Continuous Water-Quality Monitoring in Karst Basins – Issues in Assessing Nitrate-Nitrogen and Dissolved Solutes Concentrations

Joseph L. Taraba
Biosystems and Agricultural Engineering

Alex Fogle
Kentucky Geological Survey

University of Kentucky

Summary of Presentation

- University of Kentucky Animal Research Center (ARC) Monitoring Objectives
- Conclusions of previous studies
- Watershed description
- Data collection sites
- ARC land use
- Sond probe QA/QC for continuous monitoring
- Diurnal variability of stream water quality parameters
- Future BMPs

ARC Watershed Monitoring Objectives

- To document quality of groundwater and surface water leaving the ARC:
  - as affected by the landuse changes from pasture and hayland (1992) to intensive row crop and animal production research farm.
  - as affected by implementation of BMPs on cropland and along stream corridors.
- To document quality of water entering the ARC.

Water Quality Monitoring Strategy Objectives

Utilize continuous monitoring with periodic grab sampling and flow weighted storm sampling:

- ✓ To establish sampling protocols to obtain TMDL values within the watershed
- ✓ Determine if storm chasing is necessary with a systematic sampling strategy to make solute mass load estimations in a small uplands karst basin.
- ✓ To determine sampling frequency and sample time of dayto reduce data variance for significance testing of BMP impact in ARC streams
- ✓ To determine instrument calibration protocols

Sampling Strategies

- Usually designed at beginning of study.
- Goal is to maximize information gained within given cost and time constraints.
- Strategies vary widely, depending upon study objectives (daily, monthly, utilize historic data, develop rating curve, storm flows, etc.).

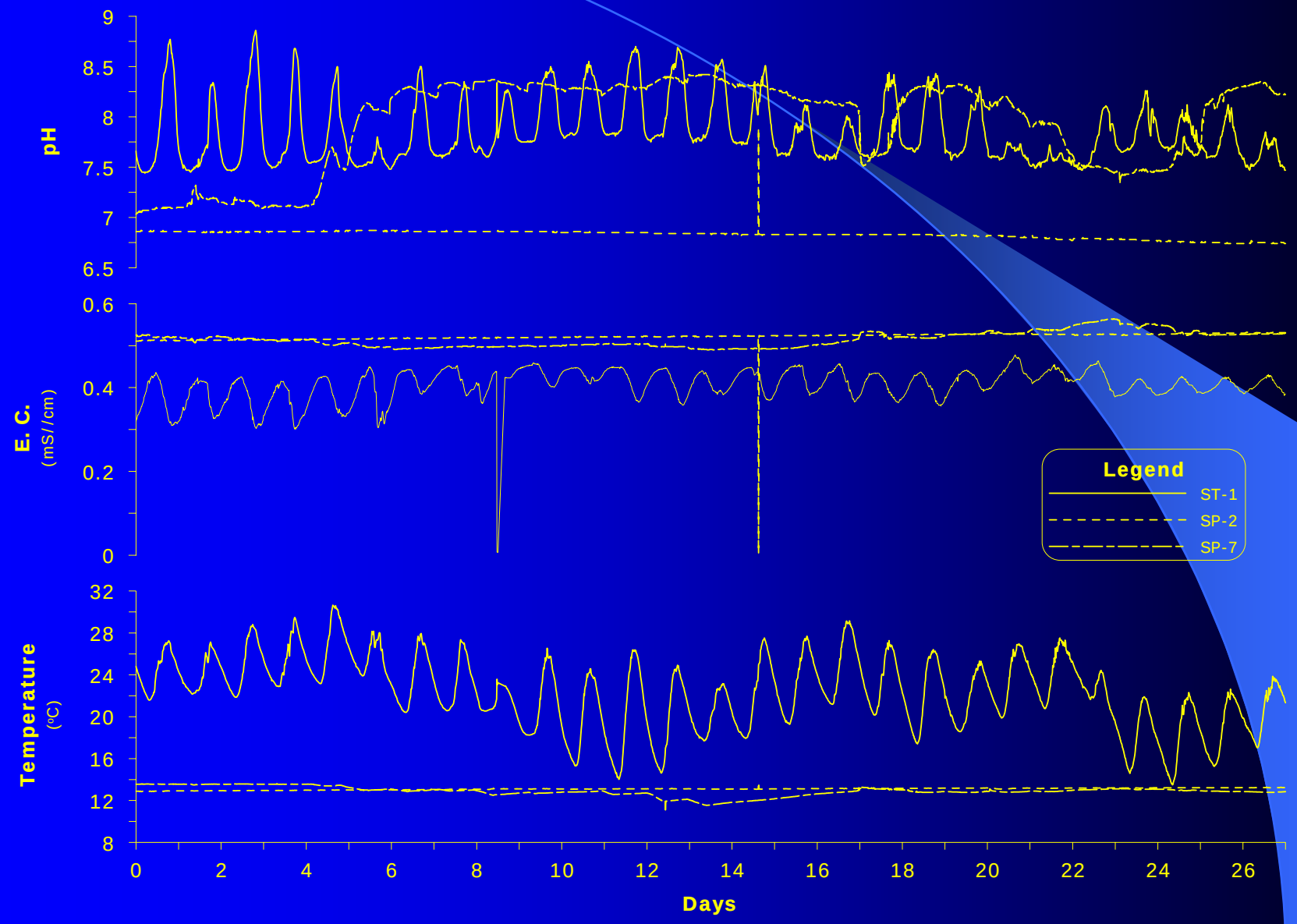
Sampling Strategies

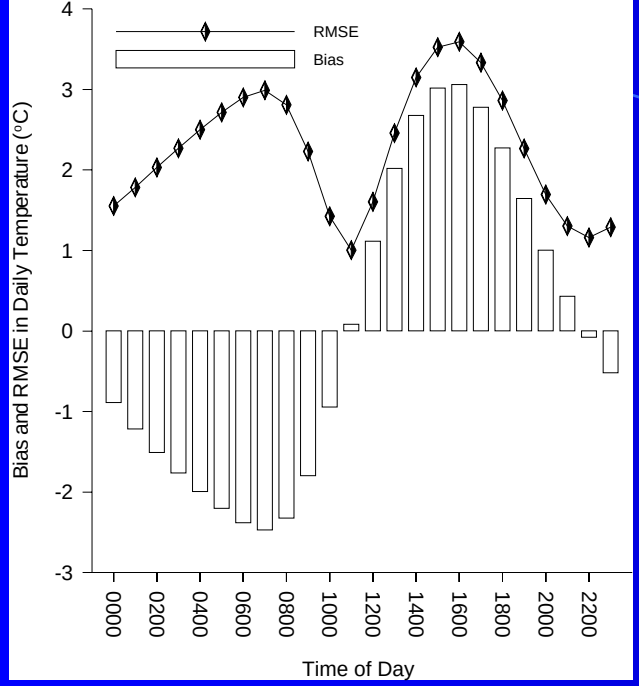
- Diurnal variations were considered negligible to seasonal and other types of variability (Taylor and Hamilton, 1994)
- Flow stratified sampling more precise than unstratified, fixed frequency sampling for load estimation in small watersheds (1400 to 11,000 ha.) (Richards and Holloway, 1987)
- Fixed period systematic sampling, plus storm chasing gave more precise load estimations (Robertson and Roerish, 1999)
- Load estimation errors in range of 15-50%.

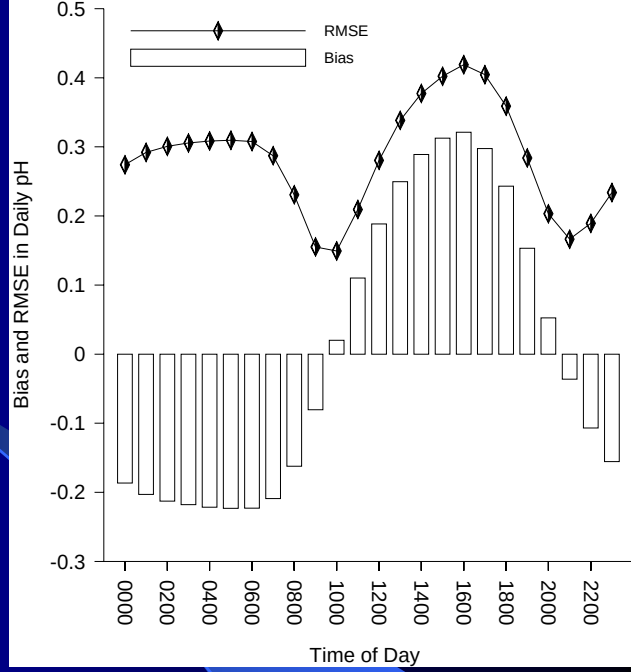
Diurnal Variations

- Water quality variations are due to air temperature, solar radiation, plant and benthic exchanges, photosynthesis, reaeration, and others.

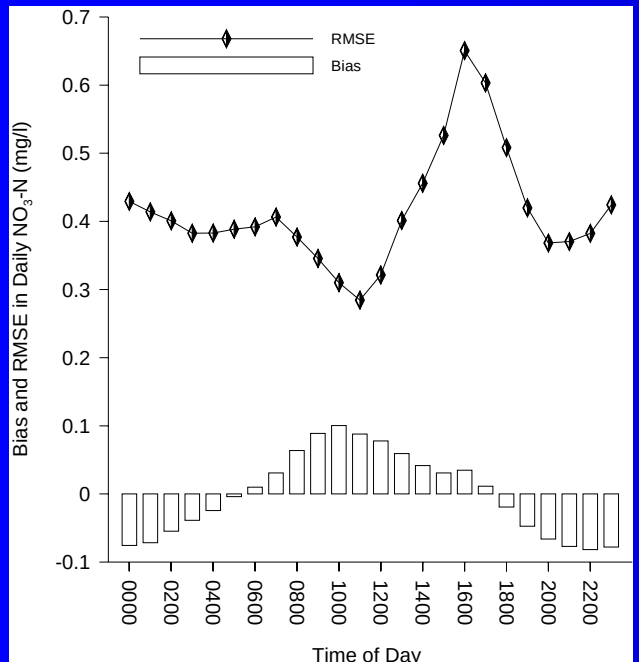
Comparison between ST-1 and SP-7 and SP-2

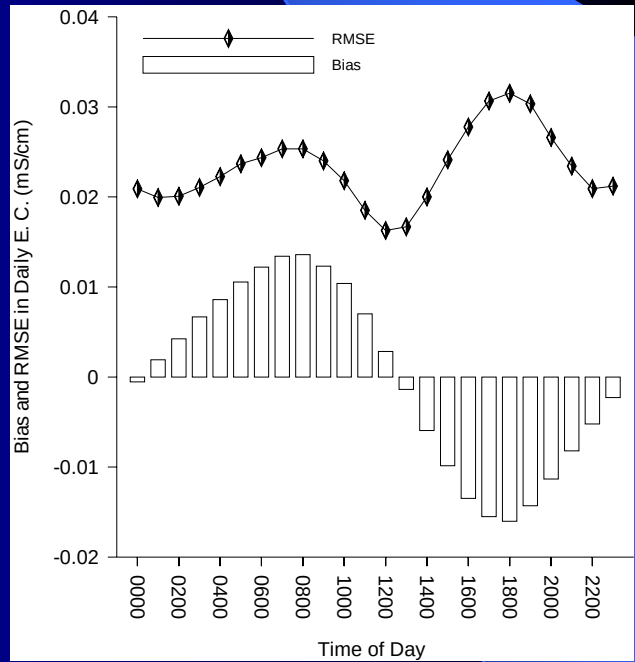






Bias and RMSE in daily values of temperature, pH, NO_3-N, and E. C. at each hour of the day.





Diurnal Variations

- Sampling strategies that give statistical confidence when comparing subwatersheds and pre-BMP and post-BMP implementation.
- Assessing strategies that will minimize monitoring costs.

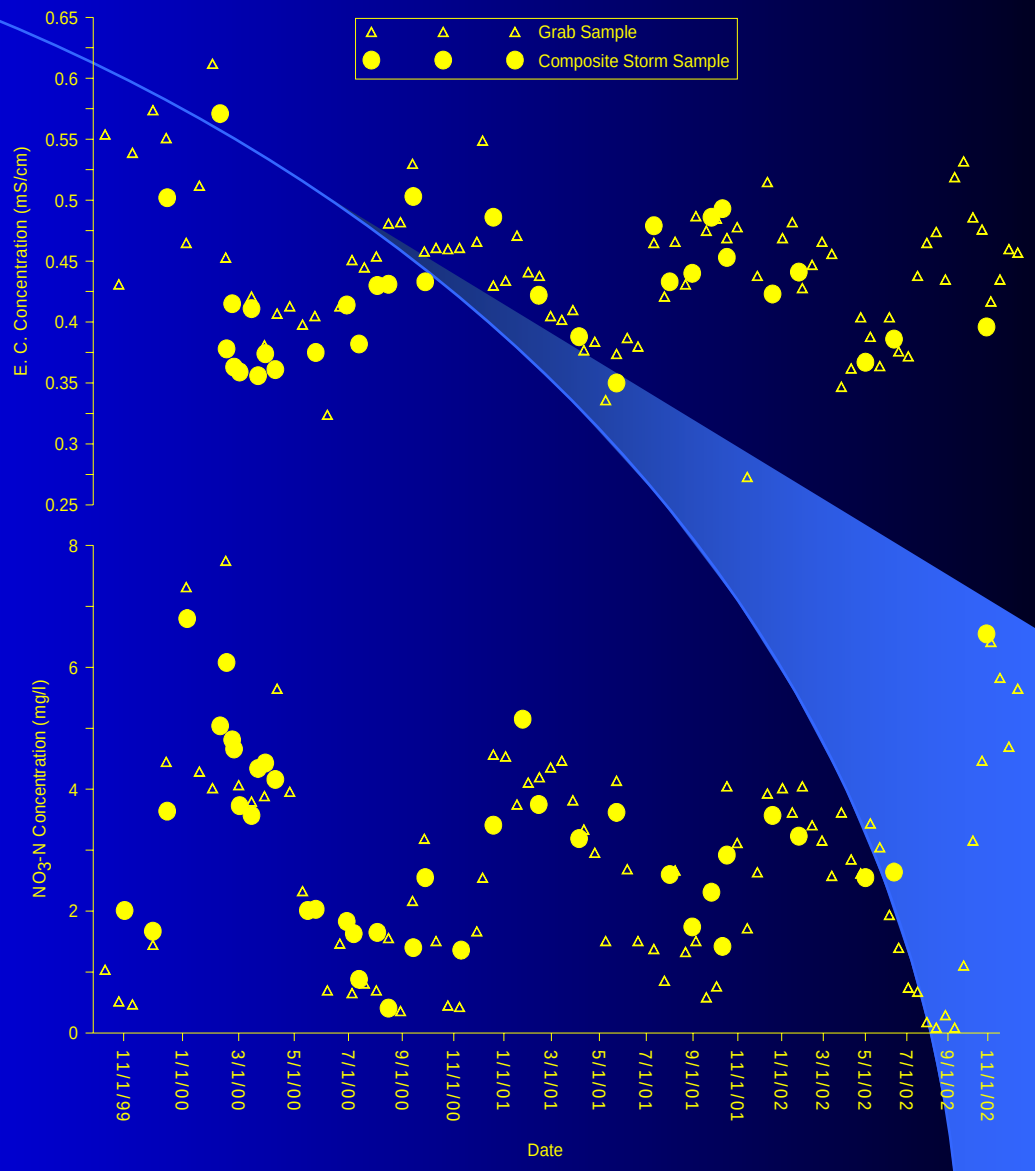
Conclusions from Previous Study

- Sampling time should be a consideration. Taylor and Hamilton's 0.1 CV threshold was consistently exceeded by temperature, E. C., and NO_3-N, except pH.
- The optimal time for collecting one aliquot and analyzing daily means of temperature, E. C., NO_3-N, and pH was near 1100 hours.

Conclusions from Previous Study

- A harmonic to noise ratio was proposed as a means of determining when stream's diurnal variability is significant.
- Storm sampling is not necessary for estimating solute mass loads.
- Systematic grab sampling at weekly, biweekly, and monthly (4 week) intervals with continuous flow consistently gave load estimates less than 10% from true load.

Comparison of Grab Sample and Composite Storm Concentrations



Camden Run Watershed Description

Aerial Photo of ARC Area

Animal Research Center Aerial Photos

Animal Research Center

Geology

Lexington Limestone Series located in the Bluegrass Physiographic Region of Kentucky

- High phosphorus content
- Most members units have minor shale bedding with one upper significant member interbedded with shale
- Broad, shallow sinkholes with caverns and underground drainage ways

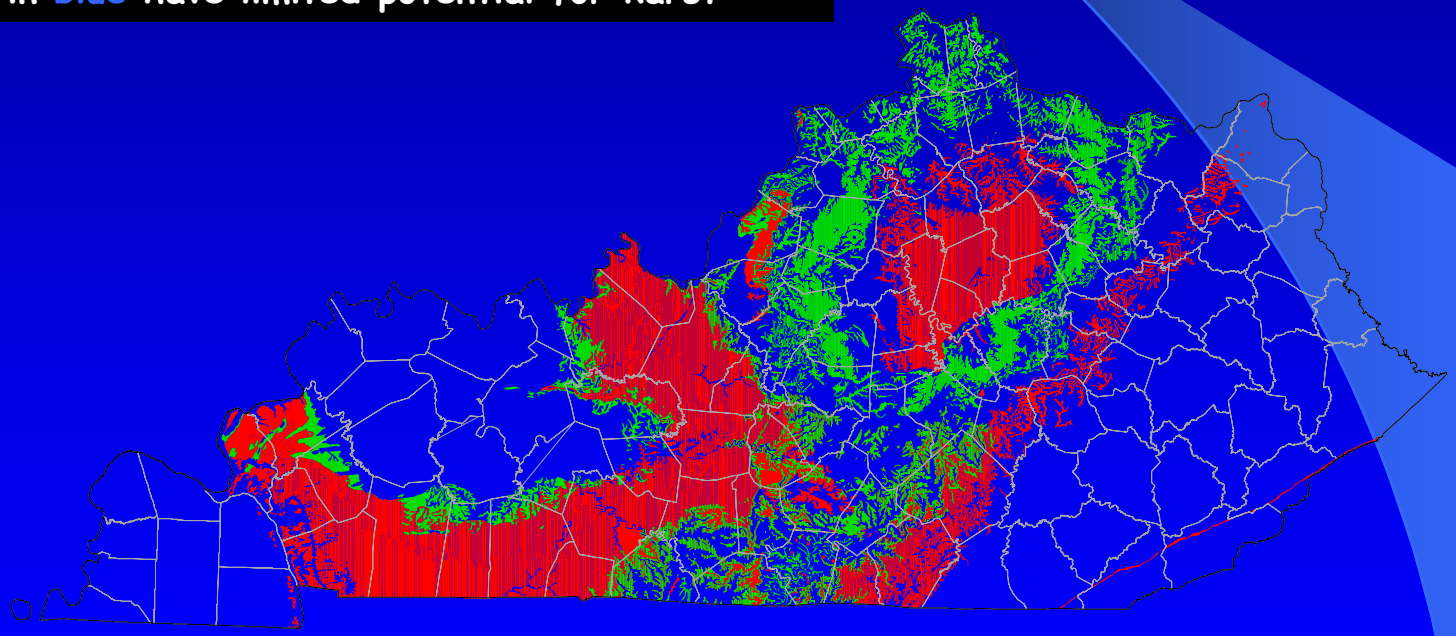
Areas of Shallow Soluble Bedrock in the Conterminous States

20 percent of the area of the 48 states is underlain by karst.

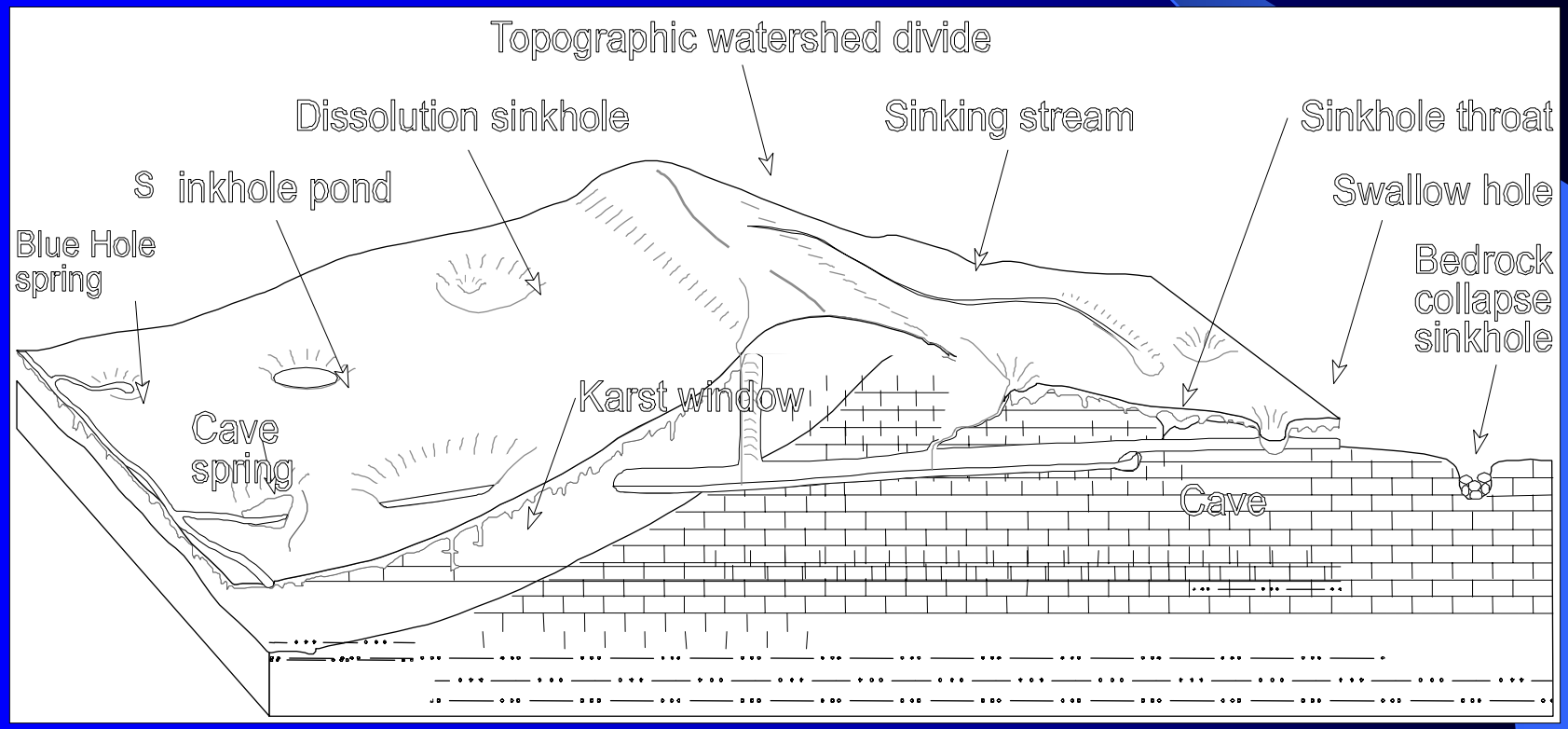
Karst in Kentucky:

Fifty-five percent of the state has potential for karst.

Areas shown in red have high potential for karst
Areas shown in green have moderate potential for karst
Areas shown in blue have limited potential for karst



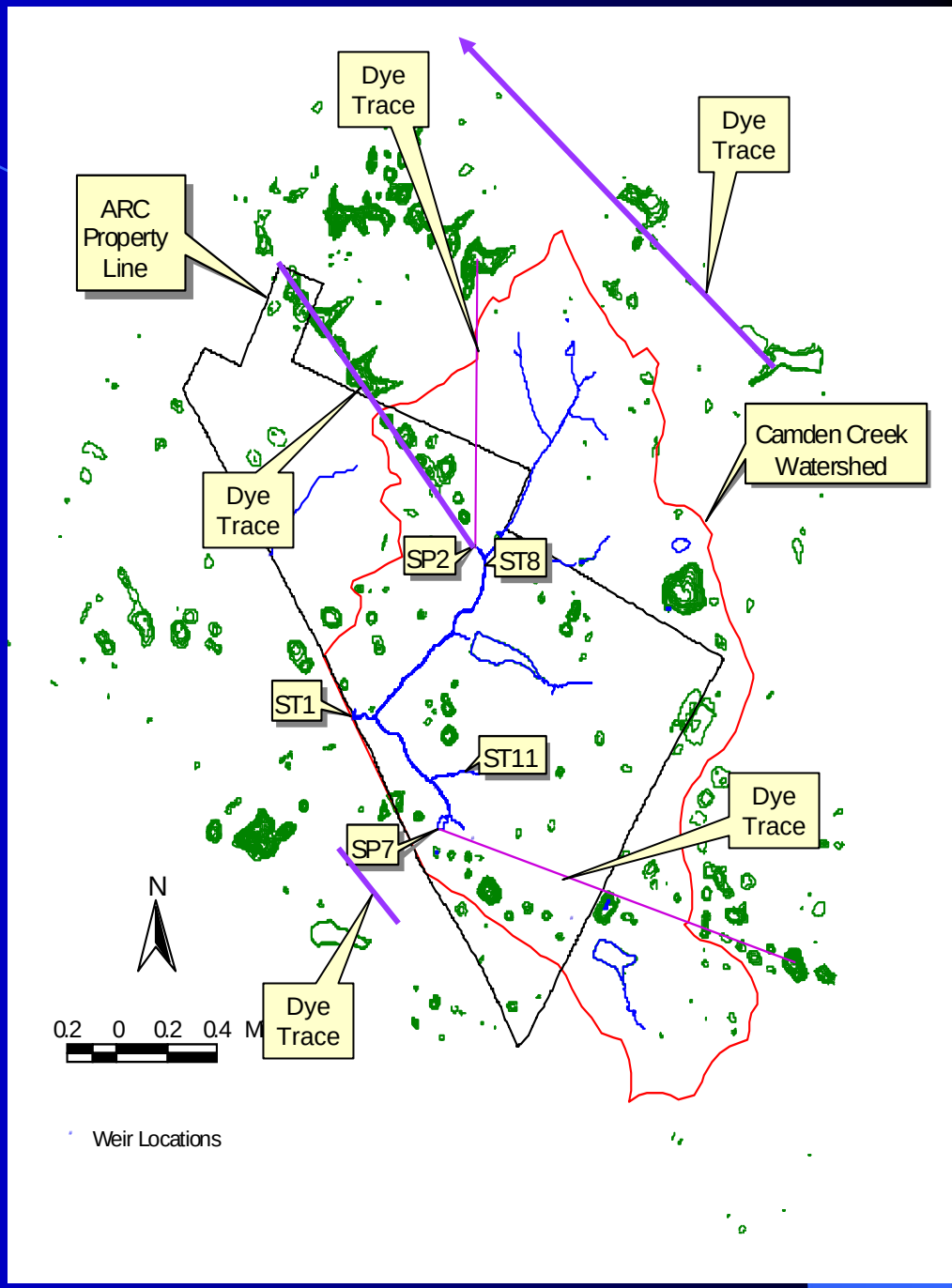
Generalized Schematic of Karst Terrane



Dye Tracing in Karst Terrain

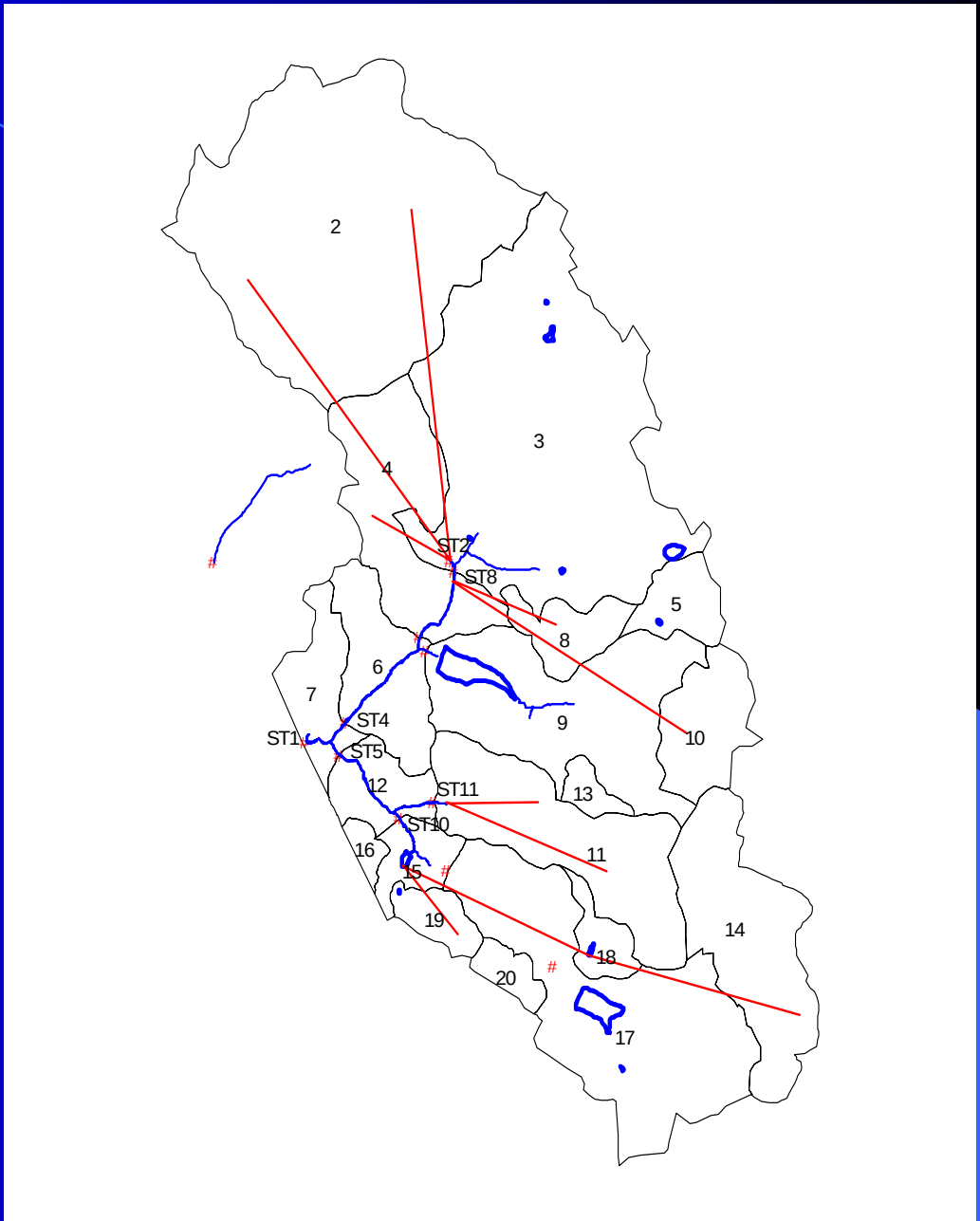
ARC Study Area

- Surface basin
- Sinkholes
- Dye traces



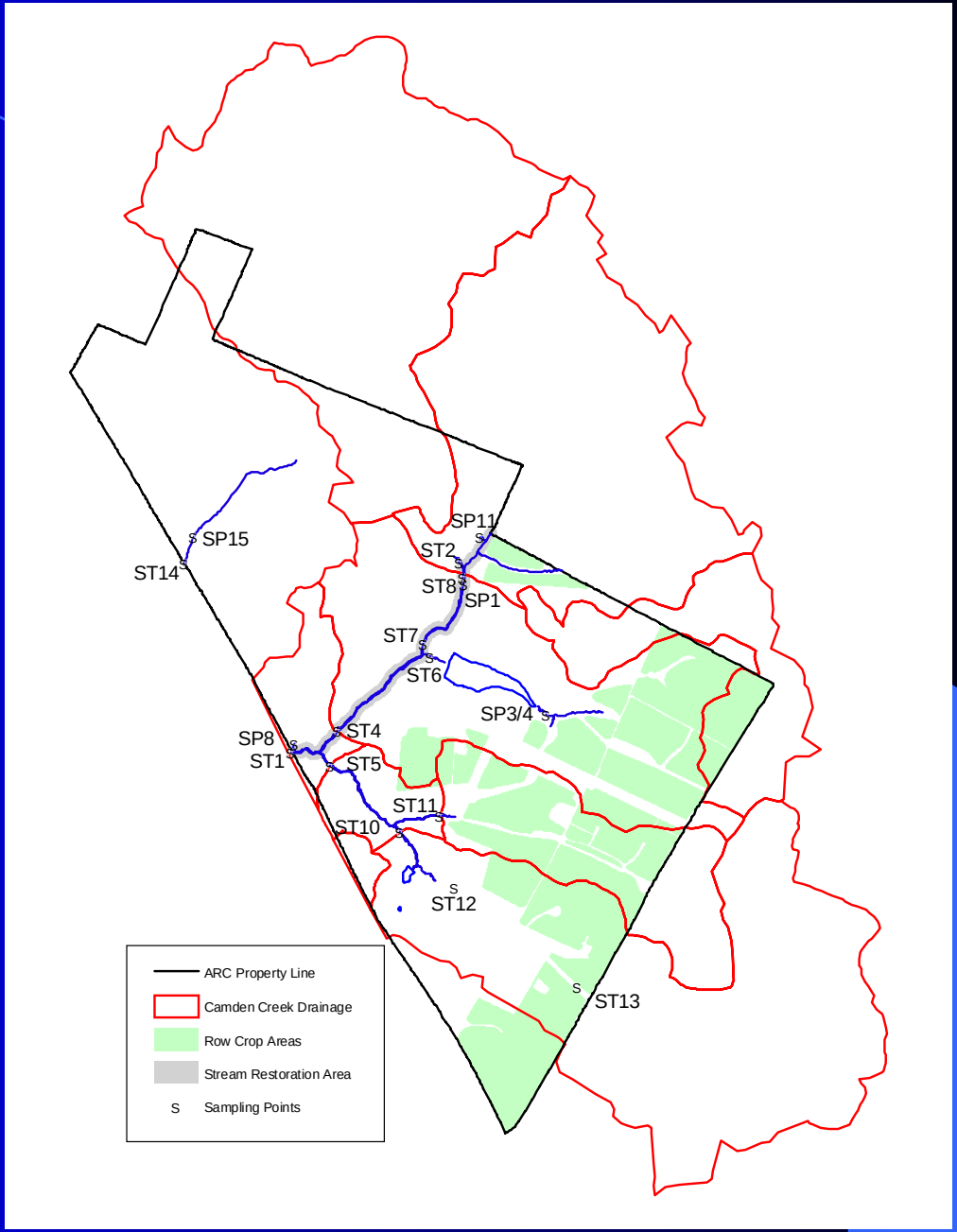
Subwatersheds

- as determined by dye tracing



Subwatersheds

- Landuse
- Sampling sites with drainage basins
- Future stream restoration corridor



ARC Watershed Areas
2000-2003

Table 1. Camden Run Watershed Landuse

	Drainage Area Above Site (Ac)	Row Crop Area Above Site (Ac.)	% Row Crop
ST1	2640	328	12.4%
ST4	1752	163	9.3%
ST5	830	165	19.8%
ST8	1177	13	1.1%
ST10	583	70	12.1%
ST11/SP6	185	93	50.1%
ST2/SP2	715	0	0.0%
ARC **ST1-(ST4+ST5)**	880	245	27.8%

Soils

Moderate to well-drained silt loams derived from high phosphatic limestone

- Maury soils: cover 70% of the area and are deep (10-15 ft. over bedrock) with silty-clay subsoil, fertile and located on broad ridge tops.
- McAfee soils: cover 15% of the area and are shallow (3 ft. or less over bedrock) with silty-clay subsoil, and are located on moderately steep slopes.

Land Use on the ARC

- Row crop acreage increased from 200-225 Ac pre 2000 to 325 Ac in 2000-2001.
- Increased use of precision nutrient management to match nutrients (NPK) to soil crop yield potential.
- Limiting cattle access to ARC streams after 2000.

Concentrations Trends of Springs on the ARC (1997-2003)

	Nitrate-N		o-Phosphate-P	
Spring	Trend	P-value	Trend	P-value
SP1	0.00190	N.S.	-0.00009	0.000
SP11	-0.01330	0.012	-0.00120	0.000
SP15	0.01680	N.S.	-0.00110	0.000
SP2	-0.02660	0.000	-0.00130	0.000
SP3/4	0.03750	0.000	-0.00090	0.000
SP6	0.02310	0.001	-0.00160	0.000
SP8	-0.03300	0.021	-0.00058	0.037

Riparian Research Pastures

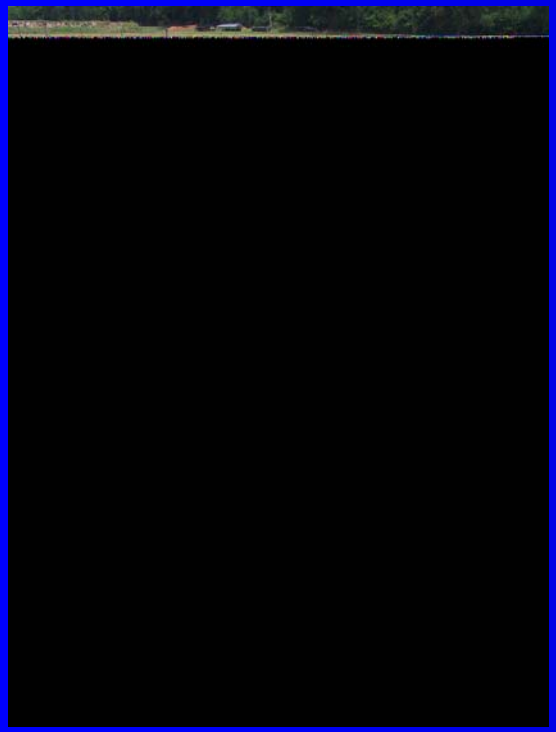
Established - 2000

2003

Data Collection

Stream V-Notch Weir

Water Quality Monitoring Sites



Streams

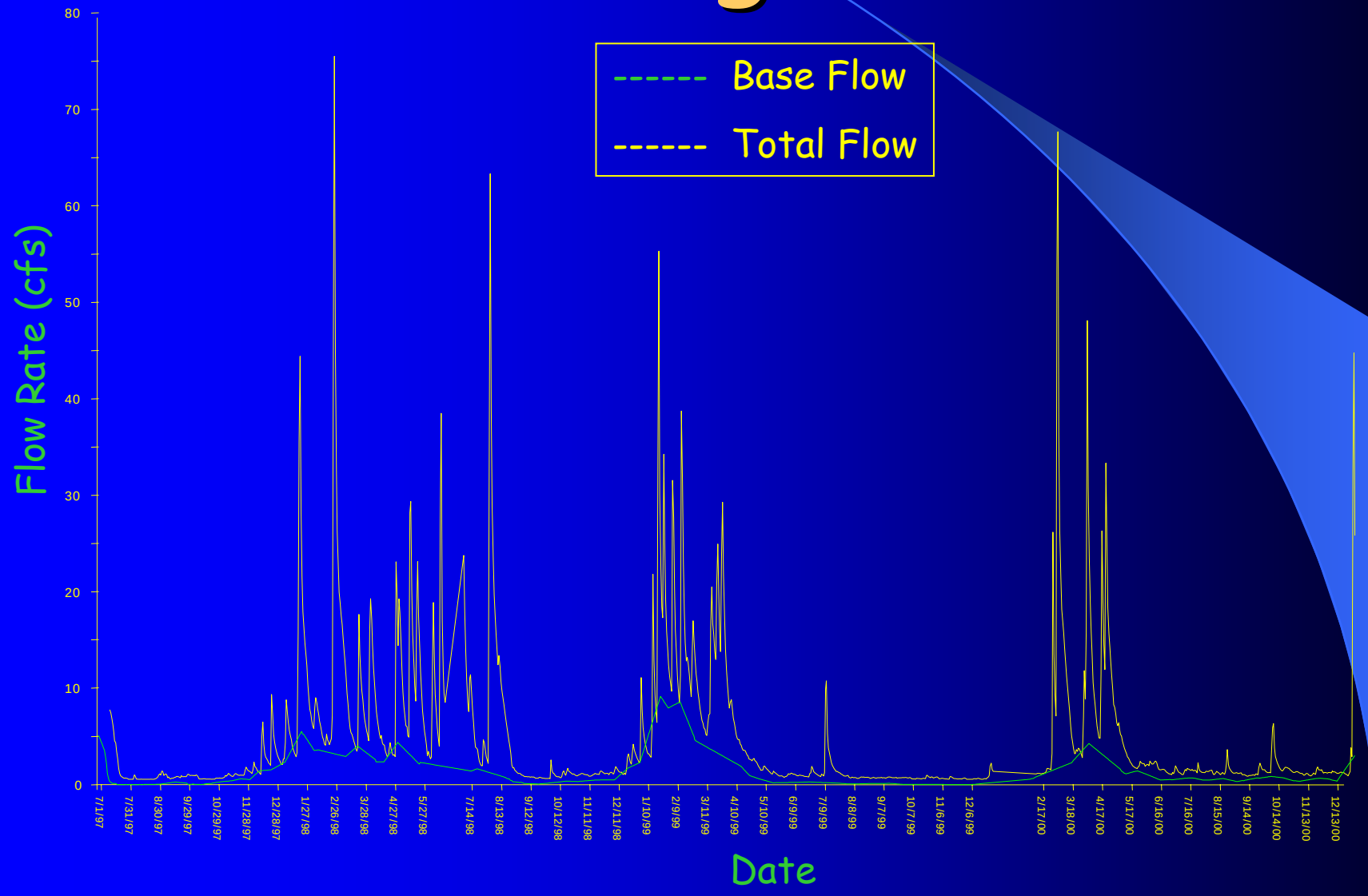
Monitoring

- Monitored constituents: ammonia-N, nitrate+nitrite-N, Total-N, organic-N, Total-P, phosphate-P, TOC, TSS, metolachlor, and triazine
  - Measured biweekly (grab)
  - Flow composited storm event (ISCO)
- Flow volume measured every 10 or 15 minutes at 7 stream sites (ISCO)
- Site ST-1 has continuous monitoring of nitrate-N, E.C., temperature, and pH (YSI)

YSI 6000UPG Water Quality Monitor

- Temperature
- pH
- Electroconductivity (E.C.)
- Dissolved Oxygen (D.O.)
- Nitrate Nitrogen (NO_3-N)
- Turbidity

ARC Camden Run Discharge Rate



Sampling Strategies

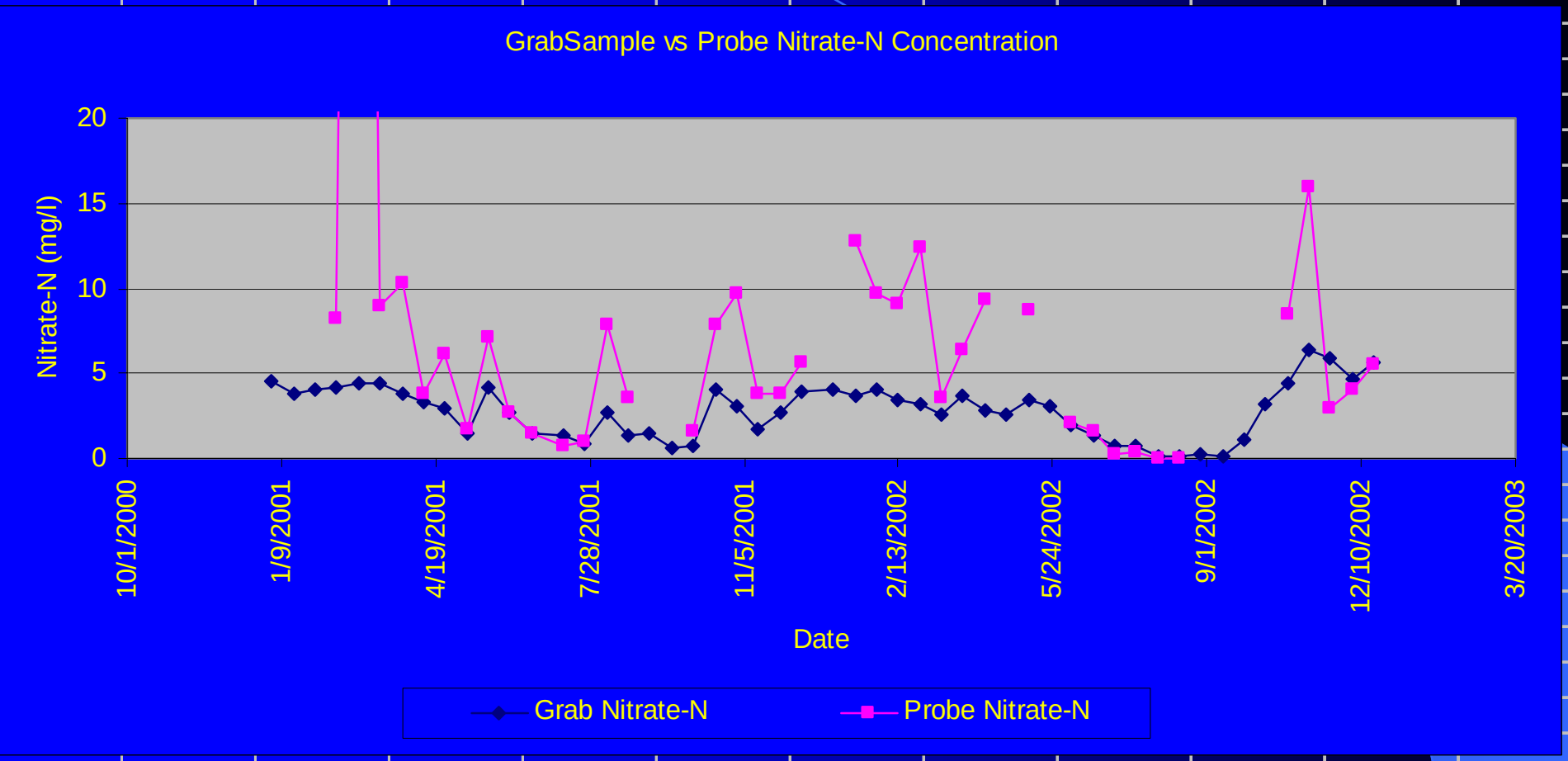
- Goal is to maximize information gained within given cost and time constraints.
- Strategies vary widely, depending upon study objectives (daily, monthly, utilize historic data, develop rating curve, storm flows, etc.).
- Load estimation errors in range of 15-50%.

Diurnal Variations

- Sampling strategies that give statistical confidence when comparing subwatersheds and pre-BMP and post-BMP implementation.
- Assessing strategies that will minimize monitoring costs.

Data Handling

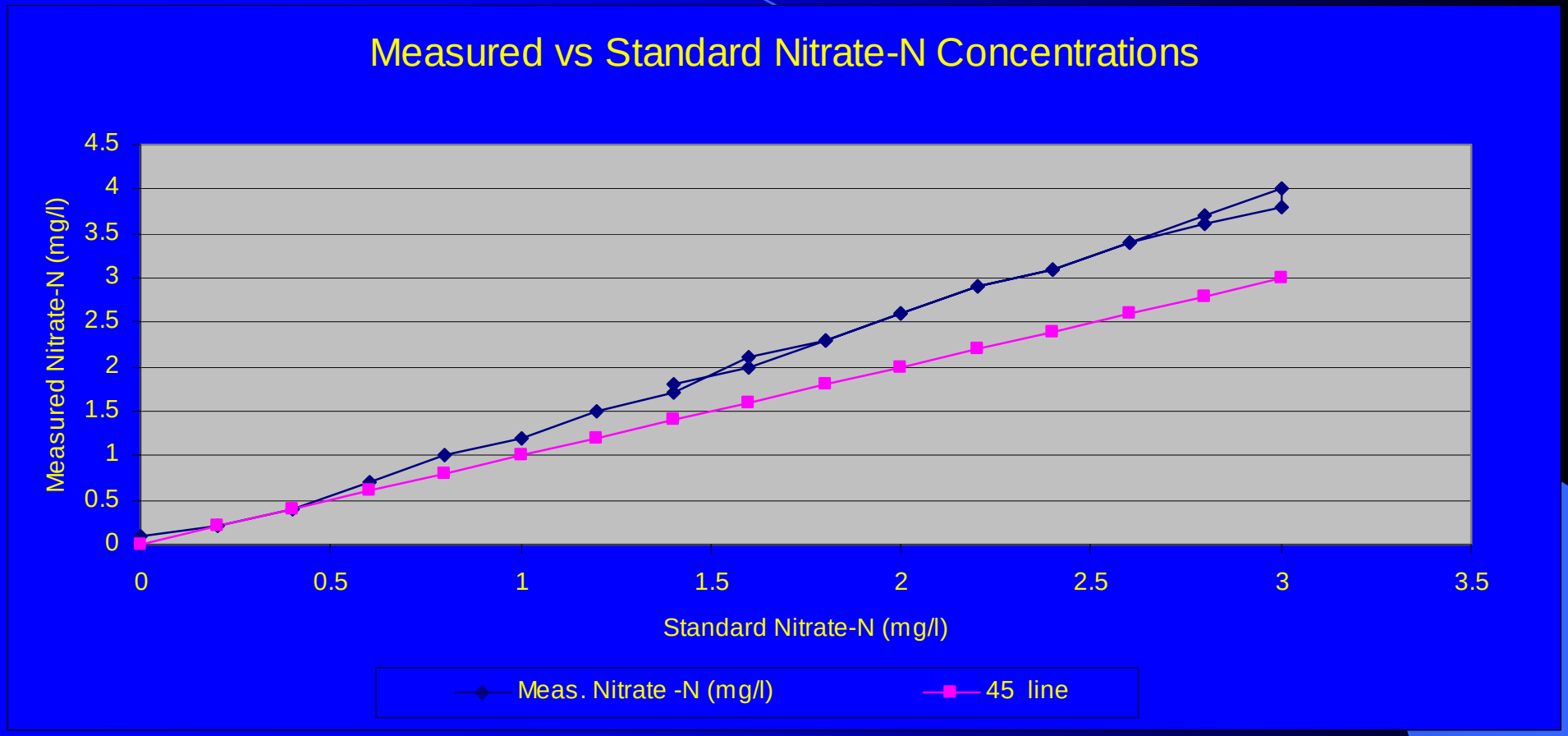
- YSI sensors subject to drift.
- Data was compensated for drift using bi-weekly grab data per YSI 6000 Instruction Manual
- Periodic calibration (every 2 weeks)


GrabSample vs Probe Nitrate-N Concentration
Nitrate-N (mg/l)
20
15
10
5
0
10/1/2000
1/9/2001
4/19/2001
7/28/2001
11/5/2001
2/13/2002
5/24/2002
9/1/2002
12/10/2002
3/20/2003
Date
Grab Nitrate-N
Probe Nitrate-N

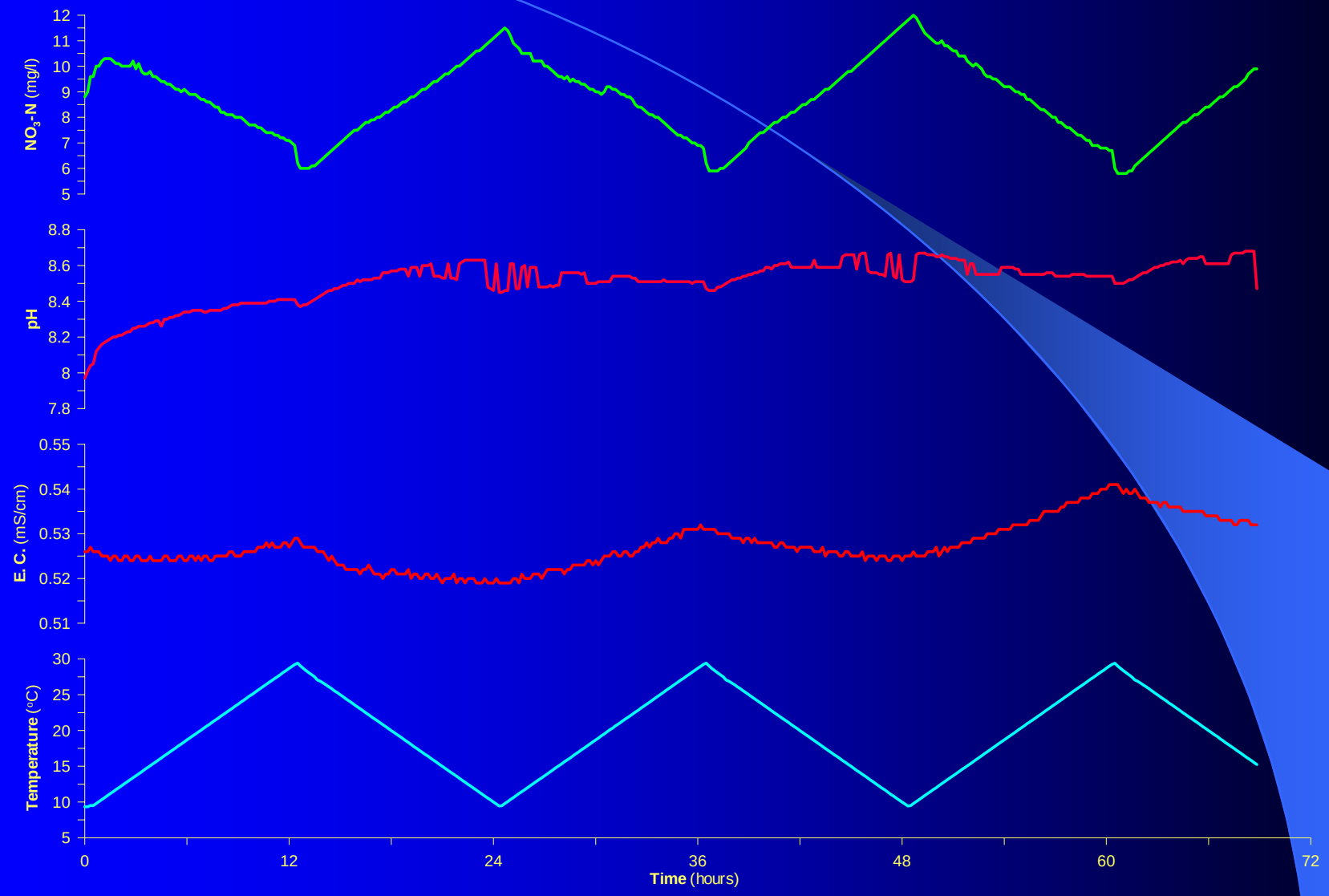
Calibration of YSI Nitrate Probe

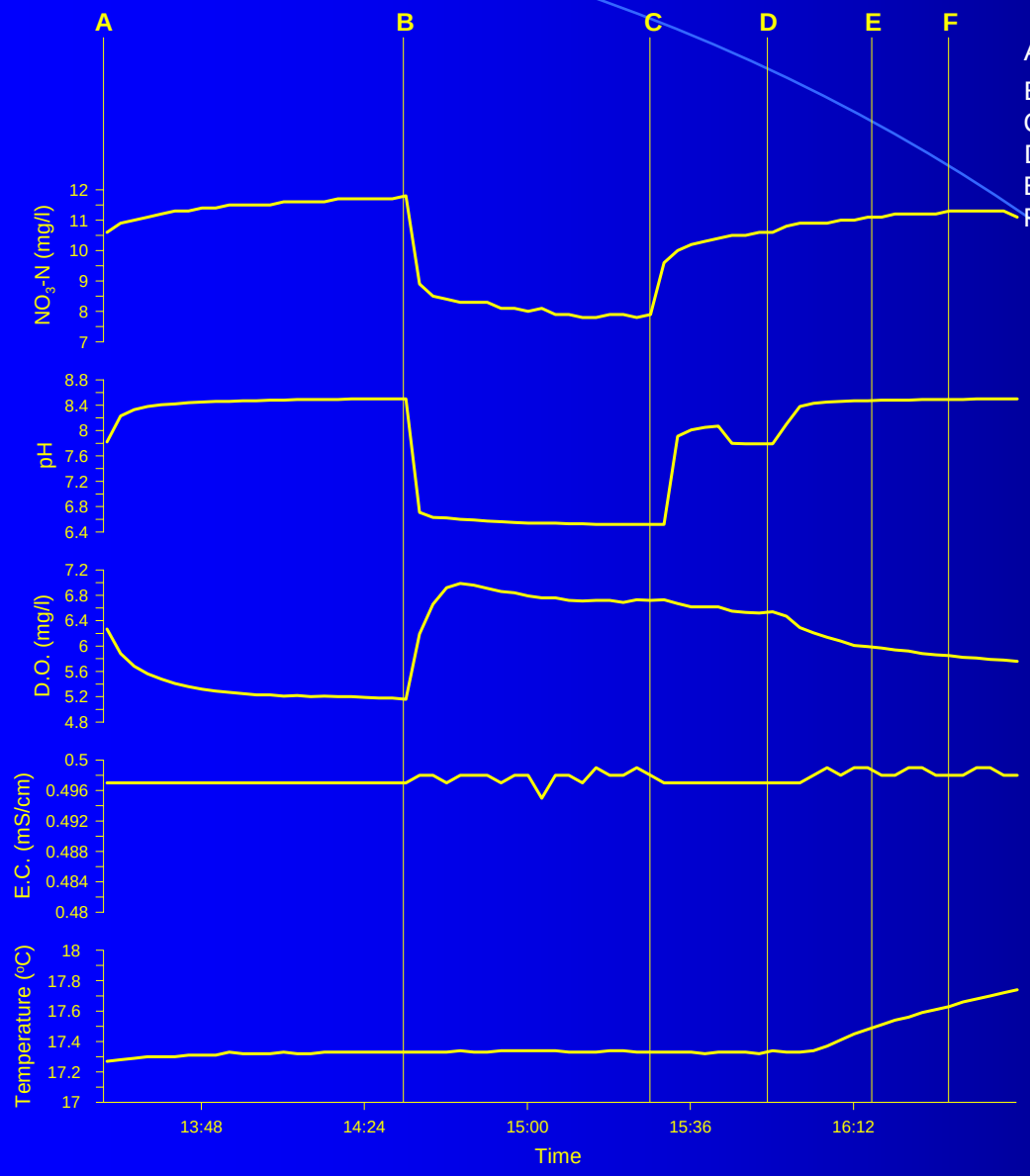
		Nitrate-N (mg/l)			
		1	4	7	10
Temperature C	22	1.5	5.0	8.5	12.8
	14.5	1.4	4.6	8.8	11.7
	8	1.2	4.7	7.7	11.0

Average % normalized error = 22%



Average % normalized error = 29%


NO3-N (mg/l)
12
11
10
9
8
7
6
5
pH
8.8
8.6
8.4
8.2
8
7.8
E. C. (mS/cm)
0.55
0.54
0.53
0.52
0.51
Temperature (°C)
30
25
20
15
10
5
0
12
24
36
48
60
72
Time (hours)



A - Isolated Sonde in unattended mode in water bath.

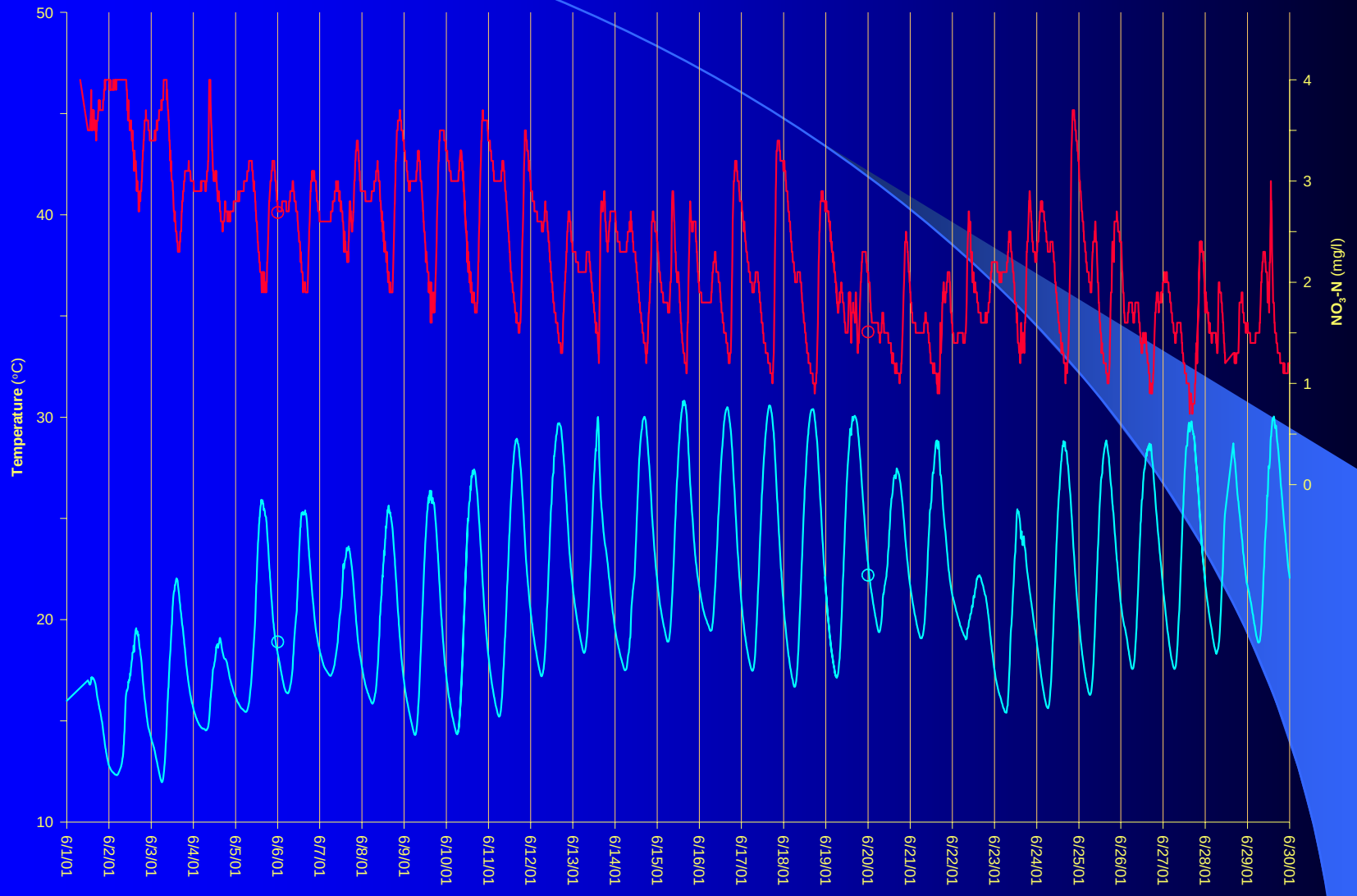
B - Sonde connected to plugged-in laptop.

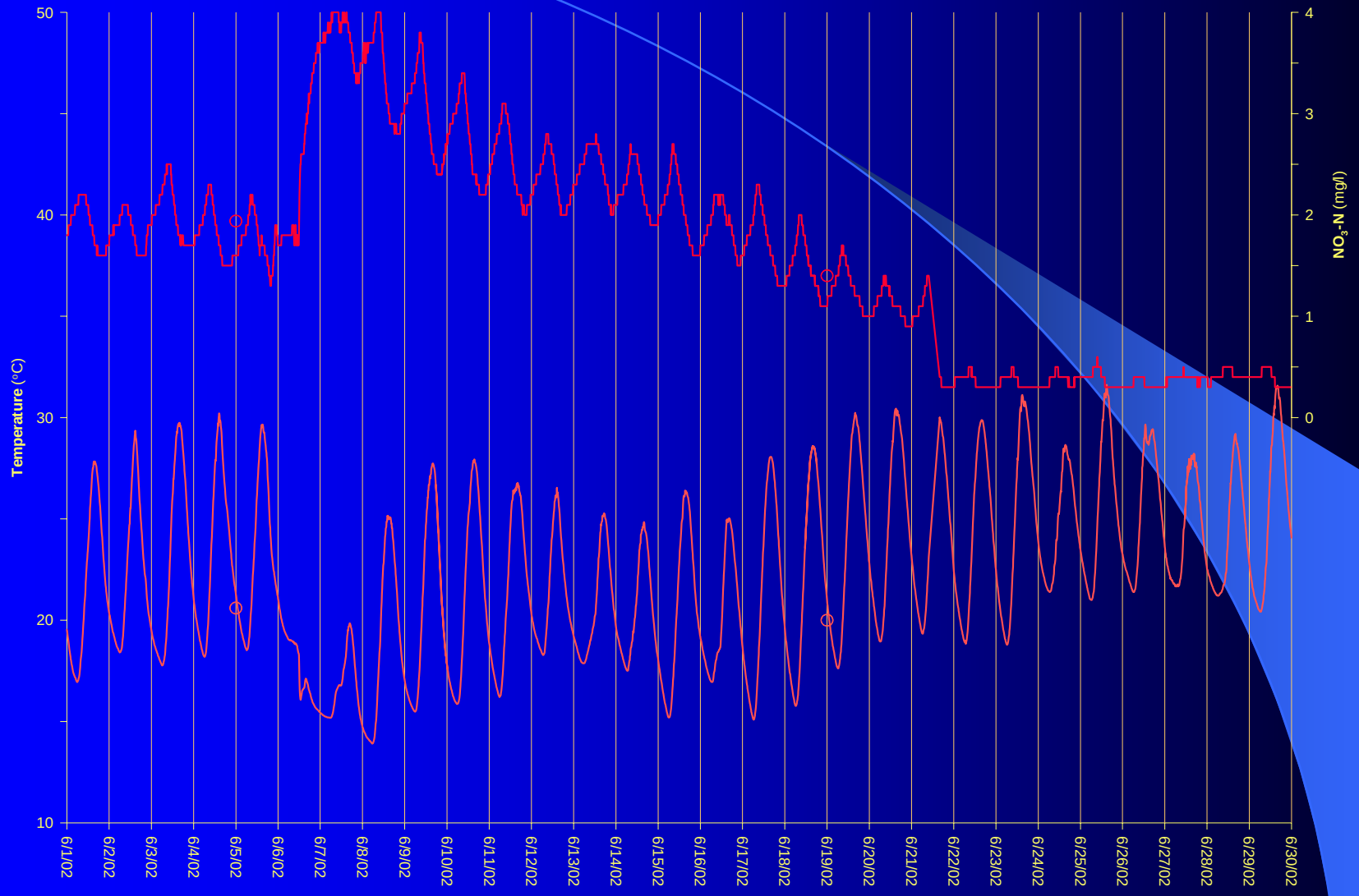
C - Laptop disconnected from AC power.

D - Water bath disconnected from AC power.

E - Sonde disconnected from laptop.

F – Water bath reconnected to AC power but shut down.

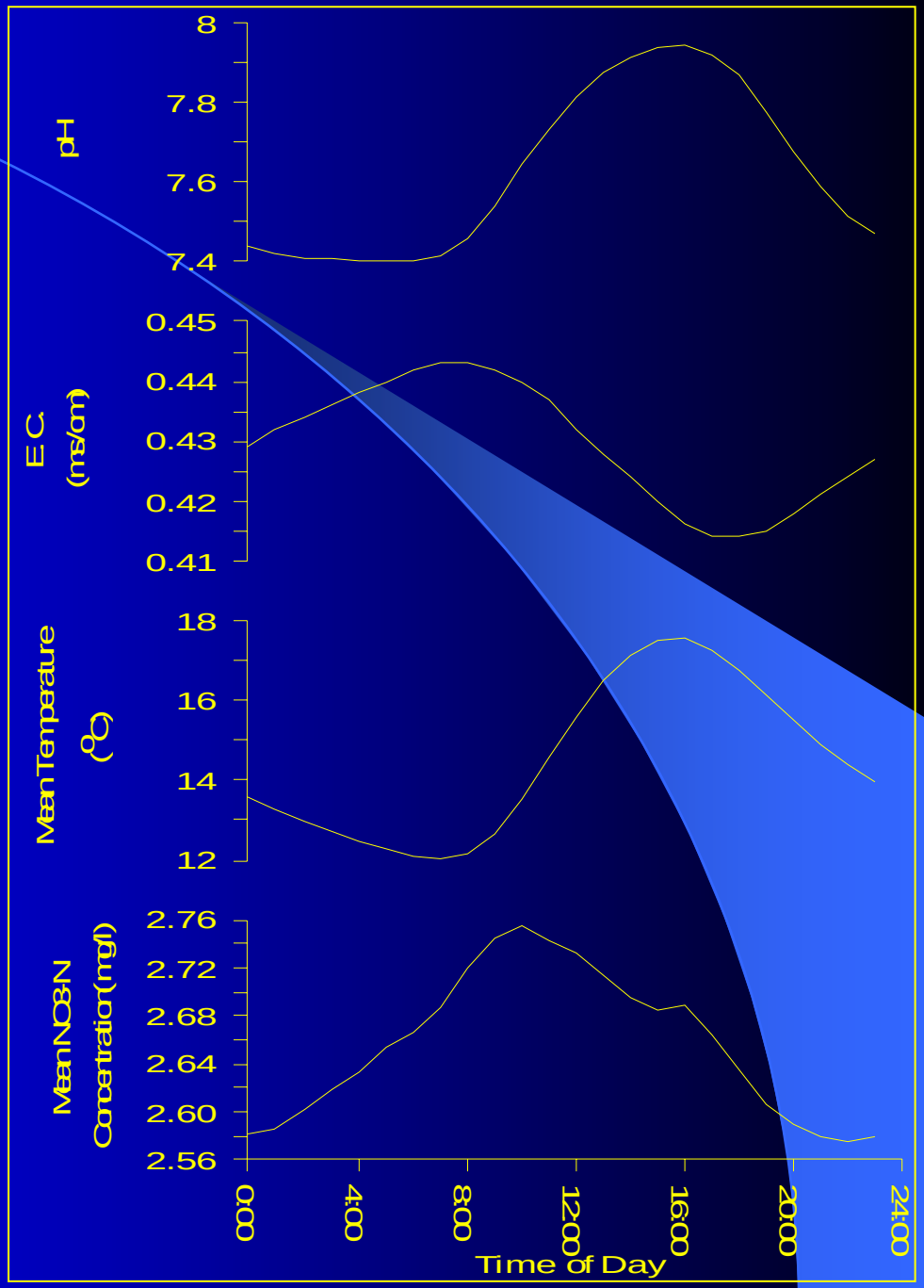

Temperature (°C)
50
40
30
20
10
NO_3-N (mg/l)
4
3
2
1
0
6/1/01
6/2/01
6/3/01
6/4/01
6/5/01
6/6/01
6/7/01
6/8/01
6/9/01
6/10/01
6/11/01
6/12/01
6/13/01
6/14/01
6/15/01
6/16/01
6/17/01
6/18/01
6/19/01
6/20/01
6/21/01
6/22/01
6/23/01
6/24/01
6/25/01
6/26/01
6/27/01
6/28/01
6/29/01
6/30/01


Temperature (°C)
50
40
30
20
10
NO_3-N (mg/l)
4
3
2
1
0
6/1/02
6/2/02
6/3/02
6/4/02
6/5/02
6/6/02
6/7/02
6/8/02
6/9/02
6/10/02
6/11/02
6/12/02
6/13/02
6/14/02
6/15/02
6/16/02
6/17/02
6/18/02
6/19/02
6/20/02
6/21/02
6/22/02
6/23/02
6/24/02
6/25/02
6/26/02
6/27/02
6/28/02
6/29/02
6/30/02

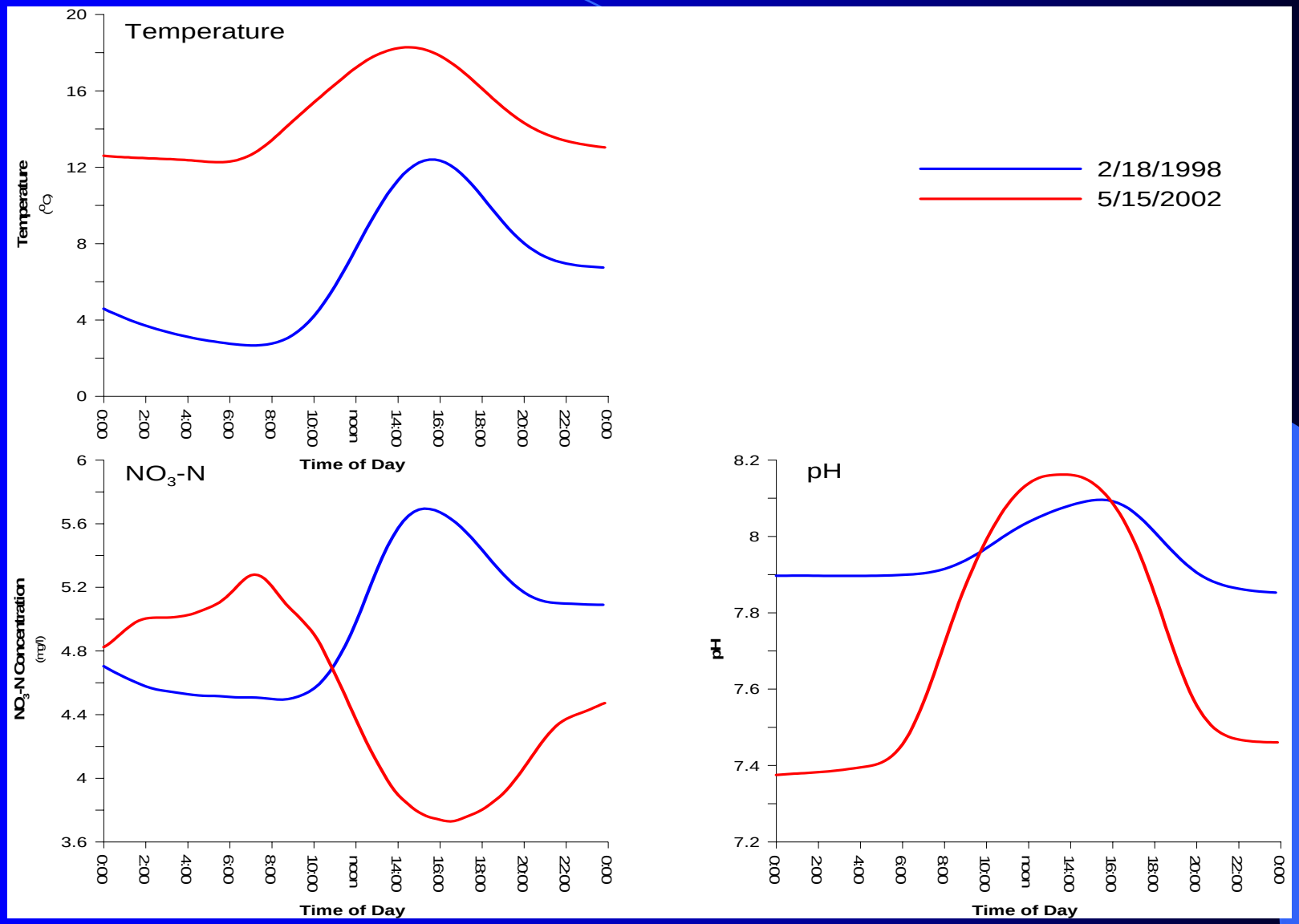
Probe Maintenance and Calibration

- Biweekly probe calibration.
- Be alert for significant nitrate probe drift particularly after 4 months.
- Replacement pH probe after 12 months may be required.
- Grab sampling needed for data adjustment.
- Be alert for electrical ground loops that can significantly affect probes during calibration, testing and field deployment.

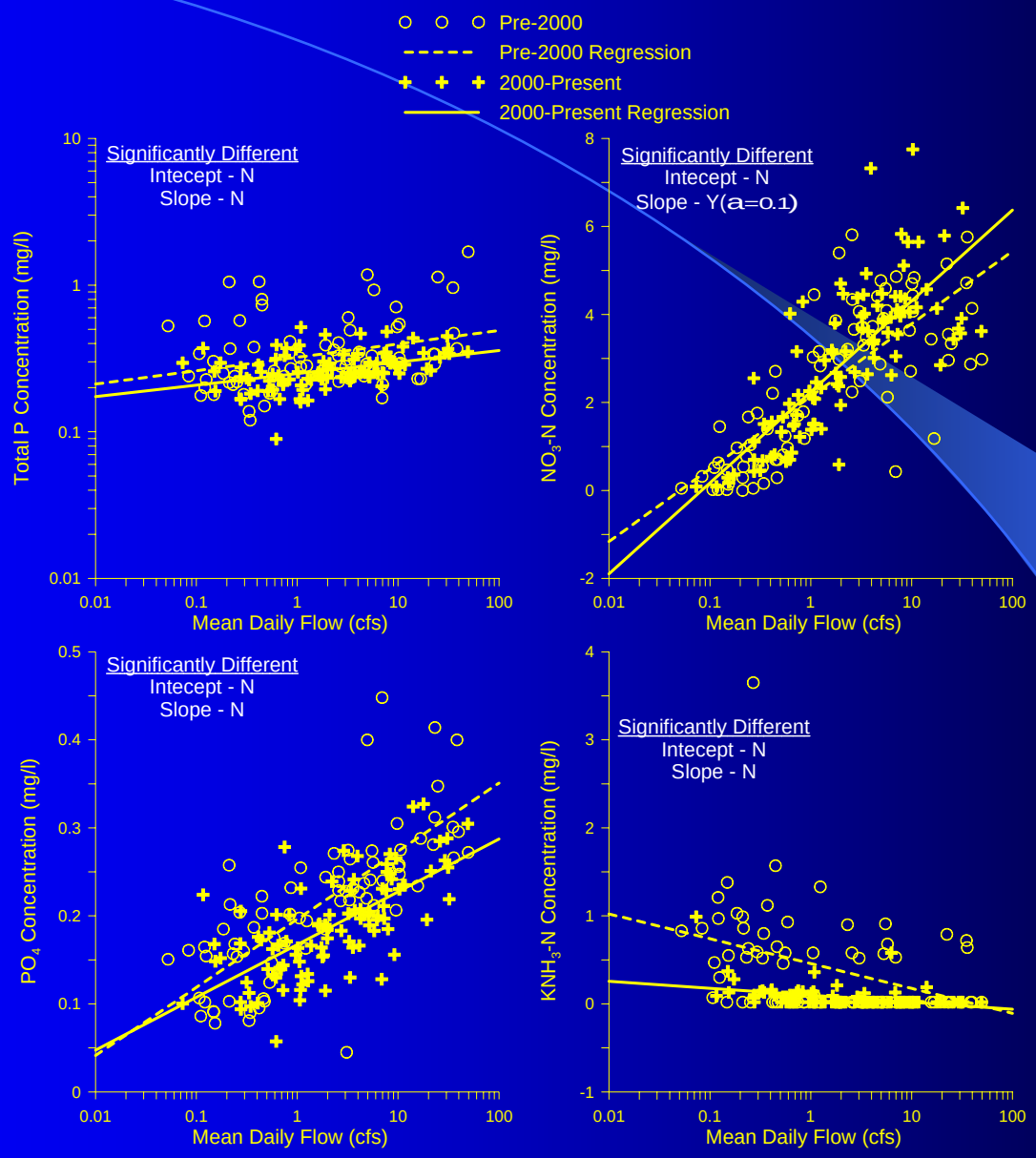
Mean values of Temperature, pH, NO_3-N, and E. C. at each hour of the day.

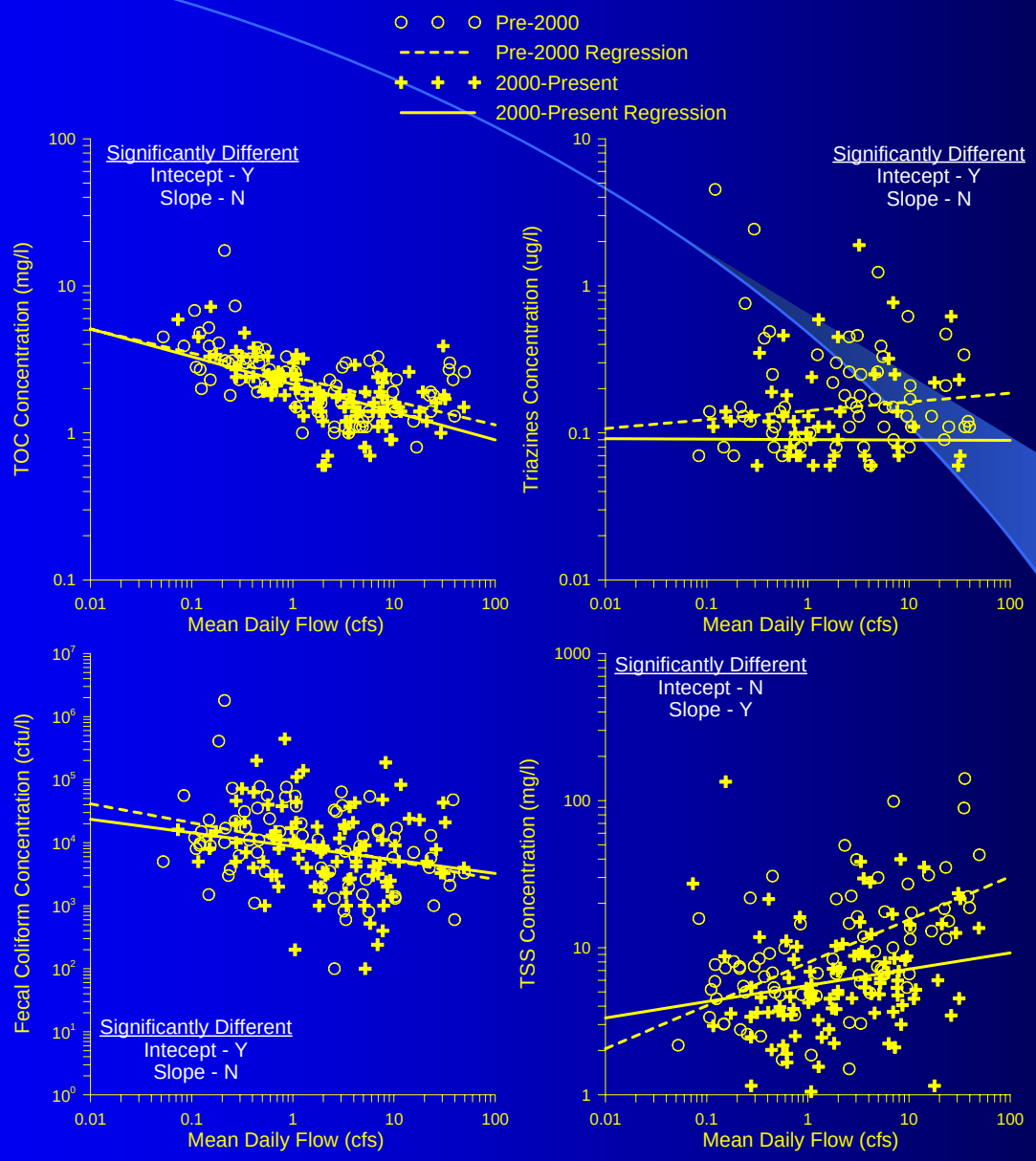


Typical Max/Min Pre and Post 2000



Impact of Cattle Restriction from Stream

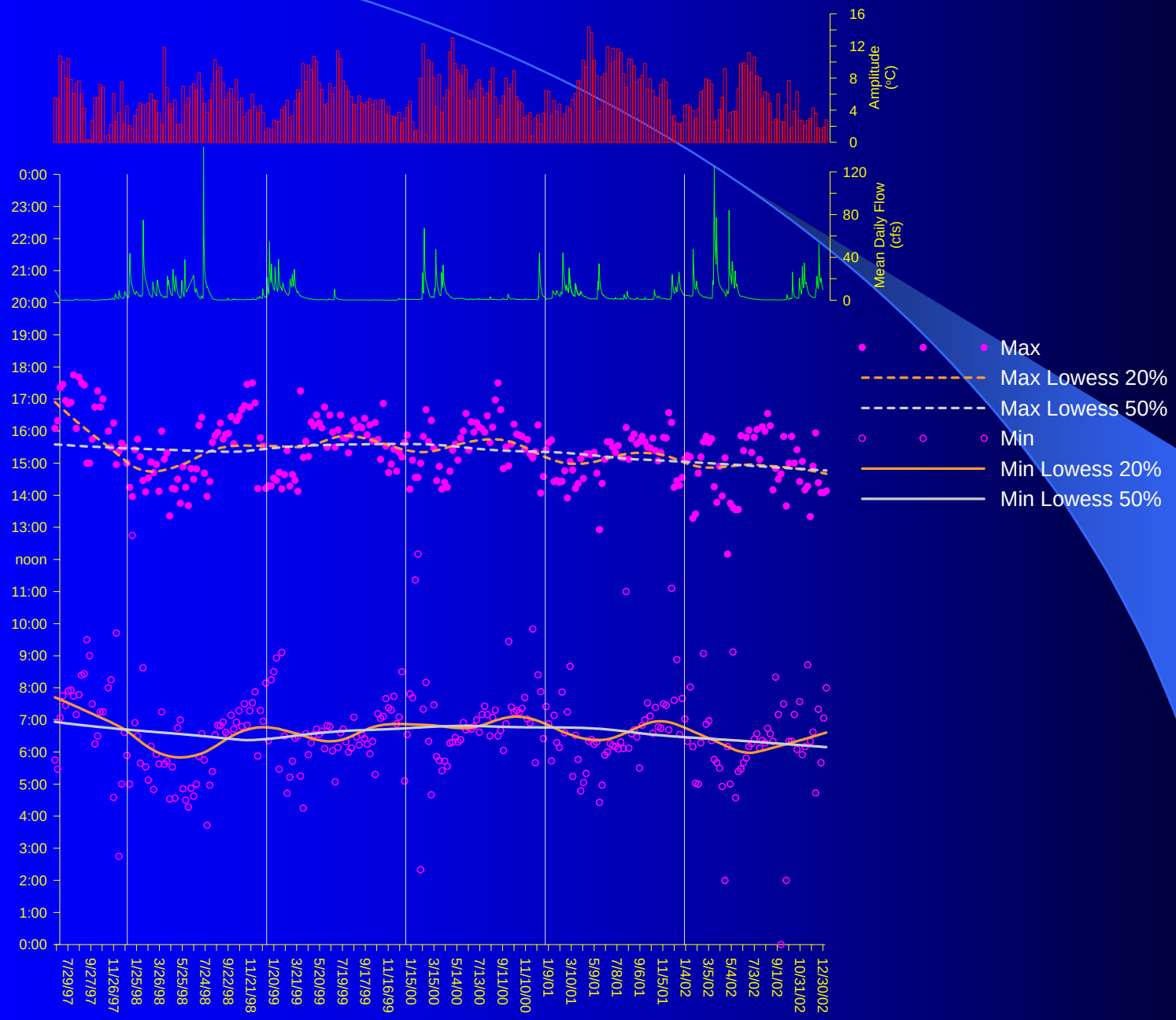

Pre-2000
Pre-2000 Regression
2000-Present
2000-Present Regression
Significantly Different
Intecept - N
Slope - N
Total P Concentration (mg/l)
Mean Daily Flow (cfs)
Significantly Different
Intecept - N
Slope - Y(a=0.1)
NO3-N Concentration (mg/l)
Mean Daily Flow (cfs)
Significantly Different
Intecept - N
Slope - N
PO4 Concentration (mg/l)
Mean Daily Flow (cfs)
Significantly Different
Intecept - N
Slope - N
KNH3-N Concentration (mg/l)
Mean Daily Flow (cfs)

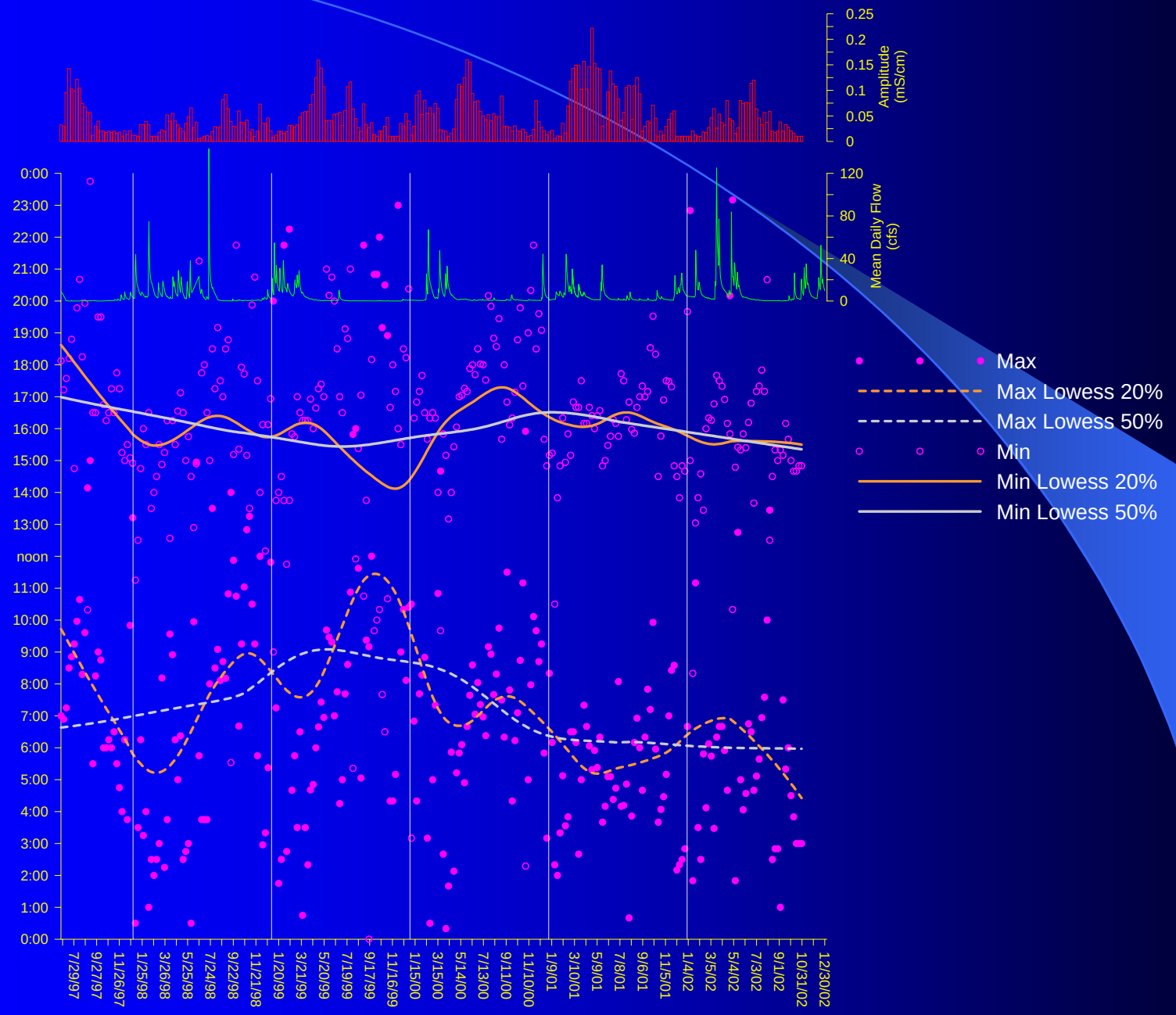

Pre-2000
Pre-2000 Regression
2000-Present
2000-Present Regression
Significantly Different
Intecept - Y
Slope - N
TOC Concentration (mg/l)
Mean Daily Flow (cfs)
Significantly Different
Intecept - Y
Slope - N
Triazines Concentration (ug/l)
Mean Daily Flow (cfs)
Significantly Different
Intecept - Y
Slope - N
Fecal Coliform Concentration (cfu/l)
Mean Daily Flow (cfs)
Significantly Different
Intecept - N
Slope - Y
TSS Concentration (mg/l)
Mean Daily Flow (cfs)

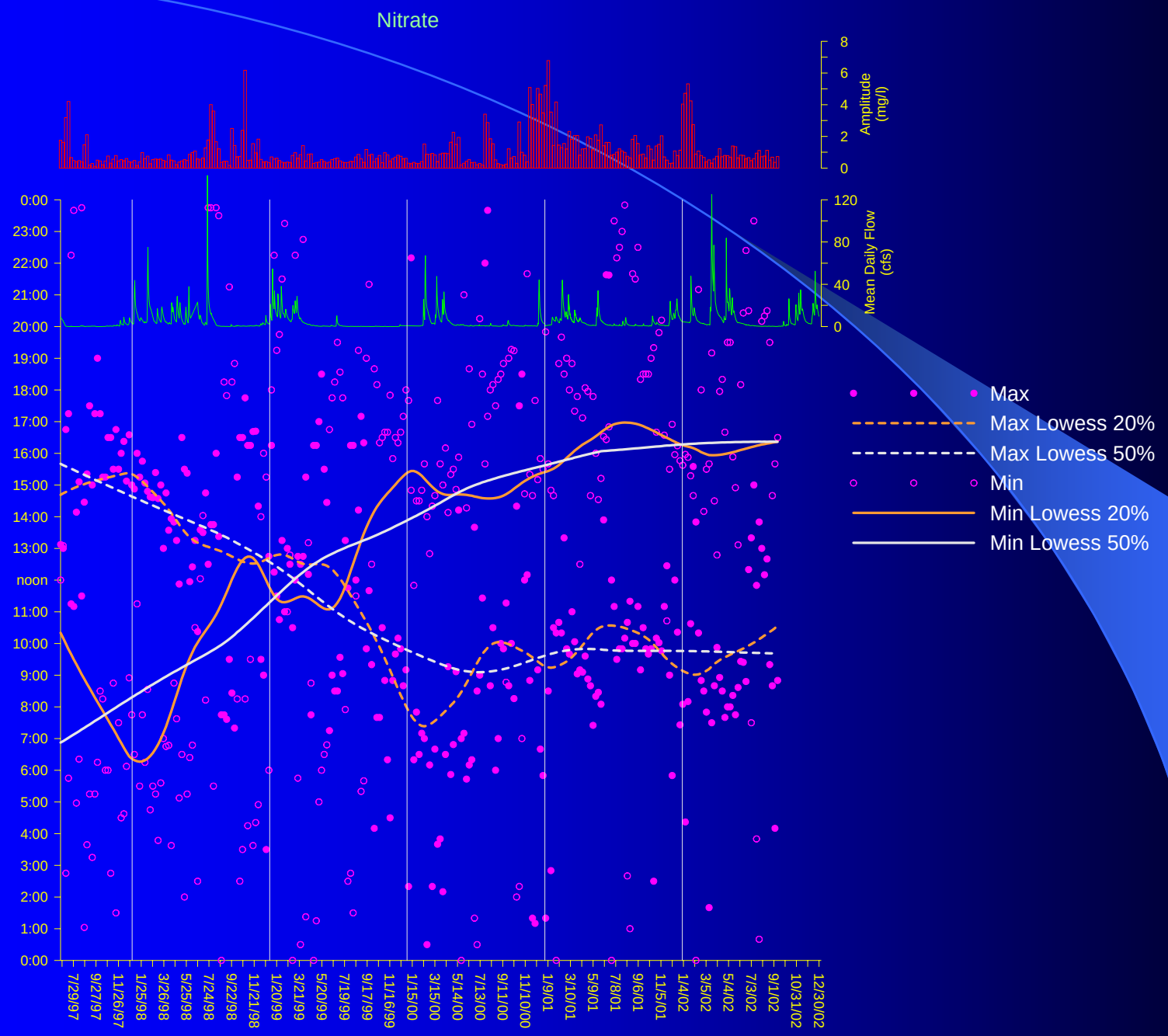
Concentrations Trends at ST1 - ARC Discharge Point

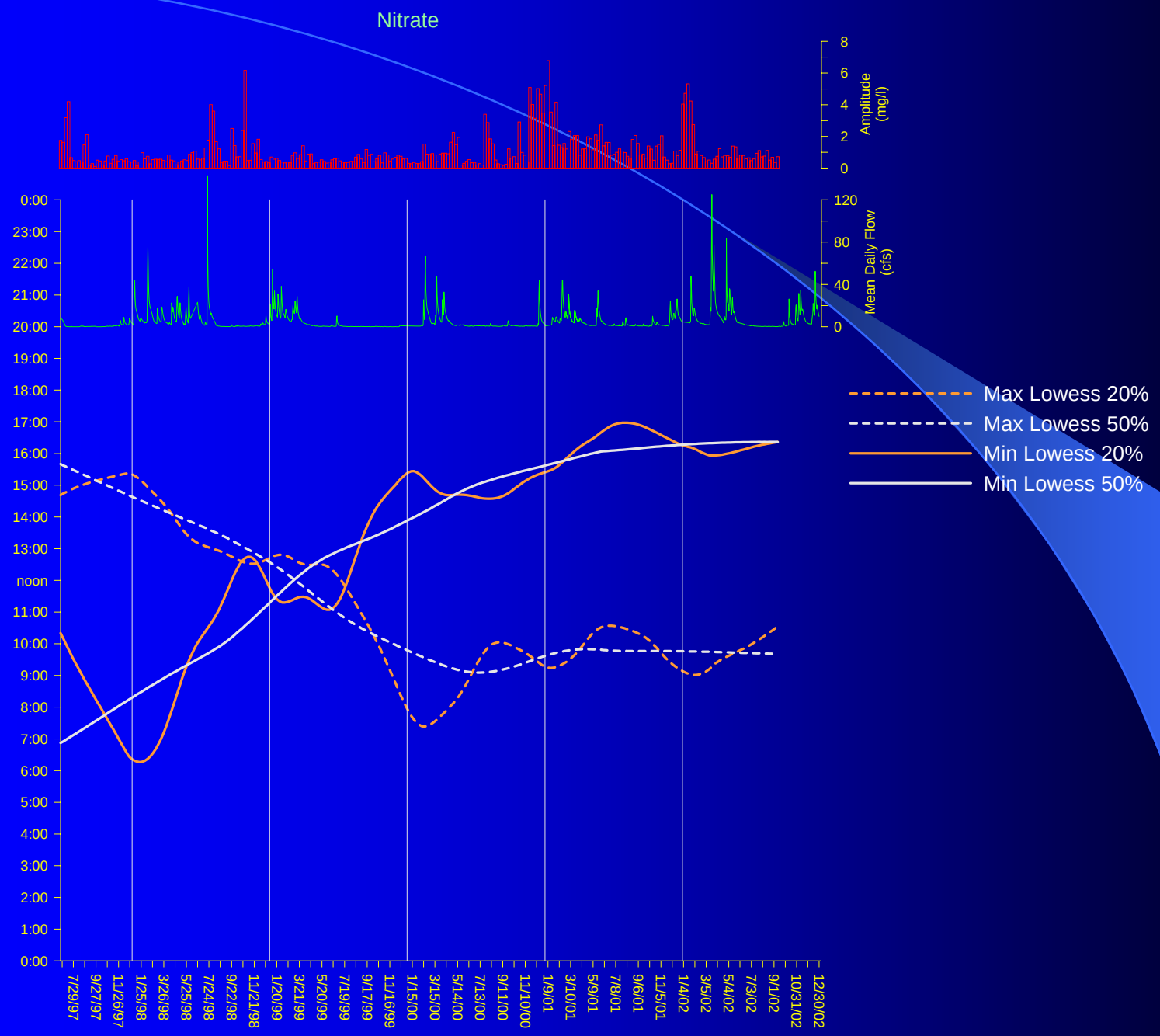
	1997-1999		2001-2003	
	Trend	P-value	Trend	P-value
F. coli	0.00170	0.034	0.00110	N.S.
Total NH3-N	-0.00003	N.S.	0.00004	N.S.
TSS	0.00340	N.S.	0.00590	N.S.
NO3-N	-0.00110	0.008	-0.00004	N.S.
PO4-P	-0.00015	N.S.	0.00002	N.S.
TOC	0.00155	0.003	0.00014	N.S.
Triazine	-0.00362	0.000	0.00080	N.S.

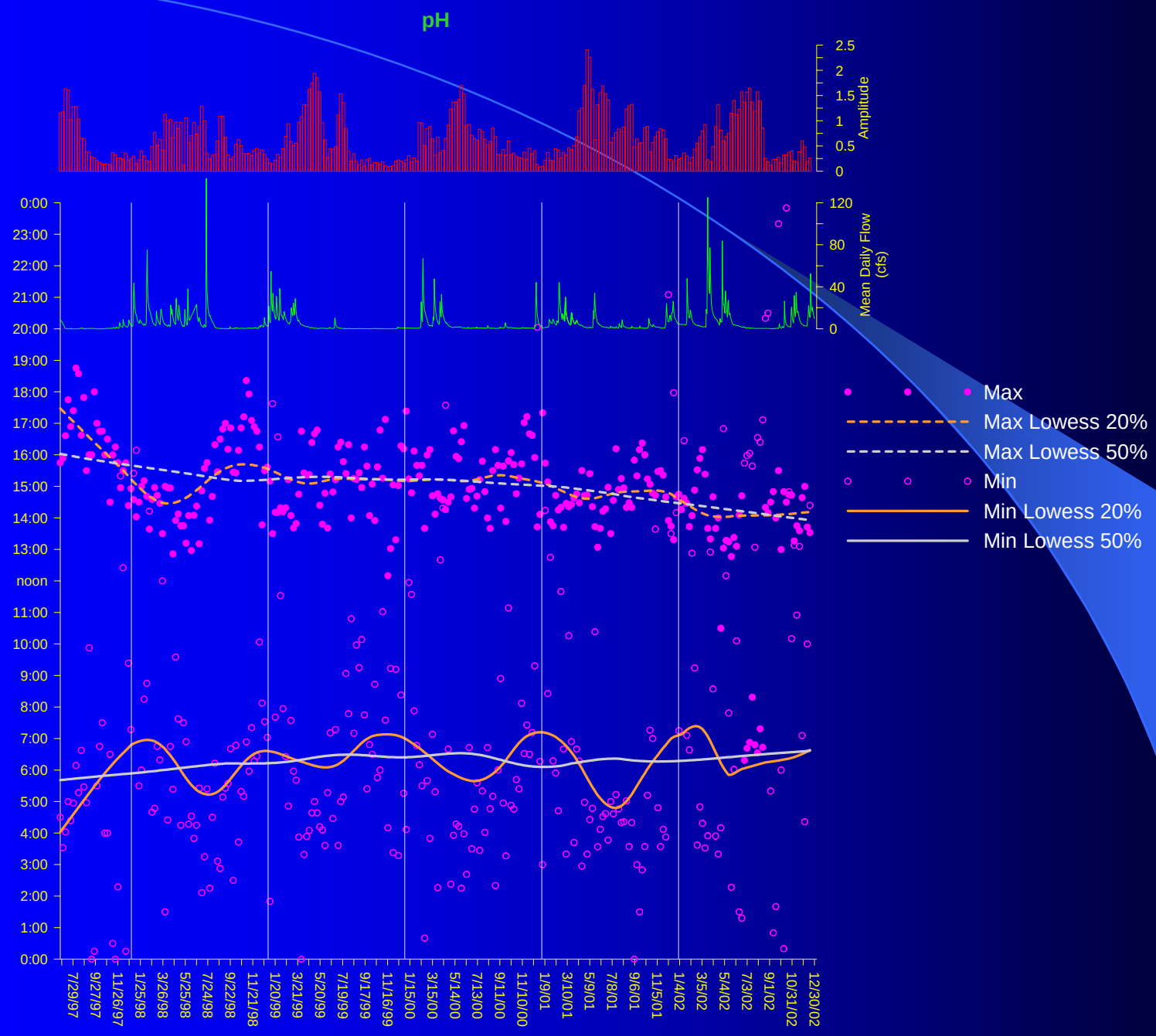
Temperature




E.C.
Amplitude (mS/cm)
0.25
0.2
0.15
0.1
0.05
0
Mean Daily Flow (cfs)
120
80
40
0
0:00
23:00
22:00
21:00
20:00
19:00
18:00
17:00
16:00
15:00
14:00
13:00
noon
11:00
10:00
9:00
8:00
7:00
6:00
5:00
4:00
3:00
2:00
1:00
0:00
7/29/97
9/27/97
11/26/97
1/25/98
3/26/98
5/25/98
7/24/98
9/22/98
11/21/98
1/20/99
3/21/99
5/20/99
7/19/99
9/17/99
11/16/99
1/15/00
3/15/00
5/14/00
7/13/00
9/11/00
11/10/00
1/9/01
3/10/01
5/9/01
7/8/01
9/6/01
11/5/01
1/4/02
3/5/02
5/4/02
7/3/02
9/1/02
10/31/02
12/30/02
Max
Max Lowess 20%
Max Lowess 50%
Min
Min Lowess 20%
Min Lowess 50%


Nitrate
Amplitude (mg/l)
0
2
4
6
8
Mean Daily Flow (cfs)
0
40
80
120
0:00
23:00
22:00
21:00
20:00
19:00
18:00
17:00
16:00
15:00
14:00
13:00
noon
11:00
10:00
9:00
8:00
7:00
6:00
5:00
4:00
3:00
2:00
1:00
0:00
7/29/97
9/27/97
11/26/97
1/25/98
3/26/98
5/25/98
7/24/98
9/22/98
11/21/98
1/20/99
3/21/99
5/20/99
7/19/99
9/17/99
11/16/99
1/15/00
3/15/00
5/14/00
7/13/00
9/11/00
11/10/00
1/9/01
3/10/01
5/9/01
7/8/01
9/6/01
11/5/01
1/14/02
3/5/02
5/4/02
7/3/02
9/1/02
10/31/02
12/30/02
Max
Max Lowess 20%
Max Lowess 50%
Min
Min Lowess 20%
Min Lowess 50%

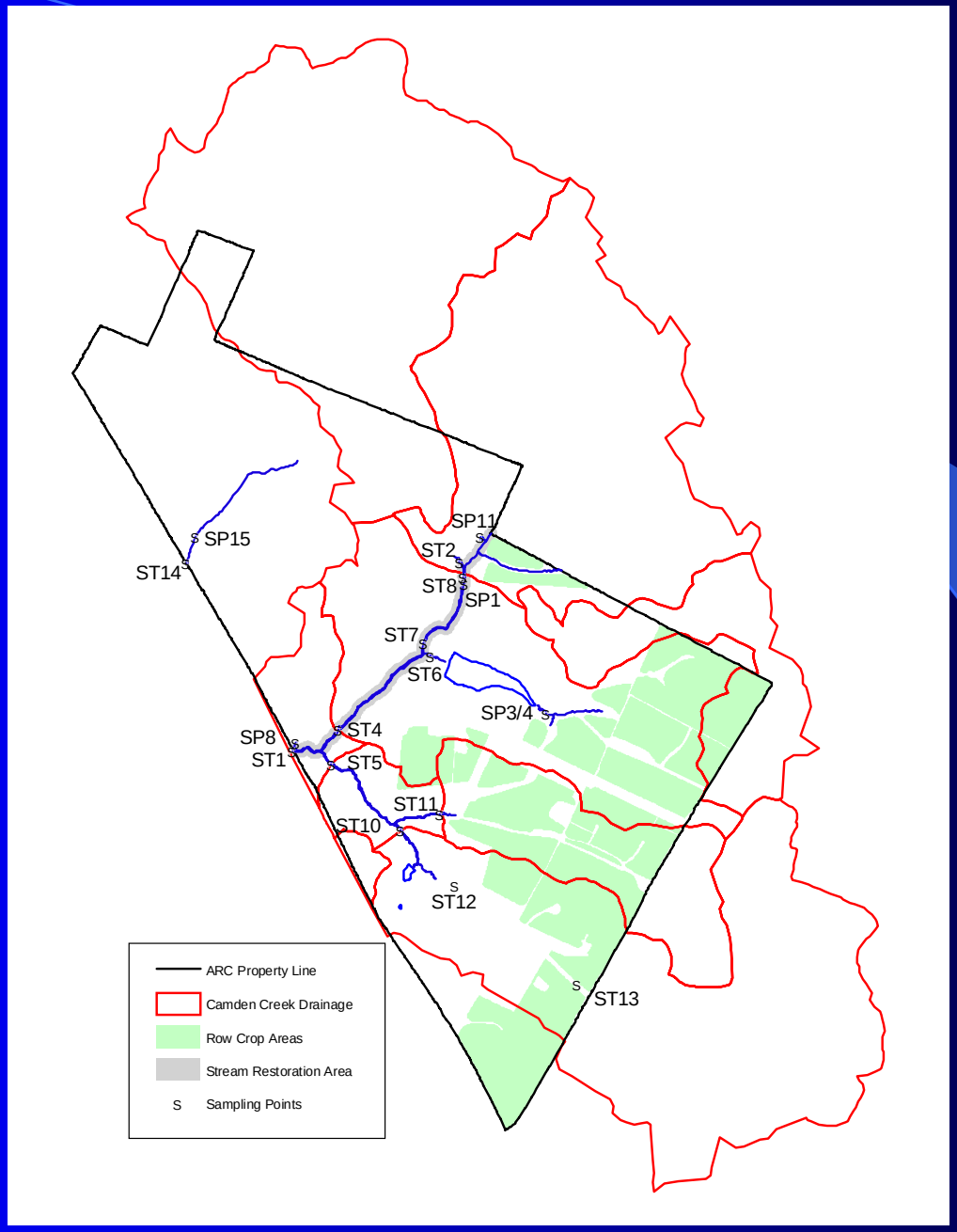

Nitrate
Amplitude (mg/l)
8
6
4
2
0
Mean Daily Flow (cfs)
120
80
40
0
0:00
23:00
22:00
21:00
20:00
19:00
18:00
17:00
16:00
15:00
14:00
13:00
noon
11:00
10:00
9:00
8:00
7:00
6:00
5:00
4:00
3:00
2:00
1:00
0:00
7/29/97
9/27/97
11/26/97
1/25/98
3/26/98
5/25/98
7/24/98
9/22/98
11/21/98
1/20/99
3/21/99
5/20/99
7/19/99
9/17/99
11/16/99
1/15/00
3/15/00
5/14/00
7/13/00
9/11/00
11/10/00
1/9/01
3/10/01
5/9/01
7/8/01
9/6/01
11/5/01
1/4/02
3/5/02
5/4/02
7/3/02
9/1/02
10/31/02
12/30/02
Max Lowess 20%
Max Lowess 50%
Min Lowess 20%
Min Lowess 50%


pH
Amplitude
2.5
2
1.5
1
0.5
0
Mean Daily Flow (cfs)
120
80
40
0
0:00
23:00
22:00
21:00
20:00
19:00
18:00
17:00
16:00
15:00
14:00
13:00
noon
11:00
10:00
9:00
8:00
7:00
6:00
5:00
4:00
3:00
2:00
1:00
0:00
7/29/97
9/27/97
11/26/97
1/25/98
3/26/98
5/25/98
7/24/98
9/22/98
11/21/98
1/20/99
3/21/99
5/20/99
7/19/99
9/17/99
11/16/99
1/15/00
3/15/00
5/14/00
7/13/00
9/11/00
11/10/00
1/9/01
3/10/01
5/9/01
7/8/01
9/6/01
11/5/01
1/4/02
3/5/02
5/4/02
7/3/02
9/1/02
10/31/02
12/30/02
Max
Max Lowess 20%
Max Lowess 50%
Min
Min Lowess 20%
Min Lowess 50%

Next Stage
Stream Corridor Restoration

Pre-Restoration

Restoration Goal


SP15
ST14
SP11
ST2
ST8
SP1
ST7
ST6
SP3/4
SP8
ST1
ST4
ST5
ST11
ST10
ST12
ST13
ARC Property Line
Camden Creek Drainage
Row Crop Areas
Stream Restoration Area
S Sampling Points