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Dry Deposition Estimates of Nitrate, Sulfate and Chloride Based on Throughfall Measurements at Black Rock Forest

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Abstract

Throughfall and precipitation chemistry measurements were used to estimate fluxes of atmospheric NO_3^-, SO_4^{2-} and Cl^- to high and low elevation deciduous and coniferous stands at Black Rock Forest in Cornwall, NY. Dry deposition was a significant pathway of NO_3^-, SO_4^{2-} and Cl^- to the forest in both types of stands during the summer of 1998, averaging 56%, 32% and 66%, respectively, of the total deposition of each ion across the three sites. Dry deposition rate estimates of NO_3^- and SO_4^{2-} for July, August and September were compared to average rates for these months calculated at nearby West Point, NY using the NDDN inferential method. Bulk wet deposition rates were compared to "wet-only" rates measured by the NADP at West Point. The sulfate dry deposition rate estimates averaged 7 kg S/ha/yr at the deciduous forest sites, and 10 kg S/ha/yr at the coniferous sites, which were higher than the NDDN average rate (4.7 kg S/ha/yr) at West Point. Nitrate dry deposition rates varied considerably among the sites. The average NO_3^- dry deposition was 14 kg N/ha/yr at the deciduous site, and 2.0 kg N/ha/yr at the coniferous site, and 4.2 kg N/ha/yr at West Point. Chloride dry deposition rates were much higher than rates reported at other experimental forests and ranged from 4 kg/ha/yr at the low elevation deciduous forest to 89 kg/ha/yr at the coniferous forest. The reasons for the high Cl^- deposition are not yet understood. Bulk precipitation inputs of all three anions generally agreed well with wet deposition estimates at West Point, however, variability between the BRF and West Point measurements increased for large volume precipitation events.

INTRODUCTION

The atmospheric input of chemicals and nutrients to forest ecosystems is rapidly changing on a global scale. Current anthropogenic nitrogen emissions roughly equal natural inputs to the atmosphere (Broad, 1996). In comparison, anthropogenic CO_2 emissions account for about 5-10% of the total atmospheric CO_2 concentration. Although acidic sulfate emissions have been reduced significantly in the U.S. in the past few decades, a doubling of global nitrogen emissions is predicted between 1980 and 2020 (Schindler, 1993). Atmospheric pollutants are delivered to forests by both wet deposition (precipitation), and dry deposition (sedimentation, impaction of aerosols, and plant uptake). Dry deposition is a significant pathway of nitrogen delivery to forests, typically ranging from about 40 to 60% of the total (Lovett, 1992). Dry deposited sulfur typically averages about 30% of the total (Lindberg, 1992). Wet deposition has been routinely measured at experimental forests in the past. Techniques for measuring dry deposition, however, have been developed only recently. In this paper, dry deposition fluxes of nitrate, sulfate and chloride were estimated from canopy thoughfall measurements at three locations in Black Rock Forest, NY that differed in vegetation type and elevation.

Background

Whereas wet deposition fluxes via rainfall are easily measured from precipitation collectors, dry deposition fluxes are rather difficult to determine. No single method of measuring dry deposition is widely accepted. However, a combination of various methods with complementary strengths may be used to estimate dry deposition to an area. The method developed by the National Dry Deposition Network (NDDN) targets gases

and small particles (<2μm), and deposition fluxes are inferred from measured atmospheric concentrations and calculated deposition velocities (Hicks et al, 1991). Deposition of larger particles is usually determined by collecting the particles on artificial surfaces. When compared to precipitation chemistry above a forest canopy, precipitation collected beneath a canopy (hereafter referred to as throughfall) can also be used to estimate dry deposition of particles.

Precipitation chemistry is altered by forest canopies by two main processes; (1) gases and aerosols that are deposited on the surface of the vegetation during dry periods can be "washed off" during a precipitation event, and (2) dissolved ions can be taken up by or leached from bark, foliage and microorganisms. It is often difficult to separate the relative contribution of these processes to throughfall chemistry. Leaching processes are generally considered more important for cation measurements than for anions, since cations in leaf tissue are readily exchanged for protons in acidic precipitation. Estimates of the relative contributions of each process have been attempted by the use of isotopic studies (Lindberg and Garten,1988; Gay and Murphy, 1989), artificial collection surfaces, and by using ratios from areas of enhanced dry deposition such as a forest edge to extrapolate to deposition on the inner forest (Beier, 1992).

Since the effects of chemical and nutrient deposition may vary widely among forest areas, the development of a large database that spans many different types of climate, vegetation, and chemical inputs is needed to assess the possible effects of changes in atmospheric chemistry on forest productivity. Mass balance approaches can be used to characterize chemical budgets in a forested watershed, and to learn how ecosystem processes vary with changing atmospheric conditions. This approach to

understanding chemical cycling and forest dynamics has been successfully applied at the Hubbard Brook Experimental Forest in New Hampshire since 1963 (Likens, 1996) and in the 13 experimental forests that participate in the Integrated Forest Study (Johnson, 1992).

Black Rock Forest (BRF), located in Cornwall, NY, has many advantages for watershed scale geochemical studies. Precipitation chemistry and dry deposition rates of major ions have been measured since 1979 at a meterological station adjacent to the forest at West Point. A long-term record of chemical fluxes in a forest area is necessary to cover a wide range of environmental conditions due to seasonal and annual variability. These measurements are particularly valuable as the data are collected as part of nationwide monitoring programs run by the National Atmospheric Deposition Program (NADP) and the NDDN, which have numerous sites across the US. The analytical protocols used by these organizations have been adopted for many forest studies, which allows direct comparison of West Point data with results obtained from a variety of forest areas, such as Hubbard Brook and the Integrated Forest Study (IFS) sites.

It is not yet known how well the dry deposition estimates at West Point represent deposition fluxes at BRF. The deposition velocities calculated with the NDDN model are measured over flat, homogeneous terrain, and may not be applicable to an area with complex topography like BRF. Throughfall techniques, however, may be used for any landscape. The goals of this study were to (1) estimate dry deposition rates of NO_3^-, SO_4^{2-} and Cl^- to the forest from thoughfall measurements, (2) identify spatial patterns in anion deposition at BRF by comparing three different sites and determine what factors

(such as elevation and species composition) affect dry deposition rates, and (3) compare the dry deposition rate estimates at BRF with estimates made with the NDDN model at West Point.

SITE DESCRIPTION AND METHODS

Study site

Black Rock Forest is a 1520 hectare mixed forest dominated by oak and maple species, with a small percentage of spruce and pine. It ranges in altitude from approximately 150 to 430m. The prevailing wind direction during the sampling period was primarily from the northeast, and occasionally from the south or southeast, with wind speeds averaging 1.5 +/- 0.8 m/s.

Three sites were chosen for throughfall chemistry measurements; deciduous forest stands at high and low elevations (HDf and LDf, respectively) dominated by Chestnut Oak (*Quecus montana)* and a coniferous forest stand (Cf) of Red Pine (*Pinus resinosa*). The HDf and Cf stands were both at an elevation of approximately 370m, and the LDf site was at an elevation of about 270m (figure 1). The Df stands were located in the Cascade Brook watershed in the southeast region of BRF, and the Cf stand was approximately 2.2km to the west. Individual trees at the Df sites ranged in age from about 35-80 years, and the trees at the Cf site were planted in 1932.

Nine precipitation events ranging from 1.1 to 39.2mm were collected for chemical analysis during the period of 7/23/98 to 10/1/98 (figure 2). The percentage of total rainfall during the sampling period for which anion concentrations were determined is approximately 80%. Chemical data was not available for events less than 1mm of

precipitation, due to insufficient volume for analysis. A total of 15 events were collected for throughfall volume measurements.

Collection buckets and sampling

Approximately 14 polyetheylene collection buckets were placed at each site to measure throughfall and precipitation volume. Each bucket was equipped with a funnel (19 cm diameter) and sealed with a polyethylene lid to reduce evaporative water loss. Nylon filters were used to keep out insects and debris. To collect throughfall at each site, buckets were placed at random under the canopy. The total number of throughfall collectors for volume measurements varied between sites (nine at HDf, ten at LDf and 8 at Cf). Three throughfall collectors at each site were chosen at random for chemical analysis.

Five buckets were placed in nearby clearings at each site to collect "bulk" precipitation. Three of the five were used for chemical measurements. Bulk wet deposition collectors differ from "wet-only" collectors in that the bulk collectors are continuously open to rainfall collection. Wet-only collectors are covered during dry periods, and are automatically exposed during precipitation events. The amount of dry deposition to the clearing bulk collectors between rainfall events was assumed to be negligible compared to the precipitation input. The bulk wet deposition to the clearing buckets was assumed to represent above-canopy precipitation inputs. To ensure that the clearing buckets were unaffected by the surrounding canopy, the buckets were placed at a distance from the forest edge where the height of nearest tree-top was at an angle less than 45 degrees from the buckets.

Samples were collected within 12 hours after the rain events, and volumes were measured on site. Each bucket was rinsed with deionized water after sampling. Samples were filtered, stored in polyethylene bottles, and kept frozen until chemical analyses. Conductivity and pH were measured within two hours of collection. Nitrate, sulfate, and chloride analyses were performed on a Dionex DX-100 ion chromatograph within two weeks of collection.

Dry deposition

Atmospheric dry deposition rates were calculated from the differences between ion concentrations in throughfall and concentrations in bulk precipitation. The intervals over which dry deposition rates were calculated were measured as the time passed since a previous precipitation event greater than 0.5mm. The rates calculated for summer 1998 were converted to annual rates for comparison with other experimental forests. It was assumed that the ions were completely washed off after events greater than 0.5mm. Leaching or uptake of NO_3^-, SO_4^{2-} and Cl^- by the canopy was assumed to be small relative to the dry deposition inputs.

Dry deposition estimates were also obtained by a different method (Hicks,1991) approximately 6-7km south of the BRF sites at an elevation of 201m at West Point. Deposition rates were calculated by the NDDN from the product of atmospheric concentrations and modeled deposition velocities. Atmospheric concentrations of SO_2 and HNO_3 vapor and small particles were measured weekly using K_2CO_3, Nylon and Teflon air filters. The dry deposition velocities of the gases and particles were calculated as a function of meteorological parameters such as wind speed, wind direction, air

temperature, solar radiation, humidity, and surface wetness. Deposition data from the 1998 summer period was not available during the preparation of this paper. Instead, average deposition fluxes from 1984 - 1995 and 1997 were used for comparison (data from 1996 was not available).

Wet-only deposition

Wet-only precipitation chemistry was measured at West Point by the NADP. Weekly composite samples were collected in polyethylene buckets and shipped to the Illinois State Water Survey Central Analytical Laboratory (CAL) where they were analyzed for major anions and cations.

Statistical analysis

Variability of rainfall volume and ion concentrations among the three collection buckets at each site was calculated from the standard error of the mean, and expressed as the percent standard error of the mean value:

$$variability = \frac{\left(std.dev./\sqrt{n}\right)}{mean} \times 100\%$$

T-tests were performed to determine the statistical significance of differences in bulk wet and dry deposition rates at the three sites.

RESULTS

Precipitation volume and canopy interception

Total precipitation volume for all 15 events measured at BRF (16.5cm) agreed within 5% of the total precipitation volume measured at West Point (17.2cm). The total precipitation volume collected in the clearings at each site for chemical analysis was

roughly 3.7L, and ranged from 2.6-3.6 for throughfall (table 1). Water loss due to canopy interception averaged roughly 30% at the three sites, based on measurements from all of the volume collection buckets. Those values agree well with the interception amounts calculated for the three buckets used for chemical analysis at HDF and Cf sites. At the LDf site, however, the percent water loss is approximately 60% less than the average calculated with all of the buckets. The average percent water loss was generally higher for small rainfall events at all sites, and ranged from about 15% to 48% per event.

Sample variability

The average variability of the water volume in the bulk precipitation collectors was less than 4% at all sites (table 2). The average variability in ion concentrations were similar at the HDf and LDf sites, and were lowest (2-4%) for NO_3^-, and highest for Cl^- (16% average). Average variability of SO_4^{2-} concentrations in the high and low Df clearing buckets was about 5%. Sulfate and chloride variabilities in the bulk collectors at the Cf site were low (4% and 9%, respectively), however NO_3^- variability was on the order of 18%.

Variability between throughfall collection buckets was generally higher than in the clearing buckets, however, the range of variability across the three throughfall sites was lower than in the clearings. Variability in throughfall volume was roughly 7% at the three sites. Sulfate variability averaged 10% and was highest (12%) at the Cf site. Nitrate variability averaged 21% and was highest at the HDf site (28%) and lowest at the

LDf site (16%). Average variability of Cl^- (22%) was similar to that of NO_3^-, and was highest at the HDf site (27%) and lowest at the LDf site (18%).

Bulk deposition

The average amounts of bulk wet and dry deposition at the three sites are compared in figure 3. Bulk deposition is estimated from concentrations measured in the clearing buckets, and is assumed to represent precipitation inputs at each site. At the high and low elevation Df sites the amount of NO_3^-, Cl^-, SO_4^{2-} and H^+ deposited by bulk precipitation is similar. Sulfate and H^+ collected in the Df clearing buckets are also the same as at the Cf site. However, bulk deposition inputs of NO_3^- and Cl^- at the Cf site differ significantly from the high and low Df sites. Nitrate deposition in the Cf clearing buckets was only about 13% of the NO_3^- collected at the Df sites, and Cl^- deposition was roughly an order of magnitude greater.

Dry deposition

Dry deposition amounts of NO_3^-, Cl^-, and SO_4^{2-} are greater at the HDf site than at the LDf site. Dry deposition of SO_4^{2-} at the HDf site is comparable to the Cf site. Nitrate dry deposition, however, is more than an order of magnitude less at the Cf site than the HDf site, and dry deposition of Cl^- is over seven times greater.

Negative dry deposition values at the Df sites indicate that the canopy was a sink for precipitation H^+. Since dry deposited H^+ is also likely to react with leaf tissue, the differences in H^+ dry deposition at the three sites are unknown. Uptake of precipitation H^+ by the canopy is greater at the LDf site than the HDf site. However, at the Cf site dry

deposited H^+ is positive, indicating either that the Cf forest receives higher H^+ dry deposition than the Df sites, or that foliar uptake is lower.

Relative contributions of deposition pathways

Figure 4 shows the relative proportions of dry deposition and bulk precipitation inputs of NO_3^-, Cl^-, SO_4^{2-} and H^+ at each site for all nine precipitation episodes. Dry deposition inputs of the three anions were greater than bulk precipitation inputs at the HDf site than at the LDf site. The percent dry deposition of Cl^- and SO_4^{2-} (approximately 75% and 39%, respectively) were comparable at both the HDf and Cf sites, but the contribution of dry deposited NO_3^- to total NO_3^- deposition was about 12% lower at the Cf site than at the HDf site. Hydrogen uptake at the Df sites generally increased with the amount of H^+ deposition. Across the sites, the percent dry deposition of each anion varied with precipitation events, and was lowest during the high rainfall episodes that occurred on 8/17, 8/26, 9/22 and 9/27.

DISCUSSION

Sulfate deposition

Comparison of BRF and West Point rates

Sulfate dry deposition was similar at the HDf and Cf sites, and nearly an order of magnitude lower at the LDf site. The annual dry deposition rates calculated for each site are 12, 10, and 1.8 kg S/ha/yr respectively (table 3). Although the NDDN data for the same time period are not yet available for West Point, an average dry deposition rate was calculated from 13 years of data (1984-1995 and 1997). The average rate for the months

July, August and September calculated at West Point is 4.7 kg S/ha/yr, which is roughly 33% lower than the average of the two Df sites (7 kg S/ha/yr). The highest deposition rate at West Point was calculated in 1984 as 10.6 kg S/ha/yr, and the next highest was significantly lower; 5.9 kg S/ha/yr. The lowest deposition rate was 3.0 kg S/ha/yr in 1994.

The sulfate deposition rate at West Point varies considerably from year to year. It is therefore difficult to directly compare the throughfall dry deposition rate calculated for summer 1998 at BRF with the historical West Point rates. The fluxes calculated for all three BRF sites are on the same order of magnitude as the rates measured at West Point, although they are outside the range of typical rates.

Deposition rate comparison with other experimental forests

Sulfate dry deposition rates at BRF calculated from throughfall for the summer sampling period are probably an upper estimate of annual rates. This is due to increased canopy leaf area and increased S deposition during the summer growing season. At Hubbard Brook, dry deposition rates calculated for 1989 by throughfall measurements were 3.3 kg S/ha/yr (Lovett, 1991), which is roughly half the average rate calculated for the BRF Df sites. During the same year, the rate modeled by the NDDN method was 2.0 kg S/ha/yr at Hubbard Brook, and a watershed mass balance approach estimated 7.8 kg S/ha/yr. In another study (Butler, 1995), throughfall dry deposition estimates were also greater than modeled deposition at a deciduous forest of maple and oak species in Ithaca, NY, in 1992. At this site, 4.5 kg S/ha/yr was estimated by NDDN and 6.0 kgS/ha/yr by throughfall methods, which is similar to the estimates made at BRF by both methods. Among the IFS sites, Huntington forest (HF) is the most suitable for comparison with

BRF. It is a hardwood forest located in the Adirondack State Park of New York, and is comprised mainly of maple species. Average annual dry deposition S fluxes for 1986-1988 were calculated as 2.1 kg S/ha/yr based on the NDDN model at HF. Coarse particles, which are not routinely measured by NDDN, contributed about 25% to the total deposition at HF. This rate is approximately half the rate estimated for West Point. Throughfall measurements were not used to calculate dry deposition fluxes at HF.

Uncertainties in S deposition rate estimates

Sulfur dioxide deposition

Plant interactions with dry deposited SO_2 may be a significant input of S in forest ecosystems and are difficult to determine. Based on the atmospheric gas and particle concentrations measured at West Point, the total S deposition that is attributed to SO_2 gas is typically about 86% during the summer. Sulfur dioxide is highly toxic to plants, and enters freely into the open stomata. Detoxification reactions occur within the cells by both metabolic and photooxidation pathways that convert SO_2 to SO_4^{2-}. Sulfur dioxide may also be reduced and incorporated into S-containing amino acids, or converted to H_2S gas that will diffuse out of the leaf (Larcher, 1995). It is estimated that roughly 30-50% of SO_2 that is taken up by foliage is re-released as sulfate (Gay and Murphy, 1989; Lindberg and Garten, 1988) in throughfall. Puckett (1998) suggested that internal leaching rates for SO_4^{2-} in a deciduous forest doubled during the growing season due to increased physiological activity and stomatal uptake of SO_2. This process of foliar SO_2 uptake would lead to an underestimate of S deposition in throughfall measurements.

NDDN model

Hicks (1988) compared calculated deposition velocities of SO_2 at West Point and at a site located at the base of Whiteface Mountain, NY to determine the effect of mountainous terrain on deposition fluxes. He found that SO_2 deposition could be underestimated by roughly 20% in complex terrain. Since the main pathway of SO_2 deposition to a forest is through stomatal uptake, vegetation (rather than wind velocity) primarily controls SO_2 deposition rates. Sulfur dioxide deposition may also be underestimated in the NDDN model due to the methods used to integrate time series data. Weekly, rather than hourly composite measurements were used in the model calculations of dry deposition and may have lead to underestimates of up to 40% (Matt and Meyers, 1993).

Bulk precipitation collectors

Comparison of the wet deposition rate of SO_4^{2-} at BRF with the West Point wet-only collectors indicates that roughly 20% of the SO_4^{2-} in the clearing buckets could be attributed to dry deposition. In figure 5 the weekly wet deposition rates calculated for each BRF site and at the West Point NADP site are compared. During low wet deposition weeks the sulfate fluxes at BRF were on average 20% higher than NADP measurements at West Point, however, the discrepancy was greater for the high volume precipitation event that occurred on 9/22 (30mm), when SO_4^{2-} deposition was overestimated by more than a factor of two.

Nitrate dry deposition

Comparison of BRF and West Point rates

Nitrate dry deposition rates varied considerably among the sites. The calculated rates were 24, 4.1 and 2.0 kg N/ha/yr at the HDf, LDf and Cf sites, respectively. The LDf estimate agrees well with the estimate from the West Point data, however, the Cf rate is 50% lower, and the HDf rate is nearly six times greater. The highest deposition rate calculated at West Point is 5.6 kg N/ha/yr in 1984, and the lowest is 3.0 kg N/ha/yr in 1987.

Deposition rate comparison with other experimental forests

Dry deposition estimates in Ithaca, NY were 3.6 kg N/ha/yr based on the NDDN model and 3.2 kg N/ha/yr based on throughfall nitrate concentrations (Butler, 1995). Both of these rates are lower than the rates calculated for Df sites at BRF and at West Point. Ammonium contributed an additional 11 kg N/ha/yr to dry deposited N at the Ithaca site. At Hubbard Brook an entirely different approach has been used to estimate dry deposition inputs (Likens, 1995). Dry deposition was calculated from a mass balance of N where precipitation inputs (6.5 kg/ha/yr), biomass storage rates (16.7 kg N/ha/yr) and stream water output (4.0 kg N/ha/yr) were estimated. The dry deposition rate at Hubbard Brook was estimated as 14.2 kg N/ha/yr, and includes both NO_3^- and NH_4^+ deposition. At Huntington Forest, NO_3^- dry deposition rates were 3.2 kg N/ha/yr based on the NDDN model, and about 16% of the total dry N deposition was from coarse particles. Nitrogen fluxes based on throughfall were 0.3 kg N/ha/yr (Lovett, 1992). Ammonium at HF contributed an additional 0.3 kg N/ha/yr.

Uncertainties in nitrate deposition rate estimates

Foliar nitrate uptake

Uptake of nitrate within both deciduous and coniferous canopies has been observed (Lovett 1986; Lovett, 1992; Neary 1994). The very low NO_3^- concentrations measured in the throughfall at the Cf site at BRF could be explained by processes occuring on the tree surface, such as uptake by epiphytic organisms. For example, at the IFS sites foliar uptake of NO_3^- was greatest in Spruce stands where epiphytic lichens were most abundant. It was suggested that nitrogen uptake balanced organic nitrogen release. However, a strong correlation was not found. Uptake of NO_3^- by the canopy at Huntington Forest was estimated as 2.8 kg N/ha/yr. In the Ithaca forest study, Butler (1995) found that organic N in throughfall contributed 3.6 kg N/ha/yr, which was about 17% to the total N flux in dry deposition. Although several of these studies have suggested foliar processes or epiphytic organisms are responsible for the uptake of nitrate deposition, the exact mechanism by which uptake occurs is unknown.

NDDN model

Dry deposition of fine particle nitrate at West Point is dominated by HNO_3 vapor. Unlike SO_2, deposition rates of HNO_3 are affected primarily by turbulence and wind speed. Meyers (1988) suggested that HNO_3 vapor deposition could be underestimated by a factor of two due to increased wind turbulence at sites located in complex terrain. The HNO_3 deposition velocities calculated by the NDDN model at the IFS sites were generally greater at windy, high elevation sites than at low elevation sites (Lovett, 1992).

Bulk precipitation collectors

The wet deposition estimate calculated from the bulk precipitation collectors at the Df sites are nearly twice the rates calculated by the wet-only collectors at West Point. At the Cf clearing, the bulk precipitation nitrate deposition was approximately 25% of the wet-only deposition measured at West Point. The reasons behind this discrepancy are unclear. As for sulfate deposition, the difference between the BRF estimates and the West Point estimates increased for the high volume precipitation event on 9/22(figure 5), when it was on average 3.5 times greater than at West Point. Rates calculated at the Cf site were lower than the other sites for every week during the sampling period, but on 9/22 the rates at agreed within 10% of the West Point rate.

Chloride dry deposition

Deposition rates at BRF

Chloride dry deposition varied considerably between the three sites and was almost nine times higher at the Cf site than at the HDf site. The annual dry deposition rates calculated for Cl^- are 12 (HDf), 4 (LDf) and 89 (Cf) kg/ha/yr. These rates are much higher than dry deposition rates measured at other experimental forests. Dry deposition inputs of Cl^- estimated from particle collectors at the IFS sites ranged from 0.2 to 7.8 kg Cl/ha/yr, and at HF averaged 0.4 kg Cl/ha/yr. The average fraction of Cl^- deposited as coarse particles at these sites was 98% of the total. Coniferous forests in the IFS study also received higher Cl^- deposition than the deciduous forest (HF).

Bulk collectors

Chloride wet deposition based on the bulk precipitation collectors at the Cf site was roughly ten times higher than at the Df sites. This suggests that the Cf clearing buckets received significantly greater amounts of dry deposited chloride, however, the source of the Cl^- is unknown. It is possible that particles that settle on the Cf canopy at low wind speeds might be blown off when wind speeds increase, and thus increase dry deposition to the clearing buckets. In figure 5, 20% of the chloride wet deposition rate is compared to rates calculated for the other sites. Whereas the wet deposition rate based on the bulk collectors at Cf is over an order of magnitude higher than the West Point rate each week, the rates at the Df sites are on average only twice the West Point rates during low deposition weeks. During the high volume precipitation event on 9/22, the Cl^- dry deposition rate was nearly five times higher at the Df sites than at West Point.

Method improvement

Although a distinct pattern has emerged of higher dry deposition at the HDf site than at the LDf site, it is unclear whether the variability is due to differences in wind regimes at the two sites. Measurements of wind speed at the HDf and LDf sites would allow site specific comparisons of the effects of wind speed on dry deposition rates.

Imperfect placement of the collection buckets must be considered, as there were only three replicates at each site. Deposition rates were not normalized to leaf area coverage above each bucket, possibly leading to bias in the samples. In addition, the number of throughfall collection buckets used for chemical analysis should be increased to better represent the canopy cover at each site. Based on statistical analysis, Kostelnik

et al (1989) found that the number of sampling buckets required varied for each ion, and that for a 10% error at the 95% confidence level, a range from 13 (to collect NO_3^-) to 382 (to collect K^+). Sulfate required an average of 40 buckets, and Cl^- required an average of 103 buckets. Depending on the month during growing season, Puckett (1990) suggested that for a mixed hardwood forest, a range of 2-41 buckets were needed for SO_4^{2-}, 10-43 for NO_3^-, and 23-143 for Cl^-.

To decrease the error in throughfall dry deposition rate estimates that is due to using bulk, rather than wet-only collection buckets, wet-only precipitation collectors should be placed at each site. This would also allow direct comparison of wet-only precipitation chemistry at BRF and West Point to see how well the West Point data matches rainfall chemistry at BRF.

CONCLUSION

Dry deposition is a significant input pathway for NO_3^-, SO_4^{2-} and Cl^- at Black Rock forest, averaging 56%, 31% and 66% of the total deposition, respectively. The modeled rate of sulfate dry deposition at West Point agreed well with rates measured from throughfall at BRF, although the rates estimated at the two high elevation sites were about twice the rate estimate by the NDDN at West Point. The average nitrate dry deposition rate at the LDf site agreed very well with the NDDN dry deposition rate estimate (both approximately 4 kg/ha/yr) , whereas the rate estimated at the HDf site was roughly six times higher, and at the Cf site it was about half the NDDN estimate.

Chloride deposition rates calculated for all three BRF sites were unusually high compared to other experimental forests, the reasons for which are unknown.

An understanding of the assumptions and limitations involved with each method of dry deposition measurement is necessary to estimate dry deposition rates to an area. Combined approaches of throughfall collection and modeled atmospheric deposition have been relatively successful at many experimental forests, and could be used in chemical cycling studies at Black Rock Forest. Additional throughfall studies are needed to investigate the effects of wind speed on dry deposition rates, seasonal differences in dry deposition rates, and annual variability.

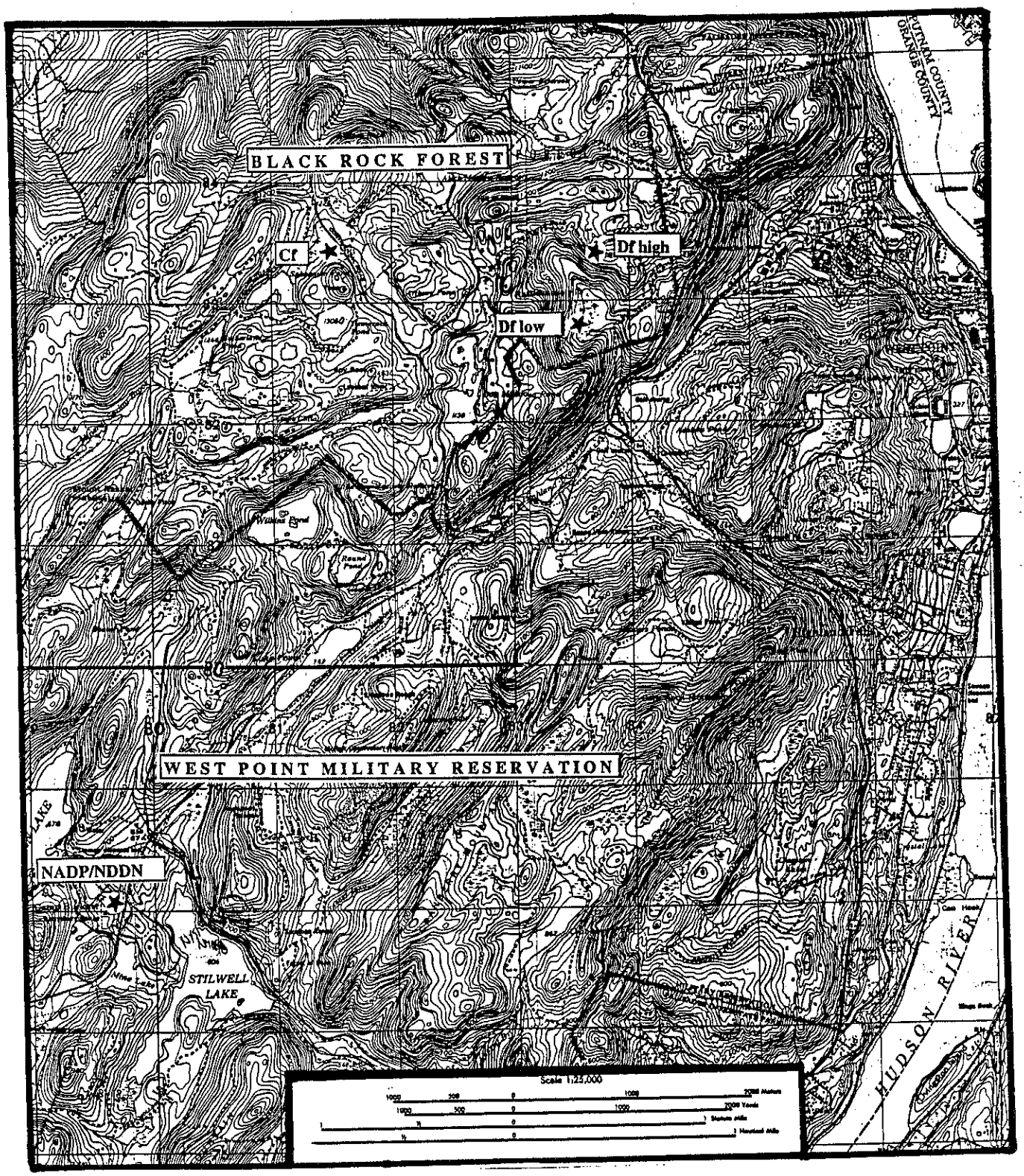

Figure 1: Location of three throughfall collection sites at BRF and the NADP and NDDN sites at West Point, NY. (Adapted from the U. S. Army Topographic Command 1970 series V821OS map, 2-TPC edition).

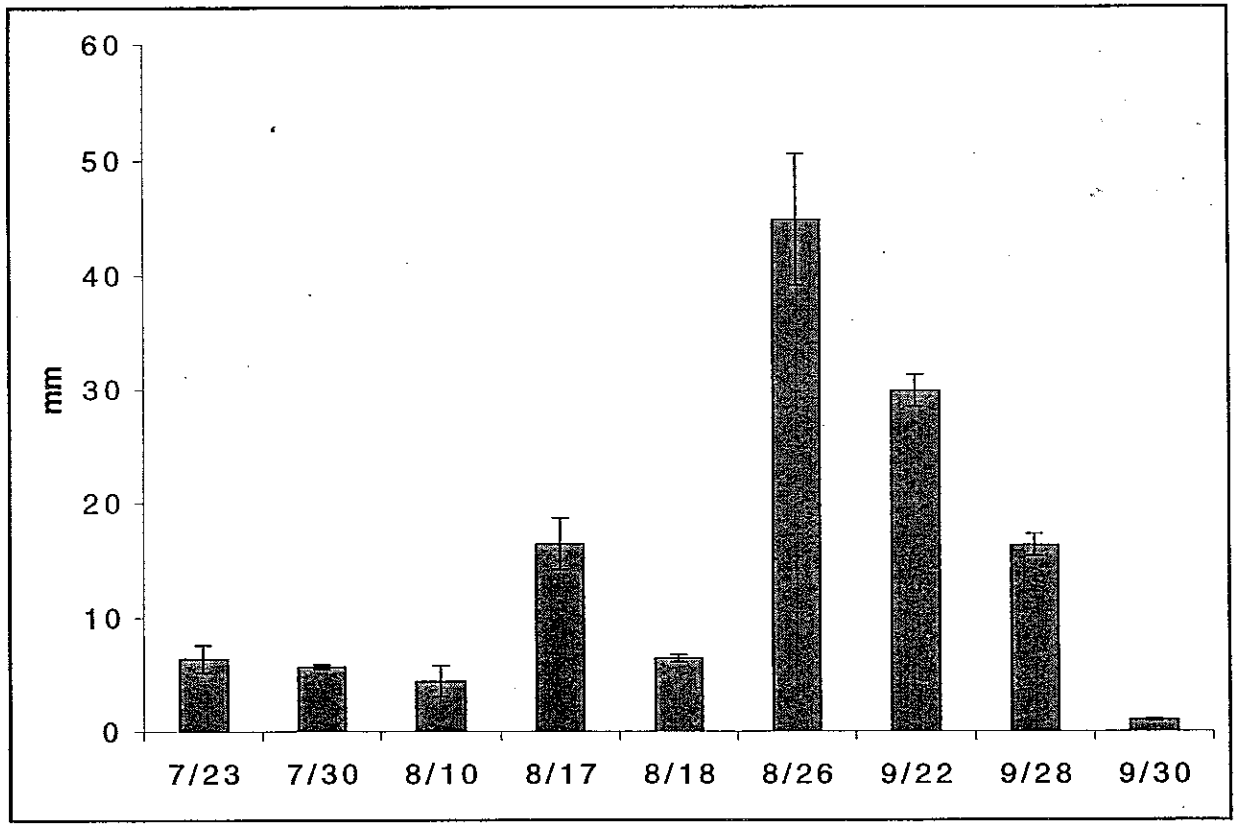

Figure 2: Rainfall amount in bulk precipitation collectors from nine events.

Table 1: Total volumes of precipitation calculated at each site during the sampling period, and average percent water loss by canopy interception. Standard errors of the means are in parentheses.

	Canopy			Clearing		
	HDf	LDf	Cf	HDf	LDf	Cf
total L	2.6	3.6	2.9	3.6	3.9	3.6
avg. % loss (3 buckets)	34(4)	11(3)	27(5)			
avg. % loss (5-10 buckets)	34(5)	27(6)	32(6)			

Table 2: Average percent variability between buckets. Percent variability is the ratio of the standard error over the mean value and is expressed as a percent.

	Canopy				Clearing			
	HDf	LDf	Cf	average	HDf	LDf	Cf	average
rain amount (5-10 buckets)	12	7	9	9	2.8	3.1	3.5	3
rain amount (3 buckets)	8	7	6	7	3.0	2.7	3.7	3
SO4	9	10	12	10	6	3	4	4
NO3	28	16	18	21	4	2	18	8
Cl	27	18	21	22	12	20	9	14

Table 3: Estimates of average wet and dry deposition rates expressed as kg/ha/yr. Standard errors of the means are in parentheses.

	NO3(N)			SO4(S)			Cl			H		
Method	HDf	LDf	Cf	HDf	LDf	Cf	HDf	LDf	Cf	HDf	LDf	Cf
dry: BRF (throughfall)	24 (7)	4.1 (0.8)	2.0 (0.7)	12 (4)	1.8 (0.5)	10 (3)	12 (4)	4 (1)	89 (31)	0.7 (0.3)	0.5 (0.2)	1.0 (0.3)
dry: West Point (modeled)		4.2 (0.2)			4.7 (0.6)							
wet: BRF (bulk collectors)	8 (3)	7 (3)	1.0 (0.4)	12 (5)	12 (5)	12 (5)	2.5 (0.7)	4 (1)	32 (13)	0.6 (0.3)	0.4 (0.3)	1.0 (0.4)
wet: West Point (NADP collectors)		4 (1)			10 (4)			1.2 (0.3)			0.6 (0.2)	

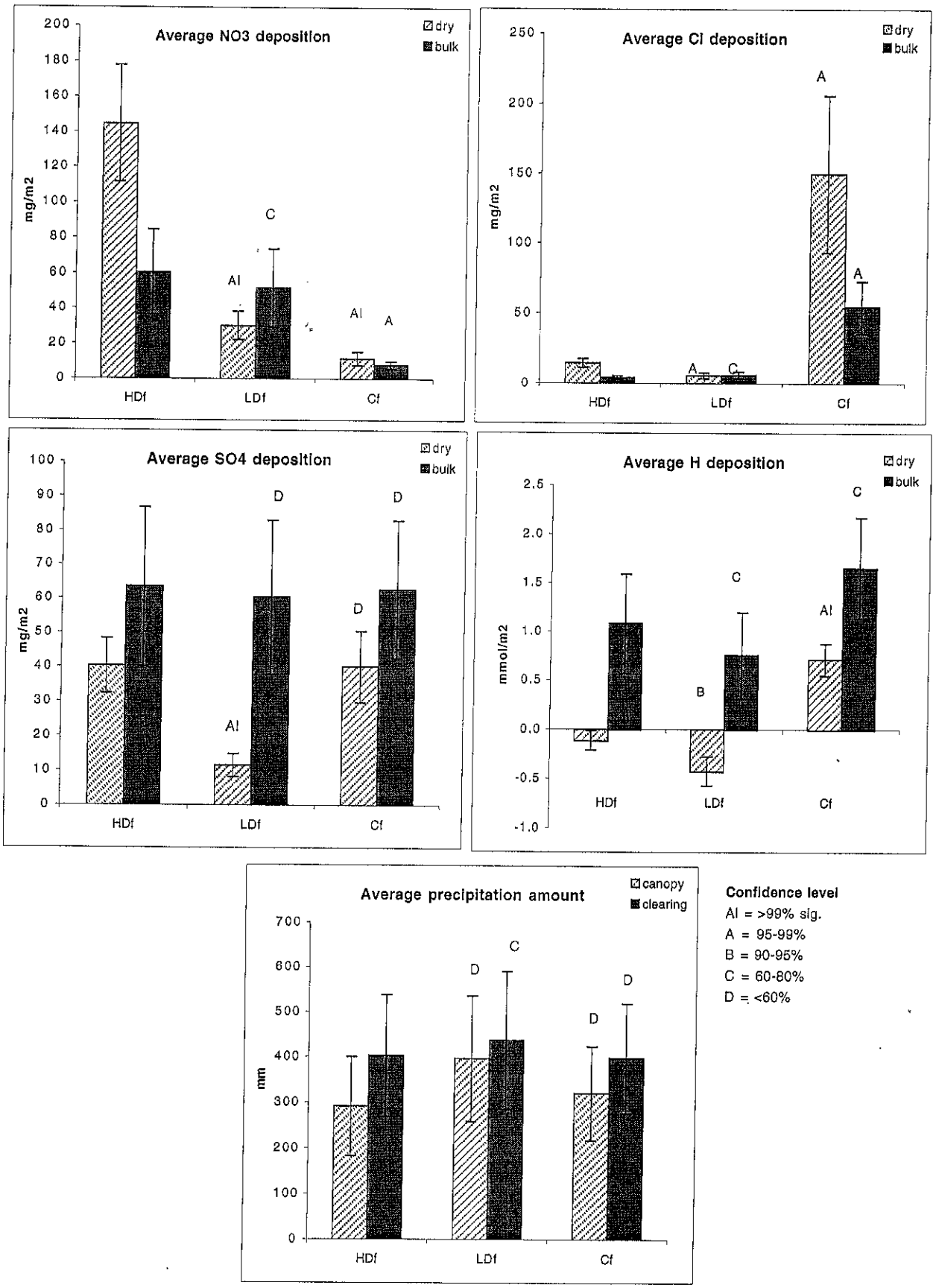

Figure 3: Average bulk and dry deposition amounts for nine events at the three sites. The confidence level of statistically significant difference is based on t-tests of each site in relation to the HDf site.

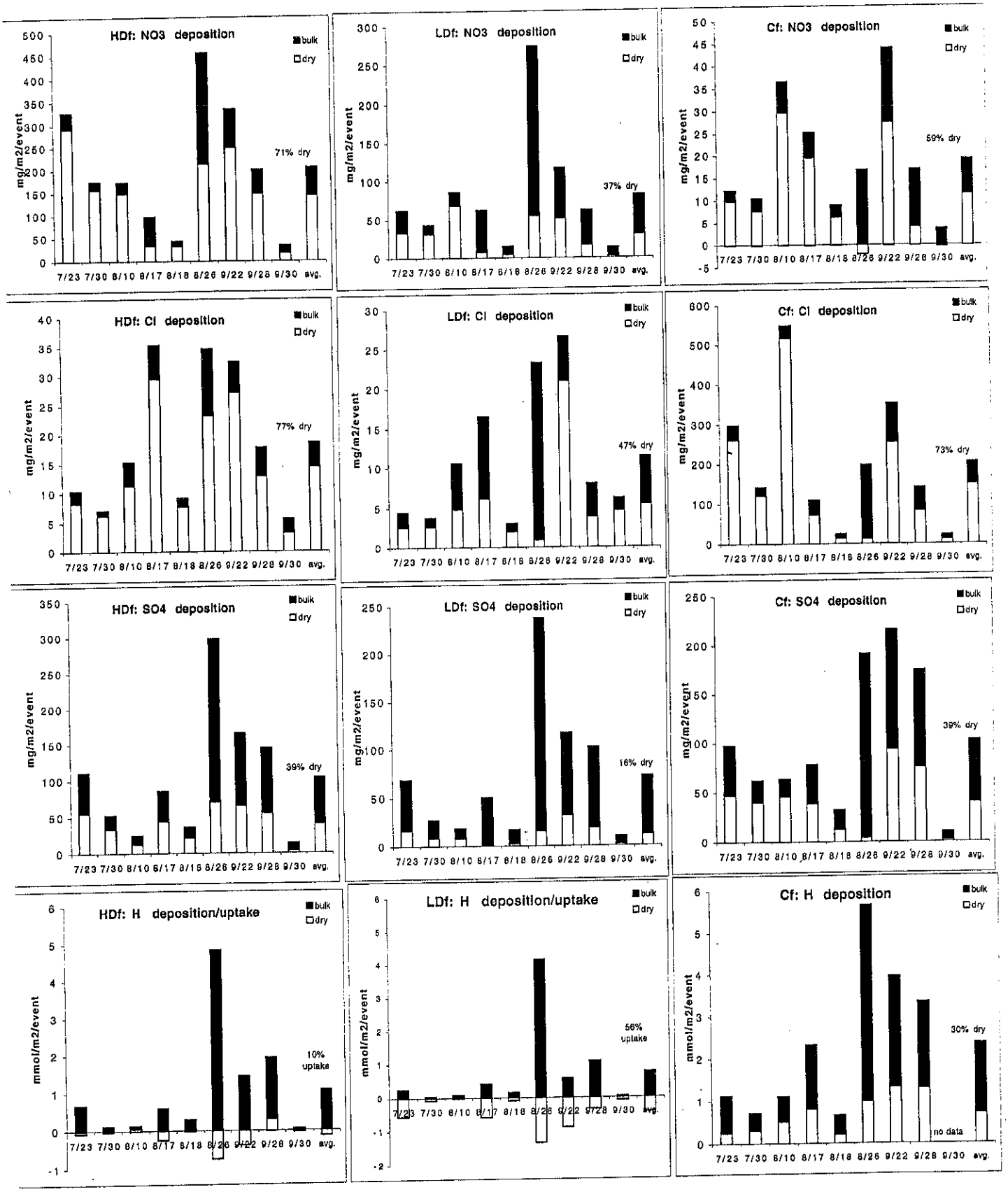

Figure 4: Proportions of dry and bulk wet depositon of SO4 , Cl , NO3 and H at each site per event. The average for all nine events and the percent dry depositon is shown in the columns at the far right .

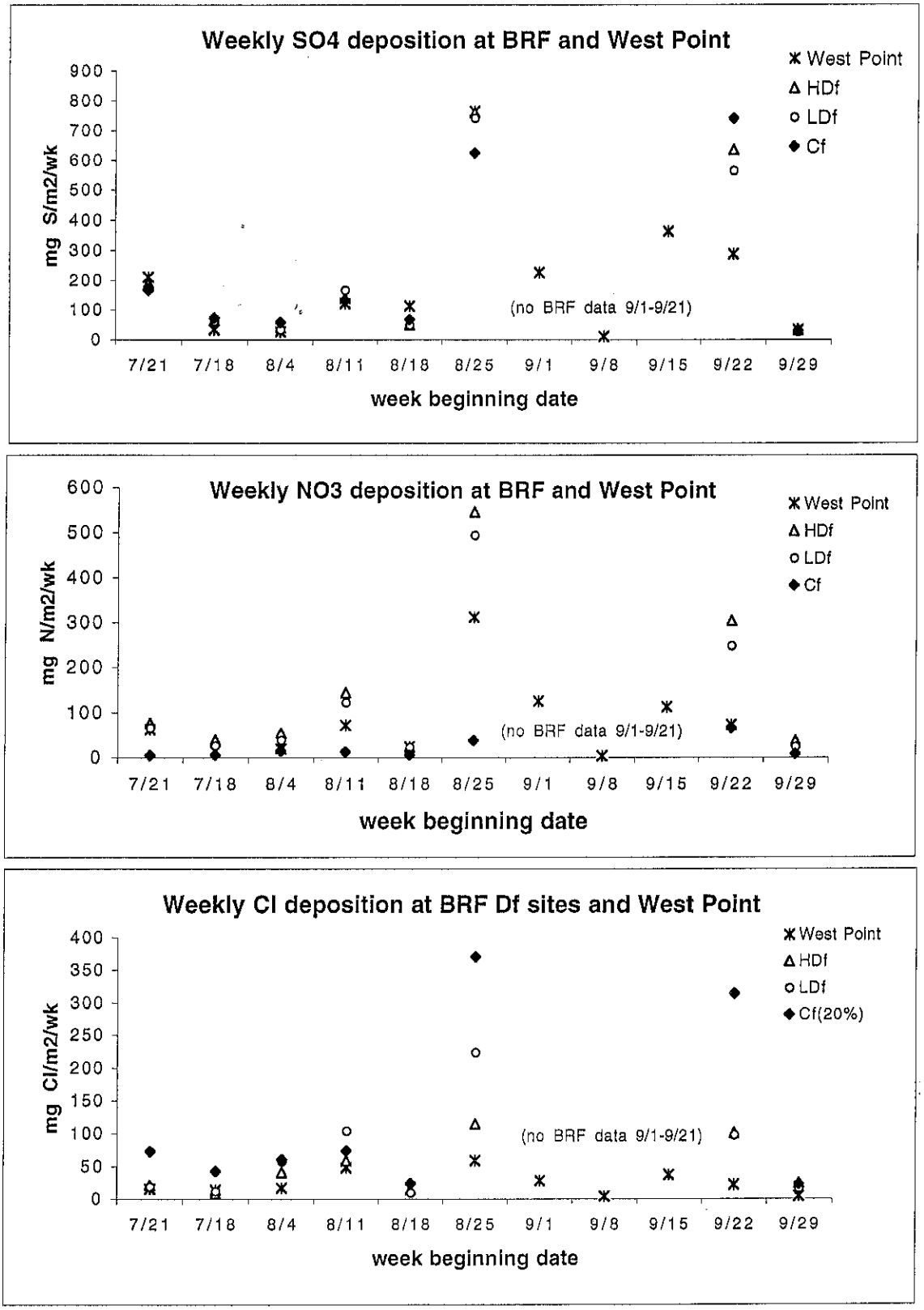

Figure 5: Comparison of weekly wet deposition rates at West Point (wet-only collectors) and BRF (bulk precipitation collectors). Chloride is plotted as 20% of the calculated deposition rate.

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