CHANGES IN FOLIAR ELEMENTS IN RED SPRUCE SEEDLINGS AFTER EXPOSURE TO SULFURIC AND NITRIC ACID MIST

J.S. JACOBSON[1], J.P. LASSOIE[2], J. OSMELOSKI[1] and K. YAMADA[1,3]
[1]Boyce Thompson Institute for Plant Research and
[2]Cornell University, Ithaca, NY USA.

ABSTRACT. Red spruce (Picea rubens Sarg.) seedlings were exposed repeatedly at a field site or in a greenhouse to acidic mist containing the major sulfur and nitrogen pollutants of wet deposition in the eastern U.S.: sulfate alone, nitrate alone or with ammonium ion, and a combination of these ions. Acidities and ion concentrations ranged from below the mean to above the maximum concentration for cloudwater in the eastern U.S. Effects on elements in current-year foliage were examined after continuous or intermittent overnight exposures to mist performed over periods of 6 to 19 weeks. Principal findings from five experiments conducted over a three-year period were that acidic mist 1) increased the foliar S and/or N content when exposures were intermittent with repeated opportunities for drying of liquid on foliage; 2) decreased foliar calcium, and/or magnesium content, especially when exposures to acidic mist were continuous rather than intermittent; and 3) gave inconsistent results for foliar iron and aluminum probably because of deposition of soil particles and contamination with metals from the mist delivery system. These results indicate that long-duration exposures to cloudwater with pH below 3 may alter foliar nutrient composition and change relationships between N, S, Ca, and Mg, with potential consequences for growth and resistance to natural stress factors.

1. INTRODUCTION

Foliar levels of elements are affected by 1) uptake from soil and atmosphere; 2) translocation to and from other tissues within the plant; and 3) loss by leaching or volatilization (van den Driessche, 1974; Miller, 1984; Johnson et al., 1985). Some non-woody plant species are highly responsive to the deposition of S and N from the atmosphere, with significant consequences for their growth and longevity (Woodin et al., 1987). High elevation forests of eastern

[3] Current address: Office of Undergraduate Admissions, University of Michigan, Ann Arbor, MI USA

Water, Air, and Soil Pollution **48**: 141–159, 1989.

North America receive unusually high rates of deposition of S and N (Scherbatskoy and Bliss, 1984; Mueller and Weatherford, 1988; Weathers et al., 1988). There is concern over the consequences of excess S (Rennenberg, 1984) and N (Aber et al., 1989) particularly for northern forests where plant growth usually is limited by N supply (Lindberg et al., 1986). Accumulation of S and N from sulfuric and nitric acids in wet deposition has been demonstrated for conifers (Westman and Temple, 1989). Depletion of K, Ca, and Mg in needles of red spruce exposed to acidic clouds has been reported (Joslin et al., 1988). However, no information is available on the influence of the acidity, S and N components of wet deposition on foliar elements in red spruce despite the well-documented decline of this species (Scott et al., 1984; Adams et al., 1985; Battles et al., In Press). The objective of this study was to determine the effects on foliar elements in red spruce produced by continuous and intermittent exposures to mist containing different acidities and concentrations of the major S and N pollutants of cloudwater and rain of the eastern U.S. Three experiments were performed to examine the effects of ions (S, N, and S/N) and acidity; one experiment examined the effects of continuous and intermittent exposures; and one experiment investigated the effects of ions, provenance, and wind during the drying period. This report is part of a larger study that included effects of acidic mist on foliar injury and shoot growth (Jacobson et al., In Press), phenology and cold tolerance (Jacobson and Lassoie, In Press).

2. MATERIALS AND METHODS

2.1. Plant Material and Culture

Availability and age of seedlings of red spruce (Picea rubens Sarg.). varied from year to year (experiment 1: 3 year old seedlings from New Hampshire; experiment 2: 2 year old seedlings from New York; experiment 3: 1 year old seedlings from Nova Scotia; experiment 4: 1 year old seedlings from New Hampshire and Nova Scotia; and experiment 5: 2 year old seedlings from Nova Scotia, New Hampshire, and Maine). When exposures to mist were initiated, seedlings were: actively growing in experiments 1, 2, and 4; at the budswell stage in experiment 3; and dormant in experiment 5. Healthy, uniform seedlings were selected and randomly assigned to treatment groups. A rain exclusion canopy prevented ambient rain and dew from contacting plants treated at the field site. Seedlings were irrigated with deionized water by hand or with an automated system. Care was taken to avoid wetting foliage during irrigation. Plastic covers were used to prevent mist or throughfall from entering the rooting media in experiments 2 through 5. Additional information on cultivation conditions have been presented elsewhere (Jacobson et al., In Press).

2.2. Exposure to Mist

Mist treatments were randomly assigned to 36 field chambers (with 4 additional chambers reserved for untreated controls) and to 8 chambers in the greenhouse. Each greenhouse chamber contained a turntable that rotated at 3 l min^{-1} to equalize mist deposition. Assignments of treatments to chambers were changed daily in the greenhouse. Exposures to mist were conducted 4 days each week (5 days in experiment 5) from late afternoon to early the next morning so that wet deposition events occurred for 12 to 35% of the total hours and 57 to 71% of the days in each experiment. The acidity and ion composition of mist varied among experiments (Table I). Water content of mist atmospheres was about 0.5 g m^{-3} for the field experiments and 0.1 g m^{-3} for the greenhouse experiments.

Mist generation was continuous in experiments 1 through 3, but intermittent in experiments 4 (1 hour on 2 hours off and 1 hour on 4 hours off) and 5 (1 hour on 4 hours off). Without fans (experiments 1 through 4), the drying time of liquid on foliage usually was about 2 hours. Fans, used in experiment 5 to increase air movement between periods of mist generation, reduced drying time to 1 hour or less. Further details concerning techniques and apparatus for generation of mist are presented elsewhere (Jacobson et al., In Press).

2.3. Sampling and Pretreatment of Foliage

Needles from lateral shoots of the upper 1st or 2nd node were sampled within three days after the final exposure to mist. Field-grown plants had terminated growth, but greenhouse-grown plants were still growing when samples were taken for analysis. Only current-year needles that expanded during the period of treatment with mist were sampled without regard to the occurrence of necrosis due to treatments. Needle samples were dried in paper bags at 80°C for 48 hours in a forced-draft oven without prior washing.

2.4. Analysis of Foliage

N determinations were performed by digestion of whole, dried needles with sulfuric acid and hydrogen peroxide (Thomas et al., 1967) and analysis with salicylate-dichloroisocyanurate reagent (Crooke and Simpson, 1971). Sulfur, phosphorus, potassium, calcium, magnesium, iron, and aluminum were analyzed by inductively-coupled argon plasma atomic emission spectroscopy (Isaac and Johnson, 1985) after ashing of whole needles in quartz test tubes in a muffle furnace at 450°C or after digestion with nitric acid-perchloric acid (for measurement of S). Insufficient tissue was available to perform S analyses in experiment 3.

2.5. Design of Experiments and Analysis of Data

Two experiments were performed in the field and three in the greenhouse in different years with different fixed factors and

TABLE I

Composition of Mist and Design of Experiments

Experiment Number	1			2			3				4	5	
Year	1986			1987			1986				1987	1988	
Location	field			field			greenhouse				greenhouse	greenhouse	
	pH of Mist												
Composition, umoles l^{-1}	2.8	3.5	4.2	2.6	3.4	4.2	3.0	3.0	4.0	4.0	2.6	2.8	2.8
Mist A. Sulfate alone	790	160	32	1260	200	32	-	-	-	-	-	790	-
Mist B. Nitrate plus	1580	320	63	3770	600	95	-	-	-	-	-	-	1580
ammonium	-	-	-	1260	200	32	-	-	-	-	-	-	-
Mist C. Sulfate plus	530	105	21	840	130	21	460	58	46	6	840	-	-
nitrate plus	530	105	21	1260	200	32	72	890	7	90	1260	-	-
ammonium	-	-	-	420	65	11	-	-	-	-	420	-	-
Experimental design	3 X 3			3 X 3			2 X 2				1 X 4	2 X 2 X 3	
Fixed effects	acidity/ions			acidity/ions			acidity/ion ratio				intermittency	wind/ions/ provenance	
Experimental units/treatment	4 chambers			4 chambers			4 racks				4 racks	4 pots	

experimental designs (Table I). Sets of seedlings not exposed to mist also were included in field and greenhouse experiments for purposes of comparison. Field experiments used a 3 X 3 arrangement of acidity and ions (S, N, and S/N). Designs of greenhouse experiments varied: experiment 3 used a 2 X 2 design with acidity and ions (S or N); experiment 4 used a 1-way design with no mist, continuous mist, and two levels of intermittency of mist; and experiment 5 used a 2 X 2 X 3 design with ions (S or N), presence or absence of wind, and provenance. Provenance by treatment interactions were not significant in experiment 4, so data from different provenances were pooled for determination of main effects. Heterogeneity of variance was checked by visual inspection of plots of treatment standard deviations against corresponding mean values. A log transformation of the data was used when necessary to eliminate heterogeneity of variance. A P-value of ≤ 0.01 was selected to indicate significance for main factors and contrasts and ≤ 0.1 for interactions in order to provide a conservative basis for conclusions.

2.6. Quality Control Tests

Mist solutions were collected in polypropylene beakers and analyzed for metallic ions to determine whether contamination occurred during passage of acidic solutions through mist nozzles and solenoid valves. One set of untreated needles was rinsed for 15 seconds in a pH 2.6 solution that was used to generate acidic mist (1:1 molar ratio of sulfate to nitrate) to determine whether elements found by foliar analysis might reside on leaf surfaces. Concentrations of foliar elements were analyzed and compared on a standard sample of red spruce needles after drying by two procedures: the standard procedure and drying for 90 minutes at 100°C followed by 46.5 hours at 70°C. Sets of needles were analyzed for elements with and without pulverization in a Wiley Mill to determine whether milling provided an extraneous source of metallic ions. Reliability of determinations of foliar elements over time was tested by analysis of subsamples of a large well-mixed sample of red spruce needles each time experimental material was submitted for analysis. National Bureau of Standards Reference Materials (Citrus SRM1572, Orchard leaves SRM1571 and Pine SRM1575) also were analyzed each time experimental materials were submitted for analysis.

3. RESULTS

3.1. Quality Control Tests

Mist solutions were enriched in Fe after passage through solenoid valves and mist nozzles. Concentrations of Fe in collected mist were highly variable and ranged from 0.1 to 2.6 ppm (mg/L) for solutions with pH values from 4.5 to 2.5, respectively. Concentrations of other metals in mist solutions were below analytical limits of detection.

TABLE II

Experiment 1. Mean Values for Foliar Elements in Needles of Red Spruce after Continuous Overnight Exposures in the Field to S and N Mist at pH 2.8, 3.5 and 4.2.

Element	Control	pH 2.8			pH 3.5			pH 4.2			P-values		
	no mist	S	N	S/N	S	N	S/N	S	N	S/N	Acid	Ion	AcXIon
N, %	2.0	2.1	1.9	2.0	1.9	2.0	2.4	2.1	2.0	1.8	0.44	0.53	0.02
S, %	0.23	0.26	0.17	0.27	0.22	0.19	0.20	0.28	0.23	0.18	0.73	0.11	0.42
P, %	0.25	0.25	0.21	0.25	0.24	0.23	0.26	0.25	0.24	0.24	0.86	0.34	0.85
K, %	1.08	0.91	0.95	0.91	0.88	0.98	1.05	0.94	0.78	0.72	0.08	0.93	0.21
Ca, %	0.59	0.47	0.41	0.47	0.49	0.43	0.48	0.50	0.48	0.50	0.61	0.51	0.99
Mg, %	0.30	0.21	0.23	0.29	0.27	0.23	0.28	0.26	0.25	0.23	0.11	0.86	0.73
Fe, ppm	157	177	225	157	169	187	215	180	246	177	0.66	0.01	0.05
Al, ppm	120	164	190	136	139	165	178	130	204	136	0.69	0.004	0.06

TABLE III

Experiment 2. Mean Values for Foliar Elements in Needles of Red Spruce after Continuous Overnight Exposures in the Field to S and N Mist at pH 2.6, 3.4, and 4.2[1].

Element	Control	pH 2.6			pH 3.4			pH 4.2			P-values		
	no mist	S	N	S/N	S	N	S/N	S	N	S/N	Acid	Ion	AcXIon
N, %	2.0	1.8	2.2	2.1	1.9	2.0	2.2	1.9	1.9	2.0	0.71	0.006	0.21
S, %	0.20	0.26	0.17	0.27	0.20	0.18	0.23	0.18	0.18	0.22	0.035	0.002	0.24
P, %	0.44	0.31	0.28	0.30	0.30	0.32	0.35	0.33	0.35	0.37	0.05	0.33	0.74
K, %	1.10	1.03	1.01	1.06	1.06	0.98	1.07	1.00	1.03	1.13	0.96	0.61	0.96
Ca, %	0.63	0.46	0.49	0.54	0.49	0.54	0.61	0.64	0.60	0.67	0.003	0.12	0.80
Mg, %	0.23	0.17	0.17	0.20	0.18	0.20	0.20	0.18	0.19	0.19	0.77	0.41	0.87
Fe, ppm	261	215	256	220	220	194	223	300	233	272	0.06	0.74	0.58
Al, ppm	245	218	238	218	221	186	214	294	227	264	0.08	0.49	0.80

1 One value for *foliar* S *in* the pH 4.2N treatment was deleted because it deviated by more than 3 standard deviations from the mean.

TABLE IV

Experiment 3. Mean Values for Foliar Elements in Red Spruce after Exposure to Mist in the Greenhouse at pH 3.0 or 4.0 with Weight Ratios of Sulfate to Nitrate of 1:10 or 10:1

Element	Control no mist	pH 3.0 1:10	pH 3.0 10:1	pH 4.0 1:10	pH 4.0 10:1	P-values Acid	P-values Ratio	P-values AcXRatio
N, %	1.1	0.99	1.1	1.1	0.95	0.63	1.0	0.18
P, %	0.23	0.23	0.22	0.21	0.24	0.87	0.77	0.50
K, %	0.74	0.81	0.59	0.63	0.74	0.13	0.58	0.89
Ca, %	0.33	0.37	0.35	0.31	0.32	0.22	1.0	0.62
Mg, %	0.20	0.20	0.21	0.14	0.21	0.23	0.10	0.20
Fe, ppm	56	85	72	43	54	0.002	0.89	0.11
Al, ppm	12	15	15	11	11	0.06	0.93	0.79

TABLE V

Experiment 4. Mean Values for Foliar Elements in Red Spruce After Continuous or Intermittent Exposures in the Greenhouse to Acidic Mist at pH 2.6

Element	Control No mist (A)	Con-tinuous (B)	Intermittent 1/2 (C)	Intermittent 1/4 (D)	P-values from contrasts A v. BCD	B v. CD	C v. D
N, %	2.9	2.8	2.9	3.2	0.84	0.01	0.007
S, %	0.19	0.29	0.29	0.32	0.0001	0.14	0.02
P, %	0.32	0.33	0.32	0.32	0.94	0.40	0.84
K, %	1.7	1.4	1.7	1.7	0.18	0.02	0.85
Ca, %	1.1	0.91	1.0	1.0	0.05	0.01	0.44
Mg, %	0.24	0.21	0.25	0.24	0.18	0.0001	0.03
Fe, ppm	108	138	151	141	0.04	0.61	0.62
Al, ppm	50	47	67	41	0.98	0.97	0.17

Washing needles with a pH 2.6 solution lowered the foliar content of Fe from 89 to 48 ppm, Al from 57 to 29 ppm, and Ca from 0.25 to 0.22%, indicating that these elements were present on foliar surfaces probably from deposition of soil particles (Al and Ca).

Concentrations of foliar elements differed by less than 5% between the two procedures for drying of needles. Pulverization of dry needles in a Wiley Mill with stainless steel blades raised the foliar content of Fe from 117 to 330 ppm and Al from 96 to 167 ppm. Consequently, needles were not pulverized prior to analysis to avoid this source of contamination.

Analyses of a standard sample of whole red spruce needles performed repeatedly over time gave coefficients of variation of 8% or less. Analyses of National Bureau of Standards Reference samples agreed closely with reported values except for Fe and Al which averaged 86% of the values reported by the National Bureau of Standards. Low recoveries of Fe and Al were obtained presumably because hydrofluoric acid was not added during wet ashing (W. Robarge, personal communication).

3.2 Nitrogen

Foliar N was significantly affected by acidic mist in 3 of 5 experiments. In experiment 1, foliar N was increased mainly by the combined sulfuric and nitric acid exposures at pH 3.5 (Table II). In experiment 2, foliar N was higher for the nitric acid (with ammonium ion) and combined nitric-sulfuric acid (with ammonium ion) exposures than for sulfuric acid alone (Table III). In experiment 4, foliar N was significantly greater for the intermittent than for the continuous mist exposures particularly when drying periods were extended (Table V). There were no significant effects on foliar N in experiment 5. However, plants treated with acidic mist generally contained less foliar N than the control no mist plants (Table VI).

3.3 Sulfur

Foliar S was significantly affected by exposure to acidic mist in 3 of 4 experiments where S was measured. In experiment 1, no statistically significant effects occurred, but there was a trend toward higher levels of foliar S with sulfuric acid mist treatments (Table II). In experiment 2, foliar S was significantly increased by exposure to sulfuric and combined sulfuric and nitric acid mist at pH 2.6 and 3.4 (Table III). In experiment 4, foliar S was significantly greater for plants treated with acidic mist than for control no mist plants. Intermittent exposures with extended drying periods gave a trend toward increased S (Table V). Foliar S was significantly increased by intermittent exposures to sulfuric acid mist especially with wind during the drying periods in experiment 5 (Table VI). In experiments 1, 2, and 5, there were indications of depletion of foliar S by exposure to nitric acid mist.

TABLE VI

Experiment 5. Mean Values for Foliar Elements in Red Spruce after Intermittent Exposures in the Greenhouse to S or N Acidic Mist at pH 2.8 with Wind or No Wind during the Drying Periods.

Element	Control	No Wind		Wind		P-values		
	no mist	S	N	S	N	Wind	Ion	WindXIon
N, %	2.4	2.1	2.1	2.2	2.1	0.20	0.67	0.34
S, %	0.18	0.25	0.13	0.39	0.12	0.0001	0.0001	0.0001
P, %	0.31	0.27	0.26	0.31	0.25	0.04	0.0001	0.001
K, %	1.3	1.2	1.0	1.3	0.9	0.80	0.0001	0.01
Ca, %	0.19	0.12	0.13	0.11	0.14	0.65	0.002	0.33
Mg, %	0.14	0.12	0.12	0.12	0.12	0.73	0.82	0.15
Fe, ppm	52	54	57	71	65	0.004	0.76	0.16
Al, ppm	48	39	38	58	38	0.002	0.0003	0.001

3.4 Phosphorus

Foliar P was significantly affected by exposure to acidic mist in 1 out of 5 experiments. In experiment 5, foliar P was reduced by nitric acid mist especially with wind during the drying periods (Table VI). Plants exposed to acidic mist contained less foliar P than control no mist plants in experiments 2 and 5 (Tables III and VI).

3.5 Potassium

Foliar K was significantly affected by exposure to acidic mist in 2 out of 5 experiments. Plants exposed to continuously to acidic mist contained less foliar K than control no mist plants in experiment 4 (Table V). In experiment 5, foliar K was reduced particularly by nitric acid mist with wind during the drying periods (Table VI).

3.6 Calcium

Foliar Ca was significantly affected in 3 out of 5 experiments. In experiment 2, increased acidity of mist decreased levels of foliar Ca (Table III). In experiment 4, continuous exposures to acidic mist reduced foliar Ca compared to intermittent treatments (Table V). In experiment 5, sulfuric acid mist reduced foliar Ca compared to nitric acid mist (Table VI). Foliar Ca was lower in plants exposed to acidic mist than in control no mist plants in experiments 1 and 5 (Tables II and VI).

3.7 Magnesium

Foliar Mg was significantly affected in 1 out of 5 experiments. In experiment 4, continuous exposures to acidic mist reduced foliar Mg compared to intermittent exposures (Table V). Foliar Mg was lower in plants exposed to acidic mist than in control no mist plants in experiments 1, 2, and 5 (Tables II, III, and VI).

3.8 Iron

Foliar Fe was significantly affected by acidic mist in 3 out of 5 experiments. In experiment 1, exposure to nitric acid mist increased foliar Fe (Table II). In experiment 3, foliar Fe was increased by higher acidity of mist (Table IV). In experiment 5, foliar Fe was increased by wind during the drying periods between exposures to acidic mist. Consistently higher foliar Fe in seedlings exposed to acidic mist than for control no mist seedlings occurred in experiments 1, 4, and 5 (Tables II, V, and VI).

3.9 Aluminum

Foliar Al was significantly affected by acidic mist in 2 out of 5 experiments. In experiment 1, foliar Al was increased by nitric acid mist except at pH 3.5 (Table II). In experiment 5, foliar Al was increased by sulfuric acid mist with wind during the drying periods (Table VI). Consistently higher foliar Al in seedlings exposed to acidic mist than for control no mist seedlings occurred in experiment 1 (Table II).

4. DISCUSSION

4.1. Accumulation of Elements from Acidic Mist

These results demonstrate that S and N pollutants in acidic mist, at concentrations that are greater than average but within the range for individual cloudwater events in the eastern U.S. (Kimball et al., 1988), can increase foliar S and N content of needles of red spruce. The specific conditions that occur during cloudwater events influence the extent to which foliar accumulation occurs. Extended periods of exposure to wet deposition with alternating wet-dry cycles increase S and N accumulation in needles. Both long-durations of wetting (Gaber and Hutchinson, 1988) and intermittent wetting and drying (Eaton and Harding, 1959) are known to increase rates of foliar penetration of solutes. Uptake of sulfate by epicuticular wax from acidic rain has been reported (Percy and Baker, 1988). The attachment, retention, and ultimate fate of S and N that are deposited on red spruce foliage from wet deposition are important questions that require further investigation. Foliar necrosis that occurs from exposure of red spruce seedlings to high sulfate, low pH mist (Jacobson et al., In Press) implies that both hydrogen ions and sulfate penetrate the cuticle.

The deposition rates of S, N, and acidity to forests of North America are highest at high elevations (Lovett et al., 1982; Kimball et al., 1988) and coastal sites (Jagels et al., In Press) where high wind speeds increase impaction of cloud and fog droplets and evaporation of water enhances the effective concentration of pollutants in liquid on foliar surfaces (Unsworth and Crossley, 1987) increasing the diffusion gradient for penetration. It is also at these locations where the greatest decline of red spruce has been observed (Scott et al., 1984; Adams et al., 1985; Battles et al., In Press). Increases in foliar accumulation of S and/or N may increase the likelihood of deficiencies of other elements such as Ca and Mg when conditions are not conducive to compensatory uptake of the latter nutrients from the soil (Zoettl and Huettl, 1986; Friedland et al., 1988).

4.2. Depletion of Foliar Elements by Acidic Mist

The results of these experiments demonstrate that repeated exposures to acidic mist can cause depletion of foliar nutrients, e.g. K, Ca, and Mg. Continuous mist events appear to be more effective than intermittent exposures with repeated wet-dry cycles for decreasing foliar content of Ca and Mg. Continuous exposures provide more total deposition of acidic mist, longer periods of wetting, and greater drainage of water from foliage. These findings are consistent with previous evidence of the importance of duration of wetting and transport of water through a canopy for removal of nutrients (McCune and Lauver, 1986).

Accelerated loss of foliar nutrients produced by exposure to pollutants in wet deposition has been suggested as a cause or contributor to decline of trees (Krause et al., 1986). Liquid on leaf surfaces and throughfall in forests are enriched in Ca, K, Mg, and other elements relative to ambient rain or cloudwater (Mengel et al., 1986; Joslin et al., 1988; Schaefer et al., 1988; Waldman and Hoffman, 1988). Accelerated loss of Ca, Mg, and K from foliage has been demonstrated after exposure of spruce to acidic pollutants in controlled experiments (Scherbatskoy and Klein, 1983). The S and N composition of wet deposition may affect loss of cations. Sulfuric acid rain removed cations from Sitka spruce more effectively than nitric acid rain (Skiba et al., 1986). With red spruce, sulfuric acid mist depleted foliage of Ca (Table VI) more than nitric acid mist while the reverse was true for depletion of P and K (Table VI).

The S and N composition of mist can affect foliar elements in another way. The toxic effects of high sulfate, low pH mist to needles of red spruce (Jacobson et al., In Press) would influence both foliar uptake and translocation of elements as well as depletion by wet deposition. Friedland et al. (1988) have provided evidence of increased foliar N and decreased Ca and Mg in red spruce from high elevation sites in the northeastern U.S.

4.3. Fe and Al in Foliage

Significant effects of acidic mist treatments on levels of foliar Fe and Al were found. However, the interpretation of these results is confounded by the occurrence of contamination from soil dust and/or the mist delivery system and the removal of surface materials by acidic mist. Extraneous sources of micro-elements must be either eliminated or accounted for in order to properly evaluate effects on foliar levels of these elements (Wyttenback et al., 1985; Krivan et al., 1987). Washing procedures that effectively remove all surface contaminants without loss of elements internal to foliar surfaces have been developed for red spruce. Dry deposition onto foliage of elements found in soil, such as Ca, Fe, and Al, remains a significant problem in the determination of concentrations of these elements accumulated by foliage (Krivan et al., 1987).

4.4 Comparison of Results Between Experiments

Foliar nutrient levels generally were in ranges considered to be satisfactory for growth of red spruce (Swan, 1971; Morrison, 1974) and above the levels reported for needles of mature forest trees (MacLean and Robertson, 1981; Friedland et al., 1987) with several exceptions. N and K were low in foliage of seedlings in experiment 3 (Table IV) and Ca and Mg were low in foliage of seedlings in experiment 5 (Table V). Fe and Al levels varied widely among experiments and were unusually low in experiments 3 and 5 for Fe (Tables IV and VI) and experiment 3 (Table IV) for Al. Zech et al. (1985) state that concentrations of S in foliage of Norway spruce above 0.12% are toxic. However, the S content of foliage of untreated red spruce seedlings in our experiments all were greater than this level (Tables II, III, V, and VI). Lord (1982) found concentrations of 0.11 to 0.22% S in foliage of red spruce in the northeastern U.S. that increased with increasing elevation.

Ammonium ions were present in mist in one field and one greenhouse experiment (experiments 2 and 4), but the influence of ammonium ions on foliar elements was not specifically studied. Elevated foliar N from exposures to acidic mist did occur in these two experiments suggesting that ammonium ions in wet deposition may make an important contribution to foliar N and unbalanced foliar nutrition (Roelofs et al., 1985).

5. SUMMARY AND CONCLUSIONS

The results of these controlled experiments indicate that high rates of wet deposition of acidity, S, and N to foliage of red spruce can increase foliar S and N and decrease Ca and Mg thereby altering nutrient relationships that may affect growth and survival. Conditions of the physical environment, namely the occurrence of wet-dry cycles and wind during the drying periods, can influence foliar levels of elements. More specific conclusions about the consequences of polluted rain and cloudwater for red spruce growing at specific locations require analysis of the 1) degree of attachment and penetration of foliar deposited S and N, 2) specific characteristics of wet-dry cycles in forests and their influence on accumulation and depletion of foliar nutrients, 3) capacity of red spruce to replenish Ca and Mg and compensate for imbalances between foliar nutrients, and 4) influence of ammonium ions in deposition on foliar nutrient relationships.

ACKNOWLEDGEMENTS

This research was supported with funds provided by the Northeastern Forest Experiment Station, Spruce-Fir Research Cooperative within the joint U.S. Environmental Protection Agency-USDA Forest Service Forest Response Program of the National Acid Precipitation Assessment Program; the Andrew W. Mellon Foundation; and the New York State Agricultural Experiment Station Regional Hatch Project NE-121. This publication has not been subject to policy review nor does it necessarily represent the policies of the supporting agencies. Important contributions to this research were made by: L. Heller, T. Bethard, M. Rutzke, K. Gerow, S. L'Hirondelle, and E. Allis.

REFERENCES

1. Aber, J.D., Nadelhoffer, K.J., Steudler, P. and Melillo, J.M. 1989. Nitrogen saturation in northern forest ecosystems. BioSci. **39**: 378-386.

2. Adams, H.S., Stephenson, S.L., Blasing, T.J. and Duvick, D.N. 1985. Growth-trend declines of spruce and fir in mid-Appalachian subalpine forests. Environ. Expt'l Botany **25**: 315-325.

3. Battles, J.J., Johnson, A.H. and Siccama, T.G. In press. Relationships between red spruce decline and forest characteristics at Whiteface Mountain, New York. In: Proceedings of the US/FRG Research Symposium: Effects of Atmospheric Pollutants on Spruce-Fir Forests in the Eastern United States and the Federal Republic of Germany. October 18-23, 1987. USDA Forest Service General Technical Report.

4. Crooke, W.M. and Simpson, W.E. 1971. Determination of ammonium in Kjeldahl digests of crops by an automated procedure. J. Sci. Food Agric. **22**: 9-10.

5. Eaton, F.M. and Harding, R.B. 1959. Foliar uptake of salt constituents of water by citrus plants during intermittent sprinkling and immersion. Plant Physiol. **34**: 22-26.

6. Friedland, A.J., Hawley, G.J. and Gregory, R.A. 1988. Red spruce (Picea rubens Sarg.) foliar chemistry in northern Vermont and New York, USA. Plant and Soil **105**: 189-193.

7. Gaber, B.A. and Hutchinson, T.C. 1988. The neutralisation of acid rain by the leaves of four boreal forest species. Can. J. Bot. **66**: 1877-1882.

8. Isaac, R.A. and Johnson, W.C. 1985. Elemental analysis of plant tissue by plasma emission spectroscopy: collaborative study. J. Assoc. Off. Anal. Chem. **68**: 499-505.

9. Jacobson, J.S. and Lassoie, J.P. In Press. Response of red spruce to sulfur- and nitrogen-containing contaminants in simulated acidic mist. In: G.D. Hertel (Tech. Coordin.) Effects of Atmospheric Pollutants on Spruce-Fir Forests of the Eastern United States and the Federal Republic of Germany. General Technical Report NE 120, USDA-Forest Service, Northeastern Forest Experiment Station, Broomall, PA. 610 pp.

10. Jacobson, J.S., Heller, L.I., Bethard, T., Osmeloski, J.F., L'Hirondelle, S., and Lassoie, J.P. In Press. Effects of sulfate, nitrate, and acidity of mist on foliar injury, shoot growth, foliar nutrients, phenology, and foliar electrolyte leakage of red spruce seedlings. In: Spruce-Fir Cooperative Winter Injury Workshop. USDA-Forest Service, Broomall, PA.

11. Jagels, R., Carlisle, J., Cronen, C., Cunningham, R.M., Gordon, G., Piatek, K.B., Serreze, S. and Stubbs, C. In press. Coastal red spruce health along an acidic fog/ozone gradient. Proc. Conference on "The Effects of Atmospheric Pollution on Spruce and Fir Forests in the Eastern United States and the Federal Republic of Germany.

12. Johnson, D.W., Richter, D.D., Lovett, G.M. and Lindberg, S.E. 1985. The effects of atmospheric deposition on potassium, calcium and magnesium cycling in two deciduous forests. Can. J. For. Res. **15**: 773-782.

13. Joslin, J.D., McDuffie, C. and Brewer, P.F. 1988. Acidic cloud water and cation loss from red spruce foliage. Water, Air, and Soil Pollut. **39**: 355-363.

14. Kimball, K.D., Jagels, R., Gordon, G.A., Weathers, K.C. and Carlisle, J. 1988. Differences between New England coastal fog and mountain cloud water density. Water, Air, and Soil Pollut. **39**: 383-393.

15. Krause, G.H.M., Jung, K.-D and Prinz, B. 1983. Forest effects in West Germany. Pp. 297-332 In: Proceedings of the Symposium on Air Pollution and the Productivity of the Forest, D.D. Davis and L. Dochinger, eds. Izaak Walton League, Washington, D.C.

16. Krause, G.H.M., Arndt, U., Brandt, C.J., Bucher, J., Kenk, G. and Matzner, E. 1986. Forest decline in Europe: possible causes and etiology. Water, Air, and Soil Pollut. **31**: 647-668.

17. Krivan, V., Schaldach, G. and Hausbeck, R. 1987. Interpretation of element analysis of spruce-needle tissue falsified by atmospheric deposition. Naturwiss. **74**: 242-245.

18. Lindberg, S.E., Lovett, G.M., Richter, D.D., and Johnson, D.W. 1986. Atmospheric deposition and canopy interactions of major ions in a forest. Science **231**: 141-145.

19. Lord, D.G. 1982. Foliar and root chemistry of declining red spruce in the Green Mountains of Vermont. Master's Thesis. University of Pennsylvania. 86 pp.

20. Lovett, G.H., Reiners, W.A. and Olson, R.K. 1982. Cloud droplet deposition in subalpine balsam fir forests: hydrological and chemical inputs. Science **218**: 1303-1304.

21. MacLean, K.S. and Robertson, R.G. 1981. Variation in the major element content of red spruce foliage with season, crown position, tree and tissue age. Commun. Soil Sci. Plant Anal. **12**: 39-49.

22. Malcolm, D.C. and Garforth, M.F. 1977. The sulphur: nitrogen ratio of conifer foliage in relation to atmospheric pollution with sulphur dioxide. Plant and Soil **47**: 89-102.

23. McCune, D.C. and Lauver, T.L. 1986. Experimental modeling of the interaction of net and dry deposition on conifers. In: Chapter 66: Aerosols. S.D. Lee, T. Schneider, L.D. Grant and P.J. Verkerk, eds. Lewis Publishers, Chelsea, MI. Pp. 871-878.

24. Mengel, K., Breininger, M.Th. and Lutz, H.J. 1986. Effect of acid fog on nutrient leaching and needle condition of Picea abies. pp. 25-33. In: Direct Effects of Dry and Wet Deposition on Forest Ecosystems - In Particular Canopy Interactions. Air Pollution Research Report 4. Commission of the European Communities. 300 pp.

25. Miller, H.G. 1984. Deposition-plant-soil interactions. Phil. Trans. R. Soc. Lond. **B305**: 339-352.

26. Mueller, S.F. and Weatherford, F.P. 1988. Chemical deposition to a high elevation red spruce forest. Water, Air, and Soil Pollution **38**: 345-363.

27. Morrison, I.K. 1974. Mineral nutrition of conifers with special reference to nutrient status interpretation: a review of literature. Canadian Forest Service Publ. No. 1343. 74 pages.

28. Percy, K.E. and Baker, E.A. 1988. Effects of simulated acid rain on leaf wettability, rain retention, and uptake of some inorganic ions. New Phytol. **108**: 75-82.

29. Rennenberg, H. 1984. The fate of excess sulfur in higher plants. Ann. Rev. Plant Physiol. **35**: 121-153.

30. Roelofs, J.G.M., Kempers, A.J., Houdijk, A.L.F.M. and Jansen, J. 1985. The effect of air-borne ammonium sulphate on Pinus nigra var. maritima in the Netherlands. Plant and Soil **84**: 45-56.

31. Schaefer, D.A., Reiners, W.A. and Olson, R.K. 1988. Factors controlling tree chemical alteration of throughfall in a subalpine Balsam fir canopy. Envir. Exper. Bot. **28**: 175-189.

32. Scherbatskoy, T. and Bliss, M. 1984. Occurrence of acidic rain and cloud water in high elevation ecosystems in the Green Mountains of Vermont. Pp. 449-463. In: The Meteorology of Acid Deposition. P.J. Samson, Ed. Air Pollution Control Assoc., Pittsburgh.

33. Scherbatskoy, T. and Klein, R.M. 1983. Response of spruce and birch foliage to leaching by acidic mists. J. Environ. Qual. **12**: 189-195.

34. Scott, J.T., Siccama, T.G., Johnson, A.H. and Breisch, A.R. 1984. Decline of red spruce in the Adirondacks, New York. Bull. Torrey Bot. Club **111**: 438-444.

35. Skiba, U., Peirson-Smith, T.J., and Cresser, M.S. 1986. Effects of simulated precipitation acidified with sulphuric and/or nitric acid on the throughfall chemistry of Sitka spruce _Picea sitchensis_ and heather _Calluna vulgaris_. Environ. Pollut. (Ser. B) **11**: 255-270.

36. Swan, H.S.D. 1971. Relationships between nutrient supply and nutrient concentrations in the foliage of white and red spruce. Woodlands Report WR/134. Pulp and Paper Res. Inst. of Canada. 27 page.

37. Thomas, R.L., Sheard, R.W., and Moyer, J.R. 1967. Comparison of conventional and automated procedures for nitrogen, phosphorous, and potassium analysis of plant material using a single digestion. Agron. J. **59**: 240-243.

38. Unsworth, M.H. and Crossley, A. 1987. Consequences of cloud water deposition on vegetation at high elevation. pp. 171-188. _In_: Effects of Atmospheric Pollutants on Forests, Wetlands and Agricultural Ecosystems. T.C. Hutchinson and K.M. Meema, eds. Springer-Verlag, Berlin.

39. van den Driessche, R. 1974. Prediction of mineral nutrient status of trees by foliar analysis. Bot. Rev. **40**: 347-394.

40. Verdouw, H., van Echteld, C.J.A. and Dekkers, E.M.J. 1977. Water Research **12**: 399-402.

41. Waldman, J.M. and Hoffman, M.R. 1988. Nutrient leaching from pine needles impacted by acidic cloudwater. Water, Air and Soil Pollut. **37**: 193-201.

42. Weathers, K.C., Likens, G.E., Bormann, F.H., Bicknell, S.H., Bormann, B.T., Daube, B.C. Jr., Eaton, J.S., Galloway, J.N., Keene, W.C., Kimball, K.D., McDowell, W.H., Siccama, T.G., Smiley, D. and Tarrant, R.A. 1988. Cloudwater chemistry from ten sites in North America. Environ. Sci. Technol. **22**: 1018-1026.

43. Westman, W.E. and Temple, P.J. 1989. Acid mist and ozone effects on the leaf chemistry of two western conifer species. Environ. Pollut. **57**: 9-26.

44. Woodin, S.J., Studholme, C.U. and Lee, J.A. 1987. Effects of acid deposition on peatlands. pp. 554-561. In: Acid Rain: Scientific and Technical Advances. R. Perry, R.M. Harrison, J.N.B. Bell and J.N. Lester, eds. Selper Ltd., London. 821 pps.

45. Wyttenback, A., Bajo, S., Tobler, L. and Keller. 1985. Major and trace element concentrations in needles of Picea abies: levels, distribution functions, correlations and environmental influences. Plant and Soil **85**: 313-325.

46. Zech, W., Suttner, T.L. and Popp, E. 1985. Elemental analysis and physiological responses of forest trees in SO_2-polluted areas of NE Bavaria. Water, Air, and Soil Pollut. **25**: 175-183.

47. Zoettl, H.W. and Huettl, R.F. 1986. Nutrient supply and forest decline in southwest-Germany. Water, Air, and Soil Pollut. **31**: 449-462.

(Received May 30, 1989; revised August 22, 1989)