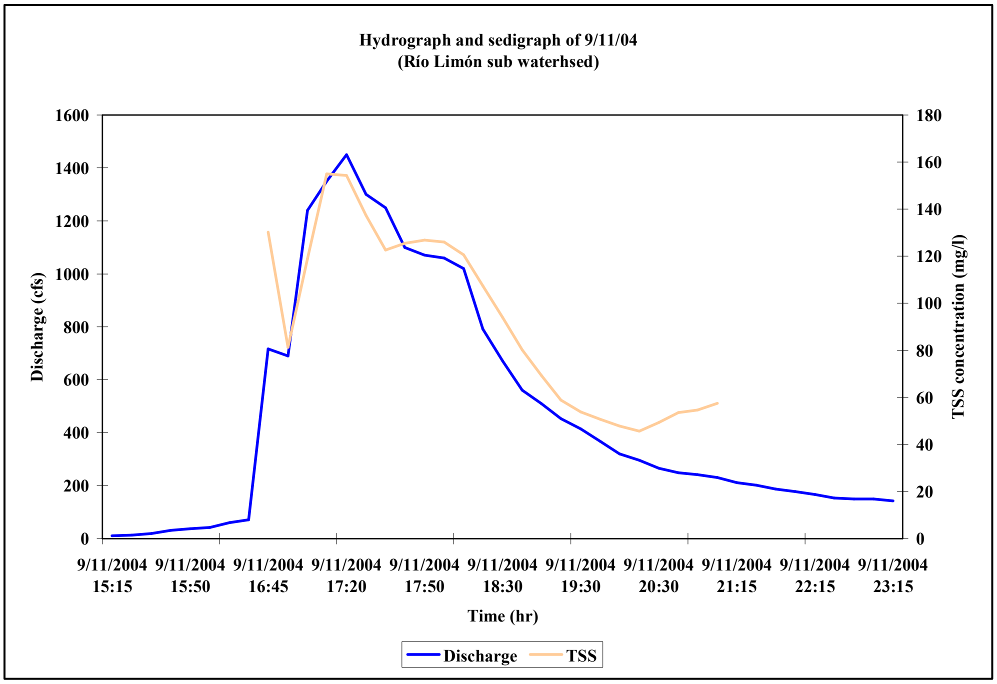


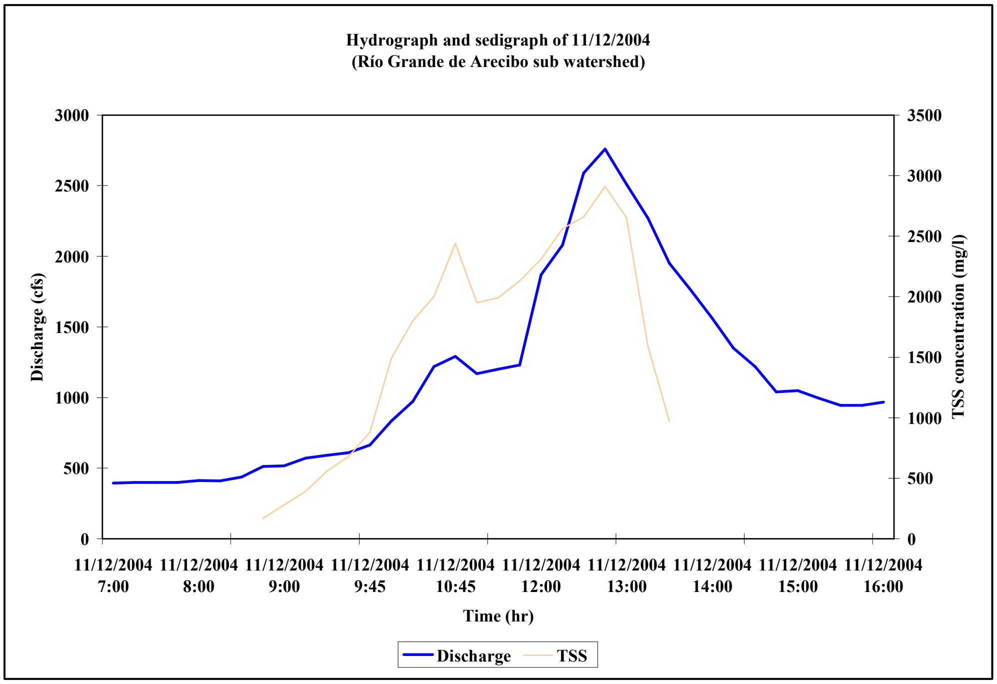
Appendix B. (Continued)



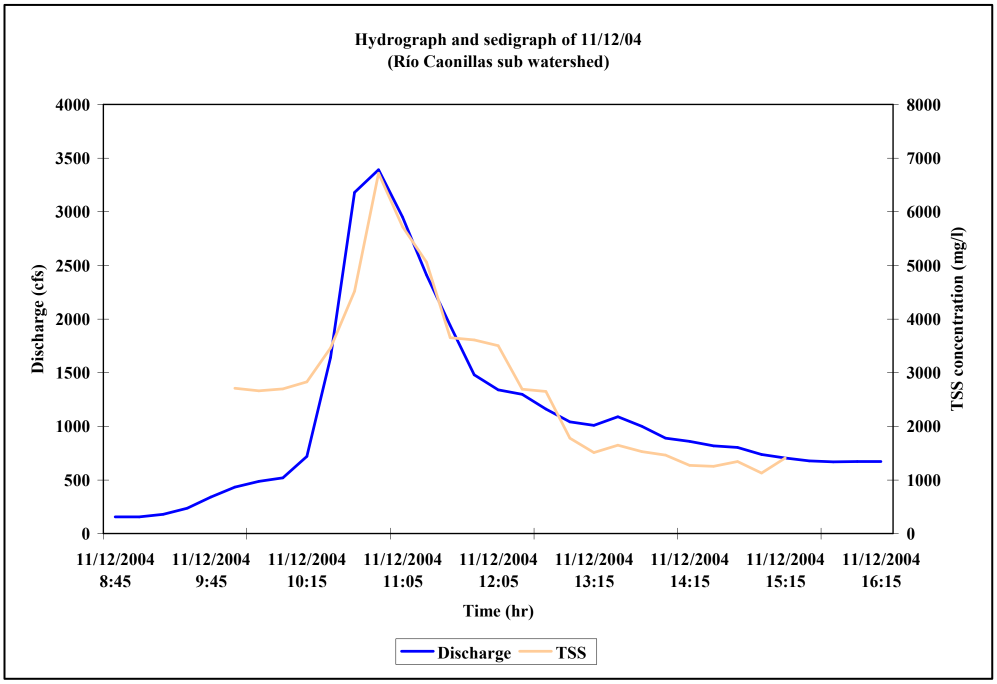


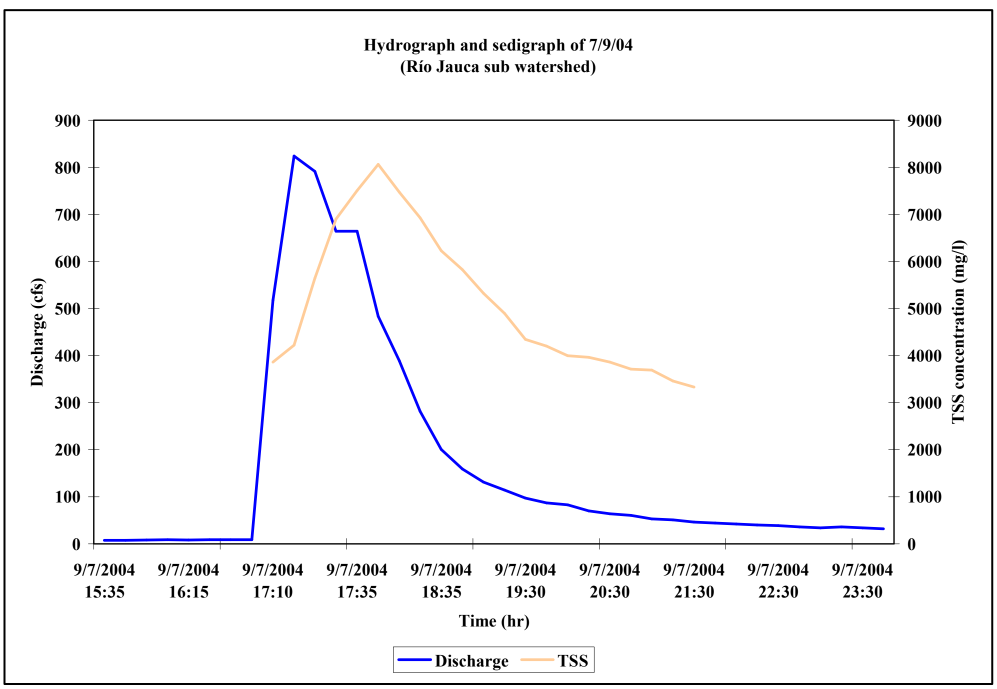
Appendix C. Example of storm event hydrographs and sedigraphs (discharge versus TSS concentration)



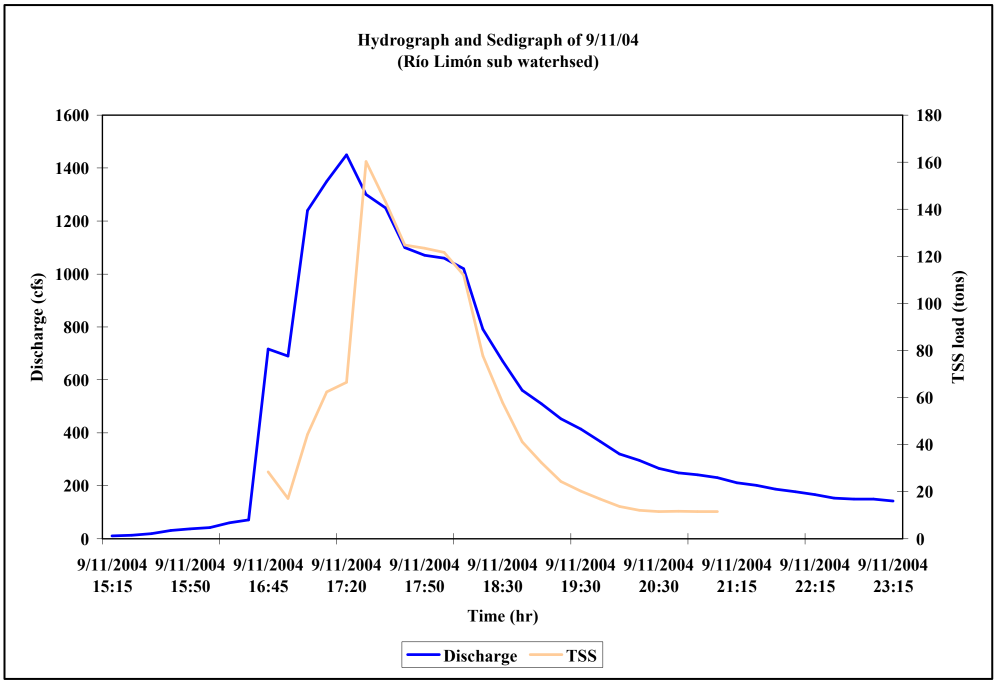


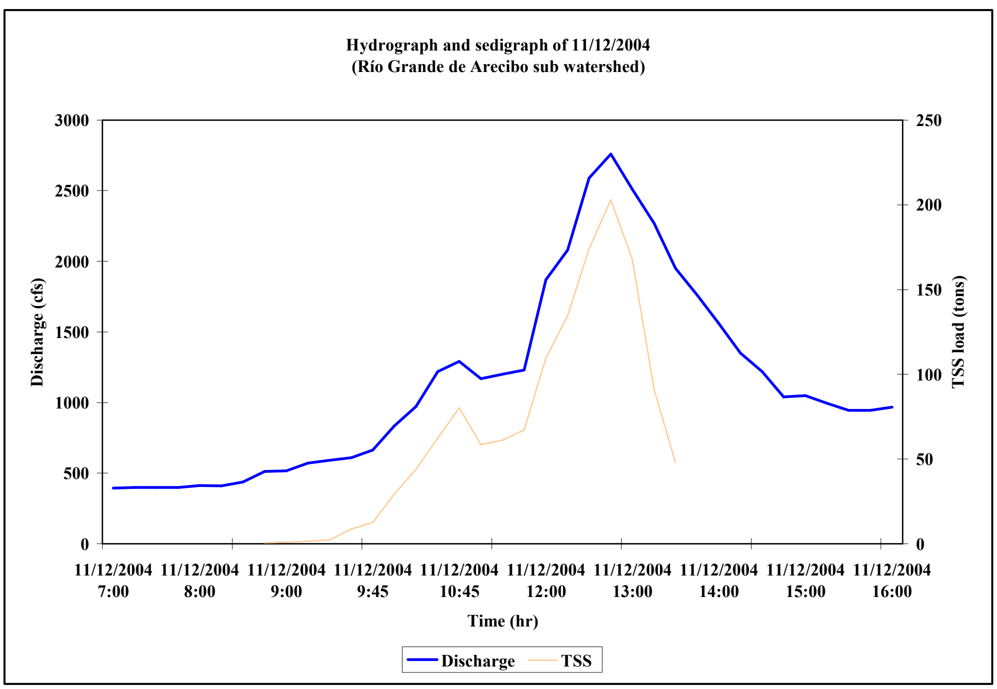
Appendix C. (Continued)



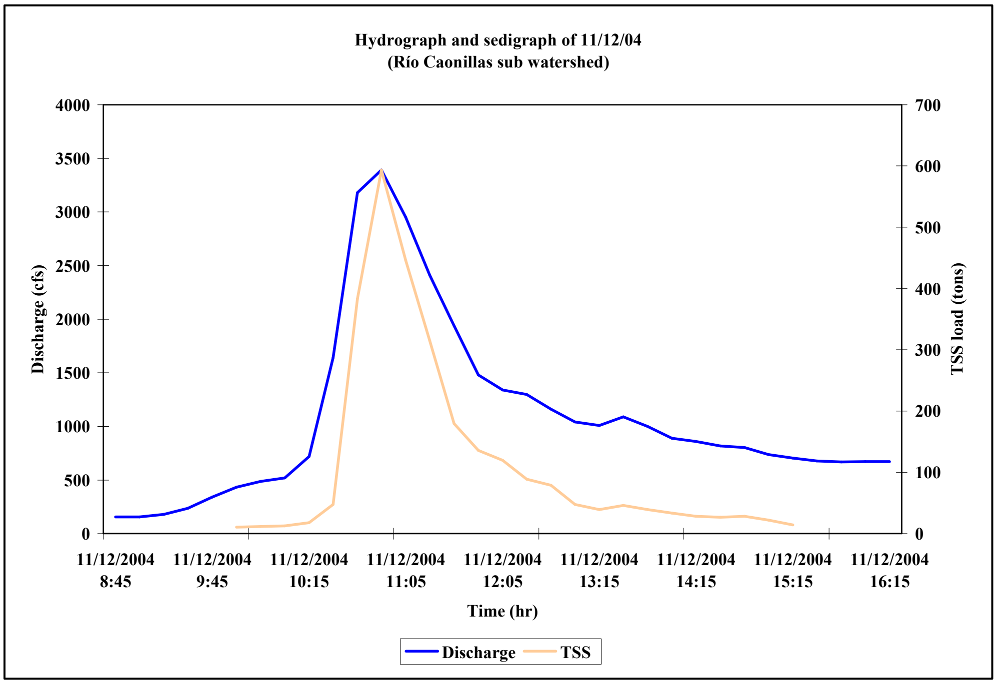


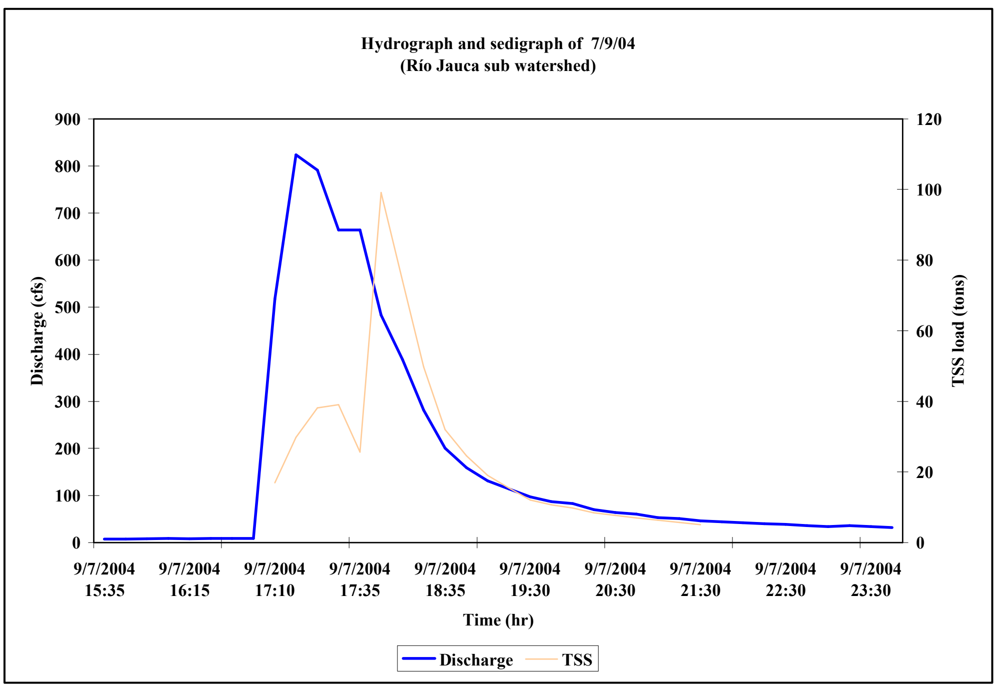
Appendix D. Example of storm event hydrograph (discharge versus TSS load)





Appendix D. (Continued)





Appendix E. Field data sheet.

Field Sheet

University of Puerto Rico
Mayagüez Campus

Site: ___________________________________
Date: ___________________________________
Time: ___________________________________

Name of Collectors:
____
____

#1 Measurements

pH Standard units	Temperature °C	Conductivity (μS/cm)

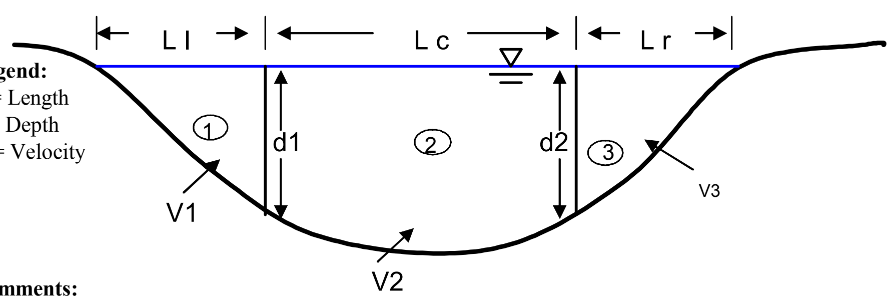
#2 Manual Sampling Data

Samples Collected	Bottle 1	Bottle 2	Bottle 3
Nutrients	Nitrogen	Phosphorous	Refill
Collected (check)			
Sediments	Left	Center	Right
Collected (check)			

#3 Measurements

Location	Velocity ft/sec.		Length ft	Depth ft
	0.2	0.8		
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				

River Section:

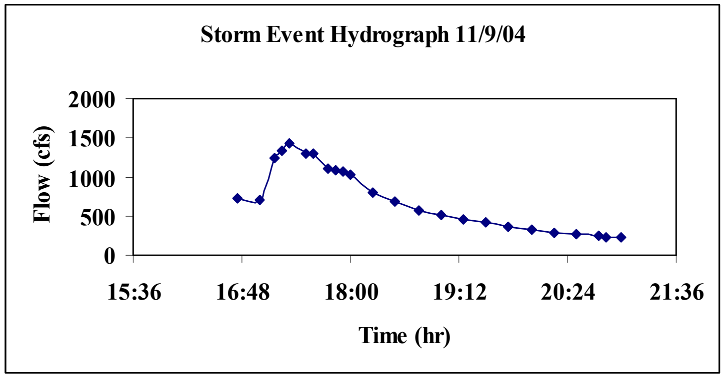


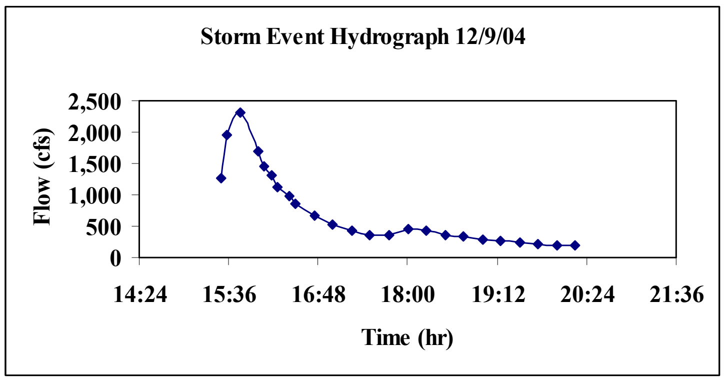
Legend:
L = Length
d = Depth
V = Velocity

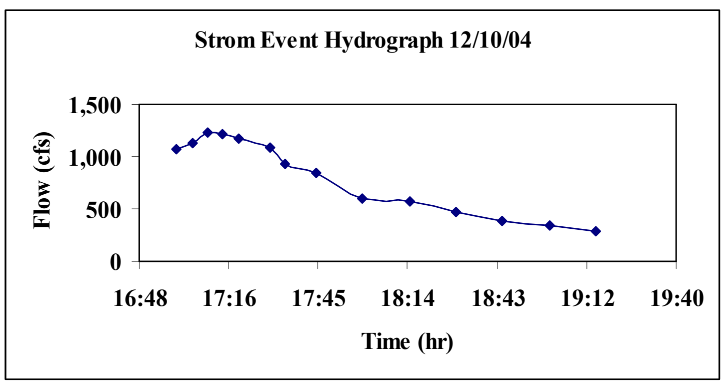
Comments:

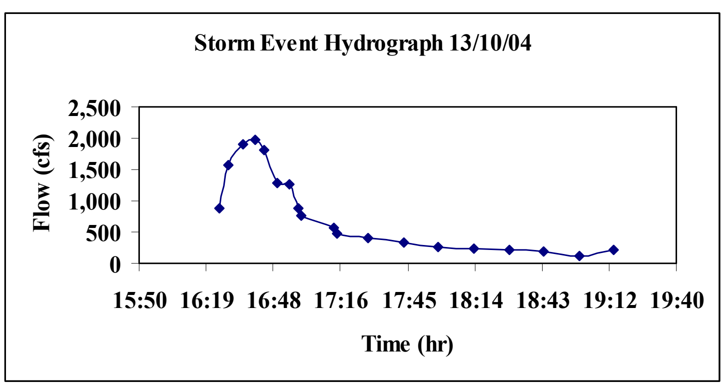
Appendix F. Storm event hydrograph (flow versus time)

Río Limón sub watershed



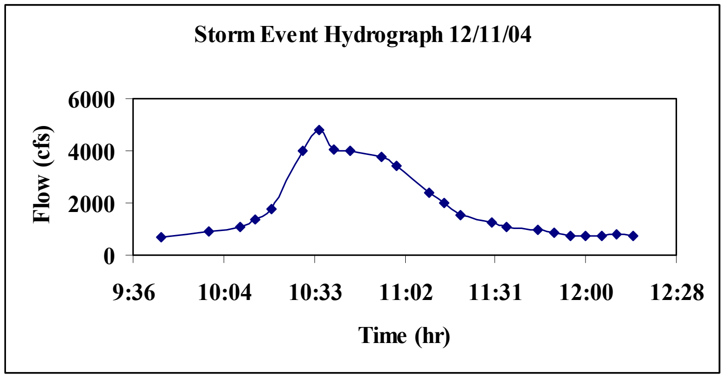


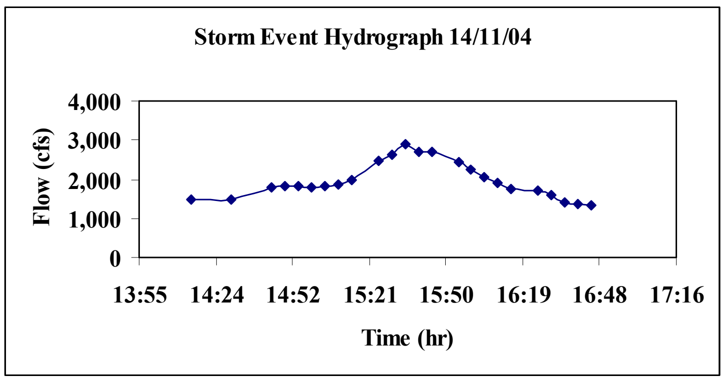


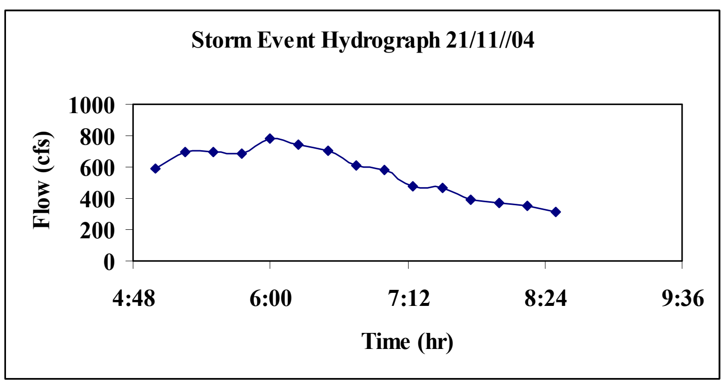


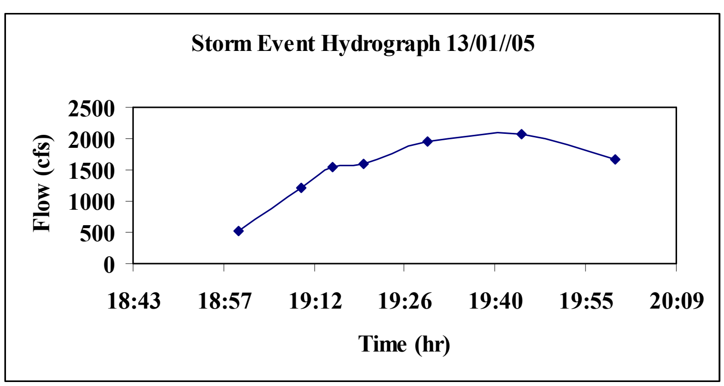
◆ **Each point in the hydrograph represents a collected sample.**

Appendix F. (Continued)



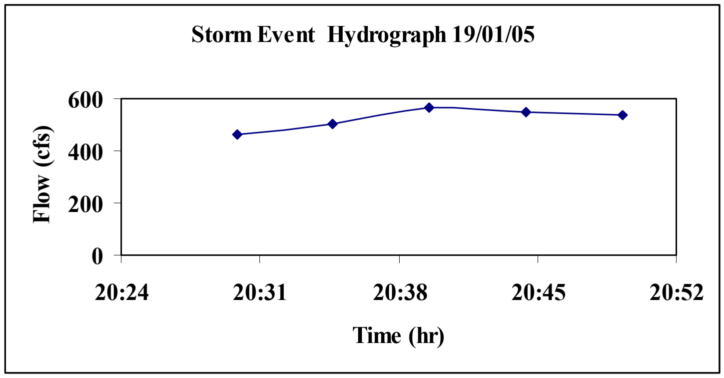


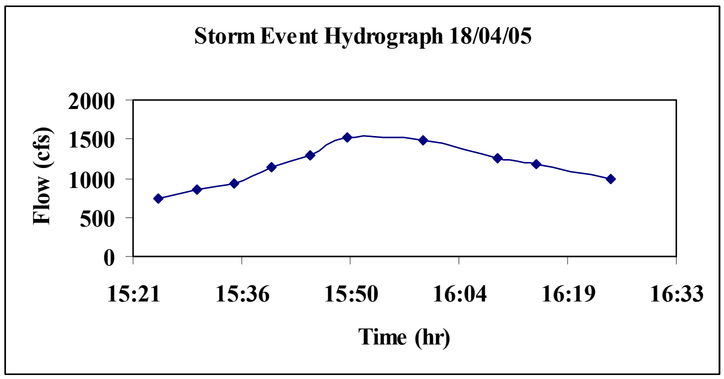


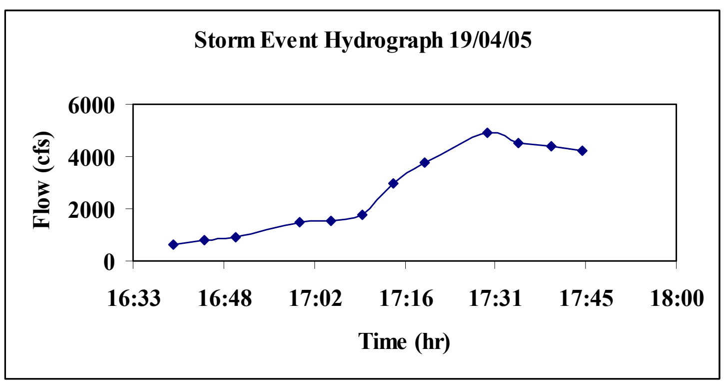


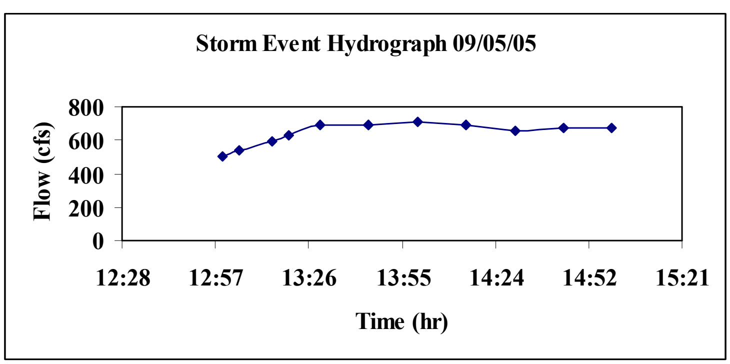
◆ **Each point in the hydrograph represents a collected sample.**

Appendix F. (Continued)





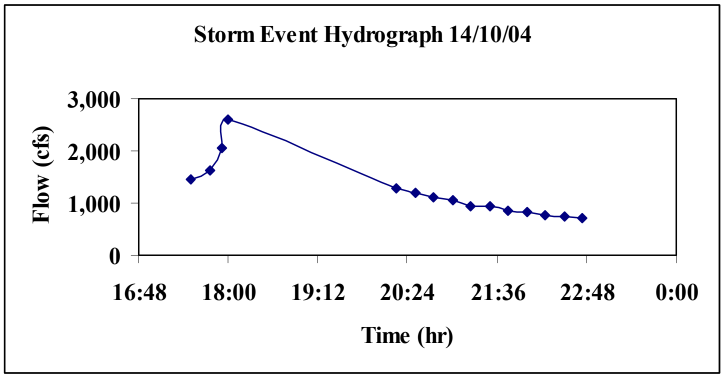


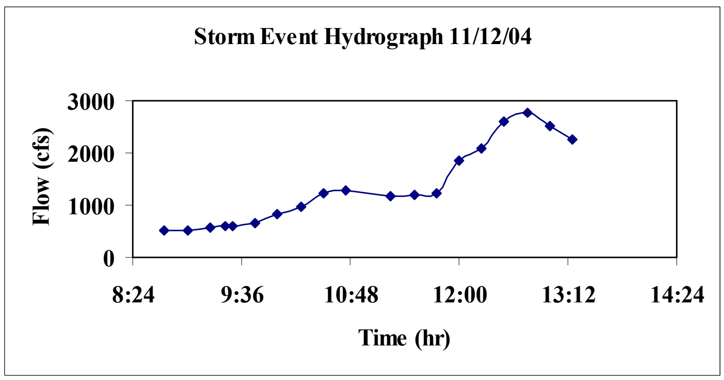


◆ **Each point in the hydrograph represents a collected sample.**

Appendix F. (Continued)

Río Grande de Arecibo sub watershed

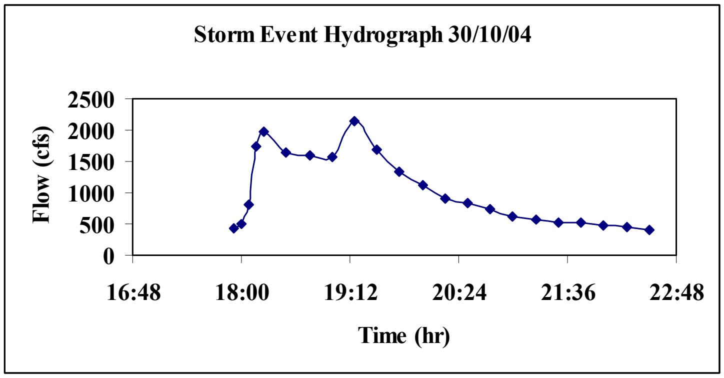


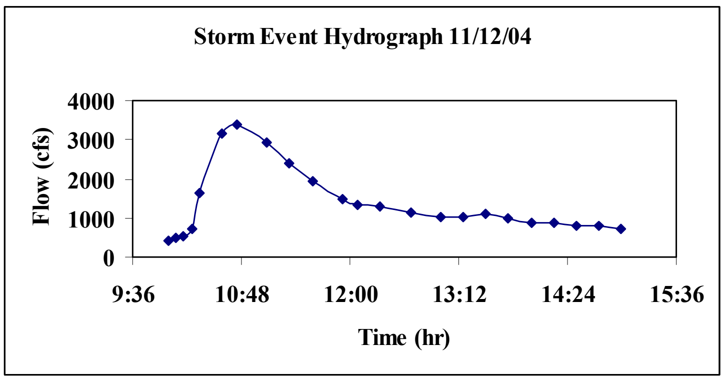


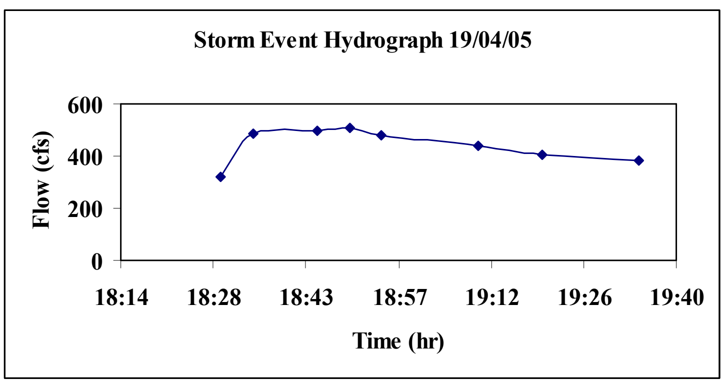
◆ **Each point in the hydrograph represents a collected sample.**

Appendix F. (Continued)

Río Caonillas sub watershed

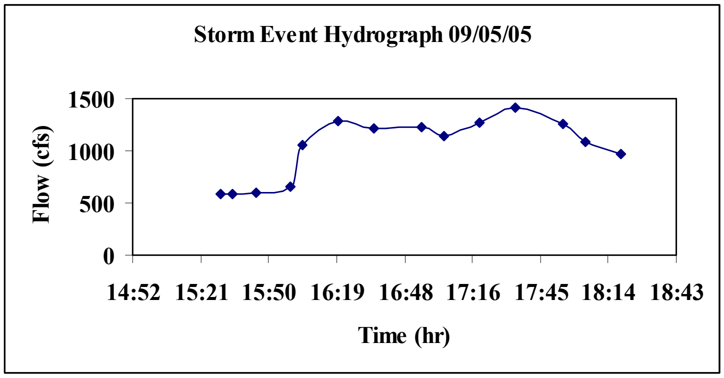


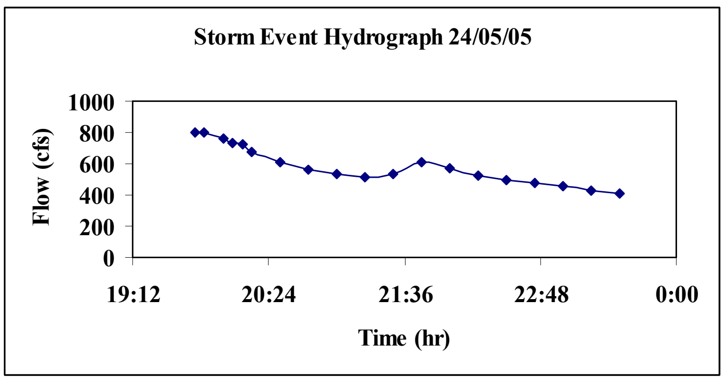


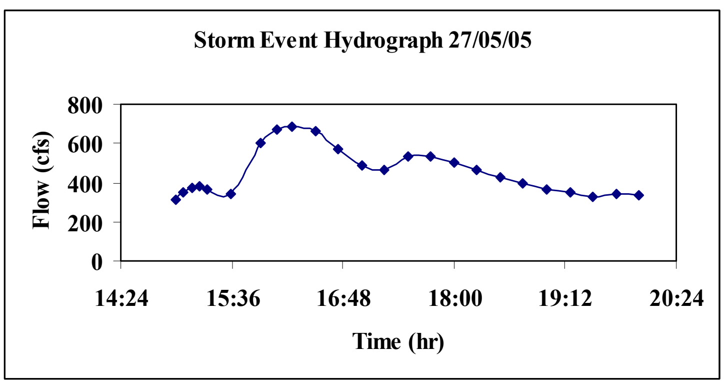


◆ **Each point in the hydrograph represents a collected sample.**

Appendix F. (Continued)



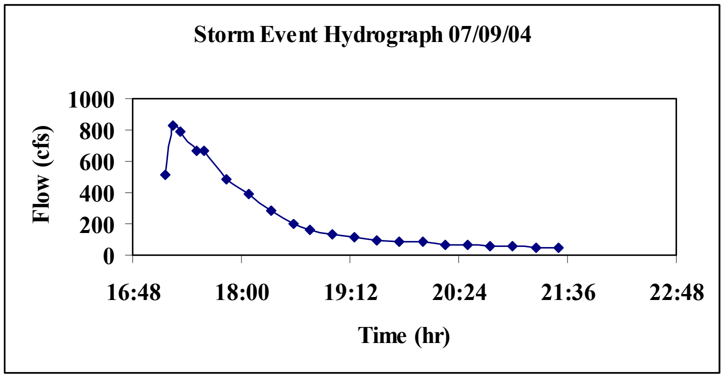


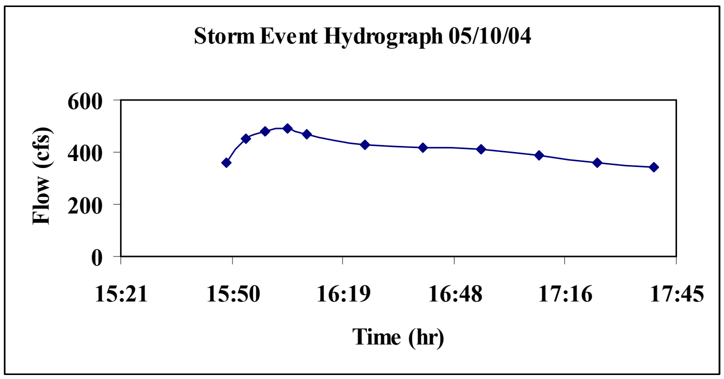


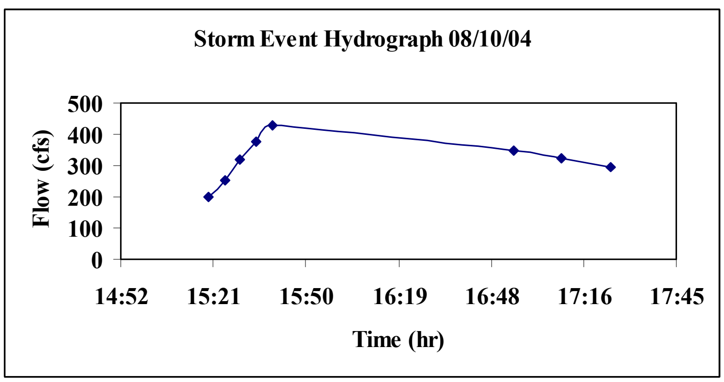
◆ **Each point in the hydrograph represents a collected sample.**

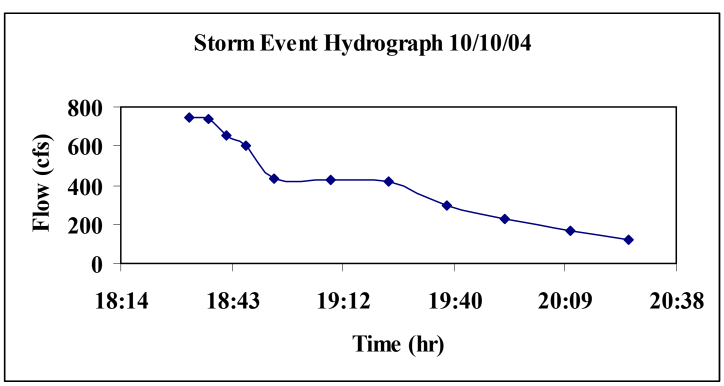
Appendix F. (Continued)

Río Jauca sub watershed



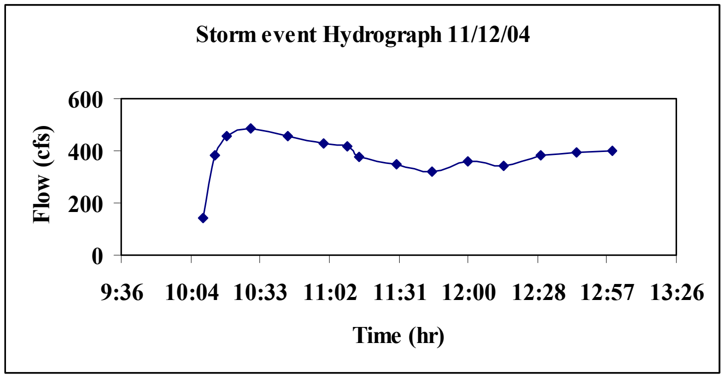


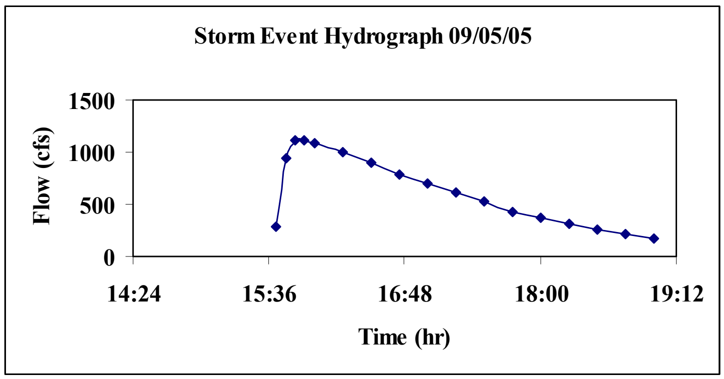


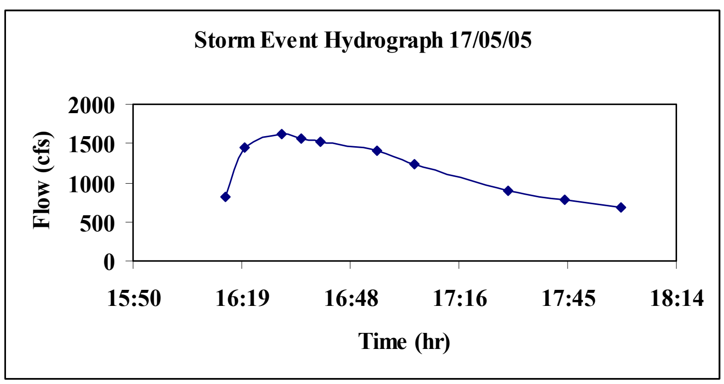


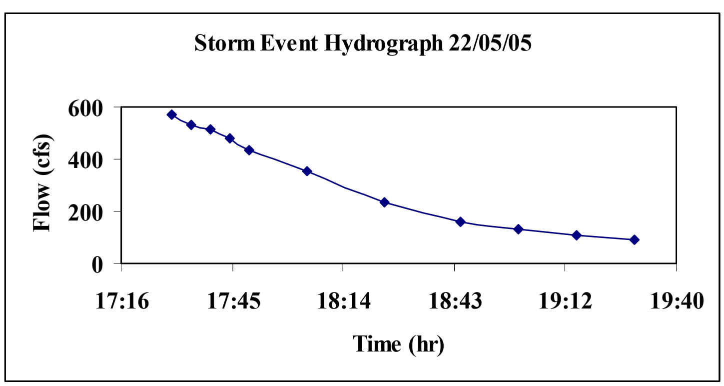
◆ **Each point in the hydrograph represents a collected sample.**

Appendix F. (Continued)



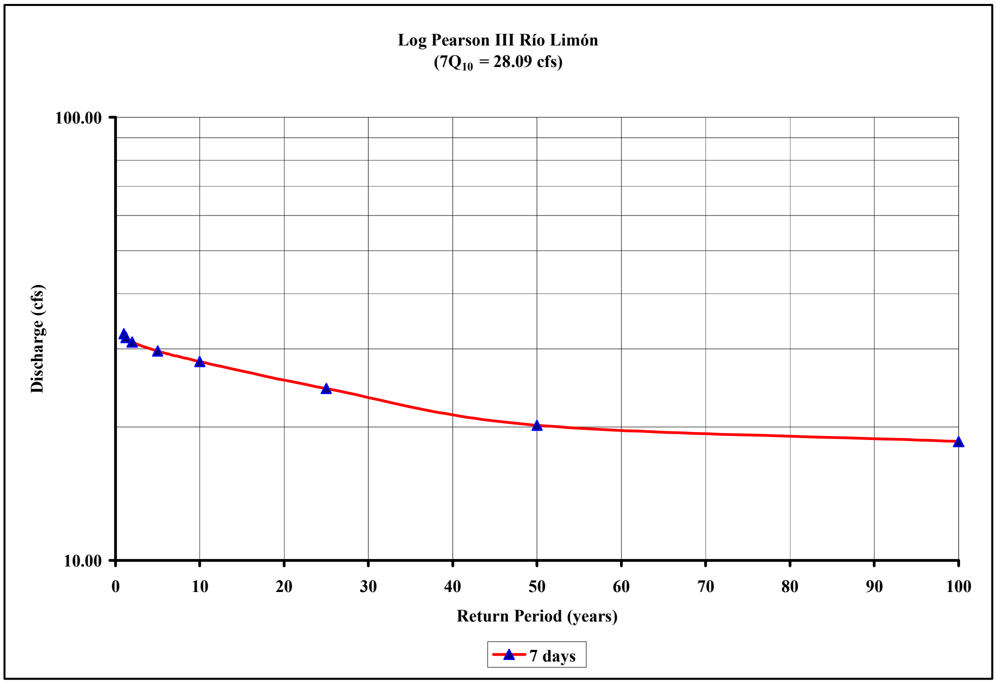


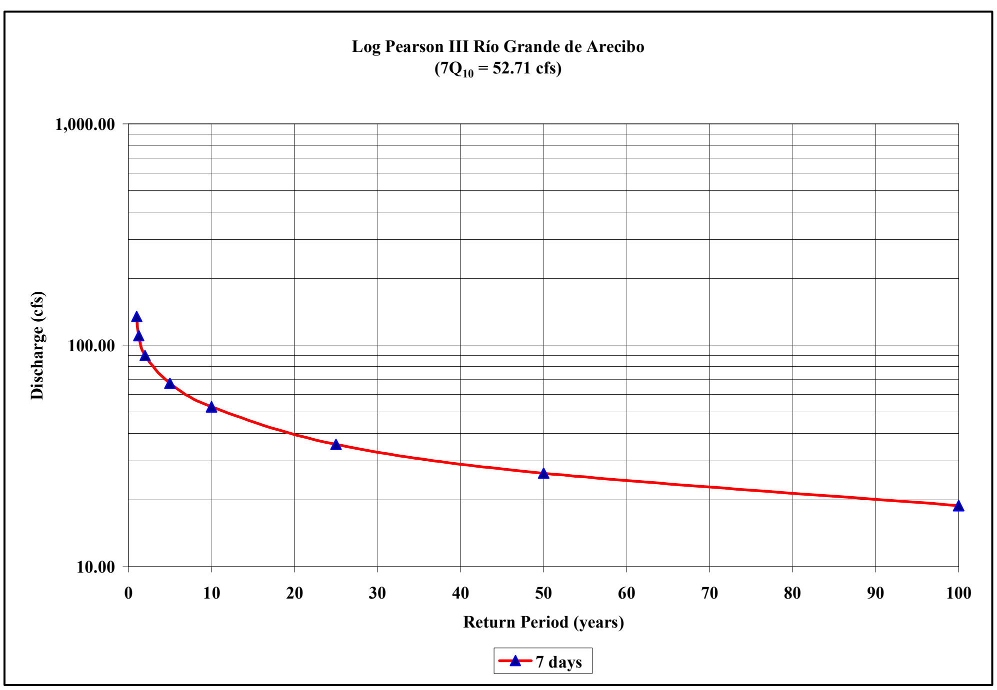




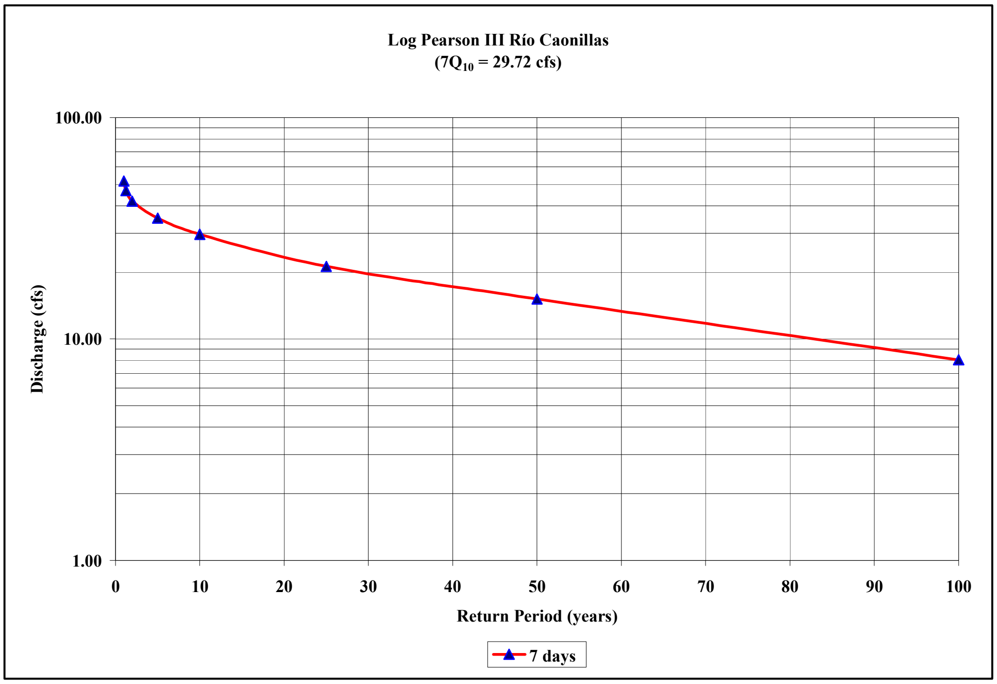
◆ **Each point in the hydrograph represents a collected sample.**

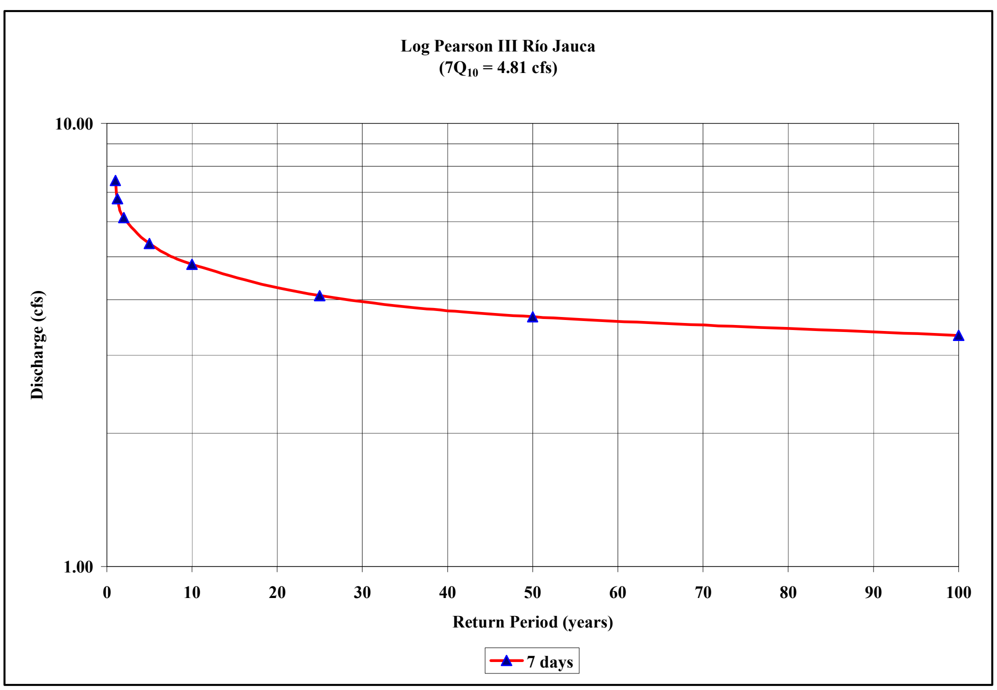
Appendix G. Log Pearson Type III distribution graph for flow separation (7 days, 10 years)





Appendix G. (Continued)





Appendix H. Grab (TP, DP, TKN, TSS) load versus flow regressions tables and graphics for Río Limón, Río Grande de Arecibo, Río Caonillas and Río Jauca sub watersheds.

	TP load versus flow regression values		
Sub watershed	**Intercept**	**Slope**	**Coefficient of determination**
Río Limón	0.1691	-1.7382	0.84
Río Grande de Arecibo	0.2623	-8.9625	0.90
Río Caonillas	0.3330	-12.5970	0.85
Río Jauca	0.1001	-0.0590	0.91

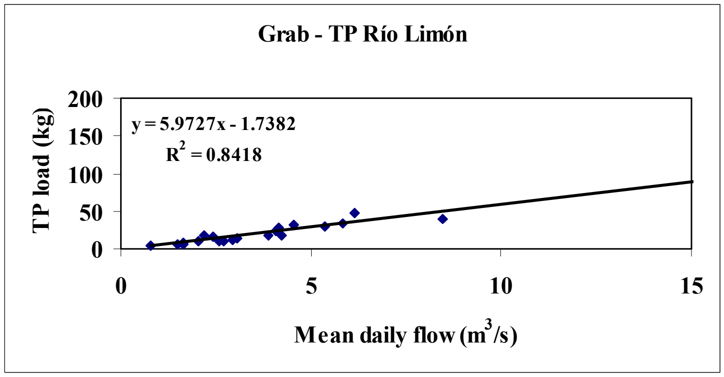
	DP load versus flow regression values		
Sub watershed	**Intercept**	**Slope**	**Coefficient of determination**
Río Limón	0.1621	-1.4281	0.67
Río Grande de Arecibo	0.1716	1.0964	0.65
Río Caonillas	0.1278	0.4565	0.89
Río Jauca	0.0544	0.4362	0.94

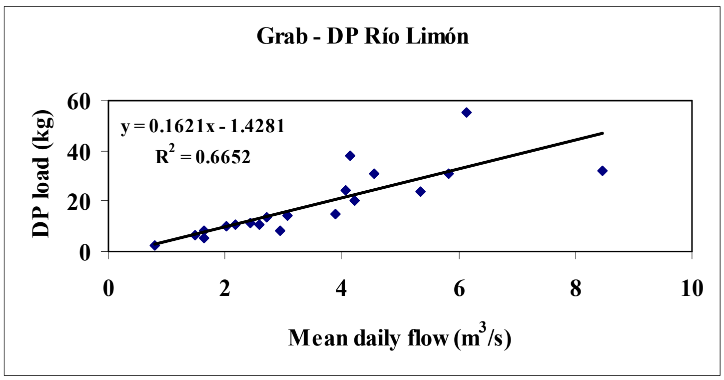
	TKN load versus flow regression values		
Sub watershed	**Intercept**	**Slope**	**Coefficient of determination**
Río Limón	0.1846	11.1180	0.51
Río Grande de Arecibo	0.7790	-31.7580	0.84
Río Caonillas	0.3257	7.2501	0.87
Río Jauca	0.0833	1.4836	0.78

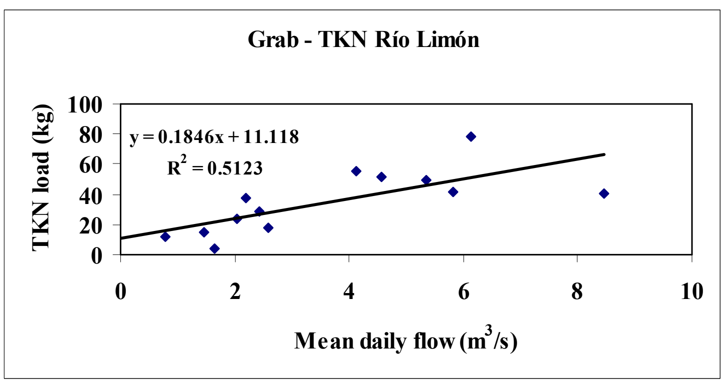
	TSS load versus flow regression values		
Sub watershed	**Intercept**	**Slope**	**Coefficient of determination**
Río Limón	0.0604	-2.2121	0.86
Río Grande de Arecibo	0.1432	-11.6800	0.88
Río Caonillas	0.0447	-0.7494	0.89
Río Jauca	0.0230	0.1066	0.88

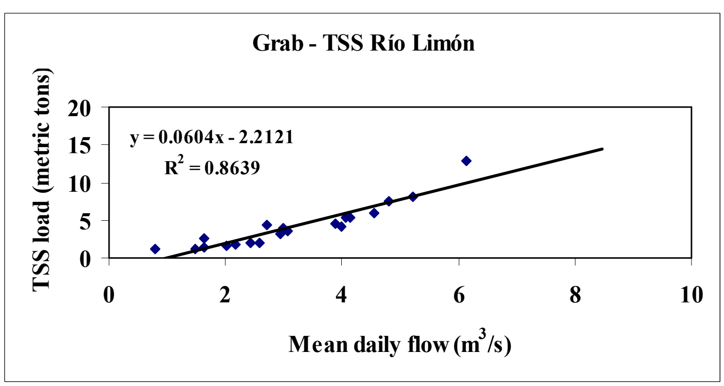
Appendix H. (Continued)

Río Limón sub watershed



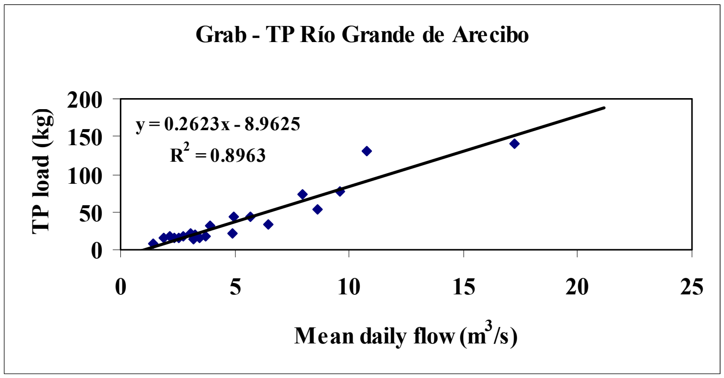


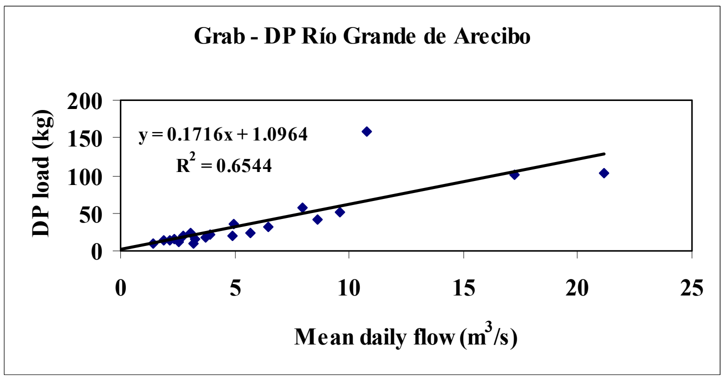


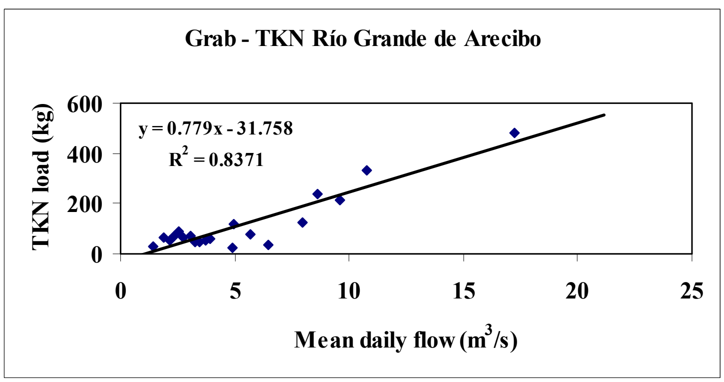


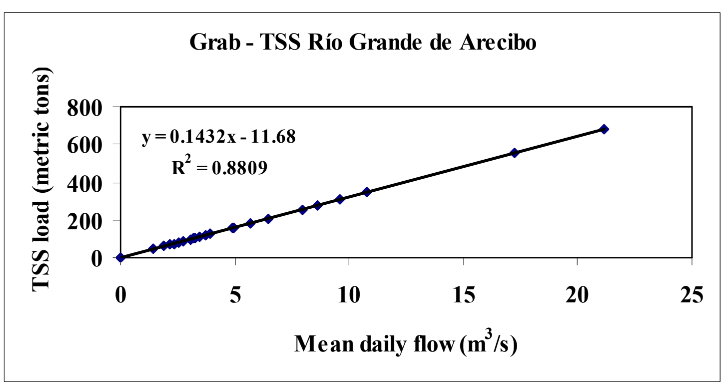
Appendix H. (Continued)

Río Grande de Arecibo sub watershed



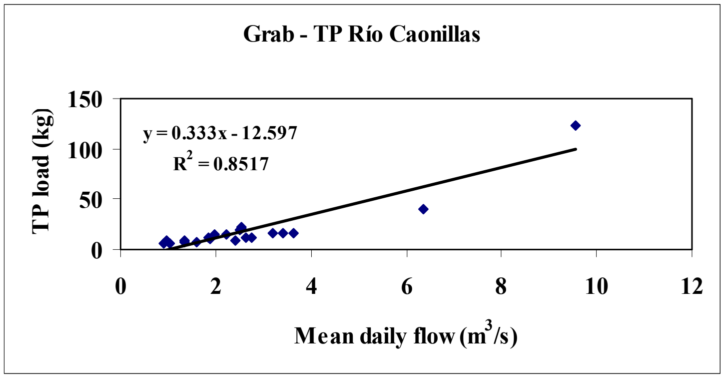


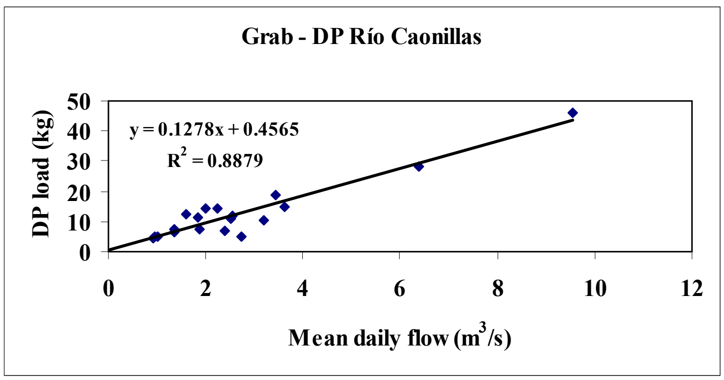


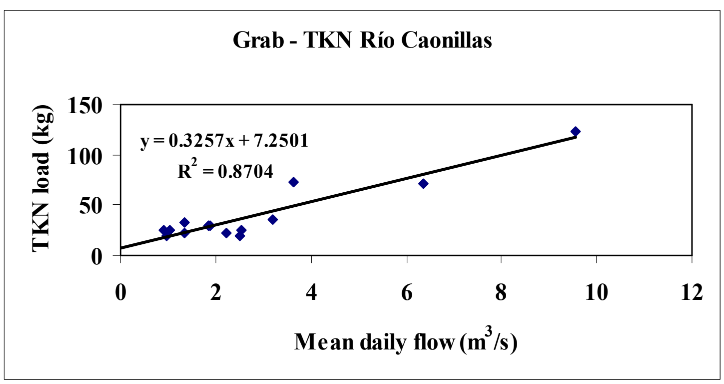


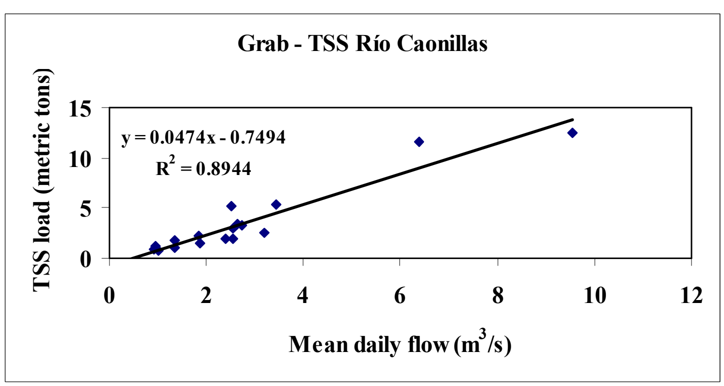
Appendix H. (Continued)

Río Caonillas sub watershed



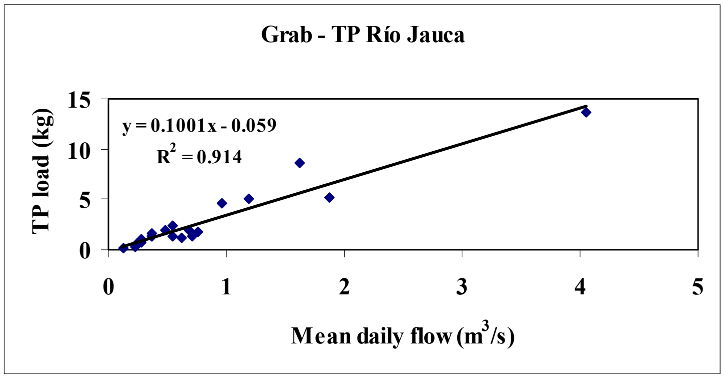


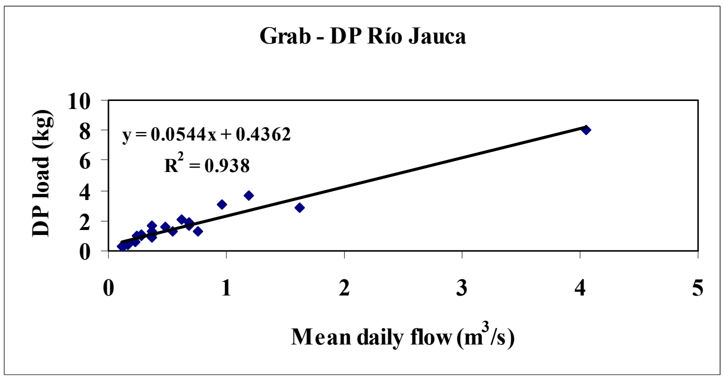


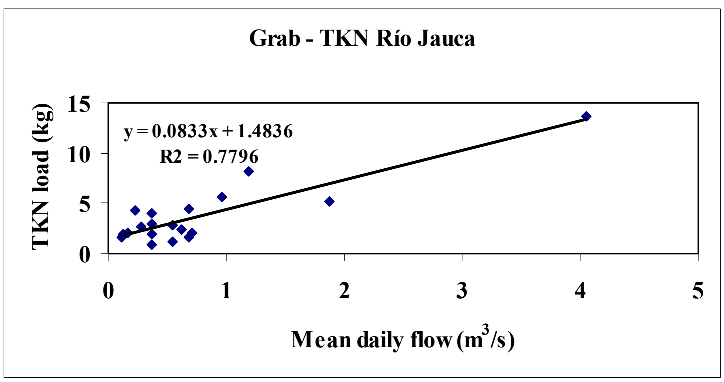


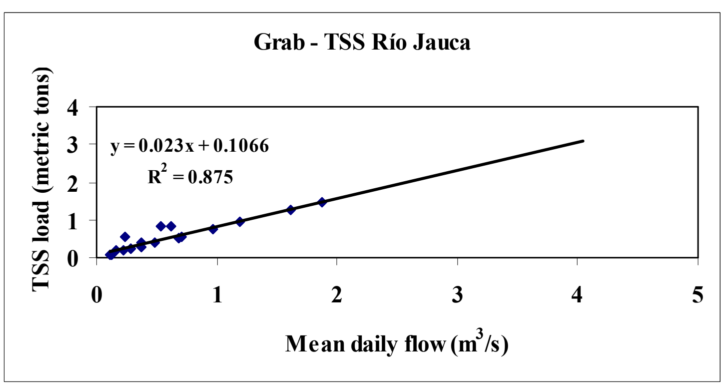
Appendix H. (Continued)

Río Jauca sub watershed









Appendix I. Storm event (TP, DP, TKN, TSS) load versus flow regressions tables and graphics for Río Limón, Río Grande de Arecibo, Río Caonillas and Río Jauca sub watersheds.

	TP load versus flow regression values		
Sub watershed	**Intercept**	**Slope**	**Coefficient of determination**
Río Limón	0.0105	-3.4740	0.81
Río Grande de Arecibo	0.0127	4.0125	0.39
Río Caonillas	0.0496	-26.8850	0.64
Río Jauca	0.0065	0.2171	0.42

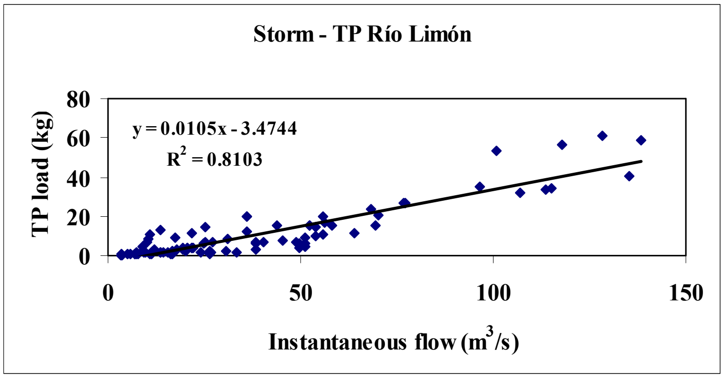
	DP load versus flow regression values		
Sub watershed	**Intercept**	**Slope**	**Coefficient of determination**
Río Limón	0.0005	0.0461	0.84
Río Grande de Arecibo	0.0043	0.4989	0.62
Río Caonillas	0.0034	-1.7395	0.73
Río Jauca	0.0029	-0.7372	0.54

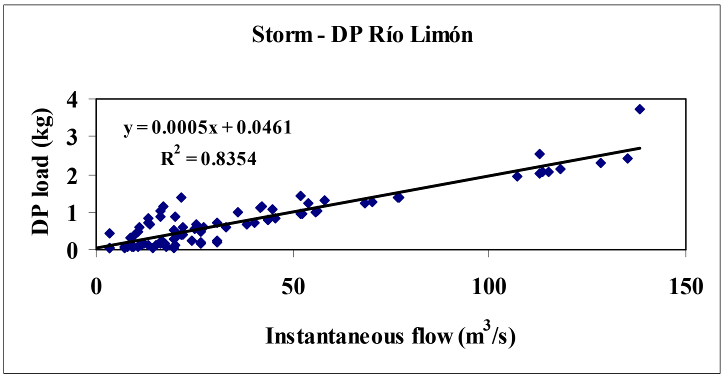
	TKN load versus flow regression values		
Sub watershed	**Intercept**	**Slope**	**Coefficient of determination**
Río Limón	0.0324	-0.9871	0.84
Río Grande de Arecibo	0.0229	4.6012	0.57
Río Caonillas	0.1330	-51.1800	0.87
Río Jauca	0.0253	6.2095	0.59

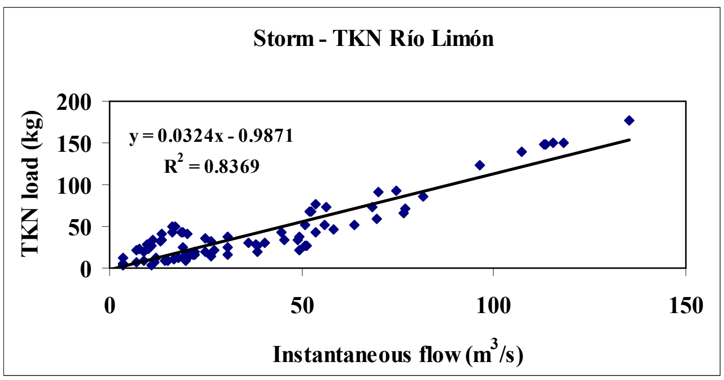
	TSS load versus flow regression values		
Sub watershed	**Intercept**	**Slope**	**Coefficient of determination**
Río Limón	0.0502	3.1808	0.76
Río Grande de Arecibo	0.0734	-36.0930	0.84
Río Caonillas	0.1535	-64.5430	0.87
Río Jauca	0.0213	6.0558	0.53

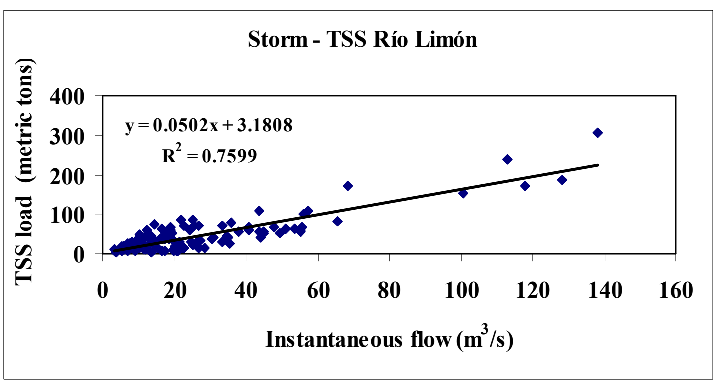
Appendix I. (Continued)

Río Limón sub watershed



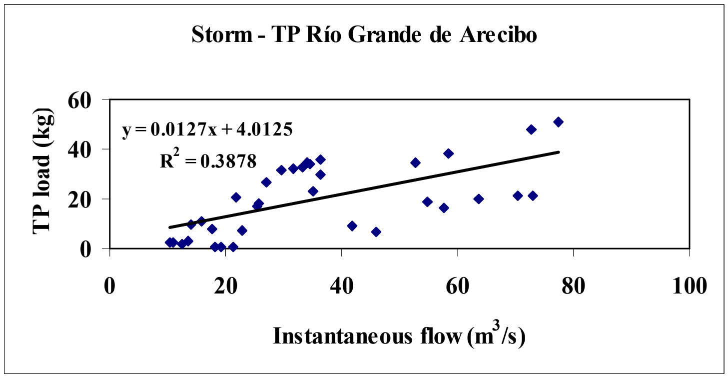


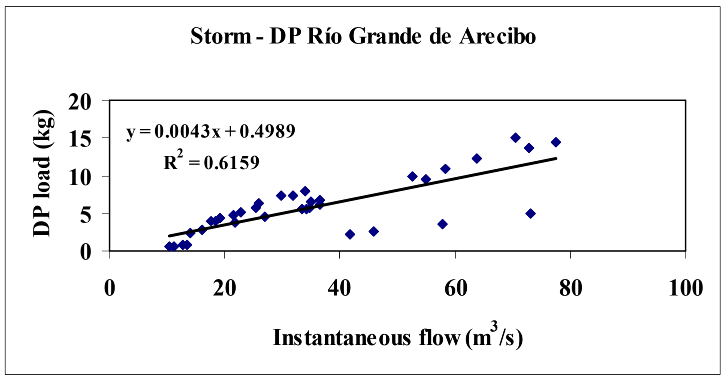


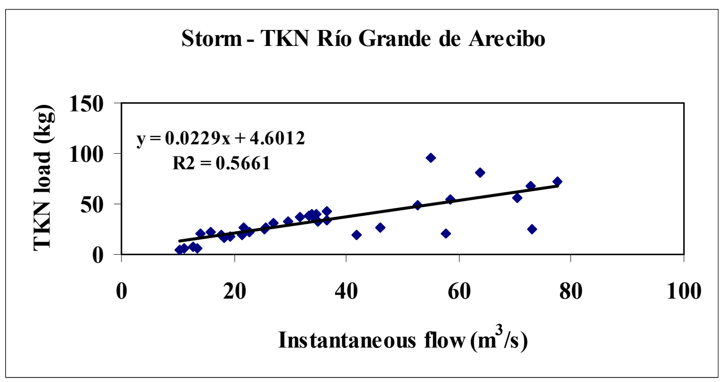


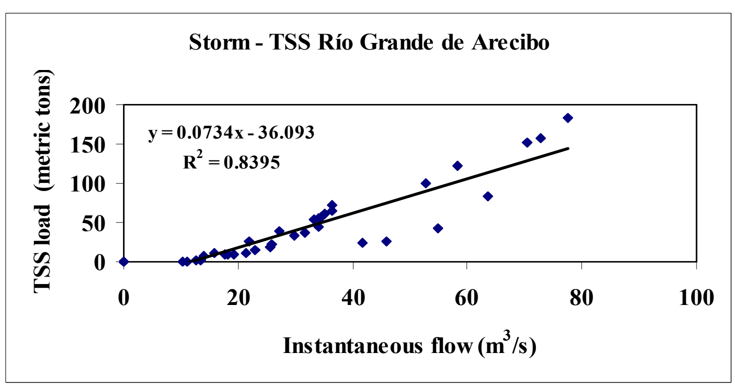
Appendix I. (Continued)

Río Grande de Arecibo sub watershed



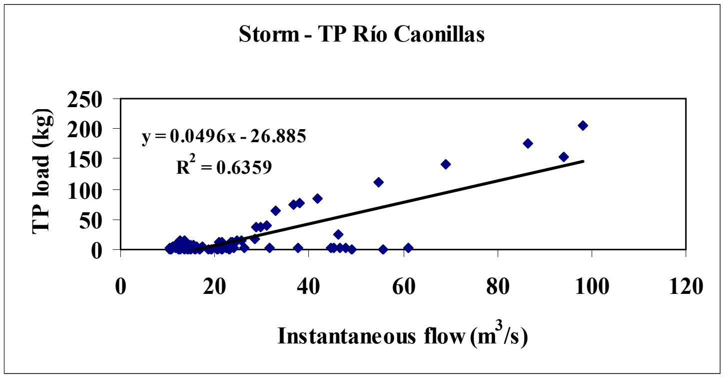


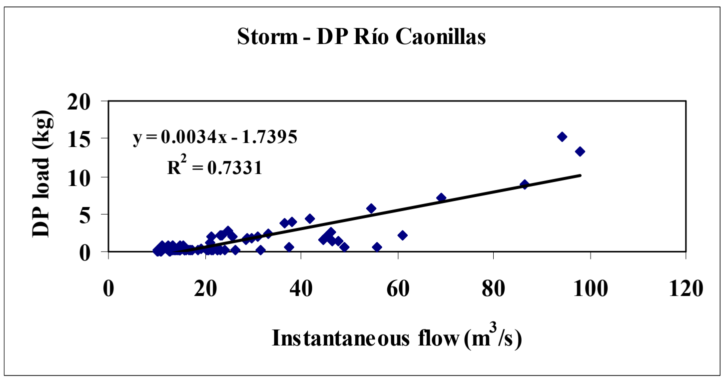


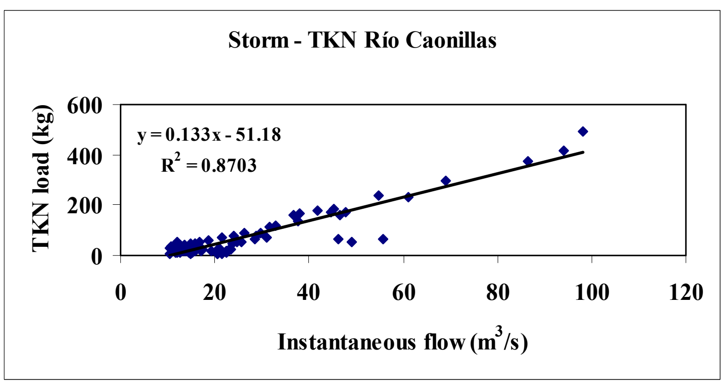


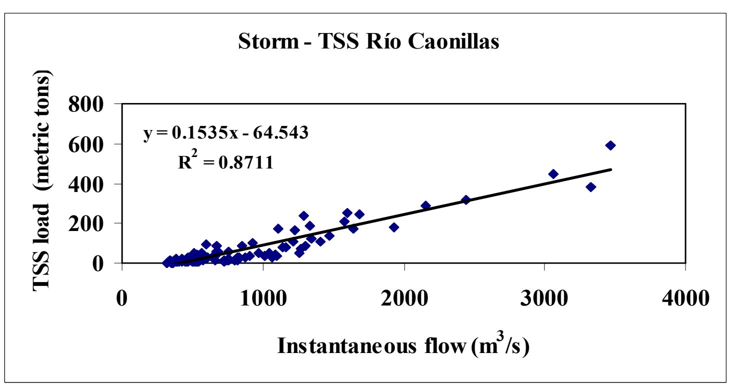
Appendix I. (Continued)

Río Caonillas sub watershed



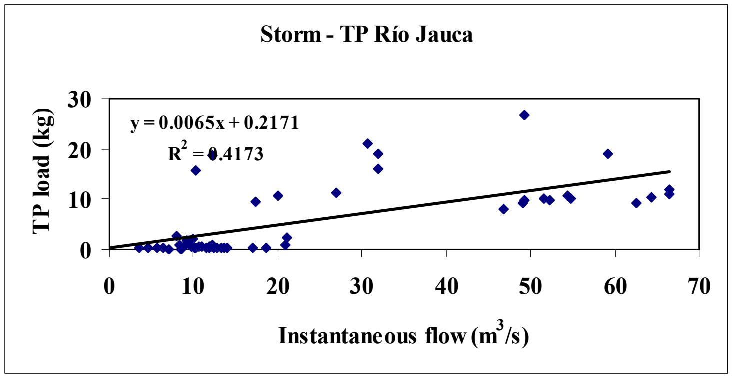


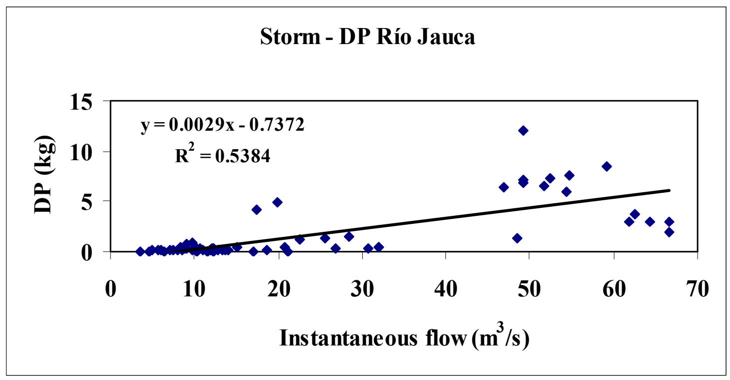


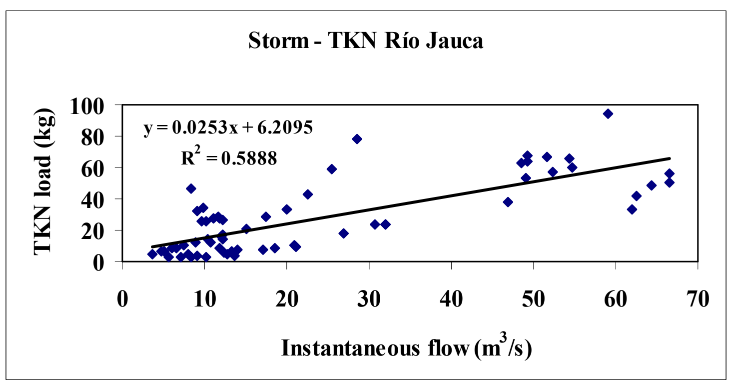


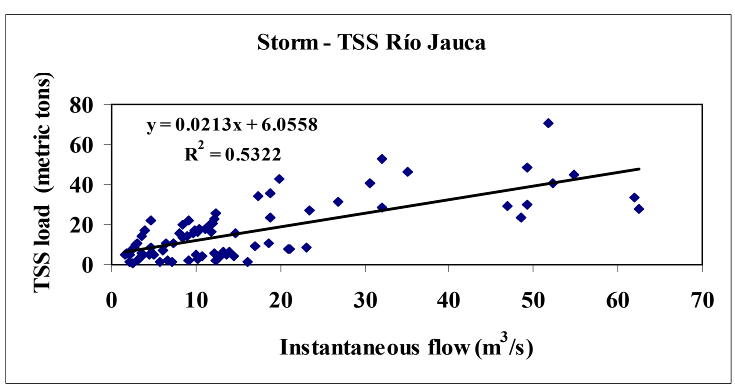
Appendix I. (Continued)

Río Jauca sub watershed



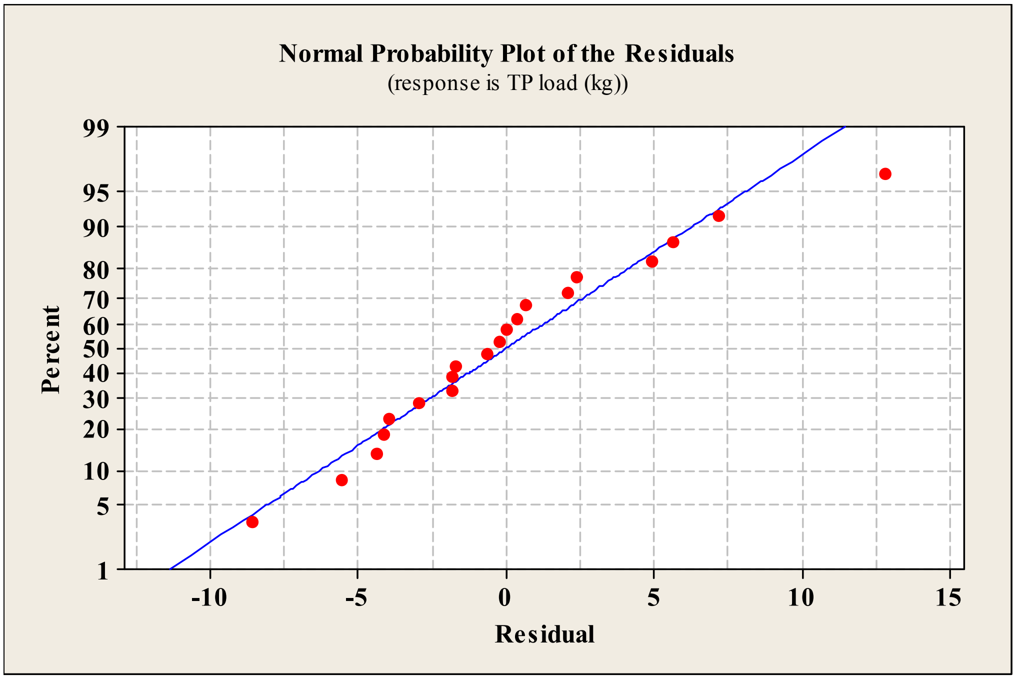


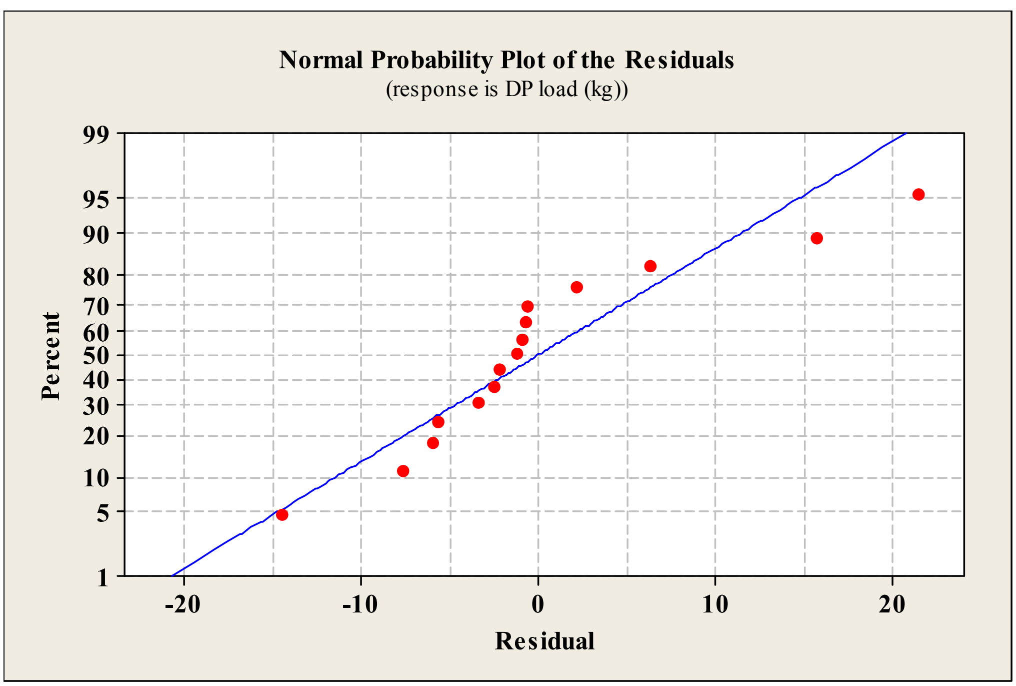




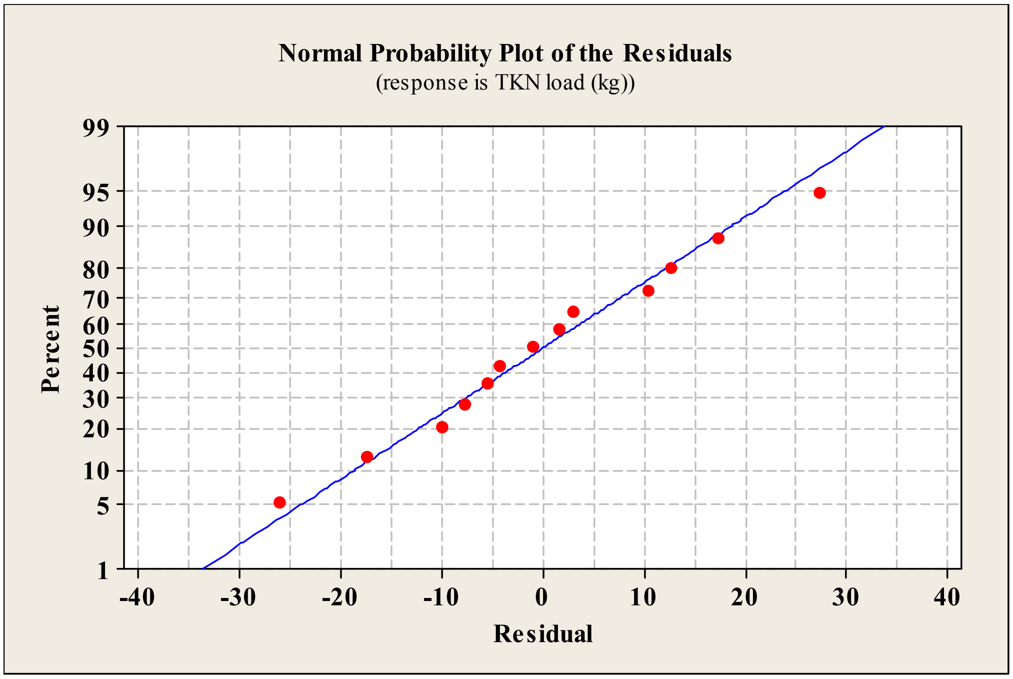
Appendix J. Grab (TP, DP, TKN and TSS) load versus flow regressions for Río Limón, Río Grande de Arecibo, Río Caonillas and Río Jauca sub watersheds.

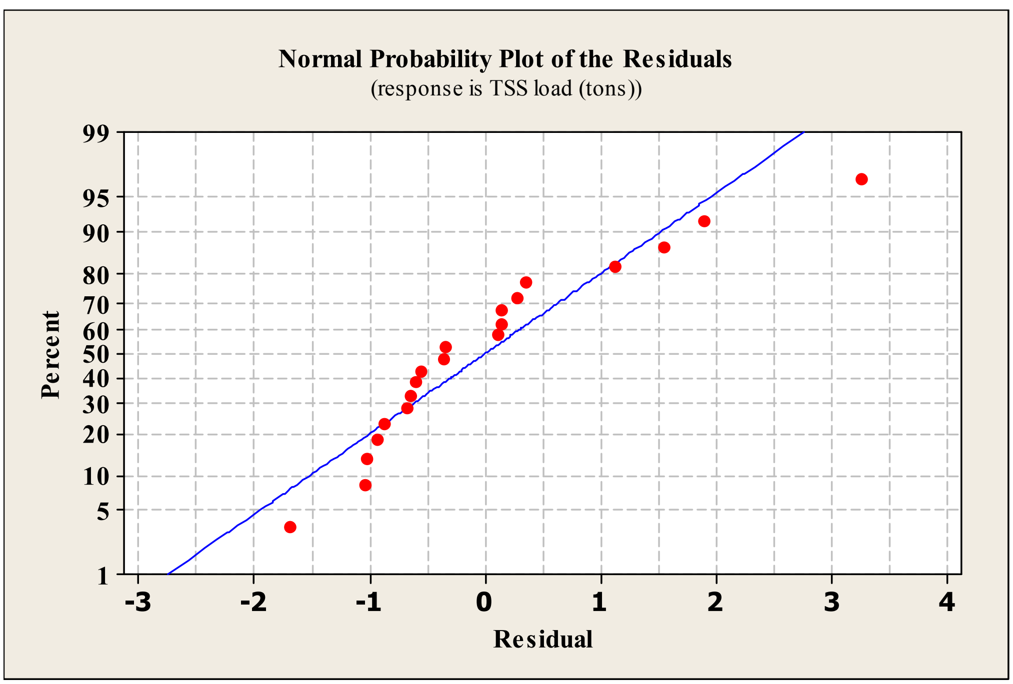
Río Limón sub watershed





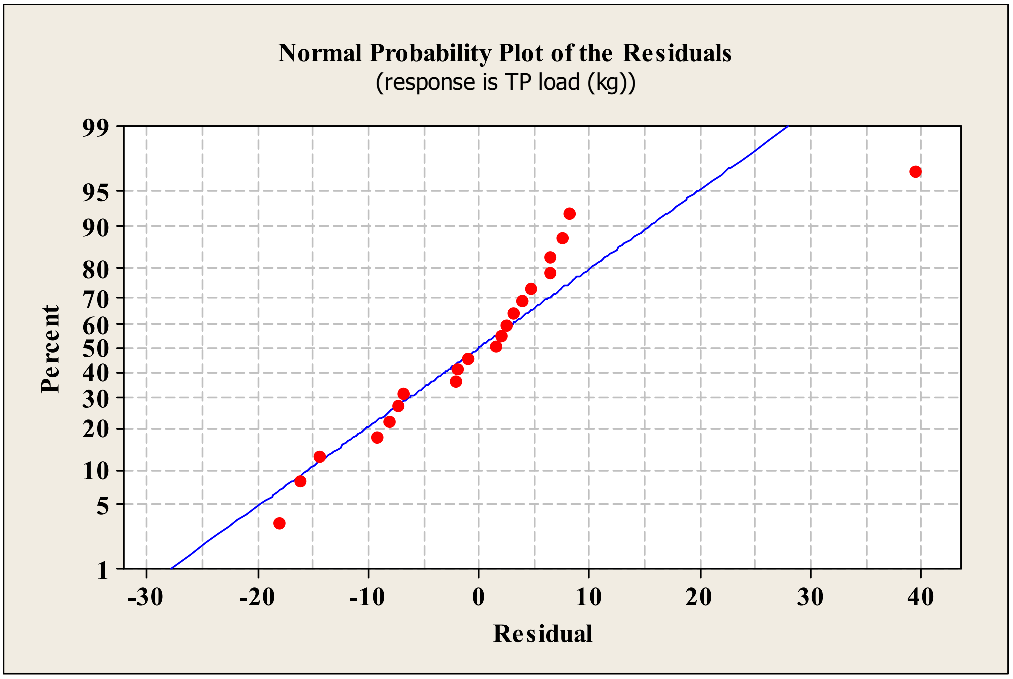
Appendix J. (Continued)

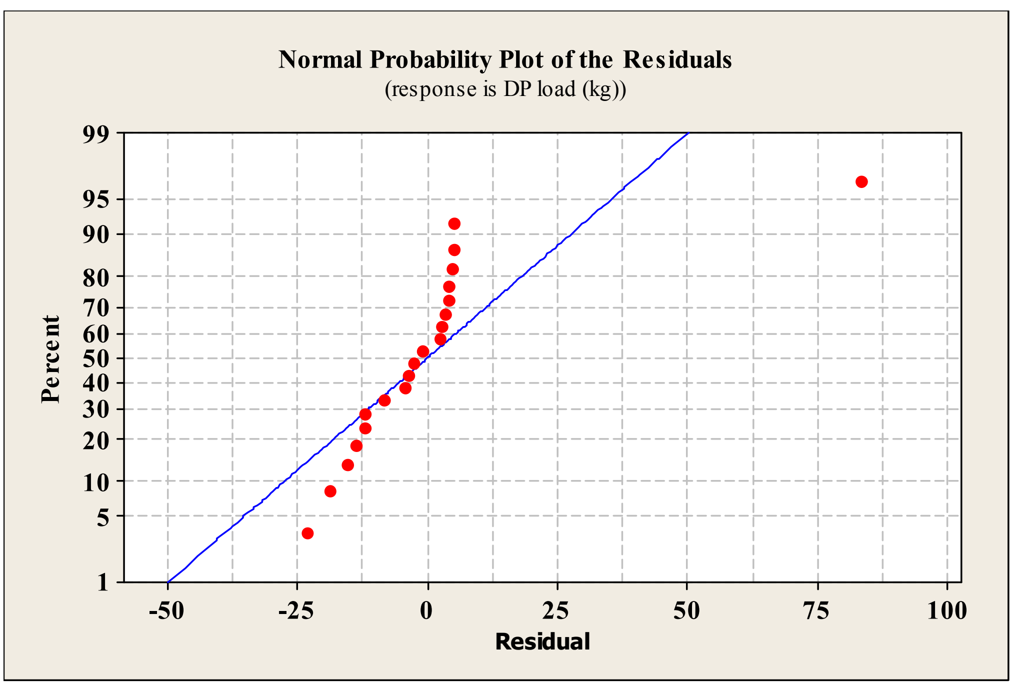




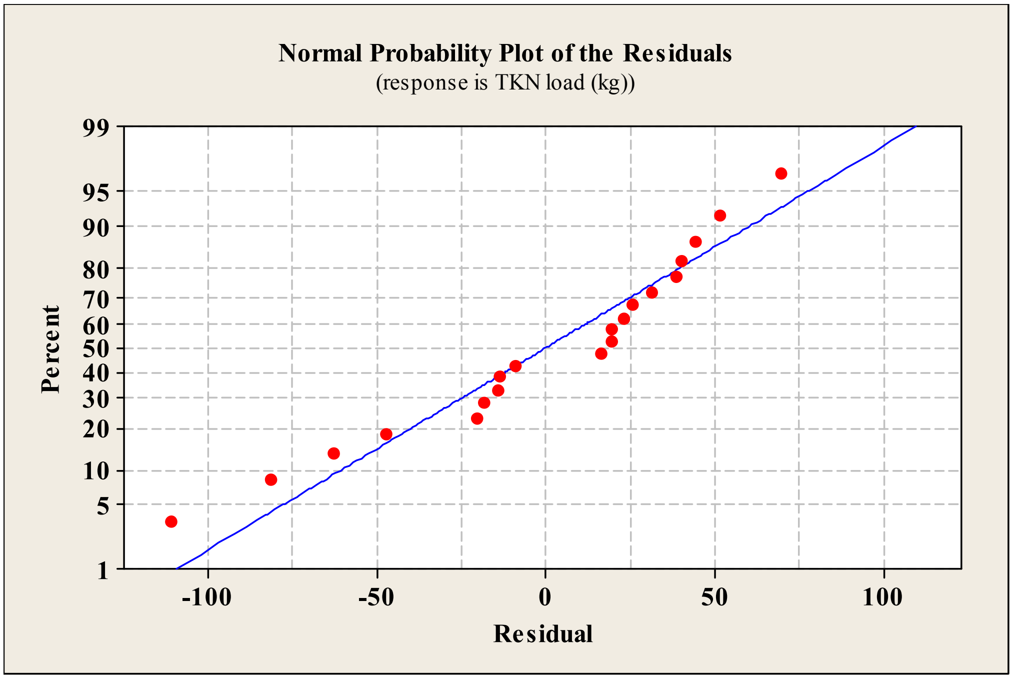
Appendix J. (Continued)

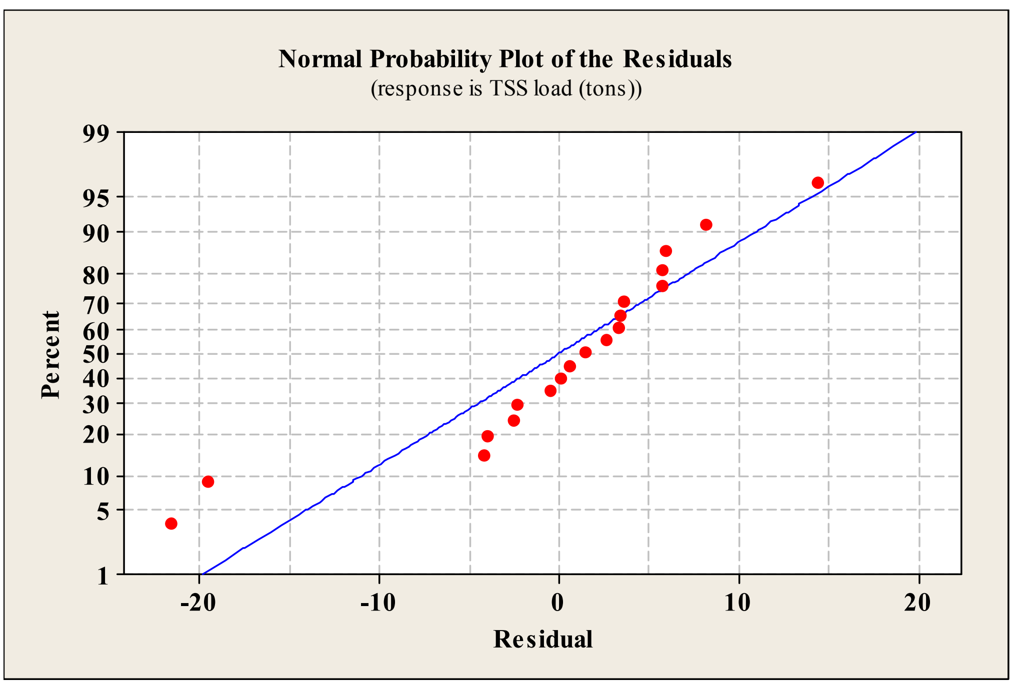
Río Grande de Arecibo sub watershed





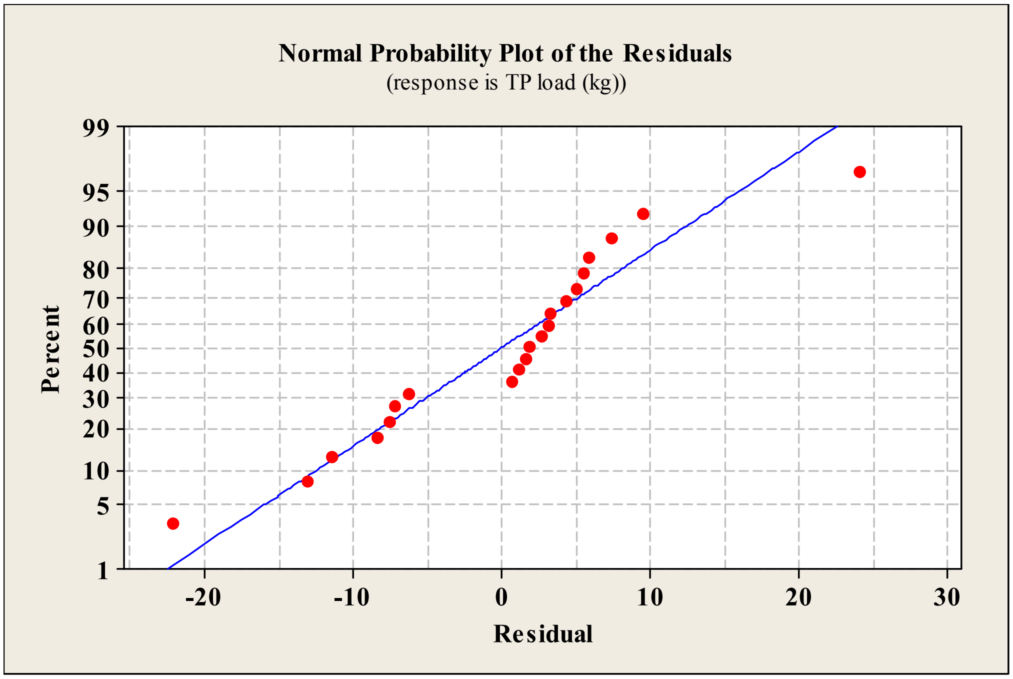
Appendix J. (Continued)

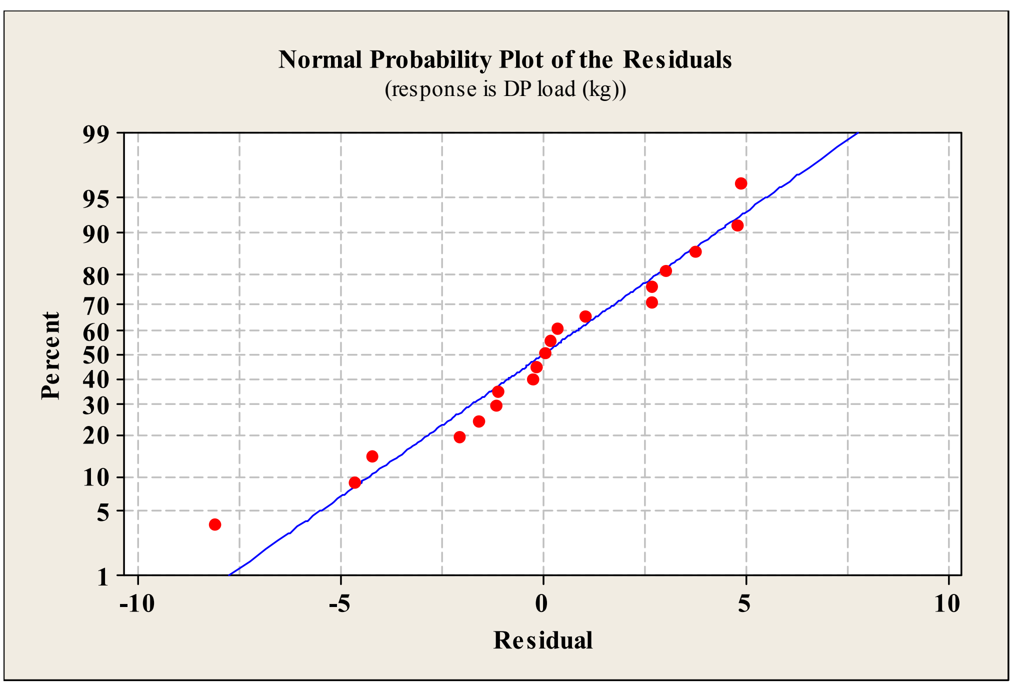




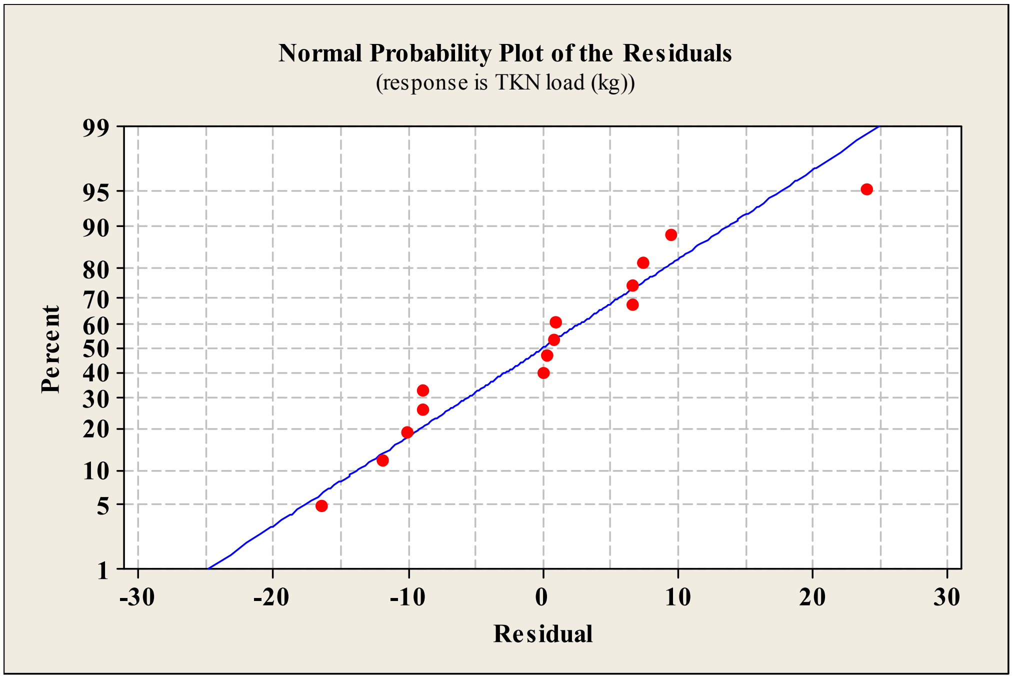
Appendix J. (Continued)

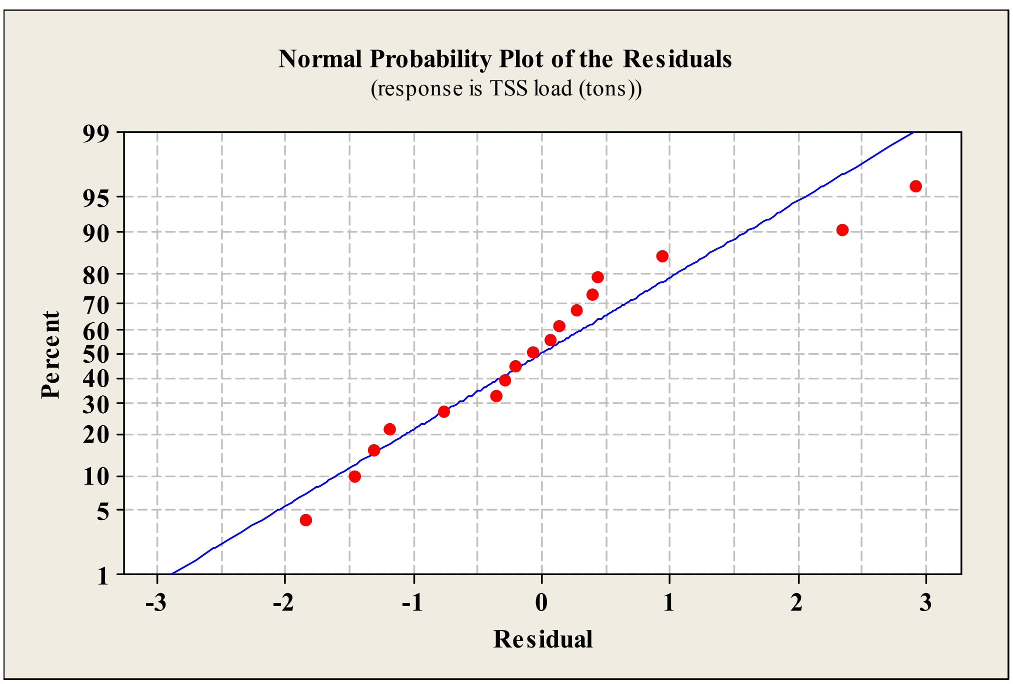
Río Caonillas sub watershed





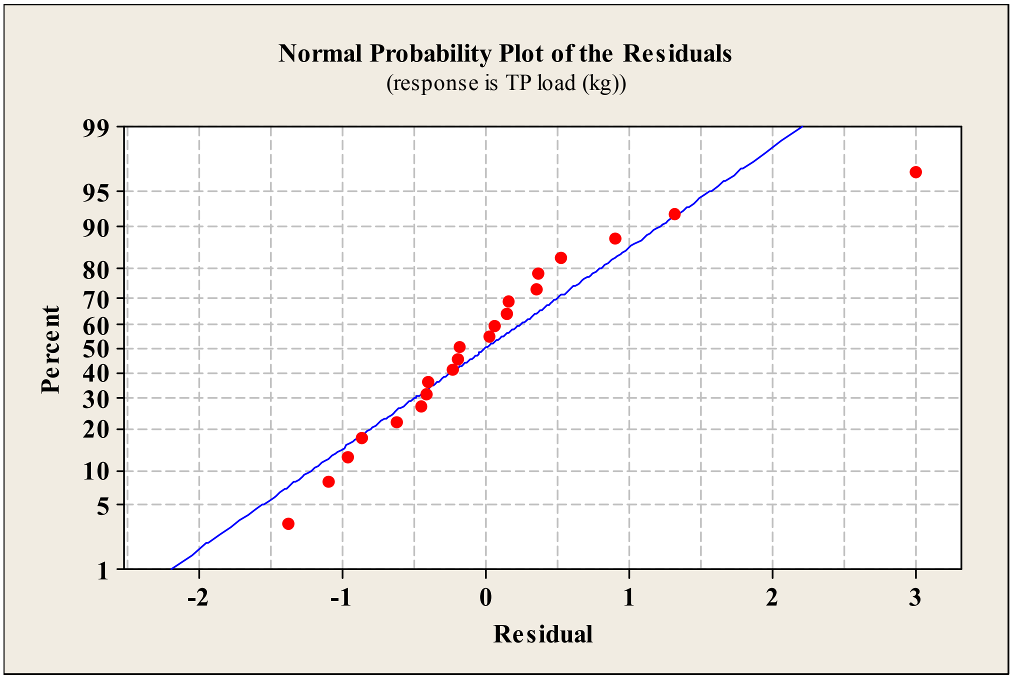
Appendix J. (Continued)

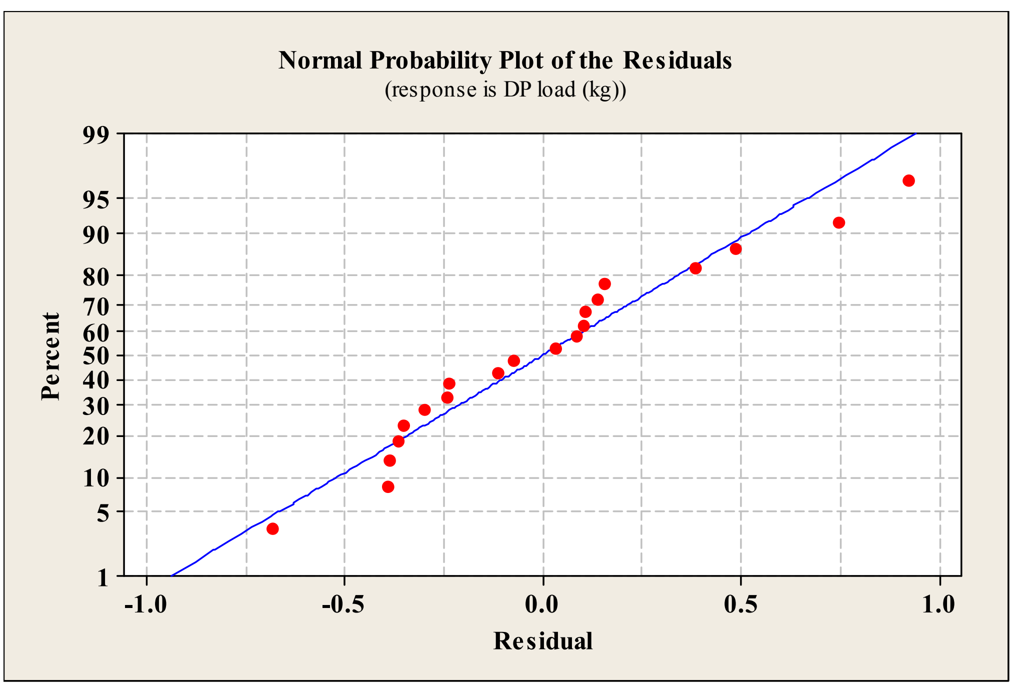




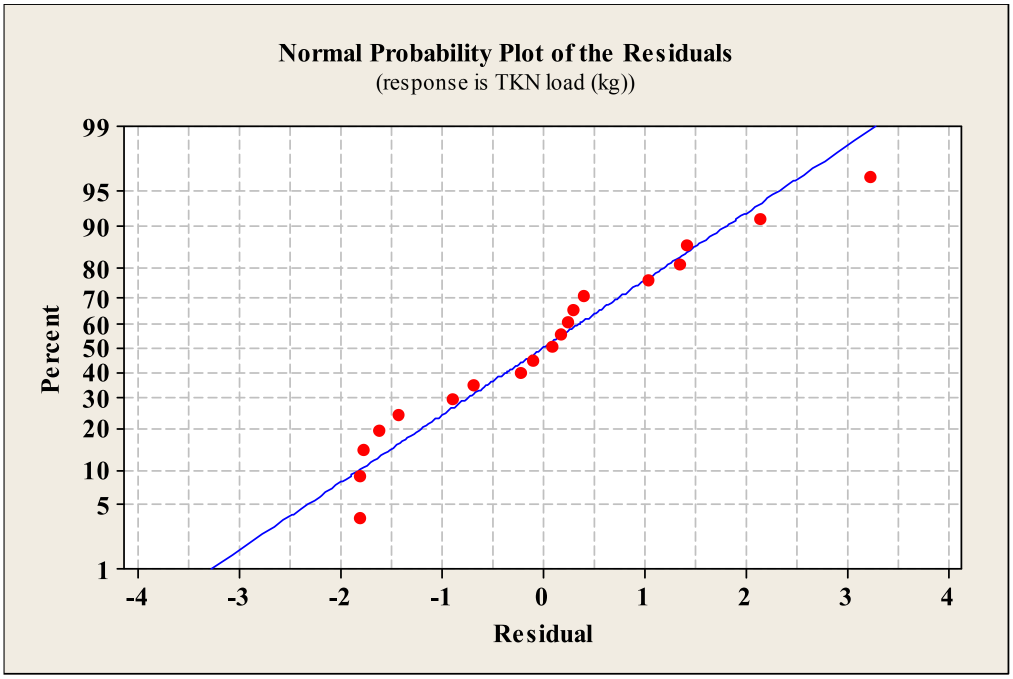
Appendix J. (Continued)

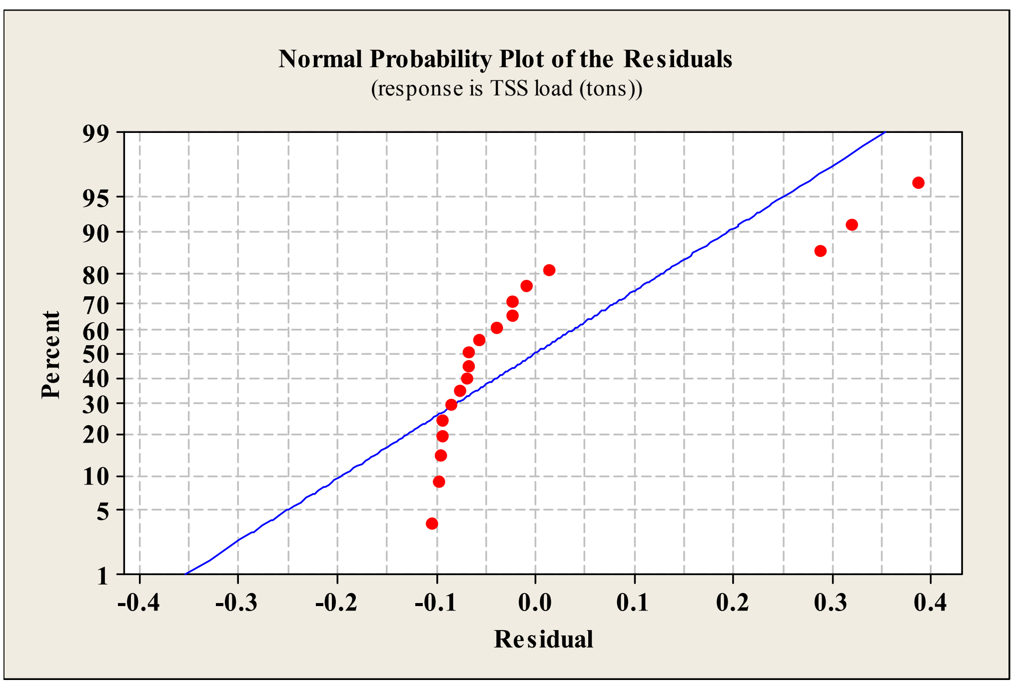
Río Jauca sub watershed





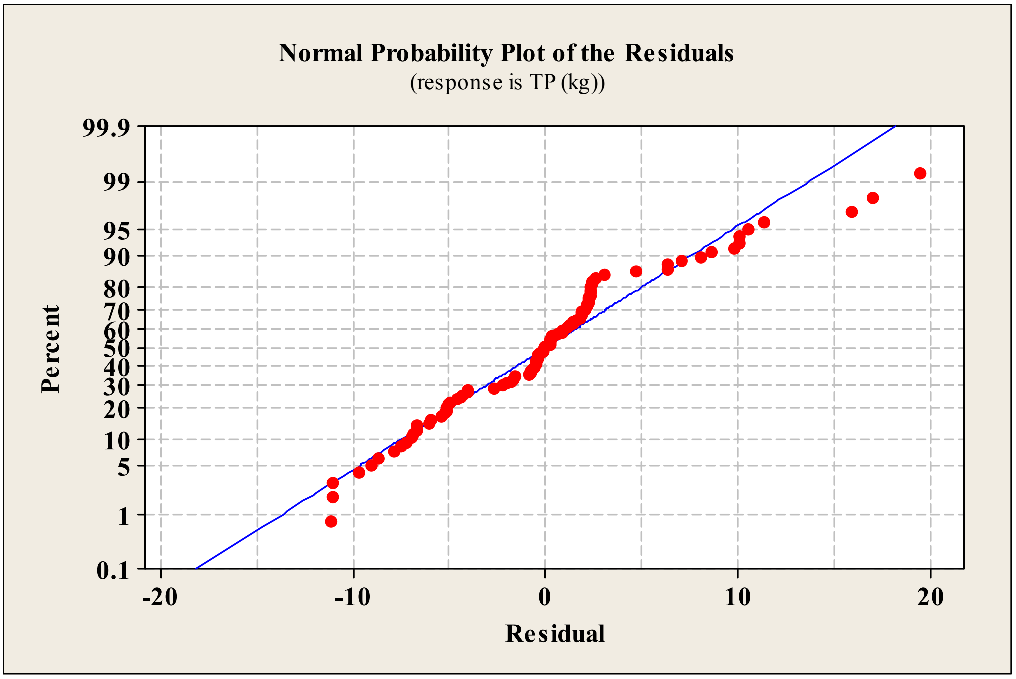
Appendix J. (Continued)

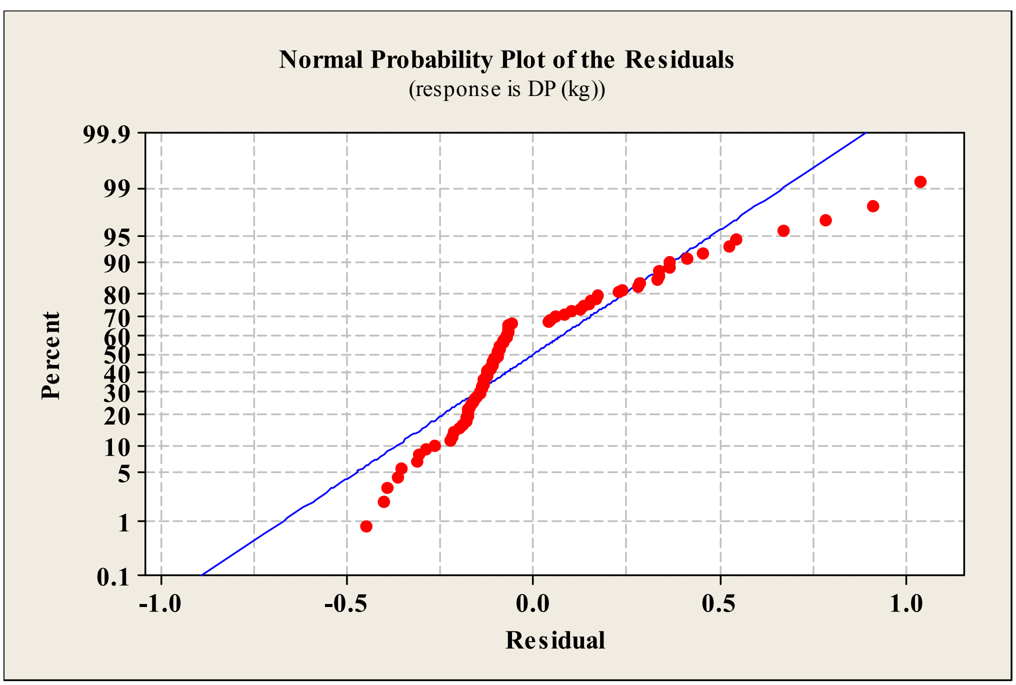




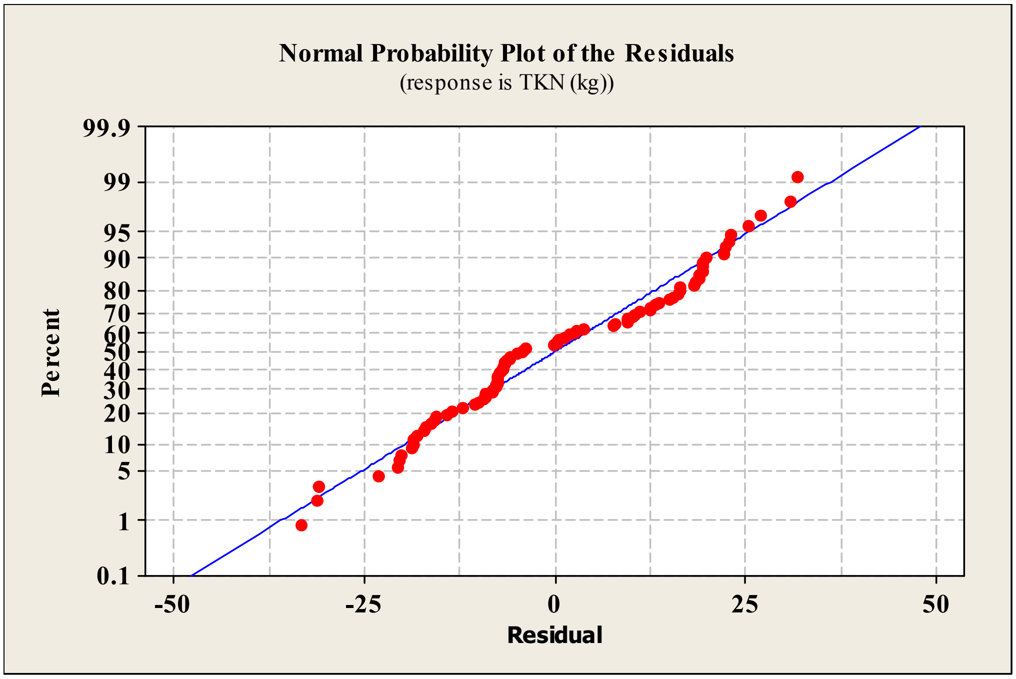
Appendix K. Storm (TP, DP, TKN, TSS) load versus flow regressions for Río Limón, Río Grande de Arecibo, Río Caonillas and Río Jauca sub watersheds.

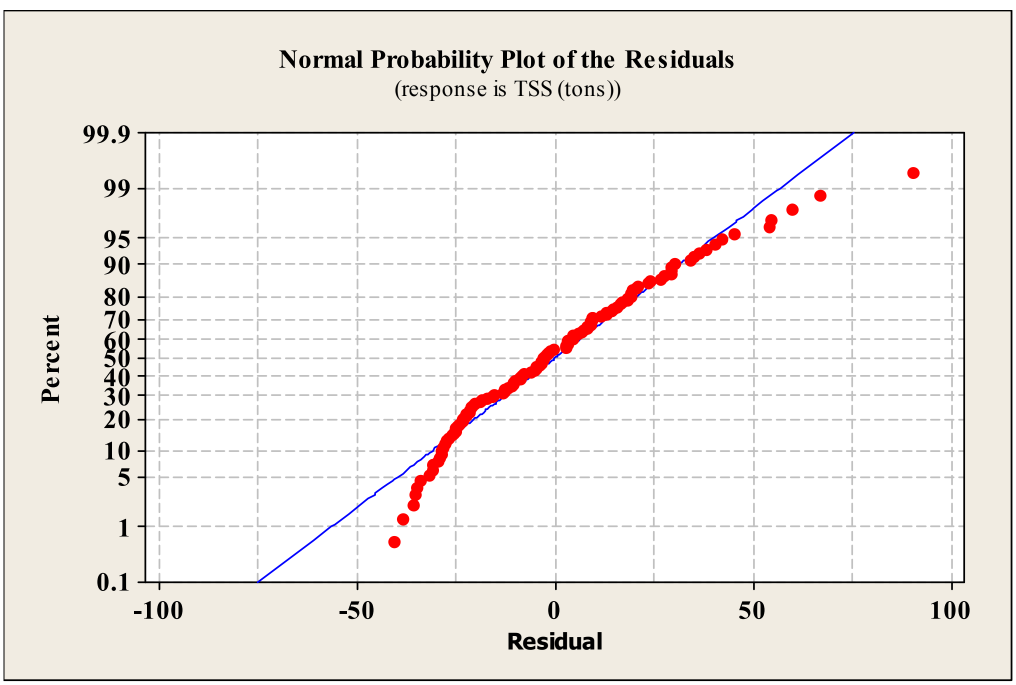
Río Limón sub watershed





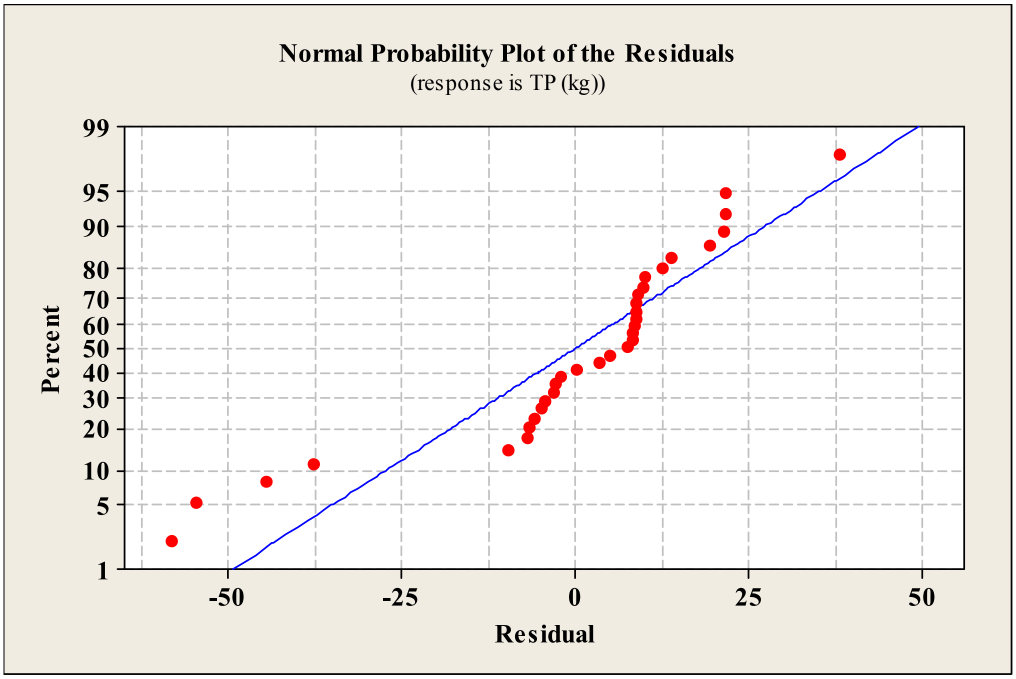
Appendix K. (Continued)

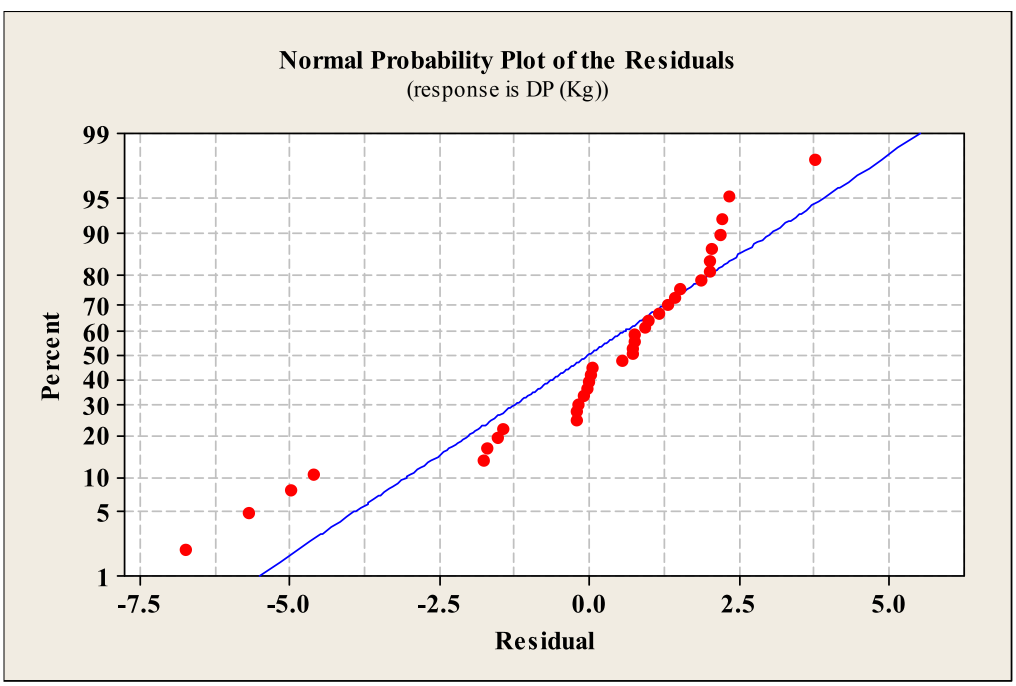




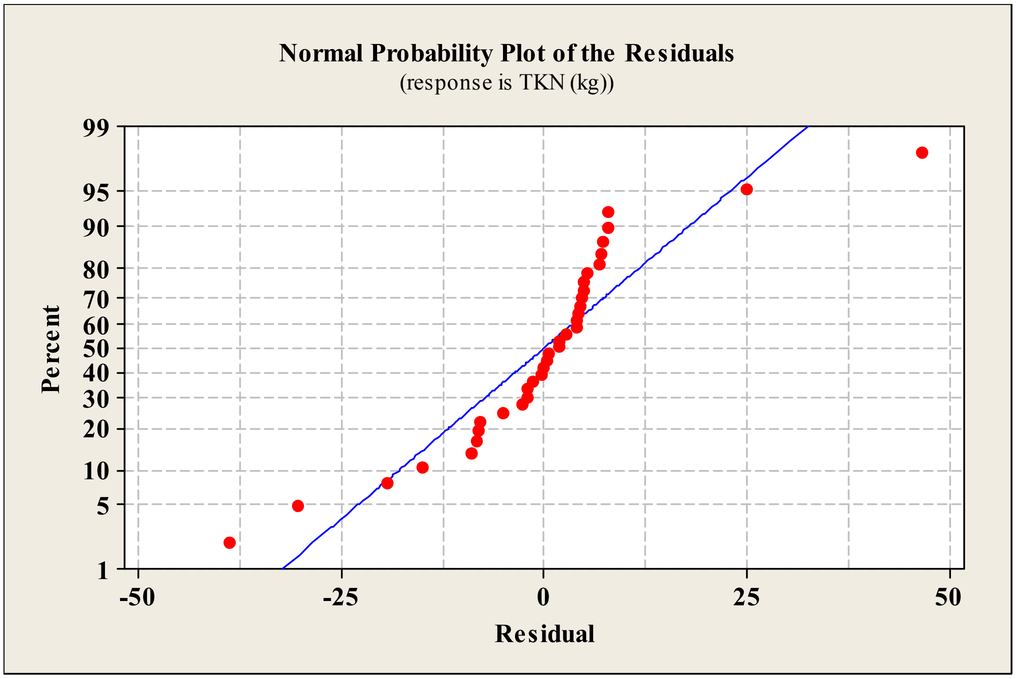
Appendix K. (Continued)

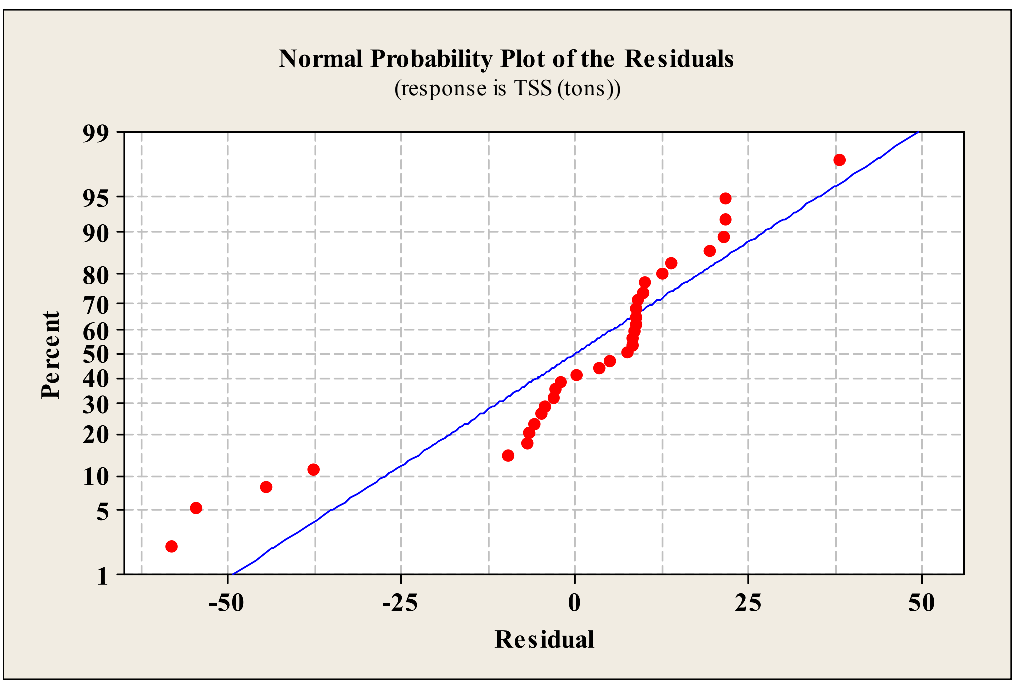
Río Grande de Arecibo sub watershed





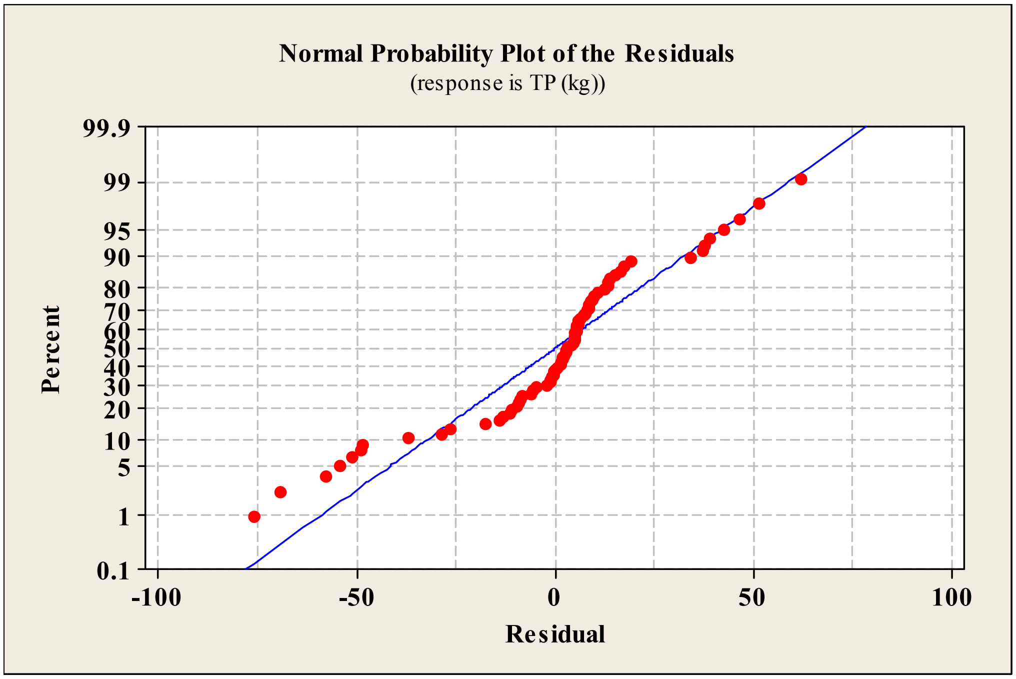
Appendix K. (Continued)

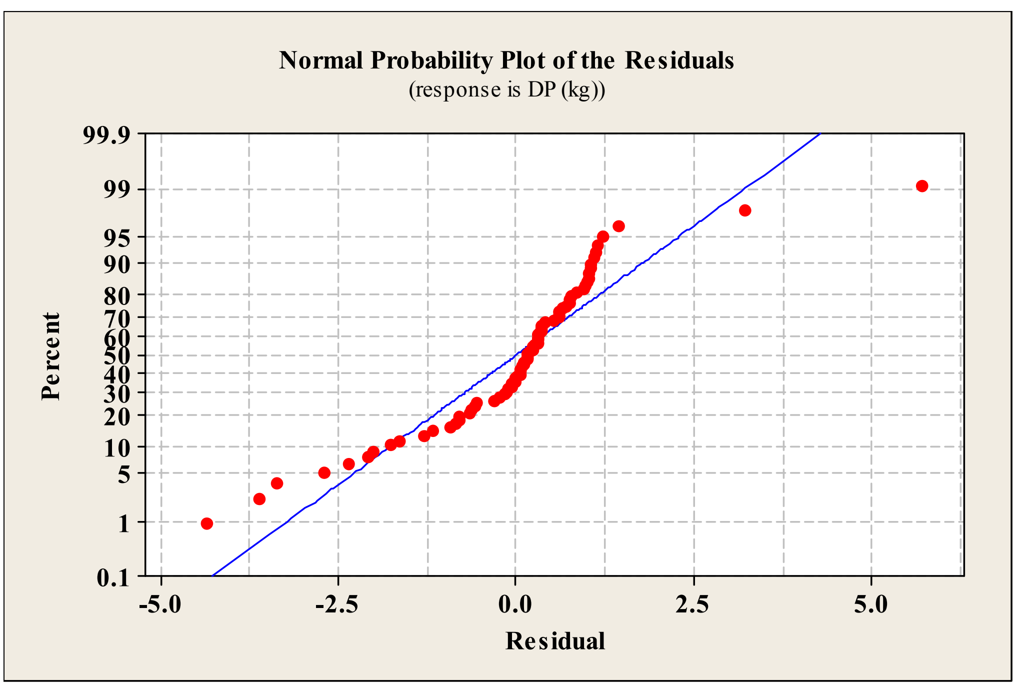




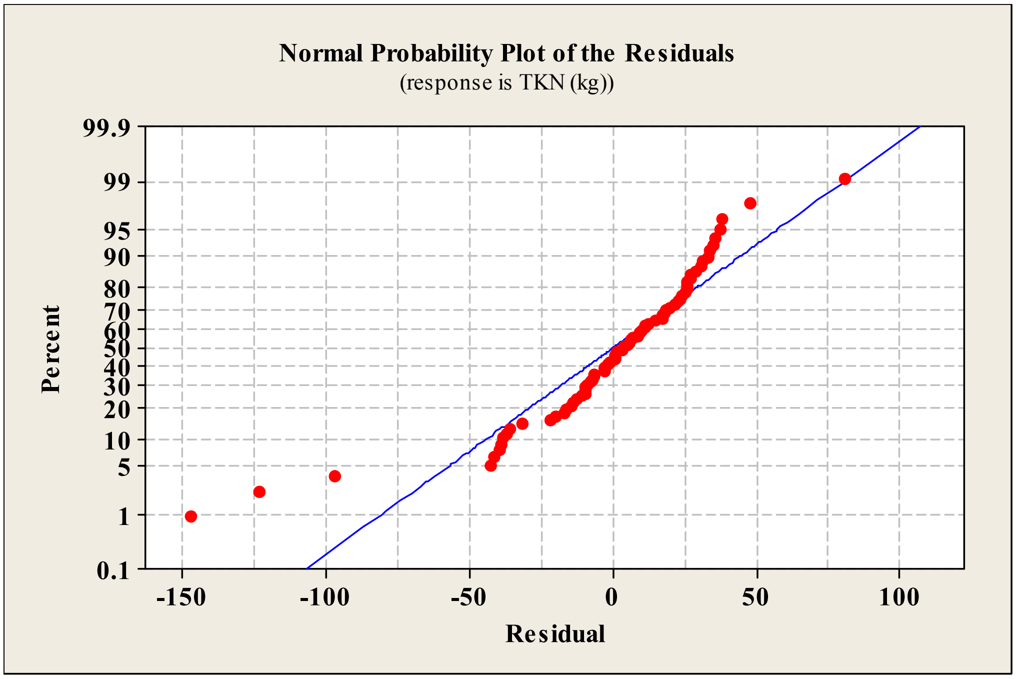
Appendix K. (Continued)

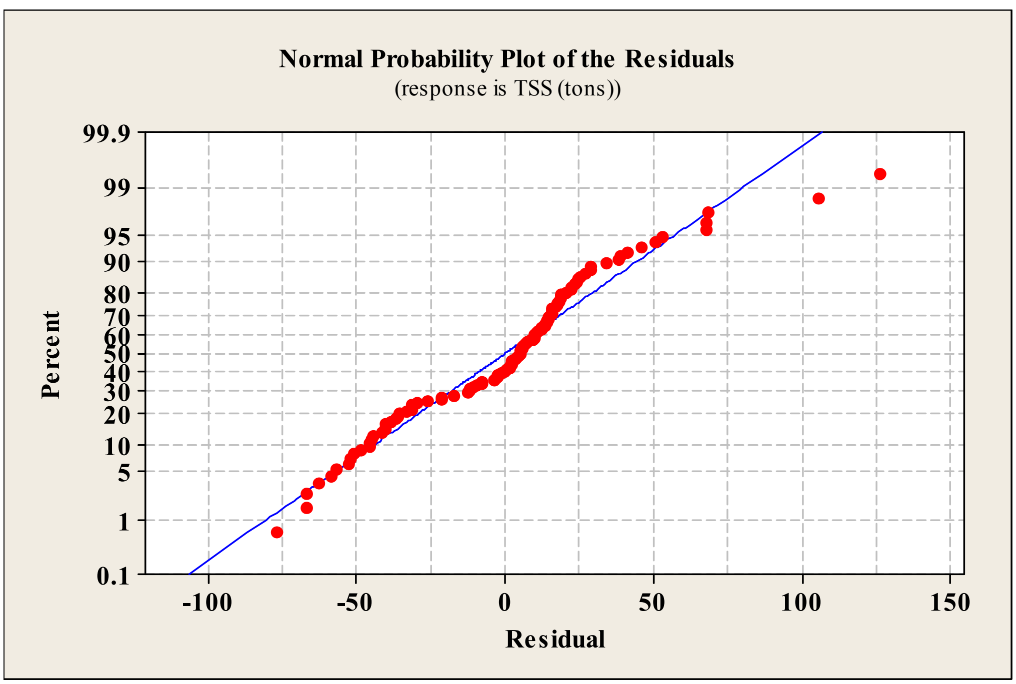
Río Caonillas sub watershed





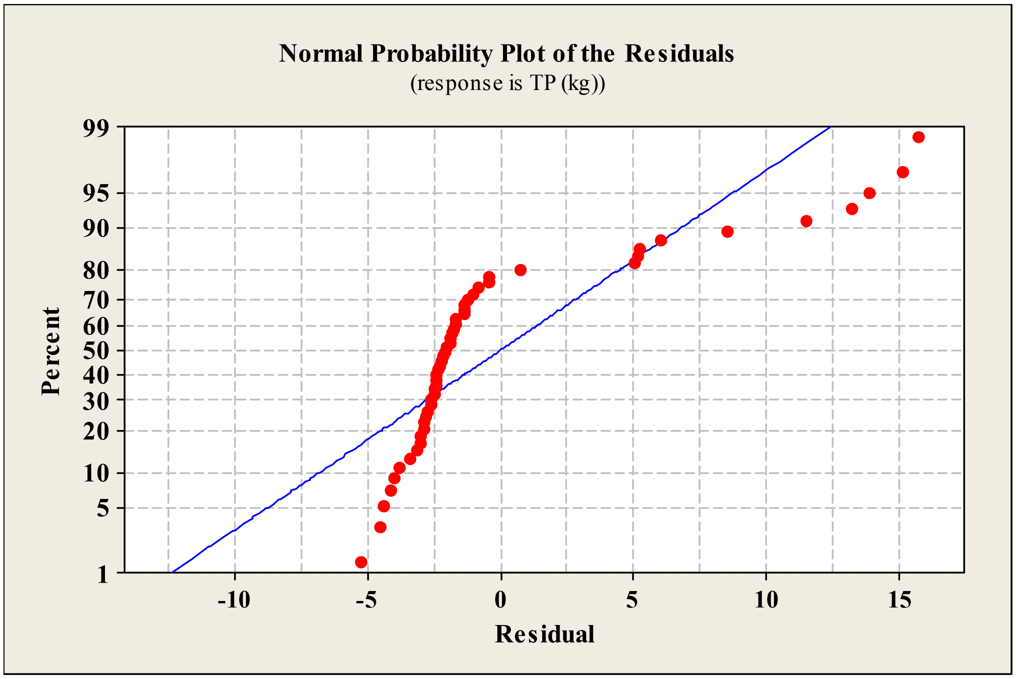
Appendix K. (Continued)

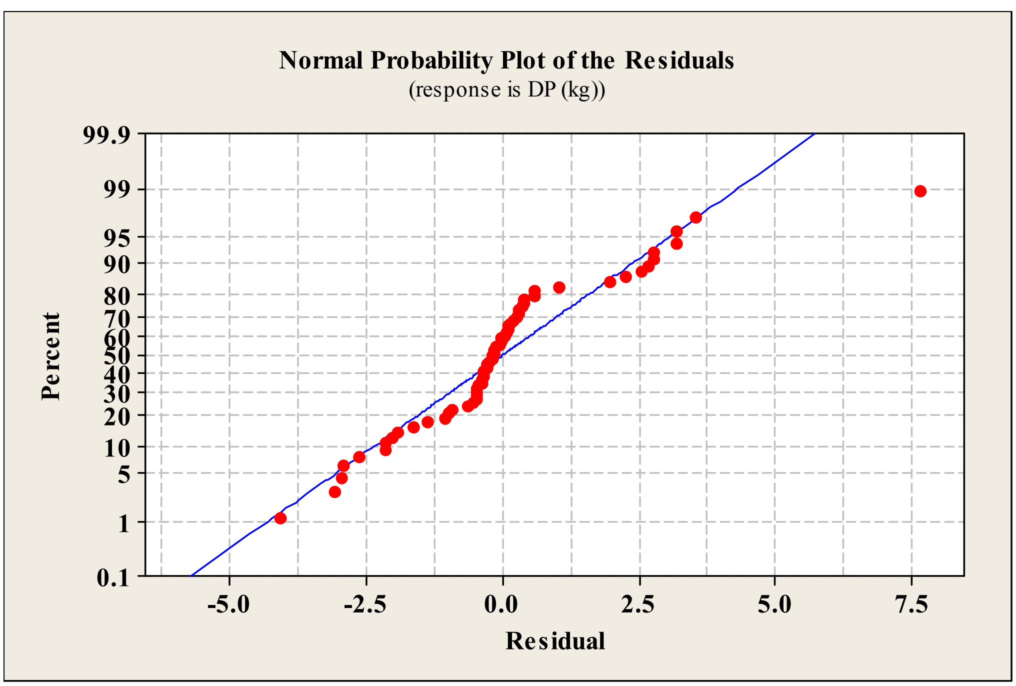




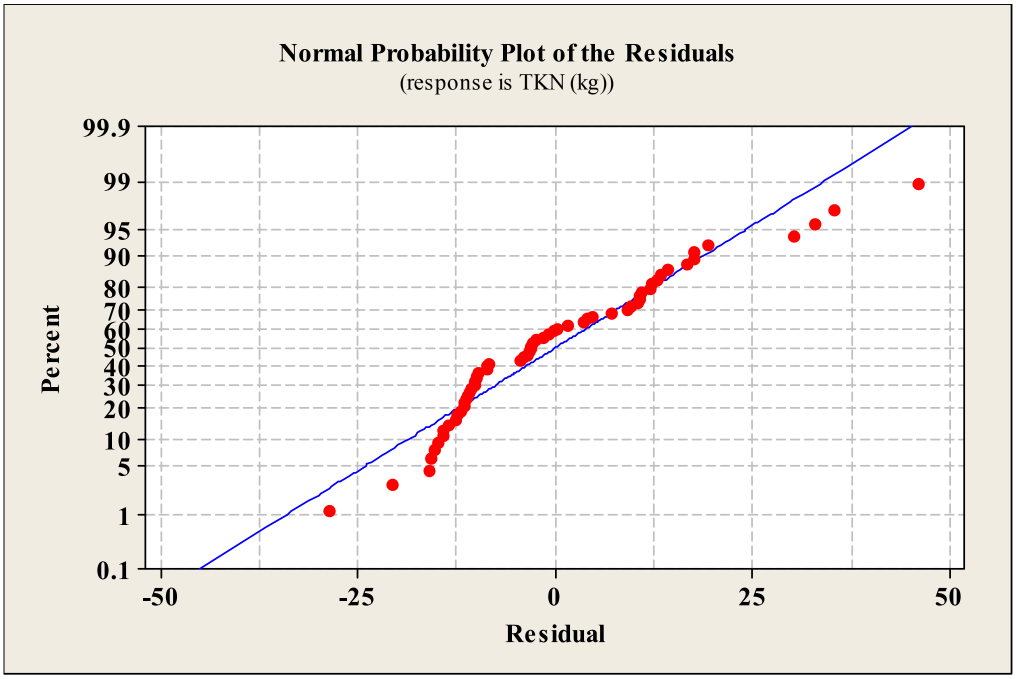
Appendix K. (Continued)

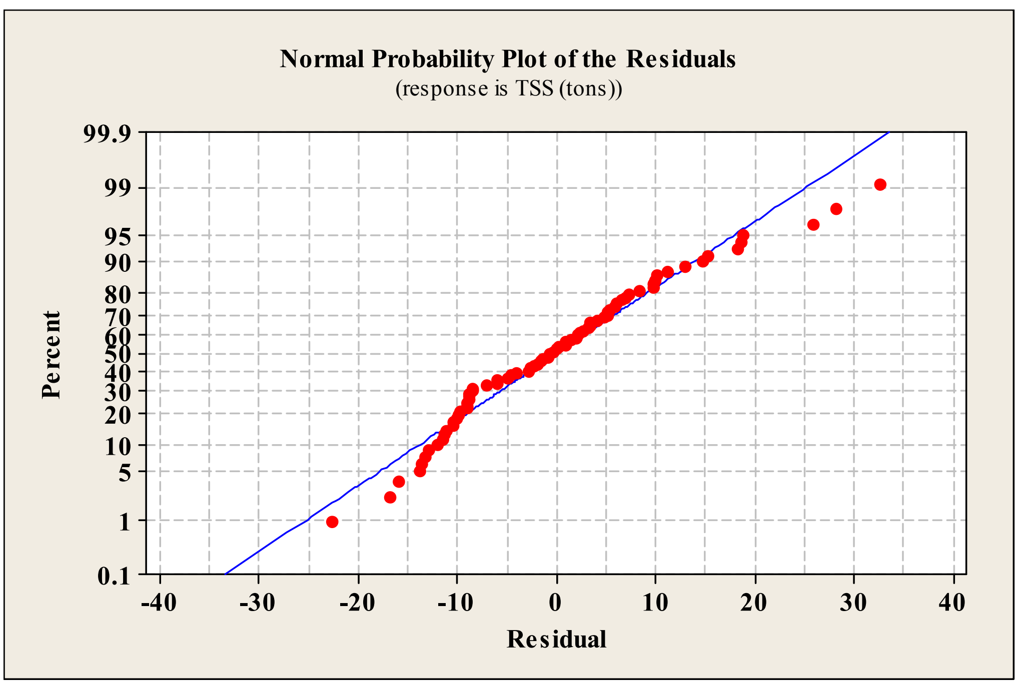
Río Jauca sub watershed



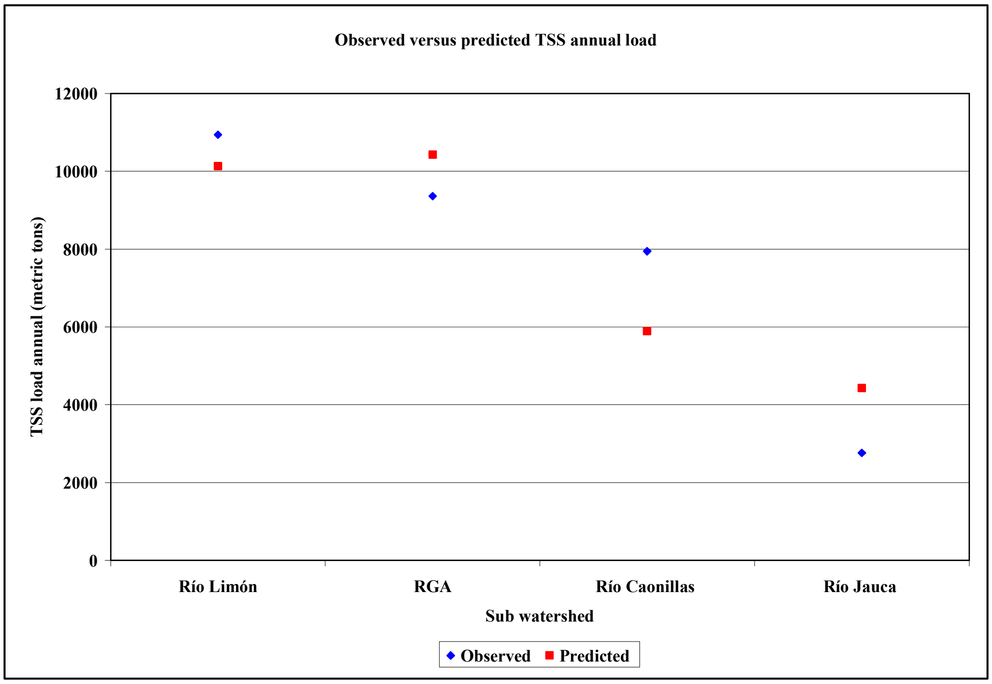


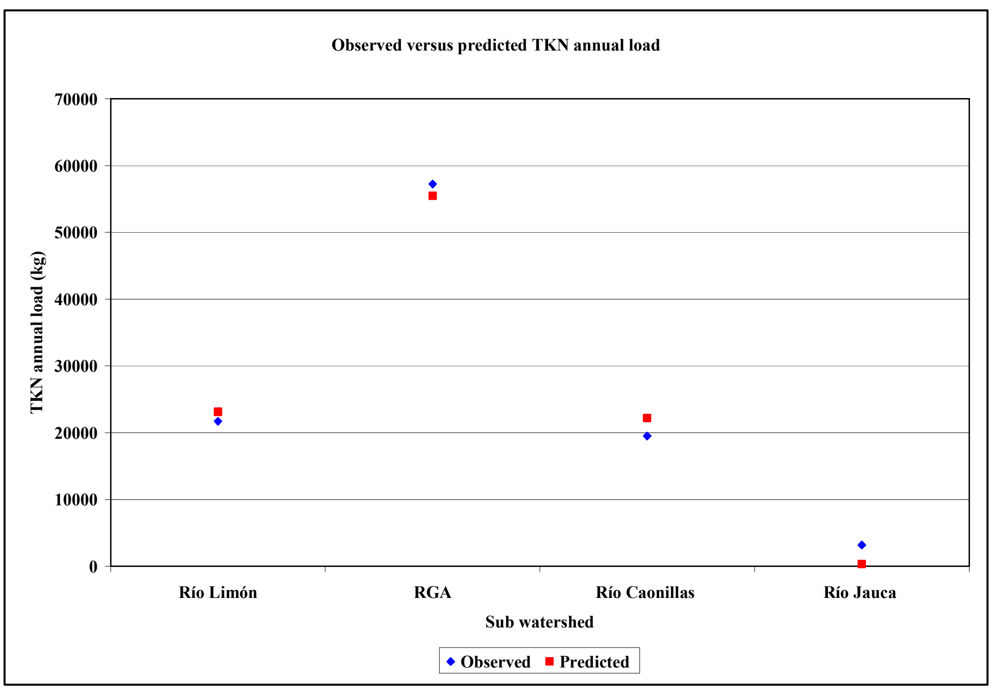
Appendix K. (Continued)



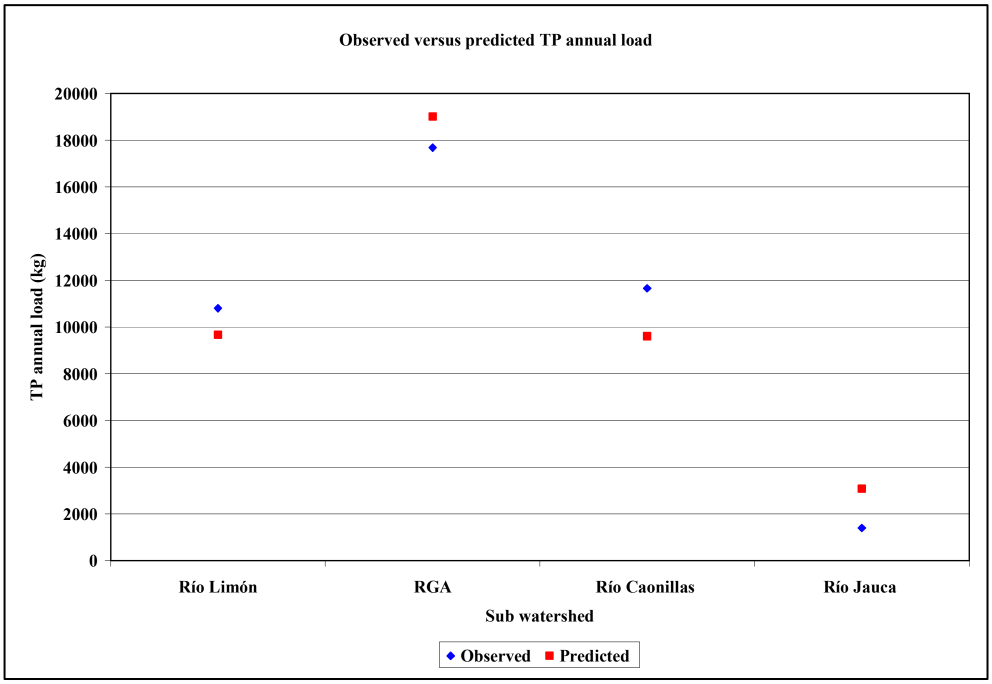


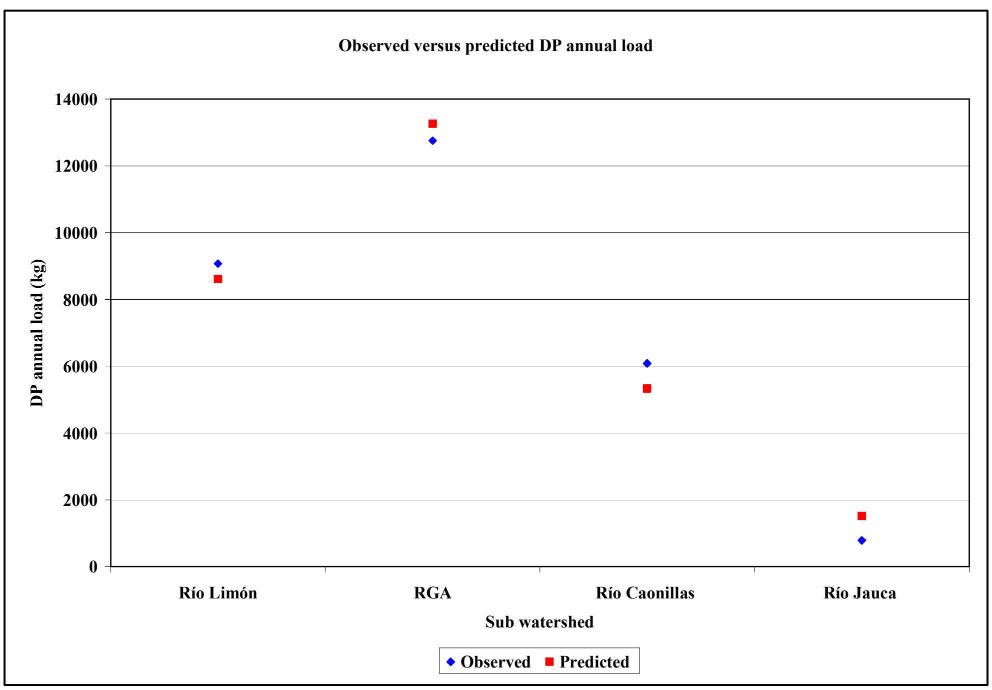
Appendix L. Observed versus predicted annual load of TSS, TKN, TP and DP





Appendix L. (Continued)





Appendix M. Statistical analysis

PLS Regression: TSS annual load (metric tons) versus drainage area, Maximum length of the channel, average land slope, average mean sea level elevation, mean annual precipitation, mean annual flow.

Number of components specified: 2

Analysis of Variance for TSS Load (metric tons)

Source	DF	SS	MS	F	P
Regression	2	28208678	14104339	1.49	0.502
Residual Error	1	9491092	9491092		
Total	3	37699769			

Model Selection and Validation for TSS Load (metric tons)

Components	X Variance	Error SS	R-Sq
1	0.714175	10572731	0.719554
2	0.978674	9491092	0.748245

Regression Coefficients

	TSS Load (metric tons)	TSS Load (metric tons) standardized
Constant	21359.9	0.000000
Drainage area	5.3	0.103105
Maximum width of the channel	20.9	0.055086
Average land slope	-31699.5	-0.154883
Mean Elev. above mean sea level	-9.8	-0.381441
Mean annual precipitation	0.7	0.105821
Mean annual flow	467.6	0.223212

Appendix M. (Continued)

Fits and Residuals for TSS Load (metric tons)

Row	TSS Load (metric tons)	Fits	Res	SRes
1	10942.3	10188.2	754.04	1
2	9364.1	10542.1	-1177.97	-1
3	7946.9	5805.5	2141.35	1
4	2763.5	4480.9	-1717.41	-1

Leverages and Distances

Row	Leverage	Distance X	Distance Y
1	0.940094	0.64558	2.81159
2	0.853797	1.03194	2.17975
3	0.516874	0.51413	1.92868
4	0.689234	1.04521	3.87619

X Scores

Row	Comp1	Comp2
1	1.12245	0.907733
2	2.24299	-0.541744
3	-1.03246	-0.505648
4	-2.33297	0.139659

Y Scores

Row	Comp1	Comp2
1	2.18991	1.76333
2	1.10588	-1.87839
3	0.13234	1.92414
4	-3.42813	-1.80908

Appendix M. (Continued)

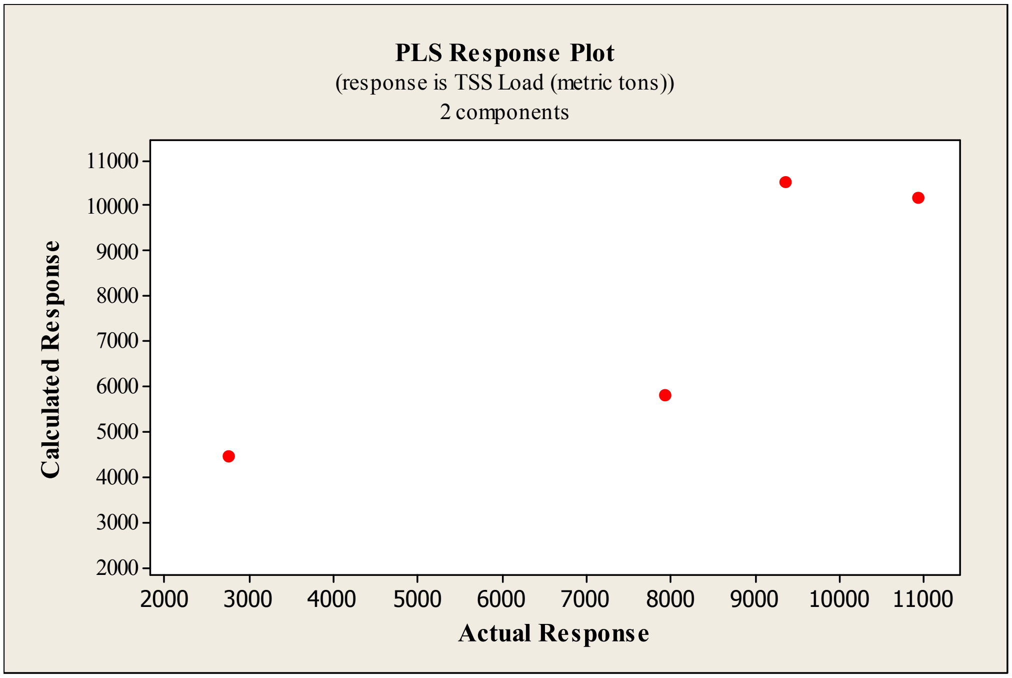
X Loadings

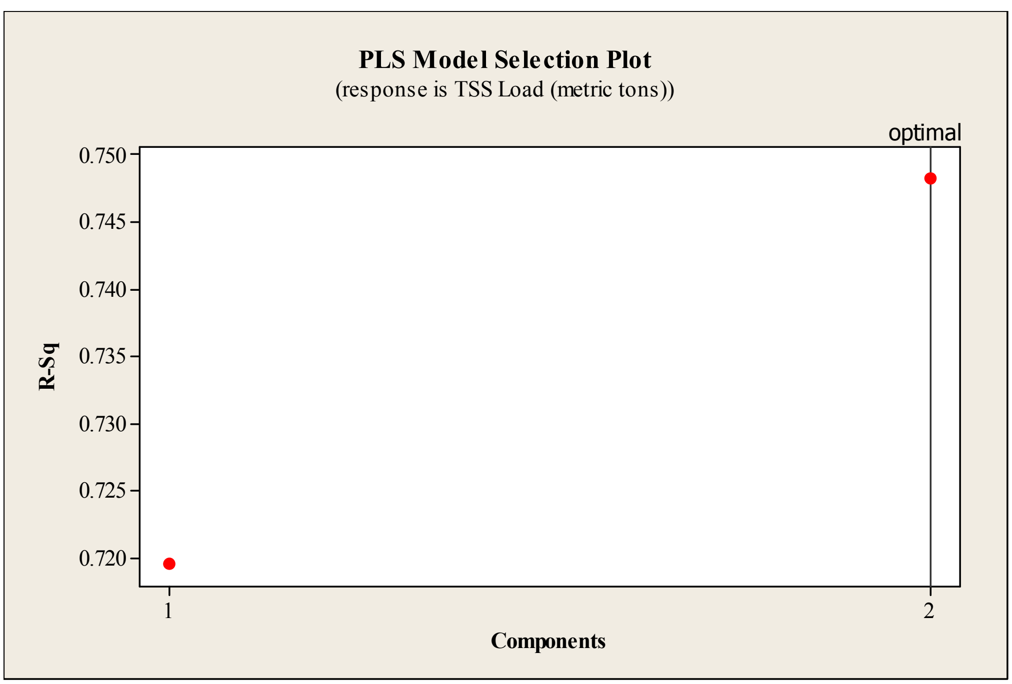
	Comp1	Comp2
Drainage area	0.431007	-0.65702
Maximum width of the channel	0.478945	-0.17530
Average land slope	-0.455412	-0.45518
Mean Elev. above mean sea level	-0.436766	-0.63269
Mean annual precipitation	0.056452	1.40843
Mean annual flow	0.433396	-0.60422

Y Loadings

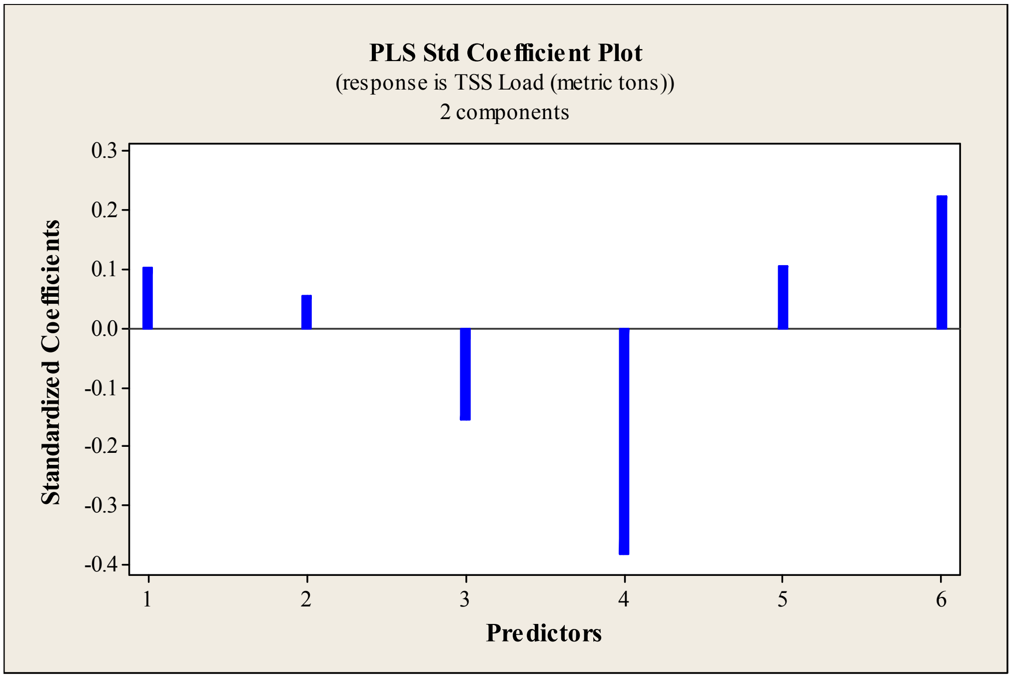
	Comp1	Comp2
TSS Load (metric tons)	0.410671	0.248606

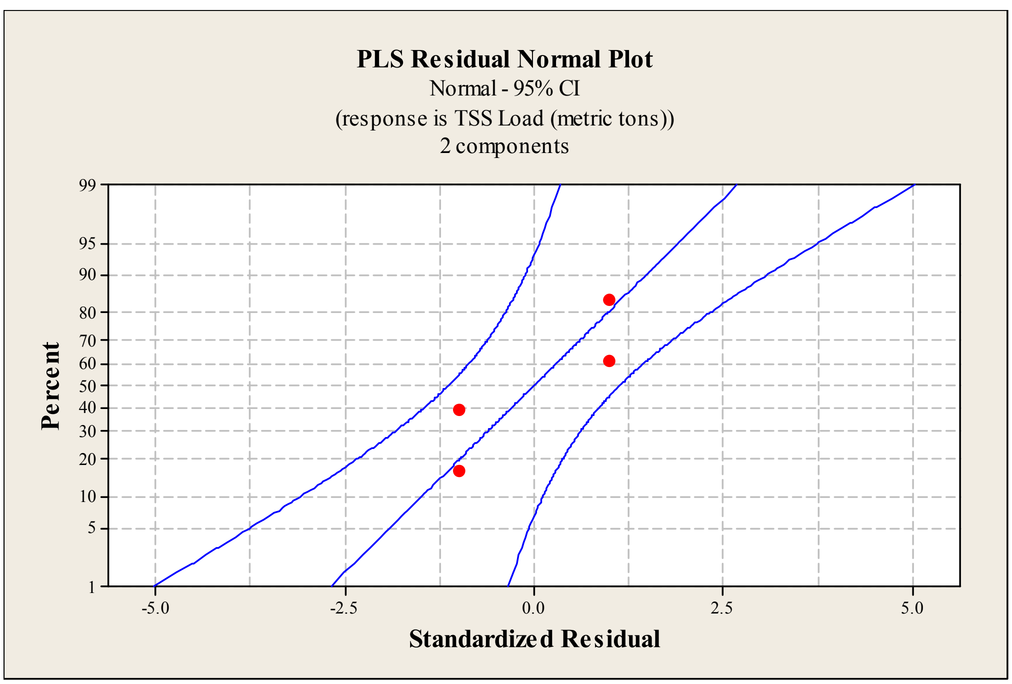
Appendix M. (Continued)



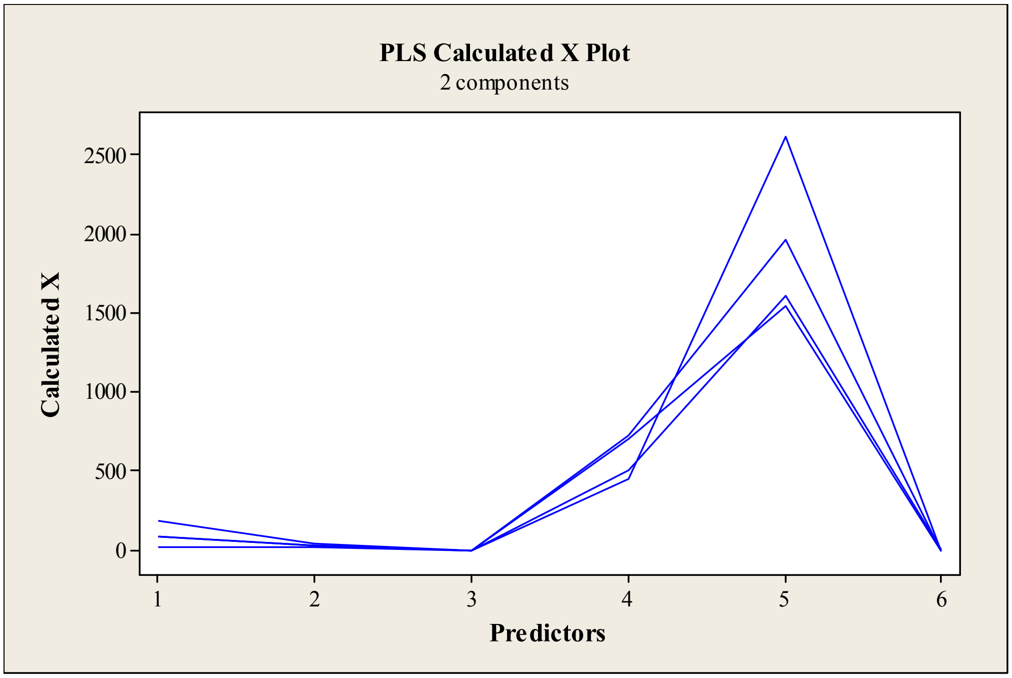


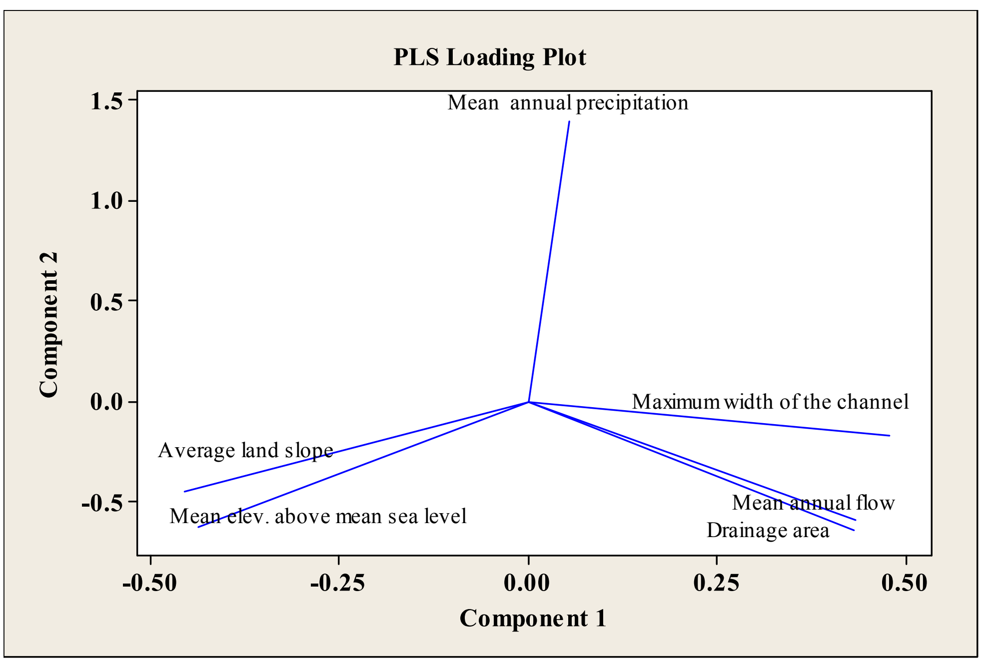
Appendix M. (Continued)





Appendix M. (Continued)





Appendix M. (Continued)

PLS Regression: TKN annual load (kg) versus drainage area, Maximum length of the channel, average land slope, average mean sea level elevation, mean annual precipitation, mean annual flow.

Number of components specified: 2

Analysis of Variance for TKN Load (kg)

Source	DF	SS	MS	F	P
Regression	2	1484513819	742256909	10.56	0.213
Residual Error	1	70299540	70299540		
Total	3	1554813359			

Model Selection and Validation for TKN Load (kg)

Components	X Variance	Error SS	R-Sq
1	0.703635	151401705	0.902624
2	0.994013	70299540	0.954786

Regression Coefficients

	TKN Load (kg)	TKN Load (kg) standardized
Constant	71559	0.000000
Drainage area	95	0.289364
Maximum width of the channel	590	0.241750
Average land slope	-161694	-0.123020
Mean Elev. above mean sea level	-10	-0.063646
Mean annual precipitation	-9	-0.203040
Mean annual flow	3632	0.269930

Appendix M. (Continued)

Fits and Residuals for TKN Load (kg)

Row	TKN Load (kg)	Fits	Res	SRes
1	21718.5	25136.0	-3417.47	-1
2	57235.7	53284.7	3951.01	1
3	19514.5	24411.0	-4896.44	-1
4	3193.9	-1169.0	4362.89	1

Leverages and Distances

Row	Leverage	Distance X	Distance Y
1	0.833867	0.80126	2.57039
2	0.777943	1.10695	3.35579
3	0.658958	0.68120	0.57717
4	0.729233	1.08122	2.25495

X Scores

Row	Comp1	Comp2
1	0.60327	-1.68706
2	2.41672	0.53493
3	-0.61442	1.39380
4	-2.40558	-0.24167

Y Scores

Row	Comp1	Comp2
1	-0.34708	-2.54685
2	2.98725	1.52895
3	-0.55399	0.16192
4	-2.08617	0.85597

Appendix M. (Continued)

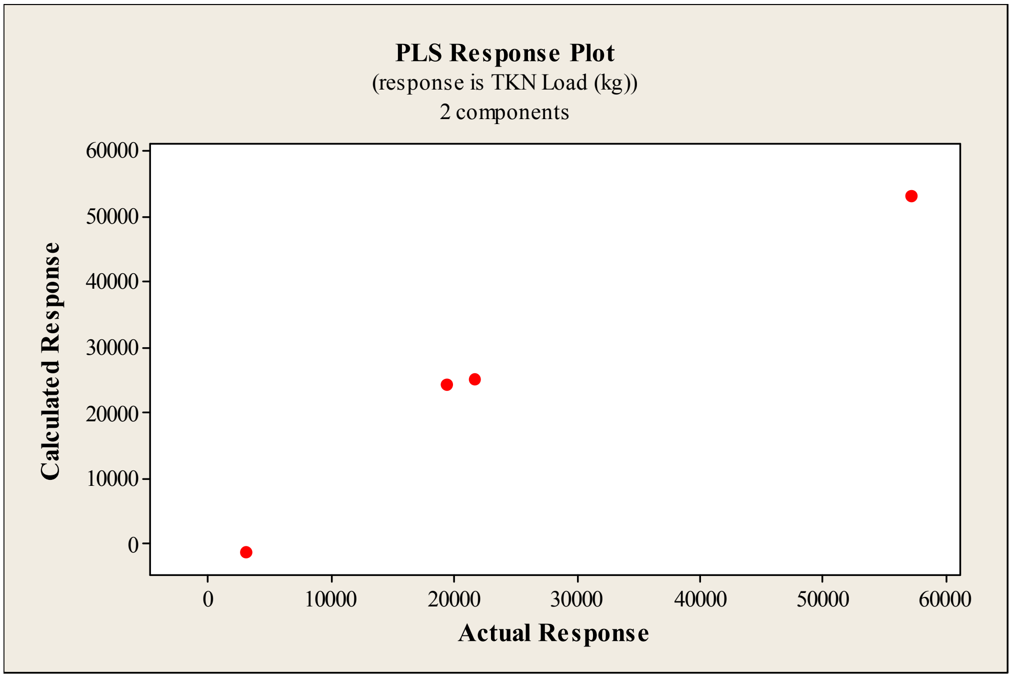
X Loadings

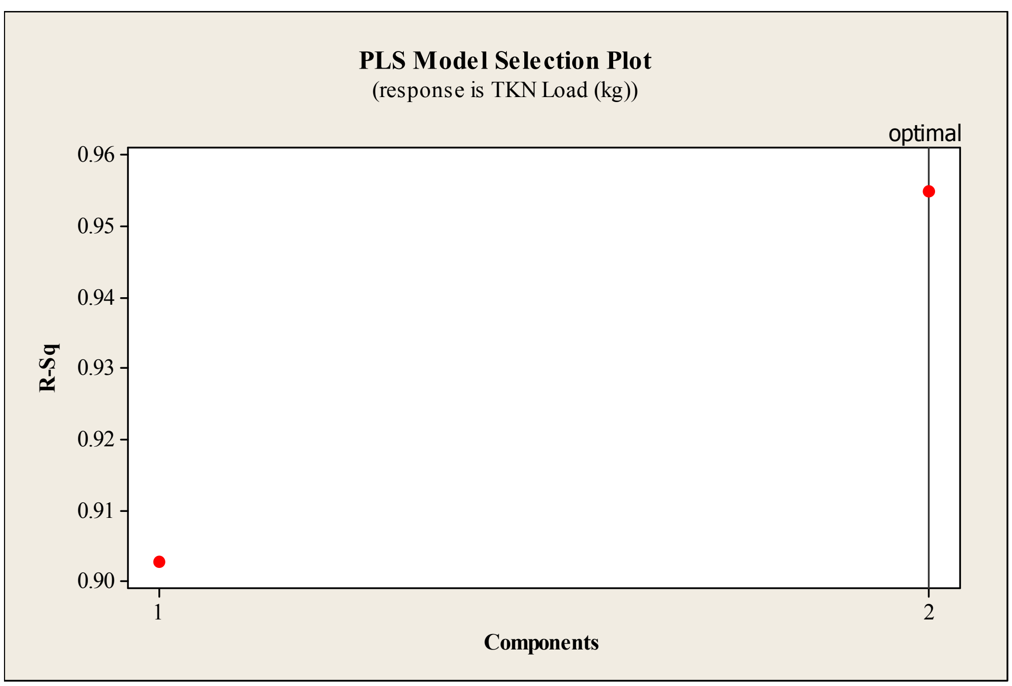
	Comp1	Comp2
Drainage area	0.473570	0.209627
Maximum width of the channel	0.487536	-0.072736
Average land slope	-0.422902	0.388738
Mean Elev. above mean sea level	-0.395967	0.446280
Mean annual precipitation	-0.038197	-0.761542
Mean annual flow	0.474268	0.196812

Y Loadings

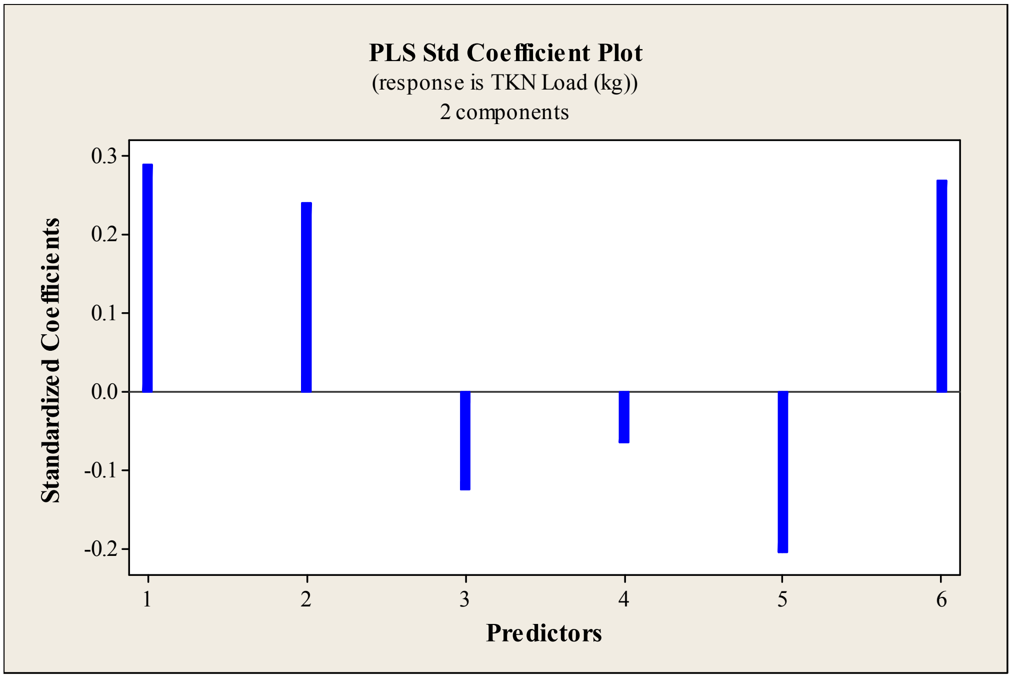
	Comp1	Comp2
TKN Load (kg)	0.467898	0.174596

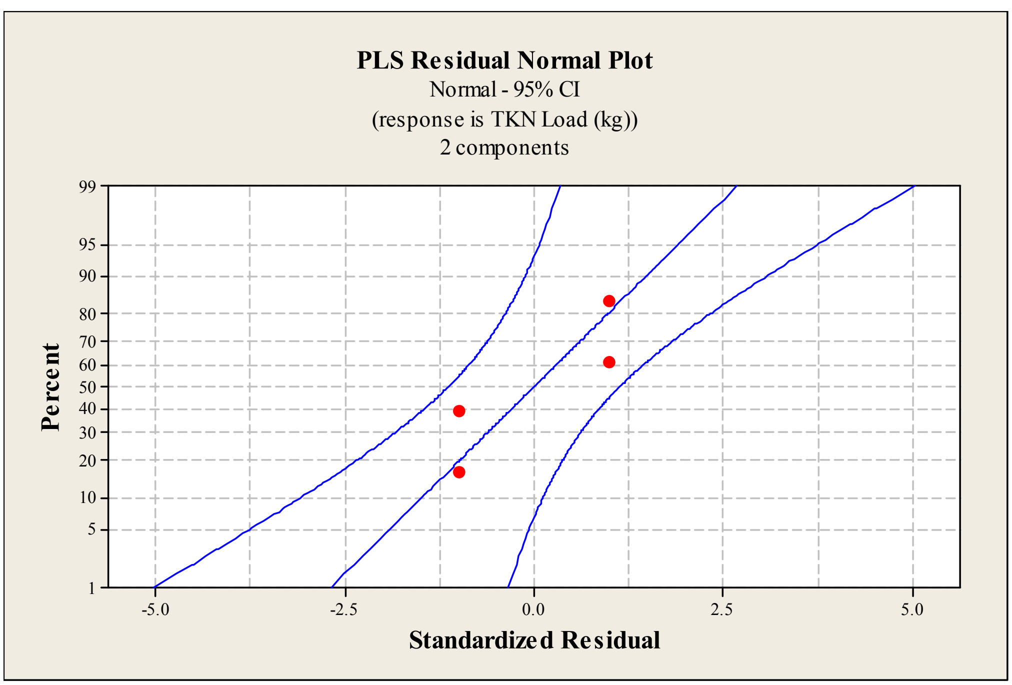
Appendix M. (Continued)



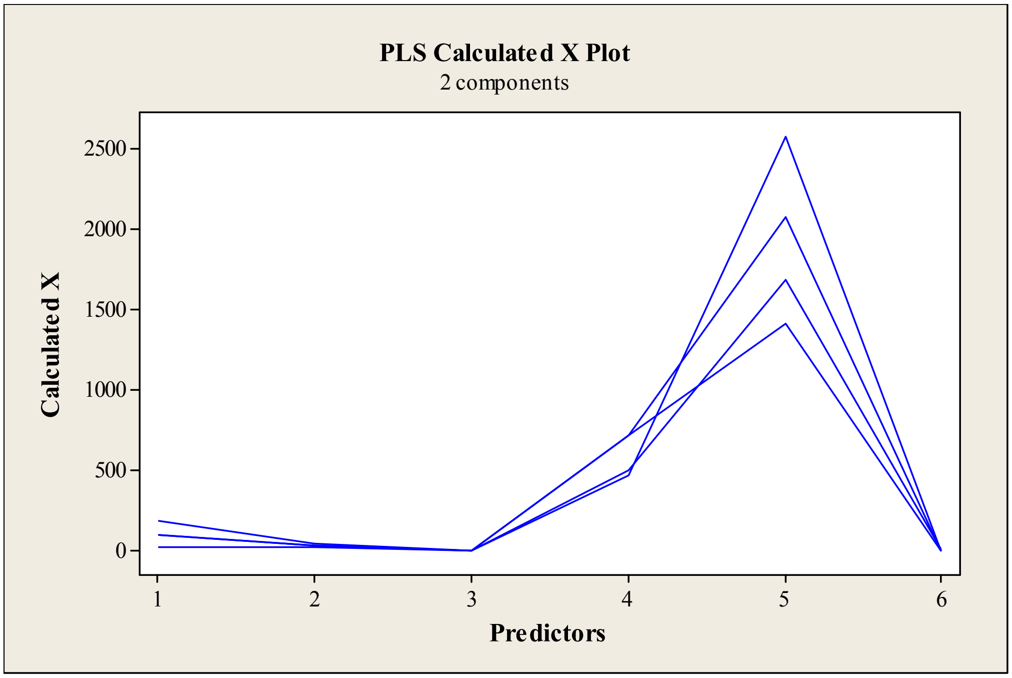


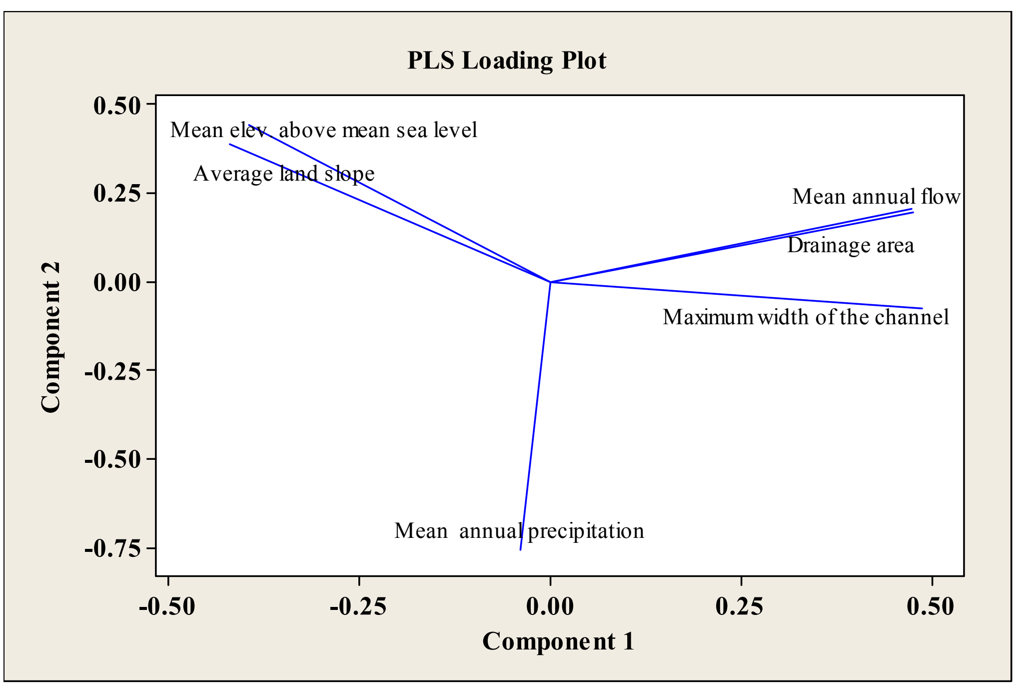
Appendix M. (Continued)





Appendix M. (Continued)





Appendix M. (Continued)

PLS Regression: TP annual load (kg) versus drainage area, Maximum length of the channel, average land slope, average mean sea level elevation, mean annual precipitation, mean annual flow.

Number of components specified: 2

Analysis of Variance for TP Load (kg)

Source	DF	SS	MS	F	P
Regression	2	131672778	65836389	16.41	0.172
Residual Error	1	4012424	4012424		
Total	3	135685201			

Model Selection and Validation for TP Load (kg)

Components	X Variance	Error SS	R-Sq
1	0.700263	12829024	0.905450
2	0.994067	4012424	0.970428

Regression Coefficients

	TP Load (kg)	TP Load (kg) standardized
Constant	21649.7	0.000000
Drainage area	28.5	0.291947
Maximum width of the channel	148.5	0.206055
Average land slope	-35679.7	-0.091892
Mean Elev. above mean sea level	-4.3	-0.089262
Mean annual precipitation	-3.2	-0.237857
Mean annual flow	1203.4	0.302782

Appendix M. (Continued)

Fits and Residuals for TP Load (kg)

Row	TP Load (kg)	Fits	Res	SRes
1	10805.9	9939.7	866.20	1
2	17683.8	18647.9	-964.11	-1
3	11660.2	10532.4	1127.80	1
4	1406.7	2436.6	-1029.89	-1

Leverages and Distances

Row	Leverage	Distance X	Distance Y
1	0.813007	0.78997	1.02075
2	0.768341	1.09983	2.31799
3	0.682999	0.69911	2.36578
4	0.735653	1.08226	3.01965

X Scores

Row	Comp1	Comp2
1	0.54573	-1.68002
2	2.41462	0.46667
3	-0.55317	1.46210
4	-2.40718	-0.24875

Y Scores

Row	Comp1	Comp2
1	0.13147	-1.01225
2	2.30143	-0.27658
3	0.40100	2.33155
4	-2.83390	-1.04272

Appendix M. (Continued)

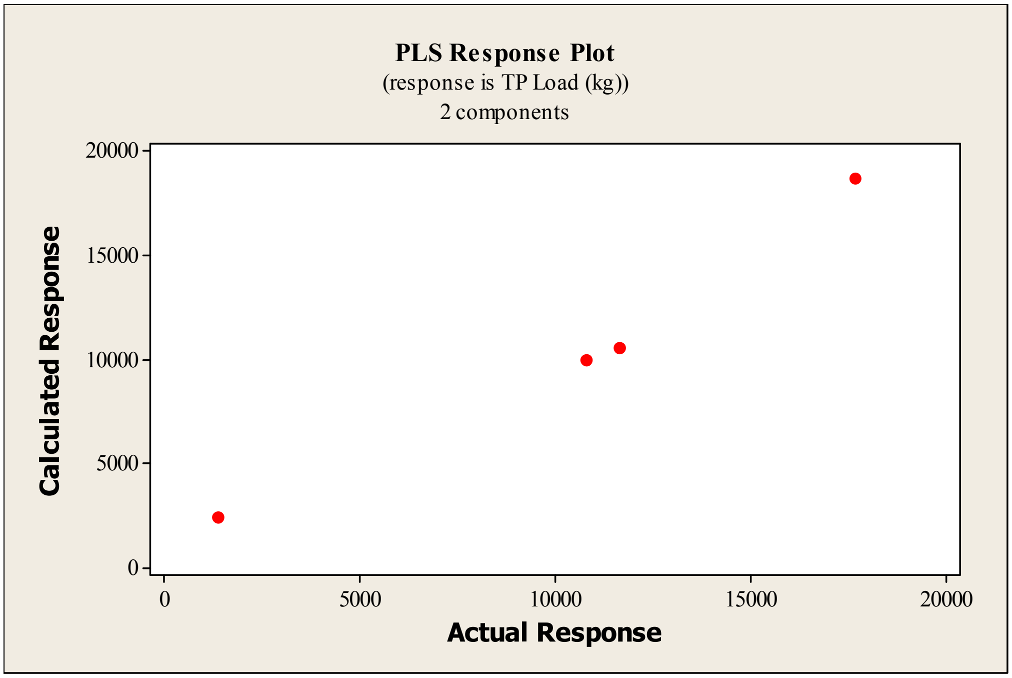
X Loadings

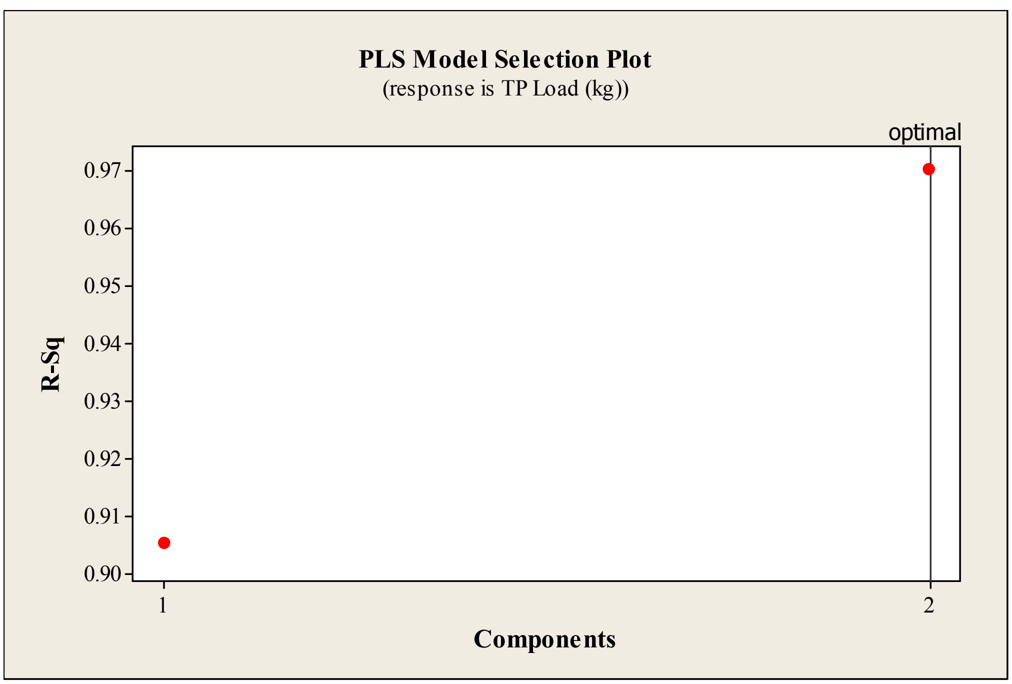
	Comp1	Comp2
Drainage area	0.479234	0.190196
Maximum width of the channel	0.488896	-0.091924
Average land slope	-0.419298	0.401074
Mean Elev. above mean sea level	-0.391716	0.452435
Mean annual precipitation	-0.049801	-0.752812
Mean annual flow	0.479930	0.179905

Y Loadings

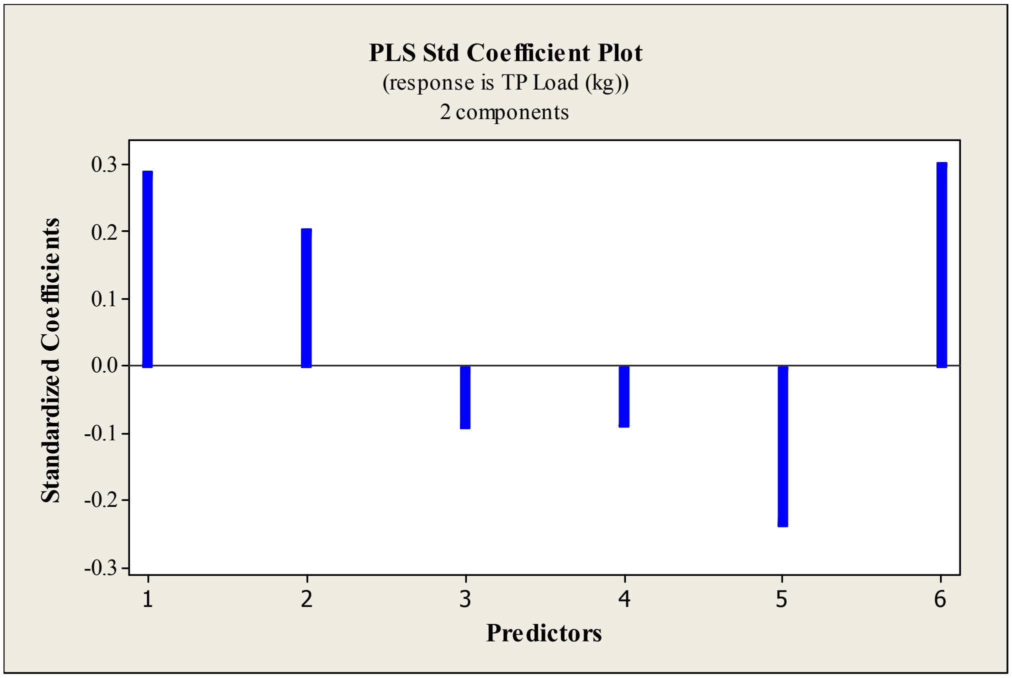
	Comp1	Comp2
TP Load (kg)	0.471306	0.192879

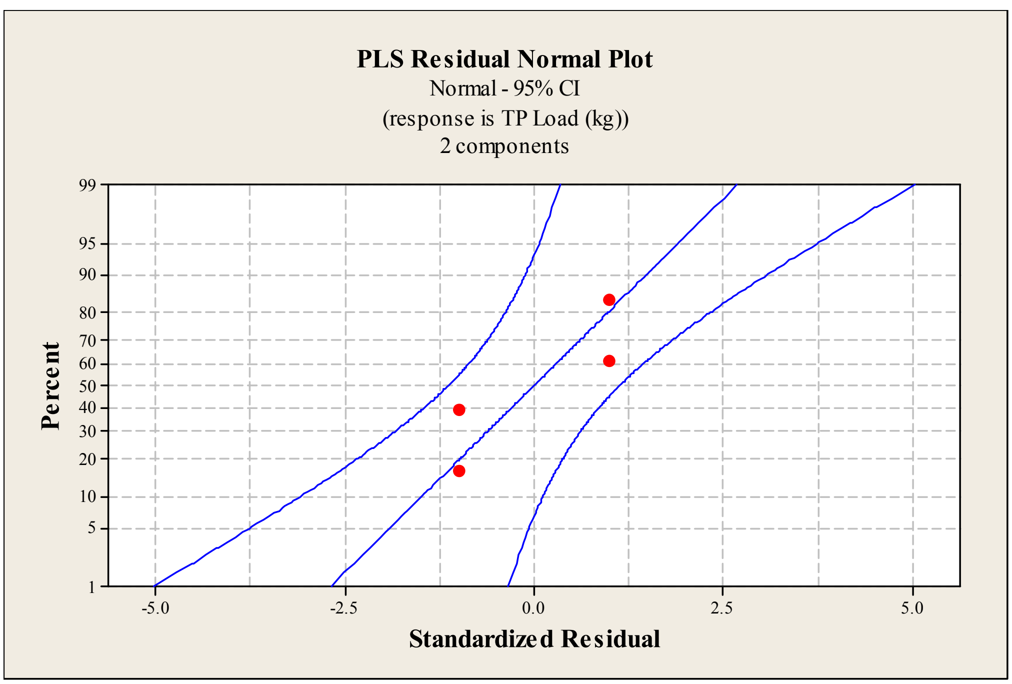
Appendix M. (Continued)



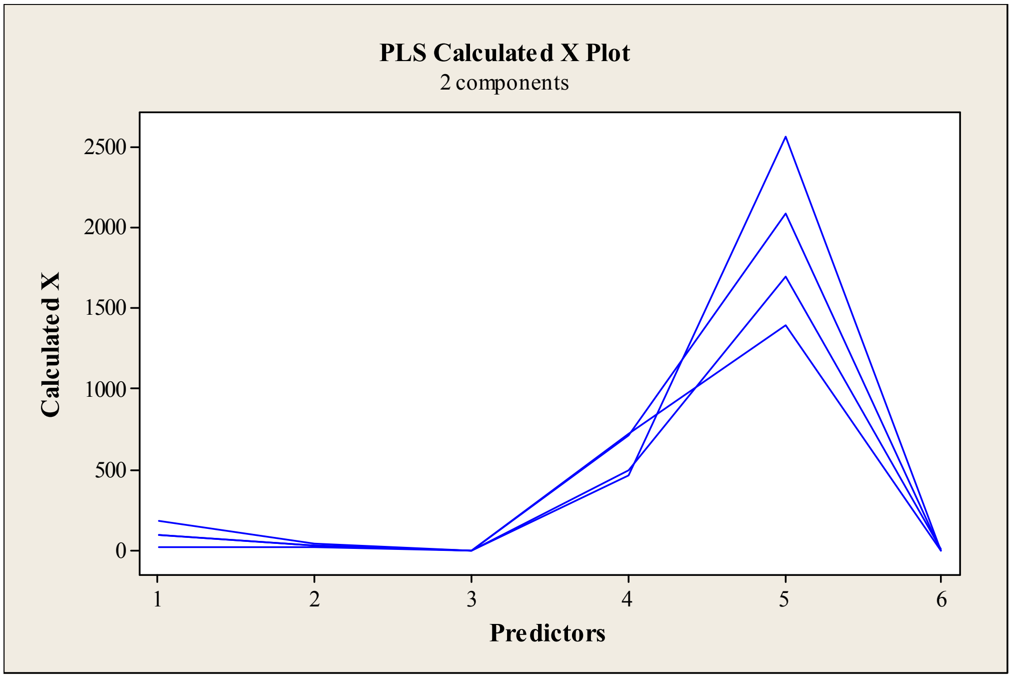


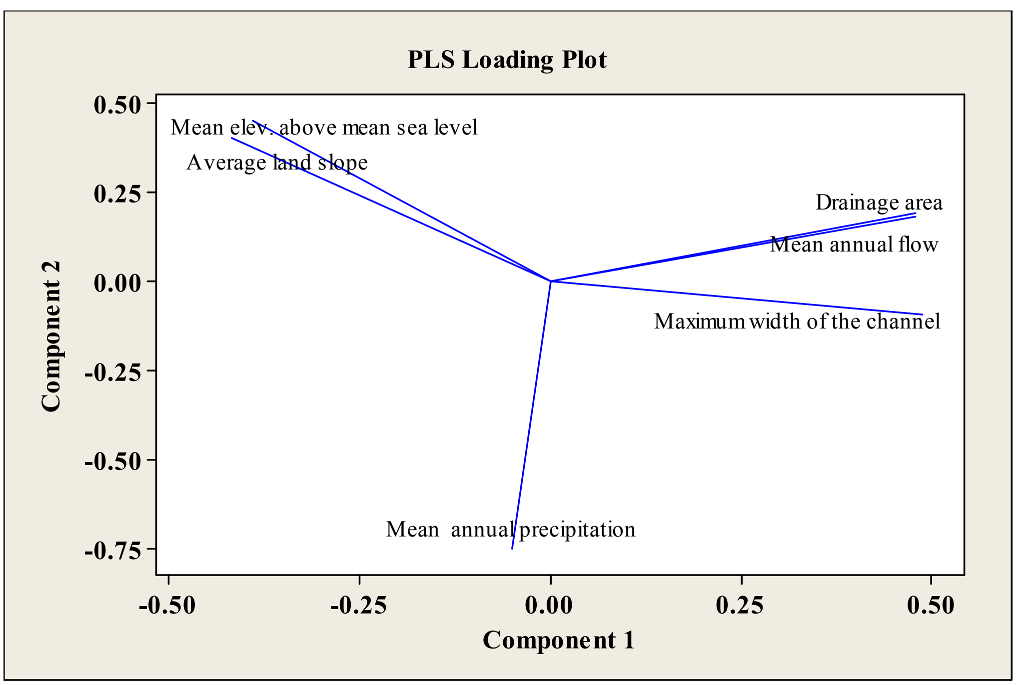
Appendix M. (Continued)





Appendix M. (Continued)





Appendix M. (Continued)

PLS Regression: DP annual load (kg) versus drainage area, Maximum length of the channel, average land slope, average mean sea level elevation, mean annual precipitation, mean annual flow.

Number of components specified: 2

Analysis of Variance for DP Load (kg)

Source	DF	SS	MS	F	P
Regression	2	76093500	38046750	60.19	0.091
Residual Error	1	632160	632160		
Total	3	76725660			

Model Selection and Validation for DP Load (kg)

Components	X Variance	Error SS	R-Sq
1	0.713154	1305481	0.982985
2	0.994001	632160	0.991761

Regression Coefficients

	DP Load (kg)	DP Load (kg) standardized
Constant	23636.3	0.000000
Drainage area	17.9	0.244841
Maximum width of the channel	122.0	0.225217
Average land slope	-51233.3	-0.175470
Mean Elev. above mean sea level	-6.3	-0.172493
Mean annual precipitation	-0.7	-0.073490
Mean annual flow	752.3	0.251706

Appendix M. (Continued)

Fits and Residuals for DP Load (kg)

Row	DP Load (kg)	Fits	Res	SRes
1	9074.8	8727.3	347.449	1
2	12751.7	13136.4	-384.719	-1
3	6084.9	5640.3	444.508	1
4	785.3	1192.5	-407.239	-1

Leverages and Distances

Row	Leverage	Distance X	Distance Y
1	0.809034	0.80525	1.00441
2	0.765869	1.09244	2.33365
3	0.687441	0.72111	2.62040
4	0.737656	1.08970	3.04920

X Scores

Row	Comp1	Comp2
1	0.87832	-1.57183
2	2.35957	0.63209
3	-0.84062	1.37600
4	-2.39727	-0.43626

Y Scores

Row	Comp1	Comp2
1	0.78276	-0.62939
2	2.29709	-0.41144
3	-0.44863	2.58171
4	-2.63123	-1.54087

Appendix M. (Continued)

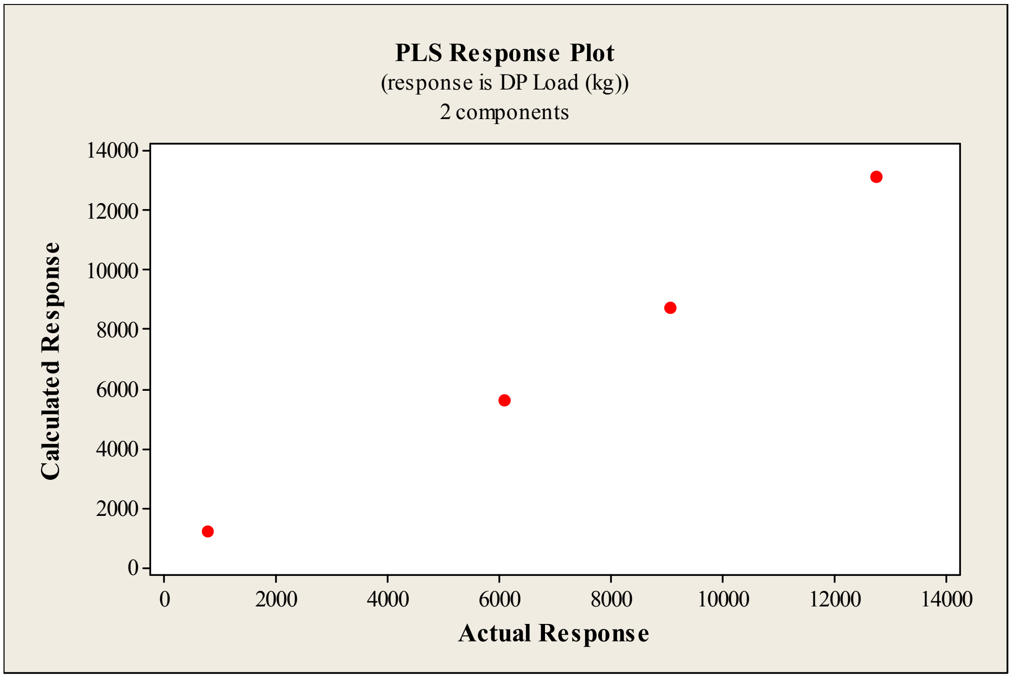
X Loadings

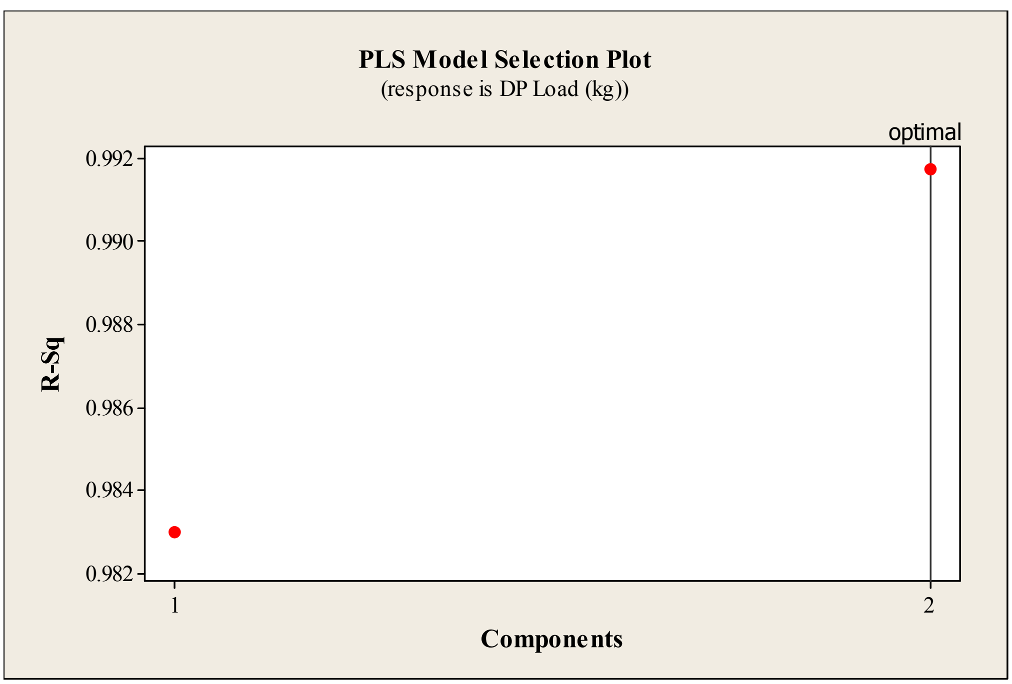
	Comp1	Comp2
Drainage area	0.450008	0.286605
Maximum width of the channel	0.481560	0.000116
Average land slope	-0.438395	0.328567
Mean Elev. above mean sea level	-0.415758	0.385372
Mean annual precipitation	0.010948	-0.777994
Mean annual flow	0.451537	0.276728

Y Loadings

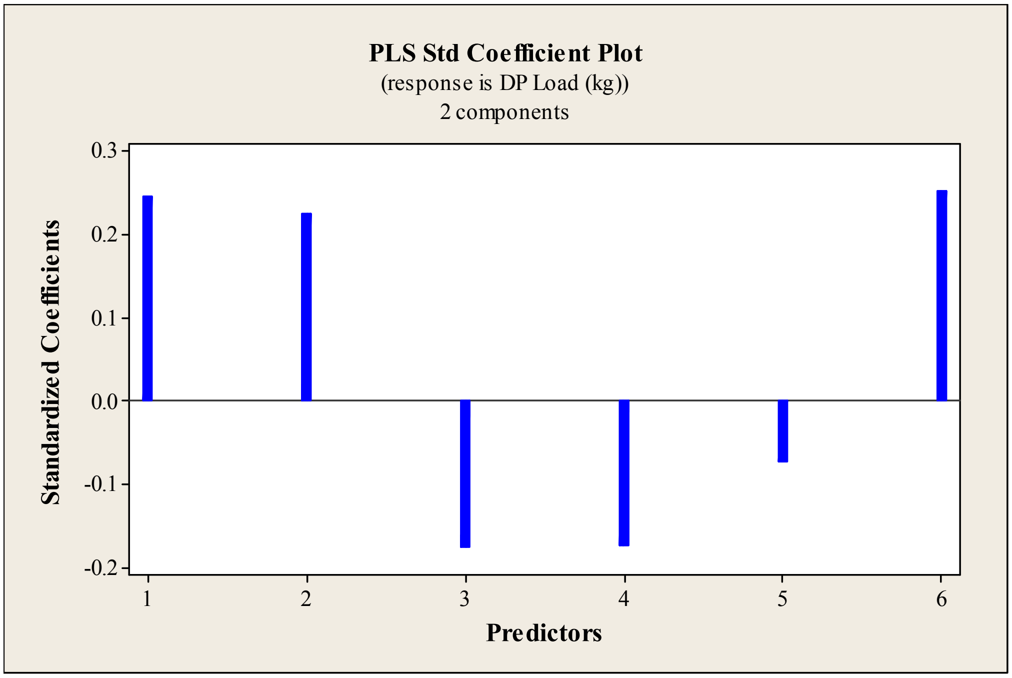
	Comp1	Comp2
DP Load (kg)	0.480127	0.0729001

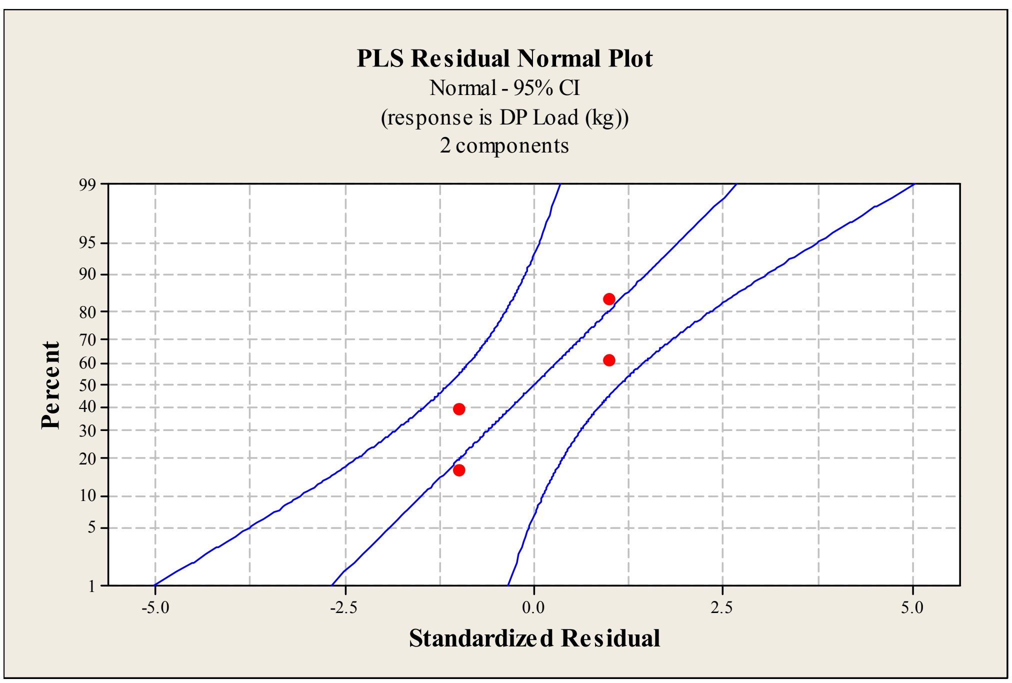
Appendix M. (Continued)



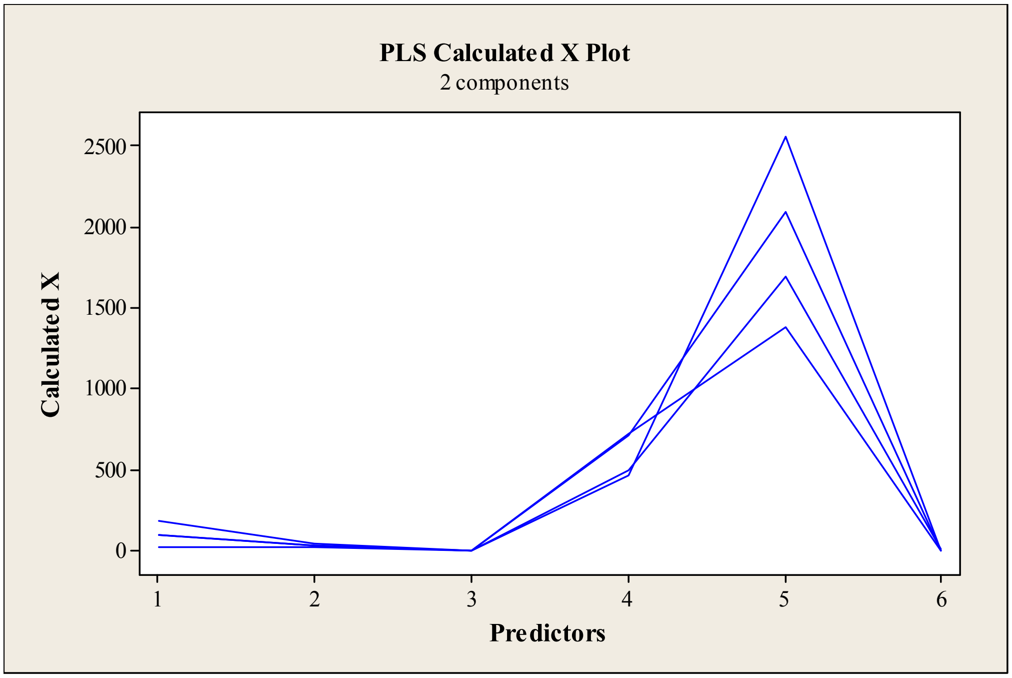


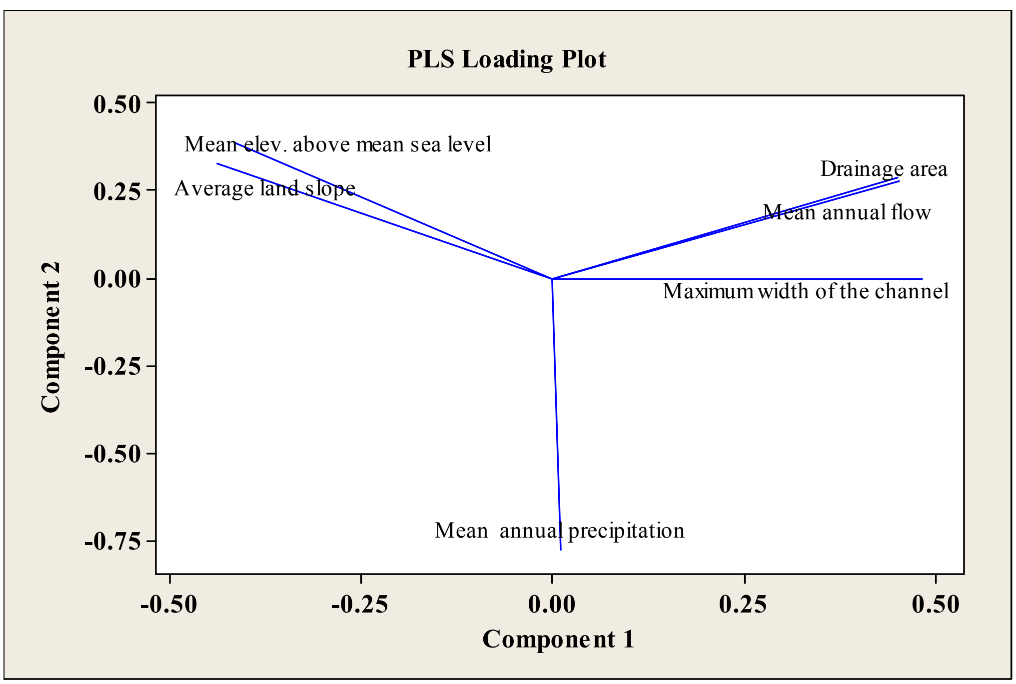
Appendix M. (Continued)





Appendix M. (Continued)





Appendix N. Flow Chart of the automated storm water sampling processes.