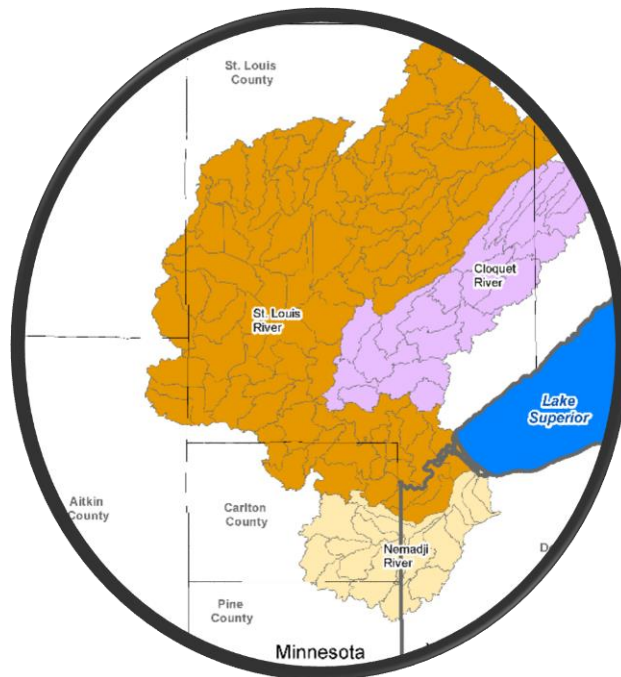


St. Louis, Cloquet, and Nemadji River Basin Models

Volume 2

Water Quality Calibration



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1 Introduction

This report is presented as Volume 2 in a set of reports that document the calibration and validation of watershed hydrology and water quality simulation models for three major watersheds in northeastern Minnesota – The St. Louis, Cloquet, and Nemadji River watersheds. Volume 1 addressed model setup and the calibration for hydrology and sediment transport. That report was initially released in 2014, but is being updated to reflect several changes in the model, including corrections to mining discharges and additional sub-basin discretization to represent some individual lakes of interest. This report (Volume II) documents the water quality calibration and validation.

The work described in this report is consistent with the objectives of Minnesota’s One Water program, which seeks to develop operational hydrology and water quality simulation models of all major watershed (8-digit hydrologic unit code [HUC] watersheds) within the state. These are basin-scale models, with sub-basin resolution resolved down to the approximately 12-digit HUC level. Models at this scale are most useful for addressing basin-scale management questions, such as the impacts of land use change within the basin on loadings of sediment and nutrients to Duluth Harbor and Lake Superior. Local-scale issues, such as headcuts in stream segments in the Nemadji River basin or streams with locally depressed dissolved oxygen in the St. Louis River basin are addressed in the model through relatively broad-scale approximations; however, development of models at finer spatial scales may be needed to correctly address localized environmental problems.

The simulation model is implemented, developed, and calibrated for the period of 1995 – 2012. Unfortunately, monitoring data are somewhat limited for this period. For various parts of the St. Louis River watershed there was intensive water quality monitoring during the 1970s and 1980s that was subsequently discontinued. For both the St. Louis and Nemadji watersheds there has been extensive data collection during the 2012 to present period in support of stressor identification and development of a Watershed Restoration and Protection Strategy (WRAPS) for these basins. Concurrent with this work, Minnesota Department of Natural Resources (MDNR) has funded an effort to extend the St. Louis, Cloquet, and Nemadji models through the end of 2014. This requires updating of meteorology input files as well as records of waste discharges, water appropriations, atmospheric deposition, and managed releases from reservoirs. Once this effort is completed the model can be compared against additional monitoring data and the water quality calibration improved.

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2 Water Quality Calibration Approach

Water quality simulation depends on the simulation of hydrology and sediment transport. Those aspects of the model are documented in detail in Volume 1 of this set. This section addresses the calibration and validation of the model simulation of water temperature, dissolved oxygen, nutrients, and algae.

Although not a primary focus of the modeling effort, water temperature simulation is important in the watershed model for several reasons: water temperature affects many biologically mediated processes that influence water quality in the streams, and the temperature of the water determines how it will mix when it enters the lake.

Daily average water temperature in shallow flowing streams is largely controlled by air temperature. Temperature cycles within the day, however, may be strongly affected by heat gain from incoming solar radiation and heat loss due to longwave back radiation. Both of these effects are controlled by the extent of cover and shading on the stream in addition to meteorological variables such as solar radiation and cloud cover.

A detailed diel simulation of stream water temperature is a complex undertaking. The timing and magnitude of heat fluxes are controlled by a variety of factors such as stream orientation and vegetative and topographic shading angles that cannot be fully represented in a basin-scale HSPF model. For example, a stream oriented east-west is likely to be exposed to unshaded solar radiation for a longer part of the day than a stream oriented north-south. Stream shading varies over the course of the year as canopy density changes, and may also change over time as trees grow, are cut, fall due to ice and wind storms, or due to fire. HSPF approximates all these complex details through the assignment of a temporally constant “surface exposed” (CFSAX) factor that represents the average fraction of tree-top solar radiation reaching the water surface. Given these issues, the stream temperature calibration was checked for reasonableness, but not constrained to achieve specific statistical targets.

Loading of nutrients that may support excess algal growth is an important concern. The major nutrients controlling algal growth are phosphorus and nitrogen. Both are simulated in detail in the model. Minor nutrients (e.g., silica, iron) may also play a role in determining algal response but are not simulated in the watershed model. (Iron may play an important role in inorganic phosphorus cycling, but is not a direct limiting factor on algal growth in this watershed). The first step in a sequential process for nutrient calibration is to verify that unit area loading rates were reasonable compared to literature values. Next, calibration to instream observations is carried out to refine the simulation. Plant growth has an important effect on nutrient balances during low flow conditions and serves to convert inorganic nutrients into organic forms; therefore, nitrogen and phosphorus species must be calibrated simultaneously with algae.

In forested watersheds, much of the nutrient load moves as a constituent of organic matter (including leaf litter, other debris, and dissolved organic compounds, such as humic acids), while stream concentrations of inorganic nutrients remain low in these watersheds. In contrast, agriculture and fertilized lawns may export significant amounts of nutrients in inorganic forms. Point source discharges can contain a mix of organic and inorganic nutrient forms dependent on the treatment process.

The approach taken is to simulate three components in loading from the land surface as general quality constituents (GQUALs): inorganic nitrogen (nitrate, nitrite, and ammonia), inorganic phosphorus (total orthophosphate), and organic matter. Each of these constituents is then partitioned at the point of entry into the stream network:

- Inorganic nitrogen is partitioned into dissolved nitrate, dissolved ammonium, and sorbed ammonium. Fractions of the dissolved constituents are set to reproduce observed data, while sorption of ammonium is simulated using equilibrium partitioning assumptions (the model connects inorganic N from the land surface to dissolved N in the stream reach, but equilibrium

partitioning to the sorbed form occurs instantaneously). Assignment of total inorganic nitrogen from the land surface to nitrate and ammonium at the point of entry to the stream is represented by a constant ratio throughout the model, but differs for agricultural land and impervious surfaces. Partitioning of ammonium between dissolved and sorbed forms depends on local suspended sediment concentrations. A small portion of the inorganic N is routed directly to organic N to represent uptake by heterotrophic organisms in low order streams (a process not explicitly simulated by the model).

- Inorganic phosphorus is partitioned into dissolved and sorbed fractions using equilibrium partitioning assumptions. As with ammonium, the fraction that becomes sorbed depends on the local suspended sediment concentration,
- Organic matter (biomass) is partitioned into labile and refractory organic carbon, organic nitrogen, and organic phosphorus components. Initial specifications were based on expected stoichiometry of forest litter, and then revised during calibration to achieve agreement with observed concentrations.

All three upland components (inorganic nitrogen, inorganic phosphorus, and organic matter) may be loaded through either surface flow or subsurface flow (interflow and groundwater discharge). The HSPF GQUAL algorithms do not maintain a full mass balance of subsurface constituents (which would require a groundwater quality model); rather, the user specifies concentration values, which may vary monthly, for interflow and groundwater. Surface washoff loading is considered from both pervious and impervious surfaces.

Inorganic phosphorus loading from pervious surfaces is simulated as a sediment-associated process because of the strong affinity of orthophosphate for soil particles. Surface loading of inorganic phosphorus is thus determined by a potency factor applied to sediment load, which may vary on a monthly basis to reflect changes in surface soil concentration associated with the annual growth cycle. (While this reflects the physical basis of surface loading of inorganic phosphorus, it does mean that any errors in the simulation of sediment loading will also affect estimates of inorganic phosphorus loading.) Subsurface flow pathways are assumed to primarily load small amounts of dissolved inorganic phosphorus. Organic matter is also simulated as a sediment-associated load from pervious surfaces, as this primarily represents the erosion of humus, leaf litter, and other detritus.

In contrast to phosphorus, inorganic nitrogen is highly soluble, and loading in surface runoff may occur independent of sediment movement (particularly where fertilizer is applied). Further, much of the nitrate load in surface runoff represents input from atmospheric deposition. Therefore, inorganic nitrogen loading from pervious surfaces is represented via a buildup-washoff process in which the user specifies a rate of accumulation, an accumulation limit, and a flow rate sufficient to remove 90 percent of the accumulated material.

As noted above, representation of plant growth is a necessary part of the nutrient calibration process. HSPF contains routines for simulating planktonic (floating) and benthic (attached) algae. Growth, respiration, and death processes are affected and potentially limited by the availability of light, availability of inorganic nutrients, water depth, and water temperature. Because HSPF represents stream segments as one-dimensional, fully-mixed reactors, the predictions of algal response are averages throughout the stream segment volume. Planktonic and benthic algae simulations differ primarily in the way that the attenuation of light availability is calculated. For plankton light availability is calculated as the average over the euphotic depth, such that all phytoplankton are assumed to be mid-depth in the reach or the middle of the euphotic zone, whichever is smaller, then adjusted to the full volume of the reach. Benthic algae are assumed to be at the average depth of the reach. These simplifying assumptions can distort the actual response in some situations. For deeper reaches, especially lakes, the phytoplankton simulation results are an average over the reach volume, which does not match well with chlorophyll *a*

observations collected from the photic zone. When the average depth is large relative to the light extinction rate benthic algal growth will be simulated as minimal, whereas significant growth may actually occur in the shallower edges of the lake or stream. The scheme does not include a representation of floating or emergent rooted macrophytes. While these can sometimes be successfully approximated with the benthic algae routines, the light availability calculations for benthic algae are not appropriate to these types of macrophytes and the program does not consider that floating/rooted macrophytes can exchange gases with the atmosphere and obtain nutrients from the sediment.

The dissolved oxygen simulation considers reaeration, the decay of organic matter (carbonaceous biochemical oxygen demand), oxidation of ammonia and nitrite N, sediment oxygen demand, and algal photosynthesis and respiration. In the slow-moving, swampy areas of the upper St. Louis, Cloquet, and Nemadji watersheds, the DO balance is largely a factor of the interplay of algal growth and sediment oxygen demand exerted by the decay of settled organic matter. The model is not designed to simulate the oxidation of reduced iron and sulfur, which could play an important role in and downstream of the Iron Range.

For most water quality constituents, it is unreasonable to propose that the model predict all temporal variations in concentration and load. The model should, however, provide an accurate representation of long-term and seasonal trends in concentration and load, and correctly represent the relationship between flow and load. To ensure this, it is important to use statistical tests of equivalence between observed and simulated concentrations, rather than relying on a pre-specified model tolerance on difference in concentrations.

Ideally, average errors and average absolute errors should both be low, reflecting a lack of bias and high degree of precision, respectively. In many cases, the average error statistics will be inflated by a few highly discrepant outliers. It is therefore also useful to compare the median error statistics.

General performance targets for water quality simulation with HSPF are also provided by Duda et al. (2012) and are shown in Table 1-1. These are calculated from observed and simulated daily concentrations, and should only be applied in cases where there are a minimum of 20 observations.

Table 2-1. Performance Targets for HSPF Water Quality Simulation (Magnitude of Annual and Seasonal Relative Average Error (RE) on Daily Values)

Model Component	Very Good	Good	Fair	Poor
Temperature	≤ 7%	8 - 12%	13 - 18%	> 18%
Water Quality/Nutrients	≤ 15%	15 - 25%	25 - 35%	> 35%

Evaluation of water quality simulations presents a number of challenges because, unlike flow, water quality is generally not monitored continuously. Grab samples at a point in space and time may not be representative of average conditions in a model reach on a given day due to either spatial or temporal uncertainty (i.e., an instantaneous measurement in time may deviate from the daily average, especially during storm events, while a point in space may not be representative of average conditions across an entire model reach). Where constituent concentrations are near reporting levels, relative uncertainty in reported results is naturally high. Accurate information on daily variability in point source loads is also rarely available.

Evaluation of relative average error is recommended, but averages are prone to biasing by one or a few extreme outliers. Therefore, it is also useful to examine median relative errors, which are less influenced by outliers.

The performance targets for water quality simulation may be applied to either concentrations or loads. Concentrations provide the most natural metric, but error magnitude may be unduly influenced by variability at low flow conditions that has little effect on cumulative loading downstream. Loads are more meaningful for impacts in downstream lakes, harbors, and estuaries but are not directly observed and need to be estimated from flow and concentration – both uncertain. Tests on loads are performed in two ways: on paired data (observed and simulated daily average concentration multiplied by flow) and on complete time series of monthly loads. For the latter approach, “observed” monthly loads are estimated using the USACE FLUX32 program (a Windows-based update of the FLUX program developed by Walker, 1996; available at <https://www.pca.state.mn.us/water/watershed-pollutant-load-monitoring-network#flux32-8f1620f5>), and are themselves subject to significant uncertainty.

Additional statistical tests are also applied as part of a weight-of-evidence examination of the water quality calibration. Two-sample *t*-tests are reported on the differences in mean concentration and mean load, with higher probability values indicating less chance that the measures are systematically different. A problem with the *t*-test is that the test is on a null hypothesis that the mean difference is exactly equal to zero, not whether the difference is physically meaningful. Therefore, a low value on the *t*-test (rejection of the null hypothesis) is generally considered of practical significance only when the mean difference is greater than 10 percent. Additional graphical tests are also performed to ensure that errors in the prediction of load and concentration do not exhibit strong correlations relative to flow magnitude and season.

3 Nitrogen and Phosphorus Calibration

3.1 NUTRIENT MODEL SETUP

The nutrient simulation follows the same general approach used in other Minnesota HSPF models and recommended by AQUA TERRA (2012). Ammonia, nitrate nitrogen, orthophosphate, and generalized organic matter are simulated on the land surface, with the first two being represented by buildup-washoff processes and the second two simulated as sediment-associated using potency factors for pervious land (with a buildup-washoff approach for impervious land). Representation of point source loads of nutrients are described in Section 3.1.2. Full nutrient kinetics are represented instream, including the decay of organic matter, uptake by and release from planktonic and benthic algae, nitrification, denitrification, exchanges with the sediment bed, and sorption to sediment of ammonium and ortho-phosphate.

3.1.1 Nonpoint Sources

As described in Section 1, the nutrient simulation for the uplands represents inorganic nitrogen, inorganic phosphorus, and organic matter as three distinct constituents. Inorganic phosphorus and organic matter on pervious surfaces are simulated using a sediment potency approach, while inorganic nitrogen on pervious surfaces and all three constituents on impervious surfaces are represented as a buildup/washoff process. Concentrations associated with subsurface flows are also included.

Within the stream reaches the model represents individual nutrient species (ammonia, nitrate, nitrite, organic nitrogen, orthophosphate, organic phosphorus, and organic carbon/BOD). The stream reach module is implemented with full nutrient simulation, including uptake by and release from plankton and benthic algae, decay of organic matter, oxidation of ammonium to nitrite and nitrite to nitrate nitrogen, bed exchanges of dissolved and sorbed nutrients, and ammonia volatilization.

The key parameters controlling the upland nutrient simulation are listed below:

MON-ACCUM: The monthly varying assignment of the build-up or accumulation of a constituent on a particular surface (lb/ac-d).

MON-SQOLIM: The monthly varying upper limit value beyond which a constituent can no longer accumulate on a surface (lb/ac).

MON-IFLW-CONC and **MON-GRND-CONC:** These parameters are used to assign the interflow and groundwater constituent concentrations on a monthly basis. The values for these parameters were estimated from the observed data with consideration of flow regime and then calibrated as necessary.

MON-POTFW: The monthly varying specification of constituent mass per sediment mass (lb/ton). For organic matter the assigned values were around 10^0 to 10^1 . The seasonal assignment for organic matter reflects the annual cycle of growth and then litter.

The sediment potency, build-up/washoff, and subsurface flow parameters were initialized for the St. Louis, Cloquet, and Nemadji watershed models based on past experience. A literature review was conducted to establish appropriate ranges for unit-area loading rates of the diverse land use categories found in the watersheds (Table 3-1). The simulated unit-area loading rates were compared to the literature-based ranges and the surface and subsurface flow parameters were revised until reasonable loading estimates were established for TN and TP. Results for the St. Louis and Cloquet watersheds were aggregated and are provided in Figure 3-1 and Figure 3-2. Results for the Nemadji watershed are shown in Figure 3-3 and Figure 3-4.

The mean simulated TN unit loading rate for forest land segments in the St. Louis and Cloquet River watersheds is 2.9 lb-N/ac/yr, which is in the center of the reported range in Table 3-1. The developed

pervious and impervious mean simulated values are 4.2 lb-N/ac/yr and 12.5 lb-N/ac/yr, respectively. These results are similar to the values reported by the Minnesota Pollution Control Agency, which range from 2-17 lb-N/ac/yr for mixed developed land use (MPCA, 2013a). The mean simulated TN unit loading rate for wetlands is 5.3 lb-N/ac/year and this is slightly higher than the literature supported range of 0.5 – 5 lb-N/ac/yr (MPCA, 2004); this can be attributed to the fact that the literature values are largely based on surface runoff whereas the model results include nitrogen loading from subsurface waters. The cropland unit loading rate is near the lower limit of the reference range at 7.6 lb-N/ac/yr. The simulated unit loading rate for croplands, however, is comparable to the average loading rate of 17 watersheds in Wisconsin, 7.5 lb-N/ac/yr (Clesceri et al, 1986).

Reference TP unit loading rates for forest are as low as 0.05 lb-P/ac/yr (MPCA, 2004) and as high as 0.5 lb-P/ac/yr (Loehr et al, 1989). The simulated TP unit loading rate for forest in the St. Louis and Cloquet watersheds aligns with the reference values at 0.17 lb-P/ac/yr. The TP unit loading rate from wetlands are higher than reference values because subsurface flows contribute to the simulated load but generally are not considered in the literature-based values. The mean simulated TP unit loading rate for croplands, 0.60 lb-P/ac/yr, aligns well with other studies that recommend use of 0.11-1.7 lb-P/ac/yr (Dodd et al, 1992; Loehr et al, 1989).

Table 3-1. Reference Ranges for the Nutrient Loading Rates of Diverse Land Use Categories

Land Use	TN (lb-N/ac/yr)	TP (lb-P/ac/yr)	Source
Forest	1.97 – 4.2	0.05 – 5	Clesceri et al, 1986; Loehr et al, 1989; MPCA, 2013a, MPCA, 2004; Reckhow et al, 1980
Wetland	0.5 – 5	0	MPCA, 2013a; MPCA, 2004
Pasture	6.1 – 23	0.11 – 0.43	Clesceri et al, 1986; McFarland and Hauck, 2001; MPCA, 2013a; MPCA 2004
Crop	7.5 – 23	0.11 – 1.7	Dodd et al, 1992; Clesceri et al, 1986; Loehr et al, 1989, MPCA, 2013a; MPCA 2004
Developed (pervious)	2 – 17	0.8 – 1.02	Loehr et al, 1989; MPCA, 2013a; MPCA, 2004; Reckhow et al, 1980
Developed (impervious)	2 – 17	0.8 -1.02	Loehr et al, 1989; MPCA, 2013a; MPCA, 2004; Reckhow et al, 1980
Barren	0.5 - 5	ND	MPCA, 2013a
Shrub	0.5 - 5	0.05 – 0.12	MPCA, 2013a; MPCA, 2004

The Nemadji watershed model was calibrated separately and results differ somewhat from the St. Louis and Cloquet model. This is in part due to the calibration data not strongly constraining exact results for individual land uses, but also may reflect some systematic differences between the watersheds. Total N loading rates are generally lower in the Nemadji, possibly reflecting greater denitrification potential in this basin's clay soils. Total P loading rates are generally higher because phosphorus is sediment-associated and erosion rates are higher in the Nemadji, on average, than in the St. Louis basin. Note, however, that the averages depend on the mix of different HRU characteristics associated with a given land use and there is a wide range of loading rates among different HRUs in a single land use class, reflecting differences in erosion rates and runoff potential.

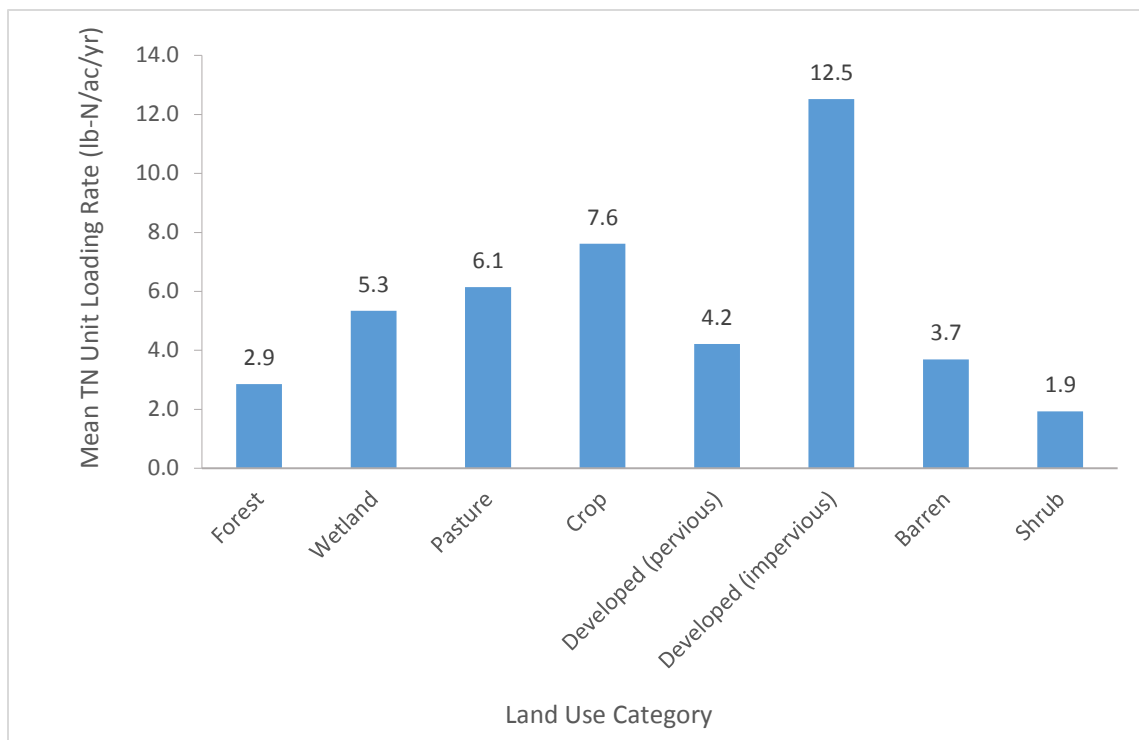


Figure 3-1. Mean Simulated Total Nitrogen (TN) Unit Loading Rates for Land Use Categories in the St. Louis and Cloquet Watersheds

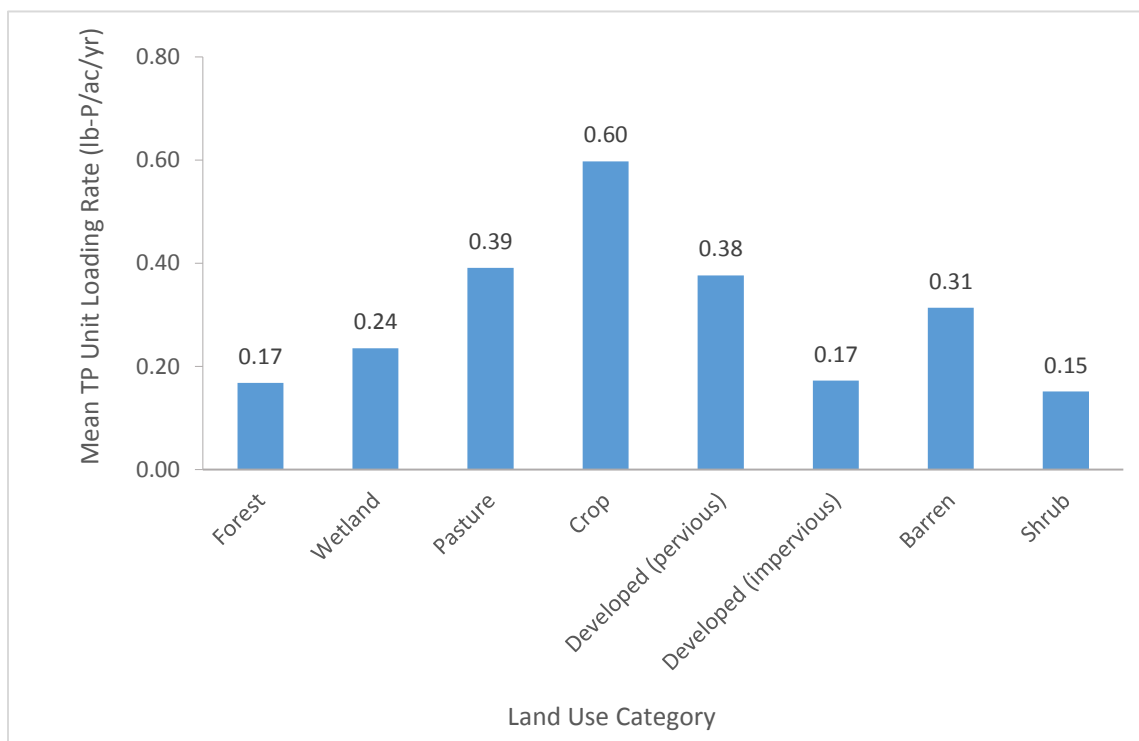


Figure 3-2. Mean Simulated Total Phosphorus (TP) Unit Loading Rates for Land Use Categories in the St. Louis and Cloquet Watersheds

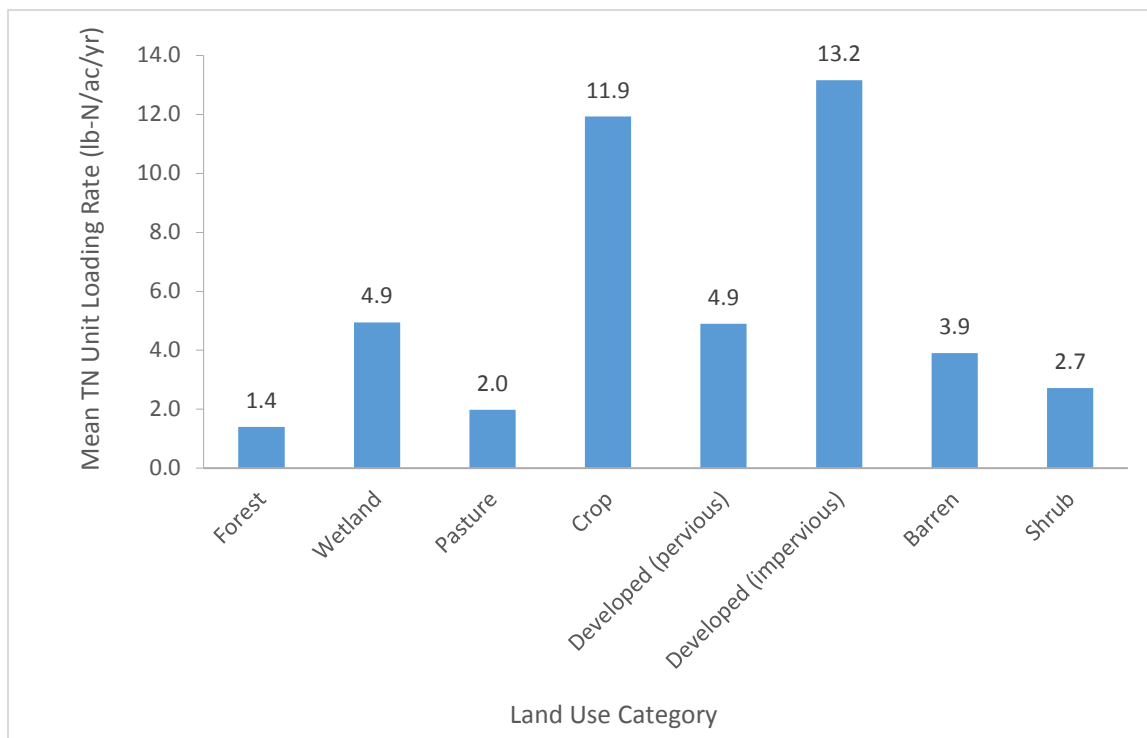


Figure 3-3. Mean Simulated Total Nitrogen (TN) Unit Loading Rates for Land Use Categories in the Nemadji Watershed

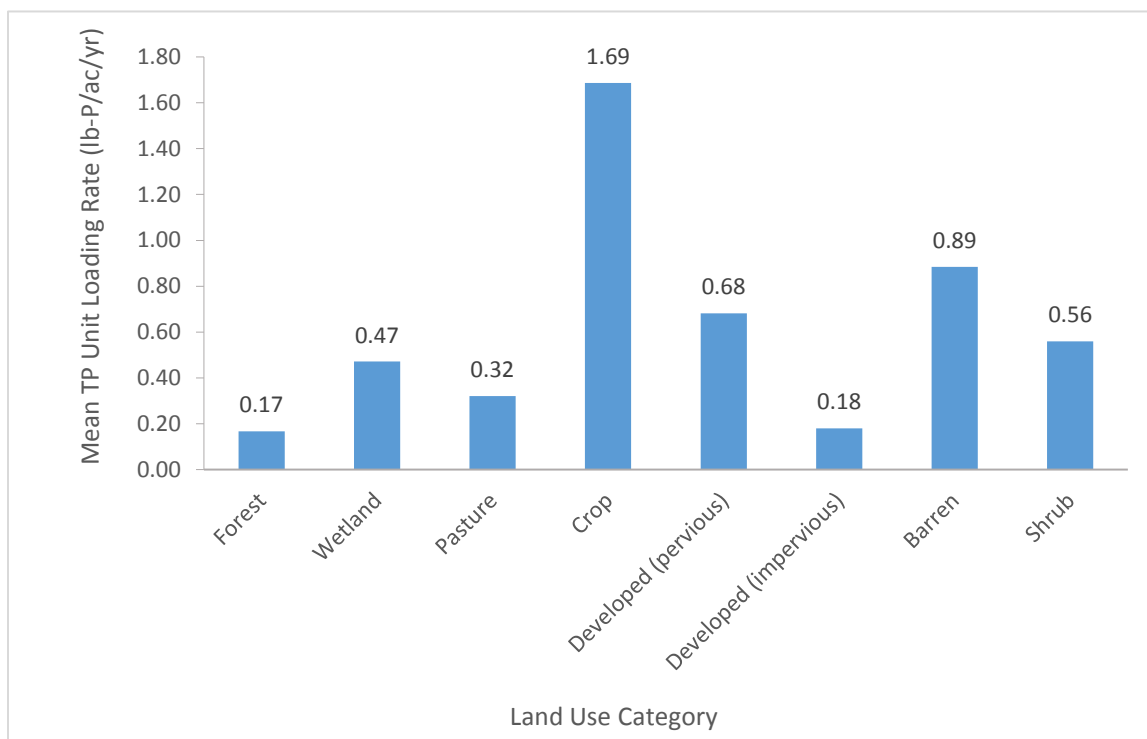


Figure 3-4. Mean Simulated Total Phosphorus (TP) Unit Loading Rates for Land Use Categories in the Nemadji Watershed

3.1.2 Point Sources

Point sources that have discharge permits in the St. Louis watershed are included in the modeling framework. Permitted point sources are not present in the Cloquet and Nemadji watersheds and, therefore, are not represented. The St. Louis-Cloquet model incorporates five major WWTP discharges and forty-nine minor point sources. The minor point sources include a variety of industrial, mining, and smaller municipal wastewater dischargers. Although classified as “minor” they include some very large discharges of non-contact cooling water and mine pit dewatering flows. The point sources included in the model are documented in Section 2.4 of Volume I of this report. The locations of the discharges are recapped in Figure 3-5. Note that the majority of the point sources are located either in the northern part of the watershed along the Iron Range or downstream in the Duluth area.

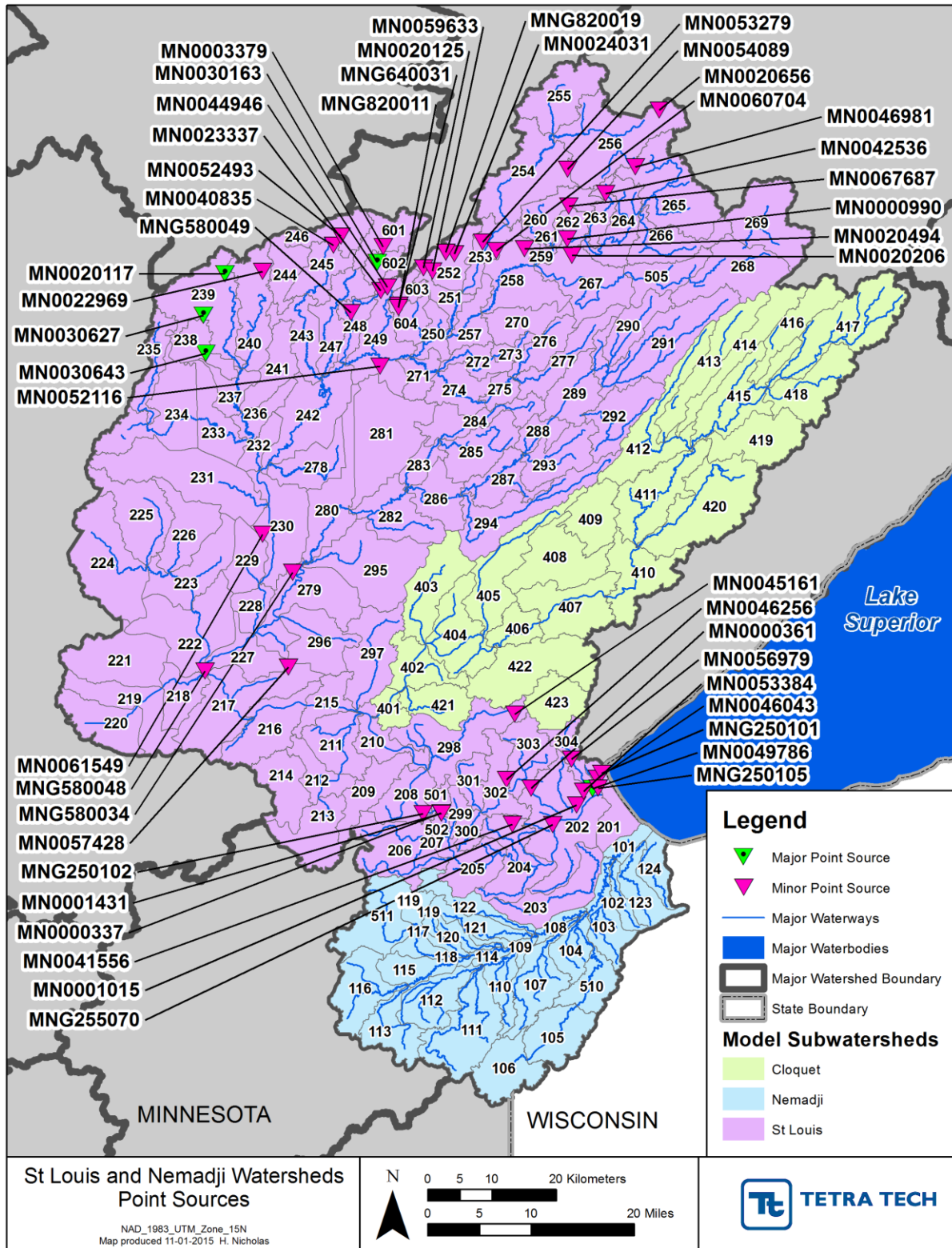


Figure 3-5. Point Source Discharges Included in the Model

Daily effluent flows are available for the major point sources and were used to create daily nutrient load series. Minor point sources rely on monthly flow and load series. Wastewater treatment plant discharges generally have monitored and reported effluent total phosphorus and ammonia concentrations in the Discharge Monitoring Reports (DMRs) commencing in 1995. These were assembled and provided by MPCA. Effluent nitrite + nitrate ($\text{NO}_2 + \text{NO}_3\text{-N}$), organic nitrogen, and phosphorus species were generally not reported. Discharge concentrations of these nutrients were established according to observations at upstream and downstream water quality stations and based on the type of discharger being represented (e.g. small municipal, industrial, mining). Large non-contact cooling water discharges that draw from and discharge back to the same reach, such as the 128 MGD discharge from the Laskin Power Plant, are simulated as having no net effect on nutrient loads. Mean nutrient concentrations simulated for the point sources are provided in Table 3-2. Phosphorus and ammonia discharge concentrations are generally low relative to concentrations observed in other parts of Minnesota. This likely reflects the influence of elevated levels of iron and sulfate in the surface and ground water supply sources of the St. Louis watershed, which in turn, respectively, may enhance complexation and removal of ortho-phosphorus and ammonia nitrogen in the wastewater systems.

Table 3-2. Mean Modeled Discharge Concentrations (mg/L) for Point Sources in the St. Louis River Watershed, 1995-2012

Discharge (Major Source or Minor Type)	$\text{NH}_4\text{-N}$	$\text{NO}_2 + \text{NO}_3\text{-N}$	Organic N	TP	$\text{PO}_4\text{-P}$	Organic P	CBOD
Chisholm-Mech.	3.53	7	2	0.42	0.23	0.2	3.62
Hibbing WWTP North Plant	0.64	10	4	0.31	0.17	0.14	2.87
Hibbing WWTP South Plant	0.56	10	4	0.35	0.19	0.16	2.84
Virginia WWTP	3	10	4	0.52	0.38	0.14	4.68
WLSSD WWTP	3.05	10	4	0.42	0.31	0.12	6.24
Minor Municipal WWTPs	1 - 4	3 - 10	2.36	0.12 – 0.85	0.09 – 0.61	0.03 – 0.24	12
Minor Industrial	2	1	1	0.12	0.1	0.02	0.5
Iron Range Industrial Discharges	0	0.25	0	0.02	0.02	0	0.5

Notes: Total phosphorus (TP) concentrations for WWTPs are based on monitoring reports, while the split between phosphorus species is based on fixed ratio assumptions. Iron Range Industrial Discharges are primarily mine dewatering flows which are expected to have low nutrient concentrations due to the presence of reduced iron and sulfur species. Nitrate plus nitrite N concentrations for minor municipal WWTPs are not monitored and are based on MPCA summaries by source type, ranging from Class D municipal discharges to ponds (3 mg/L) to Class B medium size mechanical plants (10 mg/L). Ammonia ($\text{NH}_4\text{-N}$) and carbonaceous biochemical oxygen demand (CBOD) are also based on MPCA summaries.

3.1.3 Channel Sources

Nutrients can be gained or lost through exchanges with the sediment bed – either through releases in the dissolved form or by scour or deposition of nutrients that sorb to sediment. HSPF simulates ortho-phosphate and ammonia as sorbing to sediment and also represents release of dissolved ortho-phosphate, ammonia, and labile organic matter (as BOD, with associated nutrients) from the sediment.

Based on past experience, sorption coefficients were set for ortho-phosphate as 1,000 ml/g relative to silt and clay and 600 ml/g relative to sand; the corresponding numbers for total ammonia N were 100 and 10 ml/g. Default background sediment bed concentrations for ortho-phosphate are set at 250 mg/kg for silt and clay and 100 mg/kg for sand, and, for total ammonia N, 100 mg/kg for silt and clay and 10 mg/kg for sand. Higher bed concentrations are used in the red clay portions of the Nemadji River (2,000 mg/kg of clay for ortho-phosphate and 600 mg/kg total ammonia N). Those higher concentrations are based on calibration to observed data from the Nemadji River at South Superior monitoring station, and are also qualitatively consistent with the clay sediment leaching experiments reported by Bahnick et al. (1979), who reported that “The Nemadji River particulate sample gave the largest [soluble] orthophosphate release.”¹

For the Nemadji River, comparison of monitoring data to observations suggest that there is also a significant amount of organic phosphorus that is associated with channel bank erosion. HSPF does not directly provide for this source, but it was implemented using GENER statements that associate a refractory organic phosphorus load with scoured sediment, with potency factors ranging from 8 to 20 lb/ton.

The waters of these basins tend to contain ample amounts of iron, which can enhance the deposition of phosphorus in complexes with iron hydroxide under oxidized conditions. In anaerobic sediment this complexed phosphorus can be re-released in dissolved form. This is hypothesized as likely to be a significant process in lakes of the region that develop summer stratification and oxygen depletion in the hypolimnion, and also possibly in some slower-moving stream segments. The model is therefore set up to simulate releases of orthophosphate and ammonia N from sediment in lake segments as well as the most downstream reaches of the Nemadji. These releases are somewhat speculative and could be refined with detailed mass balance studies of individual lakes.

3.1.4 Atmospheric Deposition

The model simulates wet and dry deposition of ammonia-N and nitrate-N to pervious surfaces, impervious surfaces, and water bodies. In addition, both dry and wet deposition of phosphorus to phosphorus is simulated. Atmospheric deposition of phosphorus to the uplands is not simulated because it is assumed to be implicit in the sediment potency representation of pervious land loading and the buildup/washoff representation of impervious land loading of phosphorus.

Direct phosphorus deposition to surface water is represented in the model. The phosphorus deposition rate specified is the average estimated for the Lake Superior basin in the 2007 update to *Detailed Assessment of Phosphorus Sources to Minnesota Watersheds - Atmospheric Deposition* (Twaroski, et al. 2007) of 0.115 kg/ha/yr. The wet deposition concentration for phosphorus is set at the average concentration for Fond du Lac of 10.7 µg/L given in the same resource.

Wet deposition concentrations of ammonia and nitrate N (as mg/L) are taken from seasonal data recorded at NADP station MN16 (Marcell Experimental Forest) because other NADP stations within the watershed either did not become operational until 1997 or ended prior to 2012 and thus do not cover the full time span of the model. Dry deposition rates of ammonia and nitrate N (as lb/ac) are taken from CASTNET monitoring. There are not CASTNET stations within or particularly close to the watersheds studied here,

¹ The sediment potency assigned in the model is much higher than the total P content of sediment reported in two sediment cores from the lower channel of the Nemadji by Bahnick et al. of 17.1 ppm (=mg/kg); however, these core samples were only about 20% clay and are stated to represent original glacial lacustrine depositional material that is largely unimpacted by human activities. Desorption experiments reported by Bahnick et al. released about 150 mg of dissolved orthophosphate per kg of clay from suspended particulate material from the Nemadji, but the total P concentration of these sediment samples is not reported. The average ratio of total P to TSS from monitoring samples in the Nemadji River at South Superior is about 2,300 mg/kg, consistent with the concentrations applied in the model, and assignment of higher bed sediment concentrations in the lower Nemadji mainstem provide a good fit to observed total P in the water column. Material eroded and suspended during high flows in the lower Nemadji may be enriched in phosphorus due to human activities over the last 150 years, but further understanding of phosphorus exchanges between the water column and sediment in the Nemadji is needed.

so we use the station at Voyageurs National Park (VOY413) for the period after 1996, filling in earlier dates with monitoring from Perkinstown, WI (PRK134). In all cases, reported data were converted from molar units to mass or mass-based concentration as N.

3.2 NUTRIENT CALIBRATION

Nutrients from point and nonpoint sources are loaded to the stream reaches. Within the stream reaches the model represents the following nutrient species: ammonia, nitrite, nitrate, organic nitrogen, orthophosphate, organic phosphorus, and organic carbon/BOD. The stream reach module simulates instream biogeochemical processes including nutrient uptake and release by plankton and benthic algae, decay of organic matter, nitrification/denitrification, absorption/desorption of nutrients on suspended sediment, and deposition and scour of sediment-stored nutrients.

3.2.1 Calibration Data and Locations

Water quality data have been collected at many locations within the St. Louis, Cloquet, and Nemadji watersheds. Most of these data are available in EQUIS, and MPCA provided a full download of all stations. Despite the volume of data, stations that have collected significant amounts of nutrient data over a time period coincident with the model simulation period are few and an even smaller number are at or near flow gaging stations. The model segmentation was designed to line up with available flow gage locations and monitoring sites known to have large amounts of water quality data; however, some stations with small to moderate amounts of monitoring data were not usable for calibration because a major tributary or point source discharge enters the model segment between the monitoring station and the downstream end of the segment, or because they were on tributaries or lakes that were too small for explicit inclusion in the basin-scale models. In other cases, multiple closely located EQUIS stations were combined for use in model calibration.

Ultimately, 13 locations (represented by 17 EQUIS stations) were selected as primary model calibration locations in the St. Louis, Cloquet, and Nemadji watersheds. These locations are summarized in Table 3-3 and displayed in Figure 3-6 (St. Louis and Cloquet) and Figure 3-7 (Nemadji). For the St. Louis watershed, comparison to Figure 3-5 reveals that all these stations are affected to some extent by point sources, and most are downstream of major WWTP discharges in the Iron Range. For the sparsely populated Cloquet watershed, only one station (Cloquet River near Burnett) met the screening criteria. This station has a reasonable quantity of observations, but is downstream of Island Lake and observations will be affected by in-lake processes in this large reservoir. For the Nemadji watershed a number of EQUIS stations are on reaches too small to be explicitly simulated in the model, leaving a total of six stations with significant amounts of data. The downstream station at South Superior was augmented by observations supplied by Wisconsin DNR.

Calibration is not presented here for Miller Creek or other Duluth-area monitoring stations on small streams. These are being addressed separately in a finer-scale HSPF model of the Duluth area that accounts for managed stormwater drainage. It should also be noted that significant amounts of additional data have been collected throughout these watersheds since 2012. When the model is updated to run through more recent years, additional calibration could be undertaken with more recent monitoring.

Table 3-3. Water Quality Calibration Locations

Location	Model Reach	EQUIS Station(s)
Partridge River near Hoyt Lakes	262	S007-022
Swan River near Toivola	232	S000-641
St. Louis River at CSAH 7 nr Forbes	249	S000-119
St. Louis River below Cloquet R	210	S000-023
St. Louis River at Scanlon	501	S005-089, S000-629, S000-046
St. Louis River near Fond du Lac	205	S000-021, S003-972
Cloquet River near Burnett	402	S003-968, S005-147
Deer Creek near Pleasant Valley MN 23*	118	S003-250
Rock Creek near Pleasant Valley	120	S003-251
Blackhoof R nr Pleasant Valley	511	S005-620
Nemadji River nr Holyoke	113	S005-619
Nemadji River near Pleasant Valley	115	S000-110
Nemadji River near South Superior	103	S005-115

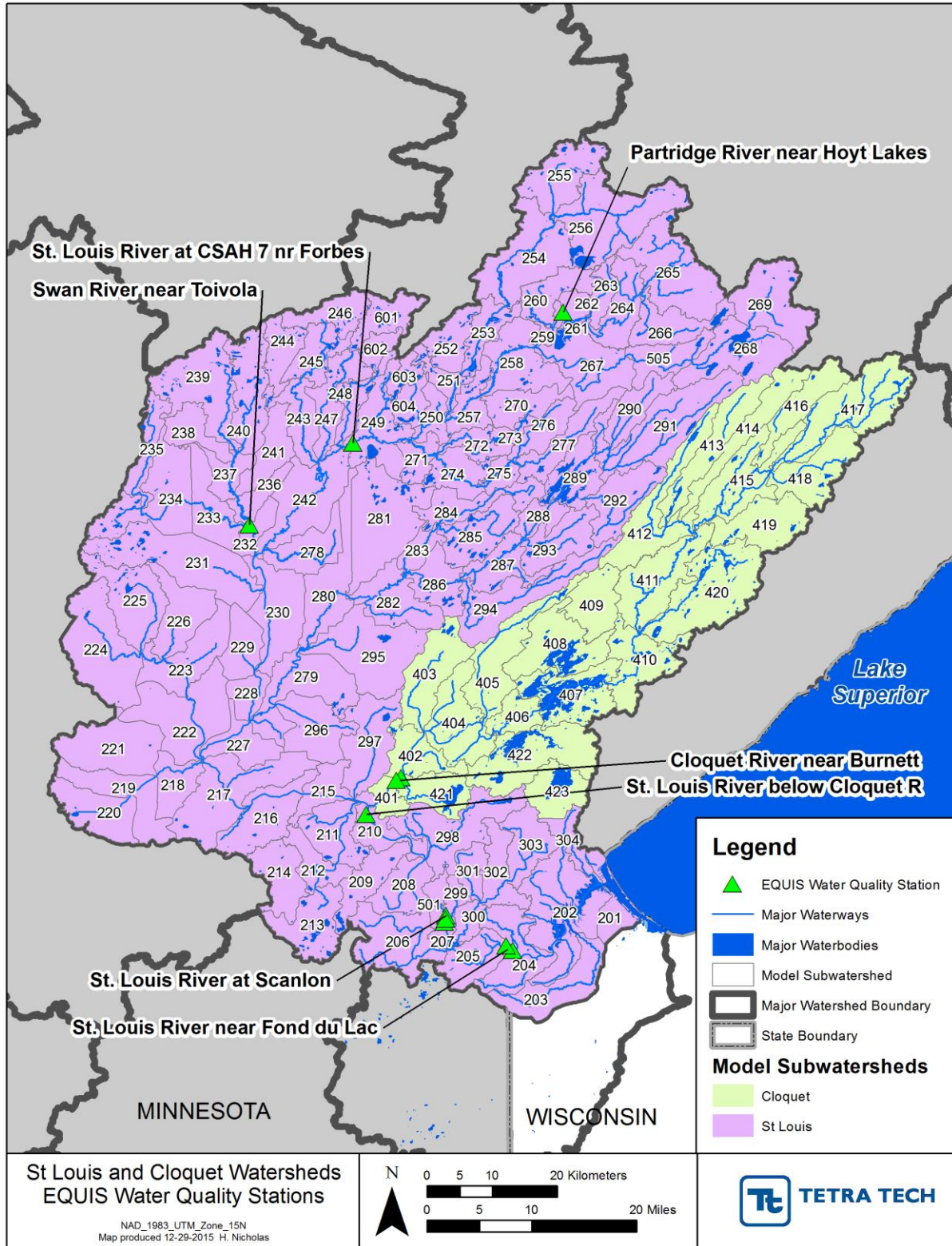


Figure 3-6. Water Quality Calibration Locations in the St. Louis and Cloquet Watersheds

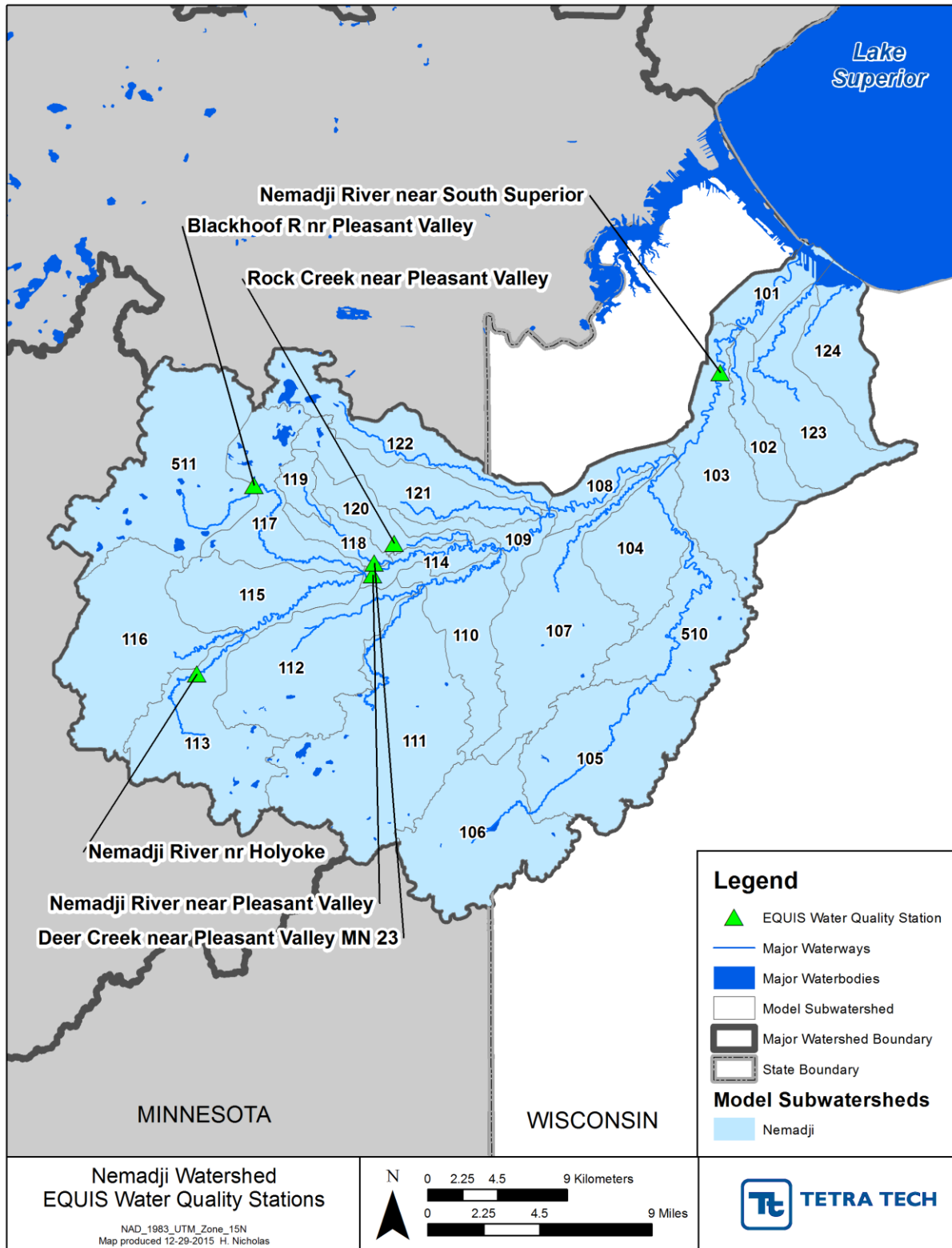


Figure 3-7. Water Quality Calibration Locations in the Nemadji Watershed

During the early stages of the calibration process efforts focused on accurately portraying nutrient concentrations at the stations located on the mainstems. In the St. Louis watershed this included the stations on the St. Louis River near Scanlon, Forbes, and Fond du Lac. Much of the St. Louis, Cloquet, and Nemadji watersheds are dominated by wetlands and hardwood forests, and the upland dynamics in the wetlands and forests complicate the modeling effort. A literature review was completed to support the selection of parameters appropriate for northern, wetland and hardwood forest dominated watersheds (see Table 3-1). The water quality calibration consisted of refining parameters that control nutrient stoichiometry (P:C, and P:N), phytoplankton and benthic algae population dynamics, nutrient transport, deposition, and scour, and nitrogen transformations (e.g. ammonification rate).

The water quality stations that are located on tributary streams had diverse location-based effects to consider; the water quality at the Swan River near Toivola station, for example, is highly influenced by major point source discharges. The water quality at the Partridge River near Hoyt Lakes and Cloquet River near Burnett are subjective to upstream lake dynamics. Specialized parameters were assigned to subbasins that have nutrient dynamics that differ from the rest of the basin.

Water quality was consistently monitored during the calibration and validation periods at the St. Louis River near Scanlon water quality station and, therefore, this site was selected to characterize the results of the water quality calibration. Similarly, the Nemadji River near South Superior was selected to showcase the water quality calibration for the HSPF model of the Nemadji watershed. Nitrogen and phosphorus were calibrated simultaneously but are summarized independently in the following sections.

3.2.2 Calibration and Validation

The nutrient calibration and validation relies on a weight of evidence approach. Upland loading rates are constrained to be in general agreement with literature values (as described in Section 3.1.1), while point source discharges are based on monitoring or recommended assumptions for unmonitored parameters provided by MPCA. Model calibration then adjusts parameters to optimize the fit between model predictions and observations at multiple stations throughout the watershed and the robustness of the fit is checked with validation tests on a different time period. Model performance is then checked against other sources of information, including information developed by MPCA on delivered loads and lake phosphorus balances.

3.2.2.1 Comparison of Model to Observations

Comparisons between model predictions and sample observations are made in terms of both concentration and inferred load (concentration times simulated or observed flow). Complete graphical and tabular statistical results for each station are provided in Appendix A (St. Louis and Cloquet River) and Appendix B (Nemadji River). Figure 3-8 provides an example of the primary types of calibration plots provided for each monitored nutrient parameter at each site, in this case showing the total phosphorus calibration for the Nemadji River at South Superior. The four panels in Figure 3-8 are:

- a. Standard time series plot, showing the observations and continuous model predictions of daily average concentrations. This shows general agreement, but can obscure biases in the simulation.
- b. A power plot comparing the relationship of observed and simulated loads versus flow. The objective here is that the relationship to flow (summarized by the power regression lines) should be similar for the model and observations. While generally true in this case, it will be noted that the simulated loads have a “hump” in the mid-range of flows. This in turn reflects the simulated relationship of flow and channel scour, derived from the channel form assumptions, which indicate a reduction in shear stress as flow spreads out onto the floodplain (see discussion in Volume I).

- c. A scatterplot of simulated versus observed concentrations shows the degree of spread or uncertainty about the 1:1 line.
- d. A plot of the residuals against flow is used to diagnose bias relative to the flow regime. In this case there is a fair balance between over and under-prediction across the range of flows, but some indication of a tendency to under-predict concentrations at the highest flows. A similar plot of residuals versus month is used to diagnose potential seasonal biases.

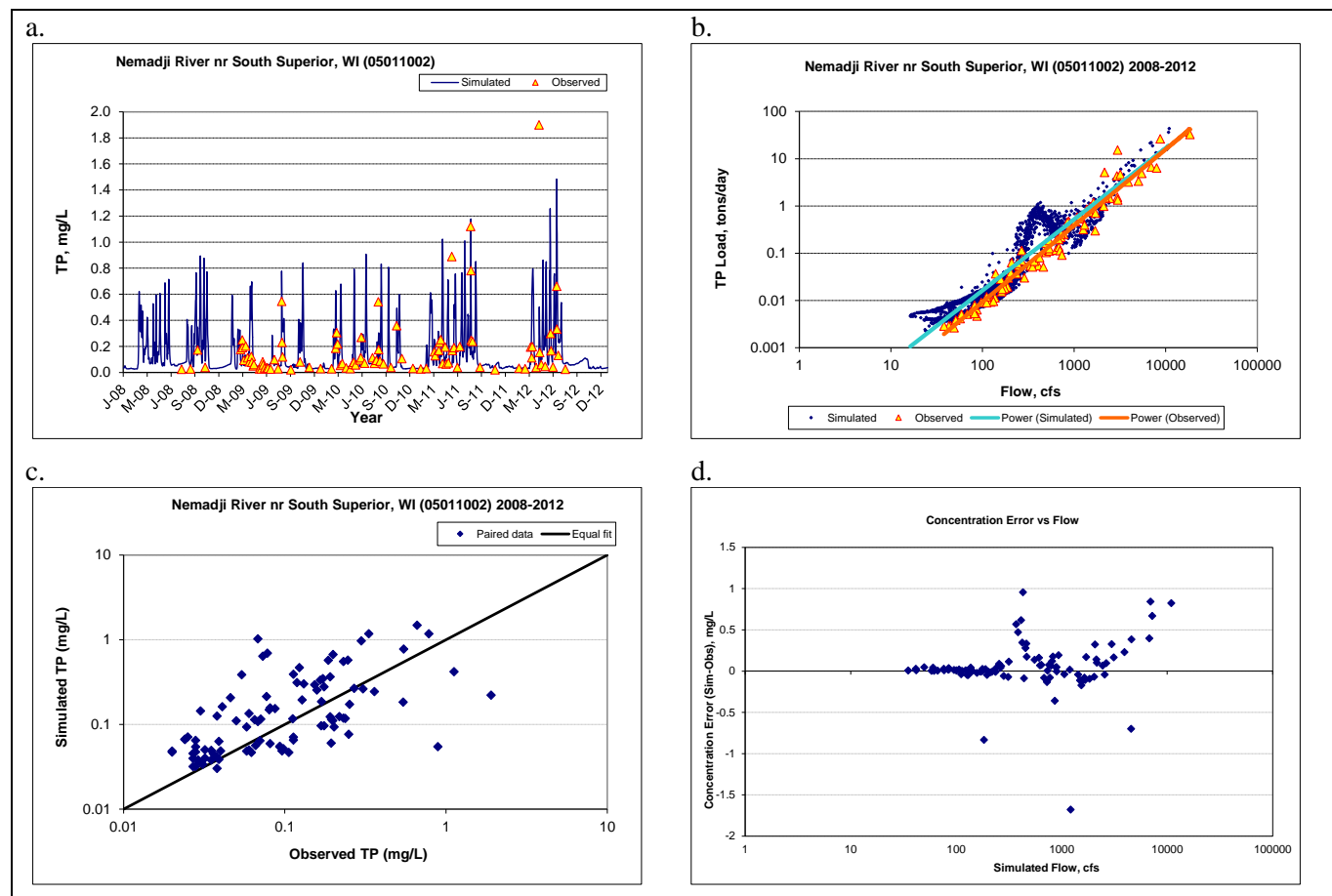


Figure 3-8. Example Calibration Plots for Total Phosphorus, Nemadji River near South Superior, WI

This section first provides an overview of the results with a focus on total phosphorus, total nitrogen, and nitrate nitrogen (nitrate nitrogen is included in the overview because it is often the predominant form of nitrogen and the number of observations for total nitrogen is limited at many stations). Results for individual nutrient species are then summarized, with full results provided in the appendices.

Summary statistics for the calibration and validation of total phosphorus, total nitrogen, and nitrate nitrogen at all stations are provided in Table 3-4, Table 3-5, and Table 3-6, respectively. Discussion by watershed and parameter follows the tables. Note that the number of samples available is relatively small, except for a few select stations.

Table 3-4. Summary Statistics for Total Phosphorus Calibration and Validation

Station	Calibration (2002-2012)*						Validation (1994-2001)*					
	Count	Average Concentration (mg/L)	Concentration Average Relative Error (%)	Concentration Median Relative Error (%)	Paired Load Average Relative Error (%)	Paired Load Median Relative Error (%)	Count	Average Concentration (mg/L)	Concentration Average Relative Error (%)	Concentration Median Relative Error (%)	Paired Load Average Relative Error (%)	Paired Load Median Relative Error (%)
Partridge River near Hoyt Lakes	18	0.025	33%	19%	31%	17%	0					
Swan River near Toivola	22	0.080	17%	-4%	-42%	-8%	0					
St. Louis River at CSAH 7 nr Forbes	50	0.029	20%	20%	5%	12%	10	0.042	6%	6%	-1%	7%
St. Louis River below Cloquet R	39	0.042	-18%	3%	-4%	1%	9	0.038	1%	11%	-2%	7%
St. Louis River at Scanlon	125	0.053	-10%	13%	-53%	3%	41	0.035	27%	22%	4%	15%
St. Louis River near Fond du Lac	50	0.036	15%	22%	7%	8%	38	0.039	13%	7%	4%	5%
Cloquet River near Burnett	80	0.033	6%	32%	-1%	18%	29	0.027	19%	34%	21%	24%
Deer Creek near Pleasant Valley MN 23*	35	0.31	-38%	1%	-79%	0%	79	0.78	-84%	-52%	-58%	-13%
Rock Creek near Pleasant Valley	63	0.12	27%	41%	53%	86%	0					
Blackhoof R nr Pleasant Valley	17	0.042	41%	53%	86%	20%	0					
Nemadji River nr Holyoke	15	0.080	16%	8%	-1%	1%	0					
Nemadji River near Pleasant Valley	100	0.20	-8%	1%	-35%	0%	22	0.12	59%	11%	35%	1%
Nemadji River near South Superior	97	0.17	31%	11%	-5%	0%	0					

Note:

* For Deer Creek the calibration period is 2008-2012 and the validation period is 1994-2006.

Table 3-5. Summary Statistics for Total Nitrogen Calibration and Validation

Station	Calibration (2002-2012)*						Validation (1994-2001)*					
	Count	Average Concentration (mg/L)	Concentration Average Relative Error (%)	Concentration Median Relative Error (%)	Paired Load Average Relative Error (%)	Paired Load Median Relative Error (%)	Count	Average Concentration (mg/L)	Concentration Average Relative Error (%)	Concentration Median Relative Error (%)	Paired Load Average Relative Error (%)	Paired Load Median Relative Error (%)
Partridge River near Hoyt Lakes	0						0					
Swan River near Toivola	0						0					
St. Louis River at CSAH 7 nr Forbes	7	0.74	1%	0%	20%	28%	6	0.92	-5%	1%	0%	0%
St. Louis River below Cloquet R	6	0.98	10%	8%	5%	4%	7	0.75	41%	33%	45%	36%
St. Louis River at Scanlon	127	1.19	-6%	-1%	-11%	2%	8	0.69	38%	37%	39%	34%
St. Louis River near Fond du Lac	7	1.08	0%	-1%	-1%	-2%	7	0.86	29%	27%	28%	10%
Cloquet River near Burnett	94	0.82	12%	18%	-10%	4%	0					
Deer Creek near Pleasant Valley MN 23*	17	0.84	17%	12%	-59%	0%	5	1.09	-30%	-38%	-23%	-16%
Rock Creek near Pleasant Valley	5	0.93	49%	47%	13%	8%	0					
Blackhoof R nr Pleasant Valley	17	0.91	-22%	-26%	26%	0%	0					
Nemadji River nr Holyoke	15	0.85	6%	-14%	5%	-6%	0					
Nemadji River near Pleasant Valley	31	1.04	11%	-17%	-4%	0%	0					
Nemadji River near South Superior	100	1.16	-1%	-5%	-23%	-1%	0					

Note:

* For Deer Creek the calibration period is 2008-2012 and the validation period is 1994-2006.

Table 3-6. Summary Statistics for Total Nitrate+Nitrite-N Calibration and Validation

Station	Calibration (2002-2012)*						Validation (1994-2001)*					
	Count	Average Concentration (mg/L)	Concentration Average Relative Error (%)	Concentration Median Relative Error (%)	Paired Load Average Relative Error (%)	Paired Load Median Relative Error (%)	Count	Average Concentration (mg/L)	Concentration Average Relative Error (%)	Concentration Median Relative Error (%)	Paired Load Average Relative Error (%)	Paired Load Median Relative Error (%)
Partridge River near Hoyt Lakes	18	0.16	-18%	-42%	-33%	-3%	0					
Swan River near Toivola	22	0.73	-2%	-10%	-57%	-49%	0					
St. Louis River at CSAH 7 nr Forbes	48	0.092	44%	55%	5%	32%	35	0.13	-34%	-26%	-41%	-11%
St. Louis River below Cloquet R	38	0.093	45%	45%	16%	25%	36	0.09	2%	14%	-8%	13%
St. Louis River at Scanlon	140	0.20	-28%	2%	-4%	1%	8	0.046	135%	120%	19%	40%
St. Louis River near Fond du Lac	49	0.10	30%	23%	5%	16%	36	0.12	0%	7%	-5%	5%
Cloquet River near Burnett	94	0.081	34%	46%	3%	18%	0					
Deer Creek near Pleasant Valley MN 23*	35	0.11	-19%	7%	-28%	0%	5	0.009	178%	63%	219%	64%
Rock Creek near Pleasant Valley	14	0.032	361%	262%	38%	12%	0					
Blackhoof R nr Pleasant Valley	17	0.19	-28%	12%	356%	-1%	0					
Nemadji River nr Holyoke	15	0.019	438%	71%	245%	20%	0					
Nemadji River near Pleasant Valley	48	0.12	-32%	-24%	-3%	-5%	0					
Nemadji River near South Superior	100	0.087	-7%	-9%	30%	-3%	0					

Note: Statistics calculated with non-detects set to one-half the detection limit.

* For Deer Creek the calibration period is 2008-2012 and the validation period is 1994-2006.

St. Louis Watershed

Ambient phosphorus concentrations in the St. Louis tend to be relatively low, with most stations having an average concentration less than 0.05 mg/L, despite the presence of point source discharges. For the calibration period, the average relative errors on concentration fall into the “Very Good” category ($\leq 15\%$) of “Good” category (15-25%) for five out of six locations, while the average relative error on load falls into these categories on three out of six locations. Results are rated only “Fair” for Partridge River, but the sample size is small. Of greater concern are the paired load relative errors for Swan River and especially Saint Louis River at Scanlon, both of which are rated as “Poor” – although the median relative errors are very good.

For Swan River near Toivola there is only a single year of monitoring data coincident with the model (2012). Concentrations appear to be under-estimated at higher flows. Nitrate nitrogen is also under-estimated at this station. The location is downstream of two major WWTPs (Hibbing and Chisolm), both of which discharge to complexes of small streams and wetlands. It seems possible that there may be historic storage of nutrients in the wetland areas near the WWTPs that is flushed out during high flows, which may bear further investigation.

The apparent load under-estimation at Scanlon is more difficult to interpret. This station is only a short distance downstream of the monitoring station for St. Louis River below Cloquet River, where the fit for load is “Very Good”. In between these monitoring stations are a series of impoundments (Cloquet Reservoir, Knife Falls, Scanlon Dam), and the monitoring point is downstream of the hydropower station at Scanlon Dam. As shown in Figure 3-9, the apparent underestimation of load is due to a small number of observations at high flow where the observed concentration is greater than the simulated concentration – such as the observation of 6/20/12 when a total phosphorus concentration of 0.344 mg/L (predominantly in non-soluble form) was reported on a flow of 35,900 cfs – versus a modeled concentration of 0.087 mg/L. Possibly this sample could represent stored material washed out of the bottom of Scanlon Reservoir by hydropower releases on the rising limb of a flood flow.

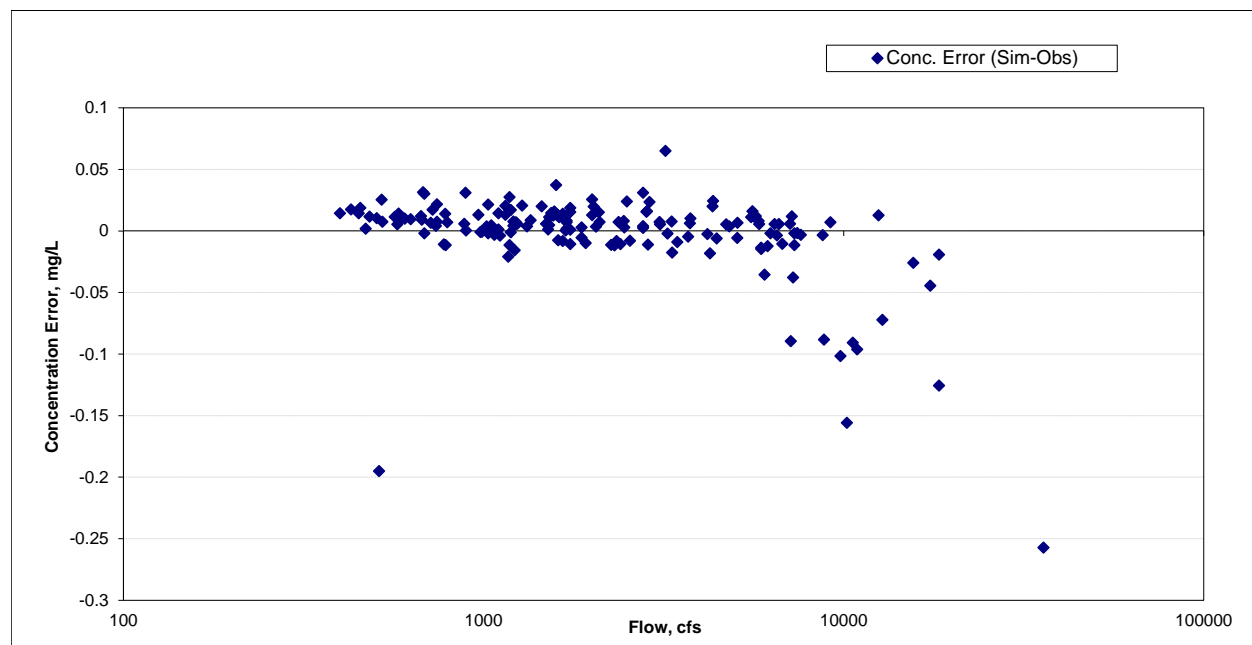


Figure 3-9. Concentration Error versus Flow for Total Phosphorus, St. Louis River at Scanlon

It was not found to be possible to simulate the reported phosphorus concentration for this or a few other similar events. It appears, however, that these may be anomalies as the model and FLUX estimates of

total load (not just paired loads) are in near perfect agreement (see Section 3.2.2.2). Further, phosphorus load at this station during the validation period is fit well. Indeed, all validation statistics for the St. Louis River stations are rated as “Good” or “Very Good.”

For total nitrogen, the average relative errors for the St. Louis stations are all in the “Good” or “Very Good” range, although sample sizes are small except for the St. Louis River at Scanlon. On the other hand, validation results (for a very small sample size) are less promising, with over-estimation by the model by similar amounts at both St. Louis River below Cloquet River and St. Louis River at Scanlon. This could be associated with the representation of point sources, for which nitrogen releases (other than ammonia) are based on generalized estimates of concentration, not measurements. Observations of nitrate N are more numerous and are fit well at Scanlon during the calibration period, but show considerable variability in results at other stations. In addition to the uncertain nitrogen loads from point sources, the model representation of kinetic transformations among nitrogen species is suspect. In particular, the amount of different inorganic species is highly sensitive to the specification of the algal preference ratio for nitrate versus ammonia nitrogen. This is a fixed ratio in HSPF, but in reality may vary over the seasons as different planktonic and benthic algae/macrophytes predominate.

Cloquet Watershed

Only one station has a significant number of observations in this watershed and it is located downstream of Island Lake, a large and deep reservoir. Processes within Island Lake and the other large impoundments in this watershed likely have a significant impact on results. For example, HSPF, as a one-dimensional model, cannot represent the impacts of seasonal stratification on nutrient loads leaving this lake.

For total phosphorus, the model achieves very good calibration statistics for average relative error, but larger median relative errors – indicating that the average is balanced out by a few observations with larger negative errors. Average relative errors during the validation period are only of “Fair” quality. Note, however, that the average concentration is only 0.027 mg/L so that an error of only 0.01 mg/L is equal to a deviation of 37 percent.

For total nitrogen, the model achieves good statistics during the calibration period, but no older validation data are available. Nitrate tends to be over-estimated, likely due to algal dynamics within the lakes.

Nemadji Watershed

Average total phosphorus concentrations at several of the monitoring stations in the Nemadji watershed are nearly an order of magnitude greater than those observed in the St. Louis River watershed. The exceptions are the Blackhoof River and Nemadji River near Holyoke stations, both of which have watersheds wholly or largely outside of the lacustrine red clay area. Thus, the higher concentrations of total phosphorus at downstream stations appear to be associated with the high erosion rates in the red clay area. This also means that the accuracy of the phosphorus simulation will be closely tied to the accuracy of the channel sediment simulation – which, as seen in Volume I, presents challenges in this dynamic basin.

Phosphorus simulation results for the downstream station, Nemadji River near South Superior, were provided above as an example of the calibration graphs used in model fitting (Figure 3-8). Average relative error statistics at this station rate as “Very Good” for load, but only “Fair” for concentration. For smaller streams, the model appears to over-predict phosphorus concentrations and loads in Rock Creek and Blackhoof River, while under-predicting in Deer Creek. This largely reflects difficulties in the sediment calibration (Volume I), where it was noted that the stream response appeared very different in the later period after 2008 as opposed to the earlier intensive monitoring of 2001-2005, which had much higher sediment concentrations. The sediment model was intentionally fit to the later period. This in turn affects the phosphorus simulation, where the model systematically under-predicts observed phosphorus in

the earlier period. It provides a much better visual fit in the later period, but average relative errors are still much less than zero due to the presence of a few outliers. For both Deer Creek and Rock Creek the excess observed phosphorus appears to be largely organic phosphorus (and indeed ortho-phosphorus is fit well in Rock Creek and acceptably in Deer Creek). Evidently there are differences in condition between these two neighboring creeks that result in higher organic phosphorus loads associated with channel erosion in Deer Creek for reasons that are not fully understood.

For Nemadji River near Pleasant Valley the model appears to under-predict total phosphorus loads based on the average relative error for paired observations and predictions. This may be misleading, however: Tetra Tech conducted a FLUX analysis of load at this station that interpolates loads as a stratified regression against flow. For the period of data collection (2003-2012) the model simulation and FLUX produce results that are within 1 percent of each other.

Statistics for total nitrogen are in the “Very Good” to “Good” range for the downstream stations on the Nemadji River (Pleasant Valley and South Superior), but the results are more variable in the smaller streams. Large relative errors are seen for nitrate plus nitrite-N at some of these stations, primarily where total nitrogen is dominated by the organic fraction. For instance, in Blackhoof River observed total nitrogen concentrations average just under 1 mg/L, but the average nitrate concentration is only about 0.2 mg/L. As with total phosphorus, the model and FLUX estimates of nitrate-N load for the monitored and gaged station Nemadji River near South Superior are close to one another, differing by only 2 percent.

3.2.2.2 Comparison of Model to FLUX Estimates of Delivered Load

MPCA’s Watershed Pollutant Load Monitoring Network (WPLMN) is designed to obtain spatial and temporal pollutant load information from Minnesota’s rivers and streams and track water quality trends. As part of this program, MPCA releases estimates of annual pollutant loads for each 8-digit hydrologic unit code basin developed using the FLUX program, as described in Section 2. MPCA estimates at the downstream gage station on the St. Louis River (St. Louis River at Scanlon), Cloquet River (at Burnett), and Nemadji River (at South Superior) are currently available for calendar years 2009 – 2011. (Most early years were judged to have insufficient data and flow gaging on the Cloquet did not commence until Water Year 2009.) Comparisons between the MPCA FLUX estimates and model simulated results are shown in Figure 3-10 through Figure 3-12 and Table 3-7.

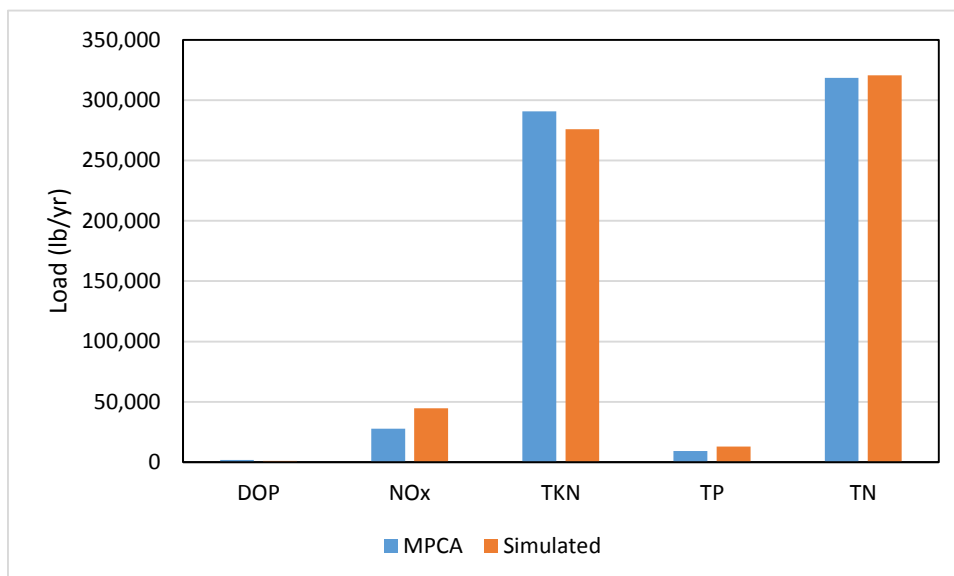


Figure 3-10. Comparison of Model to MPCA FLUX Estimates of Pollutant Load, Calendar Years 2009-2011, Cloquet River near Burnett

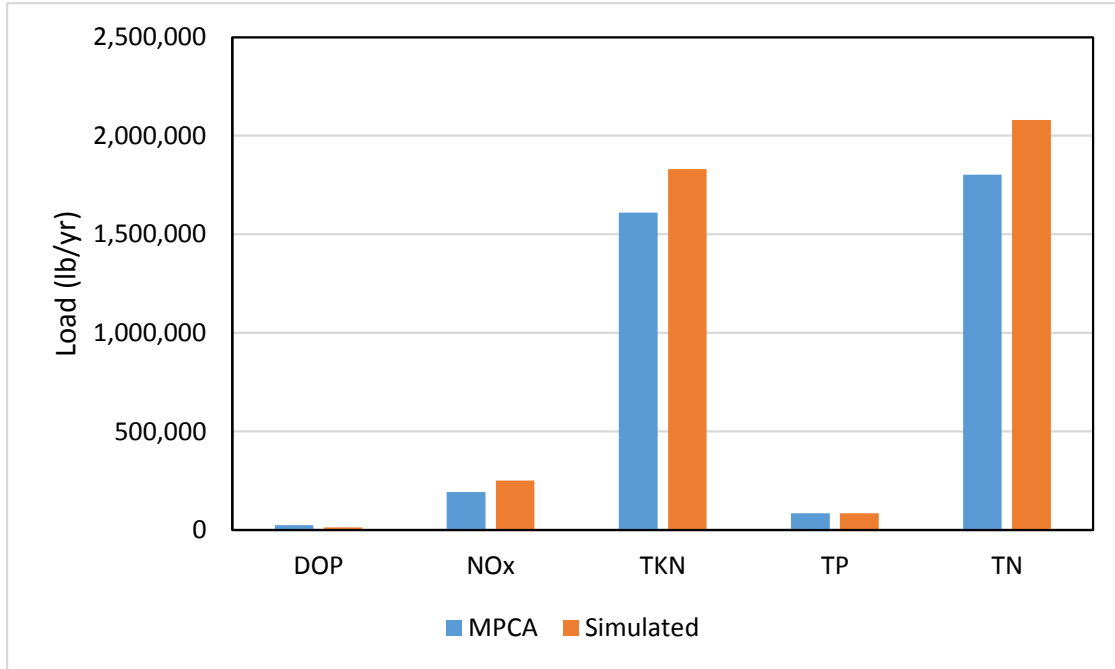


Figure 3-11. Comparison of Model to MPCA FLUX Estimates of Pollutant Load, Calendar Years 2009-2011, St. Louis River at Scanlon

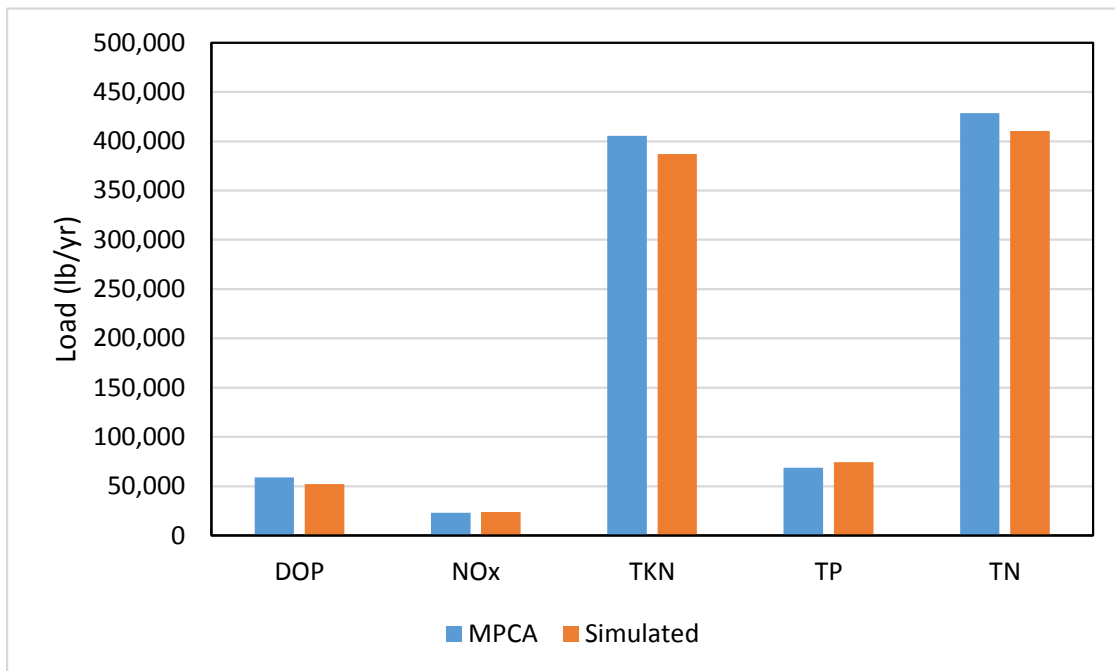


Figure 3-12. Comparison of Model to MPCA FLUX Estimates of Pollutant Load, Calendar Years 2009-2011, Nemadji River near South Superior, WI

Table 3-7. MPCA FLUX Estimates and Model Simulated Annual Nutrient Loads, Calendar Years 2009-2011

Station		Total N	Total P	Total Kjeldahl N	Nitrate + Nitrite N	Dissolved Ortho-P
Cloquet River nr Burnett	MPCA FLUX	318,431	9,374	290,598	27,834	1,920
	Simulated	320,531	12,922	275,839	44,692	1,074
	Difference	0.7%	37.9%	-5.1%	60.6%	-44.0%
St. Louis River at Scanlon	MPCA FLUX	1,801,717	84,517	1,609,440	192,277	24,597
	Simulated	2,080,380	85,720	1,830,385	249,995	13,786
	Difference	15.5%	1.4%	13.7%	30.0%	-44.0%
Nemadji River nr South Superior, WI	MPCA FLUX	428,683	68,615	405,594	23,089	58,981
	Simulated	410,495	74,571	386,865	23,630	52,031
	Difference	-4.2%	8.7%	-4.6%	2.3%	-11.8%

For total nitrogen, the match between FLUX and model simulations is rated “Very Good” or “Good” for all three basins, as is total phosphorus for the St. Louis and Nemadji River basins. The model does appear to over-predict total phosphorus load in the Cloquet River (although the total load is small). Improving this would likely require a better understanding and representation of processes within Island Lake and the other large impoundments in this basin, perhaps using a two-dimensional lake model.

Model performance is also “Very Good” for total Kjeldahl nitrogen, which is the dominant fraction of nitrogen load (primarily as organic nitrogen). The match is not as good for nitrate + nitrite nitrogen or dissolved ortho-phosphorus. Both of these constituents are very sensitive to plant/algal uptake of inorganic nutrients and release of organic nutrients, much of which occurs in wetlands. HSPF does not provide detailed simulation of kinetic processes in emergent wetlands. In addition, results for the St. Louis are sensitive to the specification of point source discharges, for which complete nitrogen species are generally not monitored, and only total phosphorus is available for most permits.

Tetra Tech used FLUX to estimate long-term loads for 1995-2012 at the two stations (Saint Louis River at Scanlon and Nemadji River near South Superior, WI) that have consistent continuous flow gaging for this period. Results have greater uncertainty than the MPCA analyses presented above because monitoring was relatively scarce in the earlier period. These results show the model slightly under-estimating nutrient loads of total P, nitrate + nitrite-N, and total Kjeldahl N for the St. Louis River at Scanlon (Figure 3-13), which is the opposite of the comparison to MDNR analyses of the 2008-2011 period. The difference for total nitrogen is -11% (within the “Very Good”) range, while that for total phosphorus is -25% (at the border between “Good” and “Fair”). The longer-term FLUX results suggest that the model may produce some under-estimation of total phosphorus and total nitrogen load in the St. Louis River, although the FLUX estimates for periods prior to 2008 are highly uncertain due to the lack of contemporaneous water quality monitoring data and limited information on some point source discharges. Similar results are provided for the Nemadji River in Figure 3-13. For the Nemadji, the differences in long-term total nitrogen loads (-14%) and total phosphorus loads (+11%) are both within the “Very Good” range.

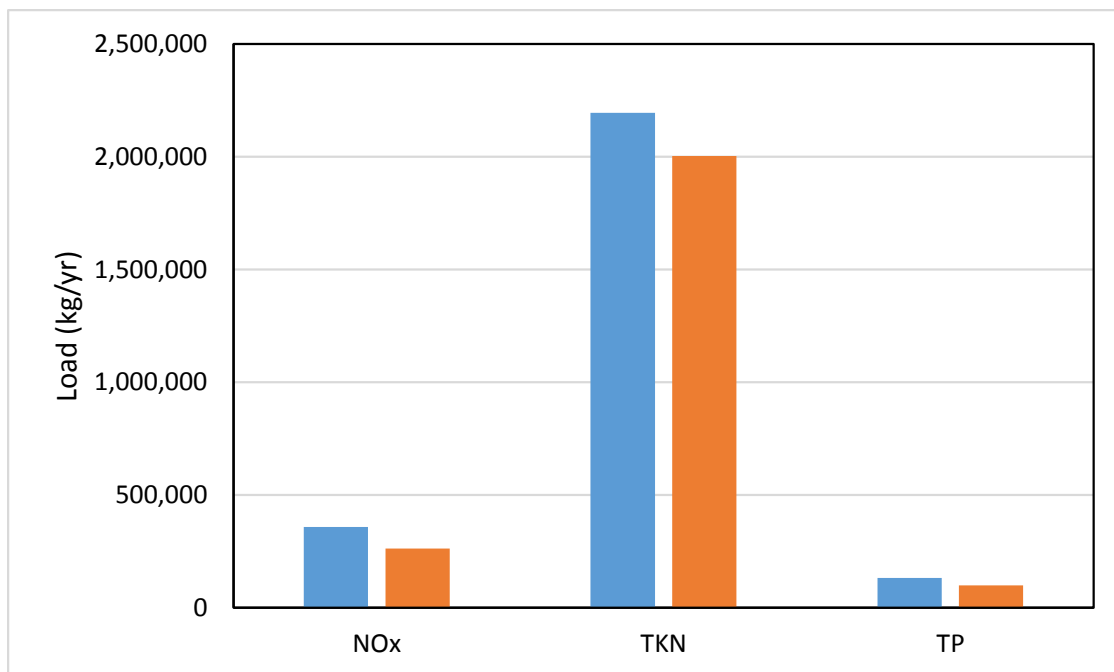


Figure 3-13. Comparison of Model to FLUX Estimates of Annual Nutrient Load, St. Louis River at Scanlon, 1995 – 2012

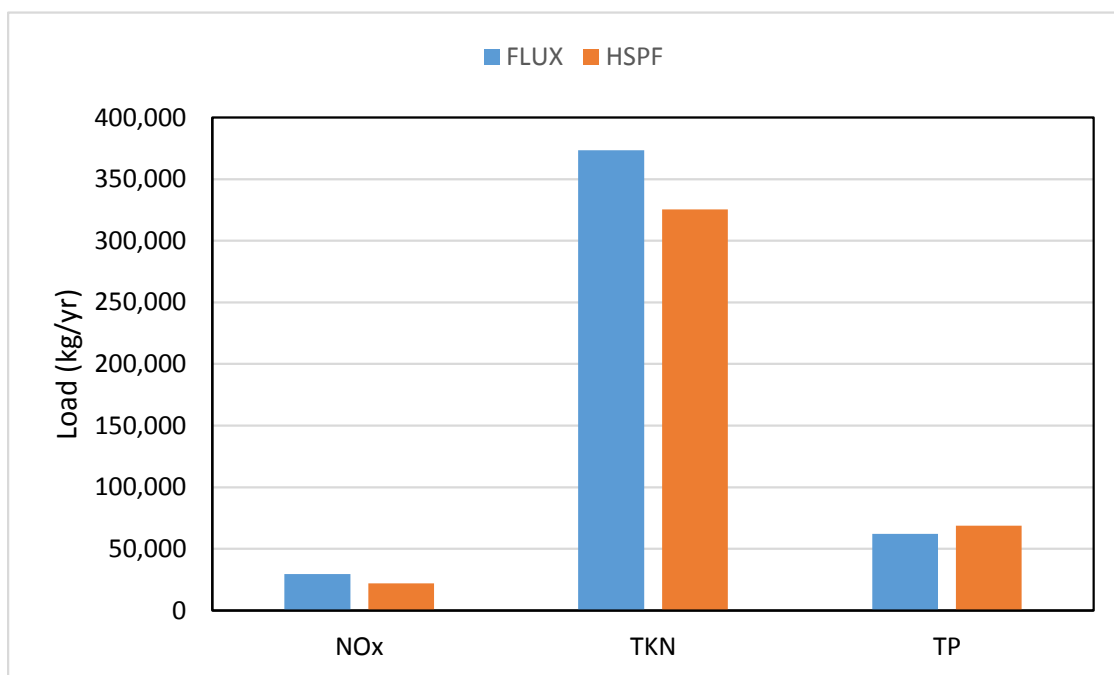


Figure 3-14. Comparison of Model to FLUX Estimates of Annual Nutrient Load, Nemadji River at South Superior, 1995 – 2012

3.2.2.3 Consistency with Lake Analyses

The St. Louis and Cloquet watersheds have a large number of lakes. In contrast, the Nemadji watershed has only a few lakes with small watersheds. Detailed nutrient balance studies are not available for most,

if any, of these lakes. MPCA has, however, conducted screening analyses of many of these lakes using the MINLEAP protocol (Wilson and Walker, 1989; MPCA, 2005). MINLEAP is designed to predict eutrophication in Minnesota lakes based on watershed area, lake depth, and ecoregional phosphorus concentrations. It is a scoping tool designed to estimate lake condition based on minimal data that calculates water and phosphorus balance and in-lake predicted phosphorus and chlorophyll *a* concentrations, which are compared to observed concentrations.

Because MINLEAP is a scoping-level tool that is not calibrated to individual lakes it does not provide a direct basis for comparison to the basin-scale HSPF model. However, it is somewhat informative to examine the deviations between MINLEAP predictions and observed lake conditions and to interpret these relative to the HSPF model predictions.

The St. Louis, Cloquet, and Nemadji watersheds are in the Northern Lakes and Forests ecoregion, for which MINLEAP assigns a stream phosphorus concentration of 55 µg/L. This is somewhat higher than the total phosphorus concentrations observed in most of the St. Louis and Cloquet monitoring stations, although lower than observed at most monitoring locations in the Nemadji (refer to Table 3-4 above).

For the St. Louis River watershed, MINLEAP analyses of 25 lakes (MPCA, 2013b, Appendix 12) tended to over-estimate in-lake phosphorus concentrations where concentrations were less than about 30 µg/L and under-estimate in-lake phosphorus concentrations where observed concentrations were greater than about 50 µg/L. Most of the assessed lakes are smaller waterbodies that are not explicitly represented in the basin-scale HSPF model. Results for five lakes that are explicit in HSPF, but for which the model was not calibrated, are compared in Table 3-8. HSPF results are shown for 2003 – 2012 as the average for the May – September growing season, along with the range of monthly averages. The observations fall within the range of predicted monthly concentrations for three of the five lakes, but appear to predict concentrations that are too high in Long and Esquagama

Table 3-8. Comparison of Observed, MINLEAP, and HSPF Projections of Growing Season Average Total Phosphorus Concentrations, 2003-2012

Lake	Model Reach	Observed Total P (µg/L)	MINLEAP Total P (µg/L)	HSPF Total P (Growing Season Average, µg/L)	
				Average	Monthly Range
Esquagama	253	16	34	37	(25 - 58)
Long (64-0495)	275	51	40	25	(13 - 77)
Manganika	602	308	166	67	(46 - 336)
West Two River	245	42	31	25	(13 - 77)
Whiteface	289	26	30	18	(12 - 30)

Note: MINLEAP and observed results from MPCA (2013b), except that Esquagama has been recalculated by Tetra Tech using MINLEAP standard assumptions. MPCA (2013b) adjusted the inflow concentration to Esquagama based on local monitoring to achieve a predicted in-lake concentration of 12 µg/L. Phosphorus loading to Manganika Lake used in the MINLEAP analysis in MPCA (2013b) is based on wastewater discharges and not regional assumptions. HSPF results are based on May – September monthly averages for the years 2003 – 2012.

We analyzed average annual phosphorus loading rates to a subset of the assessed lakes (using the land use distribution in the drainage area of the lake where the lake was not explicitly delineated for the basin-scale HSPF model) and determined that the HSPF-predicted total average phosphorus load per year was generally greater than the MINLEAP prediction. The combination of higher watershed loads but lower

predicted in-lake concentrations for the lakes that appear in both Table 3-8 and Table 3-9 occurs because (1) the MINLEAP equations estimate a lower fraction of runoff relative to precipitation, (2) the MINLEAP analyses assume a flow-weighted concentration that applies across all flows, and (3) HSPF predicts greater deposition and retention in these lakes than the MINLEAP default calculations.

Table 3-9. Comparison of MINLEAP Total Phosphorus Loads to HSPF Simulated Phosphorus Load for Assessed Lakes in the St. Louis River Basin, 2003-2012

	HSPF Upland Load (lb/ac/yr)	HSPF Average Annual Load (kg/yr)	MINLEAP Average Load (kg/yr)
Dinham	0.175	358	224
Esquagama	0.124	5,542	4,933
Long (69-0495)	0.158	2,262	266
Manganika	0.160	373	162
McQuade	0.232	1,254	606
Mudhen	0.141	236	174
Strand	0.184	240	144
West Two Rivers	0.153	844	979
Whiteface	0.119	3,340	4,197

Note: MINLEAP results from MPCA (2013b), except that Esquagama has been recalculated using MINLEAP standard assumptions. MPCA (2013b) adjusted the inflow concentration to Esquagama based on local monitoring to achieve a predicted annual load of 1,443 kg/yr. HSPF Loads are summarized for 2003 – 2012.

For the Nemadji River watershed, MINLEAP results are given in Appendix 9 of MPCA (2014). These are compared to HSPF loads in Table 3-10. For these eight lakes the HSPF-predicted watershed loads are again higher than MINLEAP. None of these small lakes are explicitly simulated in the basin-scale HSPF model.

Table 3-10. Comparison of MINLEAP Total Phosphorus Loads to HSPF Simulated Phosphorus Load for Assessed Lakes in the Nemadji River Basin, 2003-2012

	HSPF Upland Load (lb/ac/yr)	HSPF Average Annual Load (kg/yr)	MINLEAP Average Load (kg/yr)
Bear	0.153	159	55
Chub	0.143	162	117
Hay	0.156	163	113
Lac La Belle	0.152	34	25
Net	0.239	720	324
Sand	0.223	45	24
Spring	0.226	17	14
Venoah	0.258	930	130

Note: MINLEAP results from MPCA (2014).

4 Water Temperature Calibration

Instream temperature is an important parameter for simulating biochemical transformations. The HSPF modules used to represent water temperature include PSTEMP (soil temperature) and HTRCH (heat exchange and water temperature).

Simulation of soil temperature is accomplished by using three layers: surface, upper subsurface, and groundwater subsurface. The surface layer is the portion of the land segment that determines the overland flow water temperature. The upper subsurface layer determines interflow temperature while the groundwater subsurface layer determines groundwater temperature. Surface and upper subsurface layer temperatures are estimated by applying a regression equation relative to measured air temperature. The groundwater subsurface temperatures are supplied a temperature which reflects the average subsoil temperature for the region. Initial parameters for the St. Louis, Cloquet, and Nemadji models are based on recommendations in the Long Prairie example file provided as part of MPCA's HSPF modeling guidance (AQUA TERRA, 2012).

Soil temperature is only used to determine the water temperature of the three different flow paths (surface outflow, upper subsurface/interflow outflow, lower subsurface/groundwater outflow) as the water is contributing to stream flow. Once the water is in the stream, the temperature is impacted by mechanisms that can increase or decrease the heat content of the water. Mechanisms that can increase the heat content of the water are absorption of solar radiation, absorption of long-wave radiation, and conduction-convection. Mechanisms that decrease the heat content are emission of long-wave radiation, conduction-convection, and evaporation. Heat exchanges between the water and stream bed are also simulated.

Stream temperature follows diel cycles and is strongly affected by the pattern of shading over the course of the day and the local microclimate, as well as specific locations of groundwater discharges to streams. Local-scale variations in hydraulics can also influence temperature readings: for instance, temperatures are likely to be different in a part of a reach impounded by a beaver dam than in a free-flowing riffle. A watershed-scale HSPF model can typically match daily average water temperature but is limited in its ability to simulate the daily cycles of water temperature at specific locations. This is because HSPF represents stream segments as one-dimensional, fully-mixed reactors. These segments are typically in the range of 3 to 15 miles in length in models built at a HUC12 scale, as is the case here and variations within the segment are averaged out. For instance, a single average value represents shading over the whole stream segment and the model does not consider the orientation or aspect of the stream segment relative to the position of the sun. HSPF, as a one-dimensional model, also does not address vertical variation in temperature, which is especially important in deeper lakes and reservoirs. In contrast, a detailed water temperature model for a stream reach (e.g., the QUAL2K model) would typically specify segments with lengths on the order of a tenth of a mile and include a detailed analysis of shading from vegetation and topography in relation to solar position throughout the day and year. For the HSPF application we used an empirical approximation fit during calibration in which the shading factor (i.e., CFSAX, the fraction of light not shaded out) is scaled relative to the fraction of forest cover in a subwatershed as $1 - 0.73 \cdot \text{fraction forest}$.

While water temperature is measured along with most water quality observations, scattered point in time measurements are of limited use for adjusting the temperature calibration due to strong diel patterns. Fortunately, there are two sources of continuous data: continuous summer data collected by MDNR at a variety of locations, mostly on smaller streams, and continuous monitoring at the USGS gage at Scanlon. The MDNR records available for this project for the St. Louis and Cloquet are from the 1999-2005 period, while those for the Nemadji run from 2000 - 2011. More recent temperature monitoring was collected in the St. Louis watershed beginning in 2011 as part of the recent stressor identification project but was not supplied in time for use in the temperature calibration of the model.

A typical comparison between the simulation and MDNR temperature probe monitoring (for Otter Creek, a tributary to the St. Louis River) is shown in Figure 2-1. HSPF captures the general trend in average temperature, but is imprecise and does not exactly represent the daily minimum and maximum. Average discrepancies by time of day (Figure 2-2) show that the model tends to over-predict during mid-day and under-predict during night, likely related to the diel pattern of shading near the observation site. In addition, the 2000 simulation suggests that peak temperature is under-estimated during August and over-estimated during an early October cold snap. These discrepancies are likely associated with differences between local and meteorological station air temperature and humidity.

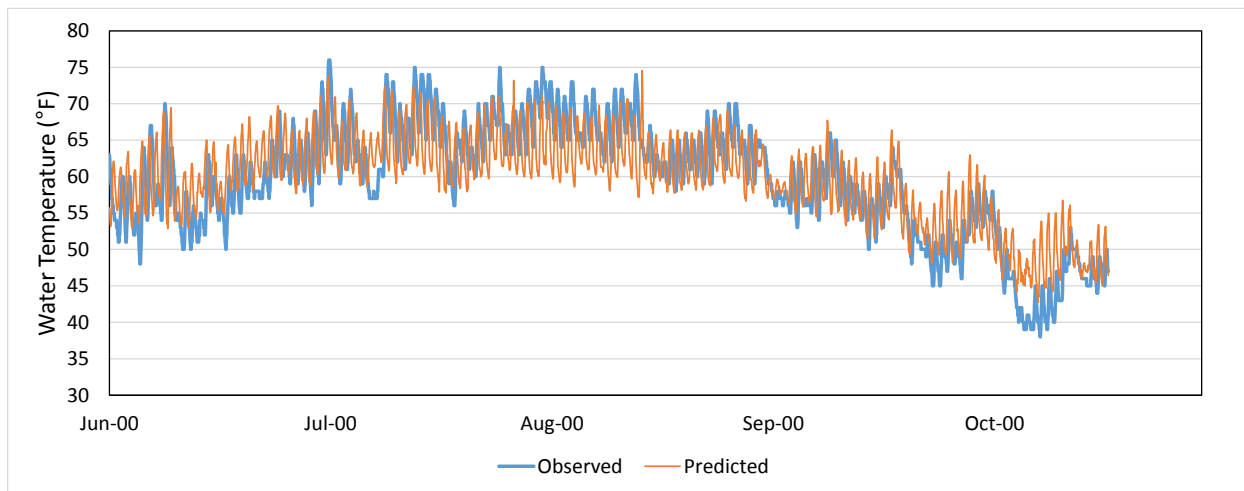


Figure 4-1. Water Temperature Calibration for Otter Creek (Reach 206)

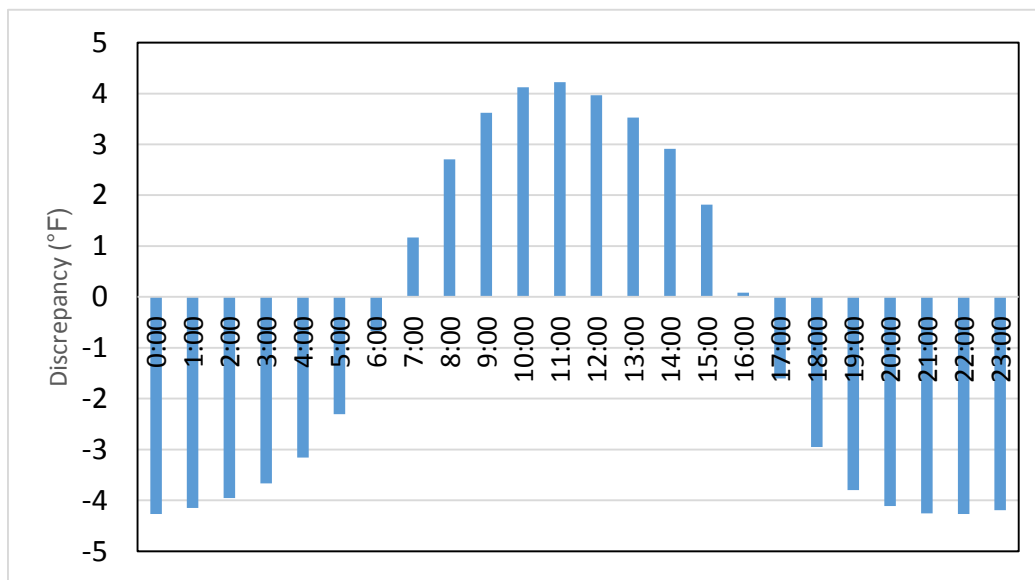


Figure 4-2. Average Water Temperature Discrepancy (Simulated minus Observed) by Time of Day for Otter Creek (Reach 206), 1999-2001

Temperature records were supplied for a large number of stations, with varying periods of record, completeness, and notes regarding quality. We selected a representative set of stations that are (1) near the downstream end of a reach that is simulated in the HSPF model, and (2) have relatively complete, longer periods of record. Results are summarized in Table 2-1. Relative average errors (a measure of bias) range between -4.85 and 2.56 percent; relative absolute errors (a measure of precision) range from

0.62 to 5.73 percent. Duda et al. (2012) state that average percent differences of less than 7 percent should be considered to represent “Very Good” model fit in HSPF – despite the fact that the model does not represent all the observed precipitation extremes. Note that the relative absolute errors are somewhat higher for the Nemadji River watershed stations. In part this is due to the fact that HSPF turns off simulation of water temperature dynamics when water depth falls below 3 inches, resulting in brief periods in which the water temperature simulation is not re-equilibrating with atmospheric temperature.

Table 4-1. Continuous Water Temperature Calibration Statistics

Station	Monitoring Period (seasonal)	Model Reach	Average Error (F)	Relative Average Error	Average Absolute Error (F)	Relative Absolute Error
Otter Creek at mouth	1999-2001	St. Louis 206	-0.80	-1.31%	1.17	1.92%
Stony Brook	2000-2002	St. Louis 211	1.50	2.56%	1.22	2.09%
Stoney Creek @ Hwy 3	2000	St. Louis 278	0.00	0.00%	0.37	0.62%
Cloquet R @ Bear Trap Cr	2003-2004	Cloquet 402	-0.66	-1.05%	1.13	1.81%
Hellwig Cr.	2002-2004	Cloquet 403	1.35	2.18%	1.92	3.12%
UsKabWanKa @ mouth	2002-2003	Cloquet 405	-1.11	-1.78%	0.87	1.40%
Cloquet R @ UsKabWanKa	2003-2004	Cloquet 406	-3.11	-4.85%	0.90	1.40%
Blackhoof R @ Hwy 104	2001-2011	Nemadji 511	0.99	1.62%	3.04	4.99%
SF Nemadji @ Hwy 23	2007-2009	Nemadji 112	1.47	2.45%	3.42	5.73%
Net River @ Hwy 8	2000-2009	Nemadji 111	-0.65	-1.06%	2.74	4.45%
Skunk Creek	2006-2008	Nemadji 115	0.09	0.15%	2.82	4.60%

Since April 2011, USGS has monitored water temperature at the Saint Louis River at Scanlon flow gage (04024000), reporting the daily mean, minimum, and maximum on the NWIS system. Interpretation of water temperature at this station is somewhat problematic, as it is located just downstream of Scanlon Dam and affected by hydropower releases from that dam, plus the Knife Falls Dam just upstream. At this station, the average error is -1.33 °F (-2.52%) and the average absolute error is 3.84 °F (7.29%). Comparison of the time series of daily means shows discrepancies in the summer, when the model under-predicts observed temperatures. This may be due to vertical variation in temperature in the reservoirs in which the surface water flowing over the dams is warmer than the vertically averaged water temperature simulated by HSPF. There are also discrepancies during winter ice conditions as HSPF predicts short-term responses to weather variability where none are observed because the presence of ice is not explicitly simulated.

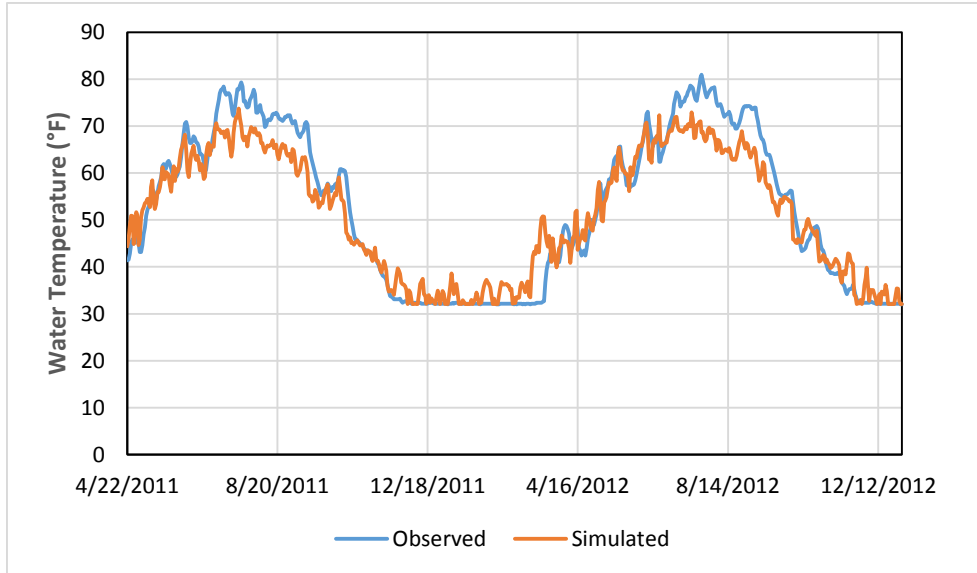


Figure 4-3. Observed and Simulated Daily Average Water Temperature, Saint Louis River at Scanlon

5 Algae and Dissolved Oxygen Calibration

Dissolved oxygen (DO) concentration in streams results from a complex interaction of reaeration rate (a function of turbulence), the oxygen concentration of inflowing water, the saturation concentration of oxygen (which depends on temperature and salinity), consumption of oxygen by bacterial breakdown of carbonaceous and nitrogenous material in the water column (biochemical oxygen demand) and at the water-sediment interface (sediment oxygen demand), production of oxygen during photosynthesis by algae and macrophytes, and consumption of oxygen during nighttime algal/macrophytes respiration. The impact of plant photosynthesis/respiration and diel cycles of water temperature result in a situation where grab sample measures of DO are not very informative for model calibration. Further, the influence of algae/macrophytes on DO means that DO and algae must be calibrated simultaneously.

5.1 ALGAE

Unfortunately, only very limited data are available on algae and macrophytes in flowing streams and wetlands of the St. Louis, Cloquet, and Nemadji watersheds. Observations of chlorophyll *a*, the primary photosynthetic pigment in most algae, are available for many lakes and serve as an indicator of planktonic algae density – but do not provide information on benthic algae and macrophytes. However, many of the monitored lakes are of small size and not explicitly simulated in the basin-scale model. Given the relative paucity of information on algal density, model calibration focused on ensuring that planktonic chlorophyll *a* concentrations were in a reasonable range.

Chlorophyll *a* is not routinely monitored at most stream stations. Four samples from St. Louis River downstream of CR 7, 1 mile south of Forbes (S000-119) show samples ranging from 1.5 to 3.1 µg/L. Average growing season simulated concentrations from streams in the St. Louis River watershed are around 2.5 µg/L.

For the St. Louis River basin the assessed lakes subject to MINLEAP modeling by MPCA (2013) had average observed (growing season) chlorophyll *a* concentrations ranging from 0.2 to 21 µg/L, with the exception of impaired Manganika Lake, which had a mean concentration of 67 µg/L and a median concentration in intensive 2004-2006 monitoring reported in EQUIS of 39 µg/L. Most of the lakes that do not have large point source inputs of nutrients fall between 2 and 12 µg/L.

While more data are available for lakes than streams, chlorophyll *a* data are not known to be available for some of the largest lakes, such as Island Lake, which controls the outflow from the Cloquet basin. In addition, much of the available data are from periods outside the model simulation period (1993-2012). Chlorophyll *a* predictions in 18 explicitly simulated lakes in the St. Louis and Cloquet models are compared to available observations for 1995 – 2012 in Table 5-1. Given the small sample sizes, the model and observations are reasonably in agreement for most of the monitored lakes. The model does appear to over-predict chlorophyll *a* in Esquagama, but, as seen in Section 3.2.2.3, phosphorus concentrations are also over-predicted in this lake. The model under-predicts observations in Long and Wild Rice lakes. Both of these lakes are very shallow with substantial rooted macrophyte growth that is not directly addressed by the HSPF code.

Table 5-1. Chlorophyll *a* Concentrations in Explicitly Simulated Lakes of the St. Louis and Nemadji River Watersheds

Lake	Model Reach	# Samples, 1995-2012	Monitored Average and Range	Simulated Average and Monthly Max
Fond du Lac Reservoir	205	ND		4.7 (8.6)
Thomson Reservoir	207	9	3.5 (1.1 - 5.7)	4.4 (6.9)
Cloquet Reservoir	208	ND		2.8 (6.6)
West Two River Res.	245	10	15.2 (4.3 - 28.6)	3.1 (36.6)
Esquagama	253	9	3.0 (1.8 – 5.0)	8.2 (17.5)
Wynne	254	5	3.1 (1.1 – 7.4)	9.4 (18.5)
Colby	262	10	2.5 (1.0 – 3.8)	10.9 (18.8)
Long (69-0495)	275	22	7.2 (0.05 – 39.8)	0.8 (7.3)
Whiteface	289	19	6.9 (1.1 -14.9)	5.2 (10.7)
Island	407	ND		0.4 (11.6)
Boulder	408	ND		0.2 (2.9)
Fish Lake Flowage	422	ND		0.1 (1.7)
Wild Rice	423	2	15 (13.3 - 16.7)	4.5 (8.7)
Knife Falls	501	ND		3.3 (6.6)
Scanlon Reservoir	502	6	4.8 (3.2 – 9.2)	3.6 (6.5)
Mashkenode	601	ND	4.8 (3.2 – 9.2)	3.2 (20.5)
Manganika	602	30	21.8 (0 – 42.7)	16.1 (38.2)
Ely	603	5	1.2 (1.0 -2.0)	2.3 (28.1)

The current version of the model does not explicitly represented any of the lakes in the Nemadji watershed due to their small size and small drainage areas. Seven of eight assessed lakes had average observed chlorophyll *a* concentrations between 2.8 and 11.2 µg/L, while Lac La Belle had an average of 43.4 µg/L (MPCA, 2014). MINLEAP screening failed to predict the high chlorophyll *a* in Lac La Belle, but HSPF predicts substantially higher phosphorus loading to this lake than would be expected from MINLEAP regional average loading rates (Section 3.2.2.3).

5.2 DISSOLVED OXYGEN

Simulation of dissolved oxygen (DO) in the stream depends on a complex interaction between reaeration, algal production and respiration, and biochemical oxygen demand (Figure 5-1). Many of these processes

also affect nutrient balances, so the DO calibration must be achieved consistent with the nutrient calibration. The oxygen balance is also strongly dependent on water temperature simulation, which affects reaction rates and determines the saturation DO concentration.

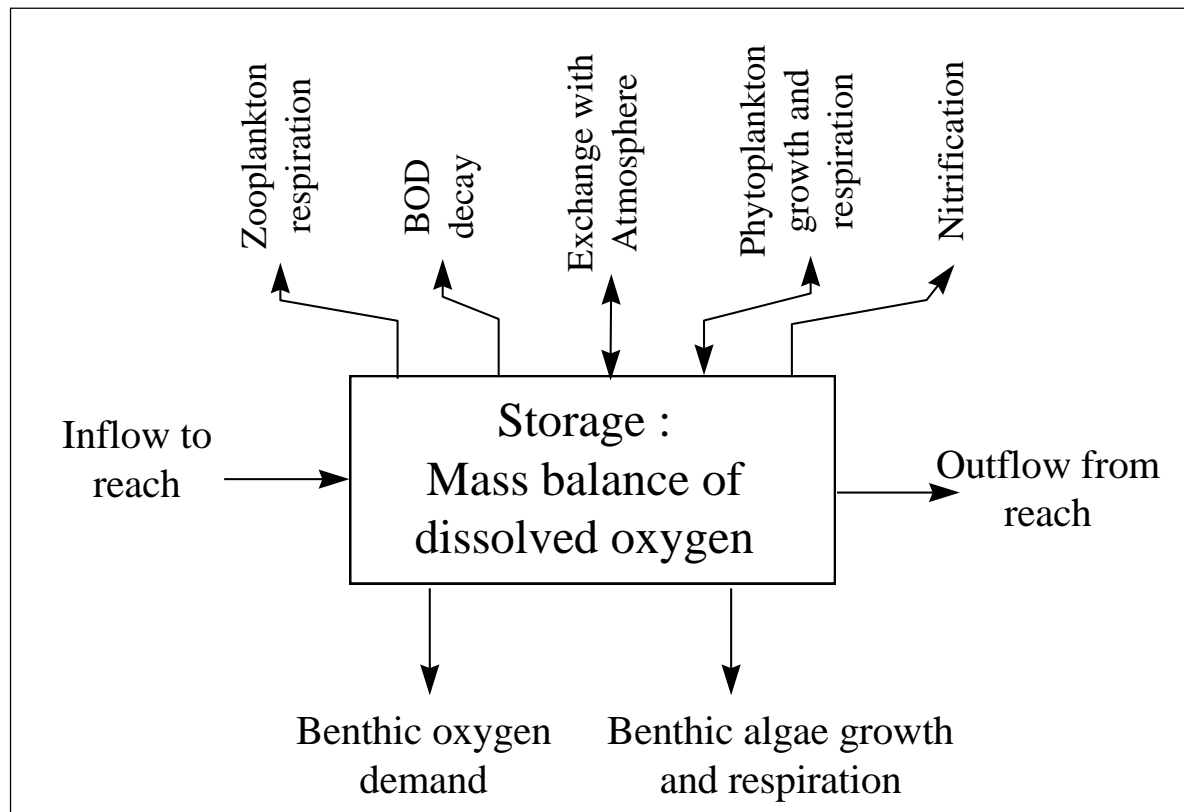


Figure 5-1. Process Diagram for Oxygen Mass Balance in HSPF

Many of the components of the oxygen mass balance in the St. Louis, Cloquet, and Nemadji watersheds have little or no available monitoring data. Specifically, there are no known monitoring data for reaeration rates, benthic oxygen demand, or benthic algal or zooplankton densities. As noted in Section 5.1, monitoring for planktonic algae in streams is very limited. While biochemical oxygen demand (BOD) data exist for many locations, the majority of observations are for 5-day total BOD, whereas HSPF uses ultimate carbonaceous BOD. Total BOD includes the nitrogenous component and may also be affected by the presence of reduced iron. As a result, the model parameters must be specified based on best professional judgment and experience with other, similar sites. The model can then be tested on its ability to reproduce observed DO concentrations.

Reaeration: When oxygen concentrations are reduced below saturation, oxygen tends to move from the atmosphere to the water, a process known as reaeration. The rapidity of reaeration depends on how well the water is mixed and the turbulence present at the water surface. HSPF provides several options for simulating stream reaeration. For the St. Louis, Cloquet, and Nemadji models the Tsivoglou energy dissipation method (Tsivoglou and Wallace, 1972) is used (with default parameters) for stream segments, while reaeration in lake segments is a function of wind speed and surface area (Bicknell et al., 2014).

Biochemical Oxygen Demand: HSPF simulates nitrogenous and carbonaceous components of biochemical oxygen demand separately, with the nitrogenous component being determined by concentrations of reduced inorganic nitrogen species (ammonium and nitrite). Carbonaceous biochemical

oxygen demand (CBOD) loading from the watershed is simulated as the labile fraction of total organic carbon, as described in Section 3.1. As the decay of CBOD results in the conversion of labile organic matter to inorganic nutrients, the representation of CBOD is largely constrained by the nutrient calibration.

The CBOD decay rate (k_d) is expected to be relatively low due both to the nature of organic carbon derived from forest and wetland vegetation, except immediately downstream of point sources. A k_d value of 0.0035 per hour (0.084 per day) appears to provide reasonable results. This is near the low end of the range of values reported nationally for streams without untreated waste input (USEPA, 1997). A higher rate of 0.01 per hour (0.24 per day) is used for segments near major WWTP discharges.

Benthic Interactions. Organic soils and sediment associated with northern wetlands affect the oxygen balance. These may both release BOD into the stream and exert a sediment oxygen demand (SOD) at the sediment-water interface. No direct measurements of SOD were identified, and these components are at this time a calibration adjustment factor. Note that in parts of the watershed the oxidation of reduced iron or sulfide could exert a significant oxygen demand. As HSPF does not explicitly address these components in the oxygen balance they are treated as part of the SOD.

Algal Dynamics: The activities of floating (planktonic) and attached (benthic) algae also affect the oxygen balance in streams. Algae produce oxygen as a byproduct of photosynthesis during sunlight hours, but are net consumers of oxygen through respiration at night. Algae can also die off, contributing to the biochemical oxygen demand.

Average CBOD concentrations predicted by the model are in the range of 1 to 2 mg/L in areas without large wastewater inputs. In stations downstream of significant wastewater discharges the predicted instream concentrations are largely a result of the BOD concentrations reported for the discharges. Comparison of simulated and observed average and maximum BOD is provided in Table 5-2. No observations are available for the Cloquet watershed, and only one stream station is available for the Nemadji. The BOD results are in reasonably good agreement, given the discrepancy between observations of 5-day BOD and model simulation of ultimate carbonaceous BOD (CBOD_u). Much higher concentrations (up to 30 mg/L) were observed in the 1960s and 1970s prior to modern wastewater treatment plant improvements.

Table 5-2. Comparison of Simulated and Observed Biochemical Oxygen Demand (mg/L)

Location	EQUIS Station	Count	Observed Average (and Maximum) BOD-5	Simulated Average (and Maximum) CBOD _u
St. Louis River at CSAH 7 nr Forbes	S000-119	22	1.4 (2.4)	2.3 (6.6)
St. Louis River below Cloquet R.	S000-023	22	1.2 (1.8)	2.7 (4.9)
St. Louis River at Scanlon	S000-629	33	1.6 (5)	2.7 (4.9)
St. Louis River nr Fond du Lac	S000-021	48	1.4 (2.4)	2.2 (4.6)
Nemadji River nr Pleasant Valley	S000-110	38	1.8 (9)	2.0 (11.9)

Calibration for dissolved oxygen presents some of the same challenges as the temperature calibration as there is likely to be significant diel variability due to the influence of algal photosynthesis and respiration that limits the information value of scattered grab samples. There may also be significant spatial

variability at scales smaller than the reaches in the basin-scale model due to local changes in light availability, substrate composition, and reaeration capacity.

Two sources of data were used for dissolved oxygen calibration. Relatively short periods of continuous DO data were collected throughout the St. Louis watershed from 2012 – 2014 as part of MPCA’s Stressor Identification process. Draft data from this effort were provided by Jeff Jaspersen of MPCA. We selected stations that were located near the lower end of reaches explicitly simulated in the model and that had good quality ratings assigned to the data. Continuous data are best for DO calibration, but these monitoring efforts typically encompass only a few weeks. We also identified several EQUIS water quality monitoring stations that had frequent, but not continuous DO data. The selected stations for the St. Louis watershed are shown in Table 5-3. Similar data were not available for the Cloquet and Nemadji watersheds.

Table 5-3. Locations and Sources of DO Calibration Data

HSPF Reach	Waterbody	source
205	St. Louis River @ Fond du Lac, S000-021 and S003-972	EQUIS
206	Otter Crk at Carlton, 4 th St. N.	Stressor ID
210	St. Louis River below Cloquet River, S000-023	EQUIS
226	Vaara Crk near Wawina, MN 73	Stressor ID
229	Skunk Crk near Meadowlands, CR 196	Stressor ID
231	Sand Crk near Toivola, CR 743	Stressor ID
236	Swan R, S000-641	EQUIS
238	East Swan Crk, Koivu Rd.	Stressor ID
241	Little Swan Crk, CR 444	Stressor ID
244	McQuade Crk near Buhl, CR 592	Stressor ID
248	Elbow Crk, CR 310	Stressor ID
249	St. Louis River at Forbes, S000-568 and S000-119	EQUIS
254	Embarrass River at Embarrass	Stressor ID
256	Embarrass River, Mattson Rd.	Stressor ID
262	Partridge River, S007-022	EQUIS
263	Wyman Crk at Hoyt Lakes, CR 666	Stressor ID
272	Mud Hen Crk near Makinen, CSAH 93	Stressor ID
274	Water Hen Crk near Makinen, CSAH 93	Stressor ID
276	Water Hen Crk near Markhamm, CR 340	Stressor ID
278	Stony Crk near Toivola, CSAH 83	Stressor ID
285	Paleface Crk at Melrude, TWP 6630	Stressor ID
402	Cloquet R @ Burnett, S003-968 and S005-147	EQUIS
502	St. Louis River @ Scanlon, S005-089, S000-639, and S000-146	EQUIS
604	Ely Crk, CSAH 95	Stressor ID

Note: Stations shown as “Stressor ID” are short-term continuous DO records collected to support the draft St. Louis River Stressor Identification Report and provided by Jeff Jaspersen of MDNR. Stations shown as “EQUIS” are sets of non-continuous grab samples stored in the MPCA EQUIS System.

Neither type of data is ideal for comprehensive calibration: the Stressor ID data cover too short a period, while the EQUIS data likely do not sample the full diel range of DO. Further, like temperature, the DO response may reflect conditions at a specific point in the stream that are not representative of the reach-averaged DO results produced by HSPF. Therefore, the calibration approach was semi-quantitative, and focused on obtaining reasonable agreement to the summer mean and minimum DO concentrations revealed by the available data.

Some streams showed a rather typical summer DO pattern with a daily average concentration that reflects temperature and the balance between reaeration and instream oxygen demand with a diel sinusoidal pattern superimposed that is a function of algal photosynthesis and respiration cycles. A good example is provided by Sand Creek near Toivola (Figure 5-2).

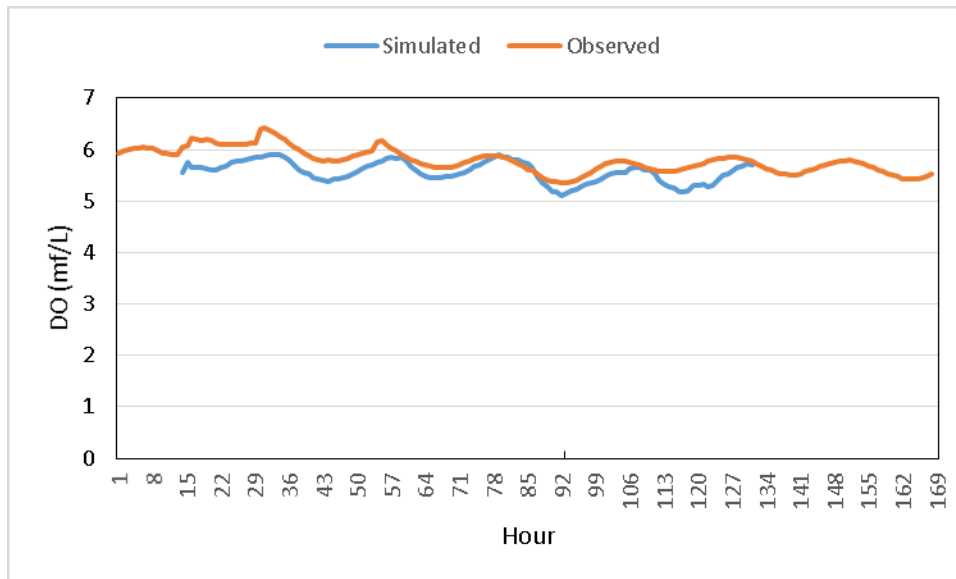


Figure 5-2. Dissolved Oxygen Calibration, Sand Creek near Toivola at CR 231, July 13 – July 18, 2012

In a series of other stream stations, especially those near the Sax Zim bog and Paleface and Mud Hen creeks, monitored DO concentrations remained near zero, with little diel variability imposed by algal photosynthesis. Assuming the data are correct, this is only possible if there is a strong source of oxygen demand within the stream that overwhelms reaeration. An example is shown for Paleface Creek in Figure 5-3. Results for this type of stream (even with an assumption of minimal DO in flow out of adjoining wetlands) could only be matched by assigning a very high SOD of 1,000 mg/m²/hr. This is higher than the SOD rates measured using *in situ* chambers and reported in USEPA (1997), which range up to a maximum of 780 mg/m²/hr, but may be enhanced by a chemical oxygen demand from the oxidation of reduced iron seeping into the stream. Oxidation of ferrous iron generally occurs quite rapidly in the presence of oxygen (c.f. Stumm and Morgan, 1996) and the discharge of reduced iron likely a contributor to the low DO and high DO deficit in these streams.

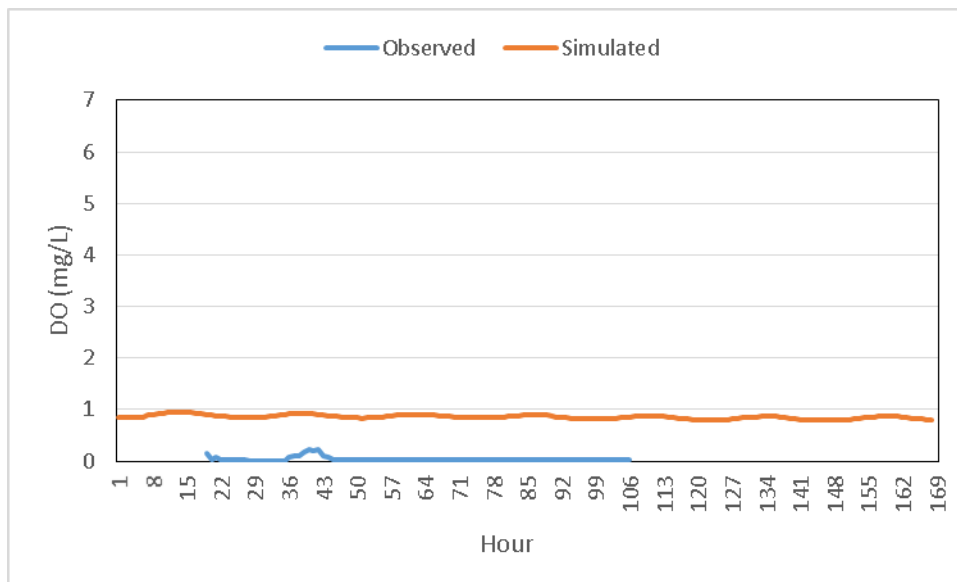


Figure 5-3. Dissolved Oxygen Calibration, Paleface Creek at Melrude TWP 6630, August 23 – August 27, 2012

The St. Louis River HSPF model does a reasonable job of representing observed astronomical summer (June 20 – September 20) mean DO concentrations in monitored reaches, with some exceptions (Figure 5-4), while also predicting minimum concentrations that are generally equal to or less than observed minima. For the mean concentrations the average difference between model and observations is -0.43 mg/L and the average absolute difference is 1.59 mg/L. One notable exception to the relatively good fit is reach 502, which is the EQUIS station just downstream of Scanlon Dam and hydropower station. There, the observed mean of 16.5 mg/L appears likely to represent supersaturated conditions due to air entrainment in the hydropower turbines. This mechanism is not incorporated into the HSPF reaeration equations, but could be described as a point source addition of oxygen mass.

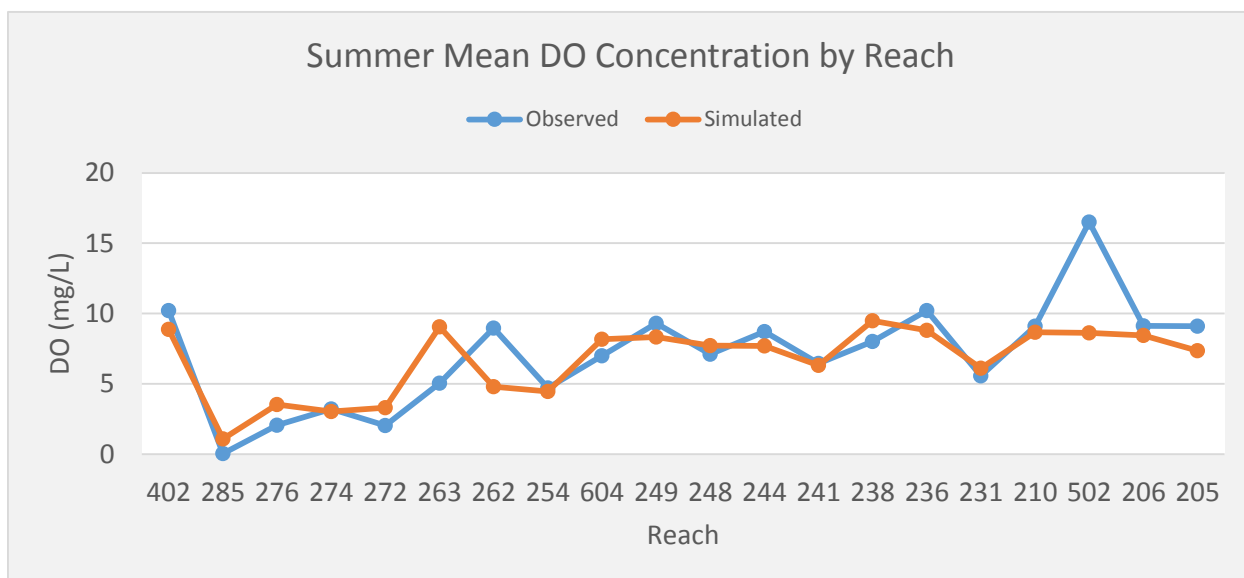


Figure 5-4. Dissolved Oxygen Calibration, Summer Daily Mean Concentration

DO calibration was not possible for the Cloquet and Nemadji watersheds at this time due to lack of monitoring data – for both DO and algae in streams. The calibrated DO parameters from the St. Louis model were transferred to these watersheds; however, benthic oxygen demand was set to the relatively low value of 100 mg/m²/hr for all reaches. These assumptions will need to be revisited as additional data become available.

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6 Potential Model Enhancements

The model calibrations presented in this report are based on model simulations through the end of 2012. Substantial amounts of data have been collected since 2012. MDNR is currently funding extension of all the model forcing time series (meteorology, point source discharges, appropriations, lake operational discharges, and atmospheric deposition) through the end of 2014. Once completed, this will open the possibility of revising model calibration with substantially more data for comparison – which is likely to result in some adjustments in calibration.

During the completion of this work it has become evident that many issues of interest to stakeholders – such as channel instability in the Nemadji or localized temperature and DO excursions in parts of the St. Louis watershed – may require analysis at finer spatial scales. Further, additional refinements to model segmentation may be needed to make use of data collected on smaller tributaries or at locations in the stream network not currently demarcated in the model. The basin-scale (HUC12-scale) models described here could be further segmented to a finer scale. Alternatively, the basin-scale model provides a framework that could be used for setting boundary conditions for more detailed local models (nested within the basin-scale model) to investigate and simulate specific areas of interest.

As is often the case in watershed models, monitoring data are not sufficient to constrain the simulation to a unique solution relative to individual source areas and processes. In the St. Louis watershed the stations with long periods of monitoring data are mostly downstream of point sources, while in both the St. Louis and Cloquet most stations with nutrient data are downstream of and affected by processes in lakes. Both factors limit our ability to calibrate source loads from individual land uses.

One area in which additional attention may be needed is the representation of wetlands and bogs. Few monitoring or flow gaging data are available to directly evaluate the representation of these land forms. Bog and wetland hydrology simulation may need to be re-evaluated when further information is available. For instance, the impacts of ditches on the hydrologic and water quality response of wetlands is potentially important but is not explicitly addressed in the model at this time.

Water chemistry in the St. Louis watershed is strongly affected by the unique geology of the Iron Range, which provides distinctive ionic signatures for surface and subsurface flows associated with mine dewatering sources and mine tailings. Sulfate and isotope work has proved valuable for identifying and validating flow pathways (e.g., Kelly et al., 2014). Ongoing work by MDNR is evaluating the ionic chemistry of the watershed in comparison to the attribution of surface and subsurface sources of flow in the model. This work may provide important evidence for refinements and enhancements to the model representation of the water balance and flow pathways. Elevated sulfate levels associated with Iron Range geochemistry are of particular interest in the St. Louis watershed due to deleterious impacts on wild rice. Sulfate chemistry is also closely tied to mercury cycling in the watershed (Berndt and Bavin, 2012). The basin-scale HSPF model could be modified in future (e.g., using the geochemical representation of the Mining Data Analysis System [MDAS; Tetra Tech, 2012]).

Surface water interactions with regional groundwater could also be enhanced. In the northern part of the St. Louis watershed the surface water hydrology is impacted by mining operations and mine pit dewatering. An initial exploration of the water balance in this area was carried out using a steady state ground water - surface water simulation model (Tetra Tech, 2014). Future development of a dynamic groundwater model for the region would further enhance representation of these processes. In the Nemadji River watershed, regional groundwater flow and the presence of clay aquitards result in artesian pressure in parts of the watershed (e.g., Deer Creek) that causes surface seeps and sediment “volcanos” that increase sediment and nutrient loads. A preliminary groundwater model application helps understanding of the water balance in this region (Barr, 2013), but awaits further improvement to better inform the surface water modeling.

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7 References

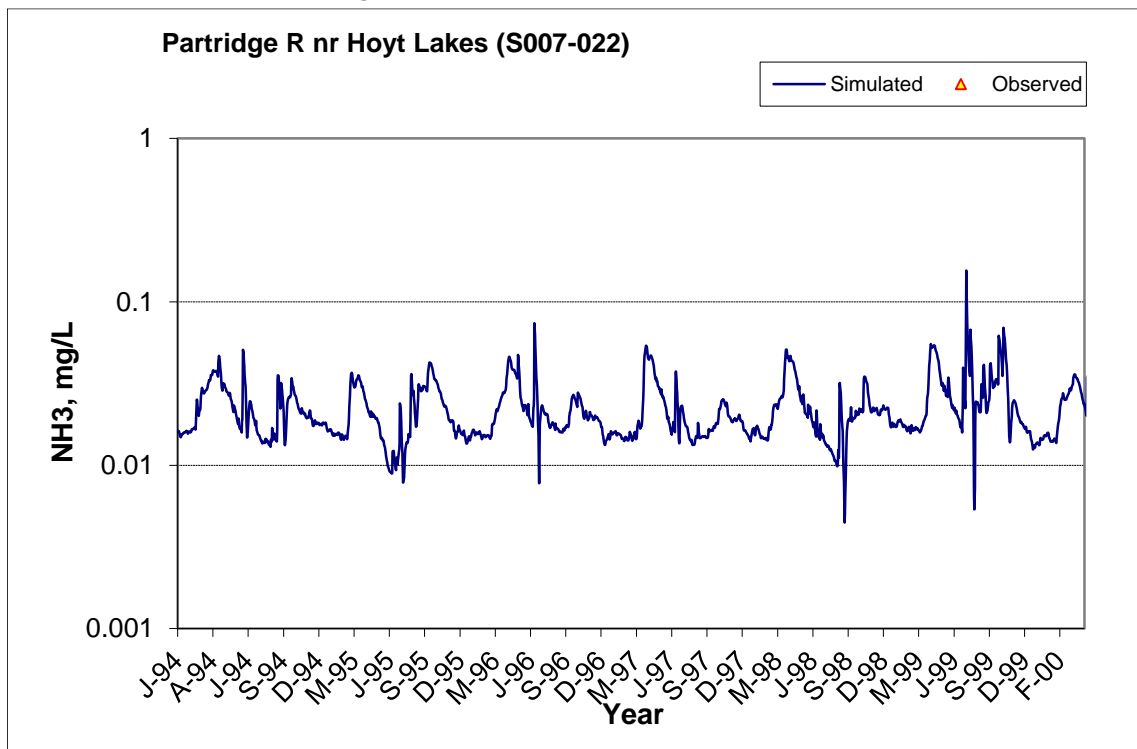
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Appendix A. Water Quality Calibration Details for St. Louis and Cloquet River Watersheds

A.1 PARTRIDGE R NR HOYT LAKES (S007-022)

A.1.1 Ammonia Nitrogen (NH₃)



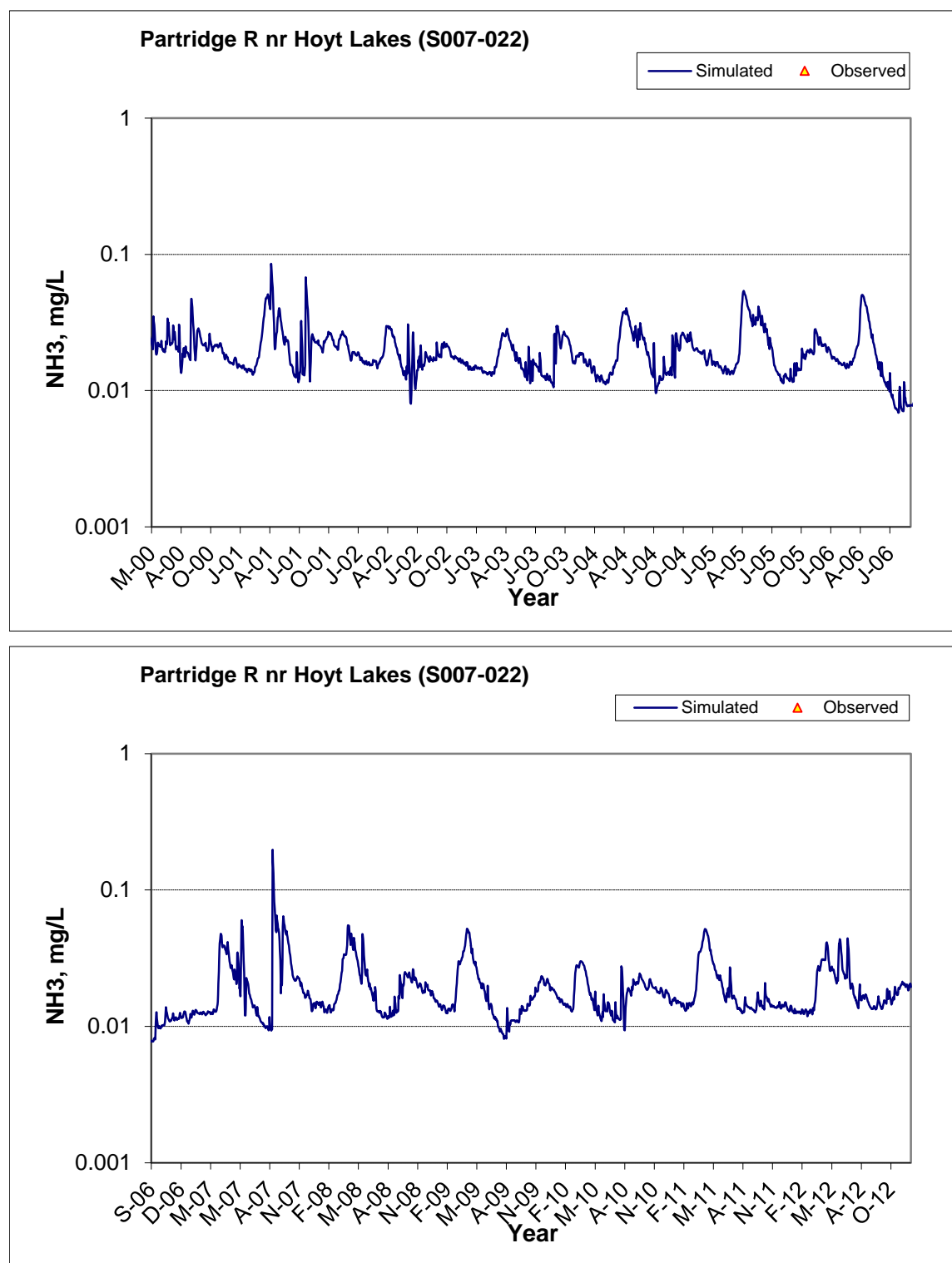
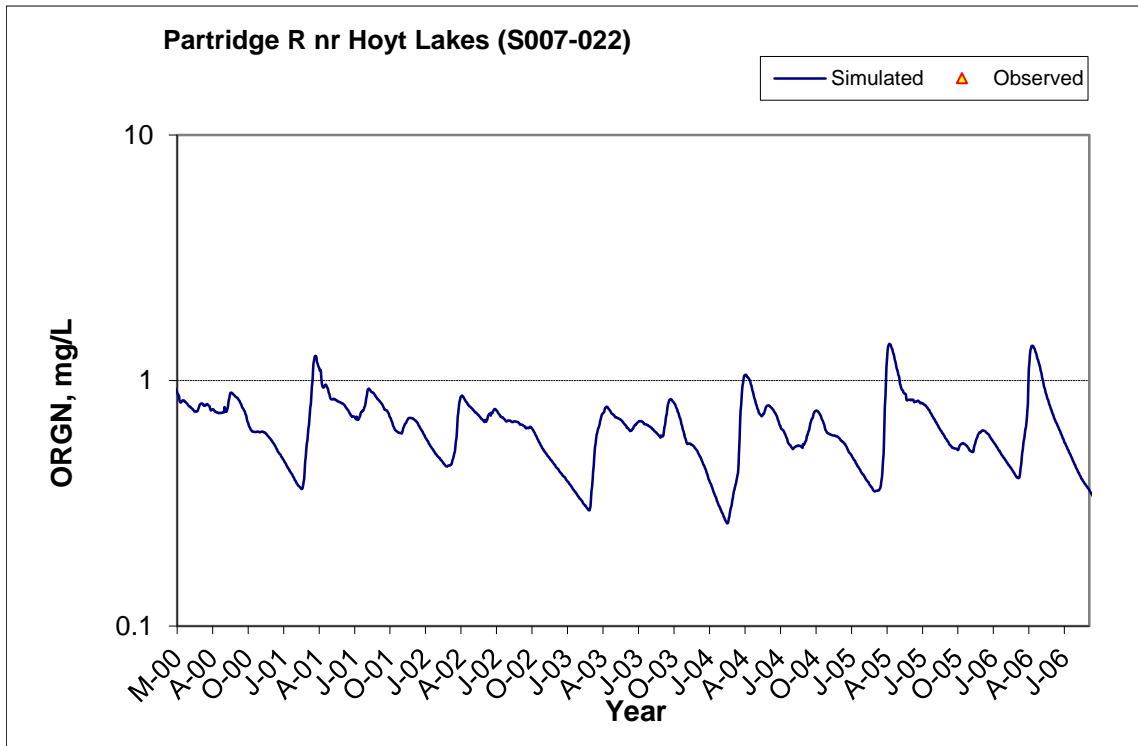
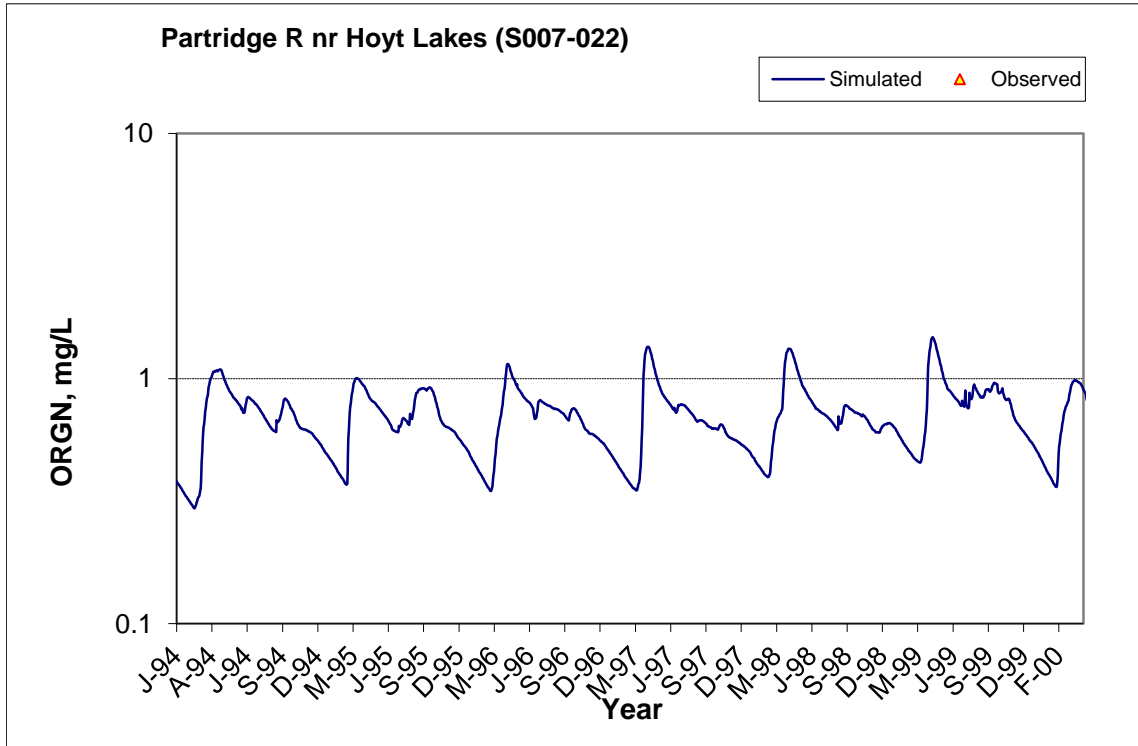


Figure A-1. Time series of observed and simulated Ammonia Nitrogen (NH₃) concentration at Partridge R nr Hoyt Lakes (S007-022)

A.1.2 Organic Nitrogen (OrgN)



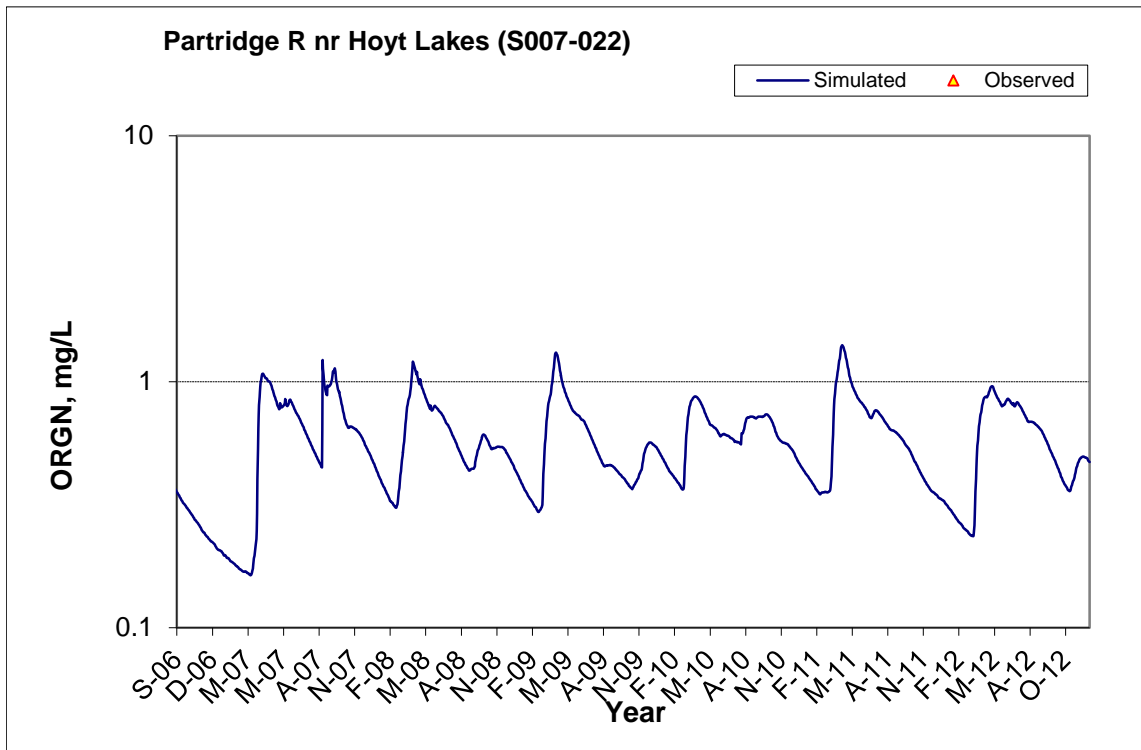
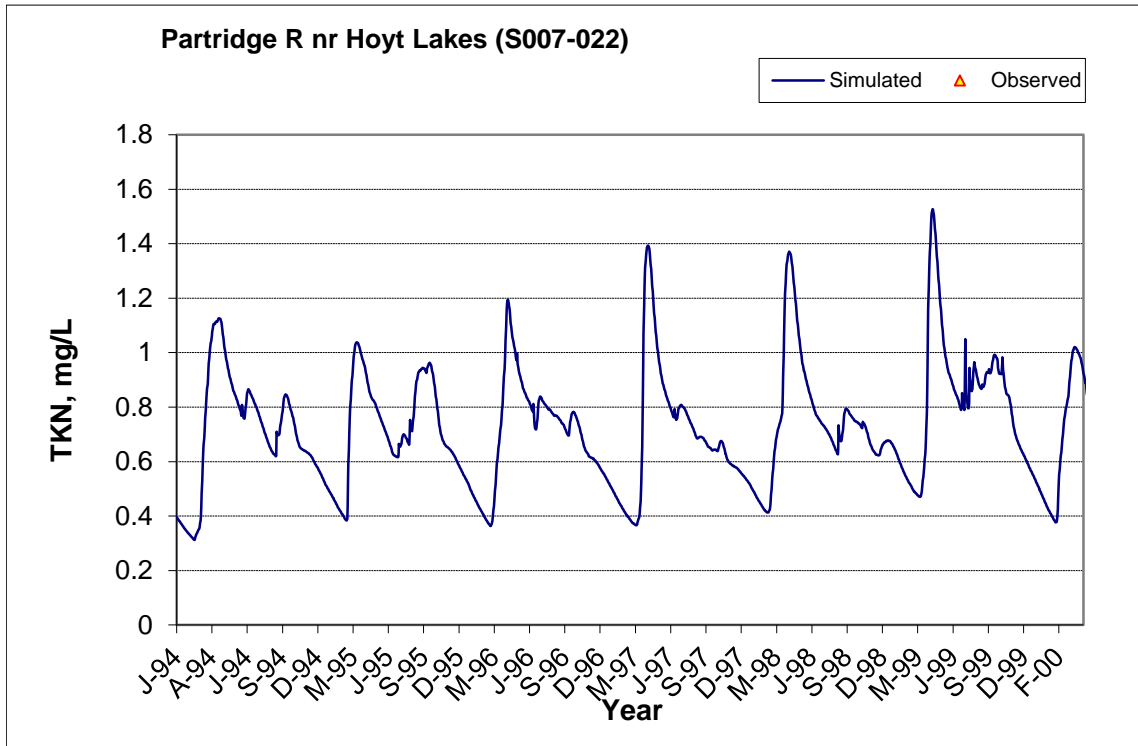


Figure A-2. Time series of observed and simulated Organic Nitrogen (OrgN) concentration at Partridge R nr Hoyt Lakes (S007-022)

A.1.3 Total Kjeldahl Nitrogen (TKN)



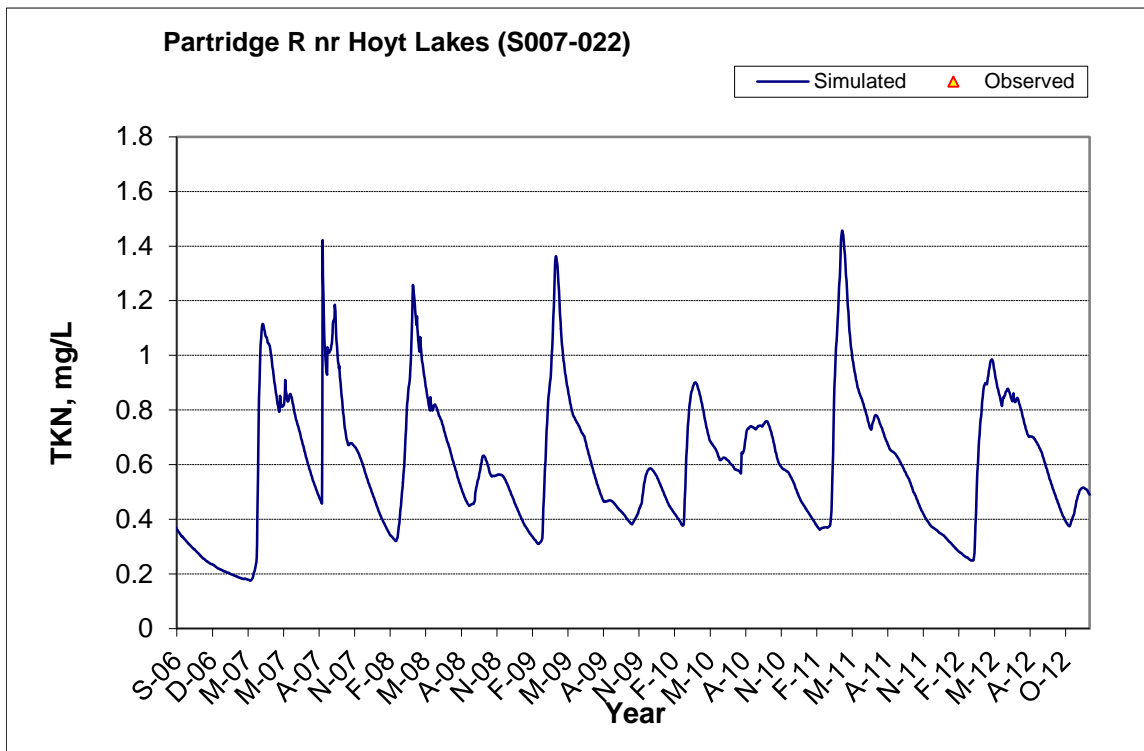
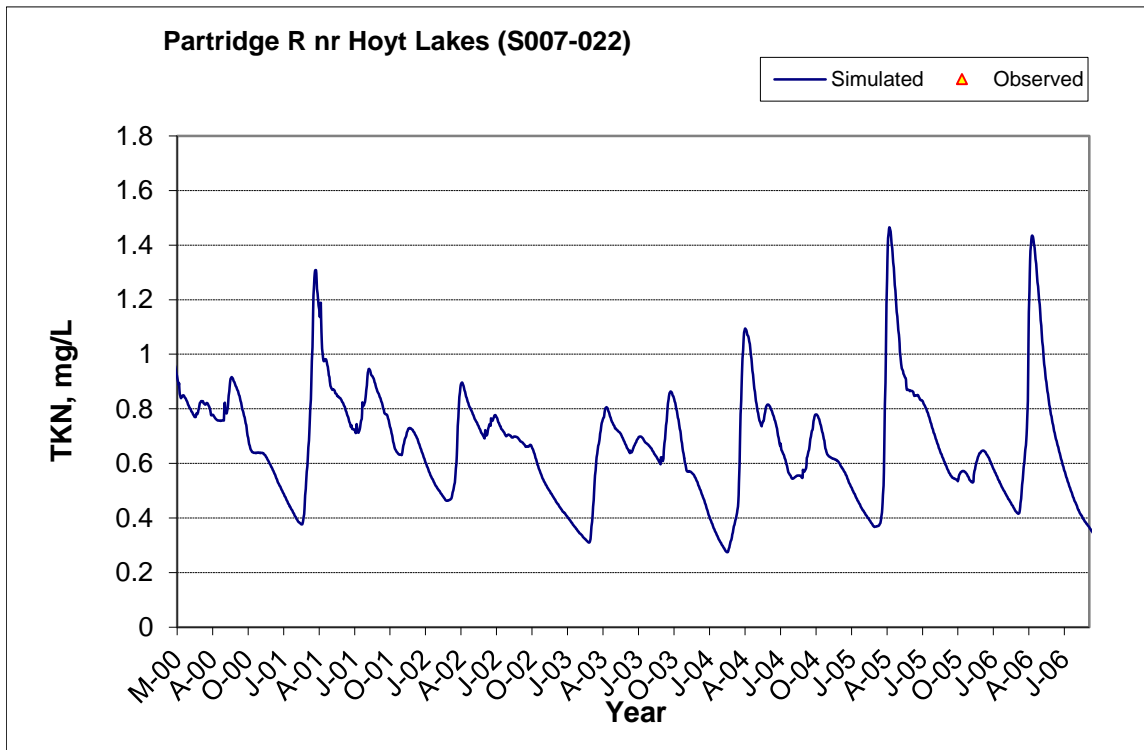


Figure A-3. Time series of observed and simulated Total Kjeldahl Nitrogen (TKN) concentration at Partridge R nr Hoyt Lakes (S007-022)

A.1.4 Nitrite+ Nitrate Nitrogen (NOx)

Table A-1. Nitrite+ Nitrate Nitrogen (NOx) statistics

Period	1994-1993	1994-2012
Count	ND	18
Concentration Average Error		-18.97%
Concentration Median Error		-41.85%
Load Average Error		-33.08%
Load Median Error		-3.21%
Paired t conc		0.54
Paired t load		0.31

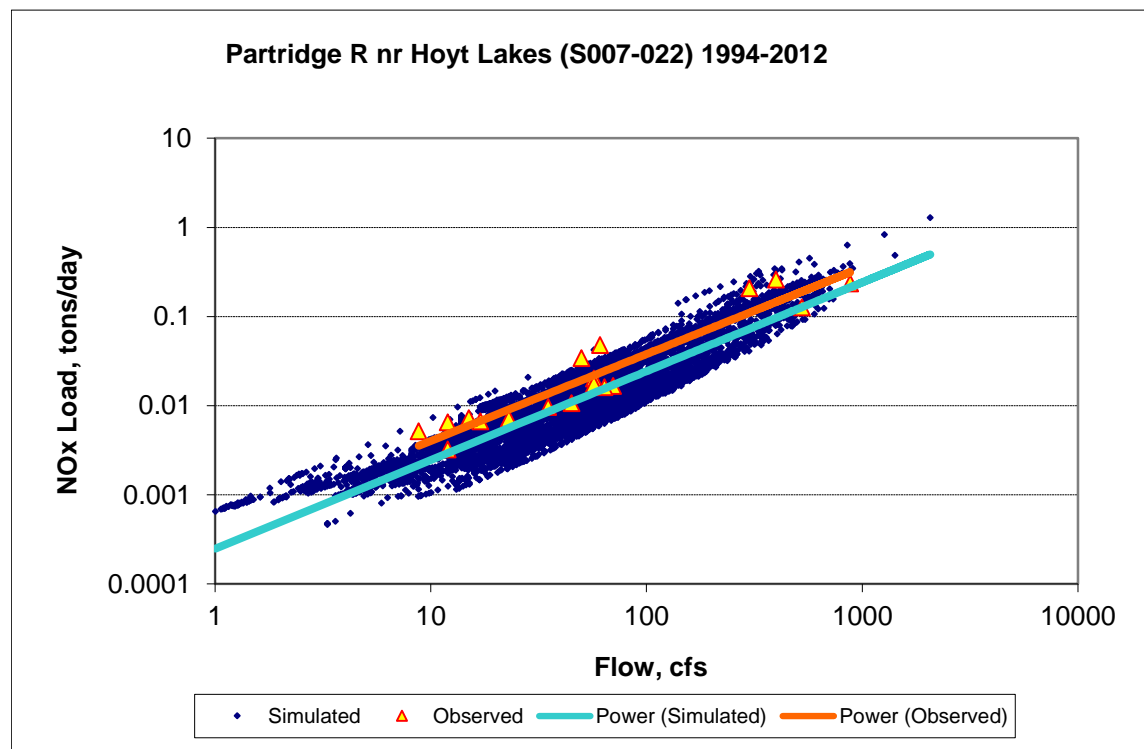
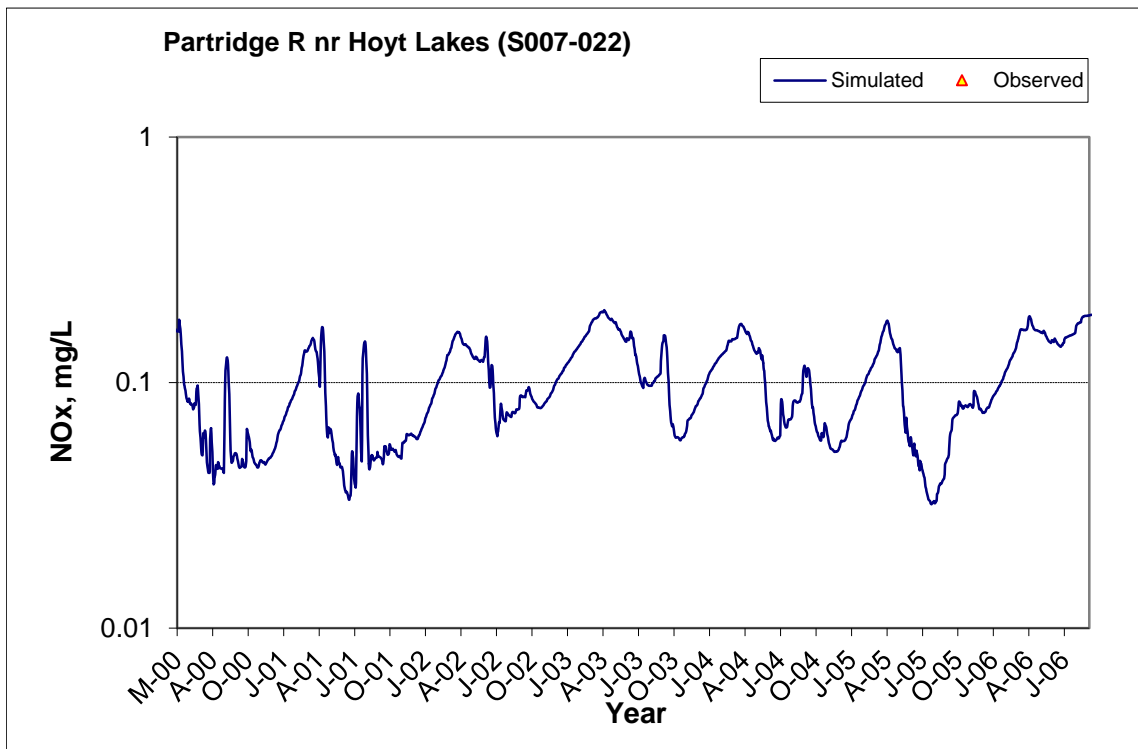
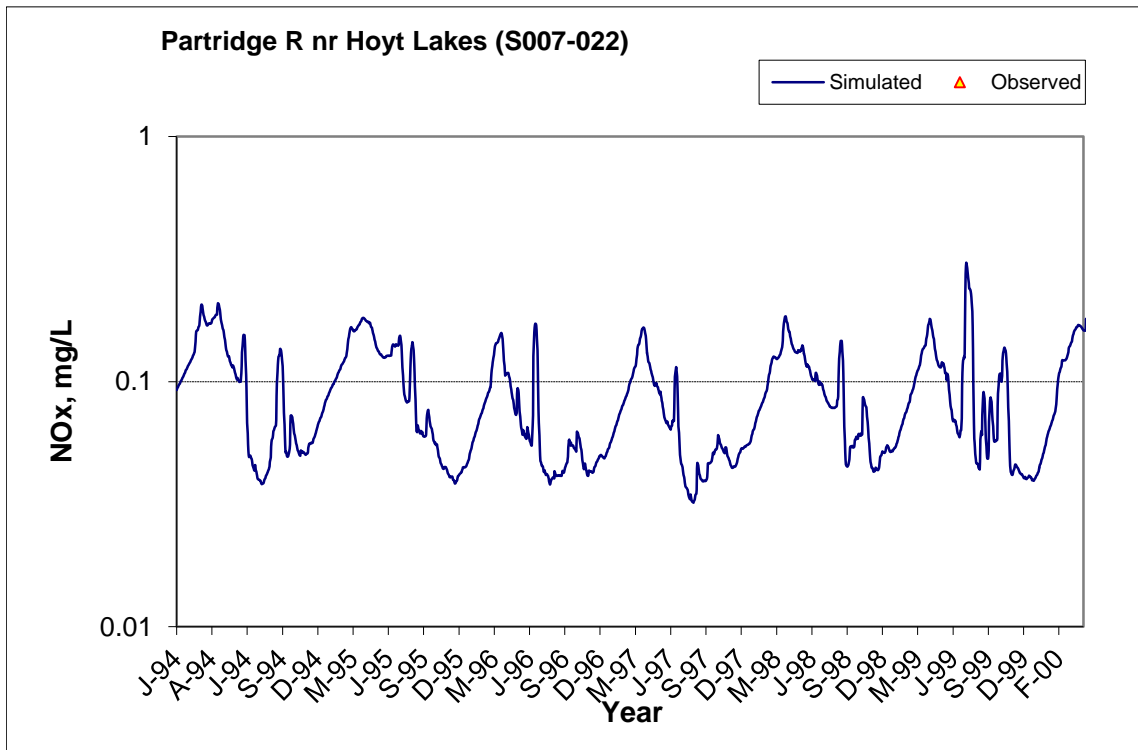


Figure A-4. Power plot of simulated and observed Nitrite+ Nitrate Nitrogen (NOx) load vs flow at Partridge R nr Hoyt Lakes (S007-022) (calibration period)



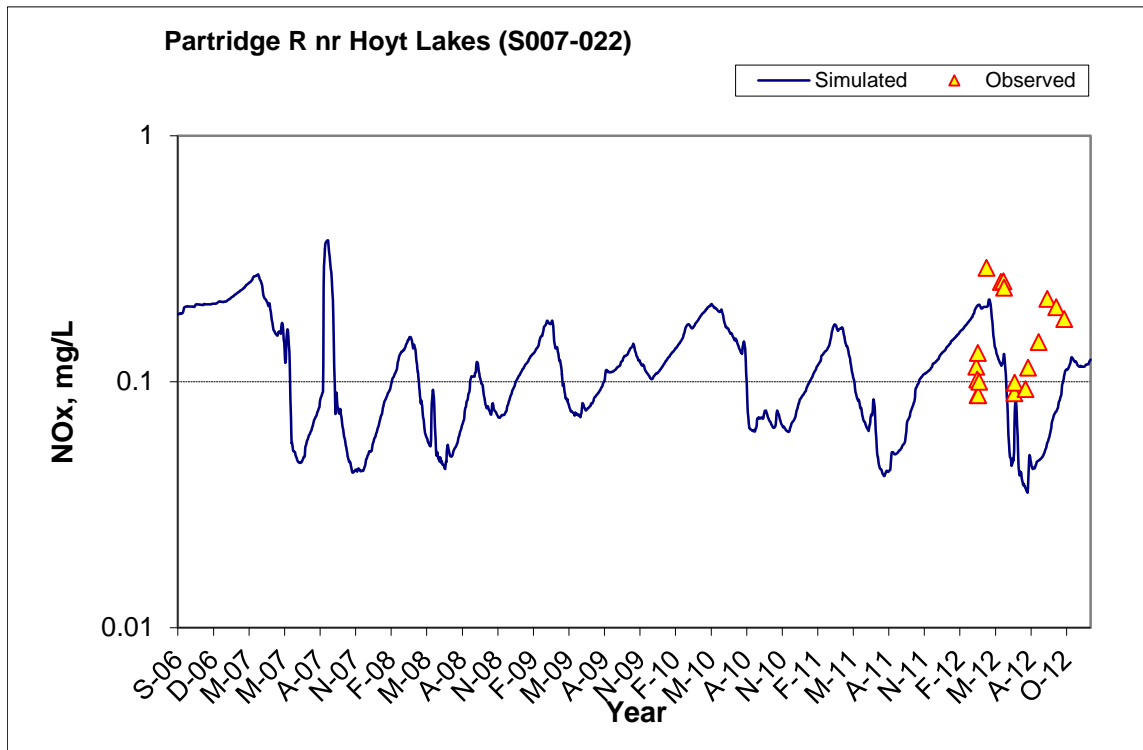


Figure A-5. Time series of observed and simulated Nitrite+ Nitrate Nitrogen (NOx) concentration at Partridge R nr Hoyt Lakes (S007-022)

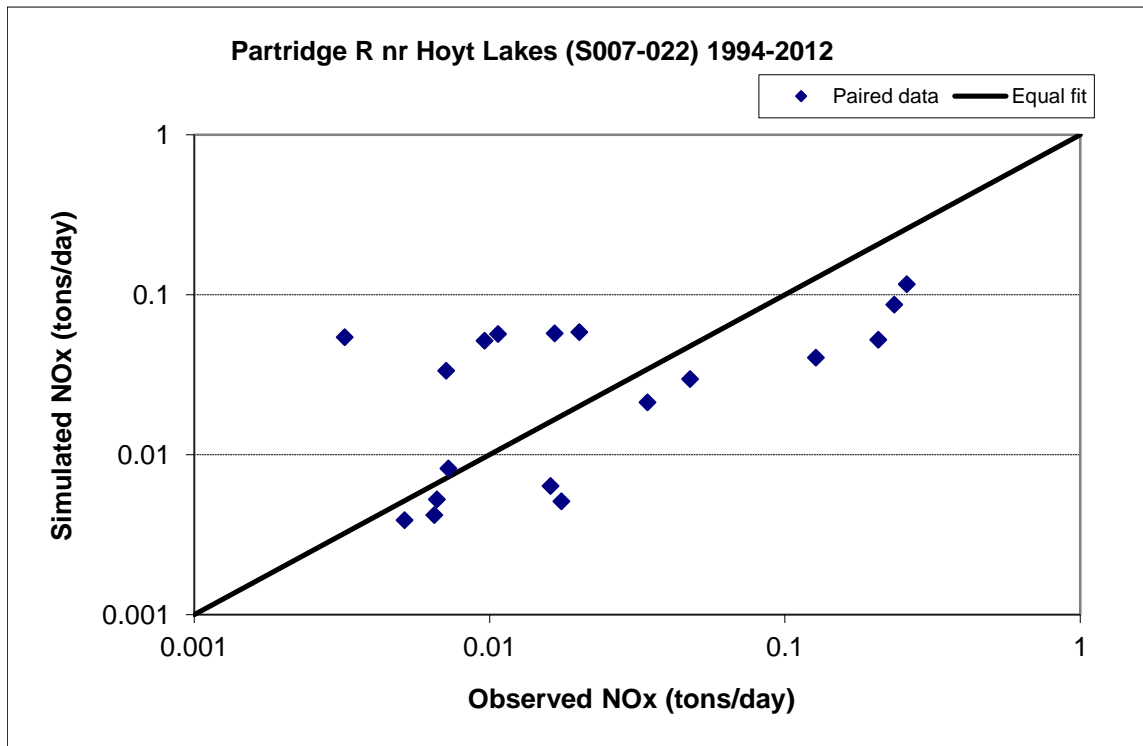


Figure A-6. Paired simulated vs. observed Nitrite+ Nitrate Nitrogen (NOx) load at Partridge R nr Hoyt Lakes (S007-022) (calibration period)

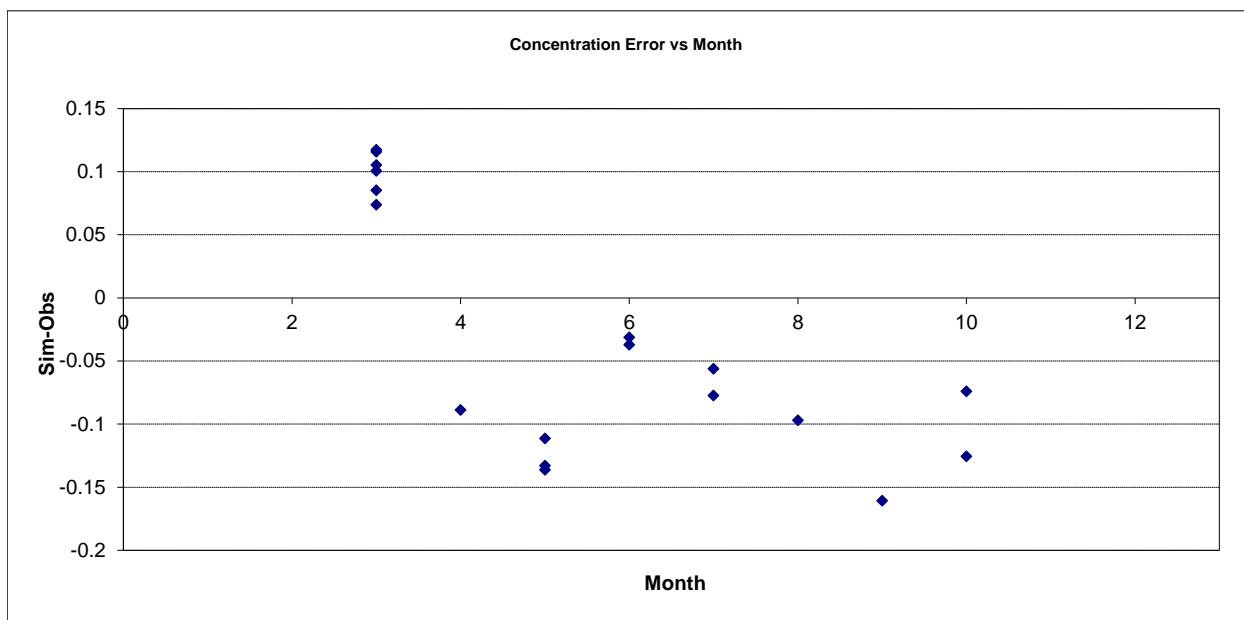


Figure A-7. Residual (Simulated - Observed) vs. Month Nitrite+ Nitrate Nitrogen (NOx) at Partridge R nr Hoyt Lakes (S007-022)

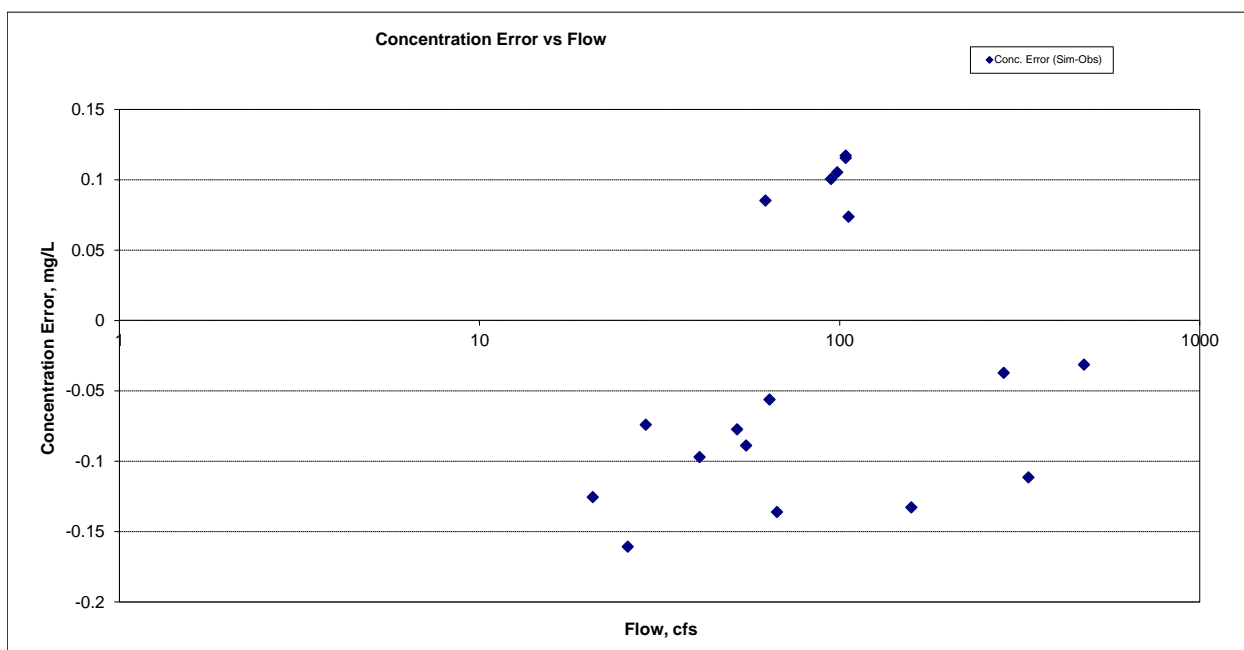
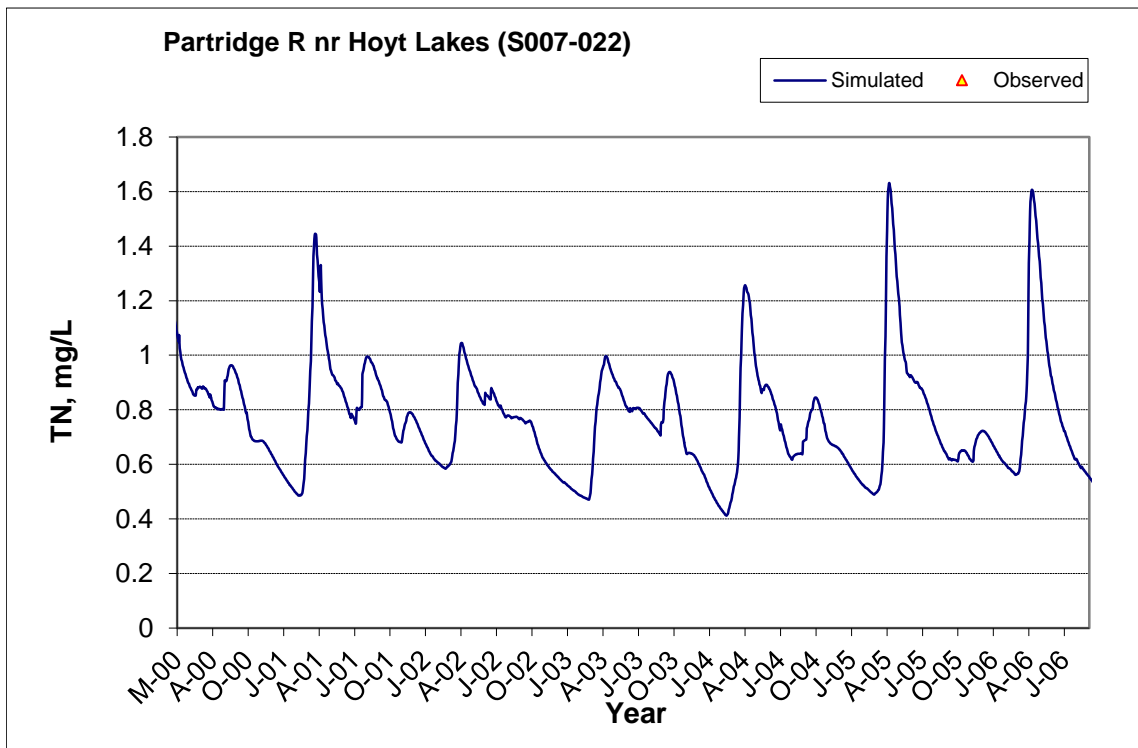
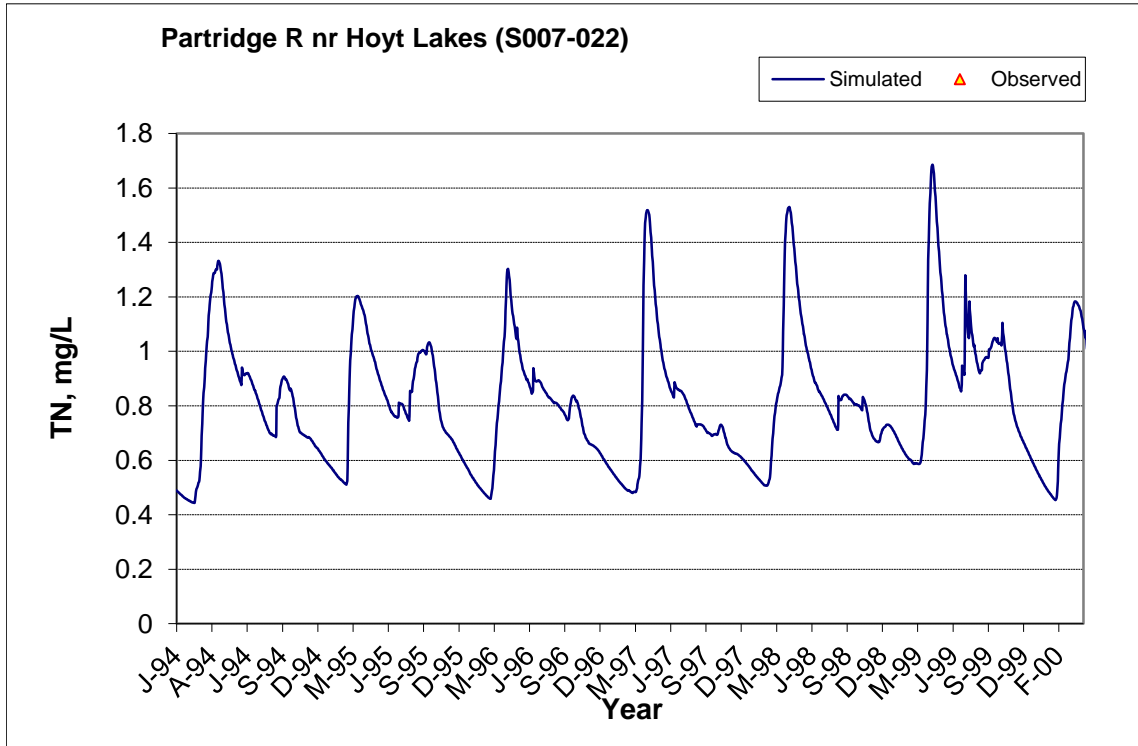


Figure A-8. Residual (Simulated - Observed) vs. Flow Nitrite+ Nitrate Nitrogen (NOx) at Partridge R nr Hoyt Lakes (S007-022)

A.1.5 Total Nitrogen (TN)



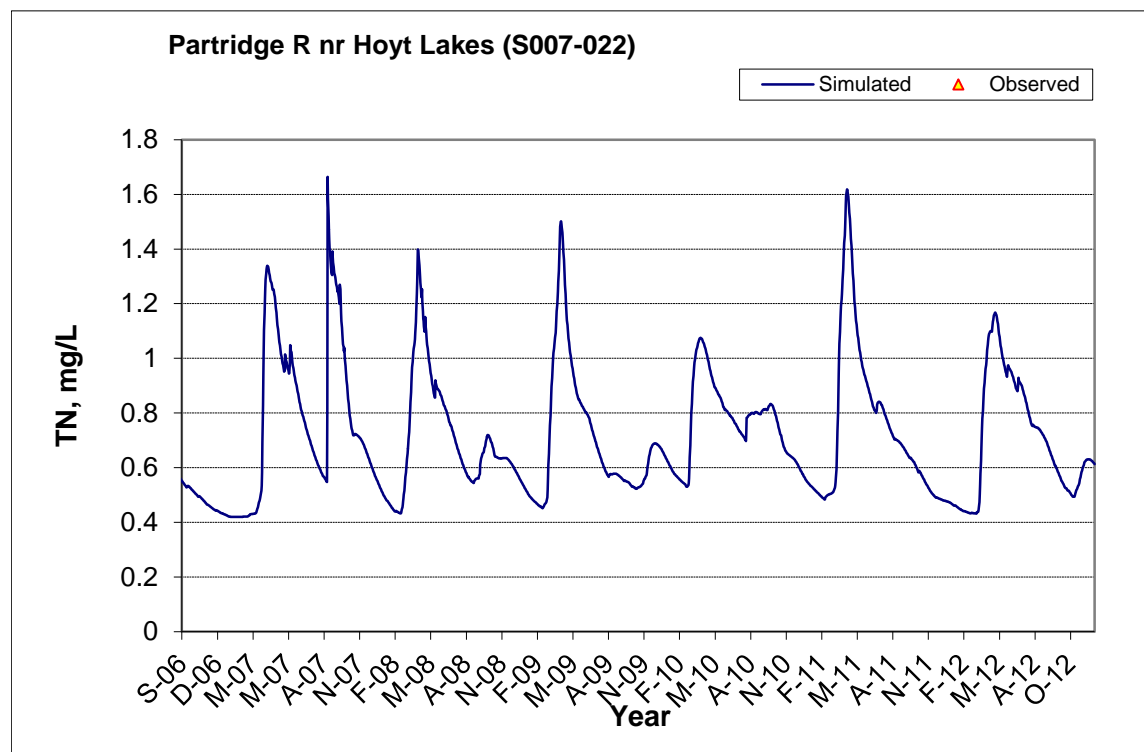


Figure A-9. Time series of observed and simulated Total Nitrogen (TN) concentration at Partridge R nr Hoyt Lakes (S007-022)

A.1.6 Soluble Reactive Phosphorus (SRP)

Table A-2. Soluble Reactive Phosphorus (SRP) statistics

Period	1994-1993	1994-2012
Count	ND	18
Concentration Average Error		-32.36%
Concentration Median Error		-24.18%
Load Average Error		13.85%
Load Median Error		-3.00%
Paired t conc		0.15
Paired t load		0.55

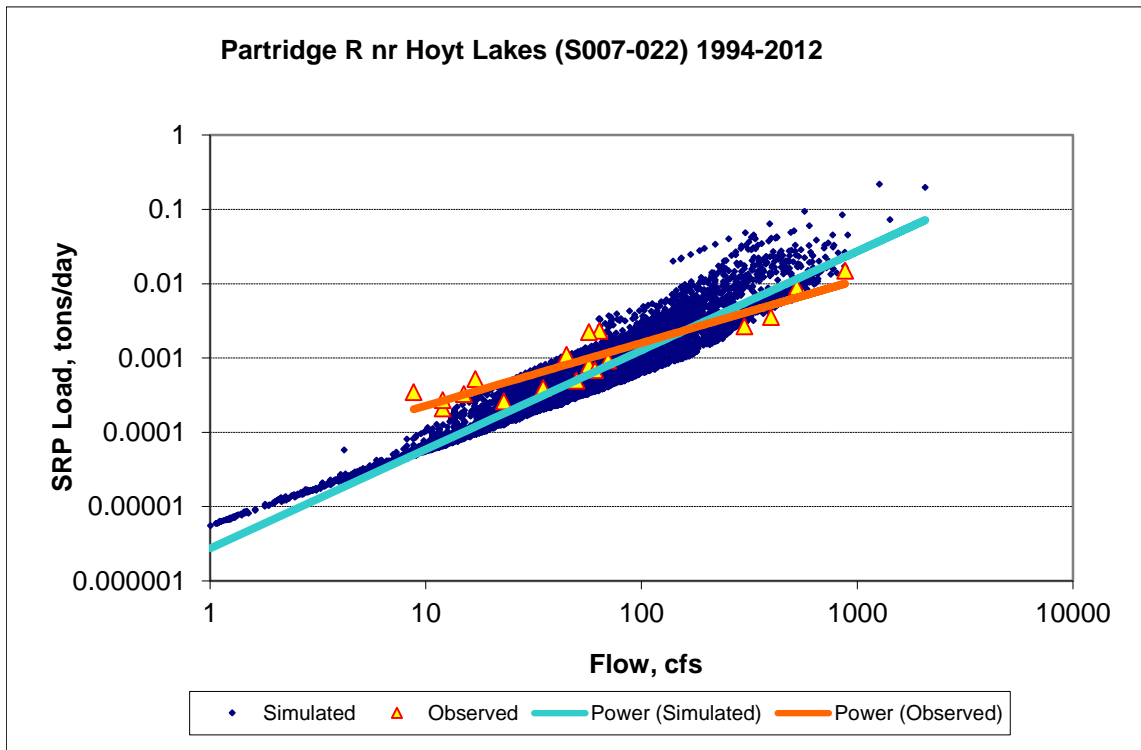
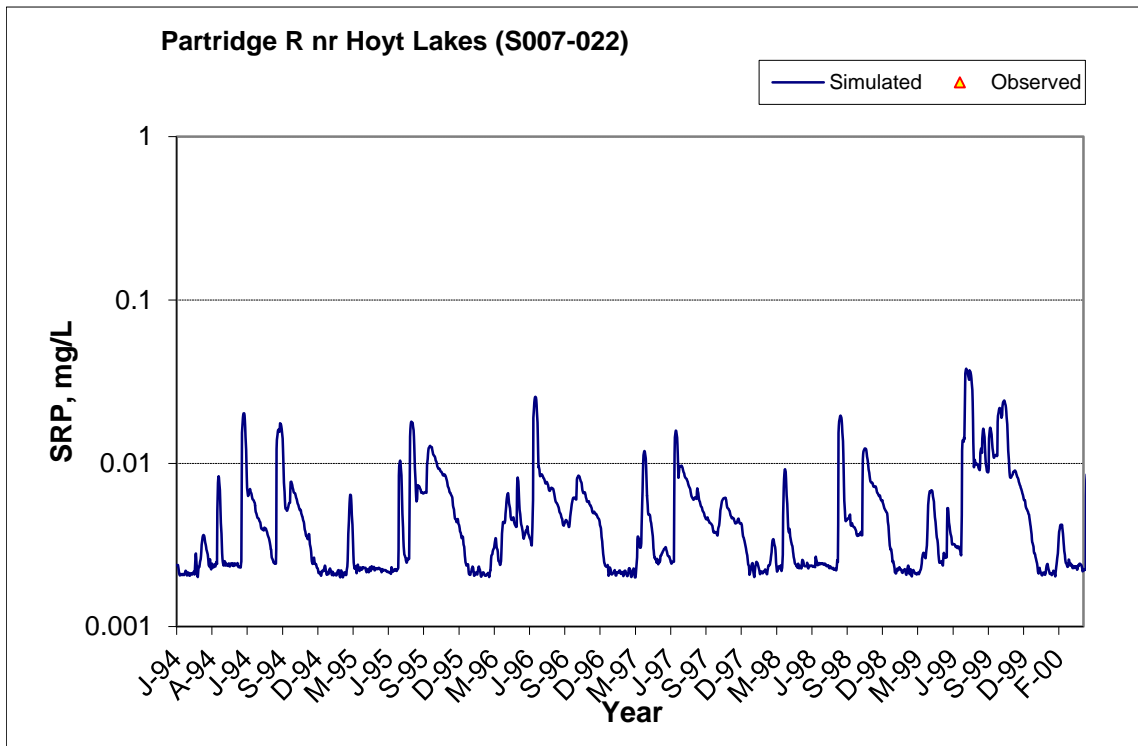


Figure A-10. Power plot of simulated and observed Soluble Reactive Phosphorus (SRP) load vs flow at Partridge R nr Hoyt Lakes (S007-022) (calibration period)



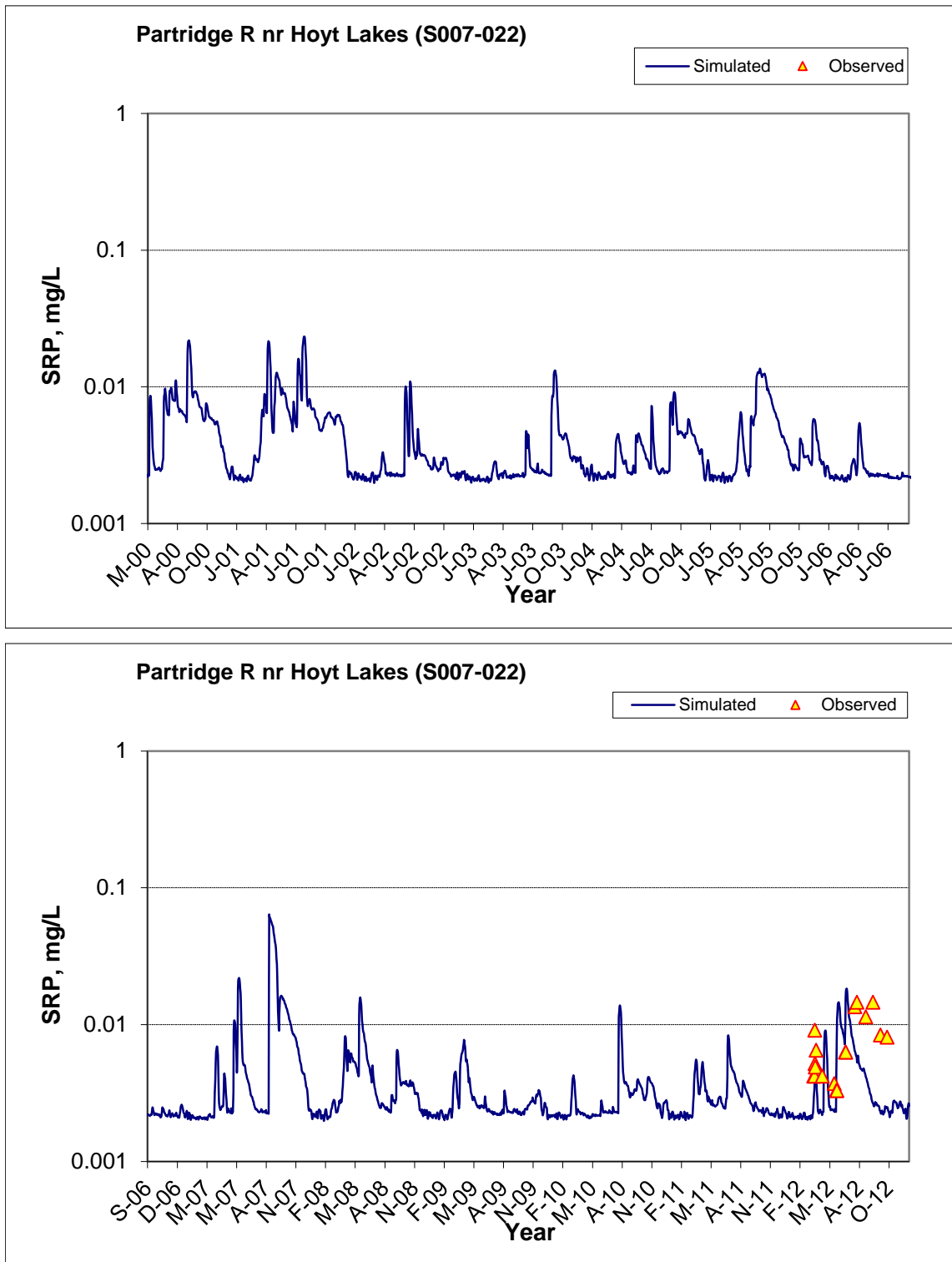


Figure A-11. Time series of observed and simulated Soluble Reactive Phosphorus (SRP) concentration at Partridge R nr Hoyt Lakes (S007-022)

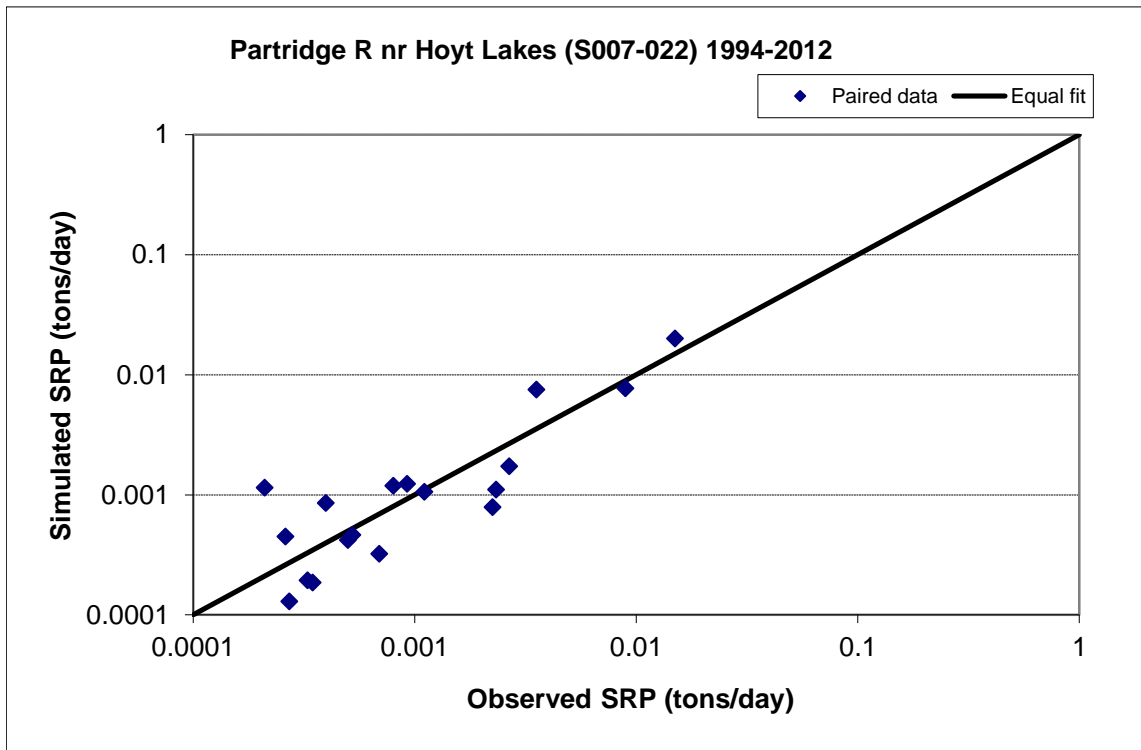


Figure A-12. Paired simulated vs. observed Soluble Reactive Phosphorus (SRP) load at Partridge R nr Hoyt Lakes (S007-022) (calibration period)

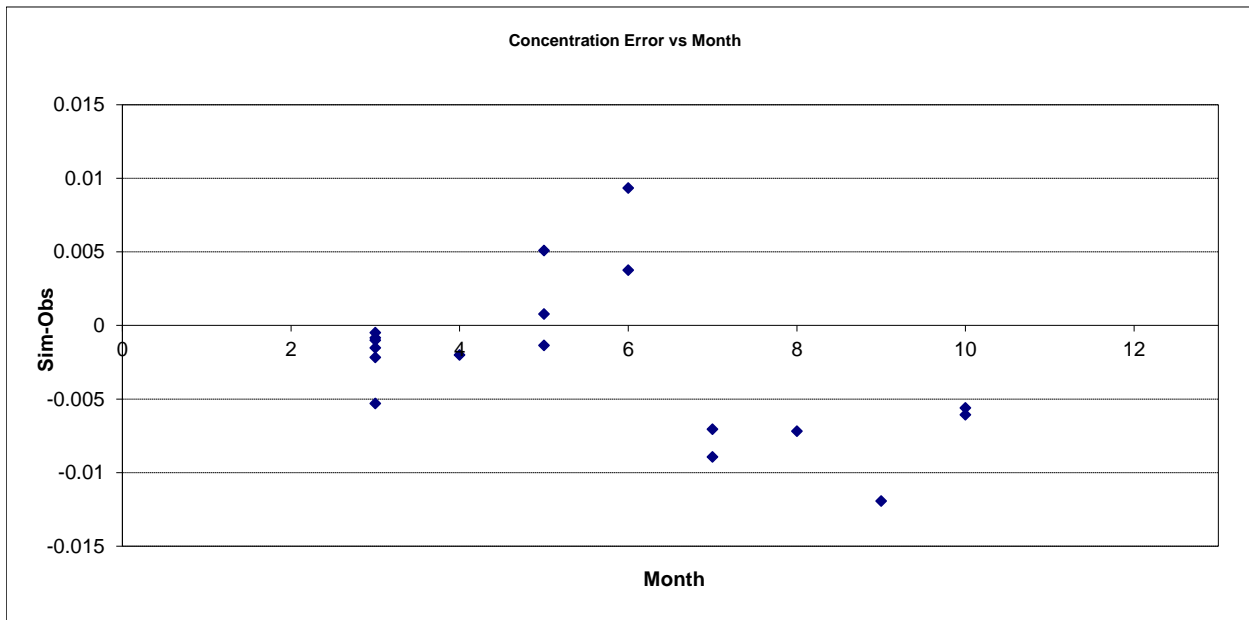


Figure A-13. Residual (Simulated - Observed) vs. Month Soluble Reactive Phosphorus (SRP) at Partridge R nr Hoyt Lakes (S007-022)

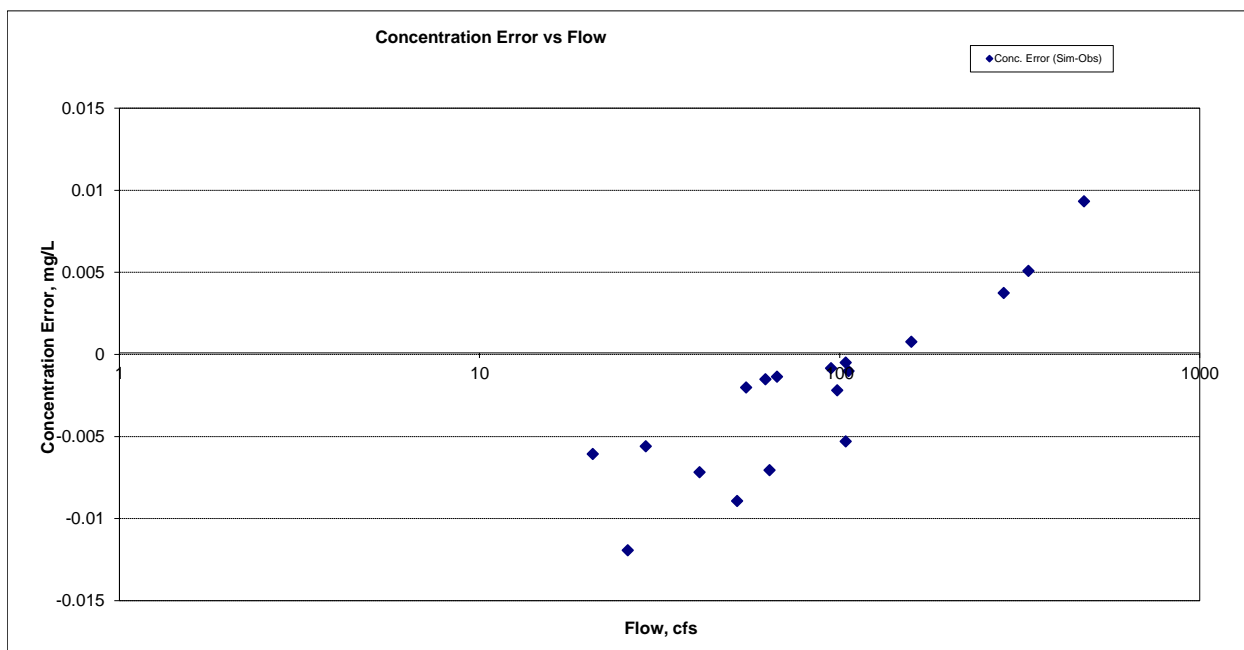
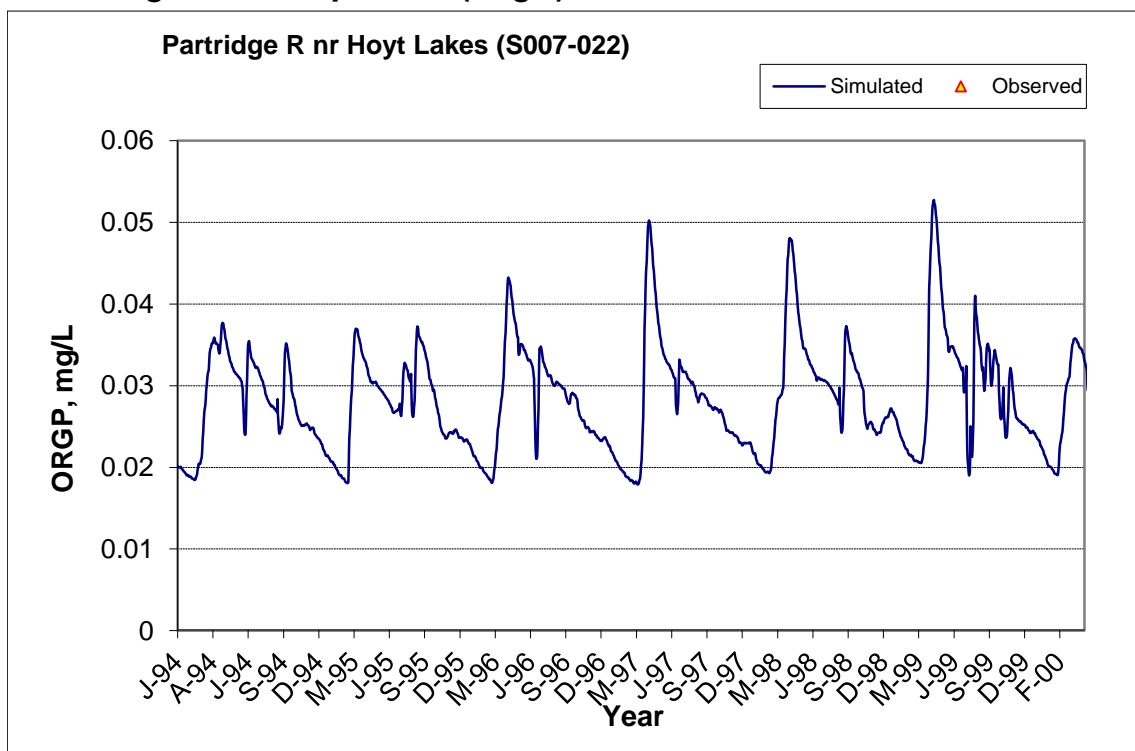


Figure A-14. Residual (Simulated - Observed) vs. Flow Soluble Reactive Phosphorus (SRP) at Partridge R nr Hoyt Lakes (S007-022)

A.1.7 Organic Phosphorus (OrgP)



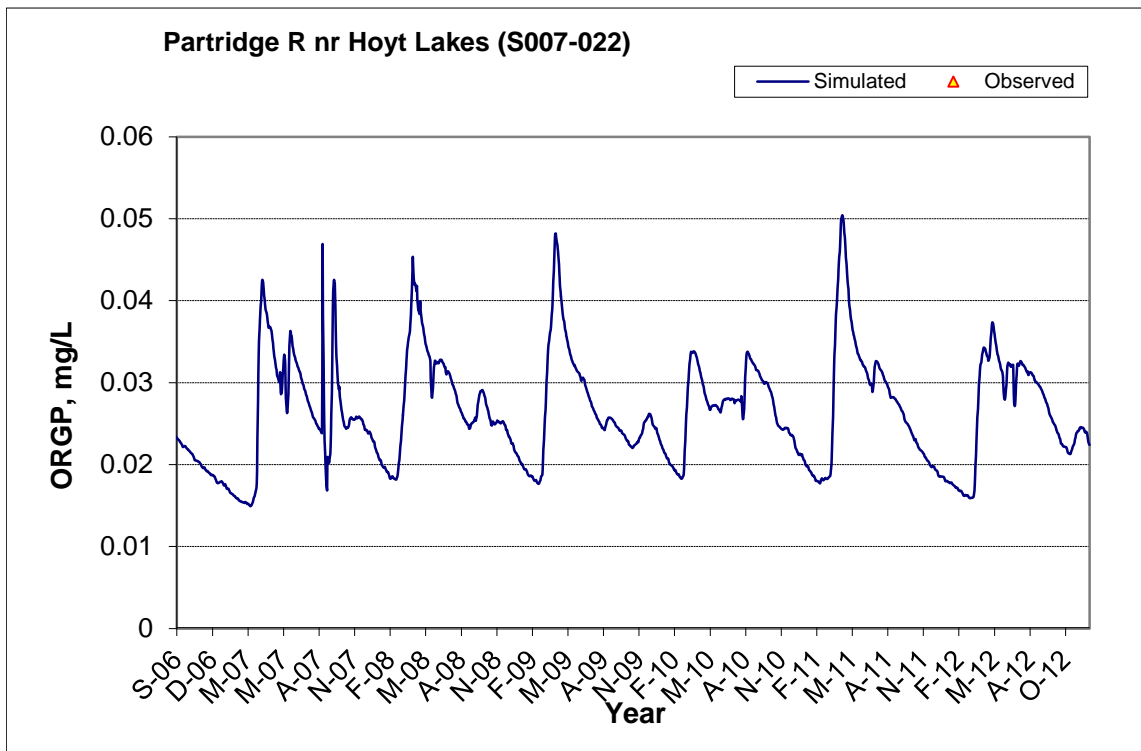
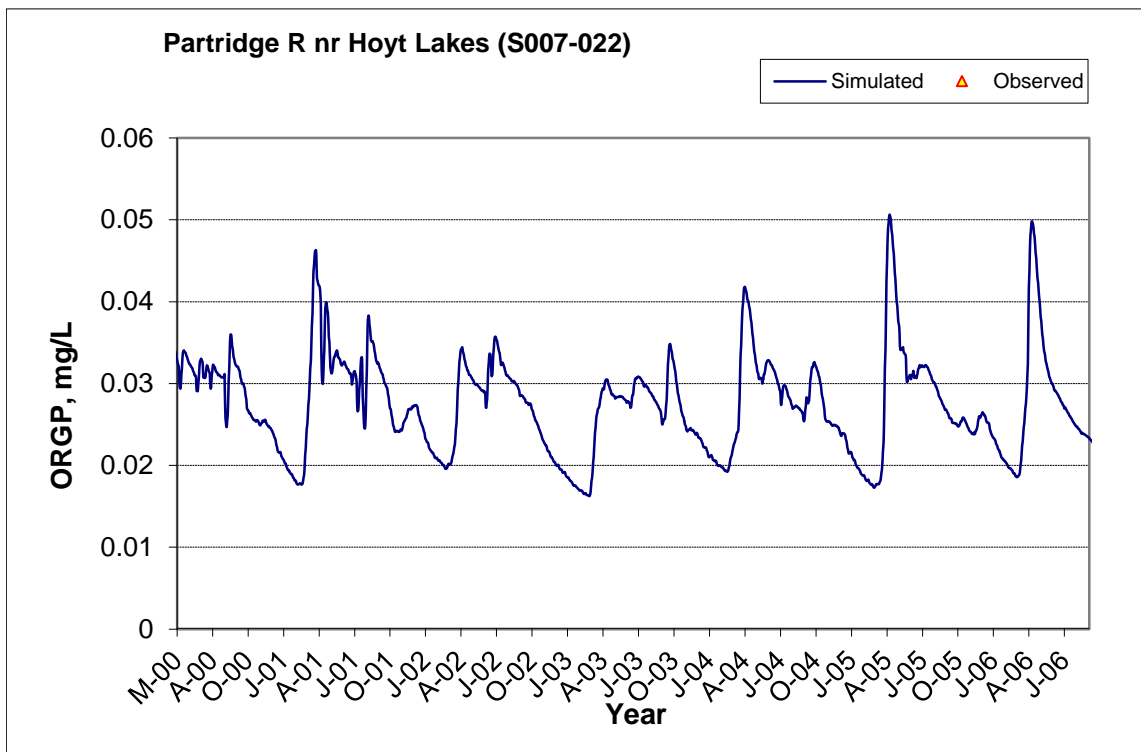


Figure A-15. Time series of observed and simulated Organic Phosphorus (OrgP) concentration at Partridge R nr Hoyt Lakes (S007-022)

A.1.8 Total Phosphorus (TP)

Table A-3. Total Phosphorus (TP) statistics

Period	1994-1993	1994-2012
Count	ND	18
Concentration Average Error		32.62%
Concentration Median Error		40.48%
Load Average Error		30.75%
Load Median Error		24.81%
Paired t conc		0.06
Paired t load		0.39

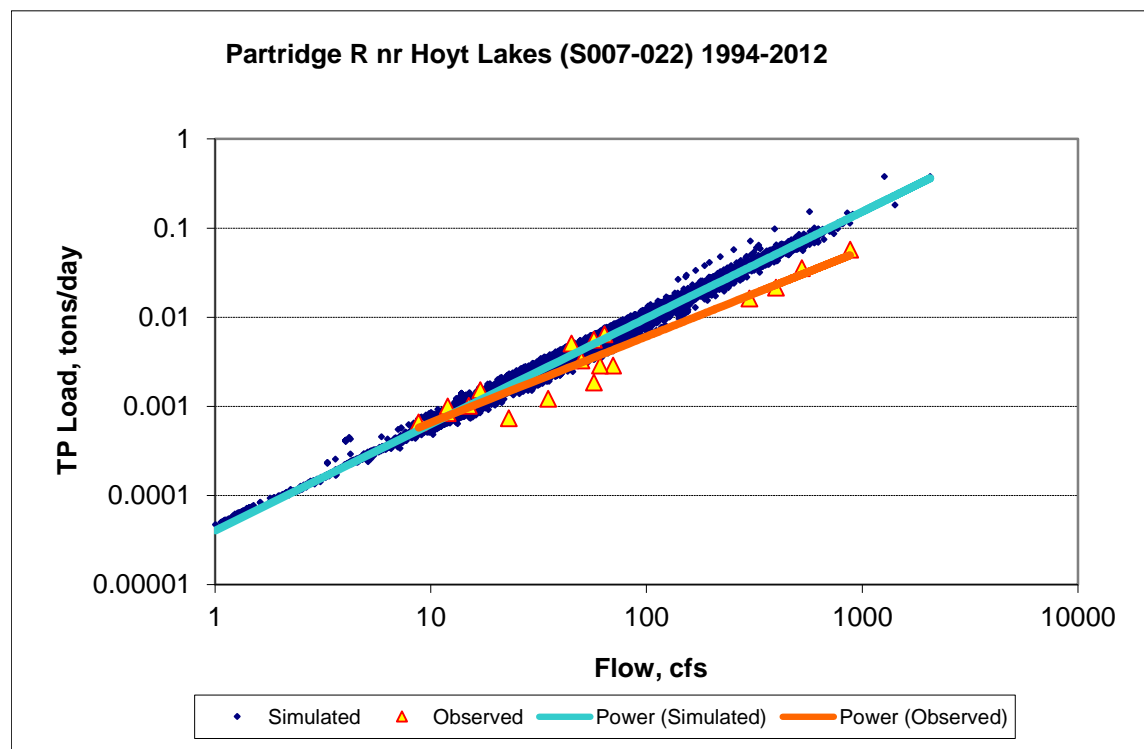
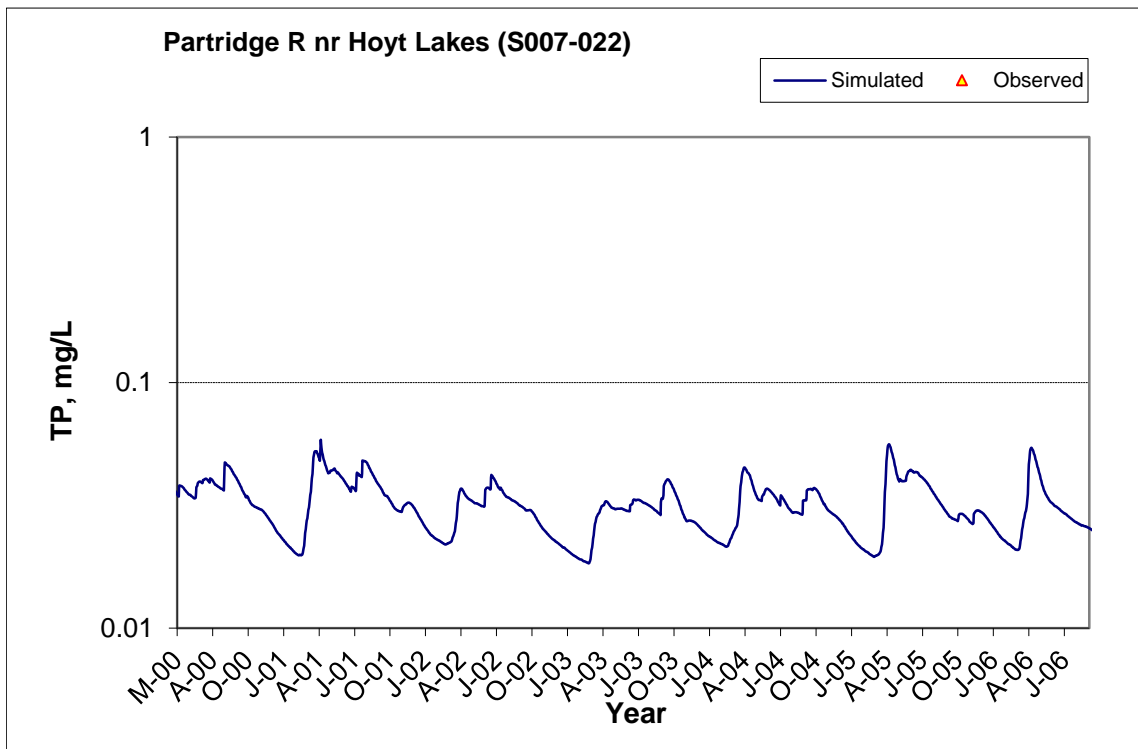
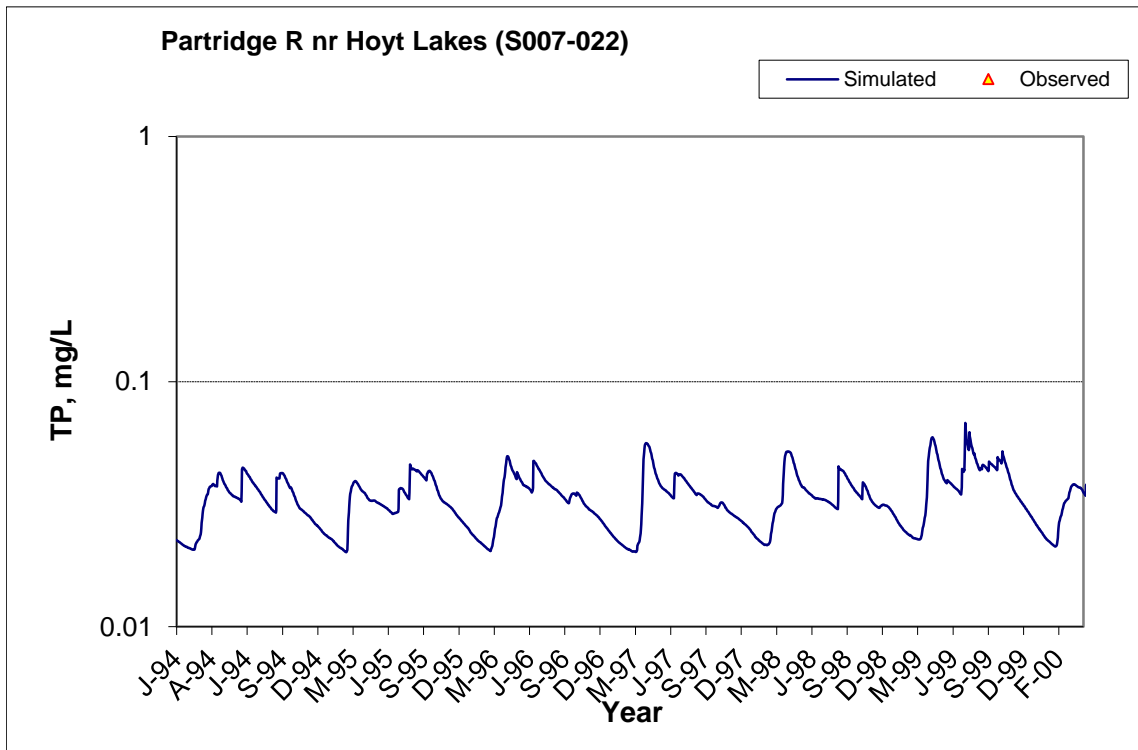


Figure A-16. Power plot of simulated and observed Total Phosphorus (TP) load vs flow at Partridge R nr Hoyt Lakes (S007-022) (calibration period)



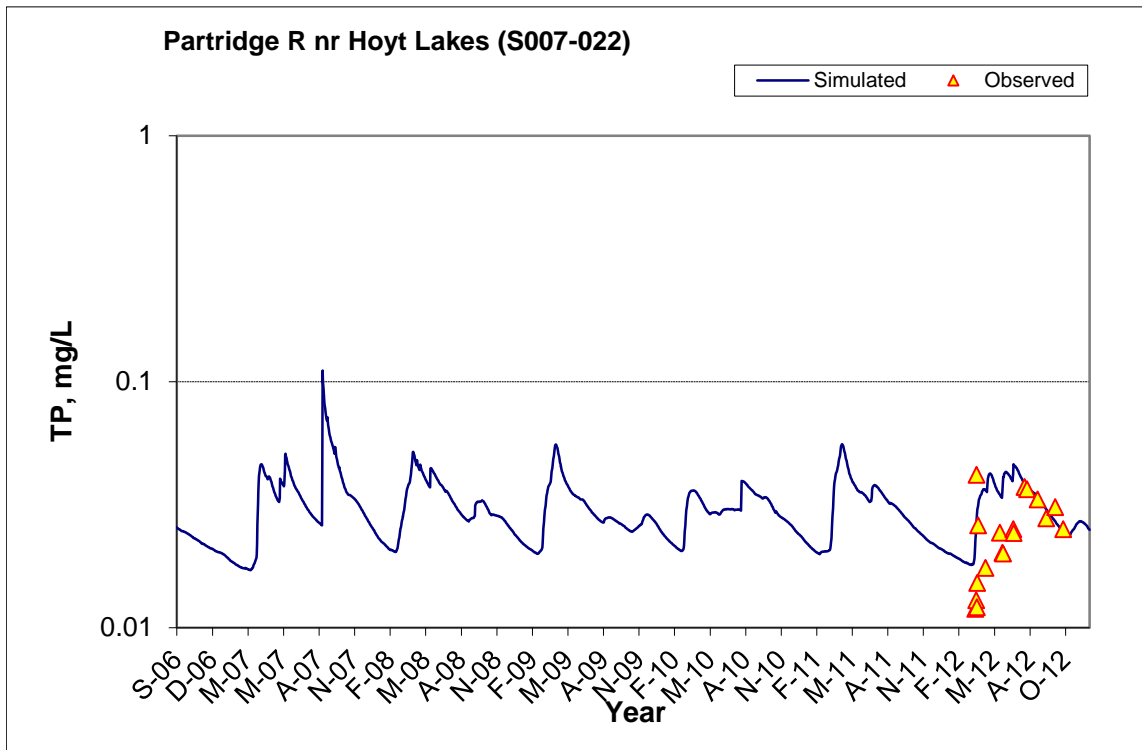


Figure A-17. Time series of observed and simulated Total Phosphorus (TP) concentration at Partridge R nr Hoyt Lakes (S007-022)

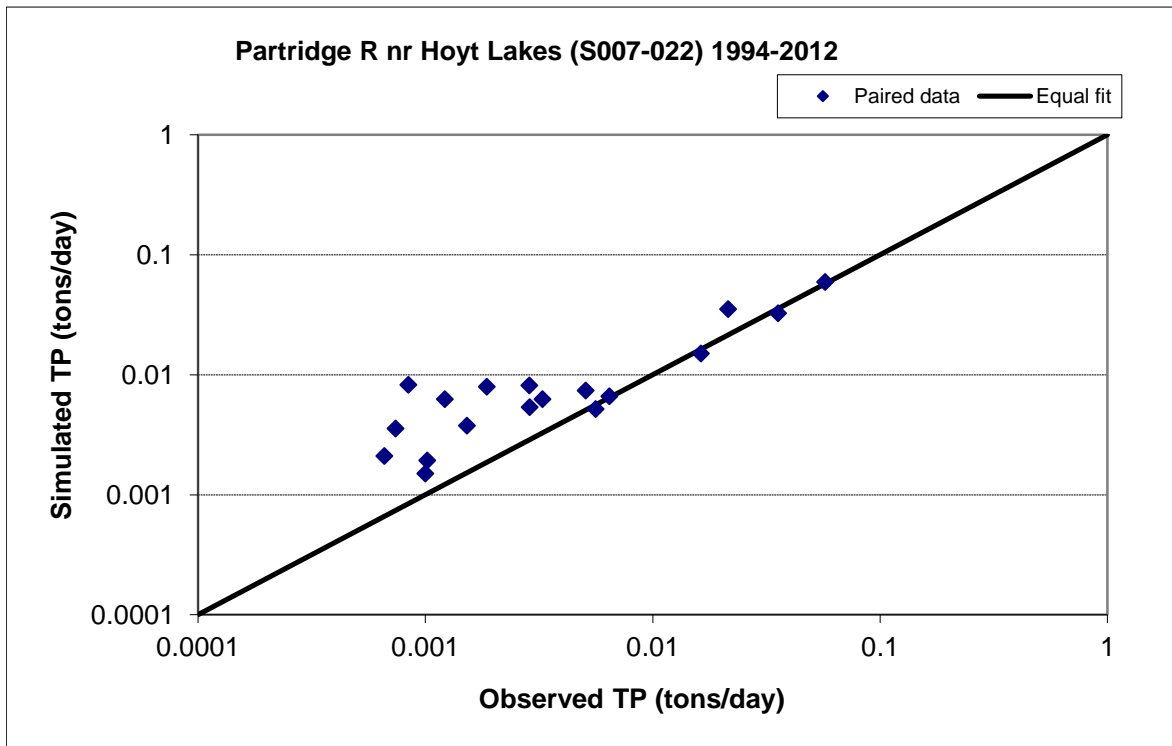


Figure A-18. Paired simulated vs. observed Total Phosphorus (TP) load at Partridge R nr Hoyt Lakes (S007-022) (calibration period)

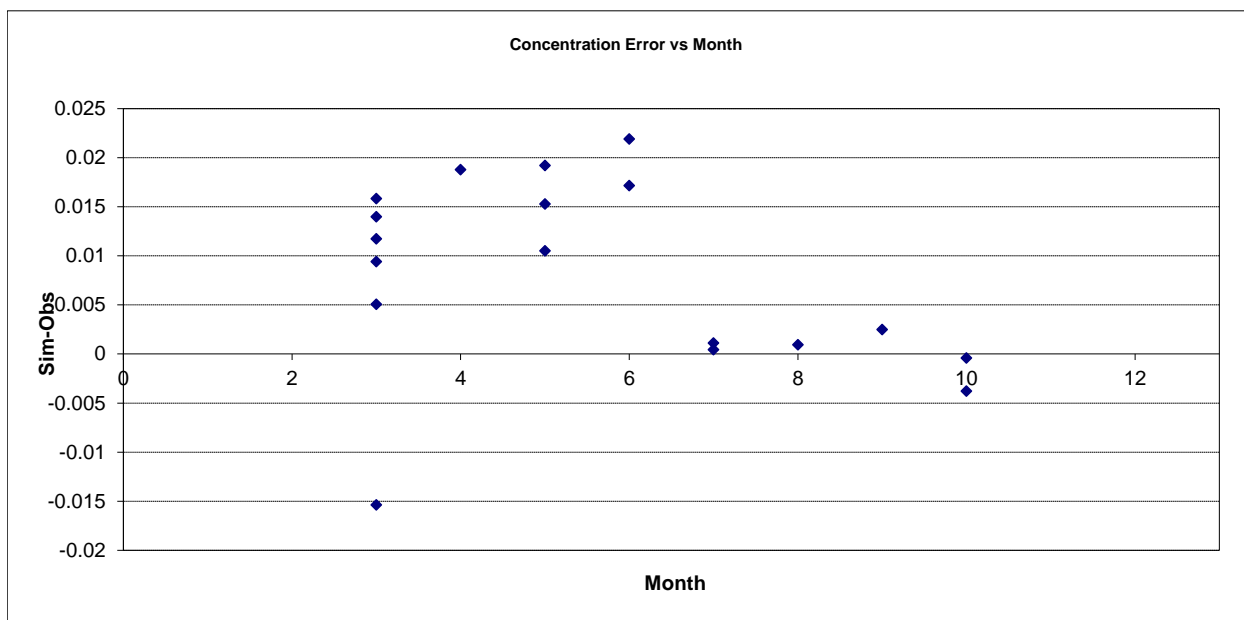


Figure A-19. Residual (Simulated - Observed) vs. Month Total Phosphorus (TP) at Partridge R nr Hoyt Lakes (S007-022)

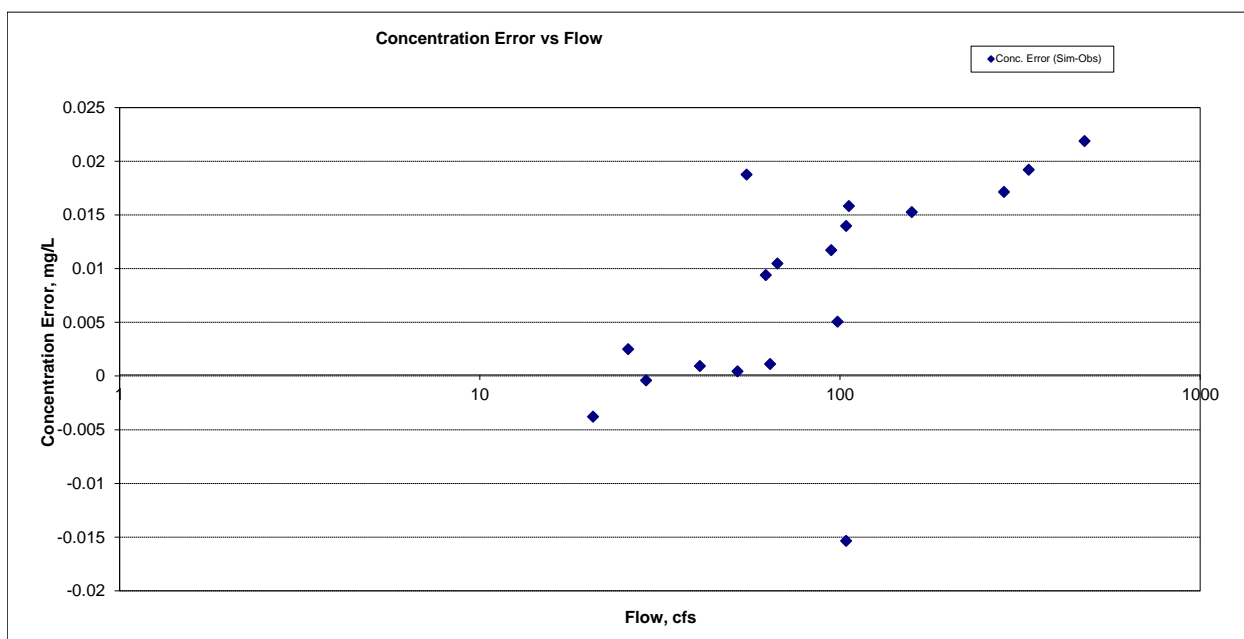
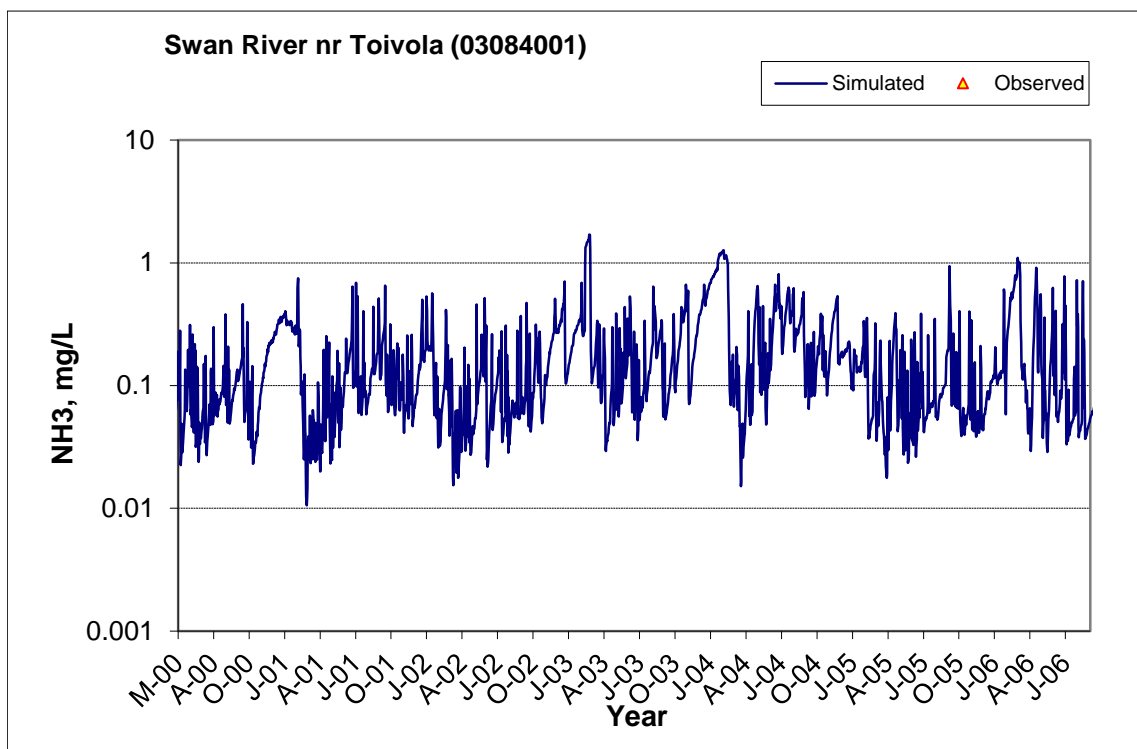
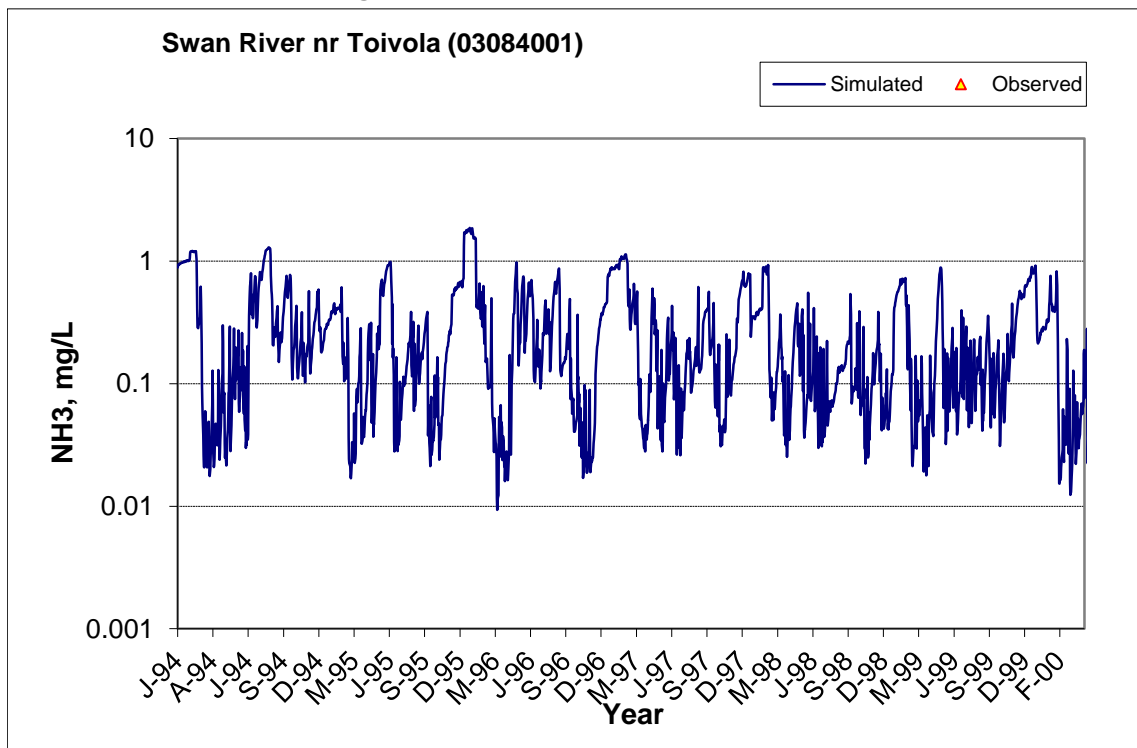


Figure A-20. Residual (Simulated - Observed) vs. Flow Total Phosphorus (TP) at Partridge R nr Hoyt Lakes (S007-022)

A.2 SWAN RIVER NR TOIVOLA (03084001)

A.2.1 Ammonia Nitrogen (NH₃)



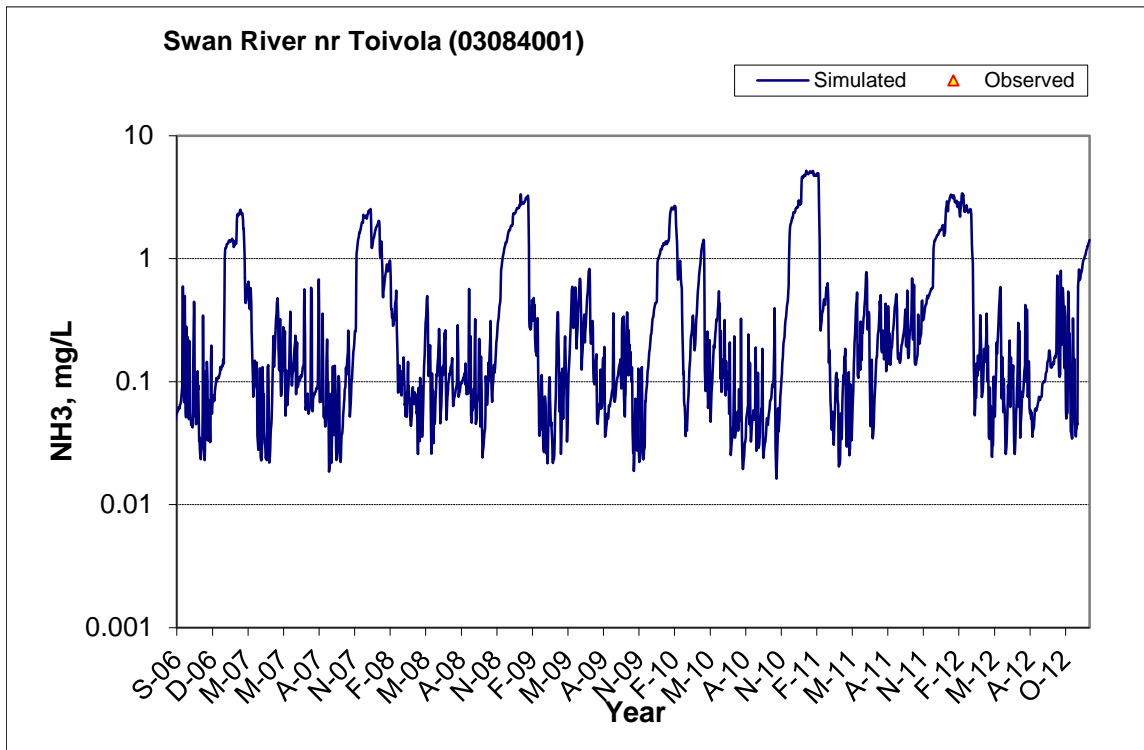
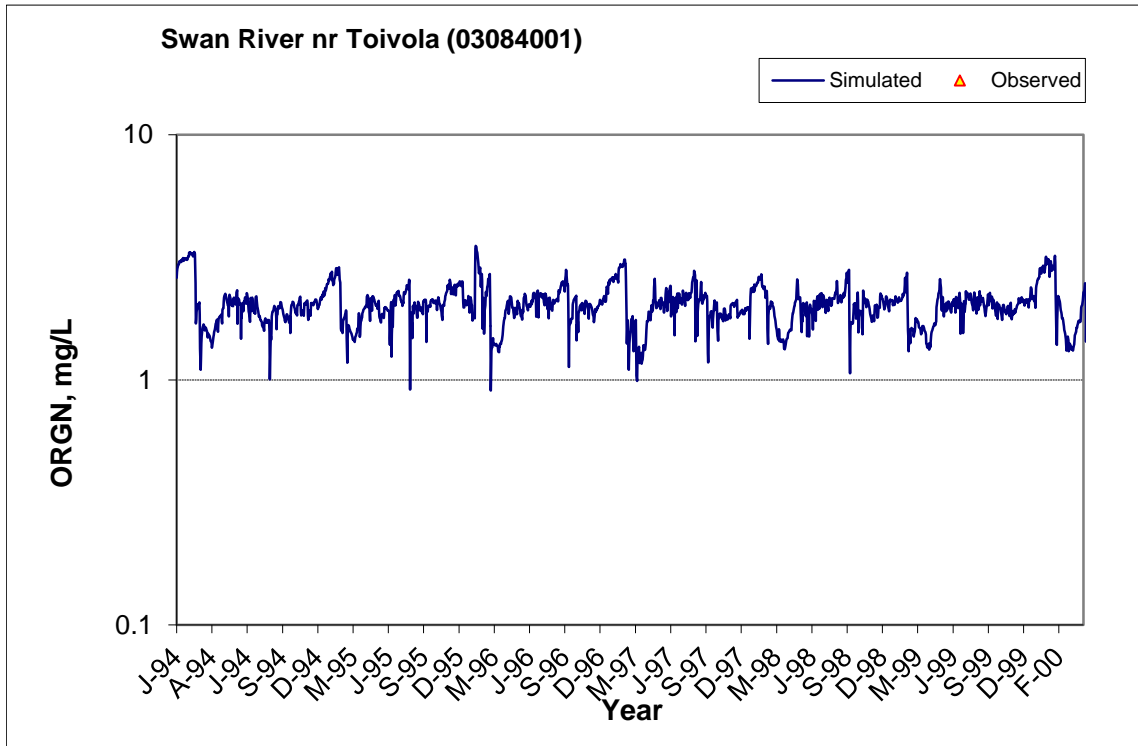


Figure A-21. Time series of observed and simulated Ammonia Nitrogen (NH3) concentration at Swan River nr Toivola (03084001)

A.2.2 Organic Nitrogen (OrgN)



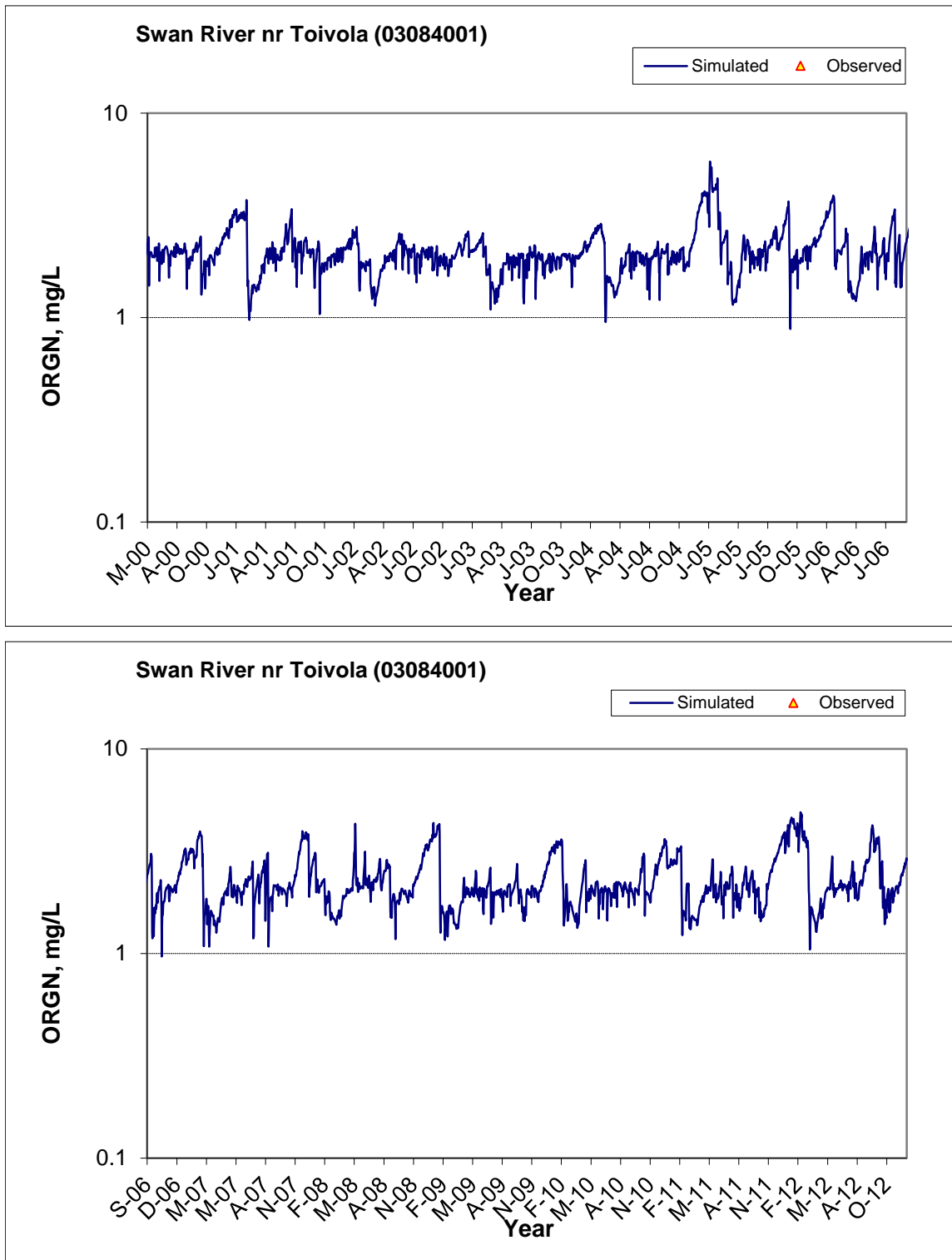
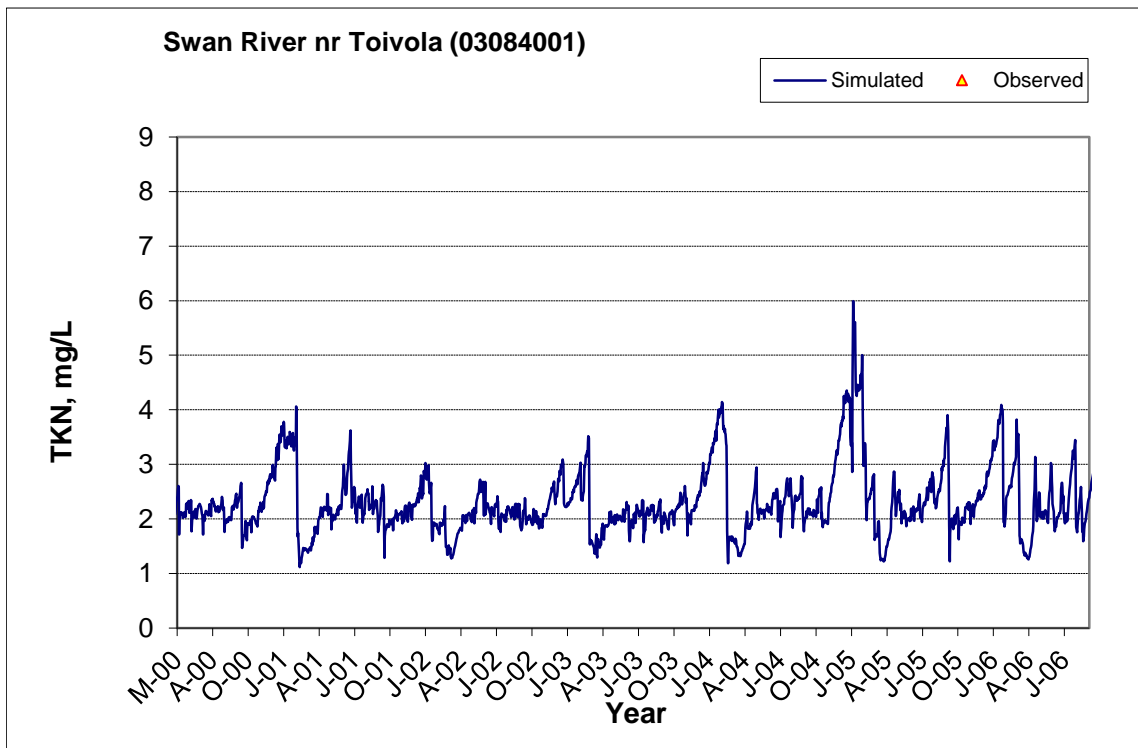
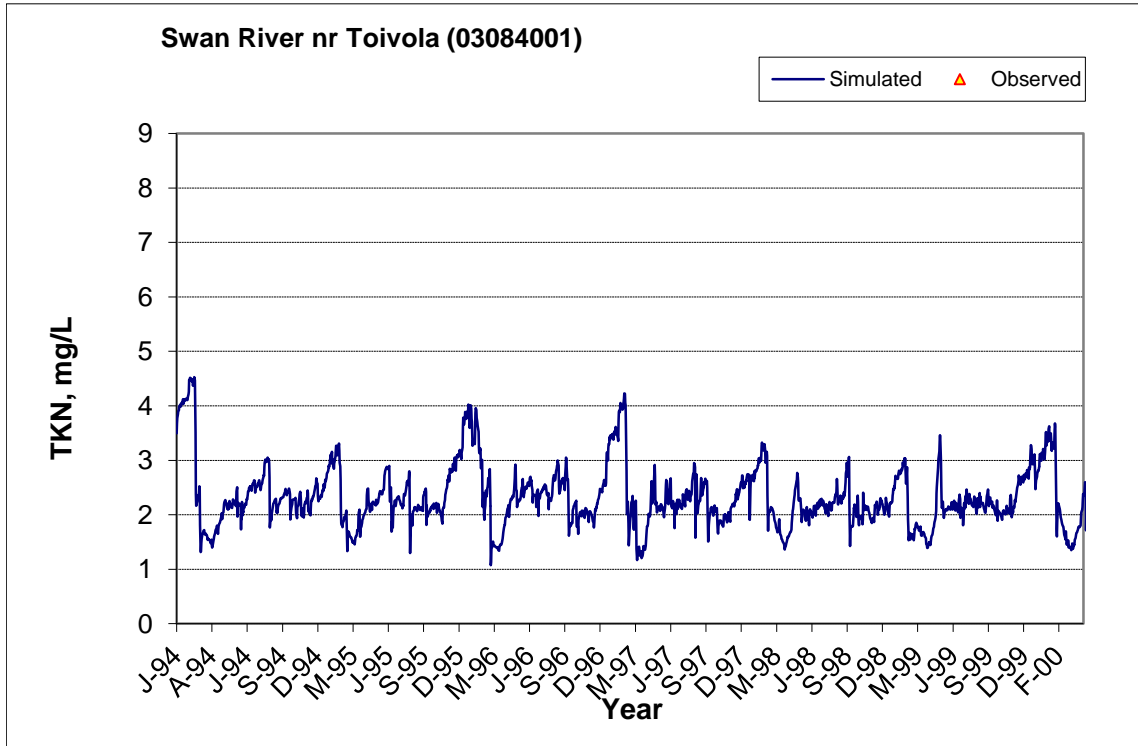


Figure A-22. Time series of observed and simulated Organic Nitrogen (OrgN) concentration at Swan River nr Toivola (03084001)

A.2.3 Total Kjeldahl Nitrogen (TKN)



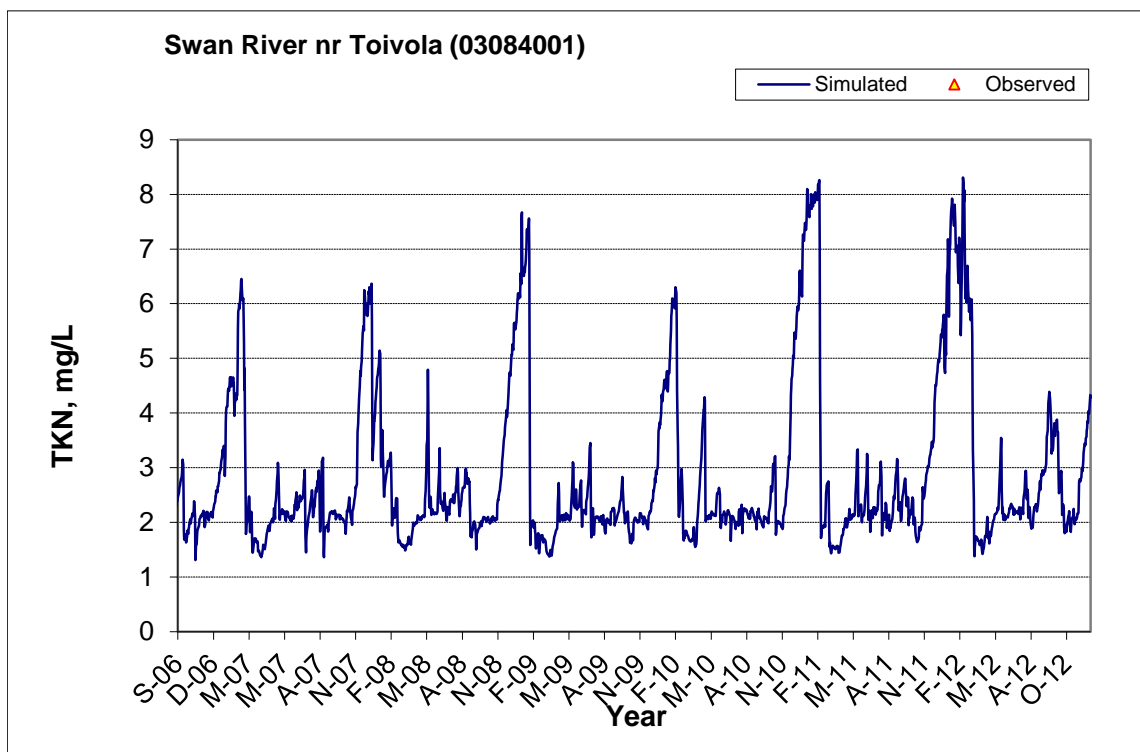


Figure A-23. Time series of observed and simulated Total Kjeldahl Nitrogen (TKN) concentration at Swan River nr Toivola (03084001)

A.2.4 Nitrite+ Nitrate Nitrogen (NOx)

Table A-4. Nitrite+ Nitrate Nitrogen (NOx) statistics

Period	1994-2001	2002-2012
Count	ND	22
Concentration Average Error		2.23%
Concentration Median Error		-7.35%
Load Average Error		-55.24%
Load Median Error		-48.10%
Paired t conc		0.78
Paired t load		0.00

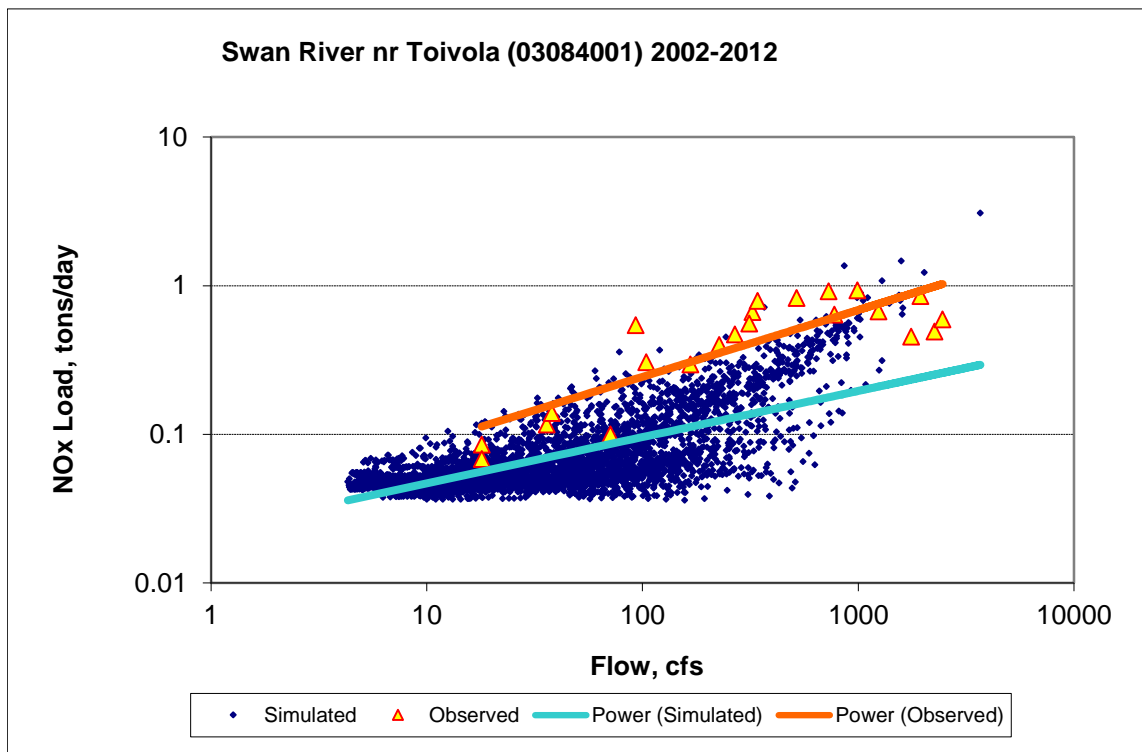
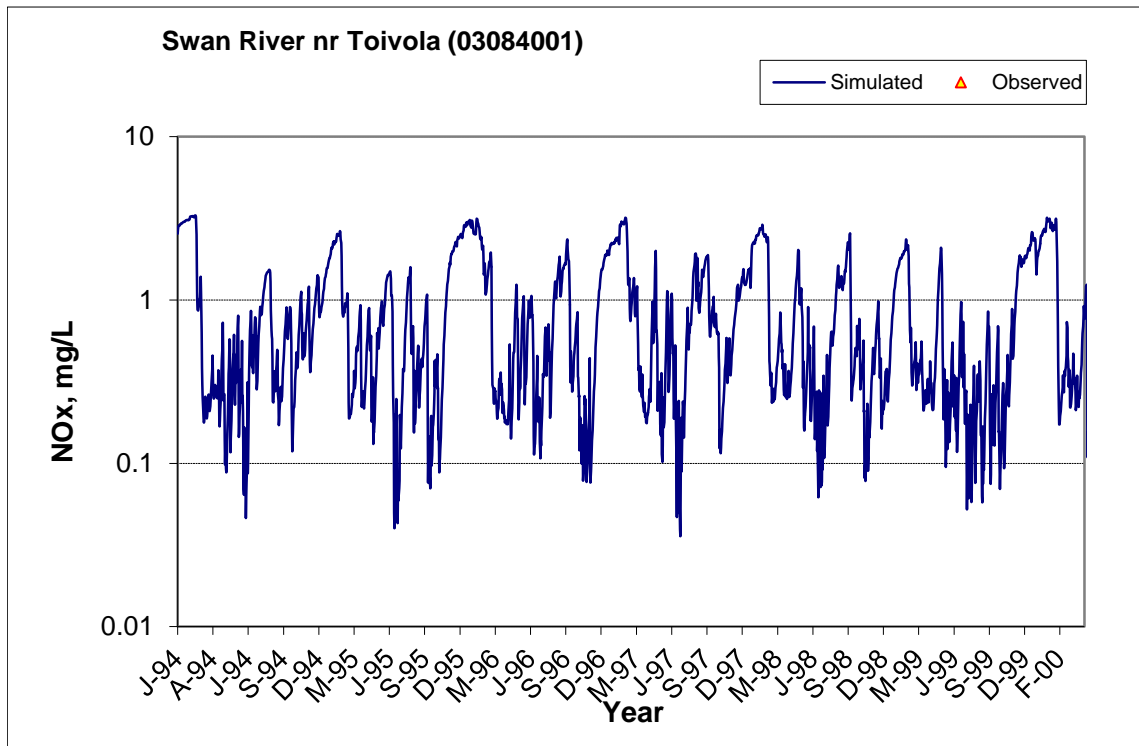


Figure A-24. Power plot of simulated and observed Nitrite+ Nitrate Nitrogen (NOx) load vs flow at Swan River nr Toivola (03084001) (calibration period)



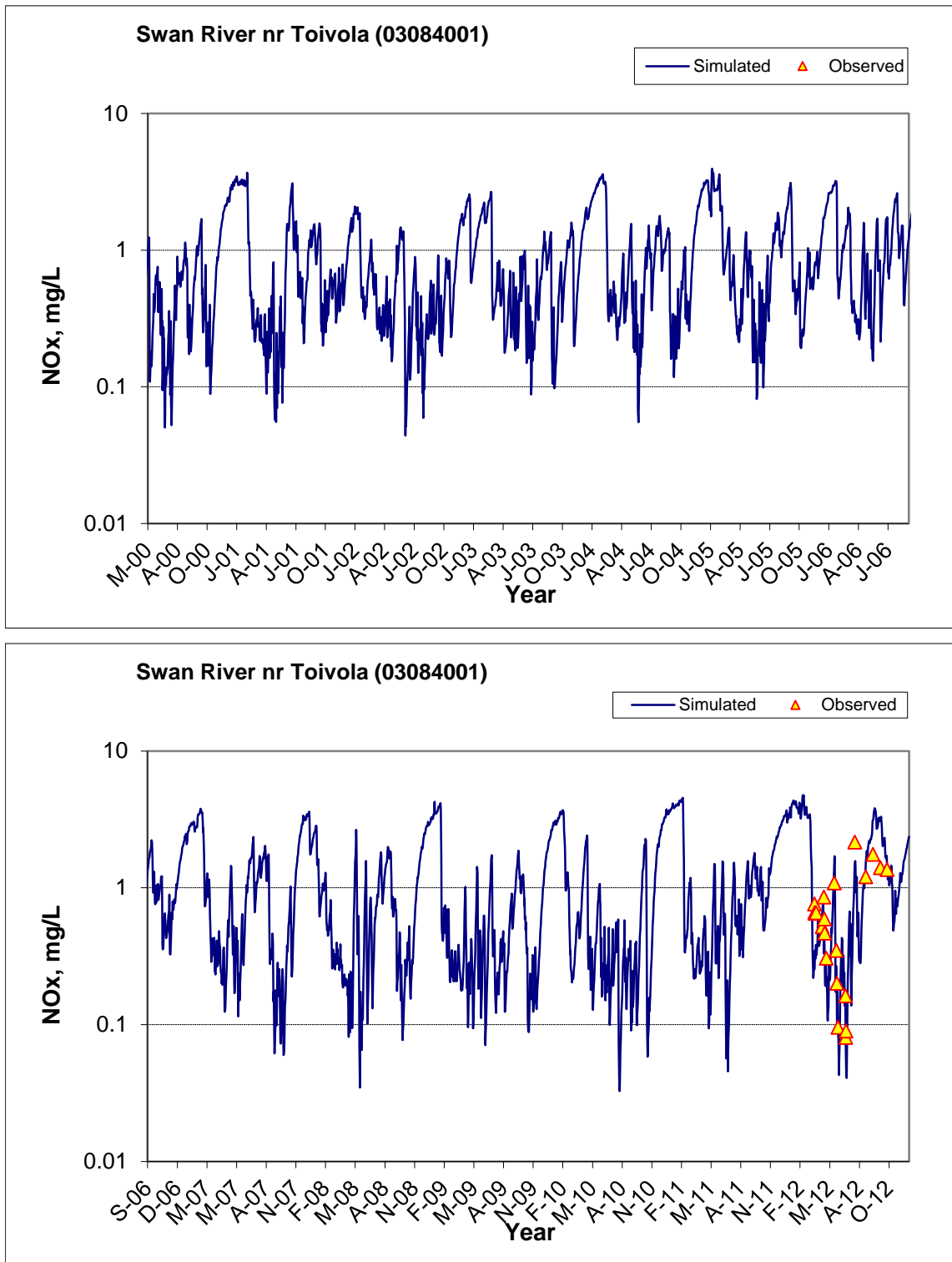


Figure A-25. Time series of observed and simulated Nitrite+ Nitrate Nitrogen (NOx) concentration at Swan River nr Toivola (03084001)

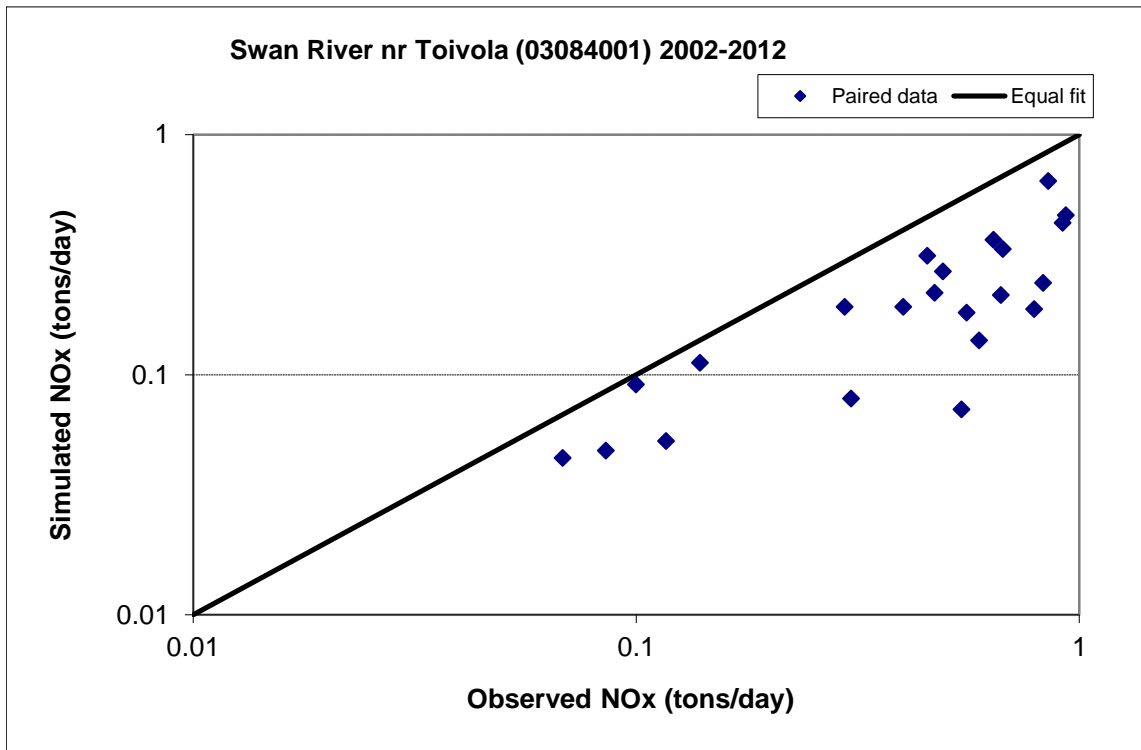


Figure A-26. Paired simulated vs. observed Nitrite+ Nitrate Nitrogen (NOx) load at Swan River nr Toivola (03084001) (calibration period)

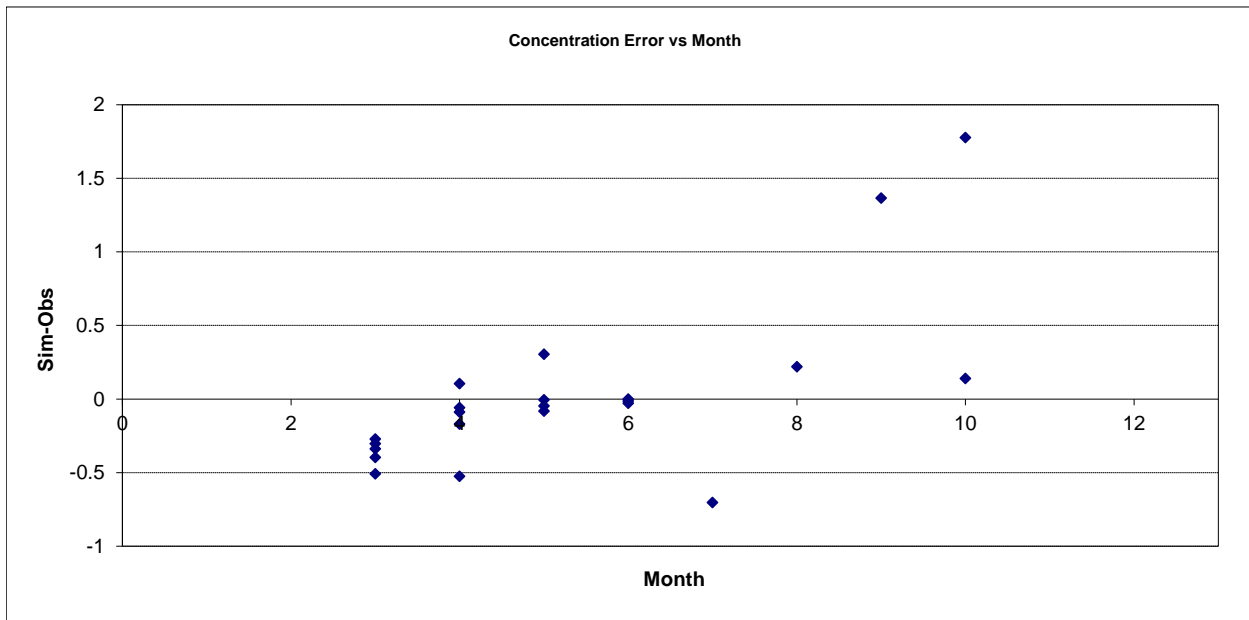


Figure A-27. Residual (Simulated - Observed) vs. Month Nitrite+ Nitrate Nitrogen (NOx) at Swan River nr Toivola (03084001)

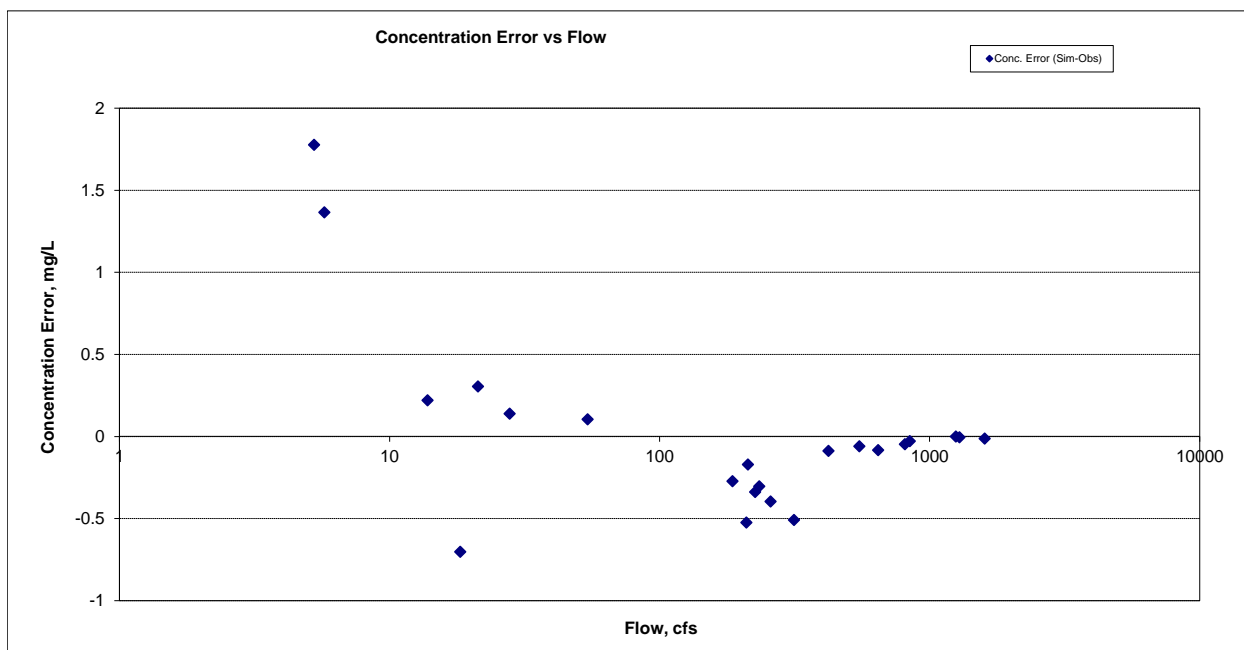
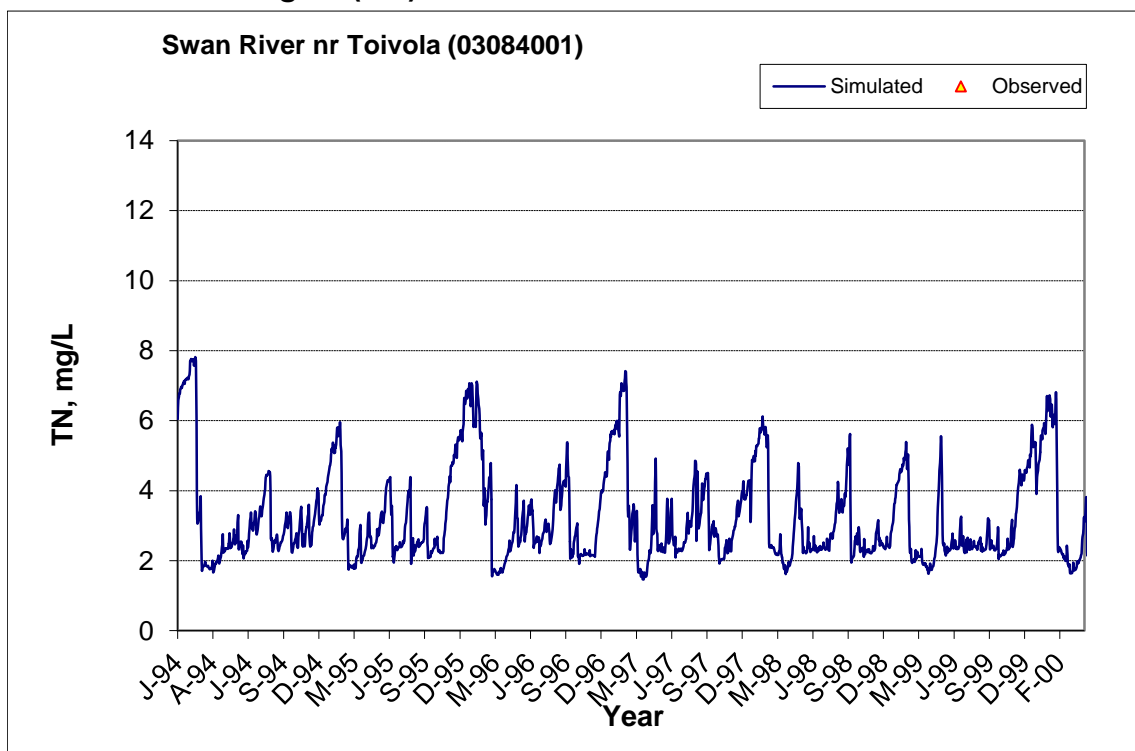


Figure A-28. Residual (Simulated - Observed) vs. Flow Nitrite+ Nitrate Nitrogen (NOx) at Swan River nr Toivola (03084001)

A.2.5 Total Nitrogen (TN)



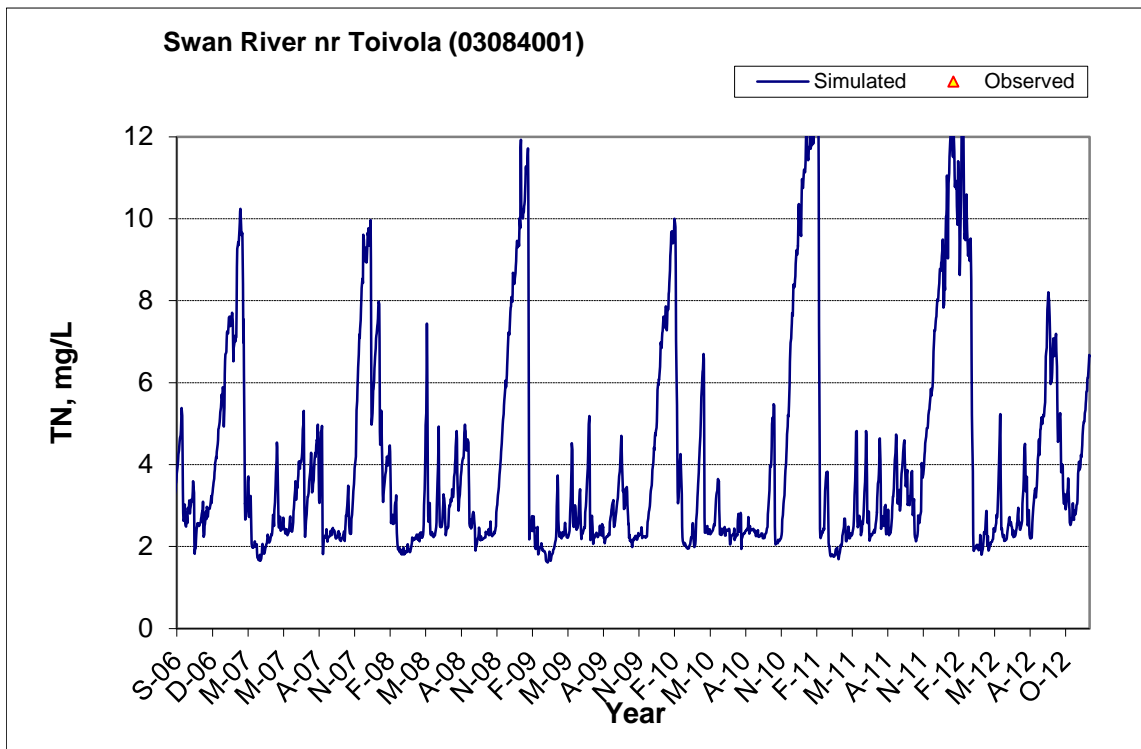
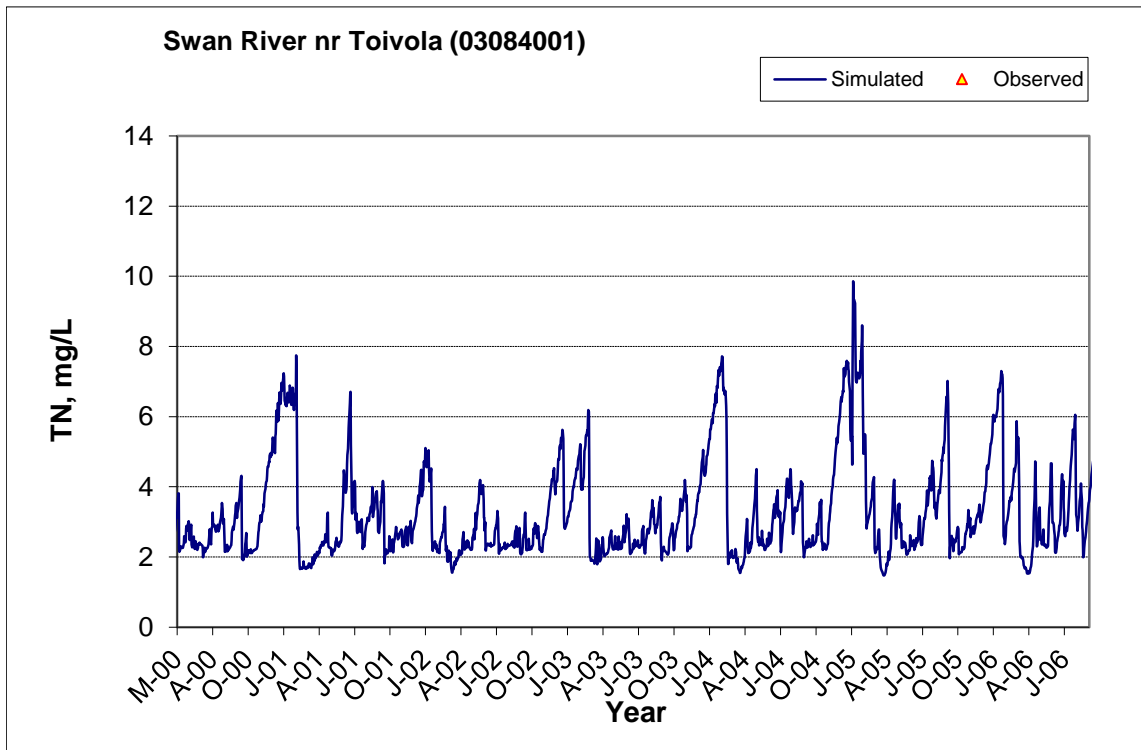


Figure A-29. Time series of observed and simulated Total Nitrogen (TN) concentration at Swan River nr Toivola (03084001)

A.2.6 Soluble Reactive Phosphorus (SRP)

Table A-5. Soluble Reactive Phosphorus (SRP) statistics

Period	1994-2001	2002-2012
Count	ND	22
Concentration Average Error		50.97%
Concentration Median Error		38.04%
Load Average Error		12.25%
Load Median Error		-6.51%
Paired t conc		0.07
Paired t load		0.57

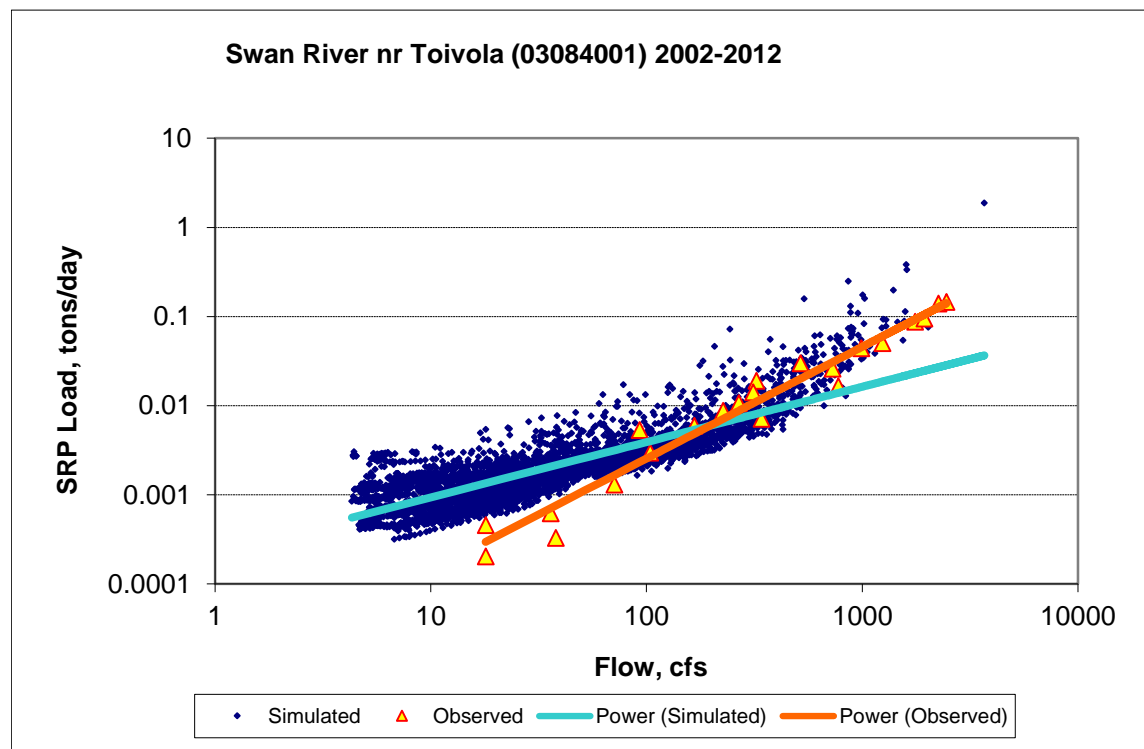
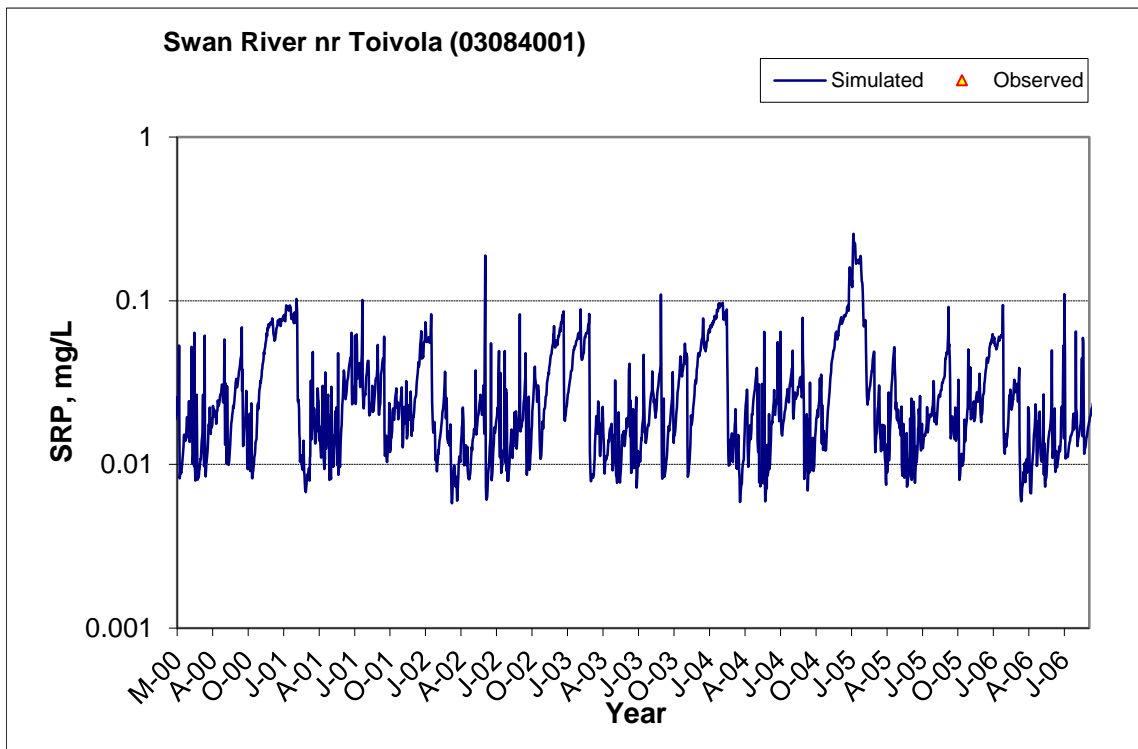
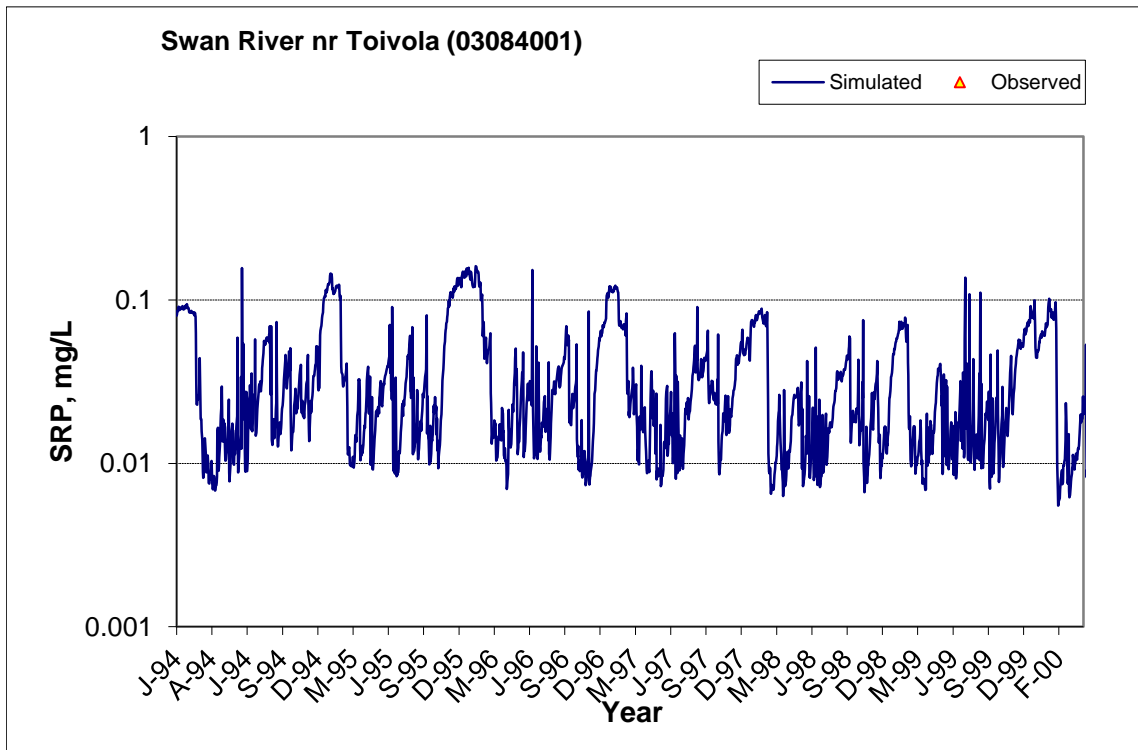


Figure A-30. Power plot of simulated and observed Soluble Reactive Phosphorus (SRP) load vs flow at Swan River nr Toivola (03084001) (calibration period)



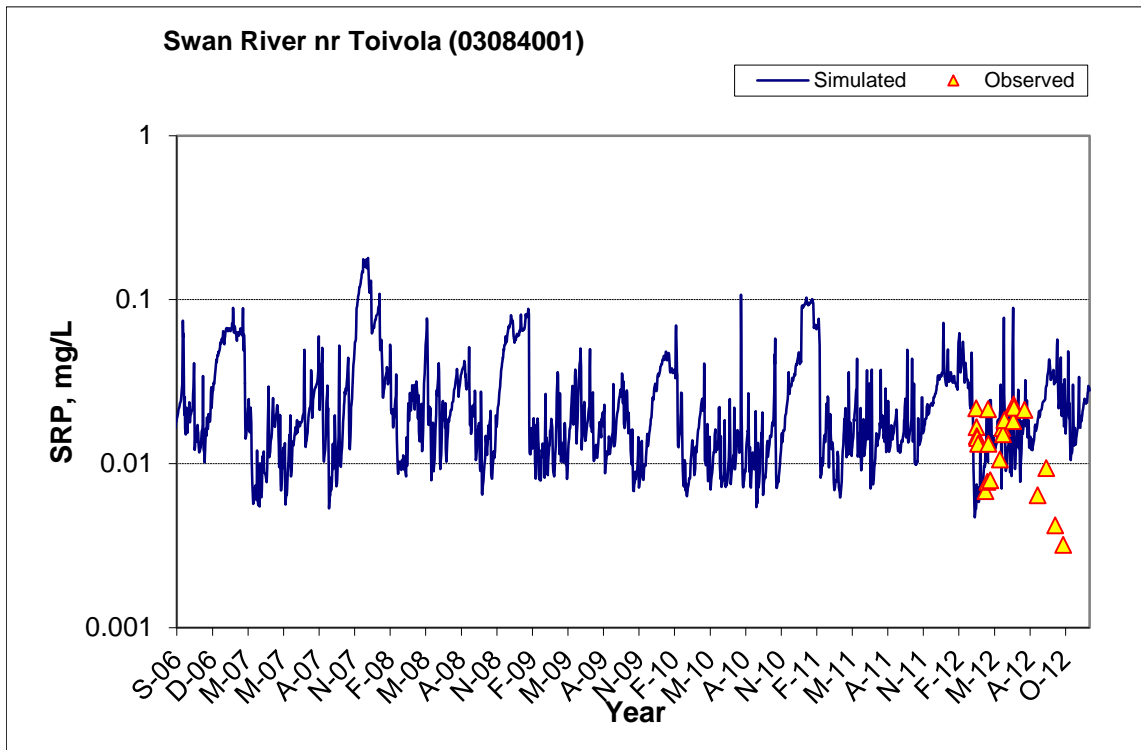


Figure A-31. Time series of observed and simulated Soluble Reactive Phosphorus (SRP) concentration at Swan River nr Toivola (03084001)

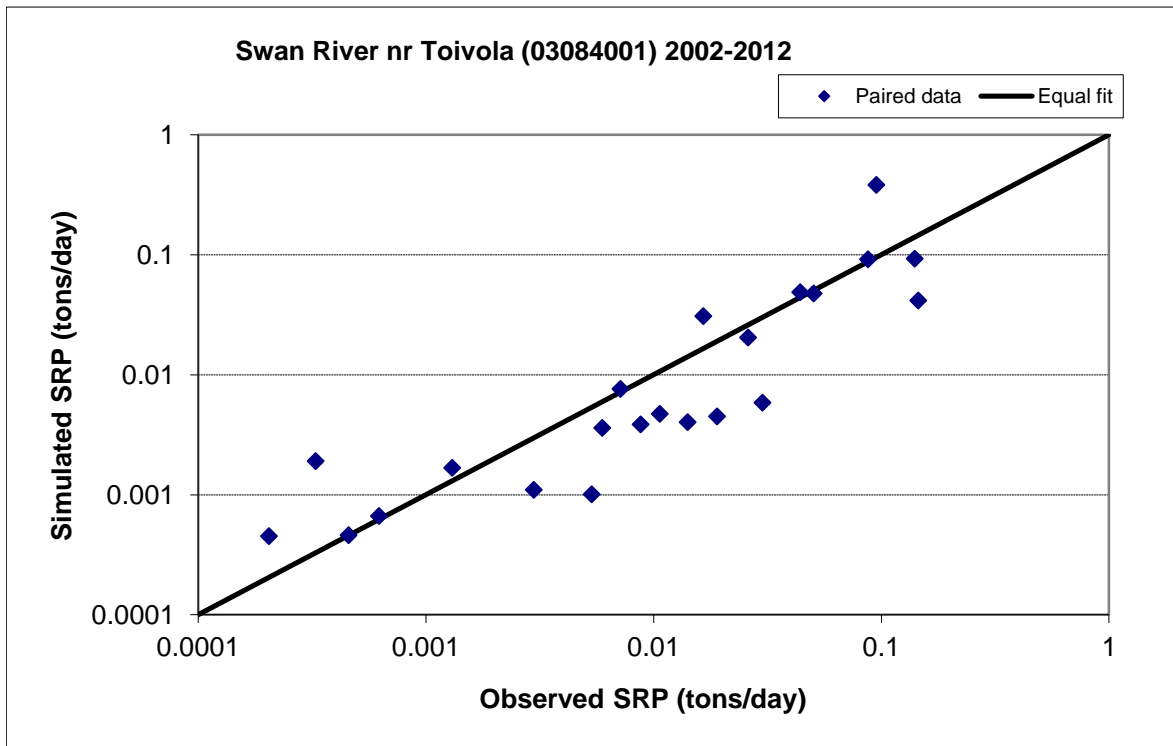


Figure A-32. Paired simulated vs. observed Soluble Reactive Phosphorus (SRP) load at Swan River nr Toivola (03084001) (calibration period)

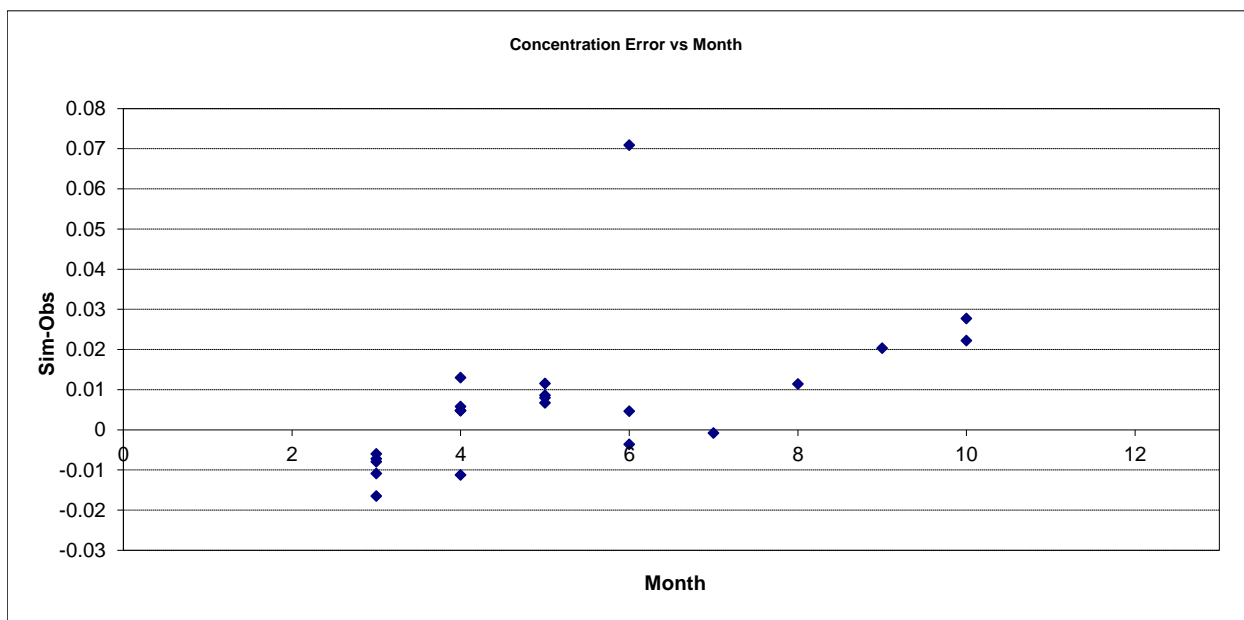


Figure A-33. Residual (Simulated - Observed) vs. Month Soluble Reactive Phosphorus (SRP) at Swan River nr Toivola (03084001)

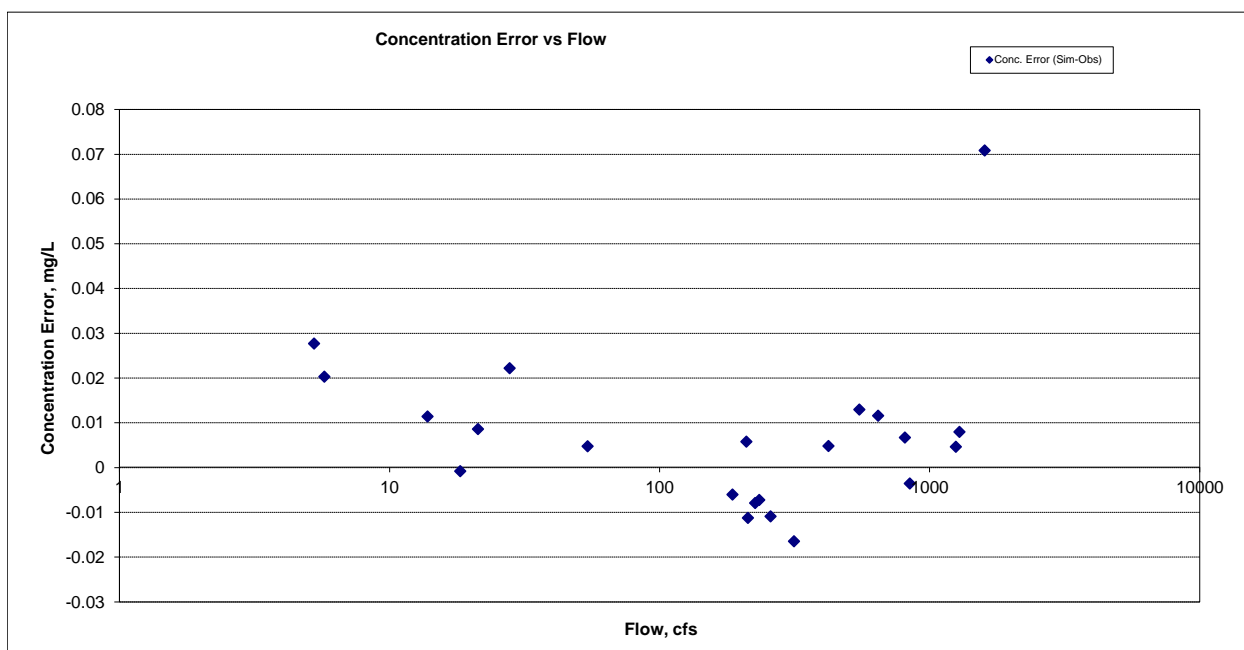
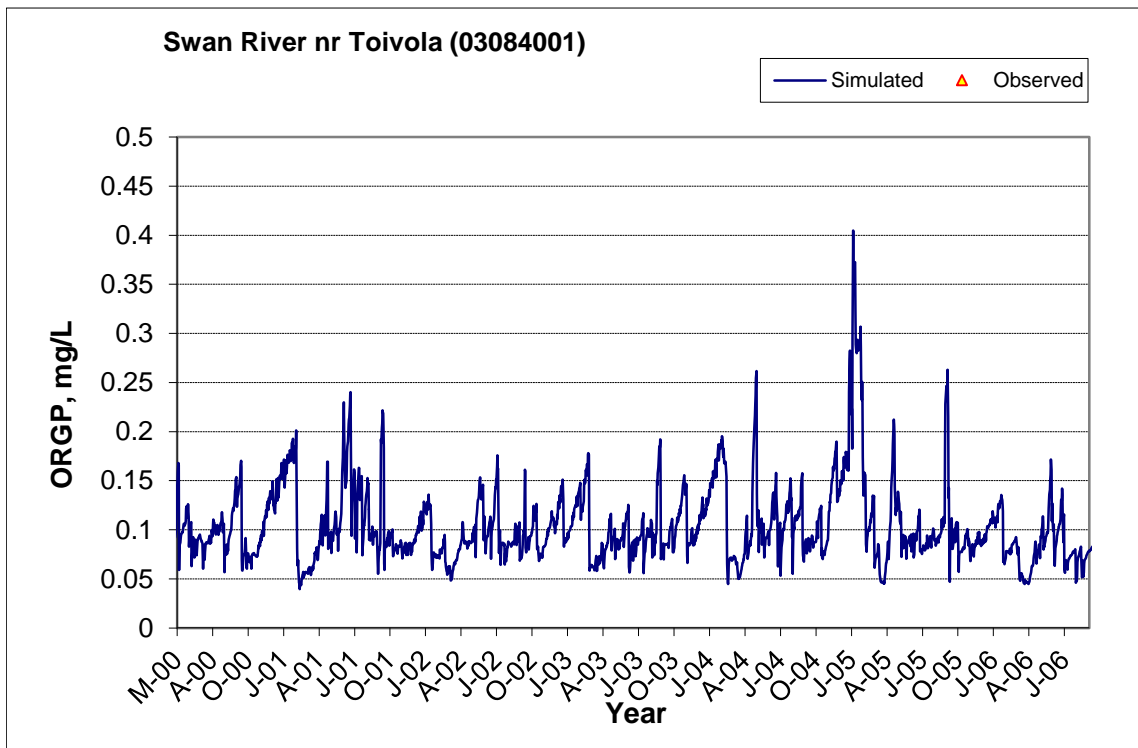
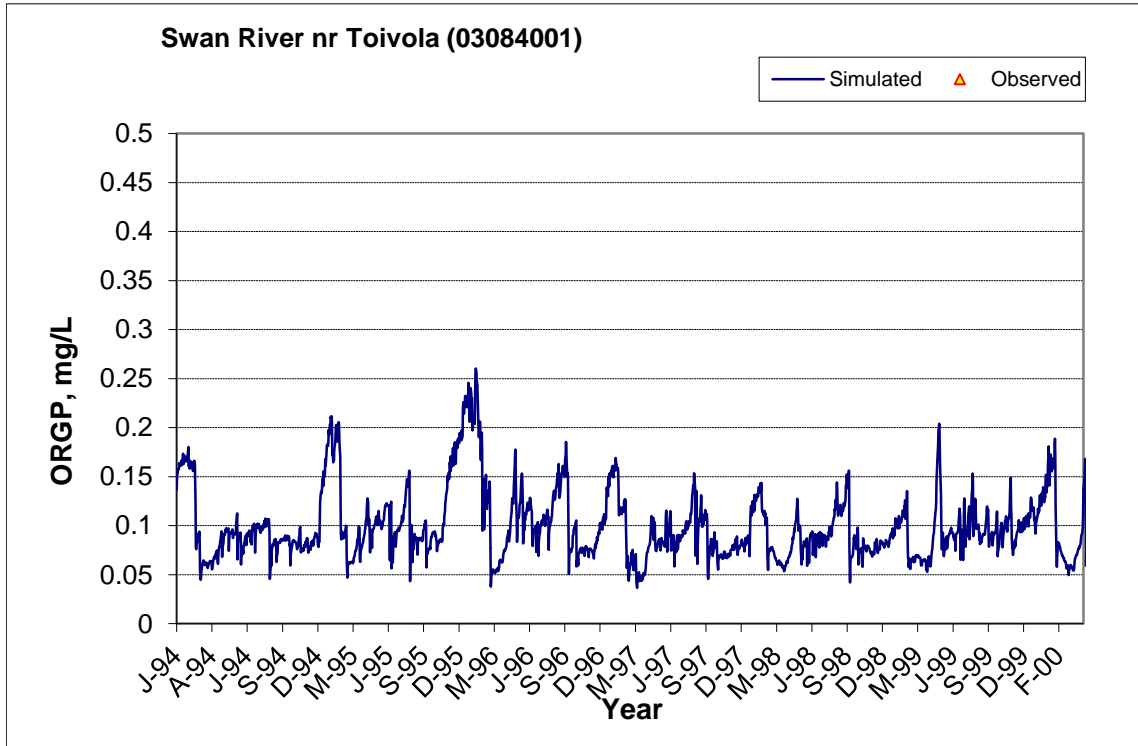


Figure A-34. Residual (Simulated - Observed) vs. Flow Soluble Reactive Phosphorus (SRP) at Swan River nr Toivola (03084001)

A.2.7 Organic Phosphorus (OrgP)



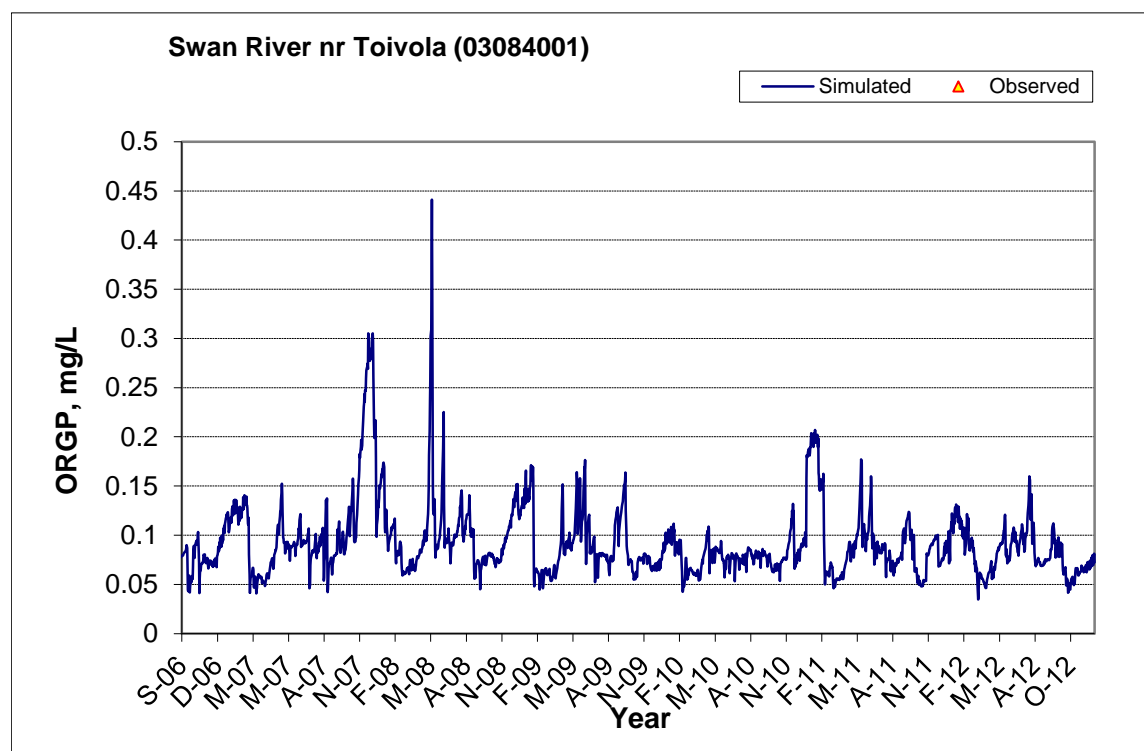


Figure A-35. Time series of observed and simulated Organic Phosphorus (OrgP) concentration at Swan River nr Toivola (03084001)

A.2.8 Total Phosphorus (TP)

Table A-6. Total Phosphorus (TP) statistics

Period	1994-2001	2002-2012
Count	ND	22
Concentration Average Error		18.07%
Concentration Median Error		-4.18%
Load Average Error		-41.22%
Load Median Error		-6.41%
Paired t conc		0.58
Paired t load		0.19

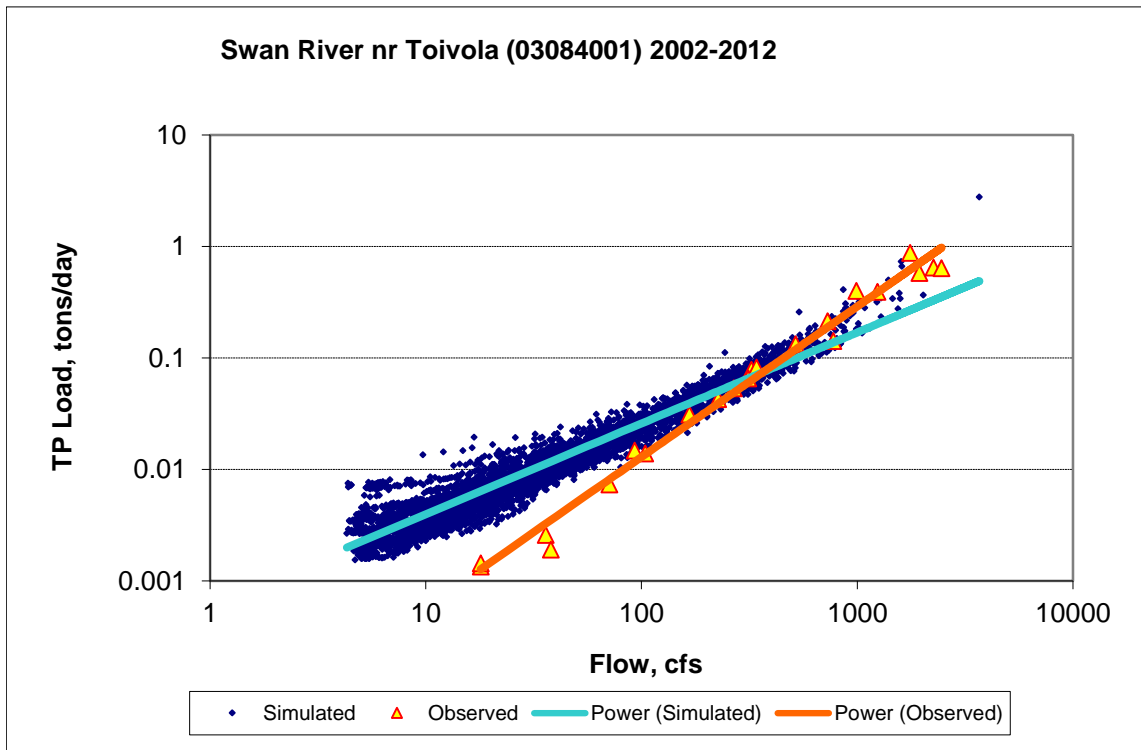
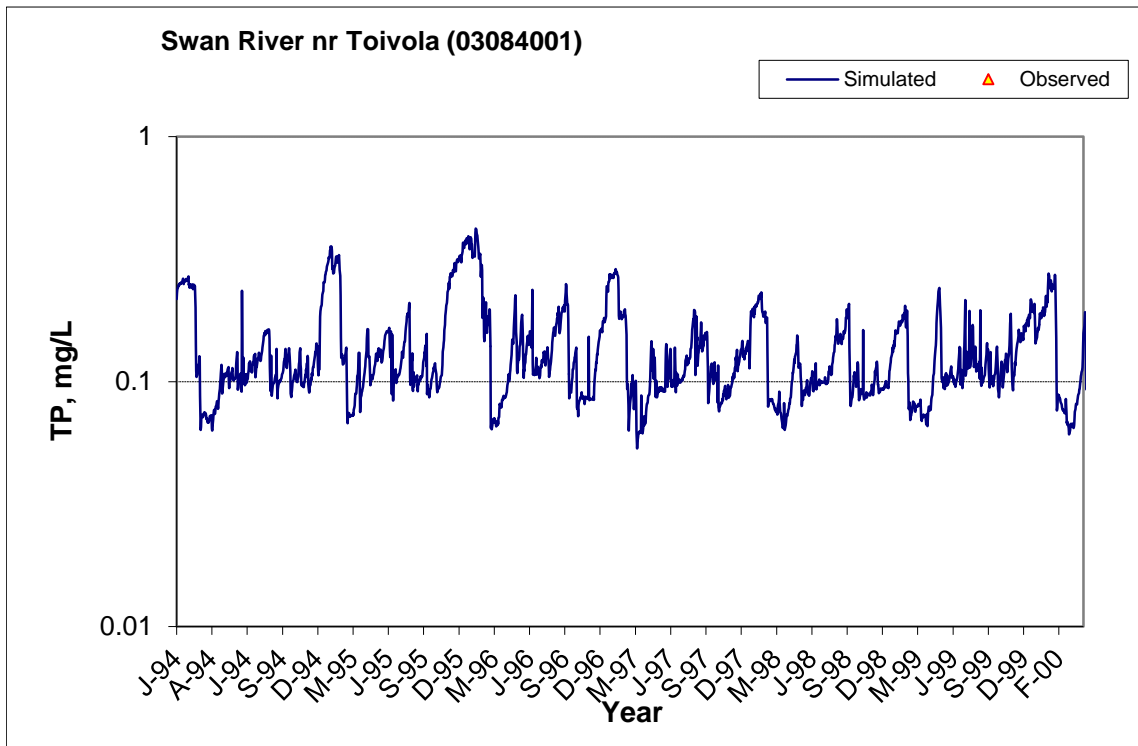


Figure A-36. Power plot of simulated and observed Total Phosphorus (TP) load vs flow at Swan River nr Toivola (03084001) (calibration period)



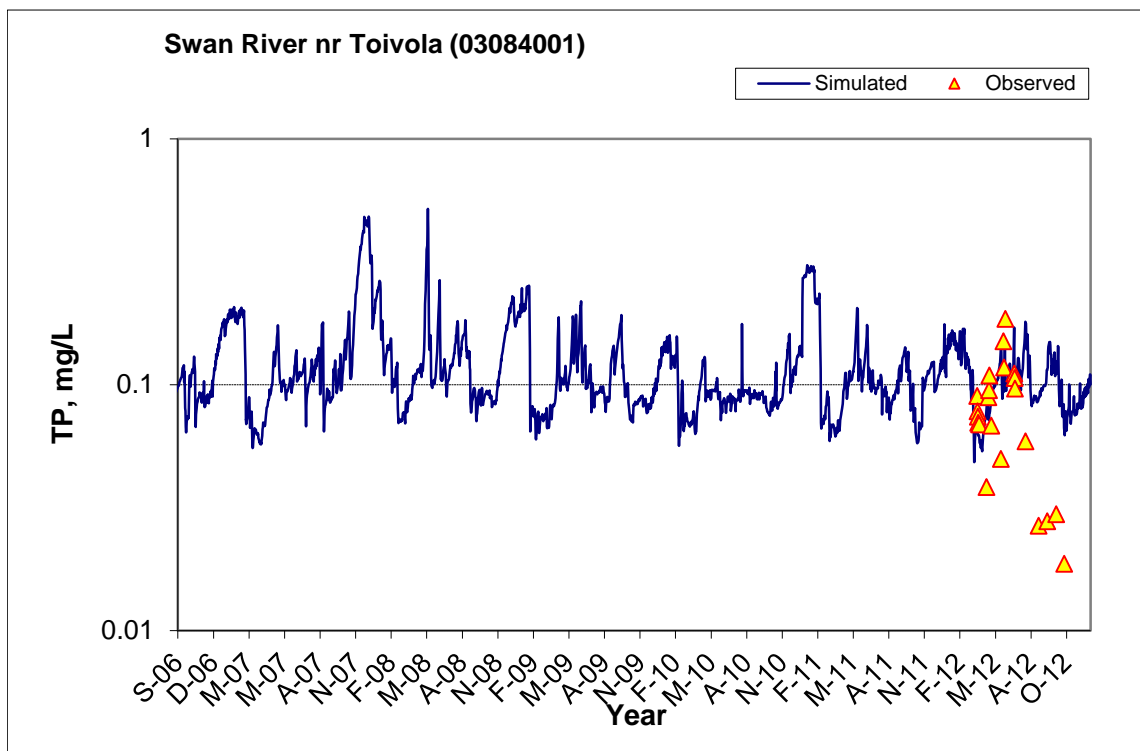
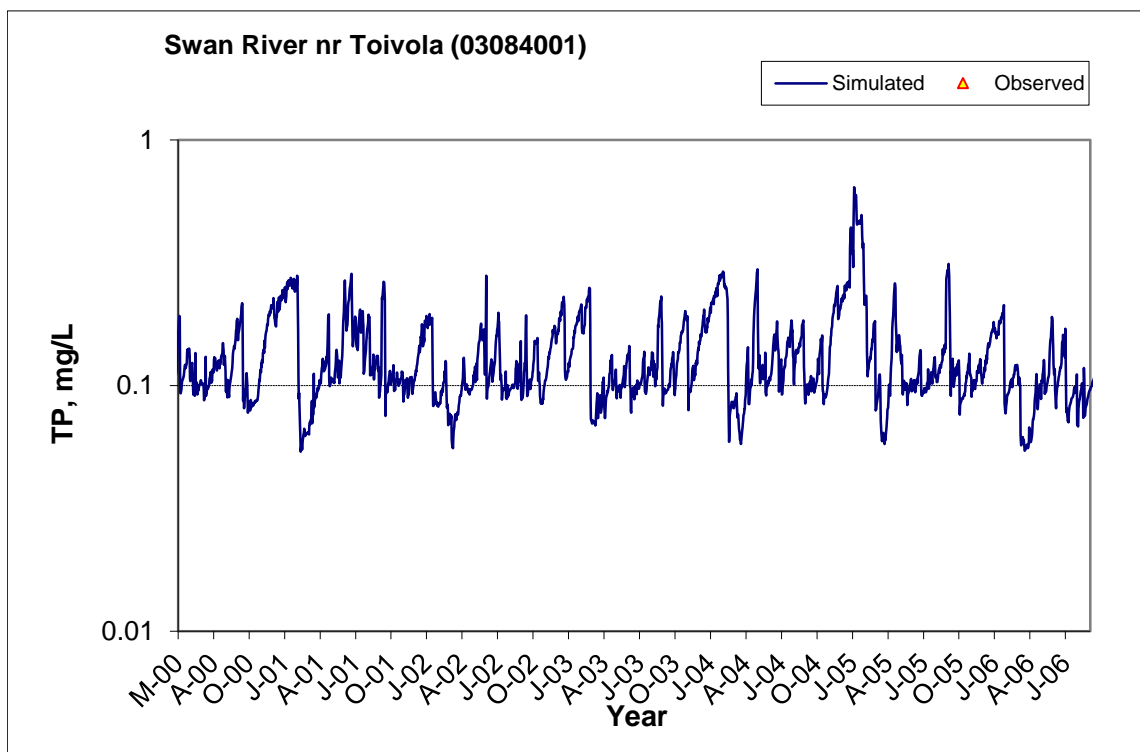


Figure A-37. Time series of observed and simulated Total Phosphorus (TP) concentration at Swan River nr Toivola (03084001)

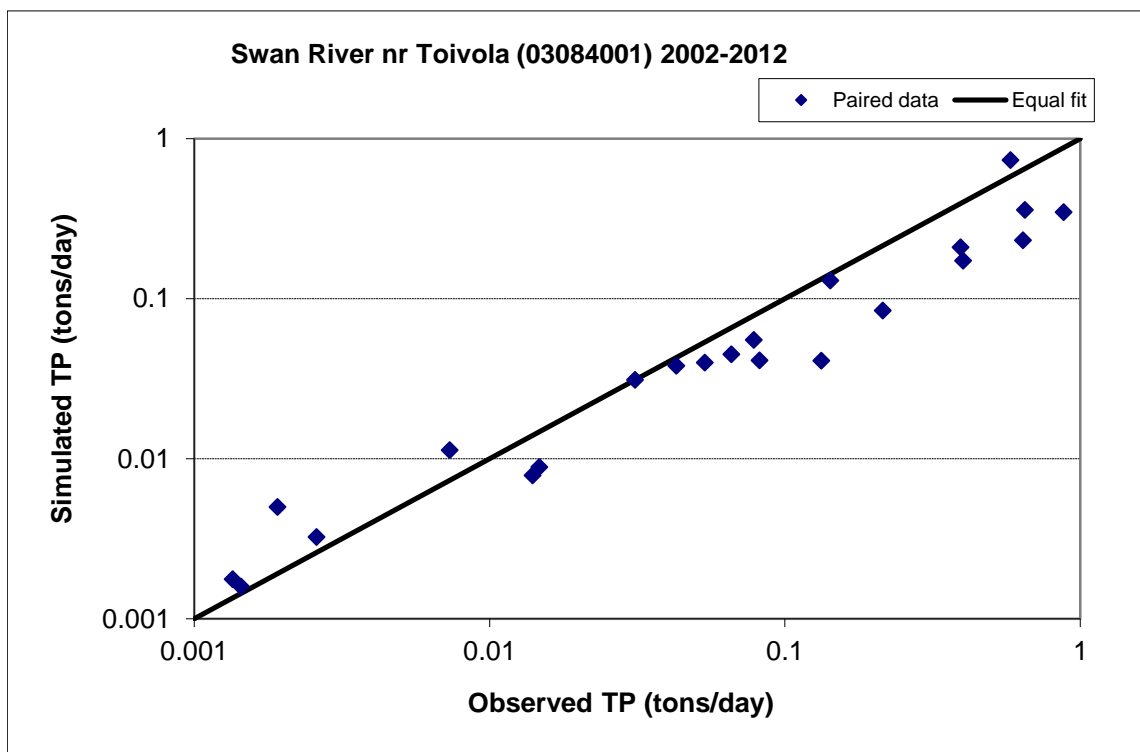


Figure A-38. Paired simulated vs. observed Total Phosphorus (TP) load at Swan River nr Toivola (03084001) (calibration period)

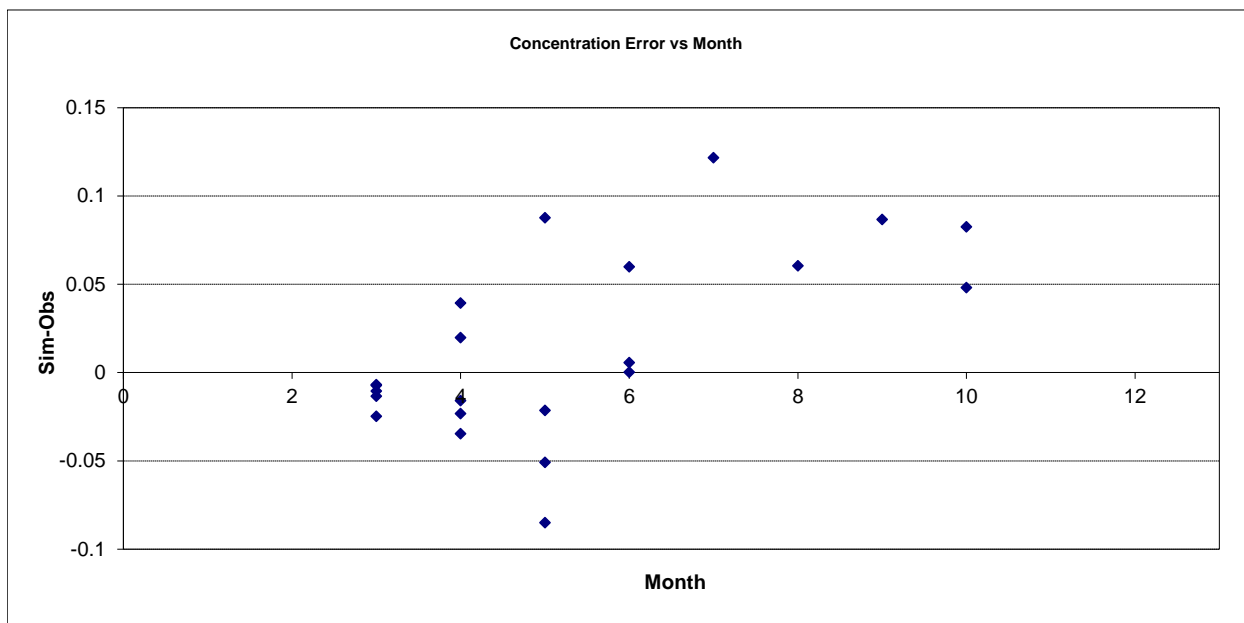


Figure A-39. Residual (Simulated - Observed) vs. Month Total Phosphorus (TP) at Swan River nr Toivola (03084001)

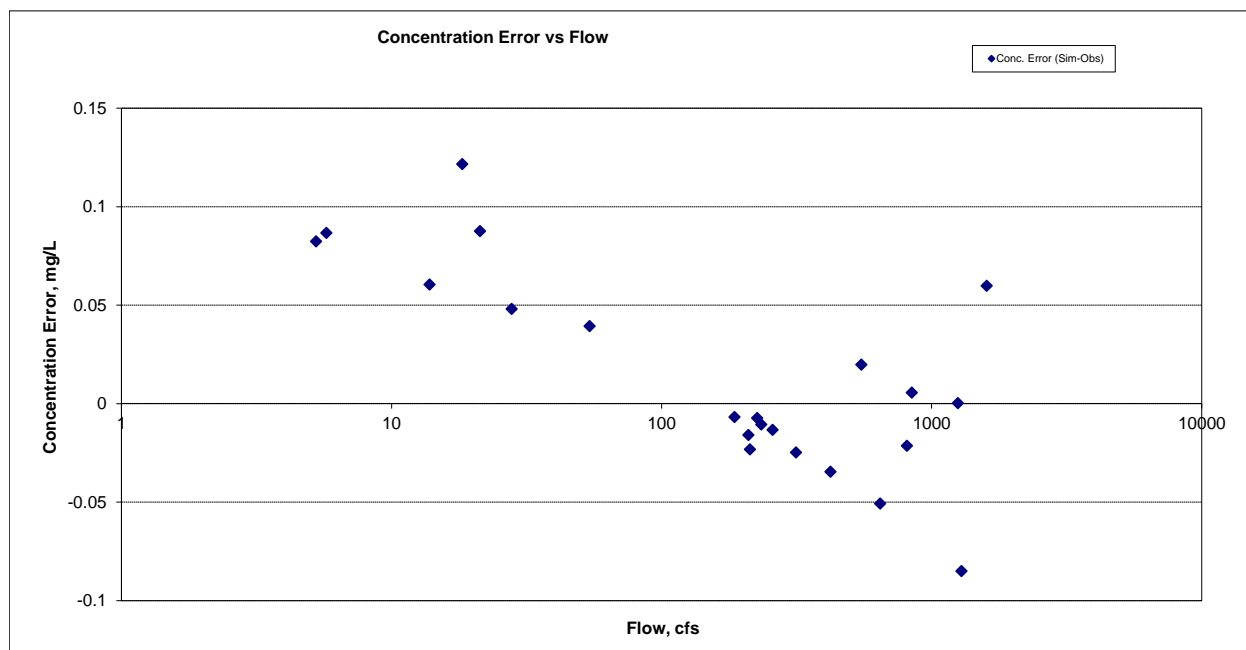


Figure A-40. Residual (Simulated - Observed) vs. Flow Total Phosphorus (TP) at Swan River nr Toivola (03084001)

A.3 ST LOUIS R BRIDGE AT CSAH-7, 0.5 MI S OF FORBES

A.3.1 Ammonia Nitrogen (NH3)

Table A-7. Ammonia Nitrogen (NH3) statistics

Period	1994-2001	2002-2012
Count	35	49
Concentration Average Error	136.20%	76.77%
Concentration Median Error	143.18%	97.38%
Load Average Error	120.54%	72.25%
Load Median Error	115.13%	65.99%
Paired t conc	0.00	0.00
Paired t load	0.00	0.03

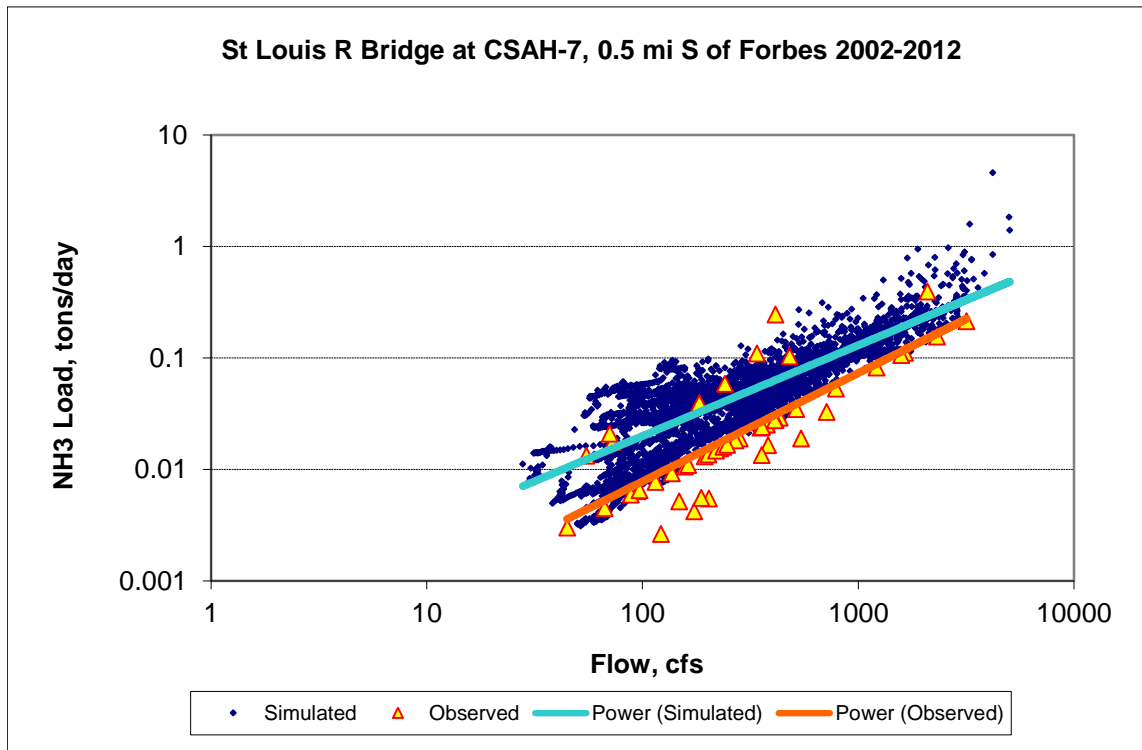


Figure A-41. Power plot of simulated and observed Ammonia Nitrogen (NH3) load vs flow at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes (calibration period)

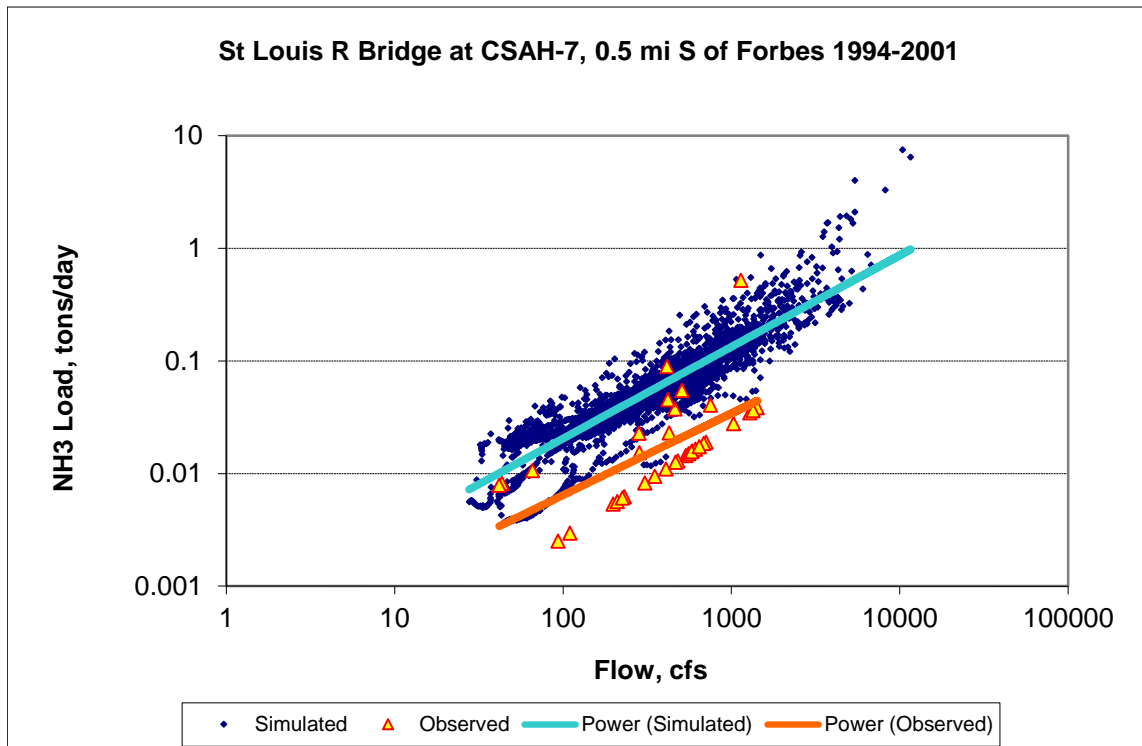
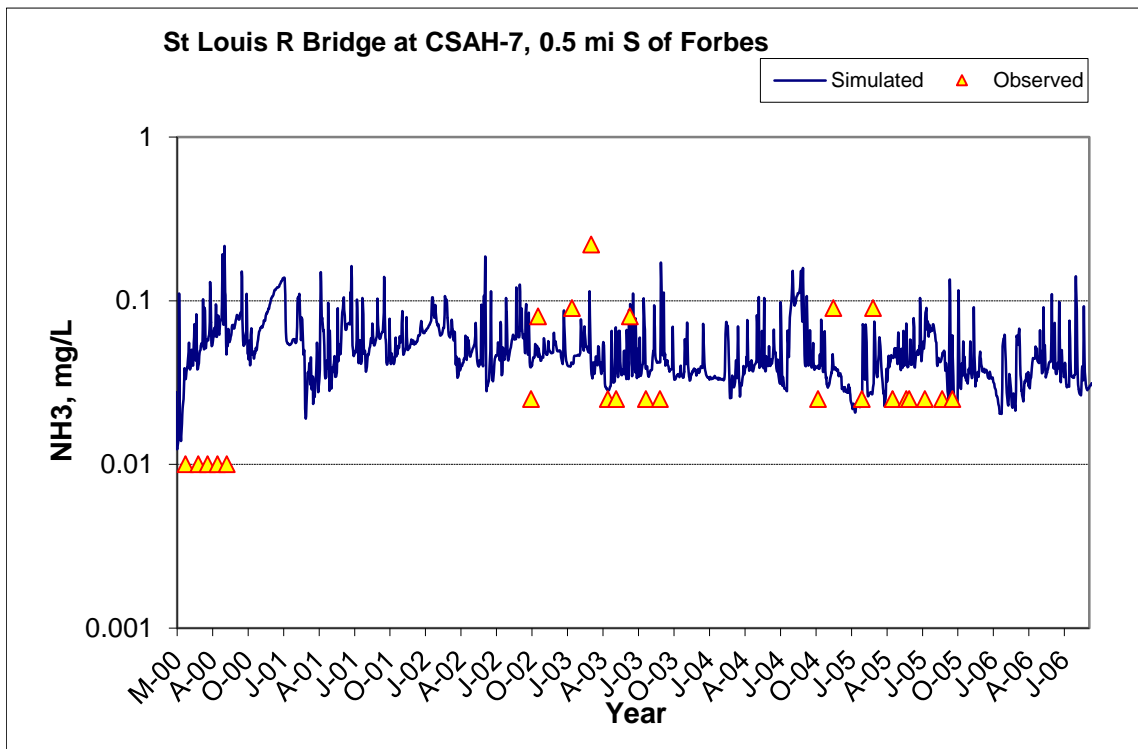
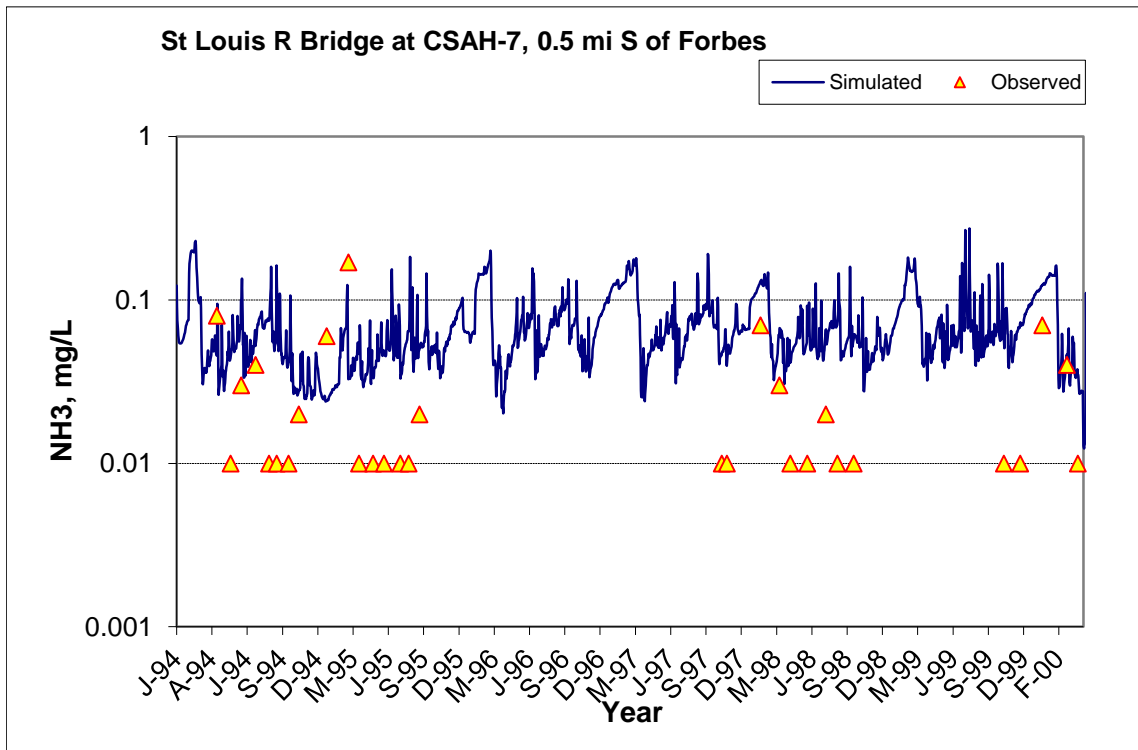


Figure A-42. Power plot of simulated and observed Ammonia Nitrogen (NH3) load vs flow at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes (validation period)



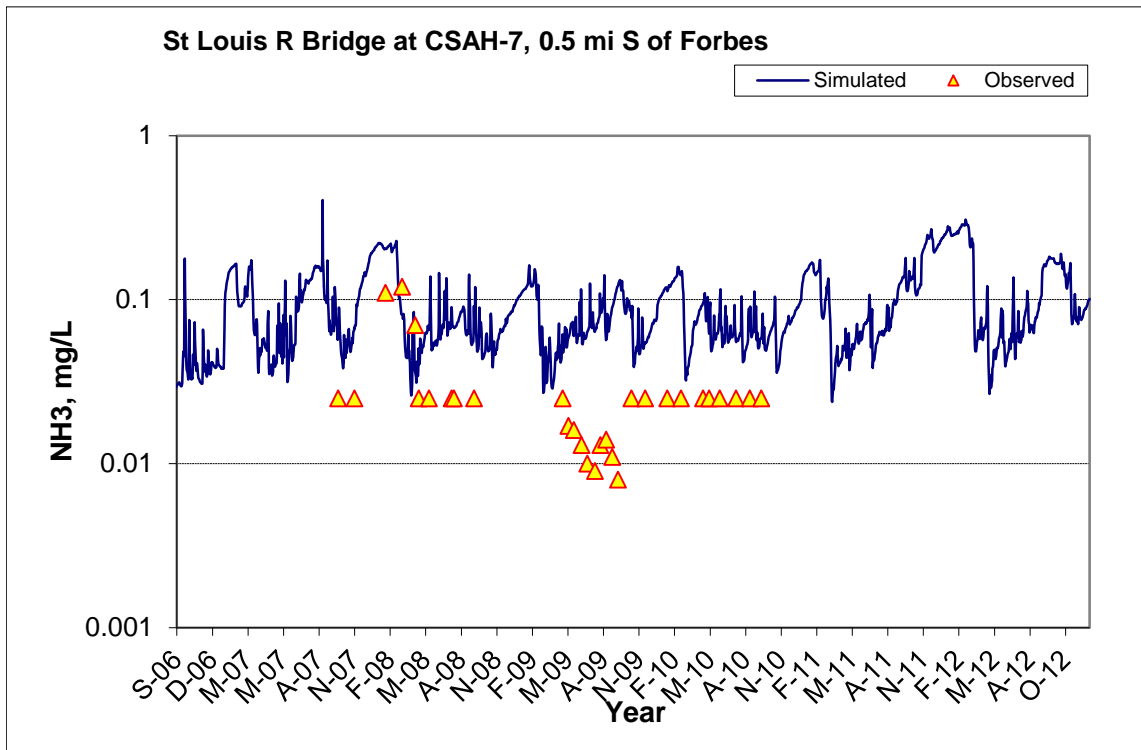


Figure A-43. Time series of observed and simulated Ammonia Nitrogen (NH₃) concentration at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes

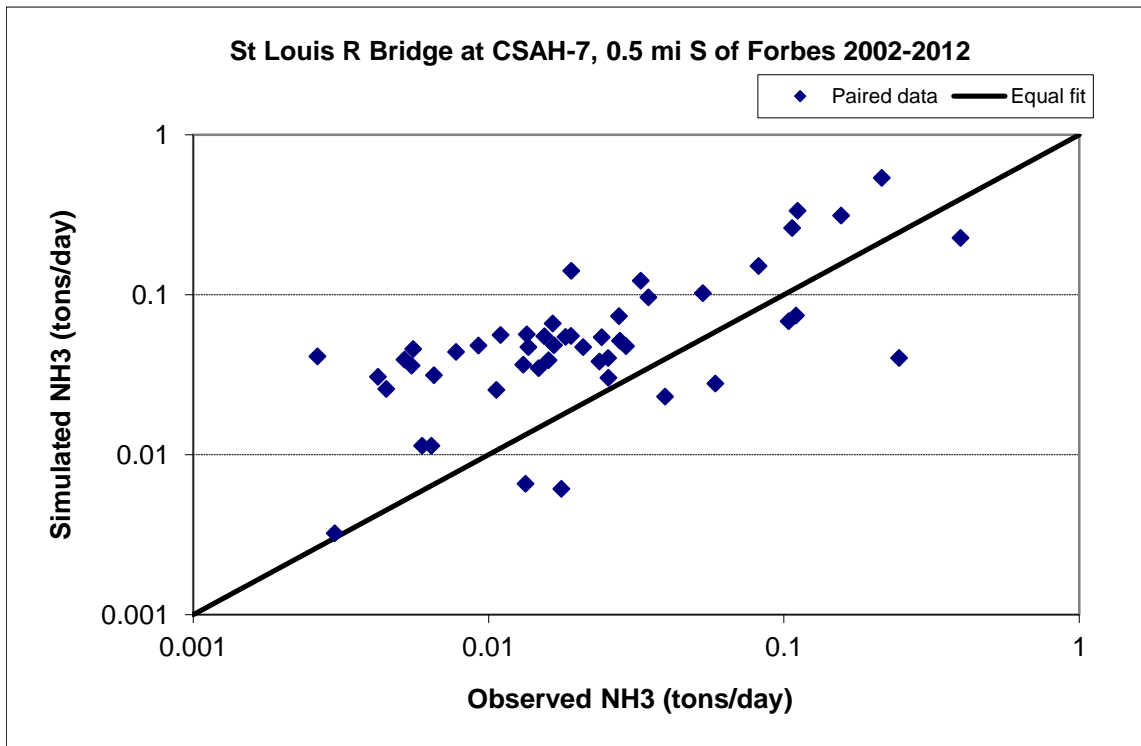


Figure A-44. Paired simulated vs. observed Ammonia Nitrogen (NH₃) load at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes (calibration period)

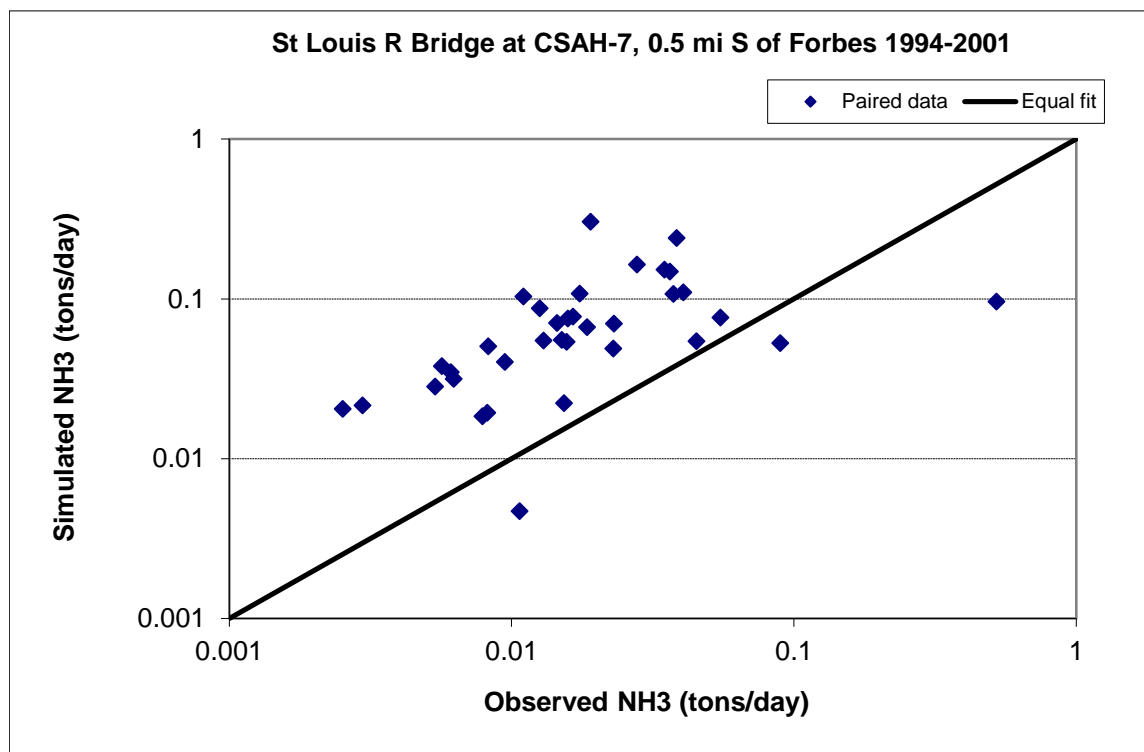


Figure A-45. Paired simulated vs. observed Ammonia Nitrogen (NH3) load at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes (validation period)

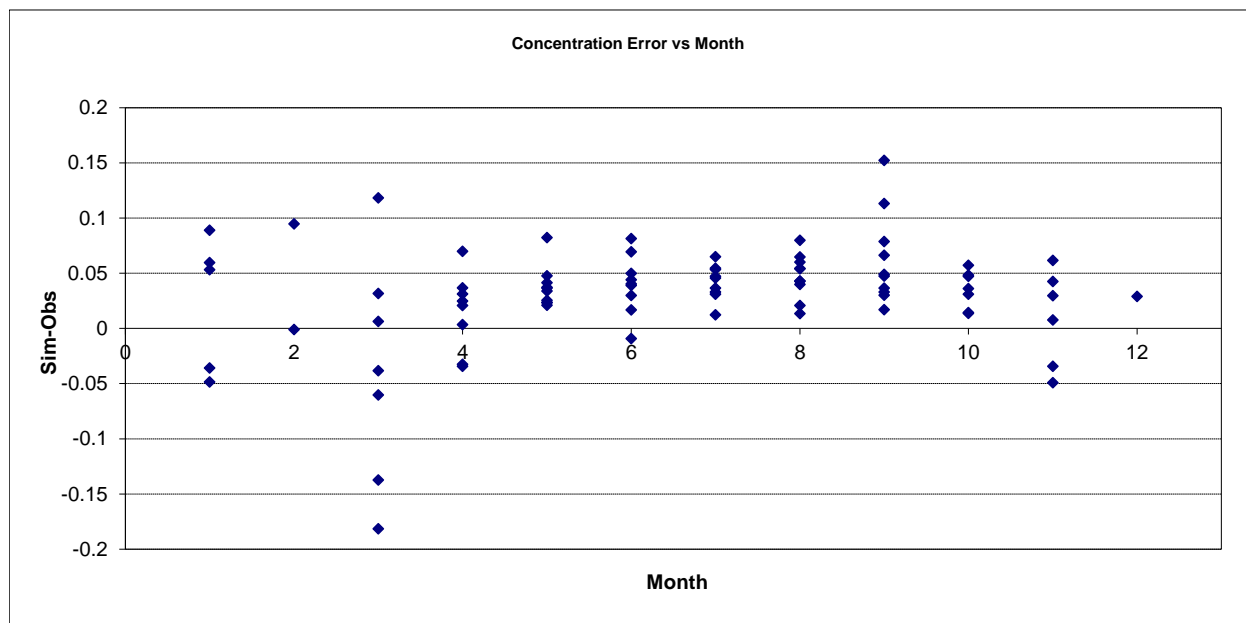


Figure A-46. Residual (Simulated - Observed) vs. Month Ammonia Nitrogen (NH3) at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes

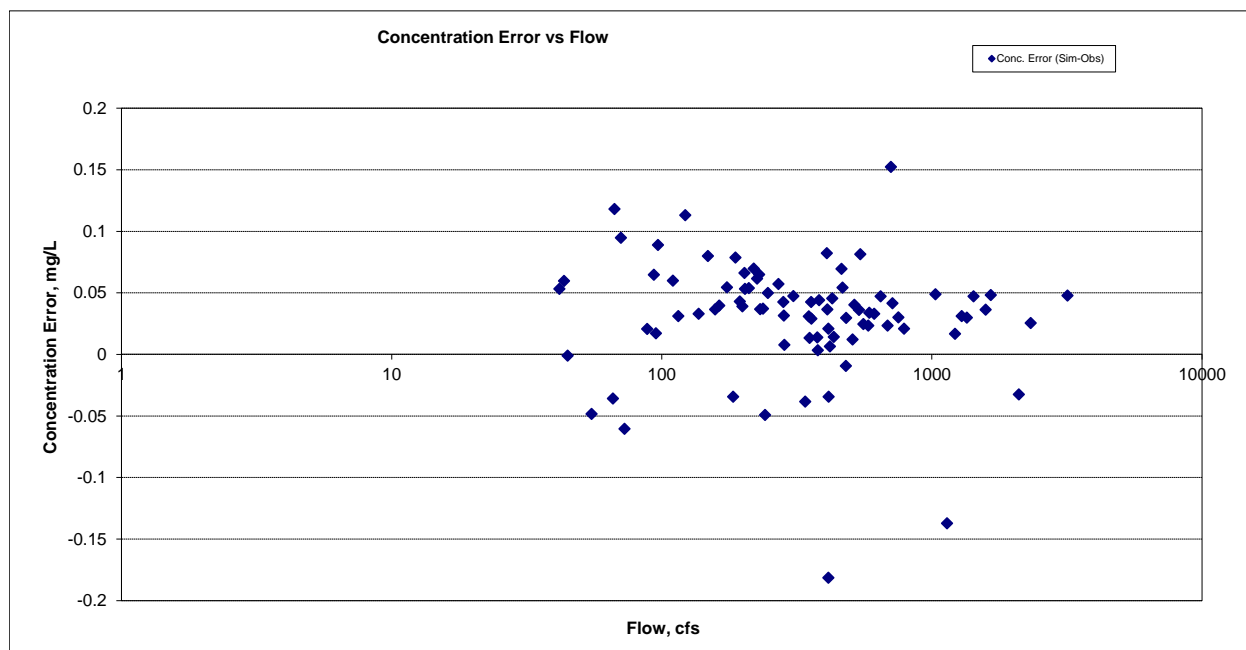
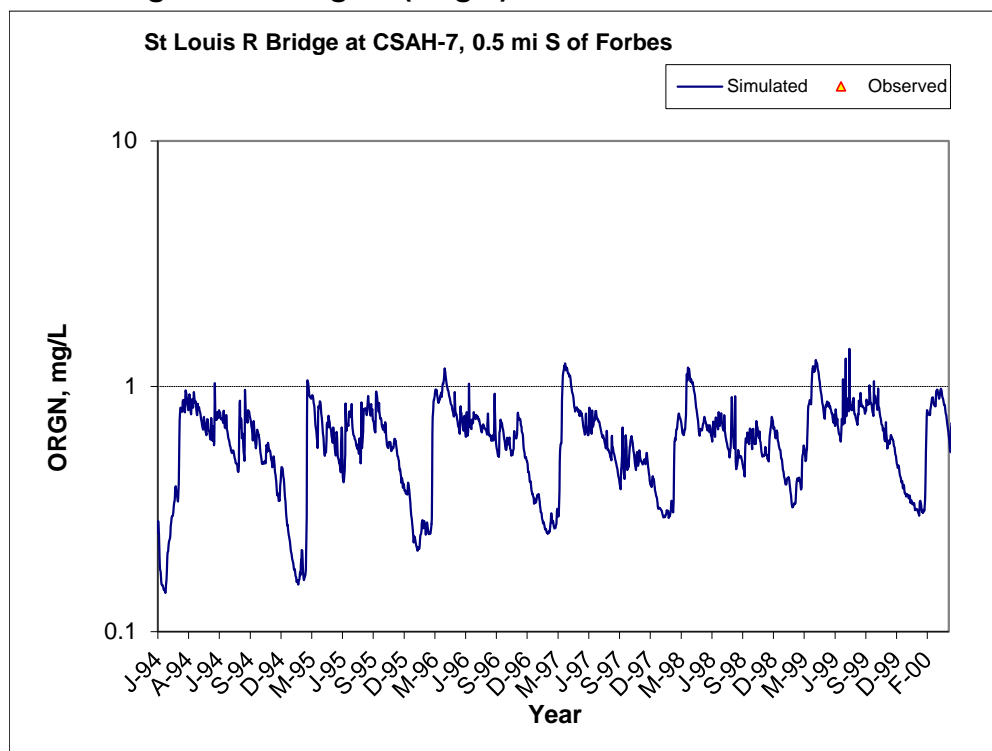


Figure A-47. Residual (Simulated - Observed) vs. Flow Ammonia Nitrogen (NH₃) at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes

A.3.2 Organic Nitrogen (OrgN)



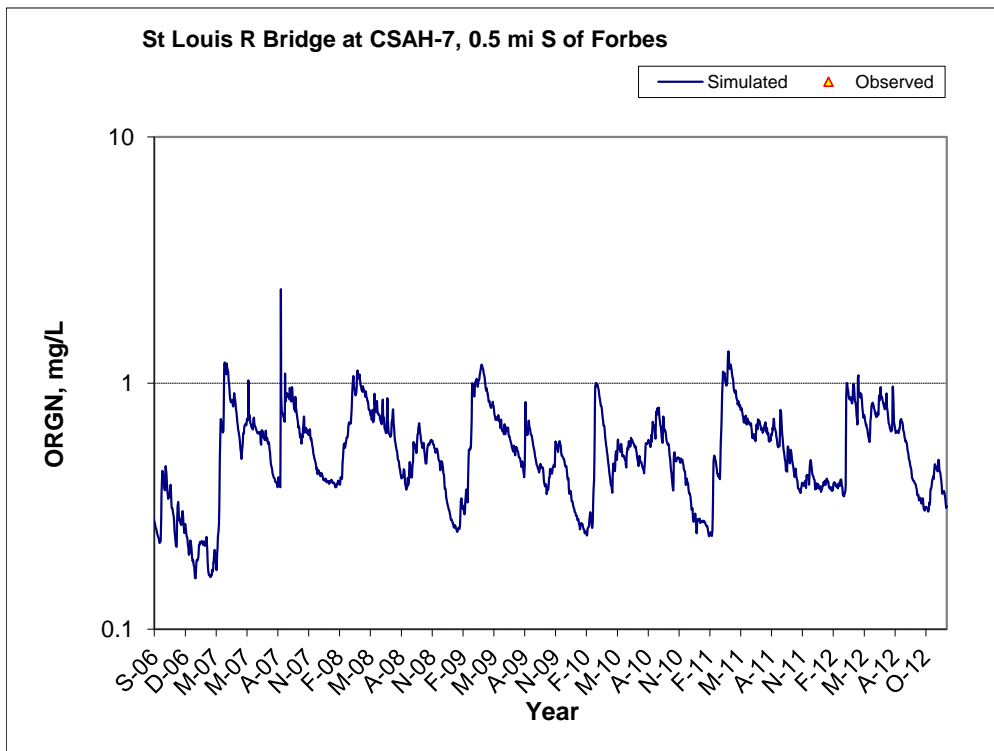
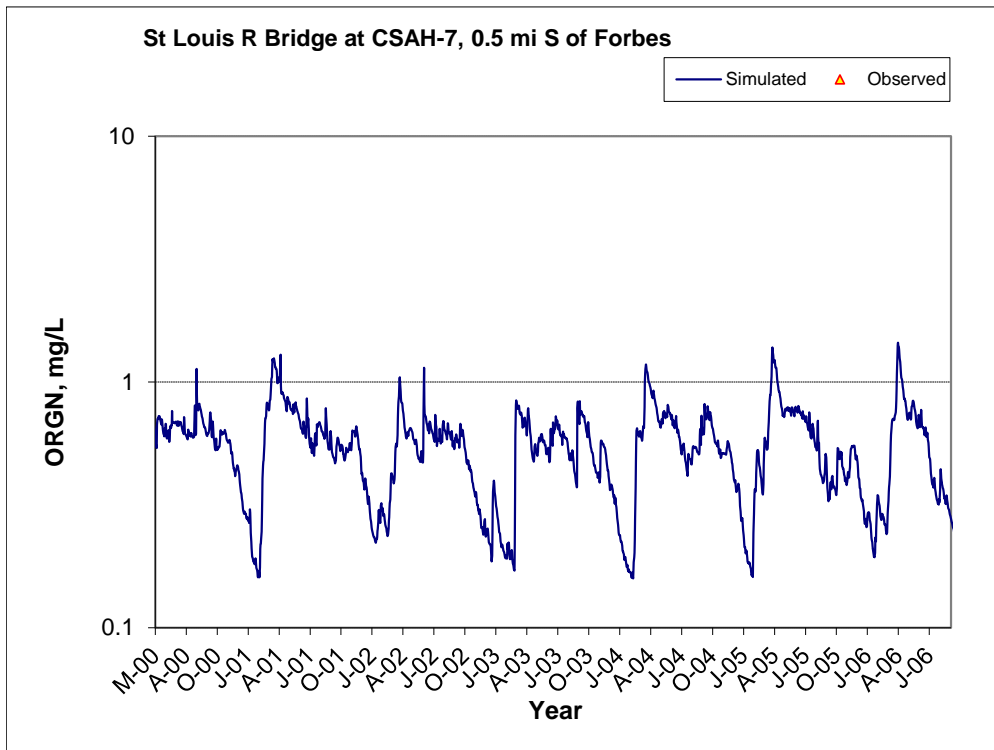


Figure A-48. Time series of observed and simulated Organic Nitrogen (OrgN) concentration at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes

A.3.3 Total Kjeldahl Nitrogen (TKN)

Table A-8. Total Kjeldahl Nitrogen (TKN) statistics

Period	1994-2001	2002-2012
Count	6	7
Concentration Average Error	-7.54%	-11.94%
Concentration Median Error	-2.63%	-22.38%
Load Average Error	-3.55%	12.63%
Load Median Error	-3.12%	22.32%
Paired t conc	0.86	0.85
Paired t load	0.73	0.55

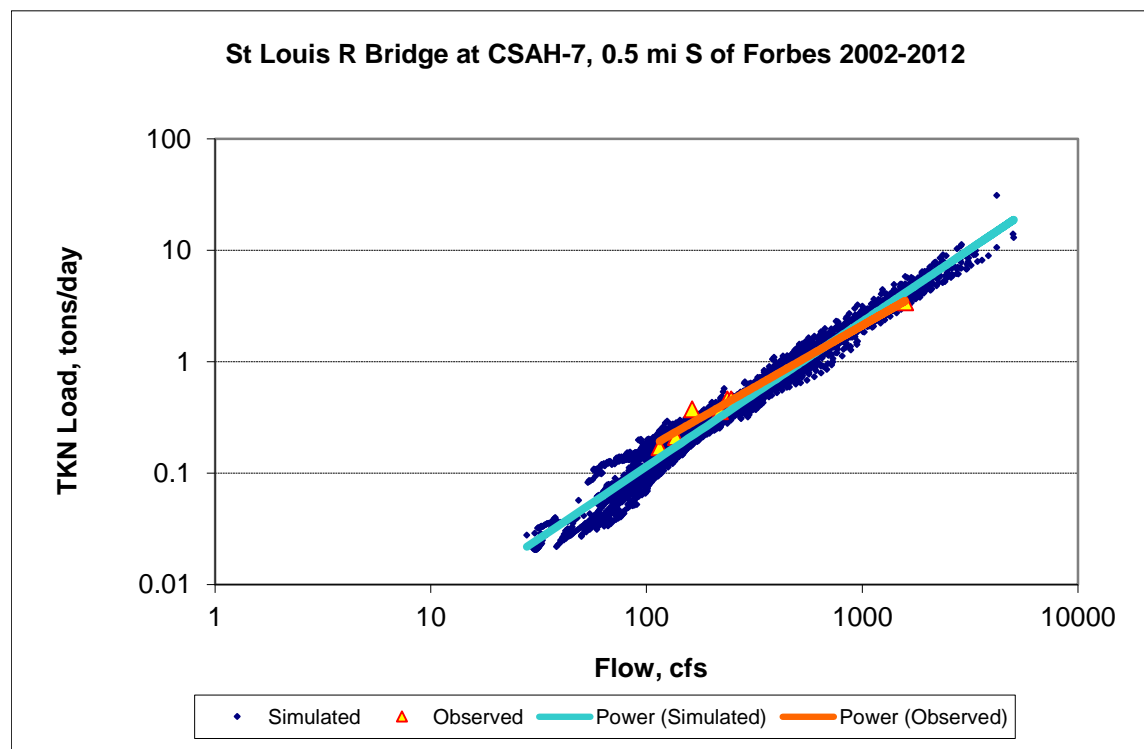


Figure A-49. Power plot of simulated and observed Total Kjeldahl Nitrogen (TKN) load vs flow at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes (calibration period)

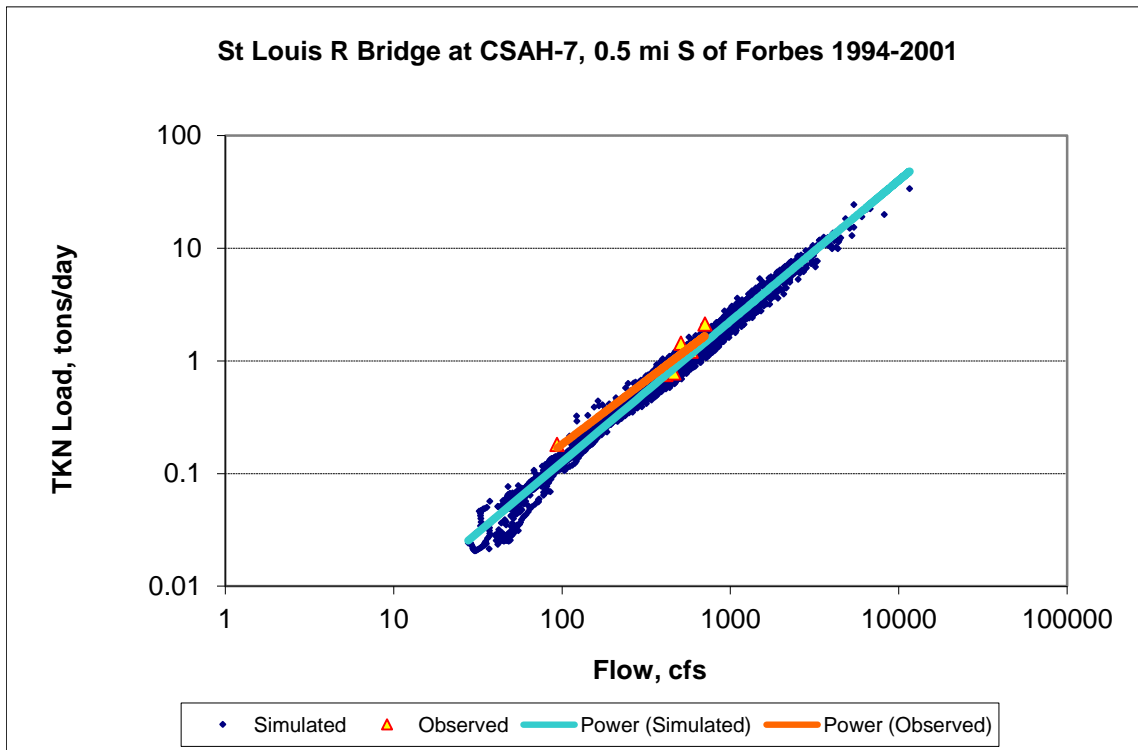
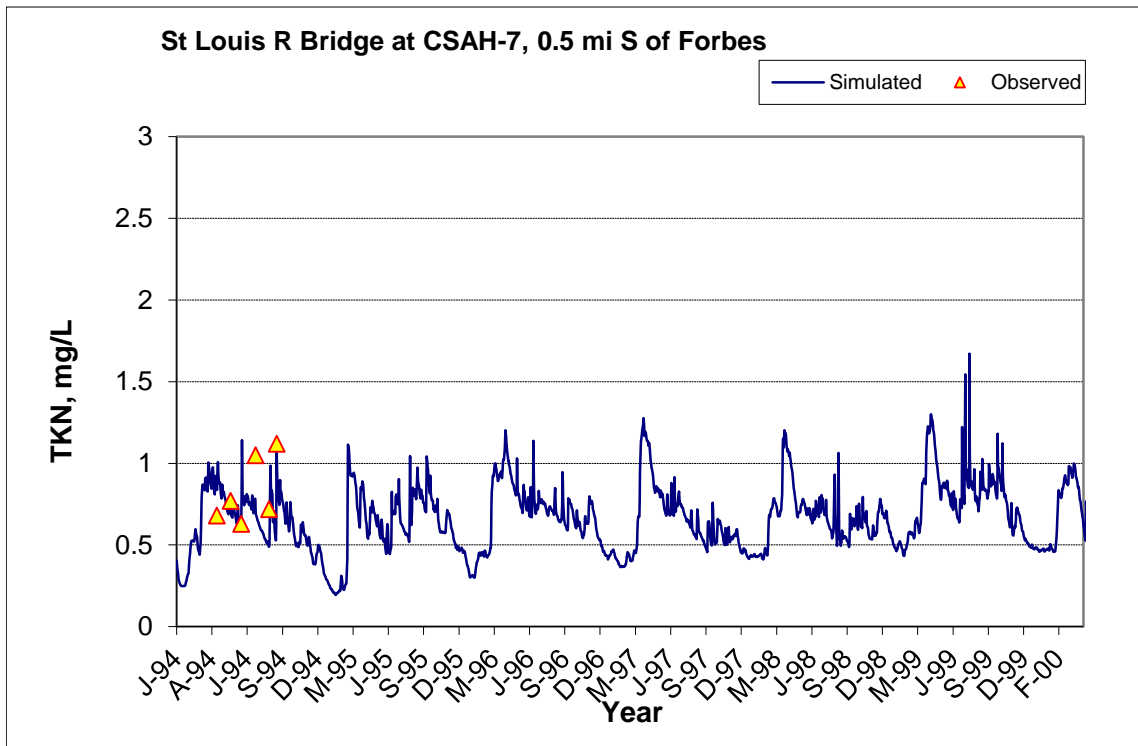


Figure A-50. Power plot of simulated and observed Total Kjeldahl Nitrogen (TKN) load vs flow at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes (validation period)



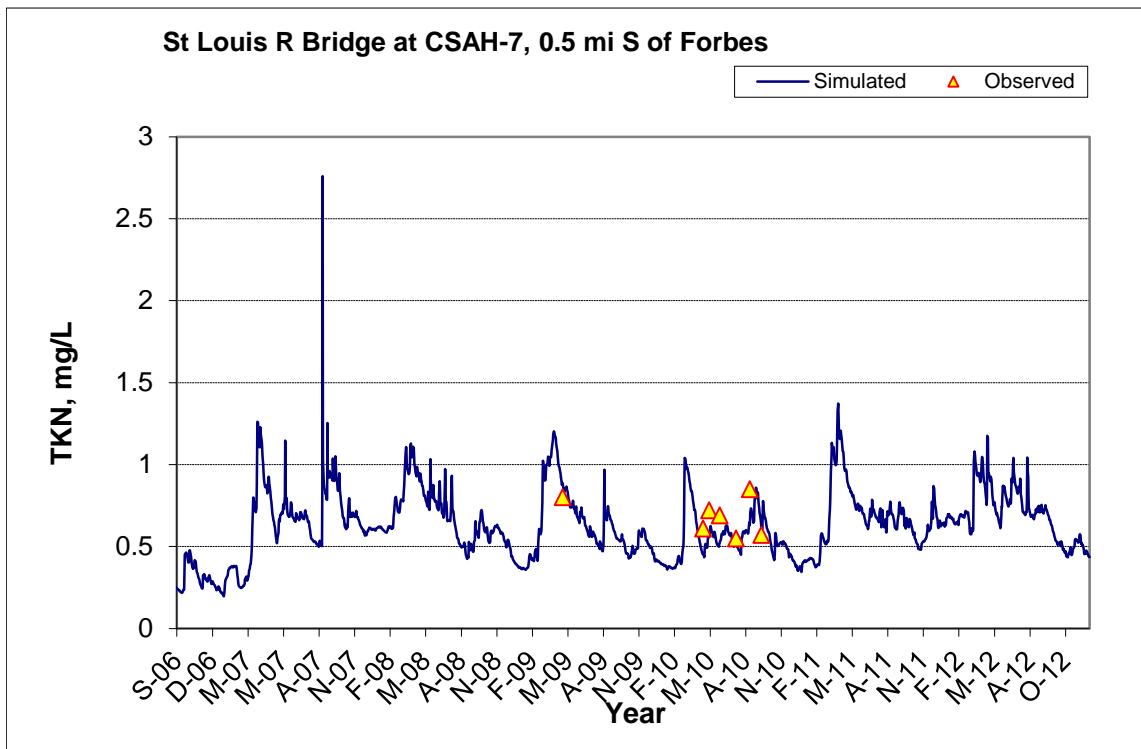
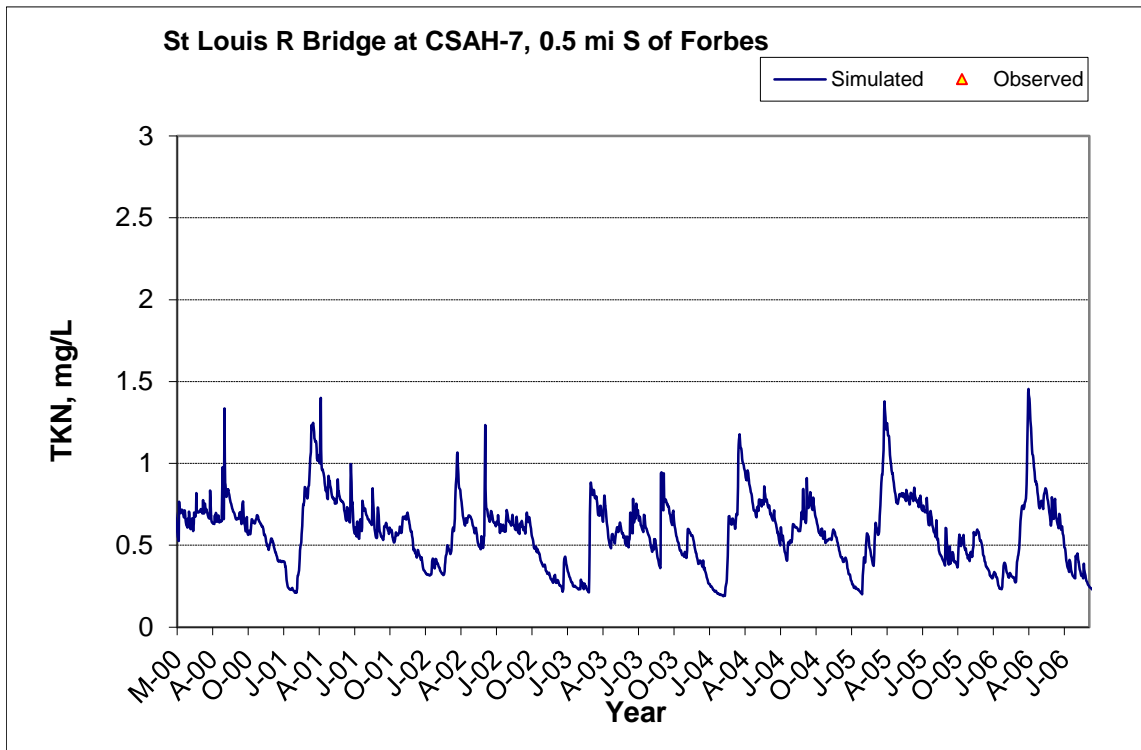


Figure A-51. Time series of observed and simulated Total Kjeldahl Nitrogen (TKN) concentration at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes

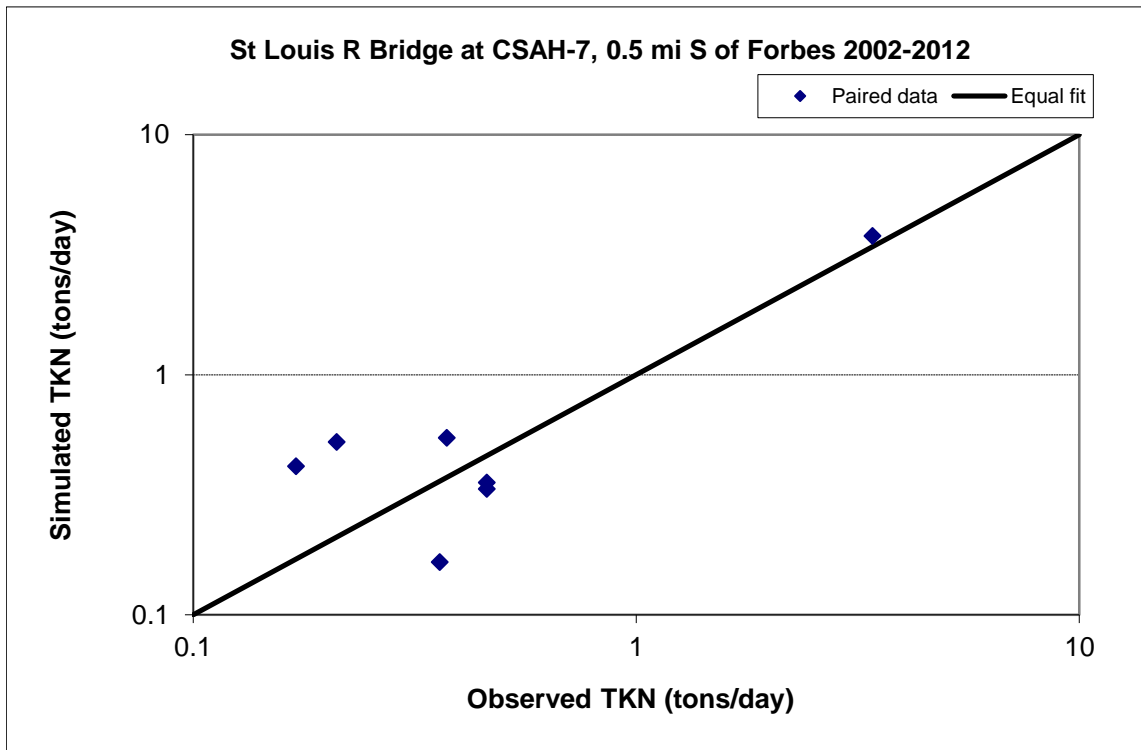


Figure A-52. Paired simulated vs. observed Total Kjeldahl Nitrogen (TKN) load at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes (calibration period)

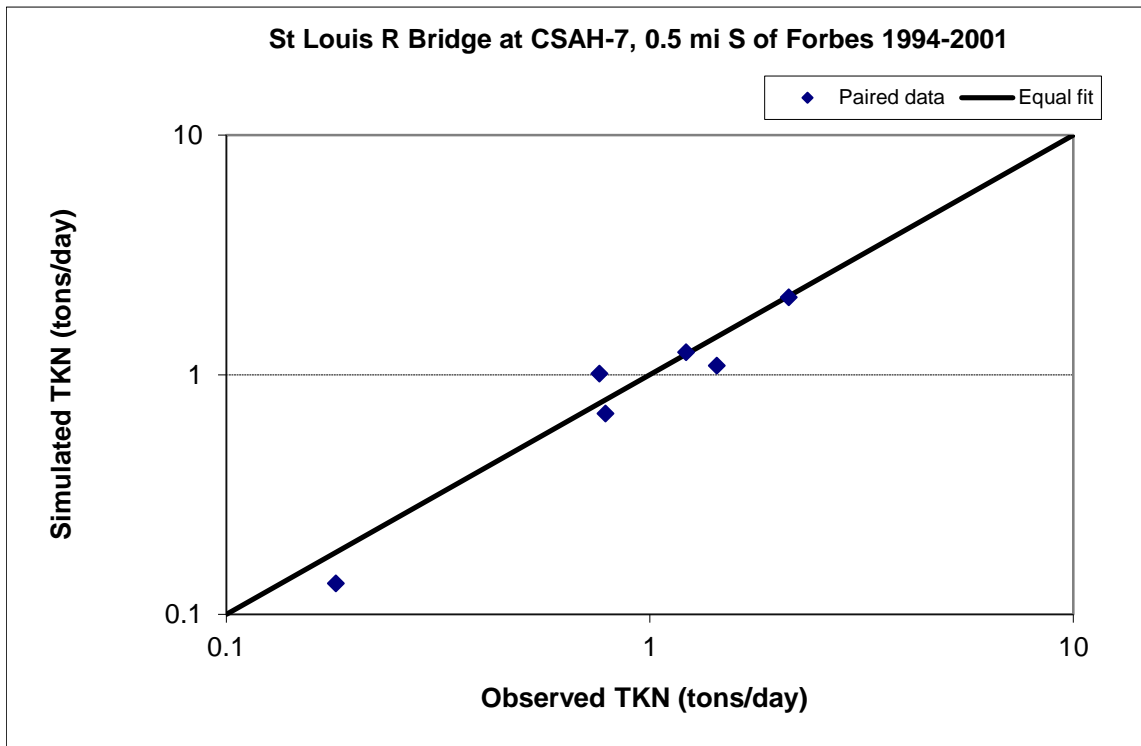


Figure A-53. Paired simulated vs. observed Total Kjeldahl Nitrogen (TKN) load at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes (validation period)

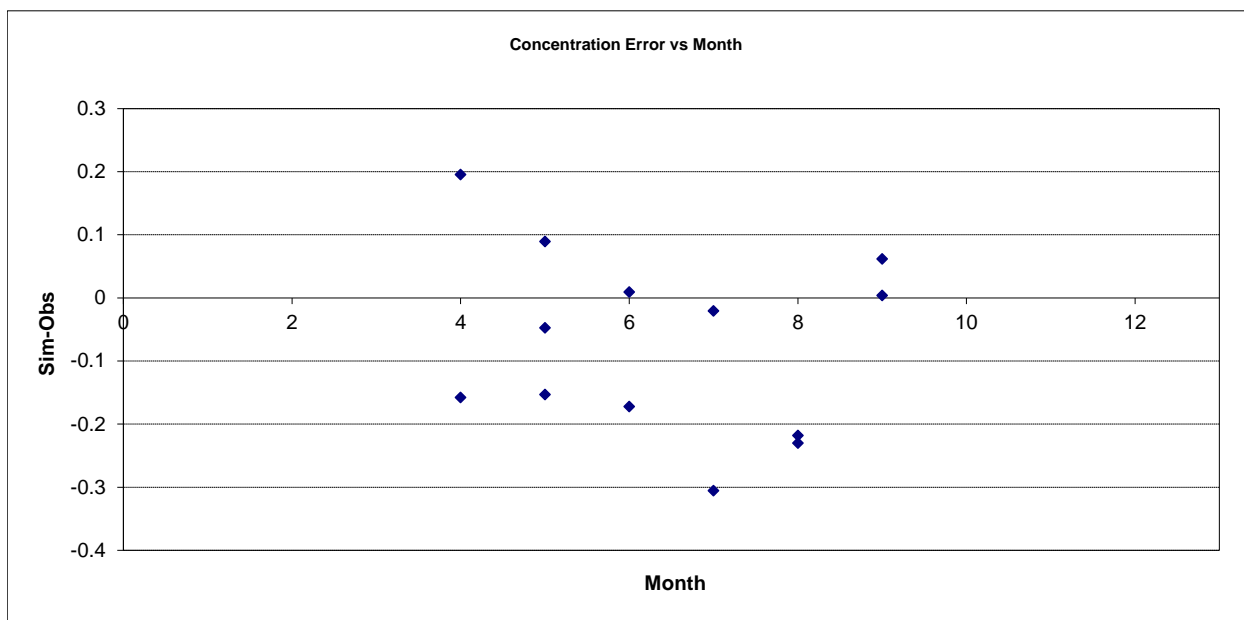


Figure A-54. Residual (Simulated - Observed) vs. Month Total Kjeldahl Nitrogen (TKN) at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes

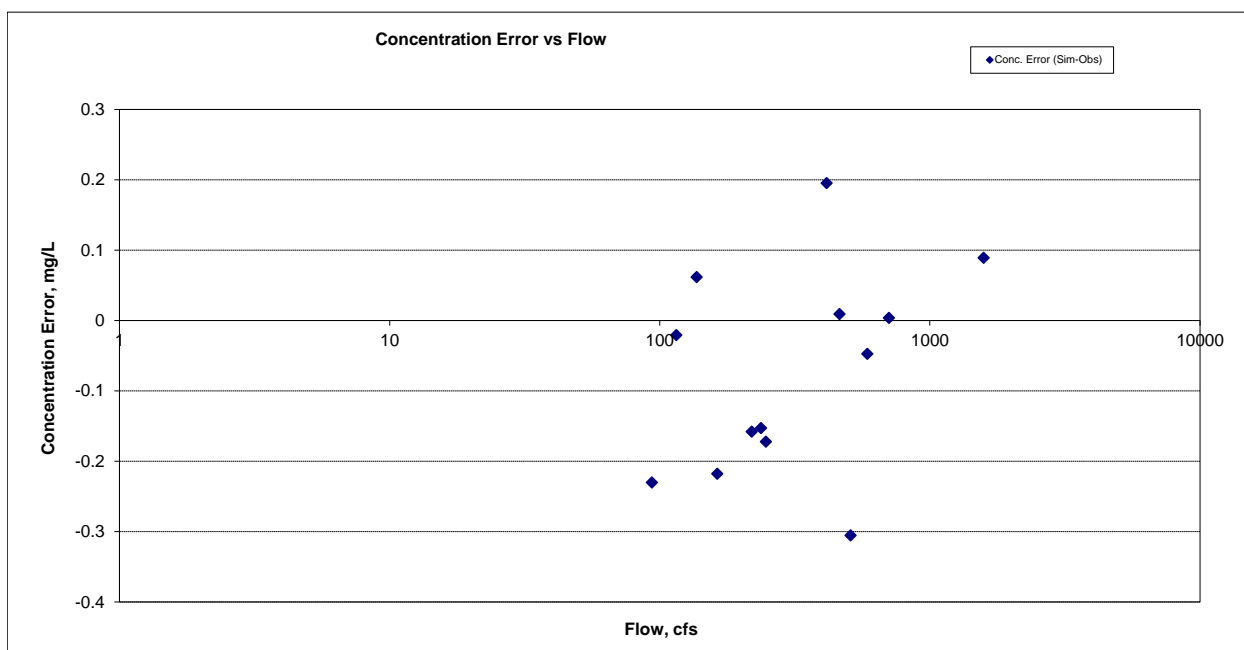


Figure A-55. Residual (Simulated - Observed) vs. Flow Total Kjeldahl Nitrogen (TKN) at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes

A.3.4 Nitrite+ Nitrate Nitrogen (NOx)

Table A-9. Nitrite+ Nitrate Nitrogen (NOx) statistics

Period	1994-2001	2002-2012
Count	35	48
Concentration Average Error	-33.89%	43.87%
Concentration Median Error	-25.84%	54.81%
Load Average Error	-40.97%	5.09%
Load Median Error	-11.20%	31.97%
Paired t conc	0.11	0.02
Paired t load	0.16	0.74

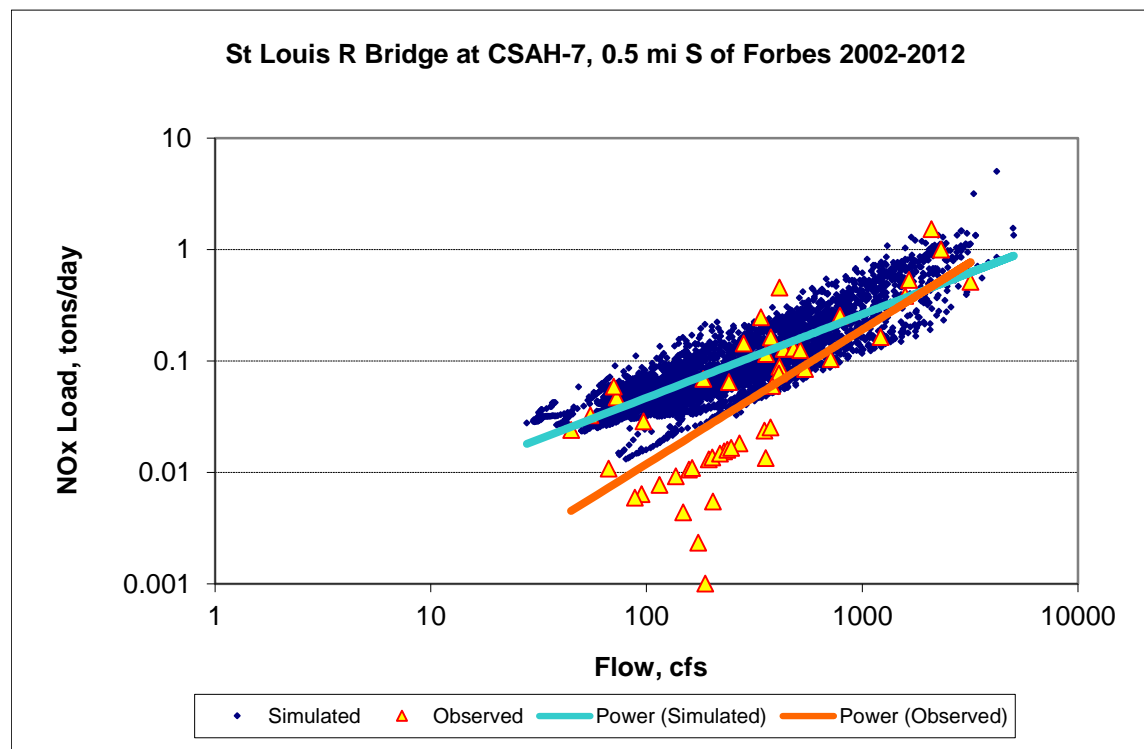


Figure A-56. Power plot of simulated and observed Nitrite+ Nitrate Nitrogen (NOx) load vs flow at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes (calibration period)

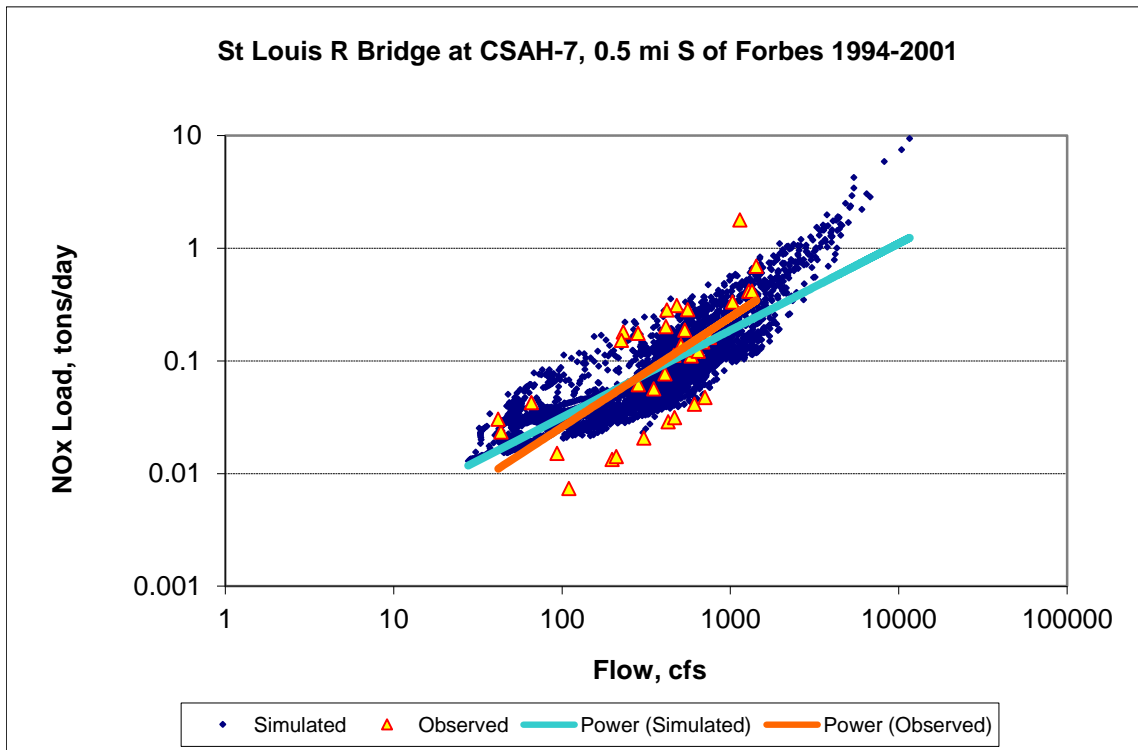
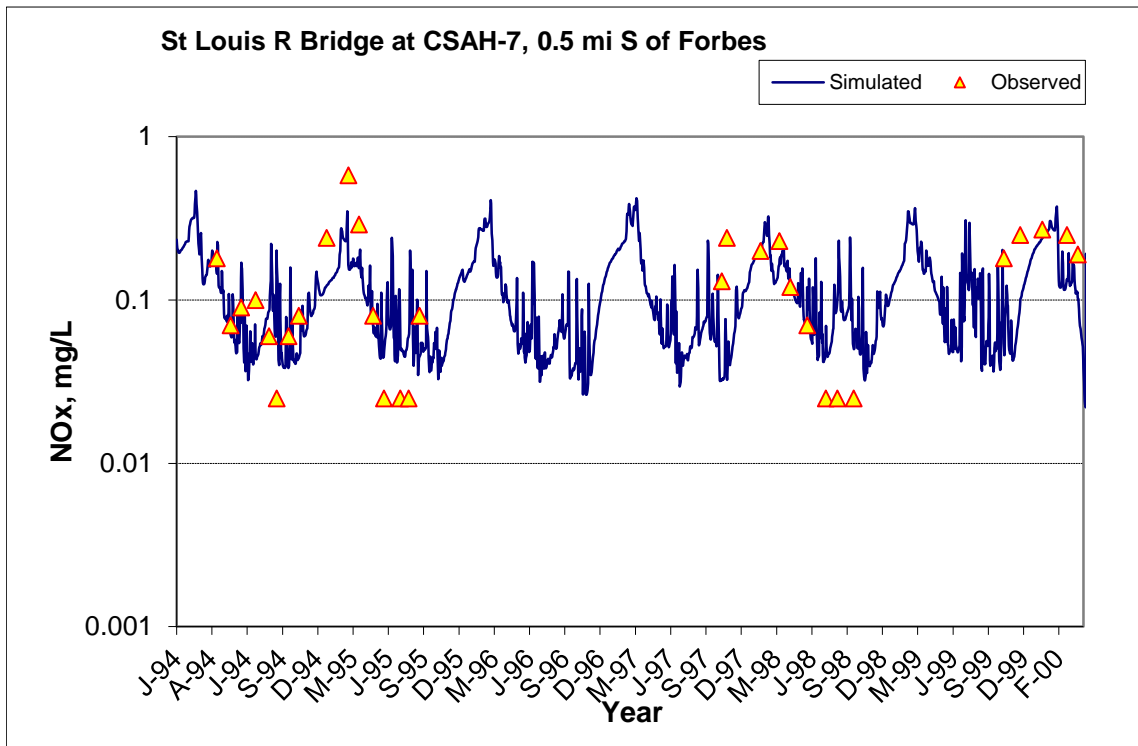


Figure A-57. Power plot of simulated and observed Nitrite+ Nitrate Nitrogen (NOx) load vs flow at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes (validation period)



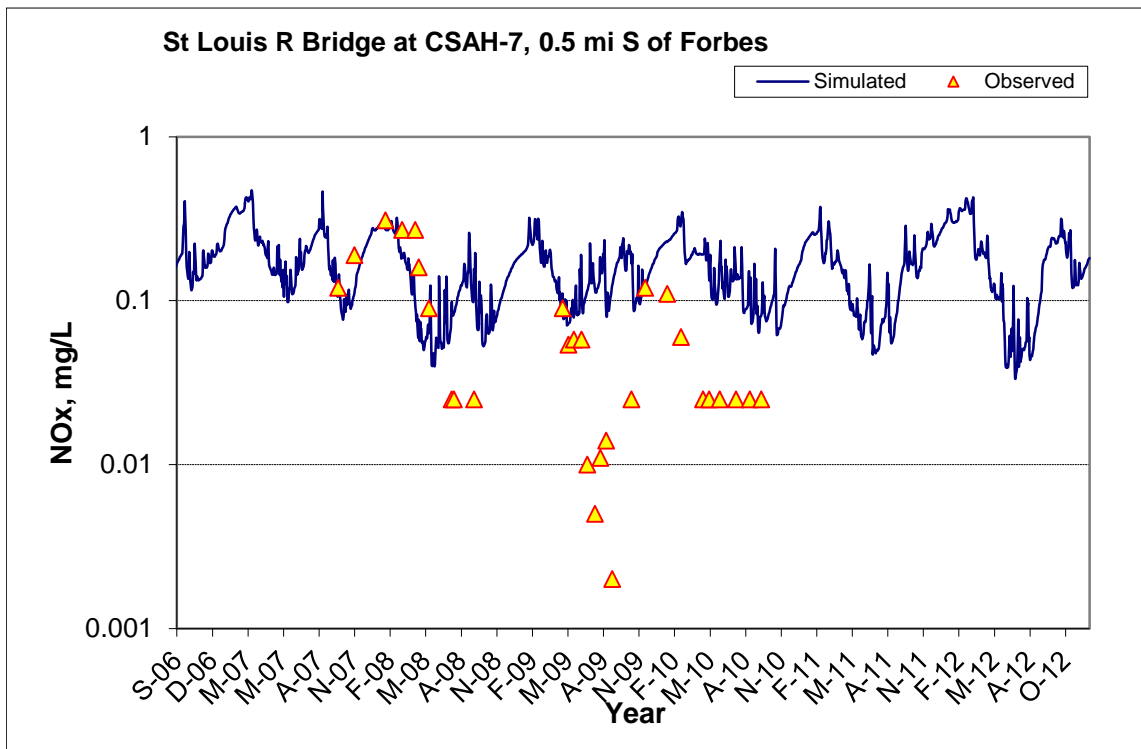
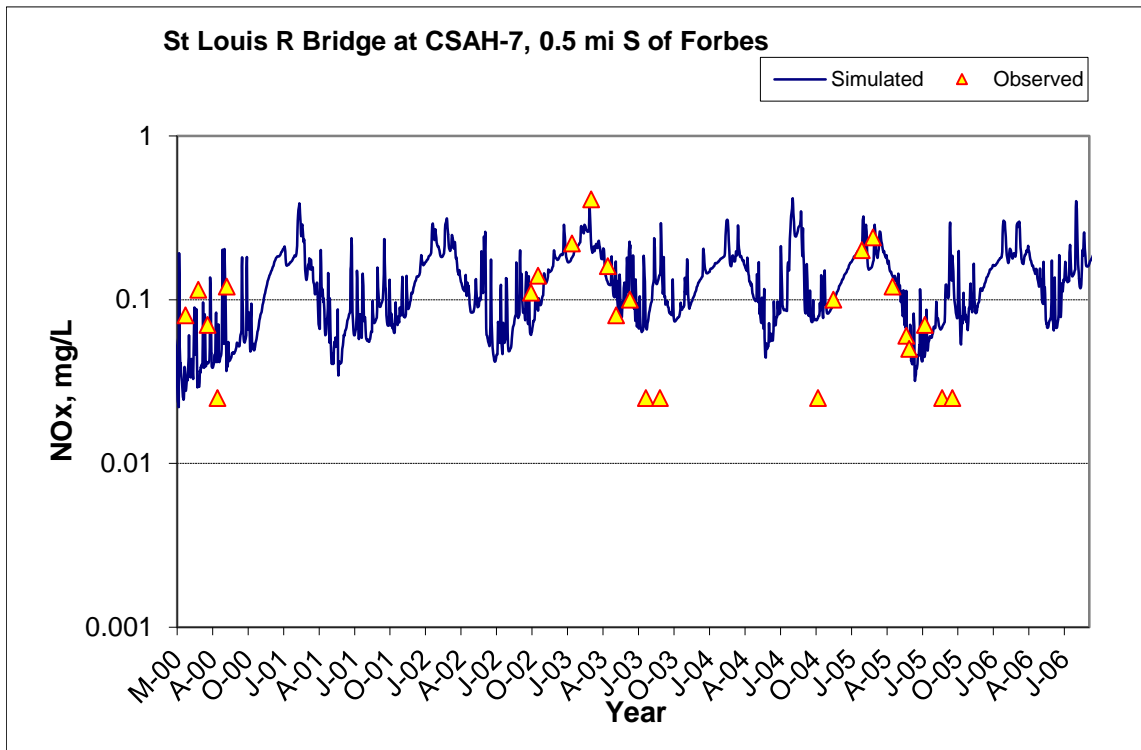


Figure A-58. Time series of observed and simulated Nitrite+ Nitrate Nitrogen (NOx) concentration at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes

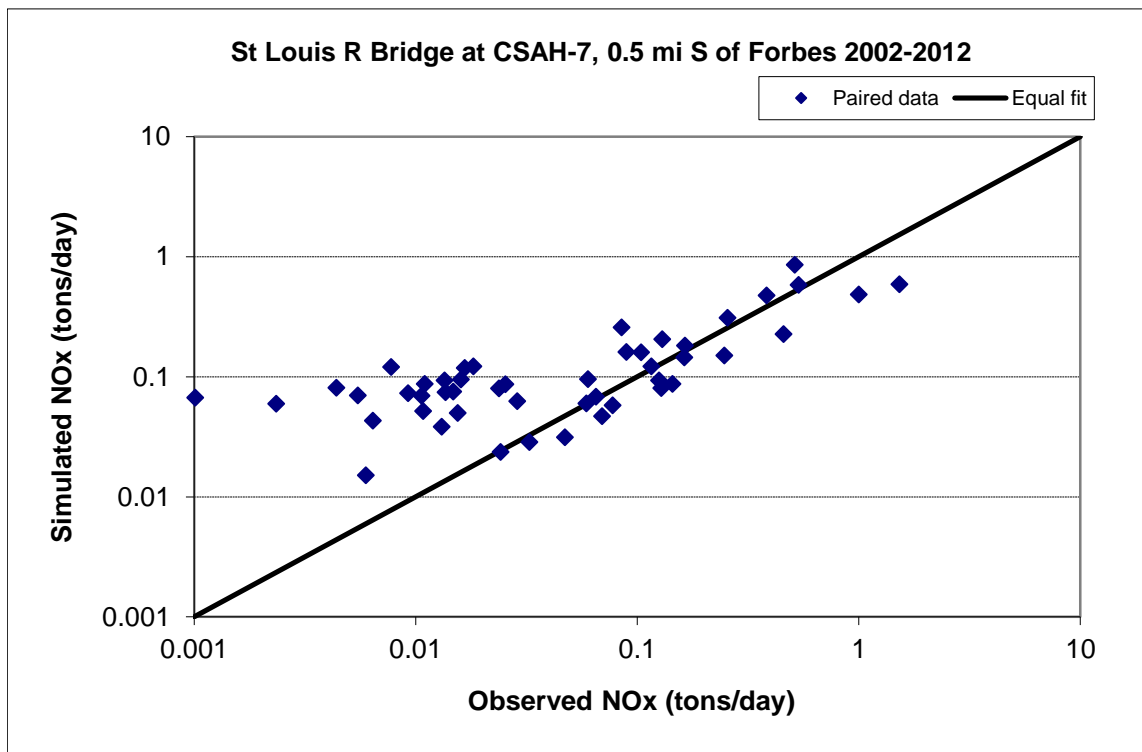


Figure A-59. Paired simulated vs. observed Nitrite+ Nitrate Nitrogen (NOx) load at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes (calibration period)

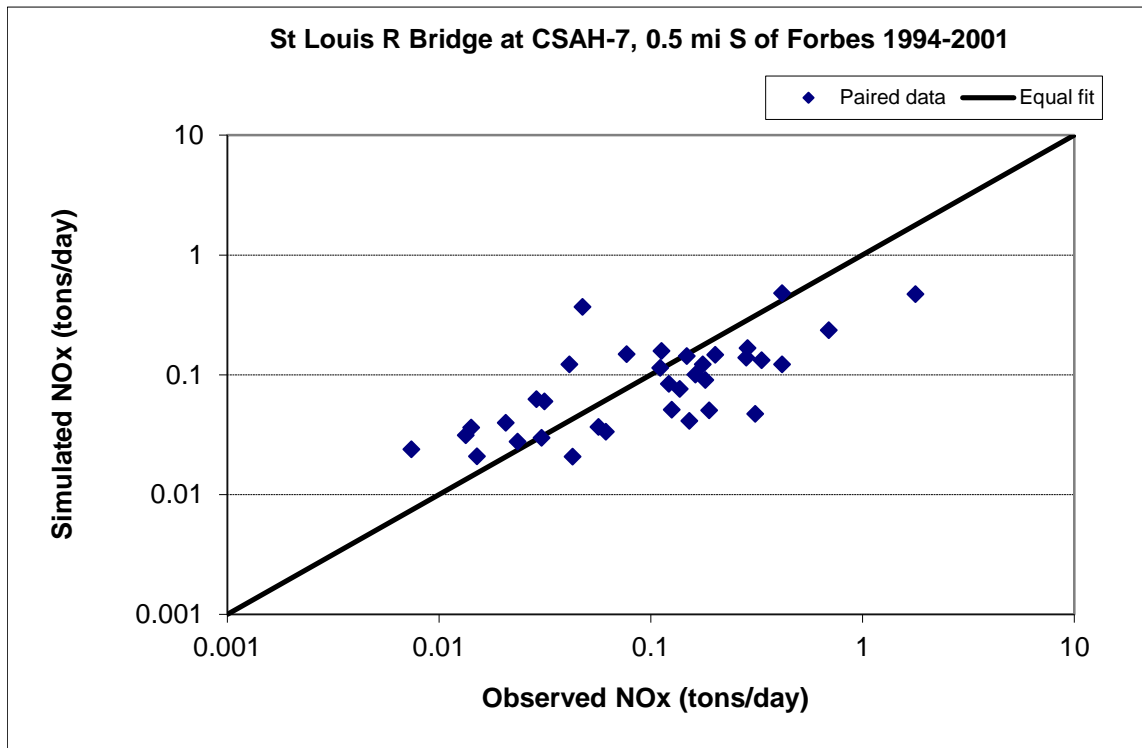


Figure A-60. Paired simulated vs. observed Nitrite+ Nitrate Nitrogen (NOx) load at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes (validation period)

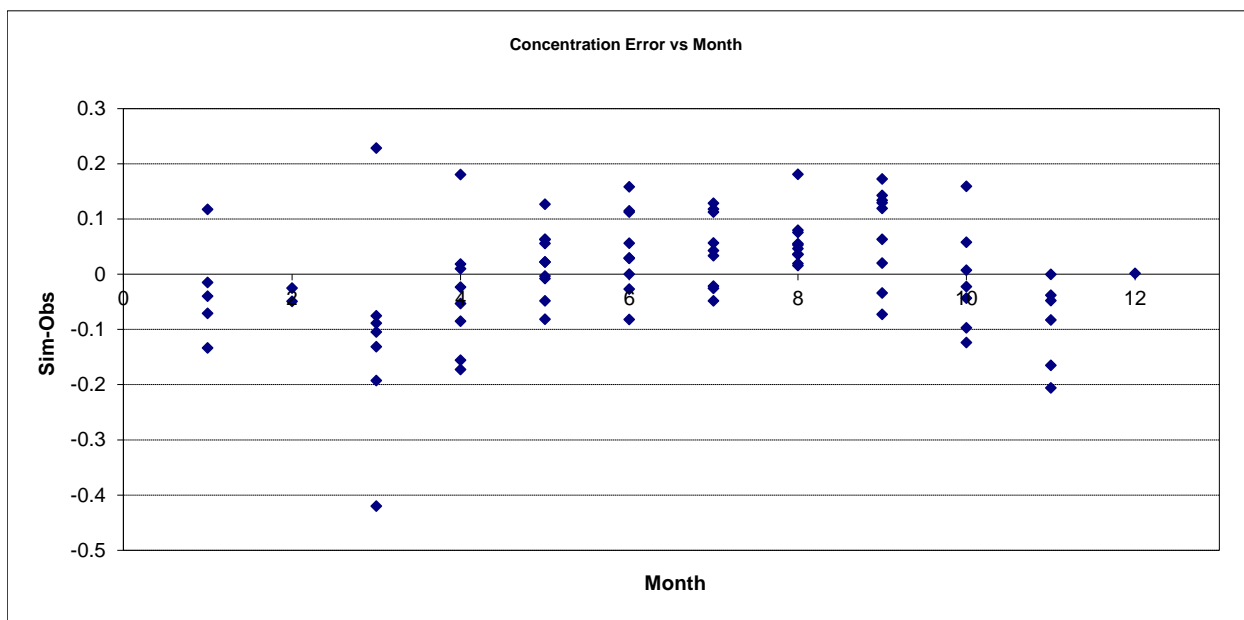


Figure A-61. Residual (Simulated - Observed) vs. Month Nitrite+ Nitrate Nitrogen (NOx) at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes

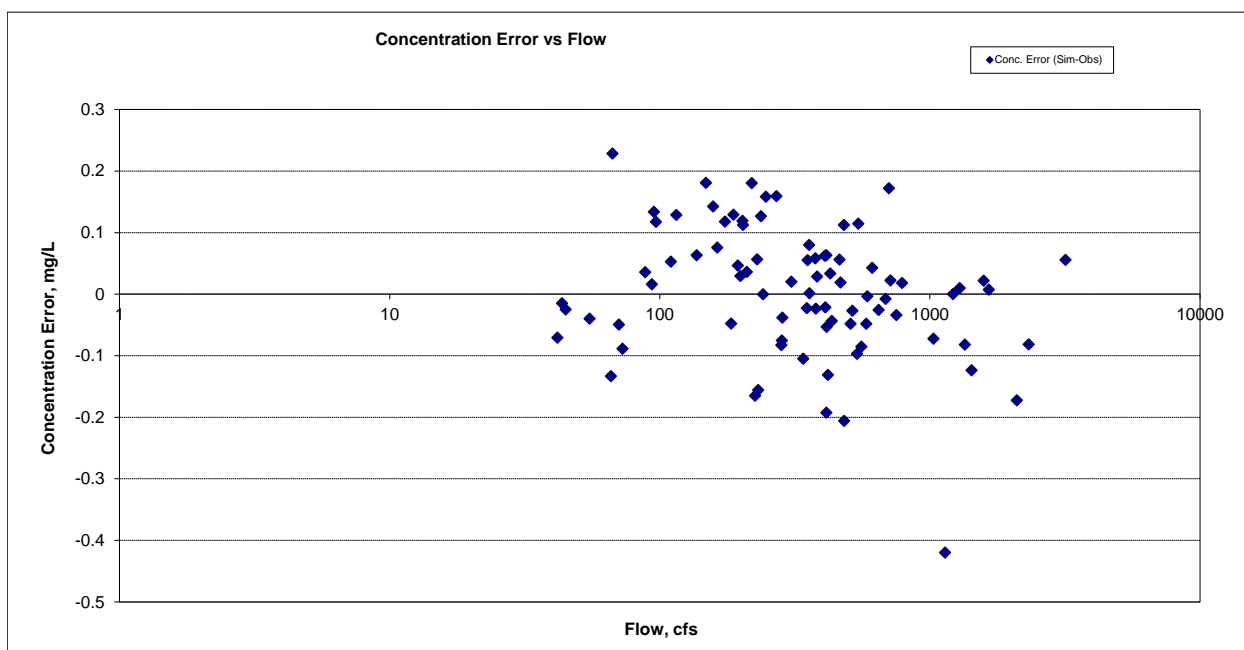


Figure A-62. Residual (Simulated - Observed) vs. Flow Nitrite+ Nitrate Nitrogen (NOx) at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes

A.3.5 Total Nitrogen (TN)

Table A-10. Total Nitrogen (TN) statistics

Period	1994-2001	2002-2012
Count	6	7
Concentration Average Error	-4.73%	0.63%
Concentration Median Error	0.78%	-0.37%
Load Average Error	-0.24%	20.07%
Load Median Error	-0.48%	27.95%
Paired t conc	0.90	0.99
Paired t load	0.77	0.50

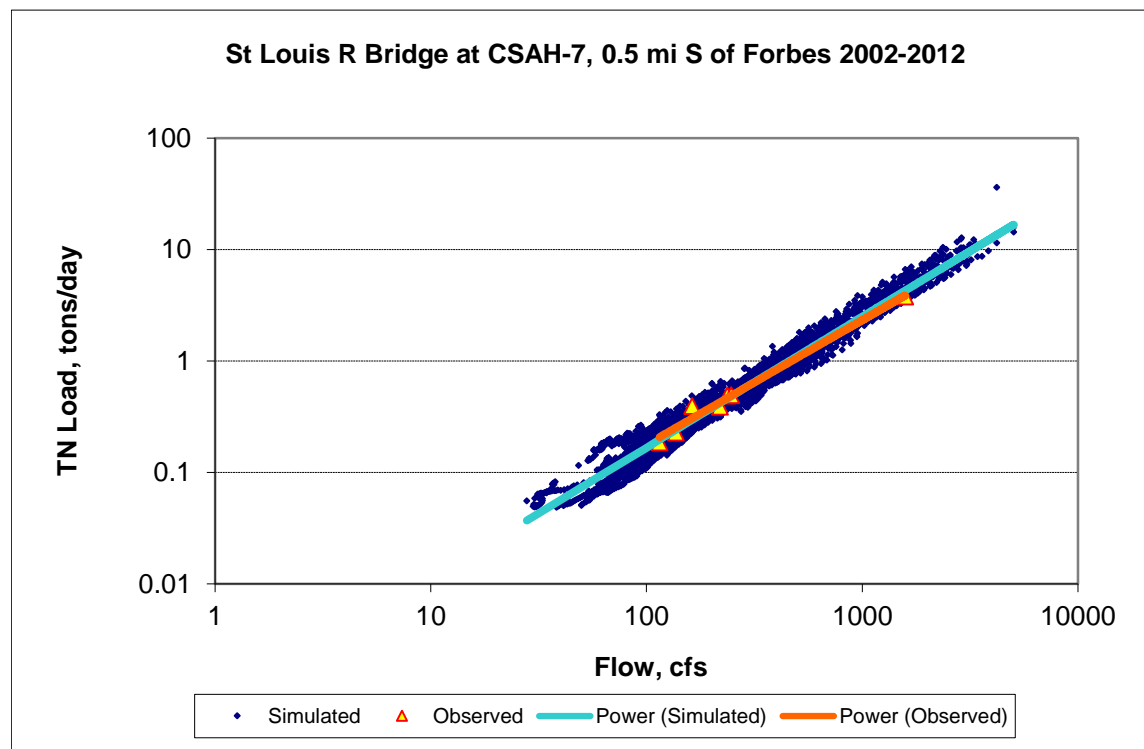


Figure A-63. Power plot of simulated and observed Total Nitrogen (TN) load vs flow at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes (calibration period)

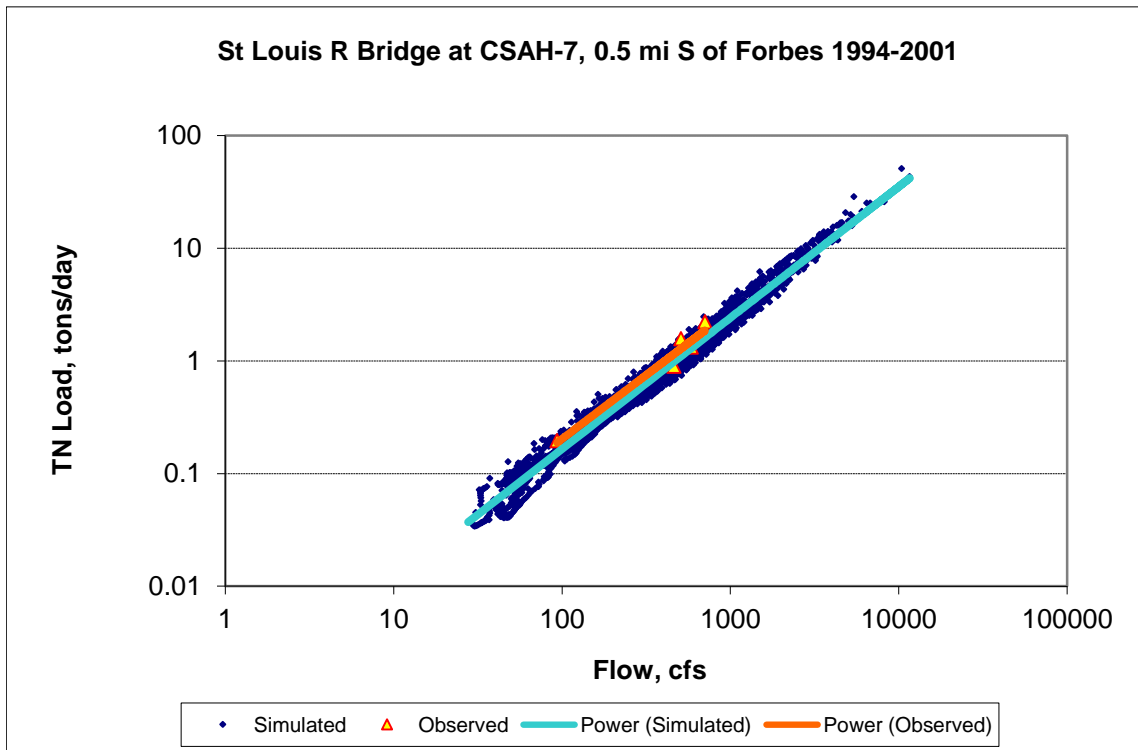
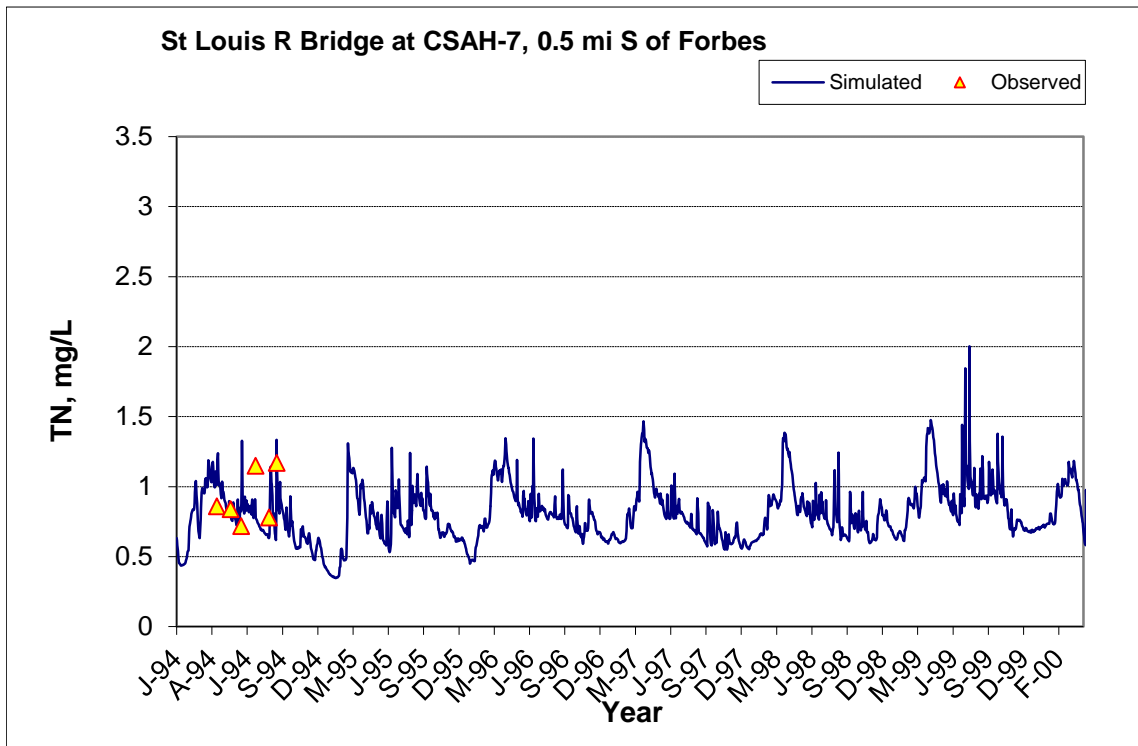


Figure A-64. Power plot of simulated and observed Total Nitrogen (TN) load vs flow at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes (validation period)



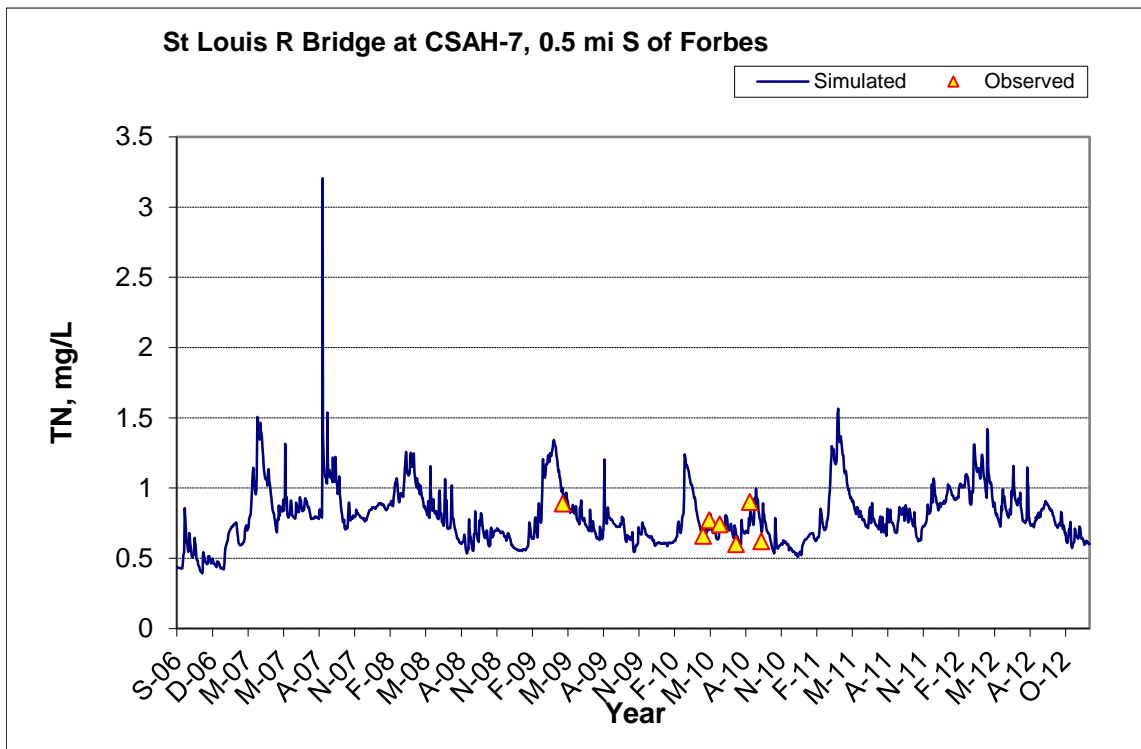
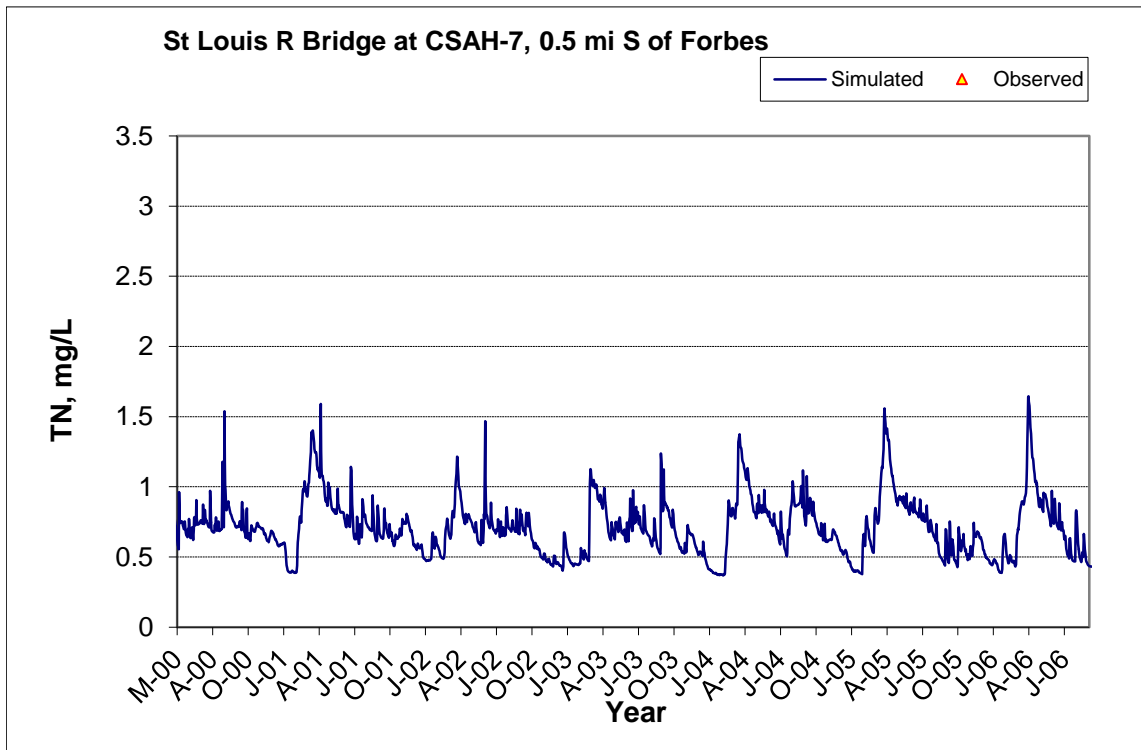


Figure A-65. Time series of observed and simulated Total Nitrogen (TN) concentration at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes

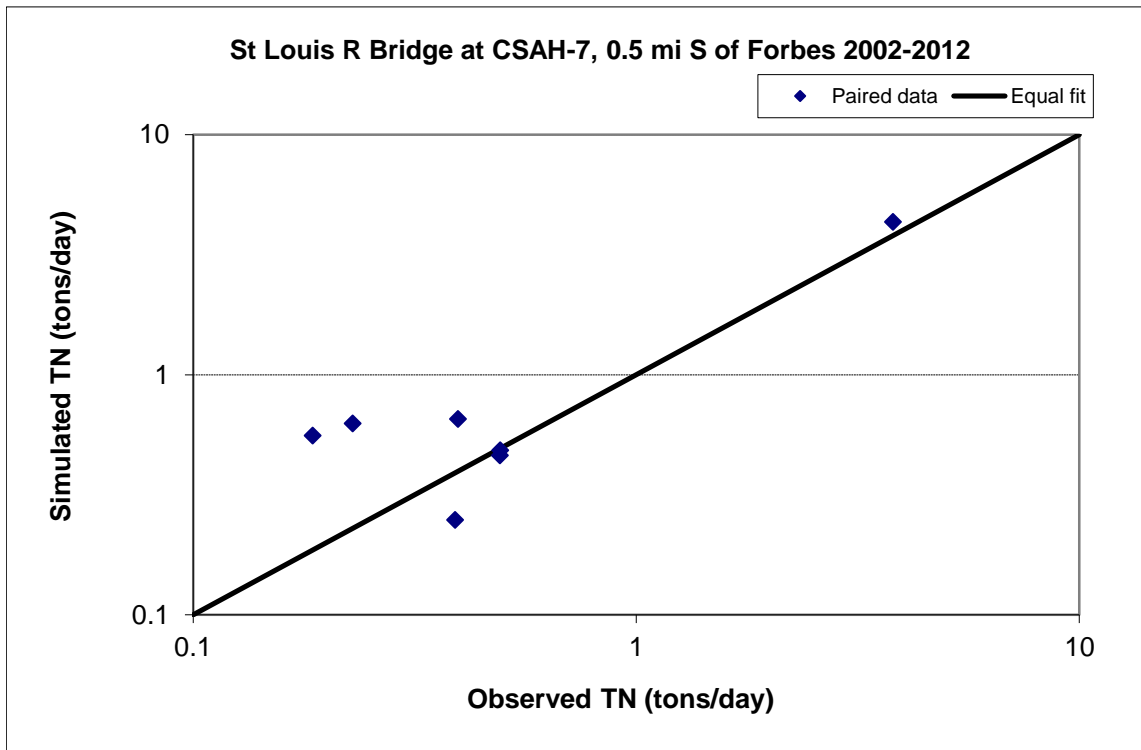


Figure A-66. Paired simulated vs. observed Total Nitrogen (TN) load at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes (calibration period)

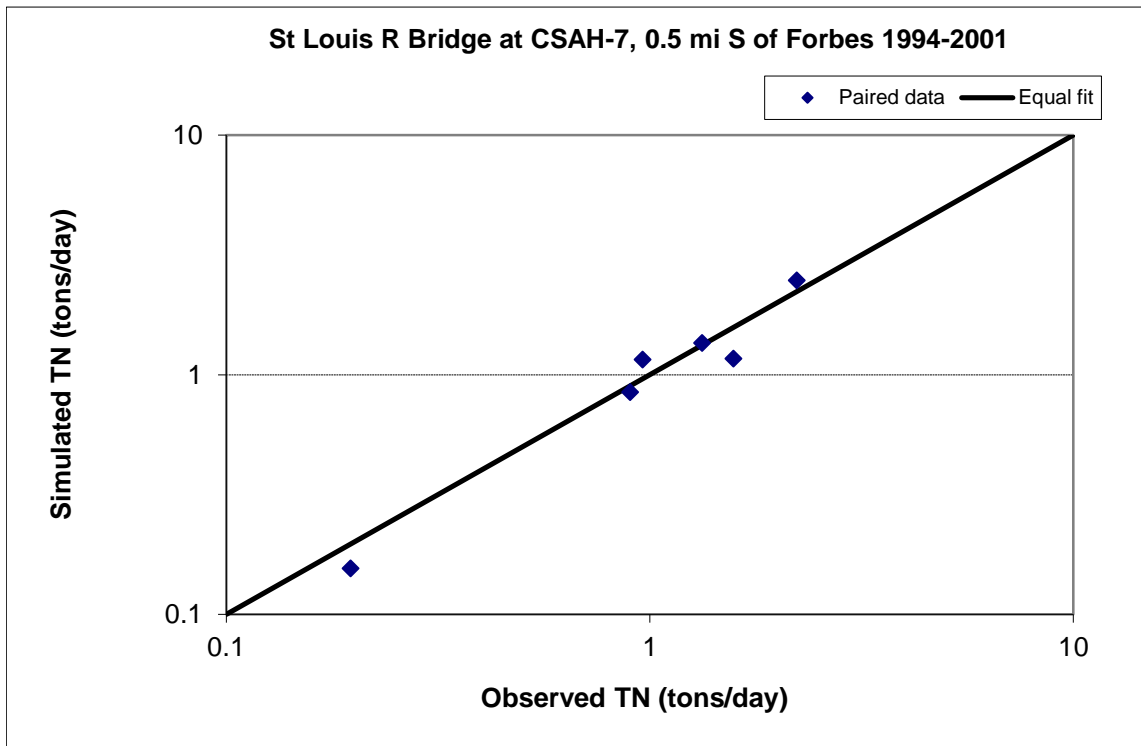


Figure A-67. Paired simulated vs. observed Total Nitrogen (TN) load at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes (validation period)

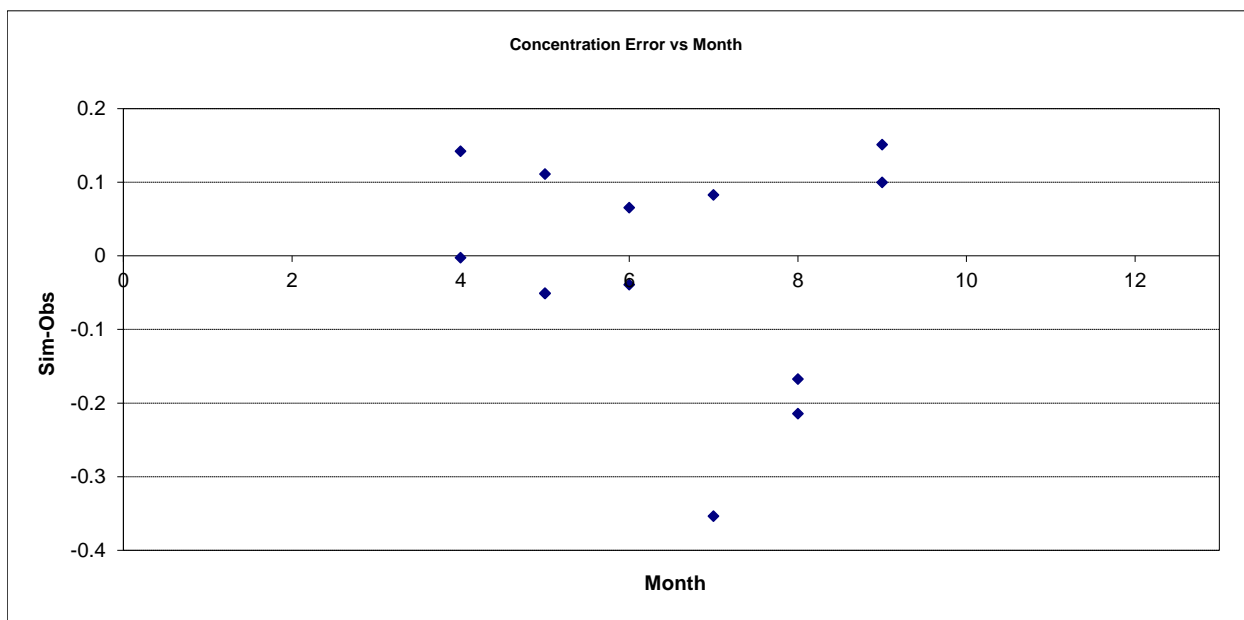


Figure A-68. Residual (Simulated - Observed) vs. Month Total Nitrogen (TN) at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes

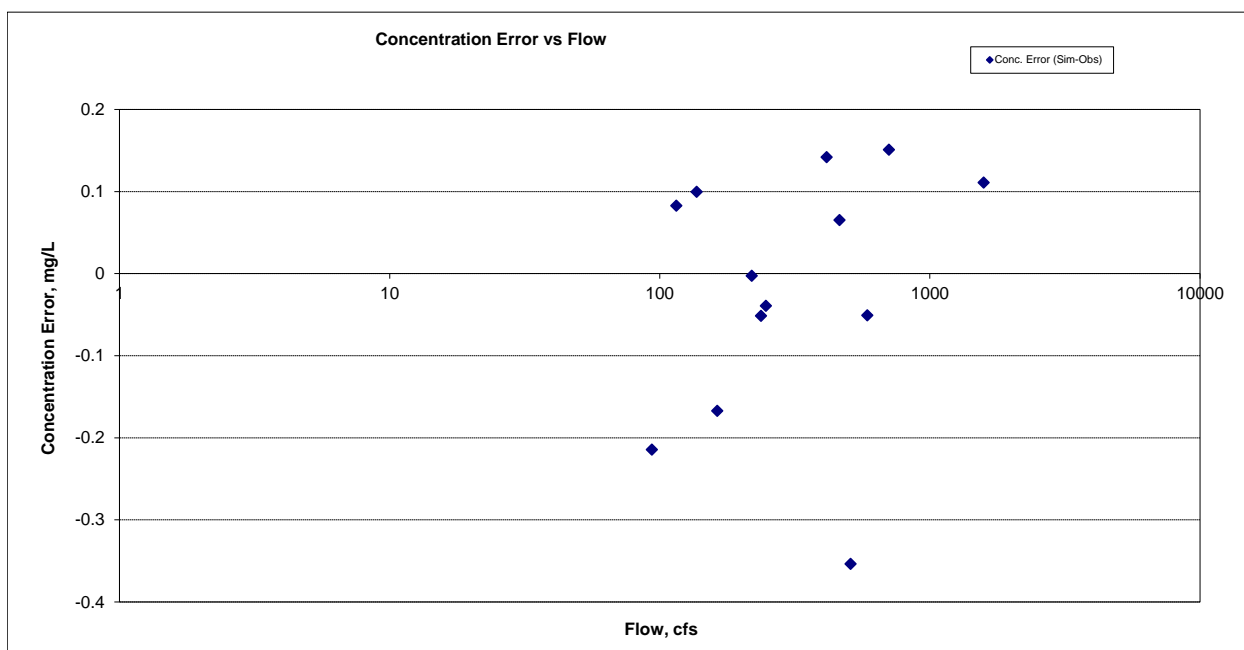
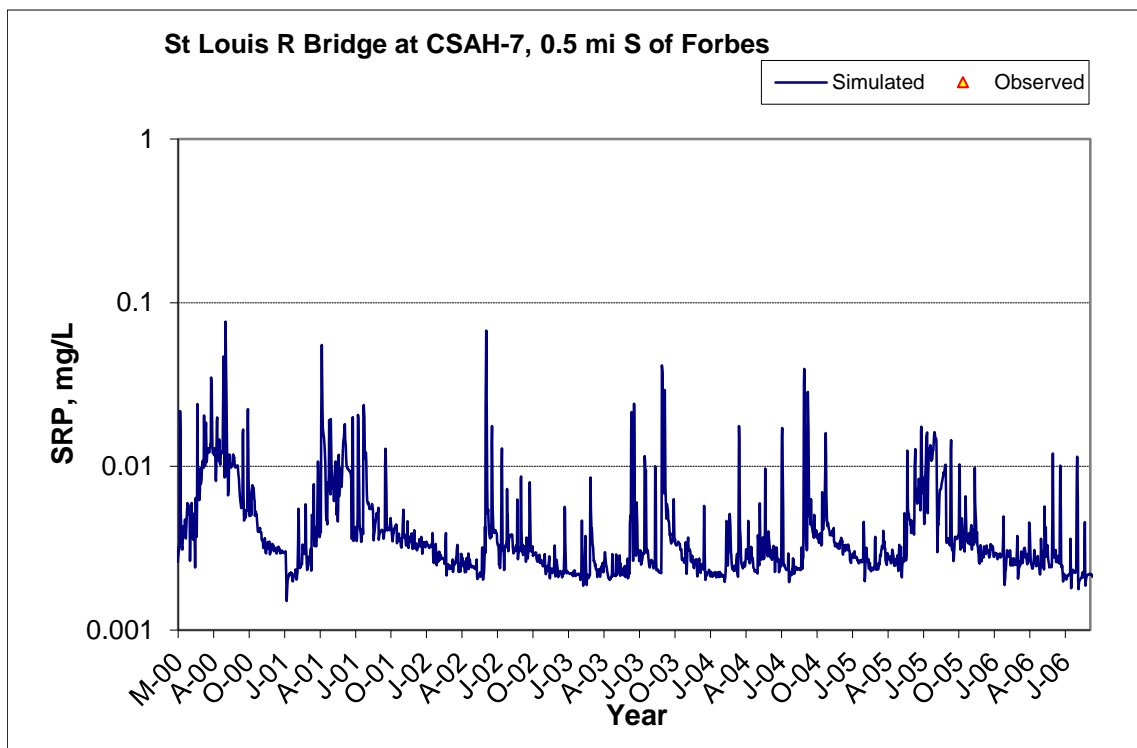
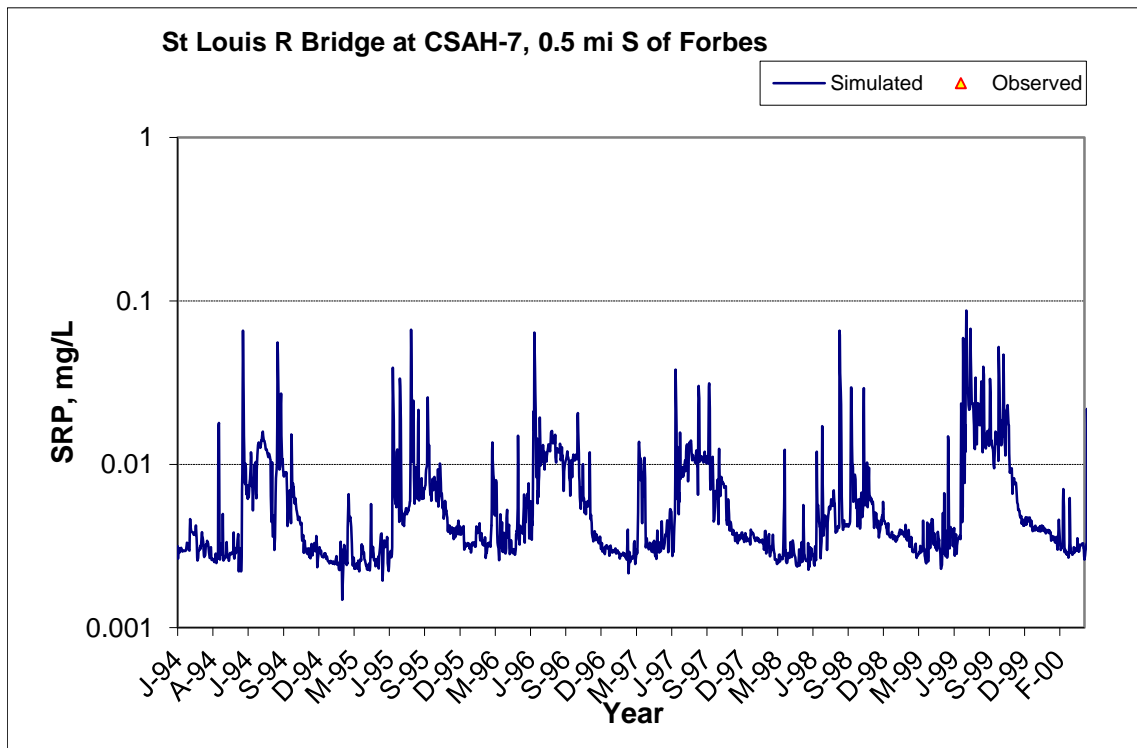


Figure A-69. Residual (Simulated - Observed) vs. Flow Total Nitrogen (TN) at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes

A.3.6 Soluble Reactive Phosphorus (SRP)



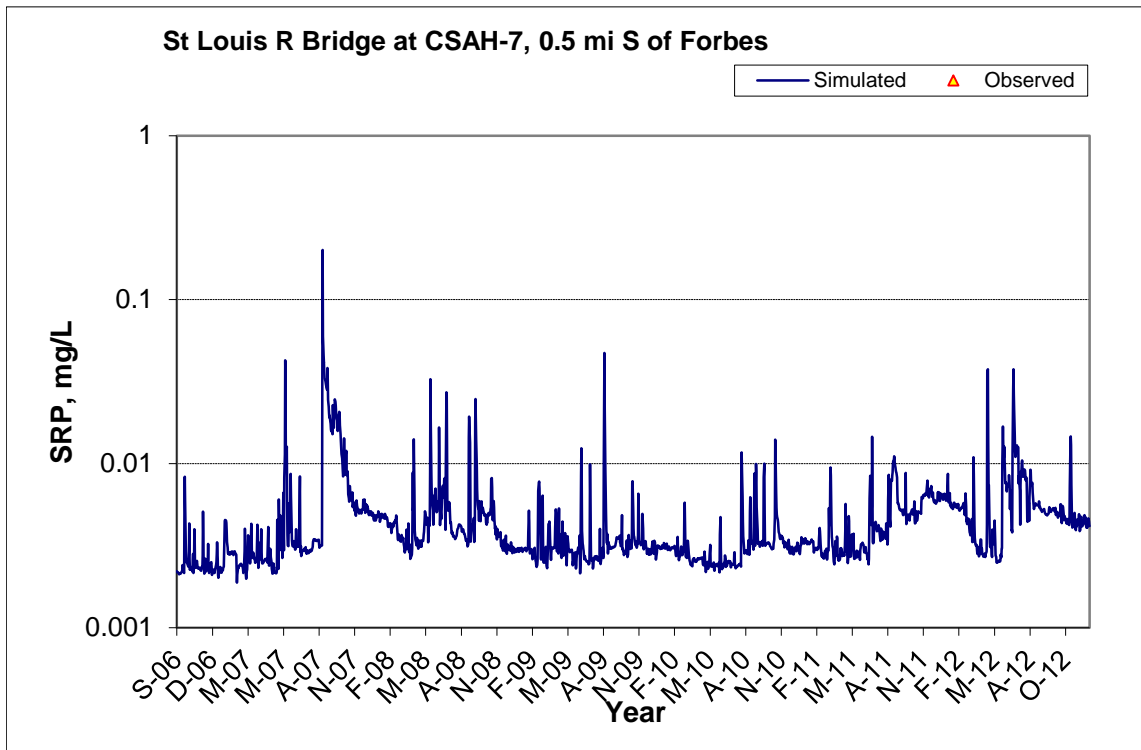
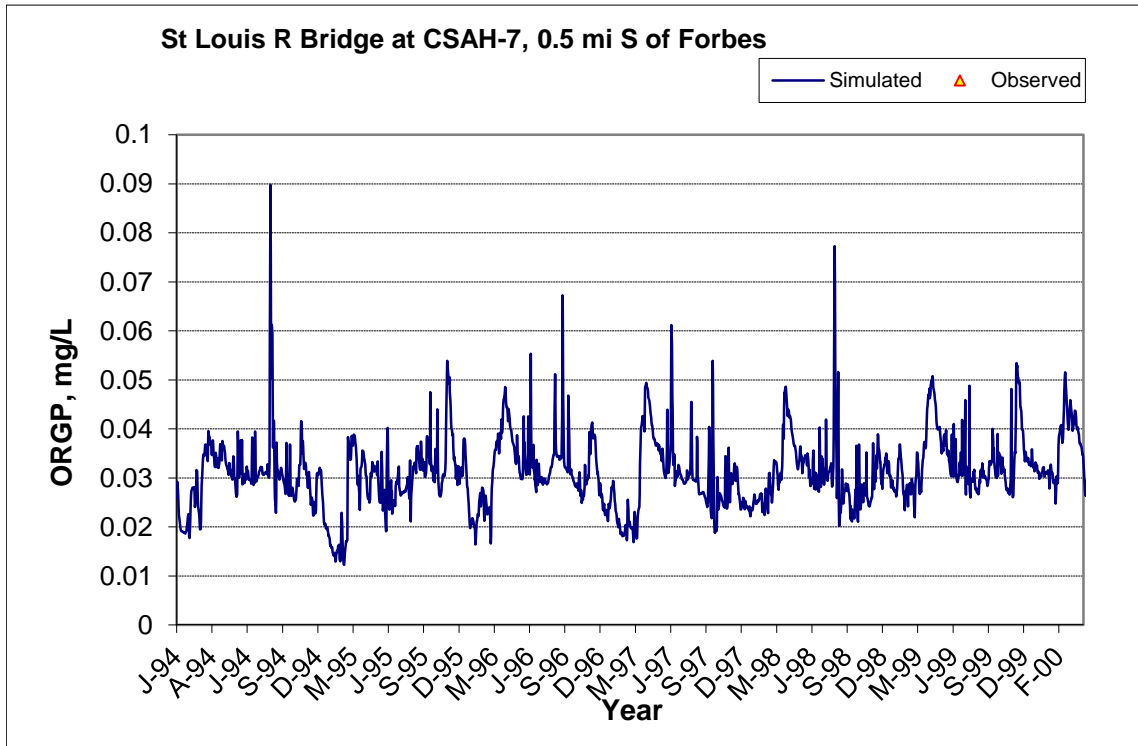


Figure A-70. Time series of observed and simulated Soluble Reactive Phosphorus (SRP) concentration at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes

A.3.7 Organic Phosphorus (OrgP)



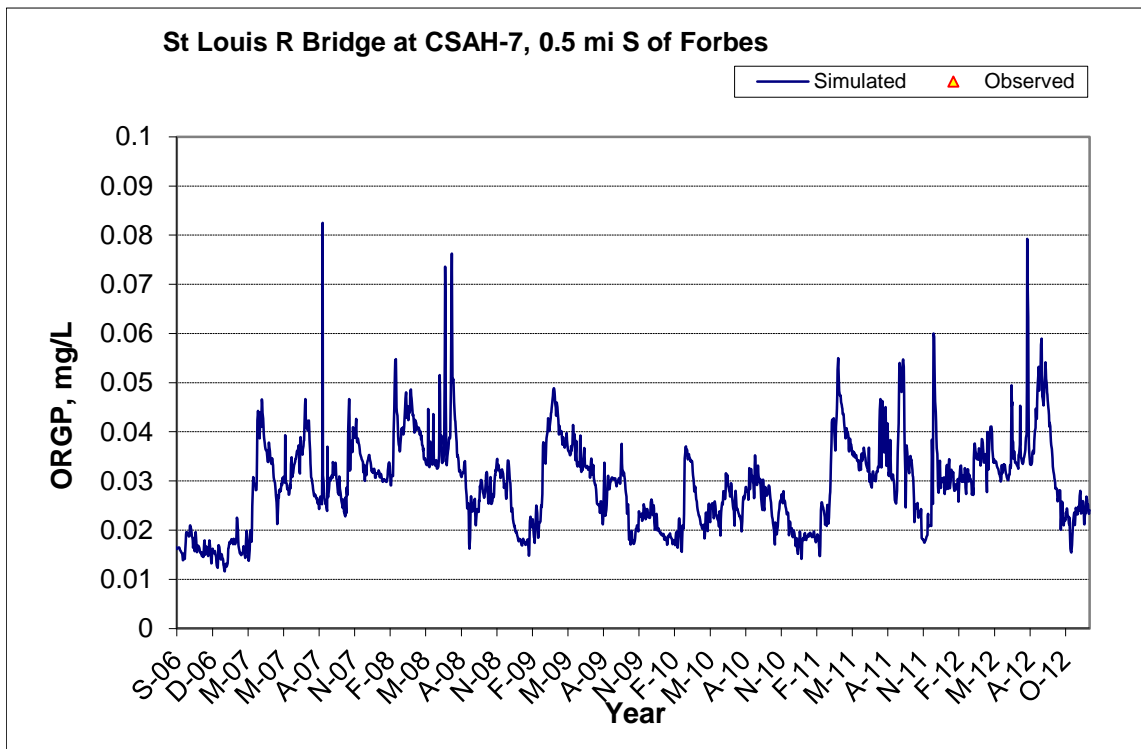
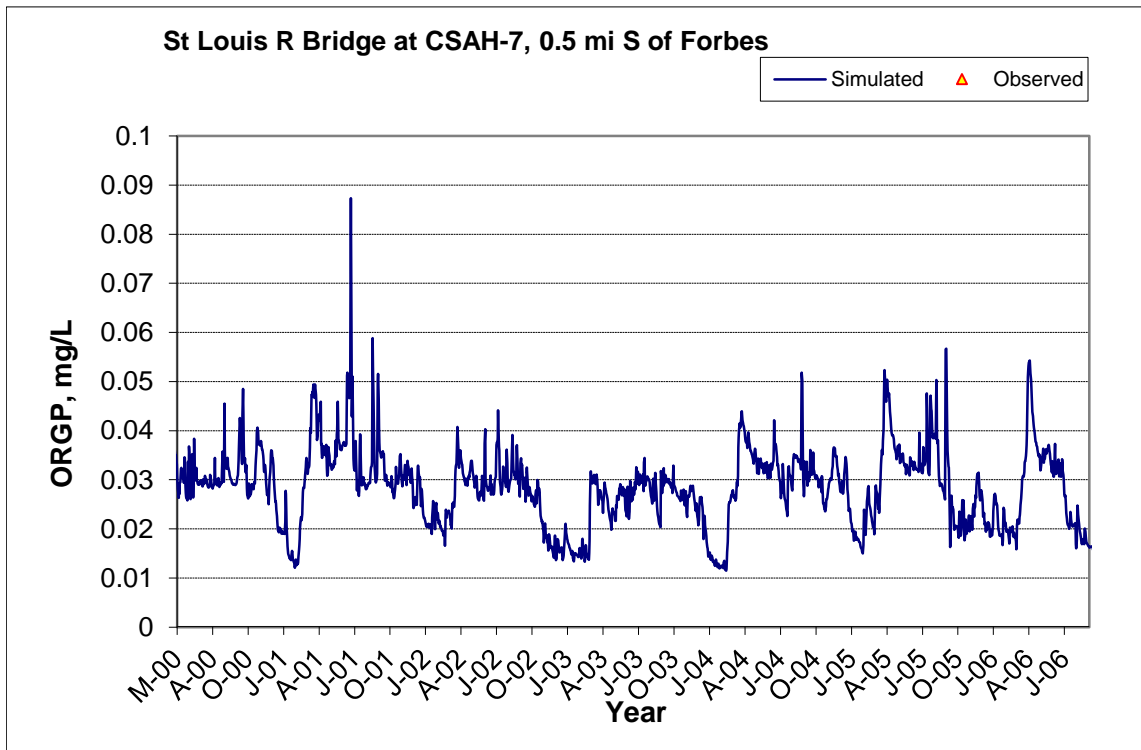


Figure A-71. Time series of observed and simulated Organic Phosphorus (OrgP) concentration at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes

A.3.8 Total Phosphorus (TP)

Table A-11. Total Phosphorus (TP) statistics

Period	1994-2001	2002-2012
Count	10	50
Concentration Average Error	6.03%	20.00%
Concentration Median Error	6.42%	20.47%
Load Average Error	-0.77%	4.92%
Load Median Error	7.11%	12.32%
Paired t conc	0.77	0.50
Paired t load	0.73	0.73

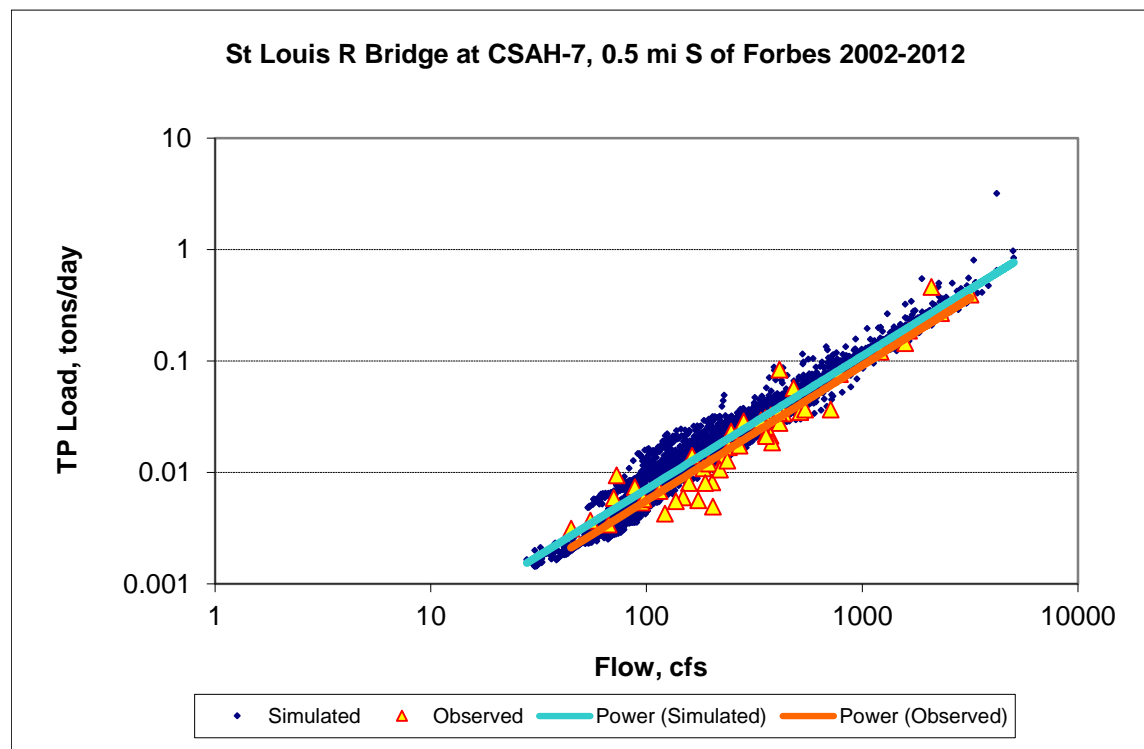


Figure A-72. Power plot of simulated and observed Total Phosphorus (TP) load vs flow at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes (calibration period)

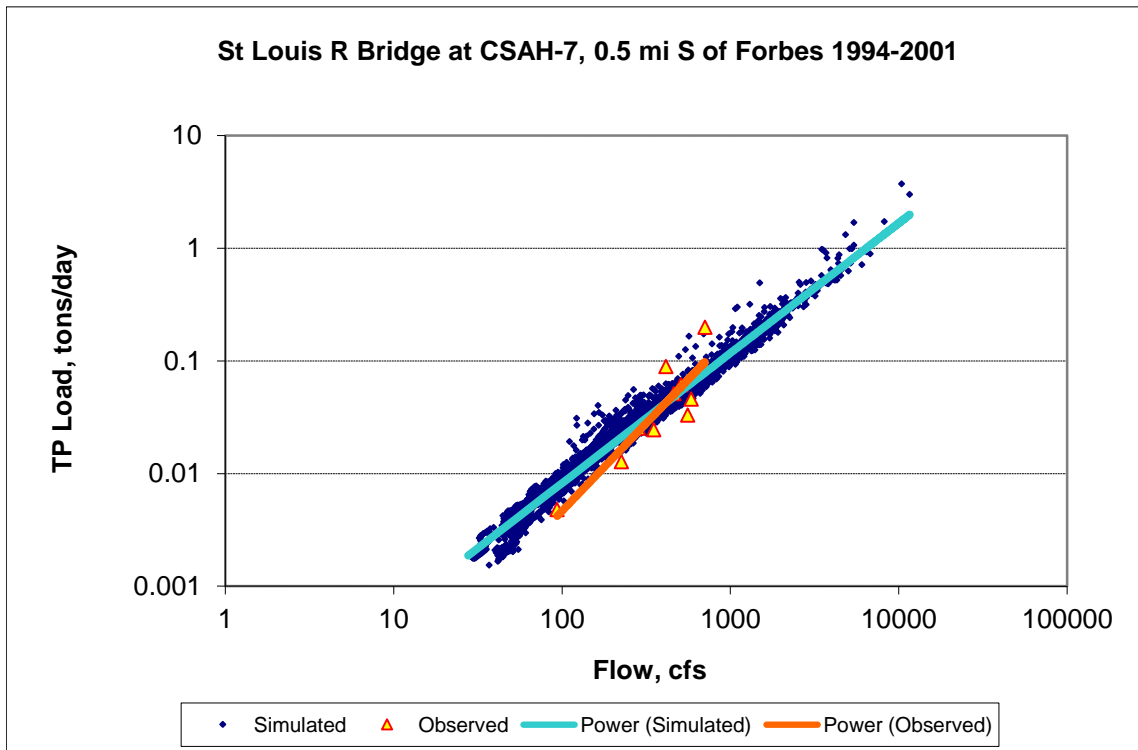
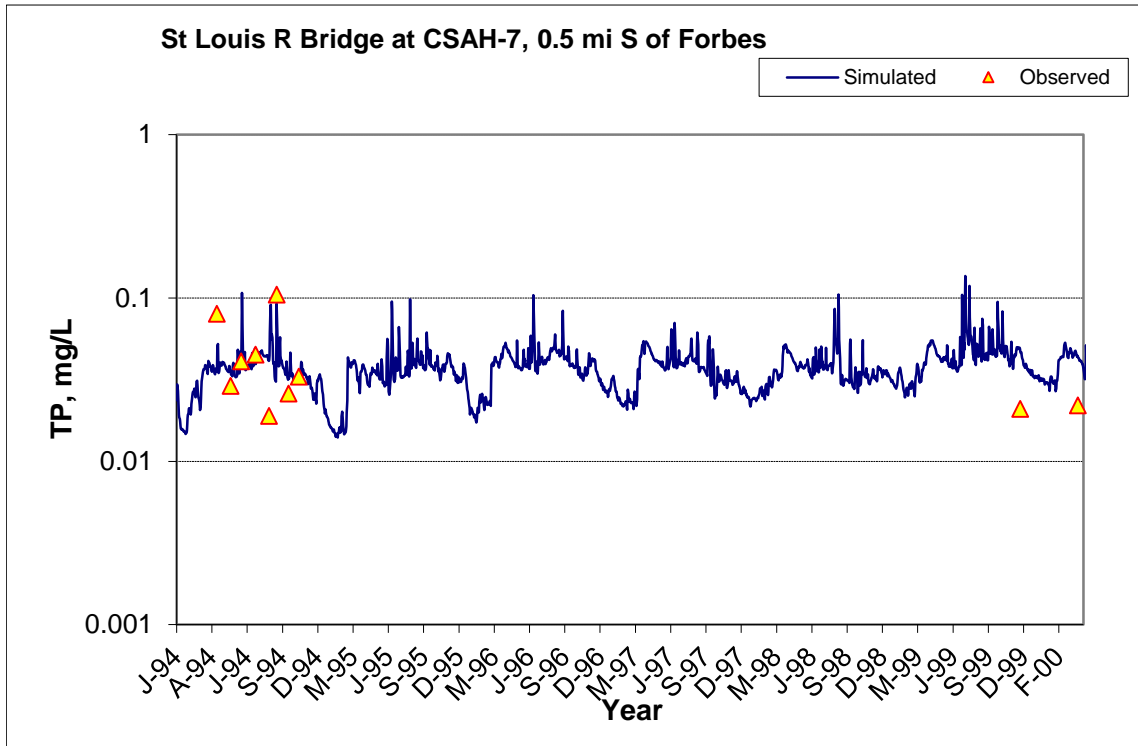


Figure A-73. Power plot of simulated and observed Total Phosphorus (TP) load vs flow at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes (validation period)



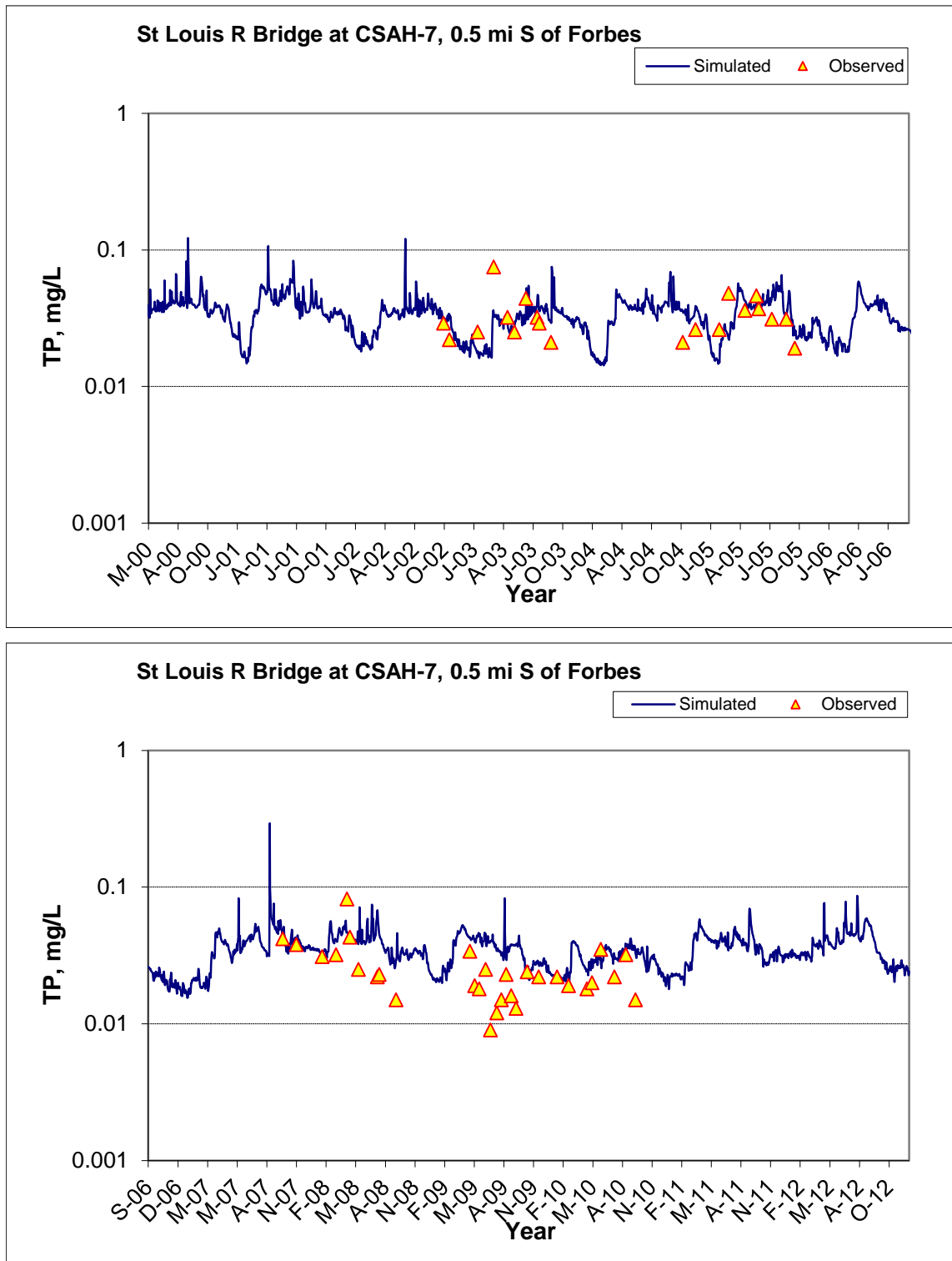


Figure A-74. Time series of observed and simulated Total Phosphorus (TP) concentration at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes

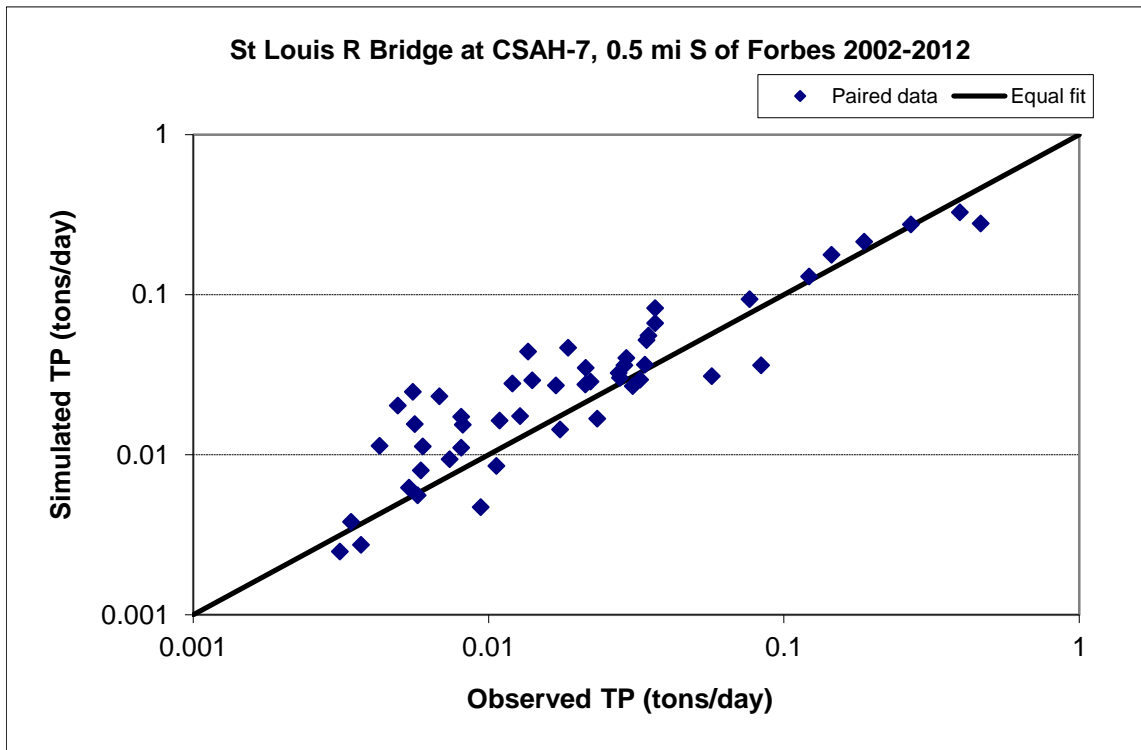


Figure A-75. Paired simulated vs. observed Total Phosphorus (TP) load at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes (calibration period)

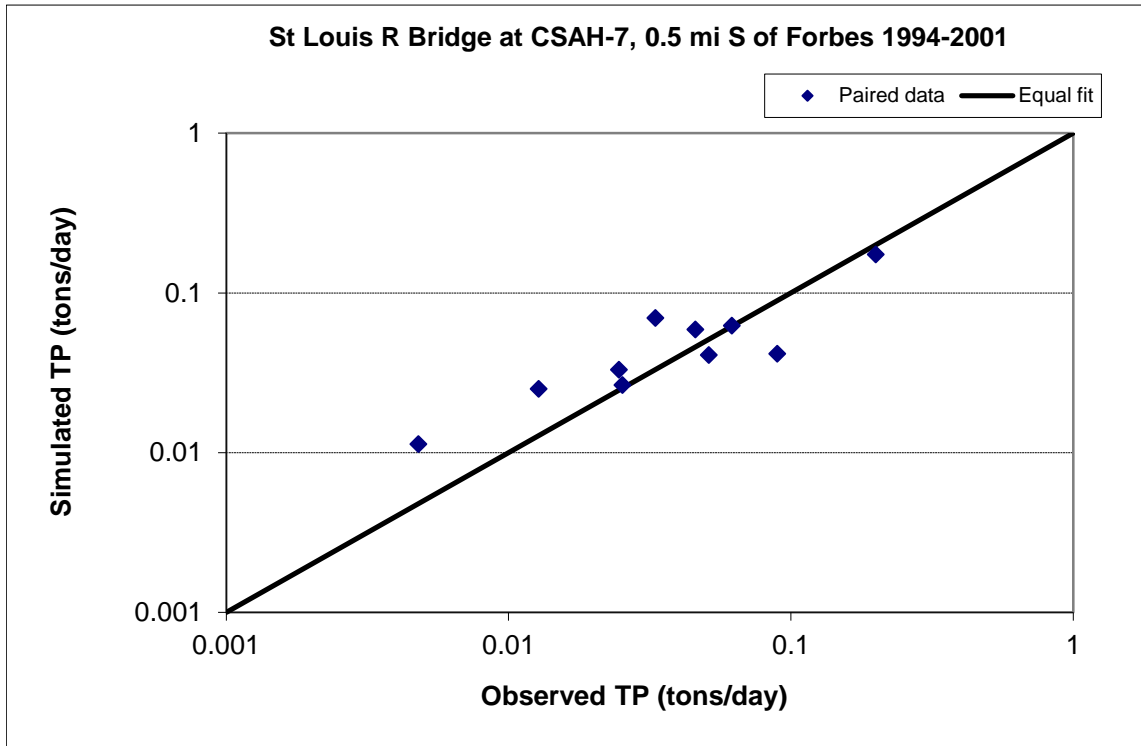


Figure A-76. Paired simulated vs. observed Total Phosphorus (TP) load at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes (validation period)

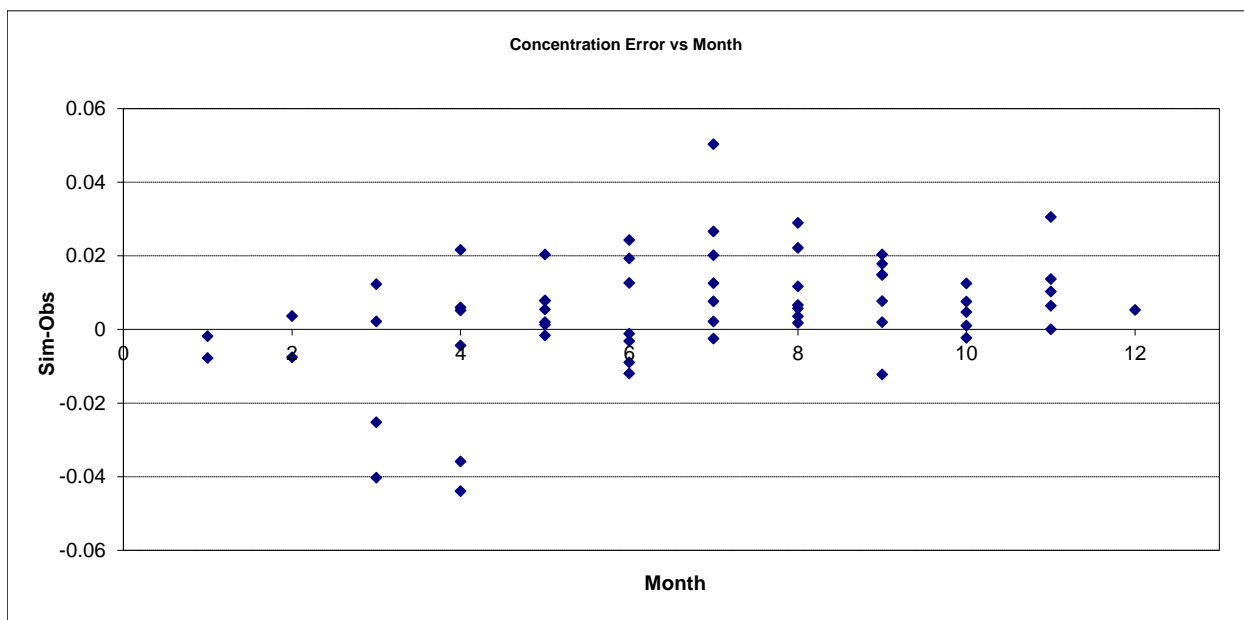


Figure A-77. Residual (Simulated - Observed) vs. Month Total Phosphorus (TP) at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes

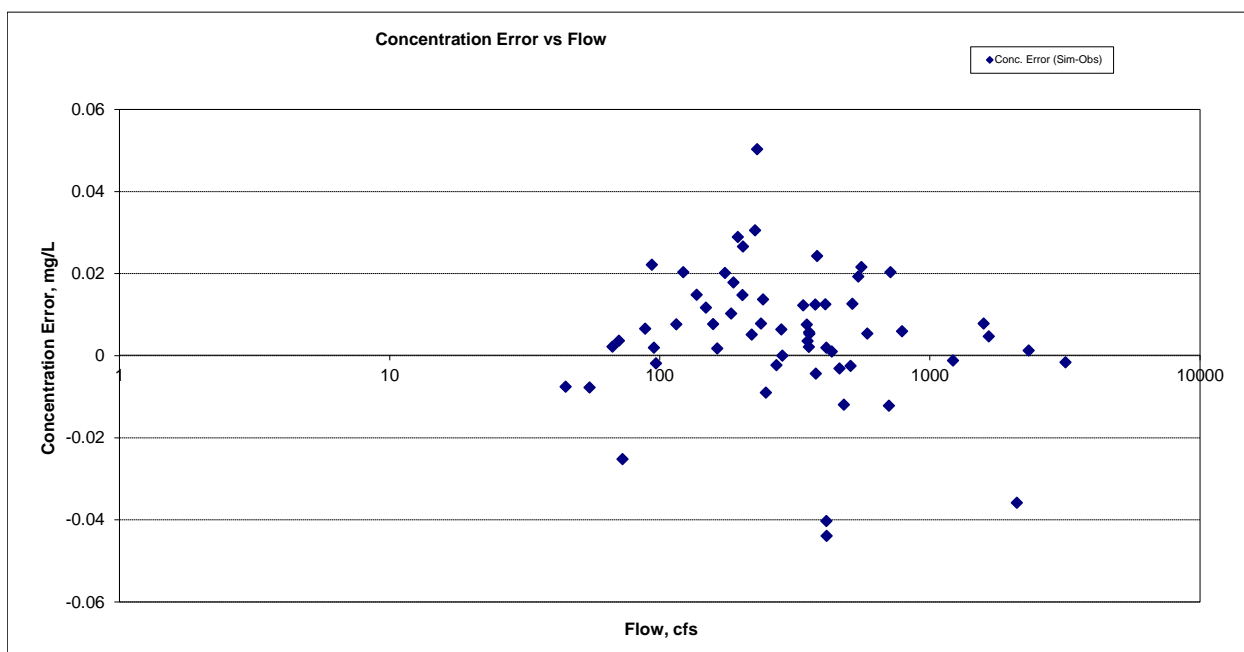


Figure A-78. Residual (Simulated - Observed) vs. Flow Total Phosphorus (TP) at St Louis R Bridge at CSAH-7, 0.5 mi S of Forbes

A.4 ST. LOUIS R BLW CLOQUET R (S000-023)

A.4.1 Ammonia Nitrogen (NH3)

Table A-12. Ammonia Nitrogen (NH3) statistics

Period	1994-2001	2002-2012
Count	36	38
Concentration Average Error	92.81%	16.55%
Concentration Median Error	105.61%	18.49%
Load Average Error	77.19%	7.75%
Load Median Error	77.60%	18.56%
Paired t conc	0.00	0.66
Paired t load	0.03	0.78

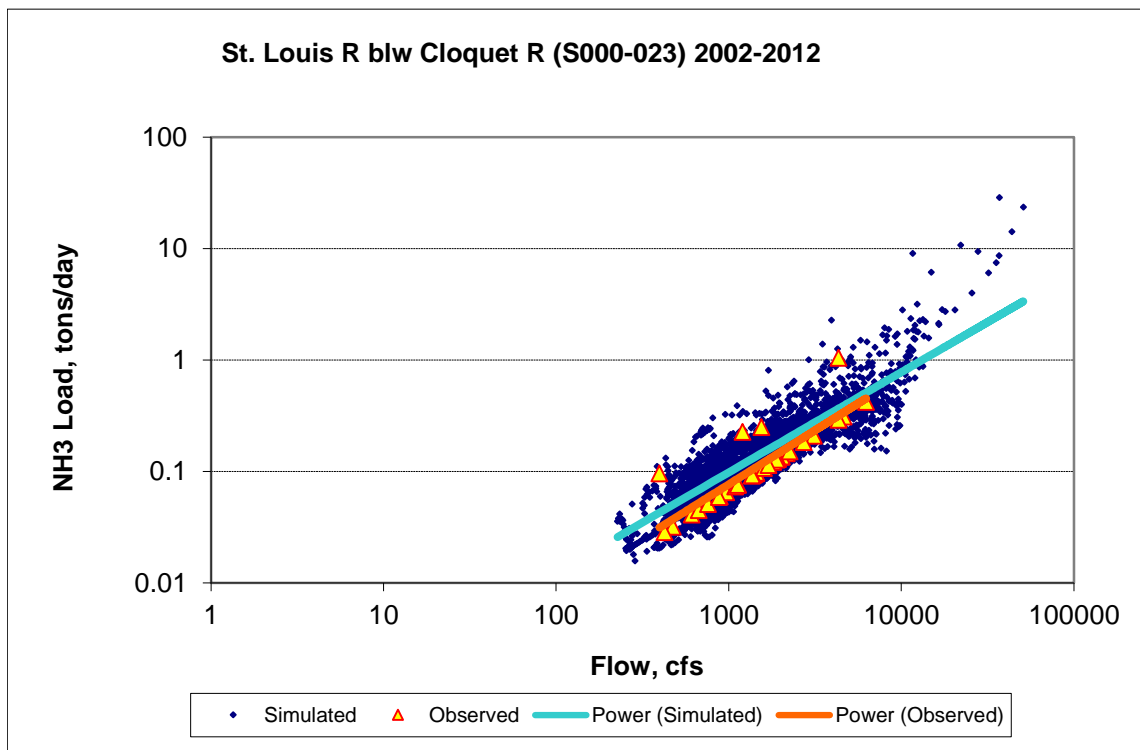


Figure A-79. Power plot of simulated and observed Ammonia Nitrogen (NH3) load vs flow at St. Louis R blw Cloquet R (S000-023) (calibration period)

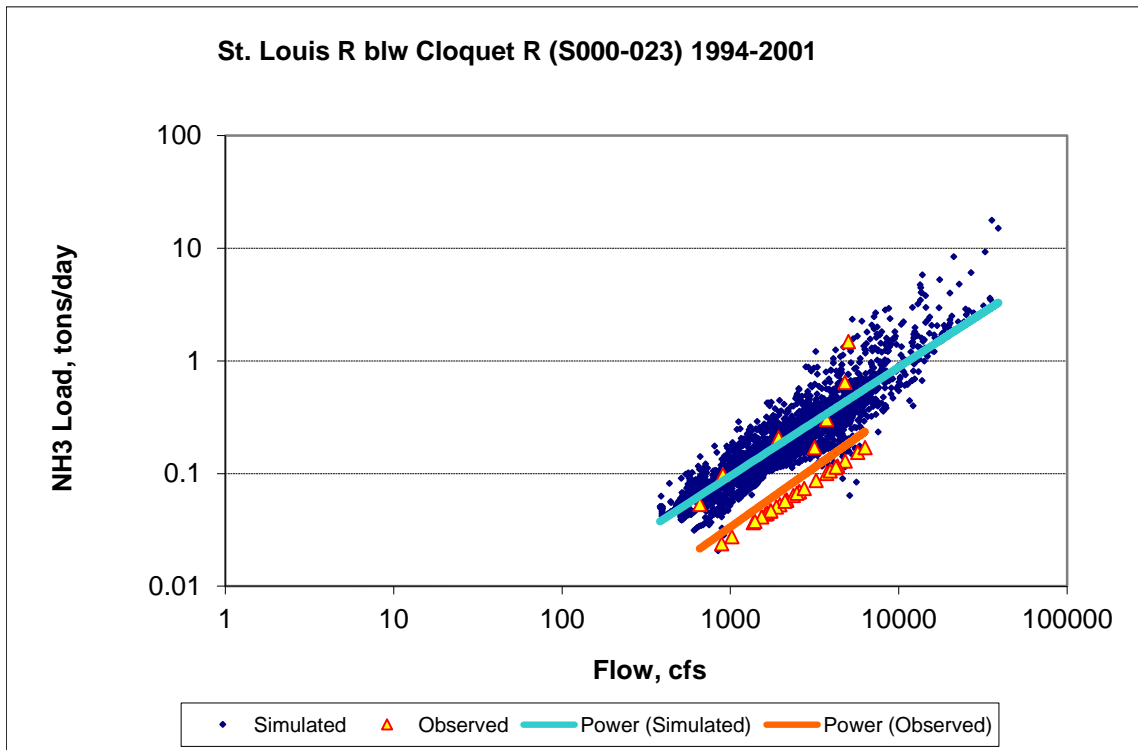
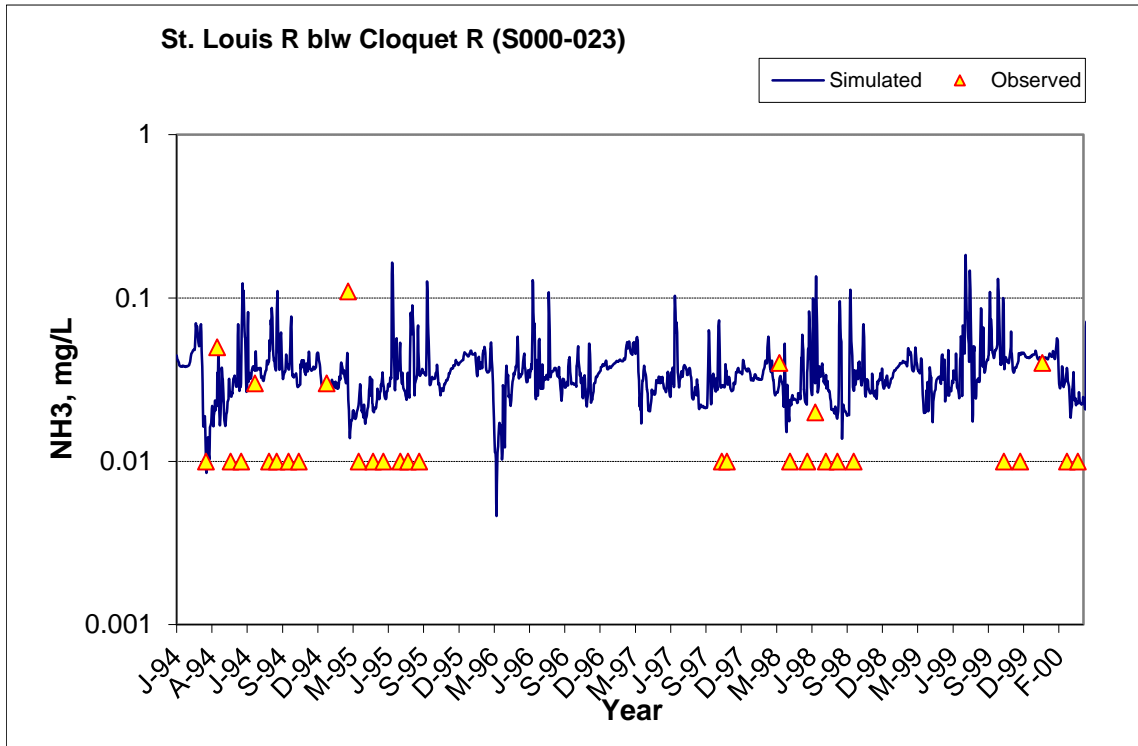


Figure A-80. Power plot of simulated and observed Ammonia Nitrogen (NH3) load vs flow at St. Louis R blw Cloquet R (S000-023) (validation period)



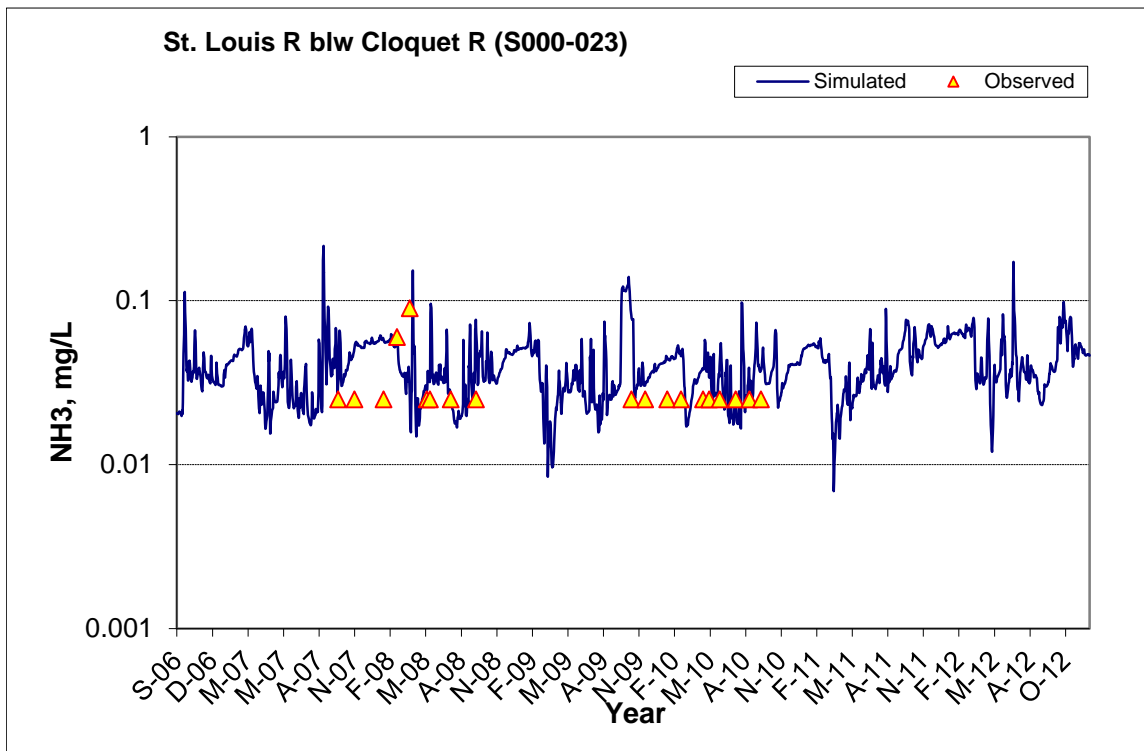
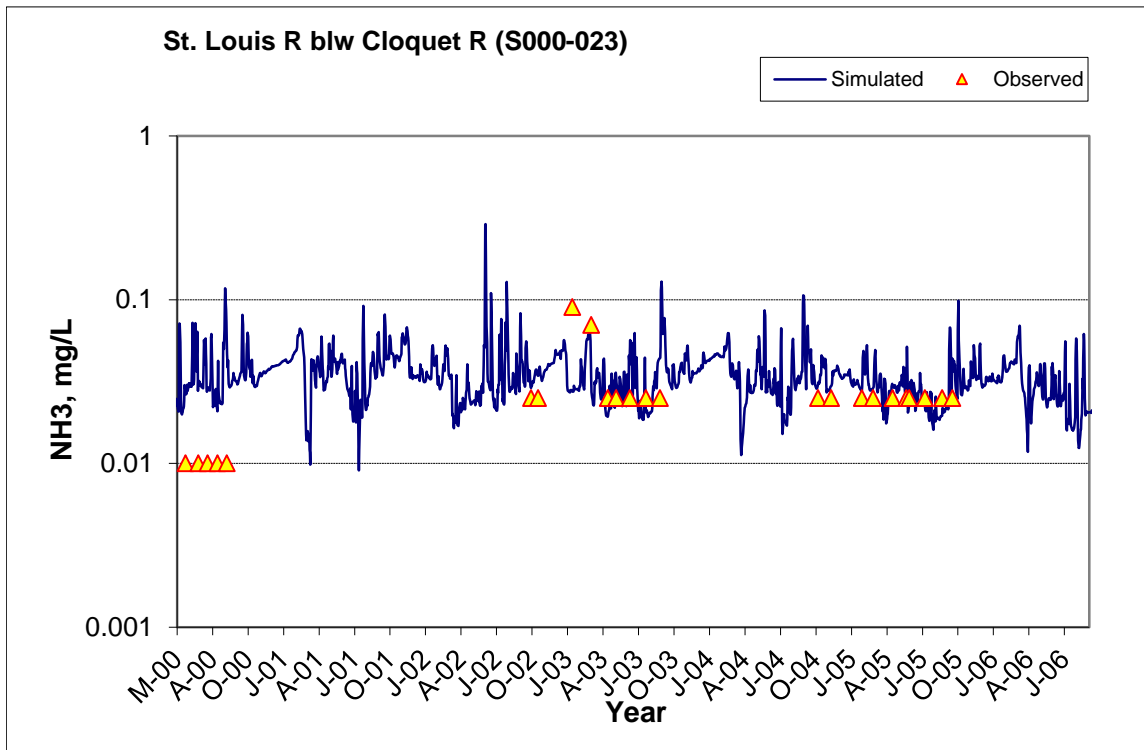


Figure A-81. Time series of observed and simulated Ammonia Nitrogen (NH₃) concentration at St. Louis R blw Cloquet R (S000-023)

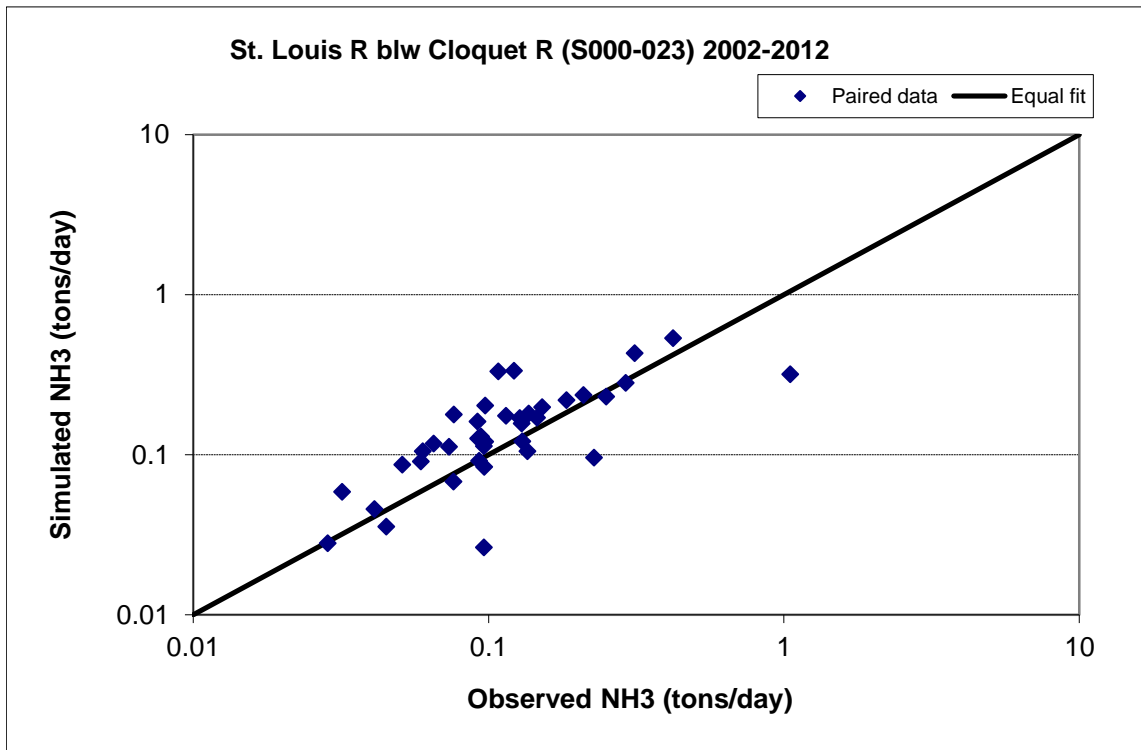


Figure A-82. Paired simulated vs. observed Ammonia Nitrogen (NH3) load at St. Louis R blw Cloquet R (S000-023) (calibration period)

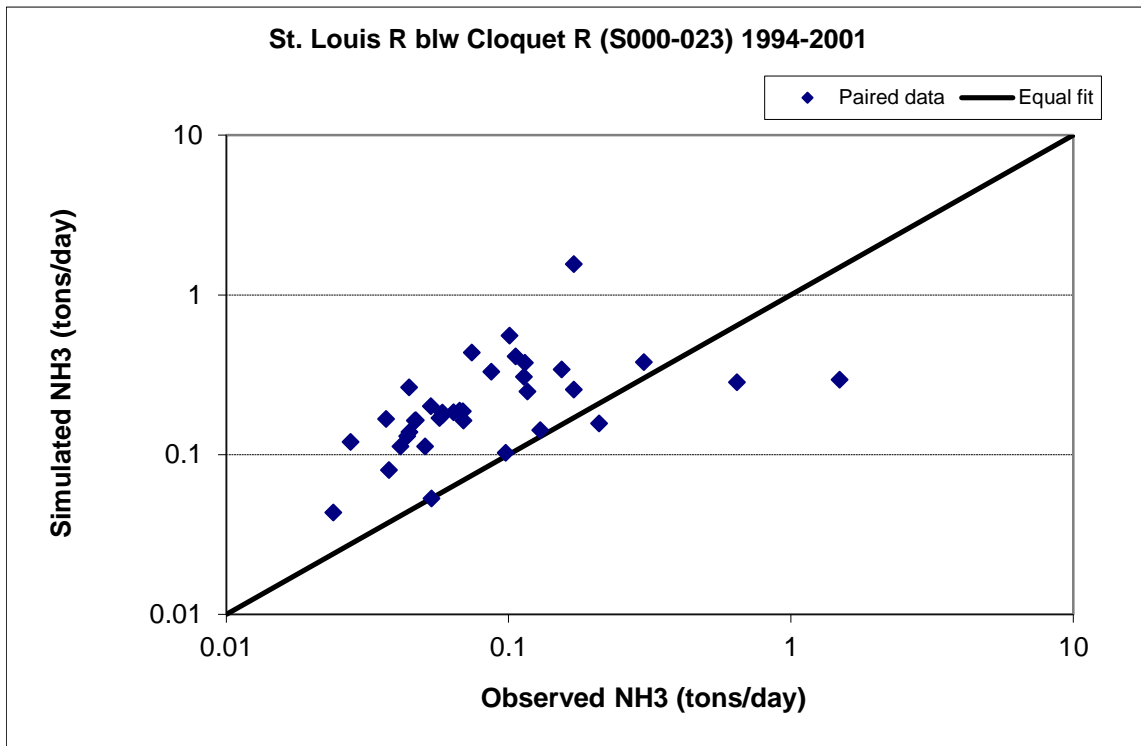


Figure A-83. Paired simulated vs. observed Ammonia Nitrogen (NH3) load at St. Louis R blw Cloquet R (S000-023) (validation period)

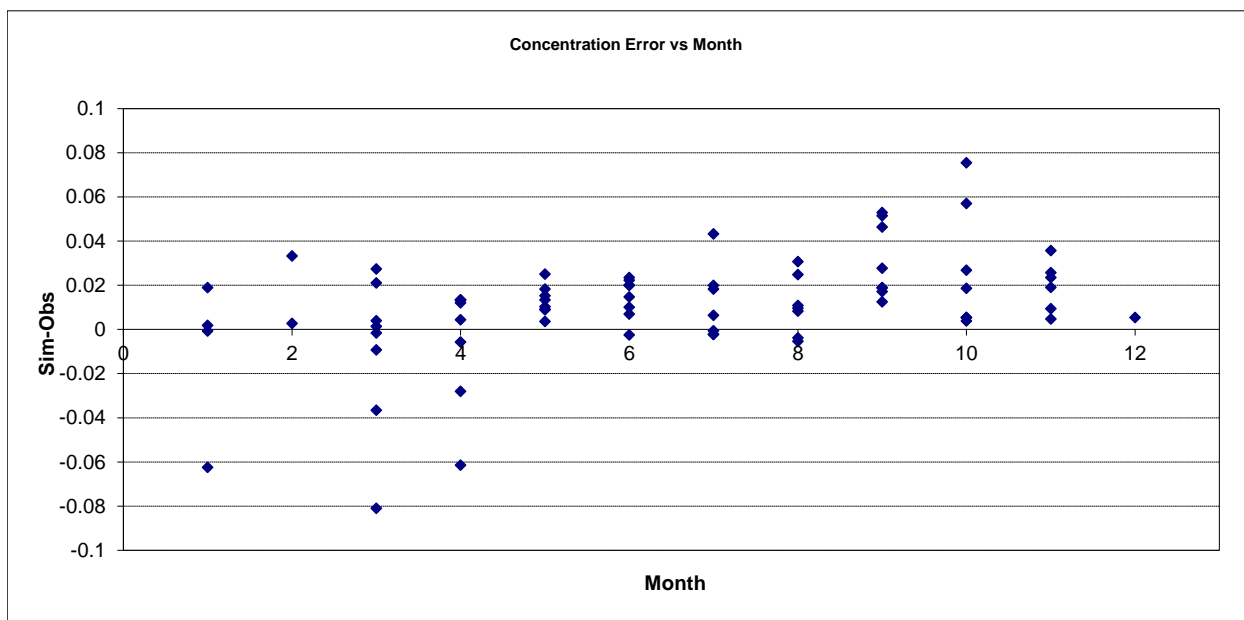


Figure A-84. Residual (Simulated - Observed) vs. Month Ammonia Nitrogen (NH3) at St. Louis R blw Cloquet R (S000-023)

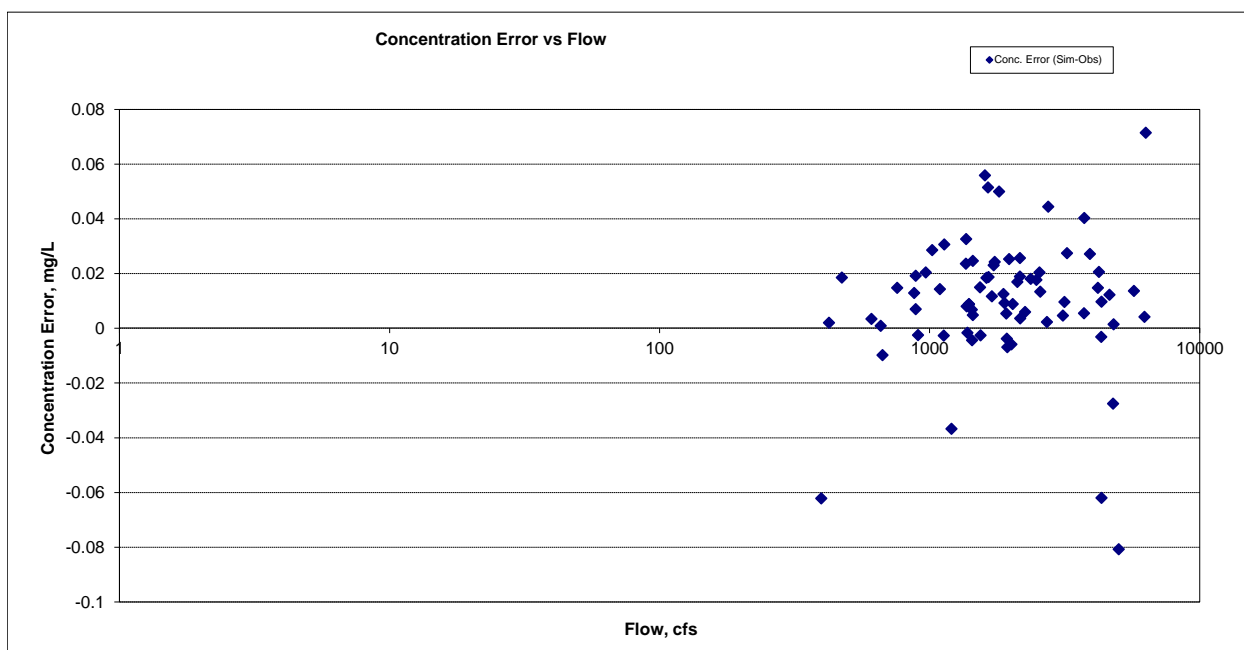
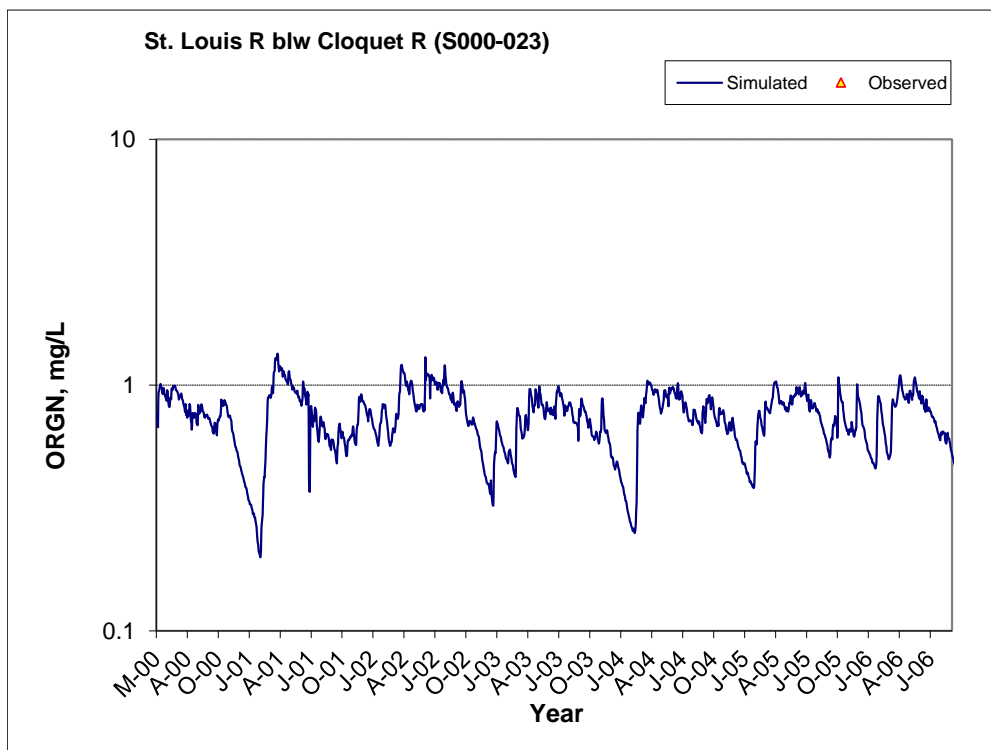
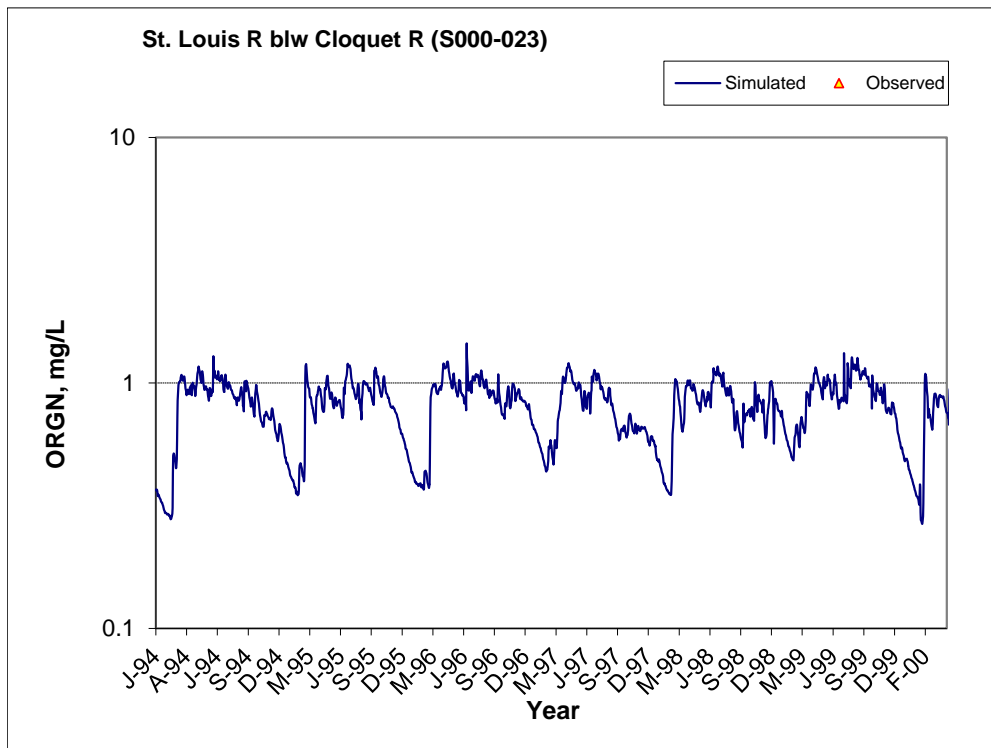


Figure A-85. Residual (Simulated - Observed) vs. Flow Ammonia Nitrogen (NH3) at St. Louis R blw Cloquet R (S000-023)

A.4.2 Organic Nitrogen (OrgN)



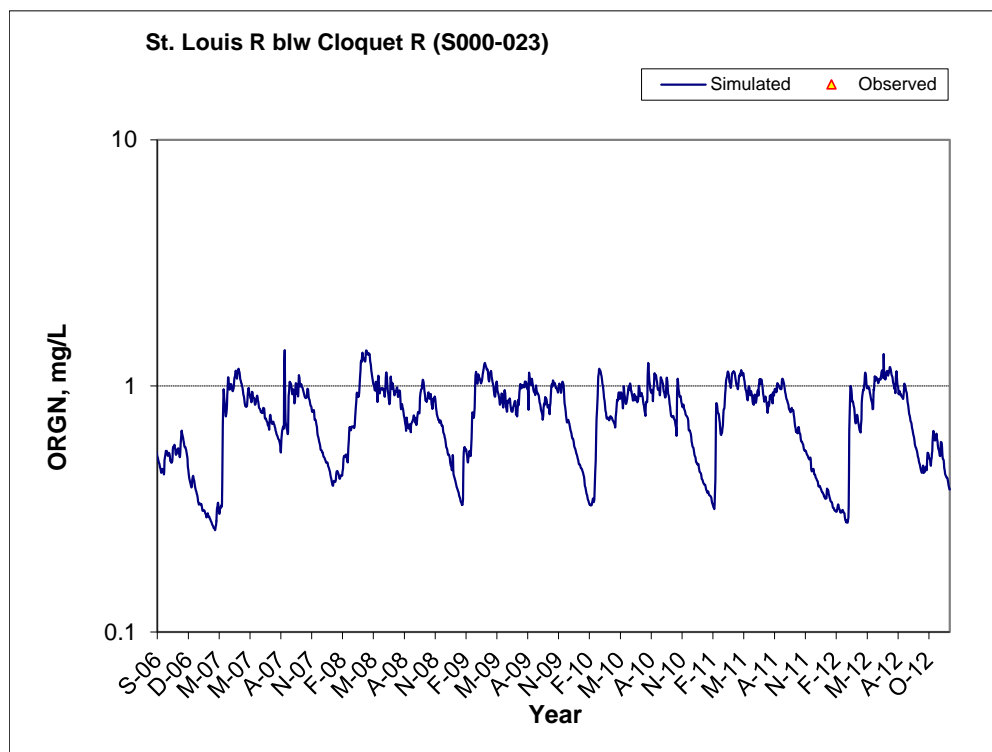


Figure A-86. Time series of observed and simulated Organic Nitrogen (OrgN) concentration at St. Louis R blw Cloquet R (S000-023)

A.4.3 Total Kjeldahl Nitrogen (TKN)

Table A-13. Total Kjeldahl Nitrogen (TKN) statistics

Period	1994-2001	2002-2012
Count	7	6
Concentration Average Error	44.41%	4.20%
Concentration Median Error	34.32%	1.49%
Load Average Error	52.50%	0.65%
Load Median Error	43.01%	-0.64%
Paired t conc	0.00	0.93
Paired t load	0.13	0.82

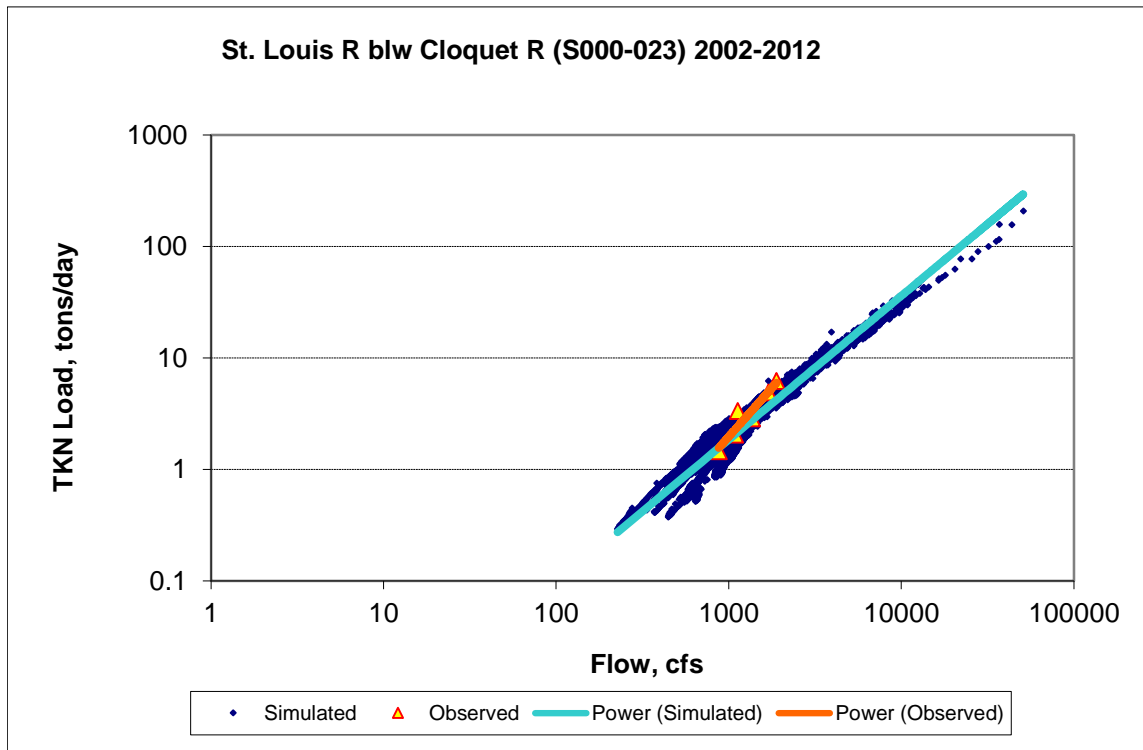


Figure A-87. Power plot of simulated and observed Total Kjeldahl Nitrogen (TKN) load vs flow at St. Louis R blw Cloquet R (S000-023) (calibration period)

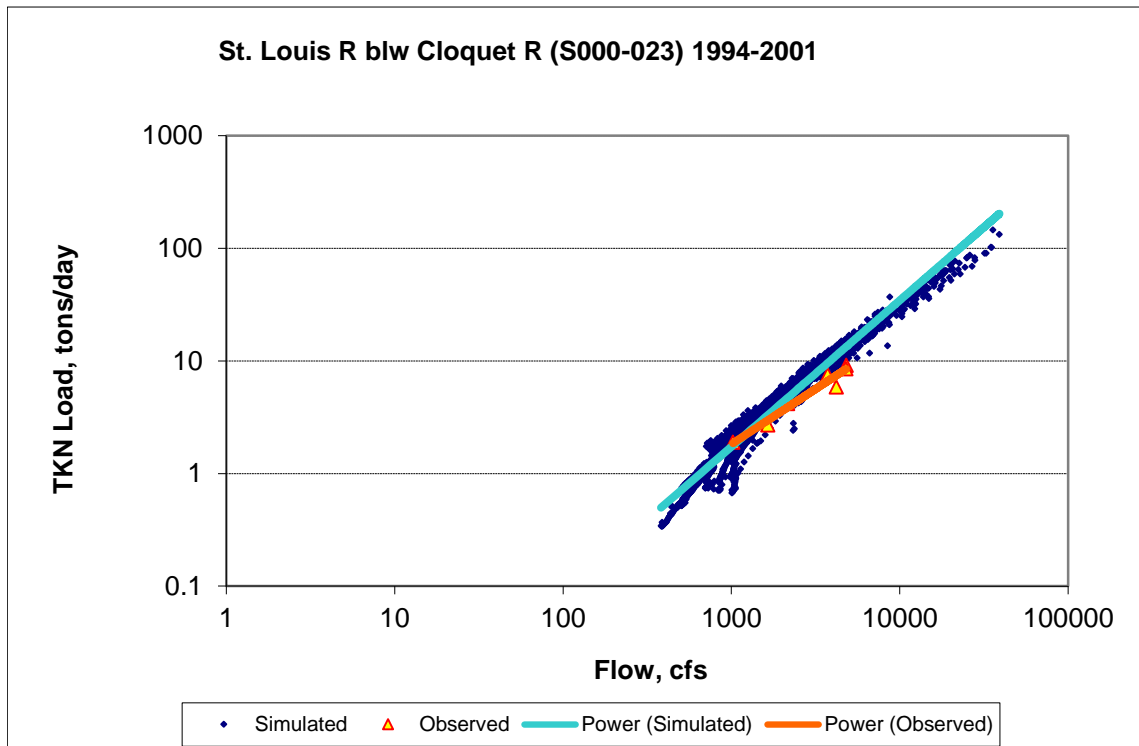
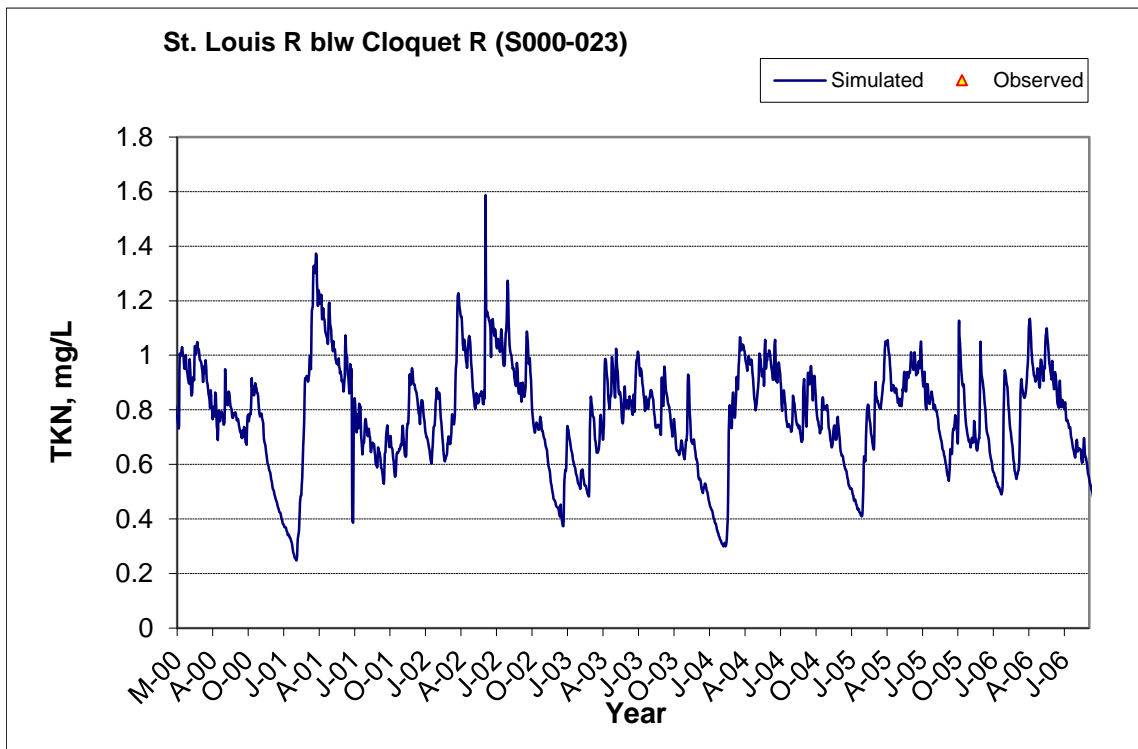
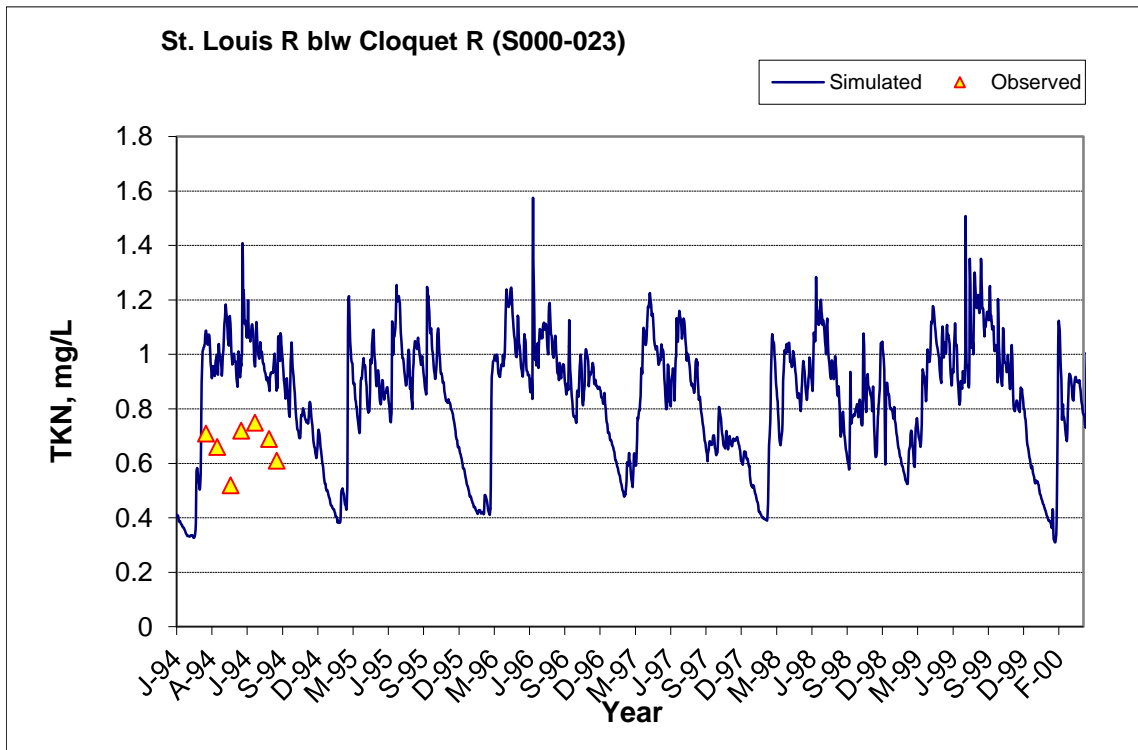


Figure A-88. Power plot of simulated and observed Total Kjeldahl Nitrogen (TKN) load vs flow at St. Louis R blw Cloquet R (S000-023) (validation period)



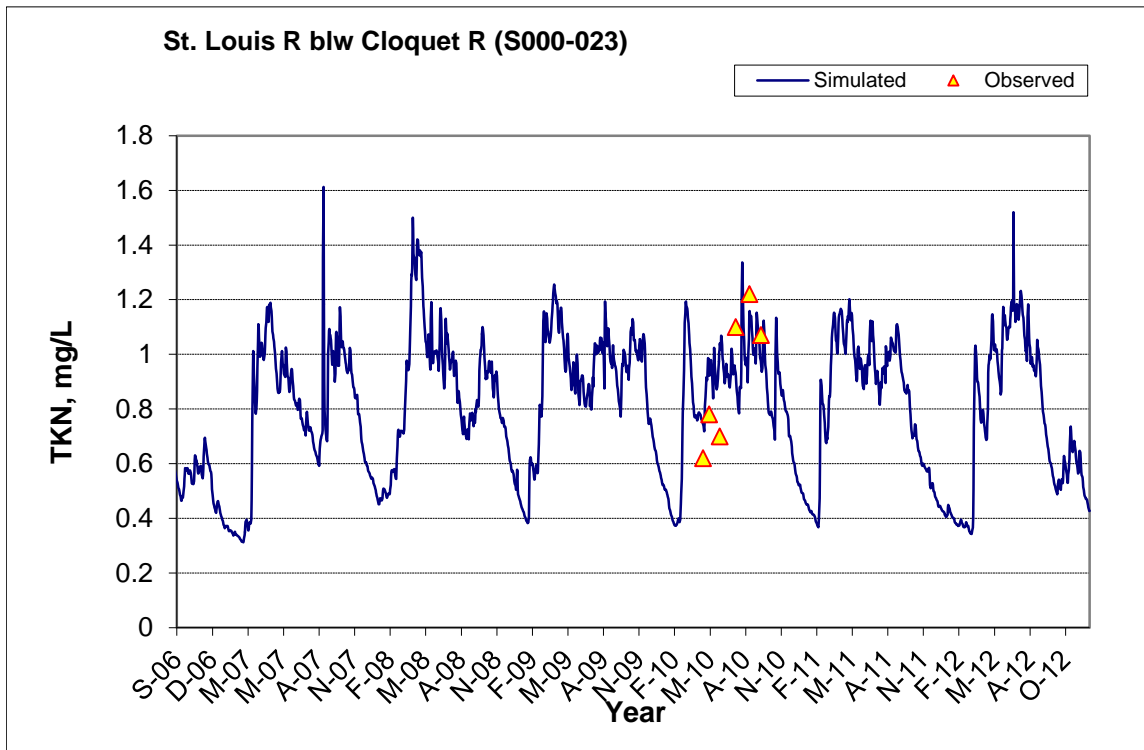


Figure A-89. Time series of observed and simulated Total Kjeldahl Nitrogen (TKN) concentration at St. Louis R blw Cloquet R (S000-023)

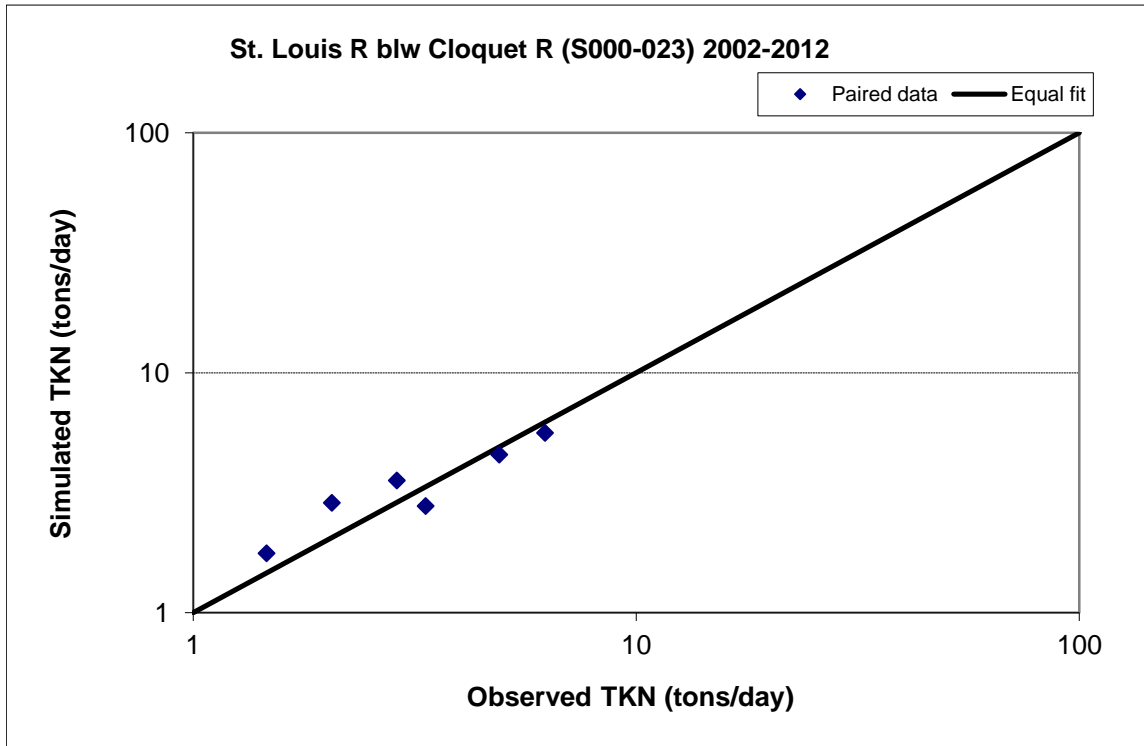


Figure A-90. Paired simulated vs. observed Total Kjeldahl Nitrogen (TKN) load at St. Louis R blw Cloquet R (S000-023) (calibration period)

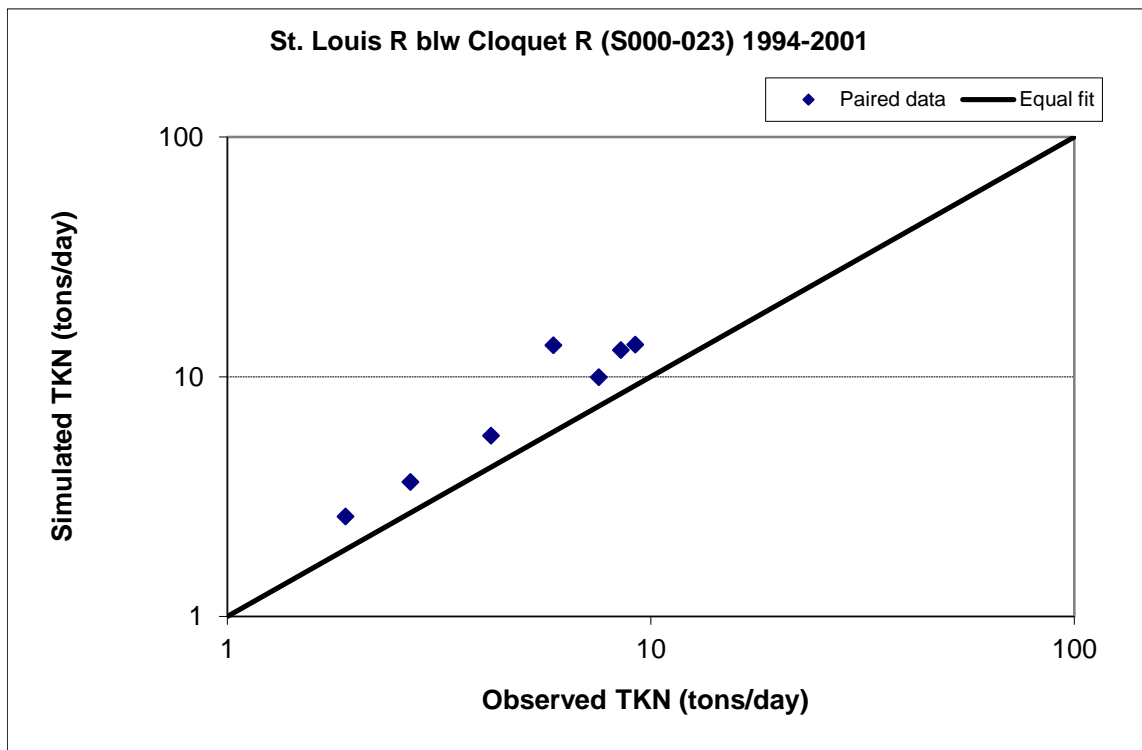


Figure A-91. Paired simulated vs. observed Total Kjeldahl Nitrogen (TKN) load at St. Louis R blw Cloquet R (S000-023) (validation period)

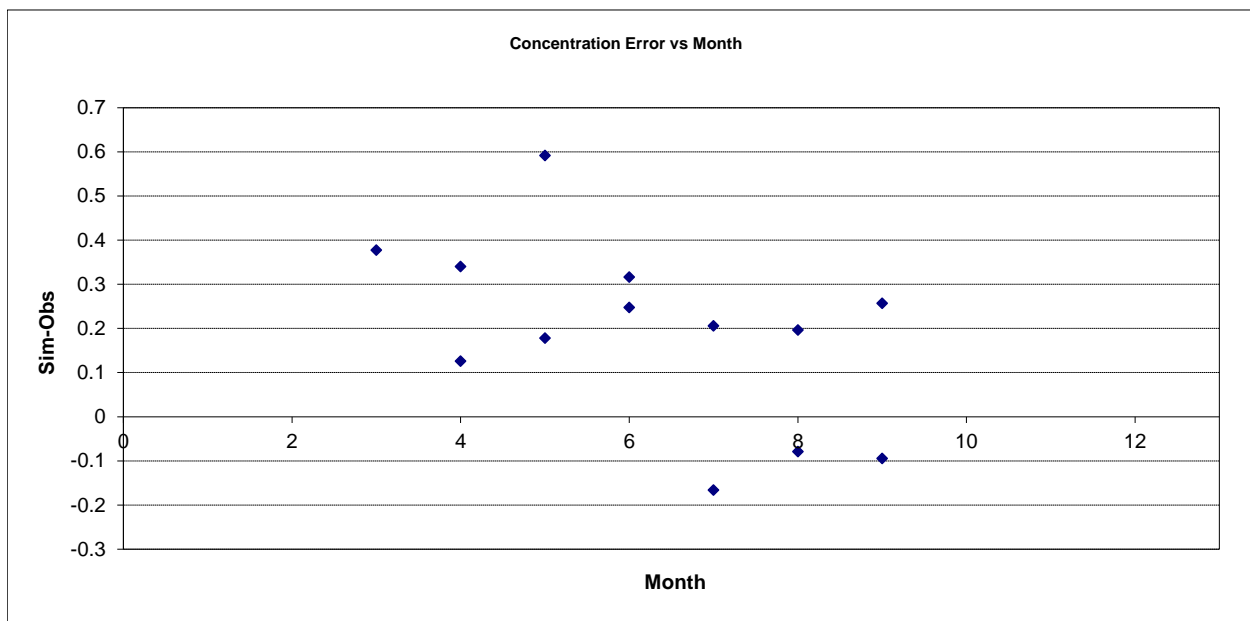


Figure A-92. Residual (Simulated - Observed) vs. Month Total Kjeldahl Nitrogen (TKN) at St. Louis R blw Cloquet R (S000-023)

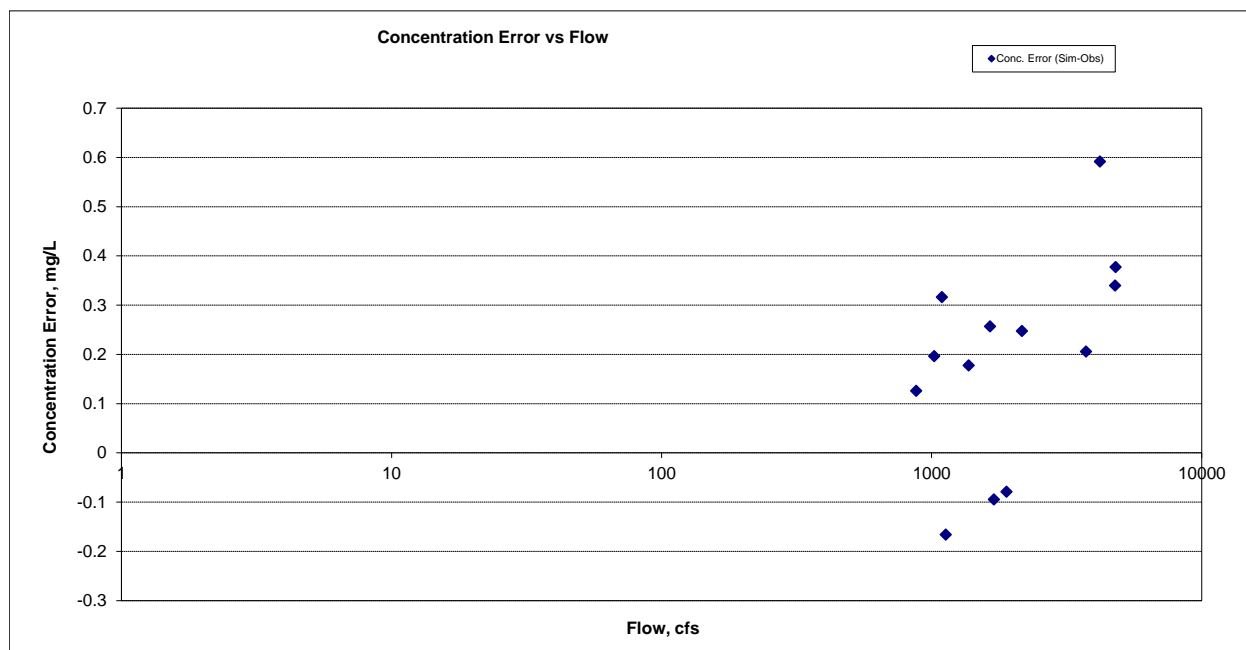


Figure A-93. Residual (Simulated - Observed) vs. Flow Total Kjeldahl Nitrogen (TKN) at St. Louis R blw Cloquet R (S000-023)

A.4.4 Nitrite+ Nitrate Nitrogen (NOx)

Table A-14. Nitrite+ Nitrate Nitrogen (NOx) statistics

Period	1994-2001	2002-2012
Count	36	38
Concentration Average Error	2.19%	45.49%
Concentration Median Error	13.72%	45.20%
Load Average Error	-8.05%	15.81%
Load Median Error	13.08%	24.58%
Paired t conc	0.90	0.02
Paired t load	0.71	0.59

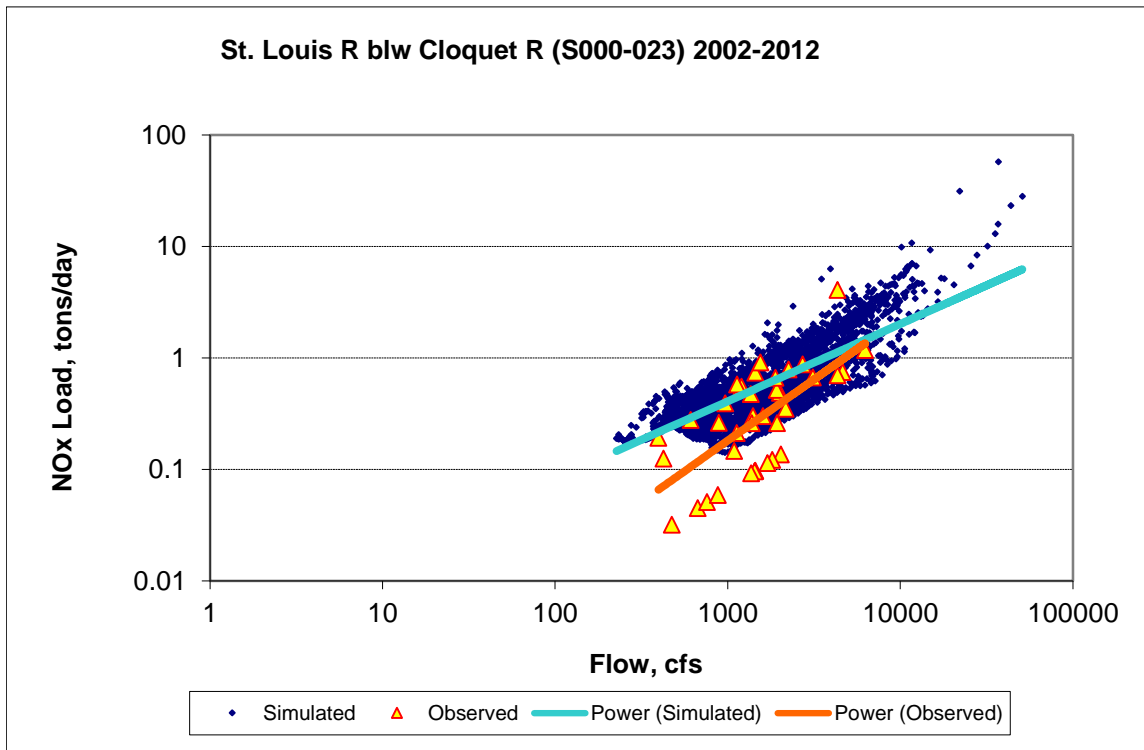


Figure A-94. Power plot of simulated and observed Nitrite+ Nitrate Nitrogen (NOx) load vs flow at St. Louis R blw Cloquet R (S000-023) (calibration period)

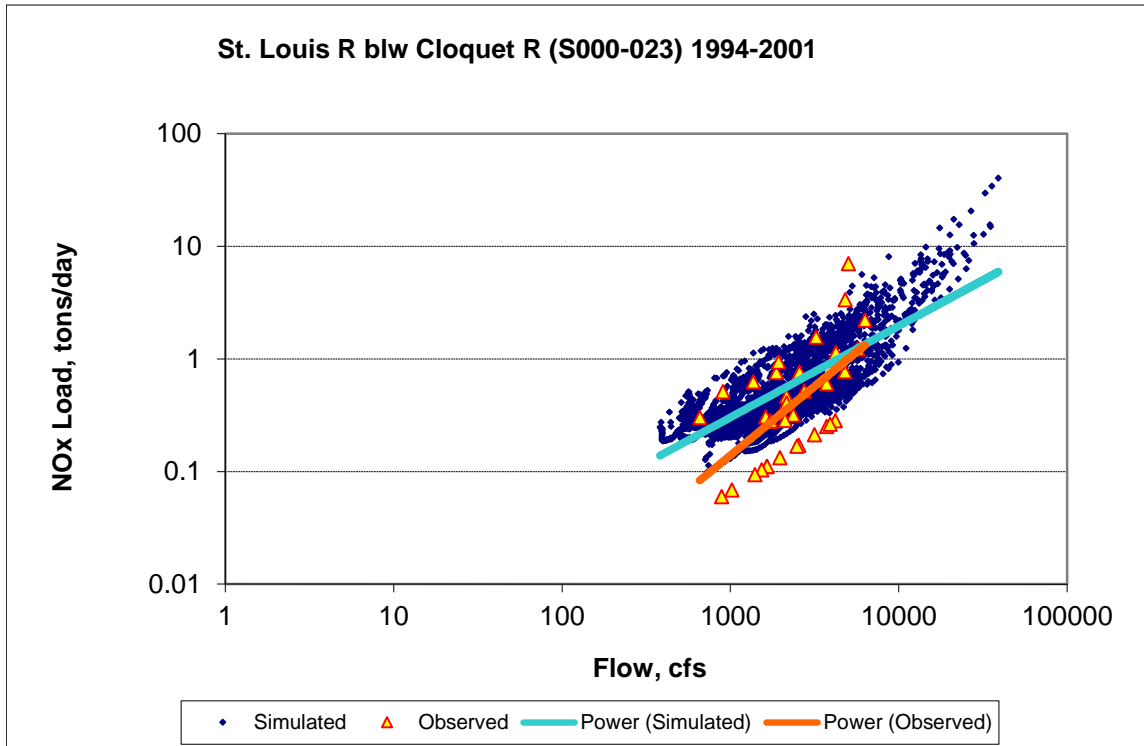
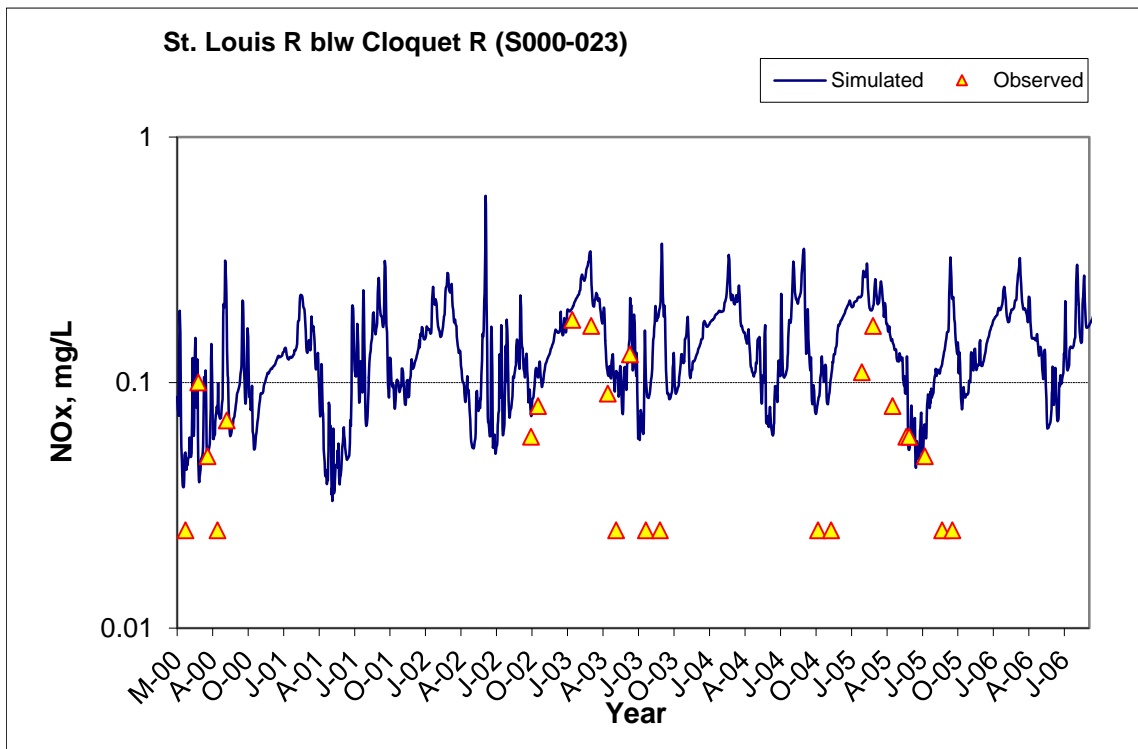
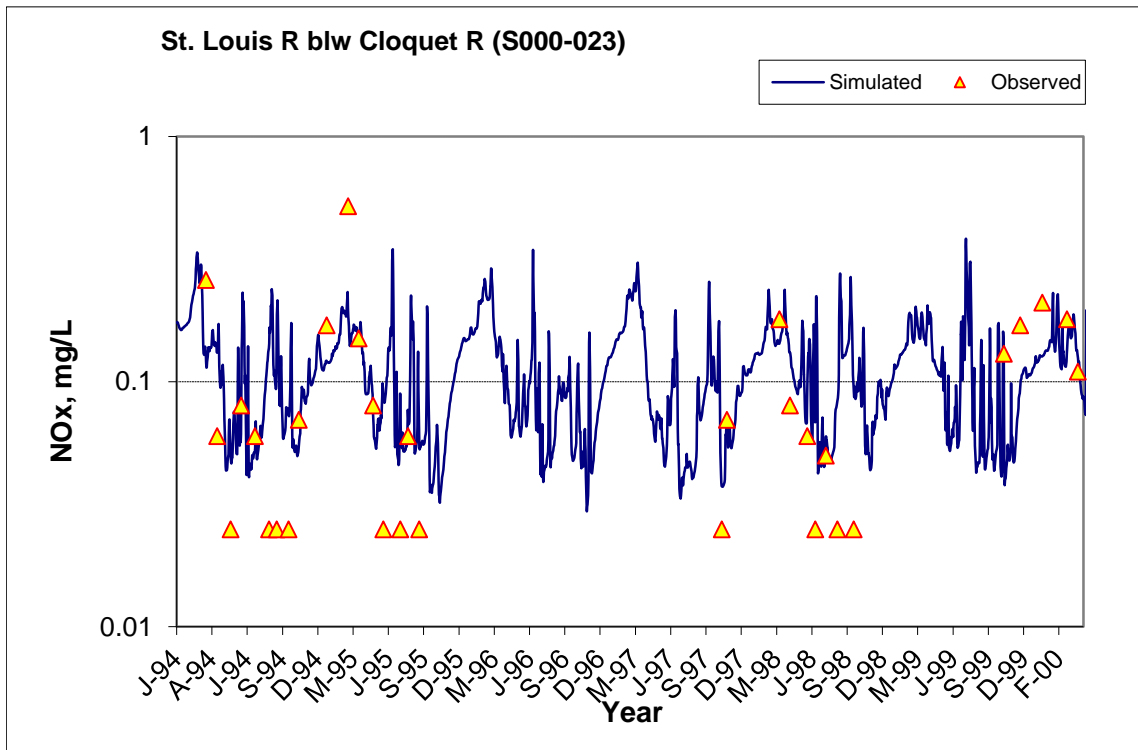


Figure A-95. Power plot of simulated and observed Nitrite+ Nitrate Nitrogen (NOx) load vs flow at St. Louis R blw Cloquet R (S000-023) (validation period)



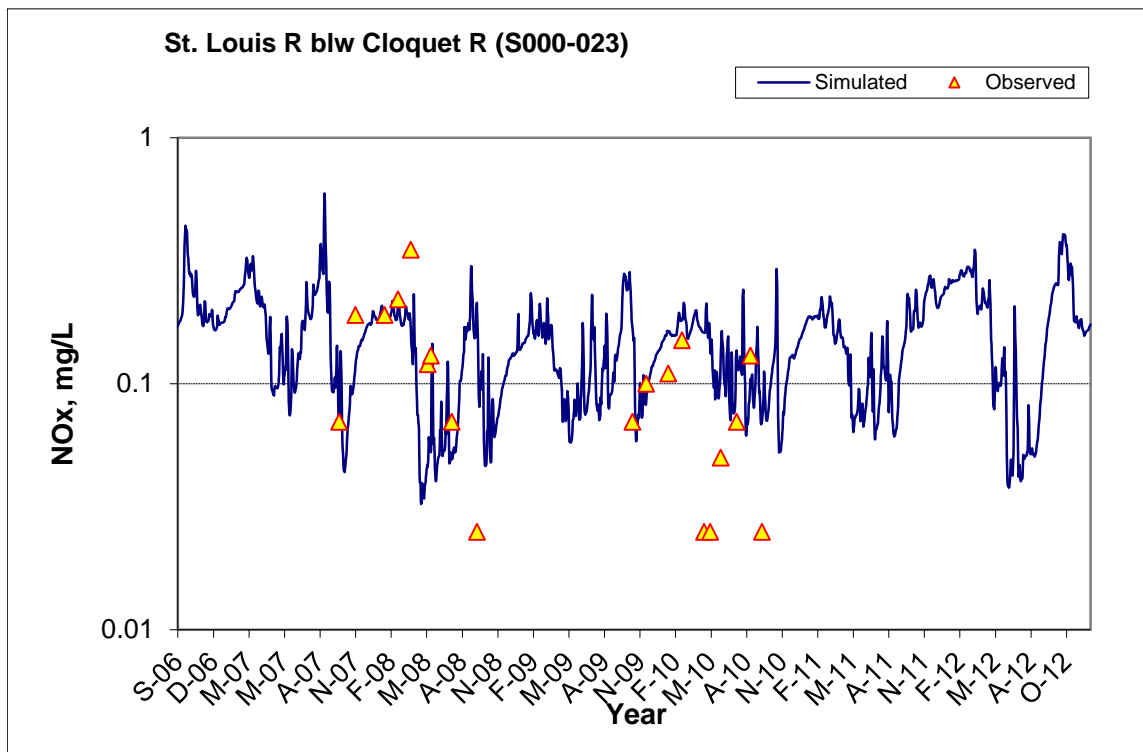


Figure A-96. Time series of observed and simulated Nitrite+ Nitrate Nitrogen (NOx) concentration at St. Louis R blw Cloquet R (S000-023)

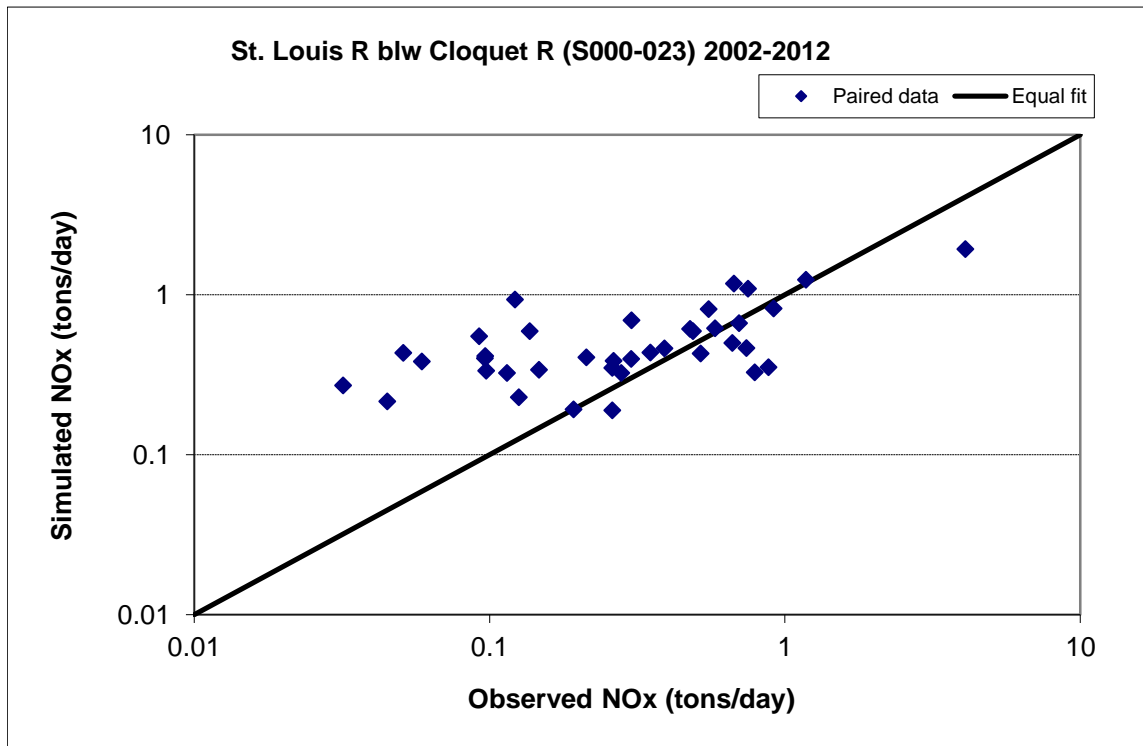


Figure A-97. Paired simulated vs. observed Nitrite+ Nitrate Nitrogen (NOx) load at St. Louis R blw Cloquet R (S000-023) (calibration period)

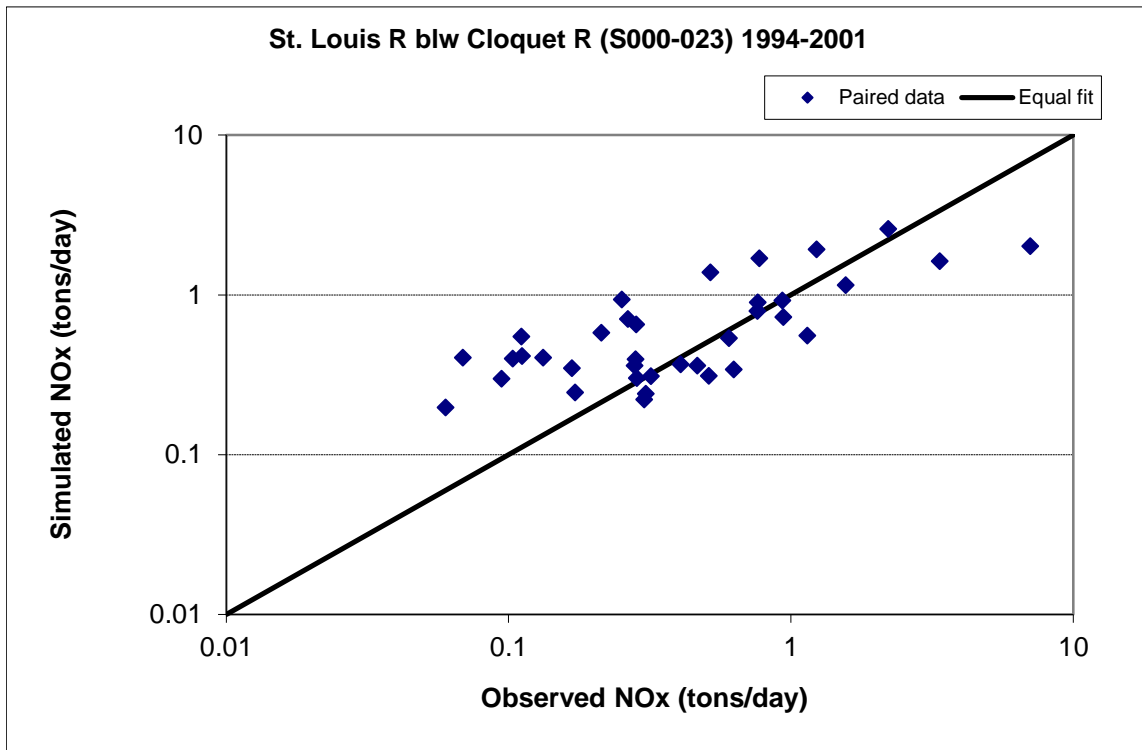


Figure A-98. Paired simulated vs. observed Nitrite+ Nitrate Nitrogen (NOx) load at St. Louis R blw Cloquet R (S000-023) (validation period)

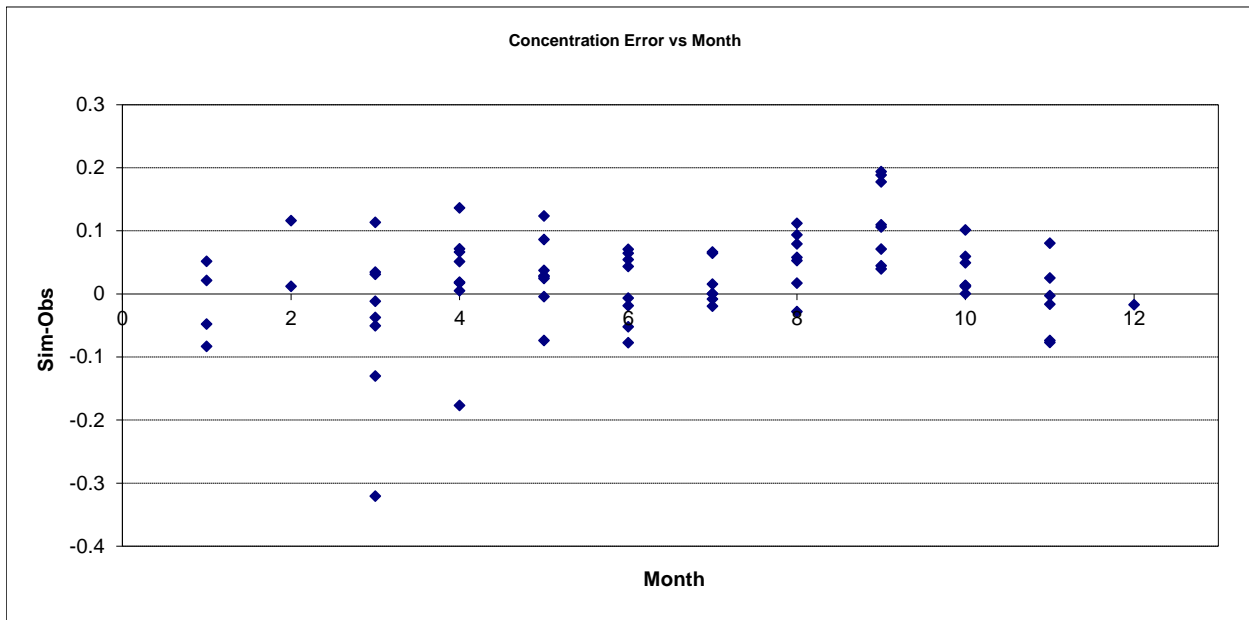


Figure A-99. Residual (Simulated - Observed) vs. Month Nitrite+ Nitrate Nitrogen (NOx) at St. Louis R blw Cloquet R (S000-023)

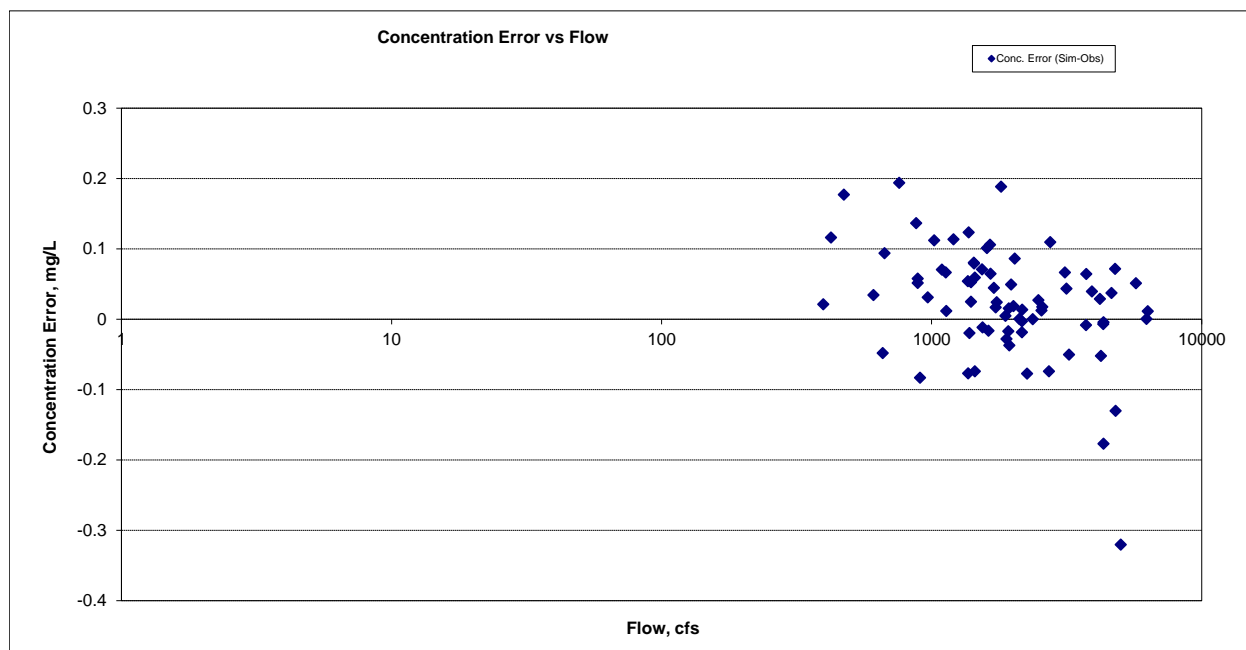


Figure A-100. Residual (Simulated - Observed) vs. Flow Nitrite+ Nitrate Nitrogen (NOx) at St. Louis R blw Cloquet R (S000-023)

A.4.5 Total Nitrogen (TN)

Table A-15. Total Nitrogen (TN) statistics

Period	1994-2001	2002-2012
Count	40.74%	9.84%
Concentration Average Error	33.42%	7.81%
Concentration Median Error	44.68%	5.01%
Load Average Error	36.15%	4.38%
Load Median Error	0.00	0.85
Paired t conc	0.19	0.77
Paired t load	40.74%	9.84%

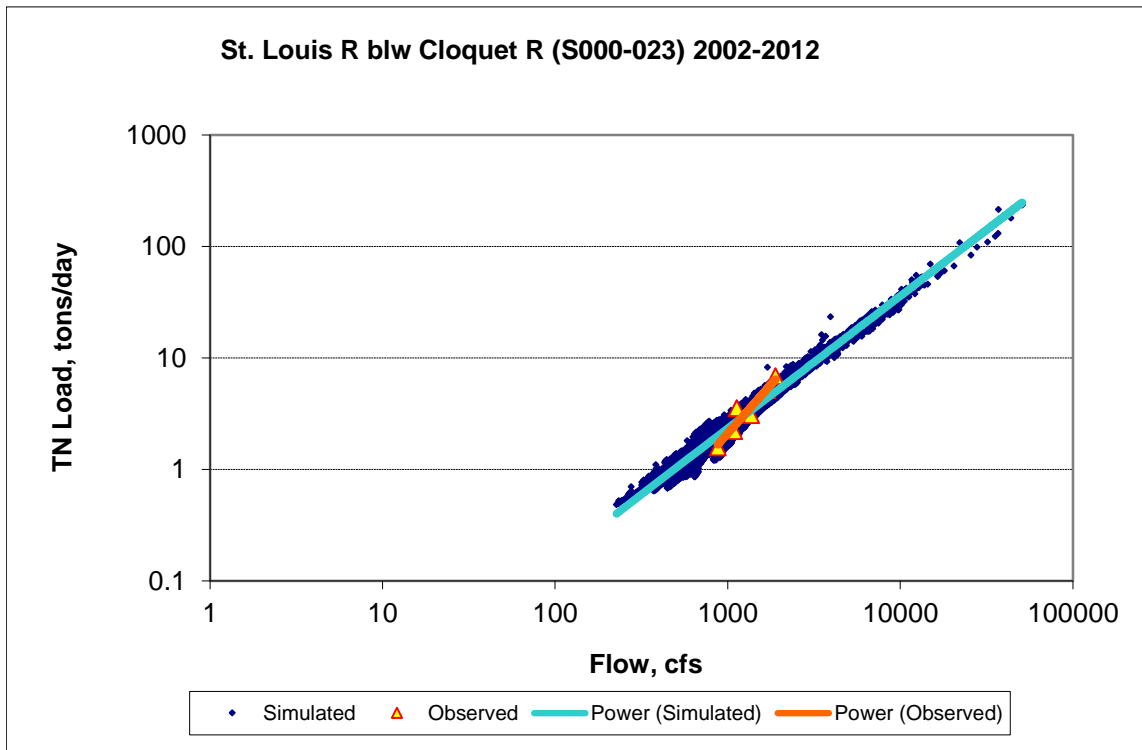


Figure A-101. Power plot of simulated and observed Total Nitrogen (TN) load vs flow at St. Louis R blw Cloquet R (S000-023) (calibration period)

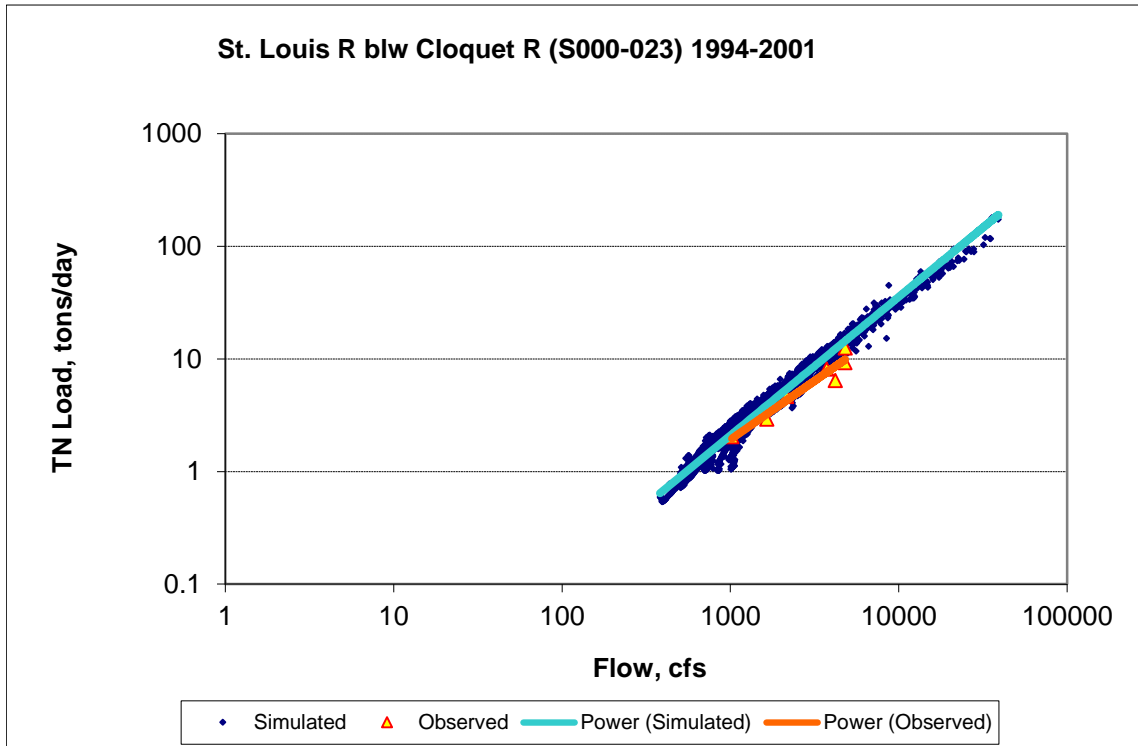
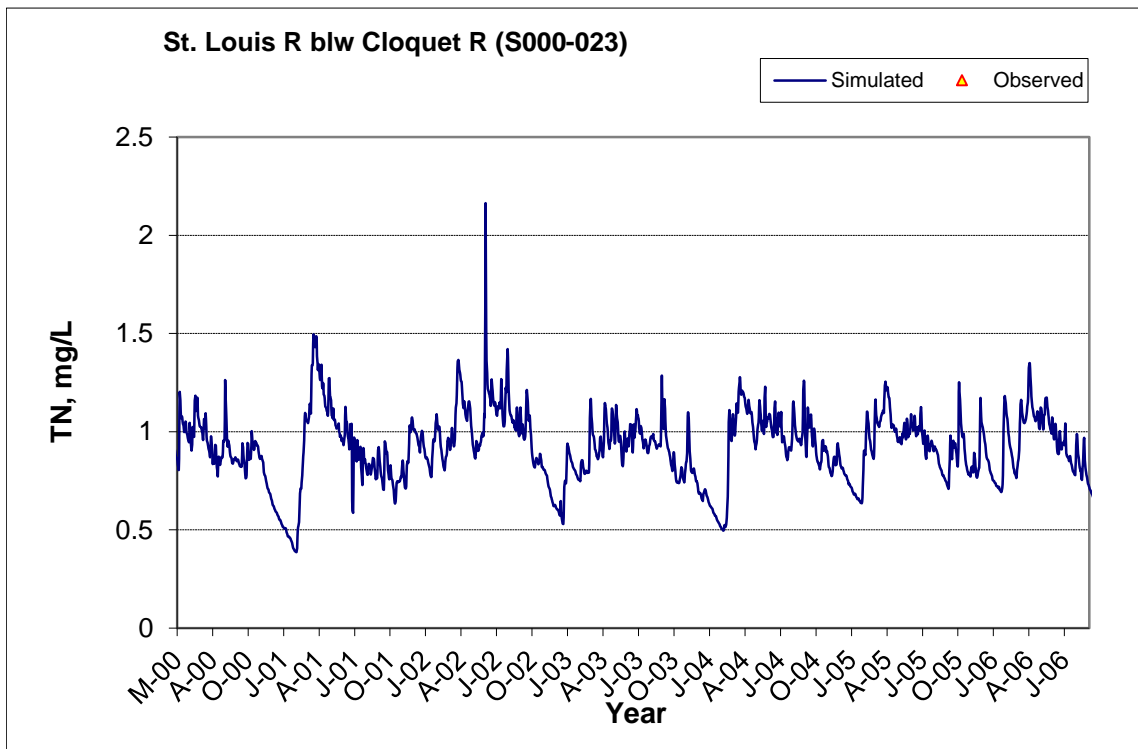
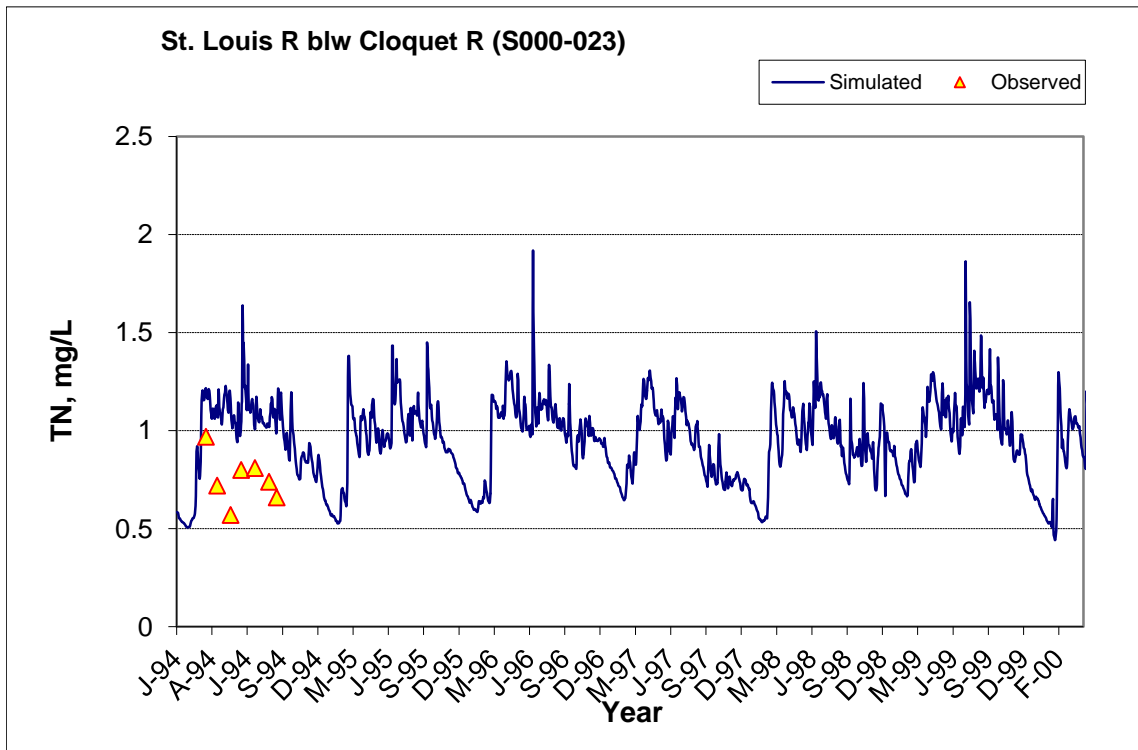


Figure A-102. Power plot of simulated and observed Total Nitrogen (TN) load vs flow at St. Louis R blw Cloquet R (S000-023) (validation period)



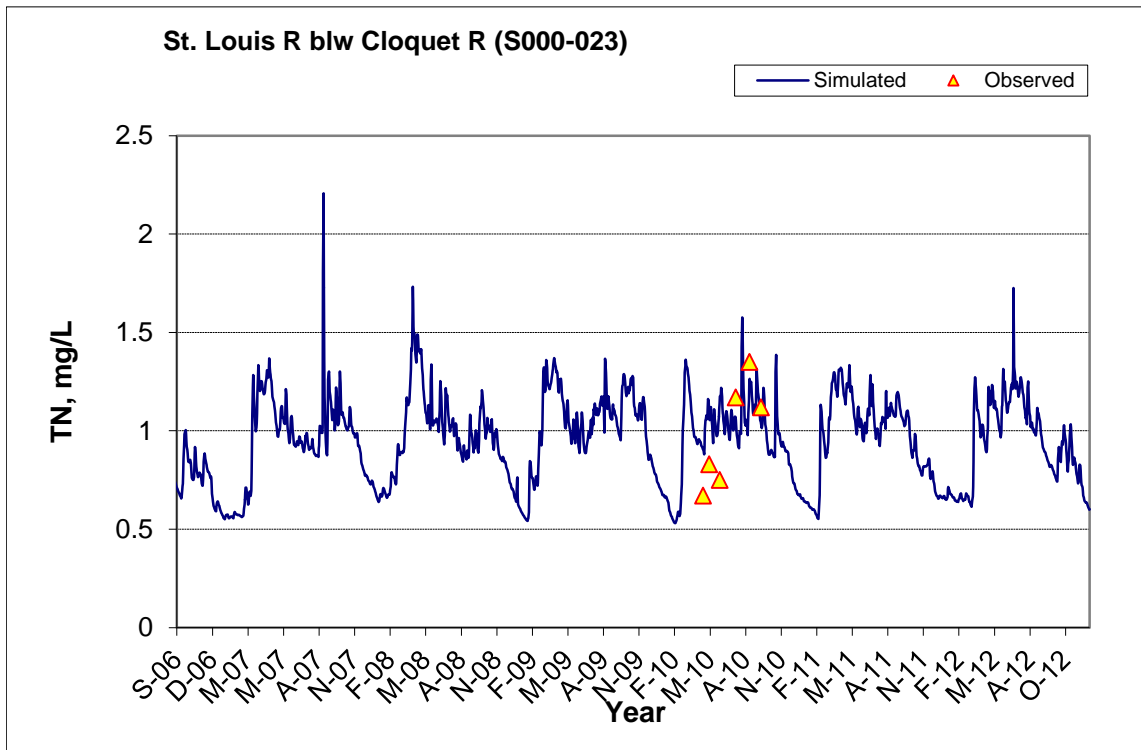


Figure A-103. Time series of observed and simulated Total Nitrogen (TN) concentration at St. Louis R blw Cloquet R (S000-023)

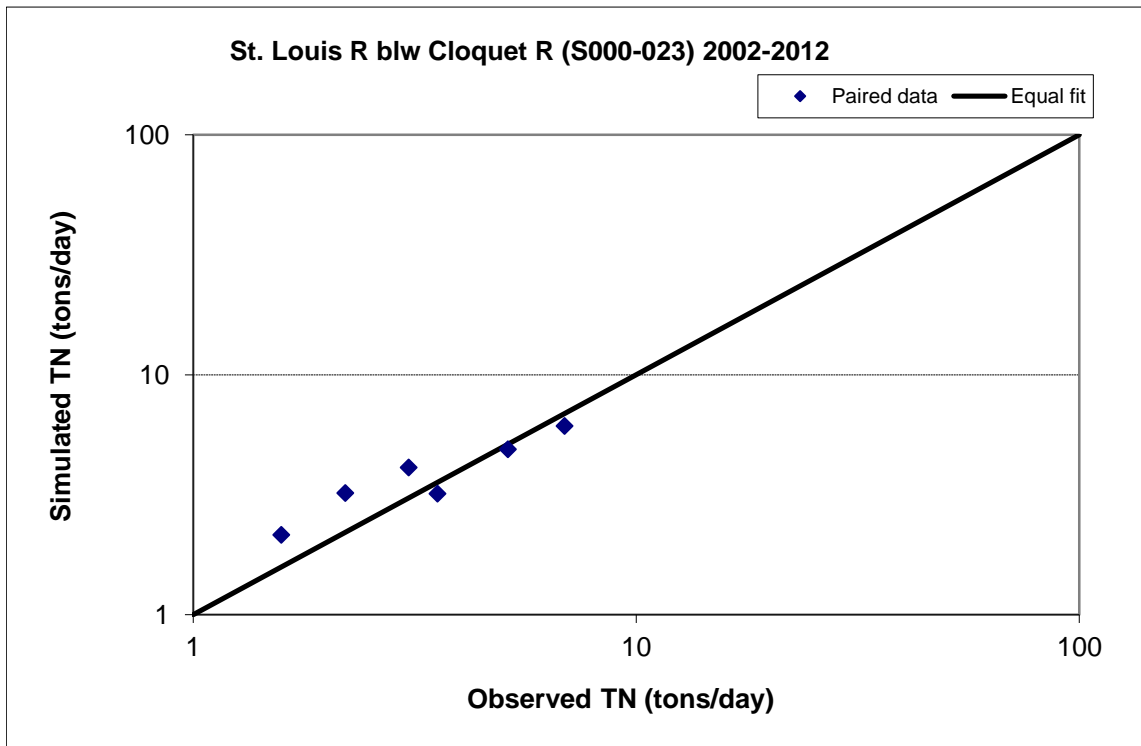


Figure A-104. Paired simulated vs. observed Total Nitrogen (TN) load at St. Louis R blw Cloquet R (S000-023) (calibration period)

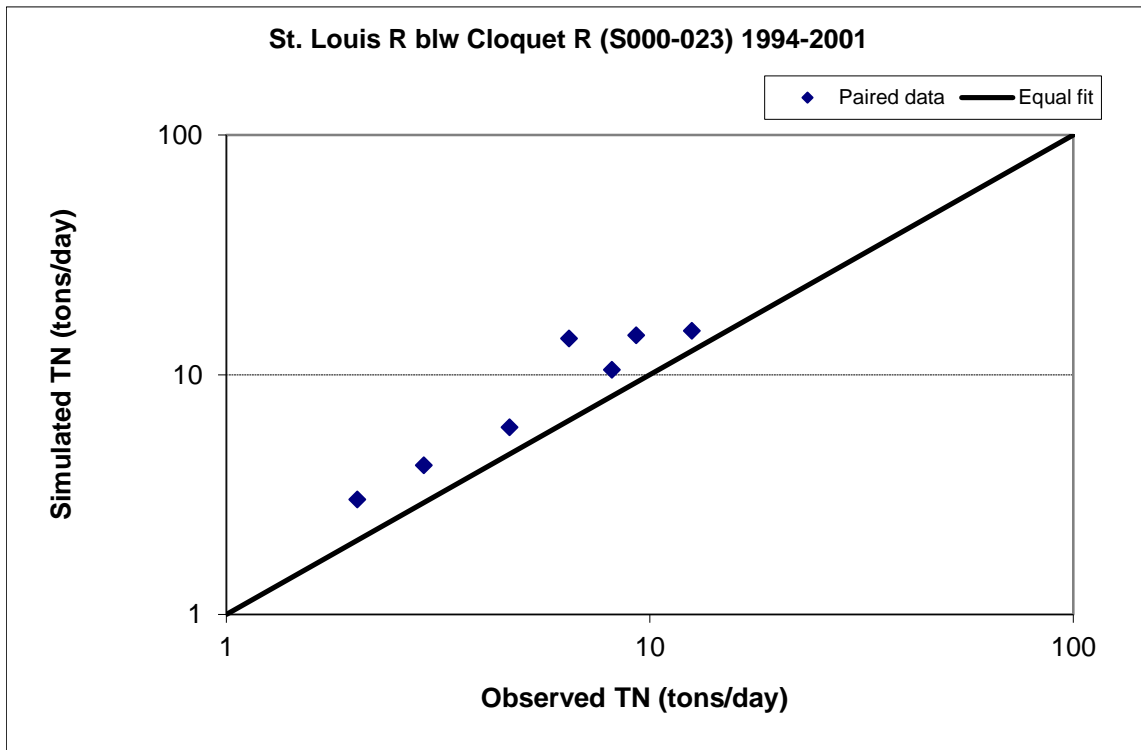


Figure A-105. Paired simulated vs. observed Total Nitrogen (TN) load at St. Louis R blw Cloquet R (S000-023) (validation period)

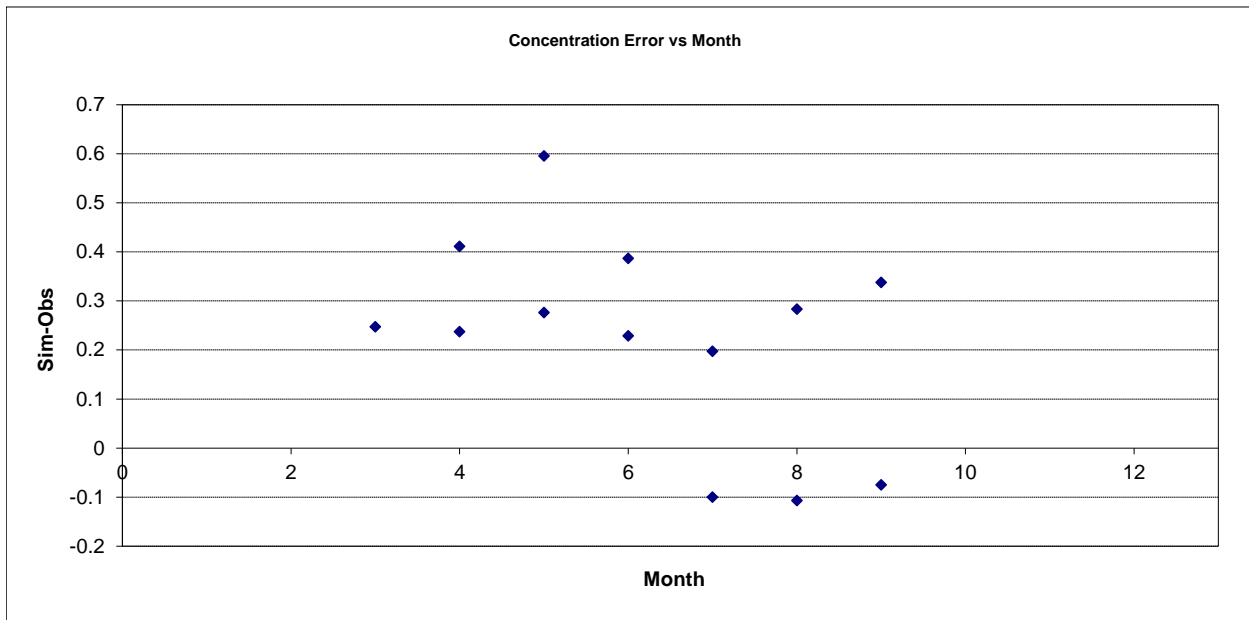


Figure A-106. Residual (Simulated - Observed) vs. Month Total Nitrogen (TN) at St. Louis R blw Cloquet R (S000-023)

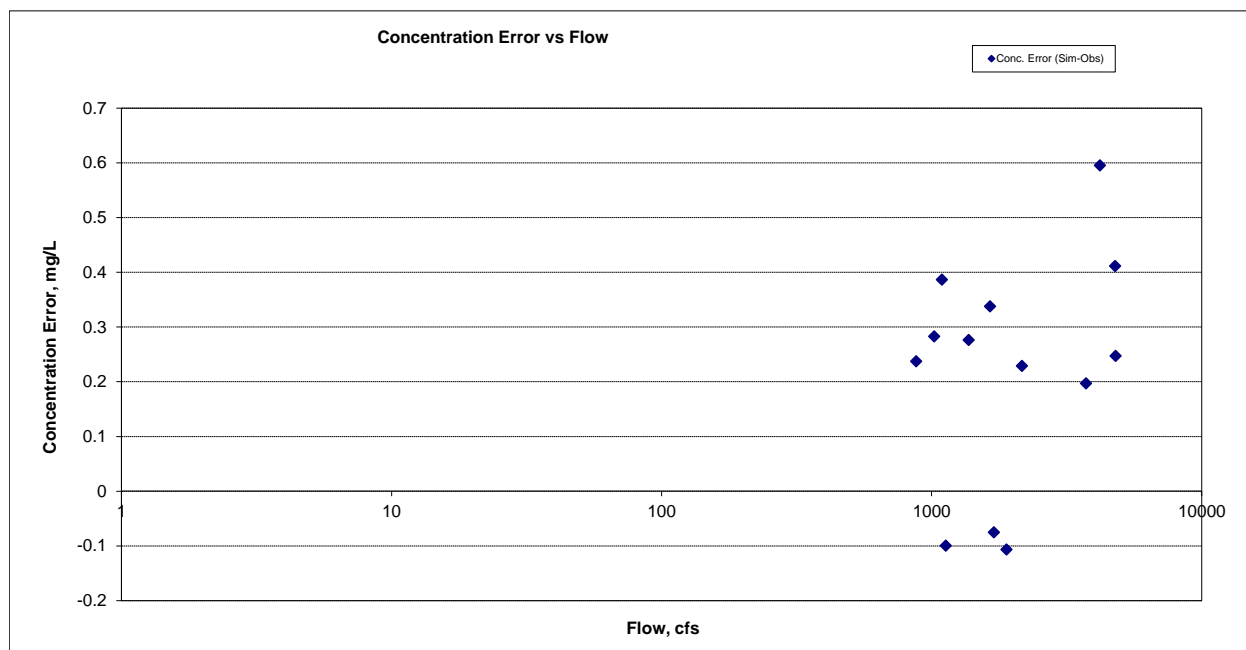
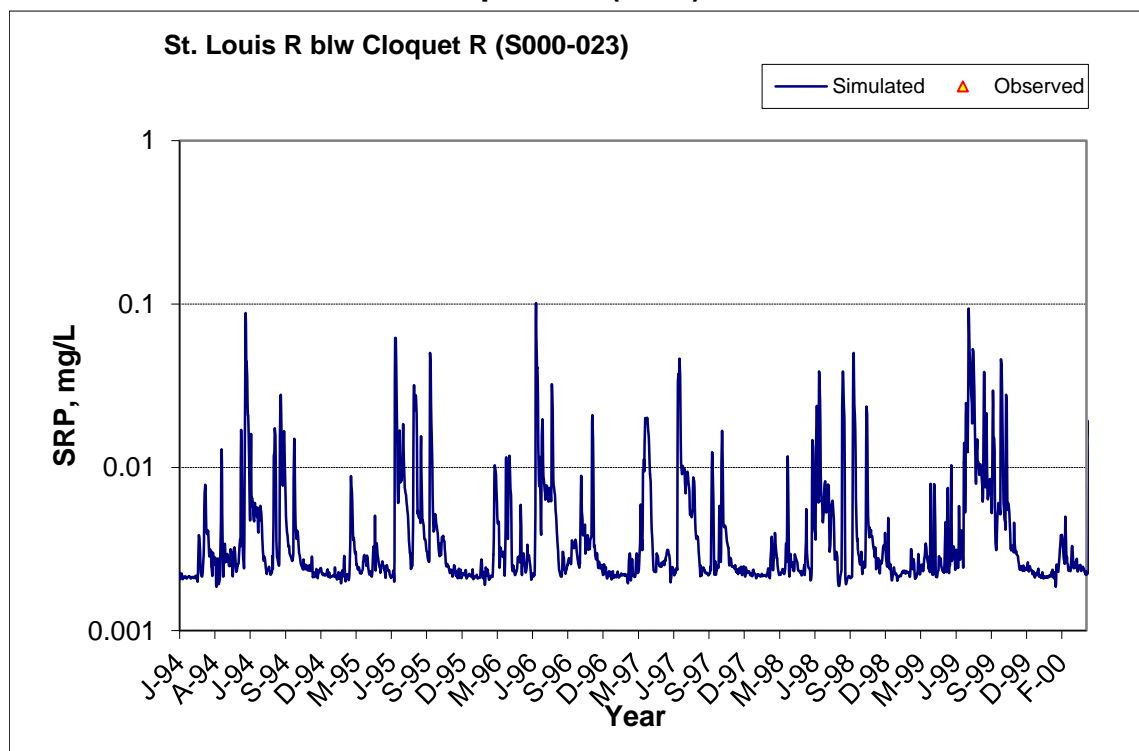


Figure A-107. Residual (Simulated - Observed) vs. Flow Total Nitrogen (TN) at St. Louis R blw Cloquet R (S000-023)

A.4.6 Soluble Reactive Phosphorus (SRP)



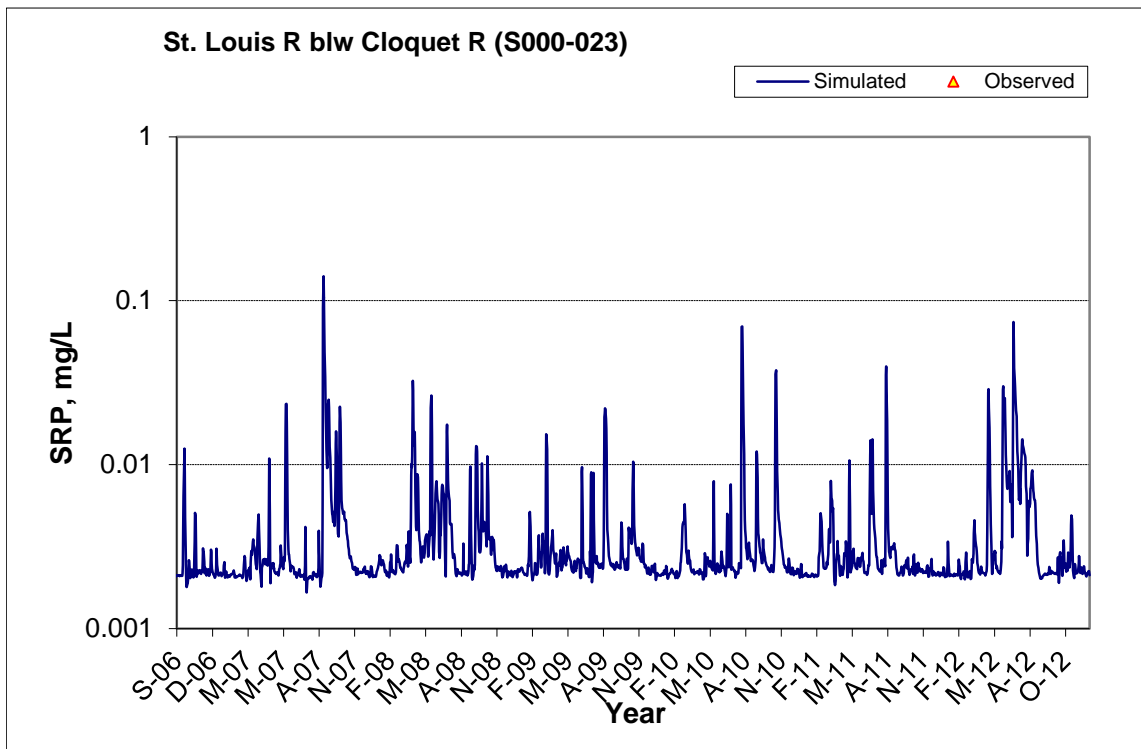
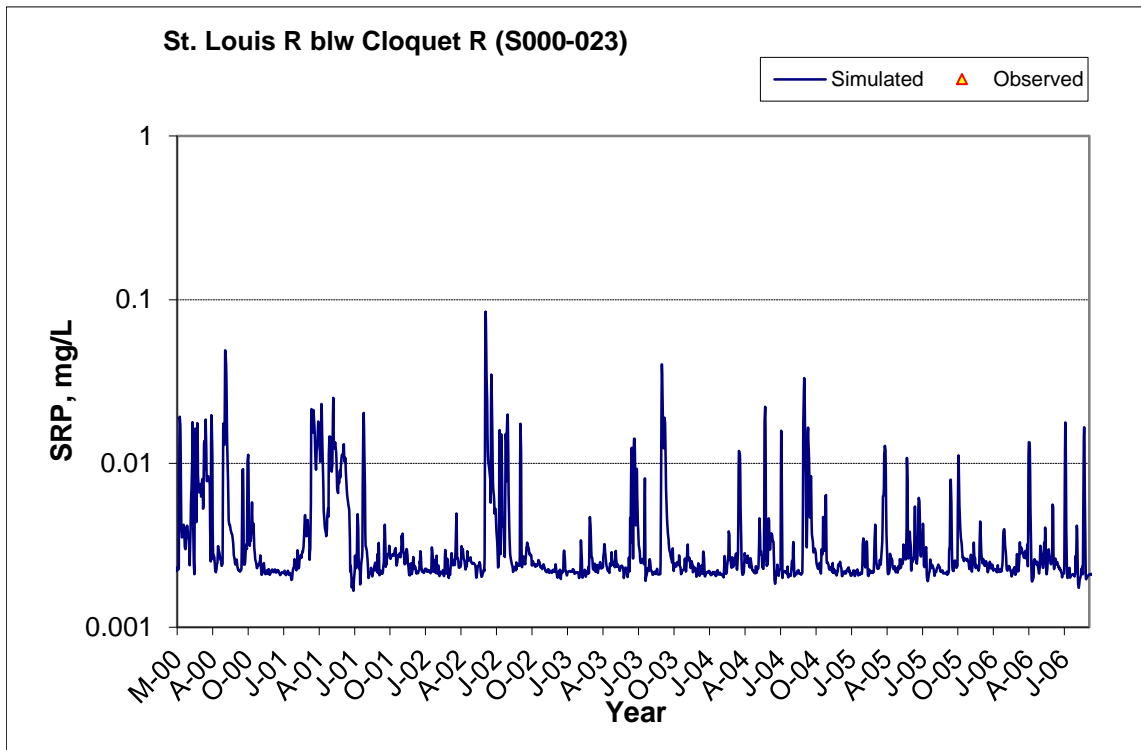
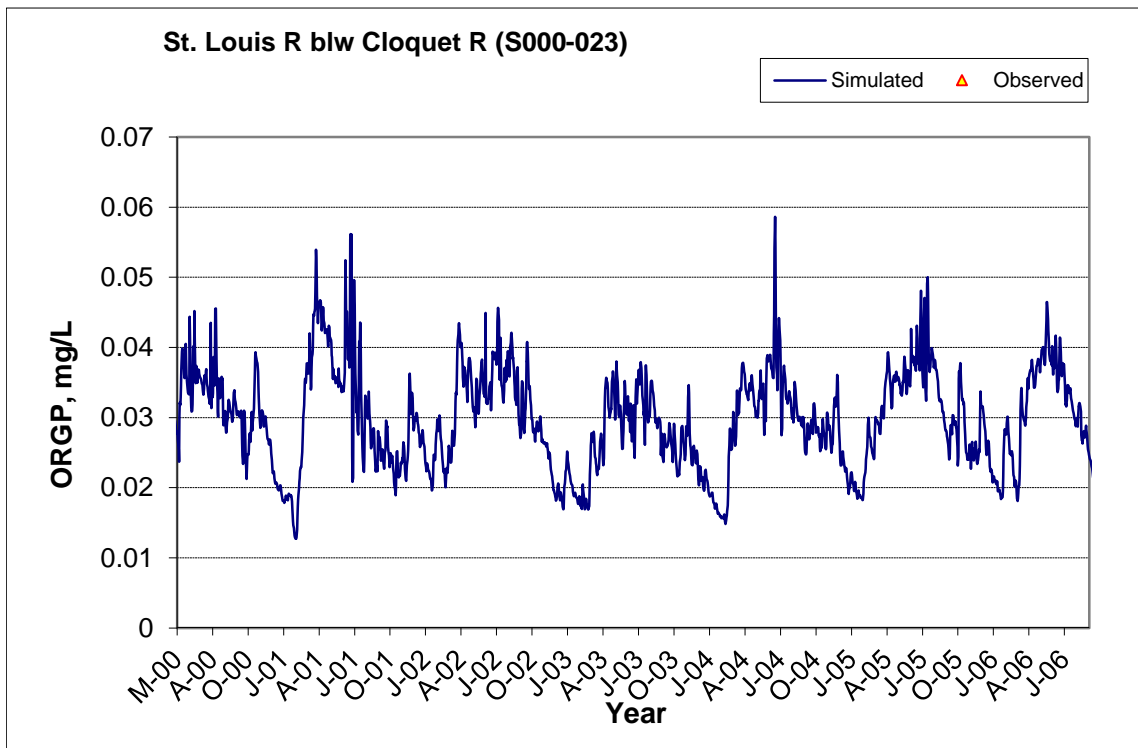
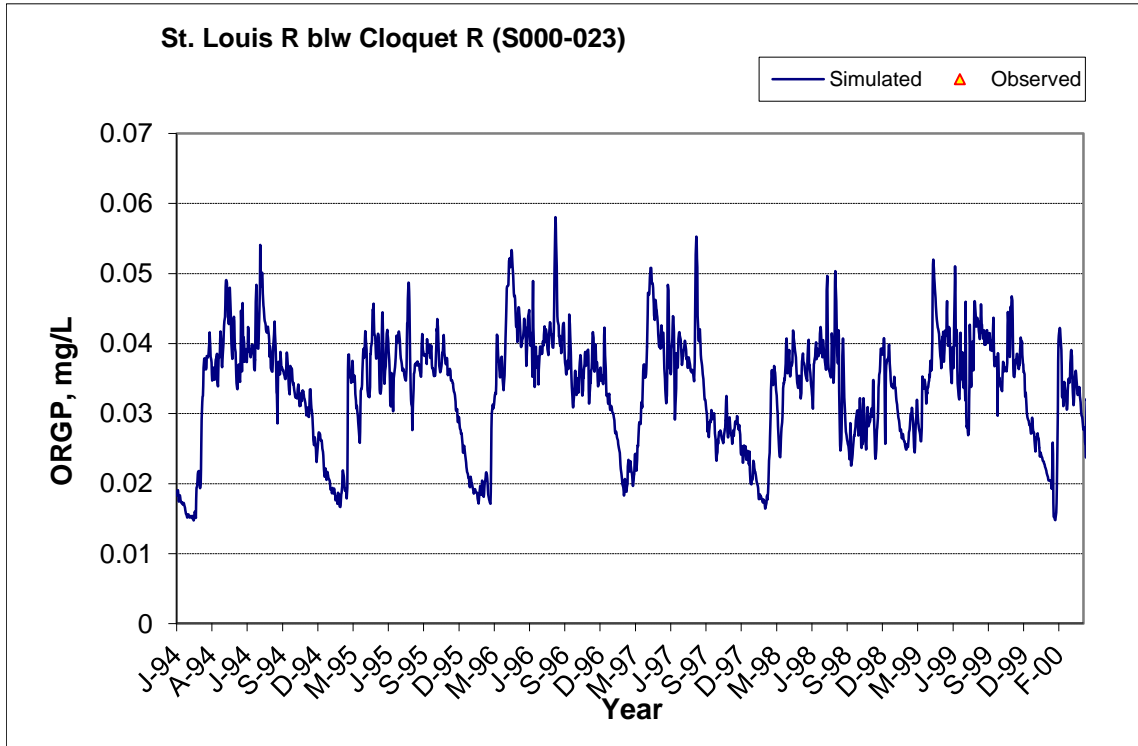


Figure A-108. Time series of observed and simulated Soluble Reactive Phosphorus (SRP) concentration at St. Louis R blw Cloquet R (S000-023)

A.4.7 Organic Phosphorus (OrgP)



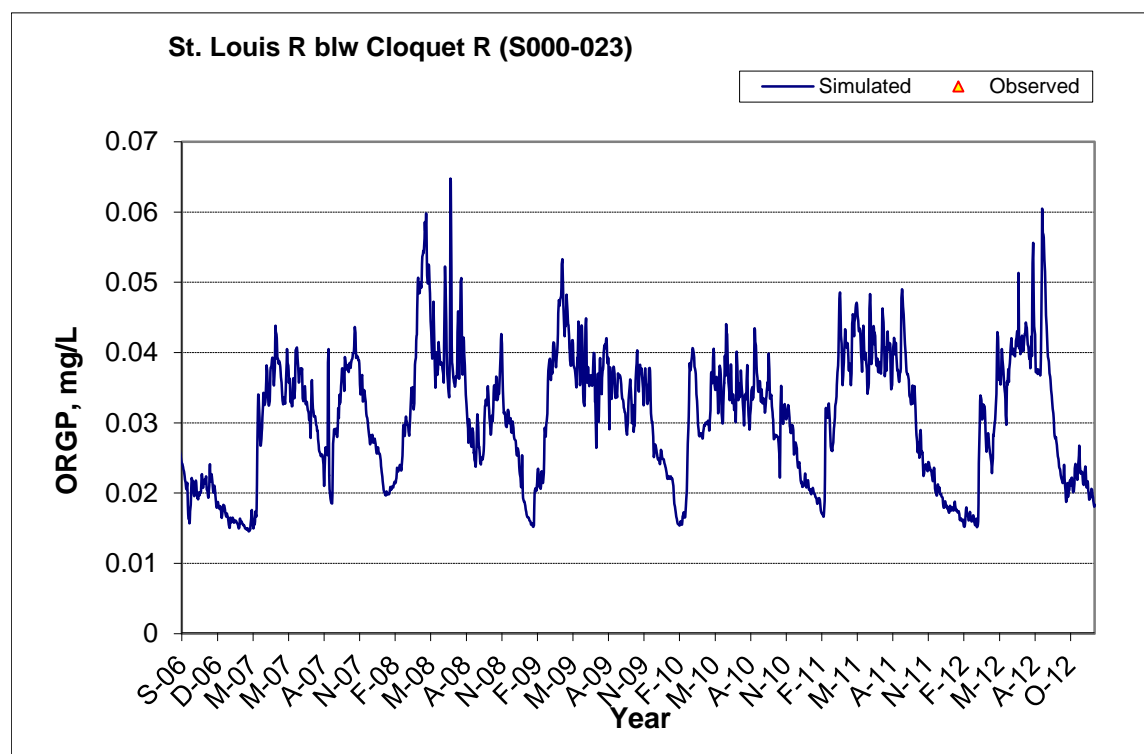


Figure A-109. Time series of observed and simulated Organic Phosphorus (OrgP) concentration at St. Louis R blw Cloquet R (S000-023)

A.4.8 Total Phosphorus (TP)

Table A-16. Total Phosphorus (TP) statistics

Period	1994-2001	2002-2012
Count	9	39
Concentration Average Error	0.91%	-17.68%
Concentration Median Error	10.54%	2.81%
Load Average Error	-3.29%	-4.43%
Load Median Error	6.72%	1.30%
Paired t conc	0.97	0.63
Paired t load	0.77	0.90

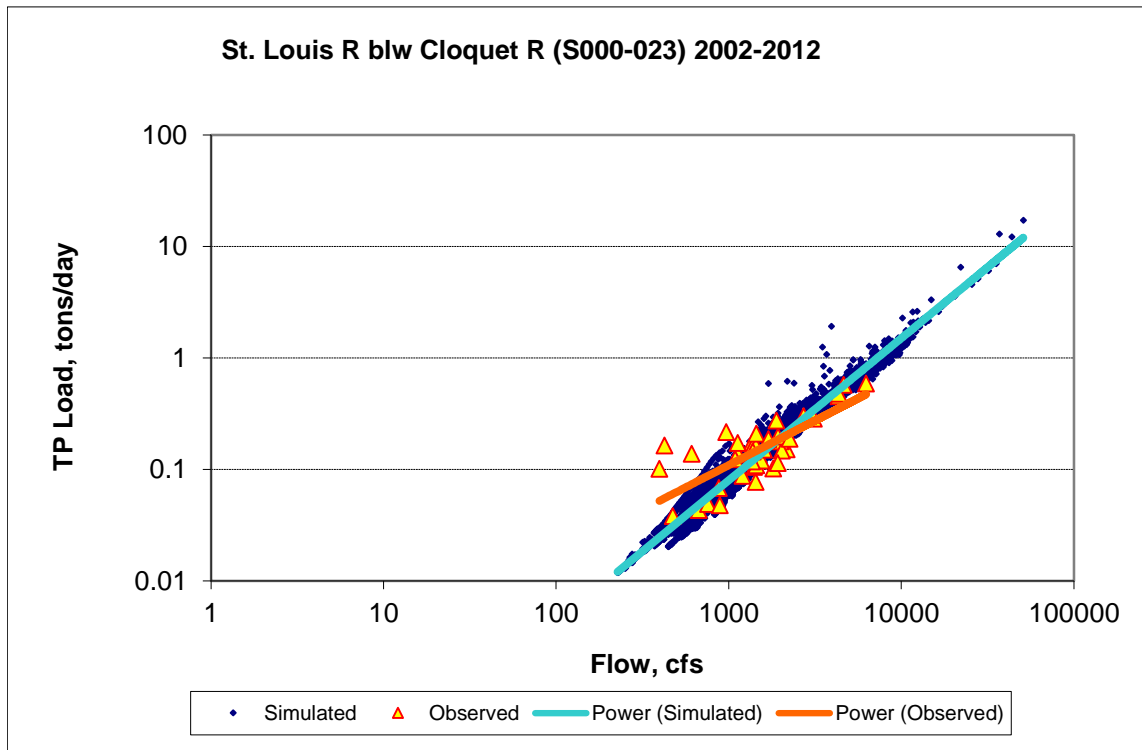


Figure A-110. Power plot of simulated and observed Total Phosphorus (TP) load vs flow at St. Louis R blw Cloquet R (S000-023) (calibration period)

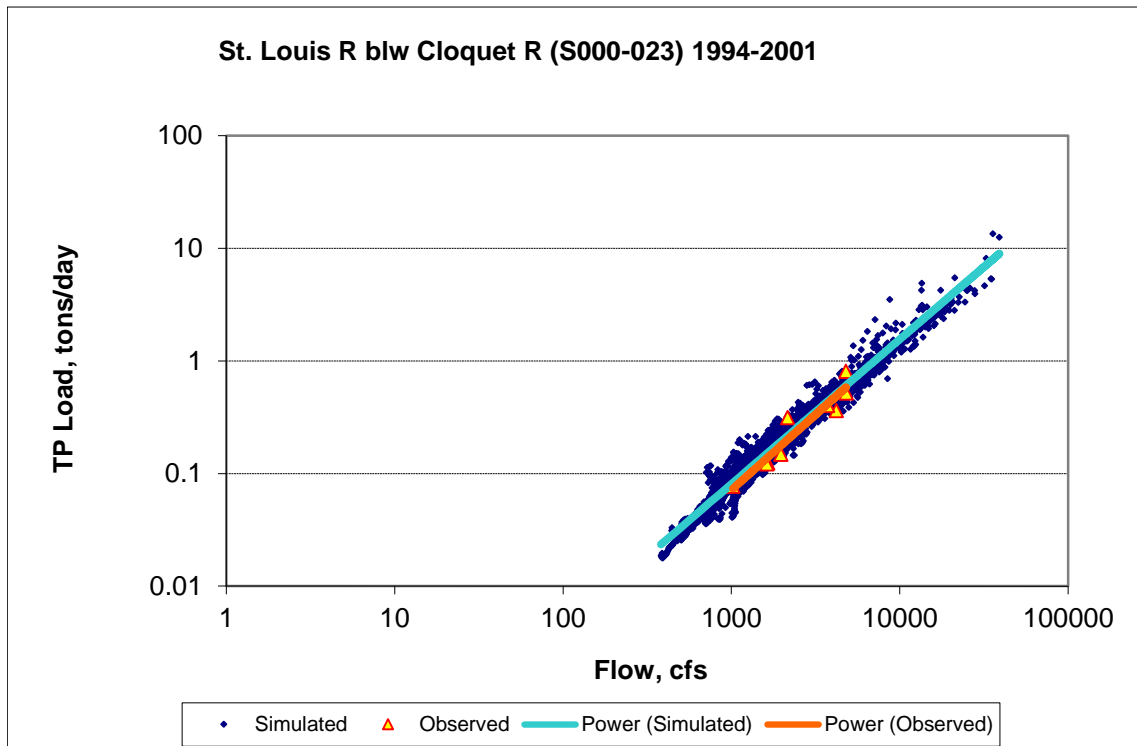
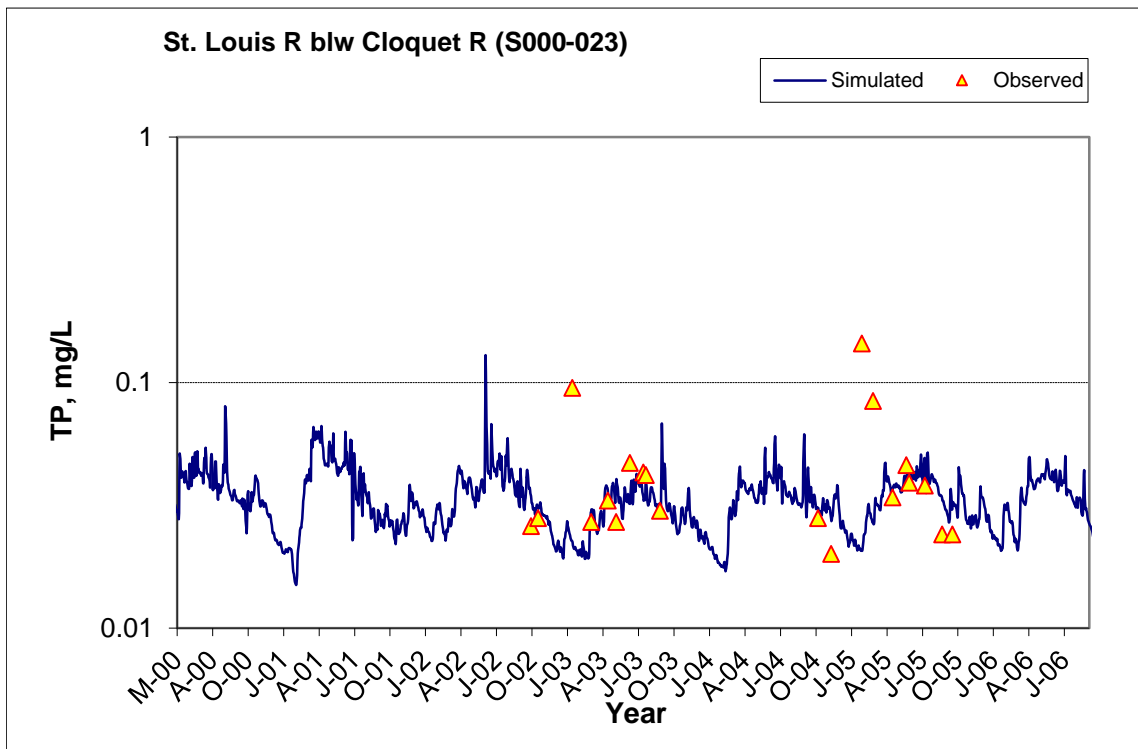
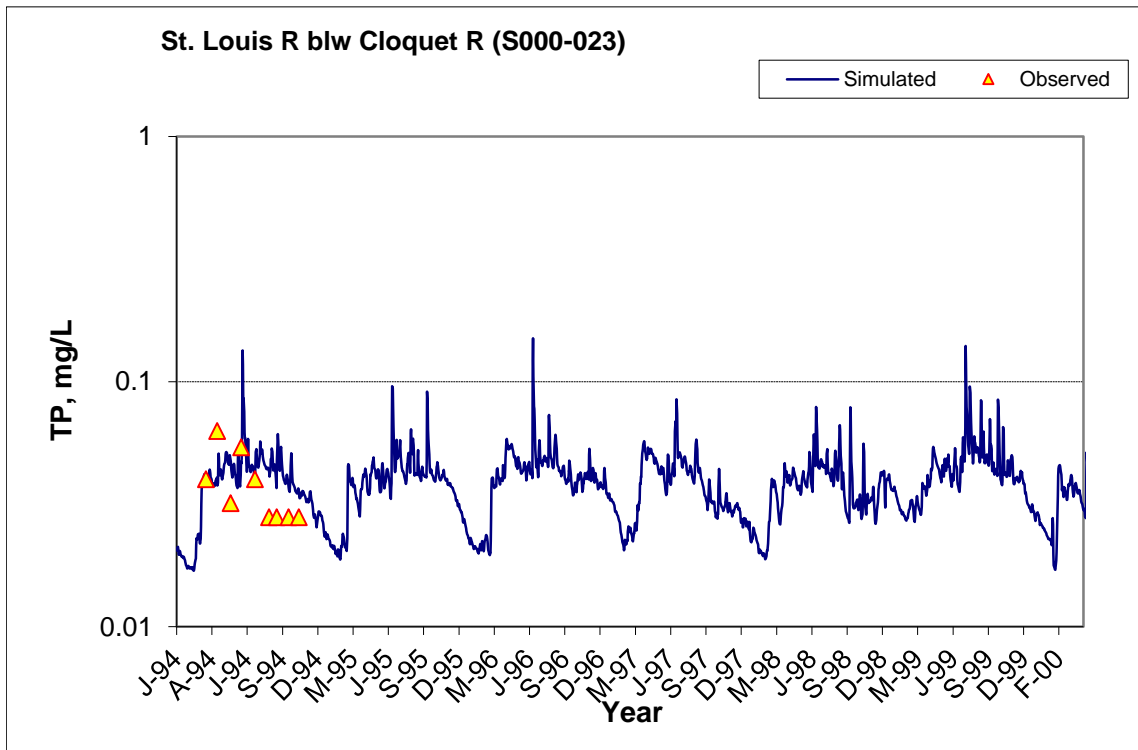


Figure A-111. Power plot of simulated and observed Total Phosphorus (TP) load vs flow at St. Louis R blw Cloquet R (S000-023) (validation period)



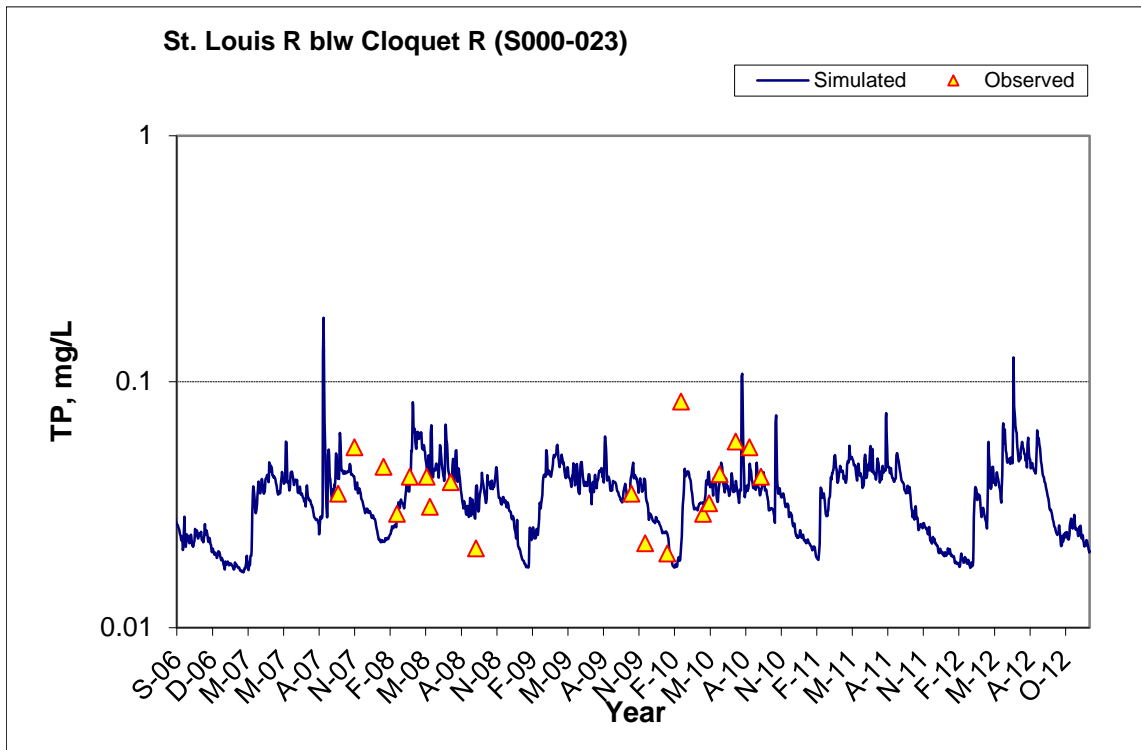


Figure A-112. Time series of observed and simulated Total Phosphorus (TP) concentration at St. Louis R blw Cloquet R (S000-023)

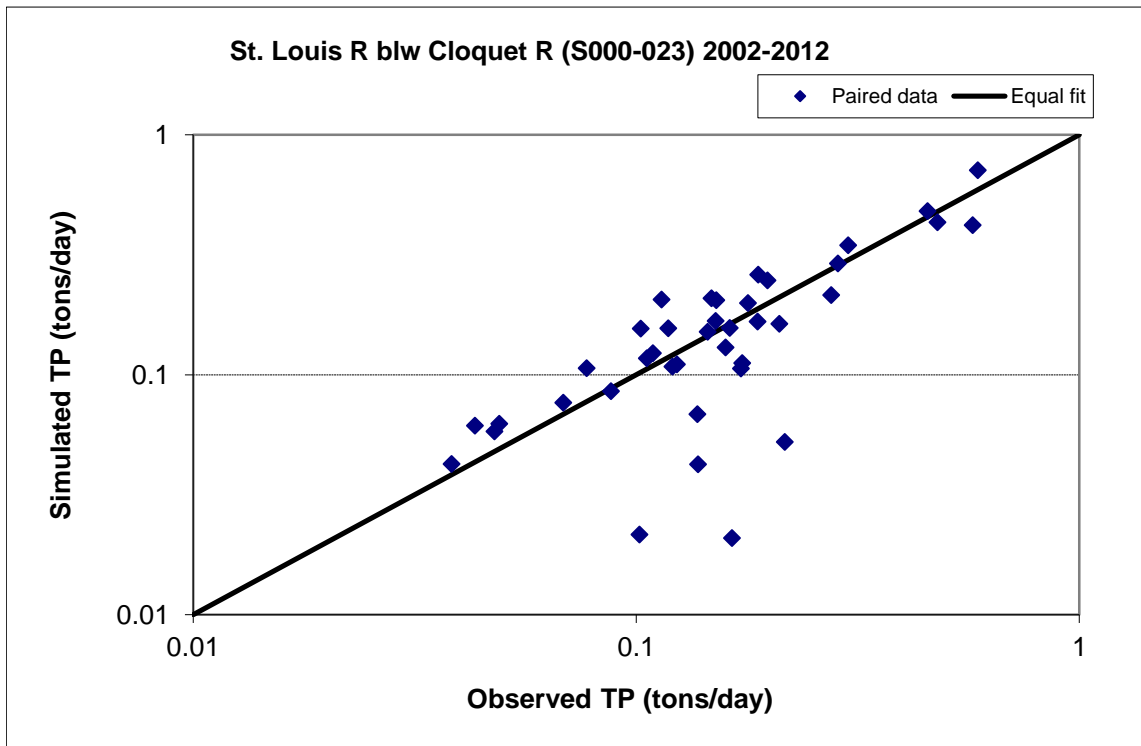


Figure A-113. Paired simulated vs. observed Total Phosphorus (TP) load at St. Louis R blw Cloquet R (S000-023) (calibration period)

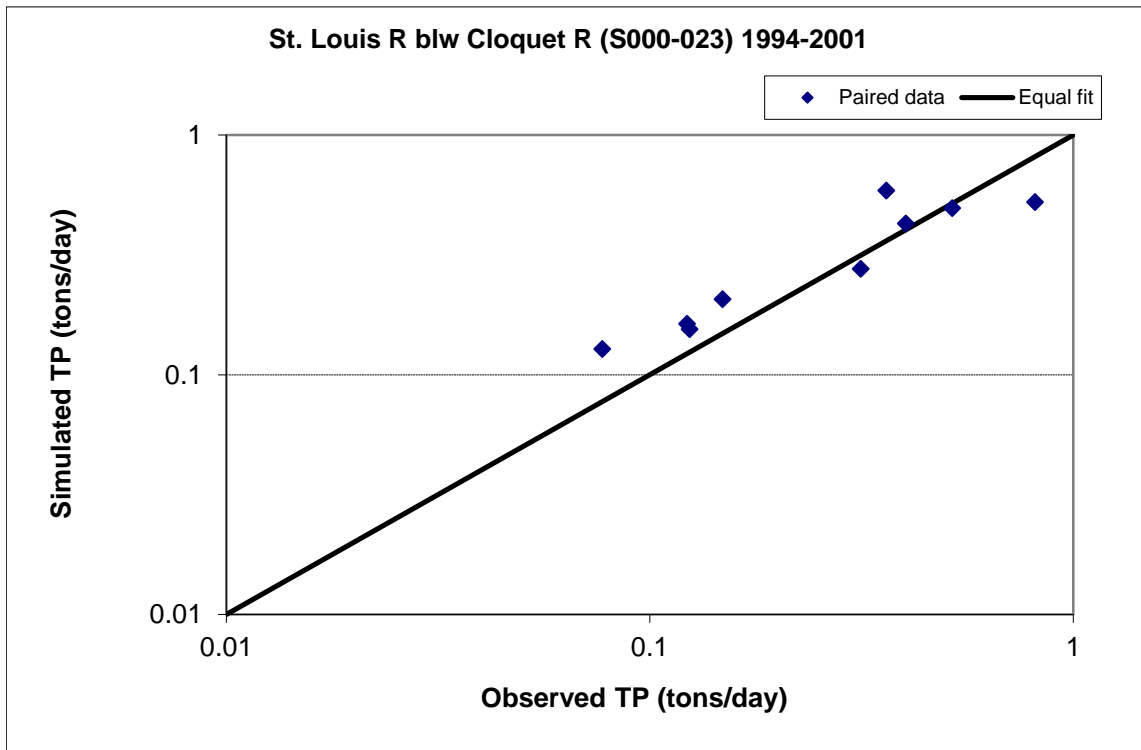


Figure A-114. Paired simulated vs. observed Total Phosphorus (TP) load at St. Louis R blw Cloquet R (S000-023) (validation period)

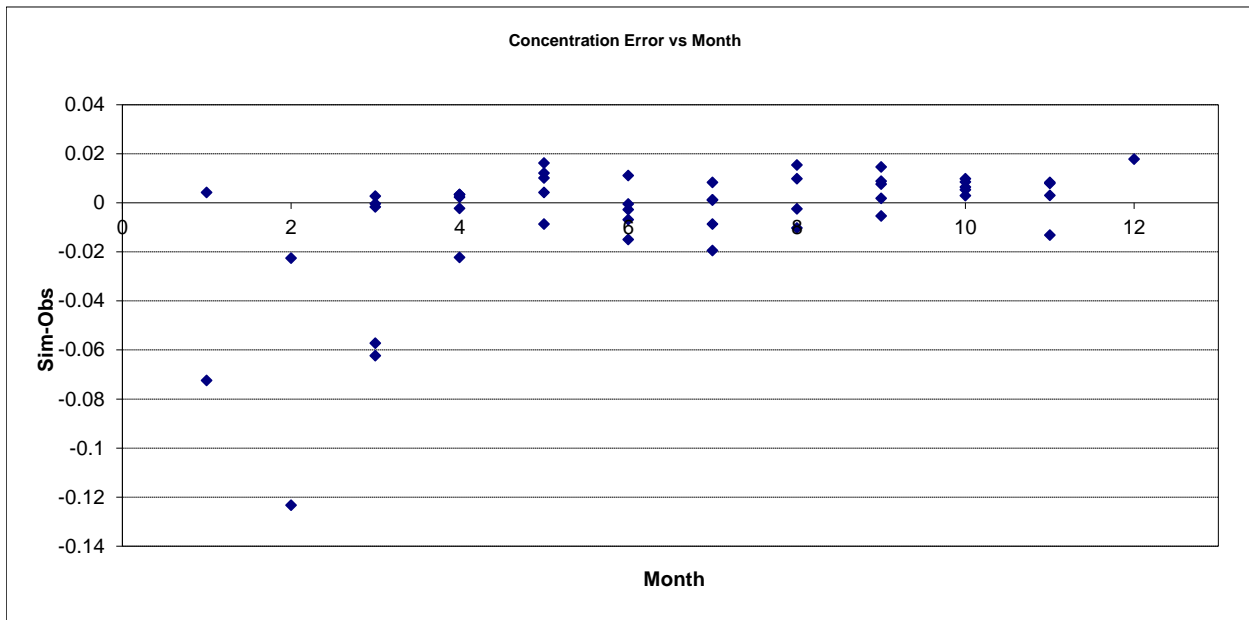


Figure A-115. Residual (Simulated - Observed) vs. Month Total Phosphorus (TP) at St. Louis R blw Cloquet R (S000-023)

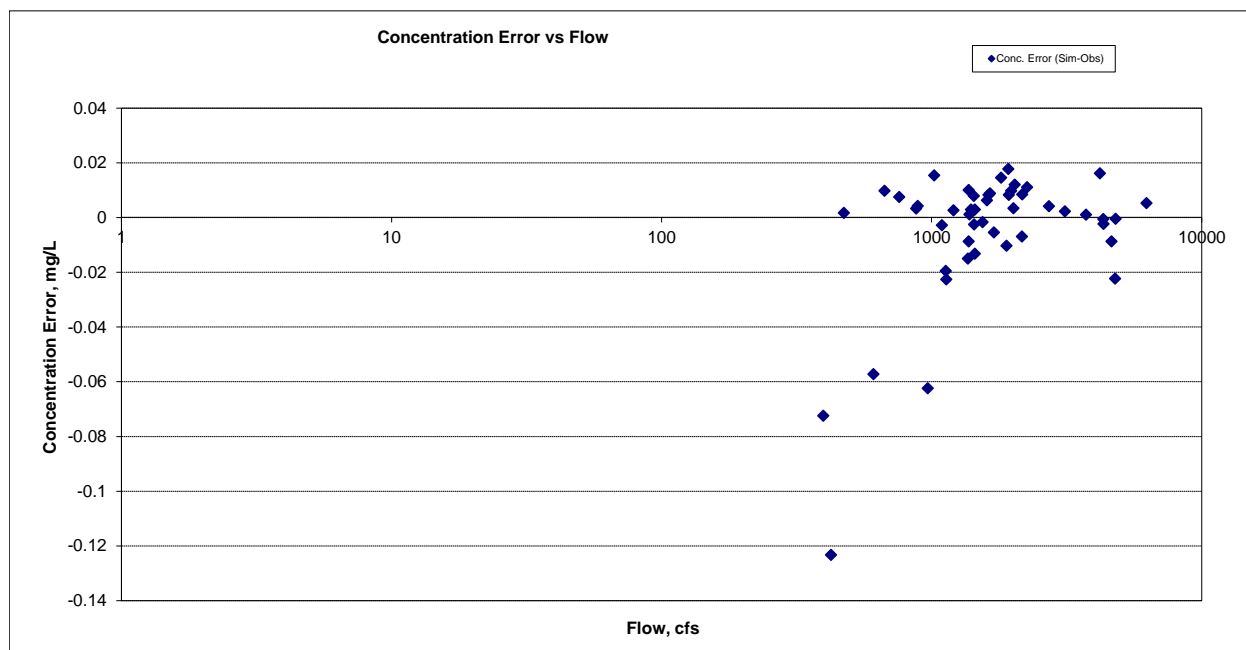


Figure A-116. Residual (Simulated - Observed) vs. Flow Total Phosphorus (TP) at St. Louis R blw Cloquet R (S000-023)

A.5 ST. LOUIS RIVER AT SCANLON, MN (03174001)

A.5.1 Ammonia Nitrogen (NH3)

Table A-17. Ammonia Nitrogen (NH3) statistics

Period	1994-2001	2002-2012
Count	17	66
Concentration Average Error	-69.31%	12.30%
Concentration Median Error	-65.21%	25.74%
Load Average Error	-74.22%	10.40%
Load Median Error	-32.56%	13.94%
Paired t conc	0.00	0.77
Paired t load	0.00	0.64

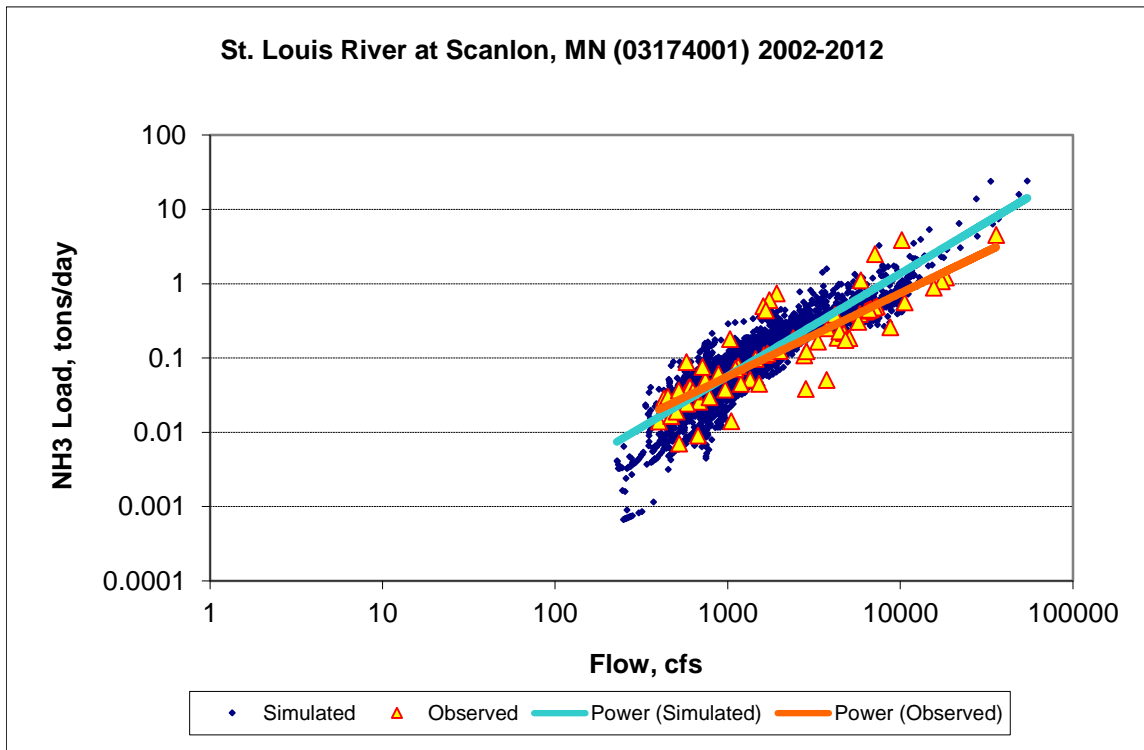


Figure A-117. Power plot of simulated and observed Ammonia Nitrogen (NH3) load vs flow at St. Louis River at Scanlon, MN (03174001) (calibration period)

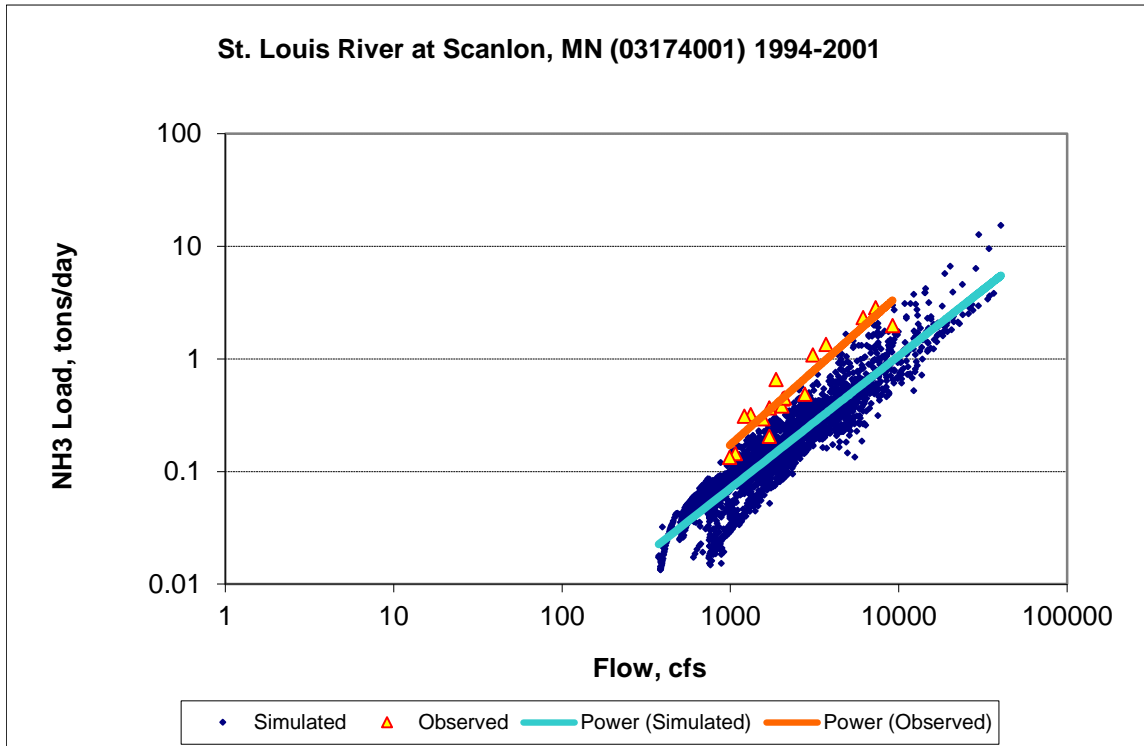
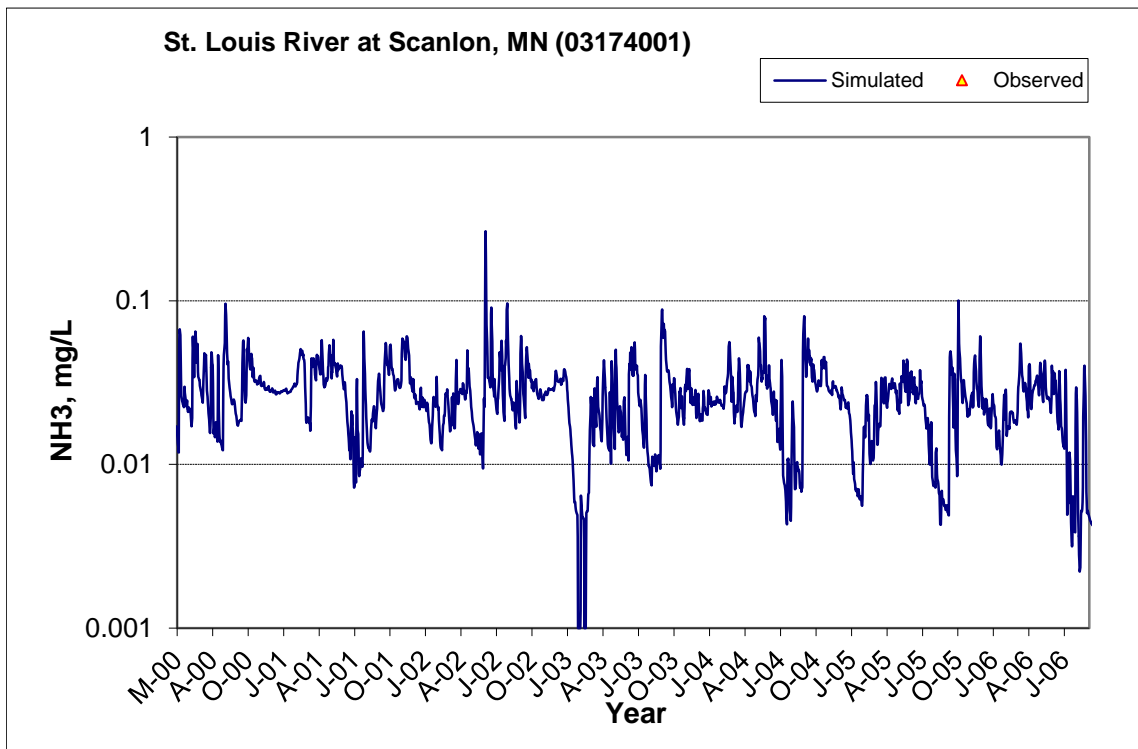
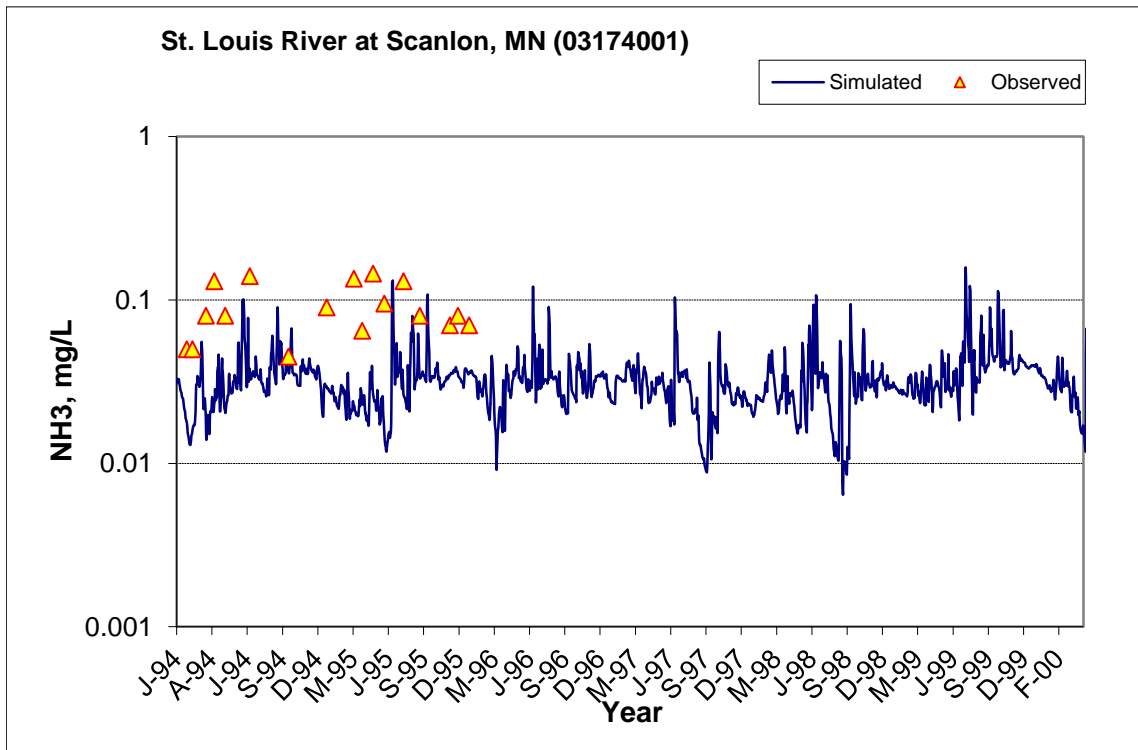


Figure A-118. Power plot of simulated and observed Ammonia Nitrogen (NH3) load vs flow at St. Louis River at Scanlon, MN (03174001) (validation period)



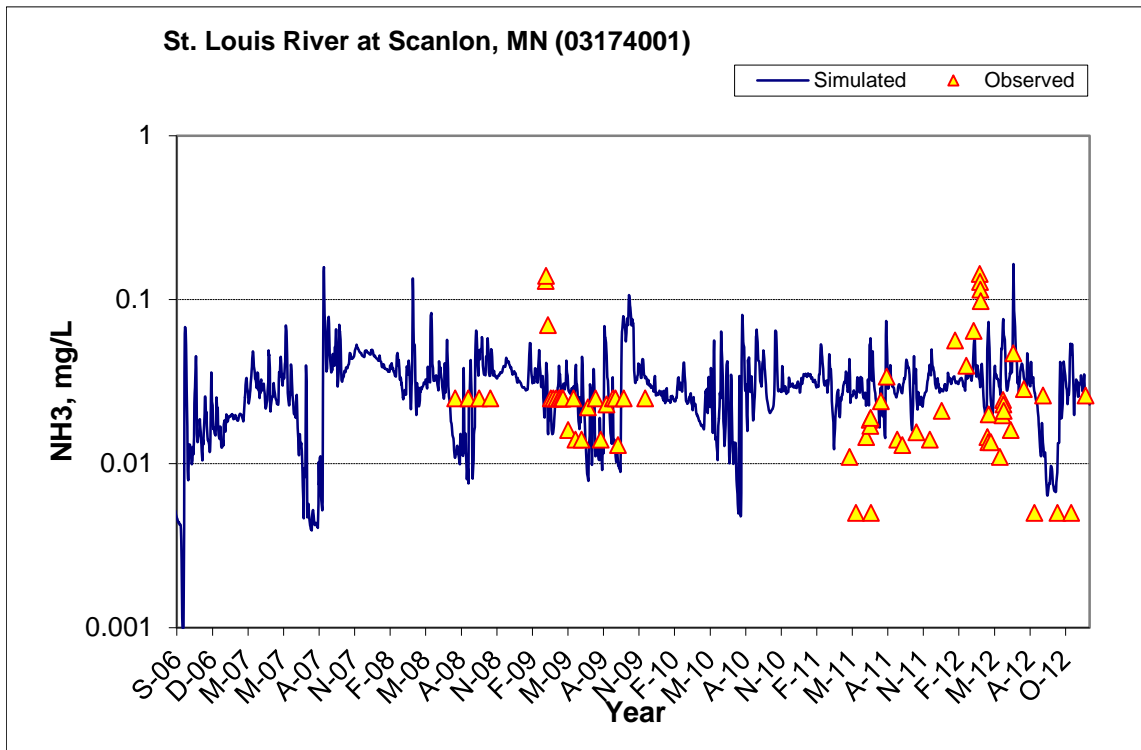


Figure A-119. Time series of observed and simulated Ammonia Nitrogen (NH₃) concentration at St. Louis River at Scanlon, MN (03174001)

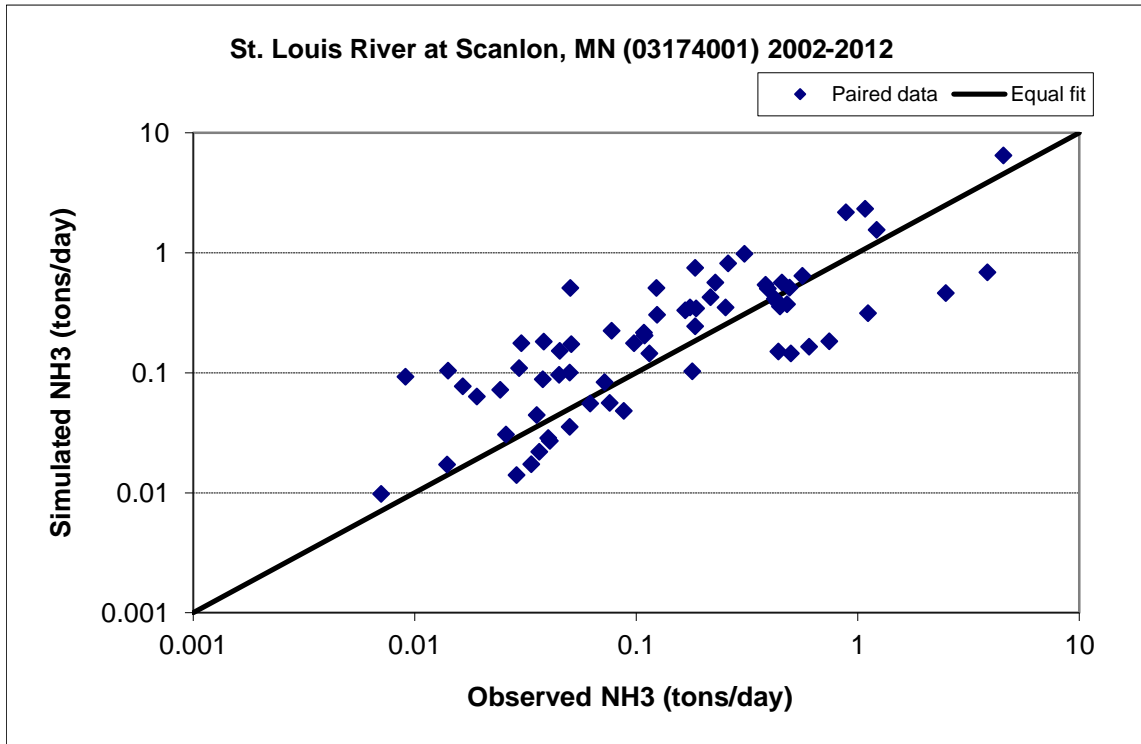


Figure A-120. Paired simulated vs. observed Ammonia Nitrogen (NH₃) load at St. Louis River at Scanlon, MN (03174001) (calibration period)

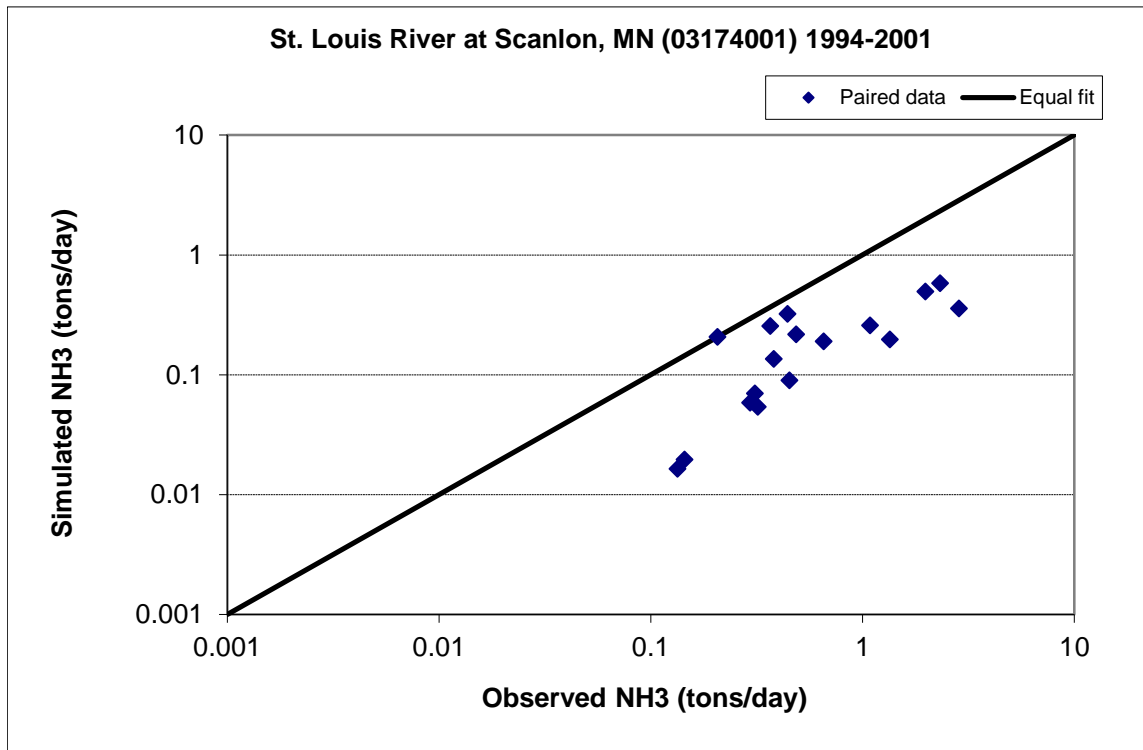


Figure A-121. Paired simulated vs. observed Ammonia Nitrogen (NH3) load at St. Louis River at Scanlon, MN (03174001) (validation period)

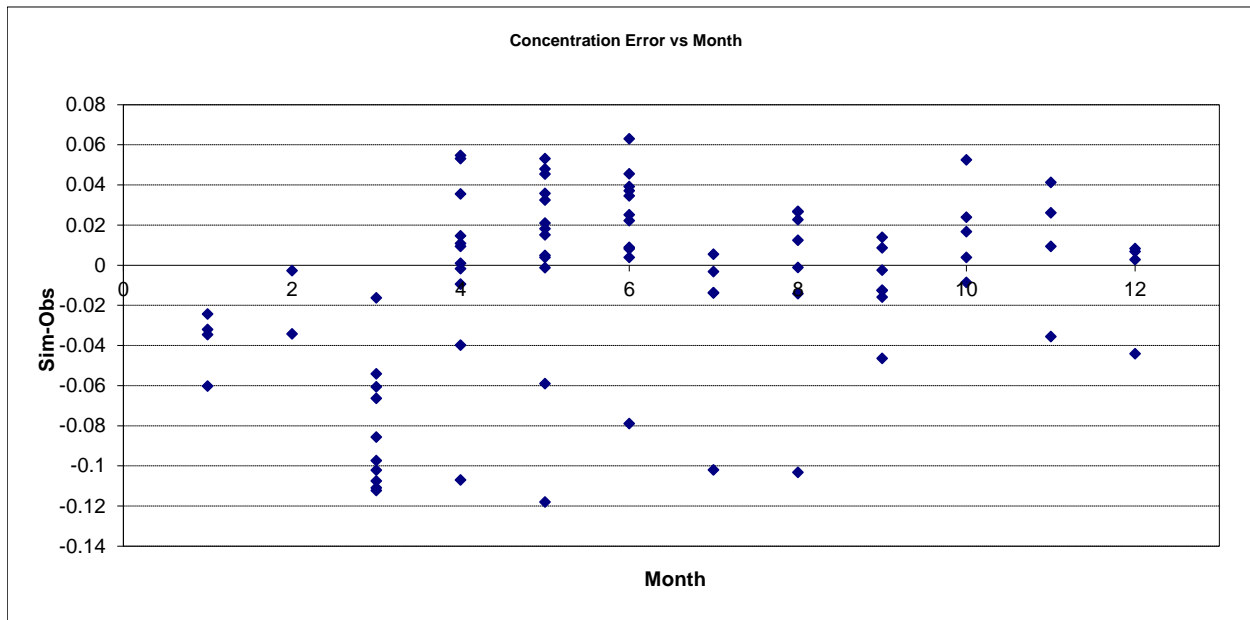


Figure A-122. Residual (Simulated - Observed) vs. Month Ammonia Nitrogen (NH3) at St. Louis River at Scanlon, MN (03174001)

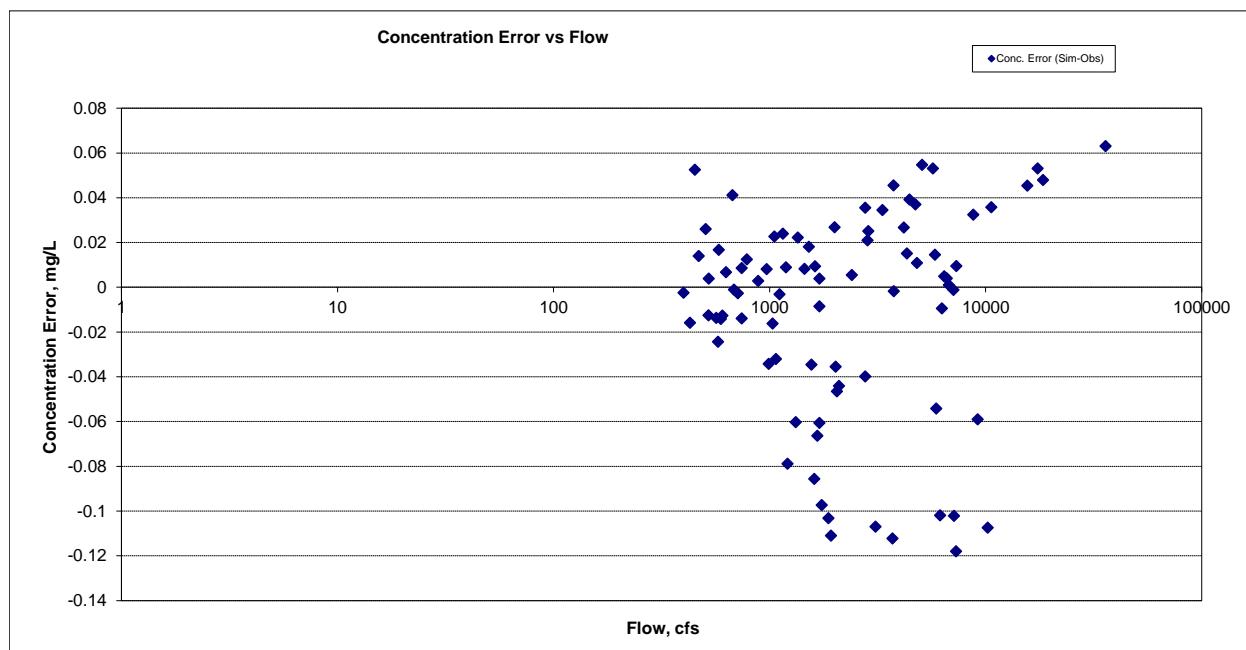


Figure A-123. Residual (Simulated - Observed) vs. Flow Ammonia Nitrogen (NH3) at St. Louis River at Scanlon, MN (03174001)

A.5.2 Organic Nitrogen (OrgN)

Table A-18. Organic Nitrogen (OrgN) statistics

Period	1994-2001	2002-2012
Count	ND	38
Concentration Average Error		7.60%
Concentration Median Error		5.13%
Load Average Error		-29.96%
Load Median Error		0.82%
Paired t conc		0.98
Paired t load		0.34

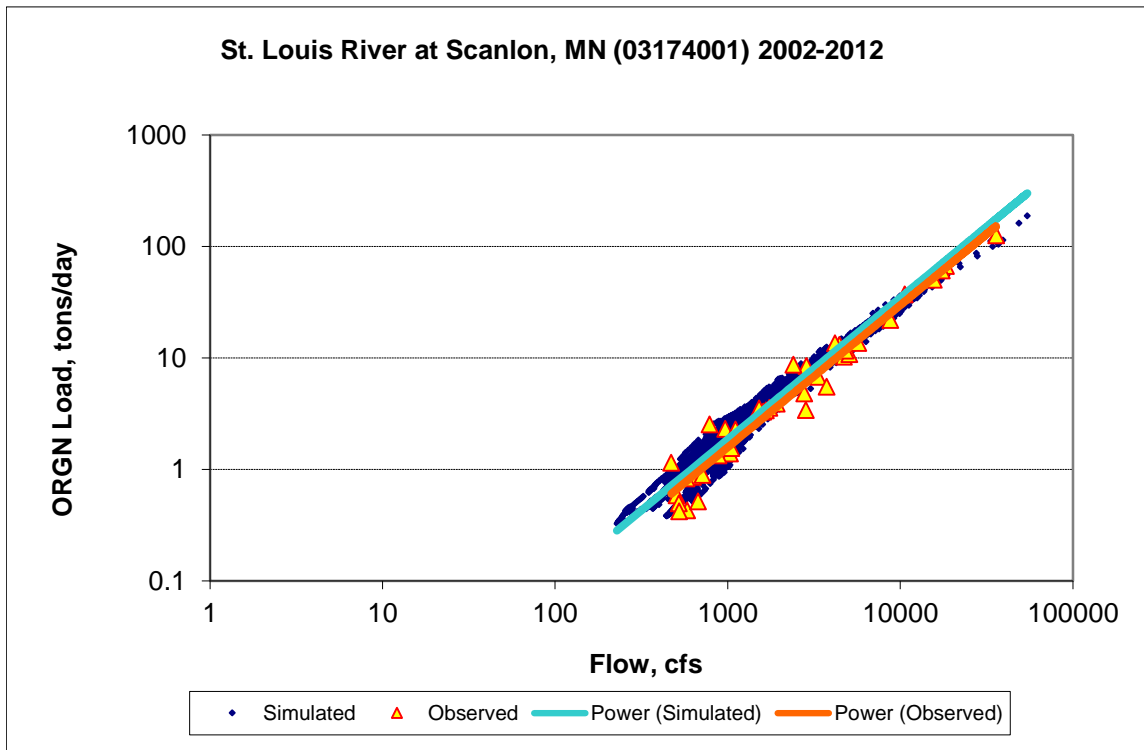
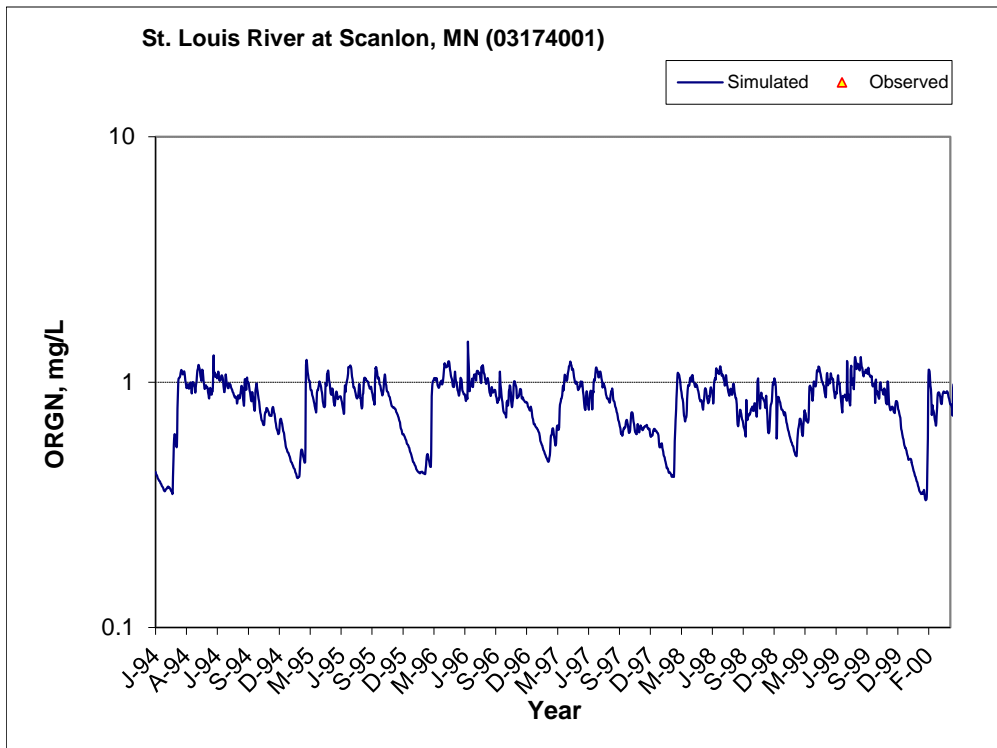


Figure A-124. Power plot of simulated and observed Organic Nitrogen (OrgN) load vs flow at St. Louis River at Scanlon, MN (03174001) (calibration period)



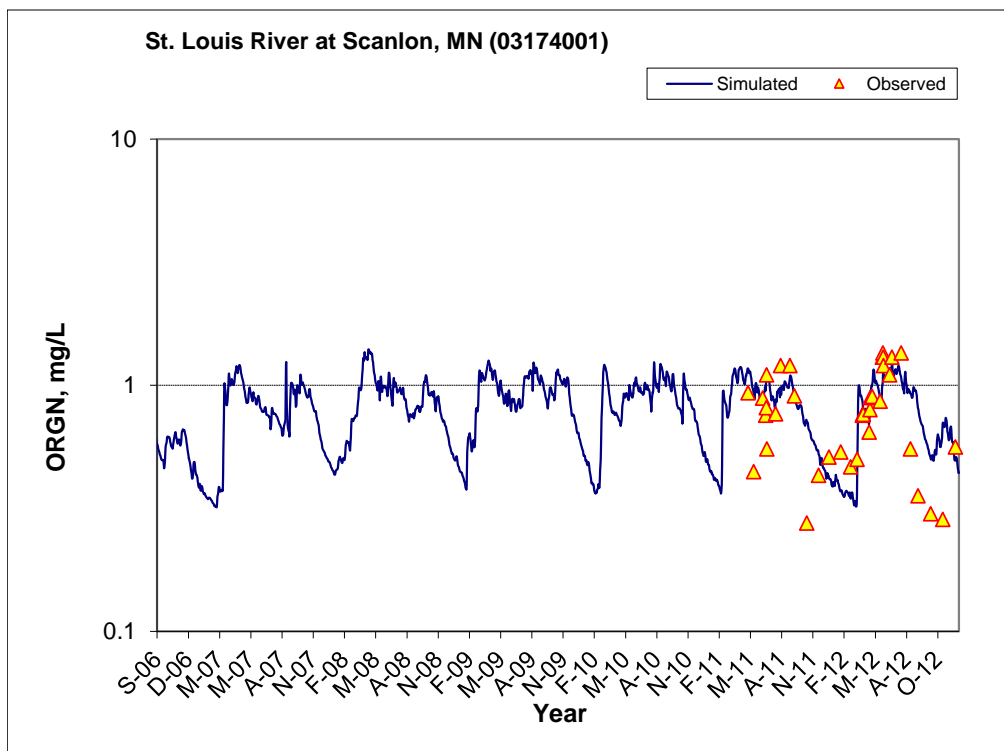
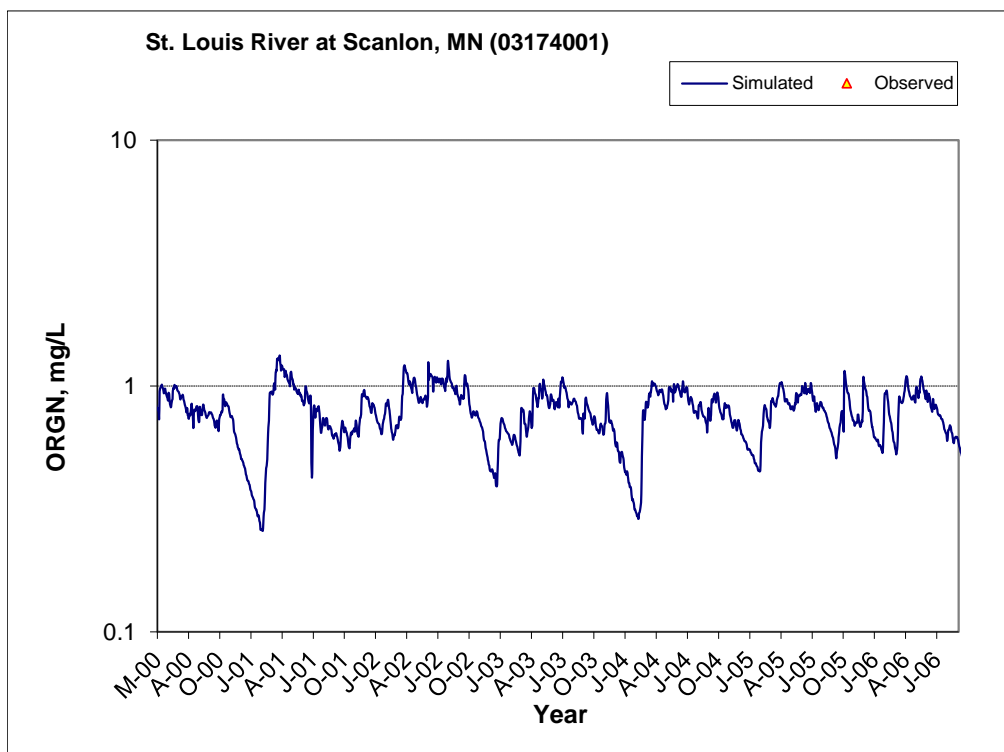


Figure A-125. Time series of observed and simulated Organic Nitrogen (OrgN) concentration at St. Louis River at Scanlon, MN (03174001)

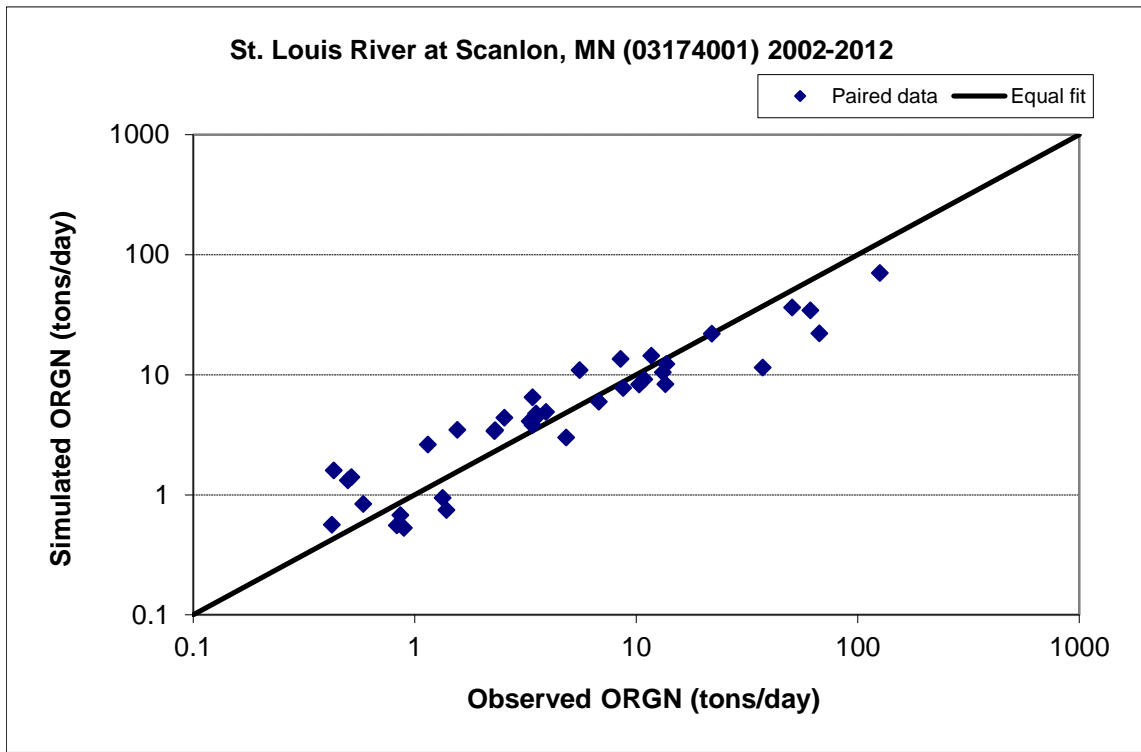


Figure A-126. Paired simulated vs. observed Organic Nitrogen (OrgN) load at St. Louis River at Scanlon, MN (03174001) (calibration period)

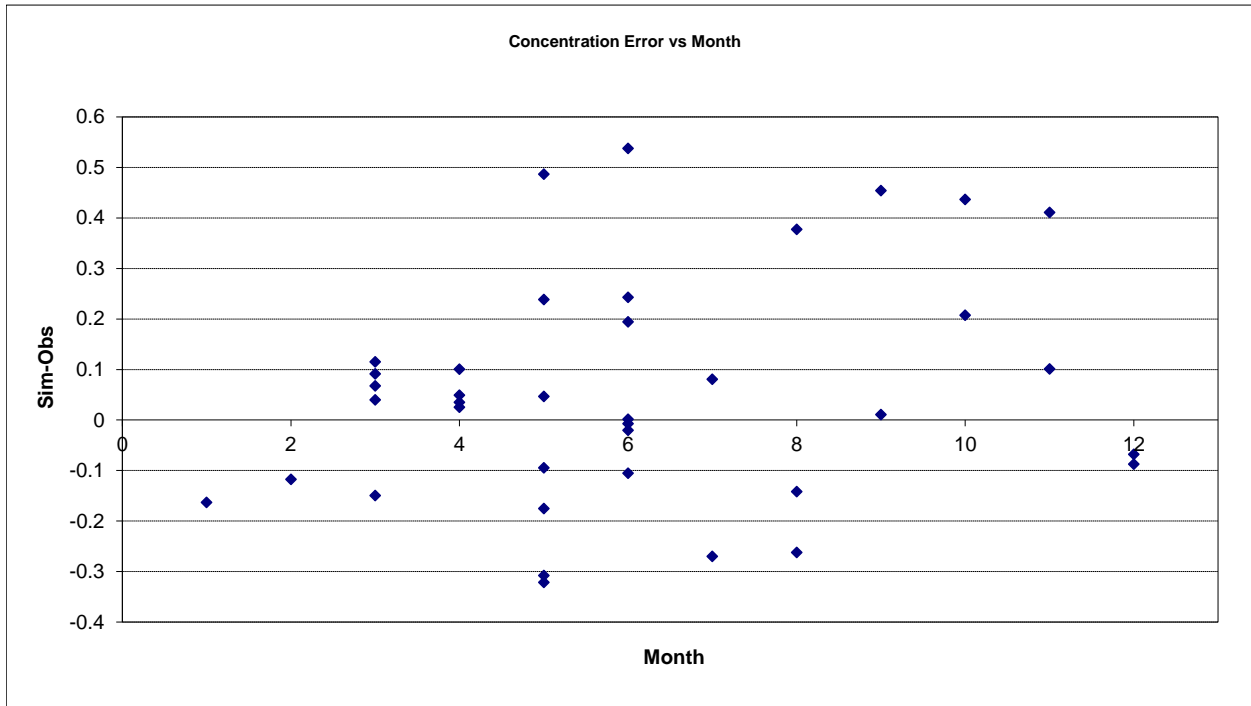


Figure A-127. Residual (Simulated - Observed) vs. Month Organic Nitrogen (OrgN) at St. Louis River at Scanlon, MN (03174001)

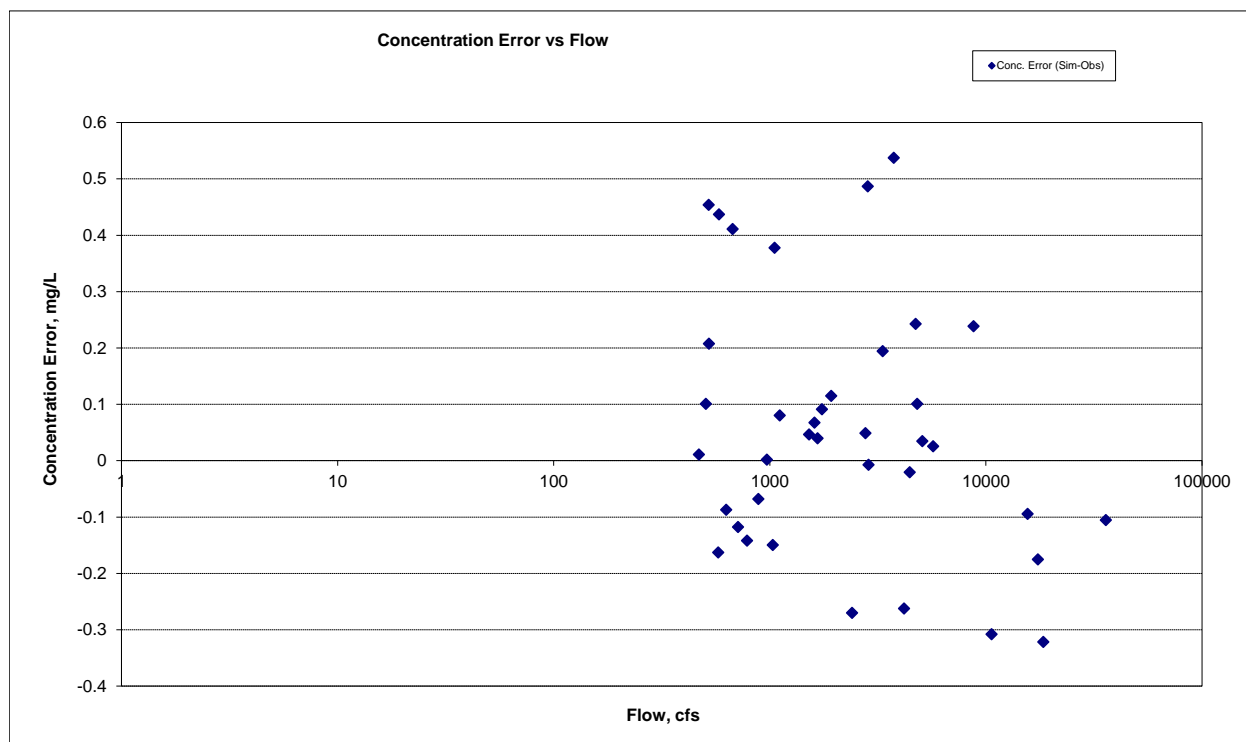


Figure A-128. Residual (Simulated - Observed) vs. Flow Organic Nitrogen (OrgN) at St. Louis River at Scanlon, MN (03174001)

A.5.3 Total Kjeldahl Nitrogen (TKN)

Table A-19. Total Kjeldahl Nitrogen (TKN) statistics

Period	1994-2001	2002-2012
Count	8	95
Concentration Average Error	34.46%	0.32%
Concentration Median Error	37.75%	2.01%
Load Average Error	41.86%	-3.87%
Load Median Error	29.30%	4.56%
Paired t conc	0.06	1.00
Paired t load	0.37	0.79

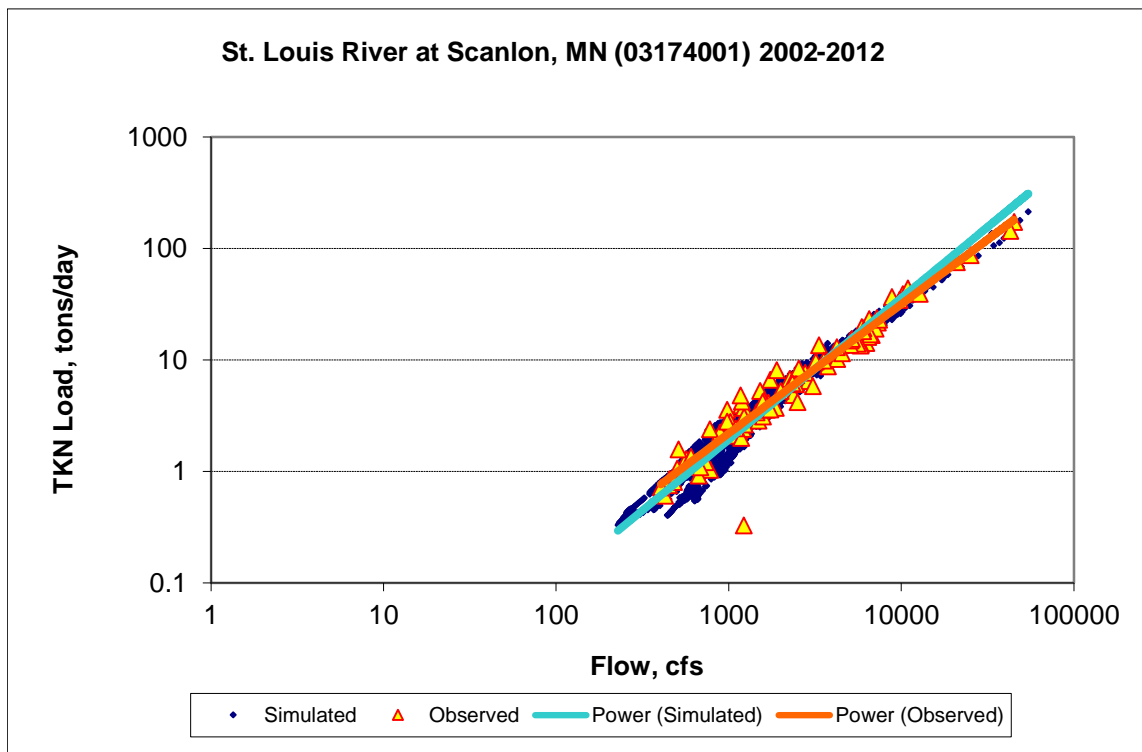


Figure A-129. Power plot of simulated and observed Total Kjeldahl Nitrogen (TKN) load vs flow at St. Louis River at Scanlon, MN (03174001) (calibration period)

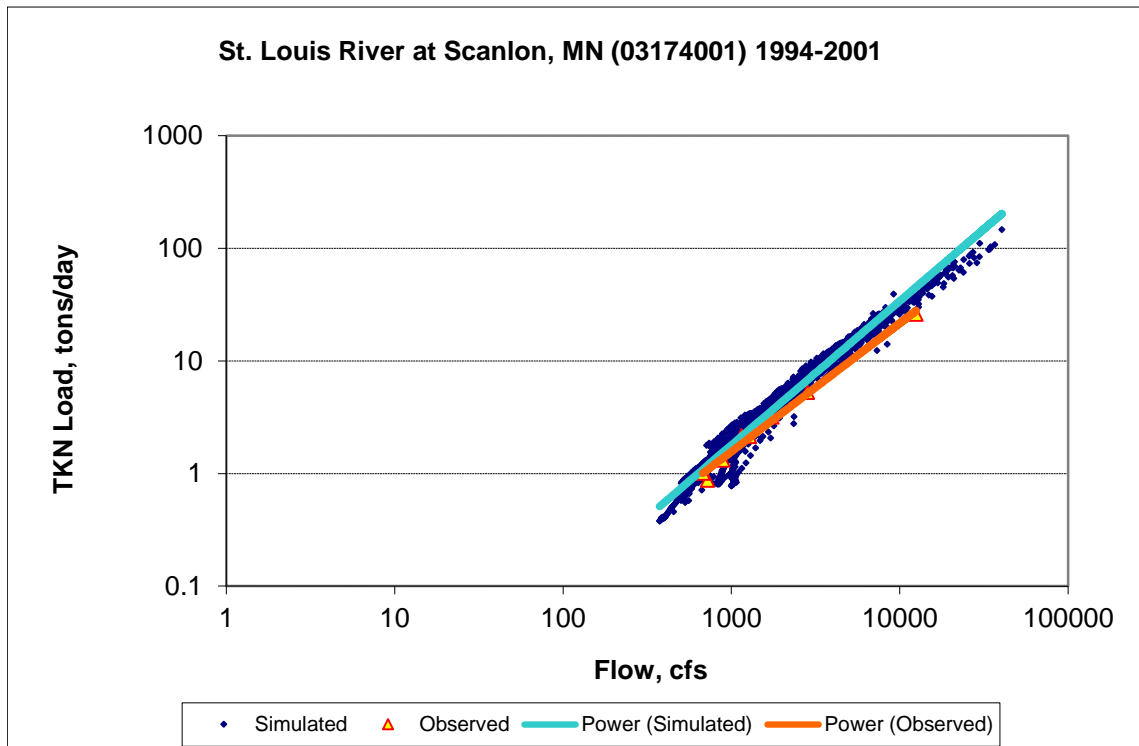
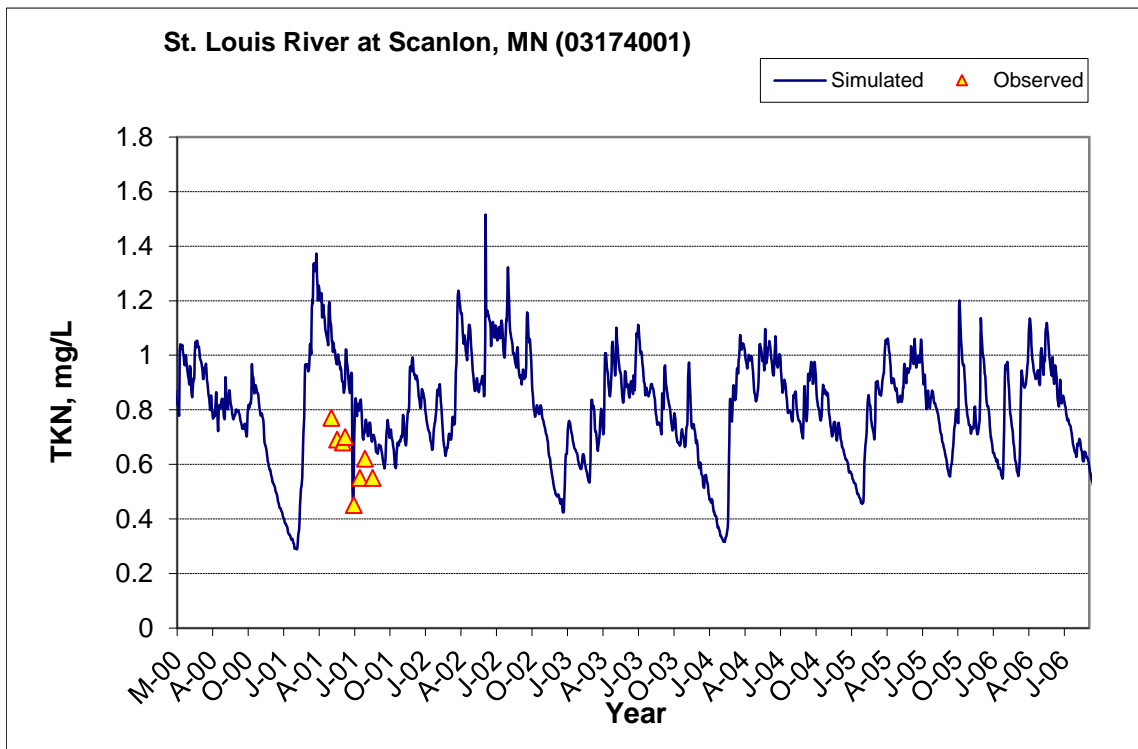
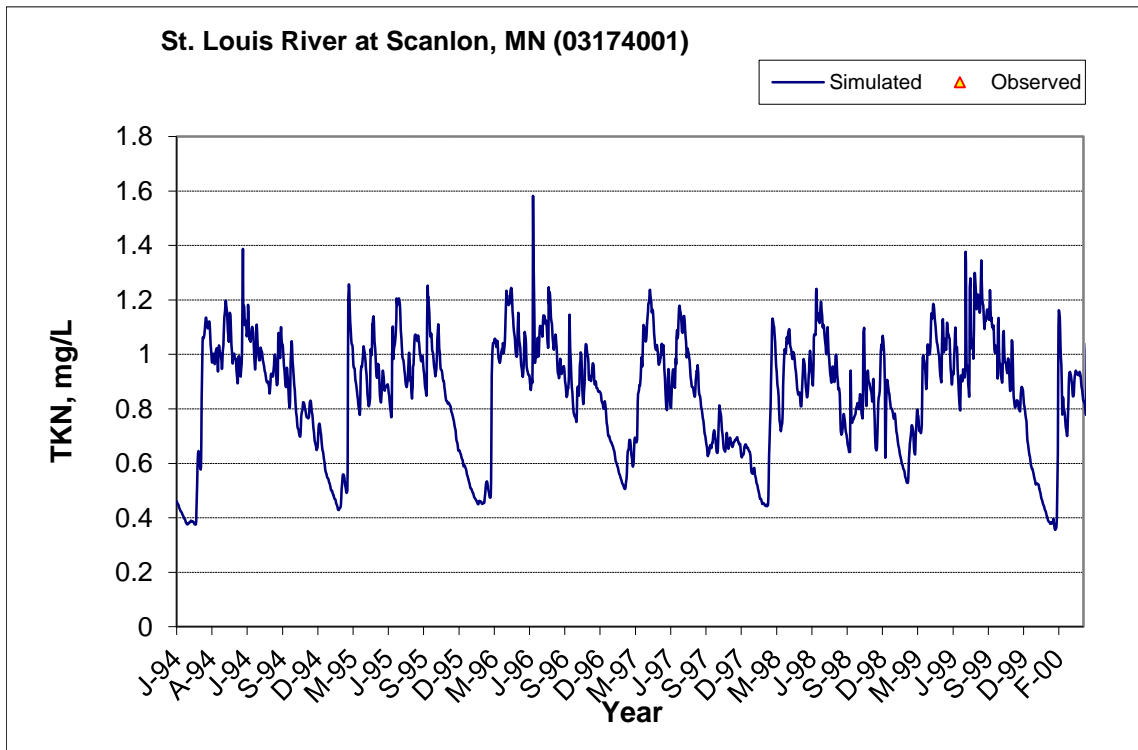


Figure A-130. Power plot of simulated and observed Total Kjeldahl Nitrogen (TKN) load vs flow at St. Louis River at Scanlon, MN (03174001) (validation period)



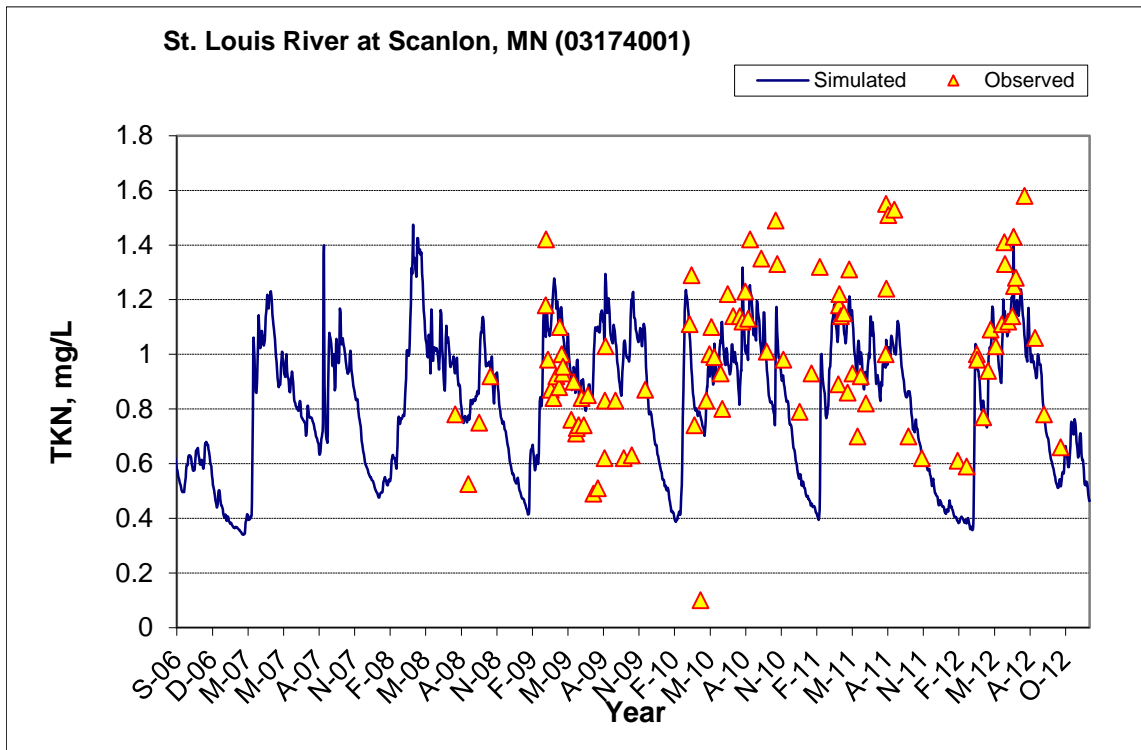


Figure A-131. Time series of observed and simulated Total Kjeldahl Nitrogen (TKN) concentration at St. Louis River at Scanlon, MN (03174001)

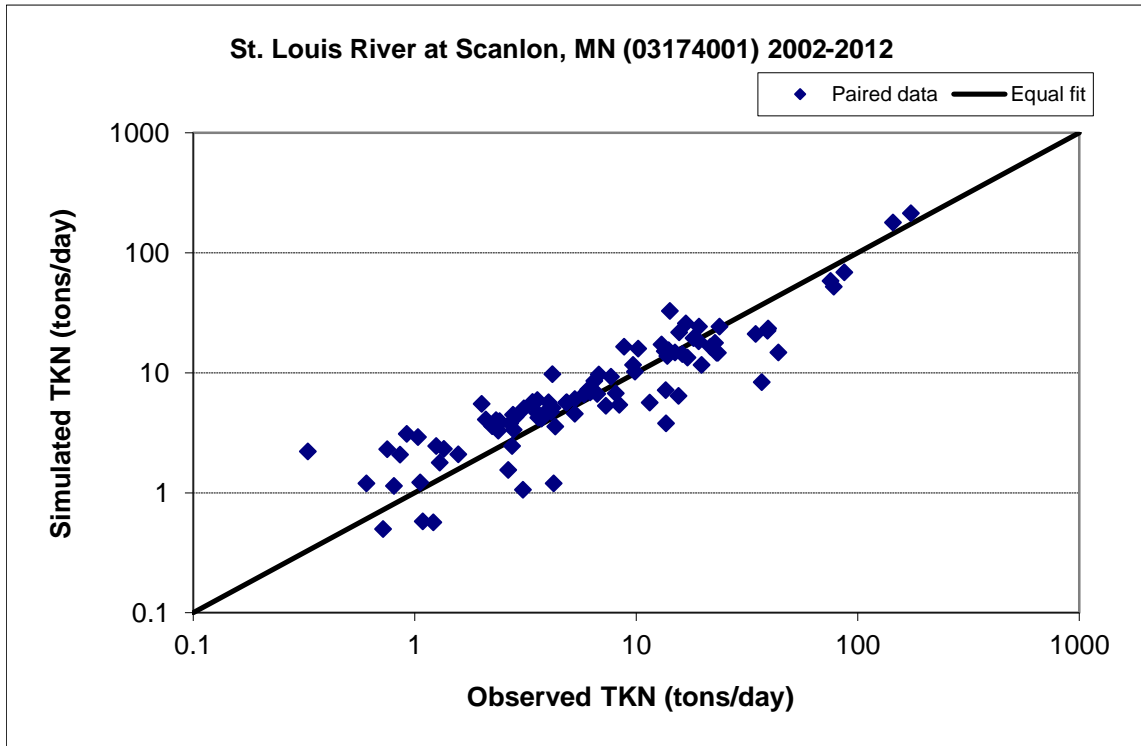


Figure A-132. Paired simulated vs. observed Total Kjeldahl Nitrogen (TKN) load at St. Louis River at Scanlon, MN (03174001) (calibration period)

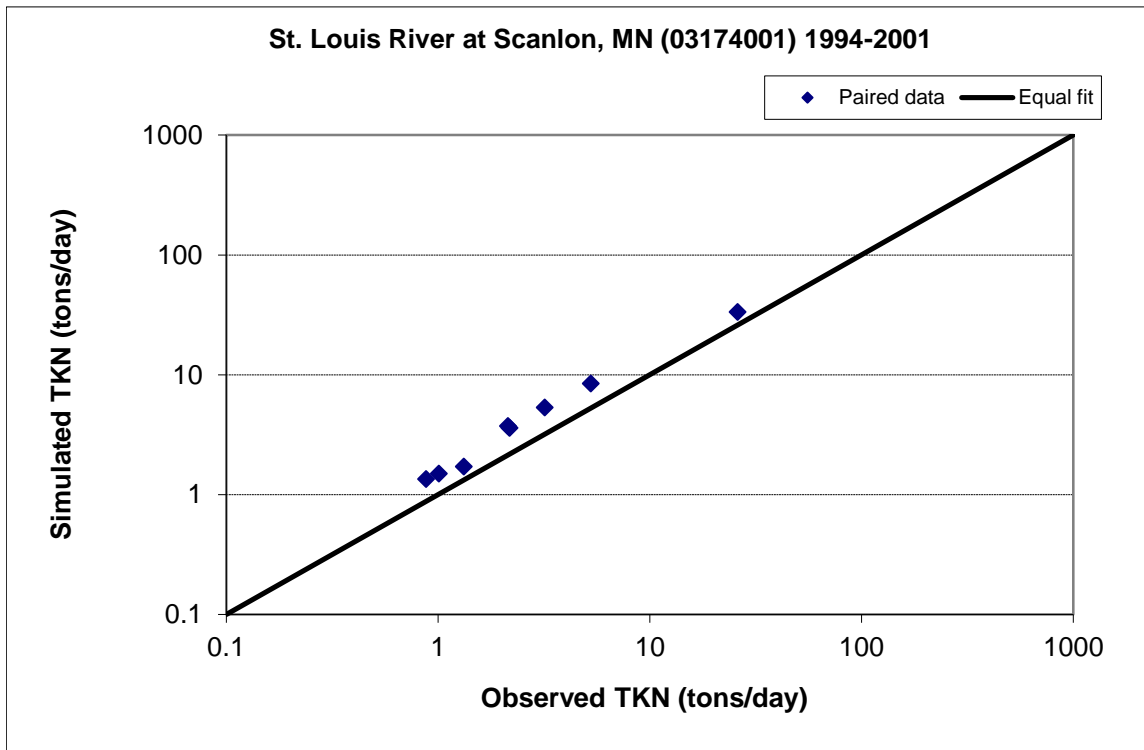


Figure A-133. Paired simulated vs. observed Total Kjeldahl Nitrogen (TKN) load at St. Louis River at Scanlon, MN (03174001) (validation period)

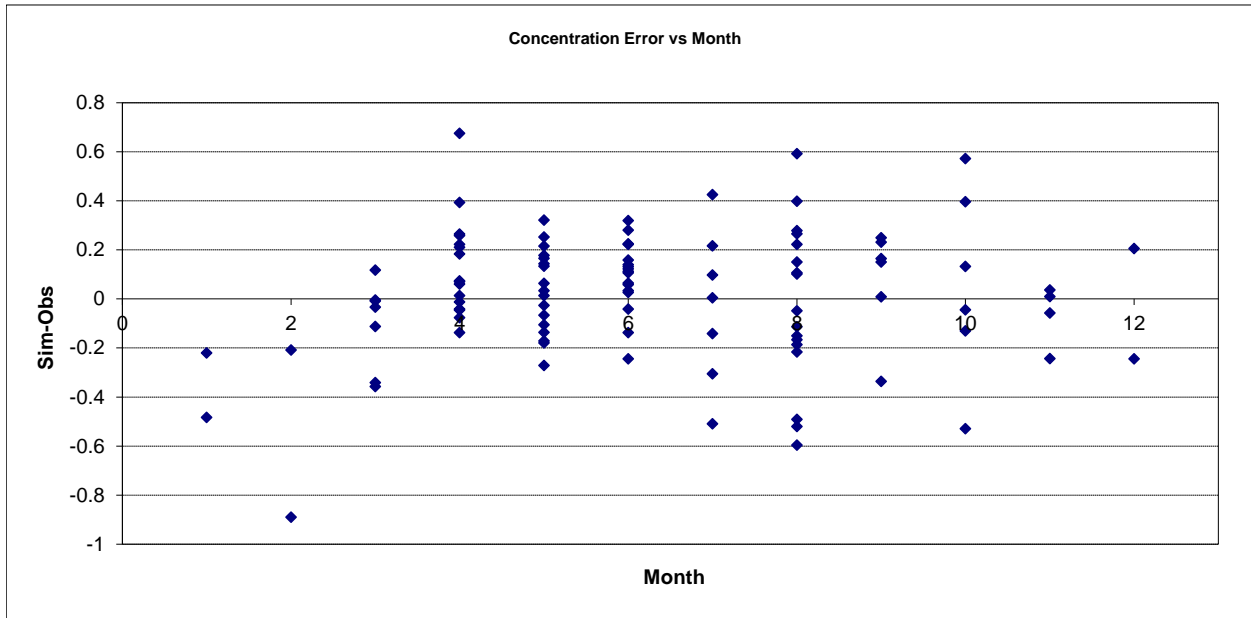


Figure A-134. Residual (Simulated - Observed) vs. Month Total Kjeldahl Nitrogen (TKN) at St. Louis River at Scanlon, MN (03174001)

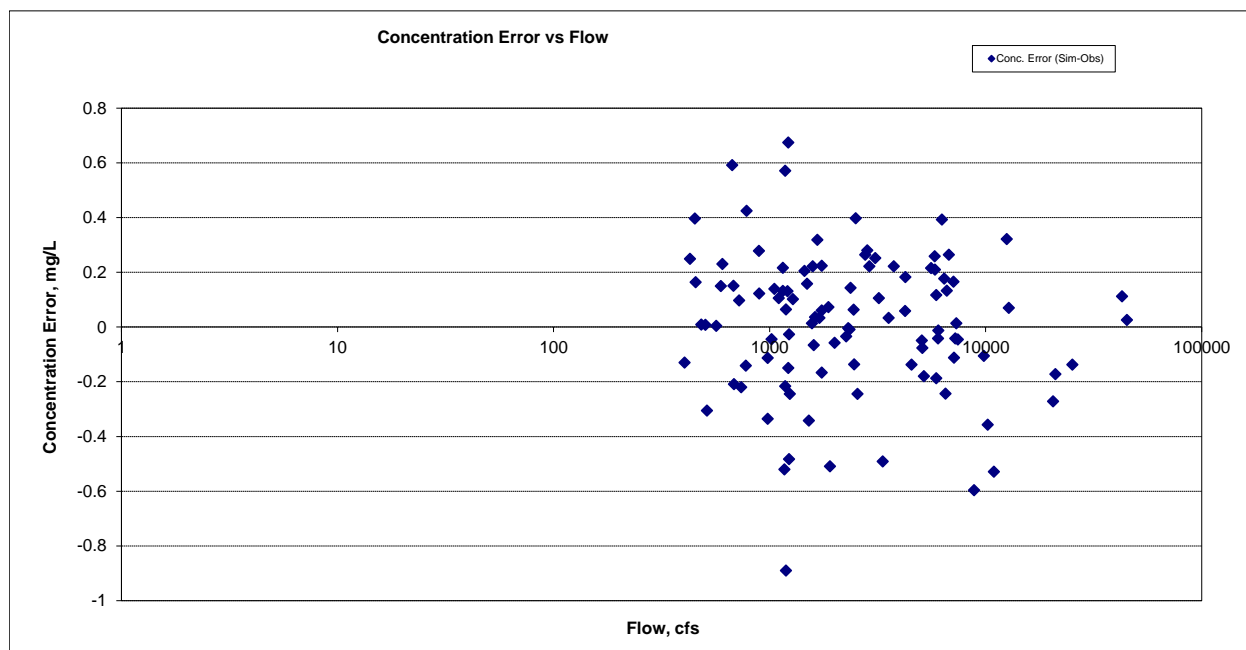


Figure A-135. Residual (Simulated - Observed) vs. Flow Total Kjeldahl Nitrogen (TKN) at St. Louis River at Scanlon, MN (03174001)

A.5.4 Nitrite+ Nitrate Nitrogen (NOx)

Table A-20. Nitrite+ Nitrate Nitrogen (NOx) statistics

Period	1994-2001	2002-2012
Count	8	140
Concentration Average Error	134.96%	-27.60%
Concentration Median Error	119.79%	1.67%
Load Average Error	18.86%	-4.46%
Load Median Error	40.17%	1.01%
Paired t conc	0.00	0.38
Paired t load	0.51	0.84

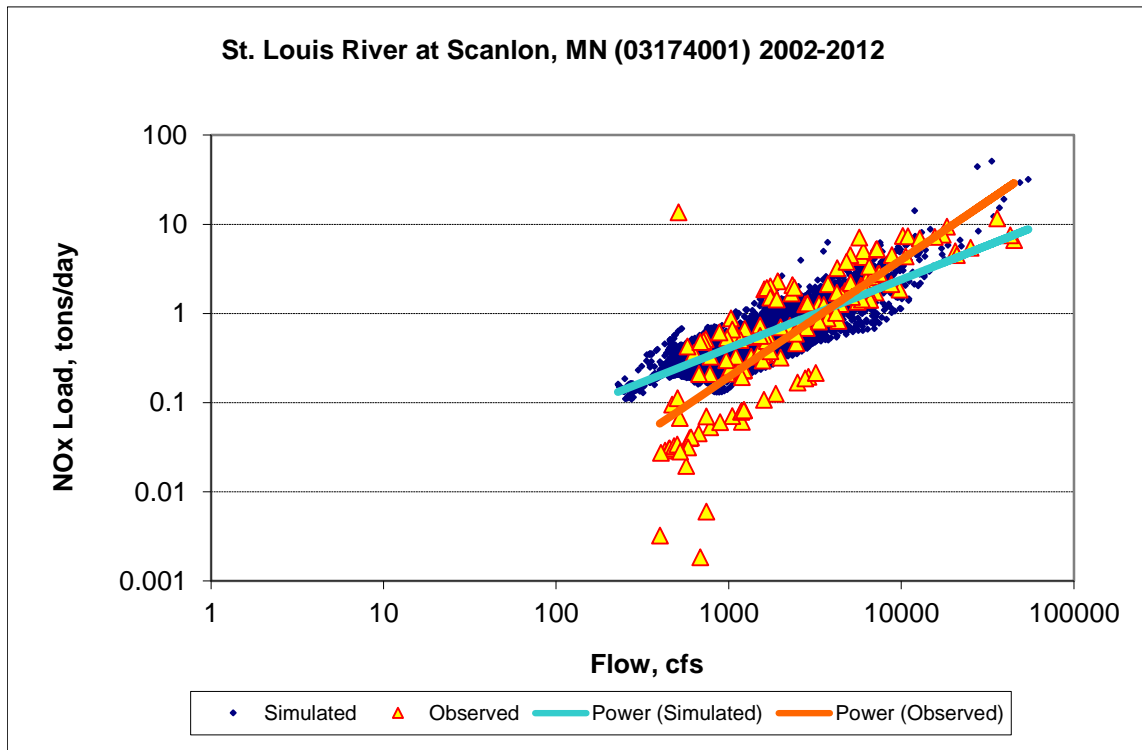


Figure A-136. Power plot of simulated and observed Nitrite+ Nitrate Nitrogen (NOx) load vs flow at St. Louis River at Scanlon, MN (03174001) (calibration period)

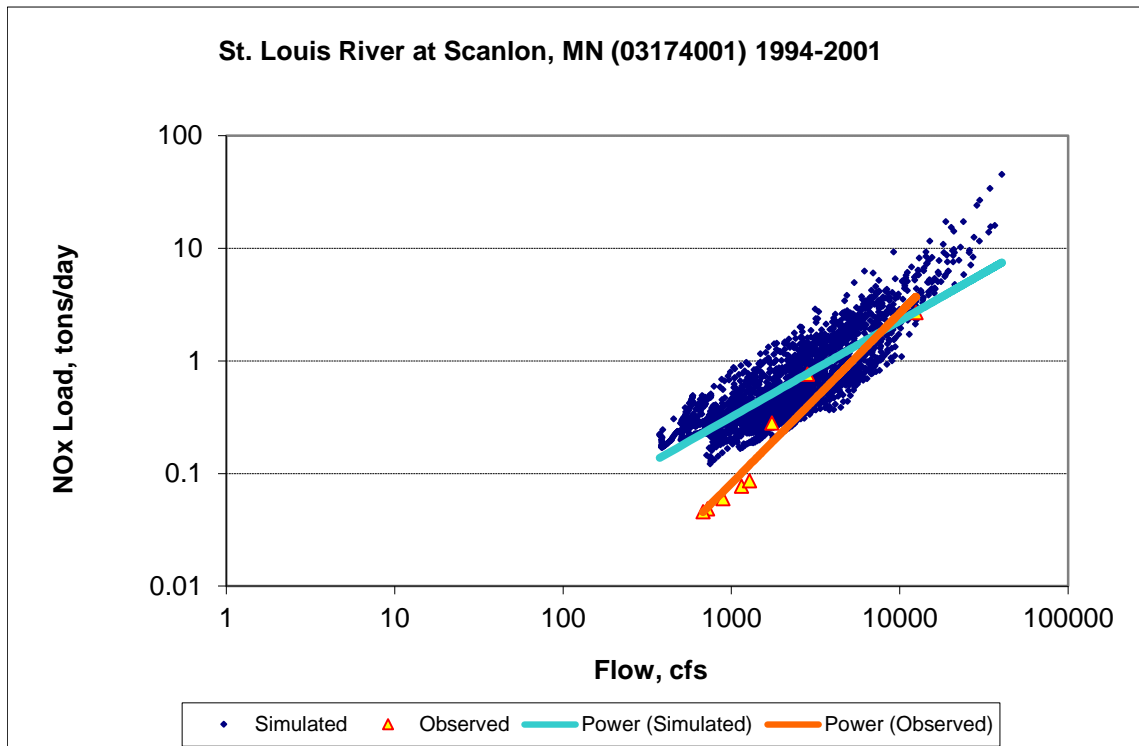
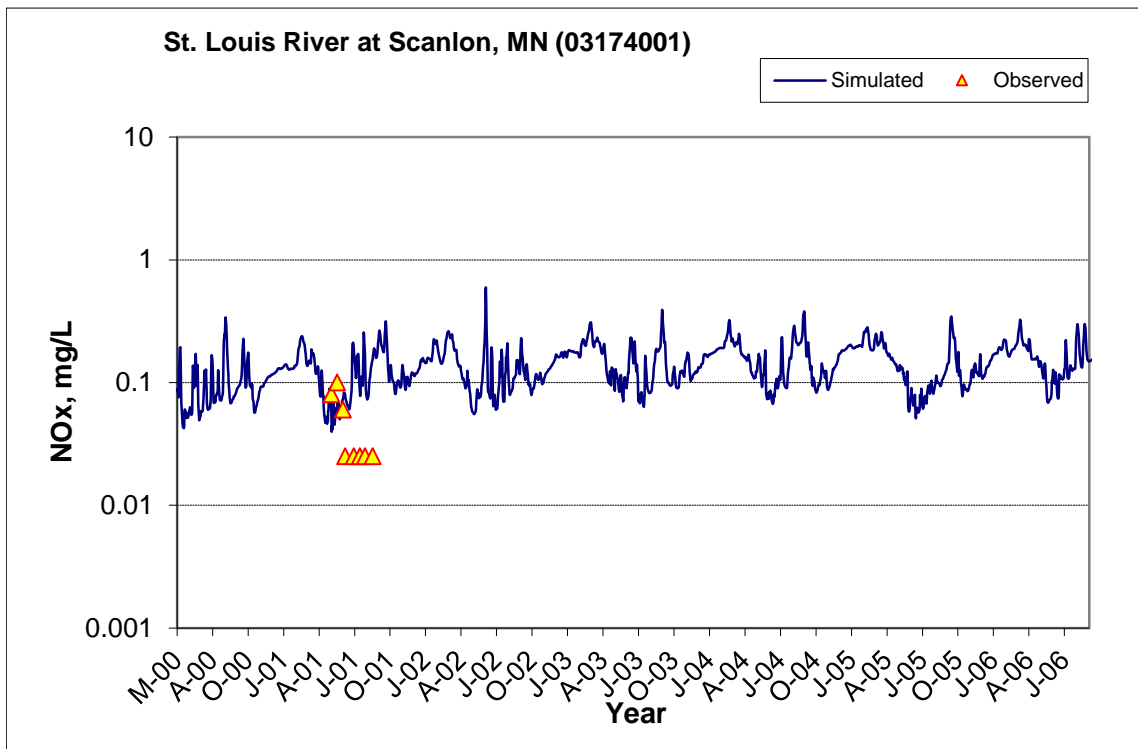
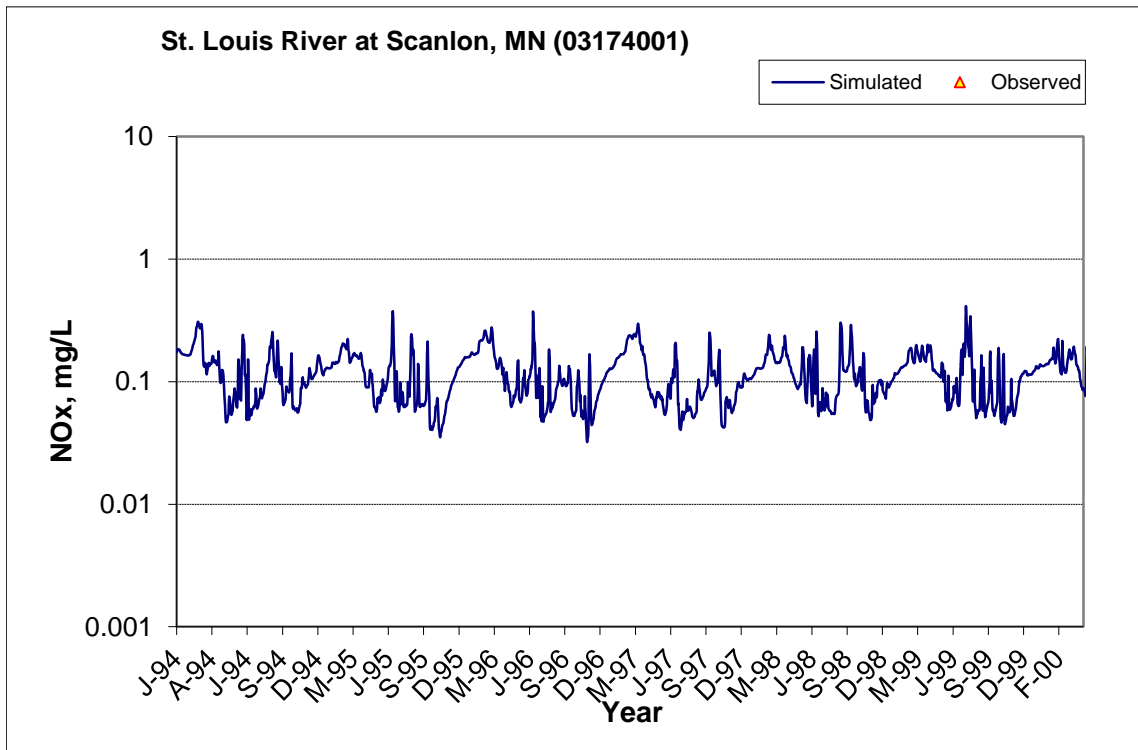


Figure A-137. Power plot of simulated and observed Nitrite+ Nitrate Nitrogen (NOx) load vs flow at St. Louis River at Scanlon, MN (03174001) (validation period)



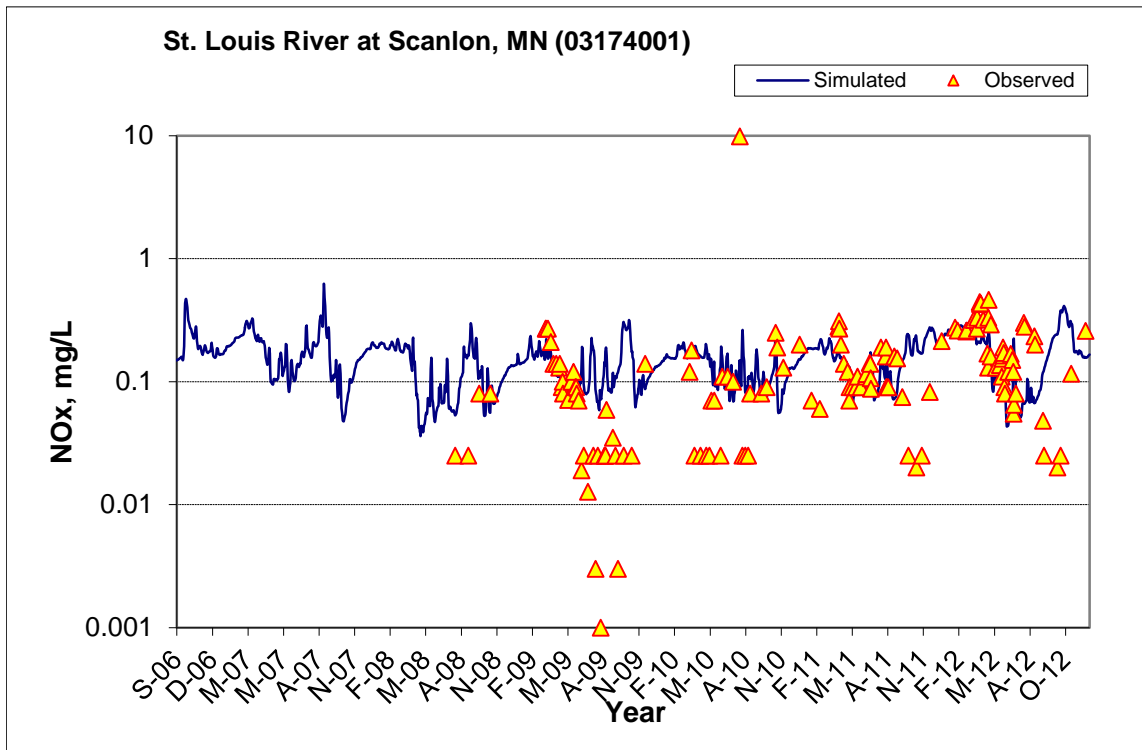


Figure A-138. Time series of observed and simulated Nitrite+ Nitrate Nitrogen (NOx) concentration at St. Louis River at Scanlon, MN (03174001)

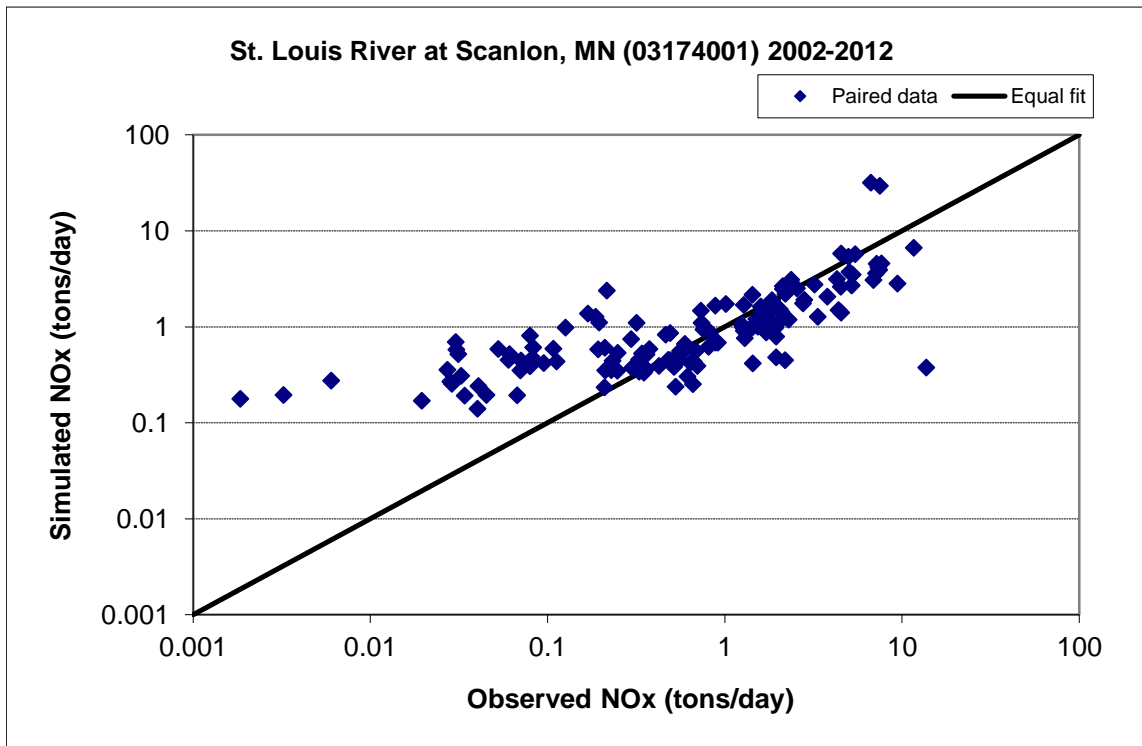


Figure A-139. Paired simulated vs. observed Nitrite+ Nitrate Nitrogen (NOx) load at St. Louis River at Scanlon, MN (03174001) (calibration period)

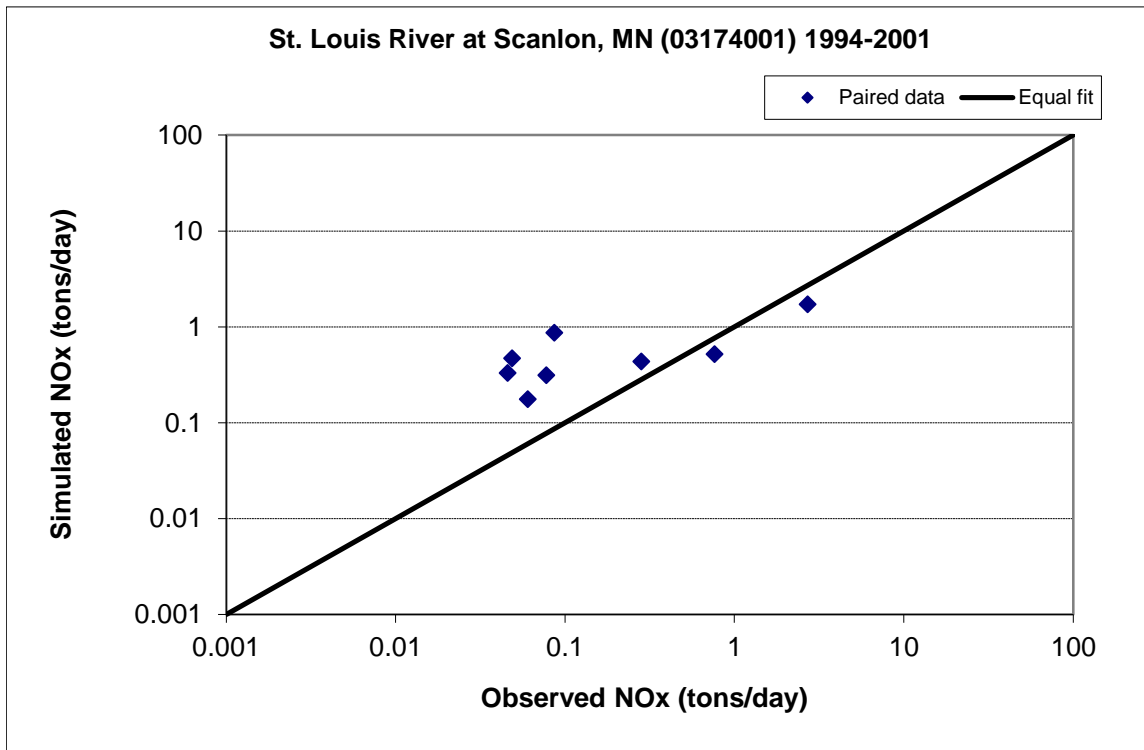


Figure A-140. Paired simulated vs. observed Nitrite+ Nitrate Nitrogen (NOx) load at St. Louis River at Scanlon, MN (03174001) (validation period)

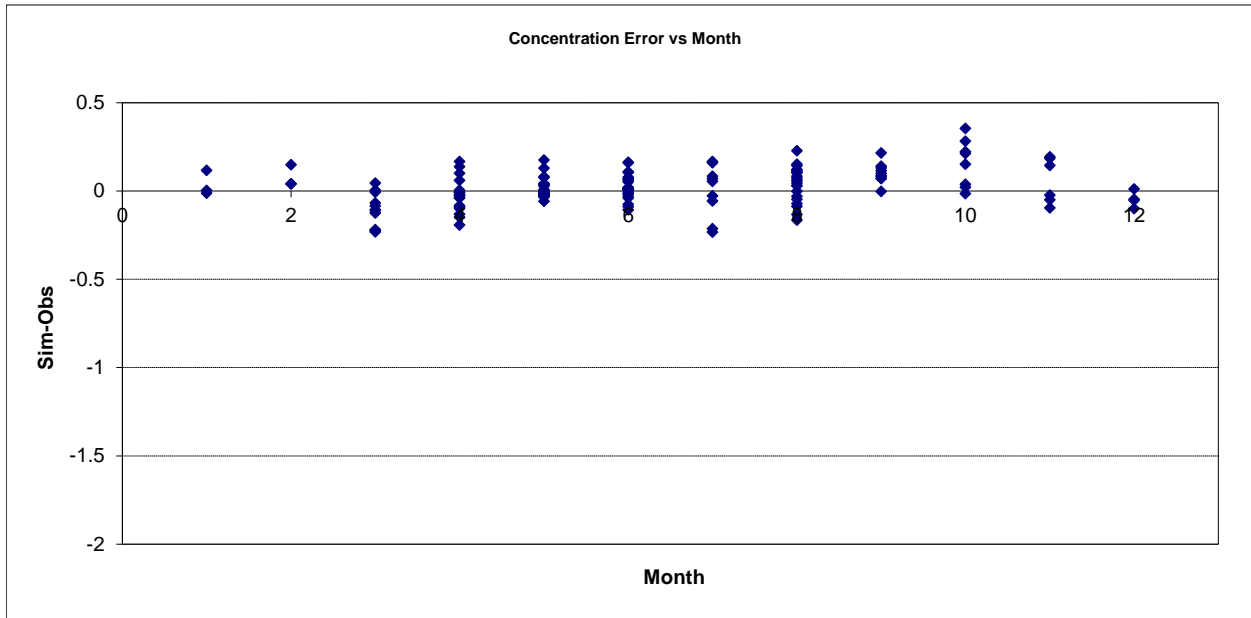


Figure A-141. Residual (Simulated - Observed) vs. Month Nitrite+ Nitrate Nitrogen (NOx) at St. Louis River at Scanlon, MN (03174001)

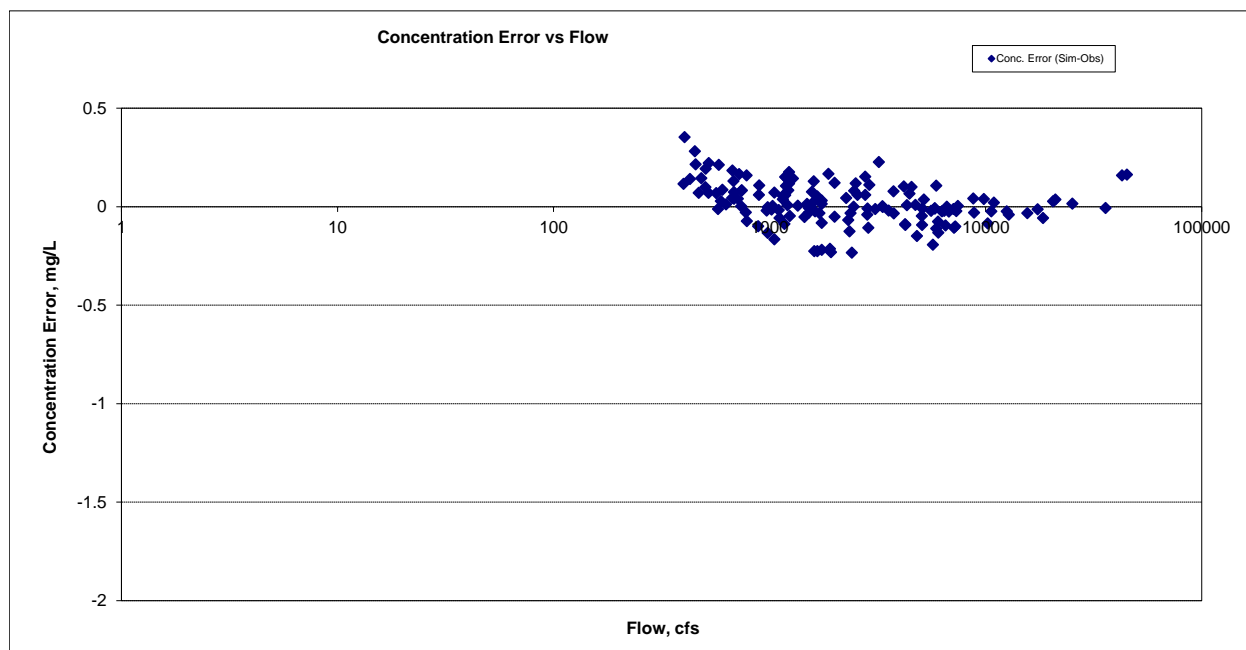


Figure A-142. Residual (Simulated - Observed) vs. Flow Nitrite+ Nitrate Nitrogen (NOx) at St. Louis River at Scanlon, MN (03174001)

A.5.5 Total Nitrogen (TN)

Table A-21. Total Nitrogen (TN) statistics

Period	1994-2001	2002-2012
Count	8	127
Concentration Average Error	38.08%	-6.14%
Concentration Median Error	37.32%	-0.54%
Load Average Error	38.87%	-10.70%
Load Median Error	33.81%	1.69%
Paired t conc	0.01	1.00
Paired t load	0.39	0.73

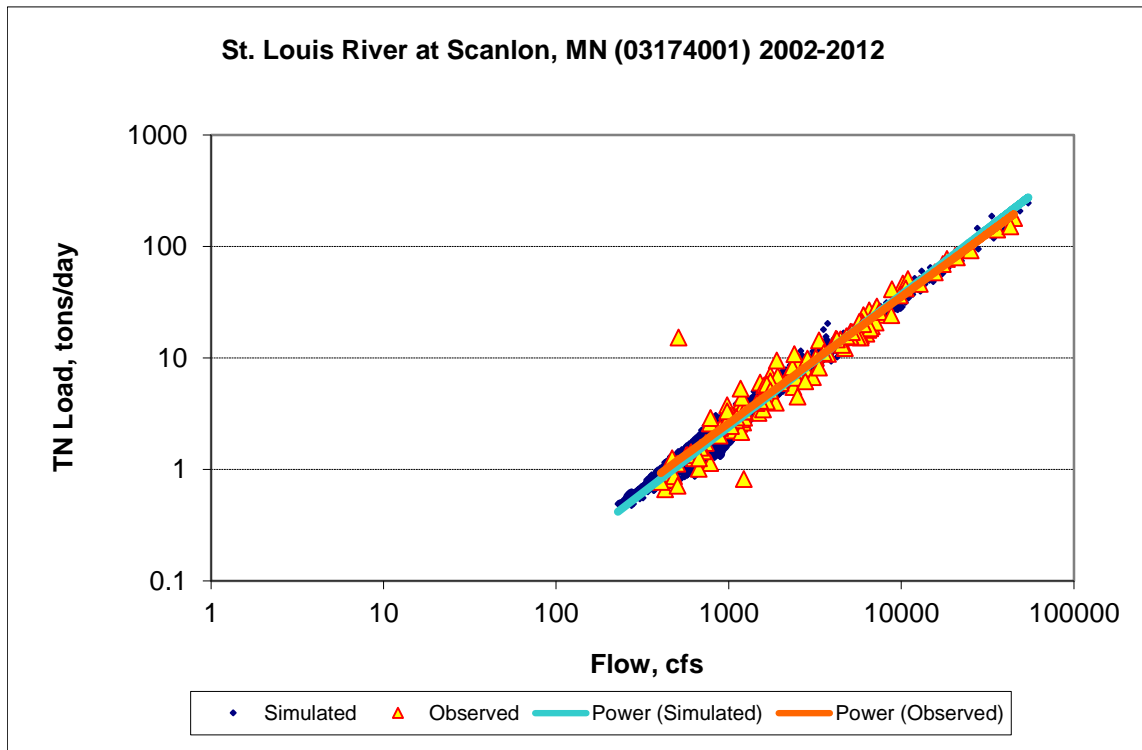


Figure A-143. Power plot of simulated and observed Total Nitrogen (TN) load vs flow at St. Louis River at Scanlon, MN (03174001) (calibration period)

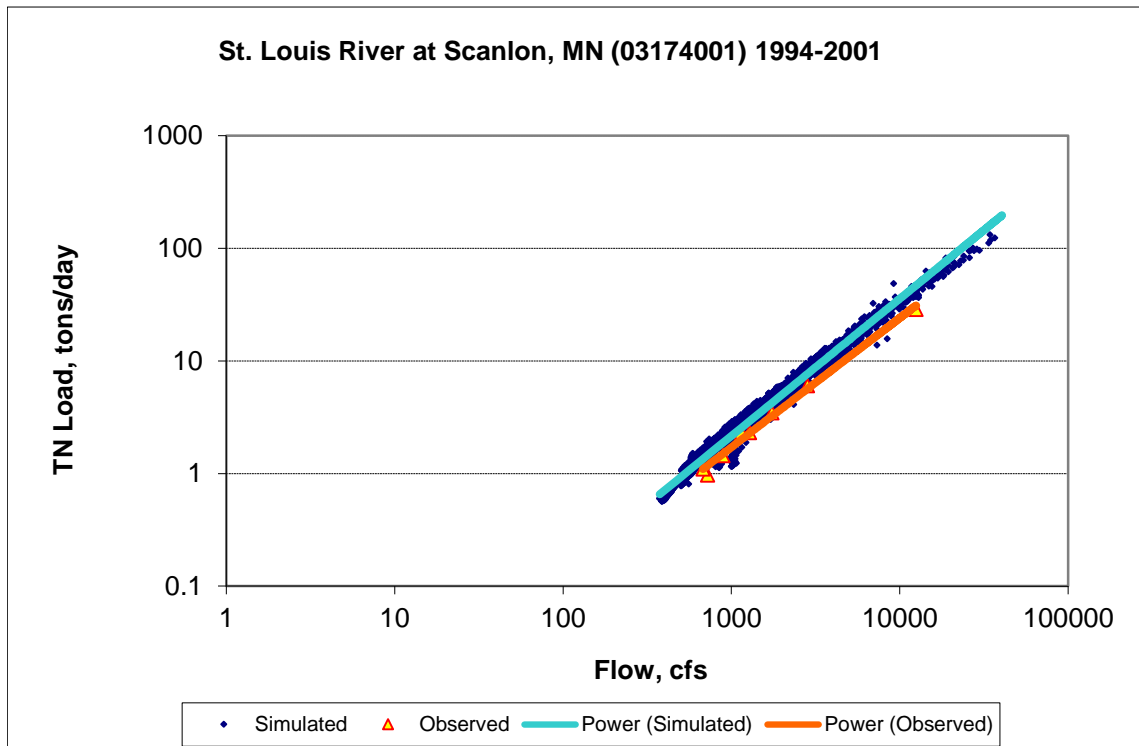
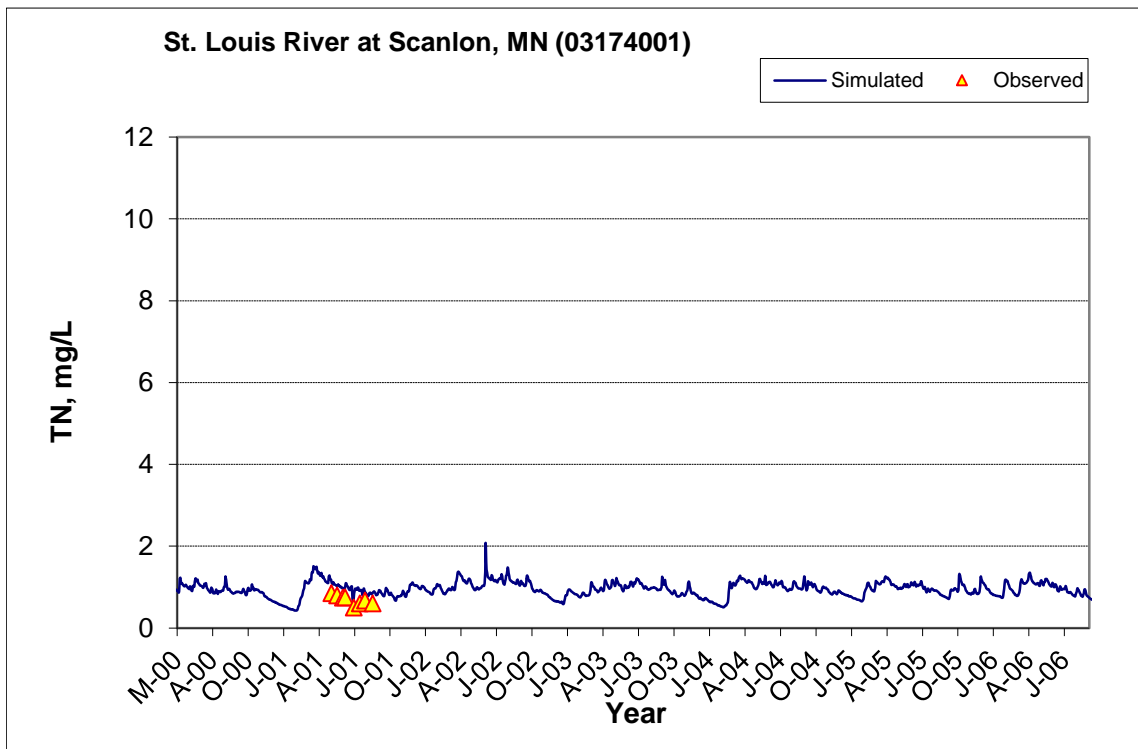
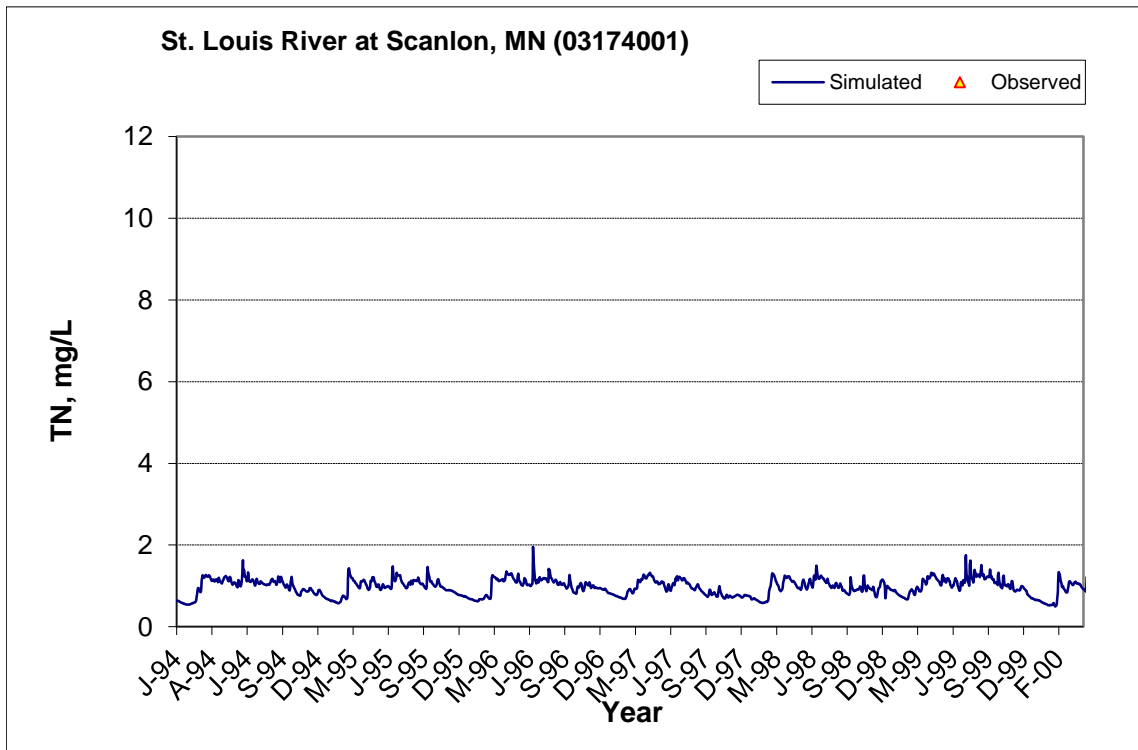


Figure A-144. Power plot of simulated and observed Total Nitrogen (TN) load vs flow at St. Louis River at Scanlon, MN (03174001) (validation period)



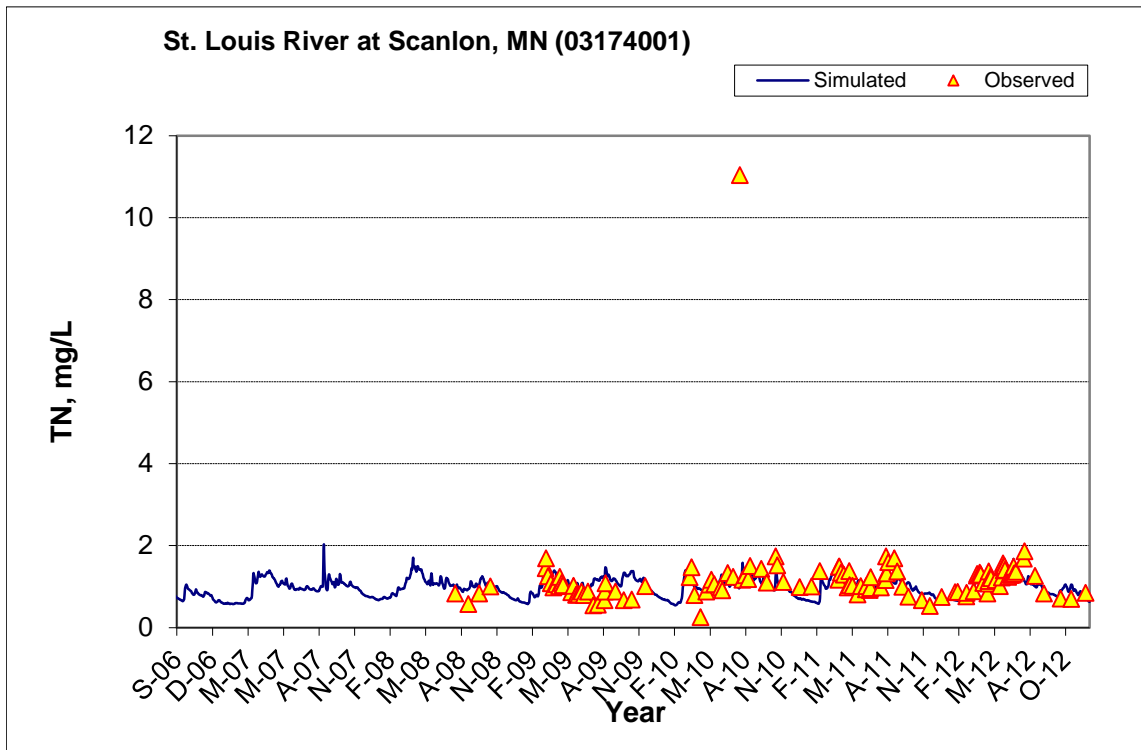


Figure A-145. Time series of observed and simulated Total Nitrogen (TN) concentration at St. Louis River at Scanlon, MN (03174001)

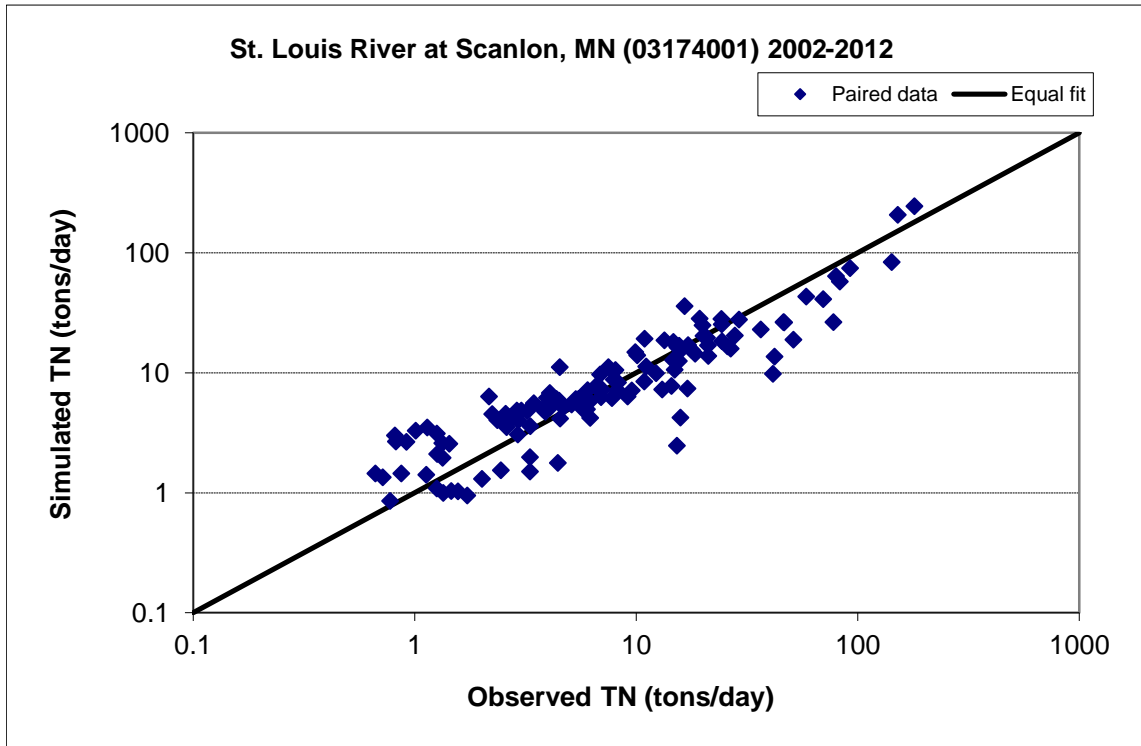


Figure A-146. Paired simulated vs. observed Total Nitrogen (TN) load at St. Louis River at Scanlon, MN (03174001) (calibration period)

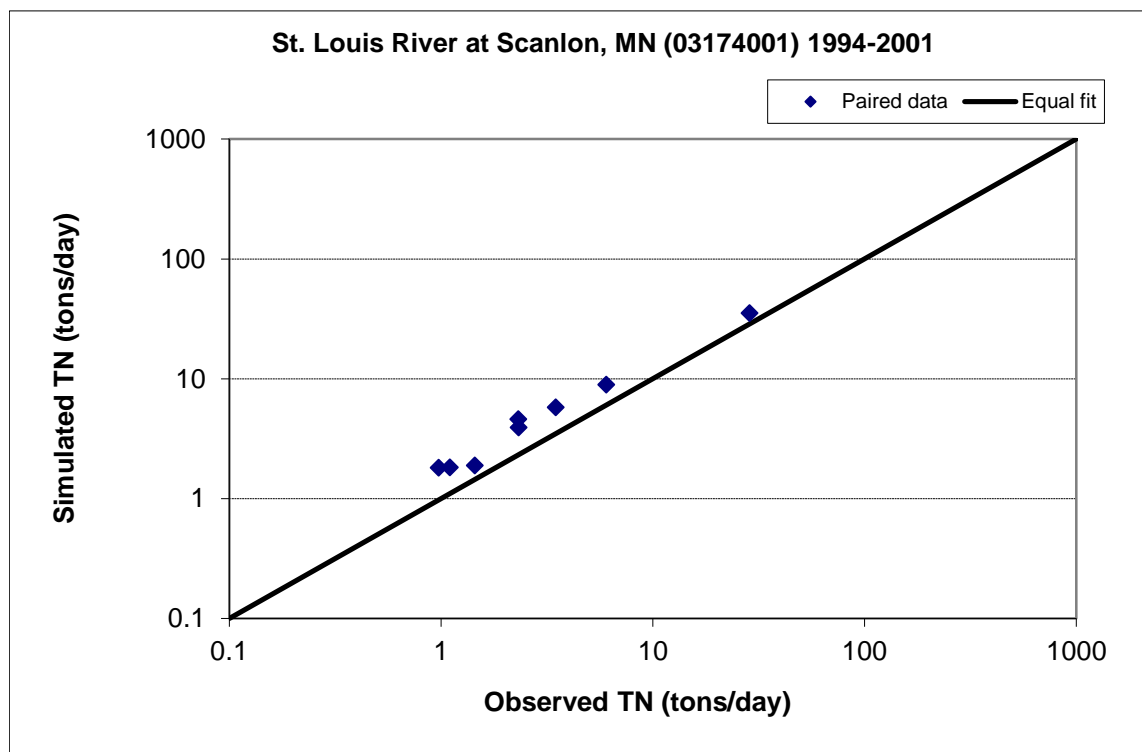


Figure A-147. Paired simulated vs. observed Total Nitrogen (TN) load at St. Louis River at Scanlon, MN (03174001) (validation period)

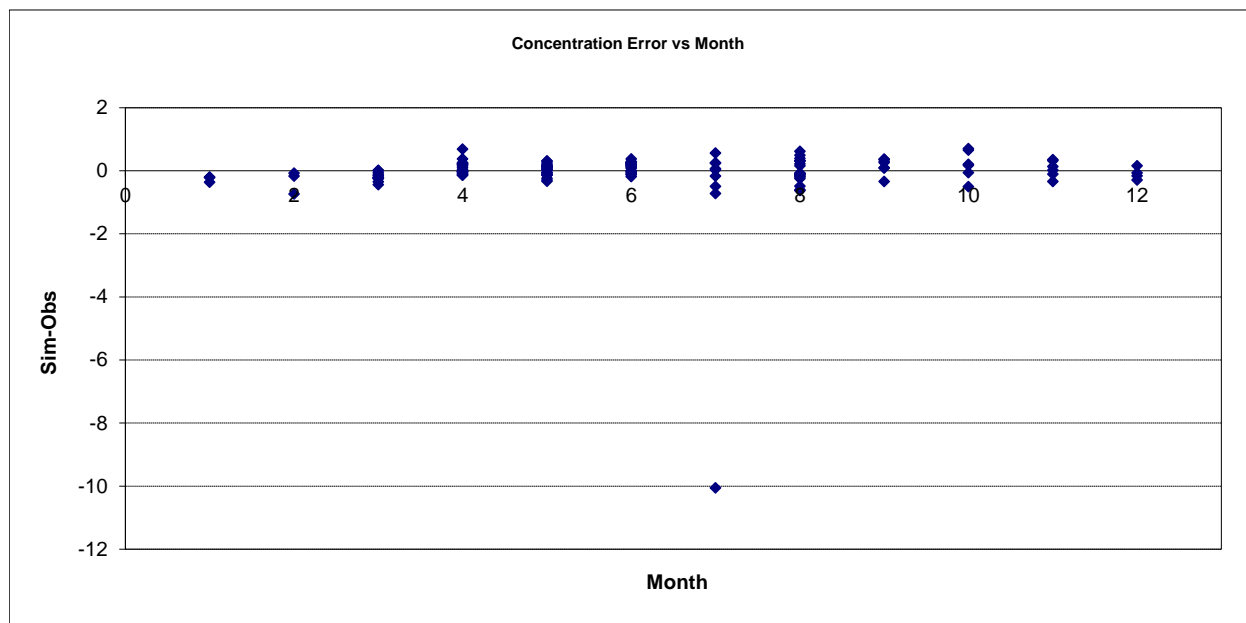


Figure A-148. Residual (Simulated - Observed) vs. Month Total Nitrogen (TN) at St. Louis River at Scanlon, MN (03174001)

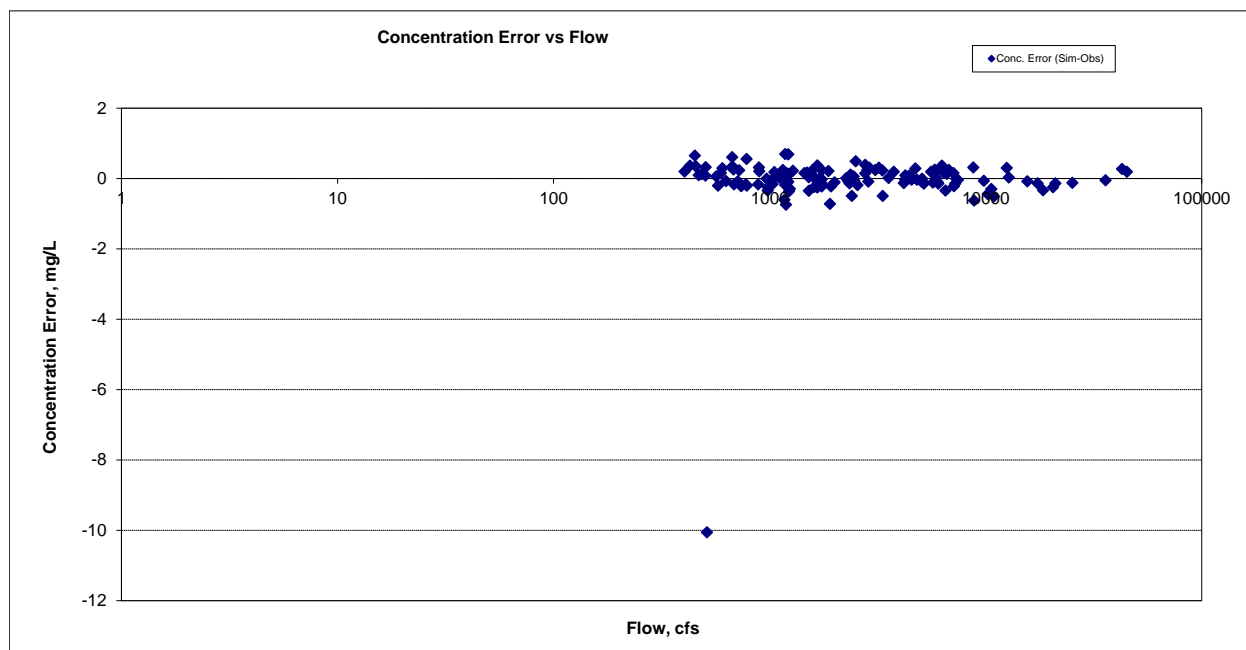


Figure A-149. Residual (Simulated - Observed) vs. Flow Total Nitrogen (TN) at St. Louis River at Scanlon, MN (03174001)

A.5.6 Soluble Reactive Phosphorus (SRP)

Table A-22. Soluble Reactive Phosphorus (SRP) statistics

Period	1994-2001	2002-2012
Count	ND	131
Concentration Average Error		-18.10%
Concentration Median Error		-24.26%
Load Average Error		13.02%
Load Median Error		-3.64%
Paired t conc		0.58
Paired t load		0.58

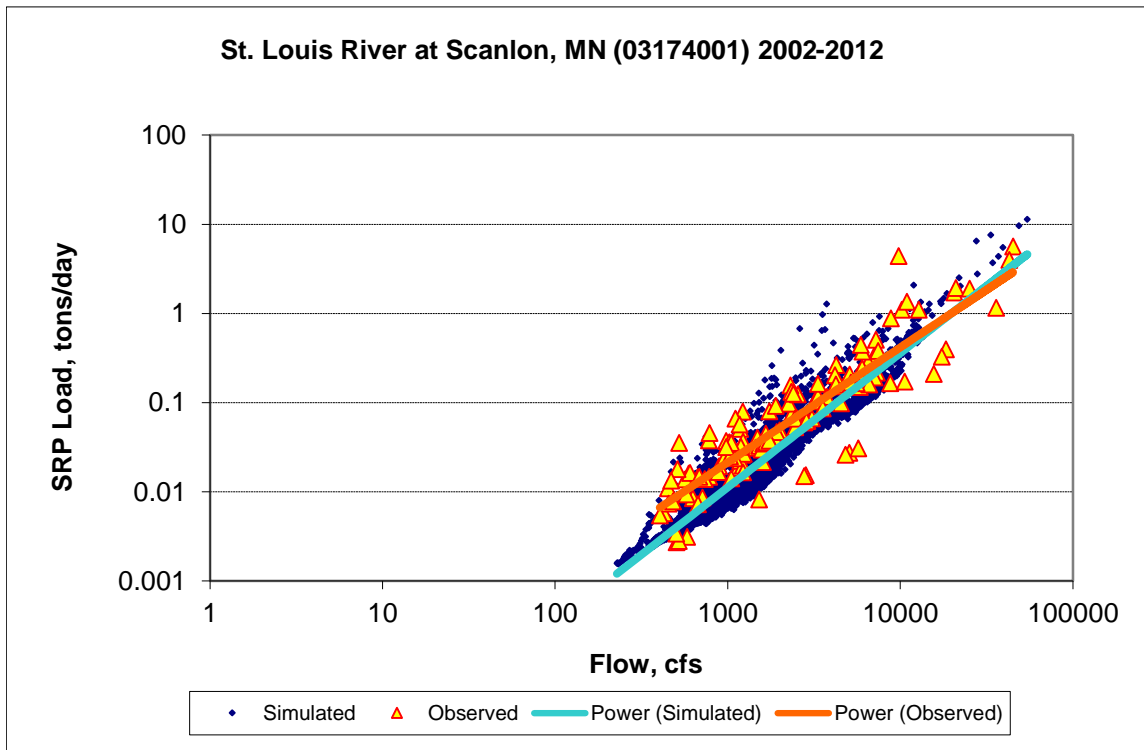
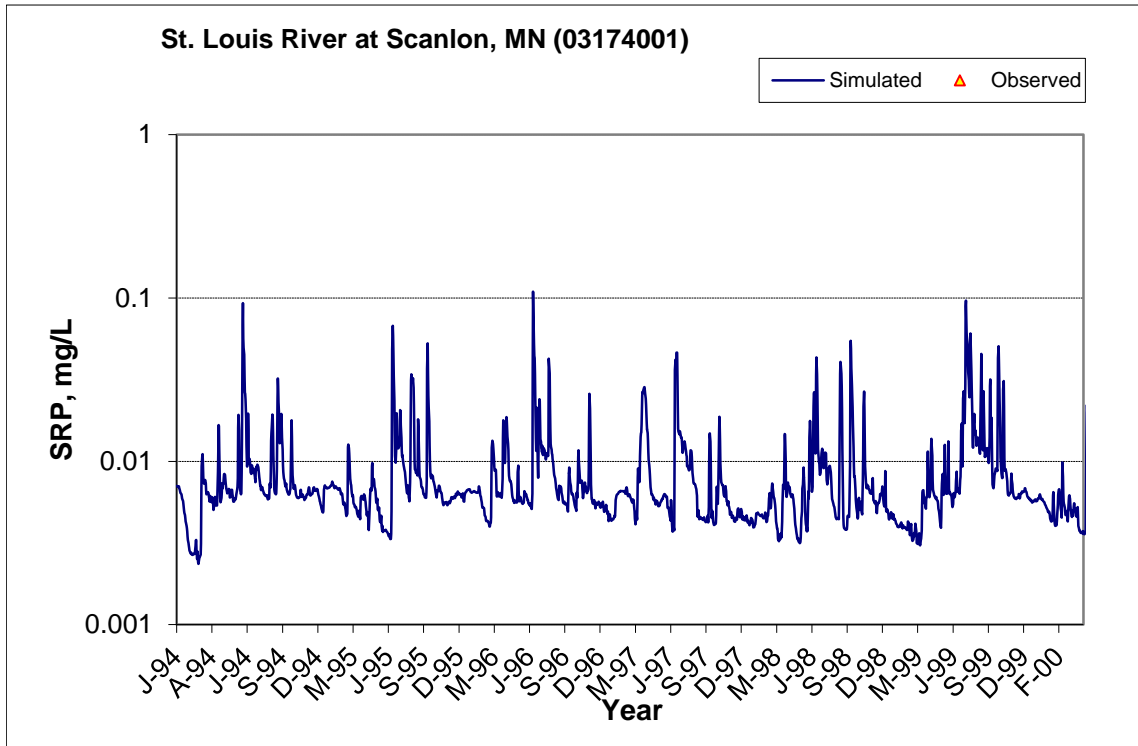


Figure A-150. Power plot of simulated and observed Soluble Reactive Phosphorus (SRP) load vs flow at St. Louis River at Scanlon, MN (03174001) (calibration period)



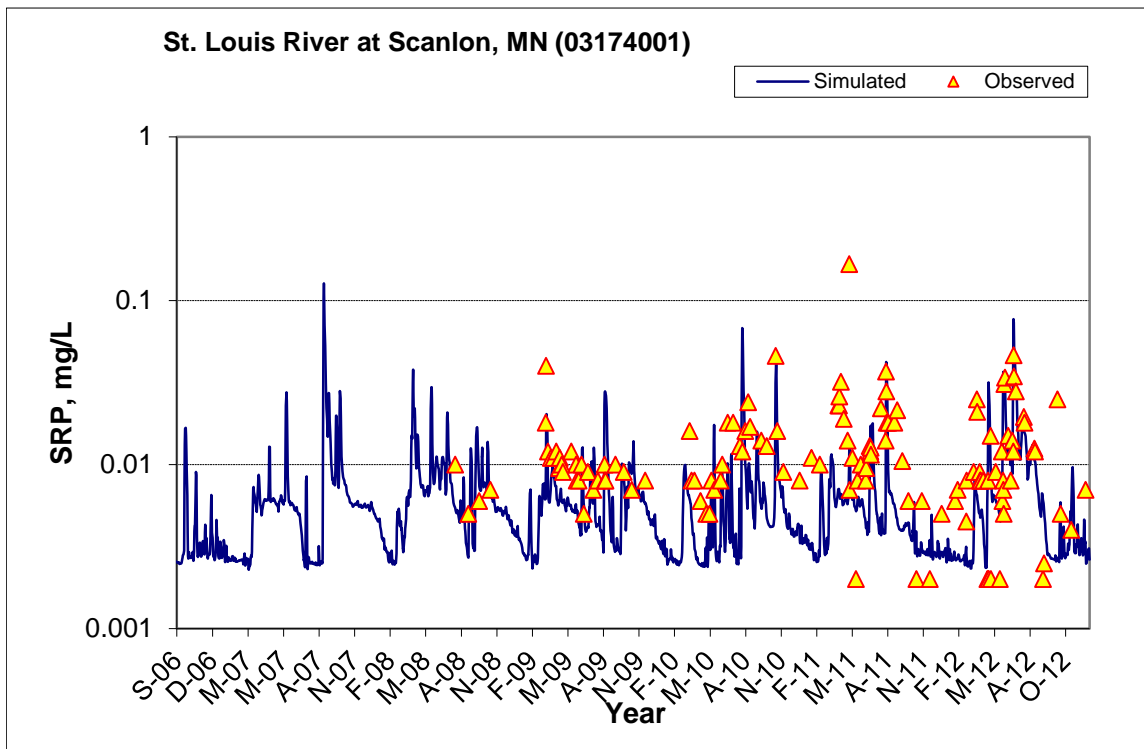
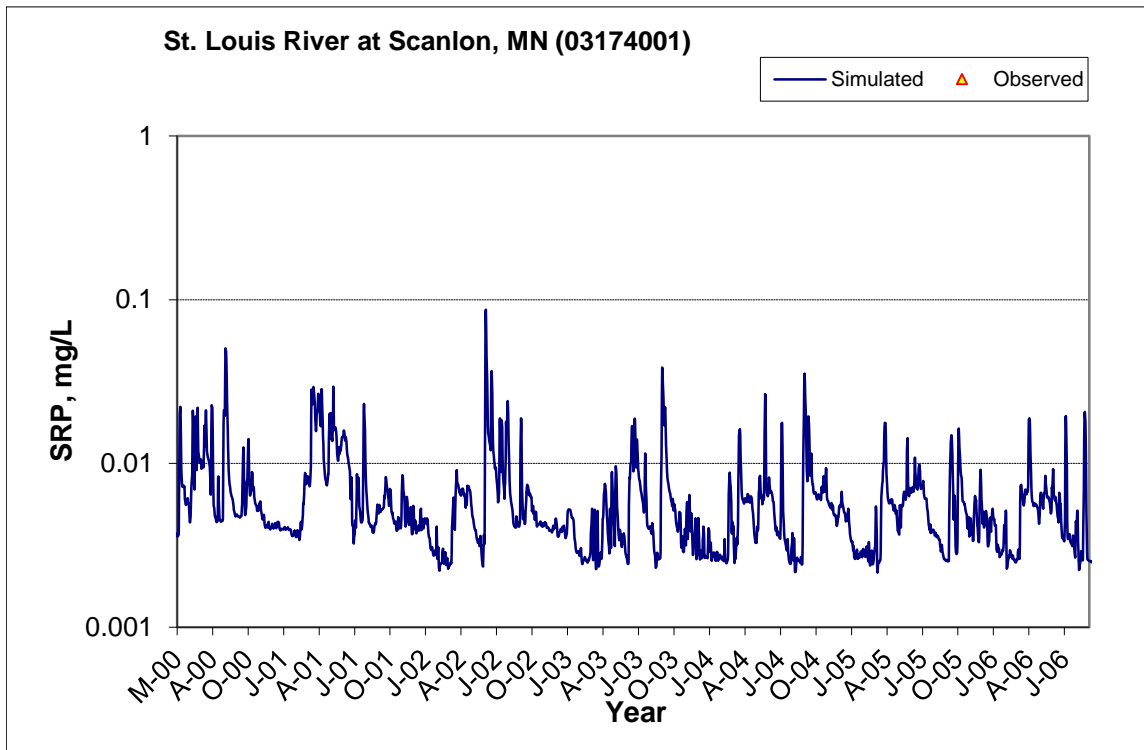


Figure A-151. Time series of observed and simulated Soluble Reactive Phosphorus (SRP) concentration at St. Louis River at Scanlon, MN (03174001)

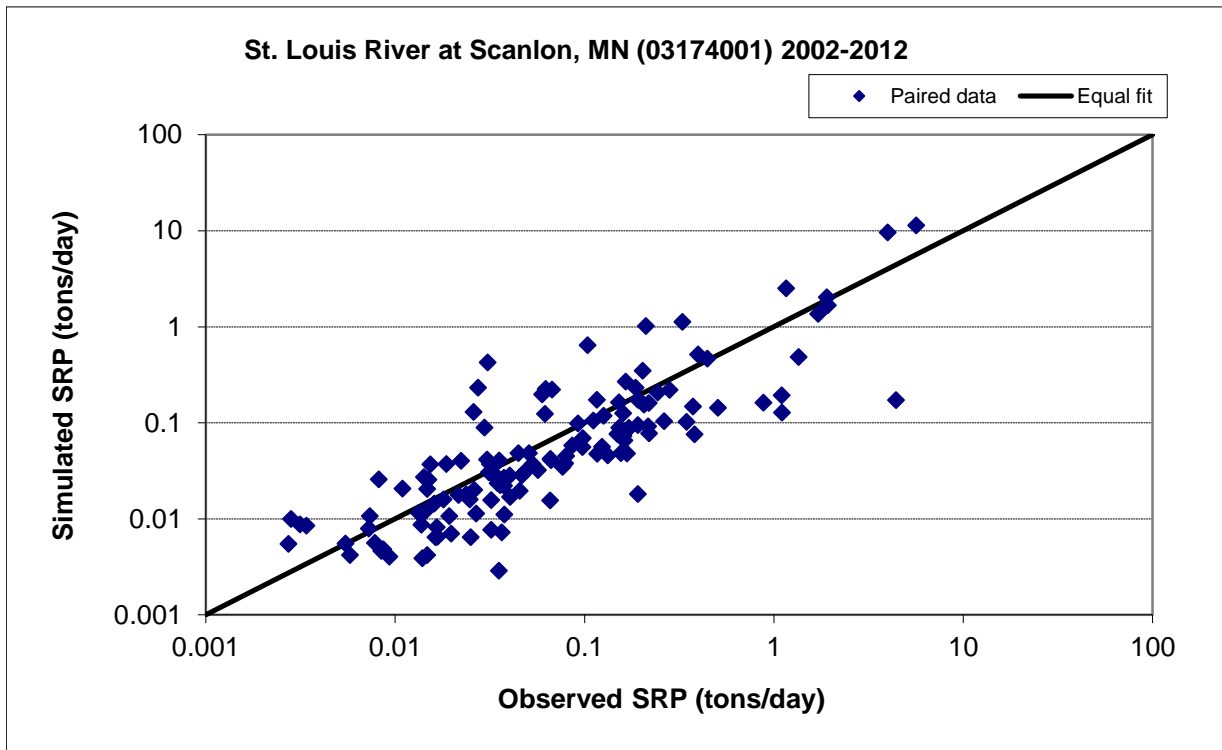


Figure A-152. Paired simulated vs. observed Soluble Reactive Phosphorus (SRP) load at St. Louis River at Scanlon, MN (03174001) (calibration period)

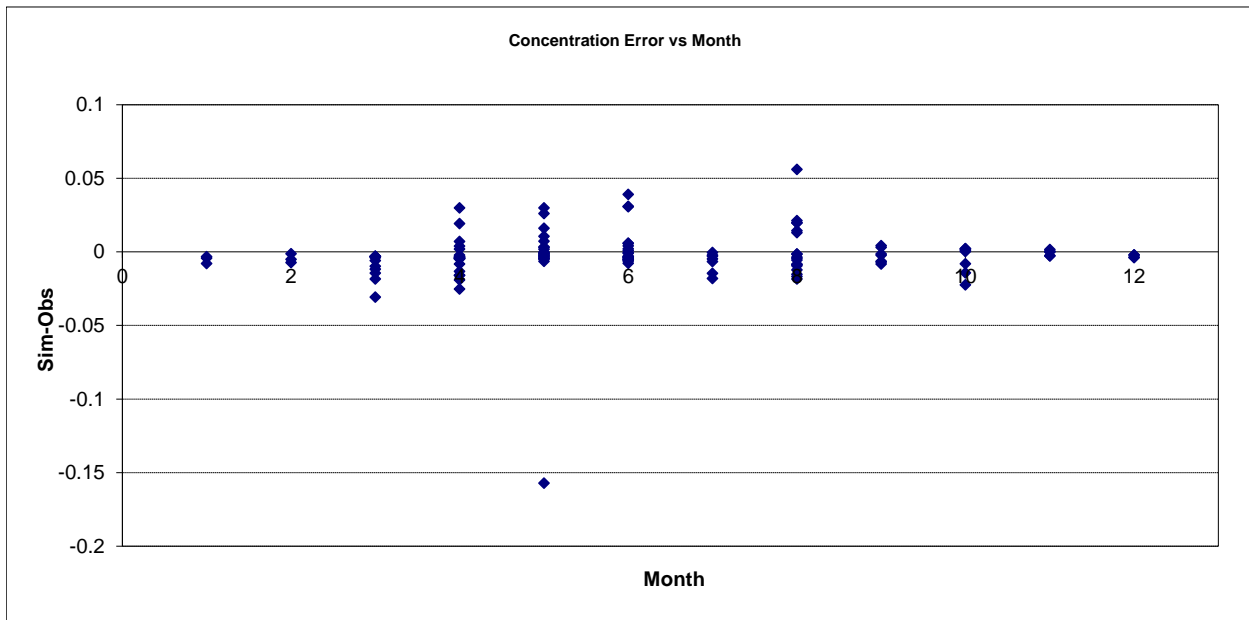


Figure A-153. Residual (Simulated - Observed) vs. Month Soluble Reactive Phosphorus (SRP) at St. Louis River at Scanlon, MN (03174001)

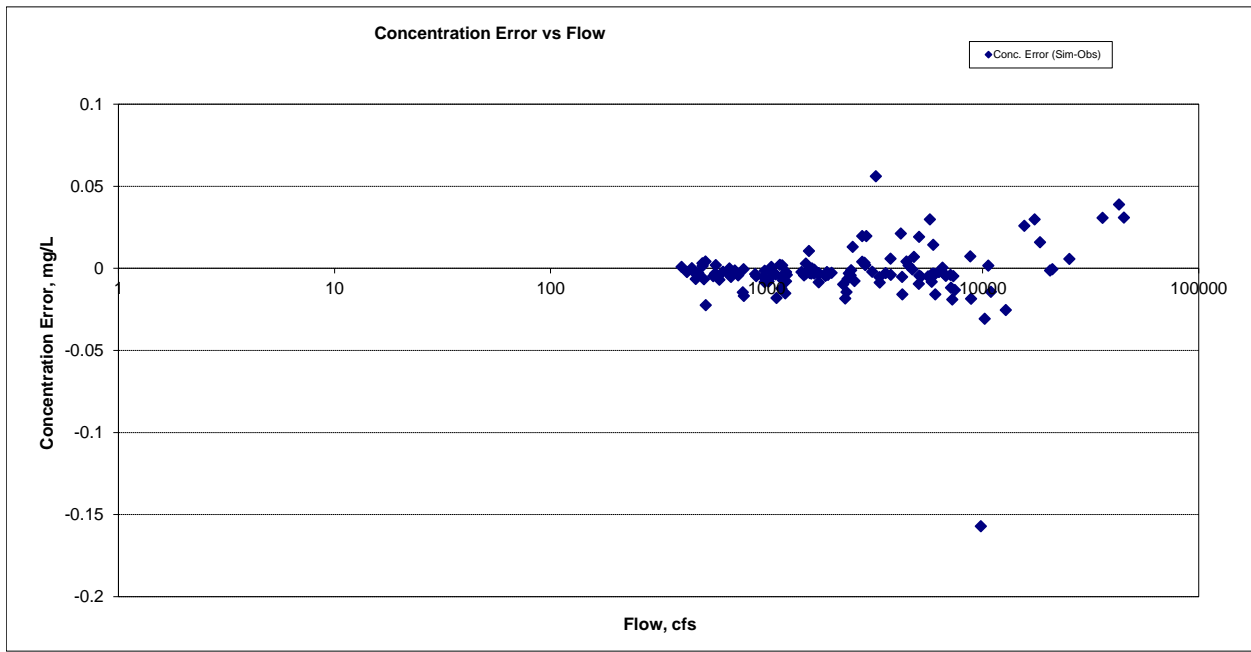
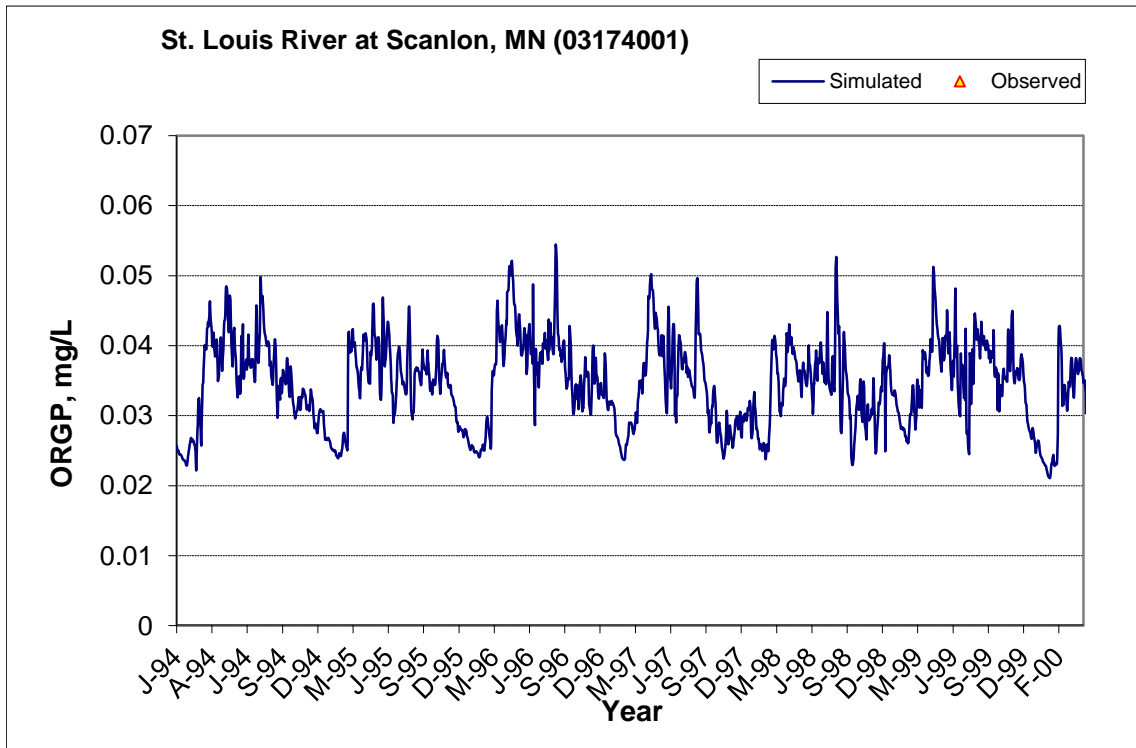


Figure A-154. Residual (Simulated - Observed) vs. Flow Soluble Reactive Phosphorus (SRP) at St. Louis River at Scanlon, MN (03174001)

A.5.7 Organic Phosphorus (OrgP)



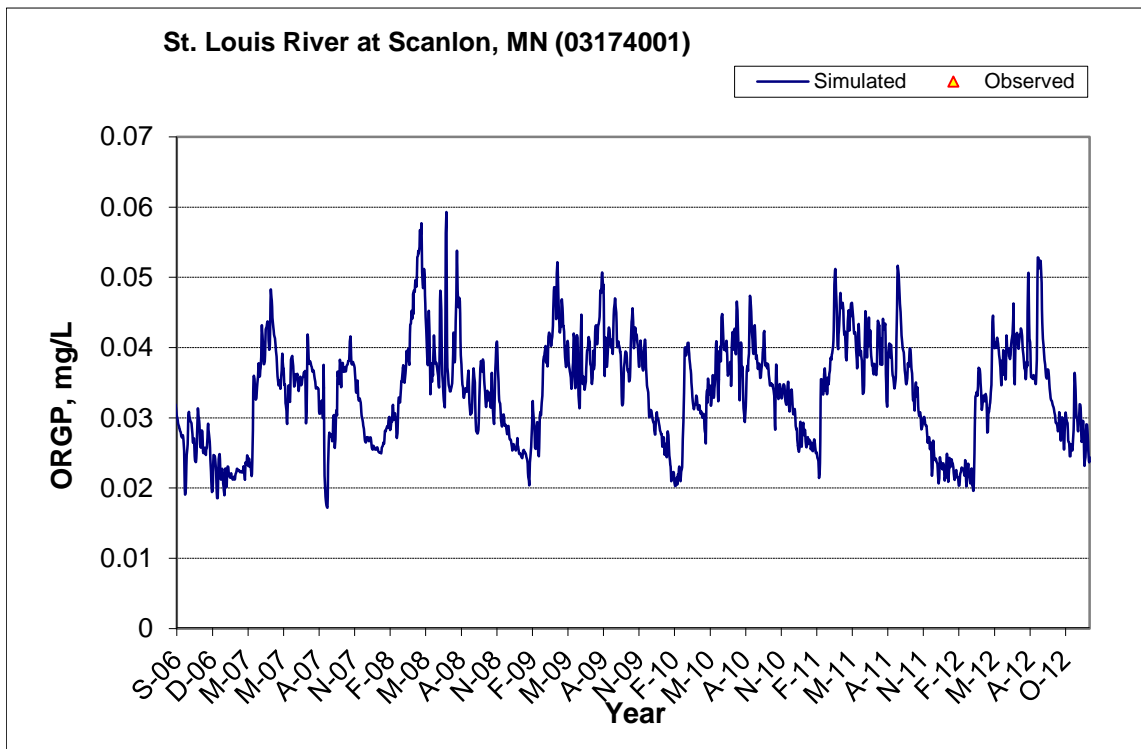
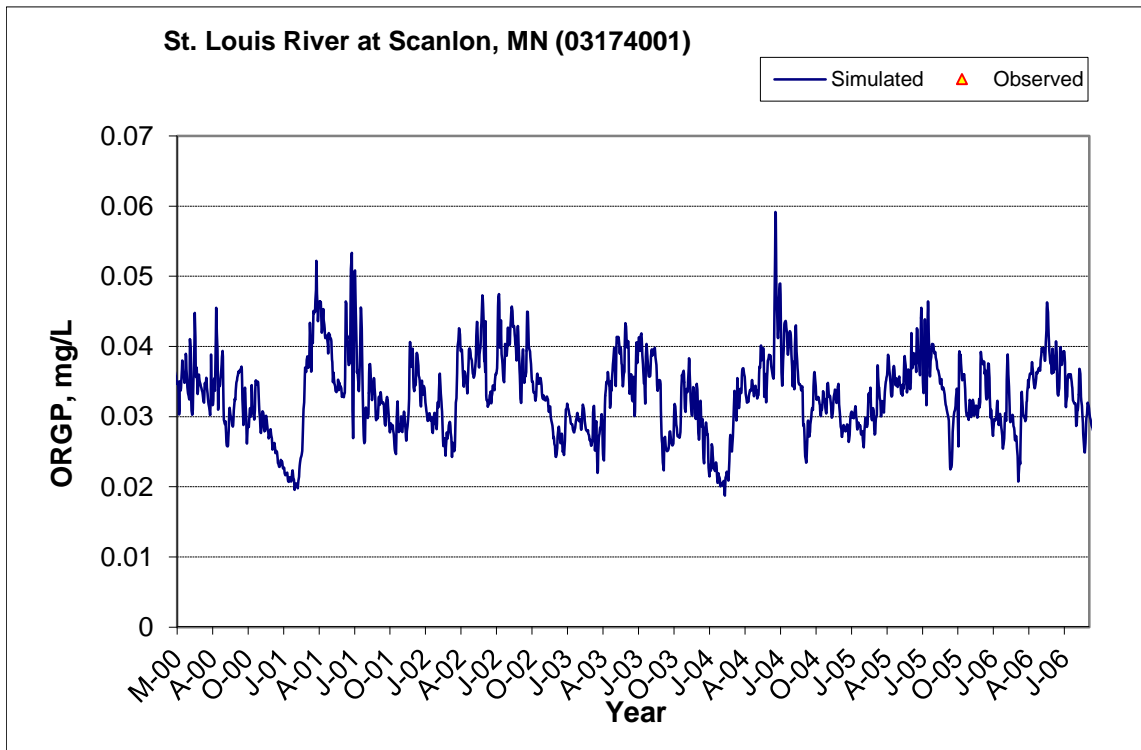


Figure A-155. Time series of observed and simulated Organic Phosphorus (OrgP) concentration at St. Louis River at Scanlon, MN (03174001)

A.5.8 Total Phosphorus (TP)

Table A-23. Total Phosphorus (TP) statistics

Period	1994-2001	2002-2012
Count	41	125
Concentration Average Error	26.65%	-10.36%
Concentration Median Error	21.70%	12.69%
Load Average Error	3.97%	-53.28%
Load Median Error	15.09%	3.26%
Paired t conc	0.10	0.95
Paired t load	0.75	0.07

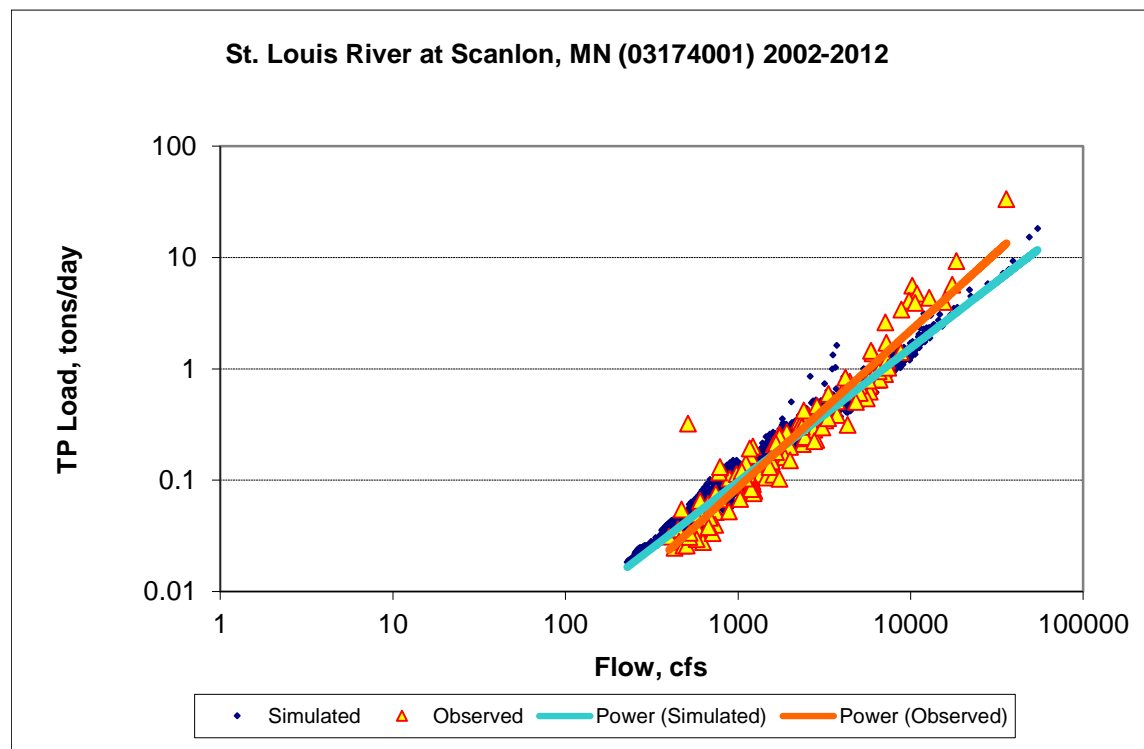


Figure A-156. Power plot of simulated and observed Total Phosphorus (TP) load vs flow at St. Louis River at Scanlon, MN (03174001) (calibration period)

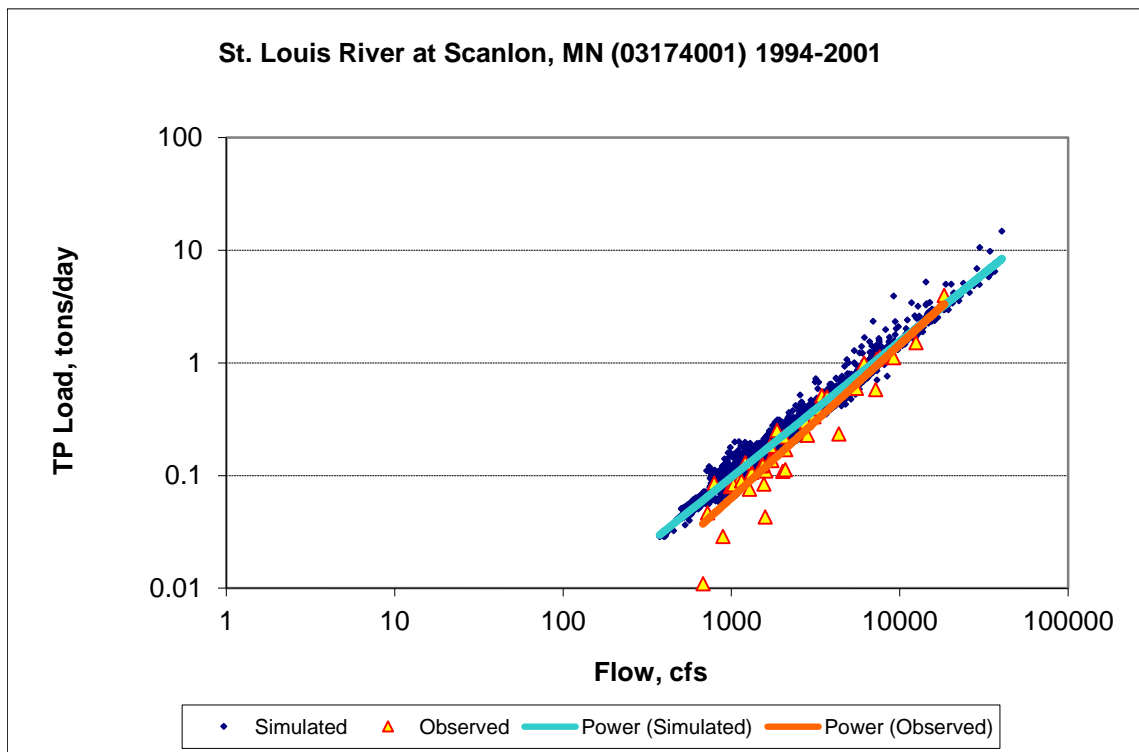
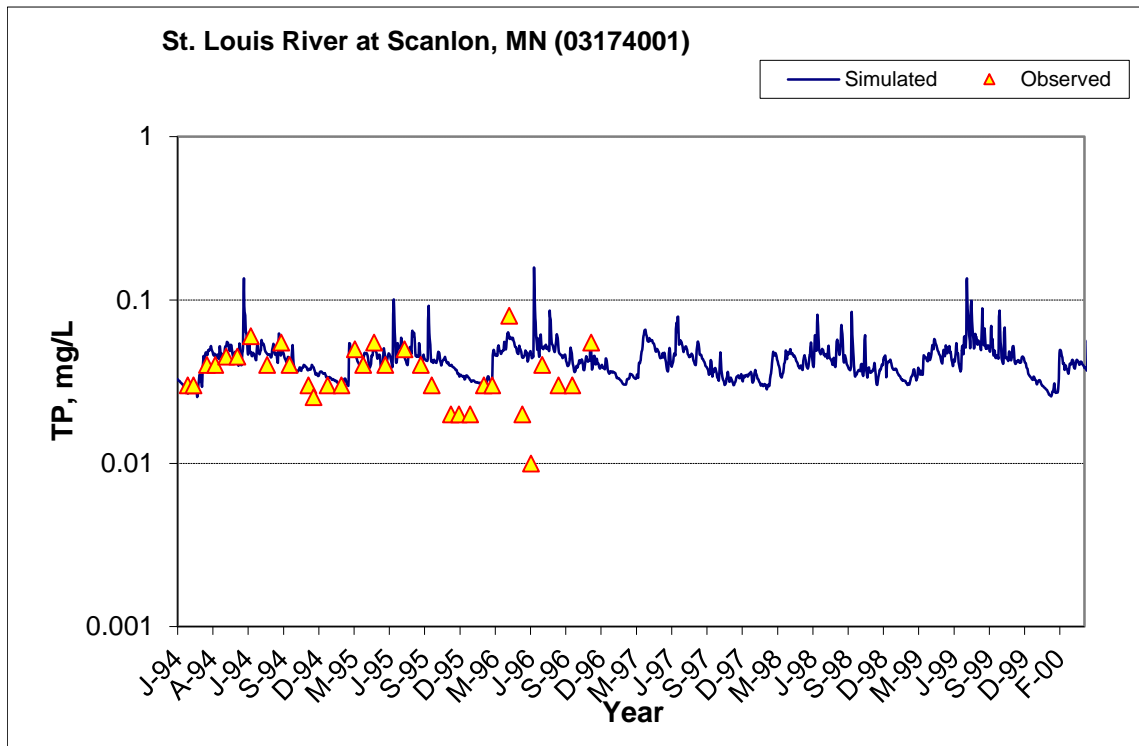


Figure A-157. Power plot of simulated and observed Total Phosphorus (TP) load vs flow at St. Louis River at Scanlon, MN (03174001) (validation period)



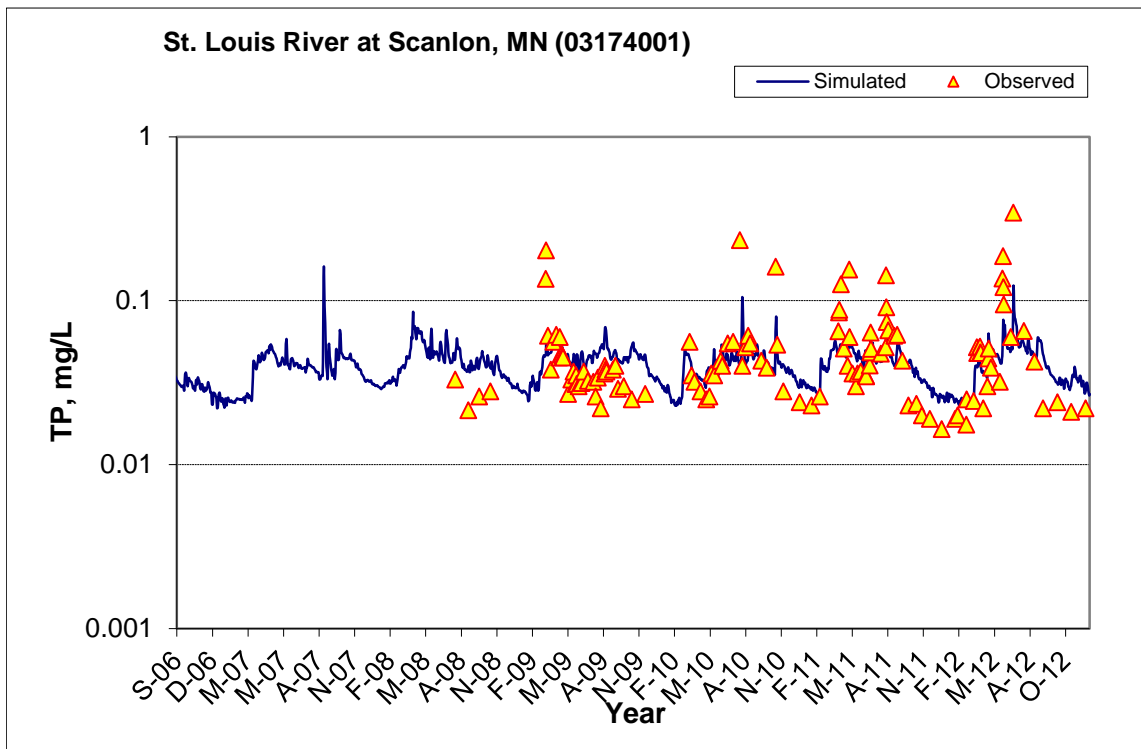
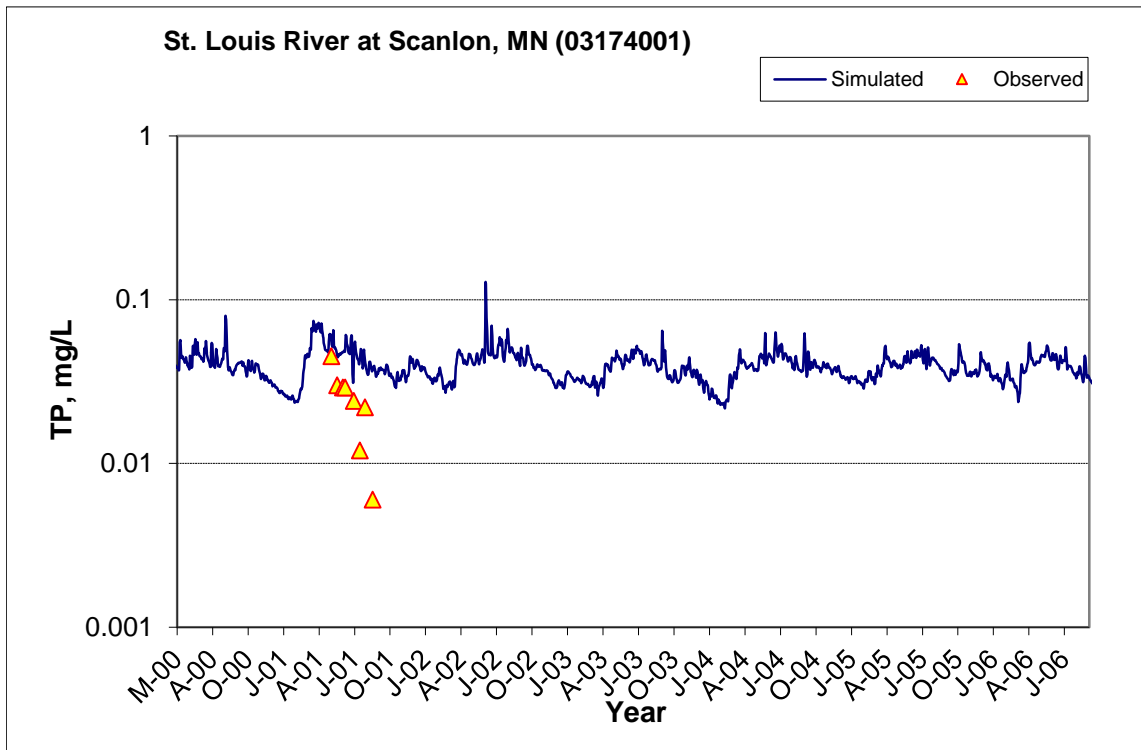


Figure A-158. Time series of observed and simulated Total Phosphorus (TP) concentration at St. Louis River at Scanlon, MN (03174001)

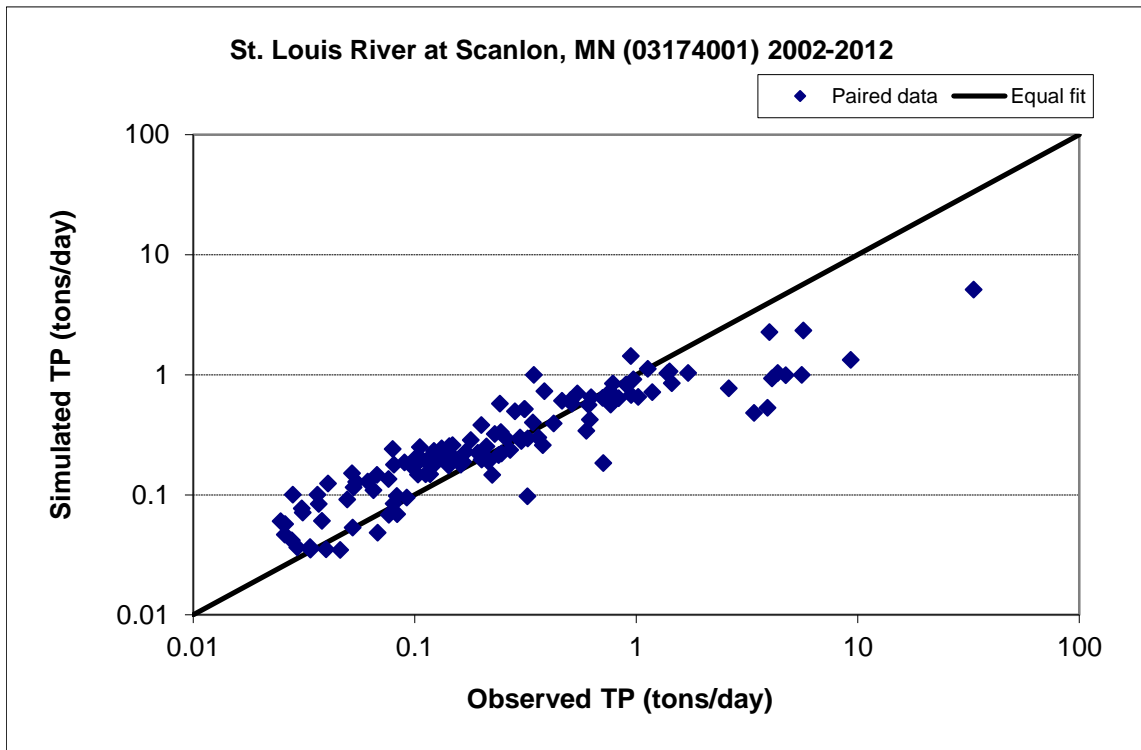


Figure A-159. Paired simulated vs. observed Total Phosphorus (TP) load at St. Louis River at Scanlon, MN (03174001) (calibration period)

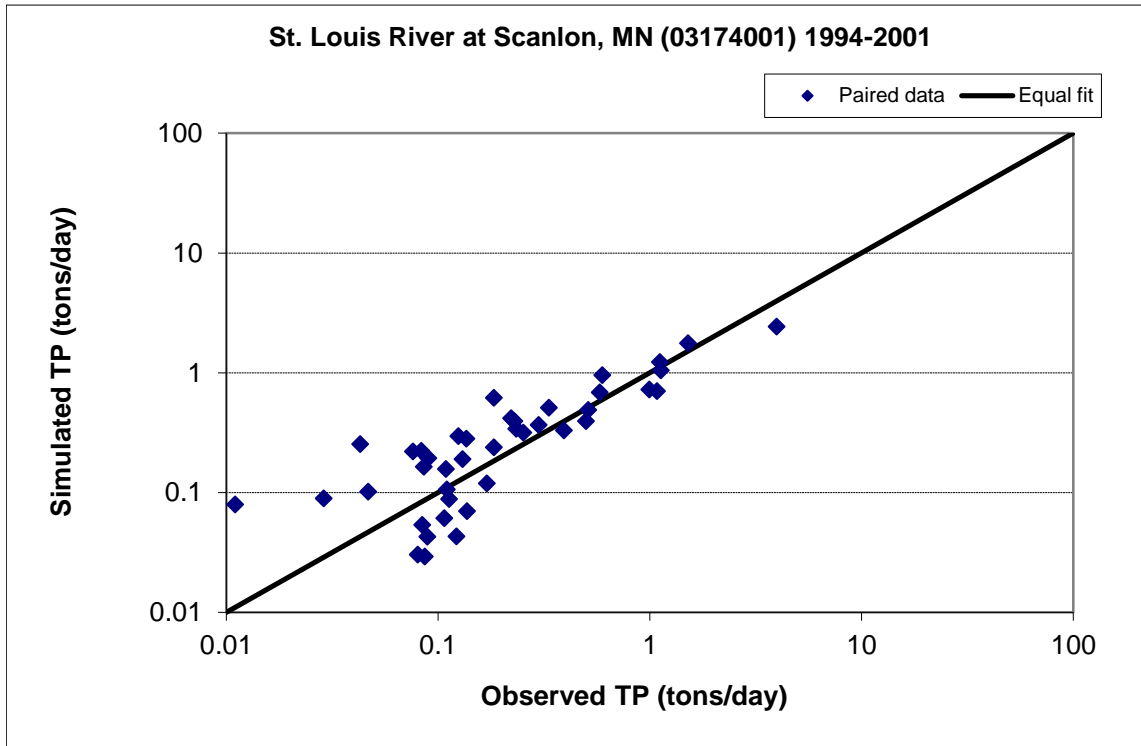


Figure A-160. Paired simulated vs. observed Total Phosphorus (TP) load at St. Louis River at Scanlon, MN (03174001) (validation period)

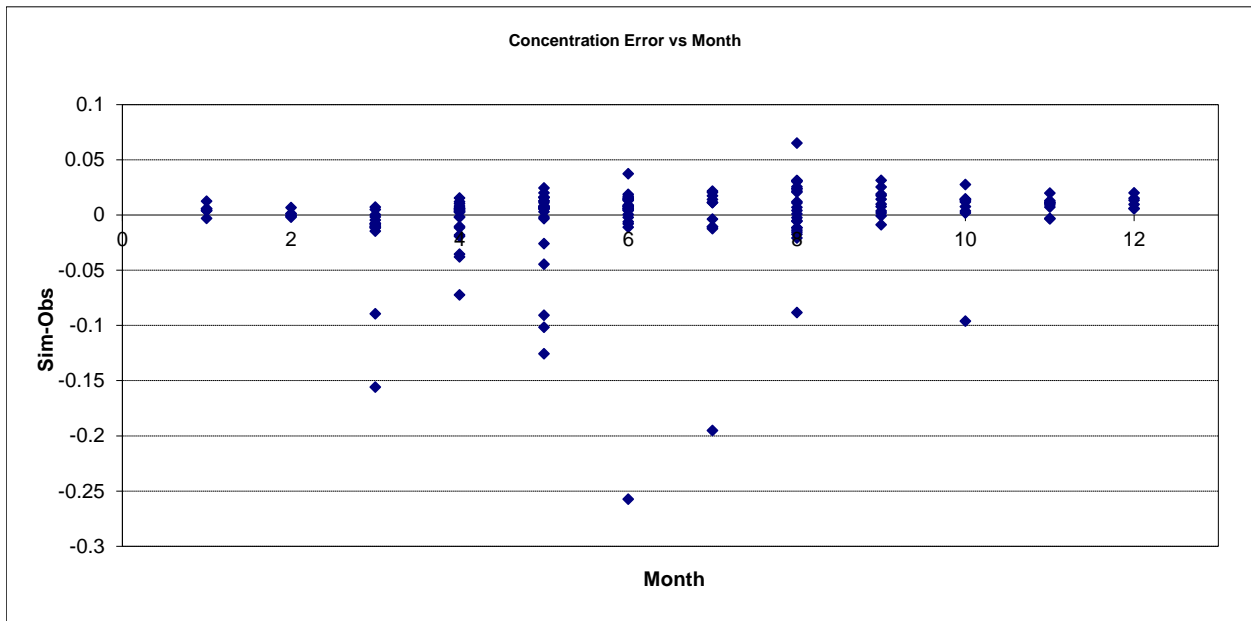


Figure A-161. Residual (Simulated - Observed) vs. Month Total Phosphorus (TP) at St. Louis River at Scanlon, MN (03174001)

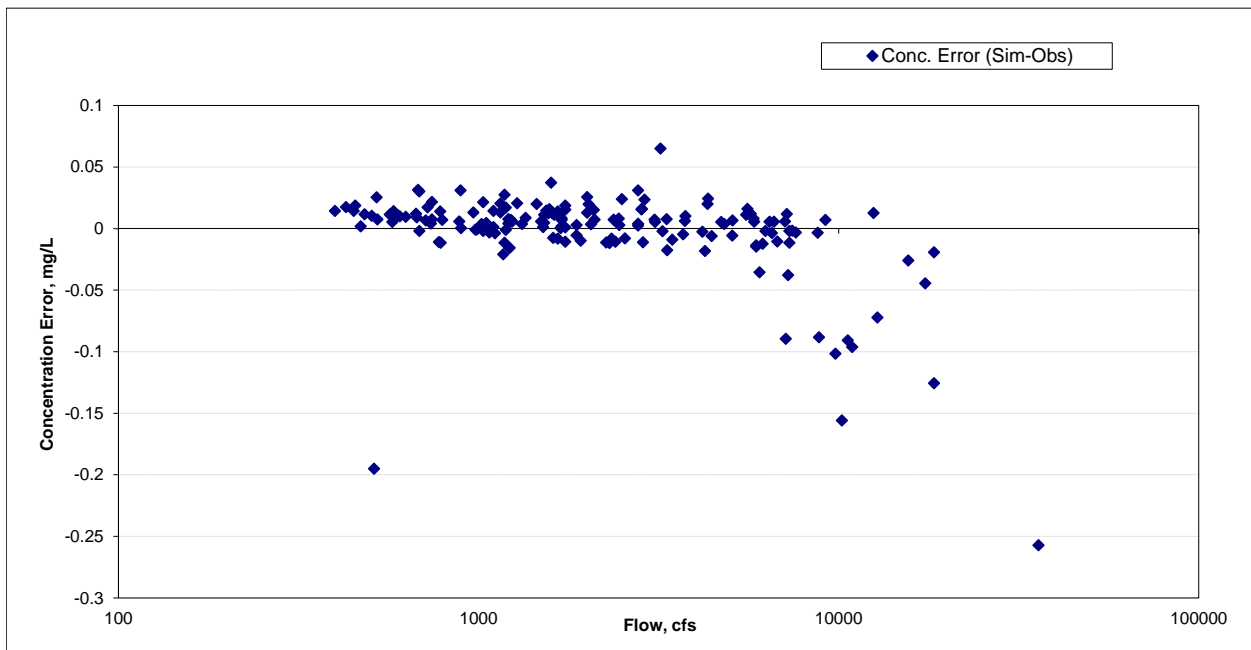


Figure A-162. Residual (Simulated - Observed) vs. Flow Total Phosphorus (TP) at St. Louis River at Scanlon, MN (03174001)

A.6 ST LOUIS RIVER AT BRIDGE ON MN-23 AT FOND DU LAC

A.6.1 Ammonia Nitrogen (NH3)

Table A-24. Ammonia Nitrogen (NH3) statistics

Period	1994-2001	2002-2012
Count	48	49
Concentration Average Error	-33.73%	6.39%
Concentration Median Error	-9.60%	8.61%
Load Average Error	-36.57%	17.11%
Load Median Error	-6.36%	3.84%
Paired t conc	0.06	0.97
Paired t load	0.09	0.55

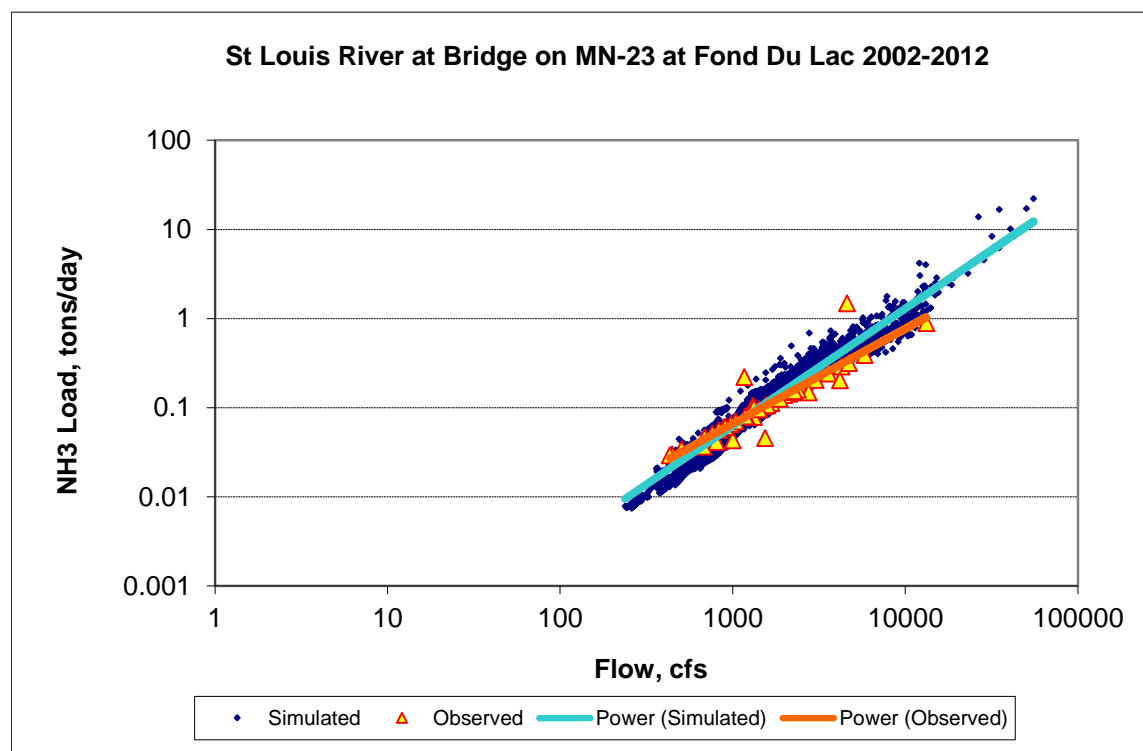


Figure A-163. Power plot of simulated and observed Ammonia Nitrogen (NH3) load vs flow at St Louis River at Bridge on MN-23 at Fond Du Lac (calibration period)

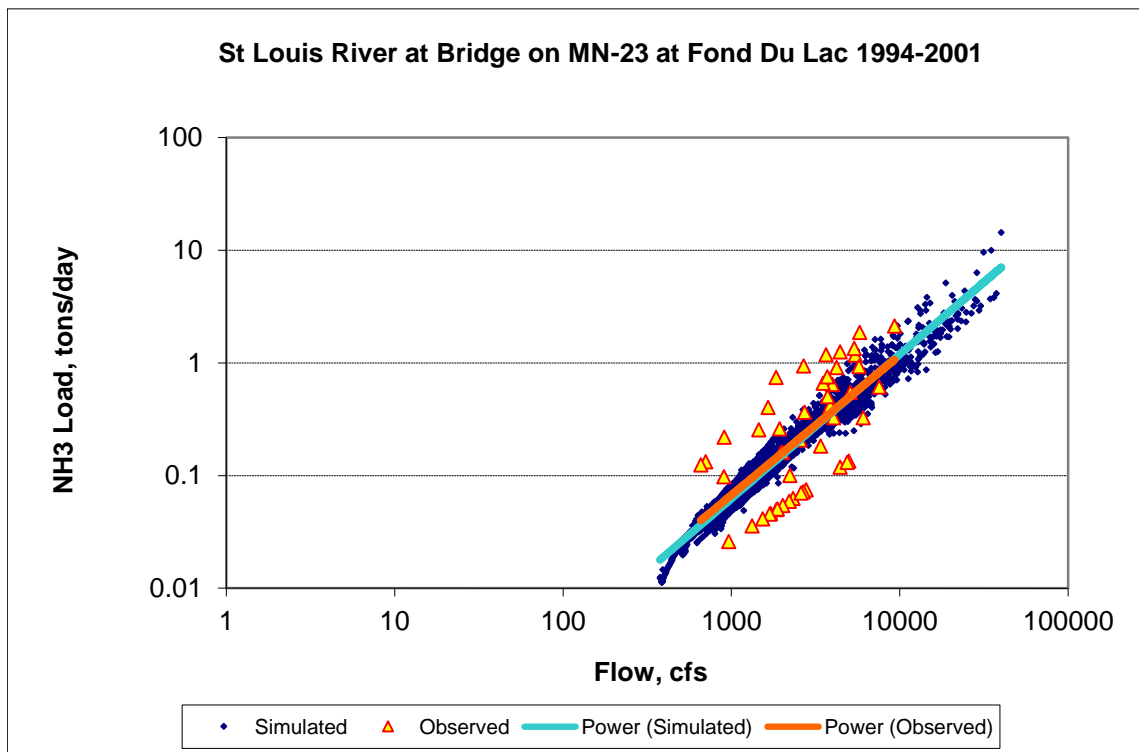
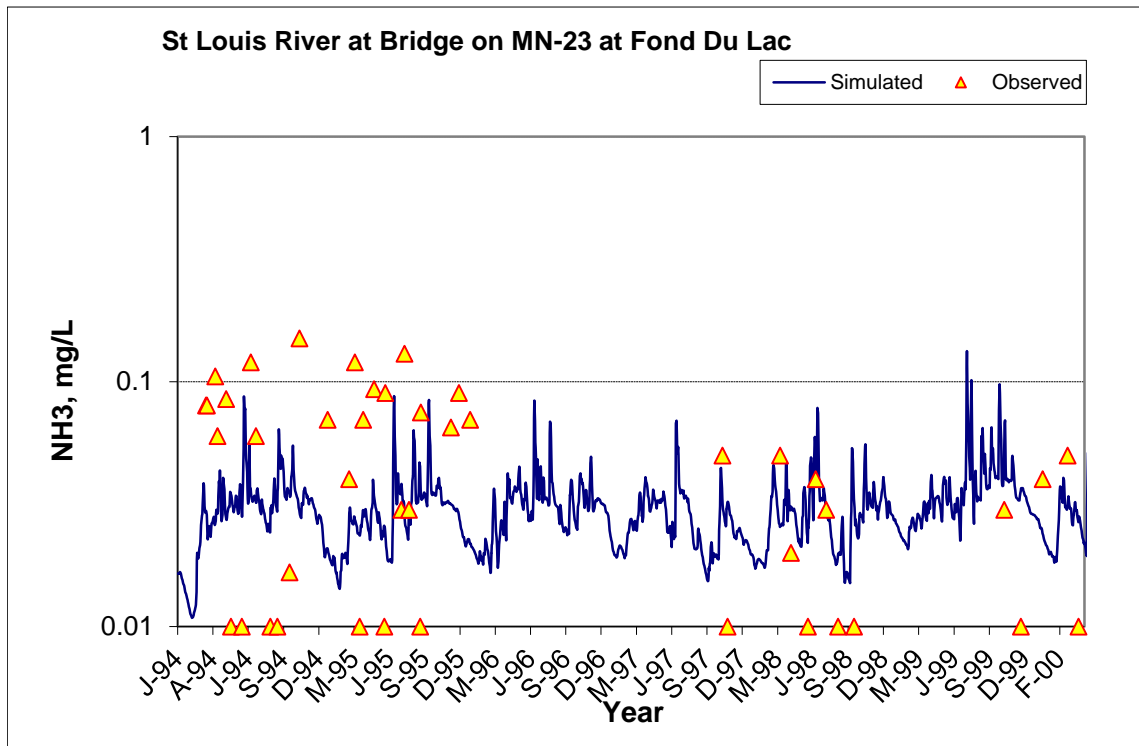


Figure A-164. Power plot of simulated and observed Ammonia Nitrogen (NH3) load vs flow at St Louis River at Bridge on MN-23 at Fond Du Lac (validation period)



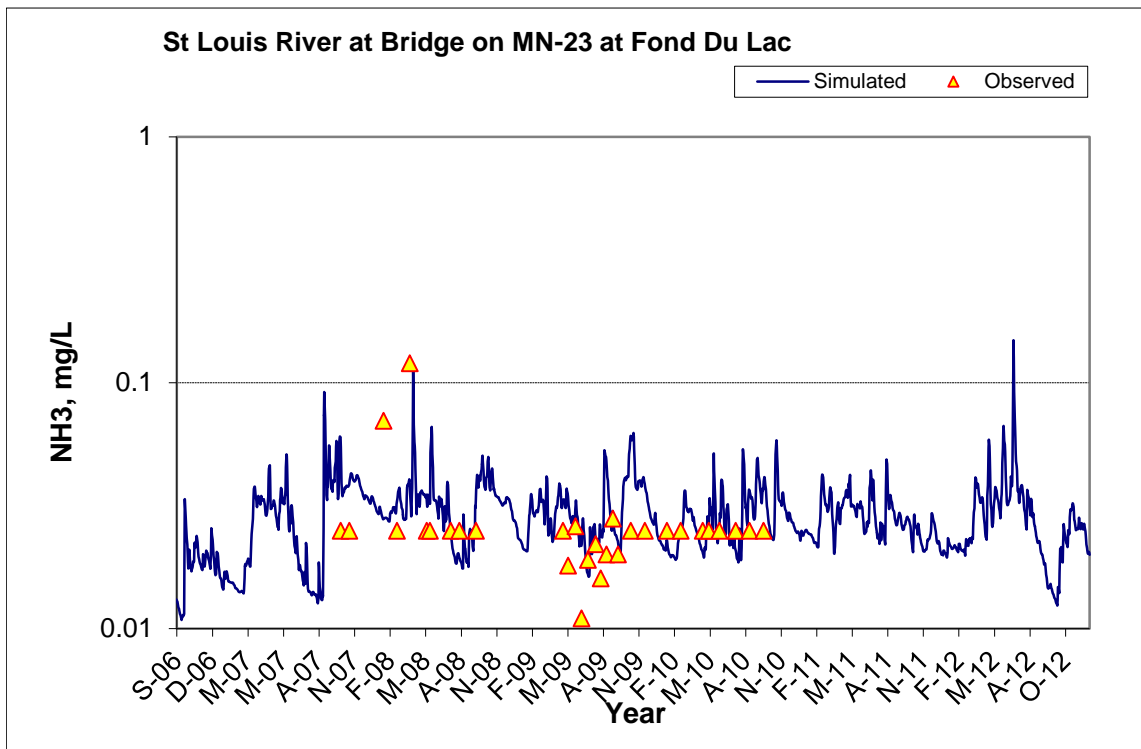
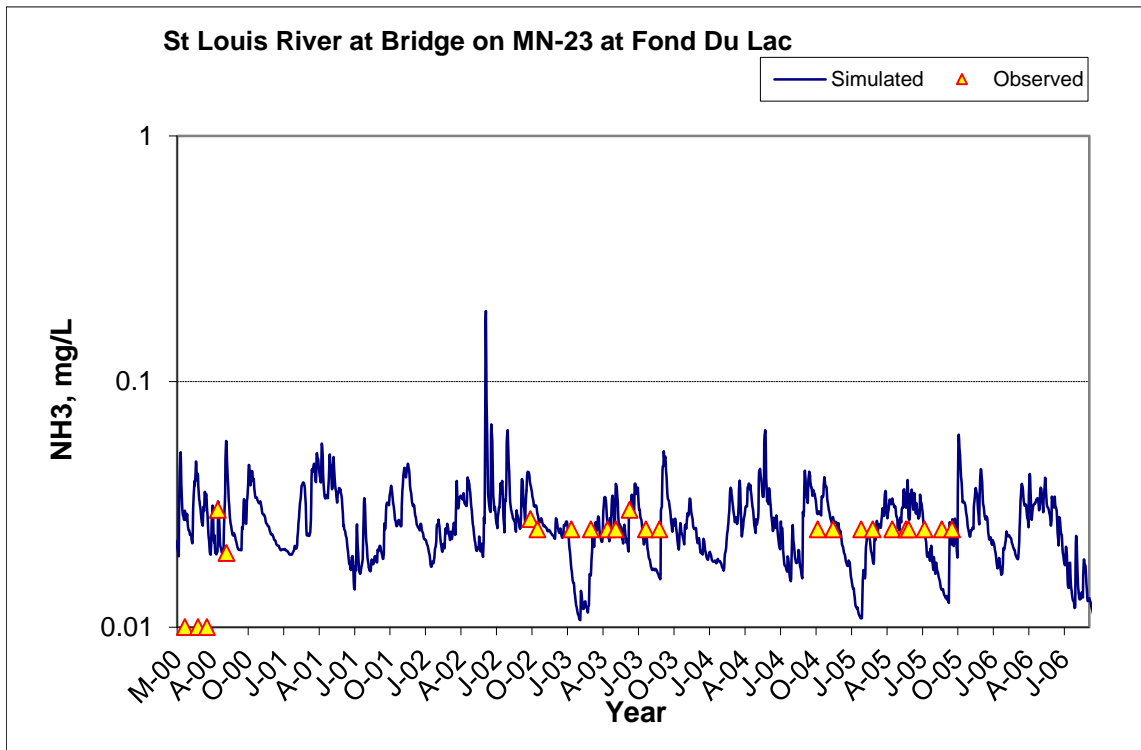


Figure A-165. Time series of observed and simulated Ammonia Nitrogen (NH₃) concentration at St Louis River at Bridge on MN-23 at Fond Du Lac

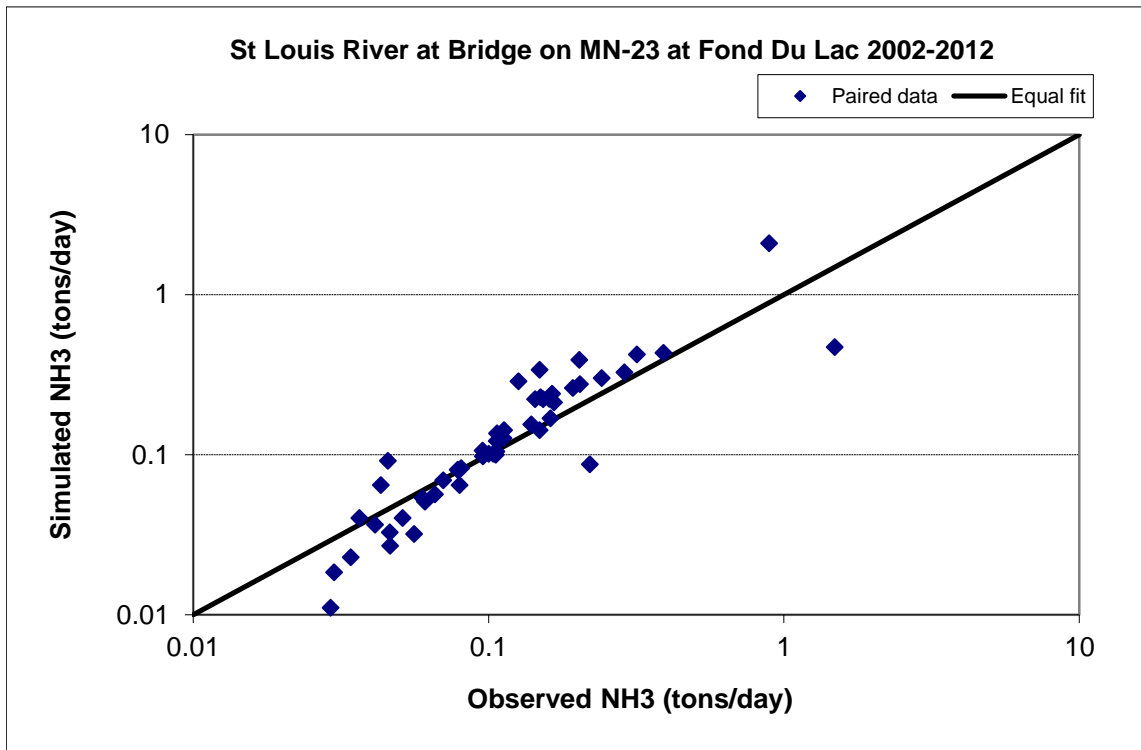


Figure A-166. Paired simulated vs. observed Ammonia Nitrogen (NH3) load at St Louis River at Bridge on MN-23 at Fond Du Lac (calibration period)

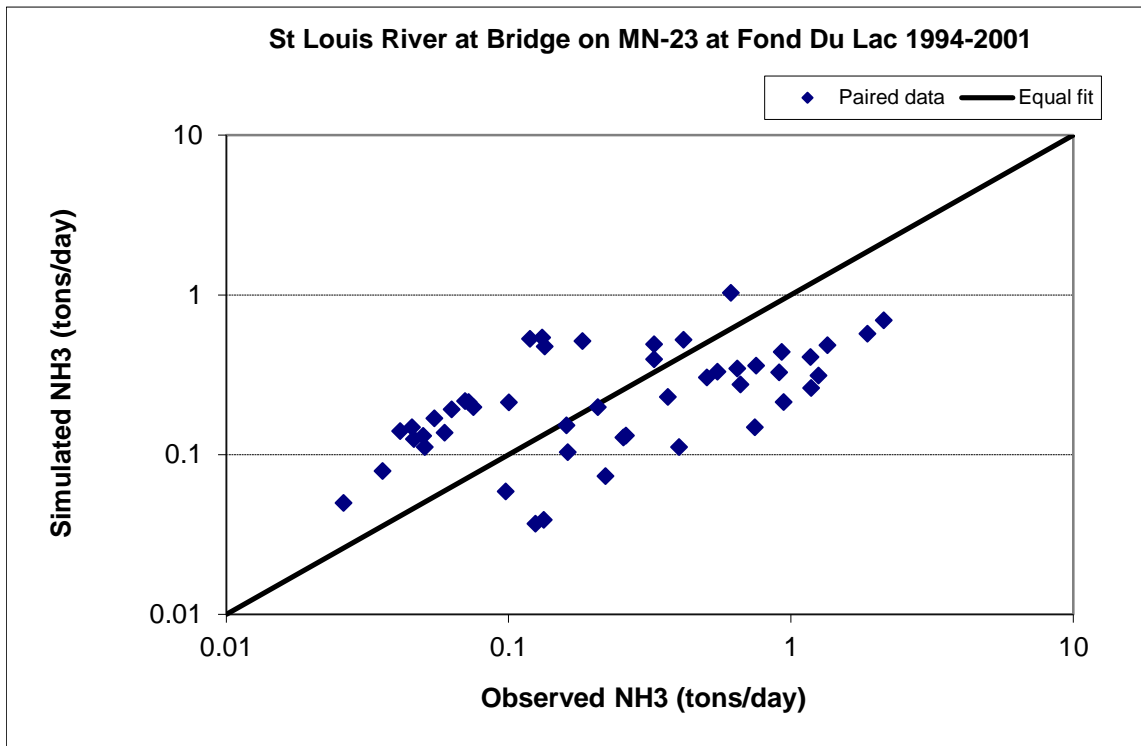


Figure A-167. Paired simulated vs. observed Ammonia Nitrogen (NH3) load at St Louis River at Bridge on MN-23 at Fond Du Lac (validation period)

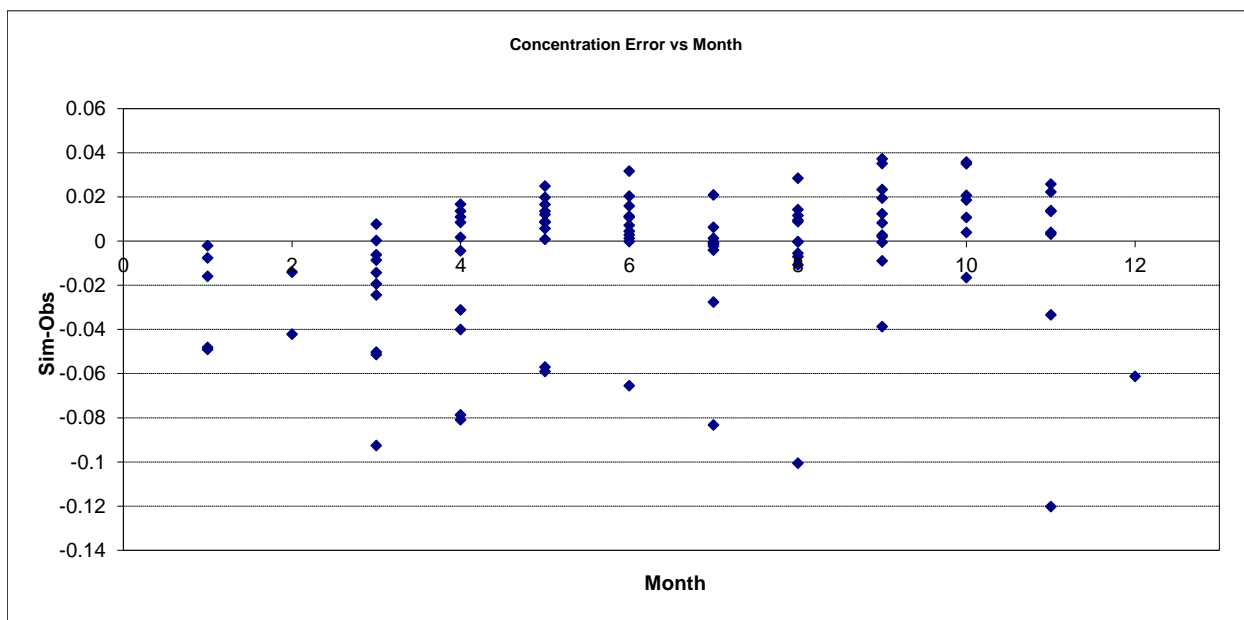


Figure A-168. Residual (Simulated - Observed) vs. Month Ammonia Nitrogen (NH3) at St Louis River at Bridge on MN-23 at Fond Du Lac

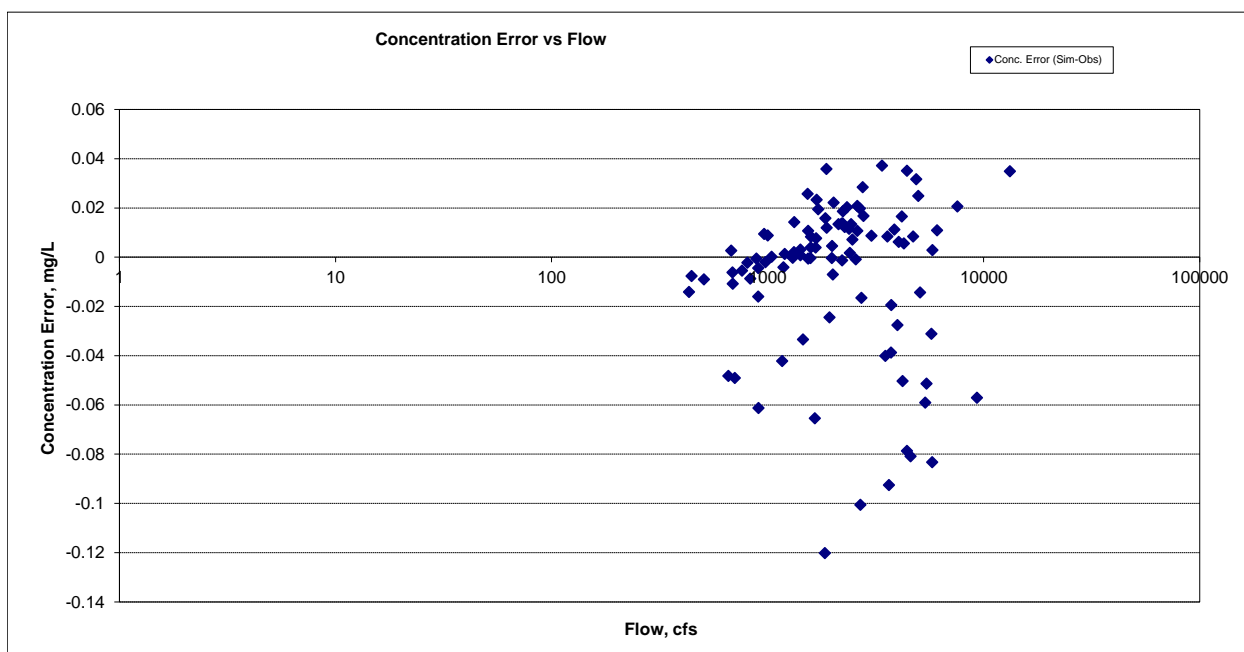
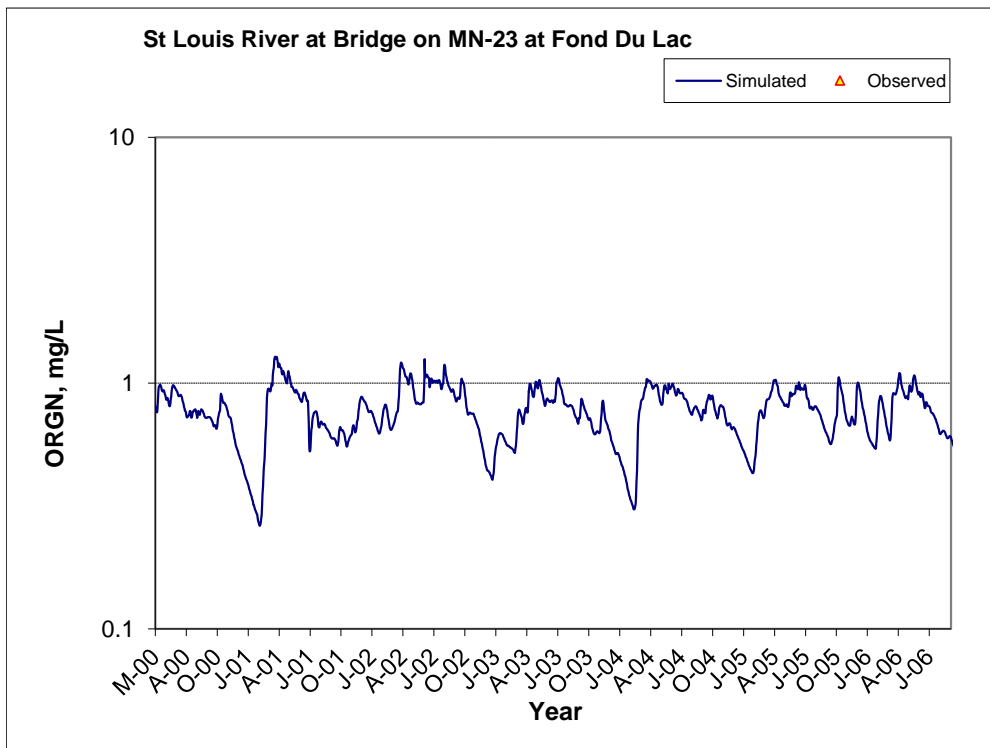
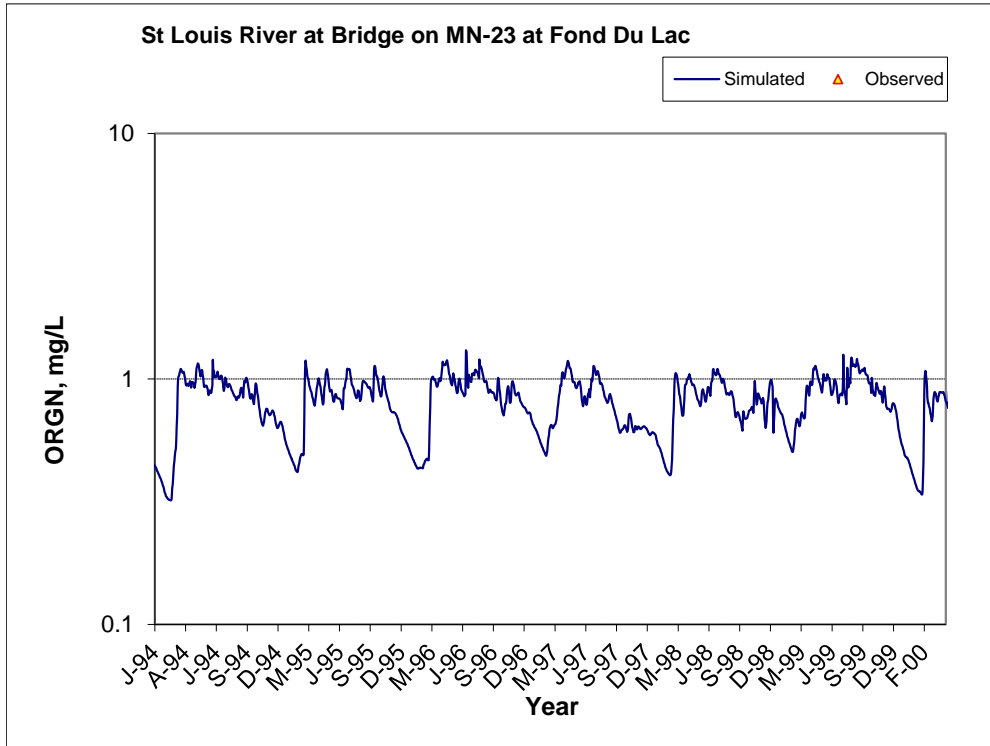


Figure A-169. Residual (Simulated - Observed) vs. Flow Ammonia Nitrogen (NH3) at St Louis River at Bridge on MN-23 at Fond Du Lac

A.6.2 Organic Nitrogen (OrgN)



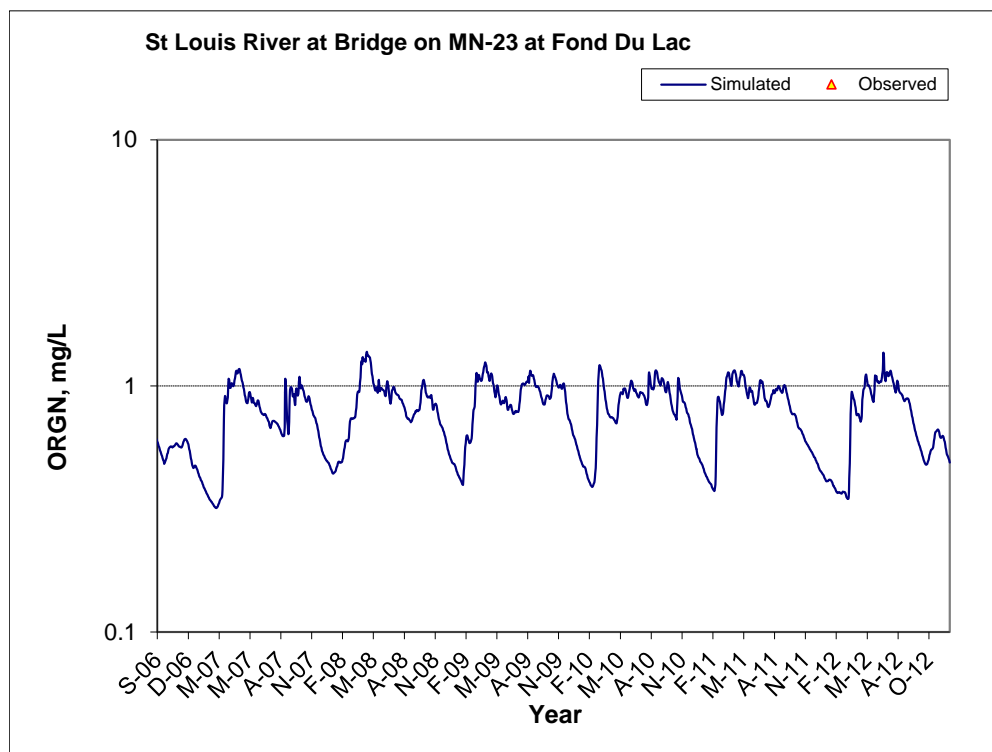


Figure A-170. Time series of observed and simulated Organic Nitrogen (OrgN) concentration at St Louis River at Bridge on MN-23 at Fond Du Lac

A.6.3 Total Kjeldahl Nitrogen (TKN)

Table A-25. Total Kjeldahl Nitrogen (TKN) statistics

Period	1994-2001	2002-2012
Count	7	7
Concentration Average Error	33.33%	-2.98%
Concentration Median Error	40.25%	-2.57%
Load Average Error	36.58%	-3.33%
Load Median Error	14.86%	-2.91%
Paired t conc	0.02	0.99
Paired t load	0.25	0.71

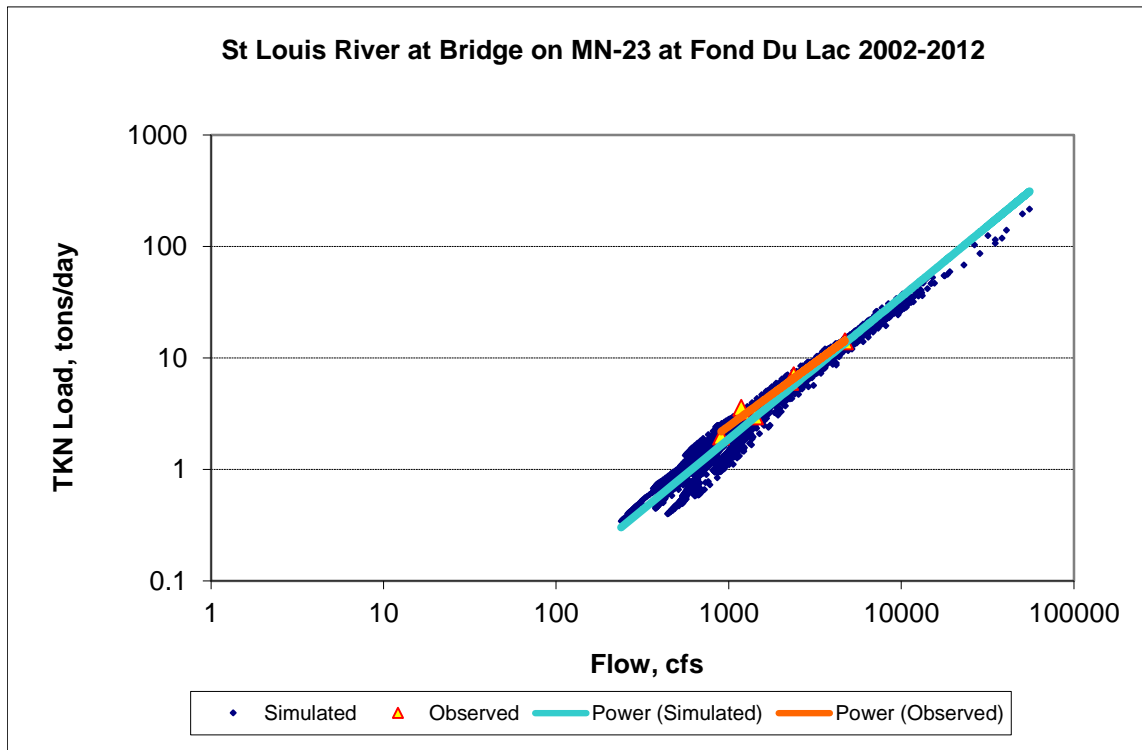


Figure A-171. Power plot of simulated and observed Total Kjeldahl Nitrogen (TKN) load vs flow at St Louis River at Bridge on MN-23 at Fond Du Lac (calibration period)

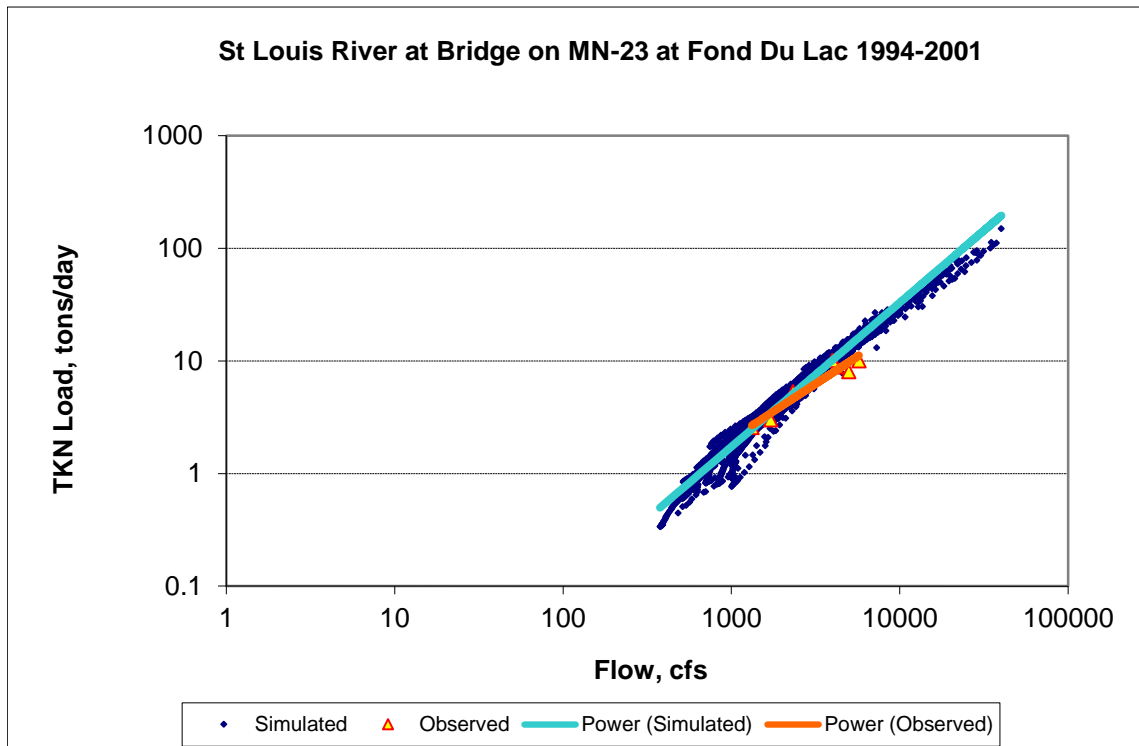
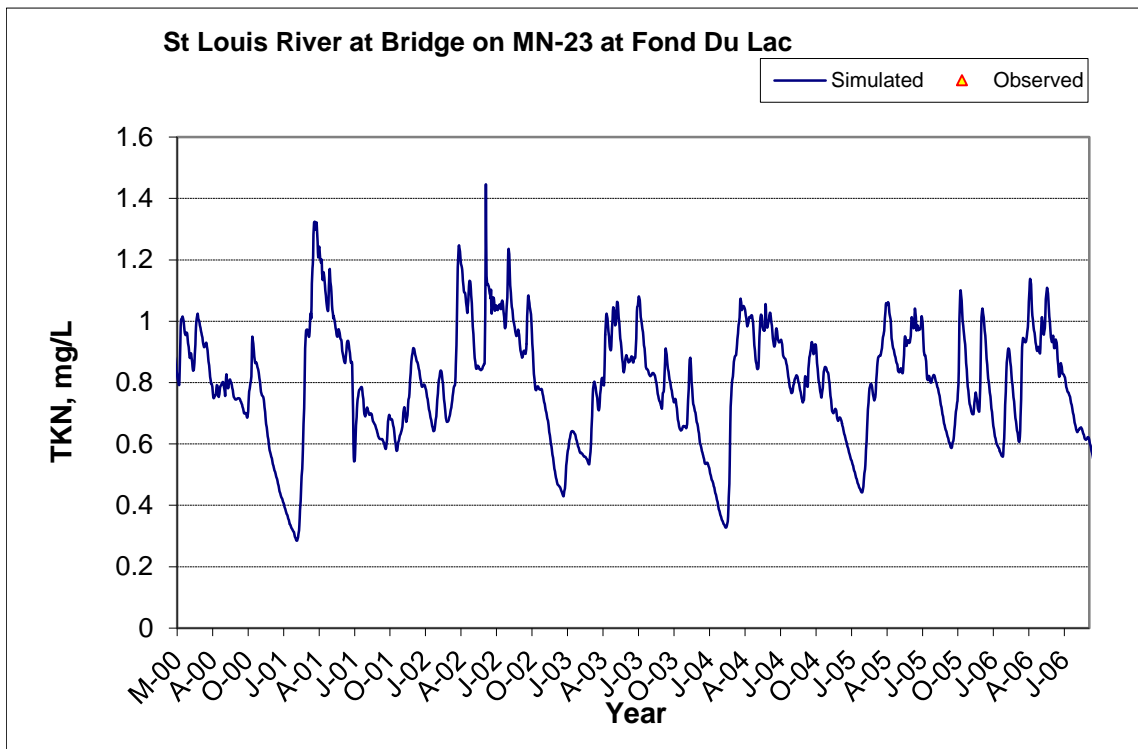
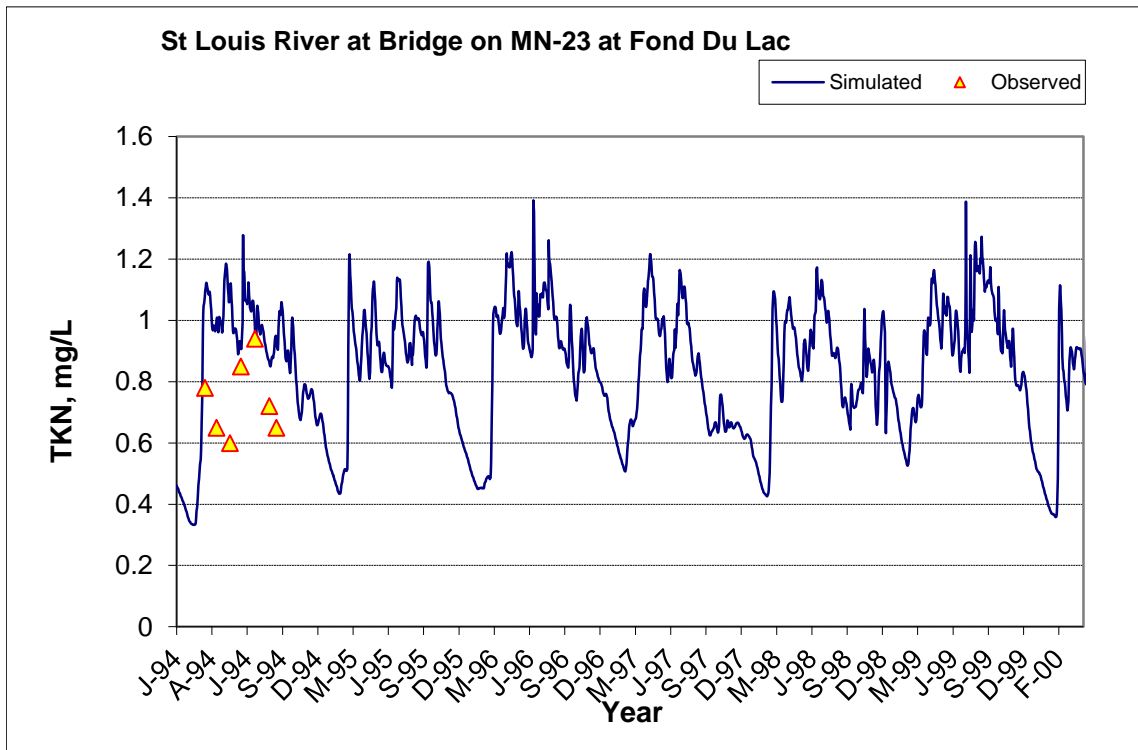


Figure A-172. Power plot of simulated and observed Total Kjeldahl Nitrogen (TKN) load vs flow at St Louis River at Bridge on MN-23 at Fond Du Lac (validation period)



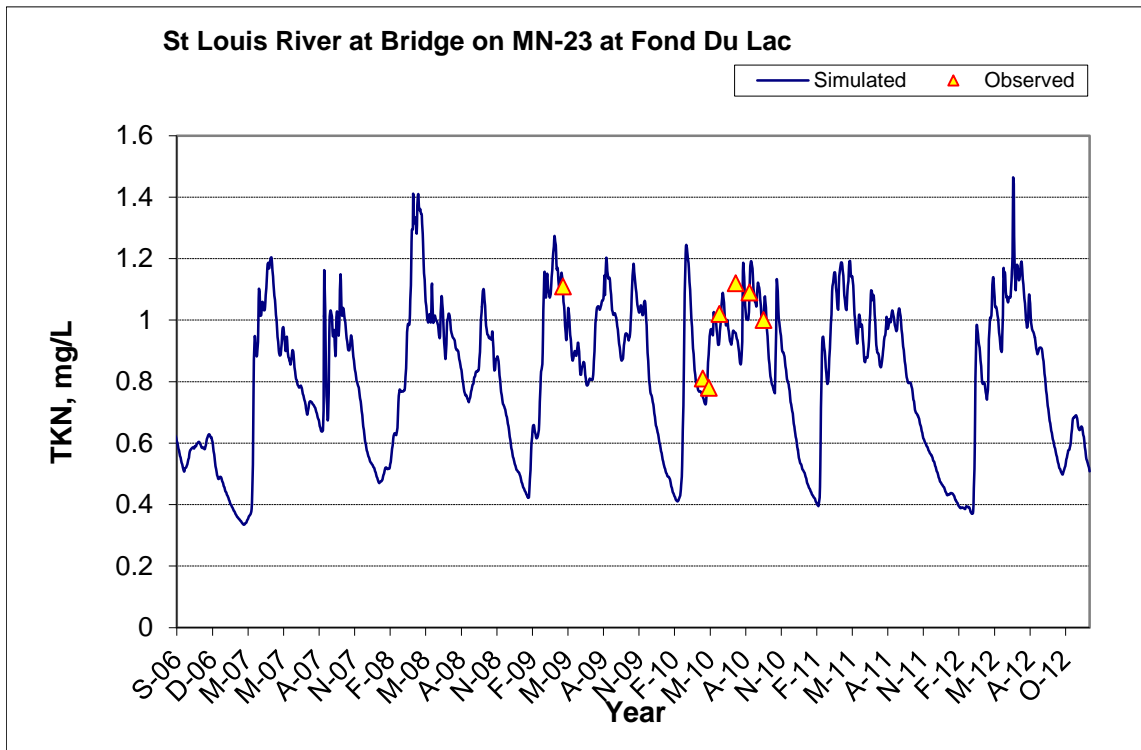


Figure A-173. Time series of observed and simulated Total Kjeldahl Nitrogen (TKN) concentration at St Louis River at Bridge on MN-23 at Fond Du Lac

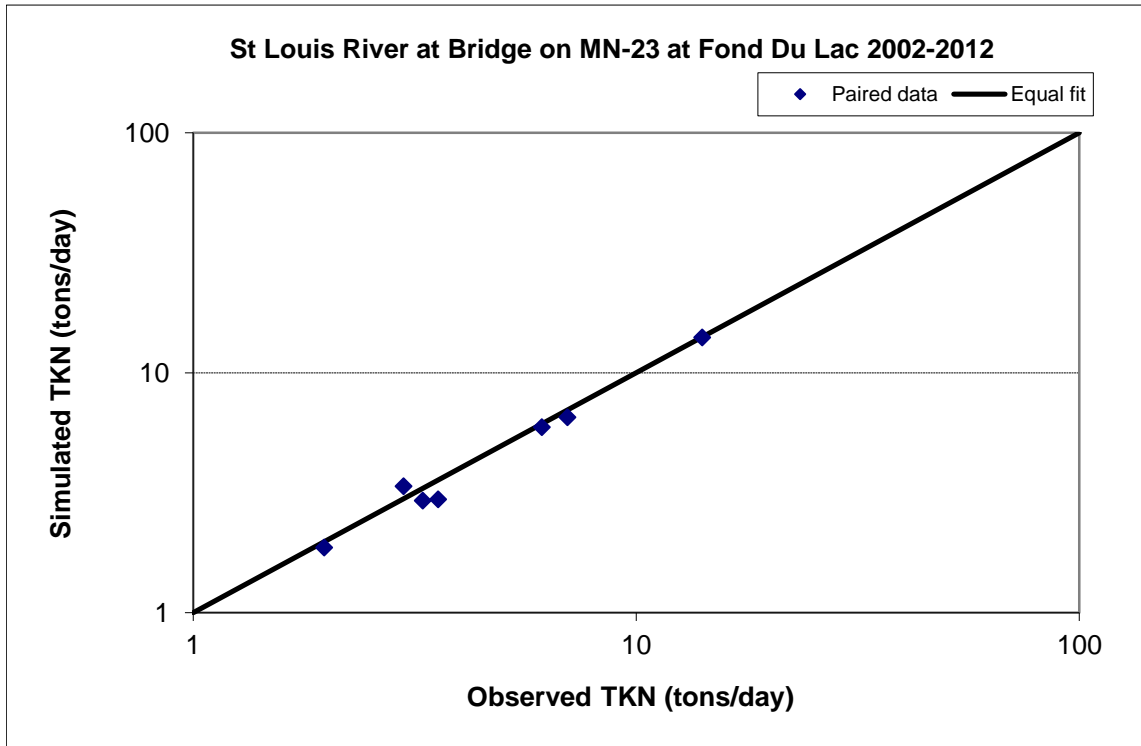


Figure A-174. Paired simulated vs. observed Total Kjeldahl Nitrogen (TKN) load at St Louis River at Bridge on MN-23 at Fond Du Lac (calibration period)

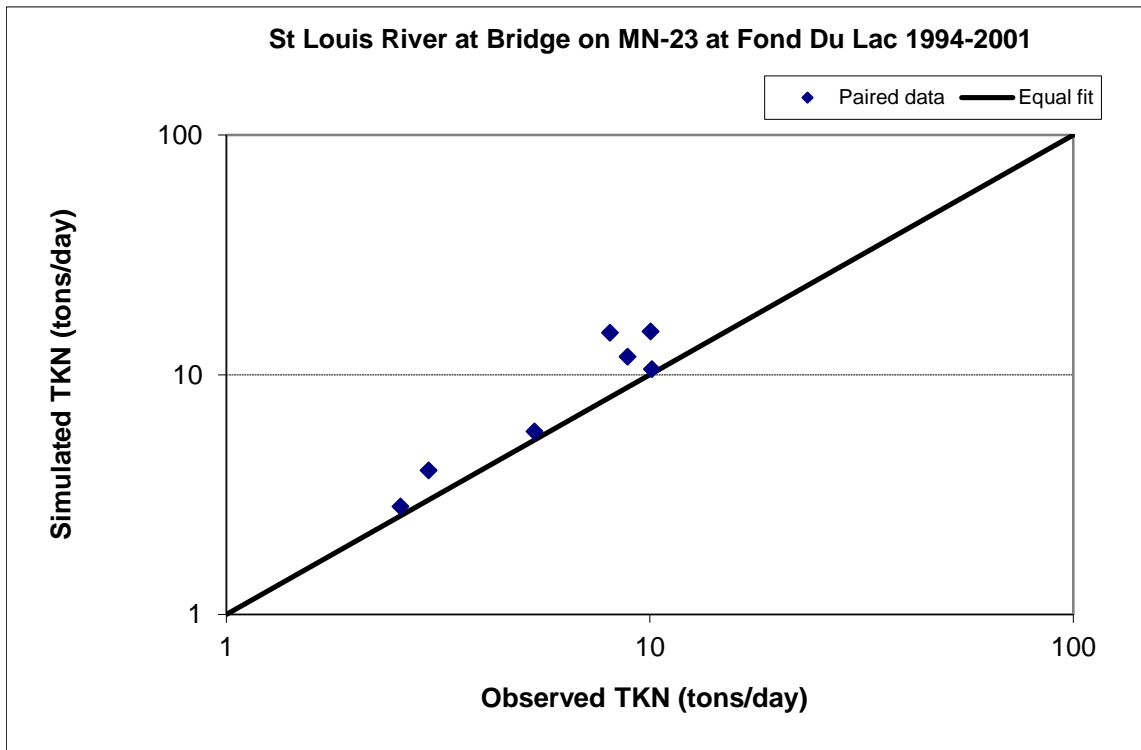


Figure A-175. Paired simulated vs. observed Total Kjeldahl Nitrogen (TKN) load at St Louis River at Bridge on MN-23 at Fond Du Lac (validation period)

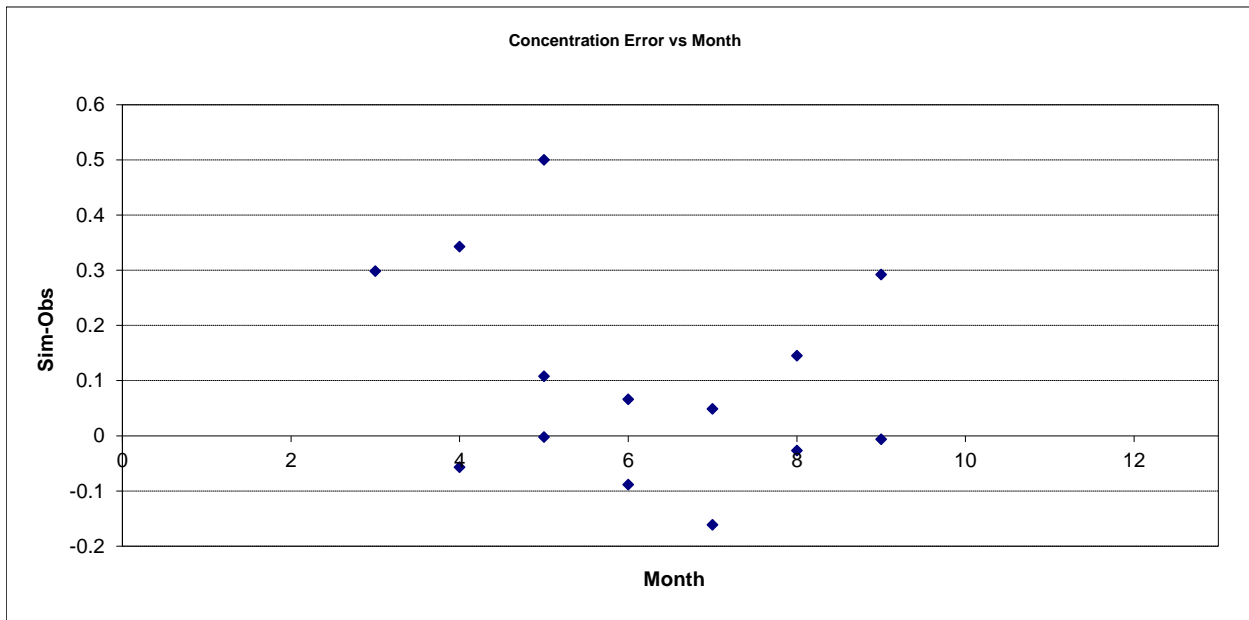


Figure A-176. Residual (Simulated - Observed) vs. Month Total Kjeldahl Nitrogen (TKN) at St Louis River at Bridge on MN-23 at Fond Du Lac

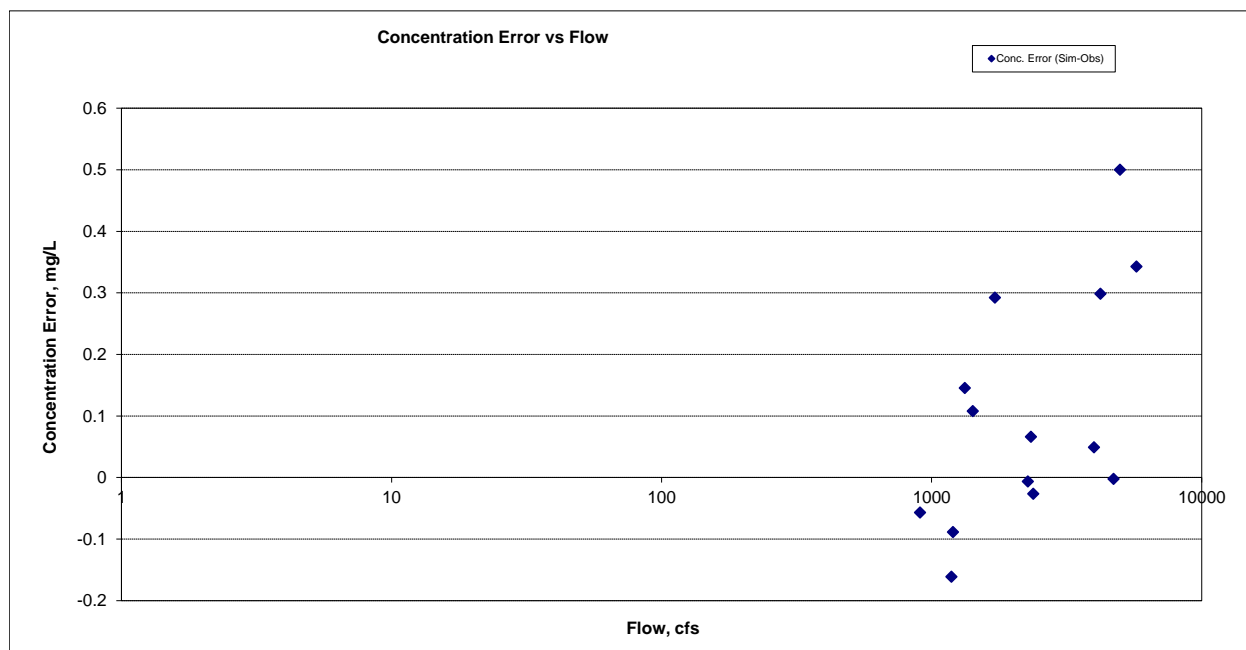


Figure A-177. Residual (Simulated - Observed) vs. Flow Total Kjeldahl Nitrogen (TKN) at St Louis River at Bridge on MN-23 at Fond Du Lac

A.6.4 Nitrite+ Nitrate Nitrogen (NOx)

Table A-26. Nitrite+ Nitrate Nitrogen (NOx) statistics

Period	1994-2001	2002-2012
Count	36	49
Concentration Average Error	0.42%	29.38%
Concentration Median Error	7.07%	23.12%
Load Average Error	-5.12%	4.83%
Load Median Error	5.14%	16.34%
Paired t conc	0.96	0.19
Paired t load	0.84	0.77

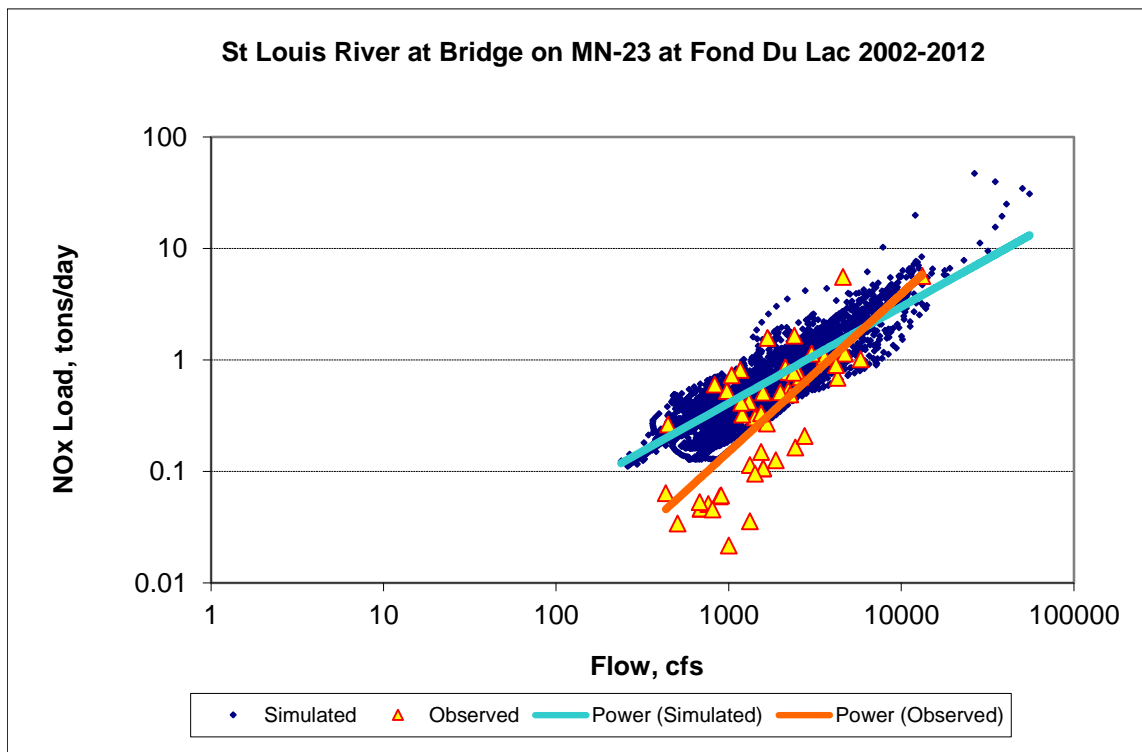


Figure A-178. Power plot of simulated and observed Nitrite+ Nitrate Nitrogen (NOx) load vs flow at St Louis River at Bridge on MN-23 at Fond Du Lac (calibration period)

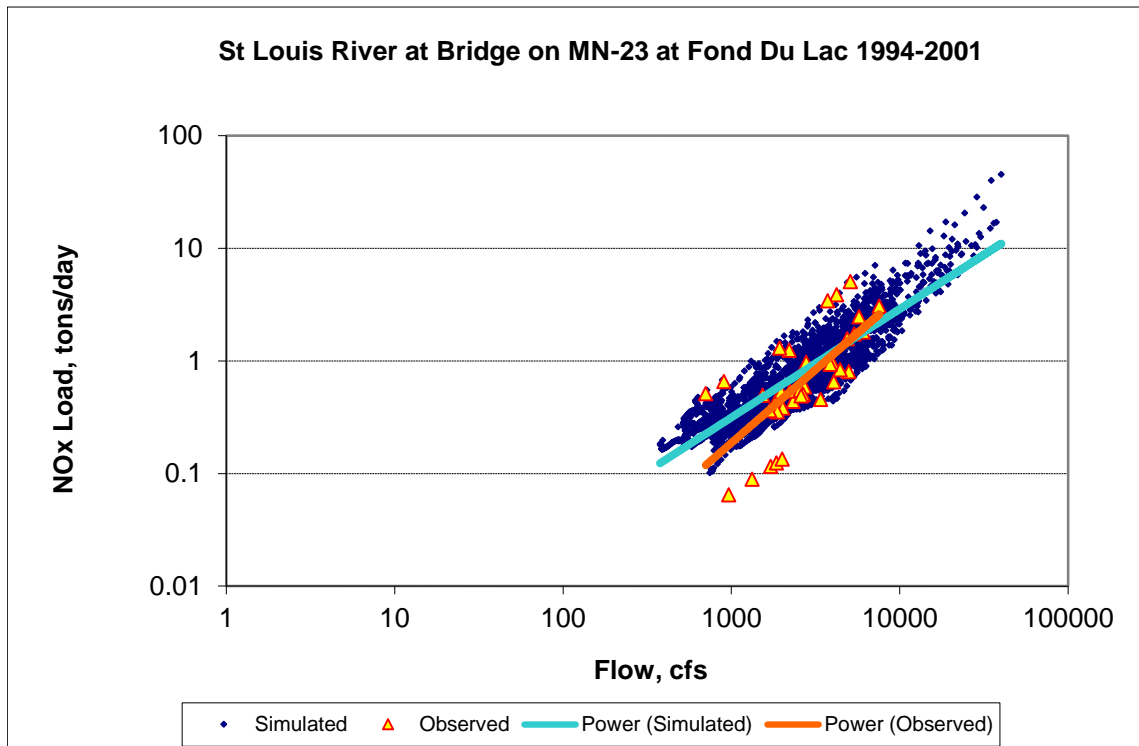
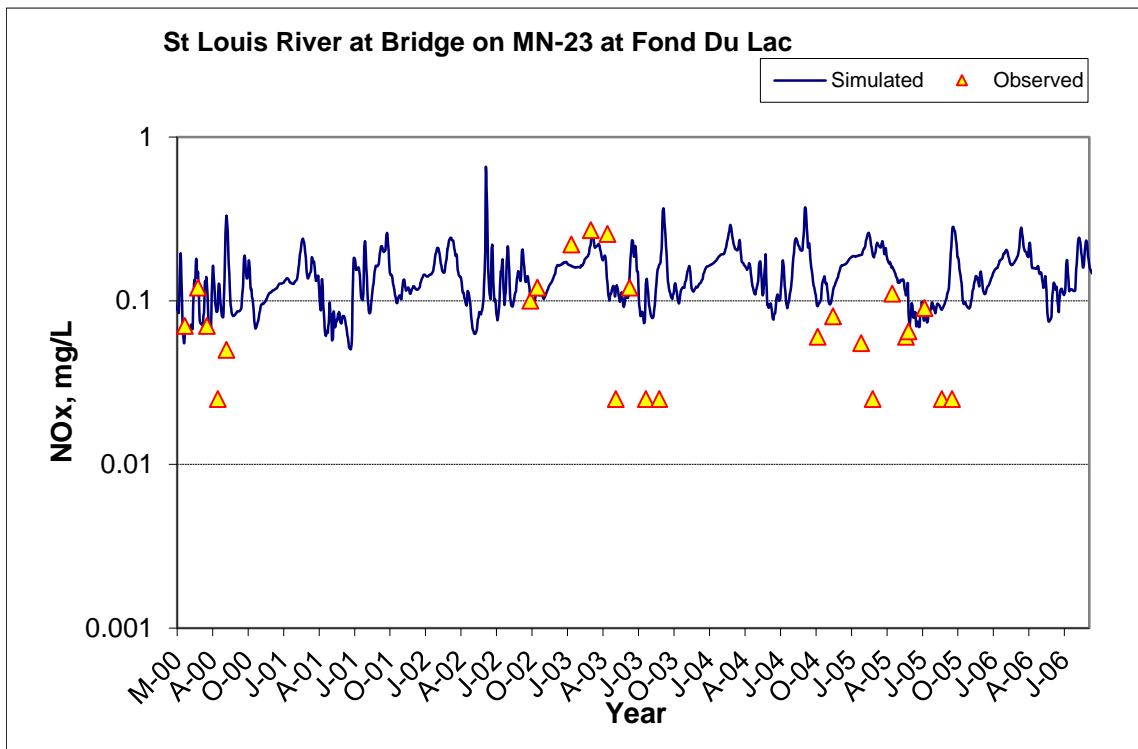
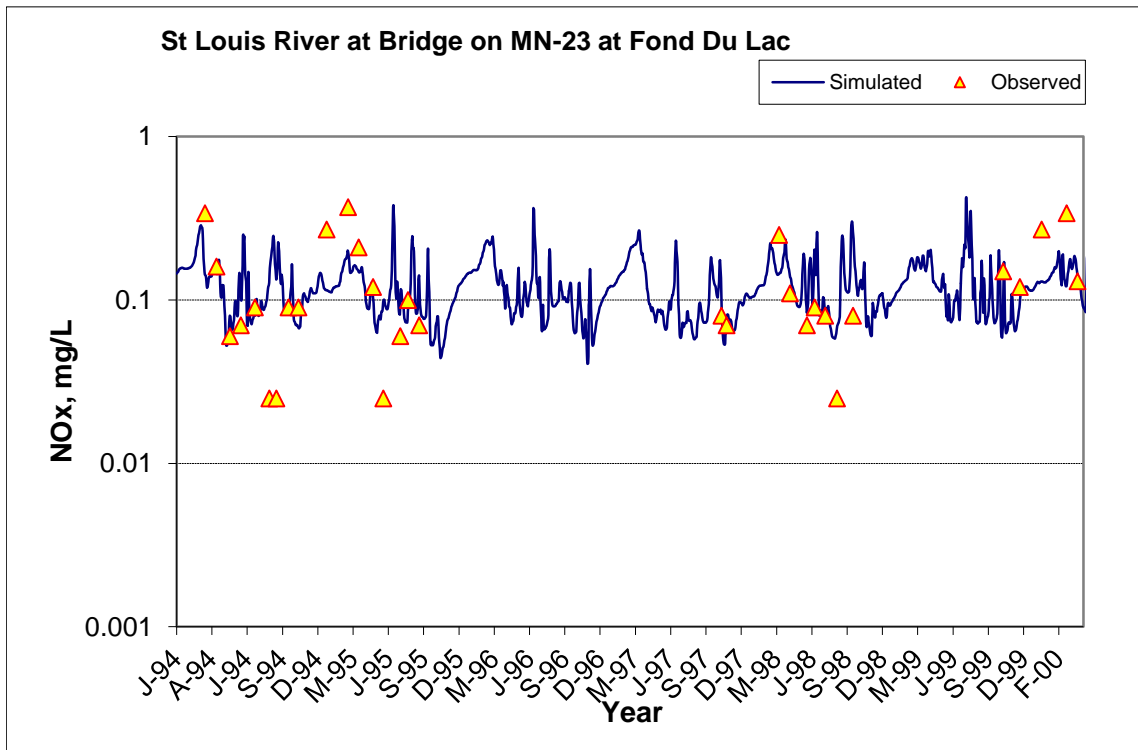


Figure A-179. Power plot of simulated and observed Nitrite+ Nitrate Nitrogen (NOx) load vs flow at St Louis River at Bridge on MN-23 at Fond Du Lac (validation period)



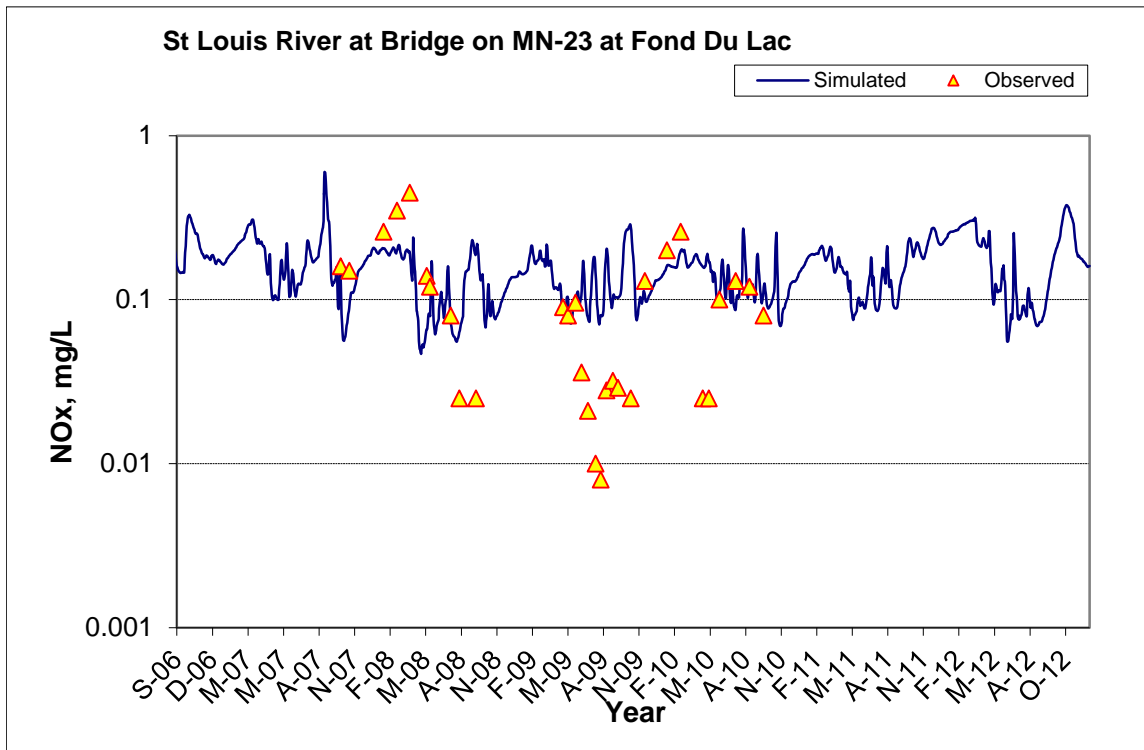


Figure A-180. Time series of observed and simulated Nitrite+ Nitrate Nitrogen (NOx) concentration at St Louis River at Bridge on MN-23 at Fond Du Lac

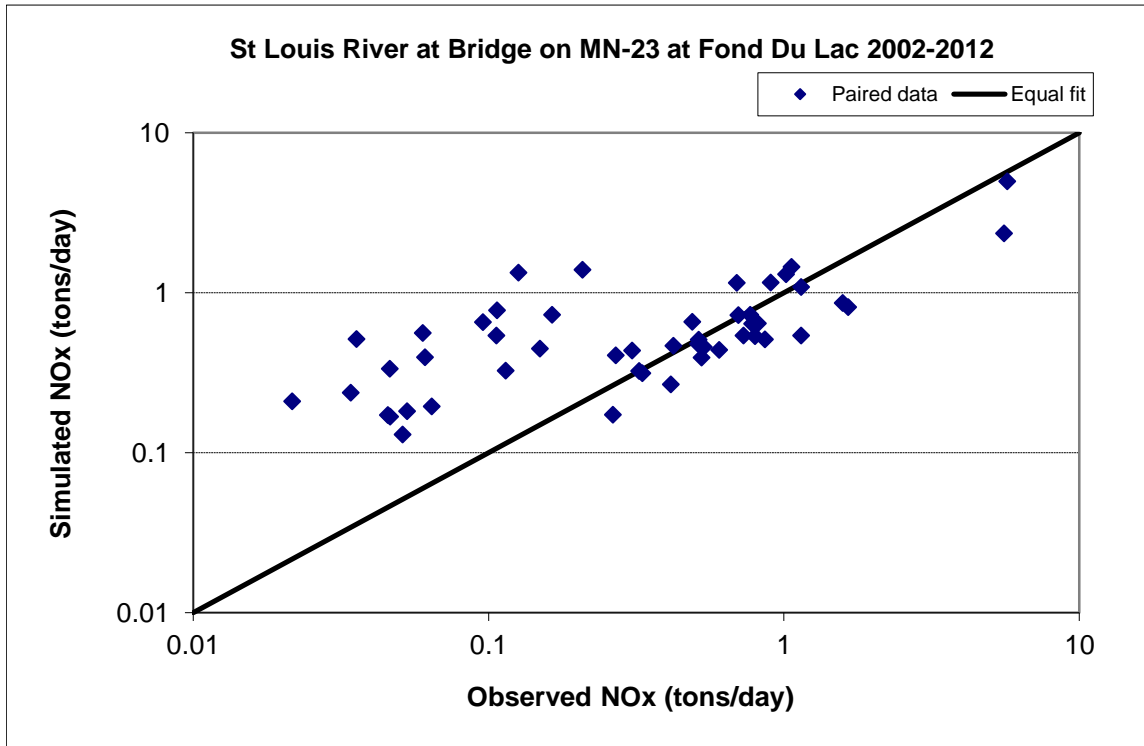


Figure A-181. Paired simulated vs. observed Nitrite+ Nitrate Nitrogen (NOx) load at St Louis River at Bridge on MN-23 at Fond Du Lac (calibration period)

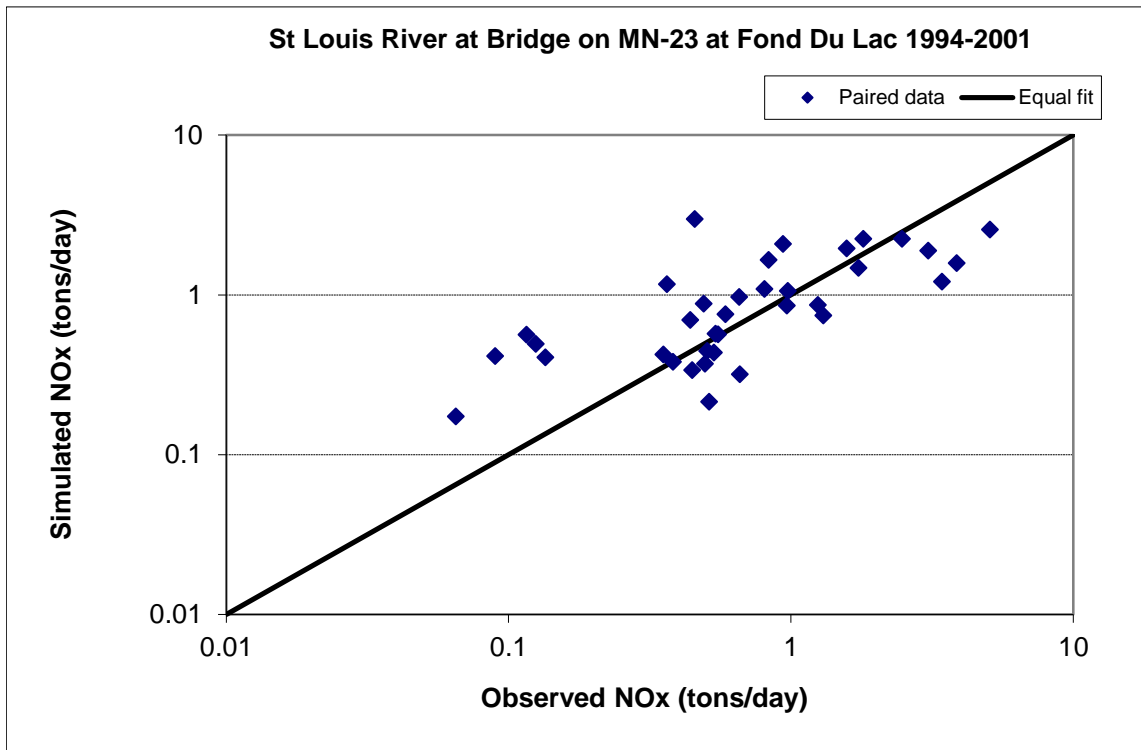


Figure A-182. Paired simulated vs. observed Nitrite+ Nitrate Nitrogen (NOx) load at St Louis River at Bridge on MN-23 at Fond Du Lac (validation period)

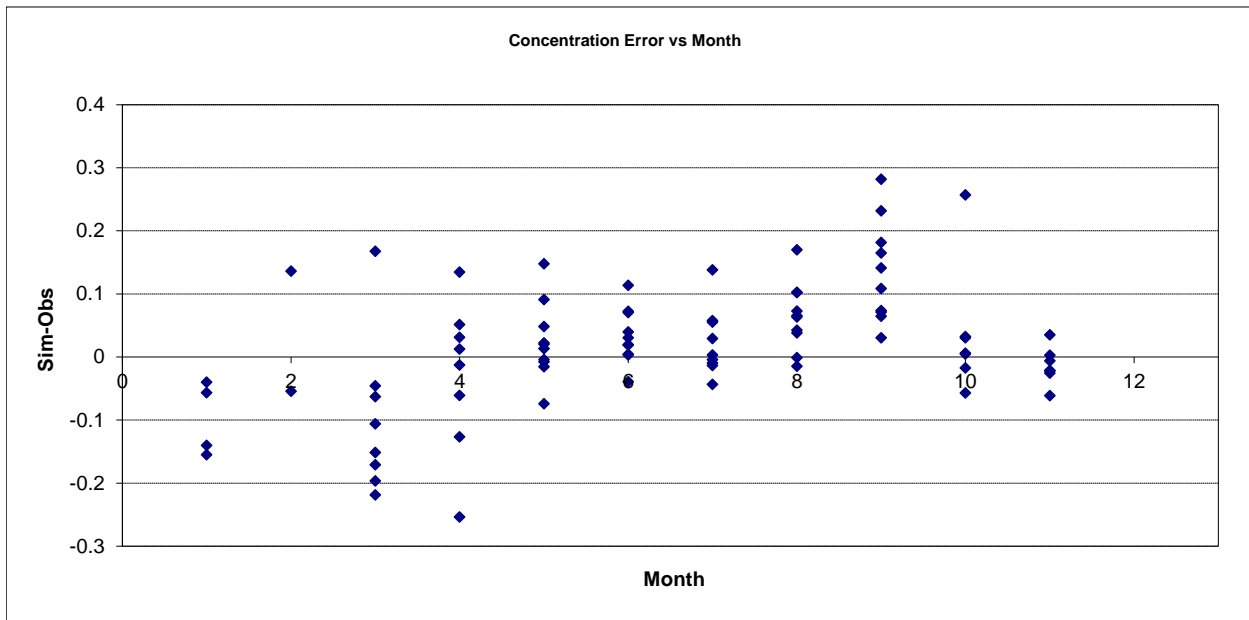


Figure A-183. Residual (Simulated - Observed) vs. Month Nitrite+ Nitrate Nitrogen (NOx) at St Louis River at Bridge on MN-23 at Fond Du Lac

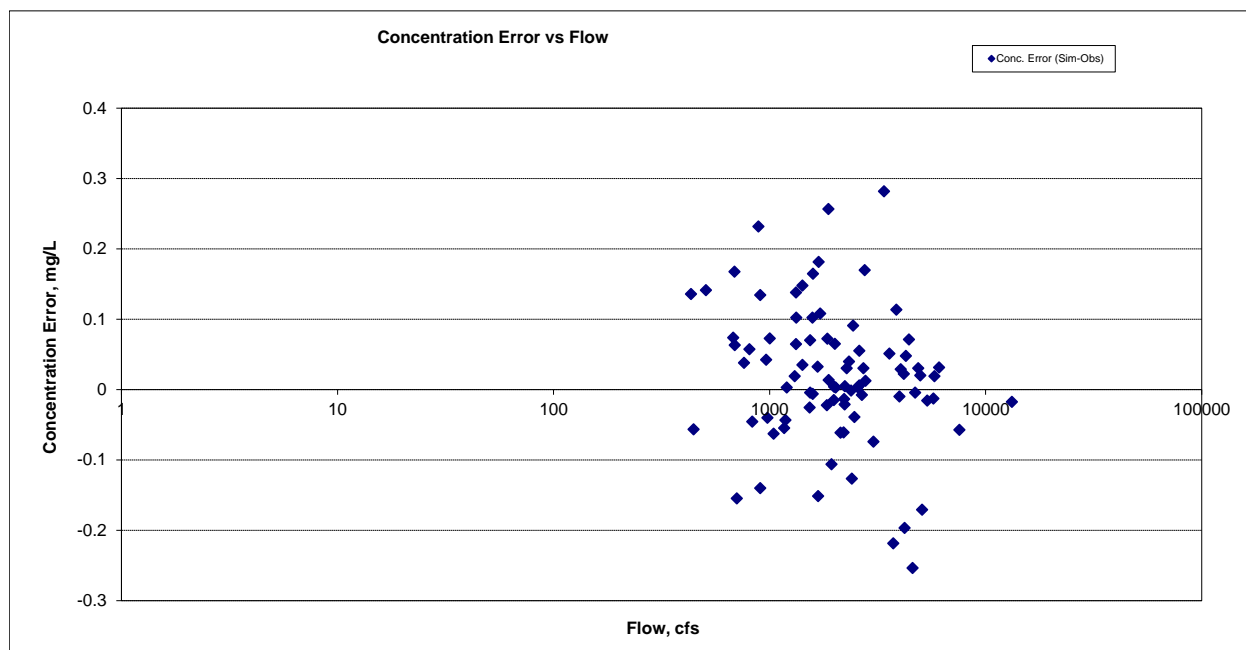


Figure A-184. Residual (Simulated - Observed) vs. Flow Nitrite+ Nitrate Nitrogen (NOx) at St Louis River at Bridge on MN-23 at Fond Du Lac

A.6.5 Total Nitrogen (TN)

Table A-27. Total Nitrogen (TN) statistics

Period	1994-2001	2002-2012
Count	7	7
Concentration Average Error	28.75%	0.22%
Concentration Median Error	27.33%	-0.76%
Load Average Error	28.13%	-1.41%
Load Median Error	9.54%	-2.03%
Paired t conc	0.09	1.00
Paired t load	0.37	0.74

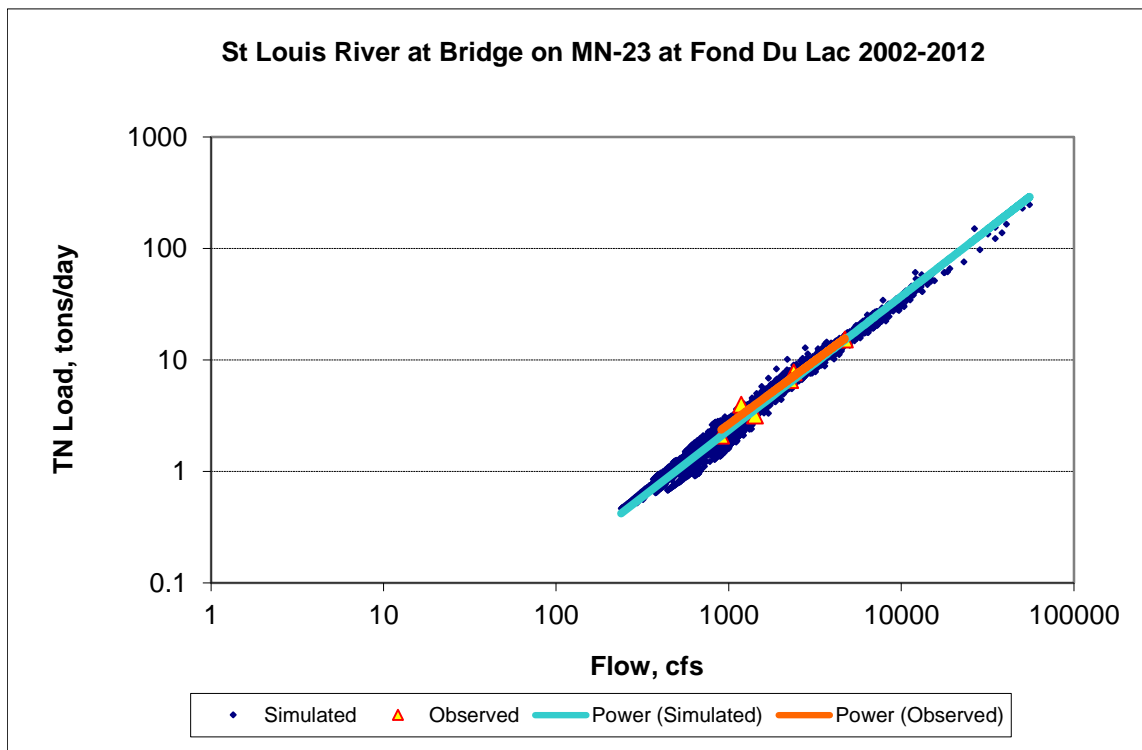


Figure A-185. Power plot of simulated and observed Total Nitrogen (TN) load vs flow at St Louis River at Bridge on MN-23 at Fond Du Lac (calibration period)

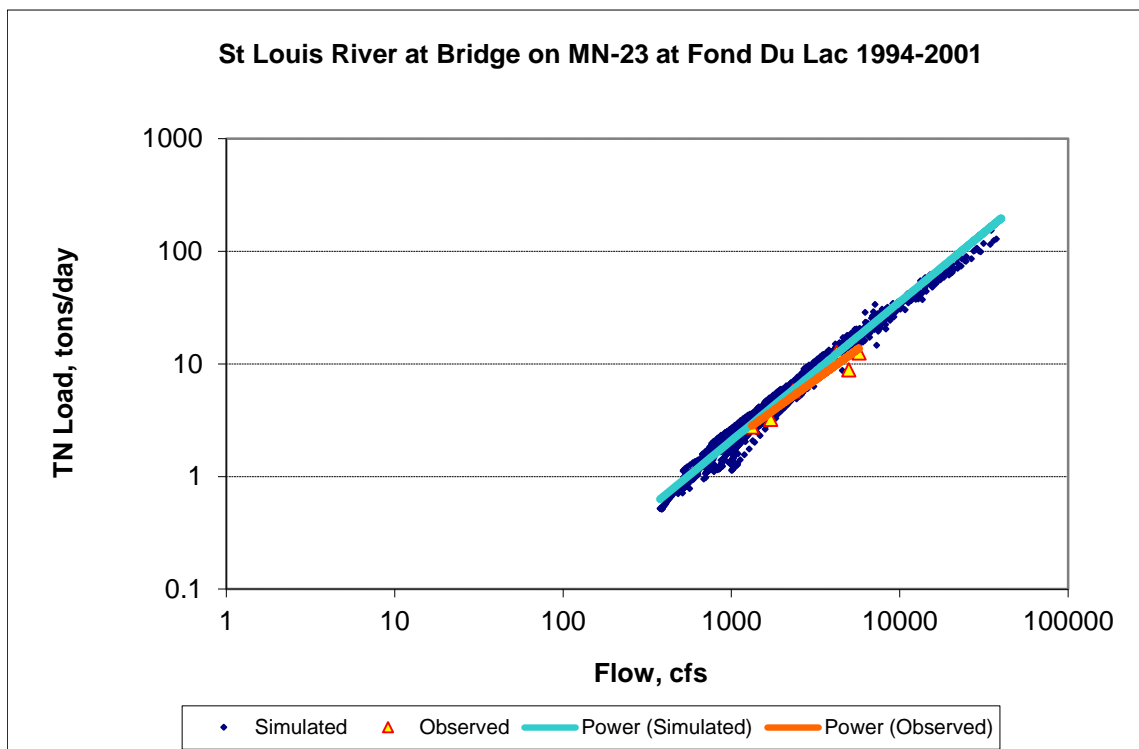
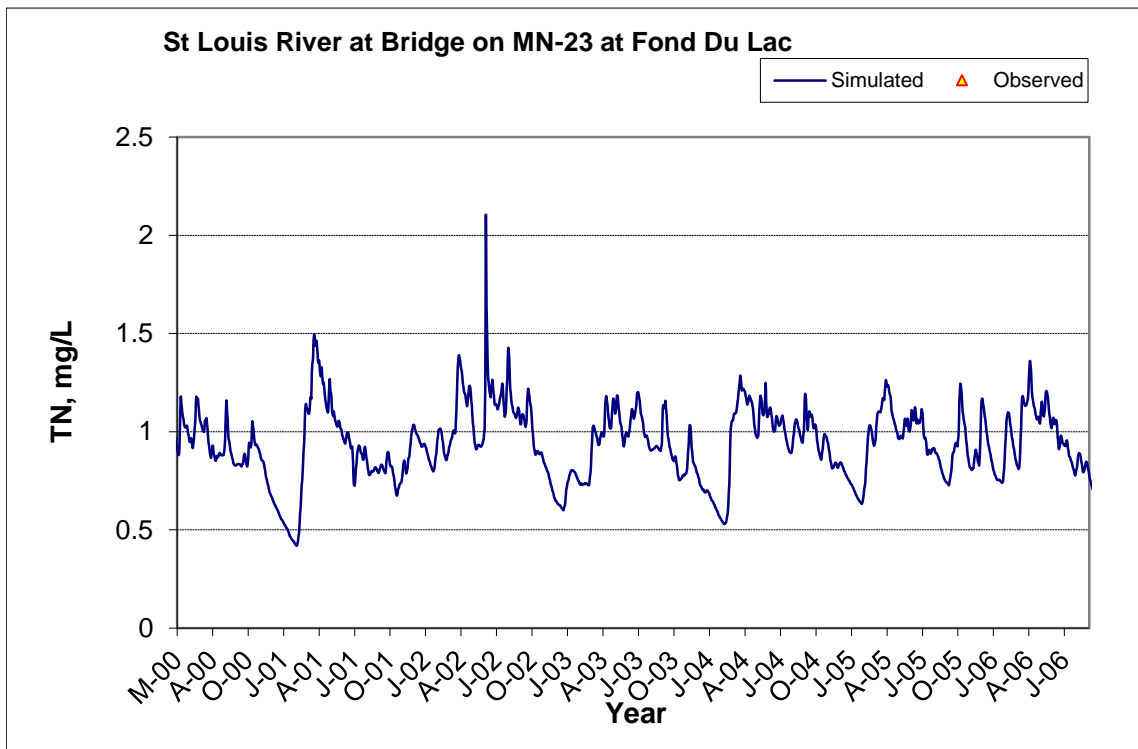
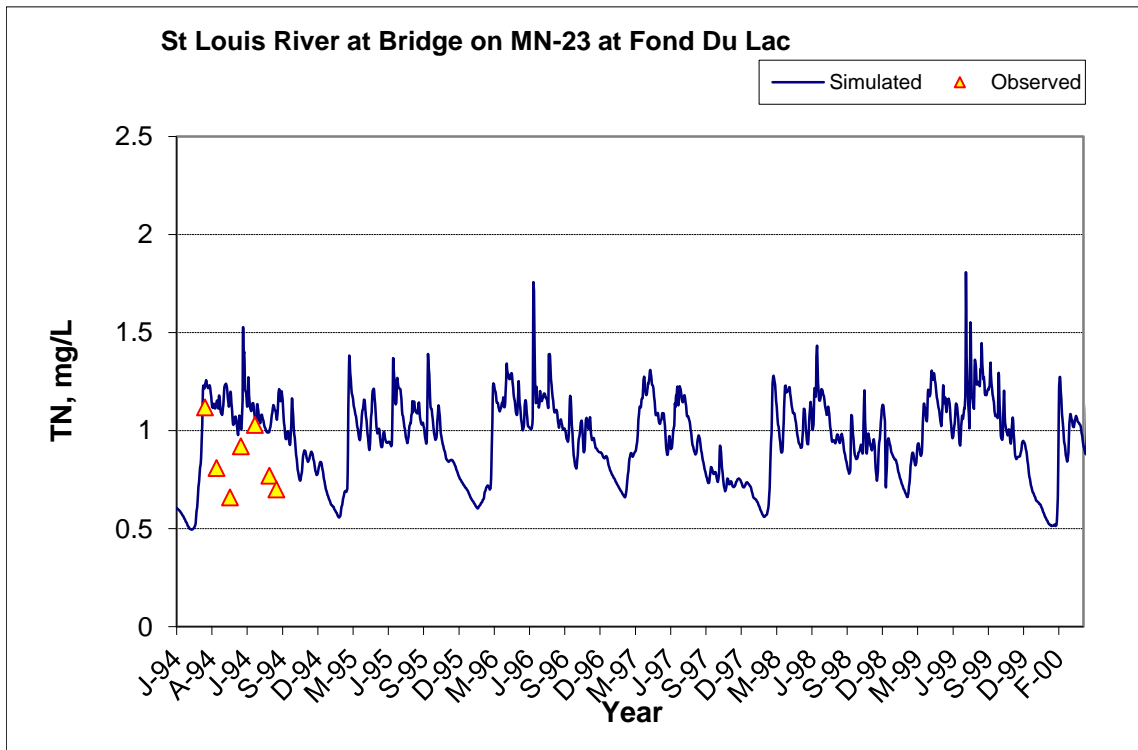


Figure A-186. Power plot of simulated and observed Total Nitrogen (TN) load vs flow at St Louis River at Bridge on MN-23 at Fond Du Lac (validation period)



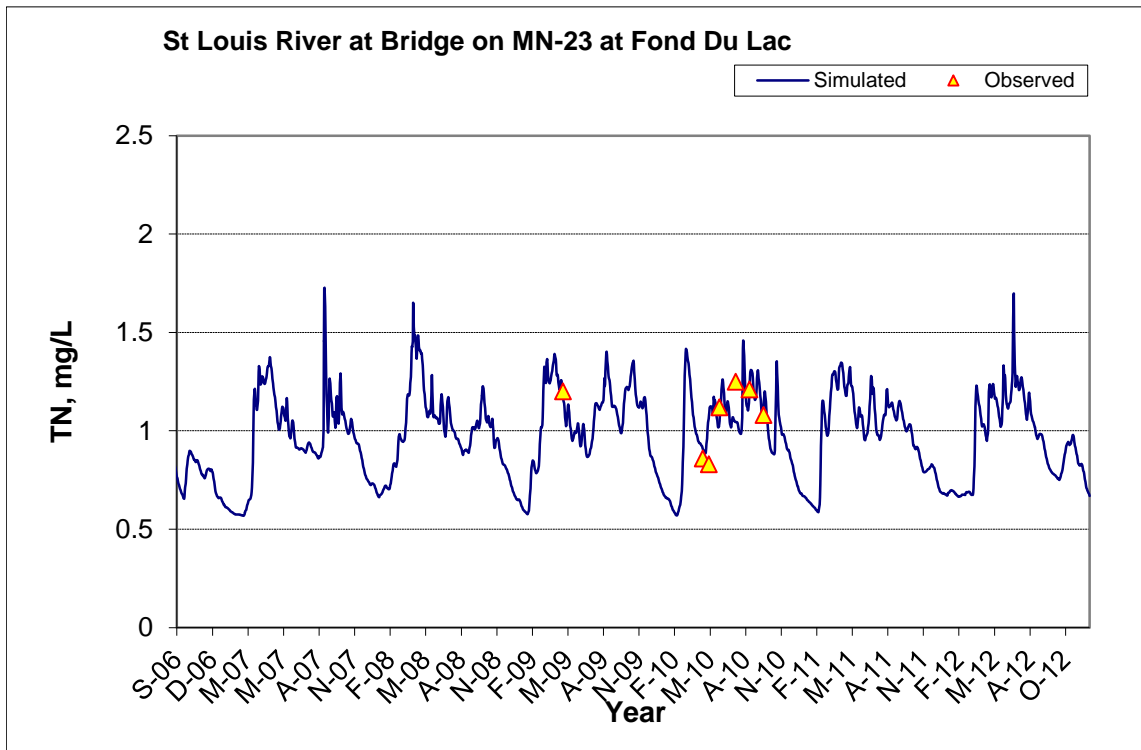


Figure A-187. Time series of observed and simulated Total Nitrogen (TN) concentration at St Louis River at Bridge on MN-23 at Fond Du Lac

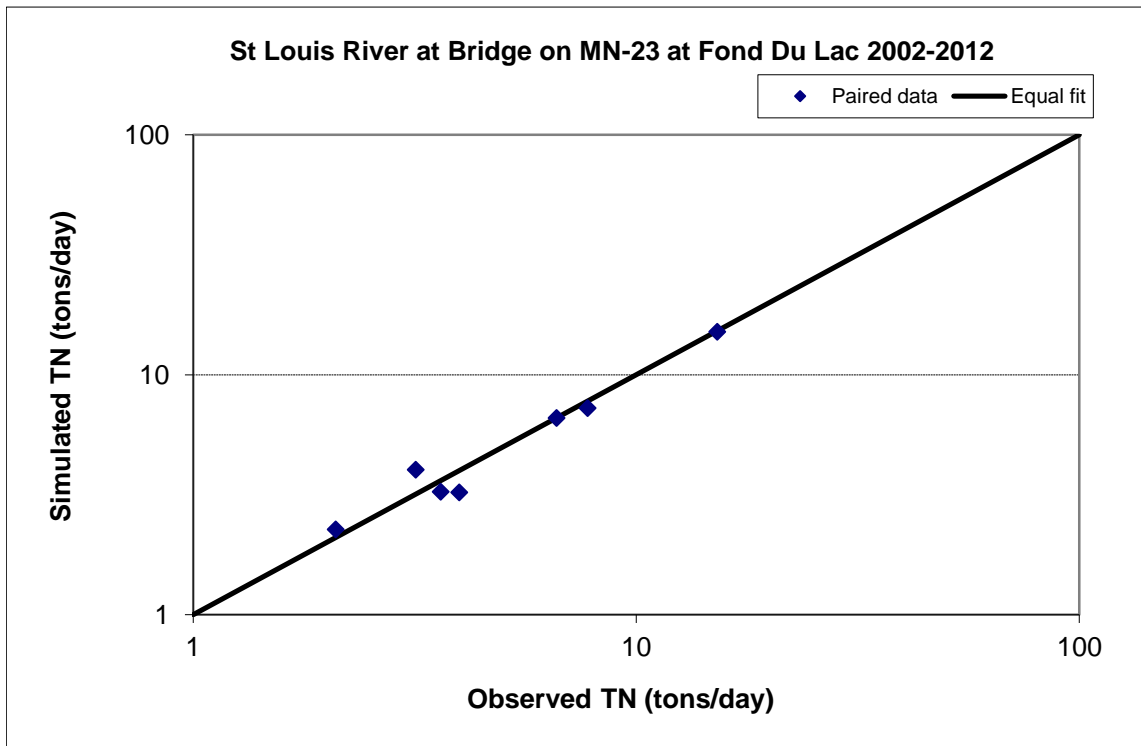


Figure A-188. Paired simulated vs. observed Total Nitrogen (TN) load at St Louis River at Bridge on MN-23 at Fond Du Lac (calibration period)

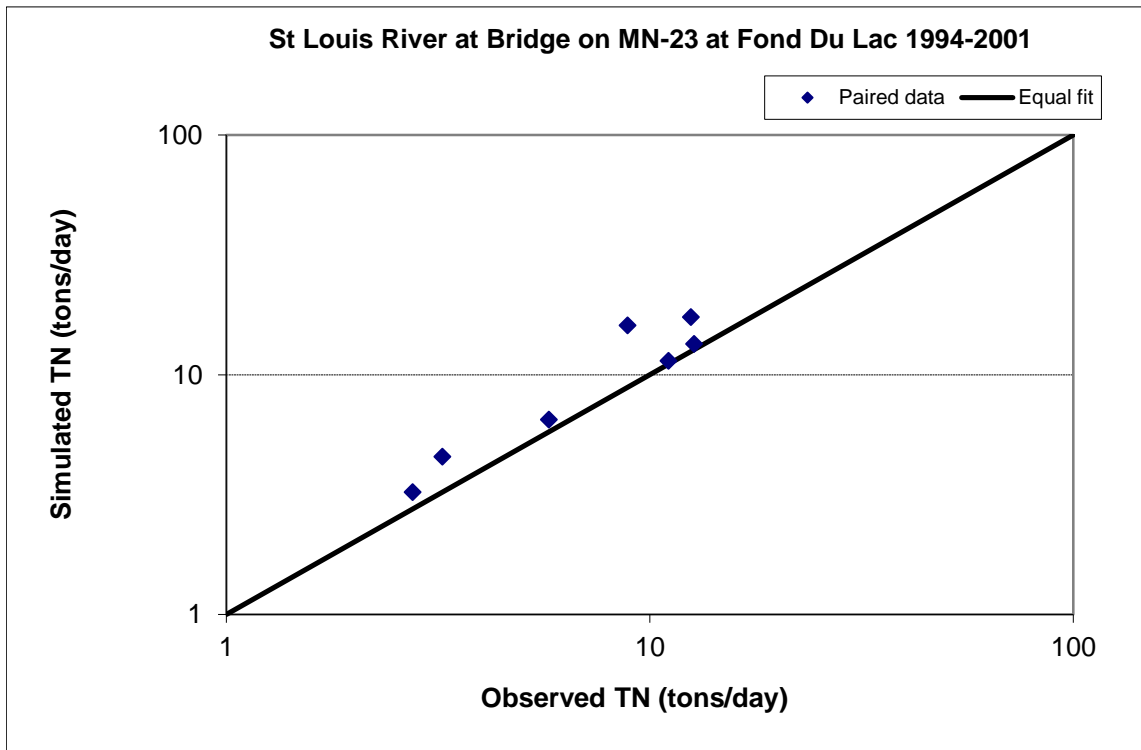


Figure A-189. Paired simulated vs. observed Total Nitrogen (TN) load at St Louis River at Bridge on MN-23 at Fond Du Lac (validation period)

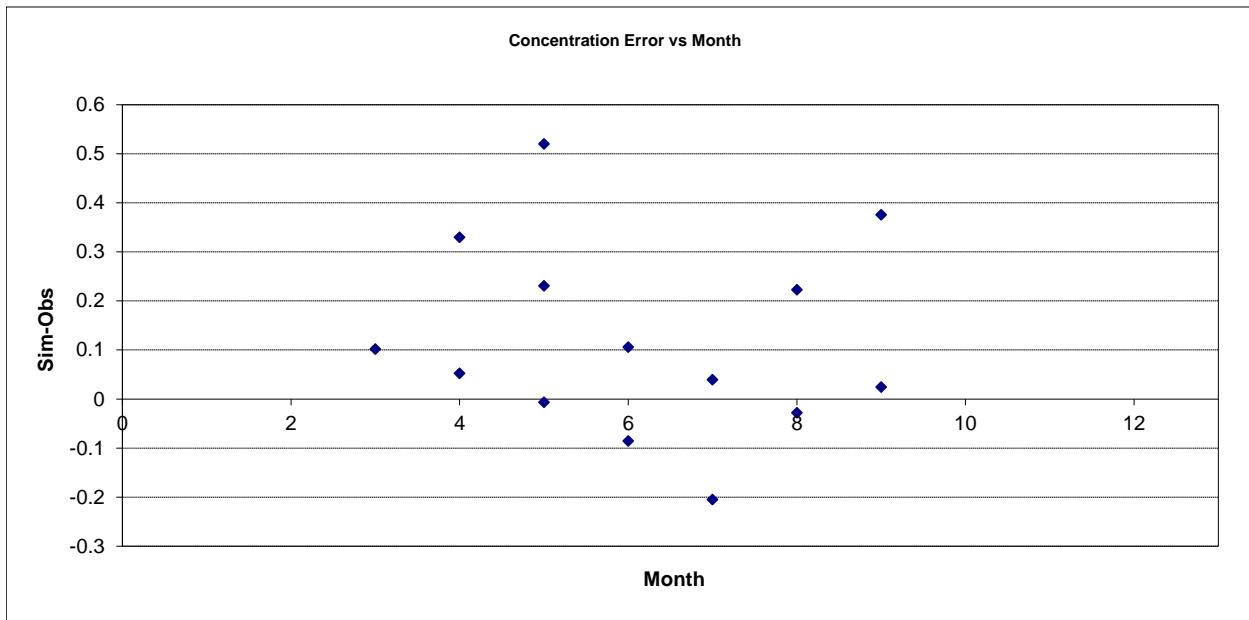


Figure A-190. Residual (Simulated - Observed) vs. Month Total Nitrogen (TN) at St Louis River at Bridge on MN-23 at Fond Du Lac

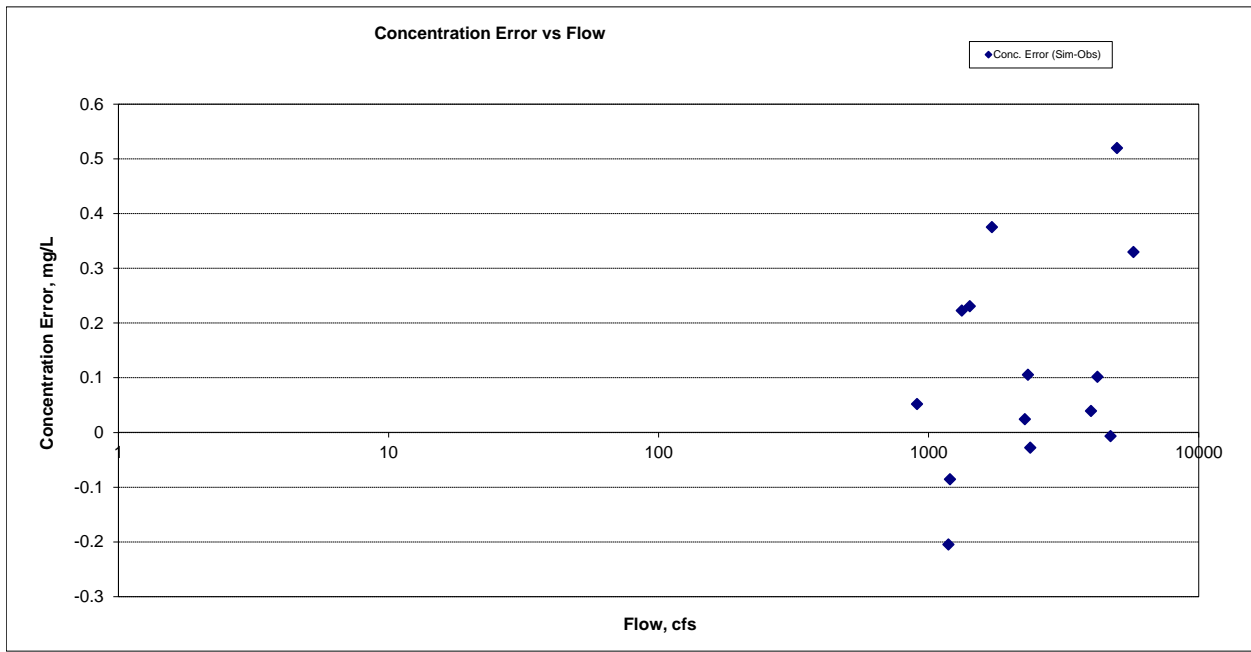
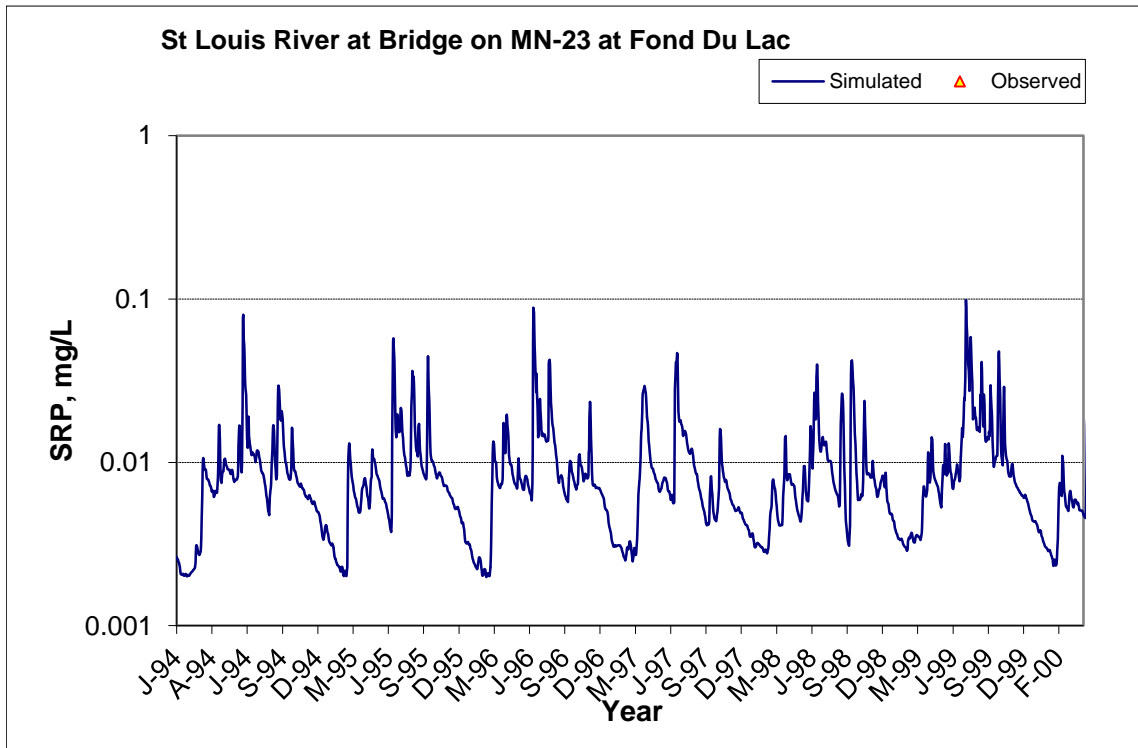


Figure A-191. Residual (Simulated - Observed) vs. Flow Total Nitrogen (TN) at St Louis River at Bridge on MN-23 at Fond Du Lac

A.6.6 Soluble Reactive Phosphorus (SRP)



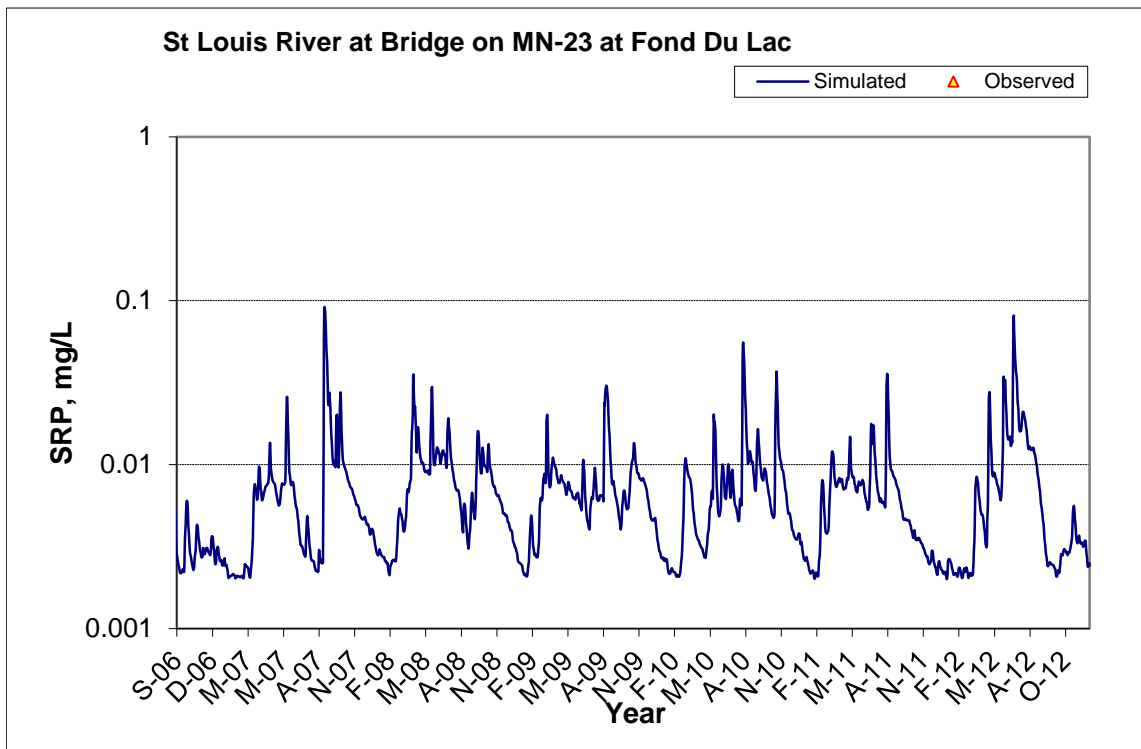
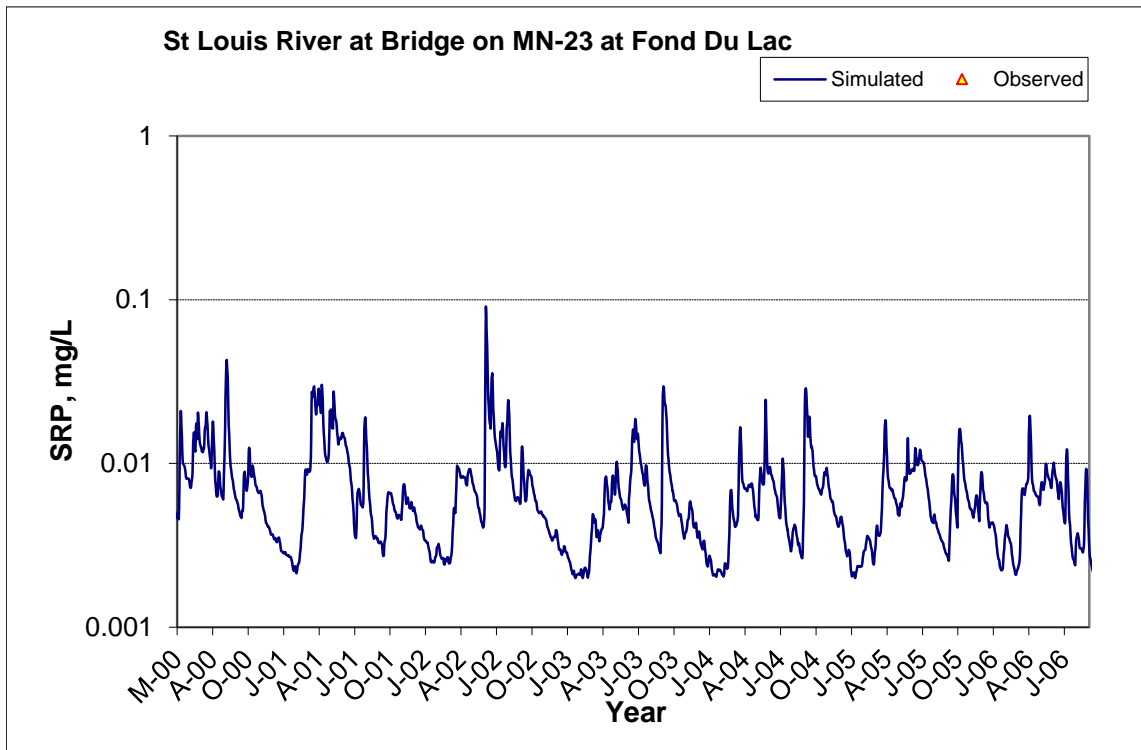
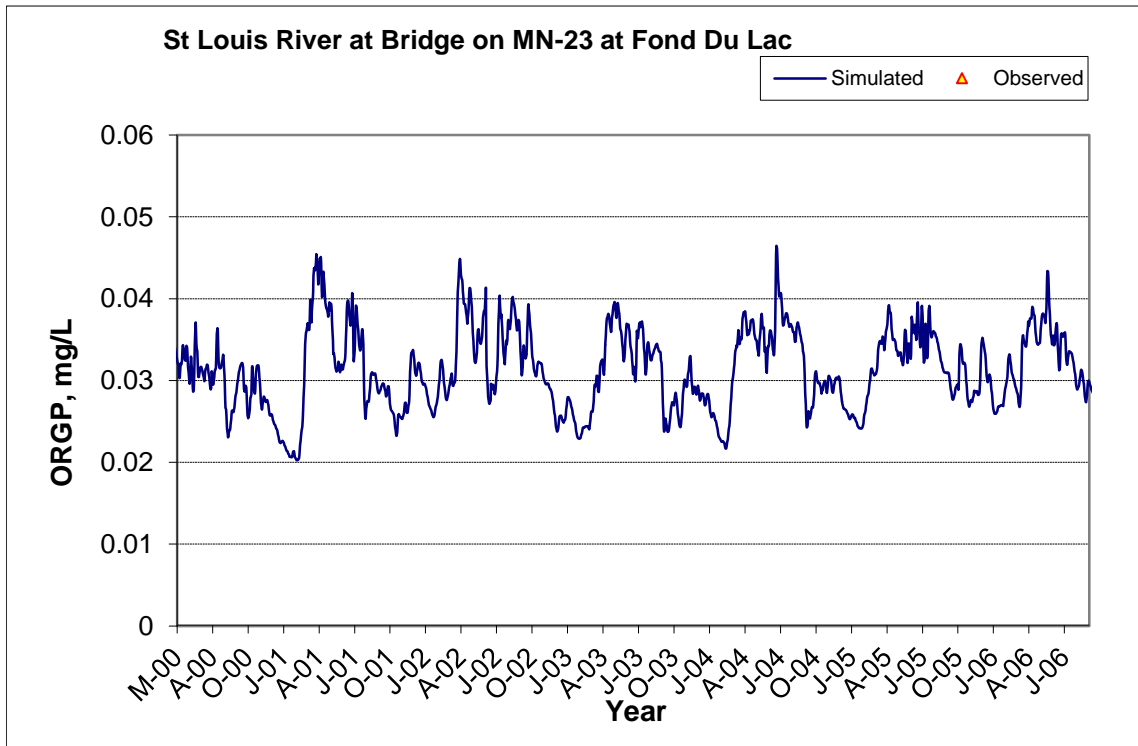
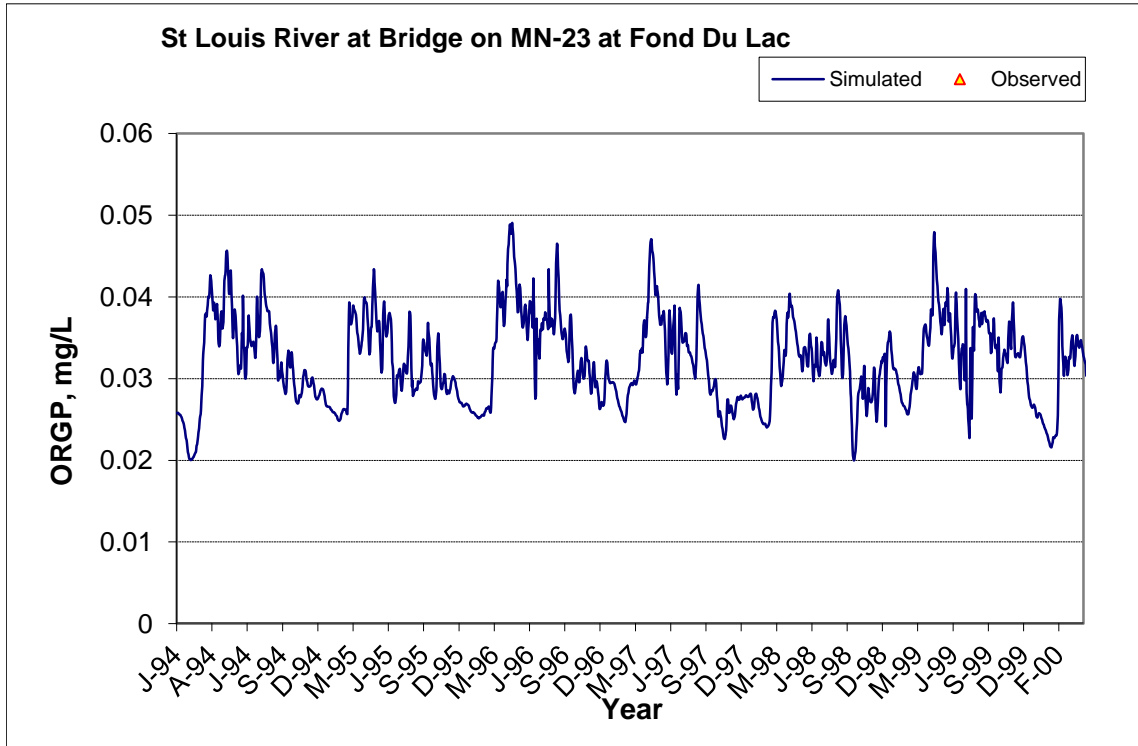


Figure A-192. Time series of observed and simulated Soluble Reactive Phosphorus (SRP) concentration at St Louis River at Bridge on MN-23 at Fond Du Lac

A.6.7 Organic Phosphorus (OrgP)



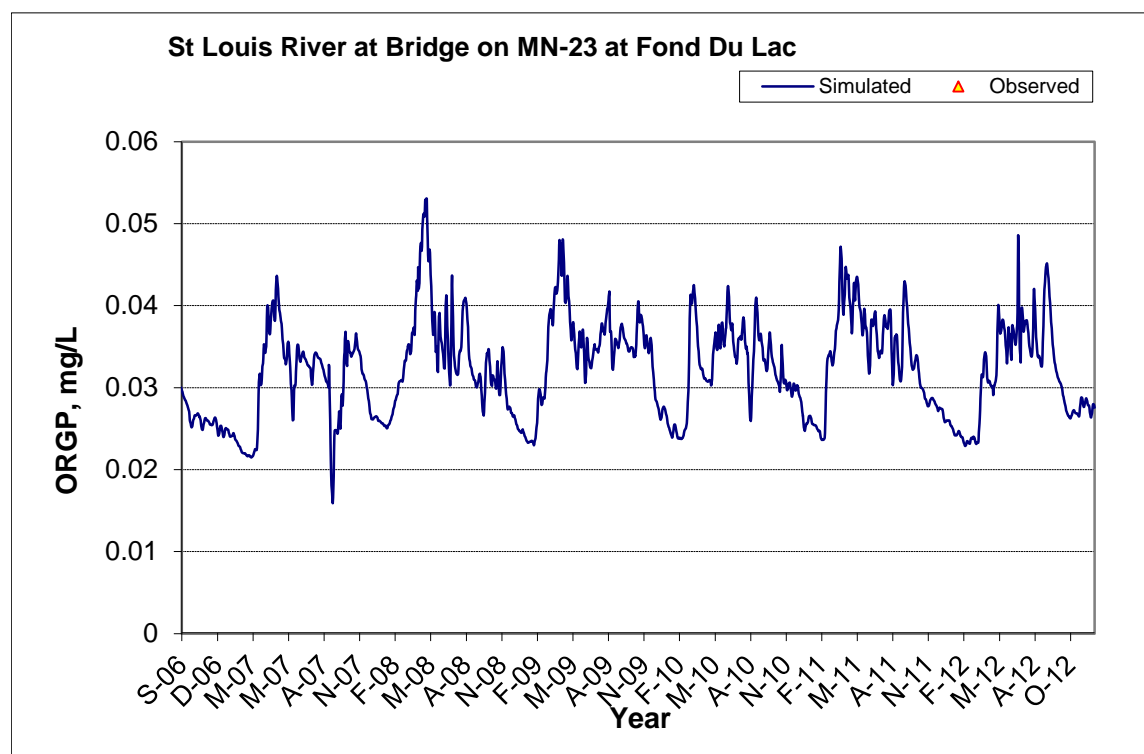


Figure A-193. Time series of observed and simulated Organic Phosphorus (OrgP) concentration at St Louis River at Bridge on MN-23 at Fond Du Lac

A.6.8 Total Phosphorus (TP)

Table A-28. Total Phosphorus (TP) statistics

Period	1994-2001	2002-2012
Count	38	50
Concentration Average Error	12.85%	15.22%
Concentration Median Error	7.03%	22.06%
Load Average Error	4.25%	7.21%
Load Median Error	4.79%	8.07%
Paired t conc	0.93	0.84
Paired t load	0.81	0.72

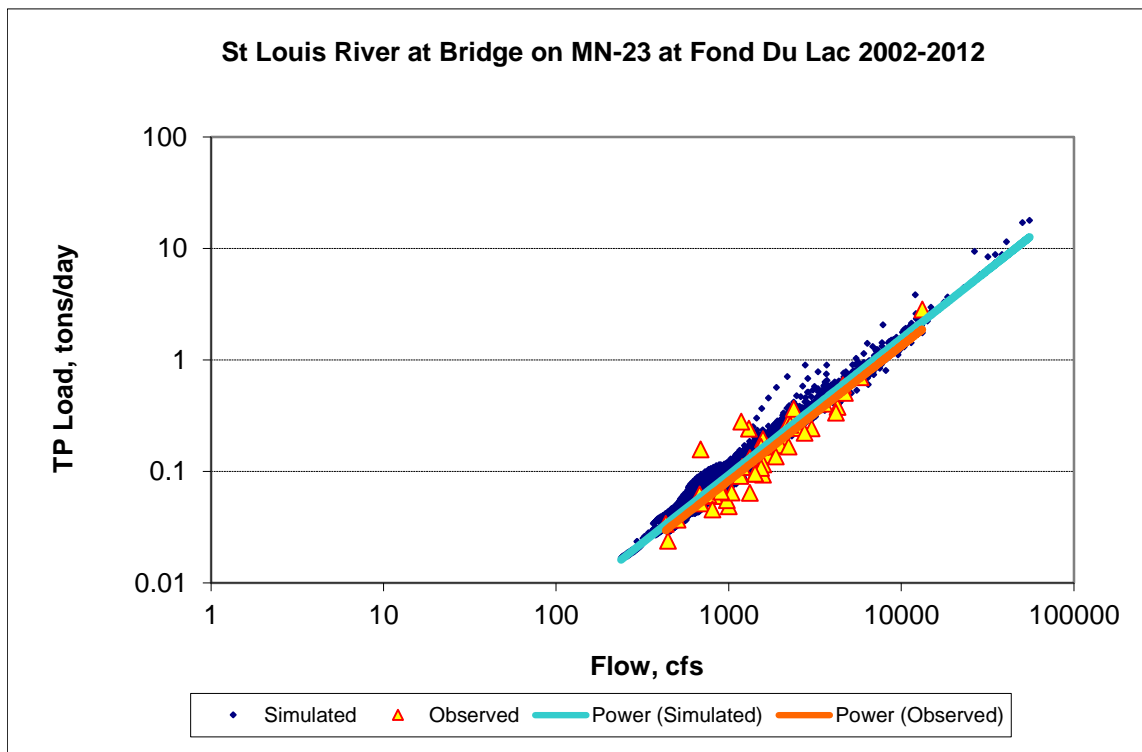


Figure A-194. Power plot of simulated and observed Total Phosphorus (TP) load vs flow at St Louis River at Bridge on MN-23 at Fond Du Lac (calibration period)

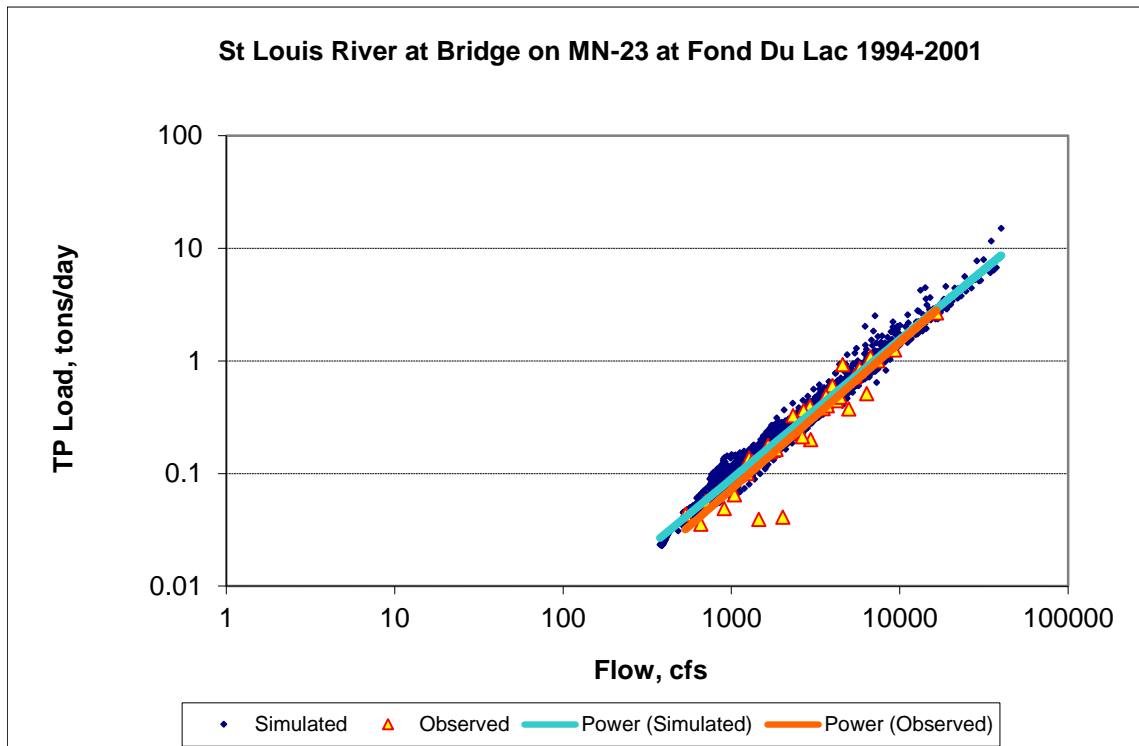
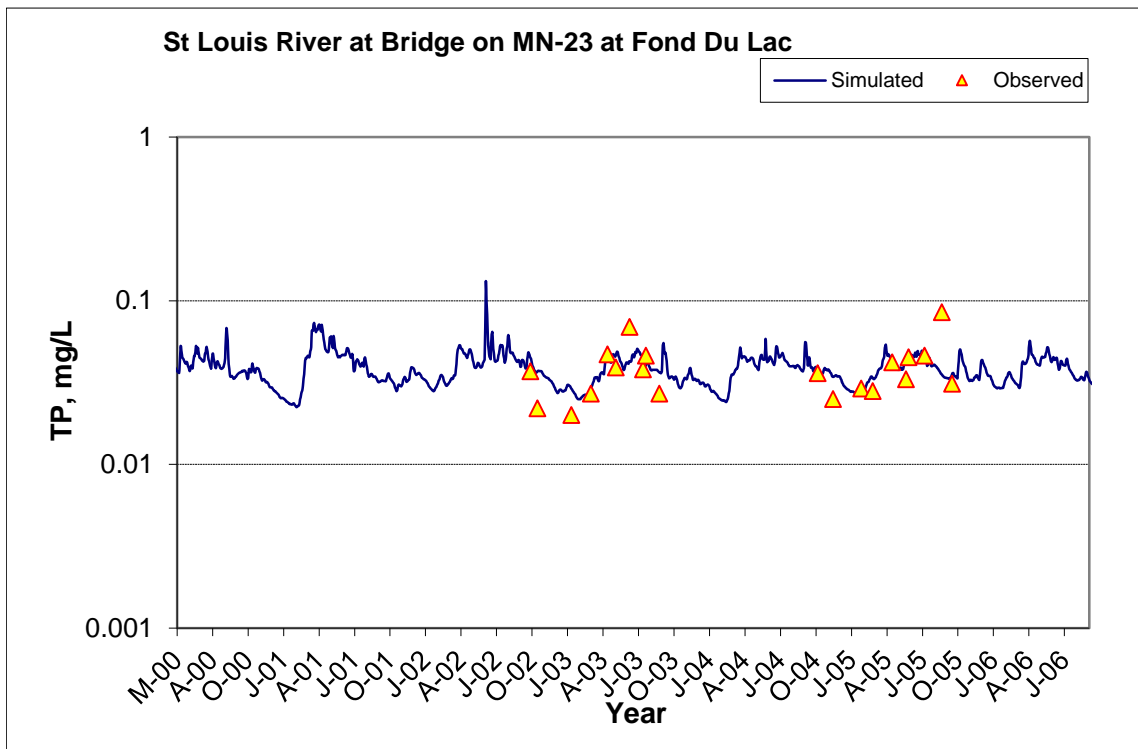
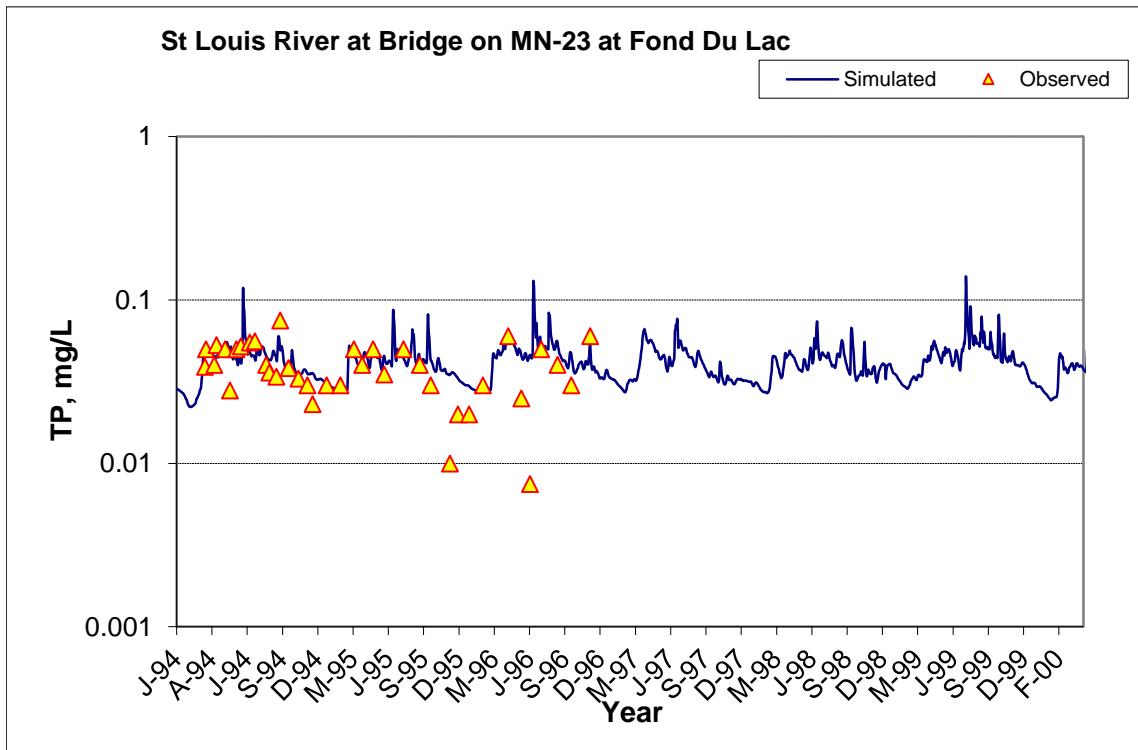


Figure A-195. Power plot of simulated and observed Total Phosphorus (TP) load vs flow at St Louis River at Bridge on MN-23 at Fond Du Lac (validation period)



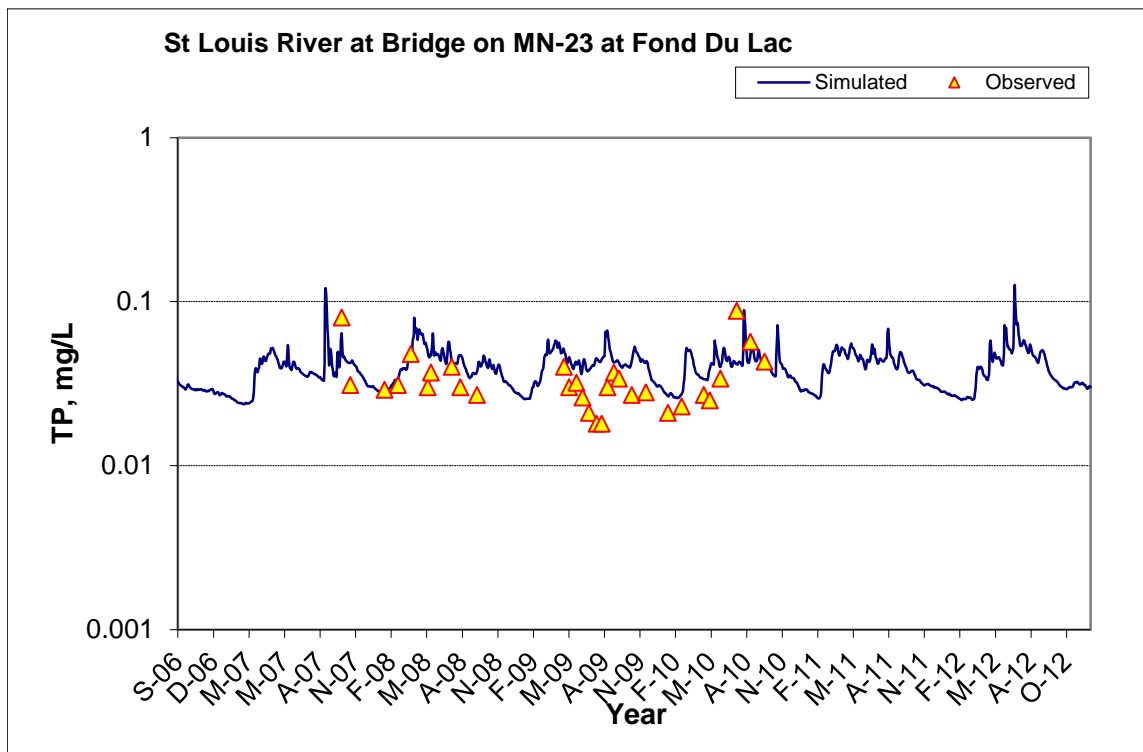


Figure A-196. Time series of observed and simulated Total Phosphorus (TP) concentration at St Louis River at Bridge on MN-23 at Fond Du Lac

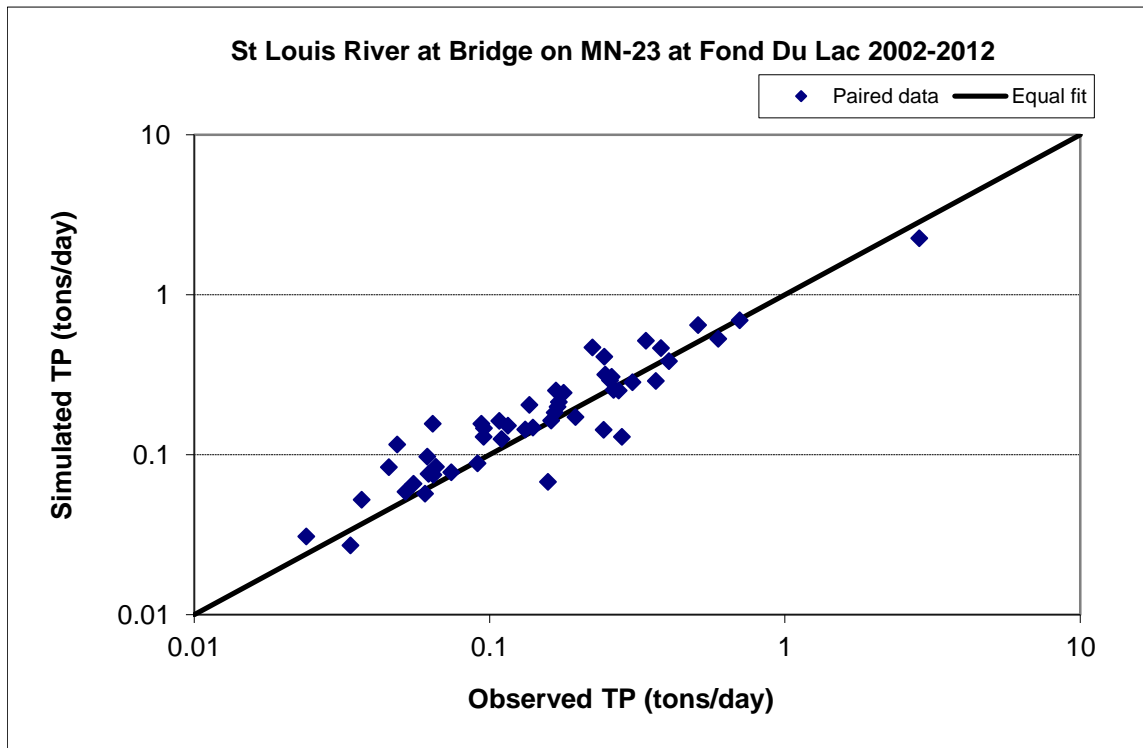


Figure A-197. Paired simulated vs. observed Total Phosphorus (TP) load at St Louis River at Bridge on MN-23 at Fond Du Lac (calibration period)

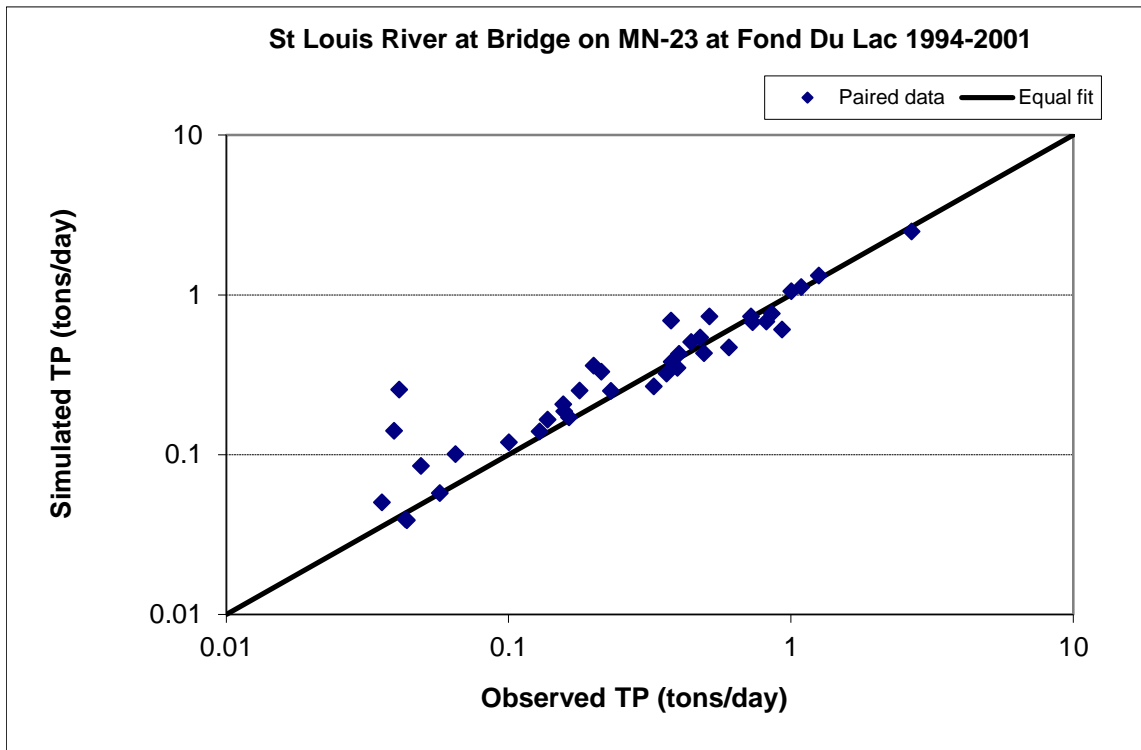


Figure A-198. Paired simulated vs. observed Total Phosphorus (TP) load at St Louis River at Bridge on MN-23 at Fond Du Lac (validation period)

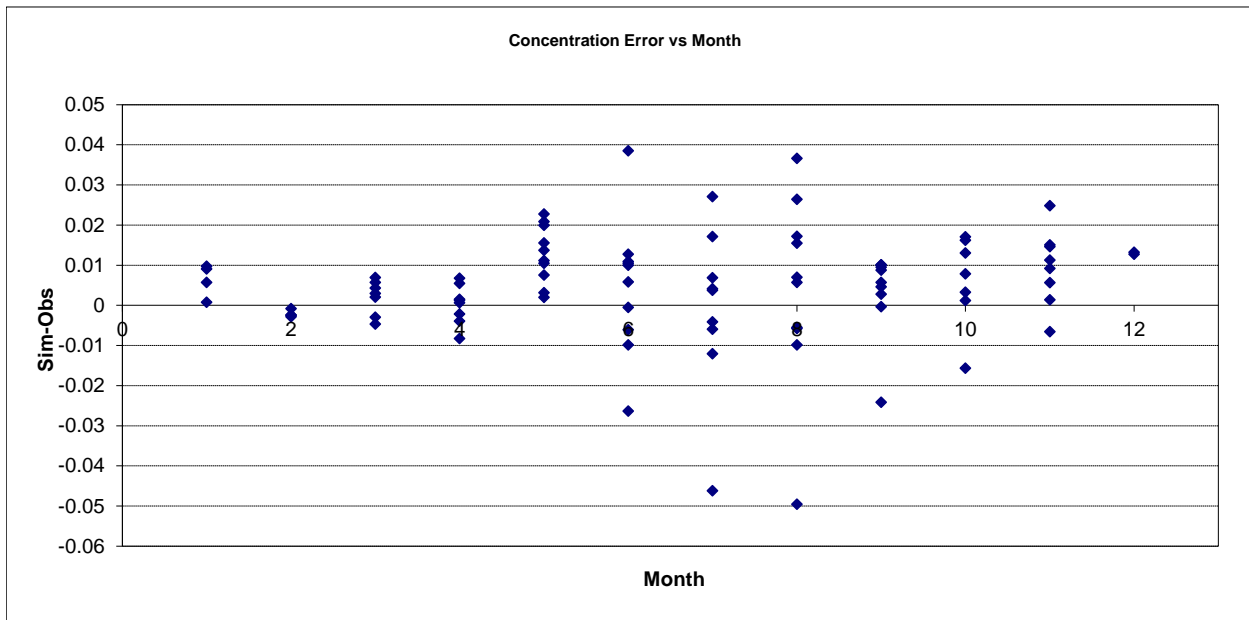


Figure A-199. Residual (Simulated - Observed) vs. Month Total Phosphorus (TP) at St Louis River at Bridge on MN-23 at Fond Du Lac

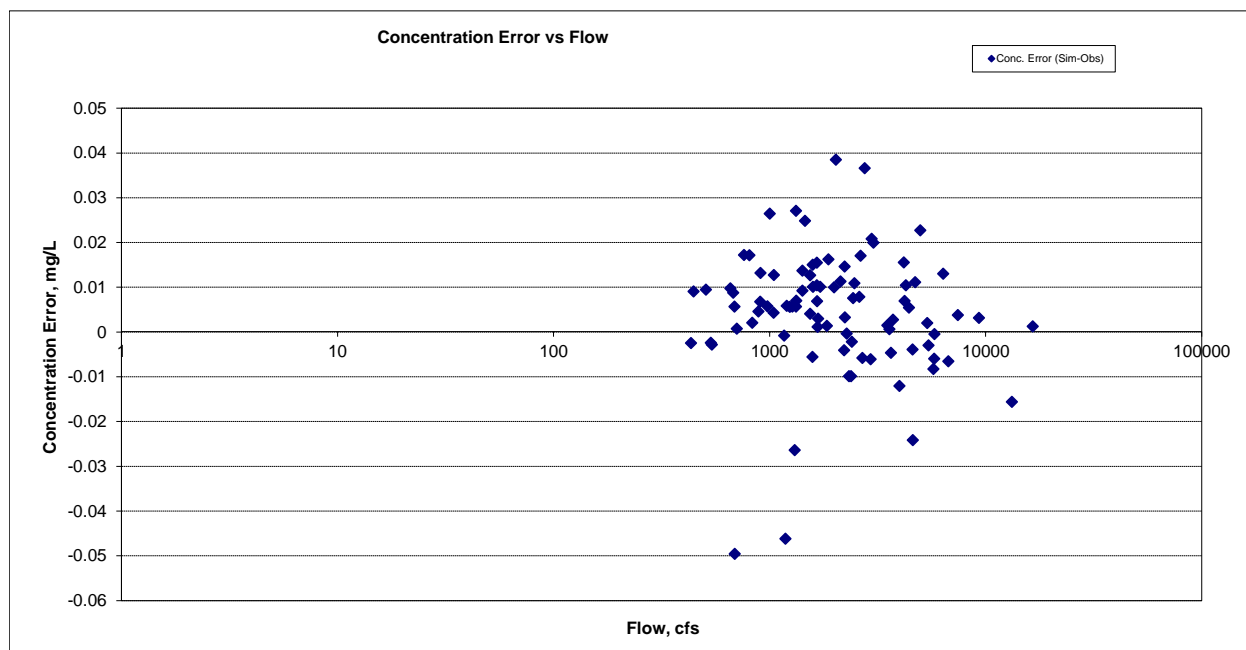


Figure A-200. Residual (Simulated - Observed) vs. Flow Total Phosphorus (TP) at St Louis River at Bridge on MN-23 at Fond Du Lac

A.7 CLOQUET RIVER NR BURNETT (04048001)

A.7.1 Ammonia Nitrogen (NH3)

Table A-29. Ammonia Nitrogen (NH3) statistics

Period	1994-2001	2002-2012
Count	13	18
Concentration Average Error	-58.42%	-17.03%
Concentration Median Error	-50.16%	-2.38%
Load Average Error	-57.17%	-19.43%
Load Median Error	-51.09%	-10.04%
Paired t conc	0.00	0.62
Paired t load	0.01	0.52

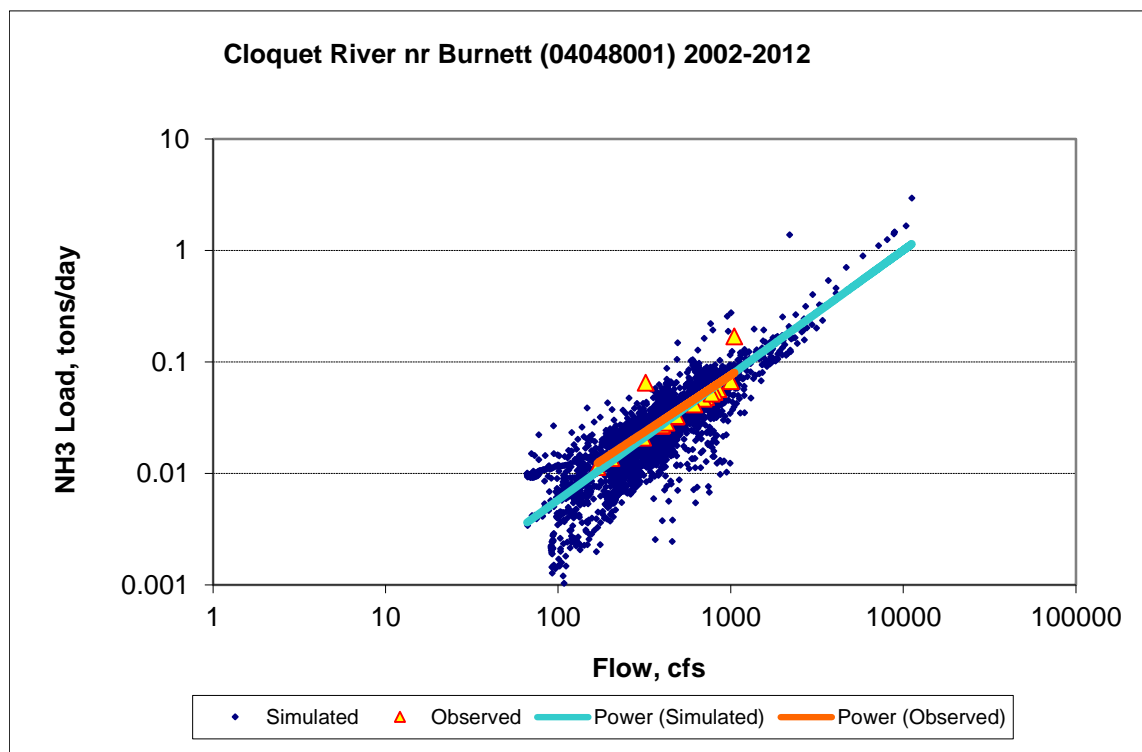


Figure A-201. Power plot of simulated and observed Ammonia Nitrogen (NH3) load vs flow at Cloquet River nr Burnett (04048001) (calibration period)

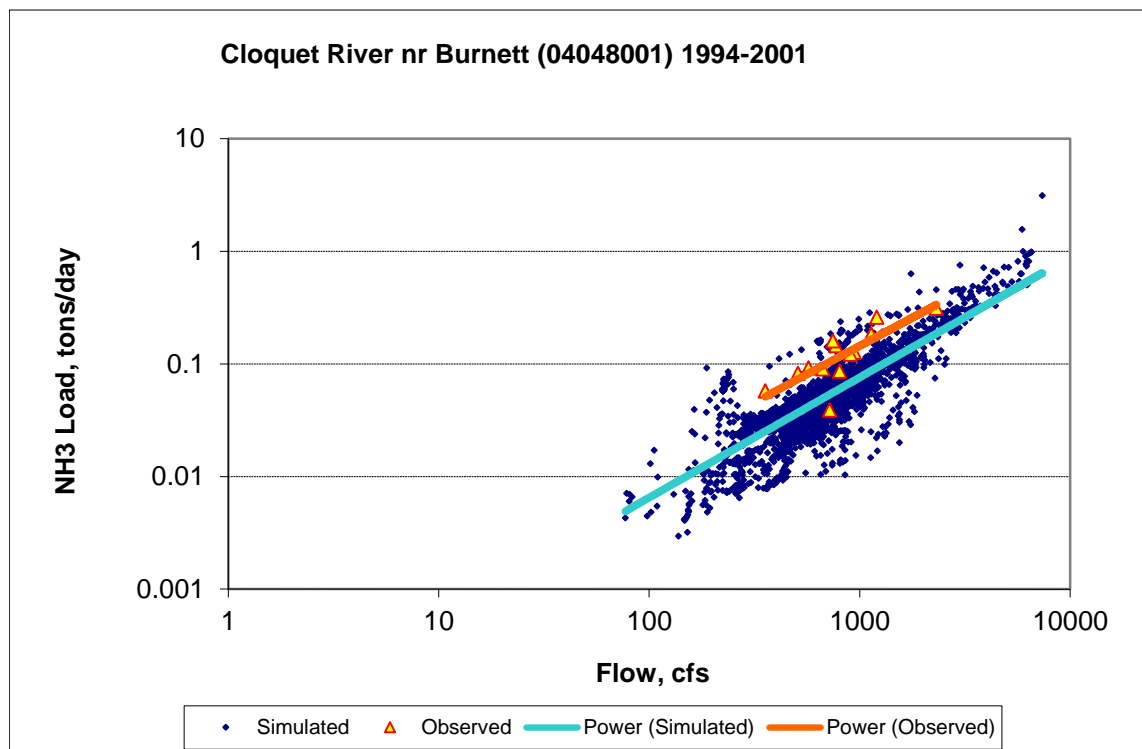
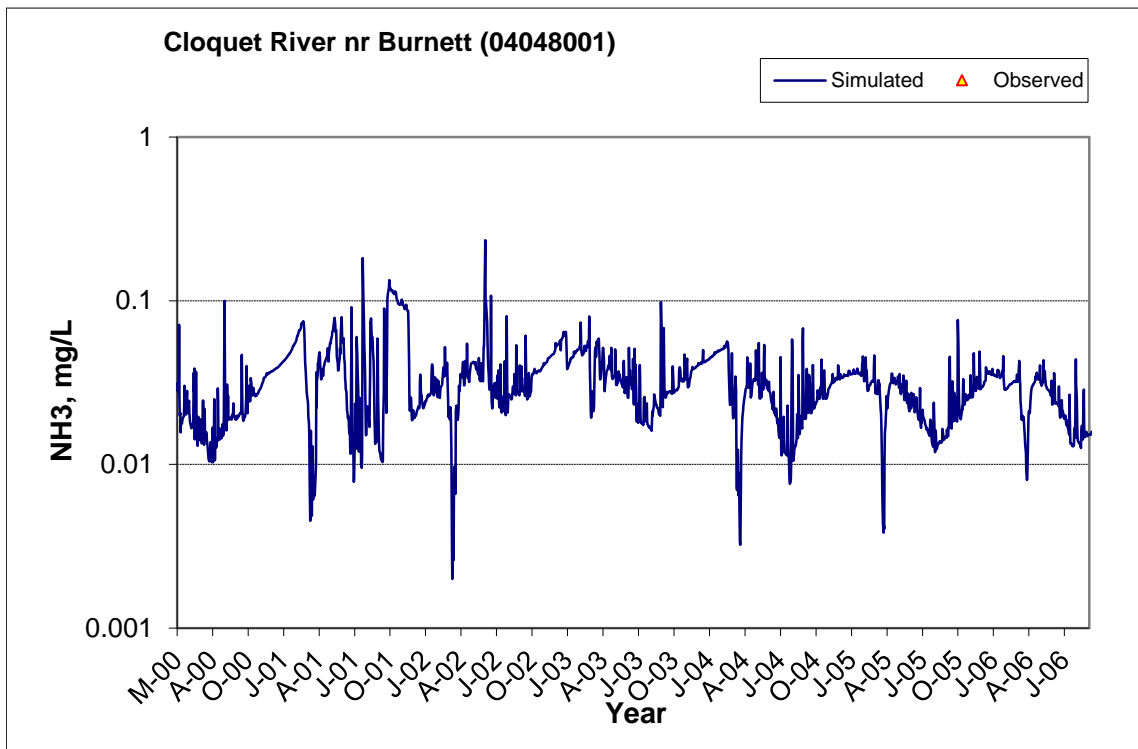
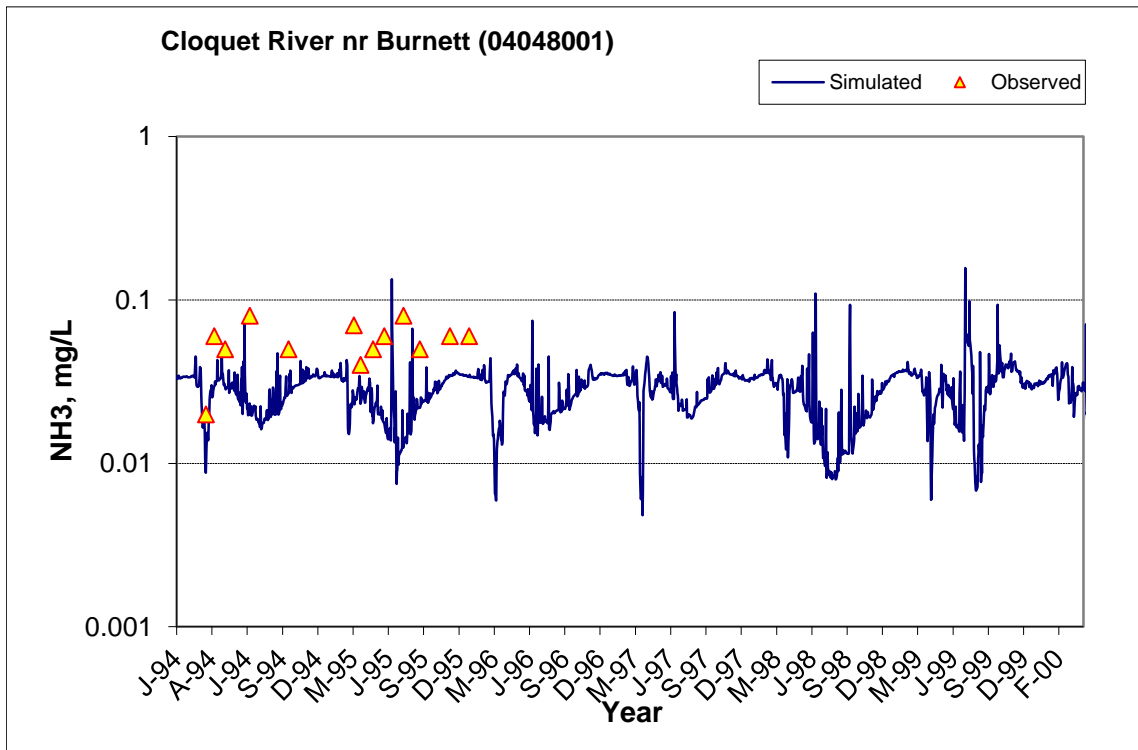


Figure A-202. Power plot of simulated and observed Ammonia Nitrogen (NH3) load vs flow at Cloquet River nr Burnett (04048001) (validation period)



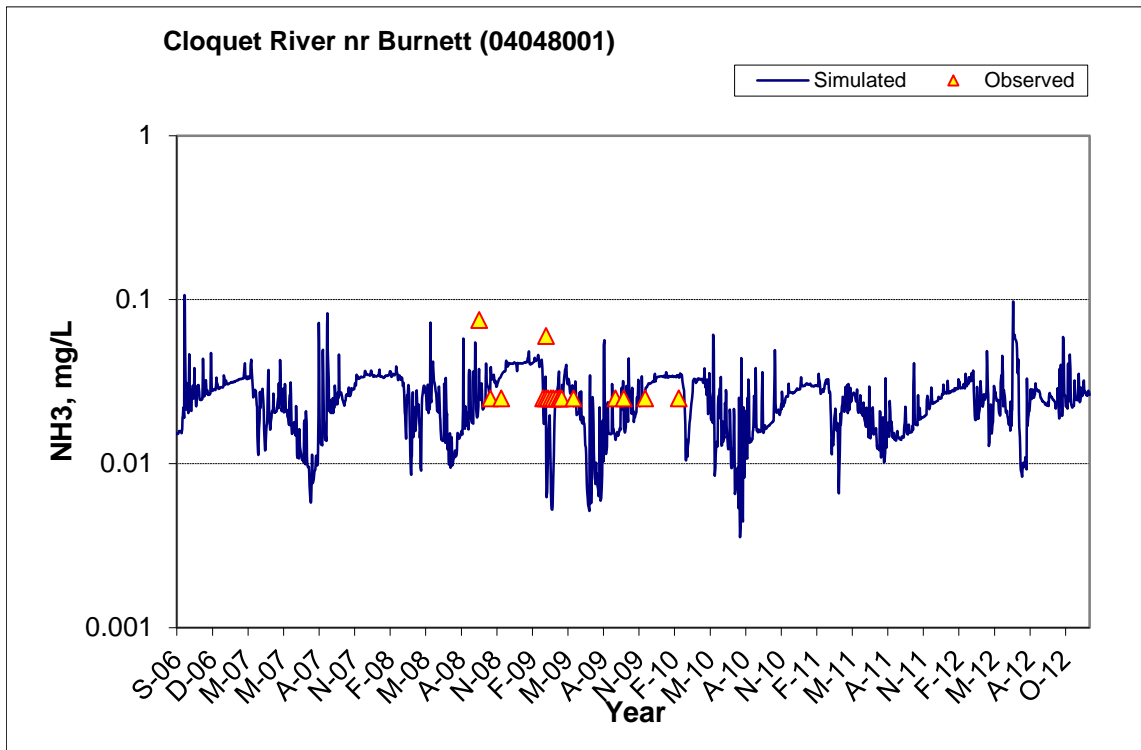


Figure A-203. Time series of observed and simulated Ammonia Nitrogen (NH₃) concentration at Cloquet River nr Burnett (04048001)

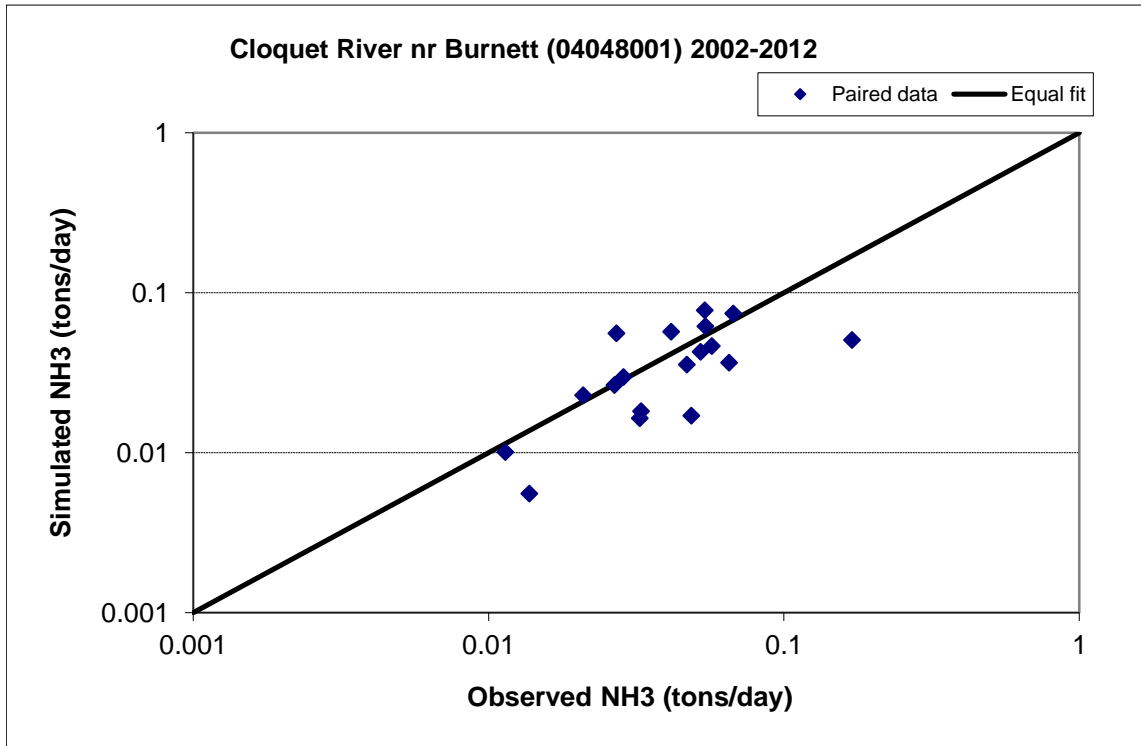


Figure A-204. Paired simulated vs. observed Ammonia Nitrogen (NH₃) load at Cloquet River nr Burnett (04048001) (calibration period)

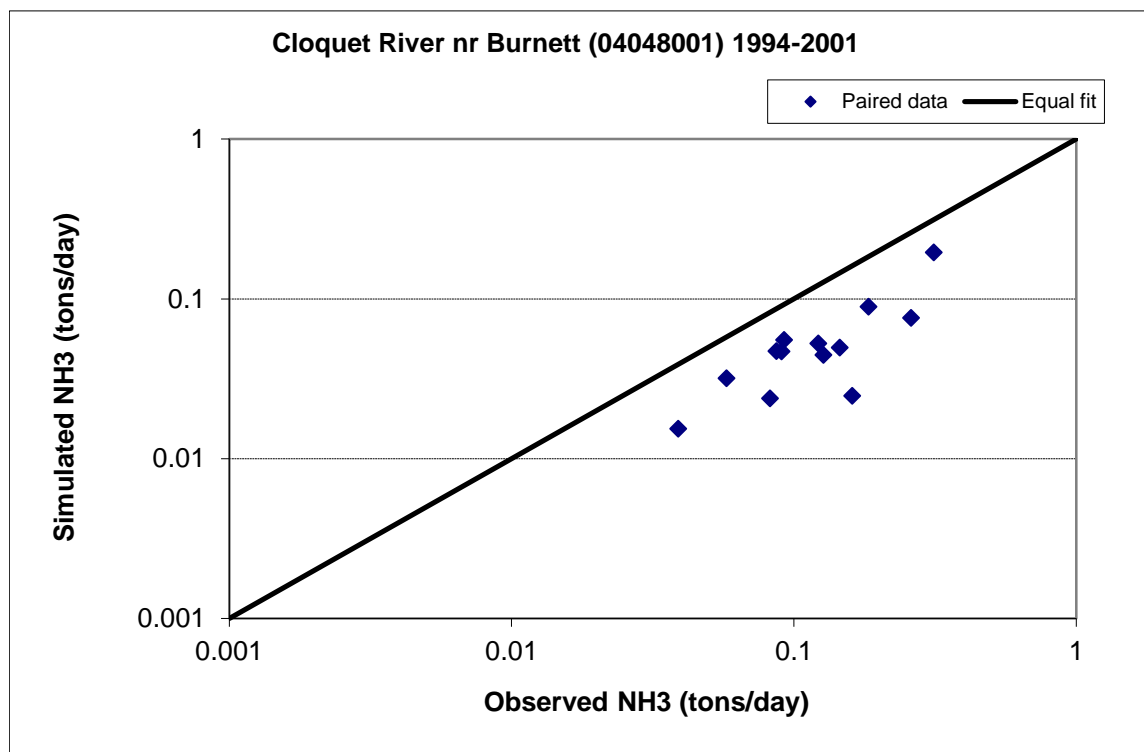


Figure A-205. Paired simulated vs. observed Ammonia Nitrogen (NH3) load at Cloquet River nr Burnett (04048001) (validation period)

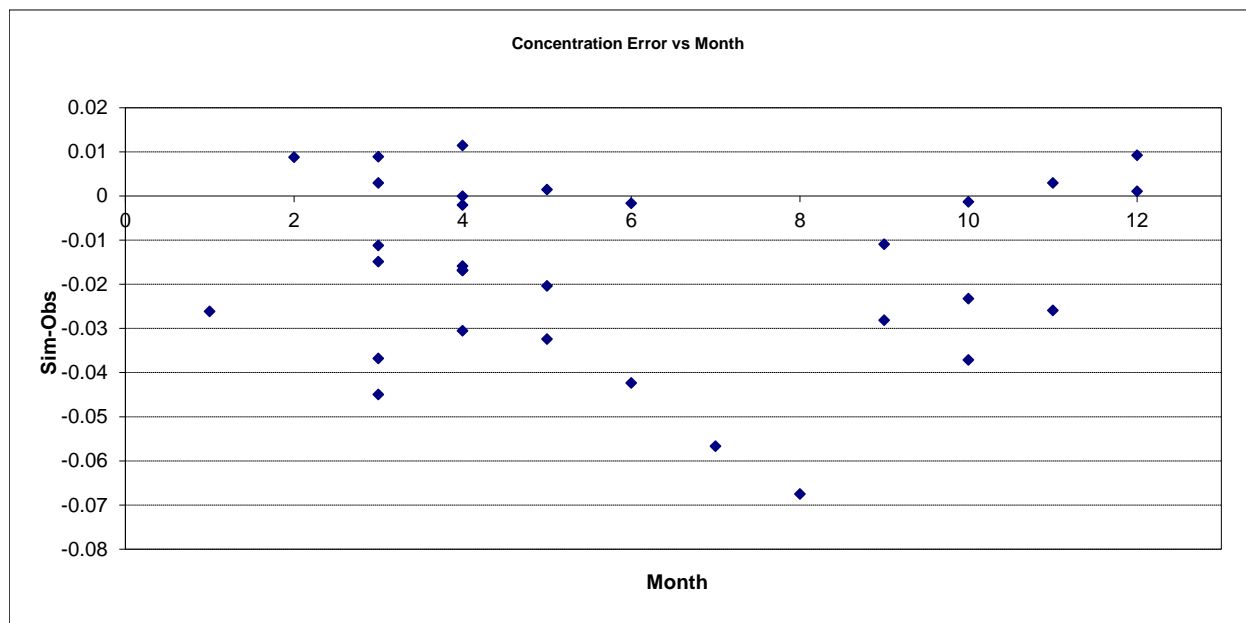


Figure A-206. Residual (Simulated - Observed) vs. Month Ammonia Nitrogen (NH3) at Cloquet River nr Burnett (04048001)

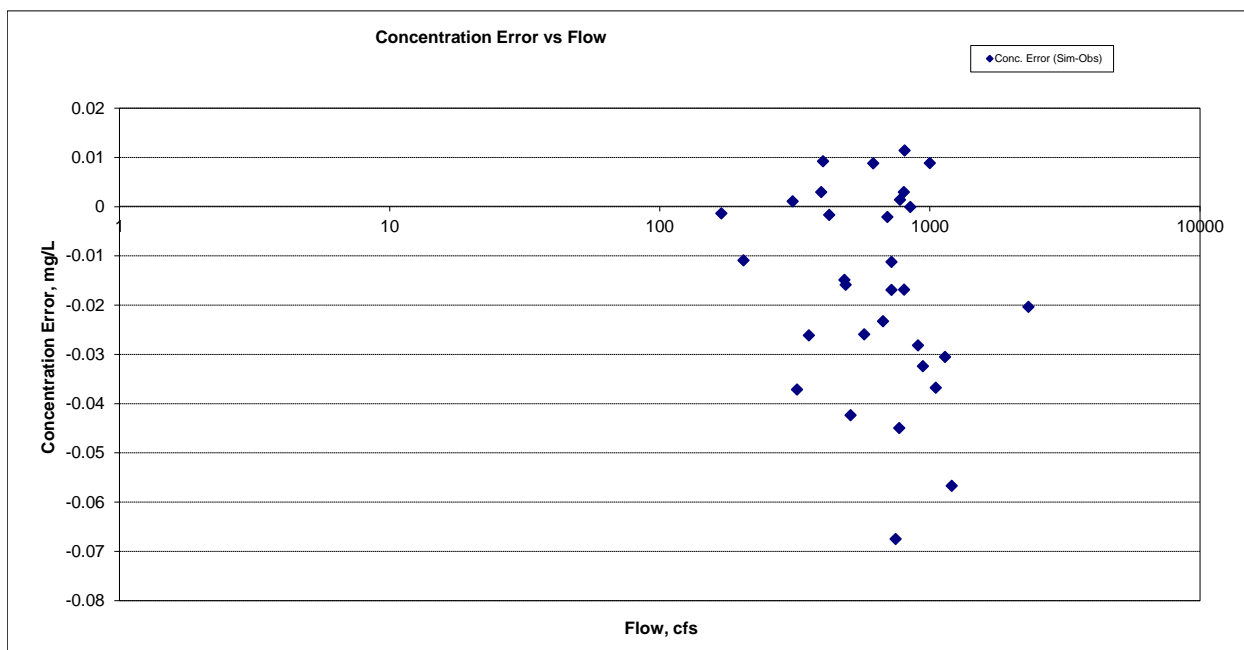
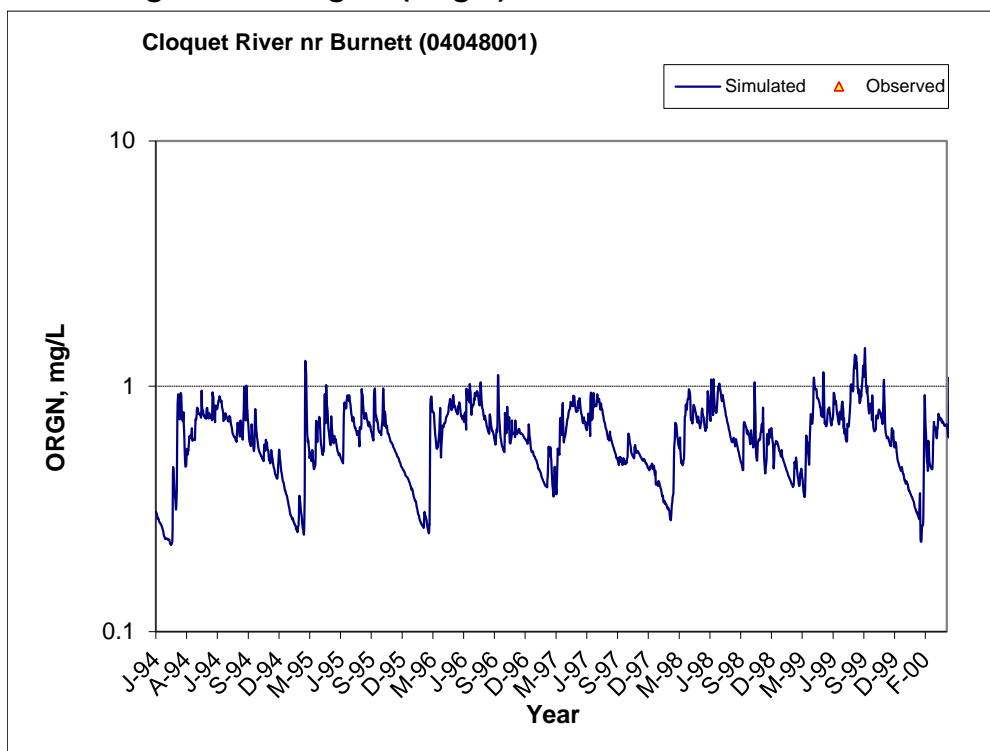


Figure A-207. Residual (Simulated - Observed) vs. Flow Ammonia Nitrogen (NH3) at Cloquet River nr Burnett (04048001)

A.7.2 Organic Nitrogen (OrgN)



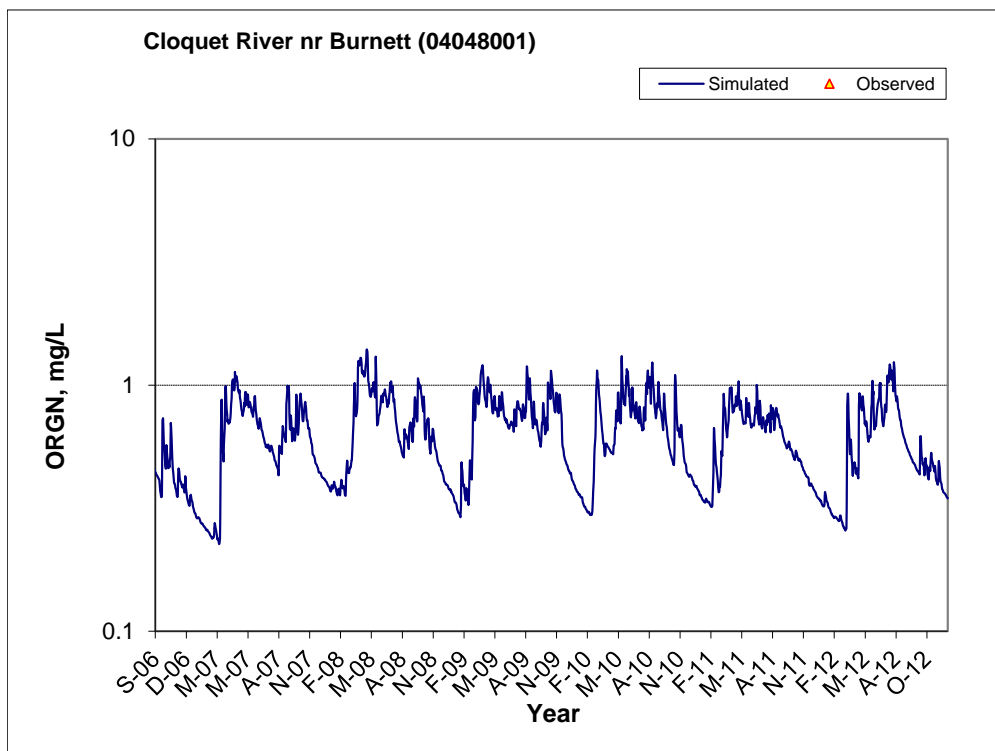
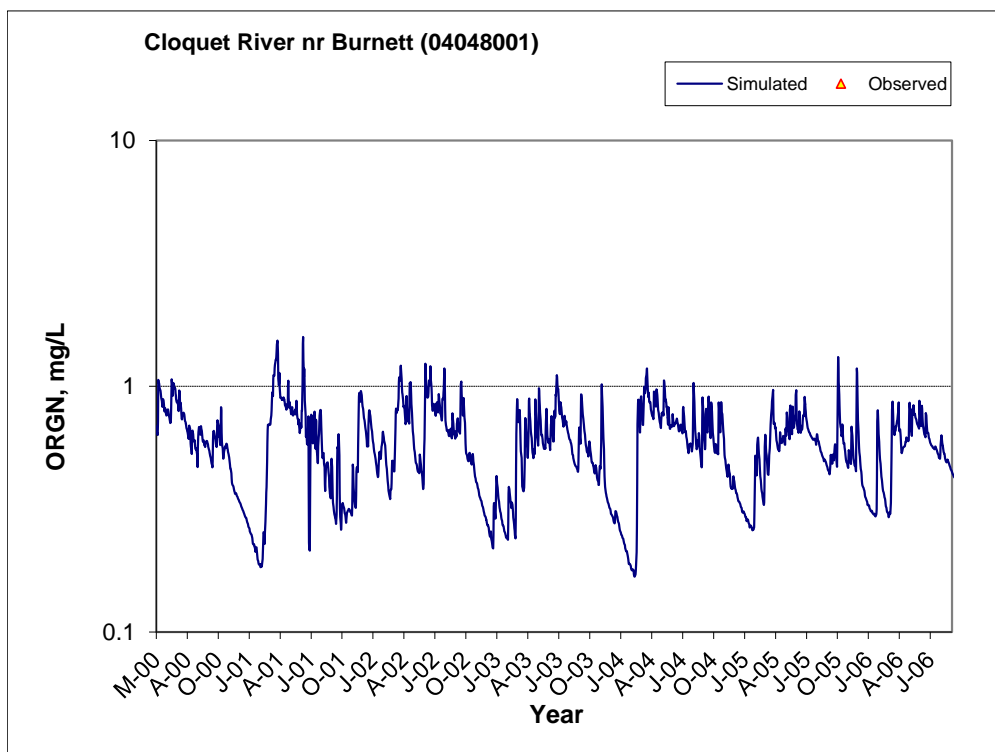


Figure A-208. Time series of observed and simulated Organic Nitrogen (OrgN) concentration at Cloquet River nr Burnett (04048001)

A.7.3 Total Kjeldahl Nitrogen (TKN)

Table A-30. Total Kjeldahl Nitrogen (TKN) statistics

Period	1994-2001	2002-2012
Count	ND	94
Concentration Average Error		10.87%
Concentration Median Error		13.29%
Load Average Error		-10.53%
Load Median Error		3.15%
Paired t conc		1.00
Paired t load		0.72

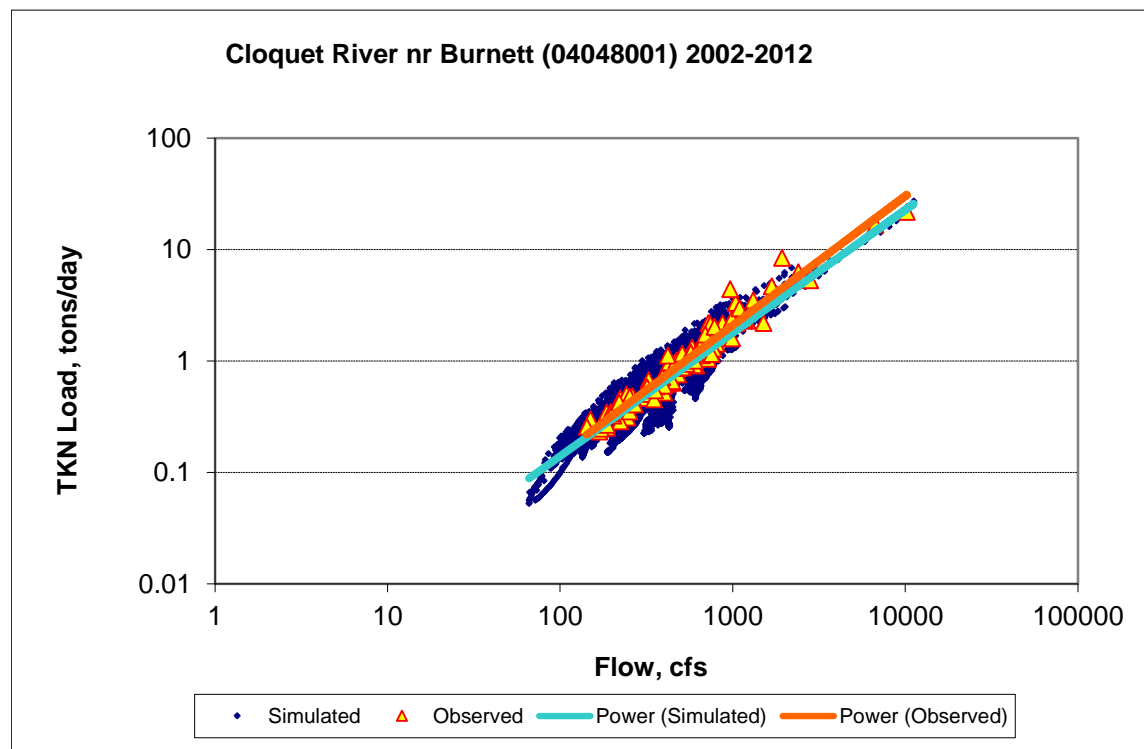
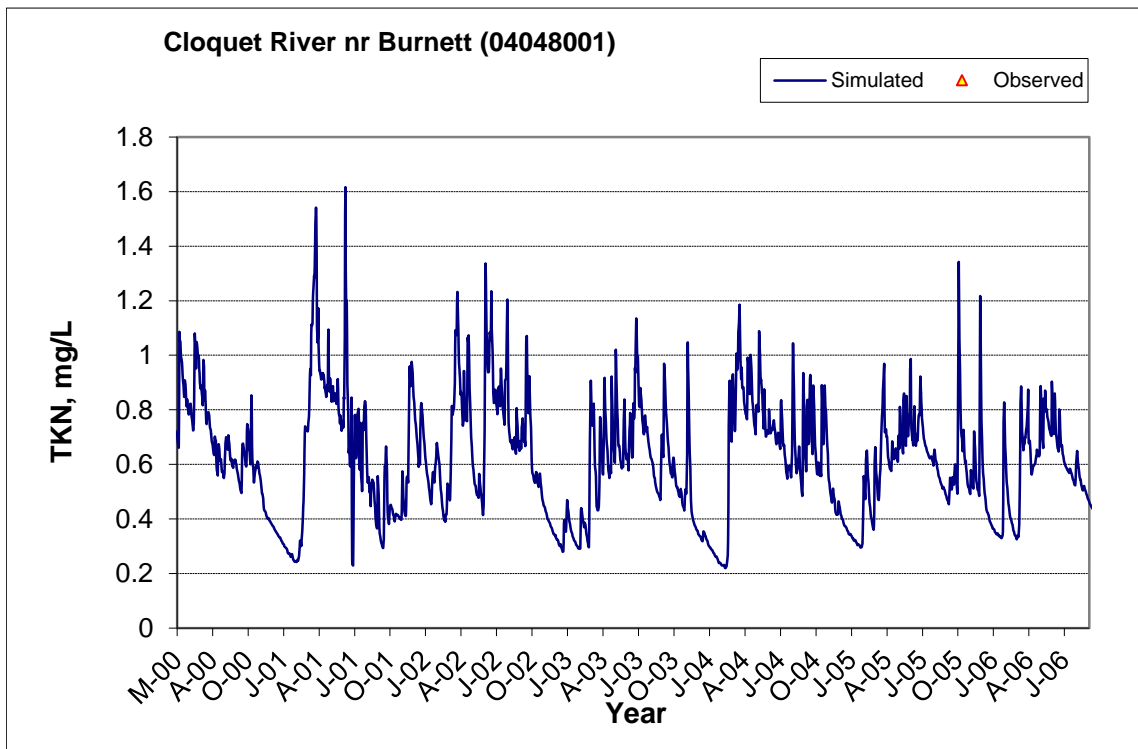
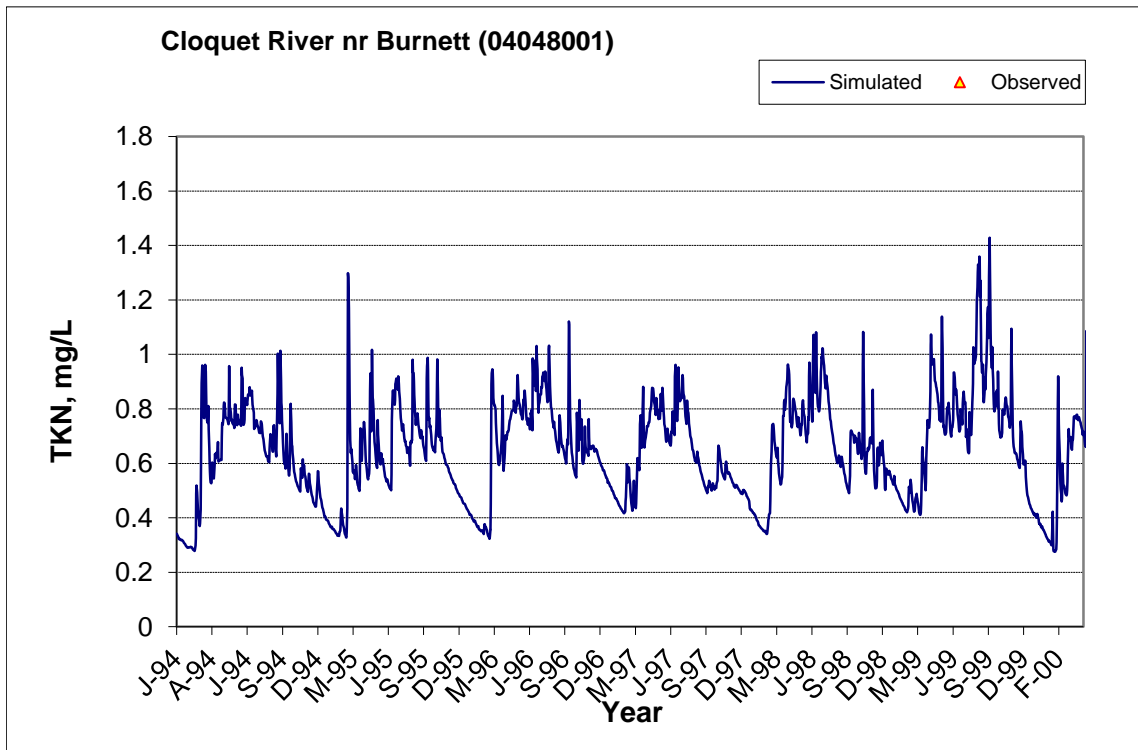


Figure A-209. Power plot of simulated and observed Total Kjeldahl Nitrogen (TKN) load vs flow at Cloquet River nr Burnett (04048001) (calibration period)



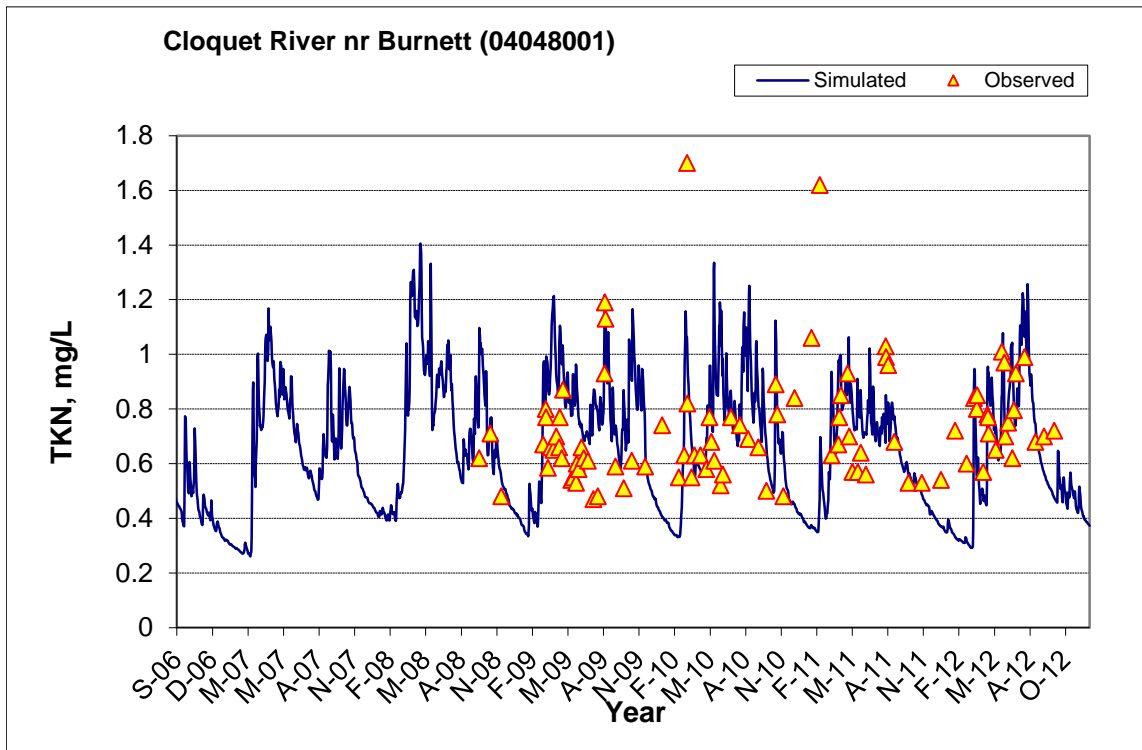


Figure A-210. Time series of observed and simulated Total Kjeldahl Nitrogen (TKN) concentration at Cloquet River nr Burnett (04048001)

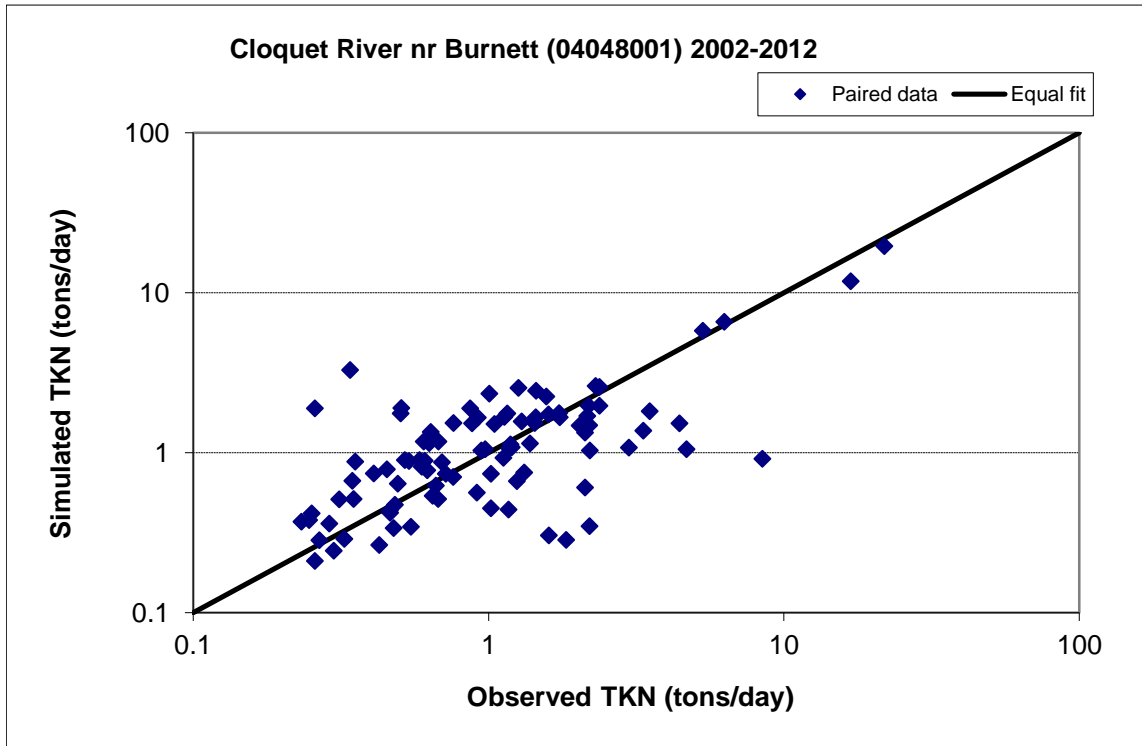


Figure A-211. Paired simulated vs. observed Total Kjeldahl Nitrogen (TKN) load at Cloquet River nr Burnett (04048001) (calibration period)

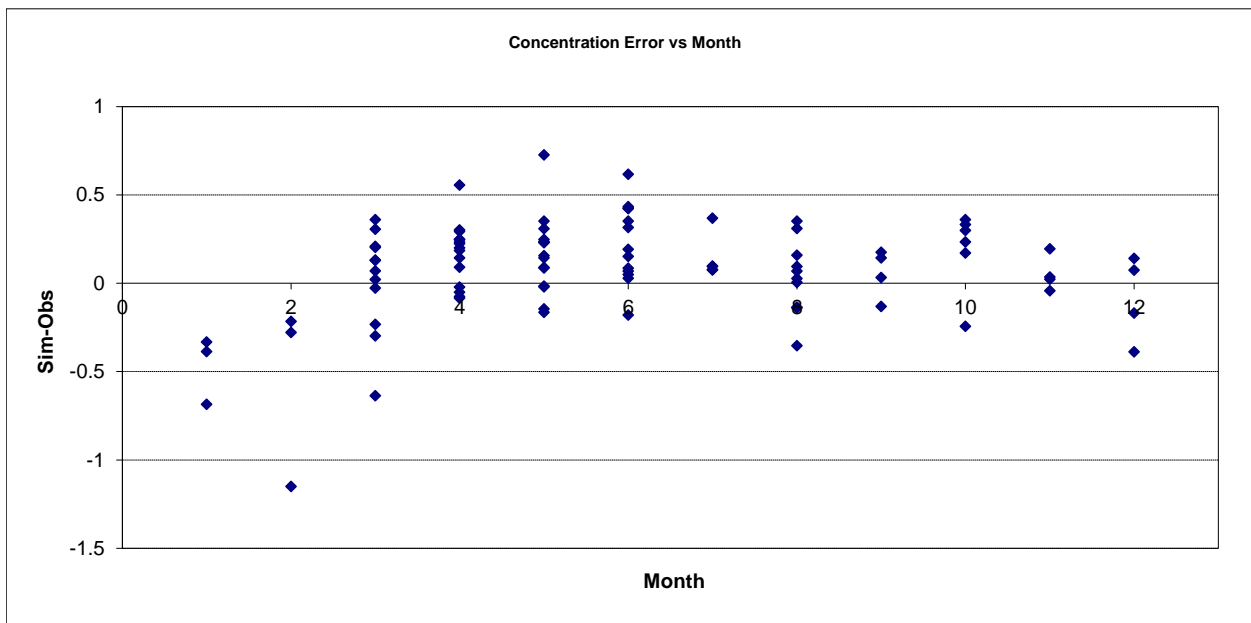


Figure A-212. Residual (Simulated - Observed) vs. Month Total Kjeldahl Nitrogen (TKN) at Cloquet River nr Burnett (04048001)

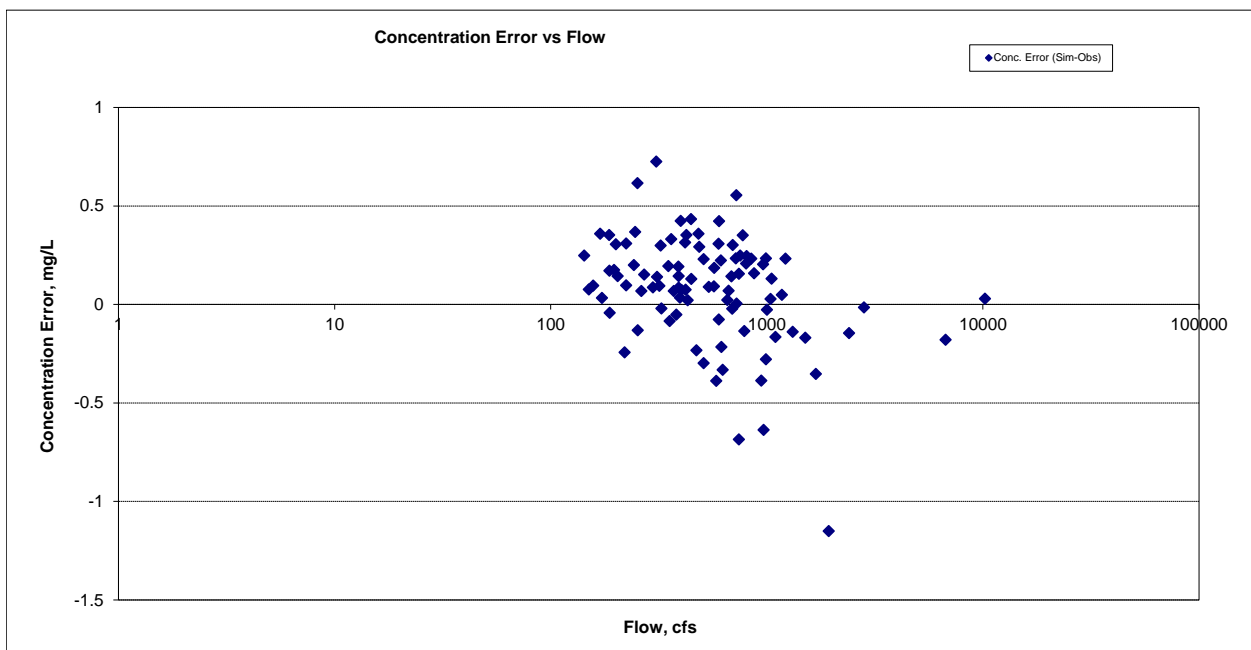


Figure A-213. Residual (Simulated - Observed) vs. Flow Total Kjeldahl Nitrogen (TKN) at Cloquet River nr Burnett (04048001)

A.7.4 Nitrite+ Nitrate Nitrogen (NOx)

Table A-31. Nitrite+ Nitrate Nitrogen (NOx) statistics

Period	1994-2001	2002-2012
Count	ND	94
Concentration Average Error		34.10%
Concentration Median Error		46.16%
Load Average Error		3.29%
Load Median Error		18.11%
Paired t conc		0.01
Paired t load		0.80

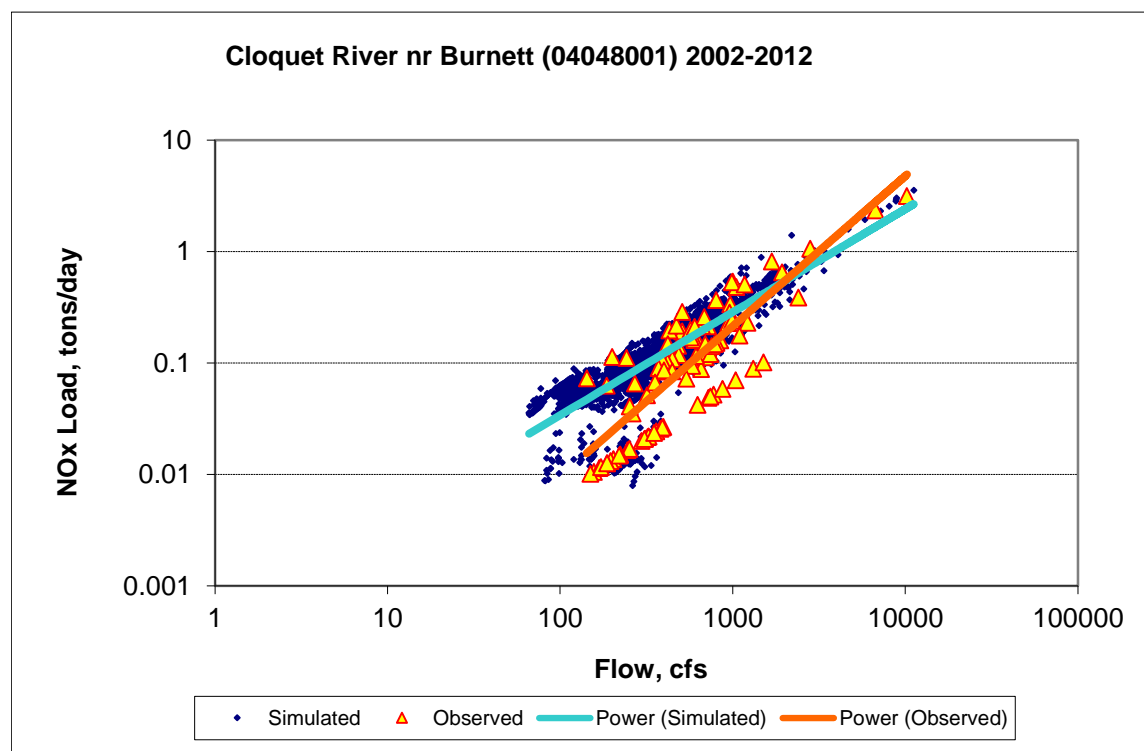
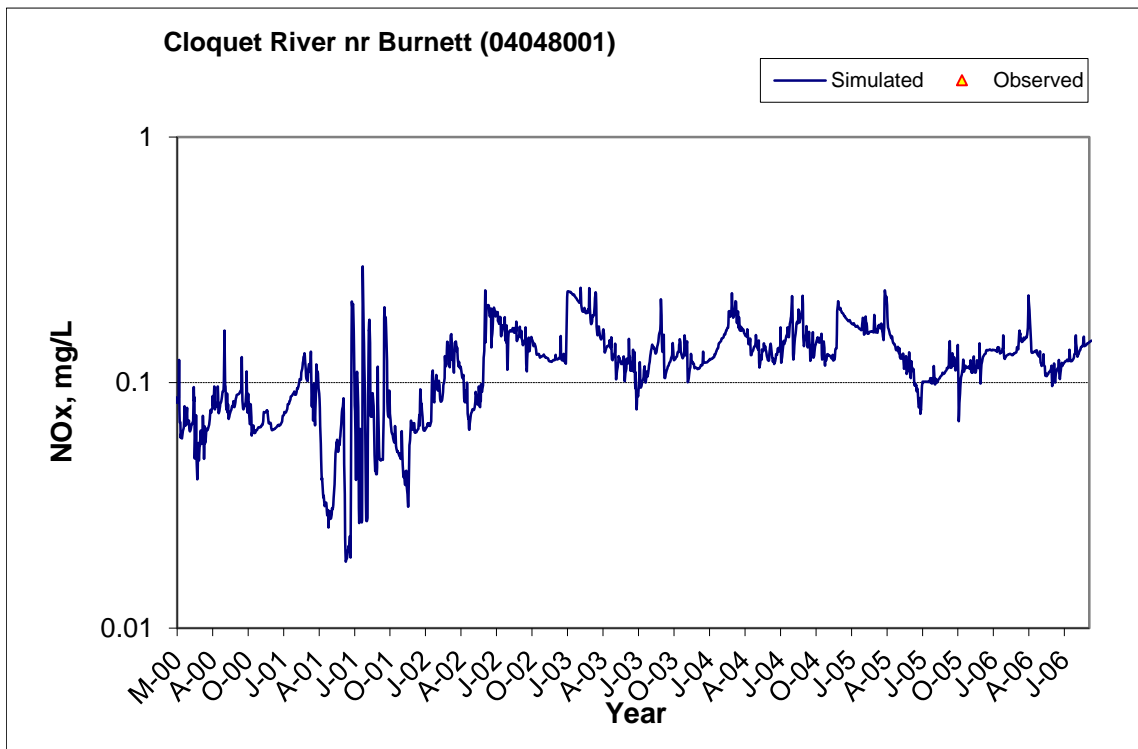
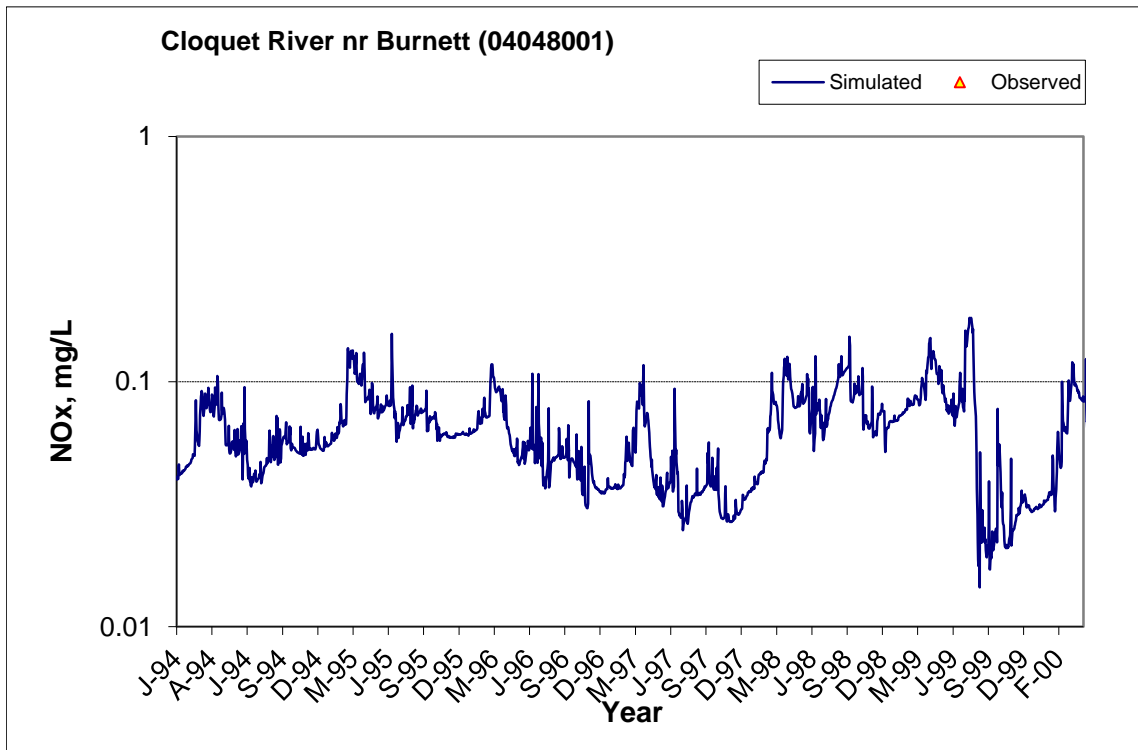


Figure A-214. Power plot of simulated and observed Nitrite+ Nitrate Nitrogen (NOx) load vs flow at Cloquet River nr Burnett (04048001) (calibration period)



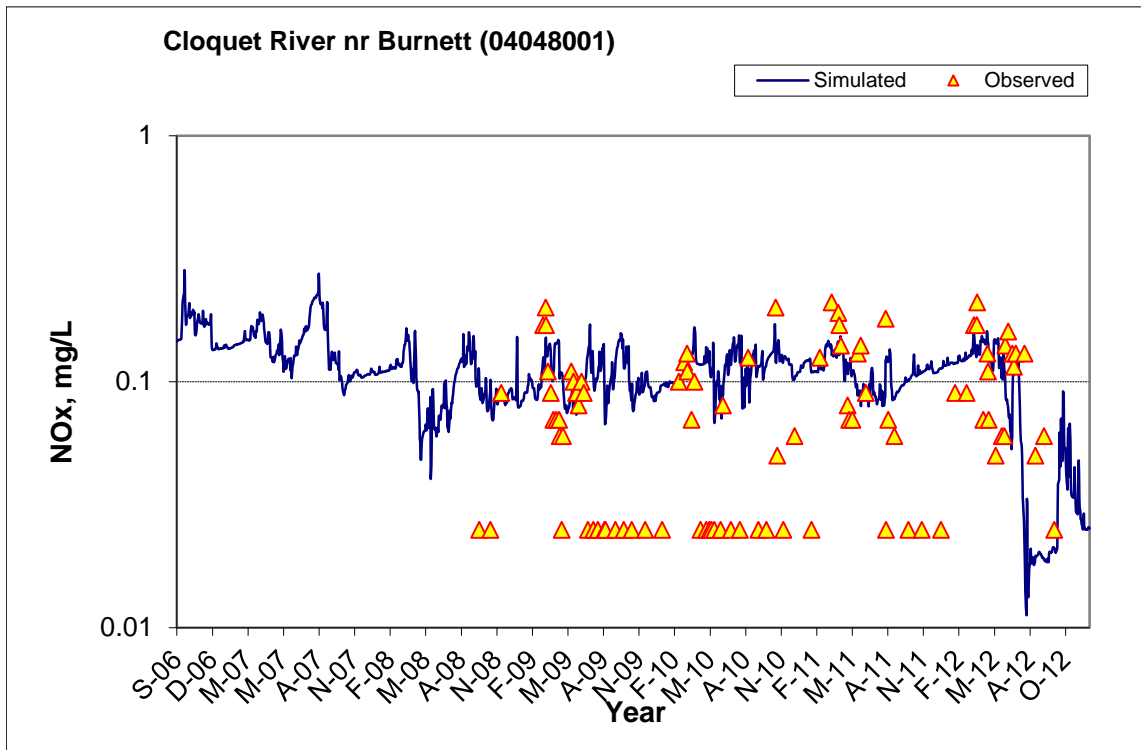


Figure A-215. Time series of observed and simulated Nitrite+ Nitrate Nitrogen (NOx) concentration at Cloquet River nr Burnett (04048001)

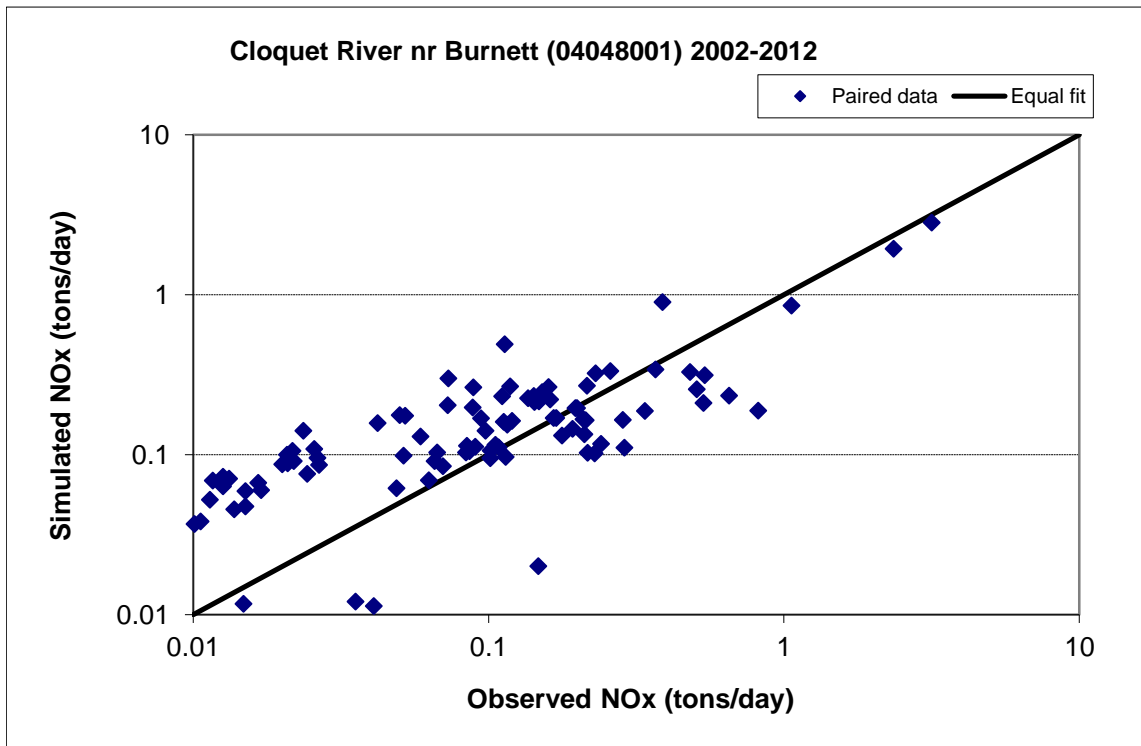


Figure A-216. Paired simulated vs. observed Nitrite+ Nitrate Nitrogen (NOx) load at Cloquet River nr Burnett (04048001) (calibration period)

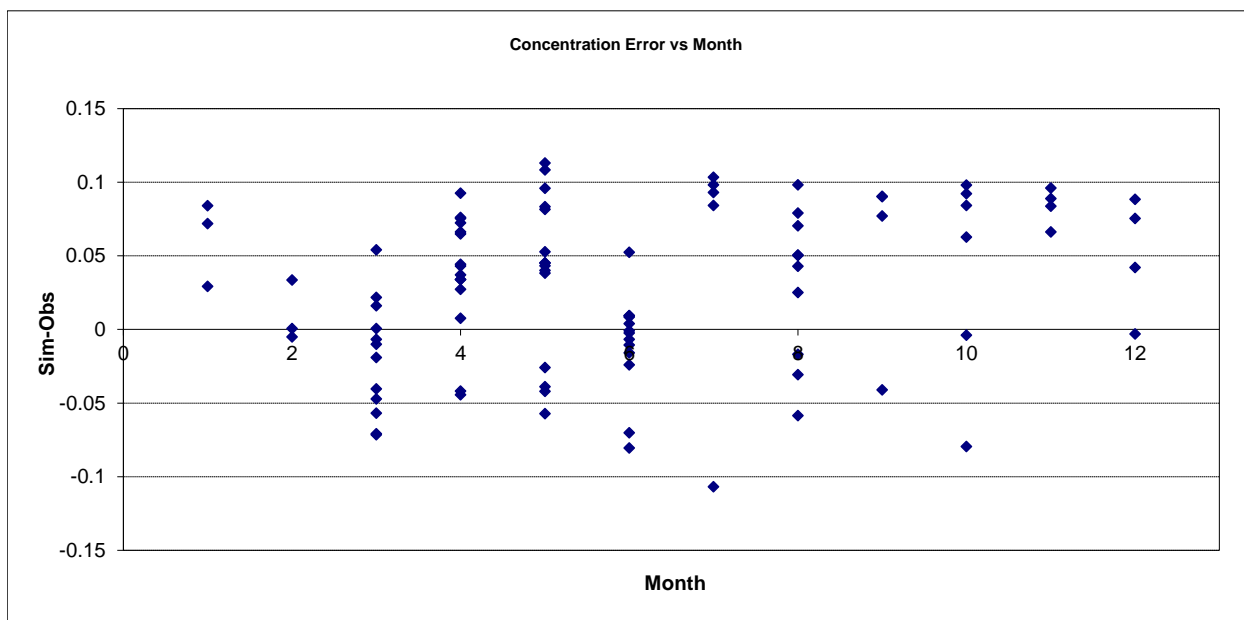


Figure A-217. Residual (Simulated - Observed) vs. Month Nitrite+ Nitrate Nitrogen (NOx) at Cloquet River nr Burnett (04048001)

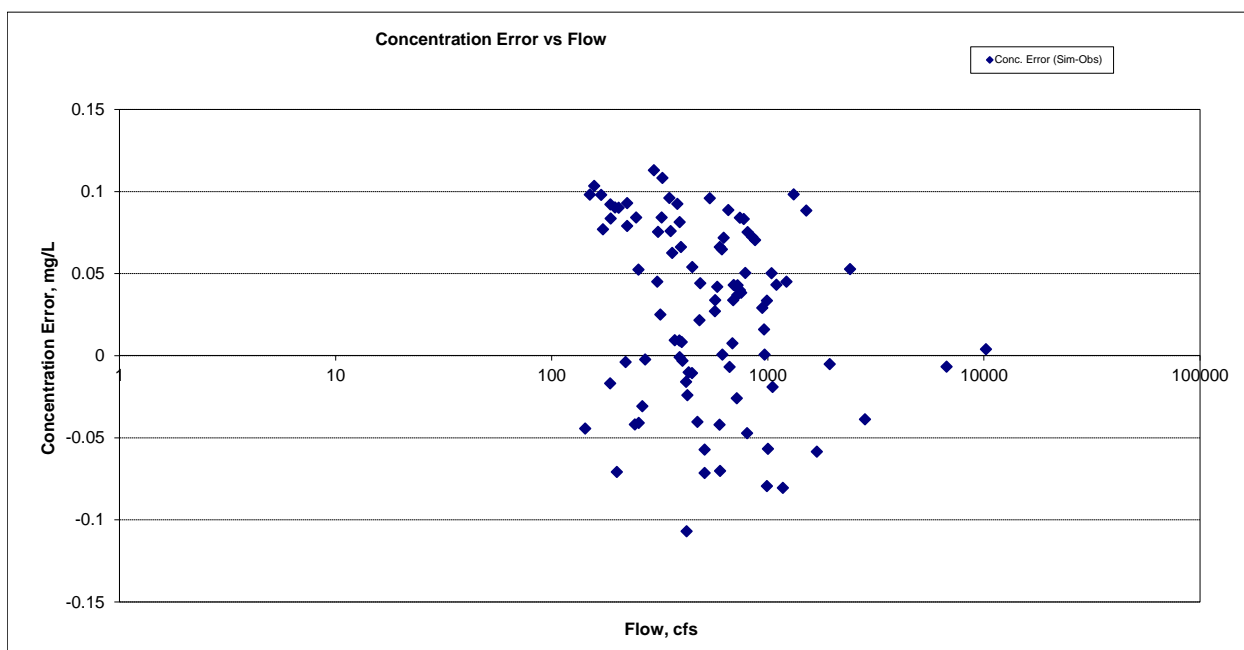


Figure A-218. Residual (Simulated - Observed) vs. Flow Nitrite+ Nitrate Nitrogen (NOx) at Cloquet River nr Burnett (04048001)

A.7.5 Total Nitrogen (TN)

Table A-32. Total Nitrogen (TN) statistics

Period	1994-2001	2002-2012
Count	ND	94
Concentration Average Error		11.71%
Concentration Median Error		18.60%
Load Average Error		-9.86%
Load Median Error		3.74%
Paired t conc		1.00
Paired t load		0.73

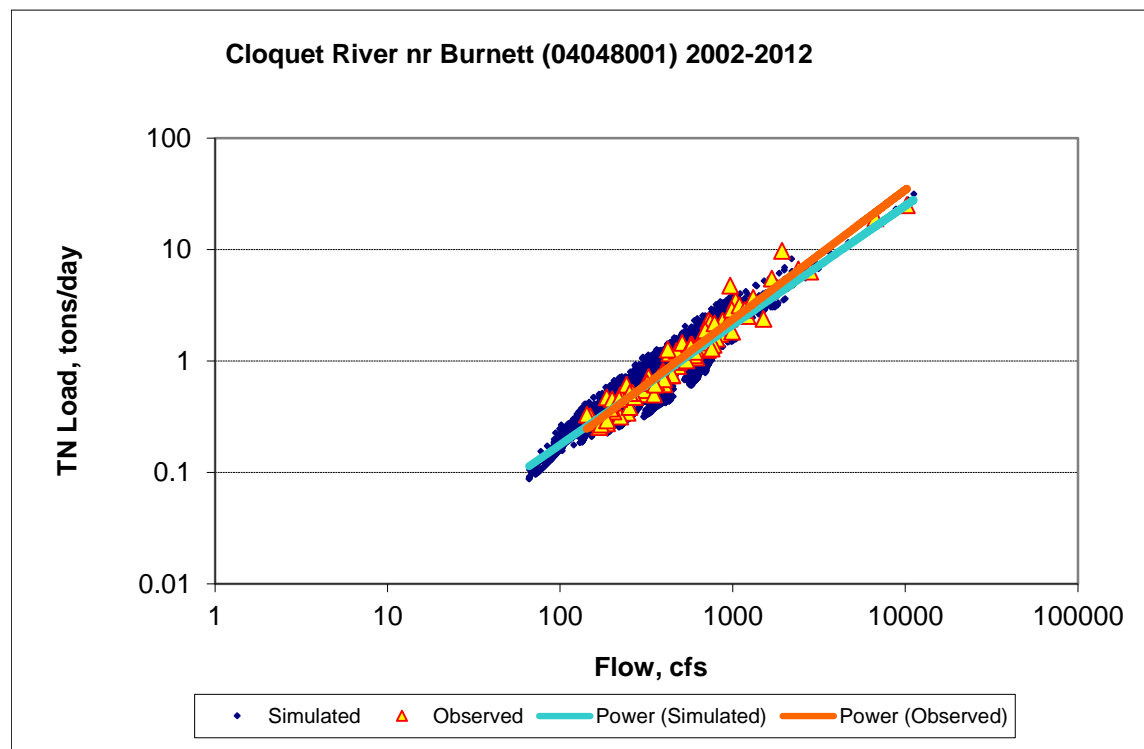
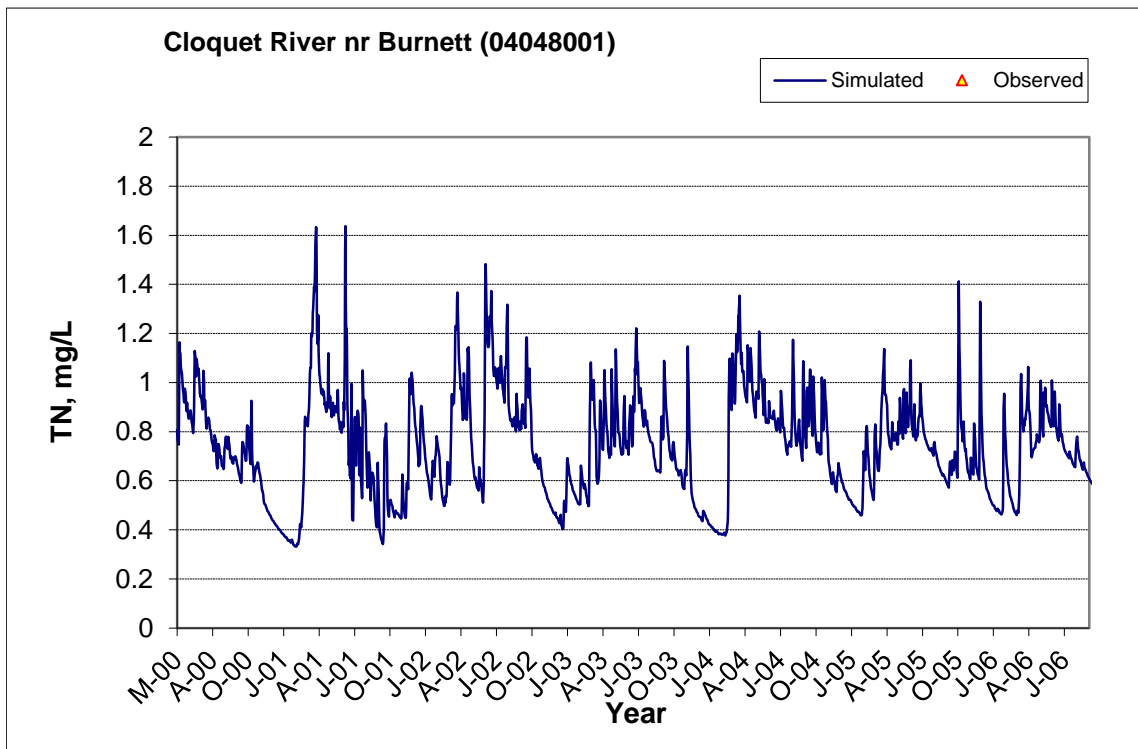
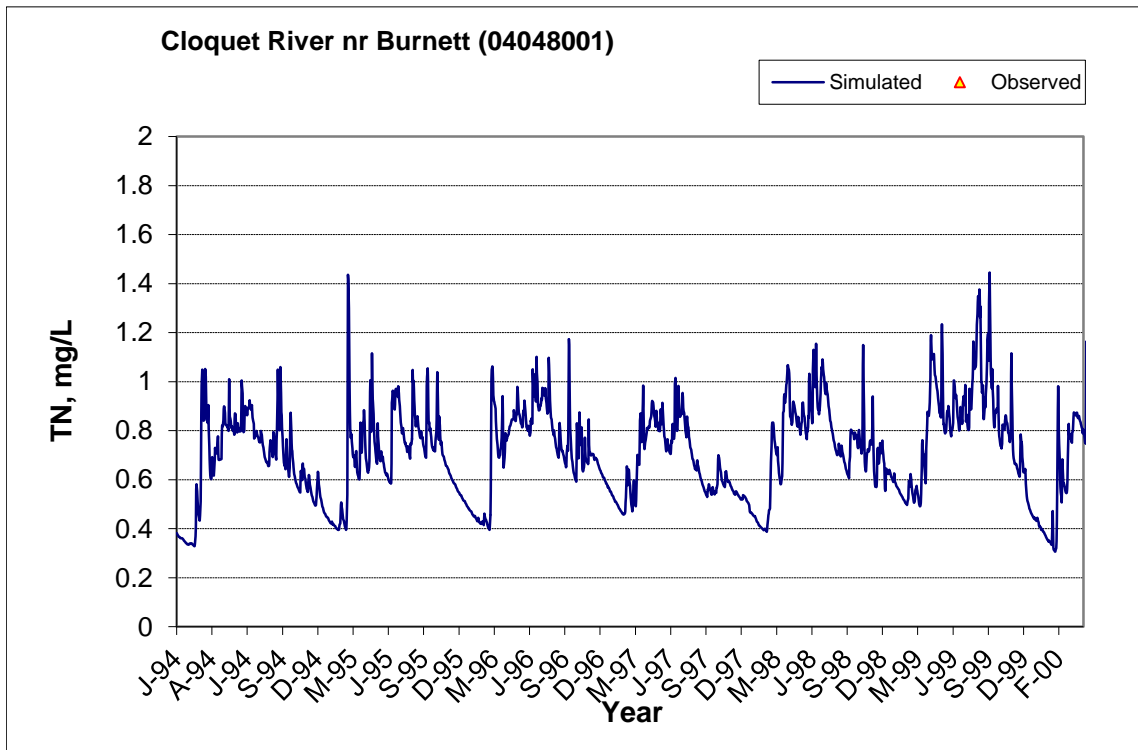


Figure A-219. Power plot of simulated and observed Total Nitrogen (TN) load vs flow at Cloquet River nr Burnett (04048001) (calibration period)



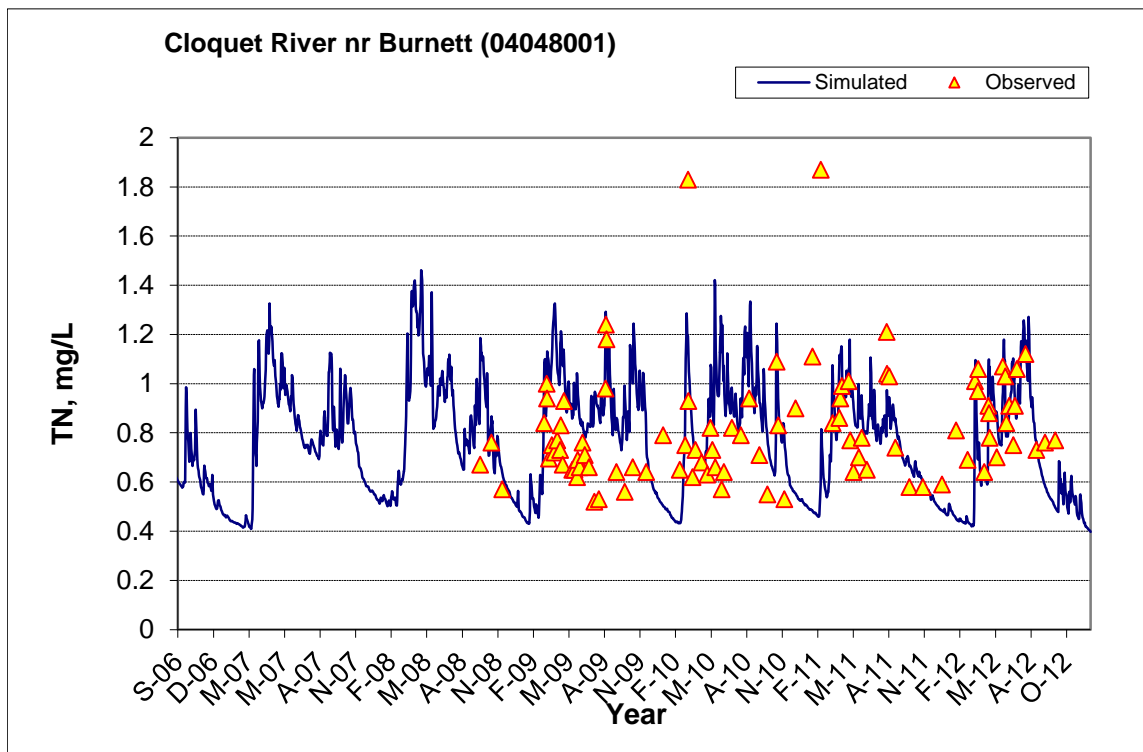


Figure A-220. Time series of observed and simulated Total Nitrogen (TN) concentration at Cloquet River nr Burnett (04048001)

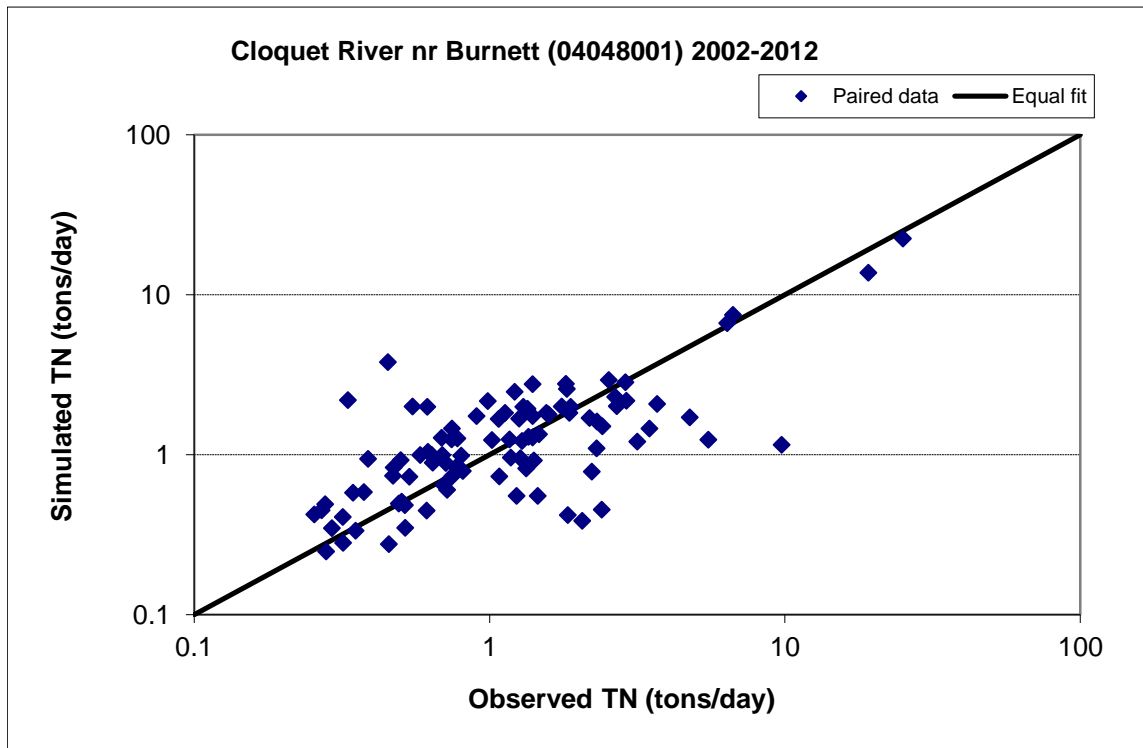


Figure A-221. Paired simulated vs. observed Total Nitrogen (TN) load at Cloquet River nr Burnett (04048001) (calibration period)

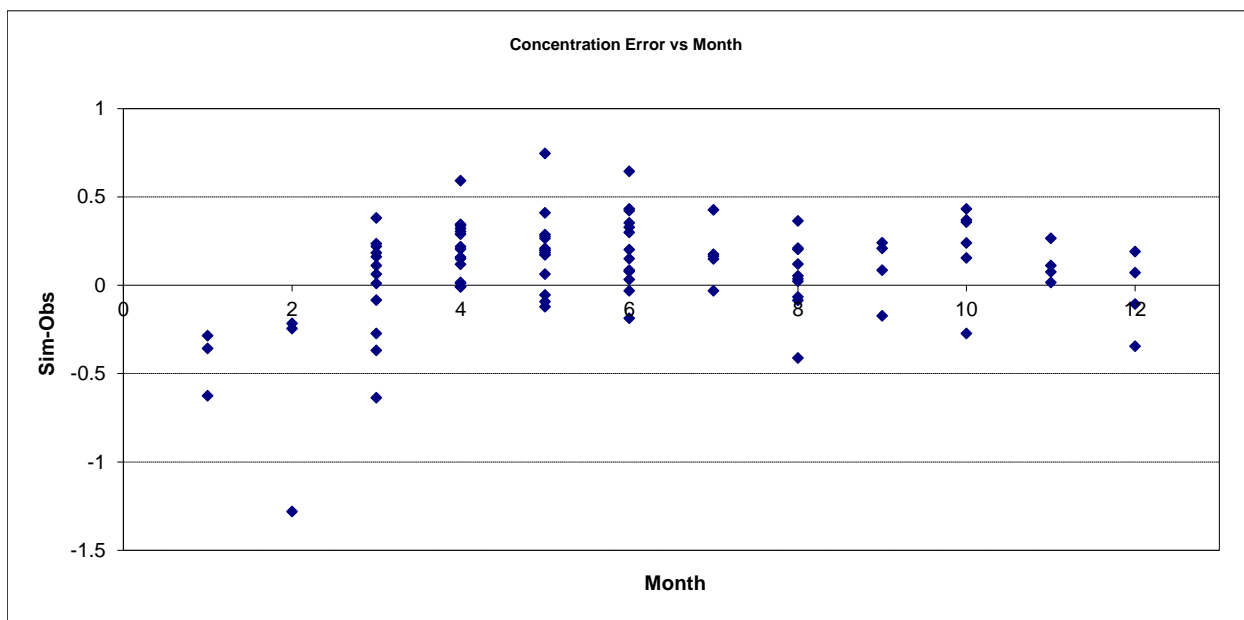


Figure A-222. Residual (Simulated - Observed) vs. Month Total Nitrogen (TN) at Cloquet River nr Burnett (04048001)

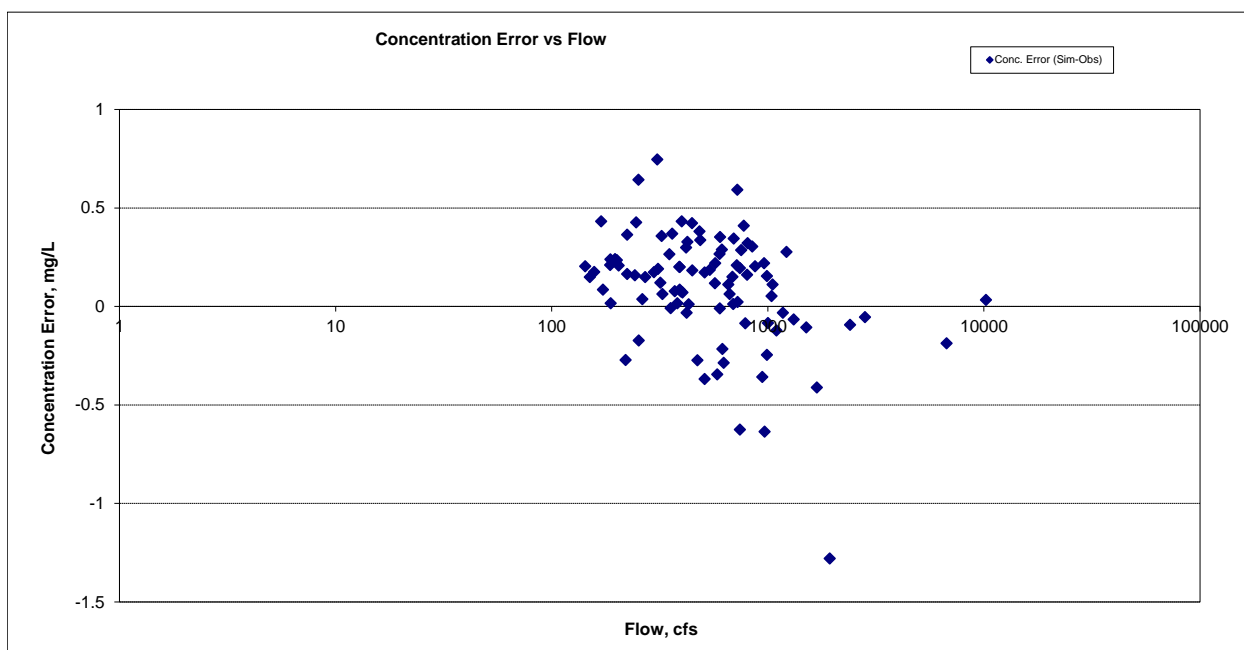


Figure A-223. Residual (Simulated - Observed) vs. Flow Total Nitrogen (TN) at Cloquet River nr Burnett (04048001)

A.7.6 Soluble Reactive Phosphorus (SRP)

Table A-33. Soluble Reactive Phosphorus (SRP) statistics

Period	1994-2001	2002-2012
Count	ND	91
Concentration Average Error		-36.73%
Concentration Median Error		-47.96%
Load Average Error		-16.43%
Load Median Error		-13.91%
Paired t conc		0.00
Paired t load		0.55

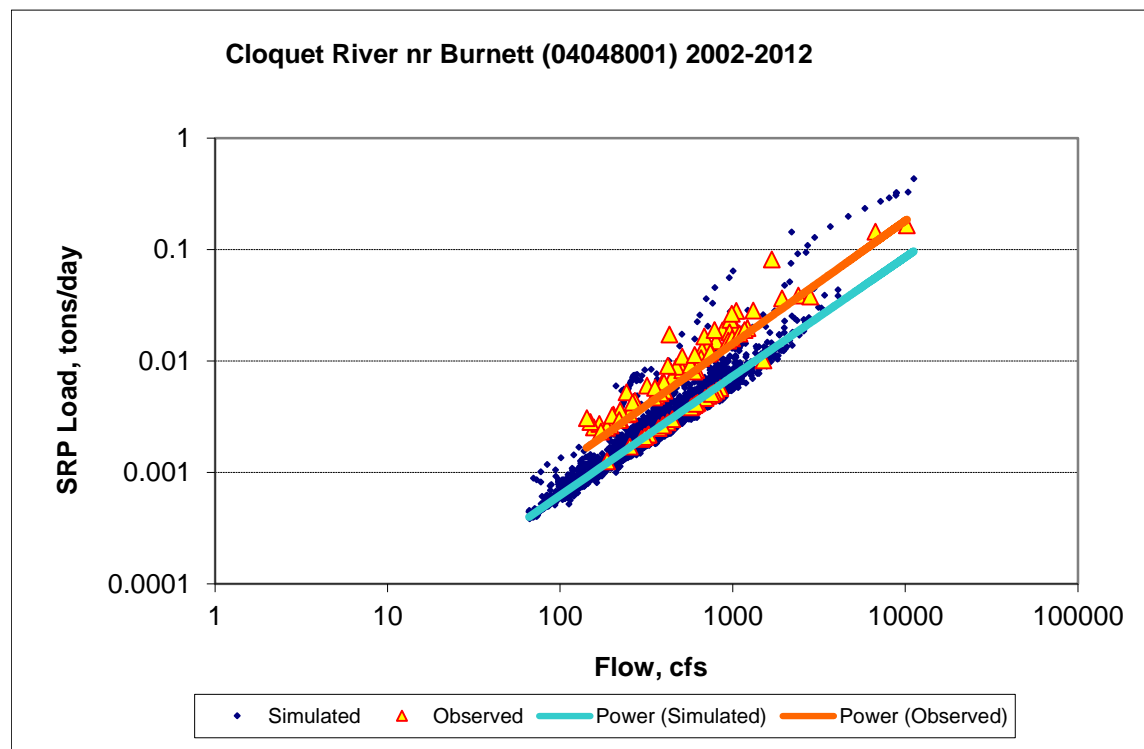
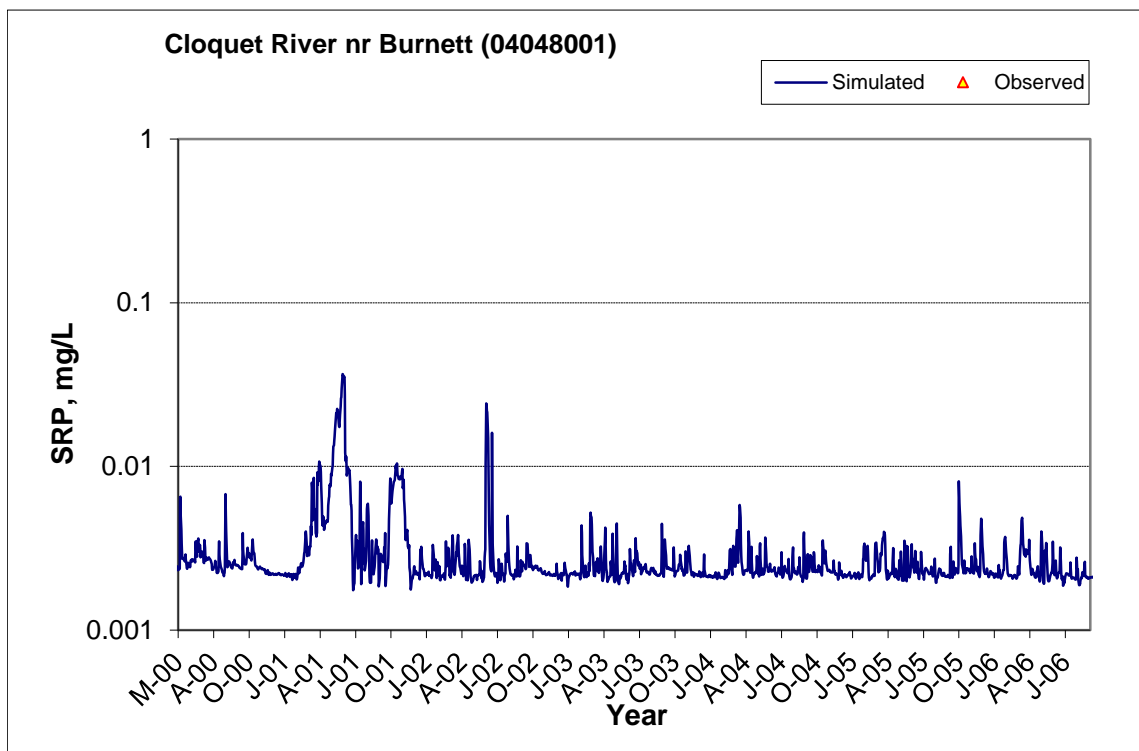
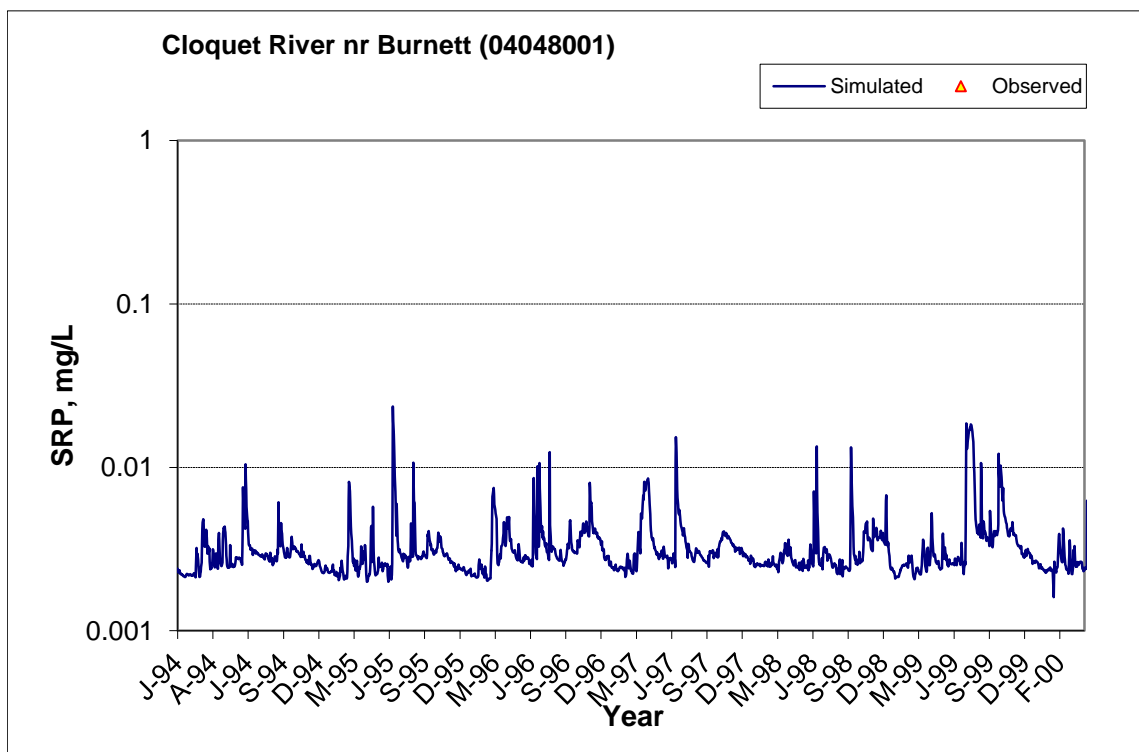


Figure A-224. Power plot of simulated and observed Soluble Reactive Phosphorus (SRP) load vs flow at Cloquet River nr Burnett (04048001) (calibration period)



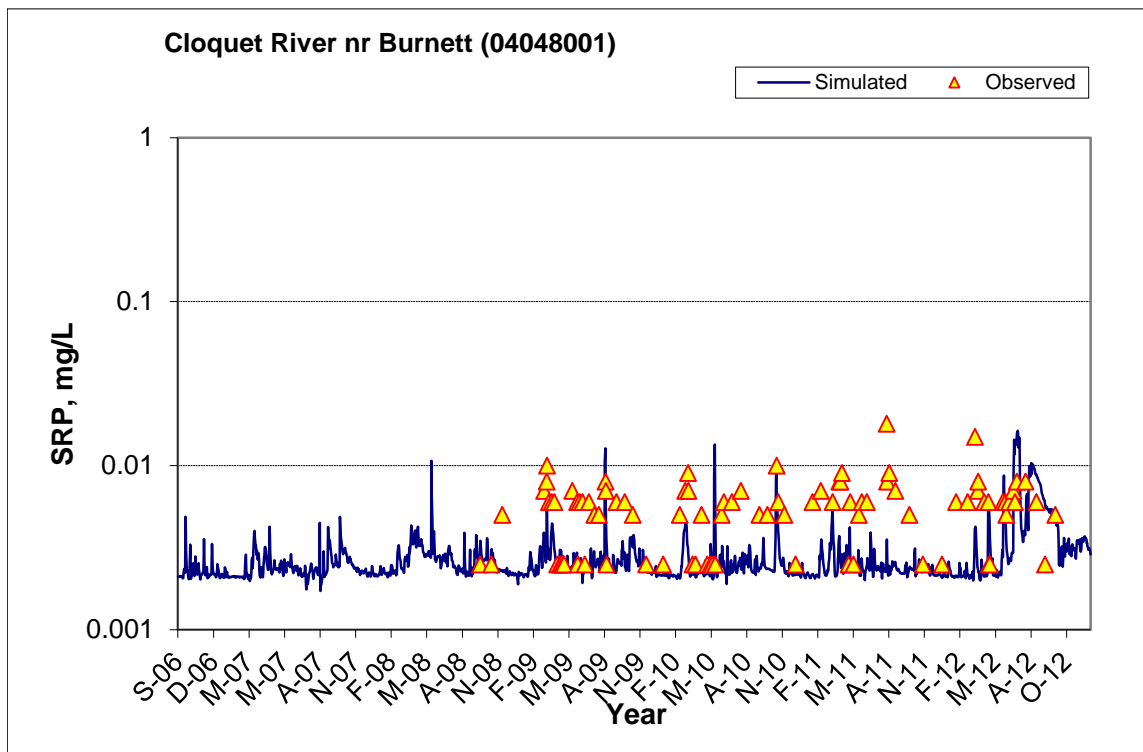


Figure A-225. Time series of observed and simulated Soluble Reactive Phosphorus (SRP) concentration at Cloquet River nr Burnett (04048001)

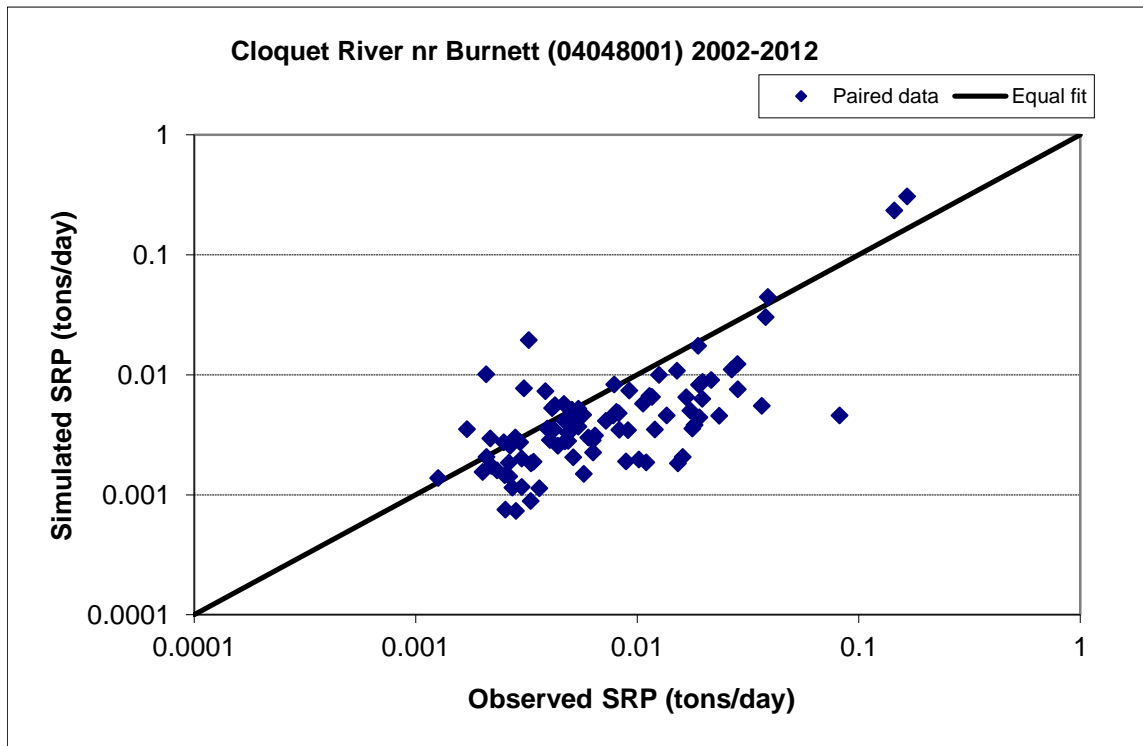


Figure A-226. Paired simulated vs. observed Soluble Reactive Phosphorus (SRP) load at Cloquet River nr Burnett (04048001) (calibration period)

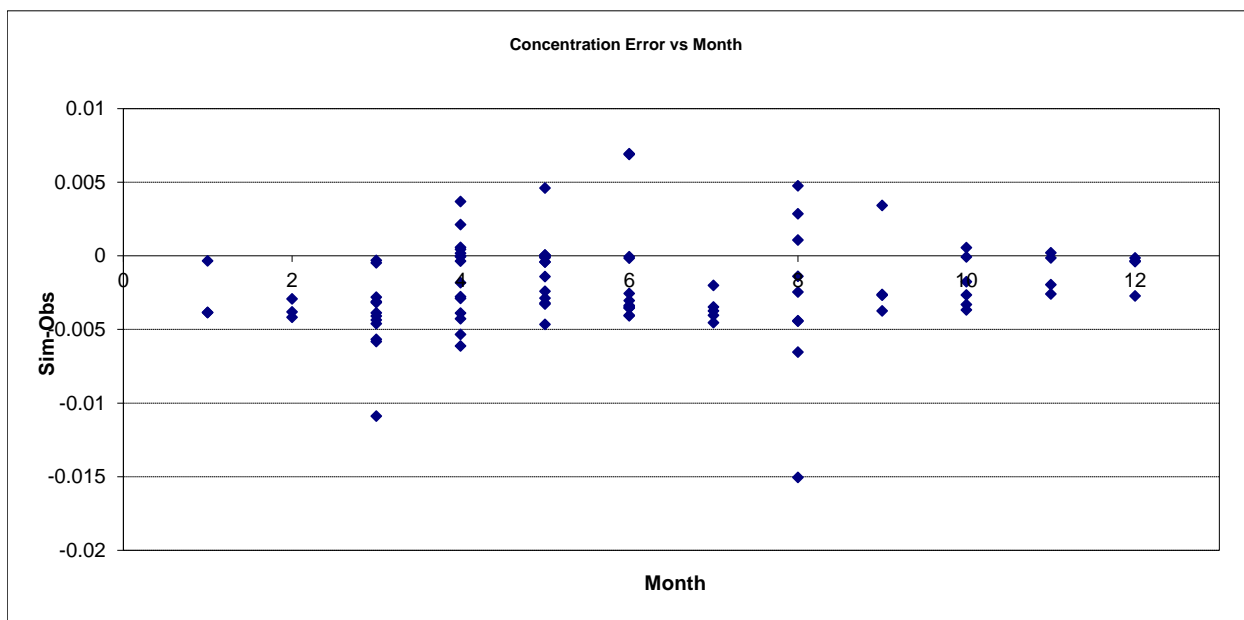


Figure A-227. Residual (Simulated - Observed) vs. Month Soluble Reactive Phosphorus (SRP) at Cloquet River nr Burnett (04048001)

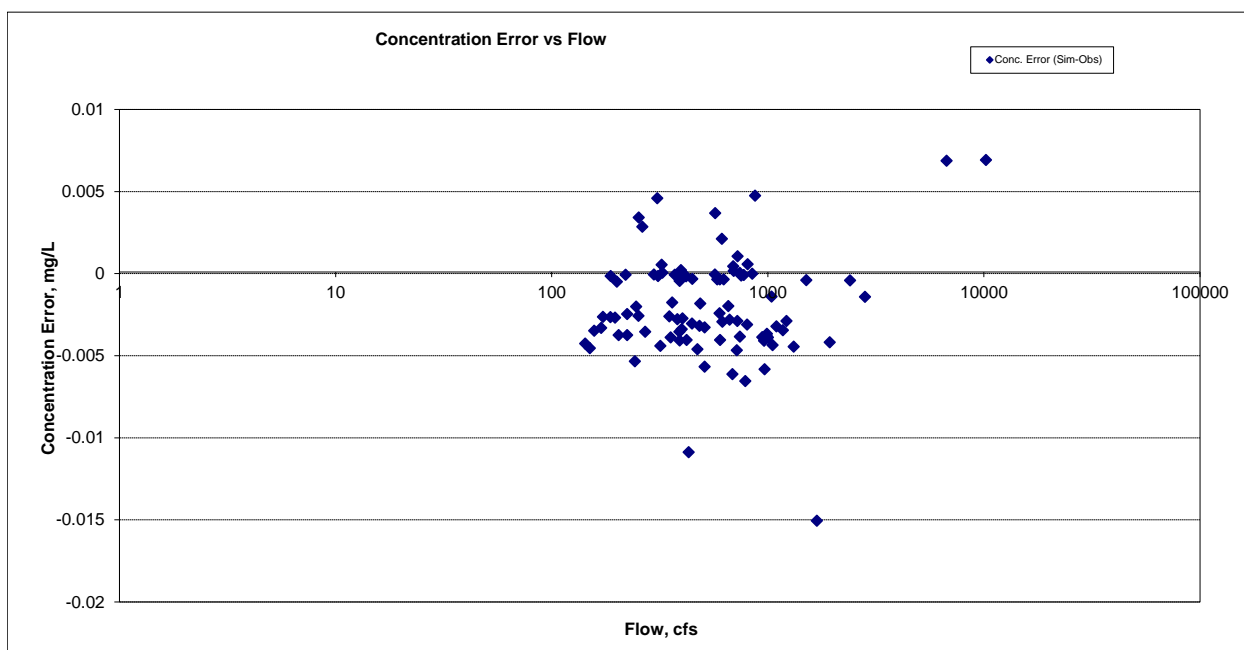
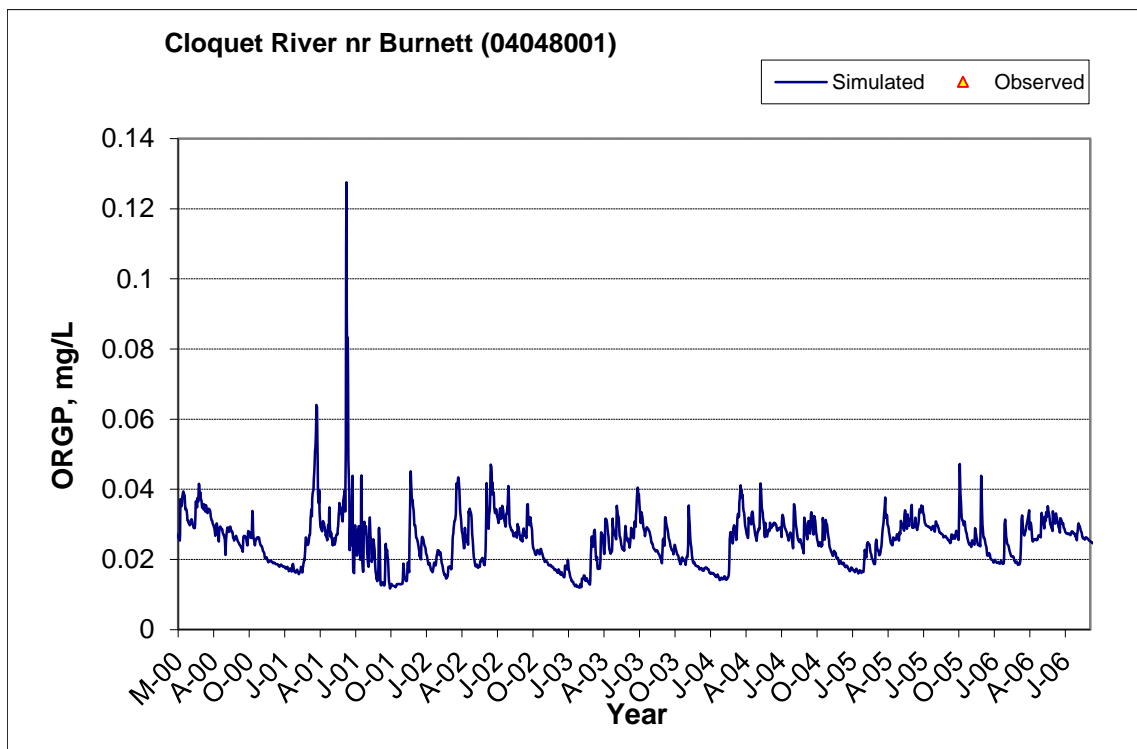
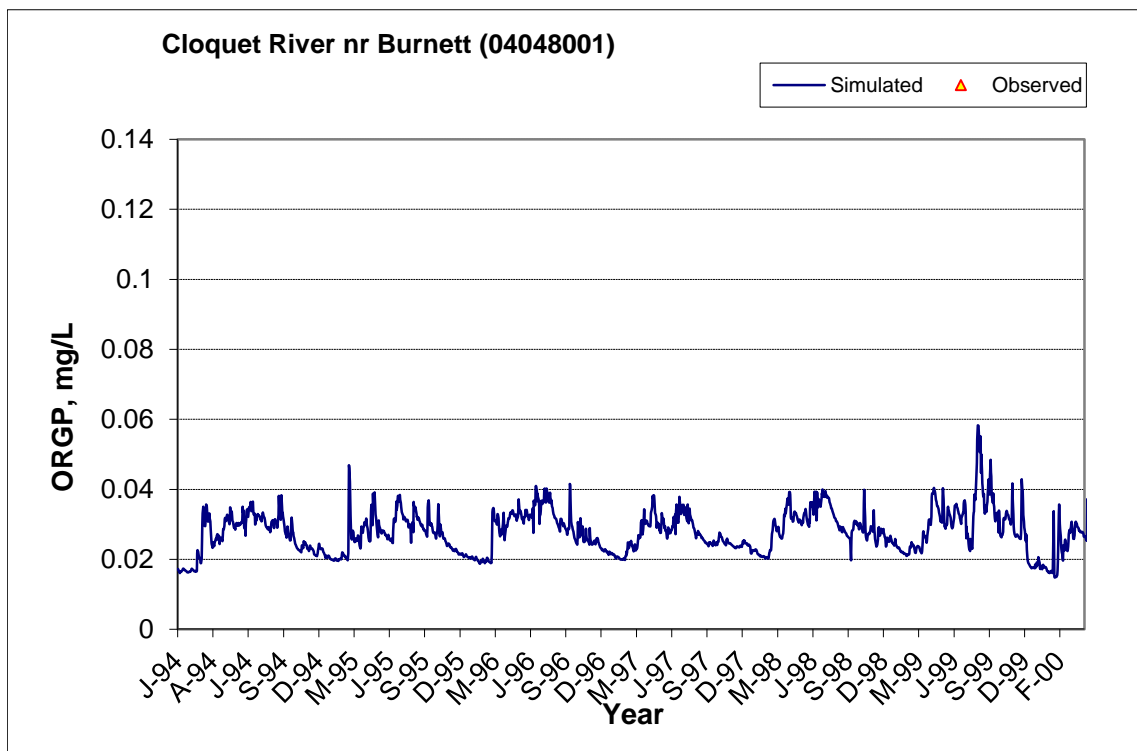


Figure A-228. Residual (Simulated - Observed) vs. Flow Soluble Reactive Phosphorus (SRP) at Cloquet River nr Burnett (04048001)

A.7.7 Organic Phosphorus (OrgP)



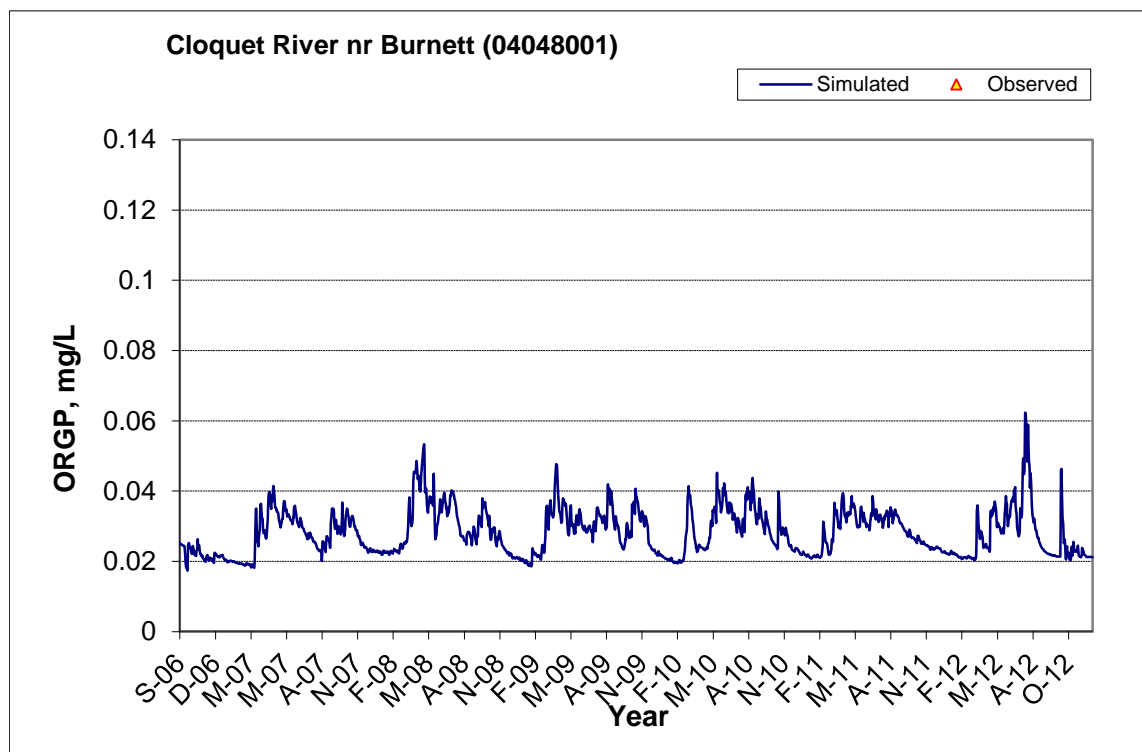


Figure A-229. Time series of observed and simulated Organic Phosphorus (OrgP) concentration at Cloquet River nr Burnett (04048001)

A.7.8 Total Phosphorus (TP)

Table A-34. Total Phosphorus (TP) statistics

Period	1994-2001	2002-2012
Count	29	80
Concentration Average Error	18.98%	6.30%
Concentration Median Error	33.88%	31.57%
Load Average Error	21.40%	-1.04%
Load Median Error	23.59%	17.80%
Paired t conc	0.57	0.82
Paired t load	0.47	0.97

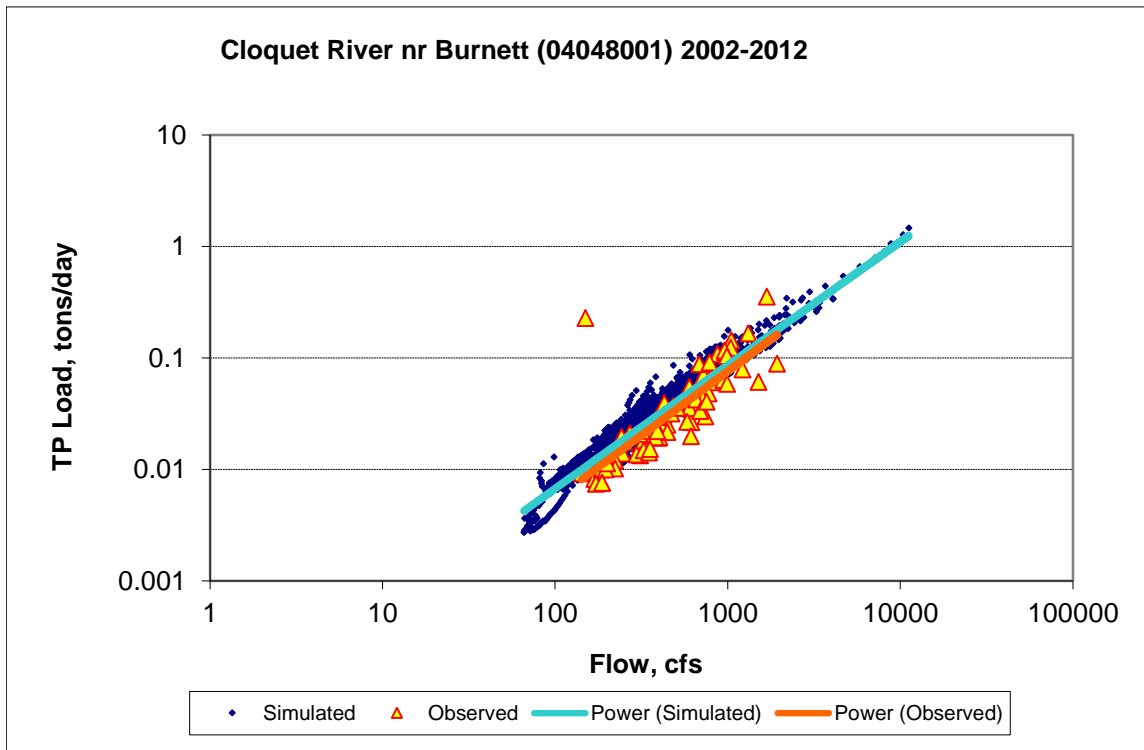


Figure A-230. Power plot of simulated and observed Total Phosphorus (TP) load vs flow at Cloquet River nr Burnett (04048001) (calibration period)

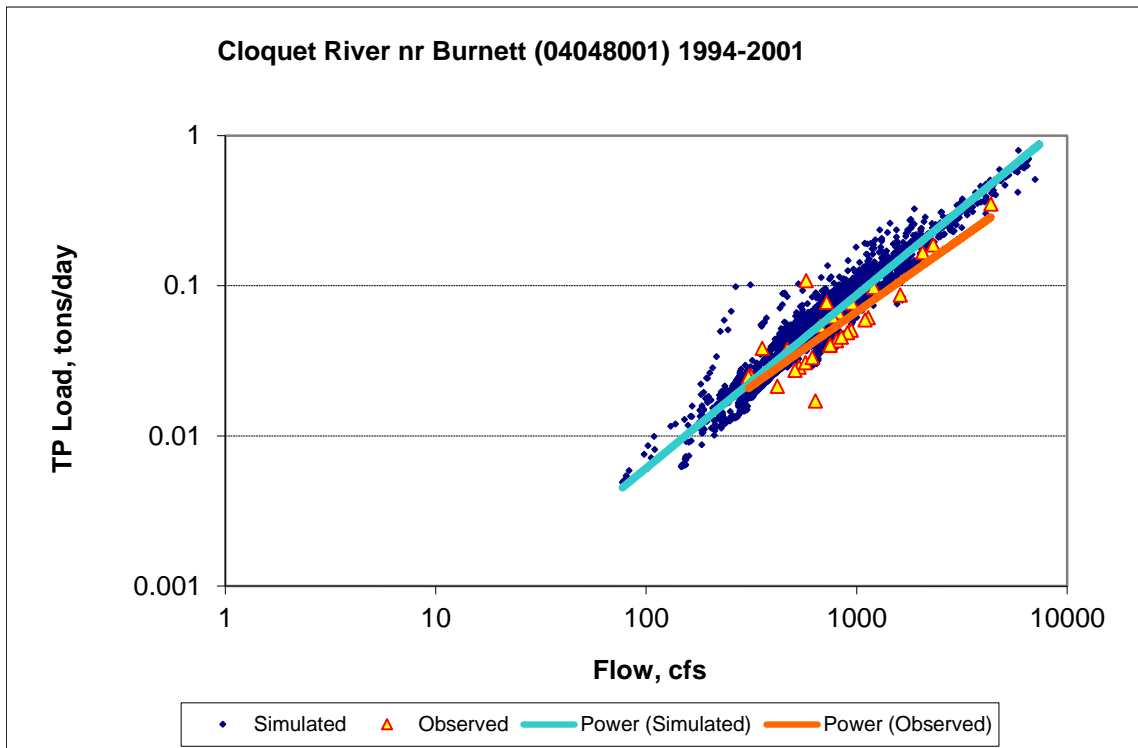
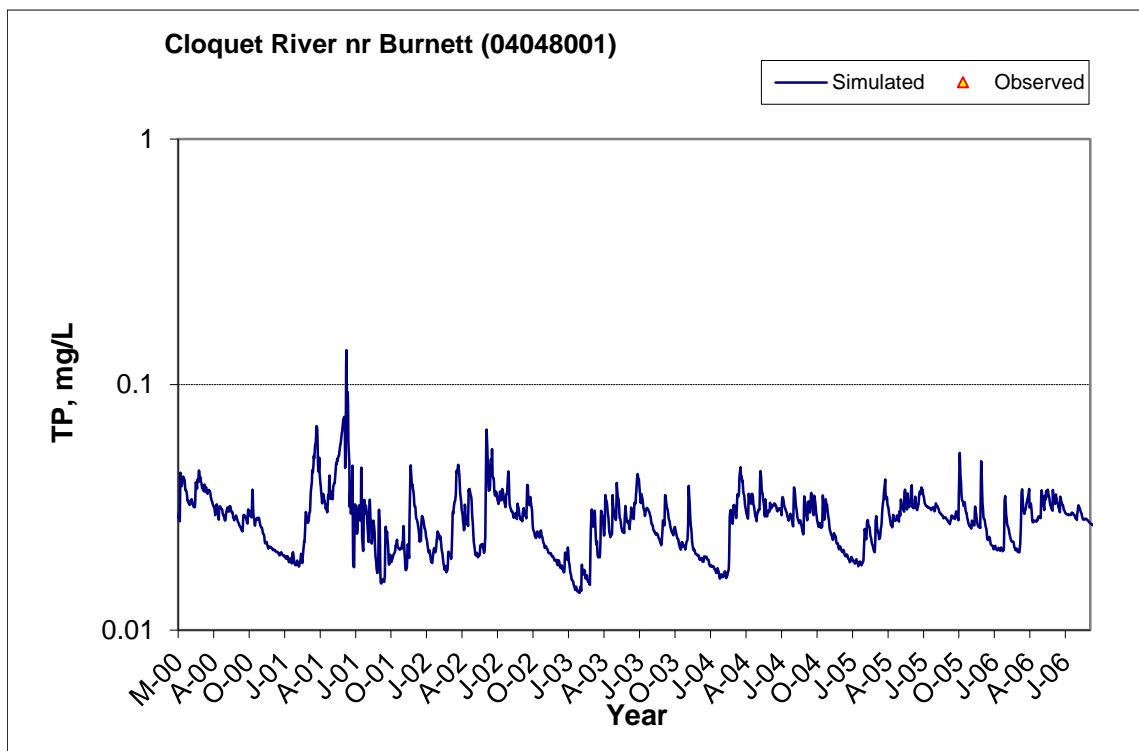
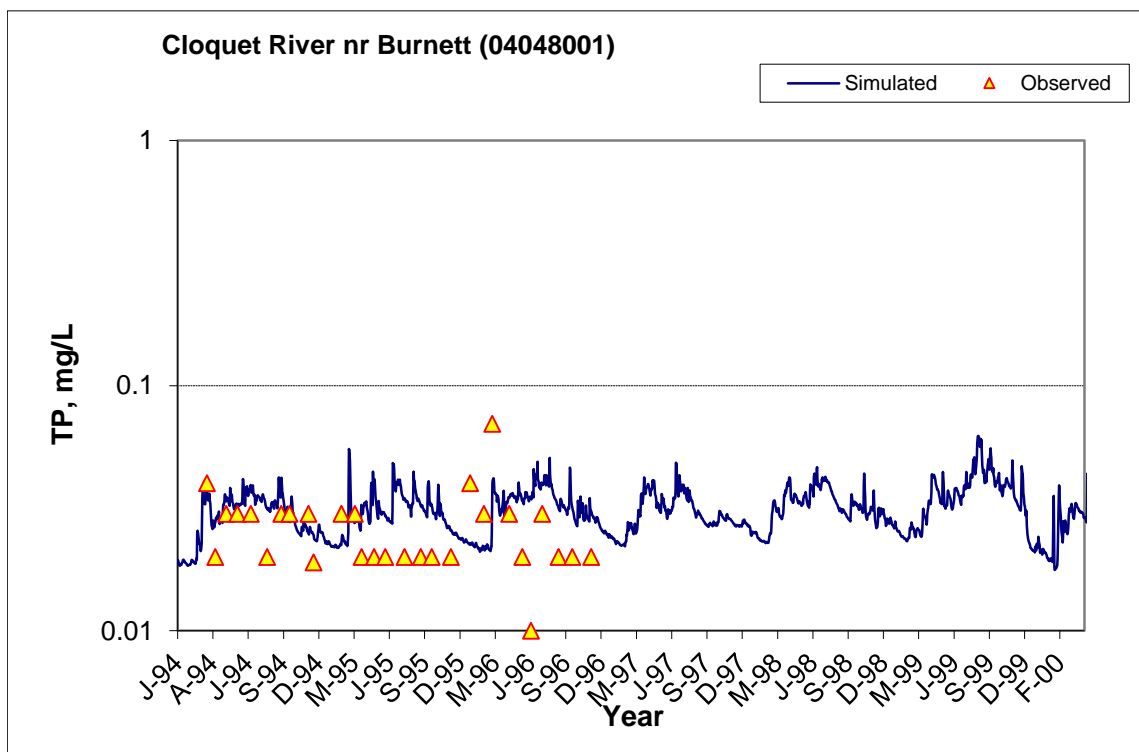


Figure A-231. Power plot of simulated and observed Total Phosphorus (TP) load vs flow at Cloquet River nr Burnett (04048001) (validation period)



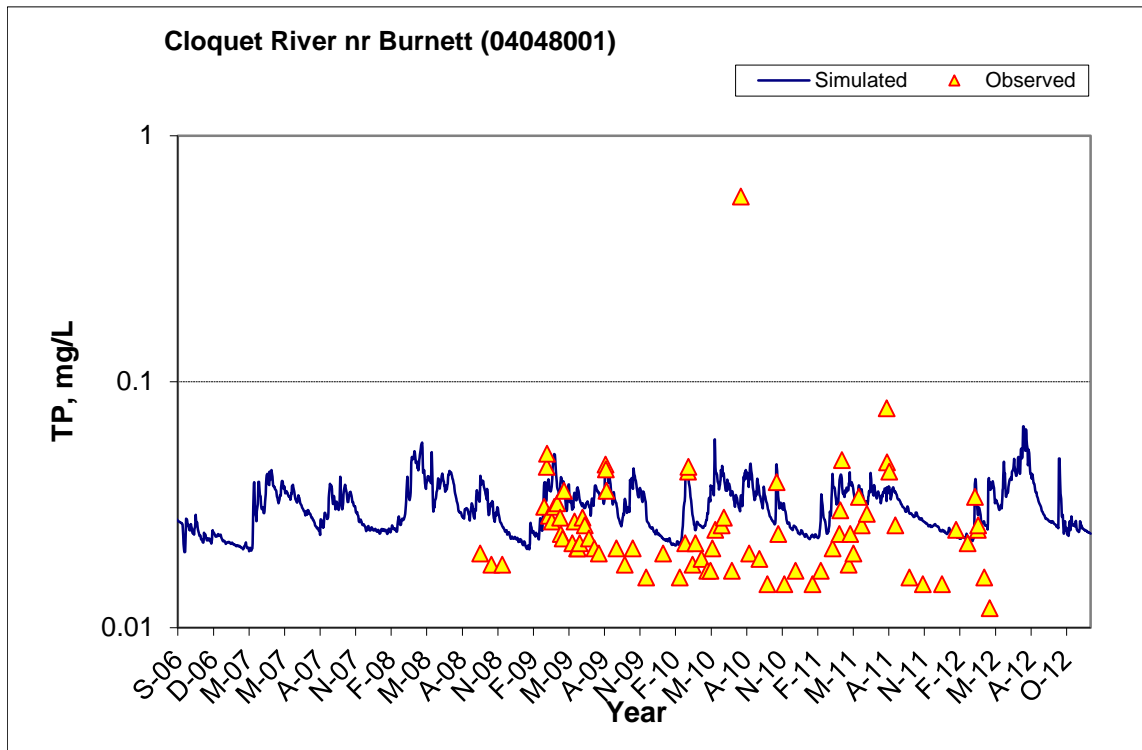


Figure A-232. Time series of observed and simulated Total Phosphorus (TP) concentration at Cloquet River nr Burnett (04048001)

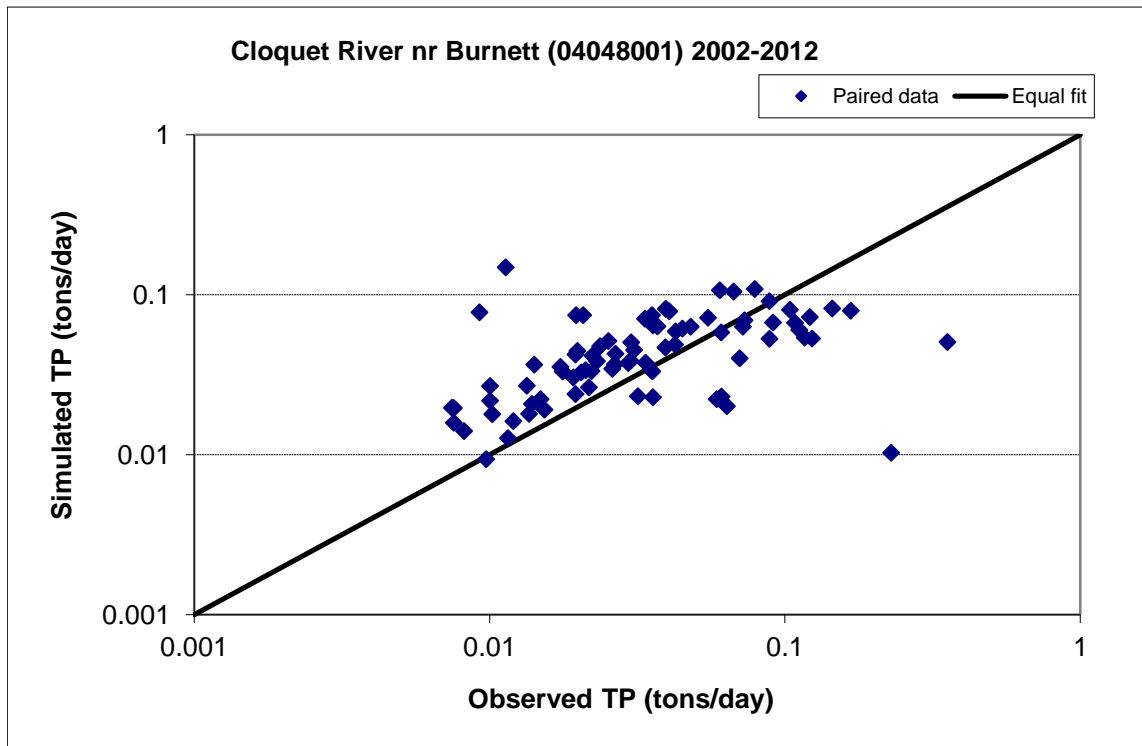


Figure A-233. Paired simulated vs. observed Total Phosphorus (TP) load at Cloquet River nr Burnett (04048001) (calibration period)

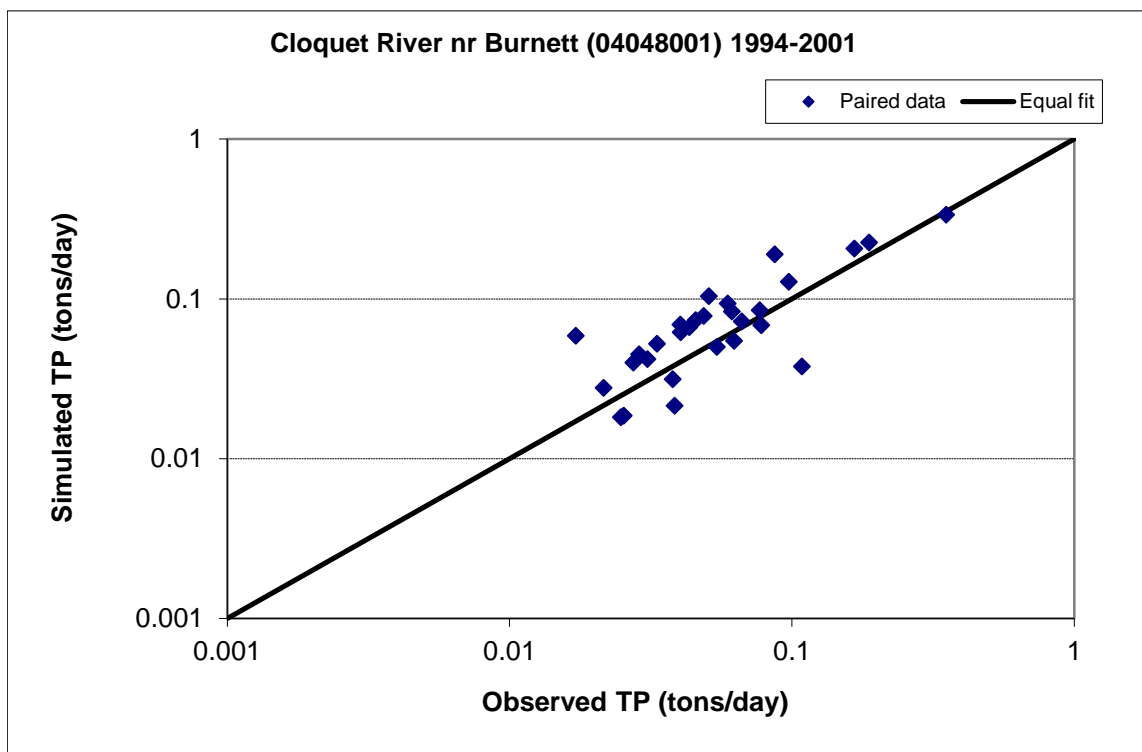


Figure A-234. Paired simulated vs. observed Total Phosphorus (TP) load at Cloquet River nr Burnett (04048001) (validation period)

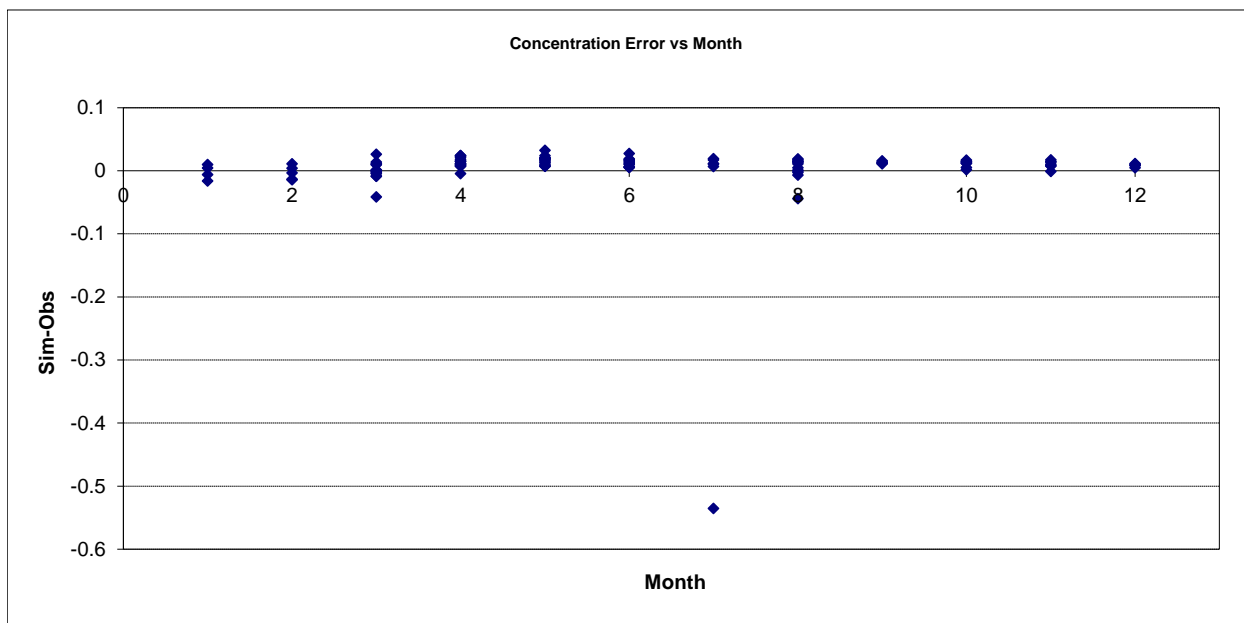


Figure A-235. Residual (Simulated - Observed) vs. Month Total Phosphorus (TP) at Cloquet River nr Burnett (04048001)

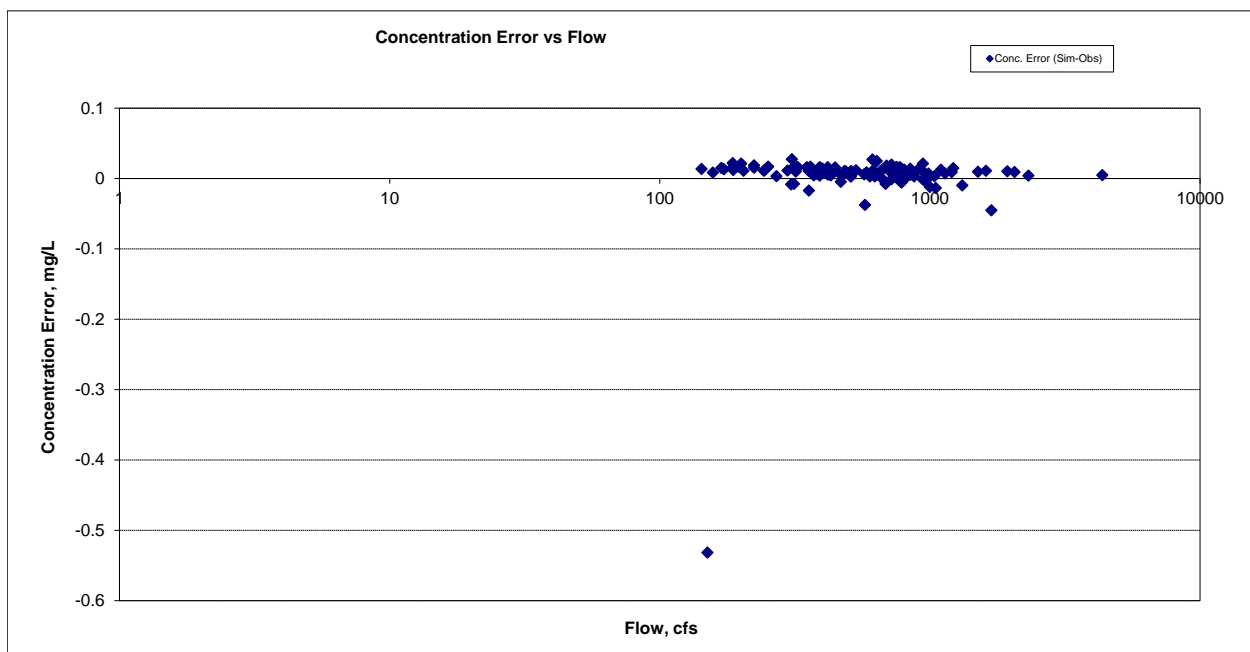


Figure A-236. Residual (Simulated - Observed) vs. Flow Total Phosphorus (TP) at Cloquet River nr Burnett (04048001)

Appendix B. Water Quality Calibration Details for the Nemadji River Watershed

B.1 DEER CREEK NR PLEASANT VALLEY, MN23 (05008001)

B.1.1 Ammonia Nitrogen (NH3)

Table B-1. Ammonia Nitrogen (NH3) statistics

Period	1994-2006	2007-2012
Count	6	18
Concentration Average Error	-44.96%	-75.09%
Concentration Median Error	-22.93%	2.22%
Load Average Error	-50.73%	8.98%
Load Median Error	-28.96%	0.82%
Paired t conc	0.11	0.19
Paired t load	0.13	0.62

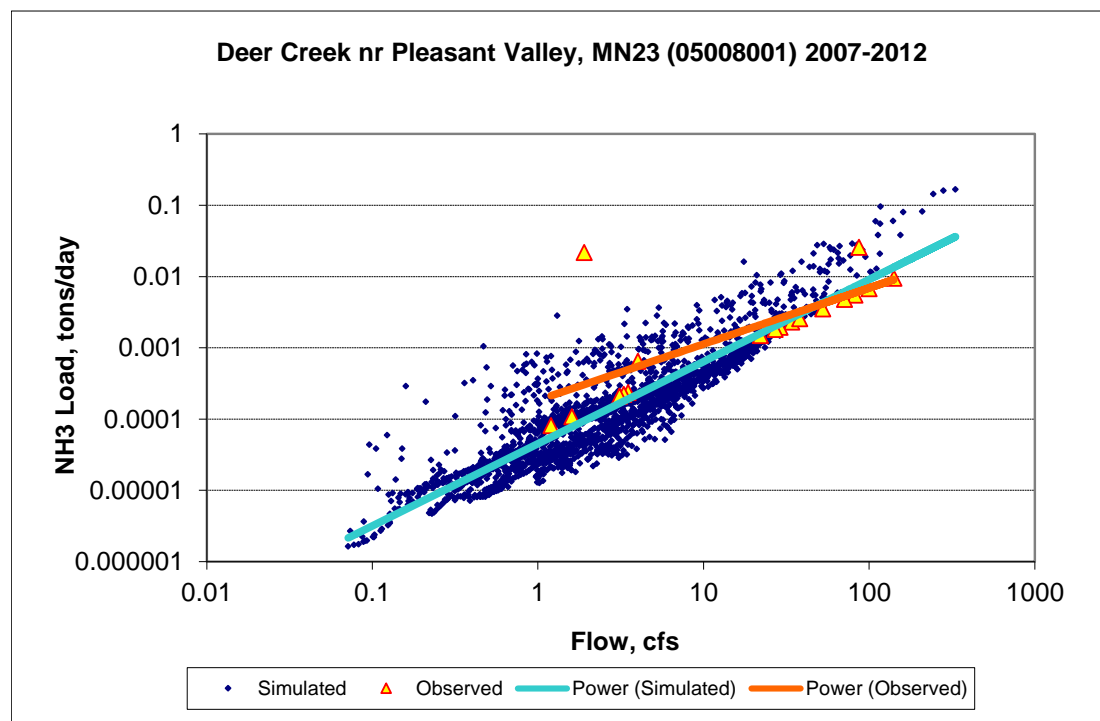


Figure B-1. Power plot of simulated and observed Ammonia Nitrogen (NH3) load vs flow at Deer Creek nr Pleasant Valley, MN23 (05008001) (calibration period)

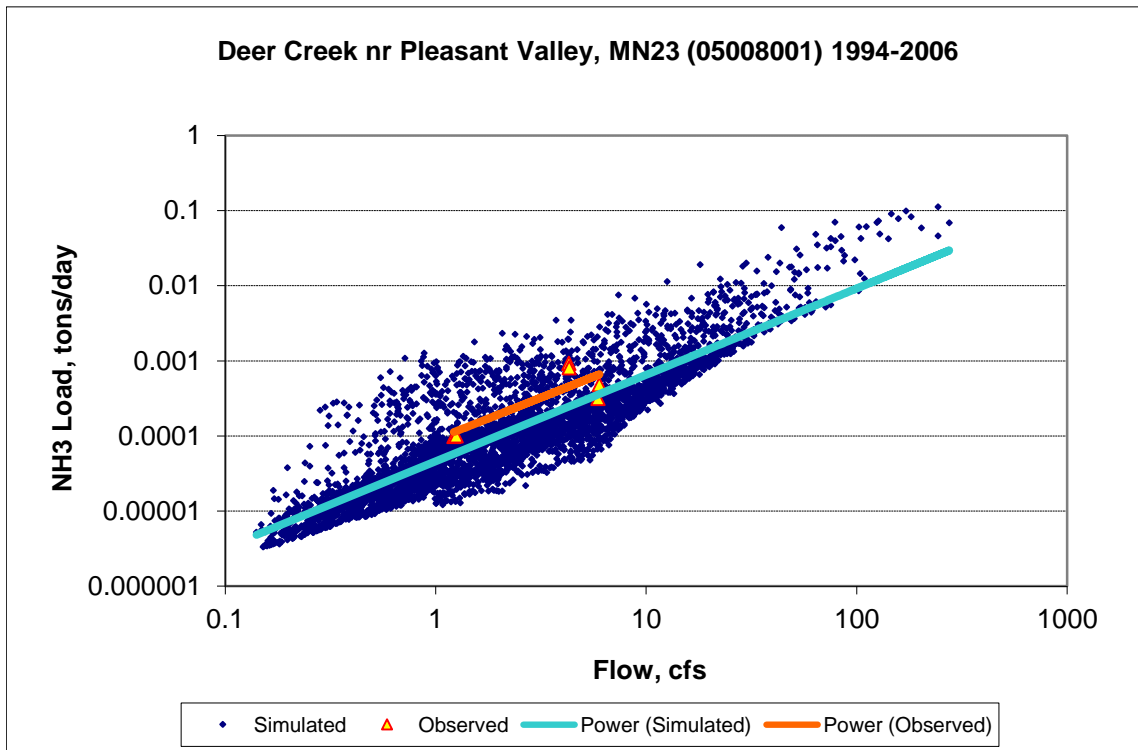
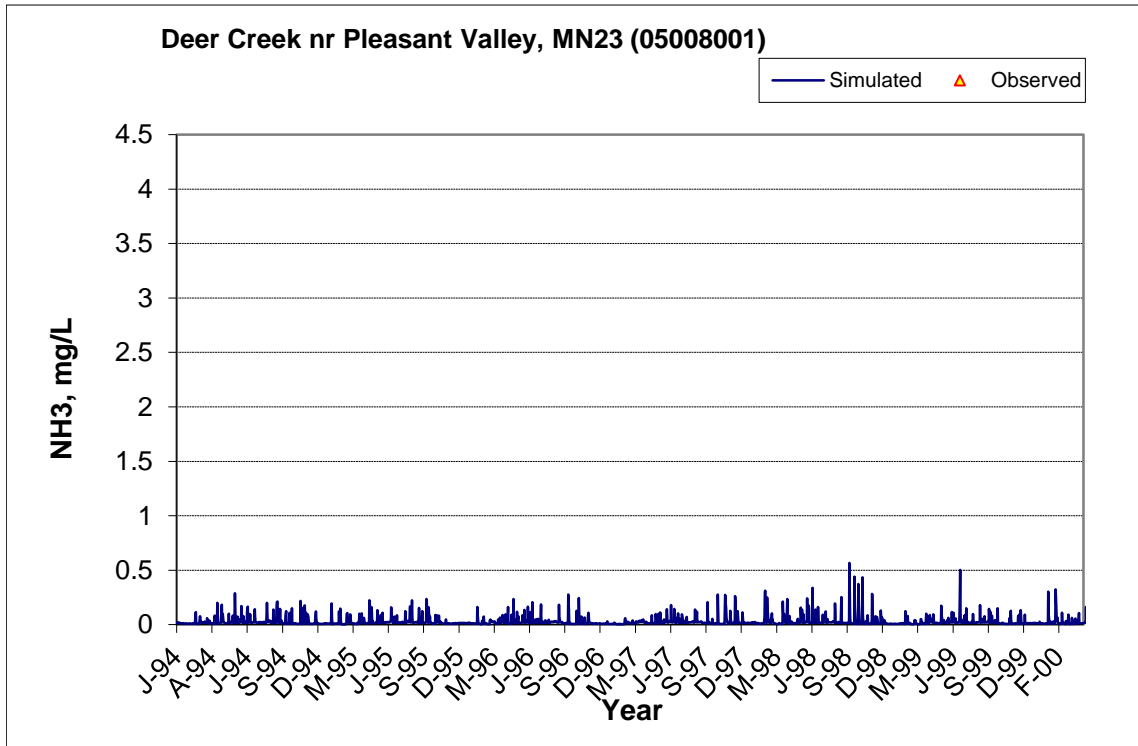


Figure B-2. Power plot of simulated and observed Ammonia Nitrogen (NH3) load vs flow at Deer Creek nr Pleasant Valley, MN23 (05008001) (validation period)



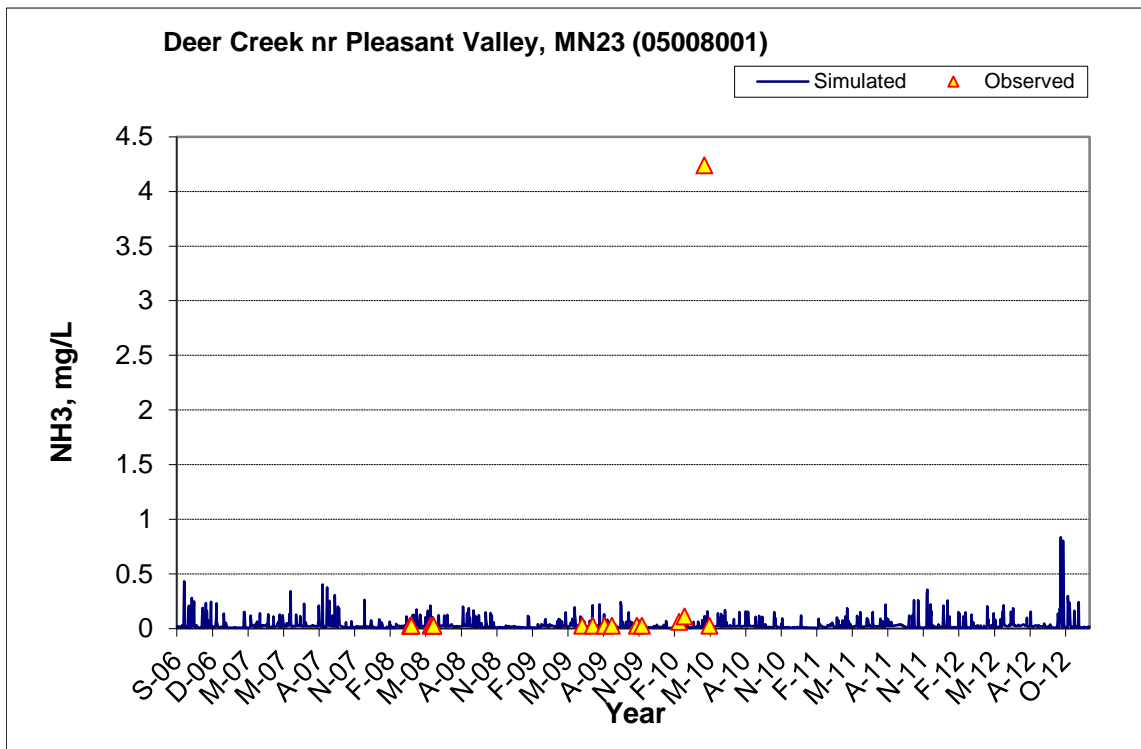
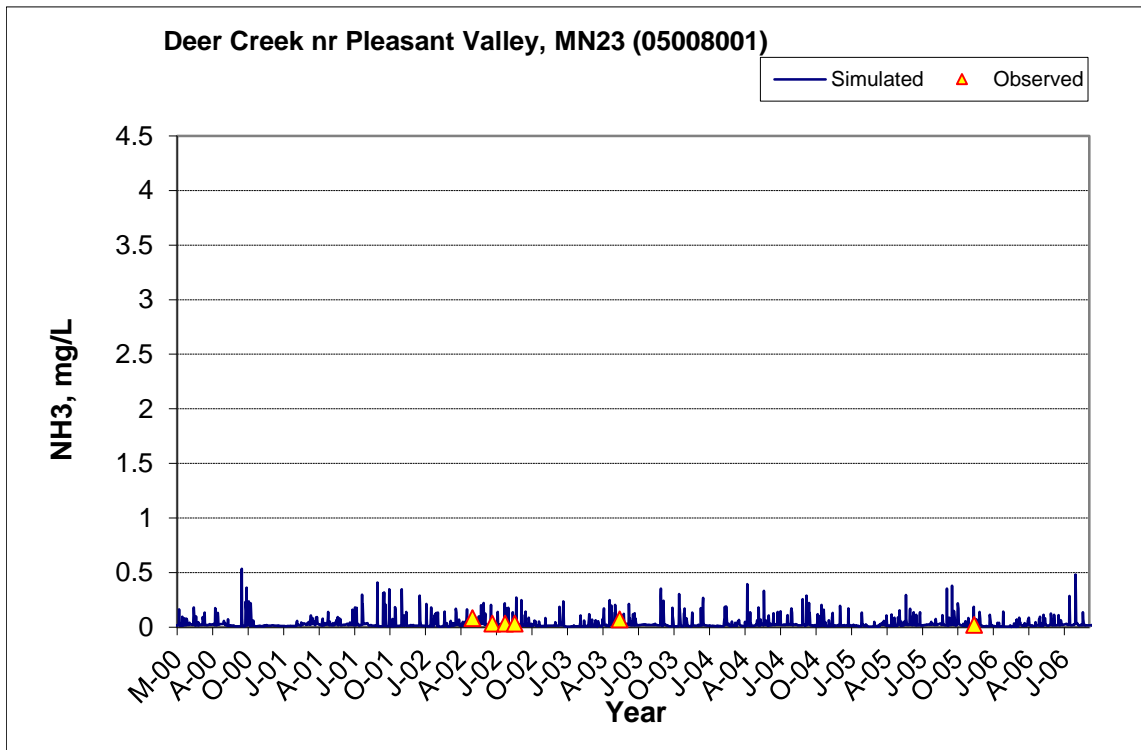


Figure B-3. Time series of observed and simulated Ammonia Nitrogen (NH3) concentration at Deer Creek nr Pleasant Valley, MN23 (05008001)

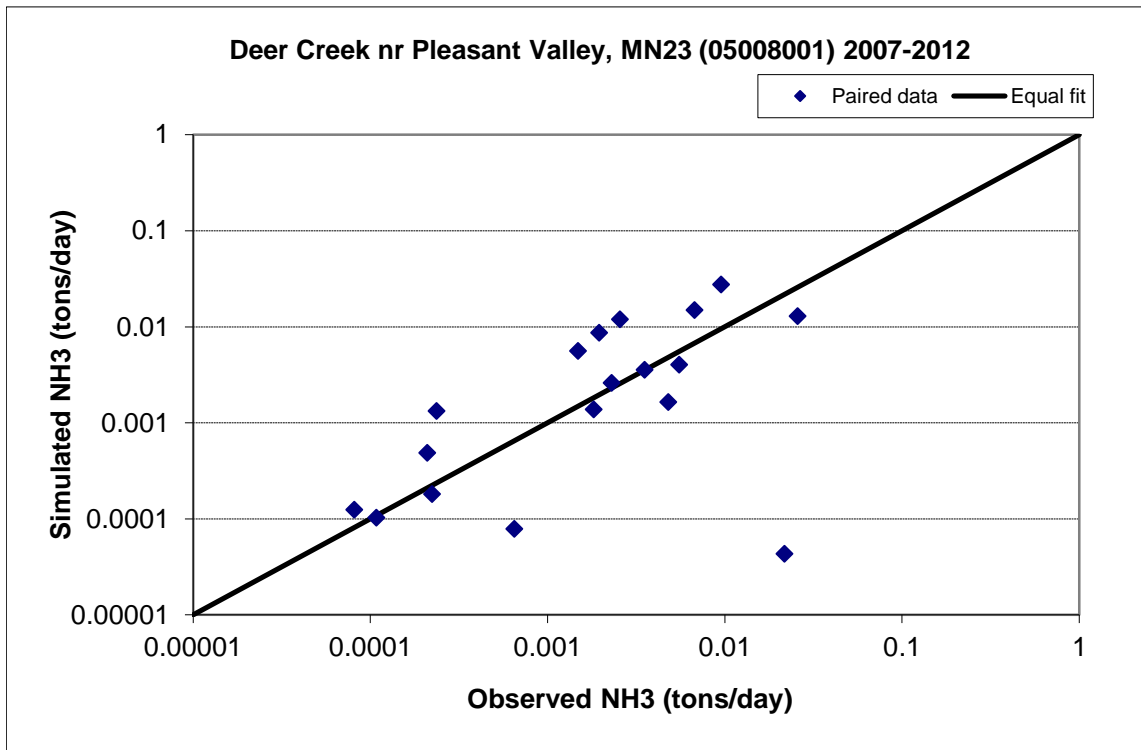


Figure B-4. Paired simulated vs. observed Ammonia Nitrogen (NH3) load at Deer Creek nr Pleasant Valley, MN23 (05008001) (calibration period)

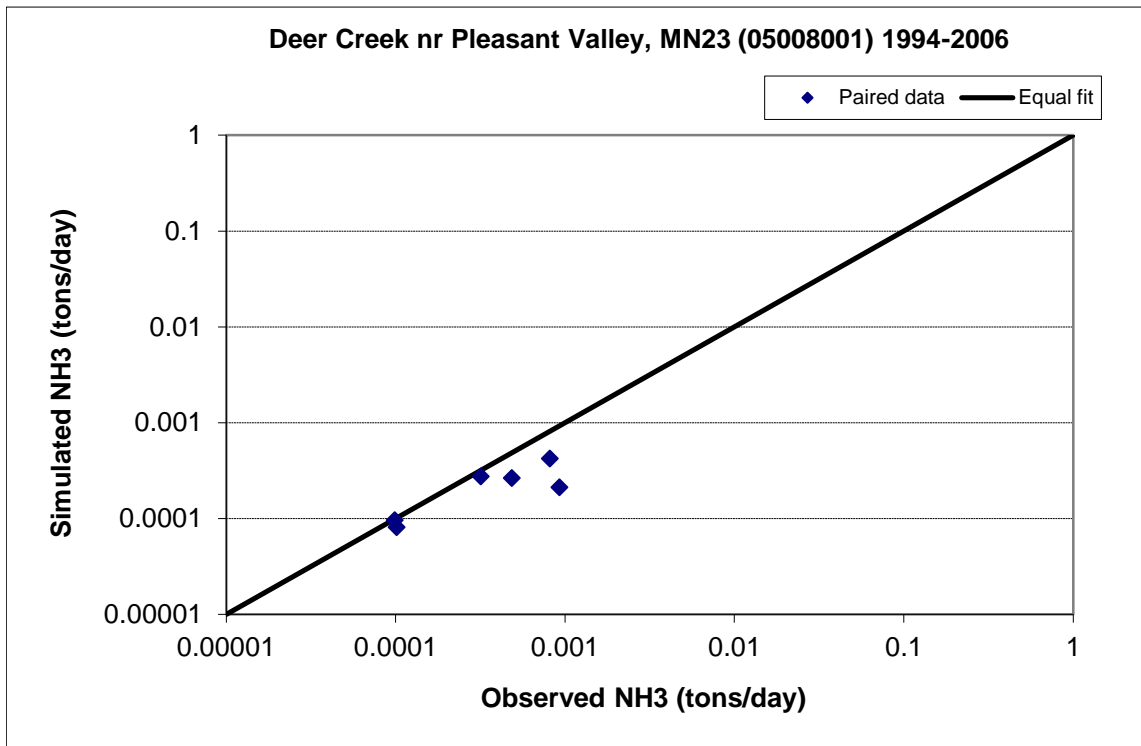


Figure B-5. Paired simulated vs. observed Ammonia Nitrogen (NH3) load at Deer Creek nr Pleasant Valley, MN23 (05008001) (validation period)

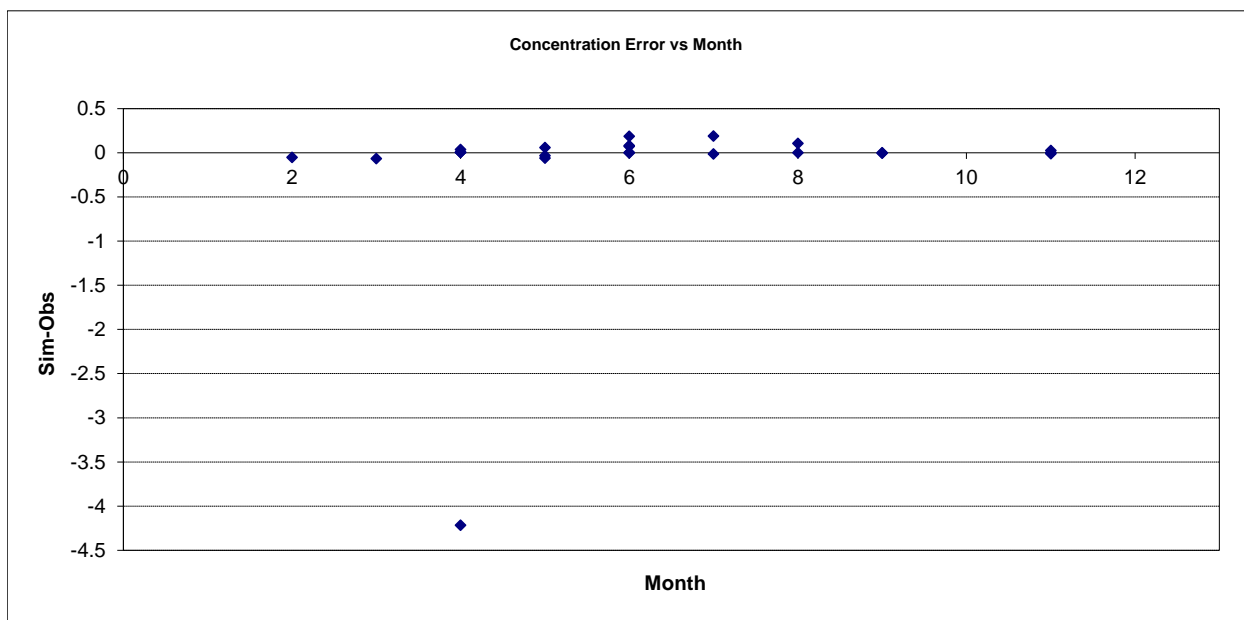


Figure B-6. Residual (Simulated - Observed) vs. Month Ammonia Nitrogen (NH3) at Deer Creek nr Pleasant Valley, MN23 (05008001)

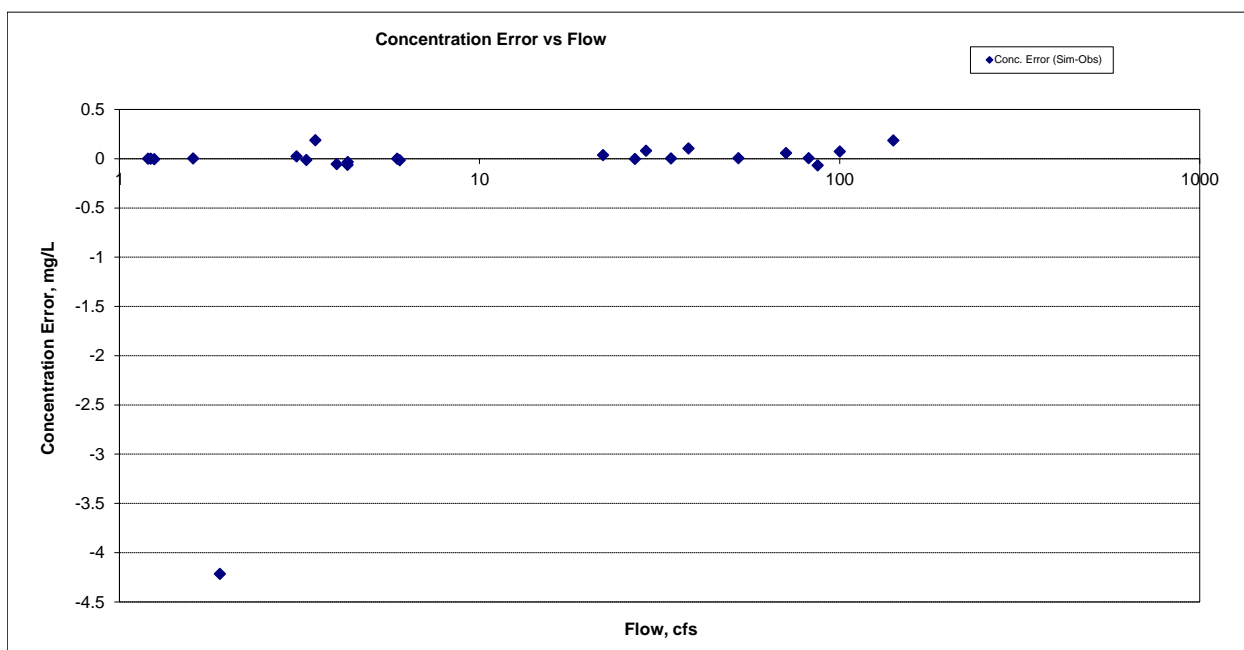
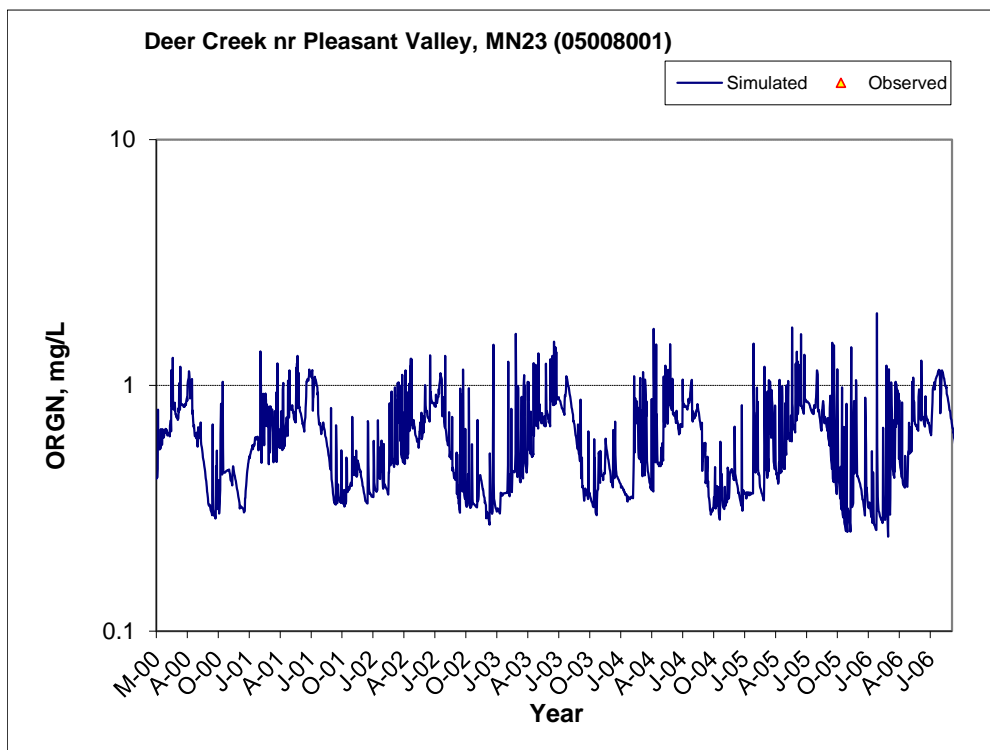
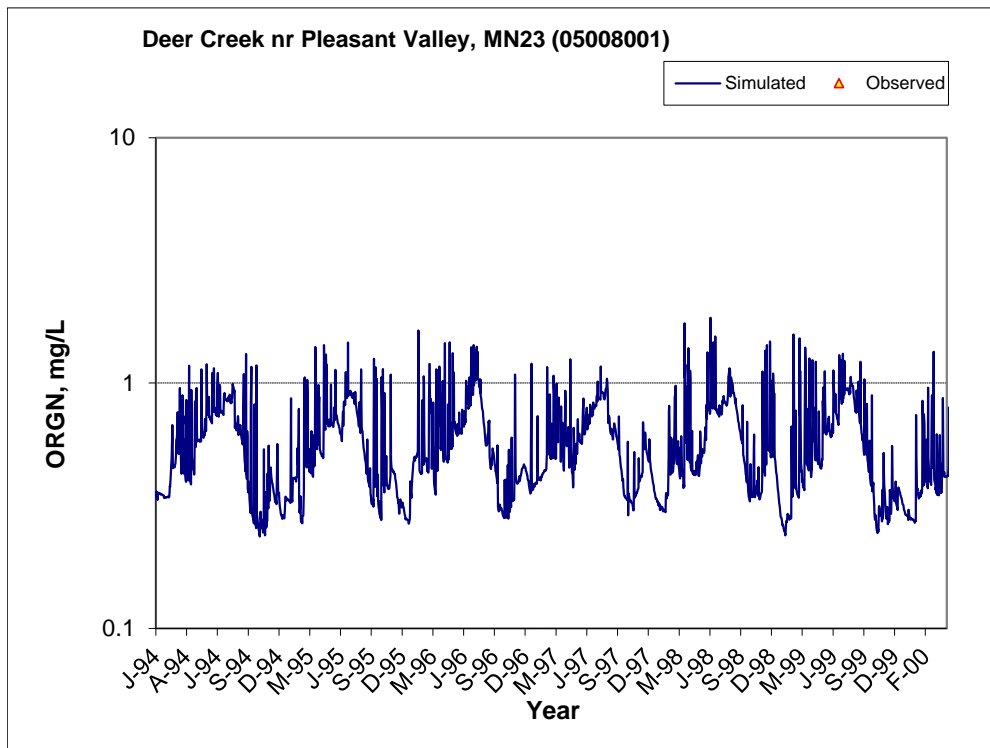


Figure B-7. Residual (Simulated - Observed) vs. Flow Ammonia Nitrogen (NH3) at Deer Creek nr Pleasant Valley, MN23 (05008001)

B.1.2 Organic Nitrogen (OrgN)



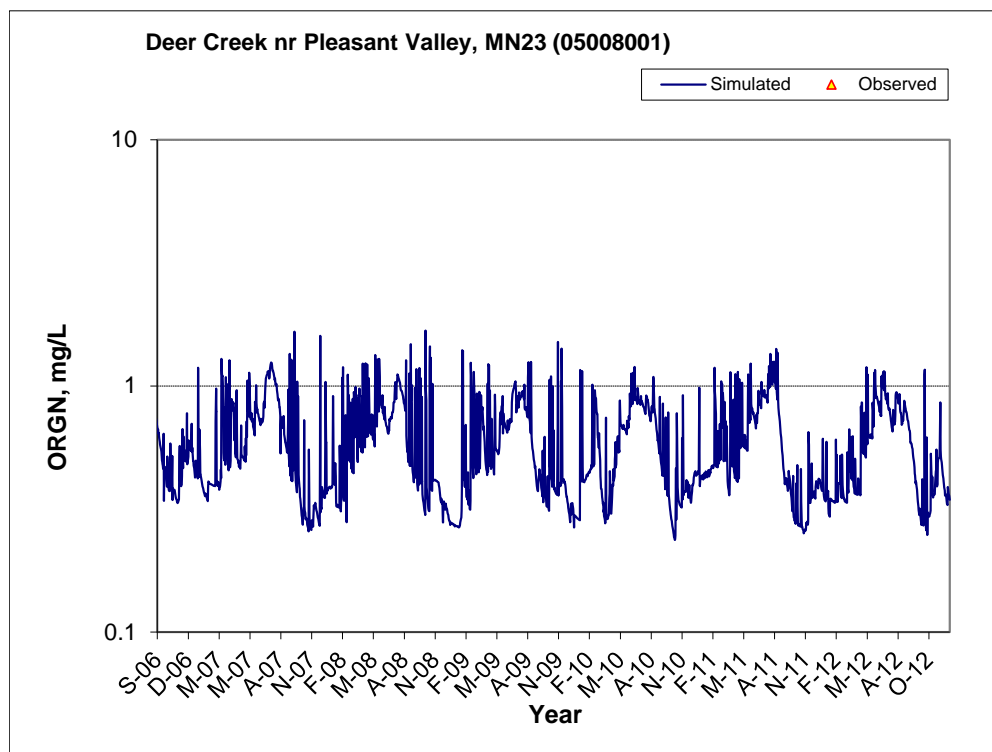


Figure B-8. Time series of observed and simulated Organic Nitrogen (OrgN) concentration at Deer Creek nr Pleasant Valley, MN23 (05008001)

B.1.3 Total Kjeldahl Nitrogen (TKN)

Table B-2. Total Kjeldahl Nitrogen (TKN) statistics

Period	1994-2006	2007-2012
Count	13	17
Concentration Average Error	-12.99%	9.43%
Concentration Median Error	-14.45%	11.94%
Load Average Error	-42.74%	-60.34%
Load Median Error	-5.25%	0.00%
Paired t conc	0.75	0.79
Paired t load	0.30	0.18

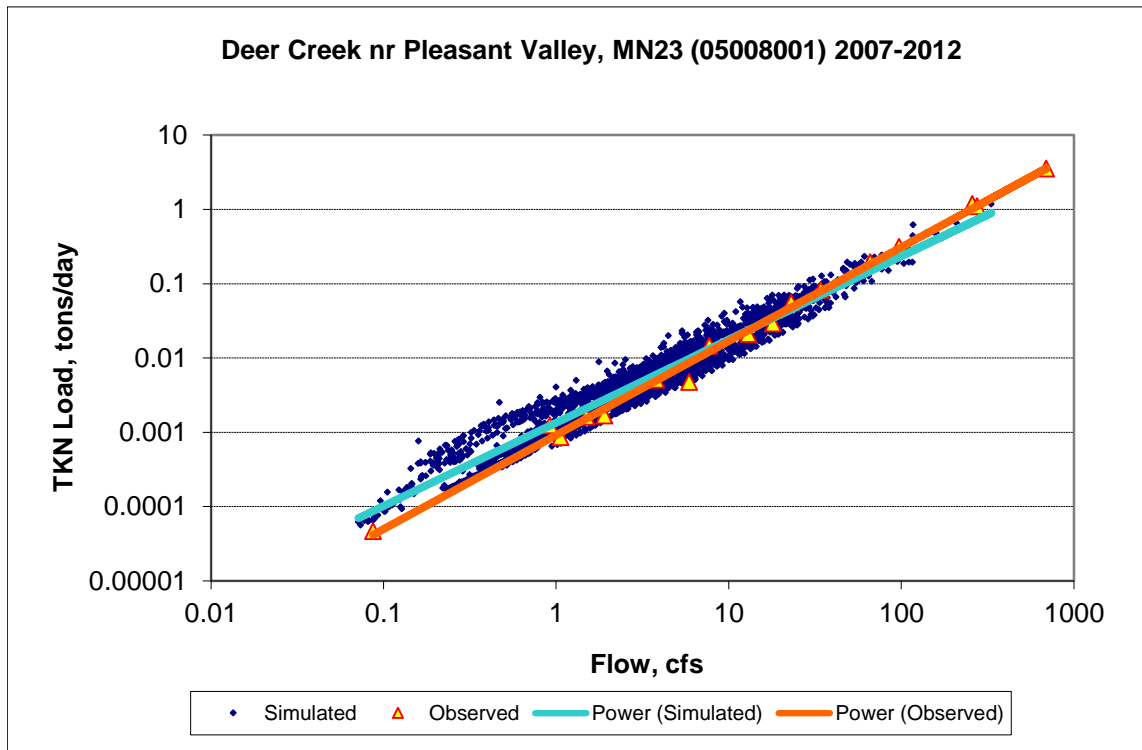


Figure B-9. Power plot of simulated and observed Total Kjeldahl Nitrogen (TKN) load vs flow at Deer Creek nr Pleasant Valley, MN23 (05008001) (calibration period)

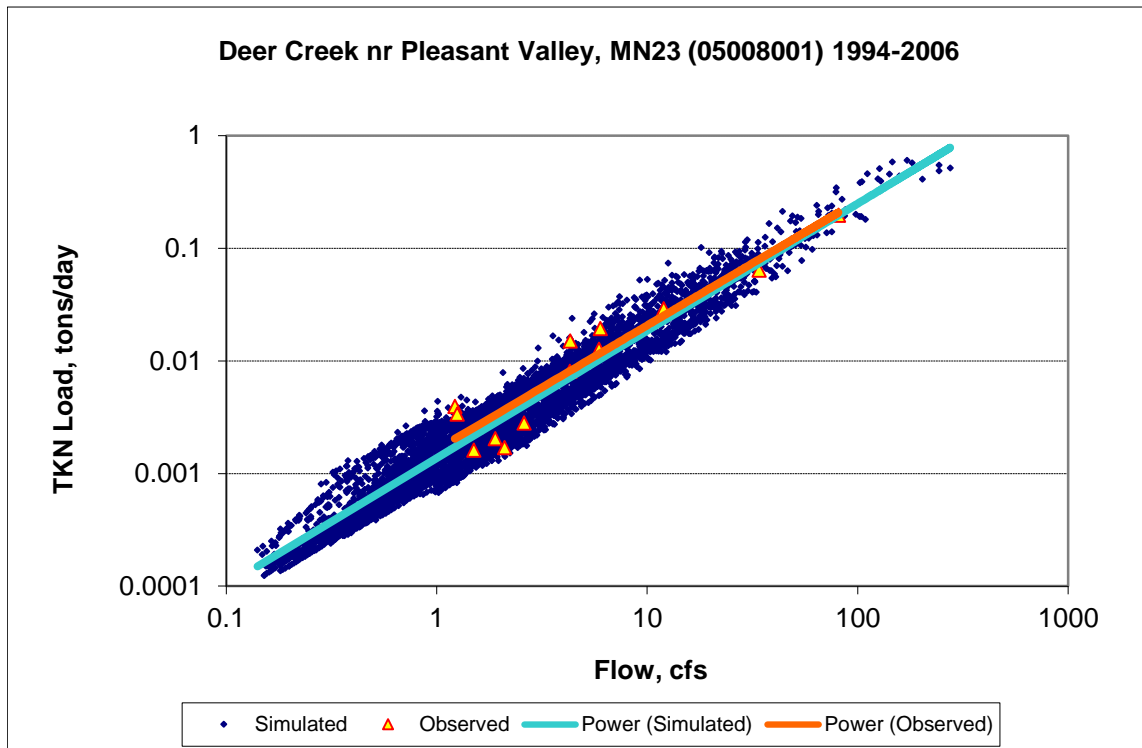
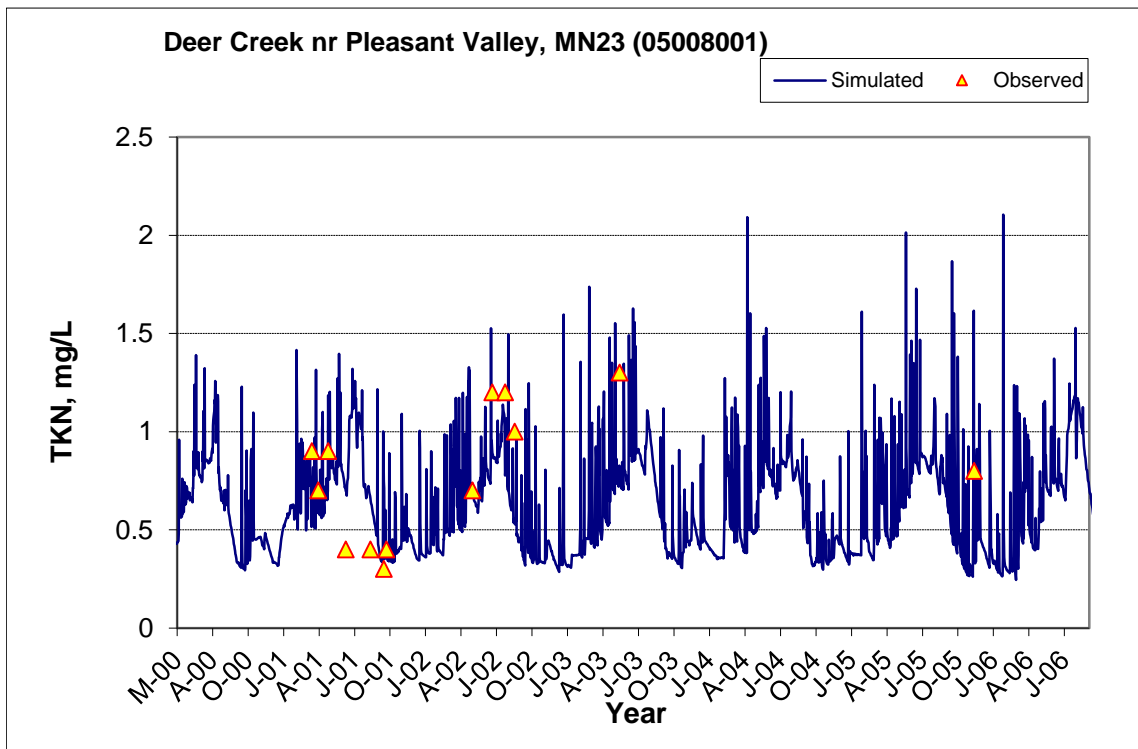
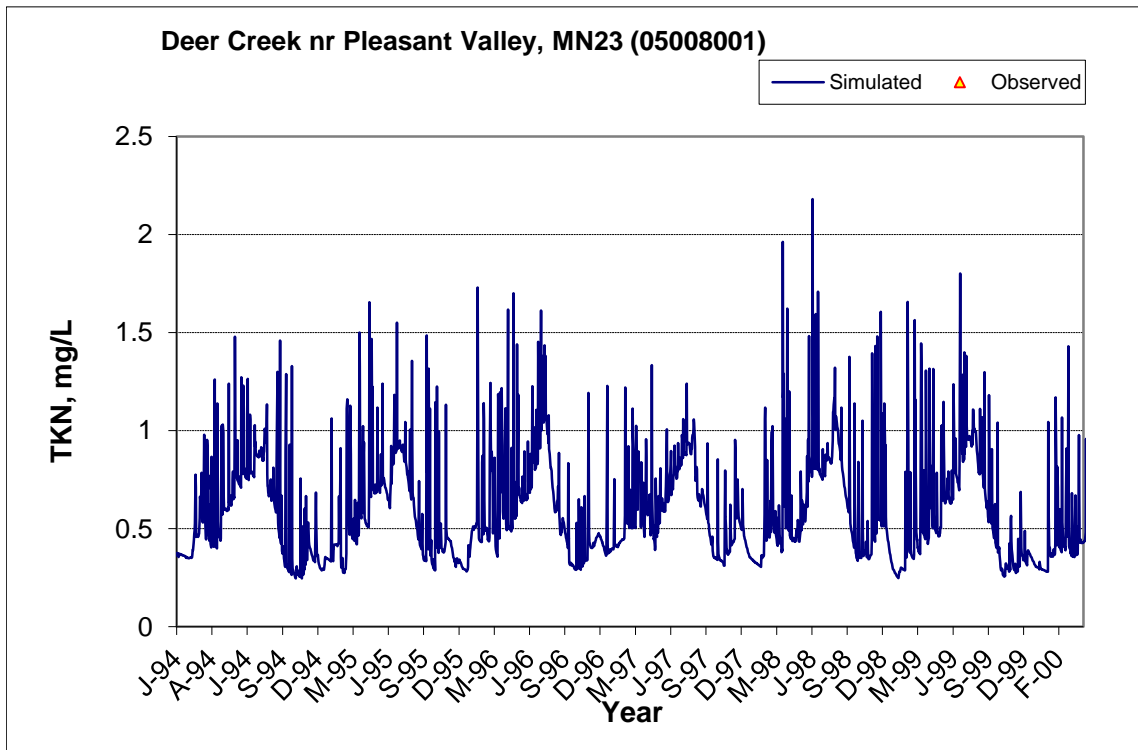


Figure B-10. Power plot of simulated and observed Total Kjeldahl Nitrogen (TKN) load vs flow at Deer Creek nr Pleasant Valley, MN23 (05008001) (validation period)



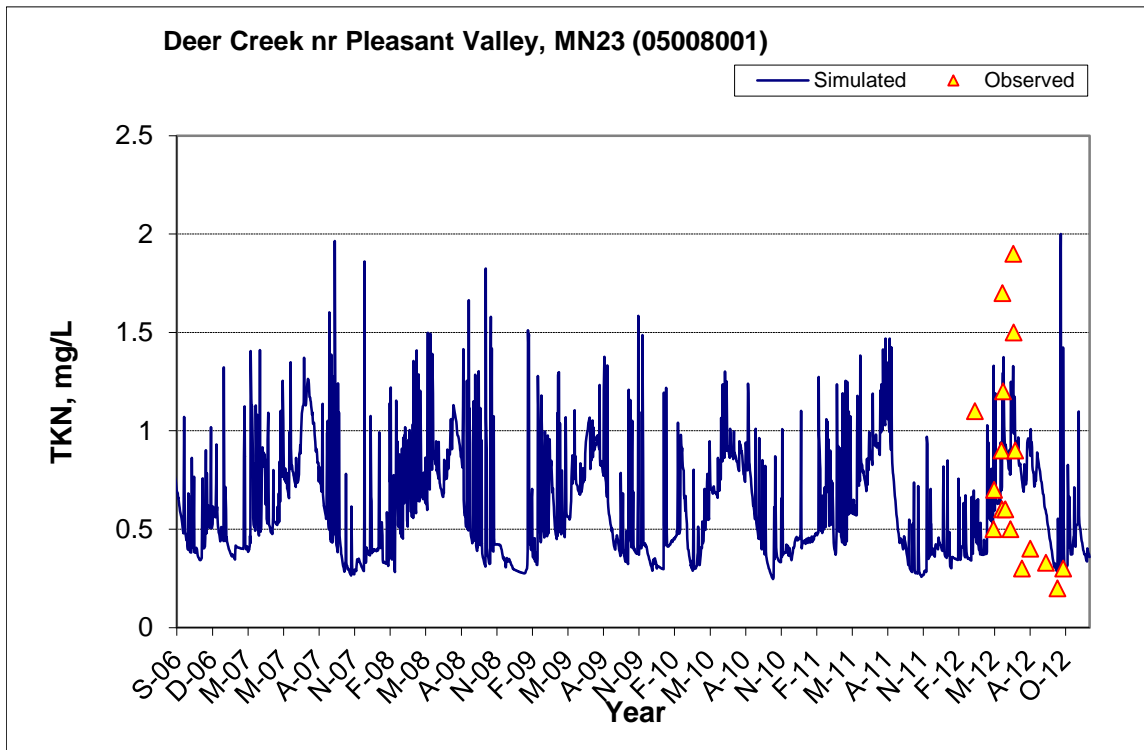


Figure B-11. Time series of observed and simulated Total Kjeldahl Nitrogen (TKN) concentration at Deer Creek nr Pleasant Valley, MN23 (05008001)

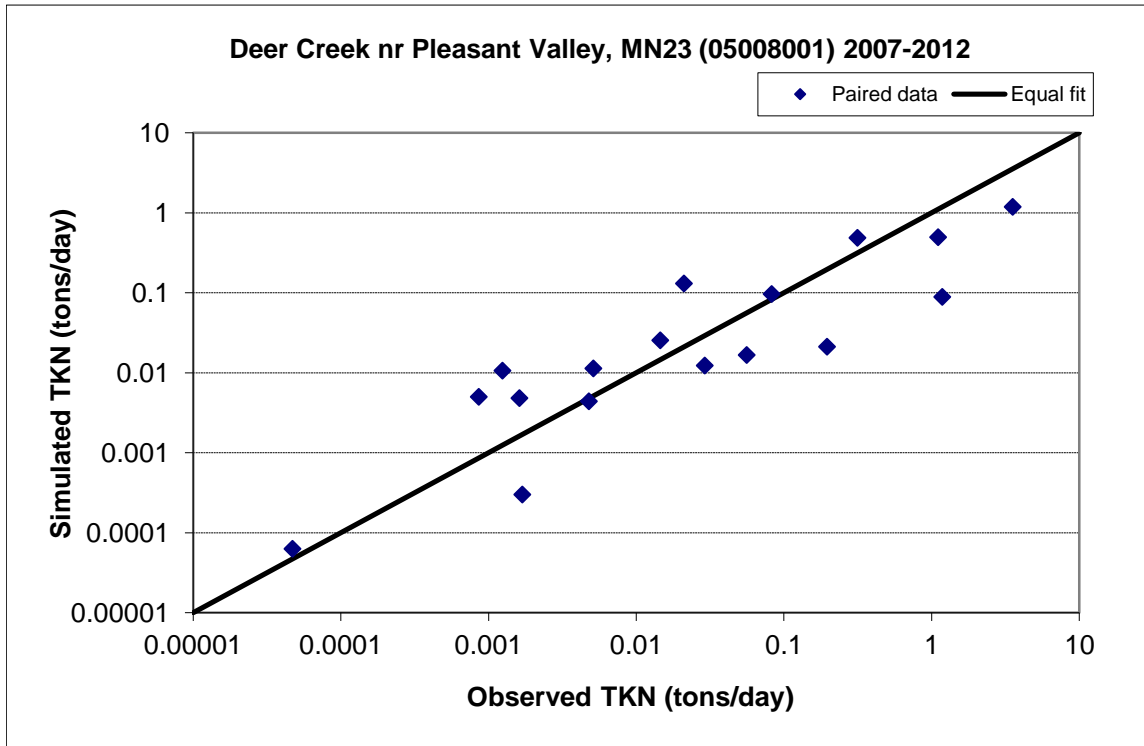


Figure B-12. Paired simulated vs. observed Total Kjeldahl Nitrogen (TKN) load at Deer Creek nr Pleasant Valley, MN23 (05008001) (calibration period)

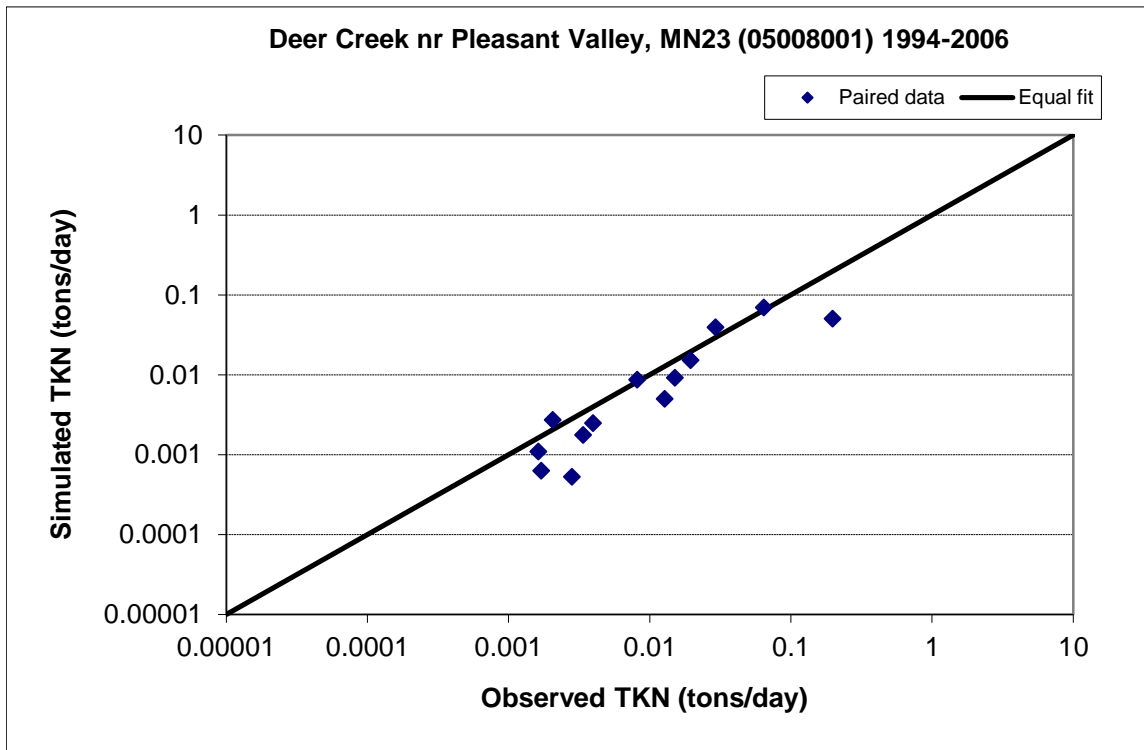


Figure B-13. Paired simulated vs. observed Total Kjeldahl Nitrogen (TKN) load at Deer Creek nr Pleasant Valley, MN23 (05008001) (validation period)

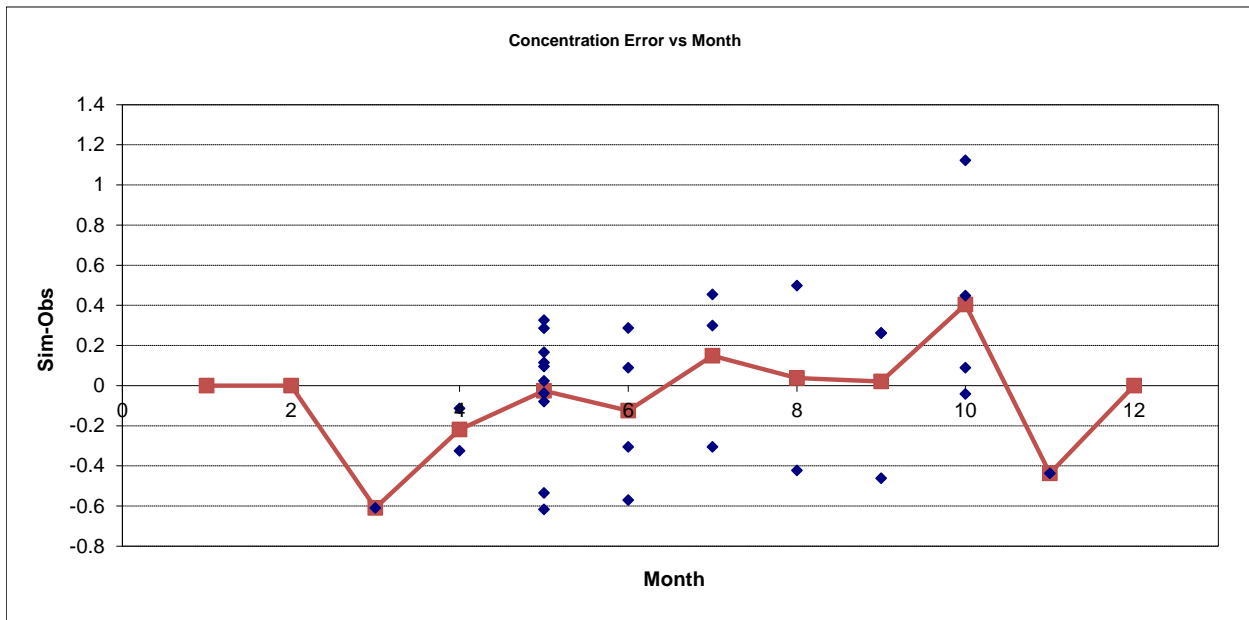


Figure B-14. Residual (Simulated - Observed) vs. Month Total Kjeldahl Nitrogen (TKN) at Deer Creek nr Pleasant Valley, MN23 (05008001)

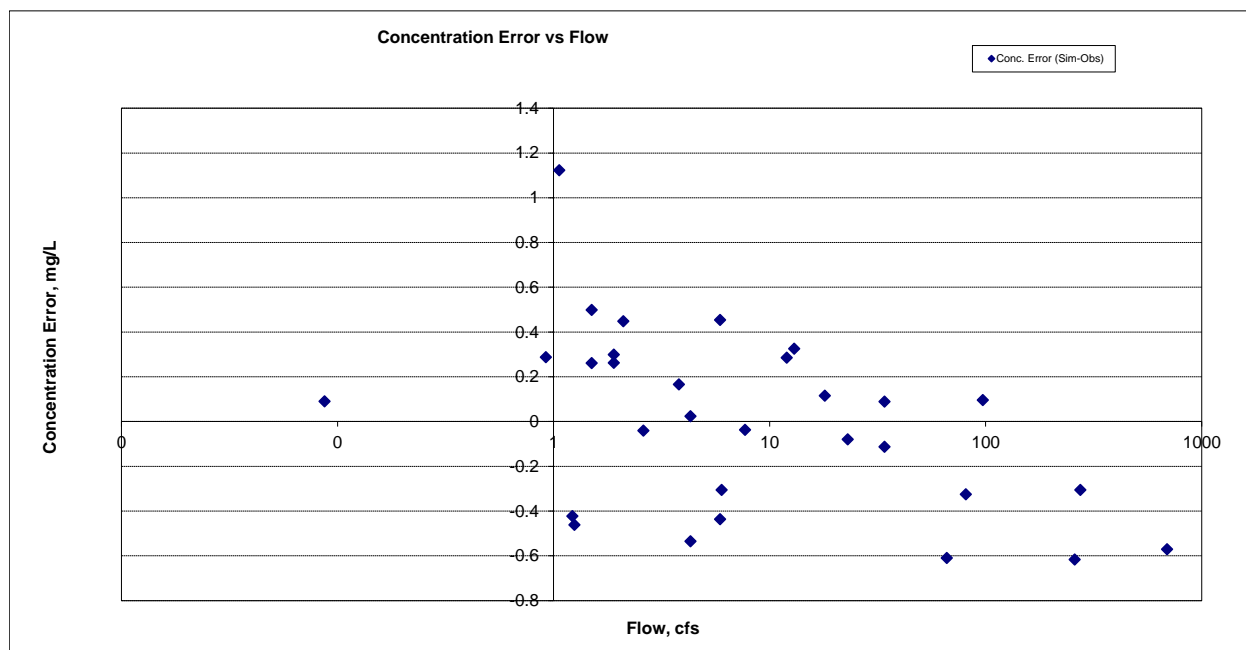


Figure B-15. Residual (Simulated - Observed) vs. Flow Total Kjeldahl Nitrogen (TKN) at Deer Creek nr Pleasant Valley, MN23 (05008001)

B.1.4 Nitrite+ Nitrate Nitrogen (NOx)

Table B-3. Nitrite+ Nitrate Nitrogen (NOx) statistics

Period	1994-2006	2007-2012
Count	5	35
Concentration Average Error	177.51%	-18.95%
Concentration Median Error	62.73%	6.72%
Load Average Error	218.54%	-27.89%
Load Median Error	63.96%	0.04%
Paired t conc	0.05	0.51
Paired t load	0.08	0.38

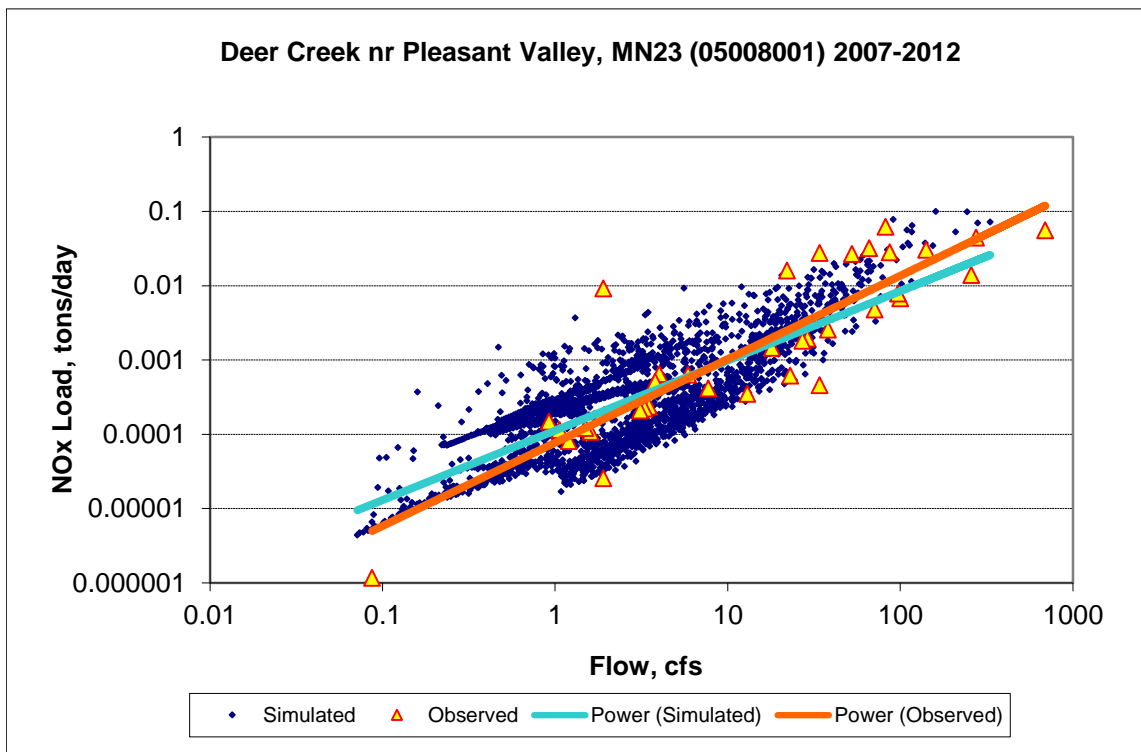


Figure B-16. Power plot of simulated and observed Nitrite+ Nitrate Nitrogen (NOx) load vs flow at Deer Creek nr Pleasant Valley, MN23 (05008001) (calibration period)

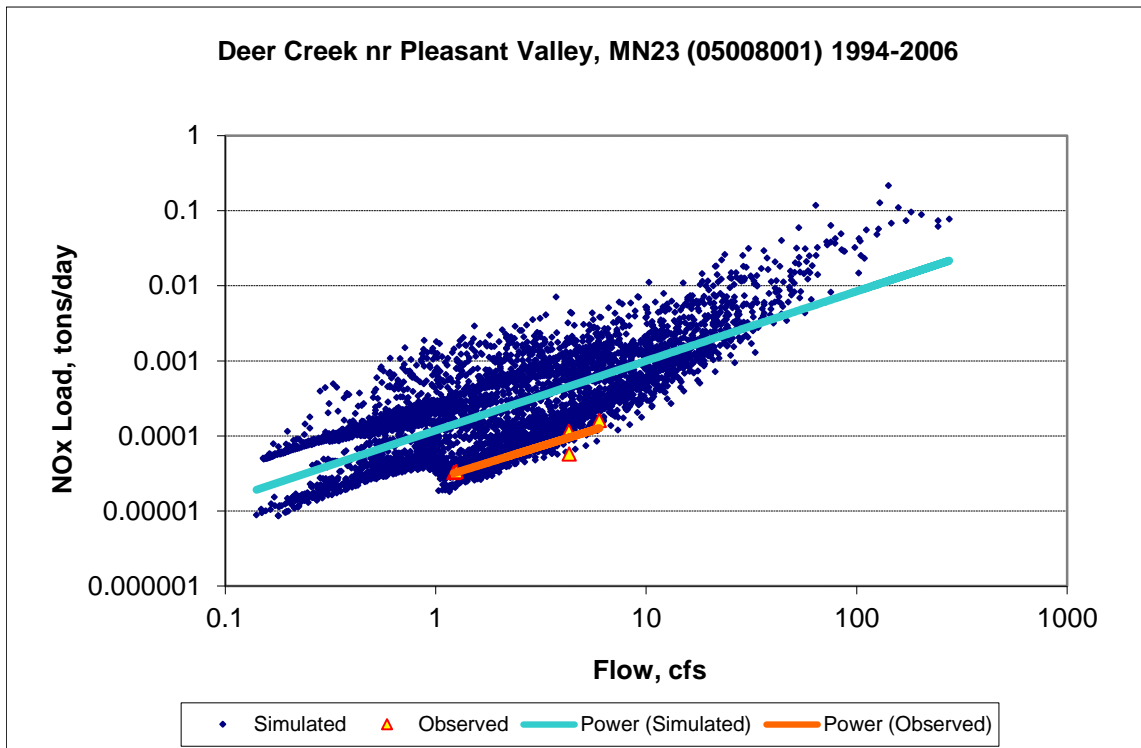
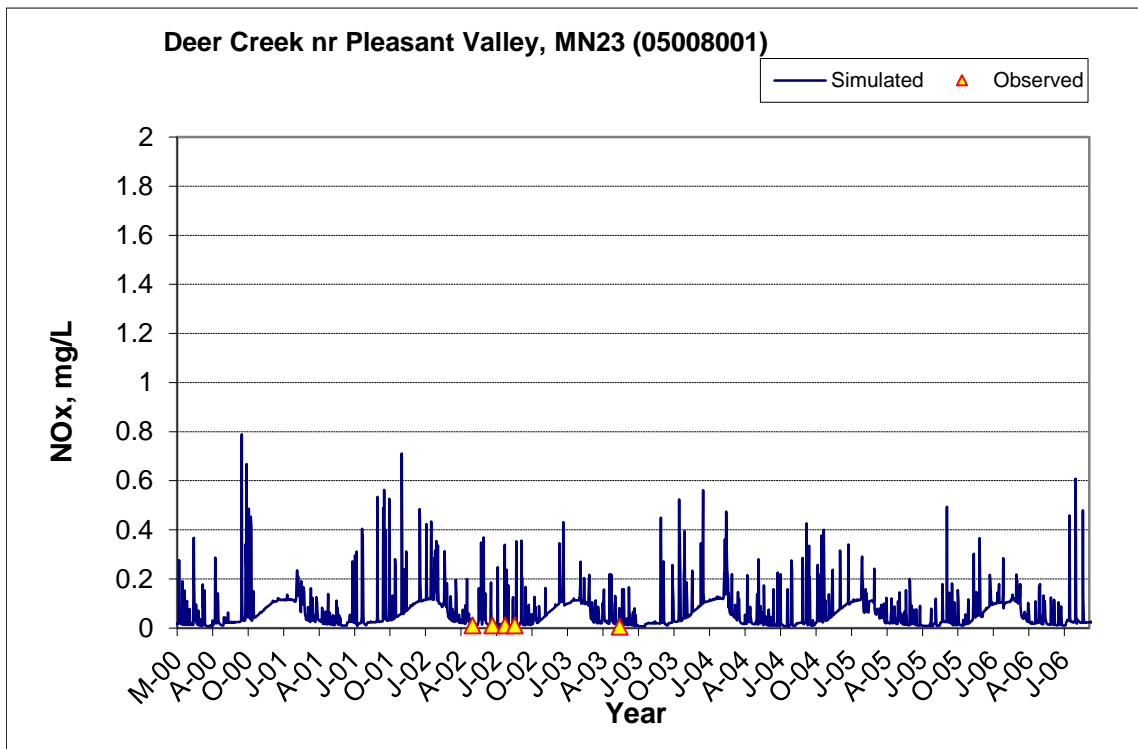
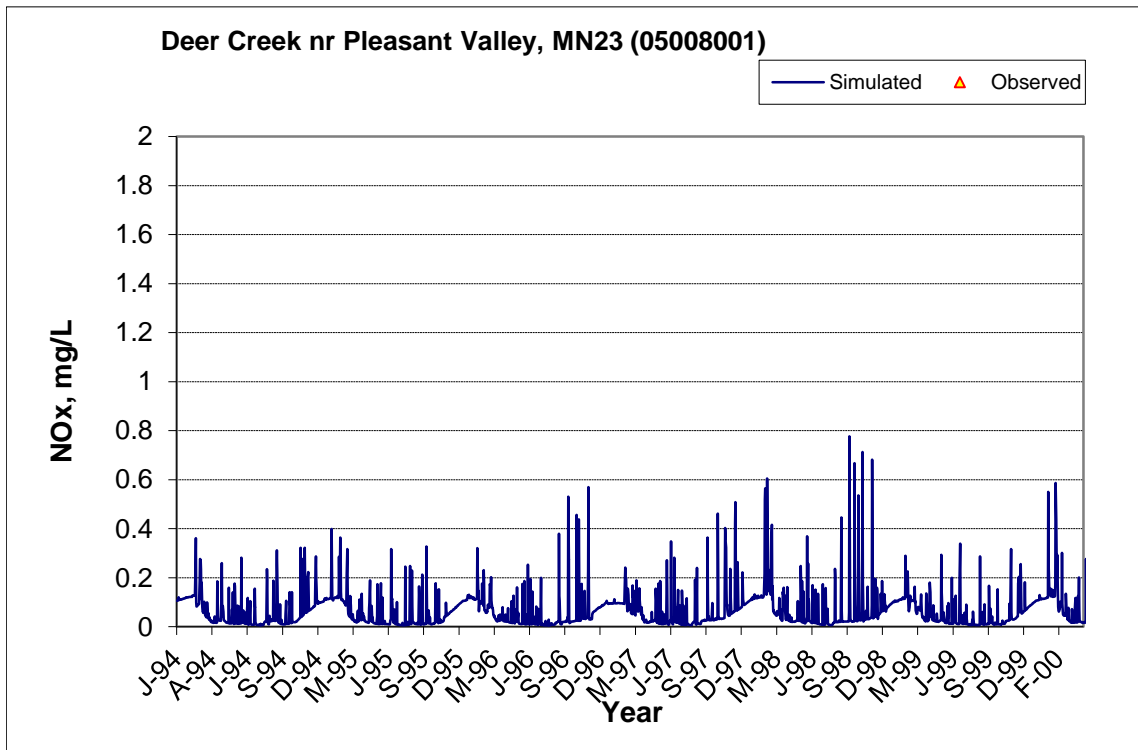


Figure B-17. Power plot of simulated and observed Nitrite+ Nitrate Nitrogen (NOx) load vs flow at Deer Creek nr Pleasant Valley, MN23 (05008001) (validation period)



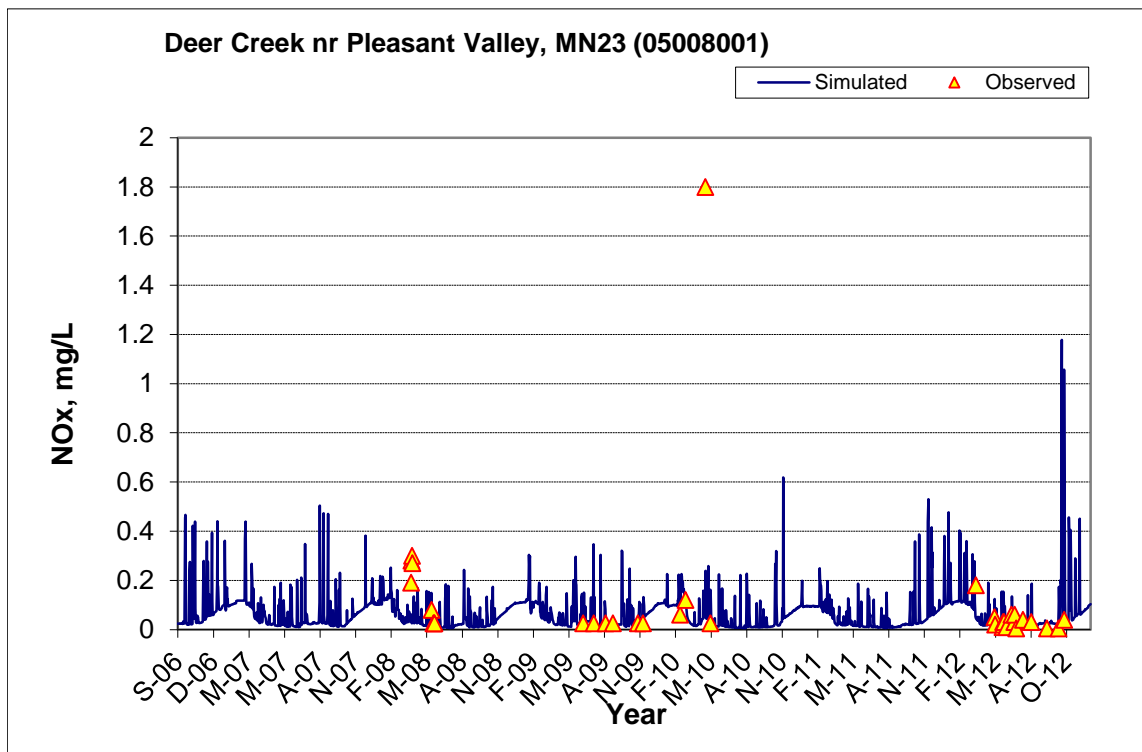


Figure B-18. Time series of observed and simulated Nitrite+ Nitrate Nitrogen (NOx) concentration at Deer Creek nr Pleasant Valley, MN23 (05008001)

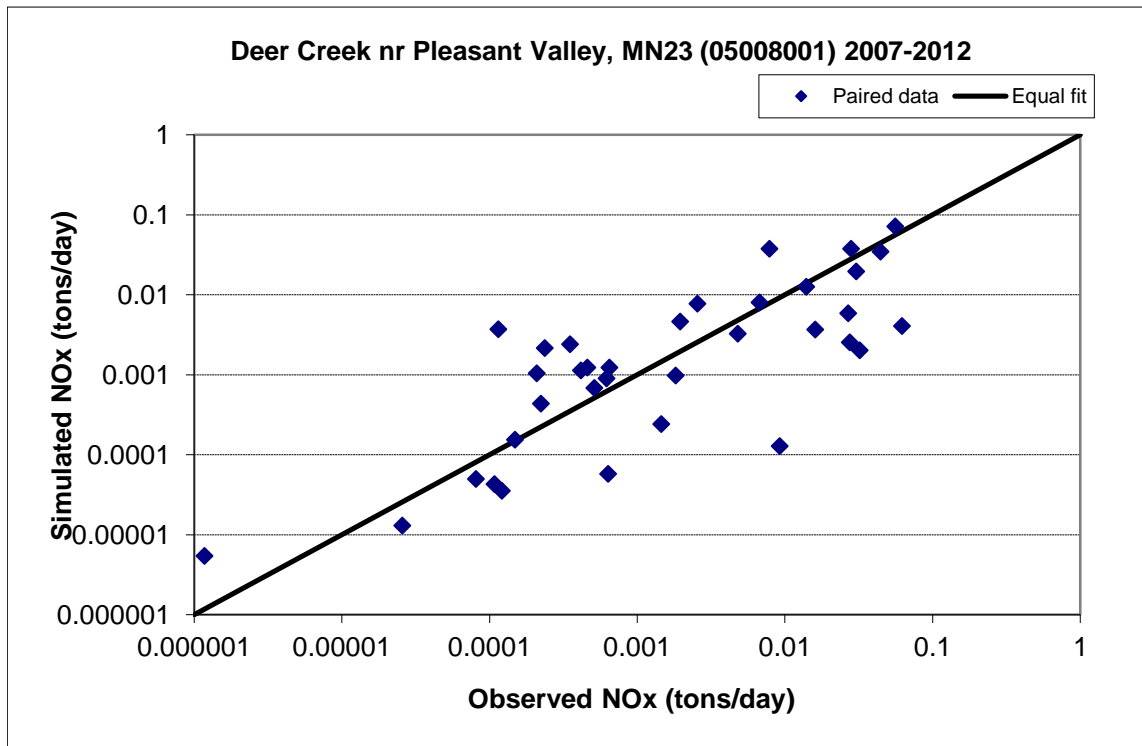


Figure B-19. Paired simulated vs. observed Nitrite+ Nitrate Nitrogen (NOx) load at Deer Creek nr Pleasant Valley, MN23 (05008001) (calibration period)

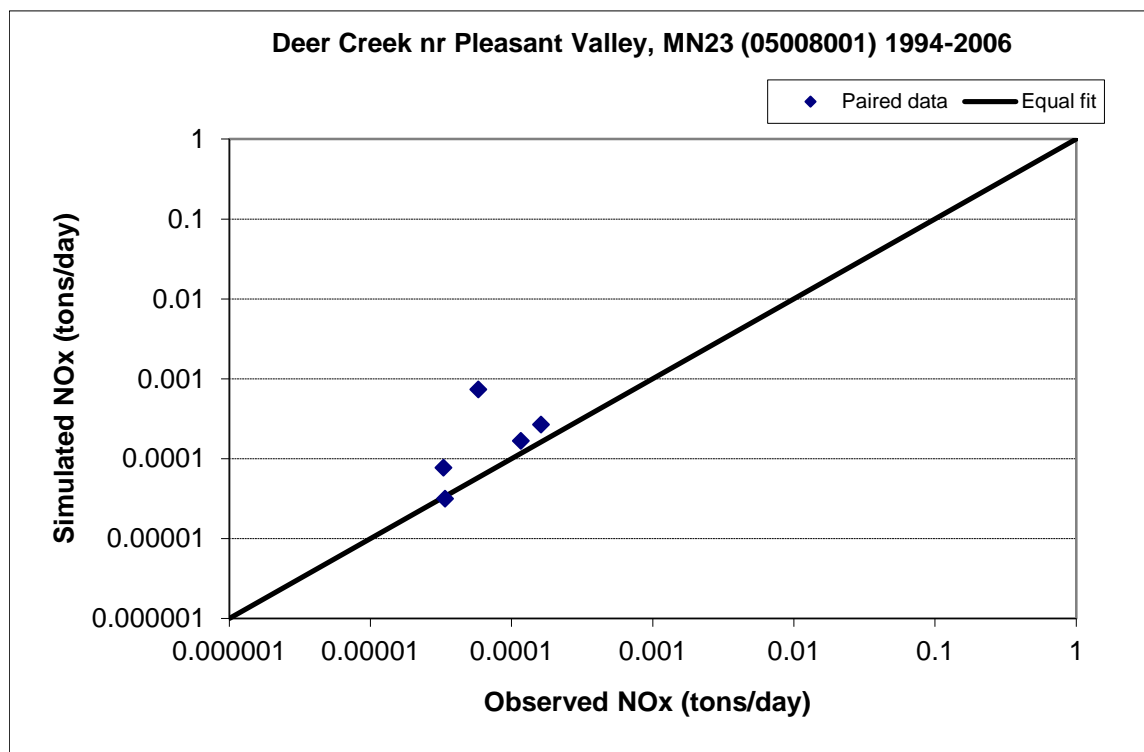


Figure B-20. Paired simulated vs. observed Nitrite+ Nitrate Nitrogen (NOx) load at Deer Creek nr Pleasant Valley, MN23 (05008001) (validation period)

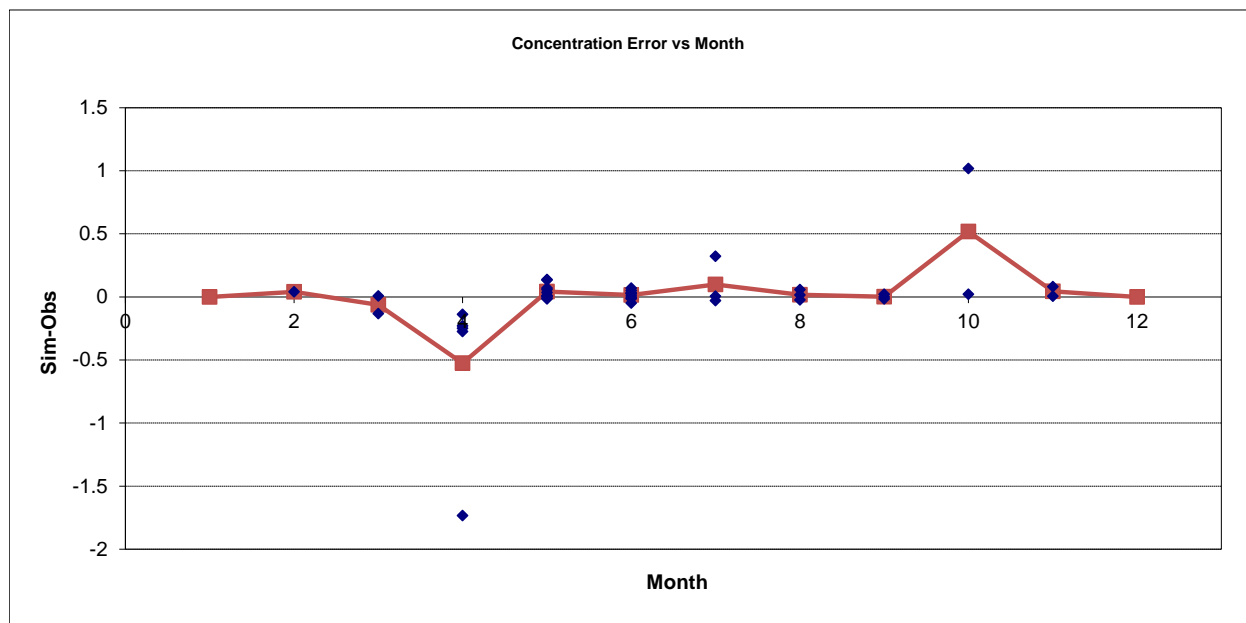


Figure B-21. Residual (Simulated - Observed) vs. Month Nitrite+ Nitrate Nitrogen (NOx) at Deer Creek nr Pleasant Valley, MN23 (05008001)

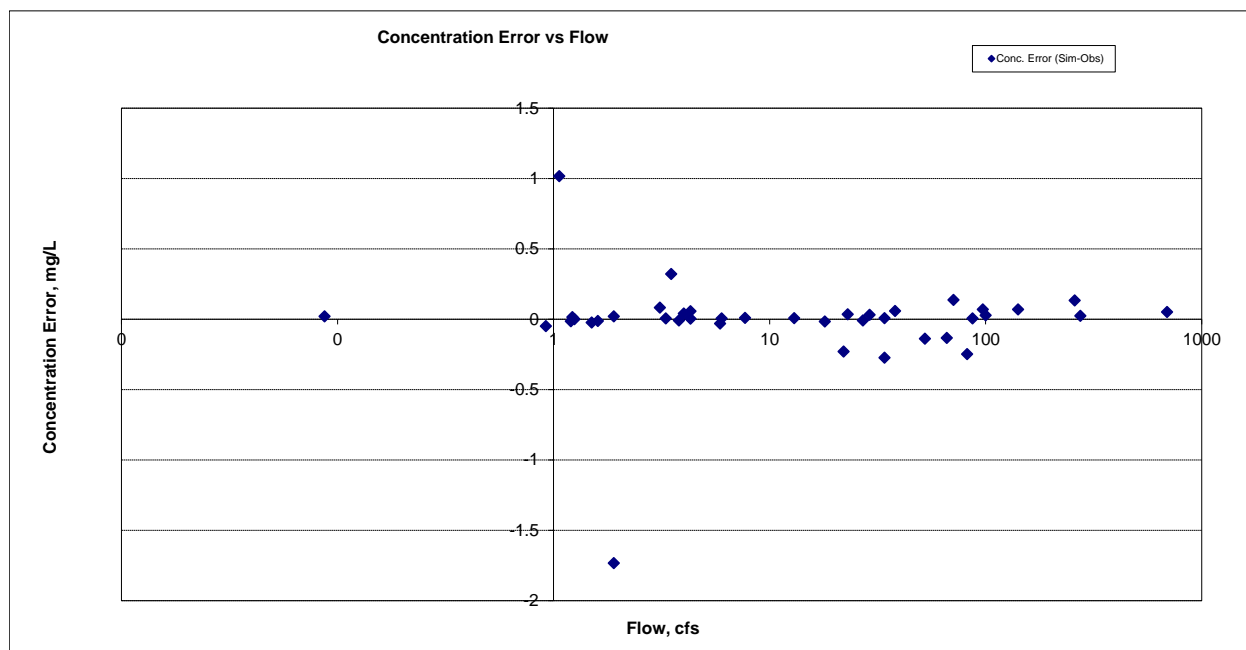


Figure B-22. Residual (Simulated - Observed) vs. Flow Nitrite+ Nitrate Nitrogen (NOx) at Deer Creek nr Pleasant Valley, MN23 (05008001)

B.1.5 Total Nitrogen (TN)

Table B-4. Total Nitrogen (TN) statistics

Period	1994-2006	2007-2012
Count	5	17
Concentration Average Error	-29.85%	16.84%
Concentration Median Error	-37.52%	12.44%
Load Average Error	-23.30%	-58.76%
Load Median Error	-15.87%	0.00%
Paired t conc	0.14	0.58
Paired t load	0.46	0.18

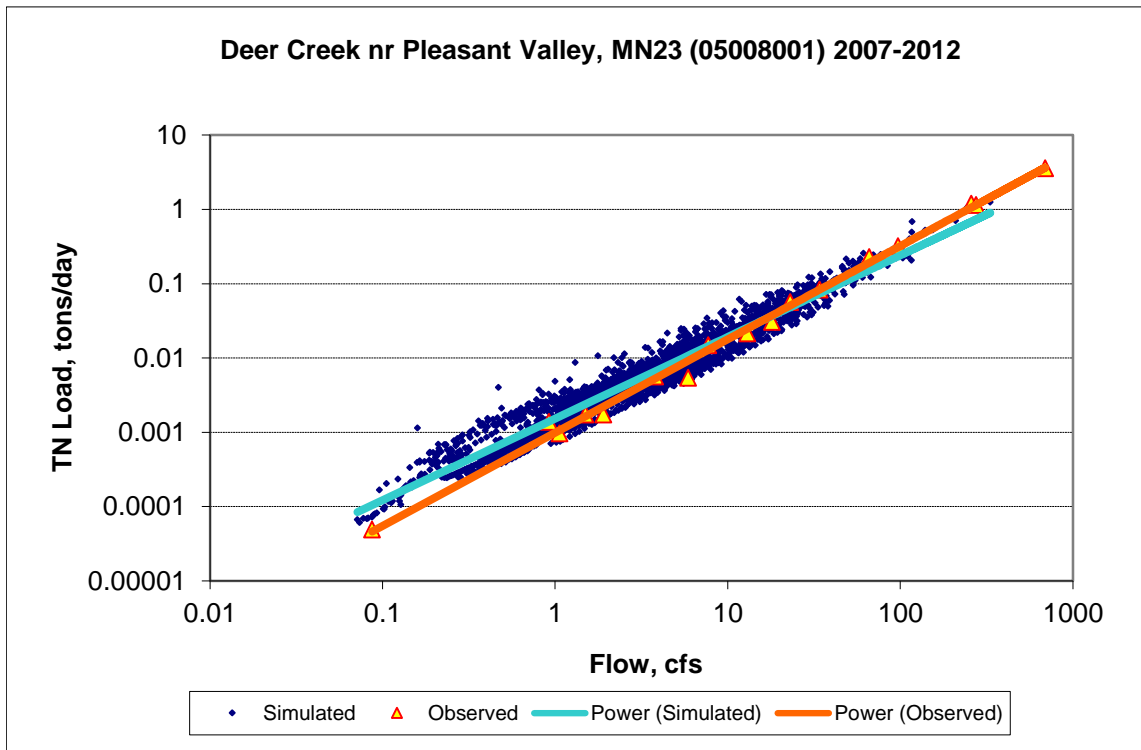


Figure B-23. Power plot of simulated and observed Total Nitrogen (TN) load vs flow at Deer Creek nr Pleasant Valley, MN23 (05008001) (calibration period)

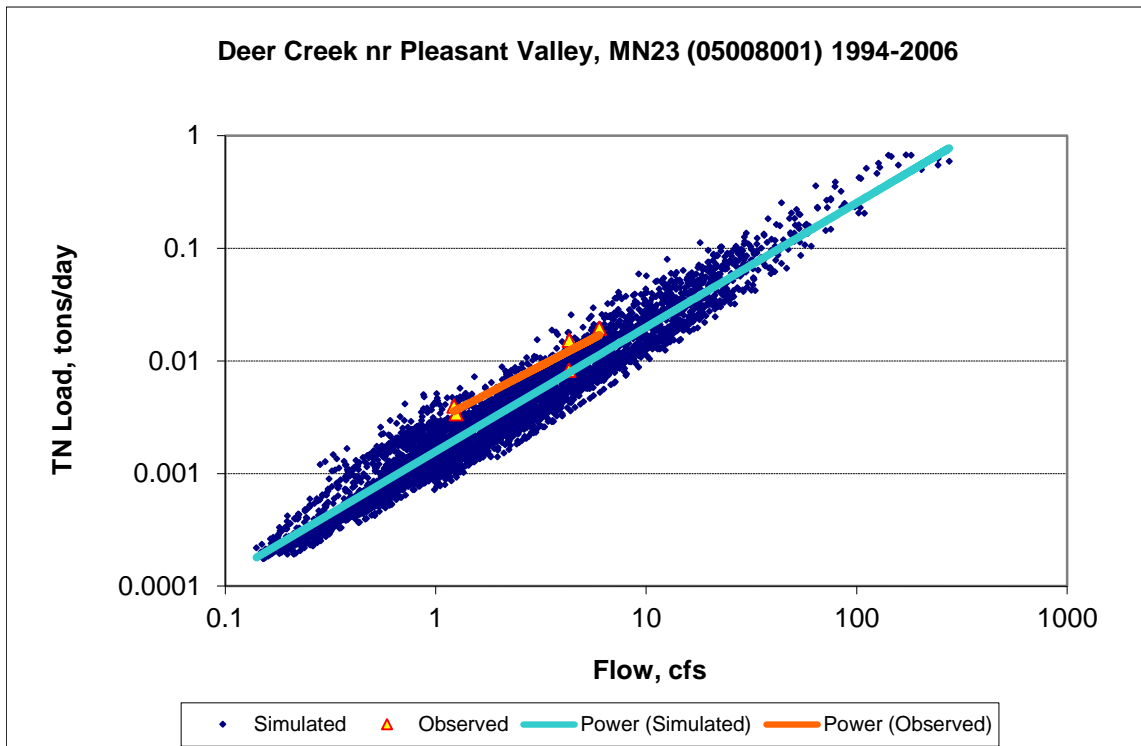
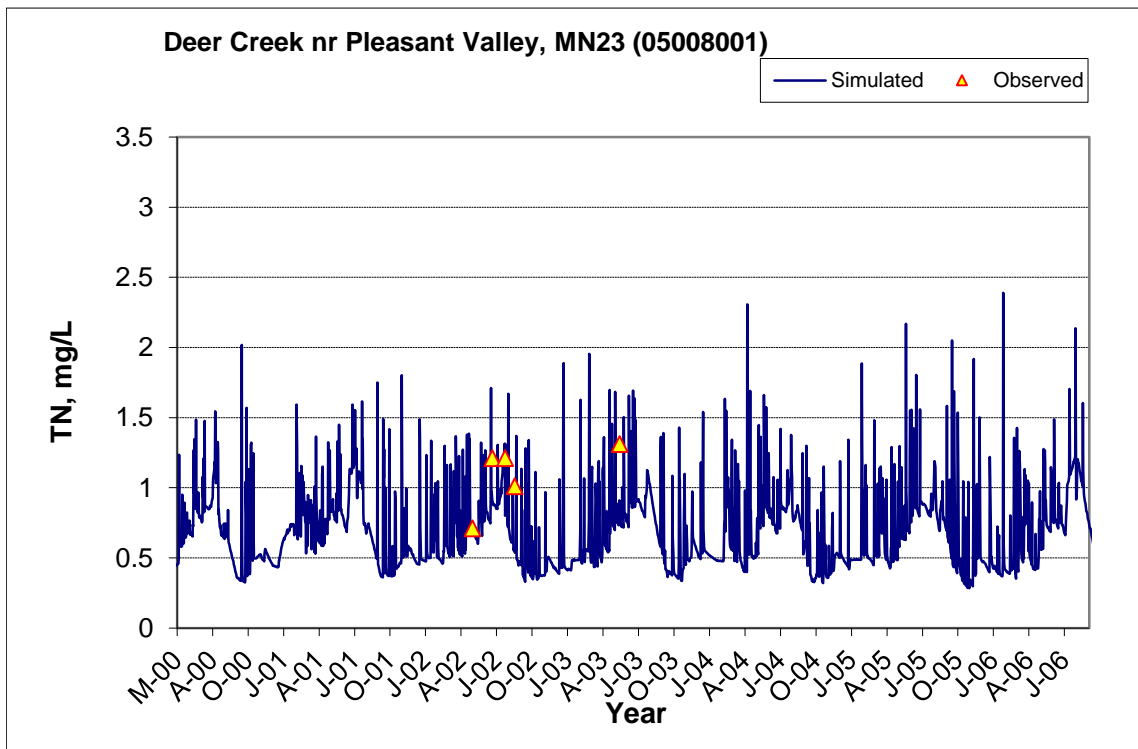
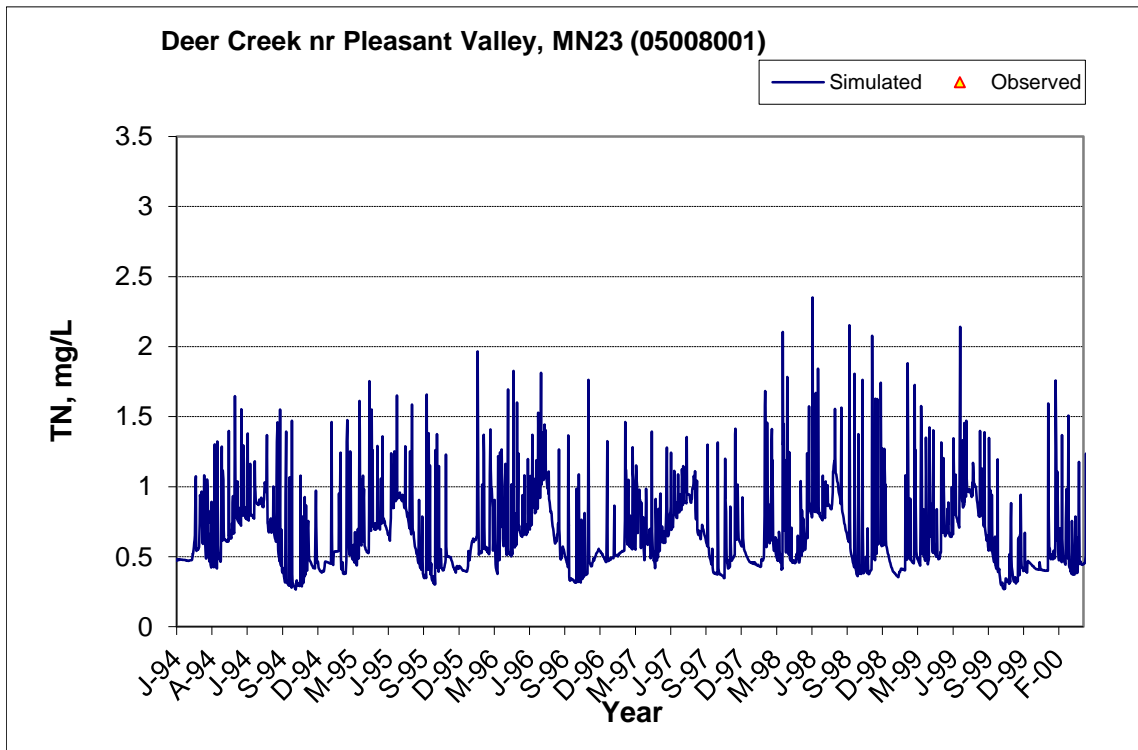


Figure B-24. Power plot of simulated and observed Total Nitrogen (TN) load vs flow at Deer Creek nr Pleasant Valley, MN23 (05008001) (validation period)



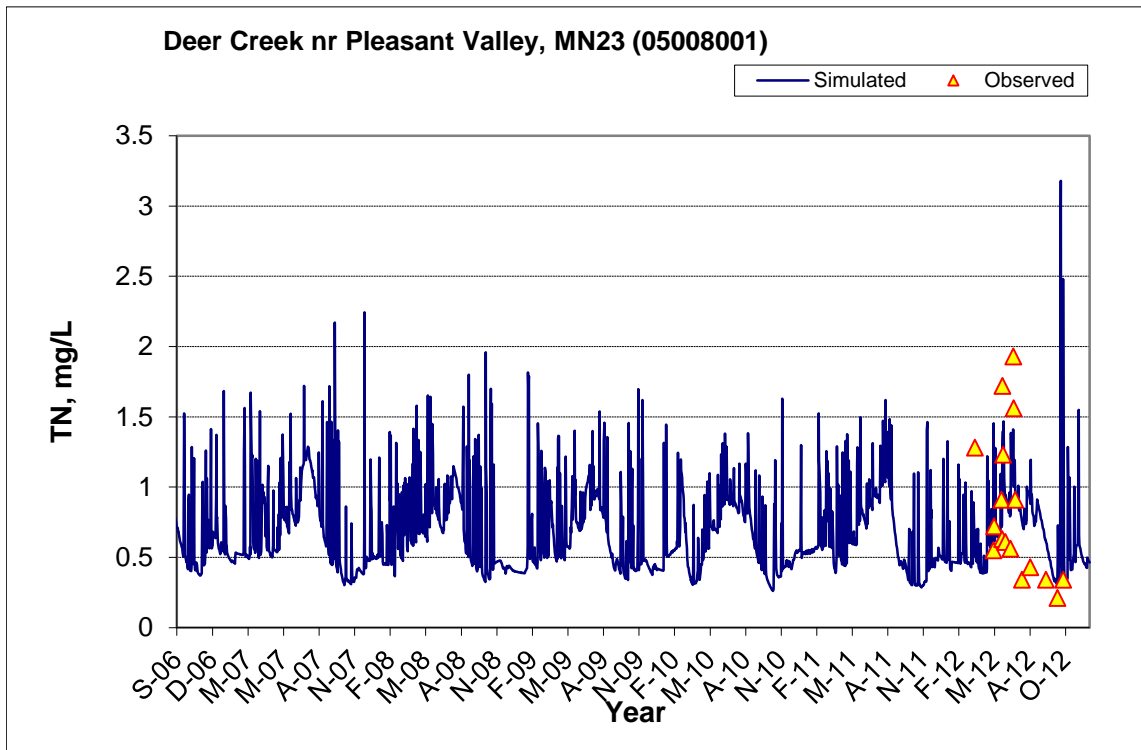


Figure B-25. Time series of observed and simulated Total Nitrogen (TN) concentration at Deer Creek nr Pleasant Valley, MN23 (05008001)

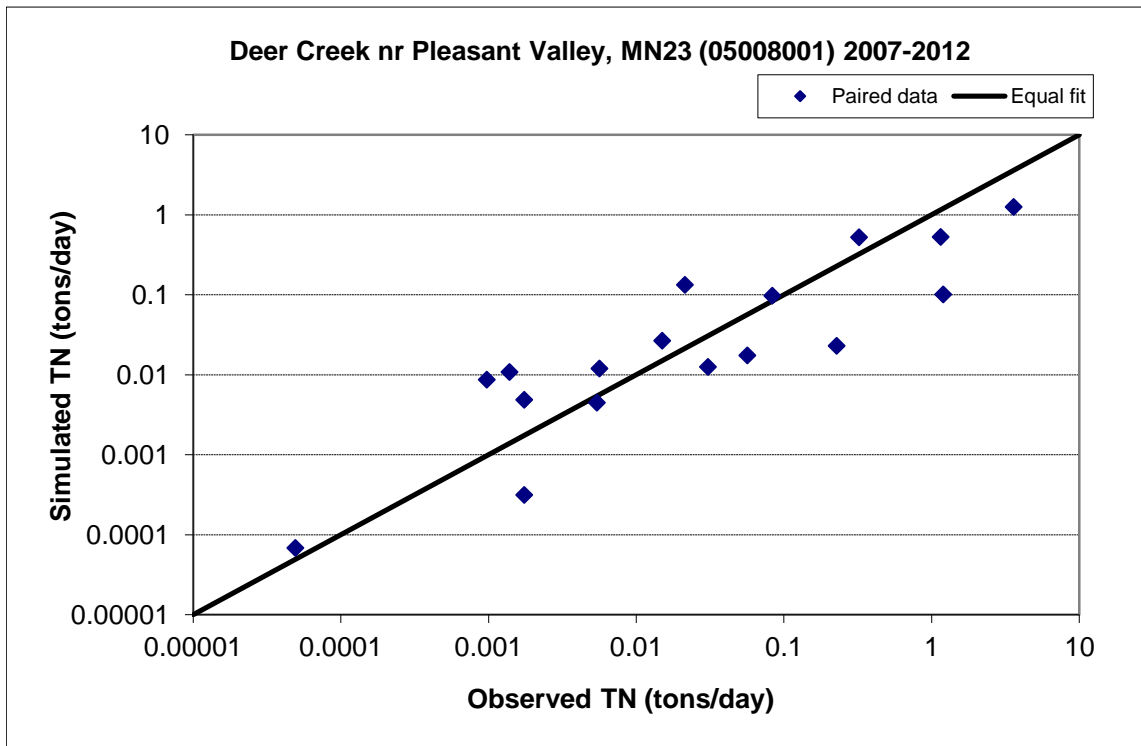


Figure B-26. Paired simulated vs. observed Total Nitrogen (TN) load at Deer Creek nr Pleasant Valley, MN23 (05008001) (calibration period)

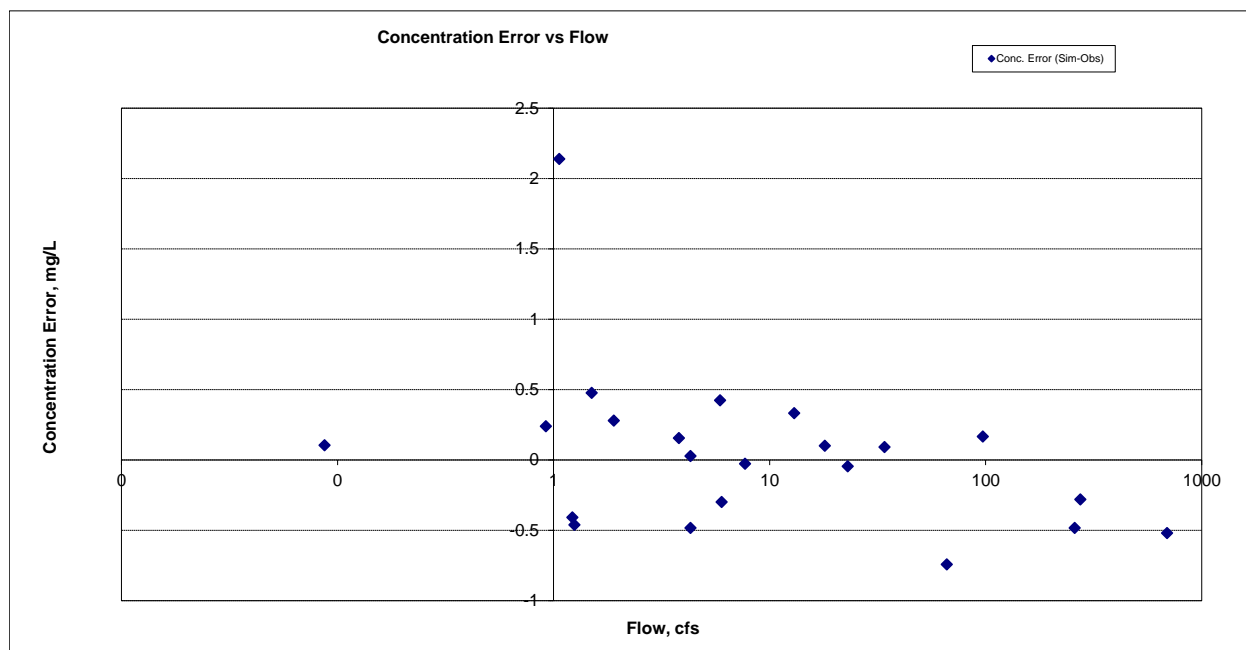


Figure B-29. Residual (Simulated - Observed) vs. Flow Total Nitrogen (TN) at Deer Creek nr Pleasant Valley, MN23 (05008001)

B.1.6 Soluble Reactive Phosphorus (SRP)

Table B-5. Soluble Reactive Phosphorus (SRP) statistics

Period	1994-2006	2007-2012
Count	6	35
Concentration Average Error	-17.99%	53.06%
Concentration Median Error	-41.71%	17.61%
Load Average Error	-19.75%	-1.05%
Load Median Error	-31.95%	0.27%
Paired t conc	0.55	0.12
Paired t load	0.50	0.67

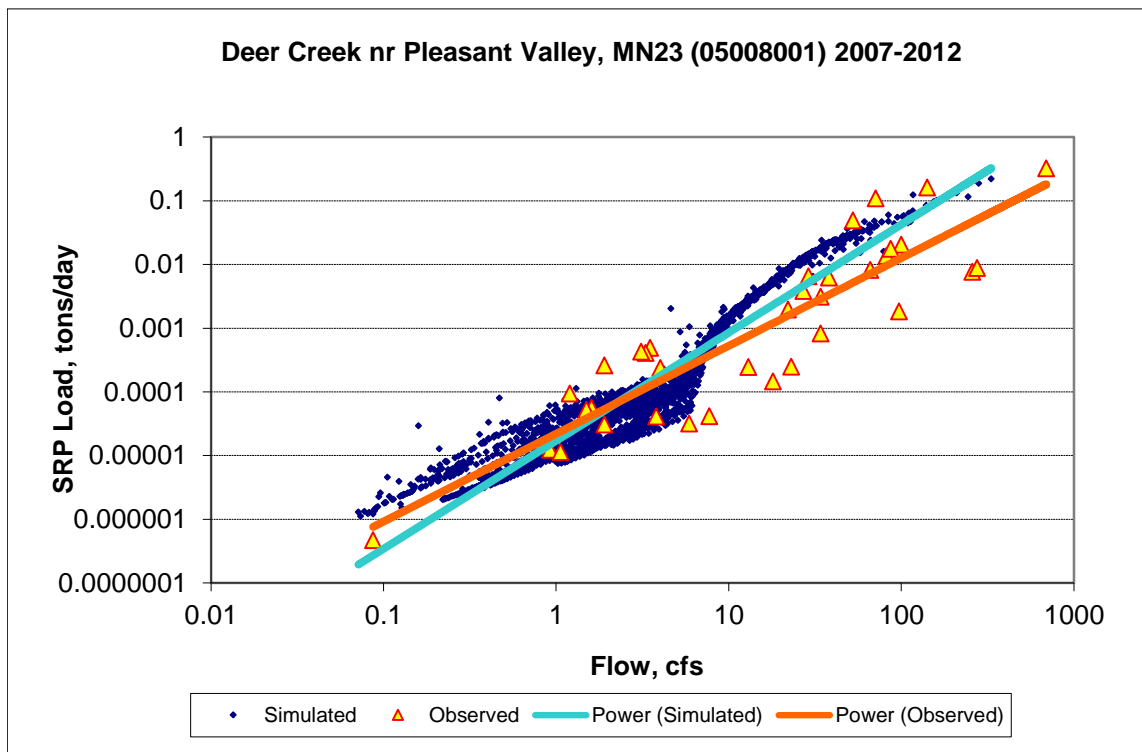


Figure B-30. Power plot of simulated and observed Soluble Reactive Phosphorus (SRP) load vs flow at Deer Creek nr Pleasant Valley, MN23 (05008001) (calibration period)

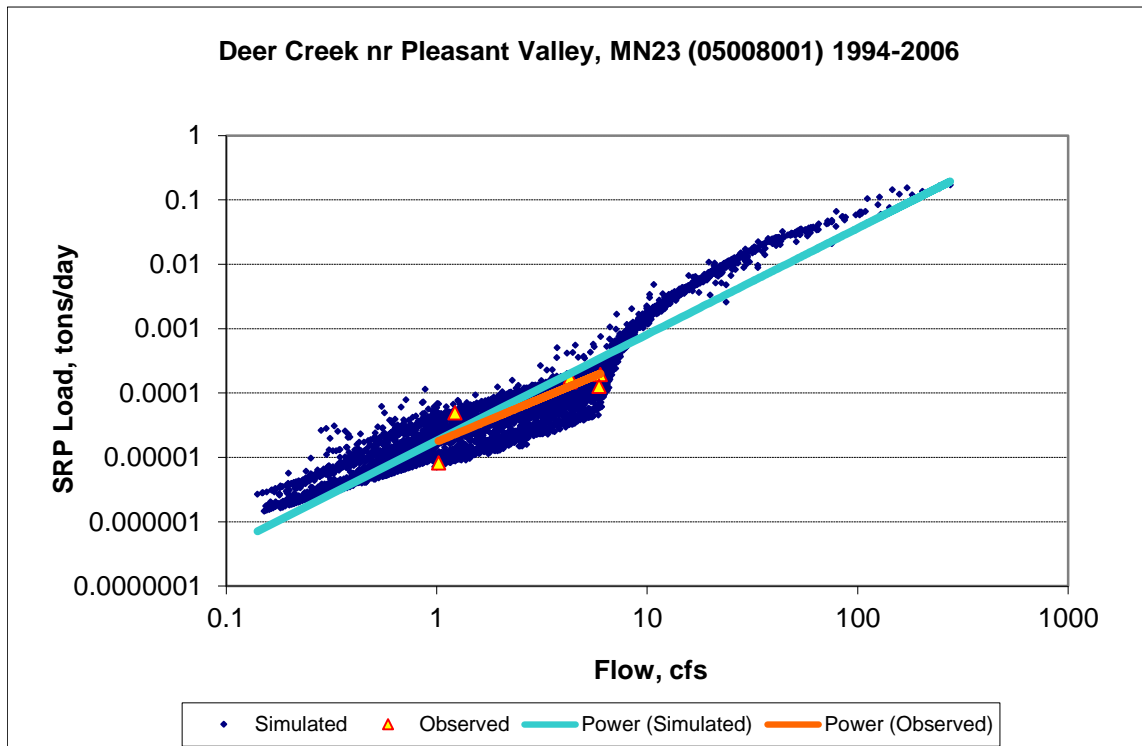
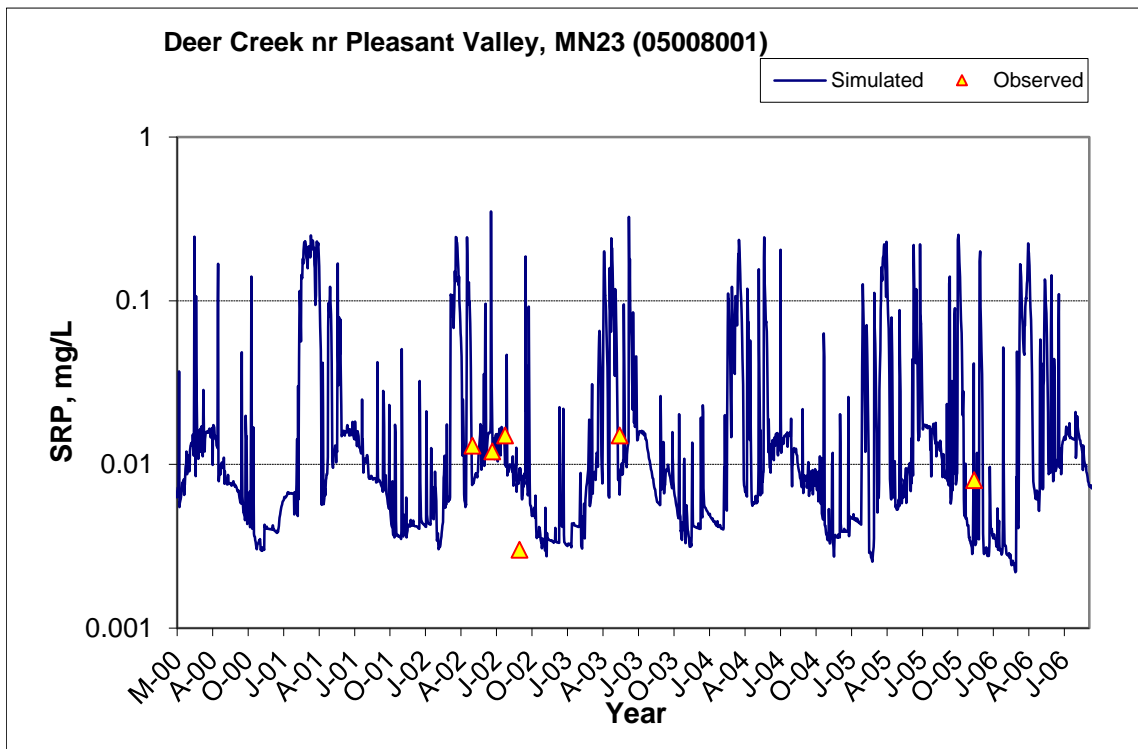
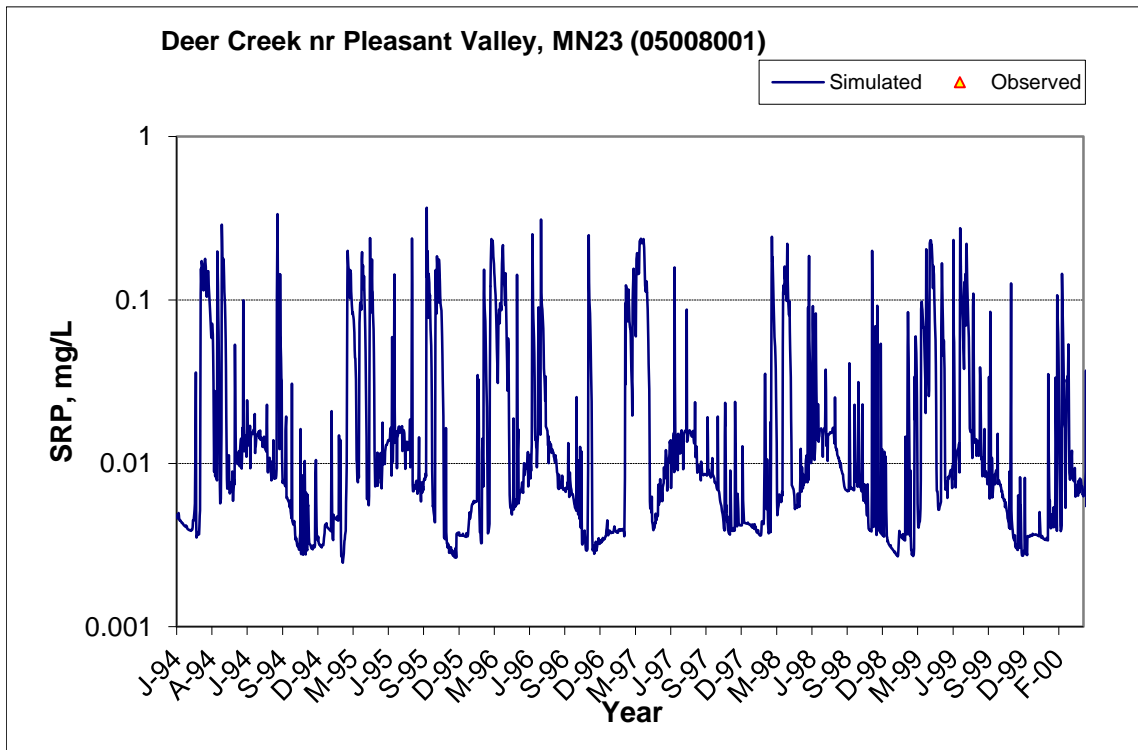


Figure B-31. Power plot of simulated and observed Soluble Reactive Phosphorus (SRP) load vs flow at Deer Creek nr Pleasant Valley, MN23 (05008001) (validation period)



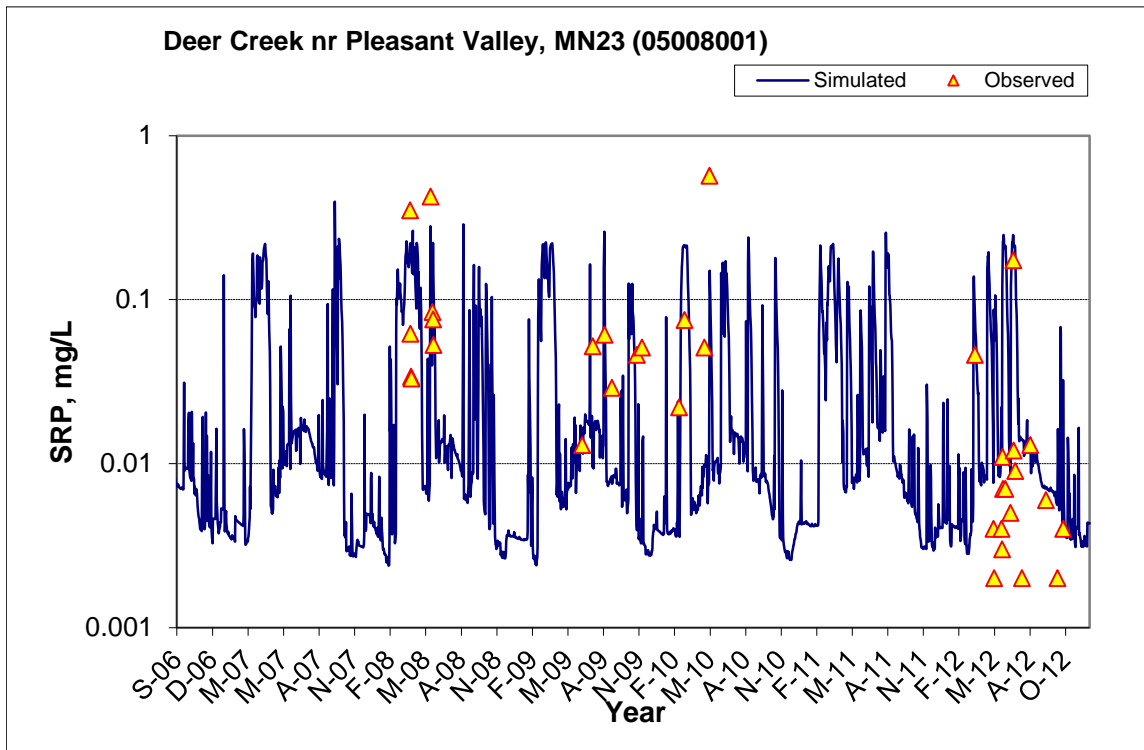


Figure B-32. Time series of observed and simulated Soluble Reactive Phosphorus (SRP) concentration at Deer Creek nr Pleasant Valley, MN23 (05008001)

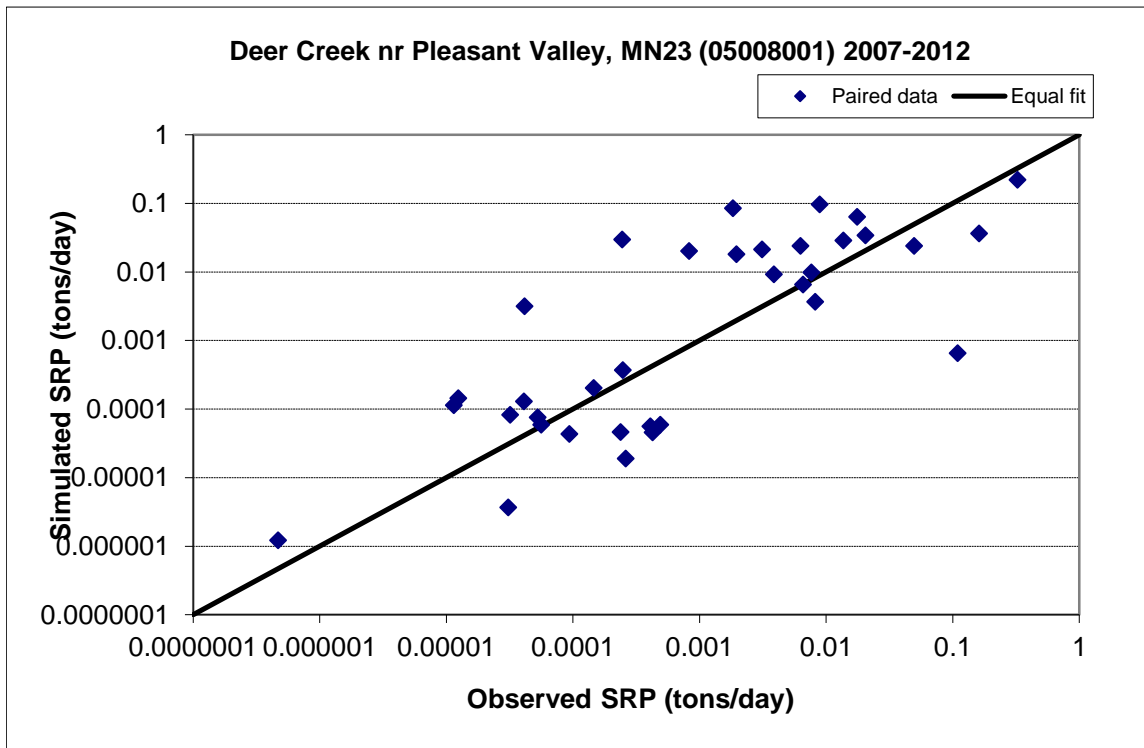


Figure B-33. Paired simulated vs. observed Soluble Reactive Phosphorus (SRP) load at Deer Creek nr Pleasant Valley, MN23 (05008001) (calibration period)

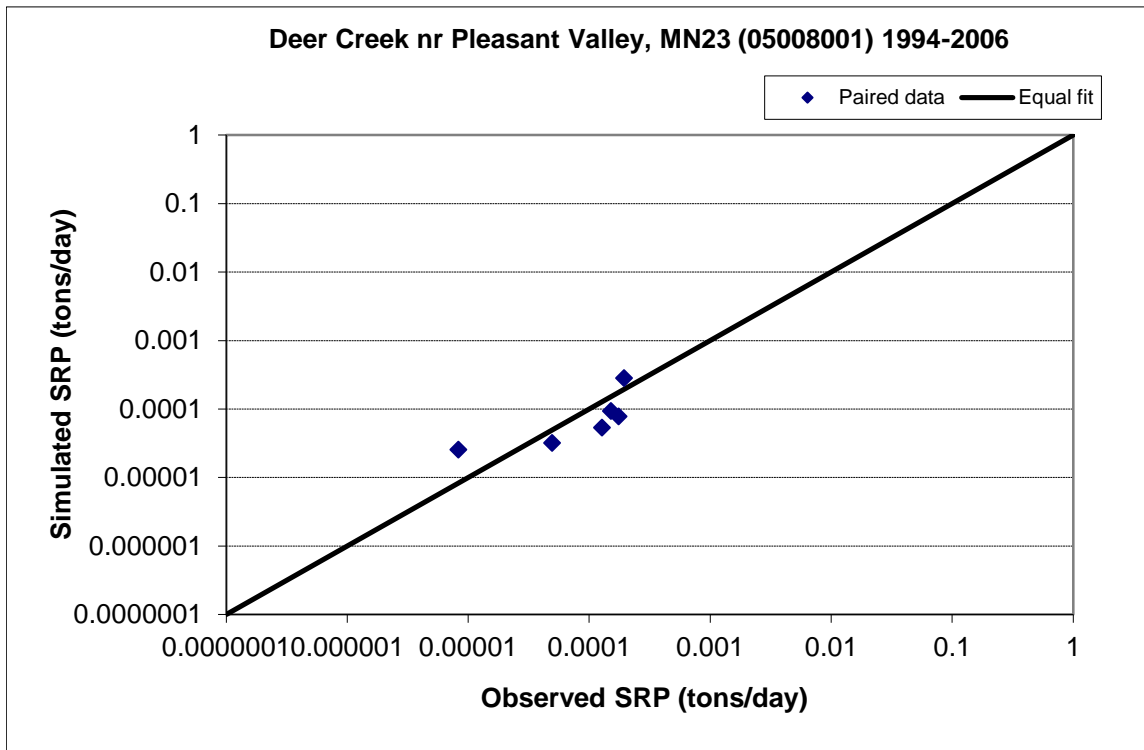


Figure B-34. Paired simulated vs. observed Soluble Reactive Phosphorus (SRP) load at Deer Creek nr Pleasant Valley, MN23 (05008001) (validation period)

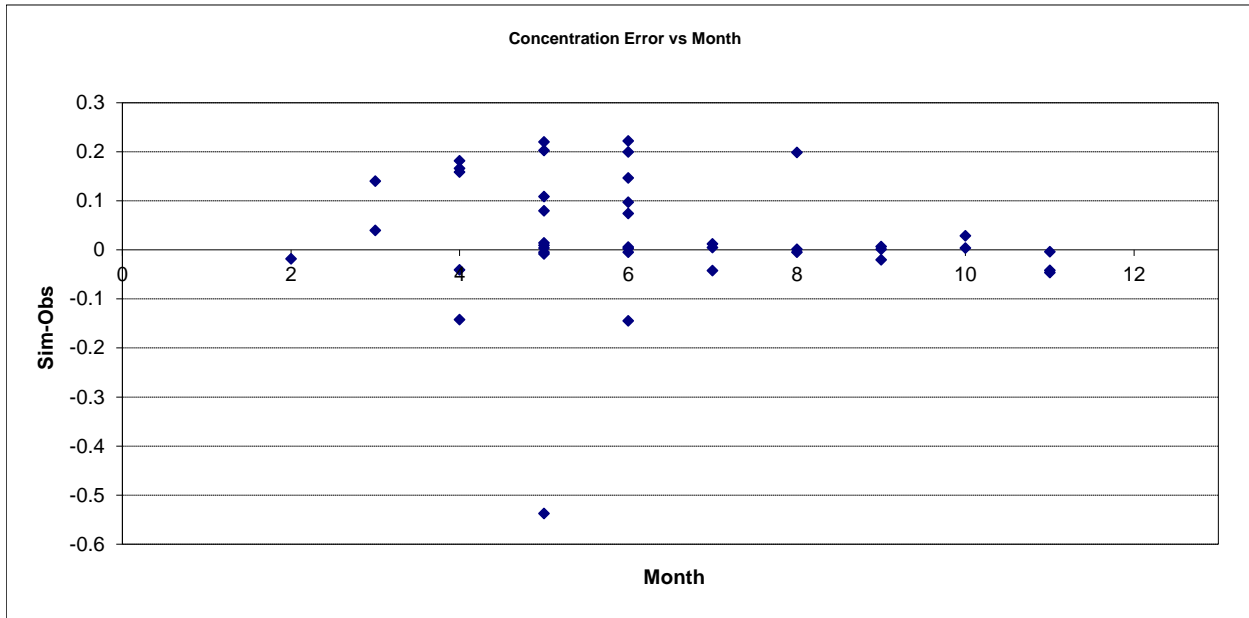


Figure B-35. Residual (Simulated - Observed) vs. Month Soluble Reactive Phosphorus (SRP) at Deer Creek nr Pleasant Valley, MN23 (05008001)

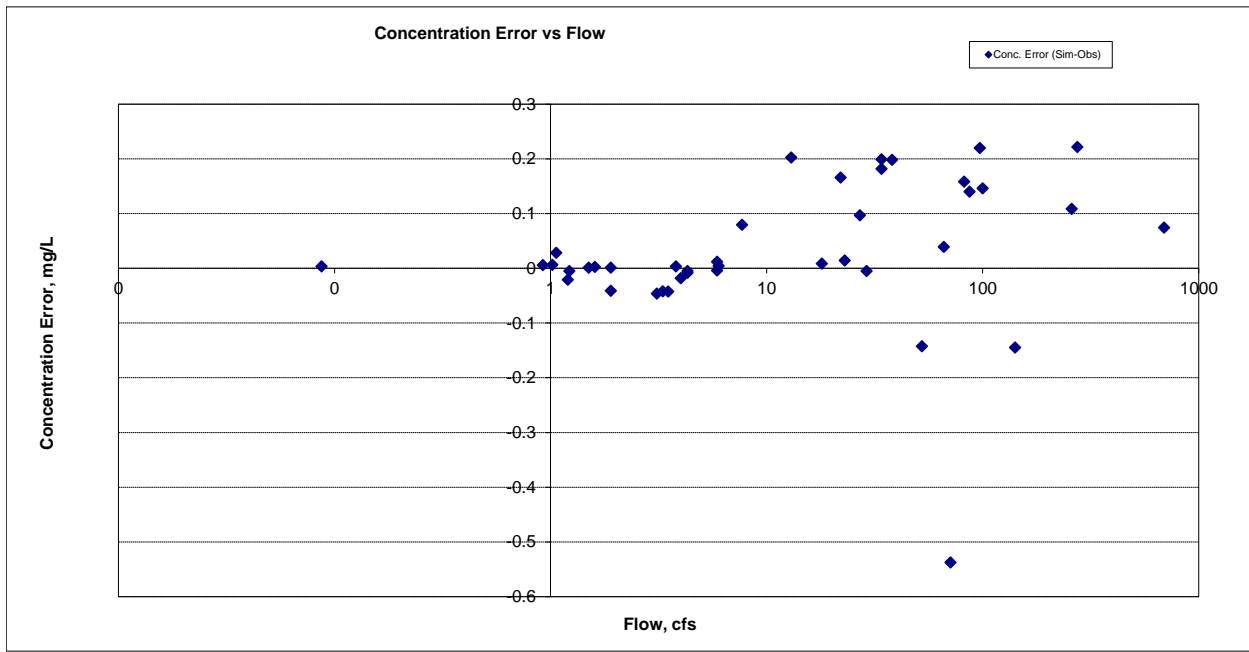
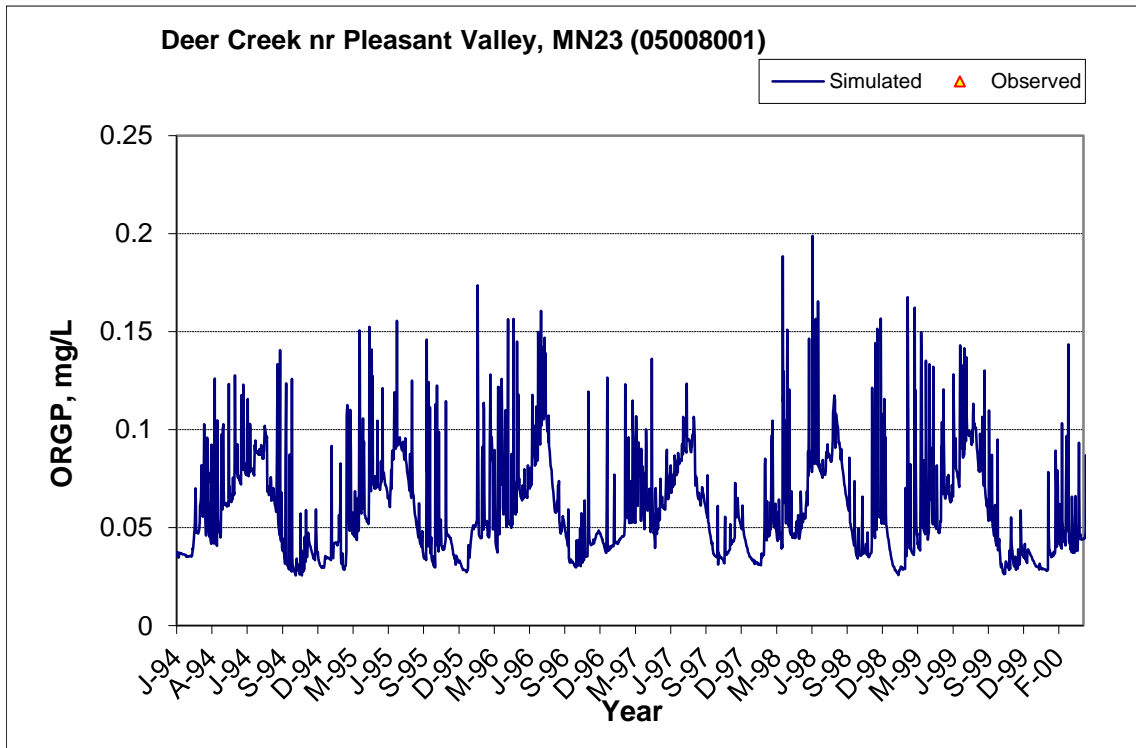


Figure B-36. Residual (Simulated - Observed) vs. Flow Soluble Reactive Phosphorus (SRP) at Deer Creek nr Pleasant Valley, MN23 (05008001)

B.1.7 Organic Phosphorus (OrgP)



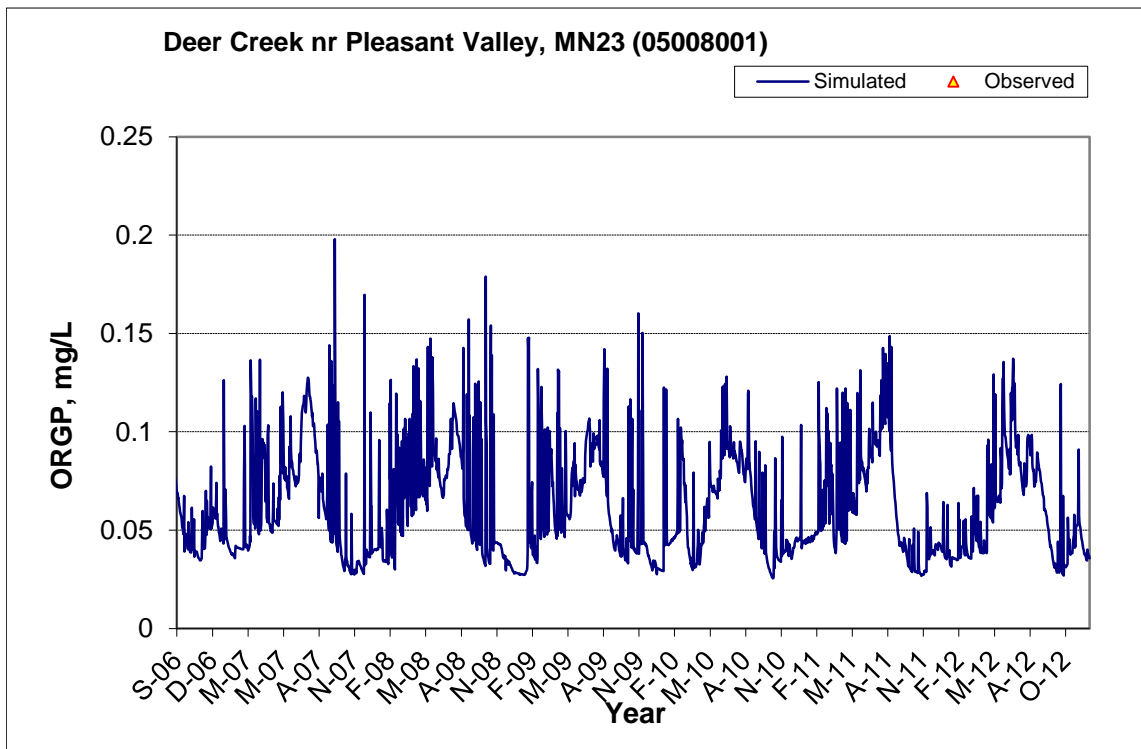
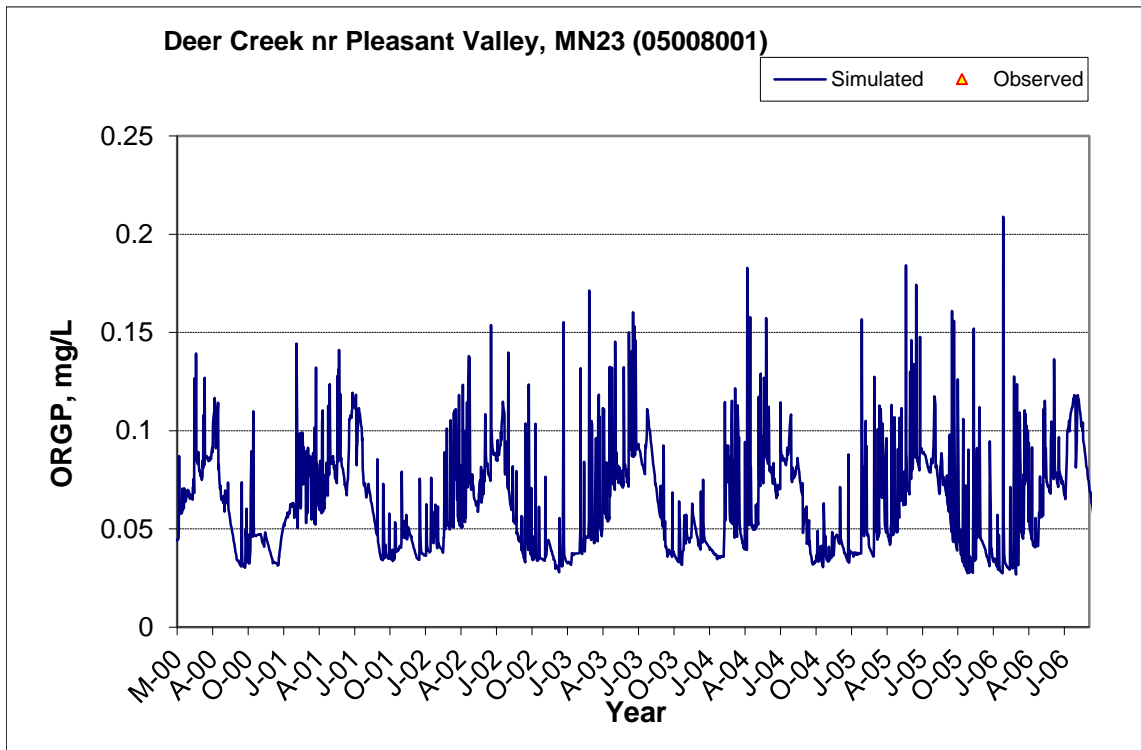


Figure B-37. Time series of observed and simulated Organic Phosphorus (OrgP) concentration at Deer Creek nr Pleasant Valley, MN23 (05008001)

B.1.8 Total Phosphorus (TP)

Table B-6. Total Phosphorus (TP) statistics

Period	1994-2006	2007-2012
Count	79	35
Concentration Average Error	-84.26%	-37.94%
Concentration Median Error	-51.62%	1.03%
Load Average Error	-57.94%	-78.55%
Load Median Error	-12.55%	0.00%
Paired t conc	0.00	0.13
Paired t load	0.06	0.06

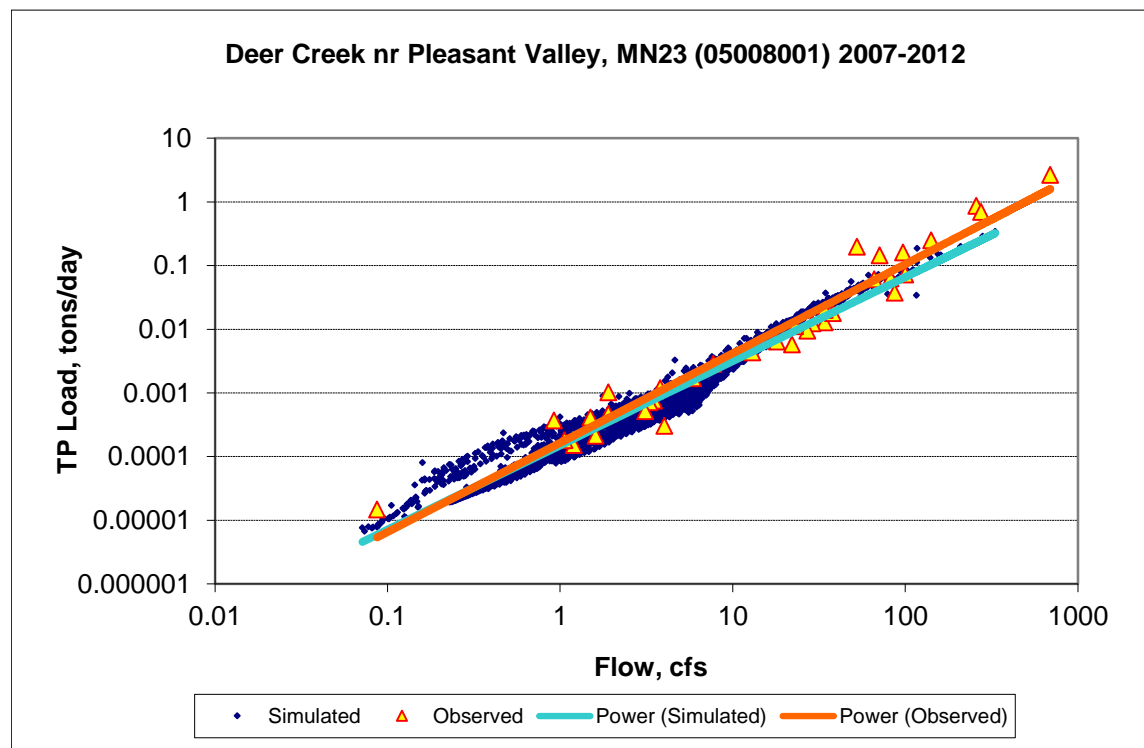


Figure B-38. Power plot of simulated and observed Total Phosphorus (TP) load vs flow at Deer Creek nr Pleasant Valley, MN23 (05008001) (calibration period)

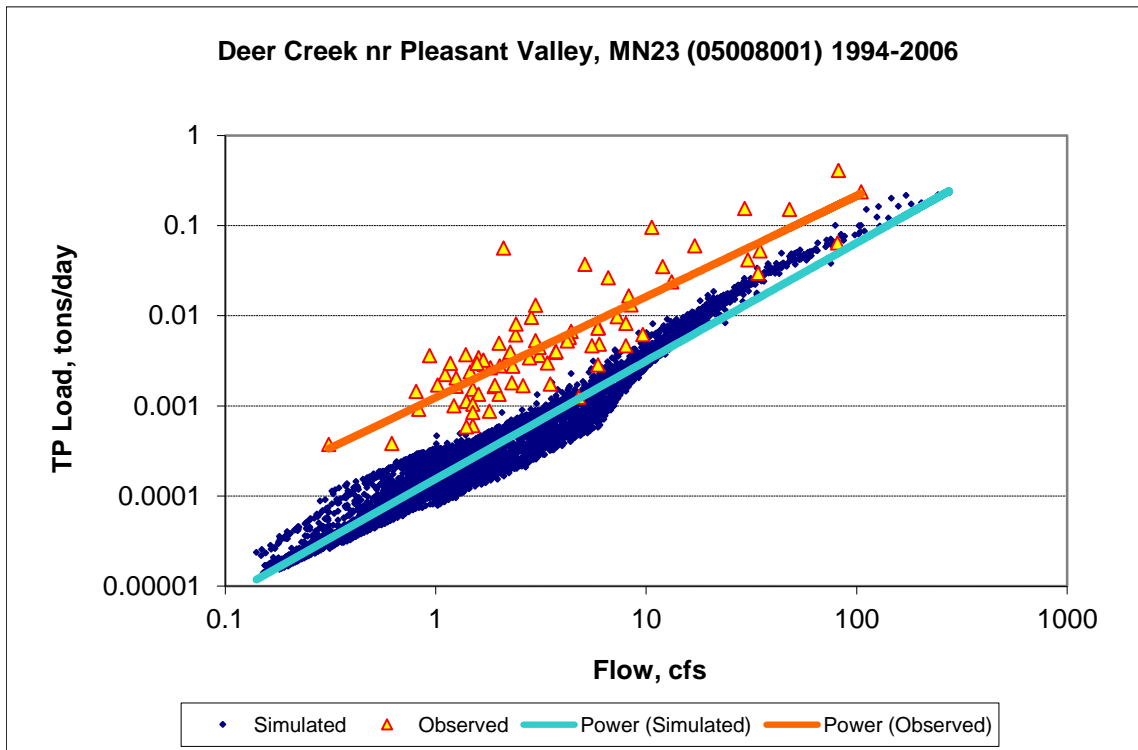
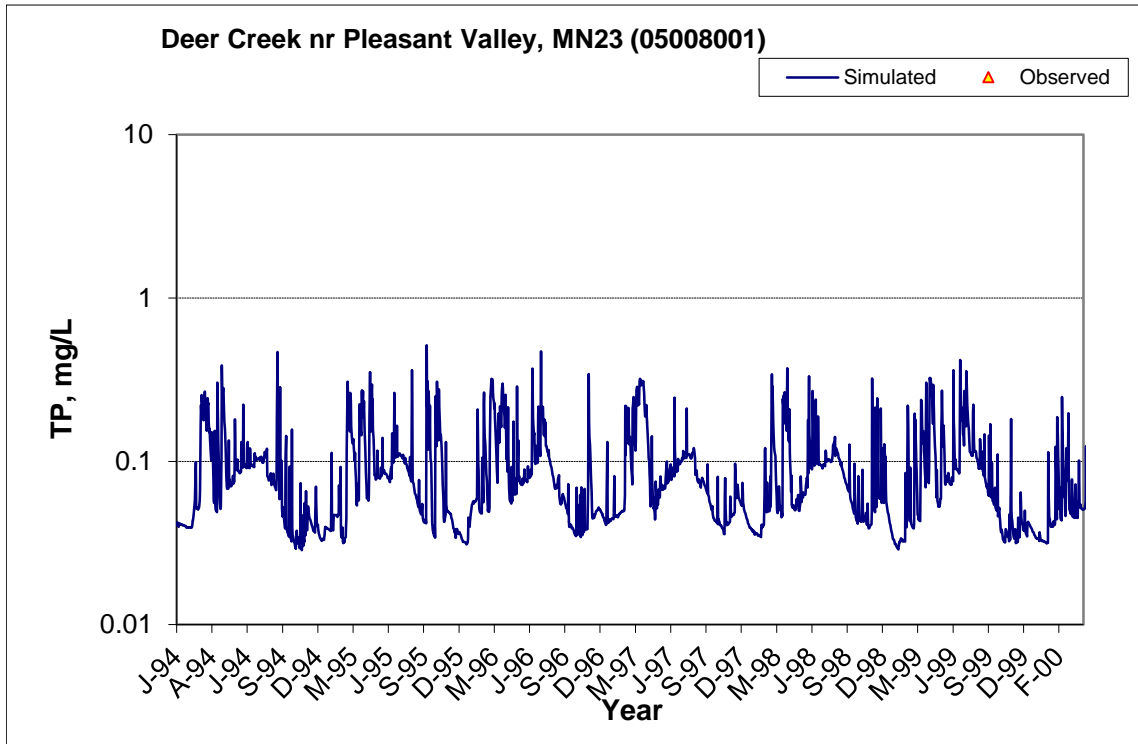


Figure B-39. Power plot of simulated and observed Total Phosphorus (TP) load vs flow at Deer Creek nr Pleasant Valley, MN23 (05008001) (validation period)



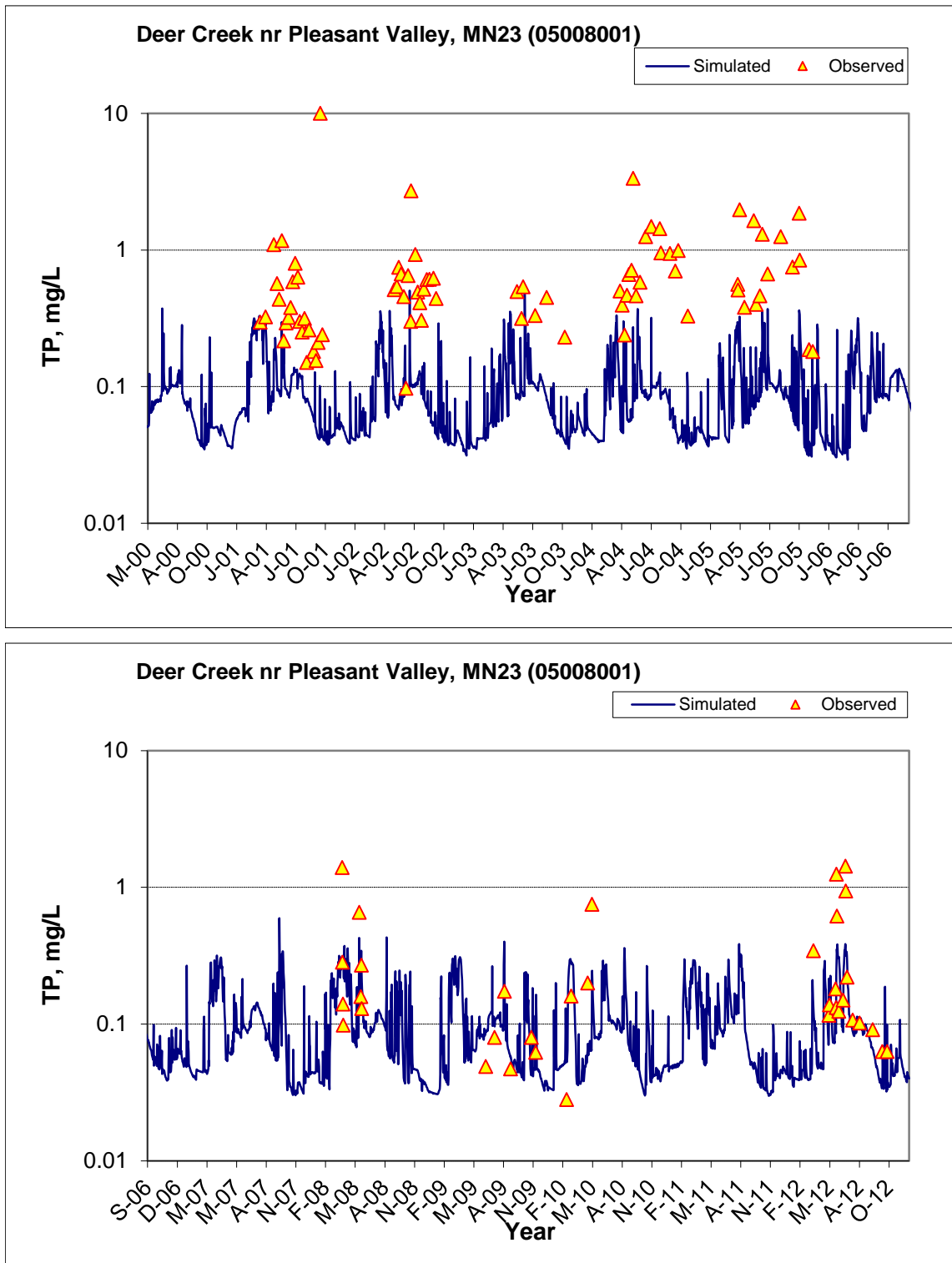


Figure B-40. Time series of observed and simulated Total Phosphorus (TP) concentration at Deer Creek nr Pleasant Valley, MN23 (05008001)

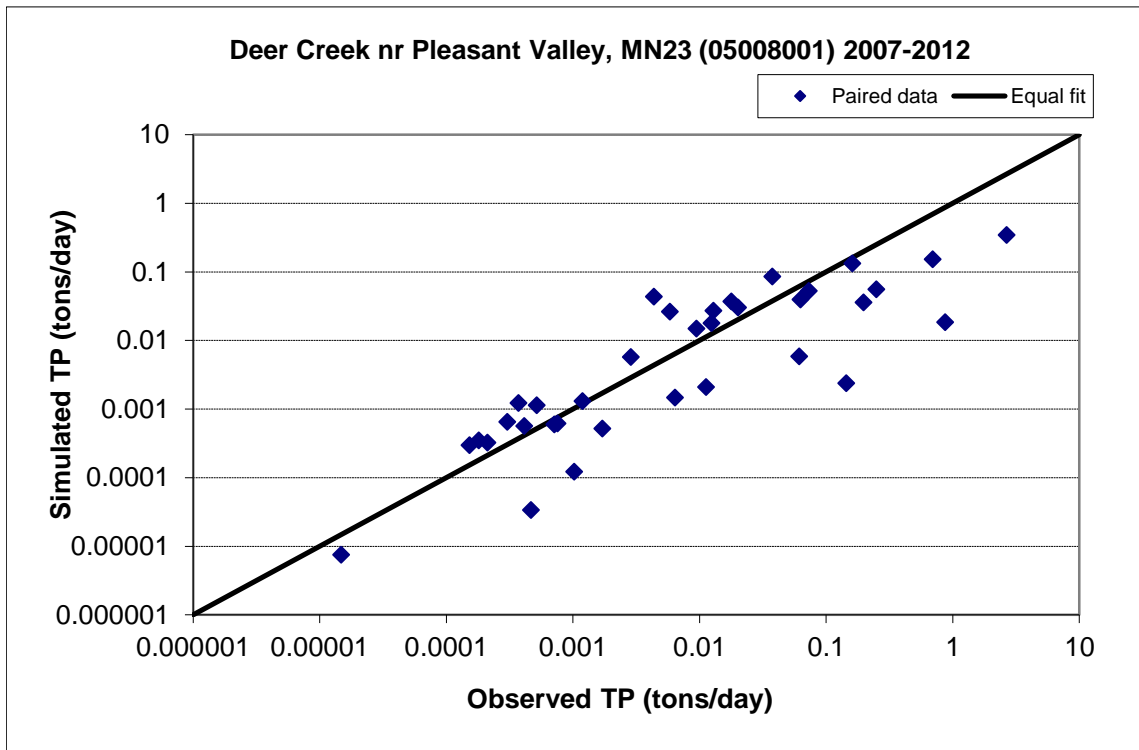


Figure B-41. Paired simulated vs. observed Total Phosphorus (TP) load at Deer Creek nr Pleasant Valley, MN23 (05008001) (calibration period)

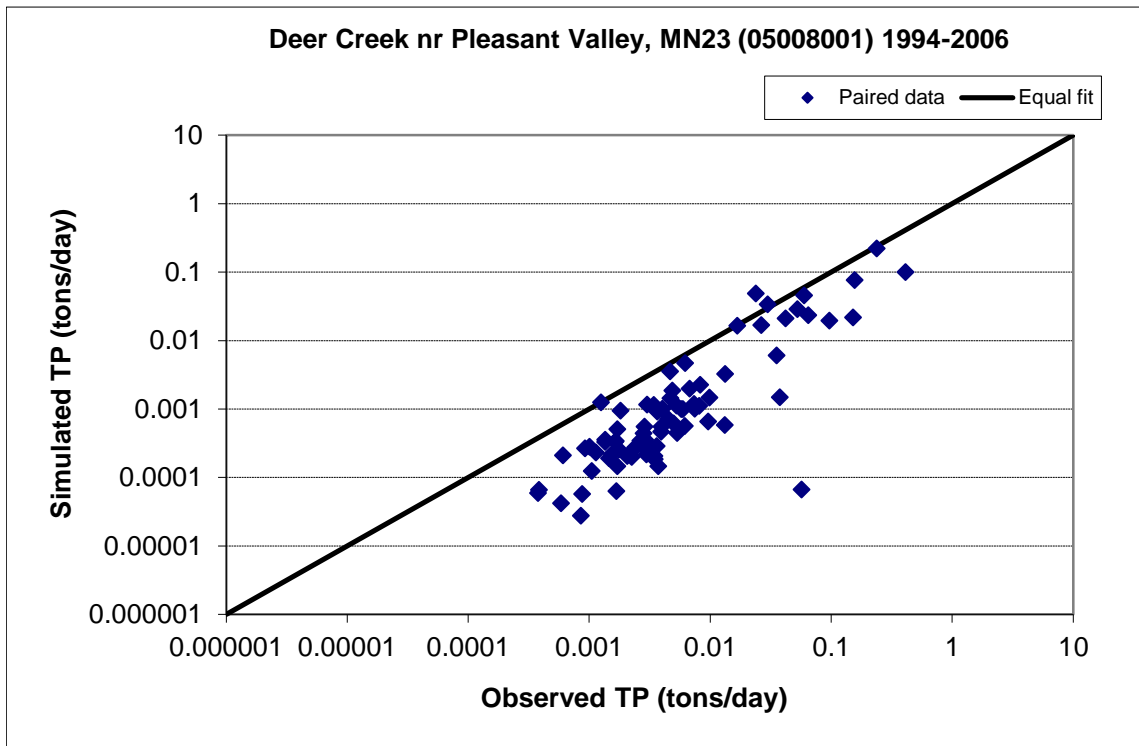


Figure B-42. Paired simulated vs. observed Total Phosphorus (TP) load at Deer Creek nr Pleasant Valley, MN23 (05008001) (validation period)

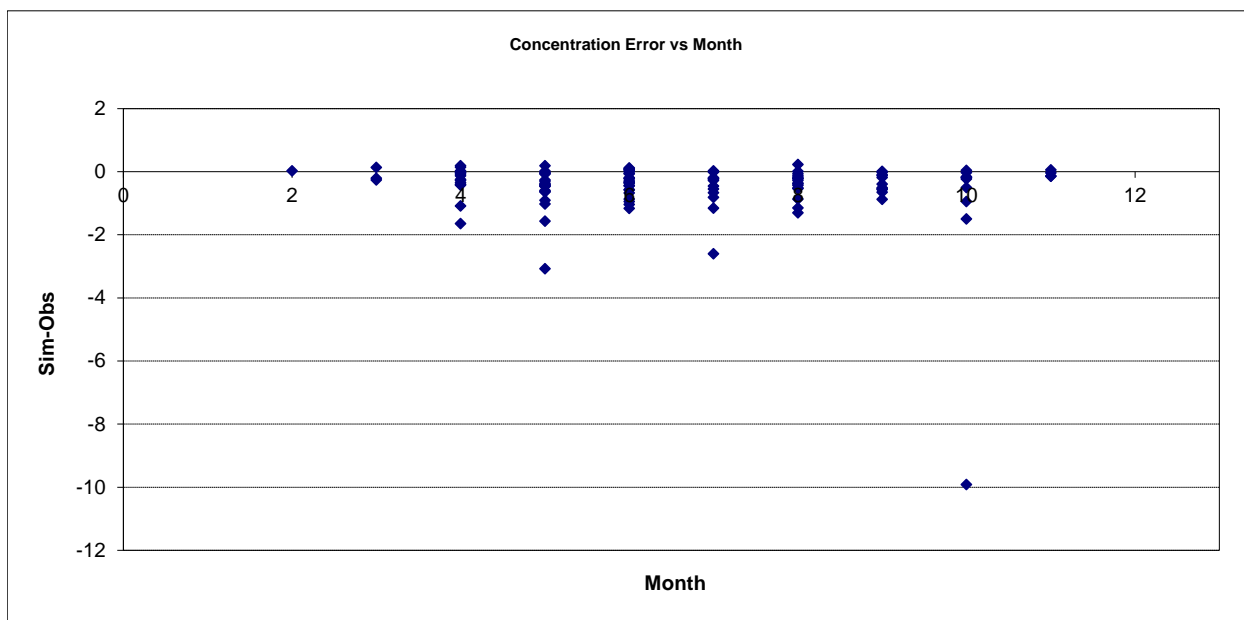


Figure B-43. Residual (Simulated - Observed) vs. Month Total Phosphorus (TP) at Deer Creek nr Pleasant Valley, MN23 (05008001)

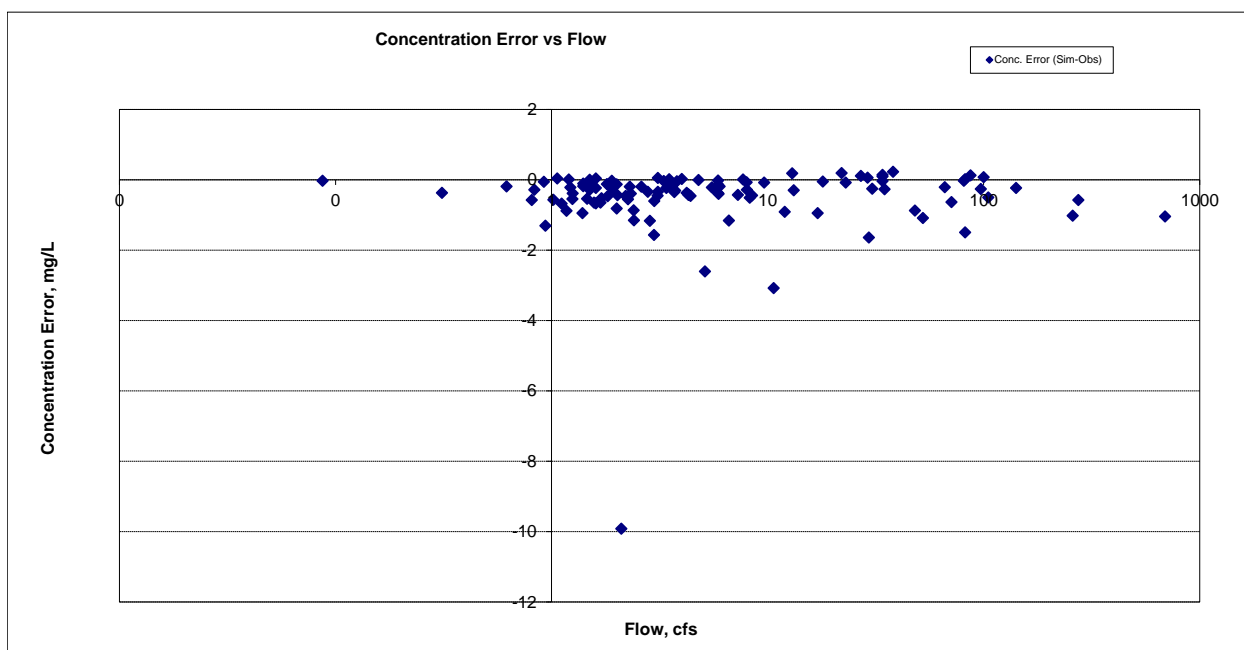


Figure B-44. Residual (Simulated - Observed) vs. Flow Total Phosphorus (TP) at Deer Creek nr Pleasant Valley, MN23 (05008001)

B.2 ROCK CREEK NR PLEASANT VALLEY (05009001)

B.2.1 Ammonia Nitrogen (NH3)

Table B-7. Ammonia Nitrogen (NH3) statistics

Period	1994-2001	2002-2012
Count	ND	15
Concentration Average Error		130.05%
Concentration Median Error		43.19%
Load Average Error		-10.12%
Load Median Error		2.18%
Paired t conc		0.02
Paired t load		0.56

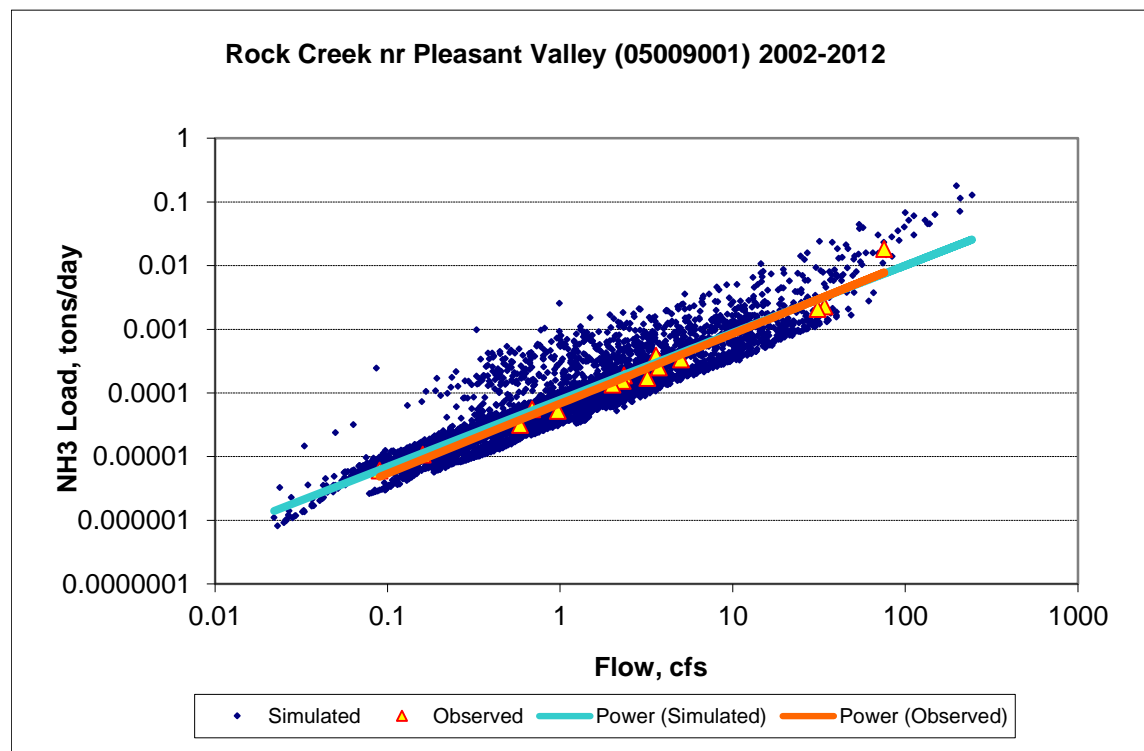
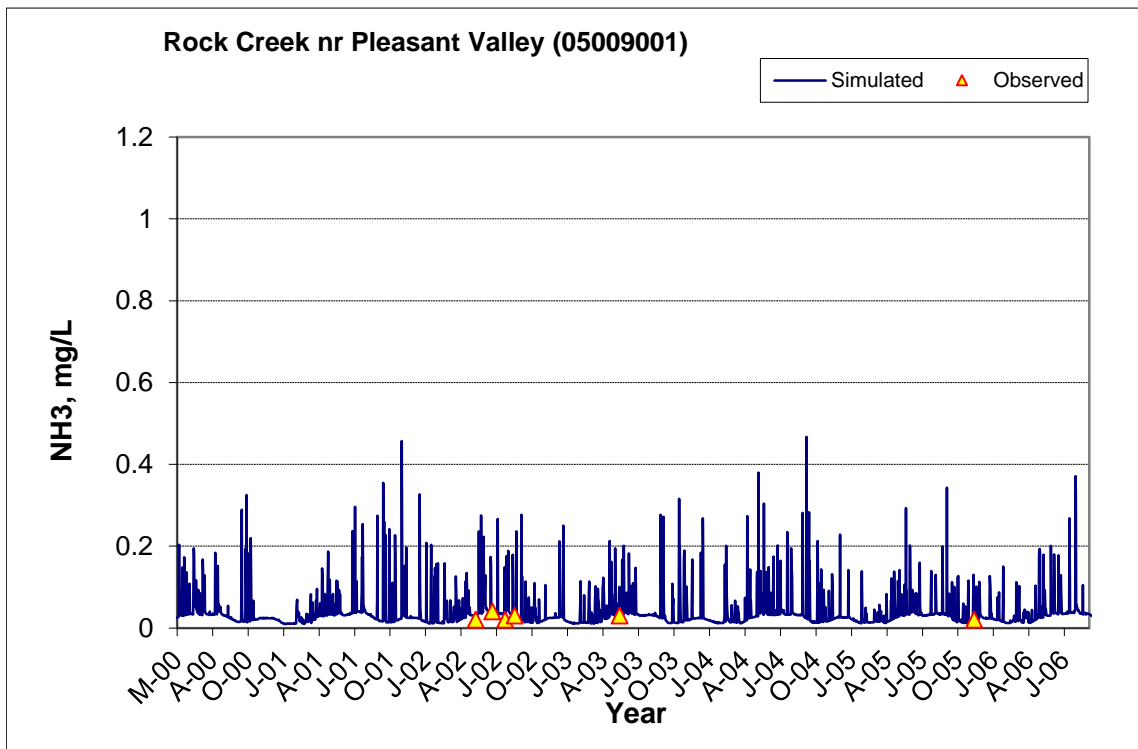
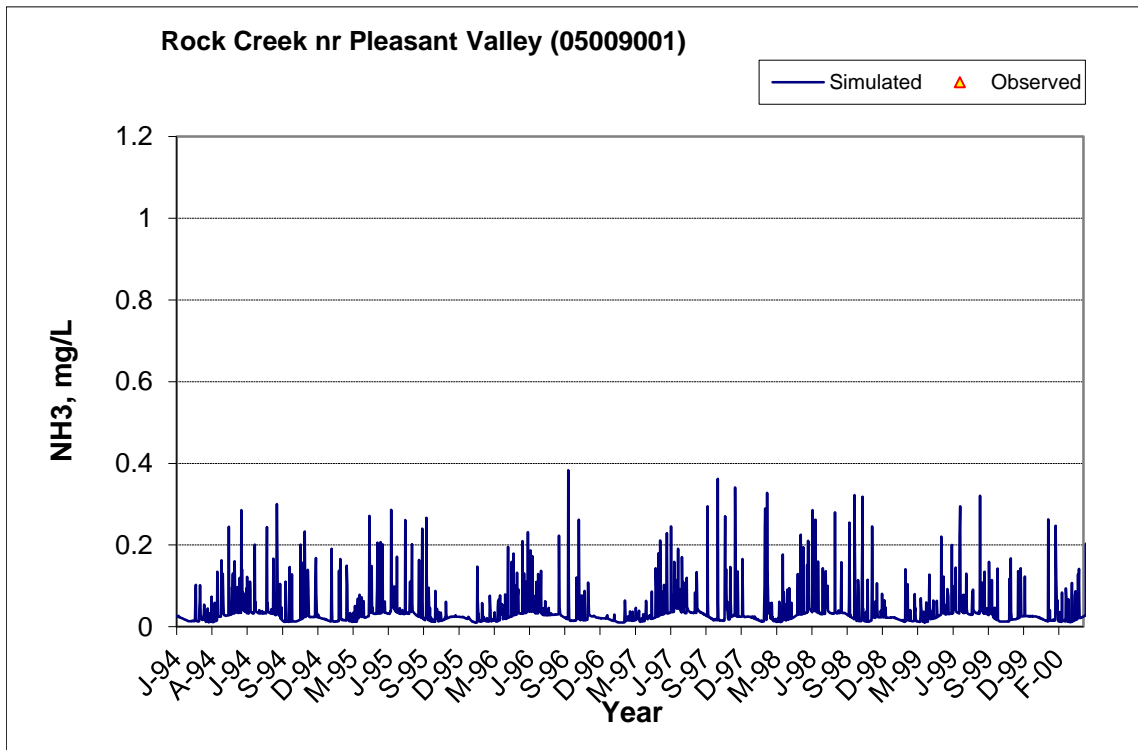


Figure B-45. Power plot of simulated and observed Ammonia Nitrogen (NH3) load vs flow at Rock Creek nr Pleasant Valley (05009001) (calibration period)



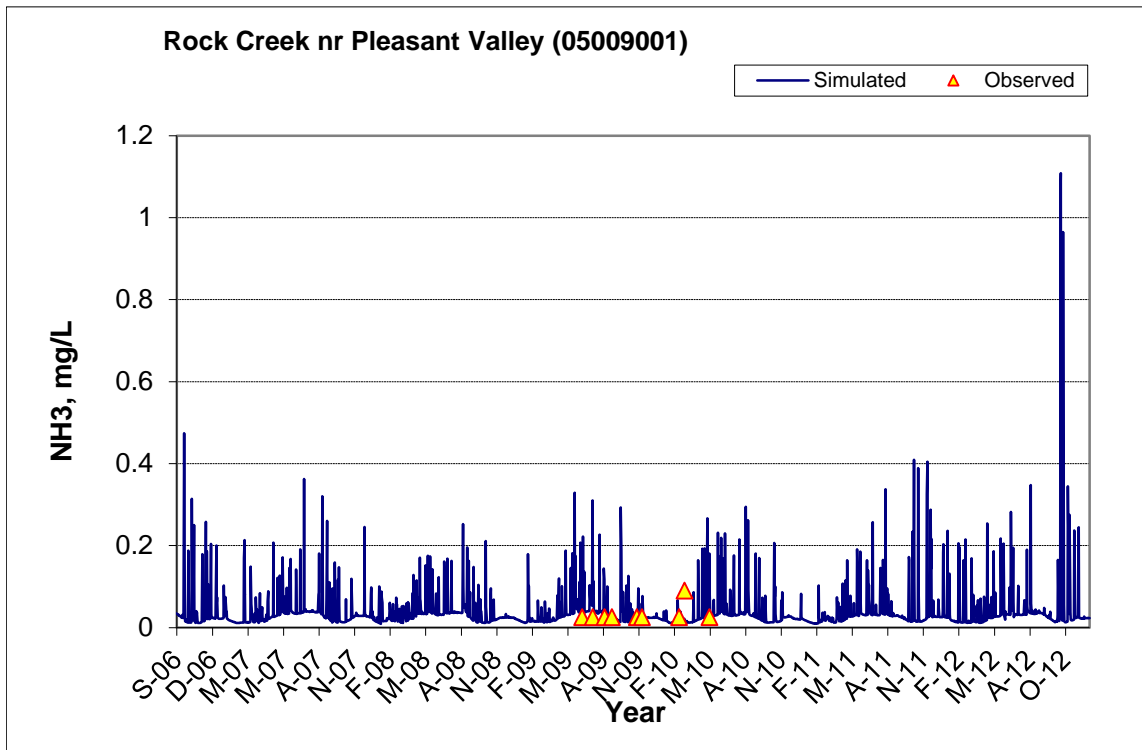


Figure B-46. Time series of observed and simulated Ammonia Nitrogen (NH3) concentration at Rock Creek nr Pleasant Valley (05009001)

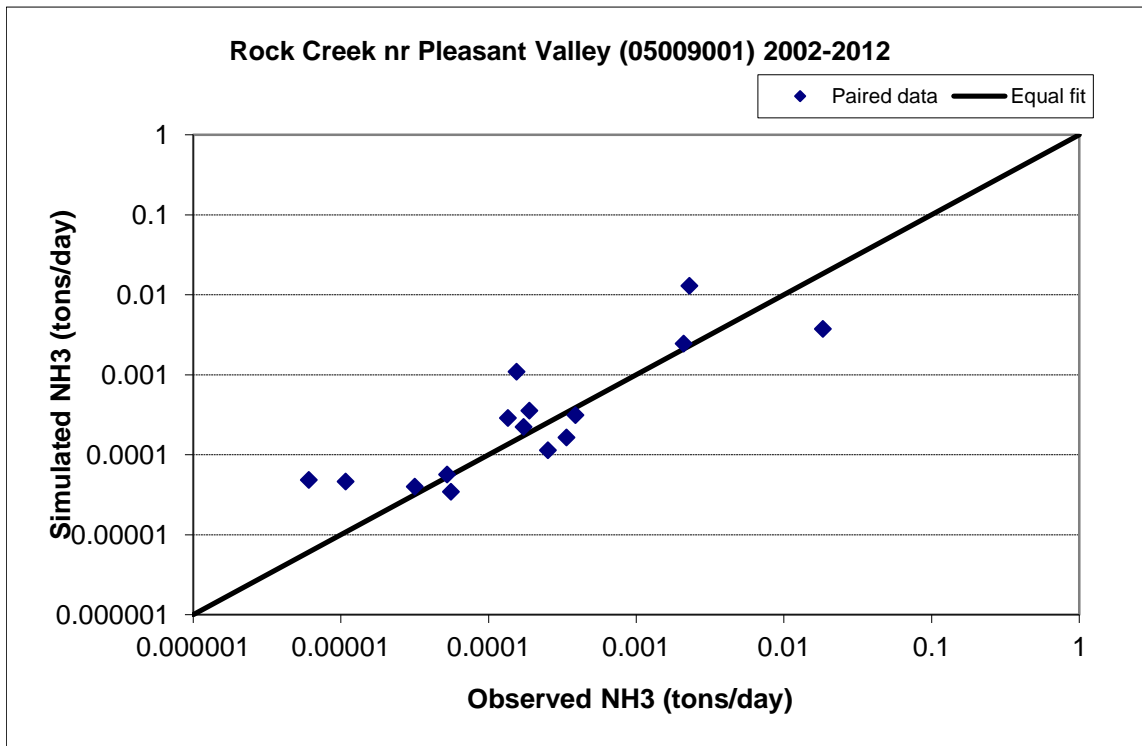


Figure B-47. Paired simulated vs. observed Ammonia Nitrogen (NH3) load at Rock Creek nr Pleasant Valley (05009001) (calibration period)

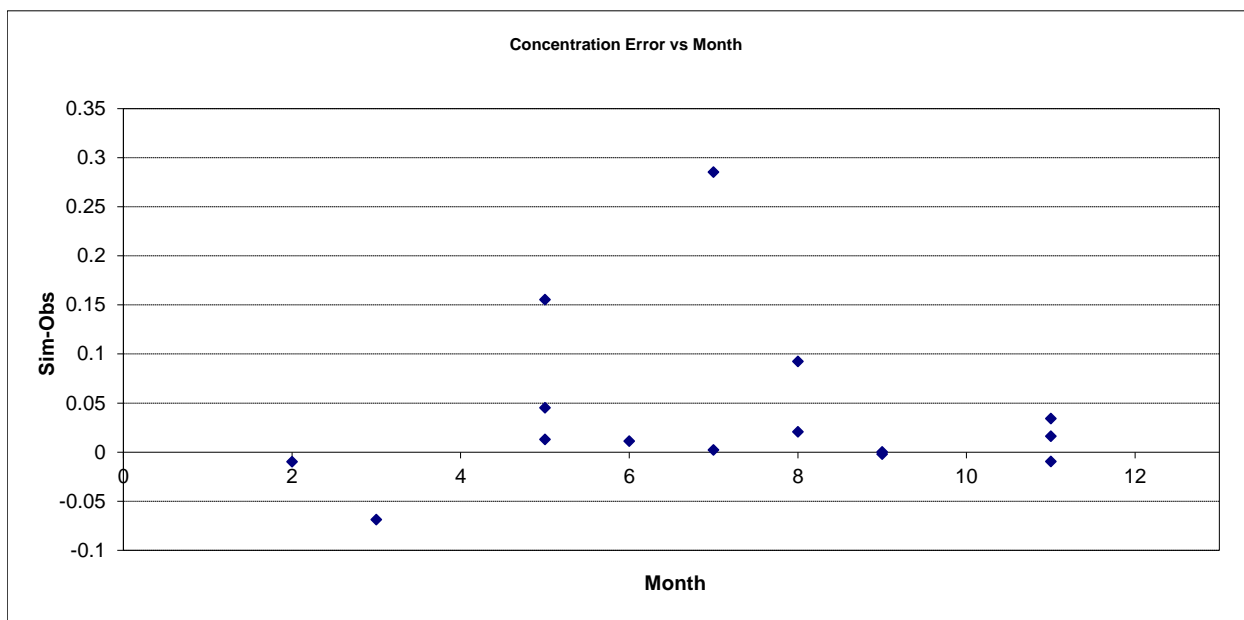


Figure B-48. Residual (Simulated - Observed) vs. Month Ammonia Nitrogen (NH3) at Rock Creek nr Pleasant Valley (05009001)

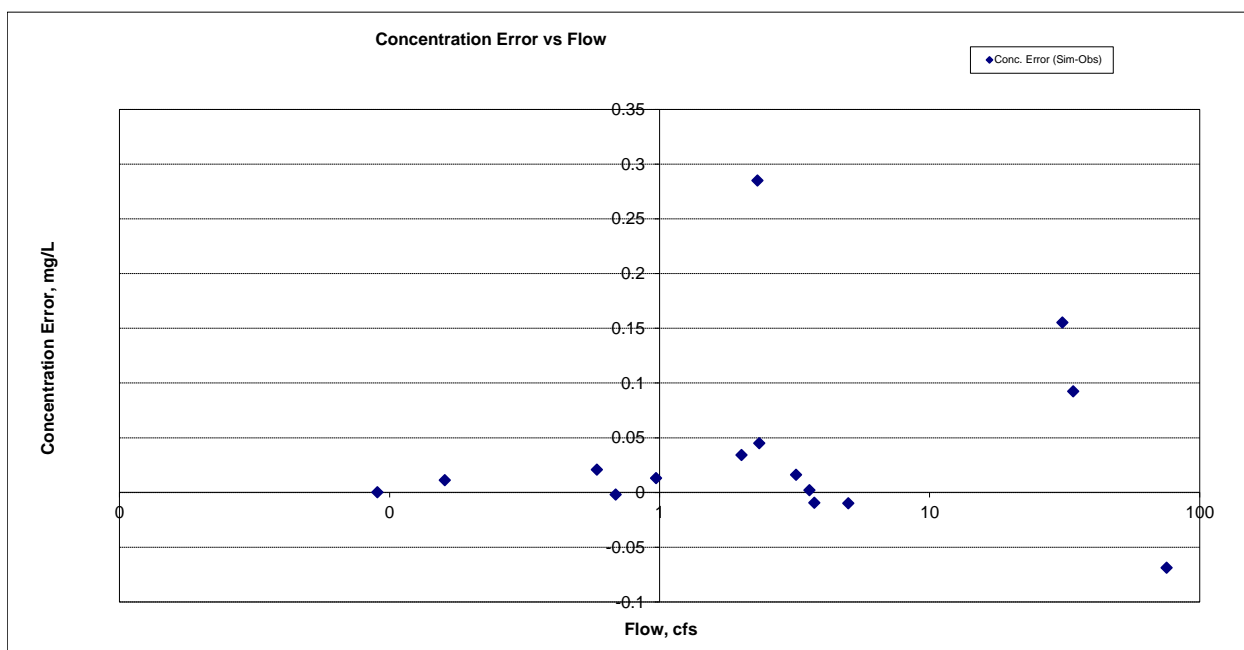
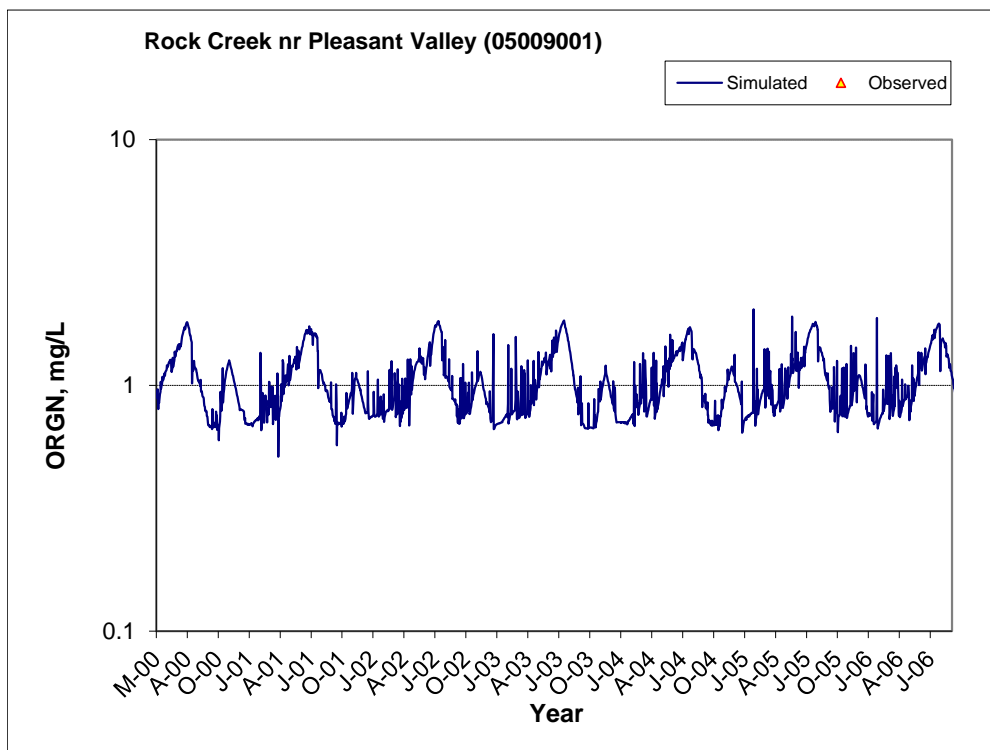
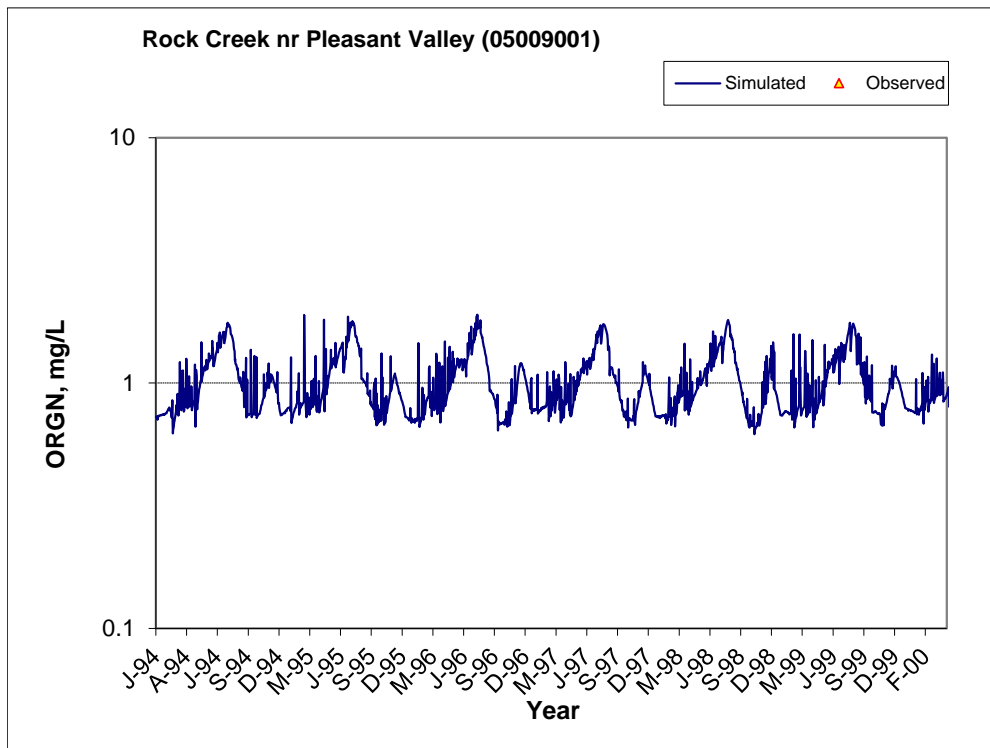


Figure B-49. Residual (Simulated - Observed) vs. Flow Ammonia Nitrogen (NH3) at Rock Creek nr Pleasant Valley (05009001)

B.2.2 Organic Nitrogen (OrgN)



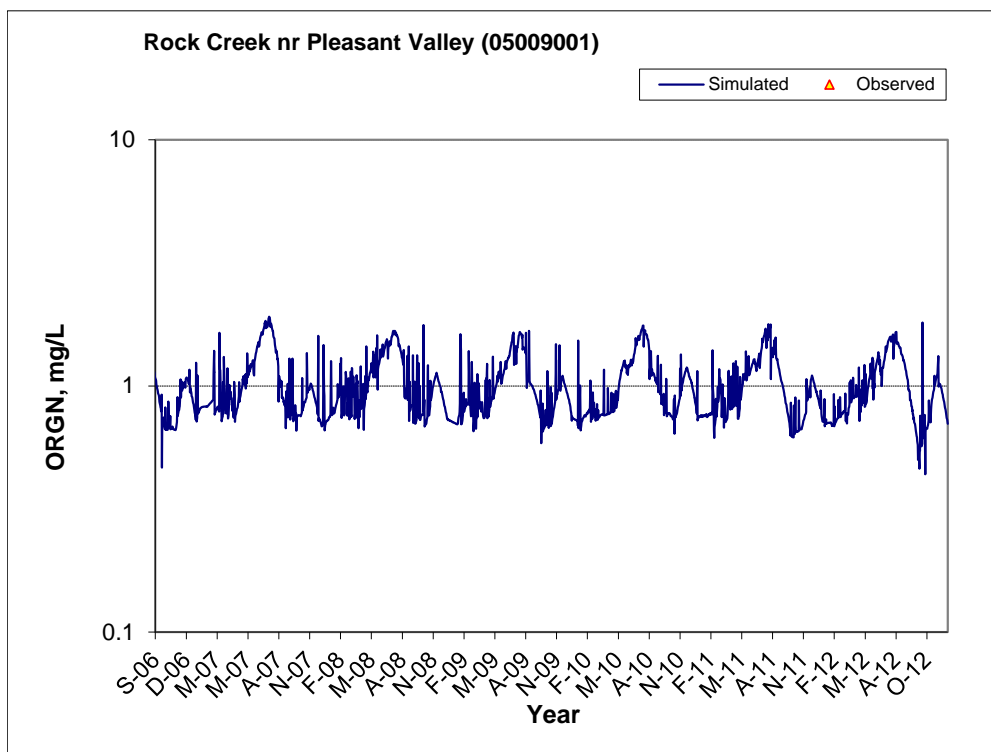


Figure B-50. Time series of observed and simulated Organic Nitrogen (OrgN) concentration at Rock Creek nr Pleasant Valley (05009001)

B.2.3 Total Kjeldahl Nitrogen (TKN)

Table B-8. Total Kjeldahl Nitrogen (TKN) statistics

Period	1994-2001	2002-2012
Count	ND	6
Concentration Average Error		36.66%
Concentration Median Error		37.56%
Load Average Error		0.50%
Load Median Error		-3.85%
Paired t conc		0.16
Paired t load		0.71

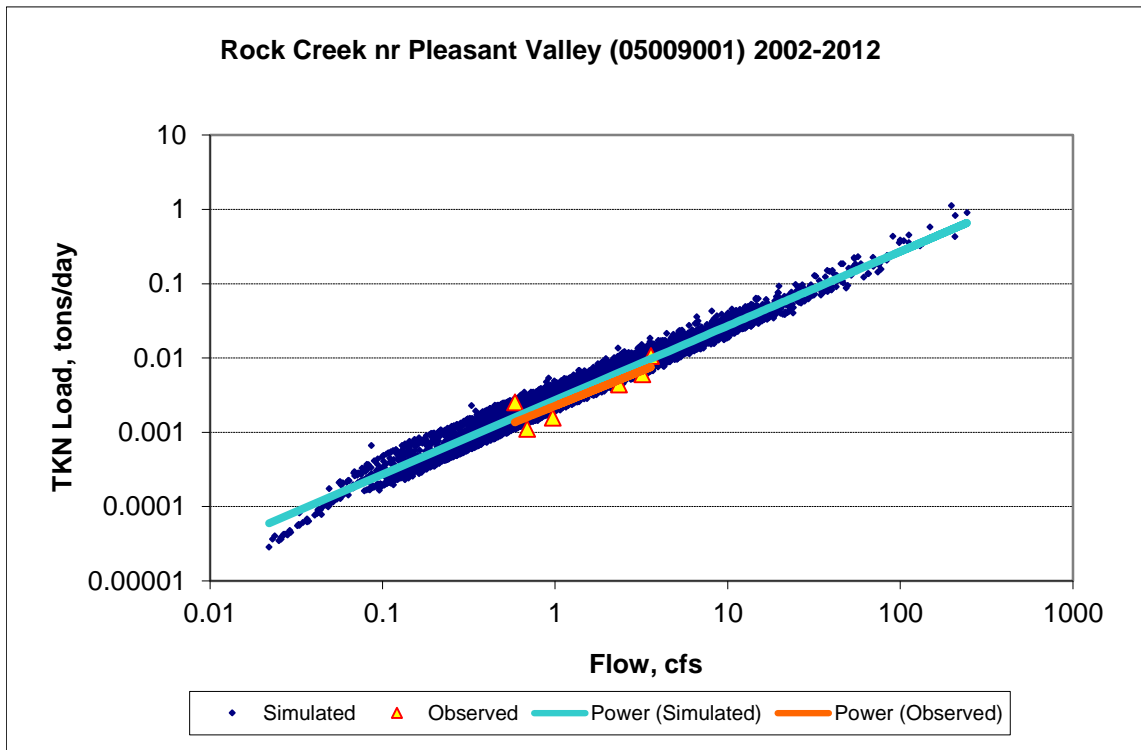
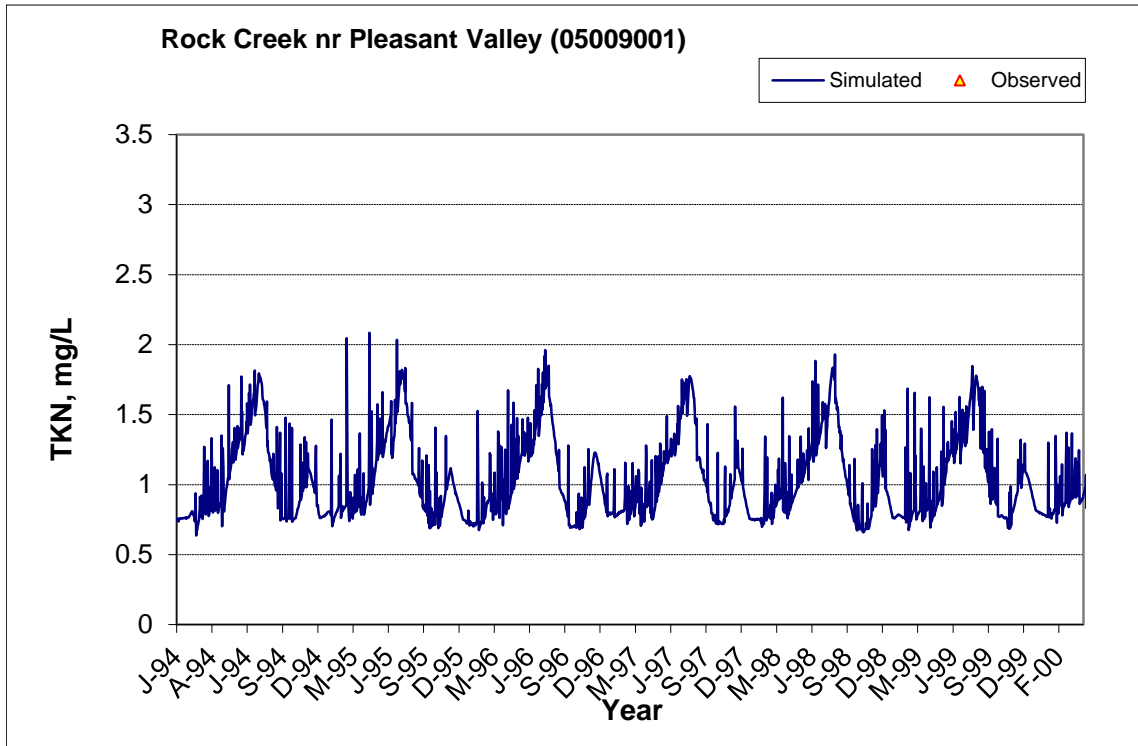


Figure B-51. Power plot of simulated and observed Total Kjeldahl Nitrogen (TKN) load vs flow at Rock Creek nr Pleasant Valley (05009001) (calibration period)



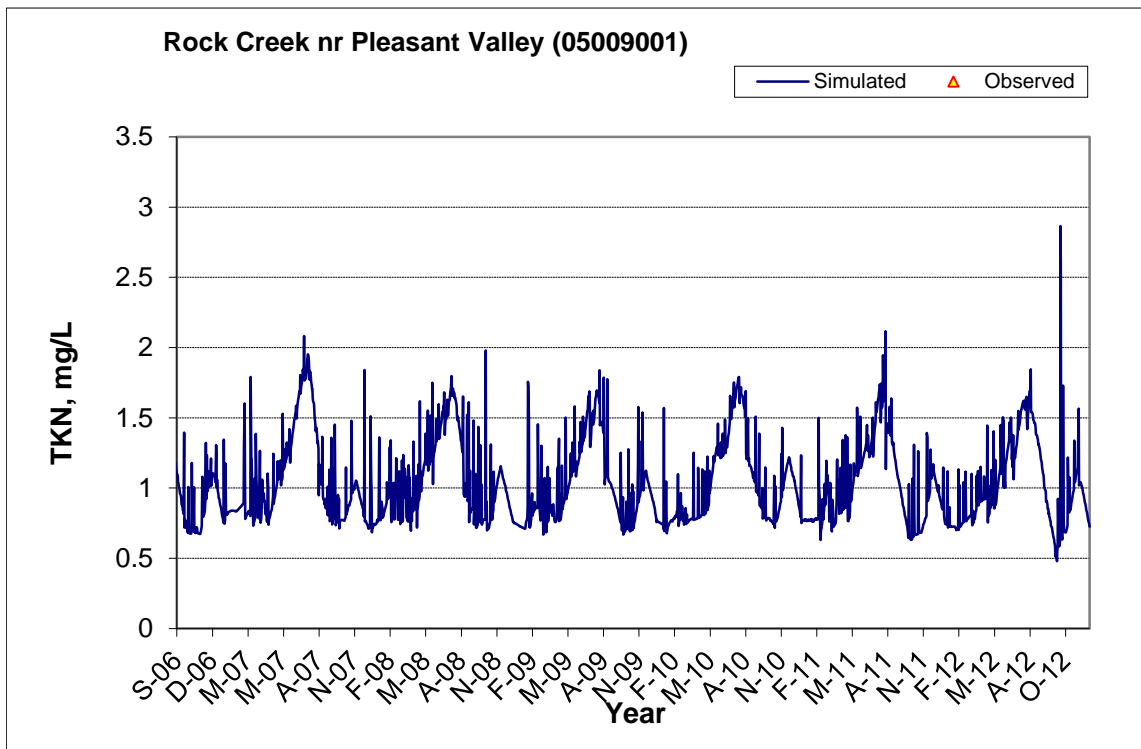
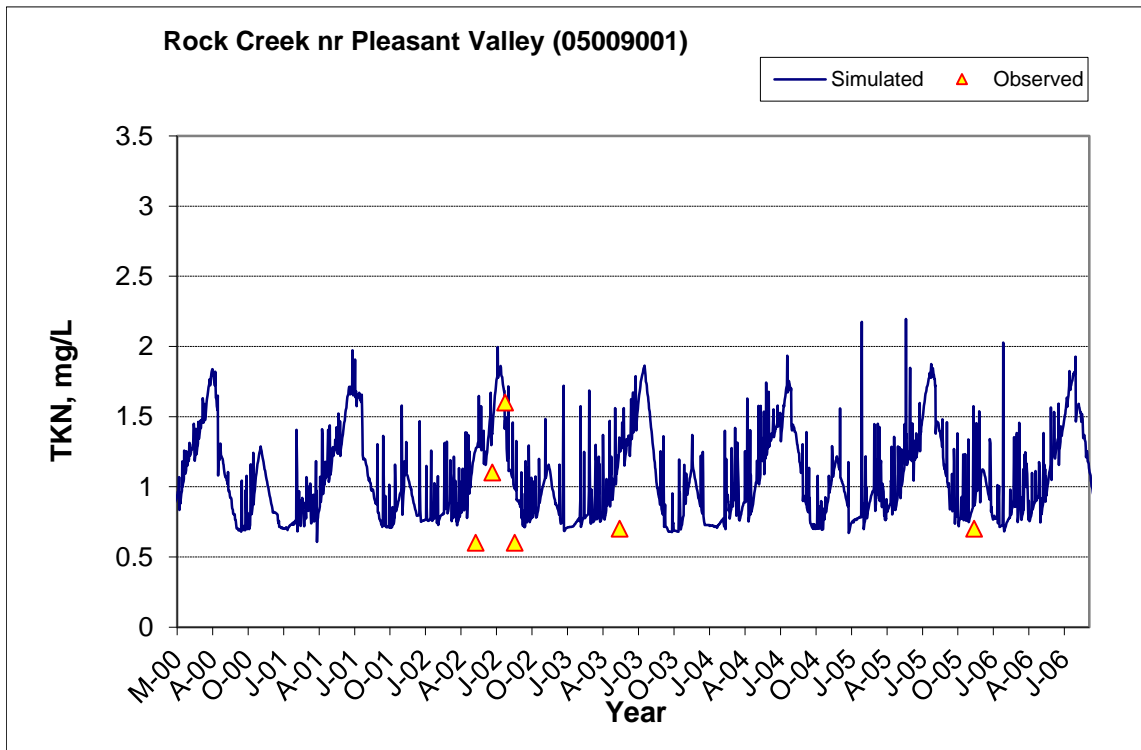


Figure B-52. Time series of observed and simulated Total Kjeldahl Nitrogen (TKN) concentration at Rock Creek nr Pleasant Valley (05009001)

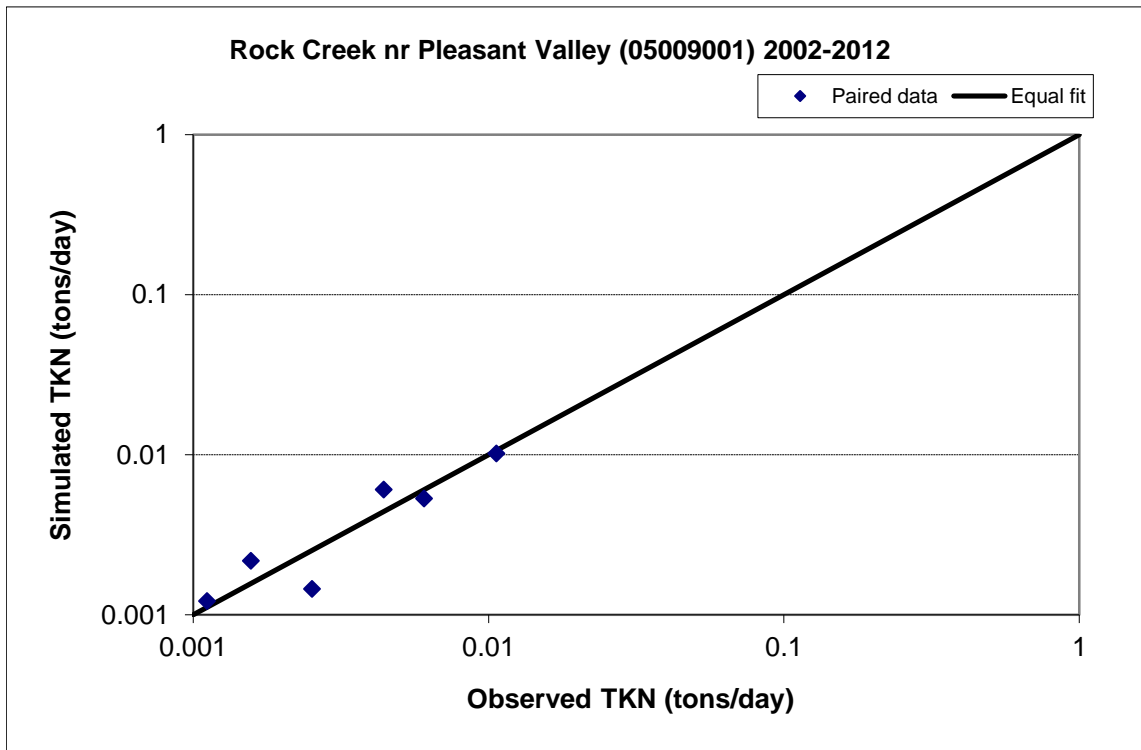


Figure B-53. Paired simulated vs. observed Total Kjeldahl Nitrogen (TKN) load at Rock Creek nr Pleasant Valley (05009001) (calibration period)

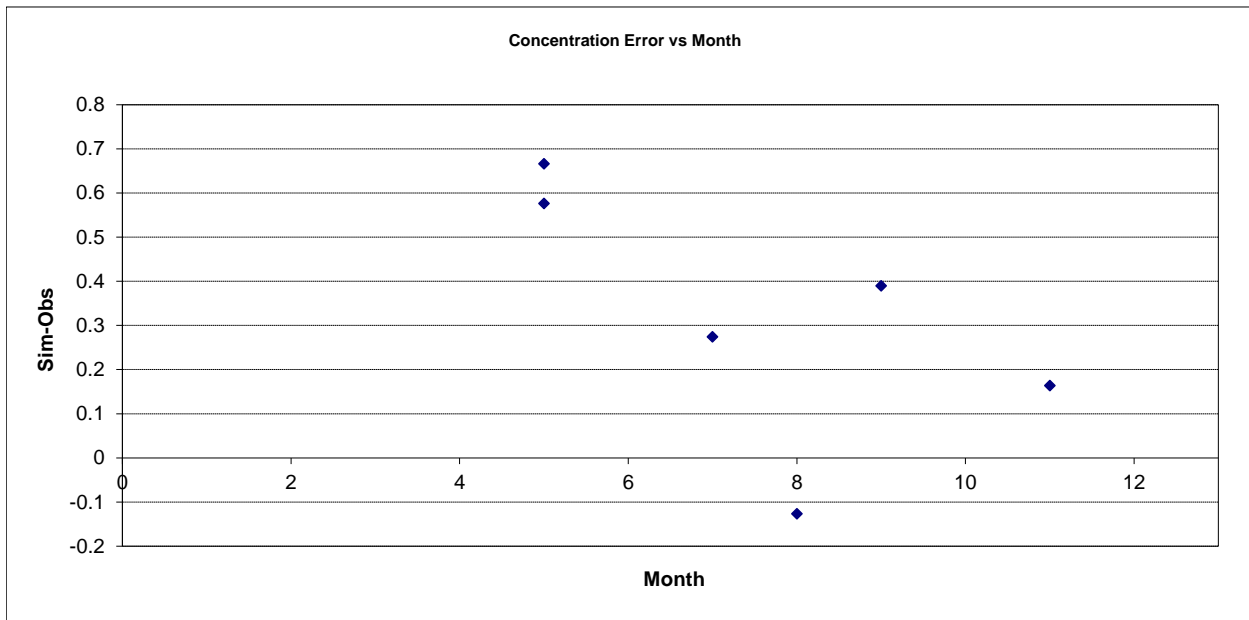


Figure B-54. Residual (Simulated - Observed) vs. Month Total Kjeldahl Nitrogen (TKN) at Rock Creek nr Pleasant Valley (05009001)

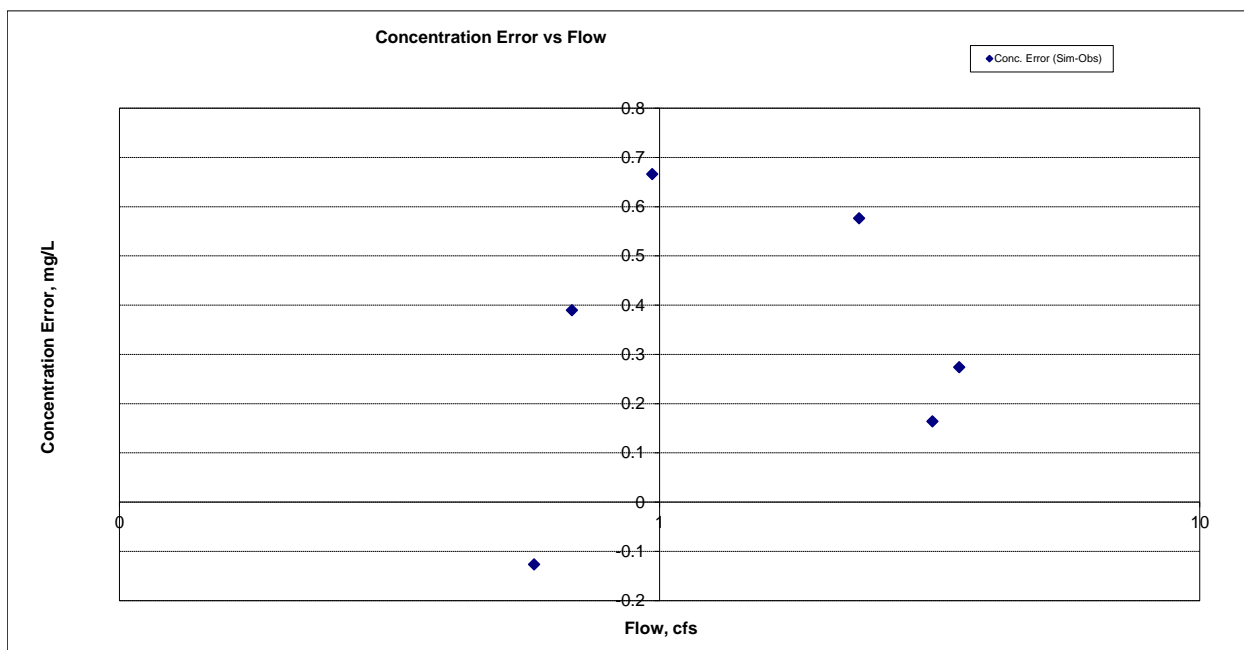


Figure B-55. Residual (Simulated - Observed) vs. Flow Total Kjeldahl Nitrogen (TKN) at Rock Creek nr Pleasant Valley (05009001)

B.2.4 Nitrite+ Nitrate Nitrogen (NOx)

Table B-9. Nitrite+ Nitrate Nitrogen (NOx) statistics

Period	1994-2001	2002-2012
Count	ND	14
Concentration Average Error		361.16%
Concentration Median Error		262.40%
Load Average Error		38.14%
Load Median Error		12.28%
Paired t conc		0.00
Paired t load		0.42

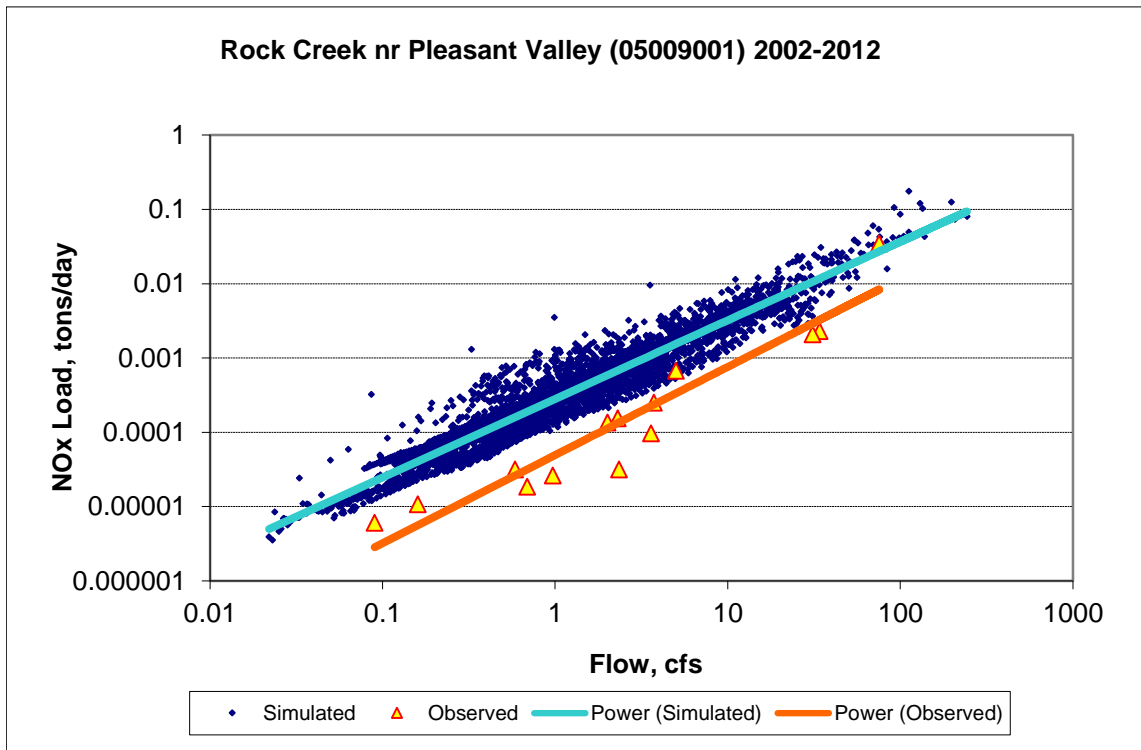
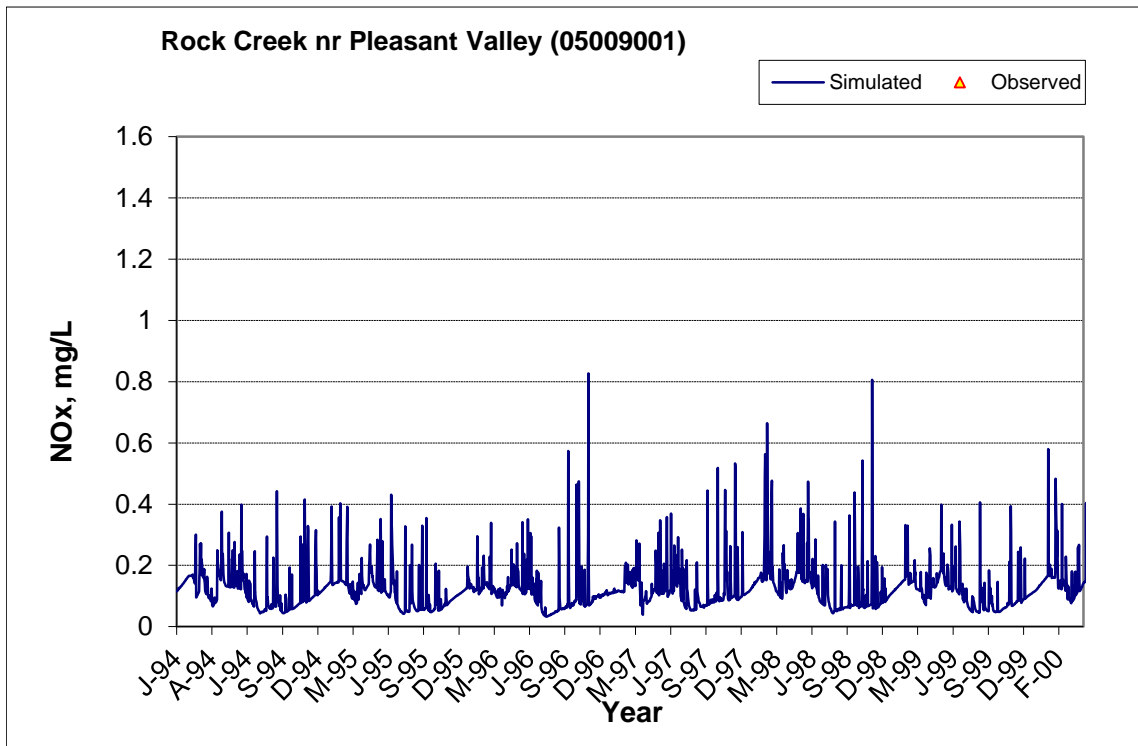


Figure B-56. Power plot of simulated and observed Nitrite+ Nitrate Nitrogen (NOx) load vs flow at Rock Creek nr Pleasant Valley (05009001) (calibration period)



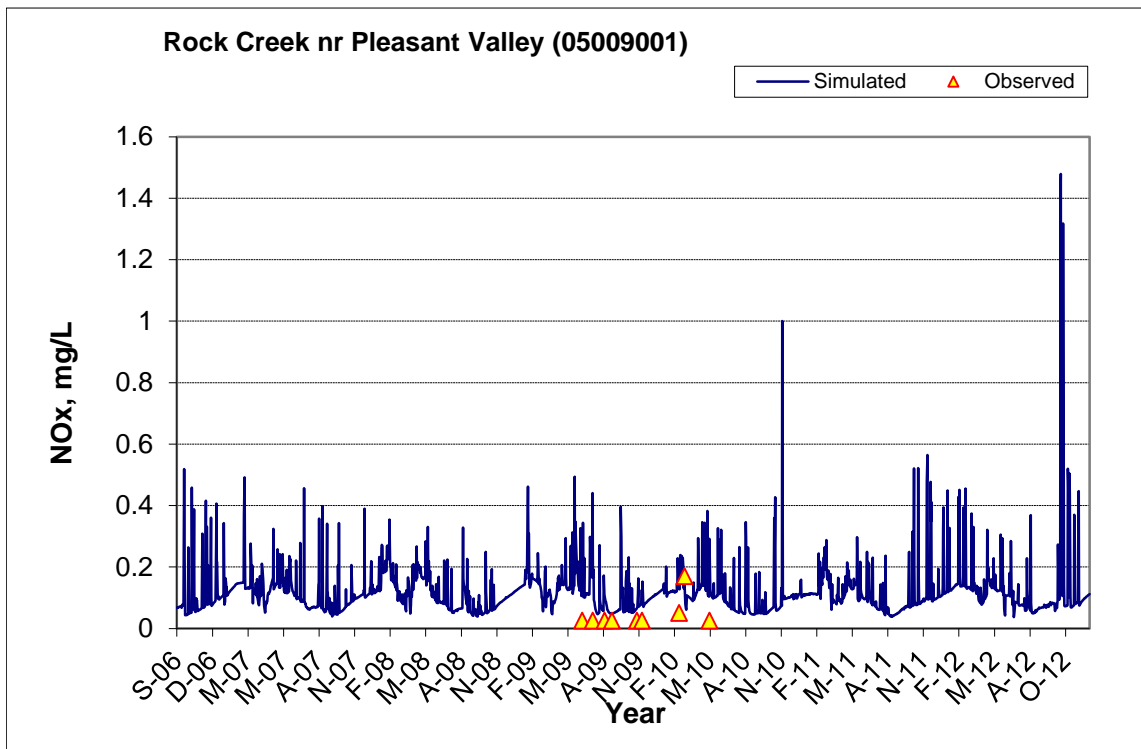
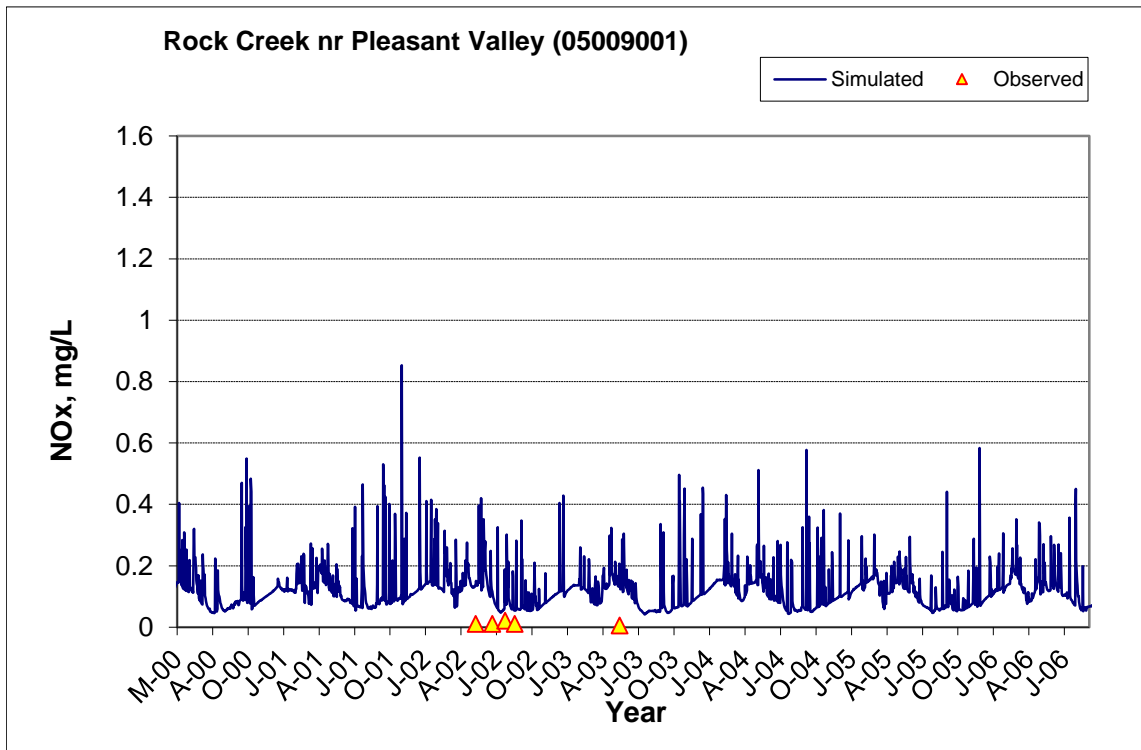


Figure B-57. Time series of observed and simulated Nitrite+ Nitrate Nitrogen (NOx) concentration at Rock Creek nr Pleasant Valley (05009001)

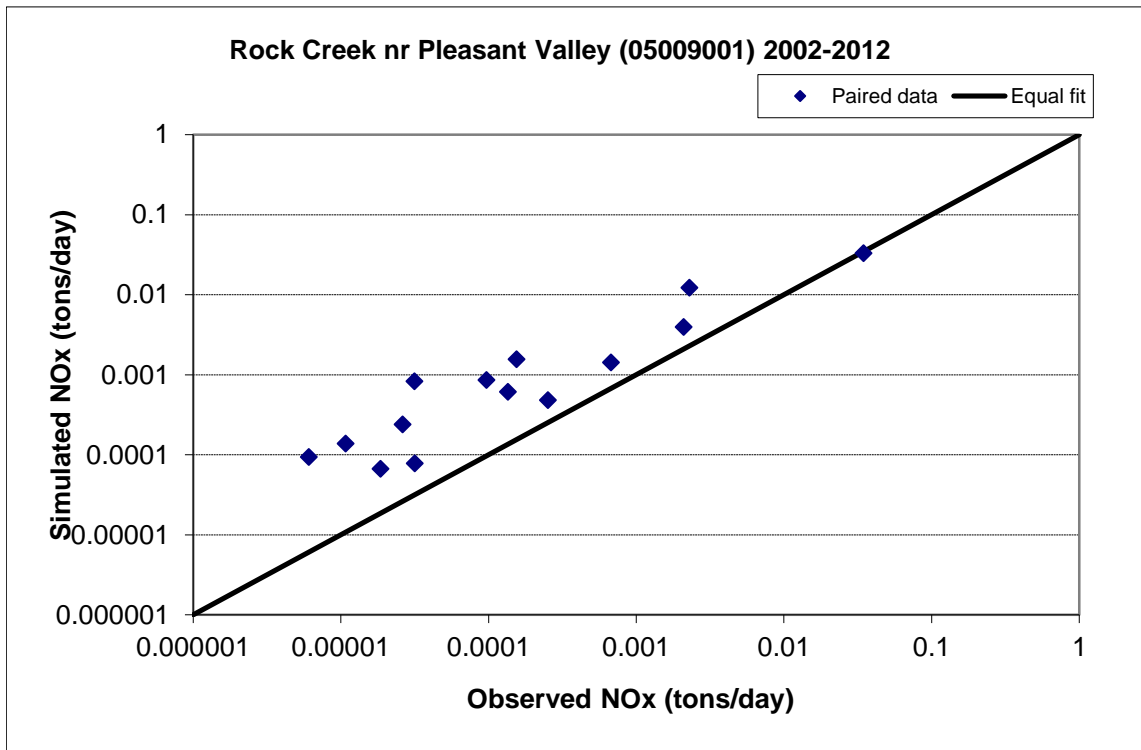


Figure B-58. Paired simulated vs. observed Nitrite+ Nitrate Nitrogen (NOx) load at Rock Creek nr Pleasant Valley (05009001) (calibration period)

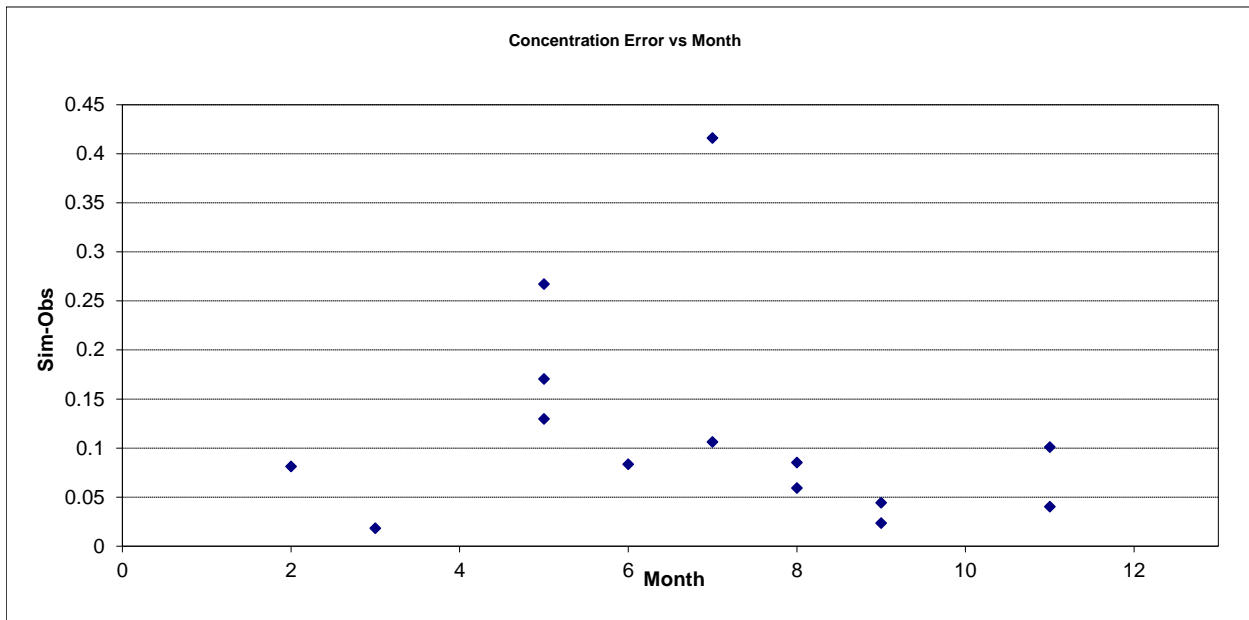


Figure B-59. Residual (Simulated - Observed) vs. Month Nitrite+ Nitrate Nitrogen (NOx) at Rock Creek nr Pleasant Valley (05009001)

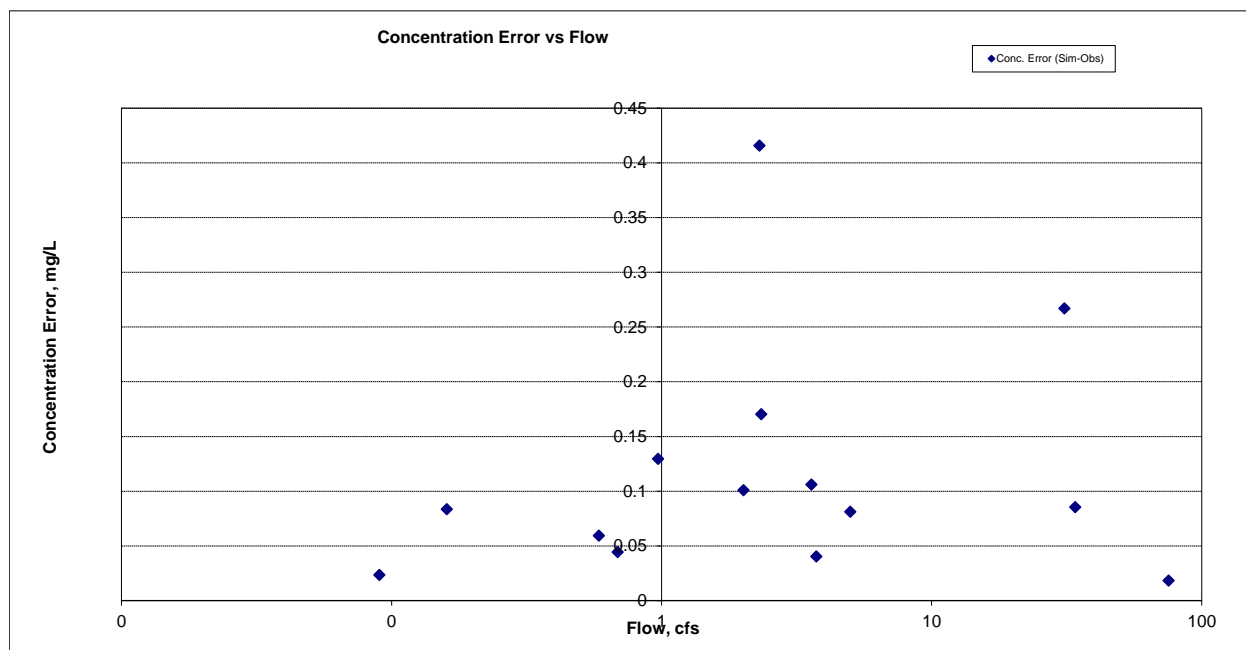


Figure B-60. Residual (Simulated - Observed) vs. Flow Nitrite+ Nitrate Nitrogen (NOx) at Rock Creek nr Pleasant Valley (05009001)

B.2.5 Total Nitrogen (TN)

Table B-10. Total Nitrogen (TN) statistics

Period	1994-2001	2002-2012
Count	ND	5
Concentration Average Error		49.01%
Concentration Median Error		46.54%
Load Average Error		13.08%
Load Median Error		7.85%
Paired t conc		0.07
Paired t load		0.56

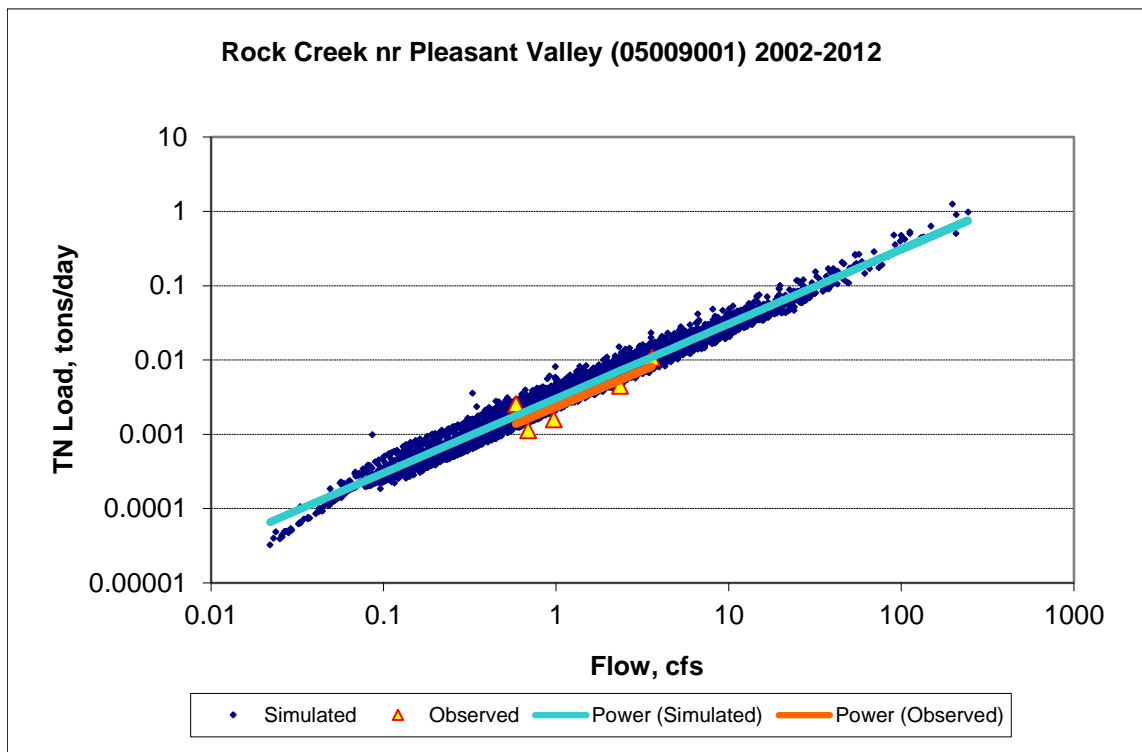
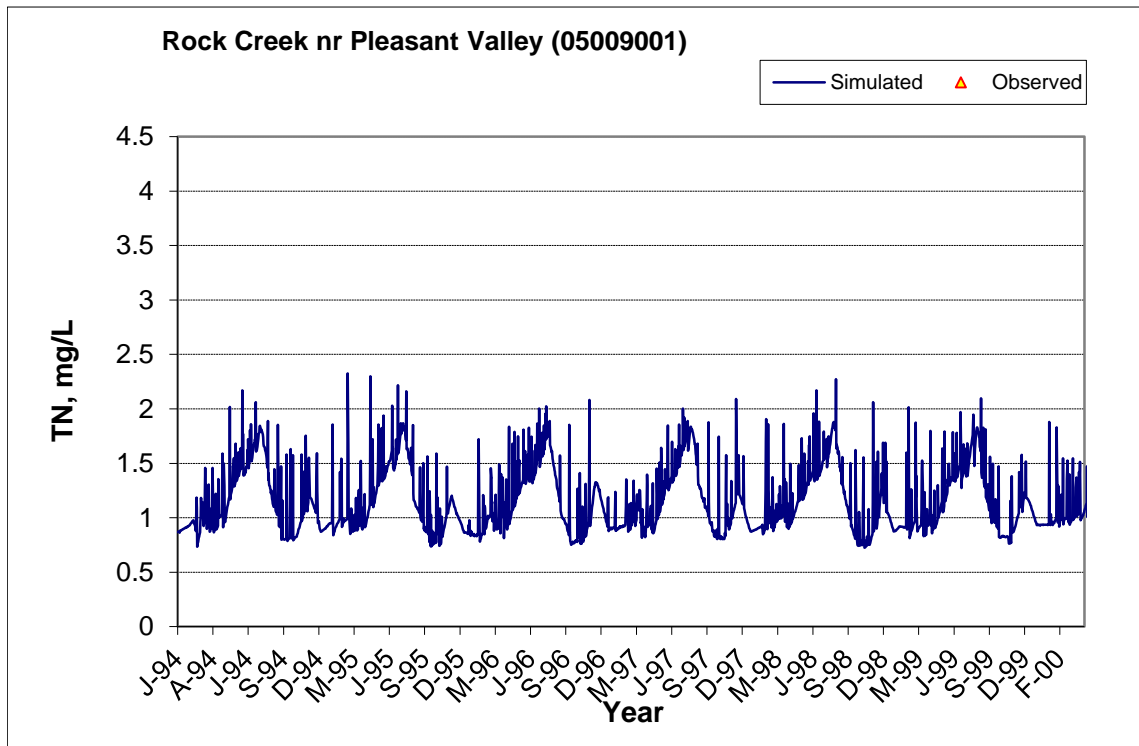


Figure B-61. Power plot of simulated and observed Total Nitrogen (TN) load vs flow at Rock Creek nr Pleasant Valley (05009001) (calibration period)



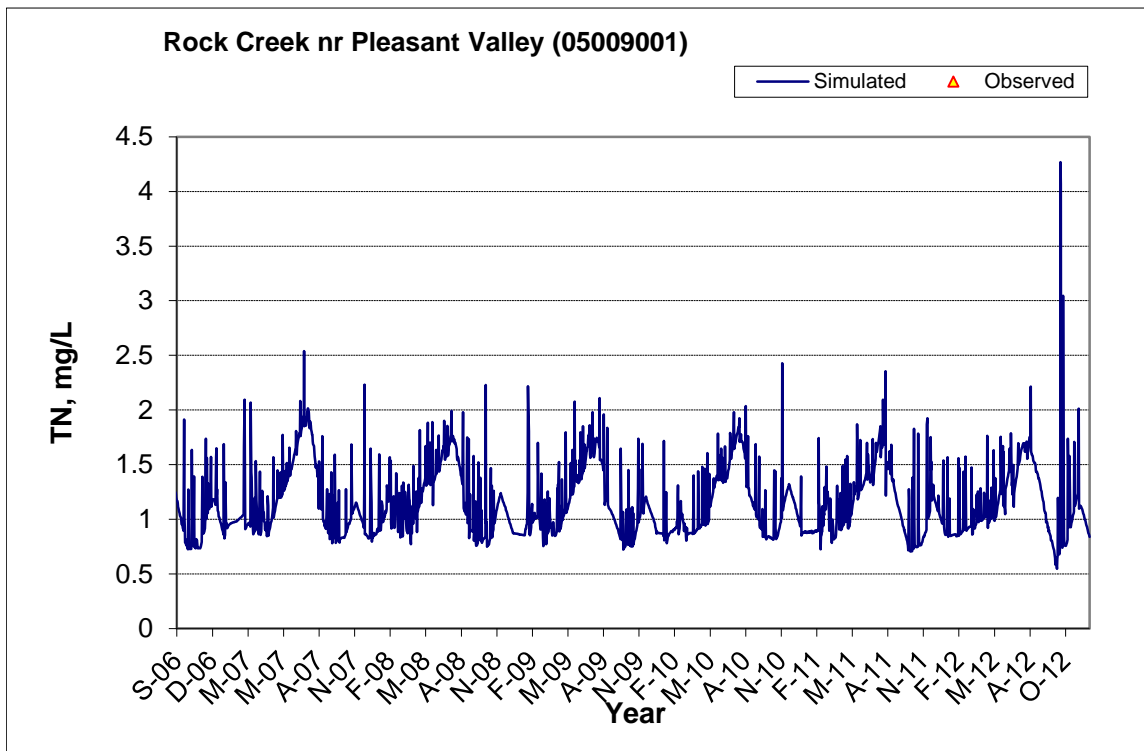
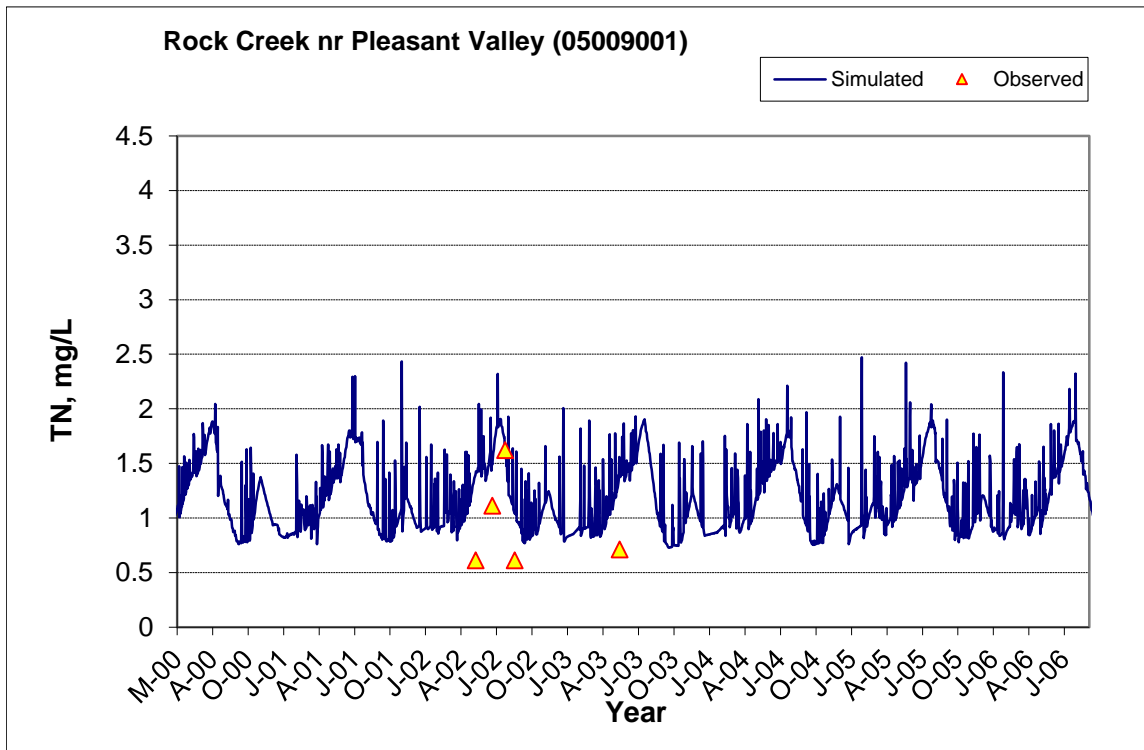


Figure B-62. Time series of observed and simulated Total Nitrogen (TN) concentration at Rock Creek nr Pleasant Valley (05009001)

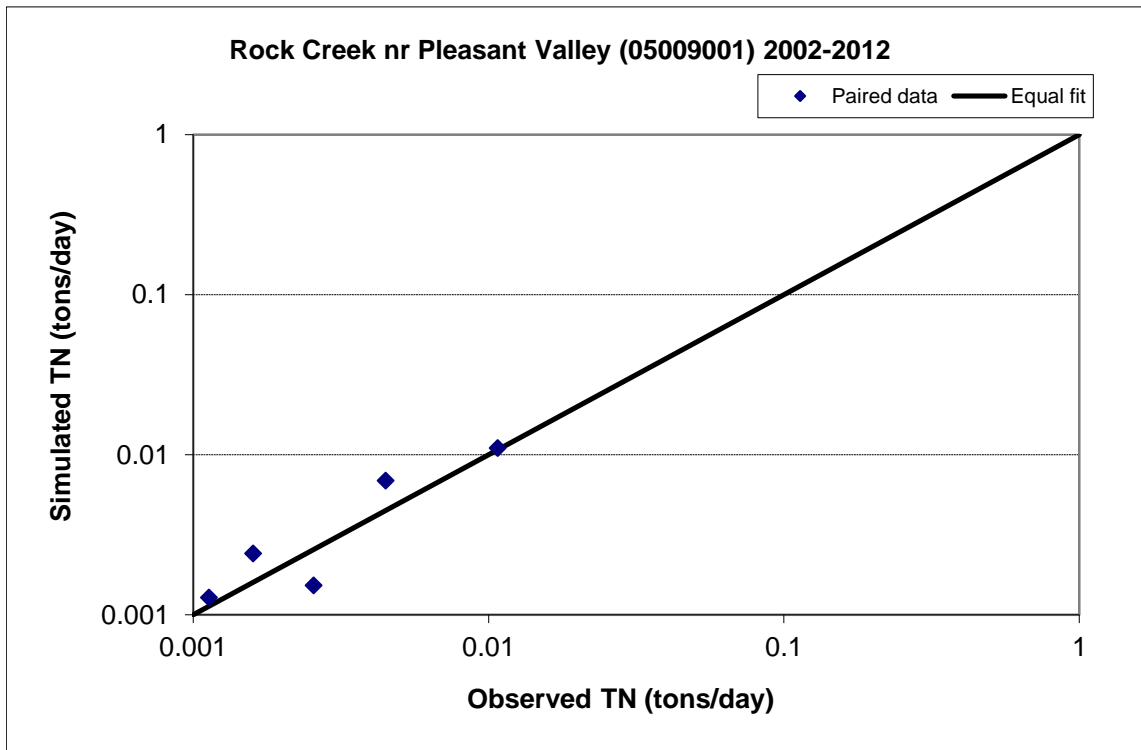


Figure B-63. Paired simulated vs. observed Total Nitrogen (TN) load at Rock Creek nr Pleasant Valley (05009001) (calibration period)

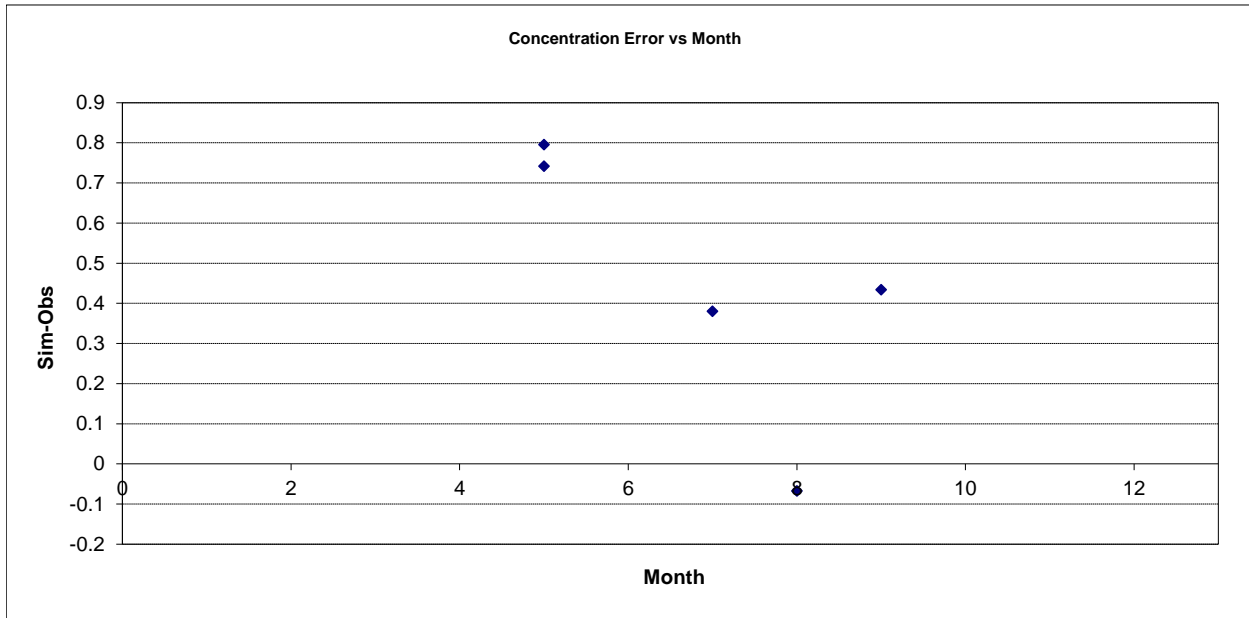


Figure B-64. Residual (Simulated - Observed) vs. Month Total Nitrogen (TN) at Rock Creek nr Pleasant Valley (05009001)

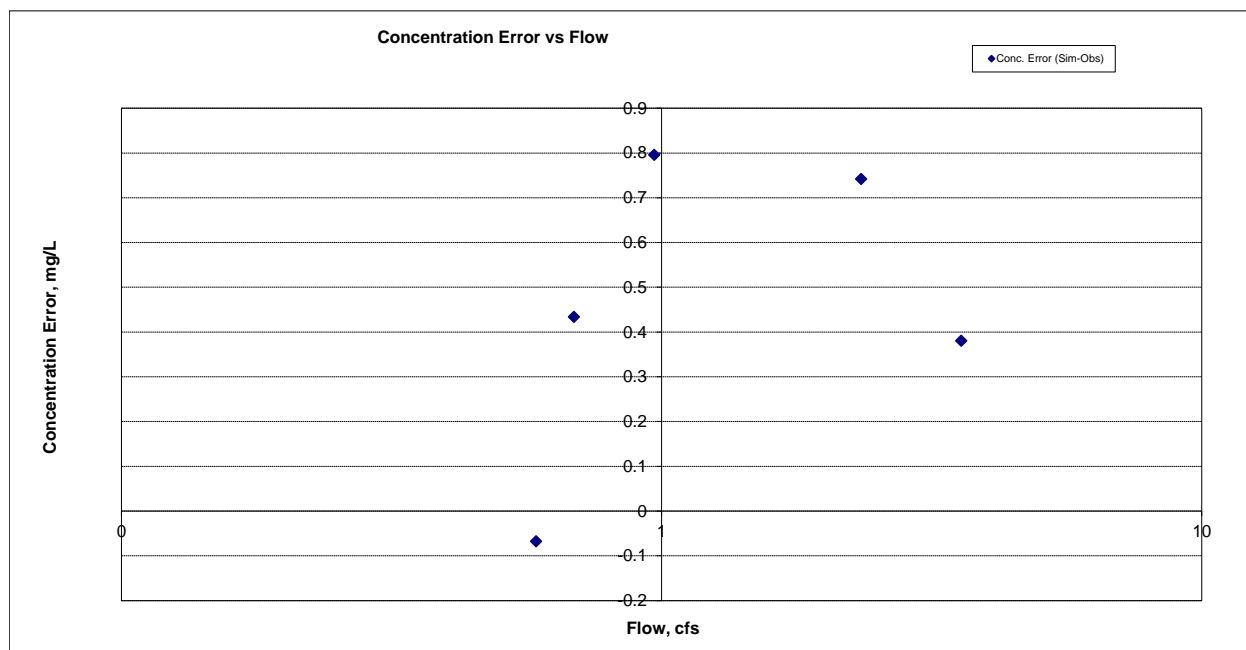


Figure B-65. Residual (Simulated - Observed) vs. Flow Total Nitrogen (TN) at Rock Creek nr Pleasant Valley (05009001)

B.2.6 Soluble Reactive Phosphorus (SRP)

Table B-11. Soluble Reactive Phosphorus (SRP) statistics

Period	1994-2001	2002-2012
Count	ND	15
Concentration Average Error		-5.82%
Concentration Median Error		32.63%
Load Average Error		-19.03%
Load Median Error		0.30%
Paired t conc		0.68
Paired t load		0.51

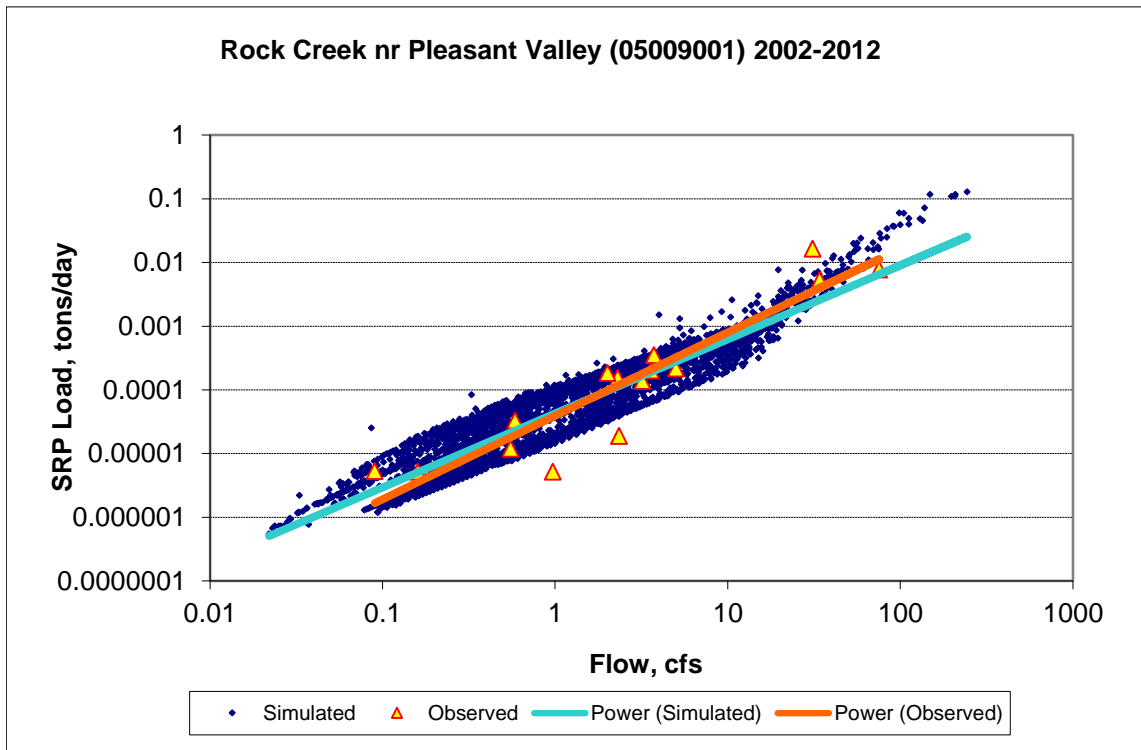
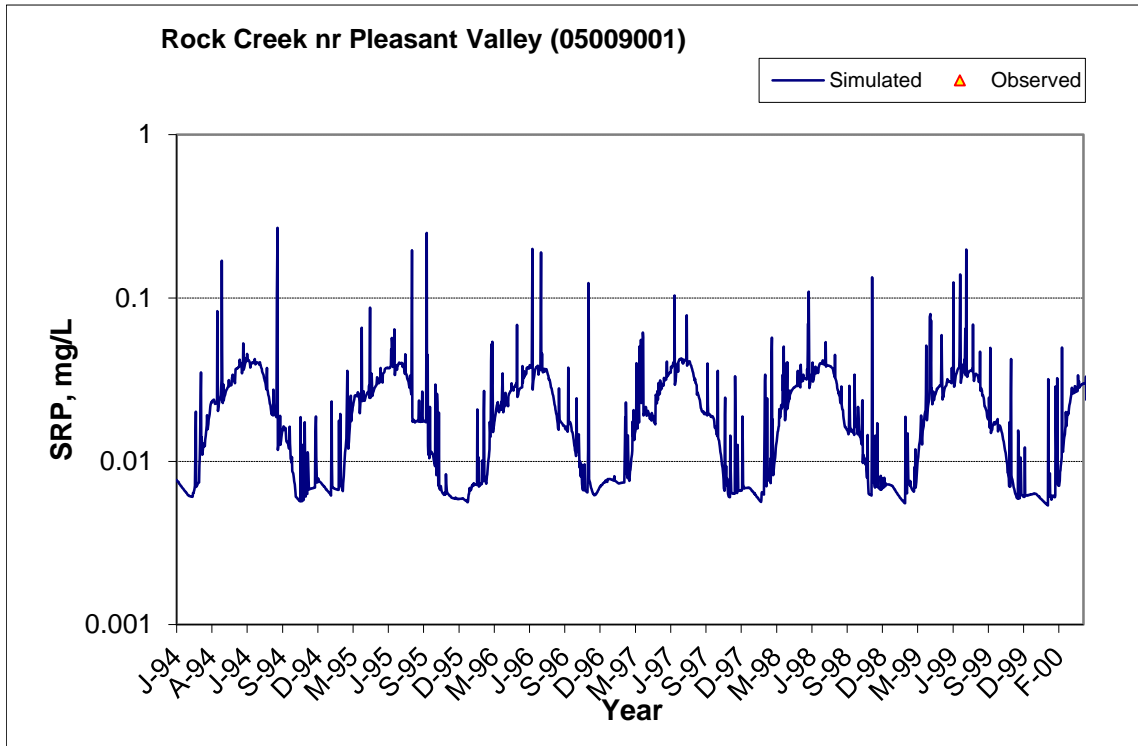


Figure B-66. Power plot of simulated and observed Soluble Reactive Phosphorus (SRP) load vs flow at Rock Creek nr Pleasant Valley (05009001) (calibration period)



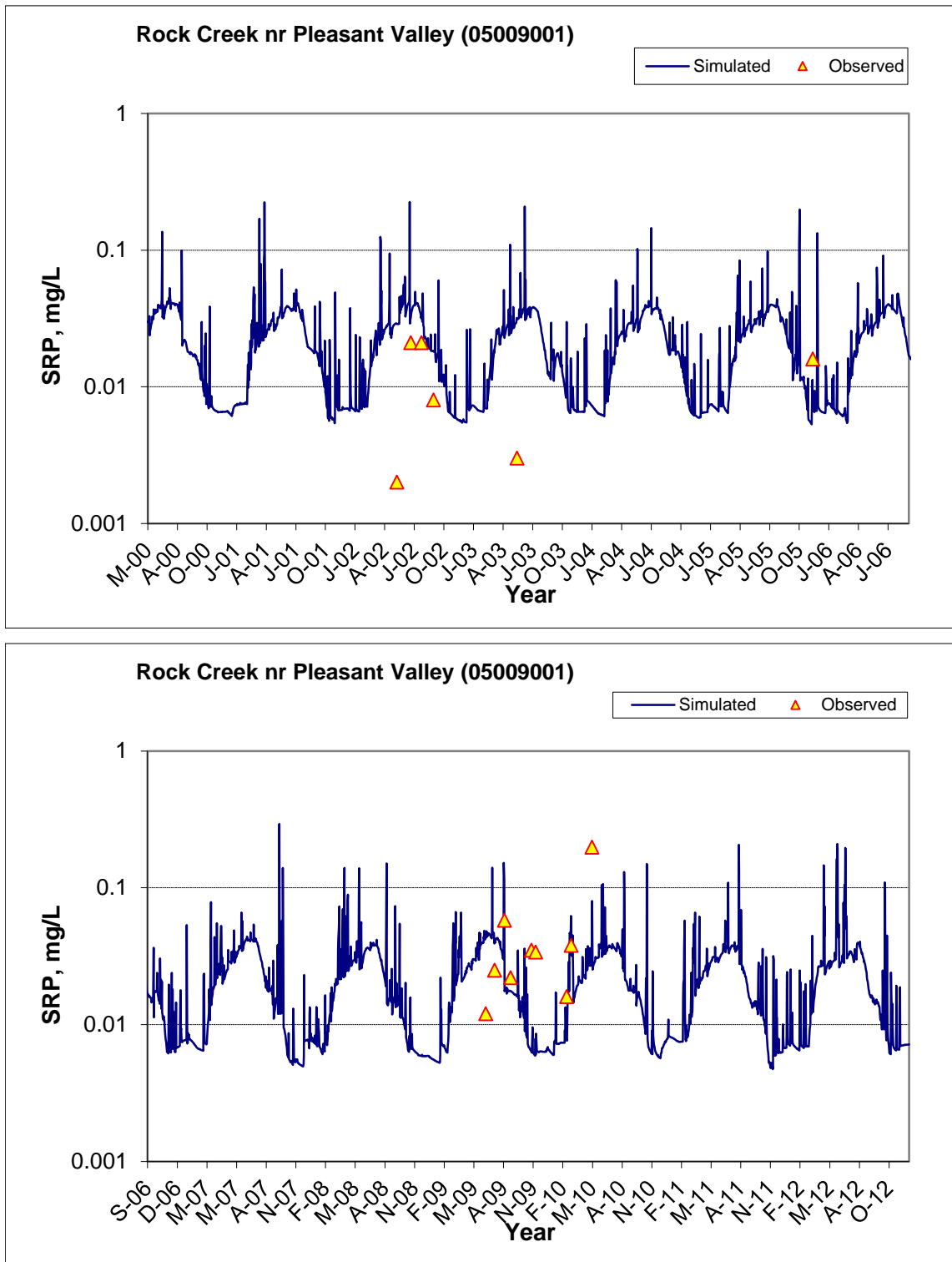


Figure B-67. Time series of observed and simulated Soluble Reactive Phosphorus (SRP) concentration at Rock Creek nr Pleasant Valley (05009001)

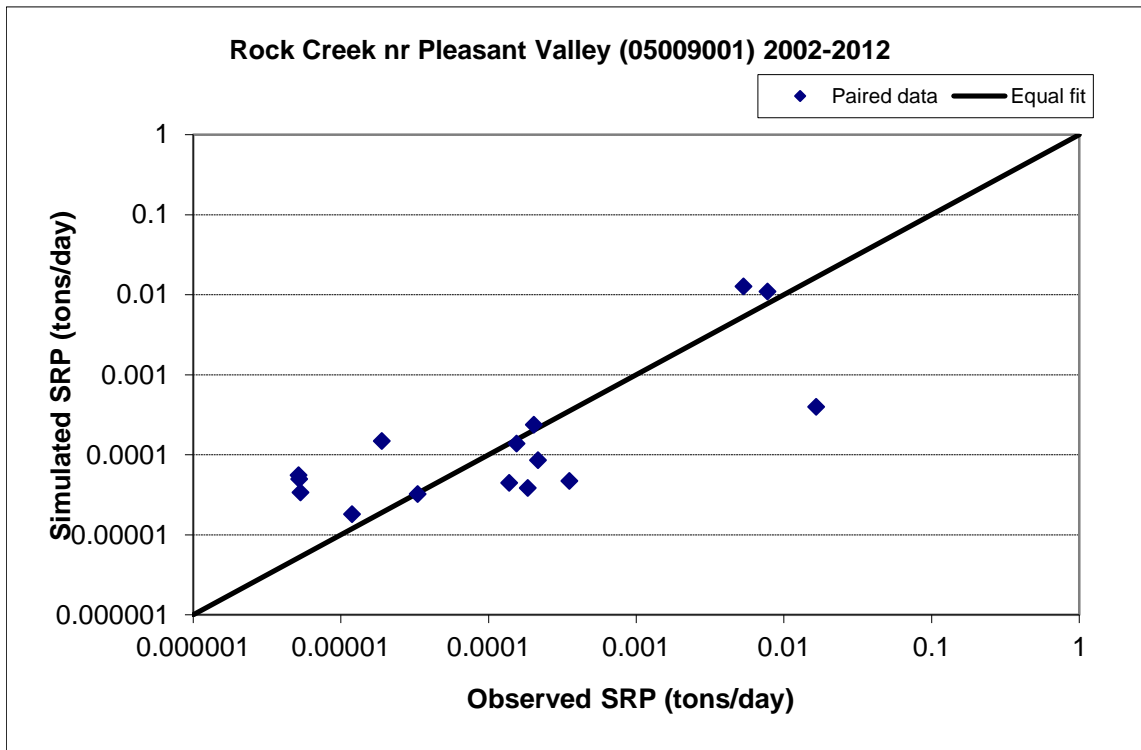


Figure B-68. Paired simulated vs. observed Soluble Reactive Phosphorus (SRP) load at Rock Creek nr Pleasant Valley (05009001) (calibration period)

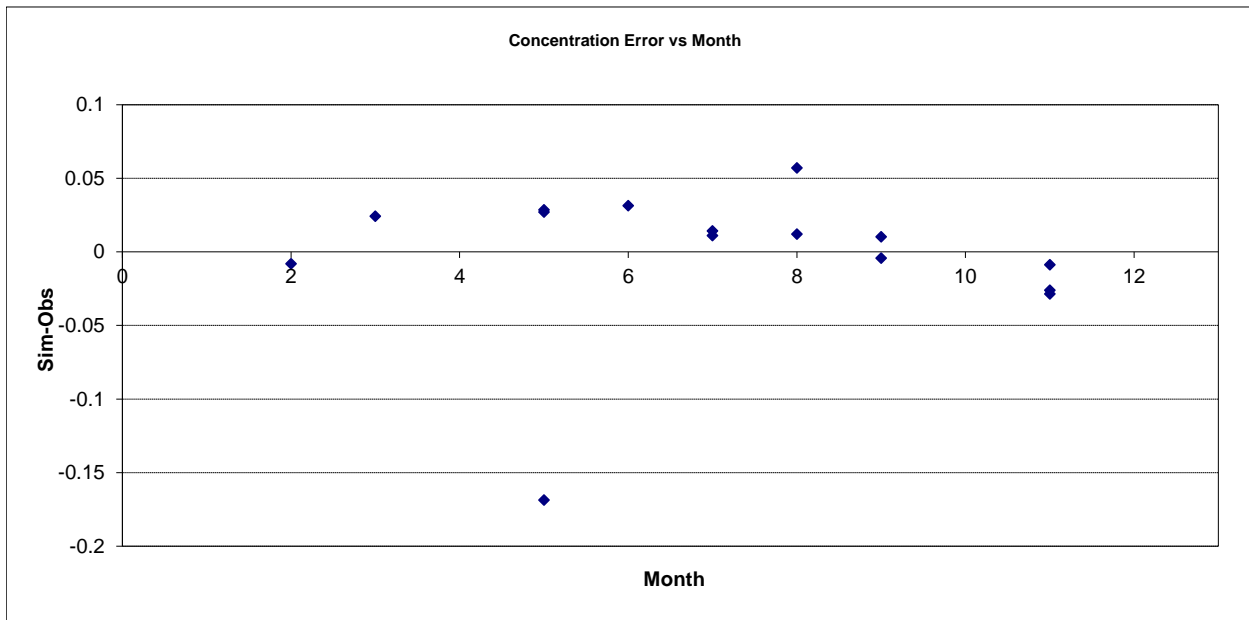


Figure B-69. Residual (Simulated - Observed) vs. Month Soluble Reactive Phosphorus (SRP) at Rock Creek nr Pleasant Valley (05009001)

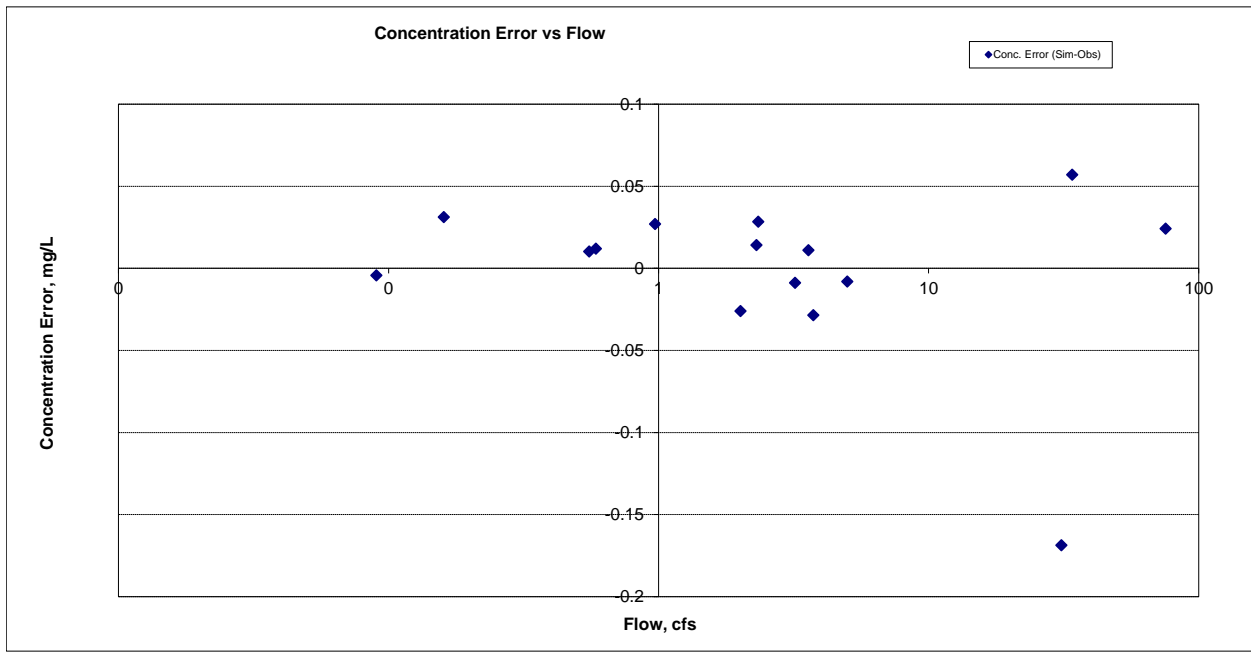
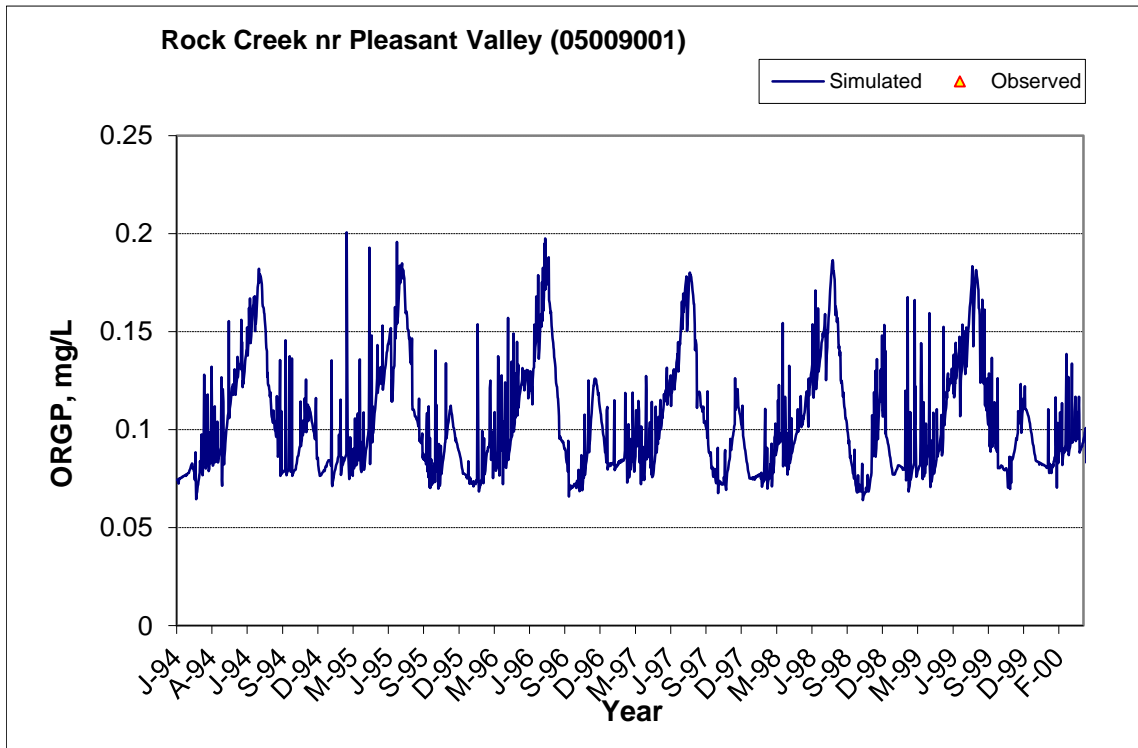


Figure B-70. Residual (Simulated - Observed) vs. Flow Soluble Reactive Phosphorus (SRP) at Rock Creek nr Pleasant Valley (05009001)

B.2.7 Organic Phosphorus (OrgP)



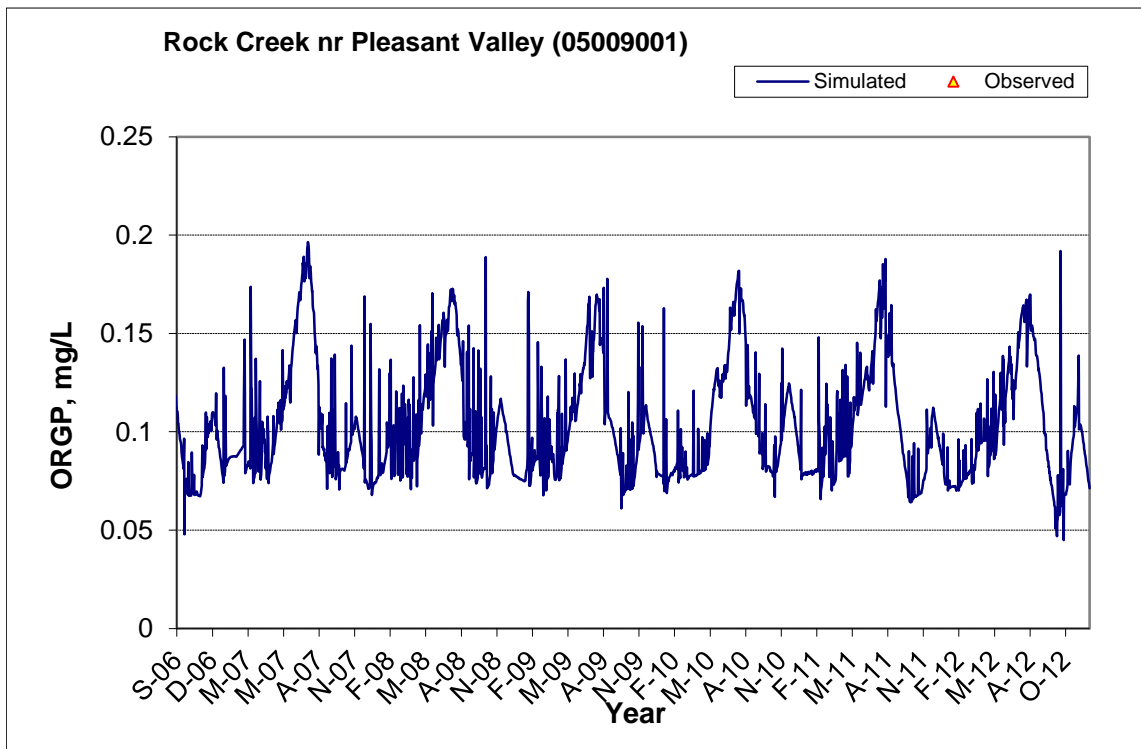
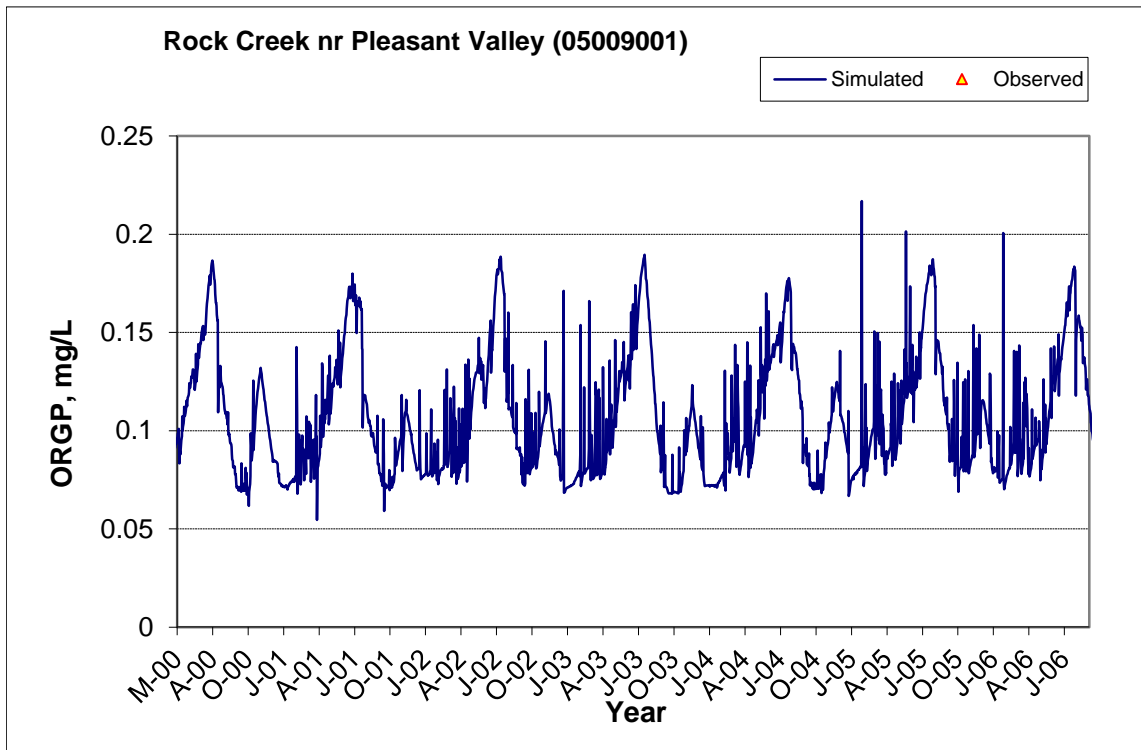


Figure B-71. Time series of observed and simulated Organic Phosphorus (OrgP) concentration at Rock Creek nr Pleasant Valley (05009001)

B.2.8 Total Phosphorus (TP)

Table B-12. Total Phosphorus (TP) statistics

Period	1994-2001	2002-2012
Count	ND	63
Concentration Average Error		27.12%
Concentration Median Error		40.97%
Load Average Error		2.65%
Load Median Error		1.62%
Paired t conc		0.18
Paired t load		0.65

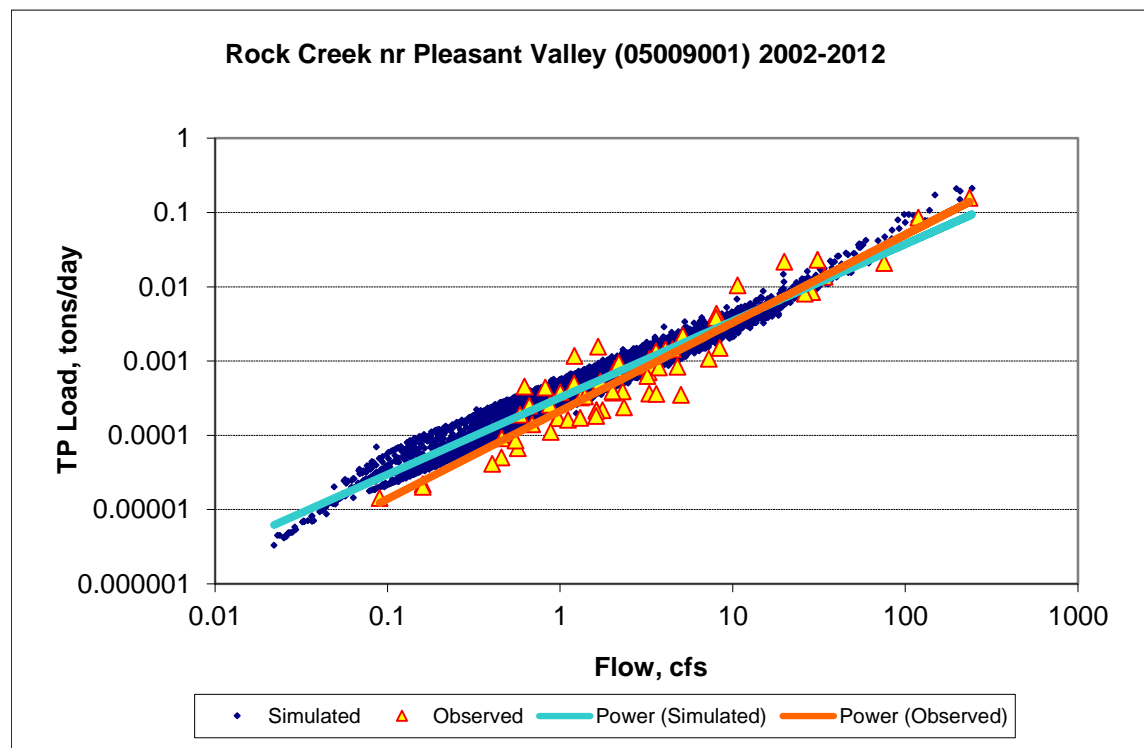
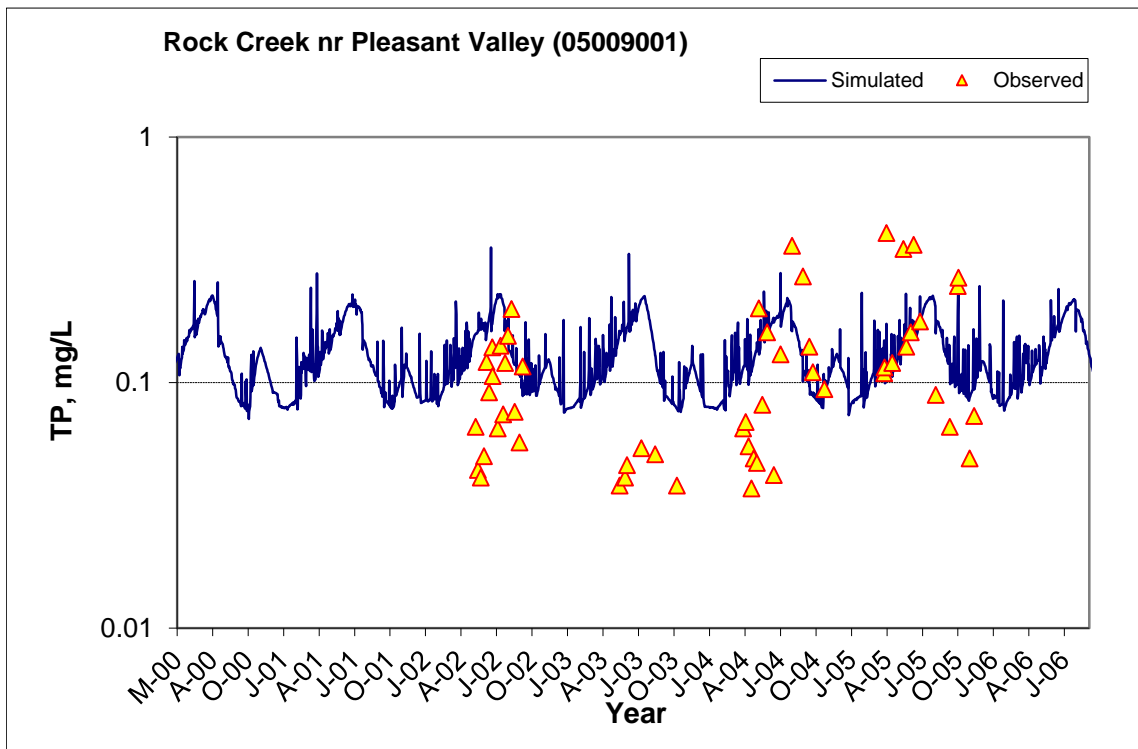
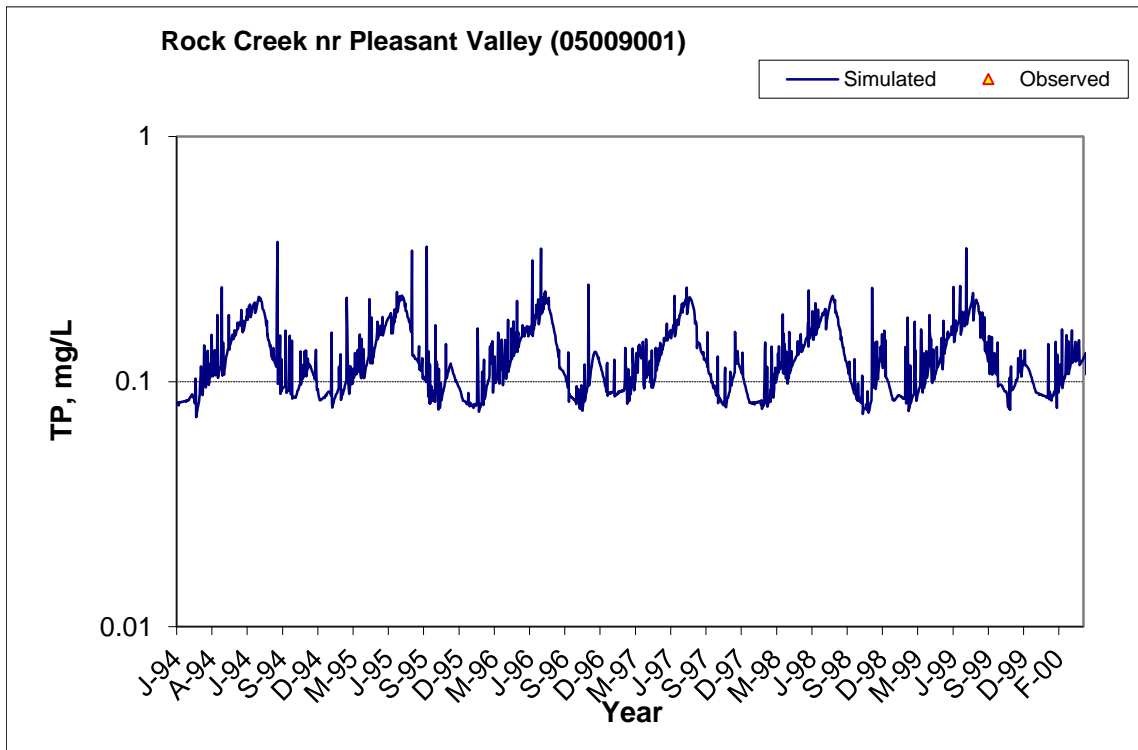


Figure B-72. Power plot of simulated and observed Total Phosphorus (TP) load vs flow at Rock Creek nr Pleasant Valley (05009001) (calibration period)



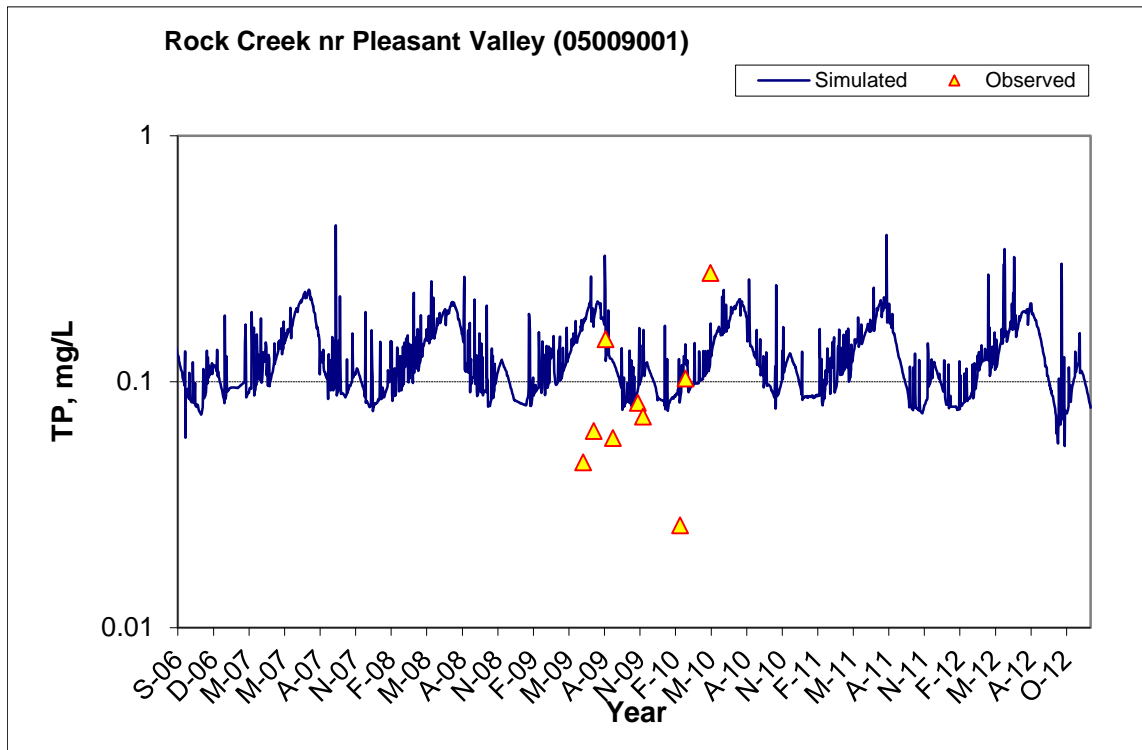


Figure B-73. Time series of observed and simulated Total Phosphorus (TP) concentration at Rock Creek nr Pleasant Valley (05009001)

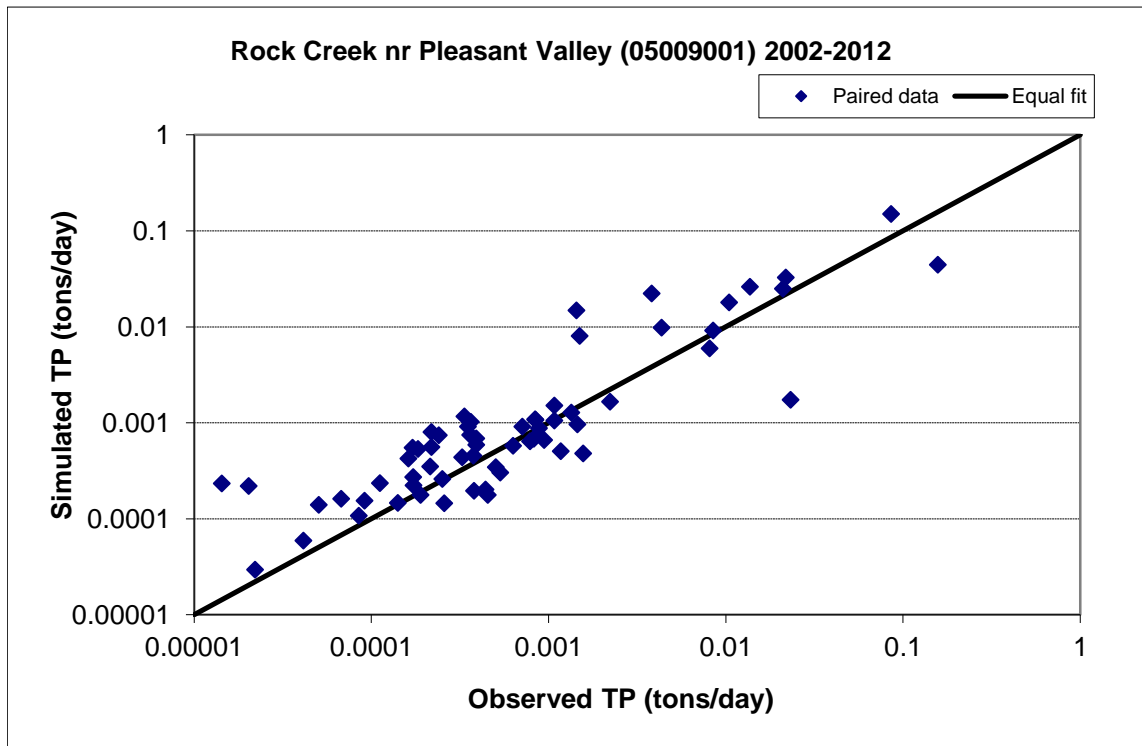


Figure B-74. Paired simulated vs. observed Total Phosphorus (TP) load at Rock Creek nr Pleasant Valley (05009001) (calibration period)

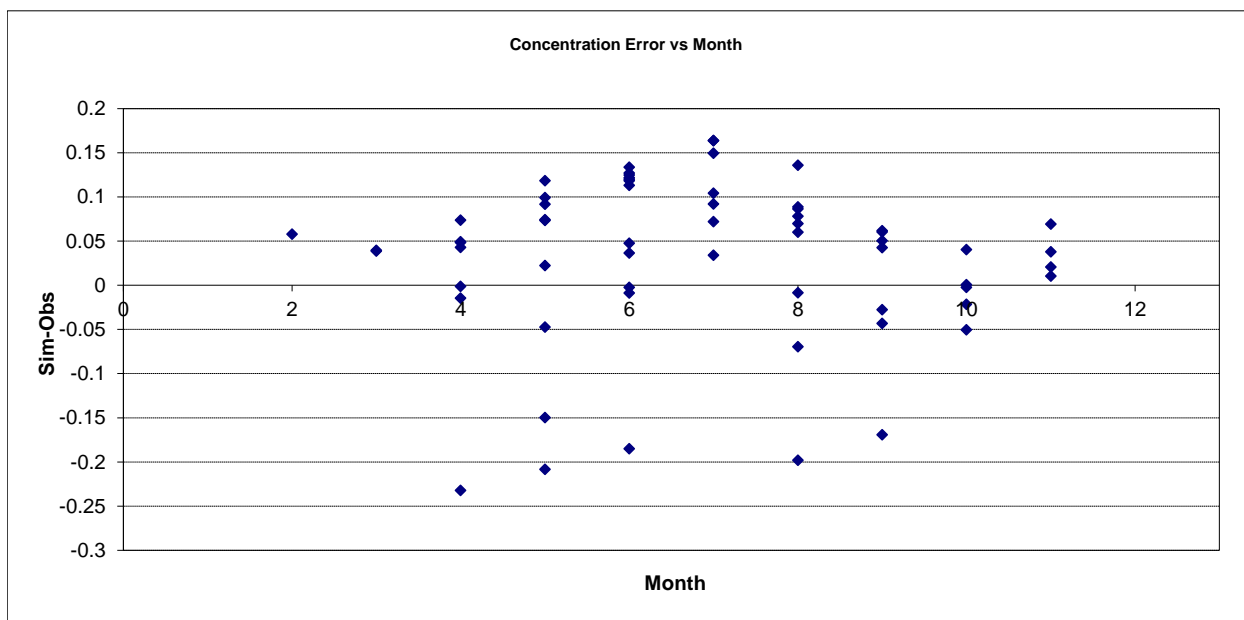


Figure B-75. Residual (Simulated - Observed) vs. Month Total Phosphorus (TP) at Rock Creek nr Pleasant Valley (05009001)

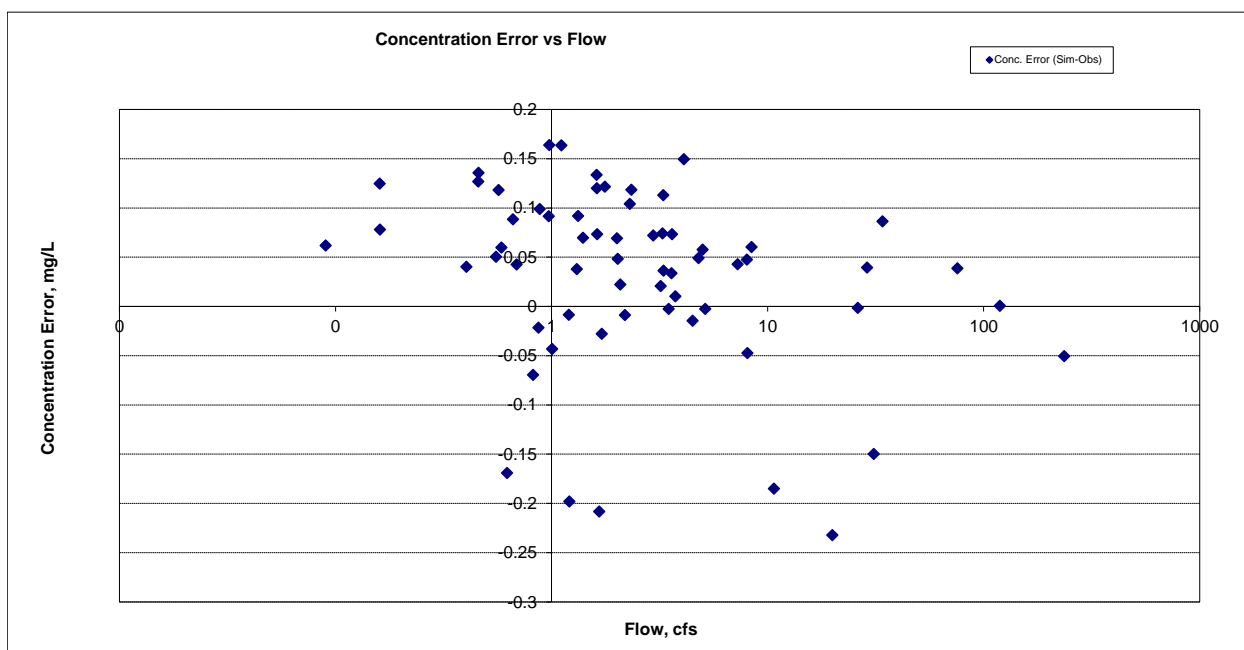
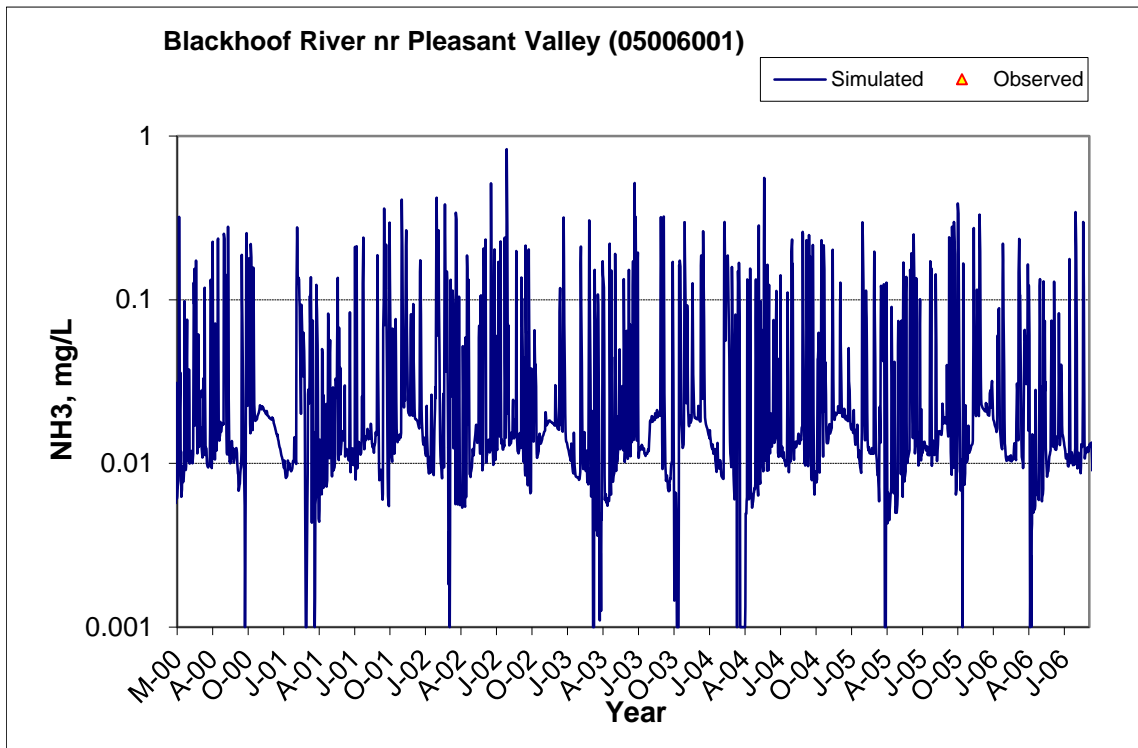
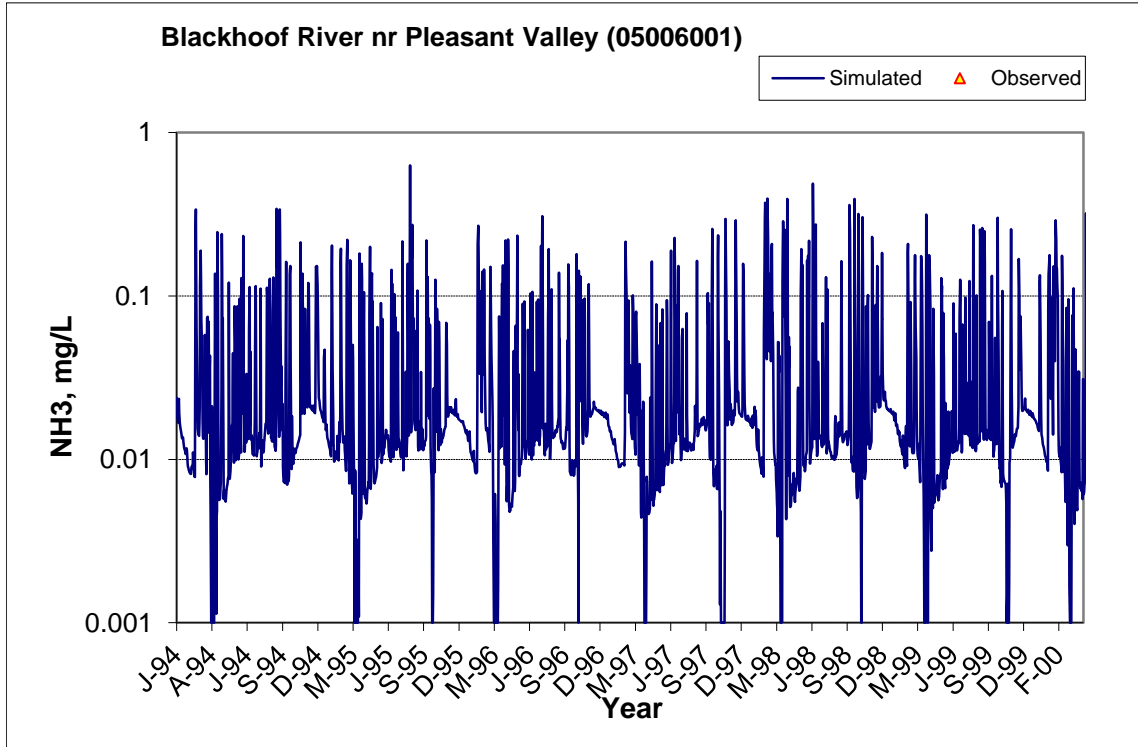


Figure B-76. Residual (Simulated - Observed) vs. Flow Total Phosphorus (TP) at Rock Creek nr Pleasant Valley (05009001)

B.3 BLACKHOOF RIVER NR PLEASANT VALLEY (05006001)

B.3.1 Ammonia Nitrogen (NH3)



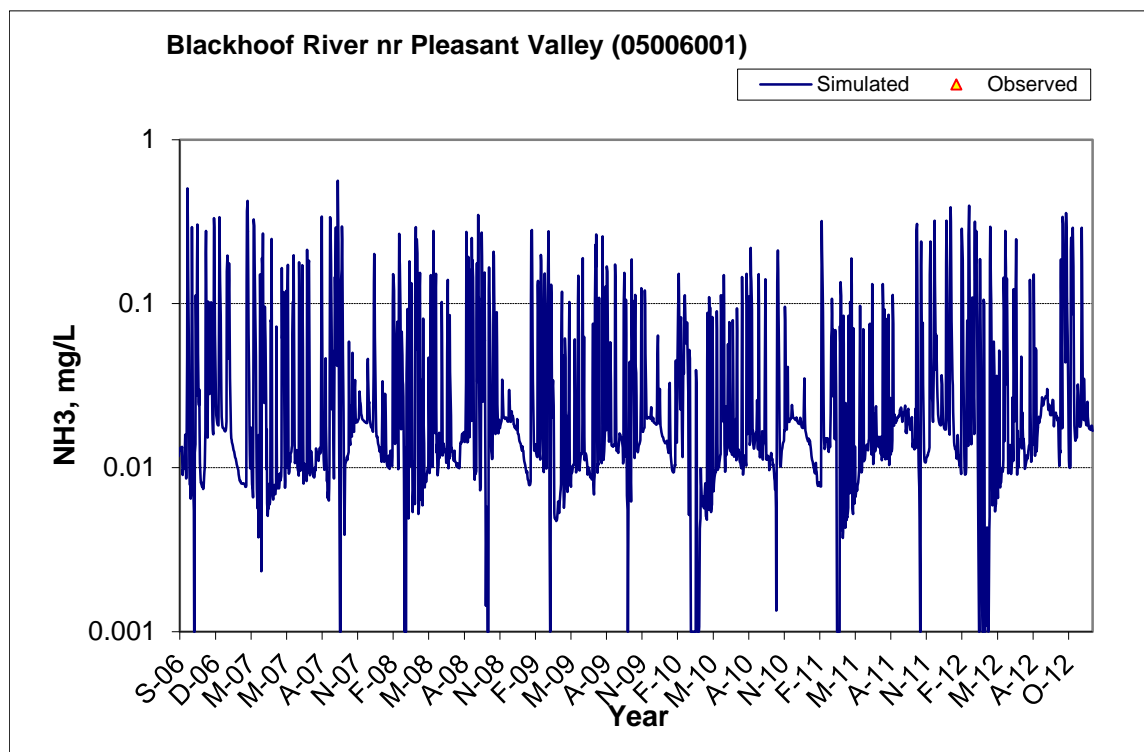
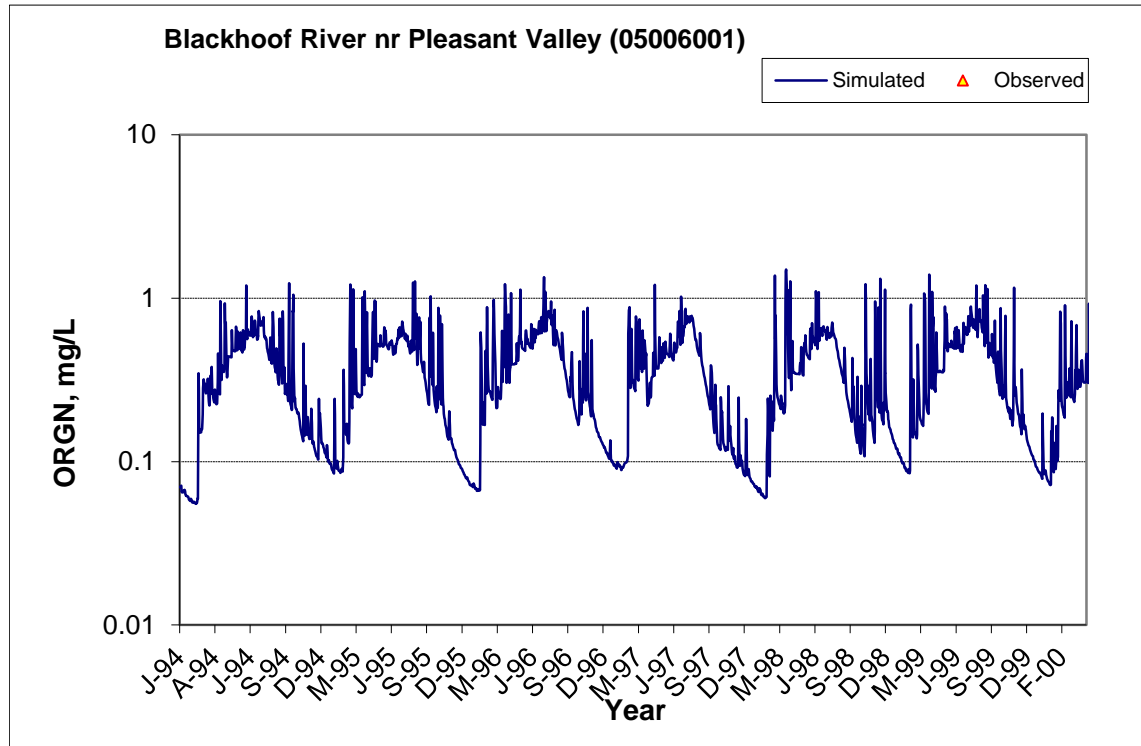


Figure B-77. Time series of observed and simulated Ammonia Nitrogen (NH₃) concentration at Blackhoof River nr Pleasant Valley (05006001)

B.3.2 Organic Nitrogen (OrgN)



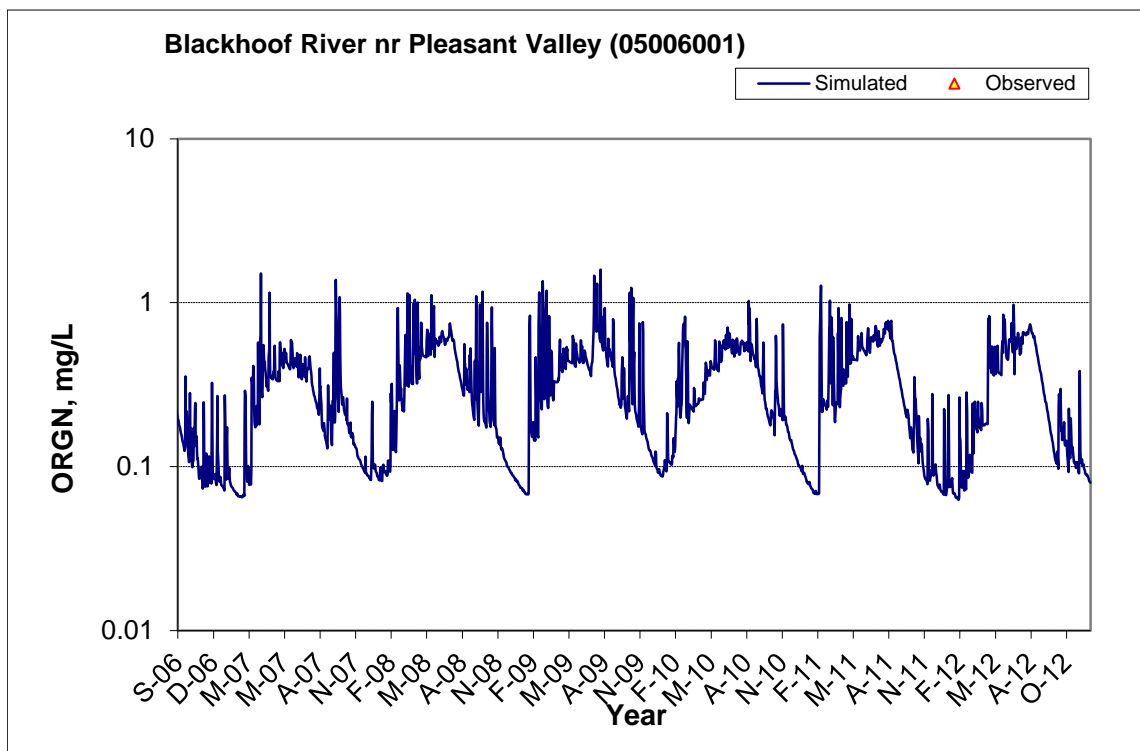
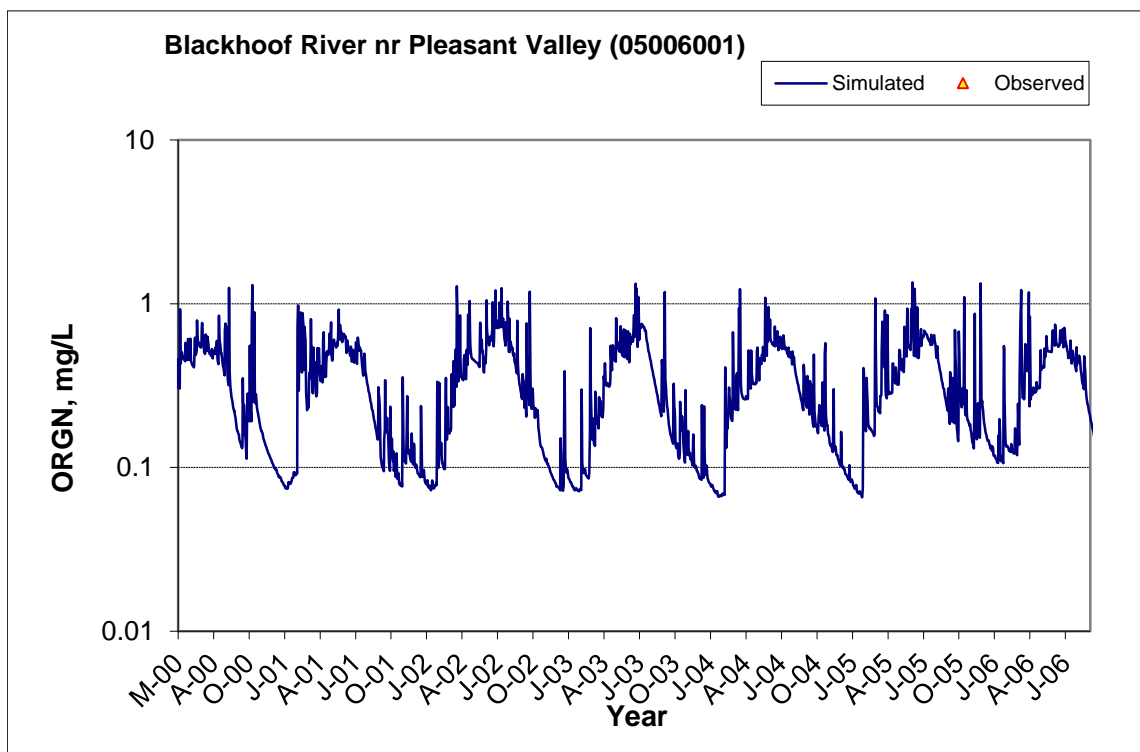


Figure B-78. Time series of observed and simulated Organic Nitrogen (OrgN) concentration at Blackhoof River nr Pleasant Valley (05006001)

B.3.3 Total Kjeldahl Nitrogen (TKN)

Table B-13. Total Kjeldahl Nitrogen (TKN) statistics

Period	1994-2008	2009-2012
Count	ND	17
Concentration Average Error		-19.82%
Concentration Median Error		-16.12%
Load Average Error		9.11%
Load Median Error		-0.40%
Paired t conc		0.51
Paired t load		0.58

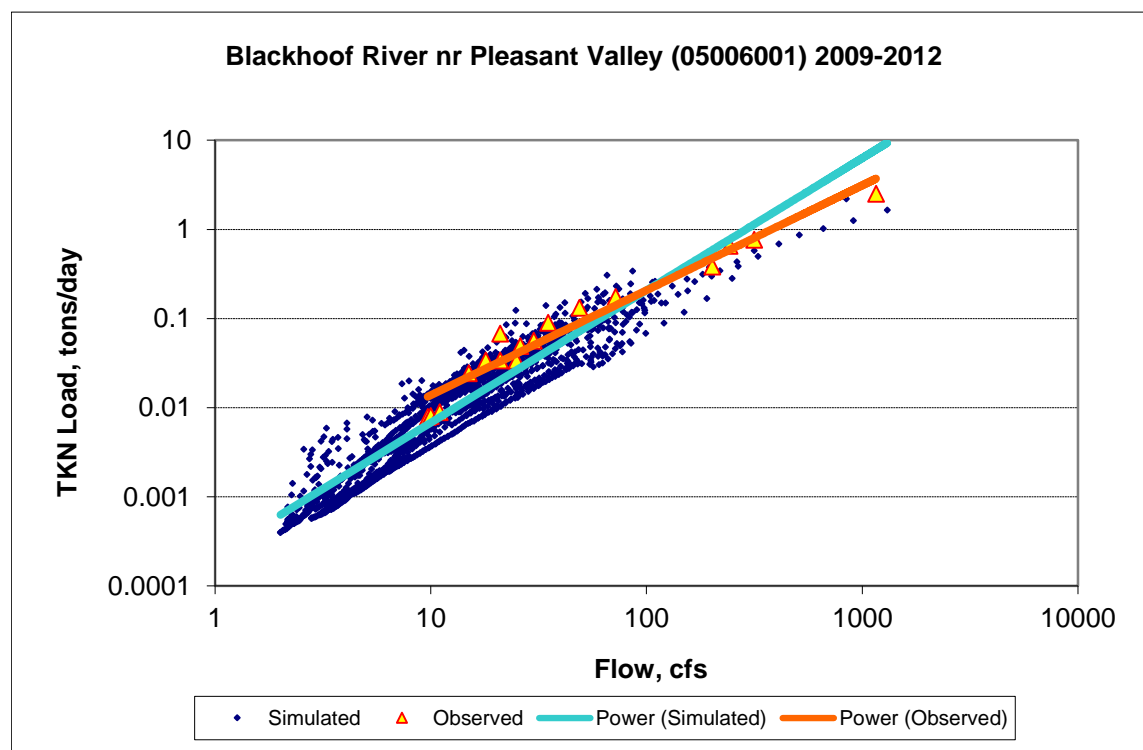
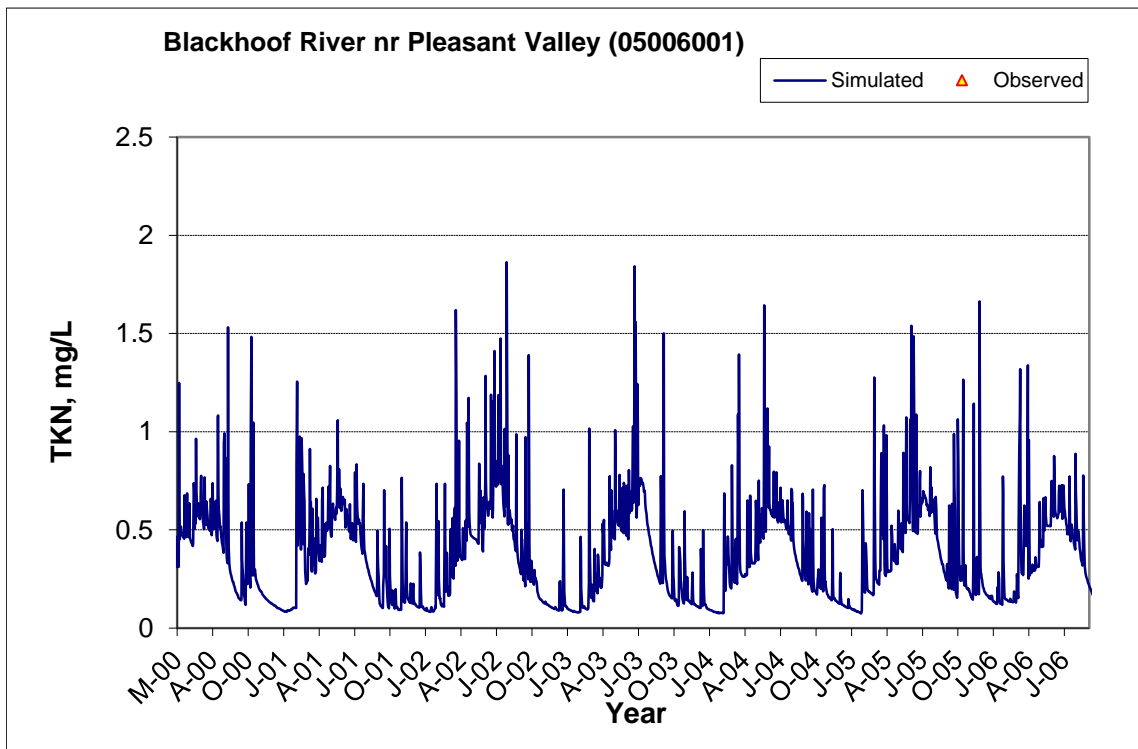
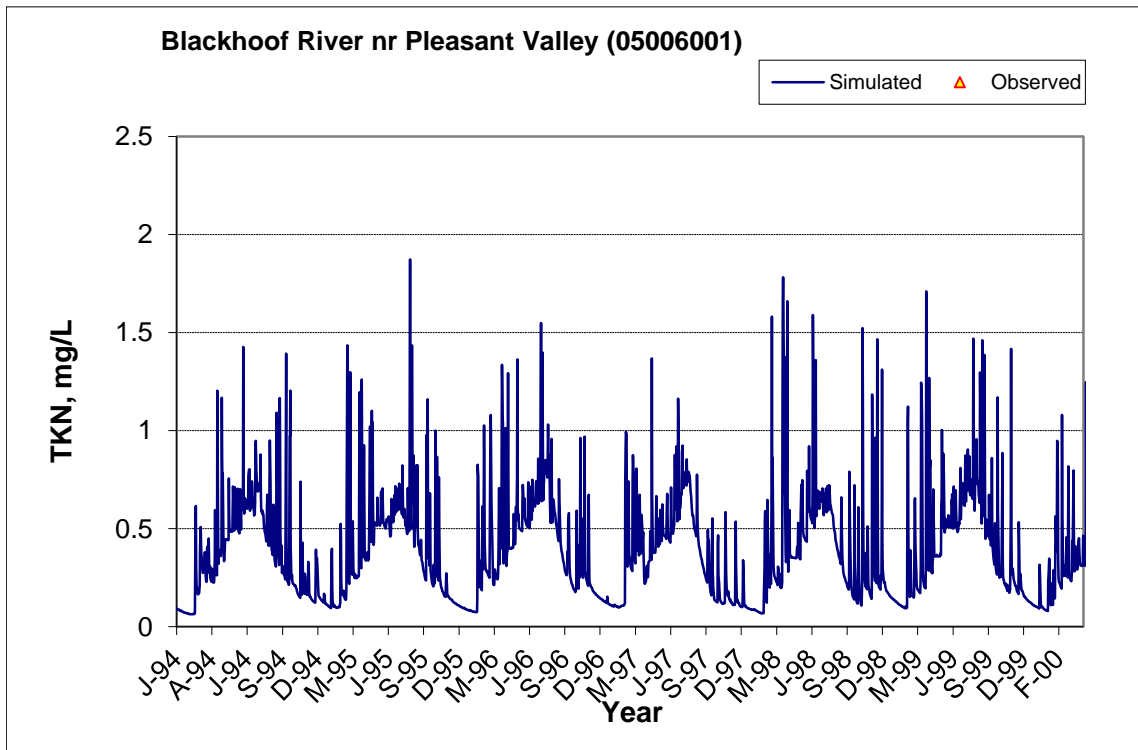


Figure B-79. Power plot of simulated and observed Total Kjeldahl Nitrogen (TKN) load vs flow at Blackhoof River nr Pleasant Valley (05006001) (calibration period)



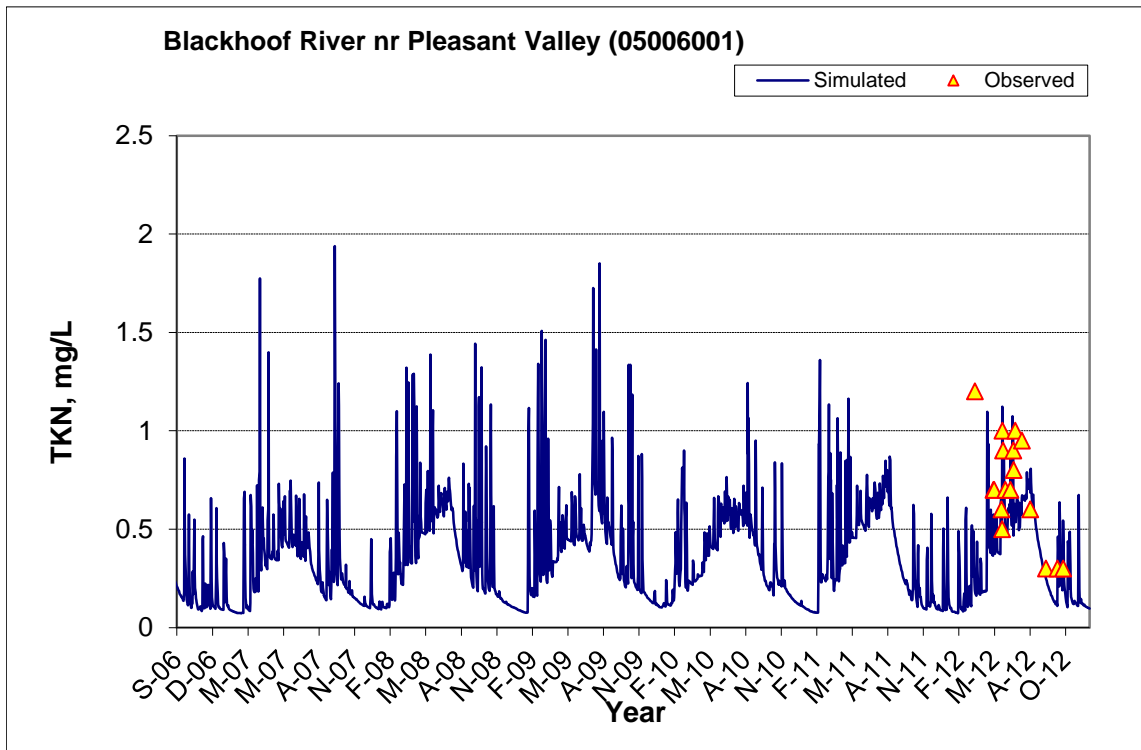


Figure B-80. Time series of observed and simulated Total Kjeldahl Nitrogen (TKN) concentration at Blackhoof River nr Pleasant Valley (05006001)

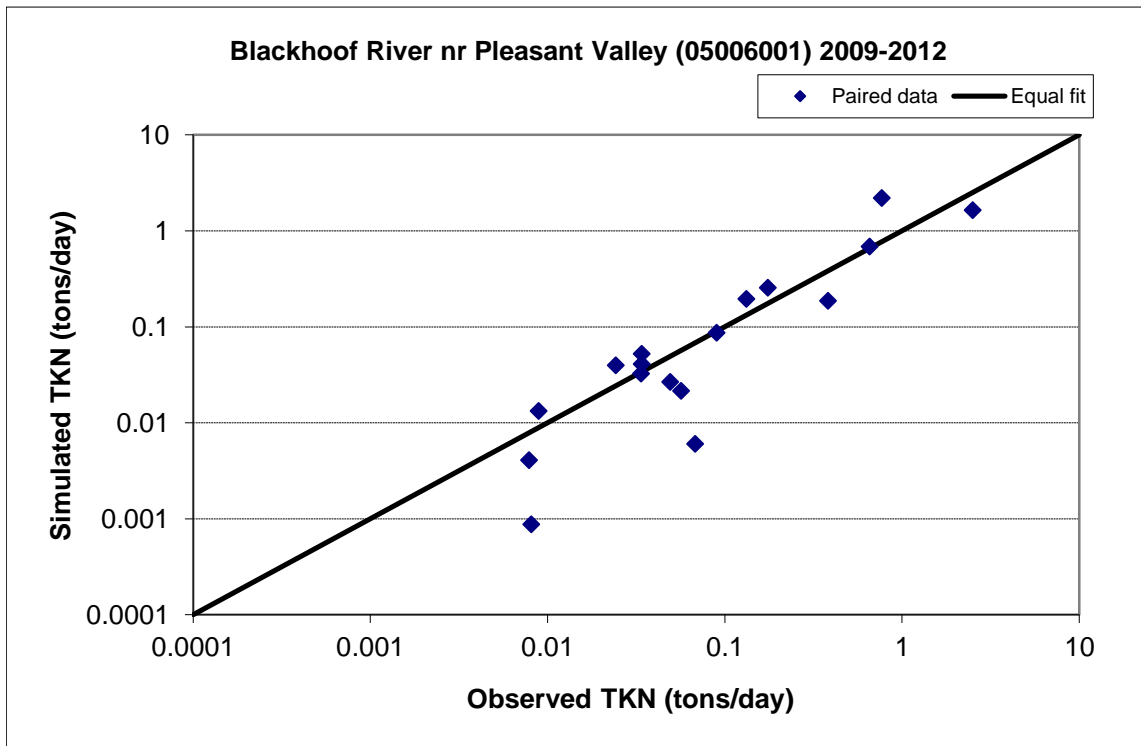


Figure B-81. Paired simulated vs. observed Total Kjeldahl Nitrogen (TKN) load at Blackhoof River nr Pleasant Valley (05006001) (calibration period)

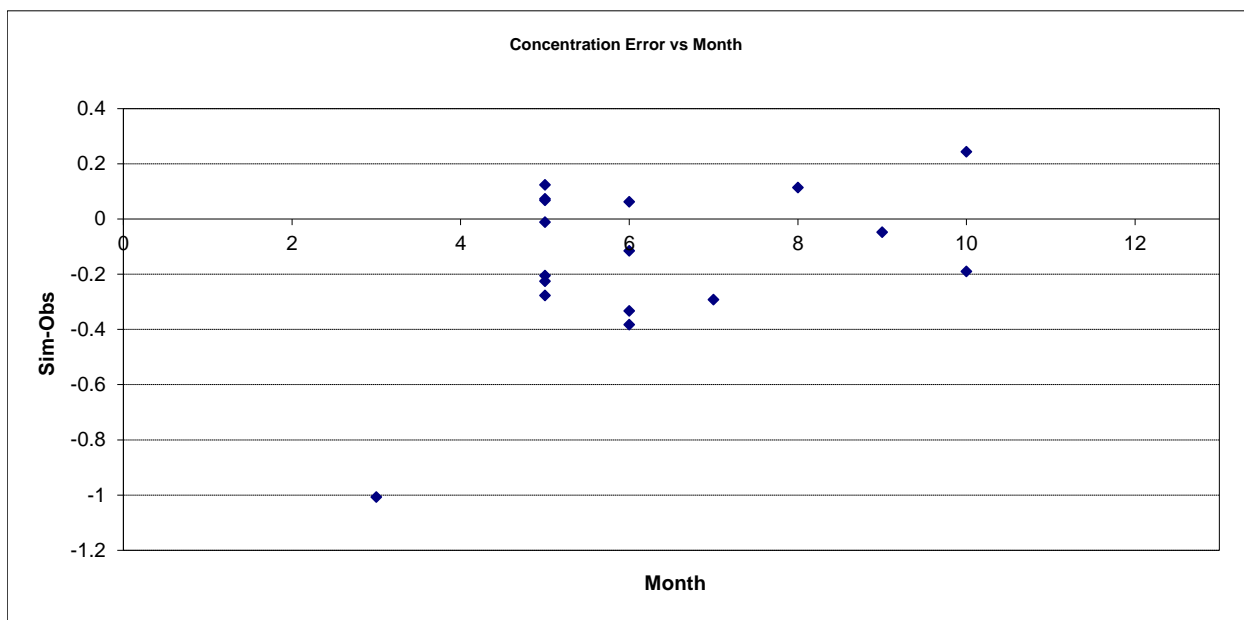


Figure B-82. Residual (Simulated - Observed) vs. Month Total Kjeldahl Nitrogen (TKN) at Blackhoof River nr Pleasant Valley (05006001)

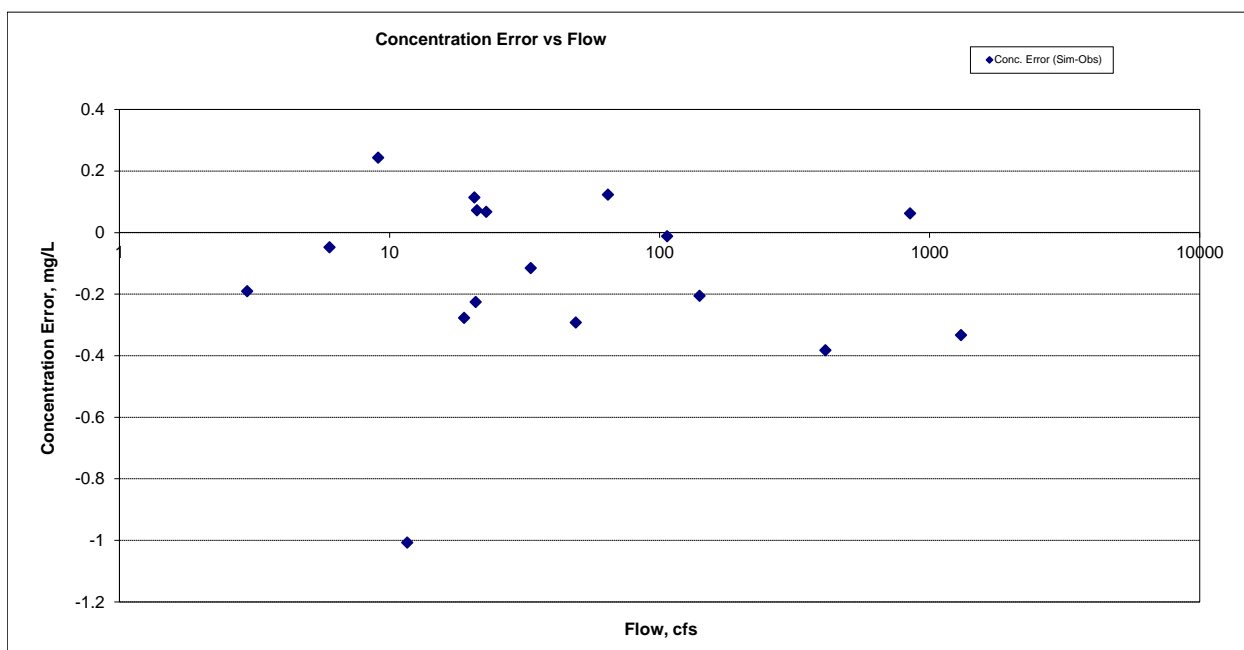


Figure B-83. Residual (Simulated - Observed) vs. Flow Total Kjeldahl Nitrogen (TKN) at Blackhoof River nr Pleasant Valley (05006001)

B.3.4 Nitrite+ Nitrate Nitrogen (NOx)

Table B-14. Nitrite+ Nitrate Nitrogen (NOx) statistics

Period	1994-2008	2009-2012
Count	ND	17
Concentration Average Error		-28.46%
Concentration Median Error		12.34%
Load Average Error		356.44%
Load Median Error		-1.04%
Paired t conc		0.33
Paired t load		0.04

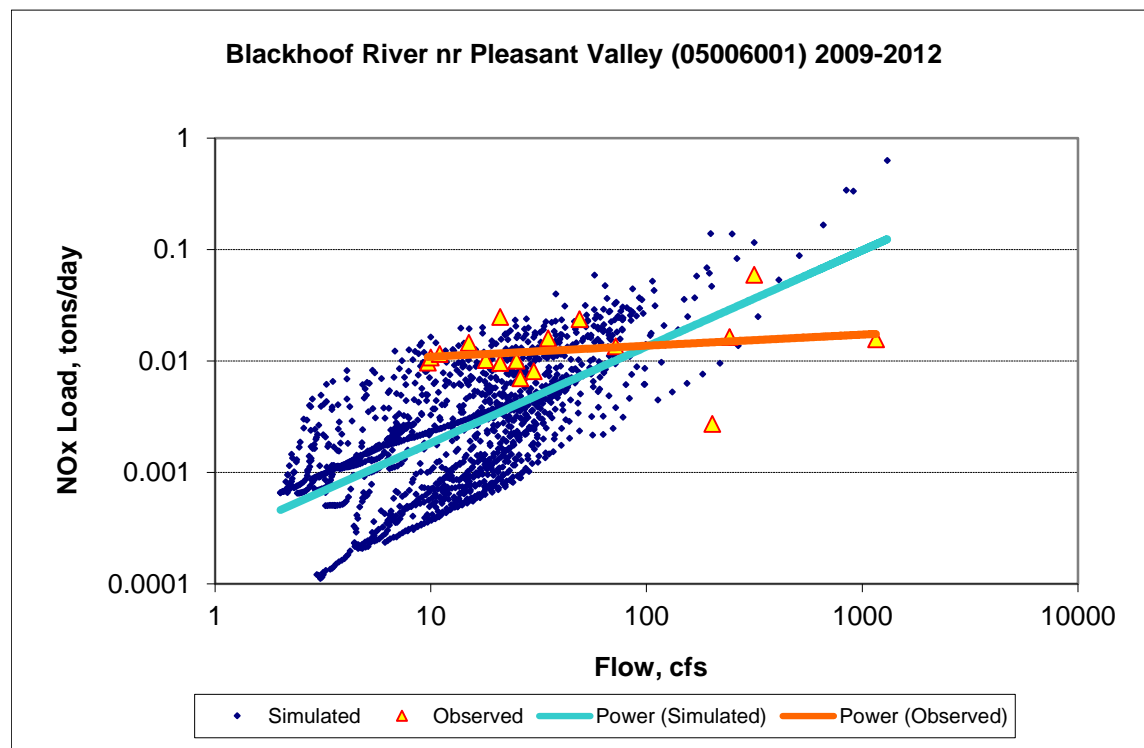
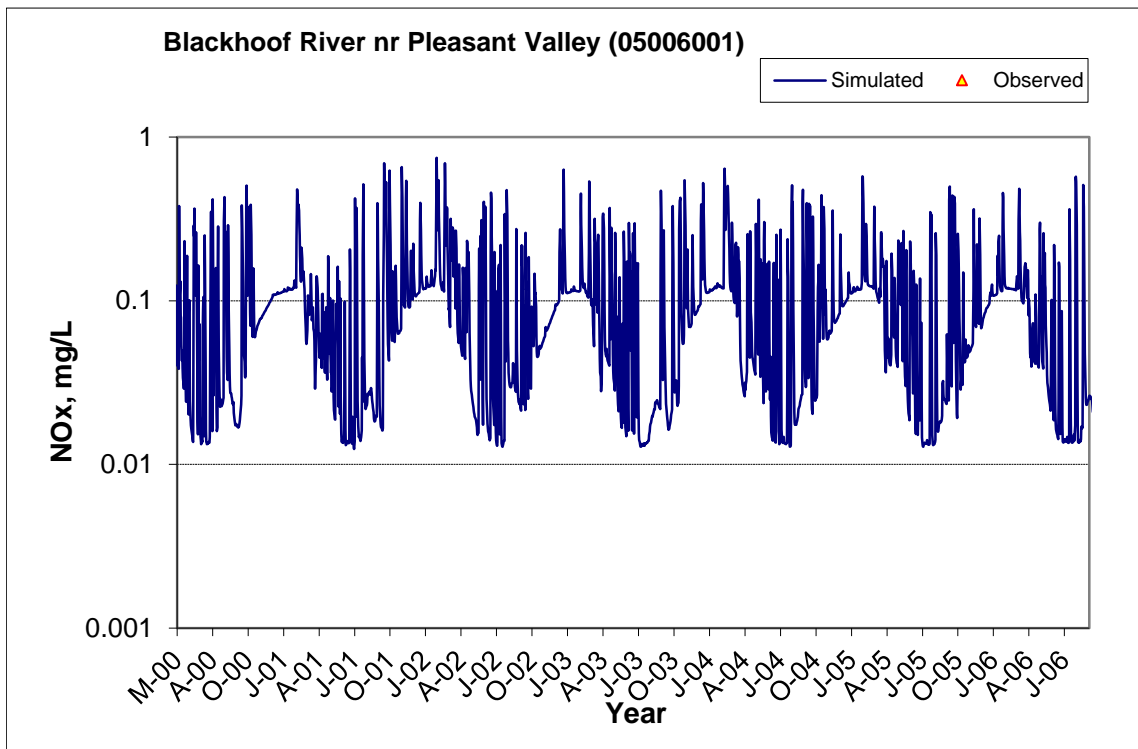
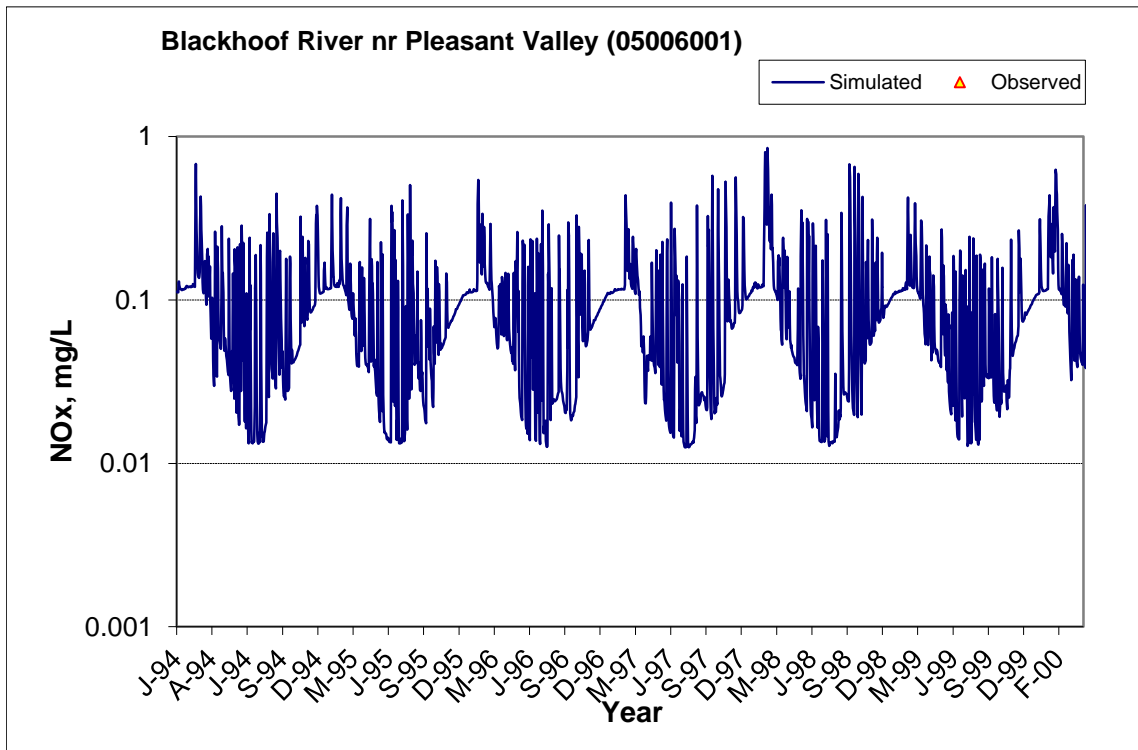


Figure B-84. Power plot of simulated and observed Nitrite+ Nitrate Nitrogen (NOx) load vs flow at Blackhoof River nr Pleasant Valley (05006001) (calibration period)



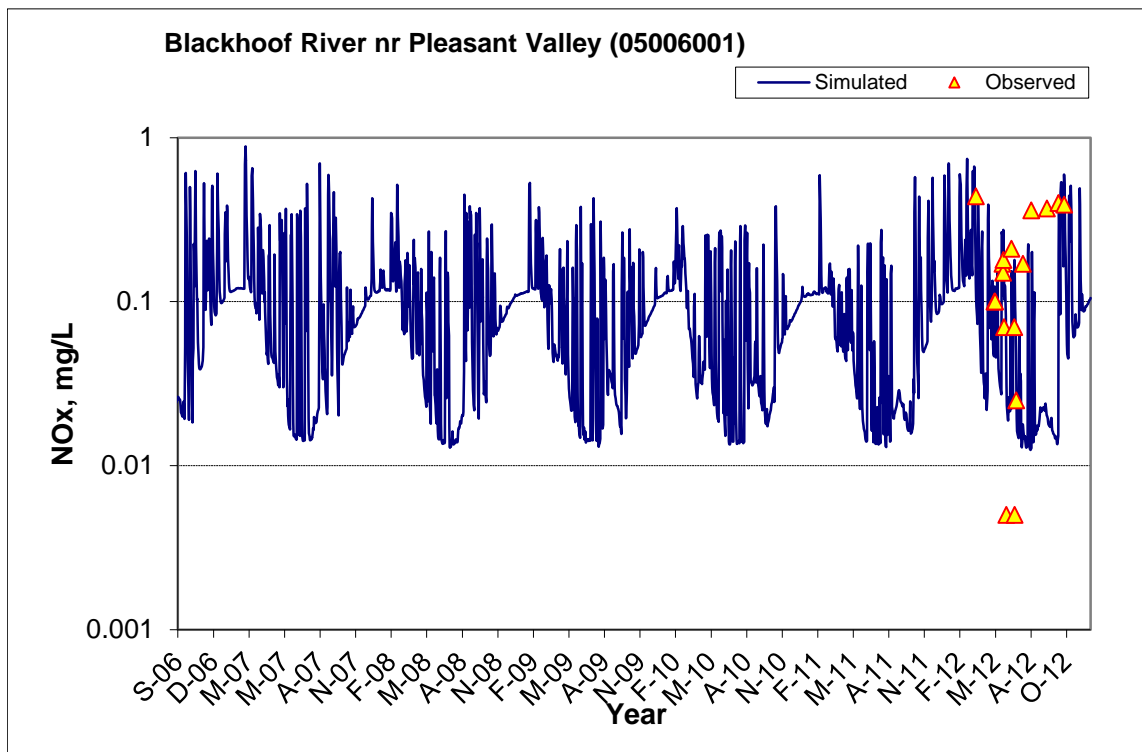


Figure B-85. Time series of observed and simulated Nitrite+ Nitrate Nitrogen (NOx) concentration at Blackhoof River nr Pleasant Valley (05006001)

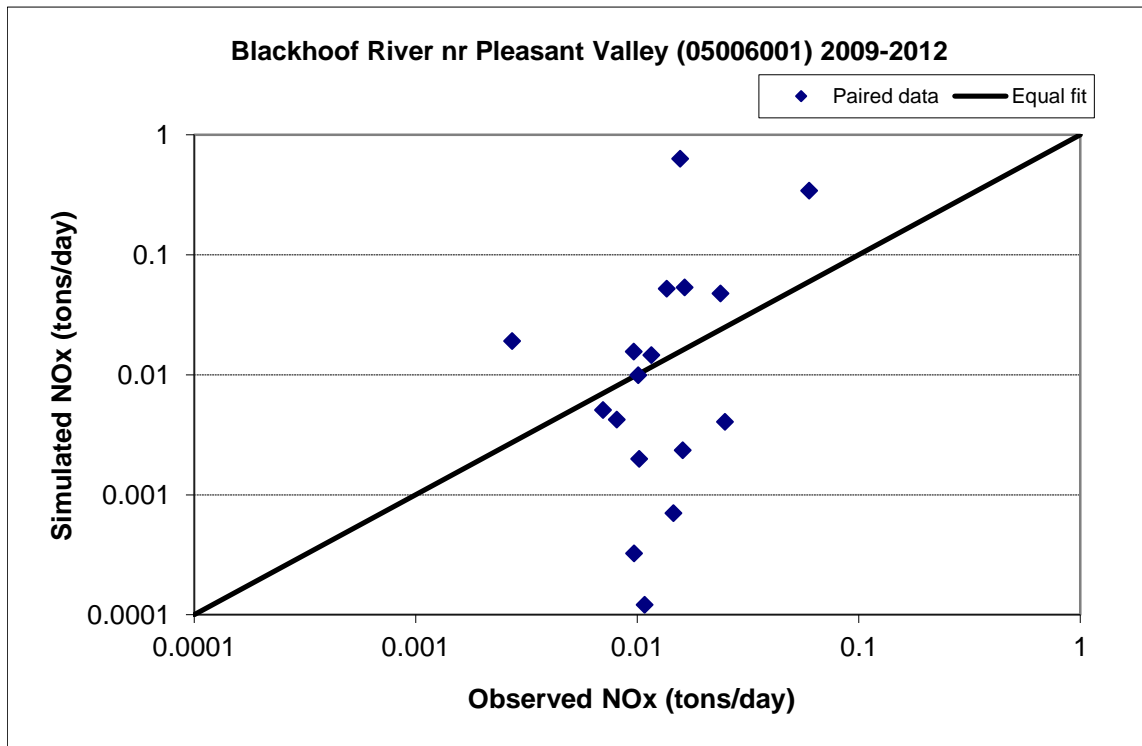


Figure B-86. Paired simulated vs. observed Nitrite+ Nitrate Nitrogen (NOx) load at Blackhoof River nr Pleasant Valley (05006001) (calibration period)

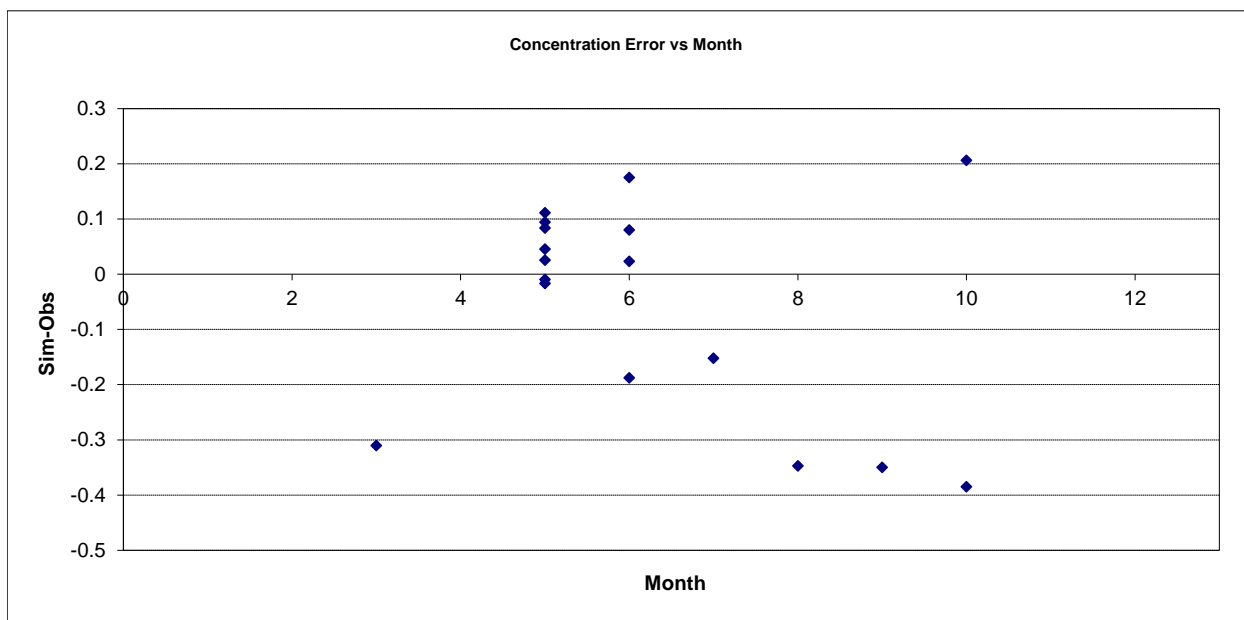


Figure B-87. Residual (Simulated - Observed) vs. Month Nitrite+ Nitrate Nitrogen (NOx) at Blackhoof River nr Pleasant Valley (05006001)

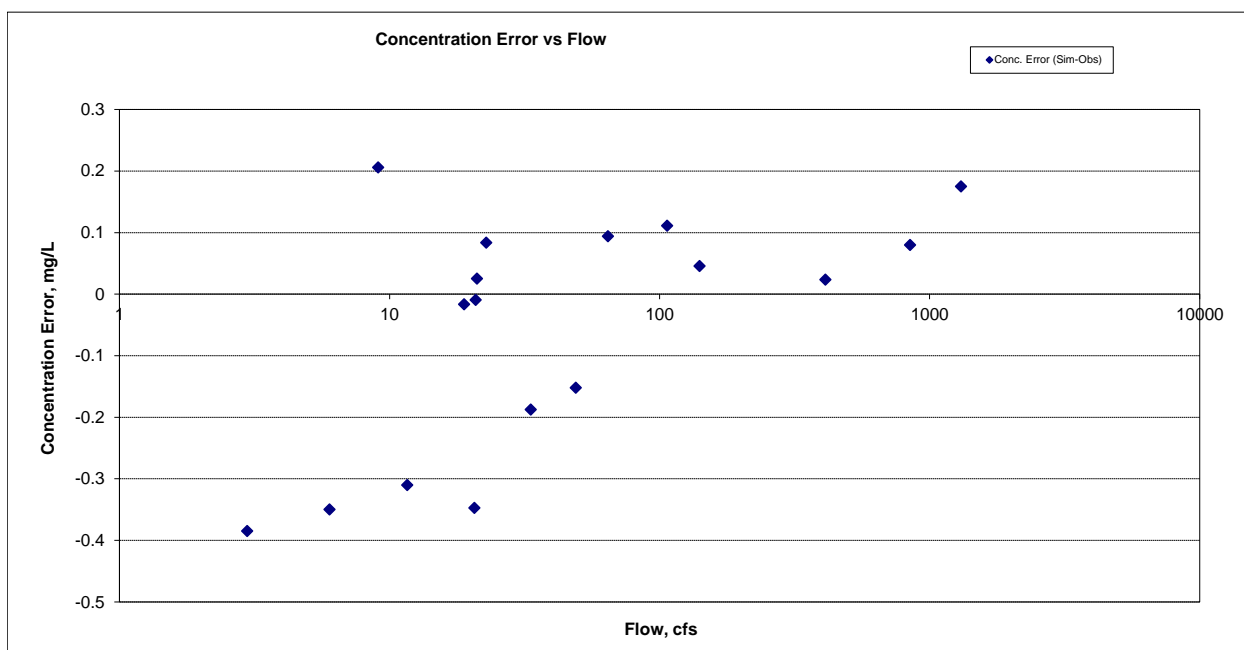


Figure B-88. Residual (Simulated - Observed) vs. Flow Nitrite+ Nitrate Nitrogen (NOx) at Blackhoof River nr Pleasant Valley (05006001)

B.3.5 Total Nitrogen (TN)

Table B-15. Total Nitrogen (TN) statistics

Period	1994-2008	2009-2012
Count	ND	17
Concentration Average Error		-21.80%
Concentration Median Error		-25.79%
Load Average Error		25.63%
Load Median Error		-0.43%
Paired t conc		0.41
Paired t load		0.46

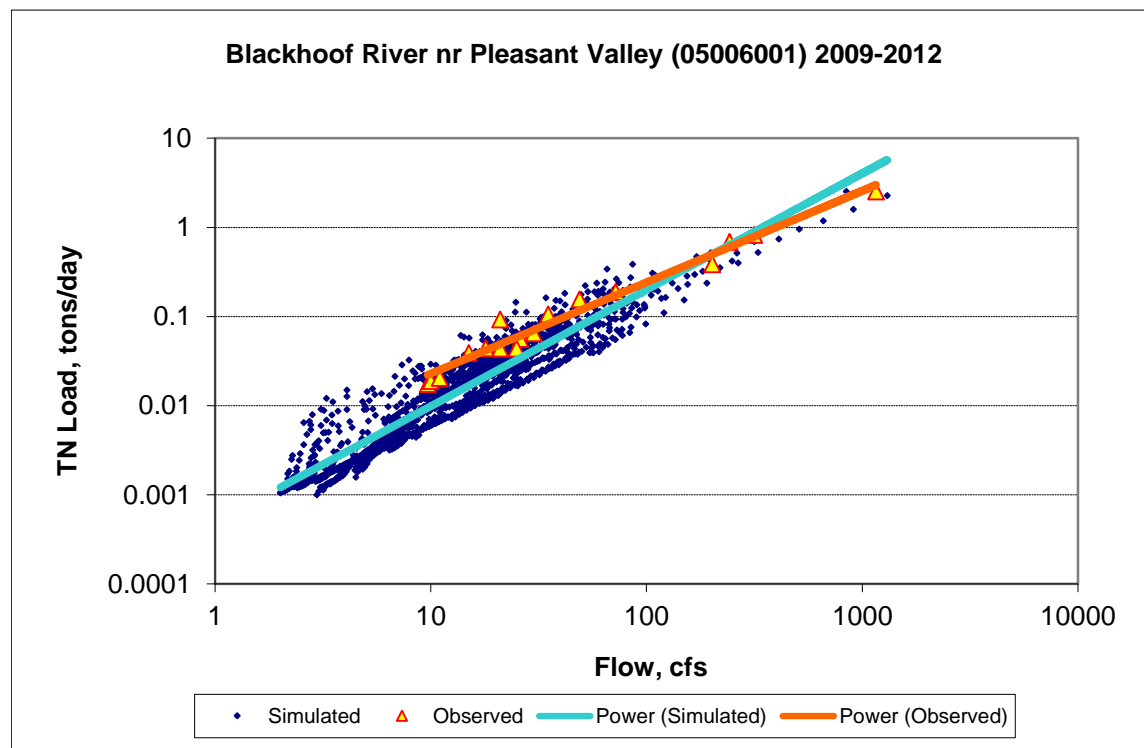
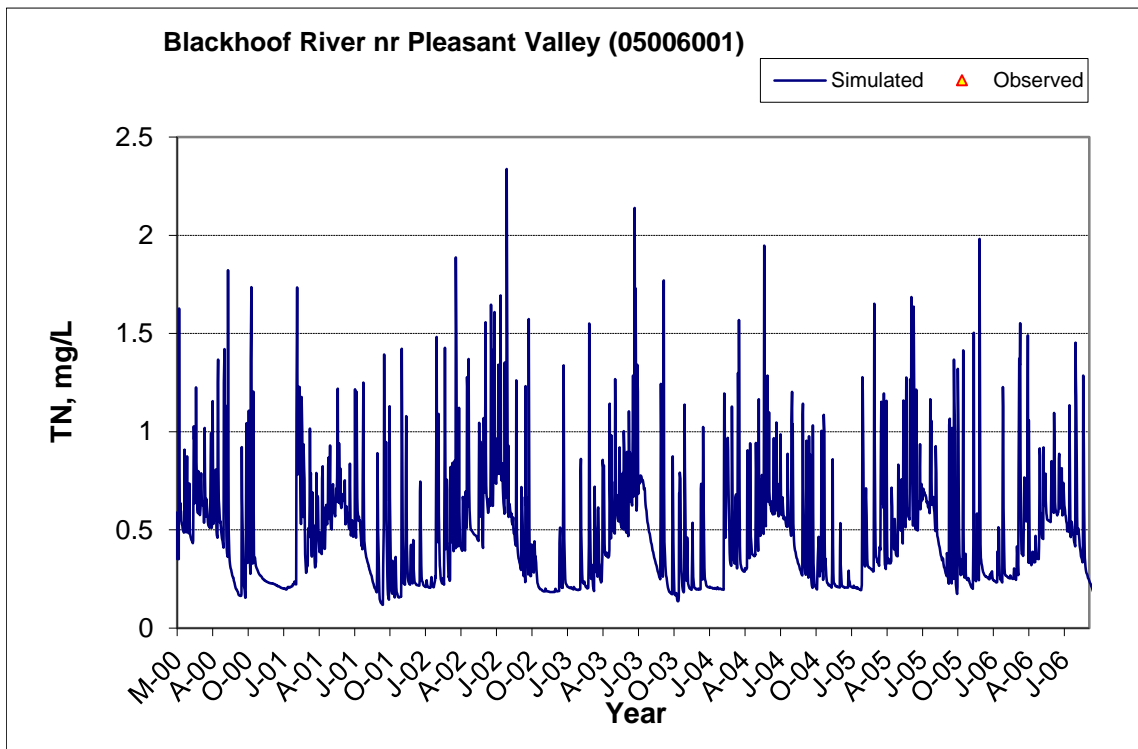
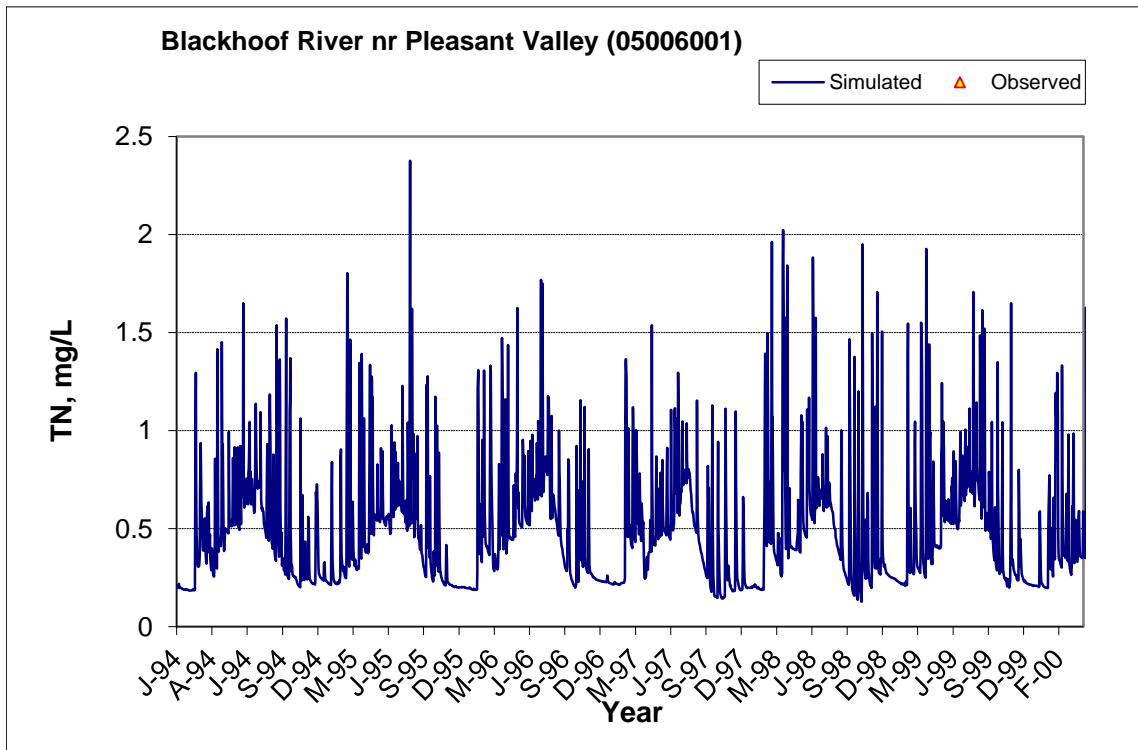


Figure B-89. Power plot of simulated and observed Total Nitrogen (TN) load vs flow at Blackhoof River nr Pleasant Valley (05006001) (calibration period)



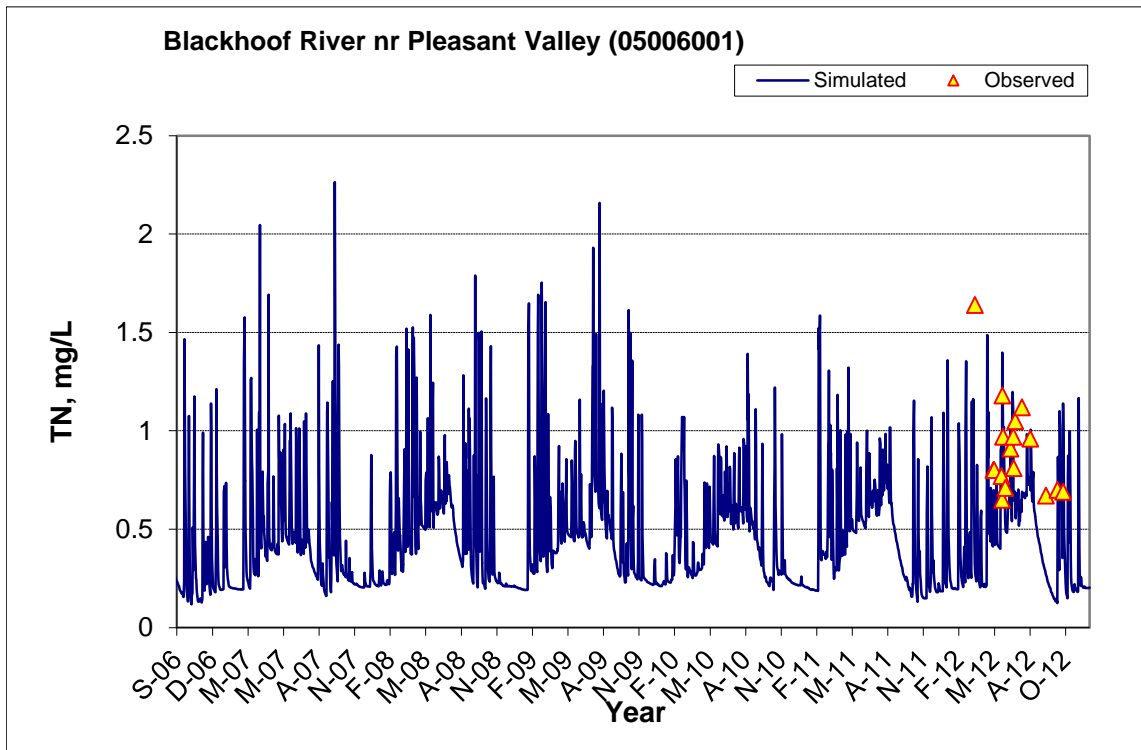


Figure B-90. Time series of observed and simulated Total Nitrogen (TN) concentration at Blackhoof River nr Pleasant Valley (05006001)

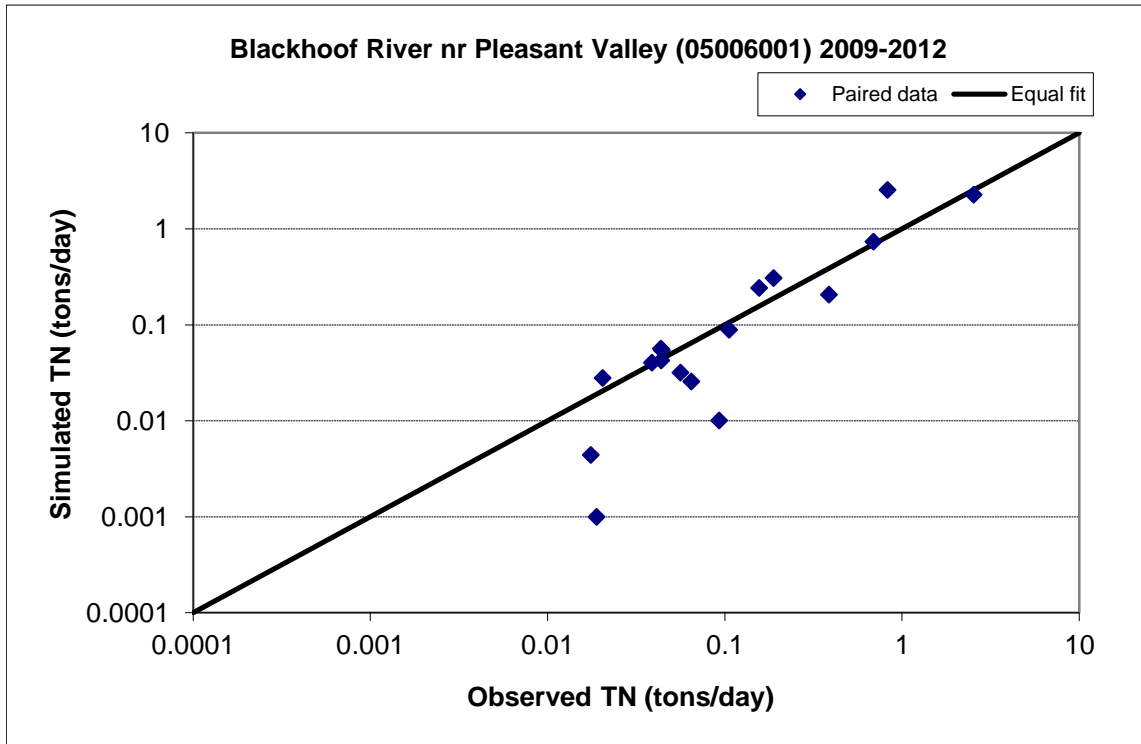


Figure B-91. Paired simulated vs. observed Total Nitrogen (TN) load at Blackhoof River nr Pleasant Valley (05006001) (calibration period)

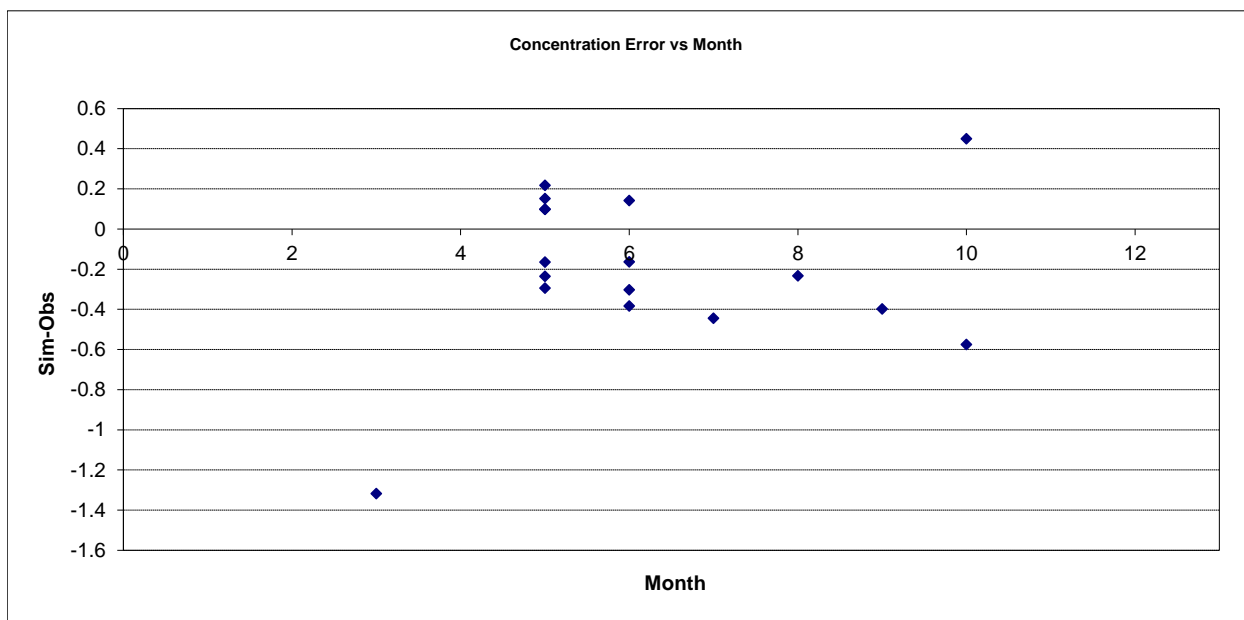


Figure B-92. Residual (Simulated - Observed) vs. Month Total Nitrogen (TN) at Blackhoof River nr Pleasant Valley (05006001)

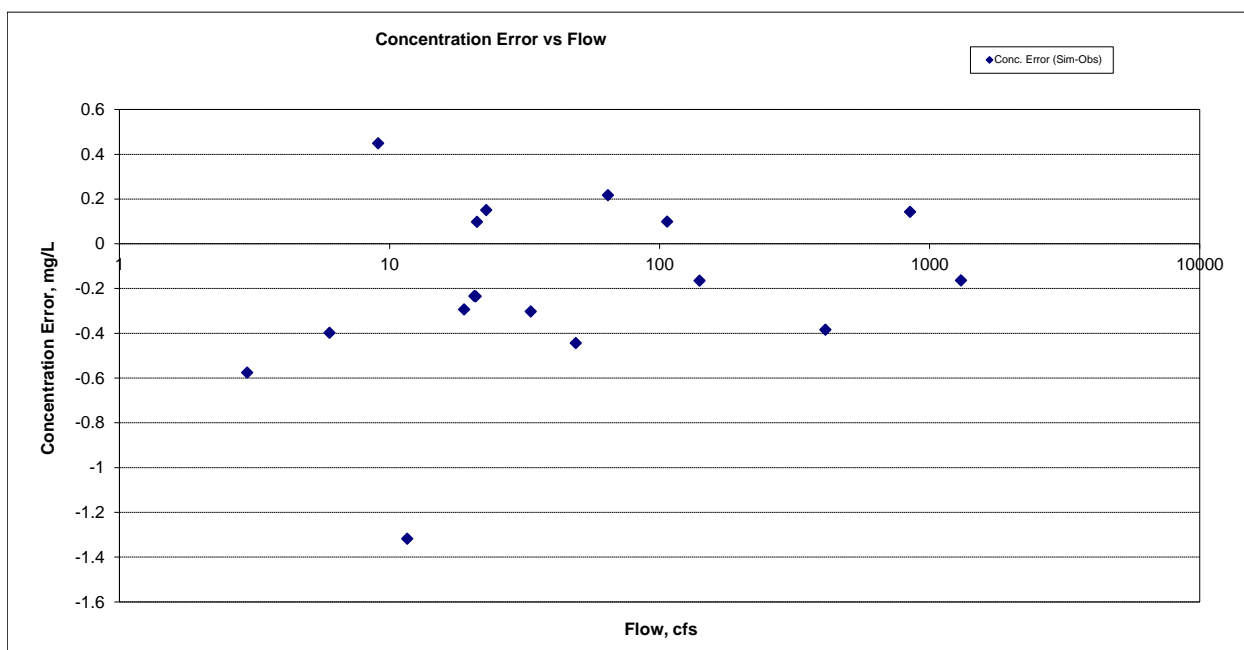


Figure B-93. Residual (Simulated - Observed) vs. Flow Total Nitrogen (TN) at Blackhoof River nr Pleasant Valley (05006001)

B.3.6 Soluble Reactive Phosphorus (SRP)

Table B-16. Soluble Reactive Phosphorus (SRP) statistics

Period	1994-2008	2009-2012
Count	ND	17
Concentration Average Error		-6.87%
Concentration Median Error		7.05%
Load Average Error		72.34%
Load Median Error		0.83%
Paired t conc		0.78
Paired t load		0.25

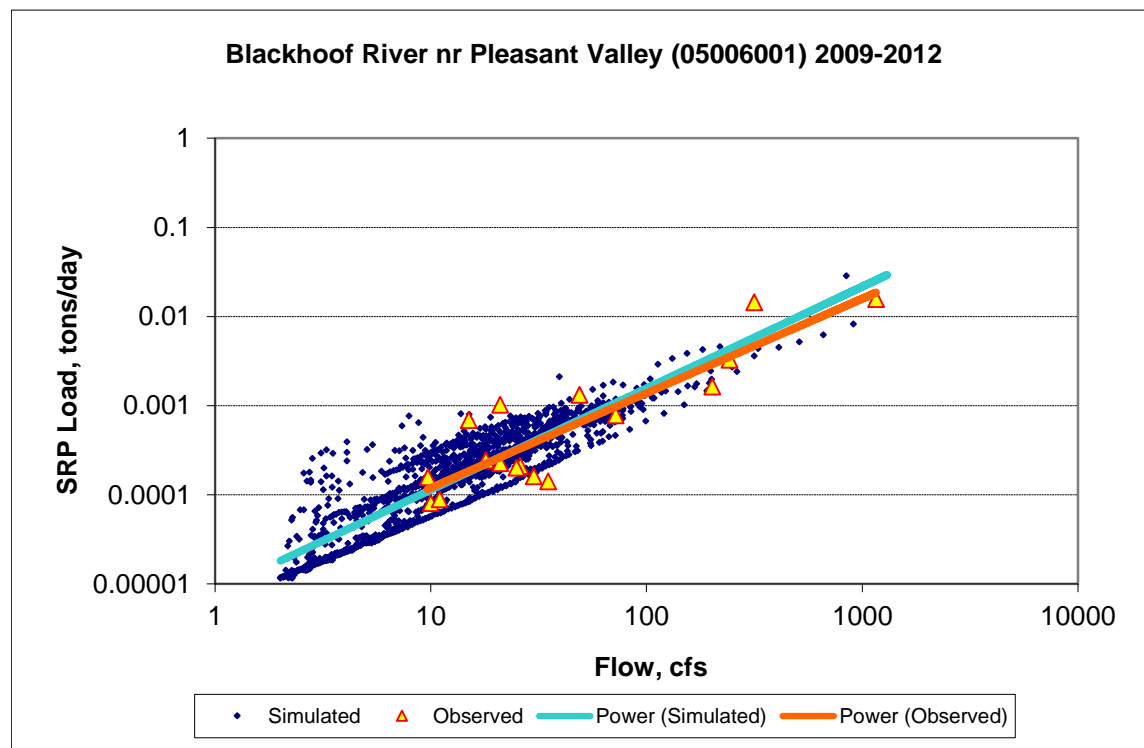
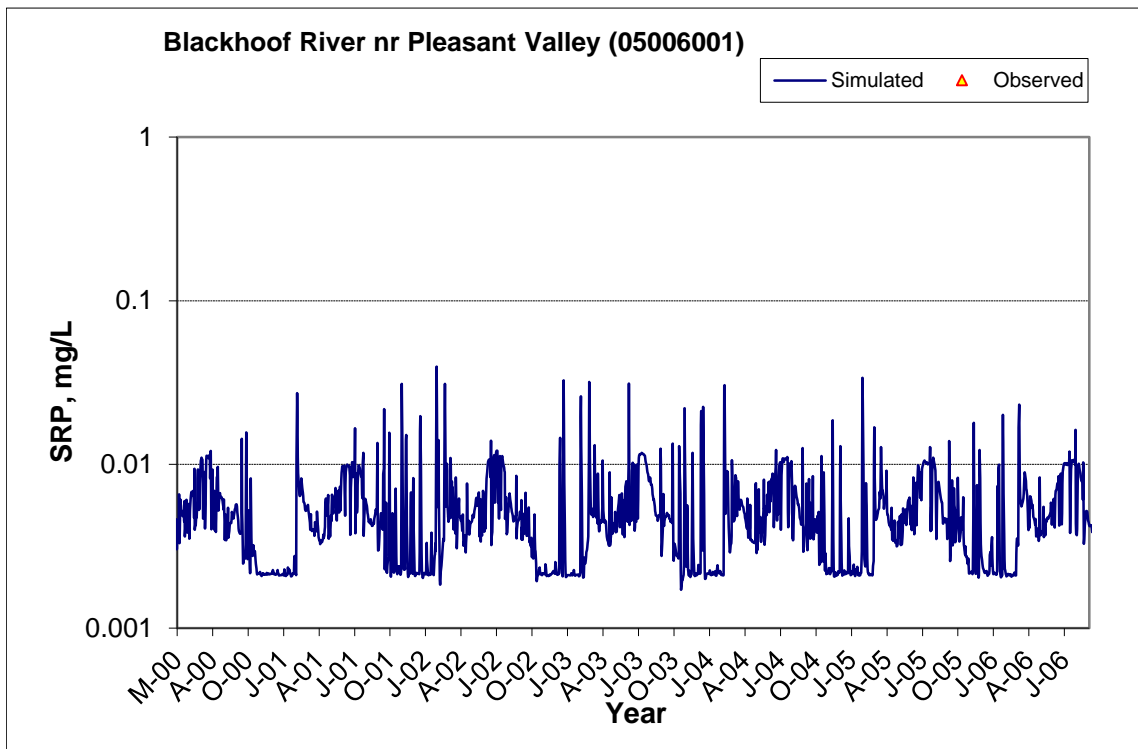
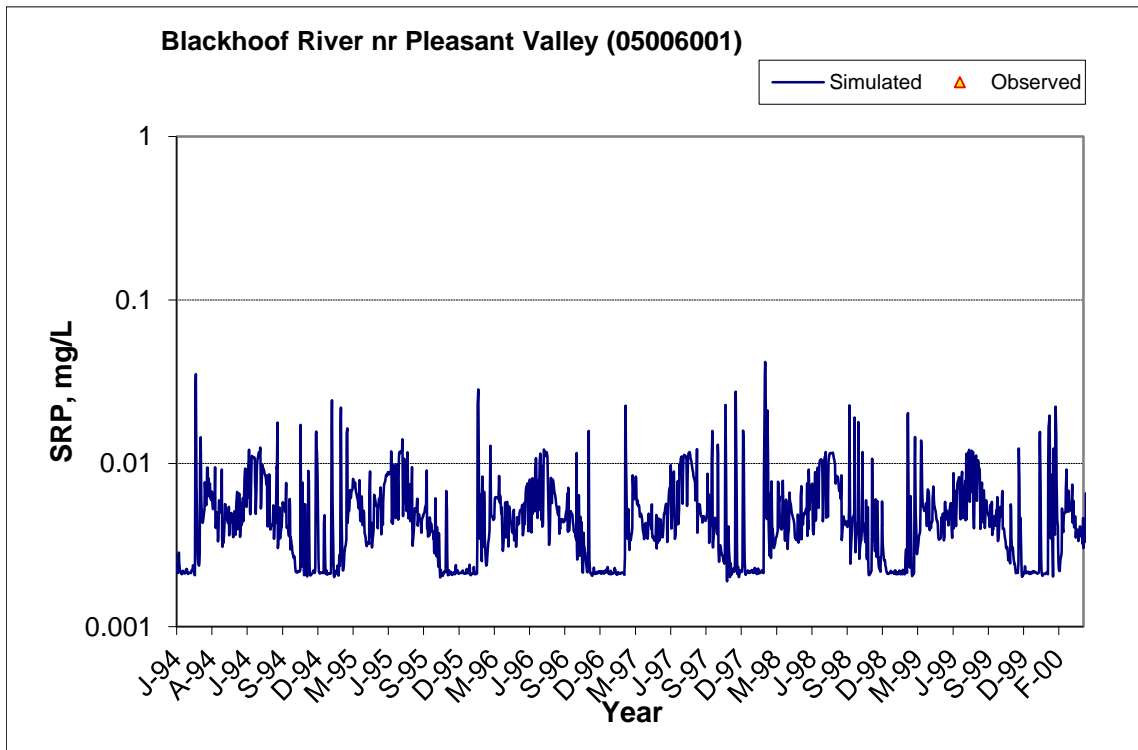


Figure B-94. Power plot of simulated and observed Soluble Reactive Phosphorus (SRP) load vs flow at Blackhoof River nr Pleasant Valley (05006001) (calibration period)



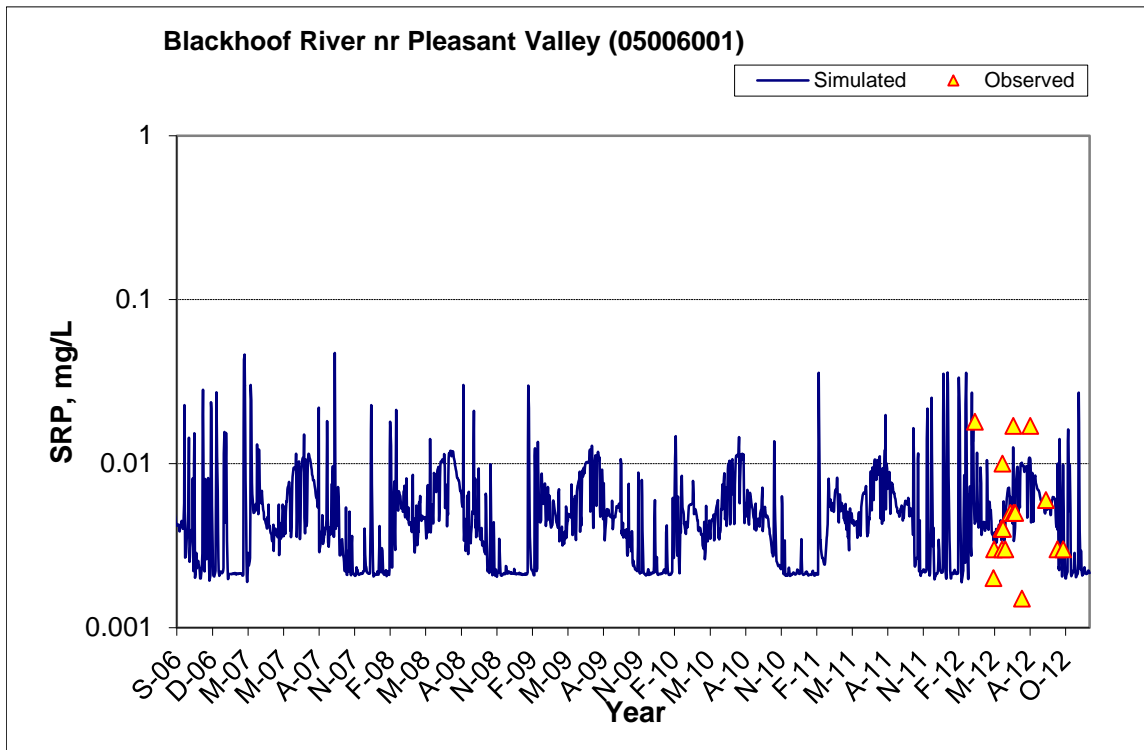


Figure B-95. Time series of observed and simulated Soluble Reactive Phosphorus (SRP) concentration at Blackhoof River nr Pleasant Valley (05006001)

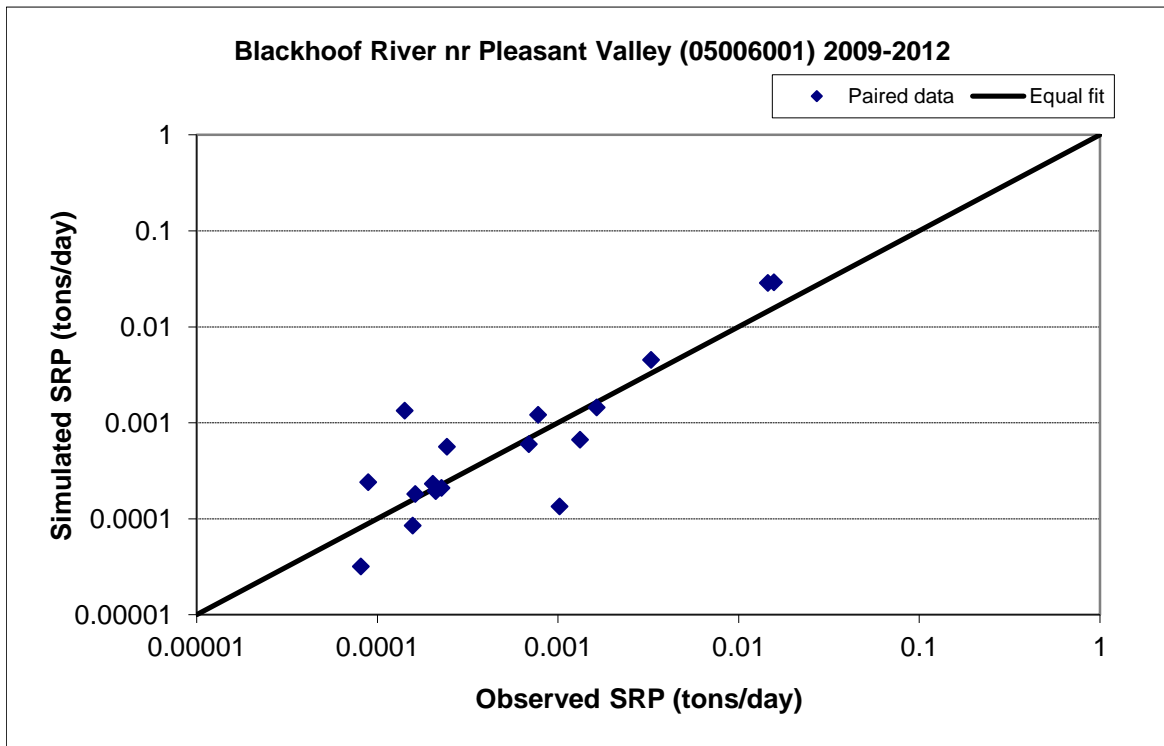


Figure B-96. Paired simulated vs. observed Soluble Reactive Phosphorus (SRP) load at Blackhoof River nr Pleasant Valley (05006001) (calibration period)



Figure B-97. Residual (Simulated - Observed) vs. Month Soluble Reactive Phosphorus (SRP) at Blackhoof River nr Pleasant Valley (05006001)

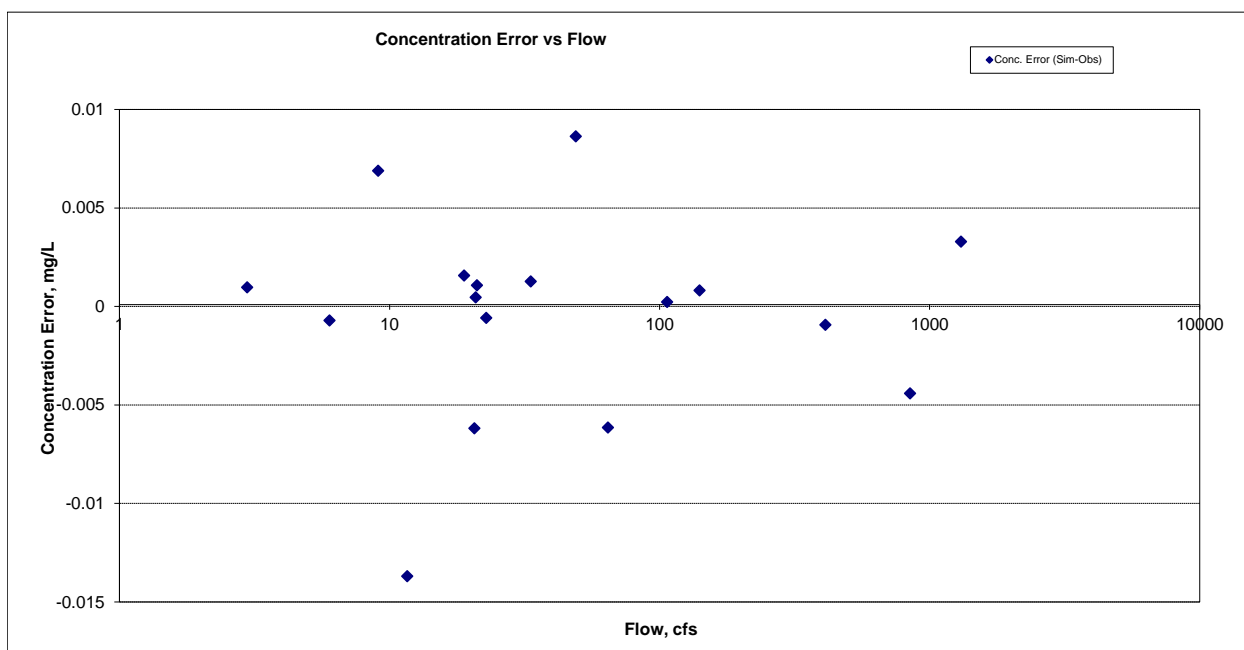
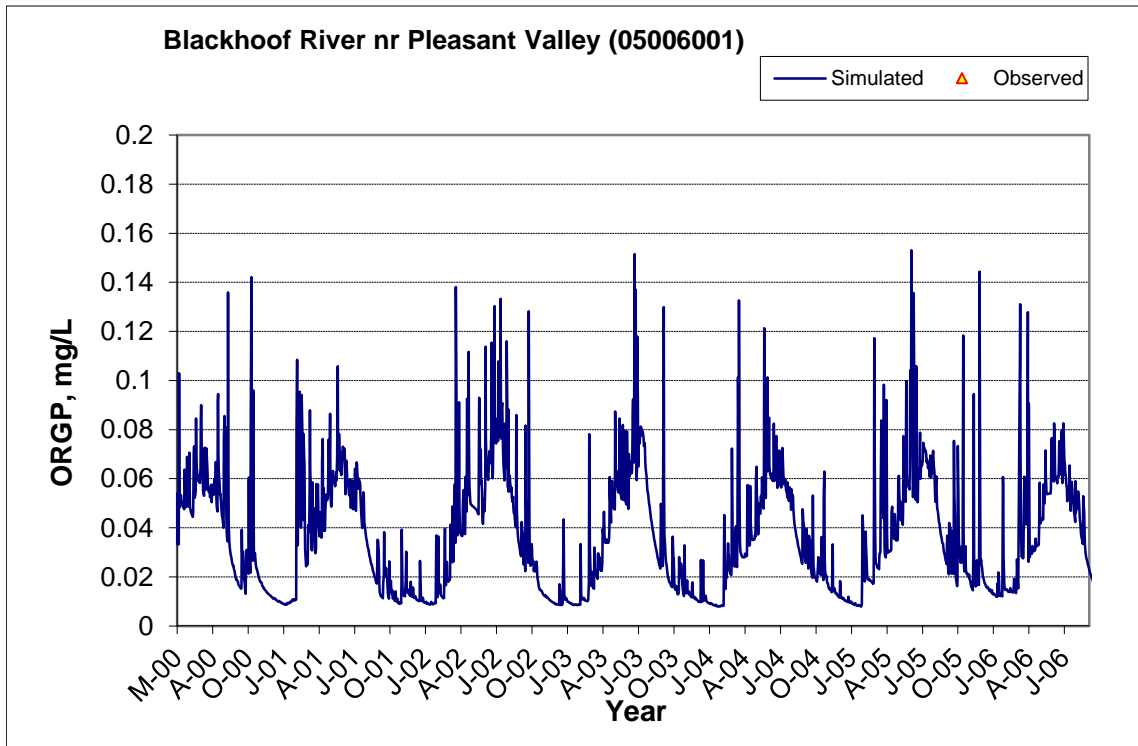
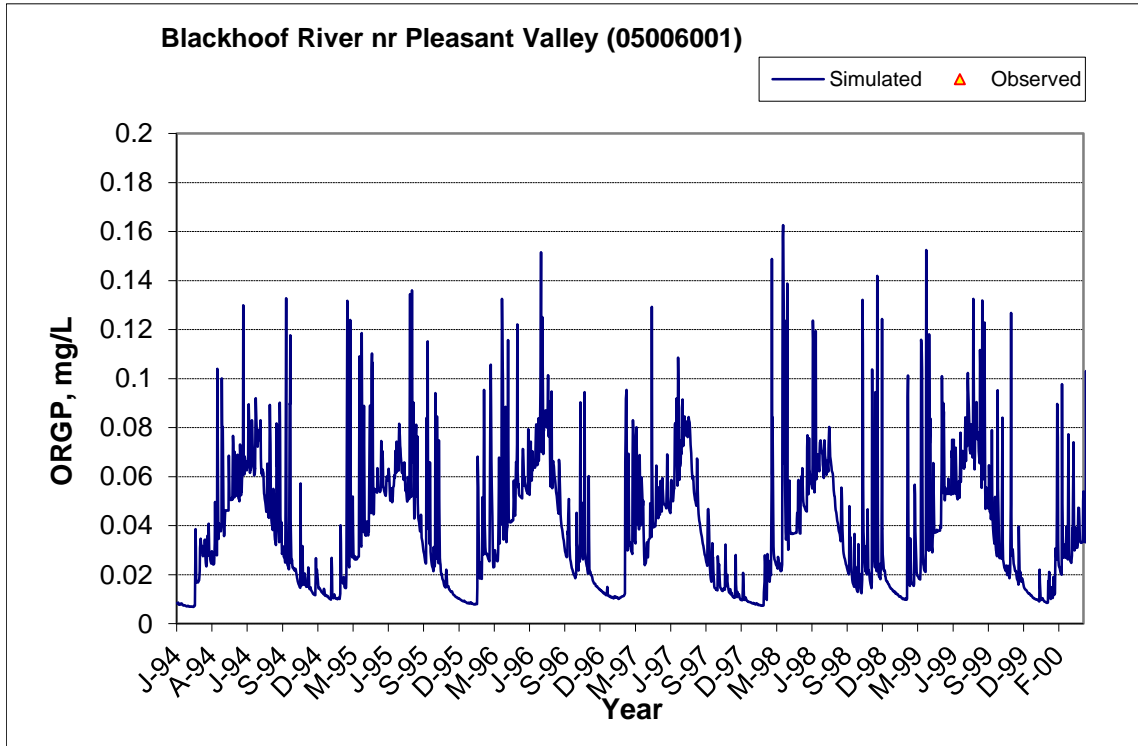


Figure B-98. Residual (Simulated - Observed) vs. Flow Soluble Reactive Phosphorus (SRP) at Blackhoof River nr Pleasant Valley (05006001)

B.3.7 Organic Phosphorus (OrgP)



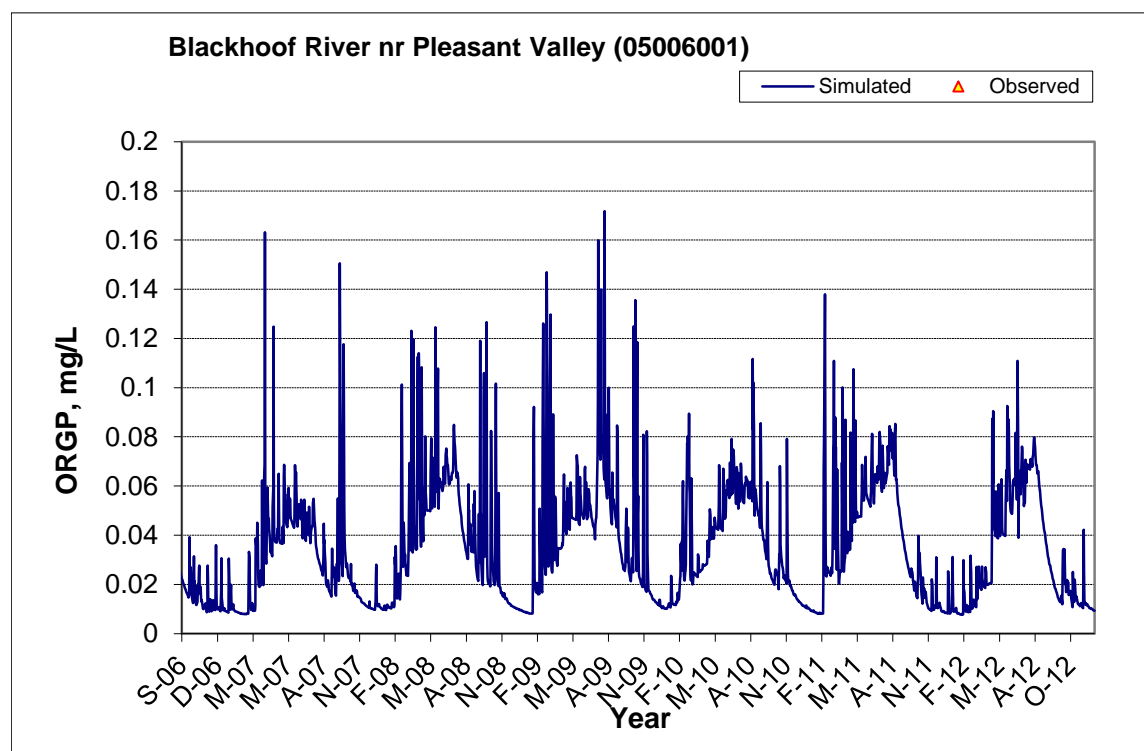


Figure B-99. Time series of observed and simulated Organic Phosphorus (OrgP) concentration at Blackhoof River nr Pleasant Valley (05006001)

B.3.8 Total Phosphorus (TP)

Table B-17. Total Phosphorus (TP) statistics

Period	1994-2008	2009-2012
Count	ND	17
Concentration Average Error		41.06%
Concentration Median Error		53.49%
Load Average Error		85.96%
Load Median Error		19.65%
Paired t conc		0.09
Paired t load		0.18

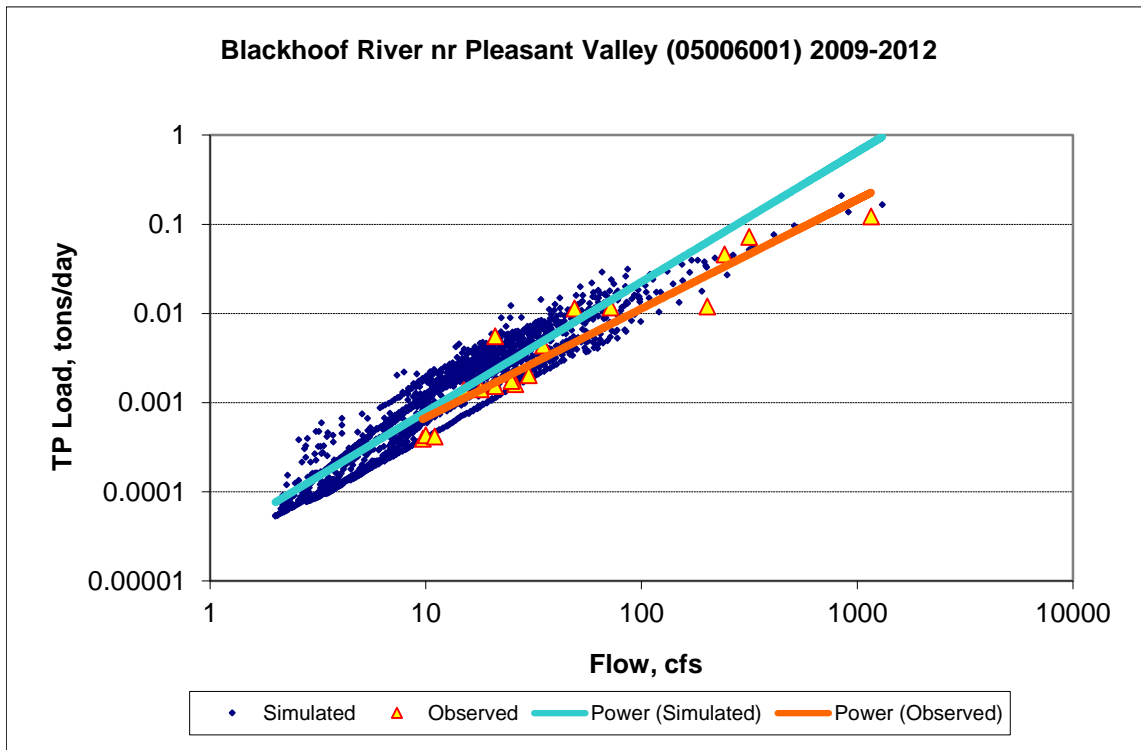
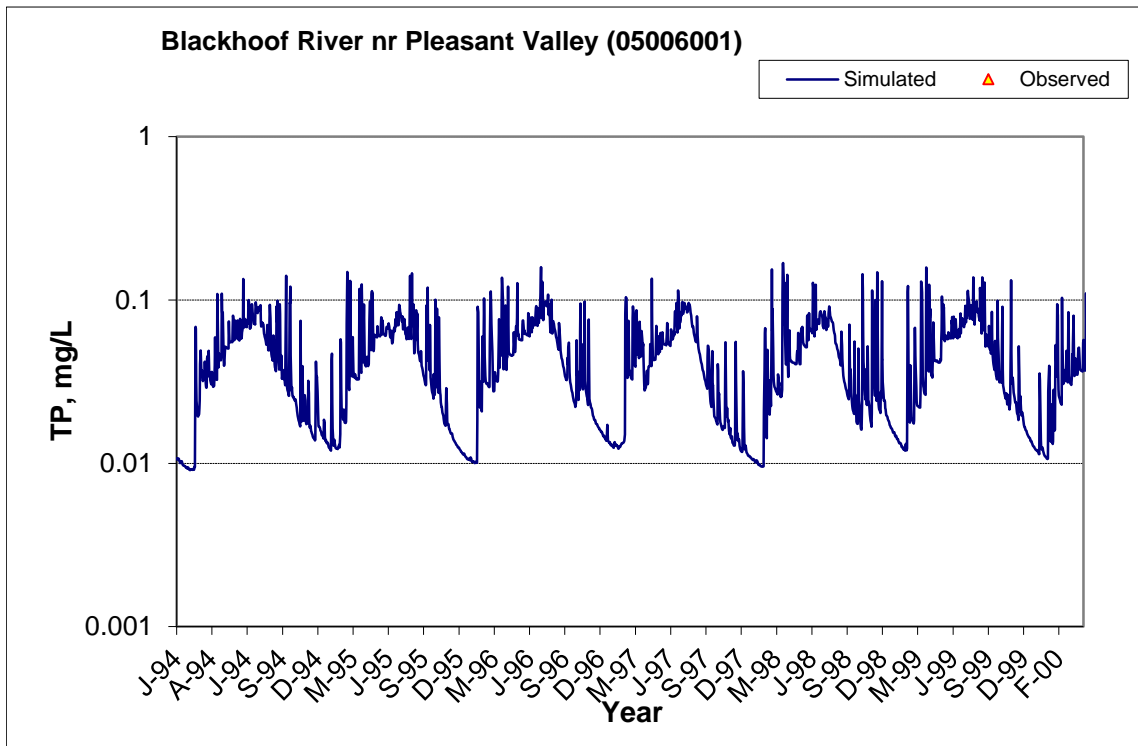


Figure B-100. Power plot of simulated and observed Total Phosphorus (TP) load vs flow at Blackhoof River nr Pleasant Valley (05006001) (calibration period)



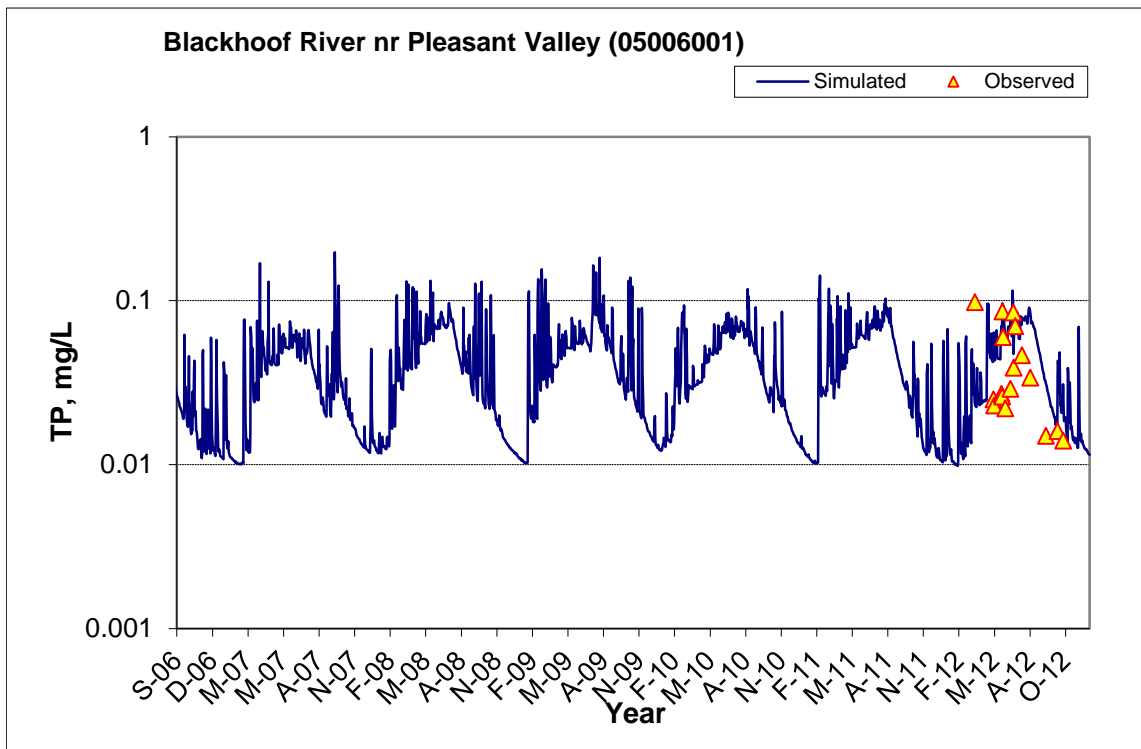
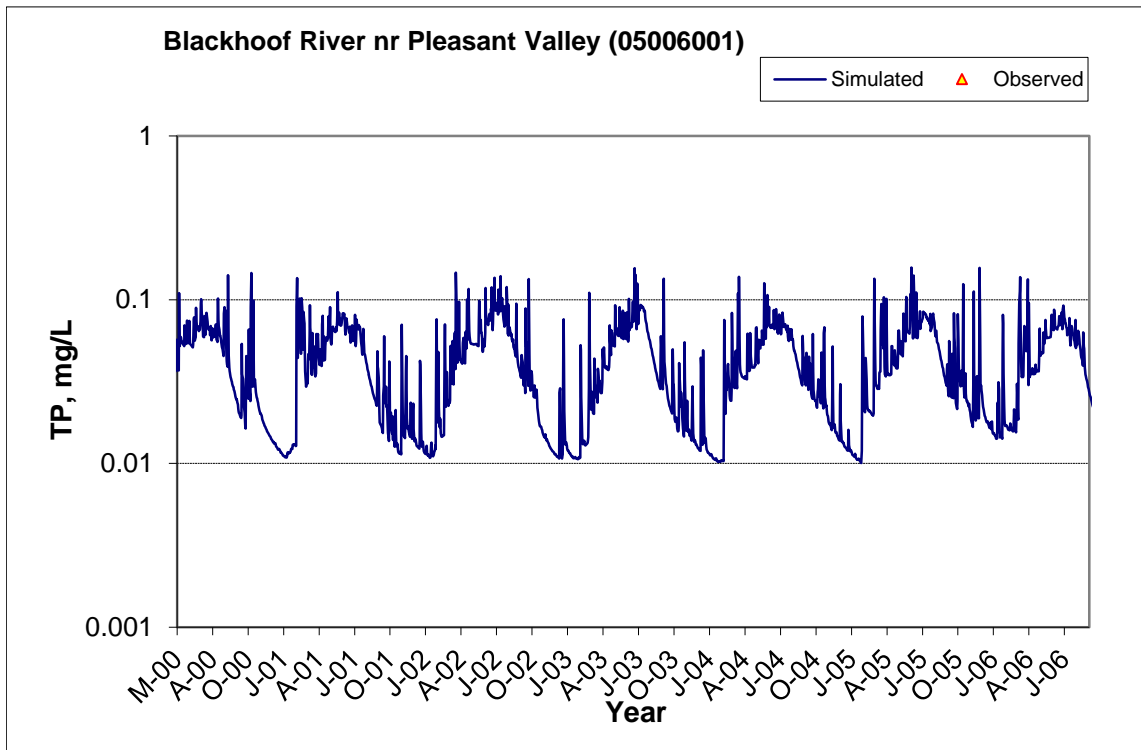


Figure B-101. Time series of observed and simulated Total Phosphorus (TP) concentration at Blackhoof River nr Pleasant Valley (05006001)

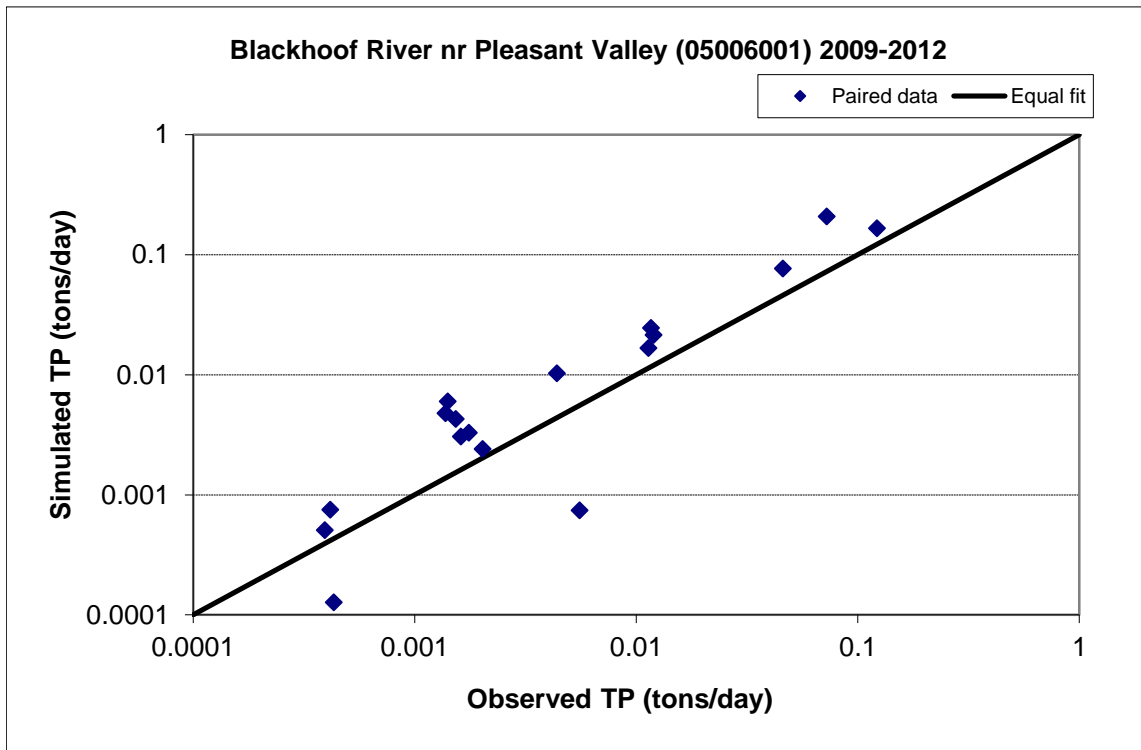


Figure B-102. Paired simulated vs. observed Total Phosphorus (TP) load at Blackhoof River nr Pleasant Valley (05006001) (calibration period)

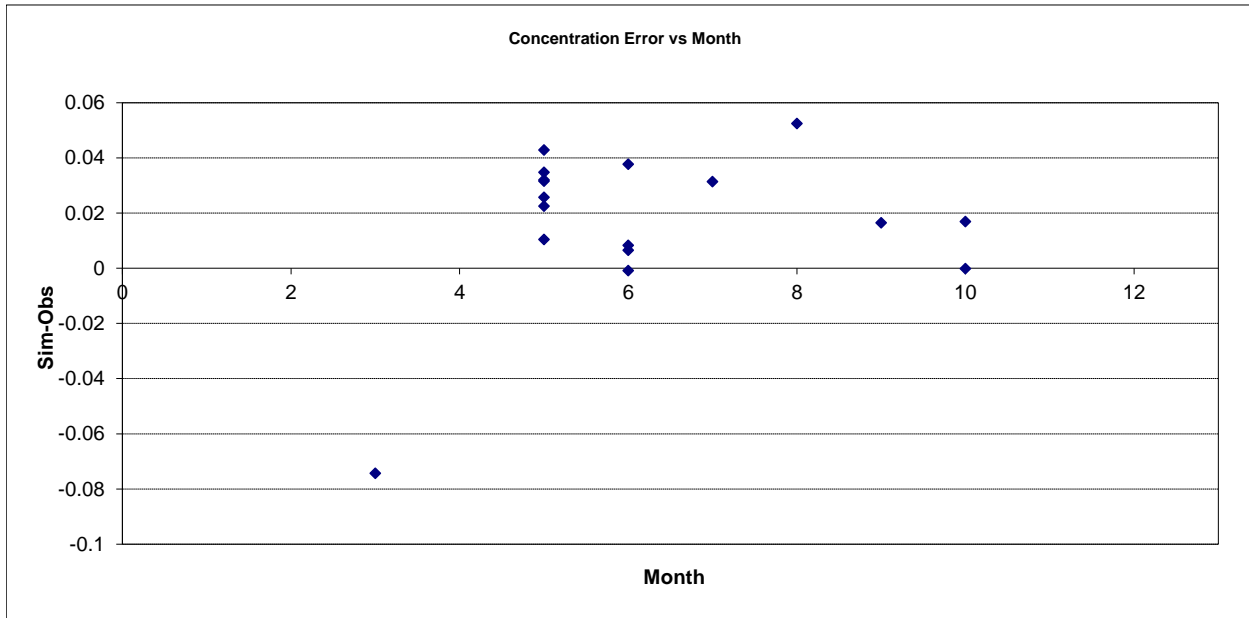


Figure B-103. Residual (Simulated - Observed) vs. Month Total Phosphorus (TP) at Blackhoof River nr Pleasant Valley (05006001)

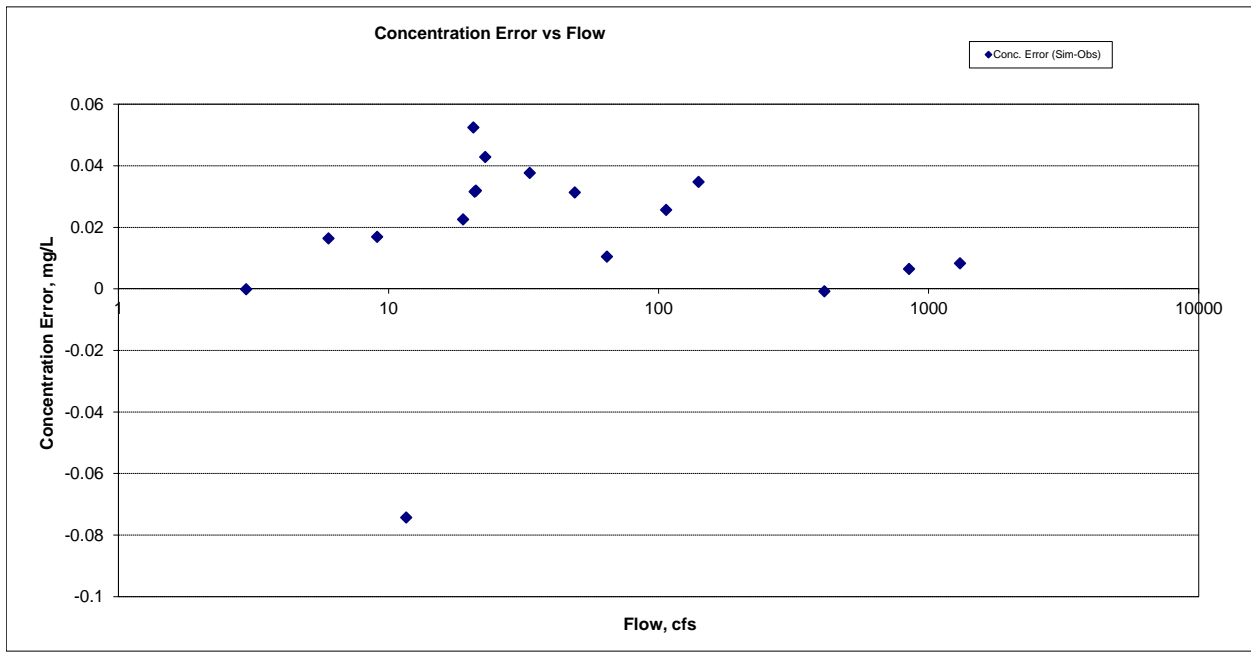
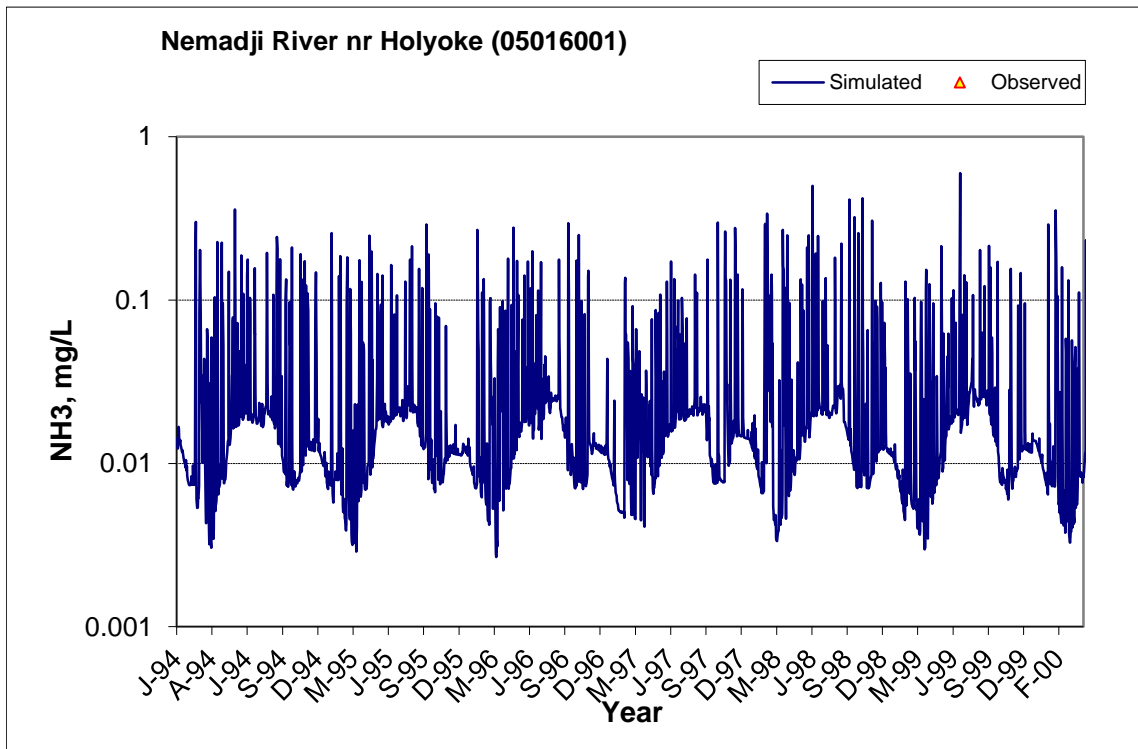


Figure B-104. Residual (Simulated - Observed) vs. Flow Total Phosphorus (TP) at Blackhoof River nr Pleasant Valley (05006001)

B.4 NEMADJI RIVER NR HOLYOKE (05016001)

B.4.1 Ammonia Nitrogen (NH3)



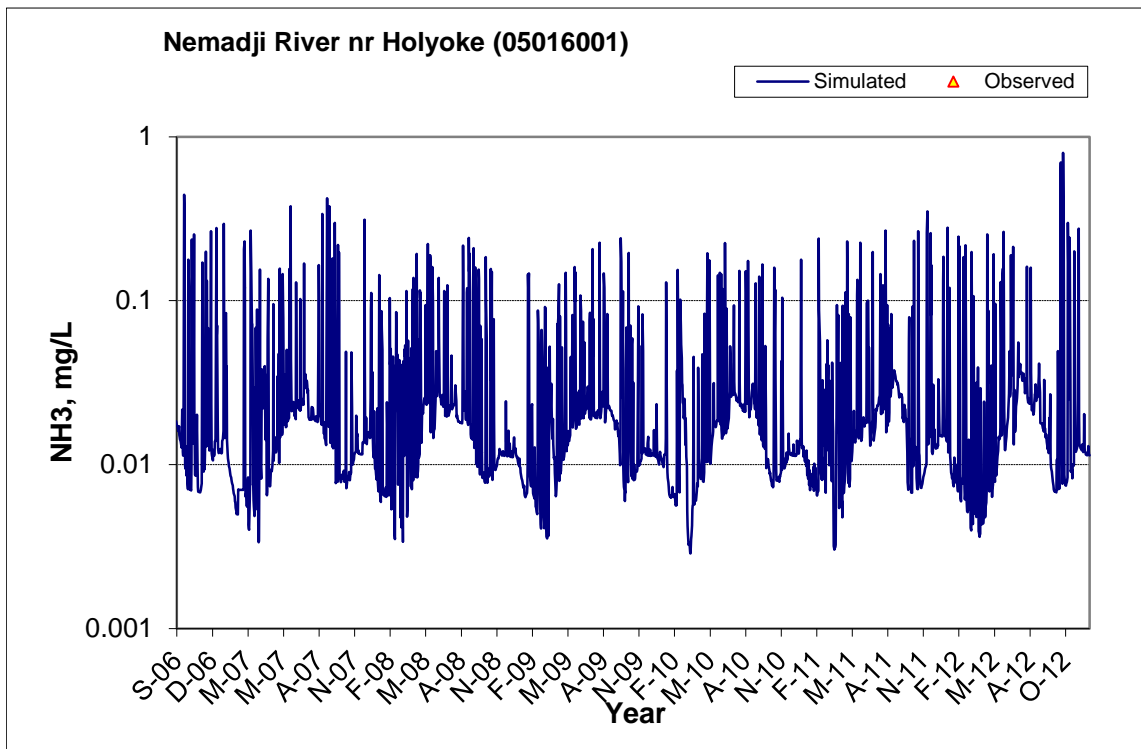
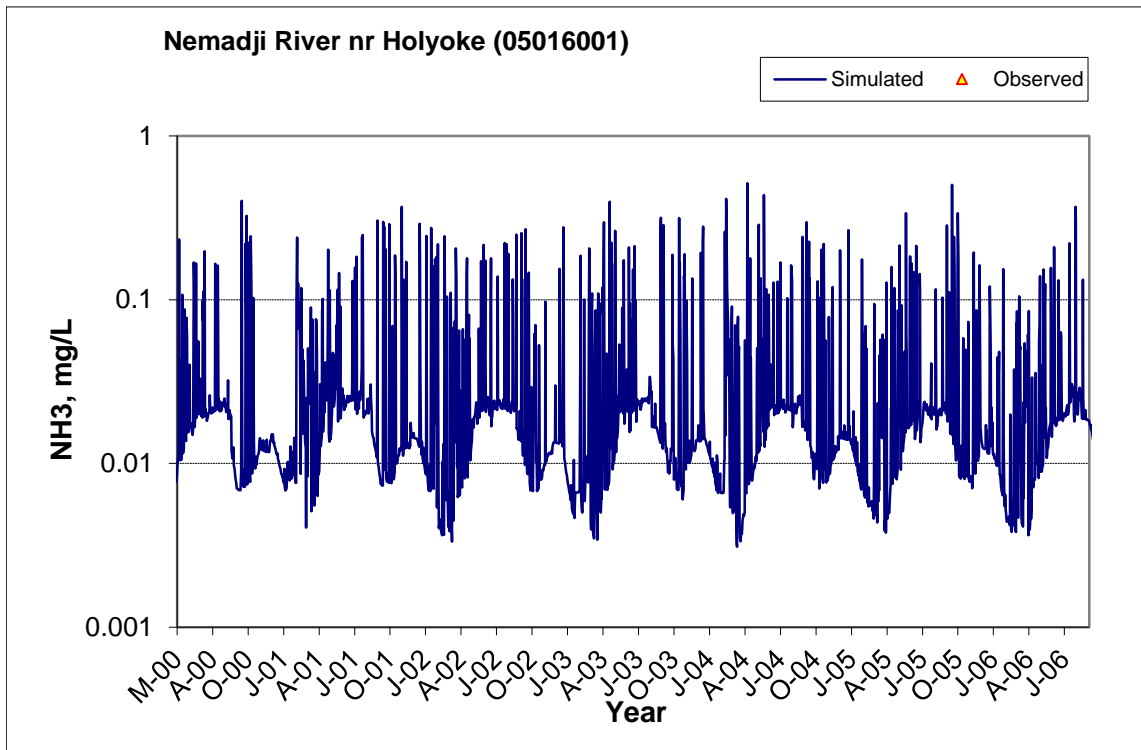
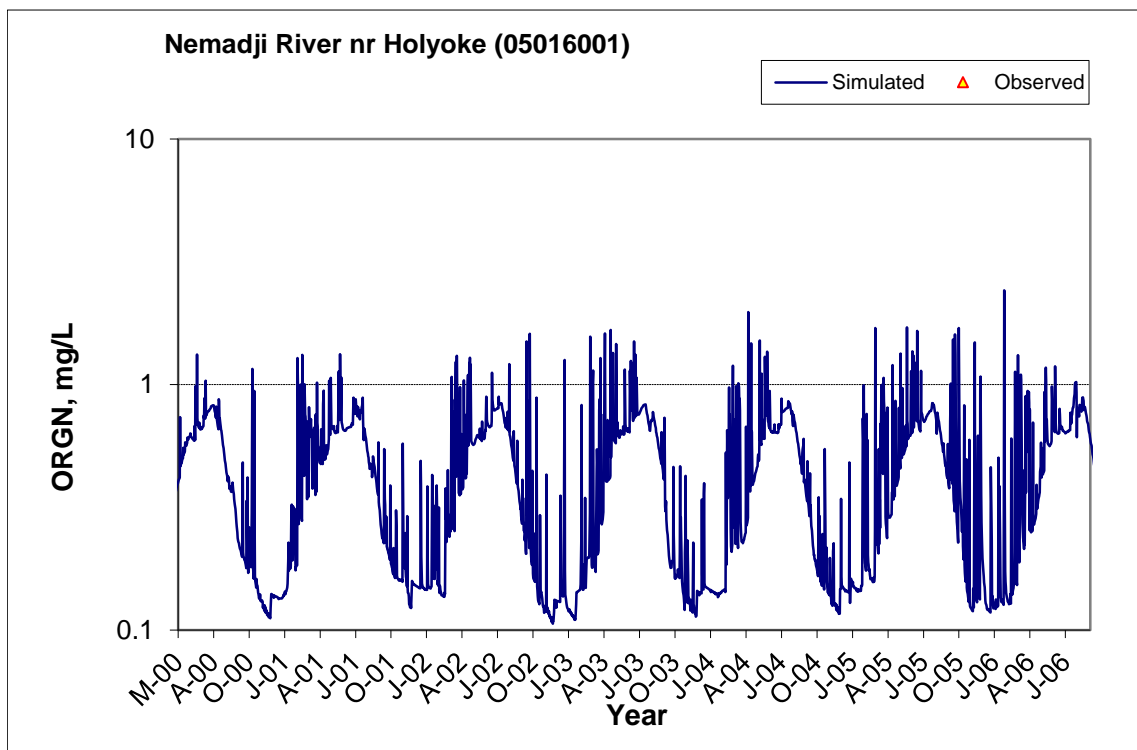
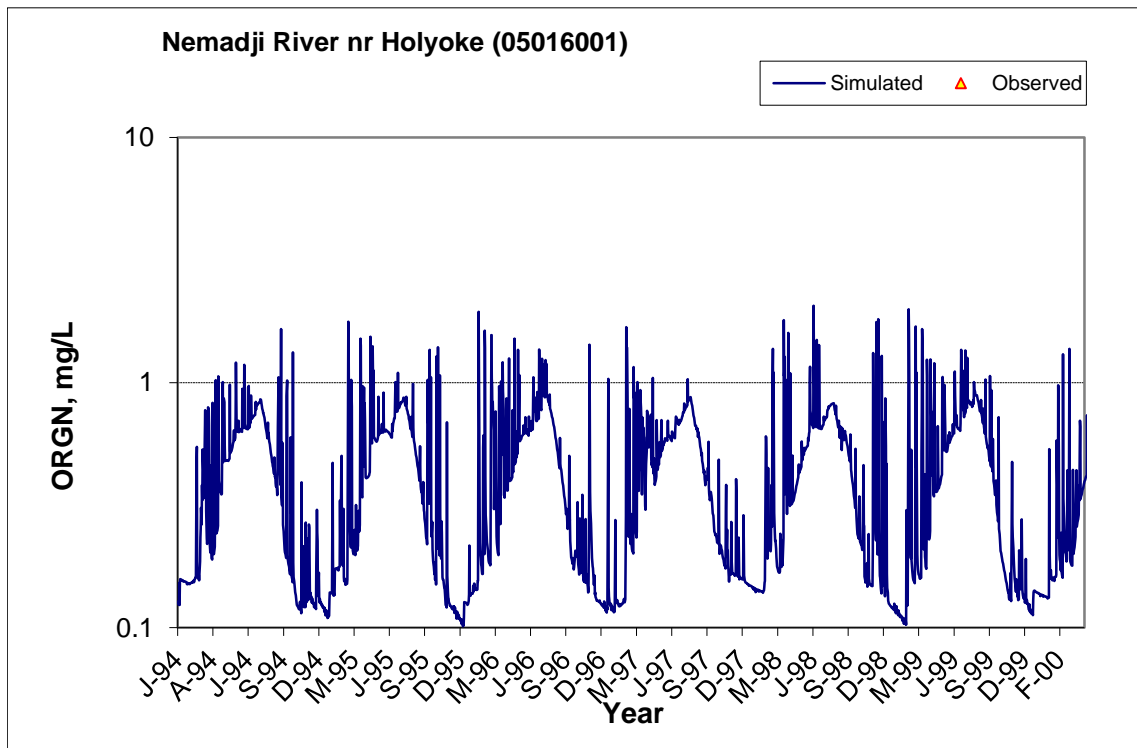


Figure B-105. Time series of observed and simulated Ammonia Nitrogen (NH₃) concentration at Nemadji River nr Holyoke (05016001)

B.4.2 Organic Nitrogen (OrgN)



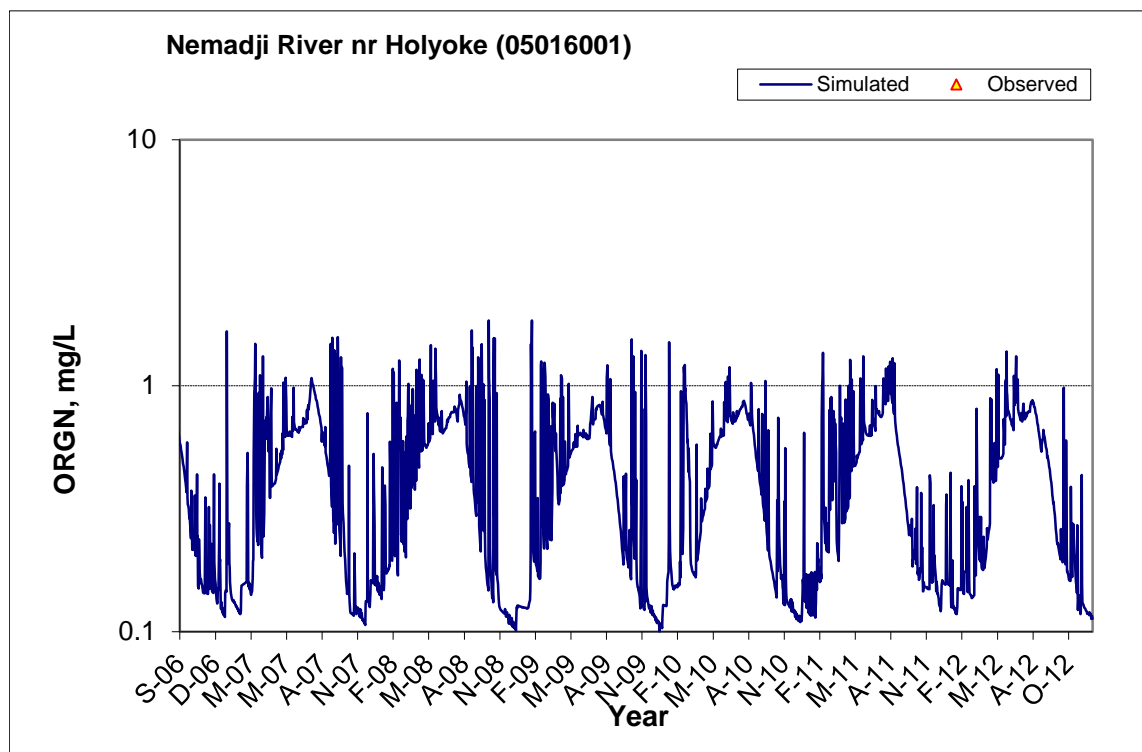


Figure B-106. Time series of observed and simulated Organic Nitrogen (OrgN) concentration at Nemadji River nr Holyoke (05016001)

B.4.3 Total Kjeldahl Nitrogen (TKN)

Table B-18. Total Kjeldahl Nitrogen (TKN) statistics

Period	1994-1993	1994-2012
Count	ND	15
Concentration Average Error		-3.76%
Concentration Median Error		-10.92%
Load Average Error		2.04%
Load Median Error		-6.02%
Paired t conc		0.94
Paired t load		0.64

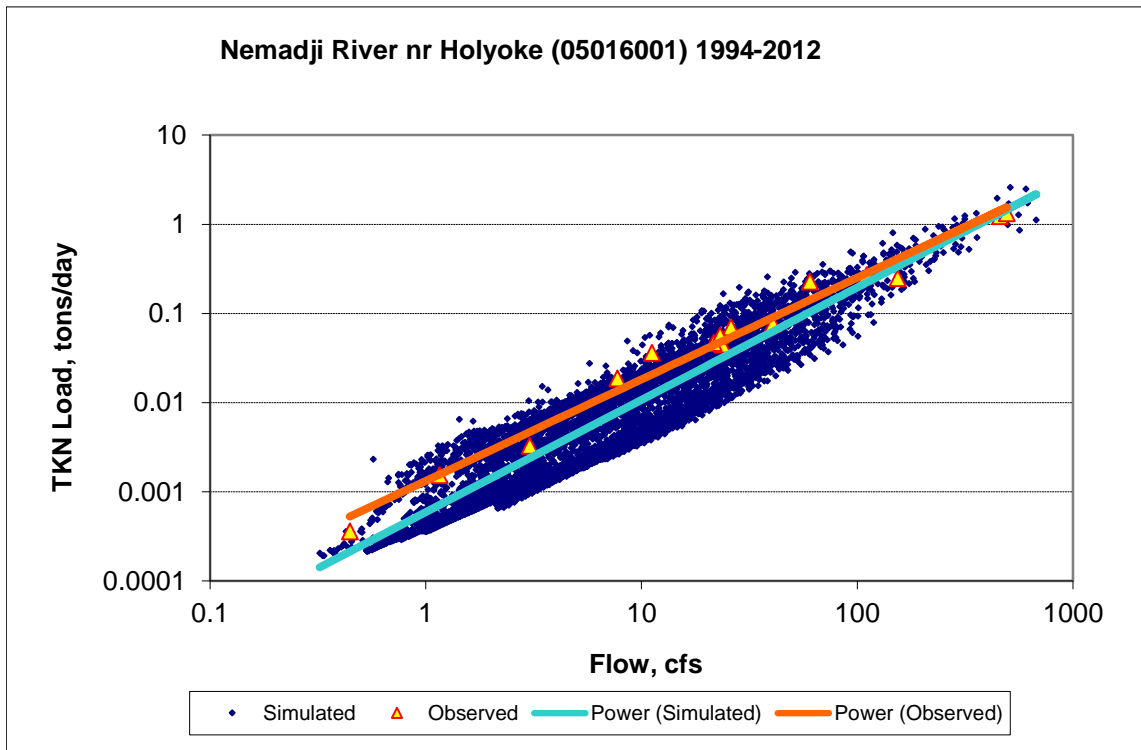
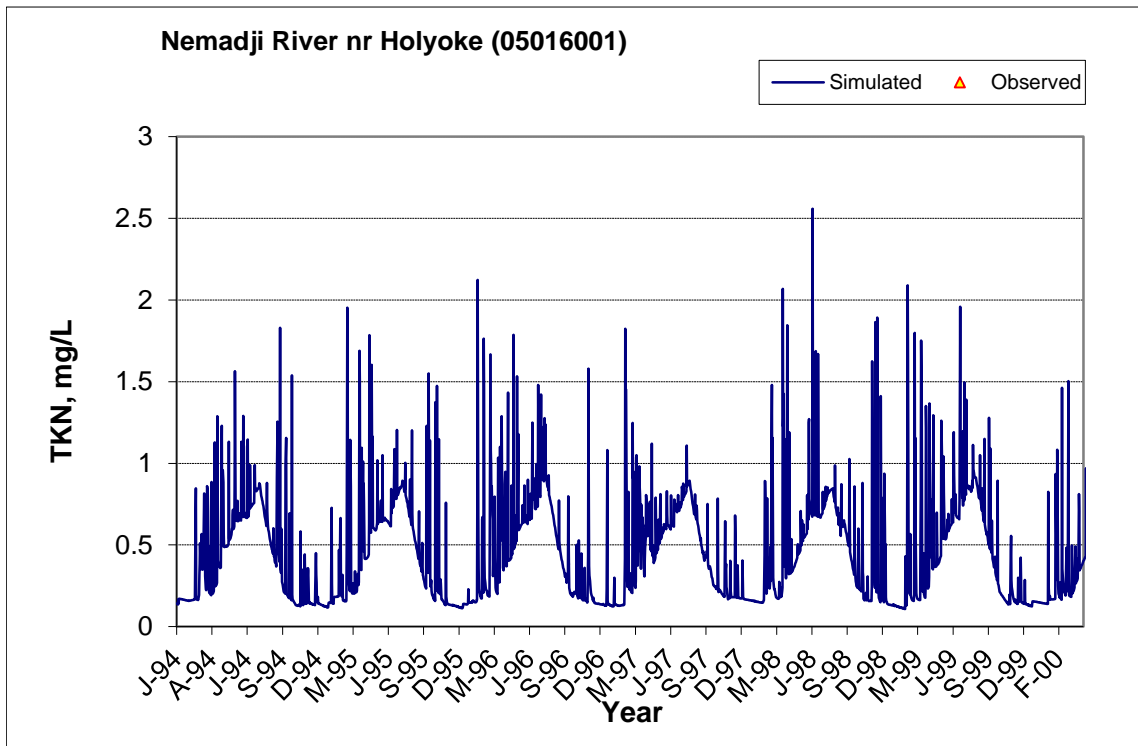


Figure B-107. Power plot of simulated and observed Total Kjeldahl Nitrogen (TKN) load vs flow at Nemadji River nr Holyoke (05016001) (calibration period)



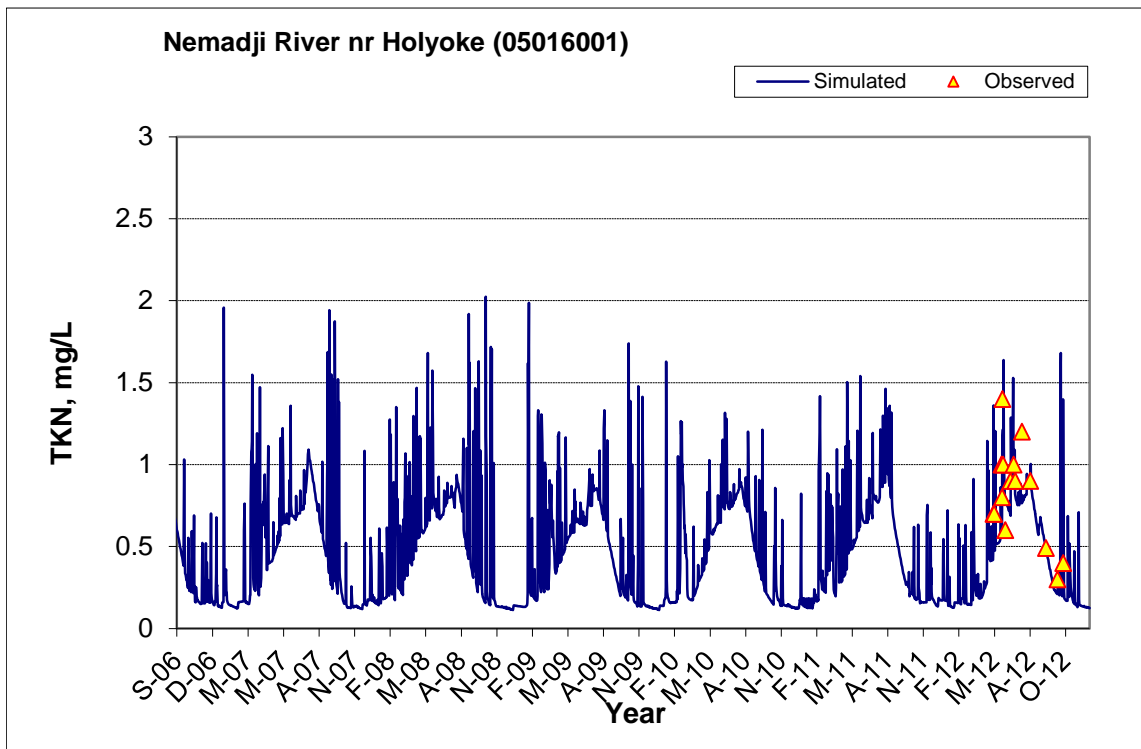
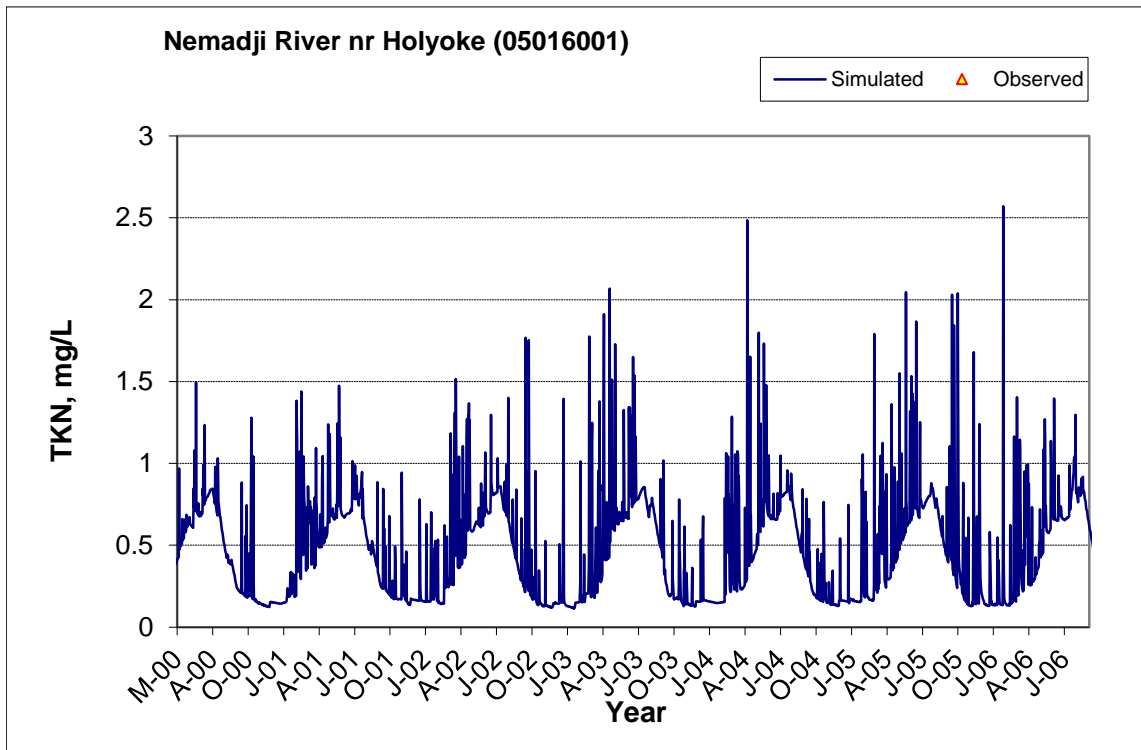


Figure B-108. Time series of observed and simulated Total Kjeldahl Nitrogen (TKN) concentration at Nemadji River nr Holyoke (05016001)

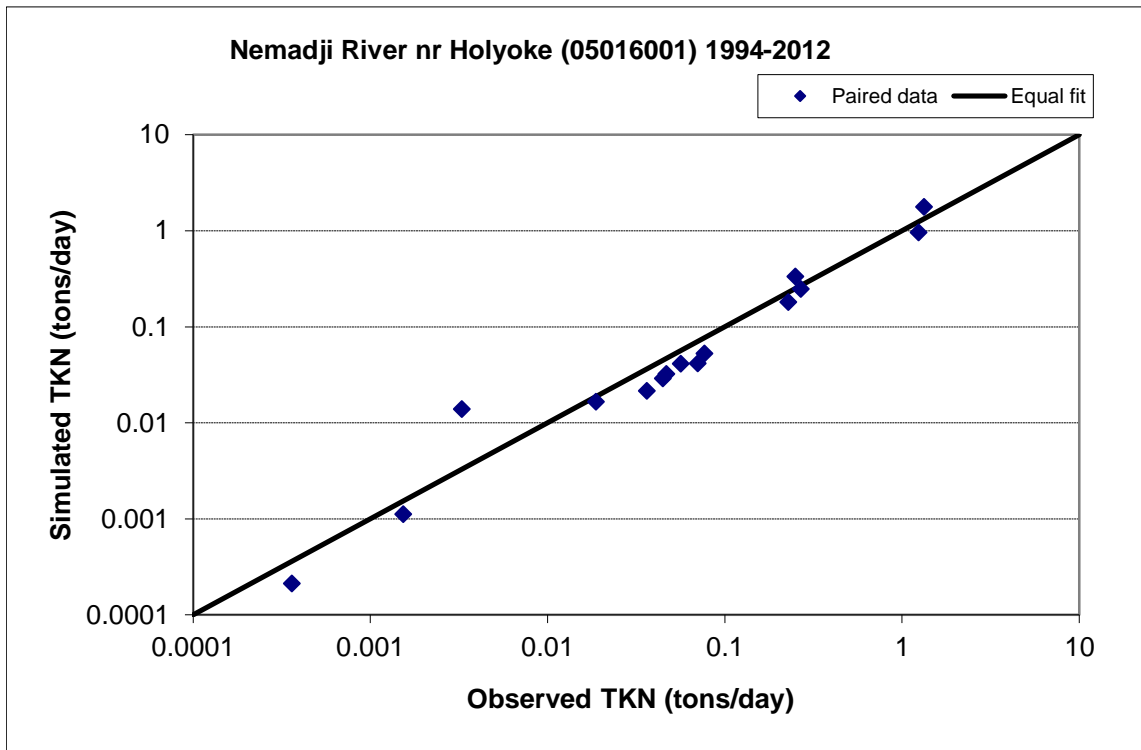


Figure B-109. Paired simulated vs. observed Total Kjeldahl Nitrogen (TKN) load at Nemadji River nr Holyoke (05016001) (calibration period)

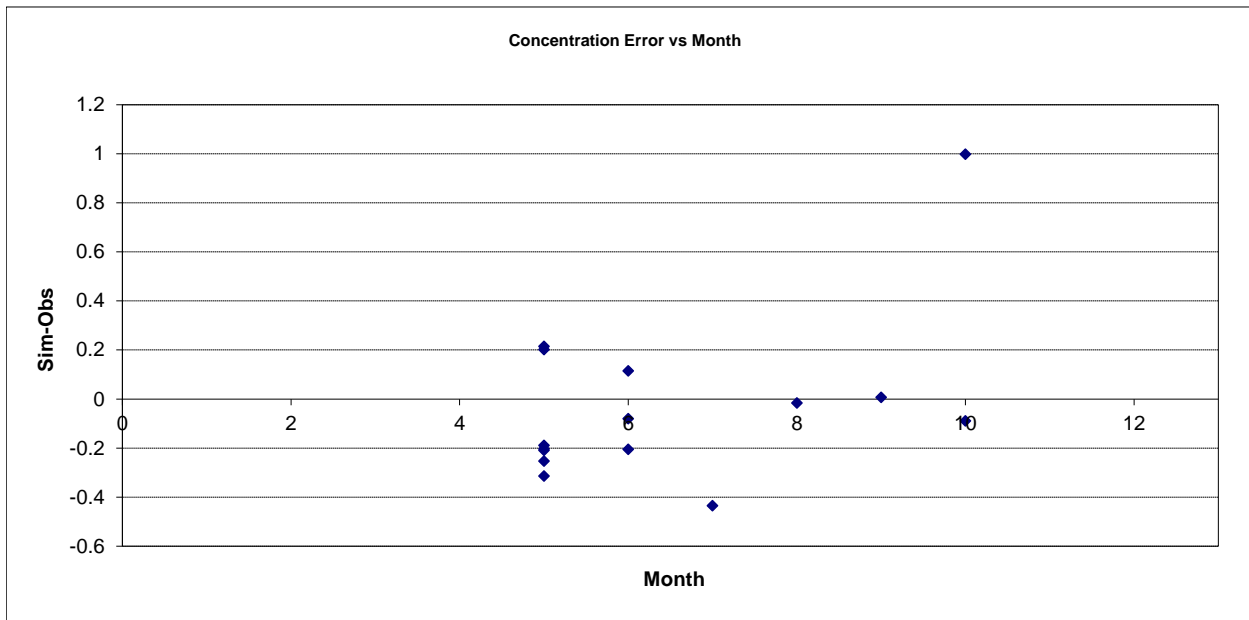


Figure B-110. Residual (Simulated - Observed) vs. Month Total Kjeldahl Nitrogen (TKN) at Nemadji River nr Holyoke (05016001)

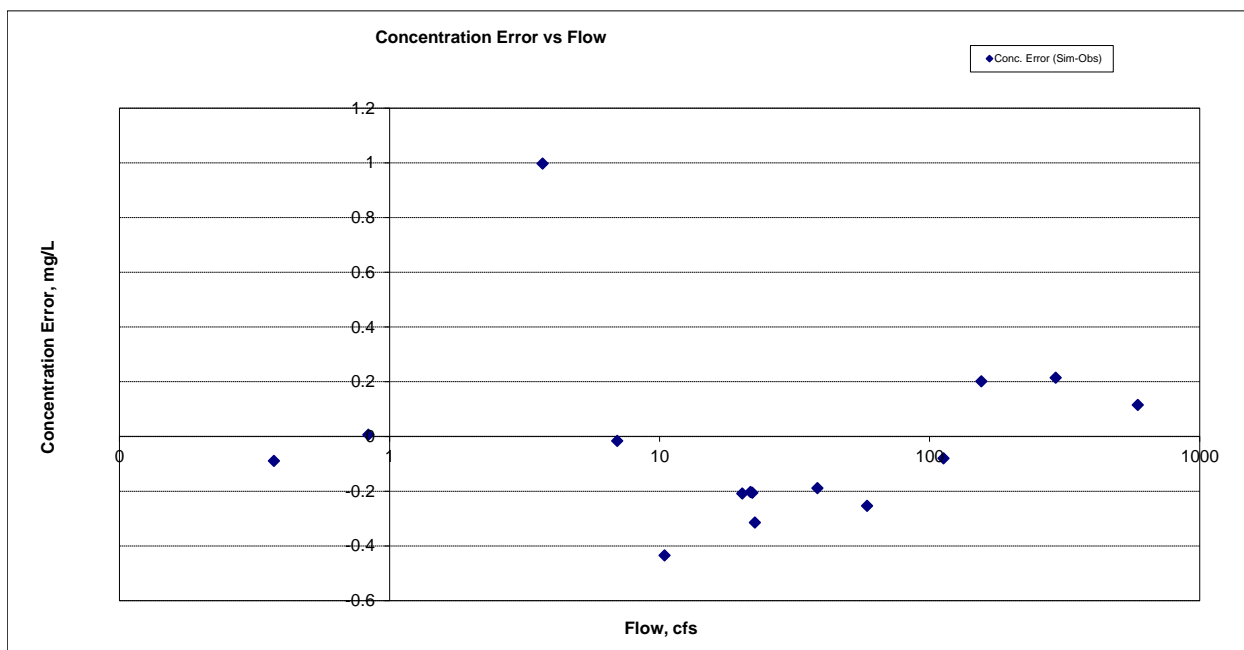


Figure B-111. Residual (Simulated - Observed) vs. Flow Total Kjeldahl Nitrogen (TKN) at Nemadji River nr Holyoke (05016001)

B.4.4 Nitrite+ Nitrate Nitrogen (NOx)

Table B-19. Nitrite+ Nitrate Nitrogen (NOx) statistics

Period	1994-1993	1994-2012
Count	ND	15
Concentration Average Error		437.85%
Concentration Median Error		71.51%
Load Average Error		244.77%
Load Median Error		20.09%
Paired t conc		0.05
Paired t load		0.05

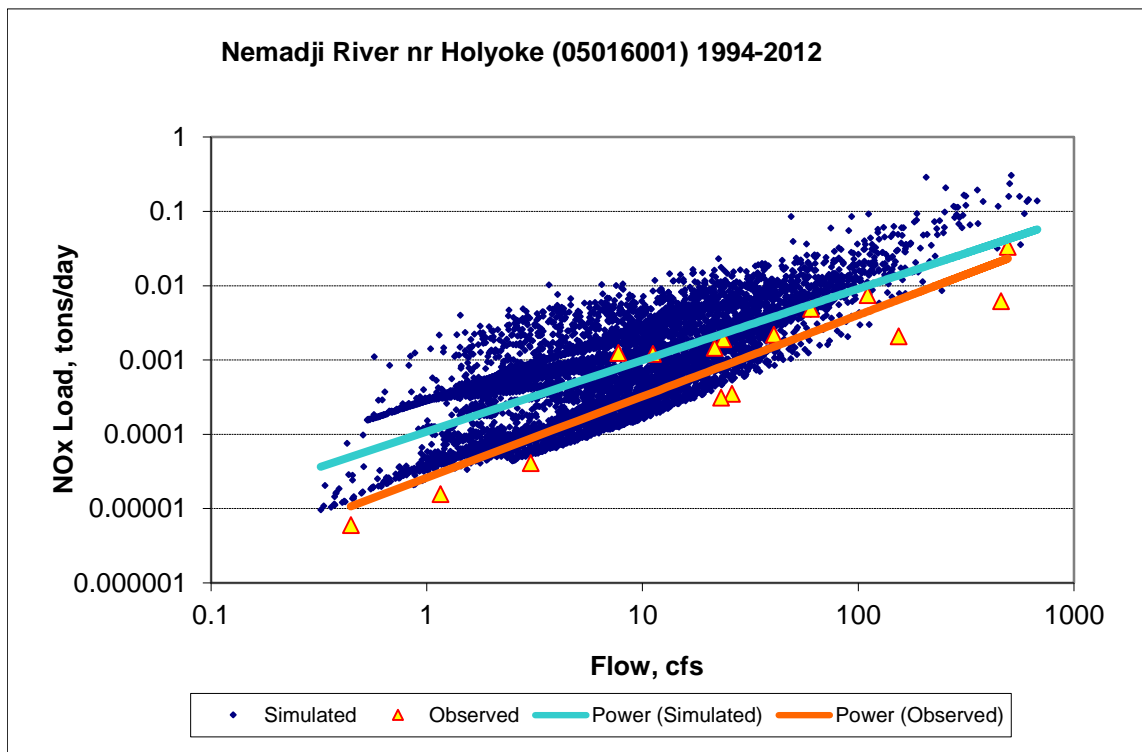
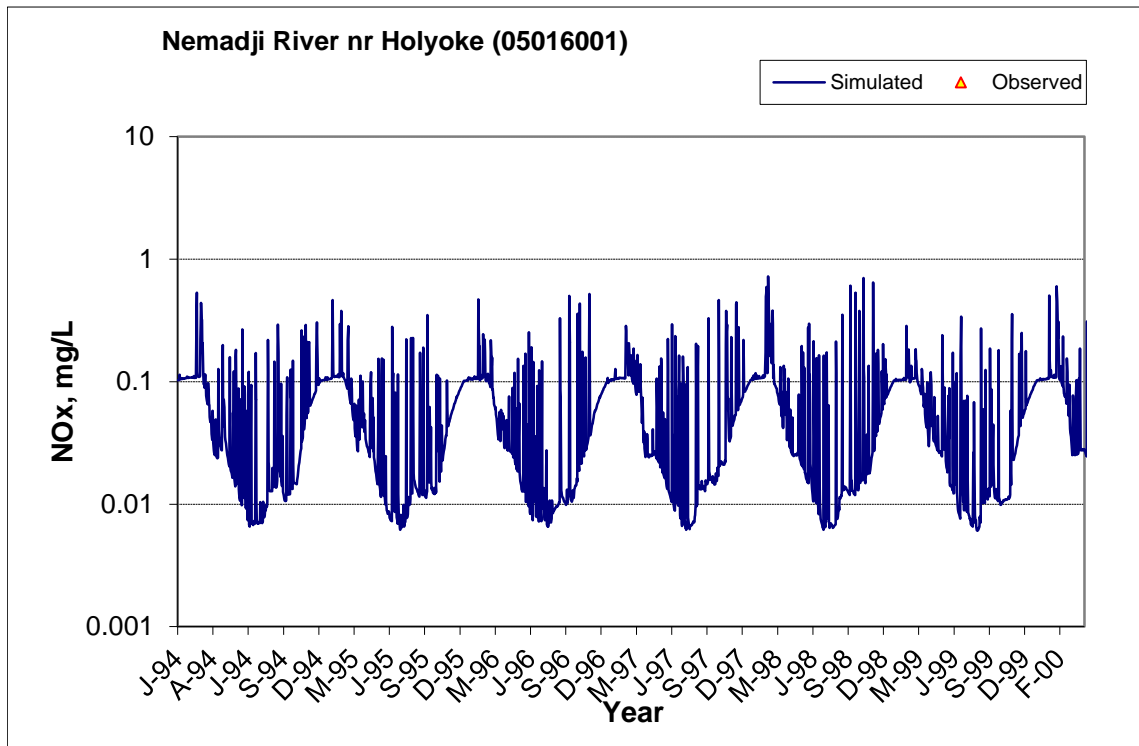


Figure B-112. Power plot of simulated and observed Nitrite+ Nitrate Nitrogen (NOx) load vs flow at Nemadji River nr Holyoke (05016001) (calibration period)



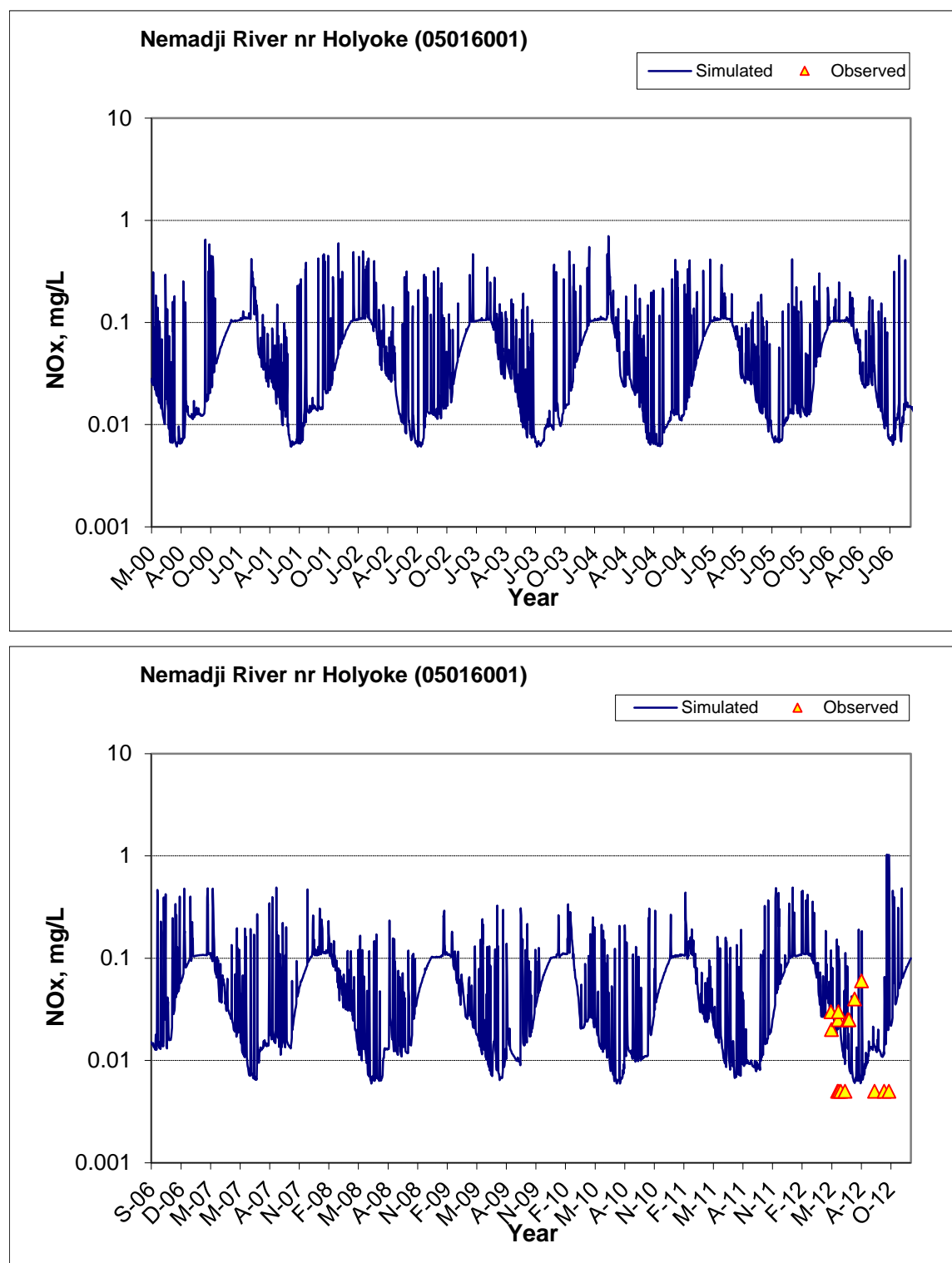


Figure B-113. Time series of observed and simulated Nitrite+ Nitrate Nitrogen (NOx) concentration at Nemadji River nr Holyoke (05016001)

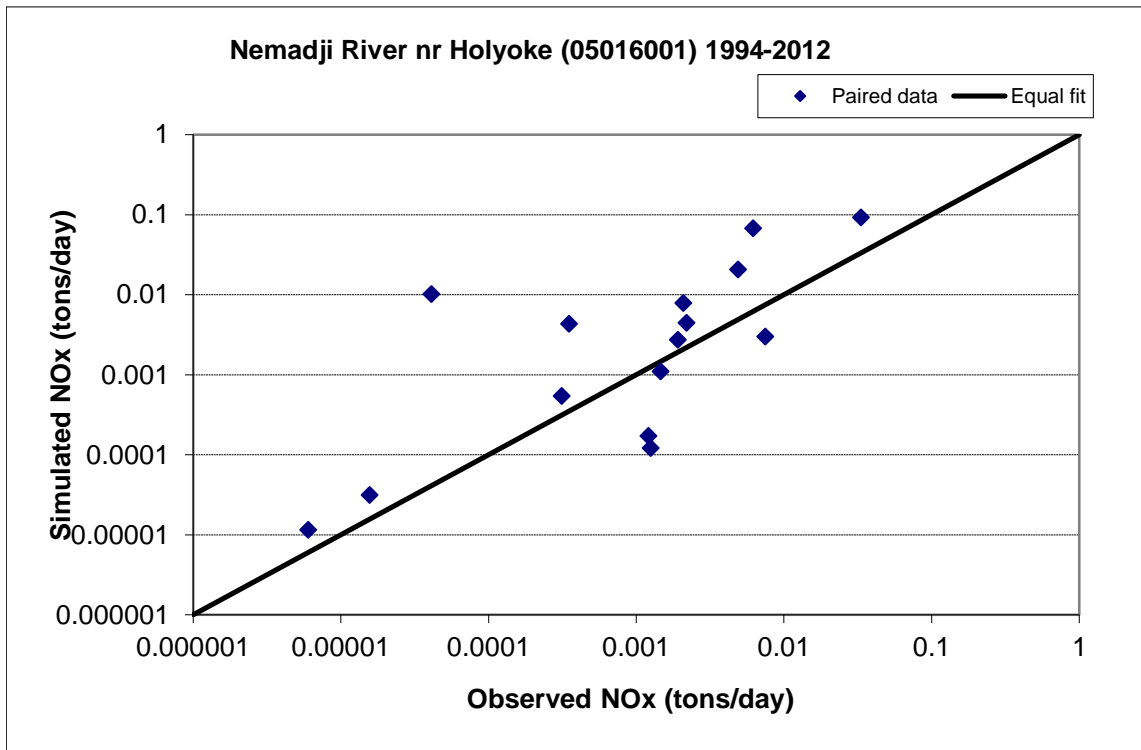


Figure B-114. Paired simulated vs. observed Nitrite+ Nitrate Nitrogen (NOx) load at Nemadji River nr Holyoke (05016001) (calibration period)

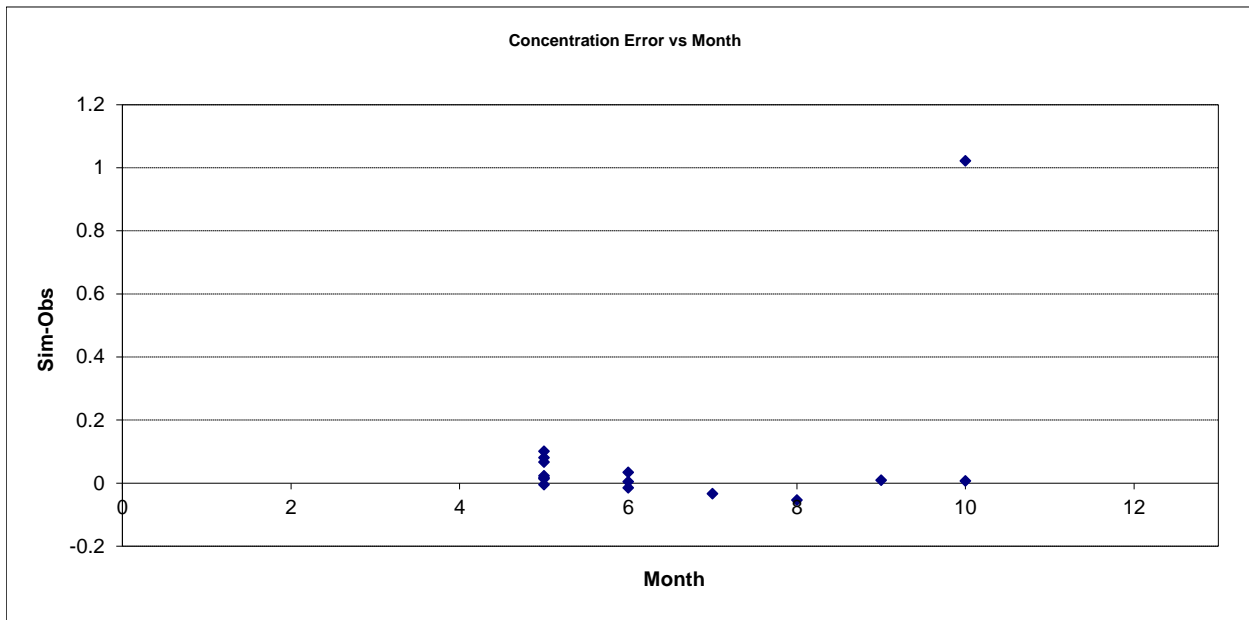


Figure B-115. Residual (Simulated - Observed) vs. Month Nitrite+ Nitrate Nitrogen (NOx) at Nemadji River nr Holyoke (05016001)

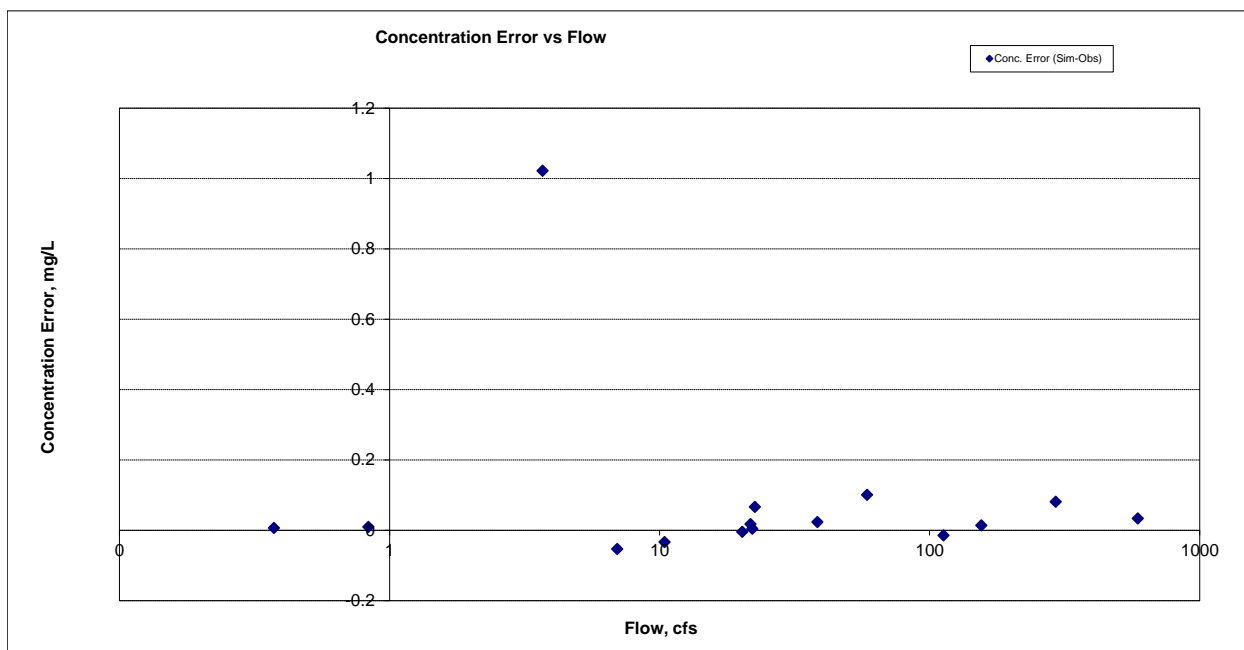


Figure B-116. Residual (Simulated - Observed) vs. Flow Nitrite+ Nitrate Nitrogen (NOx) at Nemadji River nr Holyoke (05016001)

B.4.5 Total Nitrogen (TN)

Table B-20. Total Nitrogen (TN) statistics

Period	1994-1993	1994-2012
Count	ND	15
Concentration Average Error		5.50%
Concentration Median Error		-14.25%
Load Average Error		4.68%
Load Median Error		-5.98%
Paired t conc		0.86
Paired t load		0.62

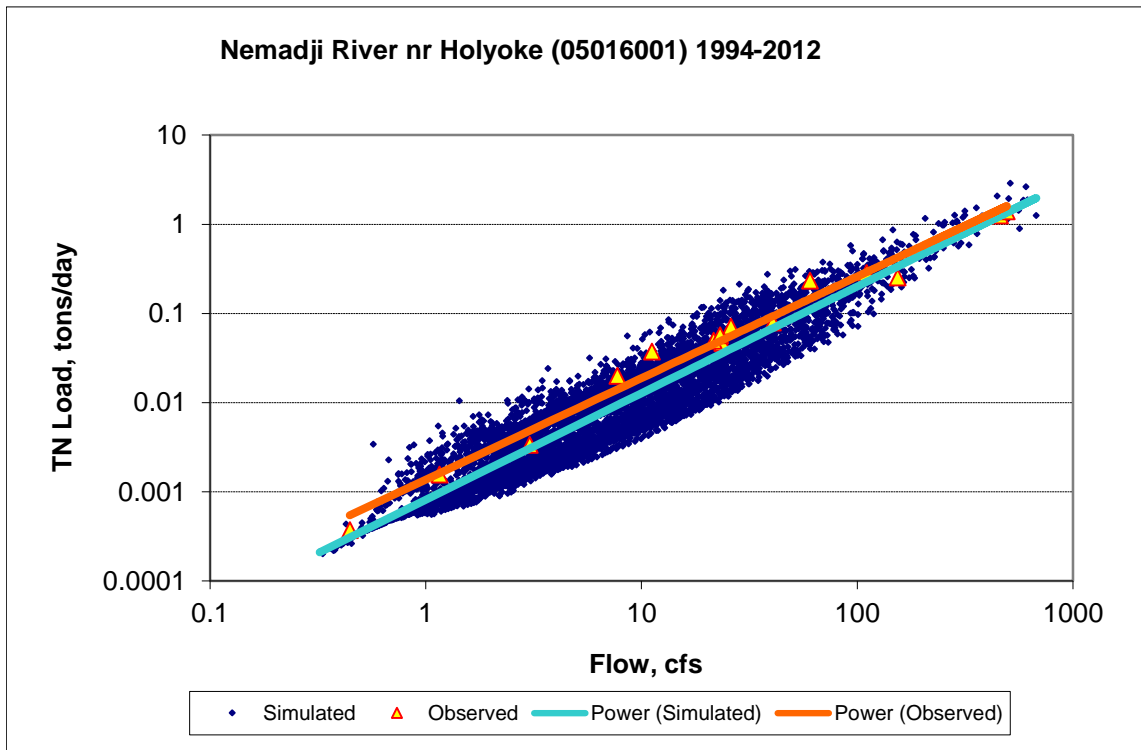
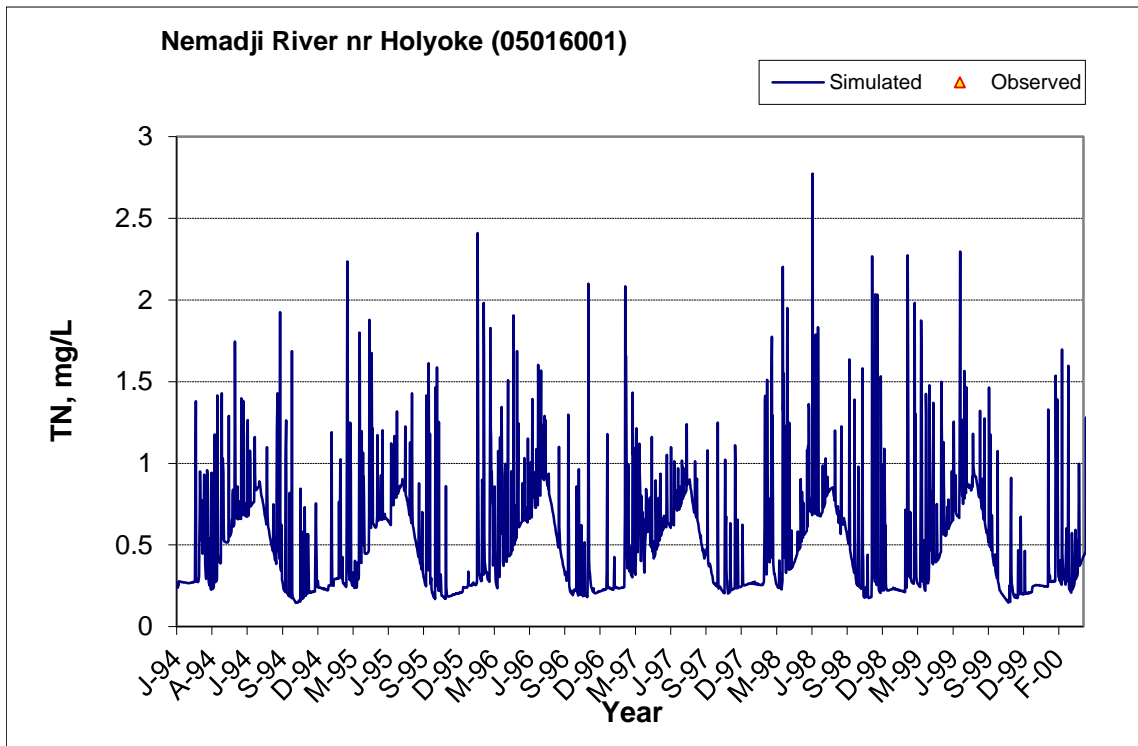


Figure B-117. Power plot of simulated and observed Total Nitrogen (TN) load vs flow at Nemadji River nr Holyoke (05016001) (calibration period)



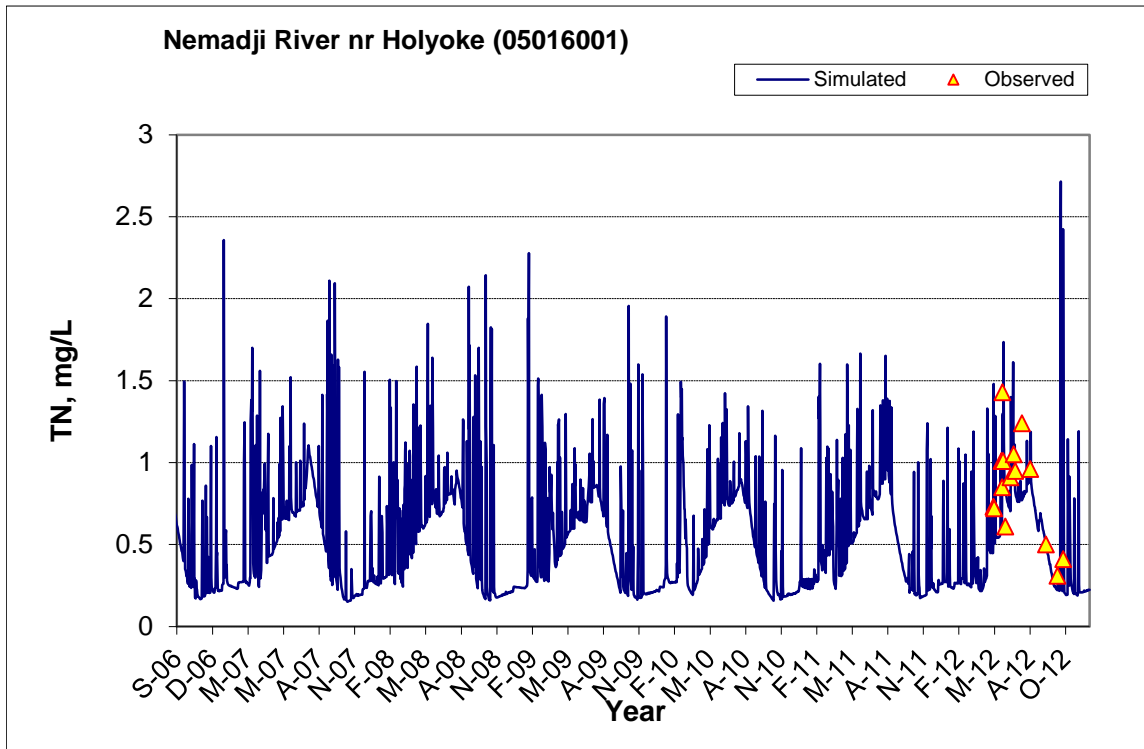
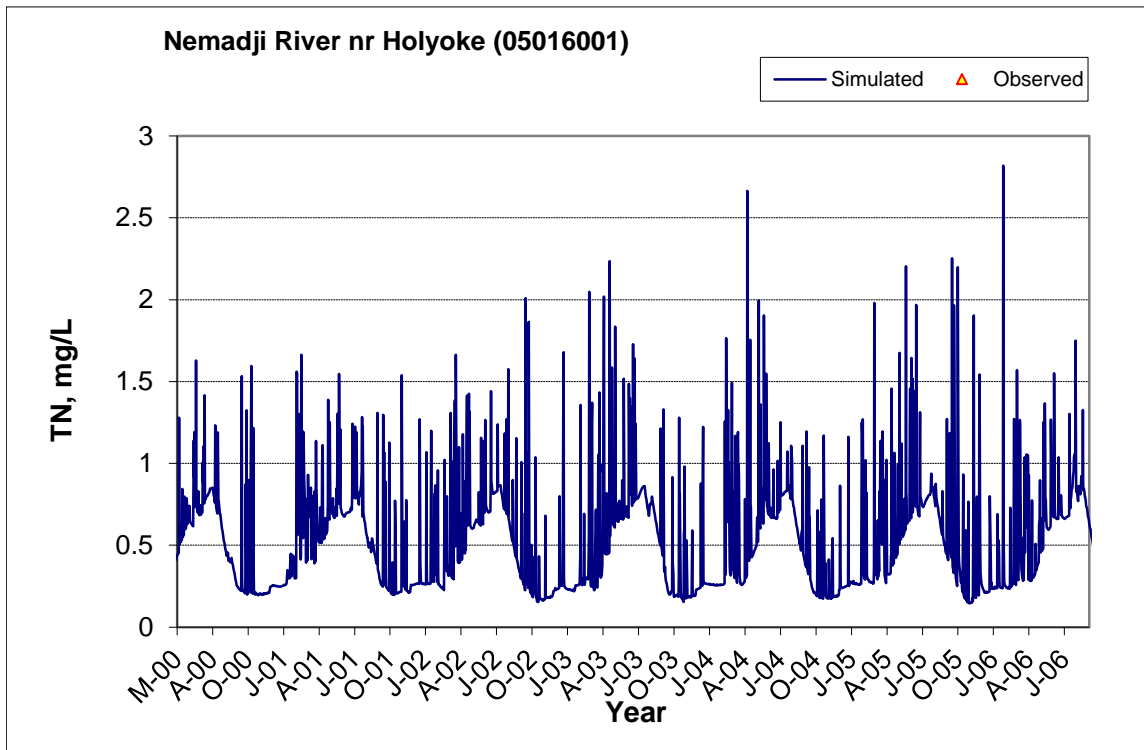


Figure B-118. Time series of observed and simulated Total Nitrogen (TN) concentration at Nemadji River nr Holyoke (05016001)

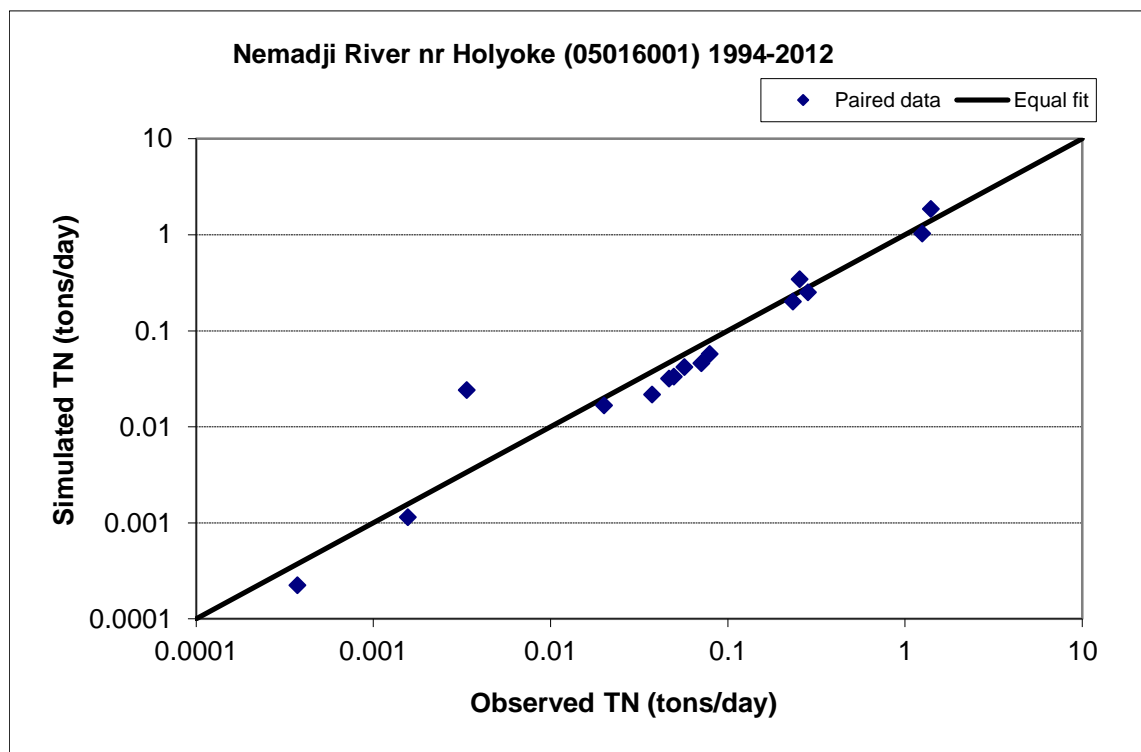


Figure B-119. Paired simulated vs. observed Total Nitrogen (TN) load at Nemadji River nr Holyoke (05016001) (calibration period)

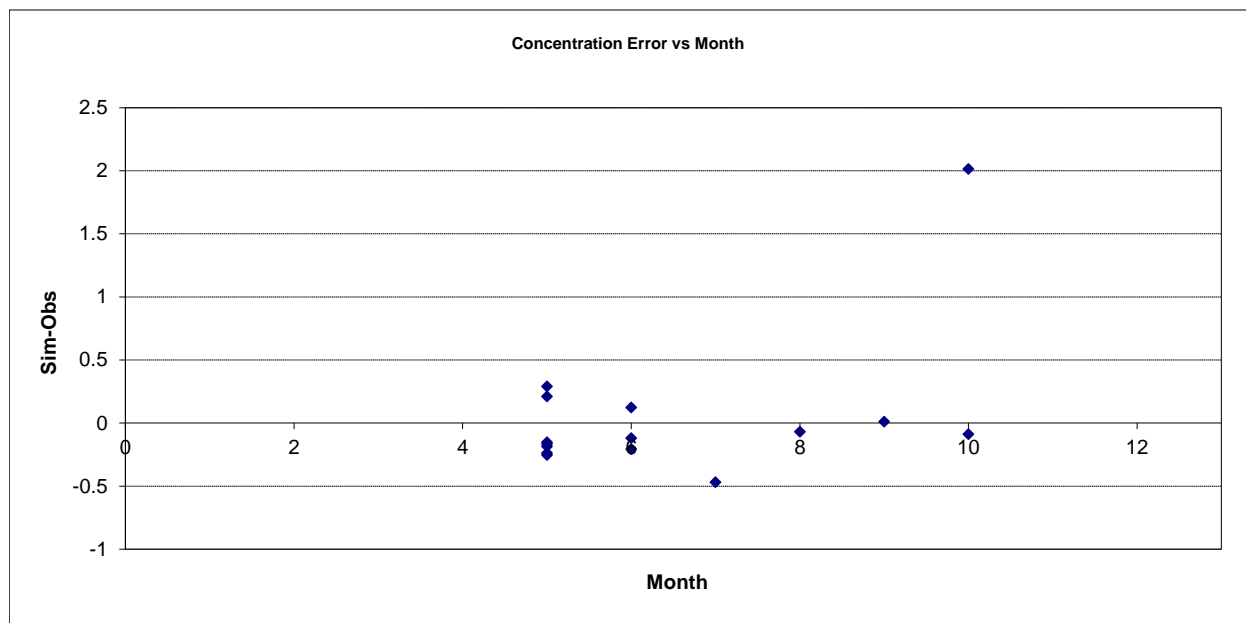


Figure B-120. Residual (Simulated - Observed) vs. Month Total Nitrogen (TN) at Nemadji River nr Holyoke (05016001)

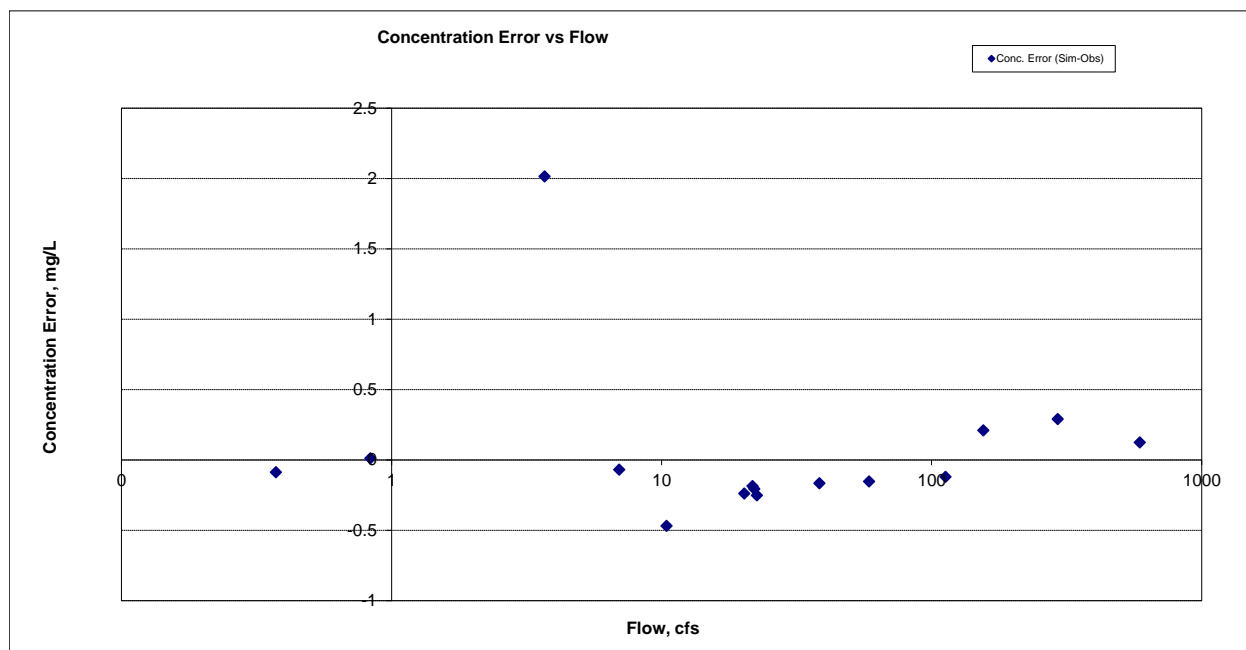


Figure B-121. Residual (Simulated - Observed) vs. Flow Total Nitrogen (TN) at Nemadji River nr Holyoke (05016001)

B.4.6 Soluble Reactive Phosphorus (SRP)

Table B-21. Soluble Reactive Phosphorus (SRP) statistics

Period	1994-1993	1994-2012
Count	ND	15
Concentration Average Error		187.65%
Concentration Median Error		44.52%
Load Average Error		736.70%
Load Median Error		11.52%
Paired t conc		0.01
Paired t load		0.04

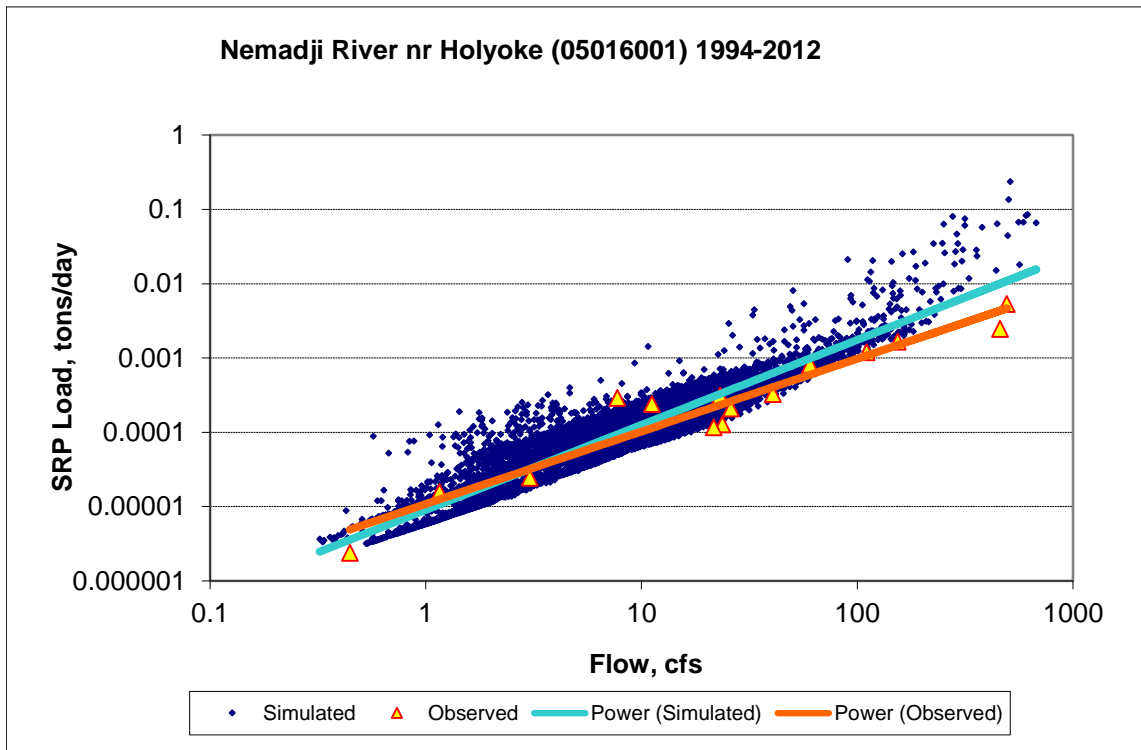
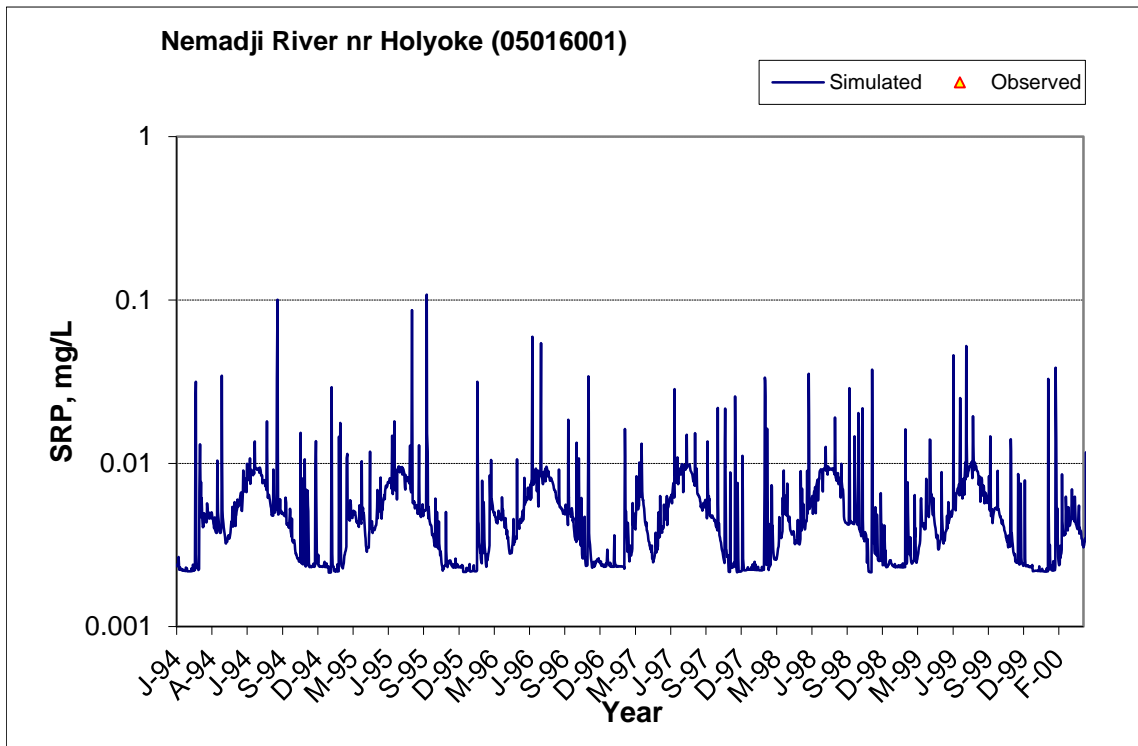


Figure B-122. Power plot of simulated and observed Soluble Reactive Phosphorus (SRP) load vs flow at Nemadji River nr Holyoke (05016001) (calibration period)



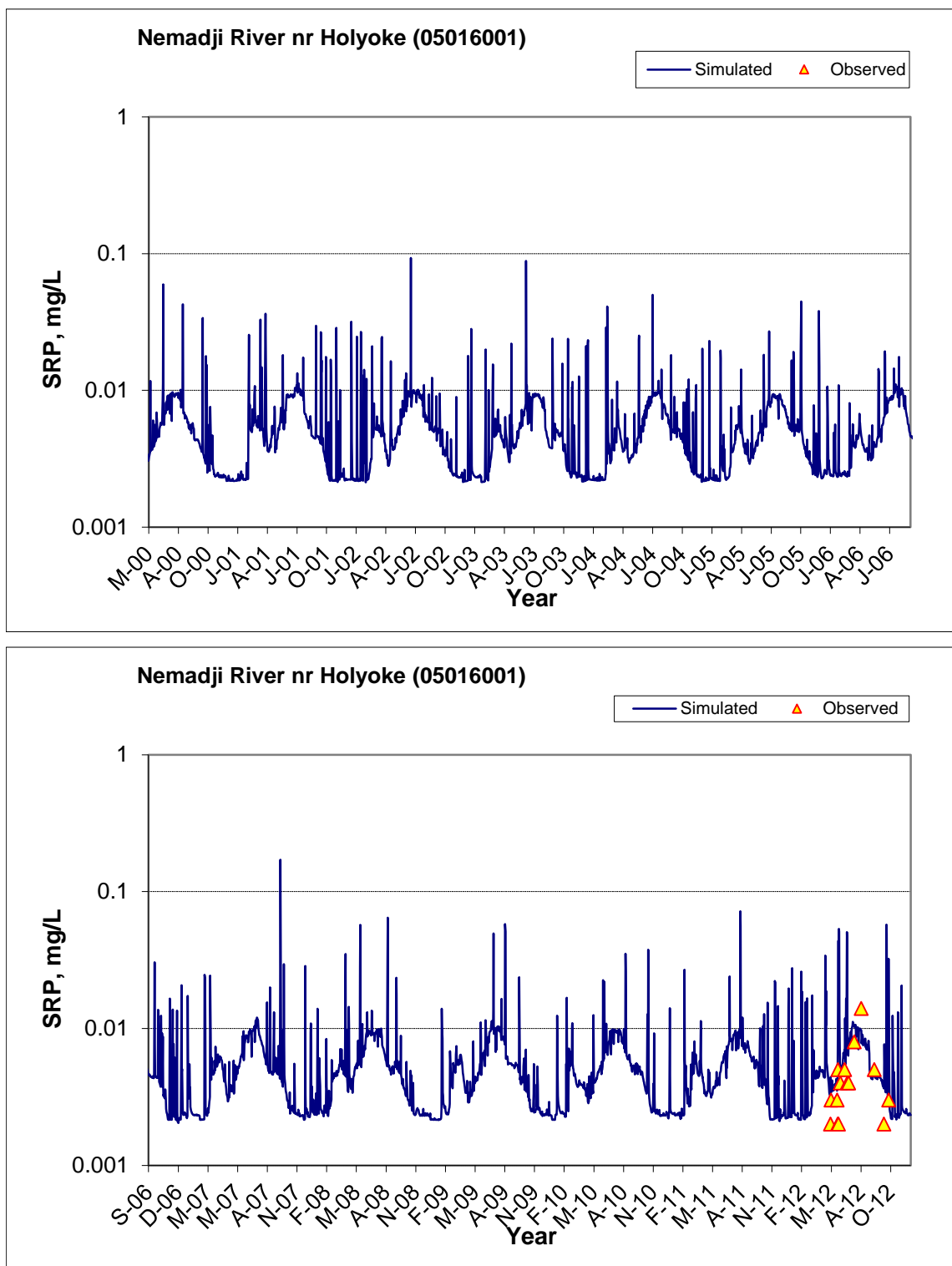


Figure B-123. Time series of observed and simulated Soluble Reactive Phosphorus (SRP) concentration at Nemadji River nr Holyoke (05016001)

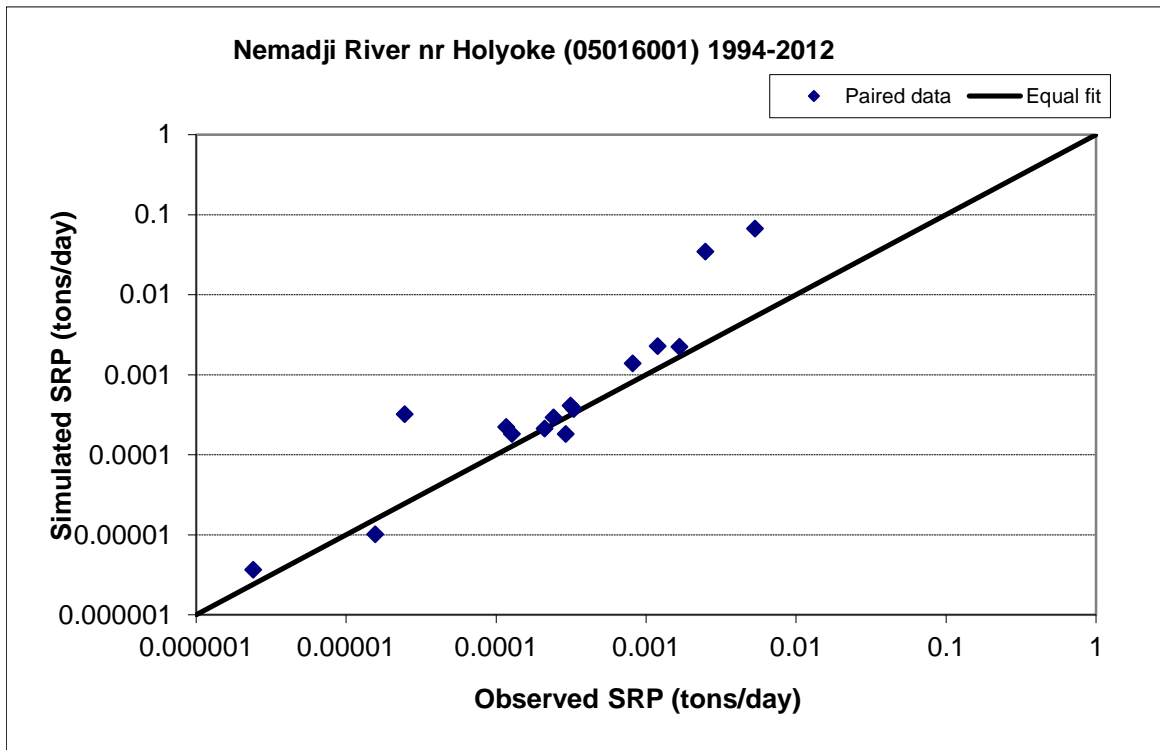


Figure B-124. Paired simulated vs. observed Soluble Reactive Phosphorus (SRP) load at Nemadji River nr Holyoke (05016001) (calibration period)

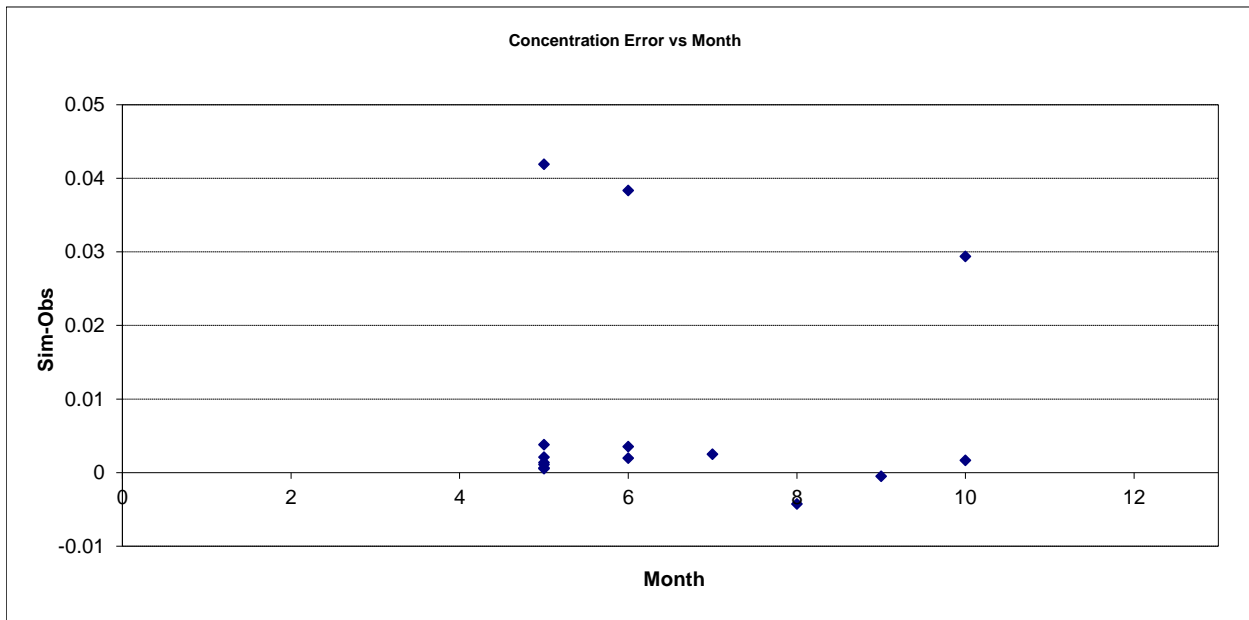


Figure B-125. Residual (Simulated - Observed) vs. Month Soluble Reactive Phosphorus (SRP) at Nemadji River nr Holyoke (05016001)

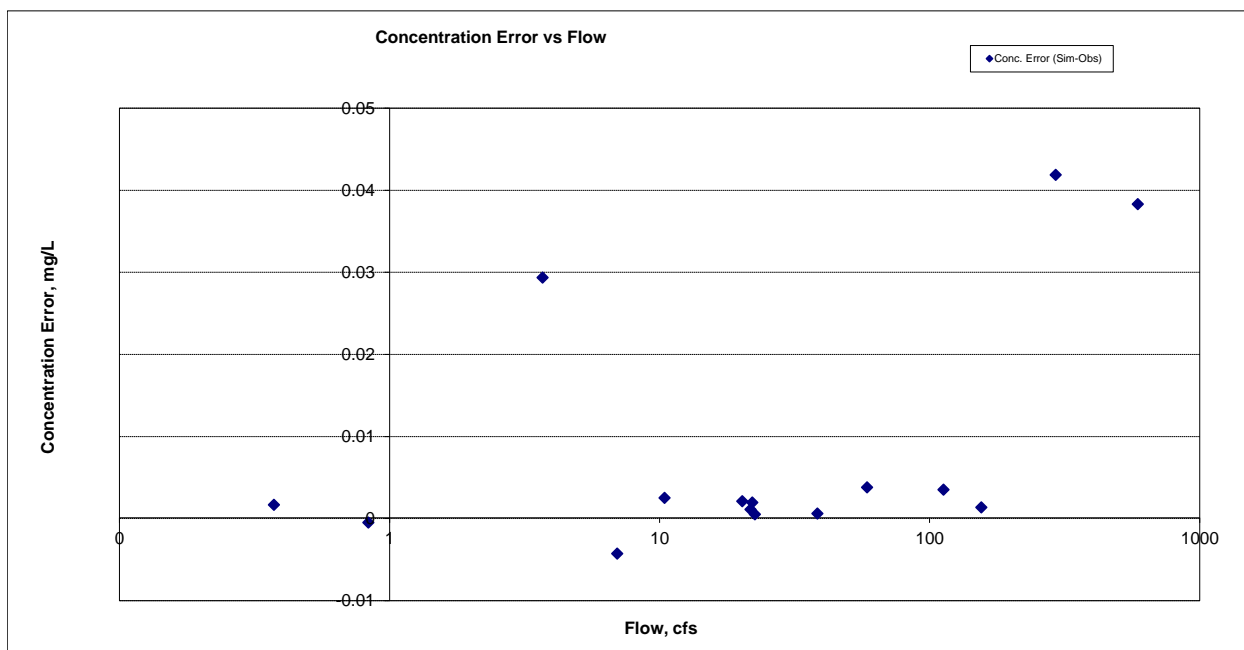
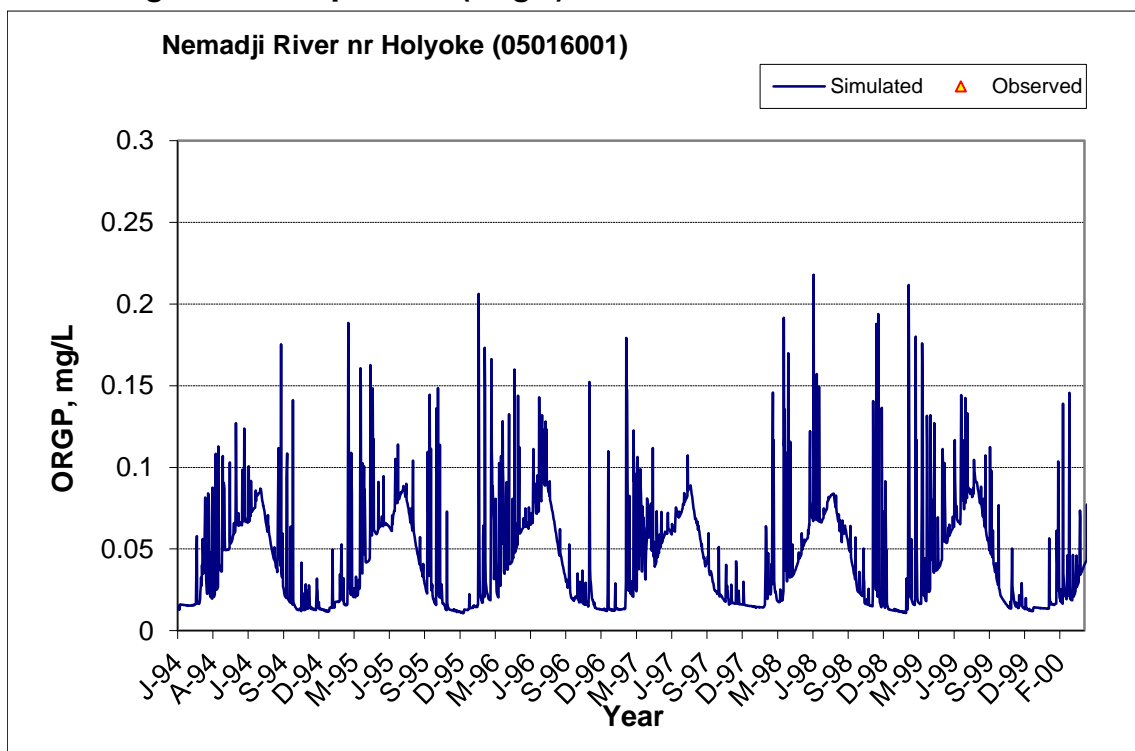


Figure B-126. Residual (Simulated - Observed) vs. Flow Soluble Reactive Phosphorus (SRP) at Nemadji River nr Holyoke (05016001)

B.4.7 Organic Phosphorus (OrgP)



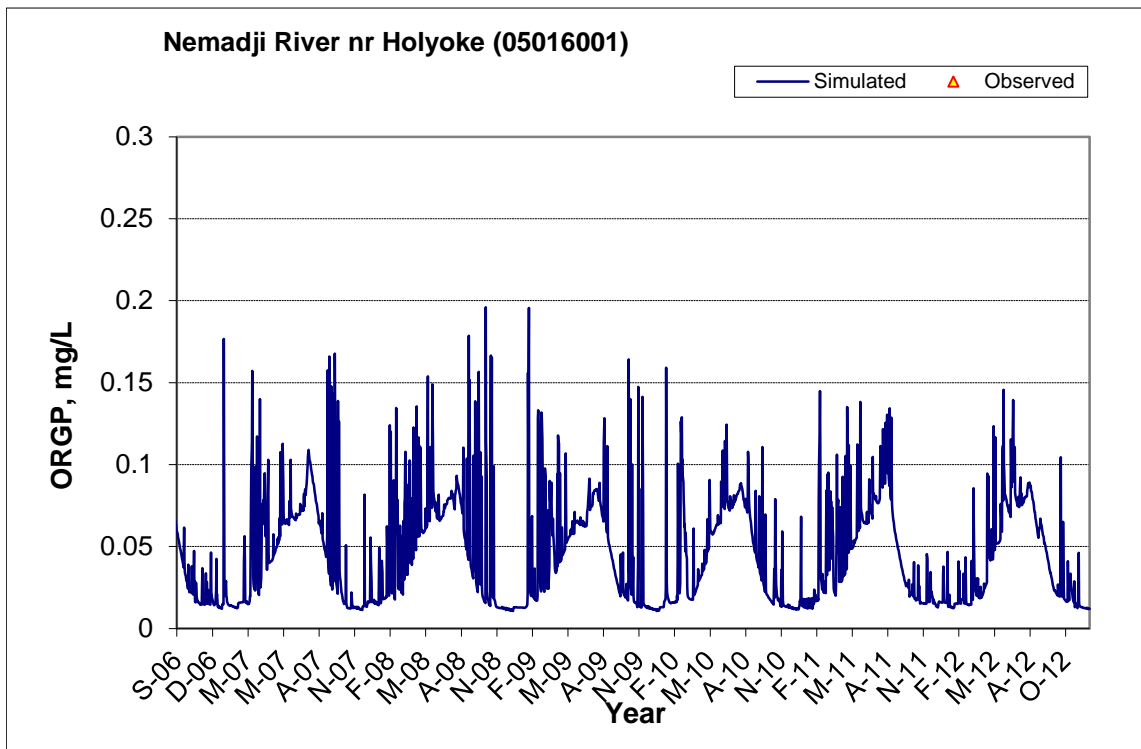
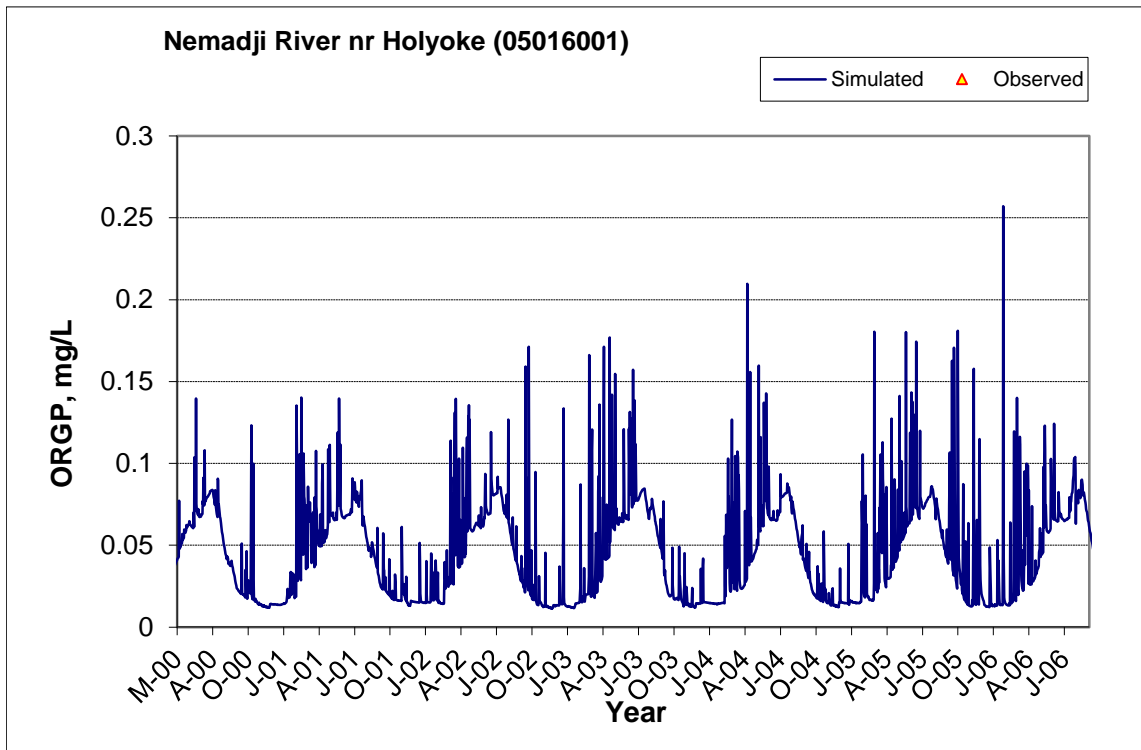


Figure B-127. Time series of observed and simulated Organic Phosphorus (OrgP) concentration at Nemadji River nr Holyoke (05016001)

B.4.8 Total Phosphorus (TP)

Table B-22. Total Phosphorus (TP) statistics

Period	1994-1993	1994-2012
Count	ND	15
Concentration Average Error		6.15%
Concentration Median Error		18.38%
Load Average Error		-1.38%
Load Median Error		0.82%
Paired t conc		0.75
Paired t load		0.64

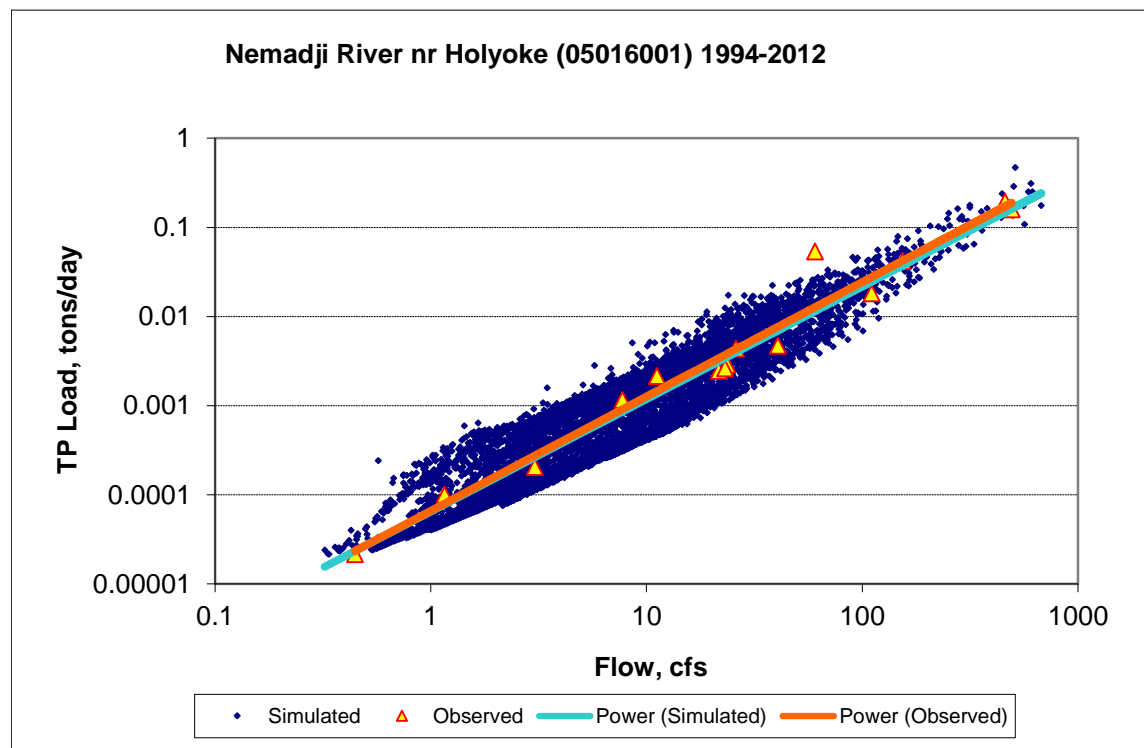
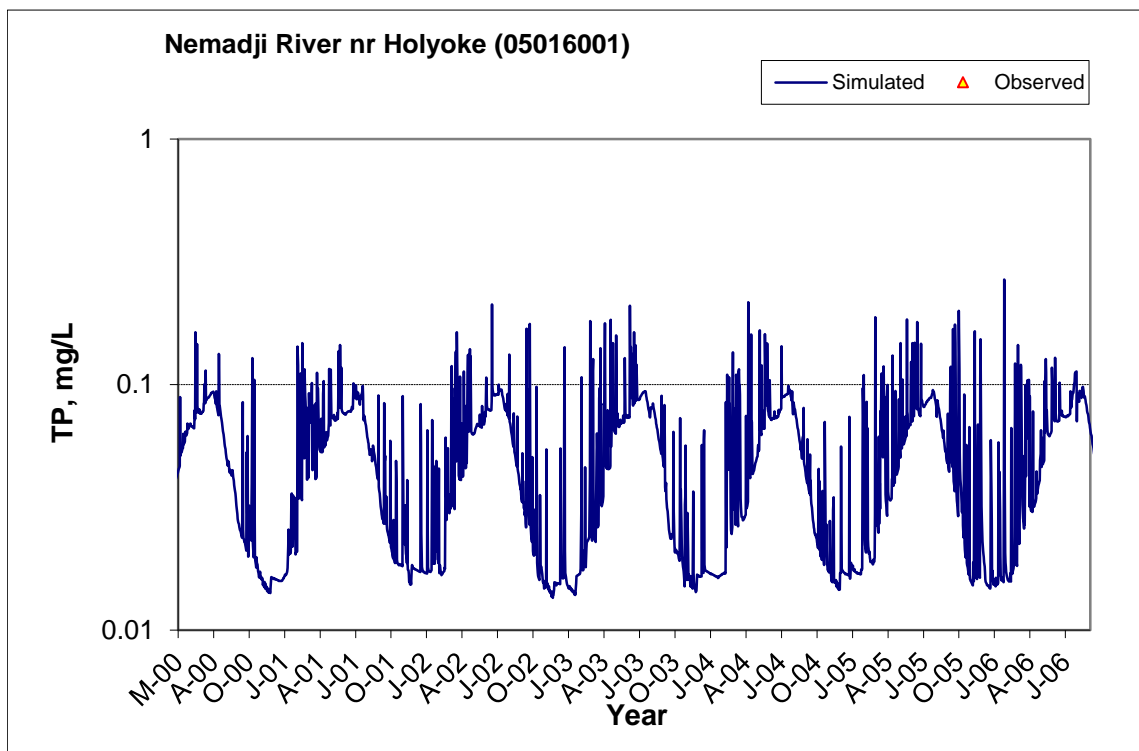
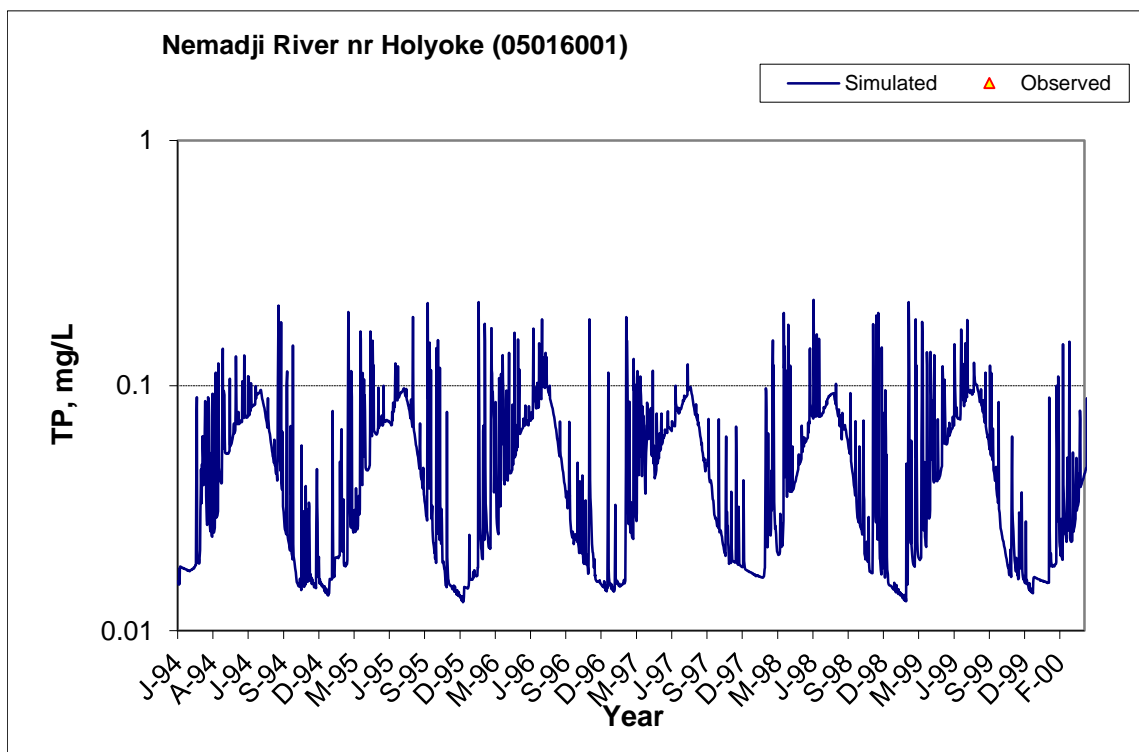


Figure B-128. Power plot of simulated and observed Total Phosphorus (TP) load vs flow at Nemadji River nr Holyoke (05016001) (calibration period)



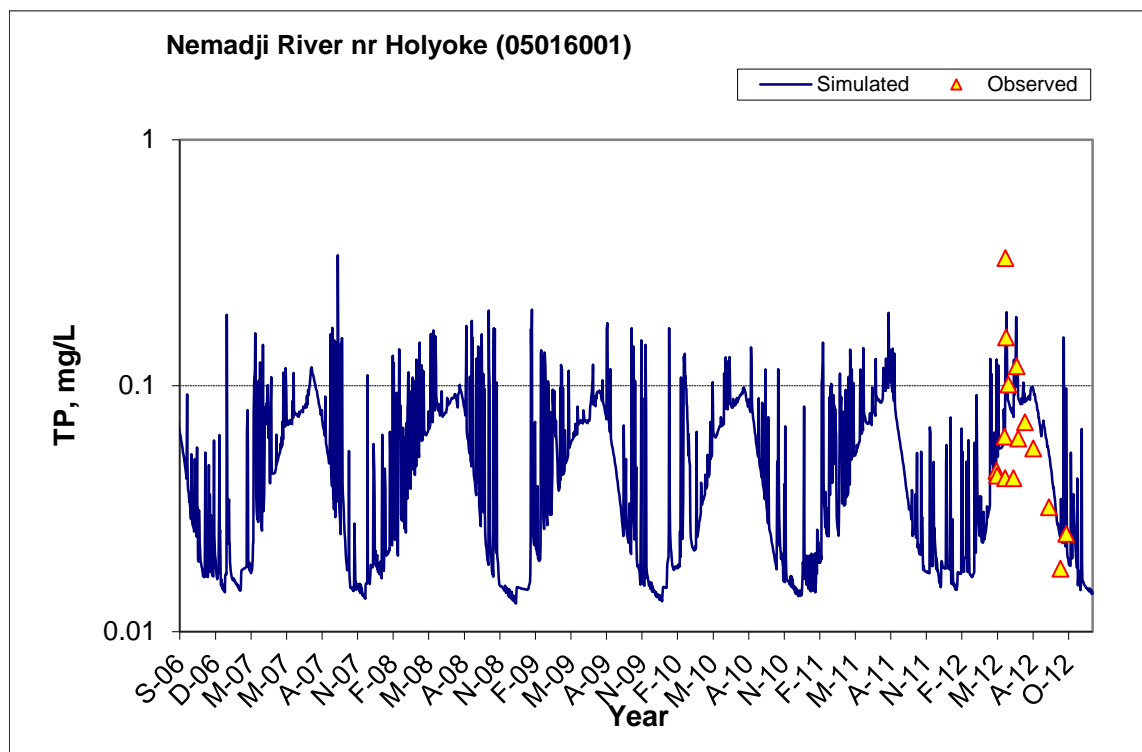


Figure B-129. Time series of observed and simulated Total Phosphorus (TP) concentration at Nemadji River nr Holyoke (05016001)

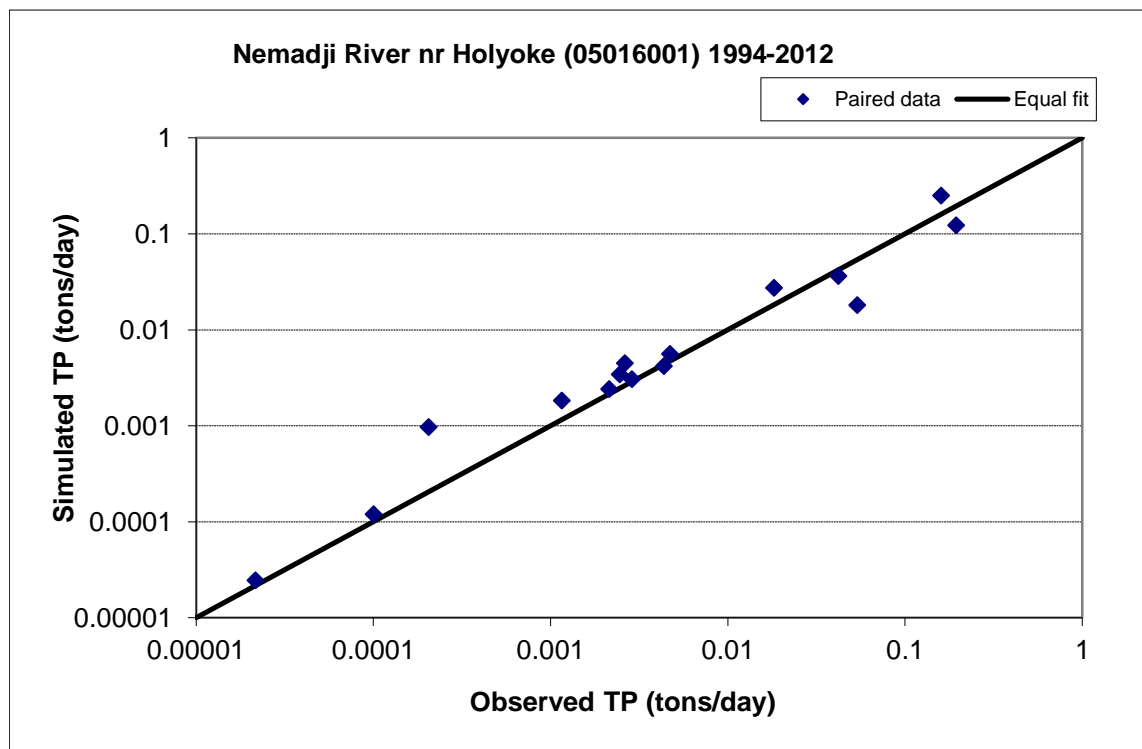


Figure B-130. Paired simulated vs. observed Total Phosphorus (TP) load at Nemadji River nr Holyoke (05016001) (calibration period)

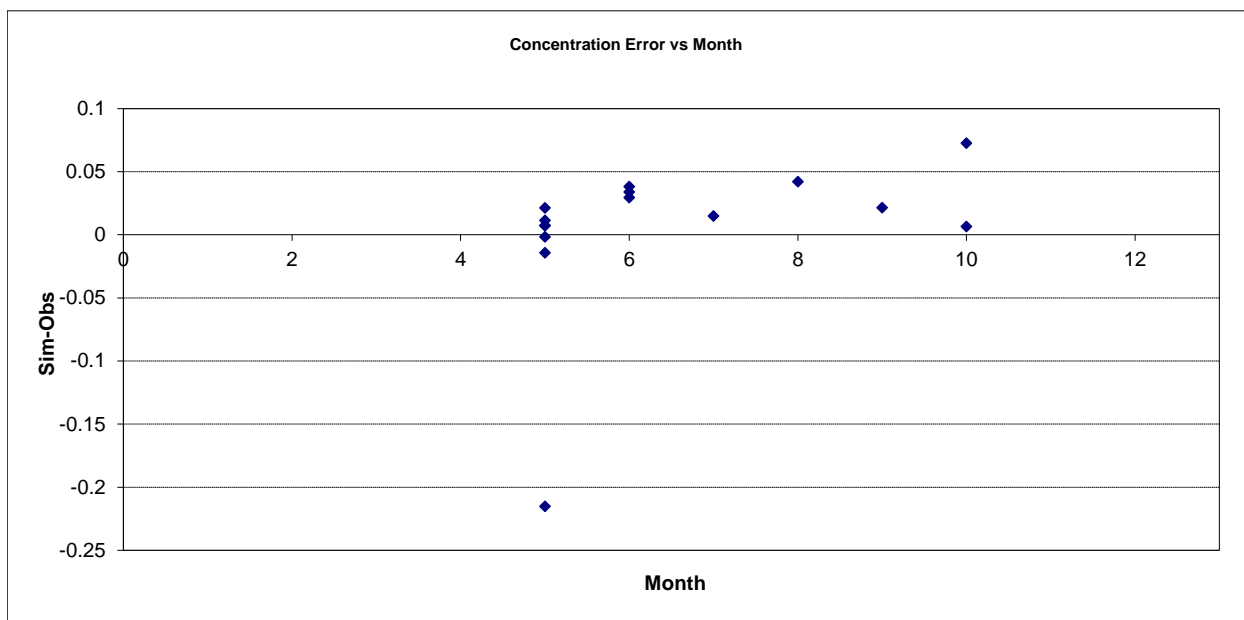


Figure B-131. Residual (Simulated - Observed) vs. Month Total Phosphorus (TP) at Nemadji River nr Holyoke (05016001)

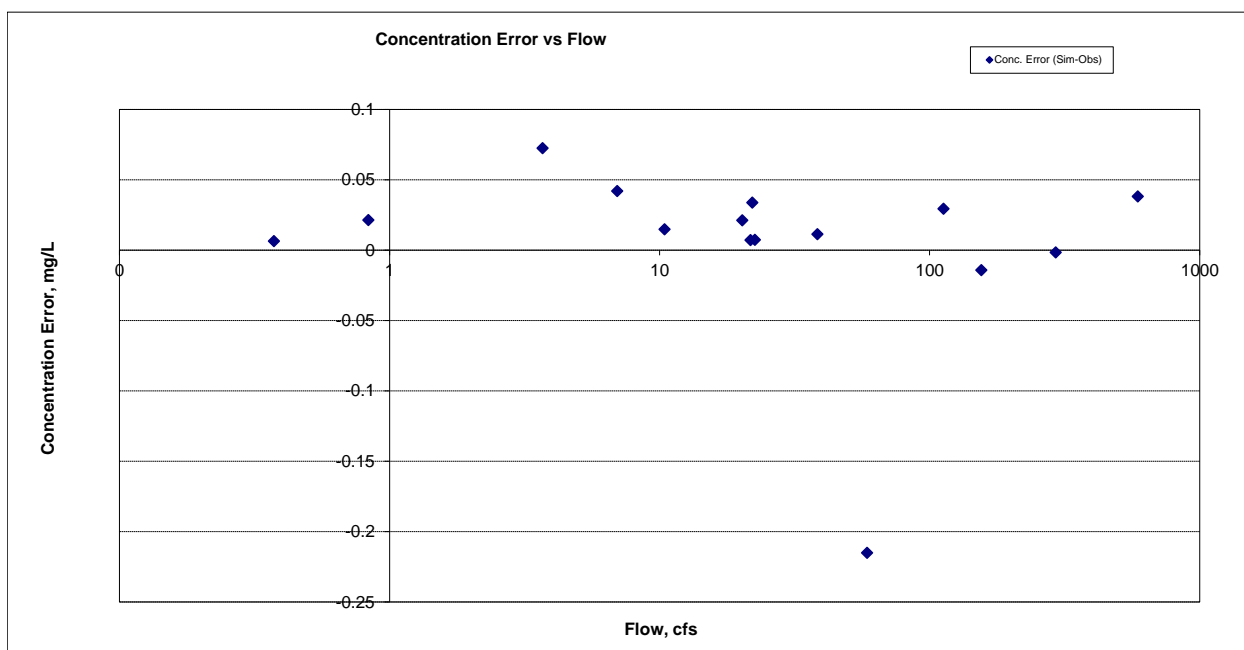


Figure B-132. Residual (Simulated - Observed) vs. Flow Total Phosphorus (TP) at Nemadji River nr Holyoke (05016001)

B.5 NEMADJI RIVER NR PLEASANT VALLEY (05011001)

B.5.1 Ammonia Nitrogen (NH3)

Table B-23. Ammonia Nitrogen (NH3) statistics

Period	1994-2001	2002-2012
Count	ND	31
Concentration Average Error		29.35%
Concentration Median Error		5.20%
Load Average Error		17.49%
Load Median Error		1.40%
Paired t conc		0.36
Paired t load		0.52

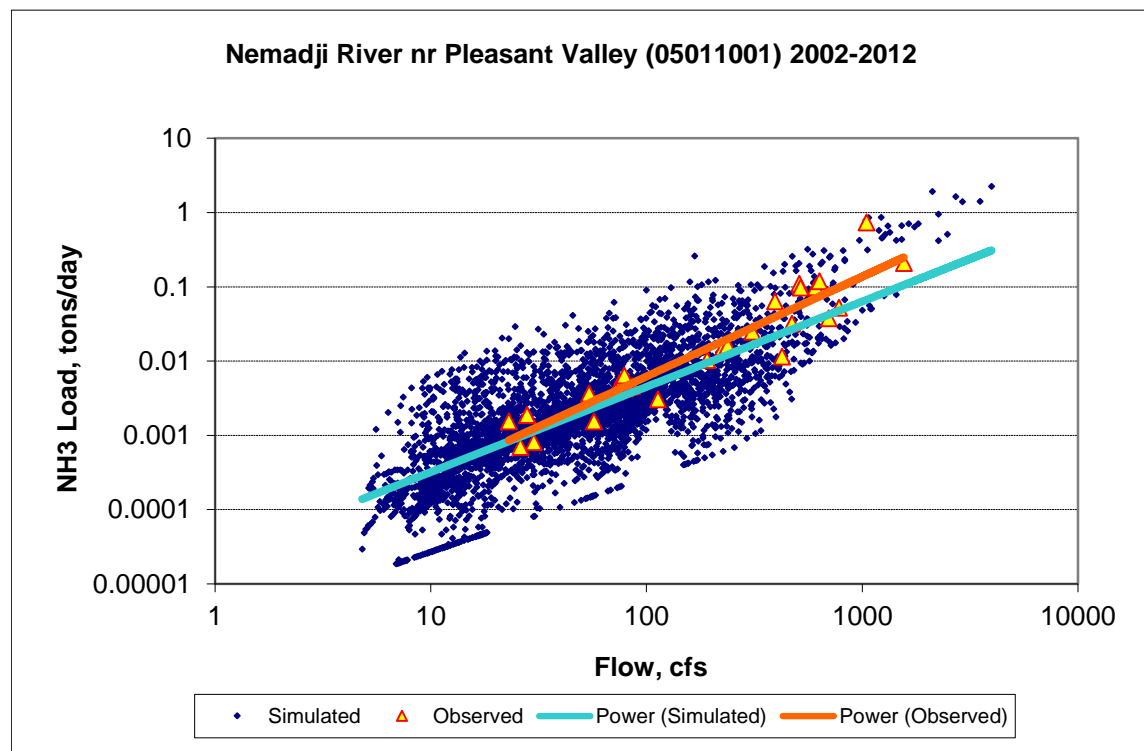
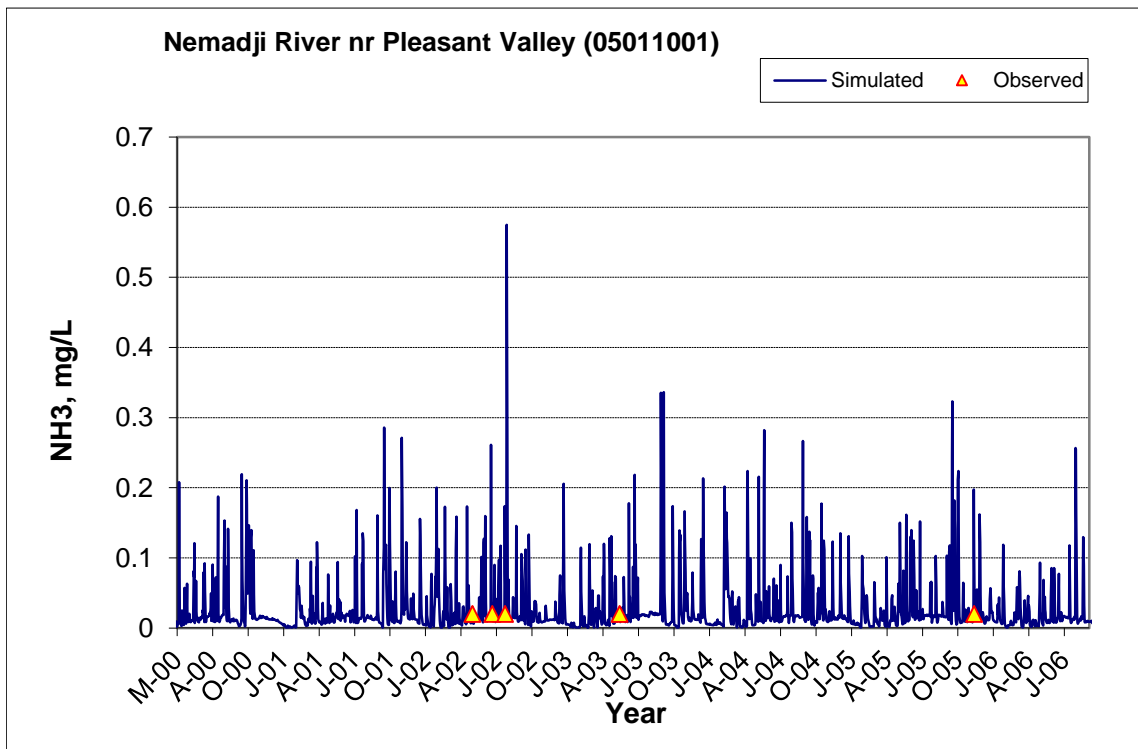
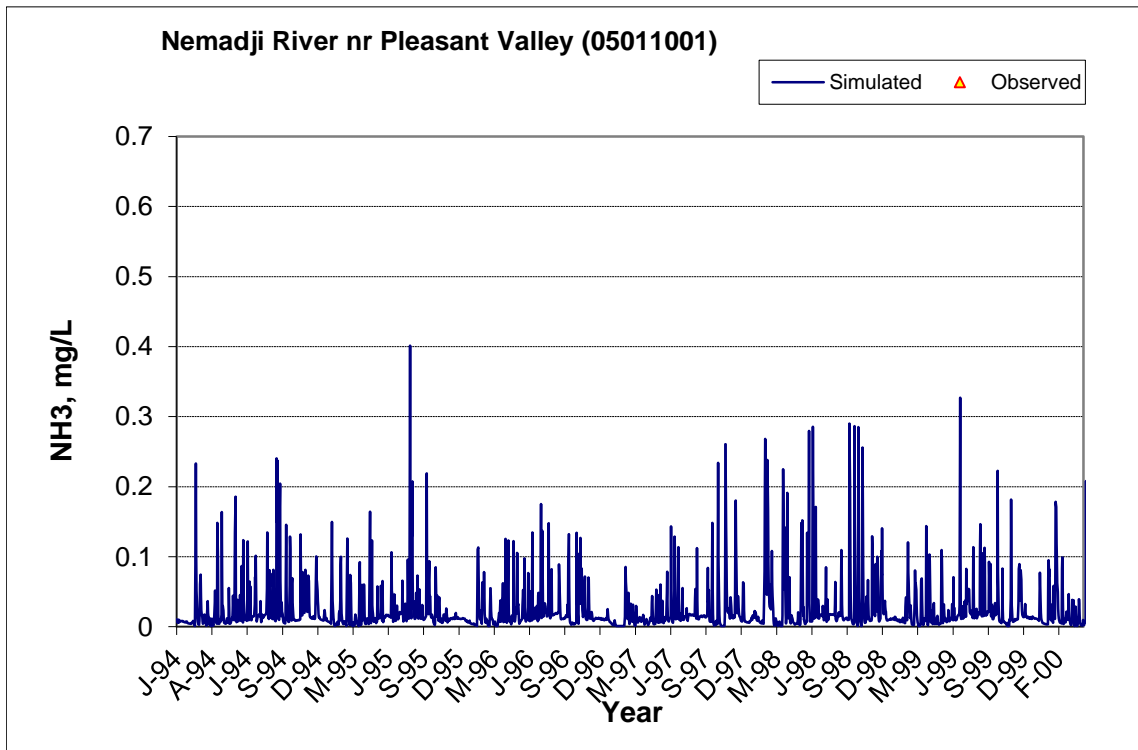


Figure B-133. Power plot of simulated and observed Ammonia Nitrogen (NH3) load vs flow at Nemadji River nr Pleasant Valley (05011001) (calibration period)



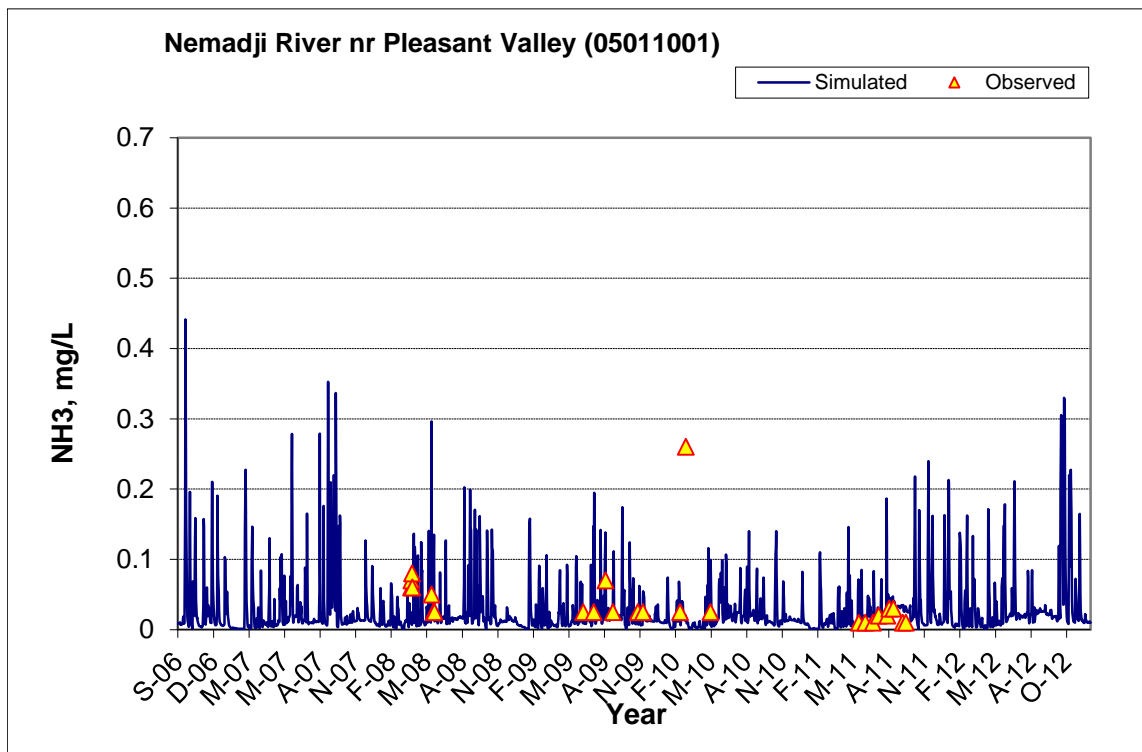


Figure B-134. Time series of observed and simulated Ammonia Nitrogen (NH3) concentration at Nemadji River nr Pleasant Valley (05011001)

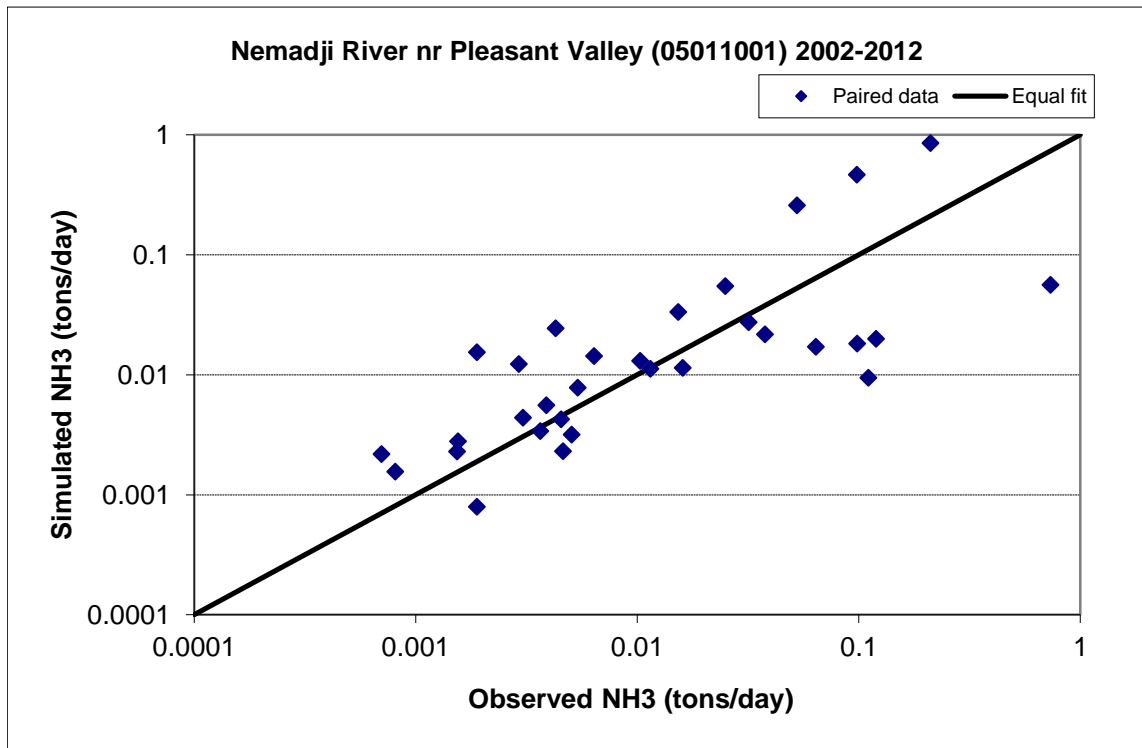
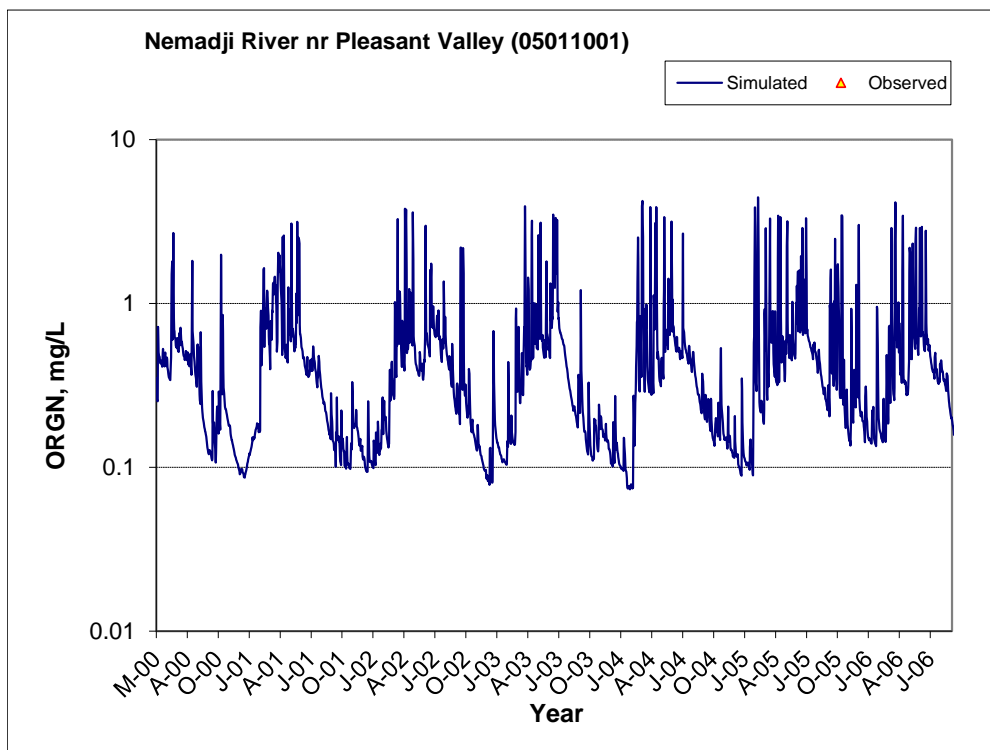
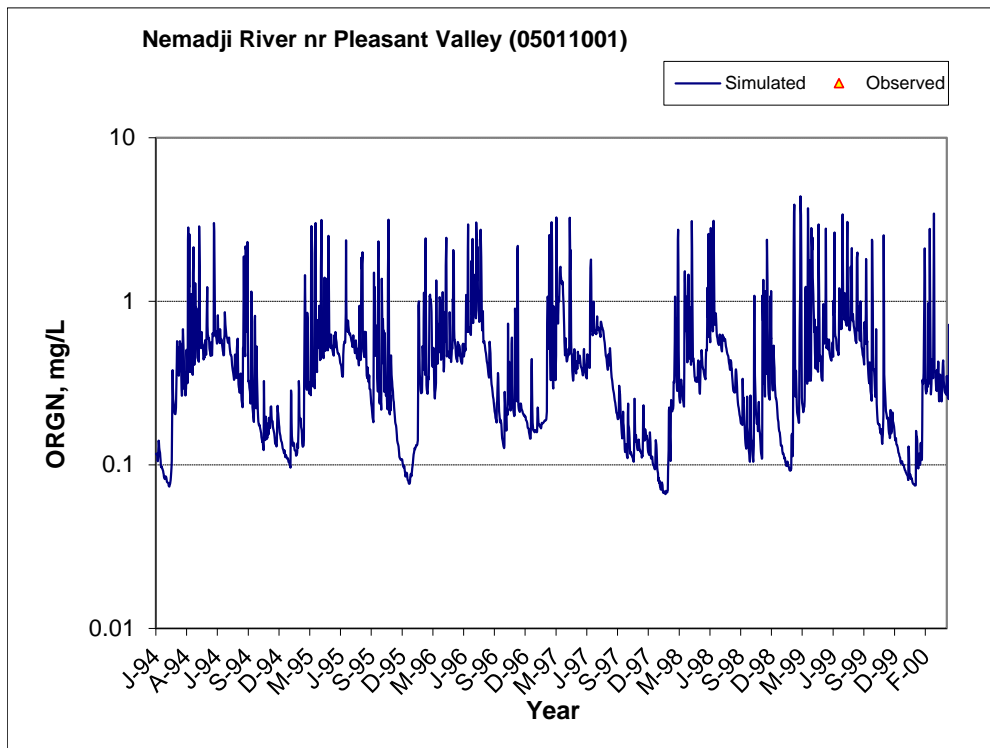


Figure B-135. Paired simulated vs. observed Ammonia Nitrogen (NH3) load at Nemadji River nr Pleasant Valley (05011001) (calibration period)

B.5.2 Organic Nitrogen (OrgN)



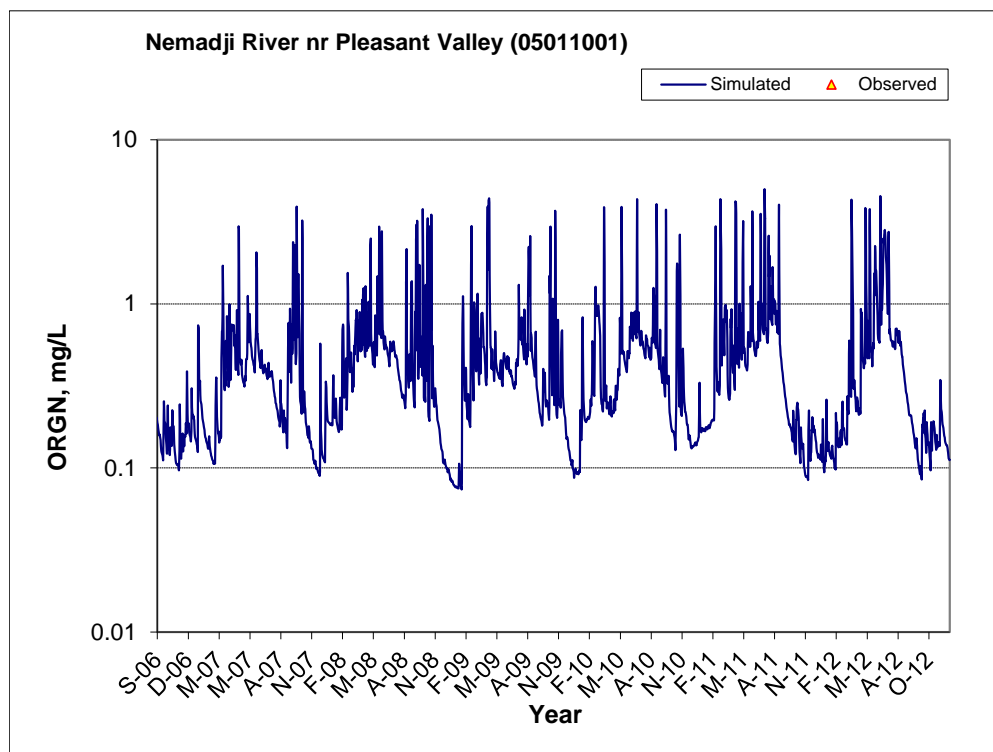


Figure B-138. Time series of observed and simulated Organic Nitrogen (OrgN) concentration at Nemadji River nr Pleasant Valley (05011001)

B.5.3 Total Kjeldahl Nitrogen (TKN)

Table B-24. Total Kjeldahl Nitrogen (TKN) statistics

Period	1994-2001	2002-2012
Count	7	32
Concentration Average Error	36.52%	13.63%
Concentration Median Error	7.09%	-1.52%
Load Average Error	89.06%	-5.58%
Load Median Error	0.21%	0.20%
Paired t conc	0.33	0.68
Paired t load	0.26	0.62

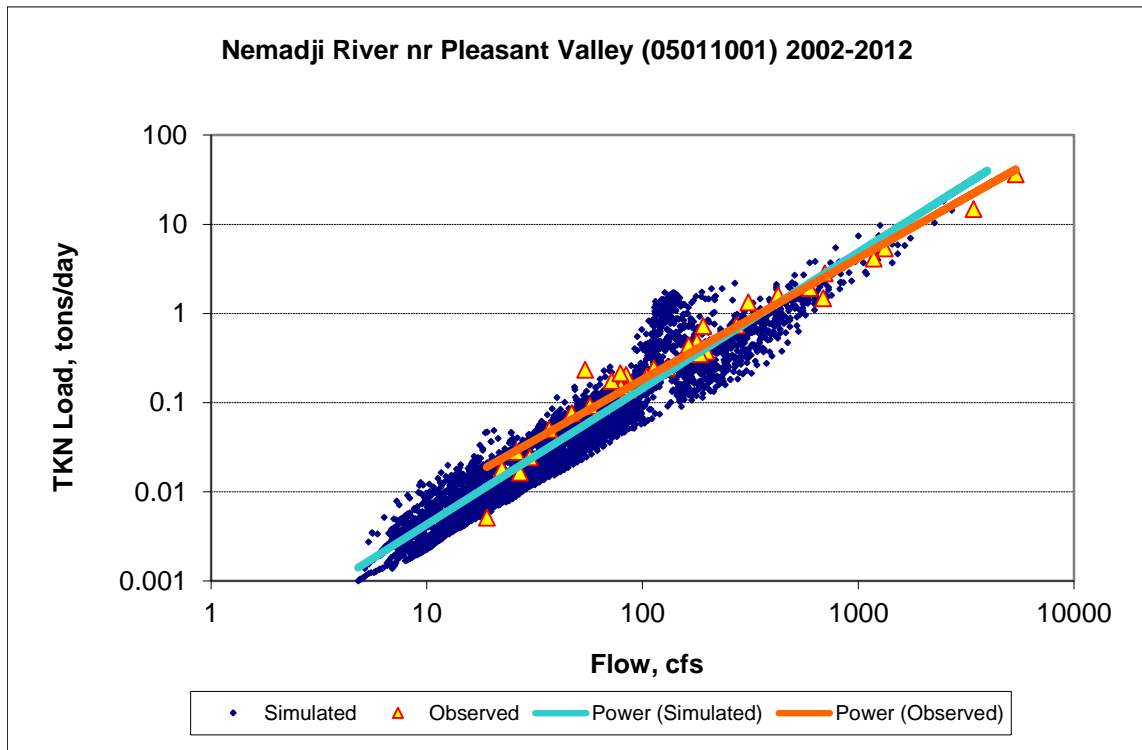


Figure B-139. Power plot of simulated and observed Total Kjeldahl Nitrogen (TKN) load vs flow at Nemadji River nr Pleasant Valley (05011001) (calibration period)

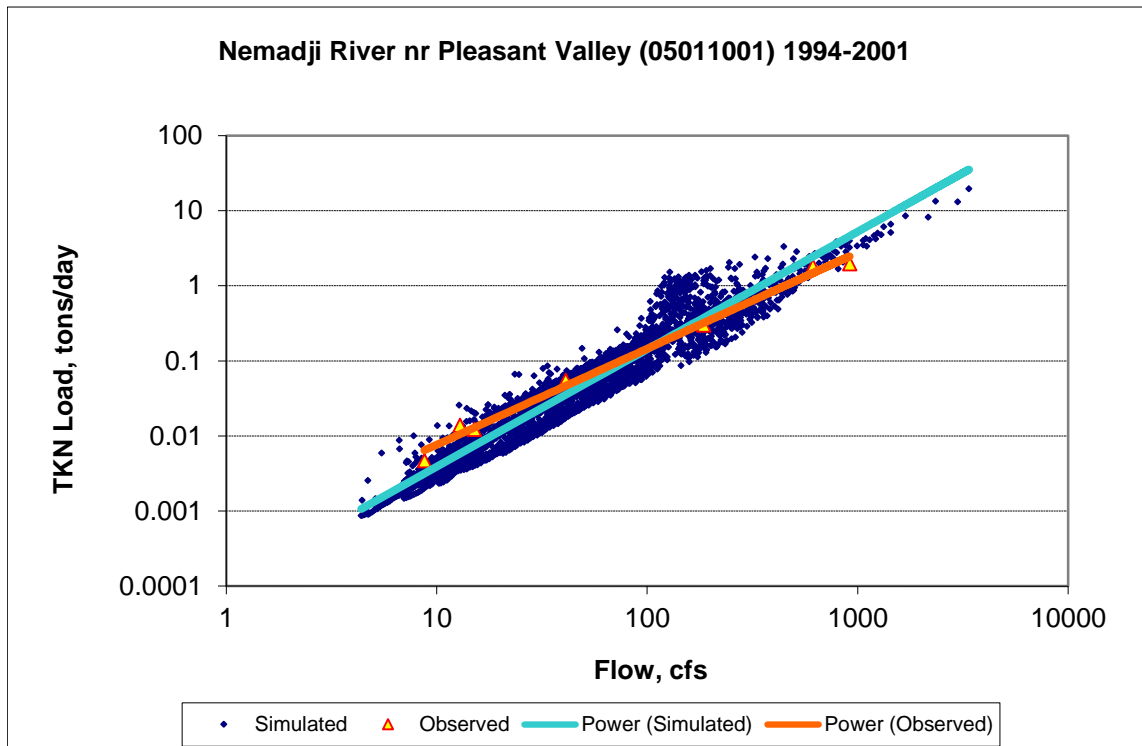
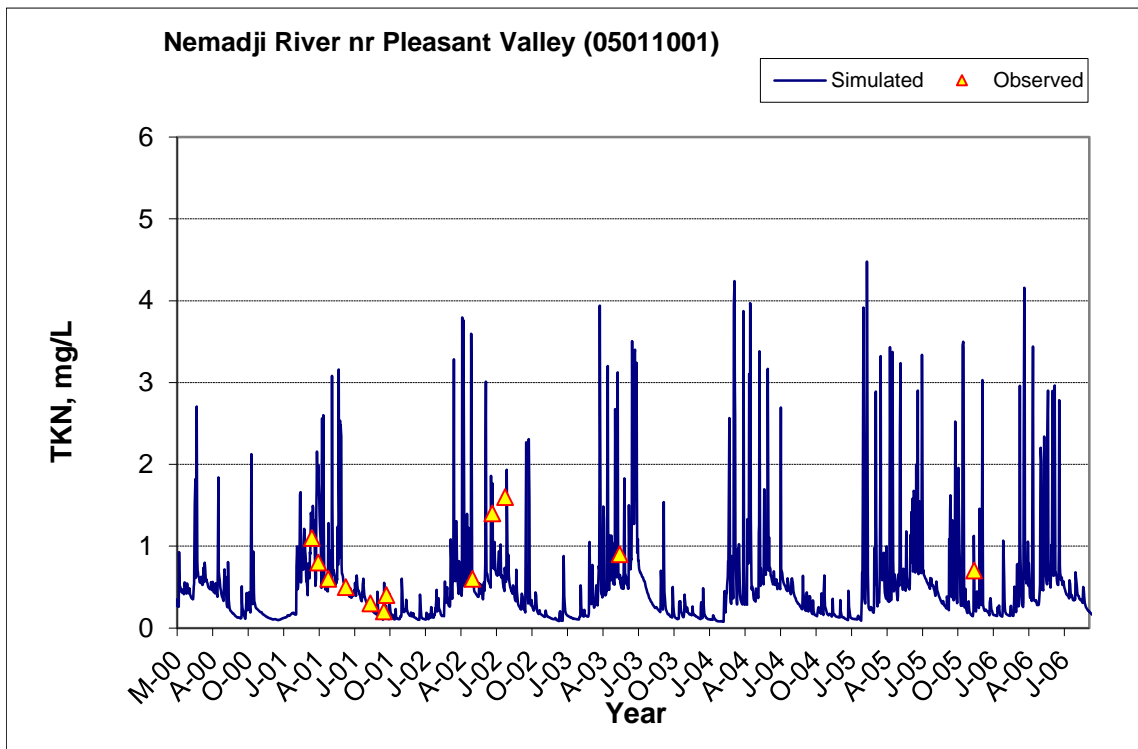
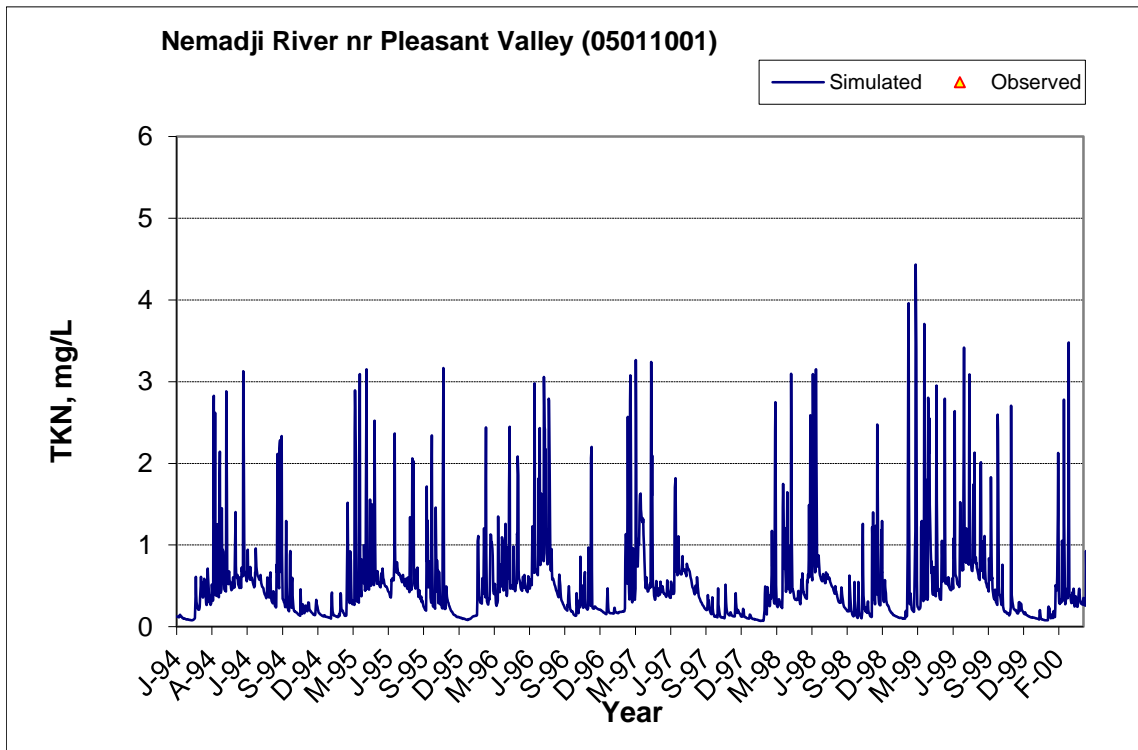


Figure B-140. Power plot of simulated and observed Total Kjeldahl Nitrogen (TKN) load vs flow at Nemadji River nr Pleasant Valley (05011001) (validation period)



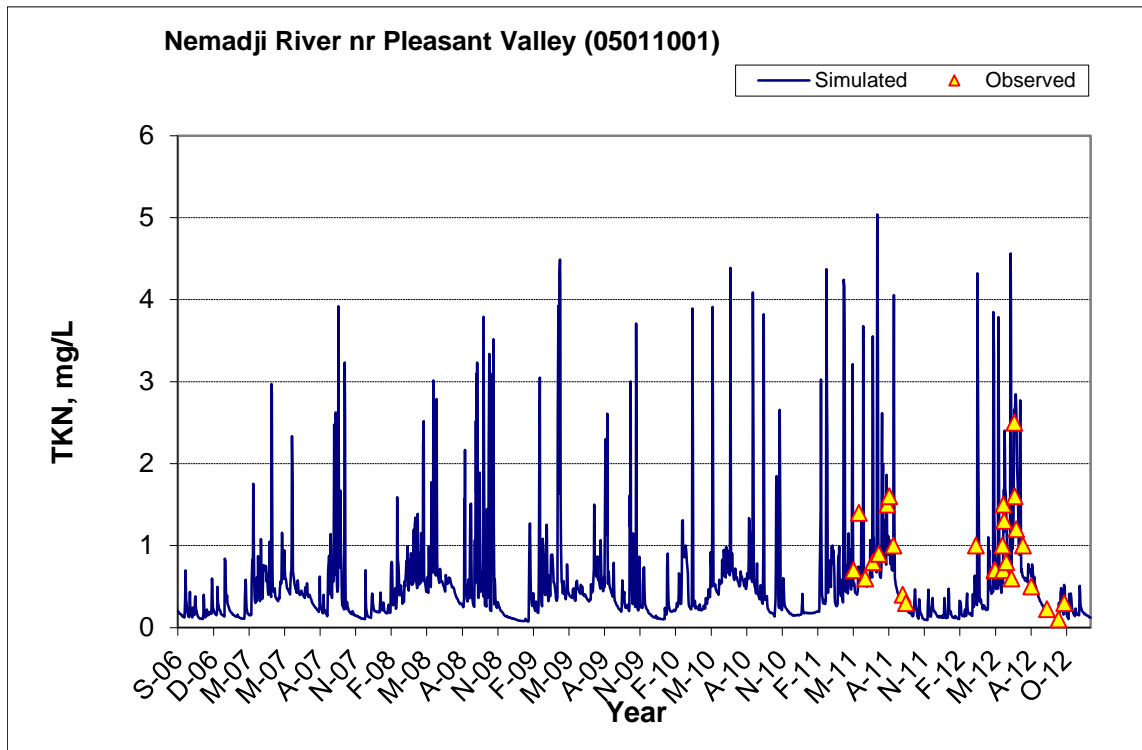


Figure B-141. Time series of observed and simulated Total Kjeldahl Nitrogen (TKN) concentration at Nemadji River nr Pleasant Valley (05011001)

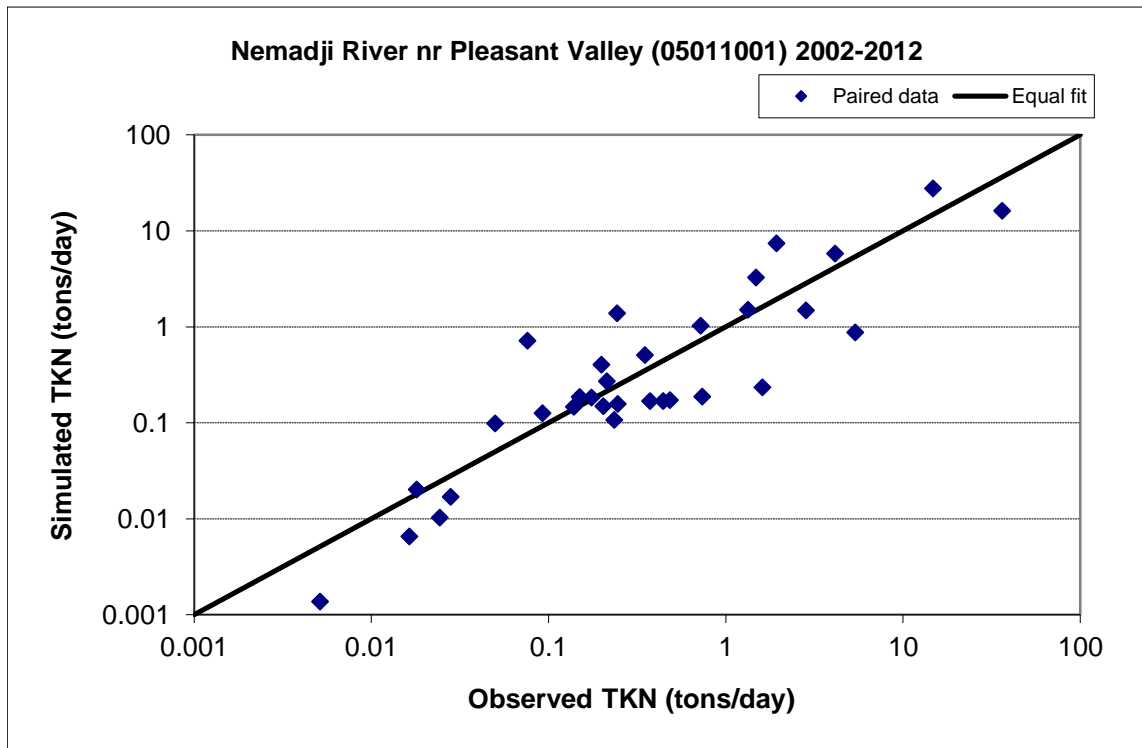


Figure B-142. Paired simulated vs. observed Total Kjeldahl Nitrogen (TKN) load at Nemadji River nr Pleasant Valley (05011001) (calibration period)

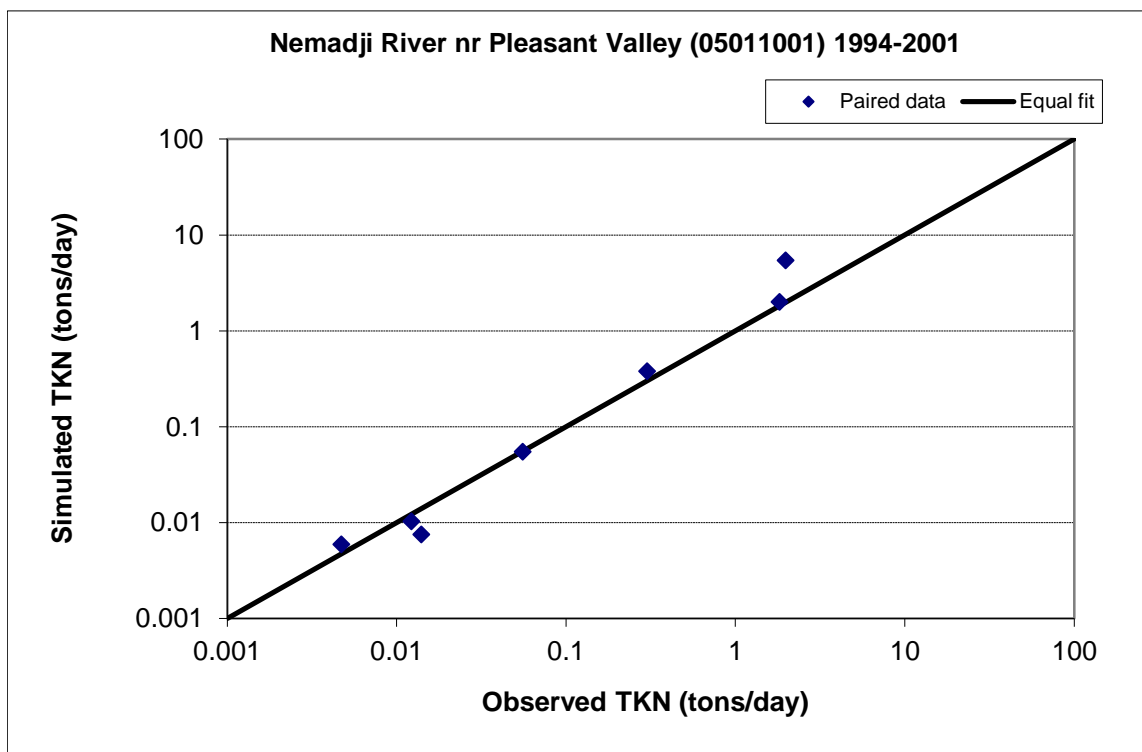


Figure B-143. Paired simulated vs. observed Total Kjeldahl Nitrogen (TKN) load at Nemadji River nr Pleasant Valley (05011001) (validation period)

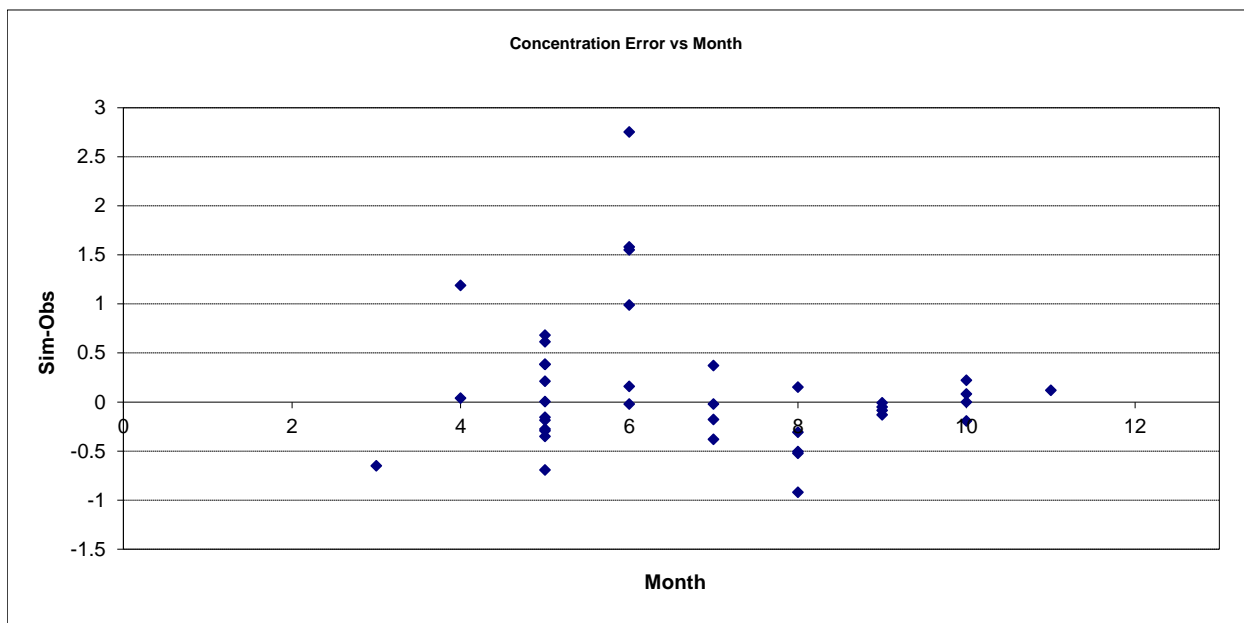


Figure B-144. Residual (Simulated - Observed) vs. Month Total Kjeldahl Nitrogen (TKN) at Nemadji River nr Pleasant Valley (05011001)

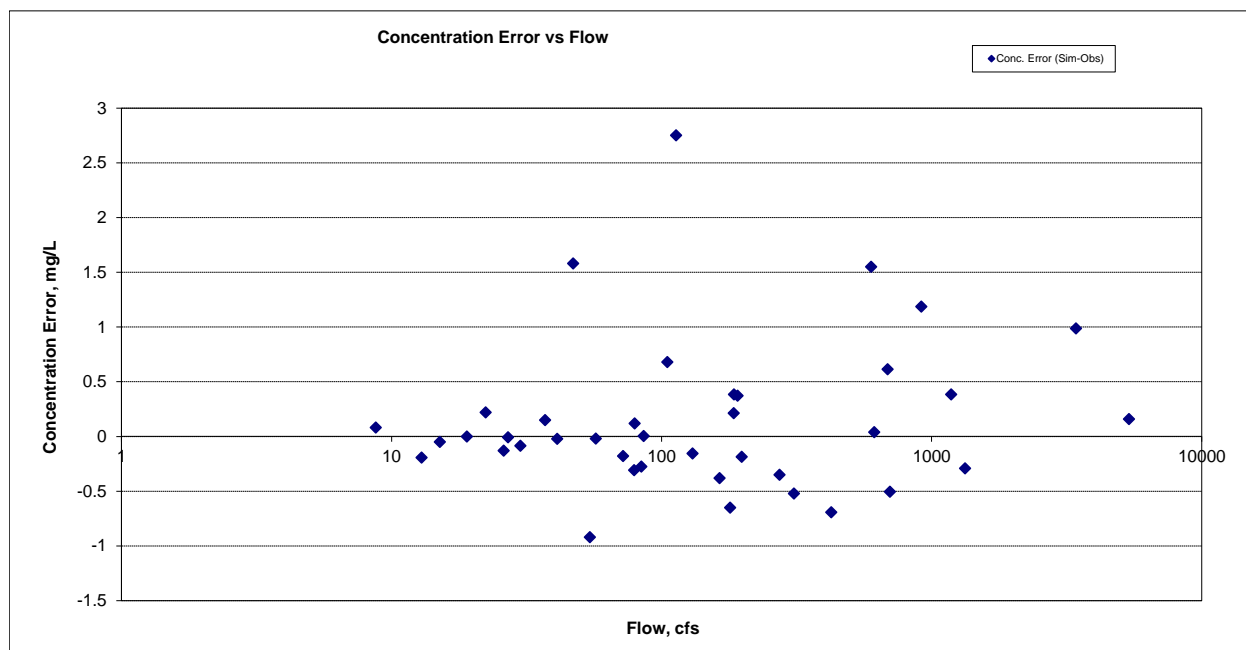


Figure B-145. Residual (Simulated - Observed) vs. Flow Total Kjeldahl Nitrogen (TKN) at Nemadji River nr Pleasant Valley (05011001)

B.5.4 Nitrite+ Nitrate Nitrogen (NOx)

Table B-25. Nitrite+ Nitrate Nitrogen (NOx) statistics

Period	1994-2001	2002-2012
Count	ND	48
Concentration Average Error		-32.35%
Concentration Median Error		-23.60%
Load Average Error		-2.75%
Load Median Error		-5.39%
Paired t conc		0.15
Paired t load		0.70

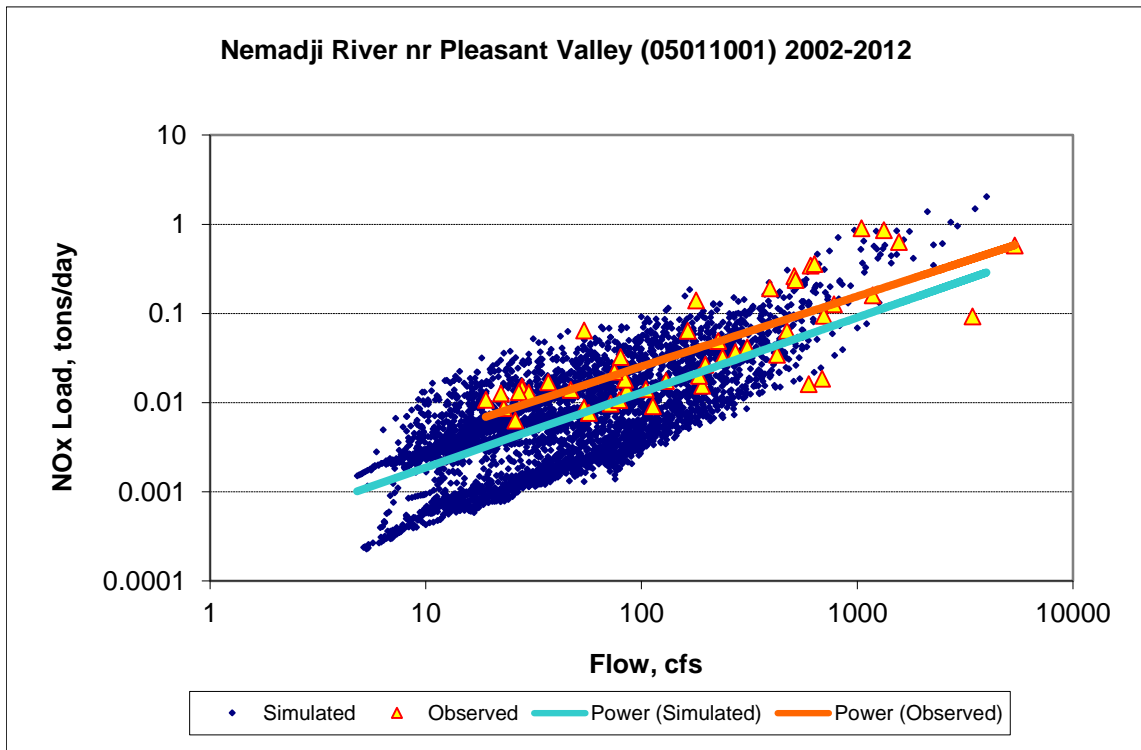
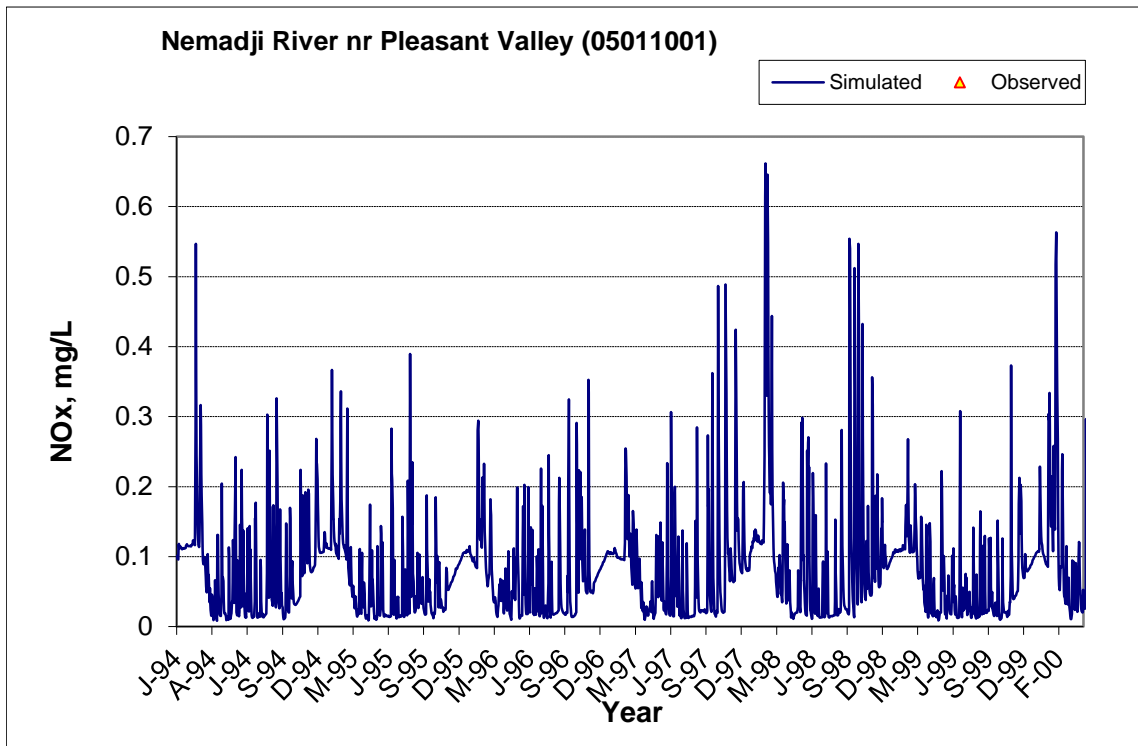


Figure B-146. Power plot of simulated and observed Nitrite+ Nitrate Nitrogen (NOx) load vs flow at Nemadji River nr Pleasant Valley (05011001) (calibration period)



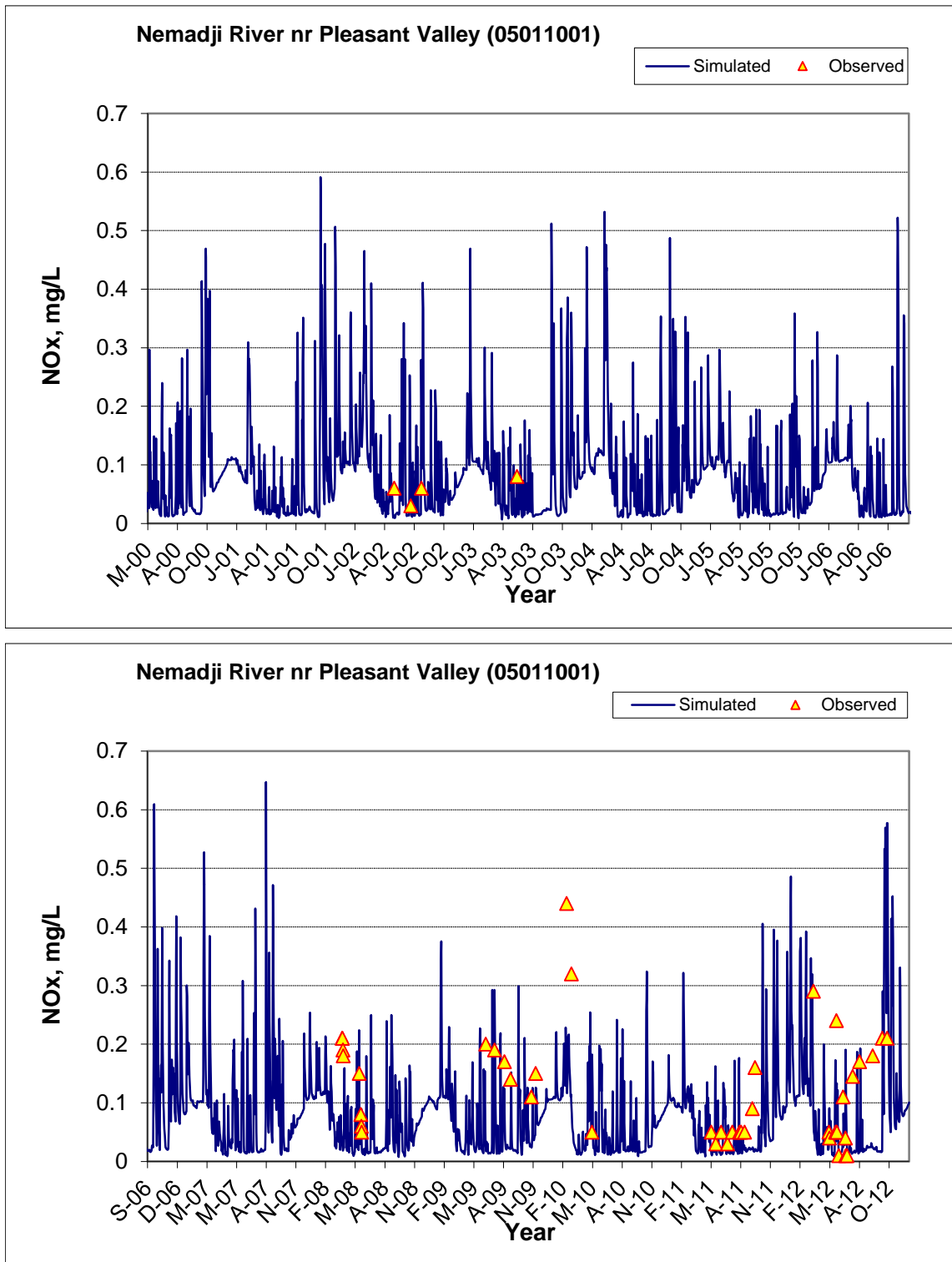


Figure B-147. Time series of observed and simulated Nitrite+ Nitrate Nitrogen (NOx) concentration at Nemadji River nr Pleasant Valley (05011001)

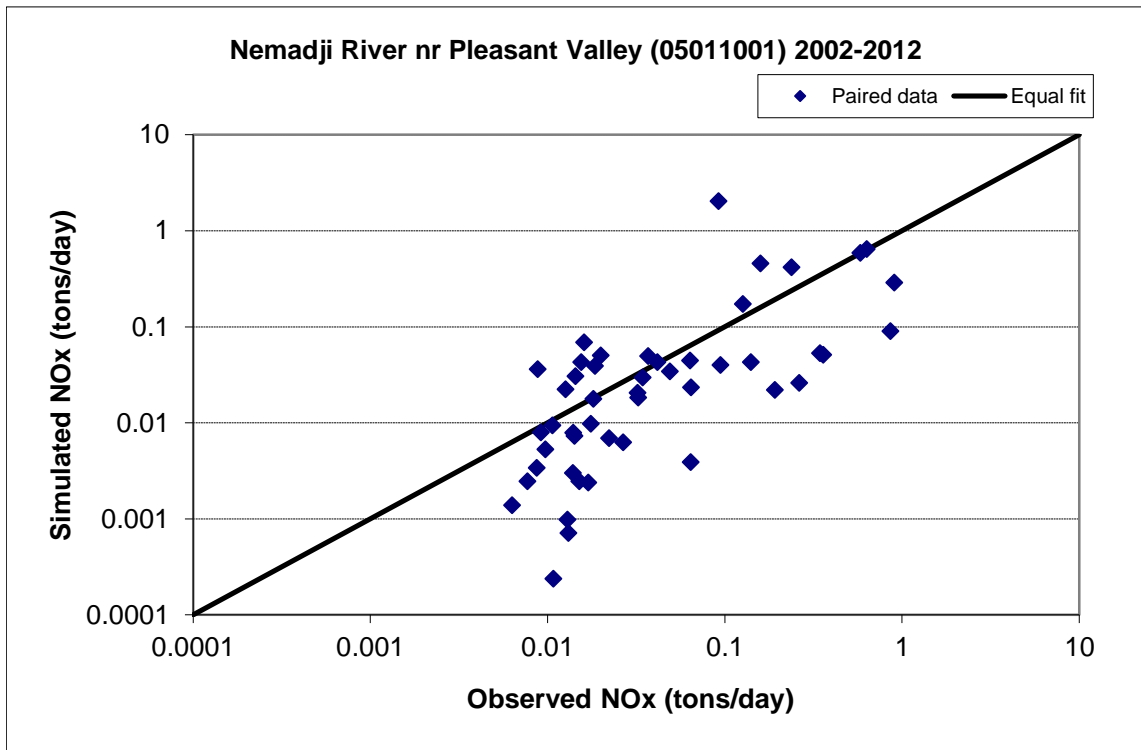


Figure B-148. Paired simulated vs. observed Nitrite+ Nitrate Nitrogen (NOx) load at Nemadji River nr Pleasant Valley (05011001) (calibration period)

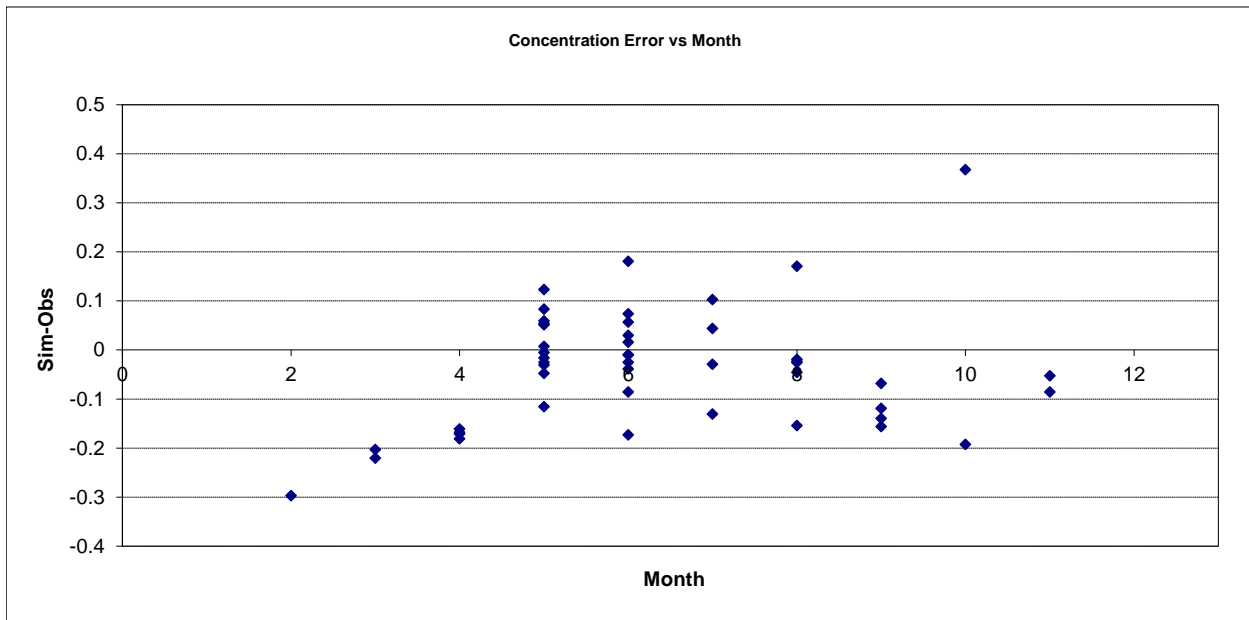


Figure B-149. Residual (Simulated - Observed) vs. Month Nitrite+ Nitrate Nitrogen (NOx) at Nemadji River nr Pleasant Valley (05011001)

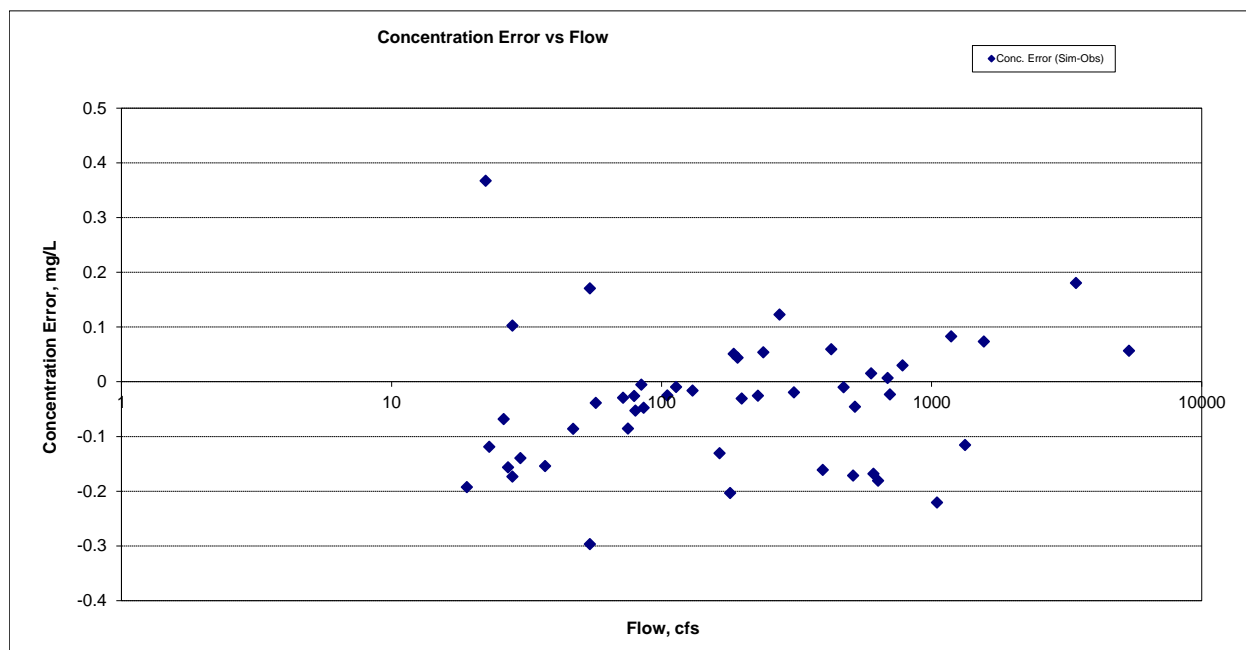


Figure B-150. Residual (Simulated - Observed) vs. Flow Nitrite+ Nitrate Nitrogen (NOx) at Nemadji River nr Pleasant Valley (05011001)

B.5.5 Total Nitrogen (TN)

Table B-26. Total Nitrogen (TN) statistics

Period	1994-2001	2002-2012
Count	ND	31
Concentration Average Error		11.29%
Concentration Median Error		-16.71%
Load Average Error		-3.90%
Load Median Error		-0.12%
Paired t conc		0.76
Paired t load		0.63

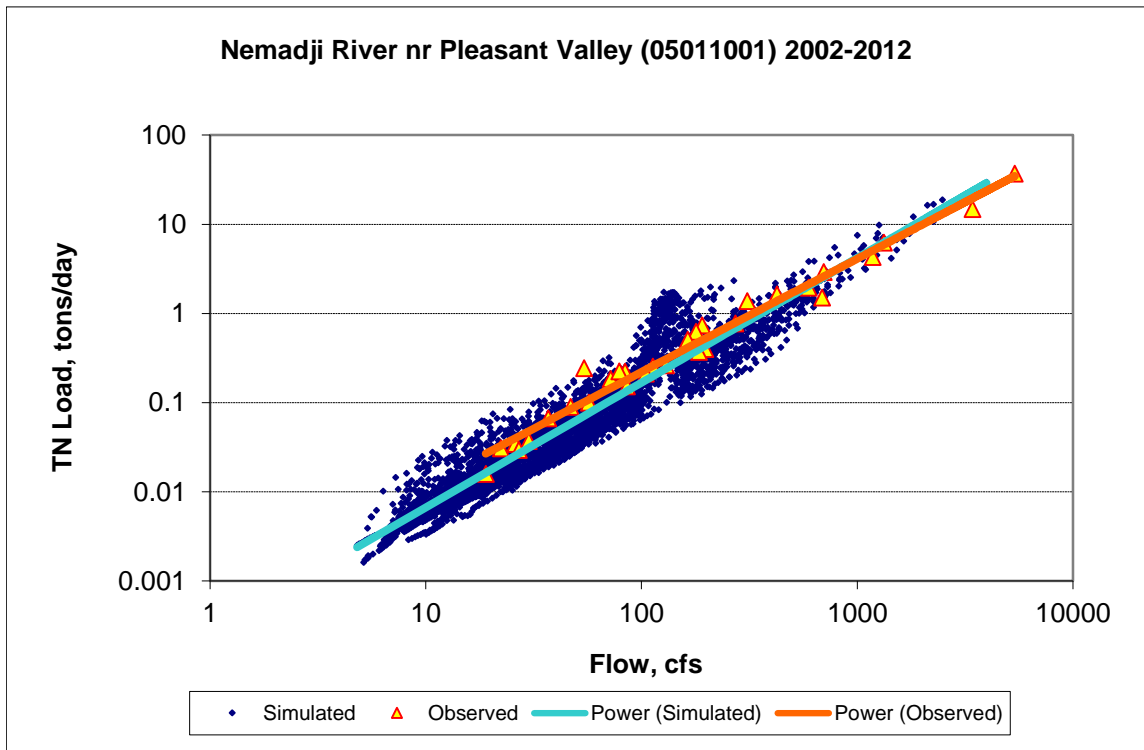
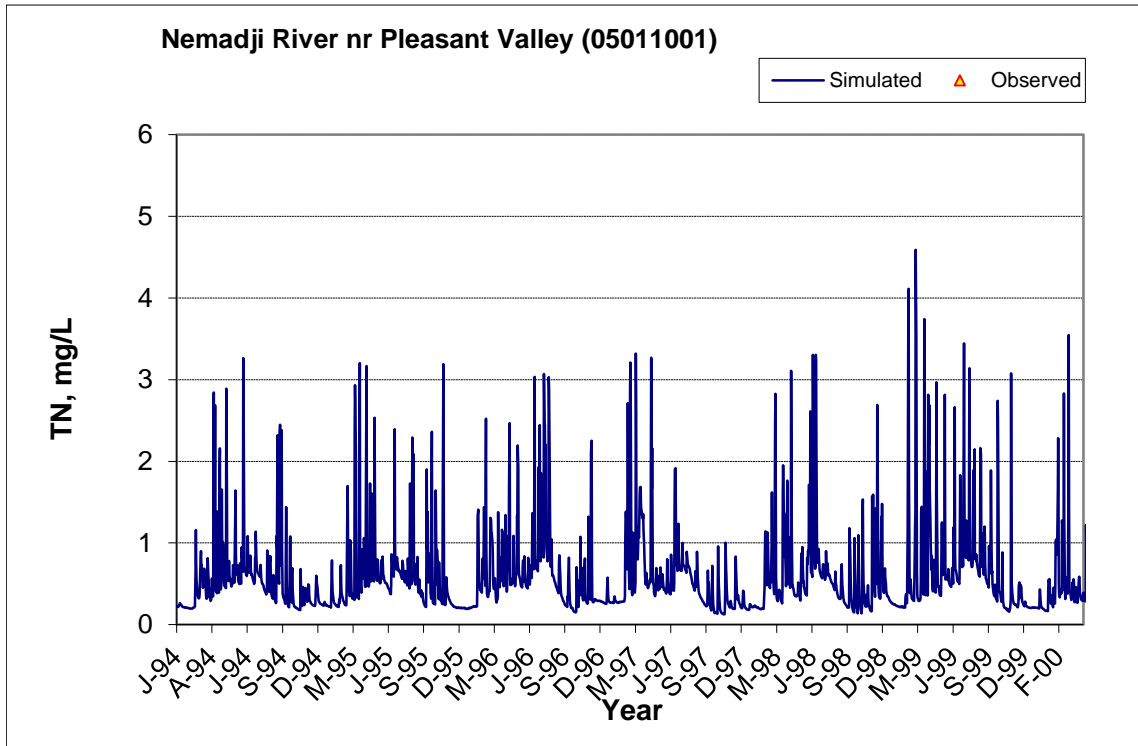


Figure B-151. Power plot of simulated and observed Total Nitrogen (TN) load vs flow at Nemadji River nr Pleasant Valley (05011001) (calibration period)



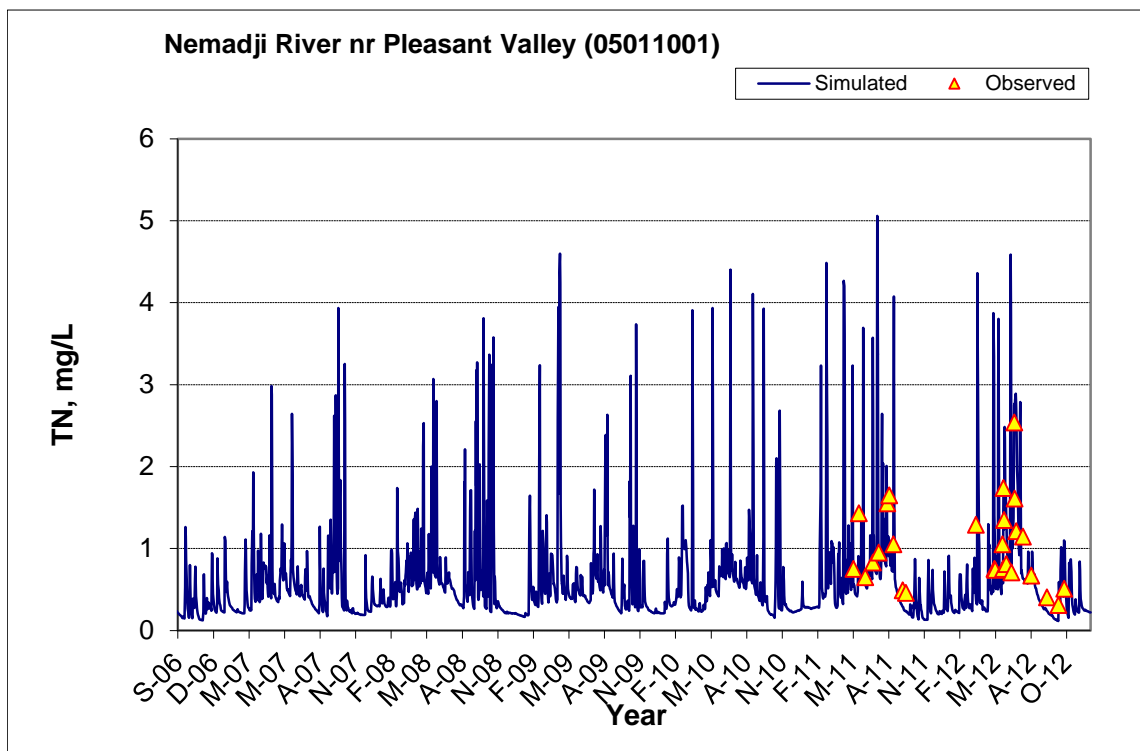
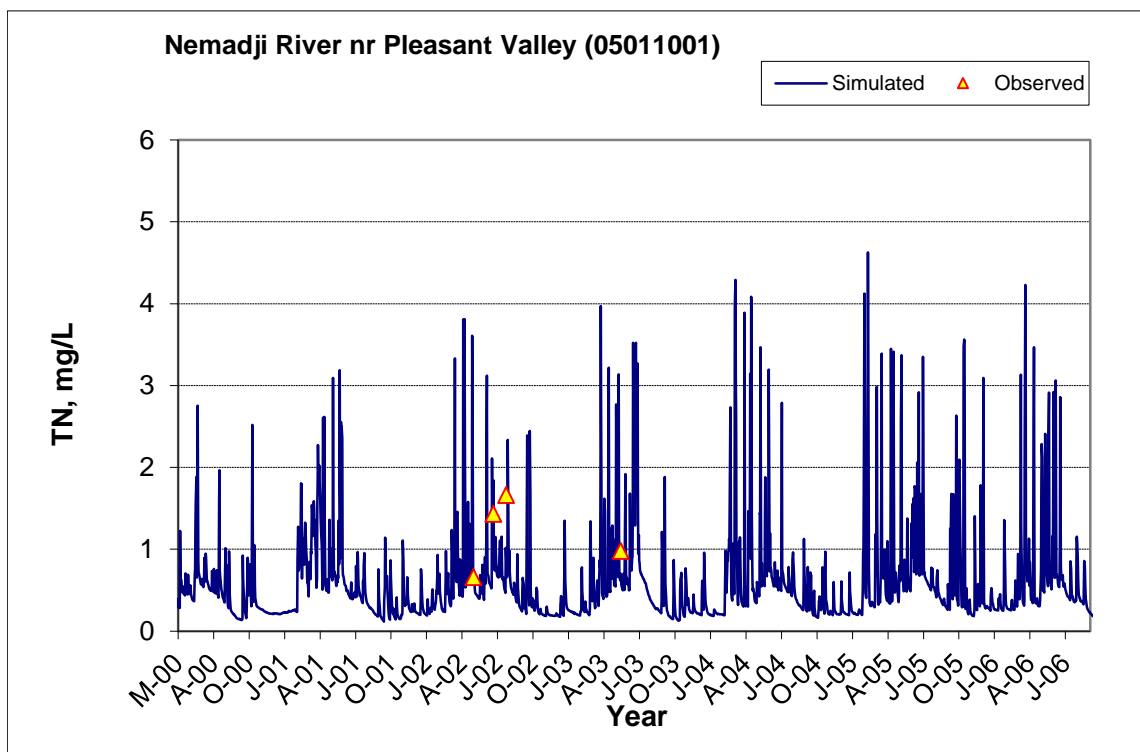


Figure B-152. Time series of observed and simulated Total Nitrogen (TN) concentration at Nemadji River nr Pleasant Valley (05011001)

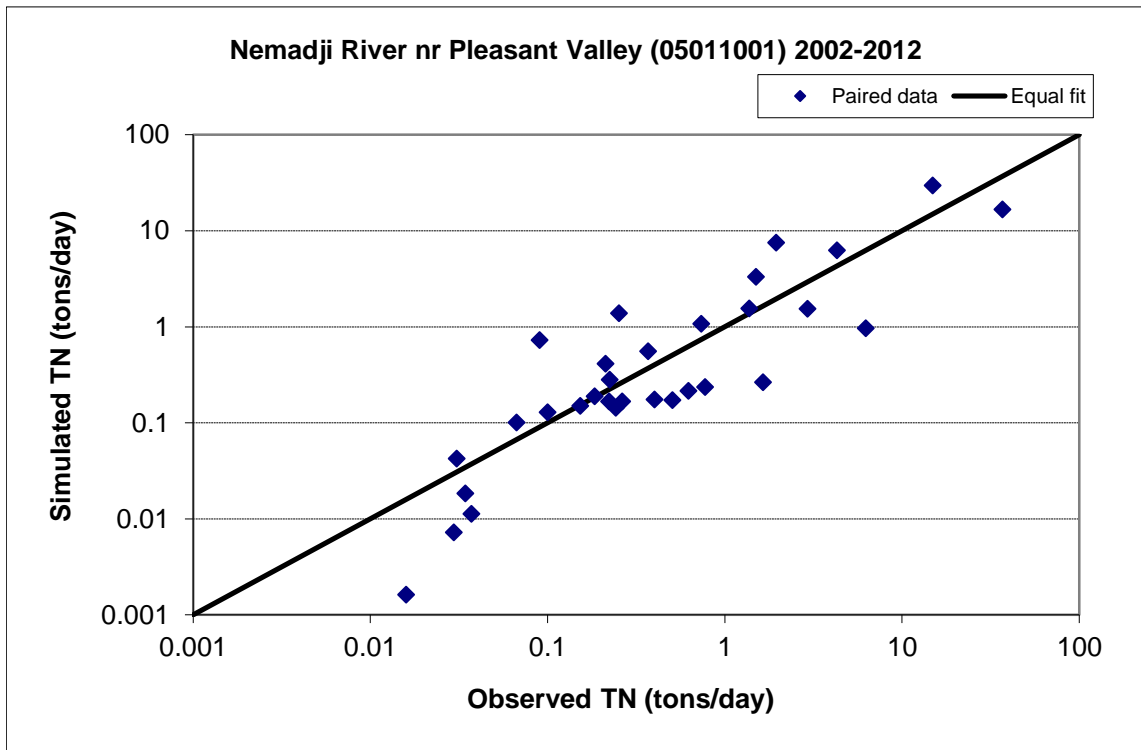


Figure B-153. Paired simulated vs. observed Total Nitrogen (TN) load at Nemadji River nr Pleasant Valley (05011001) (calibration period)

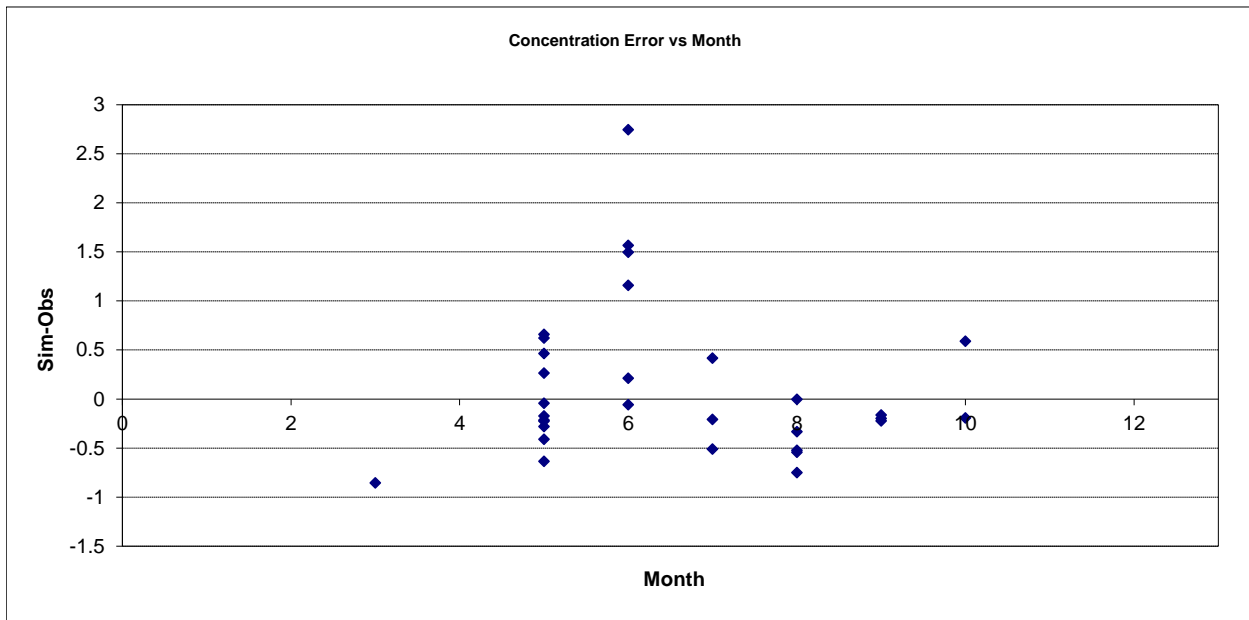


Figure B-154. Residual (Simulated - Observed) vs. Month Total Nitrogen (TN) at Nemadji River nr Pleasant Valley (05011001)

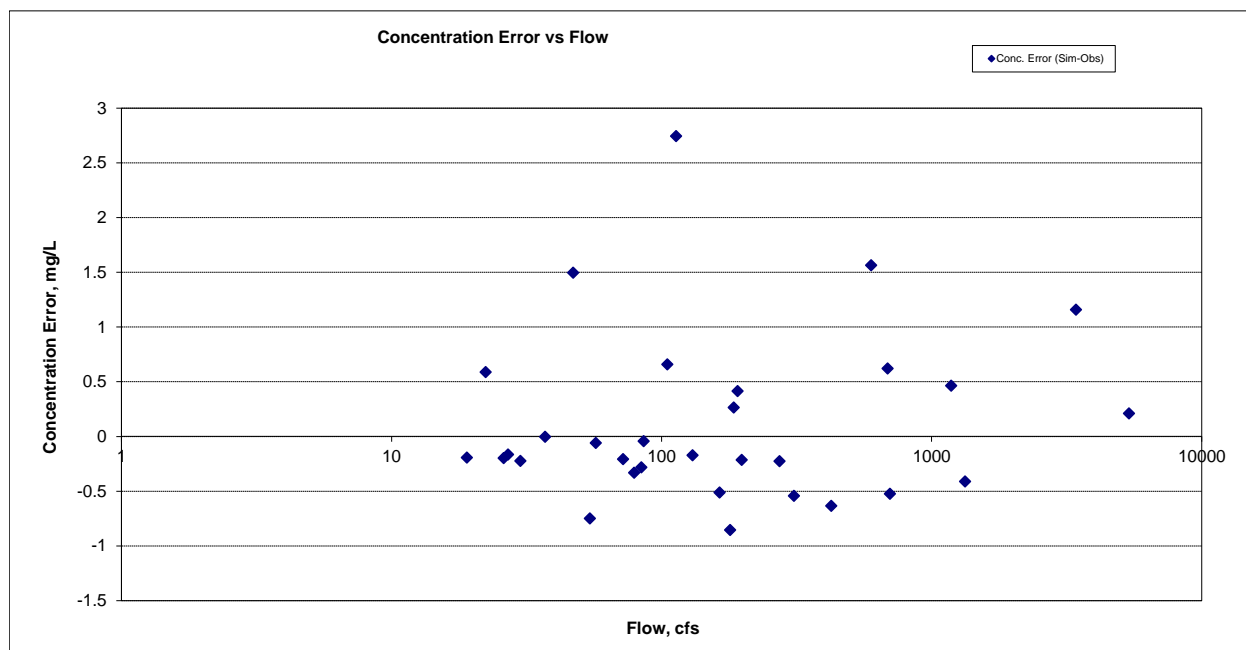


Figure B-155. Residual (Simulated - Observed) vs. Flow Total Nitrogen (TN) at Nemadji River nr Pleasant Valley (05011001)

B.5.6 Soluble Reactive Phosphorus (SRP)

Table B-27. Soluble Reactive Phosphorus (SRP) statistics

Period	1994-2001	2002-2012
Count	ND	39
Concentration Average Error		20.78%
Concentration Median Error		5.59%
Load Average Error		37.02%
Load Median Error		-0.03%
Paired t conc		0.49
Paired t load		0.40

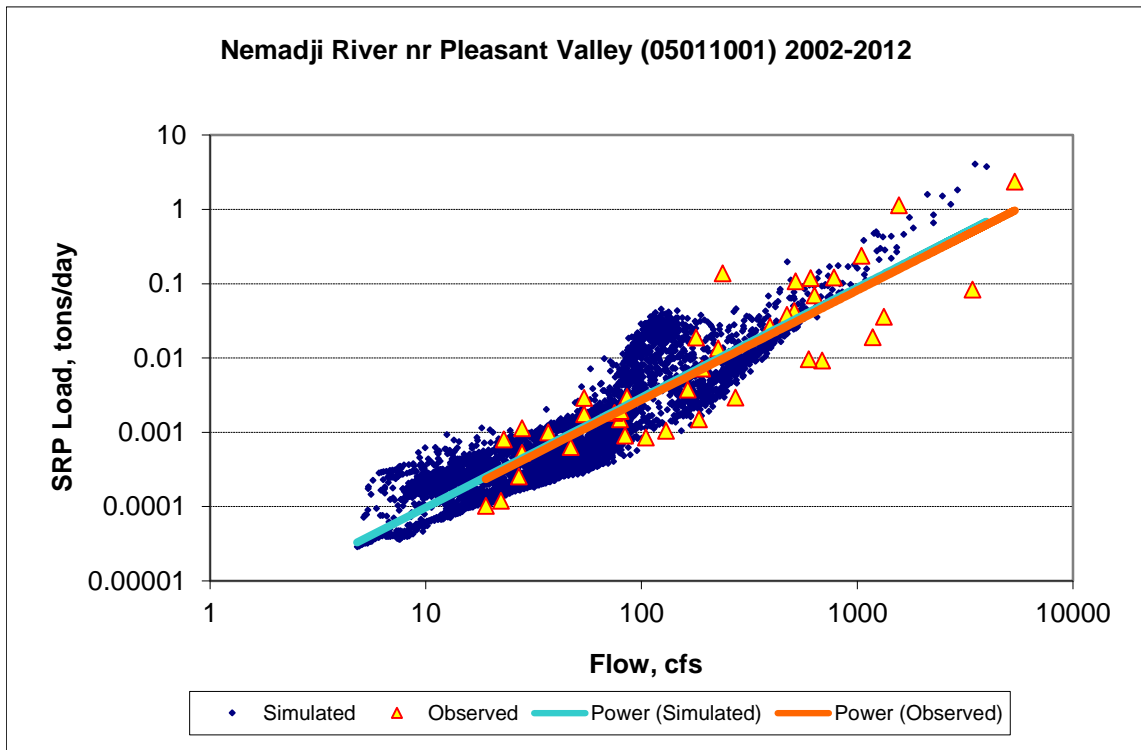
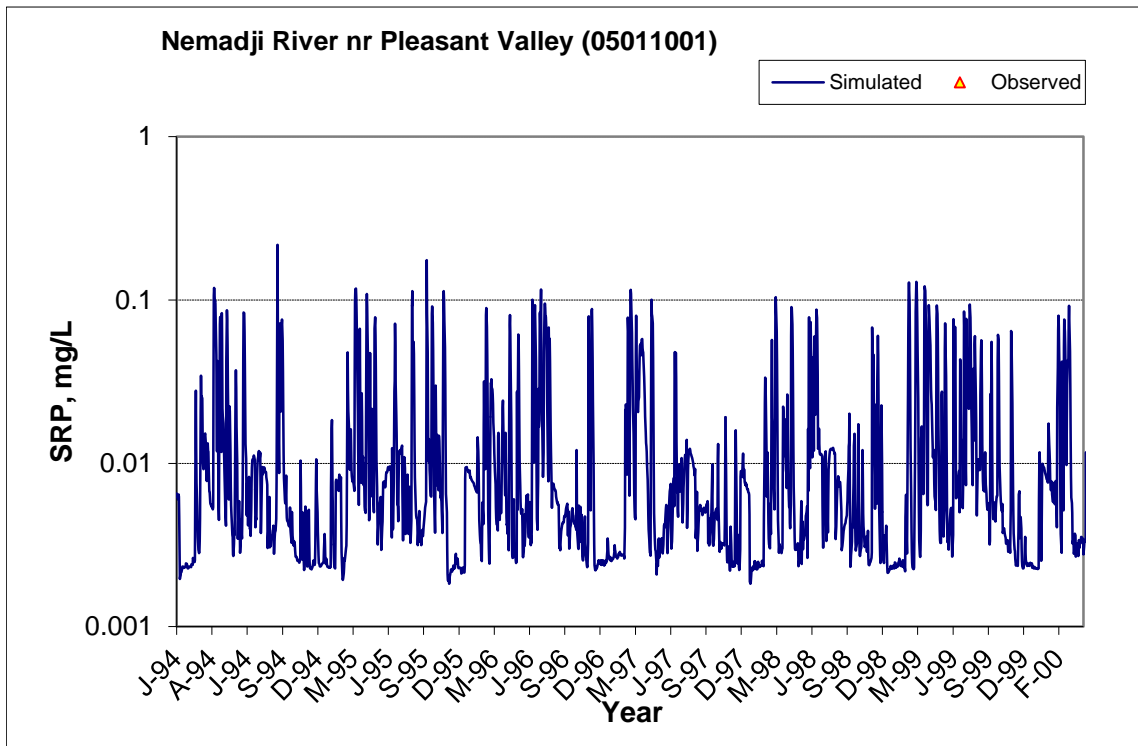


Figure B-156. Power plot of simulated and observed Soluble Reactive Phosphorus (SRP) load vs flow at Nemadji River nr Pleasant Valley (05011001) (calibration period)



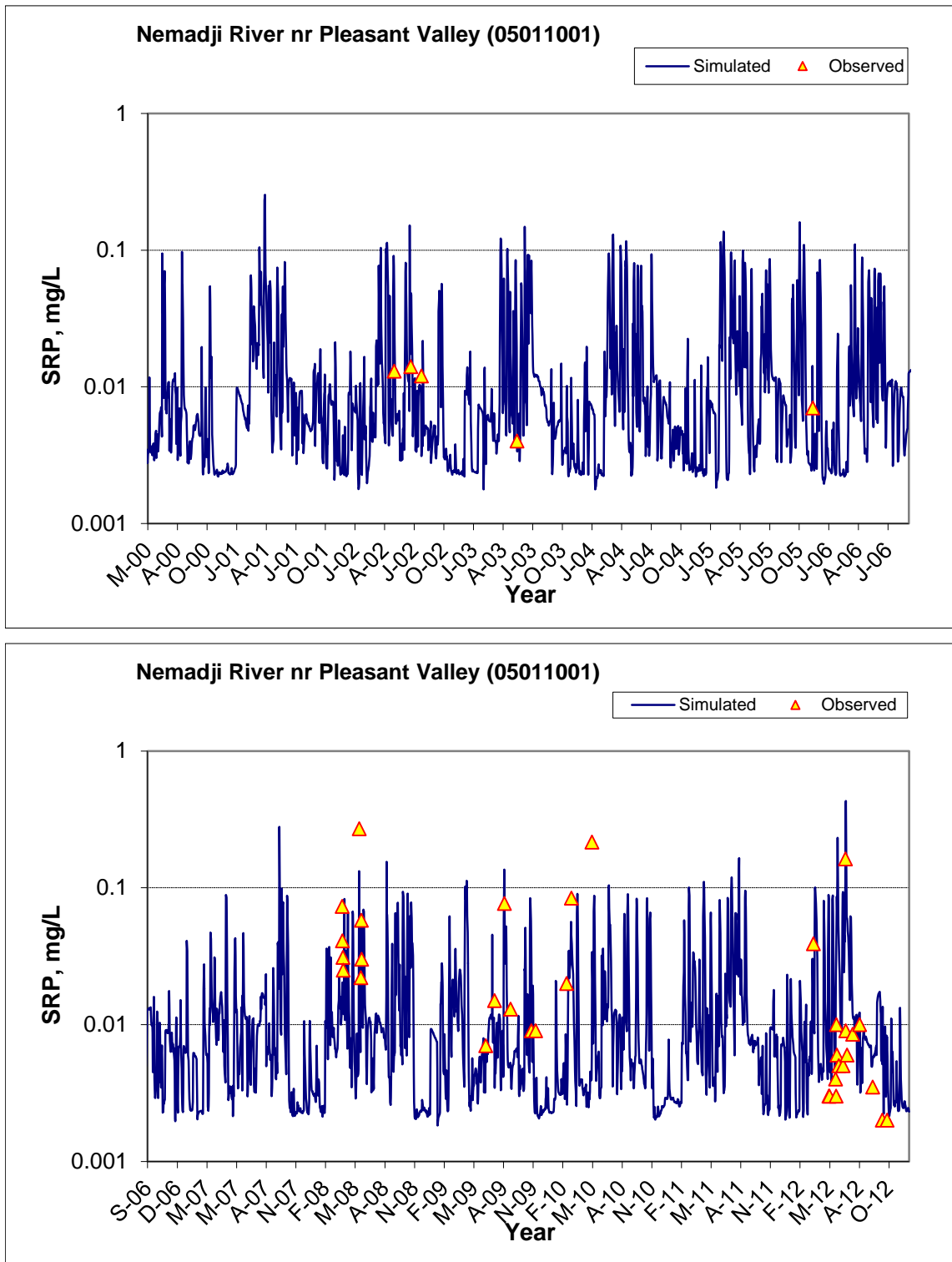


Figure B-157. Time series of observed and simulated Soluble Reactive Phosphorus (SRP) concentration at Nemadji River nr Pleasant Valley (05011001)

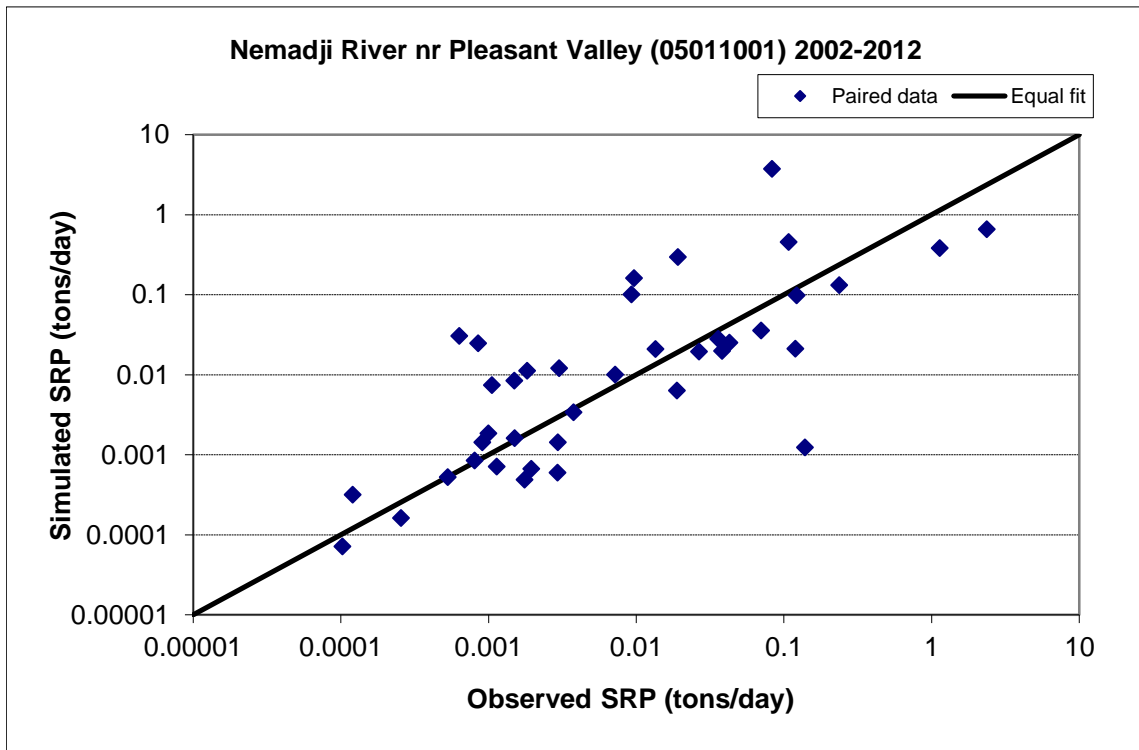


Figure B-158. Paired simulated vs. observed Soluble Reactive Phosphorus (SRP) load at Nemadji River nr Pleasant Valley (05011001) (calibration period)

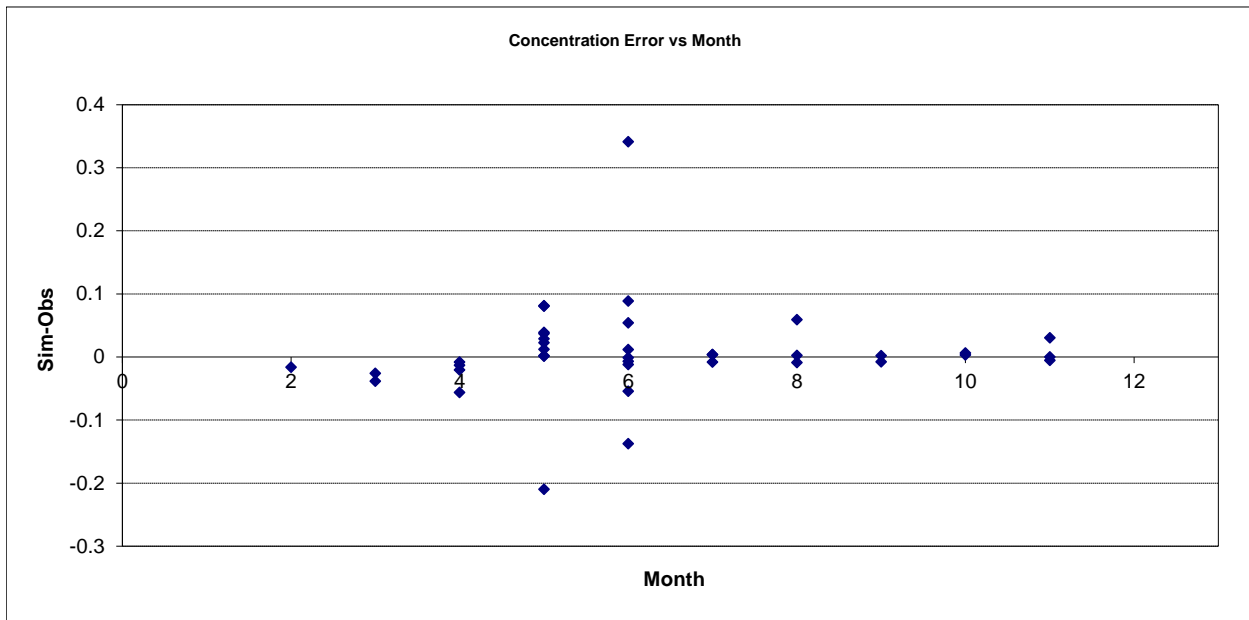


Figure B-159. Residual (Simulated - Observed) vs. Month Soluble Reactive Phosphorus (SRP) at Nemadji River nr Pleasant Valley (05011001)

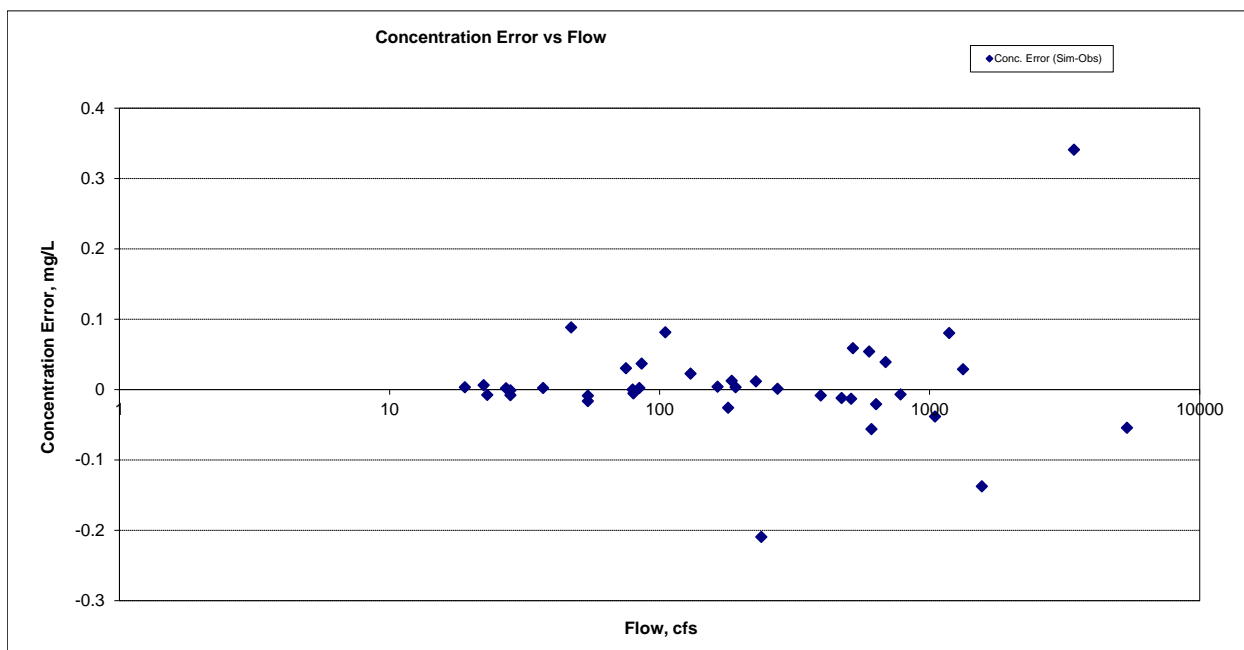
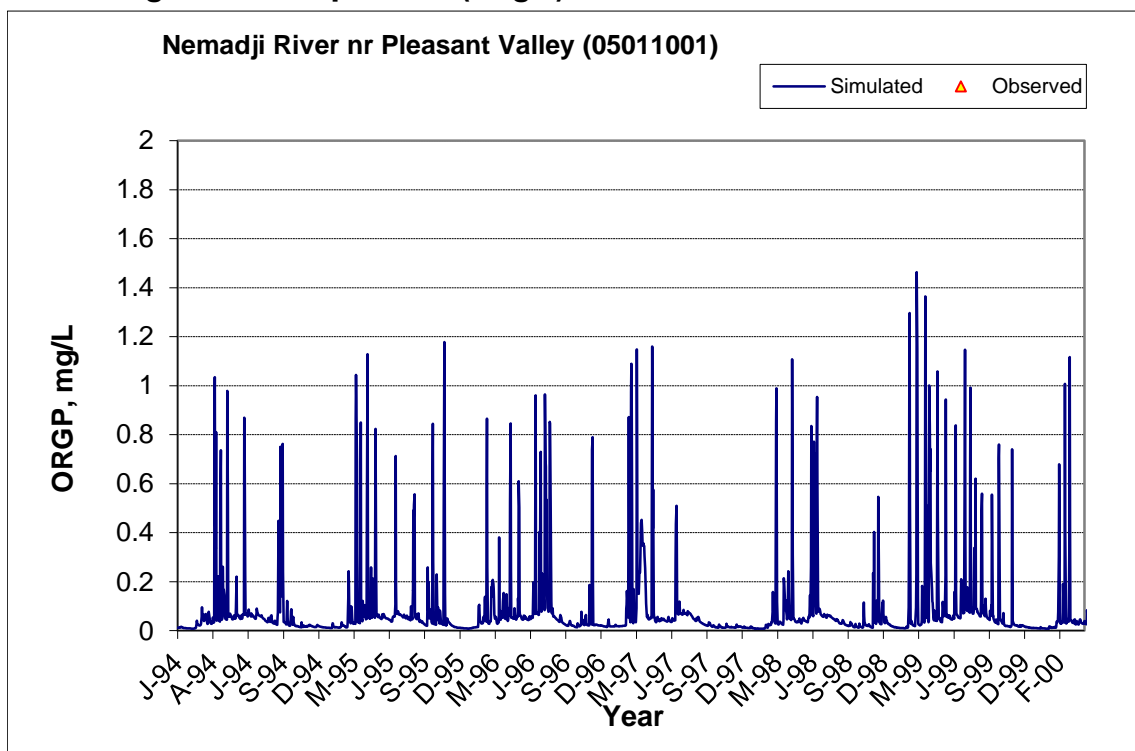


Figure B-160. Residual (Simulated - Observed) vs. Flow Soluble Reactive Phosphorus (SRP) at Nemadji River nr Pleasant Valley (05011001)

B.5.7 Organic Phosphorus (OrgP)



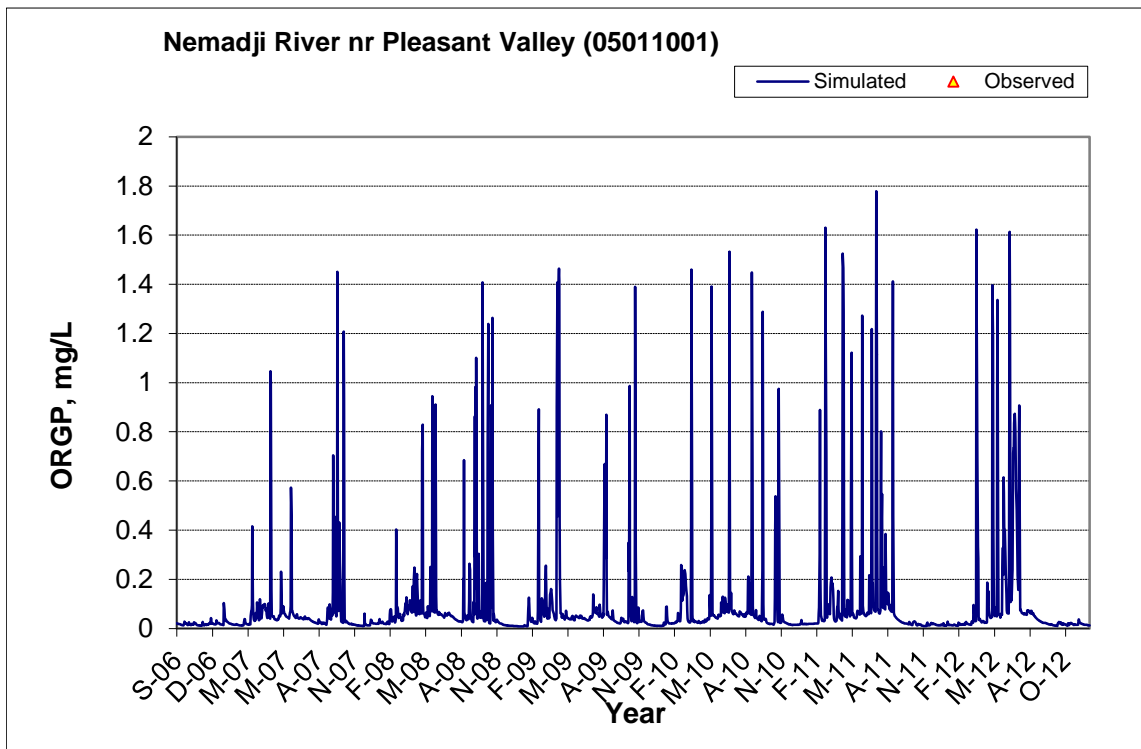
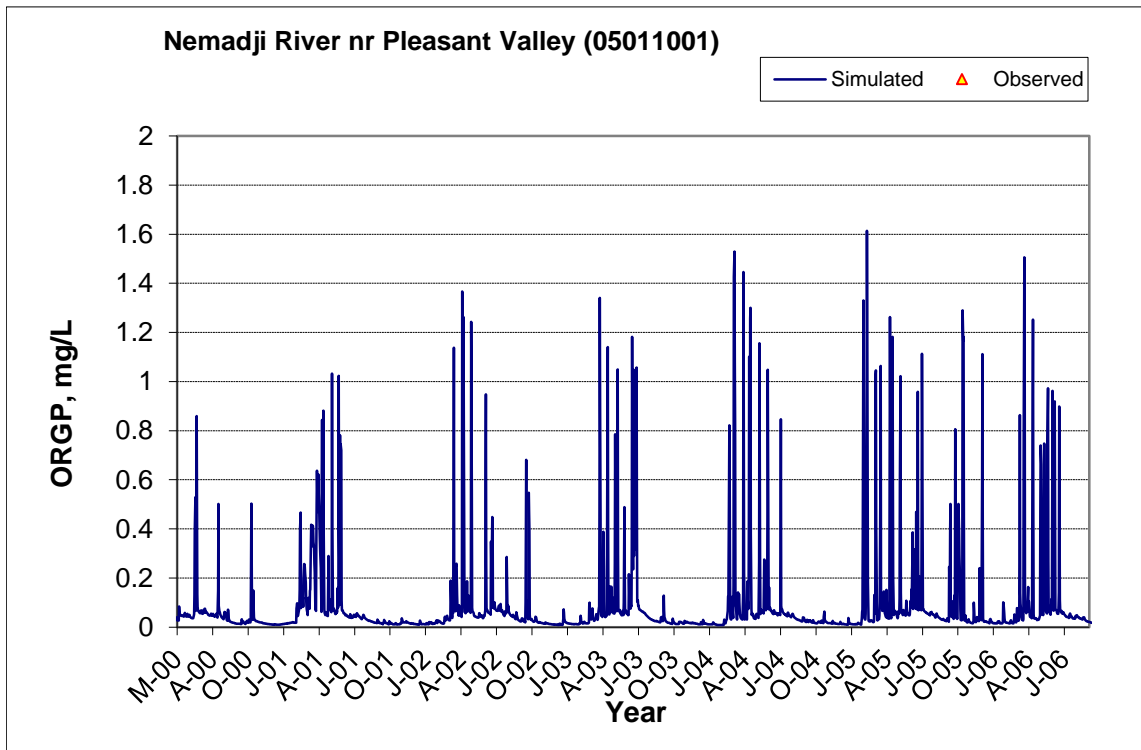


Figure B-161. Time series of observed and simulated Organic Phosphorus (OrgP) concentration at Nemadji River nr Pleasant Valley (05011001)

B.5.8 Total Phosphorus (TP)

Table B-28. Total Phosphorus (TP) statistics

Period	1994-2001	2002-2012
Count	22	100
Concentration Average Error	59.18%	-8.31%
Concentration Median Error	11.38%	0.53%
Load Average Error	35.16%	-35.49%
Load Median Error	0.81%	-0.03%
Paired t conc	0.20	0.82
Paired t load	0.41	0.33

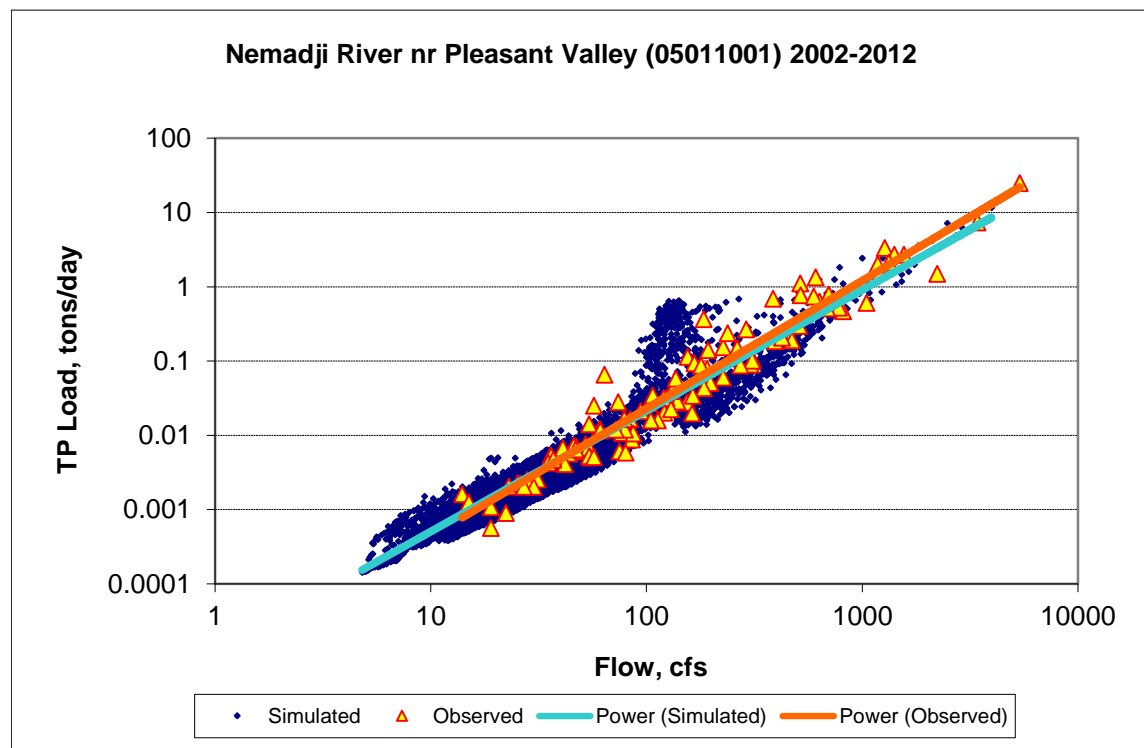


Figure B-162. Power plot of simulated and observed Total Phosphorus (TP) load vs flow at Nemadji River nr Pleasant Valley (05011001) (calibration period)

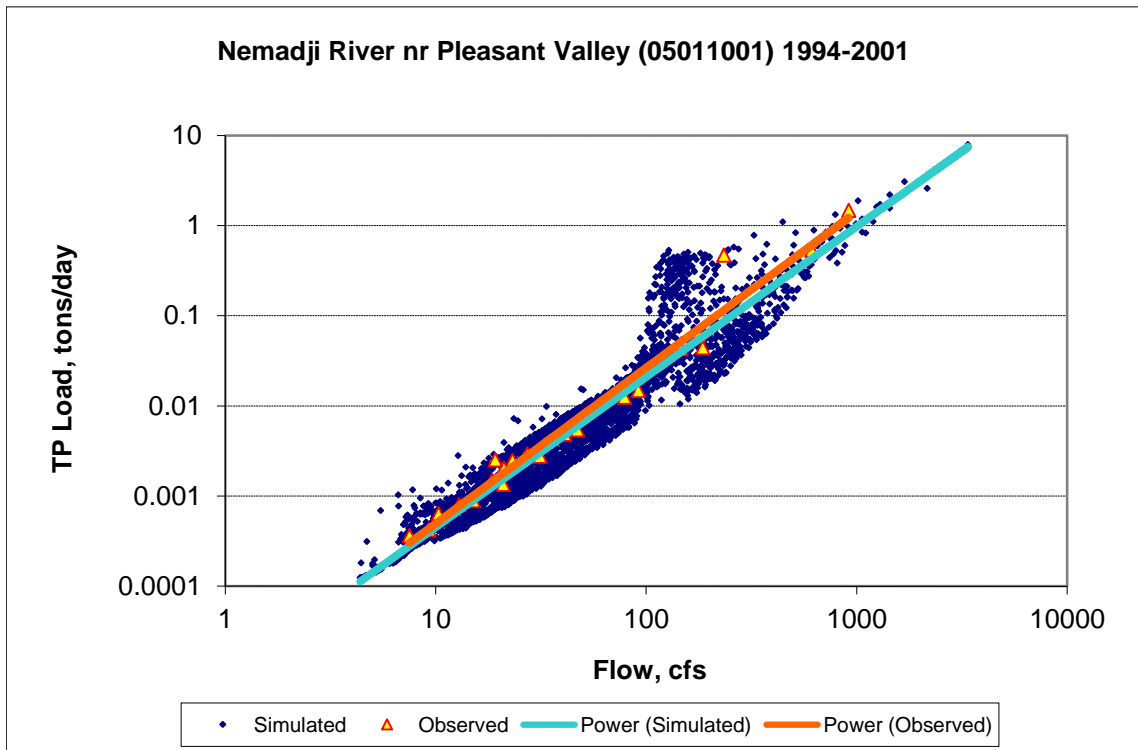
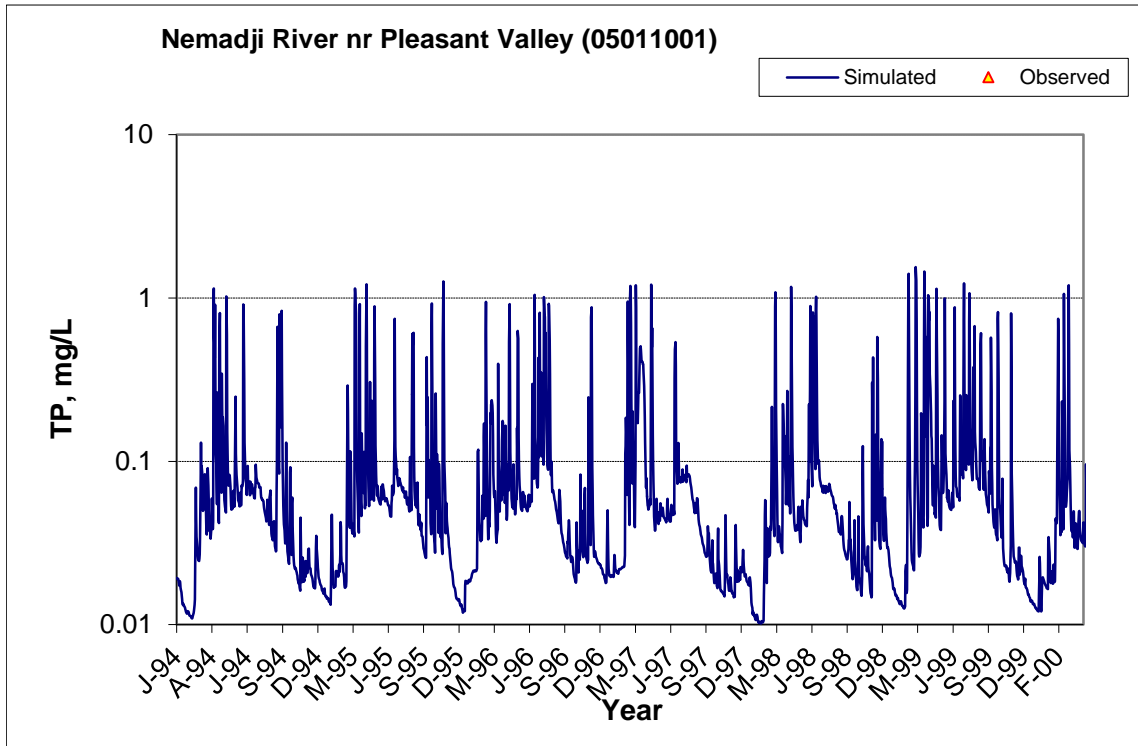


Figure B-163. Power plot of simulated and observed Total Phosphorus (TP) load vs flow at Nemadji River nr Pleasant Valley (05011001) (validation period)



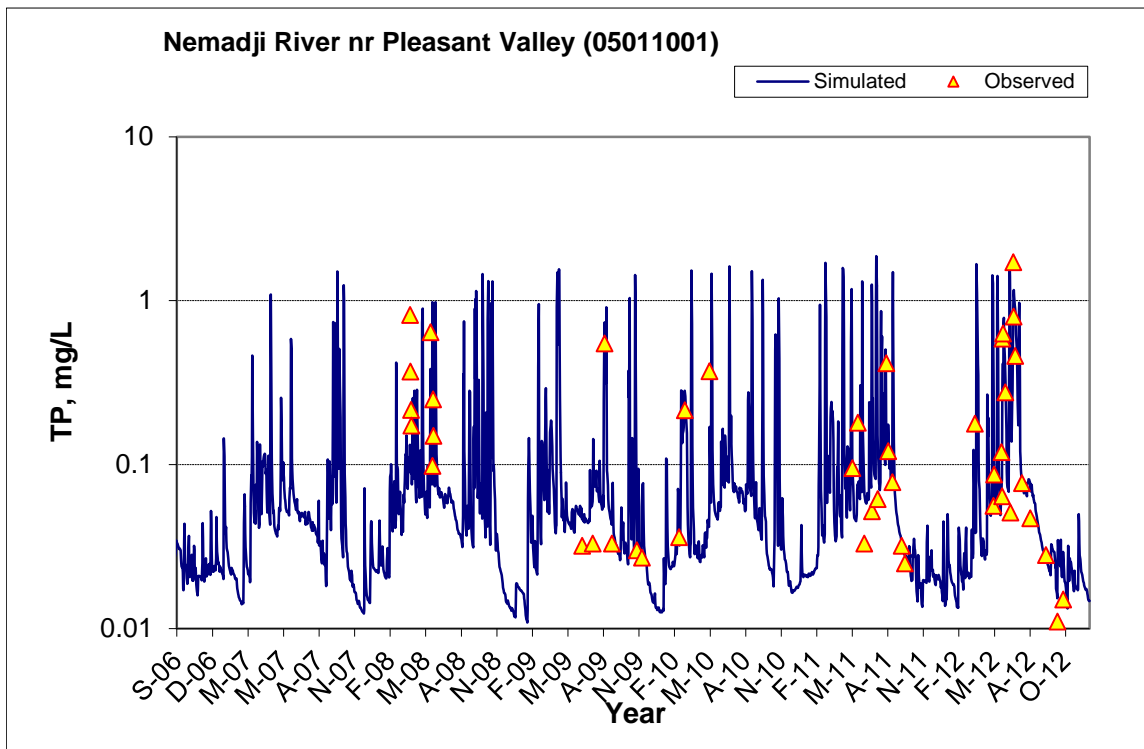
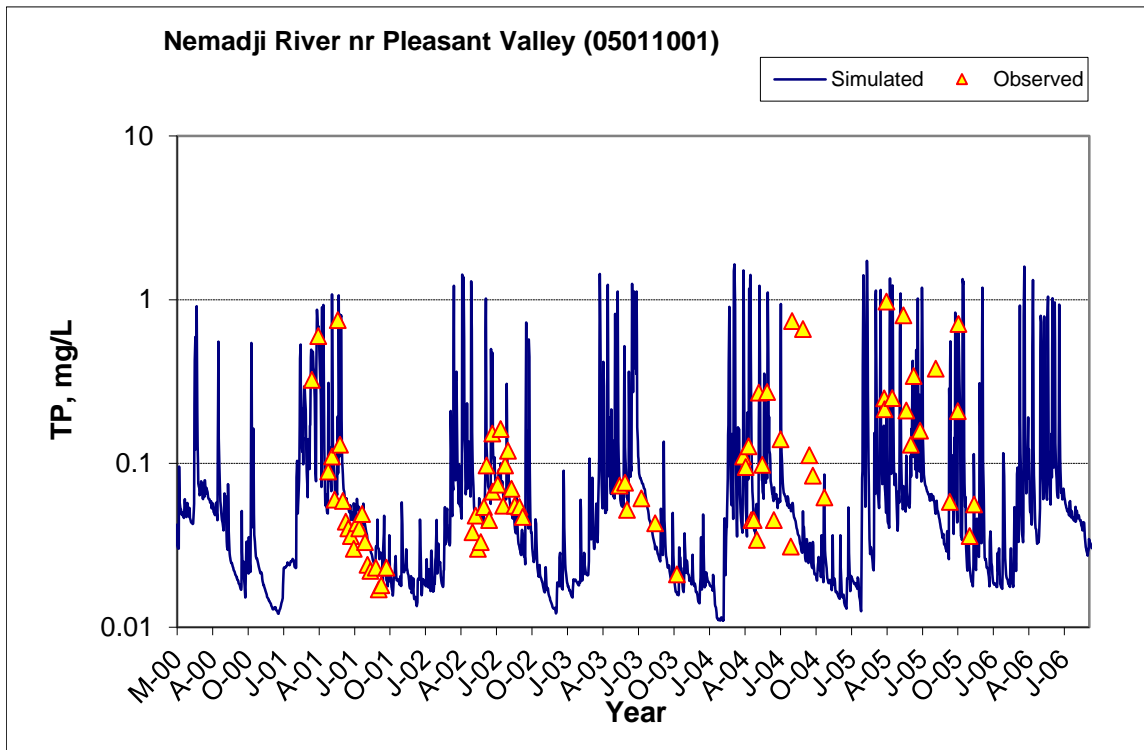


Figure B-164. Time series of observed and simulated Total Phosphorus (TP) concentration at Nemadji River nr Pleasant Valley (05011001)

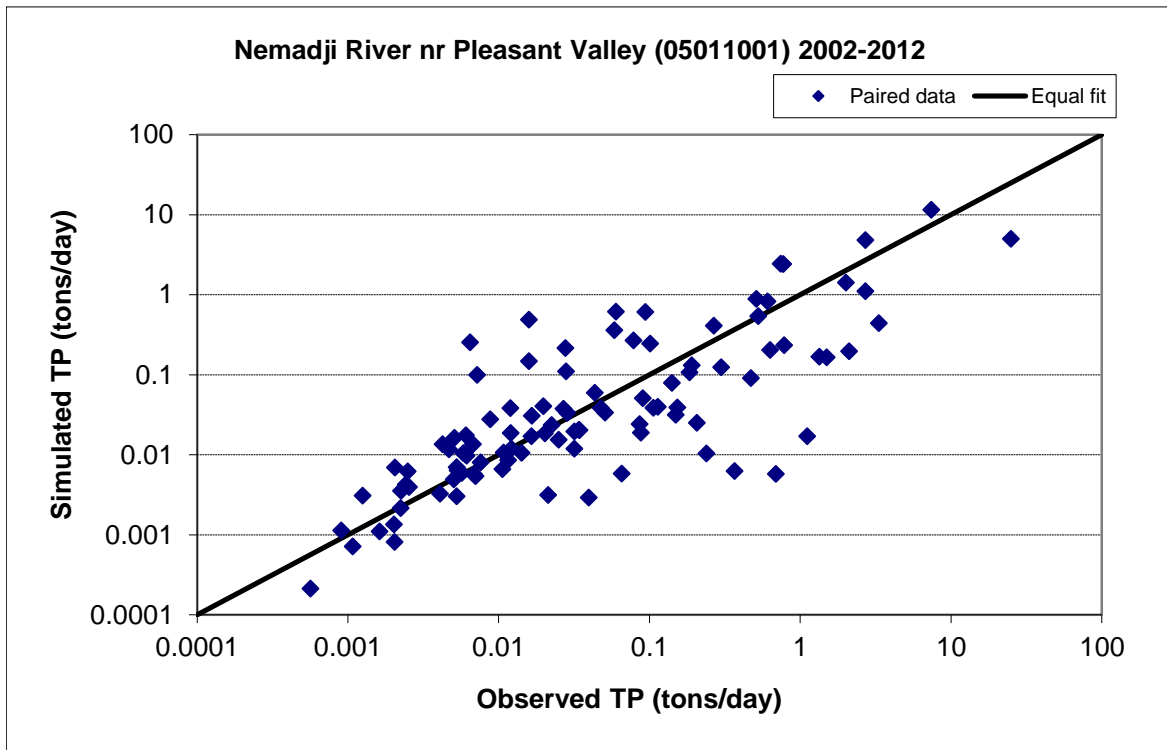


Figure B-165. Paired simulated vs. observed Total Phosphorus (TP) load at Nemadji River nr Pleasant Valley (05011001) (calibration period)

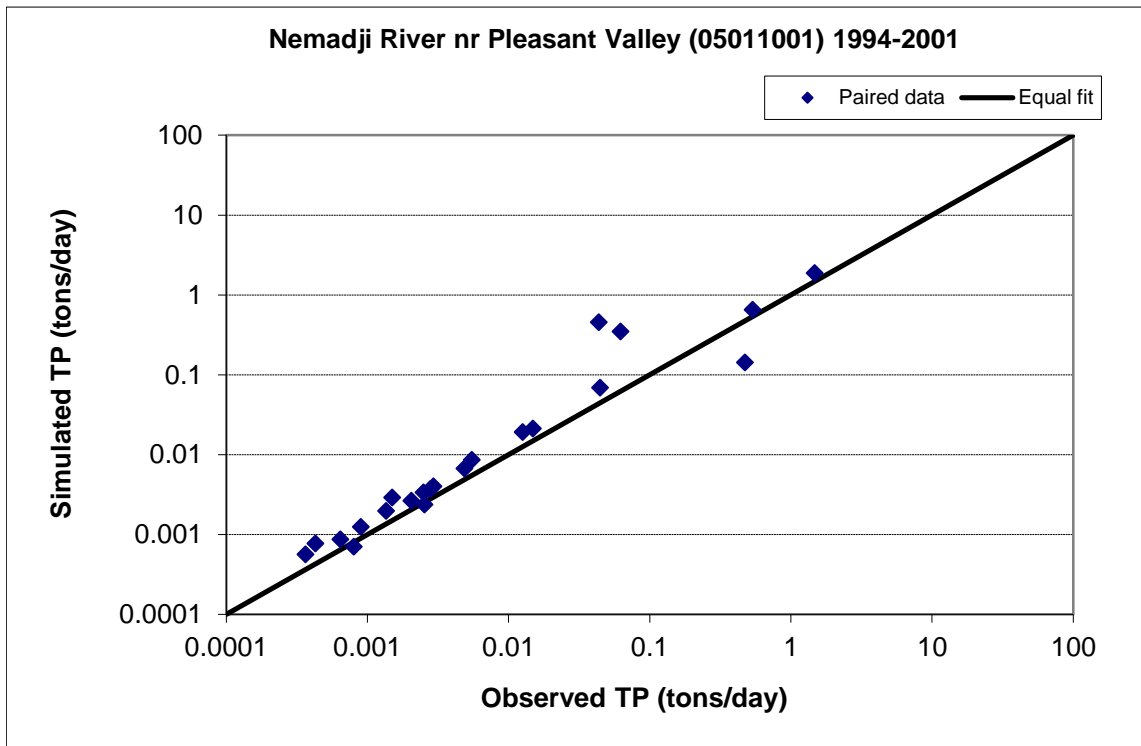


Figure B-166. Paired simulated vs. observed Total Phosphorus (TP) load at Nemadji River nr Pleasant Valley (05011001) (validation period)

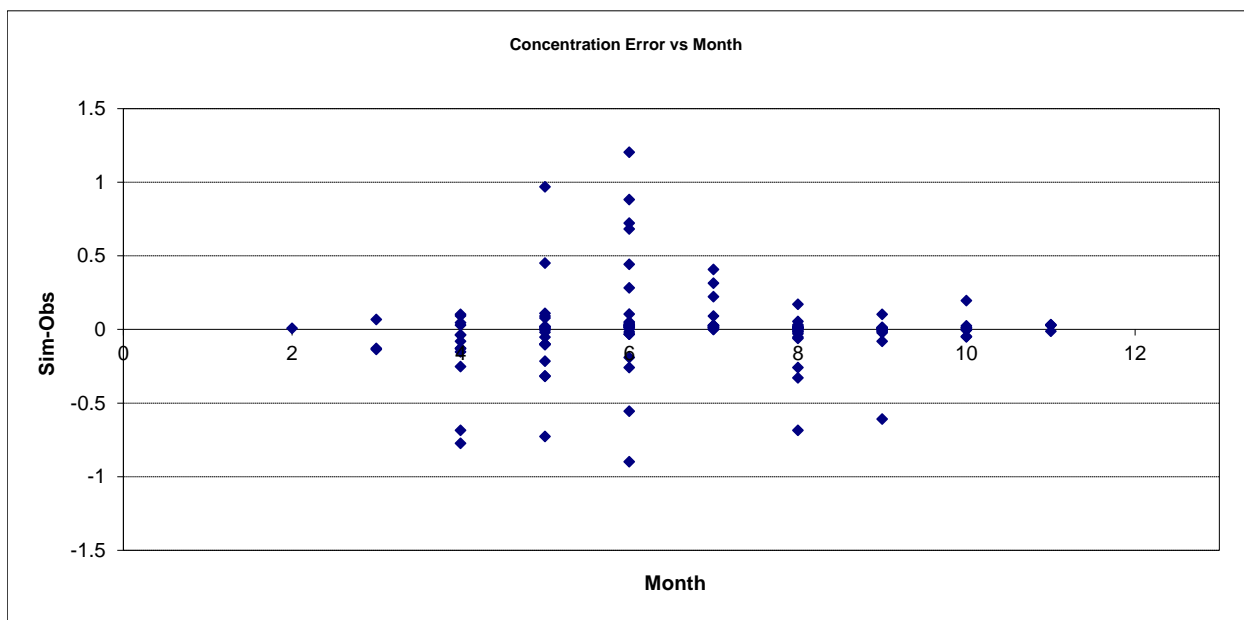


Figure B-167. Residual (Simulated - Observed) vs. Month Total Phosphorus (TP) at Nemadji River nr Pleasant Valley (05011001)

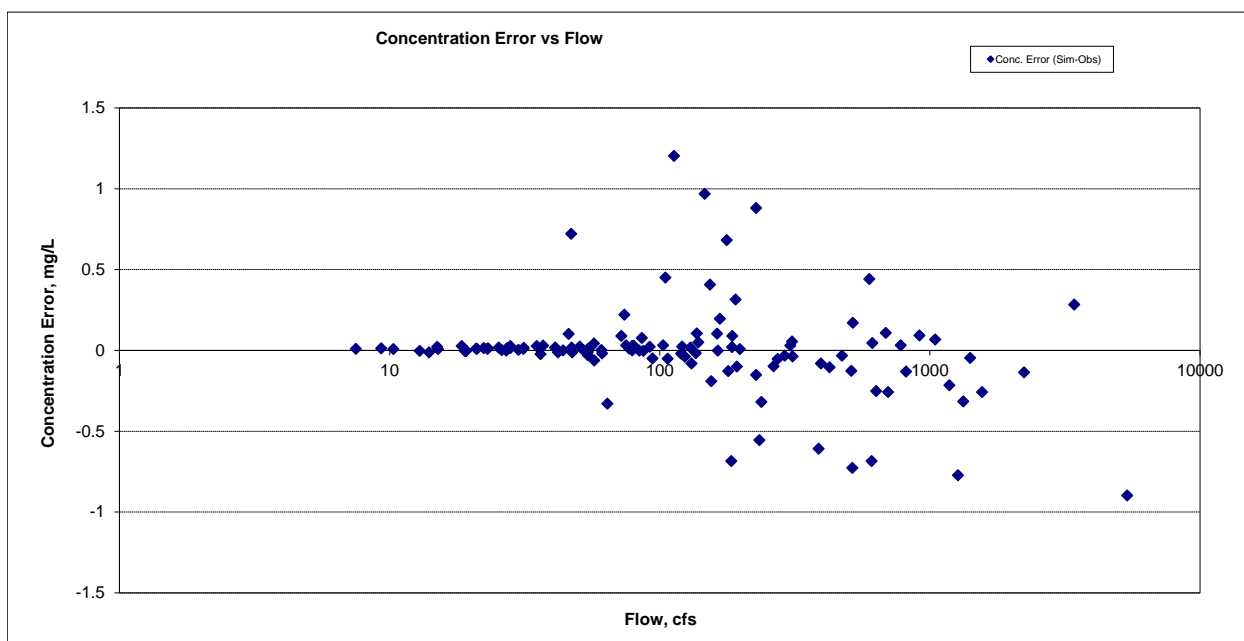


Figure B-168. Residual (Simulated - Observed) vs. Flow Total Phosphorus (TP) at Nemadji River nr Pleasant Valley (05011001)

B.6 NEMADJI RIVER NR SOUTH SUPERIOR, WI (05011002)

B.6.1 Ammonia Nitrogen (NH3)

Table B-29. Ammonia Nitrogen (NH3) statistics

Period	1994-2007	2008-2012
Count	ND	19
Concentration Average Error		23.61%
Concentration Median Error		44.39%
Load Average Error		-43.44%
Load Median Error		11.07%
Paired t conc		0.44
Paired t load		0.24

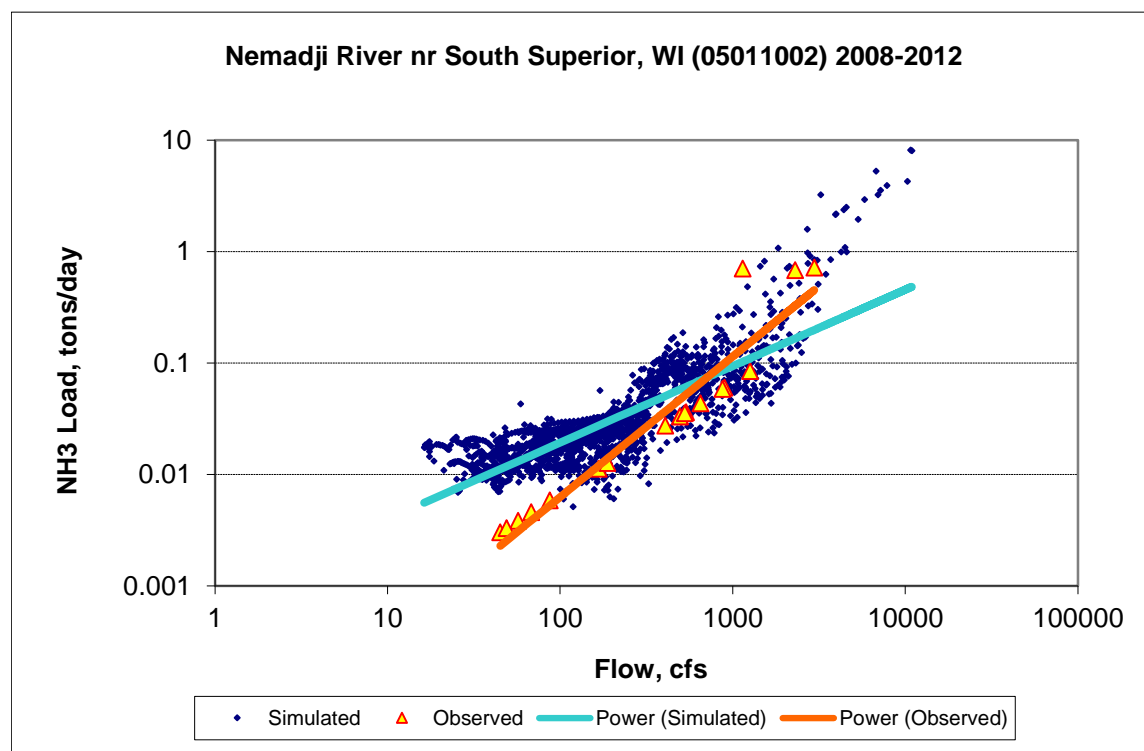
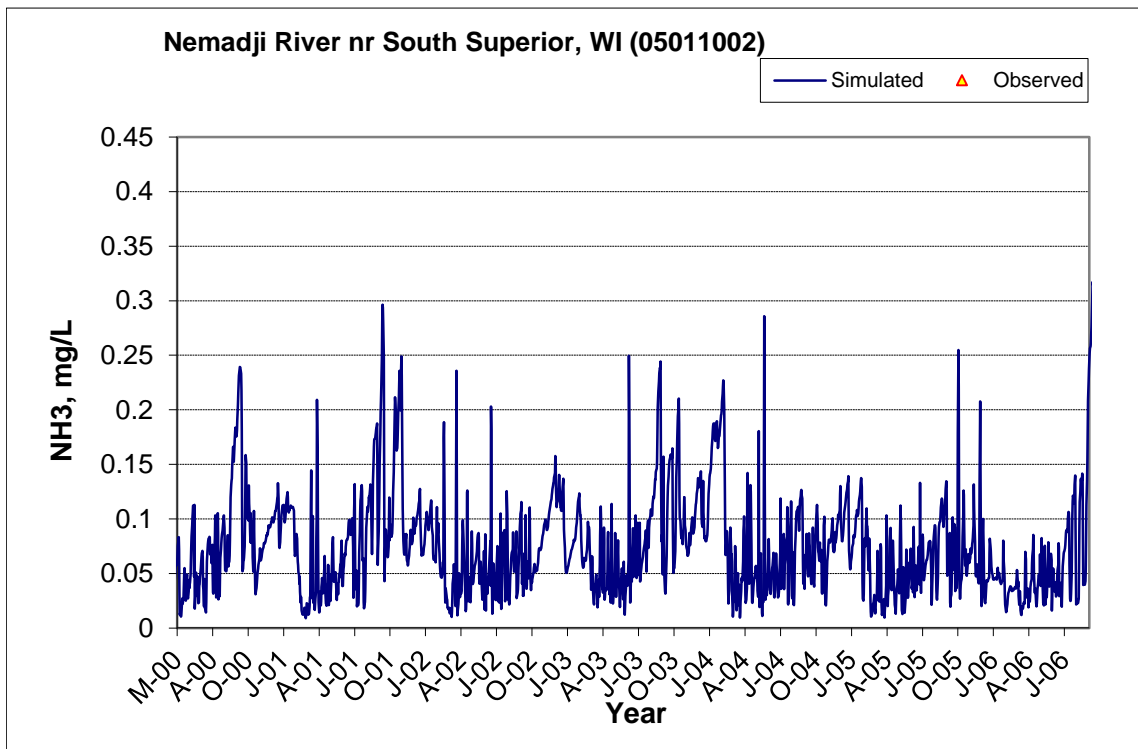
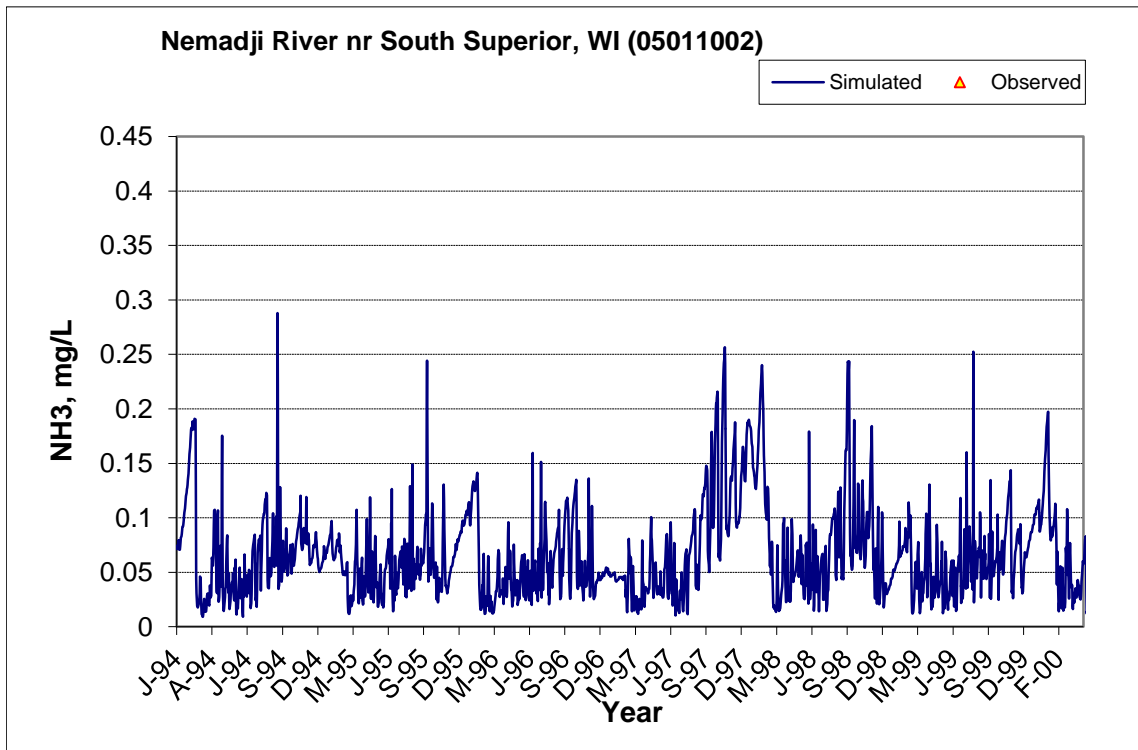


Figure B-169. Power plot of simulated and observed Ammonia Nitrogen (NH3) load vs flow at Nemadji River nr South Superior, WI (05011002) (calibration period)



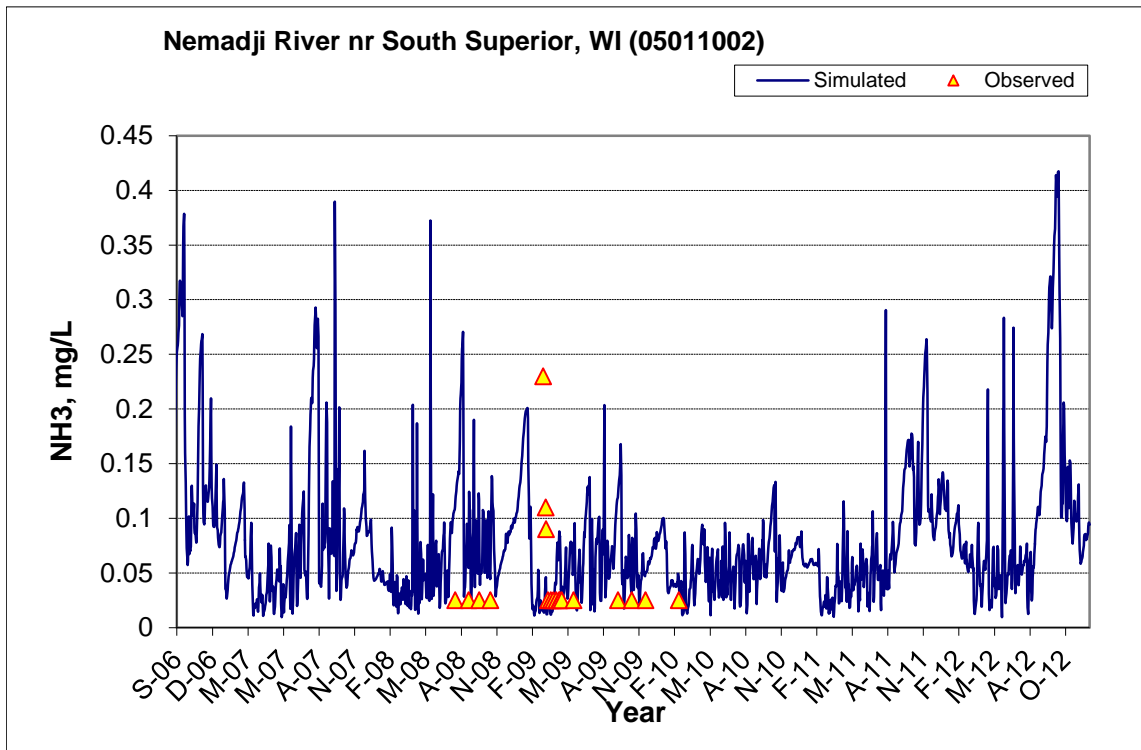


Figure B-170. Time series of observed and simulated Ammonia Nitrogen (NH3) concentration at Nemadji River nr South Superior, WI (05011002)

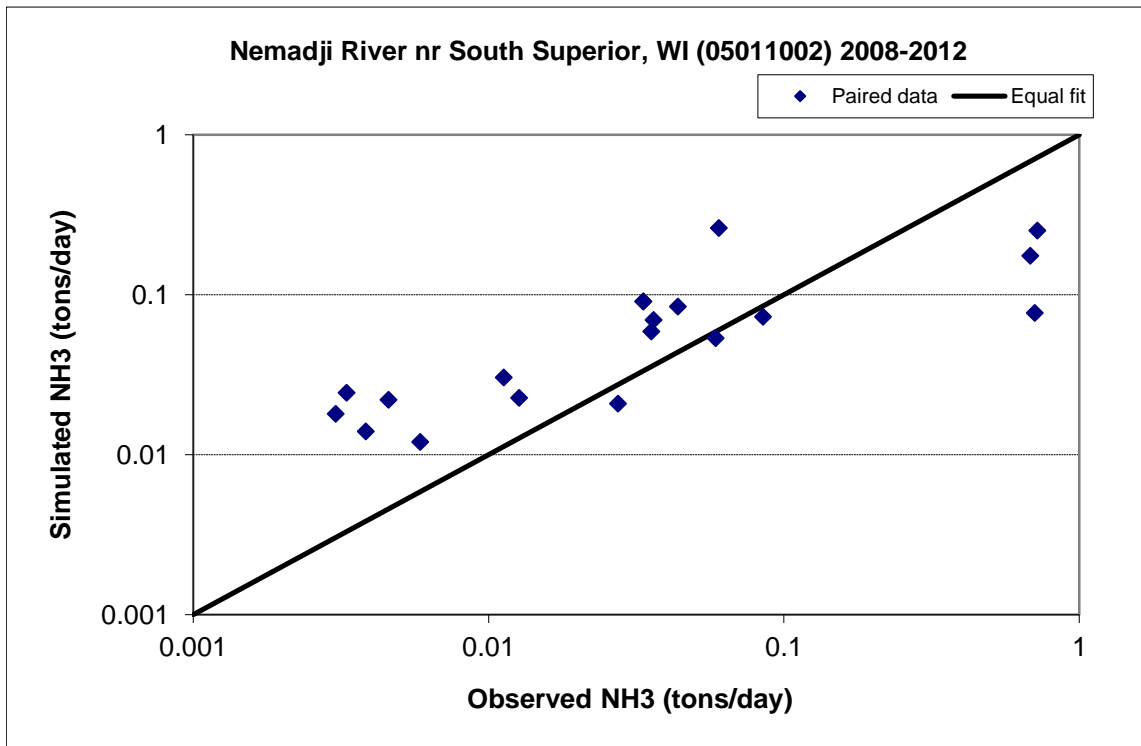


Figure B-171. Paired simulated vs. observed Ammonia Nitrogen (NH3) load at Nemadji River nr South Superior, WI (05011002) (calibration period)



Figure B-172. Residual (Simulated - Observed) vs. Month Ammonia Nitrogen (NH3) at Nemadji River nr South Superior, WI (05011002)

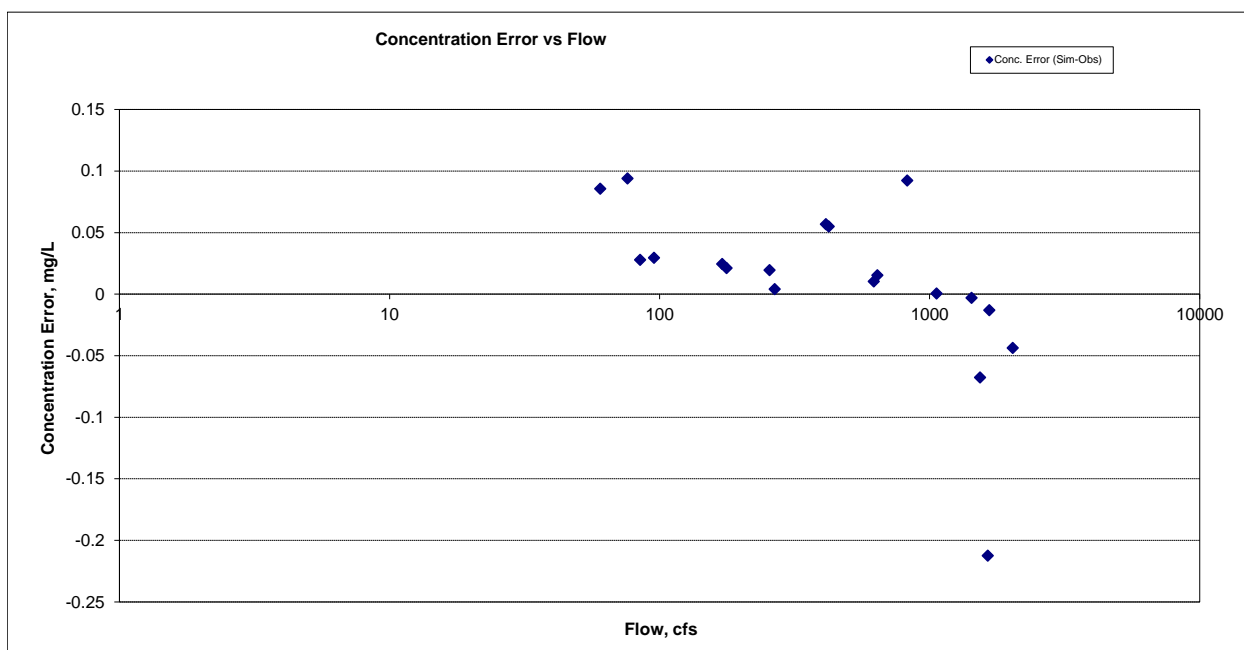
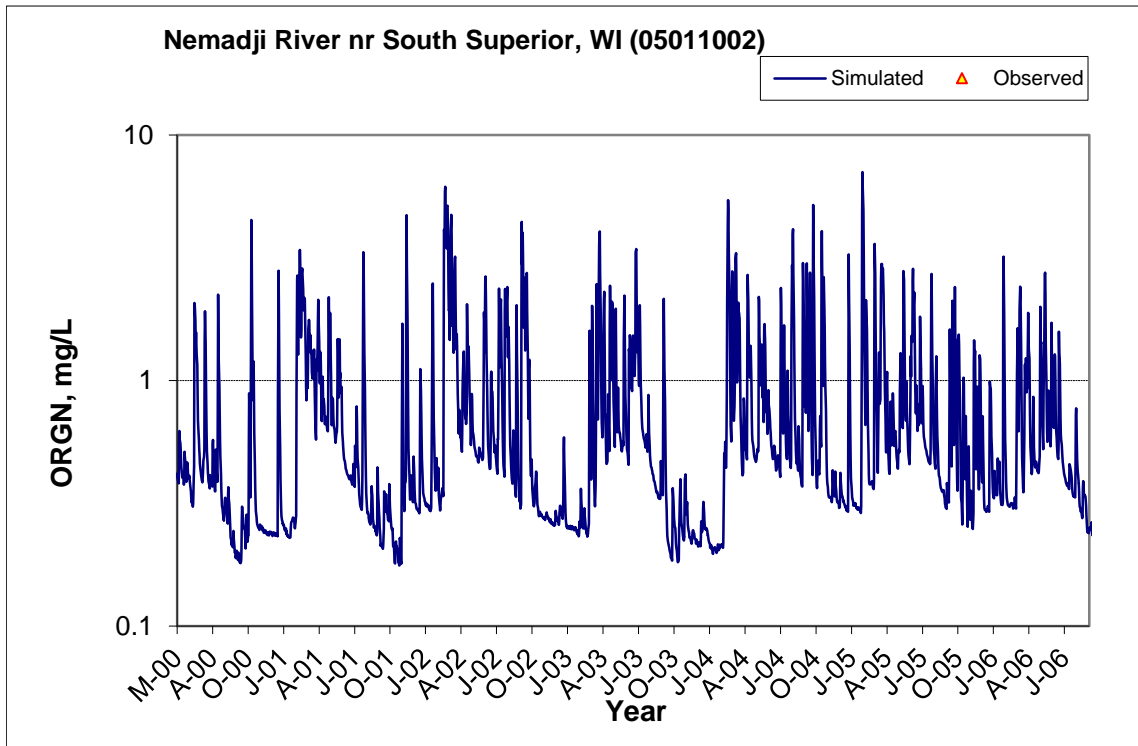
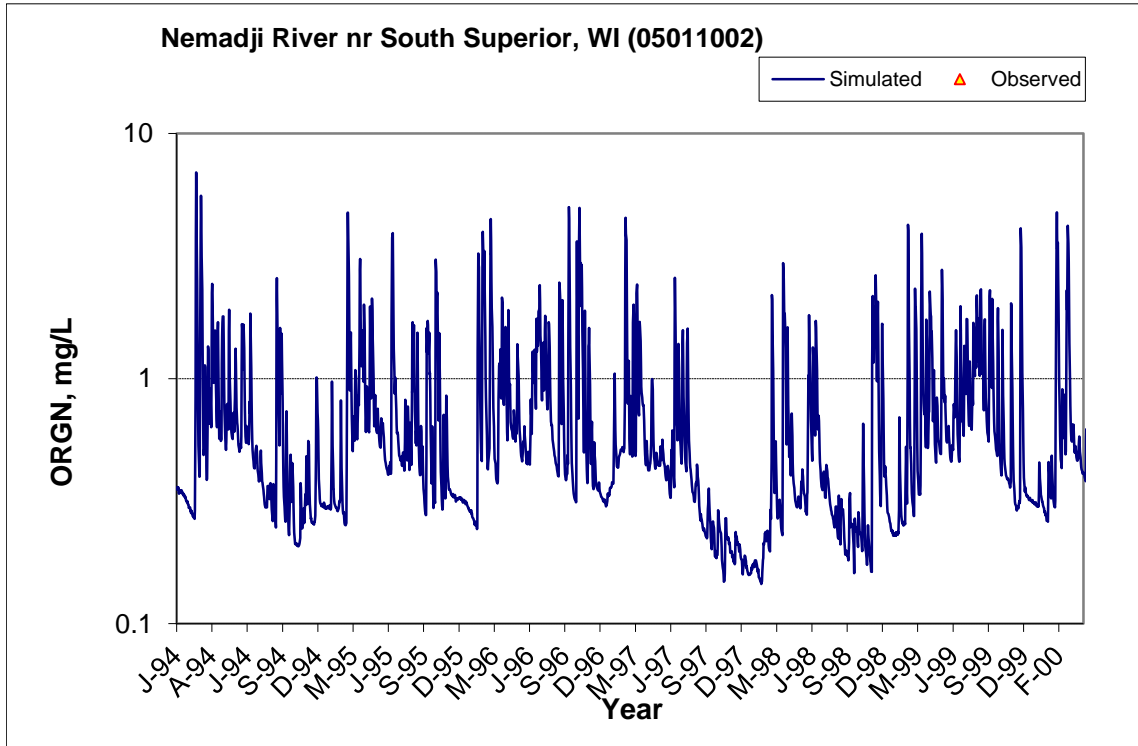


Figure B-173. Residual (Simulated - Observed) vs. Flow Ammonia Nitrogen (NH3) at Nemadji River nr South Superior, WI (05011002)

B.6.2 Organic Nitrogen (OrgN)



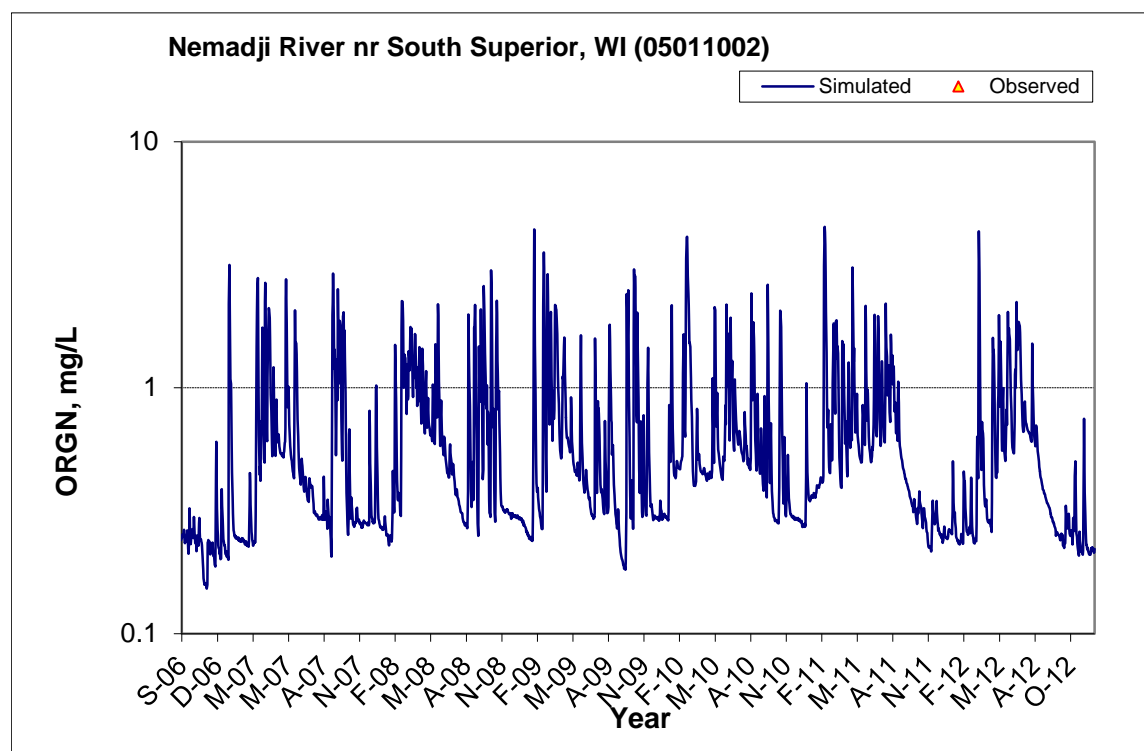


Figure B-174. Time series of observed and simulated Organic Nitrogen (OrgN) concentration at Nemadji River nr South Superior, WI (05011002)

B.6.3 Total Kjeldahl Nitrogen (TKN)

Table B-30. Total Kjeldahl Nitrogen (TKN) statistics

Period	1994-2007	2008-2012
Count	ND	100
Concentration Average Error		0.05%
Concentration Median Error		-3.23%
Load Average Error		-24.43%
Load Median Error		-1.17%
Paired t conc		1.00
Paired t load		0.42

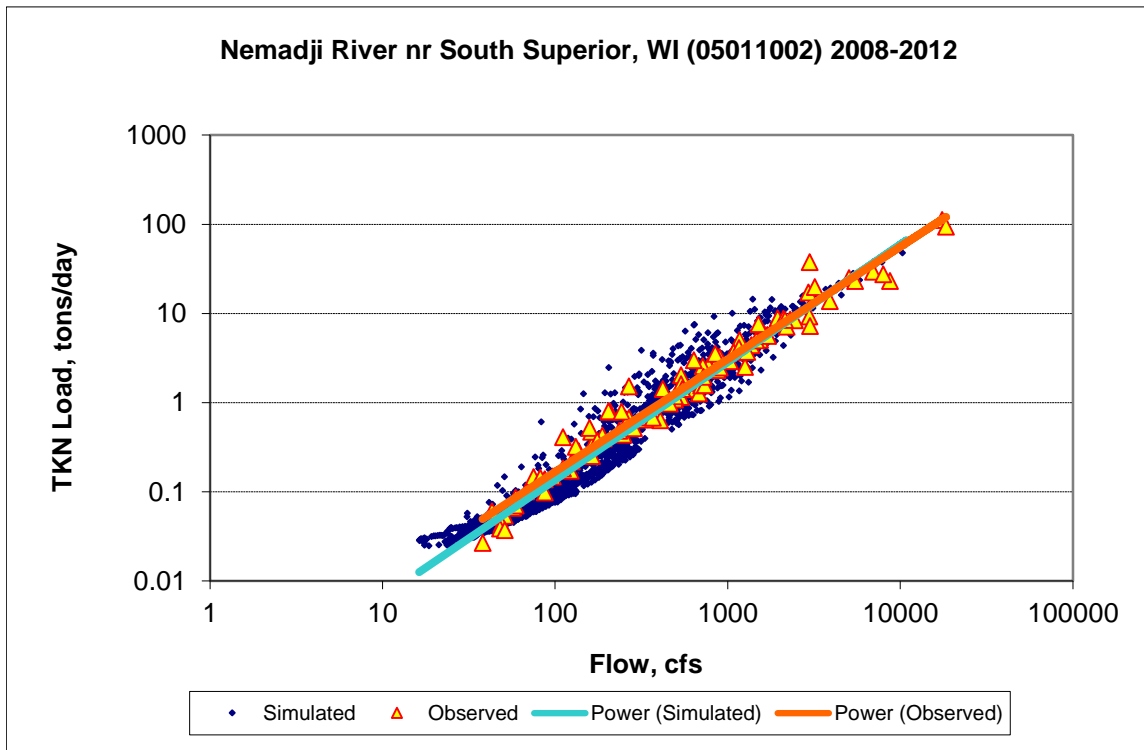
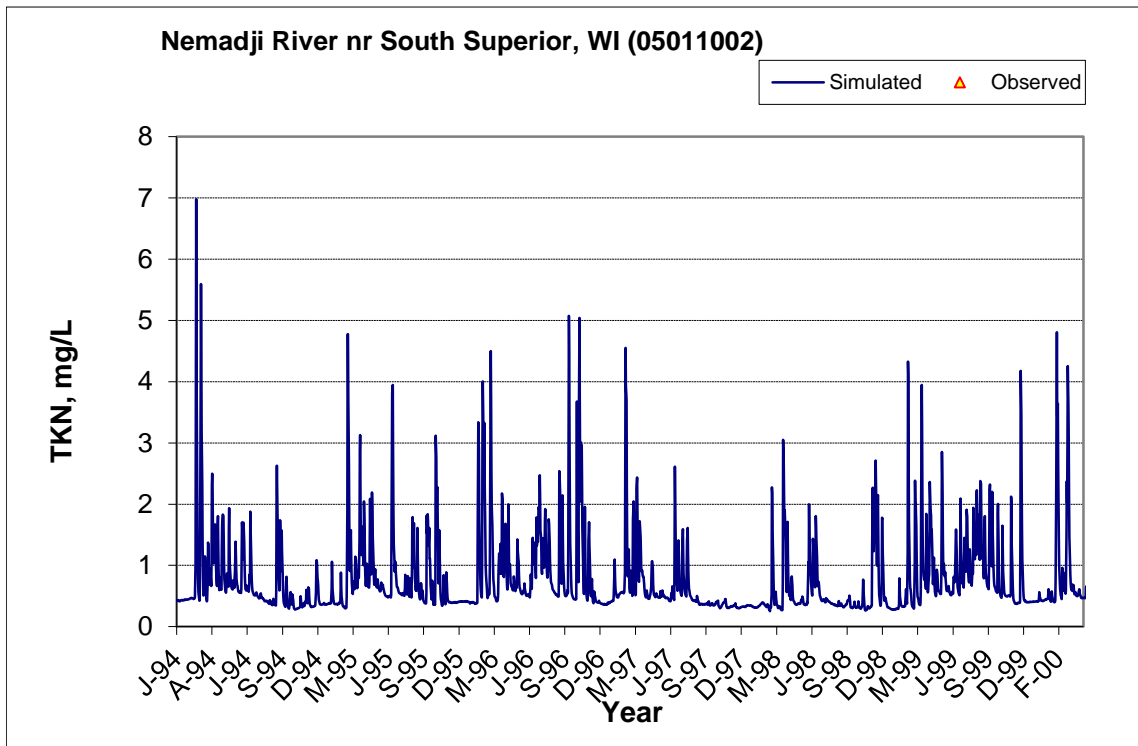


Figure B-175. Power plot of simulated and observed Total Kjeldahl Nitrogen (TKN) load vs flow at Nemadji River nr South Superior, WI (05011002) (calibration period)



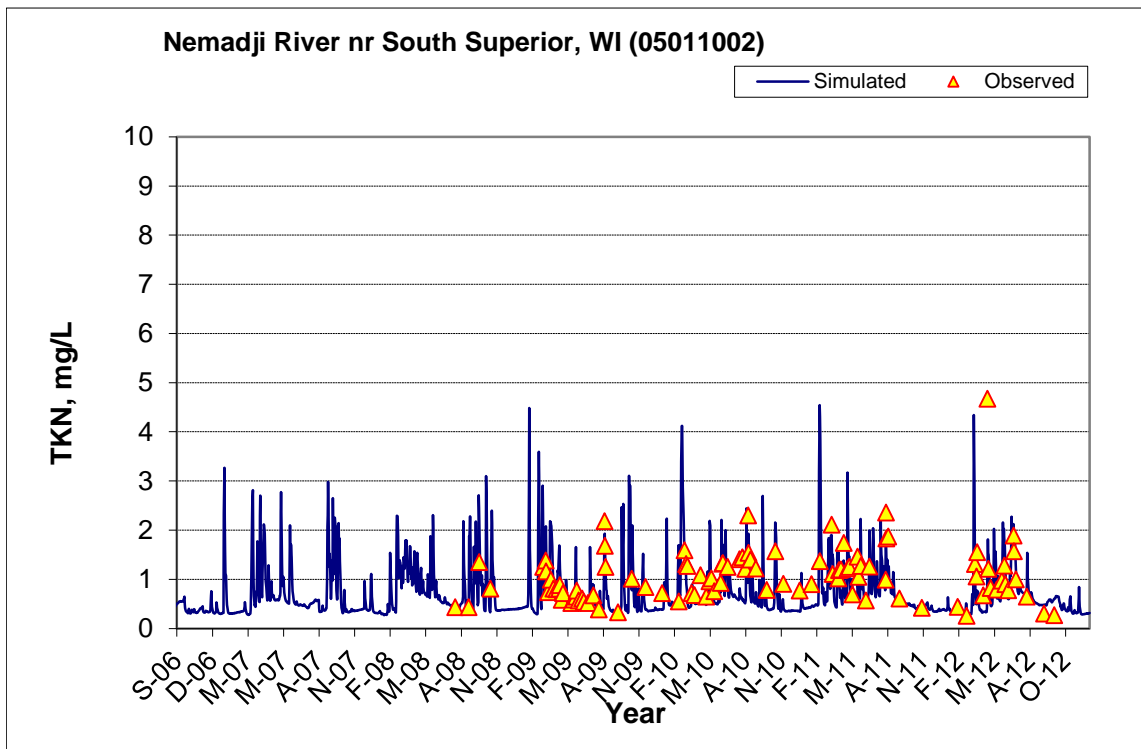
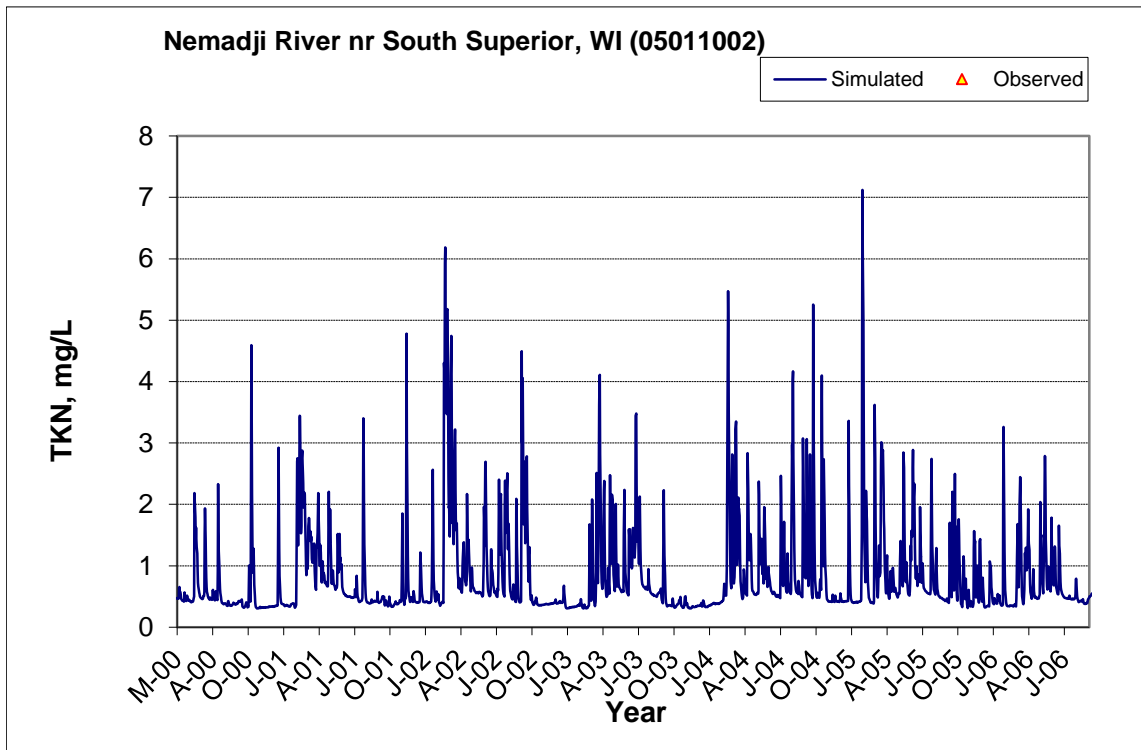


Figure B-176. Time series of observed and simulated Total Kjeldahl Nitrogen (TKN) concentration at Nemadji River nr South Superior, WI (05011002)

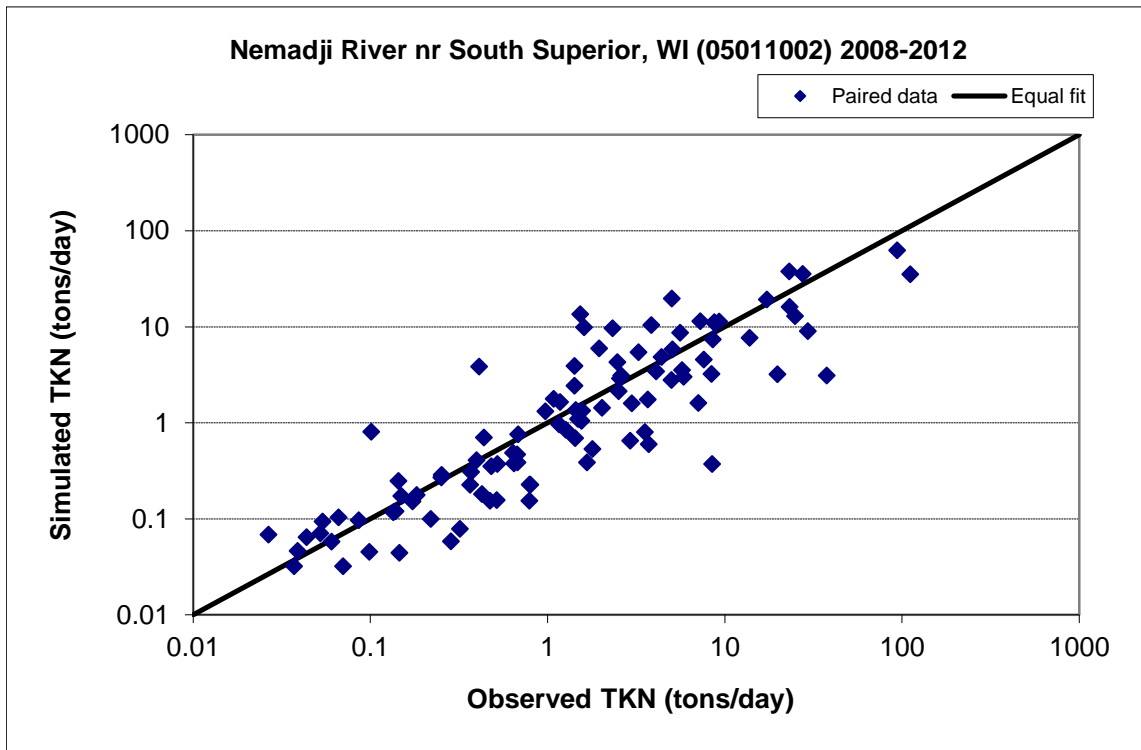


Figure B-177. Paired simulated vs. observed Total Kjeldahl Nitrogen (TKN) load at Nemadji River nr South Superior, WI (05011002) (calibration period)

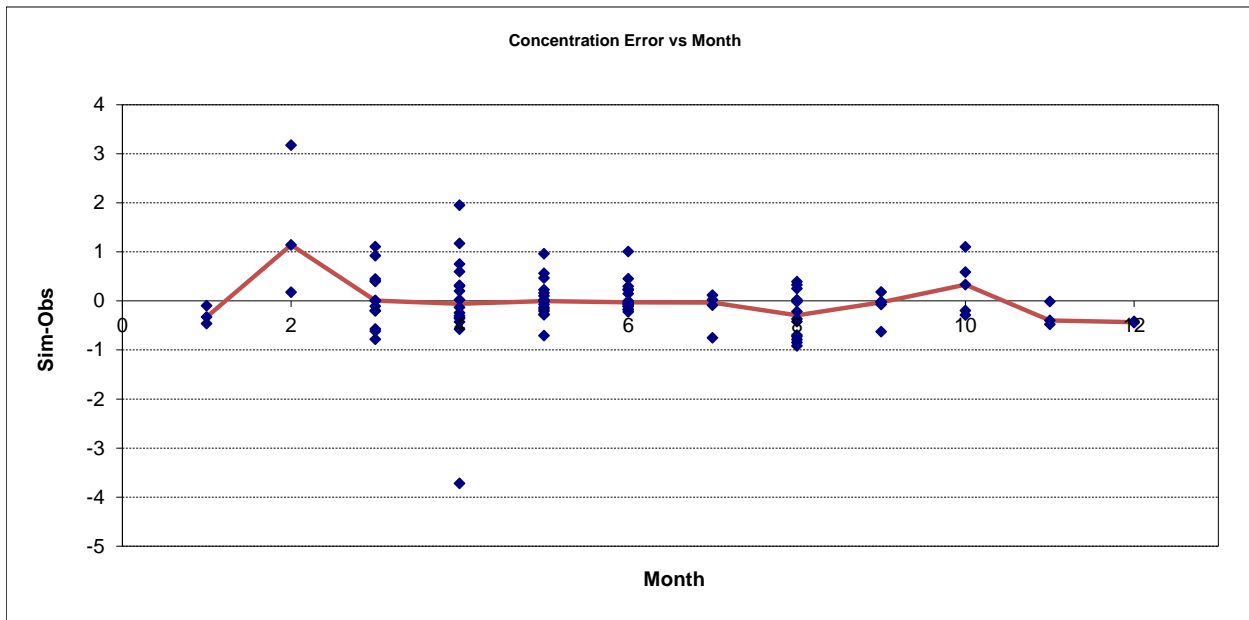


Figure B-178. Residual (Simulated - Observed) vs. Month Total Kjeldahl Nitrogen (TKN) at Nemadji River nr South Superior, WI (05011002)

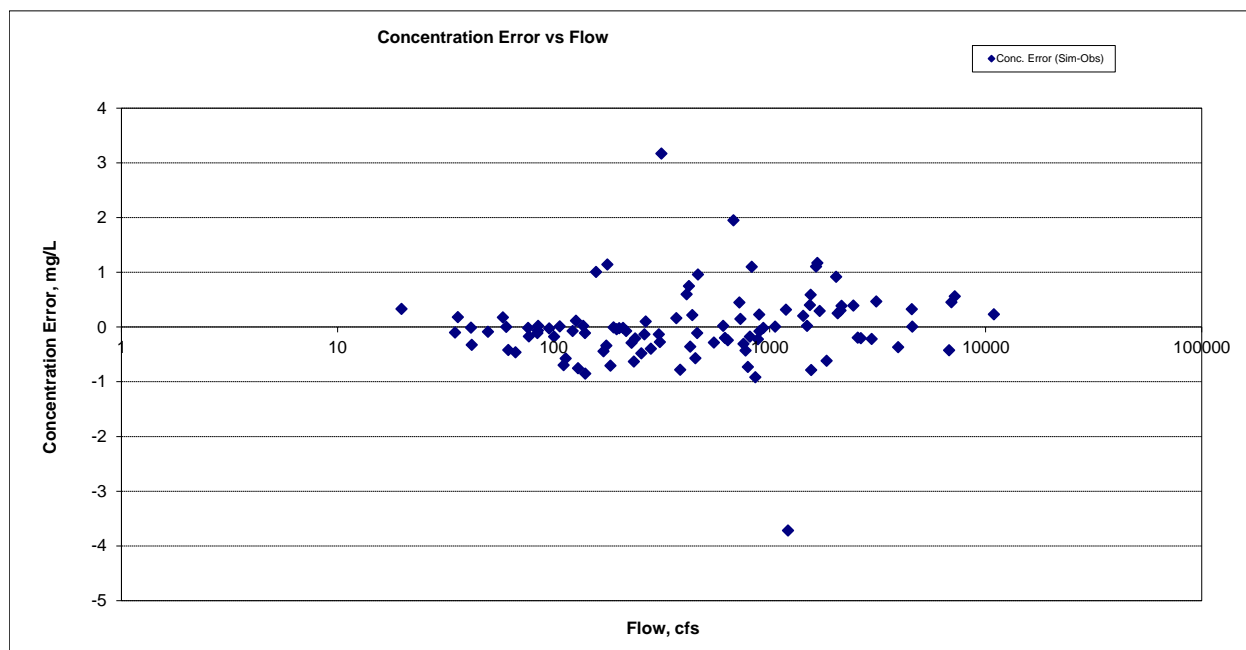


Figure B-179. Residual (Simulated - Observed) vs. Flow Total Kjeldahl Nitrogen (TKN) at Nemadji River nr South Superior, WI (05011002)

B.6.4 Nitrite+ Nitrate Nitrogen (NOx)

Table B-31. Nitrite+ Nitrate Nitrogen (NOx) statistics

Period	1994-2007	2008-2012
Count	ND	100
Concentration Average Error		-6.99%
Concentration Median Error		-9.00%
Load Average Error		30.40%
Load Median Error		-2.57%
Paired t conc		0.94
Paired t load		0.35

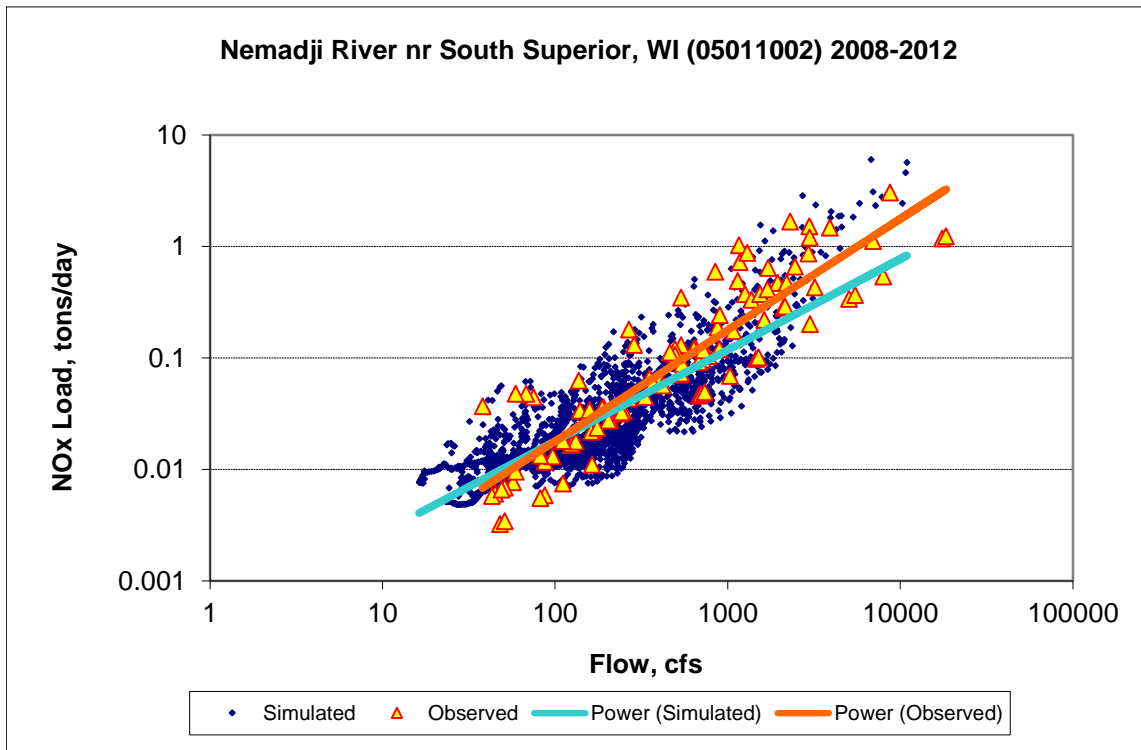
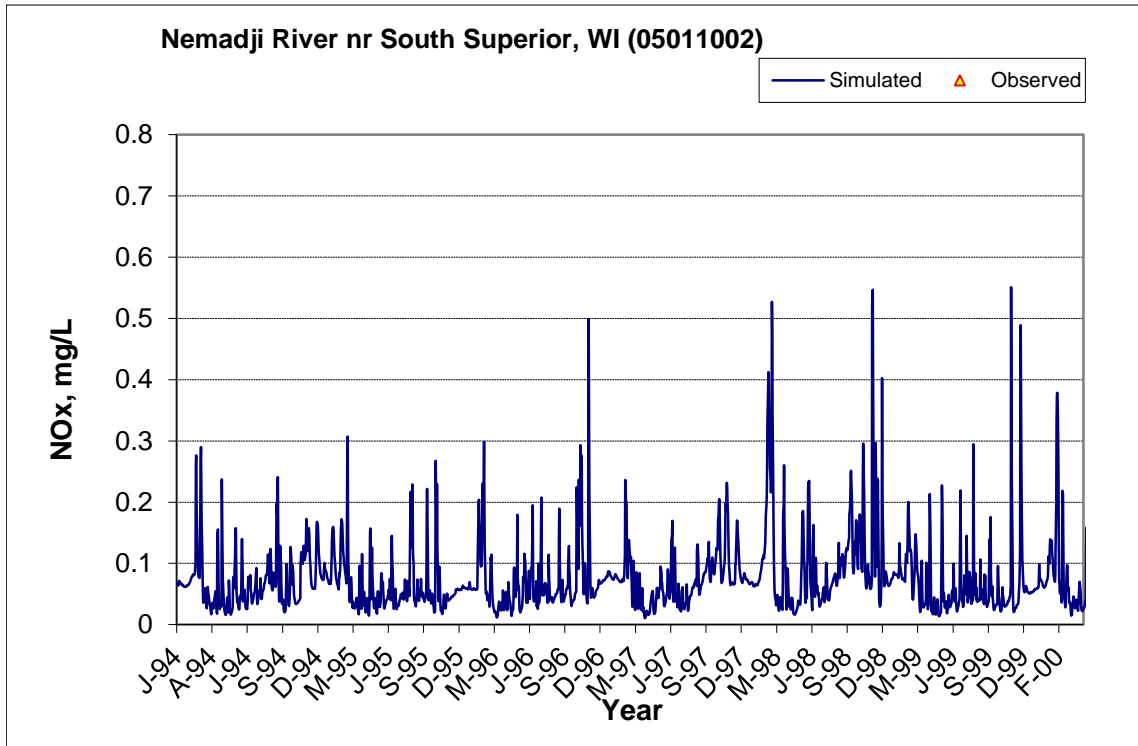


Figure B-180. Power plot of simulated and observed Nitrite+ Nitrate Nitrogen (NOx) load vs flow at Nemadji River nr South Superior, WI (05011002) (calibration period)



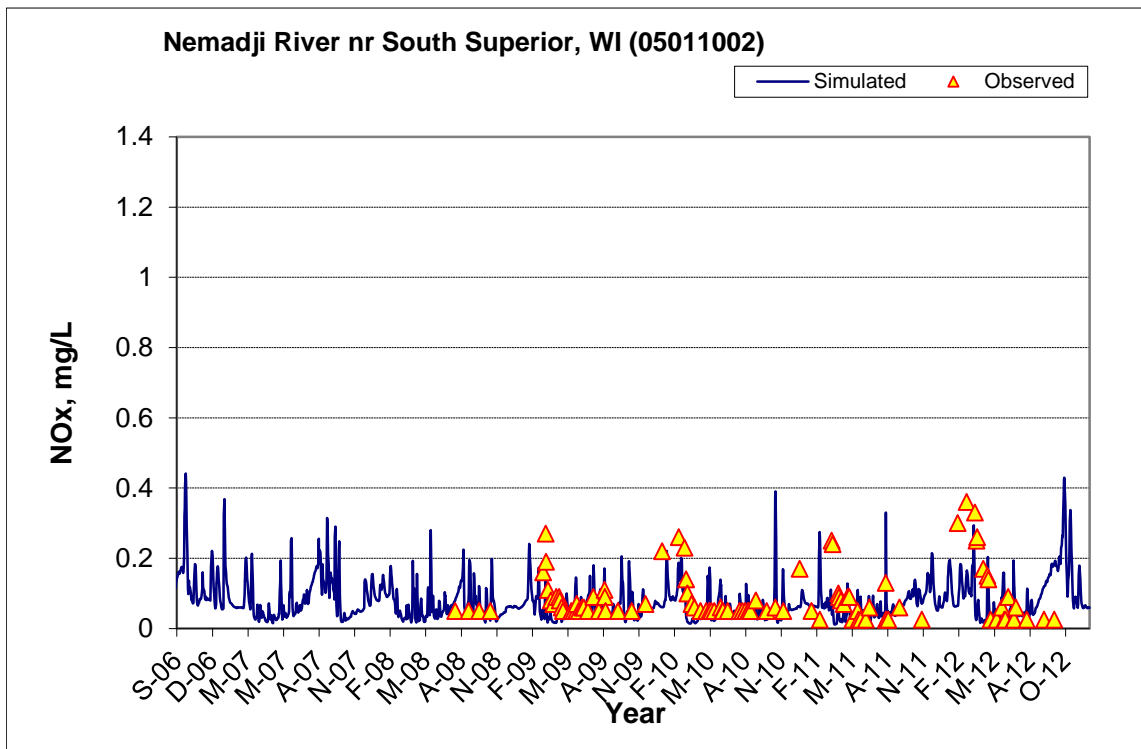
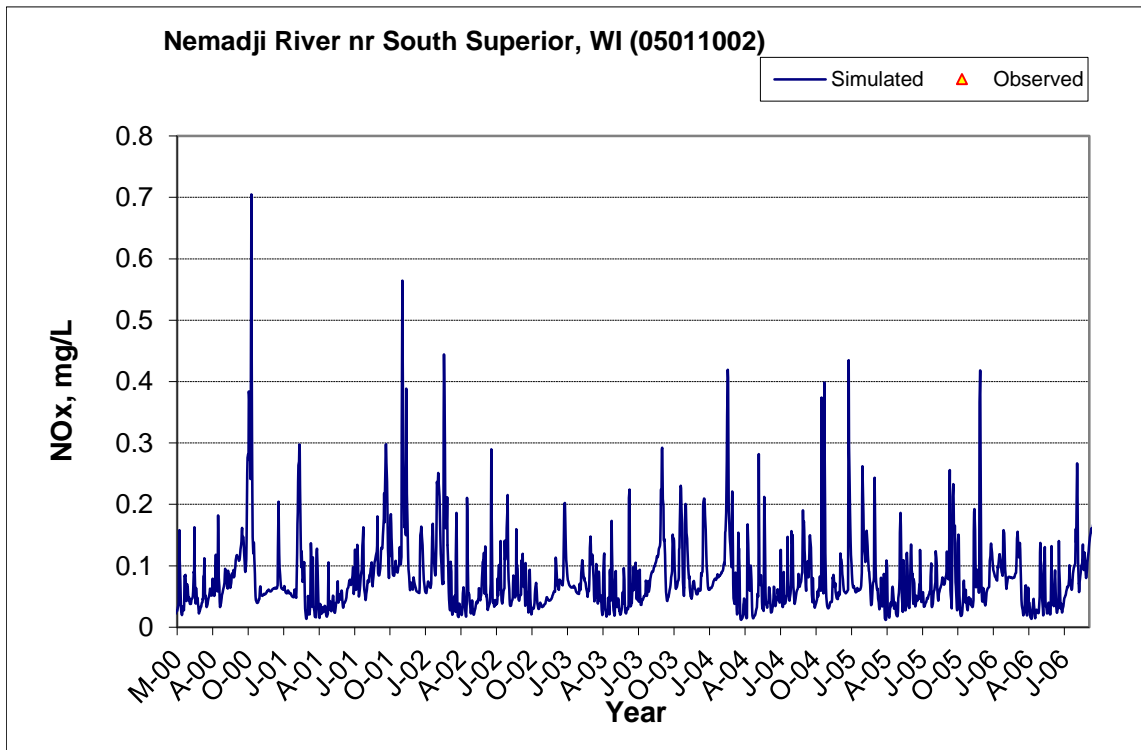


Figure B-181. Time series of observed and simulated Nitrite+ Nitrate Nitrogen (NOx) concentration at Nemadji River nr South Superior, WI (05011002)

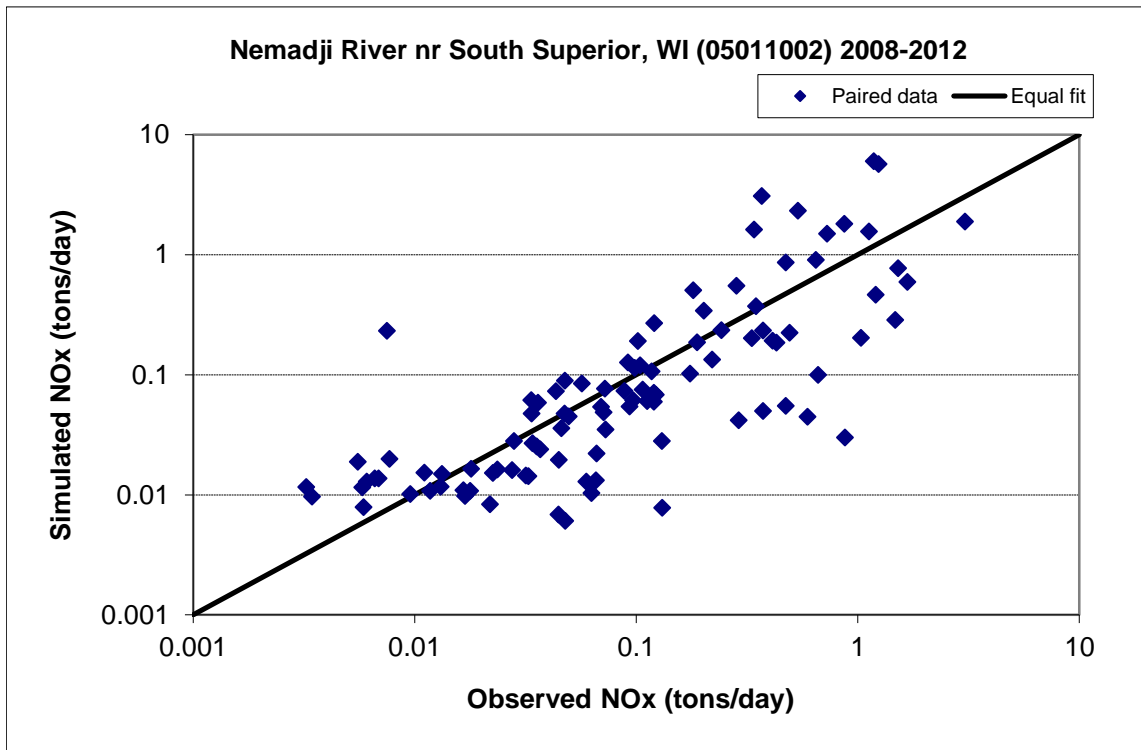


Figure B-182. Paired simulated vs. observed Nitrite+ Nitrate Nitrogen (NOx) load at Nemadji River nr South Superior, WI (05011002) (calibration period)

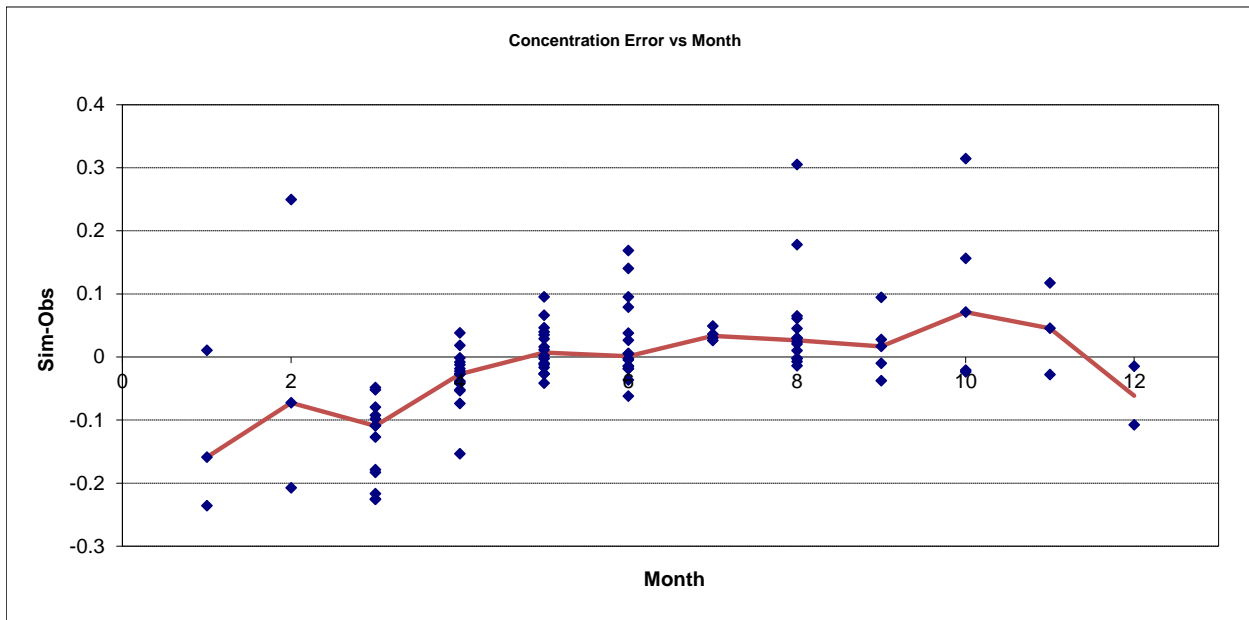


Figure B-183. Residual (Simulated - Observed) vs. Month Nitrite+ Nitrate Nitrogen (NOx) at Nemadji River nr South Superior, WI (05011002)

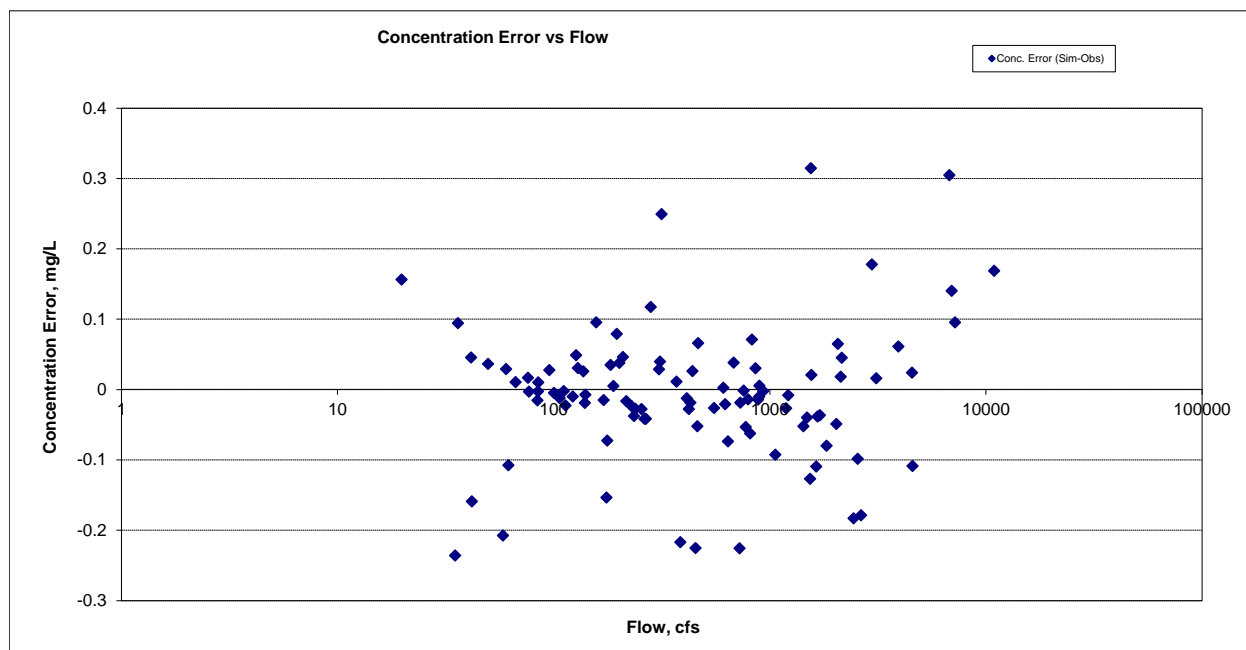


Figure B-184. Residual (Simulated - Observed) vs. Flow Nitrite+ Nitrate Nitrogen (NOx) at Nemadji River nr South Superior, WI (05011002)

B.6.5 Total Nitrogen (TN)

Table B-32. Total Nitrogen (TN) statistics

Period	1994-2007	2008-2012
Count	ND	100
Concentration Average Error		-0.78%
Concentration Median Error		-5.07%
Load Average Error		-22.56%
Load Median Error		-1.42%
Paired t conc		1.00
Paired t load		0.45

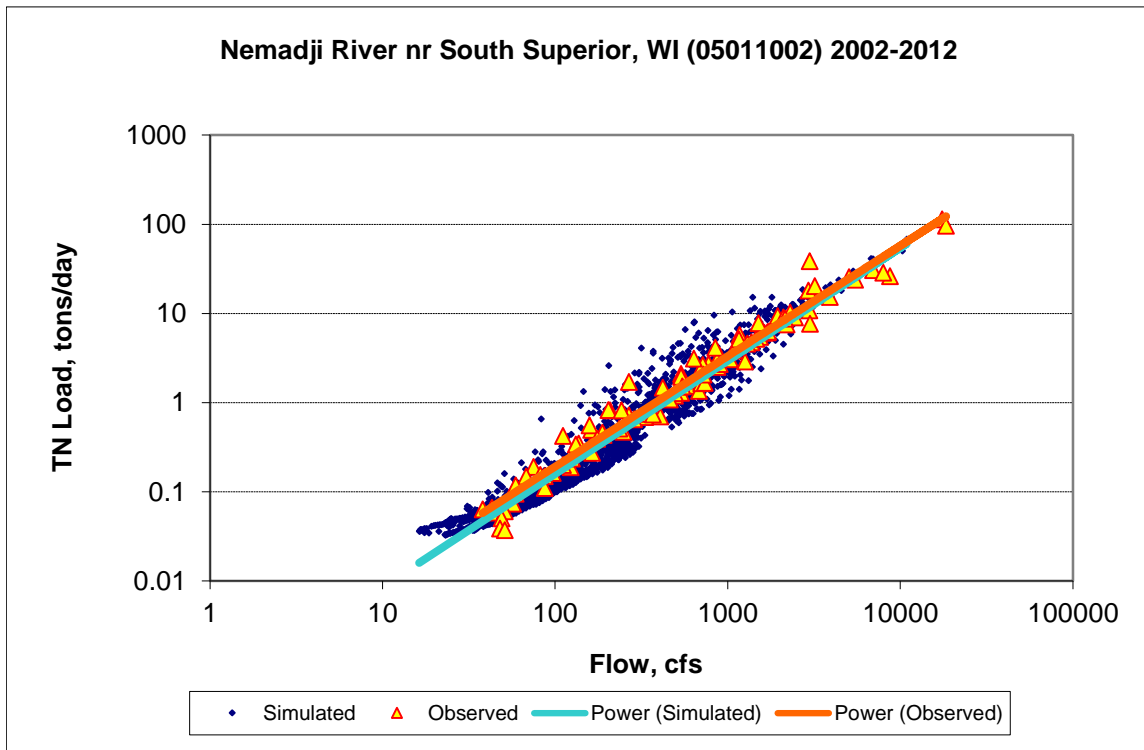
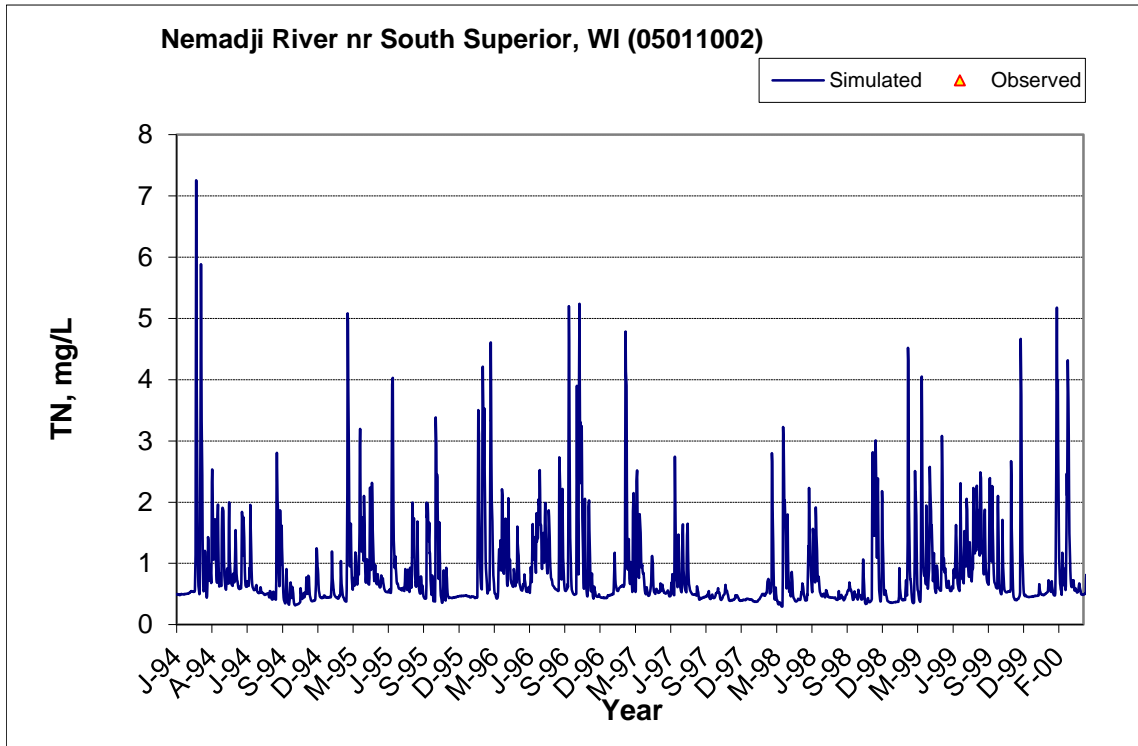


Figure B-185. Power plot of simulated and observed Total Nitrogen (TN) load vs flow at Nemadji River nr South Superior, WI (05011002) (calibration period)



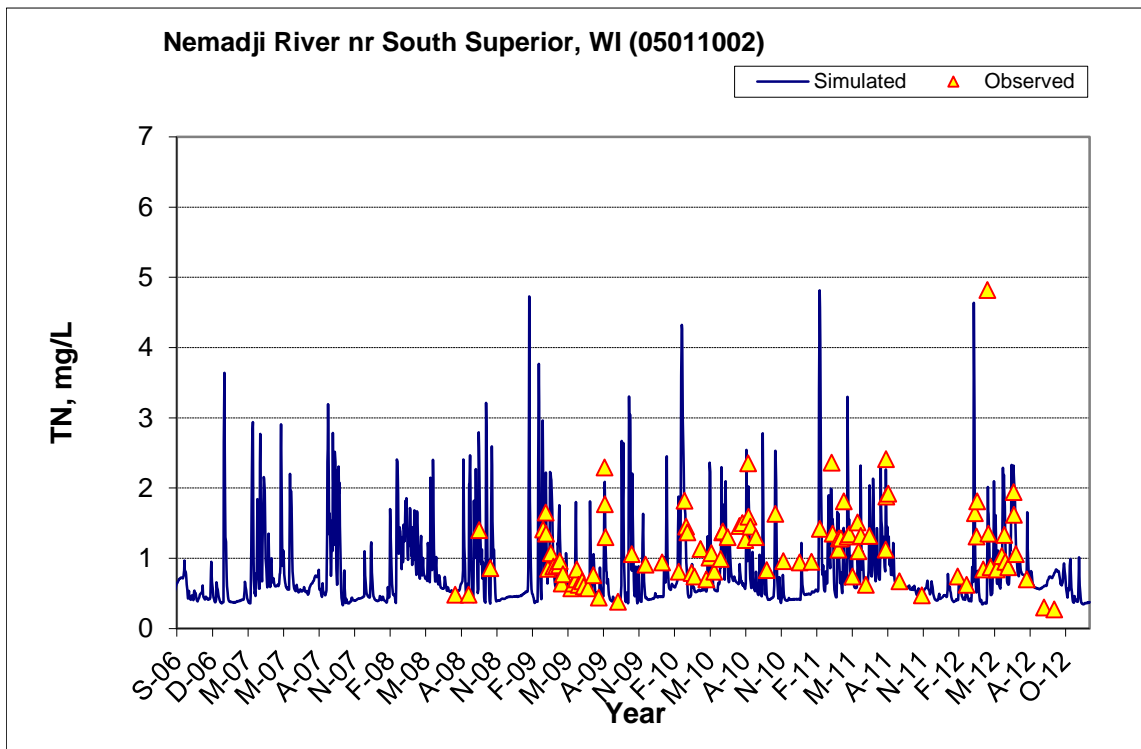
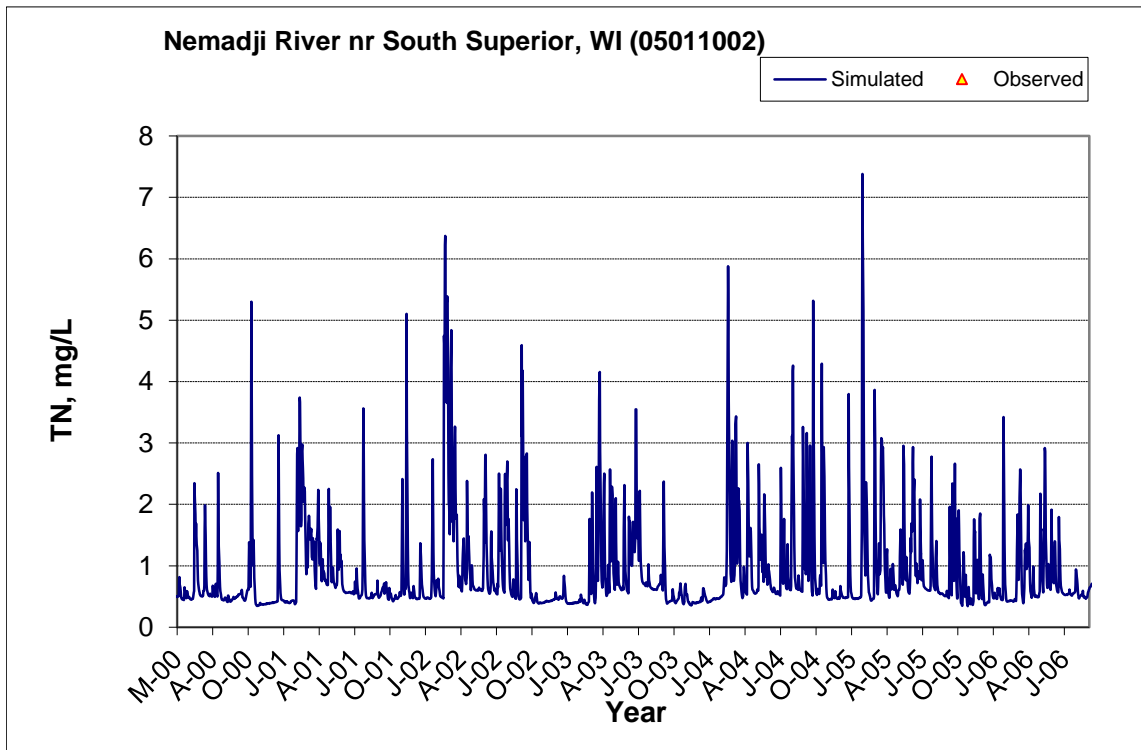


Figure B-186. Time series of observed and simulated Total Nitrogen (TN) concentration at Nemadji River nr South Superior, WI (05011002)

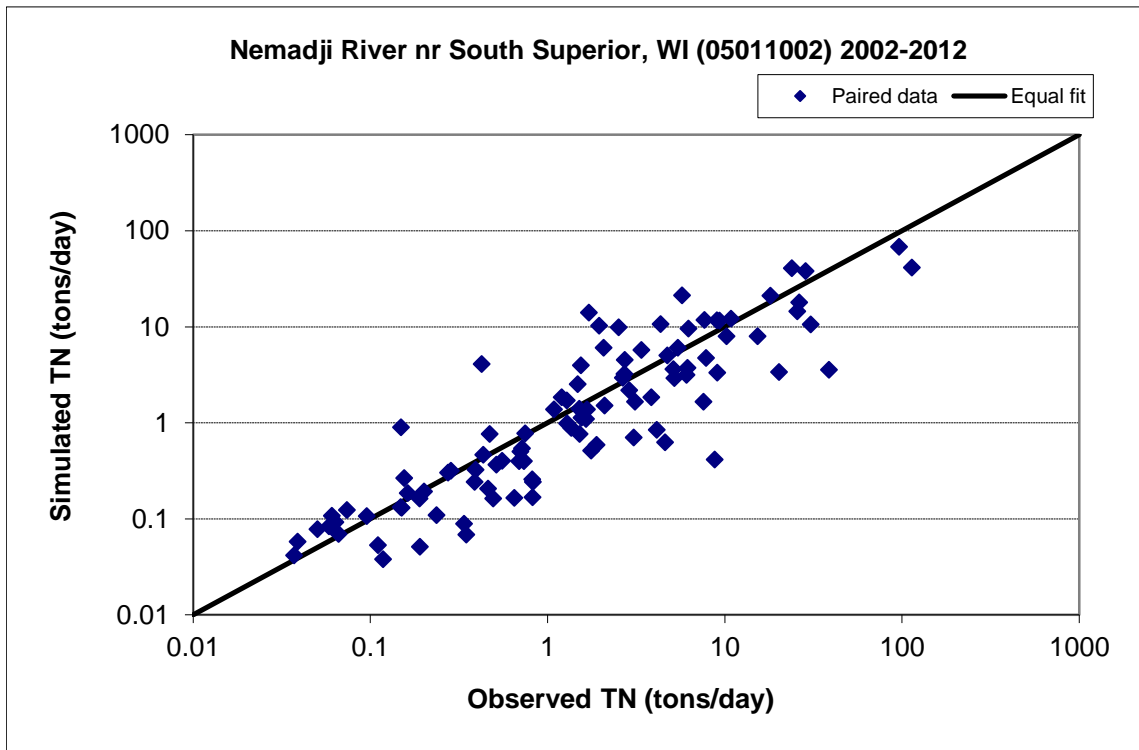


Figure B-187. Paired simulated vs. observed Total Nitrogen (TN) load at Nemadji River nr South Superior, WI (05011002) (calibration period)

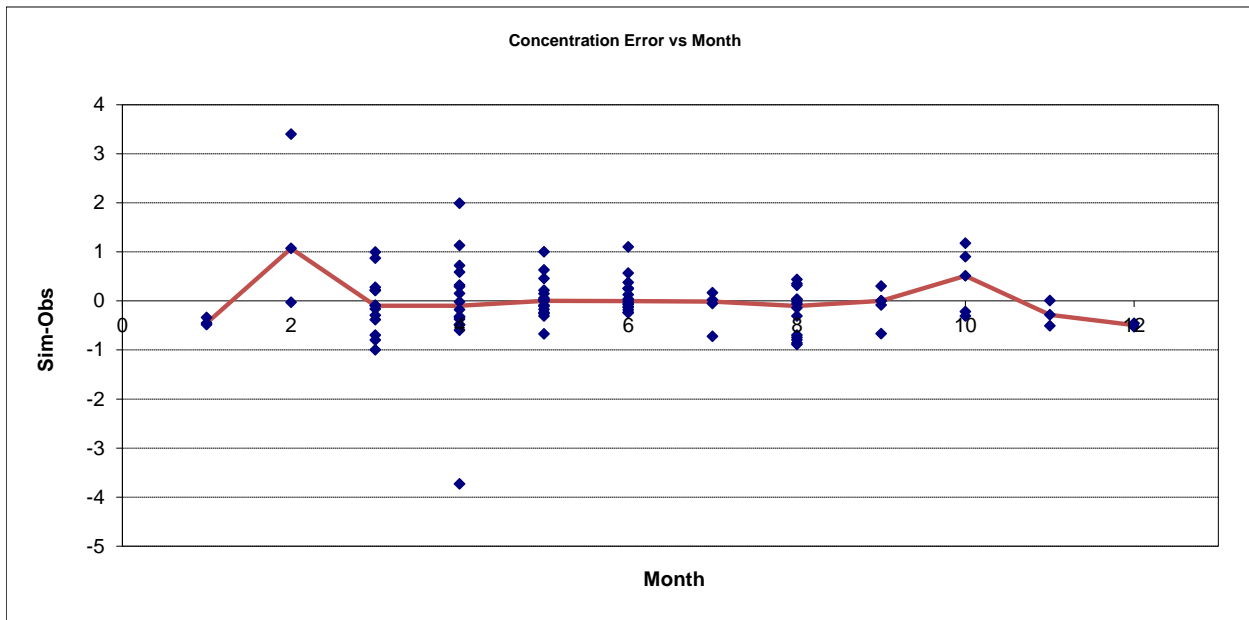


Figure B-188. Residual (Simulated - Observed) vs. Month Total Nitrogen (TN) at Nemadji River nr South Superior, WI (05011002)

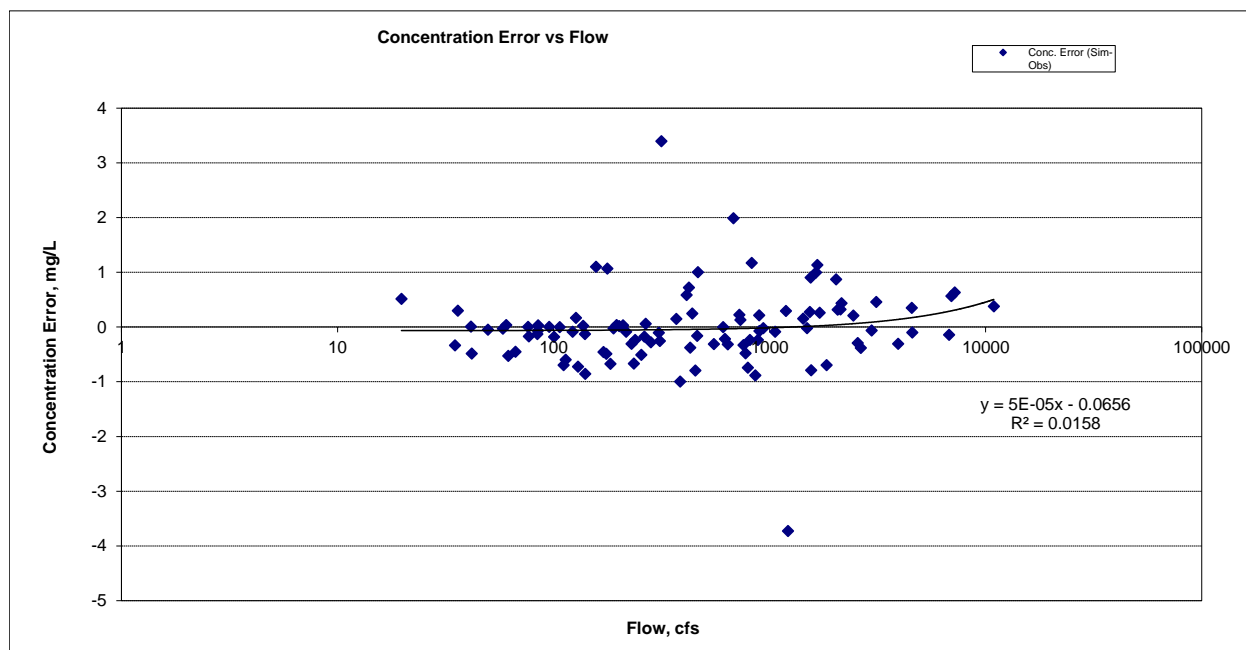


Figure B-189. Residual (Simulated - Observed) vs. Flow Total Nitrogen (TN) at Nemadji River nr South Superior, WI (05011002)

B.6.6 Soluble Reactive Phosphorus (SRP)

Table B-33. Soluble Reactive Phosphorus (SRP) statistics

Period	1994-2007	2008-2012
Count	ND	96
Concentration Average Error		0.10%
Concentration Median Error		1.26%
Load Average Error		-44.48%
Load Median Error		-0.03%
Paired t conc		0.88
Paired t load		0.22

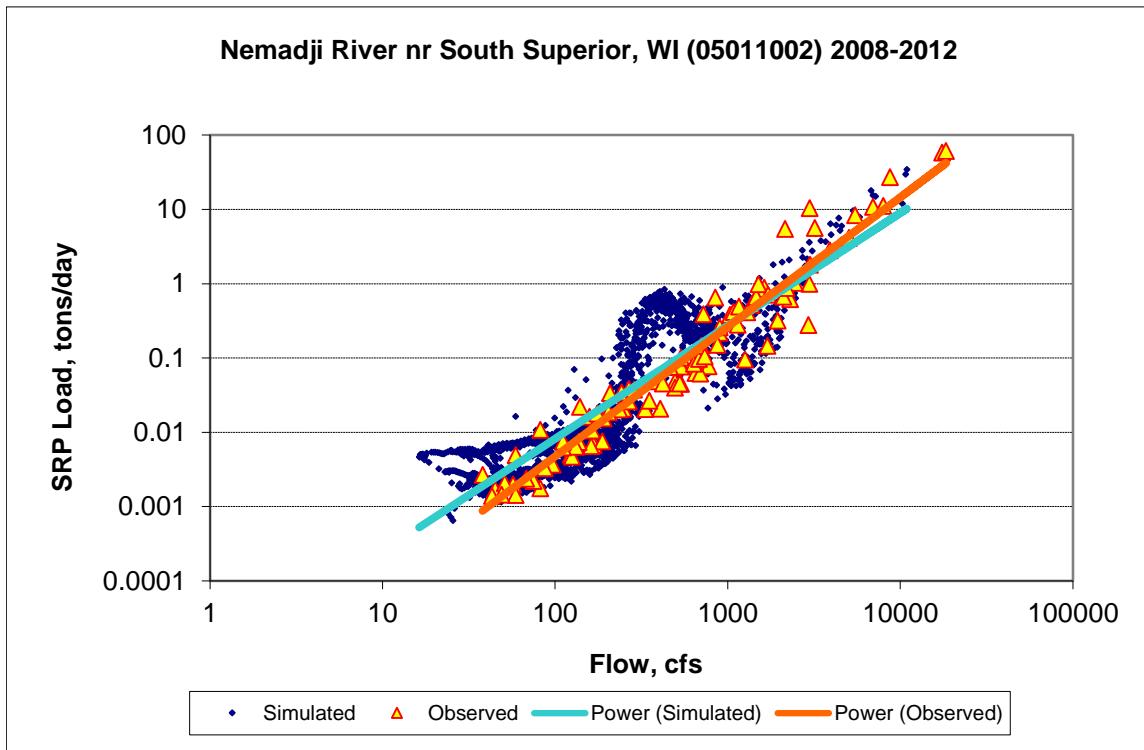
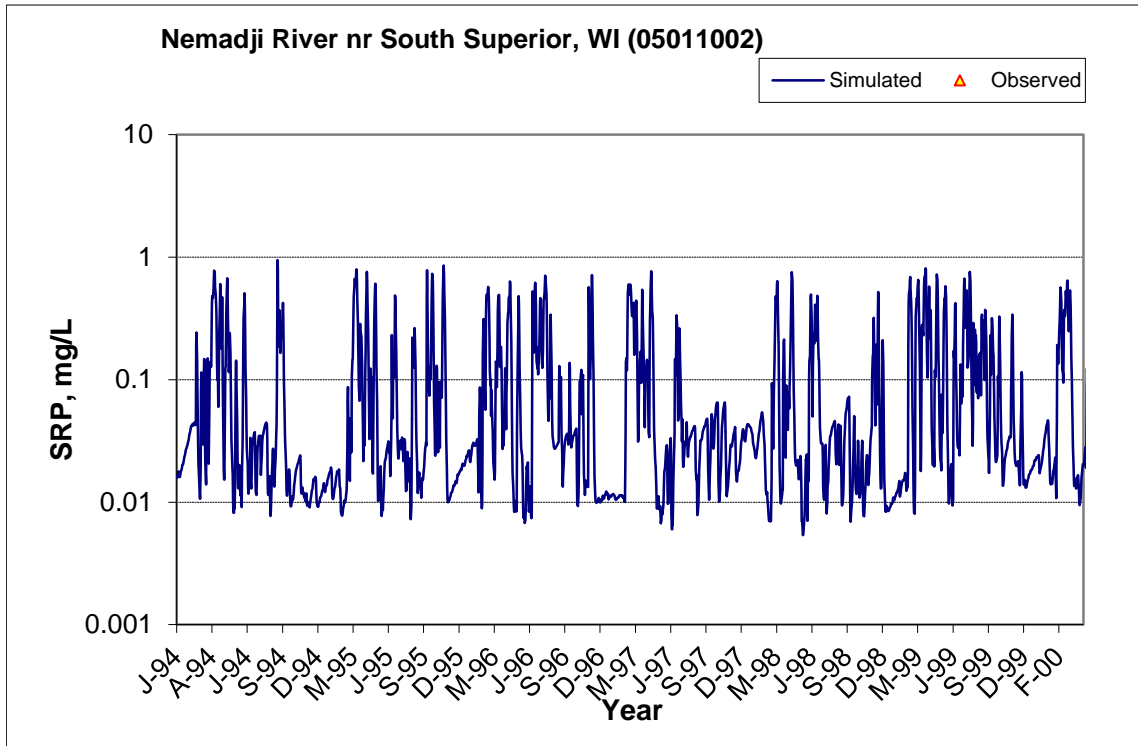


Figure B-190. Power plot of simulated and observed Soluble Reactive Phosphorus (SRP) load vs flow at Nemadji River nr South Superior, WI (05011002) (calibration period)



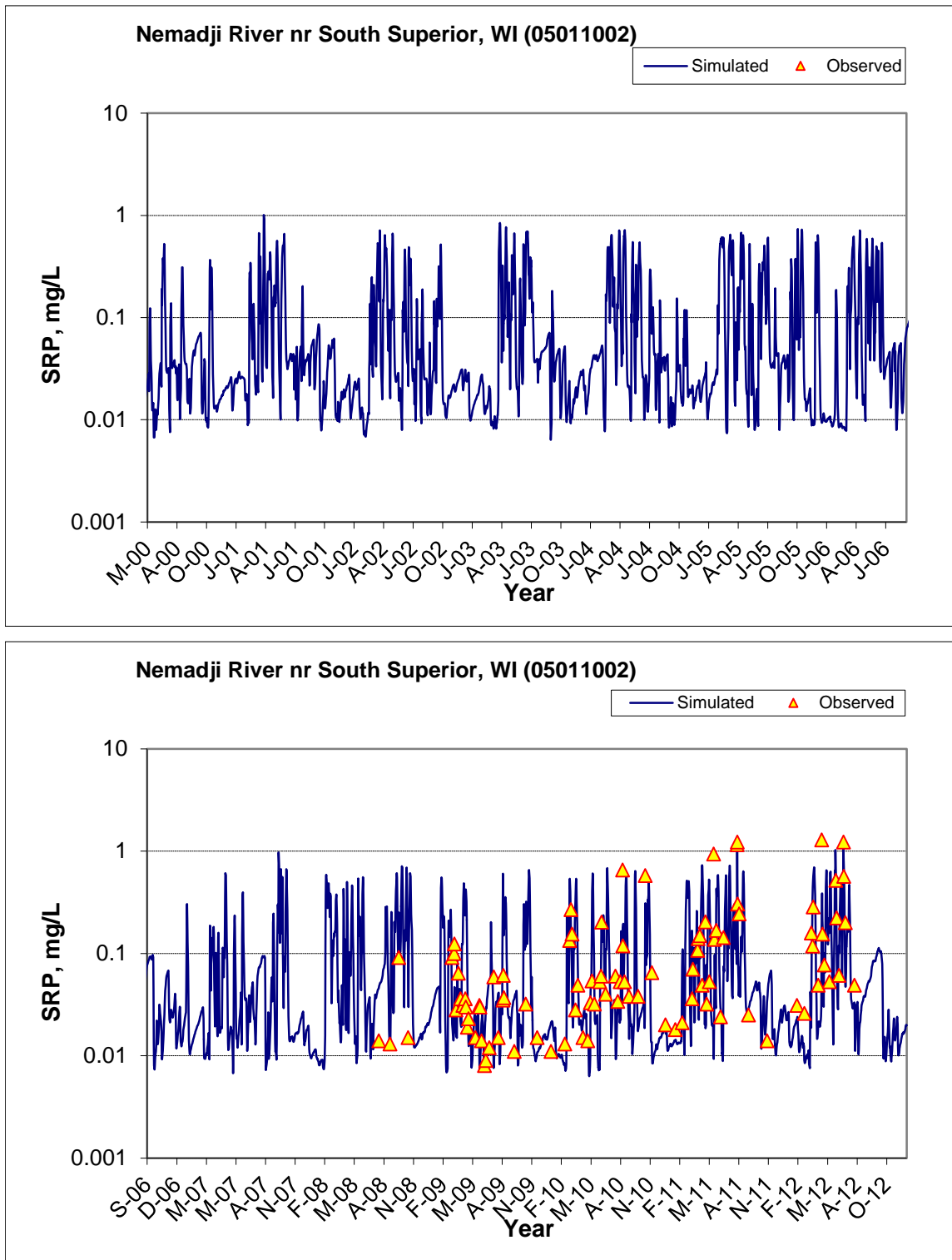


Figure B-191. Time series of observed and simulated Soluble Reactive Phosphorus (SRP) concentration at Nemadji River nr South Superior, WI (05011002)

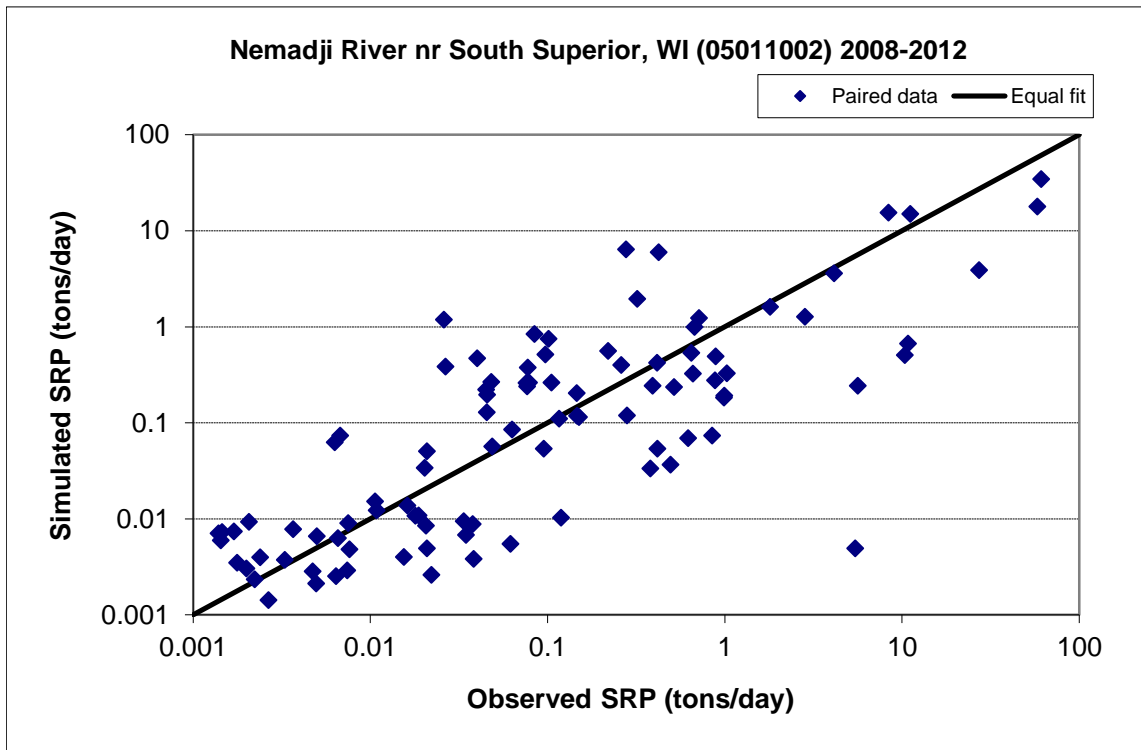


Figure B-192. Paired simulated vs. observed Soluble Reactive Phosphorus (SRP) load at Nemadji River nr South Superior, WI (05011002) (calibration period)

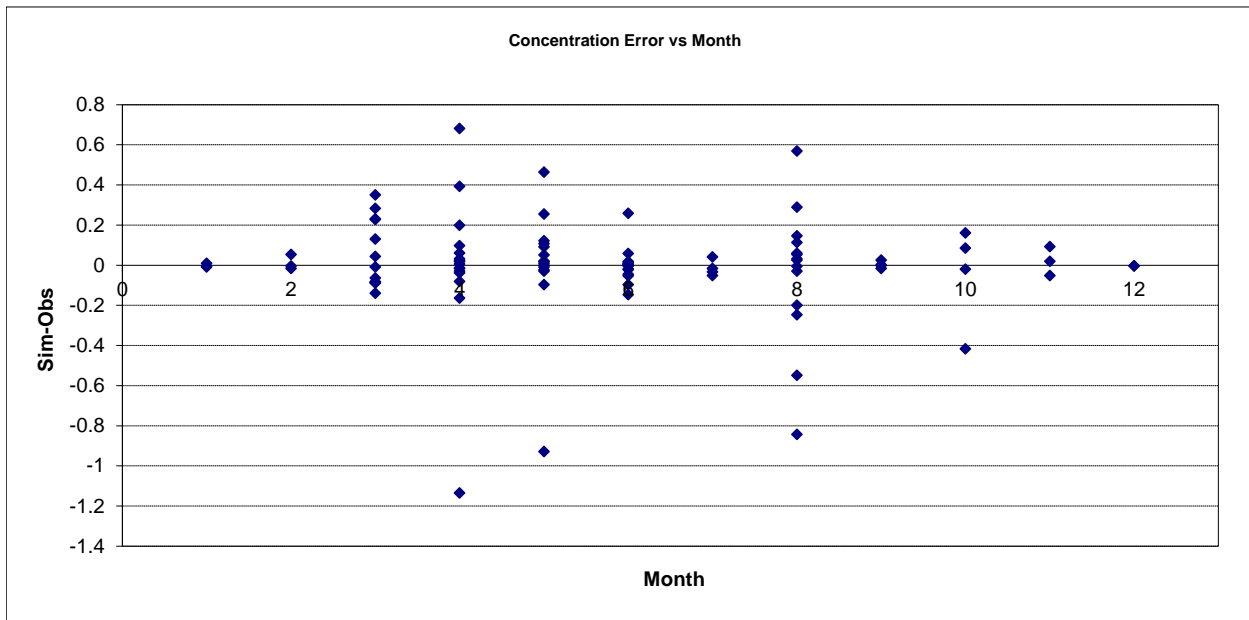


Figure B-193. Residual (Simulated - Observed) vs. Month Soluble Reactive Phosphorus (SRP) at Nemadji River nr South Superior, WI (05011002)

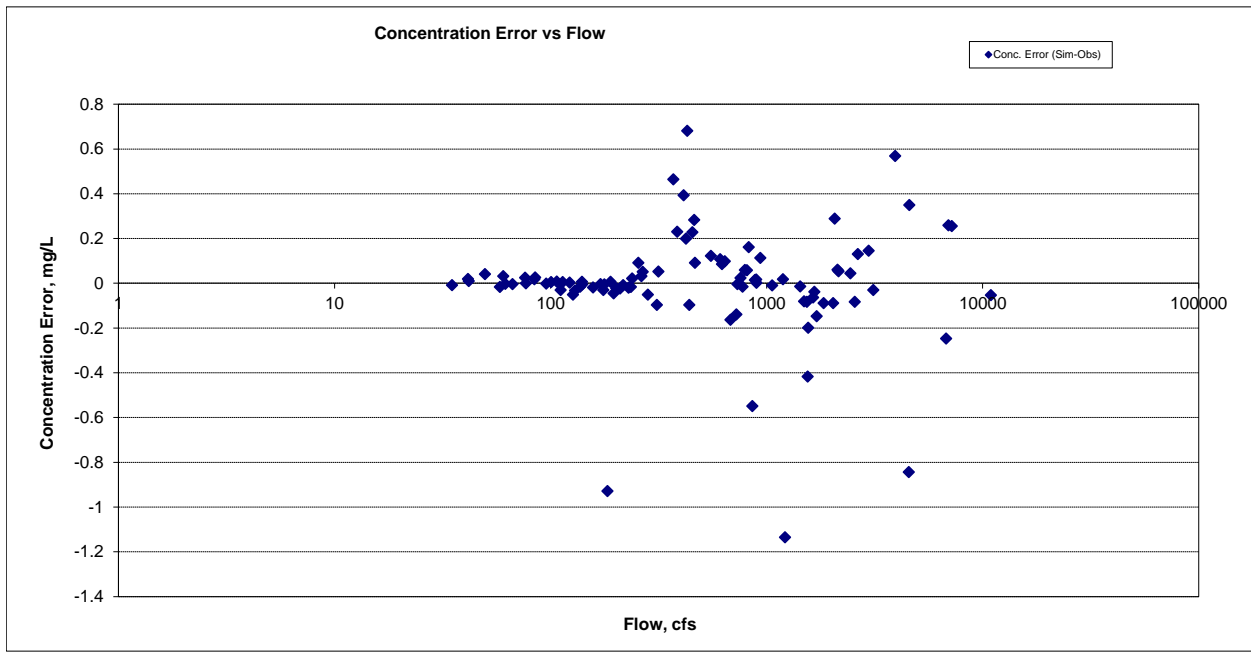
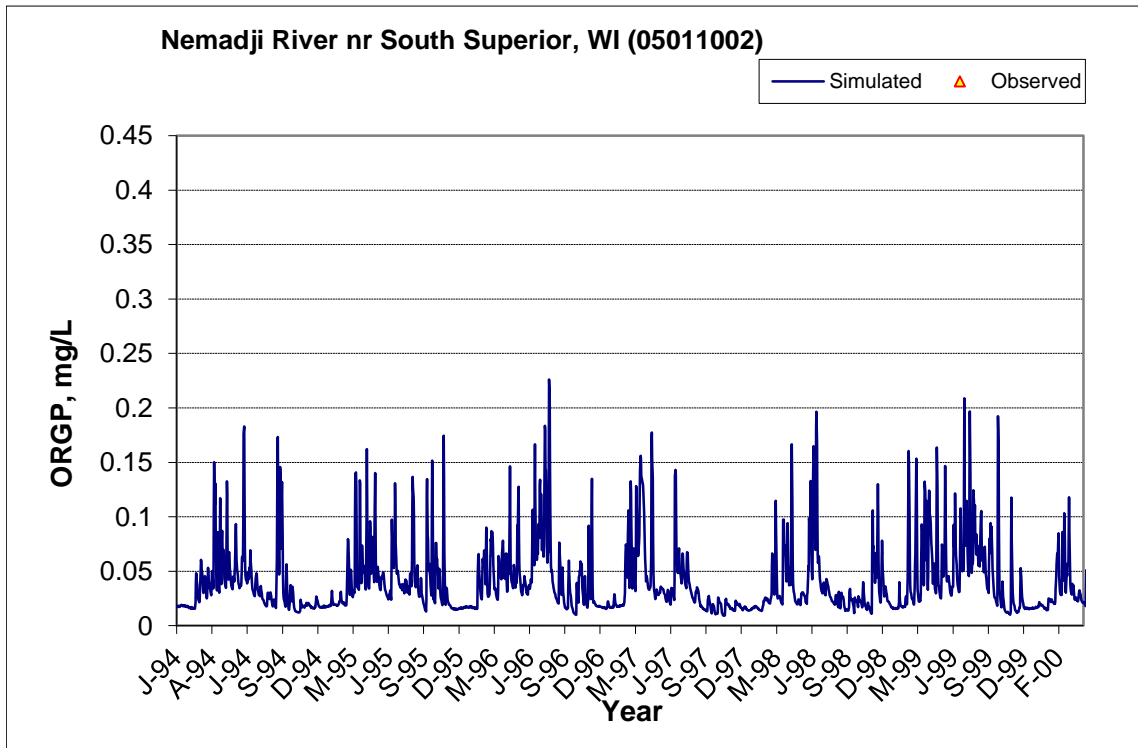


Figure B-194. Residual (Simulated - Observed) vs. Flow Soluble Reactive Phosphorus (SRP) at Nemadji River nr South Superior, WI (05011002)

B.6.7 Organic Phosphorus (OrgP)



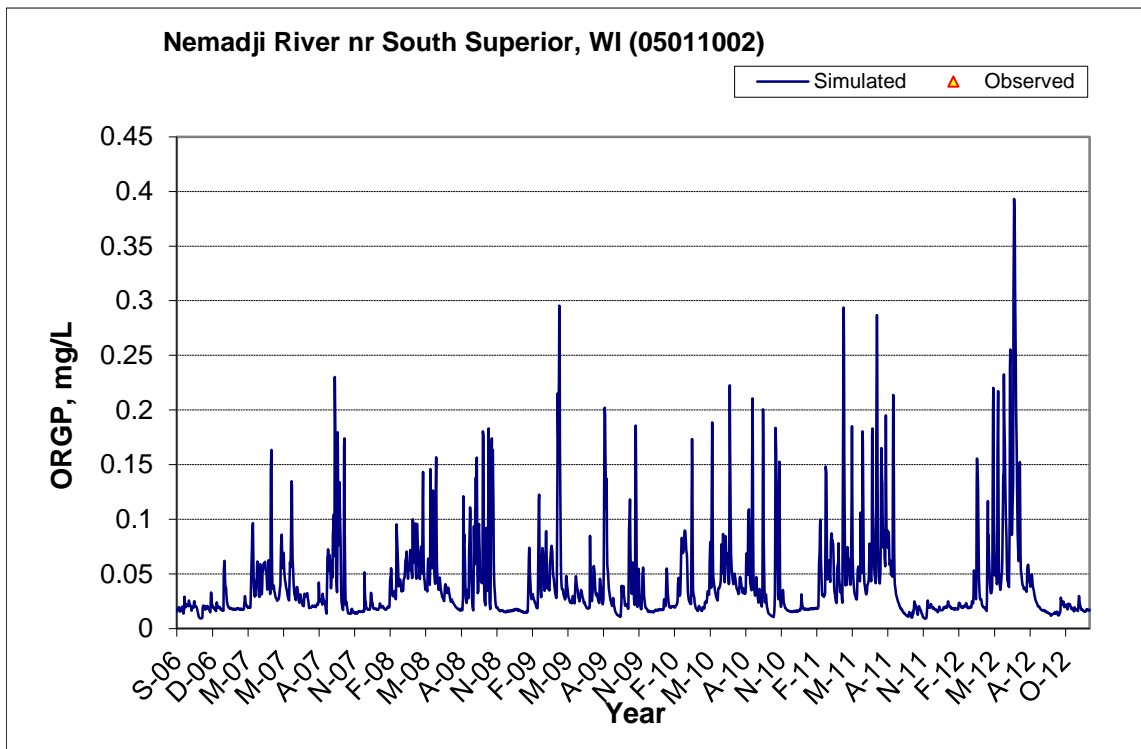
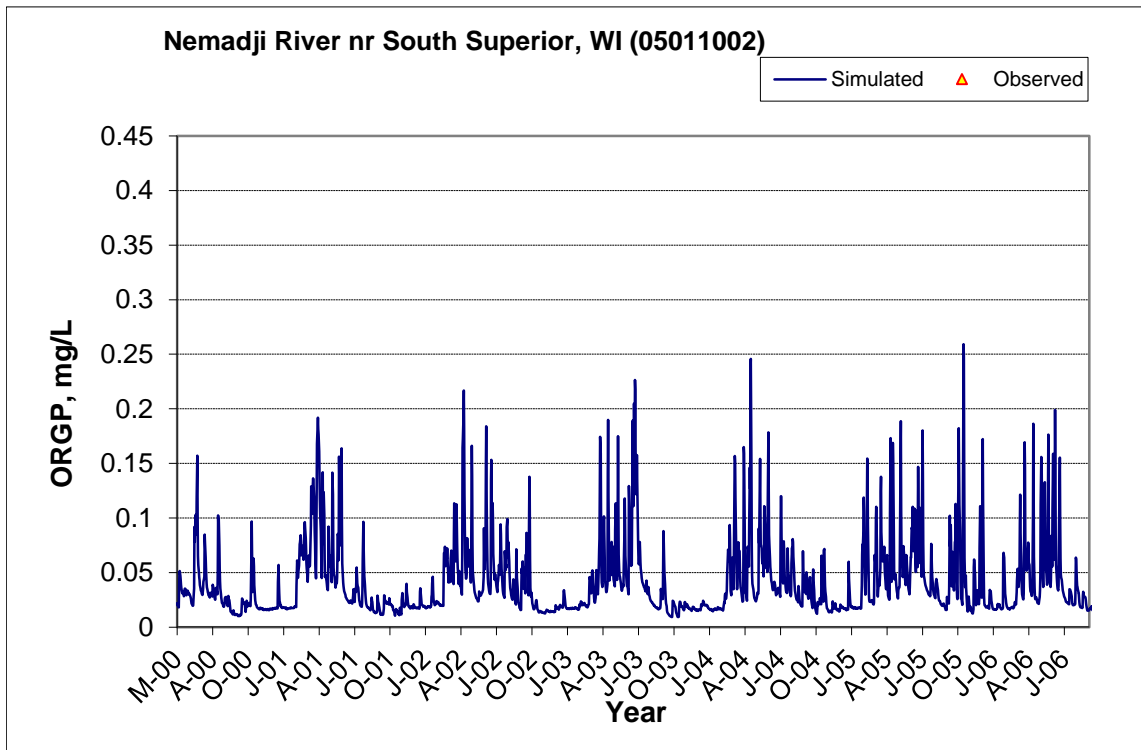


Figure B-195. Time series of observed and simulated Organic Phosphorus (OrgP) concentration at Nemadji River nr South Superior, WI (05011002)

B.6.8 Total Phosphorus (TP)

Table B-34. Total Phosphorus (TP) statistics

Period	1994-2007	2008-2012
Count	ND	97
Concentration Average Error		31.15%
Concentration Median Error		10.75%
Load Average Error		-5.04%
Load Median Error		0.35%
Paired t conc		0.25
Paired t load		0.68

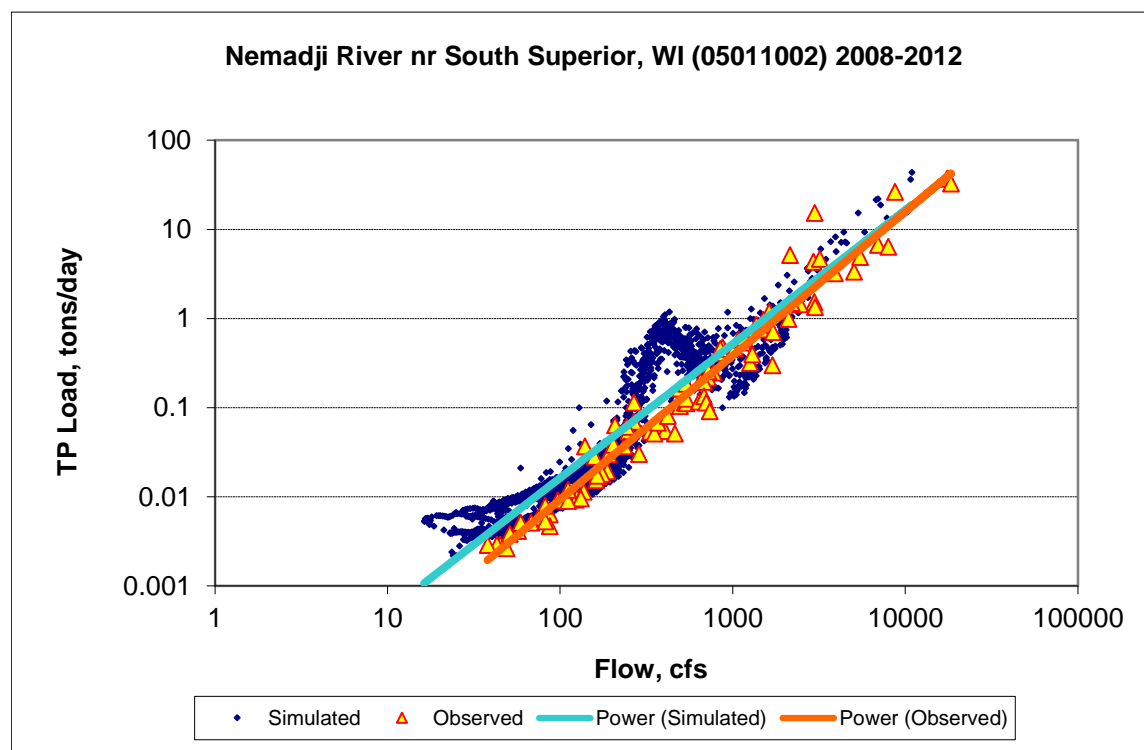
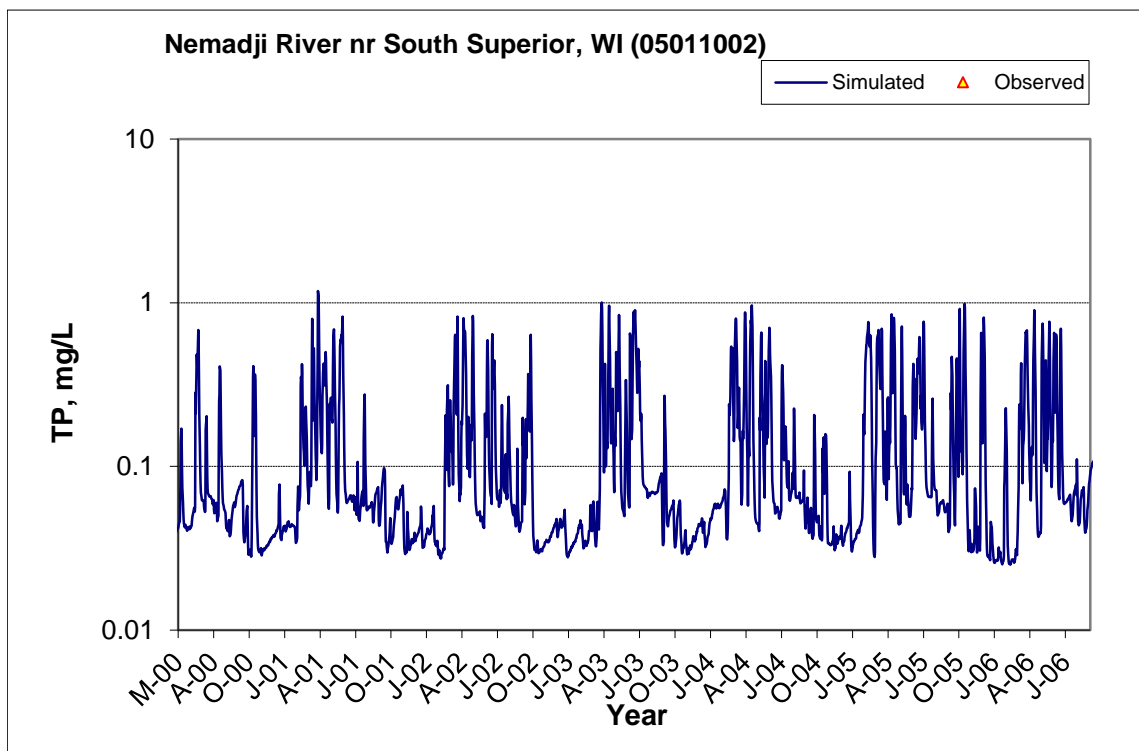
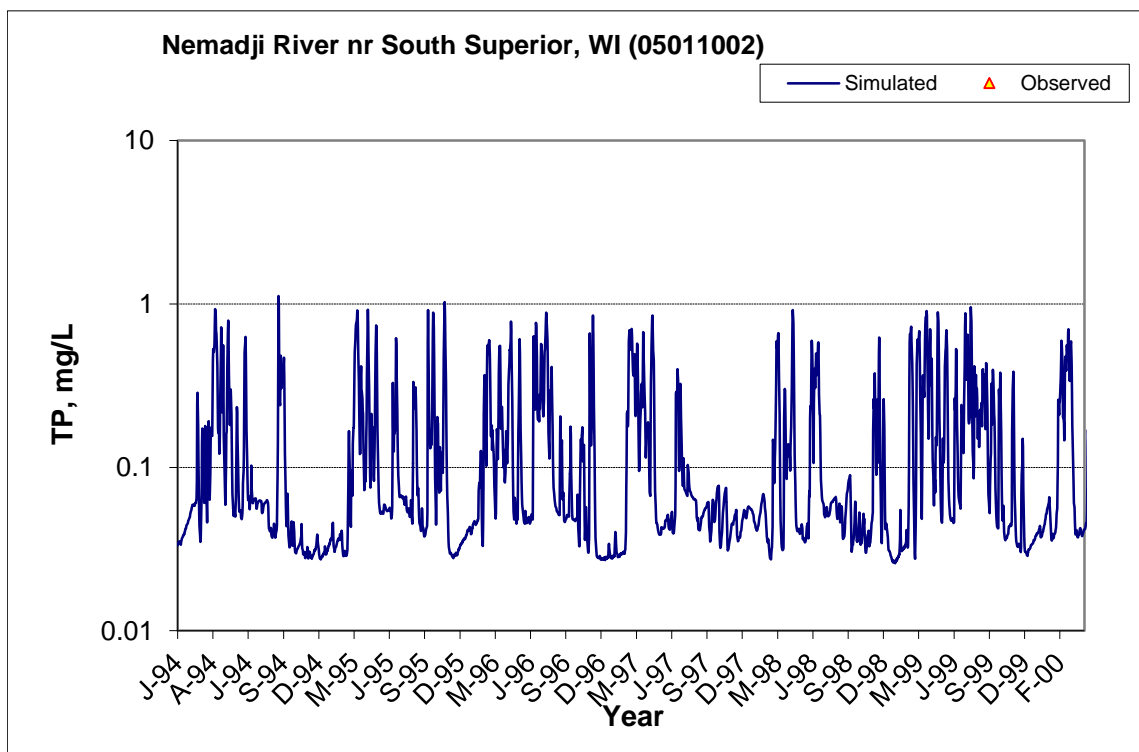


Figure B-196. Power plot of simulated and observed Total Phosphorus (TP) load vs flow at Nemadji River nr South Superior, WI (05011002) (calibration period)



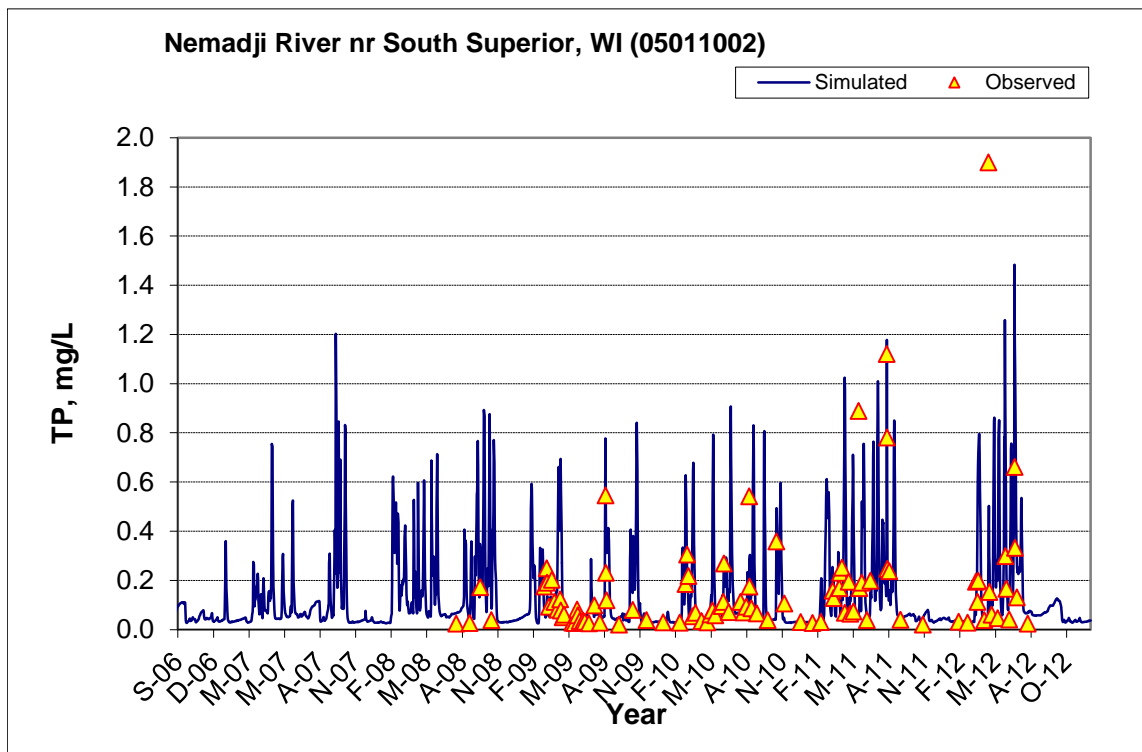


Figure B-197. Time series of observed and simulated Total Phosphorus (TP) concentration at Nemadji River nr South Superior, WI (05011002)

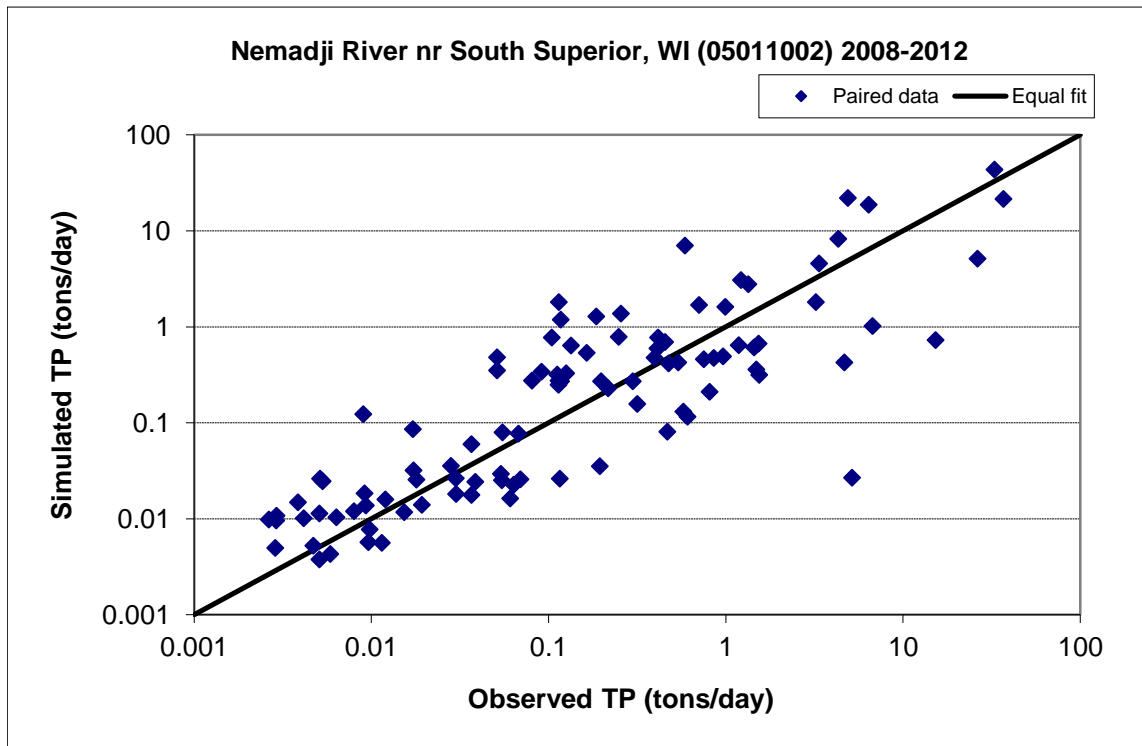


Figure B-198. Paired simulated vs. observed Total Phosphorus (TP) load at Nemadji River nr South Superior, WI (05011002) (calibration period)

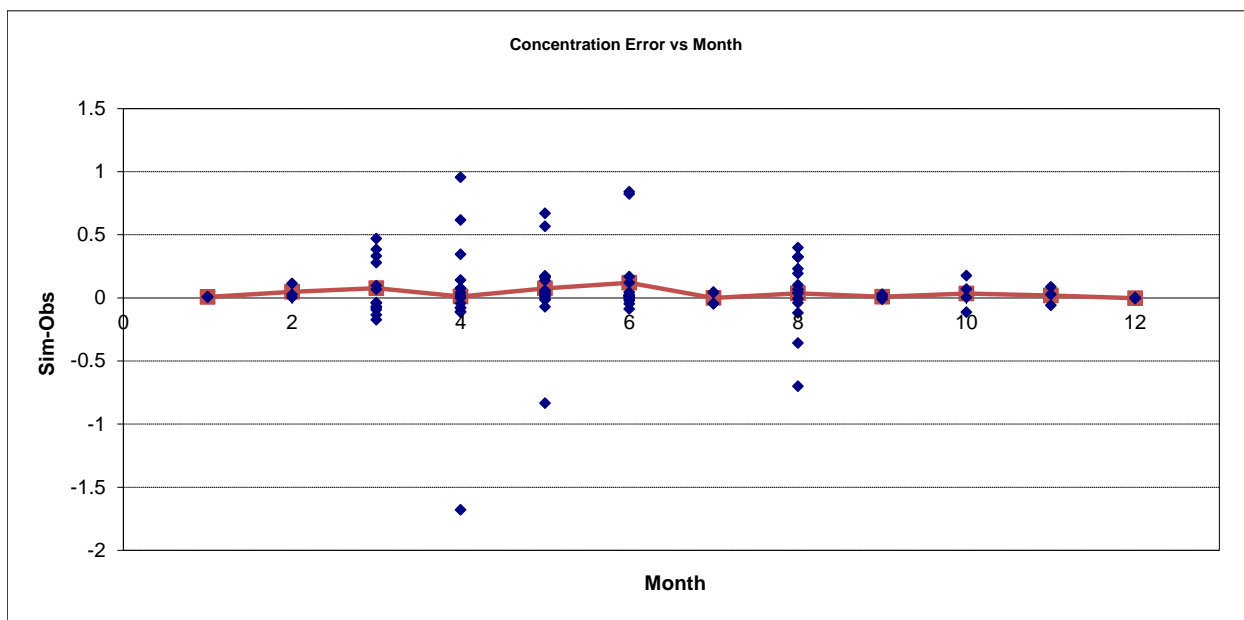


Figure B-199. Residual (Simulated - Observed) vs. Month Total Phosphorus (TP) at Nemadji River nr South Superior, WI (05011002)

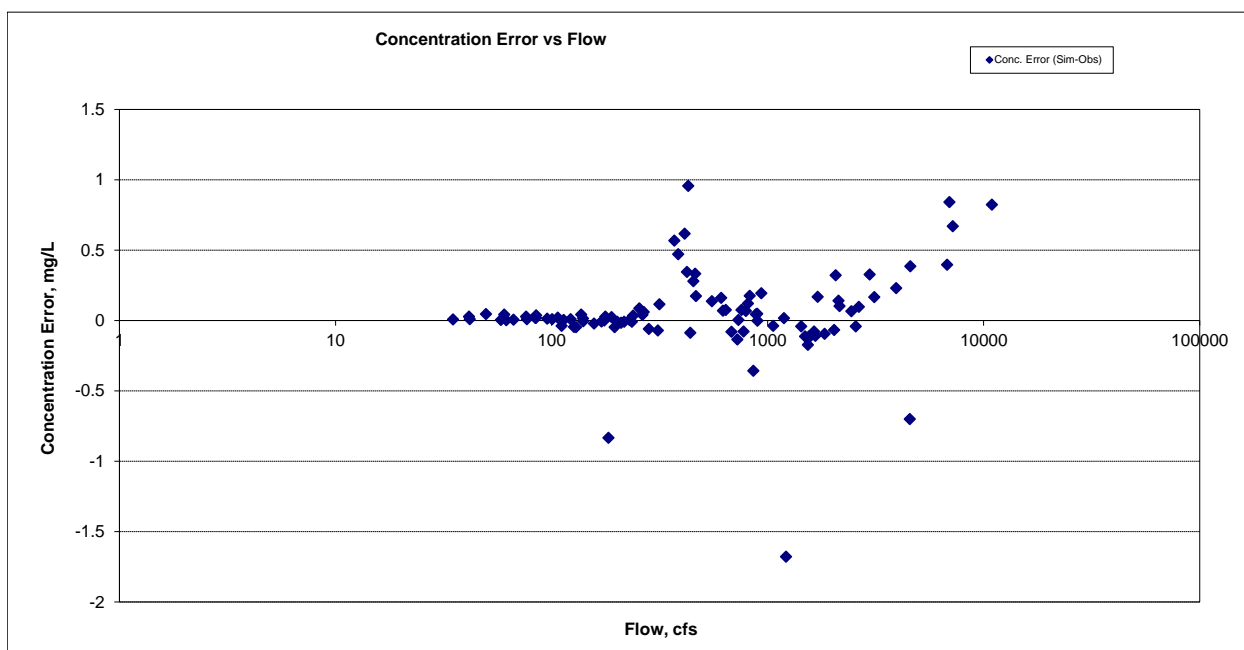


Figure B-200. Residual (Simulated - Observed) vs. Flow Total Phosphorus (TP) at Nemadji River nr South Superior, WI (05011002)