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**Ecological Responses of Streams to Anthropogenic Stressors, and Watershed
Cause-Effect Modeling in the Mid-Atlantic Highlands Region of the United
States**

Yushun Chen

Dissertation submitted to the
College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements
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in
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Approved by
Lian-Shin Lin, Ph.D., P.E., Committee Chairperson
Donald D. Gray, Ph.D., P.E.
Robert N. Eli, Ph.D., P.E.
Xinchao Wei, Ph.D., P.E.
Department of Civil and Environmental Engineering
&
James T. Anderson, Ph.D.
J. Todd Petty, Ph.D.
Division of Forestry and Natural Resources

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Keywords: Anthropogenic stressors; Appalachian Corridor H; Acidic deposition; Mid-Atlantic Highlands; Stream biotic and abiotic conditions; Watershed hierarchical approach; Landscape and riverscape; structural equation modeling (SEM); latent growth curve modeling (LGM)
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ABSTRACT

Ecological Responses of Streams to Anthropogenic Stressors, and Watershed Cause-Effect Modeling in the Mid-Atlantic Highlands Region of the United States

Yushun Chen

Urban sprawl and related habitat disturbance and acidic deposition are major anthropogenic stressors in the Mid-Atlantic Highlands region of the United States. Little information is available about the impacts of these stressors and cause-effect relationships between these watershed stressors and stream biotic/abiotic conditions in this region. A 10-year study (1997-2006) in the Lost River watershed and a 6-year study (2002-2007) in a South Branch Potomac River watershed were conducted to assess the impacts of Corridor H highway construction on stream biotic and abiotic conditions. Also, a three-decade study (1980-2006) using data from 5 wet deposition stations and 21 major stream sites in West Virginia was conducted to assess long-term stream chemical responses to reduced acidic deposition and the role of watershed attributes in regulation of the responses. In these studies, long-term stream monitoring, laboratory chemical and biological analysis, basic (e.g., paired t tests, analysis of variance or ANOVA, chi-square analysis, and trend analysis) and advanced (e.g., principal components analysis or PCA, structural equation modeling or SEM, and latent growth curve modeling or LGM) statistical methods, and geographical information system (GIS) techniques were used to assess impacts; detect long-term trends; and model watershed cause-effect relationships.

Construction of the Appalachian Corridor H highway in the Lost River watershed had statistically significant effects on seven major water quality parameters identified by the PCA analysis. Those parameters include turbidity, total suspended solids (TSS), and total iron during the construction; chloride and sulfate during and after the construction; and acidity and nitrate after the construction. The highway construction had statistically significant impacts on the scores of stream benthic macroinvertebrates index (i.e., WVSCI) after the construction, but the impacts did not change the overall good biological condition. In the South Branch Potomac River 3 watershed, the highway had no significant effects on major water quality parameters during the first year's construction. Only episodic impacts of the highway construction on turbidity, TSS, iron, and aluminum were observed.

The trend analysis found that reduced acidic deposition in the region resulted in homogeneous chemical improving trends in the West Virginia streams for sulfate, alkalinity, hydrogen ion, and total aluminum during the period of 1980-2006. The decreased deposition of acid anions and hydrogen ion explained the increase of pH and alkalinity. The SEM-based LGMs quantified most stream chemical (i.e., chloride, nitrate, sulfate, pH, hardness, and alkalinity) initial conditions (i.e., intercepts) and their changing rates (i.e., slopes) in the 1980s, 1990s, and 2000s in the central Appalachian Mountains. The slopes or trends identified by all acceptable unconditional LGMs were generally consistent with the trends detected by the trend analyses. Watershed area, mean elevation, percentage of developed, percentage of grassland, percentage of shale and sandstone, percentage of barren land, and percentage of soil type Gilpin-Upshur-Vandalia (GUV)

regulated streams' sensitivity to the reduced acidic deposition, and further influenced stream chemical initial conditions and their changing rates in these mountain watersheds.

Overall, results of these studies advanced our understanding of stream biotic and abiotic responses to urban sprawl and related habitat disturbance and acidic deposition in the Mid-Atlantic Highlands region of the United States. Construction-impacted water quality parameters should be considered for developing mitigation strategies and refining currently implemented BMPs for future highway constructions in the Mid-Atlantic Highlands region. Special attentions should be paid to those episodically impaired water quality parameters which may temporally stress aquatic organisms in the streams. Further improvements in the chemical and biological conditions of the West Virginia streams may require additional controls of power plants emissions to further reduce acidic deposition in this mountain region. Stream restoration strategies for remediation of acidic deposition impacts should consider the difference of watershed attributes in different areas.

Dedication

This dissertation is dedicated to my wife, Jinyan Sun. She, a woman, like most others, left her parents and relatives, gave up her past job, flew 15 hours to the opposite of the Pacific Ocean, just for love and for her man. This woman accompanied the man for his Master study and Doctoral study periods which are the most important periods in the man's research career and his whole life. Her smiles inspired my new ideas in solving problems in research. Further, I am indebted to her for the later period of my doctoral study when she began her dual roles, a wife and a mother. She did almost all the things in the spring of 2008 when our son David was born in this quiet, beautiful, wild, and wonderful Morgantown. Finally, I would like to dedicate this to our parents who taught us over the phones for taking care of each other, for understanding each other, and for managing our love, marriage, and the new founded family. They trained me and my wife to become good parents for the new generation.

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Chapter 1 – Introduction

1.1 Anthropogenic Stressors and Stream Ecological Conditions in the Mid-Atlantic Highlands Region of the United States

1.1.1 The Mid-Atlantic Highlands (MAH) Region of the United States

The Mid-Atlantic Highlands region of the United States encompasses about 79,000 square miles and ranges from the Ohio River in the west to the Blue Ridge Mountains in the east, and from the state of Virginia in the south to the Catskill Mountains in the north (Figure 1; USEPA, 2000a). It includes the state of West Virginia, parts of Virginia, Maryland, Pennsylvania, and New York (Figure 1; USEPA, 2000a; Canaan Valley Institute, 2002). This region is home to approximately 11.5 million people (USEPA, 2000a). Small streams dominate the total stream length in the region and contribute to the quality and condition of larger streams and rivers (USEPA, 2000a). For example, first order streams (based on Strahler system) occupy more than 63% of the total stream length (i.e., over 51,000 stream miles) in this region (USEPA, 2000a). Major watersheds in this region include the Chesapeake watershed, Allegheny-Monongahela watershed, and Kanawha-Upper Ohio watershed (USEPA, 2000a).

1.1.2 Anthropogenic stressors in the MAH region

Human activities have potential to affect the health of aquatic ecosystems. Reported anthropogenic stressors that were ranked based on percentage of stream miles impacted in this Highlands region were non-native fish (32%), channel sedimentation (25%), riparian habitat disturbance (24%), mine drainage (14%), acidic deposition (11%), fish tissue contamination (10%), total phosphorus (5%), and total nitrogen (5%) (Bryce et al.,

1999; USEPA, 2000a). In the state of West Virginia, for example, stressors and their rankings were channel sedimentation (18%), riparian habitat disturbance (26%), mine drainage (13%), acidic deposition (14%), fish tissue contamination (1%), total phosphorus (15%), total nitrogen (1%), and non-native fish (22%) (USEPA, 2000a).

1.1.3 Stream ecological conditions in the MAH region

Overall ecological health of an aquatic ecosystem depends on its biological, chemical, and physical conditions. Conditions of biological organisms such as fish, aquatic insects, and other animals integrate and reflect the total effects of all of the stressors to which they are exposed (USEPA, 2000a). To assess the overall condition of a stream, a multiple metric index (e.g., fish-based or aquatic insect-based index of biotic integrity) is usually used in regional or sub-regional monitoring and assessment studies (Karr et al., 1986; Karr and Chu, 1999; USEPA, 2000b). In this Mid-Atlantic Highlands region, over 31% of the stream miles were in poor condition based on a fish Index of Biotic Integrity (IBI) and 27% of the stream miles were in poor condition based on aquatic insect indicators according to the USEPA Environmental Monitoring and Assessment Program (EMAP) which studied 500 stream reaches during 1993 and 1994 (USEPA, 2000a). In the state of West Virginia, 44% of the stream miles were rated as poor based on the fish IBI and 25% of the stream miles rated as poor based on the aquatic insect index (USEPA, 2000a).

1.1.4 Statistical methods for linking stressors to ecological conditions

Researchers are interested in establishing hierarchical links from landscapes to riverscapes and links from watershed factors or anthropogenic stressors to aquatic biotic

and abiotic indicators (Hunsaker and Levine, 1995; Johnson and Gage, 1997; Allan and Johnson, 1997; Gergel et al., 2002; Allan, 2004; Novotny et al., 2005). But researchers may face several potential problems such as (1) covariation of anthropogenic and natural gradients in the landscape; (2) the existence of multiple, scale-dependent mechanisms; (3) nonlinear responses; and (4) the difficulties of separating present-day from historical influences when characterizing these links (Allan, 2004).

Novotny et al. (2005) listed 4 types of potential landscape parameters or watershed factors that may affect integrity of surface waters: (1) watershed morphological characteristics (e.g., area, altitude, latitude, slope of land segments, and distance of disturbed land segment from the water body), (2) watershed pedological and geological characteristics (e.g., soil type and texture, bedrock, and type of bedrock geology), (3) watershed land use land cover (e.g., % urban or % imperviousness, % agricultural or crops, % forest, % wetland, rate of wetland drainage, % area under construction, % transportation, and mining and mining spoils), and (4) stream morphology (e.g., stream order, velocity, slope, depth, frequency of bankfull flow or channel flow capacity, pool and riffle sequence, bottom substrate texture, organic content of sediments, channel alteration, and riparian vegetation and stream side cover). Tools of geographic information system (GIS) were commonly used to collate these data. To establish the hierarchical links or detect watershed impacts, Johnson and Gage (1997) listed 15 potential univariate and multivariate statistical techniques: (1) analysis of variance (ANOVA); (2) regression analysis; (3) principal components analysis (PCA); (4) correspondence analysis (CA); (5) multidimensional scaling and non-metric ordination (NMDS); (6) canonical correspondence analysis (CCA); (7) redundancy analysis (RA);

(8) R-mode linked to Q-mode (RLQ) analysis; (9) cluster analysis; (10) discriminant function analysis (DFA); (11) randomized intervention analysis (RIA); (12) before-after-control-impact pairs (BACI); (13) path analysis; (14) structural equation modeling (SEM); and (15) kriging.

In the literature, applications of methods other than those mentioned above were also reported. For example, simple Pearson correlation or Spearman's rank correlation was used to link watershed pollution sources to water quality and biotic integrity in a couple of studies (e.g., Roth et al., 1996; Hall and Killen, 2005; Handler et al., 2006; Chow et al., 2007). Some studies used a combination of multivariate analysis of variance (MANOVA) and t-tests to find links between watershed land use and macroinvertebrates condition in Charlotte, North Carolina (e.g., Gage et al., 2004). But most of the reviewed studies used a combination of correlation or ANOVA, PCA, and simple or multiple regression analysis to quantify the hierarchical links (Comeleo et al., 1996; Townsend et al., 1997; Lammert and Allan, 1999; Crosbie and Chow-Fraser, 1999; Jones et al., 2001; Griffith et al., 2002; Meador and Goldstein, 2003; Van Sickle, 2003; Strayer et al., 2003; Siwek and Chelmsicki, 2004; King et al., 2004; Van Sickle et al., 2004; Frimpong et al., 2005; Pinto et al., 2006; Frost et al., 2006a; Bhat et al., 2006; Lussier et al., 2008; Bahar et al., 2008; Morrice et al., 2008). For applications of multiple regressions in ecological studies, Nally (2000; 2002) presented detailed information about model building and identification of predicting variables. There were also applications of generalized additive models (e.g., Yuan and Norton, 2004), classification and regression tree (CART) analysis (e.g., King et al., 2005), and path analysis (e.g., Burcher et al., 2007) for watershed hierarchical studies.

For identifying these hierarchical links, however, some researchers suggested that possible spatial autocorrelations should be considered in the analysis (Legendre, 1993; Koenig, 1999). Legendre (1993) defined spatial autocorrelation as "... the property of random variables taking values, at pairs of locations a certain distance apart, that are more similar (positive autocorrelation) or less similar (negative autocorrelation) than expected for randomly associated pairs of observations." Legendre (1993) provided several solutions to address the issue of spatial autocorrelation: (1) remove the spatial dependency among observations so that the usual statistical tests can be used; (2) modify the statistical method in order to take spatial autocorrelation into account; and (3) rely on permutation tests, where the significance is determined by random reassignments of the observations. Cook and Pocock (1983) presented a revised multiple regression method that took account of spatially correlated errors. King et al. (2005) used a partial mantel test (Mantel, 1967) to link watershed land cover to ecological indicators in coastal plain streams of Maryland. To avoid confounding effects, Liu et al. (2000) incorporated one single type of land cover at a time in separated regression models as a predictor for stream water chemistry in the Chesapeake Bay watersheds. Dodds and Oakes (2006) used mixed linear models to account for spatial autocorrelation in linking land use and riparian cover to nutrients in prairie streams in Kansas. To account for spatial autocorrelation in the analysis of species distributional data, Dormann et al (2007) reviewed and compared the following methods: (1) autocovariate models; (2) spatial eigenvector mapping (SEVM); (3) generalized least squares (GLS); (4) autoregressive models (conditional autoregressive models or CAR and simultaneous autoregressive models or SAR); (5) spatial generalized linear mixed models (GLMM); and (6) spatial generalized estimating

equations (GEE). There were also increasing applications of canonical correspondence analysis (CCA) and redundancy analysis (RDA) in watershed hierarchical studies (Johnson et al., 1997; Sliva and Williams, 2001; Townsend et al., 2003; Feld and Hering, 2007).

1.1.5 Studies linking stressors to ecological conditions in the MAH region

Many monitoring programs and studies have reported the watershed links from stressors to aquatic ecological status in this region. For example, the West Virginia Department of Environmental Protection (WVDEP) conducted a series of integrated water quality monitoring and assessment programs to monitor watershed stressors (e.g., mine drainage, bacterial contamination, and atmospheric deposition), and to list impaired streams for total maximum daily loads (TMDLs) development in the state (WVDEP, 2004 and 2006). Efforts linking land cover and land use (e.g., agriculture and urban) to aquatic ecological conditions have also been extensively reported in this region (e.g., Ator and Ferrari, 1997; Jones et al., 1997; Herlihy et al., 1998; Pan et al., 1999; Debrewer et al., 2008). Further, Petty and colleagues conducted many stream assessment studies related to acid mine drainage in this mountain region (Petty and Barker, 2004; Stout III, 2004; Freund and Petty, 2007; Merovich and Petty, 2007; Merovich et al., 2007). However, little information is available about studies related to channel sedimentation and riparian habitat disturbance (e.g., highway construction) in this highland region (Chisholm and Downs, 1978; Hedrick et al., 2007). For acidic deposition, there was also no regional information available in the mountain areas of West Virginia even though extensive studies have been conducted in the Shenandoah National Park, western

Virginia, western Maryland, and Catskill Mountains of New York (Webb et al., 1989; Driscoll et al., 1998; Driscoll et al., 2001a; Driscoll et al., 2003; Webb, 2004; Web et al., 2004; Kline et al., 2007).

1.2 Ecological Responses to Highway Construction

1.2.1 Highway construction and urban development

As urbanization proceeds, new highways are constructed for transportation and development, and stream ecosystems within highway corridors are susceptible to impacts from the construction activities. In the United States, more than 6.2 million km of public roads are used by more than 200 million vehicles for transportation and linking local areas (National Research Council, 1997). It was estimated that about 19% of the total land area in the nation has been affected by these roads system (Forman, 2000). In the U. S. Mid-Atlantic Highlands region, urban sprawl and its related highway construction was one of the major concerns for habitat destruction (USEPA, 2000a).

1.2.2 Biotic and abiotic impacts of highway construction

As one of the major non-point pollution sources, construction of new highways can have short- and long-term effects on stream biotic and abiotic conditions (Barton, 1977; Chisholm and Downs, 1978; Cline et al., 1982; Taylor and Roff, 1986; Anderson and Potts, 1987; Stout III and Coburn, 1989; Wellman et al., 2000; Hedrick et al., 2007). Spellerberg (1998) reviewed 388 references for ecological effects of roads and traffic. It was found that the research gaps included effects of heavy metal accumulation and the processes and effects of habitat fragmentation. Angermeier and colleagues (Angermeier et al., 2004; Wheeler et al., 2005) proposed a conceptual model for assessing impacts of roads on aquatic biota and a three-step framework for the assessments (i.e., initial highway construction, highway presence, and eventual landscape urbanization).

In the Hanlon Creek of southern Ontario, Taylor and Roff (1986) found increased populations but decreased diversity of invertebrates at downstream sites 2.5 years after a highway construction. Specifically, *Trichoptera* and *Diptera* increased but *Plecoptera* and *Ephemeroptera* decreased or did not change at the downstream sites (Taylor and Roff, 1986). In the Falling Water Creek and North Chickamauga Creek of southeastern Tennessee, Stout III and Coburn (1989) found lower leaf processing and decreased number of shredders at downstream sites of a highway construction. It was concluded that the highway construction removed streamside vegetation, increased stream temperatures, reduced the amount of natural leaf accumulations, and thereby reduced shredder habitat (Stout III and Coburn). In 41 streams in middle and eastern Tennessee, however, fish diversity, abundance, and richness were not statistically different between streams with bridges and streams with culverts, nor among control stream reaches (Wellman et al., 2000). In the Joe Wright Creek of the Rock Mountains, a highway construction reduced algal species diversity and modified taxonomic composition of macroinvertebrates (Cline et al., 1982). In the Mid-Atlantic Highlands, Hedrick et al. (2007) investigated two tributaries in the Lost River and found no significant difference of macroinvertebrate metrics between upstream and downstream sites during a three-year study. In the coastal plain streams in southern Maine, roadway crossings increased litter loss rate and impacted biomass of important shredder taxa (Woodcock and Hury, 2004). In the forested wetlands of North Carolina, increased percentage of herbivores and algal grazers (i.e., mayflies *Caenis* sp. and *Callibaetis* sp.) were found near highway crossings (King et al., 2000). In an estuary in Hilton Head of South Carolina, lower embryo production and embryo hatching rates, and a higher level of DNA strand breaks of grass

shrimp (*Penaeus monodon*) were observed in sediments near highway runoff (Lee et al., 2004).

For abiotic impacts of highway constructions, sedimentation or increased total suspended solids is one of the most common problems that have been reported by almost all the highway construction studies (Burton et al., 1976; Barton, 1977; Beschta, 1978; Helm, 1978; Hainly, 1980; Cline et al., 1982; Helsel, 1985; Downs and Appel, 1986; Anderson and Potts, 1987; Koebel et al., 1999; Wellman et al., 2000; Colangelo and Jones, 2005; Hedrick et al., 2007; Sugden and Woods, 2007). Another concern due to highway construction is nutrients (nitrogen and phosphorus) from runoff (Barrett et al., 1998; Wu et al., 1998; Kim et al., 2006). Highway construction and highway runoff can also cause heavy metal pollution (e.g., zinc, lead, nickel, and cadmium) and polycyclic aromatic hydrocarbons (PAHs) in water and sediments (Van Hassel et al., 1980; Hoffman et al., 1985; Boxall and Maltby, 1995; Maltby et al., 1995; Boxall and Maltby, 1997; Krein and Schorer, 2000). Finally, road salt applications resulted in high concentrations of chloride and other ions in water and sediments (Amrhein et al., 1992; Williams et al., 1999; Koryak et al., 2001; Interlandi and Crockett, 2003).

1.2.3 Best management practices (BMPs)

To minimize the environmental impacts from human activities, various best management practices (BMPs) have been developed and implemented for watershed management. Vegetated buffers (e.g., vegetative filter strips, riparian buffers, and grassed waterways), fertilizer or manure management, rotational grazing or crop rotation, and constructed wetlands were often used for controlling agricultural pollutants (e.g.,

Lowrance et al., 1984; Djodjic et al., 2002; Davis et al., 2003; Sharpley et al., 2004; Bishop et al., 2005; Braskerud et al., 2005; Muenz et al., 2006; Liu et al., 2008). For highway and urban pollution, vegetated buffers and mulches, porous pavement materials, retention or detention basins and ponds, silt fence, seeding, and natural riparian wetlands have been implemented as BMPs to treat runoff and control soil erosion (Burton et al., 1976; Barton, 1977; Taylor and Roff, 1986; Pagotto et al., 2000; Benik et al., 2003; Gillilan, 2003; Van Bohemen and Janssen Van De Laak, 2003; Han et al., 2005; Li et al., 2006; Hogan and Walbridge, 2007; Houser and Pruess, 2009). However, effectiveness of some of those implemented BMPs on water quality protection is still unclear (Easton, et al., 2008).

1.3 Ecological Responses to Acidic Deposition

1.3.1 Acidic deposition: definition, causes and patterns

1.3.1.1 Definition

Acidic deposition refers to deposition from the atmosphere to a surface of the hydrosphere, lithosphere, or biosphere (i.e., any portion of a watershed) of one or more acid-forming precursors which may include oxidized forms of sulfur (S) and oxidized or reduced forms of nitrogen (N) (Sullivan, 2000). It is a dilute solution of sulfuric acid and nitric acids derived from all the forms (gases, particles, rain, snow, clouds, and fog) of compounds of sulfur dioxide (SO₂), nitrogen oxides (NO_x) ammonia (NH₃), by-products of the combustion of fossil fuels and agricultural activities (Driscoll et al., 2001a; Driscoll et al., 2001b; USEPA, 2003).

1.3.1.2 Causes

Human activities have fundamentally changed the natural cycling of S, N, and C across large areas of the earth since the last century. Soil and surface waters can be acidified by both S and N (Sullivan, 2000). Electric utilities, transportation sources, and livestock waste and fertilized soil contribute the greatest proportions of sulfur dioxide, nitrogen oxide and ammonia, respectively (Driscoll et al., 2001b).

1.3.1.3 Patterns

Atmospheric deposition includes wet deposition, or the deposition as dissolved SO₄²⁻, NO₃⁻, and NH₄⁺ in rain or snow and the dry form, when gaseous or particulate forms of S or N are removed from the atmosphere by contacting watershed features, especially vegetative surfaces (Sullivan, 2000). In some environments, particularly at high

elevations, a substantial component of the total deposition of S and N occurs as cloudwater is intercepted by exposed watershed surfaces (Sullivan, 2000).

1.3. 2 Atmospheric emissions, environmental concerns, and deposition monitoring

1.3.2.1 Emissions and related environmental issues

Smith and Alexander (1986) found a strong correlation between the atmospheric sulfur dioxide emissions and stream sulfate concentrations in eastern United States from 1967 to 1980. It is also found that streams in northeastern United States received larger fraction of regional sulfur emissions than those in the southeastern United States. Driscoll et al. (2001a) associated the environmental problems of coastal eutrophication, mercury accumulation, decreased visibility, climate change and tropospheric ozone with the emissions of sulfur dioxide and nitrogen oxides.

1.3.2.2 Emissions control and related environmental issues

In 1990, Congress passed the Federal Acid Deposition Control Program as Title IV of the Clean Air Act Amendments (CAAAAs). The objective of Title IV was to reduce the adverse effects of acidic deposition by reducing the emissions of sulfur dioxide in particular and to a lesser extent nitrogen oxides. The Acid Rain Program (ARP), established under Title IV, requires major reductions of SO₂ and NO_x emissions from the electric power industry. Title IV was implemented with Phase I beginning in January 1, 1995, and Phase II beginning in January 1, 2000. The goal is a 10 million ton reduction in SO₂, and 2 million ton reduction in NO_x, by 2010, compared to the baseline year of 1980 (USEPA, 2003).

In 2006, total SO₂ emissions were reduced by more than 6.3 million tons from its 1990 levels and NO_x emissions were 3.3 million tons below its 1990 levels (USEPA, 2007). From 1990 to 2006, the six states with the greatest annual reductions in emissions of SO₂ were Ohio, Illinois, Indiana, Missouri, Tennessee and West Virginia. Each of these states reduced emissions by more than 500, 000 tons per year (USEPA, 2007). Nine of the 13 states with a NO_x emission reduction of more than 100,000 tons were in the Ohio River Basin (USEPA, 2007).

The 1970 and 1990 CAAAs led to a 38 percent decrease in sulfur dioxide emissions nationwide, in turn causing them to drop from 32 million tons annually in 1973 to approximately 20 million tons in 1998 (Driscoll et al., 2001b). But nitrogen emissions have not changed substantially region-wide and have increased in some areas of the eastern United States (Driscoll et al., 2001b). With the passage of the 1970 CAAA and the 1990 Title IV of the Acid Deposition Control Program of the CAAA, many research opportunities became available for investigating the effects of the three decades of clean air legislation on emissions reductions; studying the trends, air pollution levels, and chemical effects of acidic deposition; and studying the recovery of ecosystem from the reduced acidic deposition (Driscoll et al., 2001a).

1.3.2.3 Deposition monitoring

The National Atmospheric Deposition Program/National Trends Network (NADP/NTN) operates more than 200 monitoring sites in US. The NADP/NTN program only monitors wet deposition. For dry deposition, about 70 sites were monitored by EPA Clean Air Status and Trends Network (CASTNet, 2007) and 13 sites were monitored by the National Oceanic and Atmospheric Administration AIRMoN (NOAA, 2007). The U.

S. Environmental Protection Agency (EPA) published annual reports to update the public on compliance with the Acid Rain Program (ARP), its status of implementation, and progress toward achieving environmental goals.

Acid deposition has declined significantly from levels measured before ARP, with corresponding improvements of water quality in lakes and streams (USEPA, 2007).

Nilles and Conley (2001) analyzed the chemistry of precipitation from NADP/NTN sites in US from 1981 to 1998 and found sulfate declined at 100 of 147 sites but no consistent trends in nitrate concentrations. It is also found that calcium at 64 sites exhibited significant increasing trends and no site exhibited a decreasing trend. In acid sensitive regions of northern and eastern US, sulfate deposition declined significantly at a rate ranging from -0.75 to -1.5 $\mu\text{eq L}^{-1}\text{year}^{-1}$ during 1990-2000 (USEPA, 2003).

Wet deposition of sulfate decreased 35 percent in the Northeast, 33 percent in the Midwest and 28 percent in the Mid-Atlantic during the observation periods between 1989-1991 and 2004-2006 (USEPA, 2007). Wet deposition of inorganic nitrogen decreased 25 percent in the Northeast, 16 percent in the Mid-Atlantic and 9 percent in the Midwest during the same periods (USEPA, 2007).

1.3.3 Sensitive ecosystems and variables of concern

1.3.3.1 Sensitive ecosystems

The sensitivity of surface waters to acidification in a region depends on regional deposition characteristics, surface water chemistry, and watershed factors (Sullivan, 2000). Soil and bedrock composition, and watershed hydrology are important factors to be considered in defining acid-sensitive regions (Sullivan, 2000). Large populations of

low-ANC (Acid neutralizing capacity) lakes and streams in US include portions of the Northeast (particularly Maine and the Adirondack Mountains), the Mid-Appalachian Mountains, northern Florida, the Upper Midwest, and the western US (Sullivan, 2000).

The regions most impacted by acidic deposition are downwind of the documented sources of industrial sulfur emissions in the Midwestern states and are located in geological-sensitive areas in the Northeast, Mid-Atlantic and Upper Midwest regions (USEPA, 2003). The central Appalachian Mountain region, defined as the mountainous areas of Virginia and West Virginia, is exposed to among the highest acidic deposition levels in the United States (Webb, 2004).

1.3.3.2 Concerned ecosystem variables

Sulfate and nitrate are the most important acid anions found in acid deposition (Sullivan, 2000). ANC is the principal variable used to quantify the acid-base status of surface waters. Acidic waters are defined as those with ANC less than or equal to zero. pH is one of the major controlling variables for chemical and biological response. The ANC of surface waters lacking high-DOC (dissolved organic carbon) concentrations is determined primarily by differences between the concentration of base cations and mineral acid anions (Sullivan, 2000). Aluminum (Al) is an important parameter for evaluation of acidic deposition effects in drainage systems because of its influence on ANC, and also because of its toxicity to aquatic biota (Sullivan, 2000). The most important chemical parameters that cause or contribute to the adverse effects of acidification on aquatic biota are decreased pH (increased H^+), increased inorganic Al, and decreased Ca^{2+} concentrations (Sullivan, 2000).

1.3.4 Effects of acidification

1.3.4.1 Effects on soils

Acidification trends of soil and surface water in eastern North American and Europe was attributed to the superposition of acid deposition from atmosphere upon natural acidifying processes in soils (Reuss, et al., 1987). Driscoll et al. (2001b) listed the effects of acid deposition on soils in the Northeast US: leaching of base cations from soils, accumulation of sulfur and nitrogen in soils, and increasing dissolved inorganic aluminum concentrations in soil waters. It has long been recognized that elevated leaching of base cations by acidic deposition might deplete the soil of exchangeable bases faster than they are resupplied via weathering (Cowling and Dochinger, 1980). In the White Mountains and Adirondack region of northeastern US, acid precipitation resulted in soil leaching of Al and elevated concentrations of dissolved Al in surface and ground waters (Cronan and Schofield, 1979). Fernandez et al. (2003) studied the soil samples with nine years' acidification treatment with $(\text{NH}_4)_2\text{SO}_4$ in West Bear watershed in Maine and found acid deposition resulted in depletion of exchangeable base cations in soils. Bailey et al. (2005) studied soil samples from four sites of the Allegheny Plateau, Pennsylvania in 1967 and 1997 and found acid deposition resulted in significant decreases of exchangeable calcium, magnesium and pH, and increases of exchangeable aluminum concentrations. Sullivan et al. (2006) analyzed the acid-base characteristics of soils in the Adirondack Mountains in summer of 2003 and found low exchangeable base cations, low base saturation and low soil pH in the study soils. It was suggested that these chemical conditions in soils will restrict the magnitude of surface water recovery from acidification.

1.3.4.2 Effects on trees

Acid deposition has contributed to the decline of red spruce trees throughout the eastern US and sugar maple trees in central and western Pennsylvania (Driscoll et al., 2001b). The symptoms of tree decline include poor crown condition, reduced tree growth, and high levels of tree mortality (Driscoll et al., 2001b).

1.3.4.3 Effects on surface waters

Compared with lakes, streams and rivers were affected more by episodic acidification because these ecosystems experience large abrupt changes in water chemistry and provide limited refuge areas for fish (Driscoll et al., 2001a). Acid deposition impaired the water quality of lakes and streams by lowering pH levels, reducing ANC, and increasing Al concentrations (Driscoll et al., 2001b). In the southern Shenandoah National Park (SNP), Deep Run and White Oak Run were investigated by Ryan et al (1989) from 1980 to 1987. It was found that acidity increased and the increasing slope of sulfate was $2 \mu\text{eq L}^{-1} \text{yr}^{-1}$ in stream water during the study period. It was also estimated that both studied watersheds retained about 65% of deposited sulfate. Webb et al. (1989) investigated 344 streams of two physiographic provinces in Virginia in spring 1987. It was found that 93% of the studied streams were sensitive (defined as alkalinity $\leq 200 \mu\text{eq L}^{-1}$) and the catchments retained 68% (median) of deposited sulfur from atmosphere. Fitzhugh et al. (2001) investigated the sources of stream sulfate in Yellow Creek watershed, which is located within the Otter Creek drainage basin in northeastern West Virginia, and found atmospheric sulfur deposition was the dominant source of stream sulfate, and thus stream acidity in that watershed. Sulfate is the dominant acid anion associated with acidic streams in the central Appalachian Mountain region (Webb, 2004). In the Como Creek

watershed of northcentral Colorado, Lewis and Grant (1979) found the acidification of precipitation increased the output of sulfate, nitrate, ammonia and dissolved organic matter, and decreased the output of bicarbonate and total cations from the watershed.

1.3.4.4 Effects on aquatic biota

In acidified Adirondack waters, inorganic Al was the major chemical form of concern with regard to Al toxicity to fish and that total Al concentrations overestimated the potential Al-induced toxicity (Driscoll et al., 1980). Fish production would be successful in lakes and streams with low pH and high total Al concentrations but high organic carbon concentrations. 41 percent of lakes in the Adirondack Mountain region of New York and 15 percent of lakes in New England exhibited signs of chronic and/or episodic acidification (Driscoll et al., 2001b). Bulger et al. (1998) reported that 6 percent of the 304 Virginia trout streams were chronically acidic and unable to support brook trout or other fish species. Webb (2004) found stream water ANC was correlated with fish diversity in Shenandoah National Park, and that increased sulfur deposition resulted in most streams in Otter Creek and Dolly Sods Wildernesses too acidic to support fish.

Schindler et al. (1985) studied an experimentally acidified lake (pH was regulated from 6.8 to 5.0 in 8 years' acidification) in northwestern Ontario and found that lake acidification changed phytoplankton species, stopped fish reproduction, prevented the appearance of benthic crustacean and induced the appearance of filamentous algae. Forty six lakes were studied by Locke and Sprules (1994) in the La Cloche Mountains of Ontario. Stability of zooplankton food webs were found to be affected by lake acidification. Vrba et al (2003) studied the acidification and recovery of eight Bohemian

Forest lakes in central Europe and found atmospheric acidification reduced biodiversity in all the lakes.

1.3.5 Extent and magnitude of surface water recovery from reduced acid deposition

Reducing emissions of sulfur and nitrogen oxides would be beneficial to aquatic and probably terrestrial ecosystems (Schindler, 1988). Ecosystem recovery is a phased process that involves the reversal of degraded chemical and biological conditions (Driscoll et al., 2001b). Stoddard et al. (1999) analyzed the chemical recovery from acidification in North America and Europe for the periods of 1980s and 1990s. It was found that 7 of the 8 studied regions showed decreased concentrations of sulfate in lakes and streams, but not nitrate. It was also found most regions showed a stronger downward trend of sulfate in the 1990s than in the 1980s. Skjelkvåle et al. (2001) investigated 95 water sites from the International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP Waters) from 1989 to 1998 and found all of the regions had highly significant decreasing trend of sulfate concentrations but no regional trend of nitrate. The relatively small recovery of pH and ANC at the North American International Cooperative Programme (ICP) sites was attributed to sharply declining base cation concentrations (Skjelkvåle et al., 2001).

1.3.5.1 Northeastern US

Mattson et al. (1997) analyzed surface water of 330 streams in Massachusetts from 1983 to 1993 and found the streams were recovering from acidification with +0.021 pH units/year for pH and +2.4 $\mu\text{eq L}^{-1} \text{ year}^{-1}$ for ANC. Driscoll et al. (2003) investigated surface water of 52 lakes in the Adirondack region of New York from 1983 to 1999 and

found all lakes showed marked decreases in concentrations of sulfate which coincide with declines in atmospheric sulfur deposition. In the Adirondack lakes, stoichiometric correspondence was found between declines in sulfate and nitrate and decreases in base cations (Driscoll et al., 2003). It is also found some lakes in that region still exhibited low pH values and high inorganic monomeric Al concentrations that are critical to aquatic biota. Four of five acid sensitive regions (except the Ridge/Blue Ridge province in the mid-Atlantic) showed significant declines of sulfate concentrations in surface waters, with rates ranging from -1.5 to $-3 \mu\text{eqL}^{-1}\text{year}^{-1}$ (USEPA, 2003). ANC increased in the Adirondacks, Northern Appalachian Plateau and Upper Midwest at a rate of $+1 \mu\text{eqL}^{-1}\text{year}^{-1}$ even though there was a decline in base cations in each region (USEPA, 2003). It was suggested that decline in base cations offset some of the decline in sulfate, and thus limited the increase of ANC or pH. In the Adirondacks, Upper Midwest and Northern Appalachian Plateau, about one-quarter to one-third of formerly acidic surface waters were no longer acidic, even though still with very low ANC (USEPA, 2003). In the Adirondack Long-term Monitoring Program (ALTM) lakes, Al shifted in chemical speciation from toxic inorganic form toward less toxic organic forms with declines in atmospheric deposition and increases in dissolved organic carbon (DOC) concentrations (Driscoll et al., 2003).

Stoddard et al. (1998a) conducted a regional analysis of acid deposition and lake responses in northeastern US from 1982 to 1994. It was found that sulfate deposition decreased significantly while there was no change in nitrate and ammonia deposition occurred. It was also found that all lakes exhibited strong declines in sulfate concentrations. Warby et al. (2005) analyzed 130 lakes in five subregions (Adirondacks,

Catskills and Poconos, Central New England, Southern New England and Maine) of the northeastern US between 1984 and 2001 and found significant decreases of sulfate, calcium and total Al in all subregions. It was also found that only the lakes in Adirondacks exhibited significant increases of nitrate. The lack of recovery in alkalinity in the Adirondack/Catskill Mountains was attributed to stronger decreases in base cation concentrations than the declines in sulfate concentrations (Stoddard et al., 1999). It was found that ANC increased in the New England but no increase in the Adirondack and Catskill subregion was observed (Driscoll et al., 2001a). The reason for the difference was attributed to a higher decrease in the sum of base cations in the Adirondack and Catskill subregions than in the New England subregion. Driscoll et al. (1998) analyzed 1469 lakes in the Adirondack region of New York and found a uniform declining rate of sulfate in lakes across the region in response to decreased sulfate precipitation. However, no systematic increase of pH or ANC was found in the region. The mechanisms were the depletion of basic cations in soil, inputs of sulfate to watersheds from weathering of sulfur minerals, increased leaching of nitrate and pH buffering related to increased concentrations of aluminum and/or naturally organic acids. ANC recovery was found in the New England lakes but not in the Adirondack lakes. The different responses of base cations between the New England lakes and the Adirondack lakes were attributed to three mechanisms: soil cation depletion, reduced base cation deposition, and decreases in nitrate concentrations (Stoddard et al., 1998a). In northeastern US, no recovery of the Adirondack and Catskill surface waters was found when compared with the surface waters in New England (Driscoll et al., 2001a). The difference was attributable to the lower acidic deposition loading in most of New England compared to New York.

Stoddard et al. (1998b) found ANC recovery was evident in lakes of the New England region, but not in the Adirondack lakes. It was also found that the magnitudes of downward trends of base cations were always smaller in the New England lakes than in similar Adirondack lakes. Likens et al. (1996) studied the long-term (1940 - 1990) effects of acid rain on the Hubbard Brook Experimental Forest and found that a large depletion of base cations from the soil retarded the recovery of the forest ecosystem in response to declining emissions of sulfur dioxide. Driscoll et al. (2003) estimated that the recovery time of chronically acidic ($\text{ANC} < 0 \mu\text{eq L}^{-1}$) lakes to reach an ANC of $50 \mu\text{eq L}^{-1}$ was about 25 to 100 years.

1.3.5.2 Appalachian Mountains

In 1998, Kentucky, Ohio, Pennsylvania and West Virginia were 4 of the 10 states with the highest sulfur dioxide emissions in the United States (Driscoll et al., 2001a). Many high elevation streams, particularly in the mid-Appalachian portion of the Appalachian Mountain region, have chronically low-ANC values and the region receives one of the highest rates of acidic deposition in the U.S. (Herlihy et al., 1993). Despite the reductions in acid-causing air pollution required by the 1990 Amendments to the Clean Air Act, many of Virginia's brook trout streams are part of acid-sensitive ecosystems in Appalachian forests and continue to be stressed by acid deposition (Bulger et al., 1998).

Acidic and low ANC streams are more prevalent in the northern part of the region in Virginia and West Virginia, than in the south. This gradient is owed, at least in part, to the highest rates of S and N deposition and the lower S adsorption of soils in the northern part of the region. Throughout the region, acidic and low-ANC stream water is confined to small (less than 20 km^2) upland, forested watersheds in areas of base-poor, weathering-

resistant bedrock (Herlihy et al., 1993). In the central Appalachian Mountains, it was found that many streams were continuing to be acidified, and the degree of observed recovery was small in relation both to the magnitude of historic acidification and to surface water recovery observed in northeastern regions of the United States (Webb, 2004). Webb et al. (2004) suggested that the central Appalachian region, including western Virginia, was a transition zone with respect to recovery from acidification.

Only 5% of the southern Blue Ridge lakes had an ANC value less than 50 $\mu\text{g/L}$ and none was acidic. In the Valley and Ridge Province, low ANC streams are generally absent from the valleys which frequently contain limestone bedrock. Ridge streams are often acid sensitive, and about one-fourth are low in ANC (less than or equal to 50 $\mu\text{g/L}$) in their upper reaches (Linthurst et al., 1986; Kaufmann et al., 1988). Webb et al. (1989) found the streams in the Valley and Ridge province had lower alkalinity and lower sulfate than that in the Blue Ridge province. It was also found that streams with crystalline bedrock types had higher alkalinity than that with silicoclastic bedrock types. Webb et al. (2004) investigated 65 streams in western Virginia and 14 streams in Shenandoah National Park (SNP) from 1988 to 2001 and found significant regional decreases of sulfate and increases of ANC in SNP but not in western Virginia. The different response of stream base-acid constituents to acid deposition was attributed to the difference of soil sulfur retention in the two regions. There was no significant trend of nitrate and sum of base cations in both of the two regions during the study period.

In the central Appalachian Mountains, the most-acidic and most-sensitive streams were associated with forested mountain watersheds (Webb, 2004). It was indicated that the variations of stream response to acidic deposition in this region was mainly attributed

to differences in the properties of watershed soil and bedrock (Webb, 2004). Little correspondence was found between rates of sulfate decline in streams and deposition in the Ridge and Blue Ridge provinces. This was attributed to the adsorptive capacity of the soils in that region (USEPA, 2003). Kline et al. (2007) analyzed streams in western Maryland before and after the 1990 Clean Air Act Amendments (CAAAAs) and found little trend in the magnitude of episodic acidification over that period. The mechanisms of episodic acidification were attributed to sulfate accumulation in the watershed before the CAAAs and base cation dilution after the CAAAs. Fitzhugh et al. (1999) studied stream acidity in Yellow Creek watershed from June 1994 to March 1995 and found sulfate concentrations controlled variations of stream acidity in that watershed. It is also found that the transport rate of sulfate from soils to stream water was faster than the rate of base cation release, which resulted in chronic stream acidification.

1.3.5.3 Florida

Florida lakes are located in marine sands overlying carbonate bedrock and the Floridan aquifer, an extensive series of limestone and dolomite that underlies virtually all of Florida (Sullivan, 2000).

1.3.5.4 Upper Midwest

Characterized by numerous lakes created by repeated glaciations, the Upper Midwest region shows little topographic relief and the deep glacial overburden results in little or no exposed bedrock. Lakes in the Upper Midwest exhibit considerable spatial gradients in pH, ANC, base cations, and DOC, all of which decrease from west to east. Most of the acidic and low-ANC lakes in the upper Midwest are seepage type (Sullivan, 2000). In

Little Rock Lake of Wisconsin, the complete recovery of zooplankton community was observed 10 years after cessation of lake experimental acidification (Frost, et al., 2006).

1.3.5.5 West

In the far West, the areas that are sensitive to adverse effects of acidic deposition form two nearly continuous ranges, the Sierra Nevada in California and the Cascades starting in California and extending through Washington. The Rocky Mountains, in contrast, are discontinuous ranges with highly variable geological composition (Sullivan, 2000).

1.3.5.6 Outside US

In Whitepine Lake of Canada, it was found that reduced sulfur emissions resulted in recovery of lake trout (Gunn and Keller, 1990). Jeffries et al. (2003) assessed the effects of reduced acidic deposition on lake recovery in the Atlantic provinces, Quebec and Ontario of Canada and found sulfate concentrations decreased but little increase of pH and alkalinity in those lakes. The delayed acidity response was attributed to reduced base cation concentration, drought-induced mobilization of sulfate, damaged internal alkalinity generation mechanisms, and increased nitrate or organic anion levels. Soulsby et al. (1995) investigated ten streams of the River Dee in northeast Scotland from 1983 to 1994 and found that reduced acid deposition resulted in decrease of sulfate concentrations and increase of ANC in streams. Majer et al. (2005) conducted two synoptic stream surveys (1991 and 2001) in the Slavkov Forest and found marked declines of stream sulfate ($-30 \mu\text{eq L}^{-1}\text{yr}^{-1}$), nitrate ($6 \mu\text{eq L}^{-1}\text{yr}^{-1}$), chloride, calcium and magnesium, but no widespread increase of pH was found. Mörtz et al. (2005) studied soil chemistry in the Lake Gårdsjön area and found the mineralization of organic sulfur in soils retarded the

catchment recovery from reduced anthropogenic acidification. Evans et al. (2001) investigated the surface water trends of the 1980s and 1990s in 56 sites from eight European countries and found most sites showed decreased sulfate ($-1.92 \mu\text{eq L}^{-1}\text{yr}^{-1}$) and soluble Al ($-0.6 \mu\text{g L}^{-1}\text{yr}^{-1}$) and increased ANC ($+1.29 \mu\text{eq L}^{-1}\text{yr}^{-1}$), but ANC was partly offset by decreased base cations ($-0.90 \mu\text{eq L}^{-1}\text{yr}^{-1}$ of Calcium) and no significant trend of nitrate was observed. Abundance of acid-sensitive mayflies increased with the reduced acidic deposition in some streams except the most chronically acidified systems in northeast Scotland (Soulsby et al., 1995).

Although the chemical trends in surface waters are often attributed to reduced acidic deposition, researchers should be cautious in interpreting the observed surface water chemistry as a direct response to estimated changes in S and/or N deposition (Sullivan, 2000). Some effects of changing deposition can exhibit significant lag periods before the ecosystem comes into equilibrium with the changed or cumulative amount of S and N inputs. For instance, watershed soils may continue to release S at a higher rate for an extended period of time subsequent to a reduction in atmospheric S loading. Thus, concentrations of sulfate in surface waters may continue to decrease in the future as a consequence of deposition changes that have already occurred (Sullivan, 2000). Moreover, if soil base cation reserves become sufficiently depleted by long-term S deposition inputs, base cation concentrations in some surface waters could continue to decrease irrespective of any further changes in sulfate concentrations. This would cause additional acidification (Sullivan, 2000).

1.3.6 Prediction models

To describe regional scale of acid deposition, three categories of models were broadly used: statistical, Lagrangian, and Eulerian (Schwartz, 1989). The most current prediction models are MAGIC and PnET-BGC.

1.3.6.1 MAGIC

MAGIC is a lumped-parameter model to predict the long-term effects of acid deposition on chemistry of soils and surface water. Wright et al. (1990) applied the MAGIC model to manipulated catchments in Norway and found that MAGIC was successful predicting future acidification. Larssen et al. (2003) used the MAGIC model to predict recovery of lakes in Killarney Park of Ontario due to reduced acid deposition. It was predicted that there was still large potential for lake water quality improvement in Killarney.

1.3.6.2 PnET-BGC

PnET-BGC is an integrated biogeochemical model. Chen and Driscoll (2005) applied the PnET-BGC model to 37 forest lake watersheds in the Adirondack region of New York and testified that the model was able to capture the observed changes in water chemistry in the period of 1984 and 2001. Gbondo-Tugbawa and Driscoll (2002) used the PnET-BGC to model the effects of atmospheric emission controls from the 1970 and 1990 Amendments of the Clean Air Act on soil and stream chemistry of a northern forest ecosystem. It was predicted that soil base saturation would have increased, soil sulfur would have continued to accumulate, and stream concentrations of sulfate, nitrate and calcium would have been higher, and stream ANC would have been $\leq -15 \mu\text{eq L}^{-1}$ without the CAAAs.

1.3.6.3 Other models

Deviney et al. (2006) used time series and recurrence interval models to predict the acid vulnerability of streams to episodic acidification in Shenandoah National Park, Virginia, and found that the most vulnerable catchments were small catchments and underlain by less carbonate bedrock. Logistic regression models were used by Sullivan et al. (2007) to investigate the relationships between stream acid sensitivity and watershed features in the southern Appalachian Mountains. It was found streams with siliceous geology (sandstone and quartzite) were mostly acid-sensitive and had values of $ANC \leq 20 \mu\text{eq L}^{-1}$. It was concluded that streams in an area with 100% siliceous geology had 17 times greater odds of being acid-sensitive than those without siliceous bedrock. It was also concluded that an increase in elevation of 154 m and a decrease in watershed size of 50 km^2 will increase the odds of being acid-sensitive by a factor of 3.2 and 3.4, respectively (Sullivan et al., 2007).

1.4 Cause-effect Search: A General Introduction to Structural Equation Modeling (SEM) and Latent Growth Curve Modeling (LGM)

1.4.1 Definition, history, and statistical basis

Structural equation modeling (SEM) is an advanced multivariate statistical approach with which a researcher can construct theoretical concepts; test multivariate relationships within and between observed (measured) and latent (unobserved or conceptual) variables; and confirm proposed causal relationships based on two or more structural equations (Bollen, 1989; Mitchell, 1994; Hoyle, 1995; Malaeb et al., 2000; Reckhow et al., 2005; Grace, 2006). Structural equation modeling can be traced back to the research of the biologist Sewall Wright (1921, 1934). Later development of SEM has been conducted by Karl Jöreskog and Dag Sörbom (Jöreskog, 1981; Jöreskog and Sörbom, 1982).

SEM depends on a correlation or covariance matrix to find the causal relationships between or among variables. However, correlation is not simply equal to causation (Wright, 1921; Blalock, 1961). For a given correlation between two variables (e.g., X and Y), Shipley (1999) presented three general causal explanations for this statistical associations: (1) X might cause Y, possibly indirectly through some intervening variables; (2) Y might cause X, possibly indirectly through some intervening variables; and (3) none of them are causes of the other and the statistical association results from some common causes of both X and Y. To reasonably infer that X caused Y, Kline (2005) recommended three necessary conditions: (1) X precedes Y in time; (2) the direction of the causal relation is correctly specified; and (3) the association between X and Y does not disappear when external variables such as common causes of both are held constant. SEM is an “a priori” statistical approach, where researchers hypothesize and test a

structure or mechanism that reflects existing knowledge, previous experience, or sound theory (Iriondo et al., 2003; Reckhow et al., 2005; Grace, 2006; Arhonditsis et al., 2006). The hypothesized covariance structure is tested against the observed covariance matrix from actual data.

SEM was developed from path analysis, factor analysis, and regression analysis (Malaeb et al., 2000; Kline, 2005). As in path analysis, the specification of an SEM allows tests of hypotheses about patterns of causal effects (Kline, 2005). Unlike path models, causal effects can involve latent variables because a SEM incorporates a measurement model that represents observed variables as indicators of underlying factors, just as in confirmatory factor analysis (Kline, 2005). Compared with other methods such as multiple regression, traditional path analysis or PCA, SEM provides more support for the question of causation because of its capabilities of modeling measurement error and eliminating estimated bias and distortion (Pugesek and Tomer, 1995; Iriondo et al., 2003). The null hypothesis (H_0) formulation of a SEM is:

$$H_0: \Sigma = \Sigma(\theta),$$

where Σ is the observed variables-based population or sample covariance matrix; $\Sigma(\theta)$ is a specified model-implied covariance matrix; and θ is a vector that contains the free parameters of the model (Bollen, 1989; Bollen and Long, 1993). Governing equations of SEM were provided by Jöreskog and Sörbom (1997; Appendix 1). SEMs minimize the differences between the observed covariances and the model predicted covariances (Malaeb et al., 2000). In contrast to testing hypotheses in linear models (e.g., ANOVA) where one tends to reject the null hypothesis in favor of the alternative hypothesis, SEM

seeks the acceptance of the null hypothesis which indicated that specified model fits the data (Bollen, 1989; Bollen and Long, 1993; Malaeb et al., 2000).

1.4.2 Model development and evaluation of model fit

There are five common steps that characterize the model development of most applications of SEMs: (1) model specification, (2) model identification, (3) parameter estimation, (4) testing model fit, and (5) respecification and modification of the model (Bollen and Long, 1993; Malaeb et al., 2000). At first, based on theory or the modeler's previous experiences in the research area, the modeler needs to specify an initial model which includes formulating latent variables, hypothesizing relations between and within these latent variables and observed variables, choosing their indicators, and possibly setting part of the factor loadings. Model identification is the determination of whether unique estimates of the model parameters can be obtained. For model identification, there are two basic requirements: (1) there must be at least as many observations as free model parameters; and (2) every latent variable must be assigned a scale (Kline, 2005). For a common SEM, Kline (2005) presented the identification as: the number of observations, which equals $v(v+1)/2$, where v is the number of observed variables, must equal or exceed the number of free parameters. Parameters are counted as follows: the total number of (1) variances and covariances of exogenous variables (measurement errors, disturbances, and exogenous factors), and (2) direct effects on endogenous variables (factor loadings of indicators, direct effects on endogenous factors from other factors) equals the number of parameters (Kline, 2005). For a mean structure model (e.g., latent

growth curve model), the number of observations equals $v(v + 3)/2$, where v is the number of observed variables (Kline, 2005).

Parameter estimation is the estimation of the model parameters using one of several estimation methods such as Maximum Likelihood, Generalized Least Squares, and Two-stage Least Squares. After the parameter estimation, the modeler can test whether the model fits the data. Many indices have been reported in the literature and choosing which indices to report usually depends on preference of the researchers. In the environment of LISREL (Linear Structural Relationships) software, values of the following indices are usually given along with the model results: chi-square (χ^2), root mean square error of approximation (RMSEA), 90 percent confidence interval for RMSEA (CI₉₀), expected cross-validation index (ECVI), 90 percent confidence interval for ECVI, independence AIC (Akaike's information criterion), model AIC, saturated AIC, independence CAIC (Consistent AIC), model CAIC, saturated CAIC, normed fit index (NFI), non-normed fit index (NNFI), parsimony normed fit index (PNFI), comparative fit index (CFI), incremental fit index (IFI), relative fit index (RFI), critical N (CN), root mean square residual (RMR), standardized RMR, goodness of fit index (GFI), adjusted goodness of fit index (AGFI), and parsimony goodness of fit index (PGFI). The chi-square (χ^2) test is usually used to test the overall fit of the model. Models are acceptable if the χ^2 values have an associated p -value greater than 0.05. Values of the RMSEA and its accompanying 90 percent confidence interval falling below about 0.05 to 0.08 indicate good model fit (Browne and Cudeck, 1993; Curran and Hussong, 2002). However, for data departing from multivariate normality and having small sample sizes, both chi-square test and other goodness of fit indices should be explained (Bollen, 1989; Bollen

and Long, 1993). A fit index value (e.g., NFI, CFI, and GFI) larger than 0.9 indicates an acceptable fit of the model (Bollen, 1989). If the model does not fit the data well, the specified model may need to be respecified or modified to improve the model fit (Bollen and Long, 1993; Malaeb et al., 2000; Hershberger et al., 2003; Grace, 2006).

1.4.3 SEM Applications

Since its initial application in the early 1920s and 1930s in the natural sciences (Wright, 1921; 1934), SEM has been intensively developed in the social sciences, especially in sociology, education, and psychology (Tanaka, 1987; Bollen, 1989; Bollen and Long, 1993; Jöreskog and Sörbom, 1993; Hoyle, 1995; Bentler, 1995; Mueller, 1996; Kaplan, 2000; Kline, 2005; Hancock and Mueller, 2006).

After the 1990s, especially the late 1990s, however, there is an increasing trend of applications of SEM in natural sciences (Mitchell, 1992; 1994; Petraitis et al., 1996; Smith et al., 1997; Pugesek and Grace, 1998; Palomares et al., 1998; Grace and Pugesek, 1998; Shipley, 1999; Pugesek et al., 2003; Iriondo et al., 2003; Vile et al., 2006; Grace, 2006; Laughlin et al., 2007; Harrison and Grace, 2007; Grace and Bollen, 2008). This increasing application trend of SEM is also found in aquatic sciences in the past decade (Grace and Pugesek, 1997; Malaeb et al., 2000; Stow and Borsuk, 2003; Reckhow et al., 2005; Arhonditsis et al., 2006; Arhonditis et al., 2007).

1.4.4 Relations between SEM and LGM, and applications of LGM

Most applications of SEM rely on cross-sectional data or data points collected at the same time. However, ecological problems are usually long-term in nature and have a

temporal pattern. Ecologists are interested in long-term trend, or the dynamic pattern of ecological parameters. Many statistical methods, including repeated measures *t*-tests, analysis of variance (ANOVA), analysis of covariance (ANCOVA), multivariate analysis of variance (MANOVA), multiple regression, path analysis, multilevel/hierarchical linear model, latent growth curve model (LGM, LGC, or LCA), autoregressive crosslagged model (ARCL), survival/event history analysis, latent transition model and time-series analysis, have been implemented in studies that examined long-term behaviors by various researchers (Hser et al., 2001; Curran and Hussong, 2002; Duncan et al., 2006). The SEM-based LGM has the capacity to explicitly model measurement error (Kline, 2005). But ANOVA assumes that error variances of repeated measures variables are equal and independent. Data from repeated measures variables often violate both of these requirements (Kline, 2005). Multiple regressions can accommodate continuous or categorical predictors, but it has the same restrictive assumptions about error variance (Kline, 2005). For MANOVA (multivariate ANOVA), it shares with ANOVA a crucial limitation: both techniques analyze changes only in observed group means and consequently treat differences among individual cases in their growth trajectories as error variance (Kline, 2005).

The LGM is an extension of structural equation modeling (Kaplan, 2000; Curran and Husson, 2002; Duncan et al., 2006). LGM models initial conditions and changing rates of a variable of interest, and searches predictors for the variable. Similar to traditional SEMs, LGMs can also be applied with multiple populations or groups, categorical variables, and missing data (Duncan et al., 2006). The LGM work can be traced back to the work of Rao (1958) and Tucker (1958), later formally defined and developed by McArdle and Epstein

(1987) and Meredith and Tisak (1990). The methodology was further implemented and developed by Willett and Sayer (1994), Duncan and colleagues (e.g., Duncan and Duncan, 1994; Duncan et al., 1994; Duncan and Duncan, 1996; Duncan et al., 1997; Li et al., 2000; Duncan et al., 2006), Curran and colleagues (e.g., Curran et al., 1996; Chassin et al., 1996; Biesanz et al., 2004), Muthén and colleagues (e.g., Muthén, 1997; Muthén and Khoo, 1998), Barnes and colleagues (e.g., Barnes et al., 2000), and Stoel and colleagues (e.g., Stoel et al., 2004).

Like the traditional SEMs, however, most of these applications of LGMs are found in social sciences. Only a few studies document applications of LGM in natural sciences (Pugesek et al., 2003; Grace and Keeley, 2006; Grace, 2006). According to our knowledge, there is no published document that reported applications of LGM in aquatic ecosystems or aquatic sciences.

1.4.5 More details about LGM

Several features of LGM make it an attractive method. These features center around the method's capability of (1) testing both linear and nonlinear growth functions; (2) incorporating time-invariant and time-varying variables or covariates; (3) modeling interaction effects; and (4) modeling multiple behaviors or variances, covariances, and means simultaneously over time (McArdle and Epstein, 1987; Li et al., 2000; Kaplan, 2000; Stoel et al., 2004; Duncan et al., 2006).

Kline (2005) listed three requirements for SEM analysis using LGM: (1) a continuous dependent variable measured on a minimum of three occasions; (2) unstandardized scores (Kline, 2005) that have the same units across time; and (3) data collected at the same

intervals. To analyze LGM with matrix summaries, either covariances or correlations and standard deviations, and means of all observed variables must be included in these matrix summaries (Kline, 2005).

LGMs often include two modeling steps: (1) modeling change or unconditional growth modeling, and (2) predicting change or conditional growth modeling (Curran and Hussong, 2002; Kline, 2005; Duncan et al., 2006). The first step analyzes a “change” model (i.e. intercept-slope model) that includes only the repeated measured variables. Each repeated measurement is represented as an indicator of two latent growth factors, initial status or intercept and linear change or slope (Kline, 2005). Unstandardized factor loadings of all indicators or measurements on these two latent growth factors are pre-fixed. The loadings of all indicators on the first latent factor (i.e., intercept) are usually fixed to 1.0 (Kline, 2005; Duncan et al., 2006). In contrast, loadings on the second latent factor (i.e., slope) are usually fixed to positive and evenly spaced constants corresponding to the repeated measurements (i.e., assuming a positive linear trend) (Kline, 2005; Duncan et al., 2006). The loading of the time 1 measurement on the slope is fixed to 0 which means the slope will be defined based on this time 1 measurement (Kline, 2005). So, the settings of loadings on the intercept are 1, 1, 1, 1, ..., 1 and the settings of loadings on the slope are 1, 2, 3, 4, ..., n or 1, 2, 4, 6, ..., n depending on the overall trend of the data. The initial level can also be based on the time 2 measurement (Kline, 2005; Duncan et al., 2006). So, the settings of loadings on the slope may become -1, 0, 1, 2, ..., n. Other forms of loadings settings are presented in detail by Duncan et al (2006). Model results at this step usually include means and standard errors of the intercept and the slope, covariance and its standard error between the intercept and slope, variances and

their standard errors of the intercept and slope, and measurement errors for each of the measurements (Kaplan, 2000; Curran and Hussong, 2002; Kline, 2005; Duncan et al., 2006).

The second analysis step involves adding variables or predictors to the intercept-slope model that can predict the latent variables over time. Some of these predicting or explanatory variables are assumed to be invariant over time and are measured only once (i.e., time-invariant variables), and the others vary over time and are measured repeatedly like the indicators in the intercept-slope mode (i.e., time-varying variables) (Kaplan, 2000; Curran and Hussong, 2002; Kline, 2005; Grace, 2006). In addition to the results of the intercept-slope model, model results at this step may also include means and standard errors of predictors, direct effects from predictors to the intercept and slope, variances and covariances of these predictors (Kaplan, 2000; Curran and Hussong, 2002; Kline, 2005; Duncan et al., 2006).

1.4.6 Guidelines for implementation of SEM and LGM

Kline (2005) provided 44 possible mistakes when using SEM for problem solving (Appendix 2). MacCallum and Austin (2000) reviewed about 500 published SEM papers in psychology from 1993 to 1997 and highlighted a list of shortcomings in those publications: (1) incomplete reporting of parameter estimates (e.g., only standardized estimates were reported); (2) unspecified input matrix (i.e., covariance or correlation matrix); and (3) unclear description of the indicators of latent variables. In ecological studies, Petraitis et al. (1996) reviewed 26 papers in ecology that applied path analysis

from 1972 to 1994 and found some limitations (e.g., collinearity, sample size issue, and categorical variables issue) of those analyses.

One of the common issues in implementation of SEM is the number of observations or sample size. Geweke and Singleton (1980) suggested the sample size of SEM can be reduced to 20. Tanaka (1987) suggested a sample size of 50 may be sufficient for hypothesizing a model with one single latent variable underlying four measured indicators. In the SAS environment, the sample size should be 5-20 times the number of parameters being estimated (SAS Institute Inc., 1990). Kline (2005) presented three scales of sample sizes: (1) small, $N < 100$; (2) medium, N between 100 and 200; and (3) large, $N > 200$. Based on model complexity, Kline (2005) then recommended a desirable ratio of the number of cases to the number of free parameters as 10:1 or 20:1. However, the number of cases or observations has no bearing on whether a SEM model is identified (Kline, 2005). The role of sample size is that results obtained from larger samples have less sampling error than smaller samples (Kline, 2005). In SEM studies, an appropriate sample size depends on variable types, number of variables, number of parameters estimated, and data normality (Bentler and Dugeon, 1996; Yuan and Bentler, 1997; Pugesek and Grace, 1998; Grace, 2006). In ecological studies, the interested or studied ecological units may be large and replication may be challenging (Grace, 2006). Due to its handling of measurement errors, SEM allows for using smaller samples than other multivariate methods (Boomsma, 1982; Raykov and Widman, 1995; Pugesek and Grace, 1998; Grace, 2006).

Another common problem faced by SEM modelers is nonpositive definite matrix (i.e., not all the numbers on the matrix diagonal are positive) (Wothke, 1993). There are two

approaches available for smoothing an indefinite matrix. The first approach is smoothing by adding a ridge. This approach involves multiplying the diagonal (the ridge) of the matrix with a constant greater than unity. It may be repeated until negative eigenvalues disappear. The second approach is principal component smoothing. This approach involves three steps (i.e., determine the eigenvalues and eigenvectors of the indefinite matrix; using all positive eigenvalues and associated eigenvectors to calculate the semidefinite components of the matrix; and if all variances in the diagonal of the original indefinite matrix were strictly greater than zero, then rescale the reproduced matrix to these original variances) (Wothke, 1993).

1.4.7 Software applications

There are significant number of computer programs and statistical software extensions available for the analysis of SEM. These programs or software packages include LISREL, Amos, EQS, Mplus, CALIS, Mx Graph, RAMONA, SEPATH, R sem package, and others. A brief review of the functions of these software packages is provided in the following paragraphs.

1.47.1 LISREL

LISREL (Linear Structural Relationships) is a software distributed by Scientific Software International, Inc. (Lincolnwood, IL, USA; Jöreskog and Sörbom, 1993; du Toit and du Toit, 2001). LISREL 8 was written by Karl G. Jöreskog and Dag Sörbom. It accepts two different command languages which include LISREL input and SIMPLIS input (Jöreskog and Sörbom, 1993). A PRELIS (a preprocessor for LISREL) is designed to screen raw data files and prepare matrix summaries for the analysis in LISREL or SIMPLIS. A path diagram option is also offered in the command. There are published

examples of SEM applications using LISREL (e.g., McArdle and Epstein, 1987; Johnson et al., 1991; Buncher et al., 1991; Mitchell, 1992 & 1994; Willett and Sayer, 1994; Byrne, 1995; Mueller, 1996; Grace and Pugesek, 1997 & 1998; Li et al., 2000; Malaeb et al., 2000; von Eye and Fuller, 2003; Stoel et al., 2004; Kline, 2005; Duncan et al., 2006).

1.4.7.2 Amos

Amos (Analysis of Moment Structures) is a software distributed by SPSS Inc. (Chicago, IL, USA). Amos 5 was written by James L. Arbuckle (2003). It does not have a matrix-oriented specification format. Also, it is not specifically designed for the analysis of ordinal data (Duncan et al., 2006). There are published examples of SEM applications using Amos (e.g., von Eye and Fuller, 2003; Duncan et al., 2006).

1.4.7.3 EQS

EQS (Equations) is a software distributed by Multivariate Software, Inc. (Encino, CA, USA). EQS 6 was written by Peter M. Bentler and Eric J. C. Wu. It uses simple and straightforward specification commands and provides extensive syntax error checking (Duncan et al., 2006). There are published examples of SEM applications using EQS (e.g., Duncan and Duncan, 1994; Duncan et al., 1994; Byrne, 1995; Chassin et al., 1996; Mueller, 1996; Duncan and Duncan, 1996; Duncan et al., 1997; Barnes et al., 2000; von Eye and Fuller, 2003; Kline, 2005; Duncan et al., 2006).

1.4.7.4 Mplus

Mplus is a program distributed by Muthén & Muthén (Los Angeles, CA, USA). Mplus 3 was written by L. K. Muthén and B. O. Muthén (2004). It has specific capabilities of individually varying times of observations, growth mixture modeling, specific procedures for growth modeling with ordered categorical outcomes, and Monte

Carlo procedures for power estimation (Muthén and Muthén, 2003; Duncan et al., 2006).

There are published examples of SEM applications using Mplus (e.g., Kaplan, 2000; Curran and Husson, 2002; Kline, 2005; Grace and Keeley, 2006; Duncan et al., 2006; Vile et al., 2006; Laughlin et al., 2007; Harrison and Grace, 2007).

1.4.7.5 CALIS

CALIS (Covariance Analysis and Linear Structural Equations) procedure is available in the SAS/STAT statistical software package under Microsoft Windows (SAS Institute Inc., Cary, NC, USA, 2000). There are published examples of SEM applications using CALIS (e.g., Liu et al., 1997; Palomares et al., 1998; Torres et al., 2002; Liang et al., 2002; Iriondo et al., 2003; Kline, 2005).

1.4.7.6 Mx Graph

The Mx (Matrix) Graph is a free program over the internet (Richmond, VA, USA; Neale et al., 2002). Mx Graph has the ability to calculate confidence intervals and statistical power for individual parameter estimates and analyze special types of latent variable models (Kline, 2005).

1.4.7.7 RAMONA

RAMONA (Reticular Action Model or Near Approximation) is within the SYSTAT 10 statistical software package (Chicago, IL, USA). The user interacts with RAMONA in SYSTAT by submitting a text or batch file with commands that specify the model and data or by typing these commands at a prompt for interactive sessions (Kline, 2005).

1.4.7.8 SEPATH

SEPATH (Structural Equation Modeling and Path Analysis) procedure is within the STATISTICA statistical software package (Tulsa, OK, USA). SEMs are specified in

SEPATH with a text-based PATH1 programming language that simulates the appearance of a model diagram based on McArdle-McDonald RAM symbolism (Kline, 2005). There are published examples of using SEPATH for SEM applications (e.g., Kline, 2005).

1.4.7.9 R sem package

R sem package is within the R, a free language and environment for statistical computing and graphics (R Development Core Team, 2005). There are published examples of using R sem package for SEM applications (e.g., Fox, 2006).

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Figures

Fig. 1. The Mid-Atlantic Highlands region of the United States (the highlighted area in the figure; USEPA, 2000a; Canaan Valley Institute, 2002)

Chapter 2 - Effects of highway construction on stream water quality and macroinvertebrate condition in a Mid-Atlantic highlands watershed, USA

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Abstract

Refining best management practices (BMPs) for future highway construction depends on a comprehensive understanding of environmental impacts from current construction methods. Based on a before-after-control-impact (BACI) experimental design, long-term stream monitoring (1997-2006) was conducted at upstream (as control, $n = 3$) and downstream (as impact, $n = 6$) sites in the Lost River watershed of the Mid-Atlantic Highlands region, West Virginia, USA. Monitoring data were analyzed to assess impacts during and after highway construction on fifteen water quality parameters and macroinvertebrate condition using the West Virginia Stream Condition Index (WVSCI). Principal components analysis (PCA) identified regional primary water quality variances, and paired t -tests and time series analysis detected seven highway construction-impacted water quality parameters which were mainly associated with the second principal component. In particular, impacts on turbidity, total suspended solids, and total iron during construction, impacts on chloride and sulfate during and after construction, and impacts on acidity and nitrate after construction were observed at the downstream sites. The construction had statistically significant impacts on macroinvertebrate index scores (i.e., WVSCI) after construction, but did not change the overall good biological condition. Implementing BMPs that address those construction-impacted water quality parameters can be an effective mitigation strategy for future highway construction in this highlands region.

Keywords: Best Management Practices (BMPs), non-point source pollution, urbanization, highway construction, water quality, macroinvertebrates

1. Introduction

As urbanization proceeds, new highways are constructed for transportation and development, and stream ecosystems within highway corridors are susceptible to impacts from construction activities. In the United States, about 19% of the total land area has been directly affected by public roads system (Forman, 2000). As one of the major non-point pollution sources, the construction of new highways can have short- and long-term effects on stream biotic and abiotic conditions (Barton, 1977; Chisholm and Downs, 1978; Cline et al., 1982; Taylor and Roff, 1986; Anderson and Potts, 1987; Stout III and Coburn, 1989; Wellman et al., 2000; Hedrick et al., 2007). These effects mainly result from sedimentation, habitat degradation, changing of leaf processing, and inputs of toxins from construction materials (Barton, 1977; Chisholm and Downs, 1978; Stout III and Coburn, 1989; Eldin, 2002).

Various best management practices (BMPs) have been developed and implemented to prevent environmental impacts of human activities. Vegetated buffers (e.g., vegetative filter strips, riparian buffers, and grassed waterways), fertilizer or manure management, rotational grazing or crop rotation, and constructed wetlands are often used for controlling agricultural pollutants (e.g., Lowrance et al., 1984; Djodjic et al., 2002; Davis et al., 2003; Sharpley et al., 2004; Bishop et al., 2005; Braskerud et al., 2005; Muenz et al., 2006; Liu et al., 2008). For highway and urban pollution, vegetated buffers and mulches, porous pavement materials, retention or detention basins and ponds, silt fence, seeding, and natural riparian wetlands have been implemented as BMPs to treat runoff and control soil erosion (Burton et al., 1976; Barton, 1977; Taylor and Roff, 1986; Pagotto et al., 2000; Benik et al., 2003; Gillilan, 2003; Van Bohemen and Janssen Van De Laak, 2003; Han et al., 2005; Li et al., 2006; Hogan and

Walbridge, 2007; Houser and Pruess, 2008). However, the effectiveness of some of those implemented BMPs on water quality protection is still unclear (Easton, et al., 2008).

In the U.S. Mid-Atlantic Highlands, habitat destruction is of great concern due to urban sprawl and land use change (USEPA, 2000a). However, few studies have reported the effects of highway construction on biotic and abiotic conditions in this highlands region. One section of a new four-lane paved highway, the Appalachian Corridor H, was constructed from June 2000 to August 2003 in the Lost River watershed, northeastern West Virginia. The West Virginia Division of Highways (WVDOH) implemented silt fencing, sedimentation ponds, mulches and grass seeding as BMPs to mitigate possible environmental impacts from the Corridor H construction (Gillilan, 2003; Hedrick et al., unpublished data; Will Ravenscroft, personal communication). Hedrick et al. (2007) found no significant effects of this highway construction on fine sediment and benthic macroinvertebrate metrics in two tributaries of the Lost River neither during construction nor one year after construction (from 2002 to 2004). However, longer-term effects of highway construction on water quality and biotic conditions at the watershed level are still unclear.

In this paper, data collected during three time periods at nine stream sites were used to assess the effects of the highway construction on water quality and biological conditions in the Lost River watershed. Research questions addressed in our study include: (1) Are there any effects of highway construction on stream water quality during and after construction?; and (2) Are there any effects of highway construction on stream benthic macroinvertebrates index scores during and after construction?

2. Materials and methods

2.1. Study area, experimental design, and site characteristics

The Lost River watershed, with an area of 472.8 km² and elevation ranging from 304 m to 1,006 m, is located in Hardy County, northeastern West Virginia (Fig. 1). Lost River flows from southwest to northeast of the area. A four-lane highway (i.e., the Appalachian Corridor H) was constructed from June 2000 to August 2003 across the northern part of the watershed. The before-after-control-impact (BACI) design was used to assess environmental impacts of the highway construction (Stewart-Oaten et al., 1986; Underwood, 1994). Based on habitat similarity (i.e., similar cumulative habitat scores which were calculated from rating ten physical habitat parameters; Hedrick et al., unpublished data; Barbour et al., 1999), nine sites along the highway were selected to monitor water quality and macroinvertebrate conditions in selected streams with similar stream orders (Table 1a; Fig. 1).

According to field observations and Geographical Information System (ArcGIS software 9.2, ESRI, Redlands, California, USA), 6 sites (HC-1, HC-3, HC-4, HC-5, HC-6 and HC-8) were downstream sites (i.e., stream sites within the highway impacted drainage area), and 3 sites (HC-2, HC-7 and HC-9) were upstream sites (i.e., stream sites upstream of the highway impacted drainage area) (Fig. 1). HC-1 and HC-2 were located on the main stem of the Lost River. HC-3 was located downstream of Baker Run and a tributary of Baker Run which was crossed by highway (Fig. 1). HC-4 was located on Baker Run and downstream of confluence of Baker Run and Long Lick Run (Fig. 1). HC-7 was located upper Baker Run and upstream of the confluence. HC-5 and HC-6 were located on Long Lick and one of its tributaries, respectively (Fig. 1). HC-8 was located on another tributary of the Long Lick and downstream of the highway. HC-9 was located on Kimsey Run which is a tributary of the upper Lost River (Fig. 1). Distances from highway construction ranged from 33 to 1,047 m at the downstream sites, and from 584 to 11,300 m at the upstream sites (Table 1a). Similar land uses were distributed in the 9

subwatersheds which include more than 60% of forested land, less than 40% of pasture land, and about 2% of other land uses, respectively (Table 1b). Based on field observations and aerial photographs, these land use types changed little during the study period except the presence of new highway for the downstream subwatersheds (i.e., HC-1, 3, 4, 5, 6, and 8). In these downstream subwatersheds, highway length ranged from 1.6 to 16.3 kilometers (Table 1b). Monitoring activities were conducted in three time periods in reference to highway construction: before (June 1997 to May 2000), during (June 2000 to August 2003), and after (September 2003 to November 2006).

2.2. Data collection

2.2.1. Water quality data

Water samples at the upstream and downstream sites were collected every six weeks ($n = 76$ for upstream and 127 for downstream sites) before construction, every eight weeks ($n = 59$ for upstream and 120 for downstream sites) during construction, and quarterly ($n = 42$ for upstream and 84 for downstream sites) after construction. Direct field measurements were conducted at each site. Water temperature ($^{\circ}\text{C}$), pH and specific conductivity ($\mu\text{S}/\text{cm}$) were measured with a portable multi-parameter YSI meter (Model 63, Yellow Springs Instruments, Yellow Springs, Ohio, USA). Turbidity (NTU) was measured with a portable turbidimeter (Model 2100P, HACH Company, Loveland, Colorado, USA) that was calibrated before each use. Flow velocity was measured with a portable flowmeter (Model 2000, Marsh-McBirney Inc., Frederick, Maryland, USA). Discharge was determined by stretching a measuring tape across a stream, dividing the transect into convenient increments, measuring width, depth, and mean flow velocity in each increment, and summing up individual discharges from all increments (Gore, 1996). In addition,

water samples were collected and analyzed in laboratories for total suspended solids (TSS, mg/L), iron (total, mg/L), calcium (total, mg/L), sulfate (mg/L), chloride (mg/L), alkalinity (mg/L as CaCO₃), acidity (mg/L as CaCO₃), nitrate (mg/L), ammonia (mg/L) and phosphate (mg/L). The analysis procedures of the Standard Methods (APHA, 1998) were followed for these analyses. Values determined to be below the method detection limits were presented as 0.5 of detection limit (USEPA, 1998).

2.2.2. Benthic macroinvertebrates data

Benthic macroinvertebrate samples were collected bi-annually (i.e., spring and fall) before (n = 11 for upstream and 18 for downstream sites), during (n = 13 for upstream and 36 for downstream sites), and after (n = 18 for upstream and 41 for downstream sites) highway construction using a modified version of a single habitat protocol described by Barbour et al. (1999). Briefly, a 500-micron net with standard dimensions of 0.5 m wide by 0.3 m high was used to sample 0.25 m² of riffle area. The net was placed in a riffle with the stream flow perpendicular to the net. Surfaces of large rocks in the riffle area were rubbed into the water flowing into the net, and the substrate was then disturbed to a maximum depth of 4 cm (Hedrick et al., 2007). The collected samples were preserved with 95% ethanol in the field. In the laboratory, each sample was spread evenly and divided into two equal halves, one half of the sample (if the total number of the half sample was more than 200) or the whole sample (if the total number of the half sample was less than 200) was used for enumeration (Barbour et al., 1999; Hedrick et al., 2007), and macroinvertebrates were enumerated and identified to family level according to Merritt and Cummins (1996). Ecological conditions at the sampling sites were characterized by West Virginia Stream Condition Index (WVSCI) which was released by

USEPA and WVDEP in March 2000 (USEPA, 2000b). The index was able to correctly indicate biotic health of streams which were stressed by human disturbance or pollution in West Virginia (USEPA, 2000b; Merovich and Petty, 2007; Hedrick et al., 2007). The index involved calculation of six normalized metrics into an index score using family level data. The six metrics were EPT (Ephemeroptera, Plecoptera, Trichoptera) taxa, total taxa, % EPT, % Chironomidae, % top 2 dominant taxa, and Hilsenhoff Family Biotic Index (HBI). The metric scores were normalized and ranged from 0 to 100, and scores were classified into five categories of condition: 0-22 (Very Poor, VP), >22-45 (Poor, P), >45-68 (Fair, F), >68-78 (Good, G), and >78-100 (Excellent, E) (USEPA, 2000b).

2.3. Statistical analyses

To meet the assumptions of parametric tests, all parameters except pH were transformed with a logarithm function (i.e., $\text{Log}_{10} [\text{original value} + 1]$), and normality of the transformed data was examined by using Shapiro-Wilk's test (Helsel and Hirsch, 1992). Principal components analysis (PCA) was conducted in SAS (SAS version 9.1, SAS Institute Inc., Cary, North Carolina, USA) to measure the water quality variance and to condense fifteen water quality parameters for further analyses. Water quality parameters included in the PCA were water temperature, turbidity, total suspended solids, conductivity, discharge (flow velocity times cross-section area), pH, alkalinity, acidity, sulfate, chloride, iron, calcium, nitrate, ammonia, and phosphate. Axis scores or principal component scores (i.e., PC scores) were calculated for each observation. The first axis (i.e., PC 1) encapsulated the maximum possible information content (i.e., variance) of the dataset, and the second axis (i.e., PC 2) contained the maximum information remaining (Shaw,

2003). Principal component loadings were considered significant if their values were greater than 0.30 or smaller than -0.30 (McGarigal et al., 2000).

Like all other ordination methods, PCA only summarizes the data variance and pattern. To test and contrast the significance of these variances between the upstream and downstream sites in three monitoring periods, scores of the first two PC factors (i.e., PC 1 and PC 2) were then analyzed using paired *t*-test (Helsel and Hirsch, 1992; Wellman et al., 2000; Petty et al., 2001; Shaw, 2003). The paired *t*-test is easy to explain and understand when comparing the differences of a series of paired observations from the upstream and the downstream sites (Helsel and Hirsch, 1992; Maltby et al., 1995; Wellman et al., 2000; Colangelo and Jones, 2005; Murtaugh, 2007). To identify the individual impacted water quality parameters, time series and paired *t*-tests were applied to compare differences of each parameter between the upstream and downstream sites in each monitoring period.

The paired *t*-tests were also used to test and contrast the differences of WVSCI between the two types of stream sites in each of the three monitoring periods. For each monitoring period, the paired *t*-tests used paired means (i.e., mean of upstream sites and mean of downstream sites for each sampling visit) to calculate their differences and tested if the differences were statistically different from zero in SAS (SAS version 9.1, SAS Institute Inc., Cary, NC, USA). The significant probability level was set at $\alpha < 0.05$ for all tests.

3. Results

3.1. Water quality

The PCA reduced the fifteen water quality parameters to four principal components (i.e., eigenvalues > 1.0). Table 2 lists the eigenvalues and percent variances explained by these four

principal components, PC scores, and final communality estimates of the water quality parameters. PC 1 and PC 2 explained 35.4% of the total variance of the water quality data. High positive values for PC 1 were characterized by increasing calcium, alkalinity, conductivity, pH, water temperature and chloride. High positive values for PC 2 were indicated by increasing total suspended solids, chloride, turbidity, acidity, sulfate, nitrate, conductivity, iron and decreasing pH (Table 2).

The paired *t*-tests detected a significant difference in PC 1 between the upstream and the downstream sites before highway construction ($df = 29$, $t = 4.54$, $P < 0.0001$; Table 3). No significant difference was found between the two stream types during ($df = 19$, $t = 1.25$, $P > 0.05$; Table 3), and after ($df = 13$, $t = -1.91$, $P > 0.05$; Table 3) highway construction. The tests found no significant differences in PC 2 between the upstream and the downstream sites before ($df = 29$, $t = -0.59$, $P > 0.5$; Table 3), during ($df = 19$, $t = -0.07$, $P > 0.5$; Table 3), and after ($df = 13$, $t = -0.72$, $P > 0.1$; Table 3) highway construction.

The paired *t*-tests on individual water quality parameters indicated that four water quality parameters (i.e., turbidity, chloride, acidity, and nitrate) were not statistically different before the highway construction but were different in either during or after construction between the two stream types (Table 4; Fig. 2a-2d). Comparisons of turbidity between the two stream types showed significant difference during ($df = 9$, $t = 3.26$, $P < 0.01$; Table 4; Fig. 2a) and no significant difference after ($df = 15$, $t = 0.88$, $P > 0.05$; Table 4; Fig. 2a) the highway construction. Chloride showed significant difference both during ($df = 9$, $t = 7.36$, $P < 0.0001$; Table 4; Fig. 2b) and after ($df = 15$, $t = 9.65$, $P < 0.0001$; Table 4; Fig. 2b) the highway construction. After the highway construction, there were significant difference between the two stream types in acidity ($df = 15$, $t = 2.75$, $P < 0.05$; Table 4; Fig. 2c) and nitrate ($df = 15$, $t = 2.26$,

$P < 0.05$; Table 4; Fig. 2d). Six of the fifteen water quality parameters (i.e., TSS, total iron, sulfate, alkalinity, conductivity, and total calcium) had significant differences between the two stream types before the highway construction (Table 4). TSS and total iron showed higher values at the downstream sites than those at the upstream sites during the highway construction (Fig. 3a-3b). Sulfate increased at the downstream sites during and after the highway construction but remained at the before construction level at the upstream sites (Fig. 3c). Trends of alkalinity, conductivity, and total calcium over the whole monitoring period at the downstream sites were similar to those at the upstream sites (Fig. 3d, 4a-4b). Conductivity showed significant difference between stream types in each of the monitoring periods (Table 4; Fig. 4a). Differences of alkalinity and total calcium between stream types changed from extremely significant ($P < 0.001$) before construction, to significant ($P < 0.05$) during construction, and to significant (i.e., total calcium, $P < 0.05$) or no significant (i.e., alkalinity, $P > 0.05$) after construction (Table 4; Fig. 3d, 4b). The paired t -tests found no-significant difference between the two stream types for the remaining five water quality parameters (i.e., water temperature, discharge, ammonia, phosphate, and pH) in each monitoring period.

3.2. Benthic macroinvertebrates index

The paired t -tests found that the differences of WVSCI between the upstream and downstream sites were not significant before ($df = 5$, $t = 2.26$, $P > 0.05$; Table 4; Fig. 4c) or during ($df = 5$, $t = 0.39$, $P > 0.5$; Table 4; Fig. 4c), but were significant after ($df = 6$, $t = -3.72$, $P < 0.01$; Table 4; Fig. 4c) the highway construction. Most values of WVSCI were above the good biological conditions at the two stream types in all three monitoring periods (Fig. 4c).

4. Discussion

Water quality parameters of PC 1 (i.e., calcium, alkalinity, conductivity, pH, water temperature, and chloride) were significantly different between upstream and downstream sites before highway construction, and had no statistical differences in the later two monitoring periods. The PC 2 (i.e., TSS, chloride, turbidity, acidity, sulfate, nitrate, conductivity, iron, and pH) showed no significant differences in each of the monitoring periods. Based on these results, we tend to conclude that the highway construction may only have affected the PC 1 parameters. However, the shared water quality parameters (i.e. conductivity, pH, and chloride; Table 2) in PC 1 and PC 2 may have changed the directions of the overall PC 2 variance, and hidden variances of possible construction-impacted parameters in PC 2 (Table 3). This may be one of the possible limitations when inferential tests were applied on PC scores of the current data. This also indicated that we cannot only depend on the PCA and inferential tests on PC scores to fully explain the current data. The time series and paired *t*-tests on individual water quality parameters showed that seven of them were directly affected by the highway construction (Table 4). Specifically, the highway construction had impacts on turbidity and TSS at the downstream sites during construction (Table 4; Fig. 2a and 3a). These results were consistent with those in other studies (Barton, 1977; Beschta, 1978; Chisholm and Downs, 1978; Taylor and Roff, 1986; Anderson and Potts, 1987; Colangelo and Jones, 2005). But the magnitudes of the TSS and turbidity increases in the present study were less than those reported in other studies (Taylor and Roff, 1986; Anderson and Potts, 1987). This may be attributed to the construction erosion controls (e.g., sediment fencing and ponds) implemented by the WVDOH (Hedrick et al., 2007; Will Ravenscroft, personal communication). Also, the riparian forest and pasture may partially contribute to the relative lower increases of TSS and turbidity in the current study. Effects on

total iron were also observed at the downstream sites during construction (Fig. 3b). This was in agreement with the results of Extence (1978) who found high values of iron at the downstream site of a motorway construction in the Great Britain. Highway construction had impacts on stream chloride and sulfate during and after construction, and effects on acidity at the downstream sites after construction (Fig. 2b-2c and 3c). Sulfate may have been released from disturbed soils to streams downstream of construction areas. The increased acidity after highway construction can be partially attributed to increased concentrations of sulfate at downstream sites. High concentrations of chloride were most attributed to construction activities. To our knowledge, no study has reported the effects of highway construction on stream acidity, sulfate or chloride. But our results support the conclusion that detection of highway construction impacts on stream chemical conditions may require long-term monitoring (Barton, 1977; Taylor and Roff, 1986). Statistically significant effects on nitrate were also observed after highway construction, but the differences were small (Fig. 2d). Elevated nitrate concentrations from highway construction were consistent with results from long-term monitoring of highway impacted Hanlon Creek in Southern Ontario, Canada (Taylor and Roff, 1986). The slight impacts on nitrate after highway construction in the Lost River watershed may have resulted from the use of mulches, fertilizer, and hydroseeding as best management practices (BMPs) for erosion and sediment control (Gillilan, 2003). This also can be partially attributed to riparian forested and pasture land uses instead of cropland in the current study. In Coastal Plain streams of the Chesapeake Bay, pasture was found to be less important in nitrate inputs than that of cropland (Jordan et al., 1997; Weller et al., 2003). Based on the results, managing total suspended solids, turbidity, chloride, iron, nitrate, acidity, and sulfate may be an effective strategy for protecting water quality from future highway constructions in the study region. According to the results of

the PCA, these construction-impacted water quality parameters were mostly associated with PC 2 (Table 2). Moreover, the time series of alkalinity, conductivity, and total calcium showed a consistent regional trend in the studied watershed (Fig. 3d, 4a-4b). They are the primary water quality variances (i.e., PC 1) which were identified by the PCA (Table 2). However, from the time series plots, conductivity seems more unstable at downstream sites after construction (Fig. 4a). The decreased significant difference levels of alkalinity and total calcium between stream types throughout the three monitoring periods may partially result from highway impacts (Fig. 3d, 4b). These identified construction-impacted parameters (i.e., PC 2) and primary regional water quality trends (i.e., PC 1) from the time series and paired *t*-tests testified to the powerful function of the PCA in major variances summarization.

The paired *t*-tests identified impacts of the highway construction on WVSCI scores after construction. Hedrick et al (unpublished data) analyzed the individual macroinvertebrate metrics, and found the highway construction increased the percent of chironomidae and Hilsenhoff Biotic Index (HBI), and decreased Ephemeroptera, Plecoptera, and Trichoptera (EPT). The decreases of stream condition index may have partially resulted from the construction-impacted water quality parameters at the downstream sites. However, most observed WVSCI scores indicated either Good (G) or Excellent (E) biological condition for all sites in the three monitoring periods based on the EPA's criteria (Fig. 4c; USEPA, 2000b). This was consistent with the slight effects on the water quality parameters identified above. In eastern England streams, Perdikaki and Mason (1999) also found no overall significant impacts of road run-off on the macroinvertebrate community. A significant decrease in macroinvertebrate metrics such as EPT taxa richness may need some threshold level of fine sediment accumulation (e.g., 0.8-0.9%) in these Appalachian

streams (Kaller and Hartman, 2004). Moreover, the forested and pasture riparian areas can have less impacts on macroinvertebrate assemblages than that of cropland (King et al., 2005).

Some important points emerged from this study. First, it is still unclear about the cause of the longitudinal trends of acidity, alkalinity, conductivity, and total calcium over the whole monitoring period (Fig. 2c, 3d, and 4a-4b). A possible cause is the climate related processes (e.g., acid deposition) in the Mid-Atlantic region (USEPA, 2000a). Secondly, the present study mainly focused on the effects of highway construction. Longer term monitoring is needed to illustrate the subsequent impacts such as heavy metals, nutrients, and hydrocarbon pollution from daily transportation (Hoffman et al., 1985; Wu et al., 1998; Kim et al., 2006; Kayhanian et al., 2007), chloride from deicing (Ostendorf et al., 2001), and subsequent urbanization (Angermeier et al., 2004; Wheeler et al., 2005; Line and White, 2007).

5. Conclusions

Highway construction in the Lost River watershed had statistically significant effects on seven major water quality parameters identified by PC 2 namely impacts on turbidity, TSS, and total iron during construction, effects on chloride and sulfate during and after construction, and effects on acidity and nitrate after construction. Highway construction had statistically significant impacts on the scores of stream benthic macroinvertebrates index (i. e., WVSCI) after construction, but did not change the overall good biological condition. Construction-impacted water quality parameters should be considered for developing mitigation strategies and refining currently implemented BMPs for future highway constructions in this highlands region.

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Tables

Table 1a. Sampling sites, stream order, and shortest distances to highway in the Lost River watershed, WV, USA

Site ID	Site type	Site name	Stream order	Shortest distance to highway (m)
HC-1	Downstream (DS)	Lower Lost River	3 rd	718
HC-3	Downstream (DS)	Lower Baker Run	3 rd	1047
HC-4	Downstream (DS)	Baker Run	3 rd	341
HC-5	Downstream (DS)	Long Lick	3 rd	45
HC-6	Downstream (DS)	Lower Long Lick Tributary	1 st	33
HC-8	Downstream (DS)	Upper Long Lick Tributary	2 nd	200
HC-2	Upstream (US)	Upper Lost River	3 rd	1774
HC-7	Upstream (US)	Upper Baker Run	3 rd	584
HC-9	Upstream (US)	Kimsey Run	2 nd	11300

Table 1b. Drainage area, land use, and highway length of the sampled subwatersheds in the Lost River watershed, WV, USA

Site ID	Drainage area (km ²)	Forested (%)	Pasture (%)	Other (%)	Highway length (km)
HC-1 (DS)	455.1	76	22	2	16.3
HC-3 (DS)	61.9	69	29	2	7.2
HC-4 (DS)	53.1	67	31	2	4.7
HC-5 (DS)	17.8	72	27	1	4.0
HC-6 (DS)	17.9	72	27	1	4.1
HC-8 (DS)	3.9	61	37	2	1.6
HC-2 (US)	324.9	75	23	2	0
HC-7 (US)	34.7	65	33	2	0
HC-9 (US)	75.5	75	23	2	0

Table 2. Principal component (PC) factor loadings for water quality of the monitored streams in the Lost River watershed, WV, USA

	PC 1	PC 2	PC 3	PC 4	Fina. Commu. Est.
Eigenvalue	2.97	2.34	1.58	1.34	-
% Var. Expl.	19.8	15.6	10.5	8.9	-
Water Temp.	0.394	-0.036	0.167	-0.711	0.691
Turbidity	-0.204	0.560	0.562	0.027	0.672
TSS	-0.009	0.612	0.598	-0.118	0.747
Conductivity	0.782	0.385	-0.158	0.130	0.801
Flow	-0.084	-0.235	0.309	0.655	0.586
pH	0.615	-0.413	0.265	-0.020	0.619
Alkalinity	0.844	-0.005	-0.033	-0.001	0.713
Acidity	-0.178	0.495	-0.337	-0.368	0.526
SO ₄	0.238	0.485	-0.372	0.229	0.483
Cl	0.375	0.603	-0.247	0.071	0.570
Fe	-0.117	0.359	0.249	0.022	0.205
Ca	0.860	-0.030	0.120	0.218	0.803
Nitrate	-0.275	0.429	-0.318	0.335	0.473
Ammonia	-0.061	0.198	-0.070	-0.093	0.056
PO ₄	0.057	0.294	0.436	0.100	0.290

Note: % Var. Expl. = % Variance Explained; Water Temp. = Water Temperature; Fina. Commu. Est. = Final Communality Estimate. Significant principal component loadings were highlighted.

Table 3. Paired *t*-test comparisons of water quality PC 1 and PC 2 (Mean $\pm$ S.D.) between the upstream and downstream sites in the three monitoring periods of the highway construction in the Lost River watershed, WV, USA

Parameter	Period	Downstream-Upstream difference (Mean $\pm$ S.D.)	DF	<i>t</i> -value	<i>P</i> -value
PC 1	Before (Jun./97 ~ May/00)	0.61 $\pm$ 0.73	29	4.54	<0.0001
	During (Jun./00 ~ Aug./03)	0.16 $\pm$ 0.58	19	1.25	0.2253
	After (Sep./03 ~ Nov./06)	-0.26 $\pm$ 0.50	13	-1.91	0.0787
PC 2	Before (Jun./97 ~ May/00)	-0.09 $\pm$ 0.85	29	-0.59	0.5601
	During (Jun./00 ~ Aug./03)	-0.01 $\pm$ 0.64	19	-0.07	0.9448
	After (Sep./03 ~ Nov./06)	-0.14 $\pm$ 0.73	13	-0.72	0.4856

Note: Statistically significant differences identified ($P < 0.05$) were highlighted. S.D. = standard deviation; DF = degree of freedom.

Table 4. Paired *t*-test comparisons of individual water quality parameters and West Virginia Stream Condition Index (WVSCI) (Mean $\pm$ S.D.) between the upstream and downstream sites in the three monitoring periods of the highway construction in the Lost River watershed, WV, USA

Parameter	Period	Downstream-Upstream difference* (Mean $\pm$ S.D.)	DF	<i>t</i> -value	<i>P</i> -value
Turbidity (NTU)	Before (Jun./97 ~ May/00)	0.004 $\pm$ 0.56	13	0.05	0.9627
	During (Jun./00 ~ Aug./03)	0.360 $\pm$ 0.64	9	3.26	0.0099
	After (Sep./03 ~ Nov./06)	0.067 $\pm$ 0.47	15	0.88	0.3920
Chloride (mg/L)	Before (Jun./97 ~ May/00)	0.21 $\pm$ 0.75	13	1.71	0.1103
	During (Jun./00 ~ Aug./03)	0.59 $\pm$ 0.46	9	7.36	<0.0001
	After (Sep./03 ~ Nov./06)	0.88 $\pm$ 0.56	15	9.65	<0.0001
Acidity (mg/L as CaCO ₃)	Before (Jun./97 ~ May/00)	-0.03 $\pm$ 0.40	13	-0.25	0.8057
	During (Jun./00 ~ Aug./03)	0.10 $\pm$ 0.38	9	0.86	0.4098
	After (Sep./03 ~ Nov./06)	0.10 $\pm$ 0.14	15	2.75	0.0148
Nitrate (mg/L)	Before (Mar./99 ~ May/00)	-0.12 $\pm$ 0.52	5	-1.35	0.2353
	During (Jun./00 ~ Aug./03)	0.07 $\pm$ 0.43	9	0.94	0.3719
	After (Sep./03 ~ Nov./06)	0.10 $\pm$ 0.29	15	2.26	0.0395

Note: Statistically significant differences identified ($P < 0.05$) were highlighted. S.D. = standard deviation; DF = degree of freedom. * Difference was calculated based on logarithmic transformed (i.e., Log₁₀ [original value +1]) data.

Table 4 (Continued)

Parameter	Period	Downstream-Upstream difference* (Mean $\pm$ S.D.)	DF	t-value	P-value
TSS (mg/L)	Before (Jun./97 ~ May/00)	0.30 $\pm$ 0.81	13	2.25	0.0426
	During (Jun./00 ~ Aug./03)	0.41 $\pm$ 0.50	9	4.68	0.0011
	After (Sep./03 ~ Nov./06)	0.28 $\pm$ 0.61	15	2.83	0.0126
Total iron (mg/L)	Before (Jun./97 ~ May/00)	0.10 $\pm$ 0.26	13	2.44	0.0299
	During (Jun./00 ~ Aug./03)	0.03 $\pm$ 0.08	9	2.24	0.0516
	After (Sep./03 ~ Nov./06)	0.01 $\pm$ 0.10	15	0.92	0.3714
Sulfate (mg/L)	Before (Jun./97 ~ May/00)	0.33 $\pm$ 0.48	13	4.14	0.0012
	During (Jun./00 ~ Aug./03)	0.33 $\pm$ 0.48	9	3.95	0.0034
	After (Sep./03 ~ Nov./06)	0.48 $\pm$ 0.51	15	5.87	<0.0001
Alkalinity (mg/L as CaCO ₃)	Before (Jun./97 ~ May/00)	0.32 $\pm$ 0.36	13	5.43	0.0001
	During (Jun./00 ~ Aug./03)	0.19 $\pm$ 0.34	9	3.15	0.0117
	After (Sep./03 ~ Nov./06)	0.03 $\pm$ 0.16	15	1.34	0.2017
Conductivity (μ S/cm)	Before (Jun./97 ~ May/00)	0.29 $\pm$ 0.29	13	3.73	0.0025
	During (Jun./00 ~ Aug./03)	0.25 $\pm$ 0.08	9	9.34	<0.0001
	After (Sep./03 ~ Nov./06)	0.29 $\pm$ 0.14	15	8.12	<0.0001
Total calcium (mg/L)	Before (Jun./97 ~ May/00)	0.63 $\pm$ 0.43	9	8.61	<0.0001
	During (Jun./00 ~ Aug./03)	0.25 $\pm$ 0.46	9	3.17	0.0113
	After (Sep./03 ~ Nov./06)	0.12 $\pm$ 0.25	15	2.90	0.0110
WVSCI	Before (Oct./97 ~ May/00)	2.09 $\pm$ 2.26	5	2.26	0.0731
	During (Oct./00 ~ Mar./03)	0.53 $\pm$ 3.30	5	0.39	0.7101
	After (Oct/03 ~ Sep/06)	-4.22 $\pm$ 3.01	6	-3.72	0.0099

Note: Statistically significant differences identified ($P < 0.05$) were highlighted. S.D. = standard deviation; DF = degree of freedom. * Difference was calculated based on logarithmic transformed (i.e., Log_{10} [original value +1]) data except WVSCI.

Figures

Fig. 1. Locations of highway and monitored upstream (US) and downstream (DS) sites in the Lost River watershed, WV, USA.

Fig. 2. Time series (Mean + 1S.D.) of (a) turbidity, (b) chloride, (c) acidity, and (d) nitrate in three monitoring periods of the highway construction (before, during, and after) in the Lost River watershed, WV, USA. Two vertical dashed lines are used to separate the three periods. Significance level between stream types in each period is marked as: ns ($P > 0.05$), * ($P < 0.05$), ** ($P < 0.01$), *** ($P < 0.001$).

Fig. 3. Time series (Mean + 1S.D.) of (a) total suspended solids (TSS), (b) total iron, (c) sulfate, and (d) alkalinity in three monitoring periods of the highway construction (before, during, and after) in the Lost River watershed, WV, USA. Two vertical dashed lines are used to separate the three periods. Significance level between stream types in each period is marked as: ns ($P > 0.05$), * ($P < 0.05$), ** ($P < 0.01$), *** ($P < 0.001$).

Fig. 4. Time series (Mean + 1S.D.) of (a) conductivity, (b) total calcium, and (c) West Virginia Stream Condition Index (WVSCI) in three monitoring periods of the highway construction (before, during, and after) in the Lost River watershed, WV, USA. Two vertical dashed lines are used to separate the three periods. Two horizontal dashed lines were used to separate “Good” and “Fair”, “Fair” and “Poor” biological conditions, respectively. Significance level between stream types in each period is marked as: ns ($P > 0.05$), * ($P < 0.05$), ** ($P < 0.01$), *** ($P < 0.001$).

Chapter 3 - Episodic water quality impacts from highway construction in streams of a South Branch Potomac River watershed, USA

(This chapter is written in the format of the *Water, Air, and Soil Pollution* and will be submitted for publication upon an approval from the funding agency-

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Abstract

Comprehensive understanding of impacts from current highway construction is beneficial to mitigate future highway construction impacts by refining best management practices (BMPs). Based on a before-after-control-impact (BACI) experimental design, stream water samples were collected from upstream (as control, $n=3$) and downstream (as impact, $n=3$) sites before (March 2002 ~ August 2006) and during (September 2006 ~ November 2007) a four-lane highway construction in a South Branch Potomac River watershed, USA. Statistical methods of principal component analysis (PCA) and paired t -tests were used to assess impacts of highway construction on eighteen physicochemical water quality parameters. The paired t -tests on scores of the first two principal components found no statistically significant impacts of the highway construction on the major water quality parameters during the highway construction. Episodic impacts on mean trends of turbidity (+90.08 NTU), total suspended solids (+37.73 mg/L), total iron (+0.52 mg/L), and total aluminum (+0.71 mg/L) were observed at the downstream sites. Future designs of BMPs should consider these episodically impaired water quality parameters to mitigate possible impacts from new highway construction in this Mid-Atlantic Highlands region.

Keywords: urbanization, highway construction, stream water quality, episodic impacts, BMPs

1. Introduction

Urban development and urban land use are among the major anthropogenic stressors for aquatic ecosystems (White, 1976; Wang et al., 1997; Interlandi and Crockett, 2003). Preceding urbanization, new highways are constructed for transportation and future development. In the United States, it was estimated that the public roads system impacted about 19% of the total land

area ecologically (Forman, 2000). Even though the impacts of the construction and presence of roads or highways on conditions of freshwater ecosystems have been reported (Whitney and Bailey, 1959; Burton et al., 1976; Barton, 1977; Extence, 1978; Beschta, 1978; Cline et al., 1982; Talor and Roff, 1986; Anderson and Potts, 1987; Luce and Black, 1999; Wellman et al., 2000; Woodcock and Huryn, 2004; Sugden and Woods, 2007), their impacts on water quality, especially chemical impacts are still rarely investigated (Wheeler et al., 2005; Chen et al., unpublished data).

In the U.S. Mid-Atlantic Highlands, channel sedimentation and habitat destruction are the top two stressors influencing stream conditions because of urban sprawl and land use change throughout the region (USEPA, 2000). However, there are only a few studies reporting the impacts of highway construction on streams in this highlands region. A four-lane highway, the Appalachian Corridor H was constructed in Hardy County, northeastern West Virginia since June 2000. The first section was finished in Lost River watershed in August 2003, and the second section began construction in the South Branch Potomac River 3 watershed in September 2006 (West Virginia Department of Highways, WVDOH). Short- and long-term impacts of the construction of the first section of the highway on stream conditions in the Lost River watershed were reported (Hedrick et al., 2007; Chen et al., unpublished data). However, watershed level impacts of the highway construction on water quality in streams of the South Branch Potomac River 3 watershed were not reported.

The present study was designed to investigate the physical and chemical water quality impacts of the highway construction on streams in the South Branch Potomac River 3 watershed during the first year of construction (i.e., from September 2006 to November 2007). The research will assist us in understanding the ecological impacts of highway construction on streams in the

Mid-Atlantic Highlands region. The understanding can inform best management practices (BMPs) to mitigate the environmental impacts of the continued construction of the Corridor H highway and highway construction in other regions with similar geographical and geological conditions.

2. Materials and Methods

2.1. Study area and experimental design

The South Branch Potomac River 3 watershed is one of the subwatersheds of the South Branch Potomac River watershed (Fig. 1), which is one of the headwater watersheds of Chesapeake Bay in the eastern U. S. It drains 886 km² with elevations ranging from 158 m to 969 m (West Virginia GIS Technical Center). The South Branch Potomac River flows from southwest to northeast. A 23-kilometer section of the four-lane Appalachian Corridor H highway has been under construction since September 2006 and will be open to traffic in fall 2009 (WVDOH). This section of the new highway crosses the south reach of the South Branch Potomac River 3 watershed in Hardy County, northeastern West Virginia (Fig. 1).

The before-after-control-impact (BACI) design was used to assess the water quality impacts from the highway construction (Stewart-Oaten et al., 1986; Underwood, 1994). Specifically, this experimental design involves two stream types (i.e. upstream/control and downstream/impact) and two monitoring periods (i.e. before and after an ecological disturbance). In the South Branch Potomac River 3 watershed, 3 stream sites (WB-1, WB-4, and WB-5) were downstream of the highway and 3 stream sites (WB-2, WB-3, and WB-6) were upstream of the highway according to field observations and Geographical Information System (GIS) analyses (Fig. 1). These sites were selected based on habitat similarity and to avoid potential pollution from other sources in

the watershed. Shortest distances to the highway of the upstream sites range from 797 m to 7360 m, and the shortest distances to the highway of the downstream sites range from 223 m to 845 m. Locations, site names, and shortest distances to the highway of these streams are presented in Figure 1 and Table 1. Monitoring activities were conducted for more than four years (period I; from March 2002 to August 2006) before the highway construction and about one year (period II; from September 2006 to November 2007) during the highway construction.

2.2. Field sampling and laboratory analyses

Quarterly water samples (exceptions were 6 visits in 2002 and 5 visits in 2006) were collected both at the upstream and downstream sites in period I ($n = 53$ for upstream and 63 for downstream sites) and period II ($n = 18$ for upstream and 17 for downstream sites). Field pH and specific conductivity ($\mu\text{S}/\text{cm}$) were measured with a portable multi-parameter YSI meter (Model 63, Yellow Springs Instruments, Yellow Springs, Ohio, USA). Turbidity (NTU) was measured with a portable turbidimeter (Model 2100P, HACH Company, Loveland, Colorado, USA) which was calibrated before each use. Flow (m^3/s) was measured with a portable flowmeter (Model 2000, Marsh-McBirney Inc., Frederick, Maryland, USA). In addition, water samples were collected and analyzed in the laboratories for total suspended solids (TSS, mg/L), iron (total, mg/L), manganese (total, mg/L), aluminum (total, mg/L), magnesium (total, mg/L), calcium (total, mg/L), sulfate (mg/L), chloride (mg/L), alkalinity (mg/L as CaCO_3), acidity (mg/L as CaCO_3), nitrate (mg/L), nitrite (mg/L), ammonia (mg/L) and phosphate (mg/L). The analytical procedures of the Standard Methods (APHA, 1998) were followed for these analyses. Values determined to be below the method detection limits were presented as 0.5 of detection limit (USEPA, 1998).

2.3. Data analyses

To meet the assumptions of parametric tests, all variables except pH were transformed with a logarithm function, and normality of the transformed data was examined by using Shapiro-Wilk test (Helsel and Hirsch, 1992). Principal components analysis (PCA) was conducted in SAS (SAS version 9.1, SAS Institute Inc., Cary, North Carolina, USA) to measure the water quality variance and to condense eighteen water quality variables into a few principal component factors for further analyses. Water quality variables included in the PCA analysis were turbidity, flow, pH, conductivity, TSS, alkalinity, acidity, sulfate, chloride, iron, calcium, magnesium, manganese, aluminum, nitrite, nitrate, ammonia, and phosphate. Axis scores or principal components scores (i.e., PC scores) were calculated for each observation on each axis. The first axis (i.e., PC 1) encapsulated the maximum possible information content (i.e., variance) of the dataset, and the second axis (i.e., PC 2) contained the maximum information remained (Shaw, 2003). Principal component loadings were considered significant if their values were greater than 0.30 or smaller than -0.30 (McGarigal et al., 2000).

Like all other ordination techniques, PCA only summarizes the data variance and pattern. To test and contrast the significance of these scores between the upstream and downstream sites in the two monitoring periods, scores of the first two PC factors (i.e., PC 1 and PC 2) were then analyzed using a paired *t*-test (Helsel and Hirsch, 1992; Wellman et al., 2000; Petty et al., 2001; Shaw, 2003). The paired *t*-test is easy to explain and understand when comparing the differences of a series of paired observations from the upstream and the downstream sites (Helsel and Hirsch, 1992; Murtaugh, 2007). We used this test to test impacts of highway construction on downstream sites. Significant probability level was set at $\alpha < 0.05$ for all tests.

Finally, a water quality trend was calculated based on the difference between the means of each water quality parameter in the two monitoring periods for the two stream locations (upstream and downstream). Because both stream types showed similar trends from period I to period II (i.e., both of them are positive or negative) for most water quality parameters, parameters with a large trend difference (i.e., more than five times) between the upstream and downstream sites were highlighted. These impaired water quality parameters were considered as impacted parameters from the highway construction and were further analyzed in time series plots.

3. Results

3.1. Water quality variance and differences between stream types

The PCA condensed the eighteen water quality parameters into four important components with eigenvalues greater than 1.0. Eigenvalues and percent variances explained by these four principal components, PC scores, and final communality estimates of the water quality variables are listed in Table 2. PC 1 and PC 2 explained 43% of the total variance of the water quality data. High positive values of PC 1 were characterized by increasing iron (+0.889), turbidity (+0.883), manganese (+0.817), TSS (+0.793), aluminum (+0.789), sulfate (+0.551), nitrite (+0.533), flow (0.383), and chloride (+0.378). High positive values of PC 2 were indicated by increasing calcium (+0.833), alkalinity (+0.785), magnesium (+0.769), conductivity (+0.738), nitrate (+0.384), phosphate (+0.351), and decreasing flow (-0.396) (Table 2).

The paired *t*-tests found no significant difference between the PC 1 scores of the upstream and downstream sites before (DF = 48, $t = -1.07$, $P = 0.2896$; Table 3) and during (DF = 12, $t = -0.71$, $P = 0.4933$; Table 3) the highway construction. The paired *t*-tests detected no significant

difference between the PC 2 scores of the two stream types before ($DF = 48$, $t = -0.97$, $P = 0.3394$; Table 3) and during ($DF = 12$, $t = -0.58$, $P = 0.5738$; Table 3) the highway construction.

3.2. Water quality trends and episodic impacts

Most stream water quality variables showed similar trends (i.e., increasing or decreasing mean values) from period I to period II both at the upstream and downstream sites (Table 4). In particular, both stream types showed increasing turbidity, pH, conductivity, TSS, alkalinity, acidity, sulfate, chloride, iron, calcium, magnesium, aluminum and nitrite, and decreasing flow, nitrate, and phosphate (Table 4). Concentrations of manganese showed no trend at the upstream sites but decreased (-0.01 mg/L) at the downstream sites (Table 4). Ammonia decreased (-0.006 mg/L) at the upstream sites but increased ($+0.004$ mg/L) at the downstream sites (Table 4).

The identified highway construction impacted water quality parameters are turbidity (an increase of $+8.83$ NTU and $+90.08$ NTU at the upstream and downstream sites, respectively), TSS (an increase of $+1.47$ mg/L and $+37.73$ mg/L at the upstream and downstream sites, respectively), iron (an increase of $+0.05$ mg/L and $+0.52$ mg/L at the upstream and downstream sites, respectively), and aluminum (an increase of $+0.14$ mg/L and $+0.71$ mg/L at the upstream and downstream sites, respectively) (Table 4). The time series plots showed these larger increasing trends mostly resulted from episodic increases during the highway construction (i.e. August 2007; Figure 2a, 2b, 3a, and 3b). In the August 2007 samples, turbidities were 850 NTU and 954 NTU at the downstream sites WB-4 and WB-5, respectively (samples in WB-1 were missed at that visit); at the upstream sites, turbidities were 12 NTU, 145 NTU, and 73 NTU at sites WB-2, WB-3, and WB-6, respectively. At the same time, TSS were 357 mg/L and 440 mg/L at the downstream sites WB-4 and WB-5, respectively; at the upstream sites, TSS were 7

mg/L, 41 mg/L, and 34 mg/L at sites WB-2, WB-3, and WB-6, respectively. Concentrations of iron were 9.60 mg/L and 1.89 mg/L at the downstream sites WB-4 and WB-5, respectively; 0.19 mg/L, 1.27 mg/L, and 1.29 mg/L of iron were observed at the upstream sites WB-2, WB-3, and WB-6, respectively. Concentrations of aluminum were 10.56 mg/L and 2.42 mg/L at the downstream sites WB-4 and WB-5, respectively; 0.25 mg/L, 1.46 mg/L, and 1.05 mg/L of aluminum were observed at the upstream sites WB-2, WB-3, and WB-6, respectively.

4. Discussion

The paired *t*-tests on PC 1 and PC 2 found no significant impacts of the highway construction on major water quality variables at the downstream sites during the first year of construction. But the comparisons of water quality trends between stream types identified episodic impacts from highway construction. The increase of turbidity and TSS at the downstream sites were 10 and 24 fold larger than those at the upstream sites, respectively (Table 4). In another Mid-Atlantic watershed (i.e., Lost River watershed), less than 3 fold larger increases of turbidity and TSS were observed at the downstream sites during a three year period of highway construction (Chen et al., unpublished data). The episodic event on August 21st of 2007 caused most of these differences. Peak turbidity at the downstream site WB-5 of the South Branch Potomac River 3 watershed was 954 NTU during the highway construction, which was lower than peak values of turbidity at impacted sites in Meginniss Arm Tributary in Florida (3480 JTU, Jackson Turbidity Units), but higher than those in Johnson Gulch watershed in western Montana (36 NTU) and Lost River watershed in Mid-Atlantic Highlands (54 NTU) (Fig. 4a; Burton et al., 1976; Anderson and Potts, 1987; Chen et al., unpublished data). Peak TSS at the downstream site WB-5 of the South Branch Potomac River 3 watershed was 440 mg/L during the highway construction, which was

lower than peak values of TSS observed at impacted sites in the Meginniss Arm Tributary in Florida (6780 mg/L), Hanlon Creek in southern Ontario (1390 mg/L) and Joe Wright Creek in Rocky Mountains (500 mg/L), but higher than those in the Roding River of Great Britain (178 mg/L), Johnson Gulch watershed in western Montana (70 mg/L) and Lost River watershed in the Mid-Atlantic Highlands (30 mg/L) (Fig. 4b; Burton et al., 1976; Barton, 1977; Cline et al., 1982; Anderson and Potts, 1987; Chen et al., unpublished data). Similar construction methods, materials, and BMPs (e.g., sediment fencing) were used by the West Virginia Department of Highways (WVDOH) in the Lost River watershed and the South Branch Potomac River 3 watershed. The higher peak values of turbidity and TSS observed at the downstream sites of the South Branch Potomac River 3 watershed could be partially attributed to higher flows during the field visit. In the August 2007 visit, mean flow at the downstream sites was about $0.20 \text{ m}^3/\text{s}$, which was higher than those at the impacted site in the Johnson Gulch watershed in western Montana ($0.06 \text{ m}^3/\text{s}$ or 60 L/s) and the Lost River watershed (flow was below detection limit) when the peak TSS concentrations were observed (Anderson and Potts, 1987; Chen et al., unpublished data). Higher peak turbidity in the Meginniss Arm Tributary and higher peak TSS in the Meginniss Arm Tributary, Hanlon Creek, and Joe Wright Creek were caused by higher flows during storms or snowmelt runoff (Burton et al., 1976; Barton, 1977; Cline et al., 1982). In the Johnson Gulch watershed, Anderson and Potts (1987) found highly positive significant relations between suspended sediment concentrations and discharge during the first year of road construction. In addition, the intensive highway construction activities may also have resulted in the spikes of turbidity and TSS at the downstream sites. This was supported by the results that no spikes of these water quality parameters were observed during a higher mean flow in March 2007 (i.e., $0.21 \text{ m}^3/\text{s}$; Fig. 3c).

Episodic impacts of iron and aluminum were also observed at the downstream sites during the same event in August 2007 (Fig. 3a and 3b). In the Lost River watershed, spikes of iron were also observed at downstream sites during the highway construction (Chen et al., unpublished data). But the peak value (1.04 mg/L) was smaller than values (9.60 mg/L and 1.89 mg/L) observed in the current watershed (Fig. 4c). In the Roding River of the Great Britain, Extence (1978) also found a peak value of iron with 1.25 mg/L at the downstream site of a motorway construction (Fig. 4c). To our knowledge, there is no report that documented the episodic impacts of aluminum during highway construction. The origin of the increased iron and aluminum may have resulted from disturbed soils and eroded banks from construction activities, and from the construction materials (McLeese and Whiteside, 1977; Eldin, 2002). These spikes should be considered for developing BMPs for future highway construction in the Mid-Atlantic Highlands.

The spikes of turbidity, TSS, iron, and aluminum could impact the biological conditions in streams (Barton, 1977; Cline et al., 1982; Taylor and Roff, 1986; Wellman et al., 2000; Kaller and Hartman, 2004), especially the iron and aluminum (Eldin, 2002). In addition to high concentrations, the frequency and duration of these physicochemical stressors also are important in determining their overall impacts on biological conditions in streams. We only observed one episode of these variables during the first year of the highway construction. After the episode in August 2007, values of all the four impacted variables returned back to typical preconstruction levels. This may suggest a low frequency of these spikes, which also is consistent with results in other studies (Barton, 1977; Cline et al., 1982). The current quarterly sampling plan is not sufficient for evaluating the duration of the impacts. It was noted that studies with more frequent samplings (e.g. weekly or monthly) in other areas also only found spikes of suspended solids

rather than prolonged elevated levels during highway constructions (Barton, 1977; Cline et al., 1982; Taylor and Roff, 1986). The co-occurrence of the TSS spike and those of iron and aluminum in the current study suggests short-term spikes of these two metals during the highway construction. Continued monitoring of these streams is needed to understand the overall long-term impacts of the highway construction on water quality in this Mid-Atlantic Highlands watershed.

5. Conclusion

The Appalachian Corridor H highway had no significant effects on major water quality parameters during its first year's construction in the South Branch Potomac River 3 watershed. One episodic impact of the highway construction on turbidity, TSS, iron, and aluminum was observed. These episodically impaired water quality parameters should be considered in refining BMPs for future highway constructions in the Mid-Atlantic Highlands.

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Table 1. Stream types, names and shortest distances to highway of the monitored streams in the South Branch Potomac River 3 watershed, WV, USA

Site ID	Stream type	Site name	Shortest distance to highway (m)
WB-2	Upstream (US)	Tributary of Toombs Hollow	797
WB-3	Upstream (US)	Upper Walnut Bottom Run	1568
WB-6	Upstream (US)	Tributary near Fisher	7360
WB-1	Downstream (DS)	Upper Toombs Hollow	223
WB-4	Downstream (DS)	Lower Walnut Bottom Run	718
WB-5	Downstream (DS)	Lower Toombs Hollow	845

Table 2. Principal component (PC) factor loadings for water quality of the monitored streams in the South Branch Potomac River 3 watershed, WV, USA

	PC 1	PC 2	PC 3	PC 4	Fina. Commu. Est.
Eigenvalue	4.67	3.02	1.88	1.83	-
% Var. Expl.	0.26	0.17	0.10	0.10	-
Turbidity	0.883	0.054	0.233	-0.057	0.840
Flow	0.383	-0.396	0.178	0.311	0.432
pH	-0.075	-0.112	0.139	0.743	0.589
Conductivity	0.148	0.738	-0.067	0.189	0.606
TSS	0.793	-0.074	0.424	0.125	0.830
Alkalinity	-0.263	0.785	0.390	0.004	0.837
Acidity	-0.018	0.215	-0.094	-0.794	0.685
Sulfate	0.551	-0.104	-0.717	0.125	0.844
Chloride	0.378	0.095	-0.701	-0.076	0.648
Iron	0.889	-0.070	0.193	-0.070	0.838
Calcium	-0.134	0.833	-0.015	0.081	0.719
Magnesium	0.241	0.769	-0.358	0.144	0.799
Manganese	0.817	0.136	-0.011	0.067	0.690
Aluminum	0.789	0.104	0.233	-0.190	0.724
Nitrite	0.533	0.144	0.080	-0.378	0.454
Nitrate	-0.233	0.384	0.419	-0.073	0.383
Ammonia	0.151	0.049	-0.126	0.112	0.054
Phosphate	0.219	0.351	-0.080	0.490	0.418

Note: % Var. Expl. = % Variance Explained; Water Temp. = Water Temperature; Fina. Commu. Est. = Final Communality Estimate. Significant principal component loadings (i.e., absolute values ≥ 0.3) are bolded.

Table 3. Results of paired *t*-test comparisons of water quality PC 1 and PC 2 (Mean $\pm$ S.E.) between the upstream and downstream sites in the two monitoring periods of the highway construction in the South Branch Potomac River 3 watershed, WV, USA

Variable	Period	Stream type		DF	<i>t</i> -value	<i>P</i> -value
		Upstream (Mean $\pm$ S.E.)	Downstream (Mean $\pm$ S.E.)			
PC 1	Before	-0.15 $\pm$ 0.11	0.03 $\pm$ 0.10	48	-1.07	0.2896
	During	-0.01 $\pm$ 0.31	0.43 $\pm$ 0.59	12	-0.71	0.4933
PC 2	Before	-0.17 $\pm$ 0.19	0.05 $\pm$ 0.09	48	-0.97	0.3394
	During	0.14 $\pm$ 0.28	0.26 $\pm$ 0.13	12	-0.58	0.5738

Note: Construction periods: before = March/2002 ~ August/2006, during = September/2006 ~ November/2007. Statistically significant differences were identified when $P < 0.05$. S.E. = standard error; DF = degree of freedom.

Table 4 Water quality trend (Mean $\pm$ S.E.) comparisons between the two monitoring periods for each of the two stream types in the South Branch Potomac River 3 watershed, WV, USA

Variable	Construction period and mean trend	Stream type			
		Upstream		Downstream	
		Mean $\pm$ S.E.	N	Mean $\pm$ S.E.	N
Turbidity (NTU)	Before	6.41 $\pm$ 1.40	53	12.50 $\pm$ 2.34	62
	During	15.24 $\pm$ 8.58	18	111.58 $\pm$ 72.30	17
	Trend	+8.83		+90.08	
Flow (m ³ /s)	Before	0.071 $\pm$ 0.02	52	0.146 $\pm$ 0.02	63
	During	0.032 $\pm$ 0.01	18	0.084 $\pm$ 0.02	17
	Trend	-0.039		-0.062	
pH	Before	8.01 $\pm$ 0.03	53	8.16 $\pm$ 0.03	63
	During	8.16 $\pm$ 0.06	18	8.22 $\pm$ 0.05	17
	Trend	+0.15		+0.06	
Conductivity (μ s/cm)	Before	386 $\pm$ 12.10	53	398 $\pm$ 6.39	63
	During	430 $\pm$ 18.76	18	412 $\pm$ 20.78	17
	Trend	+44		+14	
TSS (mg/L)	Before	4.74 $\pm$ 0.96	53	12.11 $\pm$ 1.44	63
	During	6.21 $\pm$ 2.74	18	49.84 $\pm$ 31.99	17
	Trend	+1.47		+37.73	
Alkalinity (mg/L as CaCO ₃)	Before	158 $\pm$ 6.55	53	186 $\pm$ 3.55	62
	During	178 $\pm$ 10.85	18	192 $\pm$ 5.92	17
	Trend	+20		+6	
Acidity (mg/L as CaCO ₃)	Before	3.44 $\pm$ 0.39	50	2.33 $\pm$ 0.31	59
	During	9.07 $\pm$ 1.49	15	7.44 $\pm$ 1.35	14
	Trend	+5.63		+5.11	
Sulfate (mg/L)	Before	64.17 $\pm$ 3.56	53	45.24 $\pm$ 2.53	63
	During	78.61 $\pm$ 8.19	18	62.55 $\pm$ 8.00	17
	Trend	+14.44		+17.31	
Chloride (mg/L)	Before	4.20 $\pm$ 0.42	53	2.33 $\pm$ 0.18	63
	During	5.32 $\pm$ 0.80	18	2.88 $\pm$ 0.28	17
	Trend	+1.12		+0.55	

Note: Construction periods: before = March/2002 ~ August/2006, during = September/2006 ~ November/2007. Water quality parameters with a trend at the downstream sites larger than five times of that at the upstream sites are highlighted in bold.

Table 4 (Continued)

Variable	Construction period and mean trend	Stream type			
		Upstream		Downstream	
		Mean $\pm$ S.E.	N	Mean $\pm$ S.E.	N
Iron (mg/L)	Before	0.20 $\pm$ 0.04	53	0.31 $\pm$ 0.04	63
	During	0.25 $\pm$ 0.09	18	0.83 $\pm$ 0.56	17
	Trend	+0.05		+0.52	
Calcium (mg/L)	Before	61.87 $\pm$ 1.99	53	66.18 $\pm$ 1.09	63
	During	69.53 $\pm$ 2.88	18	71.19 $\pm$ 1.78	17
	Trend	+7.66		+5.01	
Magnesium (mg/L)	Before	9.87 $\pm$ 0.50	53	8.58 $\pm$ 0.19	63
	During	10.62 $\pm$ 0.79	18	9.29 $\pm$ 0.36	17
	Trend	+0.75		+0.71	
Manganese (mg/L)	Before	0.03 $\pm$ 0.00	53	0.04 $\pm$ 0.00	63
	During	0.03 $\pm$ 0.01	18	0.03 $\pm$ 0.01	17
	Trend	0.00		-0.01	
Aluminum (mg/L)	Before	0.09 $\pm$ 0.02	53	0.13 $\pm$ 0.01	63
	During	0.23 $\pm$ 0.09	18	0.84 $\pm$ 0.62	17
	Trend	+0.14		+0.71	
Nitrite (mg/L)	Before	0.013 $\pm$ 0.00	53	0.018 $\pm$ 0.01	63
	During	0.018 $\pm$ 0.01	15	0.020 $\pm$ 0.01	14
	Trend	+0.005		+0.002	
Nitrate (mg/L)	Before	0.871 $\pm$ 0.17	53	0.865 $\pm$ 0.11	63
	During	0.500 $\pm$ 0.09	15	0.638 $\pm$ 0.10	14
	Trend	-0.371		-0.227	
Ammonia (mg/L)	Before	0.029 $\pm$ 0.01	53	0.032 $\pm$ 0.01	63
	During	0.023 $\pm$ 0.01	18	0.036 $\pm$ 0.01	17
	Trend	-0.006		+0.004	
Phosphate (mg/L)	Before	0.038 $\pm$ 0.00	53	0.033 $\pm$ 0.00	63
	During	0.010 $\pm$ 0.00	18	0.008 $\pm$ 0.00	17
	Trend	-0.028		-0.025	

Note: Construction periods: before = March/2002 ~ August/2006, during = September/2006 ~ November/2007. Water quality parameters with a trend at the downstream sites larger than five times of that at the upstream sites are highlighted in bold.

Fig. 1 Locations of highway and monitored upstream (US) and downstream (DS) sites in the South Branch Potomac River 3 watershed, WV, USA

Fig. 2 Variations (Mean + 1SD) of (a) turbidity and (b) total suspended solids (TSS) at the upstream and downstream sites in two monitoring periods (before and during the highway construction) in the South Branch Potomac River 3 watershed, WV, USA. A vertical and dashed line was used to separate the two periods in each graph.

Fig. 3 Variations (Mean + 1SD) of (a) total iron, (b) total aluminum (Al), and (c) flow at the upstream and downstream sites in two monitoring periods (before and during the highway construction) in the South Branch Potomac River 3 watershed, WV, USA. A vertical and dashed line was used to separate the two periods in each graph.

Fig. 4 Comparison of peak values for (a) turbidity (JTU for the Meginniss Arm Tributary in Florida and NTU for others), (b) TSS (mg/L), and (c) iron (mg/L) in different study areas. Each bar was labeled with value and flow condition. Values in other regions were obtained from literature (Burton et al., 1976; Barton, 1977; Extence, 1978; Cline et al., 1982; Anderson and Potts, 1987; Chen et al., 2008).

Chapter 4 - Responses of streams in Central Appalachian Mountain Region to reduced acidic deposition—Comparisons with Other Regions in North America and Europe

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ABSTRACT

Data from 5 wet deposition stations and 21 streams in 1980-2006 were analyzed to investigate chemical responses of streams to reduced acid deposition in central Appalachian Mountain region of West Virginia, USA. Wet deposition of acid anions (i.e., sulfate, nitrate, and chloride) and hydrogen ion decreased significantly during the studied time period. Stream sulfate showed a delayed response to the reduced atmospheric deposition, but decreased significantly in the 2000s ($-5.54 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) and the whole period ($-0.49 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$). No significant trend of stream nitrate+nitrite and chloride was observed. Stream alkalinity increased in the 1990s ($+23.33 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) and the whole period ($+7.26 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$). Stream hydrogen ion decreased in the 1990s ($-0.002 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$), 2000s ($-0.001 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$), and the whole period ($-0.001 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$). Compared with most acidic streams and lakes in the United States and Europe, lower decreasing rate of hydrogen ion and higher increasing rate of alkalinity were observed in the alkaline West Virginia streams in the 1990s. But the relative increase of alkalinity (percent increase based on the initial values) was higher in acidic streams (from negative values or zero to positive values) than that in alkaline West Virginia streams (from $800 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$ to $1200 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$). Total aluminum of the West Virginia streams decreased in the 1990s ($-0.67 \mu\text{mol}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) and the whole period ($-0.22 \mu\text{mol}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$). The current study advanced our understanding of streams' responses to reduced acidic depositions in the Mid-Appalachians since the passage of the 1970 and 1990 United States Amendments of the Clean Air Act (US CAAA).

Keywords: Acidification recovery; Alkaline stream; Regional trends; Sulfate; Alkalinity

1. Introduction

Emissions of sulfur dioxide (SO₂), nitrogen oxides (NO_x) and ammonia (NH₃) are known to cause atmospheric acid deposition and acidification of surface waters. National and international environmental regulations and agreements (e.g., the 1970 and 1990 United States Amendments of the Clean Air Act (US CAAA), the Canada-U.S. Air Quality Agreement 1991, and the Convention on Long-Range Transboundary Air Pollution of the United Nations Economic Commission for Europe (UN-ECE LRTAP)) have resulted in reductions of acid deposition and regional recovery of surface waters in North America and Europe (Stoddard et al., 1999; Evans et al., 2001; Driscoll et al., 2003; Forsius et al., 2003; Jeffries, et al., 2003; Warby et al., 2005).

In the United States, the Congress amended the Clean Air Act in 1970 to enforce regulations regarding air pollution. In 1990, the United States Congress passed Title IV of the Acid Deposition Control Program of the CAAA. Title IV of the 1990 Clean Air Act Amendments was implemented with Phase I beginning in January 1, 1995, and Phase II beginning in January 1, 2000 (USEPA, 2003). The central Appalachian Mountain region, defined as the mountainous areas of Virginia and West Virginia, was exposed to among the highest acidic deposition levels in the nation, and had many chronically acidified streams (Herlihy et al., 1993; Webb, 2004). The passage of the 1990 US CAAA caused a reduction of 28 percent of sulfate and 16 percent of inorganic nitrogen in wet deposition in this area between 1989-1991 and 2004-2006 (USEPA, 2007). Long-term and systematic studies of streams' responses to acid deposition in Virginia have been reported by various authors (Webb et al., 1989; Ryan et al., 1989; Herlihy et al., 1993;

Bulger et al., 1998; Webb et al., 2004). In West Virginia, however, there was no regional long-term study of streams' responses to the declines of acidic deposition.

In this paper, we present long-term trend results obtained from monitoring data at 5 wet deposition sites and 21 stream sites in the central Appalachian Mountain region of West Virginia. Meta-analysis was used to extrapolate the site-specific trends to regional trends for the studied area. The regional trends were compared with those reported for other regions in North America and Europe.

2. Materials and Methods

2.1. Study region

The central Appalachian Mountain region of West Virginia is surrounded by the states of Pennsylvania, Maryland, Virginia, Kentucky and Ohio in eastern United States (Fig. 1). Most of West Virginia is in the Appalachian Plateau physiographic province. The northeast part of the Appalachian Plateau province is the Allegheny Mountain Section, and the eastern boundary of this province is the Allegheny Front. East of the Allegheny Front is from the Valley and Ridge province in the west to the Great Valley subprovince and the Blue Ridge in the east (West Virginia Geological and Economic Survey, 2005). Most of the rocks in West Virginia are sedimentary, and few igneous or metamorphic rocks occur in the State (West Virginia Geological and Economic Survey, 2005).

2.2. Data collection

Wet deposition data from 5 monitoring sites (WV18, WV04, VA13, KY35, and OH49) of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN, 2006) were obtained to represent the regional acid deposition. Three of the monitoring sites (WV18, VA13, and OH49) have data since 1978, and the other two sites (WV04 and KY35) have data since 1983 (Table 1, Fig. 1). The NADP protocols were followed for precipitation collection and major ions measurements (Dossett and Bowersox, 1999; Bigelow et al., 2001). Data in other areas of the NADP/NTN in the United States were reported elsewhere (Stoddard et al., 1998a; Driscoll et al., 2003; Webb et al., 2004; Warby et al., 2005). Seasonal (i.e., winter: December - February, spring: March - May, summer: June - August, and autumn: September - November) precipitation-weighted mean concentrations of hydrogen ion (calculated from pH), sulfate, chloride, nitrate, ammonium, calcium, magnesium, potassium, and sodium were used for trend analyses. The seasonal precipitation volume-weighted concentration of an ion was computed using its ion concentrations within a season weighted by the ratios of the weekly sample volumes to the total volume of all the samples in the season. Cations of calcium, magnesium, potassium, and sodium were added up as the sum of base cations (SBC) in the present analyses (Stoddard et al., 1998a). Due to a change of sample handling/shipping procedures in 1994 for the wet deposition samples, field pHs were used to calculate the concentration of hydrogen ion except years 2005 and 2006 for which laboratory pHs were used because field measurements were discontinued in January 2005. For other ions, the U.S. Geological Survey (USGS) recommended algorithmic models were followed for making corrections to the measurements made before 1994 (Lynch et al., 1996).

Long-term stream chemical data for 21 stream sites were obtained and analyzed. These stream sites are part of the Ambient Water Quality Monitoring (AWQM) Network of the West Virginia Department of Environmental Protection (WVDEP) and have been monitored monthly or seasonally since 1960s (WVDEP, 2006). The sampling sites were located at the mouths of the West Virginia's large streams which were isolated from major industrial complexes and other potential pollution resources (WVDEP, 2006). Detailed characteristics of these stations were presented in Table 1 and Fig. 1. Watershed characteristics such as drainage area, elevation and land cover were obtained from West Virginia State GIS Technical Center using ArcGIS software 9.2 (ESRI, Redlands, California, USA). Water samples were filtered with 0.45 μm membrane filters and the United States Environmental Protection Agency (USEPA) approved methods were used in chemical analyses (USEPA, 1987). Water chemical parameters used in this study include hydrogen ion (calculated from pH), alkalinity, hardness, nitrate + nitrite, chloride, sulfate and total aluminum.

2.3. Statistical analysis

Seasonal precipitation volume-weighted deposition and seasonal stream monitoring data were used for trend analyses. For the stream data, if several values were available for a given season, then the value sampled closest to the middle of each season was used as the observation for that season (van Bell and Hughes, 1984). To assess the wet deposition trends and stream water quality trends after the passage of 1970 CAAA and the two phases of the Title IV of 1990 CAAA, and to make comparisons with other regions convenient, both deposition and stream data were analyzed for three individual time

periods in addition to the whole monitoring period. For deposition data, the three time periods are 1980s (1979-1989), 1990s (1990-1999), 2000s (2000-2006), and the whole period is from 1979 to 2006. For stream data, the three time periods were 1980s (1980-1989), 1990s (1990-1999), 2000s (2000-2006), and the whole period is from 1980 to 2006. Stream sites with fewer than three quarterly samples and less than 5 years of data per decade were excluded from the analysis (Stoddard et al., 1999). One exception was that only 4 years (1996-1999) of chloride data were available for 16 stream sites in 1990s, but they still met the suggested minimum requirement for the trend analysis (van Bell and Hughes, 1984). Detailed site and parameter information are listed in Tables 2 and 3.

The nonparametric Seasonal Kendall Test (SKT; Hirsch et al. 1982) was used to analyze trends of acid-base parameters of deposition and stream data. The SKT is the most commonly used method for detecting site-specific trends in water quality data (Stoddard et al. 1998b) because it can handle non-normal distributions, seasonality, and missing values (Hirsch et al. 1982), and a modified SKT can also accommodate serial correlation (Hirsch and Slack, 1984). The test calculated the Z statistic for each season, and the overall trend was obtained by combining the seasonal Z statistics. The median slope of trends was estimated by Sen's method (Sen, 1968). Applications of these methods were reported elsewhere (Stoddard et al., 1998b; Evans et al., 2001; Driscoll et al., 2003).

To extrapolate individual trends of the 5 deposition sites into a regional deposition trend and infer regional stream responses from the 21 stream sampling stations, a meta-analysis was used to statistically combine the results (i.e., Z scores) from the SKT (van Bell and Hughes, 1984). The heterogeneity of interests (sites, seasons, and interaction of

sites and seasons) was detected by testing the resulting sums of squares of *Z* statistics against a chi-square distribution, and the *P* value of 0.01 was selected as a threshold to define homogeneous trends (van Bell and Hughes, 1984; Mattson et al., 1997; Stoddard et al., 1999). All statistical analyses were conducted using SAS software 9.1 (SAS Institute Inc., Cary, North Carolina, USA).

3. Results

3.1. Regional trends of chemical constituents in wet deposition

The meta-analysis of the 5 NADP/NTN sites found homogeneous regional trends of all deposition chemical constituents in the three time periods and the whole period except site heterogeneity of SBC in the 1990s (Table 2). Deposition of sulfate decreased significantly in the 1990s ($-1.00 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) and the whole period ($-0.80 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) (Table 2; Fig. 2a). Deposition of nitrate decreased significantly in the 2000s ($-0.45 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) and the whole period ($-0.15 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) (Table 2; Fig. 2b). Deposition of ammonia increased significantly in 1990s ($+0.001 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) and the whole period ($+0.04 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) (Table 2; Fig. 2c). Deposition of chloride decreased significantly in the 1980s ($-0.10 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$), 1990s ($-0.05 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) and the whole period ($-0.04 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) (Table 2; Fig. 2d). Deposition of SBC decreased significantly in the 1980s ($-0.85 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) and the whole period ($-0.22 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) (Table 2; Fig. 3a). Deposition of hydrogen ion decreased significantly in the 1990s ($-1.20 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$), 2000s ($-0.94 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$), and the whole period ($-1.15 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) (Table 2; Fig. 3b).

3.2. Regional trends of stream sulfate, nitrate + nitrite, and chloride

Stream sulfate decreased significantly in the 2000s ($-5.54 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) and the whole period ($-0.49 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) (Table 3; Fig. 4a). Stream nitrate + nitrite decreased significantly in the 1990s ($-0.10 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) (Table 3; Fig. 4b). Stream chloride increased significantly in the 1980s ($+14.10 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) and 1990s ($+26.73 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$); and decreased significantly in the 2000s ($-4.21 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) (Table 3; Fig. 4c).

3.3. Regional trends of stream alkalinity, hardness, hydrogen ion, and total aluminum

Stream alkalinity increased significantly in the 1990s ($+23.33 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) and the whole period ($+7.26 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) (Table 3; Fig. 5a). Stream hardness increased significantly in the 1990s ($+63.33 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$), 2000s ($+45.00 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$), and the whole period ($+11.07 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$; this trend should be interpreted with caution because of missing values from 1986 to 1994) (Table 3; Fig. 5b). Stream hydrogen ion increased significantly in the 1980s ($+0.001 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$), and decreased significantly in the 1990s ($-0.002 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$), 2000s ($-0.001 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$), and the whole period ($-0.001 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) (Table 3; Fig. 5c). Stream total aluminum decreased significantly in the 1990s ($-0.67 \mu\text{mol}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) and the whole period ($-0.22 \mu\text{mol}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) (Table 3; Fig. 5d).

4. Discussion

Reduced acid deposition in the central Appalachian Mountain region of West Virginia resulted in chemical improvement of streams which was indicated by increased alkalinity, and decreased hydrogen ion and total aluminum, especially after the passage of the Title IV of the 1990 US CAAA. Stream sulfate in the study region did not show significant decrease until the 2000s even though atmospheric deposition of sulfate

decreased significantly in the 1990s. This was similar to the trend of sulfate in western Virginia streams where no significant trend was observed during 1988-2001 (Webb et al., 2004). But significant decreasing trends were observed in the Shenandoah National Park and northeastern US streams and lakes in the 1990s (Mattson et al., 1997; Stoddard et al., 1999; Driscoll et al., 2003; Webb et al., 2004; Warby et al., 2005). The different responses in these regions may be attributable to differences in soil sulfur retention in the eastern US (Rochelle and Church, 1987; Webb et al., 1989; Webb et al., 2004). In the Shenandoah National Park, Ryan et al. (1989) found the studied watersheds retained about 65% of deposited sulfate in the 1980s. The sulfate retained in watersheds may have been released and delayed the recovery of surface waters (Driscoll et al., 1998). Nonetheless, the overall trend of sulfate in the West Virginia streams decreased significantly for the whole period. This was consistent with the overall decreasing trend in wet deposition. Stream nitrate + nitrite decreased significantly in the 1990s while no significant trends were observed in most other study areas in US and Europe in the contemporary period (Stoddard et al., 1999; Evans et al., 2001; Skjelkvåle et al., 2001; Webb et al., 2004; Warby et al., 2005). But the deposition in West Virginia seemed to have no direct effects on this decrease because no significant deposition trend of nitrate but an increasing trend of ammonium was observed in the 1990s (Table 2). Moreover, the significant decrease of nitrate deposition in the 2000s ($-0.45 \mu\text{eq} \cdot \text{L}^{-1} \cdot \text{yr}^{-1}$) did not result in any homogeneous stream nitrate + nitrite trend in the same time period. In central European streams, inconsistency between nitrogen deposition and stream nitrate trend in the 1990s was attributed to the biotic processes in watersheds (Veselý et al., 2002; Majer et al., 2005). The inconsistent variations of nitrate between deposition and stream water

in West Virginia may be partially attributed to climate variations and related watershed processes such as nitrogen mineralization and nitrification (Murdoch et al., 1998; Driscoll et al., 2001). The significant decreases of chloride deposition in the 1980s, 1990s, and the whole period did not result in corresponding significant decreases of chloride in the streams. These stream chloride trends (i.e., trends in 1980s, 1990s, and the whole period) should be interpreted with caution because of missing values between 1985 and 1995 (Fig. 4c).

In response to declines of acidic anions and hydrogen ion deposition, streams were chemically improving and showed significant increases of alkalinity in the 1990s and the whole time period, and significant decreases of hydrogen ion in the 1990s, 2000, and the whole time period. These results were consistent with the recovery trends (e.g., acid neutralizing capacity (ANC) and pH) reported for other US regions of Massachusetts, New England, and Shenandoah National Park, and Europe (Mattson et al., 1997; Stoddard et al., 1998a; Stoddard et al., 1999; Driscoll et al., 2001; Evans et al., 2001; Moldan et al., 2001; Webb et al., 2004; Majer et al., 2005). Different stream types were considered in this study to make the comparisons of these improving trends more accurate among different regions. First, we categorized the streams or lakes into three types: acidic (i.e., $\text{pH} < 6$ and $\text{ANC} < 50 \mu\text{eq}\cdot\text{L}^{-1}$), near neutral (i.e., $6 < \text{pH} < 7$ and $50 < \text{ANC} < 500 \mu\text{eq}\cdot\text{L}^{-1}$), and alkaline (i.e., $\text{pH} > 7$ and $\text{ANC} > 500 \mu\text{eq}\cdot\text{L}^{-1}$). Based on these criteria, the West Virginia streams are alkaline streams. The streams in the Slavkov Forest are also in this category (Majer et al., 2005). Most reported streams or lakes in Europe and US are in the acidic category (Evans et al., 2001; Moldan et al., 2001; Driscoll et al., 2003; Warby et al., 2005). The reported streams in Massachusetts and

Virginia (western Virginia and Shenandoah National Park) are in near neutral condition (Mattson et al., 1997; Webb et al., 2004). Relatively higher recovery rates of alkalinity or ANC in the 1990s were observed in the alkaline streams (e.g., + 27 $\mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$ in the Slavkov Forest and + 23.33 $\mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$ in West Virginia) and more acidic streams (e.g., + 21.4 $\mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$ in 4 Swedish catchments) (Fig. 6a). Improving trends in other acidic streams and near neutral streams were relatively low (Fig. 6a). For hydrogen ion, the decreasing rates in acidic streams (e.g., -3.100 $\mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$ in 4 Swedish catchments and - 1.600 $\mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$ in 3 Norwegian catchments) were higher than in alkaline streams in West Virginia (i.e., -0.002 $\mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) (Fig. 6b). But increasing trends of hydrogen ion were observed in the Shenandoah National Park and western Virginia (i.e., +0.007 $\mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) (Fig. 6b). In the acidic streams (e.g., streams in the 4 Swedish catchments), larger decreasing rates of hydrogen ion contributed to the increase of ANC. For the alkaline streams in West Virginia, the decreasing rate of hydrogen ion was smaller. But the smaller decreasing rate in pH range of 7 – 8 as found in West Virginia streams still caused larger increases of alkalinity than those in the acidic streams based on the observed alkalinity levels in the streams and bicarbonate chemistry (Drever, 1997). The difference is that the alkalinity increased from negative values or zero to positive values in most acidic streams while from 800 $\mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$ to 1200 $\mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$ in the alkaline West Virginia streams. Limestone treatment in some acid impacted watersheds may also contribute partly to the higher alkalinity improvements in some West Virginia streams (McClurg et al., 2007).

In addition to ANC and pH, aluminum is also an important indicator of chemical recovery of aquatic ecosystems from acidic deposition (Warby et al., 2005). In the 21

West Virginia streams, total aluminum showed a significant decline in the 1990s and the whole period. Decreasing aluminum trends were also reported in the northeastern US and the 8 European Countries (Evans et al., 2001; Warby et al 2005). However, the recovery aluminum species in those acidic lakes and streams in the northeastern US and Europe were mostly toxic forms of inorganic aluminum (e.g., Al^{3+} , $\text{Al}(\text{OH})^{2+}$, and $\text{Al}(\text{OH})_2^+$) based on the reported pH range (Drever, 1997). In alkaline West Virginia streams, the nontoxic $\text{Al}(\text{OH})_4^-$ was likely the dominant inorganic aluminum for pH 7 - 8 (Drever, 1997). The solubility of gibbsite and kaolinite increases as pH increases from 7 to 8 which suggested an increasing trend of aluminum in water (Drever, 1997). However, this is not consistent with the aluminum decreasing trend in the West Virginia streams (Fig. 5d). The decreasing aluminum trend may be attributed to the significant decreasing trends of sulfate and hydrogen ions deposition over the studied time period (Fig. 2a and 3b). Reduced deposition of sulfate and hydrogen ions could result in reduction of releasing rate of aluminum from soils to streams (Reuss et al., 1987; Palmer and Driscoll, 2002).

5. Conclusions

The present study found homogeneous stream chemical improving trends for sulfate, alkalinity, hydrogen ion, and total aluminum during the period of 1980-2006. This advanced our understanding of stream chemical recovery in the Mid-Appalachians, and helped develop a blueprint for aquatic recovery in the eastern US as a result of the reduced acid deposition. The decreased deposition of acid anions and hydrogen ion may explain the increase of pH and alkalinity in West Virginia streams.

Further research is warranted by the present study. First, it is still unclear about the recovery status of streams to reduced acidification in the eastern, especially the mid-eastern part of West Virginia. Most streams in that region may have similar chemical responses to the reduced acid deposition. However, some of those streams may still have the problems with chronic acidification and low ANC values (Fitzhugh et al., 1999; Sullivan et al., 2007). Secondly, the biological recovery status of streams to reduced acidic deposition in the region is still uncertain. Complete recovery of biological conditions may require longer time, and sufficient recovery of chemical conditions in water and soils (Driscoll et al., 2001).

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Table 1 Stream monitoring sites ($n = 21$), watershed characteristics, and wet deposition sites ($n = 5$) in central Appalachian Mountain region, USA.

Site name	Code	Location	†Area (ha)	‡Elev. (m)	¶Land cover	County	State	Data period
Stream monitoring sites								
Tug Fork at Fort Gay	WTF	38°7'1"N, 82°35'54"W	31352	292	Forest	Wayne	WV	1980- 2006
Twelvepole Creek south of Ceredo	WTP	38°21'20"N, 82°31'1"W	40347	250	Forest	Wayne	WV	1980- 2006
Guyandotte River at Huntington	CGD	38°24'50"N, 82°21'40"W	34962	232	Forest	Cabell	WV	1980- 2006
Little Kanawha River at Elizabeth	WLK	39°3'19"N, 81°23'27"W	57153	269	Forest	Wirt	WV	1980- 2006
Hughes River west of Freeport	WHR	39°7'54"N, 81°22'37"W	16054	281	Forest	Wirt	WV	1980- 2006
Kanawha River at Winfield Locks and Dam	PKR	38°31'37"N, 81°54'45"W	32735	255	Forest	Putnam	WV	1980- 2006
New River at Hinton	SNR	37°39'5"N, 80°53'12"W	79835	643	Forest	Summers	WV	1980- 2006
Greenbrier River at Hinton	SGR	37°39'3"N, 80°51'31"W	35325	625	Forest	Summers	WV	1980- 2006
Gauley River at Beech Glen	FNR	38°9'3"N, 81°10'47"W	30045	542	Forest	Fayette	WV	1980- 2006
Kanawha River west of Chelyan	KKR	38°11'52"N, 81°29'47"W	38738	453	Forest	Kanawha	WV	1980- 2006
Coal River at Tornado	KCR	38°20'20"N, 81°50'27"W	7299	263	Forest	Kanawha	WV	1980- 2006
Elk River at Coonskin Park	KER	38°23'6"N, 81°35'8"W	9574	271	Forest	Kanawha	WV	1980- 2006
Cacapon River south of Great Cacapon	MCR	39°34'55"N, 78°18'33"W	14161	333	Forest	Morgan	WV	1980- 2006
Cheat River at Albright	PCR	39°29'42"N, 79°38'42"W	19196	612	Forest	Preston	WV	1980- 2006
Monongahela River north of Morgantown	MMR	39°39'29"N, 79°59'35"W	8900	354	Forest	Monong alia	WV	1980- 2006
Dunkard Creek east of Pentress	MDC	39°42'53"N, 80°6'39"W	28138	384	Forest	Monong alia	WV	1980- 2006
Opequon Creek east of Bedington	BOC	39°31'1"N, 77°53'23"W	44792	176	G/Forest	Berkeley	WV	1980- 2006
Shenandoah River at Harpers Ferry	JSR	39°19'22"N, 77°44'33"W	4805	156	G/Forest	Jefferson	WV	1980- 2006
South branch of Potomac east of Springfield	HSP	39°26'49"N, 78°39'16"W	70263	381	Forest	Hampshi re	WV	1980- 2006
Tygart Valley River at Colfax	MTV	39°26'7"N, 80°8'0"W	19259	397	Forest	Marion	WV	1980- 2006
West Fork River at Enterprise	HWF	39°25'24"N, 80°16'34"W	13986	350	Forest	Harrison	WV	1980- 2006
Wet deposition sites								
Parsons	WV18	39°5'22"N, 79°39'43"W	—	505	—	Tucker	WV	1979- 2006
Babcock State Park	WV04	37°58'46"N, 80°57'9"W	—	753	—	Fayette	WV	1983- 2006
Horton's Station	VA13	37°19'45"N, 80°33'28"W	—	916	—	Giles	VA	1979- 2006
Clark State Fish Hatchery	KY35	38°7'5"N, 83°32'48"W	—	204	—	Rowan	KY	1983- 2006
Caldwell	OH49	39°47'34"N, 81°31'51"W	—	276	—	Noble	OH	1979- 2006

Note: †Area = drainage area; ‡Elev. = elevation, i.e., mean elevation of watershed for each stream site and station elevation for each deposition site; †Land cover: G/Forest = Grassland + Forest.

Table 2. Results of homogeneity tests for volume-weighted wet deposition trends in central Appalachian Mountain region, USA

Parameter	Decade	Stations		Seasons		Station * Season		Trend		Slope ($\mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$)
		χ^2 (df)	P	χ^2 (df)	P	χ^2 (df)	P	χ^2 (df)	P	
Sulfate	1980s	4.32 (4)	ns	2.58 (3)	ns	8.58 (12)	ns	0.05 (1)	ns	+0.00
	1990s	4.22 (4)	ns	6.74 (3)	ns	7.47 (12)	ns	18.75 (1)	<0.001	-1.00
	2000s	1.52 (4)	ns	3.36 (3)	ns	12.49 (12)	ns	0.98 (1)	ns	-0.50
	Whole period	13.21 (4)	ns	3.33 (3)	ns	9.64 (12)	ns	183.38 (1)	<0.001	-0.80
Nitrate	1980s	2.07 (4)	ns	2.51 (3)	ns	10.84 (12)	ns	0.18 (1)	ns	-0.26
	1990s	12.07 (4)	ns	1.59 (3)	ns	7.87 (12)	ns	0.41 (1)	ns	+0.03
	2000s	2.78 (4)	ns	7.97 (3)	ns	11.08 (12)	ns	7.00 (1)	<0.01	-0.45
	Whole period	18.67 (4)	<0.001	8.61 (3)	ns	15.87 (12)	ns	39.5 (1)	<0.001	-0.15*
Ammonium	1980s	3.01 (4)	ns	2.03 (3)	ns	10.49 (12)	ns	0.55 (1)	ns	+0.21
	1990s	7.96 (4)	ns	2.91 (3)	ns	4.42 (12)	ns	4.37 (1)	<0.05	+0.001
	2000s	0.93 (4)	ns	5.76 (3)	ns	15.62 (12)	ns	0.05 (1)	ns	+0.19
	Whole period	6.61 (4)	ns	3.77 (3)	ns	16.38 (12)	ns	9.31 (1)	<0.01	+0.04
Chloride	1980s	0.26 (4)	ns	2.42 (3)	ns	7.20 (12)	ns	7.65 (1)	<0.01	-0.10
	1990s	4.94 (4)	ns	8.29 (3)	ns	8.97 (12)	ns	11.54 (1)	<0.001	-0.05
	2000s	1.34 (4)	ns	0.65 (3)	ns	11.32 (12)	ns	0.02 (1)	ns	-0.00
	Whole period	9.38 (4)	ns	6.56 (3)	ns	13.37 (12)	ns	86.65 (1)	<0.001	-0.04
SBC	1980s	4.36 (4)	ns	2.34 (3)	ns	3.62 (12)	ns	46.54 (1)	<0.001	-0.85
	1990s	18.14 (4)	<0.001	1.61 (3)	ns	9.33 (12)	ns	0.00 (1)	ns	-0.18
	2000s	1.82 (4)	ns	0.52 (3)	ns	4.31 (12)	ns	0.09 (1)	ns	-0.01
	Whole period	33.48 (4)	<0.001	7.50 (3)	ns	7.32 (12)	ns	84.05 (1)	<0.001	-0.22*
H+	1980s	7.74 (4)	ns	5.74 (3)	ns	8.11 (12)	ns	0.16 (1)	ns	-0.74
	1990s	5.68 (4)	ns	1.33 (3)	ns	9.66 (12)	ns	21.22 (1)	<0.01	-1.20
	2000s	7.43 (4)	ns	0.76 (3)	ns	10.88 (12)	ns	6.23 (1)	<0.05	-0.94
	Whole period	14.13 (4)	<0.01	6.07 (3)	ns	7.67 (12)	ns	144.51 (1)	<0.001	-1.15*

Notes: Significant heterogeneity is indicated by $P < 0.01$ (in bold). Significant trends are indicated by $P < 0.05$ (in bold). “ns” = not significant. “ χ^2 ” = Chi-square values (i.e., the Type I sums of squares which resulted from an analysis of variance performed on Z scores of the Seasonal Kendall Tests). “df” = degree of freedom. Trend results for variables are invalid if significant heterogeneity was detected in any of the sources of variance interested (stations, seasons, and the interaction of station and season). The unit of slope is $\mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$. SBC = sum of base cations (Ca^{2+} , Mg^{2+} , K^{+} and Na^{+}). *Trends are considered valid because all the stations showed decreasing trends.

Table 3. Results of homogeneity tests for stream surface water trends in central Appalachian Mountain region, USA.

Parameter	Decade	Streams		Seasons		Stream * Season		Trend		Slope ($\mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$)
		χ^2 (df)	P	χ^2 (df)	P	χ^2 (df)	P	χ^2 (df)	P	
Sulfate	1980s	44.68 (18)	<0.001	4.15 (3)	ns	36.45 (54)	ns	1.32 (1)	ns	+11.18
	1990s	22.28 (17)	ns	10.20 (3)	ns	39.49 (51)	ns	2.21 (1)	ns	+0.00
	2000s	25.41 (18)	ns	2.02 (3)	ns	49.55 (54)	ns	5.29 (1)	<0.05	-5.54
	Whole period	164.27 (18)	<0.001	6.77 (3)	ns	43.55 (54)	ns	15.81 (1)	<0.001	-0.49*
Nitrate+ Nitrite	1980s	40.64 (20)	<0.01	2.91 (3)	ns	65.75 (60)	ns	0.31 (1)	ns	-0.08
	1990s	18.81 (15)	ns	1.61 (3)	ns	23.71 (45)	ns	6.81 (1)	<0.01	-0.10
	2000s	41.81 (20)	<0.01	2.30 (3)	ns	48.23 (60)	ns	10.39 (1)	<0.01	+0.20
	Whole period	94.04 (20)	<0.001	24.47 (3)	<0.001	50.51 (60)	ns	0.01 (1)	ns	0.00
Chloride	1980s	18.82 (19)	ns	3.35 (3)	ns	48.76 (57)	ns	6.54 (1)	<0.05	+14.10
	1990s	14.94 (15)	ns	1.62 (3)	ns	26.82 (45)	ns	28.56 (1)	<0.001	+26.73
	2000s	28.81 (20)	ns	3.51 (3)	ns	48.96 (60)	ns	9.05 (1)	<0.01	-4.21
	Whole period	62.26 (19)	<0.001	16.13 (3)	<0.01	50.39 (57)	ns	3.31 (1)	ns	0.00
Alkalinity	1980s	28.62 (20)	ns	14.42 (3)	<0.01	56.98 (60)	ns	0.16 (1)	ns	+0.00
	1990s	47.21 (20)	<0.001	1.65 (3)	ns	32.41 (60)	ns	66.48 (1)	<0.001	+23.33*
	2000s	17.67 (20)	ns	4.66 (3)	ns	43.71 (60)	ns	0.07 (1)	ns	+0.00
	Whole period	120.09 (20)	<0.001	2.38 (3)	ns	43.92 (60)	ns	108.63 (1)	<0.001	+7.26*
Hardness	1980s	33.21 (19)	ns	7.11 (3)	ns	56.09 (57)	ns	2.36 (1)	ns	+31.67
	1990s	13.15 (18)	ns	9.75 (3)	ns	42.87 (54)	ns	14.85 (1)	<0.001	+63.33
	2000s	14.70 (20)	ns	7.88 (3)	ns	47.29 (60)	ns	25.89 (1)	<0.001	+45.00
	Whole period	114.80 (20)	<0.001	10.89 (3)	ns	40.99 (60)	ns	90.07 (1)	<0.001	+11.07* #
H+	1980s	37.34 (20)	ns	1.58 (3)	ns	31.60 (60)	ns	15.79 (1)	<0.001	+0.001
	1990s	18.06 (8)	ns	3.27 (3)	ns	11.04 (24)	ns	27.85 (1)	<0.001	-0.002
	2000s	21.76 (20)	ns	10.00 (3)	ns	51.91 (60)	ns	7.33 (1)	<0.01	-0.001
	Whole period	70.20 (20)	<0.001	5.93 (3)	ns	35.84 (60)	ns	111.25 (1)	<0.001	-0.001*
Tot. Al	1980s	7.60 (11)	ns	5.00 (3)	ns	34.28 (33)	ns	0.44 (1)	ns	-0.25
	1990s	22.68 (16)	ns	1.47 (3)	ns	35.99 (48)	ns	20.1 (1)	<0.001	-0.67
	2000s	9.57 (16)	ns	11.46 (3)	<0.01	46.35 (48)	ns	0.19 (1)	ns	-0.00
	Whole period	50.86 (16)	<0.001	2.54 (3)	ns	38.90 (48)	ns	52.69 (1)	<0.001	-0.22*

Notes: Significant heterogeneity is indicated by $P < 0.01$ (in bold). Significant trends are indicated by $P < 0.05$ (in bold). “Nitrate + Nitrite” = nitrate plus nitrite. “ns” = not significant. “ χ^2 ” = Chi-square values (i.e., the Type I sums of squares which resulted from an analysis of variance performed on Z scores of the Seasonal Kendall Tests). “df” = degree of freedom. Trend results for variables are invalid if significant heterogeneity was detected in any of the sources of variance interested (streams, seasons, and the interaction of stream and season). The unit of slope is $\mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$ except Total Al ($\mu\text{mol}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$). Tot. Al = total aluminum. *Trends are considered valid because more than 16 of the 21 streams showed either increasing or decreasing trends. # Trend of hardness in the whole period should be interpreted with caution because of the missing values between 1986 and 1994.

Fig.1 Study region and location of long-term monitoring sites for wet deposition ($n = 5$, indicated by asterisks, data from National Atmospheric Deposition Program/National Trends Network) and stream water quality ($n = 21$, indicated by triangles, data from Ambient Water Quality Monitoring Network of West Virginia Department of Environmental Protection) in central Appalachian Mountain region, USA.

Fig. 2 Wet deposition trends (median of volume-weighted concentrations from 1979 to 2006) of sulfate (a), nitrate (b), ammonium (c), and chloride (d) at five monitoring stations in central Appalachian Mountain region, USA. Significant trends ($P < 0.05$) are indicated by the regression lines.

Fig. 3 Wet deposition trends (median of volume-weighted concentrations from 1979 to 2006) of sum of base cations (SBC) (a) and hydrogen ion (b) at five monitoring stations in central Appalachian Mountain region, USA. Significant trends ($P < 0.05$) are indicated by the regression lines.

Fig. 4 Stream water trends (median of volume-weighted concentrations from 1980 to 2006) of sulfate (a), nitrate +nitrite (b), and chloride (c) at 21 streams in central Appalachian Mountain region, USA. Significant trend ($P < 0.05$) is indicated by the regression line. The gap between two parallel dashed lines is to represent the missing values.

Fig. 5 Stream water trends (median of volume-weighted concentrations from 1980 to 2006) of alkalinity (a), hardness (b), hydrogen ion (c), and total aluminum (d) at 21 streams in central Appalachian Mountain region, USA. Significant trends ($P < 0.05$) are indicated by the regression lines. The gap between two parallel dashed lines is to represent the missing values. Trend of hardness in the whole period should be interpreted with caution because of missing values between 1986 and 1994.

Fig. 6 Regional trends comparisons of alkalinity or acid neutralizing capacity (ANC) (a) and hydrogen ion (b) in different types of streams and lakes (i.e., acidic, neutral, and alkaline) in Europe and North America in 1990s. The three types of streams and lakes are separated by two horizontal lines on the Y axis labels. Results for other study regions were obtained from the literature (Mattson et al., 1997; Evans et al., 2001; Moldan et al., 2001; Driscoll et al., 2003; Webb et al., 2004; Majer et al., 2005; Warby et al., 2005).

**Chapter 5 - Watershed Attributes Regulated Stream Sensitivity to Reduced
Acidic Deposition in Central Appalachian Mountains: Latent Growth Curve
Modeling with Structural Equations**

(This chapter is written in the format of the *Ecological Modeling* and will be submitted for publication soon-

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Abstract

Little information was available about the effects of watershed attributes on long-term stream chemical responses to reduced acidic deposition in the central Appalachian Mountains. Long-term chemical data (1980 – 2006) for 21 stream sites in this region and data of 8 watershed attributes of the corresponding subwatersheds were analyzed to study such effects. Latent growth curve modeling (LGM), a structural equation modeling (SEM) approach, was conducted to quantify stream sensitivity to reduced acidic deposition, and to characterize the initial chemical conditions (intercepts) and changing rates (slopes) in three time periods: 1980s, 1990s, and 2000s. The modeled chemical trends were generally consistent with those trends which were detected by trend analyses in a previous study. Watershed attributes including area, mean elevation, percentage of developed area, percentage of grassland, percentages of shale and sandstone, percentage of barren land, and percentage of soil type Gilpin-Upshur-Vandalia (GUV) were found to affect stream' sensitivity to reduced acidic deposition with their importance in the respective order. The stream's sensitivity in turn regulated stream chemical initial conditions and their changing rates in the studied watersheds. This innovative application of LGM for modeling long-term chemical trends advanced our understanding of the role of watershed attributes in regulation of stream's responses to reduced acidic deposition in the central Appalachian Mountains.

Keywords: Acidic deposition; Watershed attributes; Structural equation model (SEM); Latent growth curve model (LGM), Stream sensitivity, Chemical trends

1. Introduction

The passages of environmental regulations such as the 1970 and 1990 Amendments to the United States Clean Air Act (USCAAA) have resulted in regional reductions of acidic deposition from the atmosphere. It also has been demonstrated or predicted that the reduced acidic deposition was the major driving force of regional recovery of North American and European streams and lakes either based on long-term trend analysis (e.g., Stoddard et al., 1999; Driscoll et al., 2001; Evans et al., 2001; Jeffries, et al., 2003; Webb et al., 2004; Chen and Lin, 2009) or watershed biogeochemical modeling (Cosby et al., 1985; Wright et al., 1990; Driscoll et al., 1994; Krám et al., 1999; Gbondo-Tugbawa et al., 2001; Gbondo-Tugbawa et al., 2002; Larssen et al., 2003; Chen and Driscoll, 2004; Chen and Driscoll, 2005). In addition to this major driving force, landscape or watershed attributes (e.g., landcover, elevation, watershed area, soil types, and bedrock geology) also can affect chemical concentrations in water bodies (Herlihy et al., 1998; Quinlan et al., 2003; Wayland et al., 2003; Williams et al., 2005; Cory et al., 2006).

In the US central Appalachian Mountains, improving trends of stream sulfate, alkalinity, hydrogen ion, and total aluminum in response to reduced acidic deposition over the period of 1980 – 2006 have been observed (Chen and Lin, 2009). However, it is still not clear how watershed attributes affected these long-term trends at the subwatershed level. Further, we did not find reasonable explanations for interpreting the inconsistent chemical trends between wet deposition and streams for chloride and nitrate (Chen and Lin, 2009). Recent studies in the Appalachian Mountains have found that watershed attributes may regulate a stream's vulnerability to acidic deposition or affect the spatial distribution of sensitive streams (Deviney et al., 2006; Sullivan et al., 2007). However, some of these studies only considered the effects of watershed attributes on stream sensitivity based on sampling data from one or a few sampling

events. To our knowledge, there was little information available about the role of these watershed attributes in a stream's long-term chemical responses to acidic deposition in these Appalachian Mountains. Further, there was little information available about how a stream's sensitivity or vulnerability to acidic deposition can be quantified.

In the current paper, long-term chemical data from 21 stream sites and watershed attributes of the corresponding subwatersheds in the central Appalachian Mountains were used to conduct latent growth curve modeling (1) to characterize the streams' initial chemical conditions and compare the modeled long-term changing rates (trends or slopes) with documented trends detected by trend analysis in a previous study (Chen and Lin, 2009); (2) to quantify stream sensitivity to reduced acidic deposition in the region; and (3) to establish causal relations among watershed attributes, stream sensitivity, and chemical conditions.

2. Materials and Methods

2.1 Background of SEM and LGM

Structural equation modeling (SEM) is an advanced multivariate statistical approach with which a researcher can construct theoretical concepts; test multivariate relations within and between observed (measured) and latent (unobserved or conceptual) variables; and confirm proposed causal relations based on two or more structural equations (Bollen, 1989; Mitchell, 1994; Hoyle, 1995; Malaeb et al., 2000; Reckhow et al., 2005; Grace, 2006). The method depends on the correlation or covariance matrix of modeled variables to find the causal relationships between the variables. The historic background of SEM can be traced back to the research of the biologist Sewall Wright (1921, 1934). Since its initial application in early 1920s and 1930s in natural sciences (Wright, 1921; 1934), SEM has been extensively developed in

social sciences, especially in sociology, education, and psychology (Jöreskog, 1981; Jöreskog and Sörbom, 1982; Tanaka, 1987; Bollen, 1989; Bollen and Long, 1993; Jöreskog and Sörbom, 1993a; Hoyle, 1995; Bentler, 1995; Mueller, 1996; Kaplan, 2000; Kline, 2005; Hancock and Mueller, 2006). After the 1990s, especially the late 1990s, there is an increasing trend of applications of SEM in natural sciences (Mitchell, 1992; 1994; Petraitis et al., 1996; Smith et al., 1997; Pugesek and Grace, 1998; Palomares et al., 1998; Grace and Pugesek, 1998; Shipley, 1999; Pugesek et al., 2003; Iriondo et al., 2003; Vile et al., 2006; Grace, 2006; Laughlin et al., 2007; Harrison and Grace, 2007; Grace and Bollen, 2008). This increasing trend of SEM applications is also found in aquatic sciences in the past decade (Grace and Pugesek, 1997; Malaeb et al., 2000; Stow and Borsuk, 2003; Reckhow et al., 2005; Arhonditsis et al., 2006; Arhonditis et al., 2007).

Compared with other methods such as multiple regression, traditional path analysis or principal components analysis, SEM provides more support for questions of causation between variables because of its capabilities of modeling measurement error and eliminating estimated bias and distortion (Pugesek and Tomer, 1995; Iriondo et al., 2003). The null hypothesis (H_0) formulation of a SEM is:

$$H_0: \Sigma = \Sigma(\theta),$$

where Σ is the sample covariance matrix of the observed variables, $\Sigma(\theta)$ is a specified model-implied covariance matrix, and θ is a vector that contains the free parameters of the model (Bollen, 1989; Bollen and Long, 1993). SEMs minimize the differences between the observed covariances and the model predicted covariances using the Maximum Likelihood algorithm (Malaeb et al., 2000). In contrast to testing hypotheses in linear models (e.g., ANOVA) where one tends to reject the null hypothesis in favor of the alternative hypothesis, SEM seeks the

acceptance of the null hypothesis which indicates that the specified model fits the data reasonably well (Bollen, 1989; Bollen and Long, 1993; Malaeb et al., 2000). There are five common steps that characterize the model development of most SEM applications: (1) model specification, (2) model identification, (3) parameter estimation, (4) testing model fit (usually a chi-square (χ^2) test is used to test overall fit of the model to the data), and (5) respecification and modification of the model (Bollen and Long, 1993; Malaeb et al., 2000). In the LISREL software environment, model results usually include indices for assessing model fit and model modification. Commonly used indices include chi-square (χ^2), root mean square error of approximation (RMSEA), and 90 percent confidence interval for RMSEA (CI₉₀). Chi-square (χ^2) test is usually used to test overall fit of the model. Models are acceptable if the χ^2 values have an associated p-value greater than 0.05. Value of RMSEA and its accompanied 90 percent confidence interval falling below about 0.05 to 0.08 indicate good model fit (Browne and Cudeck, 1993; Curran and Hussong, 2002).

Latent growth curve modeling (LGM) is an extension of SEM (Kaplan, 2000; Curran and Husson, 2002; Duncan et al., 2006). LGM models initial conditions and changing rates of a variable of interest, and searches predictors for the variable. Similar to traditional SEMs, LGMs can also be analyzed with multiple populations or groups, categorical variables, and missing data (Duncan et al., 2006). The LGM work can be traced back to the work of Rao (1958) and Tucker (1958), later formally defined and developed by McArdle and Epstein (1987) and Meredith and Tisak (1990). The methodology was then further developed and implemented by Willett and Sayer (1994), Duncan (e.g., Duncan and Duncan, 1994; Duncan et al., 1994; Duncan and Duncan, 1996; Duncan et al., 1997; Li et al., 2000; Duncan et al., 2006), Curran (e.g., Curran et al., 1996; Chassin et al., 1996; Biesanz et al., 2004), Muthén (e.g., Muthén, 1997; Muthén and

Khoo, 1998), Barnes et al. (2000), and Stoel et al. (2004). Like the traditional SEMs, however, most of these LGM applications are found in social sciences. Only a few studies documented applications of LGM in natural sciences (Pugesek et al., 2003; Grace and Keeley, 2006; Grace, 2006). To our knowledge, there was no published document that reported applications of LGM in aquatic ecosystems or aquatic sciences.

2.2 Methodology and Applications of LGM

Several features of LGM make it an attractive method. These features center around the method's capability of (1) testing both linear and nonlinear growth functions; (2) incorporating time-invariant and time-varying variables or covariates; (3) modeling interaction effects; and (4) modeling multiple behaviors or variances, covariances, and means simultaneously over time (McArdle and Epstein, 1987; Li et al., 2000; Kaplan, 2000; Stoel et al., 2004; Duncan et al., 2006). Kline (2005) listed three requirements for SEM analysis using LGM: (1) a continuous dependent variable measured on a minimum of three occasions (2) unstandardized scores that have the same units across time and (3) data collected at the same time intervals. To analyze LGM with matrix summaries, either covariances or correlations and standard deviations, and means of all observed variables must be included in these matrix summaries (Kline, 2005).

LGMs often include two modeling steps: (1) modeling change or unconditional growth modeling, and (2) predicting change or conditional growth modeling (Curran and Hussong, 2002; Kline, 2005; Duncan et al., 2006). The first step analyzes a "change" model (i.e. intercept-slope model) that includes only the repeated measured variables. Each repeated measurement is represented as an indicator of two latent growth factors, initial status or intercept and linear change or slope (Kline, 2005). Unstandardized factor loadings of all indicators or measurements

on these two latent growth factors are pre-fixed. The loadings of all indicators on the first latent factor (i.e., intercept) are usually fixed to 1.0 (Kline, 2005; Duncan et al., 2006). In contrast, the loadings on the second latent factor (i.e., slope) are usually fixed to positive and evenly spaced constants corresponding to the repeated measurements (i.e., assuming a positive linear trend) (Kline, 2005; Duncan et al., 2006). The loading of the time 1 measurement on the slope is fixed to 0 which means the slope will be defined based on this time 1 measurement (Kline, 2005). So, the settings of loadings on the intercept are 1, 1, 1, 1, ..., 1 and the settings of loadings on the slope are 1, 2, 3, 4, ..., n or 1, 2, 4, 6, ..., n depending on the overall trend of the data. The initial level can also be based on the time 2 measurement (Kline, 2005; Duncan et al., 2006). As a result, the settings of loadings on the slope may become -1, 0, 1, 2, ..., n. Other forms of loadings settings are presented in detail by Duncan et al (2006). Model results at this step usually include means and standard errors of the intercept and the slope, covariance and its standard error between the intercept and slope, variances and their standard errors of the intercept and slope, and measurement errors for each of the measurements (Kaplan, 2000; Curran and Hussong, 2002; Kline, 2005; Duncan et al., 2006). The second analysis step involves adding variables or predictors to the intercept-slope model that can predict change over time. Some of these predicting or explanatory variables are assumed to be invariant across time or measured only once (i.e., time-invariant variables), and the others vary across time or measured repeatedly like the indicators in the intercept-slope mode (i.e., time-varying variables) (Kaplan, 2000; Curran and Hussong, 2002; Kline, 2005; Grace, 2006). In addition to the results of the intercept-slope model, model results at this step also include means and standard errors of the predictors, direct effects from the predictors to the intercept and slope, variances and covariances of these predictors (Kaplan, 2000; Curran and Hussong, 2002; Kline, 2005; Duncan et al., 2006).

2.3 Study area, stream monitoring, and watershed attributes

The study area is in the central Appalachian Mountains within the state boundary of West Virginia. The study region is mostly in the Appalachian Plateau physiographic province (West Virginia Geological and Economic Survey, 2005). A detailed geographic and physiographic description of the study region is given by Chen and Lin (2009). Long-term (1980 - 2006) monitoring of 21 stream sites of the Ambient Water Quality Monitoring (AWQM) Network was conducted monthly or seasonally by the West Virginia Department of Environmental Protection (WVDEP, 2006). Detailed information of these sampling sites has been presented elsewhere (WVDEP, 2006; Chen and Lin, 2009). ArcGIS software version 9.2 (ESRI, Redlands, California, USA) was used to delineate the subwatershed for each of the sampling sites, and to collect data on watershed attributes for each of the subwatersheds. Watershed areas or drainage areas were obtained directly from the delineated subwatersheds and they ranged from 4,805 ha to 79,835 ha (Chen and Lin, 2009). Mean elevations of the subwatersheds were determined from a 30m* 30m raster cell file of digital elevation models (DEMs). Mean elevations of these subwatersheds ranged from 156 m to 643 m (Chen and Lin, 2009). Within these subwatersheds, land cover percentages were summarized based on the 2001 National Land Cover Database (NLCD). Subwatershed boundaries were overlaid on the NLCD and land cover percentages (e.g., forest, developed, grassland) were calculated in the GIS environment. Most studied subwatersheds have percentages of forest > 70% (Chen and Lin, 2009). Other land cover types were grassland (from 2% to 56%), developed (from 3% to 26%), and barren land (from 0 to 1.88%) (West Virginia State GIS Technical Center). Geology shape files were used to collect geology types which were dominated by shale (from 0 to 85%) and sandstone (from 0 to 100%) (West Virginia State GIS

Technical Center). General soils types were characterized based on the 1: 250 000 State Soil Geographic (STATSGO) database which was published in 1995 and is administered by the Natural Resource Conservation Service (NRCS). The dominant soil type was Gilpin-Upshur-Vandalia (GUV) which ranged from 0 to 82% (West Virginia State GIS Technical Center). Similar watershed data collections with GIS tools and techniques in these central Appalachian Mountains have been reported elsewhere (Chen and Lin, 2009; Chen et al., 2009).

2.4 Data treatment and analysis

Stream chemical parameters (1980 - 2006) used in this study include pH, alkalinity, hardness, nitrate + nitrite, chloride, sulfate and total aluminum (Chen and Lin, 2009). Based on published documents (e.g., Herlihy et al., 1998; Deviney et al., 2006; Sullivan et al., 2007) and preliminary analyses of our dataset, the following 8 watershed attributes were used for LGM analysis: watershed area, mean elevation, percentage of developed land, percentage of grassland, percentage of barren land, percentage of GUV soil, percentage of shale, and percentage of sandstone. To meet the requirement of normality, the 7 stream parameters, watershed area, and mean elevation were natural logarithm transformed (i.e., $\text{LN}(x)$), percentages of land covers (e.g., developed, grassland, barren land), soil type (e.g., GUV) and geology types (e.g. shale and sandstone) were arcsine square root transformed (i.e., $\text{ASIN}(\text{SQRT}(x))$ or $\text{ASIN}(\text{SQRT}(x + 1))$).

Two modeling steps were followed in the current study: (1) data matrix summary preparation, and (2) model syntax construction and model execution. The details of the first step are presented in this paragraph, followed by a detailed description for the second modeling step. In the LISREL software version 8.80 environment (Scientific Software International, Inc., Lincolnwood, Illinois, USA), stream and watershed data were imported from Excel files. The

aforementioned transformations were then performed for the individual variables, followed by descriptive statistics calculation (e.g., correlation matrix, means, and standard deviations) of the dataset with a PRELIS file (Jöreskog and Sörbom, 1993b). An example matrix summary prepared for the next step of the analysis is presented in Table 1.

2.5 Unconditional model and the concepts of intercept and slope

Stream chloride in the 1990s (i.e., 1996 – 1999 for the current dataset) was used as an example to illustrate the unconditional modeling process. In this case, intercept is the initial value of chloride (i.e., chloride in 1996), and slope is the changing rate or trend of chloride in the whole modeled period (i.e., 1996 - 1999). An unconditional model is a latent growth model which does not include any predictors. In SIMPLIS syntax (Jöreskog and Sörbom, 1993a), four observed variables (i.e., chloride in 1996 or Cl96, chloride in 1997 or Cl97, chloride in 1998 or Cl98, and chloride in 1999 or Cl99), correlation matrix, means, and standard deviations of these variables shown in Table 1, and two latent variables (i.e., intercept and slope) were used as model inputs. Commonly used methods (Kaplan, 2000; Curran and Hussong, 2002; Kline, 2005; Duncan et al., 2006) were adopted to pre-set the loadings of the four measurements on the two latent variables. The settings (from Cl96 to Cl99) of loadings on the intercept are 1.0, 1.0, 1.0, and 1.0, and the loadings on the slope are 0.0, 1.0, 2.0, and 3.0. The Maximum Likelihood (ML) algorithm was used to optimize model estimation. Similar procedures also were used for modeling chloride in the other two periods (i.e., chloride in the 1980s and 2000s) and the other 6 stream parameters (i.e., nitrate, sulfate, aluminum, pH, hardness, and alkalinity).

2.6 Conditional model and the concept of stream sensitivity

In this step of analysis, the same settings of the loadings in the unconditional model were used. In addition, the 8 watershed attributes (i.e., watershed area, mean elevation, percentage of developed land, percentage of grassland, percentage of barren land, percentage of GUV soil, percentage of shale, and percentage of sandstone) were added as predictors. The land cover data were treated as time-invariant variables in the current study because they did not change significantly based on aerial photographs taken at different times during the monitoring period (Chen and Lin, 2009). These 8 watershed variables and 4 stream chloride measurements were treated as observed variables in the SIMPLIS. Full matrix summaries of these observed variables were presented in Table 1. In addition to the previously defined intercept and slope, a modeled concept, stream sensitivity to reduced acidic deposition, was included as a latent variable. In the current chloride example, this concept was defined as an individual stream sensitivity to reduced amounts of chloride in wet deposition. In the SIMPLIS syntax, we defined sensitivity as $-1 \times \text{slope}$ which indicated that a stream would be more sensitive to reduced chloride deposition if the stream had larger negative value of chloride slope during the monitoring period. After defining these observed and latent variables, the 8 watershed attributes were treated as indicators of stream sensitivity, and pre-defined paths from the sensitivity to the intercept and the slope were added. Other analysis procedures were the same as those presented in the unconditional model.

3. Results

3.1 Unconditional model of stream chloride in the 1990s

The two-factor unconditional LGM for stream chloride in the 1990s fits the data moderately well ($\chi^2 = 10.97$, $p = 0.20$; RMSEA = 0.15, CI₉₀ = 0.0, 0.35, p (RMSEA < 0.05) = 0.23; Figure 1; Table 2). There was a significant mean estimate for both the intercept (mean = 5.05 $\mu\text{eq} \cdot \text{L}^{-1}$) and

the slope (mean = $0.19 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$) of the stream chloride (Figure 1; Table 2). Furthermore, there was a significant variance estimate for both the intercept (variance = 0.75) and the slope (variance = 0.02) of the stream chloride (Figure 1). Finally, there was a negative but non-significant correlation (coefficient = -0.04) between the intercept and the slope (Figure 1).

3.2 Conditional model of stream chloride in the 1990s

A hypothesized conditional model of stream chloride was developed and fit the data moderately well ($\chi^2 = 77.98$, $p = 0.11$; RMSEA = 0.12, CI₉₀ = 0.0, 0.20, p (RMSEA < 0.05) = 0.16). LISREL software suggested adding covariances between sandstone and shale, and between grassland and sandstone to improve the model fit. After modifications, the final model fit the data significantly better ($\chi^2 = 65.44$, $p = 0.36$; RMSEA = 0.06, CI₉₀ = 0.0, 0.17, p (RMSEA < 0.05) = 0.44; Figure 2; Table 2). There was a significantly positive path coefficient (i.e., 1.34) from stream sensitivity to the intercept (Figure 2; Table 2). All of the 8 watershed attributes positively predicted stream sensitivity. Watershed area (standardized loading = 1.00; unstandardized loading = 19.79), mean elevation (standardized loading = 1.00; unstandardized loading = 5.95), and percentage of developed (standardized loading = 0.96; unstandardized loading = 0.32) were the most relevant predictors (Figure 2; Table 2; only standardized values are presented). For the other 5 predictors, their importance to the sensitivity were percentage of grassland (standardized loading = 0.88; unstandardized loading = 0.36), percentage of shale (standardized loading = 0.84; unstandardized loading = 0.32), percentage of barren (standardized loading = 0.82; unstandardized loading = 0.55) and sandstone (standardized loading = 0.82; unstandardized loading = 0.78), and percentage of GUV (standardized loading = 0.68; unstandardized loading = 0.36) (Figure 2; Table 2; only standardized values are presented).

There were also negative covariances between percentages of shale and sandstone (standardized coefficient = -0.24; unstandardized coefficient = -0.18), and percentages of grassland and sandstone (standardized coefficient = -0.16; unstandardized coefficient = -0.06) (Figure 2; only standardized values are presented). Detailed modeled measurement and structural equations for chloride in the 1990s were presented in Appendix 3. And a sensitivity distribution map was made for the chloride in the 1990s (Appendix 4).

3.3 Model results of stream chloride in the 1980s, 2000s, and other chemical parameters

Table 2 lists model results of all the 7 stream parameters in the three decades which had acceptable model statistics. In addition to the presented model results of chloride in the 1990s, other acceptable models include chloride in the 1980s, nitrate in the 1990s, sulfate in the 2000s, pH in the 1990s, hardness in the 1980s and 1990s, and alkalinity in the 1990s (Table 2). For the unconditional models, there were significant mean estimates for both the intercepts and the slopes except the slopes of sulfate in the 2000s and of hardness in the 1980s (Table 2).

Furthermore, only the model of chloride in the 1980s showed a significantly negative correlation (coefficient = -0.04) between the intercept and the slope (Table 2). For the conditional models, there were significantly positive path coefficients from the stream sensitivity to the intercepts of chloride in the 1980s (coefficient = 9.82), sulfate in the 2000s (coefficient = 9.09), and hardness in the 1990s (coefficient = 6.30), and negative path coefficients from the stream sensitivity to the intercepts of nitrate in the 1990s (coefficient = -2.30), pH in the 1990s (coefficient = -8.19), hardness in the 1980s (coefficient = -2.56), and alkalinity in the 1990s (-3.99) (Table 2). All of the 8 watershed attributes positively predicted the stream sensitivity, and watershed area, mean elevation, and percentage of developed were the most important predictors (Table 2). For the

other 5 predictors, percentage of grassland was the most important predictor except pH in the 1990s where the percentages of grassland and shale had the same loading (i.e., 0.88) on the sensitivity (Table 2). Percentages of shale and sandstone were more important than percentages of barren land and GUV in predicting the stream sensitivity (Table 2). Percentage of GUV was the least important predictor for the stream sensitivity in all the acceptable models (Table 2). Finally, there were significantly negative covariances between percentages of shale and sandstone in 6 of the 8 acceptable models (i.e., chloride in the 1980s and 1990s, nitrate in the 1990s, sulfate in the 2000s, hardness in the 1980s, and alkalinity in the 1990s; Table 2).

4. Discussion

In the unconditional models, the significant mean estimate of the intercept of chloride in the 1990s (mean = $5.05 \mu\text{eq}\cdot\text{L}^{-1}$; Fig. 2; Table 2) indicated significant mean initial concentrations of chloride in 1996. The significant variance of the intercept (variance = 0.75) indicated significant variations of initial conditions of stream chloride among the studied streams in 1996. The similar mean estimates in other accepted models (Table 2) indicated that there were significant mean initial concentrations of chloride in 1980, nitrate in 1990, sulfate in 2000, pH in 1990 and 2000, hardness in 1980 and 1995, and alkalinity in 1990 among the streams. The significantly negative correlation (coefficient = -0.04; Table 2) between the intercept and the slope of chloride in the 1980s indicated that streams with higher initial chloride concentrations tended to have smaller magnitudes of slope in that period.

The significantly positive mean estimate of slope (mean = $0.19 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$; Table 2) and its variance (variance = 0.02) of chloride in the 1990s indicated that chloride increased significantly with site differences in the studied streams during that period. This was consistent with the

results that were obtained from the trend analysis in Chen and Lin (2009) (slope = $3.29 \mu\text{eq}\cdot\text{L}^{-1}\cdot\text{yr}^{-1}$ or LN (26.73)). Similar consistent results also were observed for trends of chloride in the 1980s (mean = $0.05 \mu\text{eq}\cdot\text{L}^{-1}$), nitrate in the 1990s (mean = $-0.05 \mu\text{eq}\cdot\text{L}^{-1}$), sulfate in the 2000s (mean = $-0.03 \mu\text{eq}\cdot\text{L}^{-1}$ but statistically nonsignificant in the current study), pH in the 1990s (mean = $0.05 \text{ pH unit}\cdot\text{L}^{-1}$; negative hydrogen ion trends in Chen and Lin, 2009), hardness in the 1980s (both of the observed trends were nonsignificant), hardness in the 1990s (mean = $0.05 \mu\text{eq}\cdot\text{L}^{-1}$), and alkalinity in the 1990s (mean = $0.05 \mu\text{eq}\cdot\text{L}^{-1}$) (Table 2; Chen and Lin, 2009).

The 8 watershed attributes were found to affect stream sensitivity to reduced acidic deposition in the studied area (Table 2). Their relative importance or contribution to stream sensitivity was generally in this order: watershed area > mean elevation > percentage of developed land > percentage of grassland > percentage of shale > percentage of sandstone > percentage of barren land > GUV (Table 2). Through the stream sensitivity, these watershed attributes influenced chemical initial conditions (i.e., intercepts) and changing rates (i.e., slopes) in the studied streams (Table 2). These results were generally consistent with other watershed-scale studies. For example, elevation, soil types, and watershed area were important watershed features that affected spatial distribution of acid-sensitive and acid-impacted streams in the Southern Appalachian Mountains (Sullivan et al., 2007). Also, the geological sensitivity classes of siliceous (e.g., sandstone) and argillaceous (e.g., shale) were the top two of the six classes which indicated streams with low acid neutralizing capacity (ANC) (i.e., $\text{ANC} < 50 \mu\text{eq/L}$) in this mountain region (Sullivan et al., 2007). Further, it was found that watersheds with smaller drainage areas or underlain by less basaltic/carbonate bedrock were more vulnerable to episodic acidification in Shenandoah National Park, Virginia (Deviney et al., 2006). In a southern Canadian lake district, it was found that bedrock types (i.e., carbonate versus non-carbonate)

strongly influenced spatial gradients of pH and other major ion chemistry (e.g., alkalinity, conductivity, calcium, magnesium, and sulphate) (Quinlan et al., 2003). For the influences from land cover and land use, urban and agriculture typically contributed to chloride, nitrate, sulfate, and ANC in streams (Herlihy et al., 1998; Wayland et al., 2003; Williams et al., 2005). These relations were verified to a certain degree by the current study in which percentage of developed was the third most important predictor for stream sensitivity (Table 2). In the Grand Traverse Bay watershed of Michigan, barren lands were associated with elevated sulfate levels in streams (Wayland et al., 2003). In the current study, however, the barren land was a relatively less important predictor for the stream sensitivity (Table 2). This may have partially resulted from the low percentages of barren land (i.e., 0.1%) in the studied subwatersheds.

Further research interests were warranted from the current study. First, no acceptable model (both unconditional and conditional) of aluminum was found in any of the three modeling periods in the current study (Table 2). However, trend analysis detected significant decreasing trends of aluminum in the 1990s (Chen and Lin, 2009). Also, effects of landscape features on stream water aluminum have been reported in other studies (e.g., Cory et al., 2006). This may reflect the possible limitations of using LGM to identify chemical changing rates and watershed-stream links in the current study. Secondly, the current study only incorporated time-invariant predictors in the LGMs. However, if long-term data with medium or large sample sizes (i.e., $n > 100$ or > 200 ; Kline, 2005) were available, incorporation of time-vary predictors (e.g., loading of acidic deposition) into the models can be performed and it is expected to provide insights into the links and interactions among atmosphere, watershed attributes, and streams.

5. Conclusions

The SEM-based LGMs quantified most stream chemical (i.e., chloride, nitrate, sulfate, pH, hardness, and alkalinity) initial conditions (i.e., intercepts) and their changing rates (i.e., slopes) in the 1980s, 1990s, and 2000s in the central Appalachian Mountains. The chemical slopes or trends identified by all acceptable unconditional models were generally consistent with the trends which were detected by the trend analyses in a previous study. Watershed area, mean elevation, percentage of developed, percentage of grassland, percentage of shale and sandstone, percentage of barren land, and percentage of GUV regulated stream sensitivity to reduced acidic deposition, and further influenced stream chemical initial conditions and their changing rates in these mountain watersheds.

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Tables and Figures

Table 1 Model inputs of correlation matrix, means, and standard deviations of stream chloride (1996 - 1999) and watershed attributes in the central Appalachian Mountains

	1	2	3	4	5	6	7	8	9	10	11	12
1. Cl96	1.000											
2. Cl97	0.955	1.000										
3. Cl98	0.928	0.963	1.000									
4. Cl99	0.834	0.903	0.929	1.000								
5. Area	0.021	-0.004	0.001	0.043	1.000							
6. Elev	0.035	0.010	0.017	0.073	0.423	1.000						
7. Devp	0.209	0.134	0.047	0.059	-0.482	-0.399	1.000					
8. Grass	0.136	0.192	0.093	0.239	-0.078	-0.436	0.460	1.000				
9. Barren	-0.289	-0.336	-0.307	-0.321	0.200	0.300	0.033	-0.117	1.000			
10. GUV	-0.033	-0.108	0.012	-0.074	-0.198	-0.348	0.014	-0.438	-0.309	1.000		
11. Shale	0.194	0.194	0.173	0.131	0.011	0.184	-0.033	-0.207	-0.123	0.190	1.000	
12. Sand	-0.329	-0.372	-0.294	-0.348	0.173	0.200	-0.206	-0.475	0.314	0.055	-0.703	1.000
Mean	5.101	5.219	5.341	5.691	19.248	5.782	0.309	0.350	0.042	0.358	0.633	0.760
S.D.	0.868	0.869	0.784	0.836	0.781	0.398	0.085	0.190	0.031	0.392	0.419	0.511

Note: The numbers of 1 - 12 in the first row represent the 12 corresponding variables that listed in the first column. Cl96 - Cl99 represent stream chloride ($\mu\text{eq}\cdot\text{L}^{-1}$) in the years of 1996 - 1999. Other abbreviations: Area = drainage area (m^2), Elev = mean elevation (m), Devp = developed (%), Grass = grassland (%), Barren = barren land (%), GUV = Gilpin-Upshur-Vandalia (%), Sand = sandstone (%), and S.D. = standard deviation. Data transformations: natural logarithm transformed (i.e., $\text{LN}(x)$) for variables 1 - 6, arcsine square root transformed (i.e., $\text{ASIN}(\text{SQRT}(x))$) for variables 7 - 9, and arcsine square root transformed (i.e., $\text{ASIN}(\text{SQRT}(x + 1))$) for variables 10 - 12.

Table 2 Results of latent growth curve models for stream chloride, nitrate, sulfate, aluminum, pH, hardness, and alkalinity in three decades (1980s, 1990s, and 2000s) in the central Appalachian Mountains

		Int	Slp	Int-Slp	Sens-Int	Sens-Area	Sens-Elev	Sens-Devp	Sens-Grass	Sens-Barren	Sens-GUV	Sens-Shale	Sens-Sand
Chloride	Uncon	5.45	0.05	-0.04									
1980s	Cond	-4.16	1.06	-9.88	9.82	1.00	1.00	0.96	0.93	0.82	0.68	0.88	0.86
Chloride	Uncon	5.05	0.19	-0.04									
1990s	Cond	3.77	1.12	-1.39	1.34	1.00	1.00	0.96	0.88	0.82	0.68	0.84	0.82
Chloride	-	-	-	-	-	-	-	-	-	-	-	-	-
2000s													
Nitrate	-	-	-	-	-	-	-	-	-	-	-	-	-
1980s													
Nitrate	Uncon	2.02	-0.05	0.0001									
1990s	Cond	3.94	0.77	2.30	-2.30	1.00	1.00	0.97	0.93	0.85	0.74	0.89	0.90
Nitrate	-	-	-	-	-	-	-	-	-	-	-	-	-
2000s													
Sulfate	-	-	-	-	-	-	-	-	-	-	-	-	-
1980s													
Sulfate	-	-	-	-	-	-	-	-	-	-	-	-	-
1990s													
Sulfate	Uncon	6.55	-0.03	0.01									
2000s	Cond	-0.94	0.78	-9.07	9.09	1.00	1.00	0.97	0.92	0.85	0.70	0.89	0.88
Aluminum	-	-	-	-	-	-	-	-	-	-	-	-	-
1980s													
Aluminum	-	-	-	-	-	-	-	-	-	-	-	-	-
1990s													
Aluminum	-	-	-	-	-	-	-	-	-	-	-	-	-
2000s													
pH 1980s	-	-	-	-	-	-	-	-	-	-	-	-	-
pH 1990s	Uncon	7.19	0.05	0.01									
	Cond	15.17	-0.91	-8.63	-8.19	1.00	1.00	0.96	0.88	0.80	0.52	0.88	0.85
pH 2000s	-	-	-	-	-	-	-	-	-	-	-	-	-
Hardness	Uncon	7.41	-0.01	-0.02									
1980s	Cond	9.76	-0.92	-2.57	-2.56	1.00	1.00	0.96	0.94	0.83	0.69	0.89	0.87
Hardness	Uncon	7.26	0.05	-0.003									
1990s	Cond	1.96	-0.79	6.30	6.30	1.00	1.00	0.98	0.92	0.83	0.74	0.89	0.87
Hardness	-	-	-	-	-	-	-	-	-	-	-	-	-
2000s													
Alkalinity	-	-	-	-	-	-	-	-	-	-	-	-	-
1980s													
Alkalinity	Uncon	6.64	0.05	-0.01									
1990s	Cond	10.08	-0.83	-4.00	-3.99	1.00	1.00	0.97	0.92	0.85	0.72	0.90	0.88
Alkalinity	-	-	-	-	-	-	-	-	-	-	-	-	-
2000s													

Note: A “-” connecting two variables in the first row represents interaction or factor loading between the two variables. Rows marked with “-” represent unacceptable model results based on model statistics. Units of chemical parameters are $\mu\text{eq}\cdot\text{L}^{-1}$ except pH (pH unit $\cdot\text{L}^{-1}$).

Abbreviations: Int = intercept, Slp = slope, Sens = sensitivity, Area = drainage area (m^2), Elev = mean elevation (m), Devp = developed (%), Grass = grassland (%), Barren = barren land (%), GUV = Gilpin-Upshur-Vandalia (%), Sand = sandstone (%), Uncon = unconditional model (i.e., model only includes intercept and slope), and Cond = conditional model (i.e., model includes intercept, slope, and predictors). Values in columns 3 - 6 are unstandardized estimates, and values in columns 7 - 14 are standardized estimates. All estimates are significant ($p < 0.05$) except the highlighted italic values.

Fig. 1 Unconditional latent growth curve model of stream chloride (1996 - 1999) in the central Appalachian Mountains. Note: measurement errors for chloride (1996 - 1999) are standardized estimates; factor loadings from intercept to chloride and from slope to chloride were set to predetermined values (i.e., values on dashed arrows); means and variances of intercept, slope, and interactions between intercept and slope are unstandardized estimates; all estimates are significant ($p < 0.05$) except the highlighted italic values; abbreviations (CI96 = chloride in 1996, CI97 = chloride in 1997, CI98 = chloride in 1998, and CI99 = chloride in 1999; unit of chloride is $\mu\text{eq} \cdot \text{L}^{-1}$).

Fig. 2 Conditional latent growth curve model of stream chloride (1996 - 1999) with watershed attributes as predictors in the central Appalachian Mountains. Note: factor loadings from intercept to chloride, from slope to chloride, and between sensitivity and slope were set to predetermined values (i.e., values on dashed arrows); value from sensitivity to intercept is an unstandardized estimate; all other values in this figure are standardized estimates; all estimates are significant ($p < 0.05$) except the highlighted and italic values; abbreviations (CI96 = chloride in 1996, CI97 = chloride in 1997, CI98 = chloride in 1998, and CI99 = chloride in 1999, (Unit of chloride is $\mu\text{eq}\cdot\text{L}^{-1}$) Area = drainage area (m^2), Elev = mean elevation (m), Devp = developed (%), Grass = grassland (%), Barren = barren land (%), GUV = Gilpin-Upshur-Vandalia (%), and Sand = sandstone (%)).

Chapter 6 - Conclusions and Management Implications

The following conclusions are drawn from the current studies:

1. Construction of the Appalachian Corridor H highway in the Lost River watershed had statistically significant effects on seven major water quality parameters identified by PC 2. The impacts included those on turbidity, TSS, and total iron during construction, those on chloride and sulfate during and after construction, and those on acidity and nitrate after construction. In addition, the highway construction had statistically significant impacts on the scores of stream benthic macroinvertebrates index (i. e., WVSCI) after construction, but did not change the overall good biological condition.
2. In the South Branch Potomac River 3 watershed, the highway had no significant effects on major water quality parameters during its first year's construction. Only episodic impacts of the highway construction on turbidity, TSS, iron, and aluminum were observed.
3. The trend analyses found homogeneous stream chemical improving trends of sulfate, alkalinity, hydrogen ion, and total aluminum during the period of 1980-2006. The reduced deposition of acidic anions and hydrogen ion may explain the increase of pH and alkalinity in the West Virginia streams.
4. The SEM-based LGMs characterized most stream chemical (i.e., chloride, nitrate, sulfate, pH, hardness, and alkalinity) initial conditions (i.e., intercepts) and their changing rates (i.e., slopes) in the periods of 1980s, 1990s, and 2000s in the central Appalachian Mountains. The slopes or trends identified by all acceptable unconditional models were generally consistent with the trends which were detected by the trend analyses. Watershed attributes including area, mean elevation, percentage of developed, percentage of grassland, percentage of shale and sandstone, percentage of barren land, and percentage of GUV soil were found to affect stream sensitivity to

reduced acidic deposition with their importance in the respective order. The stream's sensitivity in turn regulated stream chemical initial conditions and their changing rates in the studied watersheds.

The current studies have the following watershed management implications:

1. Construction-impacted water quality parameters should be considered for developing mitigation strategies and refining currently implemented BMPs for future highway construction in the Mid-Atlantic Highlands region. Special attentions should be paid to those episodically impaired water quality parameters which may stress aquatic organisms in the streams. Sediment fencing and detention ponds should be continuously employed during the highway construction. Also, the effectiveness of these BMPs should be monitored regularly, especially during and after storms. The first two targets of potential impacted water quality parameters (i.e., turbidity and TSS) should be monitored more intensively during and after highway construction. Further, techniques should be developed to mitigate the episodic impacts of iron and aluminum on aquatic organisms. Future watershed management practices should combine stream and watershed mitigation (e.g., sediment fencing and mulching to prevent or minimize impacts) and stream and watershed restoration (i.e., maintaining riparian vegetation and liming to restore stream biological and chemical conditions). Finally, watershed management policies should not consider only local restoration, but also consider watershed-scale stream mitigation and restoration.

2. Further chemical and biological improvements of the West Virginia streams may require continued and additional emission controls on power plants to reduce acidic deposition in this mountain region. Stream ecological recovery policies should consider multiple stressors (i.e.,

acidic deposition, acid mine drainage, and other human activities) and their relative importance to overall stream health in a specific stream or within a specific watershed. Stream restoration and remediation strategies for acidic deposition should consider the difference of watershed attributes in different areas. Further, restoration plans should consider the current biological and chemical conditions of a stream, historic impacts (e.g., acidic deposition, acid mine drainage, and other human activities), historic restoration practices (e.g., limestone treatment), and its recovery potential and sensitivity based on geology and soil conditions in the watershed. Finally, watershed restoration policies should not only target on one or two specific impacted parameters (e.g., pH and aluminum) in streams or soils, but also consider other chemical parameters (e.g., alkalinity, hardness, chloride, and nitrate). Only overall chemical recovery or improvements in streams and soils can guarantee complete biological recovery in streams.

Appendix 1

Governing Equations for a General SEM Model and a Path Diagram

The following contents are revised from the guide book of Karl Jöreskog and Dag Sörbom (1997). The citation of the book is “Jöreskog, K., Sörbom, D. 1997. *LISREL8: User's Reference Guide*. Scientific Software International. Inc., Lincolnwood, Illinois, USA.”

A SEM consists of two parts: the measurement model and the structural model (Jöreskog and Sörbom, 1997). The measurement model specifies relationships between latent variables or hypothetical constructs and the observed variables. It describes the measurement reliabilities and validities of the observed variables. The structural model specifies the causal relationships among the latent variables, describes the causal effects, and assigns the explained and unexplained variance (Jöreskog and Sörbom, 1997).

Three equations are typically given for a general SEM model (Jöreskog and Sörbom, 1997):

(1) The structural model:

$$\eta = B\eta + \Gamma\xi + \zeta$$

(2) The measurement model for Y:

$$Y = \Lambda_y\eta + \varepsilon$$

(3) The measurement model for X:

$$X = \Lambda_x\xi + \delta$$

Definitions of the terms in the models are as follows:

η is an $m \times 1$ random vector of latent dependent or endogenous variables.

B is an $m \times m$ matrix of coefficients of the η -variables in the structural relationship.

Γ is an $m \times n$ matrix of coefficients of the ξ -variables in the structural relationship.

ξ is an $n \times 1$ random vector of latent independent or exogenous variables.

ζ is an $m \times 1$ vector of equation errors (random disturbances) in the structural relationship between η and ξ .

Y is a $p \times 1$ vector of observed response or outcome variables.

Λ_y is a $p \times m$ matrix of coefficients of the regression of Y on η .

ε is a $p \times 1$ vector of measurement errors in Y .

X is a $q \times 1$ vector of predictors, covariates, or input variables.

Λ_x is a $q \times n$ matrix of coefficients of the regression of X on ξ .

δ is a $q \times 1$ vector of measurement errors in X .

Equations for a Path Diagram

Fig. 1 Path diagram for hypothetical model (revised from Jöreskog and Sörbom, 1997)

From the above diagram (Fig. 1), the following equations can be derived:

(1) Structural equations

$$\eta_1 = \beta_{12} \eta_2 + \gamma_{11} \xi_1 + \gamma_{12} \xi_2 + \zeta_1$$

$$\eta_2 = \beta_{21} \eta_1 + \gamma_{21} \xi_1 + \gamma_{23} \xi_3 + \zeta_2$$

(2) Measurement model equations for y-variables

$$y_1 = \eta_1 + \epsilon_1$$

$$y_2 = \lambda_{21(y)} \eta_1 + \epsilon_2$$

$$y_3 = \eta_2 + \epsilon_3$$

$$y_4 = \lambda_{42(y)} \eta_2 + \epsilon_4$$

(3) Measurement model equations for x-variables

$$x_1 = \xi_1 + \delta_1$$

$$x_2 = \lambda_{21(x)} \xi_1 + \delta_2$$

$$x_3 = \lambda_{31(x)} \xi_1 + \lambda_{32(x)} \xi_2 + \delta_3$$

$$x_4 = \xi_2 + \delta_4$$

$$x_5 = \lambda_{52(x)} \xi_2 + \delta_5$$

$$x_6 = \xi_3 + \delta_6$$

$$x_7 = \lambda_{73(x)} \xi_3 + \delta_7$$

Appendix 2

Supplemental guidelines for implementation of SEM and LGM

Kline (2005) provided 44 possible mistakes when using SEM for problem solving:

- (1) “Specify the model after the data are collected rather than before.”
- (2) “Omit causes that are correlated with other variables in a structural model.”
- (3) “Fail to have sufficient numbers of indicators of latent variables.”
- (4) “Use inadequate measures.”
- (5) “Fail to give careful consideration to the question of directionality.”
- (6) “Specify feedback effects in structural models as a way to mask uncertainty about directionality.”
- (7) “Overfit the model.”
- (8) “Add disturbance or measurement error correlations without substantive reason.”
- (9) “Specify that indicators load on more than one factor without a substantive reason.”
- (10) “Don’t check the accuracy of data input or coding.”
- (11) “Ignore whether the pattern of missing data loss is random or systematic.”
- (12) “Fail to examine distributional characteristics.”
- (13) “Don’t screen for outliers.”
- (14) “Assume that all relations are linear without checking.”
- (15) “Ignore lack of independence among the observations.”
- (16) “Respecify a model based entirely on statistical criteria.”
- (17) “Fail to check the accuracy of computer syntax.”
- (18) “Fail to carefully inspect the solution for admissibility.”
- (19) “Report only standardized estimates.”

- (20) “Analyze a correlation matrix when it is clearly inappropriate.”
- (21) “Estimate a covariance structure with a correlation matrix without using appropriate methods.”
- (22) “Fail to check for constraint interaction when testing for equality of loadings across different factors or of direct effects on different endogenous variables.”
- (23) “Analyze variables so highly correlated that a solution is unstable.”
- (24) “Estimate a complex model with a small sample.”
- (25) “Set scales for latent variables inappropriately.”
- (26) “Ignore the problem of start values, or provide grossly inaccurate ones.”
- (27) “When identification status is uncertain, fail to conduct tests of solution uniqueness.”
- (28) “Fail to recognize empirical underidentification.”
- (29) “Fail to separately evaluate the measurement and structural portions of a structural regression model.”
- (30) “Estimate relative group mean or intercept differences on latent variables without establishing at least partial measurement invariance of the indicators.”
- (31) “Analyze parcels of categorical items as continuous indicators without checking to see whether items in each parcel are unidimensional.”
- (32) “Look only at indexes of overall model fit; ignore other types of information about fit.”
- (33) “Interpret good fit as meaning that the model is proved.”
- (34) “Interpret good fit as meaning that the endogenous variables are strongly predicted.”
- (35) “Rely solely on statistical criteria in model evaluation.”
- (36) “Rely too much on statistical tests.”

- (37) “Interpret the standardized solution in inappropriate ways.”
- (38) “Fail to consider equivalent models.”
- (39) “Fail to consider nonequivalent or alternative models.”
- (40) “Reify the factors.”
- (41) “Believe that naming a factor means that it is understood or correctly named.”
- (42) “Believe that a strong analytical method like SEM can compensate for poor study design or slipshod ideas.”
- (43) “As a researcher, fail to report enough information so that your readers can reproduce your results.”
- (44) “Interpret estimates of relatively large direct effects from a structural model as proof of causality.”

Appendix 3

Modeled Equations for Unconditional and Conditional Models of Chloride in the 1990s

(1) Modeled equations for unconditional model of chloride in 1990s (Fig. 1 in Chapter 5):

LISREL Estimates (Maximum Likelihood)

Measurement Equations

$$Cl96 = 1.00 * intercept, Errorvar. = 0.034, R^2 = 0.97$$

(0.034)

0.98

$$Cl97 = 1.00 * intercept + 1.00 * slope, Errorvar. = 0.029, R^2 = 0.97$$

(0.018)

1.65

$$Cl98 = 1.00 * intercept + 2.00 * slope, Errorvar. = 0.029, R^2 = 0.97$$

(0.020)

1.47

$$Cl99 = 1.00 * intercept + 3.00 * slope, Errorvar. = 0.083, R^2 = 0.92$$

(0.048)

1.71

Note: “intercept” = Intercept, “Cl96 ~ Cl99” = Chloride in 1996 ~ Chloride in 1999,
 “Errorvar.” = Error Variance. Values in parentheses indicate standard errors and values
 just below that are t-values.

(2) Modeled equations for conditional model of chloride in 1990s (Fig. 2 in Chapter 5):

LISREL Estimates (Maximum Likelihood)

Measurement Equations

$$\text{Cl96} = 1.00 * \text{intercep}, \text{Errorvar.} = 0.027, R^2 = 0.99$$

(0.028)

0.97

$$\text{Cl97} = 1.00 * \text{intercep} + 1.00 * \text{slope}, \text{Errorvar.} = 0.025, R^2 = 0.97$$

(0.015)

1.73

$$\text{Cl98} = 1.00 * \text{intercep} + 2.00 * \text{slope}, \text{Errorvar.} = 0.018, R^2 = 0.98$$

(0.015)

1.18

$$\text{Cl99} = 1.00 * \text{intercep} + 3.00 * \text{slope}, \text{Errorvar.} = 0.10, R^2 = 0.97$$

(0.049)

2.14

$$\text{area} = 19.79 * \text{sensit}, \text{Errorvar.} = 0.29, R^2 = 1.00$$

$$(0.76) \quad (0.39)$$

$$26.06 \quad 0.74$$

$$\text{elev} = 5.95 * \text{sensit}, \text{Errorvar.} = 0.12, R^2 = 1.00$$

$$(0.24) \quad (0.054)$$

$$24.77 \quad 2.14$$

$$\text{devp} = 0.32 * \text{sensit}, \text{Errorvar.} = 0.0081, R^2 = 0.93$$

$$(0.025) \quad (0.0029)$$

$$12.41 \quad 2.81$$

$$\text{grass} = 0.36 * \text{sensit}, \text{Errorvar.} = 0.037, R^2 = 0.78$$

$$(0.050) \quad (0.013)$$

$$7.15 \quad 2.82$$

$$\text{barren} = 0.044 * \text{sensit}, \text{Errorvar.} = 0.00093, R^2 = 0.67$$

$$(0.0078) \quad (0.00033)$$

$$5.58 \quad 2.83$$

$$\text{GUV} = 0.36 * \text{sensit}, \text{Errorvar.} = 0.16, R^2 = 0.46$$

$$(0.10) \quad (0.056)$$

$$3.63 \quad 2.83$$

$$\text{shale} = 0.65 * \text{sensit}, \text{Errorvar.} = 0.17, R^2 = 0.71$$

$$(0.11) \quad (0.062)$$

$$6.07 \quad 2.82$$

$$\text{sand} = 0.78 * \text{sensit}, \text{Errorvar.} = 0.31, R^2 = 0.67$$

$$(0.14) \quad (0.085)$$

$$5.51 \quad 3.65$$

$$\text{Error Covariance for sand and grass} = -0.06$$

$$(0.023)$$

$$-2.70$$

$$\text{Error Covariance for sand and shale} = -0.18$$

$$(0.065)$$

$$-2.76$$

Structural Equations

$$\text{intercep} = 3.77 + 1.34 * \text{sensit}, \text{Errorvar.} = 0.76, R^2 = 0.70$$

$$(0.22) \quad (0.20) \quad (0.28)$$

$$17.08 \quad 6.61 \quad 2.75$$

$$\text{slope} = 1.12 - 1.00 * \text{sensit}, \text{Errorvar.} = 0.016, R^2 = 0.98$$

$$(0.039) \quad (0.0099)$$

$$28.77 \quad 1.58$$

Note: “intercept” = Intercept, “Cl96 ~ Cl99” = Chloride in 1996 ~ Chloride in 1999, “Errorvar.” = Error Variance, “area” = drainage area (m²), “elev” = mean elevation (m), “devp” = developed (%), “grass” = grassland (%), “barren” = barren land (%), “GUV” = Gilpin-Upshur-Vandalia (%), and “sand” = sandstone (%). Values in parentheses indicate standard errors and values just below that are t-values.

Appendix 4

Sensitivity Map for Chloride in the 1990s

Fig. 1 Stream chloride sensitivity distributions in 1990s in central Appalachian Mountains. Note: sensitivity values (i.e., <7, 7-8, and 9-10) are calculated from the modeled measurement equations based on the relations between sensitivity and individual watershed attributes (Appendix 3). A larger sensitive value indicates more sensitive of a stream to reduced acidic chloride deposition.

Appendix 5

Peer-reviewed Journal Publications

Peer-reviewed journal publications:

1. Articles in press or published

Hedrick, L. B., Welsh, S. A., Anderson, J. T., Lin, L.-S., **Chen, Y.**, Wei, X. Response of benthic macroinvertebrate communities to highway construction in an Appalachian watershed.

Hydrobiologia, In press.

Chen, Y., Viadero, R. C. Jr., Wei, X., Fortney, R., Hedrick, L. B., Welsh, S. A., Anderson, J. T., Lin, L.-S. 2009. Effects of highway construction on stream water quality and macroinvertebrates condition in a Mid-Atlantic highlands watershed, USA. *Journal of Environmental Quality*, 38, 1672-1682.

Chen, Y., Lin, L.-S. 2009. Responses of streams in Central Appalachian Mountain Region to reduced acidic deposition - comparisons with other regions in North America and Europe. *Science of the Total Environment* 407: 2285-2295.

Chen, Y., Lin, L.-S., Viadero, R. C., Gang, D. 2007. Non-point source pollution: review. *Water Environmental Research* 79(10): 2032-2048.

Chen, Y., Li, Z. 2007. Analysis of environmental and economical effectiveness in planting lotus in typical fish ponds in areas along the Middle Reaches of the Yangtze River. *Resources and Environment in the Yangtze Basin* 16(5): 609-614.

2. Articles submitted for review

Chen, Y., Li, Z., Lin, L.-S. Effects of a planktivorous fish (*Pseudorasbora parva*: Cyprinidae) on eutrophication of a shallow eutrophic urban lake in Central China.

3. Articles submitted or finished

Chen, Y., Lin, L.-S. Watershed Attributes Regulated Stream Sensitivity to Reduced Acidic Deposition in Central Appalachian Mountains: Latent Growth Curve Modeling with Structural Equations (Submitted).

Chen, Y., Wei, X., Lin, L.-S. Episodic water quality impacts from highway construction in streams of a South Branch Potomac River watershed, USA (Finished).

Curriculum Vitae
YUSHUN CHEN

Department of Civil and Environmental Engineering, West Virginia University, Morgantown,
WV 26505

233 Dewey Street APT 15, Morgantown, WV 26501

Tel.: 304-293-3031 ext. 2652 (Lab); 304-906-7935 (Cell)

E-mail: ychen8@mix.wvu.edu or limnologychen@yahoo.com

Education

Ph.D. Candidate, Environmental Engineering and Science, *West Virginia University*,
2006.8 - Present (expected graduation term: Summer 2009)

Dissertation title: Ecological Responses of Streams to Anthropogenic Stressors, and
Watershed Cause-Effect Modeling in the Mid-Atlantic Region of the United States

M.S., Aquatic Ecology, *Chinese Academy of Sciences*, China, 2006

Thesis title: Studies on Pond Pisciculture Modes Optimization and Exterior Nitrogen and
Phosphorus Pollution Control in Zhangduhu Wetland, Central China

B.S., Aquatic Sciences and Fisheries, *Hunan Agricultural University*, China, 2003

Thesis title: Comparisons of small-sized fish community diversity in three lake areas
under different habitats, Yangtze River Basin, Central China

Research Interests

Aquatic responses to anthropogenic stressors, non-point source pollution, water quality and
biotic health, lake eutrophication and nutrients management, quantitative ecological analysis and
statistical modeling, GIS modeling, ecological restoration, ecohydrology, aquatic ecosystem and
climate change

Software Skills Used in Research

Statistical Software: SAS, R, Statistica, SPSS

Structural Equation Modeling (SEM) Software: LISREL8

Geographical Software: ESRI ArcView 3, Arc GIS 9, GPS

Hydrological Software: HEC-HMS, WINTR55, EPA SWMM

Research Experience

August 2006 - present:

Graduate Research Assistant, Department of Civil and Environmental Engineering, *West Virginia University*.

September 2003 - July 2006:

Graduate Research Assistant, State Key Laboratory of Freshwater Ecology and
Biotechnology, *Chinese Academy of Sciences*.

February 2003 - August 2003:

Undergraduate Research Assistant, State Key Laboratory of Freshwater Ecology and
Biotechnology, *Chinese Academy of Sciences*.

Research Projects

- 2007-2009 West Virginia Department of Environmental Protection (WVDEP): Long-term Stream Responses to Reduced Acidic Deposition in the Central Appalachian Mountain Region of West Virginia
- 2006-2009 West Virginia Division of Highway (WVDOT): Long-term Stream Physical, Chemical, and Biological Monitoring of the Appalachian Corridor-H Highway Project
- 2006-2007 WVDEP, WV Environmental Quality Board, WV Nutrient Criteria Committee: Nutrient Criteria for West Virginia Lakes
- 2005-2006 China Ministry of Science and Technology (CMST): Fish-Algae Interaction and Environment in an Urban Lake
- 2004-2005 World Wildlife Fund (WWF): Strategies for Wetland Environmental Conservation and Fishery in Zhangdu Lake
- 2003-2004 Chinese Academy of Sciences (CAS): Theoretical Basis for Lake Biological Resources and Fishery Development

Teaching Experience

2008 Fall

Department of Civil and Environmental Engineering *West Virginia University* (WVUCEE), CE347 Introduction to Environmental Engineering, Taught Laboratory Session, Co-taught Lecture Session

2008 Spring

WVUCEE, CE347 Introduction to Environmental Engineering, Taught Laboratory Session

2007 Spring

WVUCEE, CE347 Introduction to Environmental Engineering, Assisted Laboratory Session

Professional Society Membership

American Society of Civil Engineer (ASCE): Since 2007

Ecological Society of American (ESA): Since 2007

American Geophysical Union (AGU): Since 2007

American Fisheries Society (AFS) WVU Chapter: Since 2007

Awards and Honors

2008 Conference Travel Grant Award, *West Virginia University*

2006-2009 Research Assistantship, *West Virginia University*

2008 Teaching Assistantship, *West Virginia University*

2007 Teaching Assistantship, *West Virginia University*

2003-2006 Research Assistantship, *Chinese Academy of Sciences*

2004 Graduate Student Scholarship, *Chinese Academy of Sciences*

2003 Outstanding Undergraduate in Hunan Province, Hunan Department of Education

2003 Top Ten Undergraduate Student Thesis Award, *Hunan Agricultural University*

1999-2003 First Prize Undergraduate Scholarship, *Hunan Agricultural University*