(H23B-1488) LONG-TERM CHANGES IN THE ACID-BASE STATUS OF WESTERN MARYLAND STREAMS

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A. Background and Objectives

Following the Clean Air Act (1975) & its amendments of 1990, decreases in acid deposition have been observed in many regions of the U.S. (Figure 1).

Following these decreases in acid deposition, decreases in surface water nitrate and sulfate concentrations have been observed (Likens et al. 1996, Clow and Mast 1999, Stoddard et al. 1999) but only more recent studies have documented any significant increases in alkalinity (Stoddard et al. 2003, Skjelkvale et al. 2005).

Using long-term monitoring data from two small streams in western Maryland, we investigated the following question:

❖ How have streams in this region responded to decreases in acid deposition?

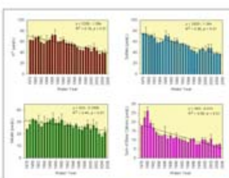

Figure 1. Average precipitation-weighted concentrations of solutes in wet deposition from three National Atmospheric Deposition Program (NADP) sites in the mid-Atlantic region (WV18, PA15, and PA42). Since 1978, significant ($p < 0.01$) decreasing trends have been observed for H+, sulfate, nitrate, and the sum of base cations (Na, K, Mg, Ca) at these three stations.

B. Methods

Data was collected from two continuously gaged, small watersheds in the Appalachian Plateau region of western Maryland (Figure 2, Table 1). NADP precipitation monitoring stations were selected based on length of record, geographic proximity to stream sites, and topographic similarity.

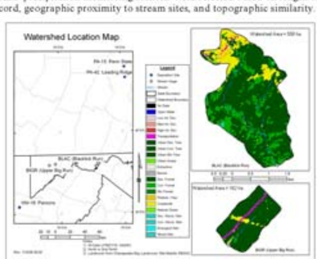

Figure 2. Locations of NADP precipitation monitoring sites and gaged streams with land use/land cover (LULC) for each watershed. Both watersheds are predominantly forested.

- Recorded hourly stage data converted to discharge.
- Grab water samples collected bi-weekly or monthly and analyzed using EPA-approved methods (Tables 2 & 3).

B. Methods, continued

- Monthly and annual discharge-weighted solute concentrations calculated using:
  - WATFLOW
  - LOADEST
- Trends analyzed using linear regression and Seasonal Kendall Tau.

Table 1. Watershed LULC summaries.

Land Cover (% of watershed)		
	BLAC	BIGR
Area (ha)	558	162
Description		
Developed / Transportation	0.8	4.7
Deciduous forest	68.0	88.7
Coniferous forest	18.4	2.1
Mixed forest	0.2	0.0
Agriculture	12.6	4.5

*Land Cover data from Chesapeake Bay Landcover Map, Mid-Atlantic RESAC

Table 2. Sample collection summary.

Annual Sample Collection Rates		
Water Year	BLAC	BIGR
1990	0	46
1991	0	40
1992	0	45
1993	0	24
1994	0	13
1995	0	8
1996	27	73
1997	43	58
1998	54	49
1999	11	11
2000	10	10
2001	11	11
2002	12	12
2003	12	12
2004	11	11
2005	13	13

Table 3. Analytical constituents and methods.

Analyte	Technique
ANC*	Gran titration
Nitrate & Sulfate	Ion Chromatography (IC)
Base Cations**	Before 1999 by IC After 1999 by Flame AA

*Acid Neutralizing Capacity
**Sum of sodium, potassium, magnesium, & calcium

C. Results

(1) Annual Fluxes of Water and Solutes at BIGR

Figure 3. Annual fluxes of water, sulfate, nitrate and ANC at BIGR.

- In general, solute fluxes related to water flux (Figure 3).
- 1996 and 2003 wettest
- 1992 and 1999 driest
- Significant ($p < 0.05$) positive trend in ANC flux.

(2) Monthly Discharge-Weighted Concentrations at BIGR

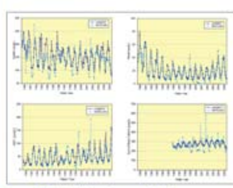

Figure 4. Monthly discharge-weighted concentrations of sulfate, nitrate, ANC, and the sum of base cations at BIGR calculated with WATFLOW and LOADEST models.

- Good agreement between WATFLOW and LOADEST for calculating flow-weighted solute concentrations.
- Seasonal pattern observed in data from Big Run.
- Overall, solutes were lowest during the late summer and early fall.

(3) Annual Discharge-Weighted Concentrations at BIGR

Figure 5. Annual trends in discharge-weighted concentrations of sulfate, nitrate, ANC, and the sum of base cations at BIGR.

- Significant ($p < 0.05$) declines in sulfate and nitrate.
- Significant ($p < 0.05$) increases in ANC and base cations.

(4) Trend Analysis at BIGR and BLAC

❖ Both sites – BIGR and BLAC:
- Sulfate is decreasing by 2 – 4 µeq L^{-1} yr^{-1} (Table 4)

❖ BIGR:
- Nitrate is decreasing by 1 – 2 µeq L^{-1} yr^{-1}
- ANC is increasing by 1 – 2 µeq L^{-1} yr^{-1}
- Cations are increasing by 3 – 7 µeq L^{-1} yr^{-1} (1997-2005 only)

❖ BLAC:
- Cations are decreasing by 3 – 7 µeq L^{-1} yr^{-1}
- No trends observed for nitrate or ANC

❖ Consistent results obtained using both trend analysis techniques and both models suggest that the observed relationships are very robust.

Table 4. Summary of trend analysis for solutes at each sampling site.

Constituent/Statistical Technique	Sampling Site/Model			
	BIGR		BLAC	
	WATFLOW	LOADEST	WATFLOW	LOADEST
Sulfate				
Linear Regression	-2.53*	-3.37*	-3.26*	-3.13*
Seasonal Kendall Tau	-2.32	-2.89*	-3.48*	-3.03*
Nitrate				
Linear Regression	-1.32*	-1.70*	NS	NS
Seasonal Kendall Tau	-1.25*	-1.23*	NS	NS
ANC				
Linear Regression	+2.19*	+1.34*	NS	NS
Seasonal Kendall Tau	+1.13*	+1.27*	NS	NS
Sum of Base Cations				
Linear Regression	+7.23*	+3.58*	-2.91*	-4.77*
Seasonal Kendall Tau	+4.34*	+3.30*	-5.41*	-6.78*

* $p < 0.05$

(5) Watershed Differences

❖ Differences in long-term trends observed between the two watersheds may be influenced by a number of factors, including watershed size, bedrock geology, land use/land cover, and disturbance history.
❖ Although both watersheds are predominantly forested, BIGR almost entirely forested with deciduous species, the BLAC watershed has almost 10 times more coniferous forest cover (Figure 2, Table 1).
❖ BLAC watershed has greater agricultural influence than BIGR.

(5) Relationships Between Flux and Wet Deposition

❖ Relationship between wet deposition and fluxes of sulfate and nitrate suggest differences between the two watersheds (Figure 6).
❖ NO3-N at BIGR is the only stream solute that does not exceed wet deposition.
❖ NO3-N dynamics at BLAC may be influenced by agricultural activity in watershed.
❖ SO4 fluxes at both sites exceed wet deposition contribution but the relationships differ.
❖ Dry deposition may help explain the difference between solute flux and wet deposition.
❖ Scavenging of dry deposition by conifers at BLAC may explain the differences between the two sites.

(5) Relationships Between Flux and Wet Deposition, continued

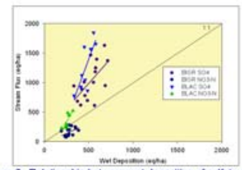

Figure 6. Relationship between wet deposition of sulfate and nitrate and stream flux. Points above the 1:1 line suggest more solute is exiting the watershed than is entering as wet deposition.

D. Conclusions

❖ Sulfate trends (↓ 2-4 µeq L^{-1} yr^{-1}) at BIGR and BLAC are comparable to literature.
❖ Nitrate trends (↓ 1-2 µeq L^{-1} yr^{-1}) at BIGR are comparable to literature.
❖ ANC recovery at BIGR (↑ 1-2 µeq L^{-1} yr^{-1}) is comparable to the more recent literature.
❖ High ANC at BLAC may be influencing the ability to observe any significant long-term recovery trends.
❖ Trends in cation concentrations at the two sites are opposite.
- Differences in cations between the two sites may be attributable to the shorter period of record for cations at BIGR compared to other solutes.
- When SBC are calculated, results suggest that cations at BIGR were actually increasing during the first half of the period of record (Table 5).

❖ Trends at BIGR appear to have shifted over time (Figure 5).
- For the second half of the monitoring period, sulfate and nitrate are actually increasing at BIGR and the slope of the ANC trend has changed.
- Further monitoring may help explain BIGR trends.

❖ Watershed differences, as well as forest disturbance, could also be playing a role in long-term trends.

Table 5. Trends at BIGR for period of 1990 through 2005. SBC are calculated.

CONSTITUENT	LOADEST*	WATFLOW*
△ ANC (measured)	1.34	2.19
△ Sulfate (measured)	-3.37	-2.53
△ Nitrate (measured)	-1.7	-1.32
△ SBC (difference)	-3.73	-1.66

*µeq L^{-1} yr^{-1}; $p < 0.05$

D. References

Clow, D.W. and M.A. Mast. 1999. Long-term Trends in Stream Water and Precipitation Chemistry at Five Headwater Basins in the Northeastern United States. Water Resources Research 35:541-554.

Likens GE, Driscoll CT, Buso DC. 1996. Long-term effects of acid rain: Response and recovery of a forest ecosystem. Science. 272:244–246.

Stoddard, J.L., Jeffries, D.S., Lukewille, A., Clair, T.A., Dillon, P.J., Driscoll, C.T., Forsius, M., Johannessen, M., Kahl, J.S., Kellogg, J.H., Kemp, A., Mannio, J., Monteith, D., Murdoch, J.S., van Dam, H., Webster, K.E., Wieting, J., Wilander, A. 1999. Regional trends in aquatic recovery from acidification in North America and Europe. Nature. 401: 575-578.

Stoddard, J.L., Kahl, J.S., Deviney, F.A., DeWalle, D.R., Driscoll, C.T., Herlihy, A.T., Kellogg, J.H., Murdoch, P.S., Webb, J.R., Webster, K.E. 2003. Response of surface water chemistry to the Clean Air Act Amendments of 1990. EPA/620/R-03/001, U.S. Environmental Protection Agency, Corvallis, Oregon.

Skjelkvale, B.L., J.L. Stoddard, D.S. Jeffries, K. Torseth, T. Hogasen, J. Bowman, J. Mannio, D.T. Monteith, R. Mosello, M. Rogora, D. Rzychon, J. Vesely, J. Wieting, A. Wilander, & A. Worsztynowicz. 2005. Regional scale evidence for improvements in surface water chemistry 1990-2001. Environmental Pollution 137: 165-176.

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