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Comparative Use of Hydrologic Indicators to Determine the Effects of Flow Regimes on Water Quality in Three Channels across Southern Florida, USA

Ikechukwu S. Onwuka , Leonard J. Scinto * and Ali Mahdavi Mazdeh

Institute of Environment and Department of Earth and Environment, Florida International University, Miami, FL 33199, USA; ionwu002@fiu.edu (I.S.O.); amahdavi@fiu.edu (A.M.M.)
* Correspondence: scintol@fiu.edu; Tel.: +1-305-348-1965

Abstract: This study determines the relationships between water flow and water quality in three types of channels in southern Florida, USA: Shark River Slough, Peace River, and Hillsboro Canal. Peace River most resembles a natural channel with floodplain connectivity, sinuosity, and uninhibited flow. Shark River Slough has a natural, shallow channel with sheet flow, while the Hillsboro Canal is the most modified channel due to dredging, straightening, and regulated flow. Hydrologic indices for each channel were estimated to characterize flow regimes and flow variability, while concentration–discharge (*C*–*Q*) relationships were determined to quantify the impact of flow regime on water quality. The greatest variability in flow occurred at the Hillsboro Canal, followed by Peace River and Shark River Slough. Connectivity to floodplains and long durations of low and high flow pulses at Peace River and Shark River Slough contributed to the dilution of water quality constituent concentrations at higher flows. Conversely, the channelized characteristics of the Hillsboro Canal resulted in an enrichment of constituents, especially during high flows. This study suggests that *C*–*Q* relationships can be used in canal discharge management to prevent water quality degradation of sensitive downstream wetland and aquatic ecosystems.

Keywords: channelization; flow regime; hydrologic changes; water quality; *C*–*Q* relationships

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1. Introduction

Human modifications of natural channels (rivers and streams) have resulted in channelization and deviation from natural flow regimes [1–4]. Channelization, or canalization, involves the straightening and shortening of existing natural channels to increase hydrologic transport capacity, and the dredging of land surfaces to create new channels for navigation, water conveyance, and drainage purposes [2,5]. Channelization includes the construction of levees and embankments along channel banks to restrict channel morphology and width, which, in some instances, results in the deepening of the channel [3]. Such changes in morphology disconnect channels from their floodplains, reduce sediment exchange capacities, prevent overbank flows, and change flow regimes [3,6,7]. Flow management via water control structures can further change the flow regimes of channels [5]. For example, pump stations, culverts, spillways, and weirs are used to regulate the flow of water within the canal networks of South Florida, USA [5,8]. Overall, flow regime changes affect the natural variability and cyclical patterns of low and high flow conditions of channels, often changing the magnitude and frequency of low and high flows [3,9,10].

A variety of hydrologic metrics have been developed to quantify deviations from natural flow regimes that are caused by human interventions. The Indicators of Hydrologic Alteration (IHA) are widely used hydrologic indices that characterize the magnitudes, timings, frequencies, and rates of changes in water flow, all of which are components of a flow regime [10]. These components are important because they regulate bedload transport, which influences channel morphology and facilitates exchanges of water quality constituents (e.g., nutrients and organic matter) between a channel and its floodplain [3]. Furthermore, flow regime changes in modified channels can cause water quality degradation by decreasing in-stream nutrient retention and increasing pollutant exports downstream to receiving ecosystems [11]. Low flow conditions can increase the residence time of water quality constituents [12], allowing biogeochemical processes such as biotic uptake, microbial reduction (e.g., denitrification), and sorption to regulate concentration variability [12,13]. Conversely, high flows can dilute the concentrations of point-sourced water quality constituents or mobilize concentrations of multi-sourced constituents, including particulates, which can then be transported downstream [12,14–16].

Regression models have been developed to predict the behavior of the concentrations of constituents that affect water quality for specified flow regimes [17]. Specifically, several studies have used concentration–discharge (*C*–*Q*) relationship models to quantify the effect of flow on the behavior of water quality constituents within natural channel networks [12,15,16,18–20]. A *C*–*Q* relationship is commonly expressed as a power-law function:

$$C = aQ^b \tag{1}$$

where a and b are model coefficients that represent the intercept (same unit as concentration) and slope (unitless), respectively, on a logarithmic scale [12]. The slope (b) represents the pattern or behavior of the constituent [18]. A chemostatic or constant pattern, where $b = 0$ [18], occurs when the concentration of a constituent is not influenced by discharge, but by other factors such as biogeochemical cycling. For instance, chemostasis can result from the abundance of a constituent in the watershed [21], stemming from nutrient legacies from agriculture [22] or active geogenic weathering [18], which act as biogeochemical controls and regulate the concentration and loading of such constituent. Conversely, a chemodynamic pattern occurs when there is an effect of discharge on the concentration of a constituent as denoted by a non-zero slope. A negative slope ($b < 0$) represents a dilution behavior in which concentration varies inversely with discharge, while a positive slope ($b > 0$) represents an enrichment or mobilization behavior where a constituent's concentration increases with increasing discharge [12,16]. Oftentimes, there are changes in *C*–*Q* patterns, observable as inflections in slopes that further delineate the processes dominating the behavior of water quality constituents. These inflections in slopes, also known as discharge thresholds, reflect the interactions of hydrologic and biogeochemical forcing on the behavior of water quality constituents, whereby hydrology is more likely to dominate at high flow and biogeochemical processes at low flow [12]. Furthermore, the presence of slope inflections in *C*–*Q* relationships can identify the ranges of discharges in a flow regime where hydrology increases the concentration and export of constituents [12,15,20]. Theoretically, there are nine classifications (archetypes) of *C*–*Q* relationship patterns based on the presence of slope inflections (Figure 1) [12].

Previous research has used the flow regime characteristics of channels to assess the impacts of flow changes caused by dams on river ecology [9,10,23,24], while few studies have addressed the effects of channelization [25]. This study expands on previous research by determining the impacts of flow regime changes on the behavior of water quality constituents in three channels in southern Florida, USA, whose channel morphologies and/or flow characteristics deviate from the flow regimes of natural channels. The objectives of this study were to (1) characterize and compare the flow regimes of a wetland slough, a river, and a flow-regulated, man-made canal; and (2) test the applicability of *C*–*Q* relationship models that have been traditionally used in channels with natural flow regimes to other channels that are different morphologically (channel) and hydrologically (flow regime). Predictions include the following: (1) the flow regime in the man-made canal will have the greatest variability compared to the slough and river; and (2) *C*–*Q* relationship models will be applicable in non-riverine channels to quantify the effect of flow on the behavior of water quality constituents.

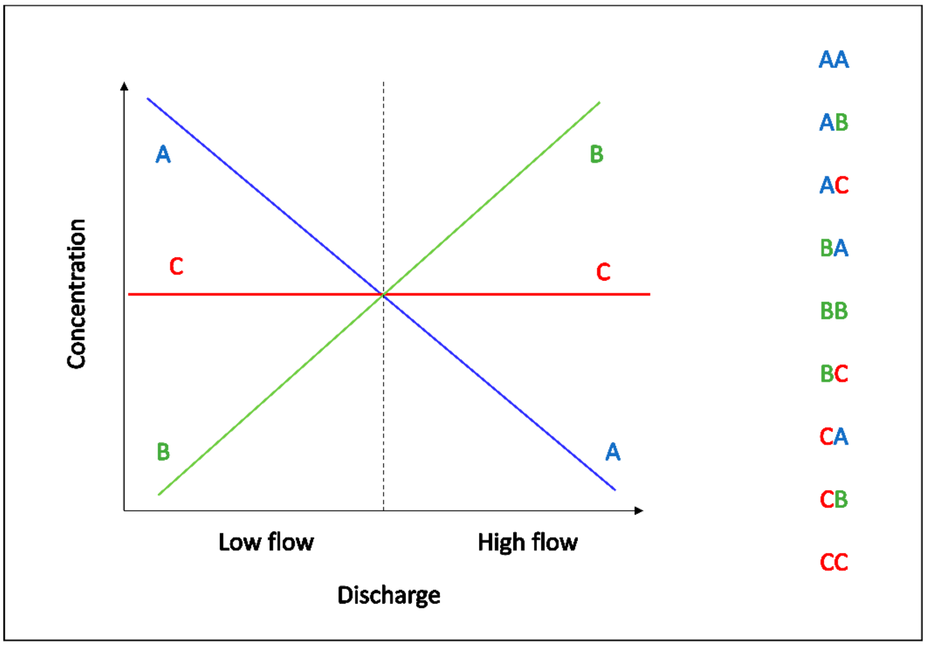


Figure 1. Nine possible archetypes for interpreting *C*–*Q* relationships with inflections in slopes (discharge thresholds) as adapted from Moatar et al., [12]. Blue, red, and green represent dilution, chemostatic, and enrichment, respectively.

2. Materials and Methods

2.1. Study Locations

Three channels were selected for this study: Shark River Slough, Peace River, and Hillsboro Canal, which are all located in southern Florida (Figure 2). This region broadly has a sub-tropical to tropical climate, relatively flat topography and is underlain by carbonate (karst) formations that hold groundwater [26,27].

Shark River Slough is within Everglades National Park (ENP), a protected ecosystem comprising fresh-water wetlands, marshes, prairies, tidal flats, and mangroves [4]. The slough is a shallow, slow-moving, broad river, with channel depths in the order of centimeters [28] and is the primary pathway for surface-water flow through ENP [4]. Everglades National Park is underlain by porous marine limestone formations, including the Miami Limestone [29,30]. As part of a larger effort to drain the larger Everglades region for agriculture and urban development, discharges into Shark River Slough have been reduced by changes in the volume, timing, and distribution of water through regional canals, which diverted freshwater flows into the Atlantic Ocean [4].

Peace River starts in south-central Florida and flows southwest until discharging into the Charlotte Harbor Estuary. The river drainage basin is 6086.47 sq km, with a length of about 168.98 km, and the basin geology consists of clastic sediments that overly carbonate rocks (Table 1) [31]. The river, although a natural watercourse, has had its flow regime modified by land use activities such as phosphate mining, urbanization, and agricultural development [32]. This has resulted in the loss and channelization of some of the headwater tributaries, and reduced surface inflows into the river [32]. However, much of the river corridor remains undeveloped; it has floodplains that support riparian vegetation, and the river flows unrestricted over its entire reach [32]. For example, the river reach at the town of Bartow, Florida, is within the upper river watershed (2139.33 sq km) and has abundant riparian vegetation and wetlands, including cypress and hardwood swamps [31]. Additionally, the channel reach is characterized by low bank heights and shallow bank slope angles [31] and is sinuous. Given these channel and hydrologic characteristics, Peace River most resembles a channel with a natural flow regime.

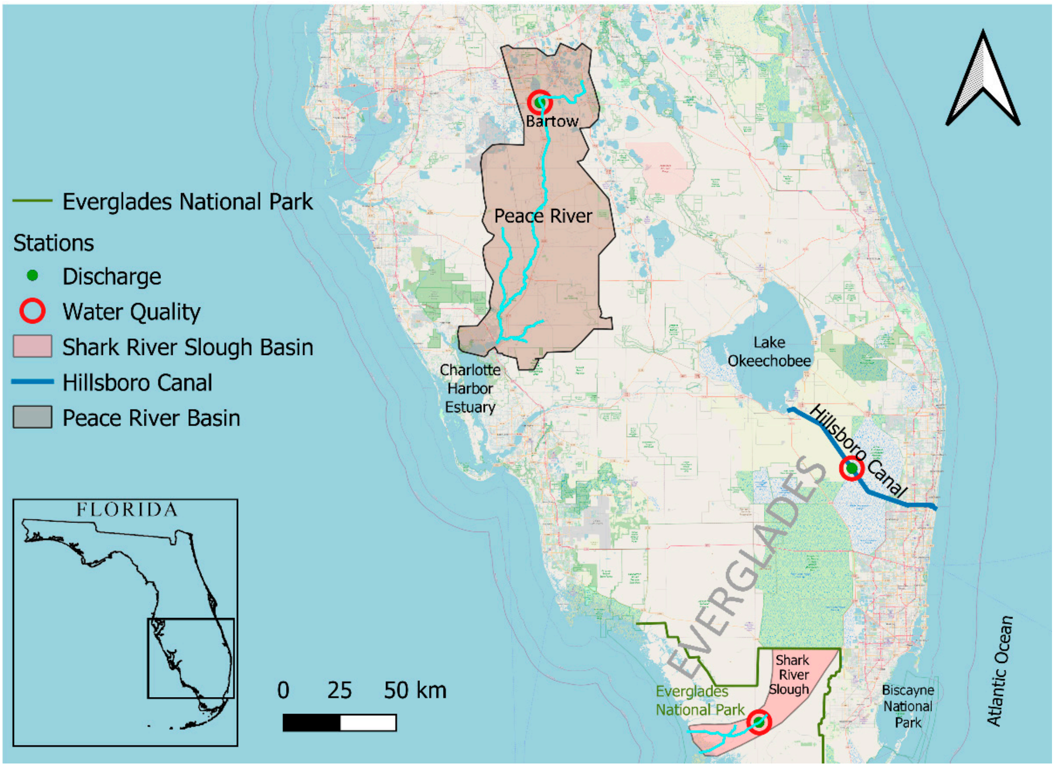


Figure 2. Locations of study sites: Shark River Slough, Peace River, and Hillsboro Canal.

The Hillsboro Canal is a major canal that originates from Lake Okeechobee and flows southeast, draining agricultural, wetland, and urban basins before discharging into the Atlantic Ocean [8]. The geology of the canal basin is made up of the Fort Thompson formation, which consists of alternating layers of limestone, shell, sand, and marl punctured by solution holes, and the southern portion grades into the more porous Miami Limestone formation [30]. The Hillsboro Canal is one of the regional canals, constructed between 1910 and 1920, that was dredged to drain the Everglades and reroute freshwater, originally headed south, eastward into the ocean [4]. Like all South Florida canals, the Hillsboro Canal lacks the natural channel features necessary to dissipate high-energy discharges, such as floodplains, but rather has levees, and steep slopes to confine the flow to the channel and prevent overbank discharge [5,8]. Discharge in the canal is managed via water control structures to prevent flooding, drain excess water from farmlands, convey watershed runoff, recharge the surficial aquifer, and prevent salt-water intrusion [5,8]. The channelization and flow regulation in the Hillsboro Canal makes it the most modified of the three channels in this study.

Table 1. General basin characteristics of the channels.

Channel	Basin Size (sq. km)	Geology	Dominant Land Use
Shark River Slough	1034	Miami Limestone	Wetland (100%)
Peace River	6086	Undifferentiated sand, shell and clay, underlain by carbonates, e.g., Suwannee Limestone and Hawthorn Group	Agriculture (40%)
Hillsboro Canal	479	Fort Thompson Formation	Agriculture (62%)

2.2. Data Collection

Discharge and water quality concentration data for fifteen years (2004–2018) were used in this study. The sites selected on the channels were Shark River Slough at Bottle Creek (SRS), Peace River at Bartow (PRB), and Hillsboro Canal at the S6 structure (HC6). Mean daily discharge data at SRS (25°28′04.8″ N, 80°51′16.2″ W), and HC6 (26°28′19.3″ N, 80°26′45.3″ W) were downloaded from the South Florida Water Management District's online data repository—DBHYDRO (https://www.sfwmd.gov/science-data/dbhydro, accessed on 12 January 2021). Mean daily discharge measurements for PRB (27°54′07.0″ N, 81°49′03.0″ W) were obtained from the United States Geological Survey-National Water Information System (https://waterdata.usgs.gov/nwis, accessed on 26 February 2020).

Water quality constituents including total phosphorus (TP), nitrate-nitrite (NN), chloride (Cl), specific conductance (SC), total suspended solids (TSS), and turbidity, which varied over a range of temporal sampling resolutions, from daily to monthly, were considered for this study. At SRS, only SC, TP, and NN were available. Specific conductance was downloaded from DBHYDRO (25°28′04.8″ N, 80°51′16.2″ W) while TP and NN were obtained from the online repository of the Florida Coastal Everglades-Long Term Ecological Research [33] (https://fce-lter.fiu.edu/data/core/, accessed on 12 December 2019) at a site 130 m upstream from the discharge station (25°28′05.5″ N, 80°51′11.8″ W). At PRB, water quality constituent concentrations were retrieved from the Water Management Information System of the Southwest Florida Water Management District (https://www18.swfwmd.state.fl.us/ResData/Search/ExtDefault.aspx, accessed on 12 February 2020) (27°54′08.6″ N, 81°49′03.4″ W) at a station 50 m upstream from the discharge station (27°54′08.6″ N, 81°49′03.4″ W) and at HC6, the water quality data were adjacent to the discharge station and were also retrieved from DBHYDRO.

2.3. Data Analysis

2.3.1. Flow Regime Characterization

The discharge data in each channel were analyzed using the IHA program developed by the Nature Conservancy [10,34]. This program is free and user-friendly. The selected groups of hydrologic indices were the magnitude of annual flow conditions, frequency and duration of high and low pulses, and rate of change in water flow (see Table 2 for definitions). The Richards–Baker Flashiness Index (R-B Index), developed to determine the fluctuations in discharge relative to the total discharge [35], was calculated as an additional index of flow variability [36]. Because hydrologic data is usually not normally distributed, non-parametric statistics were used in the IHA program to calculate the values of the hydrologic indices and the median values were reported, except for the magnitudes, which were computed as means [34].

Principal component analysis (PCA) was used to identify the dominant hydrological indices that best described the flow regimes of the three channels. Principal component analysis is a multivariate analysis tool that is primarily used to reduce the dimensionality of large data by transforming the original variables in a dataset into new uncorrelated variables known as principal components, and the new variables or axes are linear combinations of the starting variables [37]. However, PCA can also be used to determine the relationships between variables and highlight the similarities and differences between categories [38].

2.3.2. Concentration–Discharge (C–Q) Relationships

The linear expression of the concentration–discharge (C–Q) relationship is written as follows:

$$\log_{10} C = \log_{10} a + b \ \log_{10} Q \quad (2)$$

For each channel, discharge and constituent concentration data were paired by date. Since flow is regulated at HC6, the discharge data used were restricted to pumping events when the canal was flowing. The data pairs were then log-transformed and regressed to yield slopes (b) [12], which were then used to understand the influence of flow on the concentrations of the water quality constituents. Student's t-test was conducted to ascertain the statistical significance of b being different from zero, with a level of significance at $p < 0.05$ [39,40]. p values lower than 0.05 indicated a significant log (C)-log (Q) slope; otherwise, b was not different from zero, and this meant that concentration was not discharge-dependent [40]. Next, piecewise (segmented) linear regressions were conducted on C–Q relationships to detect the presence of inflections in the slopes, which would signify changes in the behavior of the water quality constituents with discharge [20]. To do this, the Davies' test from the 'segmented' package in the R programming language [41] was used to iteratively search across 10 quantiles of the explanatory variable (Q) for breakpoints in the slope (b) of the log (C)-log (Q) regression for each constituent, with $p < 0.05$ selected as the level of significance [19,39]. When the significance level was met, breakpoint analysis from the package was conducted to estimate two new regression models, separated by an inflection in b. This indicated a change in the linear relationship between concentration and discharge [42,43]. An ANOVA test of independence was then conducted on the slopes above and below the inflection points to determine if they were statistically different from zero [39]. Flow duration curves, which are one of the outputs of the IHA program, were used to calculate the probabilities of exceeding the discharge thresholds for the constituents that had slope inflections. All statistical analyses were conducted in the R programming language [41].

Table 2. Calculated Indicators of Hydrologic Alteration (IHA) [10,34] and Richards–Baker Flashiness Index (R-B Index) [35] for SRS (slough), PRB (river), and HC6 (canal) for the years 2004 to 2018.

Flow Regime Characteristics	Description	Hydrologic Indices	Unit	SRS	PRB	HC6
Magnitude	The mean (moving average) magnitude of minimum and maximum yearly flow conditions of various durations (daily to seasonal)	1-day minimum	m^3s^{-1}	0.002	0.052	0.000
		90-day minimum	m^3s^{-1}	0.111	0.580	1.538
		1-day maximum	m^3s^{-1}	0.878	27.160	76.780
		90-day maximum	m^3s^{-1}	0.782	7.147	22.980
Frequency	Number of yearly occurrences during which the magnitude of the water conditions exceeds an upper threshold (75%) or remains below a lower threshold (25%) of the long-term daily mean flows	Low pulse count	Count	2	6	0
		High pulse count	Count	4	4	20
Duration	Yearly duration of low and high flow pulses	Low pulse duration	Days	31.00	6.00	
		High pulse duration	Days	6.25	12.00	3.00
Rate of change	The rate of both positive (rise) and negative (fall) changes in the daily hydrographs during a year	Rise rate	m^3s^{-1} day^{-1}	0.03	0.12	6.31
		Fall rate	m^3s^{-1} day^{-1}	−0.03	−0.10	−6.95
Flashiness	Measurement of oscillations in discharge (day to day changes) relative to total discharge during a year	R-B Index	Unitless	0.04	0.09	0.47

3. Results

3.1. Flow Regime Characterization

Flow regime characteristics differed between the three sites (Table 2). The 1-day minimum discharge was highest at PRB (river), while the 90-day minimum, and 1- and 90-day maximum discharges, were highest at HC6 (canal). The channels SRS (slough) and PRB had low frequencies of high pulse counts while HC6 had the highest frequency of high pulse counts. SRS had the longest low-pulse duration (31 days) while PRB had the longest high-pulse duration (12 days), which was about twice (6.25 days) and four times (3 days) that of SRS and HC6, respectively. Conversely, HC6 had the highest hydrograph rise rate, fall rate, and highest flashiness (R-B Index) of the three channels. With consistently lower differences between low-flow and high-flow indices, the flow regime of SRS had the least variability, while HC6 had the greatest flow variability between the low- and high-flow indices and had the highest values across most hydrologic indices.

In the PCA, SRS and PRB were noticeably distinguished from HC6 (Figure 3). For instance, SRS and PRB were differentiated from HC6 by low pulse duration and low pulse count. Additionally, PRB was differentiated by the fall rate, high pulse duration, 1-day minimum discharge, and 90-day minimum and maximum discharges, while HC6 was differentiated by R-B Index, high pulse count, 1-day maximum discharge and rise rate (rise rate is highly correlated with R-B Index and is thus omitted for clearer illustration) (Figure 3).

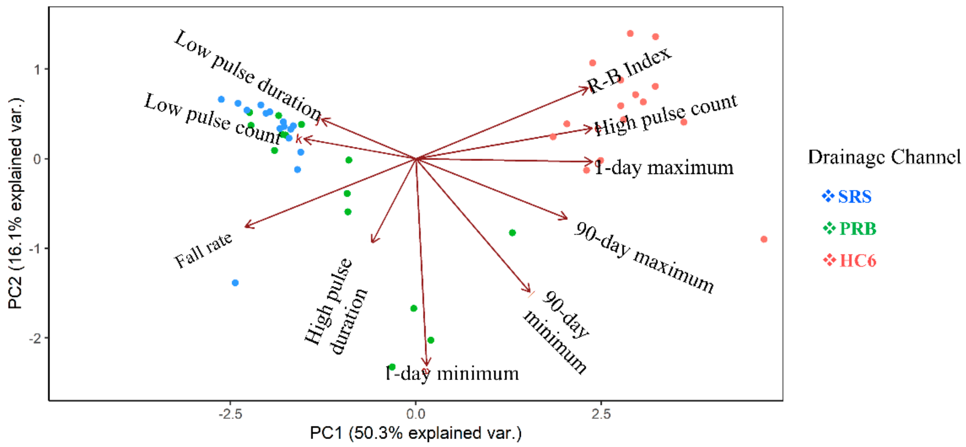
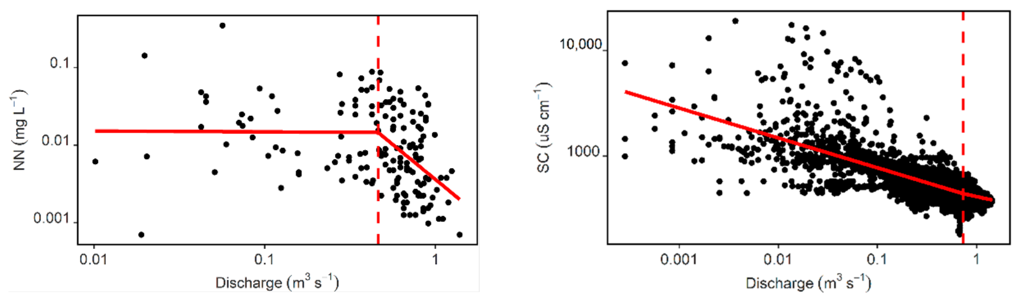


Figure 3. Principal component analysis plot of the hydrologic indices used to characterize the flow regimes of SRS, PRB, and HC6.

3.2. Concentration–Discharge (C–Q) Relationships across the Channels

The flows in the channels had quantifiable impacts on the concentrations of water quality constituents (Table 3). At SRS and PRB, dilution patterns tended to dominate with higher flows (negative *b*), particularly for TP, NN, SC, and Cl (PRB only). Conversely, turbidity and TSS were enriched with higher flows in PRB. At HC6, enrichment patterns were observed with higher flows (positive *b*) for TP, NN, and turbidity, and chemostatic patterns (*b*~0) were observed for TSS, SC, and Cl.

Piecewise regression analysis further revealed the presence of statistically significant slope inflections in the linear log (*C*)-log (*Q*) regressions for some water quality constituents across the channels (Table 4). Five of the nine possible (*C*–*Q*) archetypes were found across SRS, PRB, and HC6 combined. At SRS, NN exhibited the CA archetype; that is, chemostasis at low flow and dilution at high flow, while SC exhibited the AA archetype signifying continual dilution with discharge (Figure 4).



(**a**) (**b**)

Figure 4. Concentration–discharge (*C*–*Q*) relationship plots for water quality constituents with discharge thresholds: (**a**) nitrate-nitrite (NN) and (**b**) specific conductance (SC) at SRS.

Table 3. Log (*C*)-log (*Q*) regression slopes (*b*) for water quality constituents at SRS, PRB, and HC6 for the period 2004 to 2018.

Constituent	Channel	Data Pairs (n)	Slope (*b*)
TP	SRS	155	−0.23 *
	PRB	173	−0.06 *
	HC6	382	0.22 *
NN	SRS	157	−0.38 *
	PRB	166	−0.24 *
	HC6	302	0.20 *
Turbidity	PRB	177	0.08 *
	HC6	64	0.30 *
TSS	PRB	151	0.21 *
	HC6	42	0.06
SC	SRS	4666	−0.28 *
	PRB	177	−0.15 *
	HC6	380	0.01
Cl	PRB	179	−0.26 *
	HC6	302	−0.02

* Significant *p* values ($p < 0.05$) indicate slope is statistically different from zero.

Table 4. Piecewise (segmented) linear regression slopes (*b*) for water quality constituents that have statistically significant inflections in *b* (discharge thresholds) according to the Davies' test for the different channels.

Channel	Constituent	Davies' Test	Discharge Threshold (m^3s^{-1})	Exceedance Probability of Discharge Threshold	Piecewise Regression Slopes (*b*)		Archetype
					Low	High	
SRS	NN	$p = 0.0008$	0.46	0.56	−0.01	−1.81 *	CA
	SpC	$p < 0.0001$	0.74	0.22	−0.28 *	−0.20 *	AA
PRB	NN	$p < 0.0001$	1.05	0.58	0.51 *	−0.60 *	BA
	Turbidity	$p = 0.0004$	7.24	0.20	0.2 *	−0.32 *	BA
	TSS	$p = 0.0004$	8.91	0.17	0.36 *	−0.38 *	BA
	SpC	$p < 0.0001$	0.35	0.84	0.25 *	−0.19 *	BA
	Cl	$p < 0.0001$	1.74	0.43	−0.36 *	−0.19 *	AA
HC6	TP	$p < 0.0001$	23.82	0.15	0.12 *	0.87 *	BB
	NN	$p < 0.0001$	21.72	0.17	0.08	0.97 *	CB
	Turbidity	$p = 0.05$	4.39	0.40	0.12	0.59 *	CB
	SpC	$p = 0.04$	70.96	0.015	0.02	−4.73	CA

Significant *p* values at 0.05 (*) according to ANOVA test of independence indicating slopes are statistically different from zero.

At PRB, four of the five water quality constituents with statistically significant slope inflections (NN, turbidity, TSS, and SC) exhibited the BA archetype, which is enrichment at low flow and dilution at high flow (Figure 5). The fourth constituent, Cl, exhibited the AA archetype.

At HC6, TP exhibited BB archetype—enrichment at both high and low flow, while NN and turbidity exhibited the CB archetype, which is chemostasis at low flow and enrichment at high flow (Table 4, Figure 6). The levels of significance for a change in slope according to the Davies' test were marginal for turbidity (0.05) (Table 4). For SC, the archetype was CA and although the *p* value for the Davies' test was marginally significant at 0.04, ANOVA revealed that the slopes were not statistically different from zero. Furthermore, visual inspection of the *C*–*Q* plot shows that there is not really a definite pattern (Figure 6).

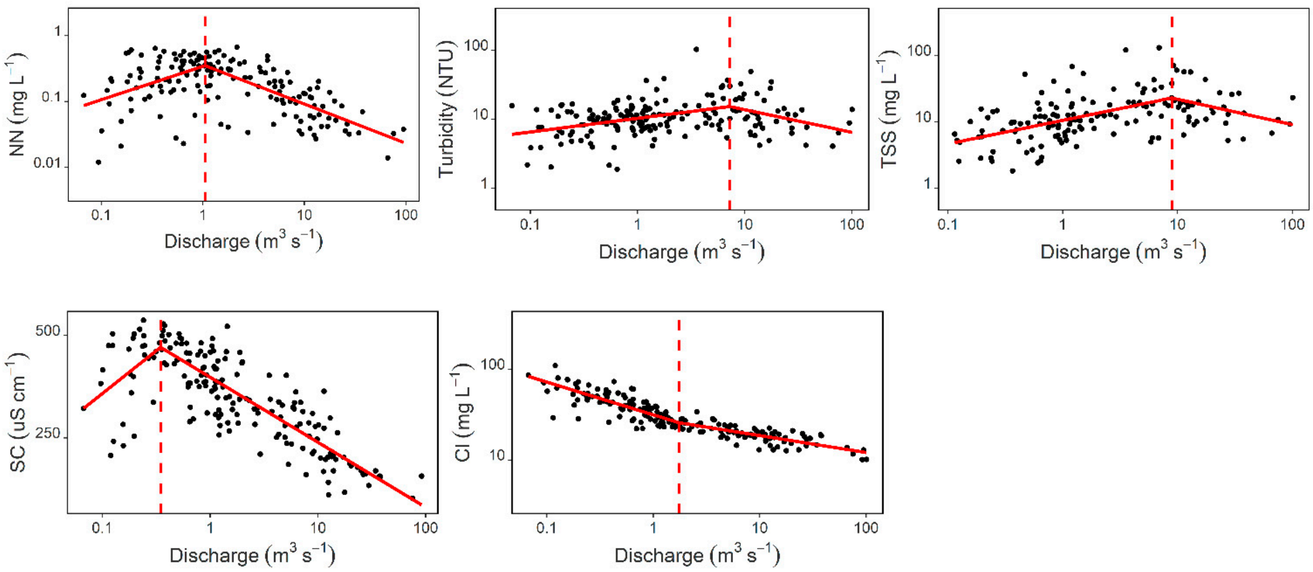


Figure 5. Concentration–discharge (*C*–*Q*) relationship plots for water quality constituents with discharge thresholds at PRB.

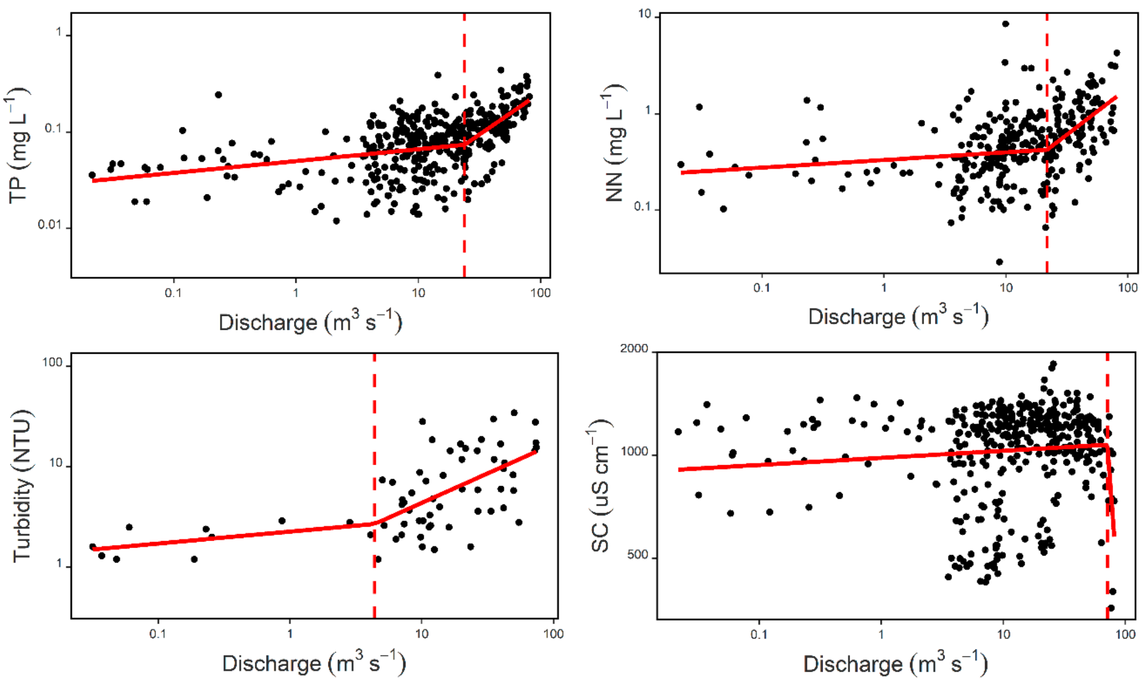


Figure 6. Concentration–discharge (*C*–*Q*) relationship plots for water quality constituents with discharge thresholds at HC6.

4. Discussion

4.1. Impacts of Flow Regime Characteristics on Water Quality in the Channels

The longer low pulse duration at SRS translates into a longer residence time of low flow conditions where biogeochemical transformation can dominate water quality constituent behavior [12]. Furthermore, the low magnitude and flow variability at SRS, combined with the low pulses, resulted in chemostatic and dilution behavior, and the absence of enrichment behavior.

At PRB, a recurring behavior of the water quality constituents was an initial enrichment in concentrations at low flow followed by dilution at high flow (BA in Table 4, Figure 5). The flow regime characteristic most responsible for this is the high pulse duration. Previous studies suggest that low flow concentration enrichment can result from the abundance and proximity of widespread constituent pools that are easily exported and mobilized to (or from) the channels [16,19,39], while the switch to dilution at high flows is indicative of constituent exhaustion (source-limitation) [12,16,19]. Key reasons for the exhaustion of constituents at PRB are the extensive high flow duration, the presence of riparian vegetation, and gentle channel slopes. As a result, there is ample opportunity for extended deposition of water quality constituents from the channels into the floodplains [9,39]. Additionally, the high frequency of low pulse at PRB indicates more in-channel sediment deposition [23,24].

The channel HC6 had the greatest flow variability that resulted in the strong enrichment behavior at high flow. The unnatural and regulated discharges at HC6 resulted in higher flashiness and steeper hydrographs that contributed to the increases in the concentrations of water quality constituents. Flashier hydrologic responses have been linked to higher concentrations of nutrients, turbidity, and TSS, from channel erosion and sediment mobilization [25]. Results from a comparative study between a rural incised (channelized) stream and an urban unchanneled stream revealed a flashier hydrologic response and higher concentrations of water quality constituents in the rural stream, for all measured components except nitrate [25]. Just as storm events are periods of high sediment mobilization [20], so are canal discharge events, which explain the predominant enrichment behavior at HC6. The higher frequency of high pulse flows at HC6 translates into a greater export of sediment loads and the constituents they contain, such as TP. Furthermore, the absence of floodplains at HC6 means that a greater volume of water quality constituents and pollutant loads can be transported downstream into ecologically sensitive ecosystems.

The clear differentiation of HC6 from PRB and SRS, as shown by the PCA, alludes to the fundamental differences between natural and man-made channels. The high discharge maximums, pulse count, rise rate, and flashiness reflect the regulated flow management in the canal as well as the channel homogeneity. This contrasts with the slough and the river that have more natural heterogenous features and generally lower values for their flow regime characteristics.

4.2. Behavior of Water Quality Constituents at Low and High Flow Conditions across the Channels

All three channels had discharge thresholds for NN. The low flow chemostasis for NN at SRS and HC6 can be attributed to greater biogeochemical control on NN availability. Nitrogen species are biogeochemically active and can have high turnover rates [44]. This rapid cycling of NN between biotic and abiotic pools can regulate availability and can lead to a chemostatic response at low flow. As for most of the water quality constituents at PRB, NN exhibited a shift from low flow enrichment to high flow dilution. In Florida, NN-rich groundwater discharge that dominates at low flow conditions may be diluted with NN-poor temporary pools (rainfall and soil water) that are activated during high flow conditions, resulting in a shift from enrichment to dilution [19,20]. Although the Upper Peace River watershed mainly recharges the groundwater, high flow periods can raise the groundwater head higher than the river stage, which then discharges into the channel, and is facilitated by the porous kart formations (sinkholes and sand-filled depressions) [27]. At HC6, the low flow chemostasis of NN reflects the biogeochemical influence from the buildup of nutrient legacy stores that is typical of managed agricultural systems [20,22]. Conversely, the high flow enrichment indicates that higher discharges are responsible for the internal release and subsequent transport of NN in the canal.

For Cl at PRB, the greater dilution at low flow and the lesser dilution at high flow can be attributed to a point source contribution from the watershed. Dilution is common for Cl because it is not significantly altered by biogeochemical processes, making it a good conservative tracer [45]. Specific conductance followed the dominant PRB pattern of dilution, but the discharge threshold occurred at a lower value compared to the other constituents, suggesting a relatively scarce pool of the constituent that is quickly diluted. Although Shark River Slough is tidal, SRS is within the upstream freshwater zone, which accounts for the dilution of SC with increasing discharge. At HC6, the high variability of SC with discharge could result from the multiple natural sources of ions in the Everglades region, including trapped seawater in groundwater intersected by canals [46]. In addition, the complexities associated with canal discharge operations may have contributed to its high concentration variability.

Of the three channels, HC6 had a discharge threshold for TP, with moderate enrichment occurring at low flow and high enrichment at high flow. At low flow conditions, more phosphorus (P) can be retained in the channel and cycled physiochemically through sorption–desorption reactions and mineral precipitation–dissolution processes, and biologically through biotic uptake and decomposition of organic matter [13]. However, as flow increases, P can be transported through advection, which can cause entrainment of sediment-bound particulate P and desorption of P from suspended particles [13,19]. Decades of continuous nutrient loading from agriculture to South Florida canals, including the Hillsboro Canal, has led to the sequestration of P, often referred to as "legacy P" in canal sediments [47]. These sediments are highly organic and have low bulk density that makes them easily entrained and susceptible to downstream transport [48,49].

At PRB, turbidity and TSS had identical behavior and discharge thresholds, indicating the similarity between the two sediment-associated constituents. The low flow enrichment of TSS results from outer bank erosion and entrainment of particles from the channel bed [20], while the change to dilution at high flow indicates an exhaustion of the eroded sediments and their deposition in the floodplains [16]. At HC6, the strong enrichment behavior at high flow for turbidity results from transport limitation, whereby higher flows allow more connectivity between the watershed and the channel, and lead to greater mobilization and transport of sediments [12].

4.3. Limitations on the Use of C–Q Relationship Models of Man-Made and Regulated Channels

Unlike natural channels that may be free flowing, the man-made canals of South Florida do not flow freely; rather, their discharges are managed to meet the water needs of the region. As a result, canals exhibit extended periods of zero flow with stagnant conditions punctuated by short durations of high flows. Therefore, the *C*–*Q* relationship models could only explain the behavior of water quality constituents for periods where there was flow. This resulted in the flow exceedance probabilities of the water quality constituents with discharge thresholds at HC6 being consistently lower than the median discharge (0.5 flow exceedance probability). The median discharge is commonly used in natural channels, especially when analyzing riverine networks, as opposed to individual channels [12,19,40]. Consequently, median discharge may not always be the appropriate metric to use as the discharge threshold in *C*–*Q* slopes for singular channels or non-riverine channels. Furthermore, at HC6, a direct interpretation for the low discharge threshold probabilities (especially for TP and NN) is that the potential of canal flows mobilizing higher concentrations of these constituents is low. This means that the flows at HC6 that can export nutrients occur infrequently; however, the discharge thresholds and their associated probabilities will vary at other locations along the Hillsboro Canal and other South Florida canals depending on discharge operations. Therefore, *C*–*Q* relationships in such canals are useful in the determination of discharge that can limit the transport of nutrients to sensitive ecosystems, which can be a potential benefit to water resource managers.

5. Conclusions

This study described the relationships between water quality and flow in three morphologically and hydrologically different channels in southern Florida: Shark River Slough, Peace River, and Hillsboro Canal. The unchanneled and shallow Shark River Slough exhibited the least flow variability, which when combined with its naturally nutrient-poor conditions, resulted in predominantly dilution behavior of its water quality constituents at higher flows. The meandering Peace River, whose characteristics most resemble a natural flow regime, exhibited intermediate flow variability. Furthermore, Peace River had the highest pulse duration that afforded an extended temporal connectivity to its floodplains and resulted in dilution behavior of all the water quality constituents at higher flows. The heavily channelized Hillsboro Canal, whose flow regime is regulated by water control structures, had the greatest flow variability, and was dominated by enrichment behavior of its water quality constituents with higher flows. This study found that *C*–*Q* relationships can be applied to canals and should be considered by water managers in discharge operations to reduce the transport of nutrient and pollutant loads downstream to ecologically delicate ecosystems.

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References

1. Schoof, R. Environmental impact of channel modification. *J. Am. Water Resour. Assoc.* **1980**, *16*, 697–701. [CrossRef]
2. Brooker, M.P. The ecological effects of channelization. *Geogr. J.* **1985**, *151*, 63–69. [CrossRef]
3. Poff, N.L.; Allan, J.D.; Bain, M.B.; Karr, J.R.; Prestegaard, K.L.; Richter, B.D.; Sparks, R.E.; Stromberg, J.C. The natural flow regime: A paradigm for river conservation and restoration. *BioScience* **1997**, *47*, 769–784. [CrossRef]
4. Sklar, F.; McVoy, C.; Van Zee, R.; Gawlik, D.; Swift, D.; Park, W.; Fitz, C.; Wu, Y.; Rudnick, D.; Fontaine, T.; et al. Hydrologic needs: The effects of altered hydrology on the Everglades. *Everglades Interim Rep.* **1999**, *2*, 1–68.
5. Carter, K.; Redfield, G.; Ansar, M.; Glenn, L.; Huebner, R.; Maxted, J.; Pettit, C.; VanArman, J. Canals in South Florida: A Technical Support Document. 2010. Available online: https://www.researchgate.net/publication/305316875_Canals_in_South_Florida_A_Technical_Support_Document (accessed on 8 May 2021). [CrossRef]
6. Schmutz, S.; Sendzimir, J. *Riverine Ecosystem Management: Science for Governing towards a Sustainable Future*; Springer Nature: Cham, Switzerland, 2018.
7. Wohl, E. Legacy effects on sediments in river corridors. *Earth Sci. Rev.* **2015**, *147*, 30–53. [CrossRef]
8. SWFMD. Canals in South Florida: A Technical Support Document. Appendix A. Basic Concepts, Hydrologic Terminology. Glossary of Terms and Abbreviations. 2010; pp. A1–A22. Available online: https://www.sfwmd.gov/sites/default/files/documents/canalssfl_appendixa-c.pdf (accessed on 8 May 2021).

9. Richter, B.D.; Baumgartner, J.V.; Braun, D.P.; Powell, J. A spatial assessment of hydrologic alteration within a river network. *Regul. Rivers Res. Manag.* **1998**, *14*, 329–340. [CrossRef]
10. Richter, B.D.; Baumgartner, J.V.; Powell, J.; Braun, D.P. A method for assessing hydrologic alteration within ecosystems. *Conserv. Biol.* **1996**, *10*, 1163–1174. [CrossRef]
11. O'Driscoll, M.; Clinton, S.; Jefferson, A.; Manda, A.; McMillan, S. Urbanization effects on watershed hydrology and in-stream processes in the southern United States. *Water* **2010**, *13*, 605–648. [CrossRef]
12. Moatar, F.; Abbott, B.W.; Minaudo, C.; Curie, F.; Pinay, G. Elemental properties, hydrology, and biology interact to shape concentration-discharge curves for carbon, nutrients, sediment, and major ions. *Water Resour. Res.* **2017**, *53*, 1270–1287. [CrossRef]
13. Withers, P.J.A.; Jarvie, H.P. Delivery and cycling of phosphorus in rivers: A review. *Sci. Total Environ.* **2008**, *400*, 379–395. [CrossRef]
14. Nilsson, C.; Renöfält, B.M. Linking flow regime and water quality in rivers: A challenge to adaptive catchment management. *Ecol. Soc.* **2008**, *13*, 18. [CrossRef]
15. Underwood, K.L.; Rizzo, D.M.; Schroth, A.W.; Dewoolkar, M.M. Evaluating Spatial Variability in Sediment and Phosphorus Concentration-Discharge Relationships Using Bayesian Inference and Self-Organizing Maps. *Water Resour. Res.* **2017**, *53*, 10293–10316. [CrossRef]
16. Zhang, Q. Synthesis of nutrient and sediment export patterns in the Chesapeake Bay watershed: Complex and non-stationary concentration-discharge relationships. *Sci. Total Environ.* **2018**, *618*, 1268–1283. [CrossRef] [PubMed]
17. Malan, H.L.; Day, J.A. Linking flow, water quality and potential effects on aquatic biota within the Reserve determination process. *Water SA* **2003**, *29*, 297–304. [CrossRef]
18. Godsey, S.E.; Kirchner, J.W.; Clow, D.W. Concentration–discharge relationships reflect chemostatic characteristics of US catchments. *Hydrol. Process.* **2009**, *23*, 1844–1864. [CrossRef]
19. Diamond, J.S.; Cohen, M.J. Complex patterns of catchment solute-discharge relationships for coastal plain rivers. *Hydrol. Process.* **2018**, *32*, 388–401. [CrossRef]
20. Rose, L.A.; Karwan, D.L.; Godsey, S.E. Concentration-discharge relationships describe solute and sediment mobilization, reaction, and transport at event and longer timescales. *Hydrol. Process.* **2018**, *32*, 2829–2844. [CrossRef]
21. Thompson, S.E.; Basu, N.B.; Lascurain, J.; Aubeneau, A.; Rao, P.S.C. Relative dominance of hydrologic versus biogeochemical factors on solute export across impact gradients. *Water Resour. Res.* **2011**, *47*, 1–20. [CrossRef]
22. Basu, N.B.; Thompson, S.E.; Rao, P.S.C. Hydrologic and biogeochemical functioning of intensively managed catchments: A synthesis of top-down analyses. *Water Resour. Res.* **2011**, *47*, 1–12. [CrossRef]
23. Hayes, D.S.; Brändle, J.M.; Seliger, C.; Zeiringer, B.; Ferreira, T.; Schmutz, S. Advancing towards functional environmental flows for temperate floodplain rivers. *Sci. Total Environ.* **2018**, *633*, 1089–1104. [CrossRef]
24. Graf, W.L. Downstream hydrologic and geomorphic effects of large dams on American rivers. *Geomorphology* **2006**, *79*, 336–360. [CrossRef]
25. Shields, F.D.; Lizotte, R.E.; Knight, S.S.; Cooper, C.M.; Wilcox, D. The stream channel incision syndrome and water quality. *Ecol. Eng.* **2010**, *36*, 78–90. [CrossRef]
26. Lodge, T.E. *The Everglades Handbook: Understanding the Ecosystem*, 3rd ed.; CRC Press: Cleveland, OH, USA, 2010; 424p.
27. Metz, P.A.; Lewelling, B.R. Hydrologic Conditions that Influence Streamflow Losses in a Karst Region of the Upper Peace River, Polk County, Florida. *Sci. Investig. Rep.* **2009**, *5140*. [CrossRef]
28. Bolster, C.H.; Saiers, J.E. Development and evaluation of a mathematical model for surface-water flow within the Shark River Slough of the Florida Everglades. *J. Hydrol.* **2002**, *259*, 221–235. [CrossRef]
29. Everglades National Park (U.S. National Park Service). Available online: https://www.nps.gov/ever/learn/nature/evergeology.htm (accessed on 31 July 2021).
30. Daroub, S.H.; Van Horn, S.; Lang, T.A.; Diaz, O.A. Best management practices and long-term water quality trends in the everglades agricultural area. *Crit. Rev. Environ. Sci. Technol.* **2011**, *41*, 608–632. [CrossRef]
31. SWFWMD. Upper Peace River: An Analysis of Minimum Flows and Levels. Volume 2: Technical Appendices. 2002, pp. 1–294. Available online: https://www.researchgate.net/profile/Clifford-Dahm/publication/267260603_A_Review_of_Upper_Peace_River_An_Analysis_of_Minimum_Flows_and_Levels_Prepared_by/links/549b39730cf2b803713719ea/A-Review-of-Upper-Peace-River-An-Analysis-of-Minimum-Flows-and-Levels-Prepared-by.pdf (accessed on 8 May 2021).
32. Kelly, M. Peace River Comprehensive Watershed Management Plan Draft. I. Brooksville, FL: N.p. Print. 2001. Available online: http://www.polk.wateratlas.usf.edu/upload/documents/PEACE%20RIVER%20CWM%20PART1.pdf (accessed on 8 May 2021).
33. Gaiser, E.; Childers, D. Water Quality Data (Grab Samples) from the Shark River Slough, Everglades National Park (FCE), from May 2001 to Present. Environmental Data Initiative. 2019. Available online: https://agris.fao.org/agris-search/search.do?recordID=QN2019001307404 (accessed on 12 December 2019).
34. Conservancy, N. *Indicators of Hydrologic Alteration (IHA) Software Version 7.1 User's Manual*; The Nature Conservancy: Charlottesville, VA, USA, 2009. [CrossRef]
35. Baker, D.B.; Richards, R.P.; Loftus, T.T.; Kramer, J.W. A new flashiness index: Characteristics and applications to Midwestern rivers and streams. *J. Am. Water Resour. Assoc.* **2004**, *40*, 503–522. [CrossRef]
36. Oueslati, O.; De Girolamo, A.M.; Abouabdillah, A.; Kjeldsen, T.R.; Lo Porto, A. Classifying the flow regimes of Mediterranean streams using multivariate analysis. *Hydrol. Process.* **2015**, *29*, 4666–4682. [CrossRef]

37. Sârbu, C.; Pop, H.F. Principal component analysis versus fuzzy principal component analysis: A case study: The quality of danube water (1985–1996). *Talanta* **2005**, *65*, 1215–1220. [CrossRef]
38. PCA basics in #Rstats. Available online: https://swampthingecology.org/blog/pca-basics-in-rstats/ (accessed on 8 May 2021).
39. O'Donnell, B.; Hotchkiss, E.R. Coupling Concentration and Process-Discharge Relationships Integrates Water Chemistry and Metabolism in Streams. *Water Resour. Res.* **2019**, *55*, 10179–10190. [CrossRef]
40. Botter, M.; Burlando, P.; Fatichi, S. Anthropogenic and catchment characteristic signatures in the water quality of Swiss rivers: A quantitative assessment. *Hydrol. Earth Syst. Sci.* **2019**, *23*, 1885–1904. [CrossRef]
41. R Core Team. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. 2019. Available online: https://www.R-project.org/ (accessed on 8 May 2021).
42. Muggeo, V.M.R. Testing with a nuisance parameter present only under the alternative: A score-based approach with application to segmented modelling. *J. Stat. Comput. Simul.* **2016**, *86*, 3059–3067. [CrossRef]
43. Muggeo, M.V.M.R. Package 'segmented'. *Biometrika* **2017**, *58*, 525–534.
44. Musolff, A.; Schmidt, C.; Selle, B.; Fleckenstein, J.H. Catchment controls on solute export. *Adv. Water Resour.* **2015**, *86*, 133–146. [CrossRef]
45. Jarvie, H.P.; Sharpley, A.N.; Scott, J.T.; Haggard, B.E.; Bowes, M.J.; Massey, L.B. Within-river phosphorus retention: Accounting for a missing piece in the watershed phosphorus puzzle. *Environ. Sci. Technol.* **2012**, *46*, 13284–13292. [CrossRef]
46. Chen, M.; Daroub, S.H.; Lang, T.A.; Diaz, O.A. Specific Conductance and Ionic Characteristics of Farm Canals in the Everglades Agricultural Area. *J. Environ. Qual.* **2006**, *35*, 141–150. [CrossRef]
47. Diaz, O.A.; Daroub, S.H.; Stuck, J.D.; Clark, M.W.; Lang, T.A.; Reddy, K.R. Sediment Inventory and Phosphorus Fractions for Water Conservation Area Canals in the Everglades. *Soil Sci. Soc. Am. J.* **2006**, *70*, 863–871. [CrossRef]
48. Daroub, S.H.; Stuck, J.D.; Lang, T.A.; Diaz, O.A. Particulate Phosphorus in the Everglades Agricultural Area: I–Introduction and Sources. *EDIS* **2002**, *1*, 1–8. [CrossRef]
49. Das, J. Characterization of Physicochemical Properties, Phosphorus (P) Fractions and P Release of the Everglades Agricultural Area (EAA) Canal Sediments. Ph.D. Thesis, University of Florida, Gainesville, FL, USA, 2010.