

A Multivariate Water Quality Investigation of Select Drainage Ditches in the Arroyo Colorado River Watershed, Texas

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Texas Water Resources Institute Technical Report No. 424

May 2012

This report was created through the Arroyo Colorado Agricultural Nonpoint Source Assessment project funded by the United States Environmental Protection Agency through a Clean Water Act §319(h) grant administered by the Texas State Soil and Water Conservation Board (TSSWCB).

Arroyo Colorado Agricultural Nonpoint Source Assessment

The report highlights the accomplishment of Task 7 of Project number 06-10 administered by TSSWCB

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List of Symbols and Abbreviations

Symbol	Description	Symbol	Description
TMDL	Total Maximum Daily Load	WPP	Water Protection Plan
CC1	Cameron County Site 1 (Harding Ranch Road 3 mi N. of 508 and 1420)	CC2	Cameron Count Site 2 (ABD Rd & FM 1479 4 mi S. of Hwy 83)
HC1	Hidalgo County Site 1 (Mile 4 North FM 491)	HC2	Hidalgo County Site 2 (3 mi. N of US Military Hwy 281 & 493)
DO	Dissolved Oxygen	CBOD	Carbonaceous Biochemical Oxygen Demand
TSS	Total Suspended Solids	OP	Orthophosphate Phosphorous
TP	Total Phosphorous	TKN	Total Kjeldahl Nitrogen
ANOVA	Analysis of Variance	KW	Kruskal Wallis
FDC	Flow Duration Curves	LDC	Load Duration Curves
ACF	Auto Correlation Function	TSSWCB	Texas State Soil and Water Conservation Board
TCEQ	Texas Commission on Environmental Quality	USEPA	United States Environmental Protection Agency
QAPP	Quality Assurance Protection Plan		

Introduction

Drainage ditches are widely used for agricultural water management to help remove excess water from fields, which mitigates the effects of water logging and salinization. These ditches act as a direct hydraulic link between the agricultural field and streams and rivers. As such, there is an increasing concern that drainage ditches can act as conduits for nutrient transport and, in conjunction with other point and nonpoint sources, can contribute to eutrophication and decreased dissolved oxygen levels in receiving water bodies. Studies have linked drainage ditches to hypoxia in the Gulf of Mexico and eutrophication of the Great Lakes (Dagg and Breed, 2003; Moore et al., 2010). However, there is also evidence suggesting that drainage ditches can help attenuate the loadings of phosphorus and suspended sediments (R. Kröger et al., 2008) and thus foster water quality improvements at a watershed scale. There is a growing interest in understanding the nutrient behavior in drainage ditches both in the United States (Bhattarai et al. 2009; Moore, et al. 2010; Ahiablame et al. 2011) as well as other parts of the world (Nguyen and Sukias 2002; Leone et al. 2008; Bonaiti and Borin 2010).

The Arroyo Colorado River is a distributary of the Rio Grande River whose flows are sustained primarily by discharges from wastewater treatment plants and nonpoint source loadings from urban and agricultural sources. The Arroyo Colorado River watershed along the US-Mexico border region is not only one of the fast-growing urban areas in the United States, but it also has a strong agricultural base. Nearly 80% of the approximately 700 sq. mile watershed is designated as cropland (Figure 1). Being in a semi-arid region, rainfall is highly erratic and often occurs as high intensity, short duration storms (Norwine et al. 2007). As such, farmers rely on irrigation to grow cotton, grain (corn and sorghum), sugar cane, citrus and vegetables. Figure 1 also depicts the labyrinth of drainage ditches within the watershed that transport water, sediment, and nutrients away from the farmlands. The tidal segment of the Arroyo Colorado River is listed as impaired for low dissolved oxygen on the State of Texas 303(d) list. The low dissolved oxygen in the tidal segment is primarily linked to high loadings of nutrients and oxygen demanding substances in the upland (non-tidal) areas of the watershed (Raines and Miranda 2002). Watershed modeling studies conducted to estimate TMDLs in the region have indicated that over 90% pollutant load reductions are necessary to improve dissolved oxygen conditions in the tidal segment (Raines and Miranda 2002; Hernandez 2007). Given the impracticality of such drastic reductions, a multistakeholder watershed planning group was designated to develop a watershed

protection plan (WPP) that seeks to improve water quality through better land and wastewater management in the watershed (ACWPP 2007).

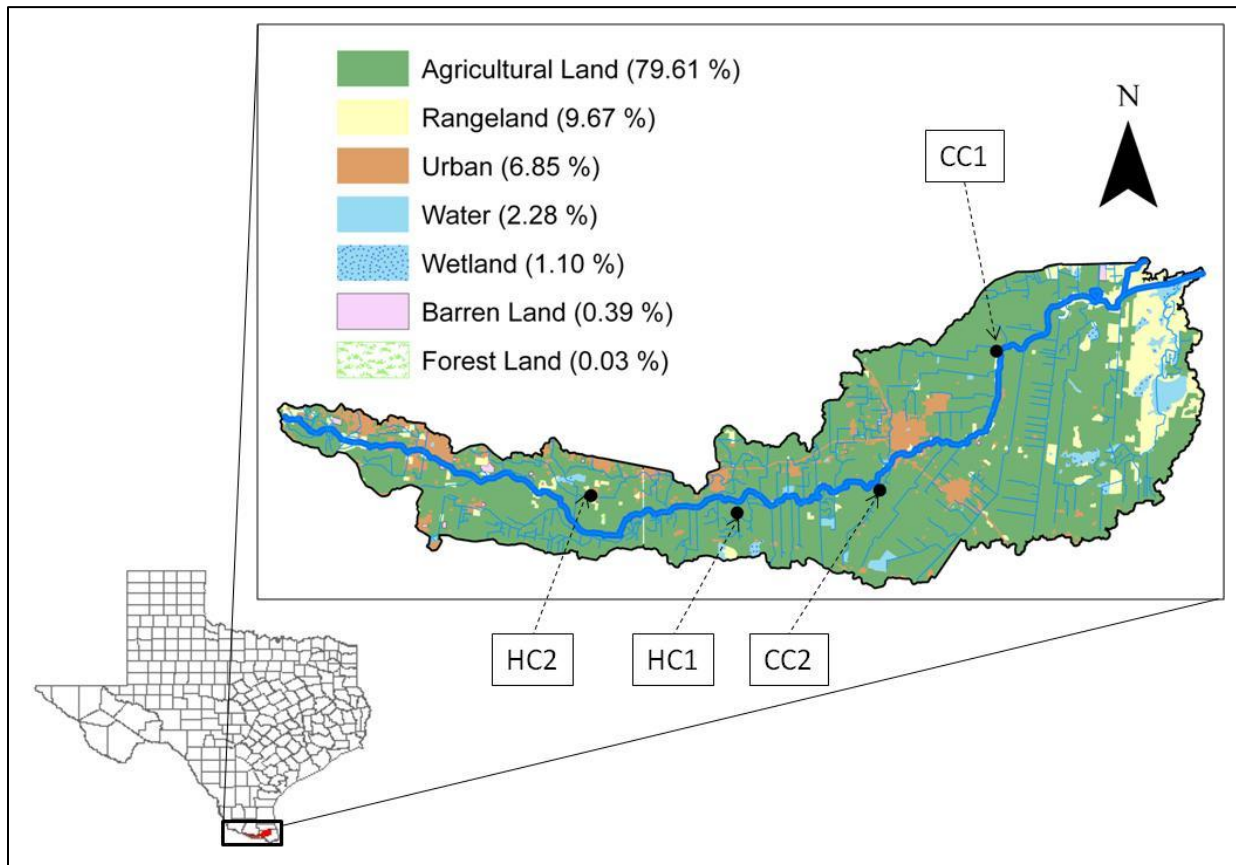


Figure 1: Land use and Land cover view of the Arroyo Colorado River Watershed, Lower Rio Grande Valley, Texas

An important component of the Arroyo Colorado WPP is to evaluate and quantify the nature and extent of nutrient loadings from agricultural activities in the region. This information is fundamental to promote best management practices and foster sustainable agricultural activities (Hernandez and Uddameri 2010). As most agricultural runoff is carried to the Arroyo Colorado River through the drainage ditches, quantifying nutrient dynamics in the drainage ditches is of paramount importance. Previous efforts aimed at quantifying nutrient loadings from drainage ditches have been limited to a few synoptic measurements and as such provide limited information. Therefore, a long-term (multiyear), multisite, multivariate water quality sampling campaign was undertaken through this study with the broad goal of understanding the spatio-temporal variability of nitrogen species (Total Kjeldahl Nitrogen (TKN), ammonia-nitrogen ($\text{NH}_3\text{-N}$), nitrite + nitrate-nitrogen), phosphorus compounds (total and dissolved phosphorus) and other water quality parameters. More specifically, the focus of the study was

to develop fundamental insights about the role of hydraulic controls (flows) on nutrient concentrations. An edge-of-field water quality monitoring program was also carried out in conjunction with the drainage ditch monitoring to evaluate whether drainage ditches attenuated or exacerbated nutrient loadings from croplands.

Field Sites and Sampling Design

Four representative drainage ditches were selected for extensive monitoring based on recommendations from the Texas State Soil Water Conservation Board (TSSWCB). Two of these sites were located in Cameron County and two were in Hidalgo County (Figure 1). Approximate contributing drainage areas (sub-watersheds) corresponding to these monitoring locations were delineated using ArcGIS V 9.3 (ESRI Inc., Redlands, CA) and integrated with recent land use land cover (LULC) data to obtain sub-watershed characteristics (Figure 2). The contributing sub-watersheds were predominantly agricultural, varied in size, and provided a representative sample of different drainage ditches in the area.

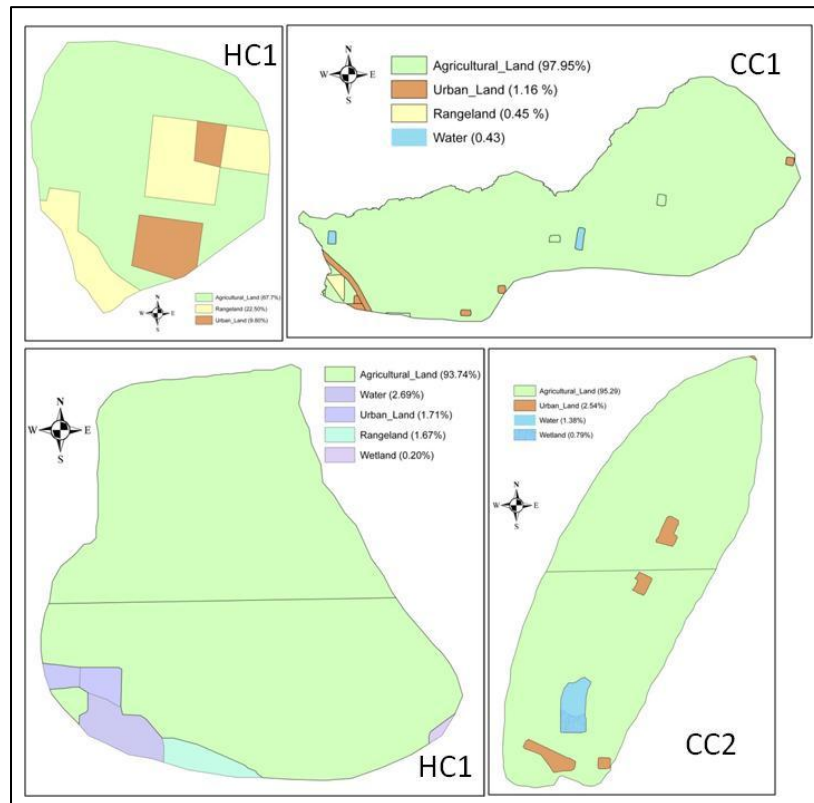


Figure 2: Contributing sub-watershed characteristics for the monitored drainage ditches

A modified, stratified, random sampling approach was adopted to collect data over time. According to this approach, sampling was carried out monthly (stratified design), but the sampling date within the

month was selected at random to avoid any sampling bias (randomized design). However, the sampling dates were spaced sufficiently far apart (at least two weeks) to minimize auto-correlation effects and ensure independence among sampling events. A total of 37 sampling events were carried out during August 2008 – November 2011. The sampling was carried out on the same day at all sites to facilitate paired comparisons. While the number of locations sampled and the frequency of sampling were clearly limited by fiscal and logistic constraints, the design captured variability over a 2-year period, which included a protracted period of drought and two major storm events (Hurricane Dolly in 2008 and Tropical Storm Ike in 2010).

In addition to monthly grab sampling, the project also evaluated the water quality characteristics of time-averaged composite samples on select dates and locations. The composite sample was obtained using a field autosampler, which took samples from the ditch every 30 minutes over a 24-hour period. The autosampler and the collection set up are presented in Figure 3. The sample was filtered at the end of the collection period and analyzed for nutrients using the same analytical methods listed in Table 2. Every attempt was made to obtain these composite samples around a major rainfall event. However, the erratic characteristics of the rainfall events (i.e., either large tropical storms that prevented access to sites) or very low intensity events that did not yield considerable runoff added difficulties to the collection process. A total of eight sampling events were carried out in all and are summarized in Table 1. However, the data from two of these events were not used in the analysis due to instrument failures in the field. A grab sample was also collected at the end of the composite sampling period to facilitate pairwise comparisons between the two sampling methods.



Figure 3: Composite sample collection set up at one of the sites (HC1)

Table 1: Summary of Composite samples collected to account for storm water events

Date	Site	Last Rainfall Event (in)	Remarks
19 September, 2009	CC1	0.06	Instrument Failure
23 January, 2011	CC1	1.22	
27 February, 2011	CC1 & HC1	0.02	
27 March, 2011	CC2 & HC1	0.01	
28 August, 2011	CC2* & HC1	0.04	*Instrument Failure at CC2; HC1 successful

Table 2: Field and laboratory protocols used to measure water quality parameters

Component	Units	Analysis Method	Equipment Used
pH	Standard Units	EPA 150.1 TCEQ SOP	YSI 556 MPS
DO	mg/L	EPA 150.1 TCEQ SOP	YSI 556 MPS
Conductivity	µS/cm	SM 2520B	YSI 556 MPS
Turbidity	NTU		HACH 2100P
Temperature	C	EPA 170.1 TCEQ SOP	YSI 556 MPS
Flow	cfs	TCEQ SOP	Marsh McBirney Flowmate
CBOD, 5-day	mg/L	5210B Standard Method	YSI 5100
TSS	mg/L	EPA 160.2	Hot oven, glass fibre filters
Ortho Phosphate	mg/L	4110 B Std. Methods	Spectrophotometer (Ascorbic Acid Method)
Total Phosphorous	mg/L	4110 B Std. Methods	Spectrophotometer (Ascorbic Acid Method)
Total Nitrite + Nitrate Nitrogen	mg/L	4110 B Standard Methods	Spectrophotometer and Nitrate Electrode method
Ammonia Nitrogen	mg/L	EPA 350.3	Ammonia Electrode
Total Kjeldahl Nitrogen	mg/L	EPA 351.3	Labconco Rapid Still II and Spectrophotometer

A suite of 13 water quality parameters, as listed in Table 2, were measured at each site using approved field and laboratory protocols. All measurements were made in duplicate both in the field and at the lab. Three sets of grab samples (one unfiltered, one unfiltered but preserved at pH < 2 and one field filtered using 0.45 µm filters) were collected in the field for laboratory analysis of nutrients, total suspended solids (TSS) and carbonaceous-biological oxygen demand (CBOD). Instantaneous velocity measurements were also made in duplicate using the Marsh McBirney FloMate[®] instrument and used to compute flow

via the area-velocity method. All field probes were routinely calibrated and maintained per manufacturer's specifications. Laboratory analysis used approved standard methods for water and wastewater analysis (AHPA, 2010) and adhered to USEPA approved QA/QC protocols as stated in the QAPP (QAPP, 2008). Consistency checks such as total phosphorus (TP) being greater than or equal to orthophosphate phosphorus (OP) and $\text{NH}_3\text{-N}$ being less than or equal to the TKN were also used as appropriate. Other relevant hydro-meteorological data such as rainfall, relative humidity and temperature were compiled from a nearest weather station located within the watershed (Agrilife Extension 2011). The edge-of-field sampling was carried out by personnel from Texas AgriLife Extension Service as part of another task in the 06-10 *Arroyo Colorado Agricultural Nonpoint Source Assessment* project.

Conceptual Model and Hypotheses Development

Three of the four drainage ditches (CC1, CC2, and HC1) exhibited perennial flow throughout the period of study even when significant drought conditions persisted in the area. One site, HC2, had a stagnant water column during the study period, but had no measurable flow. The depth of the water column and the flow rates were noted to vary considerably throughout the sampling period. The flows in the drainage ditch could therefore be conceptualized to include relatively short flow paths, comprised of overland flow near the sampling points, long flow paths, which brought water from farther portions of the contributing drainage area, and deeper flow paths. The longer flow paths (particularly the subsurface components) can be viewed as the cause for persistent flow in the ditches during dry periods while shorter flow paths (overland flow) can be envisioned to mostly control flow under wet weather conditions.

Based on the flow regime conceptualization, the concentration of pollutants between high and low flow regimes are hypothesized to be different particularly for TSS, which either are filtered out in the subsurface or settled out in the ditch under low flow conditions. Phosphorus compounds are known to undergo a variety of reactions including sorption and co-precipitation with calcite (CaCO_3) and are generally strongly correlated with suspended solids (Kadlec and Wallace 2009). Therefore, it is expected that phosphorus concentrations are also likely to exhibit differences with flow regimes. However, unlike TSS, the uptake of phosphorus by plants and subsequent release during senescence are likely to have some impacts in masking flow-related differences as periods of senescence will likely occur during months when the flows are going to be low (i.e., moisture stresses on the vegetation). Furthermore, if

the soils in the contributing drainage area are low in phosphorus, then high flow events will have a dilution effect and lead to smaller concentrations.

As drainage ditches are open to atmosphere and biologically active systems, they are generally known to contain relatively greater amounts of oxidized forms of nitrogen (nitrite+nitrate) than reduced forms (TKN). Agricultural streams in many parts of the United States are reported to be major contributors of nitrates ($\text{NO}_3\text{-N}$) to rivers and lakes (David et al. 1997; Goolsby et al. 1997; Goolsby et al. 2001; Mitsch et al. 2001; Royer et al. 2006). However, drainage ditches under investigation exhibit density-driven stratification due to the presence of salts and sediments. Therefore, the upper portions of the ditch are hypothesized to be under oxidizing conditions conducive to nitrification reactions, while the deeper sections may be under reduced conditions facilitating denitrification reactions (Jetten et al. 1997). The denitrification process in natural waters is known to occur even before all the oxygen in the water column is completely depleted (Kuenen and Robertson 1988). However, the extent of denitrification is also critically controlled by the availability of organic carbon source (Kadlec and Wallace 2009).

Based on the above discussion, it is clear that certain conditions found in the drainage ditches, such as deeper flow channels, lower flow rates (lesser oxygenation) and higher organic matter due to detritus, can facilitate removal of nitrates via the process of denitrification, particularly in comparison with direct runoff from agricultural fields where nitrate attenuation is less favorable. Therefore, it is hypothesized that nitrate concentrations in the drainage ditches are likely to be lower than those collected at the edge-of-field. The amount of dissolved oxygen in the stream is inversely correlated to temperature. Furthermore, nitrate concentrations in the stream are likely going to be lower in summer months than in winter months (if all other factors stay the same). However, the nature and extent of nitrate (oxidized nitrogen) removal in drainage ditches can be subject to several confounding factors. While deeper channels are likely to facilitate nitrate reductions, they are likely to have higher flow rates (Chapra, 1996). These higher flow rates can increase the re-aeration rate and facilitate deeper penetration of oxygen molecules, which in turn can limit the amount of denitrification. Higher flow rates can also induce rate limitations on the conversion of TKN to nitrate (nitrification step) as TKN molecules spend less time in the ditch for the reaction to go to completion. As denitrification depends upon the amount of nitrate produced, higher flow rates can also lead to limited denitrification. Considering all these factors it is hypothesized that nitrate concentrations are inversely proportional to the ratio of depth to

flow rate, which is referred to as nitrate reduction index in this study and represents the hydraulic residence time per unit area of the channel.

Statistical Analysis

Exploratory data analyses (EDA), which employs a suite of visualization tools such as box plots, quartile (Q-Q) plots, factor separated scatter plots, and autocorrelation functions (ACF) (Cleveland 1993; Qian 2010), were utilized to understand variability in the observed data. In particular, EDA techniques were used to evaluate the reasonableness of data to normality (using Q-Q plots), independence (ACF plots) and homoskedasticity, which form the underlying basis of parametric hypothesis tests (Hamilton 1994). Parametric statistical procedures including t-tests, one-way and two-way analysis of variance (ANOVA) have been commonly used to evaluate water quality data in drainage ditches (Smith et al. 2005; R. Kröger et al., 2008; Rocha et al. 2008; Bhattarai et al., 2009; Moore et al., 2010; Ahiablame et al., 2011).

The selection of statistical parametric methods over non-parametric methods is generally based on that they typically exhibit greater power to discern true changes (i.e., lower type-II errors) when the underlying assumptions are true (Hamilton 1994). While parametric methods are generally noted to be robust to deviations from normality, outliers or extreme values can still significantly impact the results of these tests (Hamilton 1994). Non-parametric counterparts to t-test (Mann-Whitney test), one-way ANOVA (Kruskall-Wallis test) and two-way ANOVA (Friedman's test) have been proposed in the literature and are useful when the dataset has considerable variability and does not fully satisfy the parametric assumptions (Conover 1980). The study area in semi-arid South Texas is known to exhibit considerable climatic variability (Norwine et al., 2007). Therefore, the flow, vegetation and water quality characteristics in the drainage ditches exhibit significant fluctuations. As such, non-parametric tests were primarily employed in this study. The statistical analyses were performed using R statistical language version 2.14.1 due to easy access to various EDA and hypothesis testing tools (Hornik 2011). The statistical data analyses were used to evaluate various hypotheses related to water quality in the ditches, the results of which are discussed next.

Results and Discussion

Exploratory Data Analysis and Evaluation of Parametric Assumptions

A comprehensive exploratory data analysis was performed to obtain initial insights into the observed dataset and evaluate the assumptions of normality, independence and homoskedasticity. Comparison of

parametric and non-parametric summary statistical measures indicated that the data are not normally distributed and typically skewed (Table 3). Chemical concentrations are known to manifest as a multiplicative effect of several random processes and as such are likely to follow log-normal distribution (Ott, 1995). Q-Q plots were therefore generated using log-transformed data and compared to theoretical normal distribution function. An illustrative Q-Q plot is presented in Figures 4-6 for one site (Q-Q plots for other sites can be seen in Appendix A, Figures AF 1 - AF 9).

The departures from normality at upper and lower quartiles is evident for most water quality parameters in Figures 4-6, and these are indicative of heavy tails and presence of extreme values in the dataset. This behavior is reflective of the climatic variability in the region, which can be gleaned from deviations in flows and temperature. Behavior such as this suggests that water quality is greatly influenced by hydro-climatic conditions, particularly flows. Also, data pertaining to concentrations of Orthophosphate-Phosphorous and NH₃-N in the drainage ditches indicate several non-detects at the sites and as such the distributions show negative skewness. Except in the case of CBOD, log-transformation of the data is not likely to be sufficient to make the water quality parameters be represented using the normal distribution.

Table 3: Descriptive statistics for the monitored water quality parameters for the drainage ditches

	Mean	Median	Std. Dev	IQR	Kurtosis	Skewness
CC1						
Temperature (oC)	22.549	23.760	5.350	8.490	-0.714	-0.573
Turbidity (NTU)	65.678	62.267	44.488	39.407	3.415	1.496
Dissolved Oxygen (mg/L)	4.748	4.520	1.832	2.006	0.159	0.018
Specific Conductance (µS/cm)	5418.024	4178.000	2659.216	4960.000	-1.237	0.582
pH	7.582	7.760	0.666	0.432	4.858	-1.701
Flow (cfs)	4.572	3.759	4.022	2.260	8.409	2.611
CBOD (mg/L)	70.579	48.880	57.064	55.746	-0.034	1.107
TSS (mg/L)	80.161	80.000	40.855	45.000	1.103	0.900
OP (mg/L)	0.045	0.010	0.065	0.053	13.288	3.276
TP (mg/L)	0.551	0.249	0.606	0.643	3.598	1.879
Total Kjeldahl Nitrogen (mg/L)	0.445	0.431	0.131	0.104	1.965	0.191
Ammonia Nitrogen (mg/L)	0.038	0.010	0.045	0.039	2.455	1.775
Nitrite + Nitrate Nitrogen (mg/L)	1.138	0.400	1.298	1.273	1.249	1.440
CC2						
Temperature (oC)	24.063	24.900	5.265	9.305	-0.792	-0.360
Turbidity (NTU)	111.043	69.500	109.370	87.699	2.643	1.757
Dissolved Oxygen (mg/L)	4.999	5.020	2.225	2.230	0.248	-0.387
Specific Conductance (µS/cm)	5310.565	4921.000	2174.413	3733.000	-0.822	0.284
pH	7.205	7.260	0.515	0.577	2.760	-1.523
Flow (cfs)	2.619	2.001	2.441	1.996	10.240	2.742
CBOD (mg/L)	69.077	64.965	40.745	62.481	-0.856	0.441
TSS (mg/L)	113.629	85.000	84.137	105.000	1.195	1.331
OP (mg/L)	0.122	0.088	0.093	0.139	0.041	0.833
TP (mg/L)	0.881	0.622	0.777	0.861	1.473	1.412
Total Kjeldahl Nitrogen (mg/L)	0.418	0.410	0.141	0.121	1.543	0.604
Ammonia Nitrogen (mg/L)	0.118	0.010	0.425	0.055	29.883	5.426
Nitrite + Nitrate Nitrogen (mg/L)	1.331	0.632	2.205	1.053	19.561	4.116
HC1						
Temperature (oC)	25.601	25.510	5.580	8.940	-0.698	-0.413
Turbidity (NTU)	154.909	149.000	73.148	103.834	-0.539	0.091
Dissolved Oxygen (mg/L)	4.521	4.790	2.067	2.645	-0.523	-0.763
Specific Conductance (µS/cm)	2785.113	2401.000	1005.133	818.000	0.761	1.236
pH	7.183	7.300	0.536	0.600	0.267	-0.561
Flow (cfs)	11.119	9.497	9.307	10.671	6.181	2.114
CBOD (mg/L)	65.502	60.281	37.625	43.235	0.984	0.848
TSS (mg/L)	118.952	115.000	55.407	67.500	0.616	0.543
OP (mg/L)	0.157	0.165	0.093	0.165	-0.633	0.103
TP (mg/L)	1.344	0.734	1.172	1.547	1.368	1.307
Total Kjeldahl Nitrogen (mg/L)	0.441	0.429	0.148	0.150	0.387	0.260
Ammonia Nitrogen (mg/L)	0.044	0.010	0.064	0.034	6.783	2.513
Nitrite + Nitrate Nitrogen (mg/L)	0.978	0.661	1.082	0.922	2.003	1.653
HC2						
Temperature (oC)	27.298	27.660	6.644	22.826	-0.547	-0.387
Turbidity (NTU)	194.929	166.000	156.738	140.365	7.500	2.390
Dissolved Oxygen (mg/L)	4.909	4.920	2.519	2.785	-0.317	-0.264
Specific Conductance (µS/cm)	4597.194	3182.000	3750.590	4383.500	3.646	1.861
pH	7.325	7.310	0.728	0.715	0.547	-0.385
Flow (cfs)	No Measurable flow					
CBOD (mg/L)	65.850	49.167	45.429	65.677	-0.555	0.690
TSS (mg/L)	181.528	135.000	137.266	117.500	0.867	1.326
OP (mg/L)	0.198	0.119	0.166	0.219	0.764	1.150
TP (mg/L)	1.810	1.360	2.133	1.594	17.034	3.715
Total Kjeldahl Nitrogen (mg/L)	0.422	0.400	0.174	0.225	0.326	0.465
Ammonia Nitrogen (mg/L)	0.034	0.010	0.037	0.039	1.138	1.506
Nitrite + Nitrate Nitrogen (mg/L)	1.431	0.686	1.511	2.053	-0.006	1.156

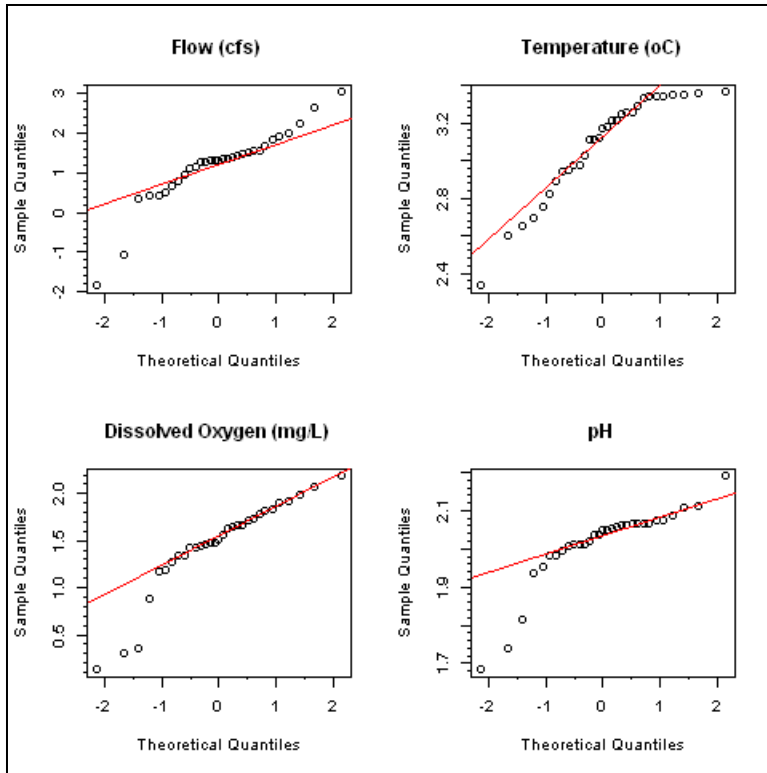


Figure 4: Q-Q plots for measured field parameters at CC1

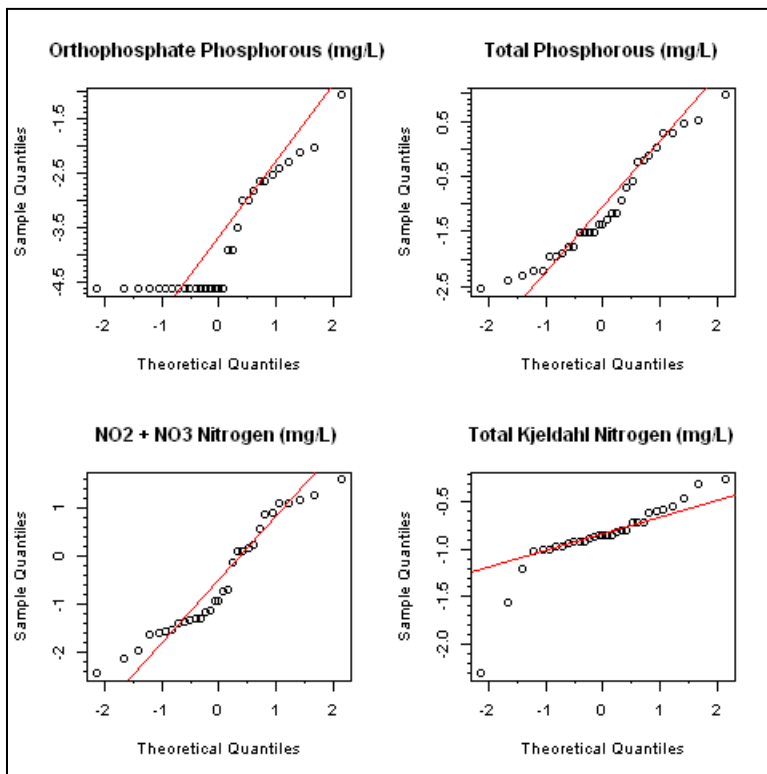


Figure 5: Q-Q plots for measured nutrients at CC1

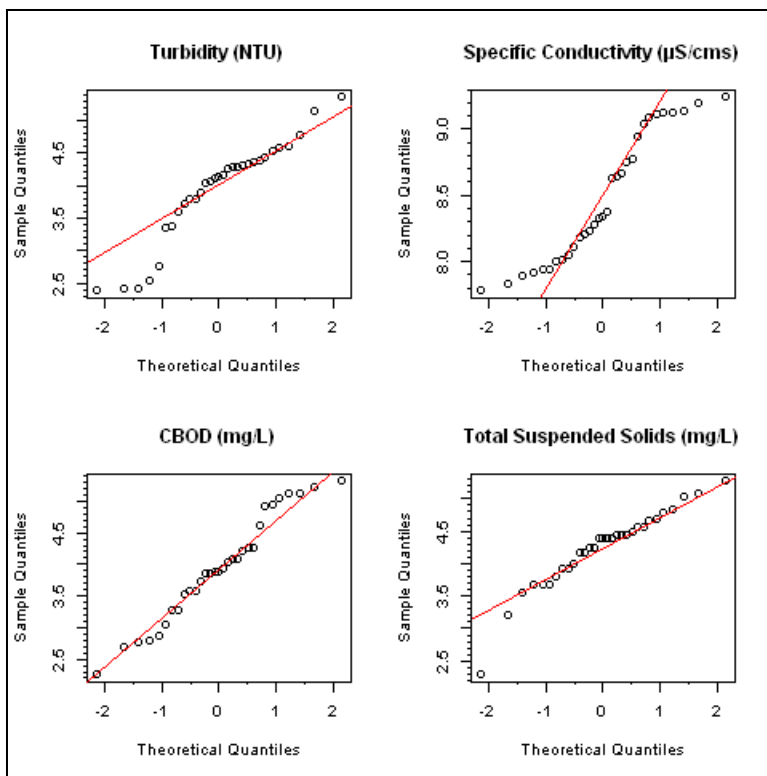


Figure 6: Q-Q plots for measured water quality indicators at site CC1

ACF plots depict how data collected at a certain time are correlated to values observed at previous times (lags). As data were collected on a monthly scale, each lag in Figures 7–9 correspond to a specified number of months (e.g., lag 1 previous month, lag 2 two previous months). ACF plots are useful to detect the presence of seasonality and independence of sampling events. The ACF plots for one site are presented in Figures 5 and 6 and the autocorrelation functions for other plots are summarized in Appendix A, figures AF 10-AF 18.

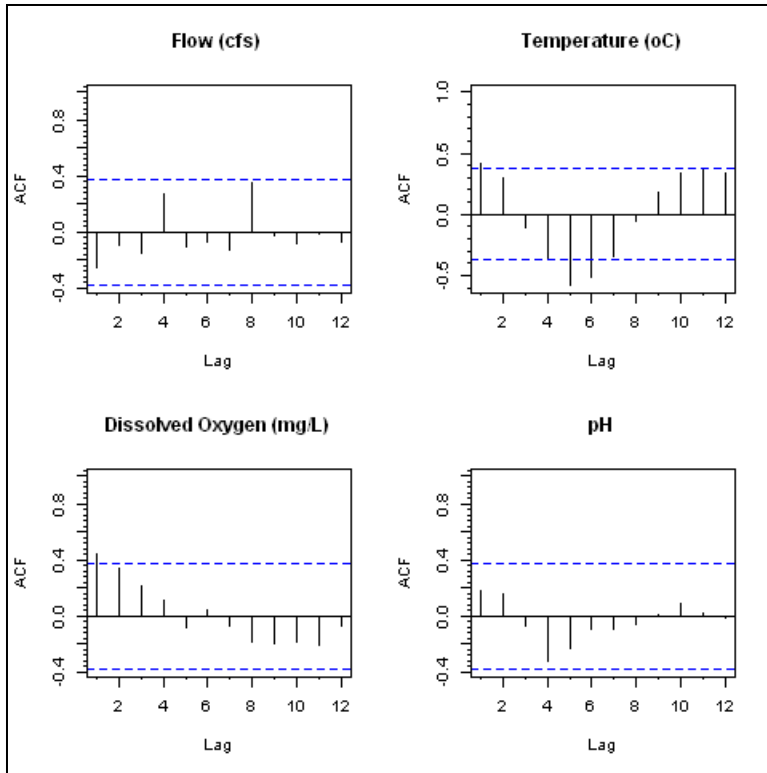


Figure 7: ACF plots for measured field parameters at site CC1

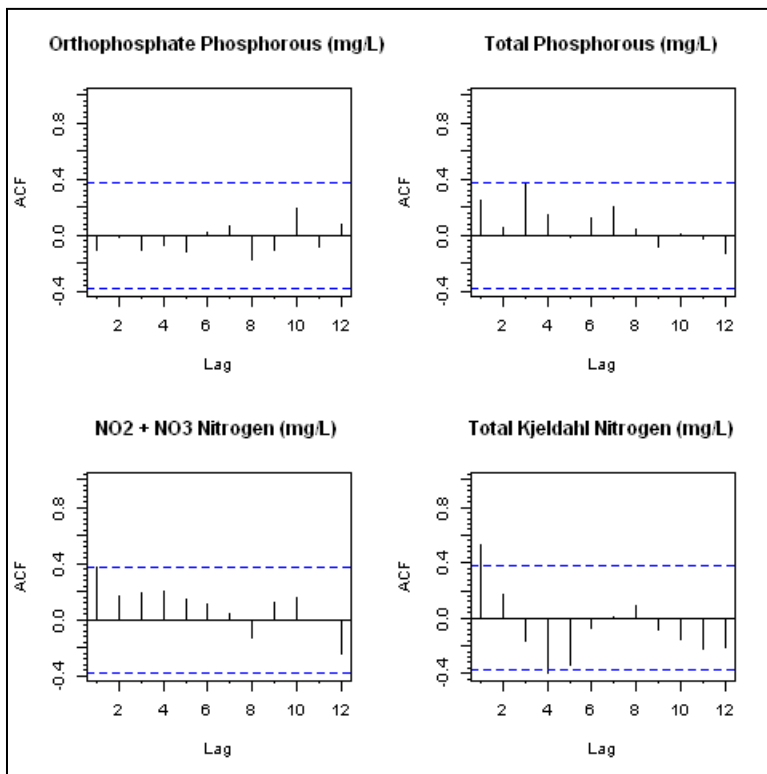


Figure 8: ACF plots for measured nutrients at site CC1

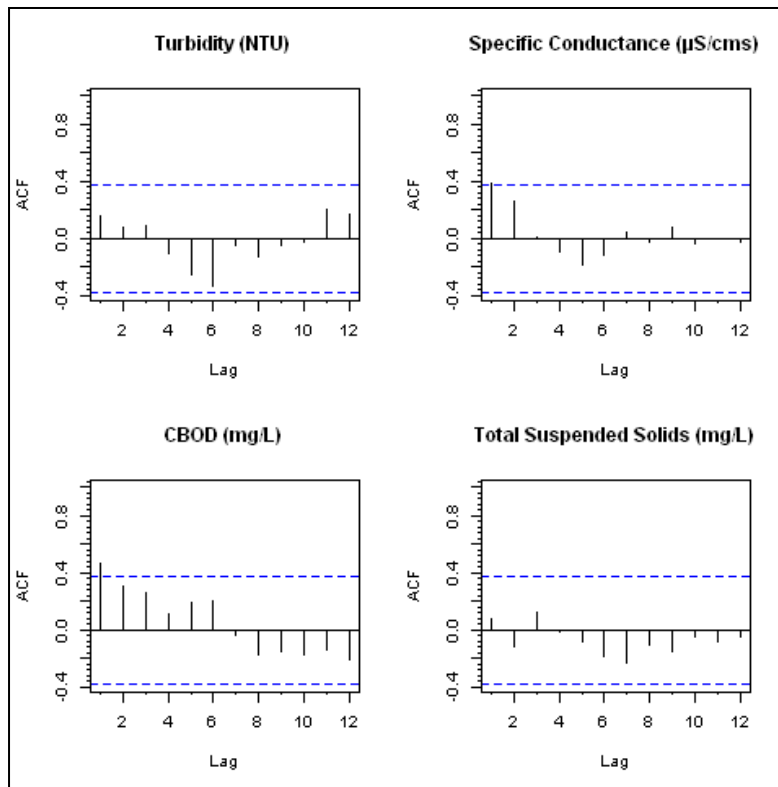


Figure 9: ACF plots for measured water quality indicators at CC1

The results presented in Figures 8 and 9 indicate that statistically significant lag-1 correlations are noted only for CBOD and TKN. This result points towards the increased persistence of physicochemical processes in the deeper (reductive) sections of the drainage ditch. In particular, sample collection at the CC1 site were carried out at a retaining wall, which led to settling and persistence of detritus and other organic matter that contribute to CBOD and TKN production. The persistence of CBOD, ammonia and TKN was also evident at HC2 site. There were no appreciable flows at the HC2 site, which also leads to persistence of detritus within the ditch. The pH data at CC2, HC1 and HC2 sites show consistent values. This result is to be expected given the buffering action of alkaline soils and sediments commonly found in South Texas. Overall results from the ACF analysis indicated that the collected samples were either minimally correlated or generally not correlated to each other and can therefore be considered independent measurements. This result validates the adopted sampling strategy as the assumption of independence is critical for both parametric and non-parametric statistical tests (Dudewicz and Lin 1981). Box-Plots were developed for all salient water quality parameters to visualize central tendencies and obtain preliminary insights with respect to inter-site and intra-site variability and are presented in Figures 10 and 11.

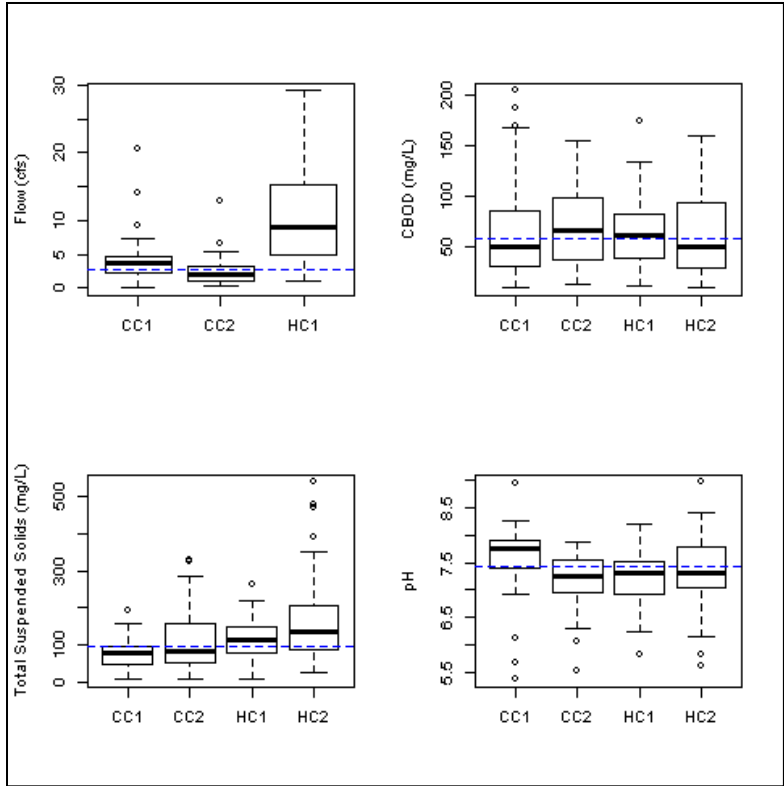


Figure 10: Inter and intra site variability of salient water quality parameters

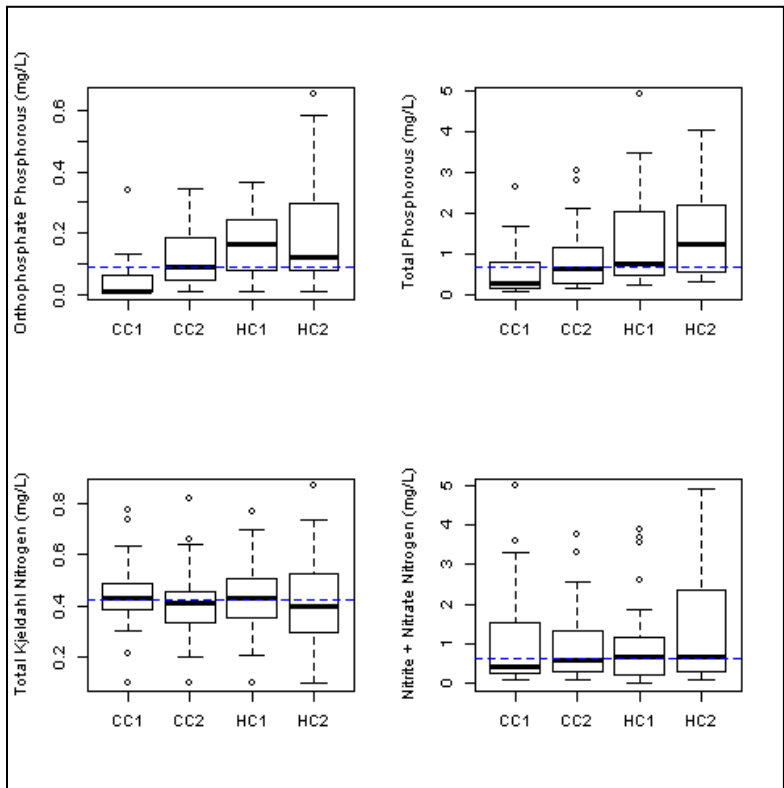


Figure 11: Inter and intra site variability for measured nutrient concentrations

A common characteristic evident in all plots presented in the Figures 10 and 11 is the high degree of variability noted at each site. Clearly, the temporal variability at each site is significantly greater than spatial variability across the sampled drainage ditches. The TSS, TP and NO_2+NO_3 were somewhat higher in the drainage ditches in Hidalgo County than those in Cameron County were. More intense agricultural activities were noted near the Hidalgo County sites during the sampling period, which partly explains the observed spatial differences. The variability of measurements at the HC2 site was generally higher than the other sites and was partly caused from measurement difficulties emanating from limited water in the ditch, which sometimes resulted in having to grab samples from near the sediment bed. As can be seen from the first box plot, the flows at the HC1 site were significantly higher than the other two flowing ditches (CC1 and CC2) and also more variable. The bottom of the drainage ditches (HC1 and HC2) were comprised of fine-grained sediments that are more amenable to settling and re-suspension and thus partially contributed to observed variability in TSS at these sites. The lower Rio Grande Valley region of South Texas experienced the effects of several major storms including Hurricane Dolly and Tropical Storm Ike and was also subject to one of the most severe droughts in recent history during the study period that spanned from 2009–2011. These meteorological events contributed to extreme values in the box plots that extend beyond the 5th and 95th percentile whiskers. The high degree of variability in the observed flow and water quality data are indicative of heteroskedasticity (non-homogeneous variances) across different flow regimes.

Flow Duration Curves (FDC) Analysis to Identify Major Flow Regimes

The pollutant loads to a receiving water body are directly related to flow patterns. Flow duration curves (FDC) plot the magnitude of flow against the frequency of its exceedance. As such, their use is recommended in total maximum daily load (TMDL) assessment studies (USEPA 2007). Figure 12 depicts the FDCs developed for the three flowing drainage ditches (CC1, CC2 and HC1) of this study.

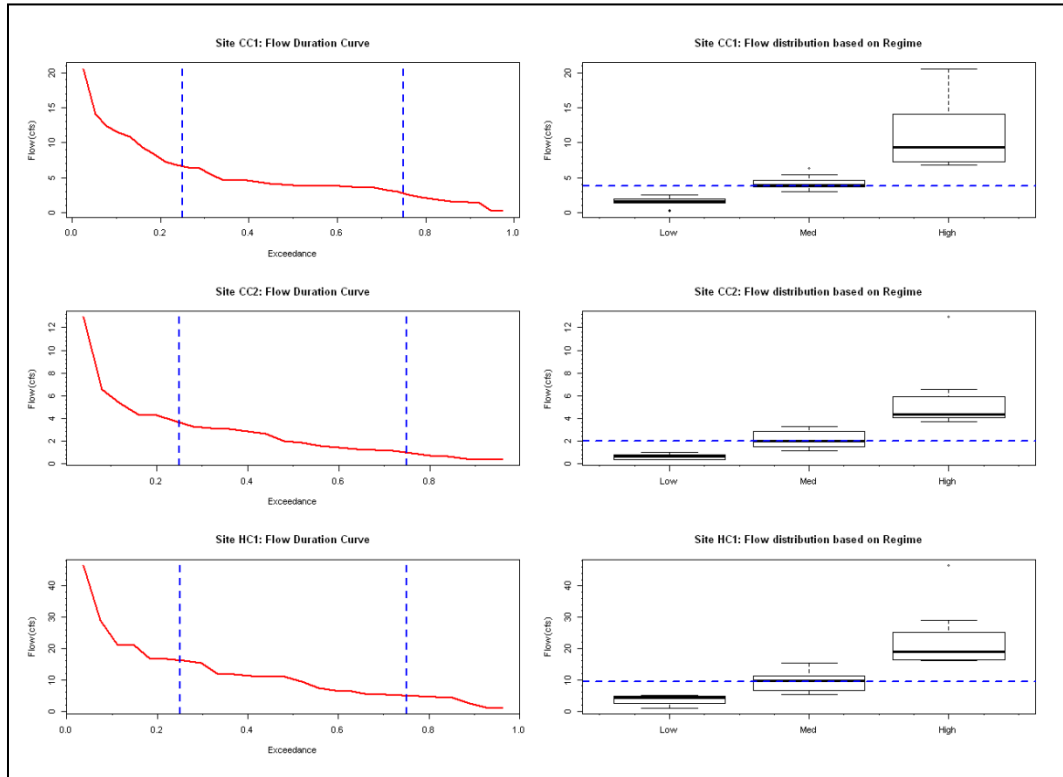


Figure 12: Flow Duration Curves and Flow Variability at CC1, CC2 and HC1 sites

The 25th and the 75th percentile exceedances were used as cut-offs to delineate high, medium and low flows. The box-plots presented in Figure 12 demonstrate that the variability in flows associated with different flow regimes (USEPA 2007). The low flows exhibit the least amount of variability, which indicates that they are controlled by sustained sources such as subsurface (shallow groundwater) discharges or unregulated peri-urban sources (colonias). On the other hand, the high flows exhibit the greatest variability and are likely controlled by intermittent rainfall and irrigation events. The variability in high flows is largest at the CC1 site, which has the largest contributing drainage area. The variability is clearly controlled by the extent of runoff generated due to rainfall variability and different irrigation events corresponding to various crops grown within the drainage area.

Role of Flow Characteristics in Defining Drainage Ditch Water Quality Behavior

As discussed earlier, higher flows correspond to direct surface runoff from contributing drainage area and lower flows are characteristic of longer subsurface flow paths. Box-Plots of various water quality parameters were constructed at each site using the flow classification developed using FDCs (Figures 13 and 14) to visually evaluate the effects of flows. From the figures, the median values of various water quality parameters, most notably—CBOD, TSS, TP, OP and NO_2+NO_3 —are higher for high flow conditions. These results provide preliminary evidence that runoff from contributing drainage areas can enhance loadings of nutrients and oxygen demanding substances in the drainage ditches. However, the box plots also suggest that there is no appreciable difference among various flow regimes with regards to reduced forms of nitrogen (i.e. TKN, $\text{NH}_3\text{-N}$), again highlighting the importance of in-stream processes (e.g. decay of organic matter) in controlling the reduced forms nitrogen.

The non-parametric Kruskal-Wallis (KW) multiple comparison tests was used to formally evaluate the null hypothesis. There is no difference in water quality parameters across different flow regimes against the alternative than there are differences between various flow regimes. The KW multiple comparison tests was then used to compare pair-wise differences (Table 4) among different flow regimes and is based on Siegel and Castellan (Siegel and Castellan 1988).

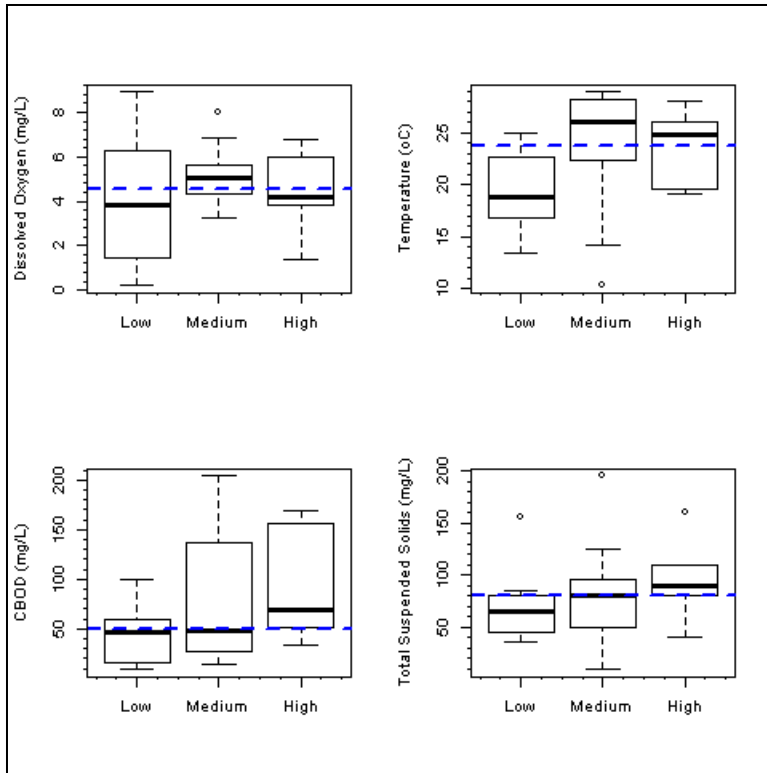


Figure 13: Water quality characteristics pertaining to different flow regimes at Site CC1

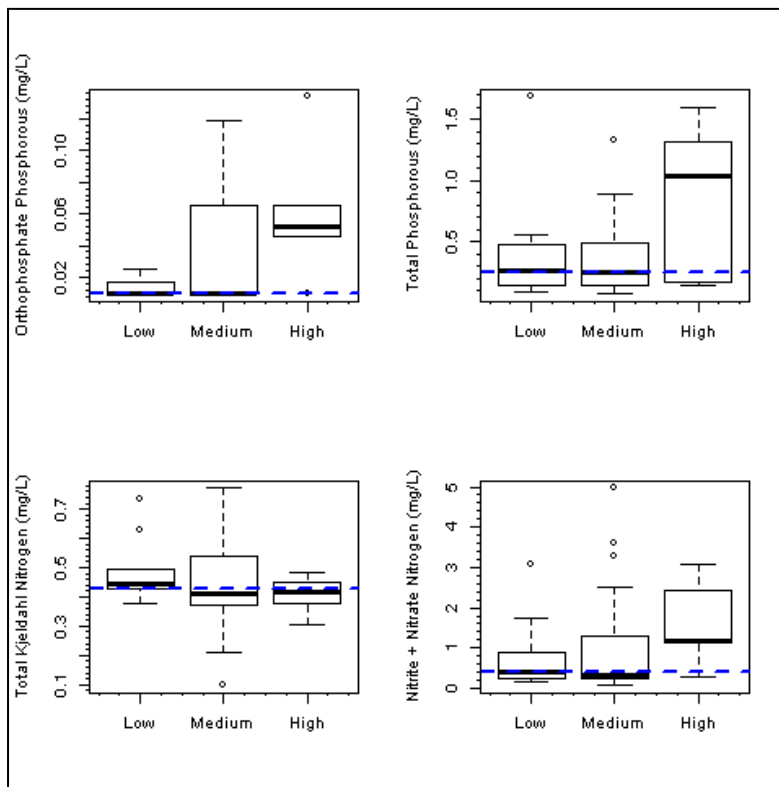


Figure 14: Nutrient characteristics pertaining to different flow regimes at Site CC1

Table 4: Results of the Kruskal-Wallis and Pairwise Comparison Tests

	Site CC1					Site CC2					Site HC1				
	KW chisq	P	Low-High	Medium-High	Medium-Low	KW chisq	P	Low-High	Medium-High	Medium-Low	KW chisq	P	Low-High	Medium-High	Medium-Low
Temperature (°C)	6.300	0.043	F	F	T	5.314	0.070	T	F	F	7.138	0.028	T	T	F
Turbidity (NTU)	2.968	0.227	F	F	F	7.988	0.018	T	F	F	2.857	0.240	F	F	F
DO (mg/L)	1.921	0.383	F	F	F	4.744	0.093	F	F	F	4.730	0.094	F	F	F
Specific Conductance (µS/cm)	2.877	0.237	F	F	F	1.770	0.413	F	F	F	1.490	0.475	F	F	F
pH	4.149	0.126	F	F	F	0.333	0.846	F	F	F	1.117	0.572	F	F	F
CBOD (mg/L)	2.714	0.258	F	F	F	1.161	0.560	F	F	F	0.196	0.907	F	F	F
TSS (mg/L)	2.079	0.354	F	F	F	7.043	0.030	T	F	F	5.748	0.056	F	T	F
OP (mg/L)	2.830	0.243	F	F	F	11.312	0.003	T	T	F	1.966	0.374	F	F	F
TP (mg/L)	1.393	0.498	F	F	F	10.070	0.007	T	T	F	5.422	0.066	T	F	F
Total Kjeldahl Nitrogen (mg/L)	1.568	0.457	F	F	F	2.494	0.287	F	F	F	2.155	0.341	F	F	F
NH3 - N (mg/L)	2.118	0.347	F	F	F	0.829	0.661	F	F	F	2.413	0.299	F	F	F
NO2+NO3 as N (mg/L)	1.886	0.389	F	F	F	4.178	0.124	F	F	F	2.048	0.359	F	F	F

The highlighted boxes indicate a significance level of less than 0.1

The hypothesis testing results in Table 4 essentially corroborate the visual analysis and particularly highlight that the loadings of TP and TSS could be controlled by runoff from surrounding agricultural areas. The visual differences noted in nitrogen compounds could not be statistically confirmed via hypothesis testing due to large observed variability. The results presented in Table 4 highlight significant temperature differences between high flow and low flow events. The statistical difference noted in temperature stems from the fact that low flows are generally observed during winter months while high flows correspond to runoff from high intensity convective storms and larger irrigation activities that mostly occur during summer months. The difference in timing between high and low flow events help explain the significant differences noted in DO at CC2 and HC1 sites using the KW test. Even though the pair-wise comparison test lacked sufficient statistical power to discern the differences, the median DO concentrations were noted to be higher for low flows than high flows at these sites (see Figures AF 19 and AF 21 in Appendix A). This result also implies that dissolved oxygen in the ditches is controlled by climate (temperature) and any additional mixing associated with increased flows are unlikely to enhance re-aeration in the ditches.

To summarize, direct runoff from contributing drainage areas generally have a significant impact on TSS and phosphorus compounds in the drainage ditch. On the other hand, the concentrations of nitrogen compounds are affected by both processes operating at both watershed and drainage-ditch scales. In particular, drainage ditch processes, such as detritus decay, could play a major role in defining the concentrations of reduced nitrogen compounds (TKN). The DO concentrations in the ditches are largely

controlled by temperature and enhanced mixing associated with higher flows are unlikely to overcome the higher de-oxygenation rates during summer months.

Evaluation of Differences between Edge-of-Field and Drainage Ditch Nutrient Water Quality

An independent field study to assess water quality characteristics of irrigation runoff from six different fields primarily growing four different crops (cotton, sugarcane, corn and vegetables) and employing different irrigation technologies commonly used in the Lower Rio Grande Valley region was carried out during the same period (2009-2010). Further details of the irrigation field sampling campaign can be found in (Ensico et al. 2011). Most importantly, water quality characteristics of the irrigation runoff at the edge-of-field were collected and analyzed using the same sampling and analytical methods used in this investigation and by the same personnel. Therefore, an evaluation of the differences in water quality observed in agricultural farm runoff and drainage ditches was carried out again using visualization and statistical hypothesis testing tools. The box-plots presented in Figure 15 clearly demonstrate that the concentration of both phosphorus and nitrogen compounds are higher in the runoff water leaving the edge of field than what is observed in the drainage ditch flows.

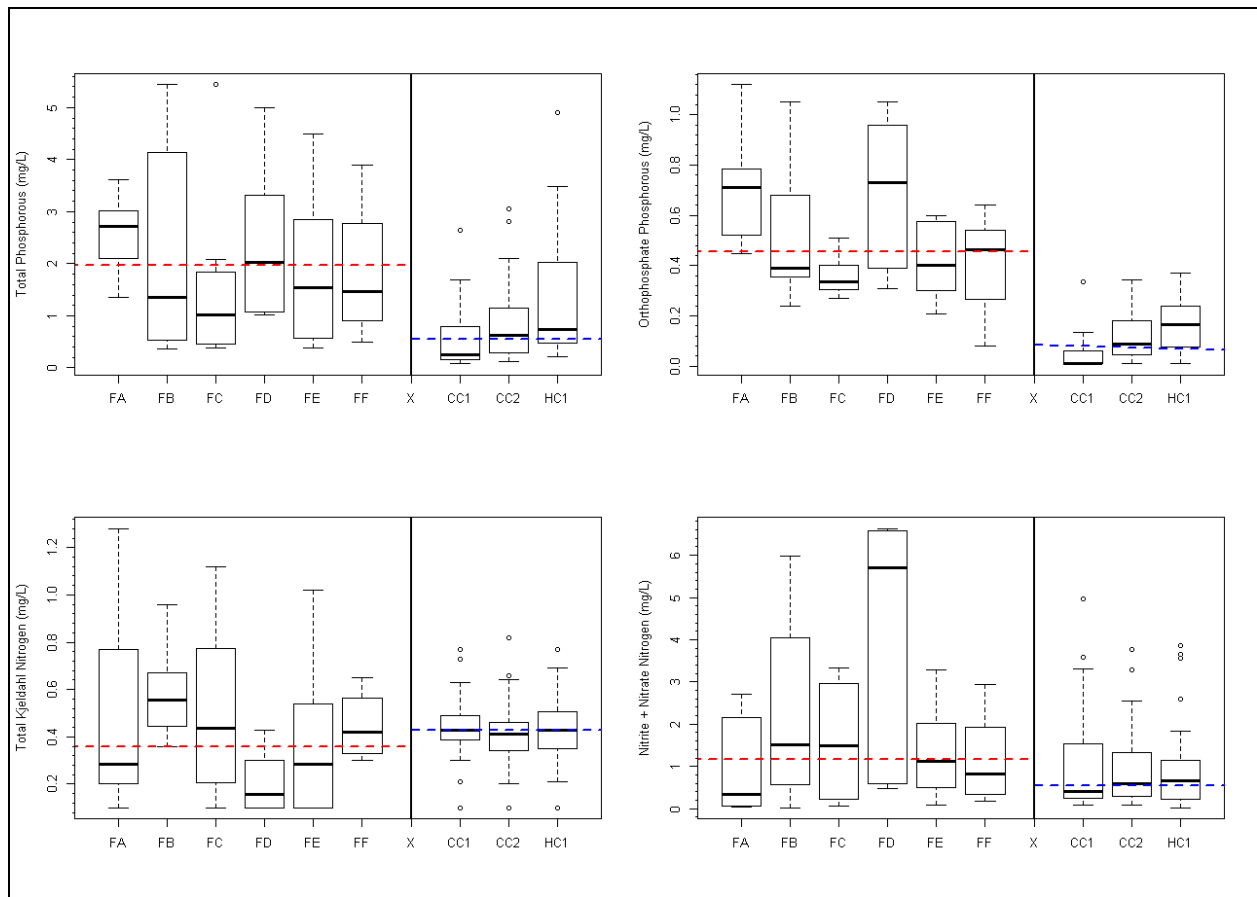


Figure 15: Comparison of Observed Nutrient Water Quality at Edge of Field Agricultural Sites and Drainage Ditches

A two-sided Mann-Whitney U test was also carried out to test the null hypothesis that the nutrient water quality leaving the agricultural farms was no different from the nutrient water quality measured in drainage ditches against the alternative hypothesis of significant differences between the two sets. The results indicated that the drainage ditch concentrations are significantly different for OP ($W = 150$, $p < 0.001$), TP ($W=1012$, $p < 0.001$) and oxidized nitrogen compounds ($W = 1688$, $p = 0.044$) than those measured in agricultural runoff leaving the farmlands. The alternative hypothesis could not be rejected for TKN ($W = 2375$, $p = 0.235$). These results once again reiterate the previous findings that the loadings of phosphorus compounds are more controlled by watershed scale processes while the reduced forms of nitrogen in the drainage ditches are influenced to a greater extent by in-channel processes. Furthermore, the large differences in phosphorus concentrations between the edge-of-field and drainage ditch measurements is consistent with reports from other studies elsewhere which indicate the ability of drainage ditches to remove phosphorus compounds (Smith et al. 2005; Bhattarai et al., 2009; Ahiablame et al. 2011).

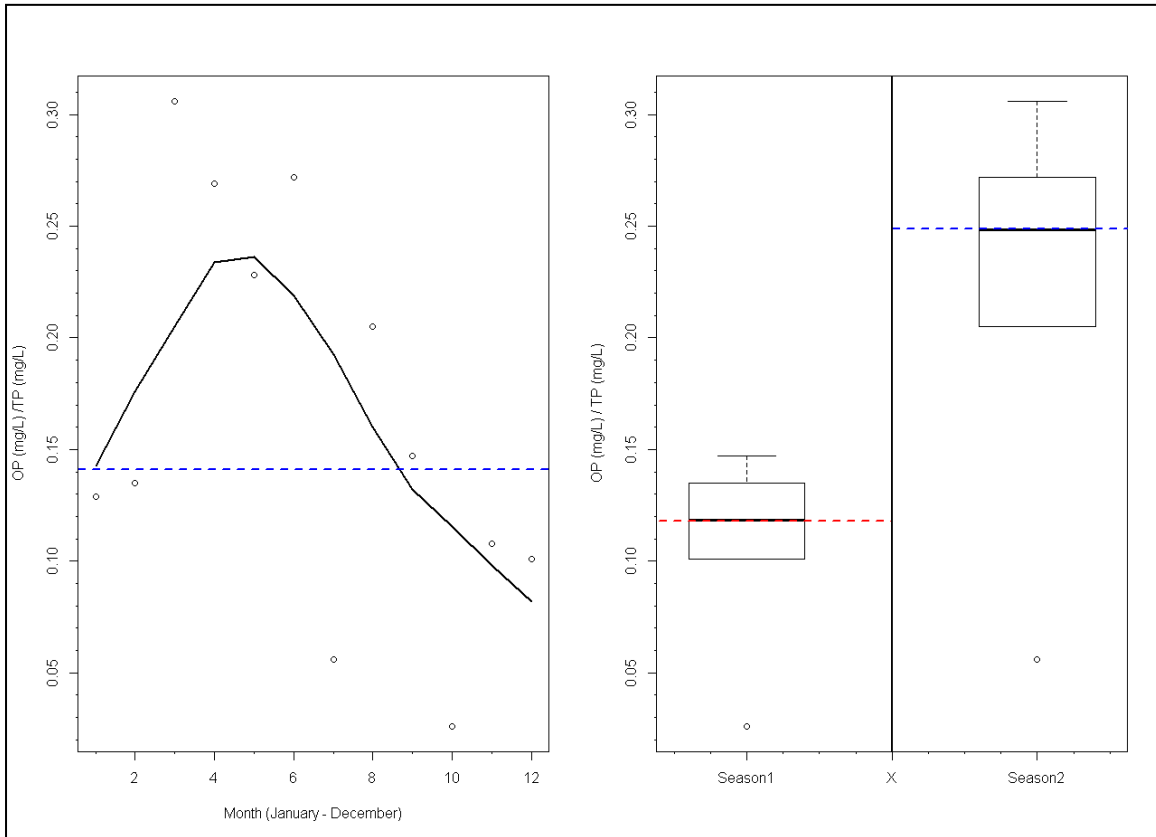
The result that the nutrient water quality in drainage ditches is generally less than those measured at the edge-of-field is certainly promising and points towards the attenuation capabilities of these ditches. However, it is important to remember that fiscal and logistic constraints precluded a paired experimental design. The data collection in the drainage ditches was systematic and occurred over a larger period while the edge-of-field monitoring was limited to specific events spanning few days each time. Even during the periods when the sampling campaigns were coordinated, logistic constraints precluded the isolation and tracking of flows emanating from the edge-of-field study sites in the drainage ditches. Generally speaking, the flows in the drainage ditches can be viewed as an agglomeration from several agricultural sites and other sources (e.g., urban runoff) within the contributing drainage area. Given these sampling limitations, it is important to not construe the magnitude of observed differences in nutrient levels as a measure of the degree of nutrient attenuation occurring within the ditches. Nonetheless, the results presented here highlight that drainage ditches play an influential role in altering the timing and extent of nutrient releases from agricultural practices to receiving water bodies. In particular, they help transform high intensity, highly variable intermittent loadings arising during rainfall and irrigation activities to a more sustained lower-intensity slow release pattern and help increase the time the nutrients spend in the watershed before being discharged into the receiving water body.

Factors Affecting Phosphorus Concentrations in Drainage Ditches

The results presented in this study indicate that drainage ditches can receive significant phosphorus loadings during irrigation and high intensity rainfall activities. The TP concentration is positively and significantly correlated to the concentration of TSS for high flow regimes. The ability of drainage ditches to settle out TSS is therefore an important phosphorus removal mechanism and this result is consistent with the findings from other studies reported in the literature (Smith et al. 2005; Leone et al. 2008; Robert Kröger and Moore 2011). However, the drainage ditches can also act as a phosphorus source when particles become re-suspended or diffuse from the sediments into base flows (i.e. groundwater discharges) that generally have lower concentrations of phosphorus.

Phosphorus is an essential but often limiting nutrient for plant growth. As such, the uptake of phosphorus by plants is another major attenuating mechanism in drainage ditches. The extent of uptake is largely controlled by the amount of dissolved phosphorus or the OP. One of the monitored drainage ditches, HC2, had no appreciable flows, but a significant amount of biomass in the form of standing

emergent vegetation (grasses). The observations at the site provided a unique opportunity to evaluate the role of vegetation in the ditches on nutrient uptake and removal without having to deal with the confounding effects of flows.



**Figure 16: Temporal Behavior of Average OP at Site HC2
(Season1 corresponds to September-March and Season2 from April-October)**

Figure 16 represents the average temporal behavior observed during each month of sampling. The OP concentrations in each month were normalized with respect to the TP concentrations to block the effects of differences in TP between different months. The seasonal variation in phosphorus concentrations is evident from the Figure 17. The concentrations are lower in season 1, which corresponds to the relatively colder months of September–February. On the other hand, the concentrations are higher during the relatively hot months of March–August. The Mann-Whitney test for differences in concentrations between the two seasons was statistically significant ($U = 5, p = 0.041$) and corroborates the box plot observations in Figure 17. Visual observations at the site indicated a larger and healthy biomass (green grass) during season 1 (cooler period) than during dry summer months where the amount of biomass in the ditch was significantly lower and unhealthy (yellow and

brown grass stalks). Therefore, it is likely that uptake of phosphorus by emergent vegetation is a significant mechanism for phosphorus removal during cooler periods. However, these plants are likely to act as sources of phosphorus (release due to biomass decay) during hot summer months. Emergent vegetation in the drainage ditches can therefore play a major role in attenuating phosphorus concentrations, but can also act as source of phosphorus.

The in-channel biomass was noted to be low in flowing drainage ditches (CC1, CC2, and HC1), and as such the relative importance of vegetation is likely to be not as prominent. Literature on constructed wetlands indicates that plant uptake accounts for about 10% of the overall phosphorus removal and can serve as an important tertiary treatment mechanism (Vyzamal 2005). As the primary purpose of drainage ditches is to reduce flooding, irrigation and drainage districts engage in periodic biomass harvesting as part of channel maintenance activities. It is recommended here that such maintenance schedules be coordinated in a manner that maximizes the plant uptake but also minimizes their ability to act as sources. This coordination should not be too difficult, as high intensity convective storms and large irrigation events are more likely to occur in the summer months, which also corresponds to lower biomass uptake. Also allowing smaller sections of healthy biomass to occur intermittently in the drainage ditches, where possible, could potentially be beneficial.

Factors Affecting Nitrogen Concentrations in Drainage Ditches

The concentrations of reduced forms of nitrogen (TKN and $\text{NH}_3\text{-N}$) were generally low in drainage ditches relative to the oxidized forms (nitrite+nitrate-nitrogen), and drainage ditches provide suitable conditions for the oxidation to take place. This result is again consistent with findings reported in the literature (Goolsby et al. 2001; Jarvie et al. 2010) where drainage ditches, as being potential sources of nitrate, have been highlighted. The comparison of edge-of-field and drainage ditch concentrations provide some evidence of nitrate reduction capabilities of the drainage ditches. Furthermore, statistically significant differences in nitrogen concentrations were noted between different flows regimes, indicating that under suitable conditions there is a potential for nitrate removal by drainage ditches. As discussed earlier, nitrate reduction occurs in the deeper sections of the ditch in the presence of sufficient organic carbon and limited oxygen conditions. Also, lower flow rates limit the amount of re-aeration and reduce the amount of oxygen in the ditch. Therefore, the average water column depth in the channel to flow ratio (d/Q) was used as a hydraulic reduction index (HRI) for assessing nitrate reduction capabilities of the ditch. The HRI represents the hydraulic residence time per unit plan-view

area of the watershed. Spearman rank correlations were established between the hydraulic reduction index (HRI) and deficit dissolved oxygen (Deficit DO) and the observed correlations $\rho = 0.341$, ($p = 0.061$) at CC1; $\rho = 0.263$, ($p = 0.152$) at CC2 and $\rho = 0.0294$ ($p = 0.105$) corroborated the utility of the developed index to characterize reduced conditions in the ditch.

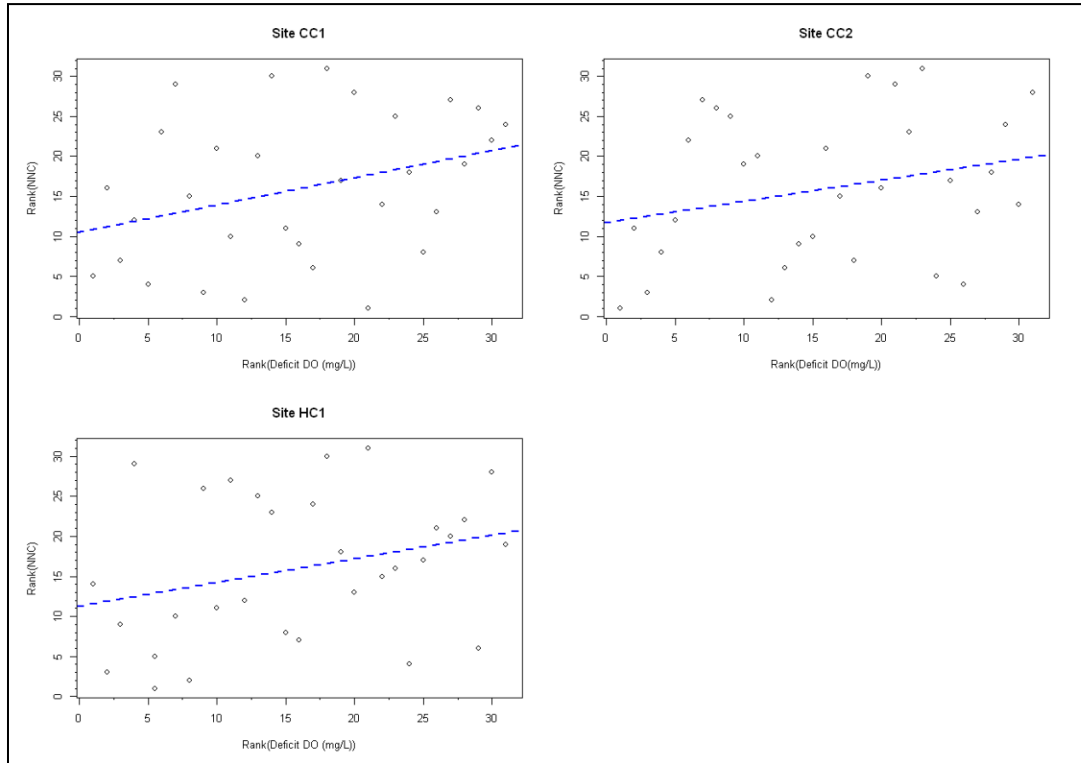


Figure 17: Correlation between Deficit Dissolved Oxygen and Normalized Nitrate Concentration (NNC)

Clearly, larger depths and/or lower flow rates result in a higher value of the hydraulic nitrate reduction index and must depict an inverse correlation to nitrate concentrations. Figure 17 plots the nitrate reduction index against the ratio of total oxidized nitrogen concentration ($\text{NO}_3 + \text{NO}_2$) to TKN. The rank transformation was used to mask the effects of outliers and highlight the correlation between the hydraulic characteristics of the ditch and the nitrogen concentrations. Again, the ratio of oxidized to reduced nitrogen forms (i.e., normalized nitrate concentrations (NNC)) were used to block for the variability in nitrate sources in the ditches. The inverse relationship between the index and oxidized nitrate concentrations is evident from Figure 18. The spearman rank correlation coefficients, ρ , between the two parameters was equal to $\rho = -0.18$ ($p=0.33$) for CC1; $\rho = -0.54$ ($p = 0.002$) and $\rho = -0.35$ ($p = 0.05$) and confirm the statistical significance of the observed correlations. The presence of internal sources (decay of detritus) at CC1 site appears to have an impact on the observed correlation.

Based on the above results, it is clear that the nitrate reduction efficiency can be enhanced by making certain structural modifications to the drainage ditches. It is therefore recommended that periodic deepening or widening of the drainage ditch channels along the length of the drainage ditch when and where possible would be beneficial as it leads to slowing of flows and creation of deeper (anoxic) zones. However, as flood control is the primary function of the drainage ditches, a detailed hydraulic evaluation of the impacts of periodic deepening (e.g., (Rodriguez et al. 2008)) is necessary to fully evaluate the feasibility of this recommendation.

Nitrogen is also an essential nutrient for plants, and therefore the uptake of nitrogen could be an important attenuation mechanism within the drainage ditches as well. Plants are known to use both ammonium and nitrate with the former being generally preferred than latter (Kadlec and Wallace 2009). However, the uptake by plants is not a sustainable removal process as decay of biomass leads to the release of nitrogen into the ditch. The role of vegetation on nitrogen compounds was studied at HC2 site, which had no confounding effects of flows. The results presented in Figure 14 demonstrate the seasonal influence of the biomass on nitrogen concentrations. As shown similarly with phosphorus, lower nitrate concentrations were noted when the standing biomass was healthy (uptake). However, the nitrogen cycle is not congruous with the phosphorus cycle possibly due to heterogeneities in the biomass types within the ditch. The Mann-Whitney U test ($U = 0$, $p = 0.002$) confirmed the differences in concentrations between the two seasons.

The results of the analysis again point towards the important role of vegetation in controlling nitrogen concentrations in the ditch. However, vegetation can also serve as a nitrogen sink and as such must be properly managed. Based on the data presented in Figure 16 and Figure 18, both phosphorus and nitrogen concentrations are simultaneously higher during the months of June–October and therefore represent the best months for biomass harvesting in drainage ditches.

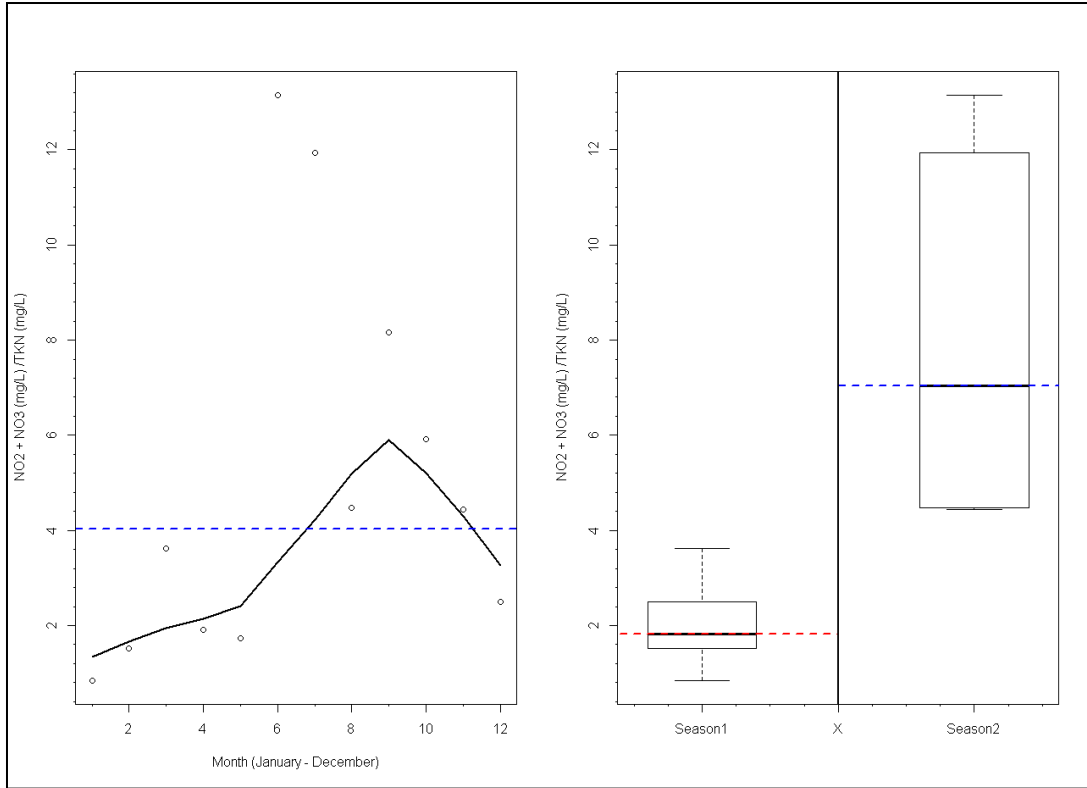


Figure 18: Cyclical Behavior of Nitrate Concentrations and Visualization of Seasonal Differences (Season1: December–May; Season2: June–November)

Comparison between Grab and Composite Sampling

The summary characteristics of the collected data are visualized in Figures 19–21. The variability in the composite samples were higher for temperature, turbidity, TSS, $\text{NH}_3\text{-N}$, OP and pH while the variability was either higher or similar for the grab samples for other compounds. This result is to be expected because temperature and TSS can exhibit diurnal fluctuations. Also, the plant metabolism varies diurnally which in turn controls the oxygen levels in the ditch and affects the uptake by the plants. This diurnal variability in uptake in turn affects ammonia and orthophosphate levels in the ditch over the short-term. The DO variability in the grab samples was noted to be somewhat higher than the composite samples and this result arises because the paired grab samples were obtained at different times at each site.

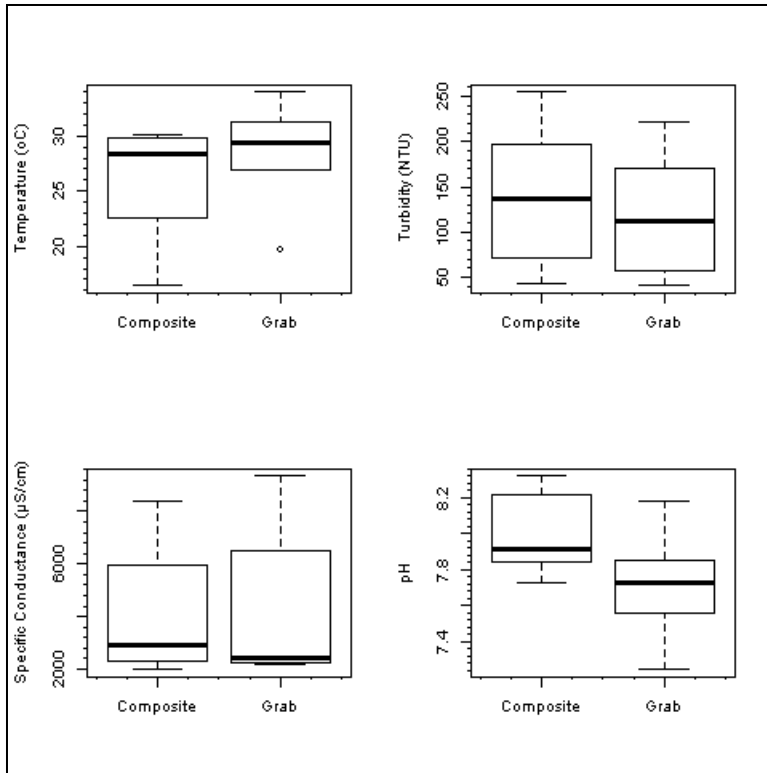


Figure 19: Measured field water quality comparison between grab and composite sampling events

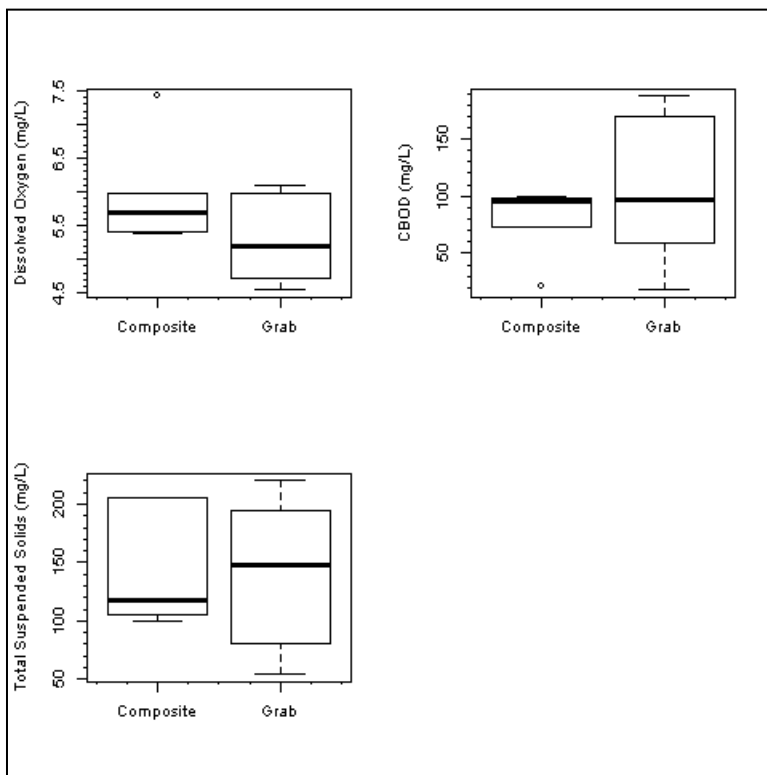


Figure 20: Measured water quality parameter comparison between grab and composite sampling events for Oxygen dependent parameters and suspended solids

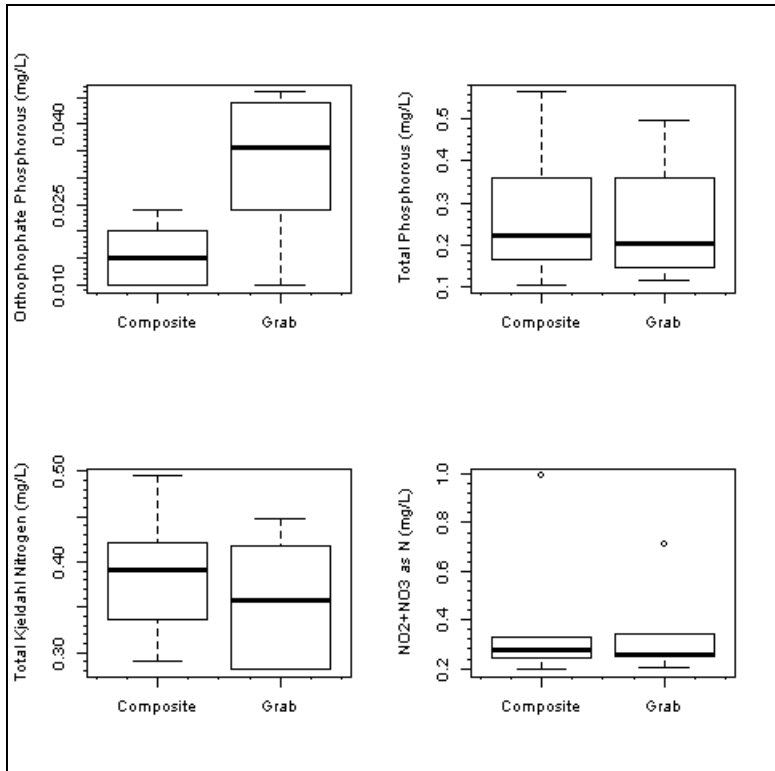


Figure 21: Comparison of measured nutrient concentration between grab and composite sampling events

The Wilcoxon Paired Rank Sum Test was used to formally evaluate the observed differences between grab and composite samples. The null hypotheses that there is no appreciable difference in the observed median values of grab and composite samples could only be rejected for turbidity at 0.05 significance levels and for temperature, OP and pH at 0.1 significance levels (see Table 5). This result again corroborates that the adopted sampling strategy is reasonable to make inferences about most water quality parameters. However, a 24-hour averaged sampling of DO and temperature is recommended for future studies.

Table 5: Mann-Whitney test results comparing corresponding grab and composite events

Wilcoxon Rank Sum Test Results		
Parameter	U	p-value
Temperature (°C)	1	0.063
Turbidity (NTU)	21	0.031
Dissolved Oxygen (DO) (mg/L)	18	0.156
Specific Conductance (µS/cm)	9	0.844
pH	19	0.094
Carbonaceous Biochemical Oxygen Demand (CBOD) (mg/L)	7	0.563
Total Suspended Solids (TSS) (mg/L)	12	0.834
Orthophosphate Phosphorous (mg/L)	0	0.059
Total Phosphorous (mg/L)	12	0.281
Total Kjeldahl Nitrogen (mg/L)	16	0.313
Ammonia Nitrogen (mg/L)	5	0.590
Total Nitrite and Nitrate (NO ₂ + NO ₃) as N (mg/L)	11	> 0.999

The highlighted boxes indicate a significance level of less than 0.1.

Summary and Conclusions

The broad goal of this study was to conduct a comprehensive multiyear, multivariate, multisite field investigation to evaluate the behavior of nutrients in the Lower Rio Grande valley region of Texas. The study used a modified, stratified random sampling design to collect flow and 11 water quality parameters including TP, OP, TKN, NH₃-N, and nitrite+nitrate-nitrogen. Three ditches (CC1, CC2, and HC1) had perennial flows, while one ditch (HC2) had no observable flows and was therefore used to evaluate the effects of vegetation on nutrient dynamics. The results from the drainage ditch monitoring program were also compared to an overlapping edge-of-field investigation focusing on characterizing water quality in runoff leaving different agricultural farm lands. A suite of statistical methods including flow duration curves, box-plots and non-parametric hypothesis testing (including Kruskal-Wallis, ANOVA, and Spearman Rank Correlation Significance tests) were used to evaluate non-random differences.

The results of the study indicate that the loadings of phosphorus and suspended solids are controlled by runoff from the contributing drainage areas. Both contributing drainage areas and in-channel processes

impact the concentrations of nitrogen compounds. The comparison of concentrations observed in agricultural runoff leaving the farms and those in the drainage ditches highlight the attenuation capabilities of the drainage ditches particularly about phosphorus compounds. The drainage ditches also effectively assimilate reduced forms of nitrogen (i.e., TKN and $\text{NH}_3\text{-N}$). The removal of oxidized forms of nitrogen (nitrate-nitrogen) is linked to the hydraulic characteristics of the ditches. Nitrate reduction is enhanced under lower flows and deeper water columns, which lead to lower dissolved oxygen and thus improved reducing conditions in the ditches. In addition to hydraulic characteristics, standing vegetation (macrophytes) can also have a significant influence on nutrient concentrations. The presence of in-channel vegetation introduces seasonality in observed nutrient concentrations. While in-channel vegetation acts as a sink during relatively cooler periods, they act as sources during hot, dry summer months. While both nitrogen and phosphorus concentration exhibit cyclic behavior, a phase-lag between phosphorus and nitrogen cycles was also noted and could possibly be due to heterogeneous biomass in the ditches.

From an operational standpoint, drainage ditches alter the flow and chemical transport characteristics of runoff emanating from agricultural fields. They help attenuate shock loadings of direct runoff from the fields and lead to a more uniform nutrient loadings that is spread out over a larger period. Therefore, drainage ditches can act as both nutrient sources and sinks. Proper maintenance and management of drainage ditches is an important regional-scale best management practice strategy for reducing nutrient loadings due to agricultural activities. Deepening certain sections of the ditch (where possible and feasible) can help improve nitrogen removal capabilities. Harvesting of biomass in the drainage ditches is routinely carried out by irrigation and drainage districts for flood control purposes. It is beneficial if these harvesting activities are optimized to minimize nutrient sources within the ditch. Biomass removal during the months of June–October could be beneficial for mitigating both nitrogen and phosphorus loadings. It is recommended that harvesting activities focus on the removal of necrophytes (dead biomass) to reduce nutrient sources within the ditches and the necrophytes be segmented to exploit the removal capabilities of plants.

Acknowledgments

The logistic support provided by Dr. V. Honnungar, D. Marek, J. R. Hernandez, M. Arreola, J. Amaya, V. Naripeddi; G. Flanders; K. Kembhavimatada; A. Nagraj; D. Cantu; R. Eti; U. Ovbiagle; O. Lyesari; C. Vera; E. Gaona and W. Allen at TAMUK was instrumental in completion of the sample collection and analysis. In addition, J. Enciso and X. Peres at Texas AgriLife Extension Service are thanked for edge-of-field data. The authors also thank the following personnel at Texas Water Resources Institute: A. Berthold, K. Wagner and C. Wagner for facilitating the project and all their logistic support. This report was funded through the *Arroyo Colorado Agricultural Nonpoint Source Assessment* project with funding support from the United States Environmental Protection Agency through a Clean Water Act §319(h) grant administered by the Texas State Soil and Water Conservation Board. The work was made possible due to the financial assistance from Texas State Soil and Water Conservation Board (TSSWCB). TSSWCB staff – A. Wendt, P. Casebolt, A. Garza, R. Ramirez are thanked for their assistance in identifying monitoring sites and for overall coordination of the project. The authors highly appreciate the time and efforts of A. Alexander in reviewing the report and suggesting improvements.

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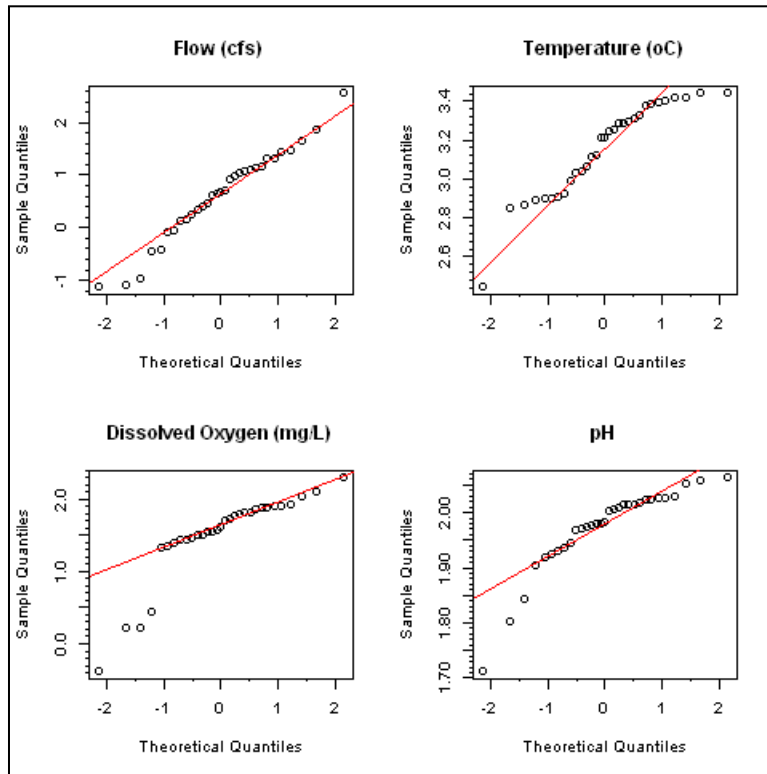
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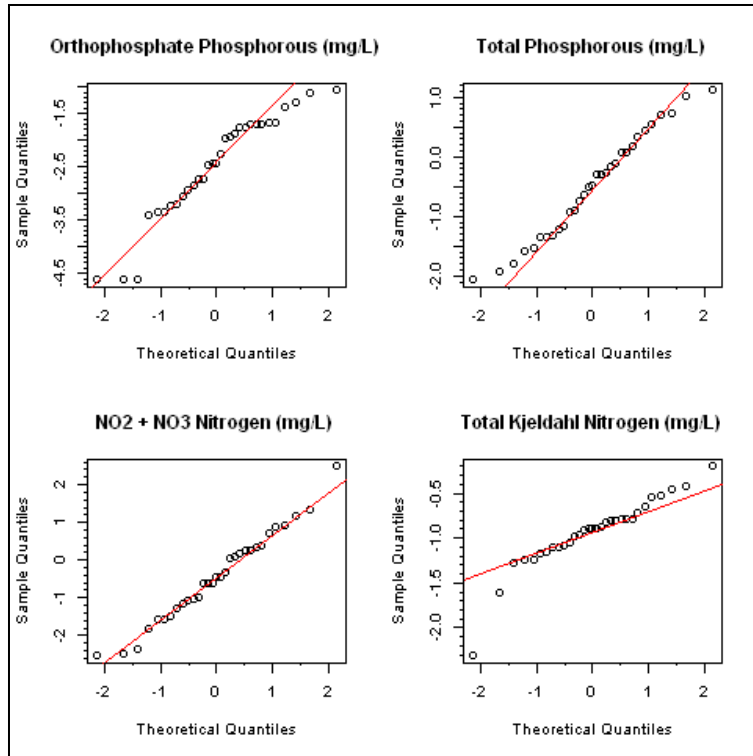
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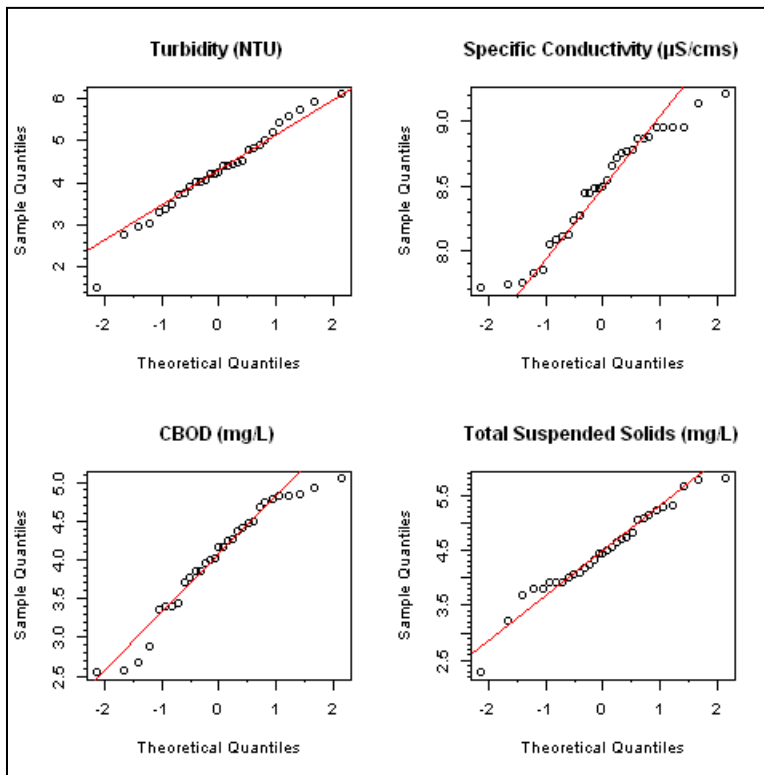
Appendix A



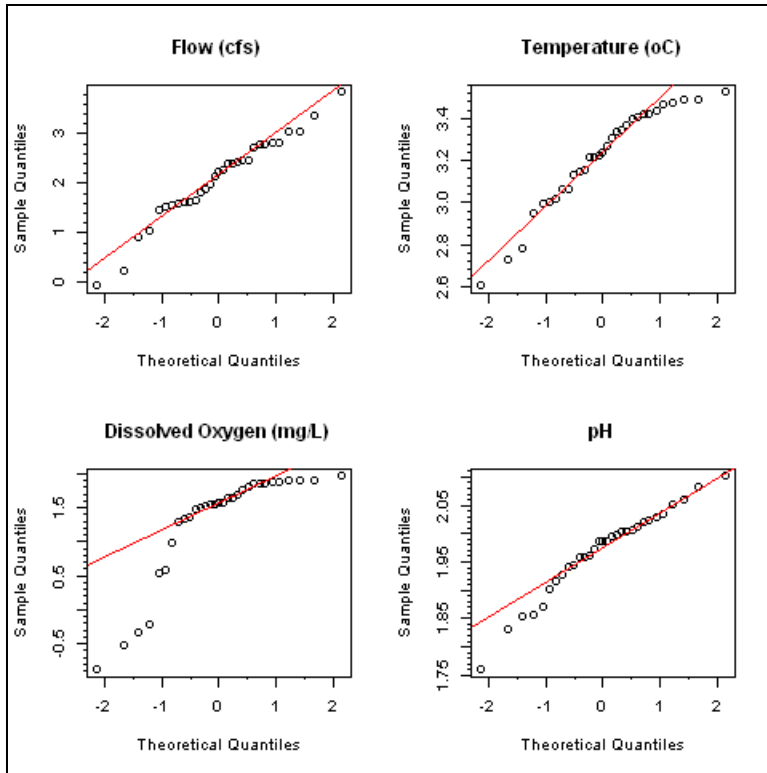
AF 1: Q-Q plots for the measured field parameters at Site CC2



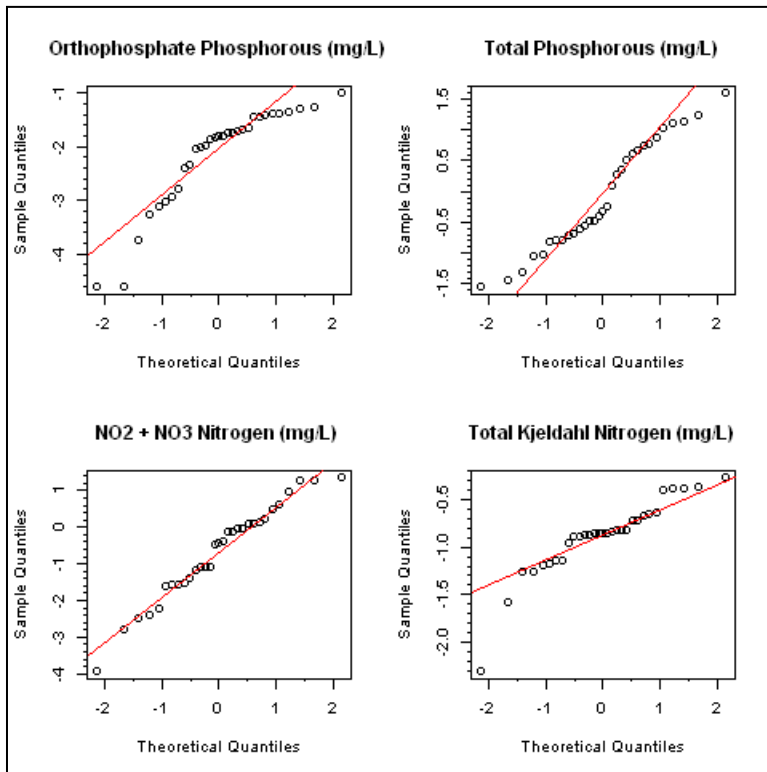
AF 2: Q-Q plots for measured nutrients at Site CC2



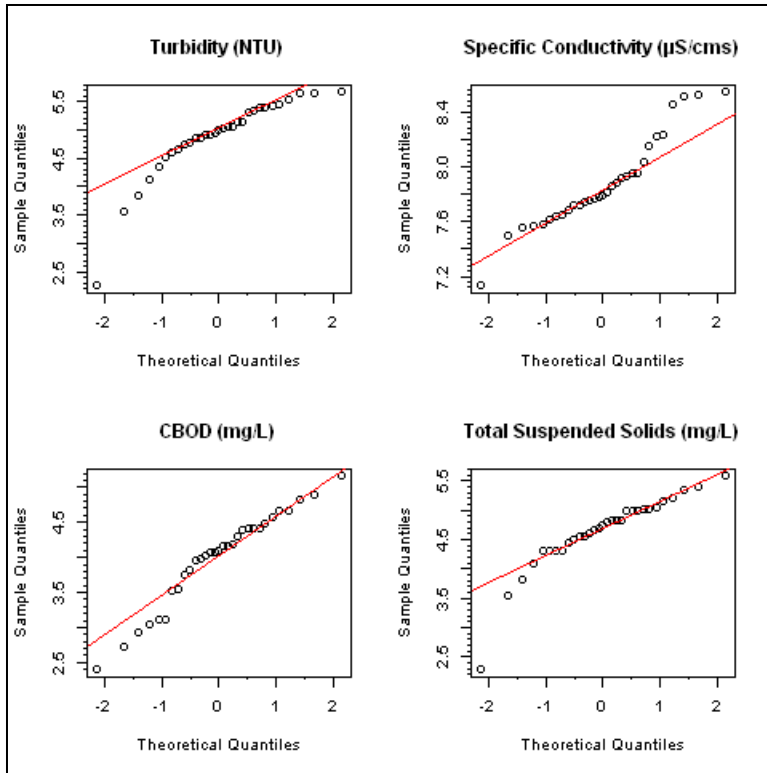
AF 3: Q-Q plots for the measured water quality indicators at Site CC2



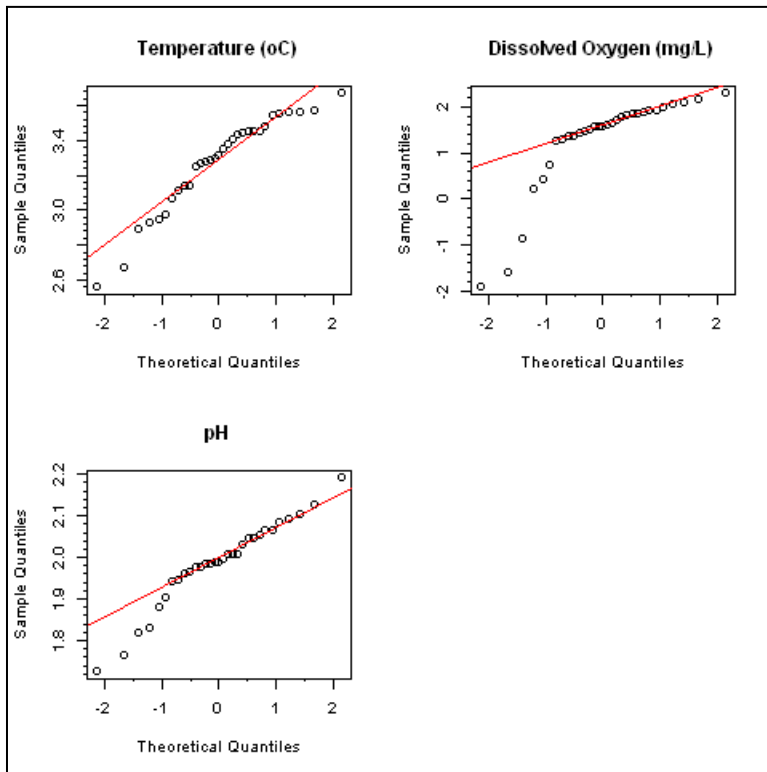
AF 4: Q-Q plots for the measured field parameters at Site HC1



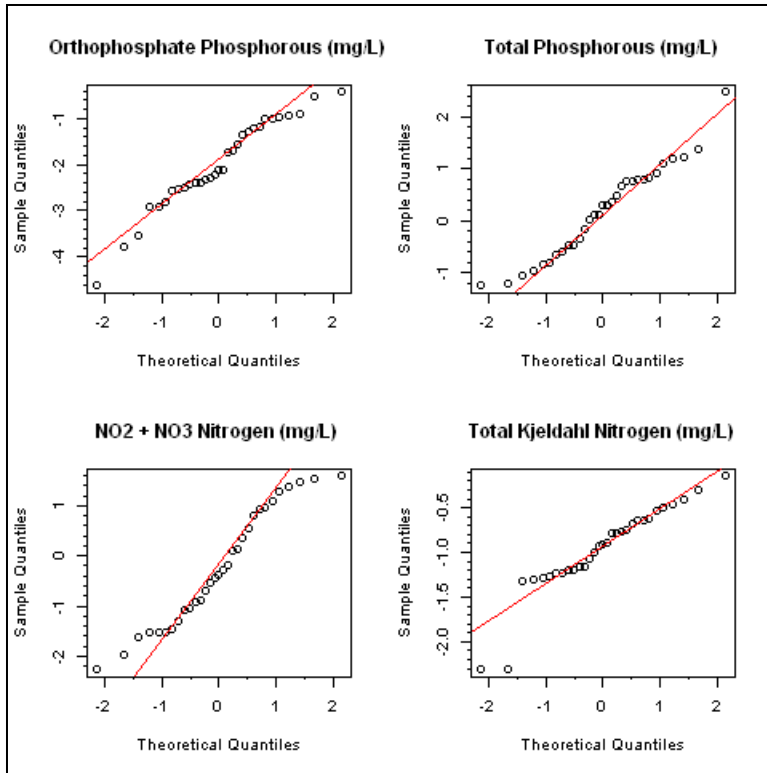
AF 5: Q-Q plots for the measured nutrients at Site HC1



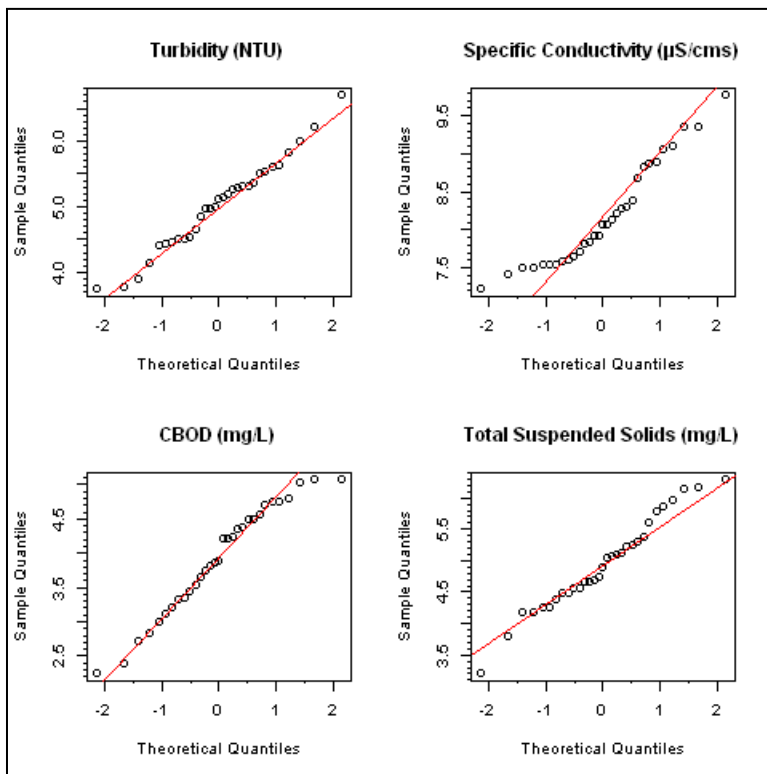
AF 6: Q-Q plots for the measured water quality indicators at Site HC1



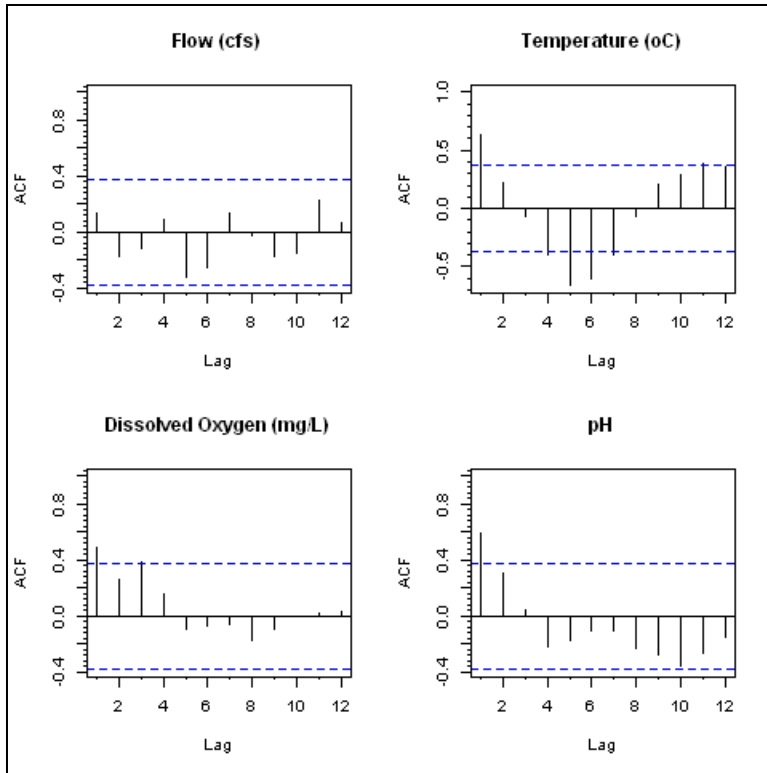
AF 7: Q-Q plots for the measured field parameters at Site HC2



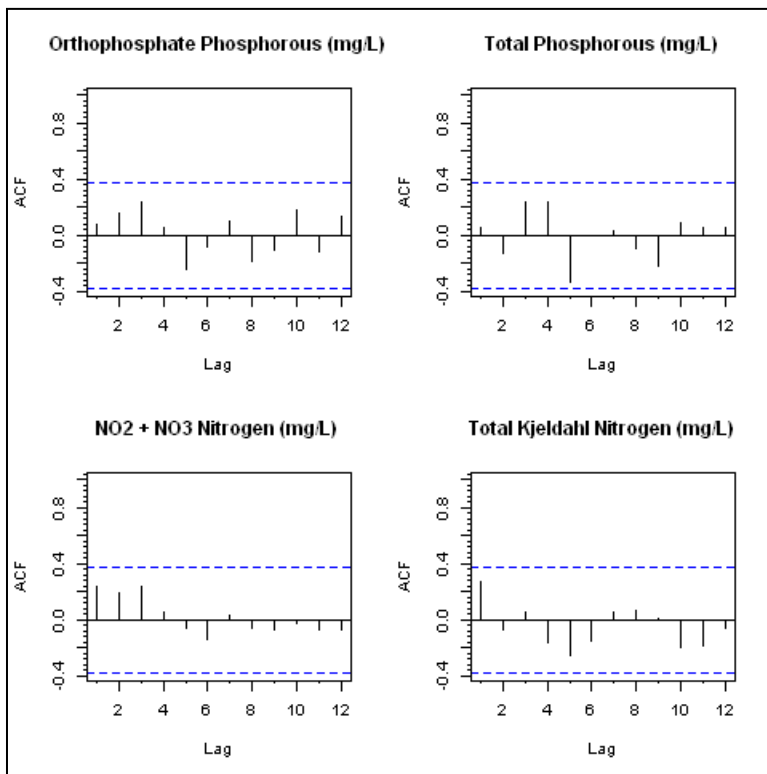
AF 8: Q-Q plots for the measured nutrients at Site HC2



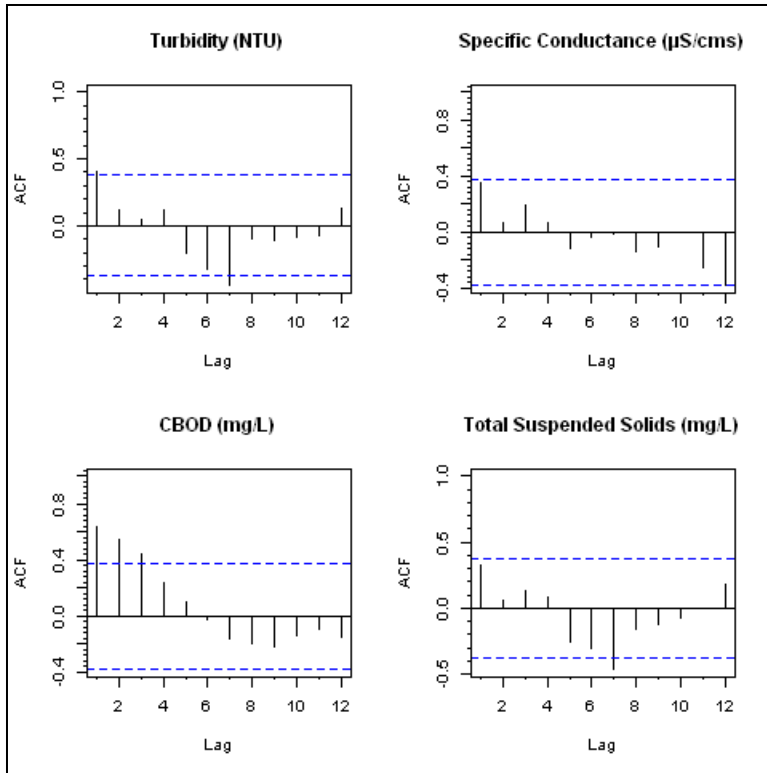
AF 9: Q-Q plots for measured water quality indicators at Site HC2



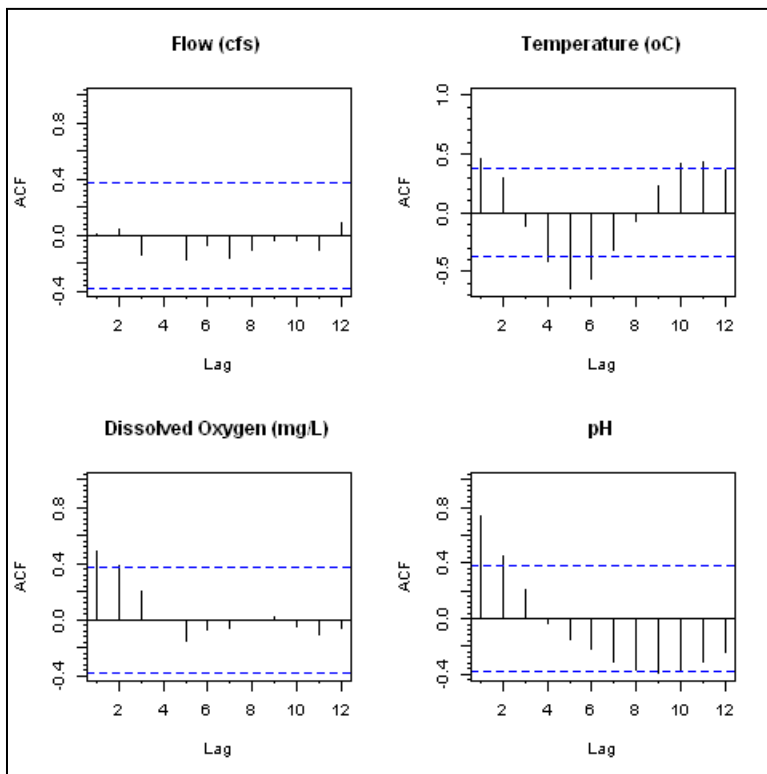
AF 10: ACF for measured field parameters at Site CC2



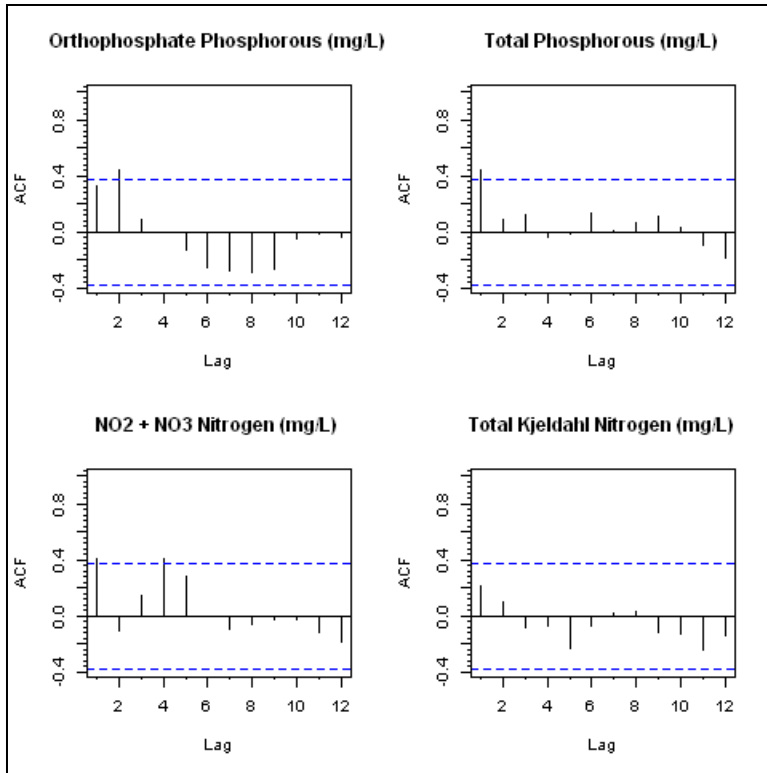
AF 11: ACF for the measured nutrients at Site CC2



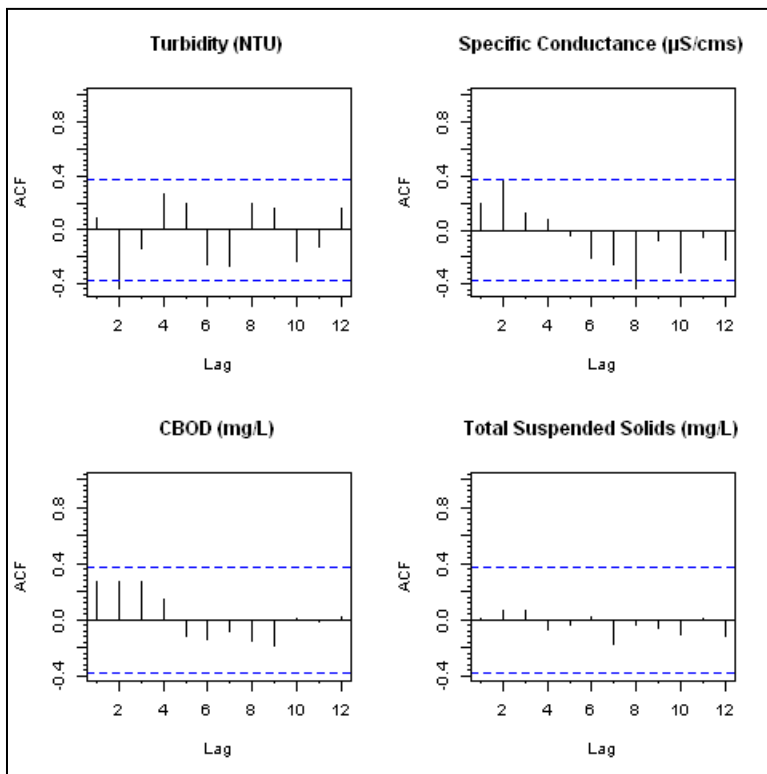
AF 12: ACF for measured water quality indicators at Site CC2



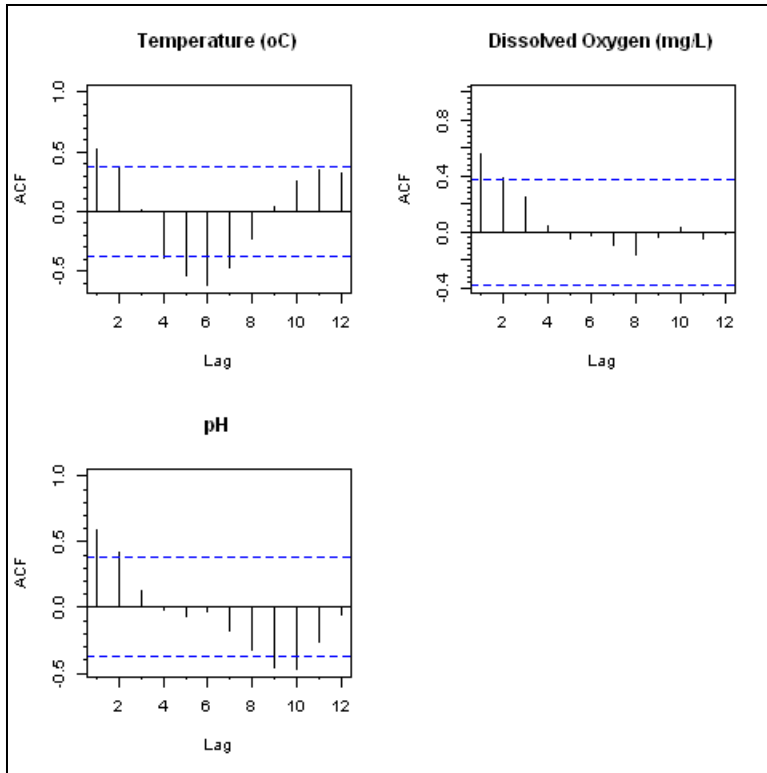
AF 13: ACF plots for measured field parameters at Site HC1



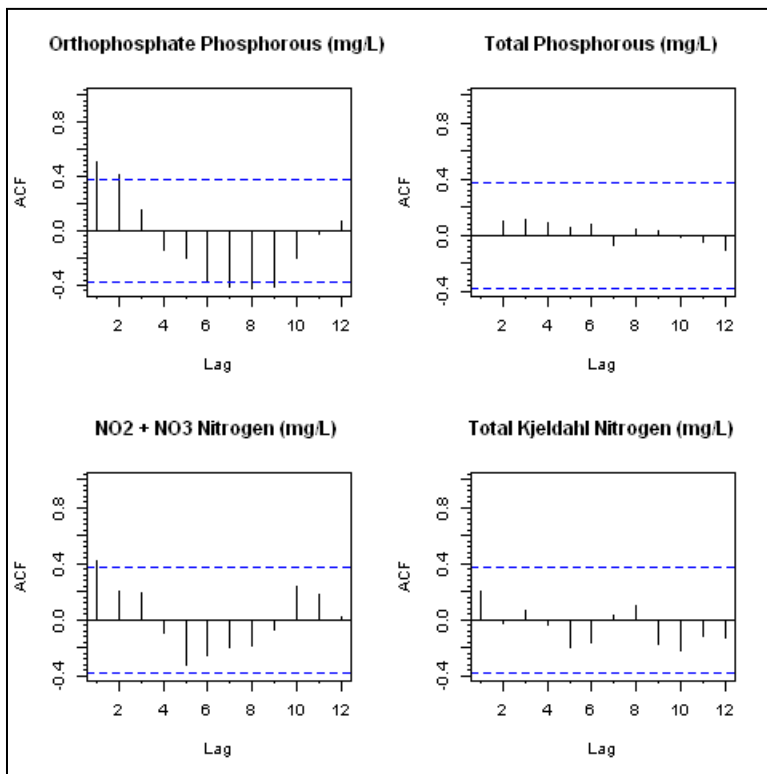
AF 14: ACF for measured nutrients at Site HC1



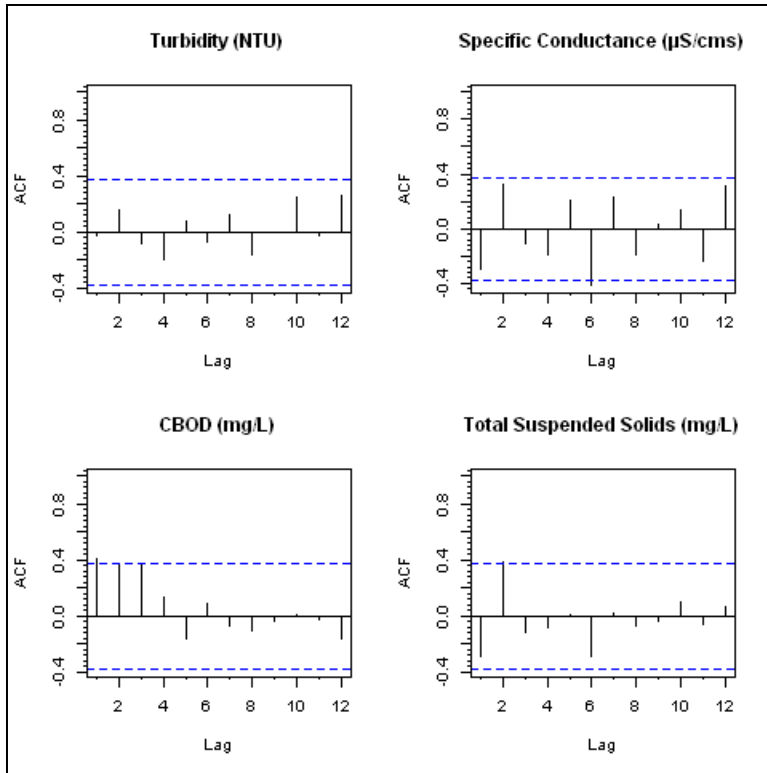
AF 15: ACF for the measured water quality indicators at Site HC1



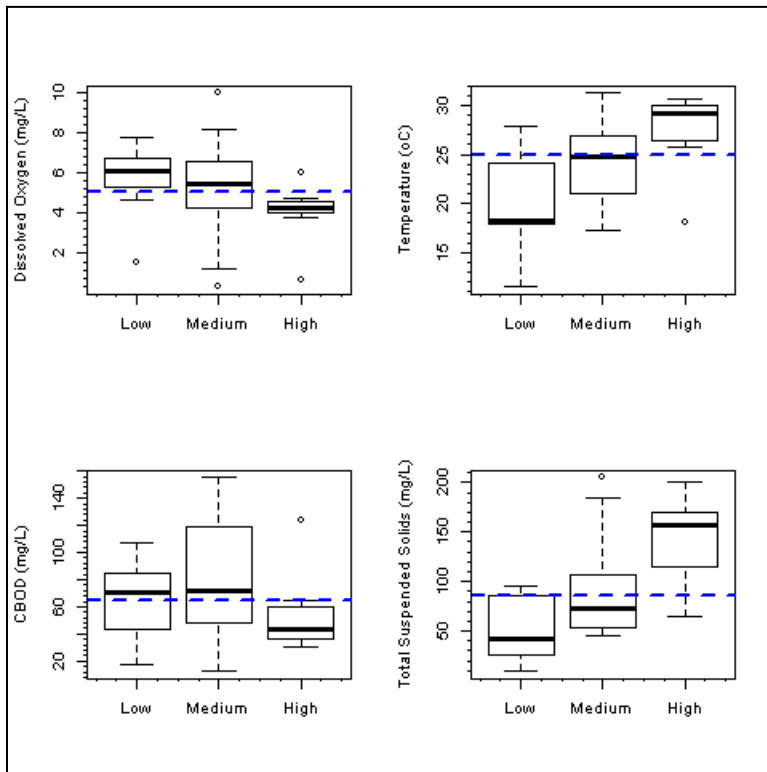
AF 16: ACF for measured field parameters at Site HC2



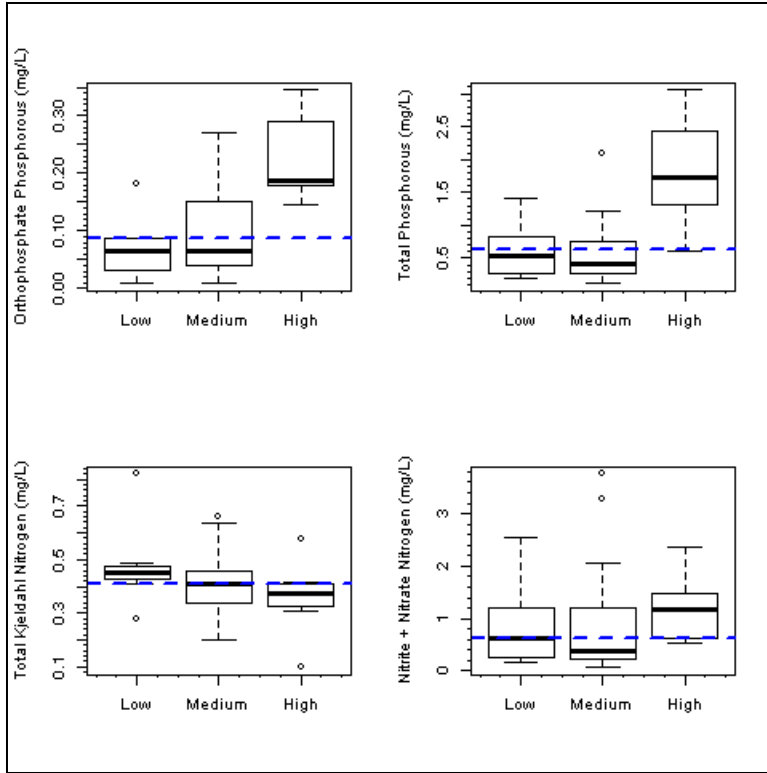
AF 17: ACF for measured nutrients at Site HC2



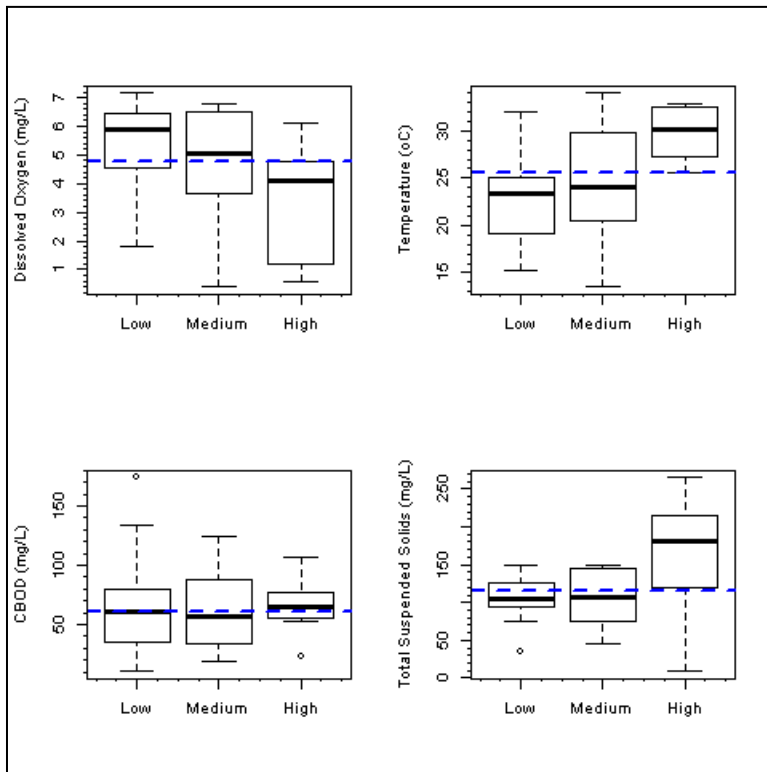
AF 18: ACF plots for the measured water quality indicators at Site HC2



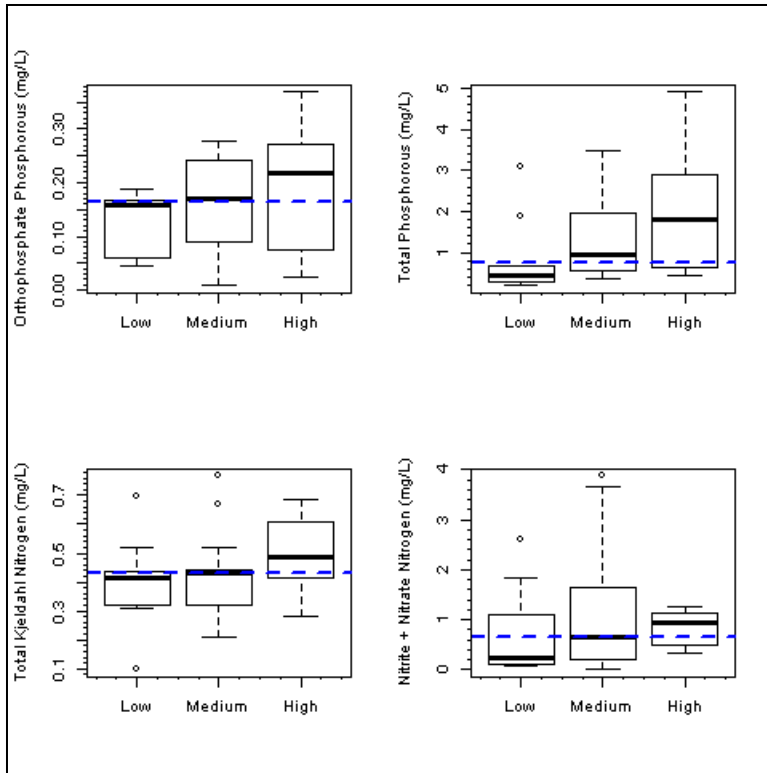
AF 19: Water quality characteristics pertaining to different flow regimes at Site CC2



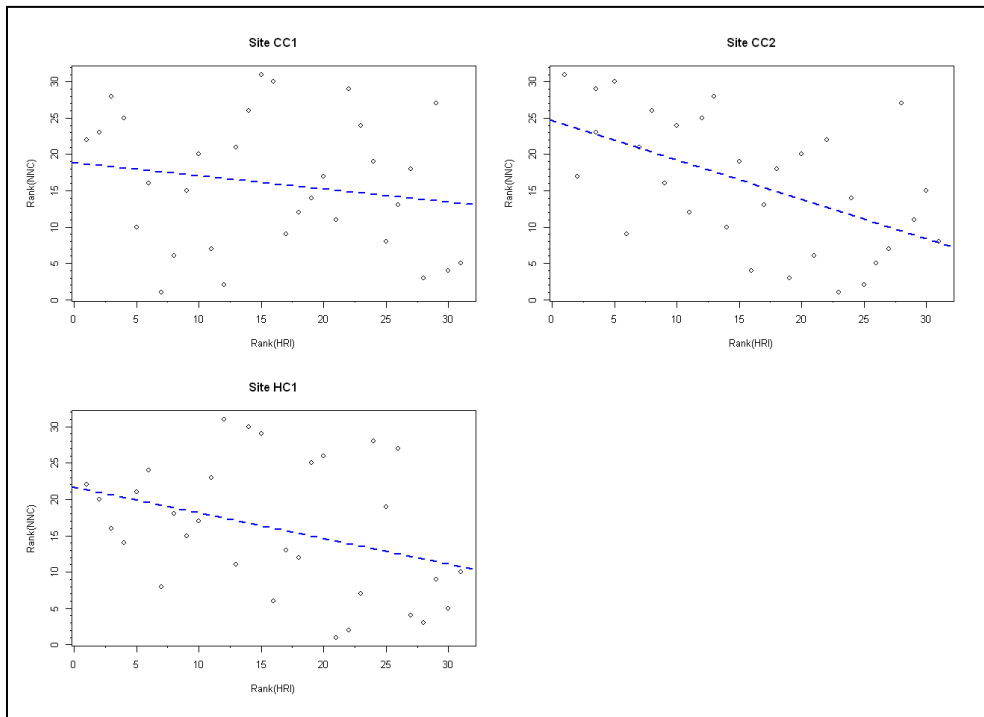
AF 20: Nutrient characteristics pertaining to different flow regimes at Site CC2



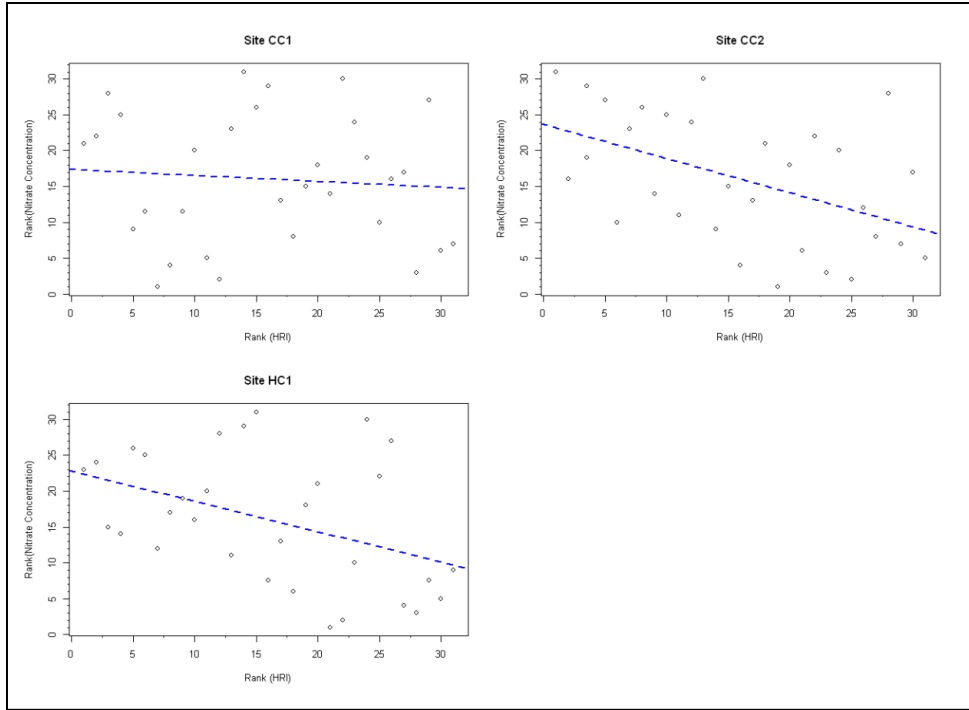
AF 21: Water quality characteristics pertaining to different flow regimes at Site HC1



AF 22: Nutrient characteristics pertaining to different flow regimes at Site HC1



AF 23: Correlation between Normalized Nitrate Concentration and Hydraulic Nitrate Reduction Index



AF 24: Correlation between Nitrate Concentration and Hydraulic Nitrate Reduction Index (HRI)