

Atmospheric deposition and corresponding variability of stemflow chemistry across temporal scales in a mid-Atlantic broadleaved deciduous forest

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ABSTRACT

Despite the fact that atmospheric deposition is widely accepted to be an important process in the biogeochemical cycling of wooded ecosystems, no single study is known that has examined stemflow chemistry in relation to atmospheric deposition across time scales, from within discrete events to season, to chronicle alterations in temporal patterns of stemflow chemistry. This research partitioned stemflow solute fluxes (K^+ , Na^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , and SO_4^{2-}) from two tree species of differing canopy form and bark morphology into their leaching and dry deposition washoff components using a modified Kazda (1990) integration model at the intra-storm scale to examine differences within and among discrete rain events. Median annual stemflow concentrations in yellow poplar (*Liriodendron tulipifera* L.) stemflow were higher than American beech (*Fagus grandifolia* Ehrh.) stemflow for all ions except NO_3^- . Beech median enrichment ratios were larger for all monitored ions than yellow poplar. All intra-storm stemflow ionic fluxes were initially high, exponentially decaying to a steady input, typically dominated by leaching contributions. With the exception of yellow poplar stemflow Cl^- and NO_3^- fluxes and beech Na^+ flux, all intra-storm mean ionic fluxes began with higher dry deposition percentages and transitioned to primarily leaching. Observations in the field implicate increased magnitude and rainfall intensity in the initiation of new stemflow flowpaths, evidenced by increased variability in the timing of stemflow ionic deposition and fluctuations in the proportion of washoff and leaching during some events. Beech stemflow fluxes were larger than yellow poplar for all ions during the leafed, leafless, and annual periods. Our results demonstrate: (1) the critical role of the initiation of new flowpaths and expansion and maturation of developed flowpaths on a tree's surface to solute enrichment and transport to the forest floor as a canopy wets-up; and (2) the importance of temporal scale in providing important insights into some effects of stemflow on biogeochemical cycling.

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1. Introduction

Temperate deciduous canopies cover about 4 billion hectares of land surface globally, with two-thirds contained in the northern hemisphere (FAO-UN, 2005). The aerodynamically rough surfaces of deciduous forest canopies have proven to be efficient scavengers of atmospheric wet and dry deposition. As a result, they provide much of the initial interface for atmosphere–biosphere

interactions within this biome (Levia and Frost, 2006). The foliar and woody components of this interface drastically alter the spatial patterning of atmospheric inputs (Ford and Deans, 1978; Staelens et al., 2008) by intercepting incident precipitation (Levia and Frost, 2006) and dry deposited materials from natural (Lovett and Lindberg, 1984) and anthropogenic (Avila and Rodrigo, 2004) sources.

Intercepted rainfall initiates flowpaths (throughfall and stemflow) within the canopy which usually become chemically enriched through the washoff of dry deposition (Kazda, 1990) and leaching of substances (Tukey, 1970). In some cases, depletion of solutes in stemflow is possible from uptake by epiphytic bacteria and lichens inhabiting bark surfaces (Houle et al., 1999; Levia, 2002; Oyarzún

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et al., 2004). As a storm event progresses, stemflow redistributes this enriched water heterogeneously over space and through time, thereby initiating and cultivating localized areas of enhanced solute flux to the forest floor (Levia and Frost, 2003, 2006). The resultant canopy-derived solute flux significantly influences ecologically valuable pools, altering the spatial patterning of soil moisture (Durocher, 1990; Chang and Matzner, 2000) and soil solution chemistry (Falkengren-Grerup, 1989; Chang and Matzner, 2000), and sometimes shaping the spatial distribution of understory vegetation (Crozier and Boerner, 1984).

Relatively few studies have examined the temporal changes of stemflow water and solute inputs within individual rain events. A much better understanding of intra-storm variation in stemflow water and solute flux to the forest floor is critically important to determine whether stemflow inputs induce or affect hot moments and hot spots of biogeochemical reactivity (McClain et al., 2003). Levia et al. (2010) found that stemflow water inputs were highly variable within particular rain events, often mirroring rainfall inputs once the bark water storage capacity was reached along preferential flowpaths of a tree's crown. Similar to throughfall (Hansen et al., 1994; Germer et al., 2007), stemflow ion concentrations have been observed to be largest at the onset of the rain event and generally steadily decrease as the event continues (Kazda, 1990). The rate of decrease in stemflow ion concentration was dependent on both rainfall intensity and amount of dry deposition (Kazda, 1990).

Hitherto, no single study is known that has examined stemflow chemistry in relation to atmospheric deposition from within a particular event to annual time scales. The specific aims of our research were to: (1) quantify and examine intra-storm stemflow washoff and leaching patterns; (2) quantify and examine event-scale stemflow washoff and leaching among discrete rain events; and (3) calculate and compare stemflow solute fluxes between leafed and leafless periods and at annual time scales. Implicit in our temporal analysis is a comparison of stemflow washoff and leaching dynamics for the two dominant tree species at our study site, American beech (*Fagus grandifolia* Ehrh.) and yellow poplar (*Liriodendron tulipifera* L.). Thus, this manuscript chronicles alterations in stemflow chemistry across temporal scales, yielding comparisons and contrasts as a function of time and species.

2. Materials and methods

2.1. Study site

The experimental plot was located within the Fair Hill Natural Resources Management Area (NRMA) in northeastern Maryland (39° 42'N, 75° 50'W) at an elevation of 70 m above sea level. Fair Hill NRMA lies within the Piedmont physiographic region, close to the Chesapeake and Delaware Bays. As a result, climate is primarily humid maritime with well-defined seasons. Frontal precipitation patterns are typical for fall, winter and spring; and convective precipitation events dominate summer. Mean 30-year total annual precipitation is approximately 1200 mm, with an average of 350 mm winter seasonal snowfall (MD Climatologist Office, 2008). The wettest season is summer (324 mm) and winter is the driest season (274 mm). Average annual summer temperature is 21.7 °C with a maximum daily mean temperature of 24.6 °C in July. Average annual winter temperature is 1.1 °C with a minimum daily temperature of -0.6 °C (MD State Climatologist Office, 2008).

The overall forest canopy at Fair Hill NRMA is deciduous with beech, yellow poplar, and *Acer rubrum* L. (red maple) as the predominant species. The study site, however, is co-dominated by beech and yellow poplar (Van Stan and Levia, 2010). The stand density of all trees within the study area ≥ 10 cm diameter at breast

height (dbh) was 225 trees ha⁻¹. Site stand basal area was 36.8 m² ha⁻¹, mean dbh was 40.8 cm, and mean canopy tree height was 27.8 m. The leafless periods for 2007–2009 lasted 6 months, beginning the first week of November and ending the last week of April. Leaf-out for both years of our study began the first week of May.

2.2. Ecohydrological monitoring and sampling

Sampling for this study occurred from fall 2007–fall 2009. A total of 27 events were sampled (15 in the leafed period and 12 in the leafless period), including 6 sequentially sampled events. Rainfall events were defined as those that generated appreciable amounts of stemflow to permit collection of chemical samples, generally >7 mm of rainfall. Rainfall depth equivalent was monitored at the Fair Hill NRMA meteorological station using a Geonor vibrating wire precipitation gage equipped with an alter-type wind shield. Stemflow volumes were monitored at 5-minute intervals using Texas Electronics TE525MM tipping bucket gages (orifice diameter 24.5 cm, 0.1 mm tip⁻¹) interfaced with a Campbell Scientific CR1000 datalogger. Care was taken to ensure that the gages remained level throughout the study and were periodically calibrated in the field.

Two beech and three yellow poplar trees were fitted with collars made of 31.8 mm outer diameter vinyl tubing, cut longitudinally and attached to the tree bole with aluminum nails and silicone sealant. Diameter at breast height (dbh) of the sampled beech trees was 10.3 and 74.9 cm, while the dbh of the yellow poplar trees was 33.7, 71.1, and 73.1 cm. The bark structure of both beech trees was smooth with little variation, whereas the bark of the two larger yellow poplar trees was rough in comparison to the smaller yellow poplar tree. The bark of the smallest yellow poplar tree was, however, rougher than both beech trees. All sample trees were located within the same plot within 30 m from each other. One stemflow collar for each species was connected to a 5 L chemically-inert high density polyethylene (HDPE) bin for bulk and manual sequential sampling, while one beech and two yellow poplar collars directed stemflow into shielded tipping bucket gages. Stemflow bulk chemistry of the selected trees was insignificantly different from the Na⁺ ($F(1,88) = 0.47, p = 0.50$; $F(1,65) = 0.35, p = 0.56$), Mg²⁺ ($F(1,88) = 1.04, p = 0.31$; $F(1,65) = 0.06, p = 0.79$), K⁺ ($F(1,88) = 0.61, p = 0.44$; $F(1,65) = 0.15, p = 0.70$), and Ca²⁺ ($F(1,88) = 0.31, p = 0.57$; $F(1,65) = 0.21, p = 0.65$) concentrations of five other comparably-sized trees for beech and yellow poplar, respectively, in the same study site over the course of a partly overlapping year, giving credence to the argument that the sample trees are representative of the broader population.

Bulk and sequential samples for chemical analysis were collected for stemflow from both species and incident precipitation at the meteorological station. Bulk samples were collected within 24 h after a rain event. Sequential samples were collected manually from individual trees, allowing the sampling intervals to be determined on an event-basis. As such, collection times for sequential stemflow samples varied for each storm event based on rainfall intensity, storm duration, and stemflow generation. As previous work has shown exponential decays in chemical washoff during storm events (Kazda, 1990), sampling intervals at the beginning of each storm event were shorter (approximately every 15 min) than at the end (approximately every hour) to accurately capture the dry deposition washoff. Variability in intra-storm wet deposition was negligible in comparison to intra-storm variability in stemflow flux. For example, the highest variability (± 1 SD) in wet deposition flux was only 2.6 meq K⁺ ha⁻¹ and the lowest for stemflow was 4956 meq Na⁺ ha⁻¹.

2.3. Chemical analyses

Bulk and sequential field samples for chemical analysis were collected from chemically-inert HDPE bins, filtered with Millipore, Durapore membrane filters (0.45 μm) and then stored at 4 °C until shipped in coolers to the State University of New York's College of Environment and Forestry (SUNY-ESF), where laboratory analyses were performed. Any samples contaminated with non-foliar organic debris were discarded. Samples were analyzed for pH by potentiometric methods using a Fisher Scientific, Accumet AR50 dual channel pH/ion/conductivity meter. Base cations (Na^+ , Mg^{2+} , K^+ , and Ca^{2+}) were determined by inductively coupled plasma atomic emission spectrometry, employing a Perkin Elmer 3300 DIV instrument. Anion concentrations (Cl^- , NO_3^- , and SO_4^{2-}) were quantified using a Dionex ICS-2000 ion chromatograph, fitted with an IonPac AS18 analytical column (4 \times 250 mm) and an IonPac AG18 guard column (4 \times 50 mm). The reliability of analytical results was ensured through the use of blanks, standards, and adherence to US government agency protocols as follows: (1) for all analyses, a blank was analyzed, and a minimum of one QC standard (of known concentration) was implemented per experimental run, which must be within 10% of the known concentration; and (2) the laboratory participates in the United States Geological Survey SRS QA/QC program two times per year.

2.4. Derivation of dry deposition and leaching

The Kazda (1990) integration technique partitions intra-storm stemflow solute fluxes into the dry deposition and leaching components using a non-linear, exponential regression to describe the convergence of solute concentrations to a constant value representative of leaching and precipitation inputs.

For all storm events, the total solute flux in stemflow was determined by integrating the entire mass curve over the length of the precipitation event:

$$\int (Ae^{Bt} + C) dt \quad (1)$$

where A , B , and C are parameters of the regression function, t is time of the event, and $B < 0$ because this is an exponential function of decay (Kazda, 1990). This overall integration can be broken into two independent integrals:

$$A \int e^{Bt} dt + C \int dt \quad (2)$$

where the first integral represents solute input from dry deposition washoff and precipitation scavenging. In accord with Kazda (1990), washoff will equal dry deposition for elements without uptake or absorption through foliar or woody surfaces of the canopy. The remaining inputs from precipitation, leaching, and absorption are quantified by the second linear integration (Kazda, 1990). The linear integration can be further separated into the leaching and precipitation contributions if solute inputs in the open area are known:

$$C \int dt = E_{fi} + Le_{ai} \quad (3)$$

where C is the total steady input of solutes from incident precipitation and leaching, E_{fi} is the input from incident precipitation and Le_{ai} is the amount of leached solutes in the stemflow (Kazda, 1990). Equation (3) differs from Kazda's (1990) method by the absence of a precipitation partitioning term because mean precipitation flux represented $<1\%$ of C on average, making it inconsequential in model calculations. In our study, C was the

average of two or more sequential chemical values that exhibited $<10\%$ decrease from the initial value in that sequence after the exponential decay. Solute input from incident precipitation (E_{fi}) was determined by the product of bulk precipitation volume and solute concentration. Leaching inputs were then calculated by changing equation (3) to:

$$Le_{ai} = C \int dt - E_{fi} \quad (4)$$

Separate integrations and decompositions were computed for each solute in stemflow of both tree species for appropriate sequentially sampled storm events.

The formulation of Kazda (1990) is valid under the specific condition of uniform stemflow pathways through the canopy and constant leaching for an event (Fig. 1a). The establishment of new pathways, however, increases wetted surface area which generates additional inputs of dry deposited washoff and enhances leaching (Fig. 1b). Therefore, we have modified the Kazda (1990) model to account for the enhanced input from new pathways, where washoff and leaching contributions from previously unwetted surfaces are determined via the storm-specific flux curve; idealized by successive increases in steady-state leaching after new flowpaths produce

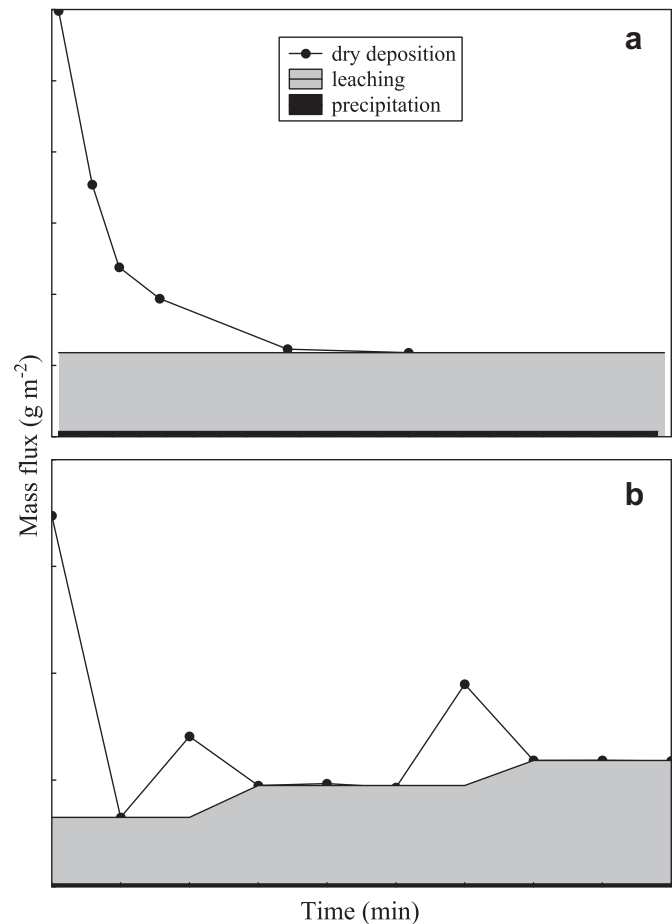


Fig. 1. Conceptual model of two temporal trends in solute mass input. Panel (a) represents the single-pathway condition valid for the integration method detailed in Kazda (1990), where the initial flush of dry deposition settles to a consistent leachate mass input composed of precipitation input and leaching. Solute mass input in Panel (b) begins with an initial flush of dry deposition and develops peaks of washoff as new hydrologic flowpaths are generated. Increased leaching from exchange processes over newly wetted surface areas becomes apparent after the establishment of each additional hydrologic flowpath.

washoff peaks as an event progresses (see Fig. 1b). All storms exhibited intra-storm trends of elemental flux that resemble Fig. 1a or 1b, hence equation (3) was used to quantify the total leachate and precipitation flux (C) after each peak in elemental flux. Dry deposition was then determined by subtracting the total leachate flux from the total flux. Equation (4) then separates total solute flux (C) into the relative contributions of Lea_i and Ef_i after each peak in elemental flux.

2.5. Enrichment ratio

During precipitation events, stemflow may be enriched or depleted, compared to the bulk precipitation. In order to quantify stemflow enrichment, the following equation is used:

$$E = (C_s S) / (C_p P_g B) \quad (5)$$

where E is the enrichment ratio of stemflow, C_s is the solute concentration in stemflow, S is the stemflow volume, C_p is the solute concentration of bulk precipitation, P_g is the depth equivalent of bulk precipitation, and B the basal area of the stemflow generating tree (Levia and Herwitz, 2000). Equation (5) permits the comparison of solute inputs between stemflow and precipitation per unit trunk basal area.

Expression of stemflow inputs using the enrichment ratio (or computation of stemflow fluxes using basal area) is a meaningful and intuitive method because basal area is the area over which stemflow is input into the soil. Stemflow inputs based on catchment area inherently under-represent and underestimate the importance of stemflow because it spreads stemflow inputs over the entire catchment rather than basal area which is the true area of stemflow input. André et al. (2008) have employed the enrichment ratio as a measure of flux based stemflow enrichment. An alternate concentration based enrichment computation would be the ratio of stemflow and rainfall concentrations (André et al., 2008). Because stemflow funnels both water and solutes to the tree base, we favor the enrichment ratio, as defined in equation (5), since it is flux based, coupling both the water and solute inputs.

2.6. Statistical analyses

Descriptive statistics were compiled for rainfall concentrations, stemflow concentrations, enrichment ratios, and fluxes. Stemflow concentrations and fluxes were not normally distributed and required the use of non-parametric Mann–Whitney U test to determine the statistical significance. T -tests were used to compare stemflow enrichment ratios as they were normally distributed.

3. Results

3.1. Overview: stemflow concentration and enrichment ratios

For both species, median annual stemflow ion concentrations were elevated in comparison to bulk precipitation (Table 1). The pH was generally more acidic for yellow poplar stemflow than beech stemflow; yet, the quartile range of pH within beech stemflow was larger than that of yellow poplar (Table 1). Both species' quartile range and median stemflow pH were at least an entire unit lower than the median bulk precipitation pH (Table 1). Median annual stemflow concentrations in yellow poplar stemflow were higher than beech stemflow for all ions except NO_3^- (Table 1). Although beech stemflow Cl^- concentrations were slightly lower than those observed from yellow poplar, the difference was practically indistinguishable (Table 1). The most enriched ion for both species was K^+ , as median K^+ enrichment ratios were well over double the

Table 1

Descriptive statistics for annual bulk precipitation, stemflow concentrations, and stemflow enrichment ratios for beech and yellow poplar (total number of discrete rain events: $n = 27$).

Chemical parameter	Concentration ($\mu\text{eq L}^{-1}$)			Enrichment ratio		
	Median	Lower quartile	Upper quartile	Median	Lower quartile	Upper quartile
Bulk precipitation						
pH	7.0	6.6	7.5	–	–	–
Na^+	21.1	13.1	40.0	–	–	–
Mg^{2+}	13.4	10.7	39.6	–	–	–
K^+	11.8	4.8	60.4	–	–	–
Ca^{2+}	22.0	14.0	38.1	–	–	–
Cl^-	13.9	8.5	44.9	–	–	–
SO_4^{2-}	37.1	22.4	53.8	–	–	–
NO_3^-	18.3	10.3	38.4	–	–	–
Beech stemflow						
pH	6.0	5.2	6.2	–	–	–
Na^+	23.0	12.6	49.7	13.1	6.5	246.4
Mg^{2+}	19.7	9.1	39.5	13.4	6.1	138.1
K^+	142.7	87.7	315.3	88.2	51.0	613.1
Ca^{2+}	39.9	14.0	98.3	15.6	5.8	147.5
Cl^-	34.6	11.3	55.6	10.9	6.1	588.9
SO_4^{2-}	117.4	60.3	400.3	37.2	16.6	307.0
NO_3^-	67.2	29.9	136.9	23.0	16.3	293.9
Yellow poplar stemflow						
pH	5.8	5.5	6.1	–	–	–
Na^+	35.2	20.9	58.4	1.0	0.5	7.0
Mg^{2+}	148.1	65.8	193.0	4.5	1.7	27.2
K^+	353.4	209.5	473.4	17.3	2.7	78.3
Ca^{2+}	136.2	65.4	172.2	3.0	1.4	15.4
Cl^-	39.6	16.8	66.7	1.2	0.4	10.4
SO_4^{2-}	251.7	109.4	334.8	3.5	1.1	26.8
NO_3^-	26.4	4.8	61.1	0.6	0.2	5.2

second-most enriched ion from either tree canopy (Table 1). Beneath yellow poplar, median enrichment ratios of the divalent ions were all between 3 and 4.5, whereas median enrichment ratios for the monovalent ions were approximately 1 with uptake of NO_3^- evident with an enrichment ratio <1 (Table 1). Beech median enrichment ratios were larger for all monitored ions than yellow poplar, yet did not exhibit the same valence trends in enrichment ratio as yellow poplar (Table 1). SO_4^{2-} and NO_3^- had the second- and third-highest median enrichment ratio for beech stemflow (Table 1). Median beech enrichment ratios for the remaining cations and anions (Na^+ , Mg^{2+} , Ca^{2+} and Cl^-) were similar, ranging between ~ 11 and 16 (Table 1). The lower-to-upper quartile range of concentrations and enrichment ratios was much larger for beech than for yellow poplar and for K^+ across species (Table 1). However, for beech stemflow, the range between lower and upper enrichment ratio quartiles was greatest for Cl^- (Table 1). Yellow poplar Mg^{2+} concentrations and enrichment ratios also exhibited a large quartile range (Table 1). The annual stemflow concentrations of most studied ions differed significantly between beech and yellow poplar (Table 2). Interspecific differences in annual stemflow enrichment ratios were statistically significant for all ions examined ($p < 0.05$, Table 2).

3.2. Intra-storm stemflow: relative proportions and fluxes from washoff and leaching

All intra-storm stemflow ionic fluxes were initially high, exponentially decaying to a steady input, typically dominated by leaching contributions (Fig. 2a,b). With the exception of yellow poplar stemflow Cl^- and NO_3^- fluxes and beech Na^+ flux, all intra-storm mean ionic fluxes began with higher dry deposition percentages and transitioned to primarily leaching (Fig. 2a,b). Yellow poplar intra-storm stemflow ionic fluxes exhibited greater

Table 2

Statistical comparison of interspecific annual stemflow concentrations and enrichment ratios between beech and yellow poplar.

	df	Concentration ($\mu\text{eq L}^{-1}$)		Enrichment ratio	
		<i>U</i>	<i>p</i>	<i>t</i>	<i>p</i>
Na ⁺	52	230.5	0.461	2.6665	0.010
Mg ²⁺	52	78.0	<0.001	3.0531	0.003
K ⁺	52	161.0	0.023	4.4003	<0.001
Ca ²⁺	52	130.0	0.003	3.5441	<0.001
Cl ⁻	52	210.0	0.452	2.1832	0.033
SO ₄ ²⁻	52	228.0	0.742	3.8945	<0.001
NO ₃ ⁻	52	108.0	0.001	4.1105	<0.001

variability in washoff and leaching proportions than beech stemflow (Fig. 2a,b). Intra-storm decay patterns in washoff were relatively strong for all primarily-leached ions monitored in beech stemflow, with slight later-event variations for Ca²⁺ and SO₄²⁻ (Fig. 2a,b). For beech Na⁺ flux and yellow poplar Cl⁻ and NO₃⁻ fluxes, the trend was opposite as the dry deposition washoff component increased throughout a storm event (Fig. 2a,b). Yellow poplar Mg²⁺, K⁺, Ca²⁺ and SO₄²⁻ fluxes appeared to have a delay in the peak percentage of dry deposition washoff with 1 h washoff proportion values slightly larger than 0.5 h values (Fig. 2a,b).

All beech stemflow intra-storm ionic fluxes, besides Mg²⁺ and Ca²⁺, were twice to ten-fold higher than yellow poplar stemflow intra-storm ionic fluxes (Fig. 2a,b). The exponential intra-event

decay in Mg²⁺, K⁺, Ca²⁺, Cl⁻ and SO₄²⁻ fluxes from the smoother-barked beech canopies were more rapid than those observed from the rougher-barked yellow poplar canopies (Fig. 2a,b). Intra-storm decays in Na⁺ and NO₃⁻ fluxes were noticeably rapid for both species (Fig. 2a,b). Many of the ionic fluxes slowly diminished as stemflow pathways matured; this is most notable for beech NO₃⁻ flux (Fig. 2b). In fact, yellow poplar stemflow NO₃⁻ flux and leaching proportions diminished simultaneously (Fig. 2b). This synchronicity was not apparent in the intra-storm beech stemflow NO₃⁻ flux pattern (Fig. 2b). Intra-storm Cl⁻ fluxes for yellow poplar were almost entirely represented by washoff (Fig. 2b). Beech intra-storm Cl⁻ flux was also dominated by washoff despite increasing leached proportions later in an event (Fig. 2b). These late-event beech stemflow Cl⁻ fluxes were quite small and, therefore, even high leaching percentages represent low flux values.

Observations in the field implicate increased magnitude and rainfall intensity in the initiation of new stemflow flowpaths (Fig. 3a). To substantiate this claim, concentrations of various solutes were plotted against 5-minute rainfall intensities within the 18 Jun 09 rain event (Fig. 3b). Following initial canopy wet-up and subsequent solute flush, Fig. 3b depicts a distinct synchronicity between increased rainfall intensity that is immediately followed by noticeable increases in solute concentrations of primarily dry deposited ions (Na⁺ and Cl⁻) and readily soluble cations (Ca²⁺, Mg²⁺), corresponding to the development of new stemflow flowpaths (Fig. 3b).

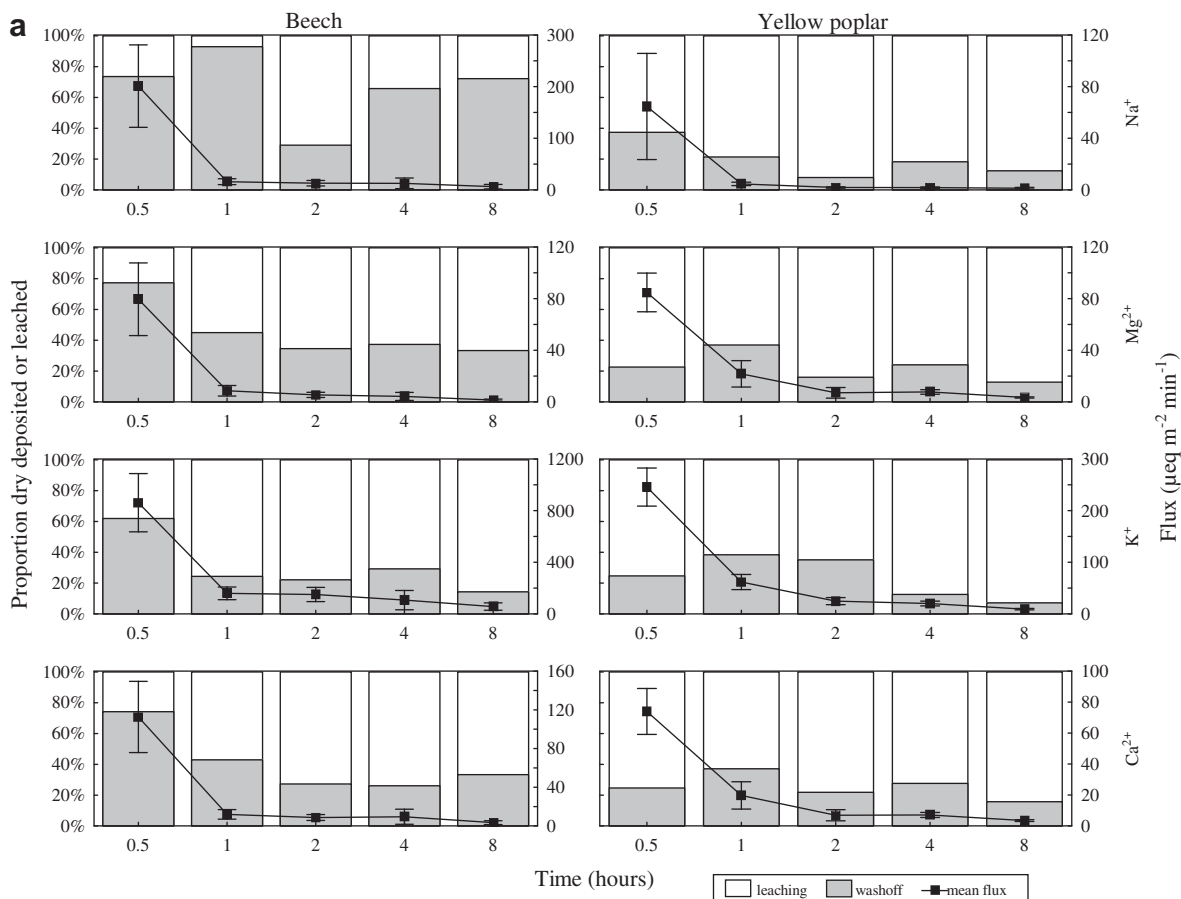


Fig. 2. Intra-storm trends in stemflow dry deposition washoff and leaching proportions and ionic flux. Total average stemflow leaching and washoff percentages and mean (a) cation and (b) anion flux ± 1 standard error for six sequentially sampled events with beech (left) and yellow poplar (right). Sample sizes in chronological order for beech are 10, 7, 4, 3, 3 and yellow poplar 10, 4, 2, 2, 2, respectively. Since the production of stemflow varies greatly between species and with meteorological conditions, the number of samples within any given time interval varied with stemflow yield. Yellow poplar sample numbers tend to be lower than beech later in an event due to diminished stemflow production.

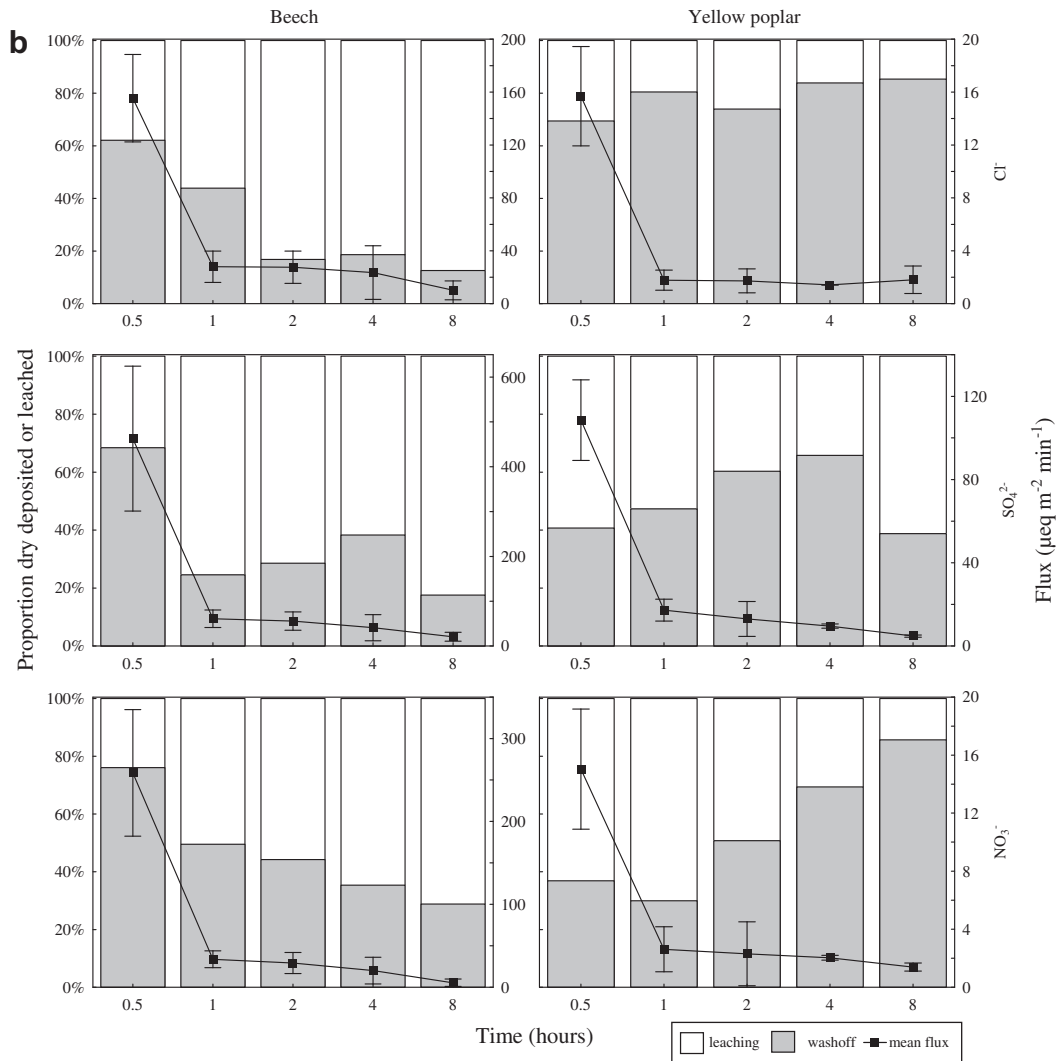


Fig. 2. (continued).

3.3. Event-scale stemflow washoff and leaching fluxes

Between-event differences in precipitation characteristics produced marked differences in stemflow concentration, enrichment ratio and ionic flux for both species (Table 3). The effects of rainfall intensity and duration were more pronounced for beech stemflow concentrations than enrichment ratio or flux (Table 3). Extremely high (20-Jul-08) and low (26-Sep-08) intensities and durations appeared to decrease all beech stemflow ionic concentrations in comparison to moderate duration and intensity (10-Aug-08) except Cl⁻ (Table 3). The short duration, high intensity 20-Jul-08 storm produced the lowest beech stemflow concentrations for all ions (Table 3). The longest duration, low intensity 26-Sep-08 storm produced the highest beech stemflow Cl⁻ concentrations but intermediate concentrations for the rest of the monitored ions (Table 3). For yellow poplar, only Mg²⁺, K⁺ and SO₄²⁻ followed the same trends between stemflow concentrations, rainfall duration and intensity (Table 3). Yellow poplar Na⁺ and Ca²⁺ concentrations were highest for the low intensity, long duration 26-Sep-08 storm, whereas Cl⁻ and NO₃⁻ yellow poplar stemflow concentrations were lowest during that event (Table 3).

Ca²⁺ enrichment ratio and ionic flux for both species were rather similar for the two events of similar precipitation amounts

(20-Jul-08 and 26-Sep-08), despite differing intensities and duration (Table 3). Yellow poplar stemflow ionic fluxes and enrichment ratios were generally largest for the rainfall event of greatest magnitude (20-Jul-08) and smallest for the event of the smallest magnitude (10-Aug-08) (Table 3). Beech stemflow ionic fluxes and enrichment ratios exhibited greater variability across events (Table 3). Beech stemflow K⁺, SO₄²⁻ and NO₃⁻ fluxes and enrichment ratios were greatest for the long duration, low intensity 26-Sep-08 storm (Table 3). The lowest magnitude 10-Aug-08 storm produced the lowest beech stemflow fluxes for all ions, yet produced the highest enrichment ratios for the beech stemflow Mg²⁺ and Ca²⁺ fluxes (Table 3).

3.4. Stemflow fluxes during leafed, leafless, and annual periods

Table 4 displays ionic stemflow fluxes for leafed, leafless, and annual time periods. In all cases, the fluxes computed using trunk basal area were larger than those computed per catchment area (Table 4). Beech stemflow fluxes were larger for all ions during leafed, leafless, and annual time periods than yellow poplar (Table 4). Interspecific differences between beech and yellow poplar during the leafed period were statistically significant for most ions (Na⁺: $p = 0.025$; K⁺: $p = 0.008$; Cl⁻: $p < 0.001$; SO₄²⁻:

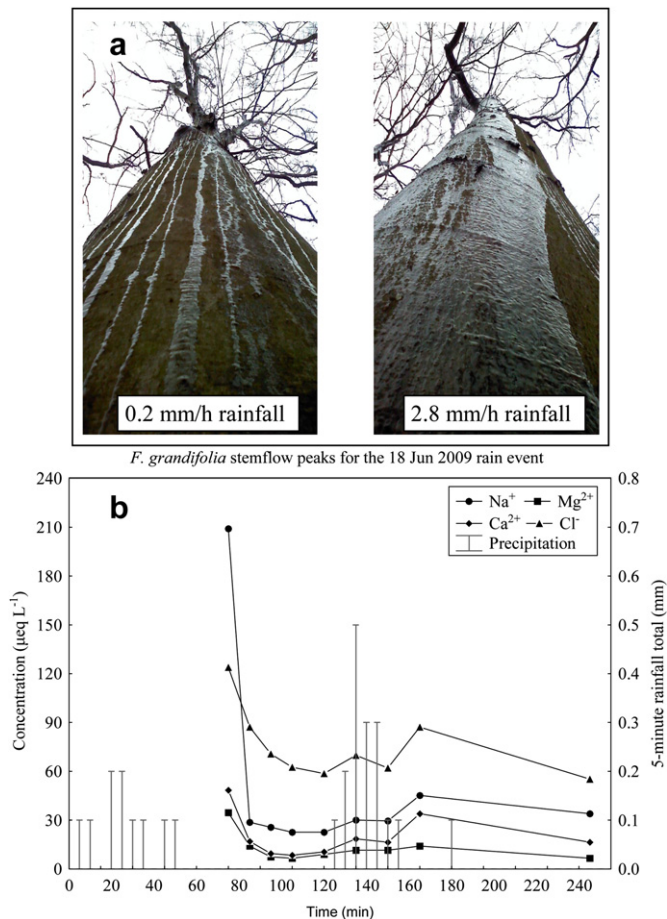


Fig. 3. Generation of new stemflow flowpaths and dry depositional flux under increased rainfall intensity. Panel (a) Beech stemflow flowpaths from the canopy are fewer and thinner during low rainfall intensities (left photograph). Under higher rainfall intensities (right photograph), these stemflow pathways expand and may wash previously unflushed dry deposition and leach solutes from the newly wetted bark surfaces. Panel (b) shows that periods of heavy 5-minute rainfall intensities immediately precede peaks in the concentrations of Mg^{2+} , Ca^{2+} , Na^+ , and Cl^- in beech stemflow regardless of exchange processes. This behavior indicates that these solute fluxes were influenced by a single mechanism and agrees with our field observations confirming the establishment of new stemflow flowpaths.

Table 3
Inter-storm comparisons between beech and yellow poplar stemflow concentrations, enrichment ratio, and ionic flux for three events of varying duration and rainfall intensity computed using trunk basal area per hectare. Parenthetical fluxes are expressed per unit catchment area.

Concentration ($\mu\text{eq L}^{-1}$)	Enrichment ratio	Ionic flux ($\text{eq ha}^{-1} \text{event}^{-1}$)	Concentration ($\mu\text{eq L}^{-1}$)	Enrichment ratio	Ionic flux ($\text{eq ha}^{-1} \text{event}^{-1}$)	Concentration ($\mu\text{eq L}^{-1}$)	Enrichment ratio	Ionic flux ($\text{eq ha}^{-1} \text{event}^{-1}$)	
20 Jul 08 (Pg: 33.5 mm, D: 1.2 h, I: 27.9 mm h ⁻¹) ^a			10 Aug 08 (Pg: 13.3 mm, D: 4.8 h, I: 2.8 mm h ⁻¹)			26 Sep 08 (Pg: 31.8 mm, D: 75.7 h, I: 0.4 mm h ⁻¹)			
Beech stemflow									
Na^+	10.4	10.0	1.1 (0.3)	149.6	7.6	0.7 (0.2)	35.2	1.5	2.1 (0.5)
Mg^{2+}	18.9	6.5	2 (0.5)	246.9	9.2	1.1 (0.3)	31.3	4.9	1.9 (0.4)
K^+	87.7	29.7	9.3 (2.2)	780.5	21.1	3.5 (0.8)	369.3	211.9	21.9 (5.1)
Ca^{2+}	25.4	6.1	2.7 (0.6)	283.9	9.9	1.3 (0.3)	42.9	4.8	2.5 (0.6)
Cl^-	12.7	14.5	1.3 (0.3)	55.6	8.9	0.2 (0.1)	63.4	5.3	3.8 (0.9)
SO_4^{2-}	69.2	24.0	7.3 (1.7)	987.1	30.5	4.4 (1)	205.1	43.7	12.2 (2.8)
NO_3^-	29.9	21.5	3.2 (0.7)	261.2	27.2	1.2 (0.3)	105.9	65.2	6.3 (1.5)
Yellow poplar stemflow									
Na^+	46.1	2.5	0.3 (0.02)	61.3	0.5	0.05 (0.004)	99.6	0.2	0.3 (0.02)
Mg^{2+}	166.2	3.2	1 (0.08)	304.5	1.9	0.2 (0.02)	239.5	1.6	0.6 (0.05)
K^+	443.0	8.4	2.6 (0.22)	1060.1	4.8	0.8 (0.07)	615.1	15.0	1.6 (0.13)
Ca^{2+}	155.2	2.1	0.9 (0.08)	167.2	1.0	0.1 (0.01)	243.5	1.2	0.6 (0.05)
Cl^-	39.6	2.5	0.2 (0.02)	40.1	1.1	0.03 (0.002)	30.1	0.1	0.1 (0.01)
SO_4^{2-}	289.5	5.7	1.7 (0.14)	368.6	1.9	0.3 (0.02)	305.1	2.8	0.8 (0.06)
NO_3^-	63.4	2.6	0.4 (0.03)	88.7	1.6	0.1 (0.01)	16.1	0.4	0.04 (0.003)

^a Pg is rainfall magnitude, D is storm event duration, and I is storm event intensity.

Table 4

Total leafed, leafless, and annual stemflow ionic fluxes standardized to the 30-year mean annual rainfall computed using trunk basal area per hectare^a. Parenthetical fluxes are expressed per unit catchment area.

Ion	Total ionic flux (eq ha^{-1})		
	Leafed	Leafless	Annual
Beech			
Na^+	24.8 (5.7)	113.3 (26.2)	138.1 (31.9)
Mg^{2+}	25.1 (5.8)	103.1 (23.9)	128.2 (29.7)
K^+	197 (45.6)	382 (88.3)	579 (133.9)
Ca^{2+}	34.1 (7.9)	155.9 (36.1)	190 (44)
Cl^-	28.9 (6.7)	185.9 (43)	214.8 (49.7)
SO_4^{2-}	139.2 (32.2)	583.4 (134.9)	722.6 (167.1)
NO_3^-	73.3 (16.9)	211.4 (48.9)	284.7 (65.8)
Yellow poplar			
Na^+	4.3 (0.3)	6.6 (0.5)	10.9 (0.8)
Mg^{2+}	12.9 (1)	26 (2.1)	38.9 (3.1)
K^+	36.9 (3)	82.1 (6.7)	119 (9.7)
Ca^{2+}	12.3 (1)	23.8 (1.9)	36.1 (2.9)
Cl^-	2 (0.2)	14.7 (1.2)	16.7 (1.4)
SO_4^{2-}	19.2 (1.6)	62 (5.1)	81.2 (6.7)
NO_3^-	3.4 (0.3)	6 (0.5)	9.4 (0.8)

^a 1200 mm yr⁻¹ (700 mm leafed period⁻¹, and 500 mm leafless period⁻¹, MD State Climatologist Office, 2008).

$p = 0.001$; NO_3^- : $p < 0.001$) except Mg^{2+} and Ca^{2+} . During the leafless period, interspecific differences in stemflow fluxes between beech and yellow poplar were statistically significant for all ions measured (Na^+ : $p < 0.001$; Mg^{2+} : $p = 0.035$; K^+ : $p = 0.019$; Ca^{2+} : $p = 0.002$; Cl^- : $p < 0.001$; SO_4^{2-} : $p < 0.001$; NO_3^- : $p < 0.001$). Annual interspecific differences in stemflow fluxes between beech and yellow poplar were statistically significant for all ions examined measured (Na^+ : $p < 0.001$; Mg^{2+} : $p = 0.038$; K^+ : $p < 0.001$; Ca^{2+} : $p = 0.004$; Cl^- : $p < 0.001$; SO_4^{2-} : $p < 0.001$; NO_3^- : $p < 0.001$). Beech and yellow poplar stemflow fluxes were much greater during the leafless period than the leafed period (Table 4). For beech, the largest annual stemflow flux was for SO_4^{2-} , with K^+ following by a difference of 143.6 eq ha^{-1} (Table 4). The beech leafed stemflow flux, however, was greater for K^+ than SO_4^{2-} (Table 4). The smallest beech stemflow flux was for Mg^{2+} (Table 4). The highest annual stemflow flux for yellow poplar was K^+ , followed closely by SO_4^{2-} (Table 4). The smallest annual stemflow flux for yellow poplar was NO_3^- (Table 4).

4. Discussion

4.1. Overview: bulk precipitation and stemflow flux

The annual bulk precipitation values from this study are representative of those reported by others in the eastern United States (Table 1). For instance, our bulk precipitation concentration of Ca^{2+} was $22 \mu\text{eq L}^{-1}$ (Table 1), whereas Mitchell et al. (1992) and Likens and Bormann (1995) reported Ca^{2+} concentrations of $30 \mu\text{eq L}^{-1}$ and of $8 \mu\text{eq L}^{-1}$, respectively. Differences in ionic concentrations are likely due to geographic locality, governing air mass provenance and proximity to industrial sources which affects bulk precipitation concentrations and ultimately elemental fluxes (Levia, 2003; Avila and Rodrigo, 2004). Stemflow leachate inputs (eq ha^{-1}) of subalpine balsam fir (Olson et al., 1981) tended to be higher than those reported for yellow poplar but lower than those reported here for beech (Table 4). The lower ionic flux values of yellow poplar and higher ionic flux values for beech are partly attributable to differences in bark morphology and stemflow production with the much larger stemflow yield for beech accounting for much of the difference (Levia et al., 2010; Van Stan and Levia, 2010).

Most Cl^- inputs via stemflow originated from washoff of dry deposition, especially for yellow poplar (Fig. 2b). Even for beech, when a greater proportion of Cl^- was computed to originate from canopy leaching in the later stages of a storm event, the total ionic flux of Cl^- was drastically reduced (Fig. 2b), indicating that the vast majority of Cl^- was dry deposition washoff. These findings are consistent with those of other studies demonstrating that Cl^- stemflow inputs were primarily dry deposition washoff, although some crown leaching could occur (Kazda, 1990; Chiwa et al., 2010).

4.2. Dynamics of dry deposition washoff and leaching across temporal scales

This study clearly shows that dry deposition and leaching differed greatly within and between discrete rain events, between leafed and leafless periods, and between species of contrasting bark morphology (e.g., Tables 3 and 4; Figs. 2a,b and 3a,b). Our finding of an exponential decay of ionic flux as a storm progresses for beech and yellow poplar has been found to mimic the exponential decay in ionic concentrations for both throughfall and stemflow of other species (Kazda, 1990; Hansen et al., 1994; Germer et al., 2007). For beech, the rapid decline in ionic flux for most ions (except Na^+) coincided with increasing leaching percentages (Fig. 2a,b), whereas for yellow poplar cation flux tended to behave similarly to beech and NO_3^- and Cl^- oppositely (Fig. 2a,b). Intra-storm diminished NO_3^- leaching for yellow poplar stemflow (Fig. 2b) may be due to canopy uptake as reported by other studies (Houle et al., 1999; Levia, 2002), and our median enrichment ratio being <1 (Table 1). Event-scale precipitation characteristics were observed to have a detectable influence on stemflow leachate concentrations, enrichment ratios and ionic fluxes (Table 3). In agreement with past studies, it was found that the most intense events produced the lowest stemflow ionic concentrations (Tukey, 1970; Crockford et al., 1996; Levia and Herwitz, 2000). Yellow poplar ionic fluxes and most enrichment ratios coincided with rainfall amount (Table 3). This trend was not as evident with beech (Table 3). This is likely due to differing bark morphologies between the two species that regulate the response of stemflow generation to changing precipitation characteristics (Levia et al., 2010; Van Stan and Levia, 2010). Our study found stemflow deposition of all ions to the forest floor to be greater in the leafless period than the leafed period (Table 4). This is attributable, in part, to the larger stemflow volumes generated in the leafless period compared to the leafed period (Levia and

Frost, 2003). Staelens et al. (2007) also observed higher leafless stemflow ion deposition, except for N-containing ions.

Within some storm events, such as 18 Jun 2009 event, dry depositional fluxes were highly variable and dependent on the establishment of new hydrologic pathways through the canopy (Fig. 3a,b). Timed field observations in conjunction with Fig. 3 suggests that increased rainfall intensities may overload pre-established stemflow pathways and initiate new flowpaths through the canopy, washing out new dry deposited materials to the forest floor. The development of these new flowpaths accounts for fluctuations in the stemflow ion concentrations and the proportion of an ion that has originated from washoff or leaching at the intra-storm scale (Fig. 3). For yellow poplar, a possible explanation for the increasing proportions of dry deposition throughout an event of Cl^- and NO_3^- (Fig. 2b), is the establishment of new stemflow flowpaths. Unlike beech which would establish new stemflow flowpaths rather quickly because of its thin, smooth bark and low bark water storage capacity, the bark morphology of yellow poplar is conducive to the wetting of bark surfaces much later in an event as up-trunk bark water storage is exceeded and stemflow progresses down-trunk. Thus, new stemflow flowpaths seem to manifest themselves in different ways for the two species; for beech, stemflow concentrations increase following the initiation of new stemflow flowpaths and then decline again, whereas for yellow poplar the stemflow concentrations are already high due to the long contact time with the bark surface and as new bark surfaces are wetted the proportion of dry deposition washoff increases.

The intra-storm empirical regression model developed by Kazda (1990) accounts for the initial flush, but neglects flux peaks and enhanced leaching generated from new stemflow flowpaths that can emerge later in an event (Figs. 1 and 3a,b). This underestimates the dry depositional and leaching fractions of total flux and inflates contributions from bulk rainfall (which were much smaller to negligible in stemflow mass fluxes for this study compared to those described in Kazda (1990), likely due to differences in geographic location).

4.3. Interspecific variability of stemflow chemistry

There are evident interspecific differences in the concentration, fluxes, and leaching/washoff proportions beneath the canopies of both beech and yellow poplar (Tables 1, 3 and 4; Fig. 2a,b). All ion concentrations and base cation leaching percentages were generally higher for stemflow fluxes from the rougher-barked yellow poplar canopy (Table 1, Fig. 2a,b), owing to greater bark microrelief and lower stemflow production values (Van Stan and Levia, 2010). Despite enhanced chemical concentrations, yellow poplar stemflow leachate fluxes were smaller than beech stemflow leachate fluxes for all ions (Table 4), primarily as a result of larger stemflow volumes of beech. Differential interspecific stemflow generation and enrichment have been attributed to a combination of branch inclination angle (Crockford and Richardson, 2000; Levia and Herwitz, 2002) and bark microrelief (Levia and Herwitz, 2005; Van Stan and Levia, 2010). The moderately-inclined branching patterns of yellow poplar generate lower stemflow volumes as it cannot funnel precipitation as efficiently as the more steeply-inclined, flexible branching patterns in beech canopies (André et al., 2008). In conjunction with higher bark microrelief and water storage capacity, the more plagiophile branching patterns of yellow poplar likely result in longer retention times for incident rainfall entrained as stemflow (Levia and Herwitz, 2002), resulting in the substantial chemical enrichment observed in this study (Tables 1 and 3). Smooth-barked, erectophile beech canopies diminish retention time over woody surfaces and increase the capture and scavenging of atmospheric dryfall, which may explain the greater

dry deposition washoff for most ions compared to yellow poplar (Fig. 2a,b).

5. Conclusion

The results of this study indicate that the temporal scale of analysis of canopy-derived fluxes can yield important insights into the transport of stemflow fluxes to the forest floor, allowing discernment on the effect of variable time scales on biogeochemical cycling. This study detailed two mechanisms affecting depositional washoff and leaching dynamics of stemflow inputs beneath two species of contrasting canopy morphology: (1) the initial flush of dry deposition; and (2) establishment of new flowpaths via stemflow and the expansion and maturation of those flowpaths as events progress. The former has been described in previous research (Kazda, 1990), but, to the knowledge of the authors, the latter has not yet been identified by the extant literature. The development of these new flowpaths in the canopy within a storm event has been shown to increase solute flux to the forest floor via dry deposited material washoff and enhanced leaching from the saturation of new vegetative surfaces. This study further illustrates that the temporal heterogeneity of canopy exchange and dry deposition rates can depend on species-specific morphology (*i.e.*, bark microrelief and branch inclination angle). At the intra-storm scale, further investigations should identify the meteorological and morphological variables associated with new stemflow flowpath initiation. If frequency relationships could be derived for meteorological variables (*i.e.*, short-term rainfall intensity) and/or canopy characteristics (*i.e.*, bark microrelief or branching architecture), intra-storm chemical variability may be modeled more accurately by stochastic methods, perhaps informing our current theories of hot moments in biogeochemical reactivity and cycling.

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