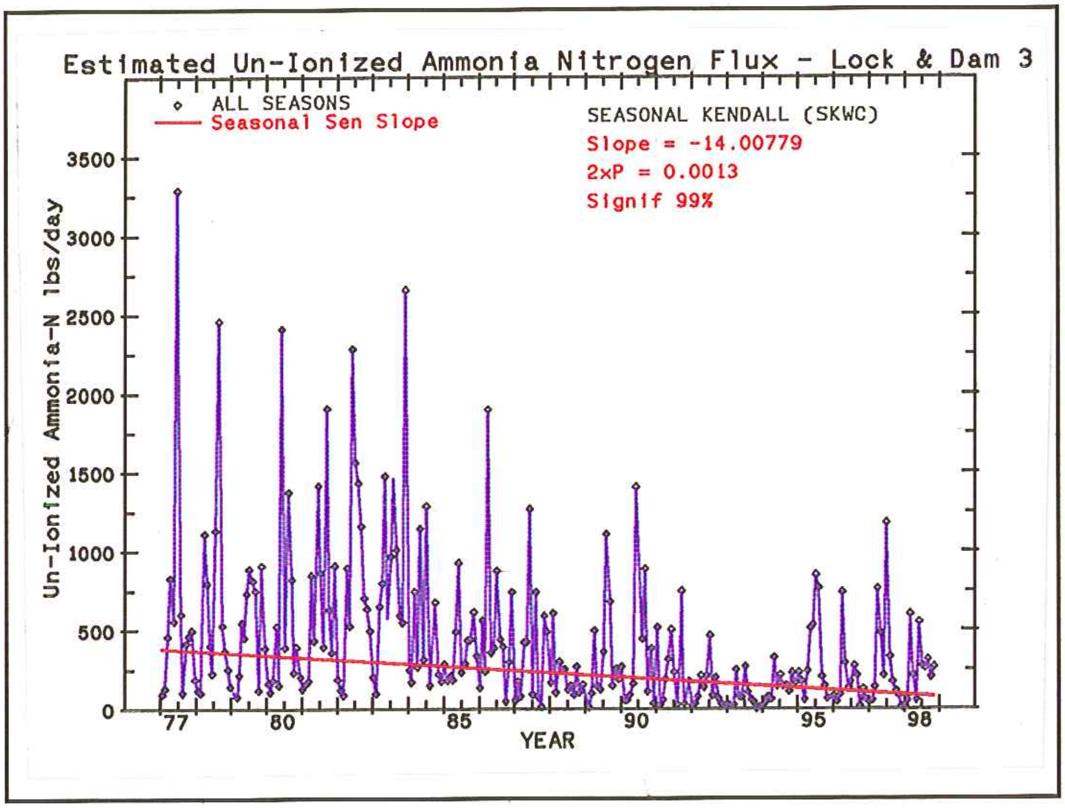
Long-Term Water Quality Trends Observed at Wisconsin's Ambient Monitoring Sites on the Upper Mississippi River



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EPA's old water quality database (STORET) provided an archive of the Department's long-term water quality monitoring data for the Mississippi River. Although the system was not easy to use compared to today's "point-and-click" software programs, this system set a standard for water quality monitoring databases that have evolved over the years. Without this centralized storage system, it is questionable whether the Department's historic water quality monitoring data would have been available in order to conduct the present trend analyses. I would like to acknowledge Carol Tiegs, our Department's STORET expert, who provided assistance with STORET use support over many years.

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INTRODUCTION

One of the most frequent questions asked by the general public, legislators, resource agencies, environmental interests and the regulated community has been, "Is the Mississippi River water quality improving or getting worse?" At first, this might seem like an easy question to answer, especially if major point and non-point source pollution efforts have been implemented and the impacted stream is small. However, when dealing with the Mississippi River mainstem, the answer is less obvious due to its large size and potential pollution inputs from its huge watershed. In addition, changes in climatic variables (temperature, flow, and precipitation) and human-induced biases (time and method of sampling or analytical changes) may confound water quality trend analyses. Finally, the existence of a sufficiently long and consistent water quality monitoring program is necessary to answer this question.

During the last two decades, the Wisconsin Department of Natural Resources (WDNR) conducted monthly water quality monitoring at three sites along the Mississippi River from Red Wing, Minnesota (Lock and Dam 3) to Lynxville, Wisconsin (Lock and Dam 9). Earlier records from the early 1960s do exist for one station (Lock and Dam 11 at Dubuque, IA), but this site was discontinued in the mid-1970s. Additional sites have been sampled during the last two decades but these records were generally limited to ten years. This river reach has also been monitored by the Minnesota Pollution Control Agency (MPCA) and a summary of both MPCA's and WDNR's monitoring efforts has been previously described (Sullivan, 1989). MPCA's monitoring effort was reduced in the mid-1990s. More recently, the U.S. Geological Survey's Long Term Resource Monitoring Program has been conducting a comprehensive water quality monitoring program on the Upper Mississippi River, but this record is limited to ten years or less. The Metropolitan Council Environmental Services has an extensive water quality monitoring program that extends back to the mid-1970s, but their Mississippi River monitoring is primarily restricted to the Twin Cities Metropolitan Area and an electronic copy of their data was not readily available.

The Department's ambient water quality monitoring program on the Mississippi began in the late 1970s. Water samples have been analyzed at the State Laboratory of Hygiene since program inception. This has assured laboratory method continuity and consistency and greatly facilitated data analysis. Data have been stored in U.S. EPA's Storage and Retrieval System (STORET) and have been accessible via dial-up or network connections. In 1999, the STORET database could no longer be used to store data due to computer coding problems dealing with the year 1999 and 2000. Since that time, a new system has been developed by EPA and will likely be used by the Department. As a result of this database transition, it was appropriate to re-evaluate Wisconsin's long-term monitoring results in 1999, while the old STORET system was still accessible.

The primary purpose of this evaluation was to assess seasonal and yearly variation in Mississippi River water quality monitoring data and to identify significant long-term trends. This assessment will be used to help guide the Department's future monitoring strategies for the river and to provide water quality information to the public and other resource agencies that are interested in Mississippi River water quality trends.

METHODS

Wisconsin DNR's long-term (1977-98) water quality data for the Mississippi River main channel was obtained from the STORET computer data base. Long-term trend analyses were restricted to stations with the longest period of record. These included the following three stations: Lock & Dam 3 near Red Wing, MN, Lock & Dam 4 at Alma, WI and Lock & Dam 9 near Lynxville, WI (Figure 1).

Field sampling for dissolved oxygen, water temperature and pH followed standardized procedures (WDNR, 1983). Water chemistry analysis was performed at the Wisconsin State Laboratory of Hygiene (WSLH), Madison, WI, following Standard Methods and/or EPA approved methods (WSLH, 1992). A summary of test methods and quality assurance information has been previously described (Sullivan, 1993). There were instrumentation and minor method changes over the 21-year period, but none of these charges were believed to introduce significant bias into the laboratory results described in this report (George Bowman, WSLH, personal communications. Sampling was conducted at monthly intervals over the 21-year period typically between mid-morning and mid-afternoon.

Field or laboratory measured parameters included: water temperature, conductivity, chloride, dissolved oxygen (DO), pH (field and lab), ammonia+ammonium nitrogen (NHx), nitrite+nitrate nitrogen (NOx), total phosphorus (TP), dissolved ortho-phosphorus, total suspended solids (TSS), dissolved silica (Si), total chlorophyll *a,* and fecal coliform bacteria. Organic nitrogen was measured prior to March 1981 or calculated from the difference between total Kjeldahl nitrogen and NHx after this period. TKN data are not presented in this report but are available in the raw data set. Calculated parameters included DO saturation, un-ionized ammonia nitrogen (UNH3), inorganic nitrogen (NHx+NOx), total nitrogen (TN = organic nitrogen + NHx + NOx), percent of TN present as inorganic nitrogen, percent of TP present as ortho-phosphorus and the TN/TP ratio. Total P and dissolved ortho-phosphorus were reported as P. Similarly, all forms of nitrogen were reported as N. Dissolved Si was reported as $Si0_2$.

Estimates of DO saturation were based on an assumed station (field) pressure of 760 mm at the time of sampling. This slightly underestimated actual DO saturation since station pressure readings are typically between 740 and 755 mm. Un-ionized ammonia nitrogen was calculated using ambient temperature and field pH. Loading estimates (flux) were derived for specific parameters by using the concentration measurements and river flows on the day of water quality sampling. Loading estimates (flux) were derived for specific parameters by using the concentration measurements and river flows recorded by the U.S. Corps of Engineers at the respective Lock and Dam monitoring site at the time of water quality sampling.

Data were transferred from STORET into Lotus 123™ spreadsheet software for initial data evaluation. Missing or questionable values were verified against hard copy laboratory records. Corrected values were re-entered into the STORET database. Values reported as less than detection were set equal to the detection limit for statistical calculations and for plotting.

Statistical analyses and plots were prepared using WQHYDRO version 2030 (WQHYDRO, 1997a). A Kruskall-Wallis test was used to test for the presence of seasonality and was automatically computed when plotting monthly box plots (Appendix A). Trend analysis was performed using a Seasonal Kendall test with (SKWC) and without (SKWOC) correction for

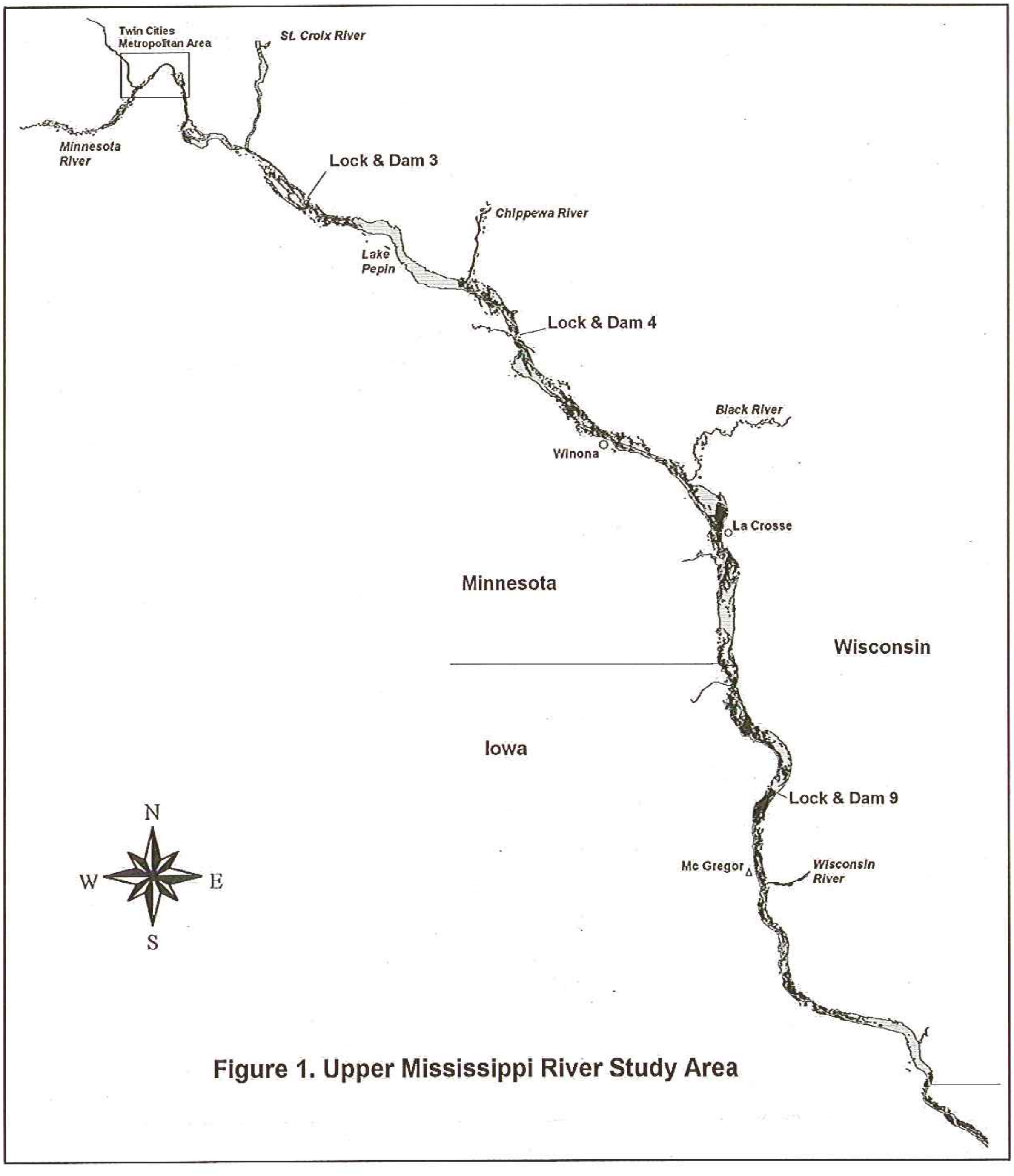

Figure 1. Upper Mississippi River Study Area

serial correlation (Hirsch et al. 1982 and Hirsch and Slack 1984). Testing for serial correlation was performed using a Spearman rank correlation of deseasonalized data. If significant serial correlation was found, the SKWC trend analysis results were used. The need to check for serial correlation was only necessary when SKWOC trend test was significant, but SKWC was not. Water quality variables that showed significant correlation (Spearman rank) to river flow were flow-adjusted using regression analysis and then the residuals were tested for trends as described above. In addition, variables that were potentially influenced by sampling time (i.e. temperature, dissolved oxygen, dissolved oxygen saturation, and pH) were also time-adjusted using a sinusoidal regression correction when the sampling time exhibited a significant temporal trend for that station.

Trend analysis was performed on monthly data spanning at least 15 years. A significance level (alpha) of 0.05 for a non-directional test (i.e. increasing or decreasing trend) was the criterion used to establish significant trends or correlations. For Seasonal Kendall tend analysis in WQHYDRO, this was denoted as 2P<0.05.

RESULTS and DISSCUSSION

Seasonal Changes in Water Quality

All water quality and physical parameters evaluated in this report showed significant seasonal (monthly) fluctuations (Appendix A). This response is typical for water quality data and is generally attributable to seasonal changes in solar radiation and hydrologic factors. Further, the annual cycle of terrestrial and aquatic plant production can also exert an influence on the quality and quantity of runoff or affect instream water quality conditions. Seasonality presents a potential problem for trend detection unless specifically addressed in the trend analysis procedure.

Parameters that showed the most pronounced seasonal variation included water temperature, river flow, DO, dissolved Si, total chlorophyll *a*, TSS and the percent of TP in the ortho-phosphorus fraction. Seasonal changes in water temperature provided a classic cyclical pattern with minimums in January and maximums in July or August.

River flow exhibited a more variable seasonal pattern with maximums typically following snowmelt runoff and spring rains (April-May) followed by a gradual decline to minimum flows during mid-winter (January-February). Increased precipitation and runoff in combination with headwater reservoir releases may result in a slight increase in flows during late fall.

Seasonal DO concentrations generally showed a seasonal pattern that was the inverse of water temperature since the solubility of DO increases as temperature decreases. As a result, DO levels were highest in winter and lowest in summer.

Total suspended solid concentrations followed a seasonal pattern similar to temperature and river flow. Lowest TSS levels were found during periods of ice cover when river and tributary flows were low and internal sources of TSS (sediment resuspension and phytoplankton) were not important. Highest TSS concentrations were usually found during periods of spring or summer runoff.

Total chlorophyll *a*, an index to phytoplankton biomass, exhibited highest levels during May and lowest levels during mid-winter. Chlorophyll data were only available for Lock and Dam 3 and 9 and for a shorter time period (1988-98). Spring phytoplankton blooms (most likely diatoms) contributed to reductions in dissolved ortho-P, Si and NHx due to nutrient assimilation. Dissolved oxygen saturation was typically highest in May and likely corresponded to increased phytoplankton photosynthetic activity.

Many of the other water quality parameters assessed in this report were influenced by temperature (i.e. biological, physical or chemical processes) and/or river flow (i.e. dilution, resuspension, mixing) and thus, also showed significant seasonal changes. The only parameter that did not exhibit significant seasonality was the sample collection time. This was expected since sampling time was generally confined to a relatively narrow window of time. Sampling time was influenced by human-induced bias attributable to travel time changes associated with the home station and field schedule of the person responsible for sampling.

Annual Changes in Water Quality

Water quality conditions in the Upper Mississippi River mainstem normally exhibited moderate to large variation from year-to-year. These fluctuations in quality were most likely related to changes in timing, amount and distribution of precipitation and land use activities in the basins receiving the precipitation. Changes in precipitation are generally reflected in the river's flow or discharge. Substantial rainfall over a basin with agricultural land use results in increased non-point source pollutant contributions such as fecal coliform bacteria, nutrients and suspended solids. In contrast, during periods of low river flow, industrial and point source inputs, groundwater inflow and internal processes (i.e. sediment resuspension, nutrient cycling and algae or aquatic macrophyte growth) may played a larger role in influencing mainstem water quality conditions. More recently, the introduction of zebra mussels to the Mississippi River has presented a another biological agent that has the potential to influence riverine water quality conditions during some years in reaches with heavy infestations (Sullivan and Endris, 1998).

A graphical summary of annual changes in water quality conditions was evaluated by preparing box plots of monthly monitoring data collected in each year (Appendix A). The yearly information has been presented alongside the seasonal (monthly) box plots to facilitate comparisons between these two temporal scales.

Annual box plots of river flow on sampling days at Lock and Dam 3, 4 and 9 showed distinct periods of low flow in 1977, 80, 87, 88, 89, and to a lesser extent 1990. High flows were obvious in 1986 and 93. The magnitude of the low or high flow periods differed somewhat between the three monitoring stations due different tributary flow contributions. The impact of a tributary's flow or pollutant contribution on a downstream monitoring site decreased as the distance and drainage area contribution increased. This was not only true of tributary-induced water quality changes in the mainstem of the river, but also applied to major point source discharges to the Mississippi such as the Metropolitan Wastewater Treatment Plant at St. Paul, MN.

An estimate of major tributary and headwater flow contributions to the Mississippi River was developed by preparing an annual average flow budget for the U.S. Geological Survey's gaging station at Mc Gregor, IA for the 21-year monitoring period (Figure 2). The major tributaries influencing the study area include the Minnesota, St. Croix, Chippewa and Black Rivers and generally accounted for 40 to 55 percent of the flow as measured at the Mc Gregor gage. Upper

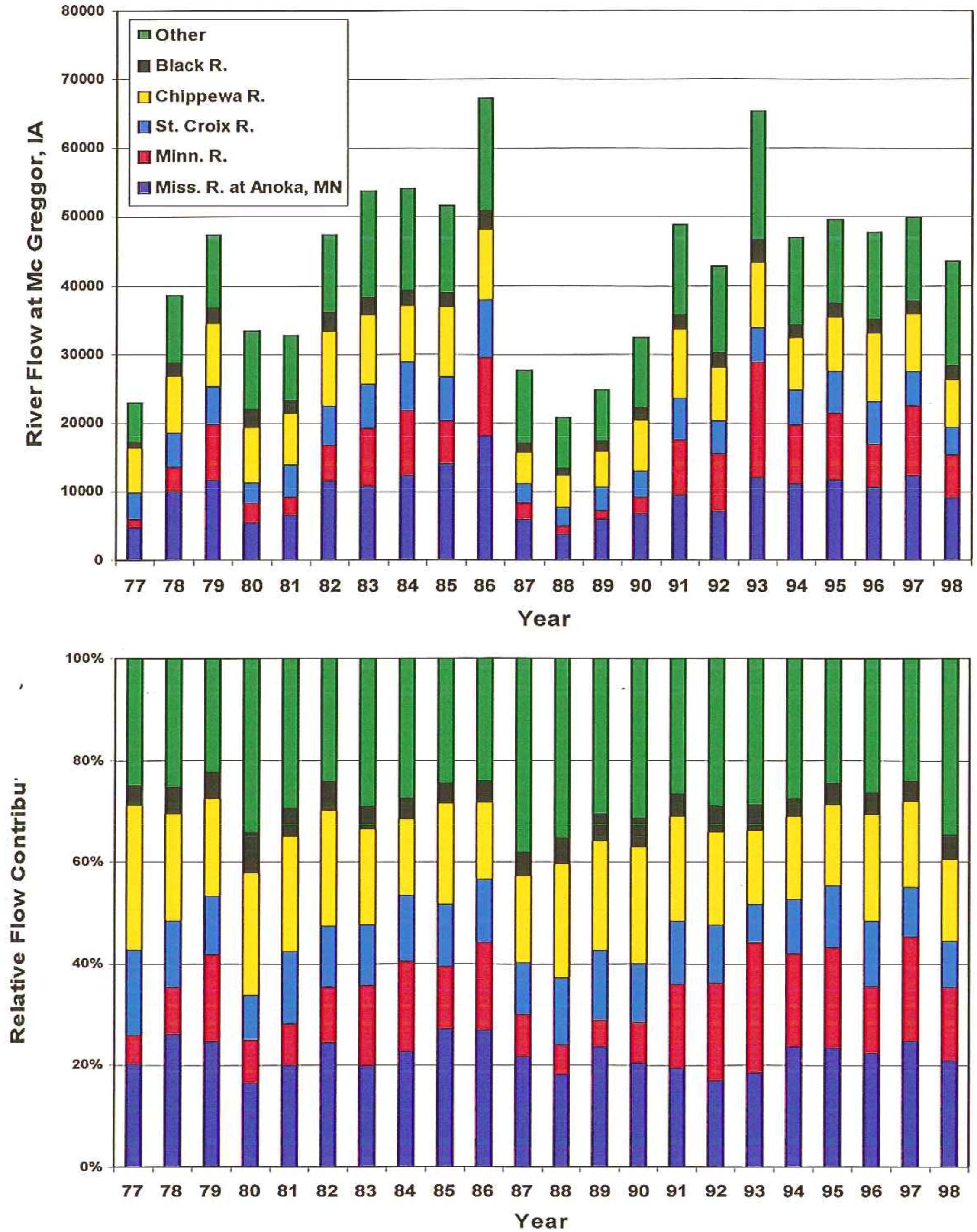

Figure 2. **Upper**. Annual average flow and estimated annual average tributary and head water flow contribution to the Mississippi River at Mc Gregor, Iowa. **Lower**. Same information but expressed as a percentage of Mc Gregor's annual mean flow. Data from USGS gaging stations in Wisconsin, Minnesota and Iowa.

Mississippi River headwater flows (Anoka, MN gage) and many smaller tributary inflows from Minnesota and Wisconsin comprised the remainder. Smaller tributaries (combined) showed large year-to-year flow contribution that varied from about 20 to 40 percent of the total flow. The Minnesota River exhibited the greatest temporal change in flow contribution and ranged from about 5 percent during low flow (1988) to 25 percent during high flow (1993) years. In general, these changes in flow contribution were likely important factors influencing temporal and spatial water quality conditions in the Mississippi River study reach.

Water quality parameters exhibiting the largest annual changes included conductivity, Cl, pH, N (all measured forms), TN/TP ratio, and percent ortho-P. This annual variation was likely influenced by the quality and quantity of surface water runoff and instream processes that changed or altered the river's water quality as the water flowed downstream. For example, during periods of low flow, the hydraulic retention time of the navigation pools increased and promoted the growth of phytoplankton (i.e. increased chlorophyll *a*) due to reduced flushing. Reduced river flow is normally associated with reduced tributary loadings of TSS and nutrients. Lower TSS concentrations may result in improved light penetration and may further enhance phytoplankton or periphyton development or promote increased submersed aquatic macrophyte growth in the shallow riverine pools or channel border habitats. The autochthonous production of organic matter by algae or macrophytes lowers dissolved nitrogen concentrations as a result of nutrient assimilation. In contrast, dissolved ortho-P may increase during summer low flows as a result of releases from anoxic sediments, especially in Lake Pepin, a natural riverine lake located in Pool 4. The combination of reduced tributary nitrogen inputs, nitrogen assimilation by aquatic plants and sediment P release resulted in lower TN/TP ratios during low flow years.

The impacts of point source discharges to the Mississippi River were more noticeable during low flow conditions when the river provided less water to dilute these wasteloads. Point source impacts were more apparent in the upper study area below the Twin Cities Metropolitan Area where the wasteloads were relatively high and the river flow was less. Annual box plots of some water quality data have indicated improved conditions associated with point source pollution abatement in the Twin Cities Area. This was most apparent with total and un-ionized ammonia nitrogen, a potentially toxic form of inorganic nitrogen, and DO saturation. Mainstem point source discharges between Lock and Dam 3 and 9 are relatively small, and tributary inflows provide more flow to dilute these wasteloads. As a result, the impacts of point source discharges in this latter reach are more difficult to quantify.

High river flows greatly diminished the influence of internal factors such as algae or submersed aquatic macrophyte growth, sediment releases or point source discharge impacts on the river's water quality. Instead, the water quality of the river at a particular site is largely influenced by the quality of runoff water from major tributaries above that location. For example, the monitoring site at Lock and Dam 3 was greatly influenced by the Minnesota River during high flow periods. This watershed is heavily influenced by agricultural landuse and contributes to high nutrient and TSS loadings to the upper study area (Stark, 1996 and Kroening, 1998). The impact of the Minnesota River on water quality measured at Lock and Dam 4 was substantially less due to greater flow contributions from other tributaries and solids settling and nutrient cycling in Lake Pepin.

Significant Water Quality Trends

Annual box plots provide an indication of year-to-year changes and some visual impression of long-term trends. However, additional analyses are required to establish if the observed temporal changes in water quality are statistically significant. The seasonal Kendall test is a widely accepted method for establishing the significance of monotonic trend (gradual change over many years) in long-term water quality records. The trend slope (i.e. change in concentration or unit value per year) presented as part of the seasonal Kendall test is an estimated value based on a median slope derived from of all the pairs of data within a particular season (WQHYDRO, 1997b).

A summary of the trend analysis of long-term water quality data collected at Lock and Dam 3, 4 and 9 is presented in Tables 1 to 3. Trend results using SKWOC were not presented since all parameters showed significant serial correlation. A graphical illustration of parameters showing significant long-term trends for the three stations is present in Appendix (B). River flow was also included for comparative purposes even though flow trends were not significant. A graphical summary of all significant trends is presented in Figure 3 where the estimated trend slope was expressed as a percentage of the parameter's median concentration or unit value (Tables 1-3). This allowed for a better comparison between monitoring stations and parameters. In the trend discussions provided below, the percentage change per year in a parameter's concentration or unit value is based in reference to the median value.

Fecal coliform bacteria provide an index to bacteria contamination in surface waters. High fecal coliform levels are usually associated with animal waste runoff and untreated domestic wastewater. However, stormwater runoff from urban areas may also contain elevated fecal coliform levels from domestic pets. Long-term fecal coliform records were only available for Lock and Dam 3 and 4. A significant decreasing trend was noted for both stations, 7.9% and 3.1% per year, respectively (Figure 3). Flow-adjustment was necessary for the trend analysis of data collected at Lock and Dam 3 (Table 1). The reduction of fecal coliform bacteria was likely associated with improved municipal wastewater treatment and a reduction of untreated domestic wastewater discharges due to the elimination of combined sanitary and storm sewers in the Twin Cities Metropolitan area between 1986 and 1995 (Cities of Minneapolis, et al. 1996). Elevated fecal coliform counts still occur, and these are most likely associated with animal waste runoff during high flow periods or during winter months when municipal wastewater effluent disinfection is not required.

Conductivity, an indirect measurement of total dissolved solids, exhibited significant increasing trends at all three monitoring stations with the average flow-adjusted trend ranging from 0.8 to 1.6% per year (Figure 3). These trends reflected an estimated 75 to 100 uS/cm increase in conductivity between 1977 and 1998. Lock and Dam 4 appeared to exhibit a greater increasing trend than that observed for Lock and Dam 3 or 9. It is not known if this larger trend is significant or what factors are contributing to this difference. A potential factor could include greater dissolved solid inputs from the Chippewa or Buffalo Rivers which enter the Mississippi a few miles above Lock and Dam 4, but this needs further evaluation.

The conductivity trends were supported by the chloride results, which also exhibited significant increasing trends (2.2 to 2.8% per year) over a somewhat shorter monitoring period (1982-98). Chloride is one of the major ions found in freshwater. Potential sources of chloride include road salt and fertilizer (potassium chloride) runoff, municipal and industrial discharges, animal waste

Table 1. Summary of flow correlation and trend analysis for Wisconsin's ambient water quality monitoring station at Lock and Dam 3 above Red Wing, Minnesota. Trend analysis was performed on monthly data using the Seasonal Kendall test with correction for serial correlation (SKWC). The term "2*P" represents the probability of a Type I error for a two-sided hypothesis test (i.e. probability that the observed trend is due to random sampling variability).

Parameter	Param. vs Flow Correlation Spearman's rho	SKWC Trend 2*P	Flow-Adj. SKWC Trend 2*P	Estimated Trend Slope unit/yr	Parm. Median Value	% Change per Year from Median
Time of Collection hr	-	0.031 +	-	-9.54	1120	-0.9
Water Temperature C	0.195 *	0.196	0.030 +@	0.05	10.7	0.5
Flow cfs	-	0.244	-	-	16100	-
Conductivity uS/cm @25C	0.193 *	0.007 +	0.005 +	3.95	485	0.8
Chloride mg/L	-0.562 *	0.004 +	<0.001 +	0.46	19	2.4
Dissolved Oxygen mg/L	-0.066	0.013 +	0.008 +#	0.05	10.2	0.5
DO Saturation %	0.159 *	0.002 +	<0.001 +@	0.43	89	0.5
pH field s.u.	0.112	0.712	0.984 #	-	8.0	-
Ammonia+Ammonium-N mg/L	-0.284 *	<0.001 +	<0.001 +	-0.013	0.16	-8.1
Un-ionized Ammonia-N mg/L	-0.297	<0.001 +	0.001 +	-0.0002	0.0028	-7.1
Nitrite+Nitrate-N mg/L	0.544 *	0.007 +	0.020 +	0.04	1.6	2.5
Inorganic Nitrogen mg/L	0.461 *	0.230	0.276	-	1.9	-
Organic Nitrogen mg/L	0.361 *	0.123	0.104	-	1.0	-
Total Nitrogen mg/L	0.525 *	0.448	0.506	-	2.8	-
% Inorganic Nitrogen	0.235 *	0.095	0.141	-	68	-
Dissolved Ortho-P mg/L	-0.281 *	0.382	0.100	-	0.093	-
Total Phosphorus mg/L	0.025	0.465	-	-	0.180	-
% Ortho-Phosphorus	-0.404 *	0.098	0.026 +	0.49	50.4	1.0
Ratio TN/TP	0.459 *	0.454	0.872	-	16.8	-
Total Suspended Solids mg/L	0.599 *	0.119	0.696	-	27	-
Fecal Col. Bact. #/100 mL	0.142 *	0.350	0.048 +	-3.17	40	-7.9

* Significant flow correlation for a non-directional test (alpha=0.05)
+ Significant trend for a non-directional test (alpha=0.05)
# Hour-adjusted only.
@ Flow and Hour-adjusted.

Table 2. Summary of flow correlation and trend analysis for Wisconsin's ambient water quality monitoring station at Lock and Dam 4 at Alma, Wisconsin. Trend analysis was performed on monthly data using the Seasonal Kendall test with correction for serial correlation (SKWC). The term "2*P" represents probability of a Type I error for a two-sided hypothesis test (i.e. probability that the observed trend is due to random sampling variability).

Parameter	Param. vs Flow Correlation Spearman's rho	SKWC Trend 2*P	Flow-Adj. SKWC Trend 2*P	Estimated Trend Slope unit/yr	Parm. Median Value	% Change per Year from Median
Time of Collection hr	-	0.247	-	-	1308	-
Water Temperature C	0.237	0.628	0.311	-	9.0	-
Flow cfs	-	0.254	-	-	26540	-
Conductivity uS/cm @25C	-0.501 *	0.007 +	<0.001 +	5.05	320	1.6
Chloride mg/L	-0.763 *	0.014 +	<0.001 +	0.31	11	2.8
Dissolved Oxygen mg/L	-0.083	0.003 +	-	0.06	10.0	0.6
DO Saturation %	0.144 *	<0.001 +	<0.001 +	0.58	88.8	0.7
pH field s.u.	-0.201 *	0.668	0.320	-	7.7	-
Ammonia+Ammonium-N mg/L	-0.208 *	<0.001 +	0.017 +	-0.0019	0.05	-3.8
Un-ionized Ammonia-N mg/L	-0.310 *	0.521	0.762	-	0.007	-
Nitrite+Nitrate-N mg/L	0.029	0.006 +	-	0.02	1.0	2.0
Inorganic Nitrogen mg/L	-0.054	0.031 +	-	0.01	1.2	0.8
Organic Nitrogen mg/L	0.180 *	0.153	0.330	-	0.8	-
Total Nitrogen mg/L	0.001	0.123	-	-	1.9	-
% Inorganic Nitrogen	-0.143 *	0.004 +	0.017 +	0.35	59.4	0.6
Dissolved Ortho-P mg/L	-0.338 *	0.325	0.021 +	0.0005	0.060	0.8
Total Phosphorus mg/L	0.013	0.590	-	-	0.129	-
% Ortho-Phosphorus	-0.547 *	0.355	0.100	-	49.0	-
Ratio TN/TP	-0.027	0.394	-	-	14.8	-
Total Suspended Solids mg/L	0.529 *	0.014 +	0.078	-	12	-
Fecal Col. Bact. #/100 mL	0.105	0.042 +	-	-2.14	70	-3.1

* Significant flow correlation for a non-directional test (alpha=0.05)
+ Significant trend for a non-directional test (alpha=0.05)

Table 3. Summary of flow correlation and trend analysis for Wisconsin's ambient water quality monitoring station at Lock and Dam 9 below Lynxville, Wisconsin. Trend analysis was performed on monthly data using the Seasonal Kendall test with correction for serial correlation (SKWC). The term "2*P" represents the probability of a Type I error for a two-sided hypothesis test (i.e. probability that the observed trend is due to random sampling variability).

Parameter	Param. vs Flow Correlation Spearman's rho	SKWC Trend 2*P	Flow-Adj. SKWC Trend 2*P	Estimated Trend Slope unit/yr	Parm. Median Value	% Change per Year from Median
Time of Collection hr	-	0.011 +	-	-4.99	1135	-0.4
Water Temperature C	0.210 *	0.156	0.088 @	-	10.2	-
Flow cfs	-	0.280	-	-	32550	-
Conductivity uS/cm @25C	-0.134 *	0.003 +	0.004 +	3.60	384	0.9
Chloride mg/L	-0.425 *	<0.001 +	<0.001 +	0.31	14	2.2
Dissolved Oxygen mg/L	-0.141 *	0.868	0.843 @	-	10.9	-
DO Saturation %	0.052	0.400	-	-	91.0	-
pH field s.u.	0.138 *	0.911	0.332 @	-	7.8	-
Ammonia+Ammonium-N mg/L	-0.006	0.812	-	-	0.05	-
Un-ionized Ammonia-N mg/L	-0.008	0.557	-	-	0.0008	-
Nitrite+Nitrate-N mg/L	0.324 *	0.189	0.229	-	1.1	-
Inorganic Nitrogen mg/L	0.300 *	0.419	0.548	-	1.2	-
Organic Nitrogen mg/L	0.278 *	0.377	0.462	-	0.9	-
Total Nitrogen mg/L	0.394 *	0.542	0.822	-	2.1	-
% Inorganic Nitrogen	0.094	0.288	-	-	58.6	-
Dissolved Ortho-P mg/L	-0.066	0.542	-	-	0.064	-
Total Phosphorus mg/L	0.254 *	0.092	0.064	-	0.160	-
% Ortho-Phosphorus	-0.250 *	0.198	0.287	-	42.6	-
Ratio TN/TP	0.050	0.165	-	-	14.2	-
Total Suspended Solids mg/L	0.486 *	0.661	0.287	-	26	-

* Significant flow correlation for a non-directional test (alpha=0.05)
+ Significant trend for a non-directional test (alpha=0.05)
@ Flow and Hour-adjusted.

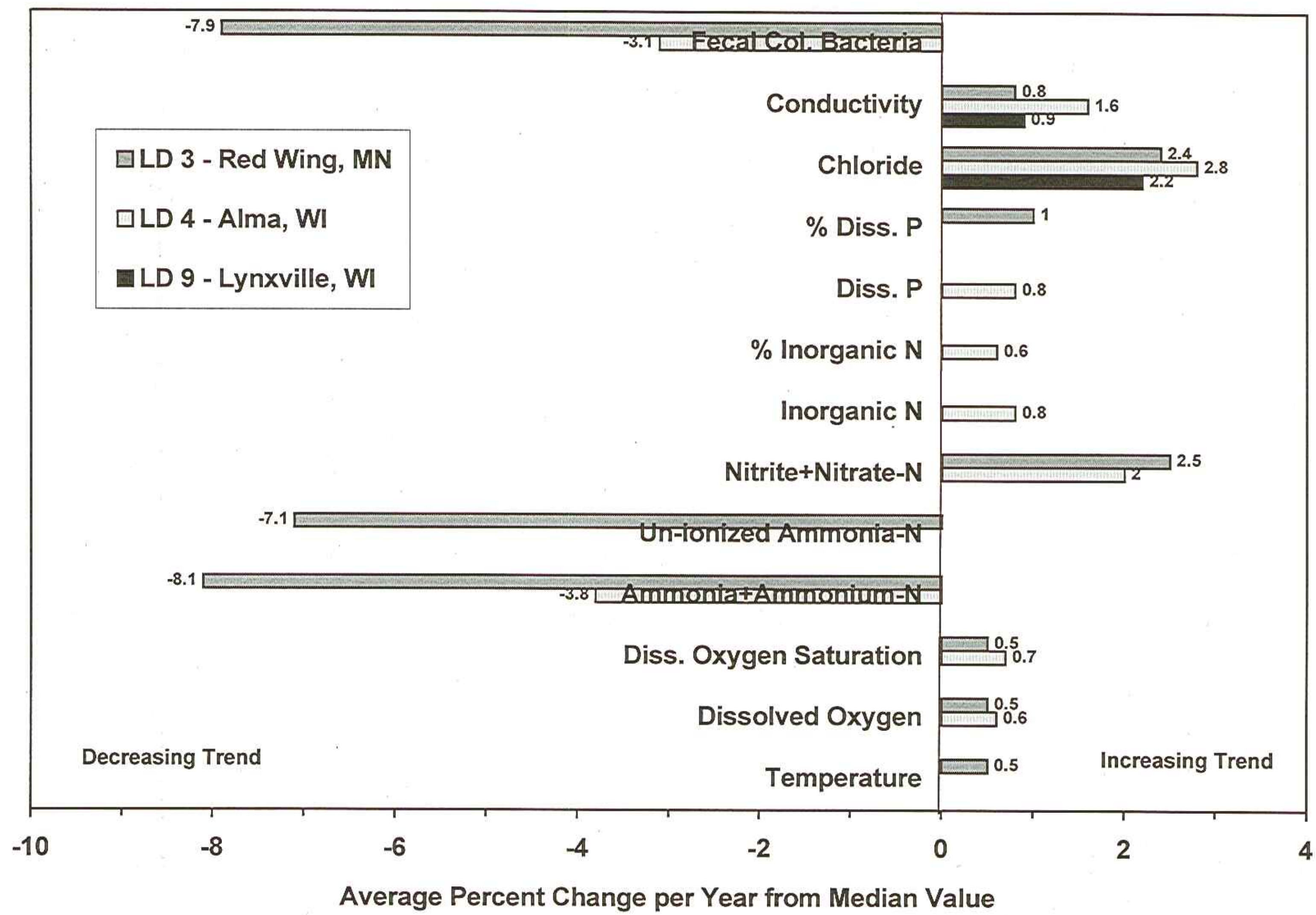

Figure 3. Summary of long-term water quality data exhibiting significant trends (apha=0.05) at Wisconsin Department of Natural Resources' ambient monitoring stations on the Mississippi River. Data were evaluated using the seasonal Kendall test.

runoff, and discharges of chloride-bearing groundwater. Chloride concentrations like conductivity were inversely correlated to river flow and thus required flow-adjustment for trend analysis. The chloride trends for the three stations yielded an estimated increase of 6 mg/L over the 16 years this parameter was measured. Although chloride levels are showing large increasing trends, median concentrations at the three monitoring sites ranged from 11 to 19 mg/L and are more than 20-fold less than Wisconsin's chronic water quality standard. Previous water quality trend results have indicated increasing chloride concentrations on a national scale and have been generally attributed to increasing use of road salt (Smith et al. 1987). However, the factors contributing the observed trend in this study have not been determined and the importance of other source inputs has not been evaluated.

Flow-adjusted NHx nitrogen trends exhibited an 8.1 and 3.8% per year decrease at Lock and Dam 3 and 4, respectively, over the 21-year monitoring period (Figure 3). Major sources of NHx nitrogen are typically associated with point source wastewater discharges. The decreasing trends observed at the two upstream monitoring stations likely reflected reduced inputs from the municipal wastewater treatment plants in the Twin Cities Metropolitan area. Kroening and Andrews (1997) also reported significant decreasing trends in total ammonia nitrogen concentrations at many surface water sites in the Mississippi River and tributaries above Lake Pepin for the 1984-93 time period. They attributed the decline to reduced inputs from wastewater treatment plants as a result of increased use of the nitrification process (ammonia removal).

Un-ionized ammonia, the form that is toxic to aquatic life, exhibited significant decreasing concentrations at Lock and Dam 3. The UNH3 trend averaged -7.1% per year and yielded an estimated reduction of 0.004 mg/L between 1977 and 1998. The fraction of NHx present as UNH3 increases with higher pH and water temperature. It is unlikely that pH influenced the decreasing trend observed at Lock and Dam 3 since a temporal trend in pH was not established. Water temperatures did show a small increasing trend slope at this site (0.05 °C/year, Table 1), but this would have contributed to a small increase in the UNH3 fraction. Therefore, the decreasing UNH3 trend observed at Lock and Dam 3 was attributed to reduced NHx concentrations.

Nitrite+Nitrate nitrogen usually represents the greatest fraction of total nitrogen in the river. This form of nitrogen has gained national attention due to its recent association with the Gulf of Mexico hypoxia problem. Concentrations of NOx increased significantly at Lock and Dam 3 and 4 over the study period. The average trend for the two sites was 2.25% per year and yielded an estimated concentration increase of approximately 0.8 and 0.4 mg/L at Lock and Dam 3 and 4, respectively, over the study period. Nitrite+Nitrate nitrogen was significantly correlated with river flow at Lock and Dam 3 but not at Lock and Dam 4.

Estimates of NOx flux (mass loading) also indicated a significant increasing trend at Lock and Dam 3 and 4 and yielded a trend slope of 4500 and 5000 Lb/d/yr, respectively (Table 4). Sources of NOx include fertilizer and manure runoff from agricultural watersheds, especially the Minnesota River basin, and point source discharge inputs, particularly municipal wastewater discharges from the Twin Cities Metropolitan area. Discharge of NOx-contaminated groundwater may be an additional source. Nitrification of municipal wastewater to abate UNH3 problems in surface water was likely an important factor influencing long-term NOx concentrations and fluxes observed at Lock and Dam 3 and 4. A similar response was absent for Lock and Dam 9 which was less impacted by NOx wasteloads originating from major point

Table 4. Trend analysis of inorganic nitrogen flux (all forms) determined at Wisconsin's ambient monitoring stations on the Mississippi River. Trend analysis was performed on monthly data using the Seasonal Kendall test with correction for serial correlation (SKWC). The term "2*P" represents the probability of a Type I error for a two-sided hypothesis test (i.e. probability that the trend is due to random sampling variability).

Site and Parameter	SKWC Trend 2*P	Estimated Trend Slope lbs/d/yr
Lock & Dam 3 - Red Wing, MN		
Ammonia+Ammonium-N lbs/d	<0.001 *	-1052
Un-ionized Ammonia-N lbs/d	0.001 *	-14
Nitrite+Nitrate-N lbs/d	0.041 *	4478
Inorganic Nitrogen lbs/d	0.171	3096
Lock & Dam 4 - Alma, WI		
Ammonia+Ammonium-N lbs/d	0.089	-124
Un-ionized Ammonia-N lbs/d	0.827	-0.30
Nitrite+Nitrate-N lbs/d	0.038 *	5022
Inorganic Nitrogen lbs/d	0.061	4424
Lock & Dam 9 - Lyxville, WI		
Ammonia+Ammonium-N lbs/d	0.829	28.5
Un-ionized Ammonia-N lbs/d	0.767	0.63
Nitrite+Nitrate-N lbs/d	0.213	3779
Inorganic Nitrogen lbs/d	0.306	3106

* Significant trend for a non-directional test (alpha=0.05)

source inputs.

Inorganic nitrogen concentrations only showed an increasing trend (0.8% per year) at Lock and Dam 4 (Figure 3) and resulted in an estimated increase of 0.2 mg/L over the monitoring period. The absence of a significant increasing trend of inorganic nitrogen at Lock and Dam 3 was likely offset by the significant decline in NHx nitrogen observed at this monitoring location. An inorganic nitrogen trend at Lock and Dam 9 was not expected since the two components of inorganic N, NHx and NOx, failed to exhibit significant trends at this site. Estimates of Inorganic nitrogen flux calculated for the three monitoring stations indicated increased loading over the monitoring period, but these trends were not statistically significant (Table 4).

The percentage of TN present as inorganic nitrogen exhibited a small increasing trend at Lock and Dam 4 (0.6 % per year), but not at the other two monitoring stations. This trend was consistent with the NOx and inorganic nitrogen results described above. The amount of TN found in the inorganic form showed substantial changes longitudinally, seasonally, and yearly (Appendix A). Inorganic nitrogen inputs, nutrient assimilation by algae and submersed aquatic macrophytes, and denitrification are likely important factors influencing spatial and temporal patterns.

Phosphorus is an important plant nutrient and is often the most critical nutrient influencing eutrophication in freshwater environments. Major phosphorus sources include runoff from agricultural watersheds and point source discharges. The two most important sources affecting phosphorus concentrations in the upper study area (above Lake Pepin) include the Minnesota River and the Metropolitan Wastewater Treatment Plant in St. Paul (Metropolitan Waste Control Commission, 1993).

No significant trends in TP concentrations were noted for the three monitoring sites. Dissolved ortho-P exhibited a small increasing trend (0.8 % per year) at Lock and Dam 4. This yielded an estimated concentration increase of 0.01 mg/l over the study period. This trend may have been influenced by sediment releases from Lake Pepin or from increased inputs from the Chippewa or Buffalo Rivers.

The percentage of TP present as dissolved ortho-P increased 1% per year at Lock and Dam 3. The median percentage of dissolved ortho-P was 50.4% at Lock and Dam 3 and the observed trend represented a 10% increase over the monitoring period. Although the fraction of dissolved P increased at this site, the concentration of dissolved ortho-P did not show an increasing trend. The reason for this response has not been determined. It may be related to changes in the characteristics of runoff or wastewater discharges or reduced utilization of available P by riverine algae. Lowest concentrations of dissolved ortho-P are typically found during May (Appendix A) when phytoplankton concentrations are normally elevated. The highest percentage of dissolved ortho-P was generally found during summer low flow conditions when point source inputs and internal flux (sediment release) were important.

Dissolved oxygen is an important water quality variable influencing fish and aquatic life habitat. Atmospheric re-aeration and aquatic plant photosynthesis represent the major source inputs. Dissolved oxygen concentrations can show substantial diurnal and seasonal fluctuations as a result of photosynthetic processes and changes in water temperature. Dissolved oxygen concentrations exhibited a small increasing trend at Lock and Dam 3 and 4, 0.3 and 0.6 percent per year, respectively. These trends resulted in an approximate DO increase of 0.6 and 1.3

mg/L during the study period. This improvement in DO, especially at Lock and Dam 3, was likely attributable to reductions in organic wasteloads from municipal and industrial point source discharges from the Twin Cities Metropolitan Area. The reason for the larger increasing trend at Lock and Dam 4 has not been determined. Potential factors could include reduced deoxgenation in the bottom waters of Lake Pepin, increased photosynthetic activity or changes in tributary DO contributions.

Dissolved oxygen saturation provides another way to evaluate DO trends and accounts for temperature-induced effects on DO concentration. The calculation of DO saturation presented here was based on an assumed station pressure of 760 mm since actual pressure levels were not recorded on the sampling days. As a result, the trend analyses presented for DO saturation assumed there were no long-term changes in atmospheric pressure at the monitoring sites.

Trends in DO saturation paralleled changes in DO concentration observed at Lock and Dam 3 and 4. The estimated DO saturation increase at these two sites was 9 and 12%, respectively, over the 21-year period. The fact that the DO saturation trends supported the DO concentration trends, and the absence of a significant DO trend at Lock and Dam 9, suggests that temperature and pressure-induced effects were not likely important.

Water temperature exhibited an increasing trend at Lock and Dam 3 (0.5% per year, Figure 3). This resulted in an approximate increase of 1 °C over the monitoring period. The lack of similar temperature trends at Lock and Dam 4 and 9 suggests this trend may not be related to climatic changes. Cooling water discharge from a nearby nuclear power plant influenced the monitoring site at Lock and Dam 3. It is suspected this facility may have contributed to the temperature increase observed at this sampling station, but this was not specifically evaluated.

The time of sample collection changed significantly over the course of the 21-year monitoring period at Lock and Dam 3 and 9. Water samples were collected approximately two to three hours earlier in the day during the late 1990s than in the late 1970s and early 1980s. This change was not intentional but was an artifact of the sampling program. In the last ten years, field staff responsible for sampling were located closer to the monitoring sites and arrived earlier in the day. This bias was an important consideration for variables showing large diurnal variation (DO, temperature, and pH).

SUMMARY and CONCLUSIONS

Water quality conditions in the Mississippi River can exhibit substantial seasonal and annual fluctuations associated with changing climatic conditions. Seasonal and annual changes in temperature and precipitation are two of the most important climatic variables that may induce temporal water quality variation in the river. The amount of precipitation is reflected by river flow which is a key factor influencing hydrodynamic (mixing, retention time, re-suspension, transport etc.) and biological (primary production) processes in a riverine system.

Tributary inflows and land use within their watersheds were important factors influencing water quality in the mainstem of the river. Runoff from basins with predominantly agricultural land use was likely a major factor influencing mainstem water quality. Point source wastewater discharges influenced mainstem water quality, but these impacts were more apparent at sites closer to the Twin Cities Metropolitan Area where river flow was less. Water quality in the river was also influenced by Lake Pepin and the navigational pools, which affect physical, chemical and biological processes. In particular, the hydraulic retention time and its negative relationship with river flow were important physical factors influencing longitudinal and temporal water quality changes.

Long-term water quality trends were evaluated by using statistical software that accounted for seasonality, time of sampling and river flow. Trend analysis was performed on approximately two decades of water quality monitoring conducted at three stations on the Mississippi River by the Department extending from Red Wing, MN (Lock and Dam 3) to Lynxville, WI (Lock and Dam 9).

Significant decreasing trends were noted for fecal coliform bacteria, un-ionzied ammonia nitrogen and total ammonia+ammonium nitrogen in the upper study area. Dissolved oxygen concentration and dissolved oxygen saturation exhibited small increasing trends over the same period. Municipal point source pollution abatement activities, particular in the Twin Cities Metropolitan Area, were important management activities influencing these positive improvements in water quality.

Nitrite+nitrate nitrogen concentrations and flux increased significantly at Lock and Dam 3 and 4 and were probably influenced by increased nitrification associated with advanced municipal wastewater treatment. However, when all forms of inorganic nitrogen were considered (NOx + NHx), only a small increasing trend in concentration (0.2 mg/L over 21 years) was observed for Lock and Dam 4. Estimates of inorganic nitrogen flux at the three monitoring sites did not indicate significant trends.

Conductivity levels and chloride concentrations increased significantly at all three stations. These were the only parameters exhibiting significant trends at Lock and Dam 9, the southern most monitoring station. Past monitoring in the nation streams by USGS had generally attributed greater chloride concentrations to increased road salt use. However, one can't discount other potential, sources including, municipal and industrial wastewater discharges, inflows of contaminated groundwater, and runoff of animal wastes and chloride containing fertilizers. These increases in conductivity and chloride do not pose a water quality problem at this time but do provide an indication of human-induced impacts on the river's water quality.

In summary, water quality conditions have shown improvements in the Mississippi River over the last two decades and can largely be attributed to point source pollution abatement activities. A vigilant and consistent monitoring program was needed to establish these trends. Greater nonpoint source pollutant control in the river's watersheds will be necessary in order achieve significant improvements in the river's water quality conditions in the future.

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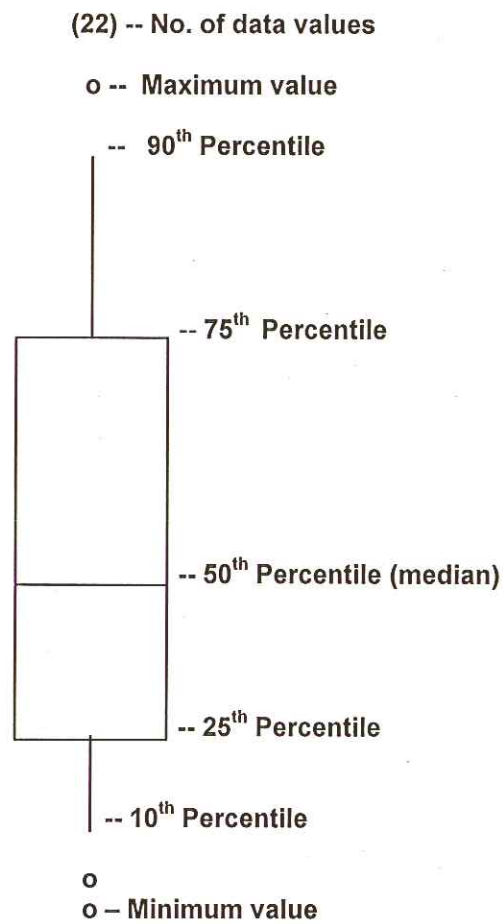
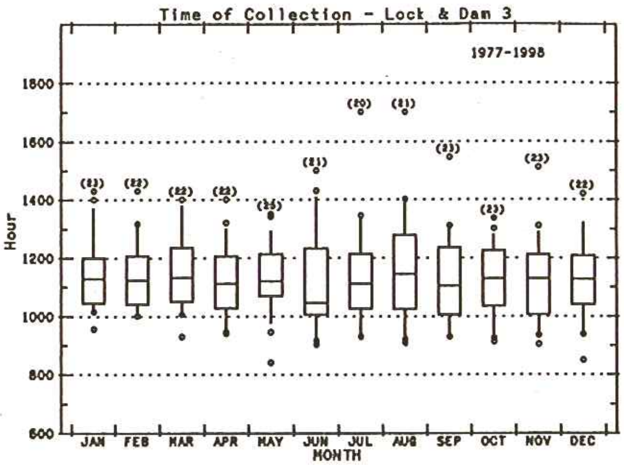
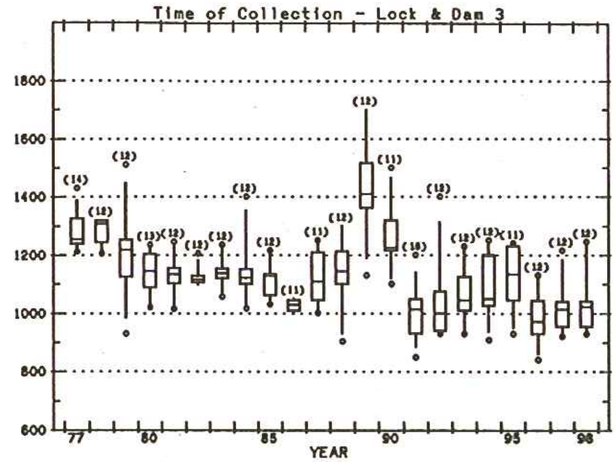
Appendix A

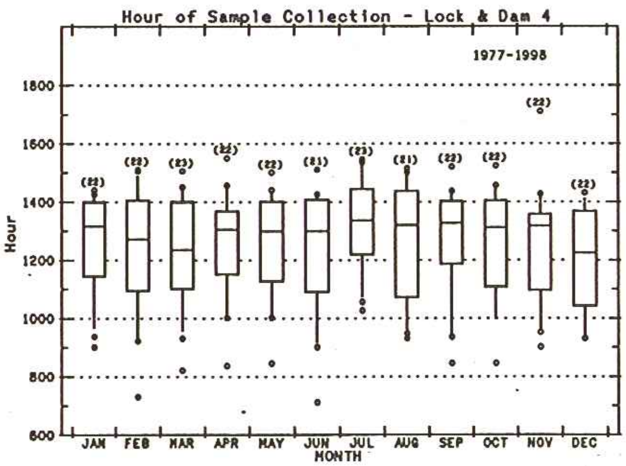
Monthly and Year Box Plots

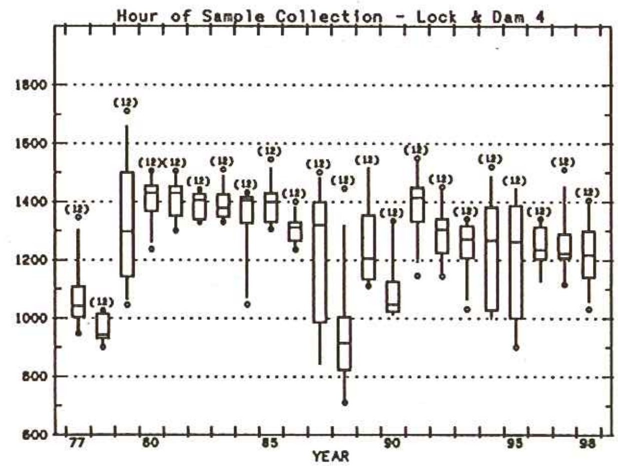


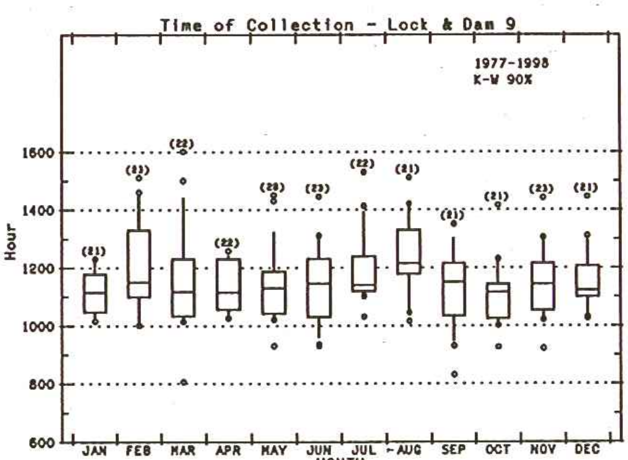
Example figure of box plot used in this report.

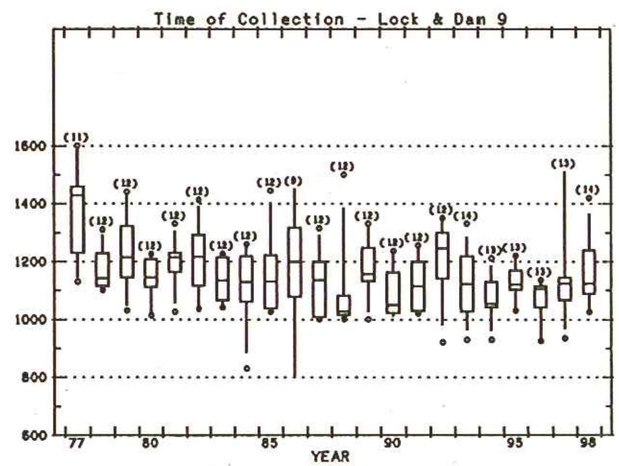












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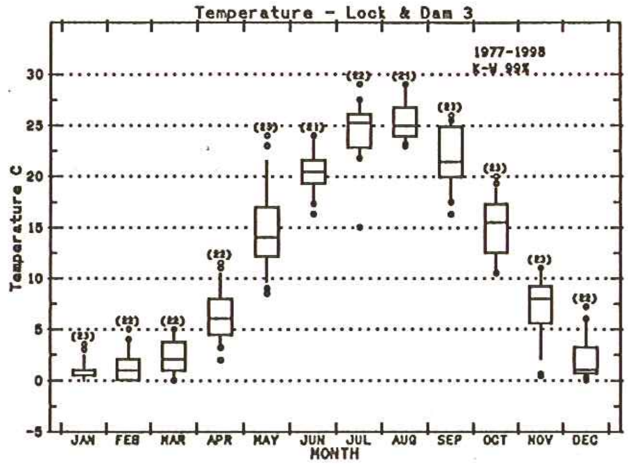

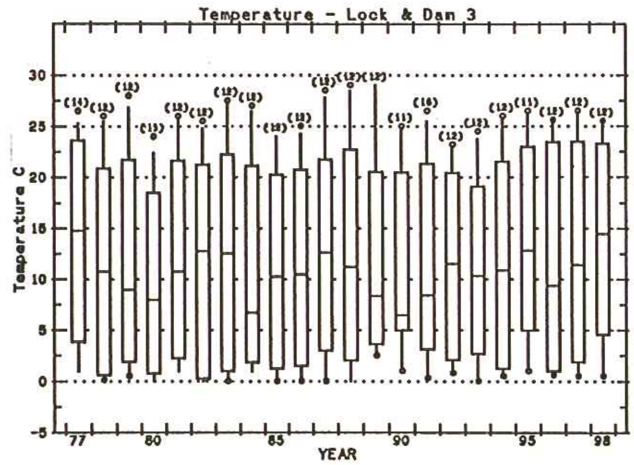

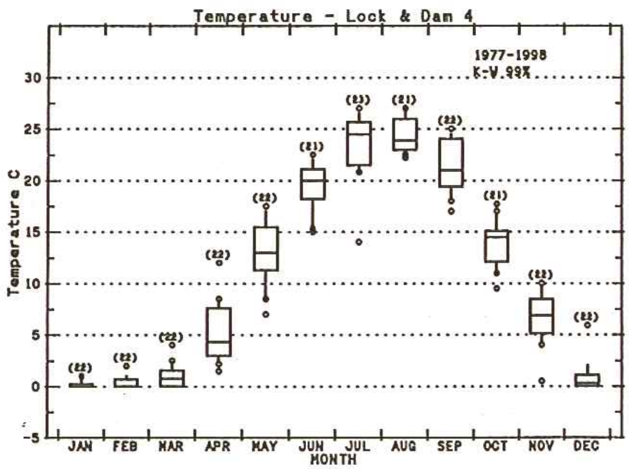

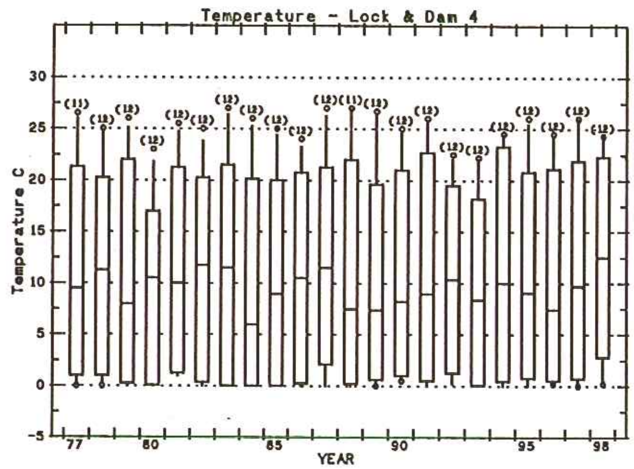

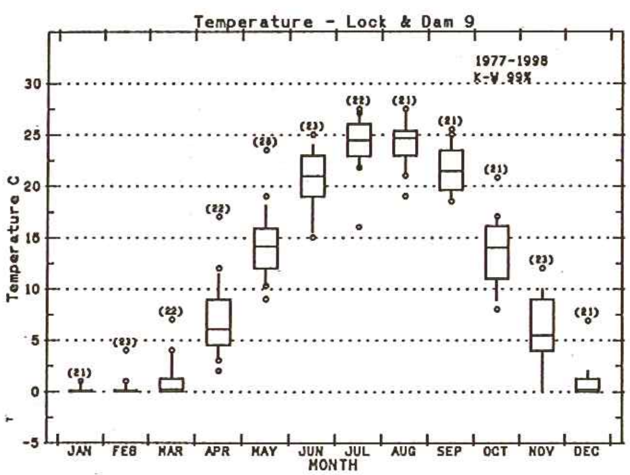

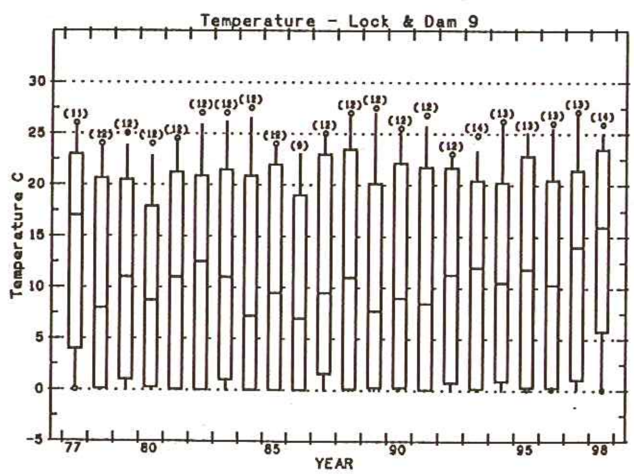

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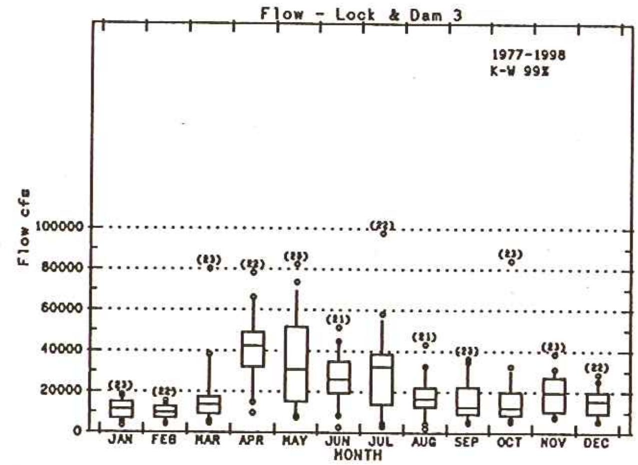

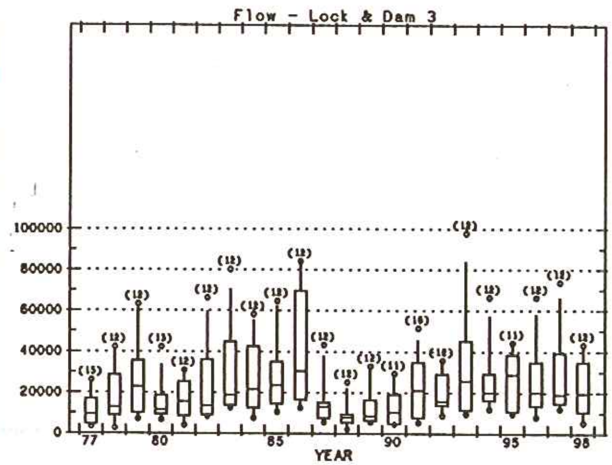

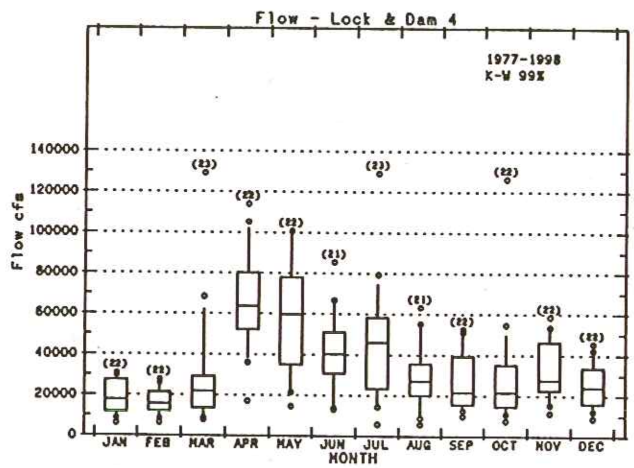

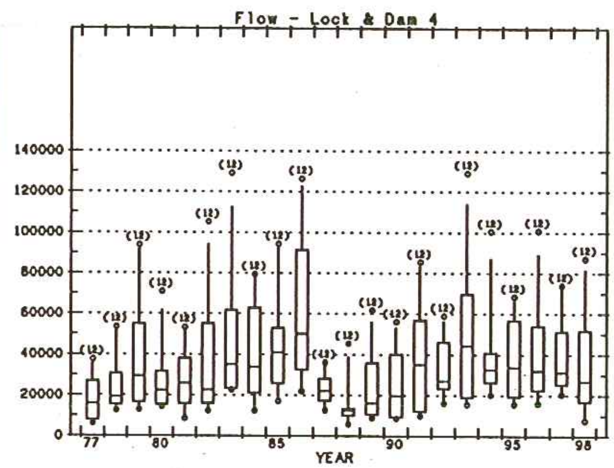

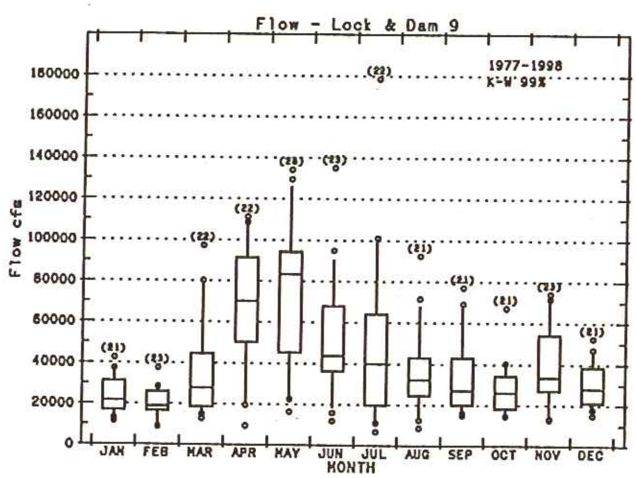

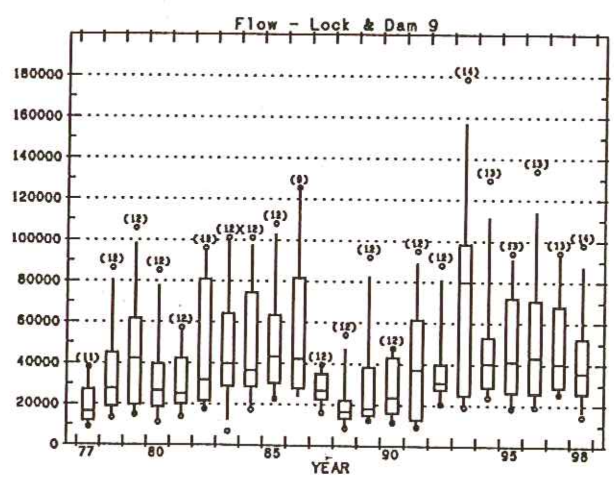

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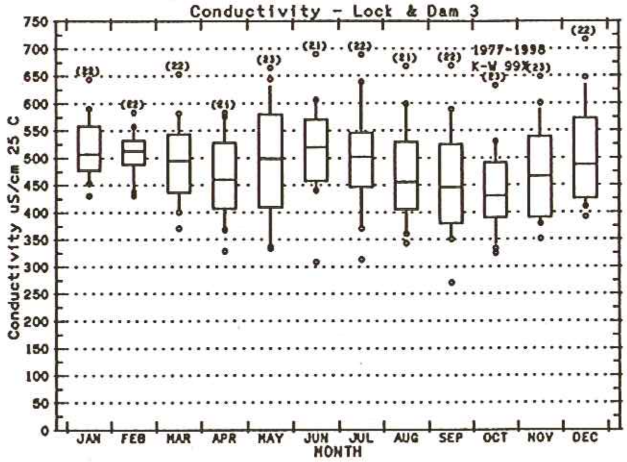

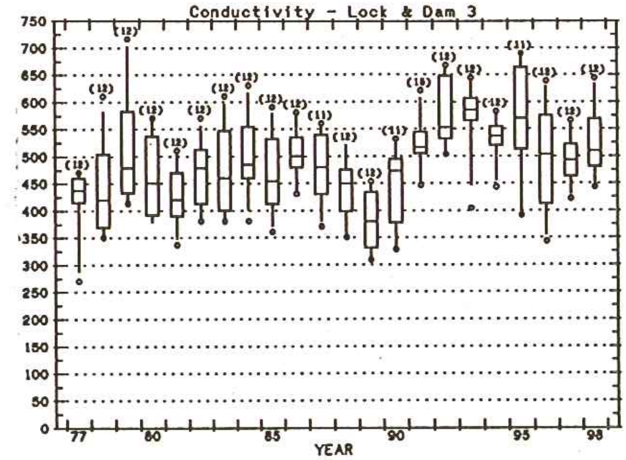

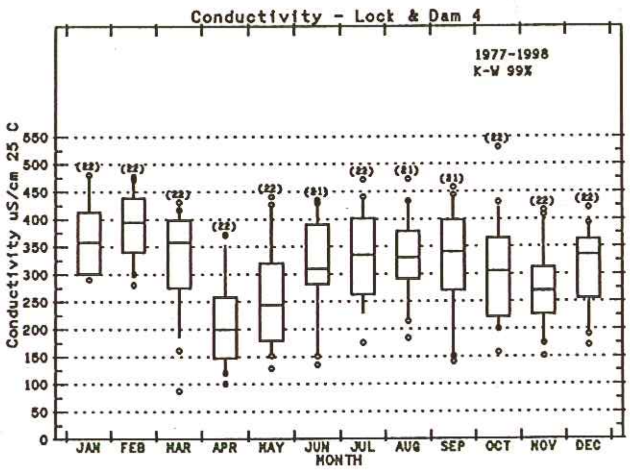

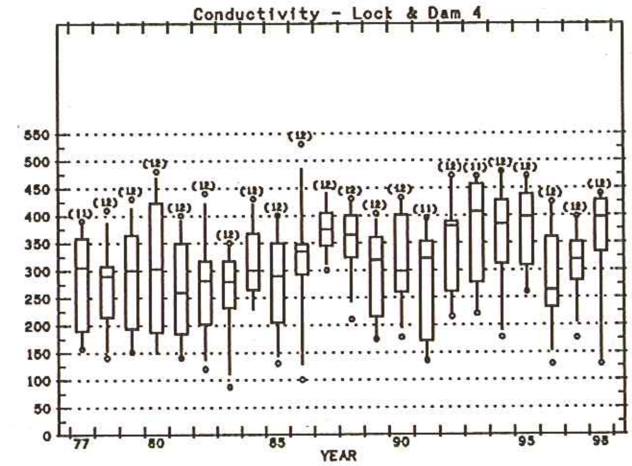

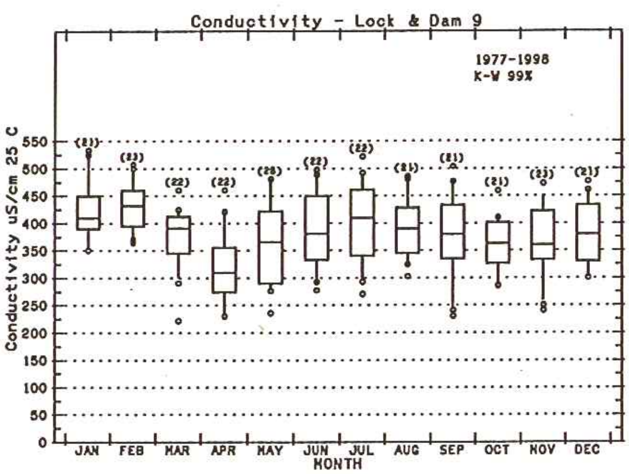

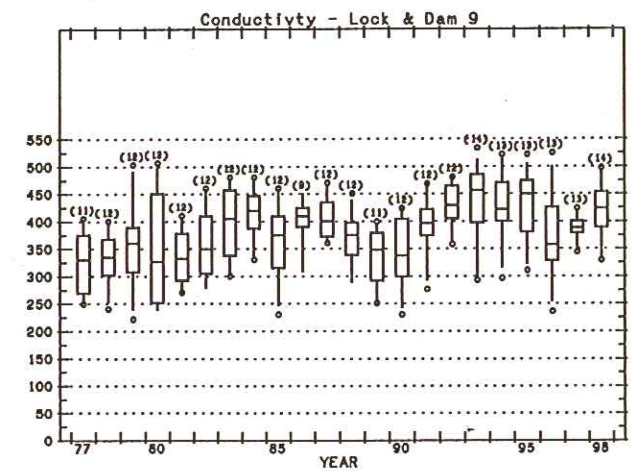

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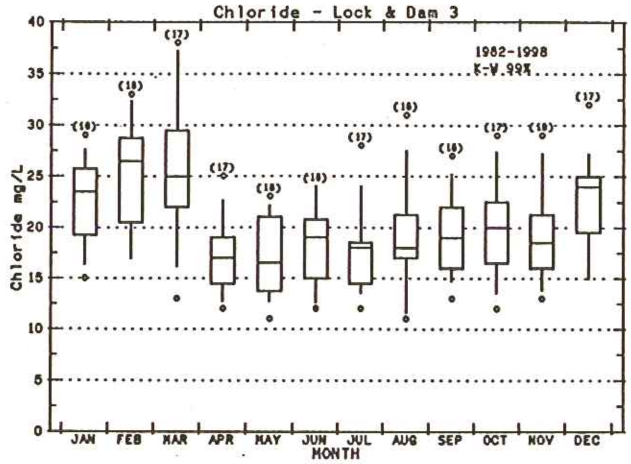

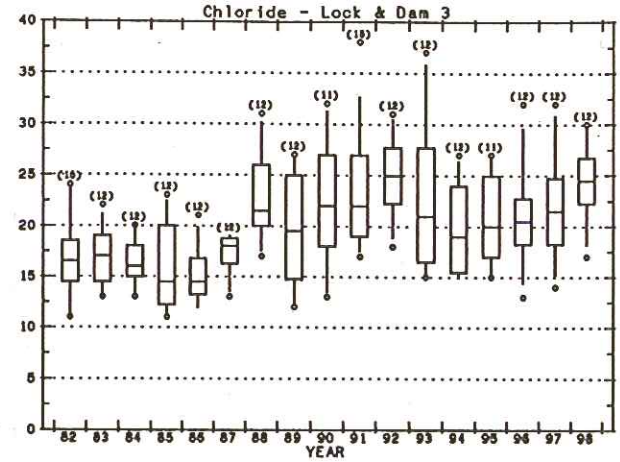

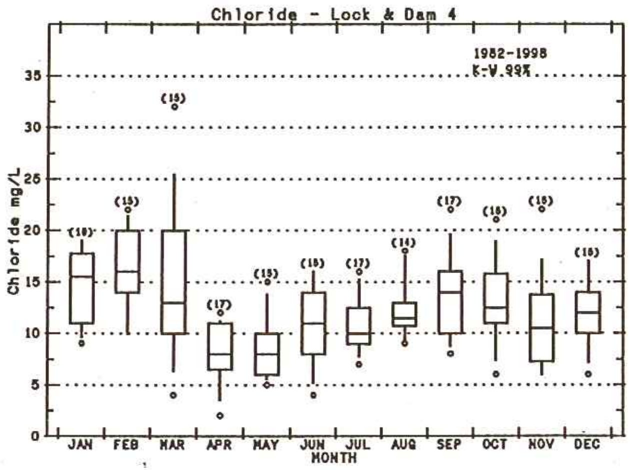

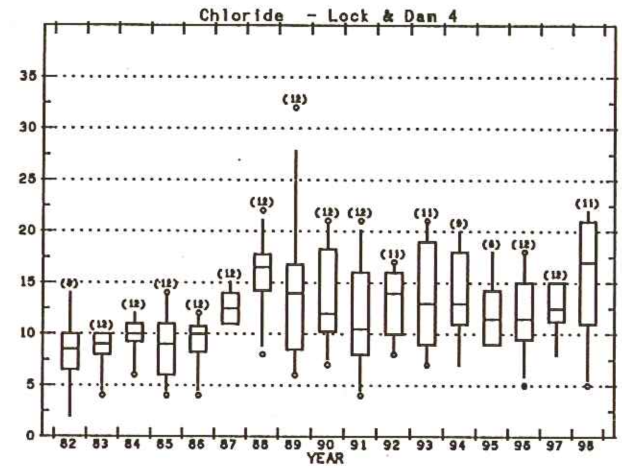

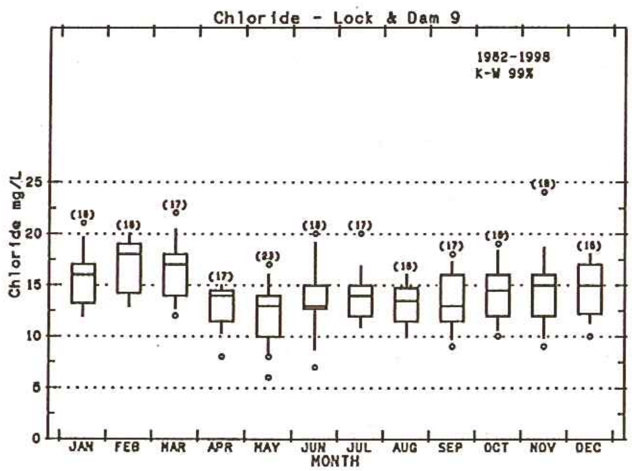

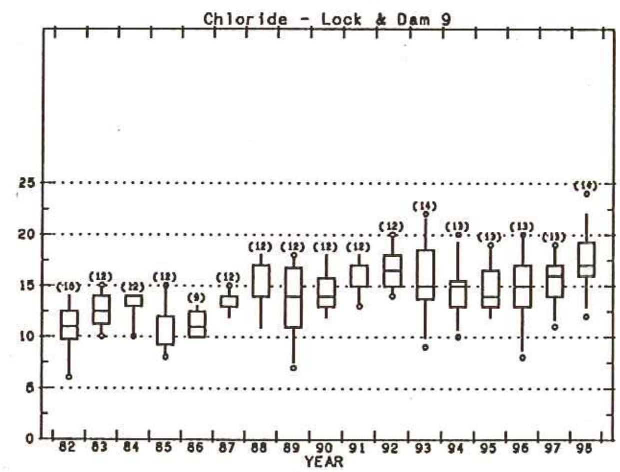

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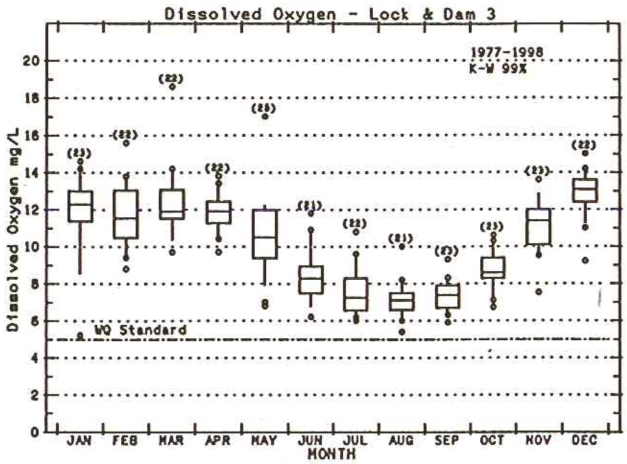

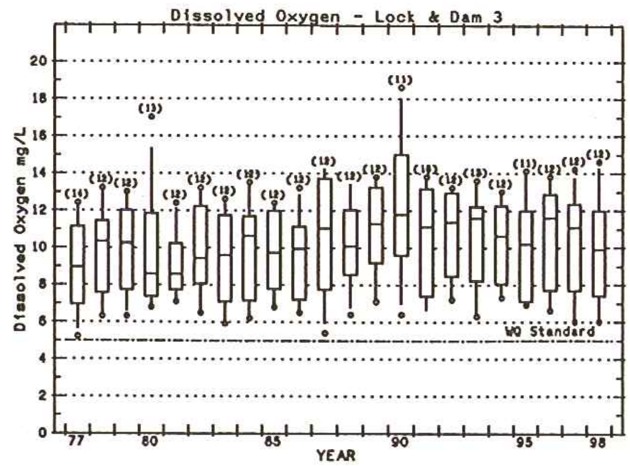

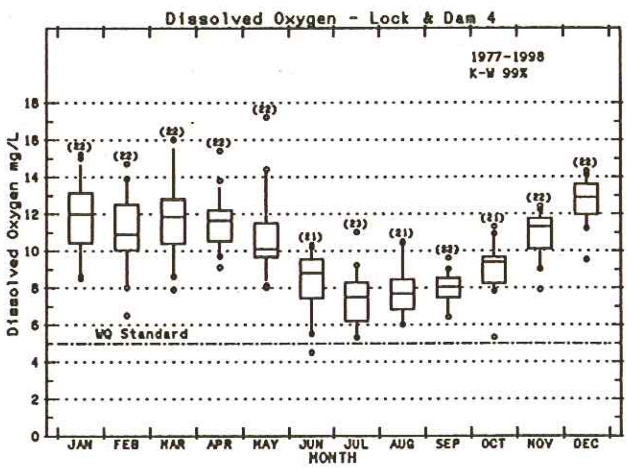

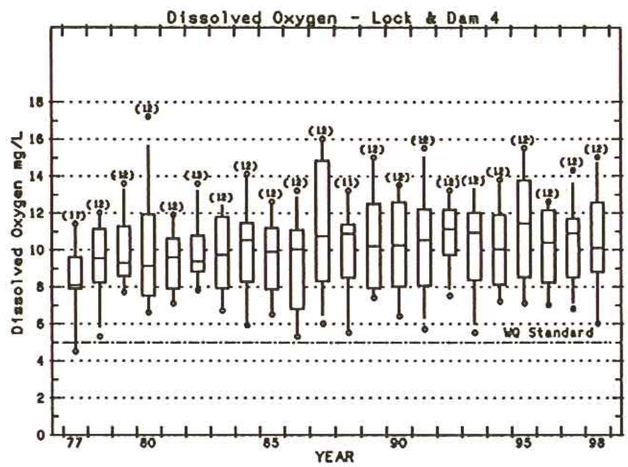

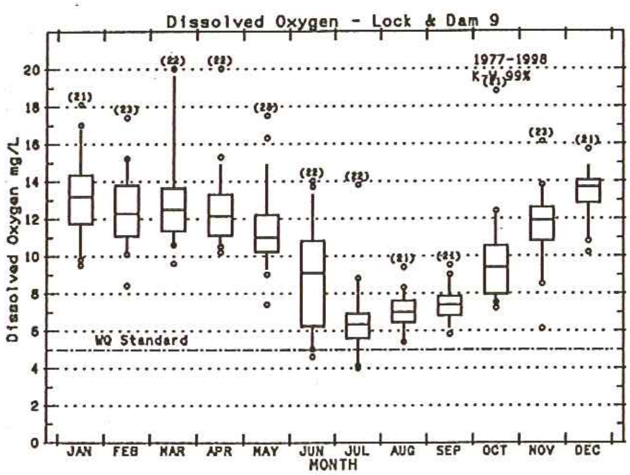

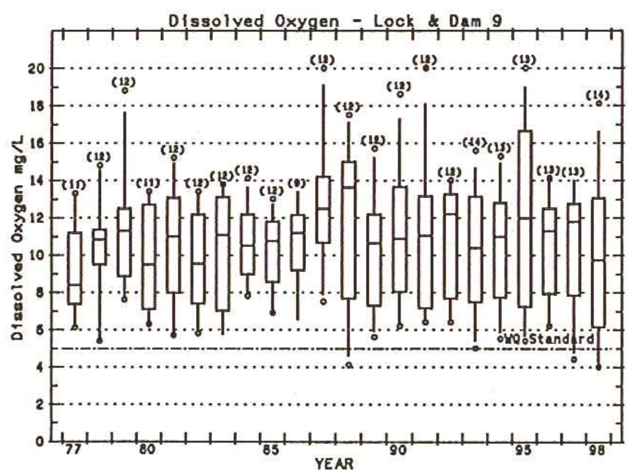

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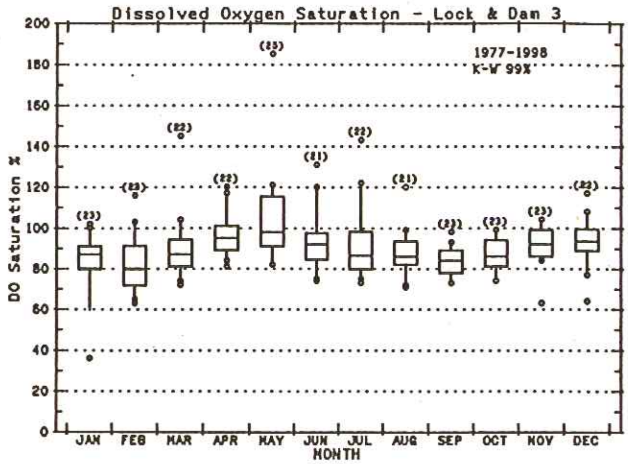

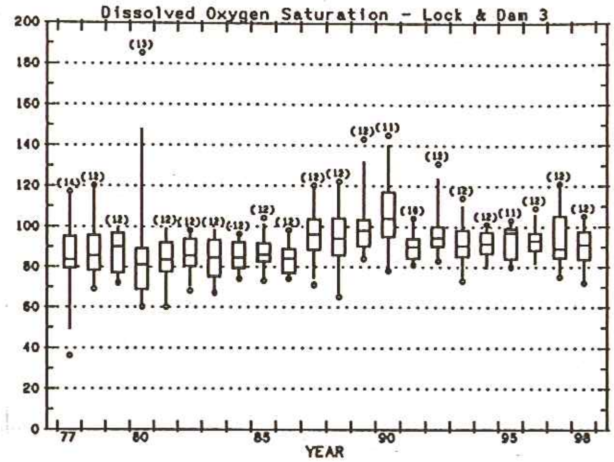

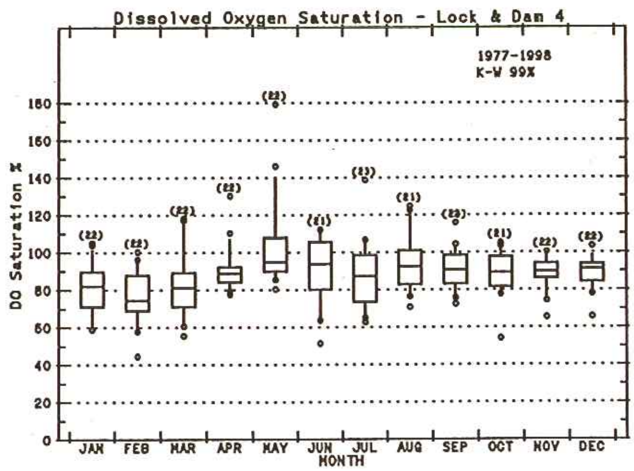

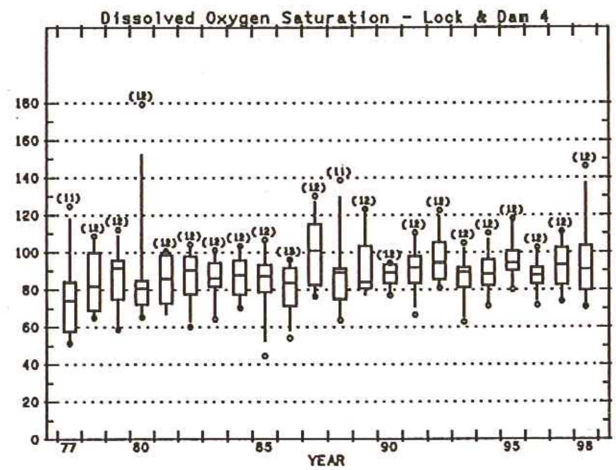

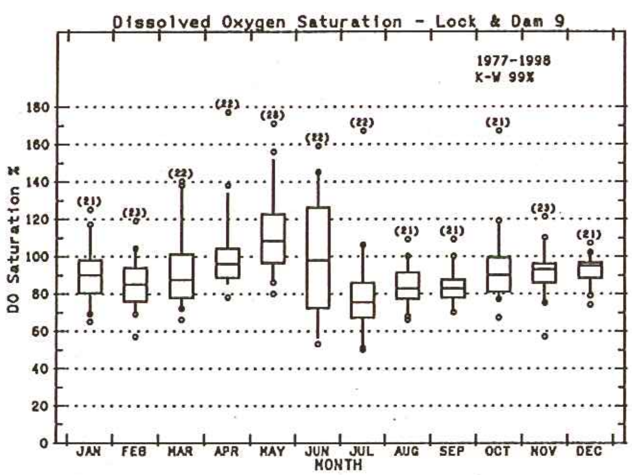

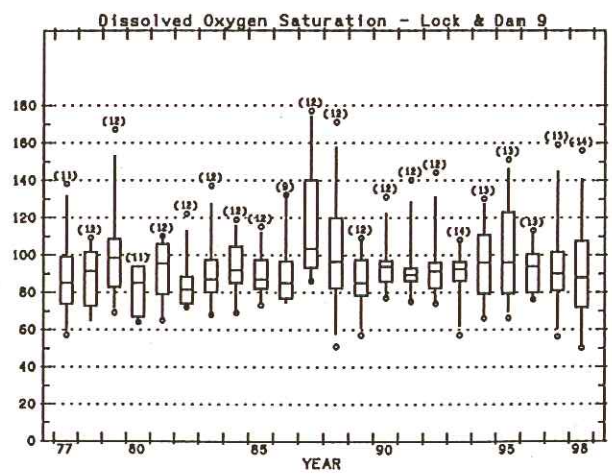

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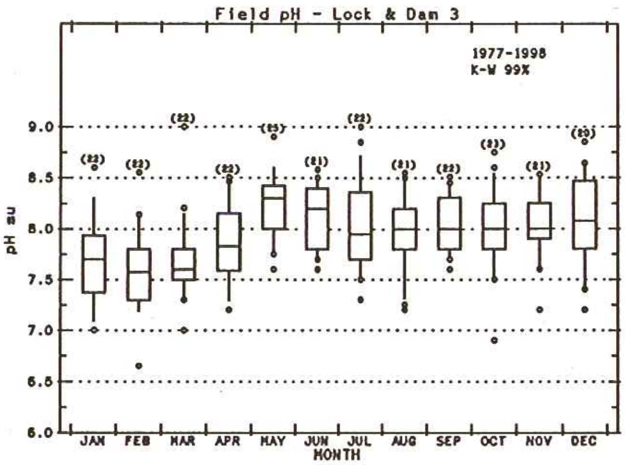

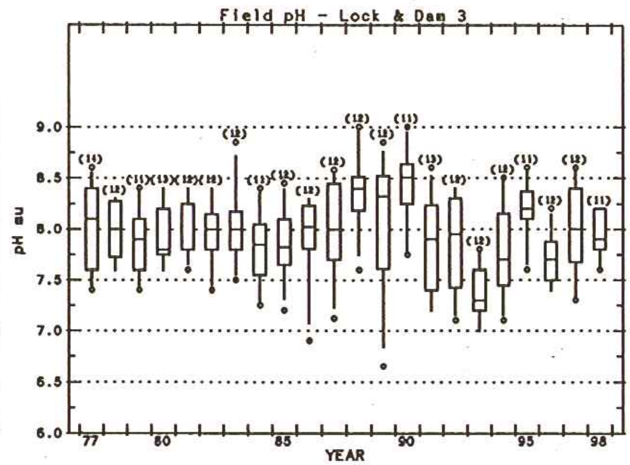

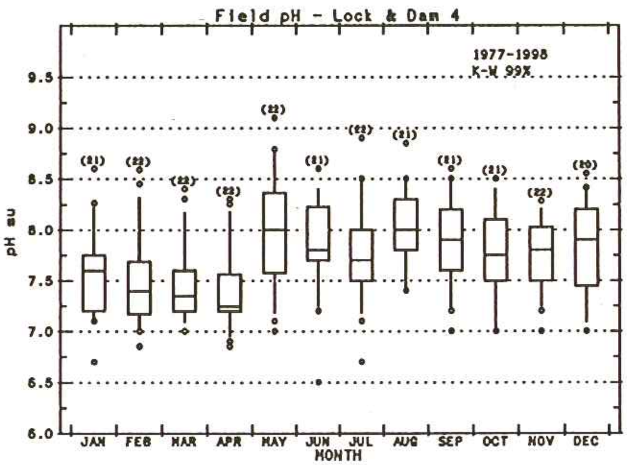

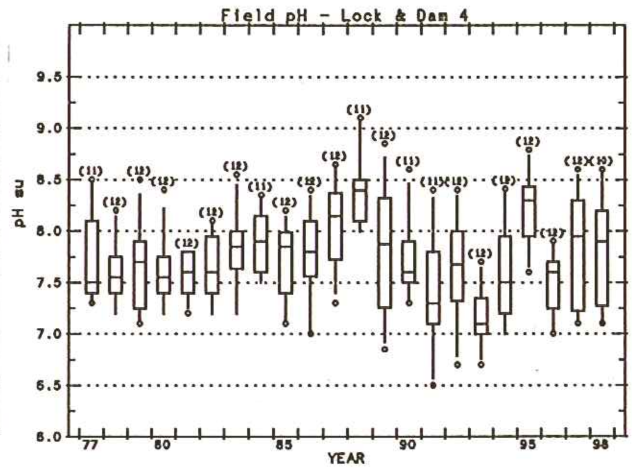

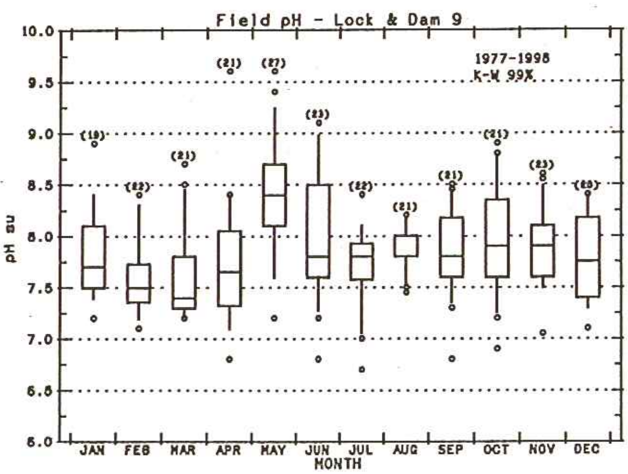

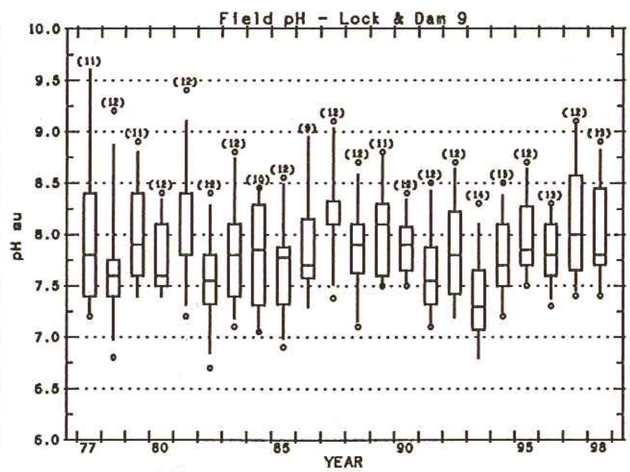

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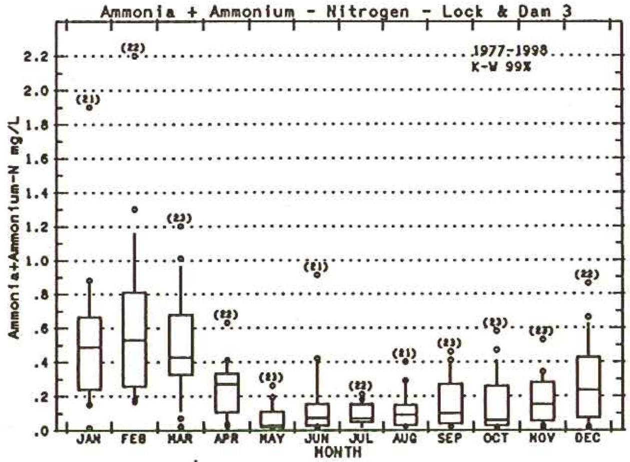

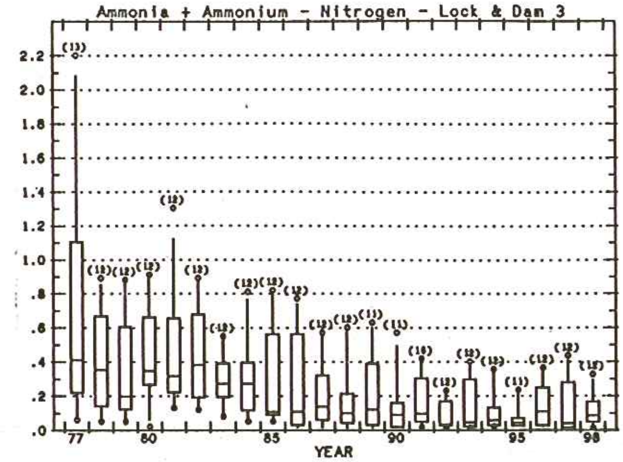

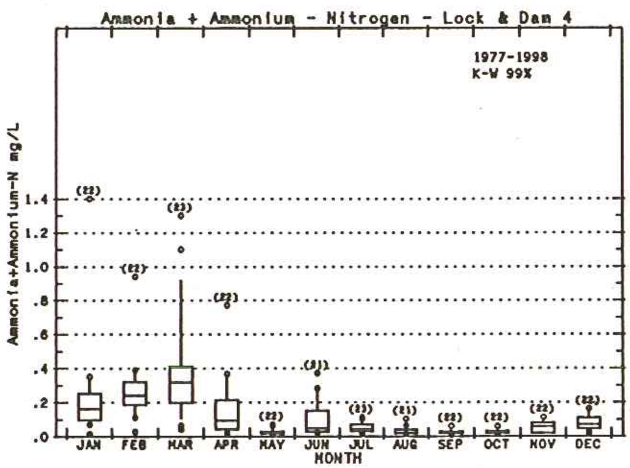

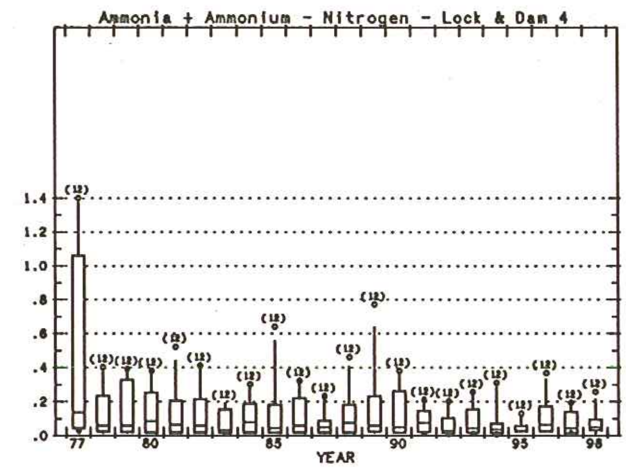

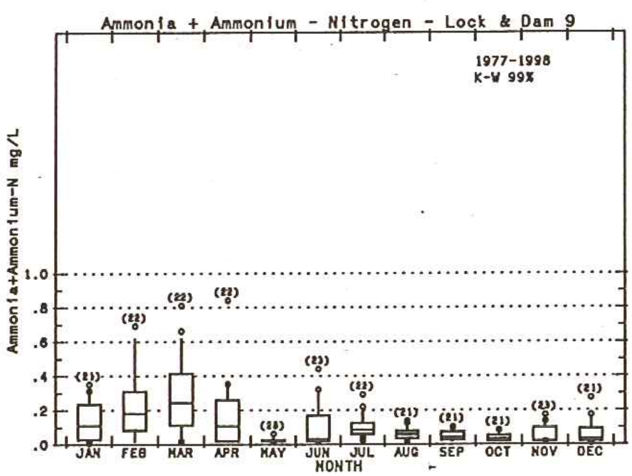

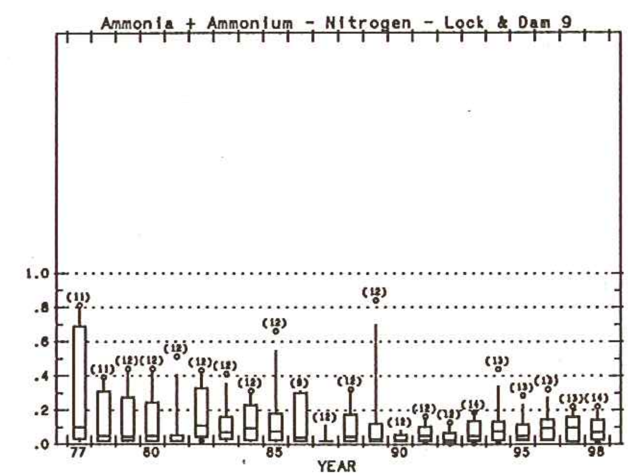

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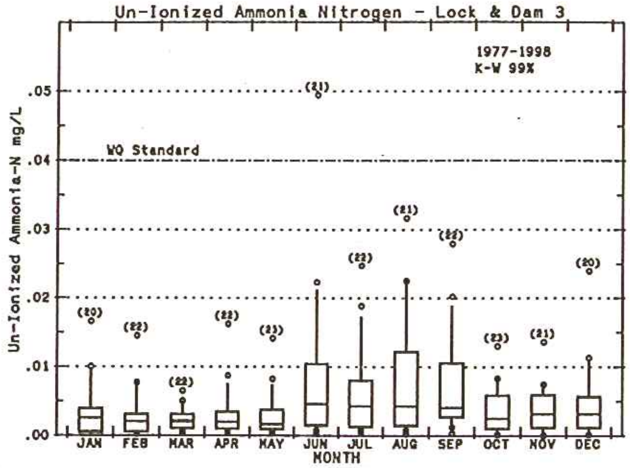

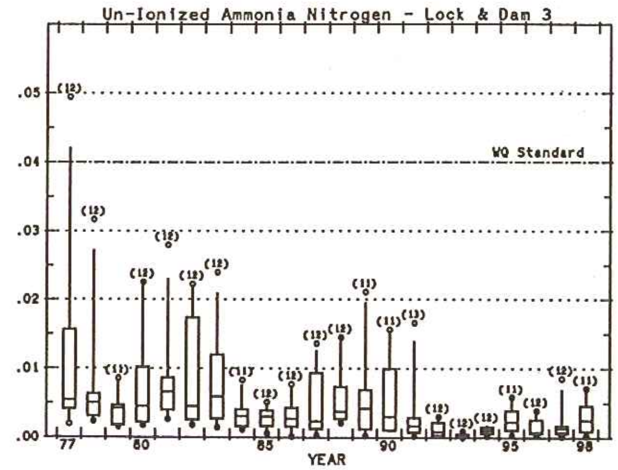

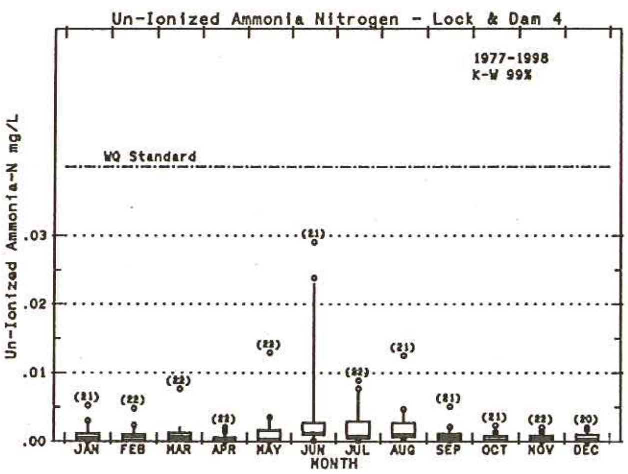

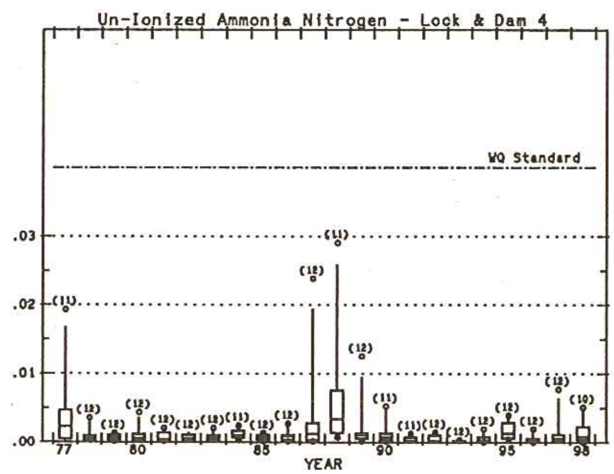

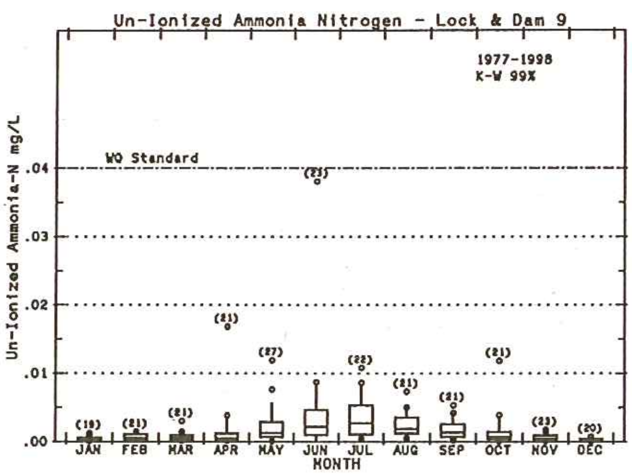

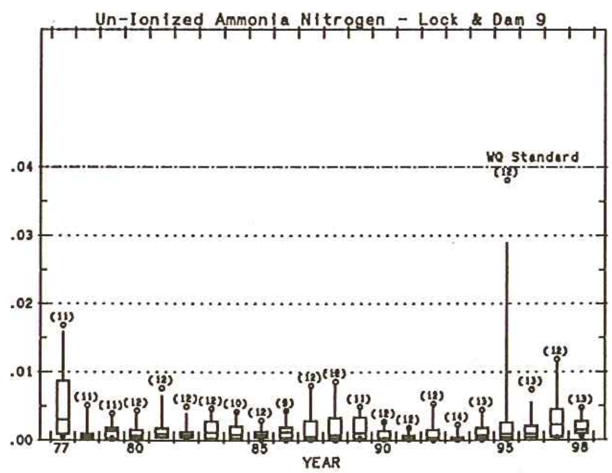

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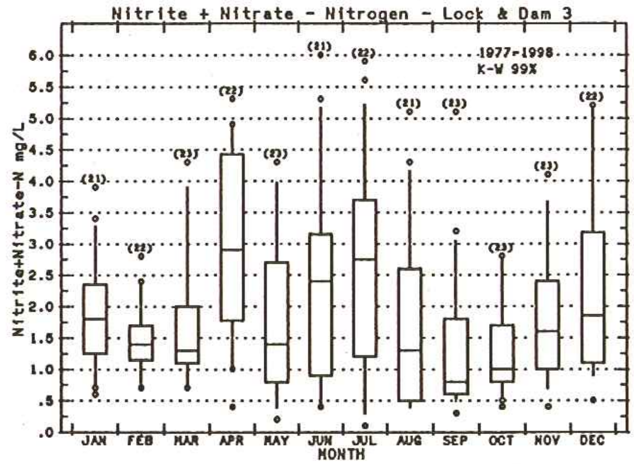

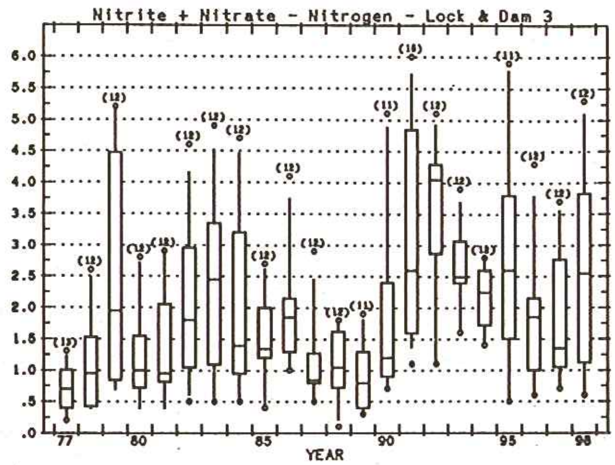

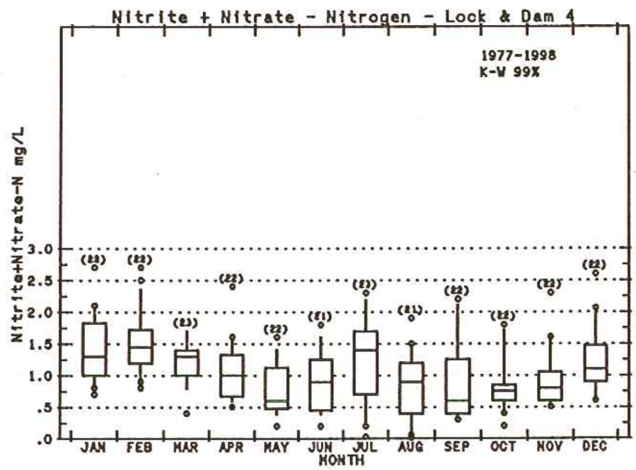

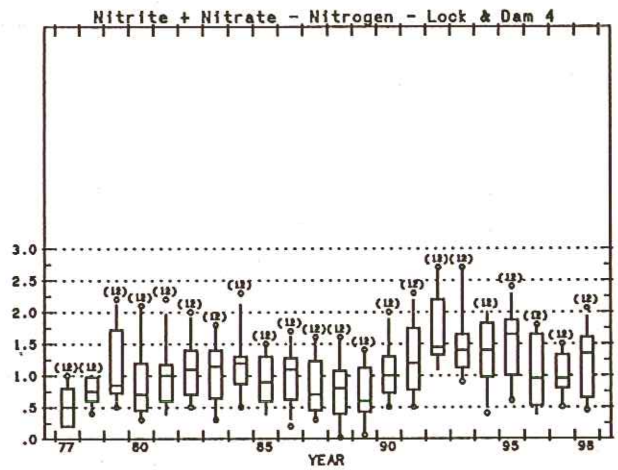

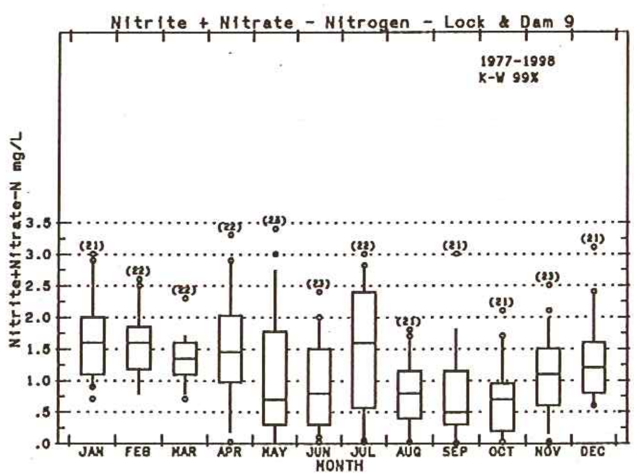

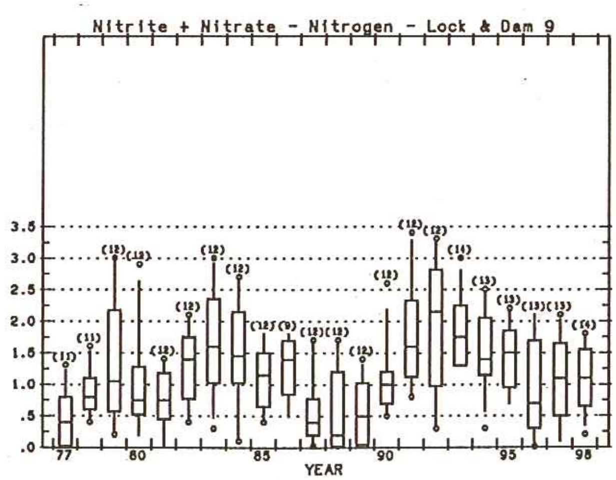

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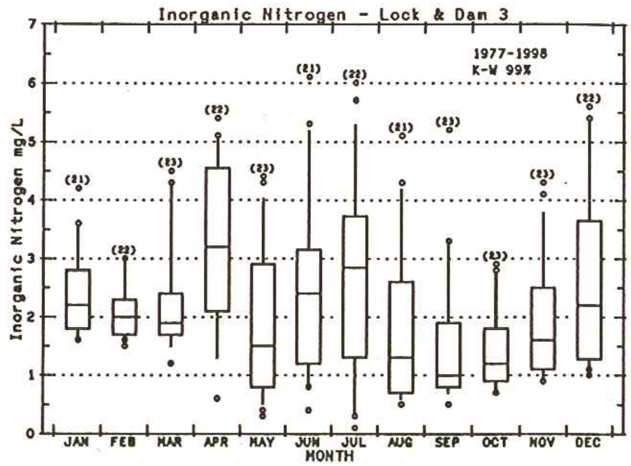

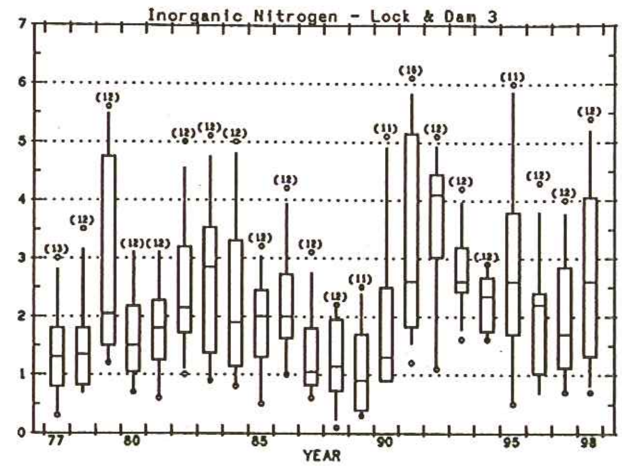

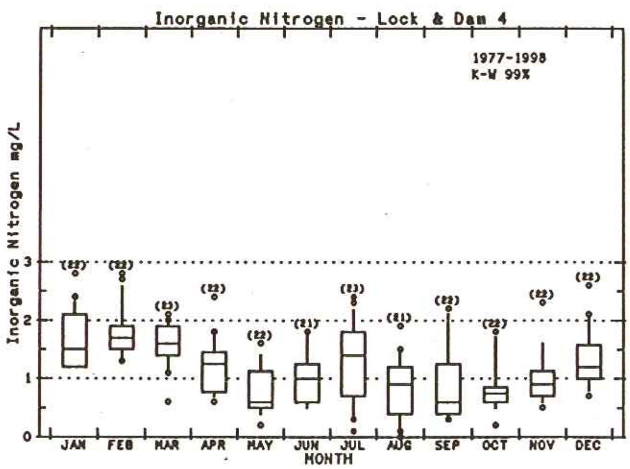

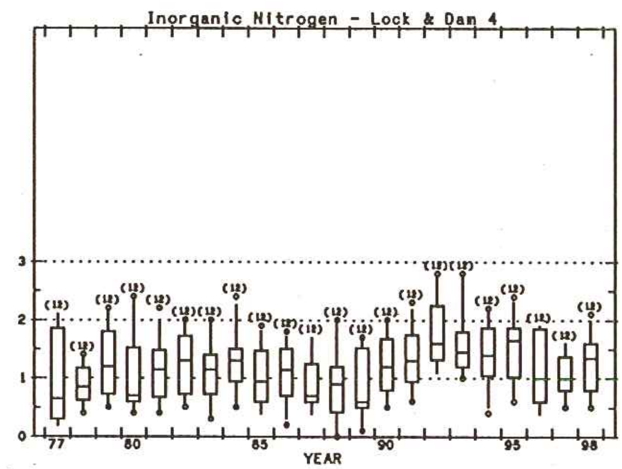

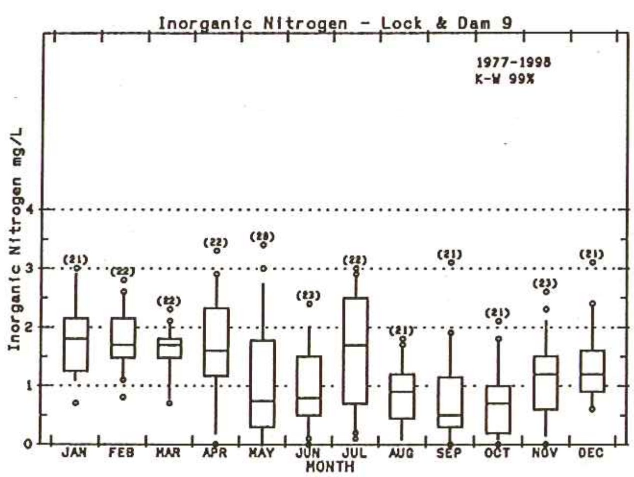

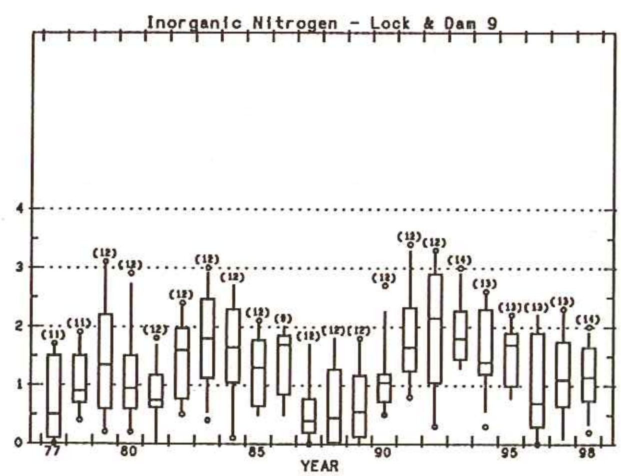

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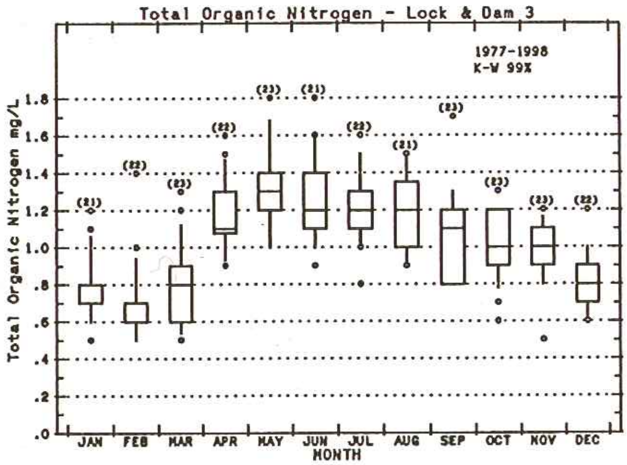

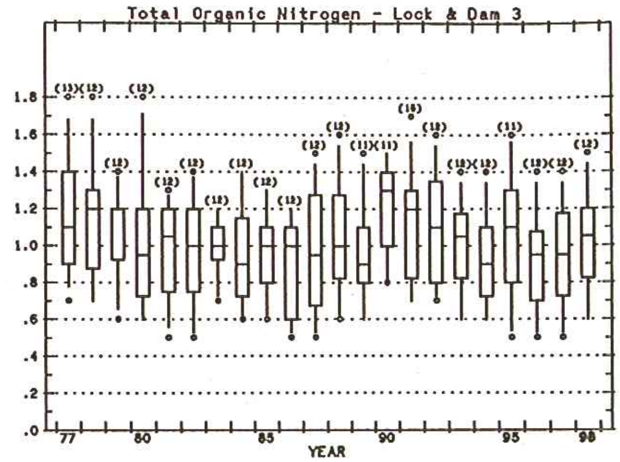

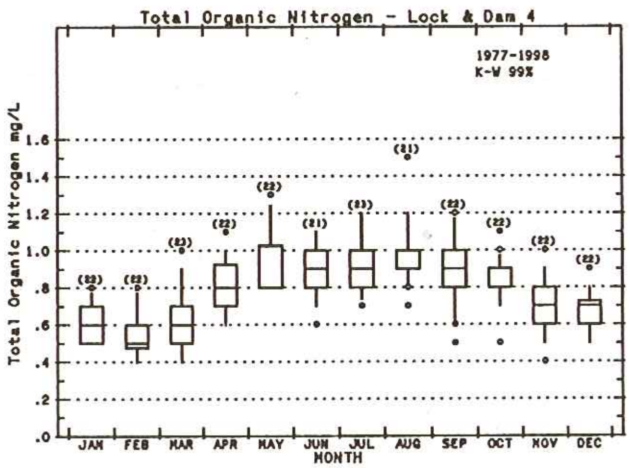

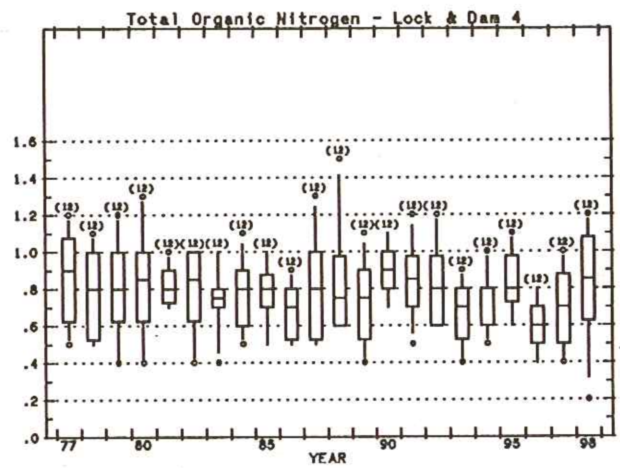

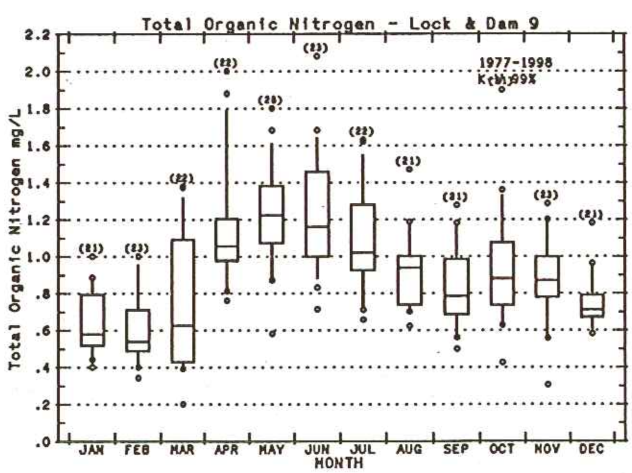

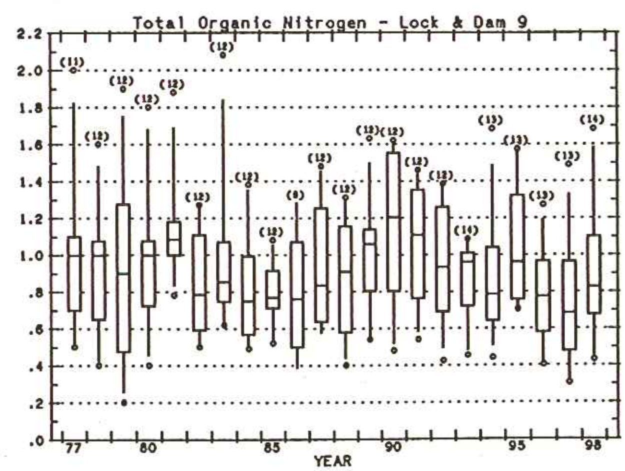

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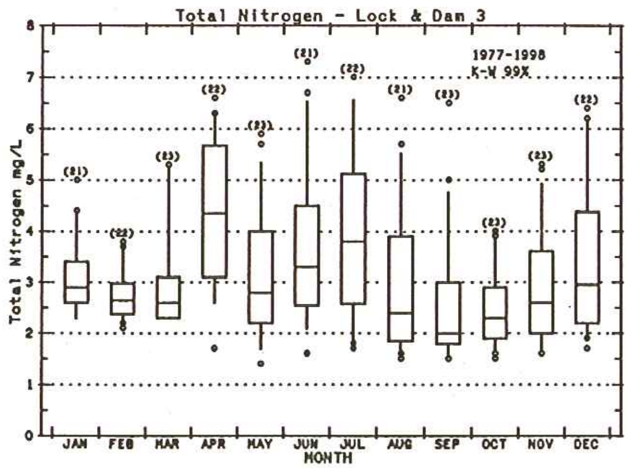

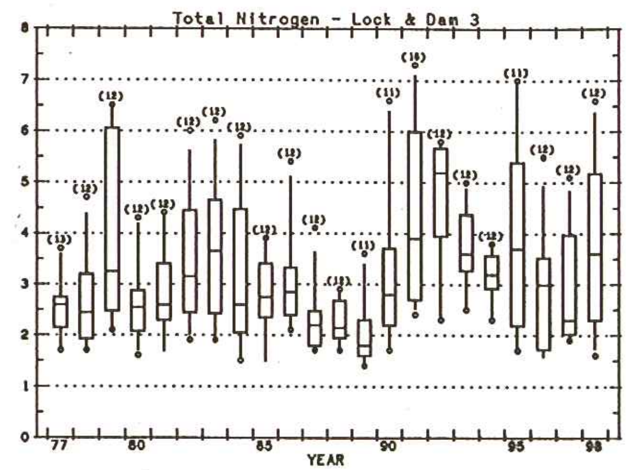

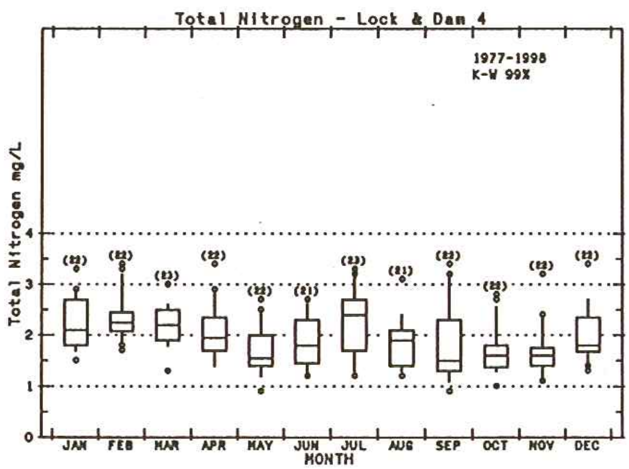

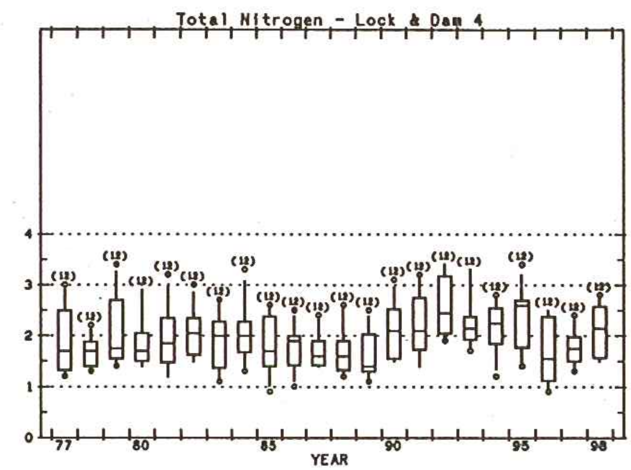

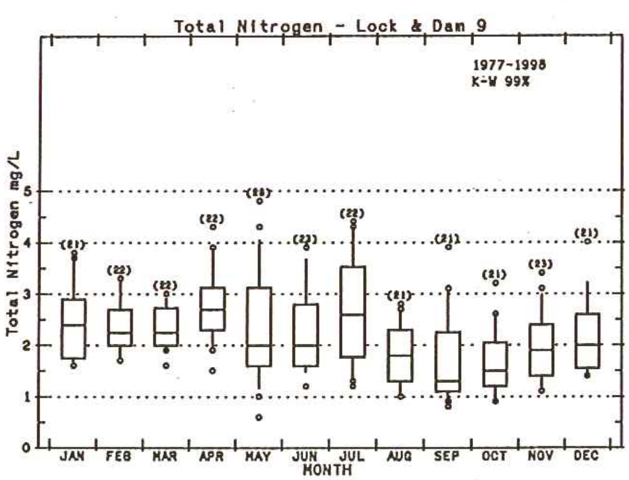

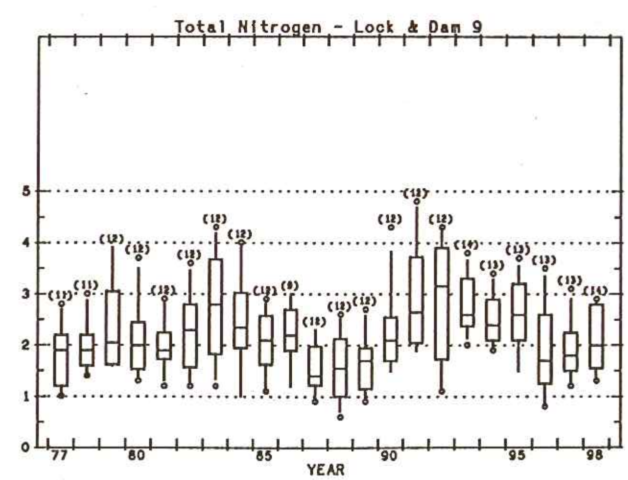

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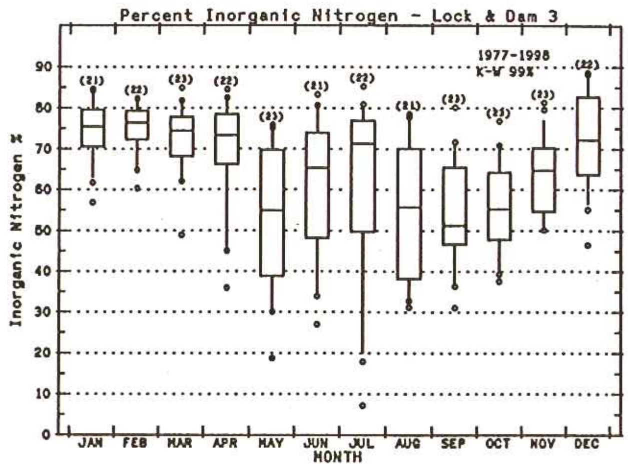

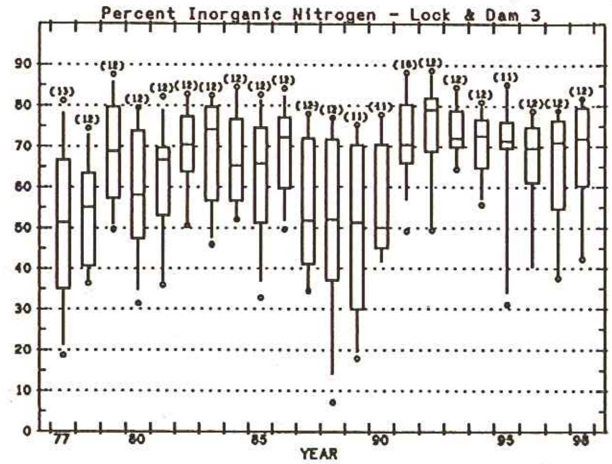

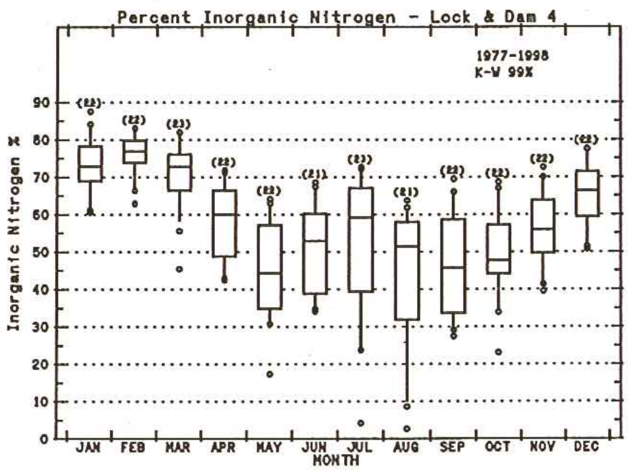

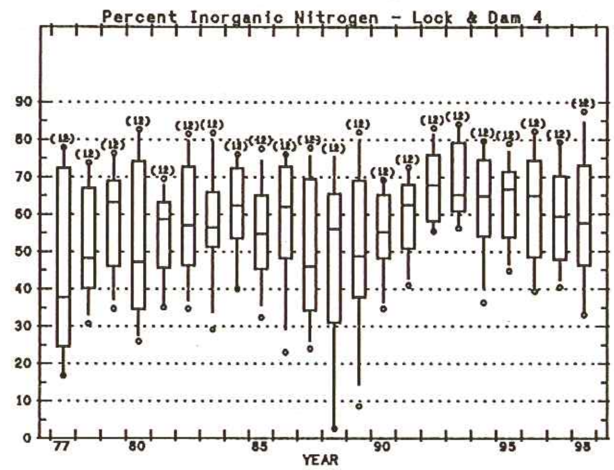

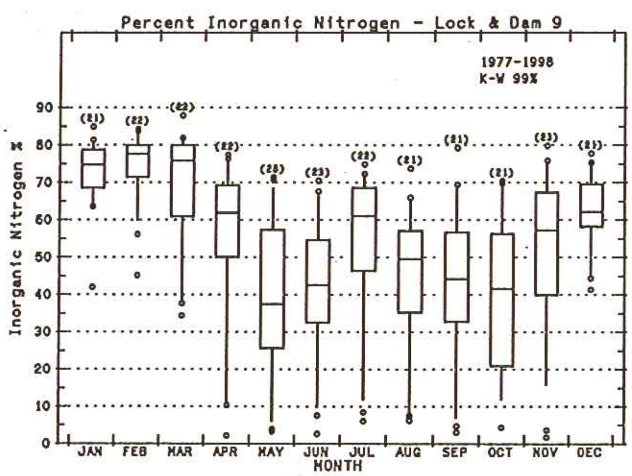

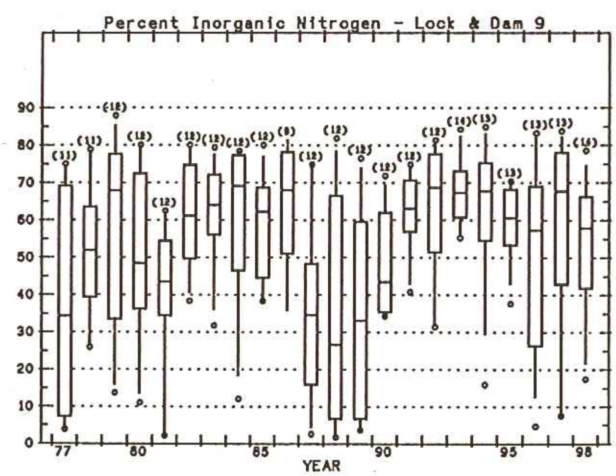

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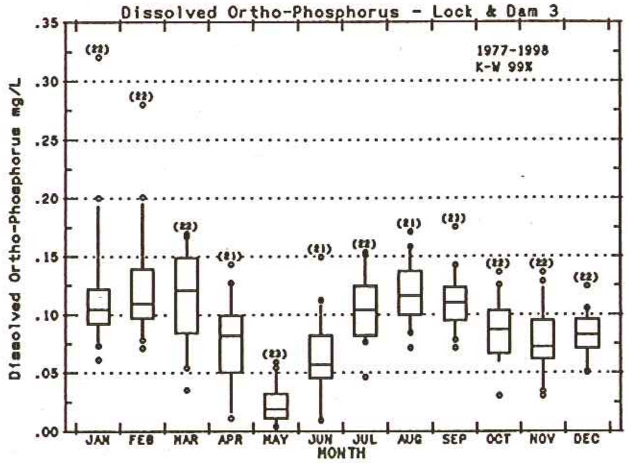

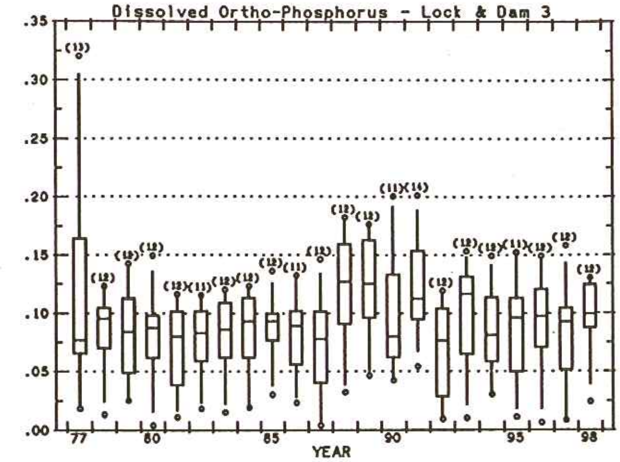

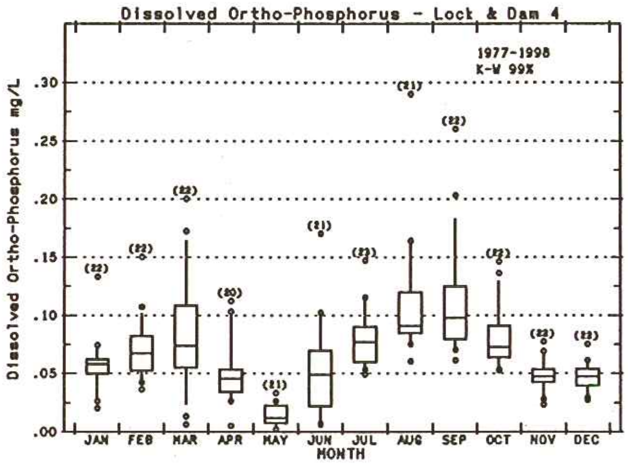

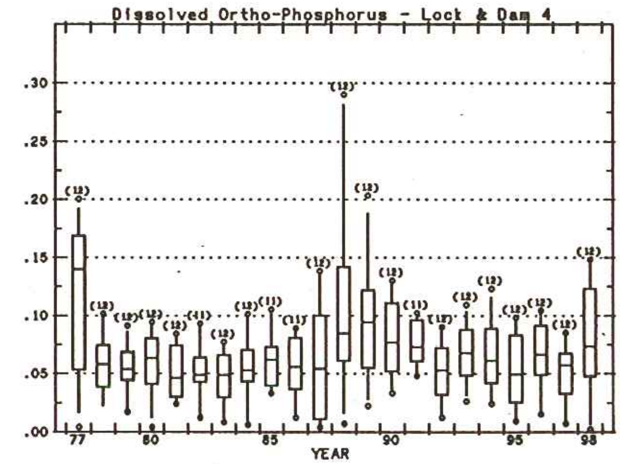

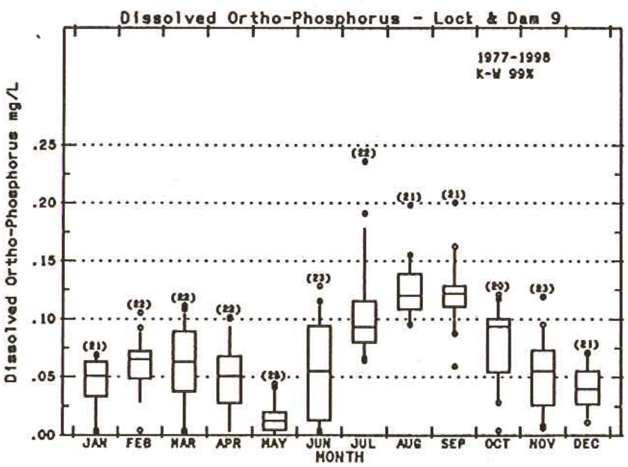

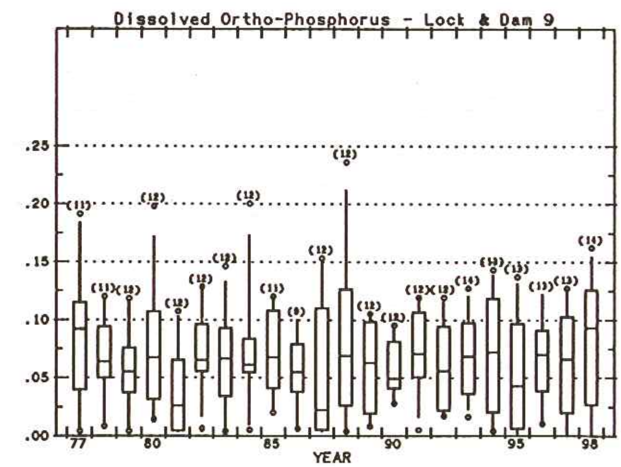

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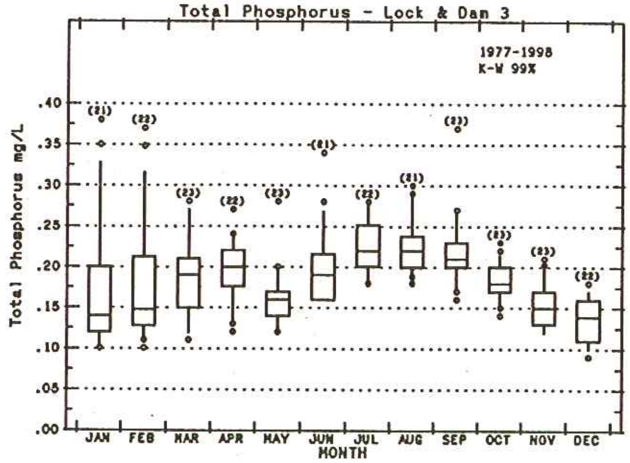

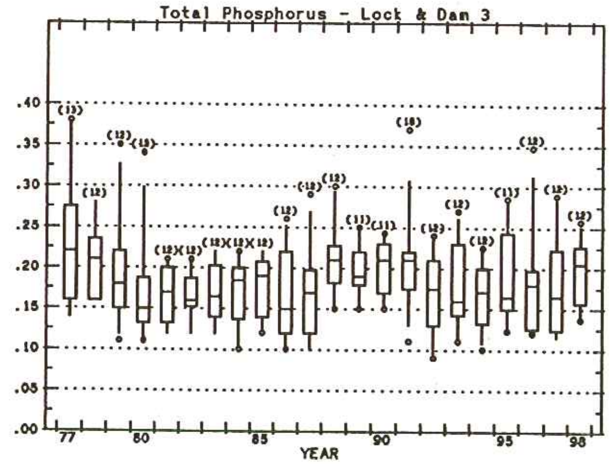

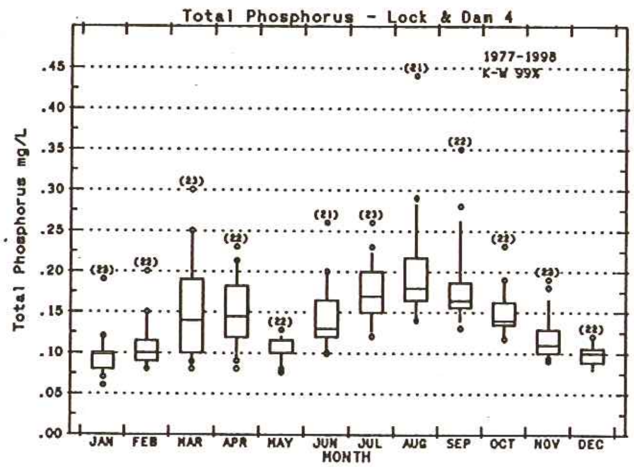

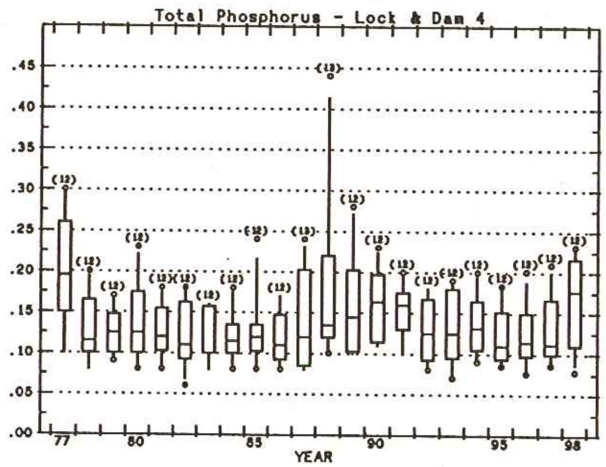

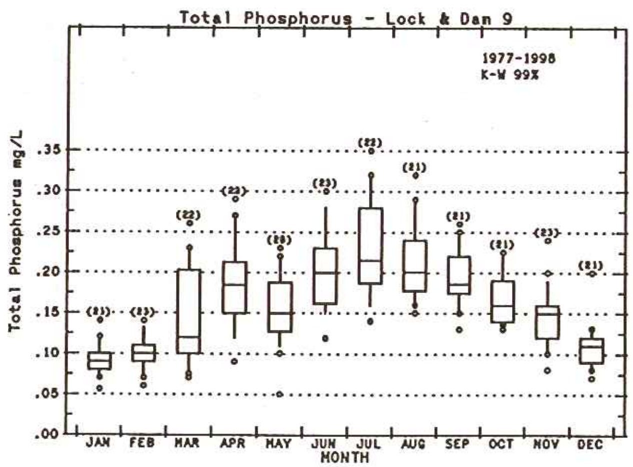

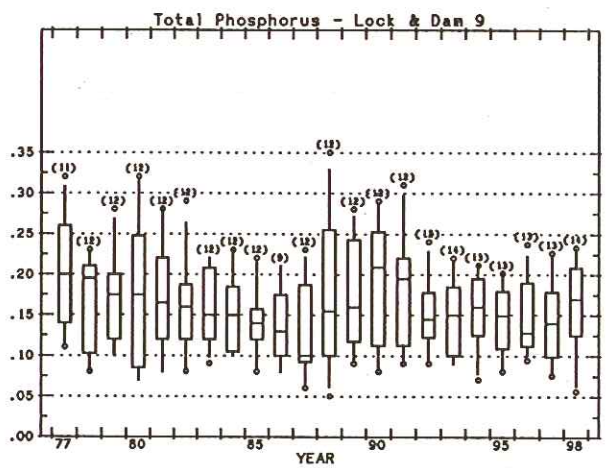

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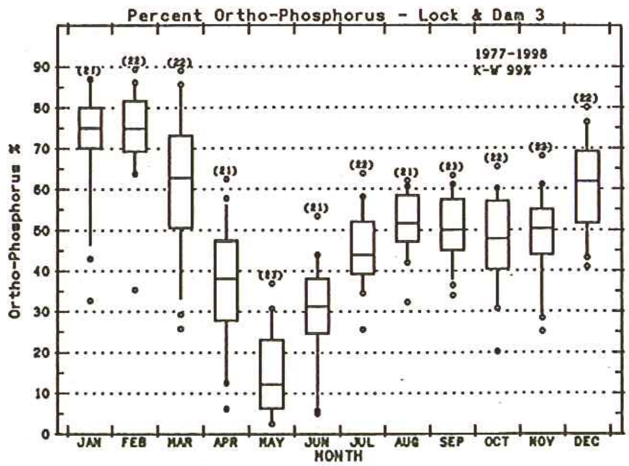

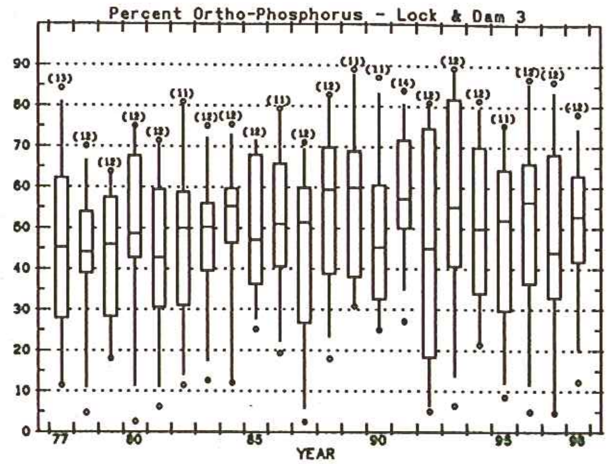

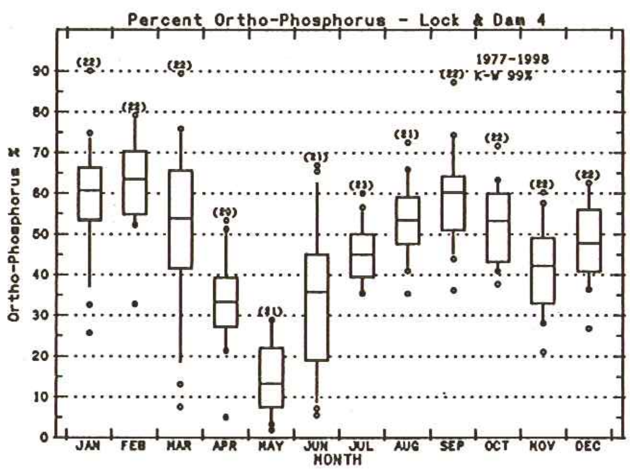

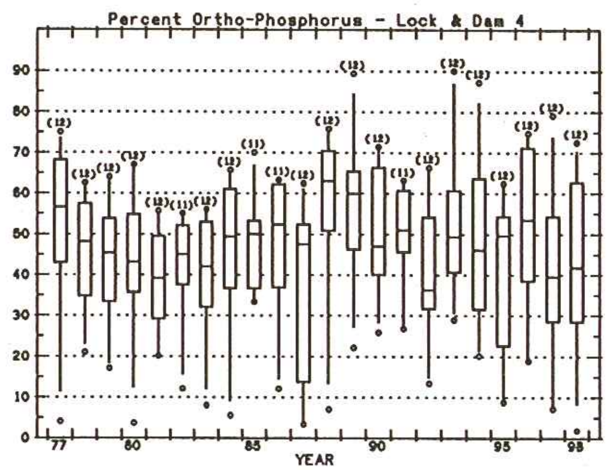

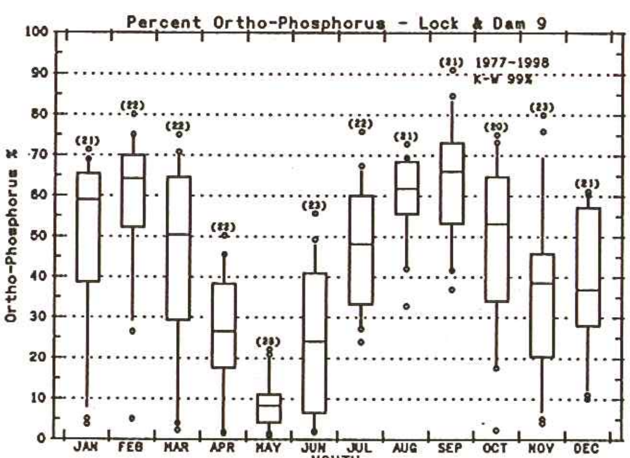

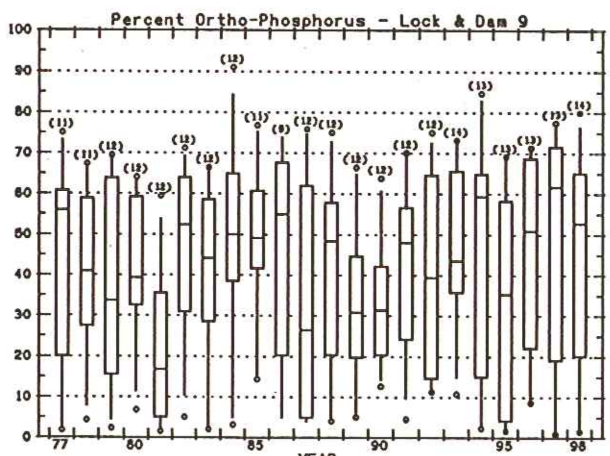

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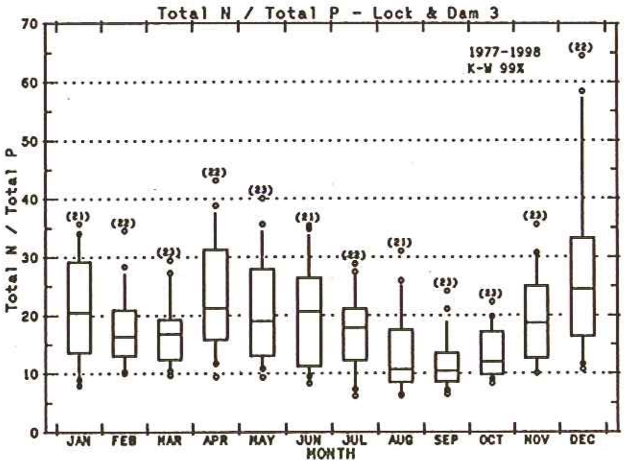
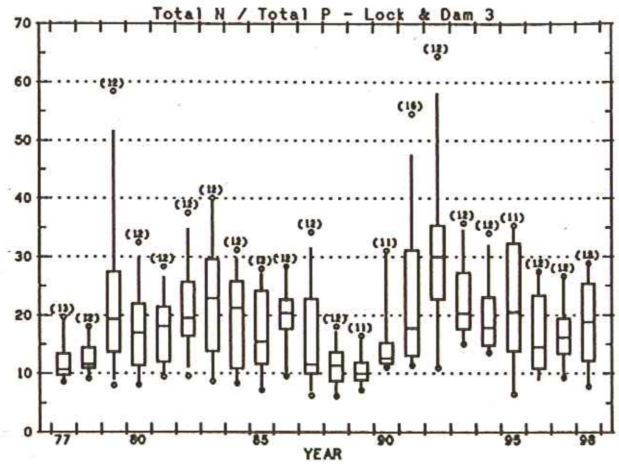
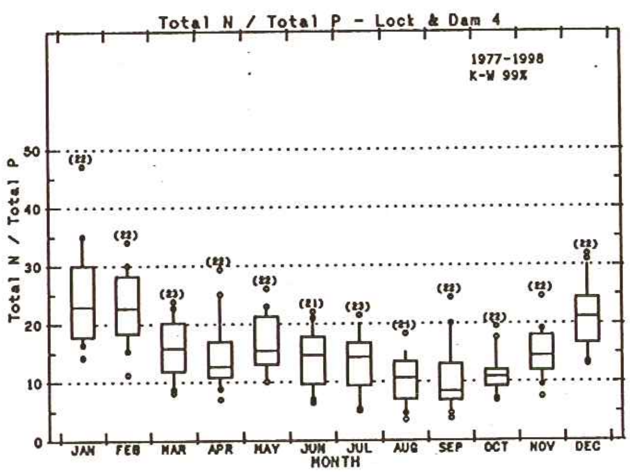
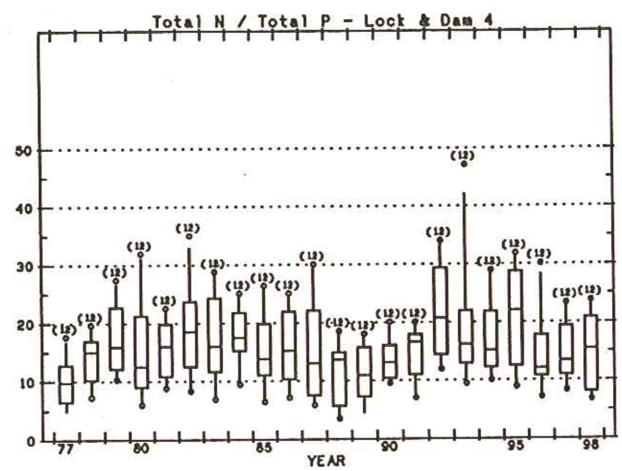
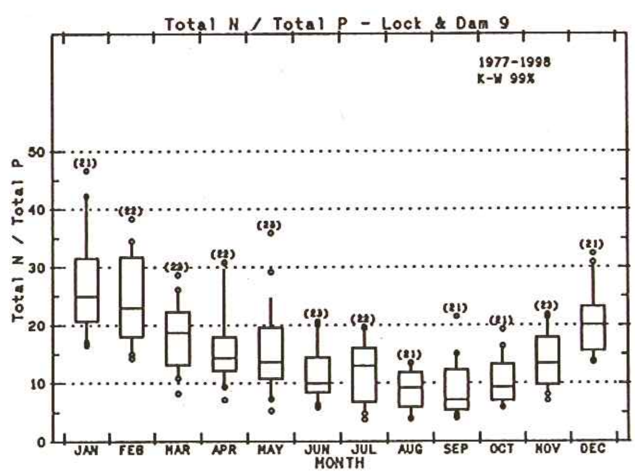
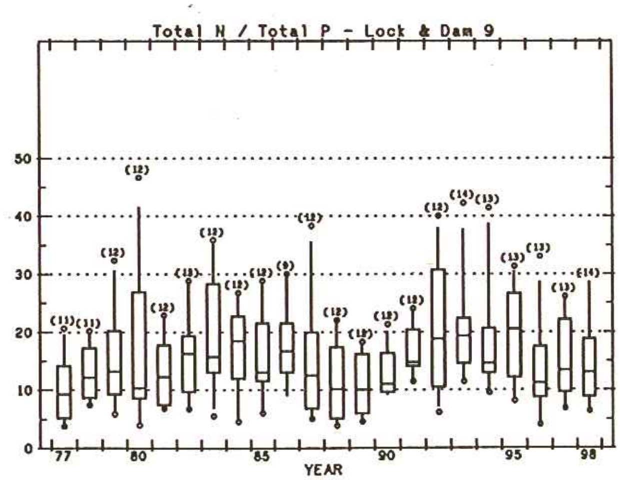




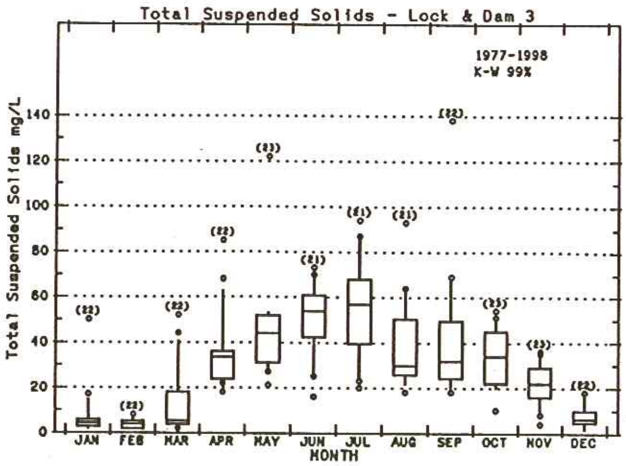


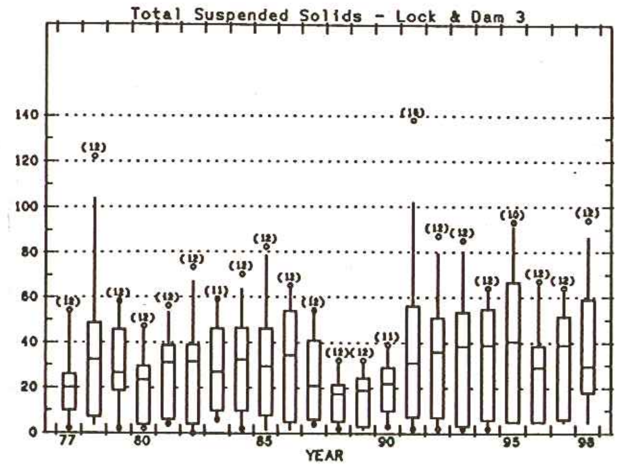


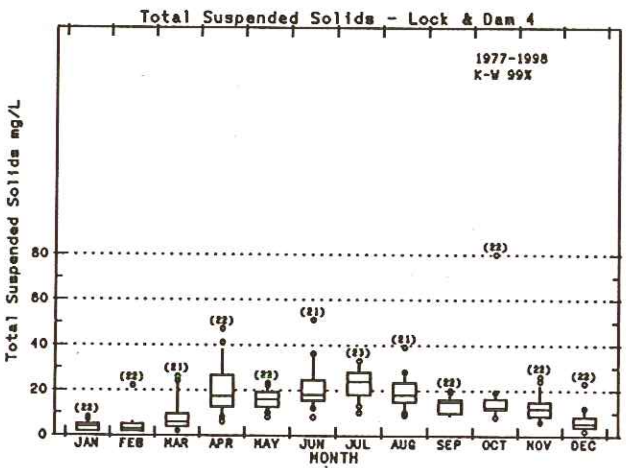


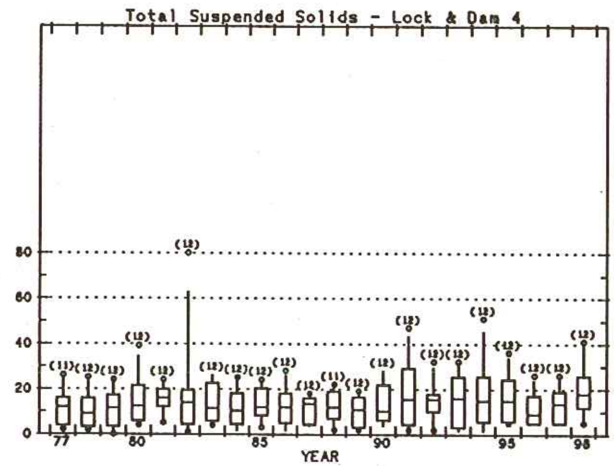


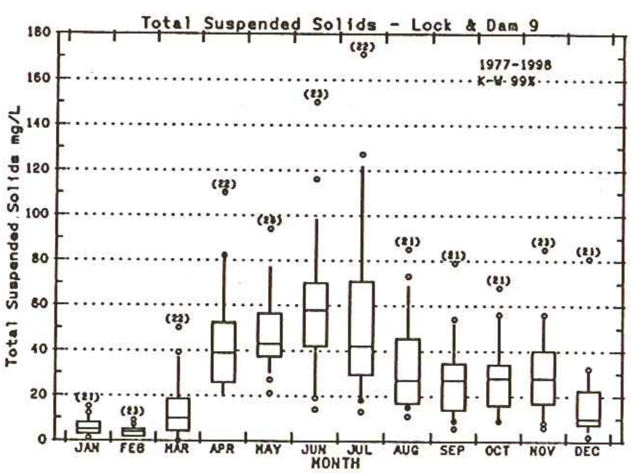
Appendix A – Continued

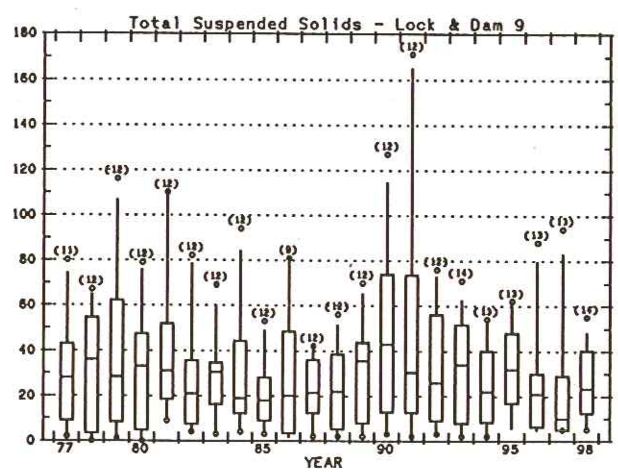




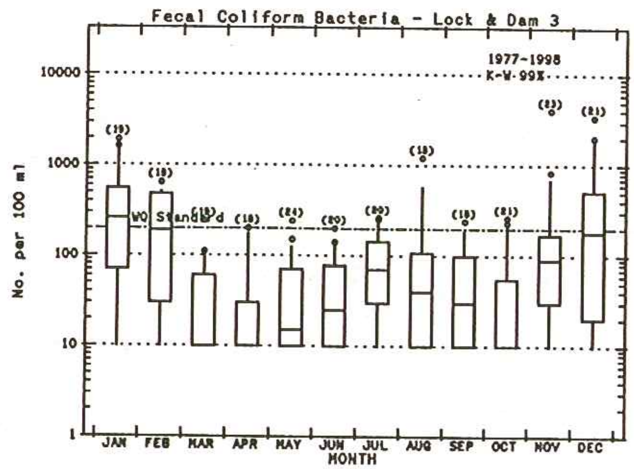


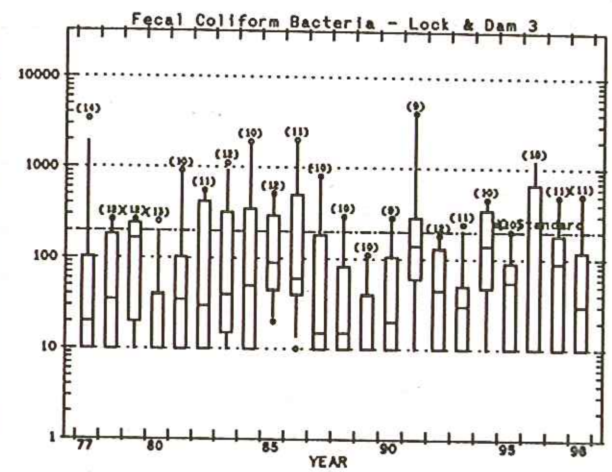


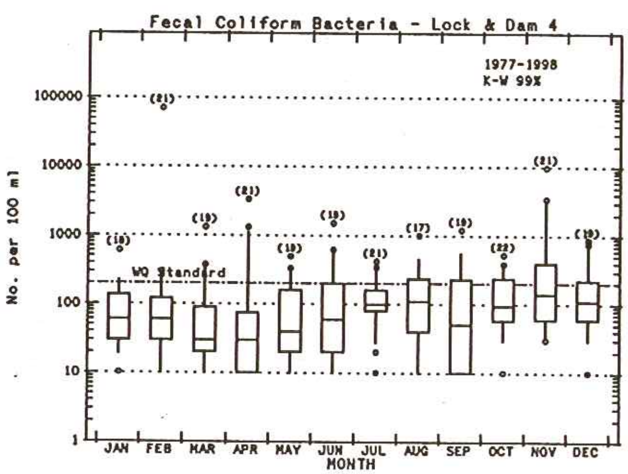


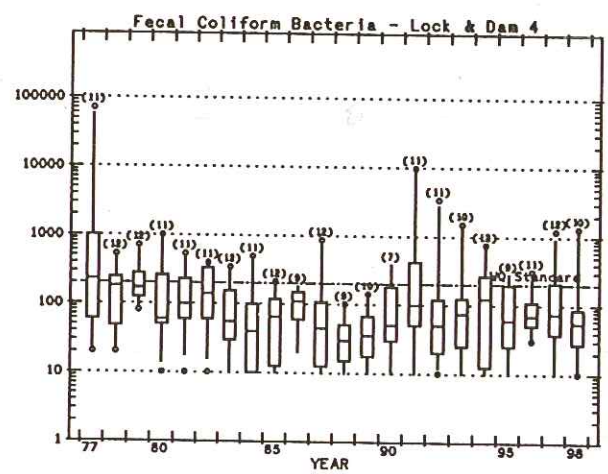


Appendix A – Continued

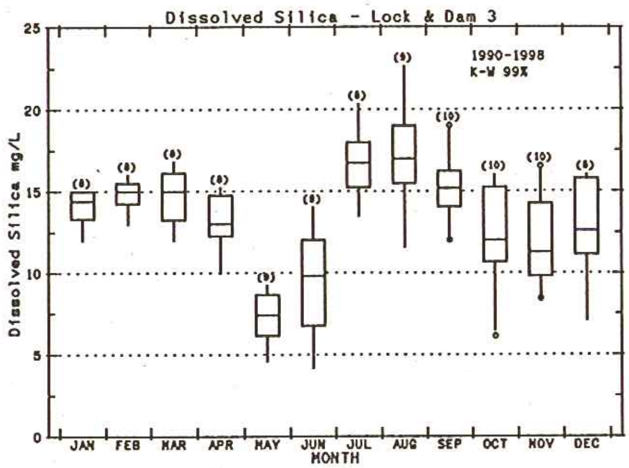


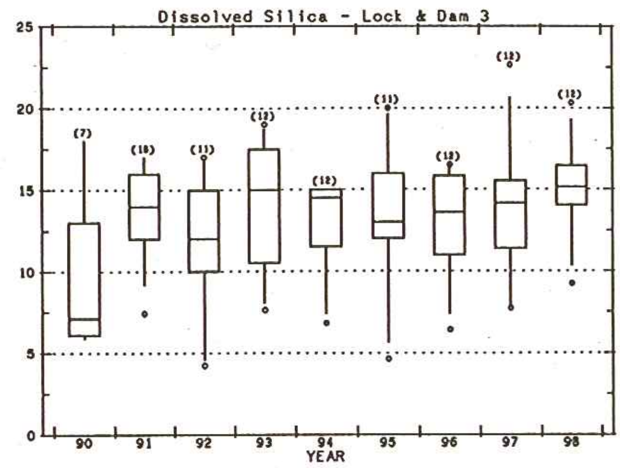


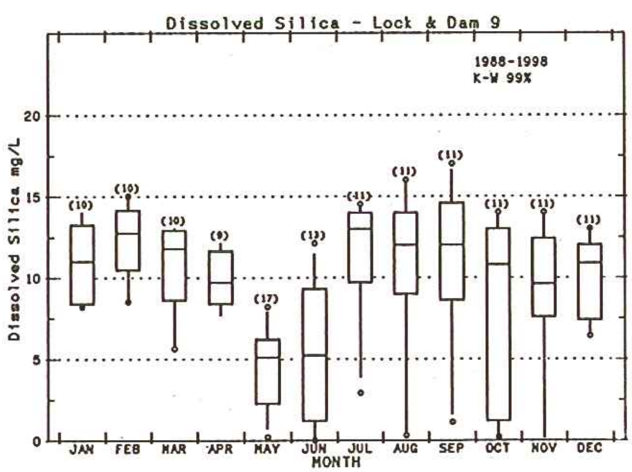


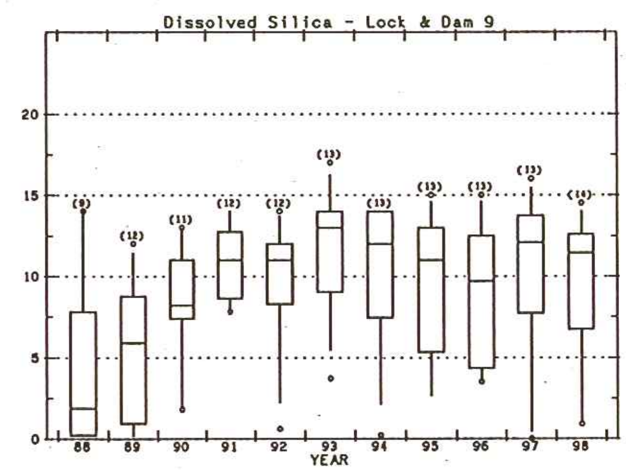


Appendix A – Continued

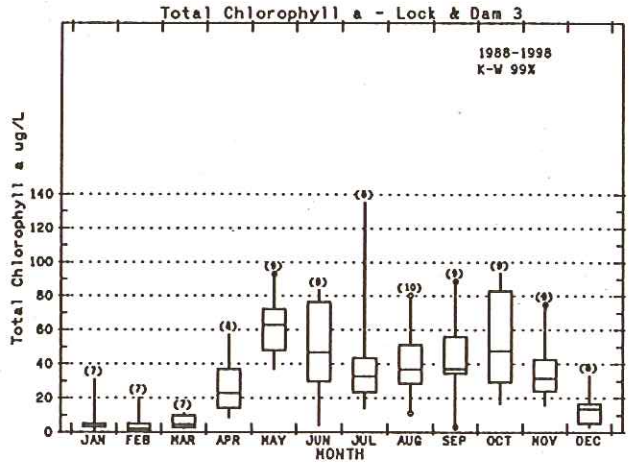


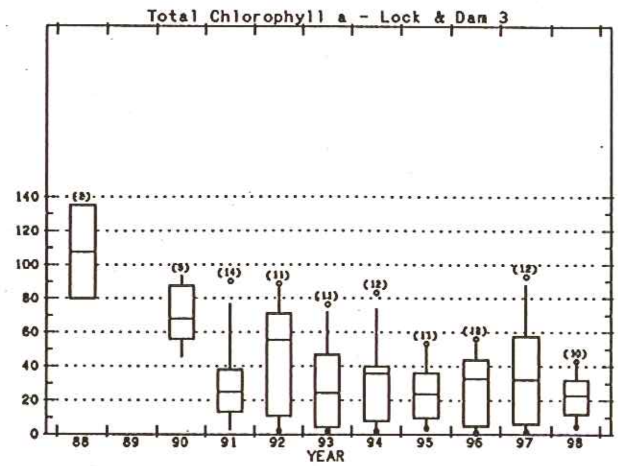


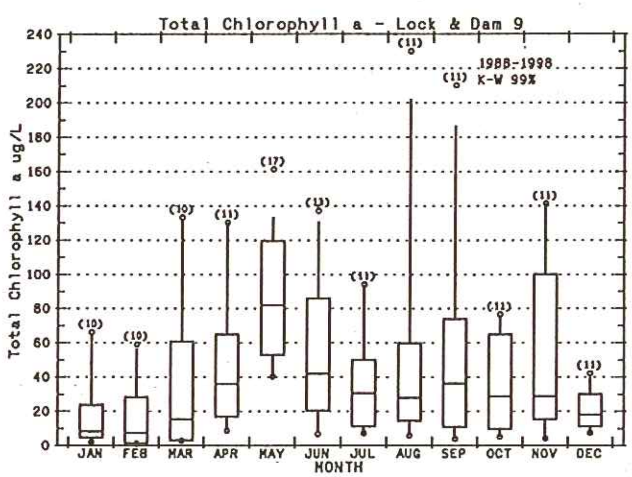


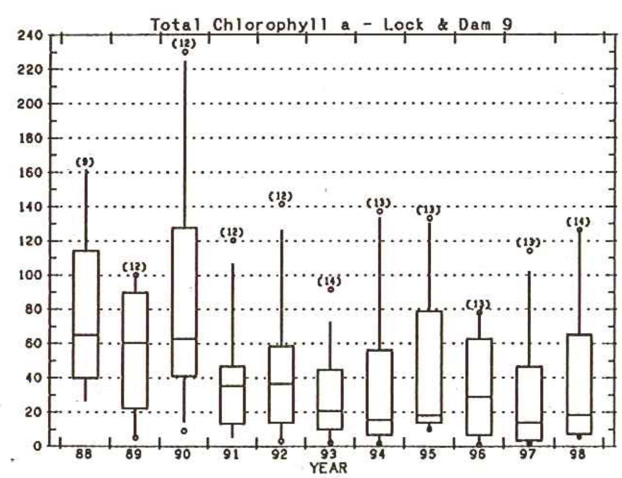


Appendix A – Continued



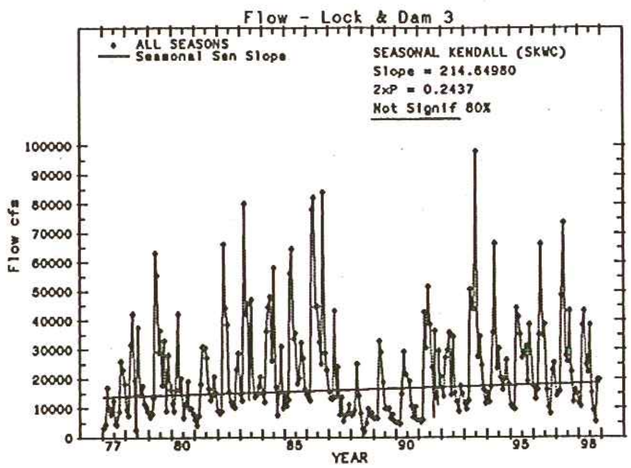


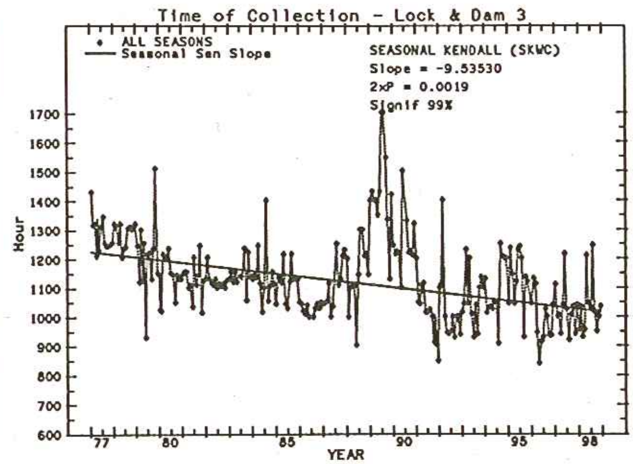


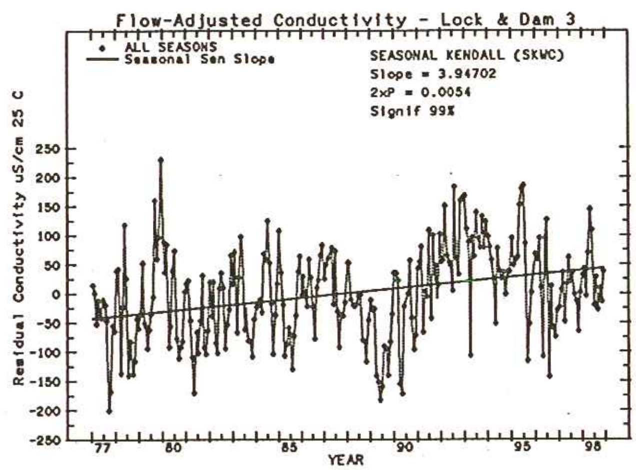


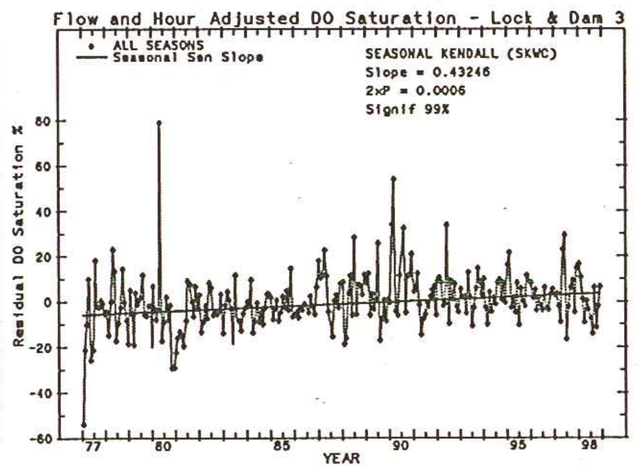
Appendix A – Continued

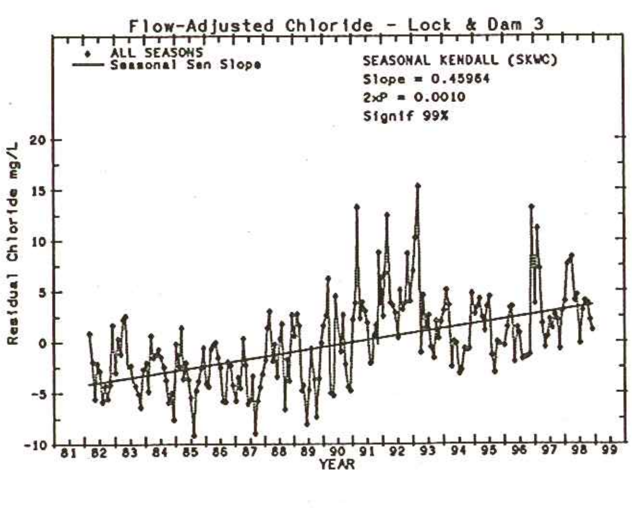
Appendix B – Seasonal Kendall Plots

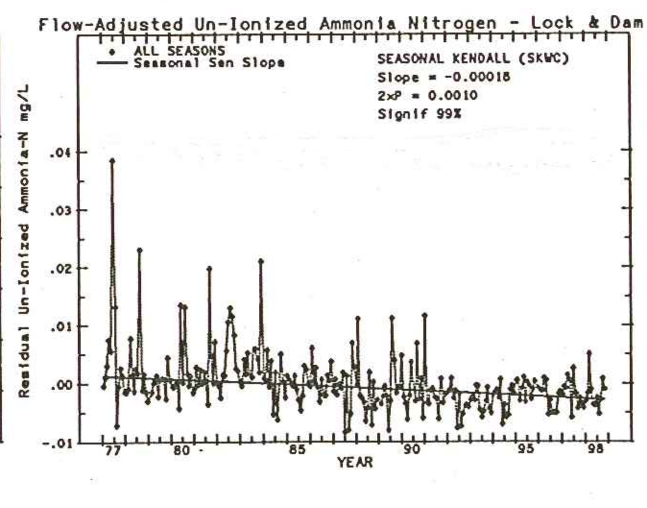


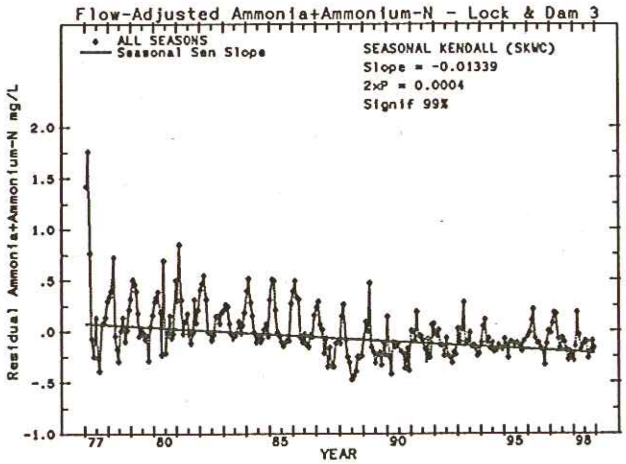


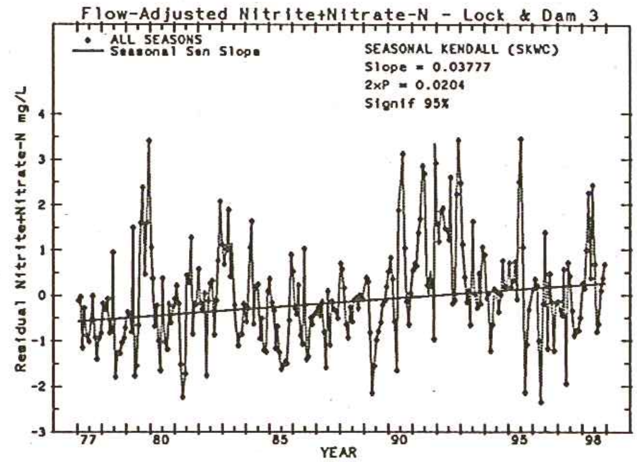


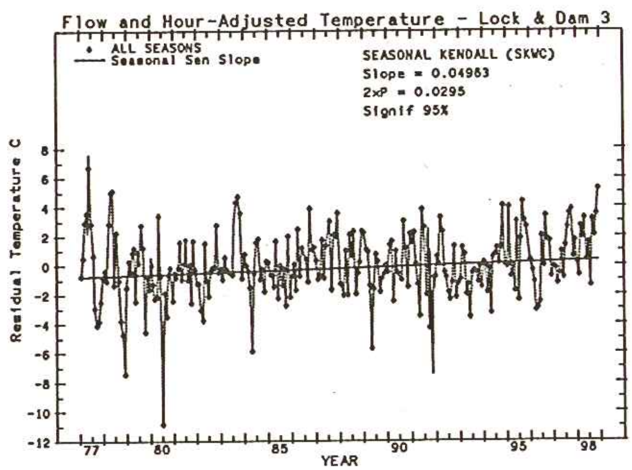


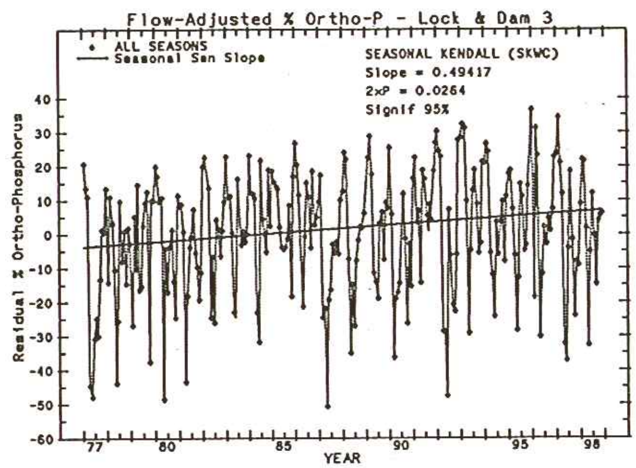


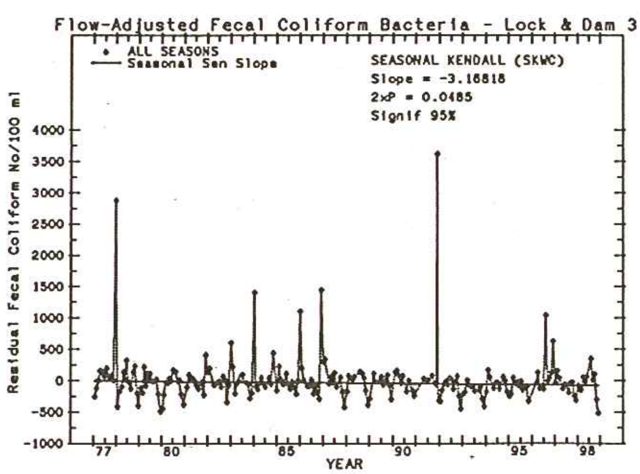


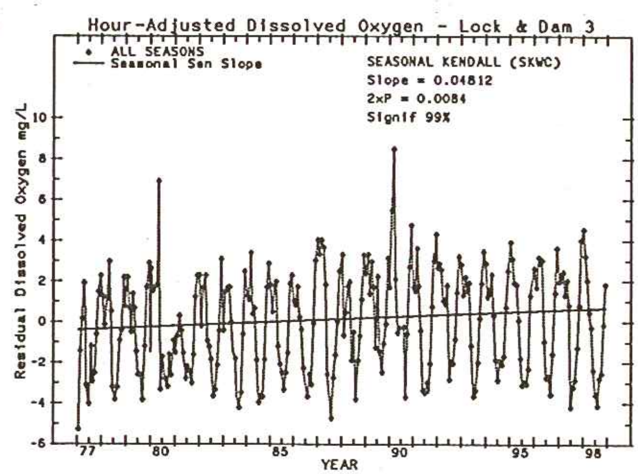




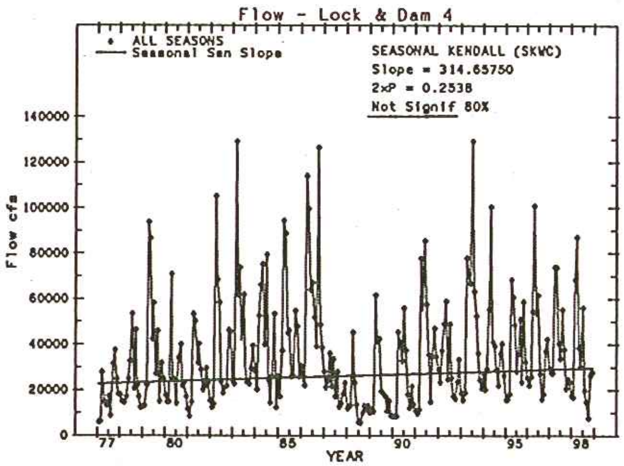


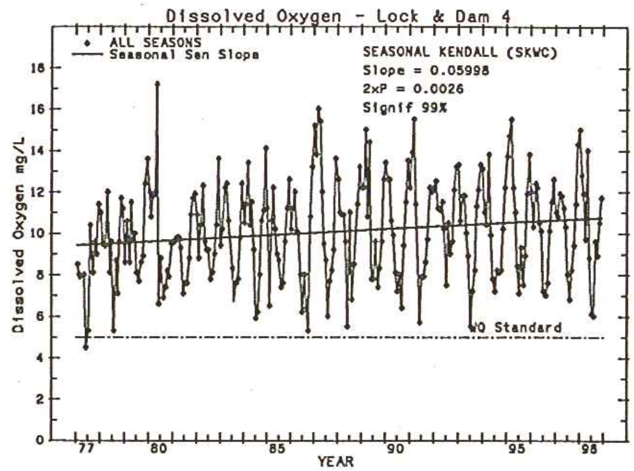


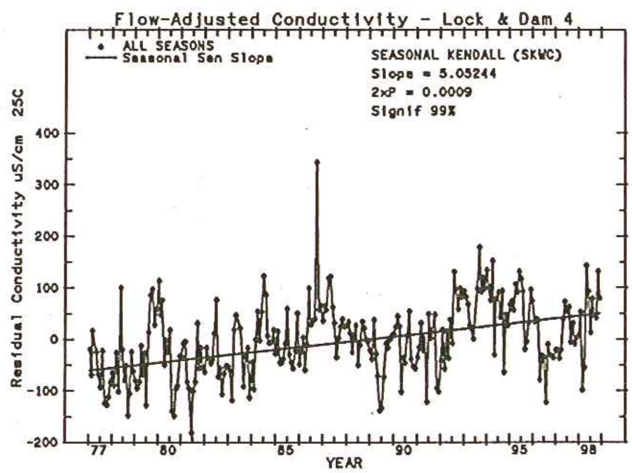


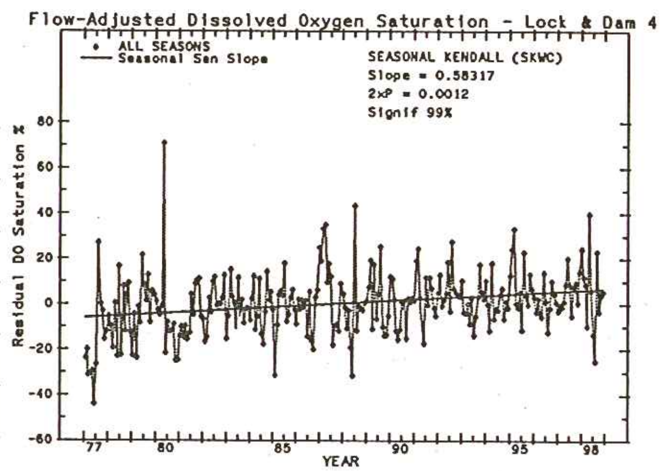


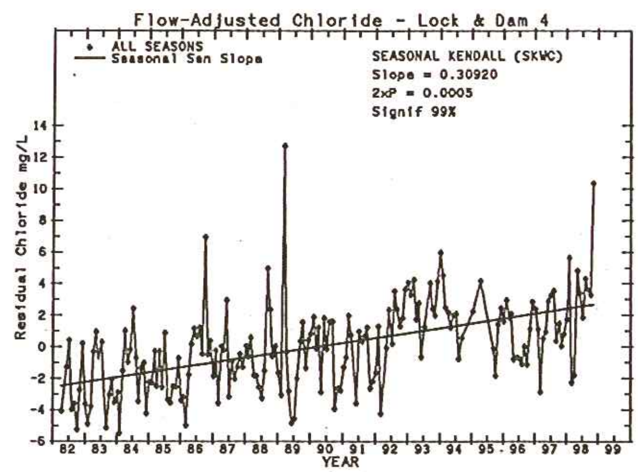
Appendix B. - Continued

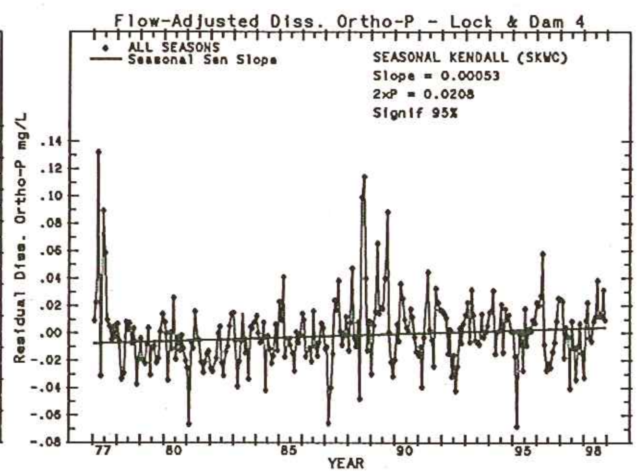




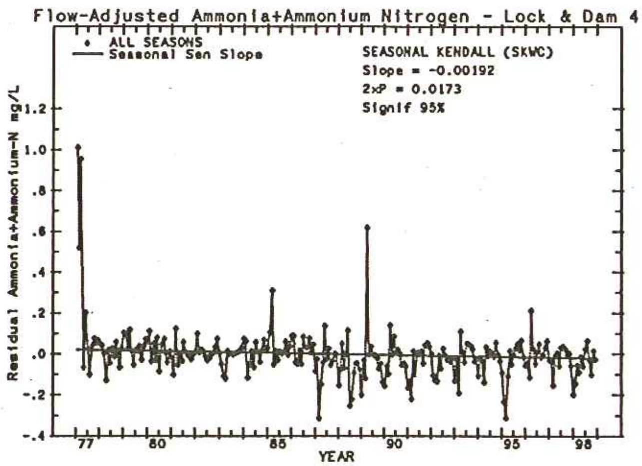


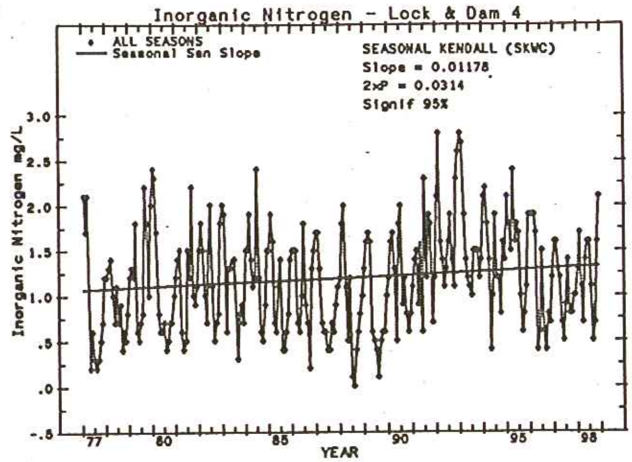


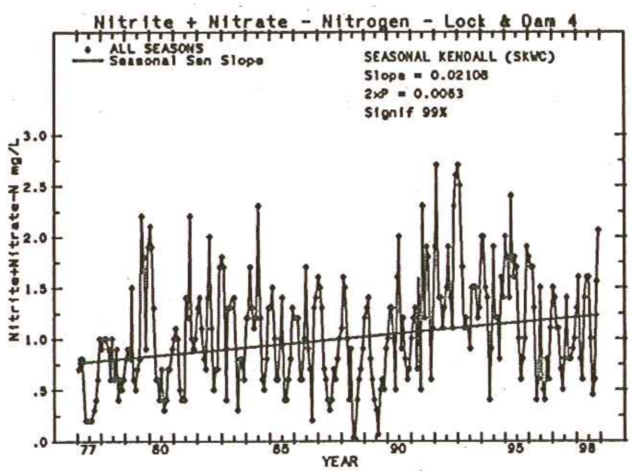


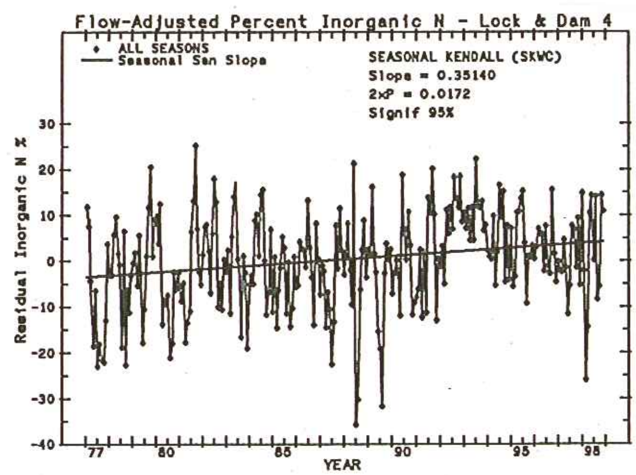


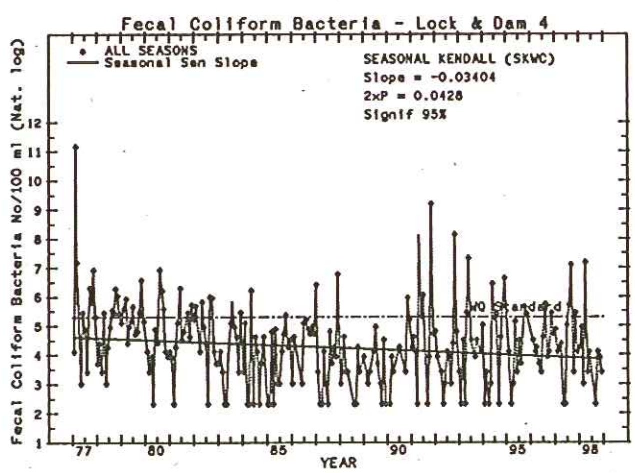
Appendix B. - Continued



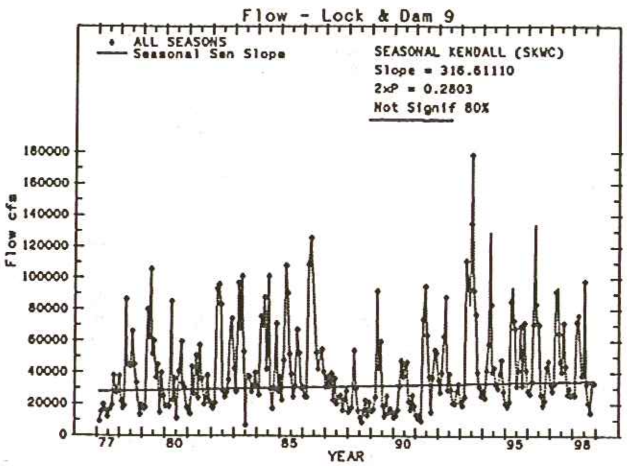


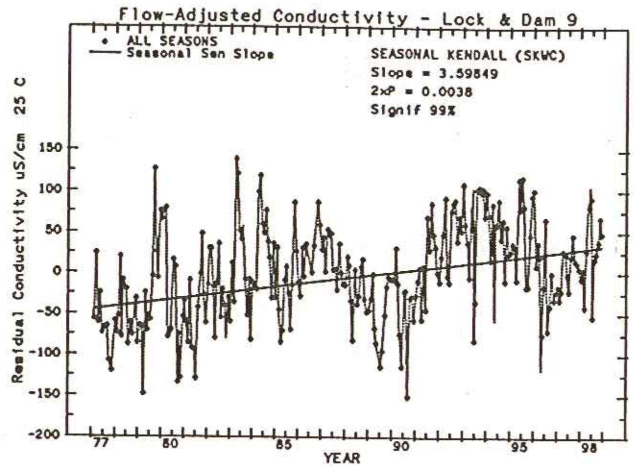


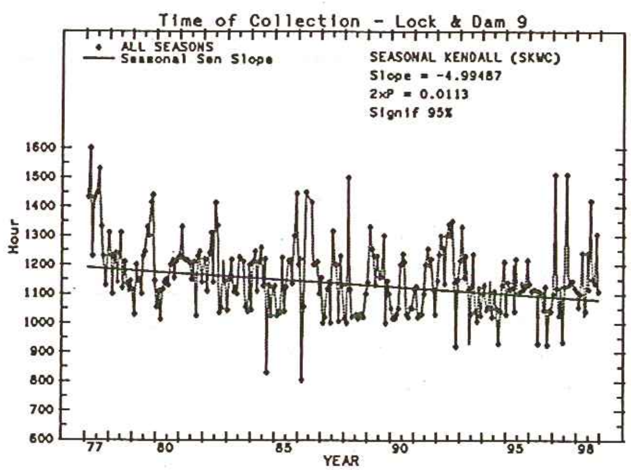


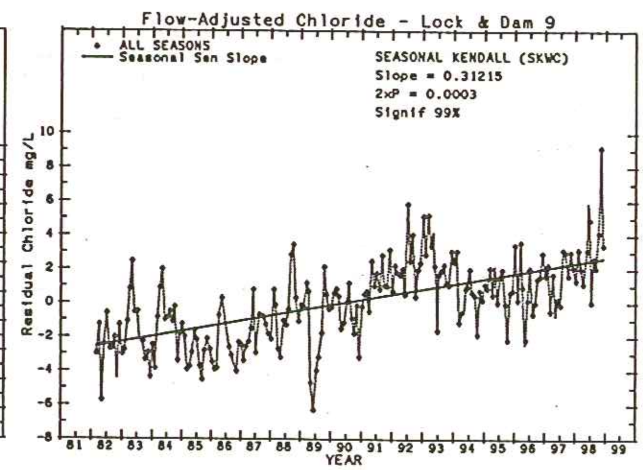


Appendix B. - Continued









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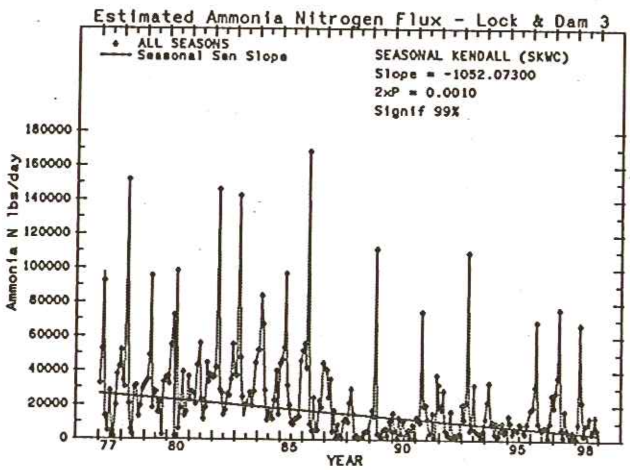

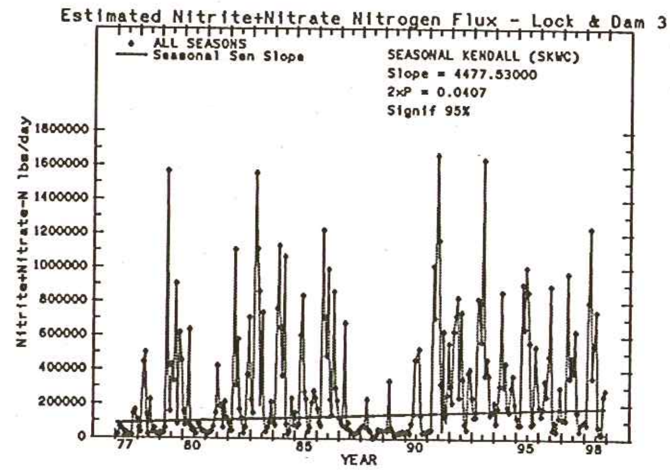

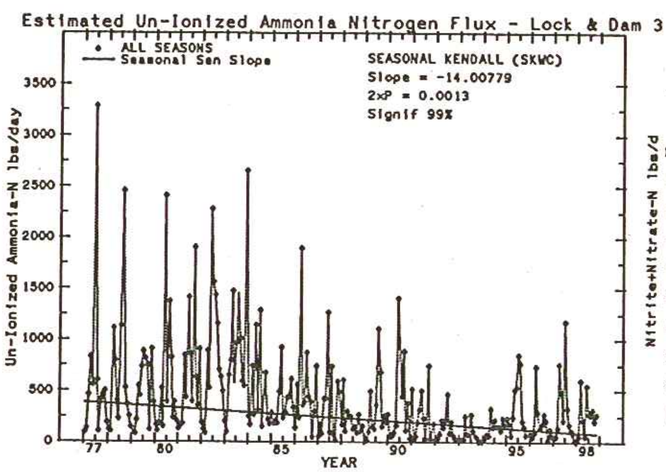

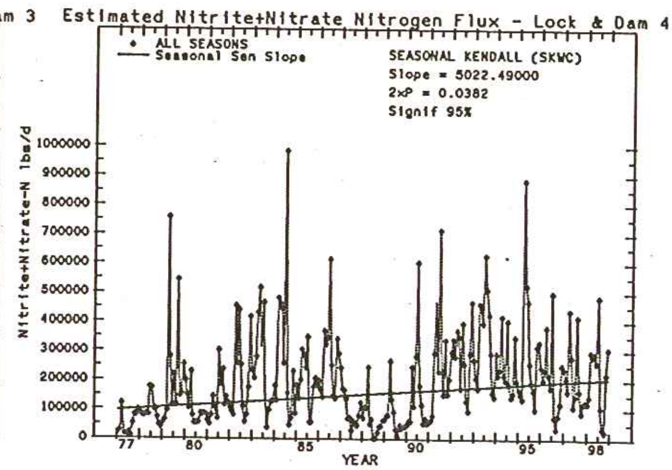

Appendix B. - Continued