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Atmospheric deposition of nitrogen and sulfur and preferential canopy consumption of nitrate in forests of the Pacific Northwest, USA

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ABSTRACT

Wet, dry and throughfall deposition of N and S were measured for 2 years in three national parks in Washington State: Olympic, Mount Rainier, and North Cascades. Throughfall was measured using ion exchange resin (IER) collectors. A major objective of the study was to evaluate the effectiveness of IER throughfall measurements for monitoring deposition inputs, including cloudwater deposition, to forest stands in national parks and other protected areas. Wet deposition (0.9–2.0 kg N ha^{-1} yr^{-1}) and throughfall (0.5–1.2 kg N ha^{-1} yr^{-1}) deposition of inorganic N in the three parks were relatively low. Wet deposition of sulfur (1.0–3.2 kg ha^{-1} yr^{-1}) was similar to wet deposition of inorganic nitrogen except at OLYM where wet deposition of S was higher than for N because of marine sources of SO_4–S. Throughfall N deposition was lower than wet deposition of N because of strong preferential canopy consumption of nitrate (NO_3–N), particularly during the wet winter periods. This phenomenon was previously reported for forests in this region, but its apparent near ubiquity in the region had not been recognized. Data on preferential canopy retention of NO_3–N from wet-deposited N is shown for 38 stands in the Pacific Northwest of which 21 are newly-reported data. Deposition of NO_3–N in throughfall at MORA and NOCA was reduced by 87% and 93% compared to wet deposition over the 2 years. In contrast, wet deposition of NH_4–N was generally increased by passage through the canopy. This strong preferential canopy retention of wet-deposited NO_3–N limits the usefulness of throughfall measurements as a N deposition monitoring approach in forests of the Pacific Northwest region of North America and in some other regions with low to moderate N deposition. As a potential remedy to this limitation, a simple method is proposed for estimating total N deposition in the study sites based on S/N ratios in wet deposition and throughfall S deposition.

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1. Introduction

Atmospheric nitrogen (N) deposition is affecting biotic communities and nutrient cycling processes in ecosystems of many regions (Bobbink et al., 2010). Empirical N critical loads and the ecological effects of N deposition have recently been reviewed for California (Fenn et al., 2010, 2011), the United States (Pardo et al., 2011), Europe (Bobbink and Hettelingh, 2011) and China (Liu et al., 2011). Nitrogen impacts on national parks and other protected areas are of particular concern. Nitrogen deposition is relatively low in much of the northwestern region of the United States, although deposition fluxes are elevated downwind of urban centers (including the greater Seattle-Tacoma, Washington and Vancouver, British Columbia regions) agricultural activities, and near transportation corridors (Geiser et al., 2010). In the Pacific Northwest (PNW) region of the United States, proximity to an urban area is the most important factor predicting increases in wet deposition of N since 1980 (Fenn et al., 2003). Transpacific transport of N oxides from Asia also contribute to the pollution load in the region (Geiser and Neitlich, 2007). Olympic (OLYM) National Park in Washington State may be affected on the east side by emissions from urban and industrialized areas along the Puget Sound, including Seattle and marine vessel traffic in the Strait of Juan De Fuca (Fig. 1). North Cascades (NOCA) National Park in northern Washington, is located in the path of prevailing westerly winds from urban, industrial and agricultural emissions in the Puget Sound, from Vancouver and the Fraser River Valley of British Columbia. Mount

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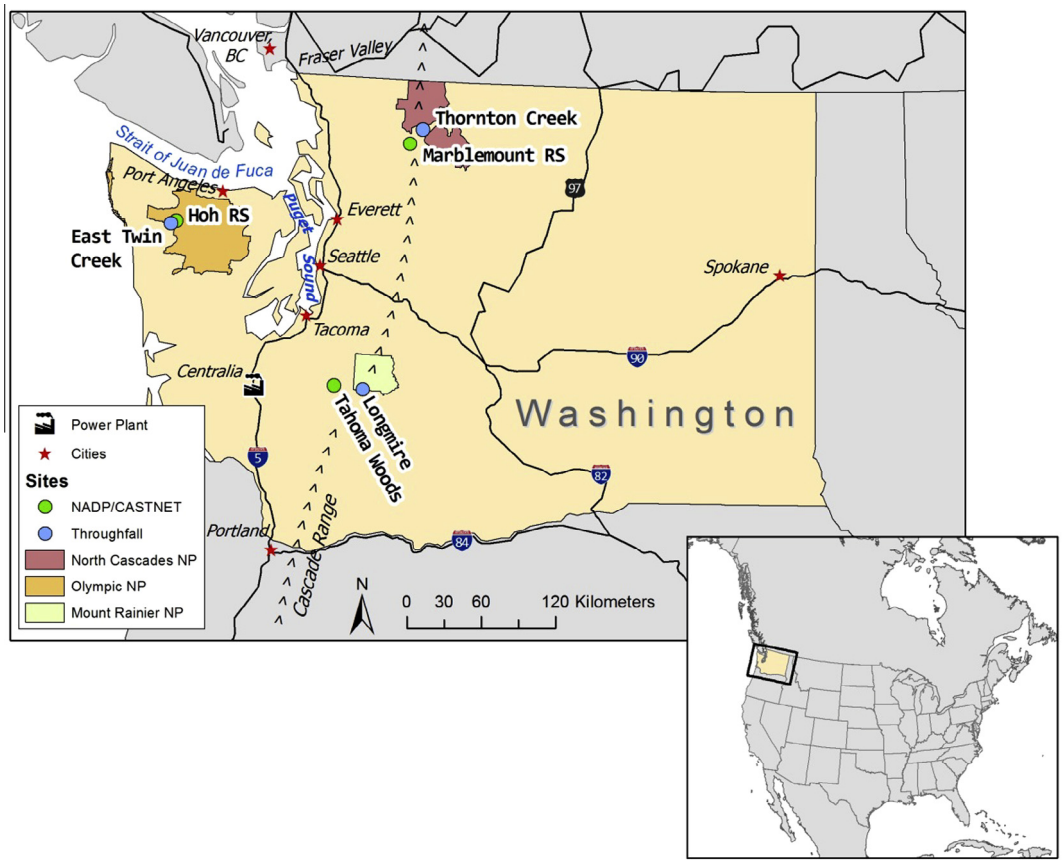

Fig. 1. Map of Washington State (USA) showing major emissions sources mentioned in the text such as urban areas, highways, and a power plant. Indicated are the location of Olympic, North Cascades and Mount Rainier National Parks and the throughfall, wet (NADP–NTN) and dry (CASTNET) deposition monitoring sites within the three parks. The wet and dry deposition sites are collocated and indicated by green dots, with the exception of Olympic National Park where the green dot indicates only the wet deposition monitoring site. The CASTNET dry deposition site in Olympic National Park was located in Port Angeles 46 km ENE of the NADP–NTN site.

Rainier (MORA) National Park is downwind of urban and industrial areas to the northwest (Seattle) and southwest (Portland, Oregon). The Centralia coal-fired power plant located 80 km to the west of MORA emits several thousand tons of N oxides per year (Fig. 1). The prevailing airflows in the Puget Sound region typically advect pollutants eastward toward the Cascade Mountains resulting in higher ozone and wet deposition of pollutants in areas east and southeast of metropolitan Seattle (Brubaker et al., 1992).

Total N and sulfur (S) deposition have been quantified in few sites in the PNW, as is true for natural areas in many regions of the world where air pollution effects are of concern to resource managers and the public. Wet deposition is monitored by the National Atmospheric Deposition Program National Trends Network (NADP–NTN; http://nadp.sws.uiuc.edu/ntn/) at six sites in Washington State and dry deposition is currently monitored by the Clean Air Status and Trends Network (CASTNET; http://epa.gov/castnet/javaweb/index.html) at one site in Washington (in MORA). However, wet deposition measurements do not adequately characterize total atmospheric deposition, particularly in much of western North America where dry deposition is a major form of deposition (Fenn et al., 2003, 2012). Likewise, dry deposition inputs estimated by CASTNET are commonly underestimated, particularly in areas exposed to moderate to high levels of dry deposition and largely because NH_3 is not included (Baumgardner et al., 2002; Fenn et al., 2009; Kolian and Haeuber, 2004; Sparks et al., 2008).

Deposition as fog or cloudwater can also be important in some areas, particularly in montane sites or coastal areas (Fenn et al., 2009). Cloudwater deposition is common in montane sites of the PNW and radiation fogs frequently occur during winter and early spring in low elevation sites in the region (Basabe et al., 1989; Duncan, 1992). In the Cascade mountain range in Washington State, forest stands may be exposed to clouds for an hour or more per day for 50–100 days during the growing season and some sites experience cloudwater events lasting more than 15 h (Basabe et al., 1989). The NADP and CASTNET networks do not measure cloudwater deposition. To measure the concentrations of the suite of N and S compounds (NO, NO_2, HNO_3, NO_3^-, SO_2, SO_4^{2-}, etc.) in the atmosphere and their deposition fluxes to forest canopies is technically and financially prohibitive, particularly when atmospheric deposition measurements are needed over large regions. Thus, more user friendly and affordable approaches are needed. Air quality models (Fenn et al., 2009) can be very useful, particularly in estimating deposition over larger regions or to evaluate changes in air pollution with different emissions scenarios. However, ground-truthing of simulated deposition estimates is needed to evaluate model performance and on-site deposition measurements are generally needed for greater certainty in evaluating cause and effect relationships.

An alternative to examining wet, dry and cloudwater deposition separately is to monitor throughfall deposition. Throughfall deposition is generally defined as the flux of nutrients or pollutants transported from vegetation canopies to the ground during precipitation events. Advantages of the throughfall method for estimating atmospheric deposition are the relative simplicity of the technique and the fact that it includes information on dry deposition, wet deposition and cloudwater deposition to the in situ deposition canopy receptor surfaces. Another advantage is that throughfall reflects the amount of N and S (and other elements)

actually affecting organisms living under the canopy as well as abiotic components (soils, etc.). Thus it's a critical link for connecting the deposition regime to biological effects in vegetated ecosystems. The major limitation of throughfall deposition methods is the uncertainty of pollutant interactions with the canopy. For example, in the case of atmospheric N pollution an uncertain amount of atmospheric reactive N, often as much as 20–40%, is typically retained by the canopy (Lovett and Lindberg, 1993). Thus, throughfall N flux is generally a lower-bound estimate of total N deposition. In contrast, studies have shown that in the case of S, total S deposition and throughfall S deposition are often similar (Butler and Likens, 1995; Joslin and Wolfe, 1992; Lindberg and Lovett, 1992).

Notwithstanding these limitations, throughfall monitoring is considered to be a highly useful estimate of atmospheric deposition inputs, particularly when considering the complexity and expense of other approaches for calculating dry deposition fluxes (Fenn et al., 2009; Sparks et al., 2008). One practical drawback of measuring throughfall deposition is the need for frequent sample collection, typically soon after each precipitation event. To eliminate this need for frequent sample collection and chemical analysis, ion exchange resin (IER) throughfall samplers have been developed that eliminate the need to collect throughfall or precipitation solutions (Fenn et al., 2009; Fenn and Poth, 2004; Simkin et al., 2004). Instead the ions of interest are captured on IER columns during an extended period of multiple precipitation events. Later ions are extracted from the IER columns and analyzed, and deposition fluxes calculated.

The major objective of this study was to determine if throughfall monitoring with IER collectors can be used to monitor atmospheric deposition inputs from wet, dry and cloudwater deposition in remote sites with relatively low or moderate levels of atmospheric deposition, such as some national parks and wilderness areas in western North America. Deposition in cloudwater or fog was of particular interest because this is not accounted for in current national monitoring networks in the United States.

2. Materials and methods

2.1. Throughfall deposition measurements

Throughfall deposition was measured at three national parks in Washington State, USA: Olympic (OLYM), Mount Rainier (MORA) and North Cascades (NOCA) National Parks (Fig. 1 and Table 1). Olympic National Park is located along a narrow coastal strip in the central portion of the Olympic Peninsula in northwestern Washington. In OLYM throughfall was measured near East Twin Creek (Hoh drainage) in a mature forest stand of western hemlock (*Tsuga heterophylla* (Raf.) Sarg.) and Sitka spruce (*Picea sitchensis* (Bong.) Carr.). Throughfall at MORA was measured at Longmire under a stand of Douglas fir (*Pseudotsuga menziesii* (Mirb.) Franco) and western hemlock. Throughfall at NOCA was measured at Thornton Creek in a western hemlock stand with a minor component of Douglas fir and Western redcedar (*Thuga plicata* Donn ex D. Don). Further site information is given in Table 1.

Throughfall was measured in the three parks with ion exchange resin (IER) samplers for slightly more than 2 years from May 2005 to August 2007 (till October 2007 at the OLYM site). The IER columns exposed in the field were changed out in the spring and fall, so that deposition data were usually collected separately for the spring/summer and fall/winter seasons. The IER methodology is described more fully in Fenn and Poth, 2004; Fenn et al. 2009. The IER columns function by adsorbing ions from throughfall or precipitation solutions that percolate through the column. Within each study area 36 throughfall collectors were installed approximately at mid distance from the bole to the canopy drip line within 4 parallel transects (9 collectors per transect), following a similar design of Houle et al. (1999a) and Fenn et al. (2000). The distance

Table 1
Location and annual average precipitation at NADP/CASTNET wet and dry deposition sites and at throughfall monitoring sites, and major overstory species at throughfall monitoring sites.

Site name	Location	Elevation (m)	Deposition type	Average precipitation (cm)[a]	Average precipitation (cm, PRISM model)[a]	Tree species
Olympic NP, NADP WA14, Hoh Ranger Station[b]	47.8597N 123.9325W	182	Wet deposition	331.0 NADP (1981–2010)	374.1	
Olympic NP, CASTNET OLY421, Port Angeles[b]	48.0975N 123.4256W	125	Dry deposition	68.19[b]	86.4	
Mount Rainier NP, NADP WA99, Tahoma Woods	46.7582N 122.1243W	424	Wet and dry deposition	132.3 NADP (2000–2010)	171.5	
North Cascades NP, NADP WA19, Marblemount Ranger Station	48.5403N 121.4460W	124	Wet and dry deposition	197.7 NADP (1984–2010)	195.4	
Olympic NP, East Twin Creek (Hoh Drainage)	47.8358N 123.9832W	157	Throughfall	284.8 Marilyn Lewis Ranch[c] (1998–2011)	314.8	*Tsuga heterophylla* (Raf.) Sarg., *Picea sitchensis* (Bong.) Carr.
Mount Rainier NP, Longmire	46.7404N 121.8136W	815	Throughfall	204.2 Longmire Coop[d] (1909–2012)	232.1	*Pseudotsuga menziesii* (Mirb.) Franco, *Tsuga heterophylla* (Raf.) Sarg.,
North Cascades NP, Thornton Creek	48.6500N 121.3361W	892	Throughfall	202.4 Newhalem Coop[e](1959–2012)	235.0	*Tsuga heterophylla* (Raf.) Sarg., with a minor component of *P. menziesii* and *Thuga plicata* Donn ex D. Don

[a] The years 1987, 1996, 2006, 2007 were excluded from the annual average precipitation at the OLYM NADP site (1981–2010), because of missing data. PRISM data for the six locations indicated in the second column (excluding the OLYM CASTNET site) are the average of the years 1895–2011. Precipitation single-point time-series data at the latitudes and longitudes shown in the second (Location) column were retrieved June 26, 2012 using the PRISM Data Explorer at PRISM Climate Group, Oregon State University, http://prism.oregonstate.edu, accessed October 29, 2012.

[b] Olympic CASTNET site (OLY421) precipitation data are the average of 1999–2004; site was discontinued in 2005. As indicated, the CASTNET and NADP sites for OLYM were not collocated (46 km apart).

[c] Marilyn Lewis Ranch (123 m elevation), an NPS operated weather station, is about 5 km west of the throughfall monitoring site. Data courtesy of Bill Baccus, OLYM.

[d] Longmire NCDC COOP Station # 454764 (elevation 841 m) is about 1 km north of the throughfall monitoring site and about 24 km east of the NADP wet deposition site.

[e] Newhalem NCDC COOP Station # 455840 (elevation 160 m) is about 7.5 km east of the throughfall site. Coop Station precipitation data were obtained from: WRCC (Western Regional Climate Center). 2012. WRCC, Desert Research Institute, Reno, Nevada, USA. http://www.wrcc.dri.edu/, accessed October 29, 2012.

between transects was 15 m and within a transect collectors were spaced approximately 7 m apart. The inner diameter of the funnels used for the IER collectors is 21.1 cm and the funnel collectors have a vertical wall 10 cm in height. Snow tubes 1 m in height with an inner diameter of 20.2 cm were inserted into the funnels in the fall of the first year of the study to allow for snow collection at NOCA and MORA. During the second year of the study snow tubes were used year-round. Snowfall is rare at the study site in OLYM so snow tubes were not used at this site.

We used Amberlite IRN-150 analytical grade mixed bed (anion + cation exchange resin) in the IER columns of the throughfall collectors. Twenty-five grams of resin were placed in PVC tubes (25 cm in length and 1.25 cm I.D.) as an aqueous slurry and then rinsed further with distilled water. After the field exposure periods the IER columns were extracted with 200 ml of 1*N* KI, followed by a second extraction with 100 ml of 1*N* KI. Nitrate and sulfate concentrations in the column extracts were analyzed by ion chromatography (Dionex DX-600, Sunnyvale, CA) using a procedure modified

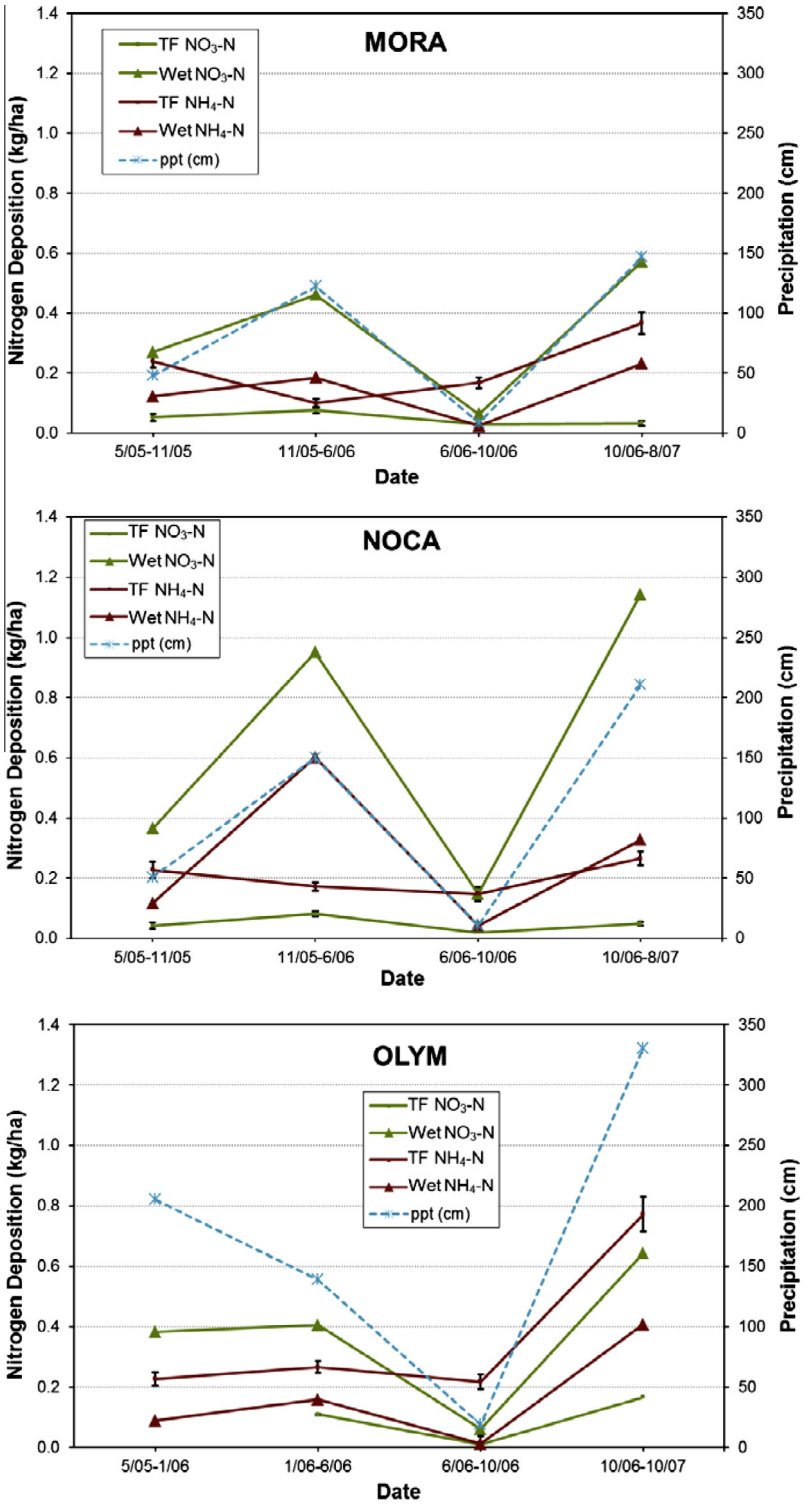

Fig. 2. Temporal trends in precipitation volume and throughfall (TF) and wet deposition of NH_4–N and NO_3–N in Mount Rainier (MORA), North Cascades (NOCA) and Olympic (OLYM) National Parks. For the throughfall data standard error bars are shown.

from Simkin et al. (2004). Due to instrumental error during the analyses for NO_3–N in the IER column extracts for the first field sampling season (Spring 2005 to fall 2006) no throughfall NO_3–N data are available for OLYM and the number of replicate throughfall NO_3–N data points was reduced from 36 to 11 and 21 for the NOCA and MORA sites, respectively. Ammonium concentrations in the KI extracts were determined colorimetrically (Technicon TRAACS autoanalyser). Quality control measures included a blank IER tube that was capped and deployed with other tubes on-site for the same length of time, in addition to laboratory standards and analysis of random duplicate samples. The detection limit for NO_3^-, NH_4^+ and SO_4^{2-} was 0.03 ppm and the range of values for these ions in the IER column extracts were: 0.04–5 ppm NO_3^-, 0.03–3 ppm NH_4^+, and 1–30 ppm SO_4^{2-}. Phosphate concentrations were also measured to aid in the detection of bird dropping contamination. Atmospheric deposition fluxes were determined by extrapolating from the area of the collector funnel opening and the amounts of inorganic N and S extracted from the IER columns. The IER columns were changed out twice per year at 4–10 month intervals, except for the last exposure period at OLYM which was for 12 months.

2.2. Wet and dry deposition measurements

Wet and dry deposition data from the three parks were also compiled for the same time periods as the throughfall measurements and compared to the throughfall data. Wet deposition data were downloaded from the National Atmospheric Deposition Program, National Trends Network (NADP–NTN) network database (http://nadp.sws.uiuc.edu/ntn/, accessed October 18, 2012). Likewise, dry deposition data were obtained from the website of the Clean Air Status and Trends Network (CASTNET) network (http://epa.gov/castnet/javaweb/index.html, accessed November 19, 2012). Atmospheric concentrations of NH_4^+, NO_3^-, SO_4^{2-}, SO_2 and HNO_3 are measured at CASTNET sites using filter packs, and dry deposition fluxes are calculated with an inferential method using modeled deposition velocities supported by meteorological data and information on land use, vegetation and surface conditions (Fenn et al., 2009). Modeled flux calculations are often biased low because of weekly integrated sampling of pollutants and because NO, NO_2, NH_3 and organic N are not measured (Baumgardner et al., 2002).

The same IER bulk deposition samplers (five replicates per site) used in the throughfall plots were also used to collect bulk deposition in forest clearings at the NADP monitoring stations. However, because of frequent contamination of the samples by bird droppings these data are not presented in this report.

Because of missing precipitation and wet deposition data for the OLYM NADP site (site WA-14) during the last sampling period at OLYM (October 2006 to October 2007), annual average precipitation and wet deposition data based on the years 1980–2010 were used to substitute for the missing data. In determining these averages, data for the years 1980, 1987, 1996, 2000, 2006, 2007, 2010 were excluded because of incomplete or inadequate data. At OLYM, CASTNET dry deposition monitoring ended in 2004 before the initiation of this study. Thus, average CASTNET dry deposition fluxes at OLYM from 1999 to 2004 were used to estimate dry deposition fluxes of N and S during the time of this throughfall study. Average dry deposition fluxes were chosen for time intervals matching those of the four throughfall sampling intervals in this study (see Fig. 2 for sampling intervals).

3. Results

3.1. Nitrogen deposition

Annual wet deposition of NO_3–N was 2.5 times greater than wet deposition of NH_4–N as an average for the three study sites in each of the 2 years of this study. In contrast, annual throughfall deposition of NH_4–N was 5.2 times greater than deposition of NO_3–N averaged over the 2 years (Table 2). However the NH_4–N:NO_3–N ratio in throughfall varied greatly between years. The average NH_4–N:NO_3–N ratio for throughfall for the three sites was 2.9 in year 1 compared to 6.8 in year 2 (Table 2), mainly because NO_3–N deposition in throughfall was about 50% lower in year 2 while NH_4–N deposition was higher. However, total inorganic N deposition in throughfall and total annual precipitation volumes were highly similar in both years (Table 3).

During the summer growing season of both years throughfall N deposition was on average 42% lower than the sum of NADP-reported wet deposition plus CASTNET-reported dry N deposition at MORA and NOCA (Fig. 3). Precipitation was low in summer (8–51 cm, but slightly higher in the summer of year 1 at OLYM where precipitation equaled 94 cm), compared to annual precipitation that ranged from 155 to 350 cm at the three sites during the entire study period (Figs. 2 and 3). In winter, throughfall N deposition was 80% lower than wet + dry deposition at NOCA and MORA. Similar results were observed at OLYM but because of incomplete throughfall N deposition data, the full results from OLYM cannot be presented. The lower N deposition in throughfall compared to wet deposition was caused by high NO_3–N retention in the canopy as described in section 3.2. On an annual basis, wet + dry N deposition was 1.9–2.6 and 4.0–4.2 times greater than throughfall N deposition for year 1 and 2 at MORA and NOCA respectively (Table 3). Averaged for all three sites and both years, annual wet + dry deposition of N (1.6 kg ha^{-1}) was more than twice as high as throughfall N deposition (0.6 kg ha^{-1}; Table 3).

CASTNET dry deposition fluxes of N were dominated by HNO_3 deposition with 79% of dry deposition occurring as HNO_3–N, compared to 4% as NO_3–N, and 17% as NH_4–N (Fig. 3). Dry deposition of

Table 2
Ratios of NO_3–N and NH_4–N deposition in throughfall and wet deposition (NADP–NTN data) at three national parks in Washington State.

Site	Year	Throughfall NH_4–N:NO_3–N	Wet deposition NO_3–N:NH_4–N
Annual data			
MORA	1	2.6	2.4
NOCA	1	3.2	1.8
OLYM	1	n.a.	3.2
Year 1 average		2.9	2.5
MORA	2	8.7	2.5
NOCA	2	6.0	3.5
OLYM	2	5.6	1.7
Year 2 Average:		6.8	2.5
2-yr average		5.2	2.5

	Year	Beginning date	Ending date	Throughfall NH_4–N:NO_3–N	Wet deposition NO_3–N:NH_4–N
Seasonal data					
MORA	1	5/25/2005	11/11/2005	4.5	2.2
NOCA	1	5/24/2005	11/4/2005	5.4	3.1
OLYM	1	5/24/2005	1/12/2006	n.a.	4.3
MORA	1	11/11/2005	6/15/2006	1.3	2.5
NOCA	1	11/4/2005	6/22/2006	2.1	1.6
OLYM	1	1/12/2006	6/16/2006	2.4	2.6
MORA	2	6/15/2006	10/18/2006	5.8	2.6
NOCA	2	6/22/2006	10/16/2006	7.5	3.4
OLYM	2	6/16/2006	10/13/2006	23.0	5.1
MORA	2	10/18/2006	8/16/2007	11.3	2.5
NOCA	2	10/16/2006	8/30/2007	5.4	3.5
OLYM	2	10/13/2006	10/26/2007	4.6	1.6
			Grand average	6.7	2.9

Table 3
Annual precipitation and deposition of N and S as wet, dry, wet + dry, throughfall and estimated total deposition. Units are (kg N or S ha^{-1} yr^{-1}).

Site	N wet deposition	N dry deposition	S wet deposition	S dry deposition
Year 1				
MORA	1.04	0.17	0.95	0.10
NOCA	2.04	0.18	1.25	0.13
OLYM	1.04	0.36	2.70	0.65
Year 2				
MORA	0.89	0.24	1.05	0.11
NOCA	1.67	0.27	1.45	0.14
OLYM	1.12	0.46	3.15	0.81
	Throughfall N deposition	Wet + Dry N deposition	Throughfall S deposition	Wet + Dry S deposition
Year 1				
MORA	0.48	1.21	1.58	1.05
NOCA	0.51	2.22	1.31	1.38
OLYM	na	1.39	4.13	3.35
Year 2				
MORA	0.60	1.13	1.56	1.16
NOCA	0.48	1.94	1.80	1.59
OLYM	1.17	1.58	4.59	3.96
		Precipitation (cm)		Total N deposition[a]
Year 1				
MORA		170.3		1.73
NOCA		200.9		2.13
OLYM		344.2		1.58
Year 2				
MORA		155.4		1.33
NOCA		221.8		2.05
OLYM		350.1		1.64

[a] Total N deposition was calculated based on S/N ratios in wet deposition, throughfall S deposition rates, and the assumption that S/N ratios for wet + dry deposition to forest canopies are equivalent to S/N ratios in wet deposition. See text for further details.

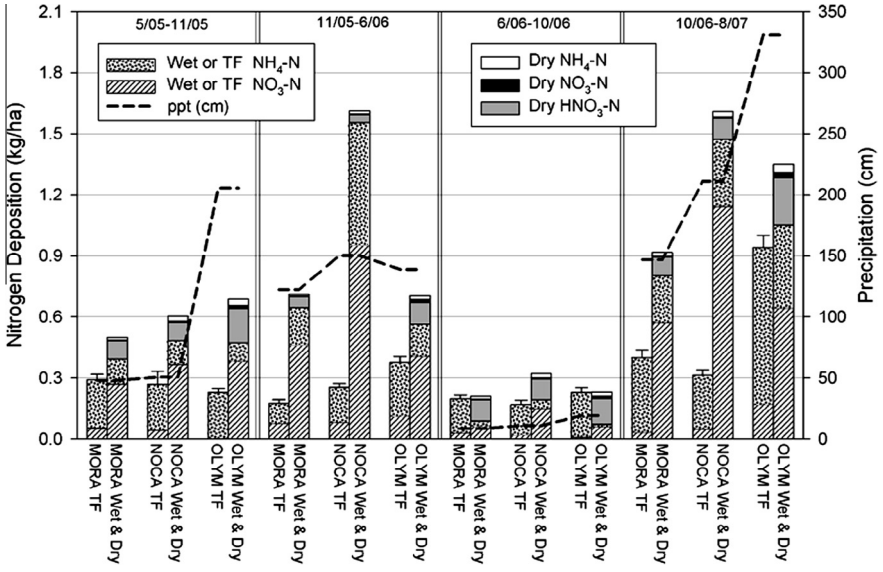

Fig. 3. Comparison of inorganic N deposition (NO_3–N + NH_4–N) in throughfall (TF) with wet + dry N deposition. For the throughfall data standard error bars are shown for total inorganic N deposition, with the exception of OLYM in the first period where the error bars are for NH_4–N deposition only. Wet deposition data are from the NADP–NTN network and dry deposition is from the CASTNET network. Apportionment of N in throughfall, wet deposition and dry deposition among reduced and oxidized species are shown as stacked bars. At OLYM CASTNET dry deposition date were not available for the period of this study, thus average fluxes from 1999 to 2004 are substituted, using data from date intervals matching those of the throughfall data in this study. Dashed lines show precipitation totals at the three sites during each monitoring period.

oxidized N at OLYM was double that at NOCA and MORA (Fig. 3). Dry deposition of NH_4–N did not vary greatly among the three sites, but tended to be higher at OLYM. Gaseous ammonia is not measured by CASTNET.

3.2. Canopy effects on nitrogen deposition

During the four deposition sampling periods, NO_3–N fluxes in wet deposition were much higher than in throughfall except during summer 2006 at MORA and OLYM when very little precipitation occurred (Fig. 2). Averaged over the 2 years of the study, NO_3 deposition fluxes in throughfall were reduced by 87% and 93% compared to wet deposition fluxes at MORA and NOCA. In year 2 NO_3 deposition in throughfall was reduced by 75% at OLYM compared to wet deposition fluxes of NO_3 (incomplete data in year 1 at OLYM). This canopy NO_3-consumption effect in reducing throughfall NO_3–N deposition was slightly greater in winter or sampling periods that included winter (92% reduction by the

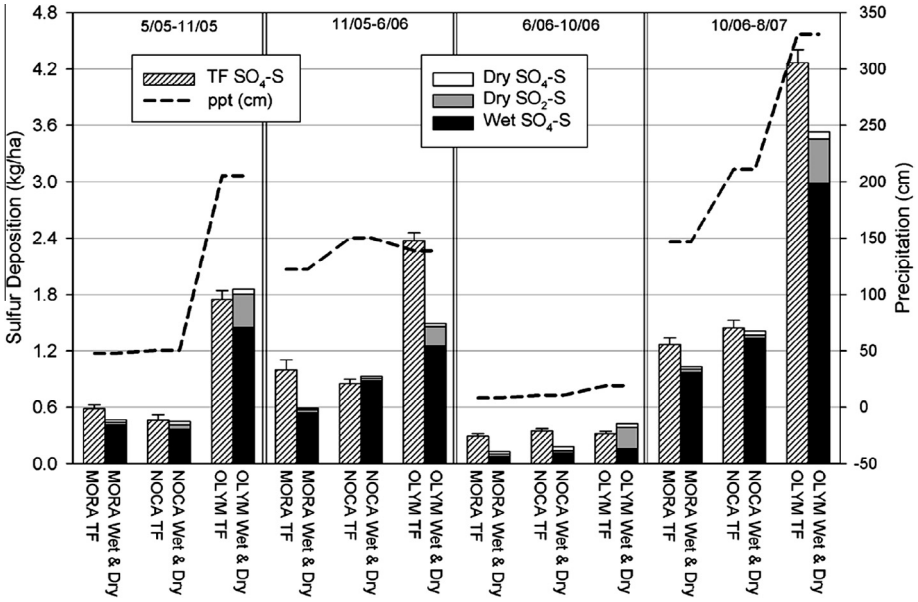

Fig. 4. Comparison of SO_4–S deposition in throughfall (TF) with 'wet + dry' S deposition. For the throughfall data standard error bars are shown for SO_4–S deposition, Wet deposition data are from the NADP–NTN network and dry deposition is from the CASTNET network. Dashed lines show precipitation totals at the three sites during each monitoring period.

canopy), compared to summer (82% reduction by the canopy; Fig. 2).

In contrast, levels of NH_4–N deposition were enhanced by passage through the canopy, except at MORA in the winter of 2005/2006 and NOCA in both winter periods (Fig. 2). Averaged over the 2 years of the study, NH_4–N concentrations in throughfall were increased by 60 and 117% compared to precipitation at MORA and OLYM, but reduced by 16% at NOCA. This different response at NOCA was a result of NH_4–N wet deposition in winter 2005/2006 (during year 1) that was the highest for any period at any of the sites during the study. In year 1 at NOCA throughfall deposition of NH_4–N was 44% lower than wet deposition of NH_4–N, but in year 2 throughfall deposition of NH_4–N was 12% greater than wet deposition of NH_4–N (Fig. 2).

Wet deposition of NO_3–N and NH_4–N followed the temporal trend of precipitation with highest wet deposition inputs during periods of high precipitation volumes. Throughfall NO_3–N only weakly tracked precipitation trends at the three sites because NO_3–N deposition in throughfall was also low in winter when precipitation volumes were greatest (Fig. 2). Throughfall NH_4–N did not track precipitation amount at the study sites, although at MORA and OLYM NH_4–N deposition was greatest in the last monitoring period when precipitation was also greatest. However, this may simply reflect the longer exposure period for the last sampling period (10–12 months; Fig. 2).

3.3. Sulfur deposition

Throughfall deposition of S was 0.9–1.5 times that of wet + dry deposition of S at the three study sites in the 2 years of the study (Table 3; Fig. 4). Averaged for all three sites and both years, annual wet + dry deposition of S (2.1 kg ha^{-1}) was 80% of throughfall deposition of S (2.5 kg ha^{-1}; Table 3). Dry deposition of S (CASTNET data) was approximately evenly divided between SO_4–S and SO_2–S at NOCA and MORA. However, at OLYM dry deposition of S from SO_2–S was six times greater than from SO_4–S (Fig. 4), possibly a result of marine vessel traffic within the Strait of Juan de Fuca (Fig. 1); The CASTNET site for OLYM is located in Port Angeles.

During the 2 years of the study, annual deposition of N in throughfall ranged from 0.47–1.17 kg ha^{-1} yr^{-1} compared to 1.31–4.59 kg ha^{-1} yr^{-1} for throughfall S deposition. Wet deposition of N ranged from 0.89–2.04 kg ha^{-1} yr^{-1} compared to 0.95–3.15 kg ha^{-1} yr^{-1} for wet deposition of S (Table 3). Annual deposition of S in throughfall was consistently several-fold greater than throughfall N deposition, particularly at OLYM. Total annual deposition (wet + dry) of N and S were equivalent at MORA, while total N deposition was slightly higher than S deposition at NOCA. However, at OLYM total (wet + dry) S deposition was more than double that of N (Table 3). Temporal trends of wet deposition and throughfall deposition of SO_4–S followed the same pattern as precipitation amount at all three study sites (Fig. 5), except at OLYM in the first sampling period of year 1 when there appears to be a slight deviation from this pattern.

4. Discussion

4.1. Canopy uptake of nitrogen

Based on NADP wet deposition data, NO_3–N deposition is two-to-three times greater than NH_4–N deposition in all three parks. The CASTNET dry deposition data also indicate a similar trend, although there is a caveat considering that for dry deposition of reduced N forms, only particulate NH_4–N is measured. Gaseous NH_3, which has a deposition velocity approximately four times greater than NH_4^+ (Flechard et al., 2011; Zhang et al., 2009) is not measured by CASTNET. However, the higher deposition of NO_3–N compared to NH_4–N is not evident in the throughfall data because of preferential canopy uptake of NO_3–N. This effect was observed at all three sites. The canopy consumption of NO_3–N was greater in winter than in summer, a temporal pattern even more clearly shown in the data of Klopatek et al. (2006) in a study in southern Washington in western hemlock, western red cedar and Douglas-fir stands. In Table 4 data from a total of eight stands in the PNW show this pattern of greater canopy NO_3–N consumption in winter.

Other studies from the PNW in Oregon, Washington, Idaho and Alaska also reported strong preferential canopy consumption of NO_3–N, in addition to studies in other low-pollution regions (Ta-

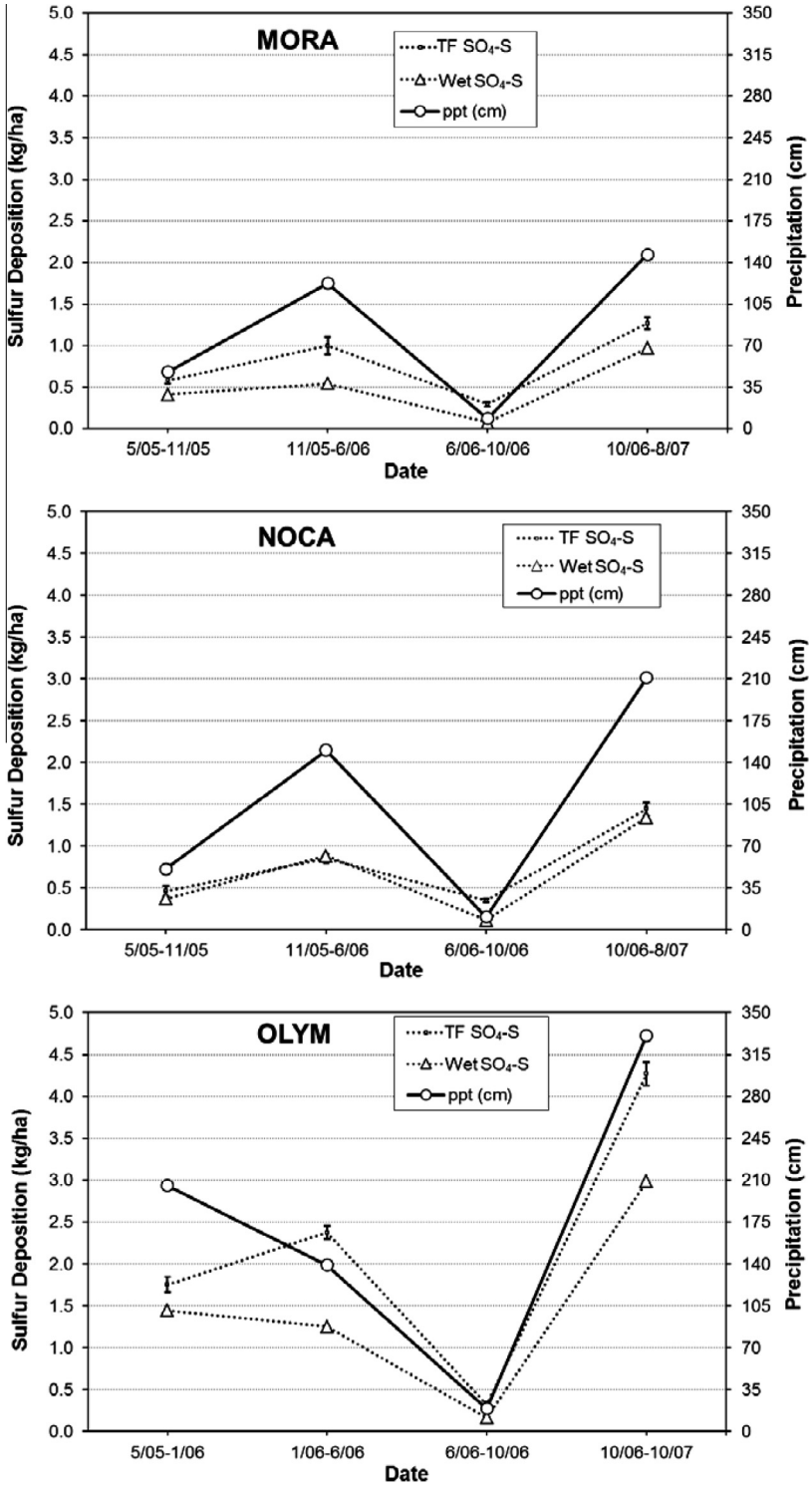

Fig. 5. Temporal trends in precipitation volume and throughfall (TF) and wet deposition of SO_4–S in Mount Rainier (MORA), North Cascades (NOCA) and Olympic (OLYM) National Parks. For the throughfall data standard error bars are shown.

ble 4). Sollins et al. (1980) found a 92% reduction in NO_3–N in throughfall compared to precipitation in the H.J. Andrews Experimental Forest in the western central Cascades in Oregon. Edmonds et al. (1995, 1998) reported a 93% NO_3–N reduction in Olympic National Park, one of our study sites. At a site in the southern Cascades in Washington, NO_3–N deposition in throughfall measured with ion exchange resin samplers was reduced by 64% and 90% compared to precipitation during the summer and winter, respectively (Klopatek et al., 2006). In southeast Alaska we found 79% reduction in NO_3–N in throughfall compared to bulk deposition in open sites, while NH_4–N was 141% greater in throughfall compared to bulk deposition (five sites, average of two field seasons; M.E. Fenn, unpublished data).

Throughfall data from 38 forest stands in the PNW region of North America and from a few other low-pollution regions are presented in Table 4 as throughfall:wet deposition ratios, a metric pre-

Table 4
Throughfall:wet deposition ratios for various studies in the Pacific Northwest and other low nitrogen deposition sites.

Site	NO_3–N	NH_4–N	References	Notes
Throughfall:wet deposition ratios				
MORA, Washington, USA	0.22	2.76	This study	Average of 2 years
NOCA, Washington, USA	0.09	1.62	This study	Average of 2 years
OLYM, Washington, USA	0.23	1.53	This study	Average of 2 years
OLYM, Washington, USA	0.07	1.58	Edmonds et al. (1995)	Average of three tree species: *Pseudotsuga menziesii*, *Tsuga heterophylla*, and *Thuja plicata*
Washington, USA	0.50	0.31	Johnson and Lindberg (1992)	55-year old *P. menziesii*
Washington, USA	0.23	0.38	Johnson and Lindberg (1992)	180-year old *Abies amabilis* Dougl. ex Forbes
Washington, USA	0.52	0.53	Johnson and Lindberg (1992)	50-year old *Alnus rubra* Bong.
Washington, USA	0.25	0.13	Klopatek et al. (2006)	Summer-old growth
Washington, USA	0.08	1.01	Klopatek et al. (2006)	Winter-old growth
Washington, USA	0.47	0.02	Klopatek et al. (2006)	Summer, 25-year old stand
Washington, USA	0.10	0.44	Klopatek et al. (2006)	Winter, 25-year old stand
Washington, USA	0.23	0.32	Fenn (unpublished data)	Summer-old growth, Wind River, close to the site of Klopatek et al. (2006)
Washington, USA	0.05	0.50	Fenn (unpublished data)	Winter-old growth, Wind River, close to the site of Klopatek et al. (2006)
Oregon, USA	0.21	1.07	Fenn (unpublished data)	Oregon Coast and Cascade Ranges and the Willamette Valley; average of eight sites with N deposition <1.2 kg ha^{-1} yr^{-1}
Oregon, USA	0.08	N/A	Sollins et al. (1980)	350–550 year old *P. menziesii* stand; Understory of *P. menziesii*, *T. heterophylla*, and other conifers and broad-leaved species
Southeast Alaska, USA	0.21	2.41	M.E. Fenn (unpublished data)	Average of five sites, two summers
Idaho, USA	0.53	0.80	Fenn (unpublished data)	Summer; three sites in Craters of the Moon National Monument and Preserve, sagebrush (*Artemisia tridentata* Nutt.)
Idaho, USA	0.15	0.83	Fenn (unpublished data)	Winter; three sites in Craters of the Moon National Monument and Preserve, sagebrush (*A. tridentata*)
Avg. of PNW sites:	0.23	0.96		
Maine, USA	0.41	0.17	Lovett and Lindberg (1993)	*Picea rubens* stand
Nova Scotia	0.32	0.96	Freedman and Prager (1986)	Average of eight stands of varying hardwood and conifer species, over a 5 month growing season; 45–100 year old stands
Norway	0.24	0.40	Lovett and Lindberg (1993)	*P. rubens* stand
Puerto Rico	0.15	4.84	McDowell (1998)	Tropical rain forest
Overall average (not including California sites)	0.24	1.08		
California, Northern Sierra Nevada Mountains	1.48	1.23	Fenn et al. (2008) and M.E. Fenn (unpublished data)	Avg of four mixed conifer sites (total throughfall 1.4–4.2 kg N ha^{-1} yr^{-1})
California, Yosemite National Park	2.24	2.12	M.E. Fenn (unpublished data)	Avg of 11 forest sites (total throughfall: 2.8–4.7 kg N ha^{-1} yr^{-1})
Central coastal California	1.71	3.70	Knops et al. (1996)	Two-year average; oak woodland
Central coastal California	1.33	3.39	Knops et al. (1996)	Two-year average; oak woodland—epiphytic lichens removed from canopy
Average of California sites	1.69	2.61		
Review/Synthesis	1.27	1.77	Parker (1990)	Data from >20 studies that include NO_3–N and NH_4–N throughfall deposition data

viously reported in a synthesis of N deposition to forests (Lovett and Lindberg, 1993). Average ratios for the low pollution regions mentioned are 0.23 for NO_3–N and 0.96 for NH_4–N (excluding the California sites), showing the strong canopy uptake of NO_3–N and on average little effect on NH_4–N. However, the canopy effect on throughfall deposition of NH_4–N was variable with enrichment in some sites or sampling periods and canopy consumption of NH_4–N deposition in others (Table 4). Included in Table 4 are eight forest stands in central Nova Scotia, Canada (Freedman and Prager, 1986) for which the average ratios of 0.32 and 0.96 for NO_3–N and NH_4–N were nearly identical to the overall average for low pollution sites in the PNW region of the United States.

We measured throughfall and bulk deposition at eight low-pollution sites (N deposition <1.2 kg ha^{-1} yr^{-1}) along a west-to-east transect from coastal Oregon through the Willamette Valley and into the Cascade Range. For these eight sites the average throughfall:wet deposition ratio for NO_3–N was 0.21 compared to 1.07 for NH_4–N (Table 4; M.E. Fenn, unpublished data). Within this same study, at four urban sites in Eugene and Portland, Oregon and in Seattle, Washington throughfall N deposition ranged from 8.1 to 21.0 kg ha^{-1} yr^{-1} and the average throughfall:wet deposition ratio for NO_3–N and NH_4–N was 6.76 and 2.80. Presumably canopy consumption of NO_3–N is also occurring in these more polluted sites, but high levels of dry deposition of oxidized N compounds in these urban environments results in much higher NO_3–N deposition in throughfall compared to deposition in open canopy-free sites. We postulate that in more polluted sites (i.e., throughfall N deposition >ca. 3–4 kg ha^{-1} yr^{-1}) elevated levels of washoff of dry-deposited NO_3–N from canopy surfaces obscures detection of canopy consumption of NO_3–N (Lovett, 1994; Lovett and Lindberg, 1993).

California sites are an exception to the trend of preferential canopy uptake of NO_3–N in low pollution sites. At four sites in the northern Sierra Nevada Mountains annual throughfall deposition of N ranged from 1.4 to 4.2 kg ha^{-1} yr^{-1}, but the average ratio of NO_3–N deposition in throughfall sampled under ponderosa and Jeffrey pine canopies versus bulk deposition was 1.48. The analogous average ratio for NH_4–N was 1.23 (Table 4). In 11 forest stands in Yosemite National Park (throughfall N deposition 2.8–4.7 kg N ha^{-1} yr^{-1}) the average ratio of annual deposition in throughfall to bulk precipitation was 2.24 for NO_3–N and 2.12 for NH_4–N. However, the ratios in these Yosemite sites were much higher for NO_3–N and NH_4–N in the summer dry season (3.40 and 3.21) than in winter (1.16 for NO_3–N and 1.23 for NH_4–N; M.E. Fenn, unpublished data). The ratio of NO_3–N in throughfall to that in precipitation was 1.71 in a coastal oak stand in California (Knops et al., 1996), similar to mixed conifer stands in northern California. The average throughfall to precipitation ratios for all these California sites was 1.69 for NO_3–N and 2.61 for NH_4–N (Table 4). Parker (1990) reported average ratios from a synthesis of

throughfall studies worldwide of 1.27 for NO_3–N and 1.77 for NH_4–N.

It is not unusual to have negative net throughfall fluxes (wet deposition > throughfall deposition) in forested areas with relatively low N deposition. However, it was unexpected to repeatedly find strong preferential canopy consumption of NO_3–N compared to NH_4–N. Many studies have shown canopy uptake of oxidized and reduced forms of N (Butler and Likens, 1995; Lovett, 1994; Lovett and Lindberg, 1993; Parker, 1990). It is more commonly reported that canopy retention of reduced forms of N is greater than oxidized forms (Lovett, 1994), although this varies widely and seems to be more applicable to sites with moderate to high levels of N deposition (Lovett and Lindberg, 1993). Based on the results summarized in Table 4 we conclude that the strong preferential uptake of NO_3–N by forest canopies is a common but not a universal phenomenon in forests with low to moderate levels of N deposition; however it appears to be the norm in northwestern North America (Oregon, Washington, Idaho and SE Alaska) and has also been reported from the state of Maine in the northeastern United States (Lovett and Lindberg, 1993), Nova Scotia, Canada (Freedman and Prager, 1986), Norway (Lovett and Lindberg, 1993) and Puerto Rico (McDowell, 1998). In two jack pine (*Pinus banksiana* Lamb.) stands in northern Alberta and Saskatchewan, Canada the average throughfall:wet deposition ratios were 0.62 and 0.92 for NO_3–N and NH_4–N over 3 years (M.E. Fenn, unpublished data); suggesting greater canopy uptake of NO_3–N than of NH_4–N, but not to the degree reported for Oregon, Washington, southern Idaho, and southeastern Alaska.

4.2. Possible mechanism for preferential canopy retention of NO_3–N

Patterns and observations that may provide clues as to the mechanism responsible for preferential canopy retention of NO_3–N in the PNW include the following: (1) NO_3–N retention is often greater in winter which is also the wet season (Klopatek et al., 2006 and others listed in Table 4), (2) foliar uptake of N, and particularly of NH_4–N, is reportedly greater during the growing season when physiological demand for N is greater (Hamburg and Lin, 1998), (3) literature reports of foliar uptake of N from wet deposition is much greater for NH_4–N than for NO_3–N (Adriaenssens et al., 2011; Brumme et al., 1992; Garten and Hanson, 1990; Harrison et al., 2000; Lumme, 1994; Wilson and Tiley, 1998), and (4) preferential canopy uptake of NO_3–N has not been reported in California (Table 4). Here we refer only to relatively low deposition sites in coastal or northern California—sites where high levels of dry deposition of N do not mask observations of canopy N retention (Lovett, 1994).

Possible mechanisms for canopy retention of N include foliar uptake, uptake by epiphytic lichens or bryophytes, absorption by bark, and microbial assimilation of inorganic N or conversion to organic N. Lovett and Lindberg (1993) evaluated most of these possibilities in the Integrated Forest Study, concluding that the evidence suggests that inorganic N consumed in forest canopies is probably taken up by the trees themselves. The capacity of forest canopies to generate organic N from inorganic N is limited, although in forests with deposition greater than 5 kg N ha^{-1} yr^{-1} the formation of organic N in the canopy can result in measurable increases in the flux of organic N in throughfall (Cape et al., 2010). Epiphytes are known to take up inorganic N, but Klopatek et al. (2006) reported strong NO_3–N consumption by the upper 5 m of the canopy of old-growth trees and also in young trees; in both situations epiphytes were virtually nonexistent. In a study in coastal central California, Knops et al. (1996) compared throughfall chemistry in oak trees with and without lichens and concluded that deposition and canopy uptake of NO_3–N and NH_4–N were not significantly affected by epiphytic lichens in their study sites.

4.2.1. N uptake by foliage, twigs and bark: seedling studies

In contrast to this study and those listed in Table 4 showing greater canopy uptake of NO_3–N than of NH_4–N from wet deposition, most studies using ^{15}N-labeled NO_3–N and NH_4–N show that foliar uptake of NH_4–N from solution is greater than for NO_3–N (Adriaenssens et al., 2011; Brumme et al., 1992; Garten and Hanson, 1990; Harrison et al., 2000, and references therein; Lumme, 1994; Wilson and Tiley, 1998). A number of studies indicate that inorganic N uptake from solution by stems, branches and twigs may be of similar magnitude as foliar uptake (Boyce et al., 1996; Bowden et al., 1989; Dail et al., 2009; Harrison et al., 2000; Macklon et al., 1996), but this can vary by species. Adriaenssens et al. (2012) found that twigs of Scots pine (*Pinus sylvestris* L.) had a much stronger affinity for NH_4–N than three deciduous species and that fully-leafed pine twigs retained more NO_3–N than fully-leafed twigs of three deciduous species. Crockford and Khanna (1997) found that NH_4–N was preferentially removed from throughfall in a *Pinus radiata* plantation in Australia but NO_3–N was preferentially taken up from stemflow solutions. Some have concluded that the net negative charge of foliar cuticles tends to repel anions such as NO_3–N and attract cations such as NH_4–N which can move between exchange sites through the cuticle (Adriaenssens et al., 2011; Marschner, 1995; Wilson and Tiley, 1998). In contrast, ion uptake in twigs can occur by simple diffusion through the bark in the region of radial rays (Katz et al., 1989) and may be important for whole plant ion balance (Klemm, 1989). Mass flow of ions in solution through splits in bark, diffusion, and exchange processes may all be important mechanisms for uptake by bark and woody tissue (Macklon et al., 1996). There are species differences in ion preference and uptake rates by foliage and woody tissues (Adriaenssens et al., 2012; Macklon et al., 1996). Species with higher wettability of foliage and bark are expected to have higher canopy uptake of N (Adriaenssens et al., 2011; Harrison et al., 2000). Wilson and Tiley (1998) reported that NH_4–N and NO_3–N uptake by woody twigs of red spruce (*Picea rubens* Sarg.) was 2–10 times greater than uptake by foliage. Uptake of NO_3–N by bark of Norway spruce [*Picea abies* (L.) Karst] seedlings was five times greater than by foliage (Katz, 1991; Macklon et al., 1996). Intercepted precipitation remains on twig surfaces far longer than on foliage (Boyce and McCune, 1992), providing opportunity for ion uptake by twigs. Bark is a more permeable barrier to ion movement than the needle cuticle due to greater wettability and lower resistance to liquid-phase diffusion (Wilson and Tiley, 1998). A concentration gradient for ions such as NO_3–N between the moistened stems or twigs and the xylem sap within may promote uptake by diffusion (Adriaenssens et al., 2012; Katz et al., 1989). Wet deposition of NO_3–N is two–three times greater than NH_4–N deposition at our study sites, which may favor canopy NO_3–N consumption.

4.2.2. Field studies of canopy N uptake

Studies of canopy uptake of N have commonly been done with immature plants; results from such studies may not adequately quantify or reveal mechanisms that affect atmospheric N interactions with mature forest stands. In a study at the Howland Integrated Forest Study site in central Maine, N was applied over three growing seasons as a fine mist of liquid NH_4NO_3 to a mature (mean age approximately 140 years) spruce-fir forest canopy by way of helicopter. The tree canopy retained much more N than the soil horizons and the most important plant sinks for NO_3^- and NH_4^+ were twigs, branches and bark (Dail et al., 2009). Eastern hemlock [*Tsuga canadensis* (L.) Carr.] bark demonstrated an unusual affinity for NO_3–N; hemlock bark was by far the most enriched plant part in the study. Retention of NO_3–N in bark was 1–2 orders of magnitude greater than NH_4–N retention by bark in eastern hemlock and red spruce, the two dominant overstory species (Dail

et al., 2009). Sixty-one percent of the applied $^{15}NO_3$–N was recovered in plant biomass (only 6.9% in soil) and 45% of the applied $^{15}NO_3$–N was recovered in the bark fraction. Less than 2% of the added N of either ionic form was retained in the foliage, which is consistent with many studies showing that a relatively low fraction of wet-deposited N is retained by canopy foliage (Adriaenssens et al., 2012; Bowden et al., 1989; Fenn and Leininger, 1995; Garten et al., 1998). Of the labeled N recovered in plant tissue within the forest stand, 91% and 80% of the $^{15}NO_3$–N and $^{15}NH_4$–N were in the bark and branch fractions (Dail et al., 2009). However, the absolute amounts of labeled N in bark and branches was 2.2 times greater in the $^{15}NO_3$–N treatment compared to the $^{15}NH_4$–N treatment. $^{15}NO_3$–N recovery in plants and in the ecosystem was nearly double the recovery of $^{15}NH_4$–N. The authors concluded that physico-chemical interactions with plant surfaces is the likely predominant mechanism of canopy N retention.

Houle et al. (1999b) measured wet deposition, throughfall and stemflow for 8 years in a deciduous stand and a coniferous stand located 50 km NW of Quebec City, Canada. The most dramatic ionic uptake from wet deposition was that of NO_3–N in stemflow. Concentrations of NO_3–N in stemflow of the coniferous stand were reduced by 93% compared to wet deposition. By comparison, NH_4–N was reduced by 58% (Houle et al., 1999b). The authors suggested this N uptake by stems may in part be due to uptake by epiphytic lichens that grow on tree trunks. Under a favorable environment corticolous lichens can reduce NO_3–N concentrations in stemflow. Such an environment includes: meteorological conditions favoring prolonged hydration of lichen thalli by nutrient solutions; air temperature range between −2 °C and 8 °C; and mixed precipitation (snow and rain) with freeze–melt cycles that increase the viscocity and surface tension of stemflow solutions, resulting in increased residence times (Levia, 2002; Levia and Herwitz, 2000). However, preferential uptake of NO_3–N in the PNW occurs in the absence of epiphytic lichens (Klopatek et al., 2006). The factors favoring N uptake by lichens also favor increased NO_3–N uptake by bark and woody tissue. Bark characterstics are also important. The boles of tree species with rough bark such as *Tsuga canadensis* L. Carr. (eastern hemlock) have greater surface area and water storage capacity than species with smooth bark (Levia and Frost, 2003), and thus a greater capacity for nutrient retention. In summary, the studies cited above and those of Dail et al. (2009) and Gaige et al. (2007) suggest that the preferential canopy NO_3–N uptake observed in our study and others (see Table 4) could be due to NO_3–N uptake by stems, branches, twigs and bark. Further work is needed to test this hypothesis. In a recent meta-analysis of ^{15}N tracer field studies, Templer et al. (2012) found that total ecosystem recovery of applied N was greater when applied as $^{15}NO_3^-$ (80.2%) than when applied as $^{15}NH_4^+$ (53.4%). They also reported that ^{15}N tracer recovery was greater when applied to plant canopies (81.7%) compared to soil applications (63.1%).

If epiphytic lichens were the primary mechanism for the preferential uptake of NO_3–N in the PNW, then lichen preference for N in the nitrate form would also be expected. Epiphytic lichens have been shown to efficiently take up both NH_4–N and NO_3–N under ambient conditions, although in laboratory studies using pure salt solutions NH_4–N is more readily utilized (Hauck, 2010). For many epiphytic lichen associations ('species') preferential uptake of NH_4–N has been reported (Dahlman et al., 2004; Palmqvist and Dahlman, 2006), although this may be related to low light conditions (higher energy cost to assimilate NO_3–N compared to NH_4–N) and the application of high N doses (Johansson et al., 2010). Thus more work is needed, but it may be that at ecologically relevant N concentrations and doses epiphytic lichens do not have a strong preference for N form (Hauck, 2010; Johansson et al., 2010).

If the hypothesis of NO_3–N uptake by stems, branches twigs and bark is correct, it may also explain why studies in the PNW show higher NO_3–N canopy consumption in winter than in summer. This region is characterized by wet winters and dry summers and frequent fog occurrence (Basabe et al., 1989). For example, Klopatek et al. (2006) describe their study site as one with over 250 cm of annual precipitation of which less than 10% occurs in summer. At our three throughfall sites, average annual precipitation ranges from 232 to 315 cm (Table 1). The longer and more frequent periods during which stems, branches and bark are wet during winter provide the necessary conditions and capacity for canopy uptake of NO_3–N (Katz et al., 1989). Although canopy retention of NO_3–N in the PNW has been reported in several instances to be greater in winter, preferential NO_3–N uptake also occurs in summer. Clouds and fog in some montane forests of the PNW are common during the growing season and at low elevations during winter and early spring (Basabe et al., 1989). Such cloudwater events are expected to favor canopy NO_3–N uptake, including N deposited as cloudwater, even during the growing season when precipitation volumes are much lower.

In the whole-forest canopy fertilization study in Maine, NO_3–N retention by the canopy was slightly higher under ambient conditions (no added N), while in the N-added plots (18–20 kg N ha^{-1} yr^{-1}) NH_4–N was more strongly retained (73–83% of inputs) compared to NO_3–N (57–75%; Gaige et al., 2007). The authors concluded that in the N-added treatments more NO_3–N than NH_4–N was washed from the canopy as throughfall, presumably because of preferential retention of NH_4–N. The authors also suggested that lower NO_3–N retention in the canopy fertilizer treatments compared to NO_3–N retention of ambient NO_3–N may have been due to canopy N retention processes that were becoming saturated. Thus, this study confirms the common experimental results of higher canopy and foliar NH_4–N retention when fertilizer-type N solutions are applied to plant canopies, but also illustrates that such N treatments are limited in their capacity to replicate ambient or field exposures to atmospheric N.

4.3. Ion exchange resin samplers for monitoring N and S deposition in remote regions

The major objective of this study was to determine if IER throughfall samplers can be used to monitor N and S deposition to forests in remote sites. An important component of this objective was to evaluate whether IER throughfall sampling could be used to estimate N deposition in its various forms to forested areas, including cloudwater deposition which is not measured in national monitoring networks. The high proportion of NO_3–N from wet deposition taken up by the canopy, in addition to unmeasured levels of canopy uptake of dry deposition, would seem to preclude the use of throughfall measurements for estimating N deposition in these forests. However, the throughfall measurements are still highly valuable for measuring N fluxes to the forest floor and for studying the effects of such fluxes. On average for the three study sites and for both years the sum of wet and dry deposition of N (1.58 kg N ha^{-1} yr^{-1}) was 2.4 times greater than throughfall N deposition (0.65 kg N ha^{-1} yr^{-1}), because of high levels of canopy NO_3–N consumption. This difference would likely be even greater if the dry deposition calculations of CASTNET included dry deposition of NH_3, a compound with a high deposition velocity (Flechard et al., 2011; Zhang et al., 2009) and which is a major driver of N deposition over widespread regions of the western and eastern U.S. (Bytnerowicz et al., 2002; Beem et al., 2010; Dennis et al., 2010). CASTNET also does not account for deposition of NO_2 (Fenn et al., 2009), which can be a significant component of dry deposition as a result of stomatal uptake, although plant uptake of NO_2 is generally lower than that of HNO_3 or NH_3 (Hertel et al., 2012).

The IER samplers gave reasonable estimates of total S deposition. The results of this study confirm many previous studies in

showing that deposition of SO_4–S as throughfall is similar to the sum of wet + dry inorganic S deposition (Lindberg and Lovett, 1992; Lovett, 1994). At our three study sites throughfall S deposition was on average 19% greater than the estimated sum of S wet + dry deposition, with absolute differences ranging from 0.1 to 0.8 kg S ha^{-1} yr^{-1}. We assume this discrepancy is due to underestimation of S dry deposition by CASTNET (Kolian and Haeuber, 2004) and possibly unmeasured cloudwater deposition. CASTNET values for dry deposition of S were very low (0.1 at MORA and NOCA; 0.7–0.8 kg S ha^{-1} yr^{-1} at OLYM). Cloudwater deposition is not accounted for in wet deposition collectors, but is measured in throughfall (Fenn et al., 2009; Fenn and Poth, 2004) except for ions that may be retained by the canopy.

Because of high levels of atmospheric NO_3–N consumption by tree canopies in this study, throughfall N deposition is not an effective measure of N deposition in low deposition environments and cannot be used directly to estimate atmospheric inputs of N to the forest canopy from dry, wet and cloudwater deposition. However, we propose that total inorganic N deposition can be calculated or estimated from the data in this study, based on two assumptions: (1) S/N ratios in wet deposition are approximately equal to S/N ratios in total deposition to the canopy, and (2) throughfall S deposition is equivalent to total inorganic S deposition to the canopy, especially in sites with low levels of SO_2 exposure (Lindberg and Lovett, 1992). If we accept these assumptions, and the latter is reasonably supported by this study, total inorganic N deposition can be calculated by solving for x in the following algebraic equation:

$$S_{wet}/N_{wet} = S_{tfall}/x$$

where x = total inorganic N deposition, and S_{tfall} is equivalent to total S deposition.

We plotted such estimated total N deposition values versus wet + dry N deposition values for the same sites. When this was done for our three sites over a 2 year period and 3 low pollution sites (from Washington and Florida) from the Integrated Forest Study (6 sites, 9 data points; Johnson and Lindberg, 1992) we obtained a regression coefficient of 0.99. When our sites and all the sites from the Integrated Forest Study were included (15 sites, 18 data points) a similar relationship (r^2 = 0.94) was found (Fig. 6).

Although calculating deposition based on nutrient ratios must be done with caution, we suggest that if one tests the nutrient or deposition relationships for the forest type under study and under the environmental conditions prevalent in the study region, this method can be used to estimate N deposition. The calculated total N deposition values for our three study sites are on average 213% greater than throughfall N deposition, but only 14% greater than the sum of wet + dry deposition of N (Table 3). These estimated total N deposition values are very reasonable considering that the CASTNET dry deposition estimate is usually a lower-bound estimate, in large part because CASTNET does not include deposition of NH_3, a highly reactive atmospheric N pollutant. Based on the estimated total N deposition, the amount of atmospheric N retained by the canopy can be estimated by subtracting throughfall N deposition. These calculations suggest that approximately 1.0, 1.6 and 0.5 kg N ha^{-1} yr^{-1} of atmospherically-deposited N were retained by the forest canopy at MORA, NOCA and OLYM.

Simulated inorganic N (2.7–3.2 kg ha^{-1} yr^{-1}) and S deposition (2.2–6.2 kg ha^{-1} yr^{-1}) values for our throughfall study sites in 2006 from the USEPA CMAQ (Models-3/Community Multiscale Air Quality) model (CMAQ5.1beta version; Byun and Schere, 2006) at a 12-km grid scale were 1.7 times greater than our calculated total N deposition and throughfall S deposition, as an average of the three study sites (CMAQ data courtesy of Robin L. Dennis, USEPA, personal communication). Average wet deposition of N and S in CMAQ for the three sites were 1.3 and 2.0 times higher than the NADP wet deposition data given in Table 3. Average dry deposition inputs of N and S in CMAQ were 7.1 and 3.7 times greater than CASTNET dry deposition data for the three study sites, supporting our conclusion that the dry deposition values in Table 3 are too low. CMAQ total N deposition was on average 5.0 times greater than throughfall N deposition in the three national parks. Separate comparisons of simulated deposition of reduced and oxidized N forms by CMAQ with throughfall data strongly confirm the phenomenon of preferential canopy uptake of NO_3–N. CMAQ annual deposition of reduced N was 2.1 times greater than throughfall deposition of NH_4–N. By comparison, simulated annual deposition of oxidized N was 15.6 times greater than throughfall deposition of NO_3–N.

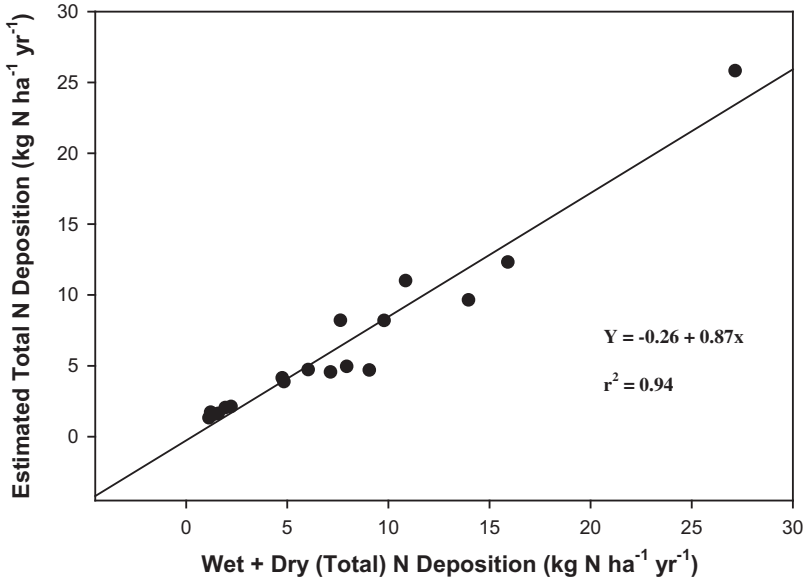

Fig. 6. Linear regression for 'wet + dry' total inorganic N deposition and estimated total inorganic N deposition. Total N deposition on the y-axis was calculated from wet deposition S/N ratios and throughfall S deposition, assuming the latter approximates total S deposition and that S/N ratios in wet deposition and total deposition to forest canopies are equivalent. Data are from this study and the Integrated Forest Study (Johnson and Lindberg, 1992; Lovett and Lindberg, 1993). See text for details.

The estimated total N deposition levels reported for the forest stands studied in the three parks (1.3–2.1 kg ha^{-1} yr^{-1}) are below the terrestrial N critical loads (CLs) reported for western Oregon and Washington, including the parks in this study (Geiser et al., 2010). The most sensitive terrestrial ecosystem response to N deposition are changes in epiphytic lichen communities. The CL for effects on lichen communities in western Oregon and Washington ranges from 3 to 9 kg ha^{-1} yr^{-1} (based on modeled deposition values), with increasing values for the CL as precipitation increases from 45 to 400 cm of annual precipitation (Geiser et al., 2010). Throughfall deposition of SO_4–S averaged 1.6 kg ha^{-1} yr^{-1} at MORA and NOCA, a low level not expected to cause detectable harm. Sulfur deposition at OLYM (average of 4.4 kg ha^{-1} yr^{-1}) was much higher, but these higher levels are largely due to non-anthropogenic sea salt deposition as has been reported previously at the NADP site in OLYM (Blew and Edmonds, 1995). This is also demonstrated in ratios of Cl^-:Na^+ (1.14) and SO_4^{2-} : Na^+ (0.61) in wet deposition at OLYM that are indicative of marine sources, while those at MORA and NOCA are not (NADP–NTN; http://nadp.sws.uiuc.edu/ntn/, accessed October 18, 2012).

5. Conclusions

Wet and dry deposition fluxes of N and S at MORA, NOCA and OLYM national parks were low as expected based on their location. Throughfall N deposition at the three parks was unexpectedly low however, because approximately 90% of wet deposited NO_3–N was consumed by the forest canopy. Preferential NO_3–N consumption by the canopy has been reported previously from low-pollution sites, but it appears to be unusually common in the PNW region of the United States. Preferential canopy uptake of NO_3–N is likely occurring in more polluted sites as well, but is not observed because of washoff of a large portion of the NO_3–N accumulated on canopy surfaces from dry deposition and from cloudwater deposition in sites where cloud impaction occurs. The mechanism for this preferential canopy consumption of NO_3–N has not been fully evaluated, but it is hypothesized to be the result of NO_3–N uptake by stems, branches and bark. This efficient canopy uptake of NO_3–N, the most prevalent inorganic N form in wet deposition in this study, may limit the usefulness of the throughfall method for monitoring N deposition in remote sites within the study region. However, we propose that total N deposition can be estimated for forests in the PNW from calculations using the S/N ratio in wet deposition and throughfall S deposition. Such calculated estimates are based on the assumptions that S/N ratios in wet deposition are similar to S/N ratios in total deposition to the canopy, and that throughfall S deposition is approximately equal to total inorganic S deposition. Further studies are needed to elucidate the generality and mechanisms responsible for the strong preferential canopy uptake of NO_3–N observed in the PNW and in some forest stands in other regions.

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