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UNIVERSITÉ DE MONTRÉAL

THE USE OF NEUTRON ACTIVATION ANALYSIS FOR ESTABLISHING HEAVY METAL AIR POLLUTION HISTORIES.

par

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ÉCOLE POLYTECHNIQUE

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ÉCOLE POLYTECHNIQUE

Cette mémoire intitulé:

THE USE OF NEUTRON ACTIVATION ANALYSIS FOR ESTABLISHING HEAVY METAL AIR POLLUTION HISTORIES

Présenté par: Reda F. ASSAAD
en vue de l'obtention du grade de: MAÎTRISE EN INGÉNIERIE
A été dûment accepté par le jury d'examen constitué de:

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RÉSUMÉ

La pollution des métaux lourds affecte de différentes manières la vie humaine sur terre et pour cette raison il est nécessaire et même primordial de surveiller et contrôler d'une façon permanente les concentrations de ces métaux.

La plupart des récentes publications scientifiques dans le domaine de la pollution affirment que les arbres sont un indicateur efficace de la pollution de l'air par les métaux lourds et offrent un grand avantage par rapport aux autres indicateurs: la disponibilité de l'information chronologique. L'intérêt des arbres réside dans le fait qu'ils montrent l'évolution de la pollution en métal lourd en fonction du temps et cela pour une longue période qui peut s'étaler sur des centaines d'années.

Le but de la présente recherche est de vérifier si les arbres sont réellement un bon indicateur de la pollution.

Notre recherche se base sur la technique de l'analyse par

activation neutronique pour l'analyse chimique d'échantillons d'arbres recueillis de différents sites aux alentours de la raffinerie de cuivre Noranda située à Rouyn-Noranda, Québec en juin 1991. Des échantillons d'écorces d'arbres et de bois ont été pris de 37 troncs d'arbres dont le plus jeune a plus de 30 ans et dont leur distribution spatiale par rapport à la raffinerie est la suivante:

5 épinettes blanches à 5.0 km au nord de la raffinerie
5 épinettes blanches à 4.5 km à l'ouest de la raffinerie
5 épinettes blanches à 6.0 km à l'est de la raffinerie
3 épinettes blanches à 10.0 km à l'est de la raffinerie
5 épinettes blanches à 11.0 km au nord de la raffinerie
4 épinettes noires à 5.0 km au sud-est de la raffinerie
3 épinettes noires à 10.0 km à l'est de la raffinerie

Les échantillons de contrôle ont été pris de la manière suivante:

4 épinettes blanches à 100 km à l'est de la raffinerie
3 épinettes noires à 100 km à l'est de la raffinerie

Deux échantillons sont recueillis de chaque arbre, un du côté est du tronc et l'autre du côté ouest à une hauteur de 130 cm au dessus du sol. D'abord, des échantillons d'écorces d'arbres de 0.8 cm de diamètre et 0.6 cm d'épaisseur sont recueillis. Par la suite des échantillons de bois sont aussi pris du même trou après une perforation supplémentaire dans le tronc d'arbre à l'aide d'une carotteuse (sonde de Pressler) de 45 cm de longueur et 0.4 cm de diamètre. Après échantillonnage et dans le but de protéger l'arbre de l'invasion des champignons ou des insectes, les trous perforés sont bouchés par des bouchons en bois. Après cette tâche, chaque échantillon d'écorce d'arbre est placé dans une fiole de plastique tandis que celui du bois est mis dans un tube de plastique. Des échantillons du sol sont aussi pris à la base des arbres et ramenés dans des sacs de plastiques pour une éventuelle analyse au laboratoire.

Au laboratoire, les échantillons d'écorces sont aussitôt soumis à l'analyse par activation tandis que ceux du bois sont emmagasinés dans des congélateurs afin d'assurer une protection contre les champignons.

L'analyse chimique des échantillons est faite grâce à la technique d'activation neutronique. L'échantillon est activé par un bombardement de neutrons produisant ainsi des radioisotopes qui à leur tour se désintègrent en émettant des rayons gamma qui sont détectés pour doser chaque élément présent.

L'analyse par activation neutronique des échantillons d'écorces d'arbres est réalisée pour des isotopes de très courte, courte, et longue période de vie. Les échantillons ont été irradiés dans le réacteur nucléaire SLOWPOKE avec un flux de neutrons stable de $5x10^{11}$ n/cm^2 sec. Les rayons gamma émis par les échantillons activés sont détectés par un détecteur au germanium couplé à un analyseur multicanal et le spectre est stocké dans le disque d'un micro-ordinateur. Les résultats de l'analyse sont traités par un micro-ordinateur grâce au logiciel EPAA conçu pour cet effet.

L'analyse a révélé la présence des éléments suivants: Al, As, Ba, Br, Cd, Cl, Cu, Mg, Mn, K, Se, Na, et le Zn.

Les concentrations des éléments sont calculées par unité de surface des échantillons d'écorces d'arbres et les résultats sont tabulés en $\mu g/cm^2$ ou en ng/cm^2 et présentés au chapitre 6.

Après avoir terminé l'analyse des échantillons d'écorces d'arbres, une analyse similaire est faite pour les 74 cylindres de bois recueillis des 37 arbres déjà cités et sur lesquels on pouvait voir clairement les anneaux annuels. Ces cylindres de bois sont ensuite découpés en morceaux correspondant chacun à 5 anneaux selon la répartition suivante 1986-1990, 1981-1985, 1976-1980, 1971-1975, 1966-1970, 1961-1965. Ces morceaux sont placés dans des fioles en polyethylene pour subir une analyse similaire aux précédentes.

L'analyse a révélé la présence des éléments suivants:
Al, As, Ba, Br, Cd, Cl, Cu, Mg, Mn, K, Se, Na, Zn, et le W.

Après l'analyse, les échantillons sont séchés et pesés. Les concentrations des éléments chimiques sont calculées par gramme de poids sec et les résultats sont tabulés en $\mu g/g$ ou en ng/g et présentés au chapitre 6.

La possibilité d'une contamination externe des échantillons d'écorces d'arbres par les outils de travail et les fioles de plastiques est négligeable; par contre on a relevé une certaine contamination de l'arsenic, tungstène, cuivre et du zinc provenant surtout des tubes et de l'extracteur de la carotteuse utilisé pour recueillir les échantillons de bois. Une analyse par activation neutronique a déterminé les rapports As/W = 0.03 et Cu/Zn = 0.002 dans les alliages du tube et de l'extracteur. De ce fait on a supposé que tout le tungstène et le zinc détectés dans le bois proviennent de la contamination et on introduit les rapports As/W et Cu/Zn dans le programme EPAA pour corriger la contamination de l'arsenic et du cuivre.

Un total de 9000 concentrations ont été déterminées. Les concentrations sont moyennées sur l'ensemble des arbres de chaque site et ceci aussi bien pour les échantillons d'écorces que pour ceux du bois.

En résumé on a remarqué que certains éléments tels que l'Al, As, Ba, Br, Cd, Cu, Cl et Se présentent des concentrations élevées dans certains échantillons recueillis à proximité de la raffinerie comparées à celles des échantillons de contrôle. Par contre les concentrations du manganèse dans certains échantillons recueillis à proximité de la raffinerie sont faibles par rapport à celles des échantillons de contrôle. Les concentrations de magnésium des échantillons pris à proximité de la raffinerie sont similaires à celles des échantillons de contrôle.

En conclusion, on peut dire que l'écorce d'arbres constitue un bon indicateur et un bon moyen de surveillance à long terme de la pollution en métaux lourds malgré l'intervention de certains facteurs naturels, tel que la pluie qui affecte d'une manière ou d'une autre l'accumulation d'éléments. Les arbres peuvent servir d'indicateurs pour la pollution en certains éléments tel que le cadmium. Par contre on peut conclure que les arbres ne constituent pas un bon indicateur de la pollution en fonction du temps car le profil de la déposition en fonction du temps n'est pas reflété dans les concentrations dans les anneaux annuels. Les informations obtenues de la Compagnie Minière Noranda montrent qu'ils ont réussi à diminuer le degré de pollution dans la région durant les dernières années en installant de nouveaux équipements dans la raffinerie. En conséquence, les concentrations en métaux lourds durant les dernières années (1986-1990) devraient être beaucoup moins élevées que celles des années ultérieures. Une tendance opposée fut observée dans les échantillons de bois pour certains éléments tels que Al, As, Br, Cl, Cu, K, Na, et le Zn.

Enfin nous recommandons qu'un travail de recherche supplémentaire soit réalisé pour explorer d'autres voies avant de se prononcer définitivement sur le rôle des arbres comme indicateurs de la pollution en métaux lourds. En particulier l'analyse des échantillons d'écorces pourrait être réalisée sur la surface externe d'une épaisseur de 0.1 cm du fait que l'accumulation en métaux lourds se fait essentiellement sur la surface externe.

ABSTRACT

Heavy metal pollution can affect human life in different ways and for that reason it is necessary to monitor and to control the concentrations of the metals.

The most recent publications indicate that trees could be considered as a good monitor for heavy metal environmental pollution with a great advantage over all other monitors: chronological information. Trees may indicate the presence of heavy metal pollution as a function of time for a very long period, as much as a hundred years.

The aim of the research of this thesis is thus to determine whether trees are good pollution monitors.

Our research depends on the Neutron Activation Analysis technique for the chemical analysis of tree samples taken from different sites around the Noranda Copper Refinery at Rouyn-Noranda, Quebec, in June, 1991. Samples of bark and wood were taken from the trunks of 37 trees at least 30 years old which

were distributed as follows:

5 white spruce 5.0 km north of the refinery
5 white spruce 4.5 km west of the refinery
5 white spruce 6.0 km east of the refinery
3 white spruce 10.0 km east of the refinery
5 white spruce 11.0 km north of the refinery
4 black spruce 5.0 km south east of the refinery
3 black spruce 10.0 km east of the refinery

Control samples were taken as follows:

4 white spruce 100.0 km east of the refinery
3 black spruce 100.0 km east side of the refinery

Two samples were taken from each tree, one from the east side of the trunk and the other from the west side at a height of about 130 cm above the ground. First, bark samples were taken with a tool which gives samples of 0.8 cm diameter and 0.6 cm thickness. Next, wood samples were taken from the same hole by boring into the trunk with a 45 cm long 0.4 cm diameter incremental corer. After sampling, the bore holes in each tree were sealed with wooden plugs to protect the tree from fungal or insect invasion. Each bark sample was inserted into a plastic vial and each wood sample into a plastic tube for transportation. Soil samples taken near the bases of the trees were also transported in plastic bags. At the laboratory, activation analysis for bark samples was started first while wood samples were stored in a freezer for protection from fungi.

The chemical analysis of the samples was done using the neutron activation technique. With this technique the sample is activated by bombarding with neutrons. The radioisotopes produced decay by emitting gamma-rays. These are detected to determine the quantity of each element.

Neutron activation analysis for the bark samples was carried out for very short, short, and long lived isotopes. Samples were irradiated in the SLOWPOKE nuclear reactor at a stable neutron flux of $5x10^{11}$ n/cm^2-sec. Gamma-rays emitted by the activated samples were detected with a germanium detector which was connected to a multichannel analyzer and the detected spectra were stored on the disk of a computer. The analysis calculations were subsequently performed using the EPAA computer program.

Elements which were determined from this analysis were: Al, As, Ba, Br, Cd, Cl, Cu, Mg, Mn, K, Se, Na, and Zn.

The element concentrations were calculated per unit surface area of the bark samples and the results are tabulated in chapter 6 in μg/cm^2 or ng/cm^2 according to the value of the element concentration.

After terminating the bark sample analysis, the wood sample analysis was started. The 74 wooden cylinders, taken from the east and west sides of the 37 trees, showed clear annual rings. They were cut into 5 year sections coresponding to years 1986-1990, 1981-1985, 1976-1980, 1971-1975, 1966-1970, 1961-1965. The pieces were placed in polyethylene vials for analysis which was done by the same method as the bark sample analysis.

Elements which were determined from this analysis were:

Al, As, Ba, Br, Cd, Cl, Cu, Mg, Mn, K, Se, Na, Zn, and W.

After analysis the samples were dried and weighed. The element concentrations were calculated per gram of dry weight and the results are tabulated in chapter 6 in μg/g or ng/g according to the value of the element concentration.

Possible external contamination of the bark samples from tools and plastic vials used was found to be negligible, while for the wood samples we determined some contamination of arsenic, tungsten, copper and zinc coming from the tube and the extractor of the incremental corer which was used in taking the wood samples from the trees. Neutron activation analysis was done for the chemical analysis of samples which were taken from the tube and the extractor where we successfully determined the ratios of As/W and Cu/Zn in the alloy of the tube and the extractor; they were found to be 0.03 and 0.002 respectively. For treating the contamination we supposed that all tungsten and zinc in the wood samples was coming from contamination and we introduced the ratios of As/W and Cu/Zn into the EPAA program to correct for arsenic and copper contamination.

A total of 9000 concentrations were determined for bark and wood samples. They were averaged over the trees from each site.

Summarizing the results of the analysis, we can say that some elements such as: Al, As, Ba, Br, Cd, Cu, Cl, and Se indicated higher concentrations in some samples from near the refinery compared to those in the control samples. The manganese concentrations in some samples from near the refinery are lower than those in the control samples. The magnesium concentrations in the samples from near the refinery are similar to those in the control samples.

From these results we concluded that bark may be considered a good monitor for long term heavy metal pollution although there are some natural factors such as rain which could affect the accumulation. Trees may be useful monitors as a function of location for some pollution elements such as cadmium but not for all elements. There is no indication that trees could serve as monitors of pollution as a function of time because the expected time-profile of deposition is not reflected in the concentrations in the annual rings. The information obtained from Noranda Minerals Inc. indicated that they have successfully decreased the pollution level in the last few years by installing new equipment in the smelter which means that the heavy metal concentrations in the last few years, i.e, (1986-1990) should be lower than those in the preceding years. The opposite trend was observed in the wood samples for some elements such as: Al, As, Br, Cl, Cu, K, Na, and Zn.

We recommend that further investigation should be carried out before trees can be used as monitors for establishing heavy metal pollution histories. Bark sample analysis should be done only for the outer surface layer with a thickness of 0.1 cm due to the fact that heavy metal pollution accumulates mainly on the outer surface.

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CHAPTER 1

INTRODUCTION

Environmental contamination is an inevitable consequence of the activities of man and a natural phenomenon as well.

Whether in an industrial society or in an agricultural society, placing waste material, partially used consumer goods and other by-products into the environment by man has characterized his activities.

Contamination is also a social phenomenon. The communal activities of man as a social being have created a new order of by products which have increased in volume at a faster rate than population, and have been concentrated by our megalopolitan tendencies. This has resulted in increasing contamination of the environment surrounding the habitats of man to the point where the natural purifying activity can no longer keep up with it and what was once contamination, now becomes pollution.

Contamination is also a historical phenomenon. Throughout the development of the industrial age and, prior to that, even during the beginning of the agricultural age, there have always been by-products returned to the environment.

Contamination must be considered an amoral phenomenon. It is neither right nor wrong; it is simply a consequence of living. However, excessive contamination is that which interferes with the health and happiness of a population; this is pollution and this is wrong.

Management of contamination, so that it does not become pollution, is essential at this time if we are to continue to grow as an industrialized world. However, a rational management program, designed to avoid adverse effects from contamination, starts with the recognition, description, and understanding of the effects of the contaminants themselves.

To understand effects, we must recognize that they are a function of the kind and quantity of contaminant that is being released into the environment. There are some contaminants that are specifically toxic to biological systems or perhaps destructive of physical systems. There are some materials that are irritants, some that are systemic poisons, some that produce abnormal growth, and some that interfere with reproduction.

Another consideration is the dose of a contaminant. The concentration and the period of time that the contaminant is exposed to a receptor system (such as a population) is the dose and it plays a significant role in the ultimate effects of this contaminant.

Finally, the sensitivity of the receptor system is important. There are some plant materials that are extremely sensitive to even very low doses of certain toxicants, whereas there are other plant systems apparently indifferent to the same dose of the same material. There are some physical systems that are not bothered by a certain material and which see it as a contaminant, and others that are extremely sensitive to it and see it as a pollutant. There are many factors which influence the sensitivity of receptor systems, such as the environmental matrix in which they exist, the innate genetics in the case of biological systems, or the innate properties of the physical system; all these play a significant role in the sensitivity of the receptor system and, consequently, in the ultimate effects.(1)

Pollution can affect human life in different ways and for that reason it is necessary to monitor and to control its concentration continually.

Several ways exist to monitor environmental pollution. Several publications have appeared throughout the world to specify new measuring methods and new monitors for different types of pollution. Some of them indicate that fish could be considered good monitors for water pollution, others indicate that plants are accurate monitors for environmental pollution.

The most recent publications indicate that trees could be considered as a good monitor for heavy metal environmental pollution with a great advantage over all other monitors: time. Trees may indicate the concentration of heavy metal pollution as a function of time over a very long period.

But trees are just a pollution receptor; in other words, if we obtain tree samples, we need a means of determining the kind and the concentration of the pollution elements which exist in these samples. Also, for trees to be used as quantitative monitor, we need to know their efficiencies for collecting various contaminants.

Different techniques have been developed for the chemical analysis needed for pollution studies, some of them depend on chemical methods and others on physical methods. Neuton Activation Analysis is one of the more modern of these techniques. Activation analysis has proven a successful method of measurement in a great many diverse disciplines. It has been used extensively in the biological sciences, in the earth sciences, in the physical sciences, and in industrial plants to name but a few. It is also being developed in such fields as environmental sciences and forensic sciences. Its role in stable-isotope tracing is growing in hydrology, petroleum, and other engineering sciences.(2)

Now, the most important question to be answered is: are trees really a good monitor for heavy metal environmental pollution ?

The aim of the research of this thesis is thus to determine whether trees are a good pollution monitor.

Our research depends on the Neutron Activation Analysis technique for the chemical analysis of tree samples taken from different sites around a source which has been polluting its surrounding area for more than sixty years. The source is the Horne Division Complex of Noranda Minerals Inc., located at Rouyn-Noranda, Quebec. In operation since 1927, it remains one of the world's largest producers of copper and precious metals.(3)

CHAPTER 2

ENVIRONMENTAL POLLUTION

2.1 **POLLUTION EFFECT**

The environmental impact of air pollutants may be broadly classified in terms of nuisance, economic, or health effects. Nuisance effects include the reduction of visibility by fugitive dust arising from resuspension or redispersion of particulates from storage piles of ash, coal, or other granular powdery materials, demolition wastes, or earth and soil from roadways and excavations; also from smoke from open burning of leaves, forest fires, agricultural materials, industrial operations, or dumps.

Economic effects range from soiling of building materials and furnishings to deterioration of property such as textiles, rubber, building stone, art treasures, books, etc. Air pollution also represents a direct economic loss through crop damage.

Health effects involve the toxicity of air pollutants for human and animal populations. They range from consideration of hazardous atmospheres (high concentration, short time) to subclinical or chronic effects associated with long-term exposure to low concentrations.

Smog may be defined in terms of several of its effects; oxidizing atmosphere, rubber cracking, reduction in visibility, eye irritation, occasional respiratory distress and damage to susceptible vegetation.

Long-lived atmospheric pollutants such as CO_2 or other combustion products, injected at stratospheric altitudes, may have future geophysical or geochemical effects in terms of the distribution and accumulation of global energy from the sun. Effects of air pollutants may occur at great distances from a source, and may affect climate and habitability of regions far from a source.(1)

2.2 SOURCES OF CONTAMINANTS

There are a variety of ways to classify the chemical contaminants found in the environment. They can be divided:

a) Into natural and anthropogenic.

b) By the medium in which they are dispersed-air, water, soil, food, etc.

c) By specific elements and/or compound classes.

d) By their state of matter-solid, liquid, gas, or dispersion.(4)

Contaminants can be classified according to their sources as primary and secondary contaminants as follows:

2.2.1. PRIMARY CONTAMINANTS

I- NATURAL CONTAMINANTS

While many "natural" contaminants can be found in areas not significantly influenced by human activity, it does not necessarily follow that the observed levels are independent of human activity. Sources of natural contaminants can be classified as follows:

- Viable Particles (such as Viruses, Bacteria, Fungi, etc.)
- Products of plant and animal metabolism.
- Products of organic decomposition.

-Erosion (wind action, wave action, man-made wind).

-Fire.

-Sea spray.

-Natural radioactivity.

-Vulcanism.(4)

II- ANTHROPOGENIC CONTAMINANTS

a) Fossil Fuel Combustion For Power Production And Space Heating

The fossil fuels contain varying mixtures of hydrocarbons and minerals such as sulfur, nitrogen, and noncombustible mineral ash.(4)

b) Transportation

In consuming energy, there is always waste. For transportation, or moving sources, these are heat, fuel spillage exhaust products, and various by-products.(4)

c) Industrial Operations

Industrial operations and processes are extremely varied and complex. The main sources of contaminations due to industrial operations are:

i- Petroleum Refining

The petrochemical industry and petroleum refining are potential sources of contaminant release such as hydrocarbons, sulfur and nitrogen.(4)

ii- Nonmetallic Mineral Industry

Components of the nonmetallic mineral industry include plants processing crushed stone, gravel, sand, and light weight aggregate; Portland cement production, concrete batching plants, and asphalt plants; talc and lime processing; coal cleaning plants; the manufacture of gypsum, clay, ceramics, refractories, frit, glass, mineral wool and other insulation; the mining and manufacturing of asbestos raw materials and products; and includes the processing of miscellaneous minerals such as phosphates, kaolin, bentonite, borax, pegmatite, fluorospar, barite, and mica.

The nonmetallic mineral industry is a source of pollution for SO_2 and NO_x.(1,4)

iii- Ferrous Metallurgical Industry

The ferrous metallurgical industry includes basic production of Fe from ore ($Fe_2 O_3$), coke, and limestone in a blast furnace, followed by reduction of C, S, and P content in an open hearth furnace or top blown basic O_2 furnace to produce steel. Major emission sources include materials handling, ore sintering and pelletizing, coke manufacturing, and furnace effluent fumes and dust.(4)

iv- Nonferrous Metallurgical Industry

The nonferrous metallurgical industry includes primary production processes for Cu, Pb, Zn, and Al; the secondary recovery and separation of these metals from scrap; and nonferrous foundry melting and casting operations.

Copper sulfide ores are mined, crushed, milled and separated from gangue by flotation. Concentrate (28% Cu) is roasted (calcined) in a multiple hearth furnace to remove moiture and some S and calcines are then smelted in a large reverberatory furnace to produce Cu_2 S and a silicate slag. Molten Cu matte is transferred to a converter and air blown through it to oxidize the S, leaving Cu. Molten Cu is then cast as flat anodes for further electrolytic refining. Principal emissions are dusts, fumes, and SO_x. Volatile trace metal values in the flue dusts (Pb, Zn, As) are recovered by settling in balloon flues and by electrostatic precipitators. SO_x control has been a continuing concern for nearly 100 years, and several plants have developed stack gas S recovery systems. The Cu smelting industry has also pioneered the use of tall stacks and meteorological control of operations to provide acceptable ground level concentrations outside the plant area.

The roasting, smelting, and refining of Cu, Pb, and Zn products usually produces smaller quantities of many other metals such as Sn, Cd, Hg, Tl, Bi, Se, and Ag-Au.(1)

d) Contaminants Resulting From Agricultural Operations

Agricultural operation creates environmental contamination sources classified as:

- -Agricultural use of fire.
- -Soil Tillage.
- -Fertilizers And Soil Conditioners.
- -Pesticides.
- -Waste Products.(4)

e) Radiological Contamination Resulting From Nuclear Fission Reactions

Contaminant radionuclides are generated as fission product and by neutron activation in the nuclear reactors and from nuclear-weapons testing.(4)

2.2.2 SECONDARY CONTAMINANTS

Many of the chemical contaminants in the environment, including some of the most important ones, such as ozone (O_3) in urban air, chloroform ($CHCl_3$) in drinking water, and aflatoxin in certain foods, are not directly released into the environment by any primary source. Rather, they are formed within the environment by chemical reactions among their precursor compounds, as in O_3 or $CHCl_3$ formation or by biological processes, as in the formation of aflatoxin by the action of Aspergillus flavus mold on stored peanuts and corn.(4)

2.3 EFFECTS OF CONTAMINANTS ON HUMAN HEALTH

The first indications that chemicals in the environment could affect human health were associations between certain diseases and specific occupations. People may be exposed to a chemical via the air they breathe, the water and food they ingest, or by skin contact with air, water, or solid surfaces. The action of chemical contaminants covers the entire range of effects, from a mere nuisance to extensive tissue necrosis and death, from generalized systemic effects to highly specific attacks on single tissues and even individual enzyme systems.

The environmental factors which affect biological response include the concentration, stability, and physicochemical properties of the agent in the exposure environment and the duration, frequency, and route of exposure.

Any organ can only respond in a limited number of ways. The following sections discuss the broad types of responses which may occur following exposure to environmental chemicals.(4)

a) Irritant Response

A pattern of generalized, nonspecific tissue inflammation and destruction may result at the area of contaminant contact. This type of reaction is caused by the class of chemicals termed irritants. The most common chemical irritants are; sulfur dioxide, nitrogen dioxide, hydrogen fluoride, formaldehyde, chlorine, ozone and numerous pesticides.(4)

b) Fibrotic Response

A number of environmental agents are etiological factors in the development of a group of chronic lung disorders termed pneumoconioses. This general term encompasses many fibrotic conditions of the lung, i.e., diseases characterized by scar formation in the interstitial connective tissue. The most common Fibrotic Agents are; Crystalline silica, Asbestos, Coal, Graphite, Iron oxide and Beryllium oxide.(4)

c) Asphyxiant Response

Some chemicals having the respiratory tract as a portal of entry can cause death by their action in preventing an adequate oxygen supply from reaching the tissues of the body. These chemicals are known as asphyxiants. Examples of these are CO_2 and CH_4.(4)

d) Allergic Response

Allergic agents, termed allergens, generally affect the respiratory tract and skin, although they may also affect other organs such as the intestines. The primary respiratory allergic reactions are bronchial asthma. The primary skin reactions are urticaria. Some chemical allergens are nickel, cobalt, arsenic and chromium.(4)

e) Mutagenic and Teratogenic Response

Mutagens are agents which produce mutations, or changes in genetic material, i.e., DNA. The most common chemical mutagens are; sodium arsenate, cadmium sulfate, and lead salts.

Teratogens produces a generative change during early embryonic development, resulting in anatomical defects or other functional or biochemical developmental errors. The most common chemical teratogens are cadmium sulfate and sodium arsenate.(4)

f) Carcinogenic Response

Cancer is a general term for a group of related diseases characterized by the uncontrolled growth of certain tissues. The most common environmental chemicals carcinogenic in man are; arsenic, nickel carbonyl, cadmium oxide, asbestos and radionuclides.(4)

g) Systemic Response

Many environmental chemicals produce a generalized systemic disease due to their effects upon a number of target sites in the human body. The most common metals producing systemic disease are; mercury, lead, cadmium, arsenic, and selenium.(4)

CHAPTER 3

TREES

Trees are the tallest, biggest and longest-lived of all plants. A tree is a perennial woody plant which can grow at least 6 m on a single stem. Trees are not a separate botanical class, but a form of growth found in many different families of plants, which may include different forms.(5) Trees are divided into two classes: coniferous and broadleaf.

3.1 **THE CONIFEROUS TREES**

Coniferous trees are a relatively primitive group, nearly all evergreen and with hard, mostly narrow leaves. They have separate male and female flowers, without petals. The wood is soft, resinous and non-porous. Viewed under a lens, the cross-section shows uninterrupted radial rows of cells between narrow dividers, called rays. These cells constitute the bulk of the tissue. They are long, tapered at the ends to fit closely together and their purpose is to transfer liquids through minute openings in their walls.

Examples of coniferous trees are; the pines, the spruces, the hemlocks, and the firs.(5,6)

3.2 <u>THE BROADLEAF TREES</u>

This second group is also known as the deciduous trees, or hardwoods. They are less ancient plants, with network veins allowing a great variety of leaf shapes. Outside the tropics most shed their leaves in winter. Some flowers have showy petals and some are combined male and female. The wood is hard, heavy and non-resinous in most species, and is partly composed of vessels. These are cells with open ends set one above the other to form continuous vertical conducting tubes. The tubes are visible in the cross-section of the wood as pores; on many species they can be seen without a lens. In some species, the cells formed during the spring are larger than those formed later in the year and, when the change from one size to the other is abrupt, a conspicuous band appears within the growth ring. Such wood is classed as ring porous. Where the pores do not vary noticeably in size throughout the growth ring, the wood is classed as diffuse porous.

Examples of broadleaf trees are; the willows, the poplars, the birches, and the oaks.(5,6)

3.3 TREE TERMINOLOGY

The different parts of a tree can be specified as follows:

3.3.1 BARK

Bark is a term given to multilayered tissue on the outside of the tree. It consists of various combinations of cell types, but especially cork cells. Epidermis is present only on the youngest stems and is quickly replaced by bark tissues. Cork cambium begins to grow on older twigs leading most commonly to scaly, furrowed bark on old branches and trunks. All trees have smooth bark when young, but most trees soon form roughened bark layers that first show up at the bottom of the trunk. The color, nature, and size of soft, corky spots and lines called "Lenticels" are the most important diagnostic features of smooth bark. Only a few trees maintain their smooth, nonexfoliating bark well into maturity.

The main mature bark characters to look for are thickness, degree and nature of roughness (smooth, scaly, exfoliating, furrowed, etc.), color of outer and inner bark, depth and breadth of fissures, width of the plates or ridges between the fissures, length of the plates, and the degree of interlacing of the ridges.(7)

3.3.2 LEAVES

Leaves are the working part of a tree, drawing the sap up from the roots and using it with the energy from light to make the food for the tree and its growth. They are therefore arranged on the shoot to catch the maximum of light. Leaf size is influenced by age, size, and vigor of the tree, the length and kind of shoot on which the leaves are borne, and habitat.

Sun leaves are those in the upper and outer crown that are exposed to full sun. They are typically smaller, thicker, more lustrous, and more dissected than shade leaves of the lower and interior crown.(5,7)

3.3.3 ROOTS AND TRUNK

The feeding roots stay within 25 cm of the ground surface over a wide area. But near the bole sinker roots may go down to various depths to give stability. On dry soils trees like beech send roots far down through the subsoil and rocks beneath to reach water, though no tree roots can grow into soil which is always saturated.

Trunks grow into the shapes best able to hold their crown against wind.(5)

3.3.4 TREE SHAPES

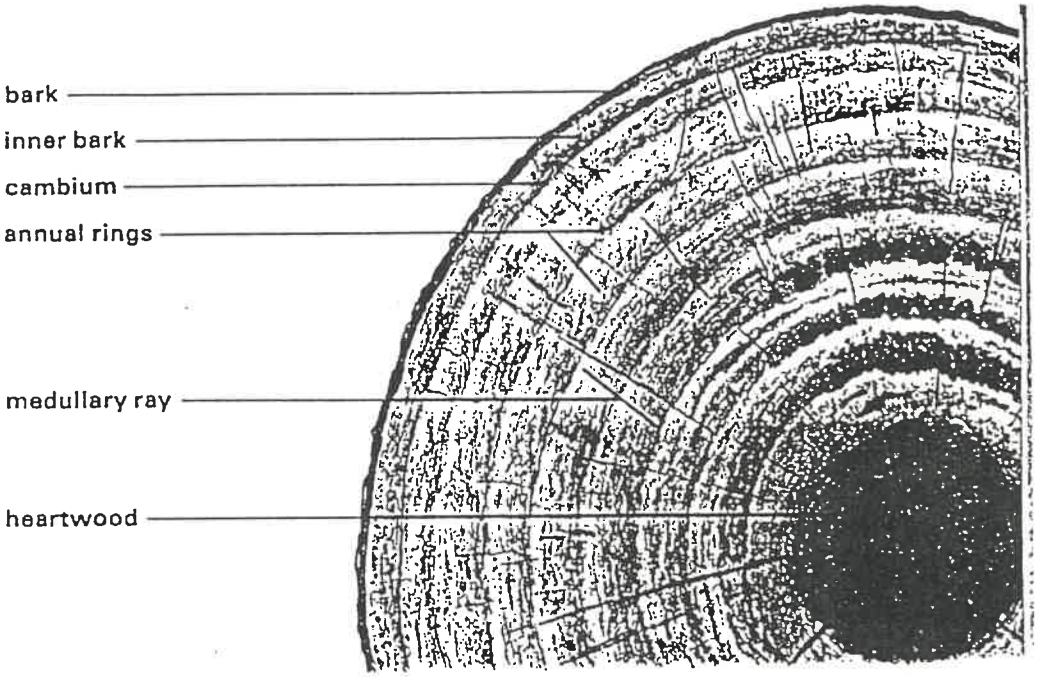
Tree shapes are set by the height at which the central stem divides, and by the length and angle of the branches. Broadleaves tend to have the more upright branching, but in conifers the branches are level with the youngest and so shortest at the top, which produces slender, conic crowns.(5)

3.3.5 WOOD

Woody plants are enclosed from shoot-tip to root-tip in a layer of cells called cambium, which moves outwards with each year's growth. Below this are the cells which conduct the sap from the roots to the leaves. They live for about 20 years, then solidify to make the heartwood that gives strength to a tree. Each year the first cells made are big and thin-walled, but the last are small with thick walls; they change as a new "ring" is made each year. Fig.(3.1) shows a cross section of a tree trunk.(5)

The general view of the structure of a tree trunk illustrates the position of the bark, cambium, sapwood, and heartwood. The "cambium" is the living meristematic sheath of cells that surrounds the trunk, branches, shoots, and roots. Toward the outside of the tree, the combium gives rise to the phloem, part of the inner bark, through which food materials and other substances are transported, mainly from the crown to stem and root tissues. Toward the inside of the tree the cambium gives rise to the water-conducting tissue or "xylem" that forms the "sapwood" . As the tree ages, the dead cells of the "xylem" become filled with resins and other compounds giving the "heartwood" a harder texture and a darker color than the sapwood.

The radial or diameter growth of trees is primarily due to the periodic formation of layers of xylem cells. In species of the temperate zones, the annual growth rings are more or less



Fig(3.1) cross-section of a tree trunk

distinguishable and enable one to determine the age of the tree.(7)

3.4 **TREES UNDER CONSIDERATION**

Our samples has been taken from white spruce and black spruce trees. The specifications of the two kinds are summarized as follows:

3.4.1 WHITE SPRUCE (*Picea glauca*)

Form

White spruce has a uniform conical crown with branches that spread or droop slightly and extend to the ground, concealing a trunk with a pronounced taper and thin scaly bark. The root system is shallow with many tough, pliable, wide-spreading laterals, but the tree has only moderate resistance to windthrow.

Habitat

White spruce is a characteristic tree of the Boreal Forest

Region, although it can be found almost everywhere in Canada.

Size

On the average, white spruce is 20 m. in height with a diameter of 50 cm., but some trees attain heights of 30 m. and diameters of up to 1 m.

Leaves

Broad needle-shaped, about 2 cm.long, stiff, with blunt ends, straight, four-sided in cross-section, green to bluish-green but often with a whitish bloom, aromatic when crushed.

Bark

Thin, scaly, light greyish-brown; inner bark silvery-white.

Wood

Light, soft, resilient, straight-grained; white, with little contrast between sapwood and heartwood.(6)

3.4.2 BLACK SPRUCE (Picea mariana)

Form

In stands, black spruce develops a straight trunk with little taper and without branches for much of its length. It has a narrow crown of drooping branches with up-turned ends. The root system is shallow and the tree is windfirm only when growing in stands.

Habitat

Black spruce grows in many different soil and climates.

Size

Usually a slow-growing tree which averages 10 to 15 m.in height and 15 to 25 cm.in diameter.

Leaves

Broad needle-shaped, 1.2 cm.long, stiff, blunt, four-sided in cross-section, dark bluish-green, without lustre.

Bark

Thin, scaly, dark greyish-brown; inner bark deep olive-green.

Wood

Moderately light, soft, relatively strong, resilient, straight-grained; nearly white, with little contrast between sapwood and heartwood.(6)

3.5 PATHWAYS OF METAL UPTAKE

Three direct pathways exist for heavy metal entry into trees, these are:

1) Uptake from the soil via the roots, with subsequent transport into woody tissue via the transpiration stream.
2) Foliar uptake, with subsequent export from the leaf via the phloem, followed by lateral movement from this tissue into the xylem.
3) Direct deposition into stem surfaces followed by lateral movement across the bark and into the wood.

The interpretation of heavy metal data obtained from the annual rings of trees is not simple. Fig.(3.2) gives an indication of the complexity involved. A tree receives fallout metal via wet and dry deposition directly on both leaves and bark. As a result of direct deposition on the soil from the atmosphere and indirect deposition via stemflow, heavy metals may enter the tree from the soil solution through the root system. The greatest contribution to the xylem may come from the root system. Leaf and bark metal may be translocated to the phloem and from there into xylem. Some of the xylem metal may be translocated to the bark. At each step towards xylem accumulation some of the metal may be lost. Hence the xylem metal content is a measure of the total environmental metal input minus what is accumulated in various tissues before the metals enter and bind in the xylem.(8,9)

3.6 **PREVIOUS STUDIES**

Previous studies had been done to monitor atmospheric pollution using trees. Tree bark has been shown to be very sensitive to environmental lead pollution. Baes and Ragsdale(9)

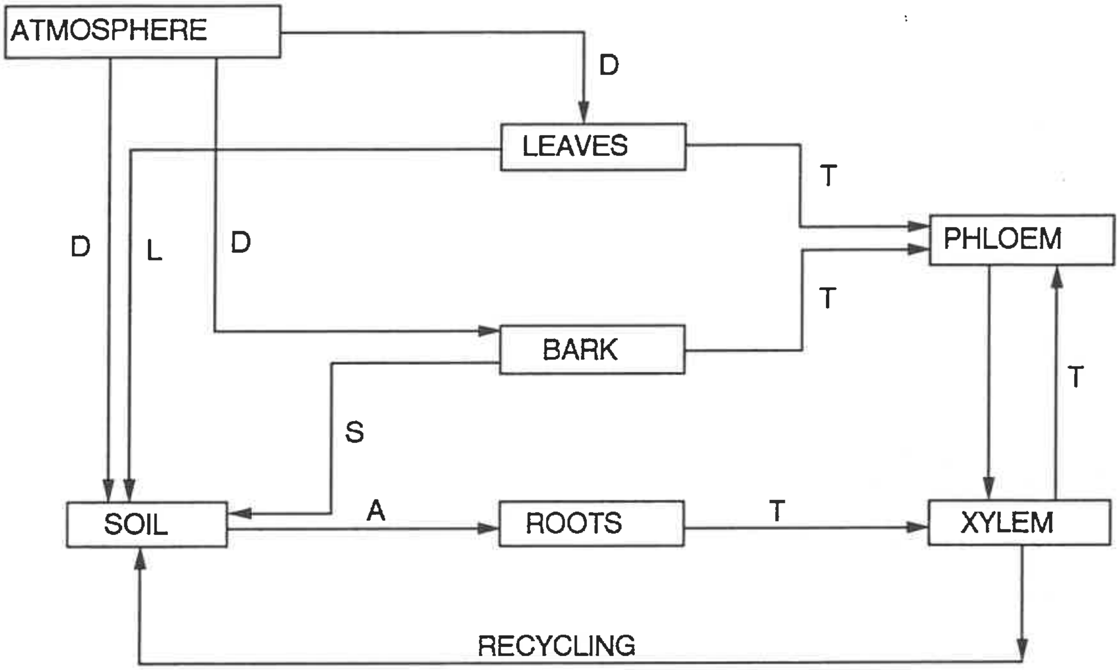


Fig.(3.2) Pathways for the deposition of metals in the xylem.
(D: deposition; T: transfer; L: leaching; S: stemflow; A: absorption)

mentioned that Barnes et al. found bark lead concentrations of various tree species to be greatest in areas of high traffic density. They also mentioned that Laaksovirta et al. found a highly negative correlation between lead concentration in white pine bark and distance from the road and a highly positive correlation with traffic density. Ward, Brooks, and Reeves(10) found bark lead concentrations higher on the sides of trees facing a road with heavy traffic than on sides facing away. Additionally, the downwind bark had significantly higher lead concentrations than the upwind bark.

While bark appears to be a sensitive monitor of environmental pollution, the question of whether tree ring analysis is useful in constructing pollution histories remains. Sheppard & Funk(11) suggested that Long-lived trees growing in intimate contact with rivers may be used to monitor variations of metal ion concentrations in rivers for times approaching a century. They had qualified success in relating metal concentrations in ponderosa pine xylem rings to mining activities along the Spokane River in Idaho. Tout,Gilboy and Spyrou(12) suggested that pollution products taken up into the tree would not remain in the quantities and positions they originally occupied, except possibly in the sapwood, which usually does not consist of more than 20 growth rings. Lepp(13) stated that many factors may influence the absolute amount of heavy metals present in woody tissues, including those which affect their uptake by the tree from soil or atmosphere, the transport form taken by the metal within the plant, and the rate at which this may bind to xylem tissue. Pathak, Love and Roy(14) found that the effects of air-pollutants may be recorded in the variations in wood chemical composition. Burton(15) found that the annual rings of trees growing in polluted environments contain elevated concentrations of a range of elements and that the potential advantage of analysing tree rings is that if the elements taken up by the tree in a particular year are retained in the wood formed in that year changes in emissions of pollutants could be documented in terms of magnitude and frequency. Baes and Ragsdale(9) mentioned that Szopa et al., working in Missouri, were unable to document lead ore hauling activities or the closing of a road through analysis of black oak, white oak, and shortleaf pine xylem. They also mentioned that Barnes et al. were unable to determine the occurrence of lead pollution from analysis of xylem from several tree species in forests and parklands in Great Britain. In addition, they mentioned that Tian & Lepp related lead concentrations to xylem growth rates in larch and sycamore, but were unable to observe evidence of environmental contamination from past mining activity.

CHAPTER 4

ACTIVATION ANALYSIS

4.1 PRINCIPLE AND SIGNIFICANCE OF ACTIVATION ANALYSIS

Activation analysis is a method for the analysis of elements. All of the atoms of any given element existing in nature have the same atomic number, however, they may have different mass numbers. Some elements are represented in nature by only one isotope, such as sodium. Other elements may have several isotopes, such as barium.

If an analytical sample is exposed to the effect of neutrons or electrically charged particles of suitable energy, nuclear reactions occur. Neutrons penetrate into the nuclei, leading to the emission of another particle, or particles, to gamma radiation, or, in some rare instances, to the nucleus being split. Thus, a new nucleus is formed out of the original target nucleus into which the neutron penetrated.

The new nucleus is very often radioactive; in these cases we say that activation has occurred. These radioactive nuclides usually emit beta and/or gamma radiation.(16) Activation analysis relies on the production of radioactive nuclides in a sample and the subsequent detection and measurement of the induced radiation.(17)

4.2 NEUTRON SOURCES

Neutrons are produced only by nuclear reactions and nuclear transmutations. Therefore a source of neutrons can exist in a device in which nuclear reactions can take place. Such devices cover a wide range of mechanisms. Neutron-producing nuclear reactions can be induced by the following:

1) Nuclear fission (and fusion) under controlled or uncontrolled conditions.
2) Charged particles and gamma radiation from accelerating devices.
3) Alpha and gamma radiations from radioactive nuclides.

These devices yield neutron sources which vary both in energy spectrum and flux. They also vary considerably in simplicity of construction, size, location, and cost from simple, low-cost, low-flux radioisotope sources to complex, expensive high-flux nuclear reactors.(2)

4.3 **NUCLEAR REACTORS**

The source of energy in a reactor is the fission of the nuclei of the fuel in a controlled chain reaction. The nuclear reactor consists of; reactor core, moderator, reflector, control rods and thermal column. Finally, of obvious importance for activation analysis, there are irradiation channels into which one can put samples for activation. These channels may be located in the reactor core, in the thermal column or in the reflector, in either a horizontal or vertical position.(16)

Neutrons produced in a reactor can be divided into fast neutrons with energy $E > 1$ MeV, resonance neutrons with 1 MeV $> E >$ 0.4 eV, and thermal neutrons with $E <$ 0.4 eV. The neutron energy distribution at the site of the irradiation is dependent on the type of moderator and on the distance traveled by the neutrons. The type of the nuclear reaction and its cross section differ greatly with the energy of the neutrons.(17)

4.4 **RADIATION DETECTION**

Once a material has been irradiated for activation analysis, it is then necessary to characterize the nature of the resulting radiations by the process of detection. Through the process of detection one can determine:

- The types of radiation being emitted by the sample.
- The energies of these radiations.
- The half-lives of the various nuclides present.
- The amount of radiation due to each radioactive component.

In many cases these characterizations can be made directly from the sample; in other cases a radiochemical separation is required(18)

Radioactive nuclides are determined qualitatively and quantitatively by the interactions of their emitted radiations with materials used as radiation detectors. A radioactivity measurement system generally consists of two parts; the detector in which the radiations interact and the associated measuring device that presents the information from the detector in a suitable form.

The two major radiation detection systems in modern practice employ detectors that are based on ionization of gases (e.g.,proportional and G.M detectors), excitation of crystals which result in luminescence (e.g.,scintillation detectors), or ionization of solids (e.g.,semiconductor detectors).(2)

Semiconductor detectors made from pure germanium are now extensively used for activation analysis. Their wide popularity is the result of the remarkable resolving power and an excellent linearity. Thus, qualitative analysis becomes very easy since gamma-ray energies can be measured with an accuracy of the order of a tenth of a keV. Moreover, very complex spectra can be analyzed and the probability for overlapping of full energy peaks is very low. As a result of the sharpness of the peaks, the calculation of peak areas by subtracting the background by linear interpolation methods results in a high precision.(17)

Radioactivity measurement systems are generally of the pulse type; that is, the output of the detector is given as a series of electrical pulses separated in time. Each pulse represents the interaction of a unit of radiation with the detector. Modern radioactivity measurement systems not only determine the number of radiations detected per unit time (i.e, the counting rate) but they also allow, to varying degrees, the separation of the radiations by type and energy. In gamma-ray spectrometers the amplitude of each electrical pulse is proportional to the gamma-ray energy deposited in the detector. Electronic sorting devices (pulse-height analyzers) can separate these pulses by amplitude.

A multichannel pulse-height analyzer, operated in conjunction with an analog-to-digital converter, an appropriate memory device, and supporting data-presentation equipment is commonly used to perform analysis of complex mixtures of gamma-ray emitting radionuclides without the need for chemical separation of the mixture by element. The memory readout may be coupled to a computer for complete data processing.(2)

4.5 ACTIVATION ANALYSIS SYSTEM AT THE I.G.E

Neutron activation at the Institut de Génie Energétique, Ecole Polytechnique de Montréal (I.G.E) is done with the institute's SLOWPOKE nuclear reactor. Samples are transfered to and from the reactor with a pneumatic system. Gamma-rays emitted by the activated samples are detected with a germanium detector which is connected to a multichannel analyzer and the detected spectra are stored on the disk of a personal computer. The germanium semiconductor detector has a volume of 75 cm^3 and resolution 1.75 keV FWHM at 1332 keV. The analysis calculations are subsequently performed by personal computer using the EPAA computer program.

4.6 THE SLOWPOKE REACTOR AT THE I.G.E

SLOWPOKE is a safe, reliable pool type nuclear reactor which can operate continuously at a flux of 10^{11} $n.cm^{-2}$ s^{-1} for 10 years on a single fuel charge. The reactor core is a compact fuel cage, 22 cm diameter and 22 cm high containing

296 fuel elements. The fuel elements are small rods of enriched uranium-aluminum alloy with a thin aluminum outer sheath. The critical mass of U-235 is 781 grams. The core is completely enclosed by the beryllium reflector.

Light water within the reactor container serves as both moderator and coolant.

The sample irradiation assembly consists of five irradiation tubes and console controls. The five irradiation tubes are located in the beryllium annulus. The irradiation tubes are directly connected to a pneumatic transfer system.

4.7 THE IMPROVED RELATIVE METHOD AND THE EPAA PROGRAM

In neutron activation analysis the concentration of an element in a sample to be analysed is calculated by comparing its gamma-ray peak area with that of a standard irradiated and counted under similar conditions. The peak area is related to the concentration by the formula:

$$\boxed{A = \frac{C\,W\,N\,\theta\,\sigma\,I\,\epsilon\,\Phi\,(1 - e^{-\lambda t_i})\,e^{-\lambda t_d}\,(1 - e^{-\lambda t_c})}{M\,\lambda}} \tag{1}$$

where:	A	is the peak area
	C	concentration of the element
	W	sample weight
	N	Avogadro's number
	Θ	isotopic abundance
	σ	effective cross-section
	I	gamma-ray intensity
	ϵ	detector efficiency
	Φ	neutron flux
	λ	decay constant
	M	atomic mass
	t_i	irradiation time
	t_d	decay time
	t_c	counting time

With the SLOWPOKE reactor it has been shown that the neutron flux is reproducible to within one percent over long periods of time. With germanium detectors, if the counting geometry can be reproduced, then the counting efficiencies will be reproducible since the intrinsic efficiency of the detector is essentially stable. Thus the analytical sensitivity for a given element, which can be thought of as peak counts per microgram, will be a constant which can be used over a period of years. For each useful gamma-ray of each element and for each counting geometry, a sensitivity constant, B, is defined which is proportional to the nuclear constants of Eq.(1) and the detector efficiency. The sensitivity factors are also defined for a reference neutron flux which is the SLOWPOKE nominal thermal neutron flux.

To calibrate an analysis system one must measure the sensitivity constant, B, for each gamma-ray line and for each counting geometry which will be used for future analysis. Several standards of each element are prepared and measured. After the standard has been irradiated and counted the sensitivity constant for a given gamma-ray is calculated with the following equation:

$$\boxed{B = A \lambda \left[M F \left(1 - e^{-\lambda t_i} \right) e^{-\lambda t_d} \left(1 - e^{-\lambda t_c} \right) \right]^{-1}} \quad (2)$$

where: M mass of the element in the standard

F neutron flux relative to the reference flux

With the sensitivity constant defined by Eq.(2) the equation used to calculate concentrations in unknown samples counted with the same geometry is:

$$\boxed{C = A \lambda \left[W B F \left(1 - e^{-\lambda t_i} \right) e^{-\lambda t_d} \left(1 - e^{-\lambda t_c} \right) \right]^{-1}} \quad (3)$$

where: A peak area measured with the unknown sample

W sample weight.

When using a SLOWPOKE reactor, an accurate value of the relative flux, F is easily obtained from the reactor power setting and measured flux distributions in the irradiation sites.

The program EPAA has been written to perform neutron activation analysis calculations on a personal computer. It reads gamma-ray spectra from disk, calculates peak areas using iteractive computer graphics, corrects interferences, and calculates the concentrations of the elements chosen by the user with the improved relative standardization method.(19)

CHAPTER 5

EXPERIMENTAL PROCEDURE

5.1 **DESCRIPTION OF THE SAMPLES**

Samples of bark and wood were taken from the trunks of trees at least 30 years old at different sites around the Noranda copper refinery at Rouyn-Noranda, Quebec in June, 1991. They were distributed as follows:

5 white spruce 5.0 km north of the refinery.
5 white spruce 4.5 km west of the refinery.
5 white spruce 6.0 km east of the refinery.
3 white spruce 10.0 km east of the refinery.
5 white spruce 11.0 km north of the refinery.
4 black spruce 5.0 km south east of the refinery.
3 black spruce 10.0 km east of the refinery.

Control samples were taken as follows:

4 white spruce 100.0 km east of the refinery.
3 black spruce 100.0 km east of the refinery.

These locations are shown on the map, Fig.(5.1). Two samples were taken from each tree, one from the east side of

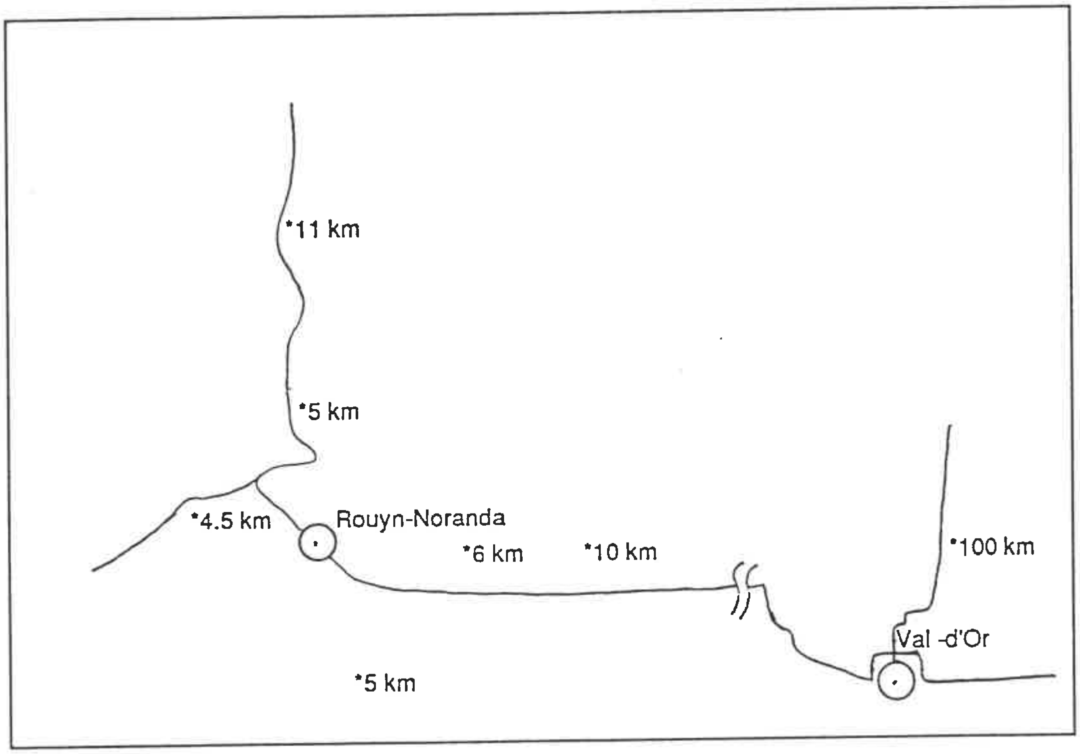


Fig.(5.1) Locations of the sampling sites the trunk and the other from the west side at a height of about 130 cm above the ground. First, bark samples were taken with a tool which gives samples of 0.8 cm diameter and 0.6 cm thickness. Next, wood samples were taken from the same hole by boring into the trunk with a 45 cm long 0.4 cm diameter incremental corer. After sampling, the bore holes in each tree were sealed with wooden plugs to protect the tree from fungal or insect invasion. Each bark sample was inserted into a plastic vial and each wood sample into a plastic tube for transportation. Soil samples taken near the bases of the trees were also transported in plastic bags. At the laboratory, activation analysis for bark samples was started first while wood samples were stored in a freezer for protection from fungi. Soil samples were also stored in a suitable place.

5.2 **BARK SAMPLE ANALYSIS**

Neutron activation analysis for bark samples was carried out for very short, short, and long lived isotopes. Samples were irradiated in the SLOWPOKE nuclear reactor at a stable neutron flux of 5.0×10^{11} n/cm^2-sec as follows:

5.2.1 Analysis With Short Lived Isotopes

After irradiation, the samples were transfered to new vials and then placed on the detector. The specifications of the analysis were as follows:

Irradiation Time (t_i) : 300.0 sec
Decay Time (t_d) : 60.0 sec
Counting Time (t_c) : 600.0 sec
Position Of Detection : 2 S (4 cm from the detector)

The elements which were determined with this analysis were; Ba, Mg, Cu, Cl, Al and Mn.

5.2.2 Analysis With Long Lived Isotopes

After irradiation, the samples were transfered to new vials and then placed on the detector with a mechanical sample changer. The specifications were as follows:

Irradiation Time (t_i) : 2.0 hr.
Decay Time (t_d) : 24.0 hr. (approximate)
Counting Time (t_c) : 3.0 hr.

Position Of Detection : 1 S (1 cm from the detector)

The elements which were determined with this analysis were; Na, Cd, Zn, Br, As and K.

5.2.3 Analysis With Very Short Lived Isotopes

The bark samples, contained in high purity polyethylene vials, were sent to the reactor and then directly to the detector with a pneumatic irradiation system. The analysis specifications were as follows:

Irradiation Time (t_i) : 30.0 sec.
Decay Time (t_d) : 3.0 sec.
Counting Time (t_c) : 30.0 sec.
Position Of Detection : 1 D (2 cm from the detector)

One element, selenium, was determined with this analysis.

Possible external contamination from tools and plastic vials used, was found to be negligible.

5.3 **WOOD SAMPLE ANALYSIS**

The 74 wooden cylinders, taken from the east and west sides of the 37 trees, showed clear annual rings. They were cut into 5 year sections coresponding to years 1986-1990, 1981-1985, 1976- 1980, 1971-1975, 1966-1970, 1961-1965. The pieces were placed in polyethylene vials for analysis. The analysis specifications were as follows:

5.3.1 Analysis With Short Lived Isotopes

Irradiation Time (t_i) : 300.0 sec.
Decay Time (t_d) : 60.0 sec.
Counting Time (t_c) : 600.0 sec.
Position Of Detection : 1 S(1 cm from the detector)

The elements which were determined with this analysis were; Ba, Mg, Cu, Cl, Al and Mn.

5.3.2 Analysis With Long Lived Isotopes

Irradiation Time (t_i) : 6.0 hr.
Decay Time (t_d) : 24.0 hr. (approximate)

Counting Time (t$_c$) : 2.0 hr.

Position Of Detection : 1 S

The elements which were determined with this analysis were; Na, Cd, Zn, Br, As, W and K.

5.3.3 Analysis With Very Short Lived Isotopes

Irradiation Time (t$_i$) : 30.0 sec.

Decay Time (t$_d$) : 03.0 sec.

Counting Time (t$_c$) : 30.0 sec.

Position Of Detection : 1 D (2 cm from the detector)

One element, selenium, was determined with this analysis.

5.4 CONTAMINATION FROM THE INSTRUMENTS

Contamination of the wood from the incremental corer was investigated and corrected with the following steps:

1) The tube and the extractor of the incremental corer were

immersed in the pool of the SLOWPOKE reactor for 7.5 hours to be irradiated in an unknown neutron flux.

2) After decay time of 24 hours, we used the radioactive tube and the radioactive extractor for taking wood samples (8 samples) from four white spruce trees from a region 30 km north of Montreal

3) The wood samples were divided into pieces of 1.8 cm length (0.154 gm dry weight) each and placed directly on the detector for detecting the radioactive elements from the tube and the extractor which contaminated the wood.

4) Samples weighing 0.102 and 0.120 gram were taken from the radioactive tube and the radioactive extractor respectively and placed on the detector for measuring the concentrations of the various elements in the two instruments.

5) From the tube's specifications, 98% of the tube's alloy is iron, so using the EPAA program we defined the irradiation neutron flux which gave that value and it was found to be 0.1×10^{11} n/cm^2.sec. We used that flux in the calculation of the following steps,

6) The wood analysis using the neutron flux calculated in

step 5 indicated a high contamination of zinc, tungsten, and a low contamination of copper and arsenic.

7) The analysis indicated that in the metal tube the As/W ratio is 0.03.

8) The analysis of the metal of the extractor indicated that its outer layer consists mainly of zinc with a small fraction of copper with a Cu/Zn ratio of 0.002.

The results obtained from the previous steps were used to correct the contamination of our samples from the icremental corer as follows:

1) We supposed that all tungsten in our samples is a contamination from the tube and we introduced an As/W ratio of 0.03 into the EPAA program to correct for arsenic contamination.

2) We supposed that all zinc in our samples is a contamination from the extractor and we introduced a Cu/Zn ratio of 0.002 into the EPAA program to correct for copper contamination.

5.5 **CALCULATION OF THE RESULTS**

For each analysis the gamma spectum was stored on disk. Subsequently, element concentrations for both bark and wood samples were calculated using the EPAA program. The SCOURT and SLONG libraries of the program were used. They contain the sensitivity constants B determined previously by measuring several standards of each element for each counting geometry.

The results of the bark sample analysis are tabulated in the next chapter in $\mu g/cm^2$ or ng/cm^2 according to the element concentration. The element concentrations were calculated per unit surface area of each sample (0.8 cm diameter).

The results of the wood sample analysis are tabulated in the next chapter in $\mu g/g$ or ng/g of dry weight according to the element concentration. Samples were weighed after drying for 3 hours at 100 C°.

CHAPTER 6

RESULTS AND DISCUSSION

6.1 **RESULTS**

The results of the analysis are tabulated in the next pages for each element in an alphabetic order. Each table contains the element concentrations of both bark and wood (east and west side of the tree) at all sites. The element concentrations are averaged over the trees from each site. They are indicated in $\mu g/cm^2$ for bark and in $\mu g/g$ for wood. For some elements which have low concentrations, the results are indicated in ng/cm^2 for bark and in ng/g for wood. The estimated experimental uncertainty of the results is indicated under each table. Also, for each site, the standard deviations of the concentrations were calculated for the N. samples of wood of the same age. The average of these standard deviations is indicated under each table. It indicates the variation in concentrations among trees at a given site. Fourteen elements were detected. Other elements may exist in the samples but were not detected because they were under the limit of detection (e.g.lead).

The definitions of the symbols used in the tables are as follows:-

E	east

W	west
N	north
SE	south east
N.	number of the trees from the site
Side	side of the tree

TABLE 6.1 ALUMINIUM CONCENTRATION

Bark: concentration in $\mu g/cm^2$
Wood: concentration in $\mu g/g$

WHITE SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
4.5 km W	5	E	46.4	4.64	2.26	1.94	2.27	2.57	2.22
		W	77.7	9.11	3.31	2.91	2.42	1.87	1.70
5.0 km N	5	E	38.6	3.23	2.50	2.71	2.68	1.79	1.44
		W	56.6	4.00	2.59	2.18	2.23	1.72	----
6.0 km E	5	E	31.2	1.76	2.51	2.43	1.89	1.96	1.52
		W	28.5	6.07	3.28	2.66	2.83	2.06	1.58
10.0 km E	3	E	33.1	3.98	2.56	1.94	1.95	2.05	1.86
		W	29.5	5.32	3.05	3.42	4.93	3.94	2.43
11.0 km N	5	E	22.6	5.04	3.10	2.13	2.12	1.63	1.59
		W	36.1	7.32	2.51	1.79	1.87	1.78	1.49
100 km E	4	E	26.2	3.74	2.53	1.97	1.64	1.29	1.56
		W	43.0	5.57	2.56	3.03	2.64	1.88	1.86

BLACK SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
5.0 km SE	4	E	61.0	8.18	4.38	9.75	3.83	4.14	----
		W	60.2	7.03	4.45	6.41	5.89	2.41	----
10.0 km E	3	E	9.0	2.47	2.23	1.36	1.52	1.33	1.10
		W	15.3	3.64	1.93	2.18	2.68	1.63	0.82
100 km E	3	E	30.3	2.05	1.97	1.15	1.37	0.96	0.61
		W	18.6	2.86	1.67	1.90	1.21	0.75	1.48

Experimental Uncertainty ± 11%
Standard Deviation ± 38%

TABLE 6.2 ARSENIC CONCENTRATION

Bark: concentration in ng/cm^2
Wood: concentration in ng/g

WHITE SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
4.5 km W	5	E	70.40	12.00	6.78	6.10	4.88	7.02	5.42
		W	187.00	10.80	4.10	6.30	6.84	8.96	5.98
5.0 km N	5	E	185.00	15.60	11.90	8.28	6.00	9.40	8.35
		W	268.00	10.40	7.90	8.40	0.70	9.83	----
6.0 km E	5	E	466.00	14.30	7.82	8.06	5.30	7.80	6.55
		W	372.00	11.00	7.94	4.28	3.96	5.46	0.15
10.0 km E	3	E	174.00	14.60	0.40	1.37	4.73	2.63	4.07
		W	296.00	11.70	0.60	2.23	2.60	3.13	n.d.
11.0 km N	5	E	117.00	31.20	14.40	13.00	13.10	11.10	7.94
		W	123.00	19.90	11.80	14.10	12.20	6.92	6.94
100 km E	4	E	n.d.	6.20	n.d.	2.95	3.03	4.45	0.15
		W	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

BLACK SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
5.0 km SE	4	E	174.00	38.20	12.10	6.30	7.83	7.67	----
		W	159.00	23.30	8.13	9.48	9.20	6.78	----
10.0 km E	3	E	241.00	15.70	2.30	5.00	5.17	5.03	6.37
		W	211.00	15.70	6.93	5.57	6.03	4.23	2.37
100 km E	3	E	n.d.	3.10	2.17	n.d.	n.d.	n.d.	n.d.
		W	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Experimental Uncertainty ± 22.4 %
Standard Deviation ± 60 %

TABLE 6.3 BARIUM CONCENTRATION

Bark: concentration in µg/cm^2
Wood: concentration in µg/g

WHITE SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
4.5 km W	5	E	60.4	15.2	18.1	19.3	20.2	20.9	27.8
		W	65.7	16.4	15.4	18.9	21.3	25.4	28.2
5.0 km N	5	E	25.0	12.0	13.9	15.6	19.7	29.5	36.8
		W	32.0	12.7	12.9	18.1	22.6	26.4	----
6.0 km E	5	E	65.4	19.6	22.1	23.2	30.2	34.8	36.6
		W	79.9	20.6	22.6	27.5	31.9	37.0	43.2
10.0 km E	3	E	42.8	12.2	16.6	13.4	18.0	13.9	14.1
		W	35.8	9.3	11.1	16.3	17.3	15.1	12.9
11.0 km N	5	E	28.8	15.2	12.4	15.4	12.4	12.0	15.4
		W	27.0	11.5	8.7	12.9	12.2	12.4	15.1
100 km E	4	E	43.9	13.7	13.1	12.5	14.3	14.1	14.6
		W	65.2	14.1	11.8	14.3	15.8	13.5	15.4

BLACK SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
5.0 km SE	4	E	53.6	23.8	26.9	29.3	29.1	28.6	----
		W	44.9	24.7	23.9	25.0	31.5	31.2	----
10.0 km E	3	E	46.8	23.4	32.6	22.2	21.4	21.9	23.9
		W	59.1	15.2	23.6	37.6	28.5	29.4	27.5
100 km E	3	E	61.7	21.5	22.4	26.3	24.9	24.5	27.0
		W	42.5	27.6	28.1	25.8	24.2	23.4	28.8

Experimental Uncertainty ± 12%
Standard Deviation ± 26%

TABLE 6.4 BROMINE CONCENTRATION

Bark: concentration in ng/cm^2
Wood: concentration in ng/g

WHITE SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
4.5 km W	5	E	361	95	43	55	49	66	53
		W	663	103	44	42	53	42	42
5.0 km N	5	E	340	98	87	67	66	41	n.d.
		W	373	88	56	52	64	27	--
6.0 km E	5	E	433	98	46	54	47	46	69
		W	335	22	23	35	24	21	30
10.0 km E	3	E	397	188	91	77	73	77	57
		W	487	106	69	72	81	59	54
11.0 km N	5	E	349	246	102	114	120	72	65
		W	429	233	61	52	63	53	68
100 km E	4	E	409	20	26	39	31	36	28
		W	410	17	28	37	29	35	34

BLACK SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
5.0 km SE	4	E	790	348	121	157	121	88	--
		W	689	251	126	112	105	100	--
10.0 km E	3	E	553	168	124	76	92	95	75
		W	696	173	85	81	101	96	69
100 km E	3	E	640	55	67	90	73	66	61
		W	534	70	66	79	92	86	60

Experimental Uncertainty ± 13%
Standard Deviation ± 43%

TABLE 6.5 CADMIUM CONCENTRATION

BARK: concentration in µg/cm²
Wood: concentration in µg/g

WHITE SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
4.5 km W	5	E	1.06	0.20	0.22	0.27	0.22	0.22	0.26
		W	1.81	0.21	0.33	0.31	0.26	0.24	0.20
5.0 km N	5	E	0.87	0.35	0.45	0.39	0.38	0.39	0.28
		W	1.26	0.42	0.40	0.46	0.54	0.63	----
6.0 km E	5	E	0.78	0.28	0.24	0.17	0.20	0.10	0.09
		W	0.84	0.30	0.23	0.26	0.22	0.22	0.21
10.0 km E	3	E	0.87	0.26	0.24	0.32	0.37	0.35	0.16
		W	1.07	0.47	0.47	0.35	0.50	0.57	0.65
11.0 km N	5	E	0.86	0.54	0.70	0.72	0.61	0.41	0.42
		W	0.96	0.66	0.83	0.86	0.69	0.56	0.39
100 km E	4	E	0.52	0.11	0.22	0.22	0.13	n.d.	0.07
		W	0.63	0.20	0.10	0.13	0.04	0.12	0.14

BLACK SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
5.0 km SE	4	E	1.18	0.63	0.70	0.70	0.62	0.46	----
		W	0.76	0.54	0.48	0.61	0.60	0.46	----
10.0 km E	3	E	1.02	0.95	1.56	1.18	0.71	0.65	0.45
		W	1.12	0.92	1.05	1.24	1.17	0.66	0.51
100 km E	3	E	0.59	0.34	0.17	0.22	0.13	0.12	0.12
		W	0.35	0.16	0.36	0.23	0.17	0.27	0.15

Experimental Uncertainty ± 18%
Standard Deviation ± 50%

TABLE 6.6 CHLORINE CONCENTRATION

Bark: concentration in $\mu g/cm^2$
Wood: concentration in $\mu g/g$

WHITE SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
4.5 km W	5	E	60.7	45.0	6.6	5.3	5.0	5.6	4.6
		W	74.3	73.5	7.2	6.3	5.2	2.3	2.9
5.0 km N	5	E	91.3	23.4	7.9	7.8	4.7	6.2	n.d.
		W	82.5	32.4	5.9	3.7	2.8	n.d.	n.d.
6.0 km E	5	E	64.8	56.4	8.1	7.1	6.0	6.1	5.3
		W	114.0	50.2	9.5	9.2	6.8	9.1	8.3
10.0 km E	3	E	69.0	53.8	9.7	6.3	10.0	6.8	n.d.
		W	65.5	53.7	16.6	9.8	11.9	5.2	3.7
11.0 km N	5	E	48.0	62.1	12.3	11.1	6.2	11.7	17.8
		W	37.1	95.5	20.3	5.8	6.8	n.d.	0.1
100 km E	4	E	25.8	21.9	7.9	n.d.	n.d.	n.d.	n.d.
		W	39.1	23.8	5.9	5.4	4.4	1.2	1.2

BLACK SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
5.0 km SE	4	E	51.0	58.5	8.87	6.7	n.d.	n.d.	---
		W	41.9	50.7	4.82	4.0	1.1	0.3	---
10.0 km E	3	E	40.5	33.1	n.d.	n.d.	n.d.	n.d.	n.d.
		W	32.4	43.7	14.4	3.0	5.5	4.0	n.d.
100 km E	3	E	46.5	23.9	n.d.	n.d.	n.d.	n.d.	n.d.
		W	41.8	2.4	n.d.	n.d.	n.d.	n.d.	n.d.

Experimental Uncertainty ± 21%
Standard Deviation ± 32%

TABLE 6.7 COPPER CONCENTRATION

Bark: concentration in µg/cm²
Wood: concentration in µg/g

WHITE SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
4.5 km W	5	E	6.75	3.06	1.77	1.50	1.39	1.66	1.44
		W	19.30	3.01	2.03	1.86	1.61	1.34	1.26
5.0 km N	5	E	10.30	3.18	2.89	2.32	2.25	1.78	1.83
		W	14.60	2.88	2.36	1.60	2.03	2.29	----
6.0 km E	5	E	7.98	3.10	2.09	1.90	1.54	1.51	1.33
		W	6.36	3.65	2.00	1.56	1.50	1.32	1.68
10.0 km E	3	E	6.94	3.45	2.26	2.22	2.26	1.61	1.76
		W	8.78	2.49	1.16	1.57	1.02	1.12	0.51
11.0 km N	5	E	4.82	8.29	3.55	3.09	3.66	2.31	3.11
		W	6.27	5.08	6.54	3.23	3.54	3.22	1.71
100 km E	4	E	3.29	2.45	2.19	1.97	1.54	1.94	1.77
		W	3.21	2.92	1.53	1.76	1.83	0.93	1.06

BLACK SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
5.0 km SE	4	E	11.90	6.62	5.35	5.43	3.54	4.03	----
		W	13.20	4.76	3.95	4.30	2.50	2.64	----
10.0 km E	3	E	3.57	2.36	3.56	2.50	2.25	2.87	2.14
		W	4.96	2.81	3.03	2.70	2.03	2.52	2.03
100 km E	3	E	3.95	2.90	3.14	2.82	n.d.	3.37	2.97
		W	3.55	3.09	2.07	1.86	3.74	3.69	2.82

Experimental Uncertainty ± 14.5%
Standard Deviation ± 15%

TABLE 6.8 MAGNESIUM CONCENTRATION

Bark: concentration in μg/cm^2
Wood: concentration in μg/g

WHITE SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
4.5 km W	5	E	182	99	92	86	95	101	102
		W	190	118	97	96	113	108	103
5.0 km N	5	E	173	107	93	100	109	116	163
		W	166	98	105	100	108	135	---
6.0 km E	5	E	178	100	85	105	94	97	113
		W	215	107	109	91	106	117	119
10.0 km E	3	E	210	133	138	126	113	117	103
		W	219	126	106	127	111	117	133
11.0 km N	5	E	170	120	112	103	89	102	118
		W	126	148	125	107	112	109	112
100 km E	4	E	129	118	97	103	107	110	100
		W	247	129	94	83	122	122	105

BLACK SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
5.0 km SE	4	E	136	105	90	104	107	105	---
		W	111	91	87	93	109	128	---
10.0 km E	3	E	151	132	112	138	143	160	148
		W	120	113	131	110	112	160	165
100 km E	3	E	171	109	95	108	144	116	117
		W	115	83	78	134	149	120	132

Experimental Uncertainty ± 16%
Standard Deviation ± 21%

TABLE 6.9 MANGANESE CONCENTRATION

Bark: concentration in $\mu g/cm^2$
Wood: concentration in $\mu g/g$

WHITE SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
4.5 km W	5	E	74	25	30	28	30	40	47
		W	68	33	36	37	35	39	45
5.0 km N	5	E	63	29	37	33	38	46	53
		W	56	23	32	30	39	63	--
6.0 km E	5	E	65	25	27	30	27	26	27
		W	58	24	31	26	27	31	31
10.0 km E	3	E	90	41	54	52	47	50	55
		W	81	37	37	48	56	59	67
11.0 km N	5	E	119	71	77	92	78	75	83
		W	102	72	88	88	78	71	71
100 km E	4	E	147	72	65	81	62	71	70
		W	128	48	44	51	59	62	60

BLACK SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
5.0 km SE	4	E	83	59	53	54	66	67	---
		W	69	49	46	48	62	76	---
10.0 km E	3	E	149	121	143	139	133	127	129
		W	164	108	146	167	181	176	180
100 km E	3	E	219	199	186	184	209	235	228
		W	235	202	221	237	280	269	318

Experimental Uncertainty ± 10.5%
Standard Deviation ± 17.5%

TABLE 6.10 POTASSIUM CONCENTRATION

Bark: concentration in $\mu g/cm^2$
Wood: concentration in $\mu g/g$

WHITE SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
4.5 km W	5	E	915	594	375	344	330	304	306
		W	924	826	429	394	354	314	322
5.0 km N	5	E	1194	526	399	314	340	313	392
		W	1217	561	379	371	337	322	---
6.0 km E	5	E	791	613	343	334	311	274	261
		W	1084	611	409	340	332	293	278
10.0 km E	3	E	688	606	383	398	437	407	356
		W	747	632	389	414	434	419	396
11.0 km N	5	E	579	735	369	315	280	237	253
		W	445	866	403	334	310	277	260
100 km E	4	E	449	432	254	223	230	222	242
		W	747	623	329	302	332	268	247

BLACK SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
5.0 km SE	4	E	571	803	305	320	317	300	---
		W	439	630	295	293	340	342	---
10.0 km E	3	E	387	538	345	308	293	286	295
		W	370	652	426	370	339	323	338
100 km E	3	E	716	475	311	311	299	287	270
		W	490	477	358	308	280	282	277

Experimental Uncertainty ± 10.5%
Standard Deviation ± 17%

TABLE 6.11 SELENIUM CONCENTRATION

Bark: concentration in ng/cm^2
Wood: concentration in ng/g

WHITE SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
4.5 km W	5	E	120	58	47	28	71	30	59
		W	233	---	---	---	---	---	---
5.0 km N	5	E	239	53	93	62	61	28	79
		W	466	---	---	---	---	---	---
6.0 km E	5	E	114	81	90	83	19	65	224
		W	149	---	---	---	---	---	---
10.0 km E	3	E	77	33	136	48	86	56	50
		W	85	---	---	---	---	---	---
11.0 km N	5	E	82	42	293	63	48	43	25
		W	126	---	---	---	---	---	---
100 km E	4	E	22	108	64	64	212	31	34
		W	14	---	---	---	---	---	---

BLACK SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
5.0 km SE	4	E	335	77	112	124	99	37	---
		W	392	---	---	---	---	---	---
10.0 km E	3	E	73	106	141	5	96	49	108
		W	135	---	---	---	---	---	---
100 km E	3	E	11	163	68	195	115	110	57
		W	29	---	---	---	---	---	---

Experimental Uncertainty ± 20%
Standard Deviation ± 64%

TABLE 6.12 SODIUM CONCENTRATION

Bark: concentration in $\mu g/cm^2$
Wood: concentration in $\mu g/g$

WHITE SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
4.5 km W	5	E	10.2	4.1	1.8	1.4	1.7	1.4	1.1
		W	24.8	5.5	2.9	2.3	1.7	1.1	1.6
5.0 km N	5	E	8.9	3.5	1.8	1.7	1.7	1.3	1.8
		W	12.9	5.0	2.9	2.2	2.1	0.9	---
6.0 km E	5	E	8.5	2.9	1.7	1.2	1.0	1.1	0.6
		W	7.4	4.1	2.2	2.1	2.0	2.1	1.8
10.0 km E	3	E	5.6	5.2	2.0	1.1	1.1	1.1	0.6
		W	7.4	7.9	4.1	2.9	4.0	2.8	1.4
11.0 km N	5	E	7.9	5.8	3.5	3.3	2.3	4.1	7.1
		W	13.4	5.5	4.0	3.9	2.5	2.0	1.1
100 km E	4	E	6.4	2.5	1.7	1.5	1.1	0.9	0.7
		W	9.6	4.2	2.1	2.3	2.1	1.4	1.3

BLACK SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
5.0 km SE	4	E	13.9	5.0	2.5	1.9	1.2	1.7	---
		W	14.3	5.5	2.6	2.2	1.4	1.2	---
10.0 km E	3	E	5.3	2.0	1.6	1.1	0.9	0.9	1.2
		W	7.3	4.1	4.0	4.0	3.4	3.0	1.2
100 km E	3	E	10.7	2.1	1.6	1.3	0.9	0.7	0.5
		W	9.1	2.7	2.5	1.6	1.2	0.6	0.6

Experimental Uncertainty ± 10.5%
Standard Deviation ± 35%

TABLE 6.13 TUNGSTEN CONCENTRATION

Bark: concentration in ng/cm^2
Wood: concentration in ng/g

WHITE SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
4.5 km W	5	E	n.d.	94	34	17	16	10	10
		W	n.d.	113	41	27	17	7	7
5.0 km N	5	E	n.d.	93	41	24	28	19	n.d.
		W	n.d.	101	61	32	23	17	--
6.0 km E	5	E	n.d.	90	53	35	18	18	14
		W	n.d.	152	36	29	26	14	8
10.0 km E	3	E	n.d.	120	54	33	34	22	7
		W	n.d.	127	50	34	35	30	18
11.0 km N	5	E	n.d.	396	156	60	127	46	56
		W	n.d.	262	252	145	74	61	27
100 km E	4	E	n.d.	168	60	37	20	11	15
		W	n.d.	94	45	28	38	14	20

BLACK SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
5.0 km SE	4	E	n.d.	157	71	42	39	52	--
		W	n.d.	143	78	31	14	23	--
10.0 km E	3	E	n.d.	82	45	13	15	13	20
		W	n.d.	143	47	37	19	53	17
100 km E	3	E	n.d.	58	33	29	26	19	5
		W	n.d.	94	81	38	13	9	8

Experimental Uncertainty ± 12%
Standard Deviation ± 35%

TABLE 6.14 ZINC CONCENTRATION

Bark: concentration in $\mu g/cm^2$
Wood: concentration in $\mu g/g$

WHITE SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
4.5 km W	5	E	78	77	45	37	37	37	33
		W	81	107	61	46	37	35	32
5.0 km N	5	E	71	71	54	48	55	47	37
		W	79	79	64	56	56	64	--
6.0 km E	5	E	76	80	59	44	39	41	33
		W	81	72	44	40	35	30	27
10.0 km E	3	E	54	125	58	35	34	32	32
		W	61	76	51	34	41	44	33
11.0 km N	5	E	52	235	136	68	101	55	57
		W	50	112	188	119	66	64	37
100 km E	4	E	38	78	50	41	27	22	21
		W	57	95	47	36	39	22	27

BLACK SPRUCE

Location	N.	Side	Bark	86-90	81-85	76-80	71-75	66-70	61-65
5.0 km SE	4	E	46	86	86	66	57	68	--
		W	50	112	80	60	49	51	--
10.0 km E	3	E	32	67	51	32	44	34	32
		W	40	130	89	42	74	73	31
100 km E	3	E	35	44	54	21	29	25	20
		W	19	74	81	65	33	25	20

Experimental Uncertainty ± 11%
Standard Deviation ± 30%

6.2 **DISCUSSION**

The results obtained lead to the following points:

1. The aluminium concentrations in the bark samples at 4.5 km W, 5 km N, and 5 km SE are significantly higher than in the control samples. The same is true for the wood samples at 5 km SE.
2. The arsenic found appears to be due to pollution since it was detected in the bark samples taken from sites close to the refinery while it was not detected in the control samples. The As concentrations in the wood samples from near the refinery are also higher than in the control samples.
3. The barium concentrations in the samples at 4.5 km W and 6 km E are higher than in the control samples, but for the other samples the concentrations are similar to those in the control samples.
4. Higher bromine concentrations are observed in the wood samples from near the refinery compared to the control samples, but the concentrations in the bark samples are similar to those in the control samples.
5. The cadmium concentrations in both bark and wood are

higher in the samples from near the refinery than in the control samples.

6. The chlorine concentrations in both bark and wood of the white spruce trees are higher in the samples from near the refinery than in the control samples. For black spruce trees, the Cl concentrations in the wood samples from near the refinery are higher than in the control samples, while in the bark samples they are almost the same.
7. The copper concentrations in the bark samples from near the refinery are higher than those in the control samples. For wood samples, Cu concentrations at 11 km N and 5 km SE are significantly higher than in the control samples, while for the other samples the concentrations are similar to those in the control samples.
8. For magnesium, there is no indication of pollution; the Mg concentrations in the samples from near the refinery are similar to those in the control samples.
9. The manganese concentrations in the samples from near the refinery are lower than those in the control samples. The reason for this unusual behaviour may be that Mn is an

essential element in trees and variations in Mn concentrations may be due to many factors other than pollution.(20)

10. The potassium concentrations in the bark samples at 4.5 km W, 5 km N, 6 km E, and 10 km E are higher than those in the control samples, while for the other samples they are almost the same.
11. The selenium concentrations in the bark samples from near the refinery are higher than in the control samples, while in the wood samples they are almost the same.
12. The sodium concentrations in the bark samples at 4.5 km W, 5 km N, 11 km N, and 5 km SE are higher than those in the control samples. For the wood samples, Na concentrations at 11 km N and 5 km SE are higher than in the control samples, while in the other samples they are almost the same.
13. Tungsten was not detected in the bark samples but it was detected in the wood samples which confirms our previous assumption that all the tungsten in the wood samples was contamination from the tube of the incremental corer.
14. Zinc was detected in both bark and wood which contradicts

our previous assumption that all zinc in the wood samples was contamination from the extractor of the incremental corer. Since this assumption and the measured zinc concentrations were used to correct copper contamination, the copper concentrations tabulated in table 6.7 are overcorrected and may be lower than the real values. Zinc concentrations in some samples from near the refinery are higher than those in the control samples which suggests that we have some zinc coming from pollution.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

From the results of the previous chapter we can conclude that further investigation is needed before trees can be used as monitors for establishing heavy metal pollution histories. The results listed below constitute cases where the levels of metals in the trees are contrary to what would be expected from an ideal monitor,

1. The bark sample analysis indicated selenium concentrations in the samples from near the refinery higher than in the control samples which agrees with the previous studies done by Glooschenko and Arafat using sphagnum moss(21), but on the other hand, wood sample analysis indicated that Se concentrations in the samples from near the refinery are almost the same as in the control samples, moreover, in some samples from near the refinery the concentrations are lower than those in the control samples.
2. The bark sample analysis indicated copper concentrations in the samples from near the refinery higher than in the control samples, but the wood sample analysis indicated that Cu concentrations in the samples from near the refinery are similar to those in the control samples

except at 11 km N and 5 km SE where the concentrations are higher.

3. The information obtained from Noranda Minerals Inc. indicated that they have successfully decreased the pollution level in the last few years by installing new equipment in the smelter which means that metal concentrations in the last few years,i.e, (1986-1990) should be lower than that in the preceding years. The opposite trend was observed in the wood samples.
4. With some elements such as manganese, concentrations are lower in the samples from near the refinery than those in the control samples.
5. In some wood samples we found dark spots several millimeters in diameter. Neutron activation analysis indicated heavy metal concentrations in these dark spots many times higher than in the surrounding wood. The origin of these dark spots is believed to be small branches which grew out of the trunk of the tree when it was young. With time these branches broke off and are no longer visible from outside the tree but they provided a pathway for the entry of pollutant elements into the wood

inside the trunk.

Considering the previous points we can conclude that bark may be considered a good monitor for long term heavy metal pollution although there are some natural factors such as rain which could affect the accumulation. Trees may useful monitors as a function of location for some pollution elements such as cadmium but not for all elements. There is no indication that trees could serve as monitors of pollution as a function of time because the time-profile of deposition is not reflected in the concentration in the annual rings.

For future studies we recommend that bark sample analysis should be done only for the outer surface layer with a thickness of 0.1 cm and not for the whole bark sample as was done in the present study because the pollution accumulation occurs mainly at the outer surface.

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