ELEMENTAL CONCENTRATIONS IN FOLIAGE OF RED MAPLE, RED OAK, AND WHITE OAK IN RELATION TO ATMOSPHERIC DEPOSITION IN PENNSYLVANIA

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Abstract: Foliage was sampled in June and late August-early September in 1988 and 1989 from the outer crowns of codominant red maple (*Acer rubrum* L.), northern red oak (*Quercus rubra* L.), and white oak (*Q. alba* L.) trees in forest stands along an atmospheric deposition gradient in north-central Pennsylvania. Leaf samples from approximately 480 trees were analyzed for concentration of macroelements N, P, K, Ca, Mg, and S, as well as microelements Al, B, Cu, Fe, Mn, Mo, Na, Pb, Si, Sr, V and Zn. Foliar concentrations of Fe, S, and Sr were generally greater in the high deposition portion of the gradient. Concentrations of other foliar elements generally were not related to the spatial pattern of atmospheric input.

INTRODUCTION

Concentrations of specific elements (e.g. sulfur and trace elements) in plant tissue have been used to indicate the magnitude of atmospheric pollutant input to forest ecosystems. Several studies have been conducted in the oak forests of Pennsylvania USA which indicate that certain elements accumulate in plant tissues subjected to elevated pollution levels. For example, the sulfur content of tree foliage in woodlands of western Pennsylvania was related to distance and direction from a complex of large coal-fired power plants (Hutnik and others, 1989). Strontium concentrations of white oak (*Quercus alba* L.) xylem in a mixed-oak forest of central Pennsylvania were related to distance from a small coal-fired power plant (Long and Davis, 1989). In addition to these point-source studies, Lynch (1990) documented the existence of an atmospheric deposition gradient in north-central Pennsylvania based on precipitation monitoring conducted since 1982. He reported that pH, sulfate, nitrate, ammonium, and calcium ions in precipitation generally followed a west-to-east pattern of decreasing concentrations. The westernmost part of this forested gradient receives high sulfate loadings, as well as some of the most acidic rainfall in the USA (Figs. 1, 2). Lynch (1990) reported that wet $SO4^{=}$ deposition varied from 38 Kg.ha-1.yr-1 in study area 1 in the west to 30 Kg.ha-1.yr-1 in study area 4 in the east. Likewise, wet $NO3^{-}$ deposition varied from 23 to 20 Kg.ha-1.yr-1 across this gradient, and mean annual precipitation pH varied from 4.07 to 4.14. Historical seasonal mean temperatures have not varied significantly across the region of this study (Kingsley, 1985), but annual precipitation varies from 109.2 cm.yr-1 in study area 1 to 96.5 in study area 4 (Davis and others, 1990). Physiographic and soil factors along the gradient have been characterized (McClenahen and Long, 1993), but have not been analyzed with respect to atmospheric deposition. Variation in heavy metal burdens within vegetation may also occur along this gradient, as evidenced by Showman and Long (1990) who reported that concentrations of Al, Cr, Cu, and Fe in lichen thalli were significantly greater in the western, more polluted part of this deposition gradient.

A multi-disciplinary research project was initiated in 1986 to examine forest health along this deposition gradient (Davis and others, 1990). Using a rigorous statistical procedure, Long and others (1991) identified 13 ecologically analogous forest stands, clustered in four distinct "core areas" on the gradient (Fig. 1). These core areas served as focal points for a series of multi-faceted studies. At or near these four core areas, elemental analyses were conducted on samples of rainfall, soils, and plant tissue collected from both the herb-layer and canopy-layer. This report deals

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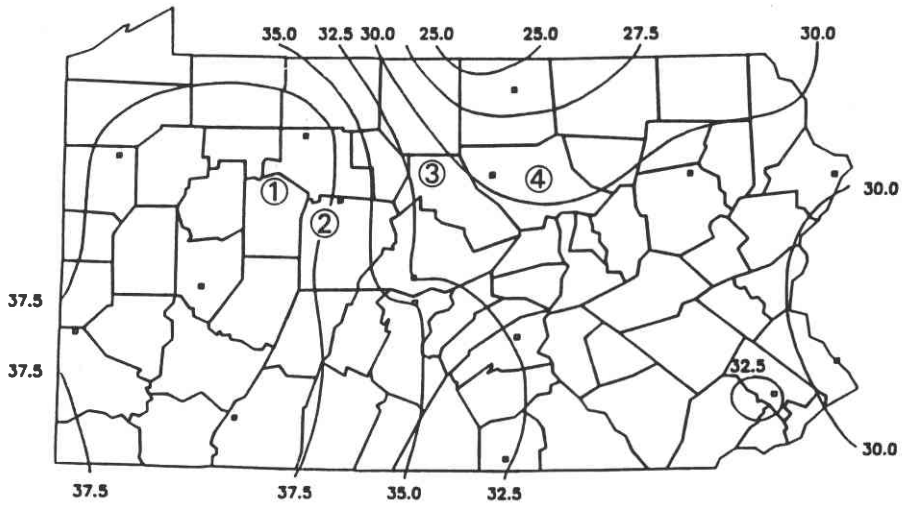

Figure 1. Spatial distribution of multiannual wet sulfate ion deposition (kg/ha) in Pennsylvania from 1982 - 1988. Numbers 1 - 4 indicate approximate location of the four core areas which served as focal points for the Pennsylvania Deposition Gradient research. The small squares represent atmospheric monitoring locations (Lynch, 1990).

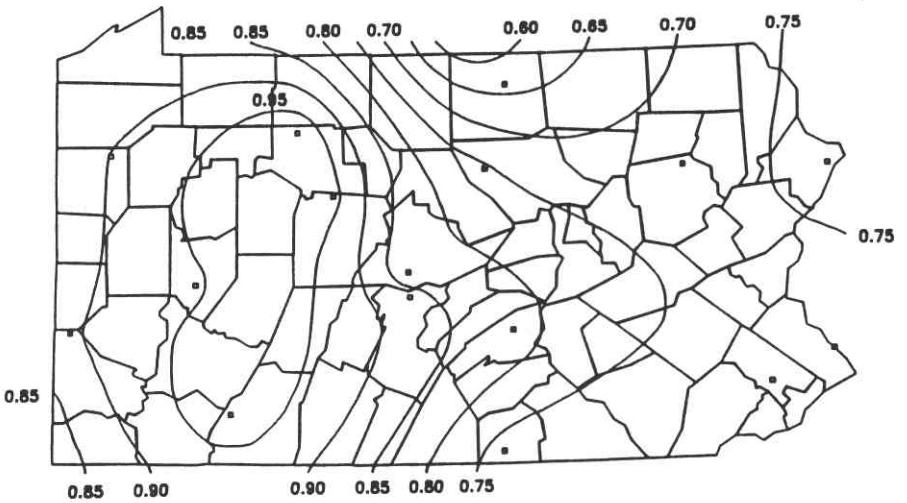

Figure 2. Spatial distribution of multiannual mean wet hydrogen ion deposition (kg/ha) in Pennsylvania from 1982 - 1988 (Lynch, 1990).

with the elemental content of the canopy-layer foliage of three native tree species. The primary objective of this study was to determine if elemental concentrations of foliage differ between the western and eastern forest stands receiving different levels of atmospheric deposition loadings. A secondary objective was to establish a database which would allow interpretation of future trends in changing elemental concentrations in forest tree foliage subjected to anthropogenic inputs.

METHODS

Four ecologically analogous forest stands, one per core area (Fig. 1), were sampled in 1988 and 1989. For this paper, "stand number" and "core area number" are identical. Ten dominant or co-dominant northern red oaks, white oak, and red maple trees growing within each stand were randomly located and tagged. Ten trees per species were tagged in all areas except in the easternmost stand, where 10 red maples, 9 red oaks and 8 white oaks were located in 1988; 10, 10, and 7 trees of each species, respectively, were tagged in stand 4 in 1989. Ten trees per species were not always present because the number of oak trees in each stand was restricted due to the number of individual trees being utilized in previously established research plots. These restrictions resulted in a total of 117 trees sampled in the four areas in each of the two years. Two samplings were conducted per year . Due to personnel constraints and inclement weather, sampling could not be done on the same dates each year. In 1988 the trees were sampled during June 21-30 and August 30 - September 2. In 1989 a different set of trees were sampled during June 27 - July 10 and August 21-25. The location of each sample tree relative to other sample trees, as well as height, and diameter of each sample tree was recorded.

Four 1-m long branches (one branch per cardinal direction) were cut from the outer canopy of each tree by a climber positioned within the crown. On the ground, excised branches were placed in plastic bags for transport to the laboratory, where 30 leaves per branch were randomly selected and removed. Leaves were not washed in order to retain external contaminants entrapped as dry (or wet) deposition. Foliage from each tree was air dried, composited per tree, ground, and sent to Micro-Macro International (Athens, GA 30607) for determination of the macroelements N, P, K, Ca, Mg, and S, as well as microelements Al, B, Cu, Fe, Mn, Mo, Na, Pb, Si, Sr, V and Zn.. Total N was analyzed using Kjeldahl digestion with generated ammonium determined by automated colorimetry. Sulfur content was determined using a LECO (LECO Corp., St. Louis, MO) sulfur analyzer. Concentrations of remaining elements were determined using dry ashing of tissue with remaining ash dissolved in dilute aqua regia, and assayed by inductively coupled plasma (ICP) emission spectrometry.

The general approach to the statistical analysis was based on results of on-going, intensive atmospheric deposition monitoring and lichen studies. The historical deposition trends (Fig. 1) are based on regional network data from Pennsylvania and adjacent states. However, intensive monitoring conducted during this study at approximately 16-km intervals along the east-west gradient revealed that depositon values at study areas 1 and 2, characterized by greater pollutant deposition loadings, were similar and were different from those monitored at 3 and 4, which in turn were similar to each other (Lynch, 1990). In complementary studies, Showman and Long (1992) concluded that lichen richness values did not form a continuum along the deposition gradient, but rather separated into two distinct groups. The lichen communities growing in study areas 1 and 2 were significantly less rich compared to those communities in study areas 3 and 4, and had significantly greater concentrations of Al, Cr, Cu, and Fe in their thalli.

Therefore, we calculated a mean concentration for each element per tree species within study areas 1 and 2, as well as within study areas 3 and 4. Significant differences between the mean concentration per element for the two areas were then tested. A GLM (Ray, 1982) analysis of variance was conducted separately for each element, tree species, and year of sampling using a factorial design, with sampling "month" (two levels = June and August-September samplings) and location (two levels = "Low" and "High" deposition portions of the gradient) as factors. Mean separation tests (Scheffe) were conducted if main effects were significant and if significant month x location interactions did not occur. Results from the two sampling times per year were combined and presented as annual means. Significance tests were conducted at $p < 0.05$.

RESULTS AND DISCUSSION

Although considerable variation existed in the data, foliar Fe, S and Sr concentrations were often directly related to the atmospheric deposition pattern, especially in red oak and red maple (Table 1). These three elements likely are emitted from the numerous anthropogenic sources such as coal-fired power plants or heavy industries located upwind in the Ohio River Valley, other states west of Pennsylvania and/or in southwestern Pennsylvania. Atmospheric S from these sources may enter Pennsylvania as gaseous sulfur dioxide (Fig. 3), or in the case of long-range transport, as sulfate. Trace metals, especially heavy metals, are most commonly associated with fine particles in contaminated atmospheres (Smith, 1981). Prevailing southwesterly winds during the growing season carry these industrial pollutants to the northeast, until they reach the front of the Allegheny Plateau in western Pennsylvania. As the pollutant-laden air masses rise up the plateau, Fe, S, and Sr are transferred from the atmosphere to the forest ecosystem through absorption by vegetation and soils as wet or dry deposition, with the greatest pollutant loadings occurring in forest stands located in the western end of the gradient (Lynch, 1990).

The use of increased foliar sulfur as a marker for delineating general polluted areas supports previous findings in Pennsylvania (Hutnik and others, 1989), in southeastern Ontario (Linzon and others, 1979), and Minnesota (Krupa and others, 1980). However, these cited studies were all conducted near point sources such as coal-fired power plants or smelters. Shriner and others (1980) reported that 82% of the sulfate deposited in Tennessee forest ecosystems, distant from point sources, was dissolved in rainfall, whereas only 18% occurred as dry particulate fallout. Similarly, it is likely that the majority of S input into the Pennsylvania forests occurs as wet sulfate, with lesser amounts occurring as gaseous sulfur dioxide. Whatever the form of deposited S, the primary available form of S in the soil solution is the sulfate anion, most of which is found in the subsoil (Jones and others, 1991). In our study, the sulfate-S of the B1 and B2 soil horizons were fairly uniform across the gradient (Davis and others, 1990). This would indicate that the greater S content of foliage in the western end of the gradient may have been due to greater foliar adsorption or absorption of wet or dry deposition.

Heavy metals are deposited in rainfall (Lindberg, 1982) but were not measured by Lynch and co-workers in precipitation sampling conducted across the study area. Likewise, Fe and Sr content of soils along the gradient were not measured. The elevated concentrations of Fe and Sr in tree foliage in the western end of the gradient could have been deposited as wet or dry deposition. Since the leaves were not washed, the Fe and Sr could have existed as particulates on the external leaf surfaces. Alternatively, soluble forms of Fe and Sr could have been directly absorbed by foliage. If deposited onto the soil, metal activity and subsequent uptake by the plant, is affected strongly by soil pH, in addition to metal equilibria among clay mineral, organic matter, hydrous oxides of Fe, Mn, Al, and soluble chelators (Adriano, 1986). Iron and Sr are more readily available in the soil solution at an acidic pH (Friedland and others, 1984). However, since the soils across the gradient were rather uniform in acidity with no east-to-west pattern (Davis and others, 1990; McClenahen and Long 1993), the ions should have been relatively available at all four stands. Soil acidity probably did not play a major role in the observed patterns of Fe, S, and Sr accumulation.

Total (Kjeldahl) N concentrations in red maple (only) foliage were significantly greater in the high deposition part of the gradient (Table 1). It has been hypothesized that elevated nitrogen inputs could promote succulent twig growth and delay hardening-off in the fall, which might lead to twig and crown dieback, and ultimately to decline (Friedland and others, 1984). We did not observe elevated twig dieback in the high deposition end of the gradient, based on observations of tree crowns (Nash and others, 1992). Perhaps the increases were not great enough to induce succulent growth. However, more detailed studies related to N accumulation and twig dieback in red maple are warranted. Alao, accumulation of N in red maple foliage may be useful as a sensitive indicator of N deposition.

The general values for elements reported herein are within the range reported in comparable studies for foliage of red and white oak (Majumdar and others, 1989) and red maple trees (Lea and others, 1980) growing in other parts of the Northeast. Thus, although the concentrations in foliage were relatively elevated in the western end of the gradient, and/or were relatively less in the eastern part of the gradient, there is no reason to suspect toxicity nor deficiency symptoms to occur in either section of the gradient. Indeed, our field observations of crowns (Nash and others,

Table 1. Concentration of elements in foliage of three species collected from the High vs Low deposition portions of the Pennsylvania gradient.

	Quercus rubra				*Quercus alba*				*Acer rubrum*			
	1988		1989		1988		1989		1988		1989	
Element	High	Low	High	Low	High	Low	High	Low	High	Low	High	Low
%												
N	2.23[a]	2.26	2.24	2.32	2.24	2.31	2.40	2.37	1.62	1.53[b]	1.66	1.54
P	0.16	0.16	0.16	0.16	0.16	0.17	0.17	0.18	0.15	0.14	0.14	0.14
K	0.85	0.84	0.75	0.72	0.77	0.82	0.71	0.71	0.71	0.75	0.62	0.55
Ca	0.39	0.44	0.46	0.43	0.43	0.55	0.41	0.53	0.37	0.37	0.37	0.34
Mg	0.08	0.09	0.11	0.10	0.10	0.10	0.11	0.09	0.09	0.09	0.09	0.08
S	0.21	0.19	0.22	0.19	0.22	0.21	0.25	0.20	0.15	0.14	0.14	0.13
ppm												
Al	52	51	44	48	42	43	42	49	34	26	24	19
B	-[c]	-	35	33	31	29	26	27	24	22	22	18
Cu	-	-	4.2	3.9	-	-	5.2	5.8	4.6	4.4	4.2	3.7
Fe	105	102	100	94	97	92	95	92	110	100	84	78
Mn	2396	2526	2240	2333	2264	2446	2184	2569	1690	1676	1565	1521
Mo	-	-	-	-	-	-	0.17[d]	0.20	-	-	0.16	0.15
Na	49	47	61	51	36	42	48	36	37	28	36	28
Pb	-	-	2.9	3.1	1.6	2.1	2.7	3.0	1.6	1.7	1.7	1.5
Si	145	132	111	112	238	259	222	252	357	358	339	278
Sr	5.1	3.8	7.6	5.4	7.0	7.1	7.9	7.8	7.6	5.9	11.7	7.2
V	0.36	0.43	0.95	0.96	0.54	0.74	0.87	0.89	0.61	0.64	0.56	0.49
Zn	18	21	27	25	13	14	18	17	17	20	23	18

[a] each mean is based on approximately 40 samples averaged across the two sampling months within a year.
[b] underline indicates a significant difference (p=.05) between mean values from "High" (core areas 1 and 2) and "Low" (core areas 3 and 4) deposition portions of the gradient.
[c] - indicates no data.
[d] significance not tested between these two means.

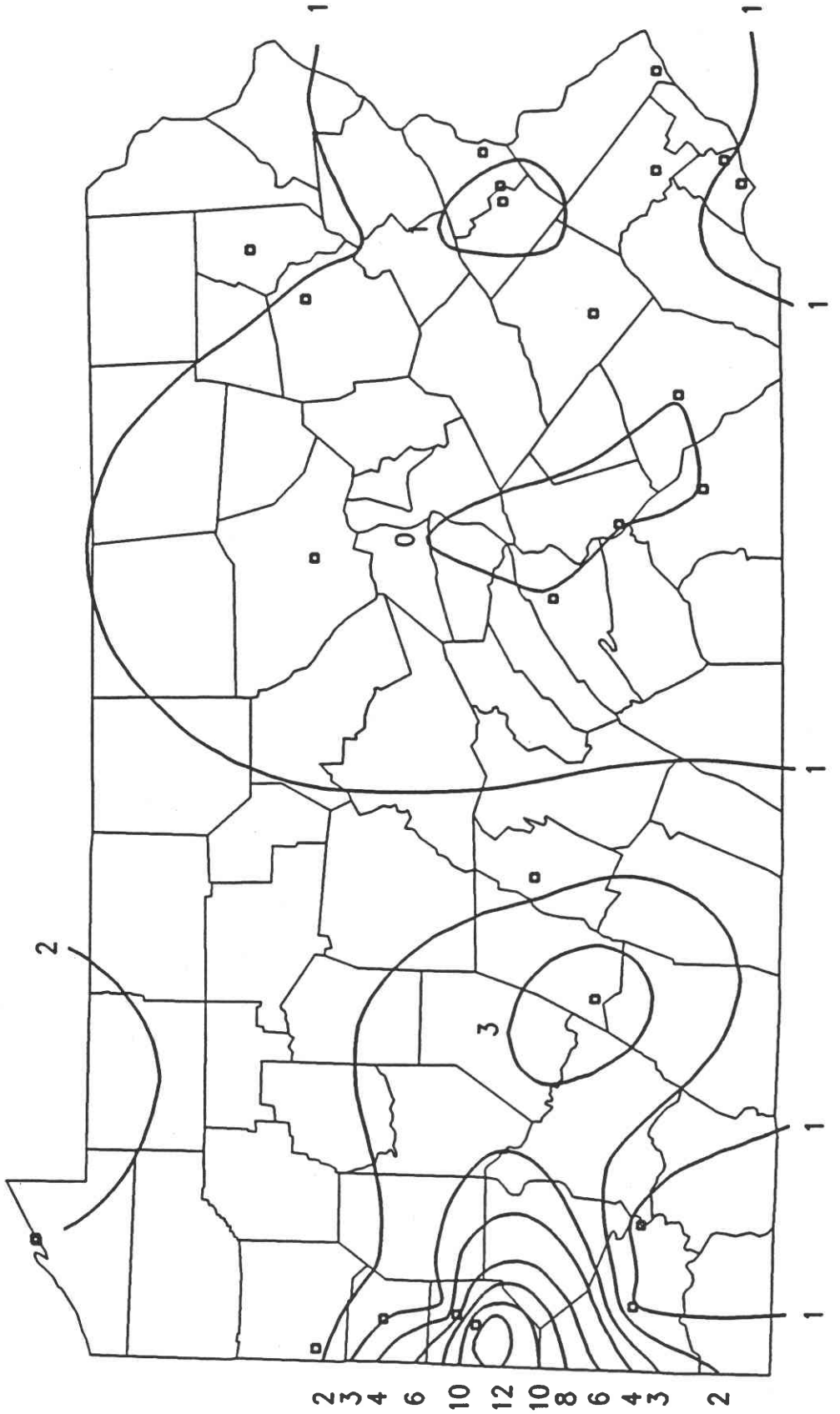

Figure 3. Percentage of hrs in 1988 that hourly-average SO2 concentrations exceeded 0.04 ppm in Pennsylvania (Data from PA Dept. Environ. Res., Bur. Air Qual. Map drawn by J. A. Lynch)

1992), as well as yet-unpublished laboratory evaluation of approximately 40,000 individual leaves indicated no apparent toxicity or deficiency symptoms.

In summary, our findings complement those of other researchers (Hutnik and others, 1989; Linzon and others, 1979; Krupa and others, 1980) who reported that S content of the foliage can be used to indicate areas affected by emissions from point sources such as coal-fired power plants and industries. Our findings extend the use of foliar S content as a marker of more widespread S or sulfate pollution. These results also complement the findings of others who reported that increased Sr content of white oak xylem (Long and Davis, 1989), sagebrush foliage (Connor and others, 1976) and grass (Wangen and Turner, 1980) as well as increased levels of Fe in grass, maple leaves, and pine needles (Klein and Russell, 1973) were increased immediately downwind from point sources such as coal-fired power plants. Since our unpublished data indicate that Fe, S, and Sr show an apparent increase during the growing season, late season collections should be utilized to ensure that concentrations of these three elements are great enough to delineate among areas of concern, and that levels are above the threshold limit for chemical analysis.

Thus, it appears that accumulations of Fe, S, and Sr may be indicative of ecosystems being subjected to atmospheric deposition originating as emissions from nearby point sources, or from pollutants which have undergone long range transport. Biological relationships between these long-term accumulations and forest health and productivity remain to be determined. In addition, the data set reported herein serves as a baseline from which future comparisons can be made as the Amended Clean Air Act goes into effect in the United States and industries reduce their emissions.

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