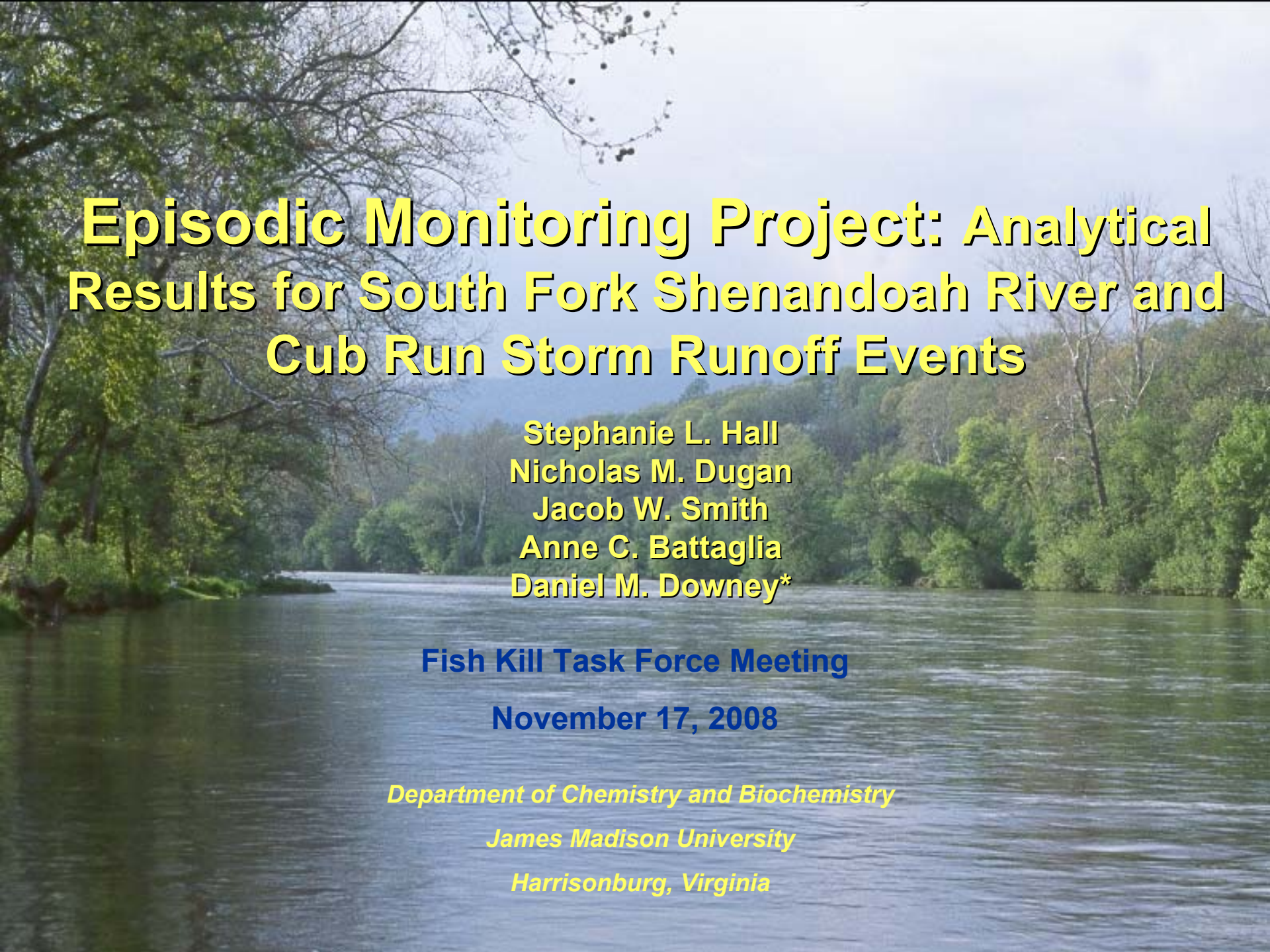


Episodic Monitoring Project: Analytical Results for South Fork Shenandoah River and Cub Run Storm Runoff Events

Stephanie L. Hall
Nicholas M. Dugan
Jacob W. Smith
Anne C. Battaglia
Daniel M. Downey*

Fish Kill Task Force Meeting

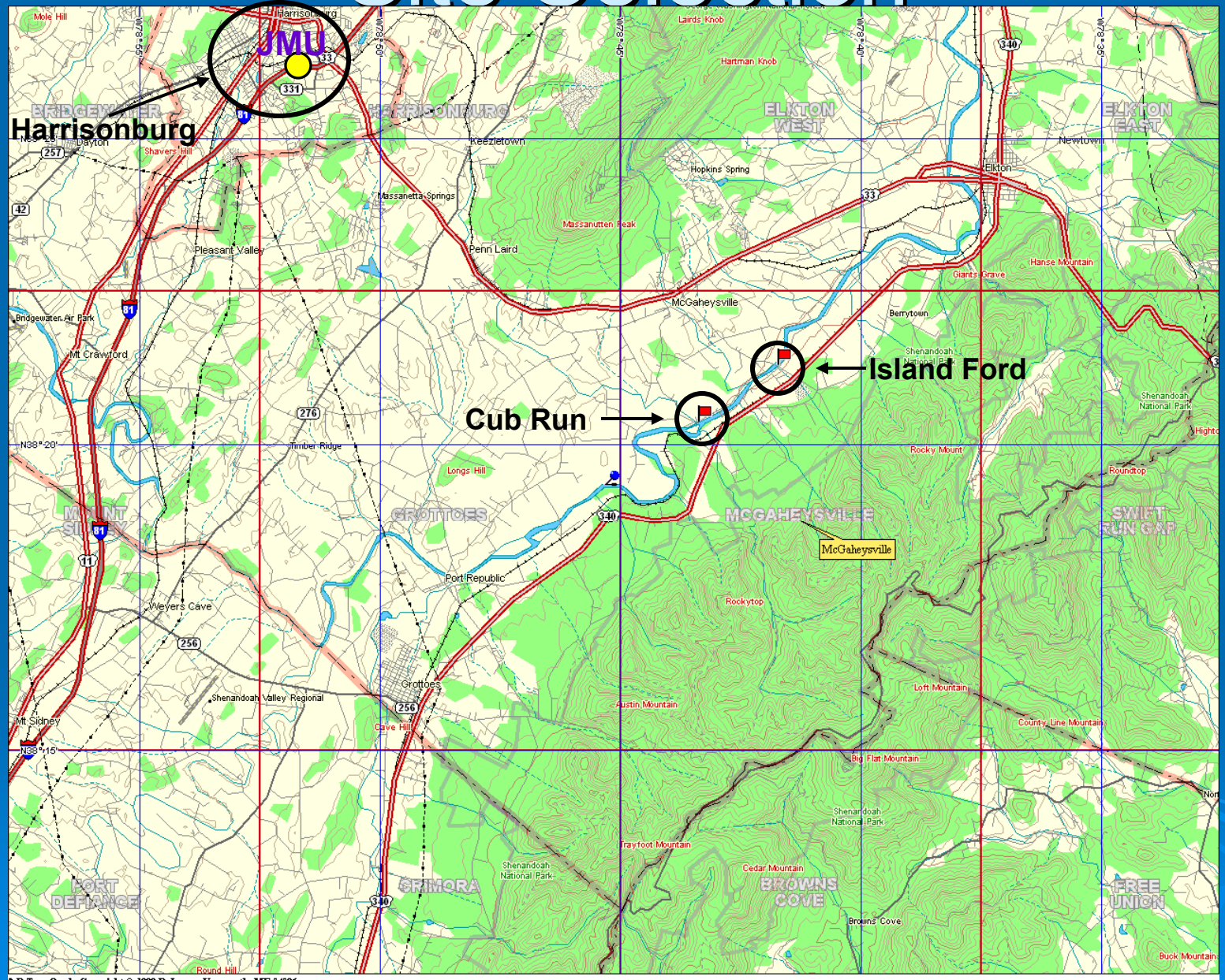
November 17, 2008

Department of Chemistry and Biochemistry

James Madison University

Harrisonburg, Virginia

Site Selection



Sample Collection

- Shenandoah River (South Fork) at Island Ford bridge
- Cub Run (tributary running into Shenandoah)

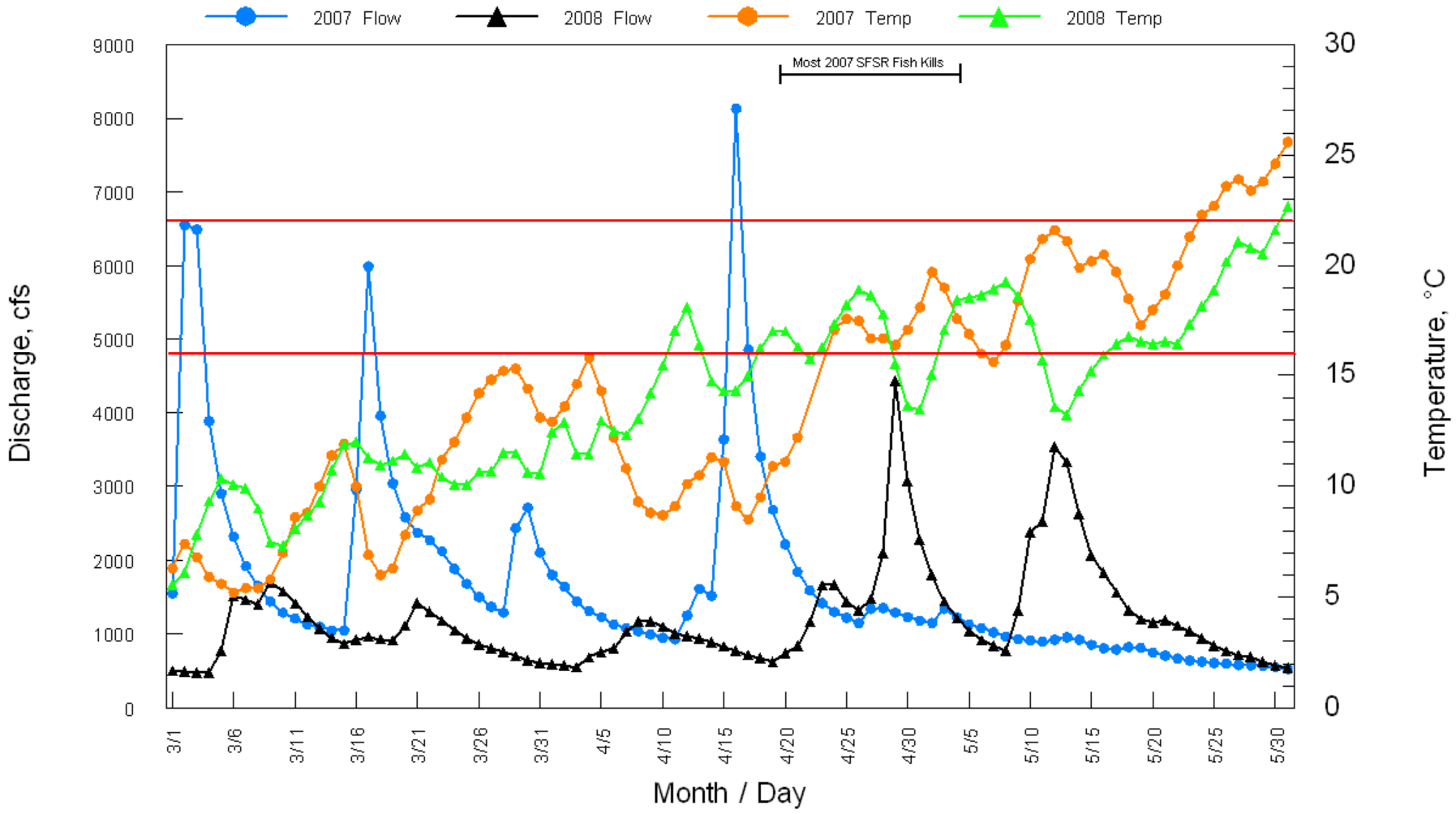
Results:

Discharge

&

Water Temperature

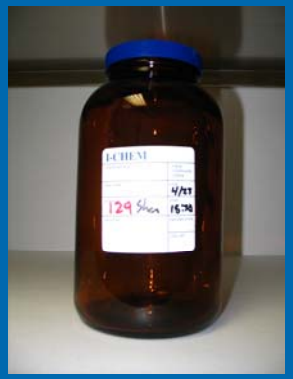
Comparison of Average Daily Flows and Temperatures 2007 & 2008
South Fork, Shenandoah River



Observations:

- Episodic discharge during fish kill period
- Annual temperature increase during fish kill period
- 2005 & 2007 greater discharge years & greater fish kills
- 2006 & 2008 lower discharge & lower fish kills
- Fish kills not observed when temperature decreases

Results: GC-ECD & GC-MS Analyses



Stephanie Hall

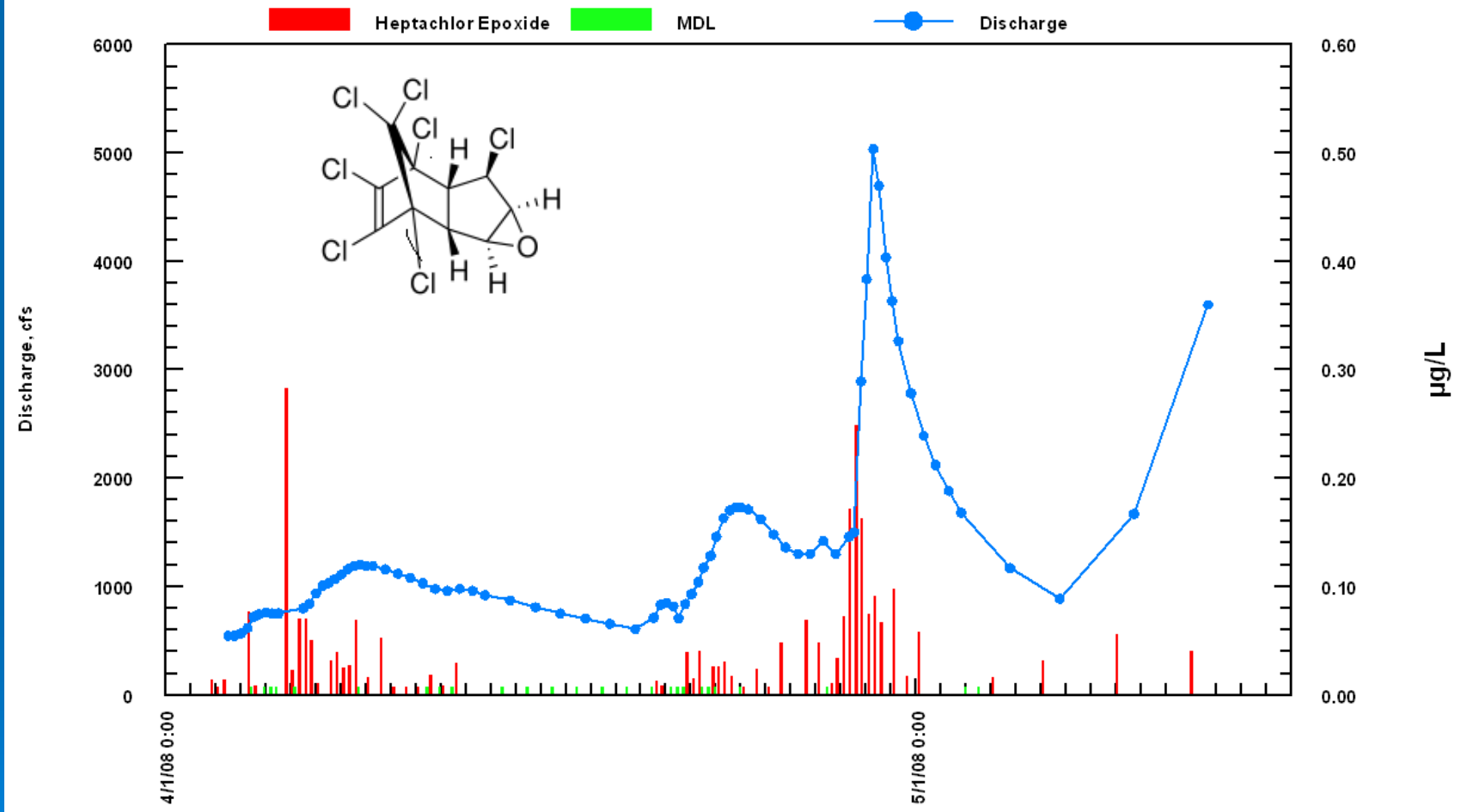
Pesticides Determined by SPE and GC-ECD & GC-MS						
Blank spaces indicate observed values < MDL						
Pesticide	**MDL**	**USGS/DEQ (10)**	**FNFSR (4)**	**JMU-IF (82)**	**JMU-CR (81)**	**JMU/DEQ (20)**
(VaWQS Acute, Chronic)	**(ng/L)**	**(#, pg/L)**	**(#, pg/L)**	**(#, ng/L)**	**(#, ng/L)**	**(#, ng/L)**
		Number of samples > MDL, concentration range				
Acetochlor	37.7			x	x	x
Alachlor	50.0					
Aldrin (3000, -)	8.0			2; 12.0-49.0	1; 40.9	
Ametryn	17.5			x	x	x
Atraton	4.4	1; 1.8		x	x	x
Atrazine	5.3	5; 26-430	4; 68-650	x	x	x
Atrazine (Desethyl-)	6.6	8; 2.0-37	4; 2.3-21	x	x	x
BHC, alpha	2.0	2; 45-47		33; 2.29-8.23	59; 2.55-181	13; 2.8-15.7
BHC, beta	9.0	4; 21-110	1; 30			
BHC, delta	7.0	1; 34	2; 74-75			
BHC, gamma (950, -)	7.0	8; 71-240.				
chlordane, alpha	7.0	6; 7.3-54	4; 4.3-10			
chlordane, gamma	9.0	9; 4.9-37	4; 5-7.6			1, 11.9
Chlorobenzilate	150.0					
Chloroneb	50.0			8; 80.9-217	9; 72.4-401	
Chlorothalonil	10.0					
Chlorpyrifos (83, 41)	30.0	9; 36-300	4; 130-550			
Dacthal (DCPA)	9.0	4; 5.7-29		1; 20.4		1, 32.9
DDD (4, 4'-)	9.0	4; 5.8-29	2; 10-15			4, 17.3-76.0
DDE (4, 4'-)	9.0	5; 13-64	4; 20-31			1, 32.4
DDT (4, 4'-)	30.0	7; 1.9-21	1; 26			
Dieldrin	9.0	6; 23-56	4; 12-24			3, 26.3-41.5
Endosulfan I	9.0	10; 48-270				
Endosulfan II	8.0	4; 180.-510	1; 65			4, 20.0-204
Endosulfan sulfate	30.0		2; 180-310			

Endrin	8.0	5; 4.8-21	3; 25-36			3, 38.8-41.7
Endrin aldehyde	8.0					2, 11,7-44.2
Etradiazole	7.0			20; 7.67-62.2	10; 7.04-69.7	5; 13.1-251.1
Heptachlor	7.0		1; 0.58			1, 8.3
Heptachlor endo-epoxide (520)	7.0	10; 2.2-42	4; 2.3-9.9			
Heptachlor exo-epoxide (520)	7.0			51; 7.60-282.	22; 7.69-238	11, 7.3-200
Hexachlorobenzene	6.0	5; 11-35	4; 3.7-10	4; 8.14-21.3	11; 6.88-18.8	
Hexachlorocyclopentadiene	4.0			3; 12.9-23.5		
Methoxychlor(-,30)	20.0	5; 13-47	1; 56	1; 48.7	1; 180	4, 87.7-272
Metolachlor	30.0	7; 0.31-7.5	2; 9.2-11			
Metribuzin	20.7			x	x	x
nonachlor, cis	8.0	6; 5.2-18	3; 0.91-2.2			
nonachlor, trans	7.0	8; 1.2-38	4; 1.8-6.9			
Oxychlordane	385?	4; 0.82-7.1	2; 3.2-3.6	x	x	x
Pendamethalin	38.9	1; 0.32		x	x	x
Pentachlorophenol (8700, 6700)	5.0					
Pentachloroanisole (PCA)	5.0	10; 2.3-59		4; 7.43-22.5	4; 7.64-75.1	
Permethrin, cis	9.4	2; 66-101	2; 88-120	x	x	x
Permethrin, trans	9.6	4; 16-140	2; 32-48	x	x	x
Prometon	5.3	6; 0.5-2.5	3; 3.1-4.2	x	x	x
Simazine	7.4	6; 1.6-13	4; 5.5-24	x	x	x
Simetryn	5.9	1; 1.8		x	x	x
Trifluralin	40.0	2; 0.42-0.94	4; 5.4-19			

x=not yet completed

Alvarez, D.A., Cranor, W.L., Perkins, S.D., Schroeder, V.L., Werner, S.L., Furlong, E.T., Kain, D., and Brent, R., *Reconnaissance of persistent and emerging contaminants in the Shenandoah and James River Basins, Virginia, during Spring of 2007*. U.S. Department of the Interior and U.S. Geological Survey, 2008; Open-File Report 2008-1231.

Alvarez, D.A., Cranor, W.L., Perkins, S.D., Schroeder, V.L., Werner, S.L., Furlong, E.T., and Holmes, J., *Investigation of organic chemicals potentially responsible for mortality and intersex in fish of the North Fork of the Shenandoah River, Virginia, during spring of 2007*. U.S. Department of the Interior and U.S. Geological Survey, 2008; Open-File Report 2008-1093.



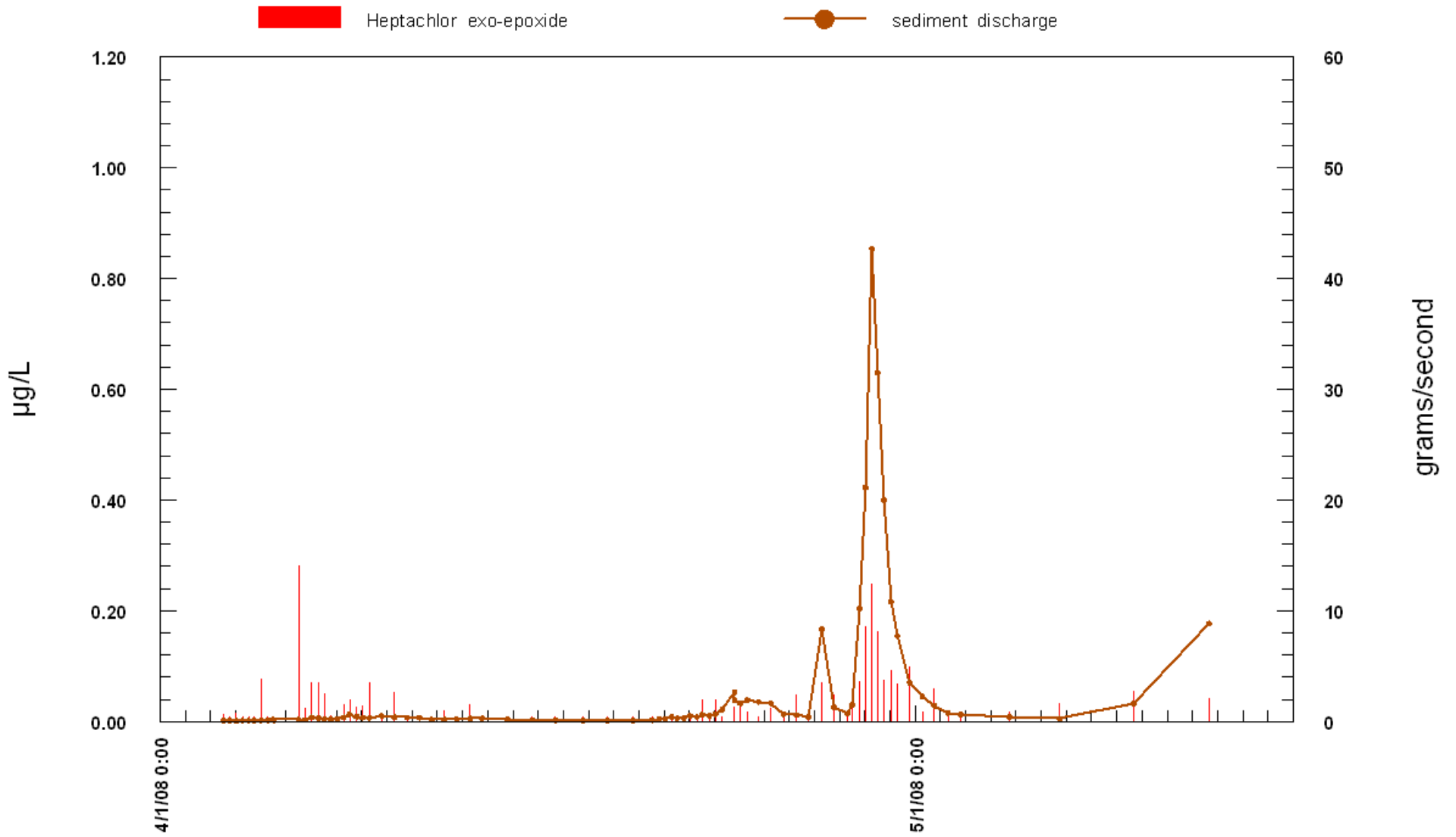
➢**The concentration of heptachlor exo-epoxide did not exceed 54% of the VADEQ acute criterion (heptachlor 0.52 µg/L)**

Source: http://www.sigmaaldrich.com/catalog/search/ProductDetail/FLUKA/34309

State Water Control Board, *Virginia Water Quality Standards*. State Water Control Board, 2007; 62.1-44.15 3a.

E.M.P. Sediment and Pesticides

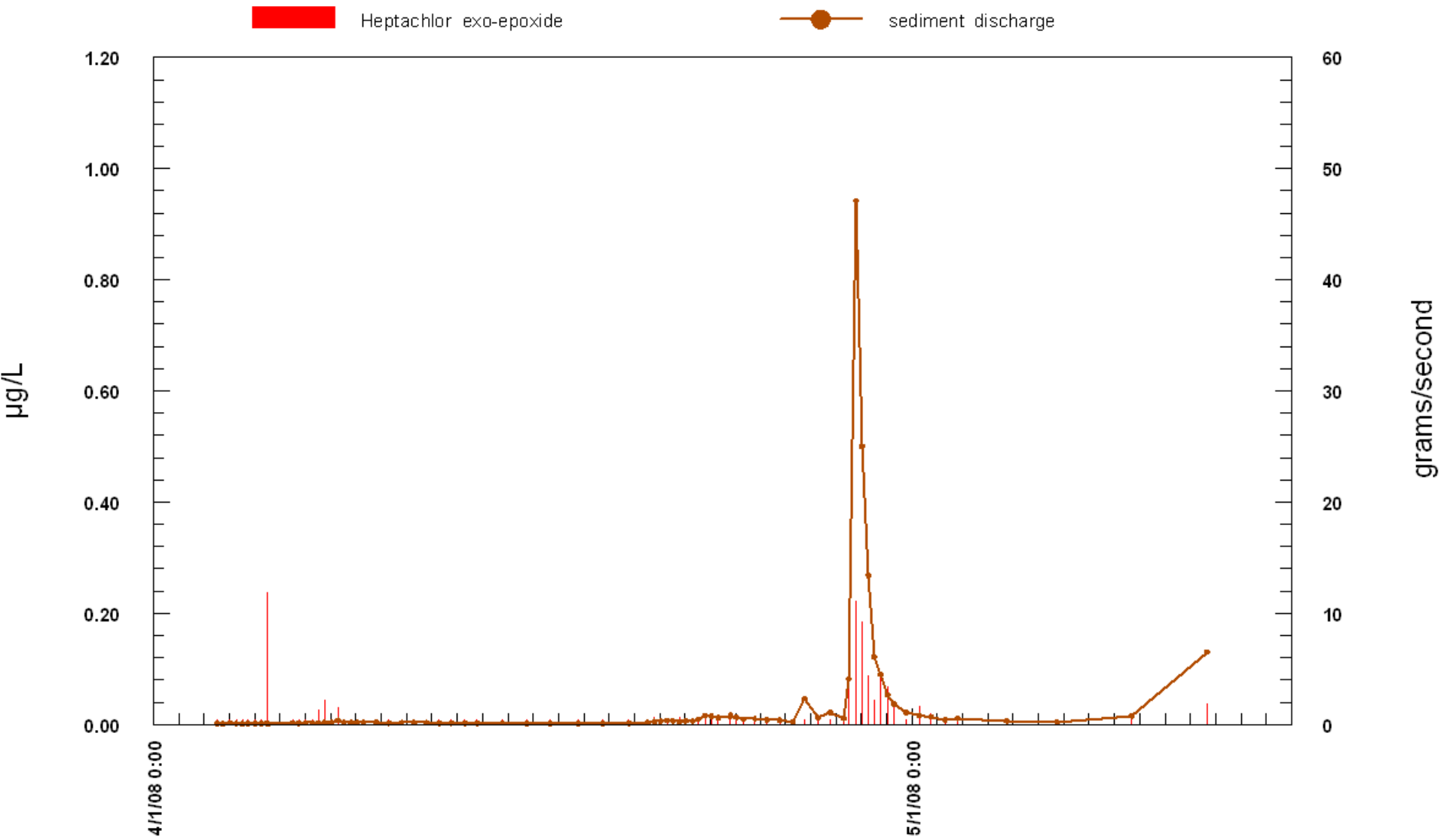
South Fork Shenandoah River - Island Ford



Spectrum Chemical Fact Sheet. http://www.speclab.com/compound/c1024573.htm (7-25-2008).

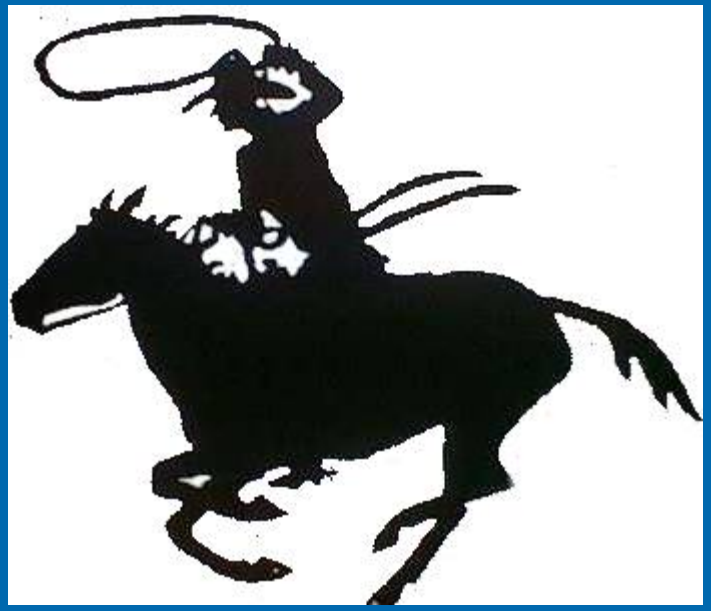
E.M.P. Sediment and Pesticides

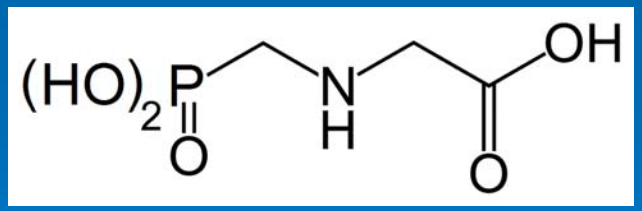
Cub Run



Spectrum Chemical Fact Sheet. http://www.speclab.com/compound/c1024573.htm (7-25-2008).

Roundup Results





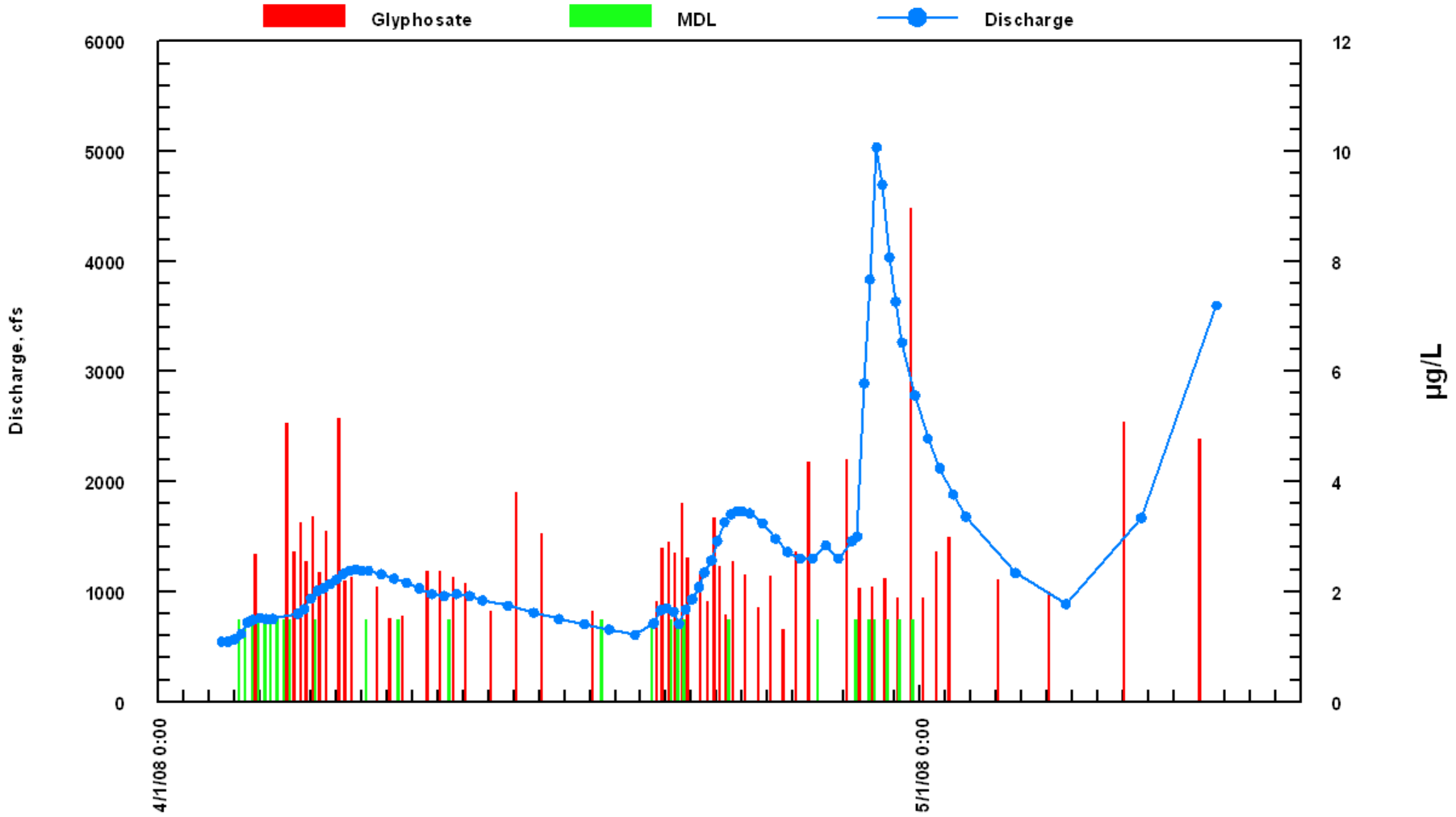
Gly - phos - ate

Jacob Smith

MDL = 1.5 ppb

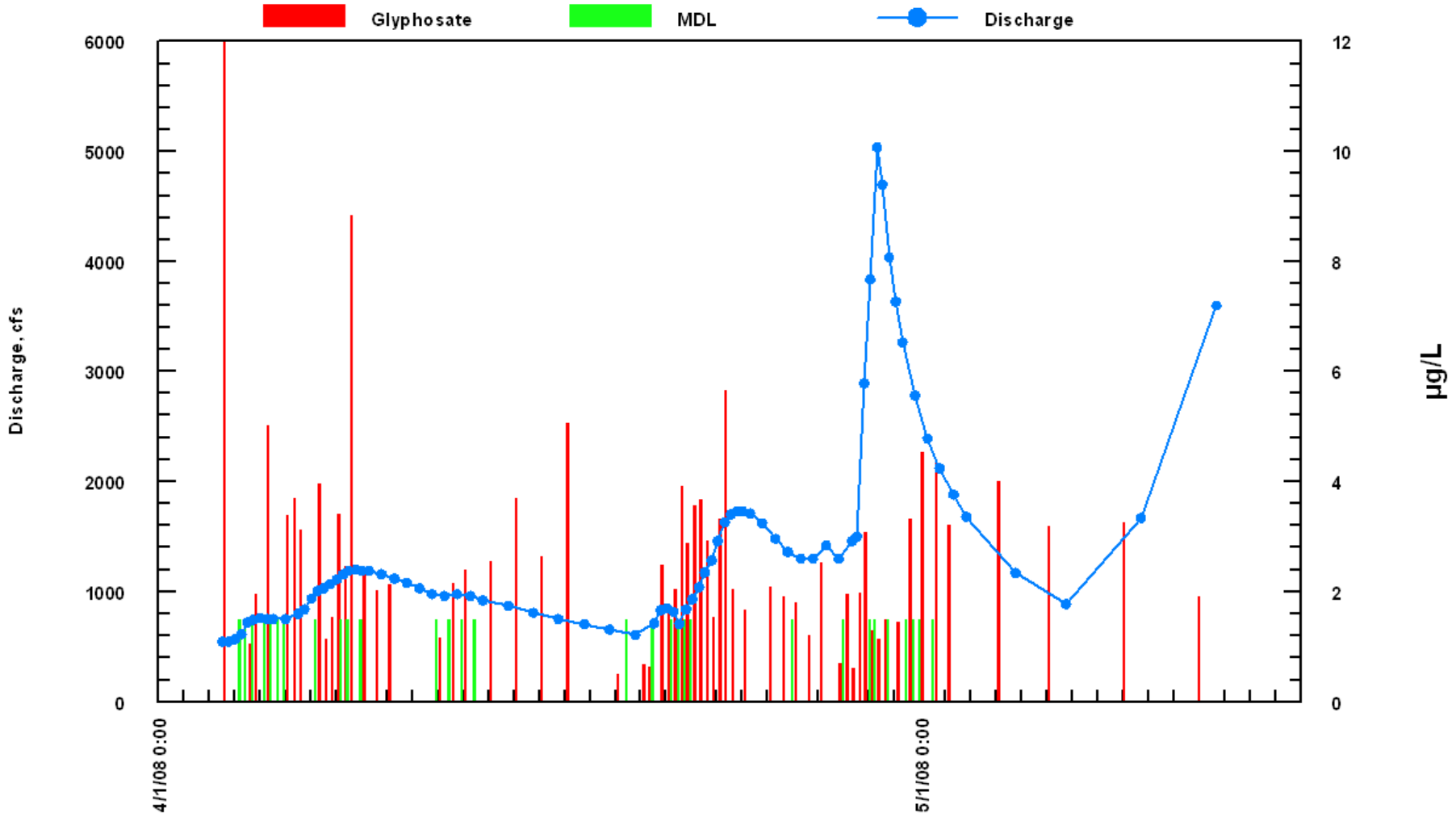
E.M.P. Pesticides and Discharge

South Fork Shenandoah River - Island Ford



E.M.P. Pesticides and Discharge

South Fork Shenandoah River - Cub Run



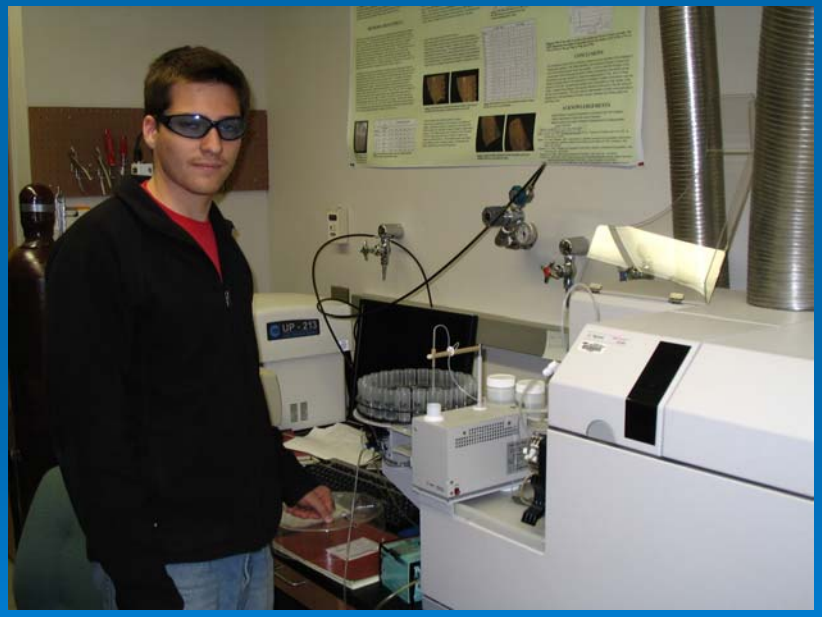
Observations:

- JMU grab sampling and passive monitoring produced complimentary results
- Other pesticide sampling indicates same
- Most pesticides BDL
- For pesticides >MDL, concentrations very low
- No correlation with discharge, but some with sediment

Recommendations:

- Discontinue future passive sampler monitoring
- Consider pesticides in low probability category as stress causative factors in the fish kills

Results: Trace Elements Analyses



Nick Dugan

Episodic Monitoring Project - ICPMS results									Blank spaces indicate observed values < detection limit										
Island Ford - SFSR																			
		27	75	9	111	59	53	63	55	95	60	208	121	82	232	205	238	51	64
		ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
ID	Date-Time	Al	As	Be	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Sb	Se	Th	Tl	U	V	Zn
MDL =		0.94	0.42	0.31	0.24	0.35	0.32	0.68	0.40	2.14	0.38	0.38	1.00	0.34	1.80	0.47	0.31	0.23	5.30
1	3/4/2008 12:54									3.05									8.06
3	3/5/2008 11:15	5.67																	9.62
5	3/24/2008 16:58	6.15																	292.30
7	4/3/2008 12:15	3.71																	224.90
9	4/3/2008 18:04	3.12																	151.70
11	4/4/2008 0:32																		107.40
13	4/4/2008 6:34																		445.70
15	4/4/2008 12:46																		158.10
17	4/4/2008 17:45																		195.40
19	4/5/2008 0:22																		142.85
41	4/5/2008 6:25	7.87	0.77				0.66			3.95	0.53			0.58	3.22		0.53		98.85

Refer to handout for the remainder of the data for Island Ford and Cub Run

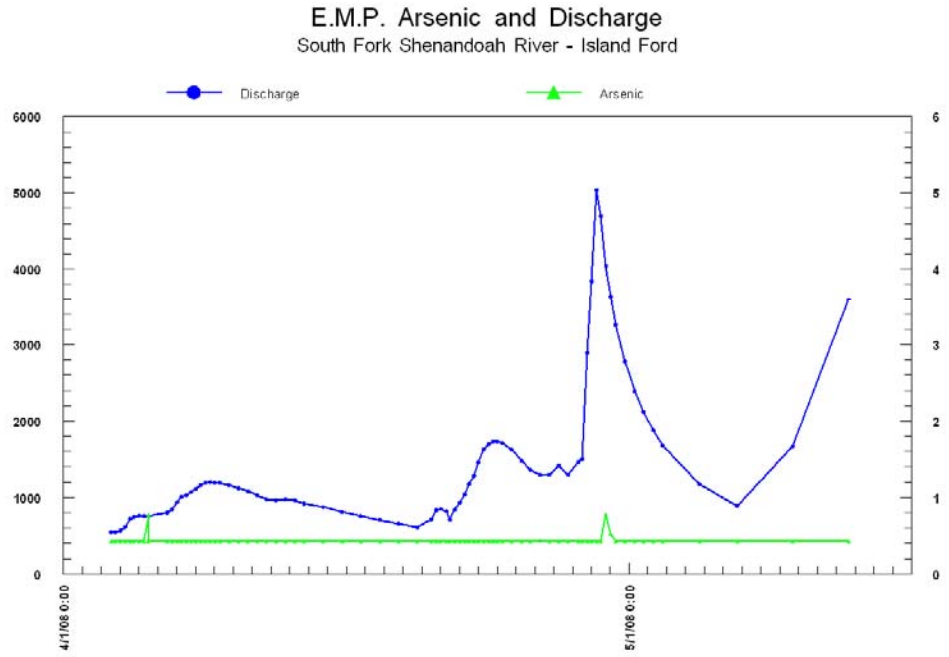
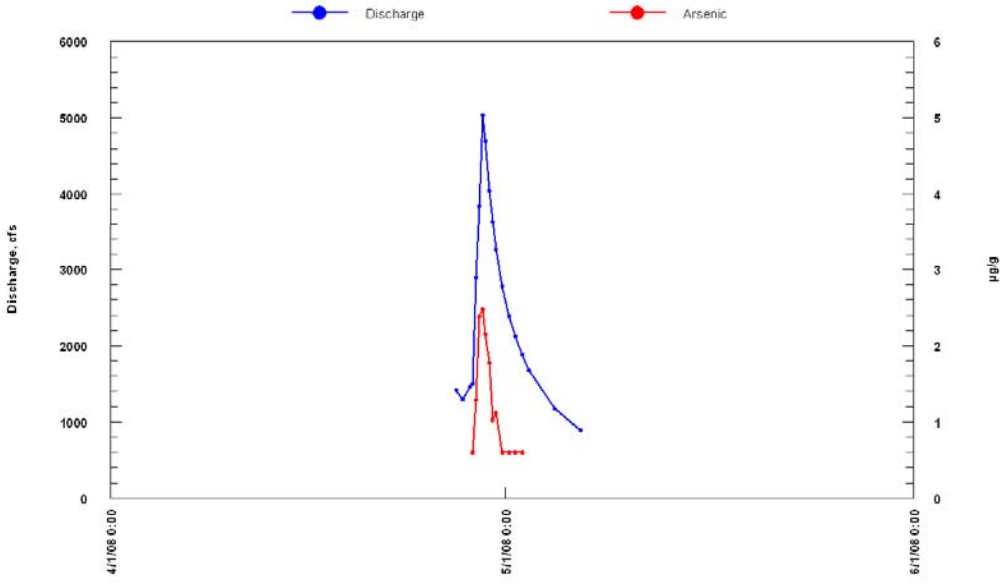


Figure 1: E.M.P. Trace Metals and Discharge
South Fork Shenandoah River - Island Ford



Observations:

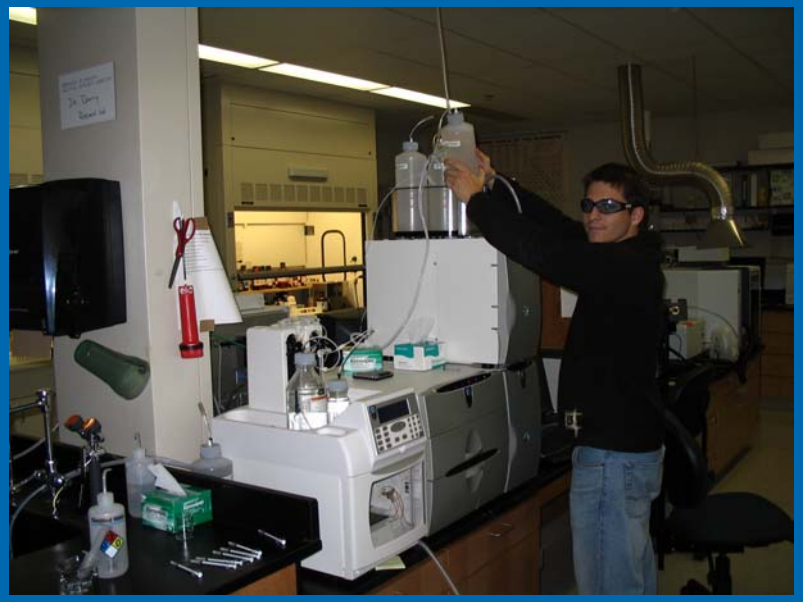
- Arsenic found in only 4/81 IF and 5/81 CR samples
- All values <1.00 µg/L
- Some As found in sediment, but values were low
- Only 1 of 336 SMB otoliths showed any As
- Very little As found in tissue, livers or otoliths of 25 SMB
- DEQ database results show low As in tissue, sediment and water samples

Recommendation:

- Consider arsenic in low probability category as a stress causative factor in the fish kills

Results: Field Tests and Major Ion Analyses

Anne Battaglia

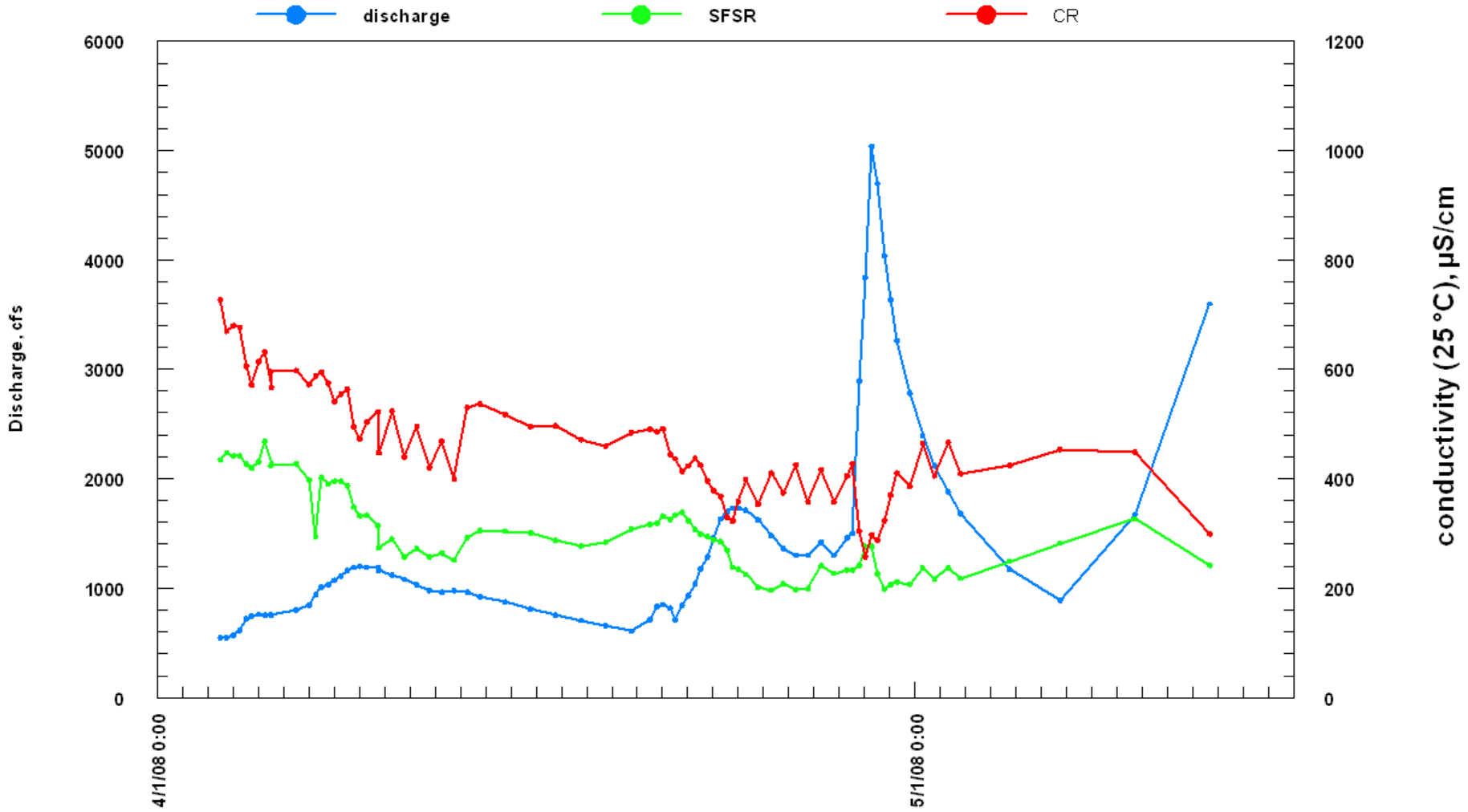


Episodic Monitoring Project - IC results							Blank spaces indicate observed values < detection limit						
Island Ford - SFSR													
						A.C.A.							
			ppm	ppm	ppm	ppm		ppm	ppm	ppm	ppm	ppm	ppm
ID	Date-Time	pH	Hardness	Na	NH4-N	NH4-N	% A.C.A.	K	Mg	Ca	Cl	SO4	NO3-N
MDL =				0.025	0.025/0.008			0.025	0.025	0.050	0.050	0.200	0.025
1	3/4/2008 12:54	8.36	173	8.42	0.17	4.20	3.99	1.62	11.23	50.95	13.95	13.32	1.18
3	3/5/2008 11:15	7.85	166	10.05	0.30	11.10	2.72	1.84	10.69	48.81	13.69	15.93	1.18
5	3/24/2008 16:58	7.94	127	12.83	0.15	9.41	1.60	1.28	7.82	38.08	9.44	25.67	0.84
7	4/3/2008 12:15	8.56	164	8.64	0.22	2.86	7.69	1.62	10.45	48.55	13.15	12.26	1.13
9	4/3/2008 18:04	8.20	169	10.87	0.37	5.73	6.44	1.78	11.22	49.37	14.08	16.48	1.12
11	4/4/2008 0:32	8.05	167	10.23	0.32	7.65	4.15	1.73	10.96	48.81	12.53	16.88	1.07
13	4/4/2008 6:34	8.27	165	8.57	0.36	5.00	7.28	1.81	10.95	48.12	13.28	12.02	1.09

Refer to handout for the remainder of the data for Island Ford and Cub Run

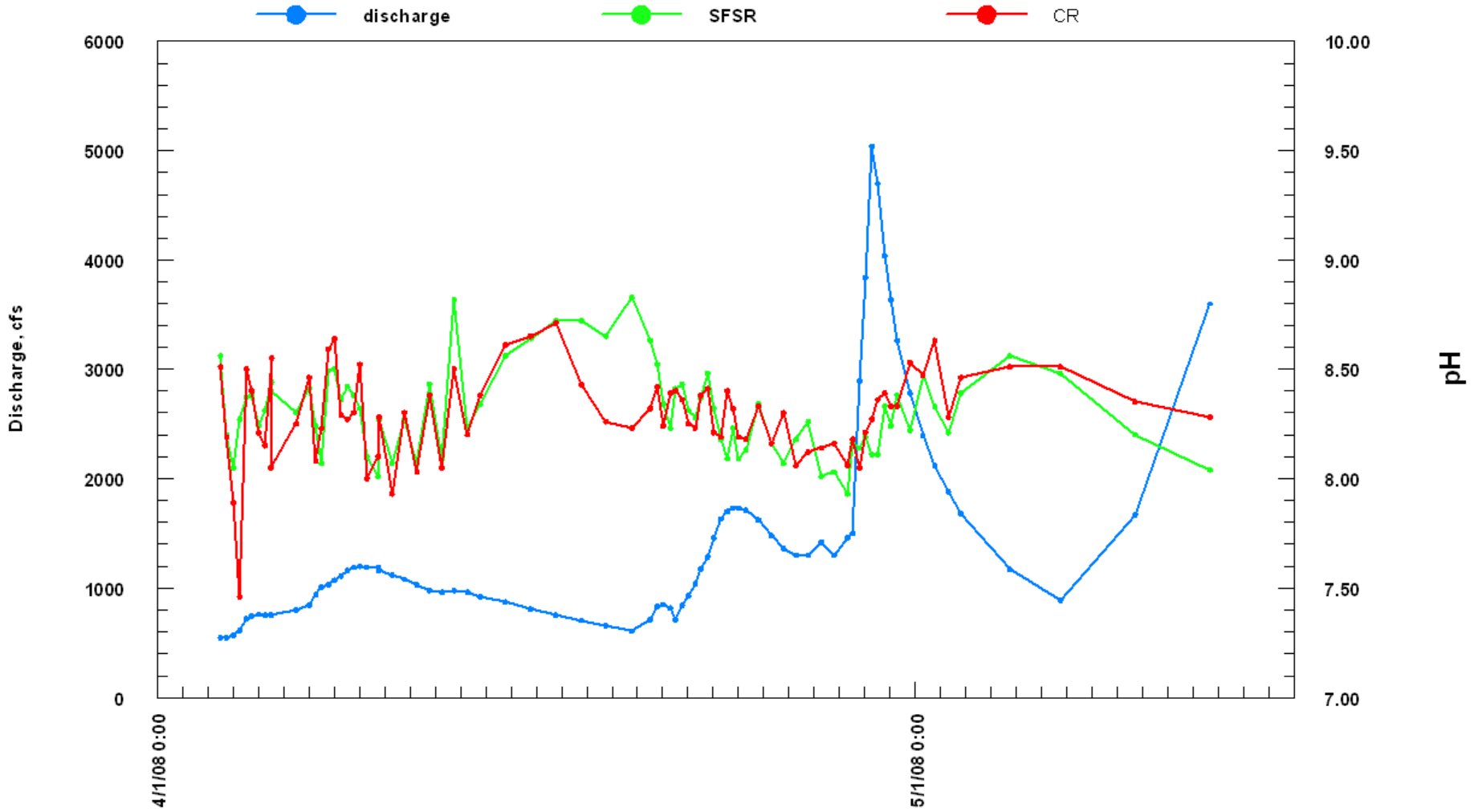
E.M.P. - Conductivity and Discharge

Island Ford - SFSR & Cub Run



E.M.P. - pH and Discharge

Island Ford - SFSR & Cub Run



Observations:

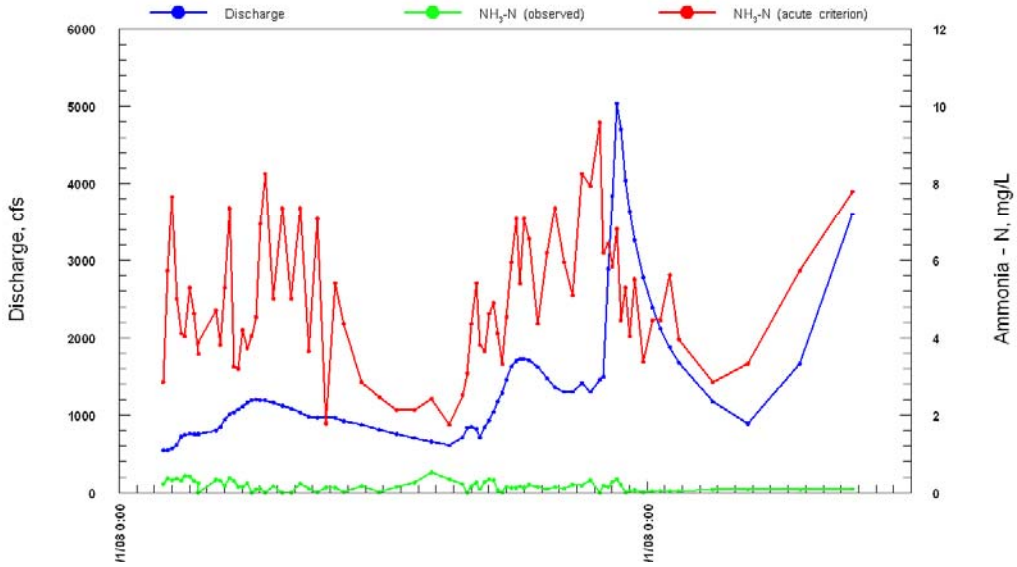
- pH values near circumneutral; not high during fish kill period
- Carbonate geology controlled
- Daily cycle due to water temperature variation, CO_2 production & consumption, ionic strength, etc.
- Probably the most common WQP, but also the least useful unless NH_3 values are elevated
- Not in the range (< 5 or > 10) where fish are stressed

Recommendation:

- Consider pH in low probability category as a stress causative factor in the fish kills

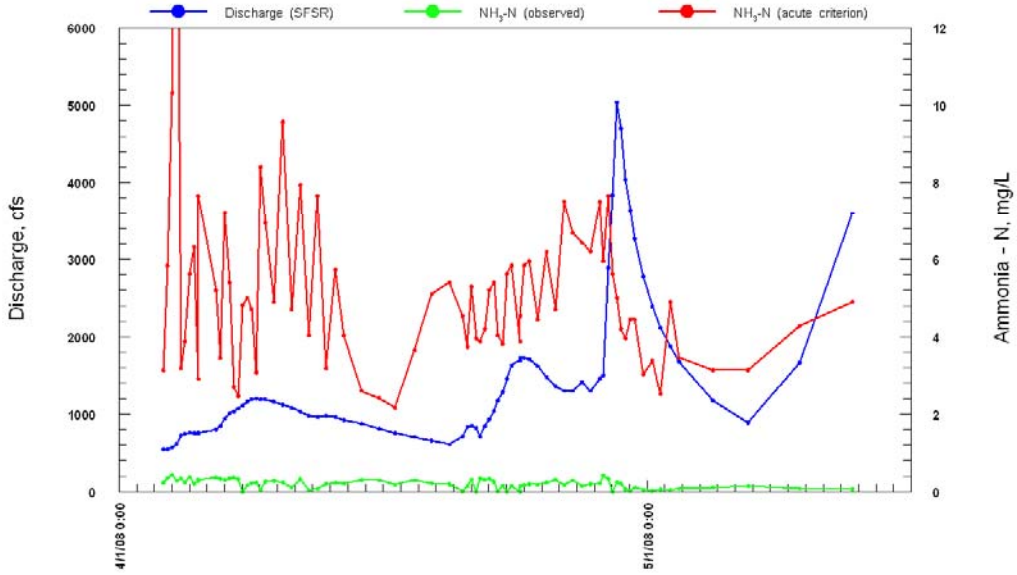
E.M.P. Ammonia-Nitrogen and Discharge

South Fork - Shenandoah River Island Ford



E.M.P. Ammonia-Nitrogen and Discharge

South Fork Tributary - Cub Run



Observations:

- Values for N-ammonia/ammonium did not increase with storm runoff
- Values were also low during base flow
- Values did not exceed 22% of acute criteria
- Most values were < 10% of acute criteria
- No evidence yet produced by any sampling to indicate ammonia has been present at lethal or near lethal levels

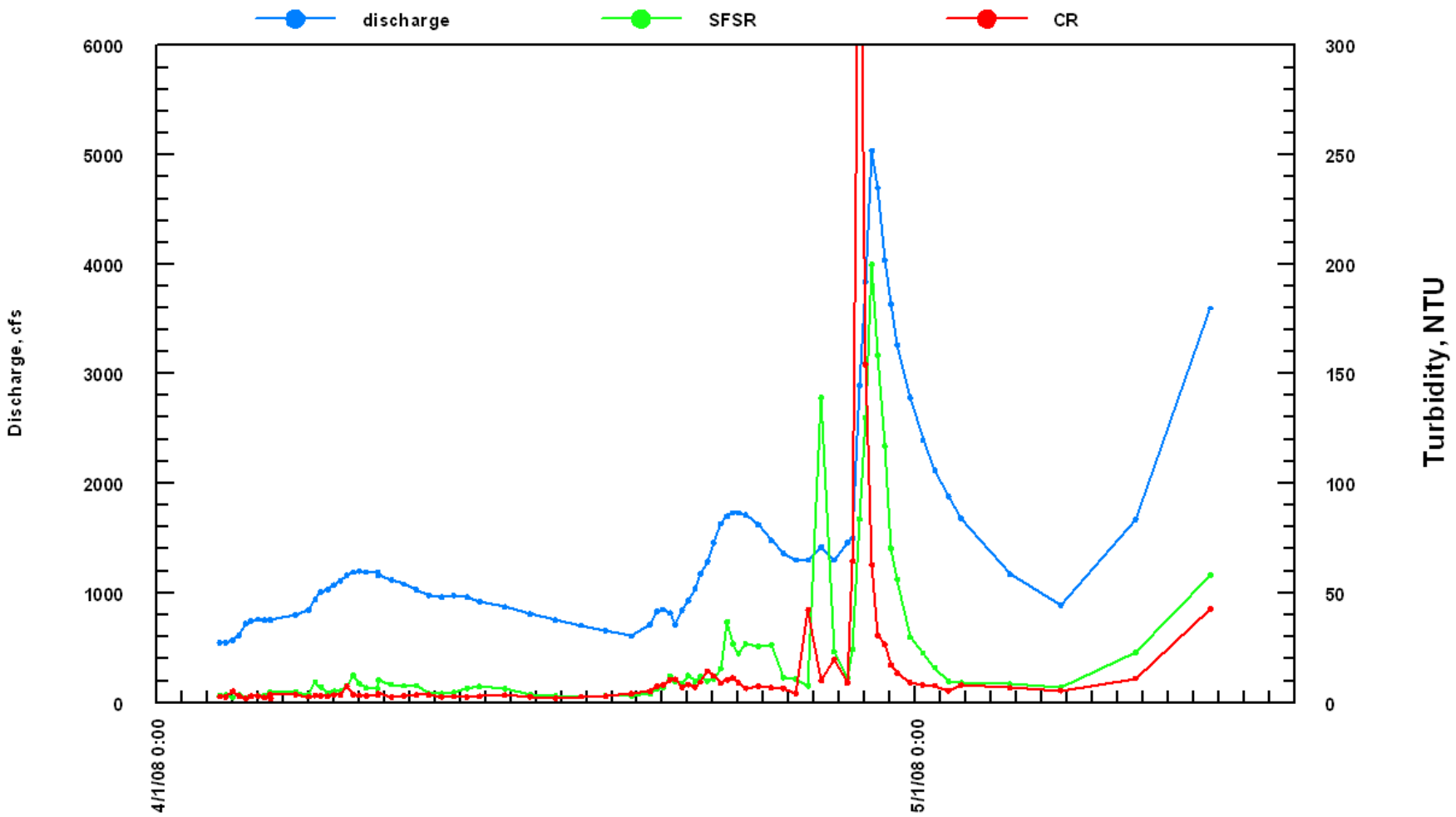
Recommendation:

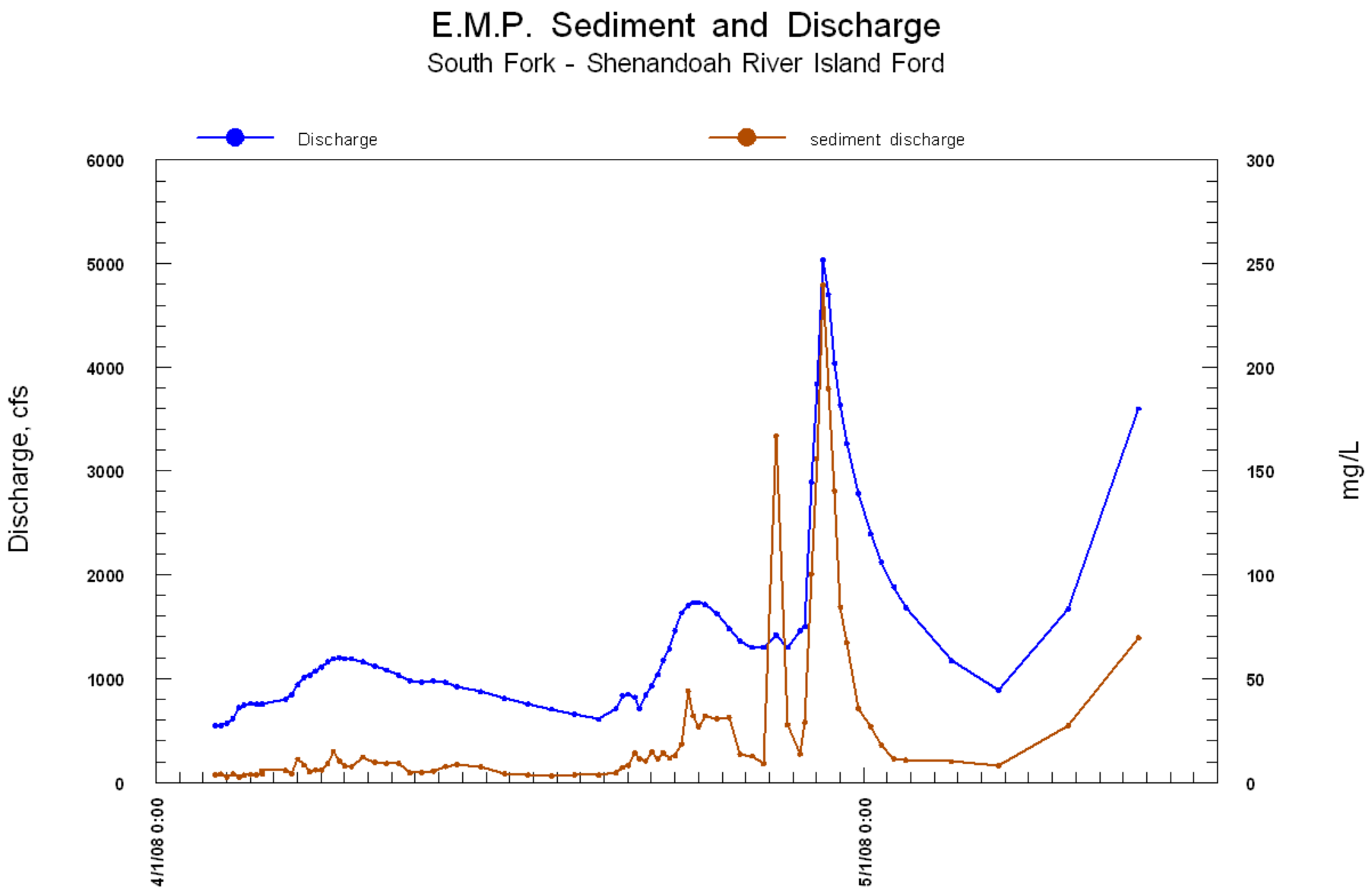
- Consider ammonia in low probability category as a stress causative factor in the fish kills


http://flickr.com/photos/21893264@N00/281427872

E.M.P. - Discharge and Turbidity

Island Ford - SFSR & Cub Run

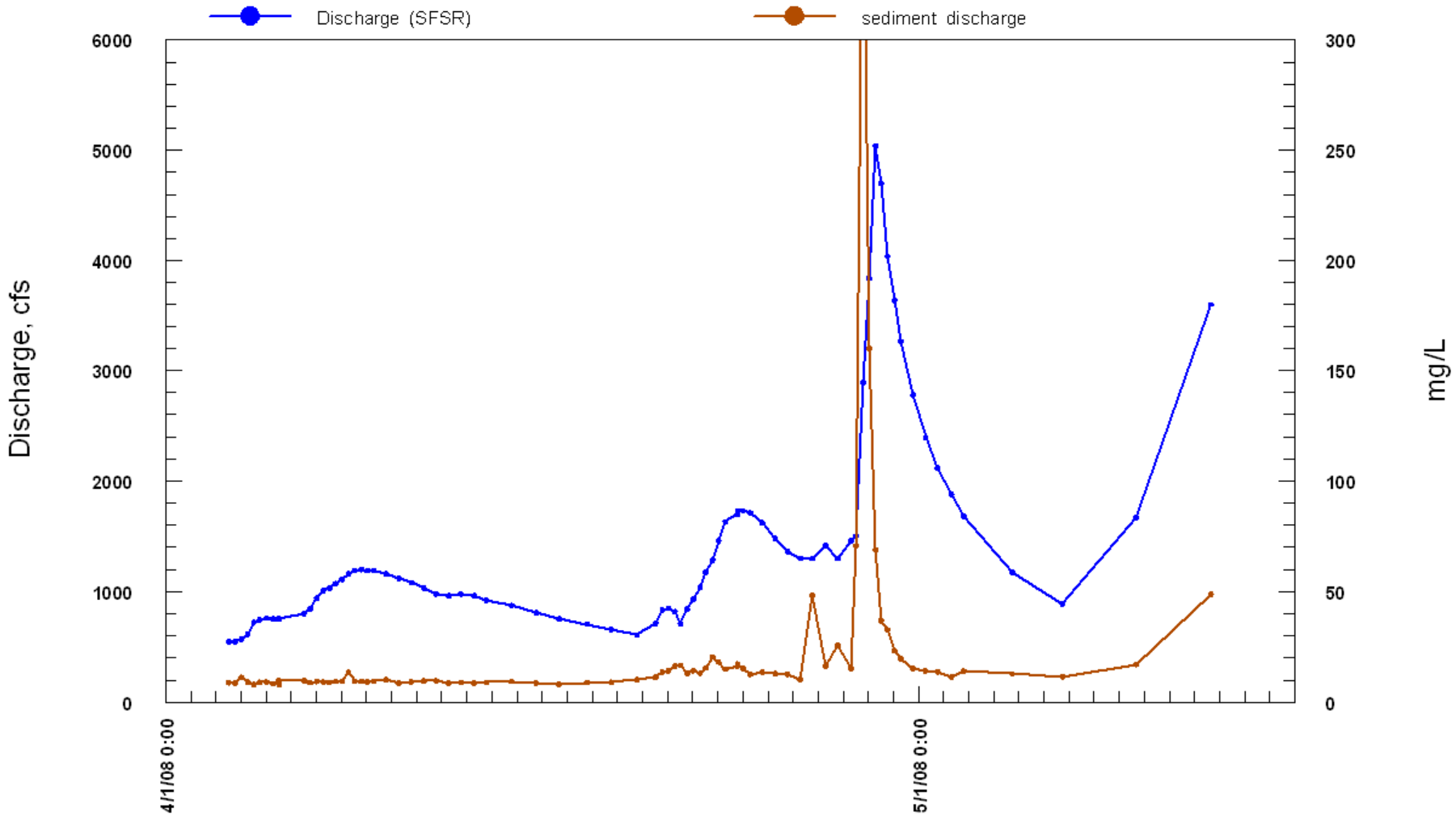




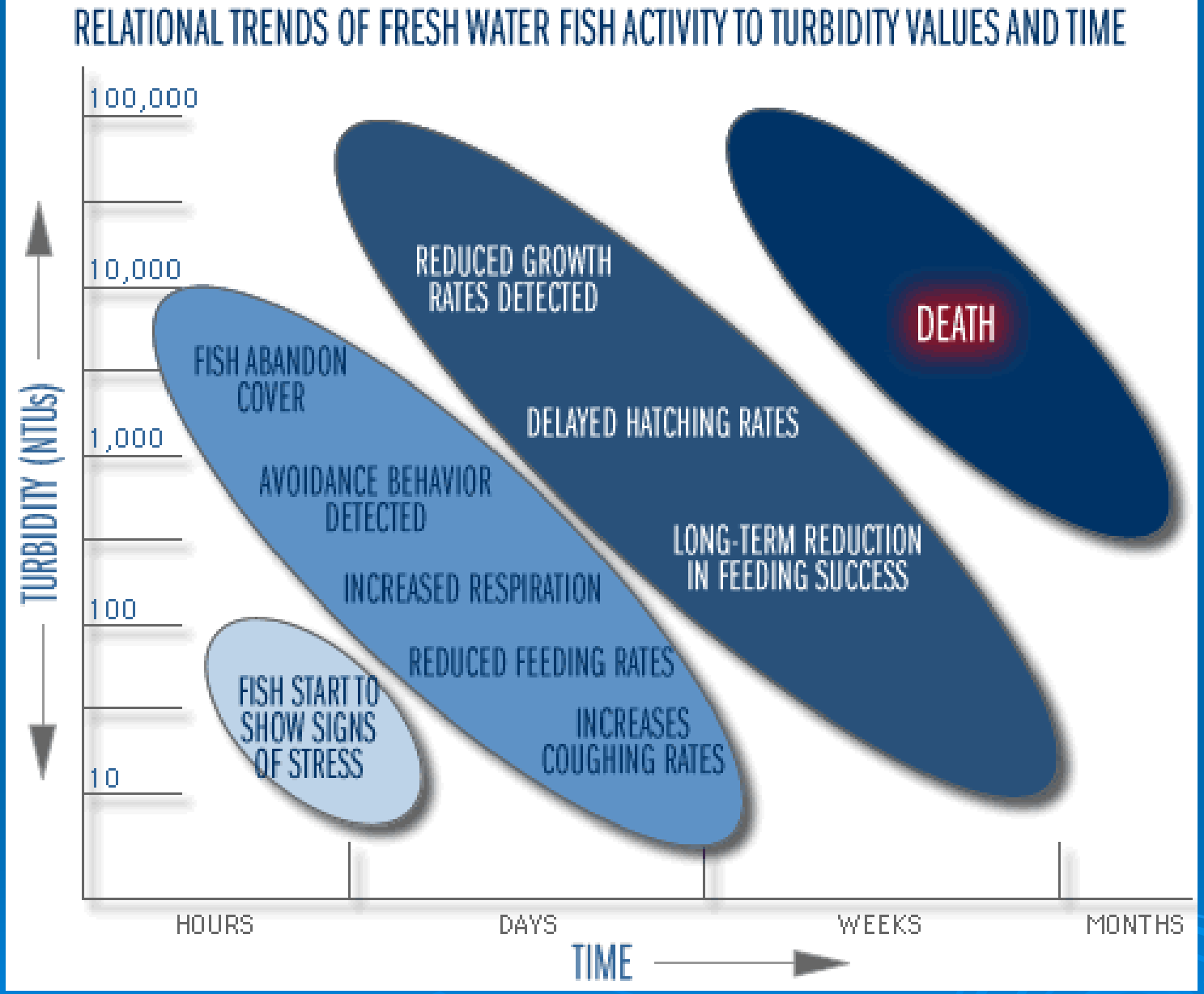
In the 8 days between April 28 and May 6, the South Fork discharged 2900 tonnes of suspended solid material at Island Ford.

E.M.P. Sediment and Discharge

Cub Run



In the 8 days between April 28 and May 6, Cub Run discharged 52 tonnes of suspended solid material; almost all of it within the first two days.



NEWCOMBE CP, JENSEN JOT (1996) Channel Suspended Sediment and Fisheries: A Synthesis for Quantitative Assessment of Risk and Impact. North American Journal of Fisheries Management: Vol. 16, No. 4 pp. 693–727.

Observations:

- Sediment loading is quite large during episodic events
- Sediment discharge increases dramatically during the initial period of the storm and maximizes before the storm discharge peak
- Values in excess of 25 ppm affect fish health
- Turbidity readings can serve as a surrogate for TSS

Recommendation:

- Consider suspended sediment (turbidity) in high probability category as an associated stress causative factor in the fish kills
- Conduct additional measurements in future storms
- Search available data
- Locate and control sources of sediment loading

Acknowledgements

- Field Sample Collectors: Brandon Ayers, Michelle Bender, Anne Battaglia, Nick Dugan, Stephanie Hall, Wesley Storm and Jake White
- Sample Processing: Anne Battaglia (Extraction), Stephanie Hall (Extraction and GC operations), Nick Dugan (IC and ICPMS) & Jacob Smith (Glyphosate)
- Instrument Specialists: Marty Mihay, Jeff Molloy, and Tom Gallaher (JMU Chemistry)
- Dr. Kevin Caran (JMU Chemistry) and Dr. Tom Benzing (JMU ISAT)
- Don Kain, Ted Turner, Billy Van Wert and Jake White (DEQ)
- Steve Reeser (DGIF)
- John Holmes (FNFSR)
- Dave Alvarez (USGS)
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