

Historical Changes in Pb concentrations and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in tree-rings of sycamore, oak and Scots Pine in north-west England.

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Abstract

Lead concentrations in tree rings of sycamore (*Acer pseudoplatanus*), oak (*Quercus robur*) and Scots Pine (*Pinus sylvestris*) sampled from trees growing in a country park in north-west England were measured in wood formed over the past 130 years. Concentrations of Pb peaked in wood formed between 1900 and 1940 in oak and Scots pine; probably a result of chemical changes during heartwood formation. In contrast, Pb concentrations in sycamore, a species that has similar heartwood and sapwood chemistry, were relatively constant in wood formed between 1880 and 1950. Lead concentrations decreased steadily in sycamore wood formed after the 1950s, and decreased more abruptly in wood formed after 1985. Furthermore, $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in tree-rings of sycamore were relatively constant, around 1.17 in wood formed prior to the 1930s, but decreased steadily thereafter reaching a minimum value of less than 1.16 in wood formed between 1975-1985. $^{206}\text{Pb}/^{207}\text{Pb}$ ratios increased sharply during the late 1980s, reflecting the reduction of Pb emitted from gasoline. Overall, these data suggest less than 10% of the Pb measured in sycamore tree rings formed over the past 120 years was derived from gasoline emissions.

Introduction

Lead concentrations and lead isotope ratios measured in ice, peat and sediment cores have been used to reconstruct historical changes in the levels and sources of atmospheric Pb deposition (1,2). Lead concentrations in tree-rings may also be used to monitor historical changes in atmospheric Pb deposition (3), although several problems exist with the interpretation of dendrochemical data, in particular the potential for lateral transport between individual rings which prevents the historical reconstruction of trace metal deposition levels (4). There is considerable uncertainty as to which tree species, if any, are suited to environmental monitoring (4). If suitable tree species are identified then there are several benefits from using dendrochemistry in environmental monitoring. Trees are widespread and can be used to monitor urban or industrial areas, unlike previous studies using ice, peat or sediment cores, which are generally restricted to areas remote from urban centers. Many tree species grow *in situ* for several hundred years, tree rings are easily dated and concentrations are relatively high and give an indication of historical changes in bio-available metal levels. In this study, Pb concentrations and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios were measured in tree-rings in 5-yr or 10-yr (before 1920) increments from cores extracted from mature sycamore (*Acer pseudoplatanus*), English oak (*Quercus robur*) and

Scots pine (*Pinus sylvestris*) at a country park in the center of a large town in north-west England. Changes in patterns of Pb concentration over time were compared between the 3 tree species and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios were measured in sycamore tree-rings. Studies conducted in the U.K. have shown that there has been a decrease in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in peat or sediment samples deposited after 1930 due to the introduction of leaded gasoline, which has a much lower $^{206}\text{Pb}/^{207}\text{Pb}$ ratio than Pb derived from urban, industrial or natural sources in the U.K. (2).

Materials and Methods

All trees (8 sycamore, 4 English oak and 4 Scots pine) were sampled in May 1998 in the grounds of Haigh Hall Country Park (OS NGR SJ588 086). The area sampled is part of a lower plantation that was established in the mid-1800s and is located about 1-km northeast of Wigan town center. Historically, mining and cotton industry flourished in the Wigan area and the population peaked in

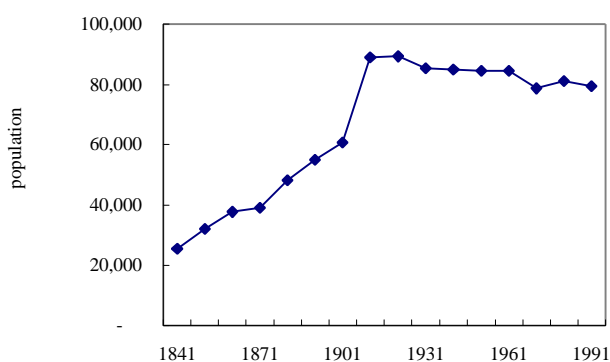


Figure 1: Population of Wigan: 1841-1991

the early 1900s (Fig. 1) coinciding with the maximum output from both industries. Tree cores were taken at breast height (1.5 m) from the south-west-facing aspect (facing the town center) of each tree using a 5-mm stainless steel increment borer. Samples were immediately sealed in dry, plastic straws and were stored at $-10\text{ }^{\circ}\text{C}$ prior to analysis. Each core was divided into 5-yr increments dating to 1920, and 10-yr increments in wood formed prior to 1920.

Increments were separated using a stainless-

steel knife, and samples were placed in pre-washed ($10\% \text{H}_2\text{SO}_4$) 50 mL borosilicate glass tubes, dried at $70\text{ }^{\circ}\text{C}$ for 24 h, weighed and then dry ashed at $400\text{ }^{\circ}\text{C}$ in a muffle furnace for 12 h. The ash was dissolved in trace-grade HNO_3 and digested under reflux at $100\text{ }^{\circ}\text{C}$ for 6 h. Samples were diluted with dd- H_2O prior to analysis using a Perkin-Elmer SCIEX ELAN inductively coupled plasma mass spectrometer (ICP-MS) under conditions described previously (5).

Precision and accuracy were confirmed by repeated analysis of NIST apple leaf standard reference material (1515). All solutions were analysed for total Pb, and three of the sycamore cores were also analysed for $^{206}\text{Pb}/^{207}\text{Pb}$ ratios. Accuracy of the spectrometer was monitored by including measurements of the Pb isotope standard SRM981.

Results and Discussion

Average Pb concentrations in sycamore, oak and pine were 3.8, 2.1 and 5.2 mg/kg, respectively (Figs 2 and 3). Temporal patterns in Pb concentration also differed among the 3 tree species. Lead concentrations in oak and pine over time were highly correlated ($r=0.83$; $p<0.001$). Weaker, but statistically significant relationships in lead concentration over time were found between sycamore and oak ($r=0.40$; $p=0.05$) and sycamore and pine ($r=0.47$; $p=0.02$). Lead concentrations in sycamore increased from 2.5 to 4.0 mg/kg during the late 1800s and remained relatively constant until the 1950s when Pb concentrations gradually decreased. The gradual

decrease in Pb concentration from 4.0 mg/kg to around 2.0 mg/kg continued until the mid-1980s after which time Pb concentrations declined dramatically. Excess $^{206}\text{Pb}/^{207}\text{Pb}$ was calculated as:

$$^{206}\text{Pb}/^{207}\text{Pb}_{\text{excess}} = [(\text{Pb}_{\text{meas}} \times ^{206}\text{Pb}/^{207}\text{Pb}_{\text{meas}}) - (0.2 \times 1.1740)] / (\text{Pb}_{\text{meas}} - 0.2)$$

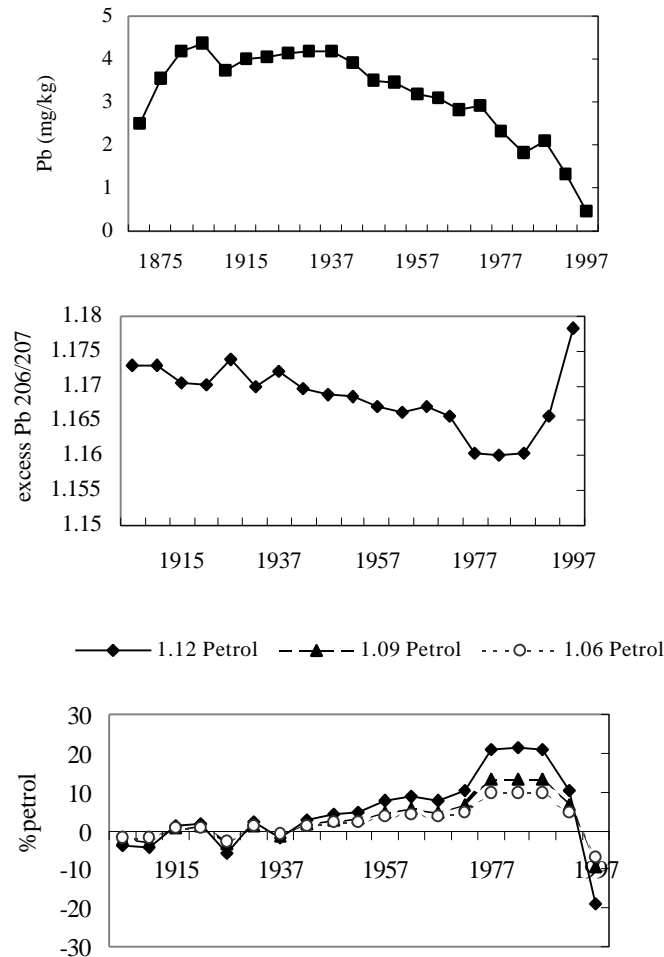


Figure 2. Pb concentration, excess $^{206}\text{Pb}/^{207}\text{Pb}$ and %petrol lead in Sycamore tree rings

$$\text{Pb}_{\text{petrol}} (\%) = [(1.169 - ^{206}\text{Pb}/^{207}\text{Pb}_{\text{excess}}) \times 100] / (1.169 - ^{206}\text{Pb}/^{207}\text{Pb}_{\text{petrol}})$$

The value 1.169 was chosen to represent the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of coal (2), and the percentage Pb contribution from petrol was determined using 3 possible scenarios which hold the $^{206}\text{Pb}/^{207}\text{Pb}_{\text{petrol}}$ ratio constant at 1.06, 1.09 and 1.12, respectively. Prior to the mid-1930s, the contribution of petrol Pb was negligible, but decreased steadily thereafter. This date agrees well with the period when Pb was added to petrol in the UK (late 1920s) and when a decrease in the $^{206}\text{Pb}/^{207}\text{Pb}$ has been reported in peat and sediment cores in the UK (2). The contribution of Pb from petrol increased steadily, peaking in wood formed between 1975 and 1985 - the period of maximum vehicular Pb production reported by the UK department of transport. The contribution of petrol

As tree cores only dated back to the late 1880s when there was already considerable Pb contamination, we used a background value of 1.174 based on data reported in Farmer *et al.* (2). Likewise, a background Pb concentration of 0.2 mg/kg was selected based on the relationship between Pb concentrations in *Acer* wood and soil pH determined at relatively uncontaminated sites in central Ontario, Canada (unpublished data). Excess $^{206}\text{Pb}/^{207}\text{Pb}$ values were relatively constant, around 1.17 prior to 1930, after which time excess $^{206}\text{Pb}/^{207}\text{Pb}$ ratios declined steadily, reaching a minimum ~ 1.16 in wood formed between 1975-1985. The excess $^{206}\text{Pb}/^{207}\text{Pb}$ ratio increased dramatically after this period and the excess $^{206}\text{Pb}/^{207}\text{Pb}$ ratio was around 1.17 in the most recently formed wood increment. These ratios may be used to calculate the contribution of petrol lead in tree rings (2), using the following equation:

Pb declined dramatically after this period, reflecting the introduction of unleaded petrol and a reduction in the Pb content of leaded petrol in 1986.

Overall, these data indicate that the chemical analysis of sycamore tree-rings provides an historical record of Pb deposition. Although background $^{206}\text{Pb}/^{207}\text{Pb}$ ratios and Pb concentrations along with the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of coal may vary slightly from the values used in this study, the results

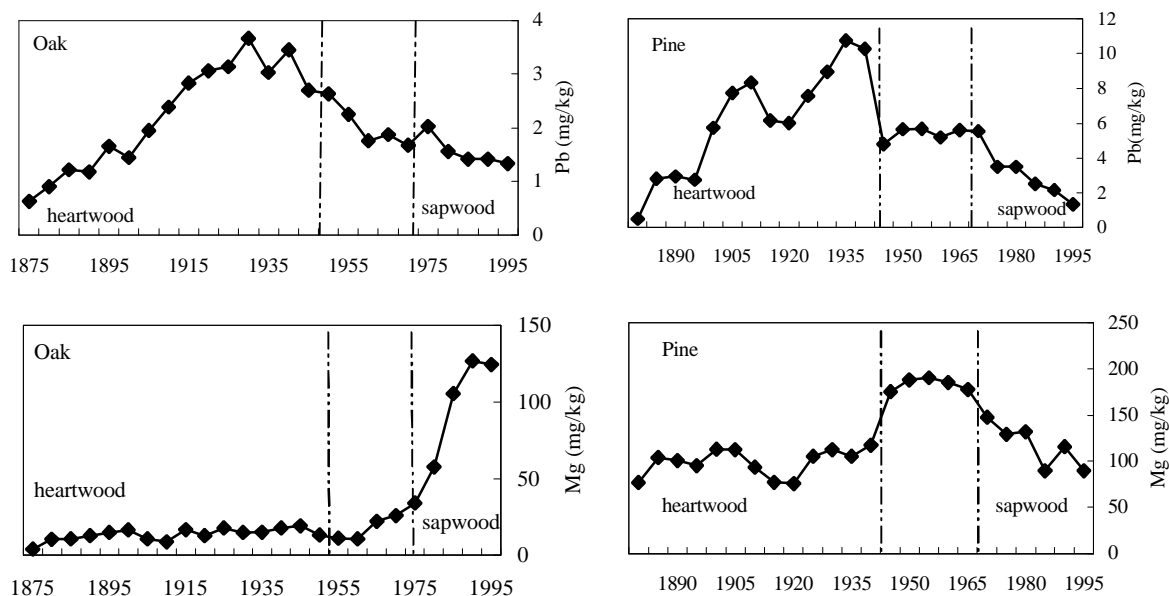


Figure 3. Lead and magnesium concentrations in tree rings.

indicate that less than 10% of Pb in sycamore tree-rings originates from vehicular emissions. It appears that the majority of Pb contamination at the park originates from urban and industrial emissions (particularly coal burning).

Patterns of Pb concentration in pine and oak were only weakly related to the pattern identified in sycamore. Peaks in Pb concentration occurred in both species in wood formed in the early part of this century. Both species have very pronounced heartwood and exhibit distinct chemical changes between the sapwood and heartwood, which do not occur in *Acer* (Fig. 3). Such chemical alterations indicate that changes in wood chemistry occurred after tree ring formation. Patterns of Pb concentration in oak and pine are likely a result of Pb accumulation in the heartwood, and do not appear to provide an historical record of Pb deposition.

References

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