Dendroanalysis of Toxic Metal Pollution from the Sydney Steel Plant in Sydney, Nova Scotia

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1.0 Abstract

The Sydney Steel Plant emitted toxic pollutants into the local area for almost 100 years. Although no paper record exists of the amount and spatial variability of the pollutants emitted, a natural record exists locked in the annual growth of native tree species in the region. Studies have shown that temperate trees can incorporate local metal pollution into their annual rings, creating a temporal and spatial record of the pollution. Six abundant species were sampled within a 5 kilometre radius of the steel plant site. Using dendrochronology, atomic absorption spectrography (AAS) and x-ray fluorescence (XRF) on white birch, *Betula papyrifera* and eastern larch, *Larix larcina*, a preliminary analysis was preformed on a new methodology to extract a pollution signal. A method of core preparation and analysis was developed that incorporated three labs to quickly find levels of pollutants in a given year. Atomic absorption spectrography did not produce accurate results with the small sample sizes, and x-ray fluorescence determined that the hardwood birch was better able to incorporate both lead and zinc than the softwood larch. In the end, a viable method of investigation has been developed and will be used in further developments.

2.0 Introduction

The Sydney Steel Plant was an essential part of the history of the City of Sydney, Cape Breton, Nova Scotia. For 100 years, the plant produced steel for global markets and employment opportunities for the local and immigrant communities. Alongside these benefits, the processes involved in converting iron ore to steel produced a variety of pollutants. Polycholrinated biphenols (PCBs), volatile organic compounds (VOCs) and toxic metals have been released throughout the time that the plant was functioning (Joint Panel Review, 2006). These toxins have been of great concern to the city's residents. However, there is no clear, available long-term record of the pollution.

Another type of record exists naturally in the Sydney area. Temperate tree populations develop a new ring of growth each year. A number of studies have shown that a tree often uptakes and incorporates local pollution into its annual ring (Nabais 2001). Using this concept, a new methodology has been to help in understanding the problem of the Sydney Steel Plant and its missing emission record through time and space.

The main goal of this project is to extrapolate the toxic metal concentrations of lead, copper and zinc in the environment of Sydney by analyzing the annual ring wood using the rapid detection method of x-ray fluorescence (XRF). In order to accomplish this task, three smaller projects were undertaken. First, the materials and methodology for the three laboratory techniques were developed and refined. Second, atomic absorption spectrography (AAS) was attempted to standardize the time-efficient XRF analysis. Third, a preliminary XRF test was completed to compare the abilities of hardwoods compared to softwoods to incorporate metals into the annual rings.

3.0 Methods

3.1 Field Methodology

3.1.1 Study Area

All samples were taken with a 5 kilometre radius of the coke ovens site (N46°08.879', W 060°10.376') within the Sydney Steel Plant grounds. This sampling region was divided into 4 quadrants by north-south and east-west axis centered on the coke ovens. In each quadrant, 5 sites were sampled with efforts taken to disperse the sample sites evenly throughout the quadrant.

3.1.2 Study Sites

An area qualified as a sampling site if it was a) a natural forested area, b) contained three of the six target species and c) was removed from direct residential and commercial contact. The target species are as follows: white pine (*Pinus strobus*), black spruce (*Picea mariana*), eastern larch (*Larix larcina*), balsam fir (*Abies balsamea*), balsam popular (*Populus balsamifera*), and white birch (*Betula papyrifera*). Red spruce (*Picea rubens*), red maple (*Acer rubrum*) and sugar maple (*Acer saccharum*) were also

sampled if available. The oldest trees available were taken although the growth of Sydney limited the availability of finding old growth (over 100 years). Although all six focal species were collected, the preliminary experiments were conducted on white birch and larch alone. These species were chosen because of their abundance throughout the study sites and the ability of both species to lose their leaves and needles annually.

Once a site qualified, two trees of each focal species were sampled. A 5.1 mm increment borer was used to extract cores with the most mass for later analysis. Two cores per tree were extracted, where the second core (B) was taken directly below the first core (A) for future matching. Cores were each labeled accordingly and stored. Coordinates, as well as distance and direction from the coke ovens site, were noted at each site.

Fig. 3.1 A photograph of Sydney with study sites plotted in relation to the coke oven site marked as “Ground Zero” on the image.

3.2 Dendrochronological Methodology

Of each pair of cores, one core was prepared for analysis of tree ring width. The core was glued into a slotted mounting board and sanded to a fine, 600n grit polish. The ring width of the core was measured using a 63X light microscope coupled to a Velmex stage measuring system which measures annual tree rings to a precision of 0.001 mm. This measurement provided information on both the age of the core and the tree’s annual radial growth rate. The polished core was then used to help prepare the second core for XRF and AAS analysis.

The unprepared second core was lined up against the fully prepared and sanded first core. The polished core was used as a template to find corresponding ring boundaries

under the microscope on the unprepared core. Once ring boundaries were noted on the unprepared core, it was cut into two-year segments using a sterile scalpel blade.

3.3 X-ray Fluorescence (XRF) Methodology

Each two-year segment was taken to the Mount Allison Medical Physics lab and analyzed using an Innovex System Alpha 2000 x-ray fluorescence instrument. The standard soil-setting was used. Each core segment was fluoresced for 3 minutes. Within this time, the instrument bombarded the atoms of the wooden segment with x-rays, causing transition of electrons. This transition causes a characteristic fluorescence photon or x-ray to be emitted. The emitted spectrum can be interpreted to reveal to the composition and concentration of elements within the segment. The Innovex instrument software calculates concentrations in ppm for any available elements, including the metals of interest – lead, zinc and copper.

3.4 Atomic Absorption Spectrography (AAS) Methodology

The wooden sample (either biannual or 1 cm segment), in a crucible, was placed in a muffle furnace. It was heated to 550˚C for 12 hours (overnight). After being cooled, the sample was weight again. In order to dissolve the ash, 1 mL of Aqua Regia ($HCl:HNO_3$ – 3:1) was added for 2-4 hours on a hot plate set at 80˚C. Once there only a salt remained, It was diluted it to make a 10 mL solution with distilled, de-ionized water in a volumetric flask. Standards were used to calibrate the Varion AA instrument and then each 10 mL sample solution was run and values (in ppm) acquired.

3.5 Project Division

With these methodologies developed, two smaller projects were developed to attain a better focus for the overall goal of the project. XRF calibration and hardwood-softwood comparisons were undertaken using the above methods.

3.5.1. Project 1: XRF Calibration

XRF allows for quick, precise analysis of elemental concentrations in the tree samples, however, it was not known if the concentrations reported by the process were accurate or if they needed to be calibrated as the instrument was made for other purposes. The first project was to develop a method of determining absolute concentrations to better calibrate the XRF values. AAS was therefore used to accomplish this task.

At the coke ovens site, a number of larch and birch cores were extracted for both AAS and XRF analysis. One core from each tree was cut into 1 cm long pieces, totaling 7 pieces overall. The samples needed to be at least 1 cm in order to provide enough mass for processing. Each piece was dried and weighed analytically (to 0.0001 g). Each piece was then analyzed for 5 minutes using XRF analysis. The sample was then processed and run through AAS. The values were complied and compared for consistency.

3.5.2 Project 2: Wood Type Comparison

Although XRF provides a time-efficient method of elemental analysis, not all samples could be run. In order to attain the best record of steel plant pollution, the two general types of trees were tested. Hardwood and birch were represented by white birch and eastern larch, respectively. One tree of each species from each quadrant were used and for three of the four quadrants, the birch and larch samples were from the same site. All samples were analyzed using XRF and compared.

4.0 Results

4.1 Dendrochronological Results

All birch and larch cores were measured and converted into decadal format. The data determined the age of each tree. See Table 8.1 for values. The tree ages were used to guide which trees were first analyzed. The oldest trees were used to obtain the oldest record for XRF analysis. The age of the tree core, and therefore, the contamination record, is examined in Section 4.3. **At the present moment, growth rates are unanalyzed due to the limited number of core samples from any given area to create a strong master chronology.**

Table 8.1 - Dendrochronological analysis of tree age for all larch and birch tree cores in a 5-km radius of the coke oven site. The samples in bold were chosen for further analysis.

Larch			**Birch**		
Tree	**Oldest Ring**	**Age**	**Tree**	**Oldest Ring**	**Age**
7ADL711	**1927**	**79**	7ADLC01	1939	67
7ADL712	1943	63	7ADLC02	1935	71
7ADL721	1955	51	7ADLC11	1948	58
7ADL722	1940	66	7ADLC12	1951	55
			7ADLC13	**1913**	**93**
			7ADLC21	1937	69
			7ADLC22	1937	69
			7ADLC31	1976	30
			7ADLC32	1957	49
7AEL701	1923	83	7AELC01	1960	46
7AEL702	1937	69	7AELC02	1961	45
7AEL711	1979	27	**7AELC11**	**1951**	**55**
7AEL712	1983	23	7AELC12	1966	40
7AEL721	1960	46	7AELC21	1966	40
7AEL722	1951	55	7AELC22	1960	46
7AEL741	**1983**	**23**	7AELC31	1952	54
7AEL742	1989	17	7AELC32	1950	56
7AFL701	**1933**	**73**	**7AFLC01**	**1960**	**46**

7AFL702	1951	55	7AFLC02	1951	55
7AFL711	1985	21	7AFLC11	1983	23
7AFL712	1988	18	7AFLC12	1974	32
7AFL731	1960	46	7AFLC21	1961	45
7AFL732	1969	37	7AFLC22	1952	54
7AFL733	1978	28	7AFLC31	1963	43
			7AFLC32	1956	50
			7AFLC41	1936	70
7AGL701	1957	49	7AGLC01	1938	68
7AGL711	1967	39	7AGLC02	1954	52
7AGL712	1963	43	7AGLC11	1967	39
7AGL721	1938	68	7AGLC12	1966	40
7AGL722	1920	86	7AGLC21	1921	85
7AGL731	**1944**	**62**	7AGLC22	1907	99
7AGL732	1949	57	7AGLC31	1951	55
			7AGLC32	**1952**	**54**
			7AGLC41	1942	64
			7AGLC42	1947	59

4.2 XRF Calibration Results

In each comparison, the dry weight value was lost for larch sample number 5, so it is excluded from the results. The wet weight was considered to be used, but thought to be less precise.

4.2.1 Lead Concentration Comparison

Lead concentrations analyzed through AAS were difficult to interpret as there were both positive and negative values. Generally, the values fluctuated around zero ppm, indicating that lead was detected using AAS. Using XRF, lead values were low, fluctuating around 1.5 ppm, yet they were detected. *Relative rises?*

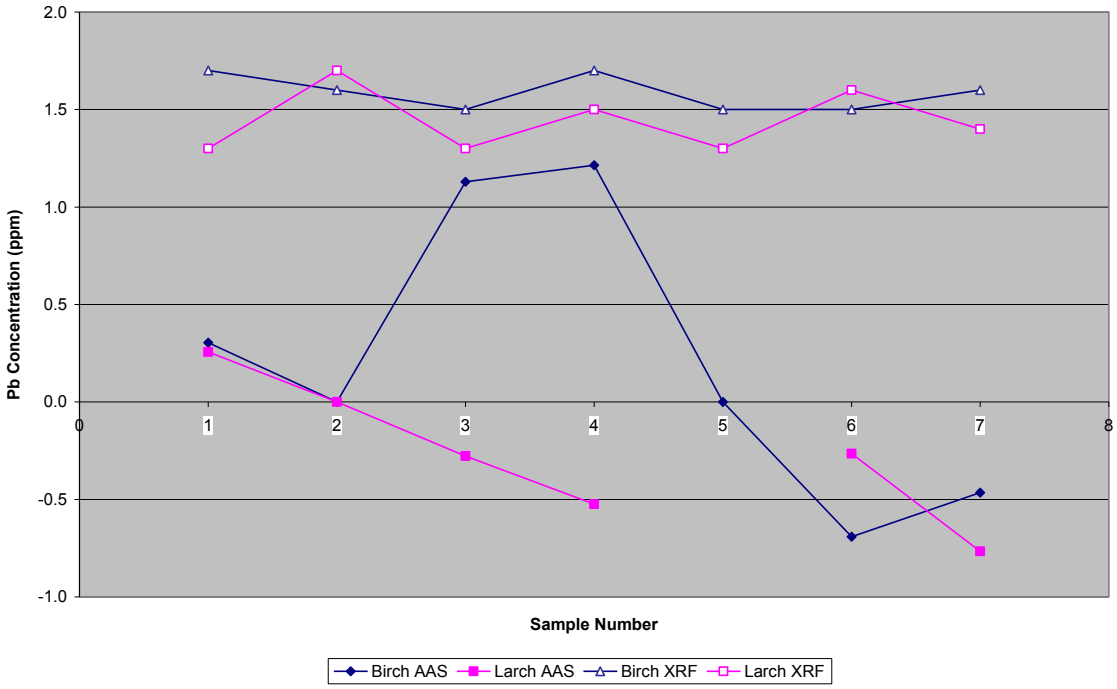

Fig. 4.1 Concentration of lead (ppm) in birch (in blue) and larch (in pink) tree cores analyzed using AAS (filled in marks) and XRF (empty marks) (N=7)

4.2.2 Zinc Concentration Comparison

In comparing the two analytical results for birch, AAS values vary a great deal more than XRF. XRF values begin low between 13-18 ppm and then peak at 43 ppm before dropping again. It creates a range of about 30 ppm which is drastically different than the AAS results. AAS produced concentration with a range of only 5 ppm from 5 to 10 ppm.

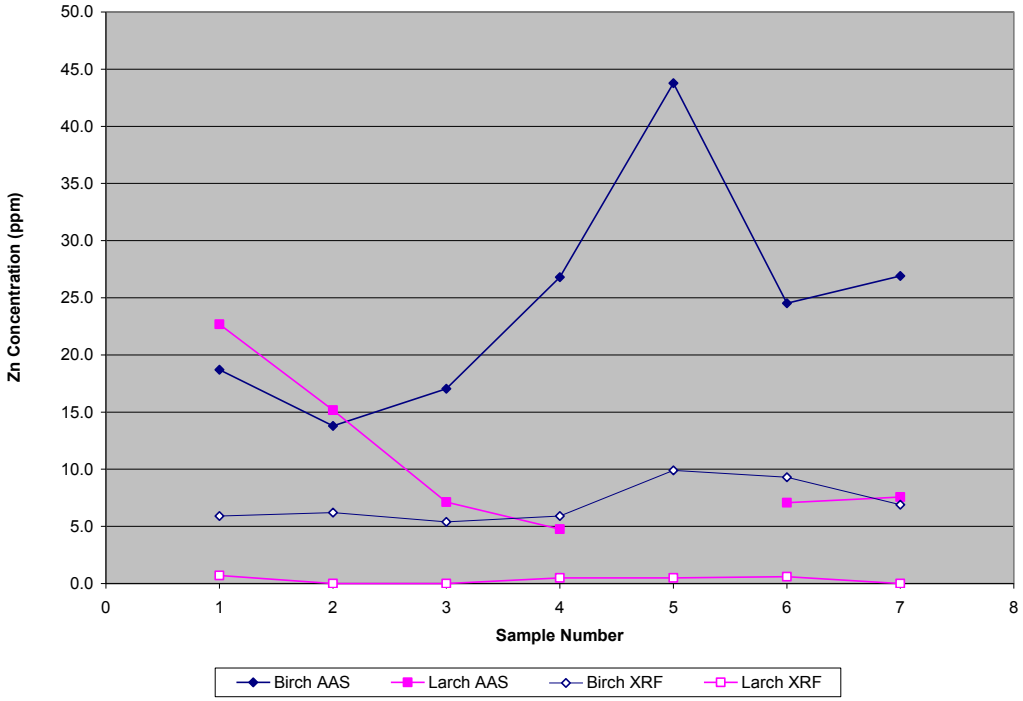

Fig. 4.2 Concentration of zinc (ppm) in birch (in blue) and larch (in pink) tree cores analyzed using AAS (filled in marks) and XRF (empty marks) (N=7)

4.2.3 Copper Concentration Comparison

Copper was detected by AAS in both larch and birch, although it was very low and fluctuated a great deal. The AAS range was about 2 ppm, between 0 and 2 ppm. Copper levels were too low to be detected by the XRF in both species for all samples.

Fig. 4.3 Concentration of copper (ppm) in birch (in blue) and larch (in pink) tree cores analyzed using AAS (filled in marks) and XRF (empty marks) (N=7)

4.3 Wood Type Comparison Results

The values given by the Innovex Alpha 2000 instrument were used directly to provide the results for this report. Although the values are not exact, the relative differences between values are true. *Future efforts will be made to standardize the values, potentially in terms of segment mass or "zero" trees taken from isolated, uncontaminated areas.*

The larch and birch within each quadrant were taken from the same site. For example, in the northwest quadrant, both larch and birch were taken from the Big Aspen Site. This consistency was maintained to theoretically keep local emission concentrations the same. The exception is in the northeast quadrant, were larch from the Frederick St. site and birch from the Shooting Range site which are 2.4 kilometers apart. The following table lists the sites and distances for each XRF core sampled.

Site	Site Name	Distance (km)
07ADLX10		4.59
07AELX40		0.81
07AELX10		3.16
07AFLX00		4.96
07AGLX30		2.09

Table 4.1 Summary of sites and distances for XRF samples

In terms of record length, birch species provided the longest record with 07ADLC13, extending back to 1928. Five records are overlapping until 1964 which the youngest segment of 07AFLC01. Larch cores have useable segments back to 1940 with the sample 07AFL701. All cores provide records back to1984, which is the first year of the youngest core 07AEL741. Overall, birch has the longest record, and its overlapping, stronger data years are longer as well.

4.3.1 Lead XRF Results

Within the existing record, larch lead concentrations range between 0 – 30 ppm, or 10-30 ppm when excluding the segments which had a concentration less than the limit of detection (< LOD). All birch lie in a range between 12 – 52 ppm and no segments contained a concentration less than the limit of detection (< LOD).

In the analysis of lead uptake in annual rings, larch and birch species are divided into two general ranges. Both species have concentrations ranging to 0 due to concentrations < LOD. However, the majority of birch segments are contained within the 25-45 ppm concentration range. The larch segments are generally found in a lower range between 10-25 ppm. Samples 07AELC11 and 07AFLC01 show a strong decreasing trend from the later 1960s to 2006. This decreasing trend is not mimicked in the other birch samples 07AFLC13 and 07AGLC32, where they are constant (fluctuating around 20 ppm) and more in the same range as the larch concentration values.

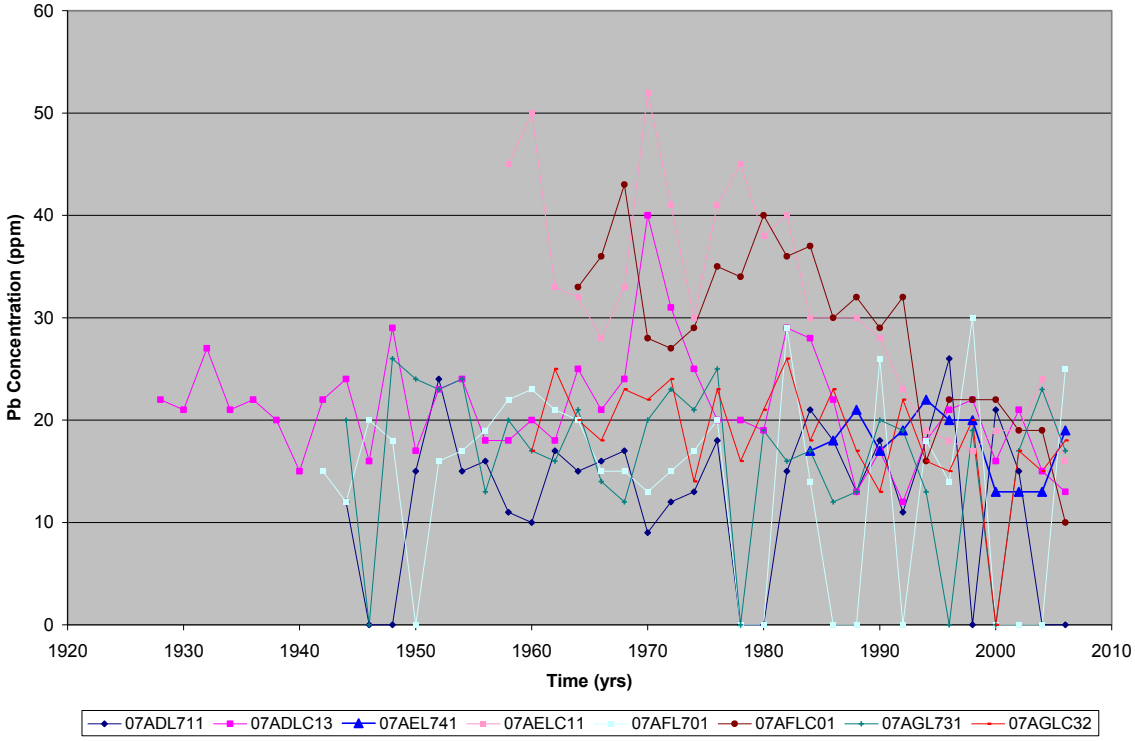

Fig. 4.4. Lead concentrations analyzed using XRF for one birch (red shades) and one larch (blue shades) tree core from each quadrant of the study site.

4.3.2 Zinc XRF Results

The zinc results for larch are low in all cores. Almost all segments have zinc concentrations < LOD. Cores 07AEL741 and 07AFL701 are the only cores with detectable zinc levels ranging from 8-16 and 13-54 ppm respectively. Birch results are in the range of 26-180 ppm, with a decreasing trend to present day in all cores over time.

The larch and birch XRF results are again grouped into two general groups. Larch concentrations are below detectable levels, and so are interpreted to center on 0 ppm. Birch has continually detectable zinc levels and has a general range between 30-160 ppm. Samples 07AELC11 and 07AFLC01 show this downward trend most strongly, followed by 07AGLC32. Sample 07ADLC13 has a less distinct trend, with only a shallow slope that could be considered horizontal.

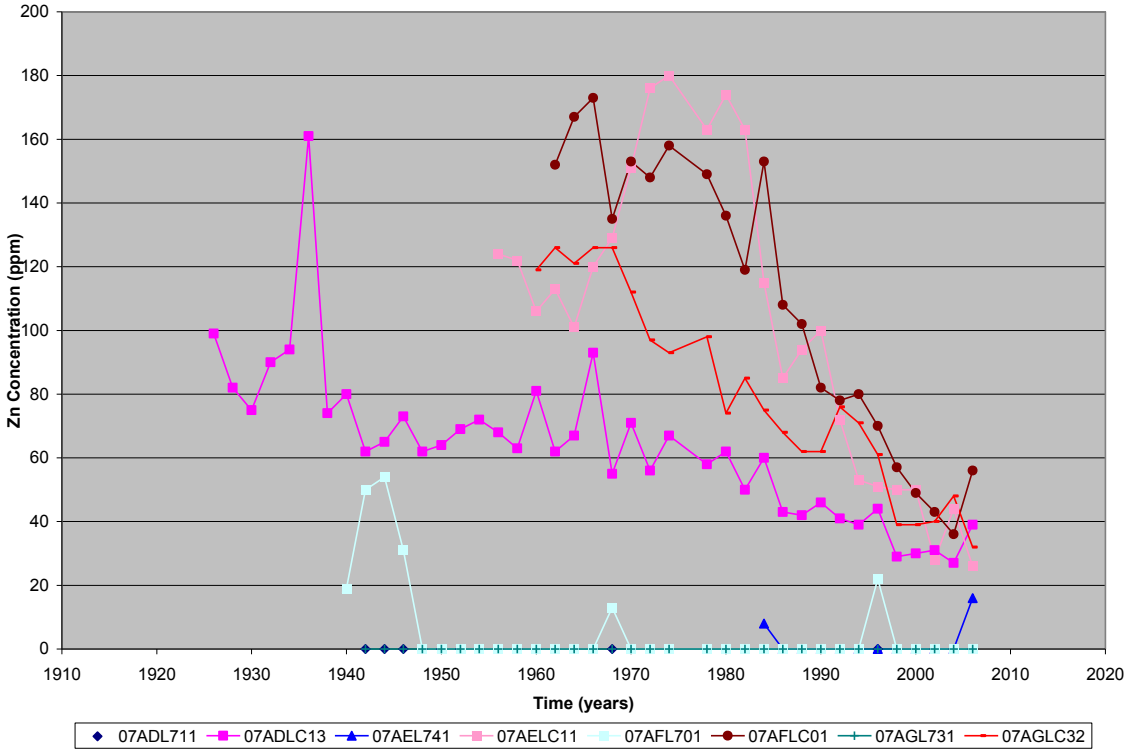

Fig. 4.5. Zinc concentrations analyzed using XRF for one birch (red shades) and one larch (blue shades) tree core from each quadrant of the study site.

5.0 Discussion

5.1 XRF Calibration

Atomic Absorption Spectrography results did not provide a consistent numerical value to calibrate the XRF results. As AAS determines absolute concentration, these values could be used to calibrate the XRF values, as the XRF has no zero value (as trees cannot be found with known metal concentrations). It was expected that the pattern of XRF results would be paralleled by the AAS results, and would be separated by some

consistent numerical value. This value could be used on all further XRF values for calibration.

However, in lead, zinc and copper analysis, there was no consistency to the AAS values. In each run, both larch and birch AAS values were found in the same range, yet there was no consistency as to whether the XRF or AAS values were higher. The increases and decreases between sample values did not match, indicating that the two sets of results did not mimic each other in an accurate way to produce a conversion coefficient.

Lead concentrations did not register using AAS. As levels were detected using XRF, lead should have been detected in this method. However, due to the inaccuracy of the muffle furnace temperature, the temperature may have increased to point where lead may have become volatile and blew off, leaving none to be detected by AAS.

Zinc and copper concentrations were detected by AAS, yet the XRF values were low and often undetectable in this method. The values were difficult to compare for this reason, especially for copper. Zinc has the closest mimic between XRF and AAS for any of the three metals.

Overall, this method did not provide the desire calibration coefficient. A major reason is the sample size. No replicates were completed due to the limited sample mass and only one core was run for each species. The low sample numbers allow for a lot of imprecision that now cannot be interpreted. If this method were to be successful, many more cores and trees should be sampled and run through both AAS and XRF. Zinc concentrations should be the focal metal, as they showed the most positive results for linking the two metal analysis methods. Due to time restrictions, this experiment cannot be completed.

No trend was found in terms of temporal concentration changes due to the gross size of the sample cuts. In terms of calibration, the AAS values did not mimic the XRF values. No consistent value difference could be determined between the two sets of results in order to allow for a numerical calibration of either species.

5.2 Wood Type Comparison

As samples from each quadrant are taken from the same site, one would expect both species to contain the same concentration of lead and zinc, as their exposure would be approximately the same over time. The difference of concentrations between the two species is indicative that birch and larch, which are representing hardwood and softwood, have different uptake abilities.

In each quadrant, the hardwood birch sample registers a higher level of lead and zinc than the softwood larch sample. With the same exposure, birch trees are able to uptake a higher concentration of the metals into their annual rings. Birch tree annual rings consist of many small, densely packed cells. Larch cells are less densely packed, and contain tracheids which allow for less concentrated water, and therefore metal, movement.

5.3 Historical Trends

In lead analysis, there is distinct decreasing trend with the cores 07AELC11 and 07AFLC01. In zinc analysis, the decreasing trend can be seen in the previously mentioned two cores as well as in 07AGLC32. This trend is indicative of the historical pollution in the area. The key year is 1988. At that time, the coke ovens, which was the largest polluter of the steel plant, was shut down. Therefore, there should be an apparent decrease after this year. Within the lead analysis, the reactive cores show a drop from fluctuating around 40 ppm to 20 ppm after 1988. In the zinc analysis, each reactive core shows concentrations over 100 ppm steadily decreasing after 1988 to a value less than 60 ppm. In each case, the bi-annual fluctuations are not significant, as they are more likely due to measurement errors. However, the overall decreasing trend is apparent and significant as it matches this historical timeline.

8.0 References