Metals in the annual rings of eastern white pine (*Pinus strobus*) in southwestern Ontario by secondary ion mass spectroscopy (SIMS)

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whole ring?

Abstract: Secondary ion mass spectroscopy (SIMS) has been used to examine the difference in metal content between different years among trees at the same site and the same year at different sites across southwestern Ontario. Significant differences are evident for each comparison. Individual differences may be attributed to site location, such as increased sodium at sites influenced by road salt.

Résumé : La spectroscopie de masse par ions secondaires a été utilisée pour examiner les différences dans le contenu en métaux entre différentes années dans les arbres d'un même site et entre différents sites pour une année donnée dans le sud-ouest de l'Ontario. Des différences significatives sont évidentes dans chaque cas. Les différences individuelles peuvent être attribuées à la localisation d'un site comme une augmentation du sodium dans les sites qui subissent l'influence du sel de déglaçage le long des routes.
[Traduit par la Rédaction]

Introduction

The analysis of the metal content of the annual growth rings in trees is well established as a means of providing a historical record of environmental pollution (see, for instance, Amatto 1988; Robitaille 1981; Eklund 1995). These analyses and others, including neutron activation analysis (NAA) (Guyette et al. 1989), proton-induced X-ray emission (PIXE) (McClenahen et al.1989), inductively coupled plasma – mass spectroscopy (ICP–MS) (Bondietti et al. 1989), and laser ablation ICP–MS (Gough et al.1995), have initiated active research in the field of dendrochemistry.

Secondary ion mass spectroscopy (SIMS) is an ion microprobe technique that can be used to analyze virtually all the elements and their isotopes in a very small volume of a solid sample. It is, accordingly, ideally suited to the study of the metal content of individual tree rings. We have demonstrated the potential use of SIMS as an analytical tool in tree-ring analysis by examining the potassium content of a single sugar maple, *Acer saccharum* Marsh. (Martin et al. 1994). These results showed only that individual rings could be probed using a SIMS instrument. In this earlier work SIMS was used to collect mass spectra at individual sites in each ring examined.

SIMS is also capable of collecting information with depth in the sample if the primary ion beam is allowed to dwell on a single spot for a period of time sufficient to ablate a significant amount of the surface while the yield of selected secondary ions is monitored with time. Subsequent measurements of the depth of the ion crater created in this way allow secondary ion yields with time to be converted to yield as a function of depth (a depth profile). This approach has two advantages. First, the long collection times possible are effective integrators of secondary ion yield. Second, a depth profile supplies information regarding the spatial distribution of the metals in the sample. In addition, the spatial distribution of preselected elements can be displayed in either two or three dimensions if the secondary ion yield is monitored as the primary ion beam and is rastered over the sample surface (Kyotani et al.1992).

In this work we have sought to determine whether SIMS analysis is capable of distinguishing (*i*) the metal content of rings from individual trees in the same year collected at the same site, (*ii*) pooled data comparing rings corresponding to different years at the same site, and (*iii*) pooled data comparing the same years at different sampling sites. In addition, we have (*iv*) sought to correlate the differences in secondary ion yields between sites with known site characteristics. Scanning electron microscopy with energy dispersive X-ray (SEM/EDX) analysis has been used as a complementary technique.

Materials and methods

Three sample sites were selected across southwestern Ontario, Canada. The first site, designated Hwy, was located at the southwest corner of the intersection between Ontario highways 401 and 73. This site was selected to determine whether road salt used on the approach ramps could be detected in tree rings. The second, site Rur, was located in a rural area at the Agriculture Canada Research Station, Delhi, Ontario. The third, site Ind, was located close to a major industrial area known to receive significant airborne material and proximate to a solid waste disposal site, which had been sealed in December 1986, on the outskirts of the town of Pellham, Ontario. No control site was required because this work seeks to measure only differences in metal content between sites.
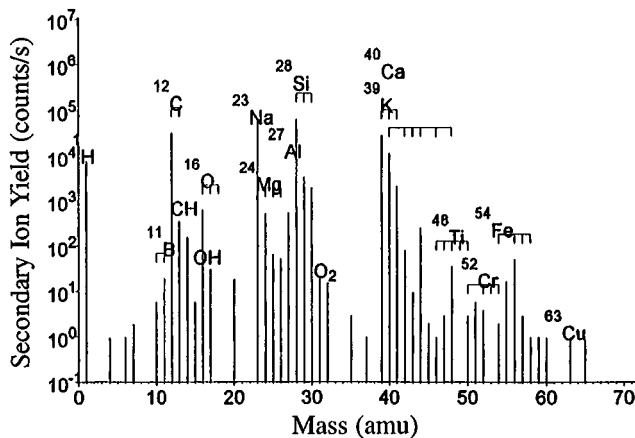
Ten core samples, one per tree, were collected in 1994 from eastern white pine (*Pinus strobus* L.) at breast height (1.5 m) using HAGLOF A 558 increment borers supplied by Canadian Forestry Equipment Limited. The resulting samples, 4 mm in diameter with a maximum length of 20 cm, were stored in plastic drinking straws for

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Fig. 1. Typical mass spectrum, 1–70 atomic mass units (amu), obtained from an annual ring.

Fig. 2. Depth profile for carbon (1), calcium (2), potassium (3), and normalized to zero (4), set to 1000 counts.
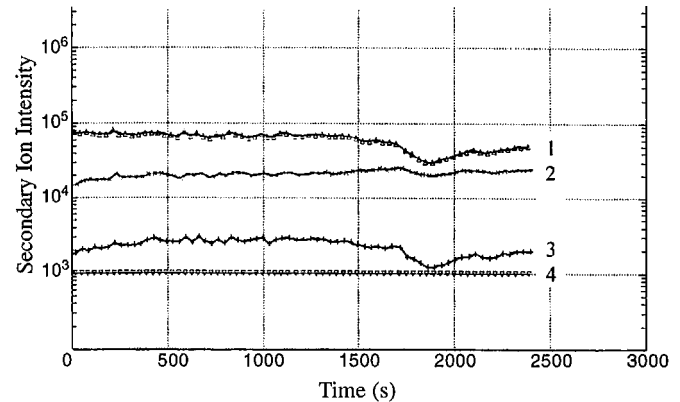
transport to the laboratory. Samples were air dried at room temperature for 48–72 h and then polished to provide a flat surface using a fresh piece of 400-grit sandpaper for each sample with doubly distilled deionized water as lubricant. The sandpaper was shown to be free of metals. The samples were dried at 50°C for 1 h, and then the annual rings were counted and dates were assigned using low-power optical microscopy. Regions of interest were removed from the cores and stored for subsequent SIMS and SEM analysis. SIMS analysis was carried out in rings corresponding to 1990 at all sites, 1965 at sites Ind and Rur, and 1970 at site Hwy. The 1990 and 1965 dates were selected to ensure that gradual changes in metal content, such as increases in sodium from road salt, would be readily detected over the 25-year span. The 1970 rings were used at site Hwy because the trees in this area were relatively young and the earlier date (1965) could not be achieved in all trees sampled. All samples were sputter coated with a thin layer of gold to help prevent surface charging during SIMS and SEM analysis.

The SIMS instrument was a Cameca IMS-3f secondary ion mass spectrometer with a 500-nA O⁻ primary ion beam rastered over a square area 250 μm on edge, while secondary ions were collected from a central area 125 μm in diameter. A 150-V bias voltage was applied to the sample holder to suppress molecular secondary ions. These conditions were used for collection of mass spectra and depth profiling. When collecting mass spectra, the ion yield of each successive integral mass between 1 and 250 atomic mass units was measured for 0.5 s. In the depth profile mode, ion intensities were measured by monitoring preselected masses for 2 s, and mass numbers were cycled according to increasing mass until all the elements selected were exhausted. The cycle was then repeated. This sequence of operations was continued for 20 min. Data collected during the first four mass cycles were rejected, since any surface contamination might have biased these results; as well, this period allowed the sample to reach equilibrium with the primary ion beam. Secondary ion yields obtained during depth profiling were normalized to give oxygen a yield of 1000 ion counts (500 cps). Secondary ion intensities measured during depth profiles rather than absolute metal concentrations were used for subsequent comparison between trees, years, and sites. A Student's *t*-test (Quattro Pro for Windows, v 5.0) was used to assess the statistical validity of averaged sets of ion yields. Measurements of the depth of the resulting ion craters using optical microscopy suggest an ablation rate for the wood samples of about 0.5 μm/min.

SEM/EDX analysis of the sandpaper in both the binder matrix and individual alumina abrasive grains failed to show any metal contamination that may have been transferred to the wood surface prior to SIMS analysis. This fact combined with our rejection of the initial data obtained during the SIMS depth profiles used for the analysis guarantees that the secondary ion yield does not contain pollutants introduced during sample preparation.

The SEM instrument, an ISI-DS130 dual stage scanning electron microscope, was used exclusively to search for possible contaminants on the surface of the sandpaper used for sample preparation.

Results

SIMS mass spectra were used to determine the metals present in highest yield and therefore suitable for further analysis using depth profiles. These spectra suggested that sufficiently high ion yields for comparison between all sites could be obtained for sodium, potassium, calcium, chromium, iron, copper, and zinc. Traces of other metals were detected but not at all sites studied. Carbon, while not a metal, is naturally abundant in the wood matrix and is included in the results.

A typical mass spectrum taken within an annual ring for the range 1 to 70 atomic mass units is shown in Fig. 1, and a typical depth profile for carbon, oxygen, potassium, and calcium is shown in Fig. 2. These figures are included to illustrate the form of data presentation in both modes of SIMS operation. SEM/EDX analysis showed only carbon, oxygen, and silicon to be present on the surface of the sandpaper used during sample preparation. This observation combined with the effective surface cleaning by the primary ion beam during depth profiling guarantees that the metals observed are present in the wood and not introduced during sample collection and preparation.

There was no statistically significant difference in the ion yields between individual trees in the same stand or between individual annual rings in the same tree, although the variability was high. No conclusions could be drawn from this comparison, and the results are not shown.

Tables 1–3 present a comparison of the average secondary ion yield for selected elements for later versus early annual rings (1990 vs. 1965 for sites Ind and Rur, 1990 vs. 1970 for site Hwy). The average represents the total secondary ion count divided by the total number of 2-s counting intervals required to obtain the count. Thus it represents all the ions counted during the depth profiles conducted in a given annual ring at each site exclusive of those counted during the initial sequence of any given depth profile, since it is during this period that the primary ion beam ablates any surface contamination.

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Table 1. Comparison of average secondary ion yields for selected elements between 1990 and 1970 at site Hwy.

Element	Avg. secondary ion yield		Difference (1990–1970)	t	Comment
	1990	1970			
C	5.19×10^4	5.60×10^4	-4.13×10^3	-1.88	No change
Na	1.18×10^5	3.92×10^4	7.89×10^4	7.80	Increase
K	1.32×10^5	7.78×10^4	5.45×10^4	5.59	Increase
Ca	1.70×10^5	2.76×10^5	-1.06×10^5	-8.65	Decrease
Cr	4.88×10^2	4.94×10^2	-6.01	-0.10	No change
Fe	8.32×10^2	6.98×10^2	1.35×10^2	1.24	No change
Cu	2.21×10	8.80	1.33×10	7.41	Increase
Zn	1.43×10	1.56×10	-1.29	-0.98	No change

Note: Student's t-test yields 95% confidence at $t = 1.98$.

Table 2. Comparison of average secondary ion yields for selected elements between 1990 and 1965 at site Ind.

Element	Avg. secondary ion yield		Difference (1990–1965)	t	Comment
	1990	1965			
C	2.05×10^5	1.54×10^5	5.08×10^4	4.4	Increase
Na	6.55×10^4	6.48×10^4	7.15×10^2	0.06	No change
K	1.07×10^5	7.97×10^4	2.74×10^4	2.18	Increase
Ca	4.32×10^5	2.22×10^5	2.10×10^5	5.58	Increase
Cr	7.44×10^2	3.87×10^2	3.57×10^2	5.26	Increase
Fe	1.46×10^3	4.12×10^3	-2.66×10^3	-2.70	Decrease
Cu	2.96×10	1.27×10	1.70×10	2.42	Increase
Zn	1.01×10	1.34×10	-3.31	-2.04	Decrease

Note: Student's t-test yields 95% confidence at $t = 1.98$.

Table 3. Comparison of average secondary ion yields for selected elements between 1990 and 1965 at site Rur.

Element	Avg. secondary ion yield		Difference (1990–1965)	t	Comment
	1990	1965			
C	9.11×10^4	7.12×10^4	1.99×10^4	5.10	Increase
Na	1.02×10^4	7.31×10^3	2.92×10^3	1.92	No change
K	2.75×10^4	1.15×10^4	1.60×10^4	4.64	Increase
Ca	7.54×10^4	5.44×10^4	2.10×10^4	2.25	Increase
Cr	1.39×10^2	1.20×10^2	1.86×10	0.82	No change
Fe	1.93×10^2	9.40×10^3	-9.20×10^3	-3.17	Decrease
Cu	2.80×10	2.5	2.55×10	2.61	Increase
Zn	6.82	1.62	5.20	1.83	No change

Note: Student's t-test yields 95% confidence at $t = 1.98$.

The average obtained in this way is representative of all the trees sampled at any given site.

Table 4 summarizes the differences in ion yield (higher or lower) between sites in the same year for 1990; for early rings the comparison is between the 1965 years for the Rur and Ind sites, while the 1970 ring is used for the Hwy site.

Discussion

While no pattern is common to all elements, there are statistically significant differences in ion yield with time at all sites studied. The behaviour of metals in trees is complex and poorly understood; consequently, comments on the changes in ion yields observed are generally speculative. It is reasonable, however, to suggest that the increase in sodium at site Hwy

between 1970 and 1990, Table 1, is due to road salt present in highway runoff. This conclusion would be consistent with other reports in the literature of salt damage to trees subjected to winter road salt (Foster and Maun 1978). This may also be the source of increased potassium, since road salt is typically 8% potassium. The calcium decrease at this site may be the result of salt damage to the trees. There is no satisfactory explanation for the copper increase at this site. Carbon, iron, chromium, and zinc fail to show any significant changes at this site.

At site Ind, Table 2, carbon and calcium yields have increased with time as well as potassium, chromium, and copper. Iron and zinc have decreased. These changes may be consistent with the closure of the waste disposal site in 1986, but it is difficult to establish a credible causal link.

Table 4. Comparison of pooled data between different sampling sites.

Comparison	C	Na	K	Ca	Cr	Fe	Cu	Zn
Hwy 1970 vs. Rur 1965	–	+	+	+	+	–	+	+
Hwy 1990 vs. Rur 1990	–	+	+	+	+	+	0	+
Ind 1965 vs. Rur 1965	+	+	+	+	+	0	+	+
Ind 1990 vs. Rur 1990	+	+	+	+	+	+	0	0
Ind 1965 vs. Hwy 1970	+	+	+	–	–	+	+	0
Ind 1990 vs. Hwy 1990	+	–	–	+	+	+	0	–

Note: + indicates a significant increase in ion yield at $p < 0.05$, – indicates a significant decrease in ion yield at $p < 0.05$, and 0 indicates no statistical difference at $p < 0.05$.

Site Rur, Table 3, shows an increase in carbon, potassium, calcium, and copper with time. There is no change in sodium, chromium, or zinc, but iron decreases.

Table 4 presents a summary of the differences in ion yield between sites in the same or comparable years. Unfortunately it is difficult to interpret the differences for all ions at all sites. Sodium and potassium are always elevated relative to the Rur site. The Hwy site is lower in these elements relative to site Ind only in the early rings (1970 vs. 1965), while it is higher in 1990. These observations are consistent with pollution of the Hwy site by road salt and the relative isolation of the Rur site (the latter is farther from roads and (or) pollution sources such as waste disposal sites than the other two sites). Site Ind is, in general, higher in chromium and iron than the other sites. This observation may be attributed to the sites proximity to a solid waste disposal site.

Conclusions

The results can now be used to address the objectives outlined in the Introduction.

(1) There is no statistical difference in the secondary ion yield between individual trees in the same stand in the same year because of the high variance in the results. Eklund (1995) has reported similar results. This observation is consistent with the large number of variables in the system. Individual trees in the same stand may be affected by different water and air movements, insect or mechanical damage, or disease, to name a few. All instrumental analytical techniques are subject to error, and in SIMS surface charging is critical. This will be affected by the local conductivity of the wood and (or) the uniformity of the gold coating. In addition, other authors have suggested that there may be significant seasonal variations in metal uptake by trees (Selin et al.1993; Yin and Arp 1994).

(2) There are significant differences between years when the data from all the trees at a site are pooled and compared for individual years. In general the metal content of the trees has increased with time. The increase in sodium at site Hwy is most notable and highway runoff is indicated. The increased potassium at this site may also originate from road salt, but since a potassium increase occurs at all sites, agricultural activity is a possible source. There is no significant change in the sodium content of trees at site Rur. This site is the farthest from major traffic. Copper has increased at all sites. Calcium has decreased at site Hwy but has increased at sites Ind and Rur; it is possible that the

high sodium at site Hwy interferes with calcium transport. The behaviour of chromium, iron, and zinc is erratic.

(3) Pooled data comparing the same year at different sites also show consistent, significant differences between sites. Comparison of sites in 1965 (1970 at site Hwy) shows site Rur to have the lowest metal burden and site Ind to be generally higher in metal content. These differences are retained, for the most part, in 1990, with the exception of the rapid increase in sodium and potassium at site Hwy. The closure of the waste disposal site near site Ind in 1986 makes interpretation of the results more difficult.

(4) The differences between sites can be generally correlated with known site characteristics. The intrusion of road salt at site Hwy is most striking. The industrial site, Ind, generally shows a higher concentration of pollutant metals, while the rural site, Rur, is comparatively clean.

(5) Finally our previous observation, that SIMS is an effective tool for probing trace elements in tree rings, is confirmed.

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