

Mapping the Sydney Steel Plant Pollution: An Application in Dendroanalysis

By

Hannah Catherine MacDonald

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ABSTRACT

The Sydney Steel Plant operated for almost a century in the middle of the growing city of Sydney, Nova Scotia. Along with its steel, the plant (specifically the Coke Ovens) produced an array of pollutants including toxic metals. Although historically relevant, there is no consistent written record of this pollution throughout the steel plant's history. The goal of this study is to produce a record of the Sydney Steel Plant pollution through both time and space.

In order to establish a record, a natural bioindicator was needed. Within the Sydney area, a previous study determined that white birch (*Betula papyrifera*) were able to incorporate varying amounts of lead and zinc from the environment into their annual growth rings. In order to access this record, 18 white birch trees were sampled within a five kilometre radius of the Coke Ovens. Two cores were extracted per tree - one processed for dendrochronological analysis and the other processed into biannual segments for dendroanalytical analysis. The dendroanalysis consisted of using energy-dispersive x-ray fluorescence to detect the lead and zinc concentrations. In order to standardize the study area samples with base level concentrations of the metals, white birch samples from two pristine sites were also analyzed in the same manner.

Lead and zinc concentration data were analyzed for spatial and temporal trends using a repeated-measures 2-way ANOVA, temporal change mapping and biannual pollution map animations. The results from this study illustrate a temporal trend of decreasing concentrations of both metals over time, especially after the Coke Ovens closure. The spatial trend indicates differential pollution distribution following the dominant wind direction. Although the results are approximate, the animations produced in this study are the most thorough pollution record for the Sydney Steel Plant. Overall, this study proved to be a successful application of dendroanalysis providing the highest annual resolution record using the energy-dispersive x-ray fluorescence technique to date.

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1.0 INTRODUCTION

1.1 Sydney Steel Plant History

The Dominion Iron and Steel Company (DISCO) produced its first steel in Sydney, Nova Scotia in December of 1901. Amidst national industrialization and immigration, the steel plant began a boom in the city of Sydney. At the time, the plant was the largest steel mill in North America with 400 coke ovens, four blast furnaces and ten open-hearth furnaces. Throughout its 99 years in operation, the steel plant changed hands and names multiple times. The structure of the plant and the coal supply also fluctuated with changing technology and economics (Barlow and May, 2000).

The population of Sydney experienced a 600% increase in size between 1891 and 1911 as thousands of workers and their families flocked to the region. The DISCO mill quickly became the focus of Sydney's economy and community, attracting a dedicated workforce and producing a vast amount of Canada's steel. With this economic prosperity came social and environment costs. The steel plant's potent emissions were a daily presence in the communities that bordered on the mill, notably Whitney Pier and Ashby (Beaton 1992). Historically, the steel mill's emissions were not a prominent environmental or health concern for a variety of reasons. Social welfare concerns at the time were more immediate, including the dangerous working conditions associated with steel production and establishing workers' rights. Further, the steel plant's emissions were often considered a necessary evil to gain economic prosperity and employment. With other concerns taking priority, there is little evidence showing that these emissions were regularly tracked or treated throughout the plant's history leaving no paper record of the amount of pollution released into the environment (Furimsky, 2002).

1.2 Steel Plant Pollution

The Sydney Steel Plant has left a legacy, not as the centerpiece of Sydney's economy, but in the form of the Sydney Tar Ponds. After decades of steel production, the Tar Ponds replaced the Muggah Creek estuary as by-products of the Coke Ovens (including tarry sludge, ammonium sulphates, benzenes, polycyclic aromatic hydrocarbons (PAHs) were disposed of on the site or in the estuary (Barlow and May, 2000). It is estimated that the Tar Ponds contain more than 700 000 tonnes of sediments contaminated with PAHs and metals (AMEC, 2005). Although the Tar Ponds are well publicized, the contaminated area extends much further than the immediate area of the Sydney Steel Plant Site.

While there were multiple sources of pollution on site, in 1975 approximately 95% of the steel plant's ground level pollutants were derived from the coking processes. This fact makes the Coke Ovens the most likely main polluter of the operation (Furimsky, 2002). The coking process involved heating coal to high temperatures in the absence of oxygen to produce coke (a hard, 90% carbon substance) which is required in iron smelting (Beaton, 1992). At this high temperature, a by-process is the volatilization of metals including toxic metals such as lead and arsenic. It was discovered that six varieties of Cape Breton coal ash (typical of coal used in the Coke Ovens for much of its operation) contained significant (> 100 ppm) concentrations of lead, arsenic, zinc and chromium. These toxic metals, once cooled and released as coke oven gas, form or deposit on particulates. Once in particulate form, the metals were wind distributed widely, far from the initial source of the steel plant (Furimsky, 2002). Although the coking of coal released lead, arsenic, zinc and chromium, a previous dendroanalytical study found that only lead and zinc left a detectable, elevated signal in Sydney area trees (MacDonald et al., *in press*).

The Sydney Tar Ponds represents the remnants of Sydney's steel production zone, and is the target area for the main clean-up processes today. Suggesting that the Tar Ponds is the only site requiring clean up post-steel production is misleading. Furimsky (2002) notes site contamination by toxic metal-containing particulates is a more serious contributor. As toxic metals are a health concern and are traceable, they are important pollutants to track.

1.3 Spatial Effects of Emissions

There have been a number of studies that have investigated the spatial distribution of the toxic metals associated with Sydney Steel Plant pollution. Lambert and Lane (2004) conducted a study comparing soil from the three closest communities to the Sydney Steel Plant and areas 5 to 20 kilometres from the Coke Ovens. The study looked at background concentrations of both toxic metals and PAHs. The study found that soil within the bordering communities of Whitney Pier, Ashby and North End Sydney contained significantly different concentrations of lead, arsenic and PAHs than those soils taken from areas 5 to 20 kilometres away. In some samples within these bordering communities contamination levels for lead, arsenic and some PAHs were still above the Canadian Council of Ministers of the Environment (CCME) guidelines many years after the Coke Ovens shut down.

The psychological impacts of the steel plant on Sydney's residents have also been studied. O'Leary and Covell (2002) investigated the concern for the environment and health in adolescents in relation to their proximity to the steel plant. They found that adolescents living in the immediate vicinity of the steel plant had more frequent environmental and health worries, which predicted depression rates. Their environmental and health worries were significantly more frequent than the comparison group living 40 kilometres from the steel plant.

Although there has been investigation into the spatial impacts of the steel plant pollution, there has been no thorough pollution record constructed through time. A sufficient record was not kept during the plant's operations as there is only sporadic documentation of pollution. Soil studies (i.e. Lambert and Lane, 2004) provide a widely-distributed set of samples, but it is only a measure of what was present at the surface when they sampled. A better measure of pollution would consist of a record which extends into the past, combined with highly-distributed measurements throughout the city.

1.4 Dendroanalysis

Most trees species in temperate regions, such as Nova Scotia, produce annual growth rings. It has long been recognized that the rings of many of these species are known to fluctuate with climate (Fritts, 1976). The knowledge of this radial growth-climate relationship has been applied to create radial growth chronologies extending knowledge of long-term regional climate (Fritts, 1976). But, the principles of dendrochronology have also been extended to look at other influences, including pollution stress.

Over the past 50 years, the concept of dendroanalysis and its utilization as an analytical tool has grown such that it is now a field unto its own. The basic assumption of dendroanalysis or dendrochemistry is that the chemical makeup of the annual woody increment at least partly reflects the chemistry of the environment during the year of formation (Watmough, 1999). The wood that is put on in annual rings partially depends on the mineral uptake of the tree – which sometimes also includes metals. By extension, the amount of mineral uptake may reflect the amount of minerals in the environment in which the tree is growing in that particular year. This

theory has allowed the exploration of trees as retrospective biomonitors of trace metal pollution (Prasad, 2001).

There has been no definitive conclusion within the scientific community as to the feasibility of dendroanalysis as a technique. Dendroanalysis has been successfully used to study pollution for a variety of regions and metals. Toxic metal pollution has been able to be successfully monitored in a variety of environmental conditions, including metal pollution from smelters (Aznar et al., 2008), pesticide production and leaded gasoline (Burnett et al., 2007) and lead mining and smelting (Patrick and Farmer, 2006). However, the results of each of these studies must be evaluated independently because of the uptake of the individual qualities of metals studied (Watmough, 1999) and each individual tree species studied (Prasad, 2001). Although there have been successful attempts to use the analysis methods, complications have also lead to unsuccessful applications of dendroanalysis. Tree physiology (Martin et al., 2000) and metal mobility (Horn et al., 1997) have hindered the ability of trees to uptake some metals and lock them in time within the growing annual ring. Without this stabilization ability, dendroanalysis cannot be used in biomonitoring. With these obstacles in mind, careful planning and testing of studies is required to allow for any dendroanalysis procedure to be properly and successfully applied.

1.5 Techniques in Dendroanalysis

There have been a variety of methods used in dendroanalysis. Graphite furnace atomic absorption spectrography (Mederios et al., 2008), inductively-coupled plasma mass spectrography (Kirchner, 2008), lead isotope ratios (Patrick and Farmer, 2006) and synchrotron radiation x-ray fluorescence (de Vives et al., 2006). Each technique analyzes metals either

within one annual ring or between multiple annual rings. However, these techniques are either expensive (keeping samples size small) or their annual resolution is low.

Similar to other x-ray fluorescence (XRF) techniques, energy-dispersive x-ray fluorescence (ED-XRF) is able to analyze different materials for a variety of elements simultaneously with relatively low detection limits. Compared to synchrotron or three-axial scanning XRF, energy-dispersive XRF is less expensive to operate which allows for higher sample size and more accessibility. ED-XRF has had limited application with dendroanalysis. This technique has been used to analyze lead and zinc in bayous, but its annual resolution was low at five years (Latimer, 1996).

In dendroanalytical studies requiring a large sample size, such as in a highly distributed pollutant study, the low-cost of ED-XRF allows for many runs covering a large number of samples, at a large number of sites. Efforts can also be made to increase the annual resolution with the newer generation equipment now available, in order to have a more precise temporal analysis of environmental contaminants.

1.6 Objective

The main objective of this project is to determine the extent of the Sydney Steel Plant toxic metal pollution across the city of Sydney through both time and space. This will be accomplished using ED-XRF analysis of lead and zinc found in annual rings of tree cores from the most abundant hardwood species in the city, white birch (*Betula papyrifera*). Using a novel dendroanalytical technique, my thesis will produce the first toxic metal concentration pollution map for Sydney for as far back in time as the tree cores will allow.

2.0 STUDY REGION

2.1 Climate

Sydney, Nova Scotia (46° 10.200' N, 60° 3.000' W) is located on the eastern part of Cape Breton Island in northern of Nova Scotia (Figure 2.1). The city borders the Sydney Harbour which opens into the Atlantic Ocean (Figure 2.1). The average daily temperature is 5.5°C, ranging from -6.5°C to 17.7°C over the year (Environment Canada, 2008). A total of 1504.9 mm of precipitation per year falls on the city, with the majority falling as rain between October and May (Environment Canada, 2008). Annually, the dominant wind direction is from the south and averages 18.6 km/h. The summer wind is mainly from the south and the winter wind from the west (Table 2.1). The only month to deviate from south and west is April with a wind from the north (Environment Canada, 2008).

Table 2.1 Monthly and annually most frequent (dominant) wind directions in Sydney, Nova Scotia based on 30 year climate normals (1970 to 2000) (Environment Canada, 2008).

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Annual
Direction	W	W	SW	N	S	S	S	S	SW	SW	W	W	S

2.2 Study Area

The Coke Ovens (46°08.879' N, 60° 10.376'W), now demolished, were located on the eastern portion of the Sydney Steel plant site. As the Coke Ovens were the main source of toxic metal emissions (Furimsky, 2002), this location became the center of the study area in this study (Figure 2.1). The sampling area was bounded by a five kilometre radius around this point. The sampling area was divided into four quadrants following the four cardinal directions, with the axes centered on the Coke Ovens.



Figure 1
 Figure 2.1 Map of the study area in Sydney, Nova Scotia, illustrating the distribution of study sites.

2.3 Sampling Site and Species

Within each quadrant, five sampling sites were chosen according to following criteria. The site must: a) be a natural forested area, b) contain the focal tree species and c) be removed from direct residential and industrial contact. The goal was to choose sample sites at a variety of distances and directions from the Coke Ovens; however the availability of natural forest area within the city led to some restrictions. The distribution of the 20 sampling sites can be seen in Figure 2.1.

The most dominant hardwood species was selected since it allowed for sampling over the widest area. A previous study in the same area determined that white birch was better able to record lead and zinc metal emissions than other tested species, and so it became the focus for this study (MacDonald et al., *in press*).

In order to establish a normal base level range of lead and zinc within white birch tree rings in the region, two pristine sites were sampled. The pristine sites selected needed to be at least 20 kilometres in the opposite direction of the dominant wind from the Coke Ovens in order to reduce the potential impact of the steel plant pollution. The two sites chosen were New Boston Road (46°58' 39.7" N, 60°01' 55.7" W) and Stirling (45°44' 35.3" N, 60°29' 08.4" W). New Boston Road is 21.9 km south-southeast of the Coke Ovens and Stirling is 51.2 km south-southwest. It should be noted that the study region includes the study area (within 5 kilometres of the Coke Ovens) and the pristine sites.

3.0 MATERIALS AND METHODS

3.1 Field Sampling

Both pristine and contaminated sites were identified, and distance and direction from the Coke Ovens were recorded using a handheld GPS unit. Two white birch trees were sampled using a 5.1 mm increment borer to extract cores, with two cores collected per tree at approximate breast height (1.3 m). After the first core was sampled, the second core was taken directly (1 cm) below the first core along the same radii direction. This sampling method allowed both cores to be as similar as possible in terms of ring-width parameters. This method was utilized as one core from the pair would be used in a dendrochronological analysis (Section 3.3) while the second core would be used in ED-XRF procedures (Section 3.4). Cores were labeled and stored in clear plastic straws, then transported to the Mount Allison Dendrochronology Laboratory for further analysis.

3.2 Dendrochronological Applications

3.2.1 Radial Width Measurement

The longest, and presumed oldest, core, was selected for dendrochronological preparation. This core was glued into a slotted mounting board and sanded to a fine polish (600 grit). The mounted cores were measured using a Nikon SMZ800 continuous zoom 63X light microscope coupled to a Velmex stage measuring system which measured annual tree rings to a precision of 0.001 mm. The measurements were captured using Measure J2X v. 3.2.1 software (VoorTech Consulting, 2004). These measurements provided information on both the age of the tree and the annual radial growth rate of each annual ring.

3.2.2 ED-XRF Preparation

The parallel extraction of cores from the trees allowed for an easily detectable similarity in ring widths between the mounted core for dendrochronological analysis to the unmounted core for ED-XRF processing. This second (shorter) core was aligned against the sanded core, and the polished sample was used as a template to determine ring boundaries on the unprepared sample. To aid in this visualization, a small amount of hand-sanding was completed on the unprepared core with fine sandpaper (200 to 600 grit). Ring boundaries were located on the unprepared cores which were then cut into two-year segments using a sterile scalpel blade. The biannual segments for each core were labeled and stored for further analysis.

3.3 Crossdating

In order to determine if the white birch rings were growing in a similar manner, the cores were crossdated. This process establishes a pattern match between annual radial growth increments. The program COFECHA 3.0 (Holmes 1983) was used to establish if the radial growth measurements from each tree had a similar signal as the collective group from a site. COFECHA does this by applying a Pearson product moment correlation at the 99% significance level to determine the quality of the pattern match between a measured series and the overall group's radial growth rate (Grissino-Mayer, 2001).

3.4 ED-XRF Analysis

The biannual segments were analyzed using an Innov-X System Alpha-4000S ED-XRF instrument (Innov-X Systems Canada, Mississauga, Ontario). Each sample was run under standard soil settings for three minutes. Throughout this time interval, the instrument bombarded

the atoms of the small wooden segment with x-rays. The emitted spectrum was then interpreted to reveal the composition and concentration of elements within the segment being analyzed (Murphy, 2006). The Innov-X instrument software calculates concentrations in parts per million (ppm) for any detected elements, including the two focal metals in this study – lead and zinc.

Limits of detection for this data were defined using the 3σ calculation method, and varied slightly between different segments. Average limit of detection in birch trees is 12 ppm for lead and 18 ppm for zinc (MacDonald et al., *in press*).

3.5 Metal Concentration Analysis

In order to determine any temporal and spatial patterns in the lead and zinc pollution records, various methods of statistical analysis were undertaken. Standard statistical analysis was completed using a repeated measures 2-way ANOVA test. To expand this analysis, mapping techniques were also used to explore any spatial and temporal trends.

3.5.1 Repeated Measures 2-Way ANOVA

To analyze the significance of spatial and temporal effects within the toxic metal data, a repeated measures 2-way ANOVA was run in SPSS v.16.0 (SPSS Inc., 2007). The metal contaminant value was the dependant variable. The tree core was the block and distance, direction and time were the independent variables. Within the independent variables, time was the within subjects variable and distance and quadrant are between subjects variables. As the years do not need to be evenly spaced for this test, but all years must have data from all samples, the years chosen were 1976, 1986, 1988, 1990 and 2006. In the ANOVA, not all assumptions of this parametric test were met meaning the results can be interpreted with caution. However, the non-parametric test equivalent, Friedman's Test, was completed to verify the results.

3.5.2 Temporal Change Mapping

To analyze the temporal effect of pollution, a linear regression was applied to the metal data of each tree core. ARSTAN (Cook, 1985) was employed to run a linear regression on both the lead and zinc data. From the regression, the slope is indicative of change in each core's metal concentration over time.

For the maps, the interval between 1966 and 2006 was selected for two reasons. A similar time period is required for each regression in order to compare the slopes. As all but one core extends back to 1966, this year provides a suitable interval. This interval is also appropriate as it encompasses 20 years before and after Coke Ovens closure.

The linear regression slopes indicate the magnitude of the change in metal concentration over time. By mapping these slopes, the spatial distribution of this temporal change between 1966 and 2006 can be better visualized. The slopes of each metal were plotted using the program SURFER v. 6.04 (Golden Software, Inc., 1997). Using contour maps, the slopes were plotted and extrapolated over the study area using the Kriging gridding method.

3.5.3 Biannual Pollution Map Animation

The biannual metal concentration data was plotted using SURFER. Contour maps were produced for each year of metal data and were then also extrapolated with the Kriging gridding method. The biannual maps were then overlaid with the spatial site locations whose data was used in producing annual maps. These maps were then compiled in yearly order using Windows Movie Maker v 5.1 (Microsoft, 2007) to produce an animated map of the changes in the study area pollution.

4.0 RESULTS

4.1 Metal Base Level Establishment

In order to determine the base level for the toxic metals in trees in the study area (i.e. within 5 kilometres of the Coke Ovens), cores from the pristine sites (i.e. at least 20 kilometres from the Coke Ovens) underwent the same testing as the study area cores. Information on lead and zinc base level concentrations were determined both by concentration values considered individually and overall trends (via linear regression).

4.1.1 Lead Base Level

Figure 4.1, illustrates that the lead concentrations from the pristine cores fluctuate between less than the LOD and 40 ppm. The average concentration for the four cores ranges from 13 to 22 ppm (Table 4.1).

In order to determine how much variation was found in lead concentration at the pristine sites, the slopes of the metal concentration records were analyzed. Table 4.1 illustrates that the slopes are shallow and fluctuate between small negative and positive values. Focusing on the two oldest cores (08TLC02,3), it can be seen that there is a very small slope (less than 0.04) in these pristine cores.

Table 4.1 Average values and linear regression slope and intercept values of lead concentration for pristine site cores.

Core	Average	Slope	Intercept
08RLC01	15	-0.089	16.05
08RLC02	13	-0.257	15.14
08TLC02	19	0.012	13.31
08TLC03	22	0.038	11.13

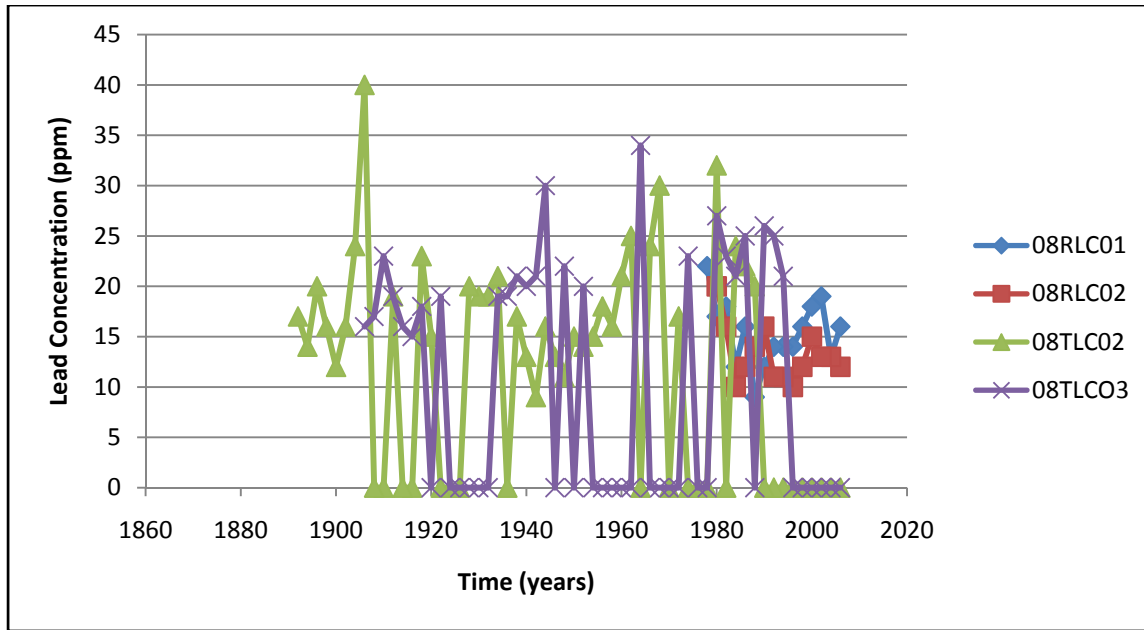


Figure 4.1 Lead concentrations (in ppm) from the four birch samples at the two pristine sites.

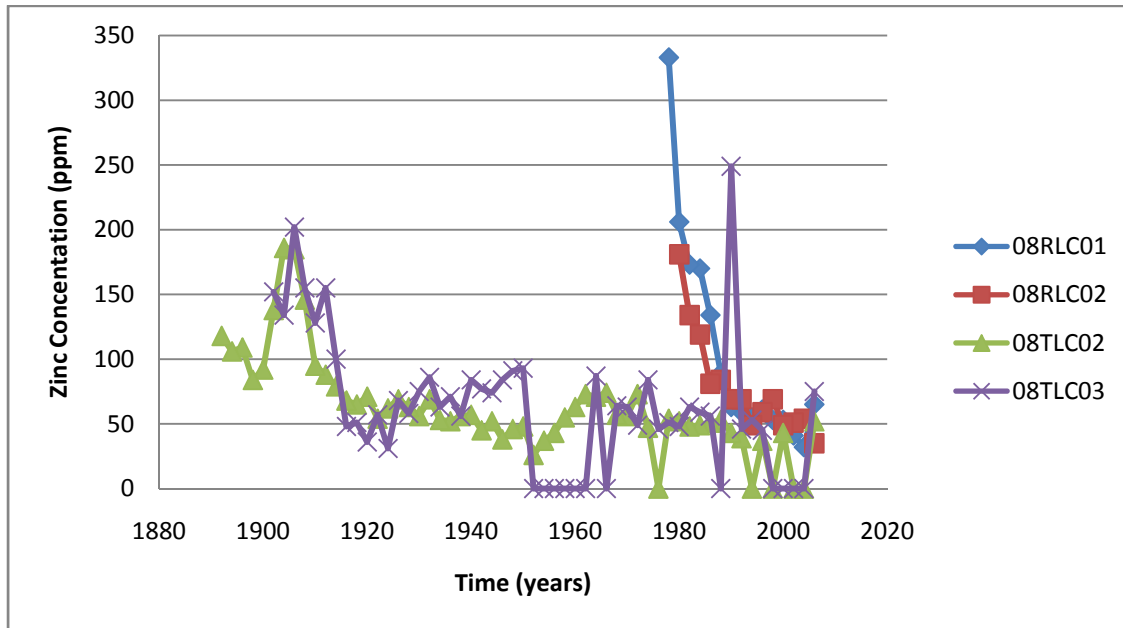


Figure 4.2 Zinc concentrations (in ppm) from four birch samples at the two pristine sites.

4.1.2 Zinc Base Level

Figure 4.2 illustrates a decreasing trend in the zinc concentrations of the samples from the pristine sites. In the first few years of growth, the concentrations are high and then decrease to eventually level out at around 60 ppm. The overall averages are artificially high when calculated for the entire core (see Table 4.2), but when the averages exclude the early extreme zinc concentration, they are dramatically reduced. In cores 08TLC02 and 08TLC03, the averages for the post-early growth period (1916-2006) are 54 and 69 ppm respectively.

The slopes of the linear regression models again provide information on long-term trends. It should be noted that all slopes which fit a linear regression are negative in Table 4.2.

Table 4.2 Average values and linear regression slope and intercept values of zinc concentration for cores from the pristine sites. N/A indicates that the data did not fit a linear regression.

Core	Average	Slope	Intercept
08RLC01	105	N/A	N/A
08RLC02	79	-8.218	140.42
08TLC02	69	-1.615	110.51
08TLC03	82	-1.508	104.25

4.2 Radial Growth Measurements

The age of the birch trees in the study area were determined to range from 23 to 93 years. The pristine site trees had an age range from 28 to 115 years. These values are illustrated in Table 4.3.

Table 4.3 – Age distribution for the sampled birch trees from within the four quadrants of the study area and the two pristine sites as determined from the annual radial width measurements.

Study Area					
Tree	Oldest Ring	Age	Tree	Oldest Ring	Age
Northwest Quadrant			Northeast Quadrant		
7ADLC01	1939	67	7AFLC01	1960	46
7ADLC02	1935	71	7AFLC02	1951	55
7ADLC11	1948	58	7AFLC11	1983	23
7ADLC12	1951	55	7AFLC12	1974	32
7ADLC13	1913	93	7AFLC21	1961	45
7ADLC21	1937	69	7AFLC22	1952	54
7ADLC22	1937	69	7AFLC31	1963	43
7ADLC31	1976	30	7AFLC32	1956	50
7ADLC32	1957	49	7AFLC41	1936	70
Southwest Quadrant			Southeast Quadrant		
7AELC01	1960	46	7AGLC01	1938	68
7AELC02	1961	45	7AGLC02	1954	52
7AELC11	1951	55	7AGLC11	1967	39
7AELC12	1966	40	7AGLC12	1966	40
7AELC21	1966	40	7AGLC21	1921	85
7AELC22	1960	46	7AGLC22	1907	99
7AELC31	1952	54	7AGLC31	1951	55
7AELC32	1950	56	7AGLC32	1952	54
			7AGLC41	1942	64
			7AGLC42	1947	59
Pristine Sites					
Tree	Oldest Ring	Age	Tree	Oldest Ring	Age
8RLC01	1976	31	8TLC01	1916	91
8RLC02	1979	28	8TLC02	1892	115
8RLC03	1940	67	8TLC03	1896	111

4.3 Crossdating

Using the program COFECHA, the birch cores from the study area were crossdated. In hopes of increasing the series intercorrelation value, the pristine trees were added into the crossdating data. The best result achieved was a series with an intercorrelation value of 0.351. For the specifications within the program (30 years lagged by 15 years), the critical (99%

confidence level) correlation value is 0.4226. Therefore, the birch trees from the study area and the pristine sites were not able to crossdate to a significant level to produce a robust master radial width chronology.

4.4 ED-XRF Analysis

From the ED-XRF analysis, raw data values were produced for lead and zinc concentrations within the biannual segments. For lead, birch trees exhibited concentrations with a range from less than the 'limit of detection' (LOD) (see Table 3.1) to 52 ppm. The average value for lead in the study samples was 13 ppm. For zinc, birch trees exhibited concentrations with a range from less than LOD to 309 ppm. The average value for zinc was 55 ppm.

4.5 Repeated Measures 2-Way ANOVA Analysis

4.5.1 Lead ANOVA Analysis

In order to run the repeated measures 2-way ANOVA analysis, the assumptions of normality, homogeneity of variance, and sphericity had to be met. Homogeneity of variance and sphericity passed, but normality did not. After a number of transformations were attempted and no improvement was made, the test was run but the results were interpreted with caution. It should be noted that there were no significant interactions within the data.

It was found that there was a significant effect of time ($p = 0.001$), but neither distance ($p = 0.752$) nor direction ($p = 0.950$) was significant. In order to determine where the significant effect for time was found, a pairwise comparison was done and the results plotted. From the pairwise comparison, it was found that there was a significant effect of time between 1976 and

2006 ($p= 0.001$). In looking at the graph in Figure 4.3, the significant effect is a decrease in lead concentration.

However, as not all assumptions of this parametric test were met, a Friedman's (non-parametric) Test was run. It also found a significant effect of time ($p= 0.000$), confirming the assumption of the repeated measures 2-way ANOVA test.

4.5.2 Zinc ANOVA Analysis

For the repeated measures 2-way ANOVA test, the assumptions of normality, homogeneity of variance, and sphericity were again tested. Homogeneity of variance passed, but normality and sphericity did not. After a number of transformations were attempted and no improvement was made for normality, the test was run but the results were interpreted with caution. For sphericity, the corrected values provided with the within-subjects effects table were used, specifically the Greenhouse-Geisser correction. It should be noted that there were no significant interactions within the data.

It was found that there was a significant effect of time ($p = 0.003$), but neither distance ($p= 0.752$) nor direction ($p= 0.203$) was significant. In order to determine where the significant effect for time was found, a pairwise comparison was done and the results plotted. From the pairwise comparison, it was found that there was no comparison with a significant difference. Therefore, the significant effect of time needed to be determined visually using Figure 4.4, which indicates a decrease over time.

As the assumptions of the ANOVA parametric test were not met, a Friedman's (non-parametric) test was run. Friedman's test also found a significant effect of time ($p= 0.000$), confirming the repeated measures 2-way ANOVA results.

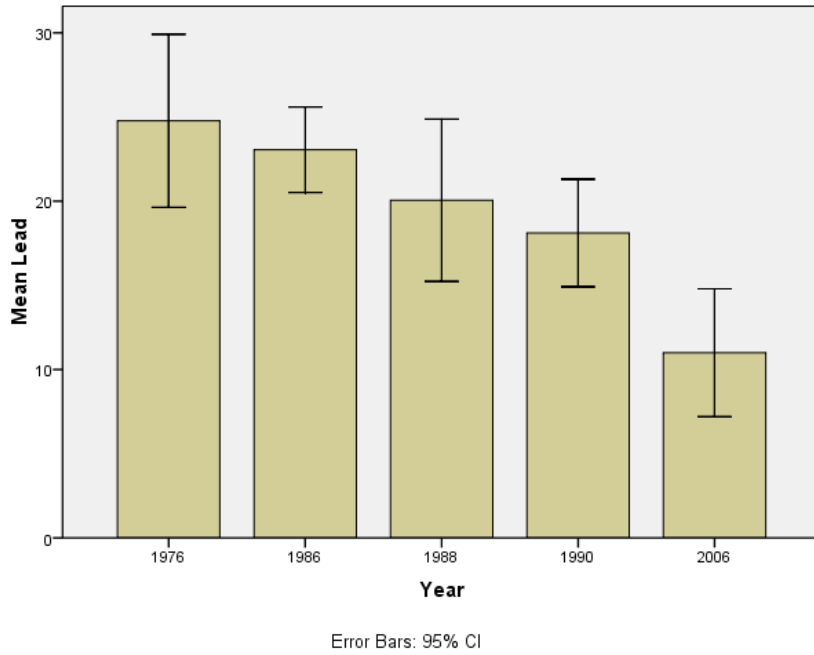


Figure 4.3 Mean lead concentrations (in ppm) over time. The error bars represent a 95% confidence interval.

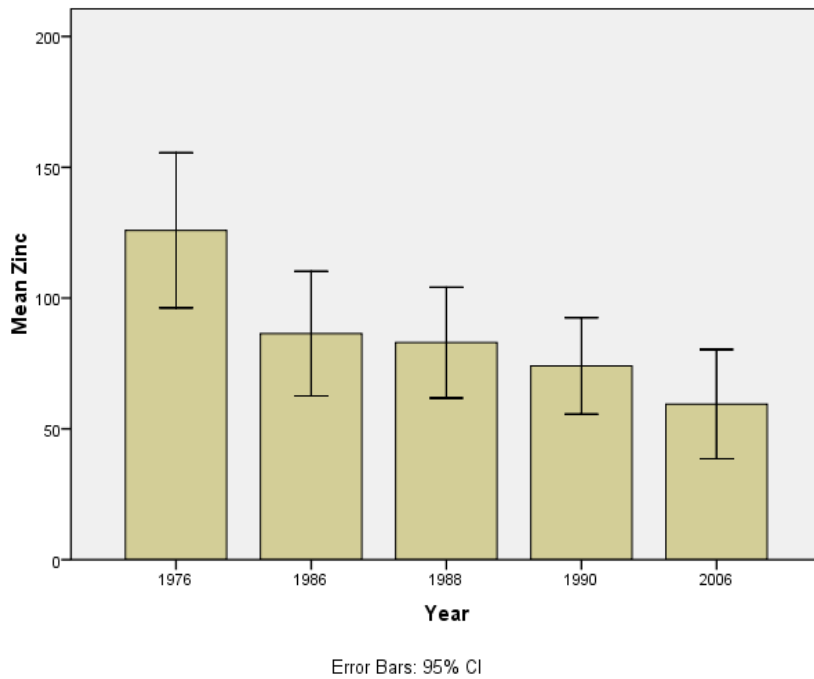


Figure 4.4 Mean zinc concentrations (in ppm) over time. The error bars represent a 95% confidence interval.

4.6 Temporal Change Mapping

From the linear regression, it was found that the slopes for lead range from -1.276 to -0.208 (Table 4.4). The slopes of zinc range from -7.797 to -0.195 (Table 4.5). It should be noted that all slopes for both lead and zinc are negative.

Table 4.4 The slope of the linear regressions for lead values for all birch cores from study area.

Core	Slope	Core	Slope
07ADLC01	-1.245	07AFLC12	-0.994
07ADLC13	-0.648	07AFLC22	-0.973
07ADLC22	-0.557	07AFLC32	-0.793
07ADLC32	-1.064	07AFLC42	-0.271
07AELC01	-0.584	07AGLC01	-0.832
07AELC11	-1.276	07AGLC12	-0.495
07AELC22	-0.712	07AGLC32	-0.208
07AELC32	-0.343	07AGLC22	-0.4
07AFLC01	-1.045	07AGLC41	-0.395

Table 4.5 The slope of the linear regressions for zinc values for all birch cores from study area. N/A indicates that the data did not fit a linear regression.

Core	Slope	Core	Slope
07ADLC01	-2.552	07AFLC12	-7.797
07ADLC13	-2.331	07AFLC22	-6.368
07ADLC22	-6.344	07AFLC32	-4.408
07ADLC32	-4.979	07AFLC42	-1.948
07AELC01	N/A	07AGLC01	-5.778
07AELC11	-6.809	07AGLC12	-6.291
07AELC22	-7.29	07AGLC32	-4.494
07AELC32	-6.844	07AGLC22	-0.195
07AFLC01	-6.971	07AGLC41	-2.509

In order to determine the spatial distribution of this temporal change over time, these slopes were plotted using contour maps. The temporal change map of lead can be seen in Figure 4.5 and for zinc, in Figure 4.6.

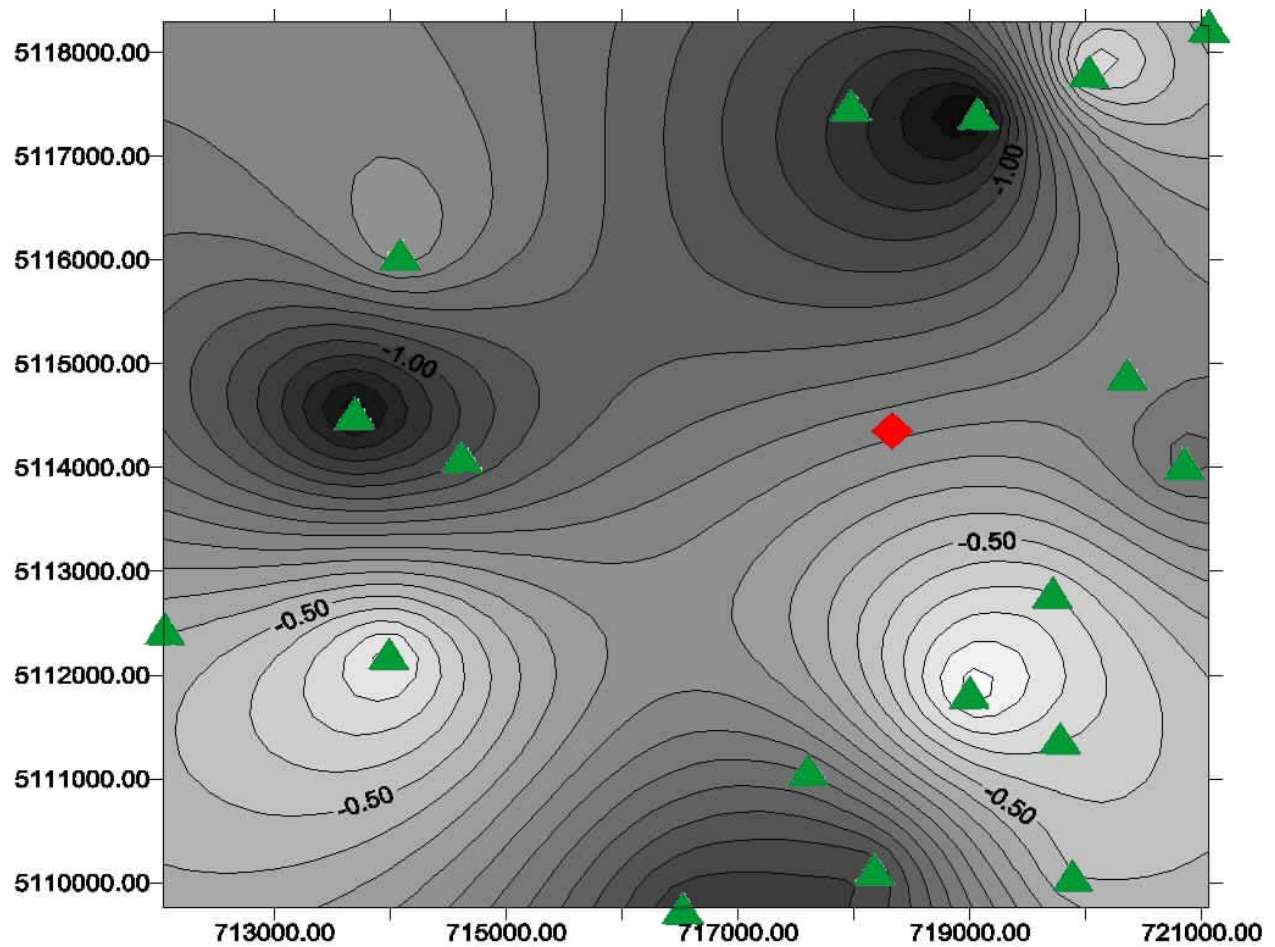


Figure 4.5 The temporal change map illustrating the slope of the lead linear regression mapped with contour lines extrapolating the slope over the entire study area. The axes are the UTM easting (x-axis) and northing (y-axis) for the 20 T quadrant. Darker areas represent a more negative slope. Overlaid are the individual study sites (green triangles) and the Coke Ovens site (red diamond).

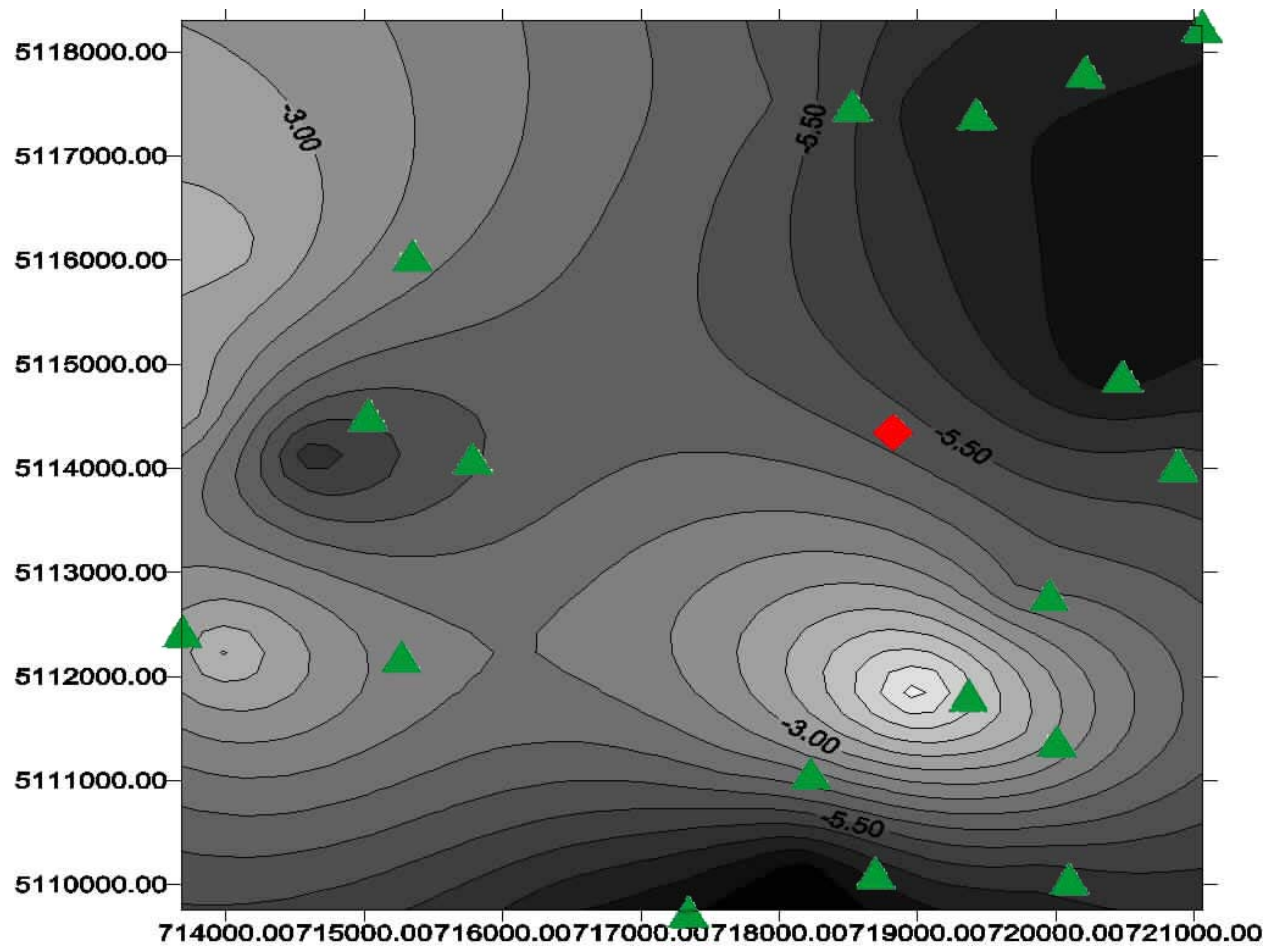


Figure 4.6 The temporal change map illustrating the slope of the zinc linear regression mapped with contour lines extrapolating the slope over the entire study area. The axes are the UTM easting (x-axis) and northing (y-axis) for the 20 T quadrant. Darker areas represent a more negative slope. Overlaid are the individual study sites (green triangles) and the Coke Ovens (red diamond).

4.7 Biannual Pollution Map Animation

The zinc and lead pollution maps can be viewed on the attached CD (Appendix A).

Within the animations, the consistently darker areas (representing elevated metal concentrations) through time should be noted.

Figure 4.7 Contour maps of lead concentration through the study area from 1950 to 2006 displayed in consecutive two-year intervals. The contour lines extrapolate the data over the study area based on 2 ppm intervals. The axes are the UTM easting (x-axis) and northing (y-axis) for the 20 T quadrant. Overlaid are the individual study sites (green triangles), the Coke Ovens (red diamond), and the dominant wind direction (white arrow) based on 30 year climate normals.

Figure 4.8 Contour maps of zinc concentration through the city of Sydney from 1950 to 2006 displayed in consecutive two-year intervals. The contour lines extrapolate the data over the study area based on 20 ppm intervals. The axes are the UTM easting (x-axis) and northing (y-axis) for the 20 T quadrant. Overlaid are the individual study sites (green triangles), the Coke Ovens (red diamond), and the dominant wind direction (white arrow) based on 30 year climate normals.

5.0 DISCUSSION

5.1 Crossdating and Climate

It was found that there was not a significant series intercorrelation for the white birch trees in the study region (both contaminated Sydney sites and pristine sites). Without a significant master chronology, it is impossible to follow standard dendroclimatological techniques and determine the influence of different climatic factors on white birch radial growth.

This non-significant result still provides valuable information in that it indicates that there is no one overriding factor affecting white birch radial growth. Without significant correlations, natural tree-to-tree fluctuations seem to be more important for radial growth rates than any specific species-wide trend. For example, this result would more than likely eliminate climate as the most influential factor in this aspect of the study.

5.2 Metal Base Level Establishment

From the pristine site analysis, it was found that base level or background concentration for white birch in the Sydney region is approximately 15 ppm for lead and 60 ppm in zinc. If this background level holds true for all white birch in the region, it would indicate that concentrations above these values would be the result of metals introduced into the environment from another source. In order to determine whether there was toxic metal pollution, lead and zinc concentrations in the tree cores sampled within study area must be elevated at least above these base level concentrations.

5.3 Metal Concentrations through Time

In order to understand any change in toxic metal levels in the trees over time, this discussion will synthesize the results of three analysis methods. Repeated measures 2-way ANOVA analysis, temporal change mapping and biannual pollution map animation are all used to determine overall temporal trends in metal concentration within the study area.

5.3.1 Lead

A significant effect of time on lead concentrations was found in the repeated measures 2-way ANOVA test. In analyzing the effect, a decrease in lead concentration was found over time. Between 1976 and 2006, the average value dropped from 25 ppm to base levels of 10 ppm (Figure 4.3). In comparing these values to the base level concentrations, lead is elevated by approximately 10 ppm in 1976, but has returned to base level concentration by 2006.

Using the temporal change map, the temporal trend becomes clearer. As can be seen in Figure 4.5, there is variation throughout the map in the magnitude of the slope (and thus the change in lead concentration). Although there is variation, every slope is negative which indicates a consistent decrease in lead concentration over time throughout the entire study area. Every tree experienced elevated lead concentrations in the early part of their growth before they returned closer to base level concentrations nearer to present day.

The lead biannual pollution map animation reemphasizes the findings of the temporal change map. The map illustrates large spatial variation in lead concentration in any individual year. However, in analyzing the maps consecutively, it becomes clearer that concentrations are higher overall (between 20-30 ppm) between 1950 and 1994 when the Coke Ovens were in operation and during the lag period post-Coke Ovens closure. This lag period runs between 1988

and 1994 when the lead, released before the closure, was still being cycled through the environment. Lead concentrations return to more natural lower levels between 1996 and 2006 when the lead has leached through the environment and was no longer easily available for uptake by trees.

Taking the results in combination, the strongest temporal trend within the toxic metal pollution is revealed. All three pieces of evidence illustrate that the lead concentration decreased over time (from 1950 to 2006) throughout the entire study area.

5.3.2 Zinc

There was a significant effect of time on the zinc concentration according to the repeated measures 2-way ANOVA test. Although there is no significant pairing in the pairwise comparison, it is clear from Figure 4.4 that a significant effect in the decrease in zinc concentration over time exists. In 1976, the average zinc concentration was 125 ppm whereas in 2006 it falls to 60 ppm. In comparing these values to the base level concentrations, zinc is elevated by approximately 65 ppm in 1976, but returns to near base level concentration by 2006.

A temporal trend can also be found within the zinc temporal change map. There is a lot of variation through space (Figure 4.6), however every slope is negative. All negative slopes indicate that every core decreased in zinc concentration from 1966 to 2006, although not all areas experienced the same level of reduction.

The zinc animation illustrates a definite decrease in metal concentrations through time. In the Coke Ovens operation and the following lag period (1950 to 1994), the metal concentrations were higher (160 to 220 ppm). After the Coke Ovens were shut down and the emissions passed

through the environment (1996 to 2006), the zinc concentrations returned to approximately base level amounts (60 to 70 ppm).

As all three analyses point to a decrease in zinc concentration over time, it provides a strong temporal trend. From the evidence, zinc concentration is elevated in the 1950's and 1960's and decreases through time to return to base levels by 2006.

5.3.3 Implications of Temporal Trends in Metals

These decreases in both lead and zinc concentrations over time have multiple implications for this study. As the pattern of pollution (a decrease to present) matches the dominant polluter (Sydney Coke Ovens) in both pollutant type and history, this experiment seems to be a successful application of dendroanalysis. White birch from the Sydney area are able to uptake lead and zinc and act as a bioindicator of the metal fluctuations through time.

In terms of the pollution impact on the environment of the study area, there are two important conclusions to be drawn. First, while the plant was in operation, levels of both lead and zinc were above their natural base level. Lead levels were heightened throughout the study area by approximately 10 ppm and zinc by elevated by approximately 60 ppm between the years 1950 to 1994. This project does not intend to examine the implications of such raised toxic metal levels, but these conclusions do beg further study. Second, the metal emissions from the Sydney Steel Plant have been leached through the environment and current levels of lead and zinc seem to have returned to more natural levels, specifically because the airborne pollution impact of the plant has ceased.

5.4 Metal Concentrations through Space

The same three analyses used in determining trends through time can be applied to another dimension – space. All three analyses used in the temporal study can be applied to extract the spatial trend.

A statistical analysis was completed but no significant effect of space was found in either lead or zinc. The repeated measures 2-way ANOVA did not find a significant effect of distance or direction. Therefore, statistically, there is no difference in metal contamination through space. However, as the sample number is very low, it is possible that there is simply not enough power to detect any spatial effect. In conducting a retrospective power analysis on lead data, it was found that 117 replicates would be needed to detect an effect of direction and 7 replicates would be needed to detect an effect of distance. These numbers clearly indicate that the current data have very low power. In understanding this low power, it is possible to continue analysis with other techniques but all results must be interpreted with caution.

Although the low power of the data did not allow for statistical analysis, it is still possible to analyze the data for spatial trends using caution in interpretation. In order to determine changes in lead and zinc through space, mapping is the most appropriate technique. This discussion will combine the results of the temporal change map and the biannual pollution map animation to provide finer scale information on the pollution levels in space.

5.4.1. Mapping Lead

The slope within the temporal change map is an important indicator of changes through space. The larger the change (i.e. the more negative the slope), the greater the decrease over time and thus the higher the lead concentration was in the early part of the study period. From the

ANOVA analysis of lead through time, it is known that lead levels returned to their approximate baseline by 2006. With all trees returning to base levels, the slopes are comparable among sites and therefore the relative size of the change in lead concentration over time can be determined.

From Figure 4.5, the temporal change map reveals three areas with the largest decline in lead concentration from 1966-2006. These areas have slopes less than -1.0 and are located in the northeast corner of the study area, to the direct west and south of the study area.

According to Figure 4.7, there are also three areas which continually show higher levels of lead while the Coke Ovens were in operation. Lead concentrations in the three areas vary between 30 and 50 ppm. The highest lead concentration is in the northeast region, followed by a zone south of the Coke Ovens and then another zone to the west with the smallest elevated concentration. These spots are the same three hotspots that were found in the lead temporal change map.

Both mapping analyses indicate the same three areas experienced higher lead levels through time. This consistent finding indicates a spatial trend in lead pollution. The three areas or hotspots of elevated lead indicate areas highly impacted by pollution. As the study area was not evenly impacted, it indicates differential pollution through space within the study area.

5.4.2 Mapping Zinc

The ANOVA analysis for zinc indicates that all concentrations return to base level by 2006. Following the same logic used in discussing the lead temporal change map, slopes in the zinc map can be compared. In comparing slopes, the changes in zinc concentration through space can be analyzed. Within the zinc temporal change map, three hotspots were found where slopes are less than -6.0. These areas are found in the northeast, the south and west, of the Coke Oven

site and decrease in elevated zinc concentration in the order as listed. The areas with the largest decrease over time are the same three areas as found within the lead temporal change map.

The spatial pattern within the zinc animation (Figure 4.8) is slightly different than the zinc temporal change map. In analyzing the animation, there is only one continuous hotspot where concentrations vary between 160 to 220 ppm – the northeast region. The south and west locations illustrate more variation with some years having elevated concentrations. However, these areas do not illustrate consistently high levels like those seen in the northeast.

Both mapping analyses point to elevated zinc pollution in the northeast region of the study area, signifying a pollution hotspot. The west and south hotspots for zinc exist only in the temporal map, but they are not as prominent as the northeast region. The lesser two hotspots are less conclusive for zinc pollution. Although only one region shows definite elevated concentrations, the northeast signal provides some evidence for differential zinc pollution through space.

5.4.3 Hotspot Explanations

The hotspots are prominent from 1950 or 1966 until approximately 1994. The elevated concentrations of these hotspots then fade into the normal range of the overall metal concentration from 1996 to 2006.

In both the lead and zinc mapping analyses, the area with the most elevated metal concentration is in the northeast quadrant of the study area. This trend may be explained through the mechanics of the pollutant emission. These toxic metals are released into and distributed by the air via particulates (Furimsky, 2002), meaning that environmental factors affecting airborne particulates may be an important factor in their distribution. The dominant wind direction in

Sydney is from the south annually and from the south and west seasonally (Table 2.1). By viewing the maps and animations, it is clear that the northeast hotspot is directly north of the Coke Ovens. The dominant winds would have consistently blown particulates emitted from the Coke Ovens to the north and east. The dominant wind could have concentrated the lead and zinc emissions such that it resulted in an elevated toxic metal levels in the northeast quadrant of the study area.

The northeast hotspot is the most prominent and has the most conclusive evidence for elevated lead and zinc concentrations. The west and south hotspots are not as prominent as they are neither as consistent nor as elevated in the maps and animations as the northwest region (especially for zinc). As the results are less conclusive, there is less certainty with their interpretation.

The hotspot to the west may also be a result of the complex interactions with the wind. The wind blowing from the south on an annual basis may have concentrated pollutants within the entire northern half of the study area. When analyzing both the temporal change map and the pollution animations, however, the evidence of pollution is not continuous from the east to the west. The northeast and west hotspots show elevated pollution levels with a discontinuity in the northwest. This discontinuity is due to the Sydney Harbour being situated in the middle of the study area (see Figure 2.1). For this north-northwest region of the study area tree core sampling is obviously impossible. The hotspot to the west may be a continuation of the northeast hotspot resulting from the annually southern wind. However, it is impossible to see any continuation in this study due to sampling restrictions

The hotspot to the south may or not be a result of Coke Ovens emissions. The inconclusive results for this hotspot allow for uncertainty in interpretation, leaving two potential (and perhaps interrelated) theories for the elevated metal concentrations.

As it falls opposite to the dominant wind direction, it does not fit the dominant wind theory. However, a non-dominant north wind occurs in April, which may drive deposition to the south of study area.

If the pollution is not a result of wind blown Coke Ovens emissions, it may be a result of a concurrent second pollutant. This hotspot is found upwind of the Trans-Canada Highway. The elevated lead levels could be a result of leaded gasoline, a practice which would have released road-side lead. This hotspot does follow the temporal trend for leaded gasoline as its usage in Atlantic Canada was decreased through the 1970's and 1980's and was altogether eliminated in the 1990's (Ernst, 2002). Although efforts were taken to sample against the leaded gasoline bias, the south hotspot may be showing that trend. Leaded gasoline would also explain the presence of the hotspot within the lead animation and its absence in the zinc animation.

Within the analysis of spatial distribution in lead and zinc, the most conclusive trend is in the northeast hotspot. Both mapping analyses and both metals indicate elevated concentrations which can logically be explained by the dominant wind. The hotspots to the west and south are both less conclusive in results and less certain in explanation. The uncertainty in these hotspots as well as the low power of the data is a result of low volume, restricted sampling. Due to time and monetary restrictions, only 18 birch trees were sampled within the study area. While the sampling was sufficient to determine temporal trends, more sampling is required to extract strong spatial trends in lead and zinc pollution. Further, urban development and the Sydney Harbour located within the 5 kilometre radius of the study site severely restricted the natural forested area

available for sampling. These sampling factors have led to the uncertainty in spatial trends within the hotspot explanations.

5.4.4 Implications of Spatial Trends in Metals

Although it is more difficult to extract with such low power, a spatial trend can be preliminarily determined. The dominant trend shows consistently higher toxic metal pollutants in that the northeast region of the study area as a result of dominant wind.

This result is important in the overall study as it confirms the hypothesis that Coke Ovens emissions caused differential pollution impact throughout Sydney. Direction from the Coke Ovens seems to influence the magnitude of the environmental impact. Again, no attempts are made in this study to directly link human health effects to this area of elevated pollutants, but obvious connections can be made (i.e. Barlow and May, 2000) and more study into this spatial connection should be completed.

5.5 Wider Application of Toxic Metal Pollution Trends

In this study, the toxic metals lead and zinc were the focal pollutants as it was feasible to track these pollutants through dendroanalysis. However, the Sydney Steel Plant emissions were not restricted to metal emissions. Volatile organic compounds and polycyclic aromatic hydrocarbons were also emitted from the steel plant (AMEC, 2005). Although the emission of VOCs and PAHs cannot be addressed through this method, the strong signal from the toxic metals may be indicative of elevated levels through time and space for all steel plant pollutants.

5.6 Technique

As the trends in lead and zinc match the probable emission history, this study finds that it was a successful application of dendroanalysis. The technique, as applied to this study, consists of applying ED-XRF to biannual white birch segments to detect lead and zinc concentration levels through time.

Although the technique was successful, the sampling strategy needs improvement before the technique can produce stronger results. A significant effect of time was determined, as the sample number ($n=18$) was large enough to detect the difference statistically, however, the sample number was too small for both distance and direction to be significantly detected. Although other methods were applied to help build evidence of the spatial effects of pollution (i.e. mapping), the results are still not scientifically conclusive.

In order to better determine any spatial effects, it is recommended that more rigorous sampling be conducted to statistically boost the weak sample size in this pilot study. Distance and direction should be clearly categorized and at least 10 trees should be sampled within each category. As well as increasing sample number, there are a variety of techniques which have been recommended in Watmough (1999) and Prasad (2001), including sampling facing the pollution source, which may also improve these results.

6.0 CONCLUSION

There are a number of key conclusions to be taken from this study regarding both the Sydney Steel Plant pollution and the dendroanalytical technique.

The original objective of this project was to create a record of the Sydney Steel Plant pollution through time and space. Although preliminary, this study provides this record through the biannual pollution map animations. These animations summarize the overall trends for lead and zinc pollution throughout Sydney between 1950 and 2006. Although the results are approximate, it provides a base upon which a more thorough temporal and spatial records can be produced. In terms of the overall spatial trends, both lead and zinc concentrations were elevated while the steel plant was impacting the environment (1950 to 1994) and decreased to base level concentrations over the past two decades. In terms of spatial trends, this study reveals one area most highly impacted by the pollution - the northeast region. The trend indicates differential pollution transport depending on the dominant wind direction.

As the trends in both metals match the probable emission history, this technique seems to have been a successful application of dendroanalysis. The technique consists of applying energy dispersive x-ray fluorescence to biannual white birch segments to detect lead and zinc concentration levels through time. This technique could provide stronger results, and therefore a more thorough pollution record, with a more a rigorous sampling effort.

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APPENDIX A

Attached to the back of this thesis is a CD containing:

- Figure 4.7 Biannual Pollution Map Animation for Lead
- Figure 4.8 Biannual Pollution Map Animation for Zinc

APPENDIX B

The following paper has been submitted to the journal *Dendrochronologia* and is currently in press. This article can provide useful background information and experiments which prefaced this current project.

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

Hannah C. MacDonald¹, Colin P. Laroque^{1}, David E.B. Fleming² and Mihai R. Gherase²*

*Corresponding Author

¹Mount Allison Dendrochronology Laboratory

Department of Geography

Mount Allison University

144 Main Street, Sackville, NB

E4L 1A7 Canada

Phone (506) 364-2390

Fax (506) 364-2625

E-mail:

claroque@mta.ca

²Department of Physics

Mount Allison University

67 York Street, Sackville, NB

E4L 1E6 Canada

Summary

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. Two abundant species were sampled within a five kilometre radius of the steel plant site. Using dendrochronology, atomic absorption spectroscopy (AAS) and energy dispersive x-ray fluorescence (EDXRF) on white birch, *Betula papyrifera*, and eastern larch, *Larix laricina*, a new methodology was developed and determine levels of pollutants in a given year. Atomic absorption spectroscopy did not produce accurate results with the small sample sizes we were able to process, but energy dispersive x-ray fluorescence determined that the hardwood birch better incorporated both lead and zinc into annual rings than the softwood larch. The technique provides an interesting area for further study, because it provides a time efficient and repeatable method of analyzing chemicals stored in wood tissue.

Keywords: energy dispersive x-ray fluorescence, atomic absorption spectroscopy, *Betula papyrifera*, *Larix laricina*, Sydney, Nova Scotia, Atlantic Canada, dendroanalysis, tree rings, environment

Introduction

Most temperate trees develop a new ring of growth each year (Fritts 1976), and a number of studies have shown that these trees often have the ability to take up and incorporate local pollution into their annual rings (e.g., Rolfe, 1974, Robitaille, 1981, Prasad, 2001).

Dendroanalysis relies on the basic assumption that the chemical makeup of tree rings reflects to some degree the chemical signal from the environment during the year of ring formation (Watmough, 1999). Dendroanalysts have debated over whether bio-monitoring using tree rings is unreliable (Garbe-Schonberg et al, 1997, Martin et al, 2000), or in fact even feasible (Watmough et al., 1998, Medeiros et al, 2008). For dendroanalysis to be applied, certain conditions of tree ring chemistry must be understood and incorporated into the study (Nabais et al., 2001). Sampling methods, study species and analytical methods must be carefully chosen, although there is no consensus on how exactly these factors interact, creating a variety of ways to apply dendroanalysis (Watmough, 1999).

A limited number of previous studies have used elaborate x-ray dendroanalytical techniques employing, for example, synchrotron radiation (Pusnshon et al, 2003, de Vives et al., 2006) or three-axial scanning x-ray fluorescence spectrometry (Larrson and Helmisaari, 1998). These instruments are, however, not easily accessible and are expensive and relatively complex to operate. This paper describes a dendroanalytical application of an energy dispersive x-ray fluorescence (EDXRF) device which is portable, relatively inexpensive, and straightforward to operate. Although EDXRF has been used to analyze lead and zinc in other environments, its annual resolution is not as high as the two-year resolution in this study (Latimer, 1996).

We hypothesized that dendroanalysis using EDXRF could provide a long-term pollution record if we could find a suitable test site. We hoped to create a map that would show the

changes of pollutants across time and space, and to do this, we would need an instrument that could run the large number of samples that would be needed for such an effort. Because of the sample number issue, the analytical instrument would have to be both straight forward to operate and readily available. The portable EDXRF used in this study provided this easily accessible, relatively inexpensive method of running multiple tree samples. Although the EDXRF instrument model we used was developed for soil chemistry applications, it has also been used for other exploratory purposes, such as arsenic detection in skin (Fleming and Gherase, 2007).

The Sydney Steel Plant was an important part of the history of the city of Sydney, Nova Scotia. From 1901 to 2000, the plant produced steel for global markets and provided employment opportunities for the local and immigrant communities (Caplan, 2005). The processes of converting iron ore to steel produced a variety of pollutants. Polychlorinated biphenols (PCBs), volatile organic compounds (VOCs), and metals were released throughout the time that the plant was functioning (AMEC Earth and Environmental, 2005). These toxicants have been of great concern to the city's residents, and today the "Sydney Tar Ponds" are a well-known environmental disaster. The known and extensive Tar Ponds pollution makes it an ideal candidate for testing our methodological hypothesis of using the EDXRF procedure to understand past chemical contaminants in the environment. This was particularly important as there is no other clear, available, long-term record of the pollution emitted by the Sydney Steel plant. High levels of metals were emitted into the environment by the working plant through time, specifically lead, copper, zinc, arsenic and thallium (Hale, 2004) and then the wind distributed these toxicants across the greater Sydney region. The metals became the focal elements for our study for their prevalence and their detectability using EDXRF analysis.

The main objective of this project was to measure the metal concentrations of lead, copper and zinc in the environment of Sydney by analyzing annual wood increments utilizing the promising, rapid detection method of a portable EDXRF instrument. In order to accomplish this task, two smaller steps were undertaken. Project I utilized the more time-consuming method of atomic absorption spectroscopy (AAS) in an attempt to properly calibrate the time-efficient EDXRF analysis. In Project II, a preliminary EDXRF test was completed to compare the extent to which white birch (*Betula papyrifera*) and eastern larch (*Larix laricina*) incorporated metals into their annual ring tissue.

Study Area and Field Methods

Study Area and Study Site Selection

All samples were taken within a five kilometre radius of the former coke ovens site (N46° 08.879', W 060° 10.376') in the heart of the Sydney Steel Plant grounds (Figure 1). The sampling region was divided into four quadrants following the cardinal directions with axes centered on the coke ovens. In each quadrant, five sites were sampled, dispersed as evenly as possible in a radial pattern across the quadrant. A specific site qualified as a sampling site if it was: a) a natural forested area; b) contained the two target species; and c) was removed from direct residential and commercial contact. The target species were eastern larch and white birch, as previous reconnaissance determined these two species to be the most common across the region.

Sampling

Once a sampling site was identified, distance and direction from the coke ovens were noted, and the two species were sampled at the site. A 5.1 mm increment borer was used to

extract cores, with two cores collected per tree at approximate breast height (1.3 m). After the first core was sampled, the second core was taken directly (1 cm) below the first core. This sampling method allowed both cores to be as similar as possible in terms of ring width parameters and ring structures. This procedure was used because one core would be used for dendrochronological analysis, while the second would be used in other analytical procedures. Cores were labeled and stored in clear plastic straws, then transported to the Mount Allison Dendrochronology Laboratory for further analysis.

PROJECT I: EDXRF CALIBRATION USING AAS

EDXRF allows for quick, precise, non-destructive analysis of elemental concentrations in a tree sample. However, as the instrument was originally intended for testing soil samples, it was not known if the concentrations reported by the procedure were accurate or if they needed to be calibrated. The method chosen to calibrate the EDXRF results was AAS, as it was expected to provide true absolute concentration values (e.g. Robitaille, 1981). Disadvantages of the AAS procedure are that it is destructive and relatively time-consuming in nature.

Methods

Dendrochronological Methodology

One core of larch and birch was cut into segments with a sterile scalpel blade. The segments weighed enough (approximately 0.5 g) to be analyzed with atomic absorption spectroscopy (AAS). The segments were approximately 1 cm in length and were not cut on annual boundaries. Each segment's temporal position was noted, and the segments were stored for further analysis.

Energy Dispersive X-ray Fluorescence Methodology

The segments were then taken to the Mount Allison Medical Physics lab and analyzed using an Innov-X System Alpha-4000S EDXRF instrument (Innov-X Systems Canada, Mississauga, Ontario). Each sample was run under standard soil settings for five minutes. Throughout this time interval, the instrument bombarded the atoms of the wooden segment with x-rays. The emitted spectrum can then be interpreted to reveal the composition and concentration of elements within the segment being analyzed (Murphy, 2006). The Innov-X instrument

software calculates concentrations in parts per million (ppm) for any detected elements, including the three metals of interest – lead, zinc and copper.

Atomic Absorption Spectroscopy Methodology

As the EDXRF procedure is non-destructive, the same samples were analyzed first with EDXRF and then taken to be analyzed with AAS. The wet weight of each wooden segment was obtained before any AAS processing. The segment was placed in a muffle furnace and was heated overnight at 550°C, converting the sample to ash. After being cooled, the sample was weighed again for dry weight. In order to dissolve the ash, 1 mL of Aqua Regia (HCl:HNO₃ – 3:1) was added for 2-4 hours on a hot plate set at 80°C. Once only a salt remained, it was made into a 10 mL solution by diluting it in a volumetric flask using distilled, de-ionized water as a solvent. Standards for each metal were used to calibrate a Varian AAS instrument and then each 10 mL sample solution was run and values (in ppm) were acquired. Hollow cathode lamps were available to test for lead, zinc and copper.

Results

Lead Concentration Comparison

Lead concentrations analyzed through AAS were difficult to interpret as there were both positive and negative values (Figure 2). Generally, the values fluctuated around 0 ppm, indicating that lead was not detected using AAS. Using XRF, lead values were low, fluctuating around 1.5 ppm, yet they were still detected (Figure 2). In each of the following comparisons, the dry weight value was lost for larch segment number five, so this data point has been excluded from the results. The wet weight was thought to be less precise, so it was not used.

Zinc Concentration Comparison

AAS values indicate that for birch, 13-18 ppm of zinc were in the more recent segments and then they peaked at 43 ppm in the middle segments before dropping again to 25 ppm in the oldest segments (Figure 3). For larch, the AAS values begin at 23 ppm in the youngest segment and then decrease to values between 5 and 10 ppm for the older segments. The total range for larch is approximately 20 ppm. Figure 3 illustrates that the XRF procedure produced concentrations of zinc varying between 5 and 10 ppm. The range is approximately 5 ppm, which is very different than the AAS results.

Copper Concentration Comparison

Copper was detected by AAS in both larch and birch, although it was very low and fluctuated a great deal (Figure 4). The AAS range was 2 ppm, between 0 and 2 ppm for larch and 1 ppm, between 0 and 1 ppm for birch. Copper levels were too low to be detected by the XRF in both species for all samples (Figure 4).

Discussion

EDXRF has no zero value or reliable scale for this project as trees cannot be found with known metal concentrations to test in the EDXRF procedure. It was hoped that the AAS results would provide a consistent numerical factor to help calibrate the EDXRF results. As AAS determines absolute concentration, these values could theoretically be used to calibrate the EDXRF measurements. This factor would then be used on all further XRF values for calibration, but ultimately our analysis did not allow this approach.

In the lead, zinc and copper analyses, there was no consistency between the AAS values and the EDXRF 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 EDXRF values or the AAS values were

higher. The trends between the larch and birch samples in both the EDXRF and AAS values did not match in any form, indicating that the two sets of analytical results did not mimic each other in a sufficiently accurate way to produce a calibration factor. Without any consistency, AAS cannot be used to calibrate the EDXRF values.

Lead concentrations did not register using AAS. The negative values in the data are indicative of an experimental problem and may be due to the error range for the instrument when detecting such low levels of lead. The settings on the muffle furnace were not in units of temperature, leading to an approximation of the temperature reached by the furnace. Due to the inaccuracy of the muffle furnace temperature, the temperature may have increased to a point where lead became volatile and left the sample, leaving none to be detected by AAS.

Zinc and copper concentrations were detected by both the AAS and EDXRF procedures, yet the EDXRF values were low or even undetectable. The values for the two methods were difficult to compare for this reason, especially for copper. Zinc has the closest relationship between EDXRF and AAS for any of the three metal tests, but still there was no clear pattern to calculate a calibration factor.

Overall, this method did not provide the desired calibration factor, with a major reason being the sample size tested (N=1 for each species). No replicates were completed (due to the limited segment mass) and only one core was run for each species (due to time and expense). The low sample numbers allow for a lot of imprecise data that cannot be interpreted. If this method were to be successful, many more cores and trees should be sampled and run through both AAS and EDXRF. Zinc should be the focal metal, as it showed the most promising results for linking the two metal analyses methods. Muffle oven temperature should also be closely monitored throughout the heating process.

The major result obtained from Project I is that since no reliable calibration factor could be determined, EDXRF results in Project II should not be interpreted as correct as absolute values, but rather viewed with respect to relative changes or differences across samples.

Project II: Hardwood and Softwood Comparison

The purpose of this experiment was to compare the metal-uptake ability to of the most abundant hardwood tree species found in Sydney (*Betula papyrifera*) with that of the most common softwood species (*Larix laricina*). The Project II test was conducted to determine which should be the focal tree species for a future project of generating a pollution map through time in Sydney.

Methods

Dendrochronological Methodology

Larch and birch tree cores sampled directly at the coke ovens site were used in this analysis. The coke ovens site was sampled as it was the pollution origin, and theoretically should contain the highest concentrations of metals. One of the two cores from each tree was processed for analyzing annual radial growth using conventional dendrochronological methods. The core was glued into a slotted mounting board and sanded to a fine polish (600 grit). The ring widths of the cores were measured using a 63X light microscope coupled to a Velmex stage measuring system which measured 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.

In Project II, instead of sampling the coke oven site, birch and larch from the five sites in each quadrant were measured and the age of each tree at diameter breast height (DBH, 1.3 m) was obtained (Table 1). The oldest trees of each species were then used in the remaining EDXRF procedure.

To prepare for the procedure, the unmounted second core was aligned against the fully prepared and sanded first core. The parallel extraction of cores from the trees allowed for an

easily detectable similarity in ring widths. The polished core was therefore used as a template to determine ring boundaries under the microscope on the unprepared core. Ring boundaries were located on the unprepared cores which then were cut in two-year segments using a sterile scalpel blade.

In total, eight cores (four birch and four larch) were cut into biannual segments to be analyzed by EDXRF. The larch and birch within each quadrant were generally taken from the same site to maintain consistency of local emission concentrations through time. The exception was in the northeast quadrant, where larch was from one site and the birch was from another site 2.4 kilometres away.

Energy Dispersive X-ray Fluorescence Methodology

EDXRF analysis was undertaken in a similar manner as in Project I. This time the segments analyzed were biannual segments and each segment was analyzed for three minutes, not five. The shorter run time allowed for relatively high precision while maximizing the number of segments analyzed. Due to the shorter measurement time and the smaller size of segments, elemental detection limits were higher for Project II. Limits of detection were defined using the 3σ calculation method, and varied slightly between different segments. Average limits of detection for lead and zinc in both birch and larch cores are presented in Table 2.

Results

Lead and zinc values are shown in the results as they were the only two metals consistently detected.

Pollutant Record Length

In terms of record length, the birch provided the longest record, from 1928 to 2006. The birch cores had a common interval dating back 42 years across the four quadrants. Larch cores had segments extending from 1940 to 2006, but all larch cores had a common interval of only 21 years.

Lead EDXRF Results

All birch exhibited concentrations of lead in a range from 12 to 52 ppm, and only one segment contained a concentration less than the limit of detection (Table 2) for the EDXRF instrument. Larch lead concentrations ranged from 10 to 30 ppm, when excluding the segments which had a concentration less than the LOD (Figure 5).

Zinc EDXRF Results

The zinc concentrations for larch were low in all cores. Almost all segments had zinc concentrations less than the LOD (Figure 6). Only two larch cores had detectable zinc levels ranging from 8 to 54 ppm. Birch results were in the range of 26 to 209 ppm, with a decreasing trend to present day in all cores over time (Figure 6).

Discussion

Lead

Lead uptake into annual rings divided the larch and birch species into two separate general ranges. Both species had concentrations ranging to 0 due to concentrations less than the LOD (Figure 5). However, the majority of birch segments exhibited lead concentrations in the 25-45 ppm concentration range. The larch segments generally exhibited a lower range of 10-25 ppm (Figure 5). Two birch cores showed a strong decreasing trend from the late 1960s to 2006.

This decreasing trend is not mimicked in the other birch samples, where they are more constant and closer to the larch range concentration values (Figure 5).

Zinc

The EDXRF results were again grouped into two general ranges by species. Larch concentrations were generally below detectable levels, and so clustered near 0 ppm. Birch on the other hand had continually detectable zinc levels in a general range of 30 to 160 ppm. Two samples strongly exhibited a downward trend through time. The two other birch cores had a less distinct pattern, but seemed to mimic a decreasing overall trend through time.

Larch-Birch Comparison

As samples from each quadrant were taken from the same or similar sites, one might expect both species to contain the same concentration of lead and zinc, since their exposure would be approximately the same through time. The distinct groupings within the results between the two species indicate that birch and larch have different metal uptake abilities.

In each quadrant, the birch samples registered a higher level of lead and zinc than the larch samples. This indicates that with the same exposure to pollution, birch trees incorporate a higher concentration of the metals into their annual rings. This result can probably be best explained by the anatomical differences between hardwood and softwood cell structures. The bulk of the cells in the xylem of softwood trees (gymnosperms) are tracheids. Hardwood (angiosperm) xylem is mostly composed of fibers as well as vessels. Angiosperm fibers have thicker cell walls and fewer pits (for liquid movement) than gymnosperm tracheids. These characteristics of fibers would allow for less liquid movement, and therefore less metal movement within that liquid, between cells and between rings. Angiosperms would be better able to maintain the metals taken up in a given year in that annual ring. Furthermore, although

angiosperm vessels and gymnosperm tracheids are both water conducting cells, the vessels contain no end walls, allowing for much less upward resistance. More water would be able to move in angiosperm vessels, leading to more metal uptake with the same exposure to root water levels. Overall, the angiosperm (birch) cellular anatomy allows for more water and metal mobility and capture into only the current annual ring (Kramer and Kozlowski, 1979). These differences in anatomy could explain the difference in metal concentration.

The EDXRF values presented are not calibrated for tree wood and so are not accurate in an absolute sense. However, the relative differences between the values are valid, and indicate strong trends. To improve the concentration data, future efforts should be taken to standardize these values. This may be accomplished by analyzing the effect of segment mass and size or by determining baseline levels of the metals by sampling and analyzing trees taken from isolated, uncontaminated areas.

Historical Trends

Both lead and zinc EDXRF results showed a decreasing trend with time (Figures 5 and 6). This trend is indicative of the known historical pollution in the area. The key year in this trend is 1988, which is when the coke ovens were shut down (Barlow and May, 2000). If this a smaller amount of emitted pollutant for the trees to potentially incorporate into their ring structures, the ring concentrations should therefore decrease after this known year. Another reason for the post-1988 decrease could be the slow leaching of pollutants out of the soil.

In the lead analysis, two birch cores showed a drop from fluctuating around 40 ppm to fluctuating around 20 ppm after 1988. In the zinc analysis, each core had concentrations over 100 ppm that steadily decreased after 1988 to values less than 60 ppm. In each case, the fluctuations between each two-year segment were not statistically significant as they were likely

due to measurement uncertainties associated with the EDXRF method throughout the whole length of record. However, the overall decreasing trend was apparent and striking as it matched the expected historical timeline of concentration depletion in Sydney.

Conclusion

The main objective of this study was to try to measure the past metal concentrations of pollutants within the environment of a site by analyzing tree cores using an EDXRF method. In this regard, the results were promising enough that further exploration is warranted.

Two important methodologies have been developed in the course of this study. First, the sampling and alignment of the polished and rough cores for accurate biannual separation has been successfully tested. Second, the use of a portable energy dispersive x-ray fluorescence unit for quickly analyzing samples seems appropriate, and promising for completing a large number of samples. Most tree cores in this study had at least 14 segments, and to complete a more conventional AAS analysis on even one core from a tree would result in the destruction of the sample and take much longer than it takes to process numerous trees utilizing the simple EDXRF process. The two methodologies introduced here work together to aid in reaching the ultimate goal of mapping the pollution both temporally and spatially.

In Project I, it was determined that atomic absorption spectroscopy did not provide a practical method for EDXRF calibration. No trend appeared in the results which could be used for calibration. AAS may be a useful technique for EDXRF calibration, but many more samples would have to be processed. However, due to time restrictions, budgetary consideration, and sample destruction, this undertaking is not always practical. Future efforts should be made to standardize the EDXRF values, if they cannot be calibrated directly. Methods for practical

standardization include comparing the data to segment mass or baseline concentrations in trees taken from unpolluted areas outside the study site.

Without calibration, the EDXRF values obtained are not accurate but the relative difference between values is valid and illustrates the promise of the technique. For example, it cannot be said that the peak value for lead was exactly 52 ppm in the northeast quadrant. However, it can be said that the average difference between birch and larch lead concentrations was approximately 57%, for a given location over the lifetime of the tree. The relative difference between birch and larch illustrate that, for both lead and zinc, the hardwood birch is better able to incorporate these metals into its annual growth.

In comparing lead and zinc results between the two projects, we found that Project II concentrations were much higher than those from Project I. All samples for Project I were taken from the coke oven site, which should be the most polluted location in all the study sites. However, trees sampled from this area had only been growing at the coke ovens since they had been shut down and demolished. Therefore, Project I trees were younger, and not exposed to the same high levels of airborne emissions as trees in the other sites potentially were. Using birch as the focal tree species and looking into new methods of standardization, the EDXRF methodology development will continue. A final goal of these developments will be to produce an accurate, long-term map of pollution through the duration of the steel plant's lifetime and over a wider spatial dimension throughout the city of Sydney.

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Tables

Table 1 - Dendrochronological analysis of tree age for all larch and birch tree cores within 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

Table 2 –Values for the limit of detection (LOD) of metals lead and zinc for birch and larch cores.

Limit of Detection	Lead (ppm)	Zinc (ppm)
Birch	12	18
Larch	13	13

Figure Captions

Figure 1 - A diagram of Sydney with study sites (marked as solid dots) plotted in relation to the coke oven site. The solid lines represent the north-south and east-west axes dividing the four quadrants.

Figure 2 - Concentration of lead (ppm) in birch (solid lines) and larch (dashed lines) tree cores analyzed using AAS (solid markers) and XRF (open empty markers). Sample 1 is the youngest segment and sample 7 is the oldest for both larch and birch (n=7).

Figure 3 - Concentration of zinc (ppm) in birch (solid lines) and larch (dashed lines) tree cores analyzed using AAS (solid markers) and XRF (open markers). Sample 1 is the youngest segment and sample 7 is the oldest for both larch and birch (n=7).

Figure 4 - Concentration of copper (ppm) in birch (solid lines) and larch (dashed lines) tree cores analyzed using AAS (solid markers) and XRF (open markers). Sample 1 is the youngest segment and sample 7 is the oldest for both larch and birch (n=7).

Figure 5 - Lead concentrations analyzed using XRF for one birch (top graph) and one larch (bottom graph) tree core from each quadrant of the study site. Larch and birch from the same quadrant have the same style of data point marker (north-east quadrant = diamond markers north-west quadrant = triangle markers, south-west quadrant = square markers and south-east quadrant = “X” markers). The bold vertical line marks 1988, the year the coke ovens were shut down.

Figure 6 - Zinc concentrations analyzed using XRF for one birch (top graph) and one larch (bottom graph) tree core from each quadrant of the study site. Larch and birch from the same quadrant have the same style of data point marker (north-east quadrant = diamond markers, north-west quadrant = triangle markers, south-west quadrant = square markers and south-east quadrant = “X” markers). The bold vertical line marks 1988, the year the coke ovens were shut down.

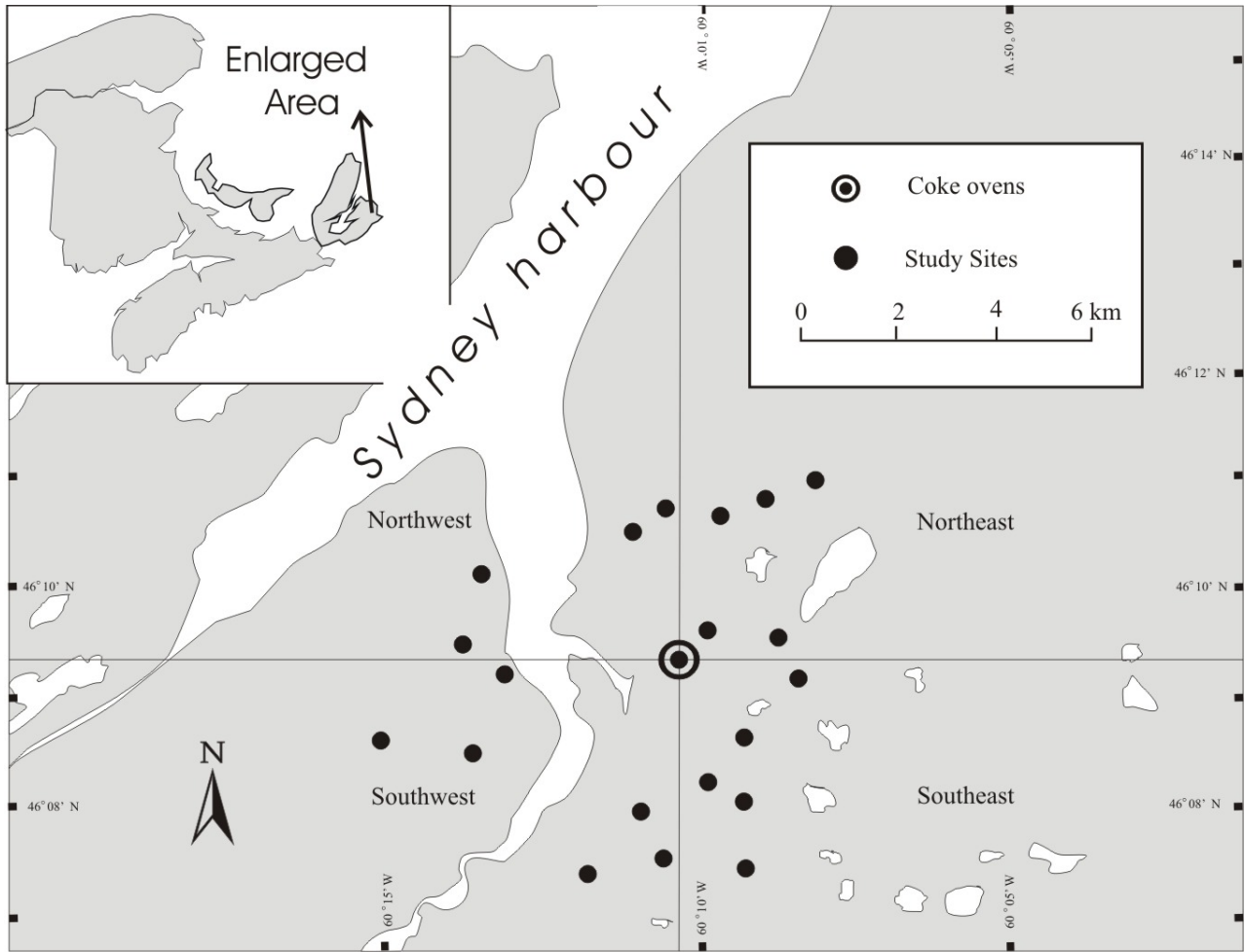


Figure 1

Figure 1

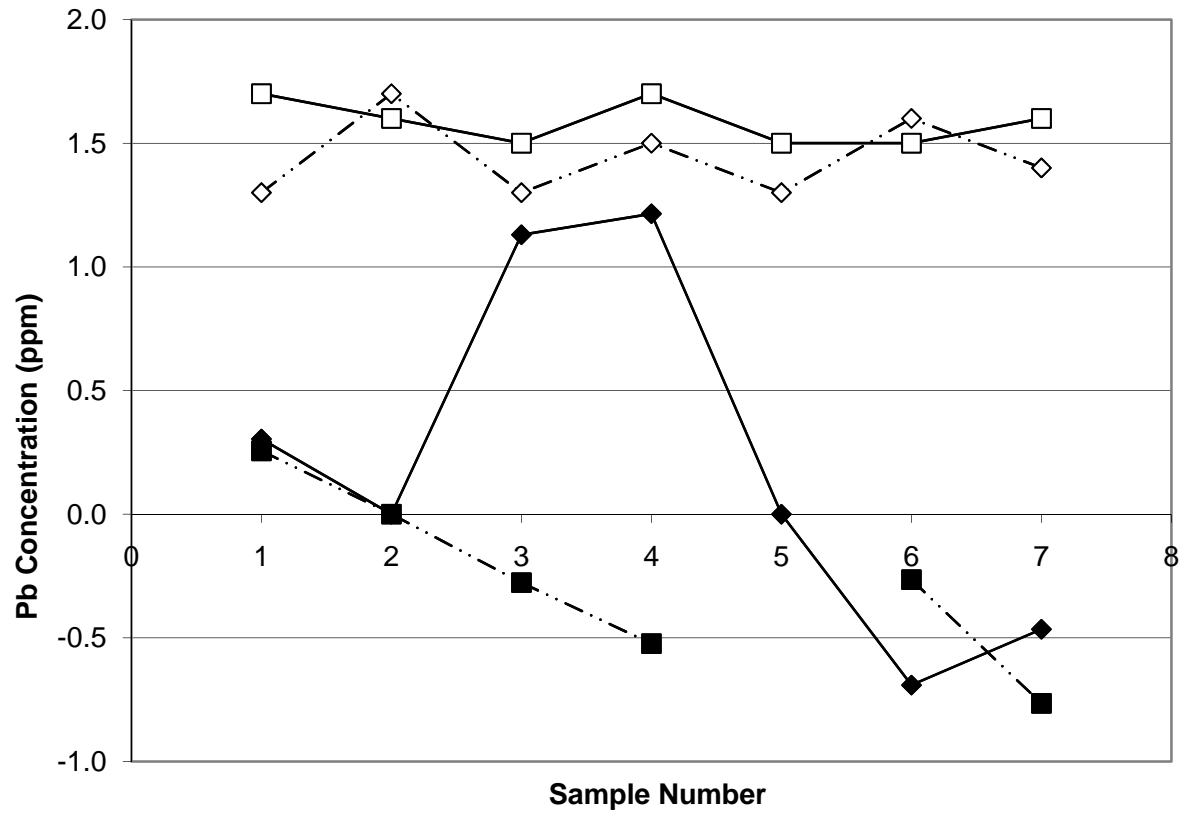


Figure 2

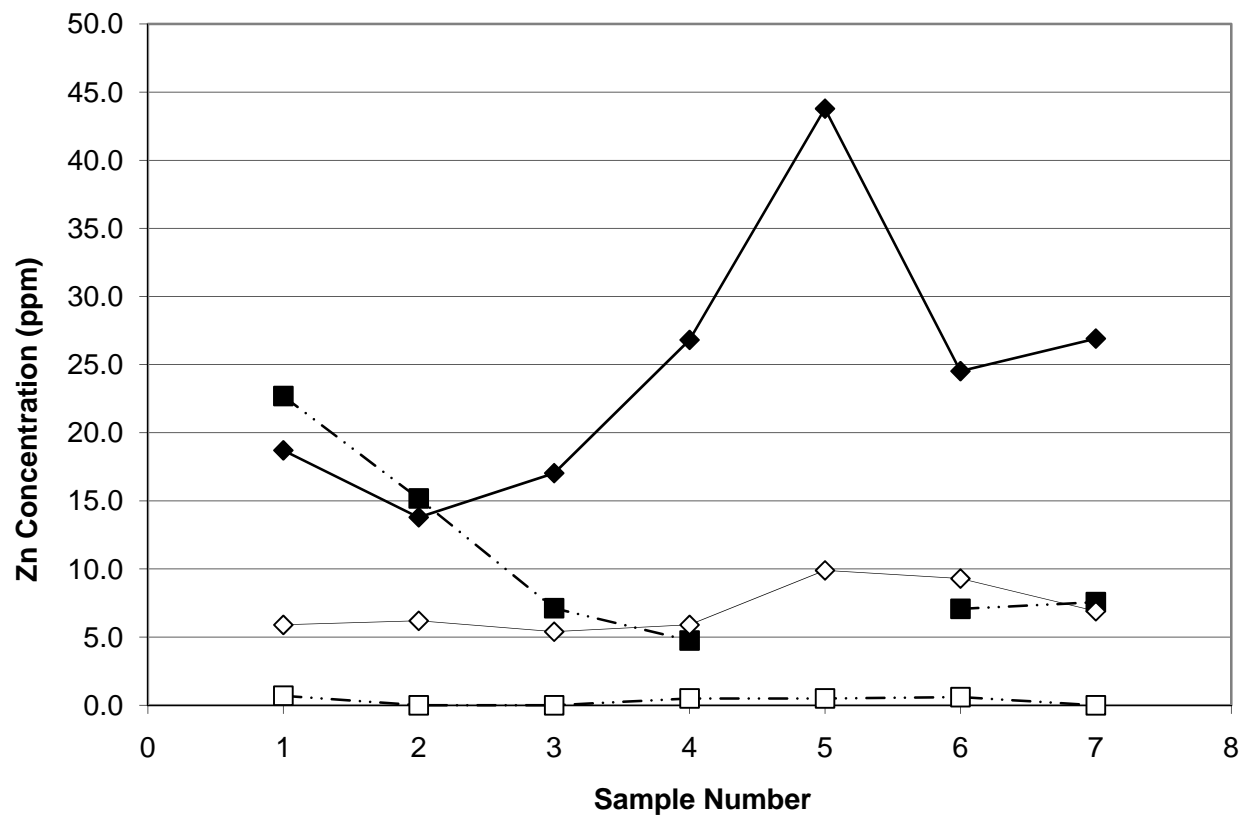


Figure 3

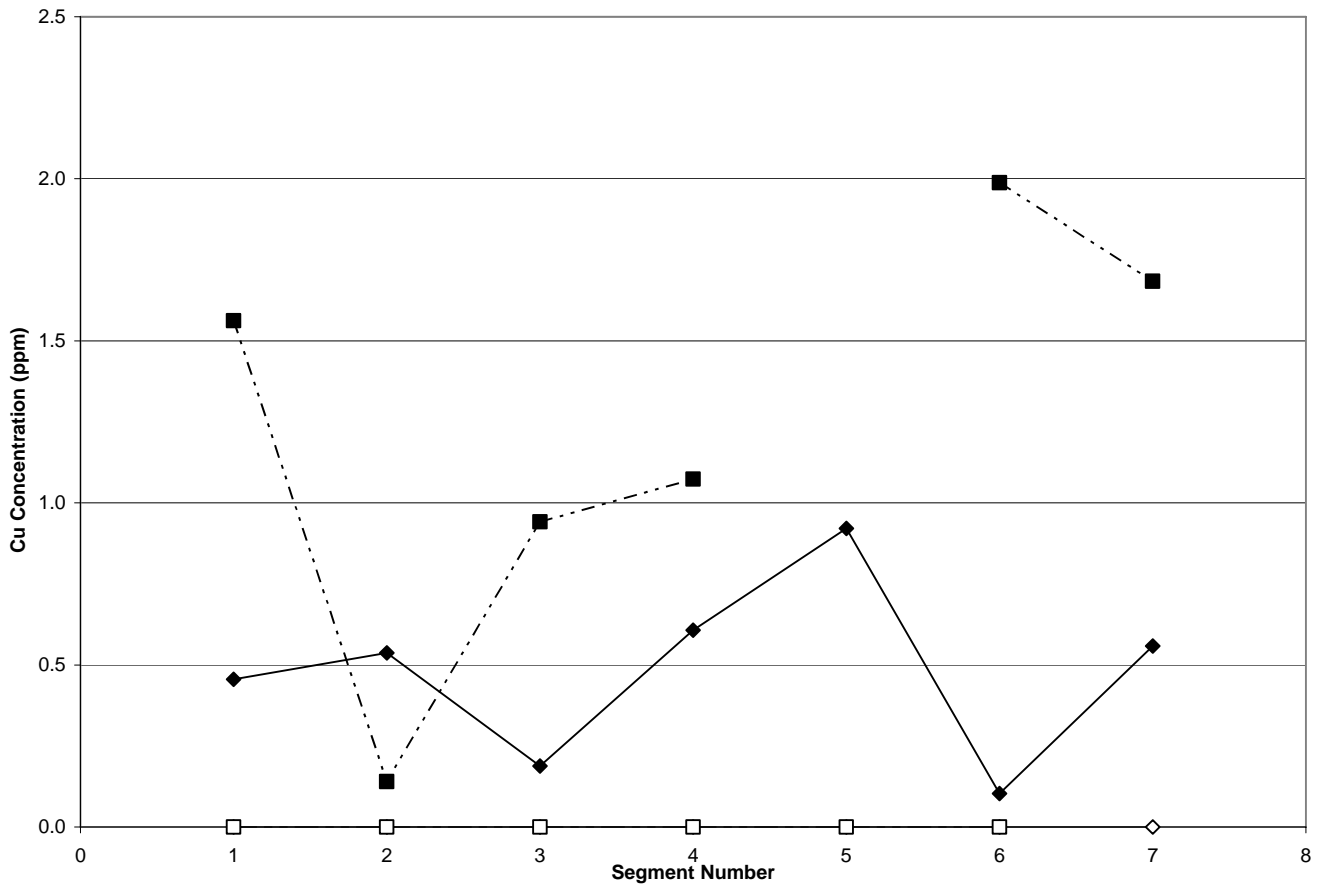


Figure 4

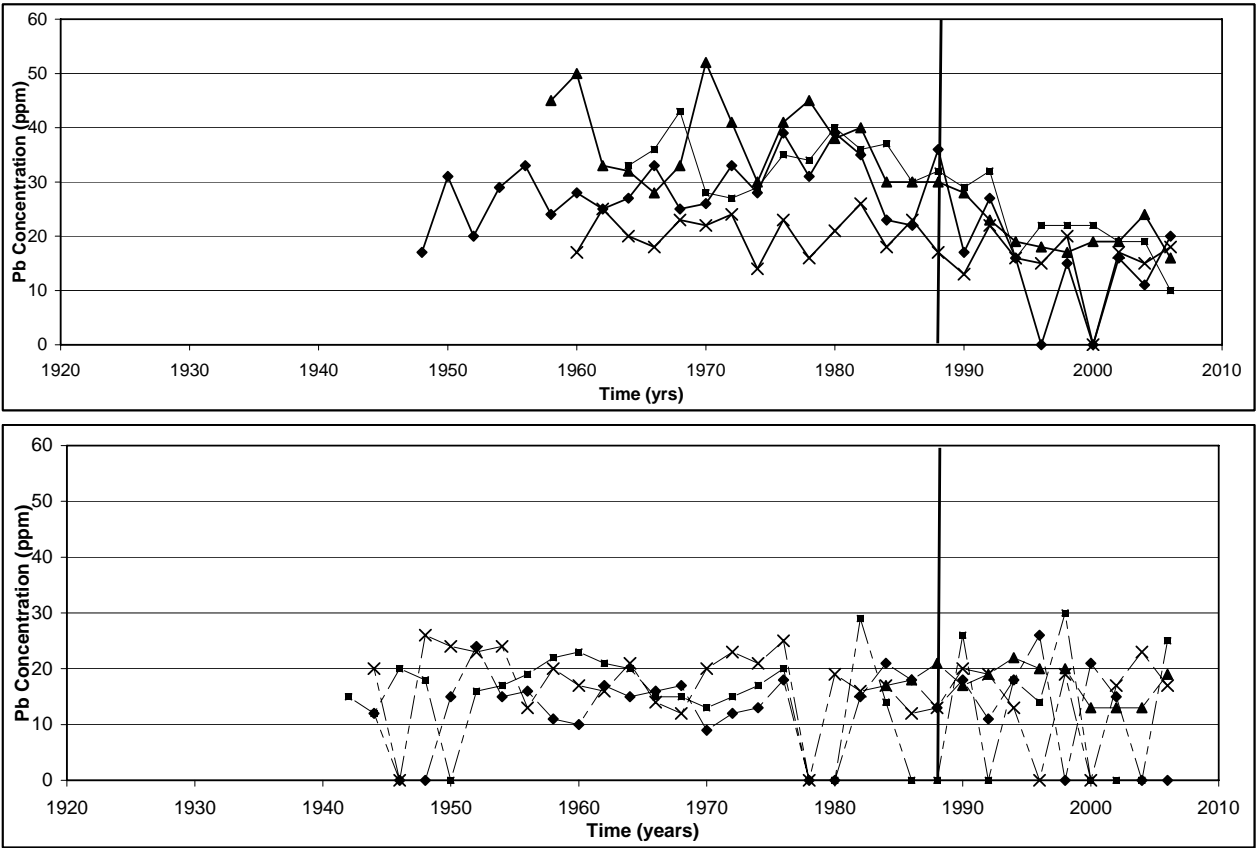


Figure 5

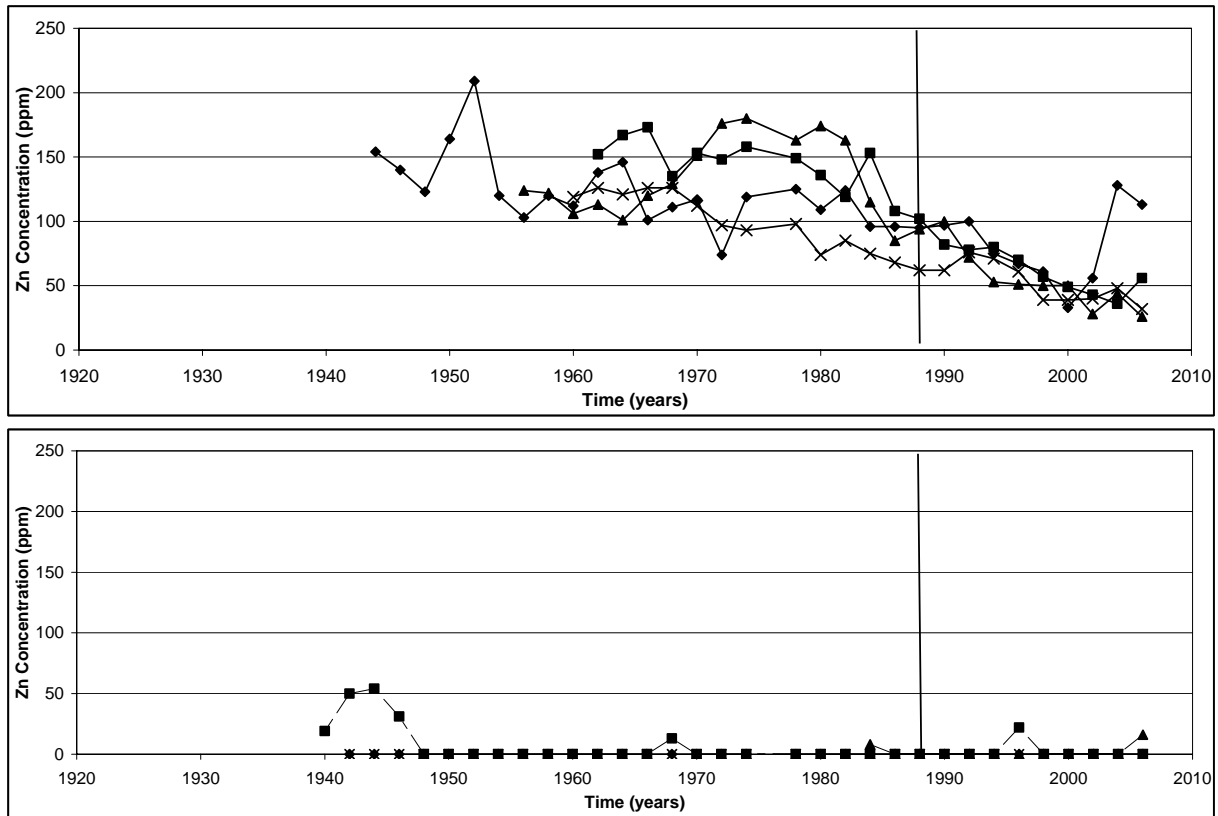


Figure 6