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# Exploring lag times between monthly atmospheric deposition and stream chemistry in Appalachian forests using cross-correlation

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## HIGHLIGHTS

- Lags between atmospheric and stream chemistry are estimated with cross-correlation.
- Time series need to be pre-whitened to remove autocorrelation before analysis.
- Lags determined varied markedly between sulfur and nitrogen on four forest basins.
- Further estimation of lags using monitoring data from other basins is recommended.

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## ABSTRACT

Forecasts of ecosystem changes due to variations in atmospheric emissions policies require a fundamental understanding of lag times between changes in chemical inputs and watershed response. Impacts of changes in atmospheric deposition in the United States have been documented using national and regional long-term environmental monitoring programs beginning several decades ago. Consequently, time series of weekly NADP atmospheric wet deposition and monthly EPA-Long Term Monitoring stream chemistry now exist for much of the Northeast which may provide insights into lag times. In this study of Appalachian forest basins, we estimated lag times for S, N and Cl by cross-correlating monthly data from four pairs of stream and deposition monitoring sites during the period from 1978 to 2012. A systems or impulse response function approach to cross-correlation was used to estimate lag times where the input deposition time series was pre-whitened using regression modeling and the stream response time series was filtered using the deposition regression model prior to cross-correlation. Cross-correlations for S were greatest at annual intervals over a relatively well-defined range of lags with the maximum correlations occurring at mean lags of 48 months. Chloride results were similar but more erratic with a mean lag of 57 months. Few high-correlation lags for N were indicated. Given the growing availability of atmospheric deposition and surface water chemistry monitoring data and our results for four Appalachian basins, further testing of cross-correlation as a method of estimating lag times on other basins appears justified.

## 1. Introduction

Understanding the lag time between changes in pollutant loads to natural systems and subsequent watershed response is critical to evaluating and refining pollutant control strategies and improving our knowledge of basic ecosystem function. When applied to understanding the effects of atmospheric deposition on stream chemistry in relatively undisturbed forest terrain, lag times account for pollutant-specific biogeochemical interactions within watershed ecosystems and time for subsurface water movement to basin outlets (Meals et al., 2010). Sulfur (S) deposition on un-farmed, forest basins with some logging is primarily translated into soil water chemical changes due to complex dynamics of sulfur adsorption/desorption processes in the soil (Edwards, 1998, Johnson, 1964, Cosby et al., 1986; Mitchell et al., 2011; Rice et al., 2014), while changes in nitrogen (N) deposition can lead to altered N cycling within the forest vegetation and soil biota (Aber et al., 1989; Driscoll et al., 2001; Galloway et al., 2003). Resultant

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changes in soil water chemistry are propagated downslope through the subsurface to groundwater at rates dependent upon precipitation, evapotranspiration and physical properties of soil, bedrock, and the overall landscape features which control watershed transit times (McGuire and McDonnell, 2006; Kirchner et al., 2001). How well lag times for chemical inputs, such as S, N and Cl, compare to transit times for water within the catchment depends on the pollutant-specific biogeochemical interactions within the catchment.

Mass balances on relatively undisturbed forest basins in the Appalachian region of Pennsylvania (Dow and DeWalle, 1997; Sweeney, 1998) indicate that S retention within most watershed ecosystems is minimal with atmospheric inputs roughly balanced by stream exports, while N mass balances suggest the opposite trend with almost complete N retention in some basins (Campbell et al., 2004; Sweeney, 1998; DeWalle et al., 2005). With minimal biogeochemical interactions, lag times for S could be dominated by transit times needed for water movement through watersheds and in fact lag time analysis could be an alternate way to estimate transit time. Once subsurface and groundwater flows are delivered to stream channels, an additional component of lag time could be biogeochemical changes within channels as water is exported to basin outlets (Seitzinger et al., 2002; O'Driscoll and DeWalle, 2010). Due to the large number of factors that can affect lag times, comparison of long-term atmospheric deposition and stream chemistry time series may offer a more direct way of estimating lag times.

Early concern with effects of acidic atmospheric deposition and impacts of pollution control strategies, prompted establishment of monitoring programs in the 1970–80s to document changes in atmospheric wet and dry deposition as well as attendant changes in surface water chemistry. In the United States, time series of atmospheric wet deposition are available from the National Atmospheric Deposition Program, National Trends Network (NADP-NTN) and time series of measured and modeled dry deposition from the Clean Air Status and Trends Network (CASTNET) data. Together with surface water chemistry time series available through U. S. EPA's Long-Term Monitoring (LTM) project or U. S. Geological Survey's Hydrologic Benchmark Network (HBN) and National Water-Quality Assessment (NAWQA) programs these data sets can help document linkages between atmospheric deposition and stream quality changes. Similar national, regional and local monitoring programs are also available across the globe.

Initial studies of such monitoring data showed positive effects of pollution control policies on atmospheric deposition which were followed by studies of the changes in surface water chemistry (Kahl et al., 2004; Stoddard et al., 1999; Burns et al., 2011; Waller et al., 2012, Fuss et al., 2015). Linkages between deposition and surface water trends were often explored by comparing rates of change in atmospheric deposition or emissions to trends in surface water chemistry (Campbell and Turk, 1988; Rogora et al., 2001; Lawrence et al., 2004; Eshleman et al., 2013). Physical models of chemical interactions between atmospheric deposition and surface waters were also developed and extensively used to predict effects of various atmospheric pollution emissions scenarios (Sullivan et al., 2008; Alexander et al., 2007; Rice et al., 2014).

While there was broad appreciation for the concept of lag time for pollutant changes to affect surface water quality in early studies, direct determination of lag times has been explored in only a few studies. Neal and Kirchner (2000) showed that cross-correlation of daily rainfall with stream concentrations of Cl and Na showed lag times of up to 3 months on small basins in mid-Wales with peaty soils. Worrall et al. (2006, 2008) used ARMA and impulse response functions to show that pulses in monthly soil water sulfate concentrations caused by atmospheric deposition did not lead to increases in DOC concentrations in runoff from a U.K. peat-covered basin. These studies suggest that cross-correlation of available atmospheric deposition and stream chemistry time series might reveal information on lag times.

Frequency of sampling affects estimates of lag time between atmospheric deposition and stream chemistry. Kirchner et al. (2004) argued for high-frequency (hourly or daily) chemical sampling of both water inputs and outputs for ecosystems in order to enhance understanding of biogeochemical processes in general. Robson et al. (1993) showed how continuous monitoring of stream chemistry enhanced understanding of within-event stream-chemistry dynamics. Unfortunately available monitoring data are often collected on weekly to monthly intervals. At longer time scales similar to available atmospheric wet deposition and stream chemistry measurements (e.g. NADP-NTN weekly and monthly LTM stream chemistry data), the issue becomes whether sufficient time resolution is available to allow detection of lag times. Clearly if dominant lag times are of the order of hours or days, then monthly resolution monitoring data are insufficient, however the data may support resolving time lags in the range of intra-annual to inter-annual time scales.

The purpose of this study was to explore the feasibility of using the cross-correlation method to help determine lag time between changes in atmospheric deposition of S, N and Cl and stream chemical responses. In particular, we tested the feasibility of using aggregated NADP-NTN weekly wet deposition data and monthly LTM stream chemistry data to define the lag time for four small forest catchments in the Appalachians of Pennsylvania.

## 2. Methods

### 2.1. Study areas

The study watersheds are located in un-glaciated portions of the Appalachian Plateau Physiographic Province in Pennsylvania (Fig. 1). Linn Run (LNN) is located in southwestern Pennsylvania and Benner Run (BNR), Roberts Run (RBT) and Stone Run (STN) are located in north-central Pennsylvania. For analysis purposes each basin was paired with the nearest atmospheric deposition monitoring station (Fig. 1): Kane monitoring station was paired with both Stone and Roberts Runs (58 and 54 km apart, respectively), Penn State monitoring station was associated with Benner Run (26 km apart), and Laurel Hill deposition site was associated with Linn Run (17 km apart). An alternative procedure of using spatially interpolated wet deposition data to represent basin conditions (Rice et al., 2014), rather than data from the nearest station, may improve cross-correlation analysis.

The region has a humid, continental climate with about 100–120 cm of precipitation per year, intermittent winter snowpacks, and mean annual air temperatures of 9–10 °C. Mean basin runoff averages about 53–66 cm per year. All watersheds are classified as second order and are about 1100 ha in area. Soils are shallow (<1 m), stony, silt loams to loamy sands derived from residuum or colluvium of acidic sandstones, shales and conglomerates. Deciduous forests covering the basins include oaks (*Quercus rubra. Q. prinus, Q. alba*), red maple (*Acer rubrum*), birch (*Betula* spp.), black cherry (*Prunus serotina*) and a mix of other species which largely represent second-growth forest remaining after extensive logging during the early 1900s. While no known anthropogenic influences on water quality in streams have occurred on these basins other than atmospheric deposition during the monitoring period, all basins except Linn Run include several seasonally-occupied hunting camps and small blocks of forest cutting prior to 1980s. Benner Run basin also is bounded partly by a ridge-top paved road subject to winter deicing salt applications and has two operating shallow gas wells from which brine could

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