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Shifts in controls on the temporal coherence of throughfall chemical flux in Acadia National Park, Maine, USA

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Abstract Major ion and mercury (Hg) inputs to terrestrial ecosystems include both wet and dry deposition (total deposition). Estimating total deposition to sensitive receptor sites is hampered by limited information regarding its spatial heterogeneity and seasonality. We used measurements of throughfall flux, which includes atmospheric inputs to forests and the net effects of canopy leaching or uptake, for ten major ions and Hg collected during 35 time periods in 1999–2005 at over 70 sites within Acadia National Park, Maine to (1) quantify coherence in temporal dynamics of seasonal throughfall deposition and (2) examine controls on these patterns at multiple scales. We quantified temporal coherence as the correlation between all possible site pairs for each solute on a seasonal basis. In the summer growing season and autumn, coherence among pairs of sites with similar vegetation was stronger than for site-pairs that differed in vegetation suggesting that interaction with the canopy and leaching of solutes differed in coniferous, deciduous, mixed, and shrub or open canopy sites. The spatial pattern in throughfall hydrologic inputs across Acadia National Park was more variable during the winter snow season, suggesting that snow re-distribution affects net hydrologic input, which consequently affects chemical flux. Sea-salt corrected calcium concentrations identified a shift in air mass sources from maritime in winter to the continental industrial corridor in summer. Our results suggest that the spatial pattern of throughfall hydrologic flux, dominant seasonal air mass source, and relationship with vegetation in winter differ from the spatial pattern of throughfall flux in these solutes in summer and autumn. The coherence approach applied here made clear the strong influence of spatial heterogeneity in throughfall hydrologic inputs and a maritime air mass source on winter patterns of throughfall flux. By contrast, vegetation type was the most important

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influence on throughfall chemical flux in summer and autumn.

Keywords Throughfall · Mercury · Winter · Atmospheric deposition · Coherence · DOC

Introduction

Scientists, policymakers, and managers have recognized the importance of quantifying total atmospheric deposition, typically defined as wet plus dry deposition, including occult (fog/cloud) inputs, in assessing effects of mass transport of anthropogenic pollutants to terrestrial and, subsequently, aquatic ecosystems. Atmospheric deposition is typically summed into an annual flux for use as the input term in watershed-scale mass balance studies, especially those that monitor long-term changes in watershed biogeochemistry and acidification (e.g., Kahl et al. 2007; Norton and Fernandez 1999; Likens and Bormann 1995). Atmospheric deposition is the largest source of nitrogen (as NO_3^-, NH_4^+), sulfur (as SO_4^{2-}), and Hg inputs, and often influences spatial and temporal patterns in export of these chemicals from many terrestrial ecosystems (Lindberg et al. 2007; Weathers et al. 2000, 2006).

Because wet-only deposition is the most readily accessible and frequently measured component of total deposition, it has been used to estimate deposition inputs to watersheds (e.g., Mitchell et al. 2011). Often dry and occult deposition inputs are inadequate or unavailable for particular watersheds. Wet-only deposition measurements such as those made by the US National Atmospheric Deposition Program/Mercury Deposition Network (NADP/MDN 2001) provide large-scale, year-round, methodologically consistent chemistry and deposition data. However, wet-only measurements underestimate total deposition for many solutes as dry deposition of some chemicals—SO_4^{2-}, Hg, and nitrogen for example—often equals or exceeds wet-only deposition, particularly at forested sites [CASTNET (http://epa.gov/castnet); Nelson et al. 2008; Johnson et al. 2007; Weathers et al. 2006].

Because of its importance, as well as challenges in obtaining accurate estimates particularly for complex terrain and over small spatial extent, measurement and modeling of dry deposition continue to be identified as research priorities (e.g., Lindberg et al. 2007). Dry deposition has been estimated with inferential techniques, micrometeorological approaches, surrogate surfaces (Rea et al. 2000; Davidson et al. 1985) and throughfall (water collected under the forest canopy) measurements (e.g., Lovett 1994). Micrometeorological and inferential methods provide standardized estimates of deposition that can complement NADP/MDN measurements of wet-only deposition; however, they are not well suited to estimate deposition in landscapes with non-uniform vegetation or topography (Weathers et al. 2000, 2006; Lindberg et al. 1994; Lindberg and Lovett 1992). Occult deposition is rarely measured, though in some locations it contributes a significant proportion of atmospheric inputs of water and solutes (e.g., Anderson et al. 2006; Ritchie et al. 2006; Weathers et al. 2000).

The throughfall approach estimates the amount of a solute deposited on the land surface after atmospheric deposition passes through and interacts with the forest canopy. Although throughfall flux is spatially and temporally variable, it has most often been quantified during the growing season and for short-duration intervals. A notable exception, Houle et al. (1999) conducted a multi-solute throughfall study across seasons in hardwood forests in Canada. As a consequence, we lack information on how local to broad scale controls such as vegetation type and phenology, elevation gradients, site aspect, and seasonal meteorological patterns (e.g., Witt et al. 2009; Johnson et al. 2007; Weathers et al. 2000; Lovett 1994) influence throughfall flux throughout the year.

Based on the literature, we had expectations regarding patterns in throughfall flux of many solutes collected in this study, and its hydrology. A major influence on throughfall flux is retention or leaching from the canopy, with effects differing by forest composition and solute. In general, ions that are "not considered limiting nutrients for tree growth" such as SO_4^{2-}, chloride (Cl^-), sodium (Na^+) (Houle et al. 1999) and Hg, are expected to be relatively conservative with respect to uptake by or leaching from forest canopies. Throughfall flux for these solutes under either coniferous or mixed canopies generally exceeds fluxes under deciduous canopies (Johnson et al. 2007; Weathers et al. 2000). Retention of foliage year-round and the greater surface area of needles as compared to deciduous leaves contribute to greater deposition at conifer sites (collectively referred to as 'scavenging efficiency') (Grigal 2002; Lovett et al. 1999). Because

of decreased canopy coverage in winter, especially in deciduous or mixed vegetation sites, we expect less throughfall flux of these solutes in winter as compared to other seasons.

In contrast to the relatively conservative ions, the base cations calcium (Ca^{2+}), magnesium (Mg^{2+}), and potassium (K^{+}) leach readily from forest canopies during the growing season, and potentially during the dormant season (Houle et al. 1999), whereas, hydrogen ions (H^{+}), ammonium (NH_4^{2+}), and nitrate (NO_3^{-}) generally are taken up by or exchanged within forest canopies only during the growing season (Houle et al. 1999; Johnson and Lindberg 1992). Although Na^{+} and Cl^{-} are considered conservative with respect to the forest canopy—especially in coastal areas where they are deposited as seasalt aerosols (Beier et al. 1992)—leaching of base cations and Cl^{-} can occur during senescence (deciduous) and dormancy (conifers) (Baumler and Zech 1997; Neary and Gizyn 1994).

Throughfall deposition is a function of both chemical concentrations and hydrologic inputs. Compared to precipitation at open sites, throughfall volume can be increased through cloud and fog interception by the canopy or decreased through evaporation and sublimation. In the growing season, rain throughfall volume generally is less than wet-only volume measured at open sites due to canopy interception (Lovett et al. 1999). In contrast, during the dormant season, snow deposition is influenced primarily by wind redistribution, presence and type of canopy vegetation, and terrain at the local scale (tens to hundreds of meters) (Pomeroy and Gray 1995).

Although both seasonal weather patterns and fine-scale watershed factors likely influence total deposition, few studies have compiled sufficient throughfall data to adequately investigate spatio-temporal patterns, particularly in winter, and seasonal controls. Given such gaps in our understanding of throughfall flux for major ions and Hg, our objectives were to: (1) quantify the similarity of temporal dynamics in throughfall deposition of 11 solutes and spatial variance in hydrologic flux in summer, autumn and winter; and, (2) infer seasonal shifts in the dominance of fine-scale (e.g., vegetation type) and broad-scale (e.g., major air mass source) controls on throughfall flux.

We analyzed event-based throughfall chemical and water flux and water volume measurements made over four years from sites located within a variety of vegetation and landcover types in Acadia National Park, Maine, USA. Our study sites at Acadia National Park are well-suited to this type of analysis: there are distinct seasonal weather patterns as well as heterogeneous vegetation patterns (Schauffler et al. 2007). In seasons when temporal dynamics were similar (e.g., strong coherence across all site pairs), we invoked the broad-scale factor of air mass source as controlling temporal patterns in the chemistry of precipitation and thus throughfall flux (Fig. 1a). If throughfall flux was not strongly coherent across all site pairs, then local or site-specific factors related to vegetation type were considered dominant controls (Fig. 1b). We then contrasted coherence among site pairs located in the same vegetation type with those in different vegetation types. This analysis framework allowed us to propose a hierarchy of local and broad-scale (regional) controls on throughfall flux by solute and season.

Methods

Site description

Acadia National Park is a 190 km^2 coastal park in the temperate-boreal transition zone in eastern North America (Fig. 2). Throughfall collection sites were located in two watersheds. The Hadlock Brook watershed (0.47 km^2) is dominated by conifer (spruce-fir, *Picea rubens–Abies balsamea*) forests with patches of northern hardwood forests and rocky balds in summit areas, which have been undisturbed by fire and harvesting for at least 200 years (Schauffler et al. 2007). The Cadillac Brook watershed (0.32 km^2) was burned in an extensive wildfire in 1947 and is comprised of mixed conifer-deciduous stands, early successional hardwoods, and rocky balds (Schauffler et al. 2007).

In Acadia National Park, mean annual temperature is 7 °C and range is <-17 °C in winter to >32 °C in summer. Although the Park is downwind from urban and industrial areas in states to the south and west, many storms track northeasterly along the Atlantic Ocean in winter. Mean monthly precipitation ranges from 7.0 cm in August to 17.1 cm in November (NCDC 2003). Average annual snowfall is 176 ($\pm$13 SE) cm and typically occurs during December–March (NCDC 2003). The Park's coastal mountains frequently are surrounded by pollutant-enriched clouds and coastal fogs (Weathers et al. 1988).

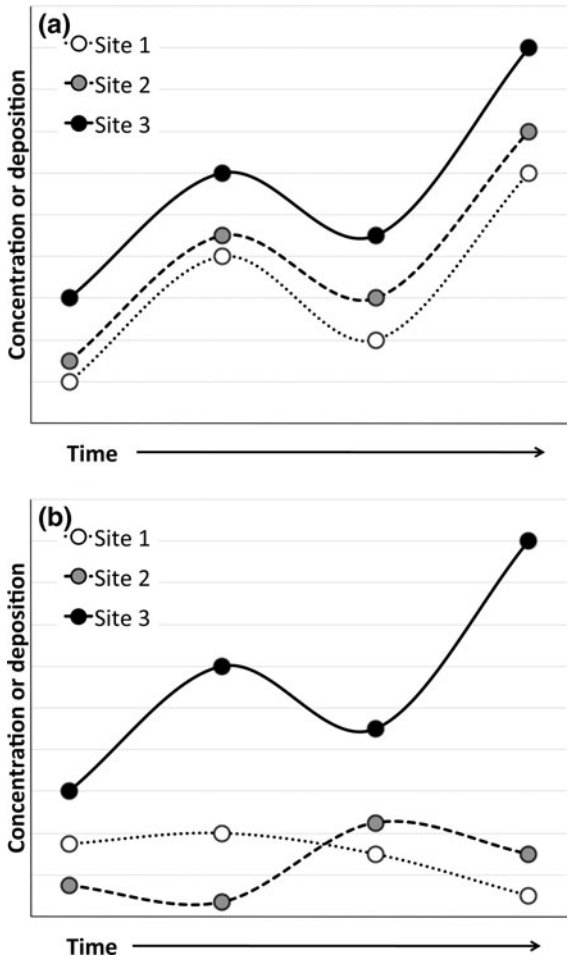

Fig. 1 **a** A hypothetical example of three sites behaving coherently; though there is variability in the magnitude of a measurement at each time period, sites behave similarly and maintain their position relative to each other. **b** A hypothetical example of three sites displaying non-coherent behavior; the pattern of increases and decreases in measurements with time does not occur similarly at each site

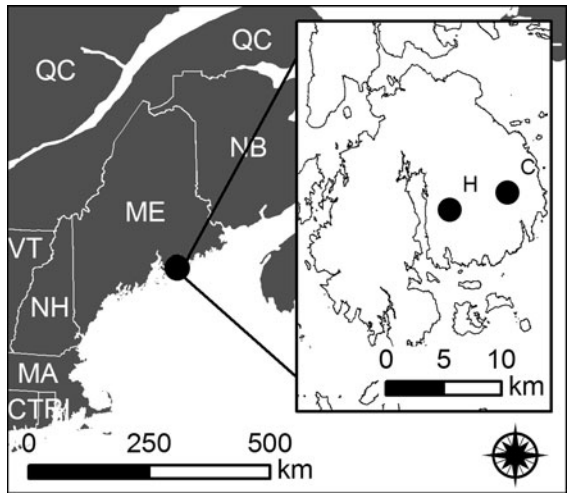

Fig. 2 Location of study watersheds in Acadia National Park on Mount Desert Island, Maine, USA. *H* Hadlock Brook watershed, *C* Cadillac Brook watershed

Field methods

Throughfall collector sites were established during 1999–2000 at a maximum of 77 locations in the Hadlock and Cadillac Brook watersheds (Fig. 2; Johnson et al. 2007; Kahl et al. 2007). These locations spanned the full range of landcover in each watershed: deciduous, coniferous, and mixed forests; shrub and krummholz sites; and open balds. One collector in each watershed was co-located with an NADP-type collector in an open, lower-elevation site, and one was co-located with the official NADP/MDN collector at site ME98. These landcover contrasts provided data for coherence comparisons between vegetation types.

Major ion chemistry samples were collected in HDPE funnel-bottle type collectors with openings 1 m off the ground during the growing season. Poly-wool (major ion collectors) or silanized glass wool (Hg collectors) was placed in funnels to exclude large litter, insects, frass, and other debris. Hg samples were collected in borosilicate glass bottles attached via Teflon® tubing to Teflon®-lined funnels during the growing season (Johnson et al. 2007). In winter, major ion and DOC samples were collected in HDPE bags lining 10 cm diameter, 60 cm depth closed-bottom tubes, and Hg samples were collected in Teflon® bags lining 10 cm diameter, 60 cm depth closed-bottom plastic tubes (Nelson et al. 2008). Loss of snow from collectors was prevented by collecting samples within 24 h of snowstorms, and loss of Hg via emission was minimized by using sample data referred to as "event-based" in Nelson et al. (2008). We used semi-clean collection methods for Hg, modified from EPA Ultraclean method 1669 (Louch 2003; Johnson 2002). The collectors were continuously open, and the samples represent the net inputs of wet deposition, dry deposition that accumulated on the funnel or bag and on the forest canopy between any rain or snow events, and canopy drip from fog or cloud water.

Throughfall samples were retrieved on 35 dates across 4 years; within a year, samples were retrieved

Table 1 Collection dates, number of collectors, and number of collection events (within the date range) each project year for major ion and mercury (Hg) throughfall samples in Cadillac Brook (CB) and Hadlock Brook (HB) watersheds in Acadia National Park, Maine

Precipitation type	Watershed	Dates	Solute group	No. of collection events	No. of collector sites
Rain	CB	08/01/99–11/19/99	Major ions	6	40
		10/20/99–11/19/99	Hg	2	13
	HB	08/01/99–11/19/99	Major ions	6	33
		10/20/99–11/19/99	Hg	2	13
Rain	CB	05/16/00–11/15/00	Major ions	10	38
			Hg		25
	HB	05/16/00–11/16/00	Major ions		36
			Hg		26
Rain	CB	05/01/01–11/17/01[a]	Major ions	6	20
	HB				17
Rain	CB	05/28/04–11/17/04[b]	Major ions	7	10
		05/28/04–10/27/04	Hg	6	
	HB	05/28/04–11/17/04	Major ions	7	
		05/28/04–10/27/04	Hg	6	
Snow	CB	12/15/04–03/15/05	Major ions	6	6
		12/15/04–03/15/05	Hg		
	HB	12/15/04–03/15/05	Major ions		5
		12/15/04–03/15/05	Hg		

Major ions included Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+, NO_3^-, SO_4^{2-}, Cl^-, pH (air-equilibrated), ANC, and DOC. Each year after 1999 included concurrent sampling at a co-located bulk collector (included in this analysis) and at NADP/MDN site ME98 (Data not reported in this analysis)

[a] Severe drought limited number of collections

[b] High elevation sites at CB were collected 11/23/04

typically 2–3 weeks apart, and each sample included one or more precipitation events. Throughfall volume was calculated from sample mass for each sample and converted to depth of throughfall hydrologic input based on the collection surface area. The number of sites and solutes measured differed over the study period, 1999–2005 (Table 1). In years lacking a full complement of sites, cluster analysis was used to choose a subset of sampling sites from the 77 established sites to represent the range of vegetation type, elevation, throughfall volumes, and chemical conductance reported in the original (1999–2000, 2001) data set (Nelson 2007). Snow (winter) samples were collected in one project year, whereas summer and autumn samples were collected in all project years (Table 1).

Laboratory analyses

Chemical analyses were performed at the University of Maine. Analyses of major ions followed standard EPA methods (e.g., Norton and Fernandez 1999), including inductively coupled atomic emission spectroscopy or ion chromatography for Ca^{2+}, Mg^{2+}, K^+, Na^+; ion chromatography for SO_4^{2-}, Cl^-, and NO_3^-; ammonium autoanalyzer for NH_4^+; persulfate oxidation and IR detection for DOC; and, air-equilibrated electrode for pH. Hydrogen ion concentration (H^+) was calculated from air equilibrated pH. Total Hg was measured with cold vapor atomic fluorescence spectrometry with EPA Method 1631 (US EPA 2002). Equipment blank Hg concentrations ranged from 0.1 ng L^{-1} (detection limit) to 1.46 ng L^{-1}, averaging 0.35 ng L^{-1}, and the value of the blank was always <10 % of the associated sample Hg concentration. Quality assurance routines included calculation of ion balance ratios and validation of field blank and laboratory replicate data. Samples were re-analyzed if ion balances were >1.20 or <0.80.

Data analysis

Throughfall flux was calculated as the product of chemical concentration and sample throughfall volume divided by the number of days for each sample period in the project years listed in Table 1. Each value used in coherence analysis represented a single collector by single collection period combination, standardized into a per-week value for statistical analyses. Throughfall flux was annualized (mass per

unit area per year) for reporting (e.g., Table 2) and comparison to other published studies. Seasons were defined as summer (leaf on; June–August), autumn (senescence; September–November) and winter (snowfall; December–March). Spring was not included, because sample collection in May of 2000–2001 was insufficient to represent temporal variance within the season. Attempted collections earlier in spring were unsuccessful due to liquid freezing in funnel-bottle collectors and insufficient snow for deploying snow collectors.

Vegetation type above each throughfall collector was determined by visual inspection by two observers. We identified shrub and tree species influencing the collector area in a cone extending upwards from the funnel walls, with an apex angle of 75°. The four species with the greatest areal coverage were ranked by majority of area to determine whether a site was considered deciduous, coniferous, mixed, shrub, or open.

We used coherence analysis to determine if temporal patterns in throughfall fluxes of the 11 solutes plus throughfall amount were similar (or coherent) across sites representing the spatially heterogeneous landscape of Acadia National Park. This approach has been used most often in landscape limnology studies to contrast control on temporal dynamics by local- and broad-scale drivers (Livingstone et al. 2010; Magnuson et al. 1990, 2004; Webster et al. 2000) and captures similarity in temporal pattern of a response variable.

We estimated coherence as the Pearson's correlation coefficient (SAS Institute Inc. 1989, Version 6.07, Cary, NC) between the time series of a response variable for every possible pair of throughfall collector sites. Only 17 of the 77 time series contained fewer than 16 observations, and only three of these 17 sites, dropped due to difficult access, contained fewer than ten observations. The remaining 60 time series used for coherence analysis contained 16–35 observations. By season, winter had the least number of observations in each of the time series ($n = 6$ for each of the 11 collector sites). There were a total of 5,527 site combinations. Response variables included throughfall depth and throughfall flux estimates for Hg and major ions. Prior to analysis, we transformed (natural log (ln)) flux values of all chemical variables except H^+ (hydrogen ion concentration) to produce near-normal distributions, confirmed with normal probability plots. We calculated the median and first and third quartiles of correlation coefficients for all site-pairs within each season and within vegetation types. An index of coherence strength (sensu Magnuson et al. 1990) was estimated as the percentage of correlations (r) that were >0.7. This value was chosen as a conservative estimate of significance across all correlations and also as a level representing roughly half of the variance (r^2 >0.49). Further inferential statistical tests with these correlation coefficients were not warranted due to the results consisting of multiple tests that were not statistically independent (Benson et al. 2000; Magnuson et al. 1990).

We compared correlations for site pairs classified as homogenous (each site in the pair having the same vegetation type) or heterogeneous (pairs with different vegetation types, e.g., a conifer-dominated site paired with a deciduous-dominated site) to determine if vegetation type influenced coherence. If homogenous pairs had greater overall coherence for a given solute than heterogeneous pairs, we concluded that vegetation type influenced throughfall, as dynamics in response to exogenous factors such as weather were similar.

We spatially interpolated throughfall depth data and quantified spatial autocorrelation in throughfall depth to relate the general spatial heterogeneity in hydrologic flux across Acadia National Park to chemical flux. We used the Geostatistical Analyst extension of ArcGIS (version 9.2, ESRI, Inc. Redlands, CA) to interpolate (ordinary kriging; spherical semivariogram with 50 m lag) throughfall depth across the two study watersheds for each of the 35 sampling periods when throughfall was collected. We interpolated throughfall depth for each watershed separately, because the watersheds were not contiguous and have different aspects. We grouped the interpolated data by season and calculated variance in throughfall depth for each season across the watersheds. The resulting maps were scaled identically so they could be visually compared to determine if seasonal differences in the variance in throughfall depths were related to coherence among sites.

Results

Throughfall flux and concentrations varied by season (Table 2). Concentrations of SO_4^{2-}, Hg, H^+, and DOC were greatest and pH was lowest in summer;

Table 2 Mean (standard deviation; *n*) of concentration and annualized throughfall flux for chemical solutes and throughfall (TF) depth determined from 35 throughfall collections made during 1999, 2000, 2001, and 2004–2005 at Acadia National Park, Maine

	SO_4^{2-} (μeq L^{-1})	Total Hg (ng L^{-1})	Cl^- (μeq L^{-1})	Na^+ (μeq L^{-1})	Ca^{2+} (μeq L^{-1})	Mg^{2+} (μeq L^{-1})	K^+ (μeq L^{-1})	NO_3^- (μeq L^{-1})	NH_4^+ (μeq L^{-1})	EqpH	DOC (mg L^{-1})
Throughfall concentration											
Summer	80.9 (59.0; 391)	21.6 (13.4; 265)	61.6 (59.6; 391)	56 (51.0; 391)	27.2 (23.5; 391)	27.7 (25.0; 391)	42.0 (44.3; 391)	26.6 (29.1; 391)	8.68 (13.5; 390)	4.5 (0.46; 387)	16.1 (12.6; 387)
Autumn	60 (42.7; 671)	11.2 (7.8; 317)	118 (125.4; 671)	89.6 (92.9; 671)	27.3 (25.1; 671)	31.8 (29.7; 671)	47.6 (61.4; 671)	29.1 (39.2; 671)	9.28 (15.3; 671)	4.76 (0.65; 644)	11.6 (14.4; 646)
Winter	31.4 (21.1; 70)	10.1 (8.2; 67)	93.2 (77.6; 70)	84.4 (66.6; 70)	10.8 (12.3; 70)	20.5 (17.9; 70)	5.5 (6.4; 70)	16.8 (14.5; 70)	5.04 (3.76; 70)	4.73 (0.25; 70)	1.6 (1.7; 70)
NADP/MDN concentration											
Summer	38.6 (29.3; 36)	16.1 (17.4; 37)	8.2 (8.73; 36)	6.31 (7.81; 36)	5.31 (8.37; 36)	2.15 (2.62; 36)	0.53 (0.98; 36)	25.2 (22.3; 36)	14.7 (16.4; 36)	4.52 (0.35; 36)	
Autumn	23.2 (17.7; 34)	6.9 (3.8; 32)	20.8 (17.6; 34)	18.4 (16.5; 34)	2.89 (2.17; 34)	3.99 (3.30; 34)	0.51 (0.37; 34)	15.4 (18.8; 34)	7.07 (9.25; 34)	4.70 (0.36; 35)	
Winter	25.9 (29.4; 10)	5.8 (6.8; 10)	50.2 (39.5; 10)	44.1 (34.3; 10)	5.12 (7.04; 10)	9.66 (7.97; 10)	1.07 (0.97; 10)	17.0 (24.2; 10)	8.19 (17.9; 10)	4.73 (0.31; 10)	

	SO_4^{2-} (kg ha^{-1} $year^{-1}$)	Total Hg (μg m^{-2} $year^{-1}$)	Cl^- (kg ha^{-1} $year^{-1}$)	Na^+ (kg ha^{-1} $year^{-1}$)	Ca^{2+} (kg ha^{-1} $year^{-1}$)	Mg^{2+} (kg ha^{-1} $year^{-1}$)	K^+ (kg ha^{-1} $year^{-1}$)	NO_3^- (kg ha^{-1} $year^{-1}$)	NH_4^+ (kg ha^{-1} $year^{-1}$)	H^+ (kg ha^{-1} $year^{-1}$)	DOC (mg ha^{-1} $year^{-1}$)	TF depth (mm $year^{-1}$)
Throughfall flux												
Summer	24.4 (14.0; 390)	15.1 (8.3; 265)	14.0 (11.4; 390)	8.32 (6.76; 390)	3.12 (2.08; 390)	2.08 (1.56; 390)	10.4 (8.32; 390)	8.84 (8.84; 390)	1.04 (1.56; 389)	0.52 (0.05; 386)	107 (78.0; 386)	47 (31; 458)
Autumn	26.0 (17.7; 662)	10.4 (7.80; 317)	45.2 (63.4; 662)	23.4 (35.9; 661)	5.20 (4.68; 661)	3.64 (4.16; 661)	15.6 (15.6; 661)	16.12 (21.3; 662)	1.56 (1.56; 661)	0.52 (0.52; 634)	109 (128; 637)	58 (30; 738)
Winter	21.8 (18.2; 70)	14.0 (10.9; 67)	47.3 (42.1; 70)	28.1 (24.4; 70)	3.12 (3.64; 70)	3.64 (3.64; 70)	3.64 (7.28; 70)	13 (11.4; 70)	1.56 (2.08; 70)	0.52 (0.05; 70)	25.5 (41.6; 70)	62 (28; 70)
NADP/MDN flux												
Summer	10.8 (5.47; 4)	7.7 (6.8; 40)	12.1 (9.55; 4)	6.87 (5.61; 4)	0.63 (0.39; 4)	0.75 (0.59; 4)	0.28 (0.22; 4)	7.79 (3.10; 4)	0.93 (0.38; 4)	0.24 (0.10; 4)		129 (60.6; 4)
Autumn	10.5 (2.95; 4)	8.5 (12.0; 37)	1.67 (0.75; 4)	0.87 (0.41; 4)	0.46 (0.02; 4)	0.14 (0.04; 4)	0.09 (0.03; 4)	7.6 (1.43; 4)	1.41 (0.34; 4)	0.22 (0.05; 4)		69 (24; 4)
Winter	11.5 (na; 1)	4.3 (3.7; 11)	25.2 (na; 1)	13.7 (na; 1)	0.84 (na; 1)	1.6 (na; 1)	0.51 (na; 1)	6.12 (na; 1)	0.56 (na; 1)	0.2 (na; 1)		130 (na; 1)

NADP and MDN concentration and flux data for site ME98 were compiled for the same time periods as in the throughfall research

concentrations of Cl^-, Na^+, Ca^{2+}, Mg^{2+}, K^+, NO_3^-, and NH_4^+ were greatest in autumn (Table 2). Peaks in throughfall flux occurred in summer for Hg, autumn for SO_4^{2-}, Ca^{2+}, K^+, NO_3^-, and DOC, and winter for Cl^- and Na^+. Throughfall fluxes of Mg^{2+} and NH_4^+ were similar in autumn and winter. Standard deviations of throughfall fluxes of base cations, Na^+, Cl^-, NO_3^-, NH_4^+, and DOC averaged ~120 % of the mean in autumn and winter, whereas they averaged ~80 % of the mean in summer.

The magnitude and among-site pair variance of coherence of throughfall flux as well as coherence in throughfall concentrations (data not shown; see Nelson 2007), assessed as the percentage considered strong (correlation > 0.7), differed with chemical variable and season (Fig. 3). In summer, coherence was greatest for throughfall depth, SO_4^{2-}, and NO_3^-; coherence was least, and variance was greatest, for K^+, NH_4^+, H^+, and DOC in summer. Coherence declined slightly in autumn for throughfall depth, SO_4^{2-}, and NO_3^- and Hg, however, coherence increased and variance decreased for all other analytes except throughfall depth, SO_4^{2-}, and Hg. In winter, variance declined for all analytes except throughfall depth, and coherence increased notably for Cl^-, Na^+, Ca^{2+}, Mg^{2+}, and DOC (Fig. 3).

Throughfall volume showed a strong seasonal pattern in coherence, total amount and spatial variance. Throughfall volume correlations were strongest in summer and weakest in autumn (Fig. 3). Throughfall depth was greater and most variable in both watersheds in winter with greatest variance occurring at a summit with krummholz vegetation and balds in Hadlock, and a mid-elevation ledge with krummholz and balds in Cadillac (Fig. 4). Variance in winter throughfall depth probably was due to re-distribution of snow, especially in windy, high-elevation or exposed sites. In contrast, throughfall depth was less and variance greatest at low-elevation sites with mixed conifer-deciduous vegetation during summer and autumn (Fig. 4). Throughfall depth also was variable near the summit (northernmost extent) of Cadillac watershed, where vegetation consisted of a krummholz-bald mixture. However, some throughfall collectors in this area were located in sheltered sites such as in a small, forested valley containing the stream headwaters.

Throughfall flux coherence was more variable in summer and autumn than in winter with respect to comparisons between heterogeneous and homogeneous site pairs (Fig. 5). In summer, the coherence of throughfall flux of chemical variables taken up by or leached from the forest canopy (H^+, K^+, NH_4^+, DOC) had the least coherence, and coherence was slightly weaker in heterogeneous than homogeneous vegetation pairs. Ions that could be sourced from maritime influences (Cl^-, Na^+, Ca^{2+}, Mg^{2+}) had moderate coherence in summer, and only slightly weaker coherence in heterogeneous than homogeneous vegetation site pairs. Solutes influenced by scavenging efficiency of the canopy (SO_4^{2-}, Hg, NO_3^-, throughfall depth) had the strongest coherence in summer compared to other ions. In autumn, the throughfall flux dynamics of K^+, DOC, NO_3^- and NH_4^+ generally were more coherent for homogeneous than heterogeneous site pairs, and coherence values were less variable overall (Fig. 5). In winter, marine-derived ions had greater coherence overall and did not demonstrate weaker coherence for heterogeneous site pairs. By contrast, solutes that responded to canopy presence and architecture (SO_4^{2-}, Hg, NO_3^-, DOC, and throughfall depth) did display weaker coherence in heterogeneous site pairs than homogeneous site pairs (Fig. 5).

Discussion

Patterns in coherence among the study sites in Acadia National Park suggest the dominant factors controlling throughfall flux are seasonally dynamic and differ by solute. Seasonally changing air mass sources, throughfall volume and spatial pattern, and vegetation type appear to have been important controls on throughfall coherence at Acadia, and each represents a different scale of control, from localized to broad-scale.

Broad scale control on temporal dynamics related to air mass source was most apparent in winter, when stronger overall coherence in throughfall flux for many solutes suggests weaker vegetation control compared to other seasons (Fig. 3). Chloride (largely marine-derived) illustrates the influence of air mass seasonality. Coastal watersheds, such as our focal study areas, are influenced by significant Na^+ and Cl^- as seasalt aerosols (Beier et al. 1992, NADP data); Ca^{2+}, SO_4^{2-} and Mg^{2+} also have significant marine sources. Chloride fluxes were greater in winter than in summer or autumn owing to this strong marine input

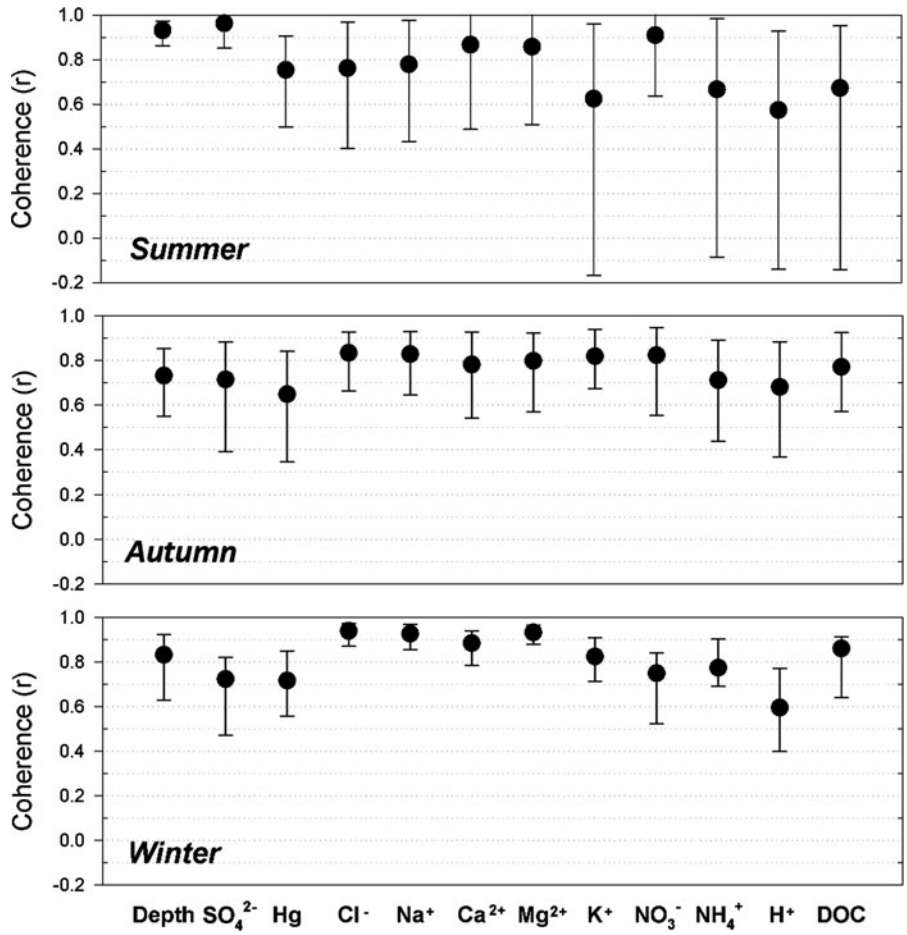

Fig. 3 Median (*dot*) and 75th and 25th percentile (*error bars*) of site-pair Pearson's correlation coefficients for a total of 35 throughfall collections divided into season. Coherence is expressed as *r*, the Pearson's correlation coefficient between all pairs of sites for each chemical variable or throughfall depth for each collection

and suggest a shift from continental to predominantly maritime events during the winter season. Our interpretation that the dominant air mass source of deposition to Acadia National Park shifts seasonally is supported by sea-salt corrected (Stumm and Morgan 1981) Ca^{2+} concentrations in throughfall. Based on these data it appears that a maritime air mass source dominated in winter, when marine Ca^{2+} averaged 62 %, while the continental air mass source combined with canopy leaching dominated in the summer, when marine Ca^{2+} averaged only 9 %.

This shift in air mass sources also influenced throughfall flux of Hg, a pollutant of concern with primary sources from both continental US air masses and global atmospheric transport (Pacyna et al. 2010). Winter Hg throughfall flux of 5.63 ± 0.38 μg m^{-2} was five times greater than either MDN network flux data (0.91 μg m^{-2}) or values reported in the literature during the same period (Nelson et al. 2008). Greater throughfall fluxes in winter could reflect greater scavenging efficiency by snow than rain, particularly in terms of accumulation of dry Hg on complex snow crystal structures. Finally, it is notable that our estimates of annual throughfall flux of Hg approximately equaled litterfall flux of Hg measured by Sheehan et al. (2006) for these same watersheds.

At the local scale, our hypothesis that coherence for site pairs with homogeneous vegetation would exceed that for site pairs with heterogeneous vegetation was supported by the data. Local control by vegetation type also was a dominant control for coherence analysis of throughfall concentrations (data not shown, Nelson 2007), especially in summer and autumn. The effect of vegetation is manifest in two ways (e.g., Grigal 2002; Rea et al. 2000; Lovett 1994). First, leaves and needles scavenge particles and gases from air masses between precipitation events. This enhancement of dry deposition has been reported for solutes such as Hg and SO_4^{2-}, which generally are considered conservative with respect to vegetation

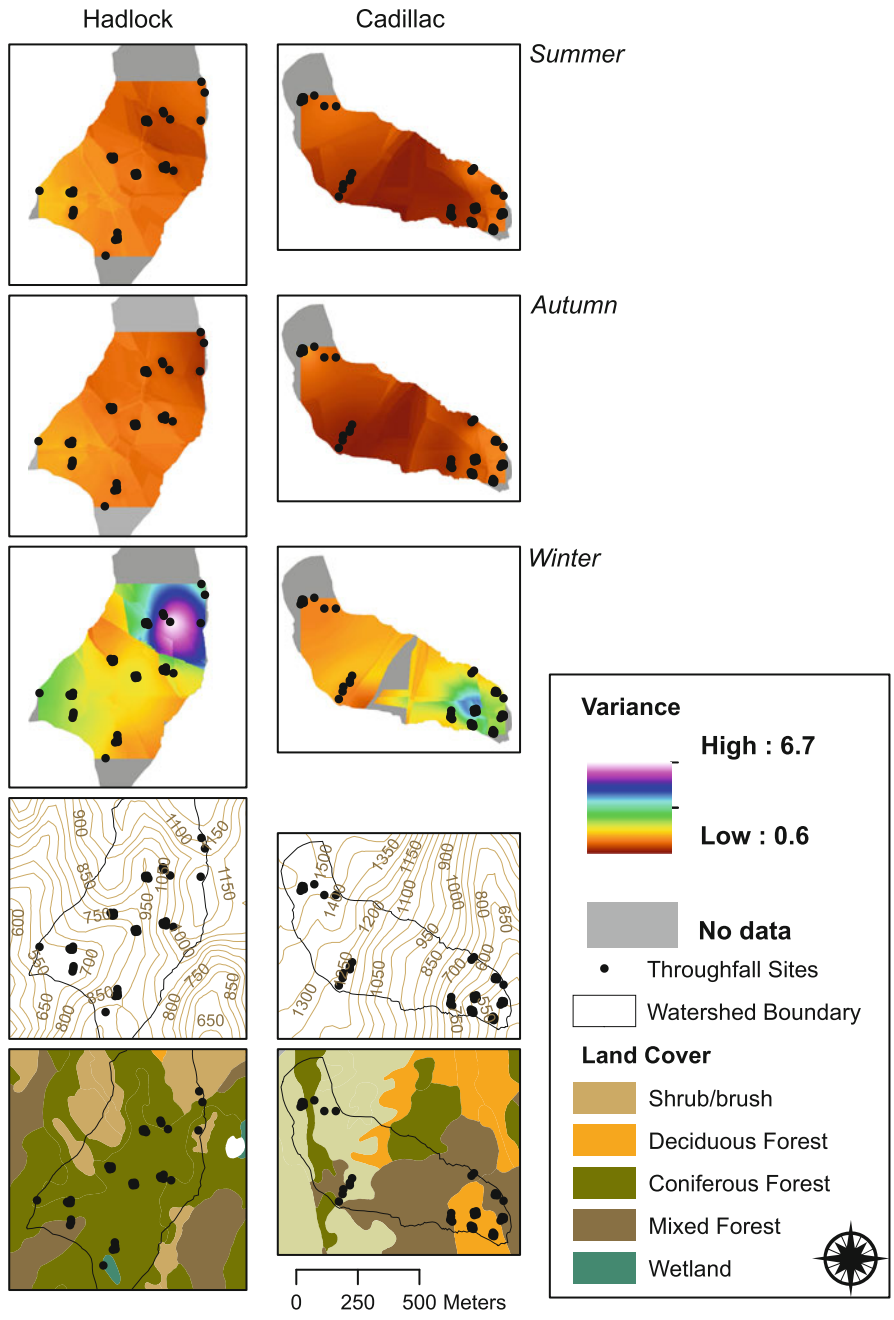

Fig. 4 Summer, autumn, and winter variance surfaces for Hadlock and Cadillac watersheds. *Dots* on each map show the throughfall collector sites. Maps were created by kriging water depth for each throughfall collection, then calculating cell statistics (mean, standard deviation) and dividing to produce the variance raster. Topographic contours (15 meter (50 ft) increments) and the Park's vegetation map are shown for each watershed. Topographic contours were provided by the National Park Service. Vegetation map provided by the USGS-NPS Vegetation Mapping Project, Lubinski et al. 2003. Map projection is NAD83, Zone 19 North

uptake (Johnson et al. 2007; Weathers et al. 2006; Rea et al. 2000; Lindberg and Lovett 1992). Second, vegetation phenology leads to enhanced nutrient uptake during the growing season and enhanced nutrient leaching during leaf senescence. We found fewer strong correlations of ions that exchange readily in forest canopies (e.g., NH_4^+, K^+) during the growing season, supporting a local scale effect of vegetation on throughfall flux at Acadia (Fig. 3).

We observed stronger coherence in dissolved organic carbon (DOC) in autumn throughfall flux compared to summer, likely reflecting leaching of DOC from senescing leaves with the onset of dormancy. Coherence in DOC flux measurements was

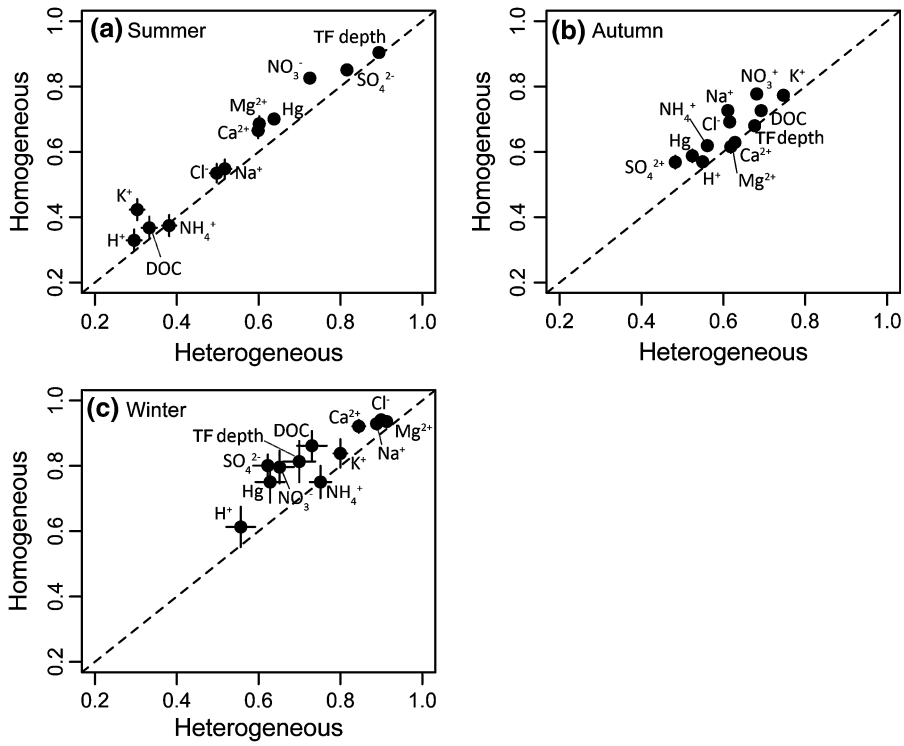

Fig. 5 Mean (with standard *error bars*) correlations between homogeneous site pairs (i.e., with the same vegetation) plotted against correlations between heterogenous site pairs (i.e., that differ in vegetation) for each chemical variable and throughfall depth in **a** summer, **b** autumn, and **c** winter. The *dashed line* is the 1:1 line

greatest in winter, presumably when vegetation plays a minimal role in DOC processing. We are unaware of published studies that report annual DOC dynamics in throughfall. Our finding of seasonal dynamics in DOC in throughfall is a focal topic for future research, particularly with the potential for increased extreme events and changes in snow patterns in winter, and as carbon storage and cycling in forested watersheds respond to changing climate (e.g., Findlay 2005).

Throughfall hydrologic flux affects patterns and interpretation of chemical throughfall flux dynamics in two ways. Chemicals are delivered and distributed across the landscape in precipitation, as well as are leached from vegetation, thus directly affecting throughfall concentrations. Sulfate illustrates the seasonal change in coherence with throughfall hydrologic delivery: coherence in SO_4^{2-} flux declined from summer to autumn but not from autumn to winter. Total flux of SO_4^{2-} remained similar in all three seasons (summer: 24 ± 14 kg ha^{-2} year^{-1}; autumn: 26 ± 18 kg ha^{-2} year^{-1}; winter: 22 ± 18 kg ha^{-2} year^{-1}). Similar flux of SO_4^{2-} across all seasons despite declining concentrations from summer to autumn to winter (Table 2) suggests that throughfall hydrologic flux plays a more important role in delivery of SO_4^{2-} in winter compared to other seasons, most likely due to greater variation in snowfall in sites with diverse vegetation. A similar effect of variation in winter throughfall volume most likely influenced DOC flux.

Our results provide insights into controls on throughfall flux in the winter, a season not often studied, especially in remote sites, due to difficult logistics. Snow is less likely to interact with the canopy in winter, bypassing it or sublimating from vegetation surfaces. Cold temperatures also can reduce dissolution of solutes at the snow-vegetation interface. The effect of the shift to a marine air mass source in winter was stronger than any effect of vegetation on dynamics as reflected by the strongest overall coherence across all site type pairs observed in winter; there is less vegetation control at deciduous and mixed sites in winter owing to leaf loss. Instead, throughfall hydrologic flux, particularly in winter

Table 3 Key broad-scale and local-scale controls for throughfall chemical variables by season, Acadia National Park, Maine

Season:	Summer		Autumn		Winter	
Chemical variable	1° control	2° control	1° control	2° control	1° control	2° control
SO_4^{2-}	AM	VEG	VEG	HYD	AM	VEG
Hg	AM	VEG	AM	VEG	AM	VEG
Cl^-	AM	VEG	AM	VEG	AM	HYD
Na^+	AM	VEG	AM	VEG	AM	HYD
Ca^{2+}	AM	VEG	VEG	HYD	AM	HYD
Mg^{2+}	AM	VEG	VEG	HYD	AM	HYD
K^+	VEG	HYD	VEG	HYD	AM	HYD
NO_3^-	VEG	HYD	VEG	HYD	AM	VEG
NH_4^+	VEG	HYD	VEG	HYD	AM	VEG
H^+	HYD	AM	HYD	AM	AM	HYD
DOC	HYD	AM	VEG	HYD	AM	HYD

Hierarchical placement of controls determined subjectively after considering results of temporal and spatial coherence and throughfall depth variance analyses

AM air mass source, *VEG* vegetation type, *HYD* throughfall hydrologic input

snowfall, was a key driver influencing variability in throughfall chemical inputs. We observed heightened variance in throughfall depth in winter as compared to summer and autumn, a result likely associated with exposed areas. Forest edges are areas where solute deposition varies greatly and may be enhanced (Weathers et al. 1995), and exposed areas are more vulnerable to snow redistribution by wind (Pomeroy and Gray 1995). In contrast, uniform throughfall depth across the sites within a season, as occurred in summer, suggests that variability in the amount of chemicals delivered to the throughfall collector is attributable to vegetation type or air mass source.

Implications

Extensive atmospheric deposition monitoring networks rarely have the resources to evaluate effects of fine-scale land cover and terrain on deposition flux to watersheds. Watershed-scale mass balance studies require spatially heterogeneous deposition estimates, and when measurements are made, they are often limited to the growing season. We evaluated summer, autumn, and winter deposition data from coastal watersheds with heterogeneous vegetation, and found that controls on throughfall chemistry differed by seasonal influence of air mass source, vegetation condition, and throughfall hydrologic flux (Table 3). Although previous research has highlighted some of these influences on throughfall fluxes, we used coherence analysis to assess shifting controls in drivers across a broad suite of analytes and through seasons in 4 years.

An analysis of spatial and temporal coherence potentially captures season-specific mechanisms for solutes important to watershed biogeochemical cycles. For example, studies to develop spatially comprehensive estimates of watershed inputs might focus more on deploying collectors under representative vegetation types in summer, and in open sites in winter, to account for hydrologic variability. In coastal sites such as Acadia National Park, winter inputs of solutes that are at least partly marine-derived (Cl^-, Na^+, Ca^{2+}, Mg^{2+}, Na^+, K^+) were enhanced in winter throughfall flux: approximately two- to seven- times NADP wet-only inputs during the same time period, and one- to three- times summer throughfall flux. Strategically placed throughfall measurements may enhance annual wet deposition measurements to obtain more representative inputs for mass balance calculations.

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