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The effect of copper smelter
effluents on vegetation

by

Gilles Robitaille

Thesis presented to the School of Graduate Studies
in partial fulfillment for the obtention of
the degree of Ph.D. in Biology



UNIVERSITY OF OTTAWA
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Gilles Robitaille, Ottawa, Canada, 1977

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Summary

The present analysis is a partial description of the environmental impact caused by 20 years of copper smelter emissions from the Gaspé Copper Mine smelter complex at Murdochville, Québec. The pollutants causing the observed impact on some of the biotic and abiotic components of the boreal forest ecosystem were gaseous sulphur dioxide (SO_2) and heavy metals such as Cd, Cu, Pb, and Zn.

The author has documented some of the latest literature on sulphur dioxide effects on lichens and bryophytes and as well has presented a description of the effects of heavy metals on these organisms. A review of the very limited literature on the use of annual rings of trees as a heavy metal monitor and indicator of pollution has also been presented.

The effects of the total pollution load, including both sulphur dioxide and heavy metals, on the epiphytic lichen and moss component of the boreal forest was first evaluated. This was done by producing an Index of Atmospheric Purity map (IAP) which showed the apparent zonation of air quality, that is, gradients of air pollution, based on the sensitivity of epiphytic lichens and mosses to pollutants. Areas close to the smelter had poor air quality (low IAP values), low numbers of epiphytes and low frequency-coverage values. These areas corresponded to high levels of ambient sulphur dioxide concentrations, to high levels of heavy metals in the stemflow of Abies balsamea and to areas of increased

acidity of both incident rainwater and stemflow.

Heavy metal accumulation by Picea mariana, Clintonia borealis, Hylocomium splendens, Pleurozium schreberi, Hypogymnia physodes and Parmelia squarrosa was greatest in regions closer to the smelter, that is in areas of low IAP, than farther away. In general, both the lichens and mosses accumulated more heavy metals than did the vascular plants.

Epiphytic lichens transplanted from a non polluted area into areas of heavy, medium, low and background pollution levels reacted predictably to the pollution loads. Decreased thallus adhesion, degree of isidial development, Trebouxia cell size and number of dividing cells and increased numbers of dead and plasmolyzed algal cells occurred in P. squarrosa thalli at increased pollution levels. Spectrophotometric analysis showed that increasing amounts of chlorophyll were lost by algal cells in lichen thalli of both transplanted P. squarrosa and naturally occurring P. squarrosa and H. physodes as pollution concentrations increased.

Acid rain occurred in the study area and this was attributed to an input of sulphur dioxide gas to the atmosphere. This acid rain engendered changes in the epiphyte substratum, that is the bark, such that the buffer capacity of the bark of Abies balsamea increased and decreased respectively; furthermore, a parallel decrease in the pH of the lichen thalli of H. physodes and P. squarrosa

was observed. It was suggested that these changes increased the proportion of toxic bisulphite and heavy metal dissolved in the stemflow bathing the lichen thalli and that this contributed to the paucity of epiphytic lichens and mosses in the area close to the copper smelter. The fact that some of the chlorophyll in these epiphytes was converted to phaeophytin and that a sharp decrease in the chlorophyll content also corresponded to an abrupt increase in the heavy metal content in the lichen thalli may support this suggestion.

A method to indicate when the pollution loading started in the study area was also tested. The heavy metal accumulation pattern in the annual rings of A. balsamea was examined as was the variation in the widths of the annual rings. It was noted that increased amounts of heavy metals in the rings corresponded with the year that the smelter operations began. Further, a concomitant decrease in the widths of the rings occurred at the polluted sites. Anomalies in these observations were explained.

It was concluded that the effects of the pollutant input on the biotic and abiotic components studied were real.

Résumé

Dans ce travail l'auteur essaie de décrire et de mettre en évidence les dégâts causés à l'environnement, surtout à la végétation, par une fonderie située au coeur de la Gaspésie. Plusieurs facteurs contribuent à appauvrir l'écosystème de cette région: l'anhydride sulfureux (SO_2) et des métaux lourds, tels Cd, Cu, Pb et Zn.

Nous avons d'abord essayé de faire une revue aussi complète que possible des publications récentes où l'on traite de l'influence de l'anhydride sulfureux sur les mousses et les lichens. Nous pensons également avoir revu toute la littérature où il est question de métaux lourds et de leur importance dans l'écologie des mousses et des lichens. Enfin nous avons résumé tout ce que nous avons pu trouver dans les publications modernes touchant la possibilité d'employer des méthodes dendrologiques, surtout les rayons annuels des arbres, pour analyser l'influence à long terme de la pollution dans la région de Murdochville.

Dans notre travail expérimental nous avons d'abord étudié l'impact total de l'ensemble de la pollution, y compris l'anhydride sulfureux et les métaux lourds, sur la végétation lichénique et muscinale de la forêt boréale. A cet effet nous avons d'abord déterminé un indice de pureté atmosphérique (IAP) pour un grand nombre de stations que nous avons alors groupées en un certain nombre de zones. Ce travail a pour base la sensibilité connue des mousses et des lichens à toute forme de pollution. Les stations

situées près de la source de pollution avaient toutes des indices faibles, possédaient très peu d'espèces épiphytiques et, lorsque présentes, ces dernières avaient un faible quotient de fréquence et de couverture. Ces stations formaient une zone où l'anhydride sulfureux était très élevé et où le pourcentage des métaux lourds était excessif, surtout dans l'eau d'écoulement (stemflow) des arbres étudiées (Abies balsamea). De plus, l'eau de pluie de la région et l'eau d'écoulement sur le tronc des arbres avaient une acidité très forte.

L'accumulation des métaux lourds par Picea mariana, Clintonia borealis, Hylocomium splendens, Pleurozium schreberi, Hypogymnia physodes and Parmelia squarrosa était toujours très élevée dans les stations près des fonderies, c'est-à-dire dans ces stations où les IAP étaient faibles. L'inverse se produit pour les stations éloignées de la fonderie et où les IAP sont très élevés. De façon générale, on remarque que les lichens et les mousses accumulent dans leurs thalles une plus grande quantité de métaux lourds que les plantes vasculaires.

Nous avons transplanté à différents endroits autour de la fonderie des morceaux d'écorce provenant d'une région non polluée et sur lesquels vivaient des mousses et des lichens. Après un certain nombre de mois les lichens placés près de la source de pollution mourraient ou montraient des signes de dégénérescence tels: un thalle qui n'adhérait presque plus à l'écorce, des isidies qui se désagrégaient,

des changements chimiques dans le chloroplaste de l'algue symbiote, etc. Les lichens transplantés assez loin de la source de pollution survécurent et même montraient un léger degré de croissance.

Nous avons remarqué que l'eau de pluie ainsi que l'eau d'écoulement le long des troncs d'arbres étaient très acides dans cette région et nous attribuons cela à la grande quantité d'anhydride sulfureux dégagée par la fonderie. Comme conséquence de cette eau acide, l'écorce de l'arbre, i.e. le substratum des lichens, subit des transformations importantes dans son pouvoir tampon et cela affecte directement la végétation épiphytique.

Nous avons également étudié le nombre et l'épaisseur des anneaux annuels de Abies balsamea et nous avons constaté une corrélation directe entre ces deux paramètres et l'année où la fonderie est entrée en fonction active.

Nous pouvons donc conclure que la fonderie de Murdochville a eu une influence néfaste sur la végétation forestière de la région en général et sur la végétation épiphytique en particulier.

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CHAPTER I

INTRODUCTION

A. Statement of Problem and Goal.

A copper smelter has been in operation since 1955 in the interior of the Gaspé Peninsula, Province of Québec, Canada. Besides discharging gaseous sulphur dioxide into the atmosphere the effluents from the smelter also contain numerous metals such as: Ag, Al, As, Au, Bi, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb, S, Sn and Zn. These pollutants are toxic to vegetation if present in excessive amounts. Although this effluent polluted the surrounding ecosystem and until 1972 the impact of this pollution on the surrounding region had not been determined.

The goal of this dissertation is to describe the environmental impact caused by pollutant loading from a copper smelter on certain abiotic and biotic components of the ecosystem.

The project was first initiated by the Gaspé Copper Mines Ltd. in May 1972 and was to have lasted for a period of one year. The contracted work specified that a survey of the current status of the environment be made, the choice of methodology being left to the contractee. In the autumn of 1972 permission was granted to the author by the Gaspé Copper Mines Ltd. authorities to expand the project as desired and to use it as the basis for a doctoral dissertation.

B. What is Air Pollution?

As used in this thesis air pollution is the presence of foreign matter (either gaseous or particulate or combinations of both) in the air which can alter certain abiotic components of the environment and be harmful to biota. This definition includes not only the direct effects of air pollution on vegetation, but also the effects which alter or damage inanimate matter essential for plant growth and reproduction. Air pollution is mostly a man made phenomenon. It would not exist if it were not for the sequence source-transport-receptor. If any one of these were missing, vegetation (or any other living or non living matter), would not be affected by pollution.

The major source of pollution in the study area at Murdochville is industrial and originates from the smelter of the Gaspé Copper Mine and from the dust of the solid waste disposal areas (tailing ponds) 6.3 km SE of the smelter.

In 1970, about 26 million tons of pollutants were **released into the atmosphere by industrial sources. This mass of pollution** represents from 0.25 to 3% of the industrial material being processed at a specific plant location (Rose 1970). Industrial sources represent the most diversified type of pollution emissions.

Air quality varies from one location to another depending on: 1) meteorological conditions, 2) geographical location, 3) industrial proximity, and 4) pollution type.

Most man made pollutants have a short life in the atmosphere and remain there for only a few hours or at most for a few weeks unless, of course, there is a constant input of pollutant. Pollutants do, however, concentrate in living tissues and are held in it (this is the concept of vegetation as a pollutant sink) until tissue death occurs or until an efficient excretion mechanism is developed.

The atmospheric transport of pollutants from the source (copper smelter) to receptor (vegetation) depends on several factors. The meteorological variables which affect the severity of an air pollution problem at a given time and location are: wind, insolation, lapse rate (temperature variation with height), mixing depth and precipitation.

Both horizontal and vertical movement of wind dissipate pollutants in the atmosphere and determine the pattern of pollutant dispersion. Precipitation can wash pollutants out of the air by the natural scrubbing action of rain and snow depositing them on the ground and vegetation. Gases that are soluble in water (SO_2) are removed by absorption by the water droplets. Particulate matter (metals) is removed by adsorption on the surface of droplets after they are impacted by the precipitation. Not only can precipitation affect atmospheric pollution, but the pollution can affect the precipitation both in the quantity that falls due to seeding action (Peterson 1969) and in its quality (becoming acid) (Likens 1976).

The atmosphere is the aerial dump for air pollution.

It can, however, purify itself up to a point by natural sources. Atmospheric dilution occurs due to wind circulation or atmospheric turbulence caused by local sun intensity (insolation). As mentioned before, precipitation may remove pollutants from the atmosphere. Gravitational fallout and chemical and physical reactions are other mechanisms of air purification. It must be kept in mind that pollutants washed from the air often contribute to water pollution.

The non-meteorological factors of type, quantity of pollutant and topography must also be considered.

In the Murdochville area the topography is a very important factor in the distribution of pollutants. The topographic features that seriously affect local atmospheric conditions in the study area are the valleys and hills. Valley effects occur due to the channeling of winds by altering normal wind flow patterns and causing the wind to flow in the general direction of the valley axis. Slope winds occur in valleys in the evenings where the air near the ground is cooler (Geiger 1965). Cold air moving down the slopes, collects in the valleys until it becomes deep enough to flow down the valley creating what are called valley winds. Any air pollution released on the slopes or in the bottom of the valley will stay in the valley if an inversion situation also exists, under normal conditions the pollution would be transported to other areas of the valley and possibly accumulate there. The onset of the valley wind usually lags several hours after the onset of the slope

wind (Geiger 1965).

Hills can cause a varying degree of influence on air pollution dispersal. A smooth hill causes the least effect on the flow of air. Rough hills, as those common to the study area, cause turbulent eddies and good mixing which promote air pollution removal. If however a mountain is sufficiently high, it will cause the wind to deflect and flow parallel to the mountain and not over the mountain. If this occurs in conjunction with slope and valley winds, as is the case in Murdochville, high ground pollution levels may be attained. Hills may also cause a reflection effect to occur, that is the pollution is turned back upon itself resulting in an increase in the concentration of air pollution. This phenomenon has been observed quite frequently in the area close to the copper smelter.

C. Literature Review.

In recent years a number of excellent literature reviews have been published on the impact of sulphur dioxide air pollution on lichens and bryophytes (Gilbert 1973; Leblanc and Rao 1974, 1975; Nieboer et al. 1976a). The responses of all types of vegetation to air pollution have also been reviewed (Mudd and Kolowski 1975). All of these reviews treat the literature to 1974. A review dealing with metal accumulation in trees has not been found. However, Smith (1976) has assembled 156 references in his treatment of lead contamination of roadside ecosystems. The effects of heavy metals on lichens and bryophytes has not been extensively reviewed. The treatments encountered were those of James (1973) and Tuominen and Jaakkola (1973).

In the present treatise the literature on the effects of sulphur dioxide and its derivatives on lichens and bryophytes will encompass the period from late 1973 to the present. Studies dealing with metal accumulation in trees will also be reviewed. An extensive bibliography on heavy metals and lichens and bryophytes is included in the dissertation.

1. Sulphur dioxide and lichens and bryophytes.

a) Some physiological effects and effects affected by morphology.

Reports on the increasing acidity of precipitation during recent years have appeared in the literature (Likens

et al. 1972; Galloway et al. 1976; Likens 1976). However, studies of the effects of increased hydrogen ion effects on lichens and bryophytes are not numerous despite the fact that sulphur dioxide has been shown to cause a decrease in the chlorophyll content of lichens (Rao and LeBlanc 1966) and bryophytes (Coker 1967; Syrratt and Wanstall 1969).

Sheridan and Rosenstreter (1973) have examined the effects of hydrogen ion concentrations on the moss Tortula ruralis. Their simulated acid rain experiments, using sulphuric acid mist (spray) of pH 1.0 - 5.0 and a distilled water control of pH 6.0, demonstrated that the highest total chlorophyll content was found at control conditions. An increase in the acidity of the simulated rain from pH 5.0 to pH 1.0 decreased the total chlorophyll from approximately 0.8 g/g dry wt. to 0.1 g/g dry wt. This was attributed to the acid hydrolysis of chlorophyll a as indicated by the reduction in chlorophyll a:b ratio with increased acidity. A sharp decline in the rate of oxygen production on a total chlorophyll a + b basis occurred between pH 2 and pH 1 and they believe that the productivity of T. ruralis would decrease by 12% per pH unit decrease. This would certainly affect the population density of this moss.

Using a different approach Türk and Wirth (1975a) determined the influence of the hydrogen ion concentration on the sulphur dioxide exposed thalli of the lichens Hypogymnia physodes and Xanthoria parietina. These thalli were submerged in buffer solutions of pH 2 to pH 8 before

being exposed to sulphur dioxide gas. This method corresponds more closely to the actual exposure sequence that would be found under field conditions. Their results showed that the deleterious effect exerted by sulphur dioxide increased with increasing hydrogen ion concentration and that at extremely low or high pH the lichens are affected even without the presence of sulphur dioxide. This is a very important observation since it indicates that lichen thalli soaked in buffer solutions of higher pH are more resistant to sulphur dioxide than those soaked at lower pH values.

The effect of sulphite on lichen and moss photosynthesis has also been studied. Sulphite affects photosynthesis in lichens and mosses (Puckett et al. 1973a; Inglis and Hill 1974) as well as respiration (Baddeley et al. 1973). Hill (1974) observed that in Usnea sp. the rate of carbon dioxide fixation was reduced to one percent of that of the controls after 30 minutes exposure to 0.2 mM sulphite and that the effect was immediate for H. physodes. The experiments indicated however that H. physodes can recover from short term effects of sulphite on photosynthesis which is significant since H. physodes is known to be relatively tolerant to sulphur dioxide pollution (Hawksworth and Rose 1970).

Sulphur dioxide resistance of lichens has been determined by carbon dioxide exchange measurements. Türk et al. (1974) exposed 12 species of lichens to 0.5, 1.0,

2.0 and 4.0 mgSO_2/m^3 of air. The most resistant species survived a treatment of 4.0 mgSO_2/m^3 for 14 hours. On this basis the most resistant species was Xanthoria parietina followed by Parmelia scortei, P. acetabulum, Hypogymnia physodes, Parmelia saxatilis, Platismatia glauca, Lobaria pulmonaria, Parmelia stenophylla and Evernia mesomorpha. Dried lichen thalli were found to resist high sulphur dioxide levels. It was also observed that the pH of the medium played an important role in damaging the lichens. At high pH a solution of $\text{Na}_2\text{S}_2\text{O}_5$ (of the same concentration as above) caused less damage than one at low pH. The degree of dissociation of this solution was pH dependant, that is, at low pH the concentration of damaging ions was high.

Lichen resistance to sulphur dioxide is not highly correlated with growth form under laboratory conditions (Wirth and Türk 1975). Various growth form groups exposed to 4 mgSO_2/m^3 of air did not clearly show that the crustose lichen form is the most resistant or that the fruticose form is the least toxitolerant. Some crustose species such as Pertusaria corallina were found to be more sensitive than some foliose species such as Xanthoria parietina, several foliose species, for example Parmelia glabratula and Lobaria pulmonaria were less resistant than the fruticose species Alectoria fuscescens and A. pubescens. The relative resistance of the lichens would seem to be more a function of the ecological amplitude of each species and on the

degree of wetness of the lichen thalli. These observations would agree with those of Farrar (1976a, b) and Farrar and Smith (1976) in that severe wet-dry cycles are required, as compared to constant wet thalli, for the maintenance of healthy thalli. Hence wet-dry cycles or prolonged dry periods would necessarily increase the sulphur dioxide resistance of lichens.

Mosses are at least as sensitive as lichens to sulphur dioxide as shown by the field studies of Rao and LeBlanc (1967) around an iron sintering plant in Wawa, Ontario and of Nash III and Nash (1974) around a zinc factory in Palmerton, Pennsylvania. It appears that the sensitivity to sulphur dioxide damage depends on the stage of the life cycle of the moss. Nash III and Nash (1974) showed without any doubt that the protonema of Polytrichum ohioense is more sensitive than the mature moss gametophyte when these are exposed to varying concentrations of sulphur dioxide. The moss protonema died after 15 days exposure to 0.2 ppm of sulphur dioxide. On the other hand the mature gametophyte had not died after exposure to 2.0 ppm of sulphur dioxide for the same duration. The most resistant mosses were Dicranella heteromalla, Polytrichum ohioense and Pottia truncata, while the most sensitive ones were Leucobryum glaucum and Dicranum scoparium. For mosses it seems that the inhibition of reproduction (i.e. protonema) is more important in limiting the presence of mature moss gametophytes in polluted areas than the actual direct

fumigation of the mature plants. Türk and Wirth (1975b) confirmed with laboratory experiments that mosses are more sensitive to sulphur dioxide than are lichens since mosses do not seem to possess the physiological buffering mechanism of lichens (Farrar 1976b).

b) Lichens and bryophytes as sulphur dioxide gauges.

Since the publication of LeBlanc and Rao's (1975) review a number of studies on the use of lichens and mosses as sulphur dioxide gauges have appeared. Pyatt (1973) used the total sulphur content of lichen thalli and moss gametophytes and correlated this with the sulphur dioxide concentration in the air finding that plant sulphur content generally decreased with increased distance from the pollution source. Anomalies were observed in that some lichen thalli collected in exposed areas away from the pollution source contained more sulphur than thalli collected closer to the source in a more sheltered habitat. This emphasizes that care must be taken to ensure a uniformity of sampling. Olkkonen and Takala (1976) have also successfully used the total sulphur content of lichen thalli of H. physodes to denote areas polluted by sulphur dioxide.

The reproductive capabilities of lichen soredia have been used for monitoring sulphur dioxide concentrations. Margot and De Sloover (1973, 1974) described this method and have demonstrated that the reproductive potential of the soredia of H. physodes, Evernia prunastri, Parmeliopsis

ambigua and Pertusaria amara previously exposed to known concentrations of sulphur dioxide was low for high pollutant concentrations and high for lower concentrations. It would seem that the method of Margot and De Sloover could be used to determine sulphur dioxide pollution patterns in the field.

A number of mapping studies on lichen distribution patterns affected by sulphur dioxide pollution have also been published. Hoffman (1974) used a modified version of the IAP method of LeBlanc and De Sloover (1970) to map the distribution of epiphytic lichens and bryophytes growing on Robinia pseudoacacia around a paper pulp mill in Lewiston, Idaho and Clarkston, Washington. It was concluded that ecological indices such as the IAP cannot be compared inter-regionally unless IAPs are normalised.

Other mapping and distribution studies by: 1) Pisut and Lisicka-Jelinkora (1974) around an aluminium plant in Slovakia, 2) Aureau and Bedeneau (1974) in the forest of Roumare, 3) Newberry (1974) on the influence of a sulphate process paper mill on corticolous lichens in Mosinne, Wisconsin, 4) Stringer and Stringer (1974) for the city of Winnipeg, Manitoba, 5) Showman (1975) around a coal fired power generating plant in southeastern Ohio, 6) Stephenson and Merriam (1975) in the Ottawa, Ontario area for lichen communities on trees in deciduous woodlots, 7) Seaward (1975) for the west Yorkshire conurbation, 8) Henderson and Seaward (1975) for Harewood House park near Leeds U.K.,

9) Skopera and Vitt (1976) in western Alberta and 10) Bégin-Robitaille (1977) for the National Capital Region of Ottawa, Canada, all indicated that lichens and bryophytes were sensitive to sulphur dioxide pollution (or to a mixture of pollutants) and that they are absent or have a reduced cover or presence in areas close to industrial emissions or in urbanized centers.

2. Heavy metals and lichens and bryophytes.

The problem of environmental pollution by heavy metals has attracted much attention in recent years. Contamination of air with specific metals comes mostly from industrial operations involved in the production of a whole range of metallic products. The particulate matter discharged to the atmosphere in any given industrial process is not the pure metal itself but is one or more of the metallic compounds present in the ore or produced in the industrial process. In addition, widespread lead pollution originates from automobile exhaust. About 70 to 80 percent of the lead which is exhausted into the atmosphere in a particulate form, usually combined with bromine and chlorine, is small enough to remain airborne for long periods of time.

Metals are non-degradable and once released into the environment, they become an integral part of the habitat. Airborne metal particles are removed from the atmosphere by rainwater, gravitational settling and impaction on various surfaces, especially vegetation, and may also be actively or passively accumulated by plants. The concentration of airborne

elements in plants is determined by their concentration in the air, the inherent ability of plants to absorb these elements, the ratio of plant surface to total plant mass, the ion-exchange capacity of plants, and the length of time of exposure.

Studies by Rühling and Tyler (1968), Hutchinson and Whitby (1974) and others have shown that plants can be used as indicators of aerial fallout of heavy metals. Accumulation of metals by vegetation can provide a rapid estimate of the degree of contamination at a large number of sampling sites within a study area. However, such methods can only give semi-quantitative results, since some of the metal particles which make contact with the plant surface either fail to adhere and are subsequently washed off by rainfall or are removed by wind (Little and Martin 1972).

Heavy metals are phytotoxic at high concentrations. Most information regarding metal toxicity and plants is obtained from studies involving metal ore deposits, mining and smelting activities (Nash III 1972, 1975), other industrial operations and from pesticide use. Roadside and urban areas are also potentially hazardous for plants mostly because of contamination from Pb (Purves and Mackenzie 1969; Smith 1976; Hutchinson 1976; Laaksoverta et al. 1976).

Lichens and bryophytes have a great capacity for retaining metals once they have been absorbed (Lounamaa 1956; Clymo 1963; Nash III 1976) and for absorbing high levels of radioactive nuclides supplied both in precipitation

and as dry deposition (Gorham 1959; Persson 1970). Mayer and Gorham (1951) analysed the content of 19 moss species from the Lake District of England and reported that these plants accumulated between 0.005 - 0.4 percent manganese dry wt. They wrote "this group of plants shows a striking tendency to accumulate iron, the highest figure being 400 mg per 100 g dry wt". Moss gametophytes also are known to accumulate iron some 5 - 10 times more than vascular plants (Czarnowska and Rejement-Grochowska 1974). In an important work on the trace-element content of lichens, bryophytes and vascular plants growing on different rock formations in Finland, Lounamaa (1956) showed that metals occurred in greater amounts in lichens than in any other group of plants. The use of carpet forming mosses has proved to be a suitable method for measuring atmospheric deposition of heavy metals over large areas and has been used in several local and regional studies on heavy metal deposition in Scandinavia (Rühling and Tyler 1968, 1970, 1971; Tyler 1971) and in England (Goodman and Roberts 1971).

As a tool for evaluating the kind and amount of airborne pollution, epiphytes have the special advantage of having no roots or root-like organs. Shacklette (1972) and Shacklette and Connors (1973) suggested that plants with no connection with soil, such as Spanish moss, seem to be useful indicators of the relative extent of airborne cadmium pollution. However, epiphytes are not totally dependent on the atmosphere for moisture and nutrients,

since stemflow and bark may also be important pathways and reservoirs of nutrients and metals.

The growing literature on heavy metals, recently reviewed by James (1973) and Tuominen and Jaakkola (1973), shows that lichens and bryophytes are efficient absorbers of these elements. Goodman and Roberts (1971) who measured airborne heavy metals in the moss Hypnum cupressiforme in industrial areas of Wales concluded "our methods are much more rapid, inexpensive and probably more meaningful than spot sampling of air filtration...".

a) Absorption and accumulation of heavy metals.

i) Absorption affected by morphology.

Certain morphological features in plants enhance or reduce their ability to absorb and accumulate airborne metals. Direct interception by plants is regarded as one of the principal methods by which contamination occurs from fallout materials. Plant surface area and density are also important factors to be considered while evaluating fallout accumulation by plants. As lichens and bryophytes have a perennially exposed plant body, are capable of absorbing water and nutrients efficiently, and have a large surface area to weight ratio, they have an unusual capacity to concentrate airborne and water soluble materials in their tissue.

Among mosses, the profusely branched and ramifying pleurocarpous species and the densely packed acrocarpous species are generally more efficient entrappers and absorbers

of particulate materials than the unbranched and erect acrocarpous species. Huckabee (1973) found a greater accumulation of mercury in Dicranum scoparium than in Polytrichum commune and he attributed this difference to their growth forms.

Besides growth form, the surface cuticle can affect the rate of absorption and accumulation of dissolved materials. Shimwell and Laurie (1972) noted that the "ectohydric" moss Dicranella varia, which lacks cuticle and absorbs water all over its gametophytic body, shows a higher heavy metal content than that of the "myxohydric" moss Philonotis fontana which has a more or less continuous cuticle with absorption taking place mostly towards the base of the gametophyte. They also found a 25 fold increase in Zn and an 8 - 9 fold increase in Pb concentration in the older tissues of myxohydric mosses. Tamm (1953) analysed the moss Hylocomium splendens for changes in the P, K, N and Ca contents associated with the increasing life span of that plant. He observed that the monovalent elements K and Na accumulated in the young moss and then decreased in concentration, Na very quickly and K at a slower rate. The bivalent and trivalent metals showed a successive accumulation from year to year in most segments of the moss plant, with or without previous accumulation in the bud. Tamm claimed that the annual shoots of this moss were nutritionally isolated, both from each other and from the soil. Further, according to Czarnowska and Rejement-

Grochowska (1974) the mineral composition of mosses is different in the haploid from that of the diploid phase. In the moss Atrichum undulatum, they observed that the concentrations of Fe, Mn, Zn and Cu were 2,000, 97, 45 and 4.5 ppm respectively in the gametophyte (haploid) and 215, 93, 76 and 7.4 ppm in the sporophyte (diploid).

Sequential drying and wetting of a lichen thallus may play an important role in the metal accumulation in view of the fact that lichens are "ectohydric". Part of the absorbed metals may be either inside the algal cells and/or stored in the walls of the lichen hyphae. Nieboer et al. (1972) suggest that the solubilized metals can be absorbed through the surface of both thallus and the rhizinal network and therefore the capacity for metal ion accumulation is dependent on the morphology and chemistry of each lichen thallus. Hence different lichens collected from the same location can exhibit varying metal contents; for example, Umbilicaria deusta showed a particularly high metal content, perhaps because its thin thallus (when dry) provides a large surface area to dry wt. ratio as compared to other species of this genus.

ii) Absorption affected by substrate.

Bryophytes can concentrate certain elements, including the rare earths, even when they grow on substrates in which the elements are found in trace amounts.

The content of an element in bryophytes generally is related to the concentration of the element in the supporting

substrate provided the substrate contains the element in greater than normal amounts. Schacklette (1965b) analyzed 38 samples of liverworts and mosses and the substrate on which they grew for 33 elements and obtained extremely high percentages of five elements in the ash of certain bryophyte samples (Table 1). Lounamaa (1956) in his study of nine species of mosses for 15 trace elements did not observe much difference between the various species of mosses in respect to their element contents.

The heavy metal accumulation in any given lichen species can vary from substrate to substrate as is evident from the data on Lecanora muralis (Table 2). Lounamaa (1965) compared the Fe, Mn and Zn contents of certain macro-lichens growing on peat, rock and bark substrates. He observed that the epilithic lichens Cladonia alpestris, C. arbuscula and C. rangiferina contained more Fe but smaller quantities of Mn than these lichens growing on peat. However, the latter contained more Zn than the epilithic lichens. In the epiphytic lichens Evernia prunastri, Hypogymnia physodes, Platismatia glauca and Pseudoevernia furfuracea, the Fe content was lower than in the epilithic lichens. The Zn content was higher than their Mn content. Both Mn and Zn were lower in epiphytic lichens than in the bark to which these were attached, but the Fe content was higher in the lichen than that of the bark substratum.

Table 1. Metal content in certain mosses and their corresponding substrates (after Shacklette 1965a).

Element	Bryophyte sp.	Plant % in ash	Substrate % in dry wt.
Ba	<u>Atrichum angustatum</u>	5	0.3 (soil)
	<u>Polytrichum juniperinum</u>	5	0.3 (soil)
Cu	<u>Anomodon rostratus</u>	0.2	0.0005 (dolomite)
Pb	<u>Dicranum scoparium</u>	2	0.01 (lithosol)
	<u>Leucobryum glaucum</u>	2	0.01 (lithosol)
Sr	<u>Polytrichum juniperinum</u>	0.15	<0.01 (soil)
	<u>Hypnum curvifolium</u>	0.1	0.01 (lithosol)
Zn	<u>Brachythecium salebrosum</u>	2.0	0.4 (soil)

Table 2. The contents of zinc and lead (ppm dry wt.) in Lecanora muralis collected from various urban and rural habitats in U.K. (based on Seaward 1974).

Habitat	Zn	Pb
Silicious rock	769	102
Silicious stone wall	789	132
Silicious stonework	710-850	375-440
Asbestos roofs		
outer suburb	1100-1860	500-1090
inner suburb	790-2470	285-3124

iii) Absorption affected by acid rain.

Normally a pH value of 5.7 (Barrett and Brodin 1955) or 5.5 (Mrose 1966) is considered as the neutral value for precipitation reaction in terms of atmospheric carbon dioxide content of distilled water at 20°C. Likens and Bormann (1974) measured rain falling on the northeastern United States and have recorded mean annual acidity values of about pH 4. Natural waters, soils and organic materials may become increasingly acidified when acidic gases are present in the atmosphere. It may result in increased rock weathering and in the leaching of soil and bark substrates. Under these conditions, lichens and mosses will not only be bathed in a dilute acid solution which may be toxic to them but, in addition, many characteristics of the substrates may be altered and therefore the epiphytes and other plants may be indirectly affected (Gorham 1955; Likens et al. 1972). Leaching can occur from the stem and branches as well as from foliage (Tukey 1971) while Wood and Bormann (1975) indicate that there is a significant increase in foliar leachate at pH 3.3 to pH 4.0 where no tissue injury was observed. Further, the process of leaching would not only influence the nutrient budget of the leached tree but also the nutrient budget of the epiphytes (Smith 1972; Lawrey and Rudolph 1975) and thus might contribute to reduced plant growth. Such an effect has been suggested for Scandinavia (Jonsson and Sundberg 1972) and for eastern United States (Whittaker et al. 1974). Nieboer et al.

(1976b) showed that Ni uptake increases with increasing pH, with the amount of Ni found per unit weight becoming independent of pH at values around pH 7. They also note that buffering action may account for the significant enhancement of Ni uptake.

In strip mine habitat under low pH conditions heavy metals are easily solubilized. In this form they are continually available for uptake by terrestrial species of lichens and bryophytes, especially during water movement (Table 3). It is suspected that small amounts of heavy metals accumulated by lichens and bryophytes are also removed by low pH rain water (Lawrey and Rudolph 1975). Therefore, accumulation of heavy metals could occur concomitantly with mobilization and release of these metals during periods of acid rain.

Rühling and Tyler (1973a) noted that in heavy metal polluted areas the spruce needle litter decomposition rate, measured in terms of dehydrogenase activity, was considerably reduced and litter and mor layers, together with mosses and lichens, when present, acted as a giant filter for heavy metal deposition. In conclusion, under conditions of acid precipitation and reduced buffer capacity; heavy metal absorption by lichens and bryophytes is increased, in other words a weakly acid medium favours accumulation of heavy metals (Czarnowska and Rejement-Grochowska 1974).

Table 3. Metal contents (ppm dry wt.) in Cladonia species and their substrates in acidic-surface-coal mine habitats (after Lawrey and Rudolph 1975).

Species	pH _S	Metals							
		Mn		Fe		Zn		Cu	
		S	L	S	L	S	L	S	L
<u>Cladonia capitata</u>	3.4	10	27	89	1315	6	33	2	8
<u>C. cristatella</u>	3.3	8	27	58	1529	2	27	1	8
<u>C. subcariosa</u>	3.5	21	59	12	385	6	37	5	18
<u>C. subtenuis</u>	3.6	13	40	98	788	4	42	1	7
<u>C. verticillata</u>	3.7	14	76	69	1085	6	36	1	7

S is substrate.

L is lichen.

iv) Absorption affected by distance.

The decrease in Pb contamination with increasing distance from roads is typical of studies that have examined Pb content of roadside plants (Smith 1976). Lee (1972) studied Pb pollution from a factory manufacturing antiknock compounds consisting of tetraethyl and tetramethyl lead. He found that the Pb content in the moss species Ceratodon purpureus, Stokesiella praelonga, Mnium cuspidatum and Calliergonella cuspidata away from the factory declined rapidly in the first 400 m and then more slowly in the next 400 m distances; at 800 m, however, the amount of Pb in the mosses was still between two and three times that in the species collected from the rural areas remote from the factory. Lee also observed that in C. purpureus the Pb content was about 320 ppm at a distance of 2 m and 185 ppm at a distance of 20 m away from a road in central Manchester. In addition, Briggs (1972) found Pb values in Marchantia even at great distances from roads, with the Pb contents corresponding to the respective traffic intensities and were without significant correlation to the Pb content of the soil. Laaksovirta et al. (1976) observed that a decrease in the Pb content of Hypogymnia physodes thalli was statistically significant between 20 m and 100 m from a highway in southern Finland, but could not be correlated with traffic density. This was probably due to effective Pb accumulation in the lichen where there was moderate traffic flow.

Rühling and Tyler (1969, 1970) and Tyler (1971) found an increase in the heavy metal content (Pb, Cd, Cu, Cr, Ni, Zn, Co and Mn) in the mosses Hypnum cupressiforme and Hylocomium splendens with increasing precipitation and decreasing distance from industrialized areas. Yeaple (1972) has shown that terrestrial mosses accumulate Hg in inverse proportion to their distances from pollution centers. Burkitt et al. (1972) found high concentrations of Zn, Cd and Pb around smelting works within the zone of prevailing winds although there was a rapid fall in metal concentration as the distance from the smelters increased. As a general rule the concentration of airborne materials decreases with distance from the source of pollution and there may be a wide variation in metal accumulation from species to species (Nieboer et al. 1972) and from habitat to habitat under different microclimatic conditions.

b) Process and pattern of accumulation.

Metal ions are retained by organic matter, either by means of simple ion exchange or by complexing or chelation with specific organic groups. According to Mellor and Maley (1947, 1948), the stability of organic chelates with divalent metal ions is mainly dependent on the properties of the metal ion and follows the average sequence: Pb>Cu>Ni>Co>Zn>Cd>Fe>Mn>Mg.

Results of cation exchange experiments with the moss Hylocomium splendens have been reported by Rühling and Tyler (1970). These authors noted that Ni accumulation was

by passive ion exchange, at least when large amounts of Ni were supplied, for Cu however, the process was not exclusively ion exchange, because only two-thirds of the copper content could be reexchanged by repeated leaching with $MgCl_2$. The sorption and retention of the heavy metals studied by Rühling and Tyler were in the order: Cu, Pb > Ni > Co > Zn, Mn. The order was shown to be independent of whether or not the ions were supplied in pure or in mixed solution. The natural carpet of Hylocomium splendens exhibited a continuous uptake of Mn, Fe and Cu from young to old tissues. The mor layer beneath the moss carpet had not enriched the heavy metals above the concentrations measured in the old moss tissue.

The moss gametophytes readily entangle and retain particulate contaminants amongst the leaves and they possess remarkable ion exchange properties. Certain mosses, especially Sphagnum, when dry, absorb and retain rainwater to a considerable extent. This facilitates ion exchange between the soluble metal and the moss cell walls (Clymo 1963).

The mechanism of metal accumulation by lichens is not clearly established. Lange and Zeigler (1963) have shown that in Acarospora sinopica Fe is concentrated in the upper cortex of the thallus. Tuominen (1967) suggested that lichen acids concentrated in the cortex have a chelating ability. He also showed that it is difficult to separate absorption through chelation from absorption by an ion

exchange mechanism. The hyphae and their associated lichen acids may act as a suitable ion exchange resin. Tuominen further demonstrated the existence of an ion exchange mechanism for Sr uptake in Cladonia alpestris thallus and proposed that uptake of alkali and alkaline earth metal ions by lichens involved simple ion exchange processes. Brown and Slingsby (1972) were able to displace Pb and K metal ions from a lichen thallus by acid solution and concluded that these accumulations are physicochemical in nature.

Puckett et al. (1973b) observed that the relative capacities of lichens, such as saxicolous or terricolous species of Cladonia, Umbilicaria and Stereocaulon, for uptake of various solutions containing a single metal ion were Fe, Cu>Ni>Pb>Co>Zn. Competitive uptake studies revealed the selectivity sequence Fe>Pb>Cu>Ni, Zn>Co. The sequences are in accord with a cation uptake mechanism involving ion exchange modified by metal complex formation. Nieboer et al. (1976c) confirmed, with equilibrium studies, for Umbilicaria muhlenbergii that the mass balance of the exchange of Ni^{2+} for Sr^{2+} , Sr^{2+} for Tl^+ and Sr^{2+} for H^+ was consistent with a cation exchange mechanism of metal-ion uptake. The data for the uptake of Ni by U. muhlenbergii suggests that the uptake is physicochemical (Nieboer et al. 1976b).

c) Response and toxicity.

Metal accumulation by lichens and bryophytes has been

well documented but the physiological effect of such accumulations are still not well understood. Relatively low concentrations of Pb, Cd, Ni and Tl may interfere with biological processes related to the general metabolism of the plant including photosynthesis (Bazzaz et al. 1974; Puckett 1976) and mitochondrial respiration (Miller et al. 1973). Minimum toxic levels for higher plants are 1,000 ppm for Pb (Lag et al. 1969), 100 ppm for Zn and 10 ppm for Cd (Jordan 1975). At these foliar metal levels toxicity remains minimal and the vegetation appears more or less normal. Seaward (1974) suggested that the values of 101 ppm Zn, 3,150 ppm Fe and 58 ppm Pb may be threshold levels for the lichen Hypogymnia physodes. However, depending on habitat, microclimate and time span of accumulation, species may have wide variations in their threshold levels. On the basis of experimental data for short periods of exposure, Nash III (1975) indicated that the threshold values for lichens to Zn or Cd may lie between 200 - 600 ppm; at low concentrations, probably all lichens will survive, at higher concentrations most species will die. Nash III further observed that in culture the lichen algae Trebouxia erici, phycobiont of Cladonia cristatella and Trebouxia anticipata, phycobiont of Parmelia carparata, are sensitive to Zn and Cd at 5×10^{-5} M concentrations. Recently Puckett (1976) has noted a burst of K efflux at certain critical concentrations of Ni, Co, Cd and Pb and that increasing concentrations of Cu, Hg and Ag caused

progressive alterations of membranes which normally retain K. These changes in membrane permeability may be detrimental to the lichen and could be a cause of toxicity.

A large number of plant toxicity studies have been made with reference to Pb, a biologically non-essential element. It is a protoplasmic poison and capable of interfering with the activity of several enzymes (Koeppel and Miller 1970; Chisholm 1971). Gullvåg et al. (1974) have stated that Pb may enter the cytoplasm of leaf cells of the moss Rhytidiadelphus squarrosus via pinocytotic vesicles which would then discharge Pb containing particles into the vacuole. Lead once released into the cytoplasm could then disrupt normal cell functions, e.g. by inhibiting enzymatic systems in the formation of chlorophyll (Hampp and Lendzian 1974). Hampp et al. (1974) have shown that two enzymes of the chlorophyll biosynthesis pathway, γ -aminolevulinic acid dehydratase (ALAD) and prothobilinogenase (PGBA) show a pronounced sensitivity towards the Pb ion: PGBA being more sensitive than ALAD at all concentrations of Pb^{2+} . One would expect a similar toxicity effect of Pb in lichens and bryophytes.

Photosynthetic reductions have been observed under the stress of metal pollution. Nash III (1975) noticed that lichen photosynthesis was depressed by much lower concentrations of Zn and Cd than was respiration. Significant reductions in photosynthesis occurred after lichen heavy metal concentration reached 308 ppm Zn and 288

ppm Cd for Lasallia papulosa and 178 ppm Zn and 320 ppm Cd for Cladonia uncialis. The compensation point occurred at metal concentrations of 482 to 3,300 ppm Zn and 863 to 7,640 ppm Cd for L. papulosa and 450 ppm Zn and 320 ppm Cd in the case of C. uncialis. Thus levels of Zn or Cd exceeding the above concentrations would cause death by starvation. The data show that C. uncialis is more sensitive to Zn and Cd than L. papulosa. Nash III observed also that this latter species could tolerate up to 2,560 ppm Zn under field conditions, whereas photosynthesis in the laboratory was depressed by Zn concentrations as low as 482 ppm. The concentration under field conditions was accumulated over a period of several years, but in the laboratory it took place in 9 days only. Thus, lichens can tolerate high concentrations of heavy metals if the rate of addition is slow. Further, the data for L. papulosa imply that Zn and Cd together depress net photosynthesis less than they do if present separately. Since both Zn and Cd are present together in the field, it is predictable that a higher concentration of Zn would be required to eliminate L. papulosa than if Zn were present alone. Puckett (1976) noted a spectral shift of 10 nm of both the red and blue chlorophyll peaks as well as bleaching (loss of absorbance) in the chlorophyll absorption spectrum of Umbilicaria muhlenbergii, when this plant was exposed to 2×10^{-2} M copper chloride for 15 hours. This change could seriously affect the electron potential in photophosphorylation and

reduce photosynthesis and hence reproduction of plant tissue.

The above mentioned photosynthetic reductions are perhaps due to chlorophyll damage by heavy metals. Location of a site with an affinity for heavy metals (lead, osmium and tungsten) on the thylakoid membranes of chloroplasts (Sabnis et al. 1969) perhaps suggests one of the methods of chlorophyll damage. Characteristic variable fluorescence of green plants (Kautsky-effect) has been used to study the effect of heavy metals on chlorophyll (Arndt 1974). By using this method Arndt has shown that, for the metabolic processes of plants, Zn is less toxic than Cu. Of all the elements found in heavy metal dusts, Cu and Mn cause particularly characteristic changes in the Kautsky-effect. After the addition of different amounts of copper chloride to the suspensions of Chlorella, a concentration dependent drop in fluorescence can be seen. The effect is dependent on the physiological condition of the alga and is especially obvious when the alga is removed from the nutrient medium and allowed to grow in a solution containing the damaging agent (Steeman-Nielsen et al. 1969). After extraction and chromatographic purification of the chlorophyll pigments of Chlorella cells grown in a culture medium containing copper chloride, a blue-green pigment is obtained which, on the basis of its absorption spectrum, is called copper porphyrin owing to its relationship to chlorophyll (see also the observations of Puckett 1976). It is presumed that the

central magnesium atom of chlorophyll is displaced by Cu. Spectral analysis of the purified pigment shows a strong Cu band but no Mg band. This exchange process has been observed in vitro (Strell and Zuther 1958). A portion of the chlorophyll is removed from the pigment system of the chloroplast in the formation of this copper complex. It cannot be used in photosynthesis as the light energy is not sufficient to stimulate the electrons. These processes necessarily lead to a drop in the Kautsky-effect.

d) Basis of tolerance and process of detoxification.

The ability of plants to colonize heavy metal contaminated sites may suggest the evolution of tolerant genotypes or the development of heavy metal ecotypes as a result of lowered competition there (Antonovics et al. 1971). On the basis of their differences in physiology and tolerance to Zn, some lichens were divided by Lambion et al. (1964) into three groups: 1) species that displayed high accumulation of Zn with no apparent injury, e.g. Diploschistes scruposus; 2) species whose Zn content varied in successive samples, e.g. Stereocaulon nanodes; and 3) species which possessed high amounts of Zn but showed pathological changes, e.g. Cladonia arbuscula, C. rangiformis, Stereocaulon dactylophyllum. The mechanisms for detoxification may be accumulation in the cell wall as well as the formation of organic complexes (possibly with acids and alcohols) (Ernst 1976). Brown and Sligsby (1972) observed in Cladonia rangiformis that excessive

quantities of Pb were almost exclusively located in the cell wall without any apparent effect on the metabolism of the lichen. They also found that Pb and K metal ions were displaced from the thallus in acid solution. They suggested that these accumulations were physicochemical without major metabolic repercussions and this perhaps was the basis of tolerance of C. rangiformis to high concentrations of heavy metals.

Lange and Ziegler (1963) proposed that inherent cytoplasmic tolerance, cytoplasmic immobilization and detoxification of ions by chemical combination, and transport of ions to regions external to the plasma membrane and even the cell wall, were the mechanisms of heavy metal tolerance in lichens. Clymo (1963) and Tuominen (1967) provided evidence in favour of a mechanism being a neutralization of ionizable anionic groups in the cell wall by added cations. These could be polyuronic acid molecules (pectic substances), considered to be an important part of the immobile phase responsible for the cation binding capacity of plant cell walls (Broda 1965). However, uronic acids, which play an important role in the cation binding of most forms of higher plants and mosses, have not been demonstrated conclusively in fungal cell walls the major component of a lichen thallus (Aronson 1965).

Detoxification through excretion of heavy metals external to the cell wall has been seen in some lichen and mosses. Noeske et al. (1970) found that Fe and Cu

accumulation within the thallus of Acarospora sinopica was in the form of a crust in and on the upper surface and sides of the areoles, and to a lesser extent, along the junction between the rock surface and the attachment of the thallus.

Coombes and Lepp (1974) have observed morphological changes in Cu and Zn stressed Funaria hygrometrica and Marchantia polymorpha and they suggest that these changes could be possible tolerance mechanisms. Funaria develops "capsule cells" and "brood cells" when subjected to high doses of Cu and Zn respectively thereby reducing the surface area of the protonema in contact with Cu and Zn. In Cu stressed Marchantia a buffering zone of outer dead cells may immobilize Cu within their walls thus preventing toxic concentrations from reaching the inner cells.

Skaar et al. (1973), in their electron microscopic studies of the leaves of the moss Rhytidiadelphus squarrosus cultured in the laboratory by watering once a day for three weeks with lead acetate solution and of samples collected in a Pb polluted area, observed accumulation within the nuclei of moss leaf cells. The binding of Pb within the nuclear membrane, as a non diffusible complex, has been suggested as the mechanism whereby the cytoplasmic concentration of diffusible Pb substances within the cell can be kept below a level that would otherwise be toxic to the mitochondrial or other Pb sensitive functions of the cytoplasm. Lead in slag

specimens of Grimmia doniana was shown to be ionically bound to an extracellular site, the cell wall, thus preventing toxic amounts of Pb from reaching or penetrating the cytoplasm (Brown and Bates 1972).

Shimwell and Laurie (1972) observed that in Dicranella varia (an ectohydric moss devoid of cuticle) most of the Pb and Zn is excreted from the gametophyte and in periods of summer drought forms a powdery crust on the moss surface. An analysis of this precipitate from Dicranella growing on shale spoil heaps produced the abnormally high values for Pb of 42,000 and 60,450 ppm.

The method of excretion by Dicranella appears to begin with an exudation at the tips of the leaves where crystals of complex metal sulphates form and gradually spread out over the surface of the leaves to form a white crust. The crust disappears rapidly into solution in periods of normal precipitation and the moss carpet remains healthy. If the period of drought and desiccation exceeds three or four weeks, some areas of the carpet die and rapidly disintegrate to form raw humus, returning the Pb and Zn to the top layers of the soil. The past existence of a moss carpet can thus greatly affect the heavy metal concentration in the soil.

Theoretically, the absorption and precipitation of heavy metals by Dicranella provides a possible natural method of detoxification of spoil heap soils.

e) Metal tolerance.

Little is known of the maximum tolerance levels of

lichens and bryophytes for individual metals. However, there are indications that particular species show differing accumulation and tolerance characteristics towards individual, or certain combinations of, cations (Noeske et al. 1970). The observations of Lounamaa (1956), and Le Roy and Koksoy (1962) suggest that the majority of lichens and mosses have an innate tendency for the accumulation of at least some metals (Fe, Pb, Zn, Ni) from their substrate and the atmosphere and that the mosses generally resemble higher plants rather than lichens in their behaviour towards certain metals.

Some species may be able to thrive only on rock rich in certain metals or in an area polluted by certain heavy metal fallout (Table 4). For instance the genus Stereocaulon appears to be rather insensitive to atmospheric pollution including heavy metal contamination. Kershaw (1963) considered that Stereocaulon pileatum possessed a great affinity for Pb and was spreading out into the industrial areas of Britain. Beschel (1959) found that S. paschale thrived in a copper swamp at North Sackville, New Brunswick, Canada. Tolerance of high Zn concentration is probably characteristic of a few lichens. In Belgium, Maquinay et al. (1961) reported that S. nanodes alone occurred on slag containing 700 ppm Zn and that the ashed lichen contained up to 3,300 ppm Zn. Lounamaa (1956) found Lasallia pustulata with 10,000 ppm Zn (ashed sample) on silicious rocks in Finland. In Japan Takeo

Table 4. Lichens and bryophytes tolerant of metal enriched environments.

Species	Nature of habitat	Thallus metal concn. (ppm max.)	Reference
<u>Iron tolerant</u>			
<u>Acarospora smaragdula</u>	Mine spoil heaps	14,400	Noeske et al. (1970)
<u>Cladonia deformis</u>	Nickel smelter soil	5,000	Nieboer et al. (1972)
<u>Lecanora muralis</u>	Urban asbestos roof	35,760	Seaward (1973)
<u>Peltigera rufescens</u>	Steel smelter soil	90,380	Seaward (1973)
<u>Stereocaulon paschale</u>	Nickel smelter soil	3,000	Nieboer et al. (1972)
<u>Zinc tolerant</u>			
<u>Diploschiste scruposus</u> var. <u>bryophilus</u>	Calamine rich soil	93,400	Lambinon et al. (1964)
<u>Lasallia pustulata</u>	Silicious rocks	10,000	Lounamaa (1956)
<u>Micarea trisepta</u>	Zinc smelter soil	23,000	Nash III (1975)
<u>Parmelia tinctorum</u>	Rock and soil	14,580	Takeo (1959)
<u>Stereocaulon nanodes</u>	Calamine rich soil	10,000	Marquiny et al. (1961)
<u>Umbilicaria pustulata</u>	Silicious rocks	10,000	Lounamaa (1956)
<u>Verrucaria nigrescens</u>	Zinc smelter soil	25,000	Nash III (1975)
<u>Lead tolerant</u>			
<u>Dicranella varia</u>	Shale spoil heaps	60,450	Shimwell and Laurie (1972)
<u>Copper tolerant</u>			
<u>Cladonia</u> sp.	Copper swamp	2,100	Dykeman & De Sousa (1966)
<u>Pohlia nutans</u>	Copper swamp	8,750	Dykeman & De Sousa (1966)

(1959) found Parmelia tinctorum with 14,580 ppm Zn (ashed sample). Nash III (1975) has shown that Verrucaria nigrescens occurring near a zinc smelter in Pennsylvania could tolerate Zn in excess of 23,000 ppm (acid digested). Lichens such as Baccidia chlorococca, Cladonia coniocraea, Endocarpon pusillum were most tolerant of the conditions around a zinc factory (Nash III 1972).

Some lichens seem to have a special affinity for Fe (Table 4). Seaward (1973) found 90,380 ppm of this metal in the terricolous lichen Peltigera rufescens near a steel smelter in England, and 35,760 ppm in thalli of Lecanora muralis collected from asbestos roofs in suburban Leeds. According to Nieboer et al. (1972), the Fe contents (dry wt.) in Cladonia deformis and Stereocaulon paschale, growing near a nickel smelter in Sudbury, Canada, was 5,000 and 3,000 ppm respectively. Noeske et al. (1970) reported a concentration of 14,000 ppm of Fe in Acarospora smaragdula on mineral rich mine spoil heaps in the Hartz area, Germany. Such high metal concentrations of the metal in lichens are often associated with 'oxydated' or ferruginose (i.e. rust red) colouring of the thallus which is a permanent feature of some species such as Lecidea silacea, Rhizocarpon oederi and Acarospora sinopica.

Huey (1973) and Lawrey and Rudolph (1975) noted that terricolous lichens, particularly those of the genus Cladonia, are among the most important early invaders on spoil material left after mining. In all species sampled

there were greater concentrations of each metal cation found in the lichen than available in the substrate (Table 3). This is important because of the fact that the high concentration of heavy metals found in strip mine spoil materials are thought to be significant in limiting the successful reestablishment of vegetation in these habitats (Berg and Vogel, 1973).

There are also some lichens which remain unaffected by high concentrations of thallus Cu in them (Table 4). Dykeman and De Sousa (1966) found that the Cu contents in Cladonia sp. and Stereocaulon paschale, growing in a copper swamp, contained 2,100 and 410 ppm Cu respectively.

Some species of mosses are known as indicators of sites of Cu enrichment in the substrate. These plants have commonly been designated 'copper mosses' in the literature. It should be remembered that although Cu is an essential plant micronutrient (Aslander 1958), it is toxic when present in excessive amounts (Sommer 1930). The 'copper moss' Mielichhoferia macrocarpa contained amounts of Cu greater than the average amounts of lithol and volcanic rocks (Shacklette 1966). 'Copper mosses' are resistant to or prefer to grow on a substratum containing Cu in amounts even 100 times higher than the trace concentration in ordinary soil. Also these mosses are able to grow on a

substratum containing Cu in amounts even 100 times higher than the trace concentration in ordinary soil. Also these mosses are able to grow on a substratum of exceptionally low pH: however the 'copper moss' Crumia latifolia was found to grow on a substratum containing 320 ppm Cu with a very high pH of 7.6 (Persson 1956). Similarly, Scopelifolia ligulata and S. cataractae (= gedeana) could grow on stones of drains from copper roofs (Noguchi 1956). It is remarkable that S. ligulata grows only on soil containing such metals as Cu, Fe, Ag or on soil moistened with sulphuric water in hot spring areas. Persson (1956) reported an average Cu content of 94.5 ppm in the substrate of 11 samples of S. ligulata collected in Java, India, Turkey, U.S.S.R., France and Switzerland, whereas Brassard (1969) reported 70 ppm Cu in organic soil supporting the growth of Mielichhoferia mielichhoferi in Arctic Canada. The substrates of M. mielichhoferi from Michigan and of M. macrocarpa from Amchitka Island (Shacklette 1961) contained about 150 ppm Cu an amount similar to those of the 'copper moss' substrates in Europe. Dykeman and De Sousa (1966) observed that Pohlia nutans growing in a copper swamp contained 8,750 ppm Cu in its tissues.

Certain species of bryophytes can successfully grow on soil derived from serpentine rock which weathers to form a soil containing as much as 4,000 ppm Ni and 900 ppm Cr. Shacklette (1965b) reports that shaded serpentine rock may be colonized with small patches of Grimmia apocarpa

var. stricta, G. tenera, Hedwegia ciliata, Thuidium abietinum, Rhytidium rugosum and Weisia controversa, but fully exposed rocks may be colonized by dense mats of Rhacomitrium lanuginosum.

f) Monitoring and mapping of metal pollution.

Lichens and bryophytes seem to possess the physical characteristics which make them ideal monitors of air quality. A good plant monitor is one possessing the characteristics of growth that enable investigators to assess quantitatively the amount of injury present and to relate this assessment to the concentration of toxicant in the air. In the present context, lichens and bryophytes should be considered as a bio-assay technique for detecting and measuring metal pollution over long periods of time.

The first step in evaluating the potential significance to lichens and bryophytes of metals introduced into the air of a city or industrial area is to establish the burden and location of various metals on or in these plants. High levels of metal accumulation by lichens and bryophytes have been detected in a wide range of species in both natural and man-made environments (Table 5).

By analyzing specimens of the mosses Hylocomium splendens, Pleurozium schreberi and Hypnum cupressiforme that were preserved in the Botanical Museum in Lund, Sweden, and that had been collected at intervals from 1860-1968 from the same locations, Rühling and Tyler (1968) were able to record the effect of human activity on the

Table 5. Accumulation of heavy metals by some lichen and moss species from terricolous and saxicolous habitats.

Species	Region	Pb	Zn	Cd	Cu	As	Mn	Ni	Fe	Reference
Lichens										
<u>Umbilicaria pustulata</u>	Finland		6500 ^a							Lounamaa (1956)
<u>Cladonia deformis</u>	Canada		95		290			380	5,000	Nieboer et al. (1972)
<u>Stereocaulon paschale</u>	Canada		70		400			300	3,000	Nieboer et al. (1972)
<u>Cornicularia muricata</u>	England	12045	5640							Shimwell and Laurie (1972)
<u>Peltigera canina</u>	England	7664 ^a	3510 ^a							Shimwell and Laurie (1972)
<u>Parmelia sp.</u>	England	1623	3271	90						Burkitt et al. (1972)
<u>Cladonia furcata</u>	England	129 ^a								Seaward (1973)
<u>Cornicularia aculeata</u>	England	134								Seaward (1973)
<u>Peltigera rufescens</u>	England	250 ^a							90,380	Seaward (1973)
<u>Hypogymnia physodes</u>	Finland		200				60		3,600	Lounamaa (1965)
<u>H. intestiniiformis</u>	Finland		130				62		4,400	Lounamaa (1965)
<u>Parmelia centrifuga</u>	Finland		180				84		3,200	Lounamaa (1965)
<u>P. omphalodes</u>	Finland		150				59		6,100	Lounamaa (1965)
<u>P. saxatilis</u>	Finland		200 ^a				79 ^a		6,050 ^a	Lounamaa (1965)
<u>P. taractica</u>	Finland		165 ^a				73 ^a		4,450 ^a	Lounamaa (1965)
<u>P. stygia</u>	Finland		120				90		7,800	Lounamaa (1965)
<u>Cladonia alpestris</u>	Finland		355 ^a				140 ^a		3,650 ^a	Lounamaa (1965)
<u>C. arbuscula</u>	Finland		320				130		3,400	Lounamaa (1965)
<u>C. rangiferina</u>	Finland		285 ^a				270 ^a		3,555 ^a	Lounamaa (1965)
<u>C. uncialis</u>	Finland		380				110		4,600	Lounamaa (1965)
<u>Cetraria ericetorum</u>	Finland		490				190		4,700	Lounamaa (1965)
<u>C. islandica</u>	Finland		320				150		4,300	Lounamaa (1965)
<u>Stereocaulon paschale</u>	Finland		230 ^a				75 ^a		5,300 ^a	Lounamaa (1965)
<u>Lasallia pustulata</u>	Finland		1445 ^a				60 ^a		2,750 ^a	Lounamaa (1965)
<u>Umbilicaria hirsuta</u>	Finland		440				90		4,600	Lounamaa (1965)

Mosses

<u>Hylocomium splendens</u>	Scandinavia	110 ^a	90 ^a	Rühling and Tyler (1971)
<u>Mielichhoferia mielichhoferi</u>	Scotland	680		Coker (1971)
<u>Saellania glaucescens</u>	Scotland	680		Coker (1971)
<u>Stokesiella praelonga</u>	England	1623	6835	Burkitt et al. (1972)
<u>Bryum pseudotriquetrum</u>	England	8870 ^a	7240 ^a	Shimwell and Laurie (1972)
<u>Dicranella varia</u>	England	6245 ^a	4228 ^a	Shimwell and Laurie (1972)
<u>Encalypta vulgaris</u>	England	2423	1660	Shimwell and Laurie (1972)
<u>Philonotis fontana</u>	England	5244 ^a	1312 ^a	Shimwell and Laurie (1972)
<u>Aulacomium palustre</u>			24 ^a	Czarnowska & Regment-
<u>Climacium dendroides</u>			31	Grochowska (1974)
<u>Atrichum undulatum</u>			5	" "
			89 ^a	" "
			209 ^a	2,075 ^a
			310	1,950
			24 ^a	2,100 ^a

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Metal concentrations 1 - 9 and 26 - 39: ppm dry weight.
10 - 25: ppm ash weight.

a = an average value.

concentration of atmospheric Pb. They wrote "from values of 20 ppm (dry wt.) in the years 1860-1875, the concentration of Pb was more than doubled between 1875-1900. During the first half of the twentieth century, no measurable changes were observed, but after 1950 there was a new increase to a present average of 80-90 ppm". Rühling and Tyler (1968, 1969, 1971, 1973b) and Tyler (1971) conducted studies of regional distribution of other airborne heavy metals by analyzing samples of mosses and they found this method to be effective in evaluating aerial metal pollution. From the increasing concentrations of metals in H. splendens from northern to southern parts of Scandinavia, Rühling and Tyler (1971) concluded that perhaps the much greater human activity in the south of Scandinavia was responsible for the measured gradients in the deposition of heavy metals (Table 6).

Robitaille and LeBlanc (unpublished data) made a historical study of accumulation of Zn, Pb, Cu, Ni, Cd and Cr in herbarium specimens of certain mosses collected from Mount Royal in Montréal, Canada, between the years 1905 and 1971 (Table 7). During this 66-year period, they found an increase of Zn concentration from 88 to 440 ppm in Mnium cuspidatum, from 87 to 330 ppm in Brachythecium salebrosum, from 100 to 120 ppm in Heterophyllum haldanianum, from 90 to 160 ppm in Anomodon rostratus and from 53 to 145 ppm in Atrichum angustatum. When the average concentration of a metal in the mosses was plotted against

Table 6. Gradient concentration (ppm dry wt.) of certain heavy metals in Hylocomium splendens from northern to southern parts of Scandinavia (after Ruhling and Tyler 1971).

Metal	Regional concentration gradient from N to S							
	N							S
Fe	250	500	1000	1500				
Zn	20	40	60	80	100	120		
Pb	10	20	40	60	80	100	120	140
Cu	4	6	8	10	12	15	20	
Ni	1	2	4	6	8	10	12	
Cr	1	2	4	6	8	10		
Cd	.063	.125	.25	.5	.75	1	1.5	
Hg	.04	.1	.2	.4	.6			

Table 7. Metal accumulation in some species of mosses collected from Mount Royal, Montréal, P.Q., Canada, between the years 1905-71.

Species	Metal	Concentration (ppm dry wt.)				
		1905/06	1910/11	1916	1925/26/28	1937 1971
<u>Mnium</u> <u>cuspidatum</u> (wet soils)	Zn	88			120	205 440
	Pb	75			56	105 85
	Cu	37			69	25 45
	Ni	35			28	13 21
	Cd	1			6	1 5
	Cr	23			36	21 27
<u>Brachythecium</u> <u>salebrosum</u> (tree bases)	Zn	87	105		155	330
	Pb	54	94		55	70
	Cu	25	37		33	27
	Ni	6	29		14	105
	Cd	1	1		7	6
	Cr	17	55		20	43
<u>Heterophyllum</u> <u>haldanianum</u> (rotten logs)	Zn	100	170		105	180
	Pb	20	50		85	110
	Cu	21	45		75	33
	Ni	14	31		27	14
	Cd	1	5		2	1
	Cr	21	37		36	36
<u>Anomodon</u> <u>rostratus</u> (rocks)	Zn	90		32	205	160
	Pb	13		4	55	34
	Cu	35		87	56	23
	Ni	21		16	30	3
	Cd	2		1	4	6
	Cr	63		7	61	19
<u>Atrichum</u> <u>angustatum</u> (dry sandy soil)	Zn	53	75		73	145
	Pb	9	18		24	37
	Cu	25	20		17	22
	Ni	22	54		25	37
	Cd	2	2		2	4
	Cr	24	24		26	27

the year of sampling it became evident that the concentration of metals with the exception of Cu, is slowly increasing in the Montréal area. This trend is perhaps an indicator of the steadily increasing heavy metal pollution in the area through urbanization and industrialization.

Roberts (1972) and Little and Martin (1974) used mosses as indicators and integrators of airborne metal levels by suspending Hypnum cupressiforme and Sphagnum squarrosum, respectively, in small nets of very fine nylon with large mesh, at a number of selected sites for a period of 3 to 4 weeks. At the end of each exposure period the mosses were analyzed for Zn, Pb and Cd. The results obtained were expressed in $\mu\text{g/g}$ or ng/g of metal collected by the moss, over and above the ambient levels. Such experiments, however, have certain limitations in that one should be careful not to expose the moss for too long a period, to avoid saturation of all the ion exchange sites (Clymo 1963), which in turn may lead to displacement of already accumulated metals by the incoming metals. Pakarinen and Tolonen (1976) have also used Sphagnum sp. for regional surveys of heavy metals in Canada and Finland.

Mosses have been used as indicators of atmospheric mercury (Weiss et al. 1971) Yeaple (1972) studied airborne Hg pollution by collecting mosses in a 128 km radius of Boston, Massachusetts. In view of the relatively low values in soil (96 ppb), Hg levels in mosses above a

concentration of 200 ppb showed their potential as a bio-indicator of Hg. Levels of Hg ranged from 250 to 1,450 ppb in the Boston area and up to 2,000 ppb in the New York area. Mondano and Smith (1974) in their study of Hg accumulation in mosses along an urban-suburban transect recorded about 4 ppm Hg in Dicranella heteromalla at the urban end of the transect and 0.2 ppm Hg in suburban rural areas. In comparing Hg values found in mosses to those found in conifer twigs and needles they are of the opinion that bryophytes probably give the more reliable indication of urban-industrial Hg fallout. It is possible to develop contour maps of specific metal levels from this type of data. Huckabee (1973) found that the Hg content of mosses was a function of the distance from smoke stacks, mean values ranging from 1.3 ppm in polluted areas to 0.07 ppm in remote areas. Experiments with radioactive mercury tagged fly ash showed that mosses take up and retain mercury to a greater extent than do grasses (Table 8).

Jaakkola et al. (1971) analysed specimens of the lichen Cladonia alpestris and of the moss H. splendens to measure airborne Cd released from a zinc refinery in Finland. Results for the moss showed 3-4 ppm Cd in the windward area while in distant areas the levels were about 1 ppm. To assess the extent of metal pollution from a zinc smelter in Pennsylvania, Nash III (1972) studied the species diversity of corticolous, saxicolous, lignicolous and terricolous lichen communities. He observed that richness and abundance

Table 8. Mercury content (ppm) in species of mosses and a grass (after Huckabee 1973).

Species	Distance from stack (km)		
	2	10	>25
<u>Dicranum scoparium</u>	1.13	-	0.118
<u>Polytrichum commune</u>	-	-	0.092
<u>Festuca eliator</u> (grass)	0.025	0.009	0.087

of species were reduced by approximately 90 percent in lichen communities near the smelter. The principal cause of the impoverished lichen flora in the area was probably the high concentration of Zn: crustose, fruticose and foliose species respectively, were found to be increasingly more sensitive to Zn pollution. Seaward (1973) found interesting configurations of terricolous lichen distribution and corresponding high metal levels around the steel manufacturing industries of Scunthrope, U.K. to strongly suggest the possibility of toxic affects.

In comparison to terrestrial species, epiphytic forms accumulate to a higher extent substances taken up via the surface and hence they are preferred for mapping airborne contaminants. Grupe (cited by Garber 1973) introduced the lichen Hypogymnia physodes as a bioindicator for the intensity of Pb pollution. At a distance of 1,000 m from a highway the thalli contained 35 ppm (unwashed) and 19 ppm (unwashed) of lead, respectively. The use of epiphytes for monitoring heavy metal pollution on a widespread basis carries with it the assumption of a uniformity of epiphyte response to a given concentration of heavy metals. Differences in epiphyte response to metal due to meteorological, physiological and genetical conditions would create erroneous data and interpretation. The epiphyte injury pattern within a heavy metal polluted area supports the idea of a consistent plant response proportional to metal concentration.

Parts of Chapters III deal with the mapping of metal distribution using plants as a bio-assay technique.

3. Heavy metals and annual rings of trees.

As can be seen from the preceding sections, lichen and moss bio-assays may be used as a monitoring technique of ambient heavy metal levels for a given time interval. The amount of metal accumulated by these lichens and mosses is indicative only of a long term accumulation of pollutant only and does not pinpoint when pollution of the environment began nor can it indicate short term fluctuations of heavy metal input, unless dated samples of extended time periods are analysed (Rühling and Tyler 1968, 1970; Lee and Tallis 1973; Robitaille and LeBlanc unpublished data, see page 47).

An appropriate indicator-monitor for metal loading would appear to be the annual rings of trees. Theoretically the amount of heavy metal accumulated in any given annual tree ring would reflect the heavy metal burden to which the tree had been exposed during that year. Although this type of analysis is very inviting indeed, it has been used sparingly, and recent renewed interest has revealed that the monitoring of heavy metals by this technique is not as simple as it appears (Lepp 1975).

The literature on this topic is extremely limited. Most studies have dealt with Pb accumulation and distribution in vegetation (trees among others) and soils of roadside ecosystems (Smith 1976). Studies dealing with heavy metals

in tree rings have come from the analysis of Pb contamination of these systems.

Litter decomposition and nutrient cycling may be reduced in heavy metal polluted forest ecosystems (Rühling and Tyler 1973b) probably due to interference with soil enzymes and microbial activity (Rühling and Tyler 1973b). Heavy metals are accumulated by trees from both the atmosphere by impaction, precipitation and gravitational settling and from the soil by root uptake from the soil solution. The most important atmospheric contribution appears to be from gravitational settling (Ewing and Pearson 1974). The highest concentration of heavy metals in soils are found at low pH values (Massey 1972), since metals are bound to soil organic matter as pH increases (Hildebrand and Blum 1974). Hence, uptake from the soil compartment via the root system appears to be at least partly pH dependant.

Rolfe (1974) has found that increment cores taken from Acer saccharum, Quercus rubra and Pinus taeda near roads had lower concentrations of Pb in the older wood than in the most recent 10 years growth. There was no change in the Pb content during these same 20 years for tree taken at remote distances from roads. Ward et al. (1974) have correlated the increase in Pb in the most recent annual rings of Platanus orientalis to increased gasoline consumption and to the introduction of leaded gasoline. For the most polluted P. orientalis (i.e.

windward to nearby high traffic density and exposed to the prevailing winds) there was an increase of 1351 ppm Pb for a 10 year period starting in 1961.

Other studies have shown that annual rings of trees are not reliable monitors of metal pollution. Analysis of Pb in tree rings using isotope composition as a natural tracer (Ault et al. 1970) revealed that the Pb-206/Pb-204 ratio for a period of 33 years in the stem of Quercus rubra was constant at approximately 17.8 which indicated constant Pb accumulation. However the actual Pb values, expressed in ppm, indicated a 2-fold increase in Pb in the outermost rings. Barnes et al. (1976) observed a decrease in the Pb content in the more recent tree rings and they believe that tree rings are not good monitors of atmospheric Pb. In their study of Pb distribution within the xylem of trees exposed to airborne Pb the data of Szopa et al. (1973) indicate that the use of tree rings of Quercus alba for documenting fluctuations of atmospheric Pb concentrations is unsatisfactory. This was attributed to the fact that radial translocation of Pb takes place and that Pb may be cycled in the stem, hence if annual rings of trees are to be used as monitors of past metal pollution it must be assumed that heavy metals are immobile in the stem (wood). Stewart (1966) indicated that the radial ray parenchyma cells of trees may translocate toxic substances, thereby excreting them into the heartwood of the tree. This could be possible in view of the fact that high Pb values have

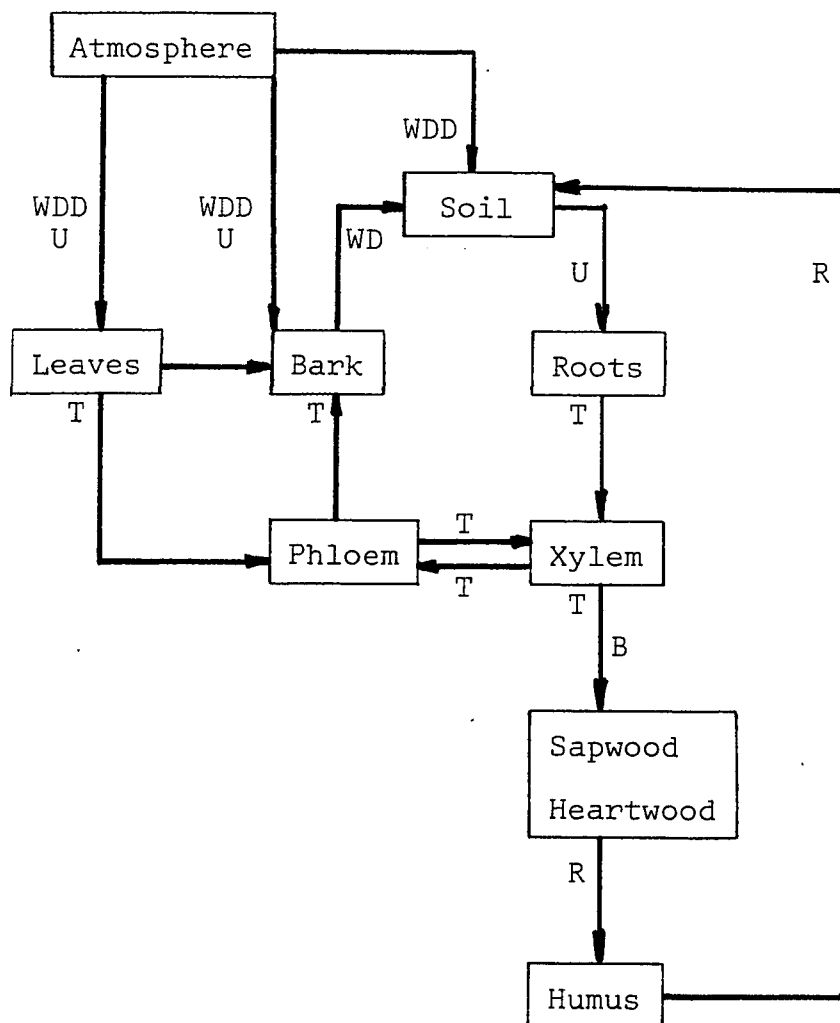
been recorded in heartwood (Hampp and Holl 1974; Dollard et al. 1976).

Application of labelled Pb to bark of Betula pubescens, Ulmus glabra, Alnus glutinosa, Fagus sylvatica and Tilia europaea indicated that Pb moves laterally from bark to xylem (Lepp and Dollard 1974a). Further studies using Acer pseudoplatanus showed that reverse translocation may also occur (Lepp and Dollard 1974b) and that free Pb ions bind more readily to the xylem than complexed Pb. Hence the transport form of Pb and probably other metal pollutants is important when assessing metal values in annual rings of trees. It has been postulated that 30 percent of the Pb present in the living wood of Robinia pseudoacacia is mobile and that this Pb may be transported towards the outer portion of the tree during wood formation (Hampp and Holl 1974). Lead and other metals may be bound in an exchangeable form to carboxyl groups of polyuronic acids (Clymo 1963; Rühling and Tyler 1970) thereby accounting for this 30 percent mobility. Heavy metals, either free or chelated may also replace Ca^{++} ions from fixed sites within the xylem tissue (Dollard et al. 1976). Depending on the amount of Ca^{++} in a given xylem tissue it would seem conceivable that the amount of metal found in an annual ring be entirely dependent upon the amount of Ca^{++} and not upon atmospheric metal concentrations. These however are preliminary results and more experimentation should clarify the process.

The interpretation of heavy metal data obtained from annual rings of trees is not simple as can be seen from the brief outline above. Figure 1 gives an indication of the complexity involved. A tree receives environmental metal input via wet and dry deposition on both leaves and bark. As a result of direct deposition on the soil heavy metals may enter the tree from the soil solution via the root system. Leaf and bark metal may then be translocated to the phloem and from there into the xylem. The greatest contribution to the xylem may come from the root system. Some of the xylem metal may be translocated into the bark. Also some of the unbound metal is accumulated in the leaves via the transpiration stream. At each step towards xylem accumulation some heavy metal is 'lost' and hence metal values observed are not a direct indication of atmospheric metal contamination although it may very easily be correlated to atmospheric input. Rather the xylem metal content is a measure of the total environmental metal input minus what is accumulated in various tissues before the metals enter and bind in the xylem.

In spite of these inherent problems, an analysis of heavy metal accumulation has been made in this thesis and is reported in Chapters III and IV.

Figure 1. The flow of heavy metals in trees showing the possible pathways by which heavy metals may reach the xylem (modified after Lepp 1975).



R = recycling to soil by death, decomposition, stemflow throughfall and by atmospheric dust.

T = translocation.

B = binding.

U = uptake.

WDD = wet and dry deposition.

(modified from Lepp 1975)

D. History and Mine Operations of Gaspé Copper Mines Ltd.

The original discovery of low grade copper mineralization in Murdochville was made in 1921. Noranda Mines Ltd. obtained the property in 1937 but World War II interrupted exploration work in 1940. Diamond drilling was resumed in 1948 and Gaspé Copper Mines Ltd. was formed to explore the property further. It was in 1951 that the decision was made to bring the property into production; that is, developing the mine, erecting a milling and smelting complex, constructing intergrated maintenance facilities and laying out the townsite of Murdochville (personal communication Gaspé Copper Mines Ltd.).

Initially, operations were confined to the higher grade deposits of porphyries of Needle Mountain, with production commencing in 1955 (Brummer 1966). Originally, 4,896 metric tons of ore per day were to be mined and milled. This was increased in 1967 to 6,803 metric tons. At the beginning of 1968, the lower grade Copper Mountain deposit was brought into production and new crushing and concentration facilities were installed to increase the throughput to 10,203 metric tons of ore per day (Gaspé Copper Mines Ltd.).

Based on the analysis of the data gathered throughout the years on the magnitude of the Copper Mountain low-grade ore deposits, the decision was made in 1971 to launch a major expansion program to bring the overall ore production up to 35,146 metric tons per day.

As of January 1, 1975, Needle Mountain reserves totalled approximately 21 million metric tons of ore grading 1.33% copper. For the same period, Copper Mountain reserves totalled 191 million metric tons of sulphide ore grading 0.39% copper and 30 million metric tons of oxide ore grading 0.45% copper.

The topography of the area adjacent to the town and the open pit mine on Copper Mountain has been changed considerably over the years. The pit excavation encompassed an area of approximately 47 hectares and extended from a height of 213 m above the valley floor, to a depth of 48 m below the original surface. Waste rock, low-grade sulphides and oxides stockpiles fill in an additional 110 hectares of valley floor to a height of 48 m.

At present there are two active suspended waste ponds (tailing ponds) with a third one being prepared for use in the near future (personal communication Gaspé Copper Mines Ltd.). The area of boreal forest land covered by the tailing ponds is 607 hectares. The water from the tailing ponds along with the surface runoff is collected in a reclaim dam and is used as process water.

In order to control sulphur dioxide emission and provide sulphuric acid for the leaching operation at the smelter, an acid plant was constructed in 1975 to reduce to 4.5% sulphur dioxide the gases coming from various parts of the smelter. The acid plant produces 93-96% acid at a maximum rate of 820 metric tons per day. Six hundred

and forty metric tons of acid are trucked to Gaspé daily where it is shipped to purchasers. A maximum of 180 metric tons is used daily at the plant.

The effluents from the smelting process pass through a stack 152 m high, 5.5 m wide stack at the top.

E. Description of Study Area.

1. Location of the study area.

The Gaspé Peninsula juts into the Gulf of Saint Lawrence at the extreme east of the Province of Quebec. It lies between latitudes $48^{\circ}00''$ and $49^{\circ}15''$ N and between longitudes $64^{\circ}15''$ and $67^{\circ}15''$ W.

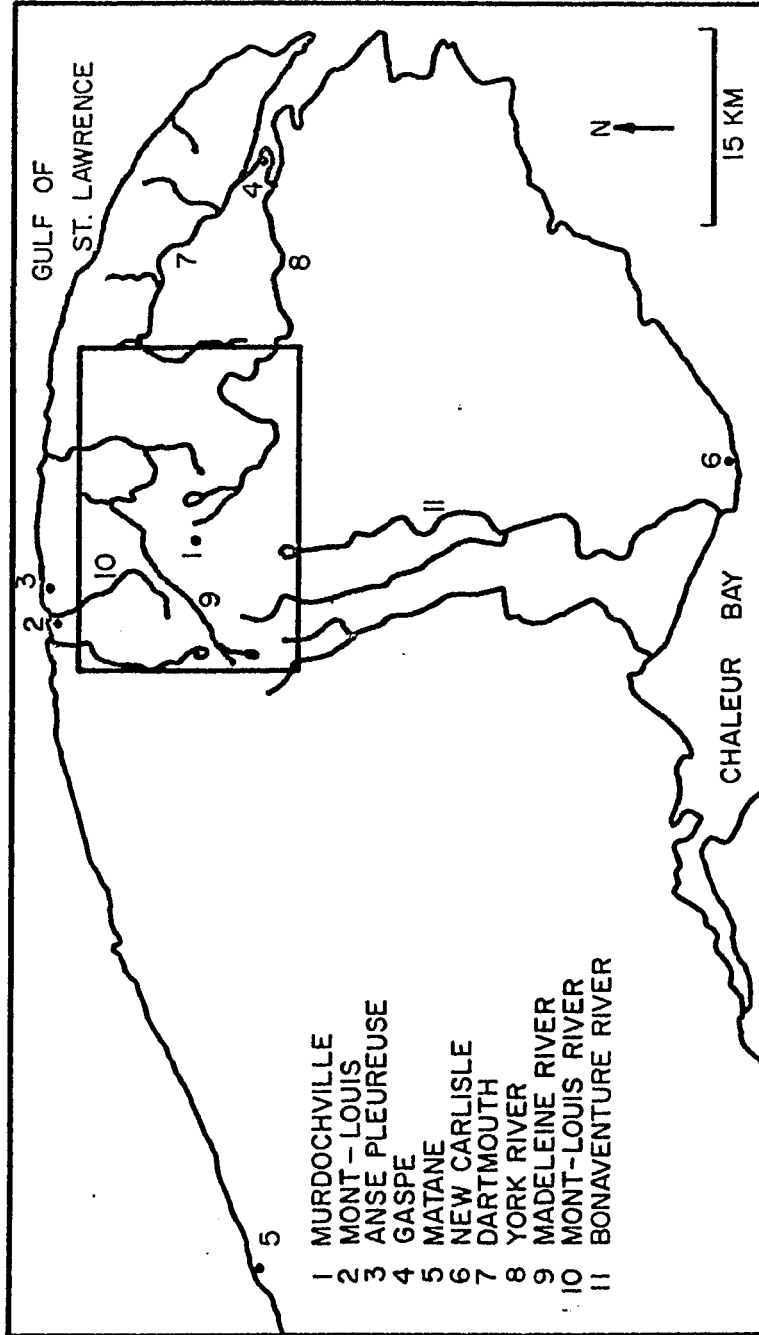
Murdochville is located in the interior of the Gaspé Peninsula, at the eastern end of the Shickshock mountain range, at latitude $48^{\circ}57''$ N and longitude $65^{\circ}31''$ W. By highways, the town is 97 km W of the town of Gaspé and 40 km S of the village of Anse Pleureuse on the shore of the Saint Lawrence River.

The study area is rectangular in shape with Murdochville approximately at its center, and occupies a surface area of $3,250 \text{ km}^2$ (approximately 10% of the peninsula; Fig. 2). Henceforth all maps referred to in the thesis (except that for the geology) will be of the surface area covered by the above mentioned rectangle.

2. Topography.

The area may be divided into two distinct topographic regions. The northern half of the region has a very rough mountain topography and is, in fact, a dissected plateau. The southern half, on the other hand, is a wide valley traversing the area in a NW-SE direction. The northern part is drained by the tributaries of the York River, which have cut parallel valleys more or less in the NW-SE axis. These valleys are those formed by the Copper and Porphyre

Figure 2. Study area showing main rivers and towns of the Gaspé Peninsula.



Rivers and by York Lake, along a series of faults (Brummer 1966).

The highest elevations are those of Mounts Needle (906.5 m), Porphyre (870.8 m), Bell (863.1 m), Miller (846.4 m), Copper (812.8 m) and York or Porcupine (799.4 m). The plateau extends towards the west to the Béland River in Bonnécamp township, and represents the vestige of a once extremely mountainous area (Brummer 1966). The elevation of the valley floor ranges between 472.7 m and 610 m above sea level and the summits of the "eroded mountains" between 762.5 m and 906.5 m above sea level. All of the main valleys have a wide rounded profile typical of morphological maturity and possible glacial action.

The sources of the York River and its tributaries are also found in the region. The York River and its main tributary, the Copper form the main river drainage systems of the region. The small secondary tributaries of the York River drainage system form the steep valley slopes while the main tributaries flow through the wider mature valleys.

The northern limits of Holland township, just north of Murdochville, is approximately at the demarcation line between the Madeleine River drainage system to the north and that of the York system to the south. The Béland, Diable and Grande Rivers, tributaries of the Madeleine River, form the basic appendages of this dendritic drainage system to the north.

There are many lakes in the region. The biggest, Lake

York, is about 4 km long and 0.8 km wide and has a maximum depth of 21.4 m. The second biggest, Lake Porphyre, is approximately 396 m long and 244 m wide and serves as the towns water supply.

3. General geology.

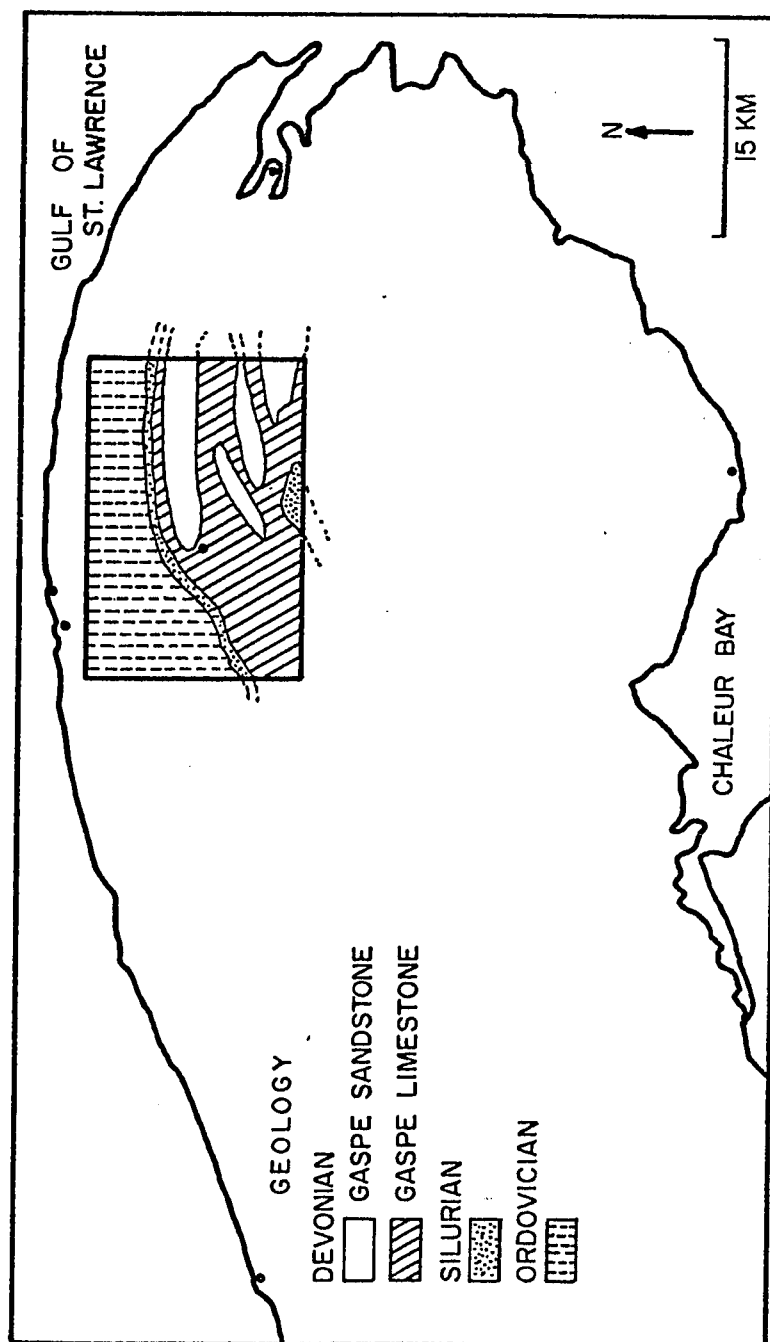
The rock formations found in the study area were formed by movements which occurred during the Acadian and Devonian time periods or possibly during the late Ordovician (McGerrigle 1954). The majority of the Devonian, Silurian, and Ordovician rocks are sedimentaries (Fig. 3). In the immediate surroundings of Murdochville are found granite porphyries which extend from the town to York Lake. Almost the whole northern half of the study area is composed of Ordovician rock, most of which is identified by the presence of fossil graptolites. It is a shale mixed with other sedimentaries and very minor amounts of volcanic rocks. A narrow continuous band of Silurian rock lies adjacent to these latter formations. The southern half of the study area is Devonian rock overlain by Gaspé Limestone and Sandstone series.

The Gaspé Copper Mines ore deposits lie in Lower and Middle Devonian sedimentary rocks, the most common of which are impure limestone and calcareous silstones, shales and sandstones.

4. Climatology.

In the classification of Köppen modified by Ackerman (1941) the Gaspé peninsula is near the demarcation line

Figure 3. Geology of the Murdochville area.



between the climatic types 'subarctic' (Dfc) and 'temperate' (Dfb). The 'subarctic' type is a climatic region of cold temperatures with a humid winter, a short and cool summer season with less than four months having temperatures higher than 10°C . The 'temperate' type has a higher annual temperature and a cool summer, where the average temperature for the warmest month is lower than 22°C . These two regions have January temperatures below zero degrees centigrade and are both characterised by the absence of a dry season.

According to Thornthwaite's (1931) classification the line between the climatic types 'taiga' (boreal) and 'humid' (denoted D' and DB'2 respectively) is found at a more northern latitude. This line corresponds to the 15.6°C isotherm for the warmest month of the year.

Villeneuve (1948), places the entire Gaspé peninsula in the 'temperate' zone but points out two sub-types: the 'maritime' climate of the Gaspé peninsula as compared to the 'continental' climate of the interior of Québec. The climate of the Murdochville study area, however, does not strictly conform with Villeneuve's 'temperate maritime' classification. A comparison of the climatic normals of selected weather stations from both 'temperate continental' and 'temperate maritime' regimes and that of Murdochville (climographs Fig. 4 and 5) will give a perspective of the climate of the interior of the Gaspé peninsula and of the study area.

Chibougamau (Fig. 4a) in the northern part of the

'temperate continental' climatic zone has seasonal differences in temperature more pronounced than changes in rainfall and the summer season tends to be slightly wetter than the winter. The mean annual temperature and precipitation range is 35.5°C and 86.3 mm respectively and is typical of these northern boreal regions. There is abundant rainfall all year round.

Val d'Or (Fig. 4b) located $3^{\circ}29''$ W and $1^{\circ}51''$ S of Chibougamau also has pronounced variations in temperature but has a much lower precipitation amplitude, 54.6 mm as compared to 86.3 mm for Chibougamau. This is mainly attributed to moisture laden winds coming from the Great Lakes region. There is no marked dry or wet season, however the bulk of the precipitation falls during the summer and winter. In general the large amplitudes of both normals (i.e. temperature and precipitation) clearly identify these two areas as having a 'temperate continental' climate.

Mount-Louis (Fig. 5a) on the other hand has a typical 'temperate maritime' climate as shown by the very narrow amplitude of the normals and by the absence of extreme temperatures, the mean annual temperature of 3.4°C is 2.4 times higher than that of Val d'Or. There are no dry seasons on the Gaspé peninsula coast, the precipitation peaks occur in summer, autumn and winter. There is, however a strong temperature gradient.

The climate of the study area (Fig. 5b) at and around

Figure 4. Climographs of selected weather stations in the province of Québec (a) Chibougamau, (b) Val d'Or.

CLIMATE TYPE : TEMPERATE CONTINENTAL

CHIBOUGAMAU

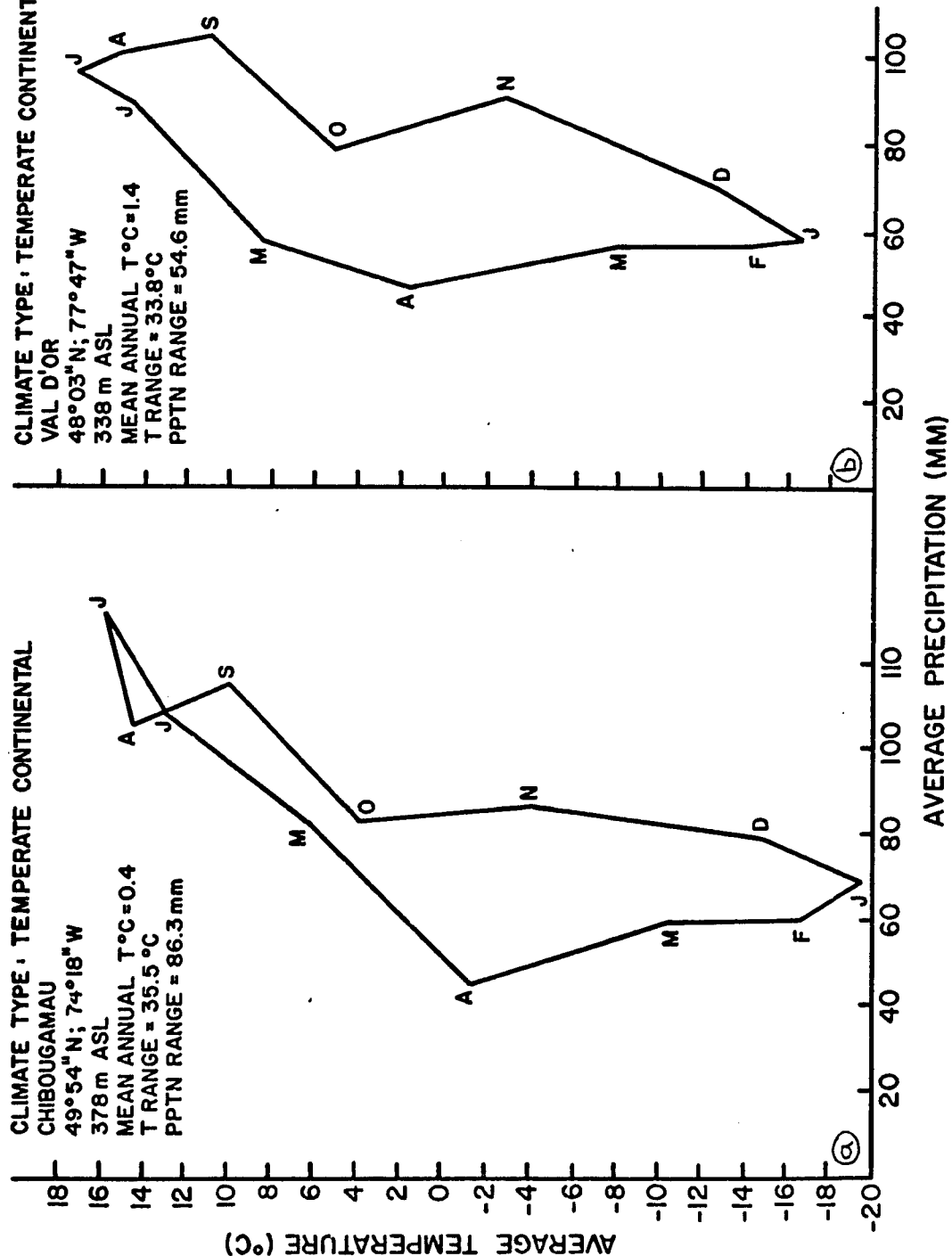
49°54"N; 74°18"W

378 m ASL

MEAN ANNUAL T°C = 0.4

T RANGE = 35.5°C

PPTN RANGE = 86.3 mm



CLIMATE TYPE : TEMPERATE CONTINENTAL

VAL D'OR

48°03"N; 77°47"W

338 m ASL

MEAN ANNUAL T°C = 1.4

T RANGE = 33.8°C

PPTN RANGE = 54.6 mm

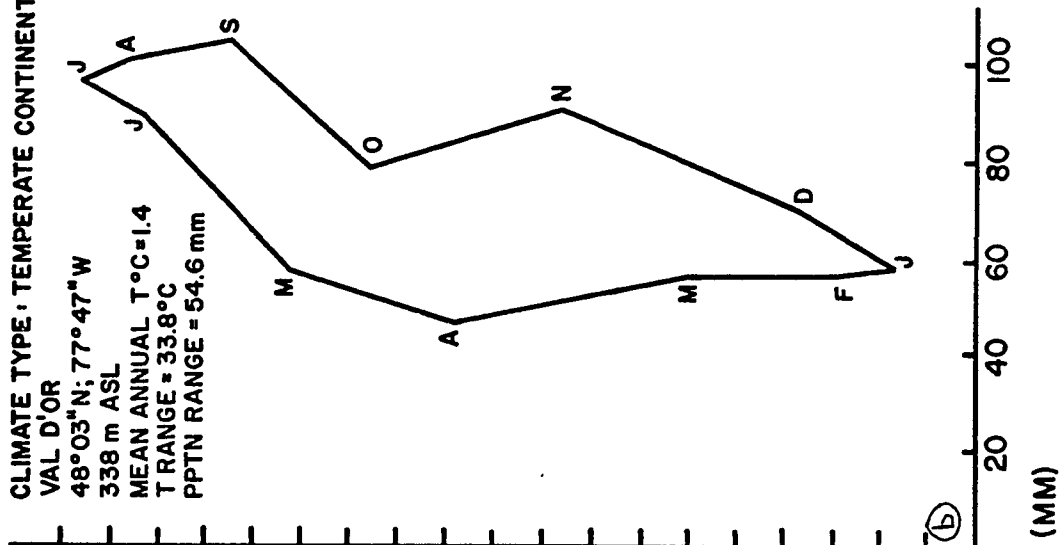


Figure 5. Climographs of selected weather stations in the province of Québec (a) Mont-Louis, (b) Murdochville.

CLIMATE TYPE : TEMPERATE MARITIME

MONT-LOUIS

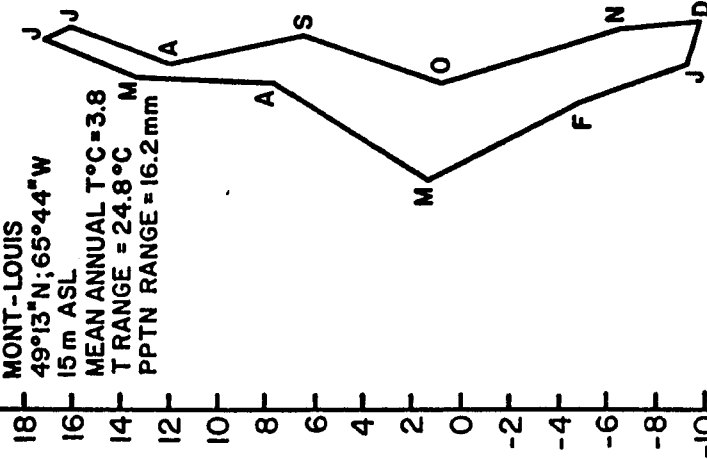
49°13'N; 65°44'W

15 m ASL

MEAN ANNUAL T°C = 3.8

T RANGE = 24.8°C

PPTN RANGE = 16.2 mm



CLIMATE TYPE : MODIFIED TEMPERATE MARITIME

MURDOCHVILLE

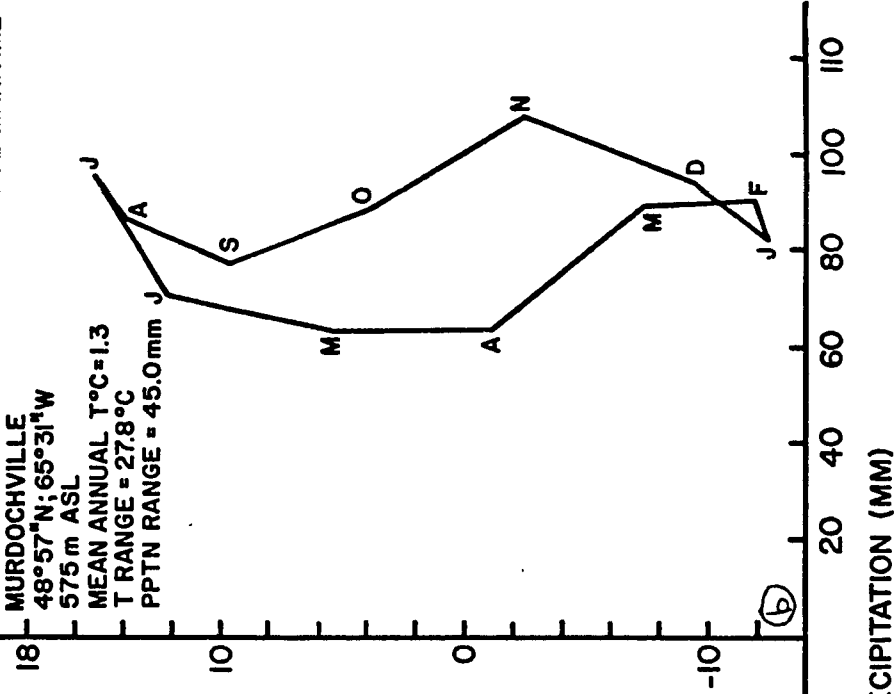
48°57'N; 65°31'W

575 m ASL

MEAN ANNUAL T°C = 1.3

T RANGE = 27.8°C

PPTN RANGE = 45.0 mm



Murdochville, previously classified as 'temperate maritime', has some continental affinities, and is classified in this work as a 'modified temperate maritime' climate for the following reasons.

The region has three peak rainfall periods, in the summer, autumn and winter, as at the maritime Mont-Louis station (Fig. 5a). But, the large precipitation amplitude at Murdochville (45.0 mm; Fig. 5b) is reminiscent of that found at continental Val d'Or (54.6 mm; Fig. 4b) and is 2.8 times larger than at Mont-Louis (16.2 mm; Fig. 5a). The total annual precipitation is higher at Murdochville (1011.0 mm) than on the Gaspé coast (902.0 mm). The dominant moisture laden NW winds (Fig. 10) and the high altitude (575 m) are probably responsible for the bulk of the precipitation, although cyclonic storms coming from the SE during the summer contribute to this total.

The temperature range in the study area (27.8°C; Fig. 5b) is similar to that on the coast (24.8°C; Fig. 5a) but the mean annual temperature (1.3°C) is considerably lower than at Mont-Louis (3.8°C) and corresponds to that of continental Val d'Or. Both Mont-Louis and Murdochville have six months of freezing weather but the latter area has two of these months below -10°C as compared to Mont-Louis which has somewhat milder winters (due to the maritime effect) with no temperatures below -10°C. Murdochville has less than four months with temperatures above 10°C, which is typical of 'subarctic' climatic regions.

The number of growing degree ($^{\circ}\text{C}$) days (Wilson 1971) at Murdochville is similar to that of Chibougamau (1800) which is located at the northern limit of the 'temperate continental' and is 400 growing degree days less than at Mont-Louis for 'temperate maritime' climates.

All of these characteristics reflect both 'maritime' and 'continental' climates due to certain influences from the Gulf of St. Lawrence and to the increased altitude in the interior.

In summary, the 'temperate maritime' climate is limited to the coast of the Gaspé peninsula. The Murdochville area which receives more precipitation, has a shorter growing season, a lower mean temperature and a greater range in the normals when compared to the true 'maritime' climate, is classified as having a 'modified temperate maritime' climate. Sanderson (1948) produced several maps of Canada on which are shown isopleths of potential evapotranspiration, moisture and summer concentration of thermal efficiency. From these maps the climate of Mont-Louis is classified as $B_4C_2'rb_1'$ (a true maritime situation) and Murdochville would be classified as a $AC_2'rb_1'$ (a modified temperate maritime climate) for the reasons given above. The fact that Murdochville has a perhumid (A) moisture index and that Mont-Louis has a humid (B_4) index shows an altitudinal influence of the interior plateau. Both stations are in the microthermal category C_2' (i.e. they have a potential evapotranspiration index of between 16.83 cm and 22.44 cm)

and both have a summer concentration of thermal efficiency between 61.6% and 68.0% which results in a displacement of C_2' to b_1' (i.e. maritime). According to these parameters Murdochville also has a 'modified temperate maritime' climate because of a higher moisture index.

5. Forest type.

Since Dansereau (1944, 1950), Dansereau and Raymond (1948, 1949) and Scoggan (1950) have previously described the flora and vegetation of the Gaspé Peninsula, detailed analysis of the vascular flora will not be given in this work. However, since part of the thesis deals with metal accumulation in certain vascular plants and since the interior of the peninsula has a very different vegetation structure than the surrounding coastal plain, a brief description of the vegetation will be given.

The modified climatic conditions of the Murdochville study area are reflected in the vegetation. Rowe (1972) classifies the vegetation as a boreal forest type subsection Gaspé. The subsection occupies the elevated region of the Gaspé peninsula. In general most of the forests have a closed canopy and are composed of Abies balsamea, Picea mariana, and P. glauca mixed at time with Betula papyrifera. The well drained areas of the interior are characterised by thin podzols, while acid Sphagnum sp. bogs occupy poorly drained situations.

All of the stands included in the present study fall within the plant association Abietetum Balsameae (Dansereau

1959). The dominant megaphanerophyte (Pg), A. balsamea, forms an almost continuous canopy, with P. mariana being present as a subordinate tree. In wetter situations the latter may be replaced by Thuja occidentalis. The shrub and herb layers are discontinuous and interrupted, Chiogenes hispidula, Linnaea borealis, Cornus canadensis, Oxalis montana, Maianthemum canadense, are the most common species. The floors of the closed stands are usually covered by extensive mats of the woodland mosses Hylocomium splendens and Pleurozium schreberi.

CHAPTER II

METHODS

A. Analysis of the Ambient Environment.

1. Survey of sulphur dioxide in the atmosphere.

The ambient sulphur dioxide concentration data for the years 1972, 1973, and to September 1974 was measured by the Environmental Monitoring Department of Gaspé Copper Mines Ltd. Sulphur dioxide was absorbed on sulphation plates exposed at specified sites in the study area. These plates are composed of circular paper discs impregnated with lead peroxide that are clipped to plastic plate covers held together by durable plastic brackets. The sulphur dioxide reacts with the lead peroxide to form lead sulphate. The following facts have been established concerning the reaction between lead peroxide and sulphur dioxide (Lack and Schnitzler 1973): a) both the reagent (lead peroxide) and the product (lead sulphate) are insoluble in water, hence the amount of sulphate produced is a reflection of the amount of sulphur dioxide in the air, b) the yield of lead sulphate is proportional to the concentration of sulphur dioxide for all concentrations up to one part per thousand (1000 ppm), c) when air containing a known amount of sulphur dioxide is blown slowly over a sulphation plate, the reaction rate is found to be constant. The resulting reading is approximately $13 \text{ mg SO}_3/100 \text{ cm}^2/\text{day}$ which is well below any of the readings obtained in the study area, d) wind speed does not significantly affect the reactivity of the plates,

e) a temperature increase of 10°C increases the reactivity by 1%, hence the accuracy of the values cited should be $\pm 1\%$, f) changes in humidity have no significant effects but if the lead peroxide surface is wet the reactivity increases slightly, and g) different batches of lead peroxide plates can have different reactivity rates. Hence, it is advantageous to use this continuous monitoring system for obtaining reliable qualitative and relative data. This type of survey provides an invaluable source of information as it is an indication of the trends in any given area.

Three sulphation plates were exposed at each site for periods ranging from one month to two months for the whole year. All of the values were corrected to a 30-day exposure period. Each plate was nailed horizontally at a height of approximately two meters above the ground onto wooden boards or exposed decapitated tree boles freed of branches. All of the plates were located away from roads and in clearings to prevent contamination from traffic and dust and to eliminate the filtering action of the vegetation. The sulphation at each site was expressed as $\text{mg SO}_3/100 \text{ cm}^2/\text{day}$. These values were converted to ppm by means of the relationship: one $\text{mg SO}_3/100 \text{ cm}^2/\text{day}$ is equivalent to 0.035 ppm SO_2 (Huey 1972). These were then converted to ppb values.

The annual averages for 51 monitoring sites (including 39 of the 40 vegetation analysis sites) are found in

Tables 9 and 10. Figures 6, 7, 8 and 9 depict the pollution isopleths for these time periods and for their summation.

It is important to note that when the exposure plate values are studied to determine the pollution trends, only two types of valid comparison can be made. Each site is either considered on its own or the yearly averages of all sites in the study area are compared.

2. Incident rainfall and stemflow analysis.

a) Study sites.

To determine the distribution pattern of expected acid rain resulting from the gaseous emissions of the Gaspé Copper Mines smelter and its consequent effects upon the epiphytic vegetation of Abies balsamea, study sites were selected in an area thought to be most affected by the emissions of the smelter because the frequency of the dominant winds was highest in this direction (Fig. 10). The area chosen was in the ESE and SE sectors.

For sampling purposes six sites were established. Five of these sites, numbered 11, 15, 21, 22 and 24, were located respectively at 6.3; 8.3, 14.9, 19.5 and 3.5 km distance along the ESE and SE direction from the pollution source. The sixth site, number 43, chosen in a relatively non-polluted area at a distance of 20.0 km SW of the smelter served as a control site (Fig. 11). At each site three 500 m² quadrats were investigated.

Table 9. Annual arithmetic means (ppb 1972, 1973) and nine-month arithmetic mean (ppb 1974) of the sulphur dioxide concentration at 51 sites in the Murdochville Gaspé Copper Mines study area ($\pm$ standard deviation).

Site	km from smelter	Ambient SO ₂ concentration (ppb)		
		1972	1973	1974
28	7.7 N	16 $\pm$ 8	13 $\pm$ 11	8 $\pm$ 4
30	11.5 N	13 $\pm$ 7	8 $\pm$ 6	5 $\pm$ 4
33	17.3 N	12 $\pm$ 5	5 $\pm$ 6	2 $\pm$ 1
331	20.0 N	4 $\pm$ 1	7 $\pm$ 9	2 $\pm$ 1
26	2.6 NNE	70 $\pm$ 39	44 $\pm$ 20	48 $\pm$ 94
25	3.7 NNE	49 $\pm$ 18	34 $\pm$ 19	21 $\pm$ 34
201	25.7 NE	6 $\pm$ 2	3 $\pm$ 3	2 $\pm$ 1
17	6.9 ENE	26 $\pm$ 19	11 $\pm$ 8	5 $\pm$ 2
20	20.0 ENE	14 $\pm$ 11	5 $\pm$ 5	1 $\pm$ 1
6	2.0 E	39 $\pm$ 11	32 $\pm$ 15	31 $\pm$ 22
7	2.6 E	80 $\pm$ 45	56 $\pm$ 68	50 $\pm$ 28
8	3.0 E	58 $\pm$ 23	40 $\pm$ 40	49 $\pm$ 40
1	3.1 E	89 $\pm$ 58	49 $\pm$ 27	42 $\pm$ 19
18	11.0 E	14 $\pm$ 6	13 $\pm$ 9	8 $\pm$ 7
19	15.9 E	2 $\pm$ 2	7 $\pm$ 8	4 $\pm$ 3
9	4.8 ESE	46 $\pm$ 15	34 $\pm$ 25	42 $\pm$ 55
16	7.5 ESE	16 $\pm$ 5	18 $\pm$ 10	10 $\pm$ 11
15	8.3 ESE	22 $\pm$ 8	17 $\pm$ 17	13 $\pm$ 8

Table 9 cont'd.

21	14.9 ESE	19 ± 6	12 ± 11	8 ± 6
241	40.2 ESE	11 ± 20	10 ± 20	3 ± 1
102	3.2 SE	55 ± 17	35 ± 17	28 ± 19
12	3.4 SE	40 ± 34	17 ± 14	11 ± 8
10	5.0 SE	25 ± 11	28 ± 18	26 ± 20
11	6.3 SE	36 ± 8	23 ± 15	32 ± 24
14	15.9 SE	17 ± 1	13 ± 11	7 ± 4
22	19.5 SE	16 ± 6	7 ± 4	5 ± 4
23	25.4 SE	18 ± 12	7 ± 5	4 ± 3
231	30.5 SE	10 ± 8	12 ± 16	5 ± 4
24	35.5 SE	10 ± 5	5 ± 3	3 ± 2
P	0.5 SSE	62 ± 21	46 ± 28	110 ± 59
V	1.1 SSE	64 ± 16	85 ± 35	111 ± 67
N	1.0 S	84 ± 37	48 ± 21	51 ± 56
101	5.0 S	30 ± 11	27 ± 23	23 ± 17
421	18.0 SSW	—	3 ± 2	2 ± 2
42	14.6 SW	9 ± 5	5 ± 4	1 ± 1
43	20.1 SW	10 ± 5	6 ± 4	1 ± 1
45	33.8 SW	6 ± 1	5 ± 4	6 ± 12
401	3.2 WSW	—	15 ± 13	5 ± 2
41	11.4 WSW	11 ± 4	13 ± 25	2 ± 2
44	25.8 WSW	9 ± 6	4 ± 3	2 ± 1
40	6.4 W	17 ± 18	6 ± 4	3 ± 4
39	6.3 WNW	20 ± 26	6 ± 5	3 ± 3
38	3.4 NW	48 ± 18	36 ± 43	21 ± 7

Table 9 cont'd.

32	20.5 NW	7 ± 3	4 ± 3	2 ± 1
35	0.9 NNW	96 ± 80	55 ± 46	39 ± 24
36	1.3 NNW	108 ± 49	77 ± 41	28 ± 11
34	1.3 NNW	65 ± 34	37 ± 28	22 ± 17
37	2.3 NNW	90 ± 45	79 ± 55	58 ± 45
27	6.6 NNW	28 ± 11	19 ± 23	15 ± 5
31	14.1 NNW	10 ± 4	7 ± 6	3 ± 1
332	23.3 NNW	8 ± 5	8 ± 7	3 ± 1

Table 10. Average of the annual and nine-month arithmetic means of the sulphur dioxide concentration (ppb) for the time interval 1972-1974 at 51 sites in the Murdochville Gaspé Copper Mines study area ($\pm$ standard deviation).

SO ₂ (ppb)			SO ₂ (ppb)		
Site	Location	$\pm$ S.D.	Site	Location	$\pm$ S.D.
28	7.7 N	12 $\pm$ 4	16	7.5 ESE	15 $\pm$ 4
30	11.5 N	9 $\pm$ 4	15	8.3 ESE	17 $\pm$ 5
33	17.3 N	6 $\pm$ 5	21	14.9 ESE	13 $\pm$ 6
331	20.0 N	4 $\pm$ 3	241	40.2 ESE	8 $\pm$ 4
26	2.6 NNE	54 $\pm$ 14	102	3.2 SE	39 $\pm$ 14
25	3.7 NNE	35 $\pm$ 14	12	3.4 SE	23 $\pm$ 15
201	25.7 NE	4 $\pm$ 2	10	5.0 SE	26 $\pm$ 2
17	6.9 ENE	14 $\pm$ 10	11	6.3 SE	30 $\pm$ 7
20	20.0 ENE	7 $\pm$ 7	14	15.9 SE	12 $\pm$ 5
6	2.0 E	34 $\pm$ 4	22	19.5 SE	9 $\pm$ 6
7	2.6 E	62 $\pm$ 16	23	24.5 SE	10 $\pm$ 7
8	3.0 E	49 $\pm$ 9	231	30.5 SE	8 $\pm$ 5
1	3.1 E	60 $\pm$ 25	24	35.5 SE	6 $\pm$ 4
18	11.0 E	17 $\pm$ 3	V	1.1 SSE	87 $\pm$ 24
19	15.9 E	4 $\pm$ 3	N	1.9 S	61 $\pm$ 20
9	4.8 ESE	41 $\pm$ 6	101	5.0 S	27 $\pm$ 4
P	0.5 SSE	72 $\pm$ 33	38	3.4 NW	35 $\pm$ 14
421	18.0 SSW	3 $\pm$ 1	32	20.5 NW	4 $\pm$ 3
42	14.6 SW	5 $\pm$ 5	35	0.9 NNW	63 $\pm$ 29

Table 10 cont'd.

43	20.1 SW	6 ± 5	36	1.3 NNW	71 ± 40
45	33.8 SW	6 ± 1	34	1.3 NNW	41 ± 22
401	3.2 WSW	10 ± 7	37	2.3 NNW	76 ± 16
41	11.4 WSW	9 ± 6	27	6.6 NNW	21 ± 7
44	25.8 WSW	5 ± 4	31	14.1 NNW	7 ± 4
40	6.5 W	9 ± 7	332	23.3 NNW	6 ± 3
39	6.3 WNW	10 ± 9			

Figure 6. Nineteen seventy two distribution of sulphur dioxide in the Murdochville study area(ppb).

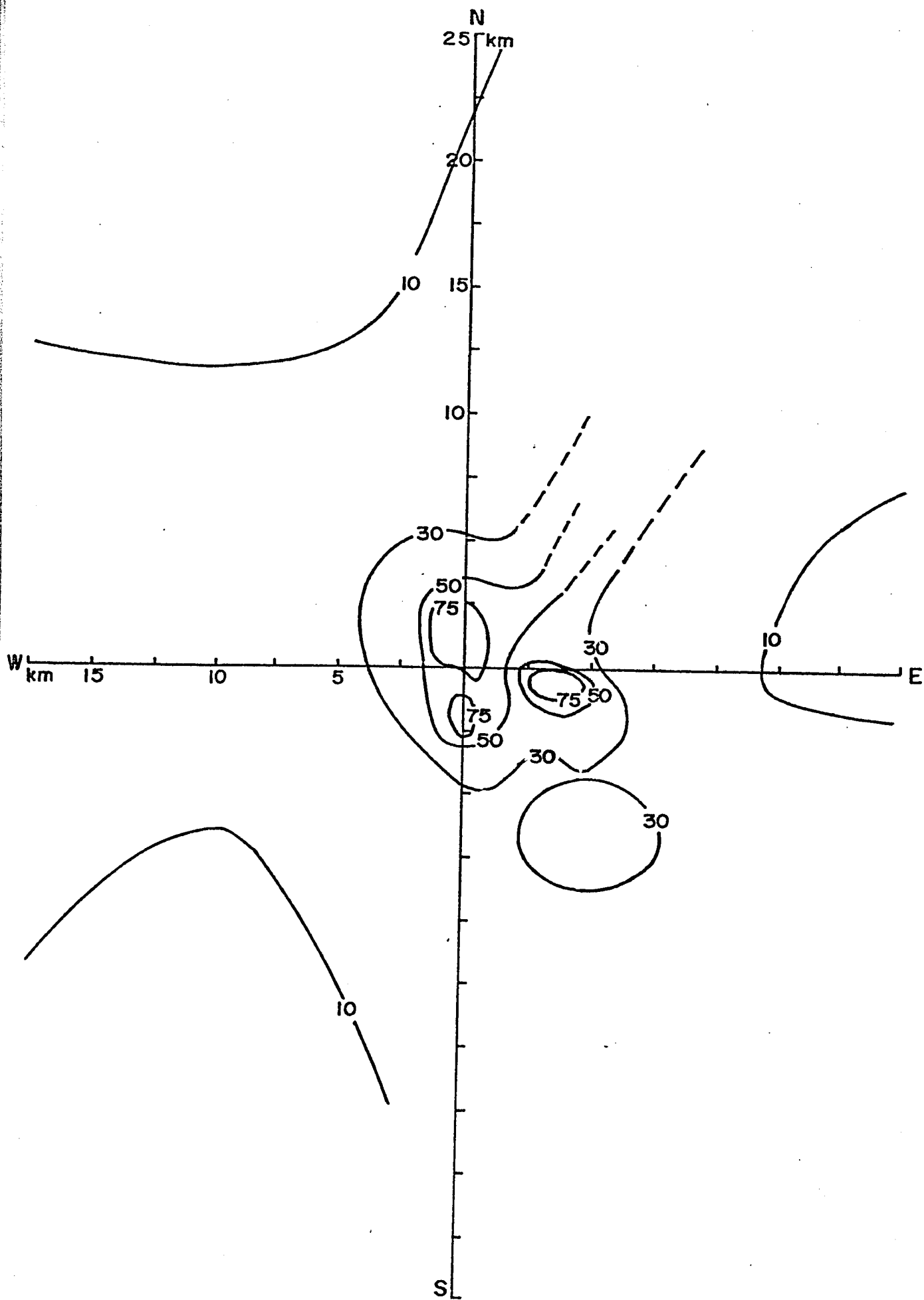


Figure 7. Nineteen seventy three distribution of sulphur dioxide in the Murdochville study area.(ppb).

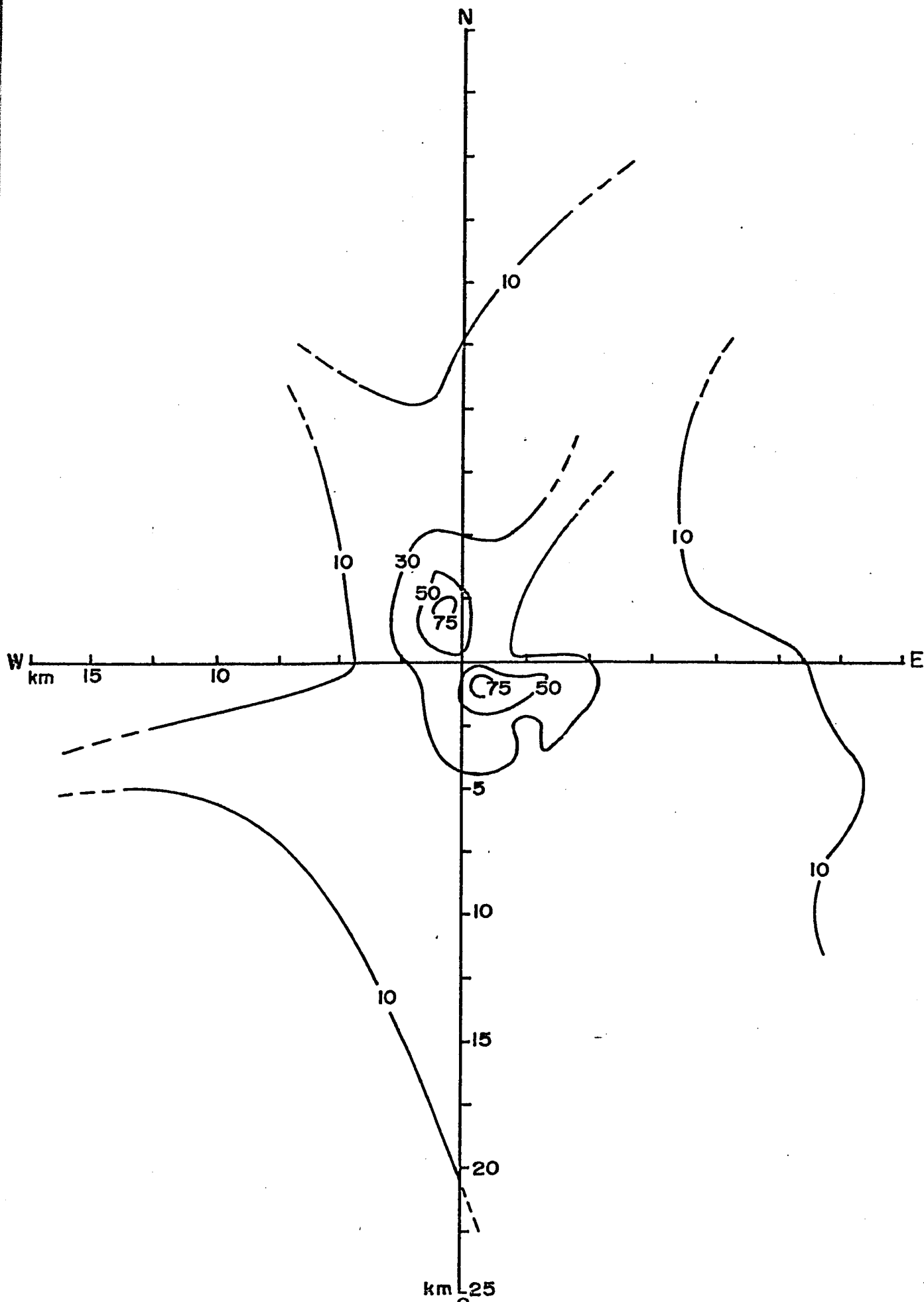


Figure 8. Nine month 1974 sulphur dioxide distribution
in the Murdochville study area (ppb).

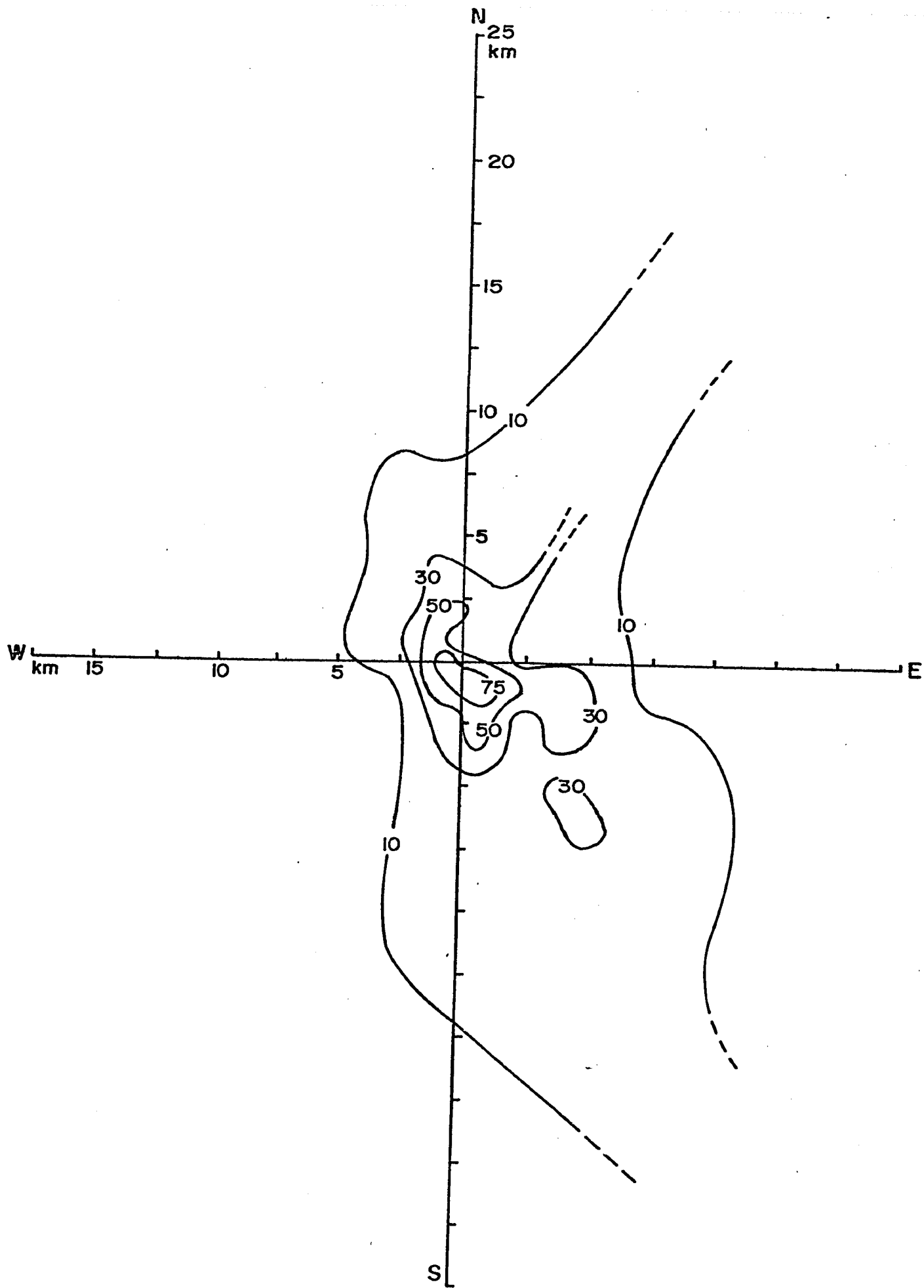


Figure 9. Thirty three month (1972 to 1974) distribution of sulphur dioxide in the Murdochville study area (ppb).

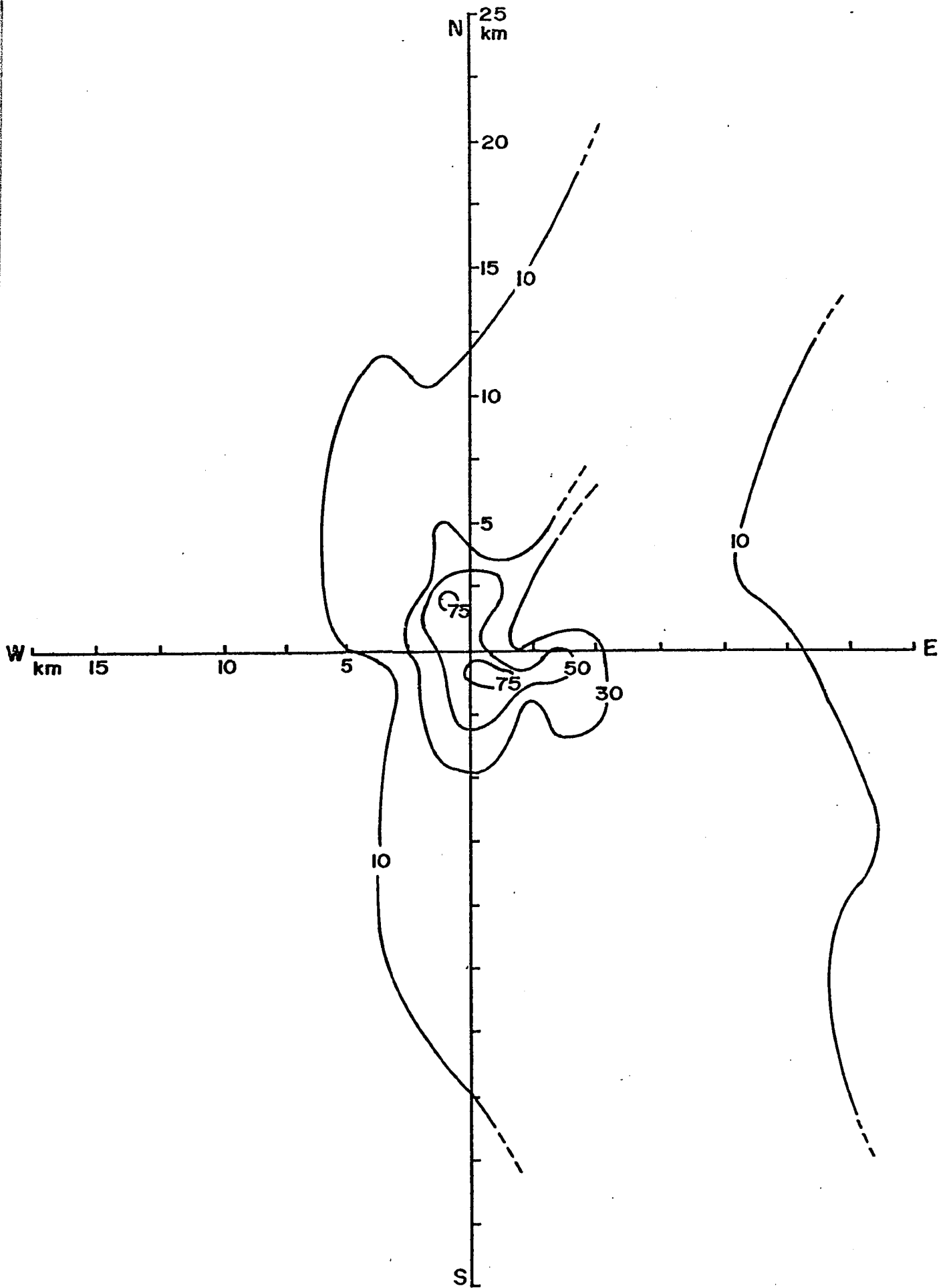


Figure 10. January 1973 wind rose for the weather station at Murdochville.

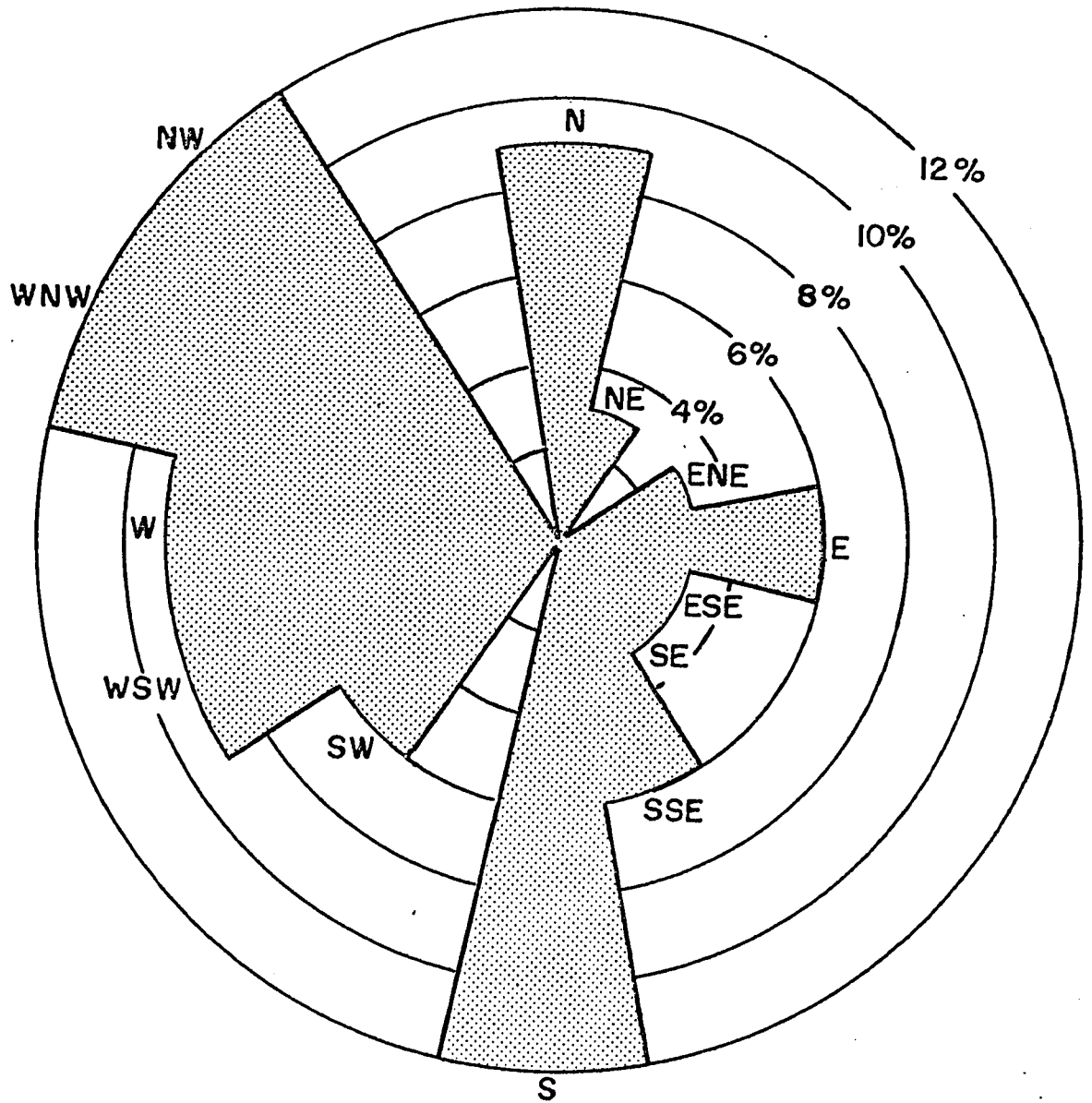
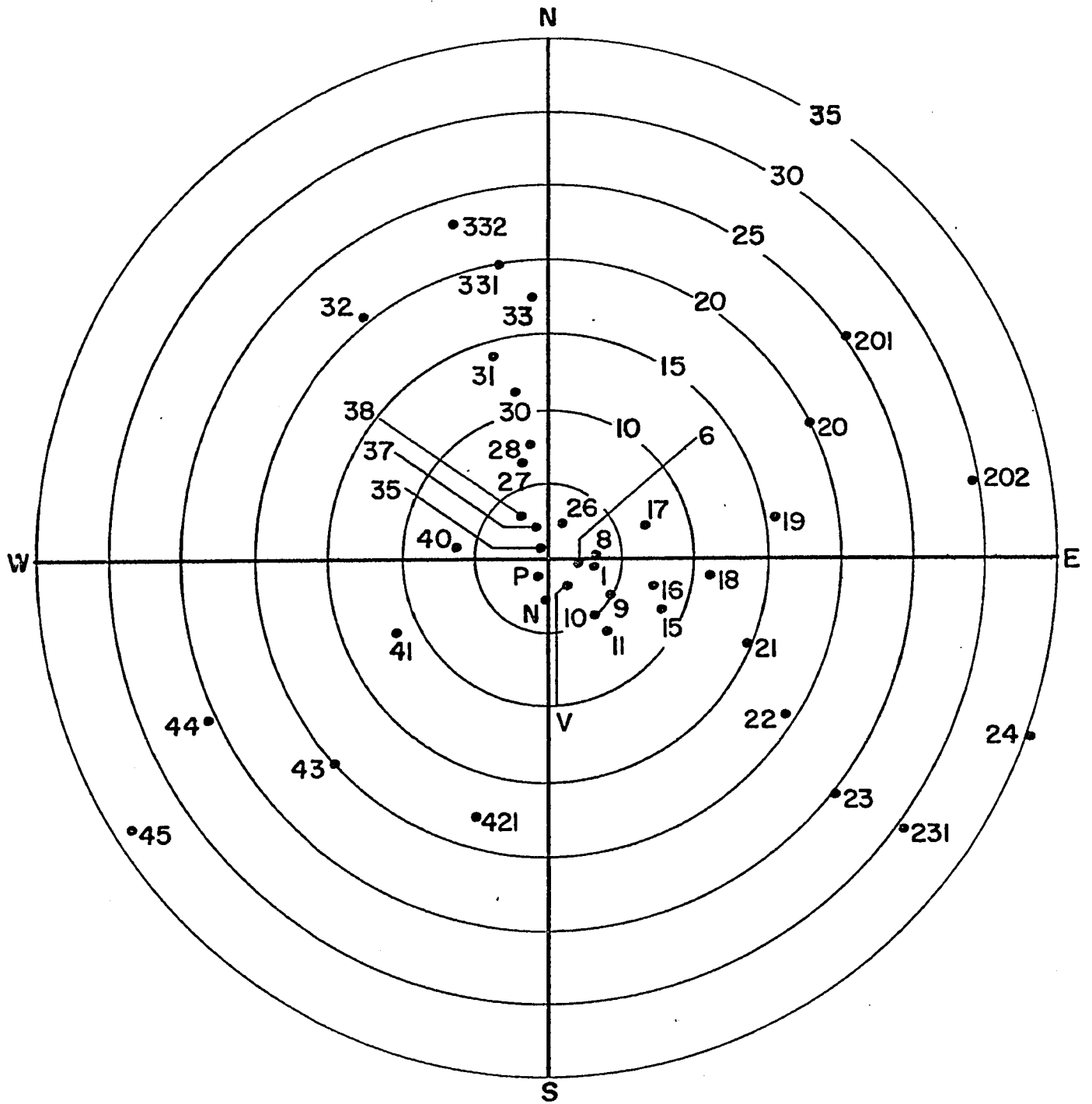


Figure 11. Polar diagram of the study sites in the Murdochville study area. The origin is the location of the copper smelter and the radii are in five km intervals.



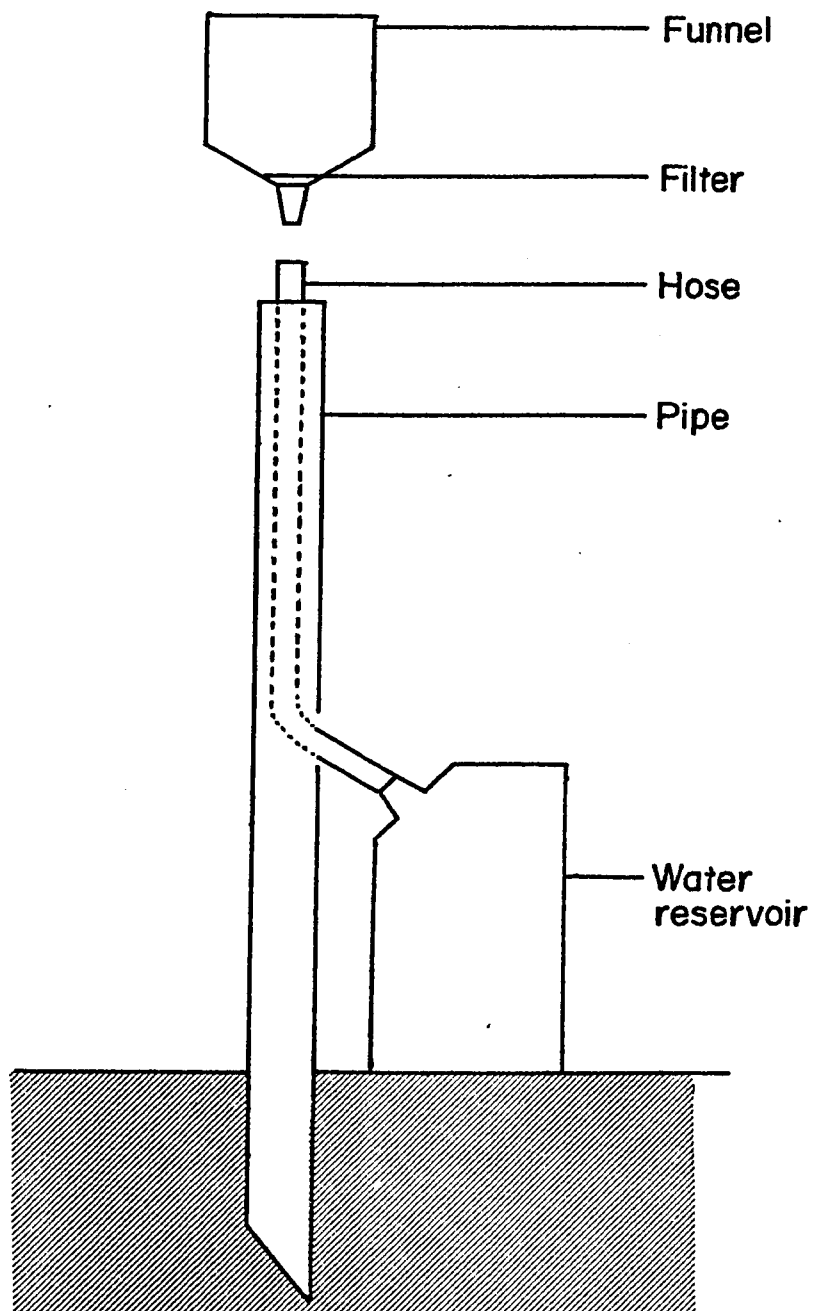
b) Sampling of incident rainfall.

At each of the six sites mentioned in the previous section, three measurements of incident rainfall were made during the course of the investigation. Rainfall collectors were set up in open fields or in clearings away from roads, so that fluctuations in water quality due to eddy currents, rain splashes from trees and contamination from dust could be avoided. The collector, consisting of a funnel of 30 cm diameter and a water reservoir of about five liter capacity, was assembled at the site. The funnel stem and the water reservoir were connected with a two cm wide polyethylene tube which passed vertically through a one meter long hard plastic pipe having a side exit at its lower end for the polyethylene tube. A polyethylene filter was placed in the funnel to separate solid contaminants from the water sample and a clean sterilized plastic bag was placed in the water reservoir to collect the rain water (Fig. 12).

c) Sampling of stemflow.

At each site six (two per stand, i.e. quadrat) tall A. balsamea trees were used for stemflow collection. The stemflow collecting apparatus was devised as follows. A 20 cm wide fine-wire-screen was affixed spirally to the periphery of the tree trunk at breast height and the lower end of the spiral was shaped into a cup like structure. A small hole was cut at the bottom of the wire-screen cup to allow a two cm wide polyethylene tube to pass through it.

Figure 12. Incident rainfall collecting device.

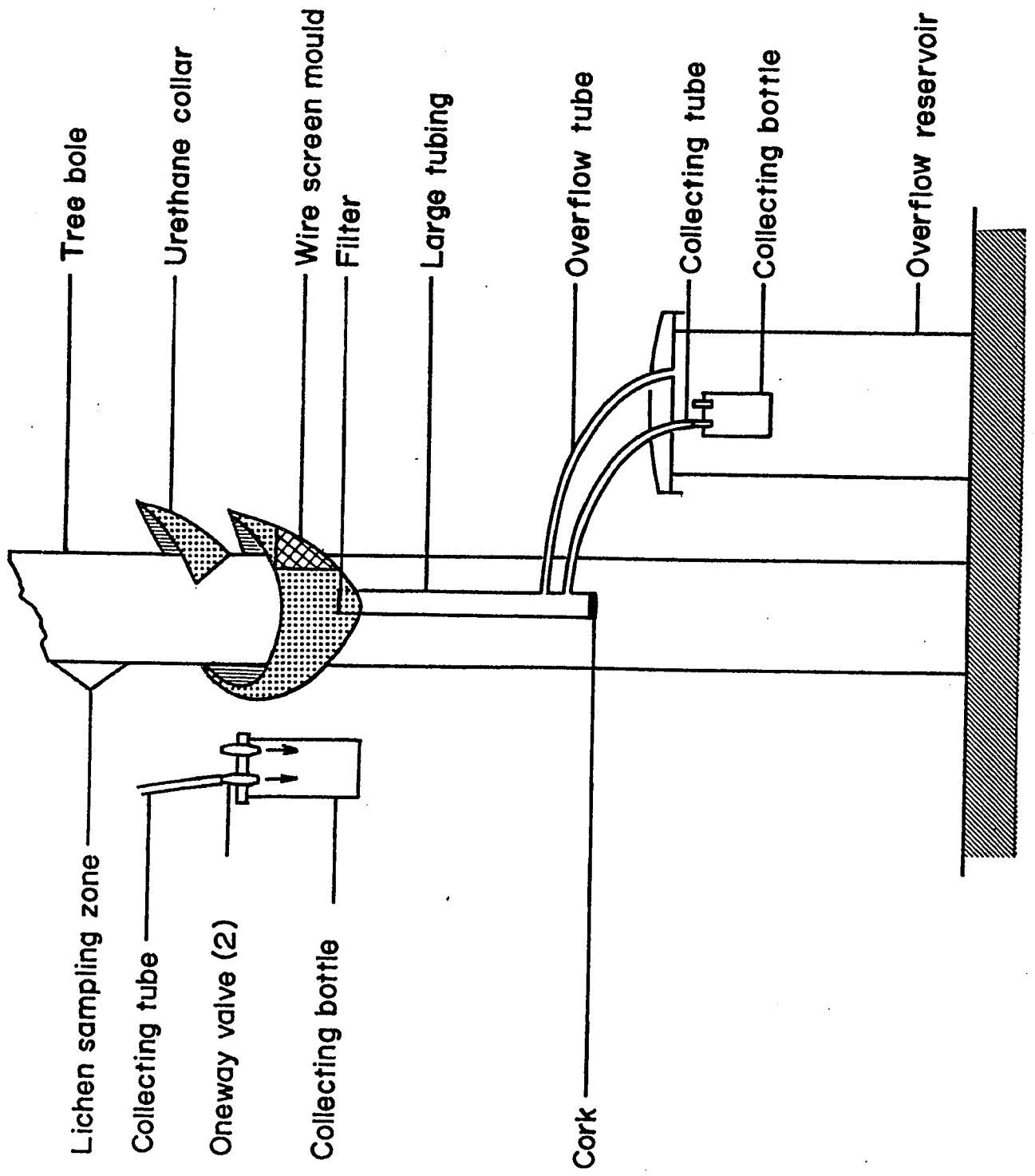


A chemically inert quick-hardening polyurathane foam was poured into the wire mold to make it a leakproof water channel. The upper end of the tube was covered with a polyethylene filter and its lower end was closed tightly with a cork. The tube was taped to the tree surface so that it did not hang loose. Two holes, each 0.75 cm wide, were cut laterally and slightly above the corked-end of the tube. In these holes plastic connectors were inserted which in turn were attached to polyethylene tubes. One of these tubes, termed the collecting tube, led via a one-way valve to a one liter polyethylene collecting bottle in which a clean, sterilized plastic bag was placed. A second one-way valve, fitted into the collecting bottle, facilitated the escape of air and prevented the loss of stemflow water. The other tube, termed the overflow tube, was connected to a 72 liter overflow reservoir (Fig. 13). A total of 90 stemflow collections were made during the entire period of the investigation.

d) Analysis of rainfall and stemflow water samples.

The volumes of water from the incident rainfall and from the stemflow were measured after every measurable rain. The water samples from the plastic bags were transferred into 500 ml narrow mouth polyethylene bottles which had been acid cleaned and rinsed with distilled water. Measurements of pH were made immediately. The samples were then acidified with five ml of concentrated nitric acid and sent to the Environmental Laboratory,

Figure 13. Stemflow collecting device.



Noranda, Québec, for determination of their total sulphur content. The stemflow samples were also analysed for Cd, Cu, Pb and Zn by atomic absorption spectrophotometry.

The analytical procedures are described below.

3. Analytical procedures.

a) Plant and wood material.

i) Heavy metals.

A five gram sample was wet digested in a 4:1 mixture of nitric-perchloric acid. The sample was first digested for two hours in the nitric acid, after which was added the perchloric acid. Digestion was continued until perchloric acid fumes were given off. If the sample was not colourless at this point 25 mls of nitric acid were added and the sample digested again to dryness.

The residue was then entirely dissolved by boiling it in a solution of five mls of hydrochloric acid and 40 mls of demineralized water. The cooled sample was then filtered and volumed to 50 mls. The sample was now ready for atomic absorption analysis for Pb, Cu, Cd, and Zn.

ii) Total sulphur.

Two grams of sample was digested as above. The acidic hydrochloric acid solution was diluted to approximately 400 mls and boiled. Ten mls of 10 percent barium chloride was added to this boiling solution, stirred and allowed to stand for approximately two hours. This was then filtered through a # 42 paper. This filter was carefully washed to remove free chlorides and transferred to a porcelaine

crucible. The filter paper was then completely charred. The residue was cooled and weighed and the total sulphur calculated as follows:

$$\% S = \frac{\text{wt. barium chloride} \times 13.74}{\text{wt. of sample}}$$

b) Water samples.

The heavy metals were determined by the direct aspiration of the water samples into the atomic absorption flame.

The total sulphur was determined by treating 20 mls of water sample in the same manner as was the dissolved plant material in the sulphur determination. The following formula was used to calculate g/l S;

$$\text{g/l S} = \frac{\text{wt. residue} \times 137.3}{\text{vol. sample}}$$

the unit used was ppm S.

B. Biotic Environment Analysis.

1. Buffer capacity and pH determinations.

a) Sampling and analysis of bark.

At each site 30 mature and healthy trees of A. balsamea were selected, taking at least 10 trees in each of three 500 m² quadrats. Strips of lichen-free bark of approximately 3 x 10 cm were cut at breast height from four sides of the trees and stored in polyethylene bags. These bark samples were used for pH and buffer capacity determinations. Sampling below breast height was avoided because such samples are often contaminated with dust and can show higher values of pH and buffer capacity (Skye 1968). No portion of wood was attached to the bark. Old and decaying trees were not studied (Barkman 1958). The samples were air-dried for 24 hrs then finely ground in a Servall Omnimixer at 14,000 rpm for 15 minutes and dried in an oven at 110°C for 48 hrs. Two grams of the pulverized oven-dried bark were placed in a 50 ml beaker containing 10 ml of deionized water. After 24 hrs of soaking, the bark-water mixture was stirred and its pH was measured with a Beckman Type Zeromatic pH meter equipped with a Fisher combination electrode having a pH range of 0 to 14. To obtain a mean pH value for each site, the pH of the bark from the three quadrats were log transformed, averaged and reconverted to a pH value (Table 28).

For measuring buffer capacity, two sets of equal amounts of bark samples (two grams) were pulverized and

soaked in deionized water in the manner described above. To one of the bark water mixtures was added 0.1 ml aliquots up to a total volume of 1.0 ml, and then 1.0 ml aliquots up to a total of 10 ml of a 0.1 N NaOH solution. The other bark water mixture was similarly treated with 0.1 N HCl. Each time, after the addition of alkali or acid, the mixture was thoroughly stirred and allowed to stand for 10 minutes before the pH was determined.

b) Sampling and analysis of lichen thalli.

Thalli of Parmelia squarrosa and Hypogymnia physodes, lichens epiphytic on A. balsamea, were collected (when present) from bark of trees selected for stemflow collection (see above) in each of the quadrats of the six sites. Care was taken to collect the lichen samples only from the region of the trunk lying above the collar of the stemflow device (Fig. 13). The method described by Skye (1968) was used for the determination of the pH of the lichen samples. Two grams of air dried lichen thalli were ground into a beaker and then twice its volume in distilled water was added. The pH of this mixture was then determined.

2. Increment measurements of annual rings of A. balsamea.

a) Collection and preparation of material.

The sites selected for the sampling of the increments were those used for the stemflow analysis (Fig. 21).

Samples were collected during a three-week period in August 1974 when the trees were approaching their dormant phase. Only the largest and most healthy specimens of A.

balsamea were sampled at each of the three quadrats, so as to obtain long term records of tree growth and metal accumulation. The tree selected for coring were first examined to find the best place to remove the cores. Areas near branches were avoided to prevent obtaining distorted ring patterns.

At each quadrat one core taken at 1.5 m above the moss mat and well below the lowest branches, was removed from each of 15 to 30 trees, with a Swedish increment borer. All of the cores were taken on the NW side of each tree bole to reduce possible differences in chronologies (Douglass 1928). This decision was influenced by the location of the copper smelter and by the wind pattern with respect to the SE transect where the majority of the sites were located.

Upon removal each core was stored in a 30 cm long plastic straw and labelled with the quadrat and tree number. After the three-week collecting period the cores were air dried for about one month and placed on a wooden mounting tray.

Each sample was examined with a Wild M5 stereoscope at low magnification. Each annual ring was measured to the nearest 10th mm and accurately cross-dated using the method of Stokes and Smiley (1968). In cross-dating ring-width patterns narrow rings are matched for each core so that a stand chronology can be established. Cross-dating is essential to ensure that similar growth rings are compared

between sites and stands.

Once dated and measured the cores were prepared for chemical analysis (see 3. a) iv)).

3. Metal and total sulphur analysis in vegetation.

The plant species chosen for metal and sulphur determinations from the various forest strata was representative of each particular stratum.

a) Manipulation of material.

i) Bryophytes.

The ground layer mosses were collected from pure patches of either Hylocomium splendens and Pleurozium schreberi towards the center of the A. balsamea stands. Approximately 500 gms of each species were collected and placed in labelled polyethylene bags and subsequently air dried for 48 hrs. The stands sampled are shown in Fig. 11.

ii) Herbs.

One leaf from each of 10 plants taken at random near the center of each Abies stand was collected in labelled polyethylene bags and dried for 48 hrs.

iii) Lichen epiphytes.

At each site 10 A. balsamea were randomly selected and at a height of about 1.5 m from the base samples of Parmelia squarrosa and Hypogymnia physodes were collected. The thalli of the lichens were freed from extraneous materials, such as pieces of bark, algae, hepatics, mosses, etc. before they were mixed together to obtain a composite sample for each site. The samples of lichen

were air-dried at room temperature for 48 hrs, divided into equal lots and stored in polyethylene bags. One lot was sent to Noranda where As, Cd, Cu, Pb and Zn were determined, while the other lot was used for chlorophyll analysis.

iv) Bark and annual rings of A. balsamea.

After the ring measurements were completed (see above) the cores were cut into groups of five annual rings starting from the outermost ring. Each group was placed in a paper envelope and labelled with an interval number. The bark plug at the end of each core was also removed for analysis.

v) Picea mariana needles.

Picea mariana needles were also sampled. The current years growth was cut off the ends of four branches from each of 10 trees at each of the 40 sites (Fig. 11) and placed in labelled polyethylene bags. After 48 hrs of air drying the needles were collected and stored in appropriately labelled envelopes.

All of this plant material was sent to the Noranda Environmental Laboratory in Noranda, Québec, for metal and total sulphur analysis.

4. Transplant experiments and chlorophyll analysis of transplanted and naturally occurring lichen epiphytes.

a) Transplants.

i) Disc preparation.

In June 1972, 360 discs were cut from A. balsamea

trees at site 43 (Fig. 11), in a relatively unpolluted area, 20.1 km SW of the copper smelter. The discs were cut with a circular saw 48 mm in diameter, attached to a Black and Decker electric hand drill number 912, with a guide wick three mm in diameter. Three species of lichens, Parmelia squarrosa, Hypogymnia physodes and an unidentified Usnea, were present on most discs.

The lichen-bearing discs were fixed in groups of six in holes 10 mm deep and 48 mm in diameter cut in a narrow rectangular board. Each disc was secured by applying grafting wax inside the hole and by driving a 2.5 cm stainless steel nail through the center.

In all, 60 boards were prepared for exposure at 28 sites. The sites were distributed in all directions within a radius of 35 km of the smelter (Table 22). At each site, two exposure boards were fixed vertically on a tall exposed tree at a height of four to six meters on the side of the tree facing the smelter. One board was removed from the tree after four months and the second after 12 months.

ii) Photographic techniques.

Each disc was separately photographed using Kodachrome II film with electronic flash. The photographs were first taken before exposure for pollutants in June 1972. In October 1972, after the transplants had been exposed for a period of four months the two boards from each site were removed and the discs rephotographed. One of the boards was again affixed to the tree for further exposure and the

other board was brought to the laboratory for microscopic, spectrophotometric and biomass analysis of the lichens. In June 1973, after eight months of additional exposure, the remaining discs were removed, rephotographed and brought to the laboratory for analysis.

iii) Comparison of transparencies.

The three sets of transparencies for each disc which were taken prior to, after four months and after 12 months of exposure respectively were simultaneously projected and the extent of damage produced on the lichens was evaluated by noting colour changes and by estimating the dead portion of the thallus cover. This evaluation was given a numerical rating as follows:

changes in colouration (% of cover of thalli)

- 1 brownish 70-100%, whitish-gray 40-70% and/or greenish-gray 0-5% (damage heavy)
- 2 whitish-gray 70-100%, brownish 40-70% and/or greenish-gray 0-20%
- 3 whitish-gray 40-70%, greenish-gray 20-40% and/or brownish 20-40%
- 4 greenish-gray 40-70%, whitish-gray 20-50% and/or brownish 5-20% (damage light)
- 5 greenish-gray 70-100%, whitish-gray 10-20% and/or brownish 0-5% (normal)

iv) Microscopic examination.

Only P. squarrosa and H. physodes were studied microscopically in detail. These plants were examined

under a stereo-microscope for external changes with respect to colour, thallus adhesion, surface cracks, rhizines, development of isidial structures and deposition of extracellular substances in the thallus. All post-exposure changes in the lichen thalli were estimated using arbitrary scales as follows:

changes in thallus adhesion (% cover attached to bark)

- 1 10-20%
- 2 20-40%
- 3 40-60%
- 4 60-80%
- 5 80-100%

degree of isidial development

- 1 very rare
- 2 rare
- 3 common
- 4 abundant

Small portions of the lichen thalli were examined at 400X for changes such as plasmolysis, chlorophyll damage, and for size and division frequency of the phycobiont cells. The living and dead status of the algal cells were determined on the basis of their reaction to neutral red and TTC (LeBlanc et al. 1971).

v) Biomass estimation (mg/cm^2).

Samples of P. squarrosa (one cm^2) were harvested from bark discs exposed at sites 27, 30, 31 and 37 located along a northern transect, at sites P (smelter), 9, 18, 21,

22, 23 and 24 along a southeastern transect and also at site 43 (control) southwest of the copper smelter (Fig. 11). Each sample was first weighed intact, then reweighed after overnight immersion in acetone. The differences of the two weights so obtained was taken as the amount of acetone soluble substances in the sample. A correlation was sought between the amount of acetone soluble substances in the lichen thallus and the pollution load to which the thallus was exposed.

vi) Spectrophotometric and quantitative analysis of chlorophyll.

Samples of 63 mg of P. squarrosa thalli were finely ground in a mortar with 10 ml of 80% acetone (acetone/water: 4/1 v/v) and one g sodium carbonate (the latter was added to prevent the degradation of chlorophyll by lichen acids). The homogenate was centrifuged for 15 minutes at 6,700 rpm and the supernatant was extracted in a separatory funnel with 10 ml of ethyl ether. The ether solution was used for determining the absorption spectrum of chlorophyll (Rao and LeBlanc 1966).

The optical density (O.D.) of the pigments was measured in a UNICAM SP1800 ultraviolet spectrophotometer equipped with a UNICAM AR25 linear recorder. A continuous trace was made between 480 nm and 700 nm. From the O.D. values at 645 nm and 663 nm the concentrations of total chlorophyll and of chlorophylls a and b in the mixture were determined using the appropriate equations from Holden (1965).

b) Naturally occurring lichen epiphytes.

The six sites used for the stemflow sampling were selected for the collection of the naturally occurring epiphytes of the same species as used in the transplant experiments. All of the study sites, except the control (43), were in the stream of the NW prevailing winds.

i) Chlorophyll analysis of lichens.

Chlorophyll extracts were prepared from 100 mg of thallus by the method already described (section 4a). The chlorophyll equations of Vernon (1960) were used for determining chlorophylls a and b concentrations. In both cases the O.D. line at 700 nm was used as a reference for the optical clarity of the solution.

5. Cartography of epiphytic lichens and mosses.

a) Epiphytic vegetation data.

The data on the epiphytic vegetation were collected at 40 sites randomly selected within a 35 km radius around the Murdochville copper smelter (Fig. 11). For a site to be retained it had to 1) be in a fairly flat humid area and have a continuous cover of woodland mosses (i.e. H. splendens and P. schreberi), 2) have a semi-closed to closed canopy, and 3) have mature trees with a DBH of between 35 and 45 cm. However some sites close the copper smelter did not strictly adhere to these criteria and were somewhat more open and better drained.

The main problem in studying the epiphytic vegetation with respect to pollution lies in the selection of suitable

phorophytes or host trees which should be common to all of the study sites. Since A. balsamea, the balsam fir, is the most abundant tree in the Murdochville area, it was decided to study the epiphytes of this tree species alone. With the choice of a single tree species, it was possible to assume that the variations in epiphytic vegetation were due to the changes in the level of pollution.

At each site 20 large fir trees located and exposed to what appeared to be similar conditions of light, temperature and humidity were selected. All species of bryophytes and lichens present on the trunks of these trees up to a height of 2.5 m from the base were listed. However, species growing on the soil-covered tree bases and dead wood were not included in the list (Table 12).

Using phytosociological characters, De Sloover and LeBlanc (1968) expanded on a method providing a mathematical formula to correlate the lichen and bryophyte vegetation of an area with the quality of its ambient air. This method, known as the Index of Atmospheric Purity or IAP method, has since been modified and improved. The IAP method has been used with success in Canada for preparing pollution maps of Montréal (LeBlanc and De Sloover, 1970), Sudbury (LeBlanc et al. 1972a), Arvida (LeBlanc et al. 1972b) and of Ottawa (Bégin-Robitaille and LeBlanc 1977, unpublished data).

The IAP method helps indirectly to assess the degree of purity or conversely the degree of pollution of a given environment by means of the following formula

(LeBlanc and De Sloover 1970):

$$IAP = \sum \frac{1}{n} (Q \times f) / 10,$$

where n is the total number of species present at a site; f is the frequency-coverage of each species at each site; Q is an ecological index or apparent resistance factor of a given species, expressed numerically by the average number of species concurrently present with a given species at the investigated sites. The sum of Q x f is divided by 10 to reduce it to a smaller and more manageable number.

The frequency-coverage (f) of each species was estimated and expressed by a number on the scale 1-5. The frequency represented the percentage of trees on which a species was physically present at a given site while the coverage was the surface area of a species at that site.

The f was:

- 1 if both frequency and coverage were less than 5%
- 2 if the frequency or coverage was between 5-25%
- 3 if the frequency or coverage was between 25-50%
- 4 if the frequency or coverage was between 50-75%
- 5 if both frequency and coverage were greater than 75%.

b) Ecological index.

From the epiphyte list of all 40 sites, an ecological index or a resistance factor (Q) for each species was determined by adding together the number of epiphytes present with a given species at the various sites and then dividing this sum by the total number of sites where that species occurred. In other words, the average number of species concurrent with each epiphyte growing on the trunk of A. balsamea in the Murdochville area was determined.

c) Index of Atmospheric Purity.

The frequency-coverage (f) and the ecological index (Q) data of the epiphytes were compiled and tabulated separately for each of the 40 sites. From these data, the IAP for every site was calculated by using the formula described earlier. The field relevé of site 20 is presented in Table 14 to illustrate the method.

d) Deliniation of IAP zones.

The IAP values were plotted on polar coordinate paper the center of which represents the Murdochville copper smelter. Then, the values of zero and those falling within ranges of 1-30, 31-60, 60-80 and greater than 80 were separated by isometric lines (i.e. isopollution lines) thus dividing the area into six IAP zones (Table 11, Fig. 14).

Table 11. Summary of site location, number of epiphytes, IAP values and annual arithmetic mean of ambient sulphur dioxide concentration (ppb) of the various sites investigated in the Murdochville area.

Site	km from smelter	Epiphytes		IAP	IAP range	SO ₂ (ppb)	IAP zone
		Lichens	Mosses				
P	0.5 SSW	0	0	0	0	72	I
V	1.1 SSE	0	0	0	0	87	I
N	1.9 S	0	0	0	0	61	I
8	3.0 E	0	0	0	0	49	I
9	4.8 ESE	0	0	0	0	41	I
10	5.0 SE	0	0	0	0	26	I
11	6.3 SE	0	0	0	0	30	I
15	8.3 ESE	0	0	0	0	17	I
18	11.0 E	0	0	0	0	17	I
6	2.0 E	0	0	0	0	34	I
1	3.1 E	0	0	0	0	60	I
35	0.9 NNW	0	0	0	0	63	I
37	2.3 NNW	0	0	0	0	76	I

Table 11 cont'd.

26	2.6 NNE	0	0	0	0	54	I
38	3.4 NW	0	0	0	0	35	I
27	6.7 NNW	2	0	4	1-30	21	II
21	14.9 ESE	11	0	22	1-30	13	II
28	7.7 N	10	2	30	1-30	12	II
16	7.5 ESE	11	2	42	31-60	15	III
40	6.4 W	13	1	45	31-60	9	III
30	11.5 N	14	3	45	31-60	9	III
20	20.0 ENE	11	2	48	31-60	7	III
22	19.5 SE	17	0	49	31-60	9	III
41	11.4 WSW	17	2	58	31-60	9	III
19	15.8 E	16	2	64	61-80	4	IV
33	17.3 N	17	1	65	61-80	6	IV
23	25.4 SE	14	2	68	61-80	10	IV
231	30.5 SE	16	3	76	61-80	8	IV
17	6.9 ENE	19	4	79	61-80	14	IV
31	14.1 NNW	17	5	81	>80	7	V

Table 11 cont'd.

202	29.5 E	21	2	82	>80	-	V
331	20.0 N	15	3	83	>80	4	V
201	25.3 NE	18	2	85	>80	4	V
43	20.1 SW	20	8	92	>80	6	V
421	18.0 SSW	18	4	97	>80	3	V
332	23.3 NNW	20	3	100	>80	6	V
24	35.5 SE	19	6	101	>80	6	V
44	25.8 WSW	19	5	104	>80	5	V
45	33.8 SW	17	9	108	>80	4	V
32	20.5 NW	20	7	110	>80	4	V

CHAPTER III

Results and Discussion

The author has divided the present chapter into five separate but somewhat related parts. Under each part a brief introduction is followed by result and discussion sections.

Part A deals with the effect of sulphur dioxide pollution on the distribution of the epiphytic flora and presents sulphur dioxide iso-pollution maps. The pollution patterns are correlated with the distribution of the epiphytic lichens and mosses in the area. It also discusses the accumulation and distribution of some heavy metals and non metals in different vegetation types.

Part B correlates the sulphur dioxide distribution pattern with changes in chlorophyll content in both transplanted and naturally occurring epiphytic lichens. Physiological effects on the lichen thalli are also discussed as are certain morphological changes.

In part C the role of acid rain as a cause for the apparent paucity of epiphytes in proximity to the copper smelter is discussed.

In part D the content of heavy metal pollutants in the stemflow of A. balsamea is related to the accumulation of these metals in two naturally occurring epiphytic lichens. The differences in accumulation are correlated with the distance from the copper smelter along a ESE to SE transect from the pollution source.

The potential of using tree rings as a monitor of heavy metal pollution is discussed in part E.

A. Biological response of lichens and bryophytes to pollution.

1. Introduction.

On approaching an urban or industrial center one often notices a decline in the number and a reduction in the growth and fertility of lichen and bryophyte species. These plant responses, which are attributed to contaminated environments, have been variously used by biologists to determine the nature and extent of ambient pollution (LeBlanc and Rao 1973a). To date, information on the subject suggests that these cryptograms, which are apparently more sensitive to polluted air than are other plant groups, have a significant indicator value. With respect to their reliability as bioindicators of pollution, corticolous species of lichens and bryophytes have proven to be superior to terricolous or saxicolous species (Barkman 1958).

Several workers in Europe and North America have used lichens and bryophytes, especially the epiphytic ones, to map sulphur dioxide pollution of cities and industrial areas (Gilbert 1969; Hawksworth and Rose 1970; Stringer and Stringer 1974; Newberry 1974). In earlier studies, mostly the empirical expression of presence or absence of species was used to delineate a polluted area into different vegetation zones which were, eventually, related to the average annual pollutant levels prevailing in that area (Sernander 1926; Barkman 1958; Skye 1957;

LeBlanc 1961; Rao and LeBlanc 1967). More recently phytosociological characters, such as frequency, coverage, density and fertility have been emphasized (De Sloover and LeBlanc 1968; Trass 1968; Skorepa and Vitt 1976).

On the basis of physical presence and coverage of lichen species on specific substrata, particularly tree bark, in certain areas of England for which the sulphur dioxide pollution levels are known, Gilbert (1969) and Hawksworth and Rose (1970) developed biological scales. These scales are suggested to be useful for the areas of Western Europe where the mean annual sulphur dioxide levels remain within the range of 30 - 170 mg/m³.

Using more phytosociological characters than just the physical presence and coverage of species, De Sloover and LeBlanc (1968) expanded on a method providing a mathematical formula to correlate the lichen and bryophyte vegetation of an area with the quality of the ambient air. This method, known as the Index of Atmospheric Purity or IAP method, has since been modified and improved. Within the last six years the IAP method or variations of it, have been used with success in Canada for preparing pollution maps of Montréal (LeBlanc and De Sloover 1970), Sudbury (LeBlanc et al. 1972a), Arvida (LeBlanc et al. 1972b), Winnipeg (Stringer and Stringer 1974) and in the province of Alberta (Skorepa and Vitt 1976).

In this part of the study the IAP method has been used to determine the pollution pattern in the Murdochville

Gaspé Copper Mine area where the environment is contaminated with emissions from a copper smelter. It is suspected that sulphur dioxide and heavy metals are the common pollutants emitted in the area.

Strong and persistent temperature inversions are common to the Murdochville valley. At night cold air drains into the valley from the surrounding mountain slopes. The prevailing wind is from the NW.

2. Results

The 1972 to 1974 distribution of ground level atmospheric sulphur dioxide in ppb are presented in Figures 6 to 8 and Table 9. Figure 9 and Table 10 represent the average sulphur dioxide levels for all three years combined. The data for these iso-pollutant contour maps were obtained from sulphation plate determinations and were supplied by the environmental monitoring section of the Gaspé Copper Mine smelter complex.

The national air quality objectives established by the Canadian government (Environment Canada 1976) for sulphur dioxide will be the basis of discussion of the air quality observed in the Murdochville study area. The national sulphur dioxide standards were set at a maximum accepted level of 0.02 ppm ($= 20 \text{ ppb} = 43 \text{ ug/m}^3$) as an annual arithmetic mean. For a 24 hr and one hr period the maximum accepted concentrations were 0.11 ppm ($= 292 \text{ ug/m}^3$) and 0.34 ppm ($= 900 \text{ ug/m}^3$) respectively.

The iso-pollutant lines (or pollution isopleths) of

Figures 6 to 9 represent sulphur dioxide arithmetic mean boundaries. Five ambient sulphur dioxide pollution boundaries were delineated using the following progression;

Zone I > 75 ppb SO₂ very heavily polluted

Zone II 50-74 ppb SO₂ heavily polluted

Zone III 30-49 ppb SO₂ polluted

Zone IV 10-29 ppb SO₂ buffer zone

Zone V 10 ppb SO₂ not polluted

The national air quality objectives dictated the choice of this scale. It was felt that a more accurate definition of the air quality in the study area would be obtained by choosing the boundaries of four of the five zones within the air quality standard for the annual arithmetic mean. Zone IV contained both values that were above and below the standard and is considered to represent a buffer zone between polluted and non polluted areas. The iso-pollutant lines are not static as may be seen by comparing Figures 6 to 8. The composite pollutant distribution map (Fig. 9) gives an overall but less accurate indication of the distribution of the sulphur dioxide levels, in that it does not take into account the dynamic aspect of the distribution.

The dynamic aspect of sulphur dioxide distribution is an important point to consider when discussing the effects on vegetation. It is imperative that the reader be aware of areas that are only sporadically but yet severely subjected to pollution if anomalies in species distribution or species

Table 12. Frequency-coverage values (f) for all sites at which epiphytes occurred on Abies balsamea.

Site number	27	28	30	31	33	331	201	16	17	19	20	202	332	21	22	23	231	24	421	40	41	43	44	45	32
Site location	6.7	7.7	11.5	14.1	17.3	20.0	25.3	7.5	6.9	15.8	20.0	29.5	23.3	14.9	19.5	25.4	30.5	35.5	18.0	6.4	11.4	20.1	25.8	33.8	20.5
	NNW	N	N	NNW	N	N	NNW	NE	ESE	E	ENE	E	NNW	ESE	SE	SE	SE	SE	SSW	W	WSW	SW	WSW	SW	NN
Epiphytes																									
Lichens																									
<u>Alectoria capillaris</u>	-	1	1	2	2	3	2	1	2	2	2	2	3	1	1	2	3	2	2	3	2	2	3	3	3
<u>A. sarmentosa</u>	-	1	1	2	2	3	2	2	2	2	2	2	3	1	1	2	3	2	3	3	2	2	3	3	3
<u>Buellia stillingiana</u>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1	2	-	-	1	1	-	1	-	1	-
<u>Cetraria orbata</u>	-	-	-	-	-	-	1	-	-	-	-	-	-	1	-	-	1	-	-	-	-	-	1	-	-
<u>C. pinastri</u>	-	1	1	1	1	2	1	1	1	-	2	1	1	1	2	2	2	-	2	1	2	2	2	2	1
<u>C. sepincola</u>	-	-	-	-	1	-	-	-	-	1	1	1	2	1	1	1	1	1	2	-	1	1	-	-	1
<u>Cladonia coniocraea</u>	-	1	1	1	-	-	2	1	1	1	-	-	-	-	-	2	1	2	1	-	1	1	2	1	-
<u>Haematomma ochrophaeum</u>	-	-	-	1	-	-	-	-	1	-	1	1	-	-	2	-	-	-	-	-	-	-	-	-	-
<u>Hypogymnia physodes</u>	-	1	3	4	4	4	4	3	4	4	4	4	4	1	3	4	4	4	4	3	3	4	4	4	3
<u>Lecanora coilocarpa</u>	-	-	-	-	-	-	1	-	1	-	1	1	2	-	-	-	1	1	2	2	1	1	-	2	2
<u>L. symmicta</u>	-	-	-	-	-	-	-	-	-	2	-	-	2	-	1	-	-	-	1	-	-	-	-	-	-
<u>Lecidia albofuscescens</u>	-	1	-	-	-	-	-	-	2	1	-	2	-	-	-	2	-	1	2	1	2	2	-	-	2
<u>L. cinnabarina</u>	-	-	1	-	-	-	-	-	-	2	1	-	-	-	-	-	-	-	-	-	1	-	2	3	-
<u>L. vernalis</u>	-	-	-	-	-	-	-	-	-	1	-	-	-	-	-	-	2	1	-	-	-	-	-	-	-
<u>Lobaria pulmonaria</u>	-	-	-	-	-	1	2	-	-	-	-	1	-	-	-	-	-	-	-	-	-	2	-	-	-
<u>Lopadium pezizoideum</u>	-	-	-	3	-	1	-	1	1	-	-	1	1	-	1	-	-	-	-	-	-	1	-	-	1
<u>Mycoblastus affinis</u>	-	-	-	-	2	-	-	-	-	-	-	-	-	-	2	-	-	-	-	-	-	-	-	-	-
<u>M. sanguinaris</u>	1	1	1	3	3	3	3	2	3	3	2	3	3	1	-	3	4	3	2	1	2	-	3	4	3
<u>Ochrolechia sp.</u>	-	-	-	-	-	-	-	1	1	-	-	-	-	-	-	-	-	-	1	-	1	-	-	-	3

<u>O. androgyna</u>	-	-	-	1	-	2	2	-	-	-	2	-	-	3	-	-	-	1	-	-
<u>O. rosella</u>	-	-	-	-	1	-	-	-	1	-	-	-	-	-	1	-	-	-	3	2
<u>Parmelia glabrata</u>	-	-	-	-	-	-	-	-	-	-	2	1	-	1	-	-	-	-	1	2
<u>P. septentrionalis</u>	-	1	-	-	-	-	-	-	2	-	1	2	-	1	-	-	-	-	-	-
<u>P. squarrosa</u>	-	-	2	3	3	4	4	-	2	4	-	2	3	2	4	4	-	1	3	3
<u>P. sulcata</u>	1	2	2	4	4	2	-	3	2	-	3	2	-	3	3	-	3	2	-	2
<u>P. trabeculata</u>	-	-	-	1	1	1	-	-	-	-	-	1	-	2	2	-	-	1	1	-
<u>Parneliopsis ambigua</u>	-	-	1	1	1	2	2	1	4	1	-	2	2	1	-	2	3	1	2	3
<u>P. hyperopta</u>	-	-	-	1	-	2	2	-	1	1	-	2	4	1	-	2	2	2	2	3
<u>Pertusaria multipuncta</u>	-	-	2	2	2	-	-	-	1	1	-	-	-	-	-	-	2	1	1	-
<u>P. pertusa</u>	-	1	1	-	1	-	1	-	1	2	-	2	2	-	-	2	2	2	2	2
<u>Platismatia glauca</u>	-	2	1	1	2	2	3	3	2	2	-	3	4	1	-	2	2	3	4	3
<u>Ramalina minuscula</u>	-	-	1	1	1	3	1	-	-	-	3	2	1	-	2	1	-	1	1	2
<u>Rinodina sp.</u>	-	-	-	-	-	-	1	-	-	-	-	-	-	1	-	-	-	-	1	-
<u>Stenocybe major</u>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1	-	-	-
Bryophytes																				
<u>Bazzania trilobata</u>	-	-	-	1	-	-	-	-	-	-	-	-	-	-	-	-	-	1	-	-
<u>Blepharostoma trichophyllum</u>	-	-	-	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
<u>Brachythecium salebrosum</u>	-	-	1	-	-	-	-	-	-	-	-	-	-	-	1	1	1	-	1	-
<u>Dicranum viride</u>	-	1	1	2	-	2	2	1	1	1	1	2	2	-	2	1	2	2	3	2
<u>Frullania eboracensis</u>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3	4	-	-	3
<u>Hylacomium splendens</u>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1	-	-	1	1
<u>Hypnum lindbergii</u>	-	-	-	1	-	2	-	-	1	-	-	2	-	-	-	-	-	-	1	2
<u>Plagiothecium roseanum</u>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1	1
<u>Pleurozium schreberi</u>	-	-	-	-	-	-	-	-	2	-	-	-	-	-	-	-	2	-	1	1
<u>Ptilidium pulcherrimum</u>	-	1	2	3	2	2	3	2	3	2	2	2	-	-	3	1	3	-	1	2
<u>Ptilium crista-castrensis</u>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1	-	-	1	-

No epiphytes were recorded at sites P, V, N, 1, 6, 8, 9, 10, 11, 15, 18, 25, 26, 35, 37, 38.

Table 13. Comparison of epiphytic data of sites 16 and 21 located at 7.5 and 14.9 km ESE of Murdochville respectively.

Epiphytes	Site 16			Site 21		
	Q	f	Qxf	Q	f	Qxf
<u>Alectoria capillaris</u>	19	1	19	19	1	19
<u>A. sarmentosa</u>	19	2	38	19	1	19
<u>Cetraria orbata</u>				18	1	18
<u>C. pinastri</u>	18	1	18	18	1	18
<u>C. sepincola</u>				19	1	19
<u>Cladonia coniocraea</u>	19	1	19			
<u>Hypogymnia physodes</u>	19	3	57	19	1	19
<u>Lopadium pezizoideum</u>	20	1	20			
<u>Mycoblastus sanguinarius</u>	18	2	36	18	1	18
<u>Ochrolechia sp.</u>	21	1	21			
<u>Parmelia sulcata</u>	17	3	51	17	2	34
<u>Parmeliopsis ambigua</u>	20	1	20	20	1	20
<u>P. hyperopta</u>				22	1	22
<u>Platismatia glauca</u>	19	3	57	19	1	19
<u>Dicranum viride</u>	20	1	20			
<u>Ptilidium pulcherrimum</u>	21	2	42			
IAP		42			22	

composition are to be explained. For example, the composite map (Fig. 9) which averages the annual sulphur dioxide values for 33 consecutive months gives no indication that in 1972 (Fig. 6) a fairly large area between 7.5 and 10 km SE of the smelter was subjected to an annual average of over 30 ppb sulphur dioxide, 1.5 times above the accepted annual arithmetic mean.

If the data are analysed zone wise for the two year nine month interval the following important characteristics are observed: 1) the general pattern of sulphur dioxide distribution was NW and SE (Fig. 9) in the general direction of the NW (winter) and SE (summer) prevailing winds (Fig. 10), 2) centers of very heavy pollution (75 ppb) may extend out to five km in the ESE direction (Fig. 6) but generally they are within a 2.5 km limit and adjacent to the copper smelter, 3) polluted areas are generally within a 7.5 km radius of the pollution source.

The composite map (Fig. 9) smooths out the erratic patterns associated with a year to year documentation of sulphur dioxide deposition. Despite the fact that some information is lost by averaging the annual and nine month sulphur dioxide values it is still possible to determine trends in the overall distribution of this gaseous pollutant. Integrated over this time interval, two centers of very heavy pollution are retained, one to the NW and the other to the SE with a maximum extension to 2.5 km NW. In general the intensity of sulphur dioxide pollution decreases

in all directions as the distance from the pollution source increases.

Trees of A. balsamea of 15 sites, distributed up to 2.6 km NNE, 11.0 km E, 8.3 km ESE, 6.3 km SE, 1.1 km SSE, 1.9 km S, 3.4 km NW and 2.3 km NNW from the copper smelter, were completely devoid of epiphytes. Beyond these distances, the tree trunks contained epiphytes whose number (n) and frequency-coverage (f) gradually rose as the distance from the copper smelter increased (Tables 11 and 12). This trend of rise in epiphyte richness at increasing distances from the copper smelter remained obscure in some instances, however. For example, at site 16, located at 7.5 km ESE, there were 13 epiphytes usually with high f scores, but at site 21, located at 14.9 km ESE, there were only 11 epiphytes mostly with low f scores (Table 13). Similarly, there were 23 epiphytes at a site (site 17 located at 6.9 km ENE) nearer to the smelter in contrast to 13 epiphytes at a site (site 20 located at 20.0 km ENE) distant from the smelter. However the f scoring of the species at these sites appeared normal, being usually higher for the sites farther away from the smelter (Table 14).

A total of 45 epiphytes, 34 lichens and 11 bryophytes, (Table 12) were recorded in the investigated area (Fig. 11). Among these, certain lichens such as Alectoria capillaris, Cetraria pinastri, C. sepincola, Hypogymnia physodes, Mycoblastus sanguinarius, Parmelia sulcata, Parmeliopsis ambigua, P. hyperopta and Platismatia glauca were present

Table 14. Comparison of epiphytic data of sites 17 and 20 located at 6.9 and 20.0 km ENE of Murdochville respectively.

Epiphytes	Site 17			Site 20		
	Q	f	Qxf	Q	f	Qxf
<u>Alectoria capillaris</u>	19	2	38	19	2	38
<u>A. sarmentosa</u>	19	2	38	19	2	38
<u>Cetraria pinastri</u>	18	1	18	18	2	36
<u>C. sepincola</u>				17	1	17
<u>Cladonia coniocraea</u>	19	1	19			
<u>Haematomma ochrophaeum</u>	18	1	18	18	1	18
<u>Hypogymnia physodes</u>	19	4	76	19	4	76
<u>Lecanora coilocarpa</u>	21	1	21	21	1	21
<u>Lecidia albofuscescens</u>				20	1	20
<u>L. cinnabarina</u>	20	1	20			
<u>Lopadium pezizoideum</u>	21	1	21			
<u>Mycoblastus sanguinarius</u>	18	3	54	18	2	36
<u>Ochrolechia sp.</u>	21	1	21			
<u>Parmelia septentrionalis</u>	18	2	36			
<u>P. squarrosa</u>	19	2	38			
<u>P. sulcata</u>	17	2	34	17	3	51
<u>Parmeliopsis ambigua</u>	20	4	80			
<u>P. hyperopta</u>	22	1	22			
<u>Pertusaria multipuncta</u>	22	1	22			
<u>P. pertusa</u>	20	1	20			
<u>Platismatia glauca</u>	19	2	38			

Table 14 cont'd.

<u>Ramalina minuscula</u>				20	3	60
<u>Dicranum viride</u>	20	1	20	20	1	20
<u>Hypnum lindbergii</u>	22	1	22			
<u>Pleurozium schreberi</u>	24	2	48			
<u>Ptilidium pulcherrimum</u>	21	3	63	17	2	42
IAP		77			48	

Table 15. Epiphytes arranged in the order of maximum Q x f values attained in different IAP zones in the Murdochville area.

IAP zones	I	II	III	IV	V
IAP range	<1	1-30	31-60	61-80	>80
SO ₂ range ppb	87-17	21-12	15-7	14-4	7-4
<u>Hypogymnia physodes</u> (19)	19	76	76	76	
<u>Platismatia glauca</u> (19)	38	57	38	76	
<u>Parmelia sulcata</u> (17)	34	57	68	68	
<u>Parmeliopsis hyperopta</u> (22)	22	44	44	88	
<u>P. ambigua</u> (20)	20	20	80	60	
<u>Pertusaria pertusa</u> (20)	20	20	40	40	
<u>Dicranum viride</u> (20)	20	20	40	60	
<u>Alectoria capillaris</u> (19)	19	57	57	57	
<u>A. sarmentosa</u> (19)	19	57	57	57	
<u>Cetraria sepincola</u> (19)	19	19	19	38	
<u>Cladonia coniocraea</u> (19)	19	19	38	38	
<u>Mycoblastus sanguinarius</u> (18)	18	36	72	72	
<u>Cetraria orbata</u> (18)	18	-	18	18	
<u>Ramalina minuscula</u> (20)		60	20	60	
<u>Pertusaria multipuncta</u> (22)		44	44	44	
<u>Lecanora coilocarpa</u> (21)		42	21	42	
<u>Parmelia squarrosa</u> (20)		40	80	80	
<u>Lecidia albofuscescens</u> (20)		40	40	40	
<u>Cetraria pinastri</u> (18)		36	36	36	

Table 15 cont'd.

<u>Haematomma ochrophaeum</u> (18)	36	18	18
<u>Ptilidium pulcherrimum</u> (21)	42	63	84
<u>Mycoblastus affinis</u> (17)	34	34	-
<u>Pleurozium schreberi</u> (24)	24	48	24
<u>Brachythecium salebrosum</u> (22)	22	22	22
<u>Parmelia glabratula</u> (22)	22	-	44
<u>P. trabeculata</u> (21)	21	21	42
<u>Ochrolechia</u> sp. (21)	21	21	63
<u>Lopadium pezizoideum</u> (21)	21	21	63
<u>Lecidia cinnabarina</u> (20)	20	20	80
<u>Rinodina</u> sp. (19)	19	-	19
<u>Parmelia septentrionalis</u> (18)	18	18	36
<u>Buellia stillingiana</u> (18)	18	36	18
<u>Lecanora symmicta</u> (17)	17	34	34
<u>Stenocybe major</u> (13)	13	-	-
<u>Ochrolechia rosella</u> (22)		22	66
<u>Hypnum lindbergii</u> (22)		22	44
<u>Lecidia vernalis</u> (20)		40	20
<u>Ochrolechia androgyna</u> (21)		63	42
<u>Lobaria pulmonaria</u> (21)			42
<u>Blepharostoma trichophyllum</u> (24)			21
<u>Frullania eboracensis</u> (24)			96
<u>Bazzania trilobata</u> (24)			24
<u>Plagiothecium roeseanum</u> (25)			25
<u>Ptilium crista-crastensis</u> (26)			52

Table 15 cont'd.

Hylocomium splendens (26) 26

No. species present in a zone	0	13	33	35	43
No. species first to appear	0	13	21	4	8

both at polluted as well as at relatively non-polluted sites. From their f scores (Table 12) and Q x f product (Table 15) it appeared that Hypogymnia physodes, Platismatia glauca and Parmelia sulcata and to some extent Parmeliopsis hyperopta were ecologically the most successful species in the area.

The majority of epiphytes were present at distances greater than 7.7 km N, 7.5 km ESE, 6.4 km W and 6.9 km ENE of the smelter. A few species, such as Lobaria pulmonaria, Plagiothecium roeseanum and Ptilium crista-castrensis could be recorded only beyond a distance of 20 km from the pollution sources (Table 15).

Hypogymnia physodes, Alectoria capillaris, A. sarmentosa, Mycoblastus sanguinarius, Cetraria pinastri, Parmeliopsis ambigua, Ptilidium pulcherrimum and Platismatia glauca were the most frequent epiphytes, as they occurred in over 50 percent of the sites investigated. Parmelia sulcata which occurred at 48 percent of the sites could tolerate an annual dose of 28 ppb sulphur dioxide as did M. sanguinarius (Tables 11 and 12). The remaining seven species tolerated up to 16 ppb sulphur dioxide. Platismatia glauca and Parmelia sulcata scored a Q x f value of 38 and 34 respectively, the highest scores attained by any species which was exposed to sulphur dioxide in the concentration range of 10 to 29 ppb (Fig. 9). The species arranged in Table 12, from Hypogymnia physodes to Blepharostoma trichophyllum, showed a gradual decline in their percentage

occurrence from 60 to 3 percent. Certain species, such as Alectoria capillaris, Cetraria pinastri, C. sepincola, Hypogymnia physodes, Mycoblastus sanguinarius, Parmelia sulcata, Parmeliopsis ambigua and Platismatia glauca, which were recorded closest to the smelter, were also the most frequent in the area.

The resistance factor (Q) of different epiphytes varied between 18 and 21 for the more frequent species as listed above. For the frequent species between 20 and 50 percent occurrence (Table 15) the Q values ranged between 17 and 22 while for the common species (10 to 20 percent occurrence) they ranged from 17 to 26. Generally, the resistance factor (Q) of a species was inversely proportional to its frequency-coverage, i.e. the lower the resistance factor the higher the frequency-coverage value.

The frequency-coverage (f) value of a species usually increased with distances from the smelter. The overall increase in the f value was fourfold for Hypogymnia physodes, Parmeliopsis hyperopta and Mycoblastus sanguinarius, threefold for Parmeliopsis ambigua, Dicranum viride, Alectoria capillaris, A. sarmentosa, twofold for Platismatia glauca, Parmelia sulcata, Pertusaria pertusa, Cetraria sepincola and Cladonia coniocraea and remained the same for Cetraria orbata as one passed from zone II to zone V (Tables 12 and 15). Surprisingly enough the f scores in the case of Haematomma ochrophaeum, Lecidea vernalis and Ochrolechia androgyna were higher closer to the smelter

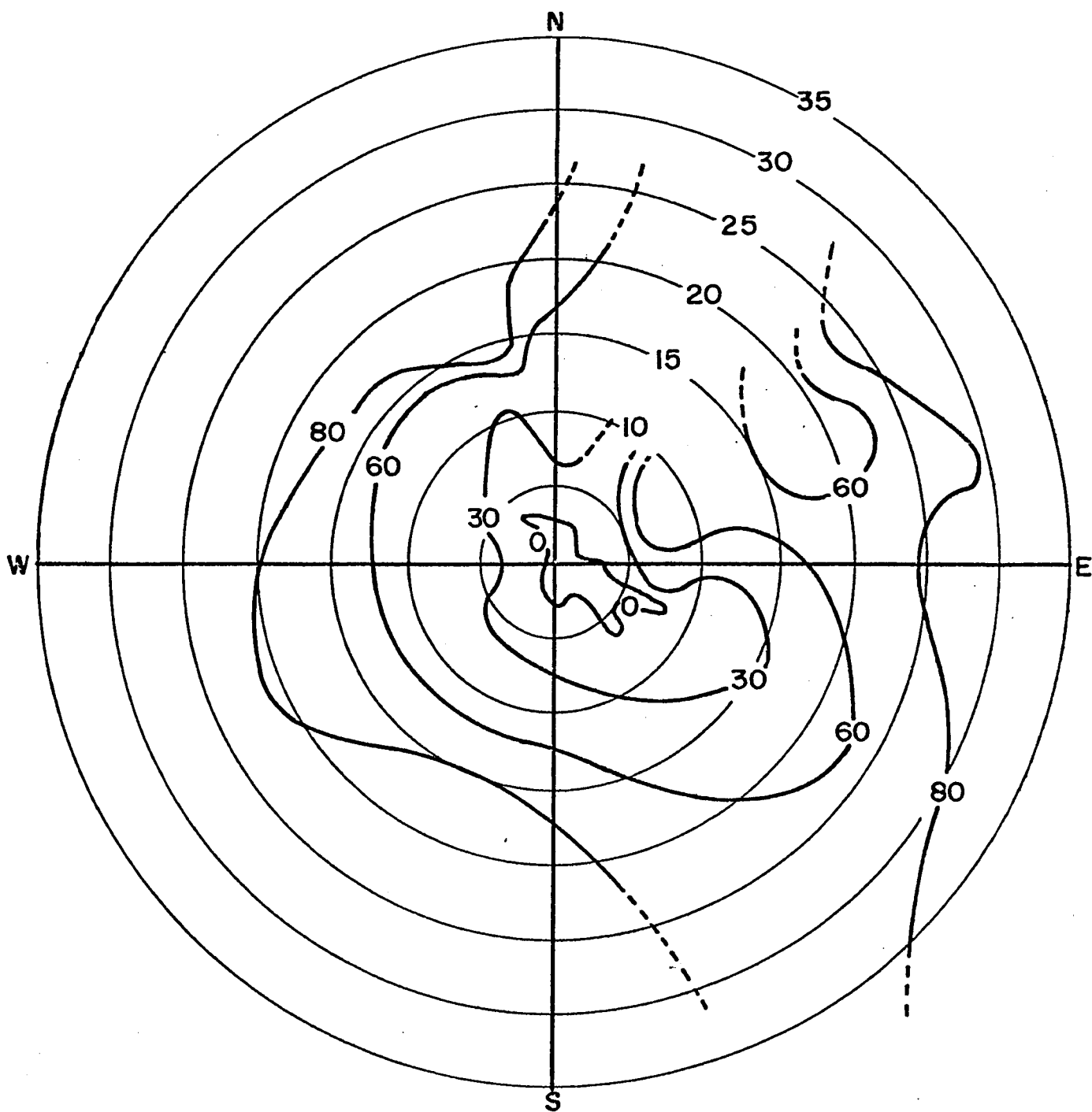
than away from it and two species completely disappeared in non polluted areas namely Mycoblastus affinis and Stenocybe major (Table 15).

The IAP values for all study sites ranged from zero to 110. Of the total of 40 sites, 15 were devoid of epiphytes and had IAP value of zero (Table 11). The IAP values for the remaining 25 sites varied considerably, depending on their location in relation to the smelter. With a few exceptions, the IAP usually increased at increasing distances from the smelter (Table 11). With respect to orientation of sites from the smelter, one may say that at similar distances the IAP increased in the order of SW=NNW>WSW=W=NW>S>WNW=N=ENE>NNE>SSE>E>SE>ESE.

The IAP values of various sites, plotted on a polar coordinate map of the Murdochville area, when grouped as zero, 1 - 30, 31 - 60, 61 - 80 and >80 and bounded by concentric lines, revealed contours of five IAP zones corresponding to the five IAP classes (Fig. 14). Zone I includes areas lying closest to the smelter while zones II, III, IV and V are progressively removed from it. The inner zones are generally kidney shaped being sharply incurved around site 16. The long axis of the zones is in the NNW and NW to SE and ESE directions, with the smelter located at the center of the axis.

The IAP zones (Fig. 14) are more or less similar to those zones traced out for the sulphur dioxide concentrations (Figs. 6 to 9). These zones and those of the IAP values

Figure 14. Polar diagram of the Index of Atmospheric Purity zones (IAP) of the Murdochville area.



were more or less inversely proportional to each other, i.e. when the level of sulphur dioxide increased, the IAP decreased (Fig. 15).

The average concentration of Pb, Cu, Zn and Cd of Picea mariana, Clintonia borealis, Hylocomium splendens and Pleurozium schreberi for each IAP zone was compared separately with the average value of the IAP for that zone. The average concentration of these heavy metals in each of the four plants was lower in areas with higher IAP values, a trend which was more obvious in the mosses than in the higher plants (Figs. 16 to 19). In all cases the mosses accumulated more heavy metal than did the higher plants. Between the two mosses at any given site, Hylocomium splendens, appeared to be a more efficient accumulator of elements than Pleurozium schreberi (Table 16).

While grading the plants with respect to their element accumulation efficiency, it is noticed that Picea mariana tops the list for As (96 ppm at site 35) (Table 17). The highest amounts of As were recorded at sites P, V, N, 8, 15, 35, 37 and 38 close to the smelter. Generally the higher plants accumulated more As, F and S than did the mosses. Clintonia borealis accumulated the greatest amounts of Cd (17.7 ppm at site 35), Zn (414 ppm at site 35) and S (3200 ppm at site P) (Table 18). The moss Pleurozium schreberi took up 1340 ppm Cu at site 15 (Table 19) while Hylocomium splendens concentrated as much as 17320 ppm Pb at site 15 (Table 20).

Figure 15. Relationship between the ambient sulphur dioxide concentration (ppb) and the IAP and km distance from the copper smelter.

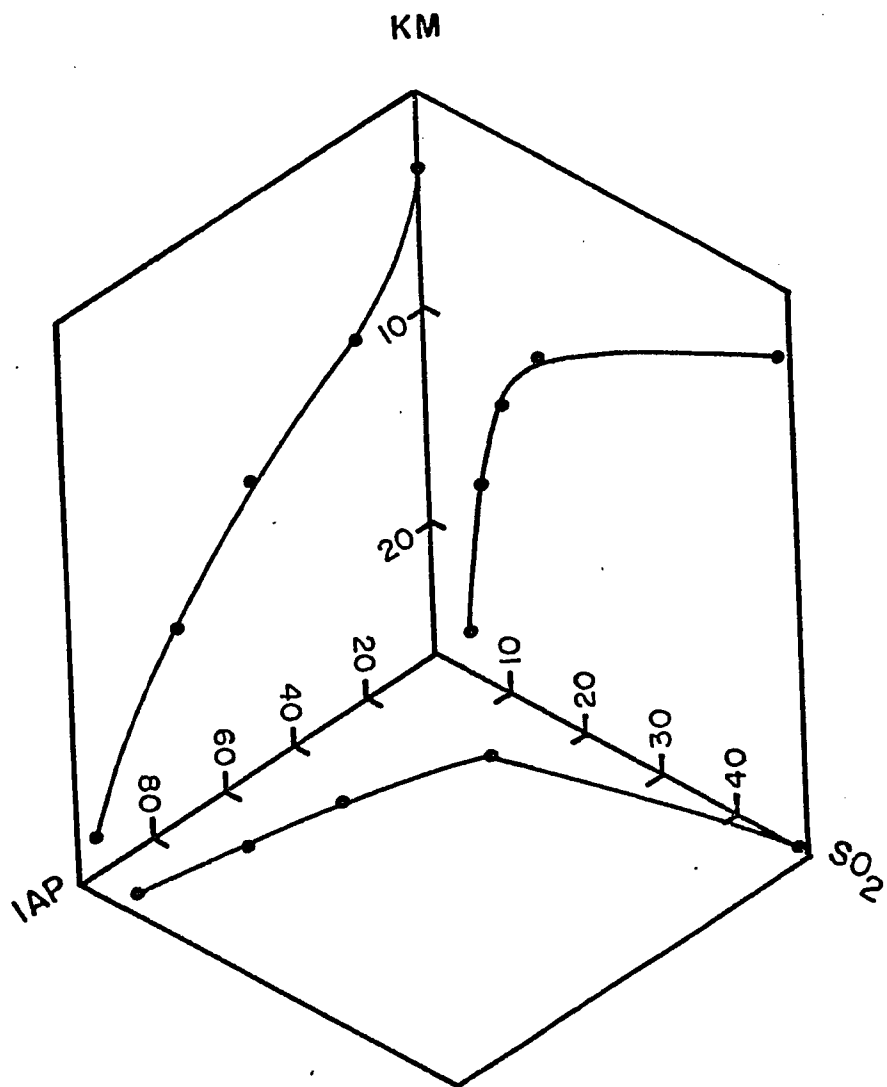


Figure 16. Lead content (ppm dry wt.) in Picea mariana (a), Clintonia borealis (b), Hylocomium splendens (c) and Pleurozium schreberi (d) in different IAP zones in the Murdochville area.

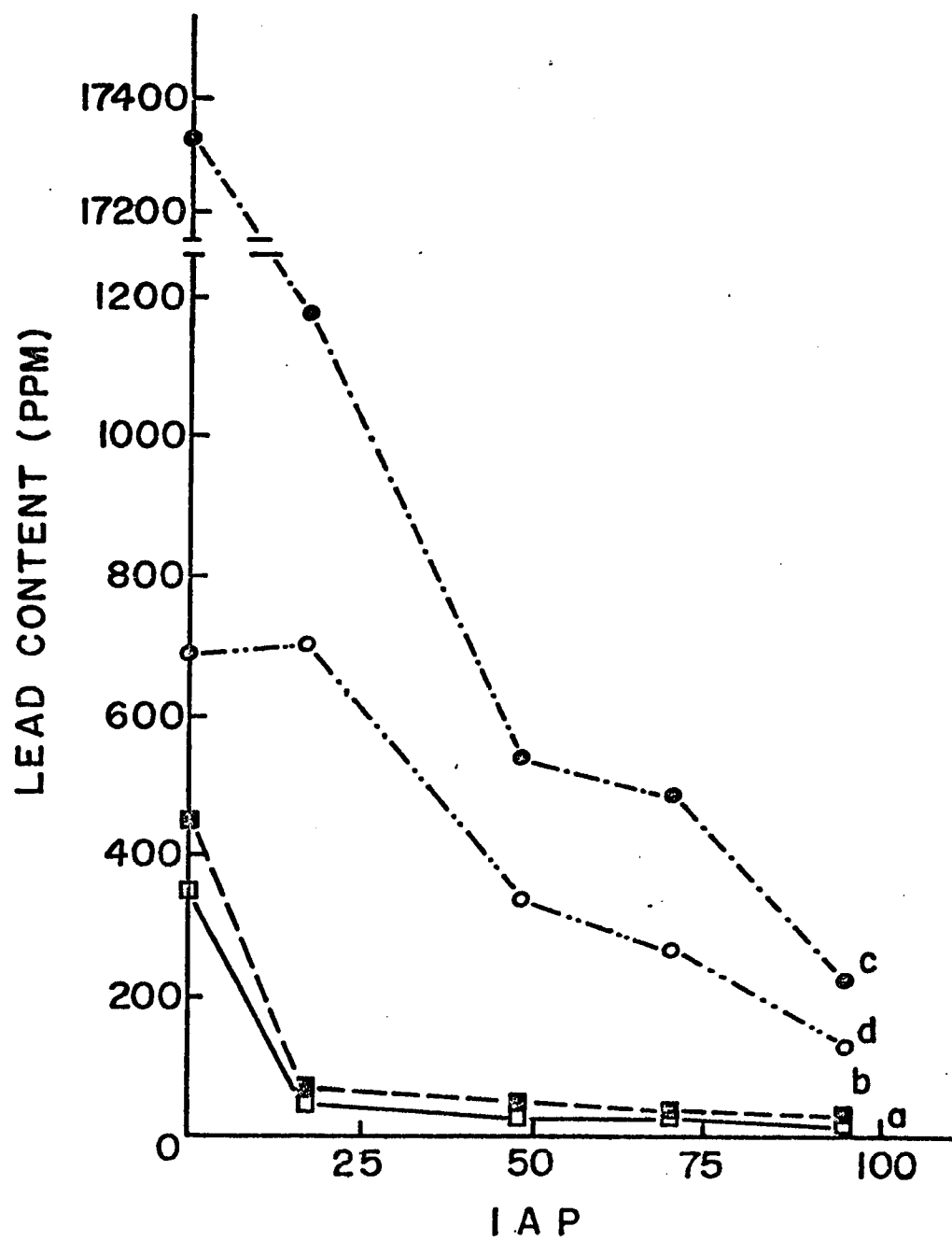


Figure 17. Copper content (ppm dry wt.) in Picea mariana (a), Clintonia borealis (b), Hylocomium splendens (c), Pleurozium schreberi (d) in different IAP zones in the Murdochville area.

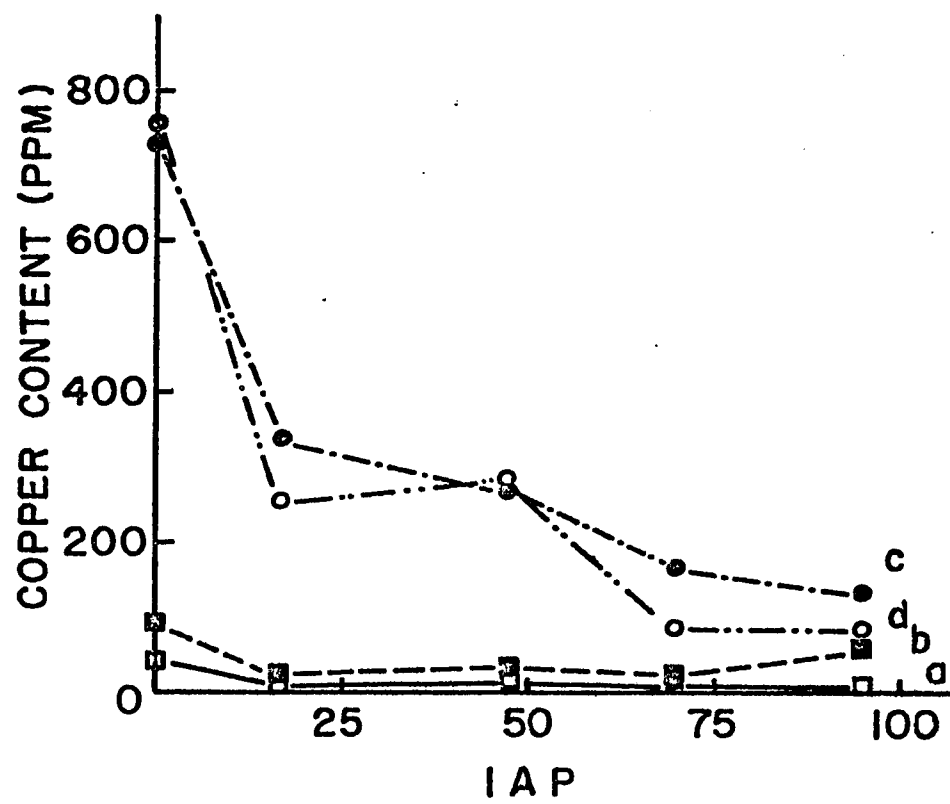


Figure 18. Zinc content (ppm dry wt.) in Picea mariana (a), Clintonia borealis (b), Hylocomium splendens (c) and Pleurozium schreberi in different IAP zones in the Murdochville area.

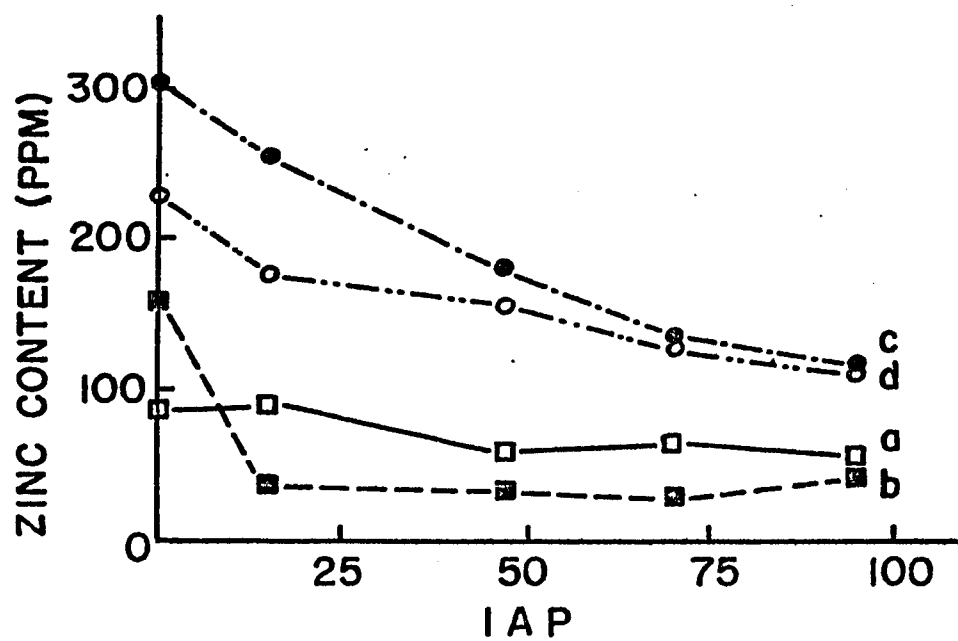


Figure 19. Cadmium content (ppm dry wt.) in Picea mariana (a), Clintonia borealis (b), Hylocomium splendens (c) and Pleurozium schreberi (d) in different IAP zones in the Murdochville area.

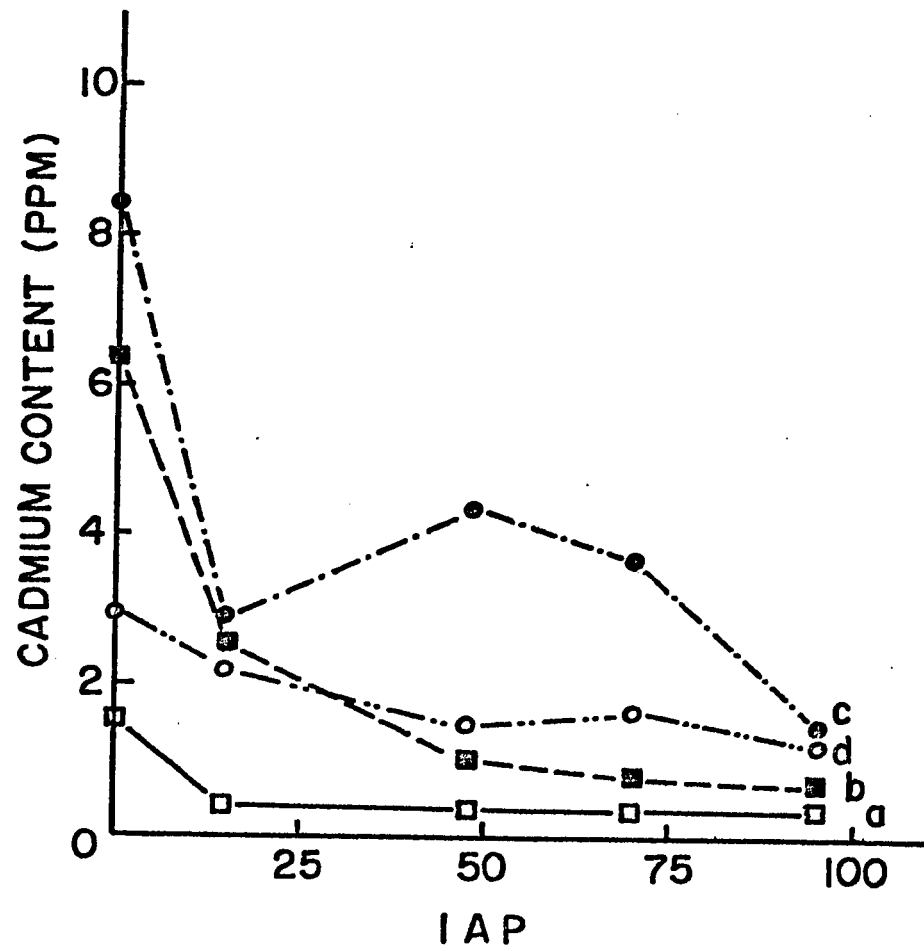


Table 16. Averages of IAP values, ambient sulphur dioxide concentration (ppb) and heavy metal and non-metal content (ppm dry wt.) in Picea mariana (a), Clintonia borealis (b), Hylocomium splendens (c) and Pleurozium schreberi (d) in different IAP zones in the Murdochville area.

IAP zone	IAP value	SO ₂ ppb	Taxa	Pb	Cu	Zn	Cd	As	S	F
I	0	48	a	349	23	84	1.6	16	1320	6
			b	459	93	157	6.2	13	1282	4
			c	17320	724	304	8.4	4	1600	7
			d	695	758	230	3.0	2	950	5
II	17	15	a	32	3	90	0.4	1	933	5
			b	70	11	34	2.5	2	533	3
			c	1178	317	255	2.9	5	900	5
			d	703	259	177	2.2	4	1267	4
III	48	10	a	14	4	57	0.4	3	633	3
			b	55	18	33	1.0	3	633	6
			c	543	267	180	4.2	6	983	8
			d	340	281	158	1.5	4	983	6
IV	70	7	a	16	3	64	0.4	1	1060	2
			b	20	13	29	0.8	4	600	3
			c	496	163	134	3.7	5	660	6
			d	276	86	130	1.7	3	580	5
V	95	5	a	7	4	57	0.4	3	618	6
			b	17	30	43	0.7	3	700	2
			c	213	138	118	1.5	2	672	8

Table 16 cont'd.

Site	92	6	d	139	82	115	1.2	2	500	8
			a	5	10	43	0.7	1	700	2
			b	26	54	24	0.4	4	200	-
			c	141	81	86	1.1	4	400	10
			d	15	45	46	0.4	3	200	10

Table 17. Heavy metals and non-metals (ppm dry wt.) in the leaves (needles) of Picea mariana collected at various sites in the Murdochville area.

Site	km from smelter	Pb	Cu	Zn	Cd	As	S	F
P	0.5 SSE	388	56	51	0.7	25	1200	4
V	1.1 SSE	611	49	55	2.3	27	1000	9
N	1.9 S	720	21	98	2.1	11	1200	5
8	3.9 E	109	16	97	1.1	10	1700	6
9	4.8 ESE	58	4	54	1.7	6	1500	11
10	5.0 SE	85	10	109	0.4	4	1600	6
11	6.3 SE	104	10	41	0.4	6	1600	12
15	8.3 ESE	29	7	111	0.4	4	1200	4
18	11.0 E	42	2	81	0.4	1	800	4
6	2.0 E	135	11	121	0.8	8	1200	6
1	3.1 E	148	12	57	1.5	7	1400	4
35	0.9 NNW	1670	65	138	6.8	96	1600	5
37	2.3 NNW	667	37	101	3.3	18	1700	5
26	2.6 NNE	317	33	69	1.1	7	1400	8
38	3.4 NW	159	14	91	1.5	7	700	7
Average Zone I		<u>349</u>	<u>23</u>	<u>85</u>	<u>1.6</u>	<u>16</u>	<u>1320</u>	<u>6</u>
27	6.7 NNW	48	5	120	0.4	1	700	6
21	14.9 ESE	31	1	77	0.4	1	800	5
28	7.7 N	17	3	74	0.4	1	1300	4
Average Zone II		<u>32</u>	<u>3</u>	<u>90</u>	<u>0.4</u>	<u>1</u>	<u>933</u>	<u>5</u>

Table 17 cont'd.

16	7.5 ESE	26	5	75	0.4	2	1000	4
40	6.4 W	12	4	50	0.4	3	500	3
30	11.5 N	4	4	72	0.4	4	1000	NSS
20	20.0 ENE	6	1	35	0.4	2	700	1
22	19.5 SE	22	7	58	0.4	1	300	3
41	11.4 WSW	15	11	49	0.4	6	300	6
Average Zone III		<u>14</u>	<u>5</u>	<u>57</u>	<u>0.4</u>	<u>3</u>	<u>633</u>	<u>3</u>
19	15.8 E	10	4	69	0.4	1	1800	2
33	17.3 N	21	1	98	-	1	900	2
231	30.5 SE	4	3	30	0.2	2	800	2
17	6.9 ENE	30	3	74	0.4	1	900	3
23	25.4 SE	17	3	48	0.4	1	900	3
Average Zone IV		<u>16</u>	<u>3</u>	<u>64</u>	<u>0.4</u>	<u>1</u>	<u>1060</u>	<u>2</u>
31	14.1 NNW	18	2	60	0.4	1	800	3
202	29.5 E	2	4	74	0.4	2	800	7
331	20.0 N	5	2	66	0.4	1	200	2
201	25.5 NE	3	2	76	0.2	2	600	7
43	20.1 SW	5	2	46	0.7	9	600	3
421	18.0 SSW	5	5	47	0.4	2	1400	10
332	23.3 NNW	2	3	39	0.2	1	400	9
24	35.5 SE	17	10	43	0.4	1	700	2
44	25.8 WSW	9	2	65	0.3	2	500	7
45	33.8 SW	3	4	59	0.4	4	300	12
32	20.5 NW	6	3	55	0.3	1	500	6
Average Zone V		<u>7</u>	<u>4</u>	<u>57</u>	<u>0.4</u>	<u>3</u>	<u>618</u>	<u>6</u>

NSS is insufficient sample.

Table 18. Heavy metals and non-metals (ppm dry wt.) in the leaves of Clintonia borealis collected at various sites in the Murdochville area.

Site	km from smelter	Pb	C	Zn	Cd	As	S	F
P	0.5 SSE	-	-	-	-	-	-	-
V	1.1 SSE	320	245	151	4.6	12	3200	5
N	1.9 S	987	108	397	15.7	24	1700	6
8	3.0 E	410	104	104	5.0	2	700	3
9	4.8 ESE	80	20	56	3.0	6	100	3
10	5.0 SE	124	40	76	3.2	2	300	3
11	6.3 SE	100	30	72	2.8	6	500	3
15	8.3 ESE	24	32	32	0.4	12	200	NSS
18	11.0 E	20	12	28	0.4	2	900	8
6	2.0 E	416	64	162	5.8	8	1000	3
1	3.1 E	372	52	178	5.2	6	1100	3
35	0.9 NNW	1592	359	414	17.8	52	2600	3
37	2.3 NNW	1456	160	334	16.0	32	1700	4
26	2.6 NNE	212	38	82	3.8	6	2300	2
38	3.4 NW	306	56	142	3.0	10	1700	3
Average Zone I		<u>459</u>	<u>93</u>	<u>157</u>	<u>6.2</u>	<u>13</u>	<u>1286</u>	<u>4</u>
27	6.7 NNW	100	20	48	4.6	2	400	<1
21	14.9 ESE	32	2	26	1.6	2	500	5
28	7.7 N	78	12	28	1.4	2	700	2
Average Zone II		<u>70</u>	<u>11</u>	<u>34</u>	<u>2.5</u>	<u>2</u>	<u>533</u>	<u><3</u>

Table 18 cont'd.

16	7.5 ESE	48	18	32	1.0	4	500	7
40	6.4 W	36	22	10	0.6	2	700	1
30	11.5 N	52	24	72	2.8	-	900	-
20	20.0 ENE	24	2	22	0.6	2	500	6
22	19.5 SE	110	32	46	0.4	2	1000	10
41	11.4 WSW	60	10	15	0.5	-	200	-
Average Zone III		<u>55</u>	<u>18</u>	<u>33</u>	<u>1.0</u>	<u>3</u>	<u>633</u>	<u>6</u>
19	15.8 E	8	9	27	0.5	3	900	-
33	17.3 N	30	10	24	1.2	2	300	1
231	30.5 SE	7	8	33	0.8	3	800	-
17	6.9 ENE	42	18	38	0.4	2	500	6
23	25.4 SE	12	18	24	1.2	8	500	2
Average Zone IV		<u>20</u>	<u>13</u>	<u>29</u>	<u>0.8</u>	<u>4</u>	<u>600</u>	<u>3</u>
33	14.1 NNW	30	10	24	1.2	2	300	1
202	29.5 E	11	8	56	0.8	-	700	-
331	20.0 N	8	9	59	0.9	3	-	-
201	25.3 NE	7	7	30	0.6	2	600	-
43	20.1 SW	26	54	24	0.4	4	200	-
421	18.0 SSW	10	22	32	0.8	-	700	-
332	23.3 NNW	9	9	53	0.8	3	800	-
24	35.5 SE	58	178	56	1.4	2	700	2
44	25.8 WSW	8	9	51	0.9	-	1200	-
45	33.8 SW	10	11	31	0.4	6	1100	-
32	20.5 NW	12	9	55	0.7	2	-	-
Average Zone V		<u>17</u>	<u>30</u>	<u>43</u>	<u>0.7</u>	<u>3</u>	<u>700</u>	<u>2</u>

Table 19. Heavy metals and non-metals (ppm dry wt.) in the leaves of the woodland moss Pleurozium schreberi collected at various sites in the Murdochville area.

Site	km from smelter	Pb	Cu	Zn	Cd	As	S	F
P	0.5 SSE							
V	1.1 SSE							
8	3.0 E							
9	4.8 ESE							
10	5.0 SE							
11	6.3 SE							
15	8.3 ESE	1160	1340	323	4.4	2	1000	6
18	11.0 E	230	165	136	1.5	1	900	4
6	2.0 E							
1	3.1 E							
35	0.9 NNW							
37	2.3 NNW							
26	2.6 NNE							
38	3.4 NW							
Average Zone I*		<u>695</u>	<u>758</u>	<u>230</u>	<u>3.0</u>	<u>2</u>	<u>950</u>	<u>5</u>
27	6.7 NNW	1160	408	282	4.0	6	1300	5
21	14.9 ESE	480	240	114	1.1	3	1300	4
28	7.7 N	470	128	136	1.6	3	1200	4
Average Zone II		<u>703</u>	<u>259</u>	<u>177</u>	<u>2.2</u>	<u>4</u>	<u>1267</u>	<u>4</u>

* Add to zone I site; N 1.9 km S no metal values

Table 19 cont'd.

16	7.5 ESE	1140	504	218	0.8	2	1300	5
40	6.4 W	185	394	224	2.1	10	800	14
30	11.5 N	280	130	185	2.2	3	1400	4
20	20.0 ENE	130	48	84	1.0	2	900	4
22	19.5 SE	215	270	139	1.5	1	900	3
41	11.4 WSW	90	345	97	1.1	5	600	8
Average Zone III		<u>340</u>	<u>281</u>	<u>158</u>	<u>1.5</u>	<u>4</u>	<u>983</u>	<u>6</u>
19	15.8 E	285	61	158	2.1	2	300	4
33	17.3 N	135	67	90	0.9	2	700	3
23	25.4 SE	530	112	180	2.3	3	500	5
231	30.5 SE	260	68	150	2.3	3	200	7
17	6.9 ENE	170	122	72	0.9	4	1200	6
Average Zone IV		<u>276</u>	<u>86</u>	<u>130</u>	<u>1.7</u>	<u>3</u>	<u>580</u>	<u>5</u>
31	14.1 NNW	80	41	77	0.7	1	1100	6
202	29.5 E	195	33	140	1.9	1	500	7
331	20.0 N	250	37	118	1.7	3	300	7
201	25.3 NE	210	47	173	2.0	1	300	2
43	20.1 SW	15	45	46	0.5	3	200	10
421	18.0 SSW	110	100	130	1.2	3	400	11
332	23.3 NNW	170	31	114	1.4	1	400	7
24	35.5 SE	110	428	132	0.5	2	1300	4
44	25.8 WSW	125	20	110	0.9	1	300	12
45	33.8 SW	70	87	85	0.4	1	200	10
32	20.5 NW	195	33	140	1.9	1	500	7
Average Zone V		<u>139</u>	<u>82</u>	<u>115</u>	<u>1.2</u>	<u>2</u>	<u>500</u>	<u>8</u>

Table 20. Heavy metals and non-metals (ppm dry wt.) in the leaves of the woodland moss Hylocomium splendens collected at various sites in the Murdochville area.

Site	km from smelter	Pb	Cu	Zn	Cd	As	S	F
P	0.5 SSE							
V	1.1 SSE							
N	1.9 S							
8	3.0 E							
9	4.8 ESE							
10	5.0 SE							
11	6.3 SE							
15	8.3 ESE	17320	724	304	8.4	4	1600	7
18	11.0 E							
6	2.0 E							
1	3.1 E							
35	0.9 NNW							
37	2.3 NNW							
26	2.6 NNE							
38	3.4 NW							
Average Zone I		<u>17320</u>	<u>724</u>	<u>304</u>	<u>8.4</u>	<u>4</u>	<u>1600</u>	<u>7</u>
27	6.7 NNW	1630	403	391	6.6	4	100	8
21	14.9 ESE	936	279	157	3.6	4	1100	4
28	7.7 N	968	268	218	5.4	6	1500	4
Average Zone II		<u>1178</u>	<u>317</u>	<u>255</u>	<u>2.9</u>	<u>5</u>	<u>900</u>	<u>5</u>
16	7.5 ESE	116	68	68	0.5	4	500	6

Table 20 cont'd.

40	6.4 W	914	466	324	12.0	8	800	12
30	11.5 N	792	152	204	4.4	8	1700	7
20	20.0 ENE	275	46	99	2.2	4	900	5
22	19.5 SE	841	516	228	5.4	4	700	4
41	11.4 WSW	318	410	154	3.6	6	1300	16
Average Zone III		<u>543</u>	<u>276</u>	<u>180</u>	<u>4.2</u>	<u>6</u>	<u>983</u>	<u>8</u>
19	15.8 E	330	60	116	1.8	1	300	12
33	17.3 N	140	56	76	5.6	4	900	3
23	25.4 SE	473	116	175	4.5	4	700	4
231	30.5 SE	325	56	102	1.5	6	300	7
17	6.9 ENE	1210	525	202	5.1	8	1100	4
Average Zone IV		<u>496</u>	<u>163</u>	<u>134</u>	<u>3.7</u>	<u>5</u>	<u>660</u>	<u>6</u>
31	14.1 NNW	154	36	77	1.4	4	1100	3
202	29.5 E	350	43	115	1.5	1	700	9
331	20.0 N	290	47	120	1.6	1	700	7
201	25.3 NE	280	67	185	2.1	1	500	10
43	20.1 SW	141	81	86	1.1	4	400	10
421	18.0 SSW	140	120	119	1.8	1	300	12
332	23.3 NNW	200	28	96	1.5	1	500	6
24	35.5 SE	252	611	174	2.0	4	1600	3
44	25.8 WSW	175	31	120	1.1	1	500	10
45	33.8 SW	95	111	92	0.5	1	200	10
32	20.5 NW	270	40	117	1.6	1	1200	8
Average Zone V		<u>213</u>	<u>138</u>	<u>118</u>	<u>1.5</u>	<u>2</u>	<u>672</u>	<u>8</u>

3. Discussion.

A complete elimination of epiphytes at the more polluted sites, such as P, V, N, 1, 6, 8, 9, 10, 11, 15, 26, 35, 37 and 38, and a reduction of their frequency-coverage values at the less polluted sites in the Murdochville area can be explained on the basis of the extreme sensitivity of lichens and bryophytes to air pollutants especially by sulphur dioxide (Rao and LeBlanc 1966; Coker 1967; LeBlanc and Rao 1973ab; Skopera and Vitt 1976).

From the data presented in Tables 11, 12 and 15, it is apparent that species richness and frequency-coverage of epiphytes at a site is affected by the proximity of the site to the smelter. As the sites investigated here are distributed over a wide area around Murdochville, the phytosociological changes indicated above create IAP gradients on all transects radiating from the source of pollution. In general, the closer the site is to the smelter, the higher its pollution level is (Tables 9 and 10; Figs. 6 to 9) and the lower is its IAP value (Table 11). From these inverse correlations it is apparent that the degree of epiphyte response vis-à-vis the IAP of an area is a reliable measure of the level of air pollution prevailing in that area.

A biological scale could also be constructed for the Murdochville area from the data much in the same way as Hawksworth and Rose (1970) have done for England. These

two distinct geographical regions cannot be directly compared, however, because of the differences that exist in species composition between North American and British floras. If such a scale were to be applied to the area studied it would be concluded that an area would have a sulphur dioxide concentration range of four to seven ppb if Lobaria pulmonaria and Blepharostoma trichophyllum, for example, formed part of the species composition of the epiphytes associated with A. balsamea (Table 15). At the other extreme the absence of all other species except those listed in Table 15 from Hypogymnia physodes to Cetraria orbata would indicate a possible sulphur dioxide pollution range of 12 to 21 ppb for a particular area.

It is interesting to note that the absence of epiphytes at sulphur dioxide concentrations of 17 to 87 ppb as well as the paucity of epiphytes at concentration range of 12 to 21 ppb roughly corresponds with the nationally accepted air quality standard of 20 ppb sulphur dioxide on an annual basis. Based on the epiphyte response at these above concentrations it would seem that the choice of this standard was a judicious one.

There are sites having the same number of epiphytes but different indices of air purity. For example, sites 16 and 20 have a total of 13 epiphytes (11 lichens and two bryophytes), but their respective IAP values are 42 and 48. Such differences in IAP mostly accrue due to changes in the frequency-coverage which is essentially an expression

of vitality or metabolic response of the epiphytic species directly to air pollution or indirectly to substrate changes caused by sulphur dioxide deposition. This emphasizes the fact that in comparison to the number of epiphytes occurring at a site, the $Q \times f$ value of the epiphytes is decidedly a better and more definite indicator of the degree of pollution.

At any given site, the sulphur dioxide concentration and the IAP are reciprocally related to each other as a function of the distance from the smelter. It is evident that a high degree of correlation exists between sulphur dioxide concentration and distance, between sulphur dioxide concentration and IAP value, and between the IAP value and distance from the smelter (Fig. 15).

The various IAP zones as outlined in Fig. 14, represent areas with different levels of pollution. As mentioned above, there is a definite correlation between the averages of the IAP values and the sulphur dioxide concentration of these zones (Fig. 14 compared to Figs. 6 to 9). A decrease in the sulphur dioxide concentration from 87 to 7 ppb, followed by an increase in the IAP from zero to 110, as seen also in the Arvida area for example (LeBlanc et al. 1972b) supports the contention that the higher the level of pollution the lower the IAP value and vice-versa. Thus, in the IAP method one has an efficient and economical tool to map pollution through time and space.

If enough data on IAP values and pollution levels on a given transect are available, it would be possible to prepare a calibration curve which may be used for the direct determination of the one from the other. The use of such a curve, however, would be restricted to similar geographical areas with comparable epiphytic floras. It would also necessitate awareness on the part of the user of factors other than pollution that might be operational in the area. Such factors may include an accidental fire or topographical singularity, which can either destroy or appreciably modify the epiphytic vegetation in the area. These factors can alter the IAP values significantly by either aggravating or subduing the effects of pollution. For example, the lack of epiphytes at site 18, located 11.0 km E of the smelter, may be attributed not so much to the level of sulphur dioxide, as to the absence of suitable host trees in the area and to changes in microclimate as a result of a combination of fire and intense logging operations in the past. Because of this, site 18 has been excluded from the IAP map (Fig. 14). The sulphur dioxide concentration at this site may vary from less than 10 ppb to a maximum of 30 ppb (Figs. 6 to 8) and corresponds to the IAP zone III where the epiphytic vegetation is well developed. Similarly, for sites 16 and 17 the IAP values of 42 and 79 appear to be high at first thought, when their proximity to the smelter is considered. These sites, in spite of their location in

the general area of high sulphur dioxide concentrations, are presumably sheltered by the 850 m high range of Miller Mountain. The inflection of the 30 ppb isopleth at about six km E of the smelter corresponds quite well to the position of Miller Mountain. The preservation of such "epiphyte cases" in areas completely or partly devoid of epiphytes, clearly demonstrates the importance of sheltered niches in the realm of pollution mapping.

The IAP zones in the Murdochville area are elongated in the WNW to NW and ESE to SE directions following the pattern of the prevailing winds. In the winter the WNW and NW winds carry the pollutants in the ESE and SE directions (Fig. 10) through the valley which provides a path of minimum resistance. The valley winds also contribute to the dispersion of the pollutants. In the summer the reverse of the above occurs. The onward transmission and gradual dilution of the pollutant plume lead to a spatial pollution concentration differential which is eventually responsible for an epiphytic gradient in the area. These epiphytic gradients in turn help in defining and delimiting the IAP zones. Since the zones based on the IAP classes of zero, 1 to 30, 31 to 60, 61 to 80 and >80 are similar to the possible sulphur dioxide zones based on the dynamic concentration ranges of <10, 10 to 29, 30 to 49, 50 to 75 and >75 ppb in the reverse order, it is apparent that the determination of an IAP provides a plausible method to monitor and describe the

long-range and cumulative impact of sulphur dioxide emissions in the Murdochville area.

The relationship between the heavy metal and non-metal concentration in plants and the IAP of a particular zone is more or less similar to that between the sulphur dioxide concentration and the IAP of that zone. A zone wise comparison of the averages of these elements and the IAP values clearly indicates that as the former increases the latter decreases. However such a correlation was more positive for Pb, Cu, Zn and Cd; less positive for S and F; and least positive for As (Figs. 16 to 19). Again, there exists a distinct relationship between the plant element content and the reciprocal of the distance from the smelter. A relationship similar to this was noticed by Nieboer et al. (1972) in their study of heavy metal contents of lichens in the Sudbury area. It is interesting to note that at site 35, located at 0.9 km NNW of the smelter exceptionally high concentrations of heavy metals were found in the plants. This situation arises due to particulate pollution in the area.

The emission of Pb, Cu, Zn, Cd, As, S and F from the Murdochville smelter increases the concentration of these elements in the air and eventually in the vegetation of the area. Studies with lichens show that the content of several heavy metals (Cu, Ni, Zn, Fe, Pb, Mn) can be explained in terms of atmospheric fallout (Nieboer et al. 1972). Among the four species of terrestrial plants

analysed, the mosses appear to be the most efficient accumulator of elements, especially of Pb, Cu, Zn and S. Shacklette (1965a) also observed that under similar habitat conditions, the element contents in bryophytes usually remain higher than in angiosperms. The order of relative absorption of heavy metals in mosses, such as Hylocomium splendens, and in higher plants, such as Picea mariana, in the Murdochville area is also different. The sorption in the former species is in the order Pb>Cu>Zn>Cd>As, whereas in the latter species it is in the order of Zn>Pb>Cu>As>Cd (Table 21). On the basis of their experimental studies with the carpet-forming moss Hylocomium splendens in southern Sweden, Rühling and Tyler (1970) concluded that this moss tissue had a great capacity for absorbing heavy metal ions selectively from dilute solutions. According to them Cu, Pb>Ni>Co>Cd>Zn>Mn represent the order of decreasing sorption of cations of the heavy metals by the moss tissue in Sweden. The variations in the cation sorption pattern of H. splendens in two areas, eastern Canada and southern Sweden, tend to indicate that the order of heavy metal sorption in a plant species is not fixed and that it may vary from one geographical region to another. However, data on heavy metal sorption by plants from many more regions should be compared before making any final judgment on this point.

It has been found that the IAP shows a better correlation with the metal contents of mosses than with

Table 21. Order of relative sorption of metals* and non-metals in Picea mariana (a), Clintonia borealis (b), Hylocomium splendens (c) and Pleurozium schreberi (d) at certain sites in the Murdochville area.

Site	Location	Taxa		
15	8.3 km ESE	a	Zn>Pb>Cu>As>Cd	S F
		b	Cu,Zn>Pb>As>Cd	S F
		c	Pb>Cu>Zn>Cd>As	S F
		d	Cu>Pb>Zn>Cd>As	S F
35	0.9 km NNW	a	Pb>Zn>As>Cu>Cd	S F
		b	Pb>Zn>Cu>As>Cd	S F
43	20.1 km SW	a	Zn>Pb>Cu>As>Cd	S F
		b	Cu>Pb,Zn>As>Cd	S F
		c	Pb>Cu>Zn>As>Cd	S F
		d	Cu>Zn>Pb>As>Cd	S F

* includes As

those of higher plants. This could be attributed to the great cation exchange capacity of their tissues and the stability of the chelates formed between heavy metal ions and their organic groups and this could qualify the mosses to be the most suitable indicators for surveying metal deposition (Tyler 1971). Similarly it has been shown that lichens can be good indicators of the amount of heavy metal fallout around industrial plants (Nieboer et al. 1972).

It is felt that cryptogamic plants or epiphytes which derive their nutrients from the atmosphere, from stemflow, or from throughfall in both wet and dry deposition can provide precise information with respect to heavy metal pollution. Martinez et al. (1971), based on their investigations of a phanerogamic epiphyte. Spanish moss (Tillandsia usneoides), have also pointed out that epiphytes show a great potential as monitors of Pb and other heavy metals in the atmosphere. Indications are that epiphytic mosses and lichens are as efficient indicators of heavy metal pollution as they are of sulphur dioxide.

On the basis of the results presented in this section it is concluded that the IAP method can be employed for mapping heavy metal pollution more or less in the same manner and with the same degree of efficiency as it has been used for mapping sulphur dioxide pollution.

B. Response of lichen transplants and two naturally occurring epiphytes to sulphur dioxide pollution.

1. Introduction.

The transplantation method has been used to study the effects of air pollution on lichens and bryophytes (Brodo 1961; LeBlanc and Rao 1966; Schönbeck 1969). In this method a lichen and/or bryophyte species, along with its substrate which may be soil, rock or bark, is transferred from a relatively unpolluted area to a polluted one and is allowed to remain there for some definite period of time. The post-exposure changes induced in the transplant are then compared, both qualitatively and quantitatively, with the original condition and with those of the control. A series of such transplants, when located along a gradient of pollution in an otherwise more or less ecologically uniform area, could help delineate a given territory into approximate isotoxic zones by relating changes to the degree of pollution prevailing in the area.

To give further information on the pollution intensity and its special distribution pattern in the Murdochville area, lichen bearing discs were transplanted onto trees at various sites as indicated in Fig. 11 in the area surrounding the copper smelter.

In conjunction with the transplant experiments it was thought appropriate that the naturally occurring epiphytes P. squarrosa and H. physodes, that is those plants that have been subjected to a pollution stress since 1955, should

also be studied. The sample sites for this part of the study, which was carried out in the field season following that of the transplant experiments, were located in sectors where the pollution load was dispersed maximally in the ESE and SE sectors of the study area (Figs. 11 and 21).

It may be confusing to the reader to note that lichens were sampled at sites 11 and 15. These sites have an IAP of zero (see previous account), and presumably no epiphytes occurred there. However epiphytes were subsequently found at site 11 in areas designated as subsite 11(2) and 11(3) as well as at site 15 in an area designated 15(4). The data in Tables 26 and 27 concerning the naturally occurring epiphytes are obtained from these subsites and designated under sites 11 and 15.

2. Results.

a) Transplants.

Simultaneous projection of the three sets of transparencies of the bark discs photographed prior to and after four and 12 months exposure, revealed that the thallus colour of both Parmelia squarrosa and Hypogymnia physodes varied from greenish-grey (the normal condition) to whitish-brown (indication of heavy damage) in a manner directly depending on length of exposure on the one hand and proximity to the smelter on the other. The colour changes after 12 months exposure, were given a numerical value (Table 22) based on an estimate of percent thallus

Table 22. Summary of external changes in Parmelia squarrosa transplants exposed for 12 months in the Murdochville area (a) colouration, (b) thallus adhesion and (c) degree of isidial development.

Site (Fig. 11)	km from smelter	(SO ₂) ^d ppb	a	b	c
V	1.1 SSE	85	1	2	1
37	2.3 NNW	75	3	2	1
1	3.1 E	74	1	1	1
26	2.6 NNE	74	3	3	1
N	1.0 S	65	1	1	1
35	0.9 NNW	59	2	1	1
P	0.5 SSW	53	1	2	1
8	3.0 E	49	3	2	1
9	4.8 ESE	44	3	2	2
38	3.4 NW	38	3	2	1
11	6.3 SE	33	3	2	2
10	5.0 SE	33	3	2	2
27	6.7 NNW	25	4	3	3
15	8.3 ESE	22	3	3	3
17	6.9 ENE	19	5	3	4
21	14.9 ESE	17	4	2	3
28	7.7 N	16	5	4	3
18	11.0 E	14	4	3	3
22	19.5 SE	13	4	3	3

Table 22 cont'd.

30	11.5 N	12	5	3	4
40	6.5 W	11	4	2	3
23	25.4 SE	11	5	3	4
31	14.1 NNW	11	5	5	4
41	11.4 WSW	10	5	4	4
33	17.3 N	10	5	5	4
20	20.0 ENE	9	5	4	4
24	35.5 SE	9	5	5	4
43	20.1 SW	9	5	5	4

-
- a) colouration (% of thallus cover)
low number $\equiv$ heavy damage
high number $\equiv$ normal
- b) adhesion (% of thallus cover attached to bark)
low number $\equiv$ adhesion low
high number $\equiv$ adhesion normal
- c) isidial development
low number $\equiv$ rare
high number $\equiv$ abundant
- d) the SO_2 concentration is the annual arithmetic mean for the time interval covering the exposure of the transplants from June 1972 to June 1973 in ppb. This concentration decreased exponentially with distance from the copper smelter (Fig. 20).

cover. The values are presented in Table 22 in order of decreasing ppb SO_2 and show a correlation of damage with SO_2 concentration. At sites more or less equidistant from the smelter however the extent of damage depended on wind direction, usually being greatest in transplants in the southeast direction. The control transplants at site 43 maintained a normal greenish-grey colouration throughout. The relation of SO_2 concentration and distance from the smelter is shown in Fig. 20.

The result of the macroscopic examination of other external changes, such as thallus adhesion and degree of isidial development are also summarized in Table 22.

The peripheral parts of P. squarrosa and H. physodes thalli transplanted in the polluted areas were often detached from the bark, having their margins upturned, shrivelled, cracked or chipped. At any given site these symptoms were more obvious in the former than in the latter species. The percentage cover of the P. squarrosa adhering to the substratum tended to decrease as the level of pollution increased (Table 22, column b). The lower surfaces of the detached thalli of P. squarrosa appeared normal both in their jet black colouration and in the presence of dense, wiry and black coloured rhizines. In H. physodes however, the detached thalli appeared normal in their non-rhizinate, brownish colouration, but appeared abnormal in their waxy appearance. The control transplants remained normal both with respect to colour and adhesion

Figure 20. The non linear relationship between the sulphur dioxide concentration (ppb) in the air and the km distance from the copper smelter.

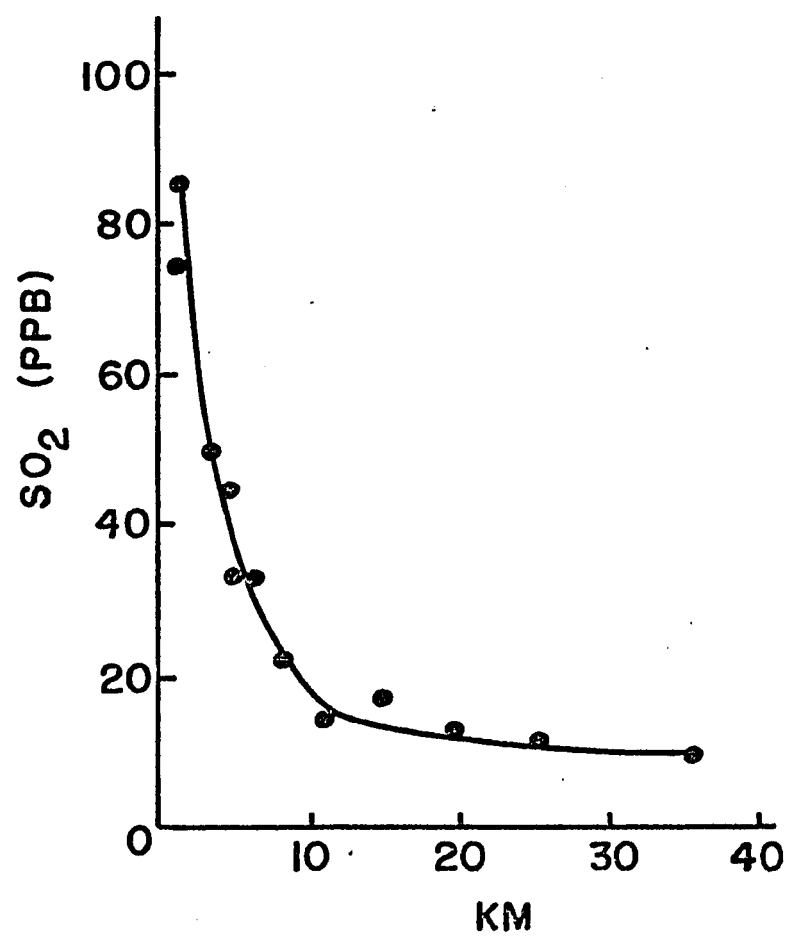
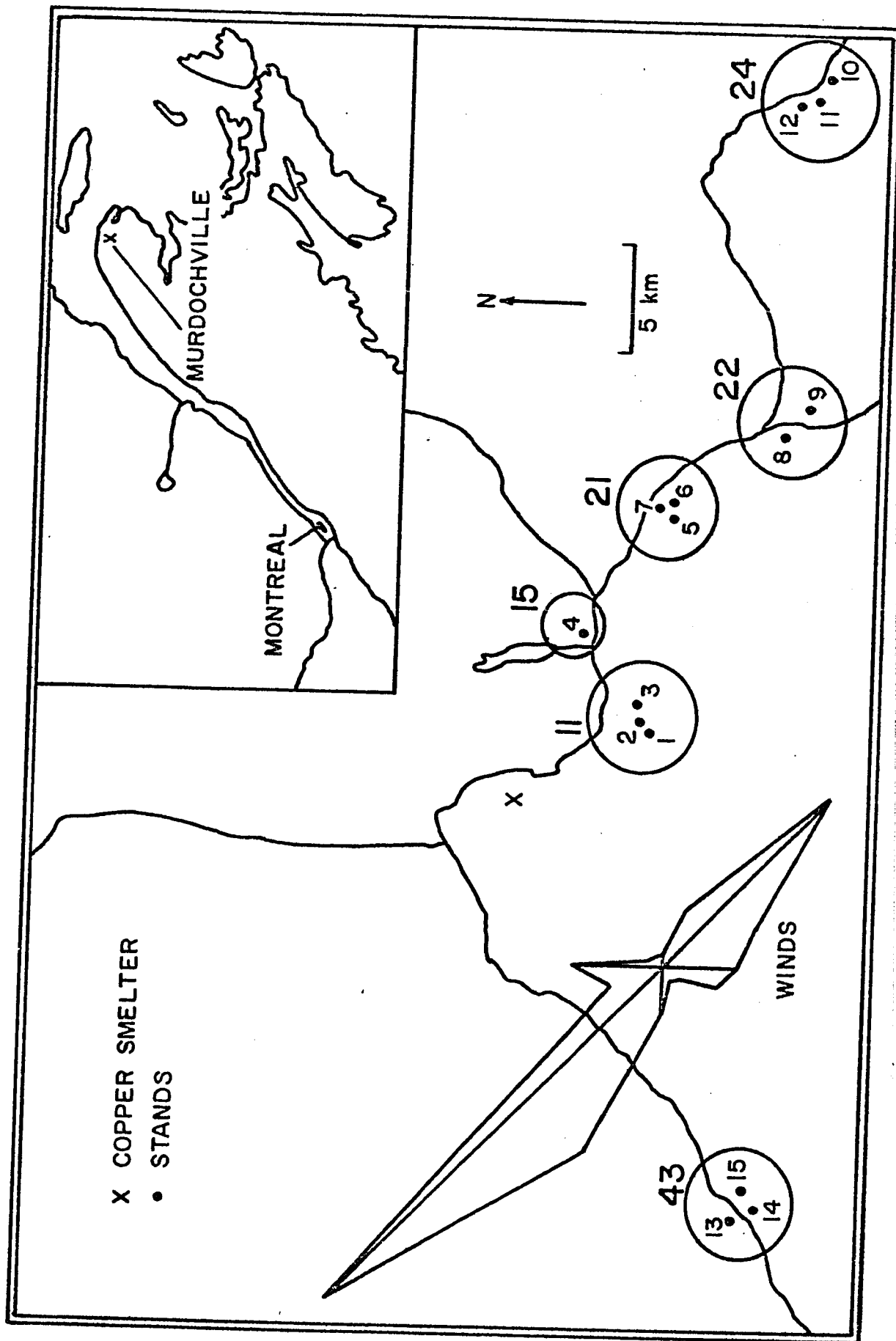


Figure 21. Site locations used for the sampling of the naturally occurring epiphytes Hypogymnia physodes and Parmelia squarrosa; for the incident rainfall (rainwater) and stemflow of Abies balsamea and for the sampling of the annual ring increments of A. balsamea.



of thalli.

In the fruiticose thalli of Usnea sp., transverse cracks were formed on their outer surfaces after transplantation in polluted areas. Such cracks, caused the cortical and algal layers of the thallus to strip off leaving the central cartilagenous strand apparently intact. These effects were severe, moderate or mild, depending on the exposure of the transplants to high, intermediate or low levels of pollution.

Isidial development (isidia are finger-like cylindrical outgrowths from the upper cortex) also was given a numerical value (Table 22, column c). Thalli of P. squarrosa transplanted in relatively unpolluted areas located beyond a distance of 10 km from the smelter had more isidia than those transplanted in highly polluted areas (Table 22, column c).

The phycobiont (the green alga Trebouxia) of P. squarrosa transplanted at sites P, 8, 11, 21, 22, 23 and 24 located between 0.5 and 35.5 km ESE and SE of the smelter was observed microscopically for cell size and presence of dead and plasmolysed cells (Table 23). The figures show fewer dead and plasmolysed cells, larger cell size and more dividing cells in areas of low pollution. With respect to these changes, the Trebouxia cells of the lichens from site 24 furthest removed from the smelter were more or less similar to those of the control at site 43.

Table 23. Summary of changes in the phycobiont (Trebouxia) of Parmelia squarrosa transplants exposed for 12 months in the Murdochville area (about 1000 cells were examined for each site).

Site	km from (SO ₂) ^f		a	b	c	d	e
	smelter	ppb					
P	0.5 SSW	54	100				
8	3.0 E	49	100				
11	6.3 SE	33	95-98	100	100	8-10	
21	14.9 ESE	17	80-90	90-95	80-90	8-12	0- 2
22	19.5 SE	13	70-80	80-90	50-70	8-15	2- 4
23	25.4 SE	11	30-50	20-30	20-30	8-18	5- 8
24	35.5 SE	9	10-15	5-10	10-20	8-20	20-25
43 ^g	20.1 SW	9	10-15	5-10	10-20	8-20	20-25

- a) dead cell as a percent of the total number of cells observed.
- b) plasmolysed cells as a percent of the living cells.
- c) degree of plasmolysis as the percent of the empty space observed between cell wall and protoplast in the plasmolysed cells (the degree of plasmolysis was considered to be 100% when the size of the empty space was ca. 3/5 of the cell size).
- d) living cell size range in μ .
- e) dividing cells as a percent of the living cells.

Table 23 cont'd.

- f) the SO_2 concentration is the annual arithmetic mean for the time interval covering the exposure of the transplants from June 1972 to June 1973 in ppb.
- g) control site.

Figure 22. Relationship between the ambient sulphur dioxide levels (ppb), mg biomass/cm² lichen thallus after the removal of acetone soluble substances (open circles) and the mg acetone soluble substances/g lichen thallus (solid circles) of Parmelia squarrosa thalli exposed for 12 months on the ESE and SE directions in the Murdochville area.

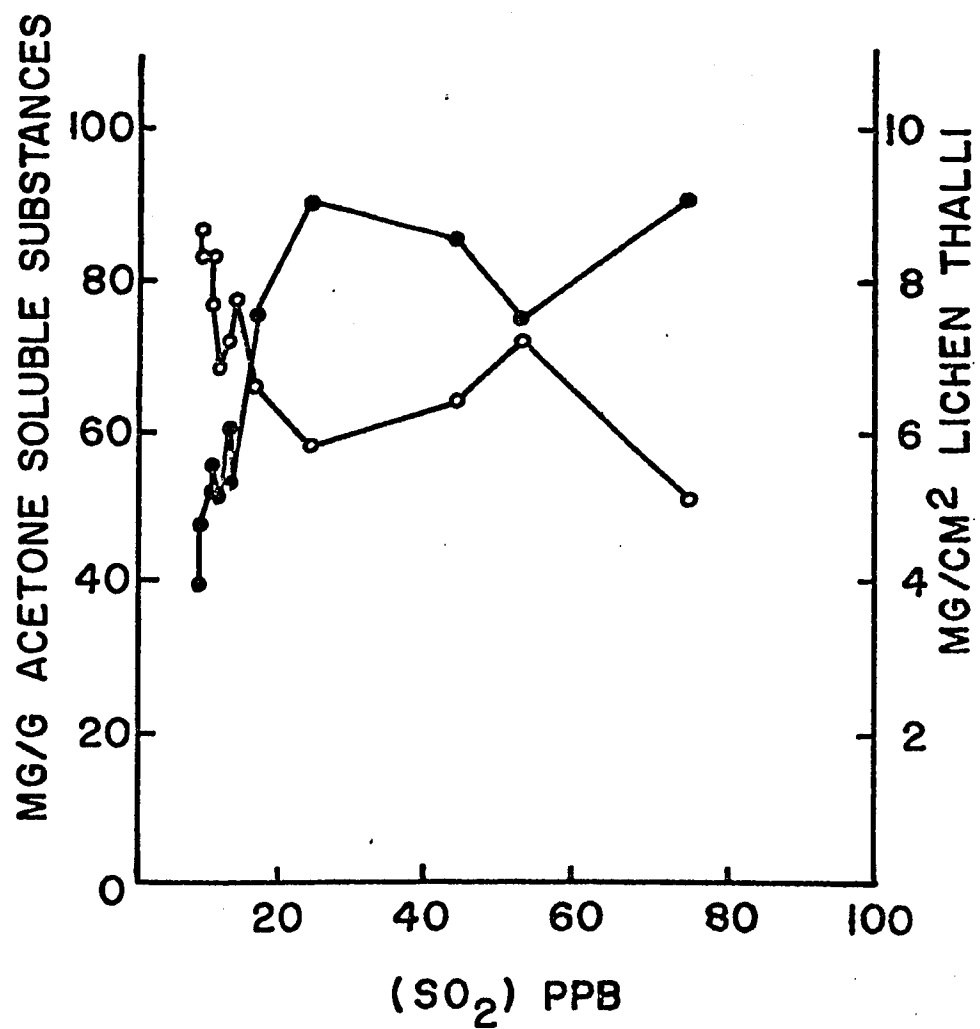


Table 24. Biomass changes in Parmelia squarrosa transplants exposed at various sites in the Murdochville area.

Site	km from smelter	(SO ₂) ^d ppb	Four months			Twelve months		
			a	b	c	a	b	c
37	2.3 NNW	75	8.72	8.37	40	5.62	5.11	91
P	0.5 SSW	53	9.24	9.17	8	7.73	7.11	74
9	4.8 ESE	44	8.11	7.67	54	6.96	6.37	85
27	6.7 NNW	25	11.80	11.42	32	6.33	5.76	90
21	14.9 ESE	17	7.12	6.66	65	7.08	6.55	75
18	11.0 E	14	7.37	7.05	43	8.08	7.65	53
22	19.5 SE	13	8.74	8.26	55	7.67	7.21	60
30	11.5 N	12	7.52	7.12	53	7.18	6.82	50
23	25.4 SE	11	8.16	7.67	60	8.08	7.63	56
31	14.1 NNW	11				8.76	8.31	51
33	17.3 N	10	8.78	8.42	41			
24	35.5 SE	9	7.80	7.55	32	8.69	8.28	47
43	20.1 SW	9	8.43	8.18	30	9.05	8.65	44

a) mg biomass/cm² lichen thallus

b) mg biomass/cm² lichen thallus (after soaking in acetone)

c) mg acetone soluble substances/g lichen thallus

d) the SO₂ concentration is the annual arithmetic mean for the time interval covering the exposure of the transplants from June 1972 to June 1973 in ppb.

The outer cortices in all lichens, regardless of their growth form were covered with an unidentified somewhat waxy material which was removed with acetone and shown to be more abundant on thalli transplanted in areas of high ambient SO_2 (Fig. 22). This substance gave a shiny and water-soaked appearance to the thallus surface in reflected light.

The biomass values (mg/cm^2) of four month and 12 month exposed transplants of P. squarrosa both before and after treatment with acetone, are shown in Table 24. The amount of extractable acetone soluble substances from the thallus seemed to increase with increasing levels of pollution while the biomass decreased (Fig. 22). This was evident for those plants exposed for 12 months. No pattern was established for the shorter exposure period. No deposition rate of these unidentified substances in the transplants exposed for 12 months in areas of high sulphur dioxide concentration was about two times higher than in the control exposed for a similar period of time.

There was a general correlation between the chlorophyll contents, expressed as a percent of the control, of the P. squarrosa transplants from various sites and the sulphur dioxide levels prevailing at those sites (Table 25). The amount of total chlorophyll, of chlorophyll a and chlorophyll b was inversely proportional to the sulphur dioxide

Table 25. The amount of chlorophyll present and lost in Parmelia squarrosa transplants after twelve months of exposure to different concentrations of ambient sulphur dioxide (ppb).

Site	km from smelter	(SO ₂) ^d ppb	Chlorophyll (% of control)					
			present			lost		
			a	b	c	a	b	c
37	2.3 NNW	75	5	2	16	95	98	84
26	2.6 NNE	74	2	1	2	98	99	95
N	1.0 S	65	1	1	3	99	99	97
35	0.9 NNW	59	1	1	3	99	99	97
P	0.5 SSW	53	7	4	19	93	96	81
8	3.0 E	49	7	4	19	93	96	81
9	4.8 ESE	44	12	9	23	88	91	77
38	3.4 NW	38	6	2	22	94	98	78
11	6.3 SE	33	6	2	22	94	98	78
10	5.0 SE	33	5	4	8	95	96	92
27	6.7 NNW	25	5	9	23	95	91	77
17	6.9 ENE	19	17	16	23	83	84	77
21	14.9 ESE	17	7	1	32	93	99	68
28	7.7 N	16	36	38	34	64	62	66
18	11.0 E	14	44	45	41	56	55	59
22	19.5 SE	13	32	32	36	68	68	64
30	11.5 N	12	34	33	36	66	67	64
40	6.5 W	11	26	26	25	74	74	75
23	25.4 SE	11	42	41	46	58	59	54

Table 25 cont'd.

31	14.1 NNW	11	27	27	27	73	73	73
41	11.4 WSW	10	43	43	42	57	57	58
33	13.3 N	10	50	50	48	50	50	52
20	20.0 ENE	9	49	45	61	57	55	39
24	35.5 SE	9	64	64	64	36	36	36
43 ^e	20.1 SW	9	100	100	100	0	0	0

a) total chlorophyll

b) chlorophyll a

c) chlorophyll b

d) the SO₂ concentration is the annual arithmetic mean
for the time interval covering the exposure of the
transplants from June 1972 to June 1973 in ppb.

e) control site

concentration. The losses of chlorophyll on the other hand were directly proportional to the concentration. At concentrations of nine ppb the lichen thalli could still lose up to 57% of its total chlorophyll, 55% of its chlorophyll a and 39% of its chlorophyll b. Above 17 ppb ambient sulphur dioxide the total chlorophyll content of P. squarrosa thalli was consistently less than 10% except in two cases where it was below 20%.

b) Naturally occurring epiphytes.

The sampling sites of P. squarrosa and H. physodes were located in the ESE and SE sector of the study area (Fig. 21).

The amounts of total chlorophyll, and chlorophylls a and b in the two lichen species were also determined and as shown in Tables 26 and 27 were found to increase with increasing distance from the smelter and with decreasing concentration of sulphur dioxide. In P. squarrosa and in H. physodes the amount of total chlorophyll at the control site (43) was 3.3 and 6.6 times higher than at the polluted site (11). For equal weights of thallus the total chlorophyll content in H. physodes was more than in P. squarrosa (the former containing 3.2 mg/g and the latter 2.2 mg/g of total chlorophyll at site 43. At the control site the amounts of total chlorophyll, chlorophyll a and b in H. physodes were respectively 69, 70 and 66% more than in P. squarrosa. However, in heavily polluted areas the percent loss in total chlorophyll, chlorophyll a and b in H. physodes as shown by comparing Tables 27 and 26 was usually more than

Table 26. Amount of chlorophyll in the epiphytic lichen Parmelia squarrosa relative to the control site, collected at various distances ESE and SE from the copper smelter.

Site	km from smelter	(SO ₂) ^d ppb	Chlorophyll (% of control)					
			Present			Lost		
			a	b	c	a	b	c
11	6.3 SE	30	30	29	34	70	71	66
15	8.3 ESE	17	67	68	63	33	32	37
21	14.9 ESE	13	62	60	69	48	40	41
22	19.5 SE	9	76	84	57	24	16	43
24	35.5 SE	6	78	74	79	22	26	21
43 ^e	20.1 SW	6	100	100	100	0	0	0

a) total chlorophyll

b) chlorophyll a

c) chlorophyll b

d) the SO₂ concentration is the arithmetic mean of all of the values up to September 1974

e) control site

Table 27. Amount of chlorophyll in the epiphytic lichen Hypogymnia physodes relative to the control site, collected at various distances ESE and SE from the copper smelter.

Site	km from smelter	(SO ₂) ^d ppb	Chlorophyll (% of control)					
			Present			Lost		
			a	b	c	a	b	c
11	6.3 SE	30	15	14	18	85	86	82
15	8.3 ESE	17	54	51	66	46	49	34
21	14.9 ESE	13	72	74	63	28	36	37
22	19.5 SE	9	72	69	81	28	31	19
24	35.5 SE	6	72	73	69	28	27	31
43 ^e	20.1 SW	6	100	100	100	0	0	0

a) total chlorophyll

b) chlorophyll a

c) chlorophyll b

d) the SO₂ concentration is the arithmetic mean of all of the values up to September 1974

e) control site

in P. squarrosa indicating a greater sensitivity of the H. physodes to SO₂ pollution.

Transplanted P. squarrosa reacted more sharply to pollution than did the naturally occurring thalli of the same species. In comparing site 11 Table 26 with site 11 Table 25, it can be seen that transplanted P. squarrosa lost 94% of its total chlorophyll while the naturally occurring thalli retained 27%. A similar comparison of sites 21, 22 and 24 can be made and again show that the naturally occurring thalli had higher chlorophyll contents. In all cases however it should also be noted that the sulphur dioxide levels were slightly higher during the transplant exposure period.

3. Discussion

The continuous in situ exposure of P. squarrosa transplants to a sulphur dioxide polluted environment produced several identifiable symptoms in the lichen thalli. These symptoms were quantified and related to the annual arithmetic mean of the sulphur dioxide concentration, between June 1972 to June 1973, prevailing at the sites, provide an interesting picture of the air pollution situation in the Murdochville area and its influence on the survival of lichens.

The degree and the area of discolouration of the thalli (Table 22), and the amount of acetone soluble substances (Table 24) imply that these plant responses directly respond to the ambient sulphur dioxide levels.

The changes in thallus adhesion and in the degree of isidial development (Table 22) also lead to the same conclusion. The annual average concentration of sulphur dioxide of nine ppb or the average for the month of October of 13 ppb sulphur dioxide at site 43 (selected as the control) would seem to represent the "normal" concentrations of sulphur dioxide that P. squarrosa can tolerate (Table 22). In comparison P. sulcata was found to tolerate only five ppb (LeBlanc et al. 1972a) Sulphur dioxide concentration, which in the Murdochville area, ranged from nine to 85 ppb during the transplant period.

Reduction in isidial development (Table 22) has been observed by others also. Pyatt (1970), LeBlanc and Rao (1973a) and Margot and De Sloover (1973) observed that the ability to produce viable ascospores as well as soredial and isidial structures was proportional to the sulphur dioxide pollution stress. Margot (1973) noted that sulphur dioxide lowers the multiplication rate of the algal cells and thus inhibits the germination of soredia.

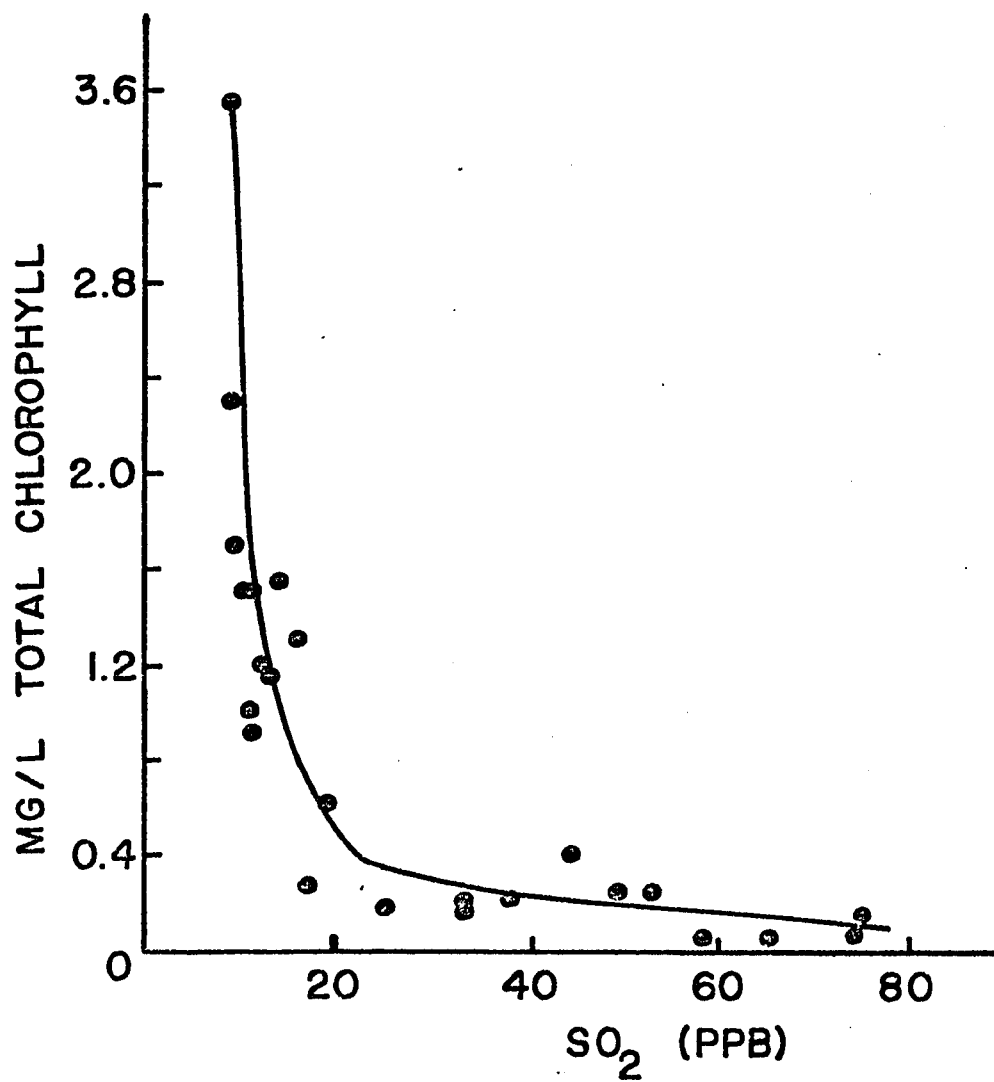
Average sulphur dioxide levels about 33 ppb killed more than 95 percent of the phycobionts of P. squarrosa (Table 23) and clearly demonstrates that sulphur dioxide has an inhibitory effect on the metabolic and reproductive functions of the lichen algae. A gradual decrease in the average concentration from 33 to nine ppb leads to a simultaneous reduction in the number of dead cells from 95 to 10 percent, of plasmolized cells from 100 to five

percent and in the degree of plasmolysis from 100 to 10 percent. This seems to suggest that under reduced pollution stress, the action of sulphur dioxide remains confined mainly to the outermost cells of the algal layer in the thallus.

It was found that with the increase in the level of pollution, there was an increase in the amount of acetone extractable (unidentified) substances and also a decrease in the total amount of thallus tissue in P. squarrosa transplants (Table 24). Similar changes were observed by LeBlanc and Rao (1973b) in P. sulcata thalli affected by iron smelter emissions in the Sudbury area. The mode of production of these substances is unknown.

A comparison of the degree of sulphur dioxide pollution and the extent of total chlorophyll damage at the various sites, shows that as the level of sulphur dioxide increases the amount of chlorophyll decreases exponentially (Fig. 23). At concentrations between 25 and 75 ppb about 95 to 99 percent of the total chlorophyll is damaged while at the other extreme, below 10 ppb, the damage is between zero and 57 percent (Table 25). It is interesting that at sites 20, 24 and 43 located respectively ENE, SE and SW of the smelter, the percentages of chlorophyll damage are not the same (Table 25), even though average annual sulphur dioxide concentrations at these sites remain at 9 ppb. Perhaps the sulphur dioxide fumigation of more than 15 ppb at sites 20 and 24 in the month of October was responsible

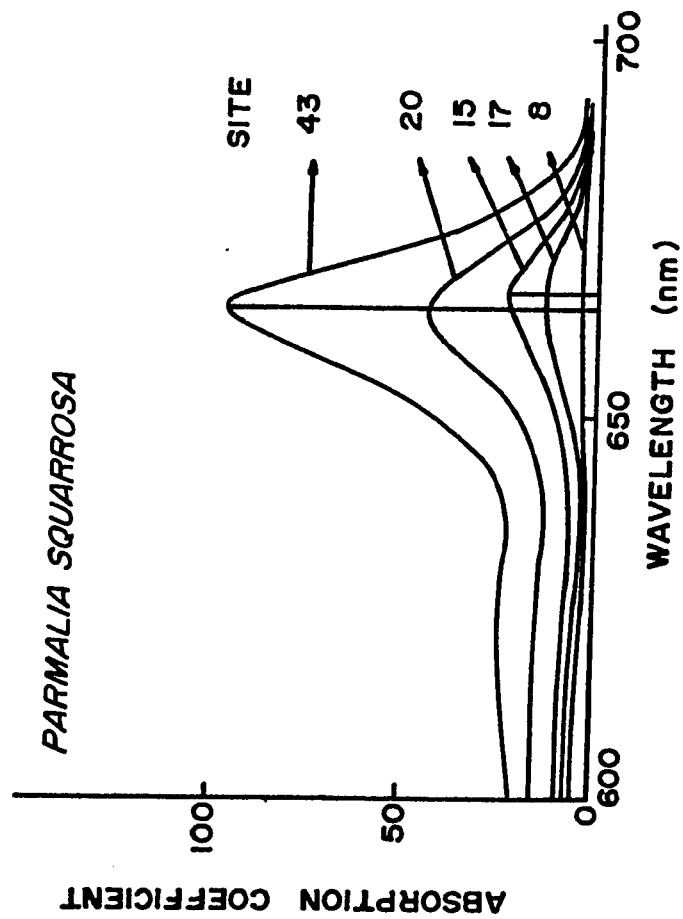
Figure 23. The relationship between the ambient sulphur dioxide concentration (ppb) and the amount of total chlorophyll (mg/l) in the lichen transplant Parmelia squarrosa.



for the increased chlorophyll damage at these sites in comparison to site 43 where the sulphur dioxide level for the same period of time remained within 13 ppb. These values indicate that a high concentration of pollutant over a short period of time may, on occasions, cause more injury to organisms than low long-term pollution levels. In general, however, it seems that the long-term low concentrations of a pollutant can also produce permanent and lethal biological injuries in lichens.

The absorption peaks of chlorophyll extracts of P. squarrosa thalli exposed for 12 months at sites 43, 20, 15, 17 and 8 are shown in Fig. 24, when considered in relation to the sulphur dioxide concentrations at these sites during the month of October 1972 when the level of pollution was rather high, offer the possibility of assessing the range of chlorophyll damage from the level of sulphur dioxide pollution. The results show that at site 43 (control site), where the pollutant concentration was 13 ppb, the chlorophyll remained normal, showing an absorption peak at 663 nm; that at site 20, where the concentration was 16 ppb, the chlorophyll, although reduced in amount, still showed a maximum peak at 663 nm; at site 15, where the concentration was 23 ppb, the chlorophyll was partly degraded into phaeophytin, showing an absorption peak at 667 nm; that at site 17 the chlorophyll showed still further degradation into phaeophytin and finally that at site 8, at a sulphur

Figure 24. Absorption spectr of chlorophyll extracts of Parmelia squarrosa thalli transplanted and exposed for 12 months at sites 43, 20, 15, 17 and 8 in the Murdochville area.



dioxide concentration of 99 ppb, the chlorophyll was completely damaged.

The transplant experiments revealed that, depending on the level of sulphur dioxide in the air, different sets of internal and external injury symptoms are produced in the lichen thalli. On the basis of these injury symptoms, especially those relating to chlorophyll degradation, it is possible to predict the extent of plant damage and further to correlate it with the level of pollution. For the development of acute injury symptoms in lichens, the short-term, high pollution concentration is certainly very real. However, the long-term, low concentrations can cause the same permanent symptoms and injuries to lichens.

The naturally occurring epiphytes P. squarrosa and H. physodes growing at sites 11, 15, 21, 22, 24 and 43 (Fig. 21) had in general the same response as the P. squarrosa transplants towards different levels of sulphur dioxide, at least as far as chlorophyll degradation is concerned (Fig. 25) (compare Figs. 26 and 27 with Fig. 24). Differences did occur however. For example; at site 15 the shift in wavelength is more pronounced in the transplant thalli than in the naturally occurring thalli of P. squarrosa despite the fact that in November 1973 the existing epiphytes was fumigated with 57 ppb sulphur dioxide as compared to 25 for the transplant; and the transplants reacted more quickly to the pollutant than did the natural epiphytes (Fig. 25 and 28). This apparent adaptability of the existing epiphytes

Figure 25. The relationship between the percent total chlorophyll lost in transplanted thalli and naturally occurring thalli of Parmelia squarrosa taken from sites in the ESE and SE directions from the smelter in the Murdochville area.

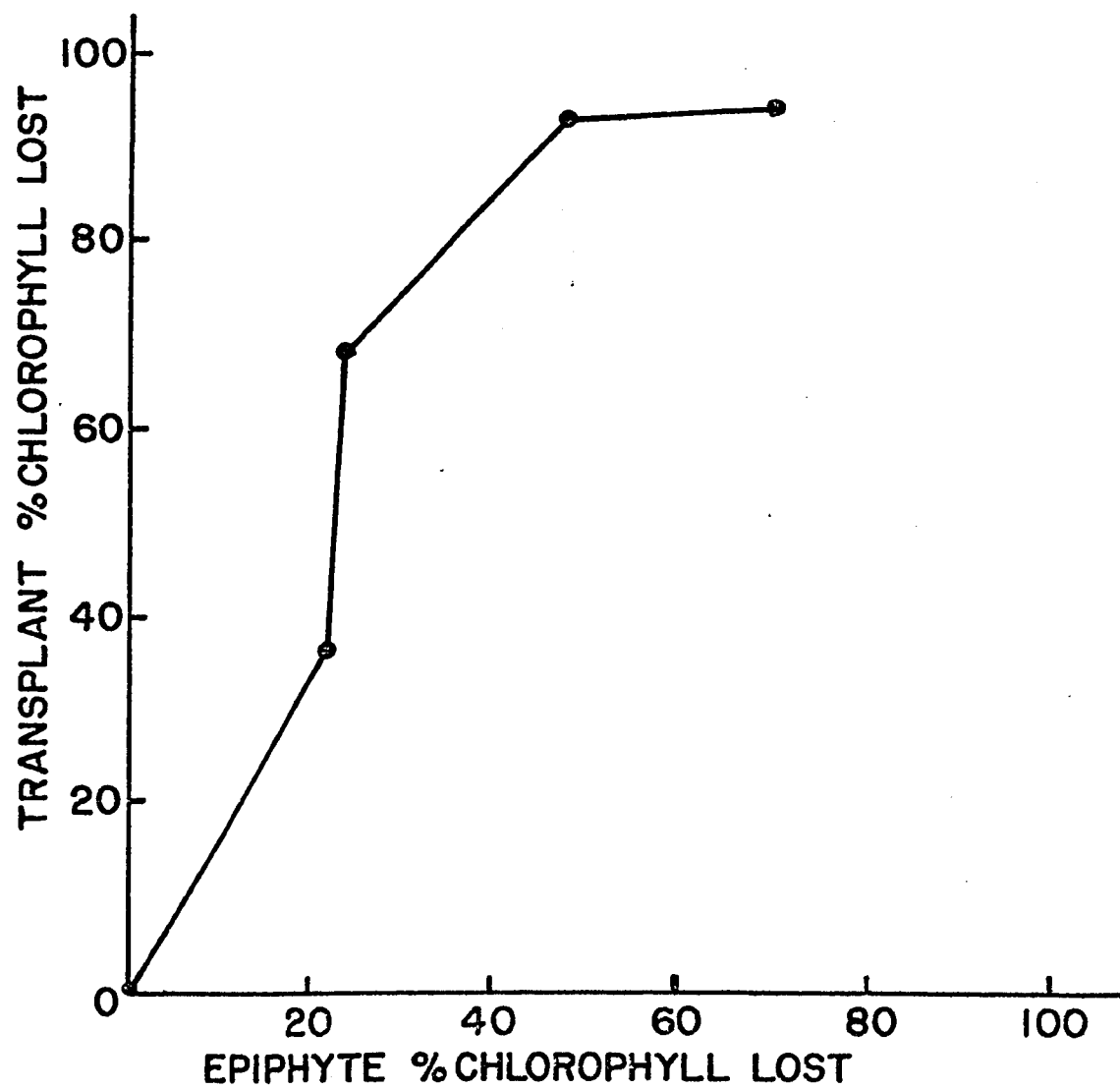


Figure 26. The absorption spectre of the naturally occurring epiphyte Hypogymnia physodes collected from sites 43, 24, 21, 22, 15 and 11 in the Murdochville study area.

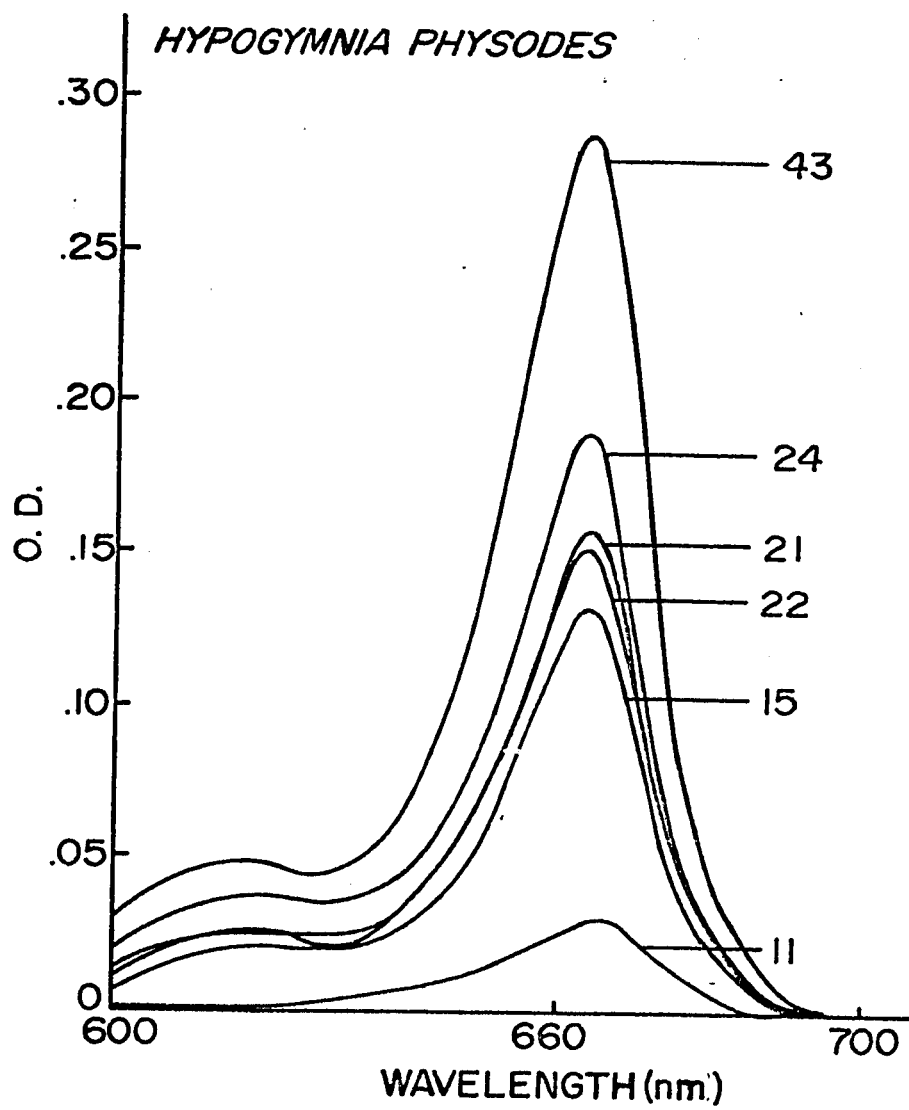


Figure 27. The absorption spectre of the naturally occurring epiphyte Parmelia squarrosa collected from sites 43, 24, 21, 22, 15 and 11 in the Murdochville study area.

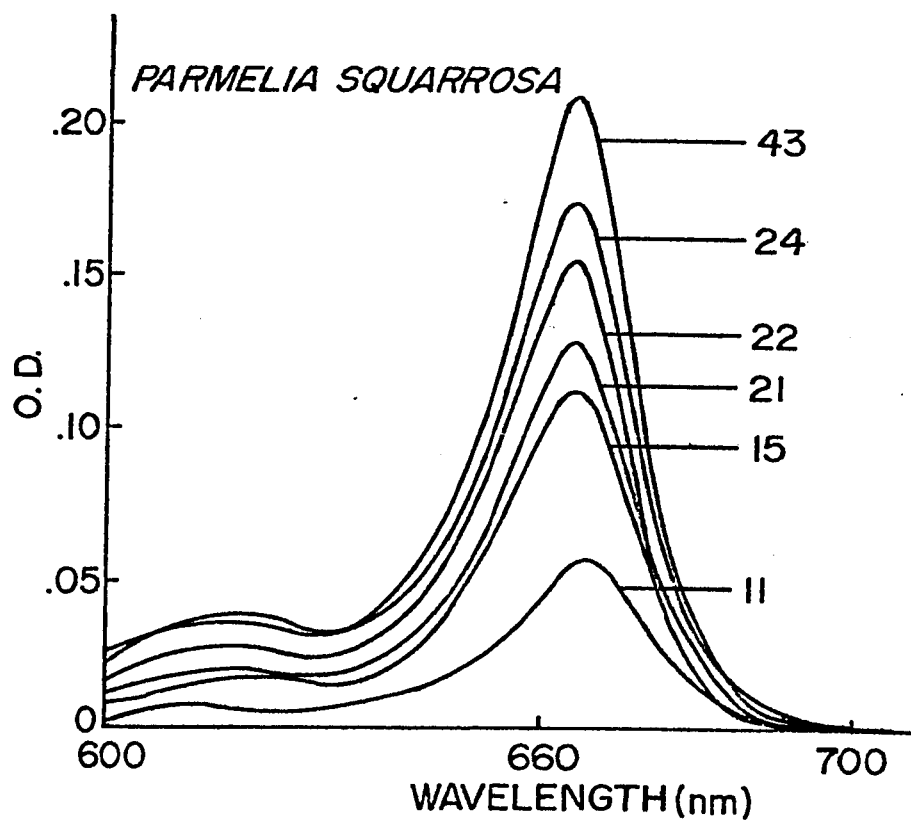
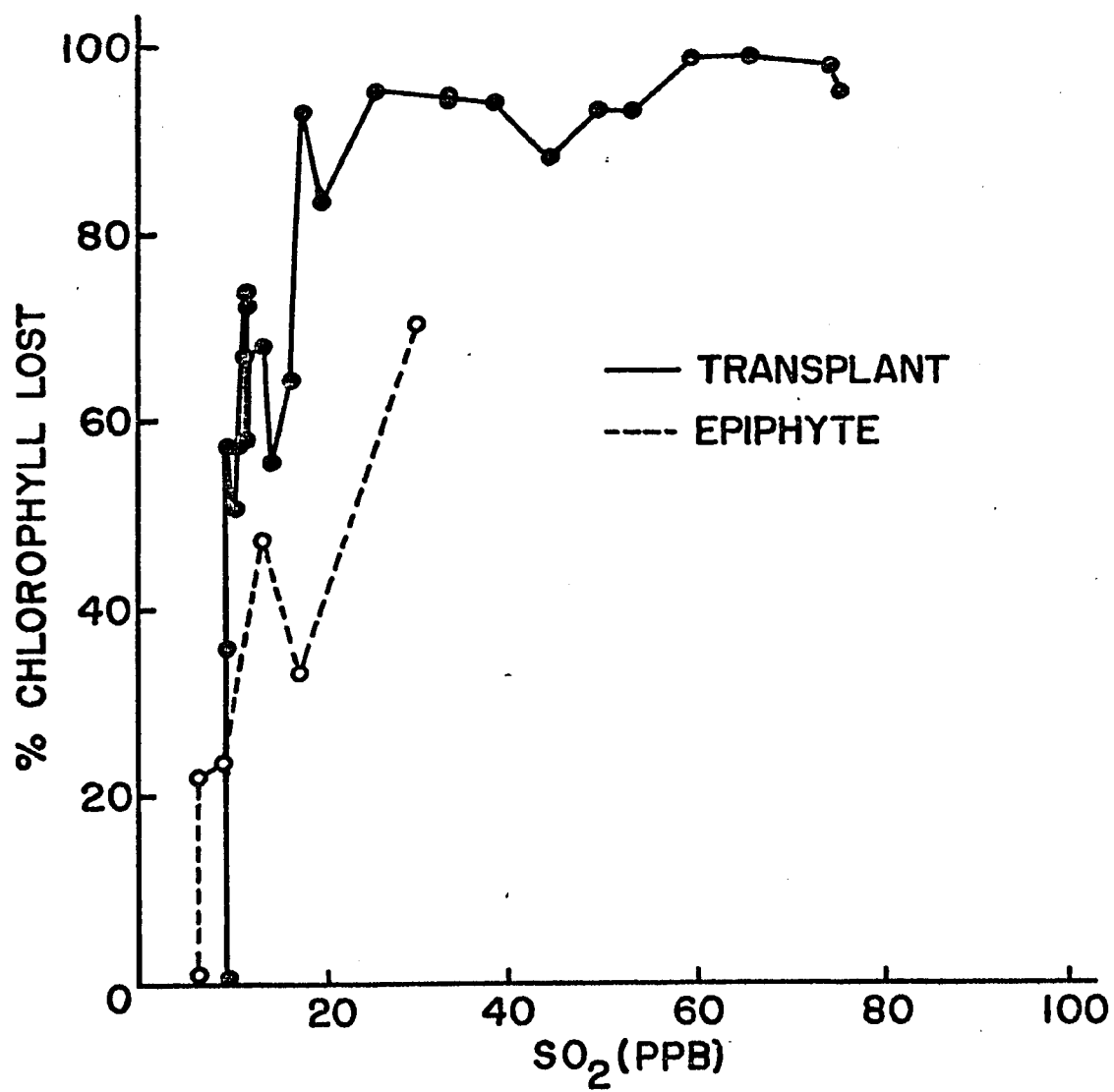


Figure 28. The relationship between the ambient sulphur dioxide concentration (ppb) and the percent chlorophyll lost in Parmelia squarrosa thalli for both transplanted (closed circles) and naturally occurring (open circles) thalli.



to better support pollution by sulphur dioxide than the transplants is interesting to speculate on.

Short-term fumigations could be more important than long-term fumigations in the degradation of chlorophyll and in the increased apparent sensitivity of transplanted thalli. It is true that an initial sulphur dioxide shock could cause a rapid decline in the natural epiphytic vegetation, but, those plants that survive, the pre-adapted ones, would prove to be resistant in the long-term. Hence transplanting lichen thalli in areas where epiphytes can still be found in spite of high ambient sulphur dioxide concentrations could make it appear that the natural existing epiphytes are more resistant than the newly transplanted thalli to sulphur dioxide fumigations. The fact that the transplants were exposed in non-sheltered places as compared to the natural habitat of the lichen may also account for increased transplant sensitivity, in that the transplants are subjected to the full brunt of the potential sulphur dioxide fumigations while those thalli growing on the bark of A. balsamea at the same site receive less gaseous sulphur dioxide due to the filtering action of the tree canopy. It could be that the normal drying and wetting cycle of the transplants has been altered to a point where the "physiological buffering" of the thalli, as expressed by Farrar (1976b), has changed thus making them (i.e. the thalli) more susceptible to injury caused by sulphur dioxide or even heavy metals. The buffering

capacity of the lichen as well as the bark discs may be reduced to a greater extent as compared to the normal bark substrate. The former more drastic change may allow for excessive amounts of toxic bisulphite and/or soluble heavy metals to bathe the transplant thalli as compared to the epiphyte in its normal habitat (this is expanded upon in the following section).

C. Acid Rain and the Paucity of Epiphytic Lichens and Mosses.

1. Introduction.

These organisms have been successfully used for mapping air pollution of urban (LeBlanc and De Sloover 1970) and industrial environments (Rose 1973; this study). It has again been shown in the previous sections that epiphytic cryptogams, especially lichens and bryophytes, are reliable bioindicators of air pollution. In the earlier studies however, it was generally the direct effect of pollutant(s), either singly or in a mixture, that was taken into consideration to assess the range of alterations in morphology, physiology, reproduction and phytosociology of these plants (LeBlanc and Rao 1975). While considering the pollution toxicity to epiphytes, little or no attention has been given to the effects induced in them via the polluted substratum, the bark, on which they are attached. This may be due to the preconceived notion that epiphytes, especially lichens, depend primarily on the air for their metabolic needs of gases, moisture and mineral elements and that they do not derive any nutritional benefit from the underlying bark. However, one should remember that pollutants are adsorbed on the bark surface, that epiphytes are occasionally flooded with rain water charged with pollutants washed out from the air, from the tree canopy and trunk, and that propagules, such as soredia and isidia, after being lodged in the bark crevices, are greatly

influenced by the physico-chemical properties of the bark during development.

Air pollutants, either in a gaseous state mixed with air or in a liquid state affected by dew, mist, rain or snow, will be noxious to lichens and bryophytes attached to the bark. Skye (1968) has shown a positive correlation between lichen growth and their pH of their bark substrate, and Gilbert (1970) observed no lichens on ash bark with pH values below 4.0. Lichens growing on the eutrophiated bark of elm show greater resistance to sulphur dioxide perhaps because of the alkaline earth metals trapped in the bark crevices, which may increase the bark buffer capacity for acids and keep up the rate of conversion of sulphur dioxide to SO_4^{2-} (Skye 1968). Studies made in several European cities indicate that, in areas of high sulphur dioxide pollution, there is a tendency towards general acidification of the bark (Staxang 1969; Johnson and Söchting 1973; Grodzinska 1971; Westman 1974).

Sulphur dioxide is a major pollutant in industrial and urban environments where fossil fuels are burned and pyrite ores are concentrated. It readily goes into solution with water. Over the concentration range of 0.81 to 8.73 mg SO_2/m^3 , the rate of solubility of the gas is a function of its concentration; the higher the concentration the greater the solubility and the more rapidly the saturation point is attained (Terraglio and Manganelli 1967). This suggests that raindrops, providing constantly new surfaces for gas

absorption, can be very effective in scavenging sulphur dioxide from the atmosphere. In this section an attempt is made to relate the incidence of acid rain in the vicinity of the copper smelter to certain changes in the physicochemical properties of tree bark and these, in turn, to the scarcity of the epiphytic lichen vegetation in the area. With this aim in view the pH and sulphur content of stemflow water and also the pH and "buffering" capacity of bark was investigated; the induced conversions of sulphur dioxide into sulphurous acid, sulphite or bisulphite ions was assessed and the overall effect of these factors on certain lichens epiphytic on Abies balsamea in the area was evaluated.

2. Results and Discussion.

The underlying theme of the discussion is that sulphur dioxide, besides affecting the epiphytes as a gas, plays an important role, when dispersed in the form of acid rain, by reducing the pH and "buffer" capacity of the bark substratum and the pH of the lichen thalli. The reduced pH will tend to increase the proportion of highly toxic sulphur dioxide derivatives in the bark substratum and in the lichen thalli, thereby enhancing the extent of injury to the epiphytes.

In the previous sections studies of pollugenic effects on epiphytic vegetation in the Murdochville area showed a high degree of correlation between ambient sulphur dioxide concentrations and atmospheric purity indices (IAP) derived

on the basis of lichen sensitivity to pollution, especially along a ESE and SE transect from the copper smelter (Table 28, column 3). It was observed that the IAP values were inversely related to the sulphur dioxide concentrations and directly related to the distance downwind from the smelter, except in areas very close to the smelter where the sulphur dioxide concentration exceeded the acute injury levels and the IAP value was zero due to the formation of an "epiphyte desert". In the present section data, obtained by sampling incident rainfall and stemflow, on acid rain in the area and on the accompanying changes in the bark characteristics of trees, especially Abies balsamea, provide a further information relative to epiphyte sensitivity to air pollution. The data is summarized in Table 28 and Fig. 29 and clearly shows that incident rainfall water, stemflow water, bark and lichen thalli alike reflect increasing concentrations of ambient sulphur dioxide in decreasing pH values (Table 28, columns 5, 6, 7, 8 and 9). Increased acidity of the bark is also indicated by the increasing amounts of NaOH needed to bring bark to neutrality, i.e. "buffer" capacity (Table 28, column 10, Fig. 30). The higher acid content of the bark from areas of high sulphur dioxide concentration is shown by the greater amount (53, 25, 14 and 16% more in the cases of sites 11, 15, 21, and 22 respectively) of NaOH required to neutralize the bark. These results are similar to those of Coker (1967), Skye

Table 28. Summary of pH and buffer capacity data collected at various sites in the Murdochville copper smelter.

1	2	3	4	5	6	7	8	9	10	11	12a	12b
11	6.3 SE	0	30	4.3	3.3	3.7	3.8	3.7	3.2	28.9	11.8	8.4
15	8.3 ESE	0	17	4.3	3.7	3.7	3.8	3.7	2.7	9.5	5.3	7.8
21	14.9 ESE	22	11	4.3	3.7	3.8	3.9	3.8	2.4	2.7	2.6	6.8
22	19.5 SE	49	9	4.3	3.7	3.8	4.0	3.9	2.3	5.5	6.0	2.7
24	35.5 SE	101	6	6.4	4.2	4.0	4.3	4.2	2.1	3.8	12.9	5.1
43	20.1 SW	92	6	5.6	4.8	4.0	4.3	4.2	2.1	2.2	11.6	1.6

1. Site number.
2. km distance and direction of site from the smelter.
3. IAP (index of atmospheric purity).
4. Ambient sulphur dioxide concentration in ppb.
5. pH of rainwater.
6. pH of stemflow of Abies balsamea.
7. pH of bark of Abies balsamea.
8. pH of Parmelia squarrosa thalli.
9. pH of Hypogymnia physodes thalli.
10. Buffering capacity of Abies balsamea bark expressed in terms of 0.1 N NaOH required to neutralize the bark to pH 7.
11. Sulphur content of stemflow water in ppb x 10³.
- 12a. Sulphur content of P. squarrosa thalli in ppb.
- 12b. Sulphur content of H. physodes thalli in ppb.

Figure 29. The relationship between the ambient sulphur dioxide concentration (ppb) and the bark neutralizing capacity of Abies balsamea and the pH of A. balsamea bark, pH of Parmelia squarrosa thalli and the pH of Hypogymnia physodes thalli.

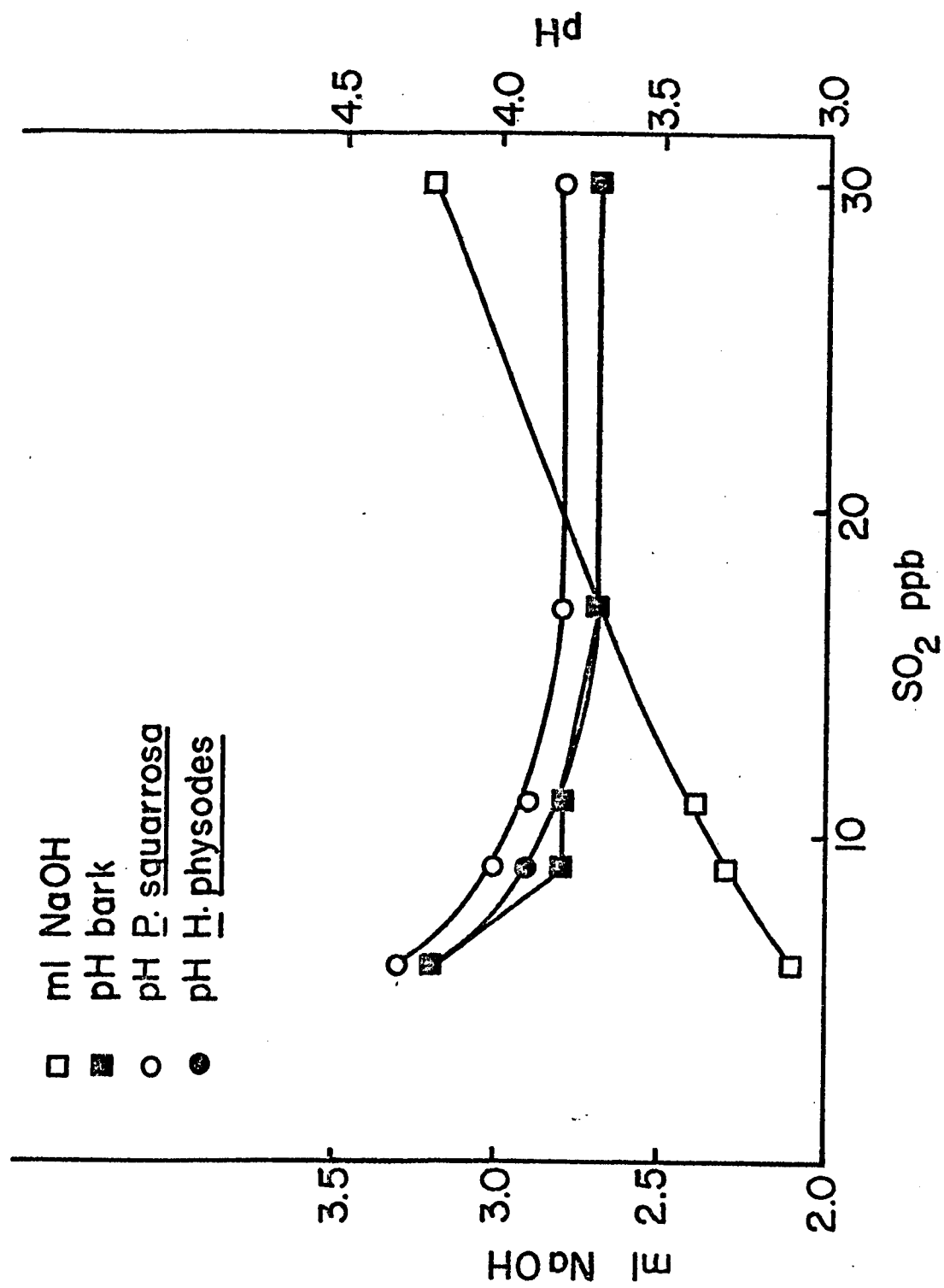
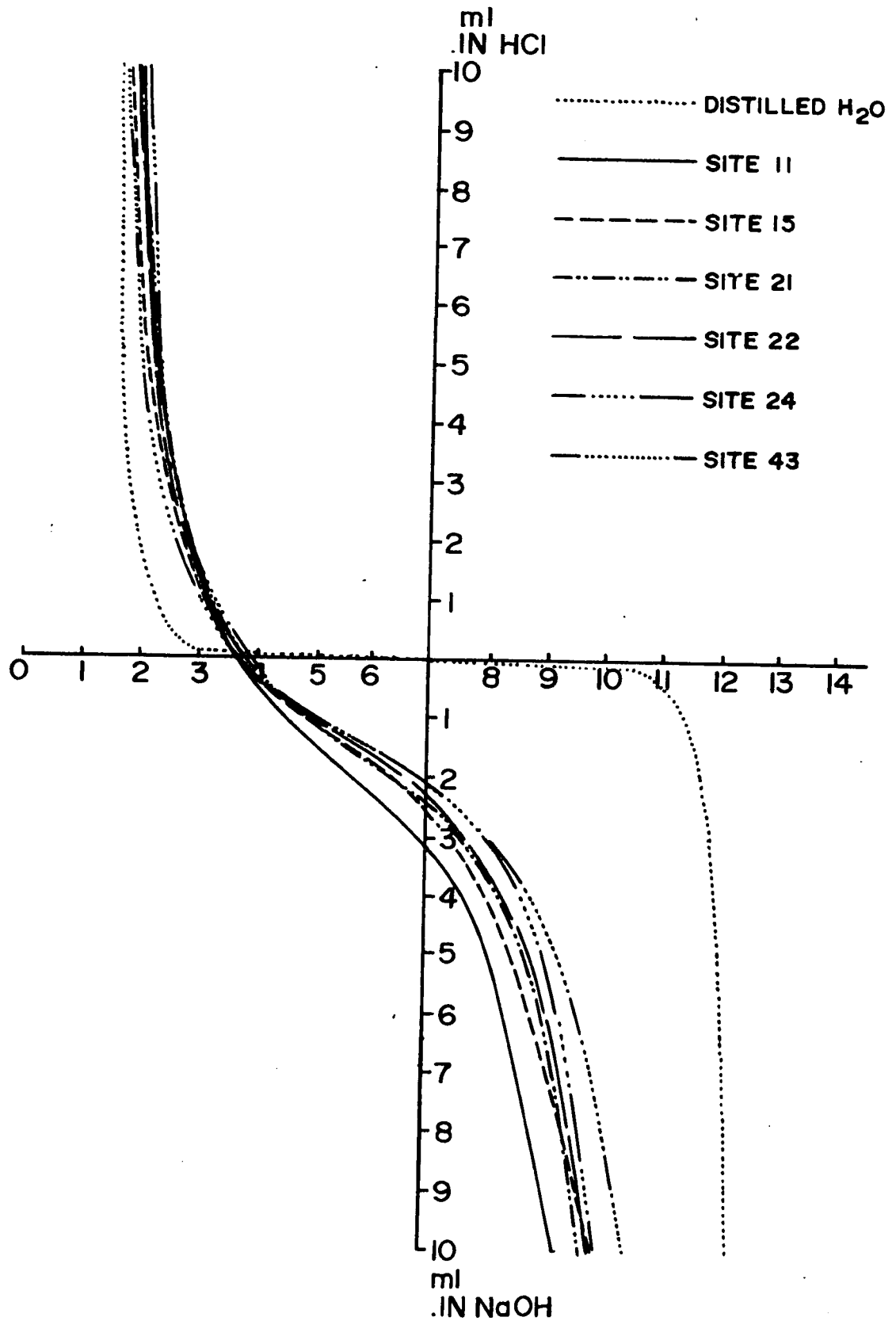


Figure 30. Buffer capacity curves for the bark of Abies balsamea from sites 43, 24, 22, 21, 15 and 11 and for a distilled water control.



(1968), Staxang (1969), Gilbert (1970) and Westman (1974).

In bark, the poorly soluble carbonates and phosphates of calcium and magnesium seem to be important in buffering capacity (Barkman 1958). In areas affected by acid rain these salts will be solubilized and leached out of the bark, thus seriously impairing its buffer capacity (Likens, personal communication). This change in the chemistry of the bark can be hazardous to epiphytes. Sulphur dioxide pollution can directly lower the pH of the epiphyte itself and upset the physiology of the organism (Skye 1968). It is known that certain epiphytes, such as Hypogymnia physodes which possess a high buffering capacity against acids (Skye 1968) are able to survive in sulphur dioxide polluted areas and can occur even in the vicinity of smelters where the level of pollution remains high (previous sections A and B).

Vas and Ingram (1949) cited by Saunders and Wood (1973) have stated that at pH 3.0 about 90 percent of the sulphur dioxide in solution is present in the form of highly toxic bisulphite ions and only about nine percent as undissociated sulphurous acid. In the sulphur dioxide polluted sites, pH values of stemflow, bark and lichen thalli dropped to below 4, and as low as 3.3 in the case of stemflow at site 11 (Table 28). Thus one would expect to find a high proportion of bisulphite ions amongst sulphur content values shown in columns 11 and 12a and 12b of Table 28.

Therefore the proportion of the pH dependent sulphur dioxide derivatives in the bark and lichen thalli becomes a

critical factor in studies of acid rain pollution effects on the epiphytic vegetation. For example, at site 11, where the bark pH was 3.7, the stemflow pH 3.3 and the lichen pH was 3.8 for Parmelia squarrosa and 3.7 for Hypogymnia physodes, about 90 percent of the 28,867 ppb sulphur in the stemflow would be in the form of highly toxic bisulphite ions (Table 28). It is the "buffering" against acid substances which seems to be critically significant (Table 29, equation 3) and on testing the bark samples from the different sites (Fig. 29) it becomes apparent that the order of increasing "buffer" capacity above pH 3.5 mirrors the order of habitat sensitivity based on the IAP (index of atmospheric purity): the lower the "buffer" capacity of the bark, the higher the sensitivity of the lichen (Table 29, equation 6 and Fig. 29).

Note that the pH of the thalli of both lichen species remained at least as high and usually higher than that of the bark on which they were attached and that it increased when the ambient sulphur dioxide concentration decreased (Table 28, columns 8 and 9 and 4; Fig. 29). Sulphur content of the lichen thalli and of stemflow from the various sites, did not show a regular trend of increasing sulphur accumulation with increasing sulphur dioxide pollution. High values of sulphur (13 and 12 ppb) at sites 24 and 43 were apparently not harmful to the lichens occurring there presumably because the higher lichen pH at sites 24 and 43, prevented the formation of toxic bisulphite ions.

Table 29. Regression analyses relating the "buffer" capacity (BC) of Abies balsamea bark to the pH of the rainwater (pH_r), pH of the stemflow (pH_s), the pH of the bark (pH_b) and the sulphur dioxide concentration in the air (SO_2) and the IAP.

Regression equation	r	R^2
(1) $\text{BC} = 1.67 + 0.05(\text{SO}_2)$	0.99	
(2) $\text{BC} = 6.77 - 1.14(\text{pH}_s)$	-0.84	
(3) $\text{BC} = 14.24 - 3.08(\text{pH}_b)$	-0.91	
(4) $\text{BC} = 20.17 - 5.02(\text{pH}_b) + 0.04(\text{pH}_r)$		0.95
BC vs (pH_r)	-0.57	
(pH_r) vs (pH_b)	0.84	
(pH_b) vs BC	-0.91	
(5) $\text{BC} = 1.72 - 0.01(\text{pH}_s) + 0.05(\text{SO}_2)$		0.98
BC vs SO_2	0.99	
SO_2 vs (pH_s)	-0.85	
(pH_s) vs BC	-0.84	
(6) $\text{IAP} = -1875.12 + 471.73\text{BC} + 45.85(\text{pH}_b)$		0.99
IAP vs (pH_b)	-0.80	
(pH_b) vs BC	-0.91	
BC vs IAP	0.97	

r is the correlation coefficient.

R^2 is the multiple correlation coefficient.

The relationship between ambient sulphur dioxide concentration and rainwater pH is not highly significant (Table 30, equation 7). Likewise relationships for sites 11, 15, 21 and 22 (Table 28) though not significantly different from each other, are highly significant with respect to sites 24 and 43. This could mean that a threshold concentration of about nine ppb of ambient sulphur dioxide would be required before a significant change in the rainwater pH occurs. Sulphur dioxide is not the only compound that may affect the level of the threshold value, other acid forming anions, such as nitrate and the presence of neutralizing substances other than those mentioned above may also be important (Likens, personal communication). The dependance of stemflow pH on rainwater pH is significant (Table 30, equation 8). Bark pH is highly dependant upon the stemflow pH (Table 30, equation 9). From equations seven to ten in Table 30, it is apparent that the bark pH is dependant on the complex interaction among sulphur dioxide concentration, rainwater pH and stemflow pH. It is important to reiterate that at low stemflow pH, the majority of the total sulphur in the stemflow will be in the form of toxic bisulphite ions. One would naturally infer that a low "buffer" capacity of the bark against acid is largely responsible for the extremely high sensitivity of the lichen community at site 11 (Table 11, Fig. 14). Similarly a low pollution sensitivity (IAP = 101) at site 24, where the bark pH is 4.0, may be attributed to the

Table 30. Regression analyses relating the pH of rainwater (pH_r) to the ambient sulphur dioxide in ppb (SO_2), the pH of the stemflow (pH_s) to that of the rainwater and the pH of the bark (pH_b) to both the pH of the stemflow and rainwater.

Regression equation	r	R^2
(7) $(\text{pH}_r) = 5.86 - 0.07(\text{SO}_2)$	-0.62	
(8) $(\text{pH}_s) = 2.32 + 0.30(\text{pH}_r)$	0.88	
(9) $(\text{pH}_b) = 2.43 + 0.37(\text{pH}_s)$	0.93	
(10) $(\text{pH}_b) = 2.49 + 0.34(\text{pH}_s) + 0.01(\text{pH}_r)$		0.87
	$(\text{pH}_s) \text{ vs } (\text{pH}_r) 0.88$	
	$(\text{pH}_r) \text{ vs } (\text{pH}_b) 0.84$	
	$(\text{pH}_b) \text{ vs } (\text{pH}_s) 0.93$	

r is the correlation coefficient.

R^2 is the multiple correlation coefficient.

high "buffering" capacity of the bark against acid, which at this site is 53 percent more than at site 11. Also, at site 24, a nearly neutral pH of 6.4 of the rainwater, might help to ameliorate the "buffer" capacity of the bark. At this point it may be hypothesized that the bark pH is directly dependant upon the pH of the stemflow and on the "buffer" capacity of the bark, which in turn depends to some extent upon the pH of the rainwater and on the ambient sulphur dioxide concentration, and that the prime factors regulating the sensitivity of the epiphytic lichens in sulphur dioxide polluted areas appear to be the relative concentrations of sulphurous acid and bisulphite ions in the stemflow (Table 30, equation 10). It must not be forgotten however, that heavy metals and other elements which are toxic to lichens when present in high concentration in their soluble form may also complicate the above interpretation. The generally high solubility of heavy metals at low pH values should be considered a factor of great importance when dealing with acidified barks. It may be that both sulphur dioxide derivatives and heavy metals complement each other as far as toxicity to the lichen is concerned.

The dependance of "buffer" capacity regulation on the ambient sulphur dioxide concentration is highly significant (Table 29, equation 1). The importance of equations six to nine in Tables 29 and 30, lies in the fact that they indicate the dependance of "buffer" capacity on the

proportions of sulphur dioxide derivatives in solution.

It is noteworthy that the rainwater pH affects the buffer capacity of the bark only indirectly (Table 29, equation 4) through its affects on pH and the sulphur content of the stemflow water (Table 30, equation 8).

On the basis of this data, it can be summarized that part of the sensitivity of an epiphytic community to an environment partly polluted by sulphur dioxide and other substances, depends to some extent on the interaction of: ambient sulphur dioxide concentration, the rainwater pH, stemflow pH, bark pH, epiphyte pH, buffer capacity of the bark and on the relative percentages of sulphur dioxide derivatives (bisulphite ions and sulphurous acid) in and around the lichen thallus. Theoretically, all of these factors, in conjunction with other pollutants that may be present, considered together in a chain would provide a sound basis for ascertaining the overall effects of sulphur dioxide and additional pollutants, on epiphytes.

In the next section the accumulation of heavy metals by two lichen epiphytes will be discussed and it will be hypothesized that the metals accumulated may affect the chlorophyll production of these lichens and hence contribute to the paucity of epiphytes in polluted areas.

D. Metal Accumulation by Epiphytes.

1. Introduction.

Lichens have a greater capacity than vascular plants for absorbing and accumulating heavy metals in their tissues (Lounamaa 1956). As a consequence of heavy metal accumulation in lichens, photosynthesis may be impaired, although this has not been proven conclusively however. In the absence of experimental evidence, it is difficult to suggest a physiological basis for the reduction in photosynthesis that seems to occur under the stress of heavy metal pollution. It could be due to a loss of chlorophyll pigments brought about either through degradation of pigments already present and/or through an inhibition of enzymes necessary for chlorophyll synthesis (Hampp et al. 1974). The author is not presenting evidence to prove or disprove this conjecture. Field observations however, in conjunction with recent work by other workers has permitted the author to conduct a somewhat philosophical discussion on the subject at hand.

Of the two constituents of a lichen thallus, the phycobiont is more sensitive to heavy metal ions than the mycobiont. Nash III (1975) observed significant reduction of photosynthesis in Cladonia uncialis that had absorbed in its thallus 178 ppm of zinc and 320 ppm of cadmium, and in Lasallia papulosa that had absorbed 308 ppm of zinc and 288 ppm of cadmium.

Since the rate of accumulation of a substance in a

lichen is a function of the quantity of metal deposition upon its thallus, these plants can successfully be employed for mapping patterns of heavy metal fallout (Nieboer et al. 1972; Nash III 1972). In section A, Chapter III it was recorded that a reduction in the growth and diversity of the epiphytic vegetation of Abies balsamea in the sulphur dioxide and metal polluted area of Murdochville occurred as the level of pollution increased. In that section the metal pollution was measured as a function of the accumulation of the metals in the woodland mosses (Hylocomium splendens and Pleurozium schreberi) as well as in the higher plants Picea mariana and Clintonia borealis (Tables 17 to 20).

Analysis of lichen thalli which are regularly bathe and drenched by acid stemflow water containing heavy metals could be used to ascertain the possible role of these metals in affecting epiphyte distribution. In this section the possible extent and nature of heavy metal accumulation in two lichens in terms of chlorophyll content of the thalli, as affected by varying metal concentration in the stemflow and lichen thalli, as compounded by sulphur dioxide pollution and/or the secondary effects of this gas as illustrated in Chapter III section C will be discussed.

The spacial distribution of the study sites used in this present analysis may be found in Fig. 21. The lichen material used for the metal determinations was the same as that utilized for the determination of the chlorophyll content in the two naturally occurring epiphytes Hypogymnia

physodes and Parmelia squarrosa in Chapter III section B. At that time the reduction in chlorophyll was interpreted as an effect of the sulphur dioxide present in the atmosphere. However the measurement of the metal content in these same thalli adds a new dimension as to the possible causes of the chlorophyll reduction. It would seem that the cause is multidimensional.

The stemflow analyzed for the metals was the same as that used in Chapter III section C in the discussion of acid rain effects.

2. Results and Discussion.

The Pb, Cu, Zn, Cd and As content of the stemflow of Abies balsamea from the different sites is presented in Table 31. Metal concentration was generally higher in samples near the smelter and lower in samples collected at distances farther away from the smelter. It was highest for Zn and lowest for Cd (or $Zn > Cu > Pb > As > Cd$).

Some metal ions in the stemflow become absorbed and accumulated by the lichen thalli as shown in Table 32. Deposition rates of Pb and Cu in the two lichen species followed a definite pattern, generally decreasing with distance from the smelter (Table 32). In comparison with the control site (43), accumulations of Pb, Cu and Zn at the most polluted site 11, were respectively 16.6, 13.5 and 1.8 times more in H. physodes and 10.5, 9.5 and 1.4 times more in P. squarrosa. H. physodes always had more Pb than P. squarrosa. Cd and As were barely detectable and

Table 31. Metal concentration (ppm $\pm$ SD) in stemflow of Abies balsamea at various distances from the copper smelter.

Site	km from smelter	Concentration ppm $\pm$ SD				
		Pb	Cu	Zn	Cd	As
11	6.3 SE	0.24 $\pm$ 0.16	0.38 $\pm$ 0.41	0.78 $\pm$ 0.41	0.02 $\pm$ 0.02	0.12 $\pm$ 0.15
15	8.3 ESE	0.08 $\pm$ 0.11	0.19 $\pm$ 0.25	0.55 $\pm$ 0.64	0.009 $\pm$ 0.003	0.04 $\pm$ 0.01
21	14.9 ESE	0.05 $\pm$ 0.03	0.05 $\pm$ 0.03	0.26 $\pm$ 0.25	0.004 $\pm$ 0.002	0.02 $\pm$ 0.01
22	19.5 SE	0.04 $\pm$ 0.02	0.03 $\pm$ 0.02	0.12 $\pm$ 0.07	0.002 $\pm$ 0.001	0.13 $\pm$ 0.33
24	35.5 SE	0.01 $\pm$ 0.01	0.04 $\pm$ 0.03	0.05 $\pm$ 0.02	0.001 $\pm$ 0.001	0.01 $\pm$ 0.01
43	20.1 SW	0.02 $\pm$ 0.01	0.02 $\pm$ 0.01	0.09 $\pm$ 0.06	0.001 $\pm$ 0.001	0.02 $\pm$ 0.02

SD is standard deviation

Table 32. Average metal concentration (ppm dry wt. $\pm$ SD) in (a) Parmelia squarrosa and (b) Hypogymnia physodes in relation to their distance from the copper smelter.

Site	km from smelter	pH Stemflow	Species	Concentration (ppm dry wt. $\pm$ SD)				
				Pb	Cu	Zn	Cd	As
11	6.3 SE	3.3	a	515 $\pm$ 131	283 $\pm$ 17	200 $\pm$ 40	3.5 $\pm$ 1.3	NSS
			b	918 $\pm$ 25	405 $\pm$ 7	168 $\pm$ 4	5.3 $\pm$ 0.6	NSS
15	8.3 ESE	3.7	a	175 $\pm$ 35	255 $\pm$ 49	260 $\pm$ 28	4.7 $\pm$ 0.1	NSS
			b	718 $\pm$ 4	210 $\pm$ 6	233 $\pm$ 4	5.4 $\pm$ 0.7	NSS
21	14.9 ESE	3.7	a	177 $\pm$ 68	91 $\pm$ 19	175 $\pm$ 27	2.8 $\pm$ 0.5	NSS
			b	244 $\pm$ 33	66 $\pm$ 15	152 $\pm$ 16	3.0 $\pm$ 0.4	3.3 $\pm$ 1.6
22	19.5 SE	3.7	a	199 $\pm$ 42	60 $\pm$ 10	138 $\pm$ 26	2.1 $\pm$ 0.8	NSS
			b	253 $\pm$ 62	57 $\pm$ 11	162 $\pm$ 22	3.4 $\pm$ 0.9	3.0 $\pm$ 1.7
24	35.5 SE	4.2	a	104 $\pm$ 36	317 $\pm$ 19	160 $\pm$ 31	1.0 $\pm$ 0.2	1.2 $\pm$ 0.5
			b	150 $\pm$ 33	215 $\pm$ 105	166 $\pm$ 28	2.0 $\pm$ 0.9	3.4 $\pm$ 0.9
43	20.1 SW	4.8	a	49 $\pm$ 8	40 $\pm$ 16	109 $\pm$ 19	0.7 $\pm$ 0.2	4.5 $\pm$ 3.7
			b	55 $\pm$ 13	30 $\pm$ 14	113 $\pm$ 8	1.7 $\pm$ 0.4	4.1 $\pm$ 0.8

SD is standard deviation.

NSS is non sufficient sample.

showed no concentration gradient in relation to the distance from the smelter. Regression analyses were done to determine the correlation of stemflow and lichen metal content. The results are presented in Table 33 and show that the Pb and Cu contents of P. squarrosa correlated well with the amounts of these metals in the stemflow (equations 1 and 2), but, the relationship with respect to Zn and Cd was rather poor (equations 3 and 4). The order of metal accumulation in H. physodes and in P. squarrosa was $Pb > Cu > Zn > Cd$.

The amounts of total chlorophyll and chlorophyll a and b in the two lichen species were found to increase with increased distance from the copper smelter (Table 34). In P. squarrosa and in H. physodes the amount of total chlorophyll at the control site (43) was 3.3 and 6.6 times higher than at the heavily polluted site 11. For equal weights of thallus the chlorophyll content in H. physodes was more than in P. squarrosa (Table 34). At the control site the amounts of total chlorophyll, chlorophyll a and b in H. physodes were respectively 69, 70 and 66 percent more than in P. squarrosa. However, in heavily polluted areas the loss in chlorophyll in H. physodes was usually more than in P. squarrosa as shown by the lower content of chlorophyll in H. physodes relative to that of P. squarrosa at site 11 (Table 34). Such pollution response variations in the two lichen species could be attributed, among other things, to differences in their thallus morphology and to

Table 33. Relationship between metal contents in the epiphytic lichens (L) Parmelia squarrosa and Hypogymnia physodes (ppm dry wt.) and in the stemflow (s) of Abies balsamea.

Species	Relationship	r	F
<u>Parmelia squarrosa</u>	$Pb_L = 67.863 + 1854.046 Pb_s$	0.97	57.188 (1)
	$Cu_L = 53.007 + 69.249 Cu_s$	0.93	19.479 (2)
	$Zn_L = 132.668 + 132.967 Zn_s$	0.75	4.995 (3)
	$Cd_L = 1.611 + 138.751 Cd_s$	0.68	3.369 (4)
<u>Hypogymnia physodes</u>	$Cu_L = 13.173 + 1032.551 Cu_s$	0.99	12786.319 (5)
	$Pb_L = 124.806 + 3611.743 Pb_s$	0.89	15.499 (6)
	$Cd_L = 2.371 + 177.683 Cd_s$	0.83	8.862 (7)
	$Zn_L = 144.211 + 69.586 Zn_s$	0.53	1.549 (8)

r is correlation coefficient.

F is the F ratio.

() indicate equation numbers.

Table 34. Chlorophyll content of the epiphytic lichens (A) Parmelia squarrosa and (B) Hypogymnia physodes collected at various distances from the copper smelter on a ESE and SE orientation in the direction of the prevailing wind.

Site	km from smelter	Species	Chlorophyll ^c		
			Chl _t	Chl <u>a</u>	Chl <u>b</u>
11	6.3 SE	A	0.67 ± 0.13	0.50 ± 0.15	0.17 ± 0.02
		B	0.49	0.34	0.13
15	8.3 ESE	A	1.48	1.16	0.32
		B	1.73	1.24	0.50
21	14.9 ESE	A	1.38 ± 0.16	1.03 ± 0.15	0.34 ± 0.02
		B	2.29 ± 0.11	1.82 ± 0.09	0.47 ± 0.02
22	19.5 SE	A	1.72 ± 0.39	1.43 ± 0.37	0.28 ± 0.10
		B	2.29 ± 0.42	1.68 ± 0.30	0.61 ± 0.13
25	35.5 SE	A	1.72 ± 0.36	1.33 ± 0.26	0.39 ± 0.11
		B	2.30 ± 0.28	1.78 ± 0.18	0.52 ± 0.01
43	20.1 SW	A	2.21 ± 0.33	1.71 ± 0.27	0.50 ± 0.07
		B	3.20 ± 0.80	2.44 ± 0.58	0.76 ± 0.22

Chl_t is total chlorophyll.

Chl_a is chlorophyll a.

Chl_b is chlorophyll b.

C means all values ± standard deviation.

higher accumulation of pollutants in H. physodes. The loosely attached, sorediate, broadlobed and ventrally perforated thalli of H. physodes may be more suited for the absorption of particulates and metals dissolved in the acidified stemflow (Table 32) water than the highly adnate and isidiate thalli of P. squarrosa. The closely attached thalli of the latter species however may facilitate particulate exchange with the bark. As shown in Table 32 H. physodes accumulated 4.1, 2.8 and 2.4 times more Pb, As and Cd than did P. squarrosa.

Nearer to the smelter, there was an increase metal content and a decrease chlorophyll content in both lichen species. This inverse relationship was stronger for Pb and Cu than for Zn and Cd (Table 34, Fig. 31).

Whether or not chlorophyll breakdown and/or reduced production of chlorophyll occurs may not be strictly related to metal content and possible toxicity, since as seen in previous sections the lichen thalli are subjected to a massive pollution insult - acid rain, sulphur dioxide and heavy metals. However, it appears that under conditions of acid rain and reduced buffer capacity (Table 28), the metal concentration in the thalli (Table 32) attained a certain minimum or threshold level before reductions in chlorophyll (Table 34) and presumably a reduction in rate of photosynthesis. As shown in Fig. 31 in H. physodes no significant loss of chlorophyll occurred until the level of Pb had exceeded 244 ppm lead (the values for Cu and Zn

are 66 ppm and 152 ppm respectively). Similarly for P. squarrosa the chlorophyll content was stable until levels of Pb, Cu and Zn exceeded 175, 255 and 200 ppm respectively (Table 32). Nash III (1975) suggested that lichen thalli treated in the laboratory at various levels of Zn and Cd, had a critical threshold for tolerance between 200 and 600 ppm - at lower concentrations all lichens were thought to survive and at higher concentrations most species would probably die. It must be emphasized that for a given lichen species, the threshold concentration of a pollutant may not be the same under short term exposure in the laboratory as for long term exposure in the field.

When the metal content in a lichen thallus increased beyond a certain limit, there seemed to be a sharp decrease in its chlorophyll content (Table 34). Both of these events occurred simultaneously at approximately 15 km from the smelter (Fig. 31) for Pb in the H. physodes thalli and at about eight km for the P. squarrosa thalli (Fig. 32). On the other hand the sharp increase in total sulphur values (Table 28 section C), which have been used by some workers as indicating sulphur dioxide pollution (Pyatt 1973), did not correspond to the sudden loss in chlorophyll. This would seem to imply that Pb and possibly other heavy metals are potentially toxic to lichens once the threshold concentration is attained. However the deleterious effects of sulphur dioxide in this area must not be underestimated. Both metal and gaseous pollution seem to

Figure 31. Relationship between the km distance from the copper smelter and the Pb content of Hypogymnia physodes thalli (ppm), the Pb content of the stemflow of Abies balsamea (ppm) and the chlorophyll lost by Hypogymnia physodes thalli collected from sites in the ESE and SE directions from the copper smelter.

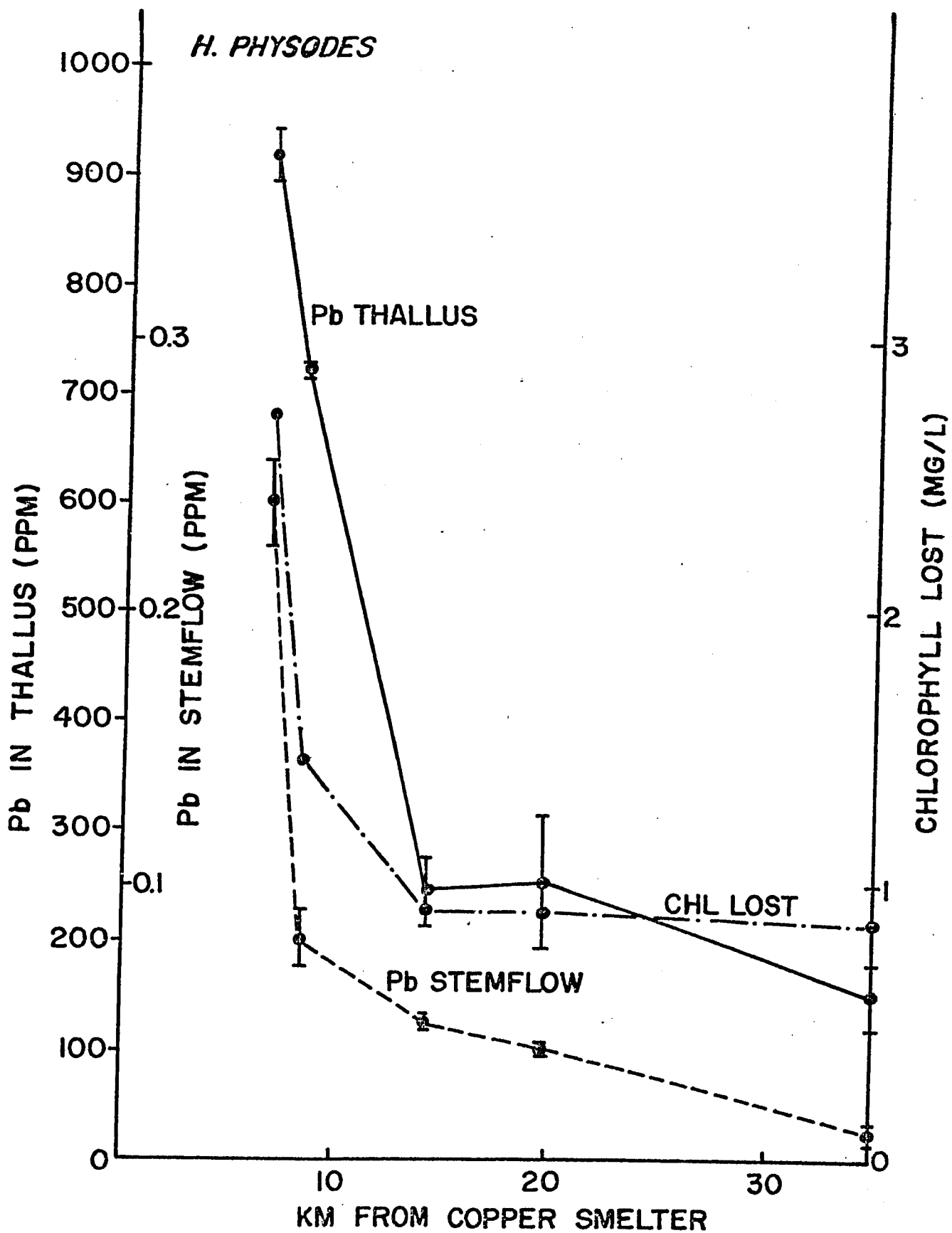
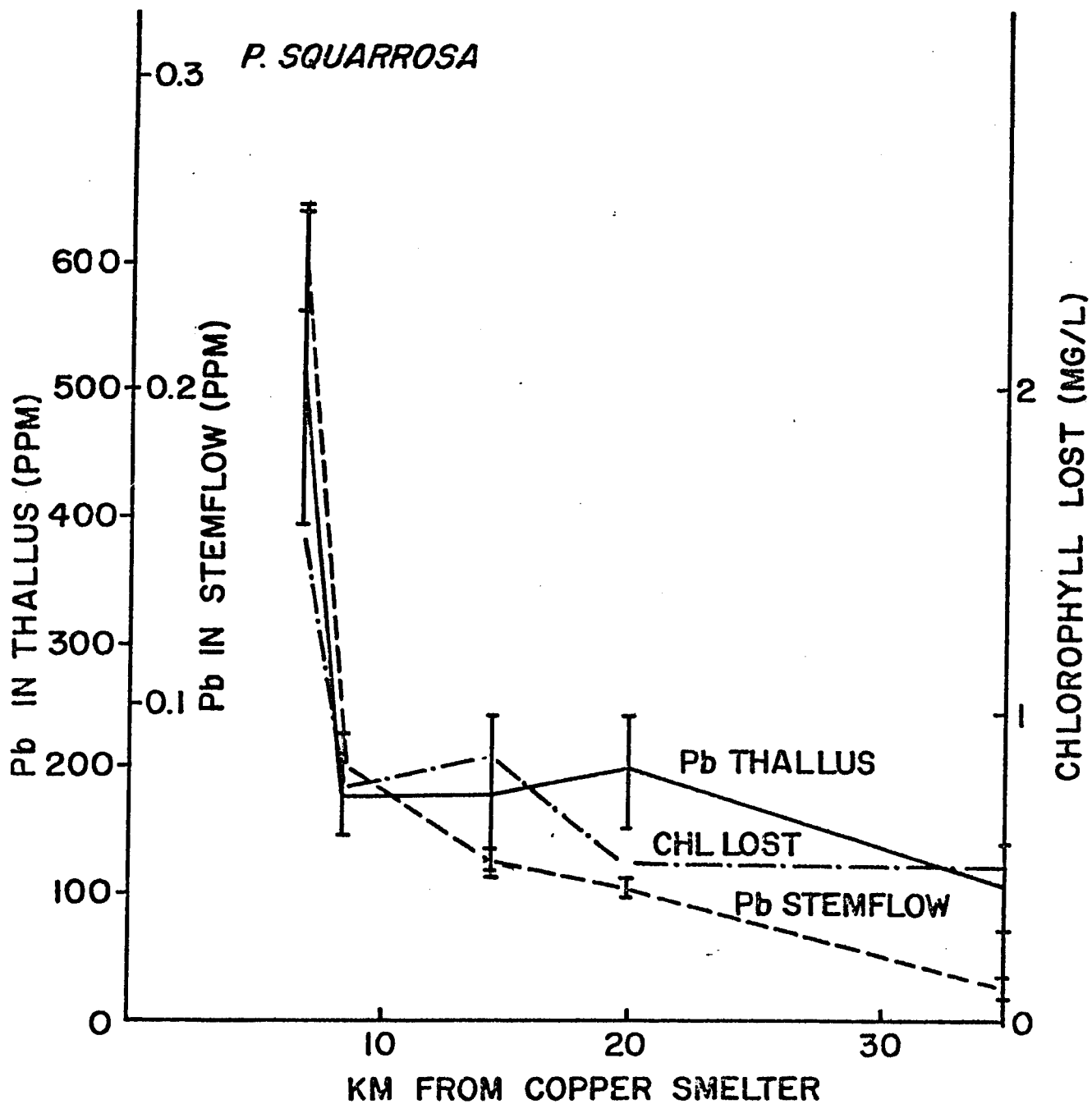


Figure 32. Relationship between the km distance from the copper smelter and the Pb content of Parmelia squarrosa thalli (ppm), the Pb content of the stemflow of Abies balsamea (ppm) and the chlorophyll lost by Parmelia squarrosa thalli collected from sites in the ESE and SE directions from the copper smelter.



be causing the environmental impact documented in Chapter III section A.

The relationship between the chlorophyll content and metal content of P. squarrosa and H. physodes thalli is shown in Table 35. An increase in Pb, Cu and Zn are all strongly correlated with a decrease in chlorophyll content. The fact that Pb and Cu are strongly correlated with decreased chlorophyll content in H. physodes does not necessarily indicate that these metals are more toxic to the lichen than is Zn. These high correlations emphasize that synergistic effects of metals may be more important in causing reductions in chlorophyll.

The mechanisms by which metal ions may cause chlorophyll reduction is not fully understood. Sabnis et al. (1969) showed that lead in plants is present in the mitochondria and chlorophyll membranes. Lead, Cd and Ni may interfere with biological processes related to the general metabolism of the plant including mitochondrial respiration (Koeppel and Miller 1970) and chlorophyll synthesis (Hampp and Lendzian 1974; Hampp et al. 1974). Using transmission electron microscopy to locate metal residues, especially Pb derived from atmospheric pollution, within plant cells and organelles, Skaar et al. (1973) found that Pb was incorporated into the nuclei of lead polluted cells. Brown and Slingsby (1972) studying the cellular location of lead in the lichen Cladonia rangiformis collected from Pb rich sites, demonstrated that Pb was probably ionically bound

Table 35. Relationship between metal (L) concentration (ppm dry wt.) and total Chlorophyll (Chl_t) content in thalli of Parmelia squarrosa and Hypogymnia physodes.

Species	Relationship	r	F
<u>Parmelia squarrosa</u>	chl _t = 2.124 - 0.003 Pb _L	-0.93	27.216 (9)
	= 2.057 - 0.004 Cu _L	-0.79	5.069 (10)
	= 2.544 - 0.006 Zn _L	-0.60	2.268 (11)
<u>Hypogymnia physodes</u>	chl _t = 2.994 - 0.002 Pb _L	-0.93	25.198 (12)
	= 2.988 - 0.005 Cu _L	-0.91	18.511 (13)
	= 4.024 - 0.012 Zn _L	-0.51	1.423 (14)

r is correlation coefficient.

F is the F ratio.

() signifies equation numbers.

L lichen thallus

within the cell wall. This led them to suggest that large quantities of a potentially toxic element may not have any direct effect on the metabolism of lichens.

A sharp decrease in chlorophyll at increasing concentrations of heavy metals in H. physodes and P. squarrosa may be evidence of heavy metal toxicity to lichens. This loss of chlorophyll may either be due to the inhibition of chlorophyll synthesis and/or due to the conversion or degradation of chlorophyll into some substances other than chlorophyll absorbing radiation at different wavelengths (Puckett 1976). Whatever the mechanism of chlorophyll reduction, heavy metals seem to take part in causing serious internal disturbances in the lichen thallus..

It is difficult to clearly mark when heavy metal effects are more important than disturbances caused by sulphur dioxide pollution and/or the secondary effects engendered by it. The concurrent emission of sulphur dioxide with rain enhances the solubility of metal salts in the dilute sulphurous/sulphuric acid stemflow, which in turn may increase the metal uptake by lichens. In Chapter III section C it was suggested that acid precipitation produces drastic changes in the chemical properties of epiphytes by reducing the pH of the stemflow (Table 28) and of the epiphytes. The increased metal concentration and percentage of chlorophyll lost in the epiphytes seemed to be affected by the acid stemflow. It is possible that, under the highly acid conditions prevailing in the stemflow

(pH 3.3), a part of or all of the ionically bound cell wall Pb, as suggested by Brown and Slingsby (1972), could be unbound and released into the cell, causing serious ionic disruptions in the protoplasm. It might be assumed that under conditions of low pH, heavy metals may be released from the cell wall and accumulated within the cell cavity by an ion exchange mechanism. It was noted that the unusually high concentrations of Cu at site 24, where the stemflow pH of 4.2 was higher than the pH at site 11, was apparently not harmful to the lichens growing there (Table 32); this could be due to the higher pH of the stemflow, the higher buffer capacity of the bark (Table 28), the higher thallus pH and to the possibility that Cu remained bound to the cell wall.

On the basis of the present data it cannot be said that heavy metals are the toxic agents in regulating lichen growth and diversity because the role of sulphur dioxide cannot be ruled out completely. It is known that the soluble form of Pb and other heavy metals can block chlorophyll synthesis (Valley and Ulmer 1972; Hampp et al. 1974) in higher plants, this could drastically reduce the potential for photosynthesis in lichens which have only a limited amount of chlorophyll. It may be hypothesized that a reduction in the chlorophyll content of lichens may occur when lichen thalli are flooded with acid heavy metal laden stemflow and that this condition may result in a gradual elimination of sensitive species (Chapter III section A).

E. Heavy Metals and Tree Rings.

1. Introduction.

a) On ring width variation.

Environmental factors which act to change or control annual ring widths are termed "signals" (Fritts 1971). Climatic influences, edaphic conditions and pollution are examples of a few of the many potential signals occurring in nature.

Annual temperature and precipitation fluctuations influence the growth of a tree at all times of the year and hence produce variations in ring widths. In the Murdochville area temperature may be the signal causing the background variation in ring width of Abies balsamea (Fig. 36). However, these same climatic signals may be closely related with ring width changes on limiting sites. Signals, such as these, received prior to the growing season may influence growth to a greater extent than those received during the active cambial period. It may be of interest to speculate at this point that such preconditioning could also be important for the growth of trees located in pollution stressed areas, since it is known that higher pollution occurs more often during the winter than the summer months.

Structural changes caused by increasing tree age and height occur from the inner to the outer rings, especially in the lower trunk, the rings near the pith being narrower and increasing in width to mid-diameter. The rings in the

area midway through the trunk to the cambium become narrower and are more susceptible to width variation from yearly signals. The greatest year to year ring width variation occurs at the tree base and reflect climatic or other environmental changes. The upper trunk reflects signals from individual branches (Fritts 1971). Hence lower trunk samples are more reliable indicators of site signals than upper trunk cores.

To compare successfully changes associated with environmental fluctuations, including pollution, it is necessary to standardize the changes in ring width due to increasing tree age. Computer programs have been devised (Nash III et al. 1975) to do this. Essentially a growth curve is fitted to the ring width data and the value of the actual ring width for each year is divided by the calculated value of the growth curve for that year to obtain a standardized value or ring width ratio. A procedure similar to this has been used for the tree ring data in this study.

Success in obtaining signal information from growth rings depends to a large extent upon ecological knowhow and on the proper application of dendrochronological principles, that is, the researcher should understand the kind of information he is after and have some ideas as to the tree's reaction to a particular signal. In such cases a random sampling effort is to be minimized as opposed to subjective type sampling. For example, if you desire to

show that heavy metal pollution is an important signal for reducing annual ring widths you must sample trees in stands that are known to be subjected to this factor. One would also need to select sites with similar local environments and trees within these sites that are likely to have similar microhabitats. If possible the tree should be of the same size class, of similar age, the spacing between trees should be uniform, the increment should be taken at the same height and the same compass direction and the trees sampled must all be at the periphery of a site or occupy a central portion so that in effect pollution load is the only local limiting signal.

b) Tree rings and pollution.

During the past decade many researchers have used a variety of plants, lichens among others, as indicators and monitors of gaseous and particulate pollution. These studies have dealt with both urban pollution (Brodo 1961; LeBlanc and De Sloover 1970) and rural pollution caused by industrial complexes (Chapter III sections A to D). The results of these studies are indicative of either long term effects of pollutants on the vegetation or of the existing status of air quality as reflected by the response of plant species to pollutants. Although the methods used give reliable results (in the present work for example), they cannot determine, even approximately, the time when the pollution stress was first felt by the vegetation. For example, the identification of air quality zones around the

copper smelter at Murdochville does not tell us that the contamination of the environment was caused by the smelter emissions since 1955. However, such studies do indicate the long term response of the epiphyte communities to a varying pollution load (Chapter III sections A to D).

At present no reliable bioassay method has been developed to establish approximately the time factor involved in a pollution situation. Recently, however, the use of tree ring analysis for monitoring heavy metal pollution patterns, with the objective of pin-pointing years of severe contamination, has been receiving considerable attention. It is argued that the amount of metal in an annual ring of a given year is a direct reflection of the pollutant load for that year in the immediate area where the tree was sampled. There is a controversy over the use of annual rings as monitors of heavy metal pollution. Recent data indicate that successive annual growth rings of trees cannot be used to document historically heavy metal pollution (Szopa et al. 1973; Barnes et al. 1976). On the other hand Vins and Mrkva (1973), Ward et al. (1974) and Rolfe (1974) give evidence that metal histories, especially that of lead near roads, can be documented using tree rings. Lepp (1975) does not discredit the technique but he does emphasize that great caution should be exercised in interpreting heavy metal patterns in tree rings since the question of uptake, transport and deposition processes of heavy metals within trees is little understood.

This investigation of the heavy metal distribution patterns present in the annual rings of Abies balsamea was approached with the assumption that these rings can be used to document the recent history of heavy metal pollution in forested areas.

The location of the sites sampled and the relation of the quadrats to the copper smelter may be found in Fig. 21. Table 36 gives an indication of the pollution status of these sites.

2. Results and Discussion.

The width of an annual ring varies from year to year depending on the growth potential of the tree which, in turn, depends on the interactions between genetic and environmental factors. Adverse seasonal climatic conditions such as reduced precipitation or a temperature below seasonal averages may result in the formation of narrow annual rings and in the occurrence of missing rings. It is not uncommon that missing rings occur especially during years of adverse environmental extremes when there is very little growth. Missing rings were not detected anywhere in the study area. From this it is assumed that climatic fluctuations in the region are not so severe as to produce rings narrow enough to cause missing rings. Nash III et al. (1975) have developed a computer technique for examining non-climatic variations in widths of annual rings. When applied to trees growing in areas of known air pollution they noticed that a decrease in tree ring width corresponded

Table 36. Location and pollution parameters of the sites investigated for the analysis of the increment cores of Abies balsamea.

Site and stand location			Air quality	Stemflow ^b		pH ^b
Site	Stand	km	zone ^a	sulphur(ppb)	pH	rain
11	1	6.4 SE	I	28,867	3.3	4.3
	2	6.1 SE				
	3	6.5 SE				
15	4	8.1 ESE	II	9,500	3.7	4.3
21	5	14.6 ESE	III	2,743	3.7	4.3
	6	15.3 ESE				
	7	14.8 ESE				
22	8	19.0 SE	IV	5,500	3.7	4.3
	9	20.1 SE				
24	10	35.8 SE	V	3,833	4.2	6.4
	11	34.6 SE				
	12	34.0 SE				
43	13	21.5 SW	V	2,227	4.8	5.6
	14	21.6 SW				
	15	20.1 SW				

- a. The air quality zones are based on lichen sensitivity to air pollution.
- b. These values of pH and sulphur content of Abies balsamea stemflow and of rain water pH are parameters indicative of pollution levels.

to known air pollution periods. However, they did specify that air pollution cannot be definitely identified as the cause of the decrease in ring width.

A change in growth rate during a single growing season may cause false rings to appear within one annual ring. Adverse local microclimate may cause this particular abnormality. Of all the sites investigated (Fig. 21) during this study only those cores taken at the polluted quadrats of site 11 had false rings and these were found exclusively after 1955, the year that the copper smelter began its operations. Thirty-seven percent of the total 1800 annual rings produced after 1955 had false rings. The absence of this abnormality at all the other sites may again be an indication that the normal variation in the width of the annual rings produced by the homogeneous regional climate overrides that caused by local microclimatic fluctuations between sites and quadrats. On the other hand, their appearance at the polluted site (11) between the years 1955 to 1974 may indicate that the pollution parameter was the controlling factor for tree growth at this site. Reports have not been encountered describing the appearance of false rings in pollution stressed trees. However, Vins and Mrkva (1973) found that there was an increase in the occurrence of missing rings in suppressed pine trees growing near a fertilizer plant and that over half of the dominant trees did not have missing rings. The fact that missing rings were not encountered in the Murdochville area

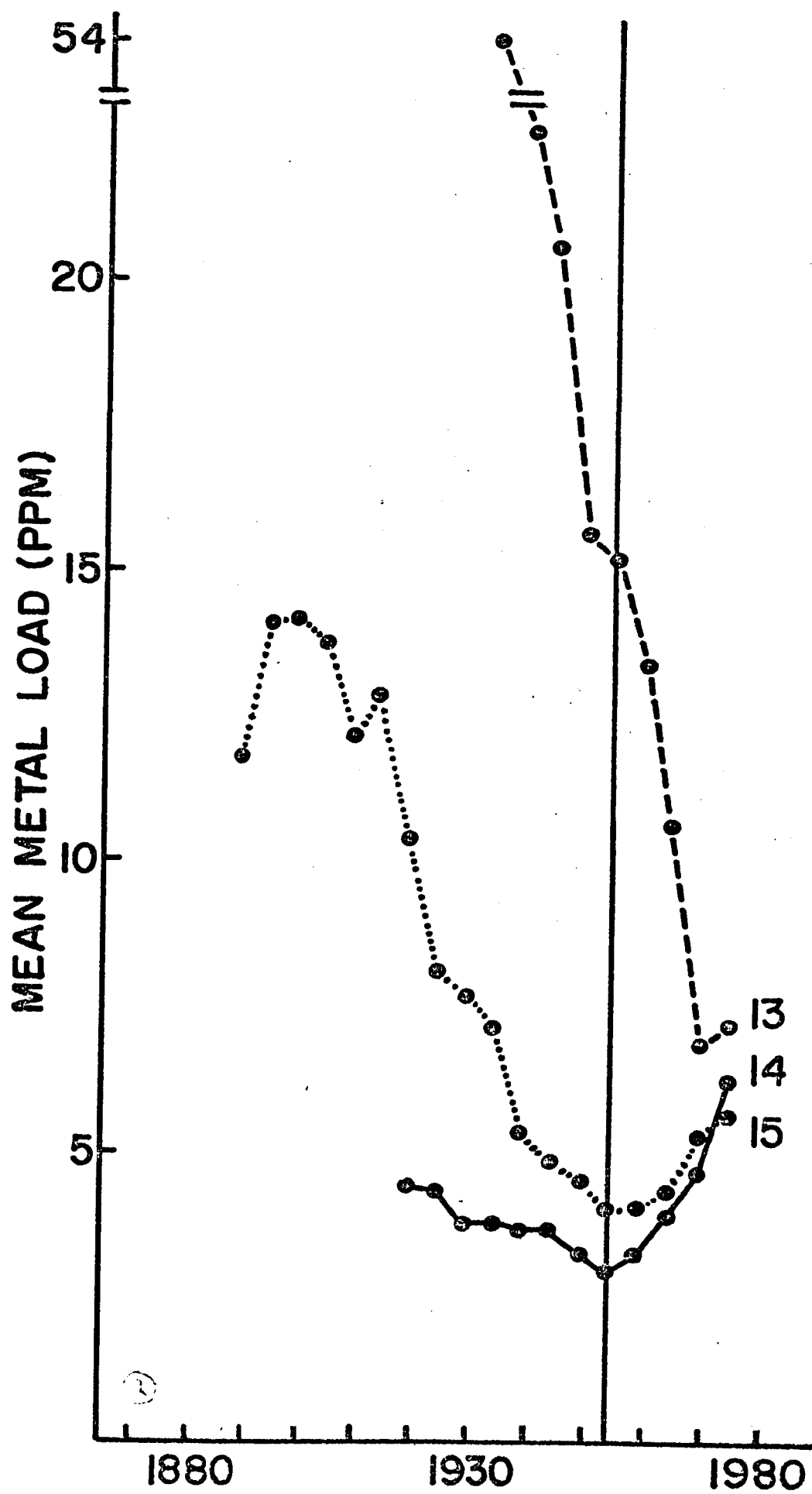
might also be a reflection of the pre-selection of dominant trees for sampling, compounded by adequate growth conditions.

a) Heavy metal pattern.

The heavy metal accumulation pattern for the total metal load, that is the average metal load of $Pb + Cu + Zn + Cd + As$ varied considerably from quadrat to quadrat (Fig. 33 to Fig. 35). The patterns are probably an expression of the total environmental effect on the groups of trees concerned as well as a reflection of changes in both soil and air quality characteristics that have occurred during the life span of each group of trees. Although it is beyond the scope of this dissertation, certain bio-physical characteristics, such as rates of metal movement between xylem elements and translocation via the transpiration stream at different seasons of the year, should be taken into account when interpreting heavy metal accumulation patterns.

The majority of the accumulation patterns are to varying degrees V-shaped. The distribution of the total metal load of the trees from quadrats 13, 14 and 15 (Fig. 33a) at the non polluted site (43) show most of the model variability that can occur in the metal accumulation patterns in trees from a given restricted geographical area and will be used as the basis for discussion. The curves for the trees in quadrats 14 and 15 (Fig. 33a) are V-shaped. The former is weighted towards the right of the 1955 introduction of

Figure 33. The relationship between the mean metal load (ppm) of the annual rings of Abies balsamea and the year the annual ring was formed (a) for quadrats 13, 14 and 15 at site 43 and (b) for quadrats 10, 11 and 12 at site 24. The vertical line at the year 1955 denotes the year that the smelter operations began.



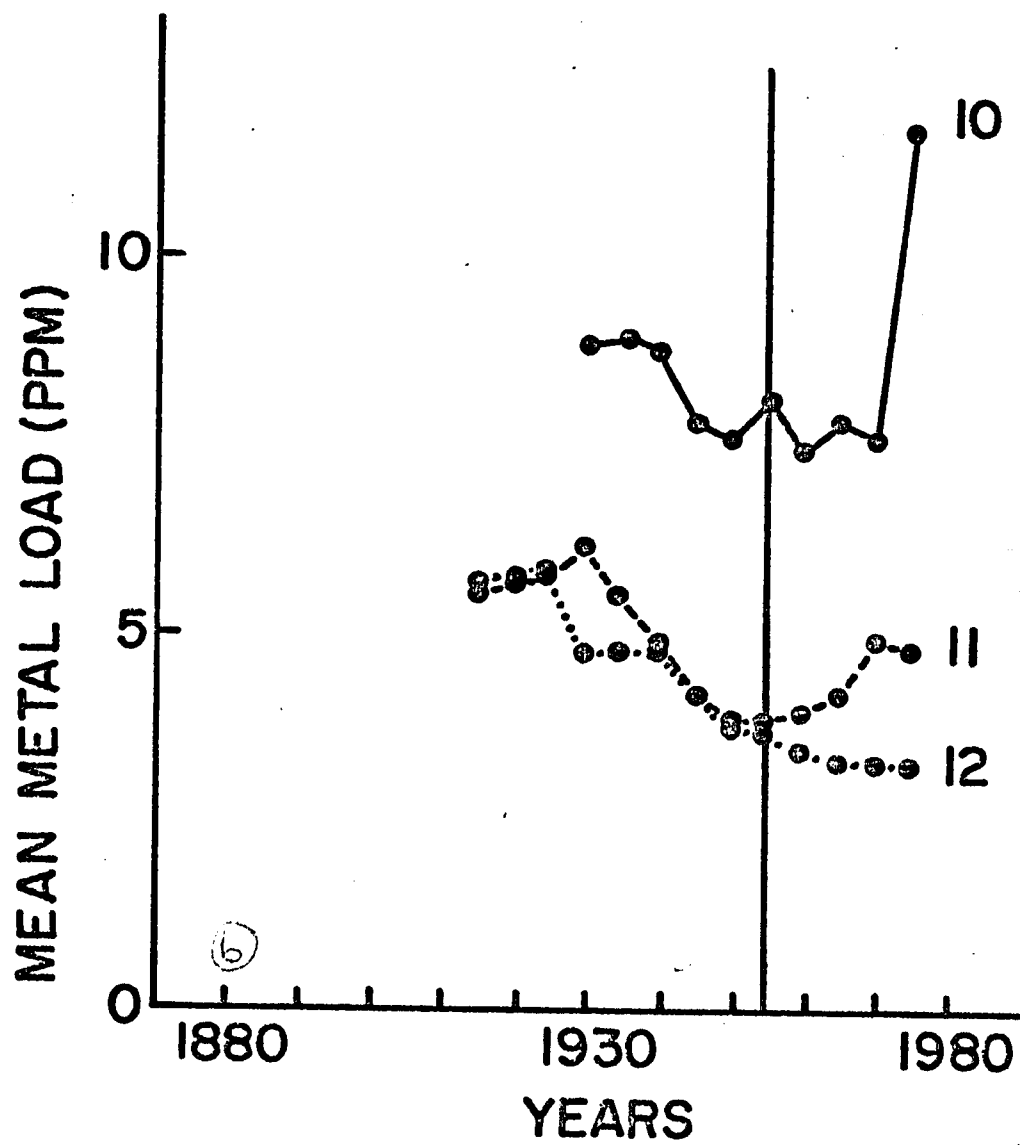
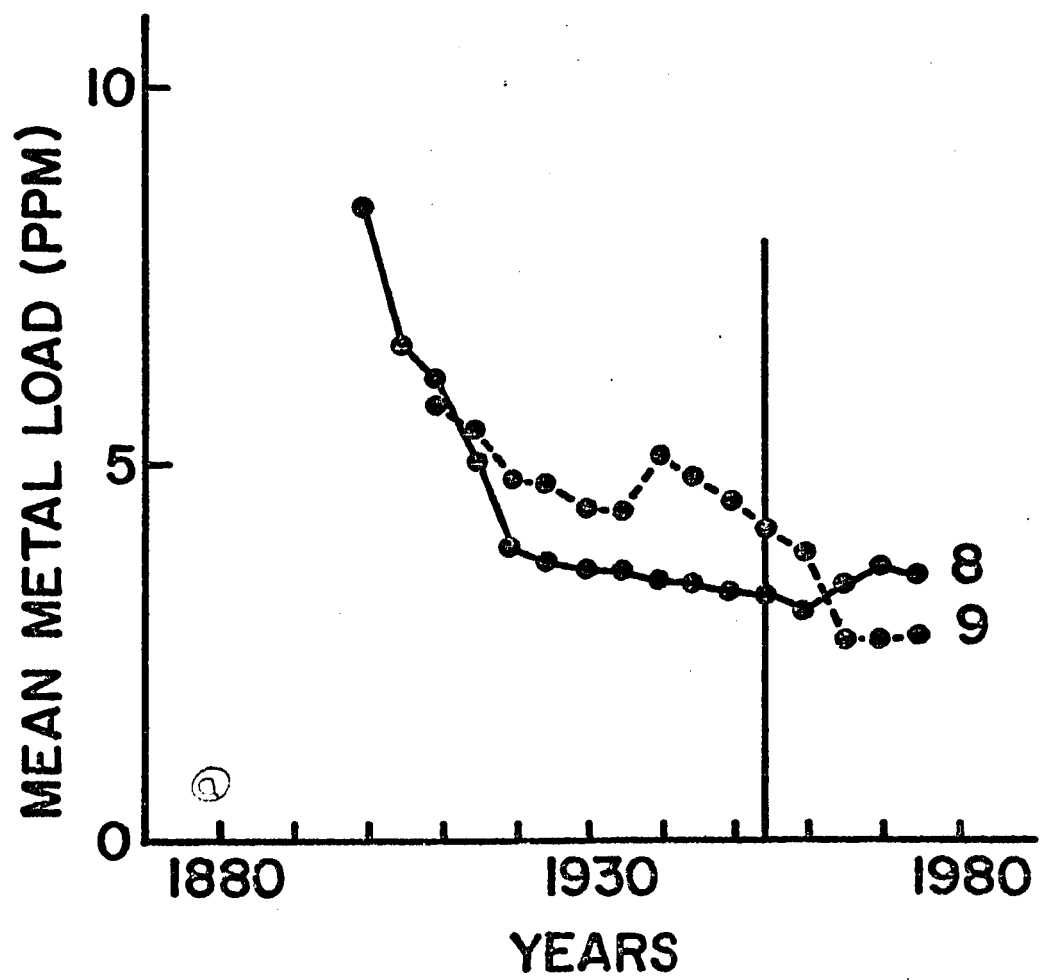


Figure 34. The relationship between the mean total load (ppm) of the annual rings of Abies balsamea and the year the annual ring was formed (a) for quadrats 8 and 9 at site 22 and (b) for quadrats 5, 6 and 7 at site 21. The vertical line at the year 1955 denotes the year that the smelter operations began.



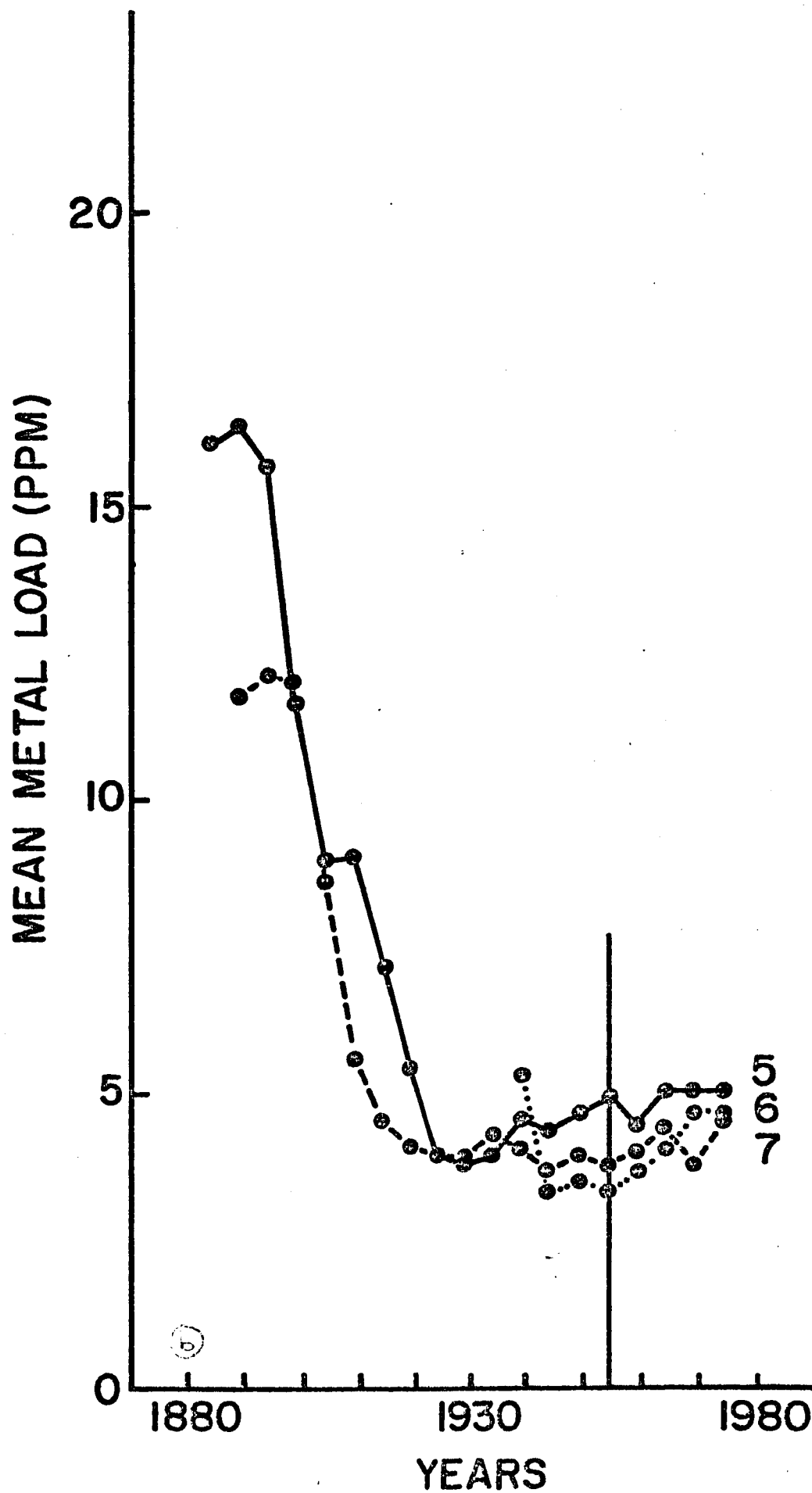
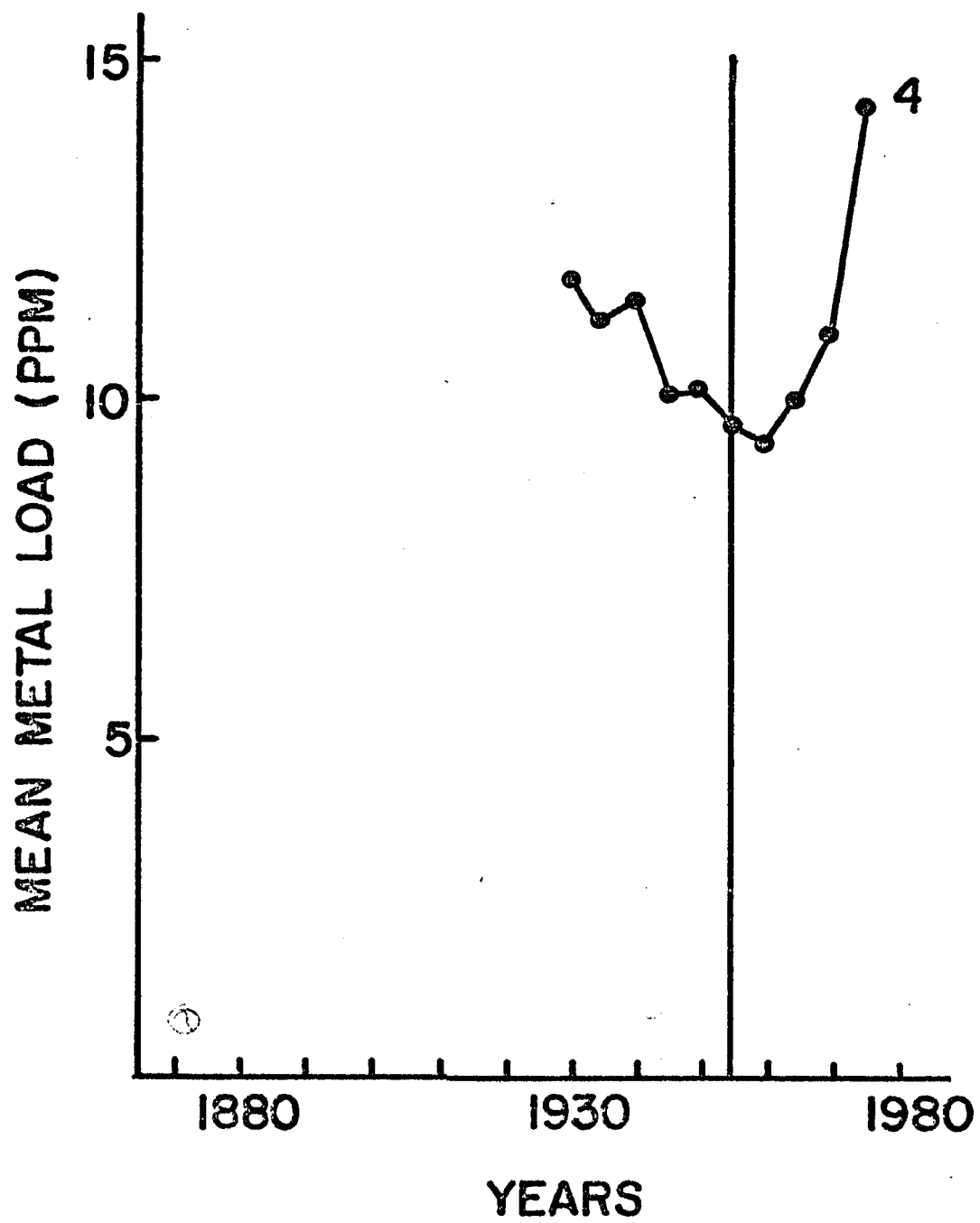
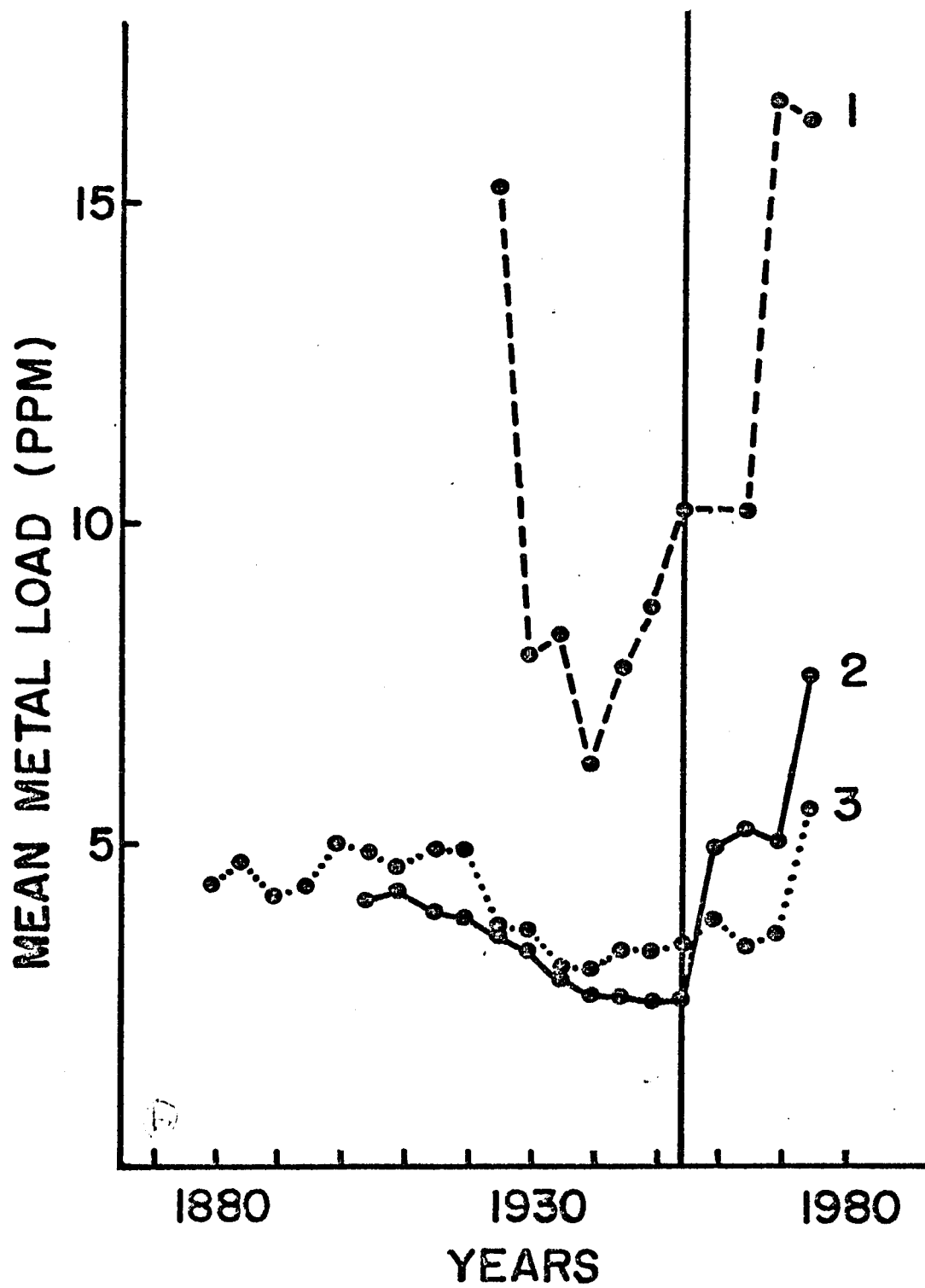


Figure 35. The relationship between the mean metal load (ppm) of the annual rings of Abies balsamea and the year the annual ring was formed (a) for quadrat 4 at site 15 and (b) for quadrats 1, 2 and 3 at site 11. The vertical line at the year 1955 denotes the year that the smelter operations began.





pollution and the latter very much so towards the left. The lowest metal values occurred at 1955 in both groups of trees. The trees occurring at quadrat 13 did not have this characteristic pattern and remained unexplained. However the fact that it also is heavily weighted with metals in the older xylem supports the contention that the high levels of metal are normal for the tissue. The type of pattern observed at site 43 may be the typical distribution model in Abies balsamea (see also curves for quadrats 5 to 6 Fig. 34b).

The fact that the older tissue generally had higher levels of heavy metals (Fig. 33 to Fig. 35) may be due to changes in soil characteristics as the tree aged. It is well known that young soils and soils that have been recently burned over, have a high mineral to organic matter ratio and that older soils have a high organic content. Young trees growing in mineral rich soils will under normal conditions accumulate these minerals (and metals) via the root system and transpiration stream in relatively high amounts. On the other hand, as the soil evolves and it becomes more and more organic, metals such as Pb (and possibly Cu and Zn) lose their mobility and solubility (Singer and Hanson 1969; Chow 1970) and form complexes with soil humic acids (Hildebrand and Blum 1974) or accumulate in both new and decomposed litter (Nilsson 1972). Trees growing in such conditions will accumulate much less metals from the roots. In such circumstances it

is not hard to imagine that the majority of the metal input would then be of atmospheric origin. It is understandable, then, that the metal levels in the most recent annual rings would be lower than in the older tissue. Metal accumulation should decrease continuously since it is bound in the soil, unless a fall out of metal occurs followed by accumulation in the aerial parts of the tree. Unwanted substances may also be excreted into the heartwood (Stewart 1966). This accumulation in the inert xylem, which may be a means of detoxification, may also, in part, account for the higher amounts of metals found in the older tissue. Holtzman (1970) indicated that Pb was found in higher concentrations in the older tissue of white and black oak. The lateral transport of Pb from bark to xylem (Lepp and Dollard 1974a) may account for some of the metal in the xylem tissue adjacent to the bark observed at most sites (e.g. site 24, quadrats 10 to 12, Fig. 33b).

The fact that the trees in quadrats 14 and 15 (Fig. 33a) showed increases in the total metal content from 1954 to 1974 may indicate that, although the site had no pollution damage characteristics (Table 36), the area (and in fact the whole region) is slowly but inexorably receiving unnatural amounts of heavy metals. The lateral transport of metals from bark to xylem may be an important process to explain the pattern observed after 1954.

Although the curve for quadrat 13 (Fig. 33a) did not

show the typical V-shaped pattern, the downward trend is interrupted at the 1955 mark and shifted towards the right to higher amounts of metal than would apparently be accumulated, Hampp and Holl (1974) showed that the sapwood of Robinia pseudoacacia contained more Pb than the outer heartwood but that the latter contained less of this metal than the inner heartwood. Higher amounts of metals in older tissue have also been reported by Holtzman (1970).

Variation in levels of total metal content in the trees occurring in the various quadrats (Figs. 34 a b) and in quadrats 11 and 12 (Fig. 33b) might be accounted for by postulating an equilibrium in the lateral transport of metals from bark to xylem (Lepp and Dollard 1974a) and from xylem to bark (Lepp and Dollard 1974b) and possibly from xylem to xylem (Lepp, personal communication).

The quadrats at the polluted site (11) however, showed a unique peculiarity. Whereas the normal pattern indicated that the higher metal values occurred in older tissue, the patterns for the trees of quadrats 1, 2 and 3 at site 11 (Fig. 35b) are reversed. Here we note the inclusion of quadrat 10 (Fig. 33b) and quadrat 4 (Fig. 35a). The V-shape is still evident but the highest metal values occurred after 1955 when pollution episodes began. Rolfe (1974) found that in cores taken near roads, significantly higher amounts of Pb were recorded in the last 10 years growth than in the earlier 10 year growth period. The coincidence of increased metal accumulation with the year that the

smelter operations began (e.g. 1, 2, 3 and 4), at a known polluted site indicates that a measure of the total metal load in the annual rings of trees (in this case in A. balsamea) may be used to show heavy metal pollution histories. The fact that the trees at a non polluted site also show an increased metal content after 1955 may attest to the sensitivity of this assay method and possibly to increased metal levels yet too low to affect mosses and lichens. Based on dendroecological reports and reviews (McGinnies 1963; Fritts 1966, 1971, 1974) it was expected that non polluted sites (43) would not show this upward metal accumulation trend.

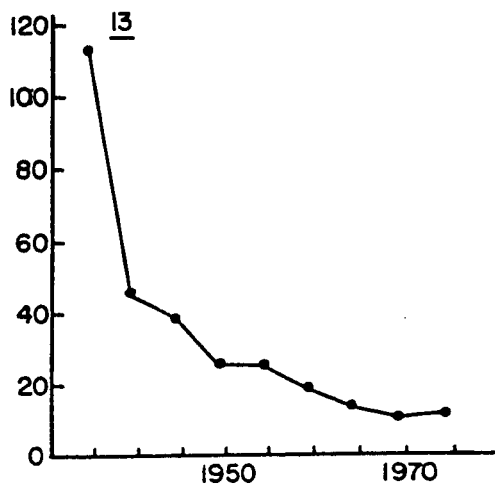
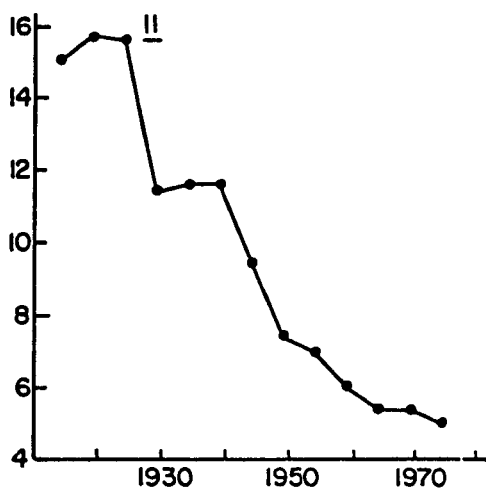
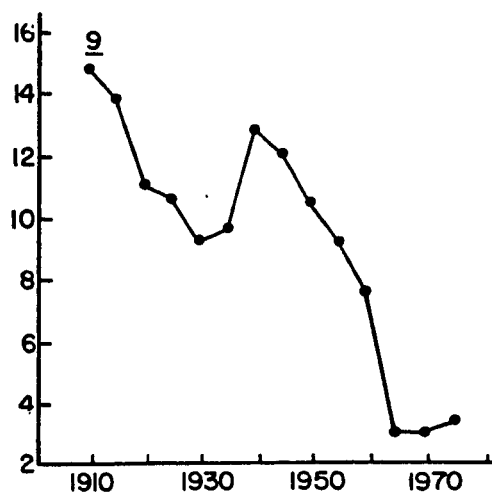
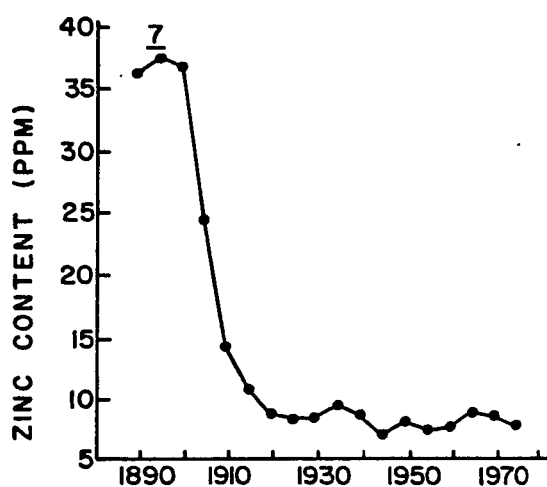
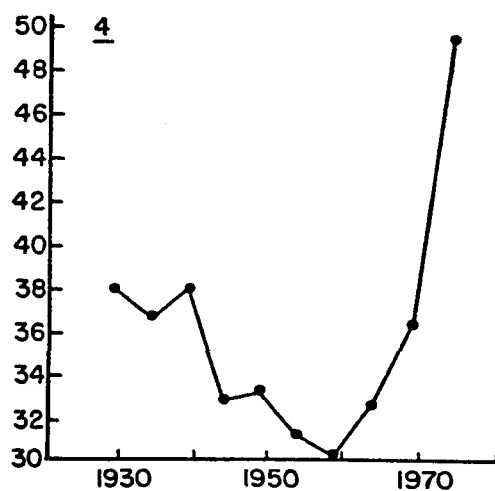
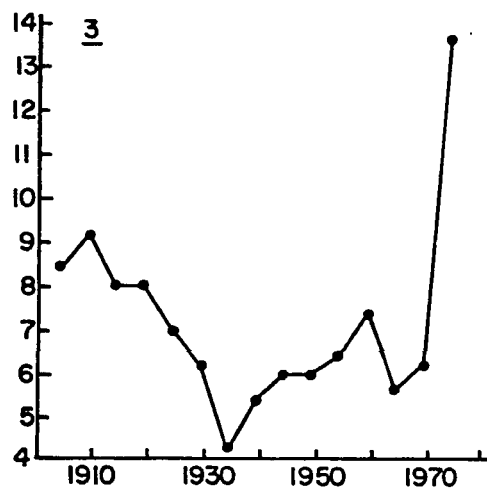
The accumulation patterns for Cu, Pb and Zn are shown in Figs. 36, 37 and 38. Values shown are near the lower limits of detection by the atomic absorption spectrophotometer. This might indicate that, as in the biogeochemical prospecting with lichens (Le Roy and Koksoy 1962), the total status of metal composition of the annual rings is more accurate in determining metal pollution histories than are observations on specific metals. These individual metal patterns are a reflection of the total metal load curves. In general, the polluted quadrats 1, 2 and 3 (Figs. 36, 37 and 38) show dramatic increases in Cu, Pb and Zn after pollution emissions began.

b) Ring width reduction.

Plots of the ring width ratios¹ (Figs. 39a and b) derived

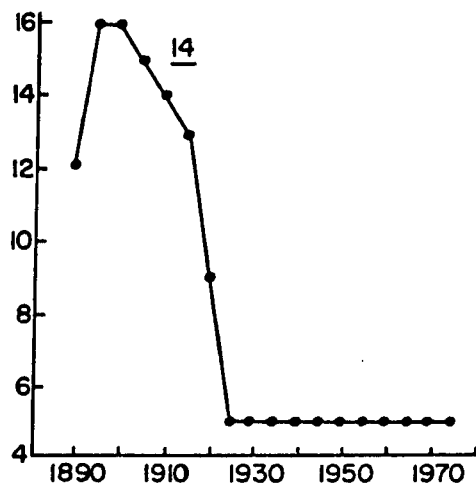
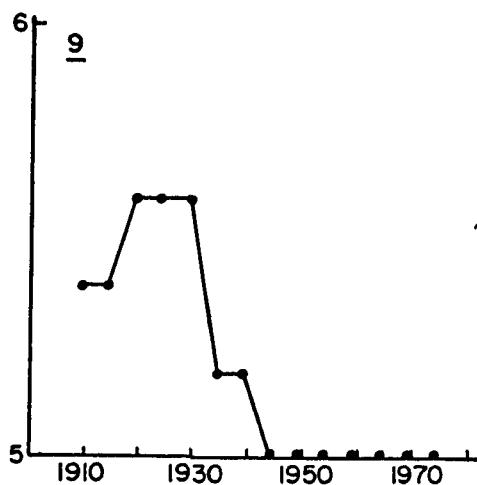
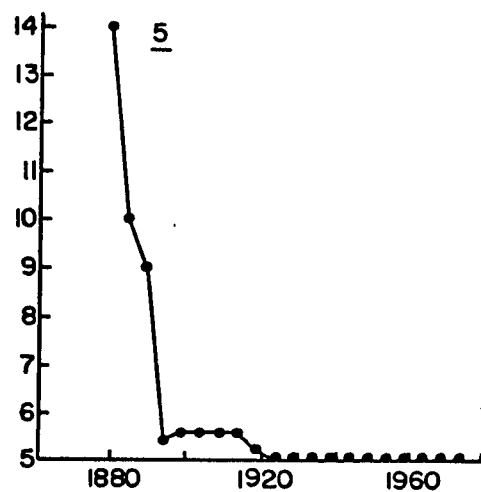
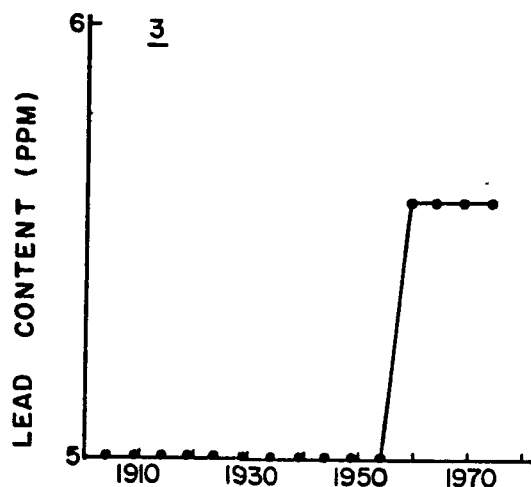
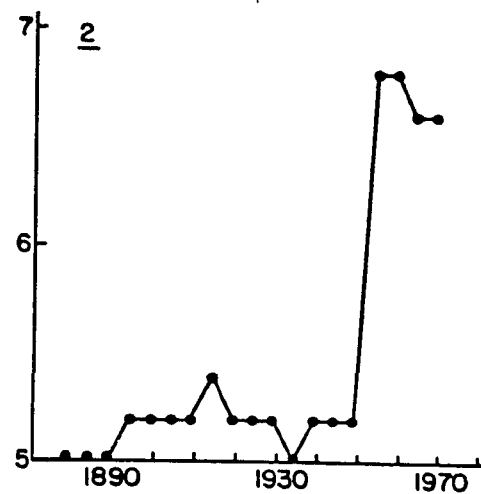
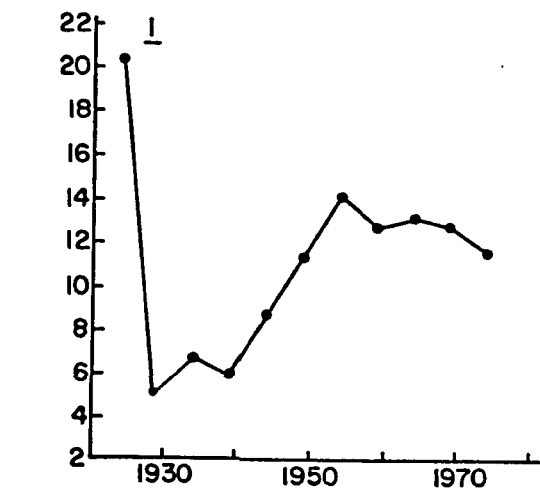
¹ The ratio is calculated as follows: five points running means are calculated for the ring width data (Tables 38 and 39), the mean for the 30 yr. width is divided into the means corresponding to the yrs. 30 to 1. This is the ring width ratio.

Figure 36. The relationship between the Zn content (ppm) in the annual rings of Abies balsamea and the year that the annual ring was formed for quadrats 3, 4, 7, 9, 11 and 13. See Fig. 21 for site locations.



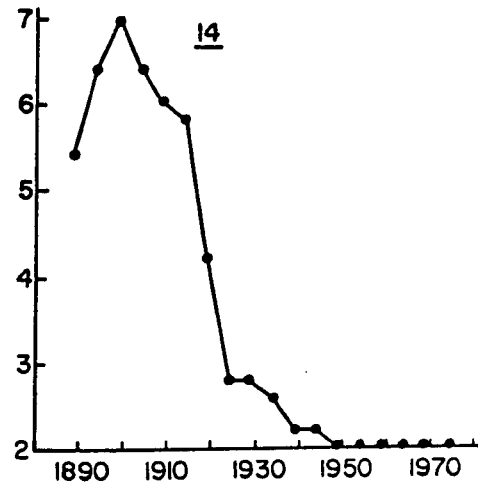
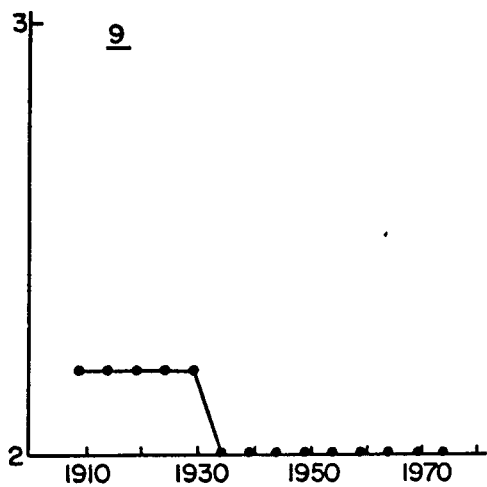
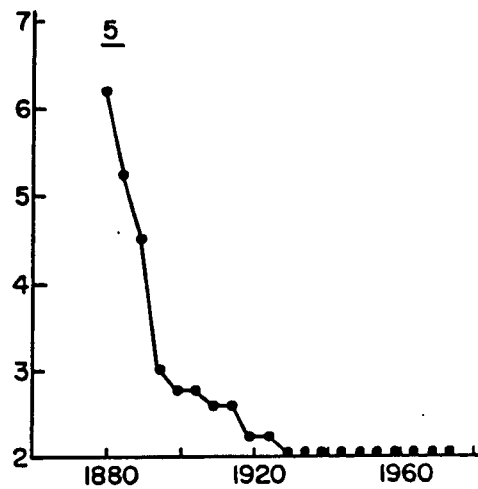
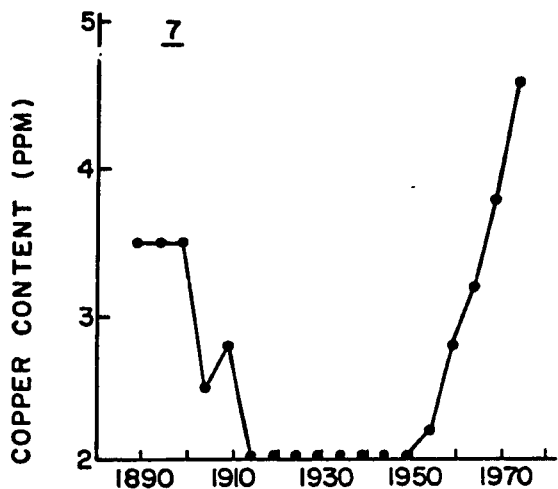
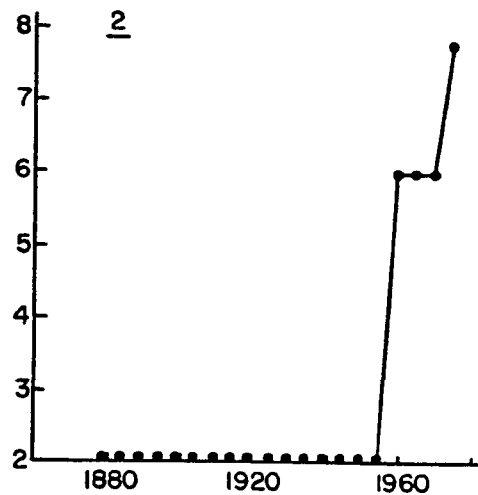
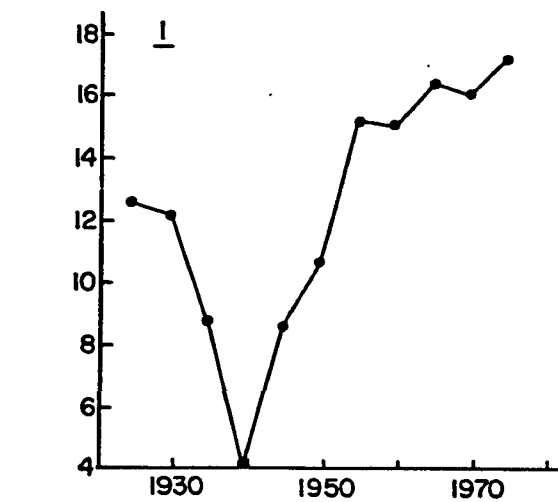
YEAR

Figure 37. The relationship between the Pb content (ppm) in the annual rings of Abies balsamea and the year that the annual ring was formed for quadrats 1, 2, 3, 5, 9 and 14. See Fig. 21 for site locations.



YEAR

Figure 38. The relationship between the Cu content (ppm) in the annual rings of Abies balsamea and the year that the annual ring was formed for quadrats 1, 2, 7, 5, 9 and 14. See Fig. 21 for site locations.



YEAR

from the ring width values in Tables 37 and 38 for the polluted and non polluted sites also indicate that the rings produced after the start of the smelter operations were narrower at the polluted site than they were previously. At the non polluted site the decrease in growth from 1944 to 1974 (Fig. 39b) was gradual. The slopes of the curves for the 10 year interval preceeding and following the input of polluted effluent into the atmosphere were 0.018 and 0.011 respectively. This would seem to indicate that these slopes are representative of normal growth reduction due to aging. In fact a slight increase in growth is indicated since the slope of the curve was smaller after 1955. On the other hand these same slopes at the polluted site were 0.012 and 0.044 (Fig. 39a) respectively, that is, there was nearly a four fold drop in the normal decrease in growth observed before pollution began. The fact that these reductions in growth coincide with increases in metal content at polluted sites gives further support to the hypothesis that annual rings of Abies balsamea may be used to demonstrate heavy metal pollution histories in forested areas.

Figure 39. The relationship between the ring width ratio of the annual rings of Abies balsamea and the number of years ago the annual ring was formed for sites 11 (polluted) and 43 (non polluted). The vertical broken line denotes the year that the smelter operations began.

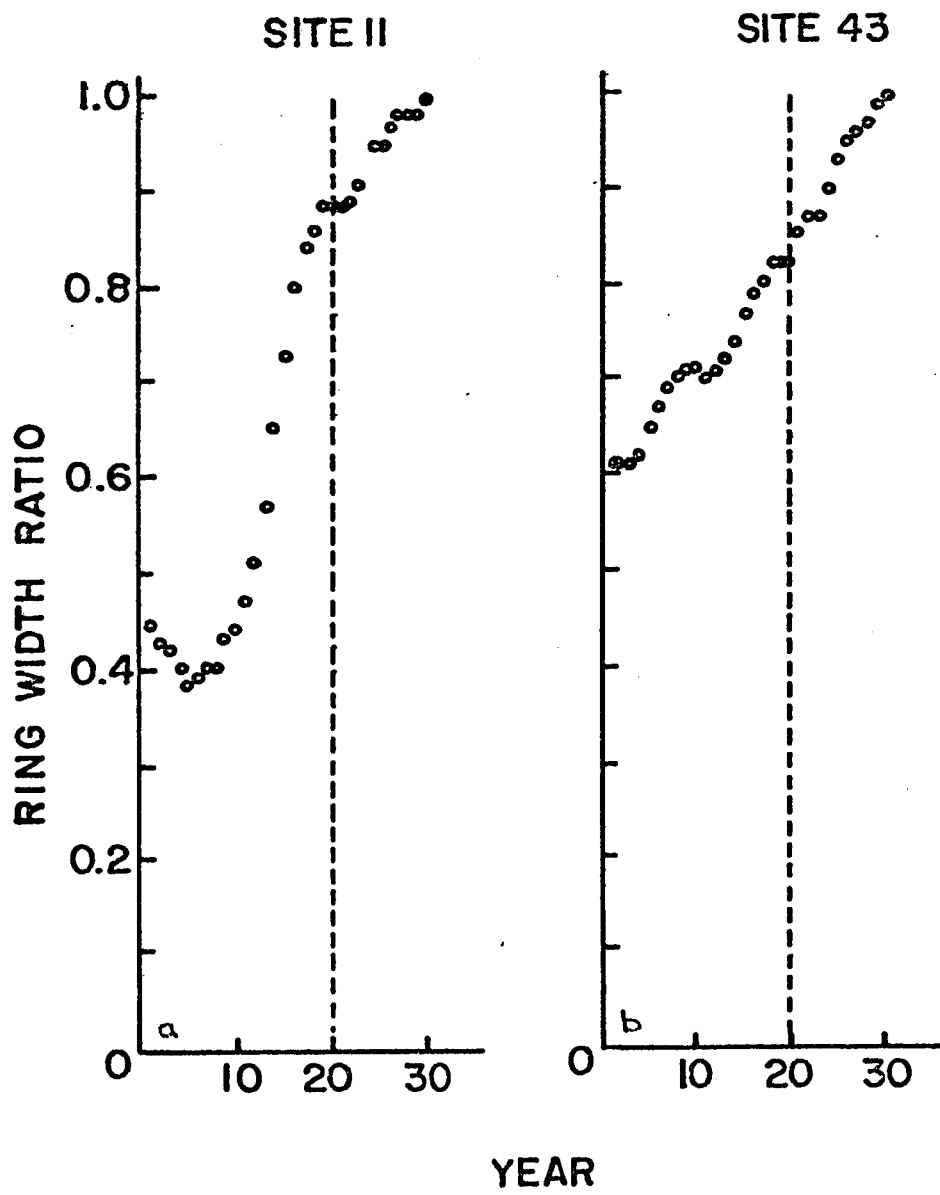


Table 37. Average ring widths by years of Abies balsamea growing in a polluted site (11) for the last 30 year period.

Year	Ring width $\pm$ SD (mm)	Year	Ring width $\pm$ SD (mm)
1	0.56 $\pm$ 0.10	16	0.88 $\pm$ 0.05
2	0.60 $\pm$ 0.13	17	0.95 $\pm$ 0.15
3	0.61 $\pm$ 0.16	18	1.03 $\pm$ 0.25
4	0.57 $\pm$ 0.09	19	1.13 $\pm$ 0.30
5	0.56 $\pm$ 0.10	20	1.15 $\pm$ 0.30
6	0.48 $\pm$ 0.08	21	1.12 $\pm$ 0.29
7	0.48 $\pm$ 0.17	22	1.13 $\pm$ 0.34
8	0.44 $\pm$ 0.09	23	1.14 $\pm$ 0.32
9	0.51 $\pm$ 0.12	24	1.15 $\pm$ 0.25
10	0.58 $\pm$ 0.12	25	1.15 $\pm$ 0.26
11	0.55 $\pm$ 0.08	26	1.20 $\pm$ 0.28
12	0.54 $\pm$ 0.07	27	1.25 $\pm$ 0.31
13	0.56 $\pm$ 0.02	28	1.27 $\pm$ 0.34
14	0.61 $\pm$ 0.04	29	1.25 $\pm$ 0.37
15	0.72 $\pm$ 0.03	30	1.29 $\pm$ 0.33

SD is the standard deviation.

Table 38. Average ring widths by years of Abies balsamea growing in a non polluted site (43) for the last 30 year period.

Year	Ring width $\pm$ SD (mm)	Year	Ring width $\pm$ SD (mm)
1	0.61 $\pm$ 0.06	16	0.72 $\pm$ 0.16
2	0.61 $\pm$ 0.08	17	0.75 $\pm$ 0.15
3	0.59 $\pm$ 0.09	18	0.78 $\pm$ 0.11
4	0.56 $\pm$ 0.07	19	0.81 $\pm$ 0.18
5	0.60 $\pm$ 0.07	20	0.79 $\pm$ 0.12
6	0.57 $\pm$ 0.06	21	0.78 $\pm$ 0.15
7	0.63 $\pm$ 0.10	22	0.82 $\pm$ 0.15
8	0.66 $\pm$ 0.11	23	0.82 $\pm$ 0.12
9	0.67 $\pm$ 0.09	24	0.81 $\pm$ 0.13
10	0.70 $\pm$ 0.09	25	0.85 $\pm$ 0.14
11	0.69 $\pm$ 0.08	26	0.88 $\pm$ 0.15
12	0.69 $\pm$ 0.09	27	0.89 $\pm$ 0.12
13	0.69 $\pm$ 0.11	28	0.91 $\pm$ 0.17
14	0.66 $\pm$ 0.13	29	0.95 $\pm$ 0.13
15	0.68 $\pm$ 0.15	30	0.97 $\pm$ 0.11

SD is standard deviation.

CHAPTER IV

General Discussion and Conclusions

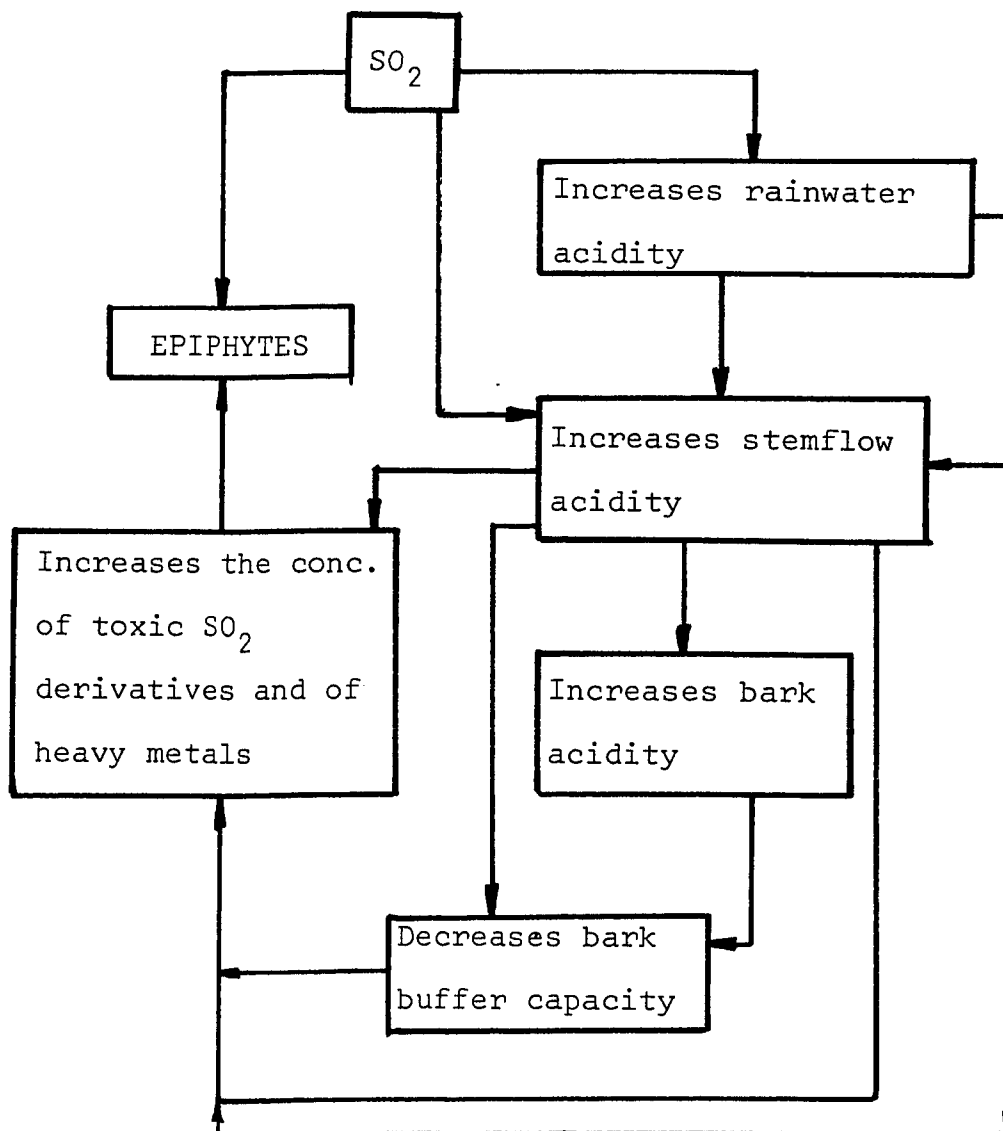
The environmental impact resulting from nearly 20 years of atmospheric effluent discharge of pollutants from a copper smelter at Murdochville Québec has been documented. The smelter discharges both gaseous sulphur dioxide and particulate metal pollutants from a stack situated at approximately 600 m above sea level in the Murdochville valley. The wind pattern (Fig. 10) plays an important role in distributing the pollutants in both the NW and SE directions (Figs. 6 to 9).

All of the biotic and abiotic compartments studied were affected to some degree by the dispersion of the pollutants into the boreal ecosystem surrounding the smelter.

The impact on rainwater was mostly affected by the sulphur dioxide emissions, which rendered it more acid (Table 28) than normal for sites close to the smelter complex. The acidity of this 'acid rain' decrease as the distance from the pollution source increased in parallel to a decline in sulphur dioxide concentration (Table 28, Fig. 20). Acid rain has been reported over northeastern United States by Likens (1976). This was the first documented report for the Gaspé region. The resultant effects of this acid rain on the epiphytic vegetation (especially lichens) and on the substratum, that is the bark, supporting

the epiphyte communities were more noticeable closer to the smelter, gradually decreasing in intensity at distances farther removed. Acid rain may reduce the diversity of the epiphytic vegetation component of the boreal forest either directly by direct deposition on the plants or indirectly by changing the physico-chemical properties of the bark substratum, that is, by lowering its pH (Fig. 28) and "buffer" capacity (Figs. 29 and 30) and/or by augmenting the concentration of toxic bisulphite in the stemflow bathing the lichen thalli. The various pathways by which the sulphur dioxide pollution signal could be perceived by the epiphytes is shown in Fig. 40. The indirect influence of sulphur dioxide via changes in rainwater, stemflow and bark acidity resulting in the formation of compounds toxic to the epiphytes and/or changing the physico-chemical properties of the epiphytes themselves (Neiboer et al. 1976a b), is probably just as important as damage caused by direct wet deposition of the gas. Whether or not the increased accumulation of heavy metals observed in the thalli of the epiphytes P. squarrosa and H. physodes (Table 32) was attributable to these pH changes has not been determined. A strong correlation did exist for stemflow pH, stemflow metal content and thalli metal content however (Tables 32 and 33), that is, an increase in the metal concentration of the thalli was directly related to a decrease in pH and to a concomitant increase in the metal concentration of the stemflow.

Figure 40. A flow chart indicating the direct and indirect pathways by which epiphytes may receive a pollution signal. In this case sulphur dioxide alters the physico-chemical properties of the epiphyte substratum which amplifies the sulphur dioxide toxicity via production and liberation of toxic compounds.



Both sulphur dioxide and heavy metals may have caused changes in the chlorophyll content of the lichen thalli. High ambient sulphur dioxide concentrations (Fig. 23) and increased thallus metal content (Figs. 31, 32 and 41) were related to a decrease in chlorophyll. Based on the present work it was difficult to separate effects caused by one or the other of these pollutants. The shift in the absorption peak of chlorophyll toward the phaeophytin wavelength (Figs. 24, 26 and 27) may indicate that sulphur dioxide was the chlorophyll reducing agent. On the other hand, the rapid increase in the Pb content of the lichen thalli P. squarrosa and H. physodes corresponds exactly with an abrupt decline in the chlorophyll content of these lichens (Figs. 31 and 32). It was speculated that both the gaseous and particulate pollutants, in conjunction with the increase in the acidity of the epiphyte substratum and the stemflow bathing the lichen thalli, contributed significantly to the apparent destruction of chlorophyll. It has been shown in laboratory experiments that both sulphur dioxide (Türk and Wirth 1975a b) and heavy metals (Puckett 1976) acting alone can reduce photosynthesis and change the chlorophyll spectrum of lichens.

A visual translation of the long term impact of these pollutants, acting together, on the epiphytic flora of Abies balsamea is presented in Fig. 14. The isopollutant lines of the IAP map clearly indicated that the distribution of the epiphytes (Table 12) was dependent on the dispersion

patterns and quantities of sulphur dioxide (Figs. 6 to 9) and that of the metals as shown by their accumulation in the woodland mosses Hylocomium splendens (Table 20) and Pleurozium schreberi (Table 19), in Clintonia borealis (Table 18) and in Picea mariana (Table 17) (see also Figs. 16 to 19).

In general lichen thalli transplanted at the different IAP sites corroborated the observations on the naturally occurring epiphytes (Figs. 26 and 27), that is, a decrease in chlorophyll corresponded to an increase in pollution and to a reduction in the IAP values (Table 11).

A summary, by IAP zones, of pollutant distribution in the atmosphere and stemflow water of A. balsamea and the accumulation of metal pollutants in selected vegetation compartments is presented in Table 39. In reading the table from top to bottom it can be concluded that a reduction in pollution levels, as shown by a decreased ambient sulphur dioxide concentration (column 3) and by a reduced concentration of heavy metals in the stemflow (column 4), was essential for normal vegetation development as indicated by an increased index of atmospheric purity (IAP, column 2). The decreased pollution from IAP zones I to V (column 1) is also reflected in the reduced amounts of metal accumulated by the different types of vegetation in that the amount accumulated showed a parallel decrease (columns 5 to 10). This decrease was especially rapid from I to zone II.

Other conclusions may be drawn by reading the table

Table 39. Summary of selected pollution data on a zone wise basis.

1	2	3	4	5	6	7	8	9	10
I	0	48	0.36	250	374	4589	422	115	179
II	17	15	0.21	174	292	438	285	31	29
III	48	10	0.09	111	116	251	195	19	27
IV	70	7	0.05	100	119	199	123	21	16
V	95	5	0.03	98	92	118	84	17	23

1. IAP zone.
2. Average IAP value for the zone.
3. Average sulphur dioxide value (ppb) for the zone.
4. Average metal content of stemflow (ppb) for the zone.
5. Average metal content in Parmelia squarrosa (ppm) for the zone.
6. Average metal content in Hypogymnia physodes (ppm) for the zone.
7. Average metal content in Hylocomium splendens (ppm) for the zone.
8. Average metal content in Pleurozium schreberi (ppm) for the zone.
9. Average metal content in Picea mariana needles (ppm) for the zone.
10. Average metal content in Clintonia borealis leaves (ppm) for the zone.

from left to right. It would appear that very low concentrations of metal in the stemflow (column 4) resulted in very high accumulations of these metals in the epiphytes (columns 5 and 6). No other evidence was presented to justify that only the stemflow contributed heavy metals, dry deposition in the form of dust would no doubt be an important factor. The cryptogams, that is the woodland mosses Hylocomium splendens (column 7) and Pleurozium schreberi (column 8), as well as the lichen epiphytes Hypogymnia physodes (column 6) and Parmelia squarrosa (column 5) accumulated more metal in each of the IAP zones than did the two vascular plants Picea mariana (column 9) and Clintonia borealis (column 10). As mentioned in previous discussions this could be related to the more efficient cation exchange capacity of the cryptogams as compared to the higher plants. In all of the zones H. splendens (column 7) proved to be the most efficient accumulator of heavy metals and as such it was probably the best indicator/monitor species in the area studied. P. schreberi (column 8) ranked second in metal accumulation efficiency followed by H. physodes (column 6), P. squarrosa (column 5), C. borealis (column 10) and Picea mariana (column 9). Bryophytes and lichens are, then, heavy metal sinks and thus retard the cycling of potentially toxic elements in these forest ecosystems.

A bioassay technique, using annual rings of Abies balsamea, to determine when pollution started in the

Murdochville area has been tested and verified. The occurrence of reduced ring widths (Table 37) and ring width ratios (Fig. 39a) in A. balsamea between the years 1955 and 1974 as compared to the 10 years prior to 1955, at a known polluted site, indicated that these annual rings can be used to determine when pollution started. The four fold reduction in the ring width ratio at the polluted site (Fig. 39a) started at the 1955 annual ring, the year that the copper smelter began operating. The control non polluted site did not show abnormal decreases in growth (Fig. 39b).

An analysis of the heavy metal pattern in these same annual rings indicated that at the polluted site a sharp increase in heavy metals generally occurred at 1955 (Fig. 36, quadrats 3 and 4; Fig. 37, quadrats 1, 2 and 3; Fig. 38, quadrats 1 and 2). This increase would seem to correspond to the reduced ring width ratios (Fig. 39a). The total metal load in each annual ring at the polluted site (Fig. 35b) gave the ^{same} results. The interpretation of the metal accumulation in the rings of trees occurring at non polluted sites proved interesting in that the distribution patterns of the metals could be explained by postulating exchange processes between bark and xylem, xylem and bark and xylem and xylem. Such exchanges have been reported in laboratory experiments using Pb tracers (Lepp and Dollard 1974a b).

The author is aware that additional information could

have been gathered both in the field and in the laboratory to clarify accumulation and cycling processes. For example, more precision as to the why of the observed heavy metal accumulation pattern in the annual rings of A. balsamea could have been achieved by analysing soil samples along a successional gradient to determine metal mobility in the soil; Lepp and Dollard type experiments could also have been made not only on the xylem and bark problem but also on the important mycorrhizal associations of roots to answer the question 'are mycorrhizae heavy metal sinks and do they prevent metal accumulation in the roots and if so does soil evolution play a role?'; data on dry deposition of heavy metals on lichen transplants could have been obtained by either exposing inert polyethylene discs adjacent to the lichen bearing discs or again by analysing the heavy metal content of the thallus washings from the transplants; the pollutant effects on the transplants could have been further verified by cultivating lichen soredia exposed to different pollutant concentrations and analysing their rate of development; epiphytic lichens could have been exposed to varying concentrations of heavy metals in the field so as to determine precisely the toxic threshold levels.

The data collected did not permit the author to detail the cycling of heavy metals in the forest stands studied. All that can be concluded positively from the metal data is that the mosses and lichens are repositories for heavy

metals and that sulphur dioxide by the indirect effect of acid rain releases these metals causing possible toxicity. The data base however is substantial and represents a unique opportunity for further research into heavy metal cycling and toxicity in boreal ecosystems. Continued efforts in the analysis of heavy metals in tree rings as pollution event indicators should also be maintained.

It is the intention of the author to exploit the data base obtained in a future impact analysis of the area and it is hoped that at that time valuable information on the reaction rates and/or adaptability of the vegetation will be acquired.

In conclusion the author has shown, both qualitatively and quantitatively, that the pollutant loading from the copper smelter has caused a marked environmental impact on specific abiotic and biotic components of the boreal forest.

Bibliography

- Ackerman, E.A. 1941. The Köppen classification of climates in North America. *Georg. Rev.* 31: 105-111.
- Antonovics, J., A.D. Bradshaw, and R.G. Turner. 1971. Heavy metal tolerance in plants. Pages 1-86 in J.B. Cragg, ed. *Advances in ecological research*. Academic Press, N.Y.
- Arndt, V. 1974. The Kautsky-Effect: A method for the investigation of the actions of air pollutants in chloroplasts. *Environ. Pollut.* 6: 181-194.
- Aronson, J.M. 1965. The cell wall. Vol. 1, 49 pp., in G.C. Ainsworth and A.S. Sussman, eds. *The fungi*. Academic Press, N.Y.
- Aslander, A. 1958. Nutritional requirements of crop plants. Vol. 4, pages 997-1025 in W. Ruhland, ed. *Encyclopedia of plant physiology*. Springer-Verlag, Berlin.
- Ault, W.V., R.G. Senechal, and W.E. Erlebach. 1970. Isotopic composition as a natural tracer of lead in the environment. *Environ. Sci. Technol.* 4(4): 305-313.
- Aureau, F. and M. Bedeneau. 1974. Essai de cartographie de la pollution à l'aide des épiphytes. *R.F.F.* 26(5): 355-359.
- Baddeley, M.S., B.W. Ferry, and E.J. Finnegan. 1973. Sulphur dioxide and respiration in lichens. Pages 229-313 in B.W. Ferry, M.S. Baddeley, and D.L. Hawksworth,

- eds. Air pollution and lichens. Athlone Press, London.
- Barkman, J.J. 1958. Phytosociology and ecology of cryptogamic epiphytes. Van. Gorcum. Assen, Netherlands.
- Barnes, D., M.A. Hamadah, and J.M. Ottaway. 1976. The lead, copper and zinc content of tree rings and bark. Sci. Total Environ. 5: 63-67.
- Barrett, E., and G. Brodin. 1955. The acidity of Scandinavian precipitation. Tellus 7: 251-257.
- Bazzaz, F.A., R.W. Carlson, and G.L. Rolfe. 1974. The effect of heavy metals on plants: Part I. Inhibition of gas exchange in sunflower by Pb, Cd, Ni, and Tl. Environ. Pollut. 7: 241-246.
- Berg, W.A. and W.G. Vogel. 1973. Toxicity of acid mine spoils to plants. Pages 57-68 in R.J. Davis and G. Davis, eds. Ecology and reclamation of devastated land. Int. Symp. on Ecology and Revegetation of Drastically Disturbed Areas. Univ. Park, Pa.
- Beschel, R.E. 1959. The copper swamps in the Aboushagen woods North Sackville, N.B. Pages 1-11 (mimeogr.) in Summary of the maritime excursion of the 9th Int. Bot. Congr., Montréal.
- Brassard, G.R. 1969. Mielichhoferia elongata, a copper moss new to North America, found in Arctic Canada. Nature 222: 584-585.
- Briggs, D. 1972. Population differentiation in Marchantia polymorpha L. in various lead pollution levels. Nature

- 238: 166-167.
- Broda, E. 1965. Mechanism of uptake of trace elements by plants. In Isotopes and radiation in soil-plant nutrition studies. I.A.E.A., Vienna. 207 pp.
- Brodo, I.M. 1961. Transplant experiments with corticolous lichens using a new technique. Ecology 42: 838-841.
- Brown, D.H., and J.W. Bates. 1972. Uptake of lead by two populations of Grimmia doniana. J. Bryol. 7: 187-193.
- _____ and D.R. Slingsby. 1972. The cellular location of lead and potassium in the lichen Cladonia rangiformis (L.) Hoffm. New Phytol. 71: 297-305.
- Brummer, J.J. 1966. Quart nord-est du canton de Holland. Ministère des richesses naturelles du Québec. Rapport Géologique 125.
- Burkitt, A., P. Lester, and G. Nickless. 1972. Distribution of heavy metals in the vicinity of an industrial complex. Nature 238: 327-328.
- Chisholm, J. 1971. Lead poisoning. Sci. Amer. 224: 15-23.
- Chow, T.L. 1970. Lead accumulation in roadside soil and grass. Nature 225: 295-296.
- Clymo, R.S. 1963. Ion exchange in Sphagnum and its relation to bog ecology. Ann. Bot. 27: 309-324.
- Coker, P.D. 1967. The effects of sulphur dioxide pollution on bark epiphytes. Trans. British Bryol. Soc. 5: 431-447.
- Coombes, A.J., and N.W. Lepp. 1974. The effects of Cu and Zn on the growth of Marchantia polymorpha and Funaria hygrometrica. The Bryologist 77: 447-452.

- Czarnowska, K., and I. Rejement-Grochowska. 1974.
Concentration of heavy metals - iron, manganese, zinc
and copper in mosses. *Acta. Soc. Bot. Pol.* 43(1): 39-44.
- Dansereau, P. 1944. Les érablières de la Gaspésie et les
fluctuations du climat. *Bull. Inst. Bot. Univ.*
Montréal 51: 1-18.
- _____. 1950. Flora and vegetation of the Gaspé Peninsula.
Wild Flower 26(2): 26-40.
- _____. 1959. *Phytogeographia Laurentiana II*. The principal
plant associations of the Saint Lawrence Valley. *Contrib.*
Inst. Bot. Univ. Montréal 75: 147 pp.
- _____, and M. Raymond. 1948. Botanical excursions in Québec
Province: Montréal - Québec - Gaspé Peninsula. *Bull.*
Serv. Biogéogr. 2: 1-20.
- _____. 1949. Observations botaniques préliminaires le long
de la rivière York, comté de Gaspé. *Ann. de l'ACFAS* 15:
106-108.
- De Sloover, J., and F. LeBlanc. 1968. Mapping of
atmospheric pollution on the basis of lichen sensitivity.
Pages 42-56 in R. Misra and B. Gopal, eds. *Proceedings*
of the symposium on recent advances in tropical ecology.
Varanasi, India.
- Dollard, G.J., T.K. Tian and N.W. Lepp. 1976. Some
approaches to the development of tree ring analysis as
a monitoring tool for heavy metal pollution. Pages 16-
25 in L. Kärenlampi, ed. *Proceedings of the Kuopio*
meeting on plant damages caused by air pollution. Kuopio,

Finland.

- Douglass, A.E. 1928. Climatic cycles and tree growth. Vol. 1 (289). Carnegie Institution of Washington, Washington, D.C.
- Dykeman, W.R., and A.S. DeSousa. 1966. Natural mechanism of copper tolerance in a copper swamp forest. Can. J. Bot. 44: 871-878.
- Environment Canada. Pages 20, 36, and 38 in Temperature and precipitation 1941-1970. Means for the period 1941 to 1970 and extremes up to 1970. Québec, Vol. 5. Environment Canada, Atmospheric Services.
- Ernst, W.H.O. 1976. Physiology of heavy metal resistance in plants. Paper presented at the Int. Conf. on Heavy Metals in the Environ., Toronto, 26 pp. (preprint).
- Ewing, B.B., and J.E. Pearson. 1974. Lead in the environment. Advan. Environ. Sci. Technol. 3: 1.
- Farrar, J.F. 1976a. Ecological physiology of the lichen Hypogymnia physodes I. Some effects of constant water saturation. New Phytol. 77: 93-103.
- _____. 1976b. Ecological physiology of the lichen Hypogymnia physodes II. 'Effects of wetting and drying cycles and the concept of 'physiological buffering''. New Phytol. 77: 105-113.
- _____. and D.C. Smith. 1976. Ecological physiology of the lichen Hypogymnia physodes III. The importance of the rewetting phase. New Phytol. 77: 115-125.
- Fritts, H.C. 1966. Growth-rings of trees: Their

- correlation with climate. Science 154: 973-979.
- _____. 1971. Dendroclimatology and dendroecology. Quat. Res. 1: 419-449.
- _____. 1974. Relationships of ring widths in arid-site conifers to variations in monthly temperature and precipitation. Ecol. Mono. 44: 411-440.
- Galloway, J.N., G.E. Likens, and E.S. Edgerton. 1976. Acid precipitation in the northeastern United States: pH and acidity. Science 194: 722-724.
- Garber, K. 1973. Luftverunreinigungen, eine Literaturübersicht. In W. Bosshard ed. Ber. Nr. 102 der Eidg. Anstalt für das forstliche Versuchswesen, Ch-8903 Birmensdorf.
- Geiger, R. 1965. The climate near the ground. Harvard Univ. Press, Cambridge, Mass. 621 pp.
- Gilbert, O.L. 1969. The effect of SO₂ on lichens and bryophytes around Newcastle-upon-Tyne. Pages 223-235 in Air pollution. Proceedings on the first European congress on the influence of air pollution on plants and animals. Wageningen, 1968.
- _____. 1970. Further studies on the effect of sulphur dioxide on lichens and bryophytes. New Phytol. 69: 605-627.
- _____. 1973. Lichens and air pollution. Pages 443-472 in V. Ahmadjian and M.E. Hale, eds. The lichens. Academic Press, N.Y.

- Goodman, G.T., and T.M. Roberts. 1971. Plants and soils as indicators of metals in the air. *Nature* 231: 287-292.
- Gorham, E. 1955. On the acidity and salinity of rain. *Geochim. Cosmochim., Acta* 7: 231-239.
- _____. 1959. A comparison of higher and lower plants as accumulators of radioactive fallout. *Can. J. Bot.* 37: 327-329.
- Grodzinska, K. 1971. Acidification of tree bark as a measure of air pollution in southern Poland. *Bull. Acad. Sc.* 19(3): 189-195.
- Gullvåg, B.M., H. Skaar, and E.M. Ophus. 1974. An ultrastructural study of lead accumulation within leaves of Rhytidiadelphus squarrosus (Hedw.) Warnst. A comparison between experimental and environmental poisoning. *J. Bryol.* 8: 117-122.
- Hampp, R., and W. Holl. 1974. Radial and axial gradients of lead concentration in bark and xylem of hardwoods. *Arch. Environ. Contam. Toxicol.* 2(2): 143-151.
- Hampp, R., C. Kriebitzsch, and H. Ziegler. 1974. Effects of lead enzymes of porphyrine biosynthesis in chloroplasts and erythrocytes. *Naturwissenschaften* 61: 504-505.
- Hampp, R., and K. Lenzian. 1974. Effect of lead ions on chlorophyll synthesis. *Naturwissenschaften* 61: 218-219.
- Hawksworth, D.L., and F. Rose. 1970. Qualitative scale for estimating sulphur dioxide air pollution in England and Wales using epiphytic lichens. *Nature* 227: 145-148.
- Henderson, A., and M.R.D Seaward. 1976. The lichens of

- Harewood. The Naturalist 1976: 61-71.
- Hildebrand, E.E., and W.E. Blum. 1974. Lead fixation by soil humic acids. Naturwissenschaften 61: 128-129.
- Hill, D.J. 1974. Some effects of sulphite on photosynthesis in lichens. New Phytol. 73: 1193-1205.
- Hoffman, G.R. 1974. The influence of a paper pulp mill on the ecological distribution of epiphytic cryptogams in the vicinity of Lewiston, Idaho and Clarkston, Washington. Environ. Pollut. 7: 283-301.
- Holden, M. 1965. Chlorophylls. Pages 461-488 in T.W. Goodwin, ed. Chemistry and biochemistry of plant pigments. Academic Press, N.Y.
- Holtzman, R.B. 1970. Discussion. Isotopic composition as a natural tracer of lead in the environment. Environ. Sci. Technol. 4(4): 314-317.
- Huckabee, J.W. 1973. Mosses: sensitive indicators of airborne mercury pollution. Atmos. Environ. 7: 749-754.
- Huey, J.S. 1973. Lichen distribution and succession on selected sites of reclaimed bituminous strip mines in Clearfield Co., Pa. PhD Thesis. Ohio State University, Columbus. 114 pp.
- Huey, N.A. 1972. Survey of air borne pollutants. Pages 25-60 in Helena valley, Montana area environmental pollution study. U.S. Environmental Protection Agency, Research Triangle Park, N.C.
- Hutchinson, T.C., and L.M. Whitby. 1974. Heavy metal pollution in the Sudbury mining and smelting region of

- Canada I. Soil and vegetation contamination by nickel, copper, and other metals. *Environ. Conserv.* 1(2): 123-132.
- Hutchinson, T.C. 1976. The impact of pollution. *Can. J. Bot. Ass. Bull. Suppl.* 4(1): 25-29.
- Inglis, F., and D.J. Hill. 1974. The effect of sulphite and fluoride on carbon dioxide uptake by mosses in the light. *New Phytol.* 73: 1207.
- Jaakkola, T., H. Taka-hashii, and J.K. Miettinen. 1971. Cadmium content in seawater, bottom sediment, fish, lichen and elk in Finland. In Trace elements in relation to cardiovascular disease. W.H.O. Mtg. Report, Geneva, Switzerland. 16 pp.
- James, P.W. 1973. The effect of air pollutants other than hydrogen fluoride and sulphur dioxide on lichens. Pages 143-175 in B.W. Perry, M.S. Baddeley and D.L. Hawksworth, eds. Air pollution and lichens. University of Toronto Press, Toronto.
- Johnson, I., and U. Söchting. 1973. Influence of air pollution on the epiphytic lichen vegetation and properties of deciduous trees in the Copenhagen area. *Oikos* 24(3): 344-351.
- Jonsson, B., and R. Sundberg. 1972. Has the acidification by atmospheric pollution caused a growth reduction in Swedish forests? *Inst. Skogsproduktion, Stoskholm, Res. Notes* 20: 46 pp.
- Jordan, M.J. 1975. Effects of zinc smelter emissions and fire on a chestnut-oak woodland. *Ecology* 56: 78-91.

- Kershaw, K.A. 1963. Lichens. Endeavour 22: 65-69.
- Koepppe, D.E., and R.J. Miller. 1970. Lead effects on corn mitochondrial respiration. Science 167: 1376-1378.
- Laaksoverta, K., H. Olkkonen, and P. Alakuujala. 1976. Observations on the lead content of lichen and bark adjacent to a highway in southern Finland. Environ. Pollut. 11: 247-255.
- Lag, T., O. Hvatum, and B. Bolvika. 1969. An occurrence of naturally lead-poisoned soil at Kastad Gjovik, Norway. Nor. Geo. Unders. 266: 141-159.
- Lambinon, J., A. Maquinay, and J.L. Ramant. 1964. La teneur en zinc de quelques lichens des terrains calminaires belges. Bull. Jard. Bot. Etat Brux. 34: 273-282.
- Lange, O.L., and H. Ziegler. 1963. Der Schwermetallgehalt von Flechten aus dem Acrosoretin sinopicae auf Erzschlackenhalde des Harzes L. Eisen und Kupfer. Mitt. Flor. Soz. Arb. gemein, N.F. 10: 156-183.
- Lawrey, J.D., and E.D. Rudolph. 1975. Lichen accumulation of some heavy metals from acidic surface substrates of coal mine ecosystems in southeastern Ohio. Ohio J. Sci. 75: 113-117.
- LeBlanc, F. 1961. Influence de l'atmosphère polluée des grandes agglomérations urbaines sur les épiphytes corticoles. Rev. Can. Biol. 20: 823-827.
- _____, and J. De Sloover. 1970. Relation between industrialization and the distribution and growth of

- epiphytic lichens and mosses in Montréal. Can. J. Bot.
48: 1485-1496.
- _____, G. Comeau, and D.N. Rao. 1971. Fluoride injury
symptoms in epiphytic lichens and mosses. Can. J. Bot.
49: 1691-1698.
- _____, and D.N. Rao. 1966. Réaction de quelques
lichens et mousses épiphytiques à l'anhydride sulfureux
dans la région de Sudbury, Ontario. The Bryologist 69:
338-346.
- _____. 1973a. Evaluation of the pollution and drought
hypotheses in relation to lichens and bryophytes
in urban environments. The Bryologist.
76: 1-19.
- _____. 1973b. Effects of sulphur dioxide on lichen and
moss transplants. Ecology 54: 612-617.
- _____. 1974. A review of the literature on bryophytes with
respect to air pollution. Soc. Bot. Fr., Coll. Bryol.,
Tome 121: 237-255.
- _____. 1975. Effects of air pollution on lichens and
bryophytes. Pages 237-272 in J.B. Mudd and T.T. Kozlowski,
eds. Responses of plants to air pollutants. Academic
Press, N.Y.
- _____, and G. Comeau. 1972a. The epiphytic vegetation of
Populus balsamifera and its significance as an air
pollution indicator in Sudbury, Ontario. Can. J. Bot.
50: 519-528.

- _____. 1972b. Indices of atmospheric purity and fluoride pollution pattern in Arvida, Québec. *Can. J. Bot.* 50: 991-998.
- Lee, J.A. 1972. Lead pollution from a factory manufacturing anti-knock compounds. *Nature* 238: 165-166.
- _____, and J.H. Tallis. 1973. Regional and historical aspects of lead pollution in Britain. *Nature* 254: 216-218.
- Lepp, N.W. 1975. The potential of tree-ring analysis for monitoring heavy metal pollution patterns. *Environ. Pollut.* 9: 49-61.
- _____, and G.J. Dollard. 1974a. Studies on the lateral movement of ^{210}Pb in woody stems. Patterns observed in dormant and non-dormant stems. *Oecologia* 16: 179-184.
- _____. 1974b. Studies on the behaviour of lead in wood. Binding of free and complexed ^{210}Pb to xylem tissue. *Oecologia* 16: 369-373.
- Le Roy and M. Koksoy. 1962. The lichen - a possible plant medium for mineral exploration. *Econ. Geol.* 57: 107-113.
- Likens, G.E. 1976. Acid rain. *Chem. Eng. News* Nov.: 29-44.
- _____, and F.H. Bormann. 1974. Acid rain. A serious regional environmental problem. *Science* 184: 1176-1179.
- _____, and N.M. Johnson. 1972. Acid rain. *Environ.* 14: 33-40.
- Little, P., and M.H. Martin. 1972. A survey of Zn, Pb, and Cd in soil and natural vegetation around a smelting complex. *Environ. Pollut.* 3: 241-254.
- _____. 1974. Biological monitoring of heavy metal pollution.

- Environ. Pollut. 6: 1-19.
- Lounamaa, K.J. 1956. Trace elements in plants growing wild on different rocks in Finland. A semi-quantitative spectrographic survey. Ann. Bot. Soc. Zool. Fenn. 'Vanamo' 29: 1-196.
- _____. 1965. Studies on the content of iron, manganese and zinc in macrolichens. Ann. Bot. Fenn. 2: 127-137.
- Maquinay, A., I.M. Lamb, J. Lambinon, and J.L. Ramant. 1961. Dosage de zinc chez un lichen calaminaire belge: Stereocaulon nanodes Turk f. tyroliense (Nyl.) M. Lamb. Physiol. plant. 14: 284-289.
- Margot, J. 1973. Experimental study of the effects of sulphur dioxide on the soredia of Hypogymnia physodes. Pages 314-329 in B.W. Ferry, M.S. Baddeley and D.L. Hawksworth, eds. Air pollution and lichens. University of Toronto Press, Toronto.
- _____, and J. De Sloover. 1973. Les sorédies lichéniques et la détection des pollutions atmosphériques. Bioindicateurs Deteriorationis Regionis II, Most-Mezibori, CSSR. Skornik Conference, Proceedings, Cast 2: 83-92.
- _____. 1974. La culture des sorédies lichéniques: un test de la vitalité des thalles soumis à la pollution. Bull. Soc. Roy. Bot. Belg. 107: 33-40.
- Martinez, J.D., M. Nathany, and V. Dharmarajan. 1971. Spanish moss, a sensor for lead. Nature 233: 564-565.
- Mayer, A.M., and E. Gorham. 1951. The iron and manganese

- content of plants present in the natural vegetation of the English Lake District. *Ann. Bot.* 15: 247-263.
- McGerrigle, H.W. 1954. An outline of the geology of Gaspé Peninsula. *Can. Mining Journ.* August: 57-63.
- McGinnies, W.G. 1963. Dendrochronology. *J. For.* 61: 5-11.
- Mellor, D.P., and L. Maley. 1947. Stability constants of internal complexes. *Nature* 159: 370.
- _____. 1948. Order of stability of metal complexes. *Nature* 161: 436-437.
- Miller, R.J., J.E. Bittell, and G.E. Koeppe. 1973. The effects of cadmium on electron and energy transfer reactions in corn mitochondria. *Physiol. Plant.* 28: 166-171.
- Mondano, M., and W.H. Smith. 1974. Mercury content of soil, mosses and conifers, along an urban-suburban transect. *Environ. Conserv.* 1(3): 201-203.
- Mrose, H. 1966. Measurement of pH, and the chemical analyses of rain, snow and fog waters. *Tellus* 18: 266-270.
- Mudd, J.B., and T.T. Kolowski, ed. 1975. Responses of plants to air pollutants. Academic Press, N.Y.
- Nash III, T.H. 1972. Simplification of the Blue Mountain lichen communities near a zinc factory. *The Bryologist* 75: 315-324.
- _____. 1975. Influence of effluents from a zinc factory on lichens. *Ecol. Monog.* 45(2): 183-198.
- _____, and H.C. Fritts, and M.A. Stokes. 1975. A technique for examining non-climatic variation in widths of annual

- tree rings with special reference to air pollution.
Tree-Ring Bull. 35: 15-23.
- _____, and E.H. Nash. 1974. Sensitivity of mosses to sulphur dioxide. Oecologia 17: 257-263.
- Newberry, G. 1974. The influence of a sulphate process paper mill on corticolous lichens. The Bryologist 77: 561-576.
- Nieboer, E., H.M. Ahmed, K.J. Puckett, and D.H.S. Richardson. 1972. The heavy metal content of lichens in relation to distance from a nickel smelter in Sudbury, Ontario. Lichenol. 5: 292-304.
- _____, P. Lavoie, R.L.P. Sasseville, K.J. Puckett, and D.H.S. Richardson. 1976c. Cation-exchange equilibrium and mass balance in the lichen Umbilicaria muhlenbergii. Can. J. Bot. 54: 720-723.
- _____, K.J. Puckett, and B. Grace. 1976b. The uptake of nickel by Umbilicaria muhlenbergii: a physicochemical process. Can. J. Bot. 54: 724-733.
- _____, D.H.S. Richardson, K.J. Puckett, and F.D. Tomassini. 1976a. The phytotoxicity of sulphur dioxide in relation to measurable responses in lichens. Vol. 1, pages 61-85 in T.A. Mansfield, ed. Effects of air pollutants on plants. Soc. Experiment. Biol. Semin. Ser. Cambridge Univ. Press, U.K.
- Nilsson, I. 1972. Accumulation of metals in spruce needles and needle litter. Oikos 23: 132-136.
- Noguchi, A. 1956. On some mosses of Merceya, with special

- reference to the variation and ecology. Kumamoto J. Sci. 2: 239-257.
- Noeske, O., A. Lachli, O.L. Lange, G.H. Vieweg, and H. Ziegler. 1970. Konzentration und Localisierung von Schwermetallen in Flechten der Erzsclarken halden des Hartzes. Vort. Bot. Ges. (Dtsch. Bot. Ges.) N.F. 4: 67-69.
- Olkkonen, H., and K. Takala. 1976. Biological monitoring of air pollution in the urban area of Kuopio. Pages 215-217 in L. Kairento, E. Ruhimaki and P. Tarkka, eds. Proc. Sec. Nat. Mtng. Biophys. Biotechnol. Finland. Espvo, Finland.
- Pakarinen, P., and K. Tolonen. 1976. Regional survey of heavy metals in peat mosses (Sphagnum). Ambio 5(1): 38-40.
- Persson, B.R. 1970. The ^{210}Pb content of lichen carpets in northern Sweden during 1961-1969. Tellus 22: 564.
- Persson, H. 1956. Studies in 'copper mosses'. J. Hattori Bot. Lab. 17: 1-18.
- Peterson, J.T. 1969. The climate of cities, a survey of recent literature. U.S. Dept. Health, Education and Welfare, Public Health Service, National Air Pollution Control Admin. (NAPCA), Raleigh, N.C.
- Pišut, I., and E. Lisicka-Jelinkova. 1974. Epiphytische Flechten in der umgebung einer Aluminiumhütte in der Mittelslowakei. Biologia (Bratislava) 29: 29-38.
- Puckett, K.J. 1976. The effect of heavy metals on some aspects of lichen physiology. Can. J. Bot. 54: 2695-2703.
- _____, E. Nieboer, W.F. Flora, and D.H.S. Richardson. 1973a. Sulphur dioxide: its effects on photosynthetic ^{14}C

- fixation in lichens and suggested mechanisms of phytotoxicity. *New Phytol.* 72: 141.
- _____, E. Nieboer, M.J. Gorzynski, and D.H.S. Richardson. 1973b. The uptake of metal ions by lichens: a modified ion exchange process. *New Phytol.* 72: 327-342.
- Purves, D., and E.J. Mackenzie. 1969. Trace-element contamination of parklands in urban areas. *J. Soil Sci.* 20: 288-290.
- Pyatt, F.B. 1970. Lichens as indicators of air pollution in a steel producing town in South Wales. *Environ. Pollut.* 1: 45-56.
- _____. 1973. Plant sulphur content as an air pollution gauge in the vicinity of a steel works. *Environ. Pollut.* 5: 103-115.
- Rao, D.N., and F. LeBlanc. 1966. Effects of sulphur dioxide on the lichen algae with special reference to chlorophyll. *The Bryologist* 69: 69-75.
- _____. 1967. Influence of an iron-sintering plant on corticolous epiphytes in Wawa, Ontario. *The Bryologist* 70: 141-157.
- Roberts, T.M. 1972. Plants as monitors of airborne metal pollution. *J. Environ. Plann. and Pollut. Cont.* 1: 43-54.
- Rolfe, G.L. 1974. Lead distribution in tree rings. *Forest Sci.* 20(3): 283-286.
- Rose, A.H. 1970. Prevention and control of air pollution by process changes or equipment. U.S. Pub. Hlth. Ser. Report A58-11.

- Rose, F. 1973. Detailed mapping in south-east England. Pages 77-88 in B.W. Ferry, M.S. Baddeley and D.L. Hawksworth, eds. Air pollution and lichens. University Toronto Press, Toronto.
- Rowe, J.S. 1972. Les régions forestières du Canada. Ministère de l'Environnement Service canadien des forêts. No. 1300F. 172 pp.
- Rühling, A., and G. Tyler. 1968. An ecological approach to the lead problem. Bot. Notiser 121: 321-342.
- _____. 1969. Ecology of heavy metals - a regional and historical study. Bot. Notiser 122: 248-259.
- _____. 1970. Sorption and retention of heavy metals in the woodland moss Hylocomium splendens (Hedw.) Br. et Sch. Oikos 21: 92-97.
- _____. 1971. Regional differences in deposition of heavy metals over Scandinavia. J. Appl. Ecol. 8: 497-507.
- _____. 1973a. Heavy metal pollution and decomposition of spruce needle litter. Oikos 24: 402-416.
- _____. 1973b. Heavy metal deposition in Scandinavia. Water, Air and Soil Pollut. 2: 445-455.
- Sabnis, D.D., M. Gordon, and A.W. Galston. 1969. A site with an affinity for heavy metals on the thylakoid membranes of chloroplasts. Plan Physiol. 44: 1355-1363.
- Sanderson, M. 1948. The climates of Canada according to the new Thornthwaite classification. Sci. Agri. 28: 501-517.
- Saunders, P.J.W., and P.M. Wood. 1973. Sulphur dioxide in

- the environment: Its production, dispersal and fate.
Pages 6-37 in B.W. Ferry, M.S. Baddeley and D.L.
Hawksworth, eds. University Toronto Press, Toronto.
- Schönbeck, H. 1969. Eine Methode zur Erfassung der
biologischen Wirkung von Luftverunreinigungen durch
transplantierte Flechten. Staub-Reinhalt. Luft 29:
14-18.
- Scoggan, H.J. 1950. The flora of Bic and the Gaspé Peninsula,
Québec. Can. Dept. Res. Develp. Nat. Museum Can. Bull.
115 (Bio. Ser. No. 39) 399 pp.
- Seaward, M.R.D. 1973. Lichen ecology of the Scunthorpe
heathlands I. Mineral accumulation. Lichenol. 5: 423-433.
- _____. 1975. Lichen flora of the west Yorkshire conurbation.
Pages 141-208 in Proc. Leeds Philosoph. Lit. Soc. Sci. Sec.
Vol. X(9).
- Sernander, R. 1926. Stockholms Natur. Uppsala.
- Shacklette, H.T. 1961. Substrate relationships of some
bryophyte communities on Latouche Island, Alaska. The
Bryologist 64: 1-16.
- _____. 1965a. Element content of bryophytes. U.S. Geol.
Surv. Bull. 1198-D: 1-21.
- _____. 1965b. Bryophytes associated with mineral deposits
and solutions in Alaska. U.S. Geol. Surv. Bull. 1198-C:
1-18.
- _____. 1966. Copper mosses as indicators of metal
concentration. U.S. Geol. Surv. Bull. 1198-G: 1-18.
- _____. 1972. Cadmium in plants. U.S. Geol. Surv. Bull.

1314-G.

- _____, and J.J. Connors. 1973. Airborne chemical elements in Spanish moss. U.S. Geol. Surv. Bull. 574-E: 1-16.
- Sheridan, R.P., and R. Rosenstreter. 1973. The effect of hydrogen ion concentrations in simulated rain on the moss Tortula ruralis (Hedw.) Sm. The Bryologist 76: 168-173.
- Shimwell, D.W., and A.E. Laurie. 1972. Lead and zinc contamination of vegetation in the southern Pennines. Environ. Pollut. 3: 291-301.
- Showman, R.E. 1975. Lichens as indicators of air quality around a coal-fired power generating plant. The Bryologist 78: 1-6.
- Singer, M.V., and L. Hanson. 1969. Lead accumulation in soils near highways in the Twin City metropolitan area. Proc. Soil Sci. Soc. Am. 33: 152-153.
- Skaar, H., F. Ophus, and B.M. Gullvåg. 1973. Lead accumulation within nuclei of moss leaf cells. Nature 241: 215-216.
- Skopera, A.C., and D.H. Vitt. 1976. A quantitative study of epiphytic lichen vegetation in relation to SO₂ pollution in western Alberta. Environment Canada, Forestry Service, Northern Forest Research Center. Info. Rep. NOR-X-161: 26 pp.
- Skye, E. 1957. Luftföroreningars inverkan på bush-och bladlavfloran kring skifferoljeverket i Närkes Kvarntorp. Svensk Bot. Tidskr. 52: 133-190.

- _____. 1968. Lichens and air pollution. Acta Phytogeogr. Suec. 52: 1-123.
- Smith, W.H. 1972. Air pollution - effects on the quality and resilience of the forest ecosystem. Paper presented at the 1972 Annual Meeting AAAS, Committee on Environ. Alterations Symp. 'Temperature, Climate, Forestry, and the Forest Ecosystem, an Environmental Issue'. Wash. D.C.
- _____. 1976. Lead contamination of the roadside ecosystem. J. Air Pollut. Cont. Assoc. 26(8): 753-766.
- Sommer, A.L. 1930. Copper as an essential for plant growth. Plant Physiol. 6: 339-345.
- Staxang, B. 1969. Acidification of bark of some deciduous trees. Oikos 20: 224-230.
- Steeman-Nielsen, E., L. Kamp-Nielsen, and S. Wium-Anderson. 1969. The effect of deleterious concentration of copper on the photosynthesis of Chlorella pyrenoidosa. Physiol. Plant. 22: 1121-1133.
- Stephenson, W.R., and H.G. Merriam. 1975. Some effects of urban impact on the structure of lichen communities on trees in three deciduous woodlot types. Urban Ecology 1: 311-323.
- Stewart, C.M. 1966. Excretion and heartwood formation in living trees. Science 153: 1068-1074.
- Stokes, M.A., and T.L. Smiley. 1968. An introduction to tree-ring dating. University of Chicago Press. 73 pp.
- Strell, M., and F. Zuther. 1958. Reaktionen in der Chlorophyllreihe. Veränderungen von Phobiden und

- Chlrinen durch komplexbildende Metalle. Justus Liebigs. Annen. Chem. 612: 264-271.
- Stringer, P.W., and M.H. Stringer. 1974. Air pollution and the distribution of epiphytic lichens and bryophytes in Winnipeg, Manitoba. The Bryologist 77: 405-426.
- Syratt, W.J., and P.J. Wanstall. 1969. The effect of sulphur dioxide on epiphytic bryophytes. Air Pollut. Proc., Eur. Congr. Influence Air Pollut. Plants and Anim., 1st.,: 79-85.
- Szopa, P.S., E.A. McGinnes Jr, and J.O. Pierce. 1973. Distribution of lead within the xylem of trees exposed to air-borne lead compounds. Wood Sci. 6: 72-77.
- Takeo, O. 1959. Inorganic constituents in plants. Gifu Yakka Daigaku Kiyo 9: 41-54.
- Tamm, C.O. 1953. Growth, yield and nutrition in carpets of forest moss (Hylocomium splendens). Medd. fran Statens Skogforskning intitit 43: 140 pp.
- Terraglio, F.P., and R.M. Manganelli. 1967. The influence on the absorption of atmospheric SO₂ by soil. Int. J. Air and Water Pollut. 10: 783-806.
- Thorntwaite, C.W. 1931. The climate of North America according to a new classification. Geogr. Rev. 21: 633-655.
- Trass, H. 1968. Indeks samblikurühmituste kasulamiseks õhu saastatuse määramisel. Eesti Loodus (Estonian Nature) 11: 628.
- Tukey, H.B. 1971. Leaking substances from plants. Pages 67-80 in Preece and Dickinson, eds. Ecology of leaf

- surface micro-organism. Academic Press, N.Y.
- Tuominen, Y. 1967. Studies on the strontium uptake of the Cladonia alpestris thallus. Ann. Bot. Fenn. 4: 1-128.
- _____, and T. Jaakkola. 1973. Absorption and accumulation of mineral elements and radioactive nuclides. Pages 185-223 in V. Ahmadjian and M.E. Hale, eds. The Lichens. Academic Press, N.Y.
- Türk, R., and V. Wirth. 1975a. The pH dependence of SO₂ damage to lichens. Oecologia 19: 285-291.
- _____. 1975b. Über die SO₂ - empfindlichkeit einiger Moose. The Bryologist 72: 187-193.
- _____, and O.L. Lange. 1974. CO₂ exchange measurements for determination of SO₂ resistance of lichens. Oecologia 15: 33-64.
- Tyler, G. 1971. Moss analysis - a method of surveying heavy metal deposition. Pages 129-132 in H.M. Englund and W. Berry, eds. Proc. Soc. Inter. Clean Air Congr. Academic Press, N.Y.
- Vallee, B.L., and D.D. Ulmer. 1972. Biochemical effects of mercury, cadmium and lead. Ann. Rev. Biochem 41: 91-128.
- Vas, K., and M. Ingram. 1949. Preservation of fruit juices with less SO₂. Fd. Mf. 24: 414-416.
- Vernon, L.P. 1960. Spectrophotometric determination of chlorophylls and pheophytins in plant extracts. Analyt. Chem. 32: 1144-1150.
- Villeneuve, G.O. 1948. Aperçu climatique du Québec. Ministère des terres et forêts, Bureau de Météorologie Québec, Bull. 10: 1-25.

- Vins, B., and R. Mrkva. 1973. The diameter increment losses of pine stands as a result of injurious emissions. Acta Univer. Agricul. (Brno), Series C (Facultas silvicul.) 42: 25-46.
- Ward, N.I., R.R. Brooks, and R.D. Reeves. 1974. Effect of lead from motor-vehicle exhausts on trees along a major thoroughfare in Palmerston North, New Zealand. Environ. Pollut. 6: 149-158.
- Weiss, H.V., M. Koide, and E.D. Goldberg. 1971. Mercury in a Greenland ice sheet: Evidence of recent input by man. Science 174: 692-694.
- Westman, L. 1974. Air pollution indications and growth of spruce and pine near a sulphite plant. Ambio 3: 189-193.
- Whittaker, R.H., F.H. Bormann, G.E. Likens, and T.G. Siccama. 1974. The Hubbard Brook ecosystem study: Forest biomass and production. Ecol. Monogr. 44: 233-252.
- Wirth, V., and R. Türk. 1975. SO₂ resistance of lichens with different growth forms. Flora 164: 133-143.
- Wood, T., and F.H. Bormann. 1975. Increases in foliar leaching caused by acidification of an artificial mist. Ambio 4: 169-171.
- Yeaple, D.S. 1972. Mercury in bryophytes (moss). Nature 235: 229-230.

B. Addendum

Sections of this dissertation have been published in whole or in part as follows:

1. Literature review on heavy metals and lichens and bryophytes.

Rao, D.N., G. Robitaille, and F. LeBlanc. 1977. Heavy metal pollution and lichens and bryophytes. Journ. Hattori Bot. Lab. Vol. 42.

2. Cartography of epiphytic lichens and mosses and biological response of lichens and bryophytes.

LeBlanc, F., G. Robitaille, and D.N. Rao. 1974. Biological response of lichens and bryophytes to environmental pollution in the Murdochville copper mine area, Québec. Journ. Hattori Bot. Lab. 38.

3. Transplant experiments.

LeBlanc, F., G. Robitaille, and D.N. Rao. 1976. Ecophysiological response of lichens transplants to air pollution in the Murdochville Gaspé Copper Mine area, Québec. Journ. Hattori Bot. Lab. Vol. 40.

4. Acid rain and the paucity of epiphytic lichens.

Robitaille, G., F. LeBlanc, and D.N. Rao. 1977. Acid rain: A factor contributing to the paucity of epiphytic lichens. Rev. Bryol. Lichénol., Vol. 43.