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Title: *Response of Balsam Fir and Red Spruce Trees to Copper and Molybdenum-rich Soils at Catheart Mountain, Somerset County, Maine*

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Response of Balsam Fir and Red Spruce Trees to Copper and Molybdenum-rich Soils at Catheart Mountain, Somerset County, Maine

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ABSTRACT

Foliage samples were collected from 26 balsam fir (*Abies balsamea* [L] Mill.) and 32 red spruce (*Picea rubens* Sarg.) growing over and adjacent to the Catheart Mountain porphyry copper-molybdenum deposit in soils that have copper and molybdenum contents ranging from 5 to 23,000 ppm and 3 to 6,000 ppm, respectively. Composite samples of the current growth of stems and needles were dried, ashed, and analyzed colorimetrically for copper and molybdenum.

A strong correlation (r = 0.94) exists between the molybdenum contents of the soil and of the plant ash for balsam fir; a range of 3-225 ppm in the ash corresponds to 3-225 ppm in the soil. Red spruce shares a positive but somewhat weaker correlation (r = 0.85) for molybdenum, but relative uptake is much less; contents of 3-150 ppm in the ash corresponds to 3-6,000 ppm in the soil. The copper content of both species (80-150 ppm in the ash), however, appears completely independent of soil copper up to a soil copper content of 2,000 ppm; beyond that level, an increase (up to 450 ppm) in plant copper was noted for fir. No data were obtained for red spruce growing in soils containing greater than 2,300 ppm copper.

Balsam fir and red spruce are common species in the forests of the northeastern United States and eastern Canada. Thus, their foliage, especially that of fir, appears to be a useful sample medium in biogeochemical surveys for molybdenum-bearing deposits, especially whenever soil sampling is not feasible or impracticable, for instance, during winter months when the ground is frozen and/or snow covered.

INTRODUCTION

Mineral exploration has been active in Maine since about 1956 and many exploration programs have utilized geochemical surveys, with soils and stream sediments being popular and useful sample media. However, in Maine, as is also true in other parts of the world, biogeochemical prospecting methods seem to be little used, although the results of one such large survey were recently published (Smith and Fournier, 1986). In the United States and Canada, the rate of use of biogeochemical methods has probably not increased greatly in the past 20 years or so, even though our knowledge of the field has certainly increased due to the publication of numerous research papers on this general topic. The reasons behind this lack of use include the impression of complexity and higher cost. The impression of complexity is partly the result of research papers that emphasize variations in metal content of various plant organs as well as seasonal variations. Vegetation normally does cost more to analyze than soils, and so soil will generally be preferred where it is an effective medium. As a result, Cameron (1986) suggested that biogeochemists must make a larger effort to tailor their product to the customer. Over 20 years ago Hornbrook (1969) suggested that research workers in biogeochemical prospecting should include an attempt to determine an application where there is no obvious competitive method. He mentions winter prospecting as a likely candidate because during that season the soil in northern areas is usually frozen and often covered with deep snow making soil sampling difficult; on the other hand, vegetation samples, except for deciduous leaves, can be collected as easily as in summer.

Winters in the northeastern United States and eastern Canada are normally cold and snowy. Mineral exploration programs conducted during this period usually do not include collection of geological materials except where rock samples are taken in drill programs. However, as pointed out by Hornbrook, a winter biogeochemical survey might be somewhat easier than a summer survey due to improved mobility coupled with the fact that working on top of a thick blanket of snow could in many areas make the branches of the larger trees more accessible. We think, therefore, that winter biogeochemical surveys in northern New England and eastern Canada should receive attention as a valuable geochemical exploration option.

The data in this paper suggest that analyzing the ash of foliage of balsam fir and red spruce trees for molybdenum would be an efficient biogeochemical method of prospecting for molybdenum-containing deposits. In vivid contrast, the data also show that the copper content of such samples is nearly independent of the copper content of the soil, and thus is of little value in searching for copper-bearing deposits.

The data used in this paper were obtained in the late sixties as part of an effort to correlate the reflectance characteristics of vegetation with concealed mineral deposits (Raines and Canney, 1980, p. 377-380). This paper was also presented orally at the 16th annual meeting of Northeastern Section of the Geological Society of America in Bangor, Maine, in April, 1981 (Canney and Nowlan, 1981). We are indebted to the landowner, Scott Paper Co., and to Noranda Exploration Co., Ltd. for access to the property and for providing data from geochemical soil surveys.

DESCRIPTION OF THE TEST SITE

The Catheart Mountain porphyry copper-molybdenum prospect was used as a test site. Catheart Mountain is a somewhat arcuate east-west trending mountain that is located in Township 4, Range 7 (Bradstreet) in Somerset County about 6 miles south southeast of Jackman, Maine (Fig. 1). It rises about 1,000 feet (305 meters) above the surrounding terrain and is heavily forested with a mixture of coniferous and deciduous species; conifers tend to predominate on the upper slopes.

The Catheart prospect, discovered in 1964, is located mostly on the southwestern flank of the mountain. It has been extensively drilled but at the present time is considered to be subeconomic both in size and grade. Incomplete assay data that have been published (Schmidt, 1974) indicate the average copper grade is probably not more than 0.25 percent and the average molybdenum grade not more than 0.05 percent. Major sulfide minerals are pyrite, chalcopyrite, and molybdenite; minor minerals include galena and sphalerite. Although traces of oxidized copper and molybdenum minerals are present in near-surface rocks, there is no well-developed zone of secondary enrichment. More complete descriptions of the deposit are given by Schmidt (1974) and Atkinson (1977).

Outcrops on the mountain are scarce due to a blanket of glacial deposits that is generally only 1 to 2 meters (3.3 - 6.5 ft) thick; data from drilling and inspection of bulldozer trenches, however, indicate that the glacial deposits are much thicker in some areas.

A well-developed podzolic soil profile is present in most areas, but is not present in areas of poor drainage. The soil horizons are variable in thickness, but the depth to the top of the C

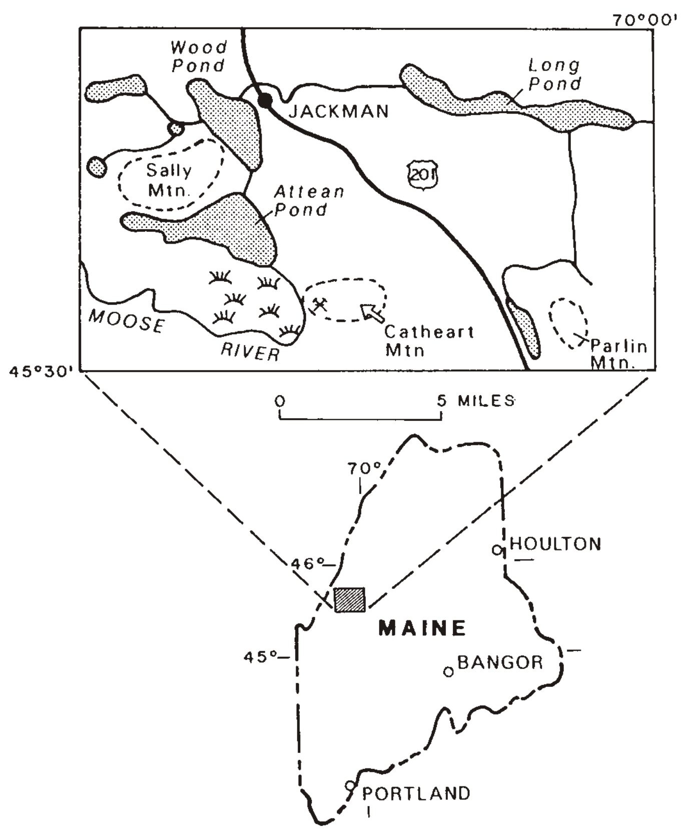

Figure 1. Location map of the Catheart Mountain copper-molybdenum deposit.

horizon is normally 30-40 cm (12-16 in.). The pH of the soil was measured at 15 sites using a slurry of soil and water, and values ranged from 3.4 to 6.7 with a median value of 4.9. In general, the more acidic values were found at sites that have excellent drainage and display very well-developed soil horizons.

Extensive geochemical soil surveys were made in the Catheart Mountain area by industrial exploration teams and the U.S. Geological Survey. In all surveys, B-zone soils, or material from the equivalent depth, were collected, sieved, and analyzed for copper and molybdenum. Data from these surveys revealed that an area in excess of 1 square mile over and adjacent to the deposit contained anomalous contents of copper and molybdenum. Copper contents ranged from 5 to 23,000 parts per million (ppm) and molybdenum contents from 3 to 6,000 ppm. In detail, the distribution patterns of these metals are erratic.

As mentioned earlier, Catheart Mountain is heavily forested and contains a variety of deciduous and coniferous trees and, in the understory, a variety of shrubs. Aerial observations of Catheart Mountain were made at different times of the year. No unusual differences were noted between that portion of the forest growing in the area of anomalous soils and that portion growing in areas containing only background contents of copper and molybdenum. Considering the rather high levels of copper and molybdenum in the soils of the Catheart Mountain site, the vegetative canopy appears healthy. Ground observations revealed that only in a very few areas where the copper content of the soil exceeds one percent are chlorotic symptoms visible.

The two species of conifers sampled in this study, red spruce (*Picea rubens* Sarg.) and balsam fir (*Abies balsamea* [L] Mill.) appear to have relatively shallow root systems based on observations of specimens of both species that have been overturned by the wind. We estimate that the bulk of the root system, especially the young absorbing roots, is in the upper 1 meter (3.3 ft) of the soil (Fig. 2). These observations tend to agree with the observations of Richards (1986), who made a study of root form and depth distribution in several biomes. Although many factors affect root system development, Richards believes that, in areas where the growing season moisture is adequate, the rooting systems will probably be shallow and that it is the upper meter (3.3 ft), or at most three meters (10 ft) of soil that the plant root system is sampling. Thus at the Catheart site, our selection of B horizon soil samples for analysis to compare with the vegetation analytical data appears to be appropriate and allows valid comparisons to be made.

Figure 2. Windblown red spruce tree at Catheart Mountain test site showing shallow root system.

COLLECTION AND ANALYSIS OF SAMPLES

Twenty-six balsam fir trees were sampled, 13 rooted in soils of background metal content and 13 growing in areas of anomalous soils. Thirty-two red spruce trees were studied, 12 growing in background areas and 20 in anomalous areas. Nineteen trees were sampled in 1968 and the remaining 39 in 1969; in both years the collections were made during the last two weeks of August. The areas of background and anomalous soils were selected after study of the geochemical-soil-survey data that were available to us. The trees selected ranged in diameter at breast height from about 6.25 cm (2.5 in) to 17.5 cm (7 in). All of the selected trees appeared to be in good health and were growing in areas of undisturbed soils. A composite sample of the foliage of each tree was collected by clipping enough of the current year's growth around its circumference to fill a 6-in. by 12-in. sample sack. In 1969, seven of the trees sampled in 1968 were resampled and analyzed; no significant differences in the two analytical data sets were noted. Because we are advocating the use of balsam fir and red spruce as sample media in biogeochemical surveys for molybdenum under winter conditions, it was necessary to test whether the anomalies found in August would also be present in the winter. Limited additional sampling was therefore done in the late winter of 1978. The group of trees sampled in 1968 could not be positively identified but the new samples were taken in areas where the soils were known to be anomalous in molybdenum. The analytical data on these samples showed molybdenum contents comparable to levels measured in 1968-69.

The entire vegetation sample was used for analysis; needles and twigs were not separated. The samples were first air dried, then pulverized, and finally ashed at 500° C in a muffle furnace. The ash contents of the samples were 3.5   0.4 (1 sd) percent for fir and 2.7   0.3 (1 sd) percent for spruce. To determine the relative amounts of twig and needle ash, needles were separated from twigs on a small group of samples and ashed separately. The results indicated that the ash samples used in the study were composed of about 75 percent needle ash and about 25 percent twig ash.

Soil samples were usually collected at each vegetation site with a soil auger. Generally, where soil conditions allowed, the sample taken was composed of four to six subsamples of B-zone soil taken from holes located around the tree at about the drip line. At a few sites, however, the rocky nature of the soil made collection with the auger impossible and it was necessary to dig holes with a shovel to locate small pockets of B-zone material. At a few sites the normal soil profile was not present and at these sites the sample was taken at the usual depth of the B-horizon. The soil samples were air dried, sieved through a 60-mesh sieve (250 micrometer opening), and the fines saved for analysis.

All samples, both plant ash and soil, were analyzed for copper and molybdenum by colorimetric procedures after a pyrosulfate fusion (Ward et al., 1963). The samples were also analyzed by a semi-quantitative emission spectrographic procedure (Grimes and Marranzino, 1968). The agreement between the copper and molybdenum contents by both the colorimetric and emission spectrographic procedures was excellent.

RESULTS AND DISCUSSION

Analyses of the soils showed, as expected, anomalous contents of copper and molybdenum in the soils overlying or close to mineralized bedrock. In some samples, extremely high values, as much as 23,000 ppm copper and 6,000 ppm molybdenum, were measured. Background values for copper in the soils were 5-20 ppm, and for molybdenum 3-8 ppm.

Over the years, in biogeochemical investigations, copper has achieved a reputation as a "difficult" element, whereas molybdenum is normally considered to be an "easy" element. A "difficult" element is considered to be one where there is little if any correlation between the content of the element in plant tissue and the content in the supporting soil. On the other hand, for "easy" elements such a correlation is good to excellent. Our data for copper and molybdenum at Catheart Mountain certainly agree with these descriptions. For both species there is no correlation whatsoever between the copper content of the ash and the copper content of the soil (Figs. 3 and 4). The copper content of the ash remains, with only a few exceptions, in the 100-160 ppm range even though soil copper increases by a factor of 400 for spruce and over 4,000 for fir. These data certainly indicate that the copper content of these species should not be used in biogeochemical surveys for copper-bearing deposits.

Both copper and molybdenum are essential elements in plant nutrition. The data in Figures 3 and 4 illustrate a rather classic response of a plant to a wide range of concentrations of an essential element in the soil, in this case, copper. The data show that both fir and spruce act as accumulator plants up to a level of about 100-120 ppm in the soil. At that level of copper content, a biological control mechanism becomes effective and both spe-

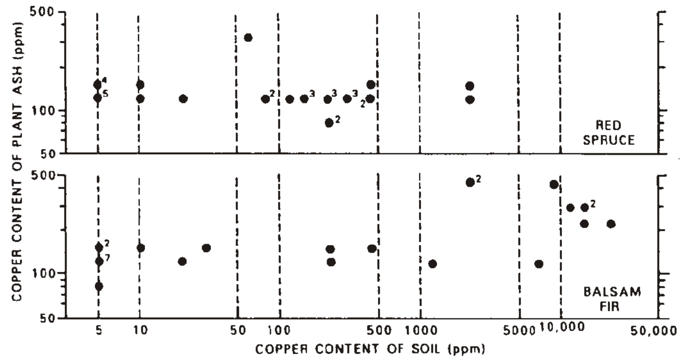

Figure 3. Relationship between the copper content of plant ash of red spruce and balsam fir and associated soils. Numeral by symbol indicates number of coincidental points.

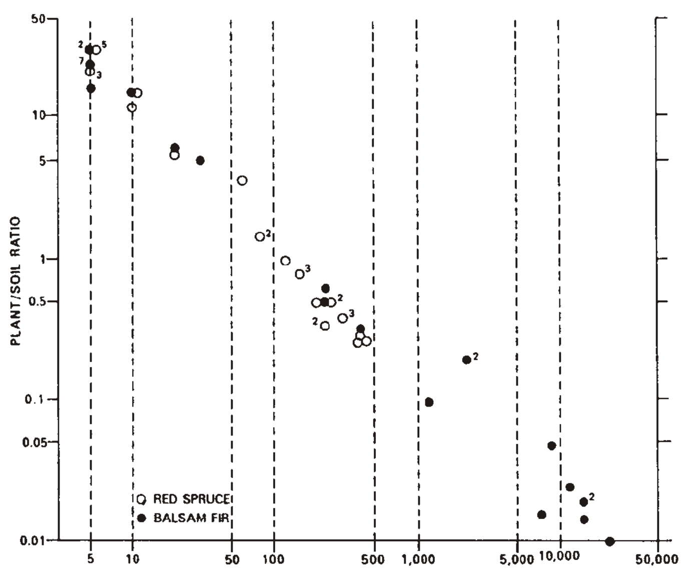

Figure 4.—Plots showing relative enrichment of copper in the plant ash of red spruce and balsam fir as a function of the copper content of associated soils. Numeral by symbol indicates number of coincidental data points. A few symbols have been shifted slightly from their true position to improve clarity.

cies become excluders. The copper content remains at that level, which is often referred to as the tolerance zone, until soil copper reaches a level of about 2,000 ppm. This concentration level for fir marks the upper limit of the tolerance zone and the beginning of the toxic zone because at this level the regulatory mechanism appears to break down as the copper content again begins to increase. Our sampling program did not locate any red spruce trees growing in soils containing more than 2,300 ppm copper, so we can not evaluate the response of spruce trees to higher soil copper contents. We do not, however, believe that this cutoff reflects the start of a lethal zone. It probably reflects the fact that red spruce trees prefer, more so than balsam fir, a well-drained soil, and the very acid character of these soils has probably resulted in, over the past 8,000-9,000 years, appreciable leaching of copper; thus the number of such soils with very high contents of copper would tend to be few.

The plots for molybdenum, for both species (Figs. 5 and 6), are strikingly different from the copper plots and they certainly confirm that, yet for two more species, molybdenum is an "easy" element. Balsam fir appears to be a near-perfect example of an ideal species to use in biogeochemical prospecting for molybdenum because there is a 1:1 correlation (r = 0.94) between soil and plant ash molybdenum contents over a concentration range of 3-225 ppm. For red spruce the correlation between soil and plant ash molybdenum is good (r = 0.85), but the relative uptake is much less than that for fir. Nevertheless, use of red spruce in biogeochemical surveys appears to be warranted. Provided that both suitable orientation studies were made in areas of known mineralization and that graphs similar to those presented in this paper were prepared, geochemical maps could be prepared in which the molybdenum content could be expressed in a uniform fashion such as "ppm soil equivalent." In the absence of suitable test sites, the data for each species would have to be analyzed separately, and means and standard deviations calculated before the two data sets could be integrated.

The tissue concentration-soil response curves for molybdenum in fir and spruce are in general accord with the data of other workers for a variety of different species (see, for example, Brooks, 1972, p. 193-199). In general the shape of the curves resembles those of the passive uptake characteristics of many non-essential elements rather than those for essential elements. For example, there is no zone of accumulation as was noted in the lower concentration ranges for copper. Brooks (1972, p. 147-148) believed that this absence may be due to the fact the physiological requirements of most plants for molybdenum is extremely low, much lower than the amounts found in most soils. Workers differ as to the toxicity of molybdenum (Carlisle and Cleveland, 1958, p. 19); some workers believe it to be completely non-toxic. Lack of toxicity would account for the absence of well-defined tolerance and toxic zones. The lower slope of the molybdenum curve for spruce (Fig. 5) might be evidence of a partial rejection mechanism, but soil pH might be the control, at least in part. Unlike copper, the availability of molybdenum to plants decreases as soil acidity increases (lower pH).

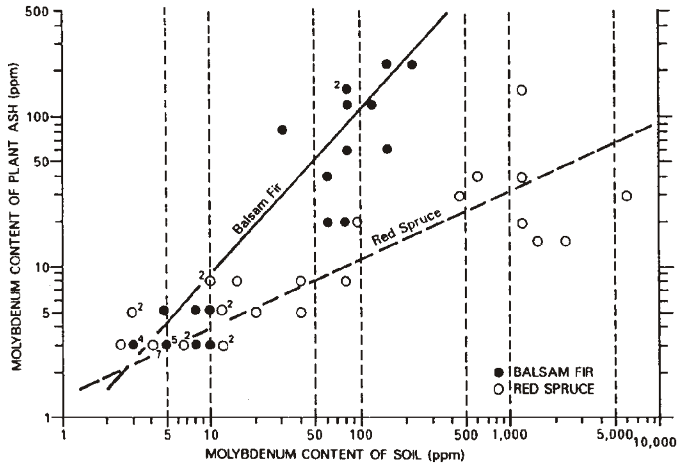

Figure 5.—Relationship between the molybdenum content of plant ash of red spruce and balsam fir as a function of the molybdenum content of associated soils. Numeral by symbol indicates number of coincidental points. Some symbols for red spruce have been shifted slightly horizontally to avoid masking by the solid symbols for balsam fir.

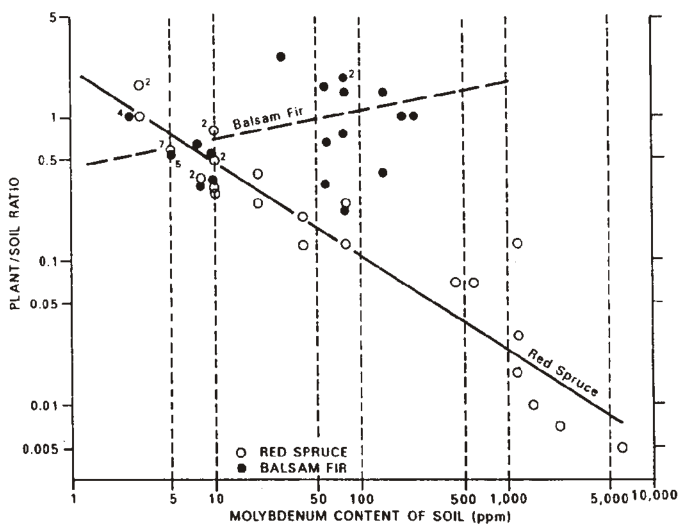

Figure 6.—Plots showing relative enrichment of molybdenum in the plant ash of red spruce and balsam fir as a function of the molybdenum content of associated soils. Numeral by a symbol indicates number of coincidental data points. A few symbols have been shifted slightly from their true position to improve clarity.

The soils containing much molybdenum are very well drained podzols and are quite acid (pH < 4.5); pH soil measurements at four of these sites revealed values of 3.4, 3.7, 4.1, and 4.4. The availability of molybdenum and its assimilation by plants would certainly be relatively less under these conditions than in soils with a higher pH. Large changes in soil pH over the area of a survey, of course, might seriously invalidate the results of a

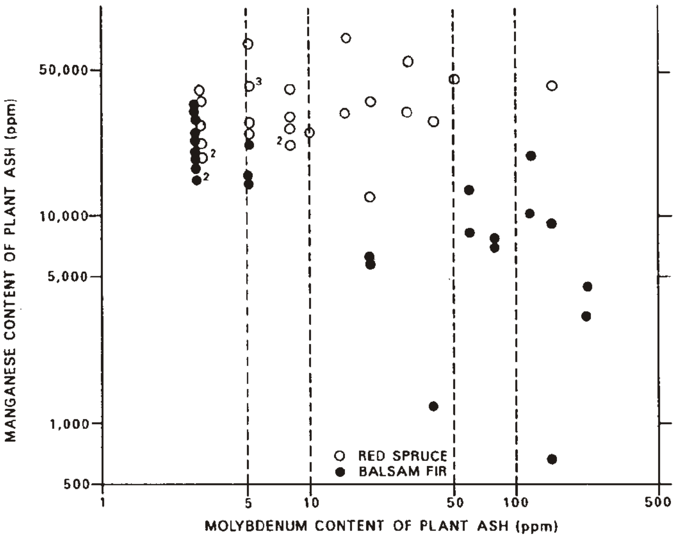

Figure 7.--Relationship between the molybdenum and manganese contents of plant ash of red spruce and balsam fir. Numeral by symbol indicates number of coincidental data points. Some symbols for balsam fir have been shifted slightly to avoid masking the open-circle symbols for red spruce.

biogeochemical survey as discussed by Brooks (1972, p. 103-106). However, we believe that in most areas and under most conditions, changes in the molybdenum content of the soil related to molybdenum mineralization would still produce a recognizable anomaly in the foliage in spite of some control by small changes in soil pH.

The data in Figure 7, at first glance, suggest that molybdenum is antagonistic to the uptake of manganese in balsam fir. Such antagonistic effects have been reported in a number of biogeochemical studies (see for example, Brooks, 1972, p. 102). We believe, however, that pH and the radically different geochemical characteristics of molybdenum and manganese may be responsible. Nearly all of the trees, both fir and spruce, are growing in soils that have very low manganese contents (<200 ppm). It is evident that most of these trees have accummulated extremely large quantities of manganese in their foliage. Only 10 samples of fir foliage ash contain <10,000 ppm. As mentioned earlier, the acidity of the soils at most sites, especially those for spruce, is quite high and therefore manganese is mostly in a soluble form that is readily absorbed by the trees; this ready absorption is reflected in the very high manganese contents in the ash of most tree samples. The 10 samples of fir that contain <10,000 ppm manganese were growing in sites that were somewhat damper than the average. Measurements of pH at two of these sites yielded values of 6.7 and 6.0. The pH at the remaining eight sites was probably similar. The manganese contents of the soils at these 10 sites were in the range of 1,000-2,000 ppm; these higher contents suggest less leaching at these higher pH values. On the other hand, molybdenum would be considerably more available to the trees at these higher pH values. Thus we believe that the apparent antagonism between molybdenum and manganese in fir is not real, but due simply to their different geochemical behaviors. An obvious conclusion that can be drawn from the above data is that, in biogeochemical surveys using copper and molybdenum, anomalies that coincide with changes in soil moisture, that is, from dry to swampy ground, should be critically evaluated.

Balsam fir and red spruce are common species in the northeastern United States and eastern Canada. In many areas, these two trees are plentiful enough so that biogeochemical surveys can be conducted using only the two species. In other areas, however, deciduous trees predominate, and conifers are either absent or too thinly scattered to use as sample media. In such areas we believe that a deciduous species can be substituted. Preliminary unpublished data for birch and maple trees, in both background and anomalous areas at the Catheart site, reveal that, like the conifers, the twigs of these deciduous species growing in anomalous soils accumulated anomalous amounts of molybdenum. The biogeochemical prospecting literature also indicates that molybdenum is absorbed by most species of plants and trees (Carlisle and Cleveland, 1958, p. 18-26) so it is probable that deciduous species other than birch and maple might also be useful sample media.

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