IMPACTS OF ARSENIC AND SULPHUR DIOXIDE CONTAMINATION FROM MINING ACTIVITIES ON FOREST HEALTH NEAR YELLOWKNIFE, NWT.

by

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ABSTRACT

Growth patterns of jack pine (*Pinus banksiana*) near Giant Mine in Yellowknife, NWT were studied in order to assess the impacts of mine activities on tree-growth and forest health during the 20th century. Differences in arsenic (As) and sulphur (S) concentrations in tree-rings and surface soil and differences in groundcover species richness (GCSR) were compared for sites downwind (contaminated) and upwind (reference) of the mine. Concentrations of As and S in soil and tree-rings were significantly higher at contaminated versus reference sites, while soil pH was not significantly different. Soil-As and soil-S concentrations decreased significantly with increasing distance of study sites from the mine. Lower GCSR at contaminated sites compared to reference sites corresponded to higher levels of soil-As concentrations. Tree-ring concentrations did not reflect changes in As emissions from Giant Mine. However, changes in calcium (Ca) concentrations in tree-rings coincided with calcine management activities. The onset of activity at Giant Mine coincided with divergences in growth patterns between mean contaminated and reference chronologies unprecedented in the pre-operational period covered by this study (1900-1948). Due to constraints in data availability, differences in the climate-growth response of jack pine at contaminated and reference sites remain uncertain.

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LIST OF CHEMICAL ACRONYMS

Abbreviation	Word in full
Al	Aluminum
As	Arsenic
As_2O_3	Arsenic trioxide
Ba	Barium
Ca	Calcium
Cd	Cadmium
Co	Cobalt
Cr	Chromium
Cu	Copper
Fe	Iron
K	Potassium
Mg	Magnesium
Mn	Manganese
Mo	Molybdemun
Na	Sodium
Ni	Nickel
P	Phosphorus
Pb	Lead
S	Sulphur
SO_2	Sulphur dioxide
SO_4^{-2}	Sulphate
Sr	Strontium
Ti	Titanium
Zn	Zinc

CHAPTER ONE

OVERVIEW AND OBJECTIVES

1.2 Introduction

Mining has been an integral part of Canadian history and economic development. Today, mining continues to be an important industry, especially in the Northwest Territories (NWT) where several diamond mines are currently being developed. Much of Canada's economy has been built on extraction and processing of a wide variety of natural resources. In association with extraction and processing in the mining industry, some environmental degradation has occurred. In the past, this environmental degradation was largely ignored. Today however, large scale mining development projects such as mines involve significant environmental planning to minimize the impact of resource extraction and processing on the environment and normally include plans to restore the area and its ecosystems to their original state (Gregor et al., 2003).

Yellowknife has been the centre of resource extraction in the NWT during the 20th century. During the early 1930s gold was discovered near Yellowknife and two significant mining sites, Con Mine and Giant Mine, were developed. This thesis will focus on the activities of Giant Mine. In the early years of operation (1938-1951), emissions containing elevated levels of arsenic trioxide (As_2O_3) and sulphur dioxide (SO_2) were released from smelter (roaster) stacks at both mines into the atmosphere and subsequently deposited onto soils, plants and waterbodies (Department of Indian and Northern Affairs (DIAND), 2006).

Although arsenic (As) is ubiquitous and harmless in small quantities, exposure to high levels of this metalloid in the environment, whether in air, soil, water or plants can cause hazards to human and ecosystem health (Dushenko et al., 1995; Dartmouth Toxic Metal Research (DTMR), 2005). Total As concentrations in soil as high as 2288 μg/g are documented on the Giant Mine property (Golder Associates Ltd., 2004). Absorption of As through leaves, bark and roots in high levels is linked to phytotoxic effects, such as chlorosis, necrosis, and growth inhibition in certain plants (Kabata-Pendias and Pendias, 1992; Dushenko et al., 1995; Lasat, 2002; Meharg and Hartley-Whitaker, 2002; Gulz et al., 2005) and can lead to plant death (Wang et al., 2002; Gulz et al., 2005).

Direct deposition of SO_2 and indirect deposition as sulphate (SO_4^{-2}) on plants and soils is of concern to forest health since they can hinder physiological and metabolic processes necessary for plant-growth (Kozlowski et al., 1991). SO_2 emissions react with sunlight and atmospheric moisture to produce acid rain that can lead to soil acidification (Bunce, 1994), subsequently increasing the potential for nutrient deficiencies, nutrient imbalances, inhibited nutrient cycling and/or root mortality that can reduce plant-growth (McLaughlin, 1998). Moreover, soil acidification can cause increased root uptake of heavy metals (McLaughlin, 1998), such as arsenic, and reduce foliar photosynthesis (Webster et al., 2004). Observations recorded in 1991 by Maynard (as cited in GNT, 1993) indicate that visual symptoms typically associated with SO_2 pollution appeared on tree foliage up to 5 km north of Giant Mine.

The extent of distribution of contaminants emitted from a point source depends on (1) stack-height (Long and Davis, 1999), (2) dominant wind direction, speed and duration

(GNT, 1993; Dion et al., 1993) and (3) size of contaminant particles (Keegan et al., 2006). Studies of the extent of atmospheric distribution of SO_2 near Yellowknife during 1990-92 (GNT, 1993) and As deposition on snow in 1975 (Hazra et al., 1977) indicate that contamination was highest near the mine and that distances traveled varied according to seasonal wind direction. Although extensive measurements are available for As content in soils within the city limits of Yellowknife, N'Dilo and Dettah (Risklogic Scientific Services Inc., 2002), Giant Mine property (EBA Engineering Consultants Ltd., 1998; INAC and SRK Consulting Inc., 2004; Golder and Associates, 2004) and north of Giant Mine along the Ingraham Trail Road (Environmental Sciences Group (ESG), 2000) and vegetation surveys were conducted in 1990 and 1991 (Maynard and Malhorta, 1990; Maynard, 1991), the impacts of As and SO_2 emissions on forest ecosystems near Yellowknife are not well known.

Previous plant ecology surveys conducted within forests surrounding Giant Mine during the mid 1970s and early 1990s indicated that early leaf-drops and yellowing foliage occurred in areas that received SO_2 emissions associated with mine activity (Kushar, 1975; Maynard and Malhorta, 1990; Maynard, 1991). Although the influence of As_2O_3 emissions on forest health has not been addressed in the Yellowknife region, a study of aquatic plants exposed to As-contaminated effluent from Giant Mine indicated that reduced stand height of cattail (*Typha spp.*) was related to diminished nutrient uptake caused by elevated As concentrations in sediments (Dushenko et al., 1995). Four years after the closure of the Giant Mine roaster stack in 1999, As concentrations above the recommended concentration of 0.1 $\mu g/g$ for consumption were found in five species of berries including blueberries (*Vaccinium sp.*), cranberries (*Viburnum sp.*), raspberries (*Rubus sp.*), rose hips (*Rosa sp.*) and gooseberries (*Ribes sp.*) within the Yellowknives Dene traditional territory (INAC, 2003b). These studies suggest that (1) SO_2 and As_2O_3 emissions from gold mine activities at Giant Mine have influenced plant health in the past and (2) regional contamination from these emissions may still be adversely impacting forest health near Yellowknife.

Since complete historical data of soil-As content and soil acidity are not available, it is necessary to find proxy data to evaluate temporal changes in As and SO_2 contamination. Tree-rings offer an alternative to historic soil data since they store elements taken up from soils, bark and foliage. Tree-rings have been successfully used to reconstruct soil pH in soil acidification studies using dendrochemical methods (Berger et al., 2006). Moreover, numerous studies have found that certain trees store metals and other elements in their rings and can provide a chronology of pollution exposure (Robitaille, 1981; Baes and McLaughlin, 1984; Guyette et al., 1991; Eklund, 1995; Watmough and Hutchinson, 1996). Tree-rings also provide information regarding temporal changes in tree-growth (Fritts, 1976).

1.2 Research objectives

The purpose of this research is to assess the impact of As and SO_2 contamination from mining activities on tree-growth and forest health in the vicinity of Giant Mine, Yellowknife, NWT. Using growth records from jack pine (*Pinus banksiana*), relations between mine activities, climate and tree-growth are investigated. In addition, groundcover species richness, tree-ring chemistry and surface soil chemistry at sites downwind (contaminated) and upwind (reference) of the roaster stack at Giant Mine are examined to assess overall forest health across the region. The main hypotheses of this thesis are:

1. Surface soil downwind of and nearest to the Giant Mine roaster stack contains elevated levels of As and sulphur (S) compared to similar sites upwind and furthest from the roaster stack.
2. Arsenic contamination of the surface soil has resulted in decreased groundcover species richness, thus sites near the mine property will contain fewer plant species than reference sites further away.
3. Trees growing at heavily contaminated sites contain higher levels of As and S in their tree-rings than trees at reference sites and tree-ring concentrations correspond to As and SO_2 exposure and subsequent uptake by trees at these sites.
4. As and SO_2 contamination from mine activities has lead to decreased growth of jack pine at heavily contaminated sites relative to reference sites during the operational period of the mine and pollution-induced stress has impacted relations between tree-growth and climate at contaminated sites during this period.

CHAPTER TWO

BACKGROUND AND LITERATURE REVIEW

2.1 Background

2.1.1 Giant Mine emissions

The Burwash gold vein was discovered in the Yellowknife Greenstone Belt (YGB) near the city of Yellowknife, NWT in 1934 (Foster and Heming, 2003). Gold in the YGB occurs in association with As- and S-rich arsenopyrite. When this ore was smelted to extract gold, As_2O_3 and SO_2 were released into the atmosphere as gaseous and solid by-products (GNT, 1993).

Gold production within present-day city limits of Yellowknife began at Con Mine in 1938 and Giant Mine in 1948. Figure 2.1 illustrates total As emissions in kg/day at Giant Mine from 1949 to 1991 and Con Mine from 1949 to 1970. Con Mine installed a wet scrubber system to control As_2O_3 emissions in 1949 and ceased using roasting equipment in 1970 due to the low S content of the ore at greater depths (GNT, 1993). Table 2.1 provides an overview of the pollution control measures implemented at Giant Mine from 1951 to 1962, and indicates corresponding total As emissions. A cold electrostatic precipitator was installed to remove dust from exhaust gases in 1951. In 1953, a second roaster stack was built and a hot electrostatic precipitator was added in 1955 to reduce the load on the cold precipitator. These measures reduced total As emissions from 7,300 kg/day to 2,700 kg/day. A baghouse gas filter was installed in 1958 along with a larger roaster and stack to replace the two older stacks, further

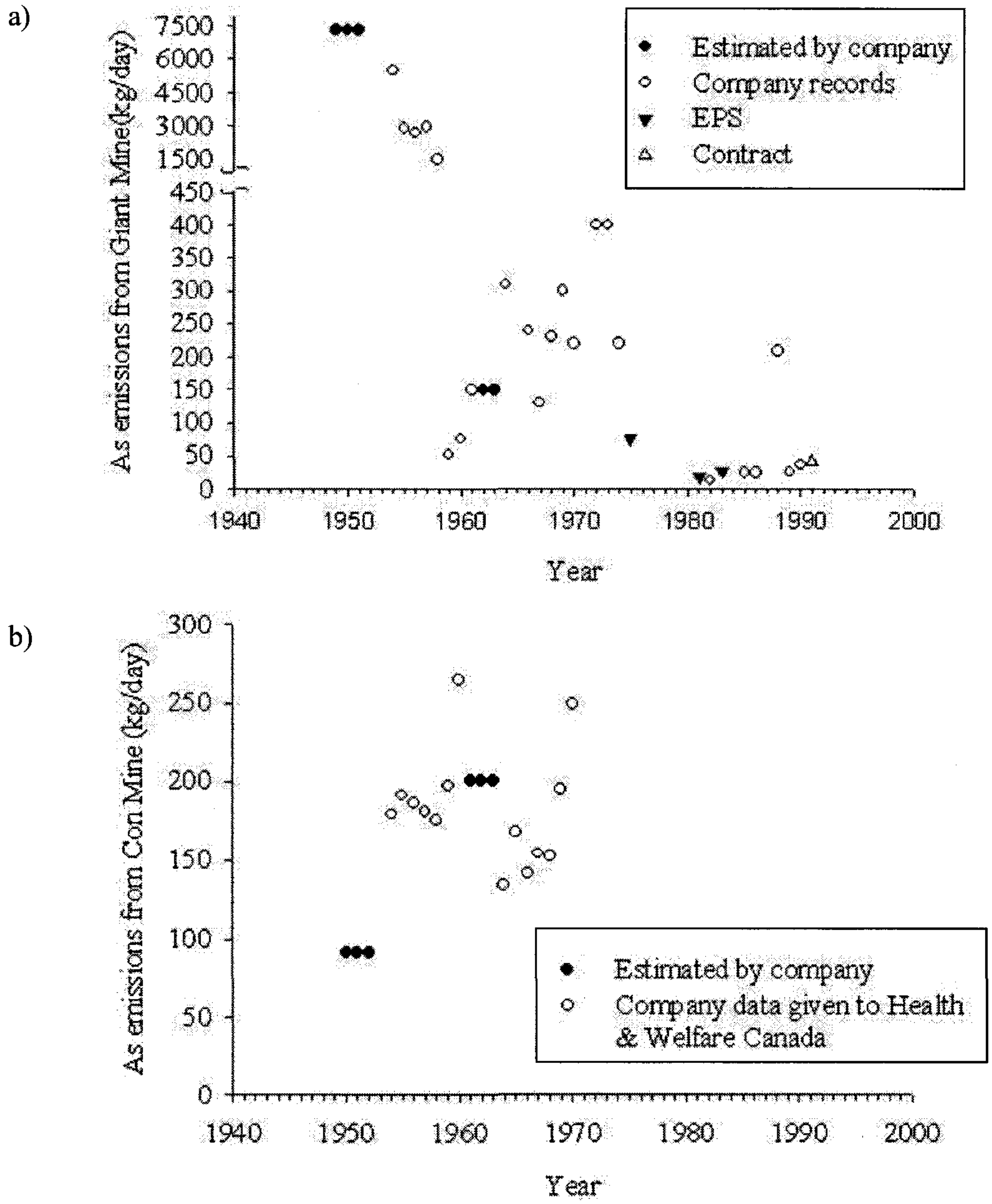


Figure 2.1: a) Arsenic emission rates from the Giant Mine roaster stack. Data unavailable for 1952, 1953, 1965, 1976-1980, 1984, 1987 and after 1991 (Data from Table 2 and 3 in GNT 1993). b) Arsenic emission rates from Con Mine roaster stack. Data unavailable for 1949, 1953 and after 1970 (Data from Hazra et al., 1977). EPS stands for the Environment Canada method of arsenic determination, EPS-1-AP-74-3.

Table 2.1: Pollution control measures implemented at Giant Mine (Adapted from CPHA, 1977).

Year	Improvement	Total As emissions of following year (kg/day)
1951	Installation of a cold electrostatic precipitator. Dust stored in underground stopes.	7,300
1953	Installation of a second roaster and a 2.7 m diameter, 45.7 m high stack.	5,500
1955	Installation of a hot electrostatic precipitator.	2,700
1958	Installation of a Dracco baghouse gas filter and two older roasters were replaced with a new, larger fluo-solids roaster.	52
1962	Converted the original cold electrostatic precipitator to hot mode of operation.	150

reducing emissions of total As to 52 kg/day. The original cold precipitator was converted to hot mode in 1962.

Production of As_2O_3 and SO_2 ceased with the closure of Giant Mine in 1999. Nevertheless, soil-As concentrations ranging from 23.5 μg/g to 2288 μg/g were recorded for soil samples taken in 2000, 2001 and 2004 on the mine and surrounding properties (ESG, 2001; Golder Associates Ltd, 2004). These were very high concentrations considering that the typical Canadian background concentration for As in soil was 5-15 μg/g (INAC, 2003a). Tailings ponds received solid and liquid wastes from mill tailings (Gregor et al., 2003). Groundwater leaching from existing storage sites was mitigated by a drainage and pumping system that was installed in the late 1970s (INAC, 2003a). Nevertheless, As concentrations in Baker Creek on June 4th, 2002 ranged from 47.4 μg/L to 232 μg/L (Dillon Consulting Ltd, 2002). Canadian Water Quality Guidelines for As at that time were 0.025 mg/L (25 μg/L) for drinking water and 5 μg/L to protect freshwater life (Canadian Council of Ministers of the Environment (CCME), 2002). Several reports have been prepared that describe Giant Mine's operations, mine-related health issues, emissions and distribution of contaminants, and remediation efforts (CPHA, 1977; Hazra et al., 1977; GNT, 1993; EBA Engineering Consultants Ltd., 1998; Risklogic Scientific Services Inc., 2002; INAC and SRK Consulting Inc., 2004; Golder and Associates, 2004).

The absence of other sources of As contamination and abundance of forested land cover in the Yellowknife area as well as numerous reports regarding the operations and distribution of contaminants from Giant Mine provided a good setting and resources to study the influence of gold mine activities on forest health in a northern boreal ecosystem.

2.2 Dendrochronology

A useful indicator of forest health is tree growth. Every year a tree adds biomass to its trunk, resulting in the formation of a ring that reflects tree-growth for a given year. Tree-rings provide chronological information regarding changes in the rate of tree-growth, which can be an indicator of environmental change. Dendrochronology, the study of tree-rings, has been widely used to reconstruct past climates (Jacoby and D'Arrigo, 1989; Szeicz and MacDonald, 1995), however numerous studies have also utilized tree-ring growth records to examine problems associated with various types of pollution. Tree-rings provide valuable proxy data regarding pollution impacts due to the relation between tree-ring formation and environmental conditions. Dendrochronological methods have been applied to study the impacts of lead (Pb) and cadmium (Cd) uptake from soils polluted by mining activity (Guyette et al., 1991) and emissions from lead smelters (Anderson et al., 2000) on tree-growth. Tree-ring analysis has also been used to study relations between tree-growth and As contamination from lead arsenate treated soils (Martin et al., 2000) and storage of arsenical pesticides (Cheng et al., 2007) as well as SO_2 emissions from regional sources (Webster et al., 2004) and local power plants (Long and Davis, 1999).

2.2.1 Dendrochemistry

Dendrochemistry draws upon the principles of dendrochronology in order to study the rates of input of contaminants into biological systems and their subsequent behaviour within these systems. This is achieved by assuming that wood formation at any given time reflects the environmental conditions in which the tree was growing at that point (Eklund, 1995). Consequently, chemical analysis of the woody tissue from a tree-ring or group of tree-rings can provide information about the levels of pollutants in the environment and subsequently taken up by the tree and stored in woody tissues. Several studies have successfully observed correlations between trace metal concentrations in tree-rings and the changes in emissions from point sources. Eklund (1995) found that the release of Cd and Pb from Swedish battery plant chimneys corresponded well to the chronology of concentrations of these metals found in rings of oak trees. Other studies found relations of Cd and Pb concentrations in tree-rings with pollution from Pb mining in southeast Missouri (Guyette et al., 1991) and Pb from spoil banks from dredging activity of an oil refining company in Louisiana (Marcantonio et al., 1998). In contrast, Dion et al. (1993) were unable to find significant correlations between aluminum (Al) concentrations in black spruce (*Picea mariana*) rings and emission rates from an aluminum refinery in Jonquiere, Quebec.

2.3 Tree-ring structure and growth

Tree-rings are produced annually under the bark of stems, in the region known as the vascular cambium. The vascular cambium is made up of phloem cells and is located between the bark and woody tissue. The woody tissue is composed of xylem cells and is referred to as xylem tissue. Three phases are involved in the formation of tree-rings - cell division, cell enlargement and expansion, and cell differentiation and maturation (Fritts, 1976). Cells produced on the outside of the cambium become new phloem cells and those produced on the inside become new xylem cells, hence increasing the diameter of the stem in a process referred to as radial growth. Xylem cells that are produced at the beginning of the growing season create a light band of wood called earlywood. The colour and density of xylem cells increases at the end of the growing season, creating a darker band of wood, called latewood. The combination of these two bands makes up the tree-ring that represents one year of growth.

Figure 2.2 shows the concentric bands of earlywood and latewood. Sapwood refers to the soft living xylem tissue that conducts water and sap through the stem. It is located between the cambium and the heartwood. Heartwood is found in the central portion of the stem and consists of non-conducting, dense, mature wood. Heartwood is distinguished from sapwood by its darker colour.

Incremental growth of tree-rings varies diurnally, seasonally, annually, with height along the tree stem and between species. Radial growth also varies throughout the lifetime of the tree (Fritts, 1976; Kozlowski and Pallardy, 1997). For instance, younger trees have been observed to grow faster than older trees (Fritts, 1976; Robitaille, 1981). Therefore, tree-rings provide chronological information regarding changes in the rate of radial growth.

2.4 Pollution and tree-ring development

Factors responsible for the variability in rates of tree growth exert their influence indirectly by hindering or facilitating physiological processes responsible for the three phases of radial growth (Kozlowski et al., 1991). Relations between pollution and tree-growth are often difficult to isolate and quantify since there are many interacting factors

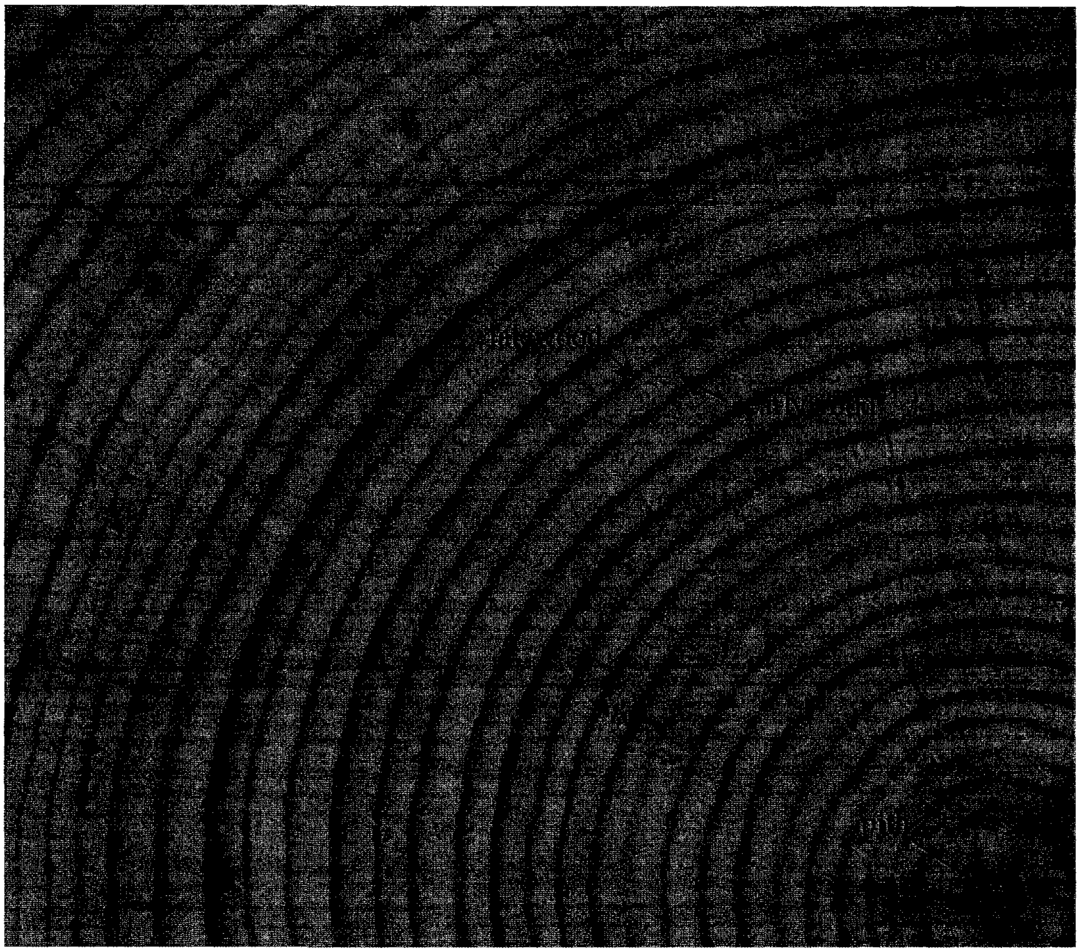


Figure 2.2: Cross section of a conifer showing the sequence of annual rings within the tree stem (Photograph by Sonia M. St-Onge).

involved in the response of tree-growth to pollution-induced stress. Factors that affect this response are identified by Kozlowski et al. (1991) as tree species and genotype, tolerance to pollutant, pollutant dosage, combined effects of pollutants, stage of tree development, environmental preconditioning, and predisposition to disease and insect attack. These factors should be considered when evaluating the impact of pollution-induced stress on radial growth in order to fully assess causality in observed relations.

Air pollutants known to influence growth of woody plants include SO_2, ozone (O_3), fluorides, oxides of nitrogen (NO_x), peroxyacetylnitrates (PAN), and particulates (Kozlowski et al., 1991). The latter includes dust, smoke, aerosols, soot and heavy metals. These pollutants impair plant growth by inducing biochemical and physiological changes in cells, plants, species and plant communities (Kozlowski et al., 1991). Physiological and metabolic processes that are affected include, i) inhibition of chlorophyll synthesis and photosynthesis, ii) alteration of stomatal aperture, cell membrane permeability and enzyme activity, and iii) changes in the amount and type of proteins and carbohydrates stored in plants (Kozlowski et al., 1991). The disruption of these reactions can adversely affect processes responsible for the three phases of radial growth.

2.5 Contaminants in the environment

Contaminants may be organic such as polycyclic aromatic hydrocarbons (PAHs) or inorganic such as heavy metals. When present at a sufficient concentration to cause deleterious effects, a contaminant is referred to as a pollutant. In order for a deleterious effect to occur, the contaminant must be biologically available for absorption into a living organism or tissue. This concept is known as bioavailability. Figure 2.3 illustrates the concept of bioavailability in soils. In the environment, contaminants are found either bound to inorganic and organic materials (bound state), or dissolved in a liquid or gas phase (released state). In the bound state, inorganic contaminants are associated to a particulate by i) the sharing of electrons; ii) electrostatic attraction; iii) precipitation of discrete particles (National Research Council (NRC), 2003). The released state entails a disassociation of the contaminant from a particle into water or air by mediation of physical, chemical or biological processes (NRC, 2003). Although contaminants are bioavailable in either bound or released states, bioavailability depends on the living organism's physiology and the phase and speciation of the contaminant (NRC, 2003).

In Figure 2.3, B and C refer to the transport of contaminants to an organism. Transport of bound contaminants occurs via entrainment in the air, suspension in water, colloidal movement in ground water, resuspension from sediments, sedimentation and burial, while released contaminants are transported via the movement of water and air or by advection (NRC, 2003). Exposure of living organisms to contaminants may occur by wet or dry deposition directly onto the organism, ingestion of or dermal contact with contaminated food, water or soil, or inhalation of contaminated air.

2.5.1 Uptake of metals by trees

Our understanding of the mechanisms involved in uptake, transport and storage of metals in trees is incomplete due to the limited number of research studies on this topic. It is generally agreed that metal uptake in plants occurs via the bark, foliage and roots, however the relative importance of each pathway is widely debated (Lin et al.,

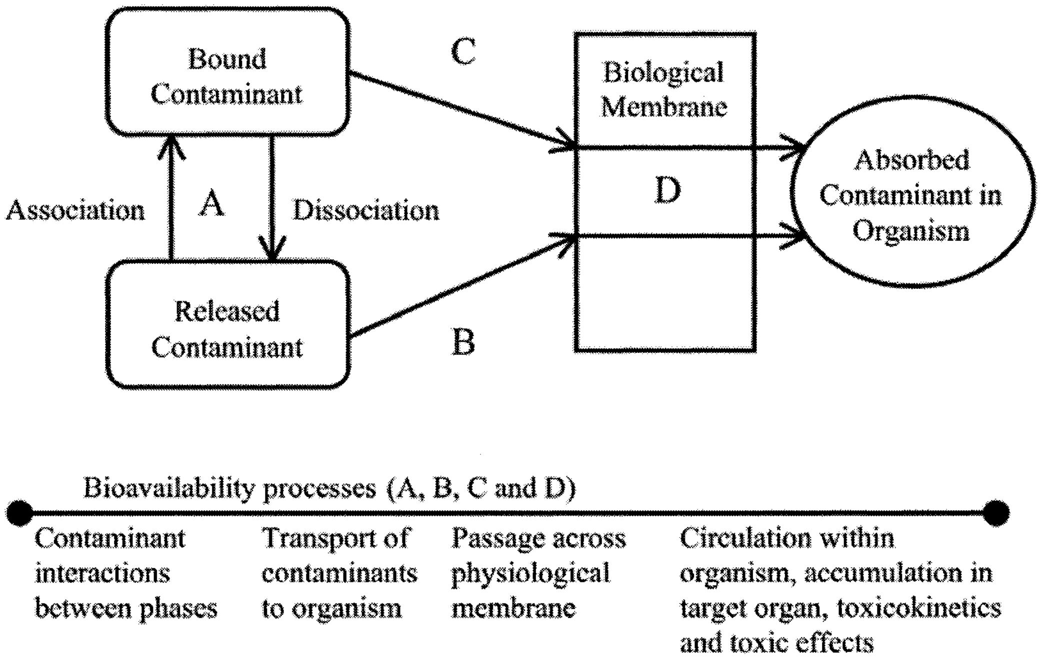


Figure 2.3: Diagram illustrating the concept of bioavailability in soils and sediments (Modified from Fig. 1-1 in National Research Council, 2003, p. 26).

1995; Watmough et al., 1999; Luyssaert et al., 2001; Watmough and Hutchinson, 2003; Watmough et al., 2005). Uptake refers to the mechanisms engaged in moving substances from the environment across a cellular membrane (Step D, Fig. 2.3). Food, minerals, water and gases that are used in growth processes of trees move through cell membranes by active transport and diffusion (Fritts, 1976). Diffusion occurs along a concentration gradient, from areas of high concentration to areas of lower concentration. This process allows atmospheric gases and ions of mineral nutrients deposited on foliage, bark and soils to penetrate the cells of leaves, twigs and roots (Kozlowksi and Pallardy, 1997).

Studies have found high concentrations of metals in the foliage of trees located in areas with high pollution loadings. Luyssaert et al. (2001) found high concentrations of heavy metals in the leaves of crack willow (*Salix fragilis*) growing in polluted soils. Field experiments that involve the direct application of metal radioisotopes (Lin et al., 1995) and stable metal isotopes (Watmough et al., 1999) onto conifer foliage show that foliar absorption varies depending on the application dosage. Leaf physiology may also influence uptake since the distribution, amount and composition of waxes on the surface of leaves can inhibit diffusion of minerals (Kozlowski and Pallardy, 1997). There is evidence that pH and metabolic processes may play a role in the mechanism of metal uptake by foliage. Watmough et al. (1999) describe that by lowering the pH of an application solution containing ^{207}Pb isotopes, an increase in absorption occurs. This study also attributes nil absorption of ^{67}Zn applied to foliage to the use of Zn as an essential element by plants. Further research is required to understand how metals released in the atmosphere are absorbed through leaf surfaces.

Existing research suggests that absorption of metals through bark varies based on tree species and bark physiology. Eklund (1995) concludes that uptake through the bark is a major pathway of Pb in oak trees near a Swedish battery plant since Pb concentrations decreased in the tree once the battery plant closed. Moreover, a field experiment tracing ^{207}Pb indicates that bark uptake is significant for sugar maple (*Acer saccharum Marsh*) and white pine (*Pinus strobus L.*), though not for white ash (*Fraxinus americana L.*) (Watmough and Hutchinson, 2003). It is suggested that metal uptake by bark may be more important than foliar uptake for deciduous trees since stems become the main deposition sites during winter months (Lepp, 1975). Watmough and Hutchinson (2003) suggest that differences in ridge size and shape, fissure depth, and furrowing of sugar maple, white ash and white pine can explain differences in Pb uptake observed for each tree. Further study of this pathway is needed in order to assess its relative importance to metal uptake and to understand the mechanism of uptake.

Several studies conclude that the root system is the dominant metal uptake pathway for trees (Robitaille, 1981; Guyette et al., 1991; Eklund, 1995; Martin et al., 2000). Reviews of the available literature on dendrochemical studies confirm that root uptake is considered the most important pathway (Lepp, 1975; Forget and Zayed, 1995; Watmough, 1997). Root absorption of mineral nutrients and water occurs by diffusion and mass movement (Kozlowski and Pallardy, 1997). The latter mode of uptake requires gravity or hydraulic pressure in order to move elements from the soil into the cells of roots. Molecules and ions of mineral salts in soils may also move into root cells by active transport which allows elements to move against the concentration gradient by anchoring themselves to a carrier molecule (Fritts, 1976).

Soil acidity is identified as a control on metal uptake by roots (Guyette et al., 1991; Eklund, 1995; Forget and Zayed, 1995; Watmough, 1997; Anderson et al., 2000; Watmough and Hutchinson, 2003). Eklund (1995) concludes that the mobility of Cd is enhanced in soils containing pore water with a pH of approximately 5, thus creating favourable conditions for root uptake by oak trees. Furthermore, alkaline soils are considered a factor in reduced uptake of Pb in a study of black oak (*Quercus negra* L.) exposed to emissions from an active smelter (Anderson et al., 2000).

2.5.2 Transport and storage of metals in trees

The mass flow hypothesis, cohesion-tension theory and radial translocation are currently accepted theories used to explain nutrient and metal transport within plants (Kozlowski & Pallardy, 1997; Stern, 2006). The mass-flow hypothesis accounts for the movement of soluble substances within the phloem column towards the xylem tissue (Stern, 2006). The cohesion-tension theory explains the transport of water within the xylem column via the transpiration stream. Radial translocation describes the movement of substances from the pith to the bark or vice-versa within the tree stem (Guyette et al. 1991).

Metals absorbed by foliage and bark follow the phloem transport stream towards the xylem tissue. Mass-flow begins from the source of absorption and moves along sieve tubes in the phloem to a sink lower in the tree, where the substance is stored for a period of time. As the substance is removed from the sink due to osmotic potential, water abandons the sink and diffuses to the xylem. Mass flow of the metal in solution continues due to the decrease in pressure created by water loss (see Fig. 9.17 in Stern, 2006, p. 160). The mass flow rate of substances from a source such as foliage and bark to the xylem is known as phloem loading. Phloem loading can delay the movement of substances within a tree thus hindering the transport of metals to the xylem (Lepp, 1975; Lin et al., 1995; Watmough et al., 1999).

Once metals are absorbed into the cells of roots they are able to move to other parts of the tree by either the transpiration stream or lateral translocation. Transpiration refers to evaporation of water from stomata at the leaf surface. The transpiration stream is the continuous vertical movement of water from the roots to the leaves in xylem tubes (Stern, 2006). In cone-bearing trees (gymnosperms) these tubes are called tracheids and in flowering trees (angiosperms) they are called vessels. Water molecules adhere to the walls of xylem tube cells and to each other as they are pulled along by conductance towards the site of transpiration due to the difference in water potentials between the soil and the air around the stomata (Stern, 2006) (see Fig. 9.10 in Stern, 2006, p. 156). If the rate of transpiration is rapid, the potential for molecule and water uptake from roots increases (Lepp, 1975).

Lateral movement of molecules within a tree is described as lateral or radial translocation and occurs by conductance in xylem rays (see Fig. 6.8 in Stern, 2006, p. 91). Rays are made of parenchyma cells that radiate out from the centre of the stem across the xylem and phloem like the spokes of a wheel allowing the lateral conduction and storage of nutrients and water towards other parts of the stem. Lepp (1975) explains that passive conductance, within xylem tubes, allows the lateral removal of metals from the transpiration stream into non-conducting tissues in the tree stem. Delays in the accumulation of these metals in tree-rings have been attributed to biochemical processes within the xylem column. It has been hypothesized that the xylem can act as an ion exchange column thus slowing the movement of free metal ions (Watmough, 1997). There is also evidence that the transport of metals may be slowed in the xylem stream during the process of metal ligand creation with amino acids (Lepp, 1975; Kozlowski et al., 1991). Hutchinson et al. (1998) describe that a lag of time occurs between root-absorption and storage of Zn and Cd, but not for copper (Cu) and nickel (Ni) in sugar maples. This may indicate that certain metals are more mobile within this species of tree than others.

The wood structure of trees can have a significant impact on the manner in which water and molecules move vertically and laterally within the stem. Ring-porous angiosperms transport water and solutes almost entirely in the xylem tubes of the current year ring (Eklund, 1995) and lateral translocation is usually minimal (Kozlowski and Pallardy, 1997). In contrast, gymnosperms and diffuse porous angiosperms transport water and solutes via active xylem tubes in many rings simultaneously (Eklund, 1995). Caution is advised when interpreting the chemistry of rings in diffuse-porous trees since lateral translocation may play a strong role in determining where metals and minerals are stored (Lepp, 1975).

Radial translocation of metals between sapwood and heartwood also confounds this analysis. Radial translocation is suspected in studies of Fe, Mo, Ti in short leaf pine (*Pinus echinata*) (Baes and McLaughlin, 1984) and studies of As in pear (*Pirus* sp.), plum (*Prunus* sp.), cherry (*Prunus* sp.) (Martin et al., 2000), pine (*Pinus* sp.) and oak (*Quercus* sp.) trees (Cheng et al., 2007). However, it is not suspected for Cu and Zn in balsam fir (*Abies balsamea*) (Robitaille, 1981), Pb and Cd in eastern red cedar (Guyette et al., 1991), or Pb in oak trees (Eklund, 1995). Knowledge of the wood structure of trees used in dendrochemistry research is useful in establishing the importance of lateral translocation.

Cutter and Guyette (1993) assess the suitability of different tree species for dendrochemical study in their review of the dendrochemistry literature. They identify three groups of suitability factors, namely habitat and species properties, xylem physiology and element properties. Tree species that possess large ecological amplitudes, well-defined rings, no injury or defoliation, year-round foliage, strip-bark habit and a substrate of well-weathered shallow soils are considered favourable habitat and species factors. Strip-bark habit is favourable because the vascular cambium is not complete around the circumference of the stem thus providing a time series without complications due to exponential growth patterns typical of most trees (Cutter and Guyette, 1993). Suitable xylem factors include large ratios of heartwood to sapwood, low heartwood permeability and low moisture content.

Table 2.2 lists the recommendations of Cutter and Guyette (1993) based on habitat, species and xylem factors. With the exception of strip-bark habit and mixed

Table 2.2: Tree species recommendations for dendrochemistry based on the criteria identified in the literature review by Cutter and Guyette, 1993 (Adapted from Table 2 in Cutter and Guyette, 1993, p. 616).

Species	**HP**	**HMC**	**NRS**	**SB**	**EA**	**L**	**GD**	**FT**	**RC**
Larix spp.	+	+	+	-	+	+	+	-	RC
Picea spp.	+	+	0	-	+	+	+	+	RC
Pinus echinata	+	+	0	-	-	0	+	+	RC
Pinus ponderosa	+	+	-	-	+	+	+	+	RC
Pinus strobus	-	+	-	-	+	+	+	+	RC
Pinus longevea	+	+	-	+	+	+	0	+	HR
Acer saccharum	-	-	-	-	+	+	+	-	NR
Populus spp.	-	-	-	-	+	-	+	-	NR
Tilia spp.	-	-	0	-	-	-	+	-	NR

HP = heartwood permeability, HMC = heartwood moisture content, NRS = number of rings in sapwood, SB = strip-bark habit, EA = ecological amplitude, L = longevity, GD = geographic distribution, FT = foliage type, RC = recommendation.

Excellent attributes for dendrochemistry are denoted by a plus sign (+), negative attributes are denoted by a negative sign (-), and mixed attributes are denoted by a zero (0). Recommendations are given to each species in the last column; HR = highly recommended, NR = recommended with limitations or not recommended, RC = recommended.

ratings for number of rings in sapwood, spruce trees are deemed to possess favourable attributes for use in dendrochemistry. Pine trees receive mixed ratings for all attributes except foliage type and are also recommended. Pine and spruce are viable subjects for the study of long-term trends in environmental chemistry, however potential lateral translocation may cause complications for developing pollution chronologies.

The mobility of elements within the stem of trees will vary depending upon certain characteristics of the tree and the element itself. Cutter and Guyette (1993) identify these factors as ion solubility, sapwood-heartwood equilibrium concentrations, charge/ionic radius ratio, essential nature of the element to plant growth, sap pH and bonding in the xylem matrix. The potential for lateral mobility within the tree stem are categorized into high, moderate and low for several elements in Table 2.3. Arsenic is listed under the high mobility category due to its solubility and ionic charge-radius ratio. As observed in the literature, physiological and biochemical factors influencing the mobility and accumulation of nutrients and metals in trees can complicate chronological analyses of concentrations observed in tree-rings. An understanding of their impacts on dendrochemical analysis is necessary in order to adequately interpret the results of tree-ring chemical analyses.

2.5.3 Arsenic

Arsenic in the terrestrial environment is mainly found in the inorganic form as either pentavalent arsenic (arsenate [As(V)]) or trivalent arsenic (arsenite [As(III)]) (Quaghebeur and Rengel, 2005). Arsenic trioxide (As_2O_3) is a trivalent form found naturally in terrestrial environments as the mineral claudetite (IPCS, 2006). It forms

Table 2.3: Potential radial mobility of some elements in xylem. Elements are categorized on the basis of solubility, ionic charge-radius ratio, and essential nature (Modified from Table 1 in Cutter and Guyette, 1993).

Degree of Mobility	**Elements**
High	As, K, Na, Mg, P, N, S, Cl, B
Moderate	Ca, Sr, Mn, Zn, Rb, Cu, Mo
Low	Fe, Mo, Ni, Sn, Sb, Ba, Al, Pb, Cd

readily when elemental metallic arsenic is heated to high temperatures or burned, as in the smelting of ore to extract copper, lead and gold (ATSDR, 1999). Arsenic and its compounds are used in agricultural and forest products, industrial manufacturing and certain homeopathic and folk remedies (IPCS, 2006; ATSDR, 1999). Traces of organic As, for instance monomethylarsonic acid (MMA), dimethyl-arsinic acid (DMA), arsenobetaine and arsenocholine are also found in soils and terrestrial plants (Quaghebeur and Rengel, 2005). Their presence is attributed to microbial activity or the local use of As-based pesticides (Quaghebeur and Rengel, 2005).

Although As is ubiquitous and thought to be harmless in small quantities, exposure to high levels of this metalloid in the environment, whether in air, soil, water or plants can cause hazards to human and ecosystem health (Dushenko et al., 1995; Dartmouth Toxic Metal Research (DTMR), 2005). Acute and chronic exposure to As has resulted in skin and lung cancer in humans (DTMR, 2005), cancer in animals (DTMR, 2005), and growth decline in various plants (Kabata-Pendias and Pendias, 1992; Dushenko et al., 1995; Lasat, 2002; Meharg and Hartley-Whitaker, 2002; Gulz et al., 2005). Moreover, As is persistent in the environment, can change from non-toxic to toxic forms through natural processes, and although it does not bio-magnify, it can bioaccumulate to high levels in a number of plants (Wang et al., 2002). Arsenic pollution can pose immediate and future risks to human and ecosystem health.

Research has been undertaken to understand the distribution, mobility and toxicity of As in terrestrial plants (Quaghebeur and Rengel, 2005). Due to this research it is known that the inorganic forms of As are the most toxic forms of this metal (Quaghebeur and Rengel, 2005) and that As phytotoxicity commonly results in growth reduction (Kabata-Pendias and Pendias, 1992). Correlations are found between the levels of As(V) in soils and within plants thus indicating that absorption by roots is a major pathway of As uptake (Patra et al., 2004).

Different mechanisms are responsible for absorption of As(V) and As(III) from soils. Gulz et al. (2005) explain that phosphate [P(V)] availability and demand in crop plants [(English ryegrass (*Lolium perenne*), maize (*Zea mays*), rape (*Brassica napus*) and common sunflower (*Helianthus annuus*)] influence As(V) uptake. Research with other terrestrial plants also suggests that As(V) in soils crosses the plasma membrane of plant cells in association with P(V) (Wang et al., 2002; Meharg and Hartley-Whitaker, 2002). At low levels, P(V) is found to displace As(V) from soil particles increasing absorption and phytotoxicity, while high levels of P(V) compete with As(V) resulting in reduced As(V) uptake and phytotoxicity (Meharg and Mcnair, 1991; Meharg and Mcnair, 1992). Wang et al. (2002) suggest that As(III) uptake by Chinese brake fern (*Pteris vittatta*) is not associated with P(V). Quaghebeur and Rengel (2005) state that recent research on *Oryza sativa* (rice) and *Saccharomyces cerevisiae* (baker's yeast) shows that As(III) is taken up through the glycerol-membrane, which transports water and solutes. Hence, the uptake of As by plant roots is determined by soil properties and As speciation.

Tu and Ma (2003) describe that low soil pH improves As and phosphorus (P) uptake in *Pteris vittatta*. However, the texture of the soil may affect the role of pH in this process. Phytotoxicity is expected to be higher in sandy soils since they have low Fe-oxide, Al-oxide, clay and organic matter content which are strong sorbents of As(V) in acid soils (Gulz et al., 2005). In alkaline soils, Ca-oxides are the primary sorbents of As(V), thus low soil Ca content could result in less bioavailable As(V) (Gulz et al, 2005). As(III) is considered more mobile from roots to shoots of *P. vittatta* than As(V) (Wang et al., 2002). The reduction of As(V) to As(III) within plants is observed in all plant uptake studies to date (Wang et al., 2002; Tu et al., 2004; Kertulis et al., 2005; Quaghebeur and Rengel, 2005). However, there is still debate about whether the reduction occurs before or after xylem loading (Wang et al., 2002). This has implications for dendrochemistry research in terms of deciding which As species to analyze within the tree and soils.

The mechanism of As phytotoxicity is receiving much study at the molecular level. Arsenicals (arsenate and arsenite) combine rapidly with dithiol groups on proteins thus inhibiting the function of enzymes that require free sulphhydryl groups (Quaghebeur and Rengel, 2005). Pickering et al. (2000) observe that arsenicals are transported to shoots via the xylem and stored as an As(III)-tris thiolate complex. Due to its chemical similarity to P(V), As(V) can bind to ADP forming arsenate-ATP analogues, depriving cells of energy sources that can lead to cell death (Quaghebeur and Rengel, 2005). Considering that many reactions in plants involve P(V) and sulphydryl groups, arsenicals have the potential to interfere with many physiological and biochemical processes that influence growth.

Patra et al. (2004) summarize the findings of several papers regarding genotoxic effects of As exposure. These studies reveal reduced mitotic index, chromosomal aberrations and clastogenic effects in plants exposed to various As compounds. Wang et al. (2002) indicate that *Pteris vittatta* can accumulate 10,000 μg/g dry weight of As before phytotoxic symptoms begin to appear. A similar study by Kabata-Pendias and Pendias (1992) suggests that the threshold of most plants is between 5 and 100 μg/g dry weight. In the case of trees, there is a lack of research on the subject of As contamination tolerances for different tree species.

2.5.4 Sulphur dioxide

SO_2 and NO_x are released into the atmosphere from the burning of fossil fuels, metal smelting and volcanic eruptions. Breathing air with 100 ppm of SO_2 can be life threatening, and lower levels can harm respiratory functions (Agency for Toxic Substances and Disease Registry (ASTDR), 1999). Once SO_2 is removed from the air it has very little impact on human health. Sulphur dioxide is removed from the atmosphere by dry and wet deposition onto the surfaces of soils, water and vegetation. Surface waters also receive SO_2 from runoff and subsurface drainage (ATSDR, 1999).

Reactions involving sunlight and atmospheric moisture can convert SO_2 and NO_x to H_2SO_3 and H_2SO_4 (reactions [1] and [2]) and HNO_3 (reactions [3] and [4]), which produce acid rain when scavenged from the air by rain droplets (Bunce, 1994). Soils exposed to acid rain may be at risk to acidification. The potential for acidification depends upon soil texture, pH, cation-exchange capacity and base saturation prior to exposure (MacLaughlin, 1998).

$$SO_2 + H_2O \rightarrow H_2SO_3 \qquad (1)$$

$$SO_2 \xrightarrow{\text{oxidize}} SO_3 \rightarrow H_2SO_4 \qquad (2)$$

$$NO_2 + H_2O \rightarrow 1/2\ HNO_2 + 1/2\ HNO_3 \qquad (3)$$

$$NO_2 + O_3 \rightarrow NO_3 \xrightarrow{XH} HNO_3 \qquad (4)$$

Acidic precipitation directly weakens the structure and function of foliar epicuticular waxes (McLaughlin, 1998). The foliage becomes more susceptible to secondary pathogenic infection and leaching of base cations thus reducing the efficiency of foliar photosynthesis (McLaughlin, 1998). It is generally accepted that visible foliar injury from SO_2 only occurs under continuous, direct exposure to precipitation with pH of approximately 3 (McLaughlin, 1998). These symptoms include necrotic patterns on leaves, chlorosis, early leaf drop and brown tipburn in conifers.

Soil acidity is determined by the relation between the amount of basic cations (Mg^{2+}, Ca^{2+}, K^+, Na^+) and acid aluminum species (Al^{3+}, $Al(OH)^{2+}$, $Al(OH)^{2+}$) on the exchange complex (Reuss and Johnson, 1986). Several studies investigate nutrients in tree-rings as an alternate method of determining soil acidity in the absence of historical soil acidity data. Berger et al. (2004) describe changes in Ca, Mg, Mn and Al concentrations in tree-rings in order to determine soil acidity and nutrient cycling under pure and mixed conifer stands. Their reconstruction of soil pH using elemental tree-ring ratios of Ca/Al (pure) and Ca/Mg (mixed) indicates that soil acidification occurred in their study area over the last 60 years. Similarly, Guyette et al. (1992) were able to reconstruct soil pH under eastern red cedar (*Juniperus virginiana*) stands using Mn in tree-rings thus indicating that reconstruction of changes in soil pH due to soil acidification is possible. Shortle et al. (1997) conclude that enrichment of Ca and Mg in stem wood of red spruce (*Picea rubens* Sarg.) is consistent with mobilization of base cations that in turn coincide with atmospheric emissions and deposition of nitrates and sulphates.

Soil acidity has implications for tree-growth since nutrient deficiencies, nutrient imbalances, inhibited nutrient cycling and/or root mortality that result from soil acidification can reduce tree-growth (McLaughlin, 1998). Acidification of soils also indirectly affects tree-growth by increasing toxic metal bioavailability and decreasing cation-exchange capacity (McLaughlin, 1998). In alkaline soils, heavy metals form insoluble oxides of sulphate, while in acidic soils they form soluble sulphates. Since the main uptake of elements by roots is from the soil solution, roots in acidic soils more easily absorb heavy metals. Conversely, uptake of nutrients by roots decreases with higher soil acidity (Stern, 2006). Webster et al. (2004) observe that reduced cation-exchange capacity due to SO_2-induced soil acidification in the Great Smokey Mountains National Park (GSMNP) is associated with reduced radial growth of red spruce in this region.

2.6 Tree-growth response to pollution

Two approaches have been taken to study the relation between tree-growth and pollution. The first approach consists of modelling ring-width chronologies at contaminated sites based on reference site chronologies. Long and Davis (1999) adopt this approach in order to assess the effect of stack height changes at a power plant on nearby white oak (*Quercus alba* L.). They develop a climate model using precipitation to predict growth of a reference chronology. The predictive ability of the reference chronology is poor prior to stack increases and stronger afterwards, thus indicating that tree-growth is likely influenced by stack heights. This method requires excellent historical information regarding changes in emissions.

The second approach entails chemical analysis of individual rings or ring groupings in order to compare a chronology of tree-ring concentrations with a ring-width chronology. This method has received mixed results due to the influence of lateral translocation on the tree-ring chemistry chronology. Relations between metal pollution and tree-growth are successfully observed for Cu in balsam fir (*Abies balsamea L. Mill*) (Robitaille, 1981); Cd in oak (*Quercus spp.*) (Eklund, 1995); Pb and Cd in eastern red cedar (Guyette et al., 1991); Ca, Mn and Zn in short leaf pine (*Pinus echinata*) (Baes and McLaughlin, 1984); and Cd in sycamore (*A. pseudoplatanus* L.) (Watmough and Hutchinson, 1996). Moreover, studies of regional soil acidification in the northeastern USA (Shortle et al., 1997) and GSMNP (Webster et al., 2004) observe relations between regional NO_x and SO_2 emissions and soil acidification based on concentrations of Ca and Mg in red spruce rings. These studies involve elements with low mobility and trees with a favourable physiology for dendrochemistry (Table 2.1 and 2.2). In contrast, studies of mobile elements, such as arsenic (Martin et al., 2000; Cheng et al., 2007), and those employing trees with unfavourable physiologies for dendrochemistry, such as black spruce (Dion et al., 1993), are unable to observe clear relations between pollution and tree-growth.

Relations observed to date indicate that increased concentrations of metals in tree-rings correspond to reduced radial growth. This is observed for studies of local pollution from Cu ore smelting (Robitaille, 1981; Baes and McLaughlin, 1984), As salt storage

(Cheng et al., 2007), and regional pollution from Pb mining (Guyette et al., 1991). Positive relations are also found between reductions of industrial emissions and decreased concentrations of their constituents in ring-width intervals (Guyette et al., 1991; Eklund, 1995; Watmough and Hutchinson, 1996). These relations reveal that tree-growth and tree-ring chemistry can indicate changes in pollution.

2.7 Summary

The reviewed literature supports dendrochemistry as a valid approach for monitoring environmental changes in northern environments. Soils in northern environments are relatively shallow, especially in permafrost zones, resulting in higher sensitivity of trees to environmental changes. Trees in these regions are at or near the limits of their ecological range. Thus, it is easier to identify the influence of climate on radial growth and subsequently remove this factor from analyses in order to observe the influence of pollution. A number of northern tree species possess longevity and many xylem factors that are suitable to dendrochemical study. Moreover, several dendrochemical studies were able to attribute changes in pollutant accumulations in trees to changes in local or regional emissions of pollutants (Robitaille, 1981; Baes and McLaughlin, 1984; Guyette et al., 1991; Eklund, 1995; Watmough and Hutchinson, 1996).

CHAPTER THREE

STUDY AREA & METHODOLOGY

3.1 Study Area

The study area consists of several sites located within a 40 km radius of Giant Mine. The mine is located on the west shore of Yellowknife Bay, 5 km north of the city of Yellowknife, NWT (62°26′32″N, 114°23′51″W). The Northwest Territories is comprised of 4 ecozones further subdivided into a number of ecoregions. Yellowknife lies within the Tazin Lake Upland ecoregion (TLU) of the Western Taiga Shield ecozone (Environment Canada, 2005) (Fig. 3.1). The TLU ecoregion extends from the East Arm of Great Slave Lake south to Lake Athabasca (Environment Canada, 2005). Ecoregions broadly divide the territory based on distinctive regional attributes such as topography, soil, climate, geology, vegetation, water and land uses.

3.1.1 Climate

The TLU has a sub-humid high boreal eco-climate, characterized by cool summers and very cold winters (Environment Canada, 2005). The 1971-2000 climate normals for Yellowknife mirror these characteristics with a mean July temperature of 17°C and mean January temperature of -27°C (Environment Canada, 2006). The mean annual precipitation for this same period was 280.7 mm with more than half falling as snow (Environment Canada, 2006). Annual snow cover begins in October and ends in late April to early May (Wedel et al., 1990). Summer precipitation occurs by convection, thus rainfall is highly variable from year to year (Spence and Woo, 2003). Conditions become cool and damp in September when the jet stream settles over the region (Spence

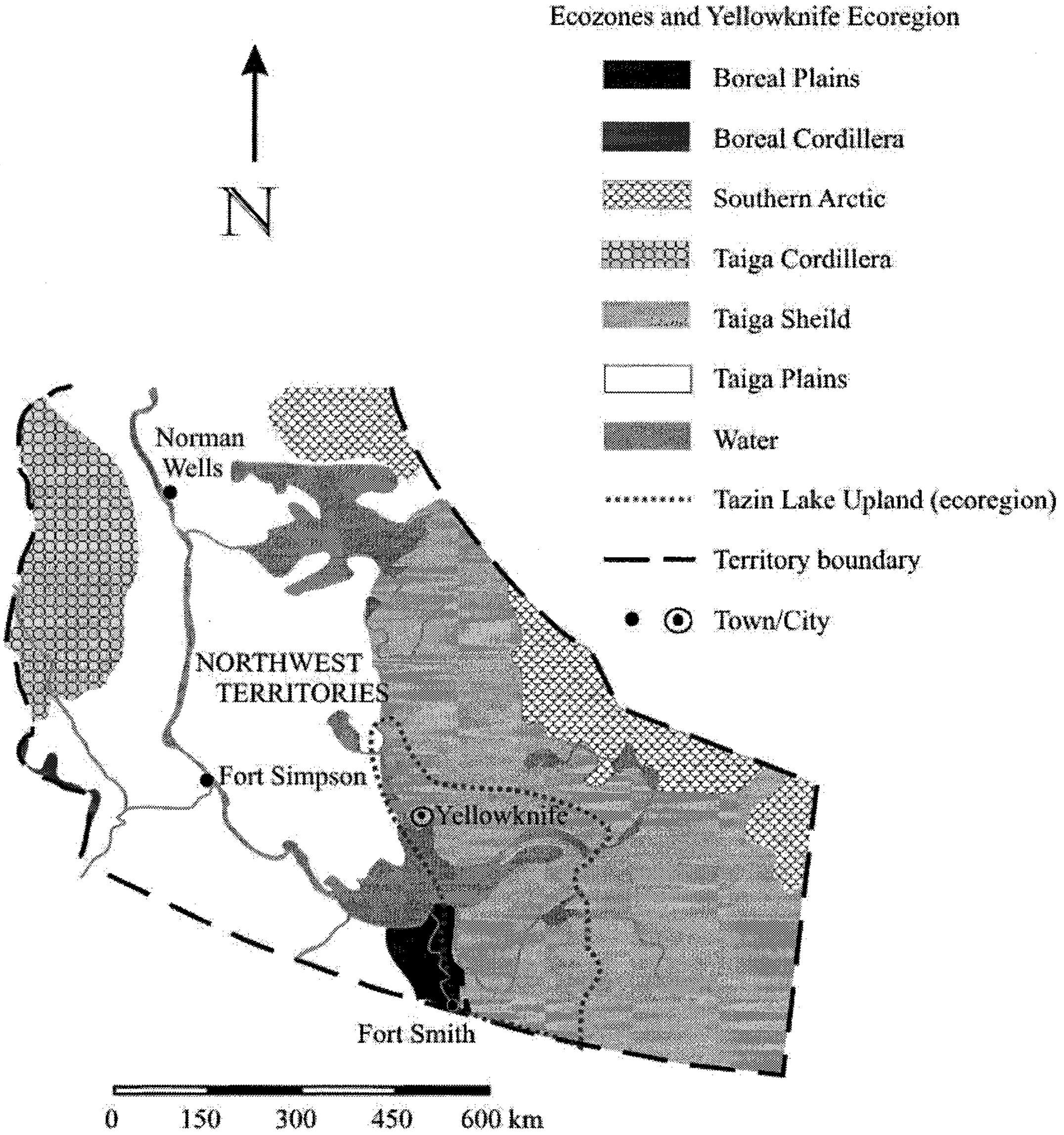


Figure 3.1: Ecozones of part of the Northwest Territories (EC, 2005) and Tazin Lake Upland ecoregion (Natural Resources Canada, 2007).

and Woo, 2003).

3.1.2 Vegetation

The study area lies within the boreal forest-tundra transition zone (Natural Resources Canada, 2003a). Vegetation in this part of the boreal forest is characterized as sub-arctic open lichen woodland. Forest stands are dominated by coniferous trees, namely black spruce, white spruce, balsam fir, tamarack (*Larix laricina*) and jack pine. Broadleaved tree and shrub species such as dwarf birch (*Betula pumila*), balsam poplar (*Populus balsamifera*), green alder (*Alnus crispa*), western mountain ash (*Sorbus scopulina*) and many willow species (*Salix* spp.) are also common. The percentage of productive forest is between 10 and 25 percent (Natural Resources Canada, 2003b). Stumps and charred trees are found throughout the region as evidence of logging and wildfire. The most recent major fire occurred approximately 60 km east of the study are in 1998 near Tibbitt Lake (Roger Fraser, NWT Energy and Natural Resources, pers. comm., 2006).

3.1.3 Soils and Geology

The TLU is dominated by uplands characterized by exposed rock outcrops covered by discontinuous veneers of sandy till and intervening valleys covered by level to gently undulating organic soils (Environment Canada, 2005). Dystric Brunisols are the dominant soil in this ecoregion, although soils in peat-filled valleys generally consist of organic Cryosols (Environment Canada, 2005). Organic deposits may overlie glaciolacustrine sediments in areas that were submerged by glacial Lake McConnell during the northeasterly retreat of the Laurentide Ice Sheet (Kerr, 2006). Turbic Cryosols are found at sites with permanently frozen ground (Environment Canada, 2005). The TLU ecoregion is located within the extensive discontinuous permafrost zone where 50% to 90% of the terrain is underlain by permafrost (Environment Canada, 2005).

Yellowknife and the study area are underlain by Precambrian shield within the southwest Slave geological province (Natural Resources Canada, 2004). The Yellowknife Greenstone Belt (YGB) extends north 50 km from Great Slave Lake and consists of Archean metavolcanics and Proterozoic intrusive rocks of the Kam and Banting groups (Kerr, 2006, Fig. 15-1, p. 214). Prosperous granite intrudes the Duncan group metaturbidites to the east of the YGB (Kerr, 2006, Fig. 15-1, p. 214). The Western Plutonic Complex of the Defeat Plutonic Suite lies to the west of the YGB (Kerr, 2006, Fig. 15-1, p. 214).

Ore in the YGB is characterized by 40-80% quartz-carbonate and less than 10% sulphide minerals, mainly pyrite and arsenopyrite (Environmental Sciences Group (ESG), 2001). Natural weathering of bedrock produces soils with high levels of As. The average background concentration for As in Yellowknife soils is believed to be 150 μg/g, with a normal upper limit of 300 μg/g (Risklogic Scientific Solutions Inc., 2002). These values are based on three separate studies performed in 2001 (Kerr, 2001; Ollson et al., 2001; ESG, 2001). Background concentrations of As in YGB soils are in stark contrast to typical background As concentrations found in Canadian agricultural soils that range from 5 to 15 μg/g (INAC, 2003a). Normal background As concentrations to the east of the YGB have not been studied.

3.1.4 Land Use

Over the last century, land use in the area has included mining, logging, parkland, urban development and First-Nations resource use. Between 1934 and 1939 individual prospectors and mining companies staked thousands of claims for potential gold mines (Foster and Heming, 2003). Logging and clearing of land was needed to build housing and amenities for the ever-growing population. Richard Finnie commented on the quick development of the area in *Canada Moves North.*

> "In 1934, flying south from the Arctic I looked down upon a maze of lakes and bush skirting the easterly shore of the North Arm of Great Slave Lake, and the only signs of life were a few widely scattered tents of Indians. In 1939, flying north from Edmonton and approaching the same locality, I saw houses, stores, warehouses, and mines; airplanes taking off and landing; power boats and barges moving to and fro. Here in the sub-Arctic a thousand people were trying to carve out careers for themselves around the town of Yellowknife" (Foster and Heming, 2003).

Urban development continued through the 1940s to present day. The current population of Yellowknife is 18,700 (2006 census, Statistics Canada, 2007). Although mining ceased in Yellowknife at the beginning of the 21st century, the city is an important hub for administration of mining and exploration further north. Yellowknife has also become a centre for government, business, transportation, arts and entertainment, and politics.

3.2 Site Selection Criteria

The general location of sites was based on distribution surveys performed during the operation of the mine and trends evident from wind roses. Snow surveys performed in the late 1970s and mid-1980s (Hazra et al., 1977; Stanley and Associates Ltd, 1986) concluded that the highest deposition of As occurred near the mine (Fig. 3.2). Figure 3.3 illustrates the results of a survey performed using a diffusion plate network to study the distribution of SO_2 from Giant Mine in the Yellowknife area during the early 1990s (GNT, 1993). Sulphur dioxide deposition was i) highest at distances < 3 km from the mine, ii) within the mid-range at 3-5 km from the mine, and iii) much lower at distances > 5 km from the mine (GNT, 1993). An earlier study using a lead candle network indicates that SO_2 levels varied between sites located at the same distance from the mine, yet in different directions from the mine (GNT, 1993). These findings reveal that the highest contamination occurred within a 10 km radius of Giant Mine. It was suggested that this was due to predominant wind direction and other variable weather conditions (GNT, 1993). The lowest concentrations of SO_2 detected by the lead candle network were found at 20 km ENE and 34 km WNW of the mine (Fig. 3.3). Thus, contaminant deposition did not occur very far east or west of the mine. Therefore, in this study sites located within a 10 km radius of the mine are considered contaminated and those over 15 km east of the mine are considered reference sites.

In order to establish predominant wind directions for Yellowknife, wind roses were prepared using hourly wind data from the Yellowknife airport (Environment Canada, 2006) for the last 20 years (1985-2005) (Fig. 3.4). Monthly wind roses for the

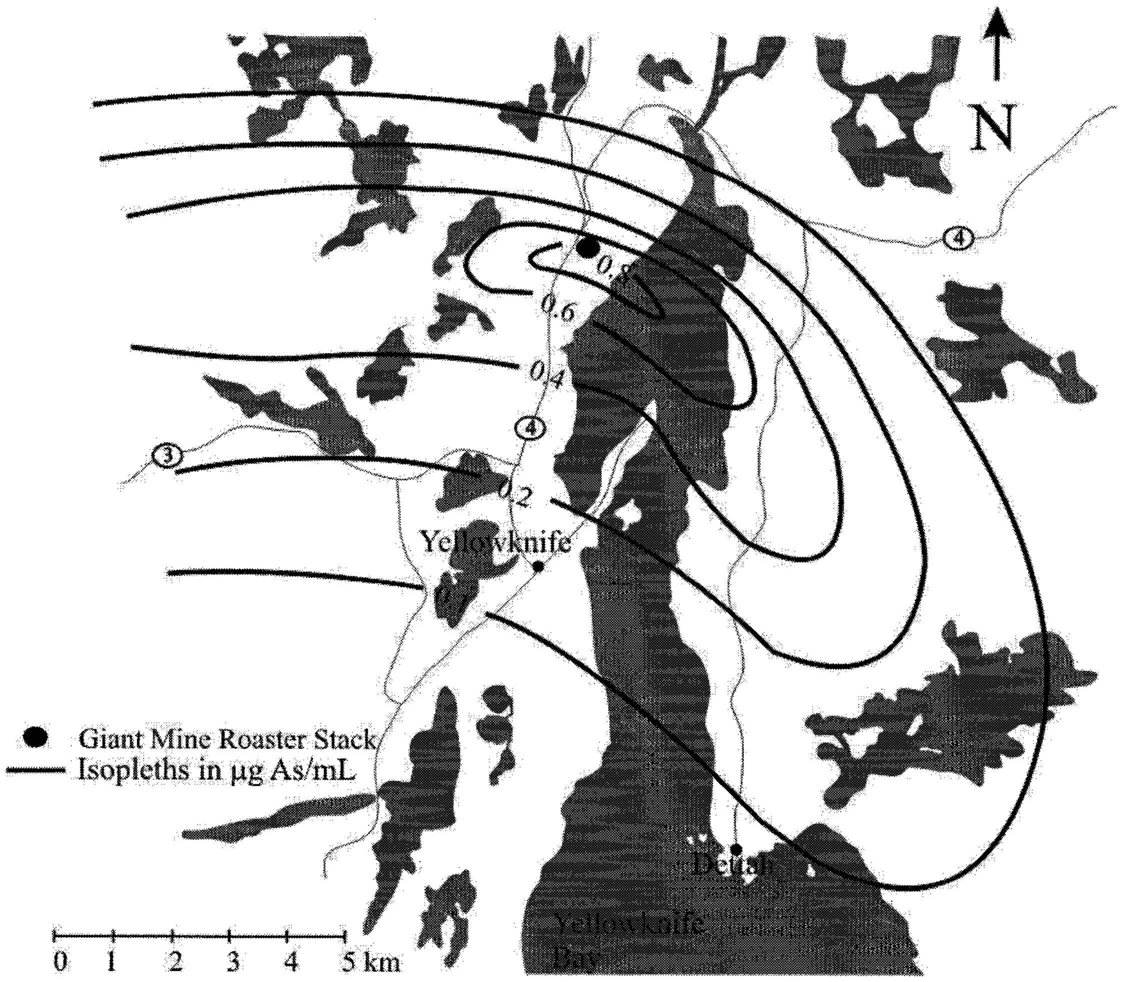


Figure 3.2: Snow arsenic distribution survey conducted in 1975 showing isopleths in µg As/mL (Modified from Fig. 7 in Hazra et al., 1977, p.18).

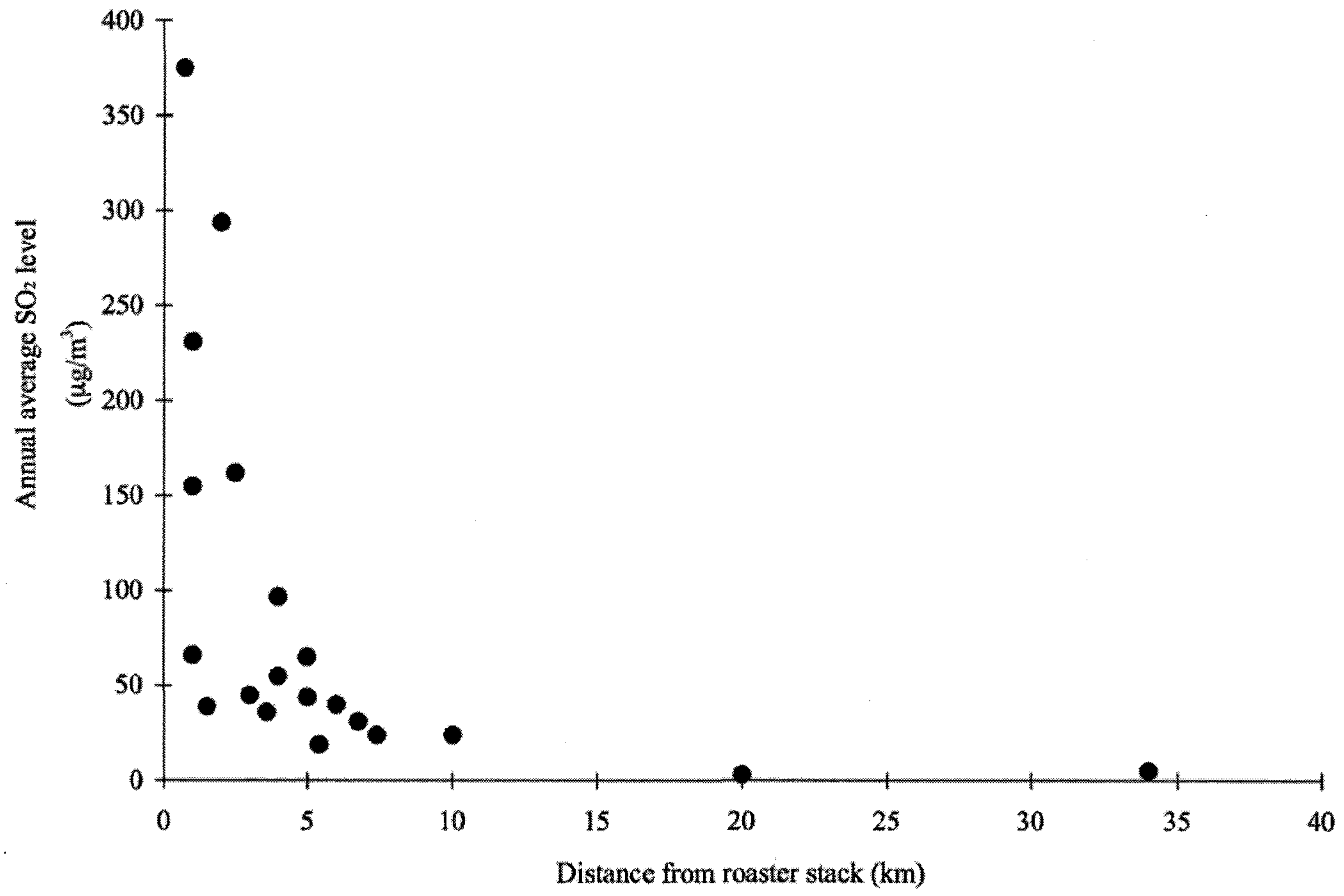
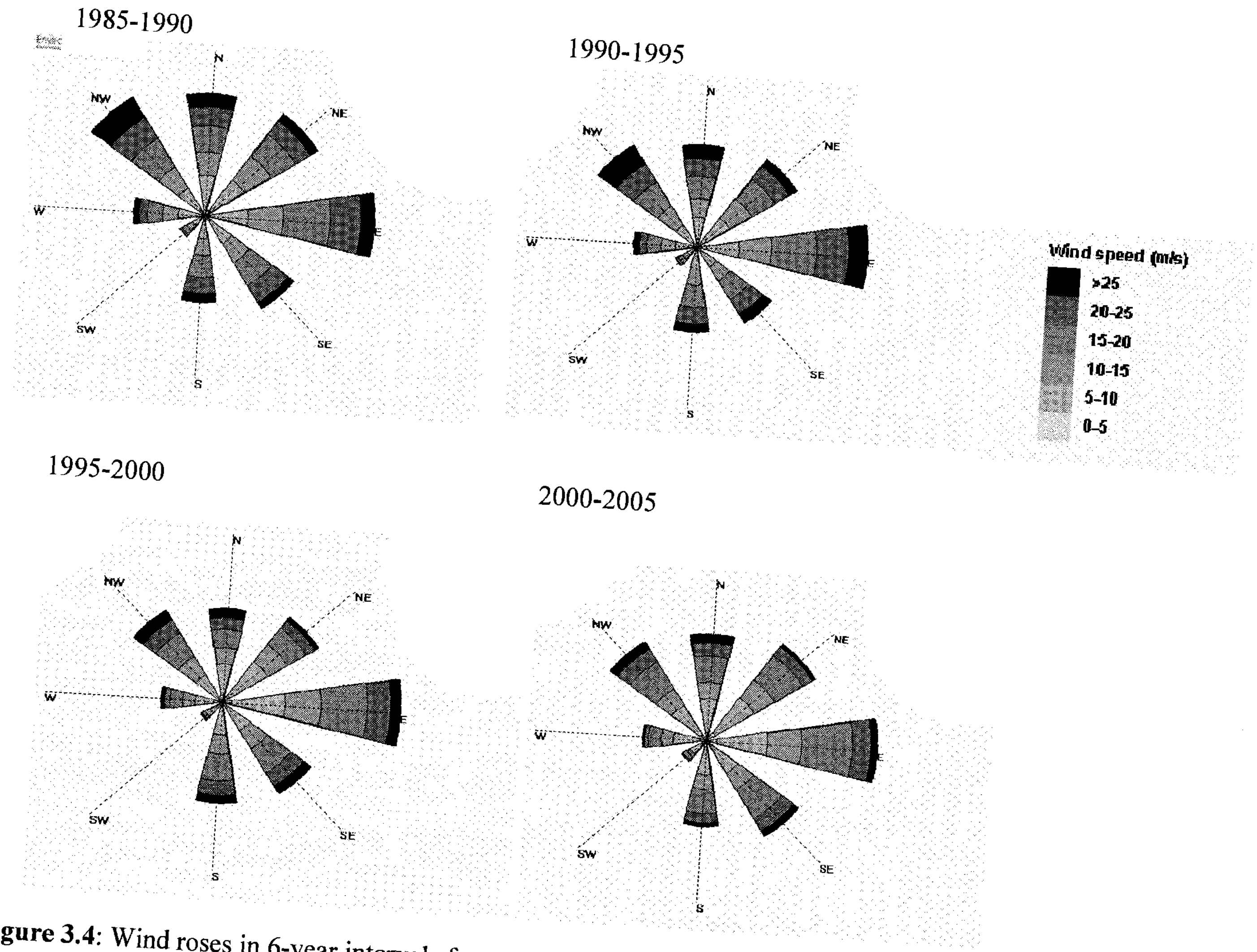


Figure 3.3: Annual average sulphur dioxide levels with distance from Giant Mine's roaster stack. Data from a diffusion plate network survey conducted from December 1991 to November 1992 (Data from Table 6 GNT, 1993, p. 17).


1985-1990

1990-1995

1995-2000

2000-2005

Figure 3.4: Wind roses in 6-year intervals from 1985 to 2005 based on hourly wind direction and wind speed data from the Yellowknife airport. Created using Enviroware Software©.

periods 1955-1966 and 1967-1972 were also examined (Hazra et al., 1977, p. 26-27). These wind roses indicate that the predominant wind directions over the last 20 years were, in decreasing order, from the east, northwest, northeast, north, southeast, and south. Although the south wind is not as frequent in these graphs, monthly wind roses show that it was the dominant wind direction in the summer months - July and August.

The selection of specific forest stands was based on topography, accessibility and presence of more than 30 trees of the same species to ensure adequate replication. Initial site selection was carried out by identifying potential tree stands and access points on National Topographic Series (NTS) maps and aerial photographs. Suitable sites were evaluated in the field for final site selection. Access to most sites was on foot from main roadways for ease of access since the boggy terrain was difficult to traverse for long distances. In these cases, sites were located at least 100 m from the roadway in order to minimize the influence of pollution from vehicles. Sites along Prelude Lake and River Lake were accessed by boat. Several sites were selected from the two dominant forest types within the study area, namely upland rock outcrops of jack pine or white spruce stands and lowland black spruce stands. Individual sampling sites consisted of 12 jack pine sites, 5 white spruce sites and 6 black spruce sites (Fig. 3.5 and Table 3.1).

Wherever possible, reference sites were located in areas with underlying geology similar to that of contaminated sites. The rationale for this was to minimize the complexity of having to account for the influence of different background levels of As on chemical analysis results for soil and tree core samples.

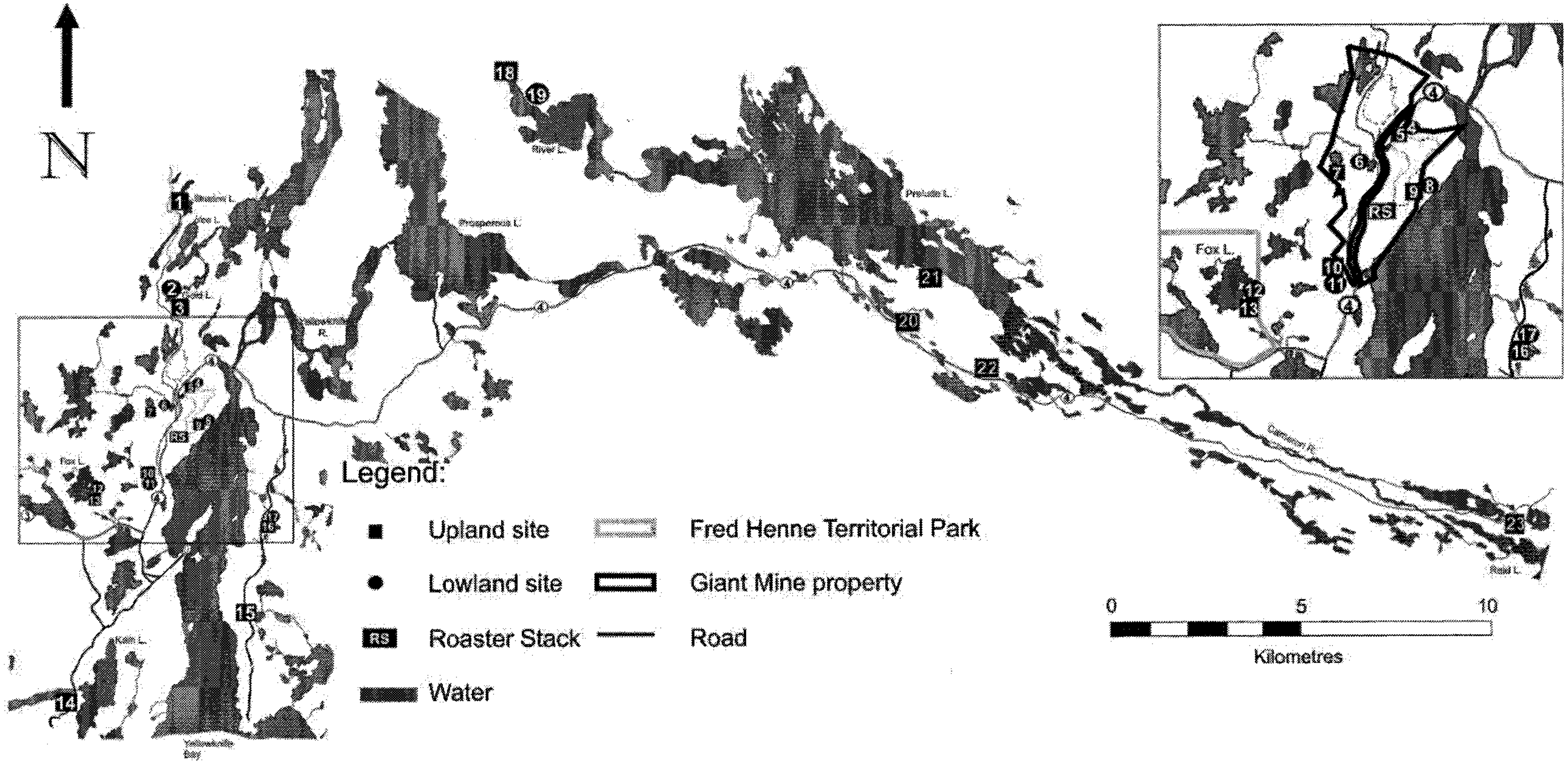


Figure 3.5: Sketch of study area indicating location of jack pine, white spruce and black spruce sites. 1) Shadow Lake; 2) Gold Lake; 3) Vee Lake Road; 4) ETP Road; 5) Settling Pond; 6) B Pit; 7) Pink Hill; 8) Cry Swamp; 9) Central Pond; 10) A Pit; 11) Raven Ravine; 12) Prospector Trail; 13) Fox Lake; 14) Kam Lake; 15) Dettah Road; 16) Dettah Road Two; 17) Boot Pond; 18) River Lake; 19) Century Pond; 20) Prelude Lake East; 21) Prelude Lake; 22) Ingraham Trail; 23) Fifty Kilometres.

Table 3.1: Summary of study area site locations.

Site #	Latitude	Longitude	Elevation (masl)	Dominant Tree Species	# Trees Cored	Distance and Direction from RS (km)
1	62°34'00.5"	114°21'29.4"	209	Jack Pine	31	8N
2	62°32'26.9"	114°21'52.3"	188	Black Spruce	31	4N
3	62°32'16.7"	114°21'42.7"	215	White Spruce	33	4N
4	62°30'53.8"	114°20'42.0"	185	Black Spruce	30	2N
5	62°30'49.3"	114°20'54.2"	189	Jack Pine	31	2N
6	62°30'22.3"	114°21'46.3"	175	White Spruce	32	1W
7	62°30'18.7"	114°22'13.4"	194	White Spruce	30	1W
8	62°30'16.4"	114°20'22.4"	186	Black Spruce	31	1E
9	62°30'12.1"	114°20'31.6"	194	Jack Pine	37	1E
10	62°29'14.8"	114°22'20.5"	211	Jack Pine	30	2S
11	62°29'09.7"	114°22'21.7"	180	Black Spruce	33	2S
12	62°28'49.1"	114°24'36.6"	202	Black Spruce	30	3SW
13	62°28'43.0"	114°24'43.0"	208	Jack Pine	32	3SW
14	62°25'04.1"	114°25'12.0"	175	Jack Pine	31	9SW
15	62°26'20.4"	114°18'39.9"	178	White Spruce	27	6SE
16	62°28'23.0"	114°18'06.0"	191	Jack Pine	24	4SE
17	62°28'24.2"	114°17'43.2"	191	Black Spruce	31	4SE
18	62°36'23.4"	114°08'05.6"	195	Jack Pine	30	15E
19	62°36'09.8"	114°06'57.6"	163	Black Spruce	24	15E
20	62°33'12.9"	113°51'22.5"	197	Jack Pine	30	22E
21	62°31'26.5"	113°49'16.0"	199	Jack Pine	31	23E
22	62°33'03.6"	113°52'07.4"	214	Jack Pine	32	24E
23	62°29'36.6"	113°26'07.5"	228	Jack Pine	31	40E

RS - refers to roaster stack

3.3 Site Descriptions

3.3.1 Contaminated sites

Contaminated sites were located to the north, west, southwest and southeast of Giant Mine within a 10 km radius of the roaster stack. These sites were considered to have received deposition of AS_2O_3 dust, SO_2 and SO_4^{2-} from Giant Mine roaster emissions, tailings ponds or contaminated soils. The mine is located approximately 5 km north of Yellowknife on the west shore of Yellowknife Bay. There are six open pits (A1, A2, B1, B2, B4, C1), four tailings ponds (Northwest, South, Central, North), two shafts (A-shaft & C-shaft), a polishing and settling pond, a mill and a 45 m tall roaster stack on the property. Highway 3 runs through the property then bends east into Highway 4, also known as the Ingraham Trail. Baker Creek flows south through the mine property and closely follows Highway 3. Several small ponds occur on the property as well as a few lakes, including Pocket Lake, Gar Lake, Trapper Lake, Vee Lake and Gold Lake.

Eight sites (SITES 4, 5, 6, 7, 8, 9, 10, 11) were located on the mine property near key areas of mining activity in pockets of conifer-dominated stands. Exposed rock outcrops at elevations of approximately 190 to 210 m.a.s.l. are dominated by jack pine-lichen communities while black spruce-moss communities are dominant in valleys of 160 to 190 m.a.s.l.. Tree species found on the property include jack pine, white spruce, black spruce, dwarf birch and tamarack. Ground vegetation consists of sparse lichen (*Umbilicaria hyperborean*, *Cladina* sp., *Cladonia* sp.), mosses, hoary willow (*Salix candida*) and bare rock. The latter is especially noticeable to the west of the mine, with large exposures of pink granite bedrock (Figure 3.6). Most of the mine property is

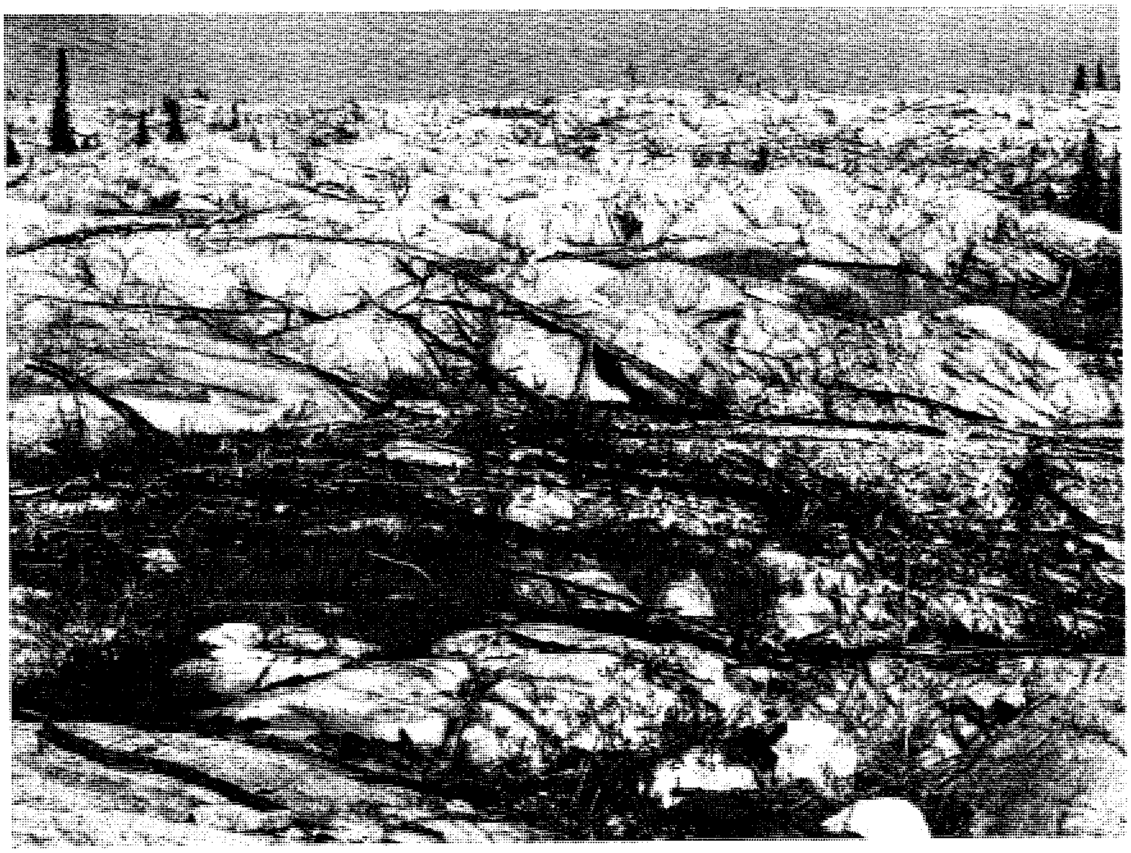


Figure 3.6: Photograph of pink granite rock outcrop to the west of the Giant Mine roaster stack (Photo by Sonia M. St-Onge).

underlain by mafic volcanic rock containing arsenopyrite in association with gold. Total As concentrations in soils on the Giant Mine property range between 11.0 µg/g to 25500.0 µg/g (Golder Associates Ltd, 2004).

In order to assess whether there is a pollution gradient with distance from the roaster stack nine sites (SITES 1, 2, 3, 12, 13, 14, 15, 16, 17) were located outside the mine property. One site was located to the north of the mine near Shadow Lake and two near Gold Lake. Two sites were selected to the southwest within the Fred Henne Territorial Park near Fox Lake. Three sites were located on the eastern shore of Yellowknife Bay along Dettah road. One site was selected to the south of the city near Kam Lake. The geology of the first three sites is similar to the mine property – mafic volcanic rock. Turbidites underlie the eastern shore of Yellowknife Bay and granitoids underlie the site at Kam Lake. Signs of past logging and fire were evident at all contaminated sites.

3.3.2 Reference sites

Six reference sites (SITES 18, 19, 20, 21, 22, 23) were located 15 to 40 km east of Giant Mine where deposition from emissions was considered unlikely. Outcrop sites ranged in elevation from approximately 190 to 230 m.a.s.l., while the valley site was approximately 160 m.a.s.l.. Three sites were selected along the Ingraham Trail, one near Prelude Lake and two near River Lake. The bedrock geology of the first four sites consists of turbidites and the last two of granitoids. Tree species at these sites are similar to the contaminated sites, however groundcover consists of dense mats of lichen (*Cladina mitis*, *Cladonia* sp., *Flavocetraria nivalis*), and moss (*Tomenthypnum nitens*). In contrast to the mine sites, bare rock outcrops occur rarely. Most of the land along the Ingraham Trail is designated Crown land or parkland. Therefore, disturbance to the forest is limited to fire and recreational use. Homes and cottages that are scattered along the shores of a few lakes rely upon alternative sources for energy and heating. Reference sites were located to the west of the 1998 Tibbitt Lake fire, however there was evidence of past fire at all sites.

3.4 Field methods

3.4.1 Sample collection

Sample collection was undertaken during July and August 2006. Tree cores were collected from 30-40 dominant living trees at each site. Upland sites were dominated by white spruce or jack pine, while lowland sites were dominated by black spruce. Tree cores were retrieved using a 14-inch Hagloff increment tree borer with an internal diameter of 4.3 mm.

The cores were placed in plastic straws, sealed and taken to the Carleton University Paleoecology Laboratory for analysis. Two to six tree cores were collected from each tree on opposite sides of the stem. Half of these samples were taken from the stem in the direction facing Giant Mine's roaster stack in order to account for uptake of contaminants via tree bark. In most cases, tree cores were collected at breast height (approximately 1.3 m), however for trees with stunted growth, cores were taken above the root collar. Evidence of wildfire and logging was present at most sites, thus a few dead trees were also sampled.

Surface soil samples were collected at each site, with the exception of Prelude Lake (SITE 20). These samples were retrieved from the rooting zone (0-30 cm depth) of three separate trees using a stainless steel trowel, placed in Nasco Whirl-Pak© bags and stored at 4°C at the Taiga Environmental Laboratory in Yellowknife, NWT.

3.4.2 Inventory of groundcover abundance

An inventory of groundcover plants was also conducted in July and August 2006 in order to characterize the vegetation assemblage at each site. Vascular and non-vascular plants were identified within a 1 m^2 quadrat with replicates of 5 per site. The location of each quadrat was randomly determined. Common and scientific names for each species follow the sources used in the handbook Plants of the Western Boreal Forest and Aspen Parkland (Johnson et al., 1995). Plant species were subdivided into 8 groups: shrubs, herbs, grasses, sedges, rushes, lichen, liverwort, and moss. Percent cover for each of these groups, as well as debris and bare rock, were estimated using a modification of the Braun-Blanquet coverage abundance scale (Mueller-Dombois and Ellenberg, 1974) (Table 3.2). This data was used to identify unique groundcover species and characterize groundcover vegetation communities. Each quadrat was documented by digital photography using a Canon digital Rebel XT, model EOS 350D.

3.5 Laboratory Methods

3.5.1 Tree-ring sample preparation and chronology development

Increment tree cores were air dried, glued to wooden core mounts, and sanded with progressively finer grit sandpaper to enhance ring boundaries (Stokes and Smiley, 1968; Fritts, 1976). Tree cores were crossdated using the method described by

Table 3.2: Modified Braun-Blanquet coverage abundance scale (Mueller-Dombois and Ellenberg, 1974).

Scale	**Cover of reference area (1 m^2)**
> 75%	More than ¾
50% - 75%	Between ½ and ¾
25% - 50%	Between ¼ and ½
5% - 25%	Between 1/20 and ¼
5%	Less than 1/20 cover or scattered with cover up to 1/20
2%	Few with small cover
1%	Solitary, with small cover

Yamaguchi (1991). Crossdating refers to the procedure of matching patterns of wide and narrow rings among trees of various ages in order to determine the specific year in which a ring was produced. Ring widths were measured to the nearest 0.001 mm using a Nikon binocular microscope and Velmex Unslide traversing table interfaced with an AccuRite digital counter at the Carleton University Paleoecology Laboratory. For quality control, crossdating was verified using the program COFECHA (version 6.02P for MacIntosh OSX, developed by Edward Cook at the Lamont-Doherty Earth Observatory, Columbia University, New York, 2004). Crossdating and measurement discrepancies were identified and corrected where possible. Tree cores that could not be adequately crossdated were omitted from analysis (85/577 = 15%).

Site chronologies were developed using standard dendrochronology methods (Cook, 1985) and the program ARSTAN (version .40c for MacIntosh OSX, developed by Edward Cook and Paul Krusic at the Lamont-Doherty Earth Observatory, Columbia University, New York, 2006). Tree-ring chronologies developed for spruce-dominant sites were not included in this study due to the lack of adequately similar reference sites and poor correlations between site chronologies.

Numerous statistical measures exist for evaluating the characteristics of a tree-ring chronology (Cook and Kariukstis, 1990; Fritts, 1976). Average Mean Sensitivity (AMS), mean series inter-correlation (r), first-order autocorrelation, sample depth, and Expressed Population Signal (EPS) were generated in order to assess whether the site chronologies were of suitable quality to merit further investigation. As AMS approaches a value of 2, tree growth is considered less complacent and more responsive to changing climate or environmental conditions from one year to the next (Fritts, 1976). Mean series inter-correlation is a measure of the strength of the relation between individual series of tree-ring widths from each core and the master series containing all individual series that will be used to create the site chronology. High first order autocorrelation values indicate a persistence or trend in the series caused by the influence of factors from the previous year, while low values suggest that environmental conditions within the growth year are the dominating influence.

Chronology quality is a function of sample depth and the strength of the common ring width signal within a chronology. Sample depth refers to the number of series or replicate samples available to calculate ring-width indices for the chronology. Replication ensures that variability observed within and between trees can be traced to common factors such as climate, site characteristics or pollution (Fritts, 1976). Thus, the ability of a chronology to accurately capture patterns of ring-width variability deteriorates as sample depth decreases. This typically occurs towards the early part of a chronology due to the ratio of old to young trees in forest stands.

EPS indicates the degree to which a site chronology portrays a hypothetical 'perfect' chronology, in terms of sample depth, back through time (Briffa, 1995). Thus, EPS values provide a quantitative estimate of the strength of the common signal within a site chronology. A minimum EPS value of 0.85 is used in this study as a conservative threshold in order to define the usable portions of the site chronologies.

3.5.2 Tree-ring chemical analysis

A subset of jack pine sites was analyzed to assess concentrations of total As, S, P, and several other elements stored in tree-rings. Four sites were chosen, two sites with very high soil-As contamination (SITES 5 and 10) and two reference sites (SITES 22 and 23). In addition to the preparation and analysis described above, the sapwood-heartwood transition of these cores was visually determined by colour. Cores were segmented into five-year increments from 1926 to 2005 using a sterile rib-back carbon steel surgical scalpel. The blade was rinsed with distilled water between cuts. Increment samples were stored separately in sealed #1 envelopes prior to analysis.

Each sample was weighed to 0.1 mg using a scientific balance then digested at 100 °C with 1.0 mL nitric acid (HNO_3) for 12-24 hours in a 50 mL Fisherbrand disposable centrifuge tube made of polypropylene (Cat. No. 06-443-18). A watch glass served as lid for the tube during digestion. Following digestion, the solution was diluted to 5.01 mL with distilled water and transferred to a 15 mL test tube. From this solution, 2 mL was transferred to a separate 15 mL test tube and further diluted with 2 mL distilled water, resulting in a total dilution of 10 mL for analysis of total As by Inductively Couple Plasma - Mass Spectrometer (ICP-MS, HP 4500, Series 100). Analysis by Inductively Coupled Plasma-Emission Spectrometer (ICP-ES, Varian, Vista-Pro) for all other elements was conducted using the remaining 3 mL of the initial digested solution. Several blanks were included in each batch of analyses. Both ICPs were calibrated by running standard solutions between every 10 samples. The detection limits for each element are listed in Table 3.3. A Wheaton pipetor (Cat. No. 851355) with 2.0 mL disposable macrotip was used for all solution transfers. Sample digestion and dilution was performed by the student at the University of Ottawa spectrometer

Table 3.3: Limit of detection for ICP-MS and ICP-ES analyses (DeSilva, 2007a; DeSilva, 2007b).

Element	**Detection method**	**Limit of detection (LOD)**
Aluminum (Al)	ICP-ES	0.005 ppm
Arsenic (As)	ICP-MS	0.04 ppb
Calcium (Ca)	ICP-ES	0.005 ppm
Magnesium (Mg)	ICP-ES	0.0005 ppm
Manganese (Mn)	ICP-ES	0.0005 ppm
Phosphorus (P)	ICP-ES	0.02 ppm
Sulphur (S)	ICP-ES	0.04 ppm

laboratory. Staff at the laboratory performed chemical analyses by ICP-ES and ICP-MS.

Concentrations of elements in wood samples (ppm) were calculated as follows: [concentration in solution (ppb) multiplied by final volume of diluted sample (mL)] divided by sample mass (mg).

3.5.3 Chemical analysis of surface soil

Surface soil samples were analyzed for total As, total S, pH, Mg and Ca at the Taiga Environmental Laboratories in Yellowknife, NWT. Total As, Mg and Ca were detected using method EPA 3050B. Total percent S was detected by LECO SC-132 Total Sulfur Analyzer. Samples were prepared by water extraction for pH analysis and detected using the McKeaque 4.1 method. The calculated method detection limits (MDL) provided by the Taiga laboratory were 0.2 μg/g for As, 200 μg/g for Ca, 100 μg/g for Mg and 0.01% for S.

3.5.4 Calculation of species richness

Species richness at each site was calculated from quadrat samples using the Jackknife estimate. This estimate is based on the observed frequency of unique species, defined as a species that occurs in only one quadrat (Krebs, 1999). The species present (1) or absent (0) in each of the random quadrats were tabulated and the sum of these numbers recorded for each species. Unique species were those with a sum of 1. With this data it was possible to calculate the Jackknife estimate of species richness (J), given as equation 3.1, where s is number of species, n, number of quadrats and k, number of unique species. The variance and 95% confidence intervals of this estimate were calculated using equation 3.2 and 3.3, respectively. The variable t_α refers to the Student's t value for n-1 degrees of freedom for 95% level of confidence, α.

$$J = s + (n - 1) / n * k \tag{3.1}$$

$$\mathrm{var}\ (J) = (n - 1/n) * [\ \sum (j^2 f_j) - k^2/n\ ] \tag{3.2}$$

$$J \pm t_\alpha * \sqrt{\mathrm{var}\ (J)} \tag{3.3}$$

CHAPTER FOUR

RESULTS

4.1 Introduction

This chapter presents results obtained from chemical analysis of surface soil and tree-ring samples, inventory of groundcover species abundance, and examination of relations between tree-growth, climate and pollution at jack pine stands located downwind (contaminated) and upwind (reference) of the Giant Mine roaster stack. The chapter is divided into four sections. The first section describes soil chemistry at contaminated and reference sites and the influence of distance on soil As and S concentrations. The second section compares groundcover vegetation composition and species richness at contaminated and reference sites, and examines relations of species richness with soil As and distance from the Giant Mine roaster stack. The following section assesses tree-ring chemistry profiles from 1926-30 to 2001-05 at contaminated and reference sites and relations between soil As and tree-ring As. The chapter concludes with an examination of tree-growth response to climate and the connection of this response with emissions of As and SO_2 in the Yellowknife area during the 20th century.

4.2 Total As, S, Ca, Mg and pH of surface soil

The mean total As, Ca, Mg concentrations, total percent S and pH levels in soil samples collected from 11 jack pine sites in the Yellowknife area are listed in Table 4.1. A soil sample was not retrieved from SITE 21. Although highly variable, on average total As, Ca and Mg concentrations, percent S and pH at contaminated sites are higher than at reference sites.

Table 4.1: Mean and standard deviation for element concentrations (As, Ca, Mg), total percent S and pH of surface soil samples (n = 3 per site) from contaminated (n = 21) and reference (n = 12) jack pine sites. Italicized values indicate that the standard deviation (SD) is equal or greater than the mean.

Site #	**Distance & direction from RS (km)**	**As (µg/g)**	**S.D.**	**Ca (µg/g)**	**S.D.**	**Mg (µg/g)**	**S.D.**	**S (%)**	**S.D.**	**pH**	**S.D.**
Contaminated sites											
5	2N	776.00	610.85	5266.67	3523.26	8333.33	5272.89	0.07	*0.07*	5.53	0.40
1	8N	504.00	439.08	3266.67	986.58	8466.67	3709.90	0.02	0.01	5.57	1.10
13	3SW	1165.67	377.76	4000.00	953.94	3633.33	1789.79	0.04	0.02	5.00	0.70
14	9SW	250.67	143.16	1466.67	230.94	5366.67	2417.30	0.03	0.02	6.87	3.24
10	2S	2055.00	1655.09	5000.00	3465.54	15800.00	11992.91	0.06	0.02	5.27	0.46
16	4SE	612.33	377.02	600.00	435.89	3933.33	2753.79	0.05	0.03	4.63	0.25
9	1E	644.67	359.92	5200.00	1907.88	3900.00	2816.03	0.06	*0.08*	5.30	0.78
Mean		**858.33**	**566.13**	**3542.86**	**1643.43**	**7061.90**	**4393.23**	**0.05**	**0.04**	**5.45**	**0.99**
Reference sites											
22	24E	13.03	7.74	600.00	200.00	5233.33	2916.05	0.01	0.00	5.50	0.53
20	22E	16.80	6.42	800.00	173.21	8233.33	5000.33	0.02	0.01	5.23	0.21
23	40E	16.03	4.45	1433.33	907.38	6700.00	3675.60	0.04	0.04	4.67	0.64
18	15E	65.30	*79.02*	825.00	*1059.48*	1325.00	650.00	0.02	0.03	4.83	0.64
Mean		**27.79**	**24.41**	**914.58**	**585.02**	**5372.92**	**3060.49**	**0.02**	**0.02**	**5.06**	**0.51**

Box and whisker plots of mean element concentrations in soil and soil pH indicate that contaminated sites have more variability, with the exception of Mg (Fig. 4.1a-e). Histograms illustrate that all soil data are positively skewed, thus a non-parametric statistical test was utilized to evaluate differences between contaminated and reference site soil chemistry. Mann-Whitney U tests reveal that mean soil pH ($p = 0.315$) and mean Mg concentrations ($p = 0.648$) are not significantly different at the contaminated and reference sites. In contrast, for soils at contaminated sites mean total percent S ($p = 0.042$), mean Ca ($p = 0.042$) and mean total As ($p = 0.006$) concentrations are significantly higher than background levels at reference sites.

Figure 4.2 illustrates the distribution of mean total As concentrations in surface soil samples of jack pine sites located to the northeast, northwest, southeast and southwest of the roaster stack. The highest concentrations occur near the roaster stack and decrease with distance away from the stack.

Figure 4.3a and b are scatterplots of mean total As concentrations and mean total percent S for all sampled sites against distance from the stack. The roaster stack is located at the 0 point of the x-axis. Trendlines fit to the data indicate a strong negative power relation ($R^2 = 0.811$) between mean total As concentrations in surface soil and distance from the mine and a weaker negative power relation ($R^2 = 0.518$) for mean total percent S and distance from the mine. Decreases are observed for mean total As concentrations and mean total percent S in soil samples from sites located at increasing distance from the roaster stack towards the north, south and east. However, mean total percent S increases for soil samples located at sites between 24 and 40 km east.

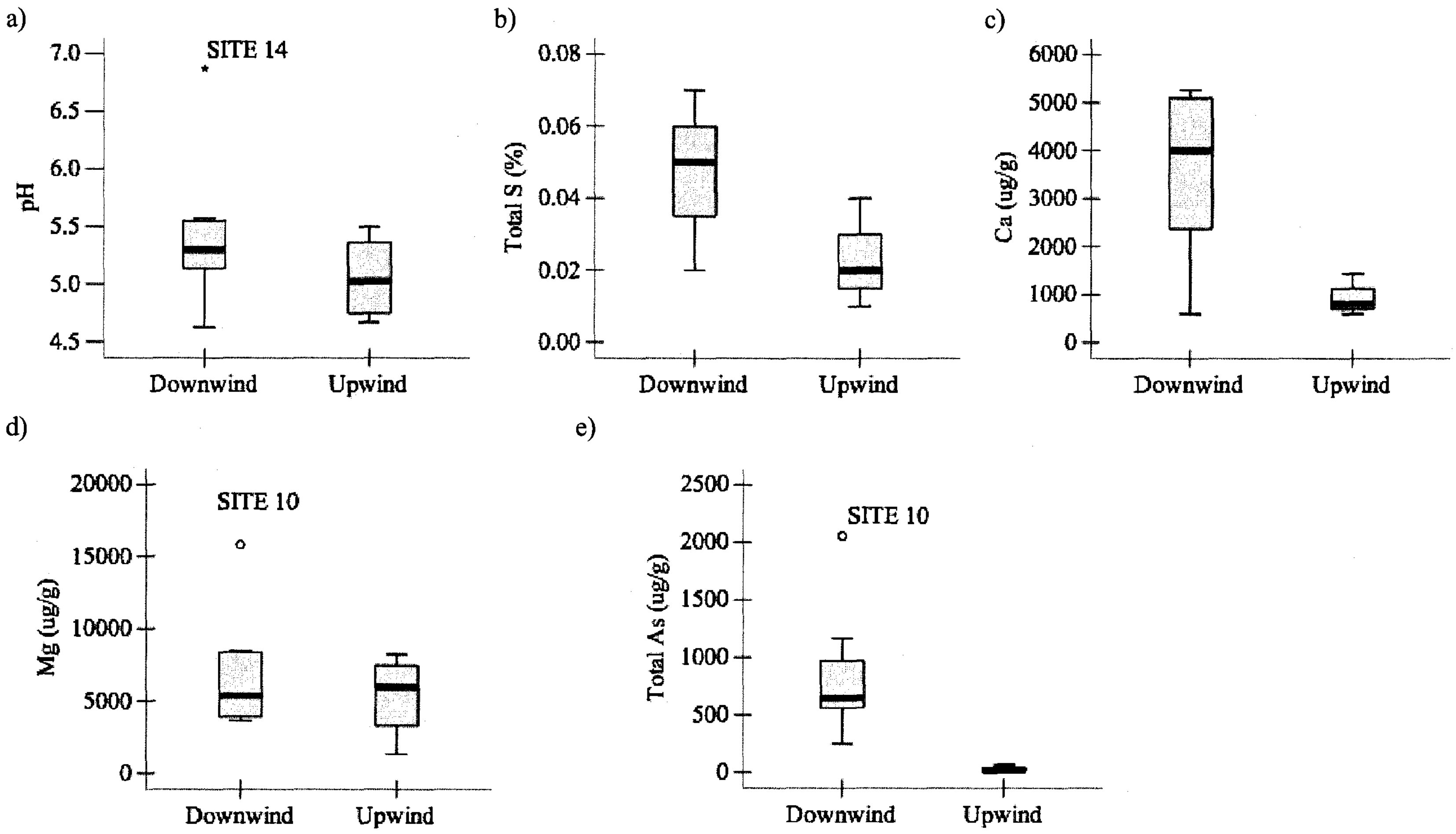


Figure 4.1: Box and whisker plots of median, maximum and minimum concentrations for various elements in surface soil samples at downwind (contaminated) and upwind (reference) sites, *n* equals 7 and 4 respectively; a) pH; b) total percent sulphur; c) calcium; d) magnesium; and e) total arsenic. Outliers are shown at SITE 10 for Mg and total As and at SITE 14 for pH.

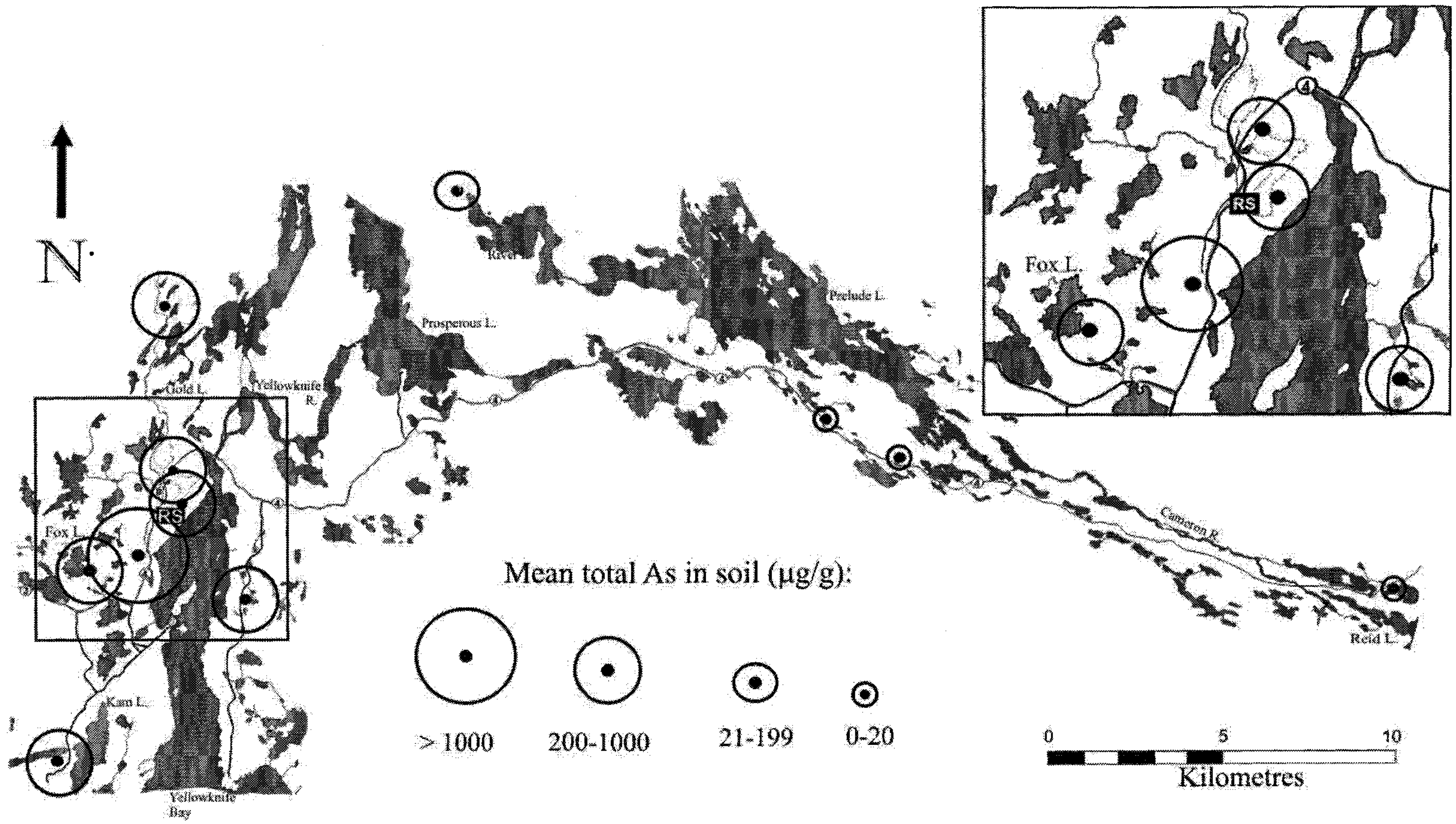


Figure 4.2: Mean total arsenic concentrations in surface soil samples collected from 12 jack pine sites. RS refers to the roaster stack.

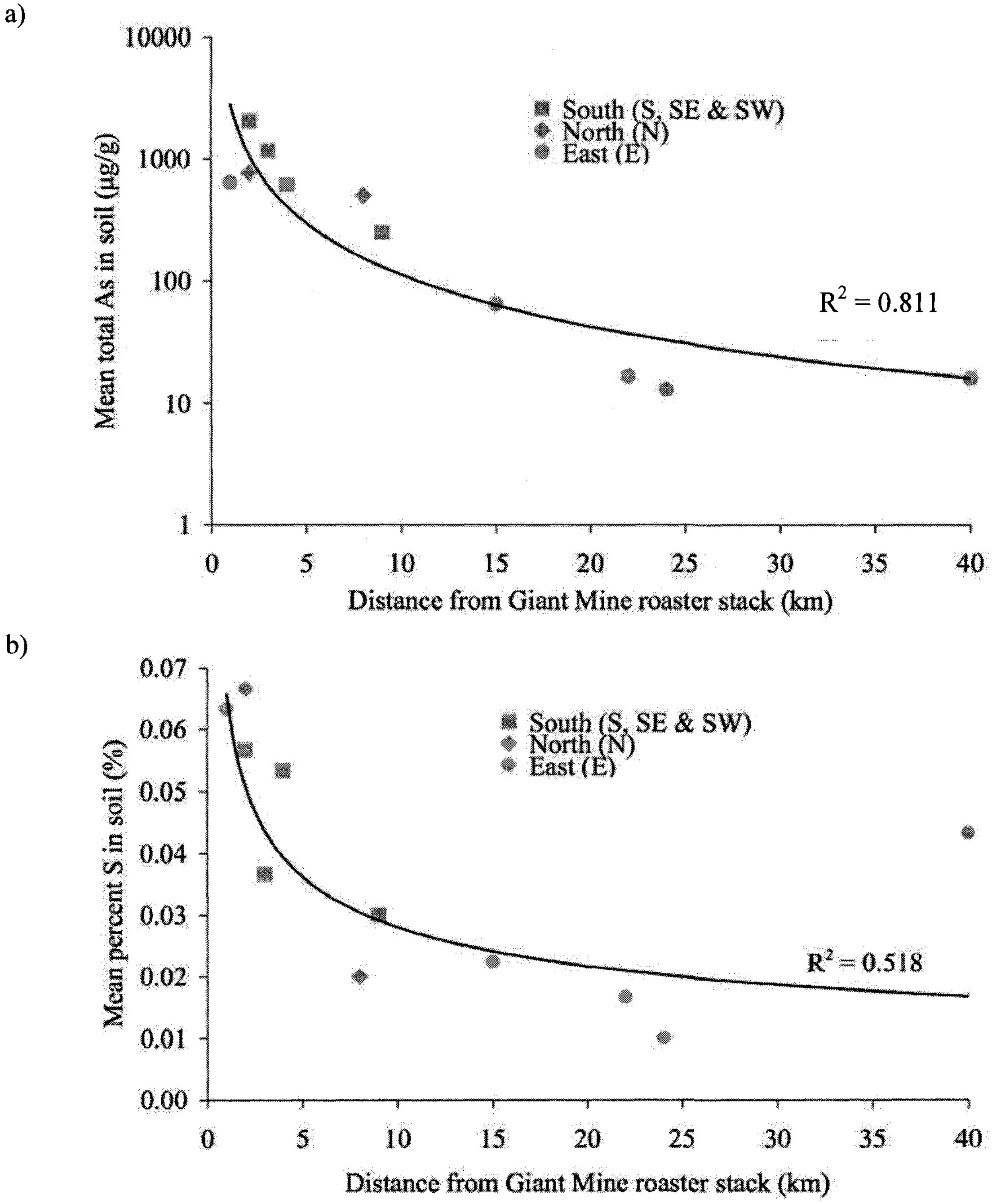


Figure 4.3: (a) Mean total As ($n = 33$) and (b) mean total percent S ($n = 33$) in study area surface soil samples by distance from the Giant Mine roaster stack for all jack pine sites (3 samples per site). The 0 point along the x-axis represents the roaster stack. R^2 refers to the squared correlation coefficien for a power regression.

Table 4.2 lists mean surface soil concentrations of each element and pH by distance from the Giant Mine roaster stack for three distance categories, < 3 km, 3 - 5 km and > 5 km. Distance categories were determined based on prior SO_2 distribution studies that showed highest deposition occurred within 3 km of Giant Mine, moderate deposition between 3 and 5 km, and low deposition beyond 5 km (GNT, 1993). All elements vary with distance from the roaster stack. A one-way ANOVA of the log-transformed soil data reveals significant differences between all distance categories for means of total As, total S, and Ca, though not for pH and Mg. Mean total As and Ca concentrations and mean percent S for the distance categories decrease with distance from the stack. Mean Mg concentrations and pH values are statistically higher at > 5 km than at 3 - 5 km. Concentrations of total As and Ca are respectively 8 and 4 times greater in the soils nearest Giant Mine (< 3 km) than in the more distant soils (> 5 km).

4.3 Groundcover inventory and species richness

The ground vegetative composition and structure is variable among contaminated and reference study sites. Short shrubs, herbs, grasses, sedges, lichen, liverwort, moss and non- vegetative cover are summarized in Table 4.3. Photographs of a subset of the study sites are given in Figure 4.4.

Short shrubs are the dominant groundcover at contaminated sites while lichen dominates reference sites. Common bearberry (*Arctostaphylos uva-ursi*) is prevalent at reference sites while ground juniper (*Juniperus communis*) is the most common shrub at contaminated sites. Herbs and grass coverage varies among all sites. With the exception of SITE 18, all reference sites have patches of saxifrage (*Saxifraga tricuspidata*) and

Table 4.2: Mean total As, Ca and Mg concentrations (μg/g), mean total percent S and mean pH in surface soil samples by distance from the Giant Mine roaster stack. High SD for Ca 3 - 5 km may be due to low sample size (n = 3 samples per site).

Element	**Distance Category**						*p* **value***
	< 3 km	S.D.	3 - 5 km	S.D.	> 5 km	S.D.	
As	1158.56	779.12	889.00	391.27	144.31	198.43	<0.05
pH	5.37	0.15	4.82	0.26	5.44	0.78	0.734
S	0.06	0.01	0.05	0.01	0.02	0.01	<0.05
Ca	5155.56	138.78	2300.00	*2404.16*	1398.61	981.90	<0.05
Mg	9344.44	6014.09	3783.33	212.13	5887.50	2620.34	0.874
n	9		6		18		

Table 4.3: Coverage abundance values of groundcover species at the jack pine study sites. Sites are arranged by increasing distance from the mine in ascending order from left to right. The coverage abundance scale is described in Table 3.3. The symbol (/) signifies that the species is included within the coverage abundance value for the group.

Scientific Name	Common Name	Coverage										
		Contaminated sites							Reference sites			
		9	5	10	16	13	1	14	18	22	20	23
Short shrubs (total)		**75**	**57**	**80**	**30**	**31**	**64**	**25**	**40**	**30**	**28**	**23**
Rubus pubescens	trailing raspberry						10				6	
Rosa acicularis	prickly rose	30		15			6	5				
Juniperus communis	ground juniper	20	28	65	20		20					
Juniperus horizontalis	creeping juniper	10					18					15
Potentilla fruticosa	shrubby cinquefoil	15										
Potentilla tridentata	three-toothed cinquefoil										2	
Picea spp.	spruce sapling		10									5
Arctostaphylos uva-ursi	common bearberry		15		10	25	10	20	40	30	20	3
Ribes oxyacanthoides	northern gooseberry		4									
Vaccinium myrtilloides	common blueberry					6						
Herbs (total)		**10**	**10**	**10**	**25**	**0**	**24**	**0**	**5**	**12**	**13**	**15**
Saxifraga tricuspidata	saxifrage	10	4	10						3	3	2
Woodsia ilvensis	rusty woodsia				20		6			9	2	8
Fragaria virginiana	wild strawberry		1									
Unidentified flower	flower (unidentified)		5						5			
Geocaulon lividum	northern bastard toadflax				5							
Corydalis sempervirens	pink corydalis										8	
Polypodium virginianum	rock polypody											5
Dryas drummundii	yellow mountain aven						15					
Aster spp.							3					

Table 4.3 (continued): Coverage abundance values of groundcover species at the jack pine study sites. Sites are arranged by increasing distance from the mine in ascending order from left to right. The coverage abundance scale is described in Table 3.3. The symbol (/) signifies that the species is included within the coverage abundance value for the group.

Scientific Name	Common Name	Coverage										
		Contaminated sites							Reference sites			
		9	5	10	16	13	1	14	18	22	20	23
Grasses (total)		**8**	**5**	**3**	**8**	**2**	**10**	**7**	**6**	**15**	**4**	**4**
Agropyron trachycaulum	slender wheatgrass	5										
Hordeum jubatum	foxtail barley	5										
Sedges (total)									**5**			**10**
Lichen (total)		**21**	**47**	**33**	**55**	**45**	**54**	**57**	**67**	**48**	**58**	**64**
Umbilicaria hyperborea	black rocktripe	/	/	/	/	/	/	/	/	/	/	/
Hypogymnia physodes	monk's hood lichen									/		
Arctoparmelia centrifuga	rippled rock frog				/		/	/	/	/	/	/
Cladonia chlorophaea	false pixie cup lichen	/	/	/	/	/	/	/	/	/	/	/
Cladina stellaris	northern reindeer lichen								/			/
Cladonia uncialis	prickle cladonia	/	/			/					/	
Rhizocarpon geographicum	green map lichen				/	/	/	/	/	/	/	/
Crust lichen	crust lichen				/		/	/	/	/	/	/
Flavocetraria nivalis	flattened snow lichen		/		/	/	/	/	/	/	/	/
Cladonia pyxidata	brown pixie cup lichen							/				/
Cladonia cornuta	horn cladonia				/			/	/	/	/	/
Cladina mitis	green reindeer lichen		/		/	/		/	/	/	/	/
Stereocaulon tomentosum	woolly coral lichen				/			/	/	/	/	/
Cladonia cariosa	ribbed cladonia			/	/		/	/	/	/	/	
Cladonia borealis	red cladonia					/		/			/	
Cladonia botrytes	stump cladonia									/	/	/
Cladonia coniocraea	tiny toothpick cladonia				/							

Table 4.3 (continued): Coverage abundance values of groundcover species at the jack pine study sites. Sites are arranged by increasing distance from the mine in ascending order from left to right. The coverage abundance scale is described in Table 3.3. The symbol (/) signifies that the species is included within the coverage abundance value for the group.

Scientific Name	**Common Name**	**Coverage**										
		Contaminated sites							**Reference sites**			
		9	**5**	**10**	**16**	**13**	**1**	**14**	**18**	**22**	**20**	**23**
Cladonia crispata	shrub funnel cladonia				/	/	/			/	/	
Cladonia scabriuscula	shingled cladonia						/			/	/	
Parmeliopsis hyperopta	grey starburst lichen							/				
Parmelia sulcata	waxpaper lichen										/	
Cladonia cenotea	powdered funnel cladonia						/				/	
Cladonia gracilis ssp.	brown-foot cladonia								/	/	/	
Xanthoria fallax	powdered orange lichen									/		
Cladina rangiferina	grey reindeer lichen									/		/
Cladonia multiformis	sieve cladonia									/		
Peltigera neopolydactyla	frog pelt									/	/	/
Hypocenomyce scalaris	common shingle						/			/		/
Liverwort									5	8		5
Moss (totals)				**10**	**12**	**20**	**6**	**21**	**10**	**15**	**17**	**10**
Ceratodon purpureus	purple horn-toothed moss			5	/	10		1				
Pohlia nutans	copper wire moss				/				/	/	/	/
Polytrichum piliferum	awned hair-cap moss	18	5	5	/	5	12	1			10	
Ditrichum flexicaule	slender-stemmed hair moss				/	/		/				
Polytrichum juniperinum	juniper hair-cap moss									/		15
Tortula ruralis	hairy screw moss									/	/	/
Mushroom												**1**
Bare Rock		41	17	39	22	35	9	14	11	12	7	11
Debris		10	13			25	10	20	1	11	9	11

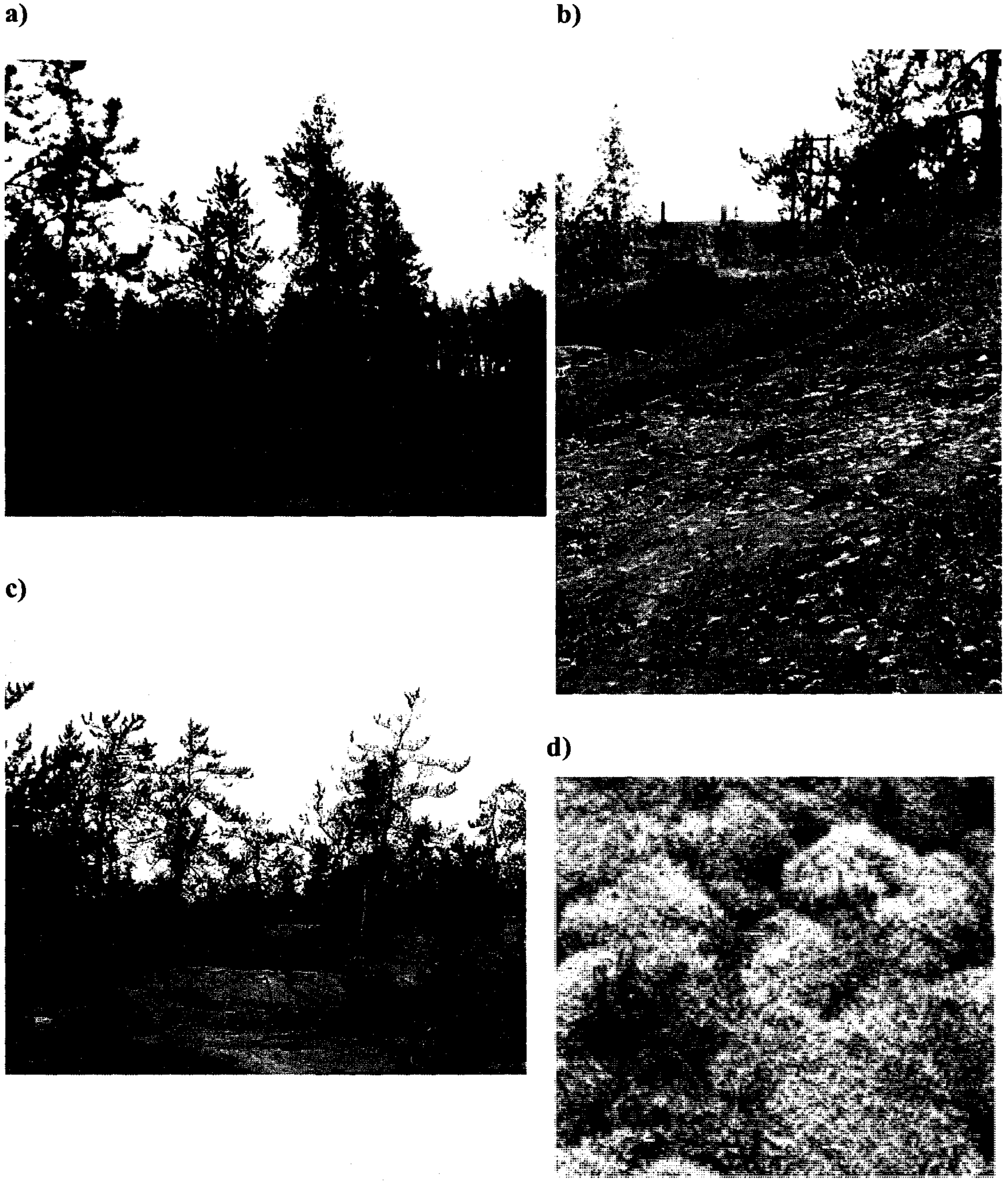


Figure 4.4: Photos of study sites; a) SITE 22, 24 km east of Giant Mine, jack pine and cushions of lichen, b) SITE 5, 2 km north of Giant Mine, ground juniper, crust lichen and bare rock, c) SITE 9, 1 km east of Giant Mine, jack pine, ground juniper and bare rock, d) SITE 23, 40 km east of Giant Mine, rusty woodsia and grey reindeer lichen (Photos by Sonia M. St-Onge).

rusty woodsia (*Woodsia ilvensis*). Sedges are only found at the reference SITES 18 and 23. Lichen coverage is consistently higher at reference sites. Moreover, several lichen species are only found at reference sites, such as four species of cladonia lichen (*Cladonia brotrytes, Cladonia gracilis spp., Cladonia sulphurina, Cladonia multiformis*), monk's hood lichen (*Hypogymnia physodes*), northern reindeer lichen (*Cladina stellaris*), grey reindeer lichen (*Cladina rangiferina*), waxpaper lichen (*Parmelia sulcata*), powdered orange lichen (*Xanthoria fallax*) and frog pelt (*Peltigera neopolydactyla*). Coverage is low for liverworts at reference sites. Moss coverage is generally discontinuous at all study sites and absent at SITES 5 and 9. Although bare rock and debris vary among sites, their spatial extent is greater at contaminated sites.

Regression analysis was performed in order to assess the relation between soil-As concentrations and groundcover species richness. Figure 4.5 shows that as soil-As concentration increases groundcover species richness decreases exponentially (R^2 = 0.655, $p \leq 0.01$). Figure 4.6 illustrates a strong positive relation (R^2 = 0.722) between groundcover species richness and distance from the Giant Mine roaster stack.

4.4 Concentrations of As and other elements in tree-rings

Table 4.4 lists mean total As, P, S, Ca and Mg tree-ring concentrations (average of all 16 5-year segments) and expresses the variability of concentrations within each core. For most elements, the standard deviation is high and in some cases exceeds the mean. This high variability may be attributed to the effects of site differences or individual tree conditions, thus in order to minimize these effects it is recommend to pool samples (Berger et al., 2006). Consequently, elemental concentrations of the 6 cores

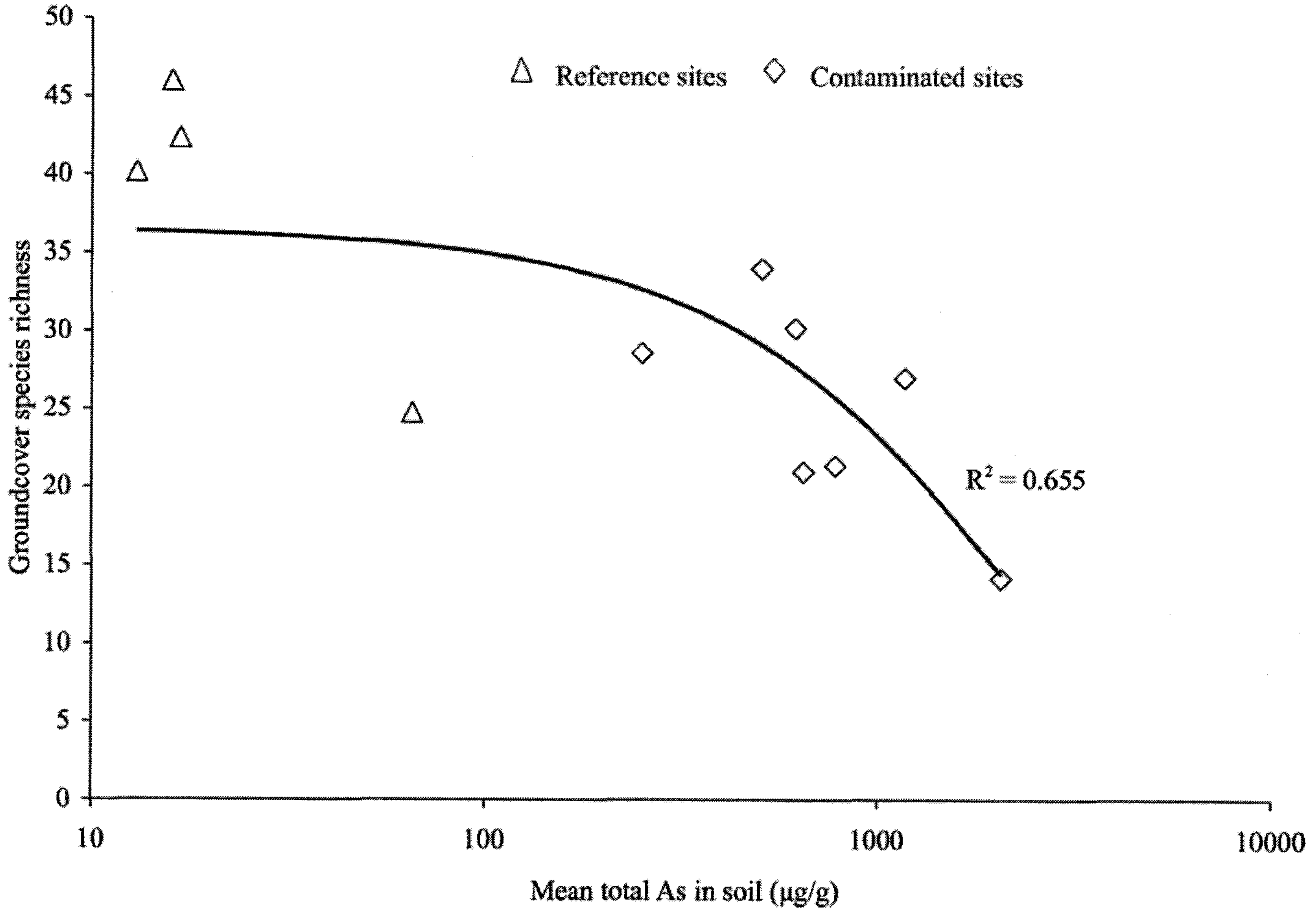


Figure 4.5: Relation between mean total As concentrations (µg/g) in soil samples ($n = 11$) and groundcover species richness showing R^2 and lines of best fit (exponential) for all jack pine sites.

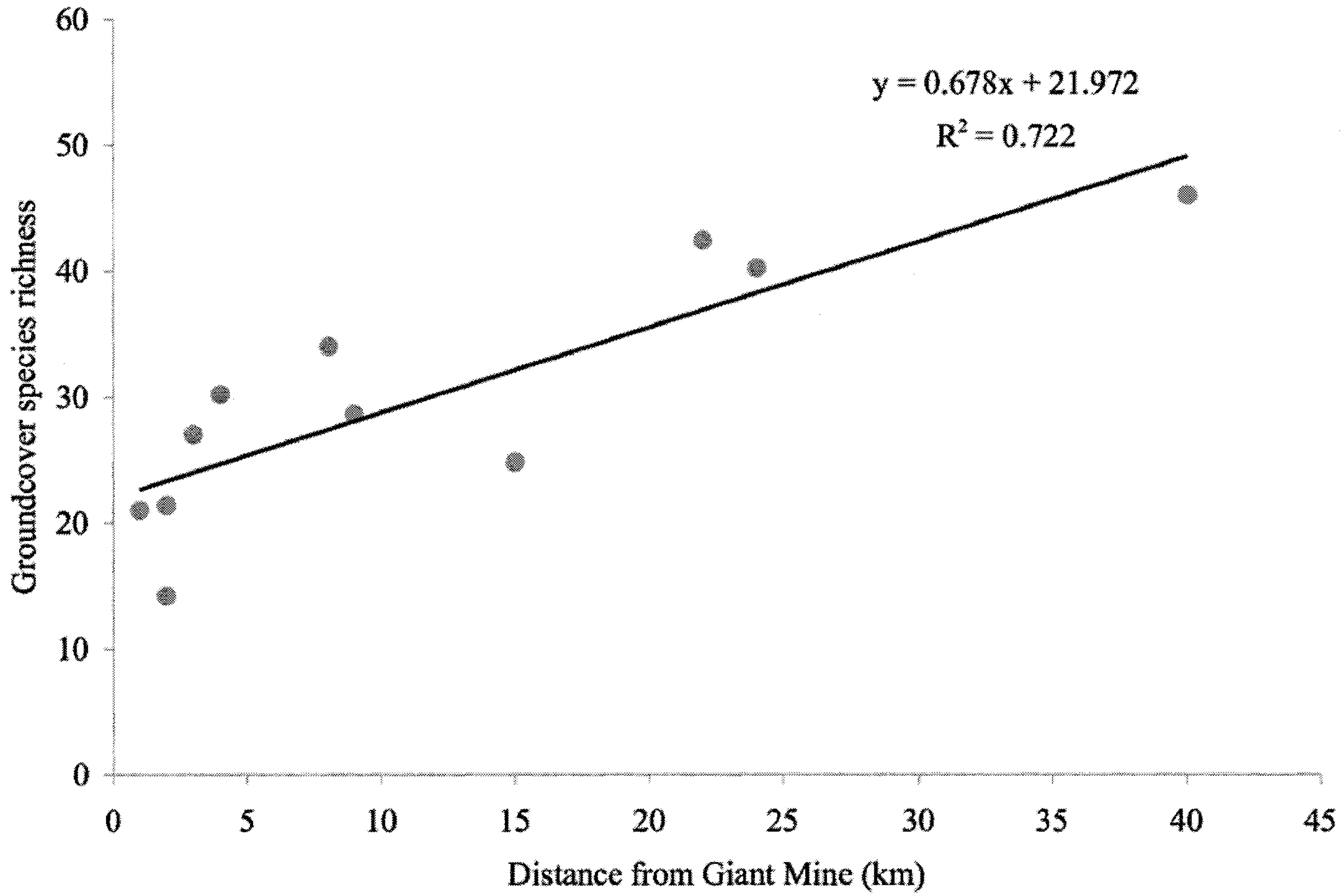


Figure 4.6: Relation between distance from Giant Mine roaster stack (km) and groundcover species richness for all jack pine sites (*n* = 11) in the study area, showing R^2 and line of best fit (linear).

Table 4.4: Mean concentrations (µg/g) of As, P, S, Ca and Mg in tree core samples (a, b,c) for contaminated and reference sites for the period 1926 to 2005 (*n* = 16 for most cores). Outliers of As were removed for 1926-30 and 1936-40 from SITE 22a (*n* = 14) due to measurement error. SITE 10 is located on the Giant Mine property 2 km south of the roaster stack; SITE 5 is located on the Giant Mine property 2 km north of the roaster stack; SITE 23 is located beyond the Giant Mine property, 40 km east of the roaster stack; and SITE 22 is located beyond the Giant Mine property, 24 km east of the roaster stack. Italicized values indicate that the standard deviation (SD) is greater than the mean. SD of S for SITE 5c is higher than mean because of a very high value for the period 1966-70.

Core #	Mean Tree As	SD	Mean Tree P	SD	Mean Tree S	SD	Mean Tree Ca	SD	Mean Tree Mg	SD
Contaminated										
SITE10a	0.194	0.079	165.6	88.6	73.9	24.5	2968.3	2707.5	182.4	64.1
SITE10b	0.429	0.157	377.3	185.8	121.9	74.4	6399.4	4493.8	252.9	78.0
SITE10c	0.107	0.057	202.1	113.0	77.3	24.0	2317.7	*2336.9*	200.9	58.4
SITE5a	0.196	0.184	154.8	77.2	73.3	21.3	1799.0	*2140.5*	106.9	60.6
SITE5b	0.278	0.126	361.2	253.9	90.3	33.1	1759.2	1385.8	135.3	55.4
SITE5c	0.316	0.197	173.7	77.6	190.3	*224.7*	2668.2	*2842.2*	160.3	48.5
Mean	**0.253**	**0.133**	**239.1**	**132.7**	**104.5**	**67.0**	**2985.3**	**2651.1**	**173.1**	**60.8**
Control										
SITE23a	0.112	0.052	101.7	36.4	72.3	12.9	3569.5	3447.6	206.1	81.9
SITE23b	0.250	0.166	280.5	187.3	88.0	40.6	3244.5	*3367.7*	204.7	79.7
SITE23c	0.051	0.038	148.1	42.5	115.6	24.2	4064.0	*4865.4*	237.6	110.6
SITE22a	0.090	0.056	270.2	44.7	80.8	12.4	2763.3	*3110.2*	189.6	60.2
SITE22b	0.097	0.046	277.2	84.6	89.1	75.6	3447.4	2888.6	222.2	70.7
SITE22c	0.271	0.201	230.7	98.1	256.9	76.6	3049.3	*3976.1*	223.3	82.1
Mean	**0.145**	**0.093**	**218.0**	**82.3**	**117.1**	**40.4**	**3356.3**	**3609.3**	**213.9**	**80.9**

corresponding to contaminated and reference sites were pooled for each 5-year tree-ring segment from 1926-30 to 2001-05. The mean total As, S, P, Ca, Mg, Mn and Al concentrations and As/P ratio in tree-rings at contaminated and reference sites are plotted in Figure 4.7. Concentrations are plotted at the mid-point of each 5-year segment. Trends of declining mean Mn, Mg and Ca tree-ring concentrations and mean As/P ratio are evident for contaminated and reference site trees. Conversely, mean P and As concentrations in contaminated and reference site trees and mean S in contaminated site trees increase towards the outer rings of the stem. No discernable trend is evident for mean Al, however a peak in Al at 1966-70 is also observed in the P and S time series.

Wilcoxon-Signed Ranks Test comparing the distribution of mean elemental concentrations in the 5-year segments of contaminated and reference site tree-rings indicate that concentrations of As, Mg and S, and the As/P ratio are significantly different for contaminated and reference sites (Table 4.5). Figure 4.8 illustrates that As concentrations in the sapwood and heartwood tree-rings from contaminated sites are higher than those at reference sites. Sapwood tree-rings at contaminated and reference sites are also more enriched in As than those of heartwood tree-rings. Furthermore, Pearson correlation coefficients indicate strong positive correlations between log soil As and mean tree-ring As in sapwood ($r = 0.964, p = 0.036$) and As in bark ($r = 0.969, p = 0.031$), however a weaker correlation occurs with As in heartwood ($r = 0.796, p = 0.204$). Linear regression did not yield significant relations. Due to low sample sizes for this analysis, these results are considered tentative.

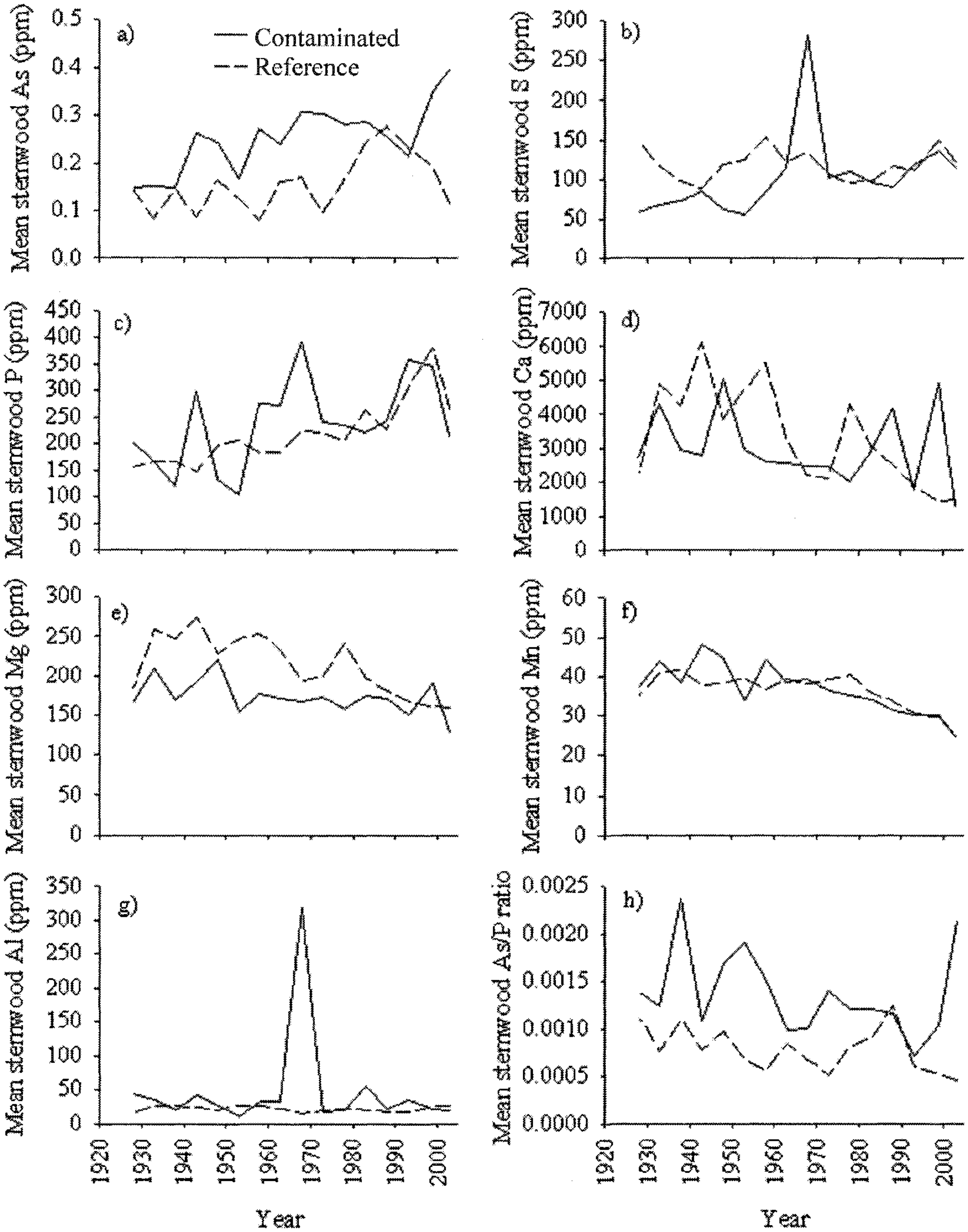


Figure 4.7: Mean As, S, P, Mg, Ca, Mn and Al concentrations and As/P ratio in tree-rings at contaminated and reference sites from 1926-30 to 2001-05 (*n=6* for each point, 3 cores x 2 sites). Concentrations are plotted at the mid-point of each 5-year segment.

Table 4.5: Summary of mean total As, P, Ca, Mg, Mn, Al and S concentrations (µg/g) and As/P ratio in tree-rings at contaminated and reference sites for the period 1926-2005. Mean contaminated concentrations are calculated using 3 cores from SITE 10 and 3 cores from SITE 5 (*n* = 6 cores x 16 segments = 96). Mean reference concentrations are calculated using 3 cores from SITE 23 and 3 cores from SITE 22 (*n* = 94). Outliers of As were removed for 1926-30 and 1936-40 from SITE22a because of measurement error.

Element	**Contaminated**	**S.D.**	**Reference**	**S.D.**	***p***
As	0.253	0.07	0.145	0.05	0.001
P	239.13	84.06	218.04	61.42	0.379
As/P	0.0013	0.0004	0.0008	0.0002	0.001
Ca	2985.30	1065.51	3356.34	1469.89	0.379
Mg	173.13	22.45	213.92	37.95	0.002
Mn	36.72	6.29	36.19	4.59	0.938
Al	46.68	73.38	21.57	4.19	0.062
S	102.91	53.22	118.73	19.74	0.044

*Wilcoxon-Signed Ranks Test, 2-tailed asymp. significance, 95% confidence level.

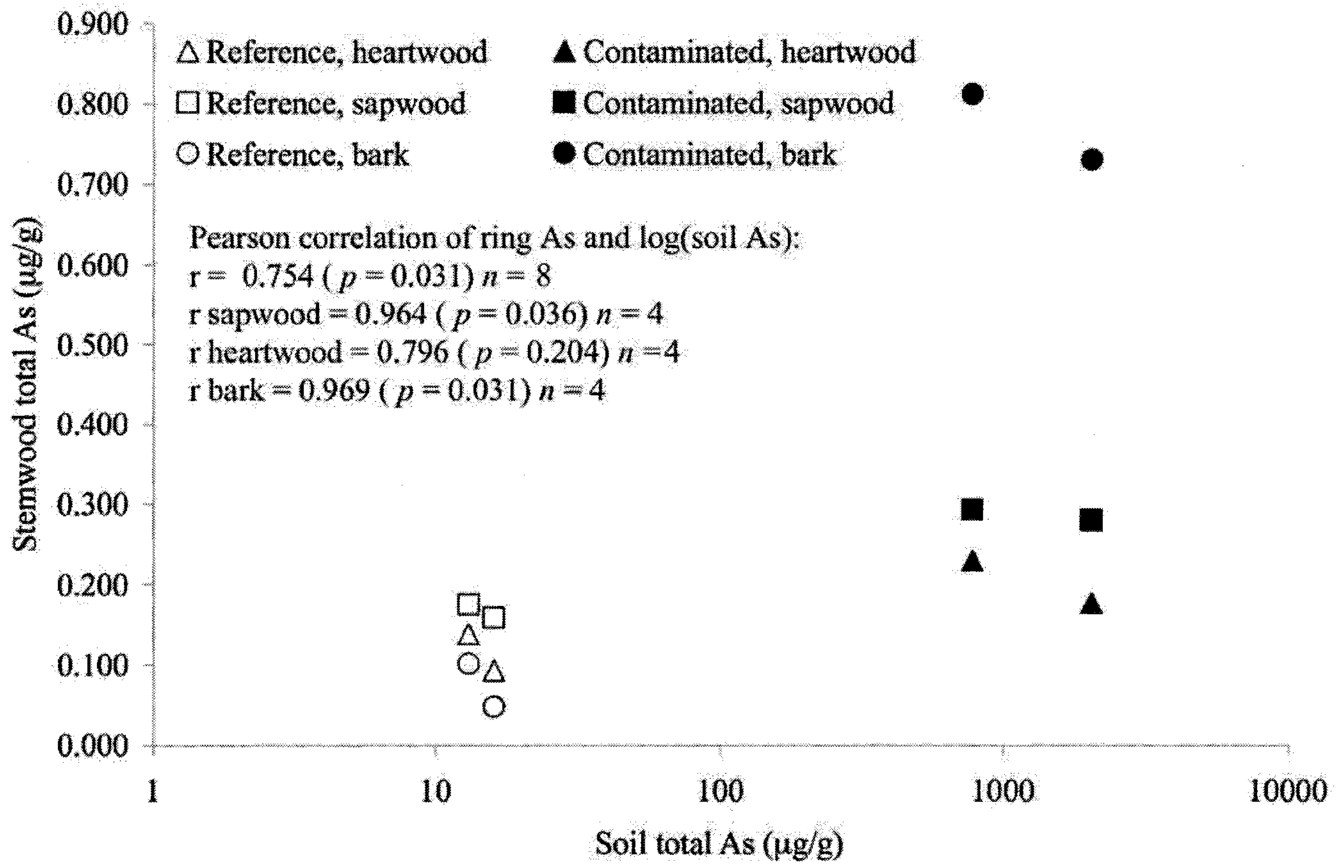


Figure 4.8: Soil-tree ring As concentration relationship. Sapwood and heartwood mean As concentrations represent average As concentrations of corresponding 5-year segments for SITE 10 (n = 31 sapwood; n = 17 heartwood), SITE 5 (n = 26 sapwood, n = 23 heartwood), SITE 23 (n = 29 sapwood; n = 19 heartwood), and SITE 22 (n = 24 sapwood; n = 22 heartwood). Mean soil total As concentrations represent average concentrations for SITE 10 (n = 3), SITE 5 (n = 3), SITE 23 (n = 3) and SITE 22 (n = 3).

4.5 Tree-growth during the 20th century

4.5.1 Assessing the common signal

The twelve site chronologies developed for this study are illustrated in Figures 4.9 and 4.10. All chronologies indicate broadly similar growth patterns. A period of above-average growth in the early- to mid-1920s and a decreasing trend in radial growth from the early-1930s to 1940 is evident for all chronologies. However, a period of below-average growth from the late-1950s to late-1970s, and a decreasing growth trend during this period is only observed for the contaminated chronologies. All sites show increases in growth from the early-1970s to the early-1980s, followed by a period of above-average growth throughout the 1980s. In the 1990s, below-average growth characterized all sites before an apparent increase in growth occurred after 2000 at most sites. Years with consistent below-average growth from one tree to another, known as marker years, are present in all chronologies for 1904, 1915, 1927, 1958, 1967, 1975, 1993, 1995 and 2004. These comparisons suggest that individual site chronologies share long-term variations in growth.

A summary of chronology statistics calculated by COFECHA for each jack pine site is provided in Table 4.6 (See section 3.5.1 for definitions of these statistics). Site chronologies range in length from 71 years (SITE 20, 1934-2005) to 326 years (SITE 13, 1679-2005). Average Mean Sensitivity (AMS) ranges from 0.337 to 0.428, indicating a high level of year-to-year variability. Series intercorrelation is highest for SITE 23 (0.712) and lowest for SITE 1 (0.627). Series intercorrelations for all chronologies are higher than other jack pine sites from other parts of Canada according to data housed

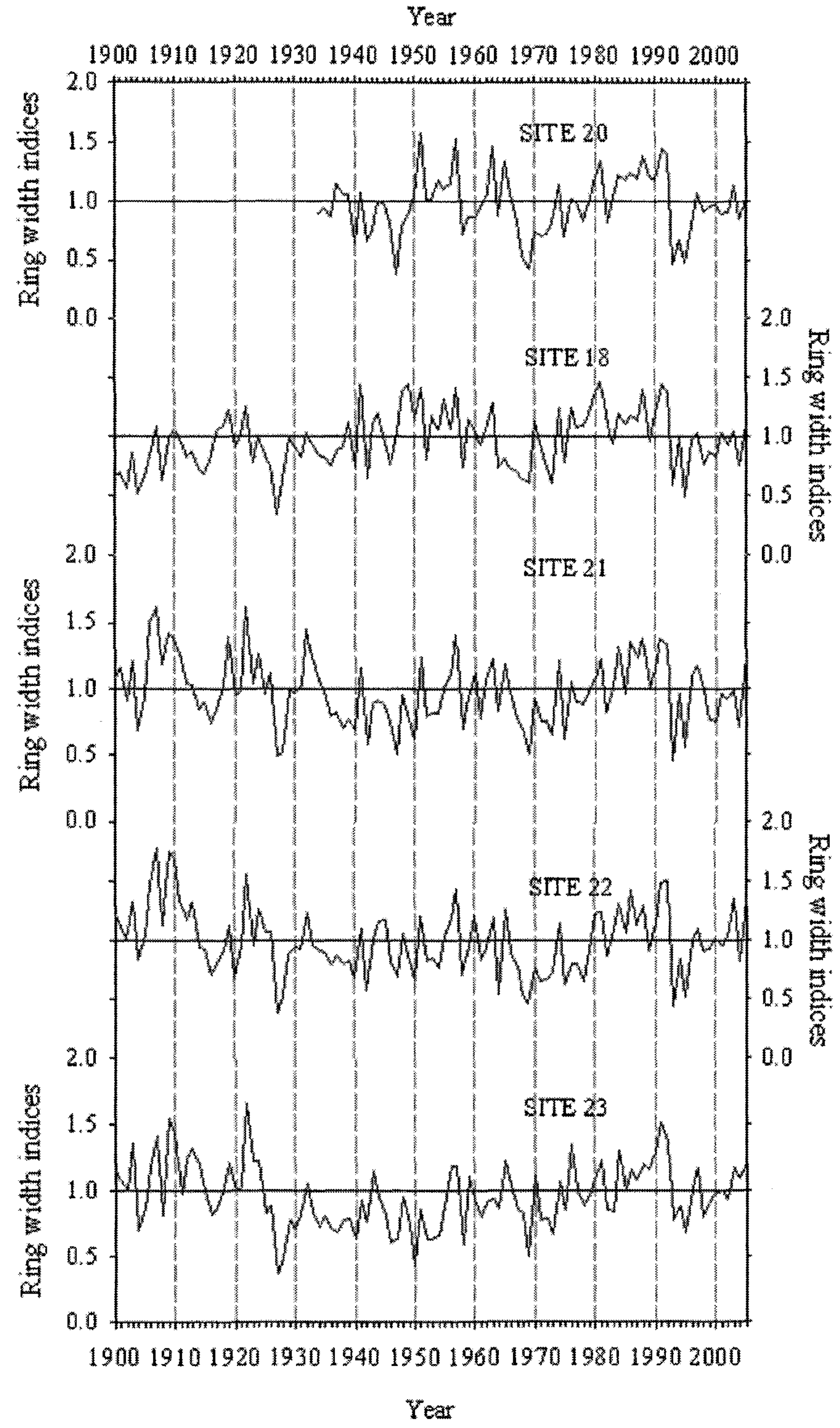


Figure 4.9: Standard site chronology time series for reference sites.

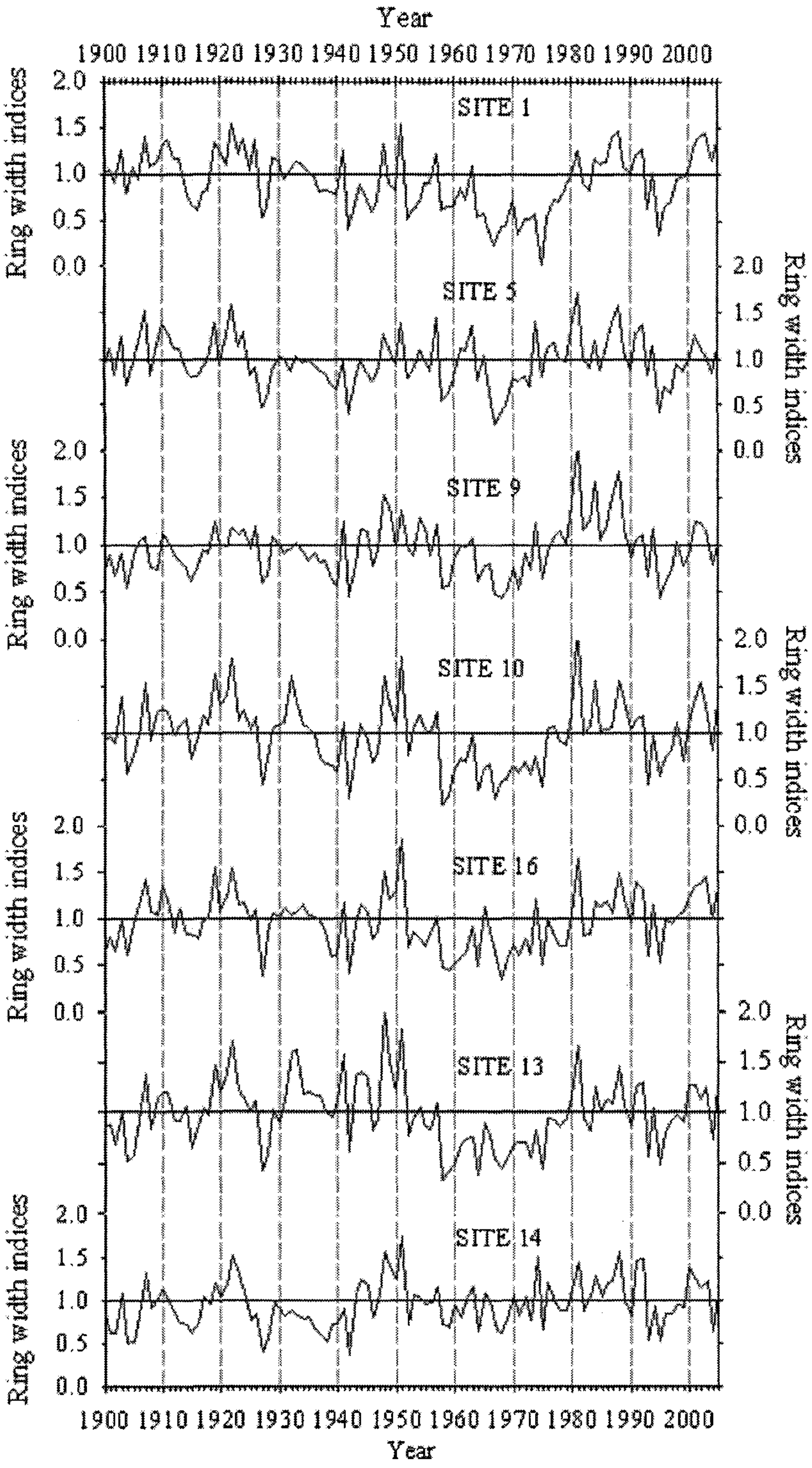


Figure 4.10: Standard site chronology time series for contaminated sites.

Table 4.6: Site chronology statistics for contaminated and reference sites.

Site #	Interval	Length of chronology (years)	n	r	Mean sensitivity	Auto correlation	Std deviation	Mean ring width (mm)	EPS >0.85
Contaminated sites									
10	1855 - 2005	150	48	0.690	0.426	0.743	0.368	0.47	1880
5	1861 - 2005	144	50	0.666	0.397	0.703	0.392	0.56	1886
9	1858 - 2005	147	48	0.676	0.405	0.656	0.558	0.76	1887
1	1868 - 2005	137	52	0.627	0.428	0.789	0.499	0.57	1893
14	1827 - 2005	178	47	0.679	0.403	0.666	0.307	0.45	1852
16	1800 - 2005	205	31	0.690	0.383	0.773	0.437	0.56	1825
13	1679 - 2005	326	49	0.678	0.398	0.687	0.311	0.44	1880
Mean		**184**	**46**	**0.672**	**0.406**	**0.717**	**0.410**	**0.54**	
Reference sites									
22	1734 - 2005	271	51	0.689	0.380	0.759	0.387	0.50	1890
20	1934 - 2005	71	44	0.650	0.354	0.654	0.453	0.83	n/a
23	1791 - 2005	214	52	0.712	0.334	0.790	0.351	0.41	1816
18	1828 - 2005	177	58	0.648	0.337	0.783	0.343	0.48	1880
21	1853 - 2005	152	47	0.699	0.363	0.753	0.358	0.48	1878
Mean		**177**	**50**	**0.680**	**0.354**	**0.748**	**0.378**	**0.54**	

n = number of series (cores)
r = series intercorrelation

at the International Tree Ring Databank (ITRDB). Auto-correlation ranges from 0.654 to 0.784. Eleven site chronologies have an EPS value above 0.9 and sample depth greater than 10 during the period 1900 to 2005 (SITES 10, 9, 1, 5, 14, 16, 18, 22, 21, 23 and 13). The exception is SITE 20 for which EPS values do not attain a value of 0.85. Considering that the common signal cannot be assessed for this chronology and it only extends to 1934, SITE 20 is omitted from further analysis.

The common growth signal among sites is assessed in order to determine whether or not contaminated and reference sites can be combined into regional chronologies. Pearson product-moment correlation coefficients for contaminated and reference site chronologies are summarized in Figure 4.11 for the period (a) 1900-2005, (b) the interval prior to Giant Mine emissions, 1900-1948 and (c) the period of emissions from Giant Mine, 1949-1999.

Correlations are generally highest between sites that are close together. This is especially evident for the period 1949-99. The SITE 18 chronology is an exception to this trend having the lowest correlations with other reference chronologies for all three periods. Nevertheless, it correlates better with reference sites than contaminated sites for the 1949-99 period. Thus, it is included in the regional reference chronology. Correlations between contaminated site chronologies are high and statistically significant for all sites and periods, thus all sites are included in the regional contaminated chronology. The regional chronologies represent the mean of site chronologies in each group. From this point forward these mean chronologies are referred to as the mean contaminated chronology and mean reference chronology.

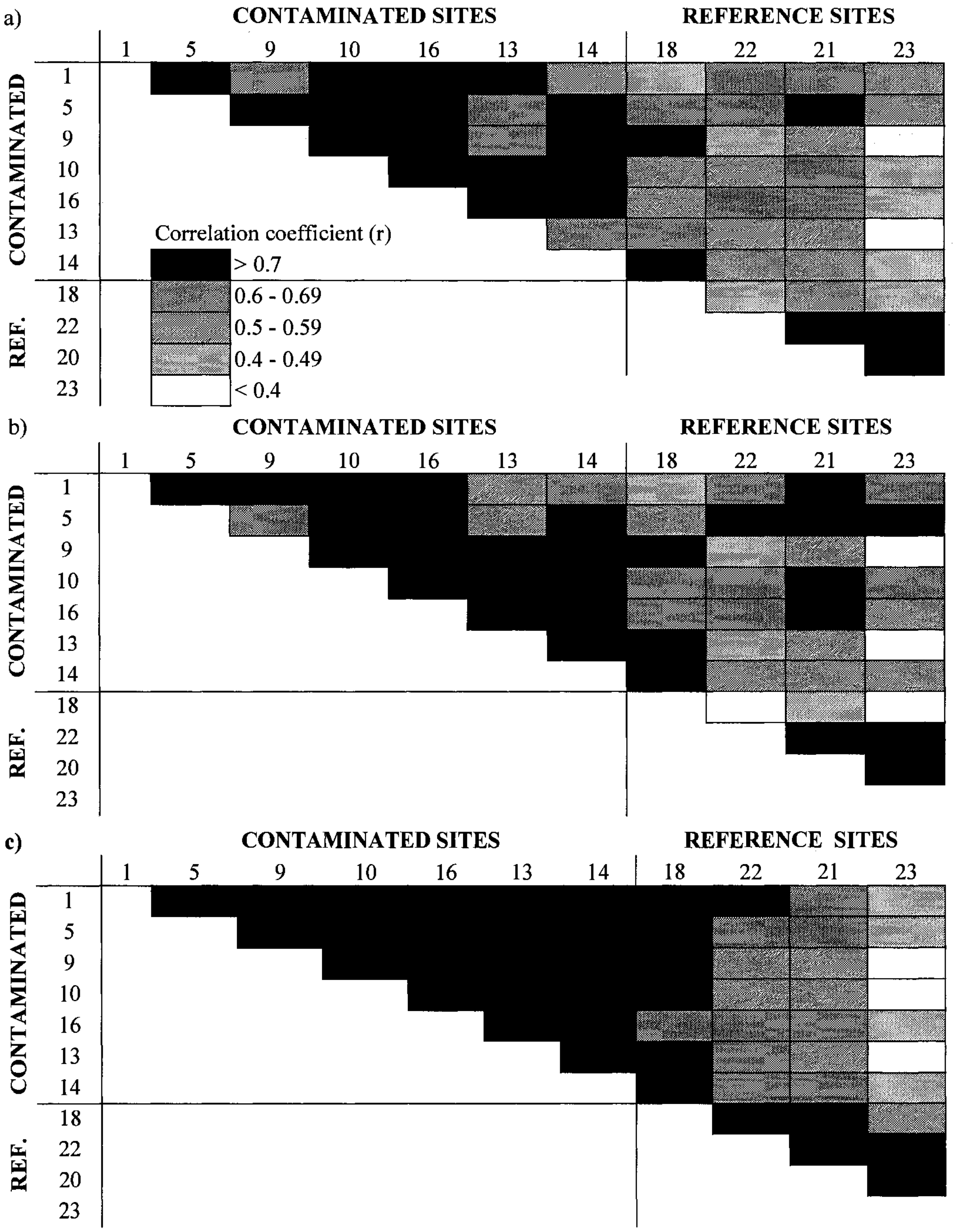


Figure 4.11: Correlation matrix for jack pine for the common period a) 1900 to 2005 (*n* = 106), b) 1900 to 1948 (*n* = 49) and c) 1949-1999 (*n* = 57). Correlations are significant at the 0.01 level (2-tailed).

4.5.2 Tree-growth and emissions during the 20th century

The mean contaminated and reference chronologies reveal considerable variability in ring-widths and growth patterns for the period 1900 to 2005 (Fig. 4.12). Both mean chronologies exhibit a decline in growth during the first few years of operations at Giant Mine (1950 to late-1960s), an increase in growth through the 1970s and 1980s, below-average growth in the 1990s and continued increasing growth in the early 2000s. Nevertheless, there are several differences between the chronologies. A growth release is observed for the contaminated chronology from 1948 to 1951 that is not present in the reference chronology. For the period of growth decline beginning at approximately 1952 and continuing into the 1970s, the mean contaminated chronology exhibits lower average growth compared to the mean reference chronology. Conversely, the mean contaminated chronology exhibits higher growth than the mean reference chronology from the mid-1910s to early 1950s, the 1980s and 2000s.

A significant positive correlation occurs between mean contaminated and reference chronologies for the periods 1900 to 2005, 1900 to 1948 and 1949-1999, with respective Pearson correlation coefficients of 0.748 ($p \leq 0.001$), 0.807 ($p \leq 0.001$) and 0.742 ($p \leq 0.001$). Tests of statistically significant differences (Wilcoxon-Signed Ranks Test) reveal that mean contaminated and reference chronologies are not significantly different ($p \leq 0.05$) for the periods 1900 to 2005 and 1900-1948. However, they are significantly different ($p \leq 0.05$) for the period 1949 to 1999, when mining activities were occurring at Giant Mine. Mean ring widths for the contaminated chronology are 5.0% and 12.3%

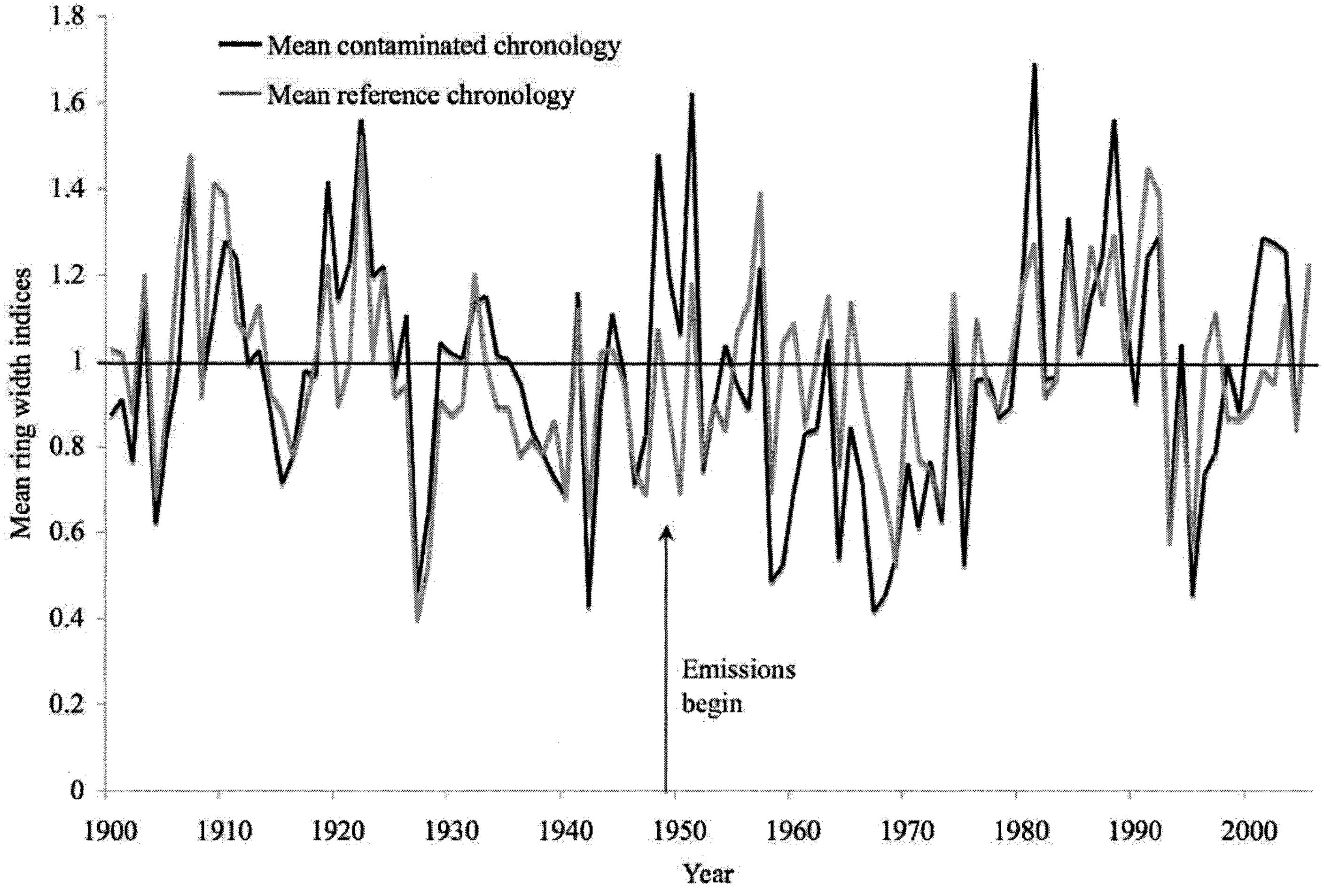


Figure 4.12: Time series of mean standard ring-width chronologies for contaminated and reference sites.

lower than those of the reference chronology for the periods 1900-2005 and 1949-99 respectively and 0.5% higher for the period 1900-48.

Missing rings refer to growth bands that may be partially absent on some portions of the stem and may indicate extreme growing conditions (Fritts, 1976). Table 4.7 provides a summary of the total number of missing rings for each site. The highest percent missing rings are observed for the contaminated SITE 10 (1.9%) and the lowest at SITE 18 (0.06%), a reference site. A Mann-Whitney U test comparing the percentage of missing rings for each contaminated and reference site indicates that contaminated sites have a significantly ($p < 0.01$) greater number of missing rings than reference sites.

4.5.3 Tree-growth, climate and emissions during the 20th century

Results of correlation analyses to compare mean contaminated and reference chronologies against temperature and precipitation records from the Yellowknife Airport are reported in Table 4.8. Correlation coefficients are generated using seventeen months of climate data, from May of the previous year to September of the growth year for three separate periods, including: a) the full climate record (1943-2005); b) prior to Giant Mine operations (1943-48); and c) during Giant Mine operations (1949-99). The pre-operational period covers only a span of 6 years, thus small sample size tempers results obtained using this dataset.

For the period of climate record (1943-2005) strong positive correlations for June precipitation with both mean chronologies are observed. Moreover, both chronologies are significantly correlated with July precipitation. For all other months, correlations are

Table 4.7: Summary of missing rings for each jack pine site. Values in brackets indicate the total number of rings examined for each site.

Site #	# Missing rings	% Missing rings
Contaminated sites		
10	83 (4430)	1.874
5	22 (4232)	0.520
9	34 (3430)	0.991
1	104 (5573)	1.866
14	30 (5292)	0.567
16	20 (3419)	0.585
13	48 (5630)	0.853
Total	**341 (32006)**	**7.256**
Reference sites		
22	32 (6207)	0.516
20	7 (2778)	0.252
23	18 (8519)	0.211
18	4 (6711)	0.06
21	25 (6176)	0.405
Total	**86 (30391)**	**1.444**

Table 4.8: Correlations of mean chronologies with climate parameters (previous May to current September). Bold values indicate significant correlations.

Climate Factor	Climate factor vs. *contaminated* mean ring width chronology		Climate factor vs. *reference* mean ring width chronology	
	r	*p*	r	*p*
1943-2005				
Monthly Precipitation (mm)				
pMay	0.098	0.448	0.010	0.940
pJun	0.043	0.739	-0.032	0.804
pJul	0.010	0.936	0.075	0.560
pAug	0.118	0.363	0.224	0.079
pSep	-0.025	0.846	-0.053	0.682
pOct	-0.123	0.339	0.018	0.888
pNov	-0.107	0.407	-0.034	0.794
pDec	-0.209	0.103	-0.006	0.963
Jan	0.055	0.671	0.203	0.110
Feb	0.017	0.893	0.073	0.567
Mar	**-0.252**	**0.047**	**-0.014**	**0.911**
Apr	-0.163	0.203	-0.027	0.831
May	0.085	0.506	0.168	0.188
Jun	**0.583**	**0.000**	**0.633**	**0.000**
Jul	**0.310**	**0.013**	**0.258**	**0.041**
Aug	-0.133	0.299	-0.136	0.289
Sep	0.032	0.802	0.009	0.946
pAug - Jul	0.227	0.073	**0.416**	0.001
Jun & Jul	**0.567**	**0.000**	**0.554**	**0.000**
Jun - Aug	**0.325**	**0.009**	**0.314**	**0.012**
Montly Temperature (°C)				
pMay	0.007	0.959	-0.042	0.745
pJun	0.009	0.947	0.146	0.258
pJul	0.135	0.297	**0.260**	**0.041**
pAug	**-0.259**	**0.042**	**-0.272**	**0.032**
pSep	0.093	0.473	-0.046	0.724
pOct	0.020	0.878	-0.156	0.227
pNov	0.125	0.334	-0.179	0.163
pDec	0.014	0.916	0.011	0.929
Jan	**0.321**	**0.010**	**0.239**	**0.059**
Feb	0.067	0.600	-0.035	0.784
Mar	0.104	0.416	-0.061	0.637
Apr	0.025	0.846	0.135	0.291
May	0.087	0.498	0.013	0.920
Jun	-0.072	0.577	-0.052	0.684
Jul	0.115	0.371	0.141	0.269
Aug	**0.254**	**0.045**	**0.209**	**0.100**
Sep	0.043	0.739	-0.109	0.393

Table 4.8 (continued): Correlations of mean chronologies with climate parameters (previous May to current September). Bold values indicate significant correlations.

Climate Factor	Climate factor vs. *contaminated* mean ring width chronology		Climate factor vs. *reference* mean ring width chronology	
	r	*p*	r	*p*
1943-1948				
Monthly Precipitation (mm)				
pMay	-0.199	0.749	-0.004	0.995
pJun	-0.175	0.779	0.185	0.765
pJul	-0.407	0.496	-0.166	0.789
pAug	0.343	0.572	0.421	0.480
pSep	0.043	0.946	-0.049	0.937
pOct	**-0.960**	**0.009**	-0.817	0.091
pNov	0.621	0.264	0.395	0.510
pDec	-0.539	0.349	-0.708	0.181
Jan	-0.735	0.096	-0.568	0.239
Feb	-0.418	0.410	-0.182	0.730
Mar	-0.481	0.334	0.026	0.961
Apr	-0.493	0.320	0.069	0.896
May	-0.396	0.437	0.105	0.843
Jun	0.547	0.262	0.635	0.175
Jul	0.785	0.065	0.645	0.167
Aug	0.642	0.169	0.332	0.520
Sep	0.745	0.089	0.319	0.537
Jun & Jul	**0.952**	**0.003**	**0.871**	**0.024**
Jun - Aug	**0.983**	**0.000**	**0.817**	**0.047**
Montly Temperature (° C)				
pMay	-0.018	0.977	0.153	0.805
pJun	-0.580	0.305	-0.250	0.685
pJul	**-0.911**	0.031	-0.762	0.134
pAug	**-0.948**	**0.014**	-0.790	0.112
pSep	-0.258	0.675	-0.060	0.924
pOct	0.585	0.300	0.870	0.055
pNov	0.624	0.260	**0.897**	**0.039**
pDec	0.427	0.473	0.794	0.109
Jan	0.631	0.179	**0.873**	**0.023**
Feb	0.166	0.753	0.630	0.180
Mar	-0.727	0.102	-0.735	0.096
Apr	-0.285	0.584	0.101	0.849
May	0.719	0.108	0.525	0.285
Jun	0.576	0.231	0.676	0.141
Jul	0.800	0.056	0.597	0.211
Aug	0.040	0.940	0.420	0.407
Sep	0.522	0.288	0.575	0.232
pJun to pAug	**-0.985**	**0.002**	-0.747	0.147

Table 4.8 (continued): Correlations of mean chronologies with climate parameters (previous May to current September). Bold values indicate significant correlations.

Climate Factor	Climate factor vs. *contaminated* mean ring width chronology		Climate factor vs. *reference* mean ring width chronology	
	r	*p*	r	*p*
1949-1999				
Monthly Precipitation (mm)				
pMay	0.127	0.376	0.037	0.795
pJun	0.114	0.427	-0.037	0.794
pJul	-0.031	0.827	0.039	0.787
pAug	0.096	0.504	0.252	0.074
pSep	-0.040	0.780	-0.105	0.462
pOct	-0.086	0.546	0.022	0.880
pNov	-0.086	0.546	-0.057	0.692
pDec	-0.175	0.219	0.065	0.649
Jan	0.157	0.272	**0.282**	**0.045**
Feb	0.064	0.653	0.072	0.614
Mar	**-0.287**	**0.041**	-0.051	0.720
Apr	-0.093	0.516	-0.055	0.702
May	0.105	0.462	0.170	0.234
Jun	**0.642**	**0.000**	**0.638**	**0.000**
Jul	0.223	0.116	0.273	0.053
Aug	-0.255	0.071	-0.200	0.160
Sep	-0.092	0.520	-0.106	0.460
pAug - Jul	0.230	0.105	**0.444**	**0.001**
Jun & Jul	**0.530**	**0.000**	**0.564**	**0.000**
Jun - Aug	0.210	0.139	**0.282**	**0.045**
Montly Temperature (^{0} C)				
pMay	0.121	0.397	0.004	0.979
pJun	0.026	0.854	0.152	0.287
pJul	0.136	0.341	0.274	0.052
pAug	-0.159	0.264	-0.206	0.147
pSep	0.098	0.494	-0.023	0.873
pOct	0.005	0.971	-0.140	0.329
pNov	0.034	0.812	-0.237	0.094
pDec	-0.041	0.774	-0.037	0.795
Jan	0.237	0.093	0.231	0.103
Feb	0.058	0.688	-0.065	0.649
Mar	0.184	0.196	-0.016	0.911
Apr	0.065	0.648	0.085	0.552
May	0.100	0.485	-0.056	0.695
Jun	-0.117	0.415	-0.098	0.493
Jul	0.071	0.619	0.148	0.299
Aug	**0.339**	**0.015**	0.200	0.160
Sep	-0.028	0.844	-0.152	0.287

inconsistent and weak. When compared with June-July precipitation, significantly positive correlations with both mean chronologies are observed. In contrast, the response to temperature across the study area for the period of climate record is not strong. A significant positive correlation with January temperatures of the growth year is observed for the mean contaminated chronology. Significant negative correlations for previous August temperatures occur with both mean chronologies. The other correlations are weaker.

Summer precipitation is a prominent factor of tree-growth for both mean chronologies during the pre-operational period (1943-48). Although correlations with the mean reference chronology are not as strong as those with the mean contaminated chronology, strong positive correlations (> 0.8) are observed for both chronologies with June/July and June to August precipitation. A strong negative correlation is also found for the mean contaminated chronology and previous October precipitation. Correlations are also significant with some temperature parameters. Significant negative correlations are observed for the mean contaminated chronology and previous summer temperatures, while significant positive correlations occur for the mean reference chronology and winter temperatures. The strength of these correlations may be misleading since sample size is below 10.

Mean chronologies for the period corresponding to emissions at Giant Mine (1949-99) also correlate strongly with summer precipitation, however, correlations with temperature parameters are weak and generally insignificant compared to the preceding period. Strong positive correlations occur for both chronologies with June precipitation and June/July precipitation. A weak positive correlation is found for the mean contaminated chronology with August temperatures.

In summary, for all three periods, both mean chronologies have a similar response to summer precipitation and slightly different response to seasonal variation in temperature. Furthermore, summer precipitation exhibits a stronger influence on jack pine growth in the Yellowknife area than seasonal temperatures for the period of study. Moreover, correlations with summer precipitation during the period 1949-99 are weaker than the preceding period (1943-48) for both mean chronologies. However, very high correlations observed for 1943-1948 may simply reflect the small sample size ($n = 6$) for this period.

CHAPTER 5

DISCUSSION

5.1 Introduction

This chapter provides a discussion of the results presented in the previous chapter with respect to the main hypotheses of the thesis. The degrees of soil-As contamination and soil acidity at contaminated and reference sites are compared to prior soil surveys, expected background levels, guidelines and typical ranges for mineral soils. The distribution of As and S over the study area is examined with consideration of wind direction and distance from the roaster stack. Next, the relations between soil-As concentrations, groundcover species richness and distance from the roaster stack are explored. This is followed by a discussion of soil chemistry and the radial profiles of As, S, P, Ca and Mg in tree-rings in order to assess As uptake pathways and determine if radial profiles can be used to develop a chronology of exposure to As and SO_2 emissions from Giant Mine. The chapter concludes by exploring the differences between mean contaminated and reference chronologies in terms of tree-growth and the climate-growth response during pre-operational and operational periods in order to assess the impact of mine activities on tree-growth.

5.2 Soil chemistry

5.2.1 As contamination and soil acidity

The Canadian Council of Ministers of the Environment (CCME) residential soil quality guideline for As is 12 μg/g (Risklogic Scientific Services Inc. (RSSI), 2002) and the typical range for As in Canadian agricultural soils is 5 - 15 μg/g (INAC, 2003a).

However, natural background levels of As in the Yellowknife area have been found to vary from 73 μg/g (Cameron and Durham, 1974) to 1560 μg/g (Kerr, 2001). The average background concentration of As in Yellowknife soils is reported as 150 μg/g (RSSI, 2004), based on three separate studies performed in 2001 (Kerr, 2001; Ollson et al., 2001; ESG, 2001). Due to the elevated levels of natural As (arsenopyrite) found in the Yellowknife Greenstone Belt, soil quality remediation objectives for Yellowknife are 340 μg/g for industrial land use, and 160 μg/g for residential and parkland land use (RSSI, 2002).

Total As concentrations in surface soil samples at sites under 10 km from Giant Mine are above the remediation objective for industrial sites (see Table 4.1). Surface soil concentrations for total As at these sites agree with concentrations reported in previous soil surveys conducted on the mine property (ESG, 2001; Golder Associates Ltd., 2004). The remediation objective for As in Yellowknife soils for residential and parkland property is exceeded at SITE 14 (250 μg/g), located within the residential area of the city, and SITE 13 (1166 μg/g), located within the Fred Henne Territorial Park. Previous soil surveys performed within the residential, commercial and recreational areas of the City of Yellowknife, found that As in soil ranged from 3.5 μg/g to 4950 μg/g (Table 4.1 in RSSI, 2002).

The current study found background levels of As at much lower levels than those reported above at sites 15 - 40 km east of the city, along the Ingraham Trail (see Table 4.1). With the exception of the reference site at the 15 km mark (SITE 18), mean total As concentrations at the reference sites are within the expected range (1.3 – 27 μg/g) for world uncontaminated soils identified by Kabata-Pendias (2001) and under the Yellowknife remediation objective for residential land use.

Mean total percent S is significantly higher at contaminated sites compared to reference sites, however pH is not significantly different. The percentage of total S in all surface soil samples is very low, not exceeding 0.07%. The pH of contaminated and reference site soils are within the extreme range of pH found for most mineral soils, ranging from slightly to strongly acidic (Soil Web, 2007). Slightly higher soil acidity at reference site soils may be related to greater amount of spruce and jack pine litter at these sites due to a denser canopy. Berger et al. (2006) found that topsoil under pure spruce forests was acidified due to litter. Conifer litter is acidic and has a high carbon to nitrogen ratio (C:N) that can decrease available soil nutrients and pH by immobilizing base cations from the litter (Van Cleve et al., 1983; Wardle et al., 2003). However, pH is considered a poor measure of the degree of soil acidity without accounting for soil buffering capacity, which requires data regarding soil Al and Fe content (Kennedy, 1992). Although this is beyond the scope of this study, soil acidity can be identified by its impact on nutrient content within affected soils. For instance, leaching of nutrients such as K, Ca and Mg from soil is an impact of soil acidity (Kennedy, 1992). Thus, low content of these nutrients in soils would confirm pH measurements.

Most soils sampled in the study area are within the typical range for Ca (700 μg/g to 500,000 μg/g) and Mg (400 μg/g to 9000 μg/g) present in soils from around the world as cited by Soil Web (Table 1, Section 1.1.3, 2007). Exceptions are SITE 10 with 15800 μg/g of Mg, and SITE 16 and SITE 22 with only 600 μg/g of Ca. Low Ca at SITE 16 and SITE 22 as well as lower Mg concentrations at most reference sites may indicate the impact of soil acidity, especially since reference sites have moderately to strongly acidic mean pH values. In contrast, Ca is significantly higher at contaminated sites than reference sites and may account for slightly less acidic soil at these sites compared to reference sites.

The high levels of Ca at contaminated sites may be due to local redistribution of iron carbonate, soluble sulphate and Ca cations from a calcine storage pond on the mine property. Calcine is a gold-bearing iron oxide that remains after smelting. Calcine tailings were released directly into Great Slave Lake from 1948-1951, redirected to the north and central tailings ponds in 1951 then deposited in its current location until 1971 (Steffen Robertson and Kristen (Canada) Inc., 2004). Although the pond was covered with 15 - 30 cm of composted manure and 9.2 m of clay, calcine was removed for gold recovery in 1997 (Steffen Robertson and Kristen (Canada) Inc., 2004). Soil samples collected near the calcine area in 2004 ranged from neutral to slightly acidic (7.92 to 5.72) (Steffen Robertson and Kristen (Canada) Inc., 2004). Interpretation of soil chemical data for this study is confined to current conditions, thus a discussion of soil acidification due to Giant Mine emissions of SO_2 and the source of Ca at contaminated sites is not possible based on soil data alone, however this topic is examined using tree-ring and soil chemistry data in section 5.3.2.

5.2.2 Soil contamination and distance from roaster stack

Arsenic concentrations and total percent S in soils are elevated near the 45 m tall roaster stack at Giant Mine and decrease significantly with distance from the stack (Figs.

4.2 & 4.3). Several studies of metals emitted from smelters and power stations also observed higher metal concentrations in soils within the vicinity of the source (Ondov et al., 1989; Sato and Sada, 1991; Anderson et al., 2000; Keegan et al., 2006). Anderson et al. (2000) observed a negative relation for Pb with distance from an active and inactive smelter in Alabama, USA. Keegan et al. (2006) also observed a decrease in As concentrations in soil with distance from a coal-burning power station in Slovakia.

In the current study, soil As concentrations within 10 km north and south of the roaster stack are above the average background concentration reported for Yellowknife of 150 μg/g (Table 4.1). In contrast, only one site located east of the roaster stack is above this background level (Table 4.1). These data reveal the importance of wind on As distribution and deposition in the area.

Wind directions with the most frequent maximum hourly speed in Yellowknife are from the northwest, northeast and north (Canadian Climate Normals 1971-2000, Environment Canada, 2007). The wind direction with the highest speed over the last 20 years is from the east (Fig. 3.5). Furthermore, the most frequent wind directions are from the northwest in winter (December to March), northeast in April, southeast in summer (May to September) and east in the fall (October to November) (Canadian Climate Normals 1971-2000, Environment Canada, 2007). Thus, emissions would have been carried furthest and most frequently towards the southeast and southwest of the mine from January to April, and would not have traveled far eastward. In the summer, emissions would also have been carried northwest. This is evident from the relatively high total As concentrations and total percent S in soil at 10 km southwest of the roaster stack, lower total As concentrations and total percent S to the north and abrupt decline of total As concentrations between 1 and 15 km east. Total percent S in soil also corresponds to this last trend, yet the decline is less apparent.

Total percent S in soil is also higher to the north and south of the roaster stack than to the east and has a significant negative relation with distance from the roaster stack (Figs. 4.2 & 4.3b). However, this relation is weaker than that for As. Moreover, total percent S in the soil increases at 40 km east. These trends suggest that deposition from Giant Mine emissions are less important to the current S content of soils than it is for current soil-As content.

Although the distance that particles travel depends on meteorological conditions, particle size and stack height also affect particle fallout (Keegan et al., 2006). Evans et al. (1980) found that for a stack of 300 m, 6% of particles emitted fell within 5 km, while 25% of particles emitted from a 40 m stack fell within 5 km and 34% within 10 km. In the current study, with a roaster stack height of 45 m, mean total As concentrations and total percent S in soils < 3 km from the roaster stack were respectively 8 and 4 times higher than at > 5 km (Table 4.2). This corresponds to results obtained from a SO_2 deposition survey conducted during the operation of Giant Mine (GNT, 1993). Keegan et al. (2006) obtained similar results for roaster stacks of 150 m and 300 m in height. They observed that As concentrations in soil were two times higher at < 5 km than at 5 – 10 km and > 10 km from the source.

5.2.3 Soil contamination and groundcover species richness

A strong negative relation between groundcover species richness (GCSR) and As concentrations in soil as well as a strong positive relation between GCSR and distance from Giant Mine are observed (Figs. 4.5 & 4.6). These relations indicate that GCSR is higher at reference sites than contaminated sites, increasing along the gradient from high to low soil-As content. Rosenberg et al. (1979) also found a significant decrease in vegetation species richness immediately downwind of a power plant and detected no effect on species richness and diversity at distances >7 km from the power plant.

Although there is a lack of literature regarding the impact of soil-As contamination on groundcover abundance and diversity, most studies on individual plants agree that in low concentrations As can be beneficial to plant growth and as concentrations of As increase in the plant As becomes toxic causing chlorosis, necrosis, inhibition of growth and finally death (Wang et al., 2002; Gulz et al., 2005). Gulz et al. (2005) observed that as soluble As concentrations increased in the soil, maize, ryegrass, rape and sunflower responded by taking up more As from their roots.

Several plant species, especially lichen, were found at reference sites that were not present at contaminated sites (Table 4.3). Patra et al. (2004) reviewed several studies of As toxicity to plants and found that in several cases plant survival is related, at least in part, to the plant's tolerance to As. However, Gulz et al. (2005) observed that As was less toxic and inhibition of growth less pronounced in plants with higher P content than in the same plants that contained less P when exposed to the same level of As. Mkandawire et al. (2004) also found that As bioaccumulation in duckweed (*Lemna gibba* L.) was higher for experimental cultures exposed to P-deficient conditions compared to P-sufficient conditions. Therefore, groundcover species richness results may reflect tolerances of plants to As and bioavailability of As.

The strength of the relations observed in this study is high and explains about 65 to 70% change in GCSR (Figs. 4.5 & 4.6). This suggests that other factors also impact GCSR in the study area. Groundcover composition is a function of canopy closure and light availability, soil nutrients and pH, forest floor heterogeneity and colonization (Hart and Chen, 2006). These factors are affected by disturbances and fire.

Based on air photo interpretation, the canopy across the Yellowknife region is relatively open, however it is slightly more open at contaminated sites. Large canopy gaps were created when the land was cleared for mine use and logging for building materials. These sites may have greater light availability and throughfall precipitation than reference sites. Greater light availability could explain the presence of certain vascular plants solely at contaminated sites since vascular plants are most limited by light availability (Hart and Chen, 2006). Greater throughfall precipitation should encourage moss and lichen abundance since this is often the limiting resource affecting their establishment and growth (Hart and Chen, 2006). However, greater lichen diversity and moss abundance occur at reference sites.

Differences in species diversity and vascular plant versus lichen abundance at contaminated and reference sites may be a function of disturbance severity. Sites near the mine show evidence of large, severe disturbances (i.e. logging, road construction) and greater shrub diversity, while minor disturbances such as windthrow and canopy dieback are the dominant disturbances at reference sites where lichen species are most diverse. This corresponds to a study of three separate groundcover communities affected by fire, logging and spruce budworm outbreak that found that logging resulted in less groundcover heterogeneity, lower species diversity and higher shrub coverage than did natural disturbances (Kemball et al., 2005). Jonsson and Esseen (1990) found that mosses colonize more effectively on small disturbance patches. Moreover, tip-up mounds and hummocks created by uprooted trees are important in controlling moss diversity since they create new microsites (Hart and Chen, 2006) thus increasing forest floor heterogeneity. Rydgren et al. (1998) maintain that forests that experience severe disturbances that cause large changes in composition and diversity may not recover for up to 25 years and that lichen and moss communities are much slower to recover. Considering that contaminated sites continue to experience disturbances due to mine reclamation activities it is possible that conditions are not suitable for lichen and moss re-colonization.

Monitoring of wildfires in the Yellowknife area began in the 1960s (Roger Fraser, ENR, personal communication, August 2006) thus information regarding wildfires prior to this time is not readily available. Nevertheless, there is evidence of past fire at all sites. According to Hart and Chen (2006) several researchers have observed that moss and lichen species richness increases with time after fire due to an increase in microsite heterogeneity. In contrast, soil nutrients and pH decrease with time after fire (Hart and Chen, 2006). Current soil pH is not significantly different at contaminated and reference sites, however Mg and Ca are higher in soils and lower in tree-rings at contaminated sites compared to reference sites, suggesting that these nutrients at reference sites were more easily mobilized for uptake by trees.

It is difficult to isolate Giant Mine As deposition as the cause of lower GCSR near the mine since observed GCSR may be due to any one or combination of the above discussed factors or other contaminants not measured. Nevertheless, As contamination and factors affected by time after fire and severity of disturbance appear to be important factors for lichen diversity. This is interesting since it is believed that moss and lichen composition drive northern boreal forest groundcover vegetation communities (Hart and Chen, 2006).

5.3 Tree-ring chemistry

5.3.1 Arsenic tree-ring contamination and uptake pathways

The radial profiles of As and As/P ratio, and the results of Wilcoxon-Signed Ranks Tests demonstrate that tree-ring As concentrations recorded at sites with high As contamination are significantly higher than those at reference sites (Fig. 4.7 & Table 4.5). This is consistent with the findings of dendrochemical studies of As contamination from a point source (Martin et al., 2000; Cheng et al., 2007). Furthermore, radial concentration profiles for As suggest that uptake by roots occurs at all sites, while absorption via bark may also be an important uptake pathway at contaminated sites.

Despite variability within the profile for contaminated sites, there is an overall increasing trend in As concentrations from older (1926-30) to younger (2001-05) rings (Fig. 4.7a). This pattern does not reflect changes in As emissions from Giant Mine for if it did As concentrations would peak around 1950, decrease gradually in following years, then decrease substantially after 1999, when emissions ceased at the mine (compare Figs. 2.1 & 4.7a). Nevertheless, an increase in As concentrations in tree-rings from 1950 to 1980 could be attributed to increased uptake of As deposited onto surrounding soil. A significant positive correlation for As concentrations in soil with those in sapwood rings ($r = 0.964$) at all sites suggests that soil-As is bioavailable and taken up by jack pine via the root system (Fig. 4.8). Moreover, high levels of As and Ca in contaminated site soils and tree-rings indicate that uptake via roots is very possible since Ca-oxides are a primary sorbent of As and are found to improve As bioavailability (Gulz et al., 2005). A number of studies found that tree uptake of As occurred via roots (Martin et al., 2000; Patra et al., 2004; Cheng et al., 2007).

Tree-ring As concentrations range from 0.051 μg/g to 0.429 μg/g, while As concentrations in surrounding soil are much higher ranging from 13 - 2055 μg/g (Tables 4.1 & 4.4). Cheng et al. (2007) and Martin et al. (2000) also observed that As concentrations in tree-rings were several orders of magnitude lower than in surrounding soils. Cheng et al. (2007) hypothesized that this discrepancy is due to discrimination of As versus P during plant uptake. They found that in contrast to As, P concentrations in the soil (mean 297 ± 230 mg/kg) were comparable to those in the sapwood rings (256 ± 167 mg/kg) for contaminated and reference sites, thus suggesting that low As uptake reflected either; i) suppression of the high P(V)/As(V) uptake system at the root-soil interface, ii) reduction of As(V) to As(III) upon entering the tree, as observed in many studies (Wang et al., 2002; Tu et al., 2004; Kertulis et al., 2005; Quaghebeur and Rengel, 2005), and/or iii) preferential transport in sapwood of P(V) over As(III). Although P concentrations for soil samples are not available for the current study, P concentrations in tree-rings at contaminated and reference sites (101 to 361 μg/g) are several orders of magnitude higher than As concentrations (Table 4.4). Nevertheless, the As/P ratios in tree-rings indicate that contaminated sites contain greater As to P compared to reference sites (Tables 4.4 & 4.5). This may indicate that soils at contaminated sites contain lower P since at low levels, P(V) is found to displace As(V) from soil particles increasing absorption and phytotoxicity, while high levels of P(V) compete with As(V) resulting in reduced As(V) uptake and phytotoxicity (Meharg and Mcnair, 1991; Meharg and Mcnair, 1992).

Interpretation of the radial profile of As with respect to Giant Mine activities is confounded by high levels of As in tree-rings formed during low periods of As emissions (Fig. 4.7a). High levels of As in the bark of contaminated sites compared to reference sites may correspond to increased levels of windblown As-contaminated soils due to ongoing remediation activities that began at Giant Mine in 2000. High concentrations observed in tree-rings formed prior to activities at Giant Mine may be the result of lateral translocation across annual rings via rays. Lateral translocation has been used to interpret concentration profiles of Fe, Mo, Ti (Baes and McLaughlin, 1984) and As (Martin et al., 2000; Cheng et al., 2007). Cheng et al. (2007) were unable to reconstruct contamination from arsenical production in pine and suggested that transport of As occurred in several sapwood rings due to the wide sapwood section of this tree species. In the current study, jack pine also had a wide sapwood section starting from the annual ring corresponding to the year 1960, on average. High levels of As in the bark and outer sapwood rings of contaminated site trees may indicate one or a combination of the following; i) absorption through bark of windblown As-contaminated soil near Giant Mine, ii) lateral translocation of As along stemwood rays, iii) transport of root-absorbed As in multiple sapwood rings. Lateral translocation and uptake of As along multiple sapwood rings could explain increased As concentrations observed during the 1980s at reference sites. A clear divergence between the reference and contaminated profile after 1991-95 and much lower concentrations of As in reference site bark, support the possibility of As uptake via bark from windblown soil near Giant Mine.

5.3.2 Radial concentration profiles of S and other elements

Radial concentrations of S are significantly different at contaminated and reference sites (Fig. 4.7b). This difference is likely due to a peak at the contaminated sites during 1966-70. This peak was not removed as an outlier since it corresponds to high concentrations of P and Al at contaminated sites. It is difficult to attribute the cause of these peaks, however, the fact that it is not observed for the reference sites suggests that site conditions unique to the contaminated sites are responsible.

A trend of increasing total S concentrations is evident for contaminated sites, with 50 μg/g in 1926-30 to over 100 μg/g in 1996-2000 (Fig. 4.7b). Conversely, the radial profile of S for reference sites has no discernable trend but fluctuates between 100 and 150 μg/g (Fig. 4.7b). Concentrations in outer rings (after 1966-70) are similar for both S profiles. Dendrochemistry studies of the effects of SO_2 on forest health did not look at S in tree-rings, instead they concentrated on reconstructing soil acidification and detecting evidence of impacts from soil acidification - namely mobilization of either Ca, Mg, Al, Mn or Fe from soil and their enrichment in tree-rings (Baes and McLaughlin, 1984; Berger et al., 2004; Webster et al., 2004).

The contaminated and reference profiles for Mn and Mg concentrations gradually decline from 1926-30 to 2001-05 and are not significantly different (Figs. 4.7e & 4.7f). Manganese profiles show narrow fluctuations while the Mg profiles exhibit greater fluctuations attesting to its higher level of radial mobility than Mn (Table 2.3). These radial profiles suggest that levels of Mn and Mg in these trees were not greatly affected by external environmental changes. It is expected that the amount of cations stored within the stemwood will decline from pith to bark due to a steady decrease of cation binding capacity with increasing distance from the pith if no external environmental changes occur (Berger et al., 2004). In contrast, a temporary increase of Mg, Ca, Al or Fe, in tree-rings may indicate cation mobilization due to acid deposition (Berger et al., 2004; Webster et al., 2004). A temporary increase is observed for Al (1966-70) for the contaminated profile and coincides with an increase in S (Figs. 4.7 b & 4.7g). More in-depth study is required in order to determine whether this indicates Al mobilization due to SO_2 and SO_4^{2-} deposition from Giant Mine emissions.

Calcium fluctuates widely for both radial profiles relative to the other elements studied (Fig. 4.7d). Furthermore, Ca concentrations in tree-rings are very high compared to concentrations in soil, especially for the reference sites, 2763 – 4064 μg/g (tree-rings) versus 600 – 1433 μg/g (soil) (Tables 4.1 & 4.4). The extremely high values in the current study either indicate error in detection of Ca using ICP-ES, or that very high levels of Ca were distributed through the atmosphere and taken up in large quantities by surrounding trees. Ca is not expected to succumb to lateral translocation, thus the Ca profile should reflect chronological uptake.

The Ca profile (Fig. 4.7d) observed for the contaminated sites profile coincides well with changes in calcine management at Giant Mine. The peak at 1946-50 coincides with calcine dumping into Back Bay. This peak in Ca may also be related to clearing of trees to erect buildings for Giant Mine during the 1940s since Ca mobilization has been observed following large-scale canopy extraction (Van Cleve and Dyrness, 1983) and thinning of managed forest land (Berger et al., 2004). Decreased Ca in tree-rings from 1951-55 to 1981-85 seem to correspond to the period when calcine was stored in a pond and covered, and the high peak in 1996-2000 seemingly corresponds to removal of several truckloads of calcine from the pond. The peaks at 1931-35 and 1986-90 cannot be explained by calcine management practices.

Webster et al. (2004) cite several papers that have observed similar changes for Ca and Mg in red spruce rings in the GSMNP and considered mechanisms to explain these observations. The first mechanism proposes that Al, with its higher charge and greater binding potential than cations with lesser charge, may prevent uptake of cations thus contributing to a decline in cation concentrations in the wood (McLaughlin and Wimmer, 1999). This does not seem to have occurred at contaminated sites near Giant Mine since the peak of Al in tree-rings is not followed by a decline in Ca and Mg. The second mechanism proposes that if cation-stripping rates exceed cation-weathering rates, base saturation will decline and plants will take up exchangeable acidity (Al or SO_4^{2-}) over exchangeable bases (Ca, Mg) (Reuss and Johnson, 1986). In the case of contaminated sites, soils received high levels of Ca, thus increasing base saturation and providing much Ca for uptake by surrounding trees. When calcine storage moved to the pond, it is possible that less Ca was redistributed over the property, potentially causing a threshold for cation-stripping versus cation-weathering, in turn causing preferential root uptake of S (as SO_4^{2-}) and acidic Al. The coinciding peak of P at this time could reflect increased acidity of the soil, since it has been documented that greater acidity facilitates P uptake by plants (Tu and Ma, 2003).

5.4 Tree-growth during the 20th century

5.4.1 Impacts of emissions from Giant Mine

During the pre-operational period (1900-1948) contaminated and reference chronologies are strongly correlated (section 4.5.2), respond to summer precipitation in a similar manner (Table 4.8) and are not significantly different (section 4.5.2). Although the chronologies remain correlated during the operational period (1949-1999), the correlation is weaker, the strength of correlations with summer precipitation decline and the chronologies are significantly different. If diminished strength of the climate-growth response is not only a function of sample size then these findings are consistent with those observed by Long and Davis (1999) in their study of changes in the climate-growth response of oak prior to and during stack emissions from a power plant in central Pennsylvania, USA. They concluded that the decline in correlation from pre-operational levels between contaminated and reference chronologies and between these chronologies and climatic conditions suggested that climate was not the only factor limiting white oak growth during a period of high ground level pollution. Similarly, Webster et al. (2004)

suggested that up to 67.1% of changes in radial growth of red spruce near ridges in the GSMNP that were exposed to acid fog could be explained by a combination of climate and regional pollution (NO_x and SO_2), while climatic conditions alone explained only 7.6%.

The shift from synchronous growth response for both chronologies during the pre-operational period (1900-1948) to non-synchronous growth at the onset of activity at Giant mine (1949-1999) suggests that mine operations may have influenced limiting factors to tree-growth near the mine (Fig. 4.12). Divergence in the chronologies is most evident for the following years 1948-1951, 1954-1977, 1981, 1988 and late-1990s to 2002 (Fig. 4.12).

A growth release is evident from 1948 to 1951 for the contaminated chronology (Fig. 4.12). This coincides with the construction of Giant Mine and unabated emissions of As (Fig. 2.1), SO_2 and calcine from the roaster stack as well as increased Ca concentrations in tree-rings of this period. Several studies have found connections between growth releases and disturbance such as fire (Lageard et al., 2000; Antos and Parish, 2002), insect outbreaks (Berg et al., 2006; Campbell et al., 2007), and logging (Motta et al., 1999). As previously discussed, removal of large patches of forest canopy has been linked to increased availability of Ca and Mg within the soil (Berger et al., 2004) as well as increased light availability (Hart and Chen, 2006). This combination of conditions may have temporarily improved accessibility to light, moisture and nutrient resources for the remaining trees, and favoured growth despite high As and SO_2 contamination.

A period of growth decline immediately follows this growth release, from the early 1950s to late 1970s (Fig. 4.12), which corresponds to the operational period prior to adequate environmental mining practices and lower radial Mg and Ca concentrations at contaminated sites (Fig. 4.7). The growth decline is also observed for the reference chronology, however average growth was greater at these sites (Fig. 4.12). As previously discussed, acid deposition from SO_2 emissions can influence nutrient bioavailability. Thus lower growth at contaminated sites than reference sites for the period of growth decline may be related to pollution-induced stress due to SO_2 emissions. Furthermore, a significantly greater number of missing rings (Table 4.7) found in jack pine at contaminated sites suggest that these trees were growing under more extreme conditions than at reference sites.

Nutrient availability appears as an important limiting factor to growth of jack pine throughout the study area. Synchronous fluctuations at contaminated sites for growth and Ca concentrations in tree-rings from the 1980s to 2000s further illustrates the role of nutrient availability to jack pine growth (Figs. 4.7d & 4.12). This is in agreement with Sheppard et al.'s (2001) findings that at sites with thin, poorly developed soils, availability of soil nutrients that affect tree-growth will play a strong role in ring-width variation. Thus SO_2 emissions could indirectly affect growth by influencing nutrient availability at contaminated sites.

Although analysis of the relation between As in tree-rings and tree-growth is confounded by the potential of radial translocation and uptake via multiple sapwood rings, increased As concentrations in tree-rings observed from 1951-55 to 1966-70 and near the end of the contaminated profile (Fig. 4.7a) correspond with reasonably expected increases in accumulation of As in soil and bark over that time due to Giant Mine emissions (Fig. 2.1).

Arsenic bioaccumulates in plants until it reaches the plant's tolerance level at which point genotoxic effects that lead to inhibition of growth occur (Kabata-Pendias and Pendias, 1992; Wang et al., 2002; Patra et al., 2004). Kabata-Pendias and Pendias (1992) suggest that the threshold of non-hyperaccumulating plants is between 5 and 100 μg/g dry weight. Although an evaluation of genotoxic effects is outside the scope of the data available for this study, it is possible to estimate the concentration of bioaccumulated As in sampled tree-rings. The total mean concentration of As accumulated in tree-rings at contaminated sites for the period of growth decline (1951-55 to 1976-80) is 1.564 μg/g. The threshold for jack pine trees is unknown, however compared to the threshold suggested by Kabatas-Pendias and Pendias (1992) it appears that As concentrations in jack pine are probably not high enough to cause growth inhibition. Cheng et al. (2007) reported As concentrations in tree-rings similar to the current study and were unable to attribute As contamination to declining tree-growth. Nevertheless, in the current study the growth decline from the 1950s to 1970s corresponds to increasing As concentrations in tree-rings while higher growth in the 1980s corresponds to decreasing As concentrations in tree-rings (Figs. 4.7a & 4.12). Although assessment of the direct impact of As on tree-growth would require a genotoxic study, these relations suggest that As may have an impact on jack pine growth at contaminated sites. These findings suggest that further research regarding the impacts of As on tree-growth is warranted.

CHAPTER SIX

CONCLUSION & FUTURE RECOMMENDATIONS

6.1 Conclusion

The objective of this research was to assess the impact of As and SO_2 contamination from gold mining activities on tree-growth and forest health in the vicinity of Giant Mine, Yellowknife, NWT. This was achieved by using growth records from jack pine to examine relations between mine activities, climate and tree-growth. In addition, groundcover species richness, tree-ring chemistry and surface soil chemistry at contaminated and reference sites were examined to assess overall forest health. The main findings that support or refute the hypotheses of this study are summarized below.

1. ***Surface soil downwind of and nearest to the Giant Mine roaster stack contains elevated levels of As and S compared to similar sites upwind of and furthest from the roaster stack.***

Total As concentrations in surface soil are significantly higher within 10 km of the mine than at sites located 15 - 40 km east and decrease significantly with increasing distance from the mine. The distribution of As over the study area corresponds to dominant wind direction and wind speed as recorded at Yellowknife and compares favourably to As fallout patterns observed by Keegan et al. (2006) that assessed As deposition from roaster stacks of 150 m and 300 m in central Slovakia. Although total percent S concentrations are significantly different for contaminated and reference sites and decrease significantly with increasing distance from the mine, soil acidity (pH) is not significantly different. Current soil acidity within the study area may not reflect historic deposition of SO_2 or SO_4^{2-} from mining activities due to the various processes that occur within the sulphur cycle of an ecosystem. Analysis of soil Ca and Mg concentrations indicate that soil buffering capacity and amount of soil litter may have a greater influence on current soil acidity than past mine emissions of SO_2.

2. ***Arsenic contamination of the surface soil has resulted in decreased groundcover vegetation species richness, thus sites near the mine property will contain fewer plant species than reference sites further away.***

Differences in groundcover species richness at contaminated versus reference sites correspond to the level of soil-As contamination as well as the type and severity of disturbances. The variability of total As concentrations in surface soil explains 65 to 70% of the variability in groundcover species richness observed in this study. Sites within 10 km of the mine property containing high soil-As concentrations have significantly lower groundcover species richness than at reference sites containing soil-As concentrations that are several orders of magnitude lower.

Vegetation species [prickly rose (*Rosa acicularis*), ground juniper (*Juniperus communis*), shrubby cinquefoil (*Potentilla fruticosa*), northern gooseberry (*Ribes oxyacanthoides*), common blueberry (*Vaccinium myrtilloides*), wild strawberry (*Fragaria virginiana*), northern bastard toadflax (*Geocaulon lividum*), yellow mountain aven (*Dryas drummundii*) and *Aster spp.*] unique to contaminated sites are vascular plants, which thrive under large canopy gaps with ample light availability. Conversely, several lichen species [cladonia lichen (*Cladonia brotrytes, Cladonia gracilis spp., Cladonia sulphurina, Cladonia multiformis*), monk's hood lichen (*Hypogymnia physodes*), northern reindeer lichen (*Cladina stellaris*), grey reindeer lichen (*Cladina rangiferina*), waxpaper lichen (*Parmelia sulcata*), powdered orange lichen (*Xanthoria fallax*) and frog pelt (*Peltigera neopolydactyla*)] which prefer to colonize small disturbance patches often caused by windthrow or canopy dieback are unique to reference sites.

Lower groundcover species richness at contaminated sites compared to reference sites corresponds to higher levels of overall contamination, the severity of logging and clearing of trees for mining operations and continued disturbance by remediation activities. Due to these disturbances, site conditions may not be suitable for lichen re-colonization and recovery.

3. ***Trees growing at heavily contaminated sites contain higher levels of As and S in their tree-rings than trees at reference sites and tree-ring concentrations correspond to As and SO_2 exposure and subsequent uptake by trees at these sites.***

Comparison of radial profiles reveal that arsenic concentrations are significantly higher in tree-rings at contaminated sites than reference sites. This may be due to higher concentrations of As and Ca in soil since Ca-oxides absorb As(V) making it more bioavailable to plants. The radial profile for As at contaminated sites does not reflect recorded As emissions likely due to lateral translocation or uptake in multiple sapwood rings. Significant correlations of sapwood As concentrations and soil-As concentrations at all sites reveal that uptake likely occurs via roots. Bark As concentrations and concentrations in outer tree-rings indicate that bark is also a possible uptake pathway at contaminated sites, while at reference sites absorption via bark is less evident. Much lower As concentrations found in tree-rings compared to surface soil indicates that much As in the soil is not bioavailable or that the trees have a threshold for As uptake.

Radial profiles of S concentrations are significantly higher at contaminated versus reference sites. A comparison of S radial profiles with changes in emissions was not possible since comprehensive records of SO_2 emissions are not available. Due to the complexity of the sulphur cycle in an ecosystem it was not possible to directly compare S in soil and tree-rings to establish changes in soil acidity. However, the radial profile of Ca at contaminated sites appears to reflect changes in calcine management. While radial profiles of other elements such as Ca, Mg, Al, Mn and P in soil are useful indicators of changing soil fertility and acidity, the level of detail obtained in this study was insufficient due to the inability to compare Al, Mn and P concentrations in soil versus stemwood since soil concentrations of these elements were not measured.

4. ***As and SO_2 contamination from mine activities has lead to decreased growth of jack pine at heavily contaminated sites relative to reference sites during the operational period of the mine and pollution-induced stress has impacted relations between tree-growth and climate at contaminated sites during this period.***

Comparisons of jack pine growth response to climatic conditions for mean contaminated and reference chronologies during the pre-operational and operational periods reveal that the climate-growth response is weaker during the operational period for both mean chronologies, however not much weight can be placed on this particular analysis since the sample size of the pre-operational period is very small ($n = 6$). Due to this constraint in data availability, it remains uncertain whether or not the climate-growth response of jack pine differs at contaminated and reference sites. Nevertheless, the onset of activity at Giant Mine coincides with divergences in growth patterns between mean contaminated and reference chronologies unprecedented in the pre-operational period covered by this study (1900-1948).

A growth release unique to the contaminated chronology is evident shortly after construction began at Giant Mine which may be due to improved resource availability for trees that were not felled during construction or possibly represent growth releases in the remaining trees. The removal of large numbers of trees would reduce competition between individuals for resources such as sunlight, moisture and soil nutrients and lead to growth releases.

Although both chronologies exhibit a decline in growth from the 1950s to 1970s, the contaminated chronology has lower growth which corresponds to increased As and reduced Mg and Ca concentrations in tree-rings at contaminated sites. Increased As in these rings indicate that As contamination may have played a role in hindering growth, however, it is unknown whether the As levels found in the trees of this study are high enough to initiate phytotoxic effects since tolerances have not been studied. Lower Mg and Ca in tree-rings may be related to pollution-induced stress due to SO_2 emissions since increased soil acidity can reduce nutrient uptake thus hindering growth. A significantly greater number of missing rings at contaminated sites also suggests that jack pine at these sites are growing under more extreme conditions than at reference sites.

6.2 Future recommendations

This study has shown that dendrochemical methods can be used to uncover information regarding the impacts of As and SO_2 contamination on tree-growth, however lack of understanding in certain key areas of tree physiology limit its applicability. This study was able to infer that certain changes in tree-ring chemistry corresponded to mine activities, such as calcine management and land clearance, yet was unable to show that tree-rings reflected changes in mine emissions. It is uncertain whether lateral translocation and high mobility of As are responsible for this disconnect since much research is yet required in order to understand As bioavailability from contaminated soils. Prior dendrochemical studies of As contamination (Martin et al., 2000; Cheng et al., 2007) affirm that further research is required to determine the role of lateral translocation in different tree species and for various elements. However, it is apparent from this study that further research is also required to understand the dynamics and mechanisms of As uptake and subsequent storage in tree-rings.

In association with toxicological study, more in-depth dendrochemical study of As concentrations in soil and tree-rings of jack pine could uncover useful information regarding As uptake from contaminated soils. This study was limited by the small sample size for soil and tree-ring data. It is recommended that a dendrochemical study that focuses on a smaller portion of the study area and includes; 1) chemical analysis of a greater number of jack pine cores, 2) a greater number of soil samples, and 3) well documented historical contamination information, would yield useful data for further study of As uptake from contaminated soils. Moreover, a comparative study of jack pine versus black spruce tree-ring chemistry could provide further information regarding As bioavailability since soil properties differ between these two forest stands.

Other avenues of research using data collected for this study could include, reconstruction of soil pH for assessment of soil acidification in the Yellowknife region and an examination of disturbance history and groundcover composition.

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