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The utility of *Pinus sylvestris* L. in dendrochemical investigations: Pollution impact of lead mining and smelting in Darley Dale, Derbyshire, UK

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Mean site dendrochemical records for Pinus sylvestris can be used to estimate the general scale and timing of atmospheric pollution episodes.

Abstract

This research investigates atmospheric pollution from an isolated and increasingly productive lead-smelting site by examining the dendrochemistry of *Pinus sylvestris* growing in the local environment and at control sites. Tree increment cores and soil in the rooting environment were analysed for lead content. Inter-site comparisons of lead-in-soil suggest that contamination of the soil may be a less important pathway for lead inclusion within wood than pathways via bark or needles. Levels of lead-in-wood (up to 38 $\mathrm{mg\,kg^{-1}}$) are at the upper end of those previously reported. There is evidence of radial translocation of lead towards the heartwood and variability in intra-site dendrochemical records. Mean site lead-in-wood records can however be related to a well-documented pollution chronology and also suggest the importance of local topography in the dispersal and deposition of particulate lead. This study demonstrates that *P. sylvestris* can be used to estimate the scale and timing of past pollution episodes in similar environmental contexts to those investigated at Darley Dale, where precisely dated pollution chronologies are lacking.

Keywords: Dendrochemistry; *Pinus sylvestris*; Lead translocation; Topography; Atmospheric pollution

1. Introduction

The chemistry of tree-rings, and in particular lead content, has been investigated since the 1960s (Schreoder and Balassa, 1961), as interest has grown in the effects of pollution on the environment and on human health. Lead has also successfully been used as a chronological marker in ice cores, lake sediments and peat deposits during the last 3000 years, suggesting synchronous temporal changes in past pollution deposition (c.f. Hong et al., 1994; Renberg et al., 2001; Rothwell et al., 2007).

Of the elements chosen for past dendrochemical assay, lead has been used in a comparatively large number of studies within the historic period, including the varying impacts of vehicle emissions (e.g. Ward et al., 1974; Orlandi et al., 2002), metal-processing works (e.g. Guyette et al., 1991; Eklund, 1995) and also in the development of isotopic studies (e.g. Åberg et al., 1999; Watmough et al., 1999; Tommasini et al., 2000; Watmough and Hutchinson, 2002; Bindler et al., 2004; Patrick and Farmer, 2006).

Studies relating to late 20th century lead pollution have however indicated differing degrees of success in the reconstruction of pollution chronologies based on tree-rings (c.f. Hagemeyer, 1993; Schweingruber, 1996; Watmough, 1999). This has been attributed to methodological pitfalls (c.f. Smith

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and Shortle, 1996). These include: uncertainties regarding elemental uptake pathways — roots, leaves, bark; preferential uptake of elements by specific tree species; the effects of soil acidity on elemental uptake (c.f. Guyette et al., 1991); radial translocation of elements within the wood structure, including differing dendrochemistry affected by the heartwood and sapwood transition (c.f. Watmough and Hutchinson, 2002 — although lead is a non-essential element for tree growth, and as such had shown previous limited tendencies for radial movement, Watmough, 1999); the impact of tree injury and pathogens; considerable variations in elemental concentrations in trees sampled close together, based on factors such as tree age; and the chemical contamination of increment cores and other wood samples (Hagemeyer, 1993; Smith and Shortle, 1996; Watmough, 1999).

Careful choice of sampling sites, tree species selected and sampling methods employed can obviate some of these difficulties (c.f. Schweingruber, 1996; Watmough, 1999), although some well-constrained research has failed to satisfactorily detect fine particulate lead produced by activities such as smelting (Sturges and Barrie, 1989).

Schweingruber (1996) states that no one tree species is ideal for constructing pollution chronologies. Site-specific factors seem to be of the utmost importance as demonstrated by Guyette et al. (1991) for Eastern Red Cedar (*Juniperus virginiana*), whilst in the UK, Sycamore (*Acer pseudoplatanus*) demonstrated a superior pollution record compared to Oak (*Quercus robur*) or Scots pine (*Pinus sylvestris*) at one site in north-west England (Watmough and Hutchinson, 2002), as the latter appeared to concentrate lead in the heartwood. Previously, Watmough (1999) had contended that conifers were best suited physiologically for the construction of heavy metal chronologies (c.f. Legge et al., 1984).

Few studies have successfully correlated tree-ring chemistry with established phases/volumes of mining and/or smelting activity (c.f. Watmough and Hutchinson, 1996). The current study tests the conflicting evidence for the suitability of *P. sylvestris* in dendrochemical assays, comparing lead-in-wood measurements to environmental monitoring data and to precisely dated historical records of changing smelter and mitigation technology.

2. Study area

Darley Dale is a valley trending north-west to south-east, which is located approximately 27 km to the south-west of Sheffield (Fig. 1). It determines the course of the River Derwent and has been incised into Carboniferous Gritstone and limestone. Both rock types are major constituents of the wider geographical area; the uplands of the Peak District. The White Peak (name relating to its limestone solid geology) is noted for its mineral veins intruded within its limestone and associated basalt lavas. Of particular importance have been lead ores, of which lead sulphide (Galena) is the most common. These lead ores have been exploited since the first century A.D. and probably in prehistoric times (Barnatt, 1999; Ford and Rieuwerts, 2000).

Mining in Saxon times is corroborated by a carving at Worksworth Church (Ford and Rieuwerts, 2000) and lead smelting is recorded by the remains of boles (small wind-blown furnaces located on hilltops) throughout Derbyshire, from the 12th to the 16th centuries (Kiernan and Van de Noort, 1992). By 1737 smelting efficiency was greatly enhanced by the introduction of the coal-fired Cupola Furnace and later by the Spanish Slag Hearth, circa 1850 (Willies, 1990; Ford and Rieuwerts, 2000).

From 1860 there was a rapid decline in lead mining in the Peak District with the exception of the Mill Close Mine, adjacent to the River Derwent, and the settlement of Darley Bridge, which was re-worked between 1839 and its closure due to flooding in 1940 (Willies et al., 1989).

Although mining activity had virtually ceased by 1940, there remained a number of sources of particulate lead that could be assimilated by trees in the Darley Dale area after this date (Willies, personal communication). These include: residual lead-in-soil and wind-blown dust from mining over many centuries in the wider local area. For instance the village of Winster 2 km to the south-west of the Enthoven site had a population of c. 2000 (with 24 inns and alehouses) in 1750 and was the third largest settlement in Derbyshire at that time (Ford and Rieuwerts, 2000).

Other potentially important local sources of lead are the spoil heaps from the Mill Close mine located opposite the Enthoven site (not owned by Enthoven and re-worked for fluorspar in the 1970s) and road movements of fluorspar (containing an estimated 3—4% Pb) from local quarries in the 1970s and 1980s, although Watmough (1999) notes that previous dendrochemical studies have been unsuccessful in determining lead pollution from such sources.

Lead from motor vehicle emissions could also be represented in the dendrochemical record, due in particular to lorry movements at and close to the site. Lead from some vehicles has however demonstrated a marked decline since the introduction of unleaded petrol in 1985 (NETCEN, 2003). Further-a-field lead-utilising industries, such as steel and paintworks, represent other possible, but unlikely sources.

In spite of potential lead contamination from other sources, the H.J. Enthoven site has remained the only active source of lead emissions in Darley Dale and its hinterland for in excess of 70 years. Whilst the Mill Close Mine was still in operation, a lead smelter was established at the site in 1934 (now the H.J. Enthoven Darley Dale smelter, hereafter referred to as the Darley Dale Smelter — Fig. 1), and since 1940 the smelter has been an isolated and increasingly productive point source of lead (production today based largely on the recycling of batteries), fulfilling the most important pre-requisite stipulated by Schweingruber (1996) and Watmough (1999) for successful dendrochemical investigations.

3. Methods

3.1. Tree-ring and soil sampling

Legge et al. (1984) contended that conifers are best suited physiologically to dendrochemical study (Section 1). It was thus fortuitous that *P. sylvestris* was the most widely available species growing at the Darley Dale Smelter site and in the surrounding area. Its generally restricted distribution in the

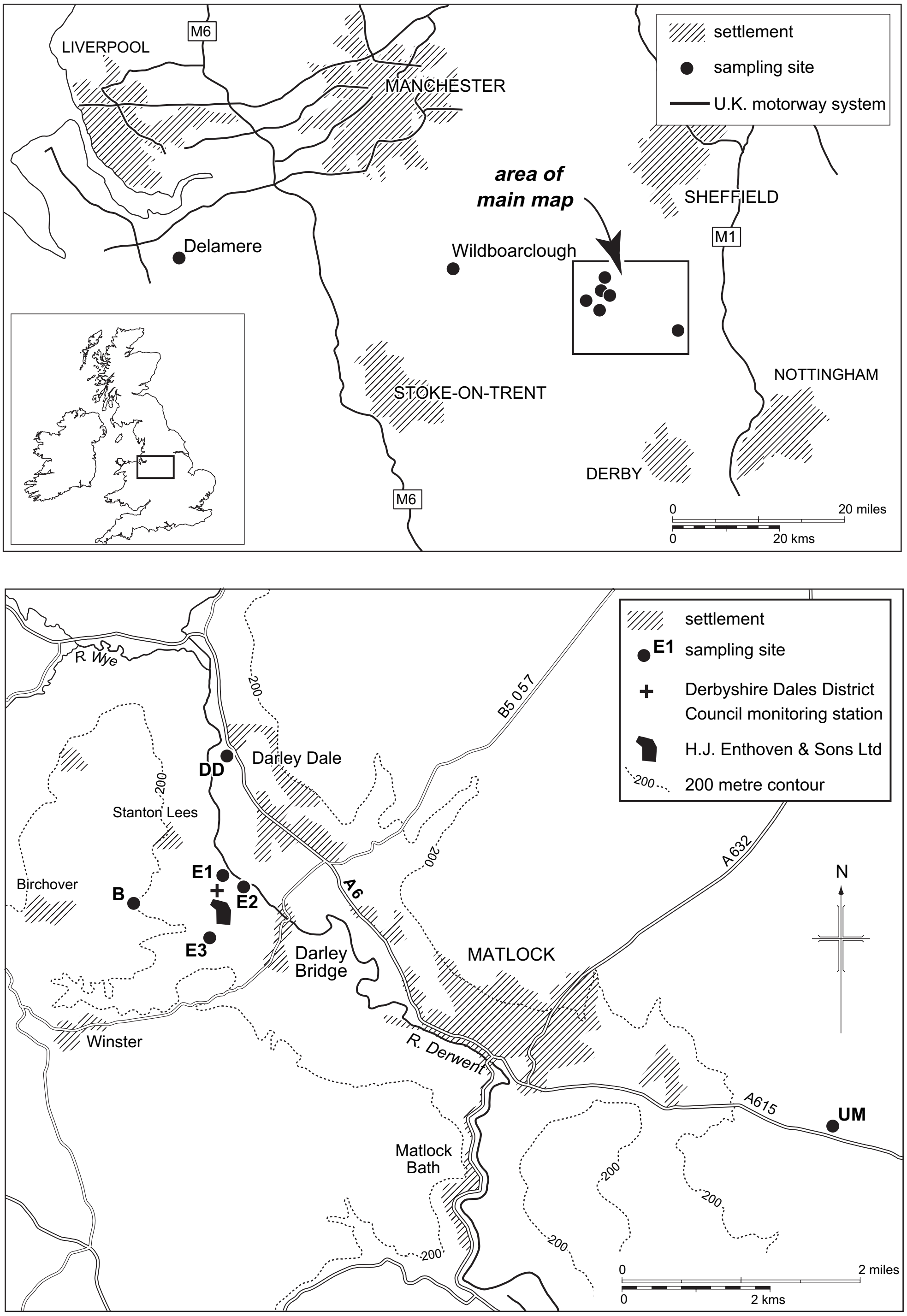

Fig. 1. Sampling locations in the main Darley Dale study area and at control sites to the west shown in relation to a map of the British Isles (inset). Site codes used in the main study area are explained in Table 2 and within the text.

wider area of the Pennine hills has been correlated with industrial pollution (linked to SO_2 deposition by Farrar et al., 1977), further emphasising the species' sensitivity and its suitability for study here.

Choice of sampling sites was, however, constrained by the general lack of trees and woodland in Darley Dale. This was in part due to the generally pastoral nature of the valley, and also to the extent of adjacent settlements (Fig. 1). Isolated groups of *P. sylvestris* did on the other hand provide greater potential for accumulating anthropogenic pollution than more dense woodland (Schweingruber, 1996). Sampling was undertaken on land owned by H.J. Enthoven surrounded the Darley Dale smelter (E 1−3). Sites further-a-field were located to the north of the settlement of Darley Dale (DD) and at hilltop locations close to Birchover (B) to the west, and at Upper Matlock (UM), over 8 km to the west south-west (Fig. 1).

Control sites thought to be unaffected by lead emissions from the main study area were chosen at Delamere and at Wildboarclough, both located in Cheshire to the west. Wildboarclough is located at the edge of the Peak District upland area. In Darley Dale the prevailing wind is from the north-west (Enthoven and Sons, 2001), whereas for the control sites it is from the south-west.

Live trees at each site were sampled at chest height by taking 5 mm increment cores using a Teflon-coated Pressler-type corer. A minimum of 2 and a maximum of 4 trees were sampled at each site. Where practicable, cores were taken from the side of the tree facing the smelter (c.f. Watmough, 1999). All cores were stored in dry paper straws and air-dried prior to further analysis. Soil was sampled underneath tree canopies in the rooting environment at each site. Bulk samples of around 50 g were taken from the top 150 mm of soil profiles and transported in plastic bags. Soil samples were also air-dried prior to further analysis.

Sites within the Darley Dale area are characterised by shallow soils and similar Gritstone substrates that are ecologically comparable (Schweingruber, 1996). The site at Wildboarclough is underlain by Gritstone, and directly comparable with the Darley Dale sites (c.f. Ford and Rieuwerts, 2000). The substrate at Delamere is fluvio-glacial sand with underlying solid geology of Triassic sandstone (Worsley, 2001).

3.2. Tree-ring and soil analyses

Ring-width measurements were made in order to facilitate cross-matching and identification of any false and or missing rings (c.f. Baillie, 1982; Schweingruber, 1988). No regional pine chronology was available for comparative purposes, but missing/false rings were not a problem in the study area. Dendrochronological procedures followed the method described in Lageard et al. (1999), using Dendro software (Tyers, 1999). For each tree core, 5 year increments were cut from the cores using a stainless steel blade, starting with the most recent tree-ring. Wood samples were soaked in 16 M HNO_3 overnight and then digested at 100 °C for 2 h using a hotplate apparatus. All digested wood samples were then filtered through Whatman No. 42 filter paper into acid-washed plastic universals and refrigerated prior to lead analysis. Wood samples were analysed for lead using ICP-AES (Varian). Three duplicate measurements were made and the precision was <6% relative standard deviation (RSD). Mean results were then calibrated according to sample weight (c.f. Watmough, 1999). Four standards (0.5, 1, 5 and 10 $\mathrm{mg\,kg^{-1}}$) were prepared from stock solution and used to calibrate the ICP-AES. After every 15 samples, each of the standards were analysed to check instrument calibration and used to correct for any instrumental drift during each batch. Blank samples (acidified distilled water passed through filter paper) were also analysed along with the wood samples. The mean Pb concentration of the blanks was 0.03 $\mathrm{mg\,kg^{-1}}$.

For each soil sample, 100 ml of de-ionized water was added to 10 g of soil sub-sample and pH was determined using a standard calibrated pH electrode, after each solution had been filtered through Whatman No. 1 filter paper. Ten milliliters of 16 M HNO_3 was also added to 1 g of dry soil and digested, filtered and stored using the same procedure as the wood samples. Analysis of soil lead concentrations was undertaken using a Flame Atomic Absorption Spectroscopy (F-AAS: Perkin Elmer PE 3110). Three replicate measurements were made for each soil sample and the RSD was 10% or better. The F-AAS was calibrated using two lead standards; 476 $\mathrm{mg\,kg^{-1}}$ and 13,773 $\mathrm{mg\,kg^{-1}}$, as used in a previous inter-laboratory calibration exercise (c.f. Eastwood and Jackson, 1984). A blank sample was also analysed and was below the detection limit of the F-AAS.

3.3. Statistical analyses

Inter-site data patterns in lead pollution were compared using *t*-tests. The degree of associations between intra- and inter-site lead records was assessed using Pearson bivariate correlations.

3.4. Secondary data sources

Lead-in-air data was provided by H.J. Enthoven and Sons (average data for 6 monitoring stations all within 0.8 km of the Darley Dale smelter – Enthoven and Sons, 2001) and by Derbyshire Dales District Council from their Warren Carr monitoring station located to the north of the smelter (Fig. 1). Individual data sets were unavailable for the Enthoven monitoring stations and the lower lead-in-air levels compared to the Enthoven average can be explained by the up-wind location of the Warren Carr site. H.J. Enthoven and Sons also provided data relating to the production of lead and alloys between 1954 and 2001, and a history of lead smelting at Darley Dale works, with reference to health and to the environment (Enthoven and Sons, unpublished chronology – Table 1). This data gave a valuable insight into production levels, as well as into the introduction of new technologies/mitigation measures.

4. Results

4.1. Air quality and Pb production

Two sets of lead-in-air monitoring data from stations close to the Darley Dale smelter show similar trends (Fig. 2). Declines between 1983 and 1988 can be directly related to the replacement of a problematic battery breaker (1983) and smelter redevelopment 1984–1988 (Table 1). Although production of

Table 1
History of lead smelting at the site of the Mill Close Mine (Darley Dale Smelter), based on H.J. Enthoven unpublished chronology

1934–1935	Mill Close Mines establish a smelter to treat lead ore Newman Hearth Furnaces, Visco Bag Filter Lime Tower Scrubber for sulphur removal, emissions at c. 20 feet Furnaces very dangerous for health of operators
1940	Mill Close Mine closed due to flooding. Prior to closure 1000 tons of ore mined per week
1941	H.J. Enthoven purchased smelter to remove lead from scrap. Shadow factory for Rotherhithe
1950–1956	2 Rotary Furnaces and one Reverberatory Furnace replace Newman Hearths
1958–1962	Smelting ceased due to shortage of scrap batteries. All smelting transferred to Rotherhithe. Darley Dale remained a collection center
1963	Large Reverberatory Furnace, new Visco Bag Filter and 150 foot tall chimney installed Tall chimney has the advantage that small quantities of lead escaping through the bag filters are dispersed over a wider area than when using the Lime Tower
1966	Blast furnace installed, chimney raised to 208 feet For first 4–5 weeks of working the fume emissions from the top of the furnace were very dense Furnace capacity reduced in response
1969	Tonolli Battery Breaker installed Proved dangerous to health of operators. High lead in air results from tests carried out by the Chemical Inspector Improvements: conveyors enclosed, Breaking drum and pits enclosed and ventilated
1983	Replacement battery breaker installed Significant improvement in costs/environment
1984–1988	Smelter redevelopment. Capacity increased from 40,000 to 70,000 tonnes p.a.
1997	Two new bag houses installed.

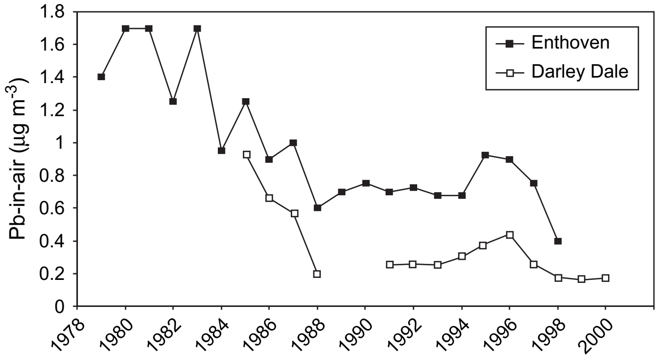

Fig. 2. Mean annual lead-in-air data from 6 Enthoven sampling stations (1979–1998) and from Warren Carr (1985–1988, 1991–2000). Data courtesy of H.J. Enthoven and Derbyshire Dales District Council.

lead and alloys rose during the latter period from 40,000 to 70,000 tonnes (Fig. 3), the redevelopment resulted in significant improvements in mitigation technologies (K. Gregory, H.J. Enthoven & Sons, personal communication, 2001). Lead-in-air levels remained steady between 1988 and 1994, rose slightly up to 1996 and declined following installation of two new bag houses (part of the filtration system designed to minimise emissions of particulate lead) in 1997.

4.2. *Soil and tree-ring chemistry*

Table 2 provides a summary of wood and soil samples, their provenance and analyses. Soil samples were generally acid to neutral (pH 3.5–6.8). Soil results indicate that the current guideline value for lead in public open spaces (450 mg kg^{-1}, DEFRA, 2002) is exceeded in all four samples taken from under trees on the Enthoven site (2033–8935 mg kg^{-1}). Soil samples from Darley Dale, Birchover and Upper Matlock ranged between 443 and 787 mg kg^{-1} and the control sites between 70 and 196 mg kg^{-1}.

The Darley Dale dendrochemical data compare well with values for lead-in-wood reported in the literature. 38 mg kg^{-1} (Upper Matlock and Enthoven) are among the highest maximum values recorded in tree-rings (Table 3). Table 3 also shows that the lowest values are comparable to cleaner/unpolluted sites. The Wildboarclough control site is located, towards the western edge of the Peak District on Gritstone geology and is more likely than Delamere to have experienced pollution from lead mining from a range of localities within the Peak District area. Despite this, the dendrochemical records of both control sites in Cheshire (over 23 km to the west) are significantly different from the four sites located within 8.5 km of each other in Darley Dale, the main study area (Fig. 4 and Table 4). Lead-in-wood measurements are generally at low levels during the study period at Wildboarclough 1–8 mg kg^{-1}, and at Delamere 1–6 mg kg^{-1} (Fig. 4).

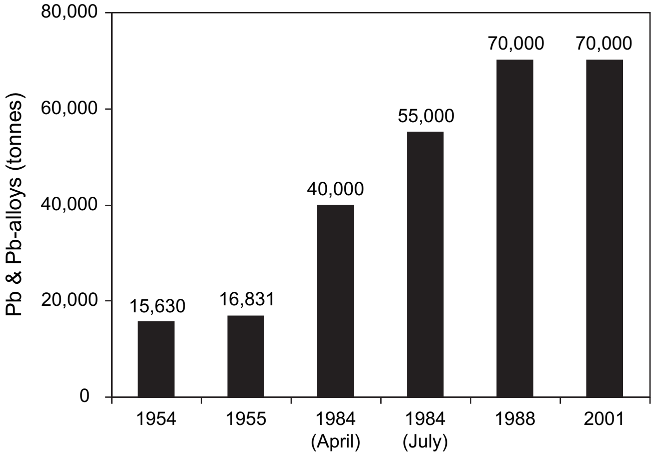

Fig. 3. Production of lead and alloys at the Darley Dale Smelter (H.J. Enthoven & Sons), 1954–2001. 1984 includes two production levels, for April and July, due to a two stage expansion of output in that year.

Trees, sampled close to the Darley Dale Smelter and in its immediate hinterland (E, DD, B, UM) show steady, and in some cases accelerated rises in lead-in-wood concentrations, from low levels of 1–4 mg kg^{-1}, to a series of peaks of up to 38 mg kg^{-1} (Enthoven tree K5, 1974–1978). These rises commence in wood laid down in the 1920s at Enthoven, Darley Dale and Birchover, but the patterns and scale of lead-in-wood cannot be replicated with annual resolution between trees (Fig. 4).

Lead records for two of the three trees from the Upper Matlock site, F17 and F5 (20 years younger), contain similar concentrations of lead in their initial growth periods (8–10 mg kg^{-1}). The record for F17 commences in the 1920s and has noticeably higher levels of lead compared to contemporary records from Enthoven. There are steep rises in lead concentrations in wood laid down in mid-1940s (F17), mid-1960s (F17 and F5) and mid-1970s (F17 and F5). F17 and F5 have very similar peak values of 37–38 mg kg^{-1} for the period 1974–1978. The record for F22, a younger tree, starts from a lower level (1 mg kg^{-1}, 1949–1953), and follows the site trend of rising lead-in-wood, especially the record of F17, but at much lower concentrations. Complacent dendrochemical responses are also a feature at the Enthoven site (tree K27) and at Birchover (F24).

4.3. *Inter-site comparisons*

Given the variability apparent between individual dendrochemical data, mean site records were created to facilitate inter-site comparison and comparisons with Pb-in-air and documentary records.

Visual comparison of the mean site data from Enthoven (E) and Upper Matlock (UM) (Fig. 5A) show good initial agreement 1939–1959, and subsequently between 1959 and 1983, although in the latter period UM has noticeably higher concentrations. The E and UM graphs again exhibit similarity between 1983 and 1998, as UM parallels the lead-in-air data trend illustrated for the Enthoven site 8.5 km up-wind (Fig. 2).

Comparison of site averages for E and Darley Dale (DD) (Fig. 5B) shows good agreement between 1909 and 1958, but although following an upward trend, DD does not mirror the sustained rise noted at E between 1958 and 1984. The E/DD curves show good agreement between 1984 and 1998,

Table 2
A summary of sampling sites, tree-ring cores and results of dendrochemical and soil analyses

Site location	Tree-ring core sample numbers	Data range: tree-rings (years AD)	Data range: Pb-in-wood ($\mathrm{mg\,kg^{-1}}$)	Soil pH	Solid geology[a]	Pb-in-soil ($\mathrm{mg\,kg^{-1}}$)
Main area						
Enthoven	K26	1954–1998	8–28	5.2	Gritstone	2033
	K8	1949–1998	4–30	3.8		3405
	K27	1909–1998	3–11	3.9		8935
	K5	1909–1998	3–38	3.5		8043
Darley Dale	D1B	1939–1998	1–35	6.8	Gritstone	787
	D3B	1899–1998	3–22	5.9		595
	D4A	1909–1998	2–28	5.8		452
Birchover	F12	1914–1998	2–30	3.6	Gritstone	443
	F24	1924–1998	1–9			
	F15	1904–1998	2–34			
Upper Matlock	F17	1919–1998	7–37	3.5	Gritstone	699
	F22	1949–1998	1–10			
	F5	1939–1998	7–38			
Control						
Wildboarclough	F13	1929–1998	2–8	5.4	Gritstone	196
	F28	1929–1998	0.6–5	5.2		141
Delamere	R6	1959–1998	0.7–6	4.2	Sandstone	70
	R6B	1954–1998	0.7–1			
	R5	1954–1998	0.4–5			

[a] Solid geology based on Harrison and Adlam (1985).

with DD at higher concentrations. The trend in the Birchover (B) curve is one of rising lead-in-wood, but there is less agreement between the specific detail of this record and those of E and UM.

Intra-site comparisons were facilitated further by using bivariate correlations (Table 4). Highest correlations were between E and UM, and between DD and B, both highly significant. Although there are also relatively strong correlations between E and both DD and B, respectively, the E/UM and DD/B subgroups seem to relate differently in comparison to the control sites, with E/UM appearing to have closer affinity to both control sites than DD/B.

Fig. 6 shows the mean lead-in-wood record for the four Enthoven trees plotted with the average Enthoven lead-in-air monitoring data for six monitoring stations (latter shown as 5 year averages to facilitate comparison). It is noticeable that lead-in-air and lead-in-wood follow a similar trend during the period where this data comparison is possible.

5. Discussion

Lead emissions from the Darley Dale Smelter, the only active point source of lead operating in the area since 1940, are difficult to quantify precisely before air quality monitoring

Table 3
Maximum lead concentrations reported in selected tree-ring research studies

Location	Context	Maximum Pb-in-wood concentration ($\mathrm{mg\,kg^{-1}}$)	Reference
Valle d'Aosta, Italy	Mountain/industrial	83	Orlandi et al. (2002)
Izmir, Turkey	Urban	57	Öztürk and Türkan (1993)
Darley Dale, UK	Mining/smelter	38	This study
Colorado, US	Mine waste	22	Witte et al. (2004)
Smolarz, Poland	Lowland	17	Opydo et al. (2005)
Wigan, UK	Parkland	10	Watmough and Hutchinson (2002)
Missouri, US	Mining	10	Guyette et al. (1991)
Onsan, Korea	Industrial	8	Kim and O (1999)
Missouri, US	Roadside	7	Szopa et al. (1973)
Alabama, US	Smelter	6	Andersen et al. (2000)
Mexico City, Mexico	Urban fringe	4	Watmough and Hutchinson (1999)
Delamere Forest, UK	Unpolluted	0.4	This study
Nikko National Park, Japan	Unpolluted	0.1	Bellis et al. (2002)
South eastern Sweden	Unpolluted	0.05	Jonsson et al. (1997)

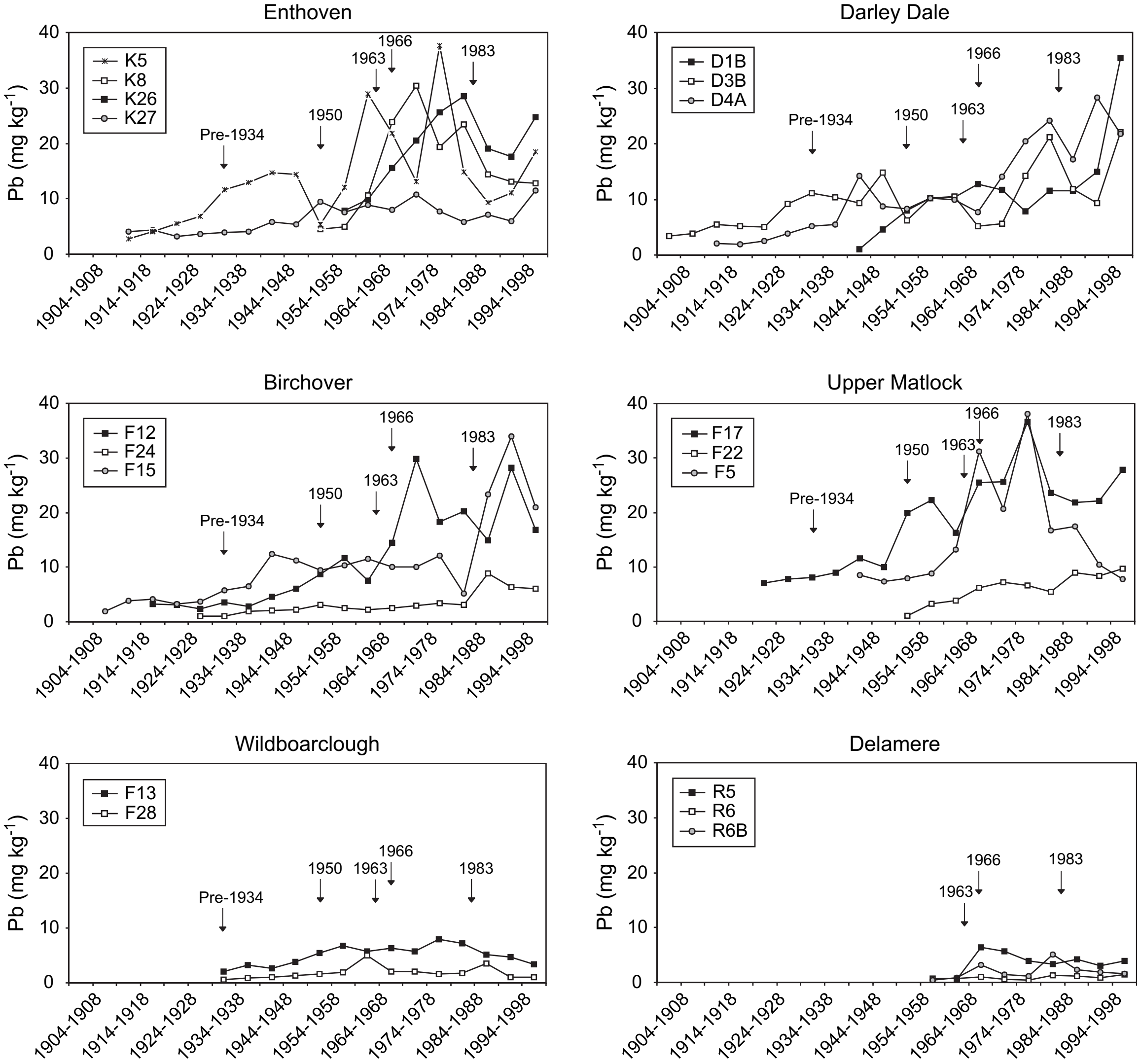

Fig. 4. Dendrochemical records showing historic variations in lead-in-wood concentrations for trees growing at the smelter site (Enthoven), in the surrounding area (Darley Dale, Birchover, Upper Matlock) and from the control sites (Wildboarclough and Delamere).

commenced in 1979. Reconstruction of the pollution chronology for the smelter is however possible, as Table 1 indicates that increasing production of lead and associated products between 1934 and 1998 (Fig. 3) was not always accompanied by successful mitigation measures. As a result, lead-in-air is expected to have risen from around 1940, with highest concentrations expected in the immediate period leading up to smelter redevelopment, which commenced in 1984. Prior to this date the ‘tall stack’ approach to pollution dispersal, widely acceptable in the 1960s and 1970s, was evidently the preferred option, and also an acknowledgement of significant emissions of particulate lead.

The introduction of more effective filtering technology was in part due to tightening of pollution control legislation, notably the 1982 EU Directive on lead in air (Council Directive 82/884/EEC, which set a limit of 2 μg m^3 as an annual mean concentration). This had a significant impact on emissions at the Enthoven site despite the redevelopment of the smelter and the associated considerable increase in lead production. Fig. 2 clearly documents an immediate reduction in lead-in air concentrations over the period 1982–1988.

When assessing the utility of *P. sylvestris* as an archive of these lead emissions from the Darley Dale Smelter, it is important to not only relate dendrochemical data to the well-dated pollution chronology, but also to consider the impact of lead from sources other than the smelter. These are listed in Section 1, and those likely to be most significant for trees sampled in this research are the adjacent Mill Close mine, its spoil heaps and also vehicle movements.

Data presented in Tables 1 and 2 represent part of a long history of lead acquisition and usage in the Darley Dale area. Today the Enthoven (Darley Dale Smelter) site includes within its perimeter the location of the Mill Close lead mine which operated up to 1940. Although few above ground features remain, there is no doubt that the mine has left a significant pollution legacy. This assertion is documented in part by data on ore output from the mine (over 550,000 tonnes 1859–1939, Ford and Rieuwerts, 2000) and also by the residual lead-in-soil at the

Table 4
Correlation and difference/similarity matrix showing relationships between sampling sites

	Calculated *t*-statistic (one tailed)					
	Enthoven	Darley Dale	Birchover	Upper Matlock	Wildboarclough	Delamere
Enthoven		0.70	1.62	0.97	5.53	6.43
Darley Dale	Similar		0.92	1.68	4.67	5.59
Birchover	Similar	Similar		2.61	3.59	4.55
Upper Matlock	Similar	Similar	Different		6.77	7.65
Wildboarclough	Different	Different	Different	Different		2.62
Delamere	Different	Different	Different	Different	Different	
	Statistical difference/similarity based on *t*-test					

Enthoven site (Table 2) that exceeds current UK soil guideline values for soils in public open spaces (c.f. DEFRA, 2002). These soil lead concentrations are as much as 10-times greater here than at the other tree sampling locations in Darley Dale (B, DD and UM). The latter are not noted for their immediate proximity to former mine sites.

The discussion relating to the precision of the dendrochemical record which follows is usefully previewed at this point. Although it is reasonable to assume that the trees sampled in this study could assimilate lead from soil contaminated by the Mill Close mine, Figs. 4, 5A and B reveal that average lead-in-wood concentrations for all the Darley Dale sites are of similar orders of magnitude over the study period (AD 1934—1998). This suggests that uptake of lead from soil by *P. sylvestris* may be a less important pathway vis-à-vis the inclusion of particulate lead in wood via bark/bark pockets (c.f. Bellis et al., 2002 using *Quercus crispula*) and via needles.

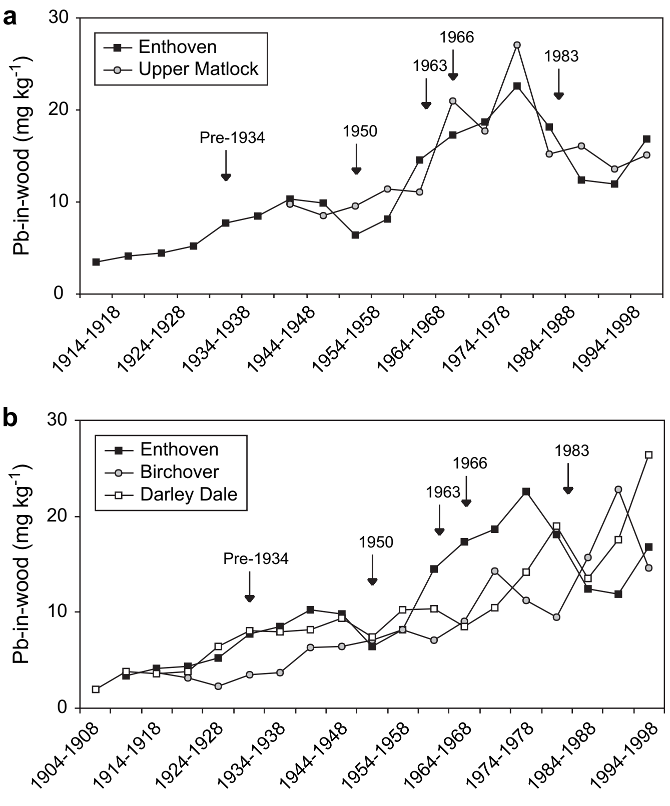

Fig. 5. (a) Location of the Darley Dale Smelter and for Upper Matlock 8.5 km to the south-west. (b) Comparison of the Enthoven mean site record to those of Birchover and Darley Dale.

5.1. Precision of the dendrochemical record

Intra-site variability in dendrochemical records is noticeable in all the Darley Dale sites. The inevitable conclusion is therefore that the dendrochemical records of individual trees do not consistently reflect concentrations of atmospheric lead. Similar was noted by Orlandi et al. (2002) who discovered unexpectedly high lead in *Larix decidua* in the Italian Alps.

It is however interesting to note that during the 20 year period when it is possible to compare lead-in-air and lead-in-wood data from the Enthoven site, both data sets follow a remarkably similar trend (Fig. 6). It is therefore possible that there may be a good agreement between the mean site dendrochemical record (5 year average) and actual lead-in-air.

Careful examination of Fig. 6 and the historical record (Table 1) from the Enthoven site does not fully support this view. A steady rise in lead-in-wood is noticeable from wood laid down in 1909. This is followed by a dip in the mean Enthoven curve between 1949 and 1958 pre-dating the cessation of smelting activities between 1958 and 1962. From 1958, lead-in-wood rises steadily to a peak of 23 mg kg^{-1} between 1974 and 1978. This secondary rise can be related to the period of peak emissions expected prior to 1984, although equally this peak is more probably expected in the period

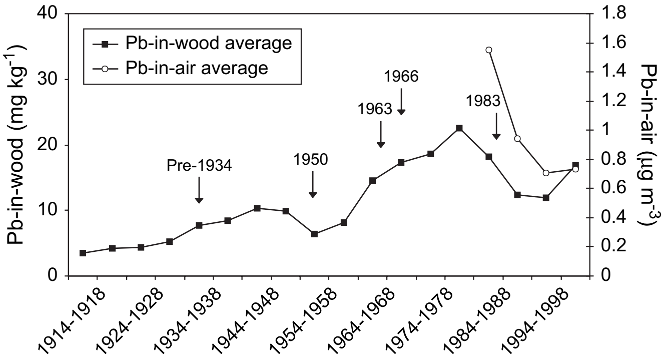

Fig. 6. Five-year mean lead-in-air data (µg m^{-3}) for the Enthoven site, plotted against the composite mean Enthoven dendrochemical record.

1979−1983. This latter contention is supported by peaks of 1.7 μg m^3 (1980, 1981, 1983) recorded by the air quality monitoring data presented in Fig. 2.

Of necessity, laboratory sampling of individual trees was undertaken in five-year increments. This approach and the subsequent creation of mean site records has an inevitably smoothing effect on the dendrochemical record and has been shown to be advantageous in demonstrating an offset between expected pollution episodes and tree-ring chemistry.

The two well-documented phases in the historic pollution chronology mentioned previously seem to be represented in the dendrochemical record, but in wood c. 5 year older than expected. Lead therefore appears to have been translocated within tree cross-sections towards the pith and this may be explained by lead sequestration in heartwood or at least movement of lead to less physiologically active areas where they could do little or no harm to the tree (P. Thomas, Keele University, personal communication, 2007). Such radial movement would also help to smear the dendrochemical record and may also account for some of the intra-site variability of lead-in-wood noted previously.

The long-term upward trends in the Darley Dale dendrochemical records do appear to reflect known pollution history, but they are out of phase with the calendrical scale. These findings support the conclusions of Watmough and Hutchinson (2002) that lead accumulates preferentially within the heartwood of *P. sylvestris*, although marked variations in lead content at the heartwood/sapwood boundary were not found in the Darley Dale trees.

5.2. Inter-site comparisons

Site records showing average lead-in-wood provide generally good agreement in terms of their overall trends (Fig. 5A and B) and the known pollution chronology (Table 1). Lead-in-wood concentrations from the four Darley Dale sites are significantly higher and also statistically different from the control sites.

Detailed visual and statistical comparison of these sites (Section 3, Fig. 5A and B, Table 1) indicates inter-site variation within the wider Darley Dale area and the following analysis demonstrates that local topography may play an important role in the dispersal and deposition of particulate lead.

The prevailing wind monitored at the Enthoven site is north-westerly, and its effects are demonstrated in Fig. 2. The Warren Carr monitoring site to the north of the smelter, mirrors the lead-in-air trends observed in the average for six Enthoven monitoring stations. Four of these are down-wind of the smelter, and Warren Carr data, collected up-wind, is therefore at a noticeably reduced level.

The dendrochemical records from the Birchover site (valley top overlooking the smelter and up-wind) and the Darley Dale (valley bottom and up-wind) are very similar (Fig. 5B and Table 4) which may point to wind circulation eddying around the smelter, largely within the confines of the valley of the river Derwent (Fig. 1).

Fig. 7. *Pinus sylvestris* growing beside the river Derwent at a lower elevation than the adjacent to the Darley Dale Smelter site.

Upper Matlock is a hilltop location, but down-wind of the smelter. Its lead-in-wood record is statistically very similar to that of the Enthoven site (Table 4). Visually these records are also comparable although the elevated nature of the Upper Matlock lead-in-wood, particularly in the 1940s, does point to additional and currently unspecified lead sources more local to the Upper Matlock site. The similarities between the Enthoven and Upper Matlock records mean that it is highly likely that trees growing at the Upper Matlock site received particulate lead from the Darley Dale Smelter, an expected outcome of down-wind atmospheric circulation channelled along the Derwent Valley.

Topography may also play a role on a microscale. Fig. 7 illustrates one of the Enthoven trees sampled in this study base and edge of a depression/hollow formed by a steep bank (possible river terrace) close to the River Derwent. This localised topographic variation is likely to disrupt atmospheric circulation near to ground, causing disturbances such as eddies. Microtopographic variations and also tree-specific morphological variability (such as bark morphology − a likely pathway for particulate lead, c.f. Bellis et al., 2002; and this study) may account for at least some of the intra-site variation in dendrochemical records noted previously.

6. Conclusions

Analyses of *P. sylvestris* growing around an isolated point source of atmospheric lead has shown that there can be considerable variation in individual dendrochemical records. In the Darley Dale area these inconsistencies may be related to variations in local topography, and to tree age and tree morphology.

Mean site records do, however, demonstrate patterns of lead-in-wood that can be related to a well-documented pollution chronology, and to known atmospheric circulation within the valley of the River Derwent. An important caveat to this is evidence of radial translocation of lead towards the heartwood, supporting previous evidence from the literature.

These results indicate that assays of lead in the wood of *P. sylvestris* can be used to estimate the general scale and timing of atmospheric lead pollution episodes in areas where historic records are absent, although calendrical precision in reconstructions may be difficult to attain.

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