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Phosphorus status of stream waters in Puerto Rico: 1989-1997[1,2]

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ABSTRACT

Elevated phosphorus (P) concentrations in Puerto Rico's surface waters are suspected to be the primary cause of observed eutrophication. This paper summarizes total P concentrations (TP), historical trends, and relationships between biological and chemical parameters at twenty-two surface water monitoring stations of eleven rivers from 1989 through 1997. Four rivers had median TP concentrations in excess of 0.1 mg P/L (which is considered a threshold limit for eutrophication). The remaining seven rivers, excluding Río Guajataca, had at least 25% of the sampling episodes exceeding 0.1 mg P/L. When all data (n = 539) were considered, TP in the central 50% of the samples (25 to 75 interquartile range) ranged from 0.04 to 0.29, with mean and median values of 0.30 and 0.09 mg P/L, respectively. Pearson correlation coefficients between TP and fecal coliform bacteria, fecal streptococcal bacteria, and total Kjeldhal nitrogen were 0.38, 0.36, and 0.84, respectively, for all the rivers combined. For rivers with the highest TP concentrations differing relationships between TP and biological and chemical parameters were obtained, thus suggesting that diverse sources were contributing to P loads in rivers. Excluding two stations in Río Grande de Añasco and Río Grande de Arecibo, the trend was for TP concentrations to decrease or not change from 1989 to 1997. Approximately half of the variation in P loads in all rivers combined was due to instantaneous hydrologic flow discharge, a finding which corroborates our hypothesis that a number

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of factors (agricultural non-point sources, background non-point sources, point sources) are contributing to the observed TP concentrations.

Key words: Eutrophication, total P concentration, surface-water quality

RESUMEN

Estatus de fósforo en aguas superficiales de Puerto Rico: 1989-1997

Los niveles elevados de fósforo (P) están implicados en la eutroficación que se observa en algunos cuerpos de agua superficiales de Puerto Rico. Este trabajo resume las concentraciones de fósforo, tendencias y relaciones entre parámetros biológicos y químicos encontradas en 22 estaciones de monitoreo localizadas en 11 ríos, entre 1989 y 1997. Cuatro ríos tenían concentraciones medianas de fósforo por encima de 0.1 mg P/L (considerado un nivel umbral para la eutroficación de aguas). Las concentraciones de fósforo en los restantes siete ríos, excluyendo el Río Guajataca, excedieron valores de 0.1 mg P/L en 25% de los episodios. Al considerar todos los datos (n = 539), el 50% de las muestras (25 a 75 percentila) tenían un recorrido de 0.04 a 0.29, con medias y medianas de 0.30 y 0.09 mg P/L, respectivamente. Los coeficientes de correlación Pearson, entre fósforo total (PT) y bacterias coliformes fecales, bacterias coliformes estreptococales y nitrógeno total Kjeldal fueron 0.38, 0.36 y 0.84, respectivamente, para todos los ríos combinados. Para los ríos con mayores concentraciones de fósforo, se obtuvieron diferentes relaciones entre PT y los parámetros biológicos y químicos seleccionados. Excluyendo dos estaciones en el Río Grande de Añasco y el Río Grande de Arecibo, se observó una disminución o ningún cambio en las concentraciones de fósforo entre 1989 y 1997. Aproximadamente la mitad de la variacion en descargas de fósforo en todos los ríos se debió a descarga hidrológica. Estos datos corroboran nuestra hipótesis de que una combinación de factores (fuentes dispersas agrícolas, fuentes dispersas no-agrícolas y fuentes precisas) están aportando fósforo a las aguas superficiales evaluadas.

INTRODUCTION

The degree of observed eutrophication in Puerto Rico's surface-waters is an issue of concern for all people preoccupied with the safety, health and quality of life. Eutrophication restricts freshwater use for fisheries, recreation, industry, and drinking because of the increased growth of undesirable algae and aquatic weeds and the resulting oxygen shortage caused by their decomposition (Sharpley et al., 2000). Coastal seas also suffer from eutrophication, where nutrient imbalances can cause blooms of noxious algal species which negatively impact recreation, commercial fishing and shell fish production (Burkhart and James, 1999).

Phosphorus (P) is the most important nutrient that must be managed to control the accelerated eutrophication of fresh waters. Although nitrogen may limit plant and algal growth during certain periods of the year, phosphorus is most often of concern because it is the limiting nutrient in fresh water areas (Correl, 1998). Furthermore, phosphorus associated with bottom sediments of surface waters can serve as a long-term reservoir and source of phosphorus to the water column once P-sorption capacities of the sediment material are exceeded (Beauchemin et al., 1996; Ramos-Ginés, 1997). The difficulty of reducing phosphorus concentrations from surface waters creates a challenging task for planners and scientists involved in water quality maintenance strategies. Thus, efforts directed towards reductions in nutrient loads rather than remediation are the best alternative.

Since the 1970s, efforts to attain clean water have been successfully directed towards reducing point source emissions in the USA. Nutrients from non-point sources have thus become the relatively major source of nutrient loads to freshwater (Van der Molen et al., 1998). Although some unsewered urban areas and seepage contribute to nonpoint nutrient emissions, agriculture seems to be the main contributor in most cases. In Puerto Rico other water quality contaminants such as sediments and the presence of high fecal coliform and streptococcal bacteria have been identified as the main water quality problems (Vachier, 1994). Reductions in point source nutrient emissions have occurred somewhat with improvements in the waste water treatment facilities and stringent controls on industrial point source emissions. Still, diverse point- and nonpoint sources such as unsewered communities in urban, suburban, and rural areas, landfills, agricultural activities, and waste-water treatment facilities (Table 1) are actively contributing substantial nutrient loads to surface waters (Vachier, 1994).

In order for local and federal authorities to implement agricultural nutrient management plans (USDA-NRCS, 1999) and to develop total maximum daily load estimates (Parry, 1998; USDA-NRCS, 1998) to impaired waters in Puerto Rico, it is important (i) to evaluate the magnitude of surface water contamination of phosphorus at selected sites in Puerto Rico, and (ii) to determine the relative contribution of diverse agricultural and non-agricultural activities as non-point sources of pollution. As a first step towards this process, this paper will summarize phosphorus concentrations and historical trends in selected surface water monitoring stations in Puerto Rico, and will examine the relation between total P (TP) concentrations and biological and chemical indices of contamination.

MATERIALS AND METHODS

The United States Geological Survey (USGS), in cooperation with local and other federal agencies, established a surface water data collection network in 1958 to assess the quality of surface waters of Puerto Rico. As of 1996, the network consisted of 83 surface-water monitoring stations (including streams, lakes, lagoons, and bays) and 22 suspended sediment stations. Water quality data obtained from analy-

TABLE 1.—*Sources, transport processes, and end products of selected constituents related to total phosphorus loading to surface waters of Puerto Rico.*

Sources	Origin	Material transported	Transport process	End product
	Non-agricultural			
Point	Industries	Treated or untreated sewage	Direct discharge	Bacteria, TKN, NO_3^-, TP
	Sewage treatment plants	Treated or untreated sewage	Direct discharge	Bacteria, TKN, NO_3^-, TP
	Communities >10,000 people	Partially decomposed or undecomposed waste water	Runoff and seepage from septic tanks	Bacteria, TKN, NO_3^-, TP
	Non-agricultural			
Non-point	Urban areas (construction sites, residential and industrial lots)	Water and eroded sediment	Runoff, erosion	TKN, NO_3^-, TP
	Secondary growth forests	Water and eroded sediment	Runoff, erosion	TKN, NO_3^-, TP
	Communities <10,000 people	Partially decomposed or undecomposed waste water	Runoff and seepage from septic tanks	Bacteria, TKN, NO_3^-, TP
	Agricultural			
	Cropland amended with inorganic fertilizer	Dissolved nutrients, sediment	Runoff, erosion	TKN, NO_3-, TP
	Cropland amended with organic sources	Dissolved nutrients, sediment	Runoff, erosion	TKN, NO_3-, TP
	Plant nurseries	Dissolved nutrients	Runoff	NO_3-
	Confined animal feeding operations	Dissolved nutrients	Runoff, direct discharge	Bacteria, TKN, NO_3-, TP

ses are published in tabulated format and include station numbers, date of sampling, description of sampling site and hydrologic unit, size of drainage area, biological and chemical parameters, suspended sediments, and stream flow rates, among other parameters (USGS, 1989-1997). The data are reported by water-year (1 October to 30 September).

This study reports on TP concentration data collected at twenty-two monitoring stations from eleven rivers throughout the island for the water-years 1989 through 1997 (Figure 1). The criteria for selecting the

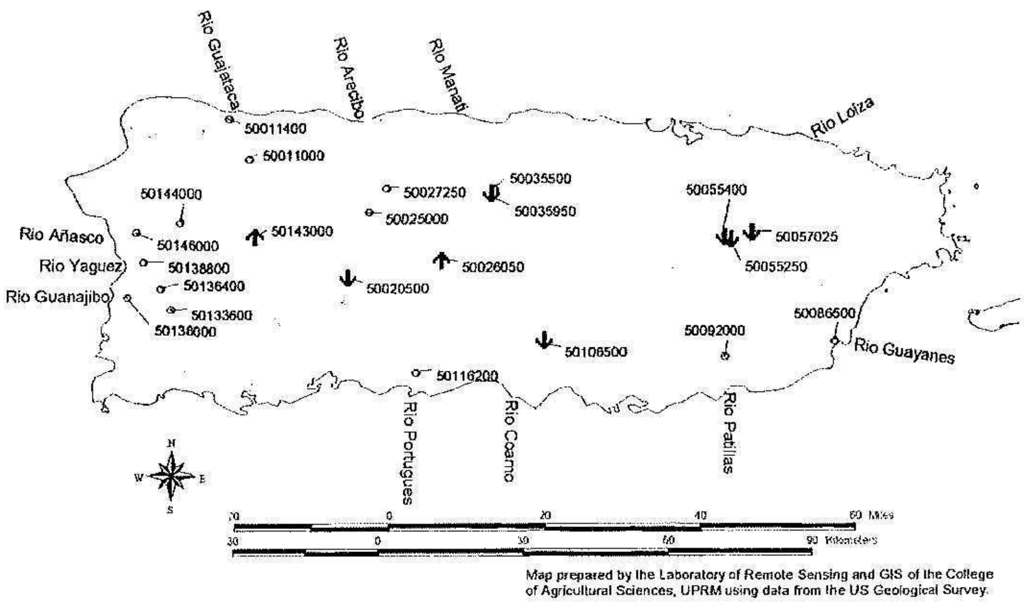

FIGURE 1. Location of selected water quality stations in Puerto Rico including trends in total phosphorus concentration stations from 1989 to 1997. An upward arrow shows that there is an upward trend, a downward arrow shows that there is a decreasing trend, and a circle denotes no trend in total phosphorus concentrations.

stations were (i) availability of data (as TP was not available for all stations); (ii) available information on land use in each area; and (iii) importance of each site to government agencies and other groups involved in water quality planning and management (USDA-NRCS, 1998). The following water quality parameters were used to infer possible sources of phosphorus contamination: stream water discharge, suspended sediments, fecal coliform and fecal streptococcal bacteria, total organic nitrogen (TON), total Kjeldhal nitrogen (TKN), and total NO_3-N (NO_3^-). Bacterial counts, designated with the letter K by the USGS to indicate colony counts outside the acceptance range, were not included in the analyses because of uncertainty associated with the results. Water sample collection was performed at quarterly intervals. Because runoff and erosion events are extraordinary and non-numerous, this sampling strategy precluded observing extremes in TP concentrations due to the relation that exists between hydrological discharge and TP concentrations during a rainfall event. Collection, transport, and analysis of water samples was performed by using standard methods approved by USGS (1989-1997) and specified therein.

To examine which areas present the greatest water quality problems we summarized the data by showing TP frequency distributions in the 11 selected rivers and their respective tributaries. To examine trends in TP occurring over the 9-yr period we performed correlation analysis between TP concentrations and month of collection (time). Total phosphorus concentration data were adjusted for changes in stream flow (instantaneous phosphorus discharge) and regressed against time, thereby eliminating the stream flow influence on phosphorus concentrations. The CORR procedure in SAS (1996) was used to calculate Spearman's rank correlation coefficients between TP and time and to calculate Pearson correlation coefficients between TP and biological and chemical parameters. Multiple regression analysis between TP and biological and chemical parameters was performed with the STEPWISE method (SAS, 1996) to select the best multiple predictors of TP.

RESULTS AND DISCUSSION

Figure 2 shows the distribution and variability in TP concentrations of eleven rivers and their respective tributaries in Puerto Rico, from 1989 to 1997. Critical concentrations of TP causing eutrophication in rivers have been suggested at 0.15 mg P/L for the European Union (Edwards et al., 2000) and at 0.1 and 0.05 mg P/L for rivers and lakes, respectively, in the USA (USEPA, 1986; Parry, 1998). Correl (1998) in-

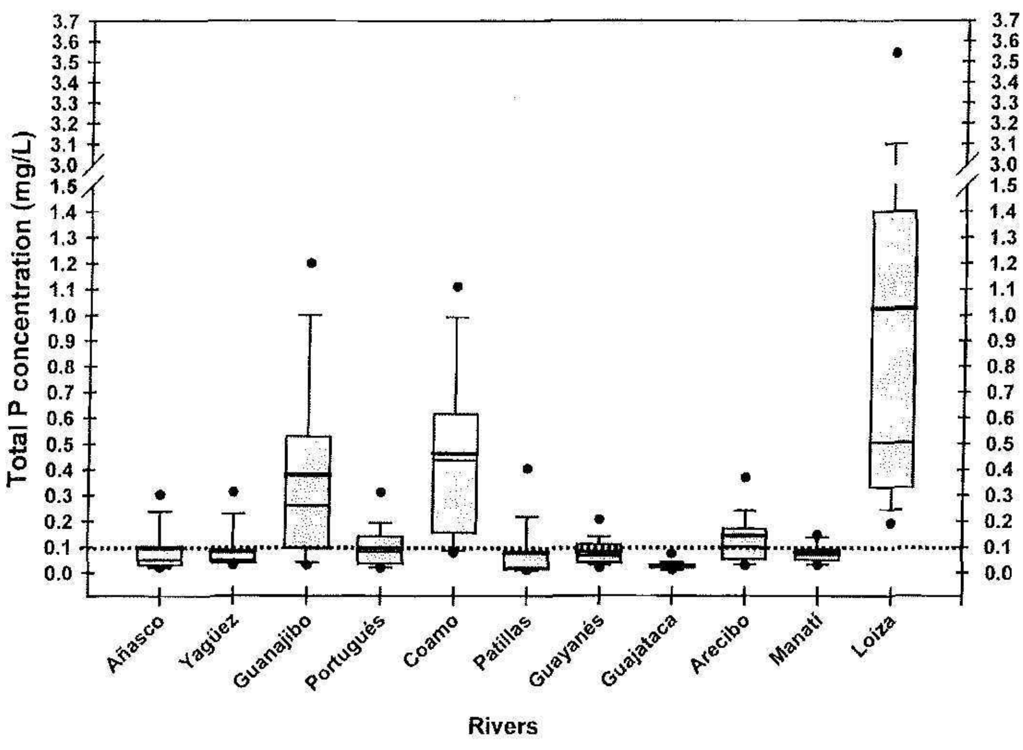

FIGURE 2. Frequency distribution of total phosphorus concentrations from 1989 to 1997 in selected rivers of Puerto Rico. Upper and lower boundaries of boxes represent 75th and 25th percentiles, respectively. Upper and lower lines on extremes of boxes represent 10th and 90th percentiles, respectively. Solid thick line and thin line within boxes represent median and mean values, respectively.

dicated that although there is no clear acceptable TP limit because phosphorus turnover, diffusion rates and N/P ratios can all interact to influence biomass growth in freshwaters, TP concentrations of 0.1 mg P/L may be unacceptably high, and that concentrations of 0.02 mg P/L are often a problem. In Puerto Rico the Environmental Quality Board has established a TP of 1 mg P/L (JCA, 1990). This limit is similar to the allowable TP effluent discharge limit for wastewater treatment plants.

Río Loíza, Río Coamo and Río Guanajibo contained the highest TP concentrations among all rivers, where at least 75% of the samples tested were higher than 0.1 mg P/L (Figure 2). In both Río Coamo and Río Guanajibo, TP concentrations in the central 50% of the data ranged from 0.15 to 0.62 and 0.09 to 0.53 mg P/L, respectively. In Río Loíza, TP concentrations in the central 50% of the data ranged from 0.33 to 1.40 mg P/L. Median values were 0.44, 0.26 and 0.51 mg P/L for Río Coamo, Río Guanajibo, and Río Loíza, respectively. In the case of Río Grande de Arecibo the central 50% of the data contained TP values between 0.05 and 0.17 mg P/L, yet mean and median values were above 0.1 mg P/L, amounts which suggest the occurrence of several high TP discharge events during the study period. The remaining seven rivers, excluding Río Guajataca, had at least 25% of the samples from 1989 to 1997 exceeding 0.1 mg P/L. When all data were considered (n = 539) the majority of samples ranged from 0.04 to 0.29 mg with mean and median values of 0.30 and 0.09 mg P/L, respectively.

Five independent studies which have evaluated TP concentrations in Lago Cidra, Puerto Rico, from 1976 to 1996 have shown TP concentrations well above the suspected threshold limit for eutrophication (Ramos-Ginés, 1997). Other studies in temperate areas have also documented the long-term deterioration of surface waters as a result of nutrient enrichment (Castillo et al., 2000; Withers et al., 2000). For example, of 96 major rivers in England and Wales, Muscutt and Withers (1996) found that 73% had TP concentrations greater than 0.1 mg P/L.

Trend analyses were performed to detect changes in stream water TP concentrations at monitoring stations over the 1989 to 1997 study period and data are summarized in Figure 1. Total P concentrations at 14 of the 22 monitoring stations selected had no clear trend. On the Río Grande de Arecibo one station reported an increase; another a decrease; and the other, no trend. At Río Loíza and Río Coamo stations, TP concentrations decreased over the eight-year period. On the Río Grande de Añasco TP concentrations increased at station 50143000.

In general, some stations had higher TP concentrations than others, within a particular river and its tributaries. For example at Rio Loíza, stations 50055250 and 50055400 had higher TP concentrations than station 50057025 (t-test, $P < 0.05$); however, the mean and median values for all three stations were in excess of 0.1 mg P/L (Figure 3A). On Río Grande de Arecibo, station 50027250 had significantly lower TP concentrations than three others (t-test, $P < 0.05$) (Figure 3B). On Río Guanajibo, station 50138000 had TP concentrations significantly lower than those of the upstream station of 50133600 (t-test, $P < 0.05$) (Figure 4A). Although data for only one station are included for Río Coamo, there was a clear decrease in TP concentrations with time (Figure 4B).

The data demonstrate that downstream stations need not necessarily reflect higher TP concentrations than those upstream. For example, in the Río Grande de Arecibo watershed, TP concentrations at station 50027250

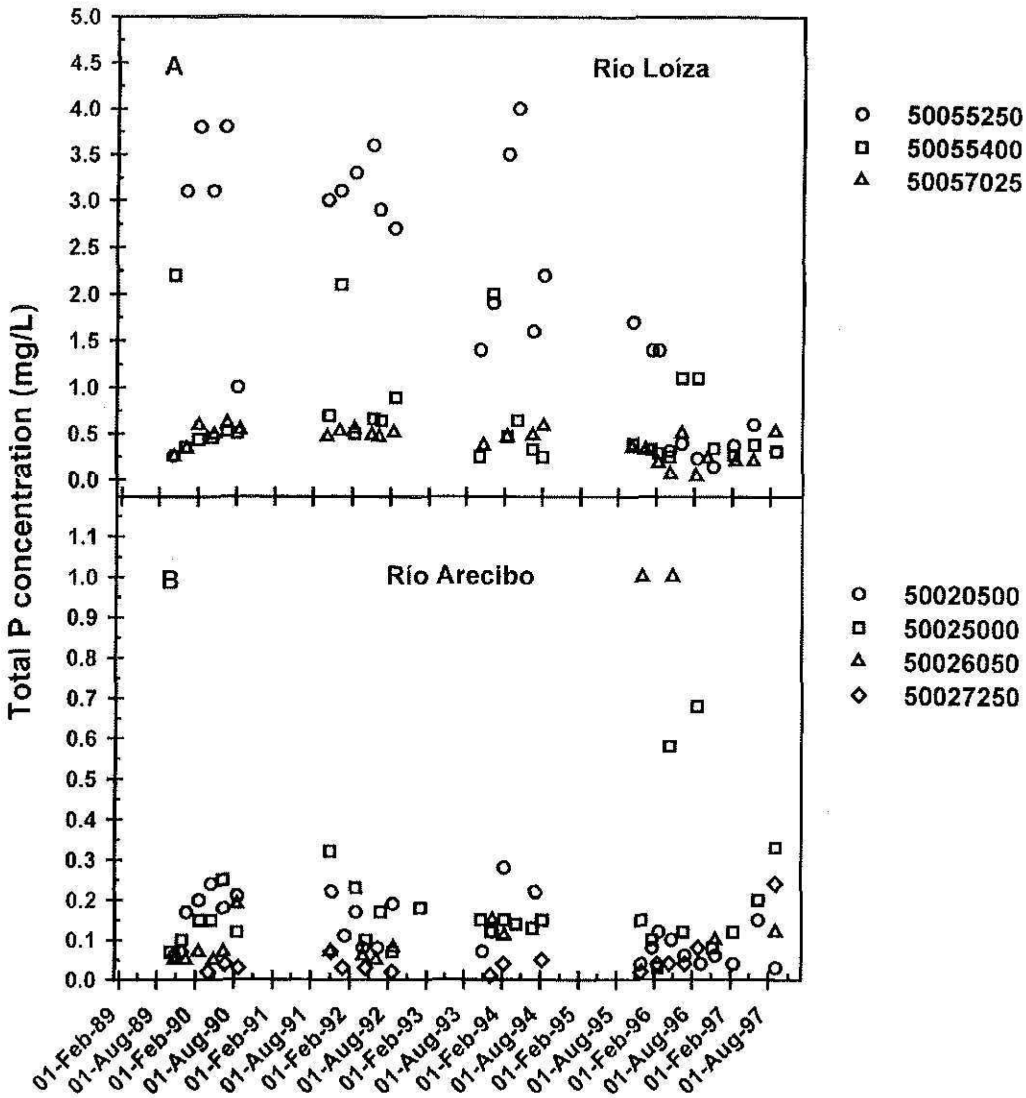

FIGURE 3. Variation in total phosphorus concentrations in (A) Río Grande de Loíza and (B) Río Grande de Arecibo, from 1989 to 1997. Station numbers locations are described in Figure 1.

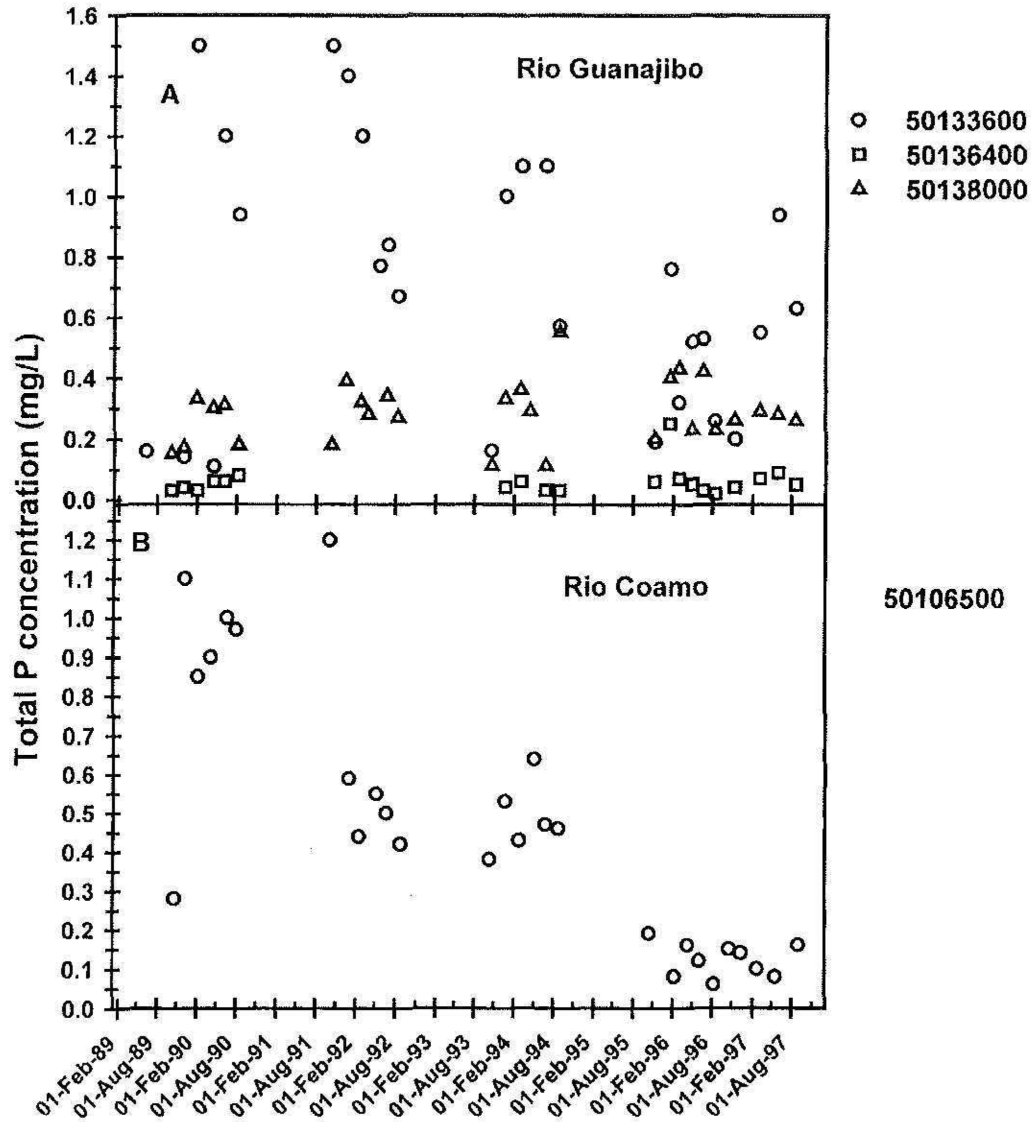

FIGURE 4. Variation in total phosphorus concentrations in (A) Río Guanajibo and (B) Río Coamo, from 1989 to 1997. Station numbers locations are described in Figure 1.

were lower than at station 5002500. This difference suggests that part of the phosphorus loads are either being deposited in bottom sediments and reservoirs or are being utilized by aquatic vegetation thus maintaining relatively lower phosphorus levels in the main water column. This condition is hypothesized to occur in the lower portion of Río Guanajibo, and in Lago Dos Bocas. In eutrophied Lago Cidra, which receives effluents from Río Bayamón and Río Sabaná, the reservoir's bottom sediments may be its major P sink, where TP concentration in the reservior's bottom sediments averaged 669 mg/kg in 1992 (Ramos-Ginés, 1997). This amount is particularly important because sediments can act as long term sources of phosphorus to the water column once phosphorus sorption capacities of the sediment material are exceeded (Beauchemin et al., 1996).

The TP concentration data and instantaneous phosphorus discharge data were plotted as a function of Julian month for all years to examine whether any seasonal tendencies could be identified. No seasonal trend was observed, neither for individual rivers nor for all rivers combined. It was initially hypothesized that an increase in phosphorus concentrations would be observed in months with higher rainfall duration and intensities (Castillo et al., 2000), if phosphorus in stream water were originating from runoff coming from soils with high soil test phosphorus levels. Increase in soil test phosphorus has been associated with soil receiving organic wastes such as dairy and poultry litter and large inorganic fertilizer phosphorus applications (Abrams and Jarrell, 1995; Simard et al., 1995). Soils rated in higher soil test phosphorus categories tend to have higher concentrations of soluble and desorbable phosphorus and have a proportionately larger pool of labile phosphorus than soils in the optimum or lower soil test categories (Pautler and Sims, 2000). Thus soils in higher soil test categories have a greater potential to release phosphorus into runoff waters or into surface waters following erosion of P-rich particles (Sharpley, 1995; Pote et al., 1996; Gburek and Sharpley, 1998). We did observe Pearson correlation coefficients ranging from 0.63 to 0.99 between instantaneous phosphorus discharge and hydrologic discharge for individual rivers. Highest values (>0.90) were obtained for Río Guayanés, Río Portugués, Río Coamo, and Río Loíza, with the latter two of special concern because of the high TP concentrations observed.

Figure 5A shows the relationship between TP concentrations and instantaneous hydrologic flow discharge obtained at each sampling station. There are episodes in which TP concentrations are high with both intermediate and low instantaneous flow discharge rates. These points were identified as those corresponding to Río Loíza. There were episodes with extremely high (>12,000 L/S) hydrologic flow discharge rates and where much variation in TP concentrations was observed. These extreme events corresponding to TP concentrations greater than 1.5 mg/L and flow discharge rates greater than 12,000 L/S were eliminated (6% of the 524 episodes), and instantaneous hydrologic discharge was re-plotted as a function of instantaneous phosphorus discharge, both on a logarithmic scale (Figure 5B). There is a linear relationship between these parameters, and 50% of the variation in instantaneous phosphorus discharge is accounted for by the variation in the hydrologic flow discharge. The solid line corresponds to a threshold value of instantaneous phosphorus discharge that would occur for every instantaneous water discharge episode at a TP concentration of 0.1 mg/L.

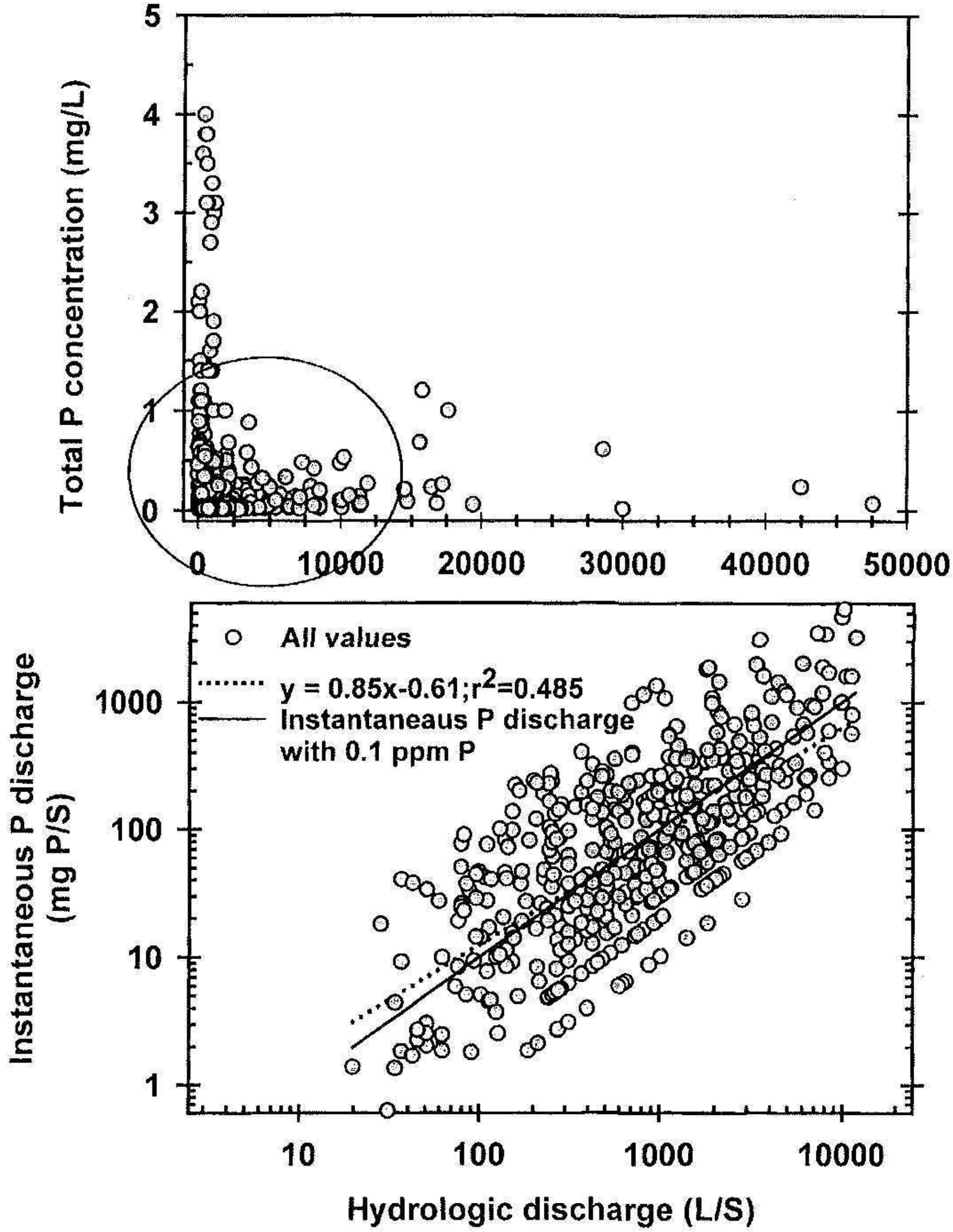

FIGURE 5. Relationship of (A) total phosphorus concentrations and (B) instantaneous phosphorus discharge with instantaneous flow discharge using data collected in 11 rivers of Puerto Rico.

More than half of the episodes are above this line, thus suggesting that these samples contain excessive phosphorus which is not reflected in the TP concentration data because of the dilution effect from hydrologic flow discharge.

Ramos-Ginés (1997) found that from 69 to 90% of the variation in TP loads to Lago Cidra was due to storm runoff discharges. The higher regression coefficients were obtained in the agricultural rural areas rather than in urban sewered and urban unsewered areas. The fact that only half of the variation in phosphorus loads in this study could be accounted for by changes in instantaneous flow discharge suggests that a combination of factors (agricultural non-point sources, background non-point sources, point sources) are contributing to the observed TP concentrations. The specific sources contributing to stream water phosphorus are difficult to ascertain. For example, in the Río Grande de Arecibo watershed, stations 50025155 and 50020500 are downstream from waste water treatment plants whereas station 50025000 apparently does not receive any direct effluents from point sources (R. Ayala, JEQ, personal communication) yet no significant differences in TP were observed among these stations.

In our analysis, we have not differentiated between base flow loads and storm event loads. Nutrient contribution from urban unsewered areas is characterized by having relatively high nutrient concentrations both during low-flow and storm-runoff events, whereas agricultural rural and secondary forest areas are characterized as having relatively low concentrations during low-flow events and high concentrations during storm events. Nearing et al. (1993) found no relationship between flow rates and phosphorus concentrations in watersheds that were primarily forest and pasture land that fed Lake Lanier in Georgia, USA. Approximately 90% of total P entering the lake was from non-point sources, about 40% of which was from agricultural sources. Further work should be directed towards differentiation of nutrient loads from varied sources to surface waters of Puerto Rico.

The correlation analysis performed with the varying water quality parameters showed that there were strong relationships between several of the biological and chemical parameters and TP concentrations (Table 2). Total phosphorus concentrations in Río Guanajibo were related only to total NO_3^- concentrations whereas at Río Coamo and Arecibo TP concentrations were significantly related only to TKN. At Río Loíza TP concentrations were related to fecal coliform and streptococcal bacteria, and TKN. At Río Añasco, TP concentrations were related to all parameters evaluated (coliform and streptococcal bacteria, NO_3^-, TKN) including total suspended sediments (data not shown). When considering all the data together, TP concentrations were significantly related to fecal coliform and fecal streptococcal bacteria and TKN, but not to NO_3^- concentrations. Results of the multiple regression analysis between biological and chemical parameters and TP concentrations indicated that the equation

$$TP = -0.0355(\log_{10} \text{discharge}) + 0.1736\ TKN + 0.173 \qquad [1]$$

explained 69% of the variation observed for all rivers combined for a discharge rate range of 20 to 10,000 L/S.

Fecal coliform and streptococcal bacteria are derived from the intestines or feces of warm-blooded animals and are often used as indicators of sewage pollution in surface waters (USGS, 1989-90). These can originate from various point and non-point sources but are expected to originate from cropland amended with organic sources such as poultry litter or inorganic fertilizers (Table 1). Although, NO_3^- as a chemical species is chemically stable in water, it is subject to immobilization by microorganisms and aquatic flora, and denitrification losses if carbon sources are available. Therefore, as residence time in water or distance from originating source is increased, NO_3^- concentrations should decrease in the water column. Very low NO_3^- concentrations (below 5 mg N/L) are indeed observed in surface waters (data not shown) of Puerto Rico.

TKN is associated with all point and non-point sources of pollution (Table 1) and can serve as substrate for aquatic microorganisms and flora through its mineralization and subsequent nitrification. TKN and fecal streptococcal bacteria were weakly correlated ($r = 0.27$; $P < 0.001$) in all rivers, suggesting that only part of the variation in TKN is associated with some form of wastewater discharges. Very high correlations (0.56 to 0.91) between TP and TKN were observed in all rivers except

TABLE 2.—*Pearson correlation coefficients between total phosphorus concentration and biological and chemical parameters in selected rivers of Puerto Rico.*

River	Coliforms[1]	Streptococci	NO_3^- total	TKN
Guanajibo	NS[2]	NS	0.689 (<0.001)	NS
Coamo	NS	NS	NS	0.816 (<0.001)
Loíza	0.335[3] (0.01)	0.411 (0.005)	NS	0.908 (0.001)
Añasco	0.474 (0.002)	0.595 (0.001)	0.444 (0.008)	0.736 (<0.001)
Arecibo	NS	NS	NS	0.579 (0.001)
All rivers	0.378 (<0.001)	0.357 (<0.001)	NS	0.844 (<0.001)

[1]Fecal coliform bacteria and fecal streptococcal bacteria were log transformed prior to analysis.

[2]NS = non significance at $P < 0.05$.

[3]Value in parenthesis is significance level from correlation analysis.

Río Guanajibo, suggesting that TP is originating from very diverse sources and not necessarily from cropland runoff. While total P originates from different sources in rivers of Puerto Rico, organic sources related to manure disposal and wastewater discharge could be the main contributors of total P to surface river waters.

As of 1999, the sedimentation and the presence of high concentrations of fecal coliform and streptococcal bacteria were the main surface-water quality problems in Puerto Rico, with the highest bacterial concentrations in stations near densely populated and industrialized areas of the island (USGS, 1999). In a National Water Summary for 1990-91, Vachier (1994) reported that Río Grande de Manatí, Río Grande de Patillas and Río Grande de Añasco all contained excessive bacteria concentrations that were attributed to discharges of domestic and municipal wastewater. The results of this study demonstrate that high TP concentrations are a water quality problem in some areas of Puerto Rico, and that it is primarily related to organic sources. The agricultural non-point source contribution cannot be discounted since the authors have observed that soil test phosphorus levels on some agricultural lands are high (unpublished data). In a recent survey, Martínez et al. (1999) showed that 67% of soil samples obtained from the poultry producing zone of Puerto Rico had phosphorus levels (Olsen-P) in excess of what is considered adequate to support crop growth. According to the P index (a diagnostic tool for evaluating the risk of phosphorus transport) all the farms evaluated had zones where nutrient runoff constituted a potential threat to the quality of the surrounding waters. It appears that reductions in agricultural non-point sources of pollution would indeed reduce phosphorus loads to surface waters in Puerto Rico, but further work is needed to discern between agricultural and non-agricultural sources before attributing responsibilities.

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