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TRACE METAL CONTAMINATION IN FORESTS OF SOUTHERN QUEBEC AND PATHWAY STUDIES OF AIRBORNE METAL DEPOSITS

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Montreal, Canada, January 1996

A Thesis Submitted to
the Faculty of Graduate Studies and Research
in Partial Fulfilment of the Requirements for
the Degree of Doctor of Philosophy

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ABSTRACT

Trace Metal Contamination in Forests of Southern Quebec and Pathway Studies of Airborne Metal Deposits

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Ph.D. in Environmental Studies. January 1996

Trace metal contamination of the air-soil-tree system was examined in southern Quebec, where acid deposition and tree dieback have been recorded in high elevation forests. Mn pollution was emphasized due to its large emission from gasoline combustion in Canada. Airborne Cu, Mn, V, and Zn showed higher concentrations than those reported for other remote locations. Significant fluctuation in Mn concentrations during the winter-spring season was explored by air mass back trajectory analysis. The study suggested that high Mn concentrations resulted from the atmospheric long-range transport from Canadian industrialized and metropolitan regions. Metal concentrations in podzolic topsoils were generally higher than their world-wide average values. Concentrations of trace metals in balsam fir [*Abies balsamea* (L.) Mill.] needles were below their suggested potential phytotoxic levels, except for Mn, which also increased with elevation. The scanning of needles with micro-PIXE showed no significant correlation between metal accumulation and epistomatal distribution on foliar surfaces.

Pathways of trace metals deposited in the soil-tree system were elucidated through application of ^{54}Mn and ^{65}Zn on shoot, bark, and soil surfaces in growth-chamber experiments with balsam fir seedlings. Uptake and accumulation by seedlings 70 days after application on the shoot surface was about 25-30% of the remaining activities for ^{54}Mn and ^{65}Zn. Less than 1% of absorbed isotopes was translocated from the bark surface to other plant organs, whereas more than 50% of the radioisotopes absorbed at the shoot moved to the rest of the seedling. Acidic wetness facilitated the metal absorption through tree surfaces. Downward movement of the radioisotopes in podzolic soils was documented, and accumulation in seedlings by root uptake was 5% of the remaining activity for ^{54}Mn and 3% for ^{65}Zn 70 days after application. No appreciable elemental migration from internal tissues to epicuticular wax layers was found, and the leaching ratio was below 0.5 and 1.0 % for ^{54}Mn and ^{65}Zn, respectively. This study helps to understand the links between atmospheric deposition and the elevated levels of Mn in trees, and potential effects of acid deposition on the bioaccumulation of toxic metal pollutants in high elevation forests in southern Quebec.

RÉSUMÉ

Contamination en métaux lourds en milieu forestier dans le Sud du Québec, et études du cheminement des dépôts atmosphériques métalliques

Zhiqing Lin, Département des sciences des ressources naturelles, Université McGill
Ph.D., Sciences de l'environnement, Janvier 1996

La contamination du système air-sol-arbre par les métaux lourds a été examinée dans le Sud du Québec où le dépérissement des arbres ainsi que les dépôts acides ont été observés dans les forêts en altitude. Cette étude a été concentrée sur le Mn en raison de sa forte émission par combustion véhiculaire au Canada. Les concentrations aéroportées du Cu, Mn, V et du Zn ont été observées comme étant plus élevées que celles rapportées pour d'autres points éloignés. Les fluctuations prononcées en Mn durant la saison hiver-printemps ont été examinées par l'analyse des trajectoires des masses d'air, qui indique que les évènements de concentration élevée sont associés avec le transport atmosphérique à grandes distances à travers les régions métropolitaines et industrielles du Canada. Le concentrations des métaux dans les horizons de surface des sols podzoliques étaient généralement plus élevées que leurs valeurs moyennes mondiales. Les concentrations dans les aiguilles du sapin baumier [*Abies balsamea* (L.) Mill.] étaient bien au dessous du niveau phytotoxique, avec l'exception du Mn, dont la concentration augmentait avec l'altitude. Le sondage des aiguilles par micro-PIXE (émission des rayon-X par protons) ne révélait aucune association spatiale entre l'accumulation des métaux et la distribution des stomates à la surface des aiguilles.

Le cheminement des métaux déposés sur les arbres a été examiné par application

de ^{54}Mn et de ^{65}Zn à la surface du feuillage et de l'écorce de semis de sapin et du sol autour d'eux, dans des expériences contrôlées au laboratoire. Les processus d'absorption à la surface du feuillage résultaient en l'accumulation de 25-30% de l'activité radioactive résiduelle du ^{54}Mn et du ^{65}Zn, 70 jours après application sur le feuillage. Moins d'un pourcent des isotopes absorbés par l'écorce ont été transportés vers les autres organes de la plante, tandis que > 50% des isotopes absorbés par le feuillage se trouvaient transportés ailleurs durant les 70 jours d'observation. L'humidité acide facilitait l'absorption par la surface des sapins. Le mouvement descendant des radioisotopes dans le sol a été documenté, et l'accumulation dans les sapins par absorption racinaire représentait 5% de l'activité résiduelle après 70 jours pour le ^{54}Mn et 3% pour le ^{65}Zn. Le mouvement des éléments du tissu interne vers la couche de cire épicuticulaire paraissait négligeable, et le lessivage < 0.5% pour le ^{54}Mn et < 1% pour le ^{65}Zn. Cette étude améliore notre interprétation des liens entre la déposition atmosphérique et les concentrations élevées du Mn dans les arbres; elle augmente également nos connaissances des effets potentiels des dépôts acides sur la bioaccumulation des métaux toxiques dans le milieu forestier en altitude dans le Sud du Québec.

Dedicated To Juan And Andrew

For Their Love And Encouragement

PREFACE

Trace metal contamination in the air-soil-tree system in southern Quebec, likely pollution source regions, and pathways of metal elements deposited in the soil-tree system are documented in this thesis, with special consideration given to the potential effects of significant acidic fog deposition on metal contamination and pathways in high elevation forests.

The interaction between forests and atmospheric trace metal deposition is complex. Therefore, only a limited number of related questions has been addressed in this thesis. Results are presented in the manuscript format with the relevant literature review contained in each section. Each manuscript is relatively independent, but serves as an integral part of the thesis, and a link to the subsequent chapter is provided at the end of each chapter. A general introduction and literature review are given in Chapters 1 and 2, respectively. The literature review summarizes the current state of knowledge of atmospheric metal contamination, dry and wet deposition of metal pollutants to forests, characteristics of metal deposits on forest surfaces, pathways of metals deposited in forests, and forms the basis for the statement of research needs. The metal contamination and the likely origins of metal elements in the air, soil, and forest compartments of high elevation forest ecosystems in southern Quebec are presented in Chapters 3, 4, and 5. In Chapter 6 deposited substances on foliar surfaces are examined, and the spatial distribution of metal deposits shown. Metal deposits on foliar surfaces have been directly determined by micro-PIXE scanning (Chapter 6), and indirectly inferred from the statistically significant differences in metal concentrations between washed and unwashed needles (Chapter 5).

Pathways of metal pollutants, in terms of surface uptake, translocation of metals in the soil-plant system, and trace metal leaching from above-ground parts of trees have been demonstrated with application of Mn and Zn radioisotopes on shoot and bark surfaces (Chapter 7) and on surfaces of podzolic soils (Chapter 8). In Chapter 9, a general summary provides an overview of this thesis, particularly in terms of biogeochemical cycling of trace metal pollutants under the effects of acid deposition.

This thesis is based on six published/accepted and one submitted refereed research papers. However, significant editorial modifications have been made to reduce repetitions and redundancies. The thesis conforms to the conditions concerning authorship, as outlined in the Guidelines for Thesis Preparation which are concerted in the Statement from the Thesis Office.

STATEMENT FROM THESIS OFFICE

In accordance with the regulation of the Faculty of Graduate Studies and Research of McGill University, the following statement excerpted from the Guidelines for Thesis Preparation (McGill University 1995) is included:

Candidates have the option of including, as part of the thesis, the text of one or more papers submitted or to be submitted for publication, or the clearly-duplicated text of one or more published papers. These texts must be bound as an integral part of the thesis.

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Additional material must be provided where appropriate (e.g. in appendices) and in sufficient detail to allow a clear and precise judgement to be made of the importance and originality of the research reported in the thesis.

*In the case of manuscripts co-authored by the candidate and others, **the candidate is required to make an explicit statement in the thesis as to who contributed to such work and to what extend.** Supervisors must attest to the accuracy of such statements at the doctoral oral defense. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to make perfectly clear the responsibilities of all the authors of the co-authored papers.*

ADVANCEMENT OF SCHOLARLY KNOWLEDGE

1. Contribution to Knowledge

To the author's knowledge, the following aspects of the thesis constitute original contributions to knowledge.

(1). Significant bioaccumulation of Mn in balsam fir needles (up to 877 mg kg^{-1}) has been demonstrated at elevated sites in southern Quebec. This has been tentatively linked to high atmospheric deposition of Mn at the site, to foliar uptake of Mn as demonstrated by radiotracer experiments, and to long-range transport of Mn contaminants from Canadian urban-industrial regions through back-trajectory analysis.

(2). Based on observations by micro-PIXE scanning, epistomatal distribution does not appear to be systematically related to the accumulation of metals on foliar surfaces of balsam fir, but spatial accumulation of Ni near the vascular endodermis or the nearby spongy parenchyma in balsam fir needles has been found by scanning to the depth 45-50 μm from the surface.

(3). Uptake of Mn and Zn through foliar and bark surfaces has been shown to be significantly affected by acidic surface wetness. Pathways of metal deposits, in terms of absorption from foliar and bark surfaces, have been quantitatively described by radioisotope studies.

(4). Translocation of Mn and Zn in the soil-tree system has been quantitatively documented. Internal cycling of Mn and Zn, such as migration of metals accumulated in shoots by root uptake from internal tissue to epicuticular wax layers and leaching of accumulated Mn and Zn from shoots in simulated acid rain of short-duration, has been found to be small.

2. Research Publications in Refereed Scientific Journals and Proceedings

(1). Lin, Z.-Q., Schuepp, P.H., Barthakur, N.N., Kennedy, G.G., and Schemenauer, R.R. 1996. On pathways of heavy metals deposited in subalpine forests in southern Quebec, Canada. *Proceedings of Third International Conference on the Biogeochemistry of Trace Elements,* 15-19 May 1995, Paris, France. INRA, Versailles. Accepted.

(2). Lin, Z.-Q., Hendershot, W.H., Kennedy, G.G., Dutilleul, P., and Schuepp, P.H. 1996. Major and trace elements in forest soils affected by acid deposition in southern Quebec. *Canadian Journal of Soil Science.* In press.

(3). Lin, Z.-Q. and Schuepp, P.H. 1996. Contamination and distribution of metal deposits on the surface of balsam fir [*Abies balsamea* (L.) Mill.] foliage by micro proton-induced X-ray emission. *Environmental Science and Technology.* 30 (1): 246-251.

(4). Lin, Z.-Q., Barthakur, N.N., Schuepp, P.H., and Kennedy, G.G. 1996. Uptake and translocation studies in balsam fir [*Abies balsamea* (L.) Mill.] with ^{54}Mn and ^{65}Zn radioisotopes applied to soil surfaces. *Journal of Environmental Quality.* 25(1): 92-96.

(5). Lin, Z.-Q., Barthakur, N.N., Schuepp, P.H., and Kennedy, G.G. 1995. Uptake and translocation of ^{54}Mn and ^{65}Zn in balsam fir seedlings [*Abies balsamea* (L.) Mill.] with radioisotope application on foliage and bark. *Environmental and Experimental Botany.* 35(4): 475-483.

(6). Lin, Z.-Q., Schuepp, P.H., Schemenauer, R.R., and Kennedy, G.G. 1995. Trace metal contamination in and on balsam fir [*Abies balsamea* (L.) Mill.] foliage in southern

Quebec, Canada. *Water, Air, and Soil Pollution*. 81: 175-191.

3. Manuscripts Submitted to Refereed Scientific Journals

(7). Lin, Z.-Q., Schemenauer, R.S., Schuepp, P.H., Barthakur, N.N., and Kennedy, G.G. 1996. Airborne metal pollutants in southern Quebec, Canada and their likely source regions. *Agriculture and Forest Meteorology*.

CONTRIBUTION OF CO-AUTHORS TO MANUSCRIPTS

The first author was in charge of experimental design, laboratory setup, experimental execution and management, data collection and analysis, preparation of manuscripts for publication, and response to the reviewers' comments.

Dr. P.H. Schuepp, the supervisor of the thesis-author's graduate study, undertook the administrative operation of all research projects, contributed through research supervision, technical assistance, editorial work, and provided extensive comments on all manuscripts.

Dr. N.N. Barthakur provided supervision in application of the radiotracer technique, editorial help on manuscripts (4), (5), (7), and comments on manuscript (1).

Dr. W.H. Hendershot contributed in general guidance on the selection of research sites, on soil sampling, provided funding for determination of four element concentrations in soils by ICP and GF-AAS, and comments on manuscript (2).

Dr. R.S. Schemenauer contributed air filter samples, data of wet and dry deposition of metal elements, and meteorological observation (raw data) at the CHEF sites, arranged for air mass back trajectories and synoptic maps, and provided comments on manuscripts (1), (6), and (7).

Dr. G.G. Kennedy provided supervision in INAA and facilities for γ-ray counting in radiotracer studies, and comments on manuscripts 1, 2, 5, and 6.

Dr. P. Dutilleul contributed through supervision on the partitioning of variation in manuscript (2).

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LIST OF TREE-SPECIES

Common Name	**Scientific Name**
Balsam fir	*Abies balsamea* (L.) Mill.
Beech	*Fagus grandifolia* Ehrh.
Eastern hemlock	*Tsuga canadensis* Carr.
Norway spruce	*Picea abies* L.
Paper birch	*Betula papyrifera* Marsh.
Quaking aspen	*Populus tremuloides* Michx
Red maple	*Acer rubrum* L.
Red spruce	*Picea rubens* Sarg.
Scotch pine	*Pinus sylvestris* L.
Silver maple	*Acer saccharinum* L.
Sugar maple	*Acer saccharum* Marsh.
Yellow birch	*Betula alleghaniensis* Britt.

LIST OF ABBREVIATIONS

Ab	Abaxial Surface
Ad	Adaxial Surface
C	Degraded Epicuticular Layer
CEC	Cation Exchange Capacity
CHEF	Chemistry of High Elevation Fog
DDW	Distilled Deionized Water
EDX	Energy Dispersive X-ray
EF(s)	Enrichment Factor(s)
F	Fungi
G	Guard Cells
GF-AAS	Graphite Furnace-Atomic Absorption Spectrometer
GMT	Greenwich Meridian Time
HDPE	High Density Polyethylene
ICP-MS	Inductively Coupled Plasma Mass Spectrophotometer
INAA	Instrumental Neutron Activation Analysis
LOD	Limit of Detection
M	Mineral Dust
MA	Morgan Arboretum of McGill University, Montreal, Canada
MMT	Methylcyclopentodienyl Manganese Tricarbonyl
NBS-SRM	National Bureau of Standard-Standard Reference Materials.
OM	Organic Matter

PAR	Photosynthetically Active Radiation
PCA	Principle Component Analysis
PIXE	Proton-induced X-ray Emission
RT	Roundtop Mountain, Sutton, Quebec
S	Stomata
SAS	Statistical Analysis System
Sb	Subsidiary Cells
SEM	Scanning Electron Microscopy
SH	Ste. Hippolyte, Quebec
Sp	Spore
W	Wax Deposits
WP	White Peak, Mont Tremblant, Quebec
XPS	X-ray Photoelectron Spectroscopy

CHAPTER 1. GENERAL INTRODUCTION

1.1. Air Pollution and Forest Decline

Trace metals originating from anthropogenic sources have greatly contributed to atmospheric contamination (Nriagu 1990; Pacyna *et al.* 1995). A buildup of toxic metals in forests has been linked to atmospheric long-range transport and deposition (Johnson *et al.* 1982; Barrie and Schemenauer 1986). The amount of airborne metal pollutants deposited from the atmosphere to forests is generally affected by characteristics and interaction of forest surfaces and trapped airborne particles, micrometeorological conditions, and local topography. Increased trace metal concentrations in forests may cause direct effects on eco-physiological functions of trees, and also may alternate biological processes in soils, such as decreasing rates of litter decomposition and soil respiration. It is a well established fact that air pollutants affect vegetation in many different ways (Bennett and Büchen 1995), including predisposing plants to abiotic and biotic stresses (Hendershot and Jones 1989).

Acid deposition may strongly affect the phytotoxicity of trace metals deposited in forest ecosystems, and also possibly affect the trees through acidification of the soil and the resulting availability of toxic metal elements. Although acid deposition was reported by Wesselink *et al.* (1995) with a decreasing trend in the 1980s in Central Europe, there was no significant change in acid deposition during 1986-1991 in southern Quebec (Schemenauer *et al.* 1995). Barrie and Schemenauer (1986) and Hendershot *et al.* (1992) demonstrated that the metal element input was particularly enhanced to the high elevation forests in southern Quebec, due to significant acid fog deposition at the high altitude sites (Schemenauer 1986). Nriagu (1990) speculated that metal pollutants affect the health of forests or mediate forest decline in some acid-sensitive areas, as may have been the case in some parts of eastern Europe.

Forest decline in North America has received considerable attention during the past two decades in the debate on ecological effects of acidic deposition and associated air pollution. Although air pollutants have been hypothesized as the causal agent for decline of red spruce populations in the high elevation forests of the northern United States (Johnson and Siccama 1983; McLaughlin *et al.* 1990), the links between air pollution and forest health in Central Europe still remain largely speculative (Kandler and Innes 1995). It is not possible to construct a theory which applies equally to different air pollutants in various ecological situations, such as studies on forest decline around the world. To what extent the occurrence of the forest damage is well correlated with the deposition of multi-metal pollutants has not yet clearly defined (Foster 1989; Edwards *et al.* 1995).

Pathways of metal pollutants on canopy surfaces and biogeochemical cycling of metals deposited in high elevation forests are important to our understanding of hypothesized contributing factors to forest health. Research on the long-term responses of forests to multi-environmental pollutants can reveal the dynamics of adaptation of the ecosystem or its components, and lead to more realistic conclusions. In particular, under the effects of acid deposition, the relative importance of metal deposition to the potentially toxic accumulation of multi-metal elements, and the pathways of metal deposits in forests, have to be considered and further explored.

1.2. Mn Contamination: A Specific Aspect of the Thesis

A specific aspect of this thesis has to some degree been stimulated by the question of Mn contamination and toxicity, that has recently been raised as a potential problem of broad concern in Canada. Since 1976, methylcyclopentodienyl manganese tricarbonyl (MMT) has become an octane-boosting additive in 'non-leaded' gasoline, and completely replaced Pb from 1990. Mn emission from Canadian MMT-related sources was about 211 tonnes, accounting for about 17% of the total anthropogenic emission into atmospheric environment in 1984 (Jaques 1987). In 1995, the total Mn emission from MMT sources may have reached about 340 tonnes, approximately 25% of the total emission in Canada. Although the Canadian government intends to ban the import and interprovincial trade of MMT, many provinces have objected to the plan mainly due to economic reasons, which will seriously hamper any effort to remove MMT from gasoline (Canadian Press 1995).

Mn pollutants from car exhausts are associated with submicron-sized particles and in the toxic form (Mn_3O_4). Therefore, the long-range transport of Mn pollutants through the atmosphere and the phytotoxicity of Mn deposits in high elevation forests must be a matter of concern (Smith 1990).

1.3. Objectives

The objectives of this thesis may be formulated as follows: (1) to investigate metal contamination in the air-soil-tree system in high elevation forests and to link it to atmospheric long-range transport of multi-metal pollutants; (2) to elucidate the most likely pathways of trace metals deposited in high elevation forests. In both these objectives, particular attention will be paid to potential effects of acid deposition on the processes involved.

CHAPTER 2. GENERAL LITERATURE REVIEW ON ATMOSPHERIC METAL DEPOSITION TO FORESTS

2.1. Metal Contamination and Transport in the Atmosphere

Anthropogenic emissions of metal pollutants to the air result in atmospheric metal contamination (Pacyna *et al.* 1995). Between 1900 and 1980, worldwide emissions of Cd, Cu, Pb, Ni, and Zn from industrial sources to the atmosphere averaged about 3,040, 10,800, 198,000, 12,240, and 136,000 tonnes per year, respectively (Nriagu 1990). Quantitative assessments of emissions of trace metals from worldwide (Nriagu and Pacyna 1988) and Canadian (Jaques 1987) anthropogenic sources to the air at the beginning of the 1980s are presented in Table 2.1, with comparison to the worldwide emissions from natural sources (Nriagu 1989). The emissions of As, Cd, Hg, Ni, Pb, V, and Zn from anthropogenic sources are generally higher than their emissions from natural sources. For Cr, Cu, and Mn, where natural sources tend to dominate over anthropogenic ones, the latter may nevertheless exceed natural emissions in or near industrialized regions. The emission figures certainly indicate that the quantity of toxic metals being discharged into the atmospheric environment is considerable.

Long-range transport of metal pollutants through the atmosphere is generally in particulate phase, but for the metalloids of As, Hg, and Se, the transport in the gaseous phase may be dominant. There has been much speculation that gases are readily oxidized onto fine particles and transported in the aerosol phase (Haygarth and Jones 1992). Nriagu (1986) reported that well over 50 % of all the trace metals getting into the Great Lakes is transported via the atmosphere. Atmospheric transport is generally affected by particle size,

Table 2.1. Annual emissions of trace metals from anthropogenic sources to the atmosphere (data from Nriagu 1989, Nriagu and Pacyna 1988, and Jaques 1987).

Elements	Worldwide Emissions [a] (10^3 t yr^{-1})		Canadian Anthropogenic Emissions [b] (t yr^{-1})
	Natural Sources	Anthropogenic Sources	
As	1.1 - 23.5	12.0 - 25.6	471
Cd	0.1 - 3.9	3.2 - 12.0	322
Cr	4.5 - 82.8	7.2 - 53.7	69
Cu	2.2 - 53.8	19.7 - 50.8	1689
Hg	0 - 4.9	0.9 - 6.2	31
Mn	51.5 - 582.2	10.6 - 66.1	1225
Ni	2.9 - 56.8	24.2 - 87.2	846
Pb	0.9 - 23.5	287.5 - 376.0	11466
Sb	0.1 - 5.8	1.5 - 5.6	75
V	1.6 - 54.2	30.0 - 141.8	- [c]
Zn	4.0 - 85.9	70.4 - 193.5	-

a: annual emission at the beginning of the 1980s
b: annual emission in 1982, except Mn in 1984
c: not available

metal chemistry, synoptic conditions, ground surface and topography.

The typical ranges of the values reported for atmospheric fallout of trace metals in Canadian urban areas were 20-980 g ha^{-1} yr^{-1} for Cu; 140-3,500 for Pb; 7-36 for Cd; and 80-4,800 for Zn (Jeffries and Snyder 1981). Average total fluxes of 12, 1, 53 and 40 μg m^{-2} d^{-1} for Pb, Cd, Zn, and Mn, respectively, were reported during July of 1986 in the Great Smoky Mountains National Park (Petty and Lindberg 1990). These studies show that atmospheric contamination, transport, and fallout of some trace metals could easily result in significant alternations of their natural biogeochemical cycling in regional environments (Pacyna *et al.* 1995).

2.2. Atmospheric Deposition of Trace Metals to Forests

Forests are an important sink for airborne metal elements originating from natural and man-made pollution sources through atmospheric wet and dry deposition. A complex variety of physical processes are involved in the transfer of metal pollutants to the surfaces of forests (Hosker and Lindberg 1982), and fog/cloud is of great interest due to its elevated concentration of pollutants (Barrie and Schemenauer 1986). Highest concentrations of trace elements are found mostly at the beginning and the end of fog episodes, when liquid water content is reduced (Schmitt 1986), or at the beginning of a rainfall (Nürnberg *et al.* 1982). Dry deposition comprises particle deposition and aerosol filtering through diffusion, sedimentation and impaction. Dry deposition is an important mechanism for the removal of particles from the atmosphere and may be a major source of trace metal input to forest ecosystems (Hicks and Johnson 1986). Petty and Lindberg (1990) reported that the monthly flux of Mn and Zn input from dry deposition to canopies in high elevation red spruce forests accounted for 65% and 62% of the total metal deposition, respectively. The study of Mayer (1983), for annual averages in Central Europe, indicated that wet deposition is the prevailing process in the case of Co, Zn, and Cd, while dry deposition is dominating for Cr, Mn and Ni.

Metal fluxes in wet deposition can be generally calculated from hydrologic flux and the metal concentrations. However, the direct measurement of dry deposition can be extremely difficult. Several indirect estimates of dry deposition have been used such as washing of deposits from tree surfaces, throughfall measurements, and modelling with deposition velocities (Dasch 1987; Lindberg and Lovett 1985; Sickles *et al.* 1983, Petty and Lindberg 1990). The deposition fluxes for Pb, Cd, Cu, Zn, Mn, Co, and Ni, reported in the literature from forests worldwide, have been summarized by Smith (1990), and the literature data on the deposition fluxes of Cu, Zn, Pb, Cd, Cr, and Ni to temperate forest ecosystems also have been extensively reviewed by Bergkvist *et al.* (1989).

2.3. Factors Affecting Deposition Fluxes of Trace Metals to Forest Canopies

2.3.1 Elevation and topography

Wet deposition tends to be evenly distributed over large areas, but in upland areas there may also be large spatial variations in wet deposition of pollutants. High pollutant deposition over elevated regions may be linked to cap clouds which often contain high concentrations of pollutants dissolved in cloud droplets (Dore *et al.* 1990). It has been shown that cloud and fog droplet deposition of certain elements to forest ecosystems at high altitude could be more important than deposition by other mechanisms (Lovett *et al.* 1982). Johnson *et al.* (1982) indicated that the measured increases in Pb levels with elevation in Green Mountain forest soil are consistent with the amount deposited from the atmosphere.

The local topography is important for the amount of metal pollutants delivered to forests as particles or aerosols by dry deposition. Hill-top and forest edges may receive a larger deposition load than low elevation stands or the interior of a forest (Hasselrot and Grennfelt 1987).

2.3.2. Micrometeorological conditions

The efficiency of washout of particles by rainfall is high for particles approximately 20-30 µm in diameter, but the efficiency of capture by raindrops falls off very sharply for particles of 5 µm or less. Apart from pollutant load and surface structures, important factors controlling the amount of dry deposition to a specific forest seem to be the aerodynamic resistance, collection efficiency and the surface area of the forest stand (Lovett and Reiners 1986; Wiman *et al.* 1990). Turbulence will be enhanced at hill sides, forest edges and transition zones between forest stands of different height (Bridgman *et al.* 1994). Interaction between tree shape, surface structures and atmospheric boundary-layer conditions, and air pollutant deposition processes have been explored in wind tunnel studies with conifer seedlings and artificial tree models (Ruck and Adams 1991; Little and Wiffen 1977). Little and Martin (1972) reported that concentrations of trace elements are usually higher on the sheltered than on the exposed sides of trees, owing to greater deposition of aerosols from slower-moving air.

2.3.3. Properties of particles and foliar surfaces

The properties of particles that are known or postulated to affect their interaction with leaf surface are size, density, and shape, chemical composition, solubility in water, and electric charge (Hosker and Lindberg 1982). Small aerosols are usually electrically charged and frequently attach themselves to other aerosols. Dochinger (1980) pointed out that forest trees are effective in intercepting suspended particles, at least in a size range where inertial impaction is significant. The micro-topography of the leaf surface and its characteristics with respects to wetness, stickiness, hairiness (pubescence), electric charge, and the position of the leaf on the tree canopy have a profound effect on deposit retention (Adams and Hutchinson 1987; Smith 1990).

The impact of acids and oxidizing agents on the structure of the coniferous wax layers might be enhanced by the highly catalytic metal oxides found on or in the epicuticular wax layer (Bermadinger *et al.* 1988). The amorphous type of epicuticular wax structures may increase the trapping efficiency of the needles to aerosols or small particles. Wedding *et al.* (1977) indicated that aerosol retention on rough pubescent leaf surfaces is a factor of 10 greater than on smooth leaf surfaces. Due to aerodynamic properties, to the greater total leaf area, and to the surface properties of the needles, conifers are much more efficient in trapping aerosols than are deciduous trees (Höfken and Gravenhorst 1982; Mayer and Ulrich 1982).

2.4. Determination of Metal Deposits on Foliar Surfaces

Simmleit *et al.* (1986) concluded that the quantity of elements occurring on needle surfaces was directly related to their atmospheric concentrations. Foliage analysis has been used as a valid indicator of air pollution (Landolt *et al.* 1989). By using effective foliage washing solutions, such as chloroform or 1:1 mixture of tetrahydrofuran and toluene, the properties of aerosol particles adhering to Norway spruce needle surfaces have been extensively studied (Wyttenbach *et al.* 1987a, b; Simmleit *et al.* 1989).

For airborne particles to affect forests, the most critical parameter is probably the retention time of the deposited metals on the leaf surface. Surface features and particle size are the major factors affecting the retention of particles (Chamberlain 1975). Recent development in surface analysis methods, such as analysis of foliage for natural radionuclides (Bondietti *et al.* 1984), can be used to quantify the amount of deposited metal elements residing on forest surface. Aerosol particles deposited on leaves have been observed by scanning electron microscopy (SEM) and characterized qualitatively by electron probe microanalysis (with EDX) (Grill and Golob 1983). X-ray photoelectron spectroscopy (XPS) analysis (on samples from Central Europe) showed that the adsorbed particles are mainly of organic origin, containing only 1.0% of Al, 0.01% of Pb and traces of Fe and Mn (Simmleit *et al.* 1989).

2.5. Pathways of Trace Metals Deposited on Forest Surfaces

2.5.1. Retention in epicuticular layers

A certain part of deposited aerosol particles is not removed by rainfall and hence irreversibly adsorbed on the hydrophobic epicuticular wax layer. The chemical and physical nature of the wax may act as a barrier to the entry of deposited metals into leaves. Lindberg *et al.* (1982) reported that the residence time of dry-deposited material is generally longer than that of precipitation-delivered material. Under the pH regime of precipitation in the canopy layer, formation of metal oxides or hydroxide and assimilation of metals by the leaf surfaces can lead to a retention of Al and Fe (Mayer 1983). Coniferous epistomatal chambers are generally occluded with finely divided wax consisting of intermeshed tubes, and are more susceptible to occlusion by deposited particles in polluted environments (Eglinton and Hamilton 1967).

2.5.2. Foliar uptake

Metal elements are deposited mainly as solid particles which may subsequently dissolve in acid precipitation at the forest surface. Dissolved metals tend to be retained partly by the canopy, on leaf surfaces and on the bark of branches. The passage of non-dissolved sub-micron aerosols through stomata with impact on sub-stomatal surfaces is theoretically possible (Buchauer 1973). Direct cuticular penetration of soluble compounds arising from deposited particles is also expected with absorbtion rates dependent on pollutant concentration gradients, cuticle thickness, hydration, and the affinity of cuticular compounds for the solutes involved (Hosker and Lindberg 1982). Kabata-Pendias and Pendias (1992) even indicated that the non-metabolic cuticular penetration could be the major route of entry for deposited trace elements to inner parts of leaves. The degree of foliar uptake of metal elements from a forest canopy has been estimated by Parker (1990), and the foliar uptake may vary as a function of the degree of forest decline (Durka *et al.* 1994).

Redox and pH may be two of the more important factors affecting metal mobility at plant surfaces (Alloway 1995). Interactions between metal particles deposited on dry leaf surfaces and subsequent acid precipitation can result in metal concentrations on leaves that are considerably higher than those in rain alone (Lindberg *et al.* 1982). The efficiency of foliar uptake may appear to follow the same ion order as for elemental leaching from forest surfaces. The rate of absorbed metal element movement among tissues varies greatly, depending on the tree species, the organ, the age, and the element involved (Huang *et al.* 1982; Lepp 1975).

2.5.3. Removal from tree surfaces

Particle deflection, rebound, and resuspension from the foliar surface are related to particle size and receptor surface characteristics. In the case of precipitation, the chemical composition of rain is modified by contact with tree canopies through the removal of particles and gases deposited on foliar surfaces and the release or adsorption of ions by leaves (Lindberg 1989; Ivens *et al.* 1990). Large particulates may be shaken off by the agitation of leaves in the wind (Juniper and Jeffree 1983). The smaller aerosol particles may be embedded deeper in the rough wax structure; they are less likely to come in contact with water and are thus not easily removed (Smith 1990). Insoluble particles will most likely behave differently than soluble or hygroscopic particles or aerosols (Hosker and Lindberg 1982). The easy removal of an element by washing may suggest a largely superficial deposit of the element on the foliar surface.

2.6. Internal Cycles of Metal Elements: Migration and Leaching

Trace metals deposited on soil surfaces may be taken up by roots, translocated to the above-ground canopy, and subsequently secreted or leached from tree surfaces in acid precipitation. This internal cycling may add metal elements to the element load of throughfall measurements, and it has to be taken into account as an internal turnover to be distinguished from directly atmospheric metal input. Juniper and Jeffree (1983) reported that when radio-labelled Zn is added to the soil, it soon appears in small particle secretion from the leaf surfaces of Scotch pine. It seems that part of the Hg load in the atmosphere may be contributed from plants growing in Hg-rich soils (Siegel *et al.* 1974). However, Smith (1990) suggested that in excess of 90% of the heavy metals deposited from the atmosphere to forest ecosystems may not be available for tree root uptake. The contribution of elemental secretion from balsam fir needles to the estimation of dry deposition has been shown to be negligible (Reiners *et al.* 1986).

The root uptake of heavy metals and their transport in the plant are regulated to a certain extent by soil and biological factors (Lepp 1975). Ion exchange, as well as diffusion, can be involved in the translocation of metals and metabolites via the cuticle to the plant surface. Mn is a relatively mobile element within the plant, so that a stronger uptake by roots and the subsequent element leaching cannot be excluded, especially in acidic soil conditions (Mayer 1983). Leaching of metabolites from plant surfaces occurs when water-soluble materials are washed off or out of the surfaces of plants by acidic rain, dew or mist, particularly after dry periods. Foliar leaching can be increased by air pollution and other ecological stresses. Fritsche (1992) reported that the leaching of K, Mg and Mn from old needles exceeded the leaching from young needles to a high degree, but the ratios between the leaching elements were almost equal. Overall, Tukey *et al.* (1958) suggested that relative to total foliar concentrations, Na and Mn are most leachable; Ca, Mg, K, and Sr are intermediate; Fe and Zn are lowest. Differences in leaching of trace metal elements can be related to their function or metabolic association.

2.7. Effects of Metal Contamination on Forest Ecosystem

Air pollution is considered to be one of several potential contributors to the decline of conifers in the high elevation forests of eastern North-America (McLaughlin *et al.* 1990; Johnson 1983). In particular, these forests are also expected to be subject to significant deposition of metal pollutants (Petty and Lindberg 1990; Lindberg *et al.* 1982; Jeffries and Snyder 1981). The complex action of atmospheric pollutant deposition in forest ecosystems may possibly affect trees by acidification of soils and the resulting availability of toxic metal elements; by the effects on the epicuticular waxes of the foliage; and by the accumulation and leaching of metal elements.

In general, only a few trace elements can cause phytotoxic injuries under certain environmental conditions, such as As, Cd, Cu, Mn, Ni, Pb, V, and Zn. However, trace metals in a mixture may interact to give a different plant responses when compared with each single element. The accumulation of metal pollutants in plant tissue may alter the plant's response to other gaseous pollutants (Ormrod 1977). Lamoreaux and Chaney

(1978) indicated that the photosynthesis and transpiration of silver maple leaves were affected by the interaction between Cd and SO_2. Low concentrations of trace elements (*e.g.*, Cd, Ni, Ti, and Pb) have profound effects on plant processes, including photosynthesis and respiration, due to interference with stomatal function (Bazzaz *et al.* 1974). The site of action may be at both the physiological and biochemical levels.

Trace element contamination of soils from industrial sources of atmospheric pollution can lead to accumulation of contaminant elements in the surface horizon (Li and Wu 1991). Heavy metal loading of the upper forest soil profile will decrease the rate of soil organic matter decomposition and soil respiration, and will reduce soil enzyme activities and nutrient uptake by roots. The direct metal toxicity to tree roots on physiology will become significant at some threshold level of dose (Smith 1990). As for acid deposition, the link between metal deposition and accumulation may be significant (Johnson and Siccama 1983).

2.8. Research Needs

No single theory can be applied equally well to different ecological cases, such as studies on forest decline around the world, involving a variety of pollutants, plant species and climate conditions. In particular, it is not yet clear to what extent the occurrence of forest decline is correlated with atmospheric metal deposition (Foster 1989). The debate on the relative contributions of dry deposition and internal cycling of metal elements in forests still continues and a question mark still hangs over the use of throughfall and stem flow measurements in estimating metal deposition to forests (Cape and Fowler 1992), especially in forests that are also subject to acid deposition. In particular, the following questions need to be better understood if the potential long-term effects of atmospheric metal deposition on forest ecosystems and the relative importance of metal deposition to toxic metal accumulation are to be properly assessed (Barrie and Schemenauer 1989; Santerre *et al.* 1990; Ruck and Adams 1991; Johnson *et al.* 1991): (1) contamination levels of multi- trace metals in the air-soil-tree system in high elevation forests, and the link between metal accumulation in forests and atmospheric long-range transport of air pollutants; (2) accumulation and spatial distribution of trace metal deposits on foliar surfaces; (3) quantitative pathways of metal deposits on tree surfaces, such as absorption of pollutants from above-ground surfaces; and (4) transfer of metal pollutants in the soil-tree system and internal cycling of trace metals, such as migration and leaching of elements from shoots.

CHAPTER 3. AIRBORNE METAL POLLUTANTS IN HIGH ELEVATION FORESTS AND THEIR LIKELY SOURCE REGIONS

3.1. Abstract

Atmospheric metal pollution in high elevation forests of southern Quebec was investigated through analysis of airborne particulates by INAA, calculation of elemental enrichment factors, and air mass back trajectory analysis. Metal concentrations (ng m^{-3}) of Al, As, Cu, Fe, La, Mg, Mn, Na, Sb, V. and Zn in the air varied significantly throughout the sampling year. The Mn concentration at Roundtop Mountain in southern Quebec was generally higher than the concentration from the Champlain Valley in northeastern U.S. Concentrations of Mn and those of Al, V, and Zn were significantly ($P \leq 0.05$) correlated. Except for likely local soil-dust origin of Fe, enrichment factors suggested that airborne metal composition could be attributed to their long range transport through the atmosphere. The wind direction frequency measured at the research site in mountain forests was not suitable for identification of likely source regions for metal pollutants. However, air mass back trajectories indicated that air parcels that moved over Canadian industrialized and metropolitan areas may contribute to Mn pollution in remote high elevation regions. This study supports the contention that the atmospheric input of toxic trace metals should be a matter of concern in the high elevation forests of southern Quebec.

3.2. Introduction

Atmospheric metal input and increased acid deposition in eastern North America may significantly affect the biogeochemistry of elements in high elevation forests (Johnson *et al.* 1982; Barrie and Schemenauer 1989). The atmosphere is a key medium in the transfer of metal pollutants from urban pollution sources to rural forest ecosystems. Comparing natural and anthropogenic sources, industrial emissions are seen to be primarily responsible for most of the trace elements in the air (Cole *et al.* 1990). Nriagu (1990) estimated that the burning of fossil fuels accounted for more than 95% of V and 80% of Ni discharged into the environment, and anthropogenic emissions of Pb, Cd, V, and Zn might exceed their fluxes from natural sources by factors of 28, 6, 3, and 3, respectively. Since 1976 when methylcyclopentienyl manganese tricarbonyl (MMT) has been used as an additive in unleaded gasoline in Canada, Mn contamination in Canadian environments has become a matter of potential concern. Loranger and Zayed (1994) reported that MMT-related Mn contamination was significantly correlated with traffic density. Airborne Mn concentrations in urban Montreal (maximum, 0.42 $\mu g\ m^{-3}$) exceeded up to 10 times that of the background level (0.04 $\mu g\ m^{-3}$), and have reached the chronic exposure limit (*i.e.*, 0.40 $\mu g\ m^{-3}$, USEPA 1990).

The multi-element analysis of airborne particulates containing trace metals may provide a methodology for detecting potentially toxic metals in the atmosphere (Sweet *et al.* 1993). Aerosol chemistry is of importance to our understanding of wet and dry metal deposition and its effects on natural ecosystems, particularly under co-occurrence of acid deposition. Airborne metal composition and source identification studies may contribute to our understanding of their atmospheric long-range transport and to impact assessment of industrial regions on more remote forest ecosystems.

As a follow-up to research on the chemistry of high elevation fog (CHEF) (Schemenauer *et al.* 1995), the objective of the present chapter was to study multi-metal contamination in the air in high elevation forests of southern Quebec, and to identify their likely pollution source regions, with special emphasis on Mn contaminants. The study may help to understand the link between atmospheric metal contamination, deposition, and the elevated levels of Mn in conifer needles found at the high elevation forests (Lin *et al.* 1995b).

3.3. Materials and Methods

3.3.1. Research site

Roundtop Mountain is located near the town of Sutton, approximately 95 km SE of Montreal, with summit elevation of 970 m. According to Schemenauer *et al.* (1988), the percentage of time that the forest is immersed in acid fog increases as a function of elevation (23, 38, and 44% at elevations of 530, 840, and 970 m, respectively). Roundtop Mountain is covered with coniferous forests of red spruce and balsam fir above 700-m elevation. Hardwood forests of sugar maple, beech, and yellow birch dominate at lower elevations. Two sampling sites were selected, at 845-m elevation on the ridge [45° 05' 19" (N); 72° 33' 25" (W)] and 250-m elevation in the valley [45° 04' 34" (N); 72° 42' 05" (W)].

Mont Tremblant is about 105 km NW of Montreal. The sampling site was selected at 860-m elevation on the summit of White Peak [46° 12' 50" (N); 74° 33' 20" (W)]. The White Peak area is covered mainly with balsam fir and paper birch above 760 m, and with balsam fir, red maple, sugar maple, and eastern hemlock below 760 m. Roundtop Mountain and White Peak have been used as two long-term research locations for the CHEF project (Schemenauer 1986).

3.3.2. Sampling of airborne particulates

Airborne particulates were sampled with Teflon filters (Millipore LS 5.0 µm), at a flow rate of 2 L min^{-1}. The filters were mounted in packs which were covered with a downward facing shield to prevent the entry of precipitation and fog (Schemenauer and Cereceda 1992). Each filter generally covered a sampling period from one to two weeks. The following filters were collected and prepared for the determination of the metal composition of airborne particulates: (1) from the ridge of Roundtop Mountain throughout 1993, and from October 1-16 of 1990 and 1991, (2) from the valley of Roundtop Mountain during May 15 to June 1, 1990 and during October 1-16, 1993, and (3) from the ridge of White Peak at Mont Tremblant from May 15 to June 1, 1990.

3.3.3. Wet and dry deposition of metal elements

Fog and rain samples were obtained from Roundtop Mountain between 30 September to 16 October, 1991. Fog samples were collected on AES/ASRC Teflon string fog collectors and the rain samples in high density polyethylene (HDPE) bags (Schemenauer *et al.* 1995). Samples were stored in HDPE bottles and preserved immediately in ultra-pure nitric acid after collection.

To study the relative importance of sedimentation in dry deposition, deposition fluxes to a vertical surface of 1125 cm^2 on the AES/ASRC fog collector (*i.e.*, the cross sectional area of the strings), and to a circular, horizontal open surface of 1963 cm^2 on the HDPE bag were determined simultaneously for a 24-hour period without precipitation (October 2, 1991) on the ridge of Roundtop Mountain. After exposure, the fog collector was rinsed with 200 mL of distilled deionized water and the HDPE bag with 425 mL.

3.3.4. Analyses of metal elements

Teflon filters were analyzed by instrumental neutron activation analysis (INAA), which precludes Pb determination, for which, fortunately, there exists an extensive literature (*i.e.*, Hutchinson and Meema 1987). The filter was put in a 1.2 mL vial, and irradiated under a neutron flux of 4.6-5.35 × 10^{11} n cm^{-2} s^{-1}. Irradiation time was 600 sec for short half-life nuclide and 450 min for long-half life ones. The analysis system and the limit of detection (LOD) for the INAA are described by Kennedy (1990). A total of 11 metal elements (Al, As, Cu, Fe, La, Mg, Mn, Na, Sb, V, and Zn), with detectability above 90%, were selected. The detectability was defined as the percentage of total filter-samples that provided metal concentrations above the limit of detection (Lin and Schuepp 1996).

The samples of fog and rain were analyzed by inductively coupled plasma mass spectrophotometer (ICP-MS). Analysis of blank samples showed concentrations below the detection limit for all elements for both fog and rain, except for mean blanks in the fog collector of 2.3 (μg kg^{-1}) for Al and 10.0 (μg kg^{-1}) for Zn. The Zn analysis for fog is, therefore, marked as questionable. Dry deposition rinse samples were analyzed by ICP-MS (Schemenauer and Cereceda 1992).

3.3.5. Enrichment factors

Enrichment factors (EFs) were calculated for the purpose of determining the most likely origin of elements in airborne particulate, fog and rainfall samples. Al in topsoils at Roundtop Mountain (Table 4.2) was chosen as the tracer element. EFs ≈ 1 are taken as an indication that elements are mainly of soil origin, and EFs ≥ 10 are considered to indicate that a substantial portion of the element has a non-soil origin, and originates most likely from anthropogenic sources (Chester *et al.* 1981; Schemenauer and Cereceda 1992).

3.3.6. Air mass back trajectory analysis

The back trajectories of air masses were determined using the LRTAP 78-4 model of the Atmospheric Environment Service of Canada (Olson *et al.* 1978). Trajectories were computed backward for two days, with air parcel positions located every six hours. The starting point of the trajectories was located at the ridge of Roundtop Mountain at the 950 mb pressure level, and the starting time was on 00:00 Z (GMT) of each day during February 15-22 and March 10-18 in 1993. These two filter sampling periods were chosen because they included the highest and the lowest Mn concentrations during the winter and spring seasons, respectively. Elemental Mn was selected following our hypothesis that ambient Mn contamination in rural mountains may be significantly affected by long range transport of pollutants from Canadian MMT-related sources.

Wind speed and direction at the ridge of Roundtop Mountain were averaged for every 15 minutes as part of the routine CHEF measurements. Rainfall was only recorded during the snow-free period of June to September.

3.3.7. Statistical analysis

Statistical analyses were performed by using SAS, including paired t-tests and the correlation analysis (SAS Institute Inc. 1988a). Element concentrations below the limit of detection were not considered in the correlation analysis.

3.4. Results and Discussion

3.4.1. Metal concentrations in airborne particulates

Airborne metal concentrations at Roundtop Mountain in 1993 are presented in Table 3.1, with seasonal means and standard deviations. The seasons are defined as December

- February for winter, March - May for spring, June - August for summer, and September-November for fall. Metal concentrations for the winter season in Table 3.1 are the average of January, February and December of 1993. Al and Zn concentrations were the highest in the spring, while Fe and Cu were the highest in the summer. Other elements did not show a large seasonal change in concentrations. However, the relatively large standard deviation indicates a high variability of metal concentrations throughout the season and the year.

Table 3.1. Metal concentrations in the air at Roundtop Mountain in southern Quebec in 1993. The means ± one standard deviation are given. Each air filter covered a sampling duration of one to two weeks. The number of filters is presented in brackets.

Element	Airborne Trace Metal Concentrations (ng m^{-3})			
	Spring (n = 12)	Summer (n = 10)	Fall (n = 12)	Winter (n = 11)
Al	72 ± 48	57 ± 56	41 ± 29	24 ± 21
As	0.3 ± 0.2	0.2 ± 0.1	0.2 ± 0.0	0.2 ± 0.1
Cu	2.7 ± 1.1	3.3 ± 1.6	2.3 ± 3.3	1.8 ± 1.4
Fe	204 ± 167	311 ± 117	154 ± 157	191 ± 129
La	0.1 ± 0.06	0.08 ± 0.04	0.07 ± 0.04	0.04 ± 0.03
Mg	270 ± 390	982 ± 345	414 ± 470	197 ± 246
Mn	2.9 ± 1.0	2.8 ± 0.5	2.0 ± 0.5	2.0 ± 1.4
Na	102 ± 60	103 ± 68	53 ± 44	105 ± 40
Sb	0.2 ± 0.1	0.3 ± 0.4	0.2 ± 0.1	0.2 ± 0.1
V	1.2 ± 0.6	1.3 ± 0.5	0.9 ± 0.3	1.2 ± 0.4
Zn	21 ± 12	14 ± 10	8.4 ± 8.9	8.8 ± 6.6

Annual means of metal concentrations in 1993 at Roundtop Mountain are given in Table 3.2, along with the ambient concentrations of trace metals reported by previous authors from other rural or remote locations. In comparison with the few data available worldwide, higher concentrations of Cu, Mn, and Zn were found at Roundtop Mountain in 1993 than the worldwide-average from other remote areas (Nriagu 1990). Table 3.2 also shows that Roundtop Mountain had higher concentrations of Fe and Na than the Dorset location in northeastern Ontario, but with similar concentrations for As, Cu, Mn, Sb, and V (Hopper and Barrie 1988). A large variation in metal concentration was also observed by Ahier *et al.* (1990) in 1988 at their Sutton sampling site, which is close to our valley site.

The average annual concentration of Mn (2.4 ± 1.0 ng m^{-3}) in 1993 at Roundtop Mountain was higher than the 1989 Mn concentration (about 1.5 ng m^{-3}) in the Champlain Valley (*i.e.*, the Underhill, VT and Whiteface Mtn., NY) (Poirot *et al.* 1991). The study on aerosol chemistry in the northeastern United States also showed a decreasing gradient in Mn concentrations from north to south. This may reflect the significant effect from Canadian Mn pollution sources.

Inter-element relationships were explored by the correlation matrix in Figure 3.1, showing correlation coefficients (r), levels of significance and the degree of freedom. It presents the statistically significant ($P \leq 0.05$) correlations among all elements, including the correlation between Mn and the elements Al, La, V, and Zn. Mielke *et al.* (1995) reported the highest concentrations of Pb and Zn from places having the largest volumes of automobile traffic. In our study, the significant correlation between Mn and Zn ($r = 0.6$, $P \leq 0.01$) may also suggest potential effects from Canadian automobile traffic due to the MMT-additive in gasoline. Small r values may indicate multiple sources, as opposed to a single source, for the metal composition in airborne particulates at Roundtop Mountain.

Table 3.2. Trace metal concentrations in airbome particulates collected from Roundtop Mountain, compared with those reported for other rural and remote locations.

Element	Eastern Canada			Worldwide Average [c]	
	Roundtop Mtn.	Sutton [a]	Dorset [b]	rural site	remote site
Al	49 ± 43	11-846	161 ± 155	-	-
As	0.2 ± 0.1	<0.10-0.93	0.84 ± 1.09	3.2	0.29
Cu	2.5 ± 2.1	-	6.1 ± 4.0	7.9	1.2
Fe	214 ± 152	11-374	55 ± 53	-	-
La	0.07 ± 0.05	-	-	-	-
Mg	449 ± 470	-	-	-	-
Mn	2.4 ± 1.0	0.6-20	2.8 ± 3.0	6.2	1.6
Na	90 ± 57	<21-647	54 ± 57	-	-
Sb	0.2 ± 0.2	-	0.23 ± 0.38	-	-
V	1.1 ± 0.5	0.3-9	1.3 ± 1.6	1.8	0.5
Zn	13 ± 11	-	-	26	6.2

All units are ng m^{-3}.
a: Ahier *et al.* (1990); Samples were collected at Sutton, Quebec, on a daily basis during 22 July - 12 October 1988.
b: Hopper and Barrie (1988); Samples were collected at Dorset, Ontario, on a daily basis during 1 October - 9 December 1984.
c: Nriagu (1990).

The elemental composition of airbome particulates may be expected to vary as a function of sampling elevation, location and sampling year. However, no significant ($P \leq 0.05$) differences were observed in concentrations between the valley (250-m elevation) and the ridge (845-m) of Roundtop Mountain during the sampling periods of May 15 - June 1, 1990, and October 1 - 15, 1993, although the Teflon-filters collected from the valley showed higher concentrations for Al and Zn than filters collected from the ridge site (Table

As										
Cu										
Fe										
La	0.5** (43)									
Mg			0.4 * (41)							
Mn	0.4** (43)				0.6** (45)					
Na										
Sb						0.4** (42)		0.4** (45)		
V			0.3 * (44)				0.4** (45)			
Zn	0.5** (37)	0.3 * (38)			0.4 * (38)		0.6** (38)			
	Al	As	Cu	Fe	La	Mg	Mn	Na	Sb	V

Figure 3.1. Inter-element correlation matrix. Degree of freedom are shown in brackets, with *, $P \leq 0.05$; **, $P \leq 0.01$.

3.3). Some of these statistically nonsignificant differences (*e.g.*, Al) may have resulted from the small sample size (n = 3).

Table 3.3. Metal concentrations in airborne particulates collected from the Valley and the ridge of Roundtop Mountain, during the sampling periods of May 15 - June 1, 1990, and October 1 - 15, 1993.

Elements	May 15 - June 1, 1990		October 1 - 8, 1993		October 8 - 15, 1993	
	Valley	Ridge	Valley	Ridge	Valley	Ridge
	ng m^{-3}					
Al	550	385	95	41	69	38
As	0.1	0.2	0.2	0.3	0.1	0.2
Cu	2.3	3.4	2.3	10	3.7	7.9
Fe	120	71	59	155	99	127
La	0.1	0.1	0.1	0.1	0.1	0.1
Mg	58	46	966	961	969	870
Mn	4.3	4	2.8	2.1	1.6	1.8
Na	60	68	50	44	67	31
Sb	0.2	0.2	0.4	0.3	0.3	0.3
V	1.4	1.3	1.8	1.3	2.2	1.7
Zn	6.4	5.8	15	7.7	8.6	6.8

Figure 3.2 shows metal concentrations at Roundtop Mountain during the October 1-15 sampling period, for three different years. Considering the logarithmic scale, considerable variability in concentration for most of the elements can be found, although the relative concentrations of the element are consistent from year to year. Figure 3.2 also

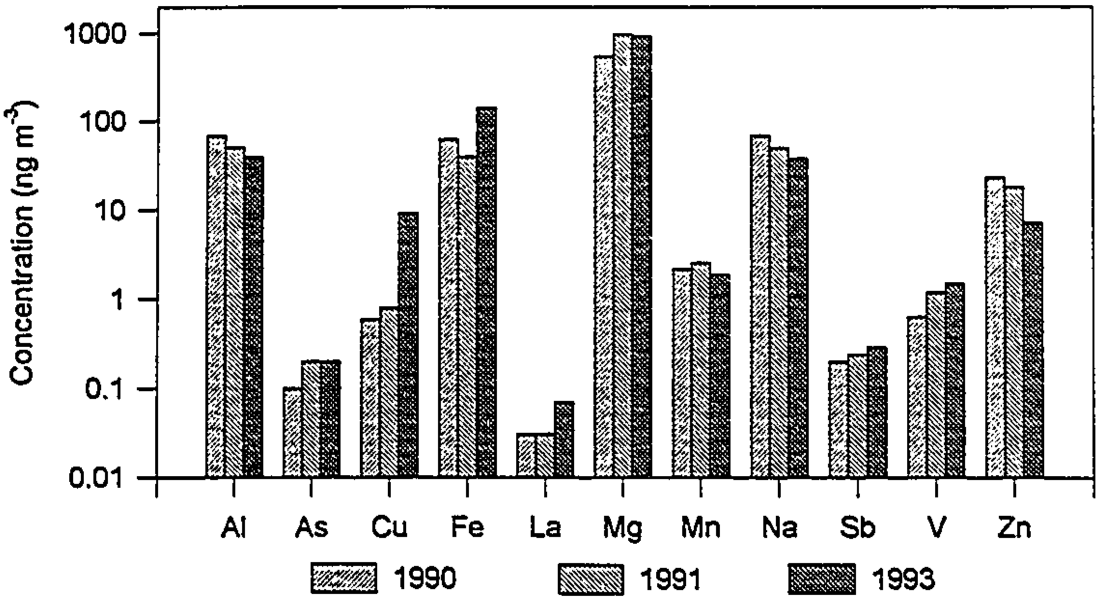


Figure 3.2. Airborne metal concentrations at Roundtop Mountain during October 1 - 15 of 1990, 1991, and 1993.

suggests increasing tendencies for Cu, Sb, and V, and decreasing tendencies for Al, Na, and Zn. These changes most likely reflect differences in pollution sources and atmospheric pathways. Some idea about the spatial variation of metal levels in the air is conveyed by the comparison of samples from Roundtop Mountain and White Peak during May 15 to June 1, 1990 (Figure 3.3). Results showed generally similar levels of metal contamination at the two locations, about 200 km apart, with the most notable exception being Zn which is more prevalent at Roundtop Mountain.

3.4.2. Origins of metal elements in airborne particulates

Except for Fe and La, the enrichment factor values (EFs) for airborne metals (Table 3.4) suggest that local wind driven soil dust may not be the most likely origin for elements such as As, Cr, Cu, Mn, Sb, V and Zn. EFs were relatively high in the winter season

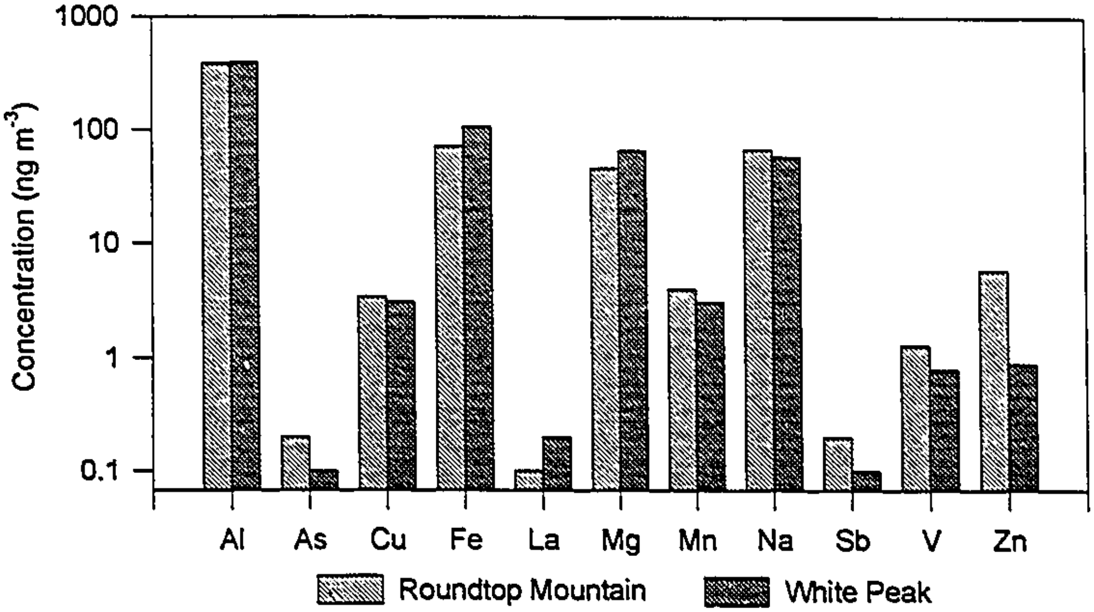


Figure 3.3. Airborne metal concentrations at Roundtop Mountain and White Peak during May 15 - June 1, 1990.

Table 3.4. Enrichment factors of airborne metal elements relative to the metals in topsoils at Roundtop Mountain during 1993. Al was selected as the tracer element. Data are presented as means ± standard deviation. Sample size (n) was given in Table 3.1.

Element	Spring	Summer	Fall	Winter
As	92 ± 155	245 ± 661	44 ± 42	314 ± 724
Cu	1545 ± 2890	4541 ± 11181	873 ± 1150	3189 ± 6587
Fe	13 ± 25	41 ± 96	8 ± 20	17 ± 44
La	8 ± 13	26 ± 65	7 ± 7	23 ± 38
Mg	87 ± 216	1818 ± 4834	83 ± 98	123 ± 214
Mn	16 ± 23	74 ± 194	11 ± 9	68 ± 115
Na	28 ± 47	163 ± 447	10 ± 10	148 ± 311
Sb	208 ± 488	3569 ± 10666	160 ± 188	717 ± 1579
V	35 ± 63	81 ± 178	22 ± 24	152 ± 275
Zn	364 ± 503	163 ± 157	84 ± 90	1200 ± 2706

Seasonal variation of EFs may result from differences in pollutant emission, prevailing wind direction, and ground characteristics, such as vegetative cover in the summer and snow during the winter.

Anthropogenic sources of air metal contamination have been further explored by the EF calculation for fog and rain samples collected at Roundtop Mountain from 30 September to 16 October, 1991 (Lin *et al.* 1995b). EFs of fog and rain samples are shown in Table 3.5, which includes Cd, Ni, and Pb. The EFs of Cd, Ni, and Pb from airborne particulates could not be obtained due to analytical limitations. EFs of several elements were comparable to those in air filter samples.

Table 3.5. Mean enrichment factors of metal elements in fog and rain at Roundtop Mountain during the period of 30 September to 16 October, 1991.

	Enrichment Factors							
	As	Cd	Fe	Mn	Ni	Pb	V	Zn
Fog	1364	8333	3	35	111	2667	123	1548
Rain	1364	41667	2	18	111	667	12	952

In general, the large EFs (»10) for As, Cd, Mn, Ni, Pb, V, and Zn suggest that metal contamination at Roundtop Mountain is significantly associated with atmospheric long-range transport of metal pollutants. For example, Mn probably originated from anthropogenic sources in Canadian metropolitan regions with industrial activity or intensive traffic. This appears to be true for fog and rain as well as for airborne particulates.

3.4.3. Annual fluctuation of airborne metal concentrations

The 1993 annual cycle of concentrations of Fe, Mn, and V is presented in Figure 3.4. Their seasonal concentrations have been given in Table 3.1. These elements were selected due to their significant correlation (*i.e.*, Mn and V), their notable sources (*i.e.*, likely soil-dust origin for Fe), and their high detectability. The two most prominent episodes of high concentrations of Mn were found during February 15-22 (5.9 ng m^{-3}) and March 26-31 (4.8 ng m^{-3}), separated by a low concentration episode during the period of March 10-18 (1.4 ng m^{-3}). The fluctuations of Mn and V concentrations appear to be correlated during the winter-spring seasons. For the entire year, the correlation coefficient between the Mn and V concentrations is 0.4 ($P \leq 0.01$).

Annual fluctuations in Mn concentration will be further examined through records of precipitation, wind velocity and direction, and the air mass movement at the Roundtop Mountain site. A back trajectory analysis was carried out for two of the above-mentioned periods of extremes in Mn concentration.

3.4.4. Wind and rainfall effects on metal concentrations

In general, weather systems moving from west to east predominate throughout Quebec, but winds from the southwest are prevalent in southern Quebec in the summer. Micrometeorological data collected at the Roundtop Mountain sampling site may, however, be affected by local topography. Figure 3.5 shows local precipitation, wind speed and direction averaged for the filter-sampling period at the Roundtop Mountain site during 1993. The means of wind speed and direction, and the distribution frequencies of wind directions, did not show significant correlation with the Mn concentrations of interest (*i.e.*, with episodes of high or low concentration). The results indicate that the individual climatic

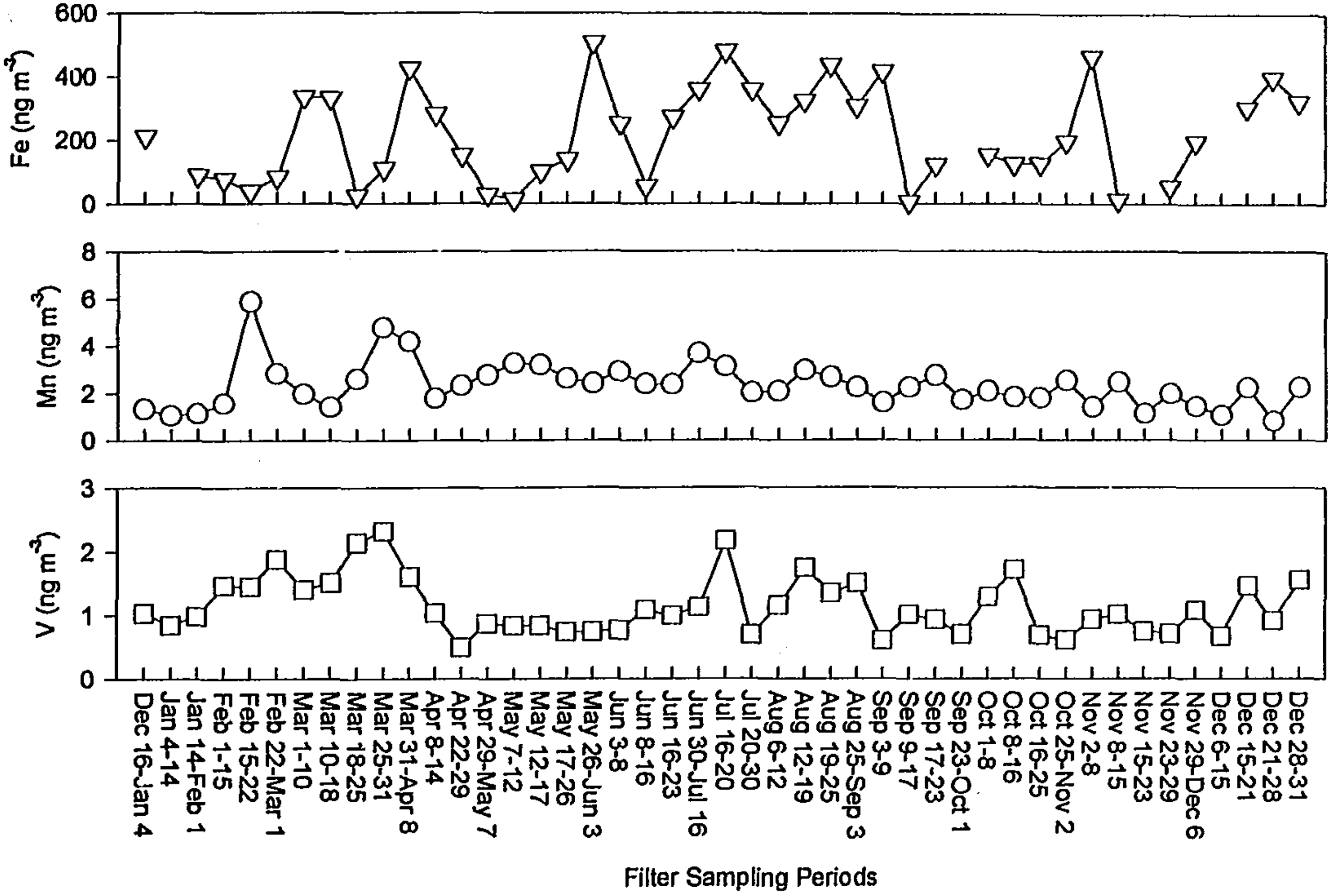


Figure 3.4. Annual cycles of airborne Fe, Mn, and V concentrations at Roundtop Mountain in 1993.

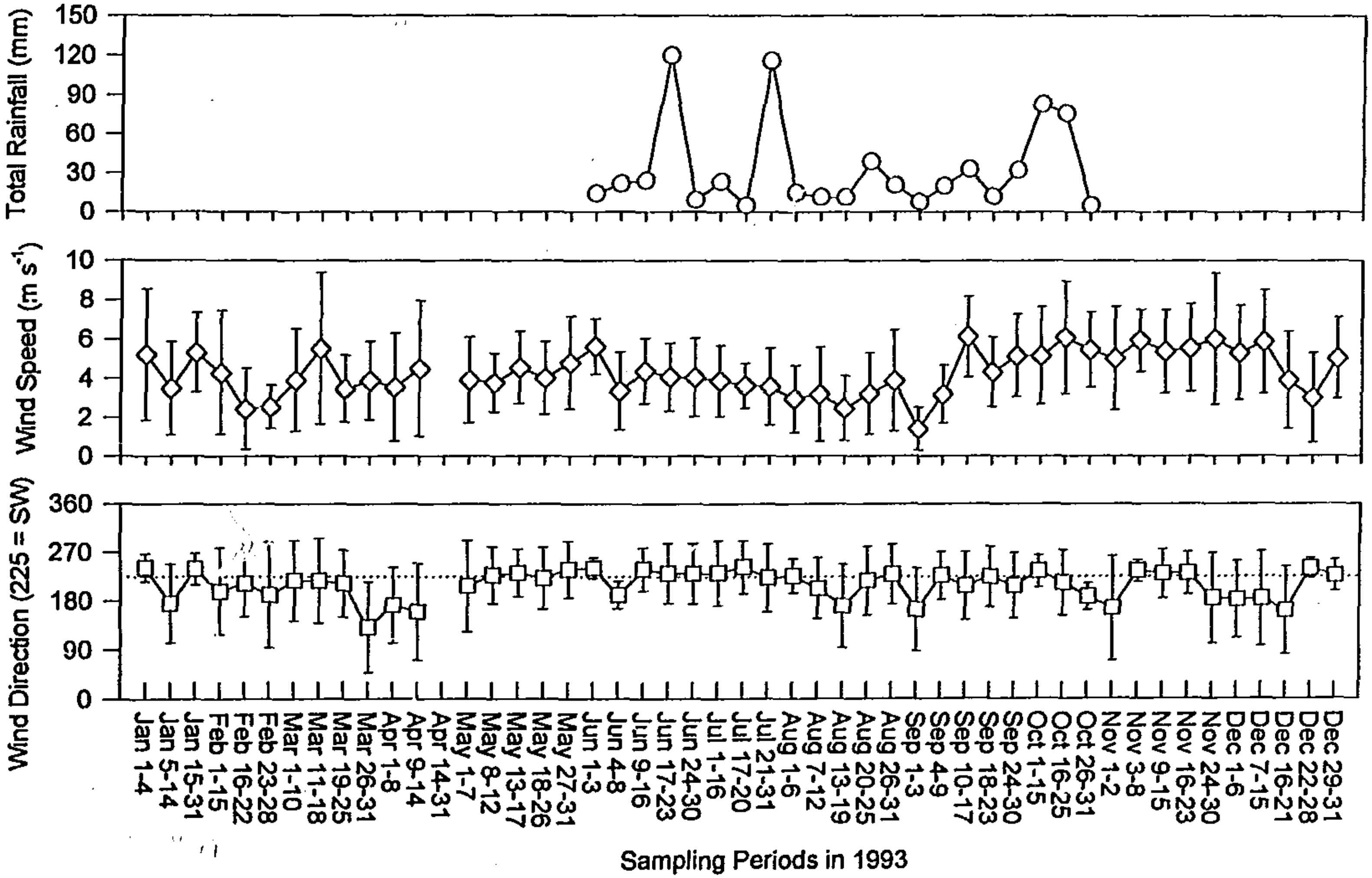
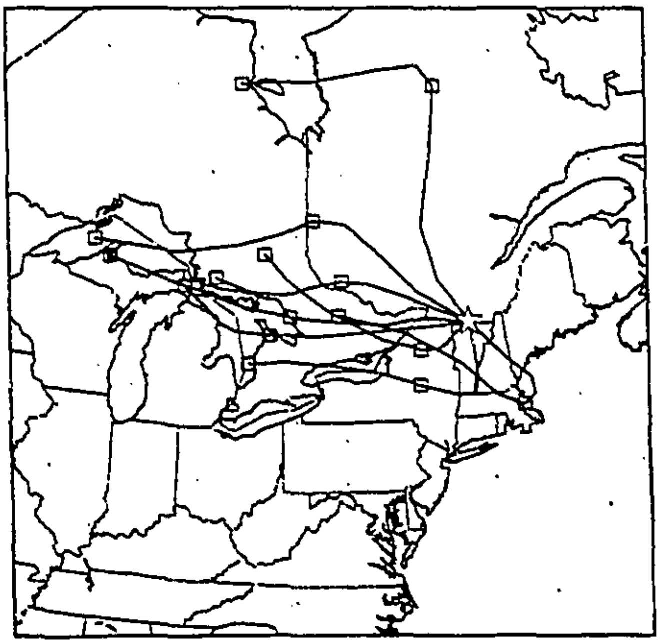


Figure 3.5. Total rainfall and the means of wind speed and direction during the sampling operation at Roundtop Mountain in 1993.

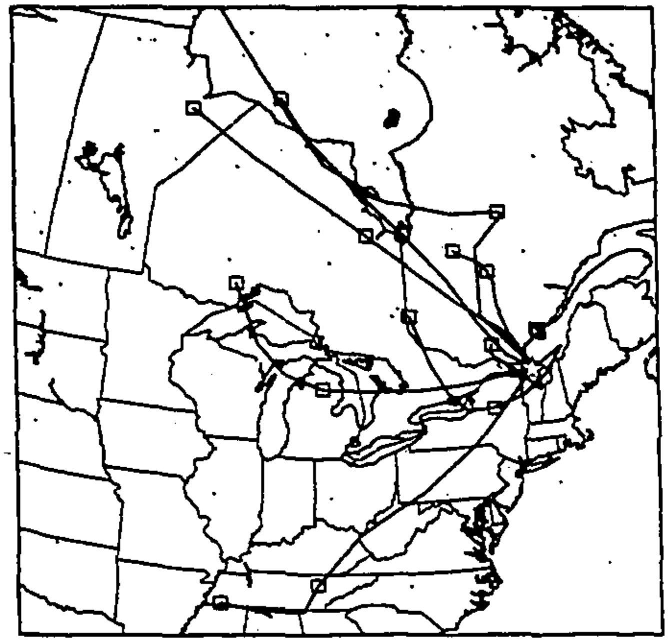
parameters of wind speed and direction, generated from observations at the site averaged over long sampling periods, are not suitable for providing a link between concentration level and pollution source. Nor did total precipitation during the sampling periods appear to be linked significantly with metal concentration, although precipitation at Roundtop Mountain was only recorded during the snow-free period from June to September.

3.4.5. Back trajectories of air mass movements

Air mass back trajectories, ending at 00:00 Z GMT of each day during the sampling periods with extremes in Mn concentration (high in February 15-22 and low in March 10-18 of 1993), are shown in Figures 3.6. The plots for the period of February 15-22 show air parcels that originated mainly from near the Great Lakes area to the west and passed eastward over some Canadian municipal and industrial regions, including the Montreal area in the Ste. Lawrence Valley. This would account for the fact that these air parcels transported significant quantities of Mn pollutant from the contaminated urban region to the observation site. In contrast, the back trajectory analysis for the period of March 10-18 showed a lower probability for air masses to pass over contaminated areas. It must also be remembered that, depending on the stability of the synoptic situation, the trajectory ending at 00:00 Z GMT is not necessarily representative of all air parcels arriving at the sampling site during the given sampling day. It is also difficult to quantify the degree of vertical mixing between near-surface sources and air parcels along the trajectories. However, back trajectory analysis allows us to speculate in a general manner about the links between the observed contamination and the likely source region.



February 15-22, 1993



March 10-18, 1993

Figure 3.6. Back trajectories of air masses during the sampling periods of February 15 - 22, and March 10 - 18, 1993, at Roundtop Mountain.

3.4.6. Wet and dry deposition of metals at Roundtop Mountain

The concentrations of selected elements in precipitation at the 840-m elevation of Roundtop Mountain are given in Table 3.6, as an indication of metal deposition to the given forest system. They show negligible values for As (<1 µg kg^{-1}) in both fog and rain, as well as for Cd (<0.5 µg kg^{-1}), with the exception of one rain sample. The mean concentrations of elements are higher in fog than in rain; for example, Mn concentration in fog is twice that in rain.

Table 3.6. Element concentrations in wet deposition of fog and rain at 840 m at Roundtop Mountain from 30 September to 16 October, 1991. Values below the detection limits are shown with a < sign. Values shown in brackets are questionable.

	Metal Deposition in Fog (n=4)			Metal Deposition in Rain (n=6)		
Element	Mean	Max	Min	Mean	Max	Min
	µg kg^{-1}					
Al	16.5	20.7	11.7	14.8	56.2	1.9
As	<1	<1	<1	<1	<1	<1
Cd	<0.5	<0.5	<0.5	1.8	8.1	<0.5
Fe	32	33.9	29.2	19.6	64.5	5.6
Mn	6.7	10	4.5	3.2	13.3	<0.5
Ni	1.6	3.5	<2.0	<2.0	<2.0	<2.0
V	3.3	6.7	0.7	<0.5	<0.5	<0.5
Zn	(21.9)	(29.4)	(15.2)	11.6	119.6	4.6

The flux of Al, Mn, and Zn deposited to the vertical (*i.e.*, the fog collector) and the horizontal (*i.e.*, the rainfall collector) surfaces were estimated from only two samples collected on the ridge of Roundtop Mountain (Table 3.7). The smaller vertical surface collected much larger amounts of metals than the horizontal surface. The high collection rates of the Teflon strings on the fog collector suggested that the metal elements are present in sizes with negligible vertical settling velocities, which might be unimportant under the windy conditions of the Roundtop Mountain site (Bridgman *et al.* 1994). Similarly, wind would be expected to lead to appreciable deposition on the surface of conifer needles of metal elements with appropriate particulate size scales.

Table 3.7. Flux of metal dry deposition on the surfaces of the fog and the rainfall collector at Roundtop Mountain during 24 hours on October 2, 1991.

	Flux of Metal Dry Deposition (μg m^{-2} hr^{-1})		
	Al	Mn	Zn
On the Fog Collector Surface	8.04	3.26	2.82
On the Rainfall Collector Surface	0.13	0.04	0.09

Hendershot *et al.* (1992) have documented significant effects of mountainous elevations on metal deposition to forest ecosystems at the same Roundtop Mountain location. They showed that wet deposition of Mn strongly depended on fog immersion time, which increased with the altitude, so that the Mn input through wet deposition at 850 m was five times higher than that at the 520-m elevation. Our study on air mass back trajectory analysis suggests atmospheric long-range transport of metal pollutants from pollution sources, which would indirectly support their conclusion, and that of other investigators focusing on the same area (Barrie and Schemenauer 1989, 1986), that the atmospheric input of toxic heavy metals, such as Mn, Pb and Zn, should be a matter of concern in high elevation forests in southern Quebec.

3.5. Conclusions

Metal concentrations in airborne particulates showed a seasonal variation, but generally fell in the concentration ranges reported for other rural locations (Nriagu 1990). Enrichment factors indicated that atmospheric heavy metals (except Fe) in southern Quebec were most likely affected by anthropogenic activities. Means of wind speed and direction averaged for the filter sampling period at the mountain site could not be used individually as meaningful parameters in the tentative identification of pollution sources. However, back trajectory analysis seems to support the hypothesis that air parcels moving across Canadian industrial metropolitan areas may contribute significantly to Mn pollution in the given mountain region.

CONNECTING STATEMENT LINKING CHAPTERS 3 AND 4:

As a consequence of air metal contamination, atmospheric metal deposition to high elevation forest ecosystem in southern Quebec is expected to significantly affect biogeochemistry of metal elements, especially when regional acid deposition is taken into consideration. Accumulation of metal elements in topsoils and their toxicities may be altered as a function of the atmospheric deposition of acidic and metal pollutants. In the next chapter, the total element concentrations in topsoils in high elevation forests of southern Quebec, will be evaluated, and effects of different elevations along the slopes of Roundtop Mountain and White Peak will be examined.

CHAPTER 4. TOTAL METAL ELEMENTS IN TOPSOILS OF FORESTS AFFECTED BY ACID DEPOSITION

4.1 Abstract

Major and trace elements (Al, As, Ba, Ca, Cd, Co, Cr, Cs, Cu, Eu, Fe, Hf, K, La, Lu, Mg, Mn, Na, Ni, Pb, Rb, Sb, Sc, Si, Sm, Sr, Ta, Tb, Th, Ti, U, V, Yb, and Zn) in forest soils were investigated from three acid deposition-affected locations in southern Quebec. Total element concentrations in the surface layer (0-20 cm) of the podzolic soils were mostly well within the range of element concentrations in Podzols reported worldwide, but with higher mean values for most elements. The mean concentrations of elements (except Zn at 124 mg kg^{-1}) were also generally comparable to the respective elemental baseline data established for Canadian soils. Element concentrations (in mg kg^{-1}) of Cs (6.2), Sc (19.8), V (106), Rb (194), K (26500), and Al (76900) in the topsoils were significantly higher at the 940-m elevation than the concentrations from the sites at 650 m and 770 m along the Roundtop Mountain slope, but Ca (1120) and Ni (4.4) were lowest at the 940-m elevation. A similar trend with elevation was not observed at the other mountain location (White Peak). Enrichment factor analysis showed significant element enrichment (EFs ≥ 10) for Cd, Rb, and Sb, but impoverishment (EFs ≤ 0.1) for Ca, Cu, and Ni, in topsoils.

4.2. Introduction

Heavy metal concentrations in soils have been shown to change significantly under the impact of environmental pollution in the past decades (Li and Wu 1991; Billett *et al.*

1991). Heavy metals deposited from the atmosphere to forests can accumulate in the upper soil horizons (Friedland *et al.* 1984; Anderson *et al.* 1980), even at sites located far from a primary pollution source (Smith 1990). Potential effects of atmospheric deposition on element biogeochemical cycles in forest soils, especially when accompanied by acid deposition, could be summarized as follows: (1) increased rate of mineral weathering with base cation release in soils (Fernandez 1985); (2) enhanced element fluxes, such as Pb, Cu, Zn, and Ni from atmospheric inputs (Johnson and Siccama 1983; Friedland *et al.* 1984); (3) facilitated base cation leaching in soil profiles (Hendershot *et al.* 1992); and (4) decreased rate of organic matter decomposition resulting from altered soil enzyme activities as a consequence of toxic metal accumulation (Tyler 1976; Binkley 1986).

In high elevation forests, the imbalance between nutrient requirements and supplies, and elemental toxicities in soil solution, may be partially responsible for some of the forest decline observed at elevated sites in northeastern North America. One might hypothesize a correlation between changes in major and trace element concentrations in soils and increasing acid deposition found along an elevational gradient on the mountain (Schemenauer 1986), because heavy metals in surface soils have been found in greater concentrations at high elevations in the northeastern United States (Johnson *et al.* 1982). The accumulation of metals in surface soils would be expected to vary with intensity of acid deposition, as a function of elevation, and with contamination level, as a function of distance from pollutant sources (Barrie and Schemenauer 1989; Lin *et al.* 1995b).

The purpose of this study was to examine the current total concentration of 34 elements in the surface soils from three locations in southern Quebec, where acid deposition has been considered to be critical. The potential effects of acid deposition on element concentrations in topsoils were evaluated particularly as a function of elevation.

Our study focuses on trace and rare earth elements (REEs) which have not been commonly investigated in such areas. This may contribute to a better understanding of the effects of atmospheric deposition to forest ecosystem on elemental biogeochemistry, both now and from the viewpoint of future long-term environmental studies.

4.3. Materials and Methods

4.3.1. Sampling locations

The Roundtop Mountain and White Peak locations have been introduced in Chapter 3. Three sampling sites at Roundtop Mountain were investigated along the mountain slope at 650-m, 770-m and 940-m elevations. Soils at Roundtop Mountain are classified as Humo-Ferric Podzols, formed on shallow materials over bedrock (Hendershot *et al.* 1992). Two sampling sites at White Peak of Mont Tremblant were located at 300 m and 825 m. Soils are Ferro-Humic Podzols. A third sampling location was chosen at the biology research station of the University of Montreal, located near the town of St-Hippolyte, about 80 km NW of Montreal (45°59'N, 74°00'W), at 345-m elevation. Soils are Ferro-Humic Podzols. The forest is dominated by sugar maple, paper birch, balsam fir and quaking aspen. One sampling site was chosen at this location.

These three forested, rural/remote locations represent a cross section of southern Quebec. They receive precipitation with an average pH of 3.7 - 4.4 at Roundtop Mountain and White Peak (Schemenauer *et al.* 1988) and an average pH of 4.5 at St-Hippolyte (Hendershot *et al.* 1985). Acid deposition observations at Roundtop Mountain and White Peak were described by Schemenauer (1986) and the soil formation at Roundtop Mountain and St-Hippolyte by Hendershot *et al.* (1992, 1985).

4.3.2. Soil sampling

During the late summer of 1992, soil samples were collected from one soil profile at 0-20, 20-40, and 40-60 cm depths (except at the 940-m elevation of Roundtop Mountain, where the maximum depth was 30 cm due to the presence of bedrock, and 0-20 and 20-30 cm samples were substituted). In keeping with the emphasis of this study on topsoils, and in order to reduce potential effects of spatial variability, two additional surface soil samples at 0-20 cm depth were collected at each sampling site, at least 15 m away from the soil profile. Soil samples from the 0-20 cm depth included the H horizon at the surface.

4.3.3. Analytical techniques

Soil pH was determined with a soil:solution ratio of 1:2 of air-dried soil and deionized water by CORNING ion analyzer 250. Organic matter was measured by the loss-on-ignition (LOI) method at 450 °C for 24 hrs (Robarge and Fernandez 1986) and cation exchange capacity (CEC), from the sum of exchangeable cations Mg, Na, K, Al, Mn, and Fe in 0.1 M $BaCl_2$ (Hendershot and Duquette 1986).

Element concentrations (except Cd, Cu, Ni, and Pb) in soils were analyzed by instrumental neutron activation analysis (INAA) with the SLOWPOKE nuclear reactor at the École Polytechnique of the University of Montreal. Air-dried soil samples, with average weight of 0.3 - 0.4 g, were sealed in 1.2 mL vials and irradiated under a neutron flux of $4.60 - 5.35 \times 10^{11}$ n cm^{-2} s^{-1}. Irradiation time was 20 s for short half-life nuclides (Al, Ba, Ca, Mg, Mn, Ti, and V) and 120 min for long half-life ones (Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Rb, Sb, Sc, Si, Sm, Sr, Ta, Tb, Th, U, V, Yb, and Zn). Gamma rays were detected and analyzed by germanium semi-conductor detector (EG&G ORTEC) and CANBERRA 35^+ multi-channel analyzer. Counting time varied from 10 min to 2 hrs. Spectra were analyzed by EPAA software (Kennedy and St-Pierre 1993) with volume correction, resulting in acceptable uncertainty (generally ≤10%) for the detection of 30 elements by INAA. Accuracy of the results was verified using standard reference materials (SRM 1632b and USGS BCR1).

Elements Cd, Cu, Ni and Pb were measured by ICP-AS (Perkin Elmer Plasma 40, with coupled ultrasonic nebulizer) and GF-AAS (Varian Spectraa-300, Zeeman), after soil samples were digested in HNO_3 with microwave acid digestion bombs (PARR®) (U.S. EPA 1986; Sauvé *et al.* 1995).

4.3.4. Enrichment factors

The enrichment factor (EF) of elements in surface soils was calculated with the element concentrations in the bedrock (Sutton Schistes) from Sutton (45°07'-10'N, 72°30'-45W) (Colpron 1987). The Al concentration in the bedrock was selected as a tracer element. EFs close to unity (*i.e.*, EFs≈1) are taken as an indication that elements are mainly of bedrock origin, and EFs ≥ 10 are considered to indicate that a substantial portion of the element has a non bedrock origin (Chester *et al.* 1981).

4.3.5. Statistical analysis

Statistical comparison of element concentrations between elevations at the Roundtop Mountain and the White Peak locations was performed using the Scheffé option of the GLM procedure of SAS (SAS Institute Inc. 1988a). Element concentrations were log-transformed when normality was rejected by the UNIVARIATE procedure of SAS (SAS Institute Inc. 1988b). The effects of sampling location and elevation on the mean element concentrations in southern Quebec were evaluated by partitioning the variation with the method described by Borcard *et al.* (1992), following Whittaker (1984). Partition of variation allows proper quantification of the fraction of variation associated with sampling elevation and location. We used three models: (M1) $Y = a_o + a_1 x_1 + \varepsilon$ where x_1, the elevation, is considered as a quantitative regression variable; (M2) $Y = a_o' + x_2 + \varepsilon'$ where x_2, the location, is considered as a qualitative ANOVA classification factor; and (M3) $Y = a_o'' + a_1'' x_1 + x_2 + \varepsilon''$ with notations similar to (M1) and (M2). The corresponding R^2 values are: $R^2_{x1} = R^2_{a+b}$ (M1), $R^2_{x2} = R^2_{b+c}$ (M2), and $R^2_{x1,x2} = R^2_{a+b+c}$ (M3); they were computed using PROC GLM of SAS. As a result, the pure elevation effects after removal of the differences among locations (R^2_a), the pure location effects after removal of the differences due to elevation (R^2_c), and the differences among locations specifically due to elevation (R^2_b) were quantified separately. It must be noted that negative R^2 values may be observed in variation partitioning (Borcard *et al.* 1992). In particular, negative R^2_b means an interaction between location and elevation that is responsible for non-significance of R^2_{a+b} and R^2_{b+c}, while the R^2 values of their respective pure effects (R^2_a and R^2_c) may be positive and large.

4.4. Results and Discussion

4.4.1. Physical-chemical properties

The soil pH, organic matter, and cation exchange capacity for the topsoil samples from the various sampling sites are summarized in Table 4.1 with the mean and the standard error from each sampling site.

4.4.2. Element concentrations

Concentrations of 34 major and trace elements in the surface layers of the soils at each sampling site are given in Table 4.2 with the overall means and standard deviations

Table 4.1. Physical-chemical properties of topsoils (0-20 cm depth with H horizon) collected from southern Quebec during the late summer of 1992. Values are mean ± standard error (n=3).

	Roundtop Mountain			Ste-Hippolyte	White Peak	
	650-m	770-m	940-m	345-m	300-m	825-m
pH (H_2O)	3.75 ± 0.09	3.75 ± 0.13	3.74± 0.03	4.82 ± 0.11	4.32± 0.15	4.20± 0.07
OM [a] (%)	18.5 ± 4.06	17.23 ± 4.39	10.05 ± 5.61	16.12 ± 0.55	15.41± 2.4	11.7± 2.75
CEC [b] ($cmol^+ kg^{-1}$)	11.85 ± 1.99	10.99 ± 1.59	8.44± 2.03	7.31 ± 1.71	8.42± 0.89	6.99± 0.67

a: Organic matter

b: Cation exchange capacity

Table 4.2. Concentrations (mg kg^{-1}) of major and trace elements in podzolic topsoils (0-20 cm). Soil samples were collected during the late summer of 1992. Elements are listed in alphabetical order. Effects of sampling elevations were evaluated at the Roundtop Mountain and the White Peak locations. Means, ± standard error (n = 3), at the same sampling location with the same letter are not significantly different ($P \leq 0.05$).

		Roundtop Mountain			Ste-Hippolyte	White Peak	
	Overall	650 m	770 m	940 m	345 m	300 m	825 m
Al	57800 ± 2660	48600^b ± 2980	48200^b ± 2548	76900^a ± 202	65100 ± 3440	52300^a ± 3820	55500^a ± 1590
As	5.07 ± 0.74	7.52^a ± 0.38	8.29^a ± 1.24	7.47^a ± 1.65	2.41 ± 0.82	1.73^a ± 0.08	3.01^a ± 0.56
Ba	530 ± 33	519^a ± 79	344^a ± 60	547^a ± 9	527 ± 8	582^a ± 84	661^a ± 108
Ca	6450 ± 946	3880^a ± 288	3790^a ± 585	1120^b ± 145	1150 ± 401	9530^a ± 1770	8880^a ± 628
Cd	12.18 ± 0.79	13.86^a ± 0.43	15.8^a ± 2.21	12.72^a ± 1.76	10.63 ± 1.75	11.73^a ± 1.90	8.33^a ± 0.13
Co	7.93 ± 0.86	10.50^a ± 2.31	7.89^a ± 1.88	4.38^a ± 1.15	10.50 ± 1.02	7.90^a ± 3.38	6.45^a ± 0.89
Cr	69.0 ± 22.0	130^a ± 31	80^a ± 7	106^a ± 2	37 ± 1	31^a ± 5	33^a ± 4
Cs	2.29 ± 0.48	2.91^b ± 0.27	2.37^b ± 0.21	6.18^a ± 0.71	0.66 ± 0.09	0.85^a ± 0.18	0.79^a ± 0.14
Cu	3.53 ± 0.57	6.27^a ± 0.96	2.74^a ± 0.67	5.78^a ± 1.94	1.57 ± 0.67	1.92^a ± 0.80	2.89^a ± 0.56
Eu	1.66 ± 0.12	1.61^a ± 0.20	1.60^a ± 0.31	0.85^a ± 0.15	1.87 ± 0.02	2.03^a ± 0.20	2.02^a ± 0.09
Fe	55600 ± 3330	55200^a ± 2720	56700^a ± 5680	42500^a ± 5060	59800 ± 4900)	68100^a ± 16300	51000^a ± 5010
Hf	11.6 ± 0.4	11.2^a ± 0.9	11.1^a ± 0.7	9.9^a ± 1.7	11.7 ± 1.1	13.7^a ± 0.7	12.0^a ± 0.3

K	19300 ± 1170	16000^{b} ± 1590	14100^{b} ± 639	26500^{a} ± 1134	16900 ± 940	19300^{b} ± 2080	23000^{a} ± 2530
La	21.00 ± 1.30	21.85^{a} ± 2.95	19.58^{a} ± 2.92	15.45^{a} ± 3.22	18.13 ± 0.82	25.14^{a} ± 3.36	25.72^{a} ± 2.55
Lu	0.45 ± 0.04	0.34^{a} ± 0.05	0.31^{a} ± 0.03	0.34^{a} ± 0.04	0.43 ± 0.04	0.64^{a} ± 0.11	0.62^{a} ± 0.08
Mg	5480 ± 322	5860^{a} ± 70	4890^{a} ± 431	6280^{a} ± 1070	6080 ± 211	5080^{a} ± 1500	4660^{a} ± 712
Mn	458 ± 65	333^{a} ± 36	394^{a} ± 28	237^{a} ± 44	387 ± 2	486^{a} ± 86	910^{a} ± 253
Na	11500 ± 671	10200^{a} ± 686	9750^{a} ± 388	7400^{a} ± 848	13200 ± 60	13900^{a} ± 1130	14700^{a} ± 379
Ni	6.48 ± 0.97	12.21^{a} ± 0.34	8.44^{ab} ± 0.59	4.38^{b} ± 1.49	5.38 ± 2.02	1.62^{a} ± 0.11	3.22^{a} ± 1.03
Pb	14.97 ± 2.20	22.67^{a} ± 3.45	21.14^{a} ± 3.75	19.73^{a} ± 941	8.32 ± 1.36	6.16^{a} ± 1.10	11.82^{a} ± 1.65
Rb	101 ± 11	103^{b} ± 4	83^{b} ± 7	194^{a} ± 21	65 ± 4	81^{a} ± 3	80^{a} ± 7
Sb	2.99 ± 0.38	3.10^{a} ± 0.45	1.94^{a} ± 0.38	2.65^{a} ± 0.39	3.55 ± 0.79	1.93^{a} ± 0.40	4.79^{a} ± 1.80
Sc	12.53 ± 0.91	11.35^{b} ± 0.42	10.55^{b} ± 1.11	19.82^{a} ± 1.09	11.25 ± 0.39	10.26^{a} ± 1.79	11.93^{a} ± 1.76
Si	270000 ± 12900	238000^{a} ± 21900	239000^{a} ± 15700	336000^{a} ± 29400	271000 ± 50300	246000^{a} ± 11100	291000^{a} ± 24900
Sm	4.33 ± 0.36	4.20^{a} ± 0.72	4.07^{a} ± 1.04	2.43^{a} ± 0.45	4.09 ± 0.31	5.77^{a} ± 1.01	5.43^{a} ± 0.39
Sr	232 ± 13	245^{a} ± 50	198^{a} ± 26	244^{a} ± 38	262 ± 33	240^{a} ± 29	203^{a} ± 21
Ta	1.44 ± 0.14	2.08^{a} ± 0.18	1.68^{a} ± 0.17	1.98^{a} ± 0.33	0.90 ± 0.14	1.24^{a} ± 0.16	0.80^{b} ± 0.01
Tb	0.66 ± 0.06	0.60^{a} ± 0.11	0.60^{a} ± 0.15	0.33^{a} ± 0.01	0.62 ± 0.02	0.93^{a} ± 0.19	0.87^{a} ± 0.06
Th	6.64 ± 0.50	7.27^{a} ± 1.01	6.40^{a} ± 1.30	9.19^{a} ± 0.69	3.70 ± 0.29	6.94^{a} ± 0.88	6.33^{a} ± 0.89

Ti	5260 ± 244	5790^a ± 209	5850^a ± 496	6320^a ± 765	4790 ± 298	4740^a ± 430	4050^a ± 208
U	1.92 ± 0.48	1.76^a ± 0.14	1.97^a ± 0.27	2.12^a ± 0.10	0.67 ± 0.10	1.32^a ± 0.27	1.12^a ± 0.07
V	79.3 ± 4.1	72.5^b ± 1.0	72.2^b ± 7.1	106.2^a ± 4.7	79.6 ± 5.4	85.9^a ± 11.3	59.6^a ± 0.8
Yb	2.59 ± 0.23	1.90^a ± 0.06	2.06^a ± 0.16	1.82^a ± 0.25	2.60 ± 0.14	3.55^a ± 0.83	3.60^a ± 0.46
Zn	124 ± 13	114^a ± 11	106^a ± 18	117^a ± 19	112 ± 10	169^a ± 79	126^a ± 14

across all sampling sites, and the means, standard errors, and the multiple comparison analysis. The statistical comparison on the means from Roundtop Mountain and White Peak sampling locations showed a significant ($P \leq 0.05$) effect of sampling elevation on elemental concentrations in surface soils for eight of the 34 elements examined at Roundtop Mountain (*i.e.*, Al, Ca, Cs, K, Ni, Rb, Sc, and V), and for two of the elements examined at the White Peak location (*i.e.*, K and Ta). At Roundtop Mountain, the concentrations of Cs, Sc, V, Rb, K, and Al in surface soils were significantly higher at the 940-m elevation than at the 640-m and 770-m elevation sites, while the concentrations of Ca and Ni were lowest at the highest elevation site. Results from the White Peak location showed a relative high K and low Ta at 867-m elevation. Calcium concentration showed significantly lower levels at Roundtop Mountain sites (at all three elevations), compared to St-Hippolyte and White Peak locations. Element concentrations at St-Hippolyte were generally comparable to the other two sampling locations.

The mean concentrations in Table 4.2 (with the exception of Zn) are generally similar to the average elemental background levels for Canadian soils, at least for the seven trace elements for which comparable data are available (McKeague and Wolynetz 1980). McKeague *et al.* (1979) examined Ferro-Humic Podzolic soils at St-Agathe, Quebec (45°57'N, 74°27'W) close to our sampling location at White Peak, with an elevation of about 450 m. Of the 15 elements studied, the concentrations of Mg, Ca, Al, Co, and Sr were higher than the corresponding concentrations from our measurements at White Peak sites, while Fe and Zn were lower, and Cr, Mn, and Ti were comparable. Concentrations of Zn, Mn (White Peak 825 m site only), and Cr (Roundtop Mountain sites only) from this study were higher than corresponding values observed in spruce fir forests in New Hampshire (Reiners *et al.* 1975). Worldwide estimates of means and ranges of total concentrations of 21 trace elements in surface podzolic soils were given by Kabata-Pendias and Pendias (1992); concentrations of As, Ba, Co, Cr, Mn, Sc, Sr, Ti, V, and Zn in Table 4.2 fall within the stated ranges, but all, except Ti, were higher than their world average mean values.

The overall mean of most element concentrations from the southern Quebec region are associated with large standard deviations (Table 4.2). These reflect a high degree of variation of metal concentration in the topsoil between different locations and elevations, due to differences in parent materials, forest composition, and other environmental factors. Confounding of location and elevation effects on metal concentrations, *i.e.*, all the locations were not sampled at the same elevations, must be expected. The variation partitioning method (Whitaker 1984; Borcard *et al.* 1992) has been specifically designed for such experimental conditions. Using a threshold of 25% for the R^2 values reported in Table 4.3, variation partitioning showed (1) pure elevation effects only for K among the total 34 elements, (2) pure location effects for Al, As, Ba, Ca, Cd, Cr, La, Lu, Ni, Mn, Na, Sm, Ta, Tb, Ti, and Yb, and (3) location effects due to elevation for As, Ba, Ca, Cs, Na, Pb, and Rb. These results suggest that metal concentrations in topsoils in southern Quebec depend

Table 4.3. Statistical analysis of elevation and location effects on metal elements in topsoils from southern Quebec.

	Effects of Elevation (M1)			Effects of Location (M2)			Effects of Elev. & Loca. (M3)		
	R^2_{a+b}	Prob.	R^2_a	R^2_{b+c}	Prob.	R^2_c	R^2_{a+b+c}	Prob.	R^2_b
Al	0.055	ns	0.209	0.117	ns	0.270	0.326	ns	-0.153
As	0.384	* *	0.012	0.782	* *	0.408	0.792	* *	0.372
Ba	0.004	ns	0.038	0.247	* *	0.281	0.285	ns	-0.035
Ca	0.526	* *	0.022	0.853	* *	0.349	0.875	* *	0.504
Cd	0.014	ns	0.106	0.364	*	0.456	0.469	*	-0.092
Co	0.165	ns	0.120	0.107	ns	0.062	0.227	ns	0.045
Cr	0.112	ns	0.002	0.361	*	0.252	0.363	ns	0.110
Cs	0.429	* *	0.057	0.587	* *	0.214	0.644	* *	0.372
Cu	0.227	*	0.010	0.370	*	0.153	0.38	ns	0.217
Eu	0.288	*	0.056	0.423	*	0.191	0.479	*	0.233
Fe	0.264	*	0.206	0.088	ns	0.030	0.294	ns	0.058
Hf	0.233	*	0.114	0.278	ns	0.160	0.393	ns	0.118
K	0.170	ns	0.269	0.094	ns	0.193	0.363	ns	-0.100
La	0.039	ns	0.020	0.346	*	0.327	0.366	ns	0.019
Lu	0.116	ns	0.001	0.690	* *	0.575	0.691	* *	0.115
Mg	0.000	ns	0.001	0.115	ns	0.116	0.116	ns	-0.000
Mn	0.003	ns	0.118	0.411	*	0.527	0.529	*	-0.116
Na	0.297	*	0.004	0.773	* *	0.481	0.777	* *	0.293
Ni	0.035	ns	0.032	0.471	* *	0.468	0.503	*	0.003
Pb	0.264	*	0.013	0.470	* *	0.219	0.483	*	0.251
Rb	0.365	* *	0.089	0.336	*	0.061	0.426	*	0.275
Sb	0.016	ns	0.183	0.076	ns	0.242	0.259	ns	-0.166
Sc	0.304	*	0.203	0.137	ns	0.036	0.34	ns	0.101

Si	0.125	ns	0.231	0.000	ns	0.106	0.231	ns	-0.106
Sm	0.149	ns	0.055	0.383	*	0.289	0.438	*	0.095
Sr	0.053	ns	0.026	0.069	ns	0.042	0.095	ns	0.026
Ta	0.143	ns	0.044	0.682	* *	0.583	0.726	* *	0.098
Tb	0.168	ns	0.046	0.491	* *	0.369	0.537	*	0.122
Th	0.239	*	0.005	0.452	* *	0.218	0.457	*	0.234
Ti	0.115	ns	0.009	0.542	* *	0.436	0.551	* *	0.106
U	0.085	ns	0.000	0.211	ns	0.126	0.212	ns	0.085
V	0.002	ns	0.010	0.083	ns	0.091	0.093	ns	-0.008
Yb	0.109	ns	0.000	0.611	* *	0.502	0.611	* *	0.109
Zn	0.044	ns	0.037	0.097	ns	0.091	0.134	ns	0.007

**: $P \leq 0.05$; ***: $P \leq 0.01$; ns: no significant difference.

more strongly on sampling location than on elevation, except for K. Such location-to-location variation in soil metal concentrations might also contribute to the variation in plant metal concentrations as reported by Sheppard (1991).

4.4.3. Enrichment factors of selected elements in topsoils

Figure 4.1 presents EFs of 25-selected elements (As, Ba, Ca, Cd, Co, Cu, Eu, Fe, La, Mg, Mn, Na, Ni, Pb, Rb, Sb, Sc, Si, Si, Sm, Sr, Th, U, V, and Zn) in topsoils at three sampling elevations along the Roundtop Mountain slope. Elements were selected based on available data for elemental composition in the bedrock from Sutton (Colpron 1987). In general, EFs of elements (except Ba, Cu, Rb, and Sc) decreased with increasing elevation. Overall, the mean of EFs shows there may be significant element enrichment (EF ≥ 10) in topsoils for Cd, Rb, and Sb, and enrichment tendency (1 ≤ EF ≤ 10) for Ba, La, Pb, Si,

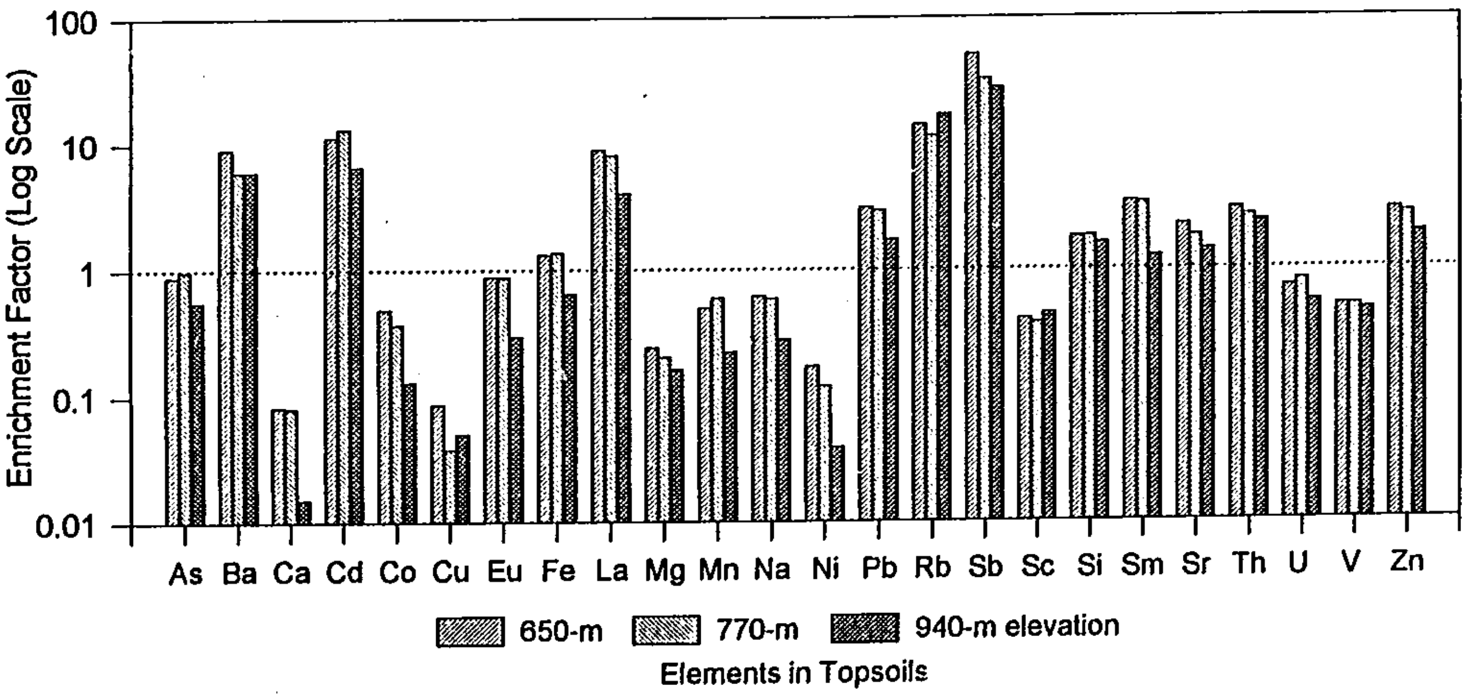


Figure 4.1. Enrichment factors of trace elements examined at the three sampling elevations along the Roundtop Mountain slope (semi-log plot).

Sm, Sr, Th, and Zn. Elements Fe and U were conservative in topsoils relative to the bedrock (EF ≈ 1). On the other hand, elements As, Co, Eu, Mg, Mn, Na, Sc, and V showed a tendency towards impoverishment in the top layer of soils ($0.1 \le EF \le 1$), which is even more pronounced for Ca, Cu, and Ni ($EF \le 0.1$).

A direct relationship has been demonstrated between elevation and the percentage of time that cloud/fog covered the forest on Roundtop Mountain (Schemenauer 1986). Soils on a transect from 520-m to 850-m elevations showed a pattern of soil solution chemistry that corresponds to the loading of acid deposition (Hendershot *et al.* 1992). The loading of K and Mn from atmospheric deposition was much higher at the 850-m elevation site of Roundtop Mountain than at the lower elevation sites (Hendershot *et al.* 1992). EFs of elements in topsoils also suggested potential effects of atmospheric deposition (*i.e.*, acid and metal pollutants) on the element enrichment (*i.e.*, Cd, Rb, and Sb) and leaching (*i.e.*, Ca, Cu, and Ni) along the SW slope of Roundtop Mountain. The enrichment of elements might result from element inputs from atmospheric deposition and element leaching from canopies (Petty and Lindberg 1990), but accelerated leaching from surface horizons might be linked to large amounts of acid precipitation, which increase the mobility of elements.

McKeague and Wolynetz (1980) documented the depletion and enrichment of microelements in Ah/Ae and B horizons relative to the C horizon of Podzolic soils. Their study showed levels of Cr, Mn, Co, Ni, Cu, Zn, and Pb were depleted in the Ae horizon compared to the associated B and C horizons, but more elements were enriched in the Ah horizon of soil profiles. In our study, the element distribution within soil profiles was only briefly examined at the 650-m and 770-m elevation sites of Roundtop Mountain. Since there was only one soil profile examined at each site with three soil layers, a proper statistical analysis could not be performed for conclusive results. Given the high expected variability in the field, the following comparisons are given for purposes of discussion only. Among the 34 elements, Mn and Fe showed consistent distribution patterns with highest levels in the second soil layers, while Ba and Si were highest in the third layers. Elements Cr, As, Cs, and Ta were most highly concentrated in the top soil layers. Other elements did not show any consistent differences between layers at both elevation sampling sites. The concentrations of elements Ba, La, Rb, Sb, Sm, Th, and Zn in the three sampling layers from the soil profiles at 650-m and 770-m elevations were much higher than the concentrations of the corresponding elements in the underlying bedrock (Sutton Schistes), while Co, Sc, V were lower and As, Eu, Sr, Ta, U were comparable. With application of enrichment factor calculation, only elements Cd, Pb, and Rb in the soil profiles showed a consistent tendency for accumulation in the upper soil layer at the two elevations, giving EF values of 16, 11, and 7 for Cd; 3, 0.7, and 0.7 for Pb; 12, 10, and 10 for Rb, in the 0-20, 20-40, and 40-60 cm soil layers, respectively, at the 770-m elevation.

4.5. Conclusions

Enrichment factors are generally used to determine the most likely origin of elements. The level of an element in soils might vary over orders of magnitude, but the EFs might remain close to the same value. The balance of enrichment versus leaching in topsoils might be element specific and affected by physical-chemical and biological characteristics in soils and subject to atmospheric acid and metal deposition. However, long-term studies of major and trace elements in soil profiles and direct measurement of metal deposition fluxes to forest soils at the research sites are needed in order to elucidate the effects of atmospheric deposition on element biogeochemical cycles in forest ecosystems.

CONNECTING STATEMENT LINKING CHAPTERS 4 AND 5:

Atmospheric long-range transport from anthropogenic sources and metal deposition to forest ecosystem result in metal contamination in forest soils. The study in Chapter 4 shows that accumulation of metal pollutants in topsoils is element specific. Enrichment of Pb and depletion of Mn in topsoils indicate that the mobility and plant availability of metal elements in soils may be significantly affected by acid deposition. In particular, Al and Mn in soils may reach the toxic level for forest physiological processes, as indicated by Smith (1990). In Chapter 5, uptake and accumulation of metal elements in trees will be examined, and the amount of metal deposits on foliar surfaces will be estimated, especially as a function of elevation. This is an essential part of any overview of metal contamination in the air-soil-plant system in high elevation forests; it should help to establish the contamination background of trace metals in high elevation forests of southern Quebec.

CHAPTER 5. TRACE METAL CONTAMINATION IN AND ON BALSAM FIR FOLIAGE

5.1. Abstract

Atmospheric trace metal contamination in and on forest foliage in southern Quebec has been investigated. Washed and unwashed foliage of balsam fir from seven sampling sites with different elevation were analyzed by INAA. Metal element concentrations in needles were generally below the suggested levels of potential phytotoxicity, except for Mn where concentrations exceeded 600 mg kg^{-1}. The variability of metal concentrations between individual trees at a given site showed the expected element-specific differences, with most CV's < 50%. The variation of metal deposits on needle surfaces (ng cm^{-2}) with elevation and sampling site depended on the element concerned. The input of Al, As, Cr, La, Sb, Sc, Sm, and V, accompanying Fe in deposits on the foliage surface, may mainly come from atmospheric deposition in the form of soil dust and air pollution.

5.2. Introduction

Air pollution is considered to be one of several potential contributor to the decline of conifers in high elevation forests of eastern North-America (Vogelmann *et al.* 1985; Mclaughlin *et al.* 1990). Since these forests are expected to be subject to significant deposition of metal pollutants (Petty and Lindberg 1990; Jeffries and Snyder 1981), including a potentially significant contribution from fog/clouds (Barrie and Schemenauer 1989), it is important to understand the link between atmospheric metal deposition and foliar uptake and accumulation. The effect of acid input may not only be observed in increasing the mobilities of most metal elements in soil for root uptake, but also in changing the elemental mobility in surface deposits and the foliar surface properties, which may affect foliar absorption particularly for high elevation forests (Johnson and Siccama 1983).

Foliage analysis has been used as a valid indicator of air contamination (Landolt *et al.* 1989). The accumulation of pollutant elements at foliage surfaces is considered to be very important in our understanding of hypothesized contributing factors to the forest decline (Simmleit *et al.* 1986). The properties of aerosol particles adhering to Norway spruce needle surfaces have been extensively studied (Wyttenbach *et al.* 1985, 1987a; Simmleit *et al.* 1989). Simmleit *et al.* (1986) concluded that the quantity of elements occurring on needle surfaces was directly related to their atmospheric concentrations and, therefore, a useful indicator of atmospheric metal deposition to forests.

Potential toxicity of atmospheric metal pollutants in the high elevation forests of eastern Canada cannot be judged adequately based on present knowledge (Santerre *et al.* 1990). As a first step towards an improved understanding of this potential problem, this paper explores current levels of metal contamination in and on coniferous foliage as a function of sampling location and site.

5.3. Observation Sites and Sampling Operations

5.3.1. Sampling sites

The sampling locations of Roundtop Mountain, Ste-Hippolyte, and White Peak have been previously described in Chapter 3 and 4. Three sampling sites at Roundtop Mountain were selected at 940-m, 770-m and 650-m elevation, respectively. The sampling site at the biological research station of University of Montreal at Ste-Hippolyte is at 345-m elevation. There were two sampling sites from the White Peak location at 825-m and 300-m elevation.

All these sites coincided with those for soil sampling (Chapter 4). In addition, one sampling site was chosen at 40-m elevation in the Morgan Arboretum of McGill University, in the near-urban SW corner of Montreal Island. Two highways are approximately 1 and 1.5 km SW from the sampling site in a managed forest stand. Soils are Luvic Gleysols.

5.3.2. Sampling operations

Balsam fir foliage samples were collected from May 30 to June 2, 1990, after more than 30 days of fair meteorological conditions (*i.e.*, no strong wind or high precipitation), at the four locations mentioned above. Meteorological conditions during the 30 days preceding the sampling dates are summarized in Table 5.1. The time of the last precipitation event and the precipitation amounts differ between the various sampling locations, which may have led to differences in element leaching from foliar surfaces, but would not likely have had a significant effect on wash off of surface deposits due to the low precipitation densities. Samples from each tree consisted of more than 20 shoots, and at each site 5 to 10 mature trees were sampled. Shoots were from branches near the middle part of the canopy (about 5-6 m above ground), on the prevailing wind (SW) side of each tree. Supplementary foliage sampling at Roundtop Mountain only was also executed in June 1991.

5.4. Experimental Methods and Quality Control of Analysis

5.4.1. Sample preparation

One-year (12 months) old shoots were separated from the branches, and randomly divided into two groups. One of these was agitated vigorously in a 1 L bottle for 30 s in about 200 ml of chloroform, followed by double rinsing with distilled deionized water

Table 5.1. Meteorological observations during the 30 days preceding the sampling date at four sampling locations.

Sampling Location	Roundtop Mtn.	Morgan Arboretum	Ste. Hippolyte	White Peak
Sampling Date	May 31, 1990	May 30, 1990	June 1, 1990	June 2, 1990
Total Rainfall (days with >1 mm)	17.4 mm (May 25, 27-29)	78.8 mm (May 5, 10-13,15,17-19, 21)	85 mm (May 6, 10-11,15,17-19, 21,27)	6 mm (May 23, Jun. 2)
Last Rain Event	0.4 mm (May 30)	0.8 mm (May 25)	2.0 mm (May 27)	2.0 mm (Jun. 2)
Wind Direction	SW	SW	SW	SW
Wind Speed (m/s)	4.9 (± 1.7)	3.9 (± 1.9)	1.8 (± 1.3)	6.2 (± 2.8)

(Riederer 1989; Wyttenbach *et al.* 1985). Samples were dried at 80°C for 48 hrs and stored in plastic bottles.

Attention to foliage washing procedures has been shown to be crucial in studies designed to distinguish external from internal tissue composition (Dasch 1987; Lindberg and Lovett 1985; Schuepp *et al.* 1988; Smith 1973). The chloroform has been used to remove the wax coating of the needles of Norway spruce without significant element leaching (Wyttenbach *et al.* 1985). In this study, the efficiency of the washing procedure for balsam fir needles was investigated under a scanning electron microscope (SEM), as illustrated by the scanning electron micrographs (Figure 5.1).

Figure 5.1. Scanning electron micrographs of the surface of balsam fir needles. (A), unwashed needle; (B), needles washed in chloroform solution.

5.4.2. Metal element analysis

Needle samples (about 1 g each) were analyzed for multi-element composition by INAA in the SLOWPOKE reactor of the École Polytechnique at Montreal. Samples were irradiated at a flux of 4.9 x 10^{11} n cm^{-2} s^{-1} for 40 s for short decay elements, and at a flux of 3.9-4.4 x 10^{11} n cm^{-2} s^{-1} for approximately 7-8 hrs for long decay elements. The γ spectroscopy was done by Ge(Li)-detectors, with counting times between 10 min and 4 hrs, after decay times varying from 120 s to 10 d. Final results (mg kg^{-1}) were produced by the software EPAA.

As a help in interpreting metal concentrations in foliage, extractable Mn, Fe, Zn, and Ni in forest soil were determined with 0.1 M HCl extracting solution by atomic absorption spectrophotometer (AAS) (Robarge and Fernandez 1986). The projected leaf area of needles from the sampling sites was estimated by a Delta-T area meter with Ikegami scanning system. About 50 - 100 needles per tree were determined to constitute a sufficient sample size for area estimates within an expected accuracy of 4% (Hungerford 1987). Such estimation was on the basis of their empirically established ratios to dry biomass (cm^2 g^{-1}), recorded for each tree at the sampling site. The ratios ranged from 41.3 cm^2 g^{-1} (Morgan Arboretum) to 57.6 cm^2 g^{-1} (Roundtop Mountain, 650-m), with an approximate error < 10 % at each sampling site.

Inter-element relationships were examined by principal component analysis (PCA), by PRINCOMP procedure of SAS with standardized raw data and R-mode. Ordination is often used as a method of clustering, and PCA is the most powerful technique for reduced-space ordination (Legendre and Legendre 1983). The two dimensional plot in this study will show the loading of the first two eigenvectors on different elements. As a multivariate technique for examining relationships among several quantitative variables, PCA has been used in revealing the inter-element relationship in spruce foliage (Landolt *et al.* 1989).

5.4.3. Analysis quality control

The NBS-SRM 1575 (pine needle) was measured with each batch of INAA measurements. Mean measured concentrations by INAA for all stated elements were located within two standard errors of the mean of the certified composition values of the standard reference materials (SRM). Paired comparisons of t-tests showed no significant difference between the two groups of values ($P \leq 0.05$).

The precision of the INAA measurement in this study was further explored through the coefficients of variability (CV) from triplicate measurements of a homogenous ground unwashed needle sample. The CV for Mg, Al, Mn, Cu, Cd, V, Zn, K, Na, Sb, La, Rb and Cs were < 5 %. The elements Ca, As, Sm, Co, Ba and Ni showed 5 % < CV < 10 %, and elements Th, Sr, Fe, Hg, W and Cr 10 % < CV < 21 %.

5.4.4. Variation of elements within a sampling site and the sampling uncertainty

The variation of element concentrations in washed needles among five trees from a given sampling site was investigated at the Roundtop Mountain location. The in-site variability can be divided into three categories: (1) CV < 20 %: K, Na, Mn, Mg, Zn, Al, Hg, Ni, Fe; (2) 20 % < CV < 50 %: V, Cd, As, Sr, La, Sb, Rb, Ba, Co, Cs; (3) CV > 50 %: Sm, Sc, Mo, Th, Cr, W. The variation of element concentrations in washed needles from four different branches on the same sampled part of a tree crown was also examined. In this case the variability could be subdivided into the following groups: (1) CV < 10 %: Al, Ba, Co, Fe, K, La, Mn, Rb, Sm, Sr, W, Zn; (2) 10 % < CV < 20 %: As, Hg, Na, Sb; (3) CV > 20 %: Cd, Cr, Ni, Sc, V.

The high variability for the last category of elements is undoubtedly attributable, to a large degree, to the small concentrations involved, reflecting various combinations of environmental and biological factors. The variability of elements in the sampling site is comparable to that reported in the literature for Norway spruce (Wyttenbach *et al.* 1985) and the sampling uncertainty is considered to be acceptable.

5.5. Results and Discussion

5.5.1. Concentrations of metal elements in foliage at different sites

Given the presumed variability of surface deposition, and in order to establish a baseline reference for current levels of metal contamination in southern Quebec, pooled needle samples were analyzed for each of the 1990 sampling sites. Equal weight of ground foliage sample was used from each sampled tree at each site.

The results shown in Table 5.2, with 25 elements, indicate that most of the element concentrations in the washed needles were below the suggested potential toxic concentrations of the elements (*e.g.*, As, 5-20; Cd and Cr, 5-30; Mn, 300-500; Ni, 10-100; V, 5-10; Zn, 100-400 mg kg^{-1}) in mature leaf tissues, as generalized for various species (Kabata-Pendias and Pendias 1992). A significant exception is Mn where concentrations in washed needles at the three rural regions reached approximate levels of 600 mg kg^{-1} in average. The high levels of Mn were confirmed by the 1991 sampling at Roundtop Mountain, which showed Mn concentrations up to 877 mg kg^{-1} in washed needles and 896 mg kg^{-1} in unwashed needles. These values clearly exceed the 286 mg kg^{-1} reported in a study on balsam fir in the maritime region of eastern Canada (Langille and Maclean 1976), and the suggested potential toxic level of 500 mg kg^{-1} (Kabata-Pendias and Pendias 1992; Adriano 1986). Mn toxicity in acidic soil could be an important growth-limiting factor (Foy

Table 5.2. Element concentrations in washed, 12 month old balsam fir needles at different sampling sites and elevations, during the sampling period of 30 May - 2 June, 1990. Values below the detection limits are shown with a < sign.

Sites	Roundtop Mountain (RT)			MA [a]	SH [b]	White Peak (WP)	
	650 m	770 m	940 m	40 m	345 m	300 m	825 m
	mg kg^{-1}						
Al	120	111	86	88	116	91	169
As	0.006	0.005	0.008	0.004	0.003	0.002	0.008
Ba	19.7	9.7	4.6	98.6	54.6	45.5	16.6
Ca	4497	3763	3529	9147	5479	4931	3529
Cd	0.16	0.09	0.15	0.10	0.09	0.10	0.13
Co	0.036	0.036	0.022	0.036	0.024	0.028	0.009
Cr	0.05	0.06	0.05	0.12	0.03	0.06	0.05
Cs	0.048	0.085	0.272	<0.004	0.074	0.059	0.099
Fe	23.5	23.9	24.4	28.2	17.0	20.3	30.1
Hg	0.014	0.009	0.009	0.016	0.008	0.005	0.010
K	4751	4567	3753	4557	4470	4354	4068
La	0.010	0.004	0.006	0.045	0.005	0.006	0.004
Mg	624	671	751	1541	743	745	647
Mn	443	466	602	191	586	556	705
Na	5.6	5.5	4.8	7.3	3.7	1.6	2.1
Ni	2.5	3.4	3.4	1.3	1.1	0.9	2.0
Rb	8.5	13.1	11.7	1.5	7.1	10.2	9.5
Sc	0.0008	0.0006	0.0010	0.0017	0.0007	0.0006	0.0006
Sb	0.003	0.001	0.007	0.003	0.002	0.001	0.002
Sm	0.0008	0.0006	0.0009	0.0046	0.0006	0.0006	0.0006
Sr	8.2	6.8	2.8	40.5	25.1	15.9	5.9

Th	<0.002	<0.002	<0.002	0.006	<0.002	<0.002	<0.002
V	<0.03	<0.03	0.04	<0.03	<0.03	<0.03	<0.03
W	<0.002	0.007	0.009	0.002	<0.002	<0.002	0.002
Zn	41.2	36.5	35.9	53.7	47.8	46.0	36.1

a: Morgan Arboretum
b: Ste-Hippolyte

and Campbell 1984; Smith 1990). However, since Mn levels equally high or higher had been found in balsam fir needles, such as 1180 mg kg^{-1} in one-year old needles (rinsed in double distilled water) from the Montmorency Experimental Forest of northwest Quebec City (Allaire *et al.* 1973), the question of Mn effective toxicity threshold, particularly for the physio- and bio-chemical processes, and the Mn tolerance of balsam fir has yet to be resolved (Horst 1988).

5.5.2. Metal concentrations in needles with elevation at Roundtop Mountain and at White Peak

The data in Table 5.2 suggest elevation-dependent variations in metal concentration in the needles. At the two locations where observations are available at more than one elevation (locations RT and WP), the concentration of Cs, Mn, and Ni increased, while the concentration of Ba, Ca, Co, Sr, K, and Zn decreased, as a function of elevation. The remaining elements in Table 5.2 show no consistent tendency with elevation at the two locations. The increase of wet acid deposition with altitude, due to increased fog/cloud immersion above the condensation level (cloud base) of approximately 600 m, has already been demonstrated at the Roundtop Mountain (Schemenauer 1986; Schemenauer *et al.* 1988); it appears to be linked to changes in soil chemistry (Hendershot *et al.* 1992) and to decrease in pollen viability (Comtois and Schemenauer 1991). The question arises whether or not changes on in-foliage concentrations with elevation could be related to local differences in acid deposition, affecting root uptake, or deposition on the foliage.

Mn is one of the elements with increased concentration at the higher sites. The results of our soil analysis (Table 5.3) at the various sampling sites showed no consistent tendency for extractable Mn concentration in the top layer of the soil to increase with elevations; an increase is indicated at White Peak, but at Roundtop Mountain the extractable Mn was lowest at the highest elevation. No significant trend of soil pH was apparent, but organic matter and cation exchangeable capacity likely decreased with altitude (Table 4.1). On the basis of our observations, it is difficult to explain the high Mn concentrations in balsam fir foliage at the higher elevations in terms of soil chemistry, especially since more Mn must be expected to be leached from an acidic soil profile in summer. However, they may be related to high bio-availability of Mn in topsoils, as well as to large input of Mn from atmospheric deposition. A precise prediction of plant available Mn in soils and the transport of Mn within plants is complex (Reisenauer 1988), including the effect of Si concentration in plants (Horst 1988). Since the absorption of Mn by trees may be increased by H^+ input (Wyttenbach *et al.* 1991), the high Mn concentrations in needles, therefore, might be not only related to root uptake from the soil but also probably to foliar uptake from atmospheric deposition (Loneragan 1988). Considering such factors, the response of metal element availability in soil to atmospheric acid input, and the element concentration in foliage as a function of altitude, possible seasonal fluctuation (Hendershot *et al.* 1992) and topographical effects, have yet to be fully explored, especially for older needles which may more likely exhibit correlations with soil chemistry.

Table 5.3. Extractable Mn, Fe, Zn, and Ni concentrations (0.1 M HCl) in topsoils. Soil samples were collected in the summer of 1992.

	Roundtop Mountain			White Peak	
	650-m	770-m	940-m	300-m	825-m
Mn (mg kg^{-1})	17.15 ± 5.30	13.58 ± 8.36	1.77 ± 0.57	3.35 ± 1.32	5.55 ± 1.90
Fe (g kg^{-1})	1.15 ± 0.29	0.85 ± 0.27	0.70 ± 0.11	0.74 ± 0.17	1.00 ± 0.13
Zn (mg kg^{-1})	5.88 ± 0.44	3.17 ±1	1.96 ± 0.38	5.26 ± 0.89	2.59 ± 0.45
Ni (mg kg^{-1})	2.81 ± 0.13	1.32 ± 0.10	0.68 ± 0.17	0.88 ± 0.14	0.85 ± 0.11

5.5.3. Element deposits on the needle surface at different locations

Surface deposits of trace metal elements at the time of sampling may be inferred from differences in concentration between washed and unwashed samples (Codzik *et al.* 1979), at least for elements with significant ($P \leq 0.01$) differences in concentration between washed and unwashed samples, including Al, As, Cr, Cs, Fe, La, Sb, Sc, Sm, Th, and V. For other elements like Mn and Zn, their surface deposits will be investigated through other techniques as described in the following chapter. Obviously, the surface metal deposits do not represent the total amount of elements deposited during the period of exposure, partly because of post-deposition transfer and exchange processes, such as foliar absorption and rinse-off by precipitation. Estimates of surface deposits refer to the net accumulation (ng or µg) per unit projected leaf area (cm^2) washed off at the time of sampling.

Observation of surface deposits as derived from the statistically significant differences in concentration between washed and unwashed needles at the given four locations (low elevation sites at Roundtop Mountain and White Peak for the sake of consistency) are illustrated in Figure 5.2 for six selected elements, which reflect the general trend found in this analysis within the same scale of absolute values. There is apparent uniformity among the three mountainous sites for As, Th, and Sb. The near-urban Morgan Arboretum site was highest for As, Sb, La, Sc (shown in Figure 5.2), V (3.15 ng cm^{-2}), Cr (4.36 ng cm^{-2}), Al (0.92 µg cm^{-2}), and Fe (0.87 µg cm^{-2}\ (not shown in Figure 5.2). Among the three rural forest regions, White Peak had the highest deposits in As, La, Cr (4.08 ng cm^{-2}), Sm (0.09 ng cm^{-2}), Al (0.74 µg cm^{-2}), and Fe (0.59 µg cm^{-2}). It should be indicated here that there are differences in the amount of precipitation and length of dry periods before the sampling date at the four locations (Table 5.1). Therefore, Figure 5.2 should be viewed only as a representation of the level of accumulated metal deposits on the foliar

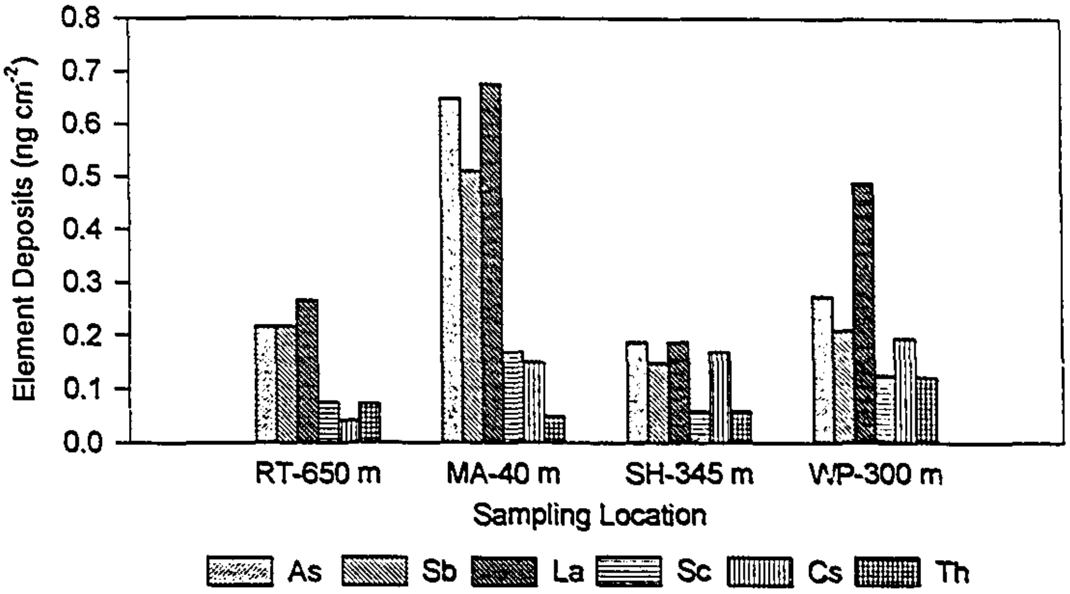


Figure 5.2. Element deposits on needle surface of one-year old balsam fir as a function of sampling location.

surface at the time of sampling, at locations that may be considered to be typical for southern Quebec. The higher level of As, Sb, V, and Sc at Morgan Arboretum may reflect local contamination from the two highways close to the sampling site.

5.5.4. Element deposits on the needle surface at different elevations

The comparison of pooled samples from different elevations at locations Roundtop Mountain and White Peak showed little systematic variations in element concentration with height. Results for As, Sb, La, Sc, Cs, and Th are shown in Figure 5.3. In general, at both locations, only the concentration of Sb and V showed any tendency to increase with height. At Roundtop Mountain, elements in the deposits showed extreme concentrations at the middle height of 770-m elevation (*e.g.*, minima for As, La, Sc, Th, Cr, Al, Fe and maximum for Cs). The general validity of these observations would have to be established through

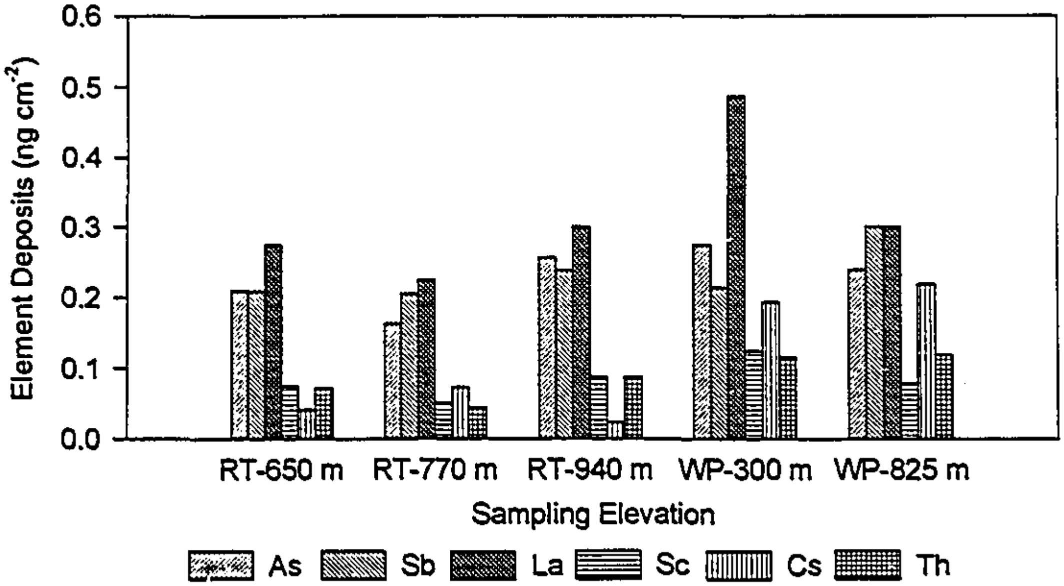


Figure 5.3. Metal deposits on needle surface of one-year old balsam fir as a function of sampling elevation at Roundtop Mountain and at White Peak.

further sampling. Element concentrations in washed balsam fir needles generally followed the trend with height shown by these surface deposits (Table 5.2). Considering that the fog/cloud immersion time increases with altitude at the Roundtop Mountain location (Schemenauer 1986), a calculation in the manner of Hendershot *et al.* (1992) would yield a Mn wet deposition five times higher at 850-m than at 520-m. This constitutes an interesting parallel to our observation which showed higher concentrations of Mn in balsam fir needles at high altitudes.

Since most elements appear in higher concentrations in fog, one would expect all elements to be present in higher concentrations at higher altitudes, if deposition and incorporation mechanisms were the same. This is not the case as we have seen (Figure 5.3). Discrepancies may be due partly to the elevated concentrations usually associated with the condensation level (cloud base), and very likely to different surface attachment and/or uptake characteristics of different elements.

5.5.5. Inter-element relationships in and on balsam fir foliage

Inter-element relationships among 11 elements which showed significant differences in concentration between washed and unwashed needles are revealed in Figure 5.4 by principal component analysis (PCA). Shown are scatter plots of the first two eigenvectors, for the washed needles and the deposits within seven sampling sites. The first two principal components account for 70.7% and 64.7% of the standardized variance in washed needles and in the deposits, respectively.

Comparing Figures 5.4 (a) and 5.4 (b), significant changes in element grouping are apparent, reflecting different inter-element relationships in and on the needles. This may suggest, in turn, significant differences in post-deposition pathways between the various elements (which may also be associated with different particle sizes), in processes of diffusion, metabolism and physical removal by wind and wetness. The most uniform cluster appears to be grouped around Fe in the deposits. Elements such as Al, As, Cr, La, Sb, Sc, Sm, and V, grouped with Fe in Figure 5.4 (b), could then perhaps be considered to originate from the same atmospheric deposition sources in the form of local soil dust (Wyttenbach *et al.* 1987b), and air pollution through atmospheric long-range transport (Hallet *et al.* 1984; Keller *et al.* 1986).

5.6. Conclusions

The variability of metal concentration in balsam fir needles among individual trees at a given site showed the expected, element-specific differences, with most CV's < 50%. Analysis by INAA of pooled needle samples among different locations in southern Quebec

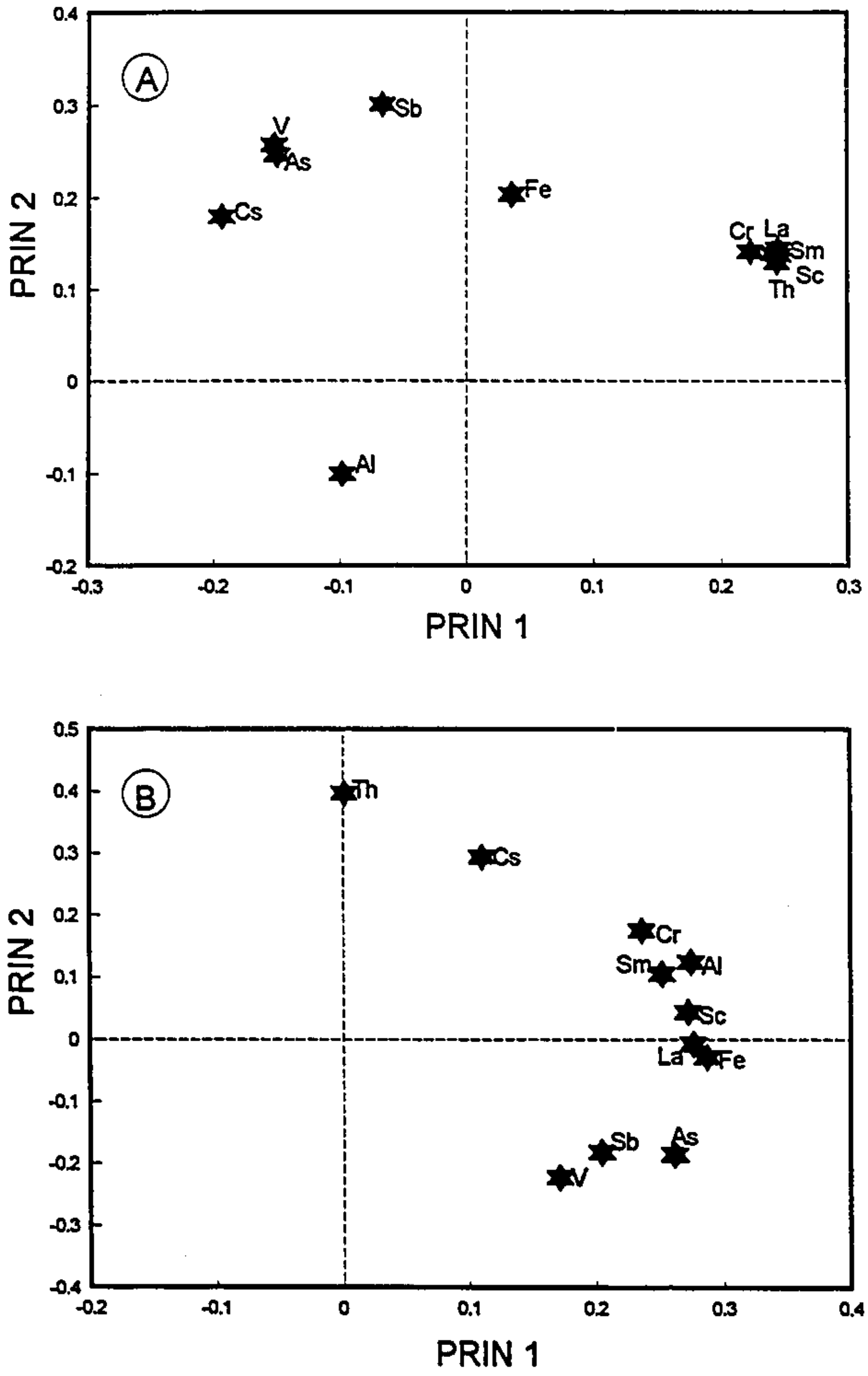


Figure 5.4. Inter-elemental relationships in (a) washed balsam fir needles, and (b) in deposits on balsam fir needle surfaces, shown by the first two eigenvectors from a principal component analysis.

exhibited location-specific element concentrations generally below the suggested levels of potential phytotoxicity generalized for various species, with the exception of Mn, where those levels were often exceeded. Manganese concentration in the washed needles showed a tendency to increase with elevation. This may possibly be the result of increased atmospheric deposition at higher elevations, for which some indirect evidence is given. It may also be linked to acid-induced increase in mobility of Mn ions in soil, corresponding to the higher incidence of acid fog (cloud) with height, although the soil analysis at the sampling sites did not permit confirmation of this hypothesis. The potential effect of biogeochemical processes on the high Mn concentrations in foliage remains to be more fully explored.

Significant ($P \leq 0.01$) differences in concentration between washed and unwashed samples were observed for Al, As, Cr, Cs, Fe, La, Sb, Sc, Sm, Th and V. The resulting estimates of deposits (ng or µg cm^{-2}) on balsam fir needles for these elements showed element-dependent variations with elevation, and between locations with different degrees of exposure. The near-urban Morgan Arboretum location was highest for As, Sb, La, Sc, V, Cr, Al, and Fe. Only the concentration of Sb and V showed any tendency to increase with height at both locations. PCA suggested that the input of elements such as V, Sb, As, Sc, Sm and Al, accompanying Fe in deposits on the foliar surface, may derive from the same atmospheric deposition sources. It is difficult to generalize findings from multi-element analysis on the basis of our present state of knowledge, because the pathways following surface deposition must be expected to be element-specific.

CONNECTING STATEMENT LINKING CHAPTERS 5 AND 6:

Accumulation of metal elements in foliage should probably be seen as a potential long-term process. Current levels of contamination for elements examined in Chapter 5 appear to be generally below the suggested levels of acute toxicity generalized for various species, with the notable exception of Mn. Chapter 5 also shows evidence for significant surface deposition of metal elements in terms of characteristic differences between concentrations in washed and unwashed needles. In order to improve our understanding how surface deposits might contribute to metal accumulation in foliage, the characteristics of surface deposits and spatial distribution of metal elements on the surface of balsam fir needles, with particular consideration of the effects of acid deposition, will be examined by scanning electron microscope (SEM) and micro proton-induced X-ray emission (PIXE) in the next Chapter.

CHAPTER 6. SURFACE DEPOSITS AND SPATIAL DISTRIBUTION OF TRACE METALS ON BALSAM FIR FOLIAGE

6.1. Abstract

Deposited substances and spatial distribution of trace metals on the surface of balsam fir needles in southern Quebec have been investigated by scanning electron microscope (SEM) and micro proton-induced X-ray emission (micro-PIXE), respectively. SEM observations showed fungi, which have been hypothesized to play a role in metal movement and accumulation at foliar surfaces, mostly on the surfaces of two years old and/or older needles at low elevation sites, but on the foliar surface of all age classes at higher elevation sites. Metal contaminations at adaxial foliar surfaces, as examined by micro-PIXE with scanning depth of 3-4 µm and scanning spacing from 15 to 250 μm^2, were significantly ($P \leq 0.05$) higher at the near-urban site than at the mountainous location for Al, Si, Ca, Ti, Fe, and Zn.

Accumulation of Mg, Al, Si, K, Mn, Fe, and Zn was significantly ($P \leq 0.01$) higher at surfaces of unwashed as compared to chloroform-washed needles, which shows significant metal accumulation in/on epicuticular wax layers. Metal deposits, except Mn, in epicuticular wax layers were significantly affected by washing with acidic solution. Distributions of Mg, K, Mn, and Zn deposits at the surface were lower around central regions than near foliar edges, while Si was higher around the central area. Scanning to the 45-50 µm depth showed significant accumulation of Ni on either side of the foliar centre groove.

6.2. Introduction

Concern over the biological significance of metal deposition to forests stems from the potential long-term accumulation of trace metals in forests and their known biotoxicity (Smith 1990). Accumulation and distribution of atmospheric metal elements deposited on forest surfaces are primarily dependent on the metal concentrations in air (Simmleit *et al.* 1986), the deposition pathways (Barrie and Schemenauer 1986) and the surface structures (Chamberlain 1975; Riederer 1991). The surface structures of foliage vary under different growing conditions (Franich *et al.* 1978), and the degradation of foliar surfaces is enhanced by air pollutants (Percy and Riding 1978). Günther and Wortmann (1966) reported that plant surfaces covered with epicuticular wax were less contaminated by deposited particles than those without wax. Substances on needle surfaces have generally been observed in the following four categories: (1) mineral dust, most likely associated with local, wind-driven sources; (2) aerosol particles, possibly from long range transport in atmospheric deposition; (3) spores, pollen grain, fungal hyphae and other biological substances (*e.g.*, bacteria and viruses), and (4) epicuticular fragments and wax deposits.

While large surface deposits (> 1μm in size) are easily washed off from foliage by precipitation, aerosols or sub-micron particles might be adsorbed and embedded in degraded epicuticular wax layers or in epistomatal chambers (Eglinton and Hamilton 1967; Simmleit *et al* 1989). Substantial amounts of metal elements have been found on the surface of Norway spruce needles by chloroform extraction after washing the needles in water (Simmleit *et al* 1986). Overall, elemental composition of surface deposits on Norway spruce needles has been investigated by electron probe microanalysis (Grill and Golob 1983), X-ray photoelectron spectroscopy (Simmleit *et al.* 1989), and the extraction of epicuticular wax layers from needles in organic solutions (Wyttenbach *et al.* 1994). By directly scanning needle surfaces, Grill and Golob (1983) reported significant differences in concentrations of Na, Mg, Al, Si, P, S, K, Ca, Mn and Fe at needle surfaces from environments with different levels of air pollution. In the semi-quantitative XPS analysis of Simmleit *et al.* (1989), the adsorbed particles on spruce needle surfaces were found to consist mainly of organic materials, with Si, Al and Pb accounting for 3%, 1% and 0.01% (on a mass basis), respectively, and Fe and Mn only present in trace amounts.

Acid fog deposition has been observed to affect metal input from the atmosphere to high elevation forests in southern Quebec (Barrie and Schemenauer 1986, 1989). Balsam fir has been found with greater fog deposition on the upper than the lower surface, but with least efficiency in fog collection compared with red spruce and Norway spruce (Jagels 1991). Considering that such disparity is mainly due to differences in the surface structure and needle orientation, the concentration and spatial distribution of metals deposited on balsam fir needles must be further explored when pathways of metal deposits are to be considered in such forests co-dominated by balsam fir and red spruce (Lin *et al.* 1995b).

The PIXE (proton induced X-ray emission) technique with micro-scanning facility is ideally suited for the study of spatial distribution of metal pollutants on forest surfaces (Hinrichsen *et al.* 1988; Campbell *et al.* 1993). Micro-PIXE has been used in determining the element concentrations at different depths below apple skin (Meyer *et al.* 1982) and the elemental distribution within roots by line-scanning along the diameter of the cross section (Makjanić *et al.* 1988). By scanning needle surfaces with micro-PIXE, our study determined metal concentrations in and on epicuticular wax layers, characterized their relationship with surface microstructure, especially the distribution of stomata. It also evaluated the effects of simulated acid rain on accumulation and distribution of metal deposits in/on epicuticular wax layers at the surface of balsam fir needles.

6.3. Materials and Methods

6.3.1. Site description and sampling

Roundtop Mountain and the Morgan Arboretum have been previously described, with characterization of soil and tree species (Lin *et al.* 1995b). The reported 1985-1991 mean pH in fog at the 845 m elevation of Roundtop Mountain was 3.9 (Schemenauer *et al.* 1995), while the Morgan Arboretum site had an annual pH of 4.3 to 4.4 in precipitation (Delisle 1990). Median age of sampled mature trees was approximately 100 yrs at the Roundtop site and about 30 yrs at the Morgan Arboretum, with median tree heights of 7-8 m and 10-11 m, respectively, at the two sites.

Sampling was carried out on October 15-16, 1993, at the 840 m elevation of the mountain site and at the Morgan Arboretum. Shoots were collected from branches near the middle part of the canopy, about 5 m above ground, on the side of prevailing wind direction (SW) and stored in plastic bottles. The meteorological observations for the 30 days preceding the sampling date are summarized in Table 6.1, showing more precipitation at the Roundtop Mountain than at the Morgan Arboretum location.

Balsam fir needles are generally 300-350 µm thick, 1.4-1.6 mm wide and 18-22 mm long. Stomata are mainly distributed on the abaxial surface, with 6-8 rows on either side of the mid-rib (Figure 6.1). The thickness of the epicuticular layer is about 3-4 µm (Delucia and Berlyn 1984). Metal concentrations at the foliar surfaces were determined in samples from 12 trees at the Roundtop Mountain location and from two trees at the Morgan Arboretum. Two trees at Roundtop Mountain were selected for the study of spatial distribution of metal deposits, and one of them was used to examine effects of washing treatments on the accumulation of metal deposits in epicuticular wax layers.

Table 6.1. Meteorological observations during the 30 days preceding the sampling date (October 15-16, 1993) at the Roundtop Mountain and the Morgan Arboretum locations.

	Roundtop Mountain	Morgan Arboretum
Total Rainfall (mm)	127	58
Rain Events (>1mm)	Sept. 24,25, 27-29; Oct. 2-5, 7-9, 11,12	Sept. 16, 24, 27, 28; Oct. 2.
Wind Direction	SW	SW
Wind Speed (m s^{-1})	4.6 ± 1.3	3.2 ± 1.2

6.3.2. Sample preparation for SEM

The needles were air-dried and stored in a desiccator with silica gel. Dried needles were covered with Au in an AKASHI VEF vacuum evaporator, prior to observation in a Cambridge Stereoscan 600 scanning electron microscope with accelerating voltage of 7.5 kV. At least four needles were randomly chosen for scanning from each treatment in two replicates. Conclusions were drawn from scanning observation around the middle parts of needles and illustrated by typical pictures taken from the randomly selected surface areas.

6.3.3. Sample preparation for micro-PIXE

Each shoot was cut into four parts, which were then randomly assigned to remain unwashed or subjected to one of the following washing treatments: (a) distilled deionized water (DDW) of pH 5.7 for 60 s, (b) in simulated acid rain, a dilute solution of H_2SO_4 (66%), HNO_3 (24%) and HCl (10%), with pH 4.0 (Wood and Bormann 1977) for 60 s, and (c) in chloroform for 15 s. The procedures (a) and (b) were intended to examine the wash -

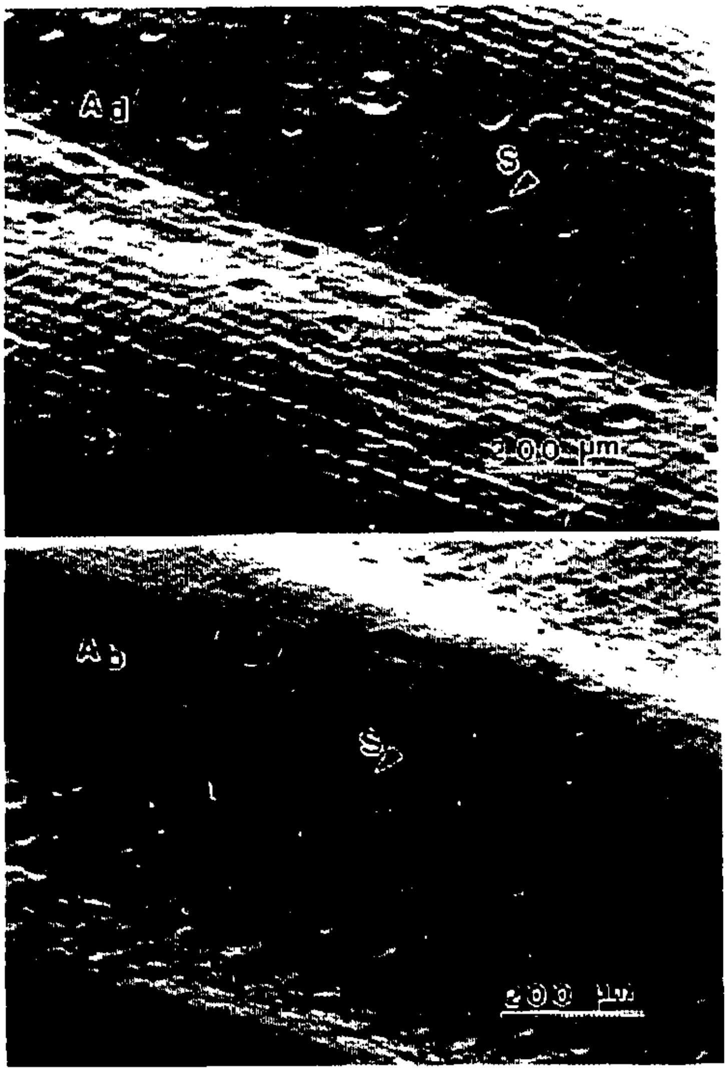


Figure 6.1. Scanning electron micrographs of adaxial and abaxial surfaces of balsam fir needles. Ad, adaxial surface; Ab, abaxial surface; S, stomata.

off of surface deposits in different acidity of washing solutions, and procedure (c) was used to determine accumulation of metal deposits on needle surfaces by removing epicuticular wax layers from foliar surfaces (Riederer 1991). Washed and unwashed shoots were air-dried in a desiccator with silicon-gel for at least 30 days. Needles removed from the shoot were attached to carbon disks (reactor grade, 2.5 cm in diameter and 0.5 cm in thickness) with conducting glue (*Q-Drop)*. Specimens were carbon-coated in an AKASHI VEF vacuum evaporator. Each treatment was replicated twice.

Knowledge of the magnitude of foliar element leaching is crucial in any attempt to distinguish surface deposits from internal element composition by needle washing (as previously indicated in Chapter 5); it was most likely negligible in this case, as will be shown at least for Mn and Zn from radioisotope studies in Chapter 8.

6.3.4. Micro-PIXE scanning

Micro-PIXE scanning lines were positioned across the needles, at the midpoint of needle length, with incident energies of 750 keV or 2.5-3.0 MeV. The acquisition of X-ray spectra from each scanning point required about 450 s at a beam current of 2.5 nA at 750 keV, and about 600 s at a beam current of 4.0-4.5 nA at 2.5-3.0 MeV. Scanning by 750 keV energy yielded the mean concentrations of Mg, Al, Si, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, As, Se and Ba down to the 3-4 µm depth from the needle surface, and the 2.5-3.0 MeV scanning detected element concentrations down to the 45-50 µm depth for Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Br, Rb, Sr, Sb, Te, Ba, Ti, Pb and Th. The precision of the micro-PIXE analysis at the sub-ppm level has been demonstrated by measurements of standard reference materials (Czamanske *et al.* 1993).

The size of proton beams (*i.e.*, scanning spacing) ranged from 15x20 μm^2 to 250x250 μm^2. Scanning lines on needle surfaces were examined by scanning electron microscope (SEM), in the attempt to relate the element concentration to the corresponding surface structure, particularly the stomatal distribution. Figure 6.2 shows the detectability of metal elements from the 750 keV and 3.0 MeV scanning. The detectability (%) is defined as the percentage of total scanned points that provided element concentrations above the

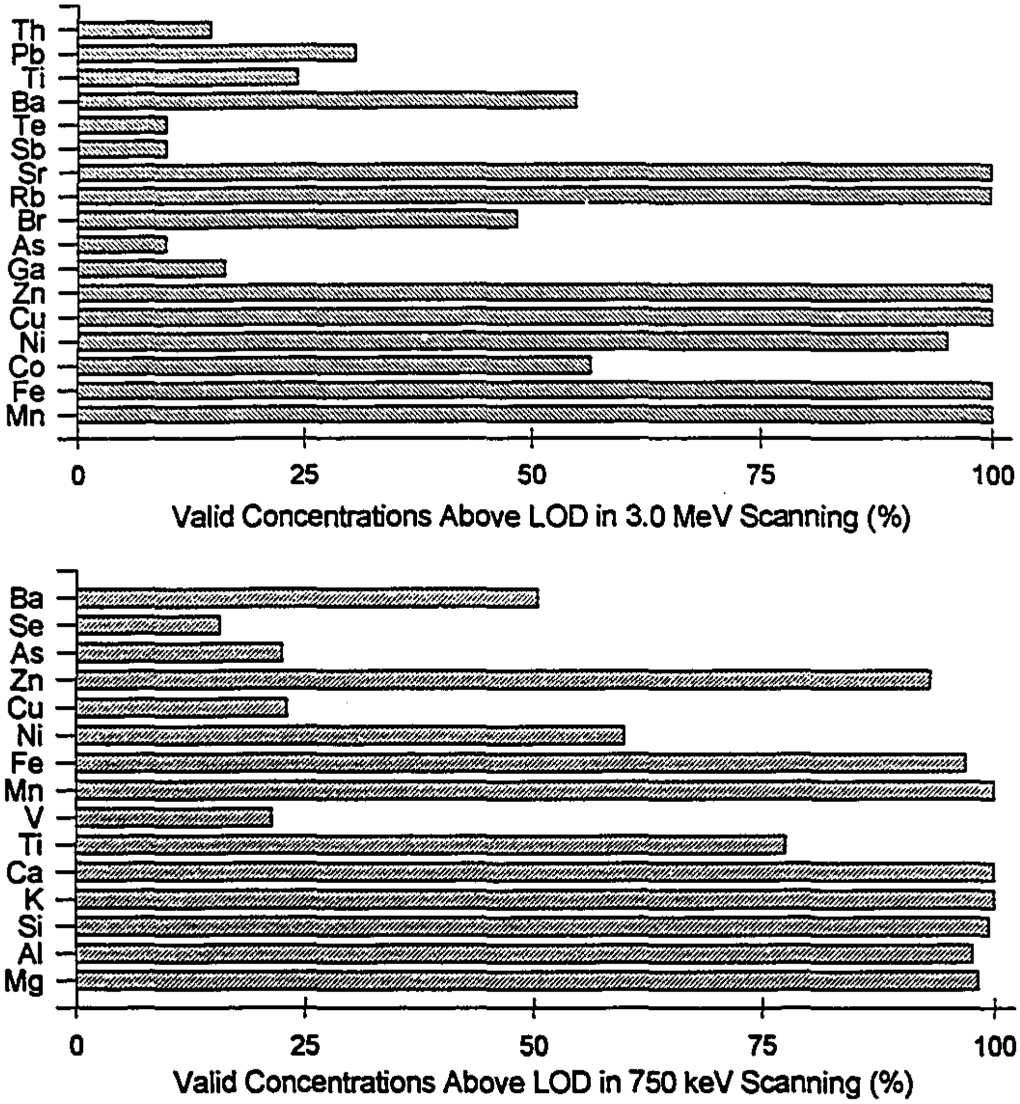


Figure 6.2. Elemental detectability by micro-PIXE scanning, showing percentage of total scanned points that provided metal concentrations above the limit of detection.

limit of detection (LOD). Only elements with more than 75% detectability are considered in our study, *i.e.*, Mg, Al, Si, K, Ca, Ti, Mn, Fe and Zn from the scanning with 750 keV; Mn, Fe, Ni, Cu, Zn, Rb and Sr from the 2.5-3.0 MeV scanning.

6.3.5. Statistical analysis

The inter-element relationship on unwashed adaxial surfaces of needles, for which most scanning was done, was examined by VARCLUS procedure in SAS (SAS Institute Inc. 1988a). Paired t-tests have been performed to examine significant differences between scanning depths and between treatments, and unpaired t-tests for differences between the two sampling locations.

6.4. Results and Discussion

6.4.1. Deposited substances on foliar surfaces

Epicuticular wax deposits, mineral crystals, spores and fungi could be easily found on unwashed needle surfaces (Figure 6.3). Deposited particles in the 15-20 µm diameter range could be retained in stomatal sub-cavities. Such particles might combine with wax deposits to occlude the stomatal chambers. Particles were less prevalent on the adaxial side of the needle than on the abaxial surface. On the needles with amorphous cuticular wax surfaces, fungi were mostly found on two- and three-year old needles, but the appearance of fungi on one-year old needles became more frequent above the 740-m elevation at Roundtop Mountain. Washing needles vigorously in 200 ml of DDW (pH 5.7) for 60 s in our study failed to show significant removal of fungi from needle surfaces. Fungi tended to be firmly attached to foliar surfaces and penetrated through epicuticular layers.

The relationships between variously sized particles, on remarkably diverse surfaces and under variable microclimate conditions, must be expected to be very complex. Little and Wiffen (1977) have demonstrated that the foliar surface texture was critical in particle capture efficiency with the rough surface more effective than the smooth surface. Surface characteristics such as the multi-faceted epicuticular texture found at the 940 m elevation

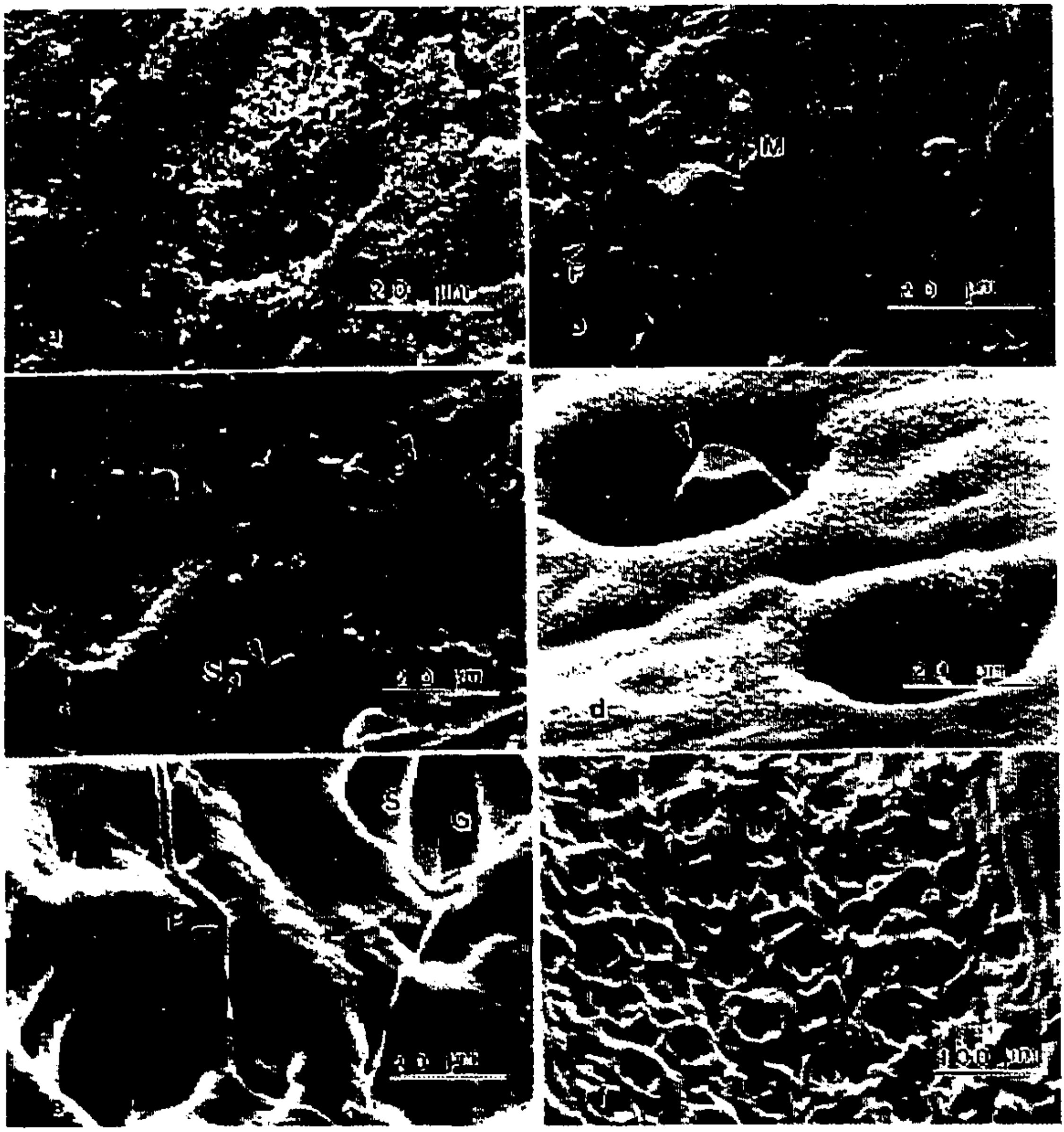


Figure 6.3. Surface deposits on balsam fir needles collected from Roundtop Mountain. F, fungi; G, guard cells; M, mineral dust; S, stomata; Sb, subsidiary cells; Sp, spore. (a) Wax deposits on adaxial surfaces; (b) Mineral crystals and fungi on adaxial surfaces; (c) fungi and spores on adaxial surfaces; (d) particles retained in stomatal chamber on the adaxial surfaces; (e) fungi on abaxial surfaces of needles washed in chloroform solution for 15 s, and (f) epicuticular topography on abaxial surfaces of needles washed in chloroform solution for 15 s.

site in this study, might be expected to increase the capture efficiency and to retain more deposited substances on needle surfaces (Wells and Chamberlain 1967). Effects of air pollution/acid deposition have been widely considered as predisposing factors. The subsequent fungal infection would be considered as a contributing factor. Penetration of fungi into needles would change or damage the barrier function of the epicuticular layer.

6.4.2. Metal concentrations at needle surfaces

Metal concentrations on adaxial surfaces of unwashed 17-month old needles from Roundtop Mountain and from the Morgan Arboretum, from 750 keV scanning (to depths of 3-4 μm) at 250 μm spacing, are summarized in Table 6.2. Significant ($P \leq 0.05$) differences in concentrations of Mg, Al, Si, K, Ca, Ti, Mn, Fe and Zn were found between the two sampling locations, with higher concentrations of Al, Si, Ca, Ti, Fe, Mn, and Zn at the near-urban sampling site than at the rural mountain site. These observations agree with previous findings in so far as analysis of surface deposits in Chapter 5 also showed Al and Fe deposits on foliar surfaces higher at the Morgan Arboretum location than at the mountain site.

Some heavy metals fell below the LOD, while others showed detectable concentrations above the LOD at least from a few scanning points, with maximum values of 238, 36 and 88 μg g^{-1} for V, Cu and As, respectively, at the Roundtop location, and 208 μg g^{-1} for Ni at the Morgan Arboretum site. These data are not included in Table 6.2. The LOD in micro-PIXE scanning to the 3-4 μm depth could be lowered by increasing scanning time and/or scanning energy. However, these options are not practicable since a higher energy will increase the scanning depth, and a longer scanning time might also result in thermal damage to foliar structures.

Table 6.2. Metal concentrations at the surface of 17 month-old balsam fir needles, to the 3-4 μm depth from the surface by micro-PIXE with 750 keV energy and 250 μm^2 scanning area. Min.: minimum value; Max.: maximum value; STE: standard error of the mean. Elements were selected with >75% of detectability from 750 keV scanning.

	Roundtop Mountain (n=46)				Morgan Arboretum (n=8)			
	Mean	STE	Min.	Max.	Mean	STE	Min.	Max.
	mg kg^{-1}							
Mg *	567	33	97	1130	407	65	192	768
Al *	216	21	25	464	392	75	80	717
Si *	435	51	36	1130	1010	213	236	2120
K *	9890	545	1340	15700	5460	945	2130	9950
Ca *	26300	1340	6140	42700	39800	3630	28100	57100
Ti *	22	4	<5	121	43	10	7	103
Mn *	1400	120	170	3250	88	15	44	173
Fe *	206	18	<25	480	388	89	65	907
Zn *	90	8	<21	172	27	5	<21	54

*: significant ($P \leq 0.05$) difference between the Roundtop Mountain and the Morgan Arboretum locations.

The metal concentrations in Table 6.2 do not represent the total accumulation of airborne metal deposits on the surface, partly due to the potential importance of root uptake on the metal concentration in needles as a whole, and partly due to the effects of post-deposition transfer and exchange processes, such as foliar absorption and rinse-off or leaching in precipitation. The difference in metal concentrations between Roundtop Mountain and the Morgan Arboretum site only reflect the metal concentrations at foliar surfaces of needles collected from different environments at the time of sampling.

Cluster analysis of elements on adaxial surfaces of unwashed needles showed the following five clusters, explaining 0.9 of the variation: (1) K, Mn, and Zn; (2) Mg; (3) Ca; (4) Al, Si, and Fe; (5) Ti. Correlated elements may result from similar origin or reflect similar pathways. This will be further explored in the following section.

6.4.3. Metal deposits and their spatial distribution at needle surfaces

Concentrations of Mg, Al, Si, K, Mn, Fe, and Zn on adaxial surfaces of unwashed needles were significantly ($P \leq 0.05$) higher than corresponding concentrations on adaxial surfaces of chloroform-washed needles, which indicates significant accumulation of the metal deposits in and on epicuticular wax layers (Figures 6.4 and 6.5). On abaxial surfaces, only Si and Ti showed such accumulation. The significant accumulation of metal deposits in and on epicuticular wax layers suggests that the metal deposits on foliar surfaces result from atmospheric deposition (Reiners *et al.* 1986).

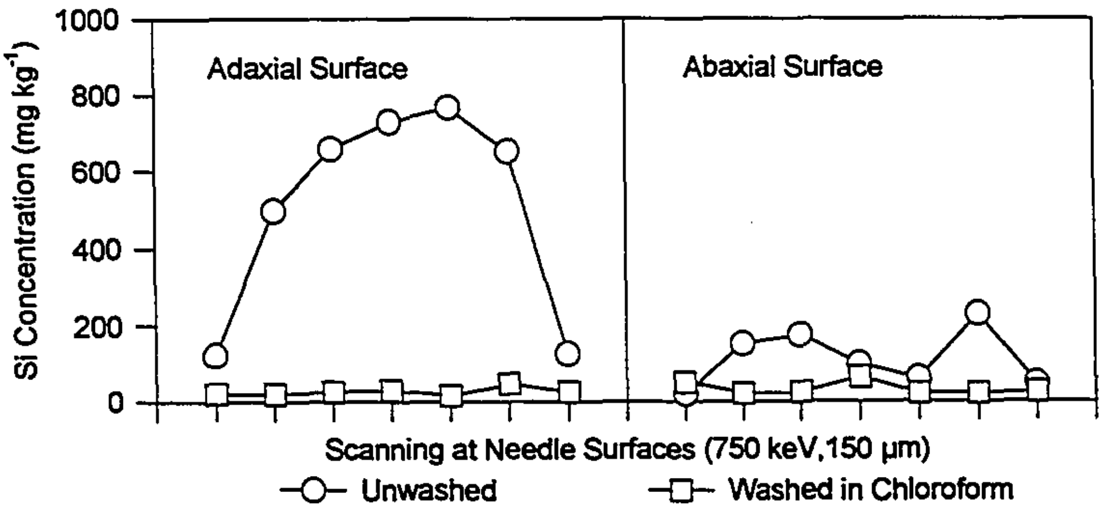


Figure 6.4. Accumulation of Si in epicuticular wax layers, scanning at adaxial and abaxial surfaces (3-4 µm depth) of unwashed and chloroform-washed needles.

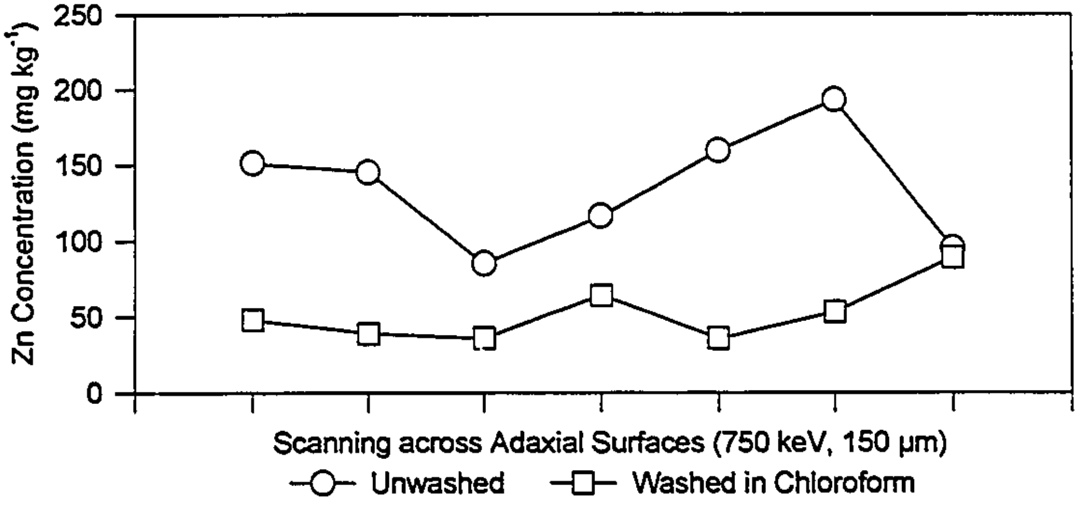


Figure 6.5. Accumulation of Zn in epicuticular wax layers, scanning at adaxial surfaces (3-4 µm depth) of unwashed and chloroform-washed needles.

Spatial distributions of metal deposits along scanning lines, with scanning spacing of 150 µm to the depths of 3-4 µm, are shown by the scans on unwashed needles (Figures 6.4, 6.5). On adaxial surfaces, Si showed higher accumulation around the centre region (Figure 6.4), while Mg, K, and Mn and Zn concentrations tended to be lower around the centre of needles (as illustrated for Zn in Figure 6.5). Al, ana Fe did not show symmetrical distributions. To what degree the distributions of Mg, K, Mn and Zn might be affected by residue in degraded epicuticular layers found preferentially away from the stomatal zone (near the top of Figure 6.6) remains an open question. By scanning surfaces at the micro-scale of 15x20 µm^2, significant fluctuation in Zn concentration has been found within 150x200 µm^2 areas (Figure 6.7). These results might suggest that the metal elements are distributed nonuniformly at needle surfaces, most likely associated with particles in the micron- or sub-micron size range. As a consequence, observed distribution patterns along scanning lines must be expected to be resolution dependent, *i.e.*, depend on size and

Figure 6.6. SEM of the adaxial surface, showing stomatal cavities and the degradation of epicuticular layers. S, stomata; C, degraded epicuticular wax layer.

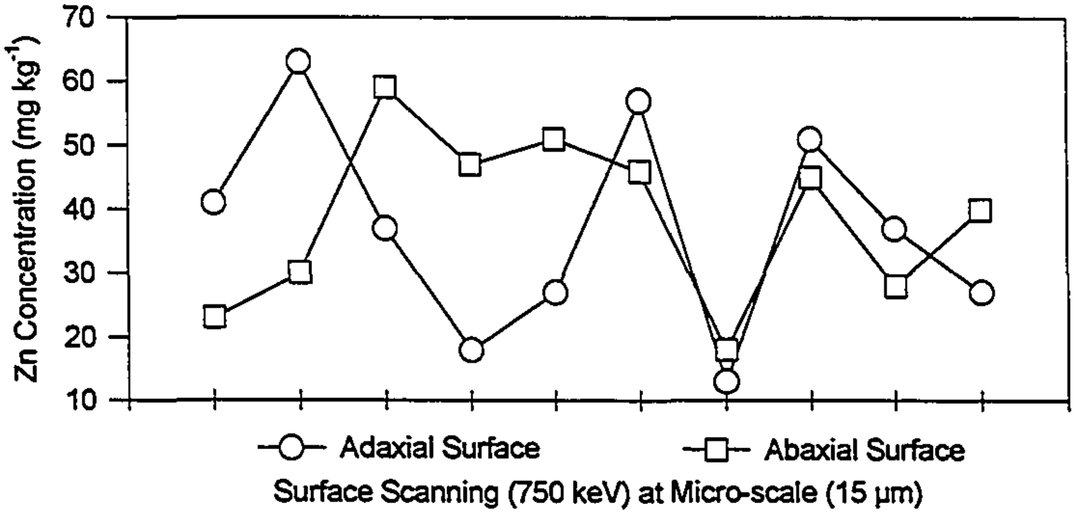


Figure 6.7. Distribution of Zn on foliar surfaces, scanning at the micro scale (15 × 20 µm^2).

spacing of scanning points.

The deposited aerosol particles containing high concentrations of trace heavy metals were hypothesized to penetrate the epistomatal chambers and enter the interior of needles (Simmleit *et al.* 1986). However, the near-surface scanning did not support this previous hypothesis that accumulation and distribution of atmospheric metal deposits on foliar surfaces might be associated with stomatal distribution (Delucia and Berlyn 1984). On the abaxial surface of unwashed needles, concentrations of K, Mn and Zn were lowest in the centre of the stomatal zone, but highest in the centre of stomatal zone of chloroform-washed needles (illustrated for K in Figure 6.8, with stomatal location shown in Figure 6.1). Obviously, this complexity in metal distribution would result in the statistically non-significant differences in metal concentrations at the abaxial surface between unwashed and chloroform-washed needles. The difference of metal deposits between adaxial and abaxial surfaces might result from differences in surface wax deposits and low metal concentrations in epicuticular wax deposits occluded in stomatal cavities on the abaxial surface. A large amount of Si detected in the scanning of needle surfaces might suggest the deposition of wind-derived soil materials, and the similar spatial distribution of Mg, K, Mn, and Zn deposits might suggest their similarity in atmospheric deposition pathways. The similarity in spatial distribution among Mn, Zn, K, and Mg on foliar surfaces generally agrees with the grouping by cluster analysis.

6.4.4. Metal concentrations in epicuticular wax layers affected by simulated acid rain

No significant difference in Mn concentration was found from the 750 keV scanning on adaxial surfaces of unwashed, DDW-washed and acid-rain-washed needles (Figure 6.9). However, the needles washed in different solutions showed different changes in the

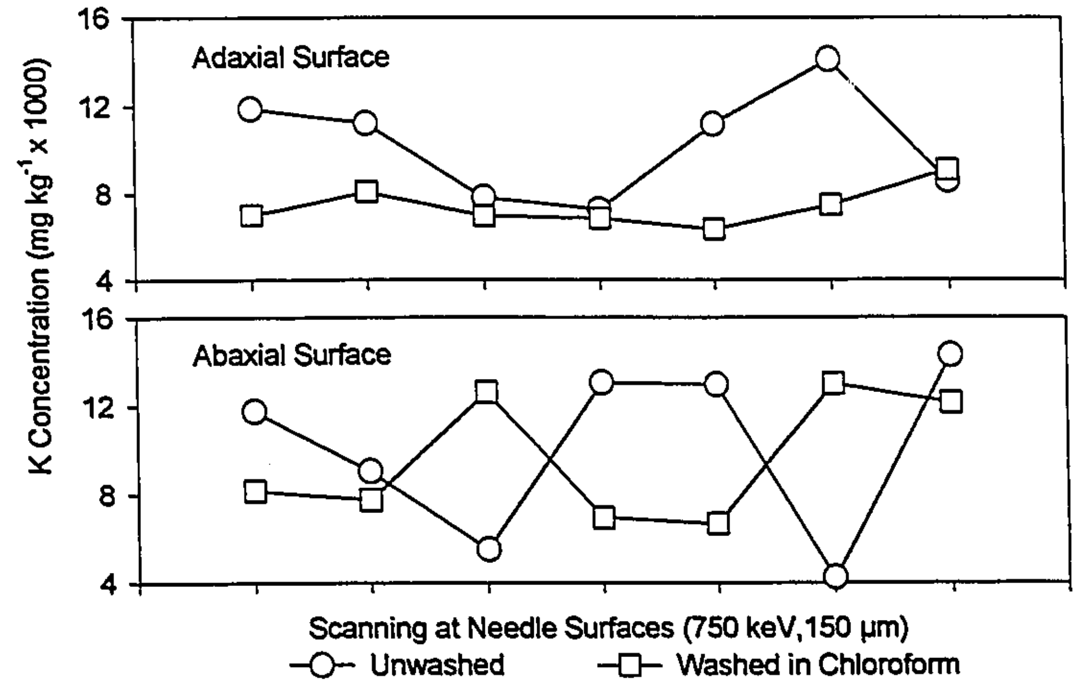


Figure 6.8. K concentrations from scanning at the abaxial surface (3-4 µm depth) of unwashed and chloroform-washed needles.

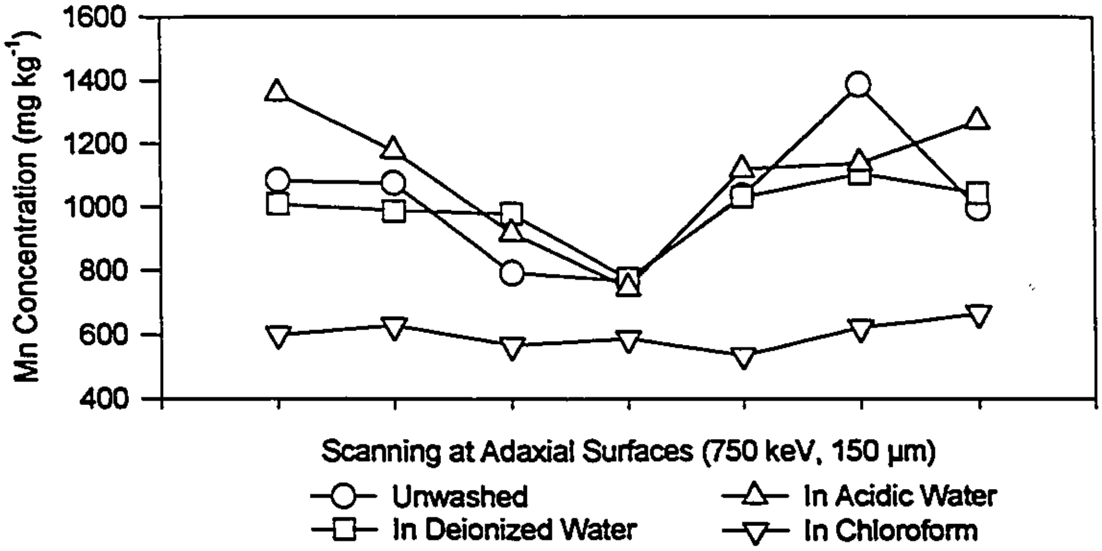


Figure 6.9. Mn at the surface of unwashed needles and needles washed in distilled deionized water (pH 5.7), in simulated acid rain (pH 4.0), and in chloroform solution.

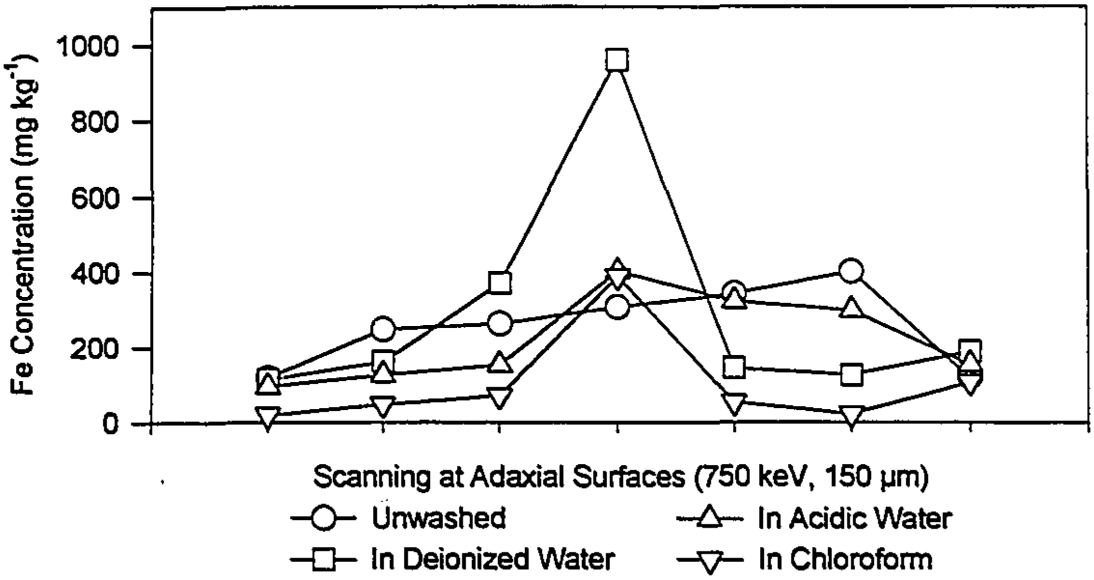


Figure 6.10. Fe at the surface of unwashed needles and needles washed in distilled deionized water (pH 5.7), in simulated acid rain (pH 4.0), and in chloroform solution.

distribution of Al, Si, Fe, and Zn at the surface (as illustrated for Fe in Figure 6.10). K concentration was significantly higher on DDW-washed needles than on unwashed needles, showing potential K leaching from internal tissue to the foliar surface. On abaxial surfaces, accumulation and distribution of all elements (including Mn) appeared to be significantly affected by the different procedures, possibly related to the more complex surface structures, including wax deposits and stomatal distribution, and to the leaching of metals from stomatal zones. Accumulation of metals, as revealed by the washing treatments, also suggested older needles might retain more metal deposits in epicuticular wax layers than younger needles.

Metal elements accumulated in epicuticular wax layers might provide evidence to support the hypothesis of cuticular penetration by metal elements deposited on needle surfaces. Foliar uptake of elements would be facilitated due to the large gradient in metal concentrations across the cuticle layer (Lin *et al.* 1995a), with higher concentrations in epicuticular wax layers (wax deposits on foliar surfaces) than in epicuticular layers (surface without wax deposits).

6.4.5. Metal concentrations in sub-surface layers

Metal concentrations to the 45-50 μm depth from foliar surfaces from 3.0 MeV scanning are summarized in Table 6.3, with concentration averaged from all 150 μm scanning points. Concentrations of Mn, Fe, Ni, Cu, Zn, Rb, and Sr were significantly higher than their average concentrations in whole needles (Lin *et al.* 1995a). Among the elements with detectability > 75 % both at the surface and in the sub-surface layer (Mn, Fe, and Zn), only Mn showed significantly lower ($P \leq 0.01$) concentration in the surface as compared to the sub-surface scanning on adaxial and abaxial needle surfaces (Table 6.4). Mn concentrations from the two scanning depths, in terms of paired scanning points along the two scanning lines separated by < 1 mm, also showed significant ($P \leq 0.01$) correlations at adaxial (r=0.54) and abaxial (r=0.57) surfaces. Zn showed such correlation (r=0.46, $P \leq 0.05$) only on the adaxial surface and no such correlation was observed for Fe.

Ni concentrations detected down to a depth of 45-50 μm ranged up to 50 mg kg^{-1} (Figure 6.11). Strong accumulation on either side of the centre groove was found on both adaxial or on abaxial surfaces with needles from the Roundtop Mountain site. However, scanning along the internal transect across the needle shows no significant accumulation of Ni near the centre of the vascular bundles. These results might suggest that the distribution of Ni might not be directly related to the xylem and phloem structure, but more likely linked to the vascular endodermis or the nearby spongy parenchyma, as suggested by Vergnano and Hunter (1953). By contrast, the significant accumulation observed for Mn

Table 6.3. Metal concentrations to the 45-50 μm depth below the surface of 17 month-old balsam fir needles from 3.0 MeV scanning with 150 μm^2 beam size. Elements were selected with >75% of the detectability from 3.0 MeV scanning.

	Mn	Fe	Ni	Cu	Zn	Rb	Sr
	mg kg^{-1}						
Mean	1011	236	21	11	110	31	13
STE [a]	87	17	4	1	26	3	1
Max. [b]	1983	359	70	19	594	66	23
Min. [c]	214	14	<0.6	2	29	7	3

a: standard error of mean (n=28)
b: maximum value
c: minimum value

around the location of the central vascular bundle may indicate root uptake of Mn from acidic soils, and above-ground translocation.

It is usually recognized that relatively low concentrations of Ni (*e.g.*, 10-50 mg kg^{-1} in dried mature leaf tissues) are toxic to a vide variety of plants (Mishra and Kar 1974; Kabata-Pendias and Pendias 1992). Mean concentrations of Ni in ground balsam fir needles (Table 5.2) varied from 2.5 to 3.4 mg kg^{-1} at Roundtop Mountain. However, such local excursions in concentrations of Ni near the vascular endodermis or the nearby spongy parenchyma region may become a matter of concern in the study of plant physiology and phytotoxicology.

6.5. Conclusions

Metal contamination and spatial distribution at the surface of balsam fir needles were quantitatively investigated by micro-PIXE scanning. Concentrations of Al, Ca, Fe, K, Mn,

Table 6.4. Metal concentrations in the surface (to the 3-4 μm depth) and in sub-surface (to the 45-50 μm depth) of 17 month-old needles with 150 μm^2 of scanning spaces. Three elements were selected with >75% of detectability above LOD in 750 keV and 3.0 MeV scanning.

	Surface (to the 3-4 μm depth)				Sub-surface (to the 45-50 μm depth)			
	Mean	STE [a]	Min.	Max.	Mean	STE [a]	Min.	Max.
	mg kg^{-1}							
<u>Adaxial Surface</u>:								
Fe *	264	13	180	401	195	13	137	390
Mn *	830	50	556	1387	1094	38	773	1384
Zn	95	10	41	193	111	17	66	372
<u>Abaxial Surface</u>:								
Fe *	221	31	58	575	167	23	14	359
Mn *	1054	89	374	1851	1392	115	214	1983
Zn *	101	10	34	169	193	35	29	594

*: significant ($P \leq 0.05$) difference in element concentrations between the surface and the sub-surface scanning.
a: standard error (n=14)

Si, and Zn at the adaxial surfaces to the 3-4 μm depth were higher than the average concentrations in whole needles, and differed between the near-urban site and the rural mountainous location. Significant accumulation of Mg, Al, Si, K, Mn, Fe, and Zn in epicuticular wax layers suggested their potential source from atmospheric metal deposition.

Accumulation of metal elements on foliar surfaces was not significantly correlated with stomatal distribution, and the spatial distribution of metal deposits at needle surfaces was elemental specific. At adaxial surfaces (3-4 μm depth), concentrations (mg kg^{-1}) of Mg, K, Mn, and Zn were higher near the edge than in the central stomatal zone. Scanning to

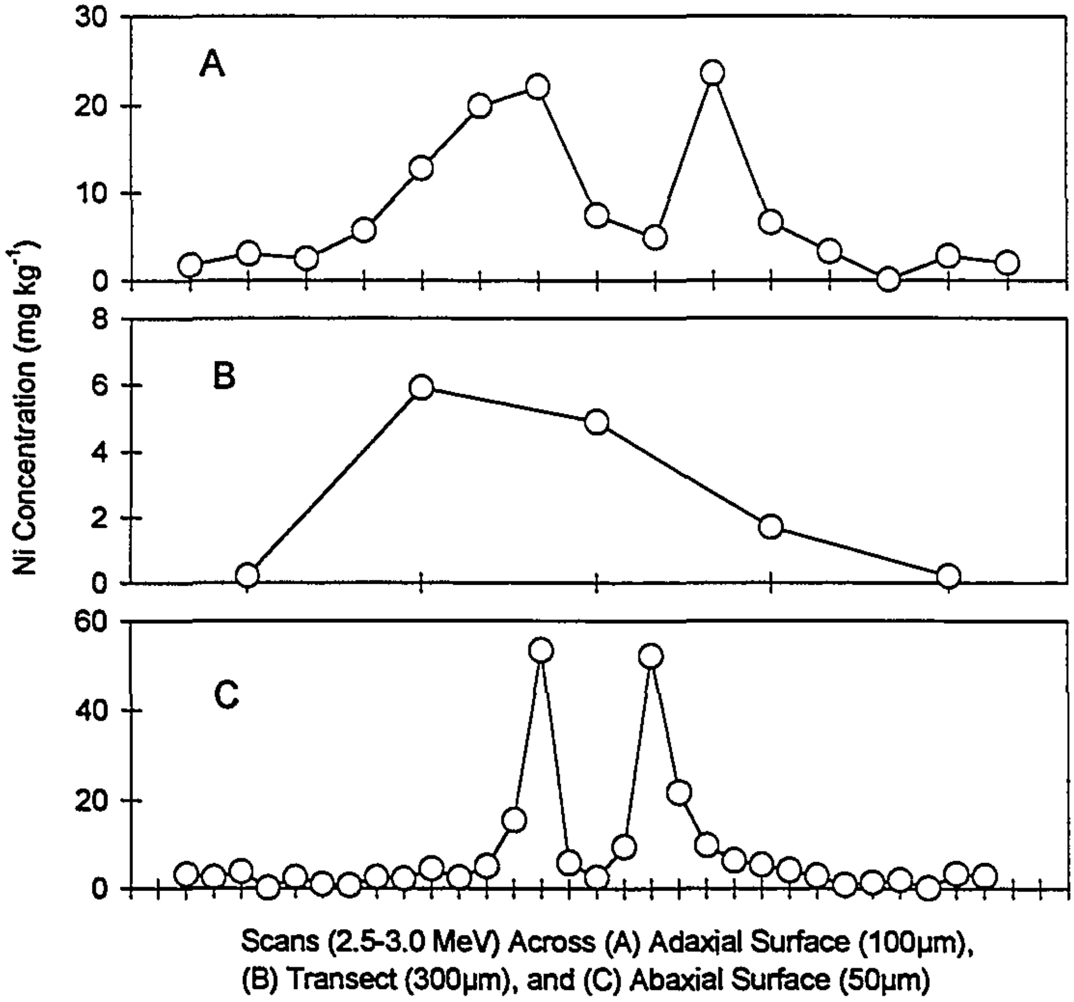


Figure 6.11. Concentrations of Ni to the 45-50 µm depth on the adaxial surface (A), along an internal transect across the needle (B), and on the abaxial surface (C) by 2.5 - 3.0 MeV scanning.

the 45-50 µm depth showed significant accumulation of Ni on either side of the centre spine of needles. Metal concentrations of the various elements in epicuticular wax layers were affected differently by washing in distilled deionized water (pH 5.7) and simulated acid rain (pH 4.0), with Mn not significantly washed off by simulated precipitation.

CONNECTING STATEMENT LINKING CHAPTERS 6 AND 7:

Surface deposits and particulates result from atmospheric deposition of aerosols, fine or coarse particles, and from wind blow soil dust. Existence of fungi may also significantly elevate metal concentrations on foliar surfaces due to bioaccumulation of metals in fungi tissues (Meng et al. 1995). The studies of metal concentration and spatial distribution of metal deposits on foliar surfaces in Chapter 6 have documented accumulation of trace metals in epicuticular wax layers and indicated the significant elemental input from atmospheric deposition. Once deposited on forest surfaces, metal pollutants may be affected by many environmental factors, and associated with different pathways. Above-ground uptake through foliar and bark surfaces is one of the most important pathways of metal deposits on trees. Such pathways will be elucidated by application of radioisotopes on tree surfaces in Chapter 7, with special consideration of surface wetness and acidity.

CHAPTER 7. UPTAKE AND TRANSLOCATION OF ^{54}Mn and ^{65}Zn APPLIED ON FOLIAGE AND BARK SURFACES OF BALSAM FIR SEEDLINGS

7.1. Abstract

Uptake and translocation of ^{54}Mn and ^{65}Zn in balsam fir seedlings were studied with the radioisotopes applied directly on shoot or main-stem surfaces in a growth chamber. Concentration and distribution of the absorbed radioisotopes in different plant parts depended on distances between source (the application site) and sink (the rest of the seedling), as well as on tissue growth activity. Acidic wetness significantly enhanced radioisotope absorption. ^{54}Mn and ^{65}Zn were found to be concentrated primarily in one-year old needles at the middle and top levels of the seedling crown. There were significant ($P \leq 0.05$) differences in accumulation (kBq kg^{-1}) between ^{54}Mn and ^{65}Zn in needles and twigs from foliar uptake. The absorption by seedlings (including the washed application shoot) 70 days after application was 24-32% of the remaining activities for ^{54}Mn and 25-30% for ^{65}Zn. Less than 1% of the absorbed isotopes was translocated from the bark application sites to other plant organs, whereas more than 54% of the activity absorbed at one-year old shoots moved to the rest of the seedling.

7.2. Introduction

Mn and Zn are recognized as important heavy metal pollutants in air (Nriagu 1990, Pacyna *et al.* 1995). Since the 1970's when MMT replaced Pb as an octane-boosting gasoline additive in Canada, a few studies have been conducted to detect Mn in its toxic oxidized forms (Mn_3O_4) in the atmosphere from automobile exhaust (Loranger and Zayed 1994). Airborne Zn, originating from tire wear, fuel additive and brake linings, in large industrial-metropolitan areas is one of the major sources of atmospheric Zn pollution. Dry deposition of Mn and Zn from the atmosphere to forest surfaces is usually estimated from throughfall measurements or foliar rinsing (Lindberg and Lovett 1985). However, the accuracy and reliability of such estimates depend on elemental accumulation and efficiency of washed-off deposited elements on forest surfaces (Potter and Ragsdale 1991). Although controlled experiments showed negligible migration of ions from internal tissues to needle surfaces during dry deposition periods (Reiners *et al.* 1986), leaching of metal elements in acid rain may contribute significantly to the estimate of dry deposition (Lindberg and Garten 1988). In general, pathways of Mn and Zn on forest surfaces, including the potential effects of surface wetness and acidity on foliar uptake and leaching processes, have to be understood if the dry deposition is to be estimated correctly.

Foliar absorption, translocation and distribution of metal elements in crops and trees have been successfully studied with radioisotopes (Huang *et al.* 1982; Bromilow *et al.* 1986; Ronneau *et al.* 1991). Field studies showed big differences in washing-off efficiency of precipitation, with 80% of ^{137}Cs remaining, while ^{103}Ru, ^{132}Te, and ^{140}La were very effectively removed (Ronneau *et al.* 1987). Large differences in surface absorption and translocation of deposited isotopes were also reported for different organs of different tree species (Huang *et al.* 1982; Ronneau *et al.* 1991).

Although foliar uptake of nutrients is of practical importance in agriculture, forest surface interception and uptake of deposited atmospheric heavy metal pollutants may have a potential impact on forest contamination (Smith 1990). In particular, the absorption of deposited metal elements on foliage and bark surfaces of conifers in southern Quebec, an area affected by acid deposition, is little understood (Lin *et al.* 1995b). We hypothesized that a significant uptake of Mn and Zn occurs from the surface of needles and barks of balsam fir, which is a co-dominant tree species of the regional high elevation forests. Acidic fog deposition will increase the mobility of metal elements deposited on tree surfaces. The translocation and accumulation of the heavy metals may be concentrated in tissues with higher growth activity. Therefore, the objectives of this study were: (a) to examine uptake and translocation of ^{54}Mn and ^{65}Zn applied simultaneously on needles or on the main stem of balsam fir seedlings; and (b) to determine the roles of surface wetness and acidity on foliar absorption of ^{54}Mn and ^{65}Zn.

7.3. Materials and Methods

7.3.1. Seedlings and radioisotopes

Four-year old balsam fir seedlings, approximately 55-60 cm in height, were grown in pots filled with 2.5 kg of air-dried ferro-humic podzolic soils collected from Roundtop Mountain in southern Quebec, which is affected by acid deposition (Schemenauer 1986). The site for soil collection was selected to study pathways of heavy metals deposited in high elevation forests. The soil characteristics were as follows: pH = 3.5; organic matter content = 31%; cation exchange capacity = 12.8 cmol$^{(+)}$ kg^{-1}; extractable Mn and Zn concentrations in 0.1 M HCl were 8.05 and 9.37 mg kg^{-1}, respectively. Experiments were conducted in a growth chamber under the following conditions: temperature 22-26°C; photosynthetically active radiation (PAR) 120 - 140 µE m^{-2} s^{-1} at seedling mid-height; day length 14 hr; relative humidity 25 - 50%; air velocity 0.5 - 1.5 m s^{-1}. Transpiration and stomatal diffusive resistance of the seedlings were measured at 4 ± 1 mg cm^{-2} hr^{-1} and 14 ± 2 s cm^{-1}, respectively, using a steady-state porometer (LI-1600) with a cylindrical chamber.

^{54}Mn and ^{65}Zn isotopes dissolved in 0.5 M HCl (Du-Pont Canada Inc.) had the following characteristics: half-life of 303 d for ^{54}Mn and 244 d for ^{65}Zn; gamma energy of 834 keV for ^{54}Mn and 1115 keV for ^{65}Zn; radionuclidic purity of 99.9% for ^{54}Mn and 99% for ^{65}Zn.

7.3.2. Application of radioisotopes

Cotton pads of 5 cm^2 projected area were used to ease the application of the isotope solution, a procedure also designed to simulate the release of metal pollutants from surface deposits. The pads were carefully attached to shoots at mid-height of the seedling crown (Figure 7.1), and to the midpoint of four-year old stems underneath the crown. The isotope sources of ^{54}Mn and ^{65}Zn were diluted and mixed before application. The cotton pads were wetted with distilled deionized water (DDW) before the mixed solution was spread uniformly on the pads using an auto-pipette on the first day of the experiments. The applied activities of ^{54}Mn and ^{65}Zn, and the subsequent wetness treatments of cotton pads with simulated acid rain (pH 4.0) (Wood and Bormann 1977) or distilled deionized water (pH 5.7), according to the requirements of each treatment, are as follows:

(1) Experiment 1: The specific activity of the radioisotope sources was 2.5 x 10^6 kBq mg^{-1} for ^{54}Mn and 1.2 x 10^5 kBq mg^{-1} for ^{65}Zn. An activity of 740 kBq of each isotope (in 500 μL of the mixed isotope solution) was applied on the cotton pad on an one-year old shoot with two replicates of seedlings, in an attempt to quantify the absorption and translocation. Pads were moistened, after application of isotopes, by the simulated acid rain two to three times a day for 70 days, with wetness from each moistening apparent to visual inspection for about 1 hr.

Figure 7.1. Application of the radioisotope solution on one-year old shoot with assistance of a cotton pad.

(2) Experiment 2: In this experiment, which is designed to explore the effects of different surface wetness conditions, one-year-old shoots were used in three treatments and each replicated three times by seedlings. The specific activity of isotope sources was 1.65 x 10^6 kBq mg^{-1} for ^{54}Mn and 6.88 x 10^4 kBq mg^{-1} for ^{65}Zn, and applied activities were 527 kBq for ^{54}Mn and 472 kBq for ^{65}Zn (in 750 µL of the mixed isotope solution) on each seedling. Pads were wetted two to three times daily for 70 days with the simulated acid rain of pH 4.0 in the first treatment. For the second treatment, daily wetting (*i.e.*, two to three times per day) was done with DDW of pH 5.7 for 70 days and, for the third treatment, the wetting frequency with the simulated acid rain of pH 4.0 was one day (two to three times per day) every two weeks during the 70-day experiment.

(3) Experiment 3: Activities of 527 kBq and 472 kBq for ^{54}Mn and ^{65}Zn, respectively,

were applied on pads attached to the stem (*i.e.*, four-year old bark) of each seedling with three replicates, wetted two to three times daily with an acidic solution of pH 4.0 for 70 days. The applied isotope had the same specific activity as in the experiment 2.

7.3.3. Sample preparation and gamma-ray counting

Seedlings were harvested 70 days after the application of the radioisotopes. Needles, and twigs were collected from the top, middle, and bottom sections of the seedling crowns, and divided into one- and two-year old age groups. The samples were dried at 80°C for 24 hr and were separately collected in 60 ml polypropylene jars for γ ray counting by a Ge semiconductor detector with a multi-channel analyzer (EG&G Ortec). Counting time was set at 5 min to about 3 hr depending on sample activity. Sample volume in jars was recorded for the correction of the counting efficiency, and sample activities were corrected for decay to the sampling date.

The absorbed isotopes remaining in the application sites were measured after agitating the shoots or the central parts of stems in 400 ml of chloroform solution for 30 sec. The washing treatment efficiently removes the epicuticular wax layers (Lin *et al.* 1995b), thereby removing non-absorbed isotopes from the surfaces. The accumulation of absorbed radioisotopes in the seedling was estimated from the biomass (kg) and the activity (kBq kg^{-1}) of the samples determined on the 70th day. The concentrations (mg kg^{-1}) of stable Mn and Zn in needles of the seedlings was determined by neutron activation analysis. The statistical comparisons between ^{54}Mn and ^{65}Zn activities (kBq kg^{-1}) in needles and twigs were made by paired t-tests with the hypothesis that the difference in concentration between two radioisotopes is significantly different from zero.

7.4. Results and Discussion

7.4.1. Absorption and translocation from foliar surfaces

^{54}Mn was absorbed and translocated to other parts of the seedling when applied on one-year old shoots at the mid-height of the seedling crown. Figure 7.2 shows the translocation of ^{54}Mn to the needles and twigs of the top, middle (*i.e.*, application height), and bottom parts of the crown, excluding the site/shoot of isotope application. The highest activities (kBq kg^{-1}) of ^{54}Mn were observed in needles from the middle section of the crown. A significant difference in isotope activities between one-year and two-year old needles occurred only at the mid level of the seedling crown. In twigs, Mn radioisotope concentrations produced similar relative distribution patterns between top, middle and bottom parts of the seedling as those in needles, but the absolute activity was significantly lower. For ^{65}Zn, the patterns of sample activity versus the needle and twig position on the seedling were similar to those for ^{54}Mn (Figure 7.3), but ^{65}Zn activities in needles and twigs were significantly ($P \leq 0.05$) lower than ^{54}Mn activities when samples were sorted according to age and position. ^{54}Mn and ^{65}Zn in stems and roots showed considerably higher activities at the top of the stem (Figure 7.4). However, there was no significant difference in activity in roots and stems between ^{54}Mn and ^{65}Zn from foliar uptake.

The fractions of initially applied activity, remaining in organs of the seedling 70 days after application, are shown in Table 7.1. The total absorption of the isotopes, including in the washed application shoot, was 32% of 631 kBq for ^{54}Mn and 30% of 607 kBq for ^{65}Zn. The translocation from the source to the rest of the seedling was about 54% of the absorbed ^{54}Mn and ^{65}Zn in the seedling. Needles accumulated the bulk of the translocated isotopes, followed by twigs, main stems and roots. Our results showed no significant difference in distribution between ^{54}Mn and ^{65}Zn from foliar or bark uptake.

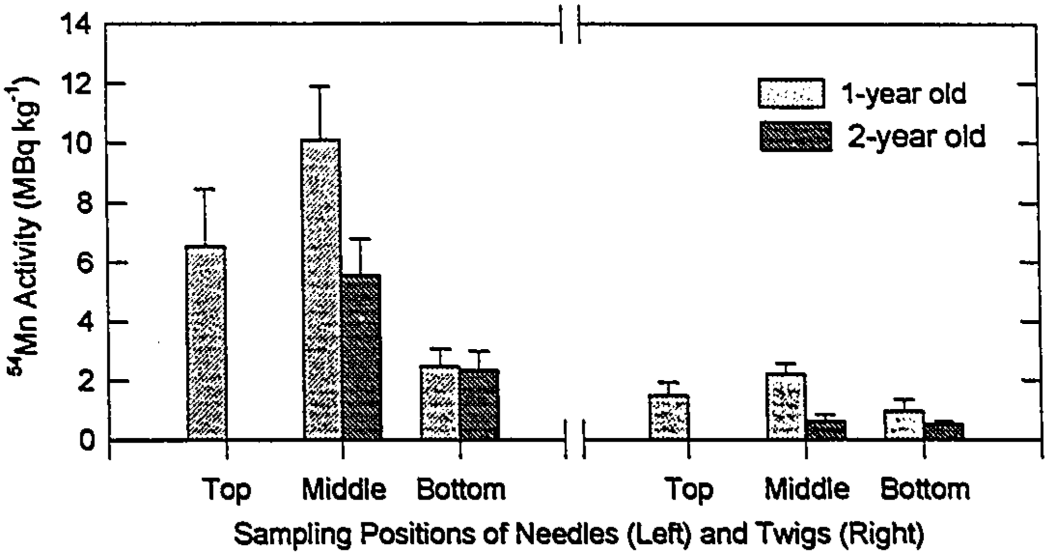


Figure 7.2. Translocation of ^{54}Mn to the needles and twigs of the top, middle (*i.e.*, application height), and bottom parts of the crown.

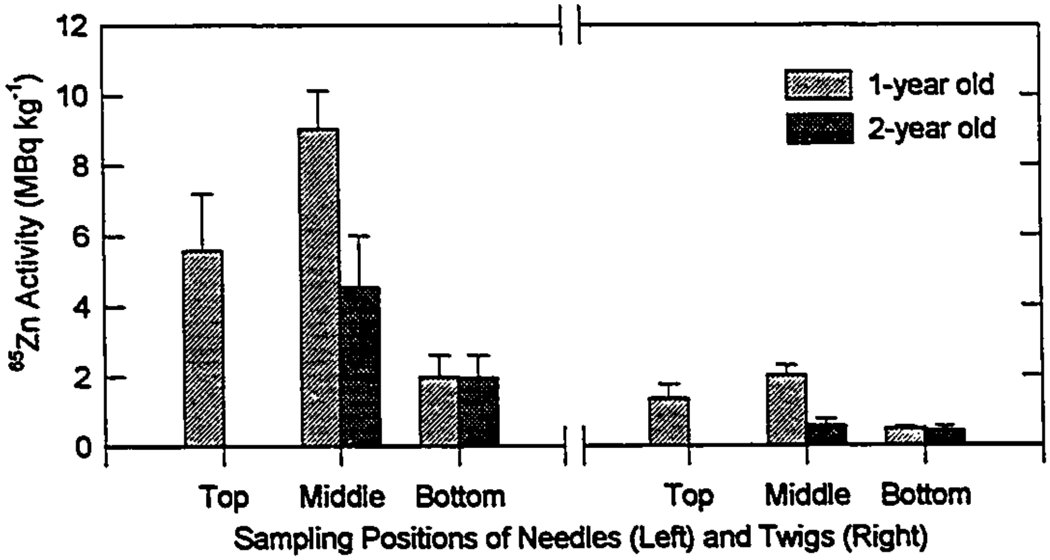


Figure 7.3. Translocation of ^{65}Zn to the needles and twigs of the top, middle (*i.e.*, application height), and bottom parts of the crown.

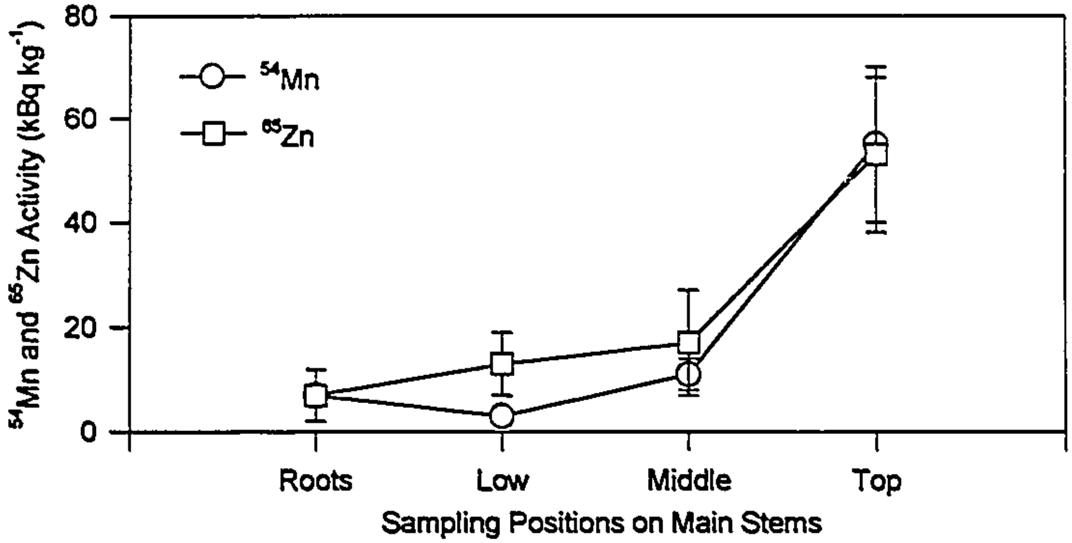


Figure 7.4. Translocation of ^{54}Mn and ^{65}Zn to roots and different heights of main stems of 4-year old balsam fir, 70 days after application on 1-year old shoots.

7.4.2. Wetness and acidity effects on foliar absorption

The absorption of two isotopes in seedlings varied as a function of wetness and acidity on needle surfaces (Table 7.2). For identical amounts of radioactivity for each isotope, daily wetting with simulated acid rain resulted in absorption of about 24% of the remaining activity, compared to about 10% for the distilled deionized water. Biweekly acidic wetting on shoots resulted in absorption of only about 1.5% of the remaining activity. The differences in accumulation (Bq) of isotopes between daily and biweekly acid wetting were significant ($P \leq 0.05$). However, the difference in absorption between the daily acidic and daily DDW wetting treatments, and between DDW and biweekly acidic treatments were significant at a lower confidence level ($P \leq 0.1$).

Table 7.1. Accumulation and distribution of ^{54}Mn and ^{65}Zn in four-year old balsam fir 70 days after application on one-year old shoots. Means were from two replicates, and ± standard errors are presented in brackets. * The total remaining radioactivity by the sampling date was 631 kBq of ^{54}Mn and 607 kBq of ^{65}Zn. † The isotope-treated shoot washed in chloroform.

Isotopes	Accumulation (kBq)		Distribution (% of Total Activity in the Seedling)				
	In Seedlings	% of Total*	Treated Shoots†	Roots	Stems	Twigs	Needles
^{54}Mn	201 ± 16	32 ± 3	45.9 ± 8.0	0.2 ± 0.2	0.2 ± 0.1	5.4 ± 1.5	48.4 ± 6.8
^{65}Zn	183 ± 12	30 ± 2	45.7 ± 5.3	0.2 ± 0.1	0.2 ± 0.0	5.5 ± 1.2	48.3 ± 4.2

Table 7.2. Accumulation of ^{54}Mn and ^{65}Zn in four-year old balsam fir 70 days after application on one-year old shoots with different wetness and acidity on the surfaces. Means were from three replicates, ± standard errors are presented in brackets. DDW stands for distilled deionized water. * Total remaining activity on the sampling date was 449 kBq of ^{54}Mn and 387 kBq of ^{65}Zn.

Accumulation in Seedlings		Biweekly Acid Wetness (pH 4.0)	Daily Acid Wetness (pH 4.0)	DDW Wetness (pH 5.6)
^{54}Mn	Accumulation (kBq)	6.21 ± 2.59	107.14 ± 28.2	41.79 ± 16.24
	% of Total Remaining Activity*	1.38 ± 0.58	23.86 ± 6.28	9.31 ± 3.61
^{65}Zn	Accumulation (kBq)	6.30 ± 2.6	94.77 ± 27.12	38.53 ± 13.68
	% of Total Remaining Activity*	1.63 ± 0.67	24.49 ± 7.01	9.96 ± 3.54

7.4.3. Absorption and translocation from bark

Bark uptake of ^{54}Mn and ^{65}Zn isotopes and their distribution (Table 7.3) showed the accumulated fractions in seedlings, including the washed application stem section, to be 58 and 63% of the remaining ^{54}Mn and ^{65}Zn applied on the stem, respectively. There was more than 99% of activity remaining at or near the application sites, with the remainder translocated to roots, other parts of the stem, twigs, and needles.

7.4.4. Discussion

Data from our experiments support the hypothesis that uptake of metal deposits from foliage and bark was significant under the effects of acidic wetness on the surface of needles and bark. Foliar uptake of Mn and Zn might involve non-metabolic cuticular absorption and also metabolic or active transport in which energy is expended in their movement across the cell membrane against a concentration gradient. Kabata-Pendias and Pendias (1992) proposed cuticular penetration of the metal elements from foliar surfaces as a major pathway of absorption although direct experimental evidence for this has not yet been forthcoming. Surface wetness with simulated acid rain in our experiments provided indirect evidence of increased absorption via the increased mobility of deposited metal elements possibly with decreased interfacial tension or with increased degradation of epicuticular layers from acidic wetness (Riederer 1991). These conditions are expected to enhance absorption through epicuticular layers on foliar surfaces.

The ^{54}Mn and ^{65}Zn may have been expected to be transported more actively towards the apex of the seedlings than in the opposite direction because the most active growth sites are usually at the top of the seedling where nutrients are most in demand (Loneragan *et al.* 1976). However, the relative distance between the source (*i.e.*, ^{54}Mn and ^{65}Zn at

Table 7.3. Accumulation of ^{54}Mn and ^{65}Zn in four year old balsam fir 70 days after isotope application on the centra part of main stem. Cottons were treated daily with acidic solution (pH 4.0). Means were calculated from three replicates, ± standard errors are presented in brackets. * The total remaining activity of isotopes on the sampling date was 449 kBq for ^{54}Mn and 387 kBq for ^{65}Zn.

	Absorption (kBq)		Distribution (% of Total Activity in the Seedlings)				
	In Seedlings	% of Total *	Treated Stems	Roots	Stems	Twigs	Needles
^{54}Mn	261± 35	58 ± 8	99.74 ± 0.04	0.08 ± 0.03	0.07 ± 0.04	0.03 ± 0.01	0.01 ± 0.01
^{65}Zn	245 ± 15	63 ± 4	99.80 ± 0.01	0.13 ± 0.04	0.03 ± 0.01	0.02 ± 0.01	0.01 ± 0.00

application site) and the sink (*i.e.*, other plant parts) appears to be an important factor in the translocation of the isotopes. When the isotopes were applied on shoots at the mid-level of the seedling crown, the concentration (kBq kg^{-1}) in needles at the mid-level was significantly higher than that in needles at the top and base. Vigorous growth of one-year old shoots relative to older tissues may explain the observed difference in activities between one- and two-year old needles at the isotope application site level. The ratio of activity (kBq kg^{-1}) in needles to that in twigs ranged between 2.5 and 8.6 for ^{54}Mn and between 4.0 and 7.8 for ^{65}Zn, and indicated that needles concentrated more isotopes than twigs, especially at the application level. These results supported our hypothesis that tissues with higher growth activity accumulated more absorbed heavy metals.

The movement of absorbed elements depends on their concentration in the plants (Kramer and Kozlowski 1979). The concentrations of stable Mn and Zn in one-year old needles of our seedlings were 299 ± 59 and 40 ± 5 mg kg^{-1}, respectively, which is lower for Mn but similar for Zn, when compared to concentrations (*i.e.*, 450-600 mg kg^{-1} of Mn and 36-41 mg kg^{-1} of Zn) found at Roundtop Mountain (Lin *et al.* 1995b). Therefore, a lower mobility than the one observed in our experiment might be expected in the field for Mn, and a similar one for Zn. Also, translocation in both directions from foliar uptake seems to be associated with both xylem and phloem vessels (Kramer and Kozlowski 1979). However, the mechanism for heavy metal internal cycles through both xylem and phloem remains uncertain (Kramer and Kozlowski 1979; Loneragan 1988), although the pressure flow hypothesis has gained some acceptance in plant physiology as a possible phloem transport mechanism (Ridge 1991; Van Goo and Wiersma 1976).

Application sites on the main stems retained 99% of applied isotopes, which indicated a strong retaining capacity of bark for deposited heavy metals, while shoots showed strong capability in translocation of ^{54}Mn and ^{65}Zn. The uptake fraction of deposited isotopes from needles varied with different application doses on shoots, probably due to the adsorption of isotopes by cotton pads. In general, our observations on ^{54}Mn and ^{65}Zn agree fairly well with a study on $^{115+115m}$Cd uptake by other conifer species (Huang *et al.* 1982), although Cd functions as a non-essential element in plants. However, when interpreting this radiotracer study we must keep in mind the considerable biological variability of tree seedlings as far as absorption and accumulation of these elements are concerned. Some statistically significant difference with lower confidence level (*e.g.*, $P \leq 0.1$) might also result from the small sampling size, in itself a reflection of experimental constraints, in spite of the suitability of radio-tracer techniques in terms of sensitivity and rapid response.

7.5. Conclusions

The accumulation of the radioisotopes in balsam fir seedlings, including in the washed application shoot, was 24 - 30% of the remaining activity of ^{54}Mn and ^{65}Zn 70 days after application with cotton pads on one-year old shoots. Bark appeared to accumulate absorbed elements with negligible subsequent translocation to other plant parts, whereas accumulation in shoots was followed by significant translocation. The relative distance between the application site and the rest of the seedling seemed to play an important role on ^{54}Mn and ^{65}Zn distribution. Surface wetness by simulated acid rain enhanced absorption of the radioisotopes from shoots.

CONNECTING STATEMENT LINKING CHAPTERS 7 AND 8:

Uptake of metal pollutants deposited on foliar and bark surfaces has been demonstrated by application of radioisotopes. In high elevation forests, metal pollutants are deposited to soil surfaces through dry and wet deposition. Metal elements deposited on forest surfaces and leached from tree foliage may be washed off in precipitation, contributing to the elemental input to soils. Pathways of metal contaminants on soil surfaces may involve metal movements in soil profiles, followed by root uptake. Such metal transfer in the soil-tree system will be examined by application of radioisotopes on soil surfaces, as described in Chapter 8.

CHAPTER 8. UPTAKE AND TRANSLOCATION STUDIES IN BALSAM FIR SEEDLINGS WITH ^{54}Mn AND ^{65}Zn APPLIED TO SOIL SURFACES

8.1. Abstract

Pathways of heavy metal deposits in balsam fir seedlings were investigated by simultaneously applying ^{54}Mn and ^{65}Zn radioisotopes on soil surfaces. Downward movement of ^{54}Mn and ^{65}Zn in soils was documented to the 14 - 16 cm depth 70 days after application. One-year old needles and three-year old twigs concentrated more radioisotopes than older needles and younger twigs, respectively, with the sample specific activity (kBq kg^{-1}) of ^{54}Mn 5 - 10 times higher than that of ^{65}Zn. The activity in seedlings on the 70th day of the experiment was 5.2% of the total remaining activity for ^{54}Mn (6,290 kBq) and 2.6% for ^{65}Zn (6,031 kBq). The distribution of ^{54}Mn in the seedling was 31% in roots, 31% in twigs, 26% in stems and 12% in needles, while roots retained 86% of ^{65}Zn. No appreciable migration of elements from internal tissues to epicuticular wax layers was found when shoots were washed in chloroform. The maximum leaching ratio was below 0.5 and 1.0% for ^{54}Mn and ^{65}Zn, respectively, when shoots were washed in simulated acid rain for 5 min.

8.2. Introduction

The direct contribution from wet and dry depositions and the indirect input from washed off elements affect biogeochemical cycles of heavy metals in forest ecosystems. Heavy metals deposited from the atmosphere to forests accumulate on forest floors

(Andersen *et al.* 1980; Friedland *et al.* 1984) and dry deposition of metal elements has been estimated from throughfall measurements in forests (Petty and Lindberg 1990). However, the accuracy of such measurements depends on whether or not there is an internal circulation of the elements and on the washing-off efficiency of precipitation for deposited elements, itself possibly a function of acid deposition. It is clear that the pathways of deposited metal elements on forest surfaces, such as foliar uptake, elemental secretion and leaching, strongly influence the estimation of their dry deposition from rinsing of leaves and throughfall measurements (Juniper and Jeffree 1983; Schaefer *et al.* 1988). In spruce forests of Eastern North America, Petty and Lindberg (1990) reported leaching of Mn from interior leaf tissues and uptake of Zn by foliar surfaces.

Radioisotope labelling allows the evaluation of the proportion of excess metal elements of internal origin, washed off from tree surfaces, versus those from atmospheric dry deposition. This technique has been used successfully to study the absorption and distribution of heavy metals in forest trees (Witherspoon 1964; Huang *et al.* 1982; Ronneau *et al.* 1991). Motivation for the study of pathways of radionuclide fallout in natural ecosystems has increased especially after the Chernobyl accident in Europe in 1986. Forest trees are of particular interest because of their effective interception of aerosols (Wiman 1986; Bunzl and Kracke 1988). Lindberg and Garten (1988) have also conducted throughfall measurements following infusion of ^{35}S radioisotope solution into tree stems to examine sulphur leaching from the canopy. Studies from an eastern Belgium forest showed that about 80% of the ^{137}Cs from atmospheric deposition had been retained by foliage, while about 100% of the other radionuclides (^{103}Ru, ^{132}Te, and ^{140}La) were washed off to the ground (Ronneau *et al.* 1991). Huang *et al.* (1982) and Benson (1966) demonstrated that root uptake and translocation of radioisotopes varied among tree species and soil properties. However, the absorption and distribution of ^{54}Mn and ^{65}Zn radioisotopes applied simultaneously on the surface of acidic forest soils in conifers have not been well investigated previously (Nadkarni and Primack 1989).

This Chapter examines the downward movement of ^{54}Mn and ^{65}Zn in forest soils, and their root uptake, accumulation and distribution in the above-ground parts of balsam fir seedlings, when the radioisotopes were applied simultaneously to the soil surface. Soil-surface applied radioisotopes were used to simulate metal deposits on forest floor, directly from wet/dry deposition and indirectly from wash-off of foliar metal deposits and internal metal leaching. An important aspect of this study is the internal cycling (*i.e.*, element migration or leaching from shoots) of ^{54}Mn and ^{65}Zn and its potential effect on the estimation of dry deposition from foliar rinsing or from throughfall measurement.

8.3. Materials and Methods

8.3.1. Seedlings and soils

Two four-year old balsam fir seedlings were grown in pots (18 cm high and 9 cm radius), each containing 2.5 kg of air-dried soils. Soil materials, originated from A and B horizons of the Humo Ferric Podzol, were obtained from Roundtop Mountain in southern Quebec, an area previously described in this thesis. Soil characteristics were identical to those specified in Chapter 7, *i.e.*, pH of 3.5, organic matter content (OM) of 31%, cation exchange capacity (CEC) of 12.77 cmol$^{(+)}$ kg^{-1} and extractable Mn and Zn concentrations (mg kg^{-1}) in 0.1 M HCl of 8.05 and 9.37, respectively. Experiments were conducted in growth chambers in the temperature range of 22-26 °C, at photosynthetically active radiation (PAR) levels of 120-140 µmol m^{-2} s^{-1} at the mid-height of seedlings, under photoperiod of 14 hrs per day, relative humidity of 25-50% and with a mean airflow (ventilation) of 0.5-1.5 m s^{-1}. In order to investigate the possible effects of acid deposition on migration of radioisotope from internal tissues to epicuticular wax layers and leaching from shoots, half of the tree crown was daily treated by spraying acid mist (pH=4.0) (Wood and Bormann 1977) twice a day for 70 days, while the remaining half was used as the control. Soil surfaces were irrigated daily with measured amounts of tap water. The total amount of water added during the 70 days of the experiment was equivalent to a rate of about 200 mm per month. Transpiration and stomatal diffusive resistance of seedlings were measured as 3.9 ± 1.3 mg cm^{-2} hr^{-1} and 13.5 ± 1.7 s cm^{-1}, respectively.

8.3.2. Application of radioisotopes

The characteristics of ^{54}Mn and ^{65}Zn isotopes (Du-Pont Canada Inc.) have been given in Chapter 7. The specific activity was 2.5×10^6 kBq (67.92 mCi) mg^{-1} for ^{54}Mn and 1.2×10^5 kBq (3.20 mCi) mg^{-1} for ^{65}Zn. The solution was diluted to 1480 kBq (40 µCi) mL^{-1} for both ^{54}Mn and ^{65}Zn. The mixed radiotracer solutions were then spread uniformly on the soil, in a ring pattern with total surface area of 250 cm^2 around the seedlings, with two replicates. Application doses of the radioisotopes on each seedling were 7400 kBq (200 µCi) for each element, equivalent to 3 µg of Mn and 63 µg of Zn in each pot.

8.3.3. Sample preparation and gamma-ray counting

The trees were harvested 70 days after application of the radioisotopes. Shoot samples were collected from the top, middle, and bottom parts of tree seedlings, and divided into one year, two year and three year age classes. Soil samples were obtained from soil layers in the pot at 4-6 cm, 9-11 cm and 14-16 cm, and passed through a 2-mm sieve for removing root residues. Shoots were separately agitated in 400 mL solutions of chloroform (for 15 s), distilled deionized water (DDW) of pH 5.7 (for 1 min) and simulated acid rain of pH 4.0 (for 1 or 5 min). Roots were washed in tap water. Washed and unwashed plant samples were dried at 80 °C for 24 hours; needles and twigs separated; stem and twigs chopped into small pieces. Extractable isotopes in treated soils were determined in 0.1 M HCl (Chapter 5). Samples were collected in 60 mL polypropylene jars for γ ray counting by a germanium semi-conductor detector (EG&G ORTEC) and a CANBERRA 35^{+} multi-channel analyzer, with counting times from 5 min to 3 hrs. The sample volume in jars was recorded and used for correcting the counting efficiency, and the activity in samples was corrected for decay.

The concentrations of stable Mn and Zn in one-year old needles of the seedlings were 300 ± 60 and 40 ± 5 mg kg^{-1}, respectively. The distribution fraction (% of total in seedling) of the isotopes in different parts of trees were calculated from the sample specific activity (kBq kg^{-1}) and the biomass (g) determined on the 70th day.

The migration of isotopes from internal tissues to the needle surfaces was estimated from the ratio (%) of activity in washing residues (*i.e.*, epicuticular wax deposits removed from foliar surfaces) to that in unwashed shoots. The epicuticular wax deposits were efficiently removed by agitating shoots in chloroform solution (in 400 mL, 15 s) (Wyttenbach *et al.* 1985; Riederer 1989). Foliar leaching of ^{54}Mn and ^{65}Zn in simulated acid rain and DDW was quantitatively estimated by the ratio (%) of activity in the washing solution to that of unwashed needles. The wash-offs from DDW (pH 5.7) and simulated acid rain (pH 4.0) differ from those of chloroform in that they do not significantly remove the wax layer.

8.4. Results and Discussion

8.4.1. Metal element movement in the soil profile

The total activities and distribution patterns of radioisotopes in three layers of soil 70 days after application (Figure 8.1, semi-log plot) showed no significant difference ($P \leq 0.01$) between ^{54}Mn and ^{65}Zn. The top layer (4-6 cm) of soils had an activity of about 13 MBq kg^{-1} on an air-dried basis. This activity on average was approximately 300 and 800 times higher than that in the second (9-11 cm) and the third layers (14-16 cm) of soils, respectively. There was no statistically significant difference ($P \leq 0.01$) in activity between the 9-11 and 14-16 cm layers.

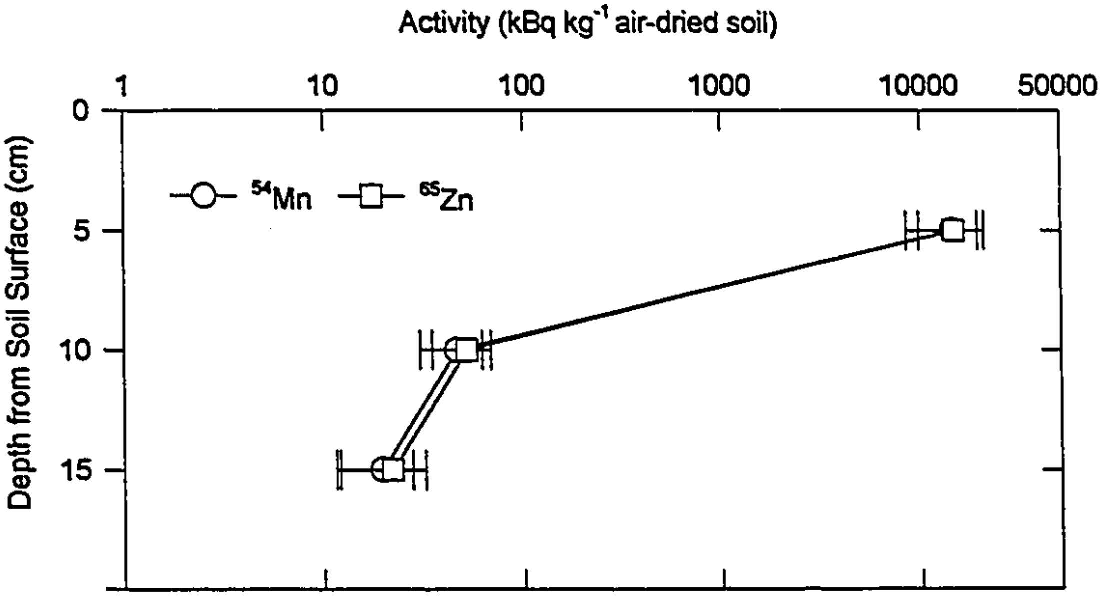


Figure 8.1. ^{54}Mn and ^{65}Zn profiles in podzolic soils 70 days after soil surface application.

The movements of Mn and Zn in the soil profile are known to be affected by pH, organic matter (OM), cation exchange capacity (CEC), redox potential and the chelating agents (Kabata-Pendias and Pendias 1992; Wallace and Mueller 1968). The Mn and Zn availability and its movement in soil become much more evident in acidic soils (Adriano 1986; Sheppard and Evenden 1989). The movement of ^{65}Zn into agricultural soils from surface application has been intensively studied in an attempt to assess the efficiency of Zn fertilizer. In general, pH and CEC were found to be important factors which controlled the initial Zn retention and its movement. The depth of downward movement was negatively related with CEC, and high concentrations of Zn were found in the upper layers of soils (Jones *et al.* 1957; Benson 1966). Our results from three subsurface layers are in qualitative agreement with their findings. These studies indicate that atmospheric deposition of Mn and Zn on soil surfaces in subalpine forests in North America may be followed by downward movement when the low pH (3.5) and CEC (12.8 cmol$^{(+)}$ kg^{-1}) of soils and strong acid deposition are considered.

8.4.2. Root uptake and above-ground translocation

Accumulated activities of ^{54}Mn and ^{65}Zn were very different, with those of ^{54}Mn (in kBq kg^{-1}) about 5-10 times higher than those of ^{65}Zn in different above-ground parts of the seedlings (Figures 8.2 and 8.3). Young needles accumulated higher concentrations of ^{54}Mn and ^{65}Zn than older needles, suggesting that concentration of the radioisotopes in needles was highly related to growth activity. However, older twigs concentrated more ^{54}Mn than younger ones, while sample specific activities of ^{65}Zn did not show any significant ($P \leq$ 0.01) difference among twigs of different age or from different parts of the seedlings. Higher activities in woody tissues relative to needles also suggest that translocation of Mn and Zn in trees is strongly dependent on xylem cells in their ability to adsorb or fix heavy metals at cell-walls. Roots concentrated less ^{54}Mn and more ^{65}Zn than the above-ground parts of

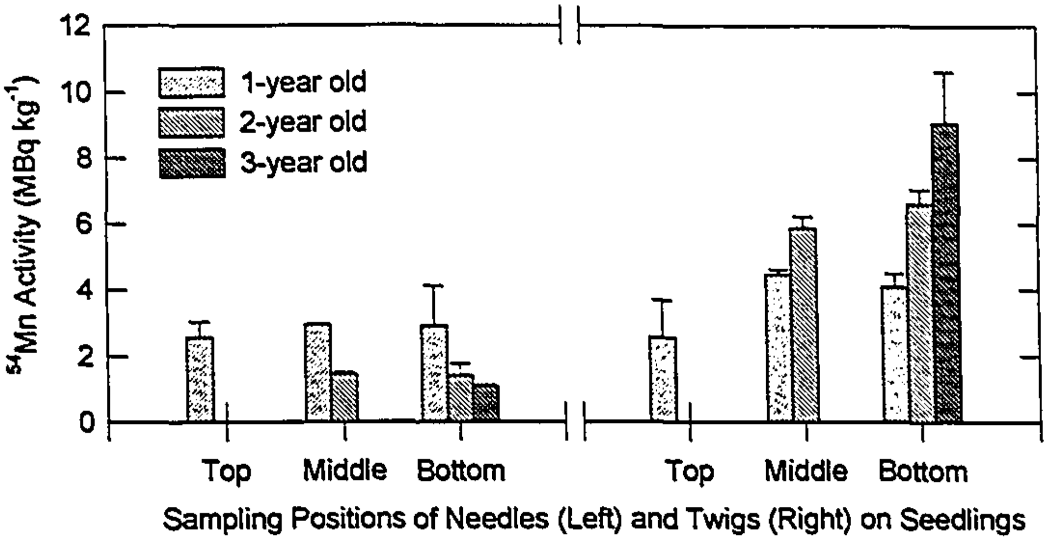


Figure 8.2. Concentration of ^{54}Mn in different-aged needles and twigs at different height of the crown of 4-year old balsam fir 70 days after soil surface application.

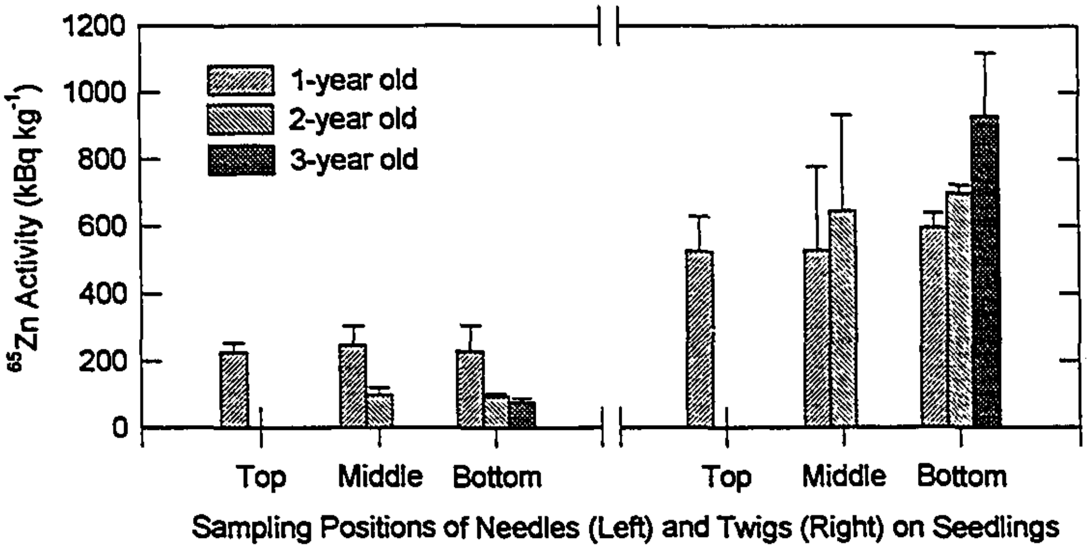


Figure 8.3. Concentration of ^{65}Zn in different-aged needles and twigs at different height of the crown of 4-year old balsam fir 70 days after soil surface application.

stems, but no significant difference between ^{54}Mn and ^{65}Zn was found in roots (Figure 8.4).

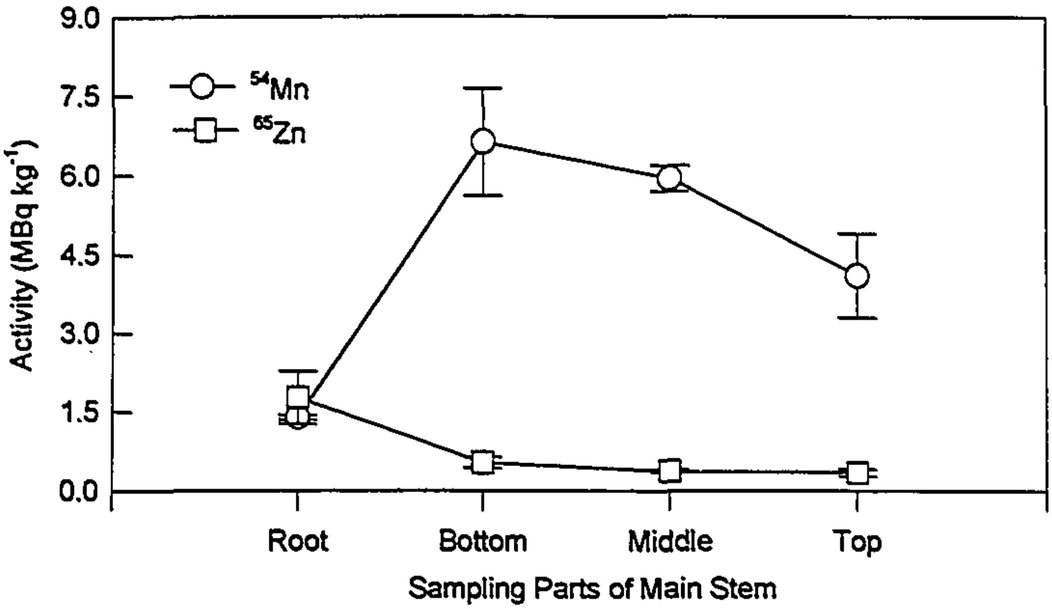


Figure 8.4. Concentrations of ^{54}Mn and ^{65}Zn in roots and at different heights of main stems of 4-year old balsam fir 70 days after soil surface application.

The distribution of ^{54}Mn accumulated in trees is fairly homogeneous in the woody tissues of roots (31%), stems (26.4%) and twigs (30.5%), but lower in needles (12%) (Table 8.1). For ^{65}Zn, roots accumulated 86.2% of the total activity, while needles only contained 2%. These results indicate that ^{54}Mn is more mobile than ^{65}Zn in balsam fir, with both Mn and Zn usually classified as intermediate in terms of element mobility (Kramer and Kozlowski 1979). Taking into consideration the plant available ^{54}Mn and ^{65}Zn, the extractable activity of isotopes represented 75% of ^{54}Mn (15 MBq kg^{-1}) and 60% of ^{65}Zn (15 MBq kg^{-1}) in the 4-6 cm soil layer. Therefore, the lower extractable ratio of ^{65}Zn and its stronger accumulation in roots might help to explain its lower accumulation in above ground parts of the seedlings.

Table 8.1. Distribution of ^{54}Mn and ^{65}Zn in balsam fir 70 days after soil-surface-application. The distribution among different plant organs is presented in percentage (%) of the total activity in the seedling. Standard errors from two replicates were shown in brackets.

	Biomass (g)	Distribution of ^{54}Mn in Tree		Distribution of ^{65}Zn in Tree	
		Activity (kBq)	% of Total	Activity (kBq)	% of Total
Needles	19.9 ± 2.6	38.6 ± 4.8	12.0 ± 0.6	3.1 ± 0.3	2.0 ± 0.1
Twigs	17.4 ± 1.5	98.4 ± 11.5	30.5 ± 1.7	11.2 ± 0.4	7.4 ± 1.2
Stems	14.9 ± 1.6	86.1 ± 15.8	26.4 ± 0.4	6.9 ± 1.2	4.4 ± 0.3
Roots	63.8 ± 5.8	102.3 ± 23.5	31.1 ± 1.9	133.2 ± 17.0	86.2 ± 1.2
Total	107.6 ± 8.5	325.5 ± 55.5		154.4 ± 18.0	

It has been indicated in Chapter 7 that the total amount of ^{54}Mn and ^{65}Zn accumulated in different parts of trees during the 70 days experiment could not be calculated precisely from the concentrations (kBq kg^{-1}) and the biomass (kg) determined on the 70th day in this study. This is mainly due to lack of knowledge in metal accumulation dynamics (*i.e.*, uptake and accumulation of isotopes as a function of tree growth) to the various parts of the seedling. Therefore, the plant-accumulated fractions of total activity remaining on the 70th day after the radioisotope application were calculated approximately as 5.2% of 6290 kBq for ^{54}Mn and 2.6% of 6031 kBq for ^{65}Zn.

A relatively large standard error in the results probably resulted from differences in the extent of root distribution, biomass, and the growth activity variations particularly in the lower and higher parts of the trees. Statistically non-significant differences ($P \leq 0.01$) among some treatments might also be due to the small sampling size and large variation.

However, the two seedlings demonstrated similar patterns in translocation and distribution characteristics. In general, root uptake and translocation of Mn to foliage have been observed to decrease through competition with Zn, Fe and Si in soils (Horst 1988). However, such interaction might be less evident in our study since soil pH values were relatively low, which favours ^{54}Mn uptake (Adriano 1986). Mineral translocation from soil to above-ground parts of plants has been expressed by soil-plant transfer factors, defined as the ratio of activity (in kBq kg^{-1}) of tree dry biomass to air-dried soil (Hoffman *et al.* 1982). But, such factors are not easy to define in our experiment due to difficulties in determining representative values for the concentrations in the soil, and due to possibly non-uniform root distributions.

8.4.3. Radioisotope migration to epicuticular wax layers

The observations summarized in Table 8.2 indicate that migration of ^{54}Mn and ^{65}Zn from internal tissues to epicuticular wax layers only accounted for 0.002-0.01% for ^{54}Mn and 0.124-0.541% for ^{65}Zn of the total radio-activities in shoots 70 days after application. The migration of ^{54}Mn and ^{65}Zn isotopes did not show significant ($P \leq 0.01$) differences between one year and two year old age classes, nor did the treatment with acid mist appear to have a significant effect on migration. This might suggest that root uptake and consequent translocation of Mn and Zn to shoots would not result in a significant contribution of these elements to the throughfall/foliar rinsing composition through physiological ion migration from internal tissues to epicuticular wax layers. These observations support our previously stated contention that washing needles in chloroform solution for 15-30 s, as used in the studies described in Chapters 5 and 6, would result in negligible metal leaching.

Table 8.2. Migration of ^{54}Mn and ^{65}Zn from internal tissues to epicuticular wax layers of balsam fir. Shoots were washed in chloroform for 15 seconds. Acid deposition was simulated by spraying acidic mist (pH=4.0) on shoots twice a day for 70 days. The unit for radioactivities is Bq.

Samples and Treatments	Activity in Shoots		Activity in Residues		Migration Ratio (%)	
	^{54}Mn	^{65}Zn	^{54}Mn	^{65}Zn	^{54}Mn	^{65}Zn
1 yr shoots, with acid spray	2080 6036	225 853	0.1 0.1	1.8 2.4	0.003 ± 0.002	0.541 ± 0.259
1 yr shoots, no acid spray	7224 8445	968 1248	0.5 1.1	2.0 3.5	0.010 ± 0.003	0.244 ± 0.037
2 yr shoots, with acid spray	4526 5707	882 1057	0.1 0.1	2.1 0.1	0.002 ± 0.000	0.124 ± 0.114
2 yr shoots, no acid spray	8670 7431	1948 1651	0.9 0.1	0.5 3.9	0.006 ± 0.005	0.131 ± 0.105

Our findings are in general agreement with those of Reiners *i.e.* (1986), who studied the migration of five cations from interior to outer surfaces of balsam fir needles under dry, inter-storm conditions in the absence of dry deposition. They concluded that most of the excess elements collected in initial rinses or throughfall measurements were derived from dry deposition, without the effects of elemental internal cycling. However, under the effects of acid deposition and other air pollutants or microbe infection (Tukey 1970), epicuticular structures could be degraded, and the barrier to surface leaching could be damaged. As a result, ion exchange and leaching of specific elements on needle surfaces might be facilitated.

8.4.4. Foliar leaching from ion exchange

Table 8.3 presents results for needle surfaces with and without the application of acid spray. It shows that washing duration played an important role in leaching, particularly for ^{54}Mn. When increasing the duration from 1 min to 5 min, the leaching ratio in the acidic washing solution increased by a factor of between 2 and 7 for Mn. For Zn, this effect was less pronounced, with longer washing times leading at most to an increase by a factor of two. There was no significant difference in ^{54}Mn or ^{65}Zn leaching from one-year and two-year old shoots, though different accumulation of the radioisotopes was found in different aged needles (Figures 8.2 and 8.3). But overall, the leaching ratio was well below 0.5% for Mn and 1.0% for Zn. In general, element leaching has been considered to involve ion exchange on foliar surfaces, with acid deposition as a contributing factor (Smith, 1990). However, the results in Table 8.3 failed to support this latter assumption for both ^{54}Mn and ^{65}Zn, at least within the constraints of the given experimental conditions. In fact, leaching of ^{65}Zn from shoots washed in distilled deionized water (pH 5.7) was considerably ($P \leq 0.01$) higher than that in the simulated acid rain. This might be due to generally low ion activities in deionized water (*i.e.*, low electric conductivity) compared with the simulated acid rain, which would increase the ion leaching through the epicuticular layer. An examination of reasons for the difference in behaviour between the two elements, however, would be beyond the scope of this thesis.

Different metal elements would be associated with different pathways on tree surfaces because of their different physical-chemical properties. Leaching of ^{54}Mn and ^{65}Zn from shoots of balsam fir seedlings agreed only partly with the field observations by Petty and Lindberg (1990), where Zn was considered as a non-leachate, but subjected to absorption by foliage, and Mn was regarded as a significant leachate in throughfall

Table 8.3. Leaching of ^{54}Mn and ^{65}Zn from balsam fir shoots. Acid deposition was simulated by spraying acidic mist (pH 4.0) on shoots twice a day for 70 days. Shoots were washed in acidic solution (pH 4.0) or distilled deionized water (pH 5.7). Leaching ratios are the means of the two replicates, and the standard errors are in brackets.

Samples and Treatments	Washing Procedure	Activity (Bq) in Shoots		Activity (Bq) in Residues		Leaching Ratio (%)	
		^{54}Mn	^{65}Zn	^{54}Mn	^{65}Zn	^{54}Mn	^{65}Zn
1 yr shoots, with acid spray	deionized water, 60s	9040 4433	770 372	0.4 6.7	7.1 3.3	0.08 ± 0.07	0.91 ± 0.02
1 yr shoots, with acid spray	acidic water 60s	7622 5818	641 646	1.8 5.7	2.3 0.7	0.06 ± 0.04	0.23 ± 0.13
1 yr shoots, no acid spray	acidic water 60s	5810 2229	902 270	4.5 1.5	0.8 2.1	0.07 ± 0.01	0.43 ± 0.35
2 yr shoots, with acid spray	acidic water 60s	6681 4590	1338 960	7.4 3.6	1.6 0.1	0.10 ± 0.02	0.07 ± 0.06
2 yr shoots, with acid spray	acidic water 300s	8024 6224	1709 1141	11.9 11.6	0.1 1.3	0.17 ± 0.02	0.06 ± 0.05
2 yr shoots, no acid spray	acidic water 60s	5069 6907	736 1776	4.6 2.4	4.1 0.5	0.06 ± 0.03	0.29 ± 0.27
2 yr shoots, no acid spray	acidic water 300s	5427 4385	1389 1122	16.6 22.2	4.3 8.1	0.41 ± 0.10	0.52 ± 0.21

measurements under old-growth red spruce canopies. The apparent contradiction between these and our own finding might be attributable to differences in the tree species and growth status studied (*i.e.*, seedlings versus mature trees), or to potential effects of insects, foliar diseases, branch leaching, and relatively long precipitation duration in the field (Tukey 1970; Smith 1990).

8.5. Conclusions

It might be suggested, according to the low migration/leaching ratio of ^{54}Mn and ^{65}Zn from balsam fir seedlings, that the estimation of Mn and Zn dry deposition would not be significantly affected by the internal element migration and ion exchange-leaching, when such estimation was carried out by ***short-duration*** rinsing of shoots or by throughfall measurements at the ***onset*** of precipitation. However, such a suggestion might be complicated and questioned by differences between seedlings from growth chambers and trees in the field, and by the size of internal pools of metals. Although this study does not in itself establish the validity of the use of throughfall measurement to estimate dry deposition of Mn and Zn, our results suggest that the proportion of metals derived from internal tissues by leaching is likely going to be very small compared to that from atmospheric dry deposition.

CHAPTER 9. ON BIOGEOCHEMICAL CYCLING OF METAL DEPOSITS IN HIGH ELEVATION FORESTS: A GENERAL SUMMARY OF THE THESIS

9.1. Metal Contamination in the Air-Soil-Tree System

Multi-element analysis techniques provide a simultaneous measurement of different metal pollutants of interest. Comparison of multi-element concentrations may give an overview on metal contamination in the air-soil-tree system, and therefore, will be helpful for future evaluation of potential synergistic phytotoxic impacts of multi-trace metals on trees. However, it is difficult to generalize findings from multi-element analysis on metal contamination in high elevation forests, such as results presented in Chapters 3, 4, 5, and 6. Different metal elements must be expected to show different characteristics in accumulation and pathways in forests due to their differences in physical-chemical properties.

Higher concentrations of Cu, Mn, and Zn in airborne particulates were found at Roundtop Mountain in southern Quebec than their worldwide averages from other remote areas. In particular, annual Mn concentration was generally higher than the reported values for Champlain Valley in northeastern U.S. Accumulation of trace metals in topsoils was mostly within the range of element concentrations in podzolic soils reported worldwide, but generally with higher mean values for most elements. In chloroform-washed balsam fir needles Mn was the only element with concentration exceeding 500 mg kg^{-1}, which has been suggested as the potential acute phytotoxic level extrapolated from observations on different species. In general, therefore, trace metal contamination in the air-soil-tree system in southern Quebec did not reach levels that would lead to expectation of acute forest damage. However, the elevated accumulation of Mn in needles (up to 877 mg kg^{-1}), especially at the higher elevation sites, and high local concentrations of Ni (up to 50 mg kg^{-1}) near the vascular bundle region, may suggest the potential for long-term toxic effects of accumulated multi-trace metals on tree physiological processes, which may become a matter of future concern.

Different statistical methods have been applied for correlation analysis among multi-trace elements involved in different samples, *i.e.*, airborne particulates, topsoils, in and on balsam fir needles. In Chapter 3, Mn in airborne particulates was significantly correlated with Al, La, V, and Zn. On the surface of balsam fir needles, a similar correlation in surface deposits has been shown for Al, La, and V by analysis of the differences in concentration between washed and unwashed needles (Chapter 5), and for Mn and Zn by direct measurement through micro-PIXE scanning of unwashed balsam fir needles (Chapter 6). Statistically significant correlation between Al and Fe has been consistently revealed by the direct (Chapter 6) and indirect (Chapter 5) measurements of metal deposits on foliar surfaces. These inter-elemental relationships may reflect atmospheric deposition sources for trace metals on foliar surfaces.

EFs of trace metals in airborne particulates show that As, Cr, Cu, Mn, Sb, V, and Zn had most likely originated from anthropogenic activities, associated with atmospheric long-range transport of metal pollutants. Trace metals in airborne particulates, fog, and rainfall showed similar elemental enrichment. However, in topsoils, most elements did not show a significant enrichment, except Cd, Rb, and Pb. The impoverishment of trace elements in topsoils may reflect effects of acid deposition on elemental distribution in forest soils.

9.2. Metal Deposits on Foliar Surfaces and their Pathways in Forests

Long-range transport of Mn from urban-industrial pollution sources to remote mountain forests and atmospheric Mn deposition may significantly contribute to elevated Mn accumulation in coniferous needles in high elevation forests. In this thesis, this aspect has been explored only through tentative back trajectory analyses which, nonetheless, seem to support that hypothesis. Significant accumulation of Mg, Al, Si, K, Mn, Fe, and Zn in epicuticular wax layers has been demonstrated by micro-PIXE scanning on adaxial foliar surfaces. Epistomatal distribution of balsam fir does not appear to be systematically related to the accumulation of metals on needle surfaces, but spatial accumulation of Ni near the vascular endodermis or the nearby spongy parenchyma has been found by scanning to the depth 45-50 μm from the surface.

Pathway studies from our growth chamber experiments reported the proportion of (1) foliar and bark uptake of metals (^{54}Mn and ^{65}Zn) deposited on tree surfaces (25-30% from foliar surfaces and about 60% through bark surfaces); (2) the root uptake of isotopes deposited on soil surfaces (about 3-5%), and (3) leaching of metals accumulated in shoots from root uptake (< 0.5-1%). It is obvious that these results could only provide some basic information for the pathway studies in the field. Very likely, uptake and accumulation of deposited metals from needles and bark surfaces are facilitated by acidic wetness on tree surfaces due to acidic fog immersion in high elevation forests. However, extended and heavy precipitation might be expected to lead to non-negligible leaching of elements. Our results on absorption of Mn and Zn radioisotopes, and negligible leaching for both, agreed only partly with the throughfall measurement by Petty and Lindberg (1990), where Mn was considered as a significant leachate, but Zn was subject to absorption by canopies.

9.3. Biogeochemical Cycling of Trace Metals Deposited in Forests

Input of trace metals from atmospheric dry and wet deposition, and effects of acid deposition on pathways of metal deposits, alter their biogeochemical cycling in high elevation forests. However, the inadequacy in existing methods for the estimation of deposition fluxes of trace metals to **different components** (*e.g.*, foliage and bark) of a complex forest system, and the complication in determination of their pathways, make it difficult to quantitatively describe the biogeochemical cycling. The laboratory studies of limited duration reported in this thesis do not permit a clear definition of wash-off efficiency of metal deposits in precipitation under field conditions, and the long-term balance between uptake and leaching of metals at above-ground surfaces of mature forest trees. Therefore, current understanding of atmospheric deposition of metal pollutants and their pathway in forests is still far from providing a solid base for the modelling of their biogeochemical cycling in the field.

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