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# Lead isotope composition of tree rings as bio-geochemical tracers of heavy metal pollution: a reconnaissance study from Firenze, Italy

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## Abstract

Pb isotope composition of tree rings (*Celtis Australis*) and urban aerosols have been determined to assess whether arboreal species can be used as bio-geochemical tracers of the evolution of heavy metal pollution to the environment. Particular care was paid to setting up a high quality analytical technique to work with arboreal species with low Pb content. **The Pb isotope composition of tree rings from 1950 to 1995 is within the range of European aerosols and is correlated with the temporal evolution of Pb isotopes measured in air particulates from Firenze.** The entire data set (tree rings and air particulates) demonstrate that Pb isotope composition of tree rings can be used successfully as a proxy of the atmospheric Pb isotope composition of urban areas. This, in turn, suggests that tree rings are potentially a powerful bio-geochemical tracer for monitoring air pollution history due to human activities. © 2000 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Atmospheric pollution from fossil fuel combustion has increased dramatically during this century (e.g., Murozumi et al., 1969; Chow et al., 1975; Lantzy and MacKenzie, 1979; Shirahata et al., 1980; Nriagu and Pacyna, 1988; Berner and Berner, 1996). The principal gaseous pollutants are CO<sub>2</sub>, CO, SO<sub>2</sub> and a number of N-oxides. Fossil fuel burning also delivers a variety of particulate matter, such as smoke particles and fly ashes, to the atmosphere. Lead alkyls, in particular,

added to gasoline for their antiknock properties, are emitted in particulate form from car exhaust and their addition to the Earth's ecosystem has long been recognised on a global scale (e.g., Chow and Johnstone, 1965; Chow et al., 1975; Manton, 1977; Nriagu, 1979; Schaule and Patterson 1981; Settle and Patterson 1982; Boyle et al., 1986; Patterson and Settle, 1987; Shen and Boyle 1987; Sturges and Barrie 1989; Hopper et al., 1991; Rosman et al., 1993; Véron et al., 1994; Hamelin et al., 1997). Over the last decades the increased awareness of environmental issues has led to the recognition that anthropogenic Pb emissions to the environment represent a serious health hazard because of the toxicity of this metal (Patterson, 1980; Pacyna, 1986; Nriagu and Pacyna, 1988).

This paper presents the results of a reconnaissance study of the temporal evolution of heavy metal pol-

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lution using Pb isotope analyses of tree rings in the urban area of Firenze, Italy. The aims are twofold: (i) to establish an analytical procedure able to produce high quality Pb isotope data in arboreal species with low Pb content; (ii) to determine whether arboreal species can be used as bio-geochemical tracers to monitor the temporal evolution of heavy metal pollution to the environment. If substantiated, this technique could be used to monitor efforts to decrease anthropogenic impact on the environment.

## 2. Rationale

The chemical element Pb ( $Z = 82$ ) is composed of 4 stable isotopes:  $^{208}\text{Pb}$ ,  $^{207}\text{Pb}$ ,  $^{206}\text{Pb}$ , and  $^{204}\text{Pb}$ . Of these four isotopes, only  $^{204}\text{Pb}$  is non radiogenic. The others derive from the radioactive decay, through a series of intermediate daughters, of  $^{232}\text{Th}$  ( $^{208}\text{Pb}$ ),  $^{235}\text{U}$  ( $^{207}\text{Pb}$ ), and  $^{238}\text{U}$  ( $^{206}\text{Pb}$ ). The abundances of  $^{208}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{206}\text{Pb}$  have, therefore, increased through time since Earth's accretion, from their primordial values to present day values depending on both the time-averaged U/Th/Pb of a given reservoir and the half-lives ( $\tau$ ) of the radioactive isotopes of Th and U that vary from 14 Ga ( $^{232}\text{Th}$ ) to 0.7 Ga ( $^{235}\text{U}$ ). The significant difference in half-lives, along with the variety of U/Th/Pb values in natural materials have produced a relatively wide range of Pb isotope ratios in the different Earth reservoirs (e.g., Faure, 1986; Dickin, 1995; Galer and Goldstein, 1996). This makes Pb isotopes an unique tool in environmental studies because of the well-established different isotopic composition of Pb emitted to the atmosphere due to human activities (*industrial* Pb) with respect to that of Pb present in rocks at the Earth's surface (*natural* Pb) (Chow et al., 1975; Shirahata et al., 1980; Maring et al., 1987; Sturges and Barrie, 1987; Church et al., 1990; Erel et al., 1990; Hopper et al., 1991; Véron et al., 1992, 1994; Erel and Patterson, 1994).

Pb in arboreal species occurs as impurities, and ranges from ppm to ppb levels (Bowen, 1979). The uptake of heavy metals by plants can occur via the foliar, cortical and radical apparatus. In the latter case, the plants take up Pb from the soil, whilst the source of Pb adsorbed via the foliar and cortical apparatus is through dry and wet deposition from atmospheric aerosol and subsequent adsorption by the plants, although the exact mechanisms and pathways of metals incorporation in tree rings is not fully understood (Lepp, 1975; Baes and McLaughlin, 1984). The Pb incorporated during the annual growth of tree rings originates from two distinct components, which are present in different proportions in the potential sources of Pb to the plants (see above). A *natural* Pb com-

ponent, which includes Pb derived from rock weathering, and an *industrial* Pb component, which includes dust from local mining activity, smelter and power plant emission and car exhaust. Car exhausts in urban areas, in particular, are known to be the major source of Pb to the atmosphere (e.g., Murozumi et al., 1969; Shirahata et al., 1980; Graney et al., 1995; Watmough and Hutchinson, 1999), despite the introduction of 'unleaded' gasoline (Pb < 0.02 g/l, Nicholson and Branson, 1993). Given the Pb content of urban aerosols (Bowen, 1979; Sturges and Barrie, 1987; Hopper et al., 1991), it is conceivable that *industrial* Pb will overwhelm the *natural* Pb component in urban areas, at least during most of the 20th century. This working hypothesis makes tree rings a potential record of anthropogenic Pb emission to the environment.

The ability of a vegetable organism to record the presence of a polluting component in the atmosphere has already been assessed (e.g., Rolfe and Jennet, 1975; Baes and McLaughlin, 1984; Sloof and Wolterbeek, 1991). Lichens, in particular, are excellent bio-geochemical tracers of environmental pollution (e.g., Lawrey and Hale, 1988; Rope and Pearson, 1990; Lawrey, 1993; Carignan and Gariépy, 1995), although, unlike tree rings, they do not record any temporal information. A few studies have used tree rings as environmental pollution monitors (Rolfe and Jennet, 1975; Baes and McLaughlin, 1984; Hagemeyer et al., 1992; Ferretti et al., 1993; Jonsson et al., 1997; Watmough and Hutchinson, 1999), although these studies only determined concentrations of a number of trace elements in tree rings. To date, only two studies have used Pb isotope composition of tree rings as bio-geochemical tracers of heavy metal pollution: Murozumi et al. (1996) in Japan, and Kalin (1996, personal communication) in Northern Ireland. The main drawback that prevents a widespread use of the Pb isotope systematics in tree rings for environmental studies is that there is no routinely accepted analytical technique to produce the low blank procedure necessary to obtain high quality data.

## 3. Sample description and analytical methods

The tree sample analysed in this study was chosen from among those periodically cut down by the City Hall of Firenze due to obstruction to roads (emerging roots, bent trunks, etc.), and is from a street heavily used by motor vehicles. The sampling site implies that car exhaust is the dominant component in the sources (i.e., soil and aerosol) of Pb to the tree, and hence it is suitable to explore the possibility of using arboreal species to monitor environmental quality. A 5 cm thick tree slice, with a diameter of ca 60 cm, was sampled

using an electric steel saw from the aliboreal species *Celtis Australis*, cut down in February 1996. The slice was successively sawed in sectors of approximately 15–20° each and one of these samples was selected for isotopic analysis based upon both the absence of fungi and visible sign of surface decay. Tree rings of the sample were then accurately counted and divided into groups of 3–5 increments following a mechanical separation using stainless-steel blades (Watmough and Hutchinson, 1999). Particular care was paid to mechanically remove the parts that had been in contact with the electric steel saw. In addition to tree rings, air particulates provided by the Regional Agency for Environmental Protection of Firenze, and representing particulate matter in 25–30 m<sup>3</sup> of air collected during 1990 (starting year of the survey by the local authorities) and 1995, were also analysed to monitor the evolution of heavy metal pollution in the city.

All chemical and Pb isotope analyses were performed at the Vrije Universiteit, Amsterdam. Special care was paid to the determination of the amount of tree material necessary for the isotopic analysis, and to the selection of material laid down in the year of growth of a given annual tree ring. First, Pb contents of the tree rings were determined on a set of samples covering the temporal range of this study (Table 1). Due to the low Pb content of the *Celtis Australis* rings (Table 1), the amount of material necessary for Pb isotope analysis was 1–2 g, yielding ~20 ng of Pb. The considerable quantity of acids used to dissolve the samples made it necessary to measure the Pb isotope composition of the reagents to check for blank contributions to the samples. The analyses of reagents were performed on the pro-analysis quality and the results

on HNO<sub>3</sub> and toluene are given in Table 2. The Pb isotope composition of the clean lab as a whole was also monitored by leaving 5 ml of 9N HBr in an open beaker for 2 weeks. Second, each tree ring sample was split into two aliquots, one of these undergoing a pre-treatment procedure to remove exchangeable Pb that may be mobile across tree ring boundaries. This procedure, developed for radiocarbon analyses of wood (Kalin et al., 1995), was tested to verify whether it was also suitable for removing exchangeable heavy metal impurities as well. The method was as follows:

1. washing of the samples, placed in 30 ml Savillex screw-top beakers, in ultrasonic bath with milli-Q water for 6 h at 50°C, and subsequently desiccating in an oven at 80°C for 2 days;
2. leaching in ultrasonic bath with distilled toluene for 6 h at 50°C to remove resins and tars, and then rinsing thoroughly with milli-Q water;
3. washing in ultrasonic bath with milli-Q water for 6 h at 50°C to remove sugars, and then rinsing thoroughly with milli-Q water;
4. drying on hotplate at 80°C.

Aliquots of samples that were not leached were processed through step 1 only. The destruction procedure, for leached and unleached samples, did not go through an ashing step as commonly used for organic matter analysis (Watmough and Hutchinson, 1999), to avoid cross contamination due to volatility of Pb and consisted of:

1. oxidation on hotplate at 120°C overnight with 10 ml of teflon distilled 14N HNO<sub>3</sub>;
2. evaporating to dryness slowly on hotplate at 80°C;

Table 1  
Pb content of tree rings (*C. Australis*) and air particulates<sup>a</sup>

| Sample              | Year      | Total particulate (µg/m <sup>3</sup> ) | [Pb]   |        |                      |
|---------------------|-----------|--|--------|--------|----------------------|
|                     |           |  | (ng/g) | (µg/g) | (µg/m <sup>3</sup> ) |
| <i>C. Australis</i> |           |  |        |        |                      |
| CA 3943             | 1939–1943 |  | 28     |        |                      |
| CA 5662             | 1956–1962 |  | 13     |        |                      |
| CA 8690             | 1986–1990 |  | 54     |        |                      |
| CA 9194             | 1991–1994 |  | 56     |        |                      |
| CA bark             |           |  | 63     |        |                      |
| Air particulate     |           |  |        |        |                      |
| 260190              | 1990      | 101                                    |        | 7383   | 0.75                 |
| 280195              | 1995      | 82                                     |        | 7577   | 0.62                 |
| 310195              | 1995      | 82                                     |        | 7923   | 0.65                 |

<sup>a</sup> Pb content in tree rings by Graphite Furnace Atomic Absorption Spectrometry, whilst in air particulates by isotope dilution thermal ionisation mass spectrometry. The volume of air sampled is between 25 (1990) and 30 (1995) m<sup>3</sup>. The Pb contents of tree rings have been corrected for a blank contribution of 2 ppb; no correction was necessary for air particulates.

3. further oxidation in a few ml of 14N HNO<sub>3</sub>, leaving the sample on the hotplate at 120°C overnight and drying slowly the following day. This step was repeated 4 times (5, 4, 3 and 3 ml of HNO<sub>3</sub>) until the complete destruction of organic matter;
4. dissolution in 10 ml of quartz distilled 6N HCl, on a hotplate at 120°C for 1 day and then drying;
5. complexing of Pb into 1 ml of teflon distilled 0.7N HBr, and centrifuging the residue as for normal Pb analyses.

Air particulate samples were processed using the standard dissolution procedure for rock samples (HF-HNO<sub>3</sub>-HCl). Lead was then separated using standard column chromatography with Dowex AG1 × 8 anion exchange resins and HBr as eluent (e.g., Manhès et al., 1978). The final Pb fraction was treated with 2–3 drops of HClO<sub>4</sub> to oxidise residual organics, which, in a first attempt, inhibited the measurement on the mass spectrometer. Finally, the samples were loaded onto single zone-refined Re filaments using the silica gel technique (e.g., Gerstenberger and Haase, 1997). The total procedural blank was < 100 pg whilst a typical sample contained ~20 ng of Pb (assuming 50% loss for the leached samples), making the blank contribution < 0.5%.

#### 4. Results

The Pb content of the tree rings of *Celtis Australis* and of the air particulates are reported in Table 1, whilst Pb isotope compositions are given in Table 2. The total procedural blank obtained for Pb isotope analyses (< 100 pg) establishes a negligible contribution to the samples. This is further corroborated by Fig. 1, in that the inverse correlation delineated by the tree ring samples on the <sup>207</sup>Pb/<sup>204</sup>Pb vs <sup>207</sup>Pb/<sup>206</sup>Pb diagram is opposite to that expected if the blank (which may reflect the Pb isotope composition of Amsterdam air at the time of analyses) contributed significantly to the Pb isotope composition of the samples. Given the amount of reagents used to dissolve the samples, this is an excellent result confirming the high quality of the procedure adopted to perform the isotopic analyses.

The Pb content in the air particulates of 1990 and 1995 is ~7500 ppm, corresponding to a Pb content in the air of ca 0.65 µg/m<sup>3</sup> (Table 1). This absolute content is higher than that measured in other urban air world-wide, such as in Belfast, Northern Ireland, in 1994 (ca 0.4 µg/m<sup>3</sup>) (Kalin, 1996, personal communication), and in Broken Hill, Australia, in 1991–1992 (0.06–0.39 µg/m<sup>3</sup>) (Gulson et al., 1994), and clearly reveals a large anthropogenic Pb emission to the en-

Table 2  
Pb isotope composition of tree rings (*C. Australis*), air particulates and blanks<sup>a</sup>

| Sample                          | Year      | Wt (mg) | <sup>208</sup> Pb/ <sup>204</sup> Pb | <sup>207</sup> Pb/ <sup>204</sup> Pb | <sup>206</sup> Pb/ <sup>204</sup> Pb | <sup>208</sup> Pb/ <sup>206</sup> Pb | <sup>207</sup> Pb/ <sup>206</sup> Pb | <sup>208</sup> Pb/ <sup>207</sup> Pb |
|---------------------------------|-----------|---------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| <i>C. Australis</i> (unleached) |           |         |                                      |                                      |                                      |                                      |                                      |                                      |
| CA 5055                         | 1950–1955 | 1056    | 38.221                               | 15.609                               | 18.253                               | 2.09406                              | 0.85521                              | 2.44863                              |
| CA 6366                         | 1963–1966 | 893     | 38.281                               | 15.623                               | 18.277                               | 2.09442                              | 0.85482                              | 2.45014                              |
| CA 8385                         | 1983–1985 | 751     | 38.144                               | 15.612                               | 18.172                               | 2.09908                              | 0.85912                              | 2.44330                              |
| CA 9195                         | 1991–1995 | 588     | 38.032                               | 15.597                               | 18.101                               | 2.10109                              | 0.86166                              | 2.43844                              |
| <i>C. Australis</i> (leached)   |           |         |                                      |                                      |                                      |                                      |                                      |                                      |
| CA 5055 T                       | 1950–1955 | 1922    | 38.329                               | 15.633                               | 18.298                               | 2.09460                              | 0.85433                              | 2.45179                              |
| CA 6366 T                       | 1963–1966 | 1894    | 38.260                               | 15.629                               | 18.246                               | 2.09695                              | 0.85657                              | 2.44809                              |
| CA 8385 T                       | 1983–1985 | 1303    | 38.182                               | 15.623                               | 18.184                               | 2.09979                              | 0.85918                              | 2.44390                              |
| CA 9195 T                       | 1991–1995 | 1092    | 38.078                               | 15.613                               | 18.117                               | 2.10180                              | 0.86178                              | 2.43893                              |
| Air particulate                 |           |         |                                      |                                      |                                      |                                      |                                      |                                      |
| 260190                          | 1990      | 0.205   | 38.141                               | 15.630                               | 18.172                               | 2.09898                              | 0.86010                              | 2.44036                              |
| 280195                          | 1995      | 0.146   | 37.899                               | 15.616                               | 17.956                               | 2.11076                              | 0.86969                              | 2.42701                              |
| 310195                          | 1995      | 0.225   | 37.809                               | 15.602                               | 17.894                               | 2.11291                              | 0.87191                              | 2.42333                              |
| Blanks (ion counting runs)      |           |         |                                      |                                      |                                      |                                      |                                      |                                      |
| HBr blank                       |           |         | 37.60                                | 15.62                                | 17.69                                | 2.1238                               | 0.8827                               | 2.4064                               |
| HBr blank                       |           |         | 37.66                                | 15.63                                | 17.75                                | 2.1230                               | 0.8816                               | 2.4080                               |
| HNO <sub>3</sub> blank          |           |         | 37.65                                | 15.61                                | 17.77                                | 2.1188                               | 0.8784                               | 2.4125                               |
| Toluene blank                   |           |         | 37.65                                | 15.61                                | 17.88                                | 2.1056                               | 0.8732                               | 2.4078                               |

<sup>a</sup> Pb isotopes were determined by solid-source thermal ionisation mass spectrometry using a Finnigan MAT 262 mass spectrometer equipped with nine movable Faradays collectors. Pb isotope compositions were measured in static mode and are presented normalised to NIST SRM981, using a linear fractionation correction of 1.4 ‰ per amu, based on repeated analyses of 20 ng of the standard. The external precision of NIST SRM981 was <sup>208</sup>Pb/<sup>204</sup>Pb = 36.501 ± 24, <sup>207</sup>Pb/<sup>204</sup>Pb = 15.426 ± 9, <sup>206</sup>Pb/<sup>204</sup>Pb = 16.890 ± 9, <sup>207</sup>Pb/<sup>206</sup>Pb = 0.91334 ± 13, <sup>208</sup>Pb/<sup>207</sup>Pb = 2.36611 ± 34, <sup>208</sup>Pb/<sup>206</sup>Pb = 2.16108 ± 61 (2σ, n = 10). The Pb isotope compositions of the blanks were determined in peak jumping mode using the ion counter.

vironment when compared to aerosol Pb from relatively remote sites such as Aspövreten in Sweden ( $\text{Pb} = 2\text{--}50 \text{ ng/m}^3$  in 1988) (Hopper et al., 1991). In Firenze, there has been  $> 500\%$  increase in Pb content with respect to the European average of the 1970s ( $0.12 \text{ } \mu\text{g/m}^3$ ) (Bowen, 1979). The result is perhaps unexpected given the introduction in the early 1990s of 'unleaded' gasoline ( $\text{Pb} < 0.02 \text{ g/l}$ ) (Nicholson and Branson, 1993), but is indicative of a dramatic increase in automobile traffic in the last decades.

The Pb content of the rings of the *C. Australis* is in the order of a few tens of ppb (Table 1), and it is noted that the measured Pb content is lower than that previously reported in other vascular plants. For example, Rolfe and Jennet (1975) reported 2–13 ppm of Pb in tree rings from Illinois; Ferretti et al. (1993) measured 0.6–7 ppm of Pb in tree rings from Italy; Murozumi et al. (1996) found 3–73 ppm of Pb in tree rings from Japan. In the general compilation of Pb content in vascular plants, Bowen (1979) reported a range of 0.9–13 ppm. Direct comparison with the present data is, however, difficult to interpret in terms of environmental pollution monitoring due to seasonal-daily variations in the concentration of Pb in aerosols, the influence of particle size and atmospheric conditions, and a number of physiological factors controlling heavy metal uptake by plants (e.g., Pacyna, 1987; Jonsson et al., 1997). In addition, the exact mechanisms and pathways of metals incorporation in tree rings is not fully understood (Lepp, 1975; Baes and McLaughlin, 1984), and different vegetable species can have different adsorption coefficients for Pb (Bowen, 1979). Overall, these parameters are difficult to quan-

tify and can lead to equivocal results when comparing the pollution history of different areas on the basis of the absolute contents of heavy metal pollutants in arboreal species. In contrast, the Pb isotope composition of plants, irrespective of Pb concentration, can be used unambiguously to trace the evolution of heavy metal pollution due to anthropogenic emissions, given the contrasting isotopic ratios of *industrial* and *natural* Pb, and the fact that Pb isotopes are not measurably fractionated during industrial or biological consumption processes (Ault et al., 1970).

## 5. Discussion

This reconnaissance study was designed (i) to establish an analytical procedure able to produce high quality Pb isotope data in arboreal species, and (ii) to assess whether arboreal species can be used as bio-geochemical tracers of heavy metal pollution.

The analytical procedure was aimed at obtaining a low Pb blank and to test the effectiveness of the leaching procedure, developed for radiocarbon analysis (Kalin et al., 1995), for removing exchangeable Pb across tree ring boundaries. The occurrence of radial (inward and outward) transport of heavy metals within the stem of trees is still controversial and may vary from species to species (e.g., Baes and Ragsdale, 1981; Hagemeyer et al., 1992; Jonsson et al., 1997; Watmough and Hutchinson, 1999). Leached-unleached tree ring sample pairs of 1950–1955 and 1963–1966 have different Pb isotope composition, whilst the two youngest leached-unleached pairs are within error

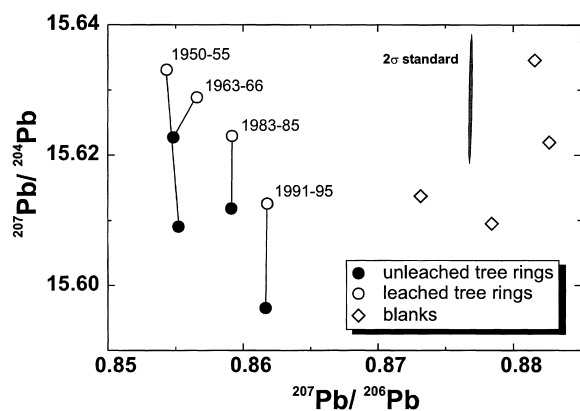


Fig. 1.  $^{207}\text{Pb}/^{204}\text{Pb}$  vs  $^{207}\text{Pb}/^{206}\text{Pb}$  diagram for the tree rings of the *C. Australis* and blanks. The trend exhibited by tree rings is opposite to that expected if blank contributed significantly to the samples. The error ellipse represents the external reproducibility of the NIST SRM981 Pb standard at 95% confidence level ( $2\sigma$ ).

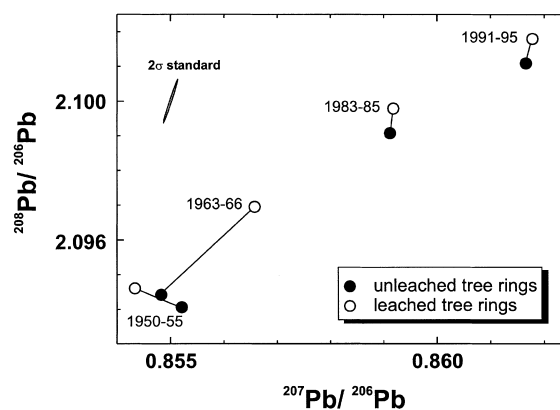


Fig. 2.  $^{208}\text{Pb}/^{206}\text{Pb}$  vs  $^{207}\text{Pb}/^{206}\text{Pb}$  diagram for the tree rings of the *C. Australis*. The two oldest leached-unleached pairs have different Pb isotope composition and provide evidence for radial transport of Pb within the stem of the *C. Australis*. The error ellipse represents the external reproducibility of the NIST SRM981 Pb standard at 95% confidence level ( $2\sigma$ ).

(Fig. 2). These data establish that in the oldest tree rings there has been some radial transport of Pb, both outward and inward, and provide evidence for the effective removal of exchangeable Pb from leached samples by adopting the same leaching procedure used for radiocarbon analysis. It is unclear why radial transport of Pb affected only the oldest tree rings, but the different isotopic composition between leached-unleached pairs (Figs. 1 and 2) implies that it is necessary to perform a leaching procedure before using arboreal species as bio-geochemical tracers of heavy metal pollution.

A compilation of relevant Pb isotope data on aerosol and gasoline, and representative Pb isotope data of sediments and Pb ores are reported in Fig. 3. On a global scale, there is the expected difference between Pb isotope abundances in natural rocks at the Earth's surface (sediments) and that of industrial Pb obtained from ore bodies. The distinct anthropogenic signatures of US, Australian and European aerosols (Fig. 3) reflect the variety of Pb ores used in different industrial activities and different countries (Chow et al., 1975; Sturges and Barrie, 1987; Church et al., 1990; Hopper

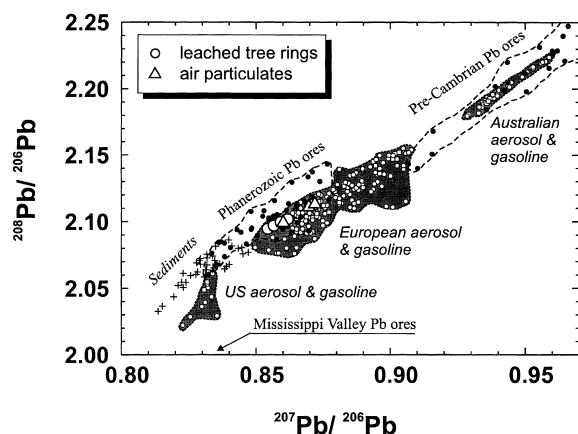


Fig. 3. Compilation of relevant Pb isotope data on aerosol and gasoline, and representative Pb isotope data of sediments and Pb ores. ○: aerosol; □: gasoline; ●: Pb ores; +: sediment. On a global scale, the distinct *industrial* Pb isotope signatures of US, Australian and European aerosols, plot on mixing lines between pre-Cambrian, Phanerozoic and the anomalously radiogenic ores of the Mississippi Valley. The Pb isotope composition of the *C. Australis* tree rings lies in the field of European aerosols, demonstrating that tree rings can be used as bio-geochemical tracers of heavy metal pollution to the environment. Data sources: (Brown, 1962; Chow and Jonhstone, 1965; Chow and Earl, 1972; Stacey and Kramers, 1975; Elbaz-Poulichet et al., 1984; Sañudo-Wilhelmy and Flegal, 1994; Maring et al., 1987; Ben Othman et al., 1989; Hopper et al., 1991; Asmeron and Jacobsen, 1993; Gulson et al., 1994; Erel et al., 1997; Véron et al., 1999). Error ( $2\sigma$ ) within symbol size.

et al., 1991; Véron et al., 1992; Craig et al., 1996; Michel et al., 1998). These aerosols lie on mixing lines between pre-Cambrian, Phanerozoic and the anomalously radiogenic Pb ores of the Mississippi Valley. The Pb isotope composition of sediments, the other potential source of aerosol Pb, is generally off these linear trends (Fig. 3), pointing to their negligible contribution to the global inventory of aerosol Pb. This is not a surprise given that the world consumption of *industrial* Pb reached  $5.7 \times 10^6$  tons in 1996 (Michel et al., 1998).

The Pb isotope composition of aerosol measured in the air particulates of Firenze is, as expected, within the range of other European aerosols (Fig. 3). The result relevant to the present study is that the Pb isotope signature of the *C. Australis* tree rings lies within the field of European aerosols (Fig. 3), demonstrating that tree rings can be used successfully as a proxy of atmospheric Pb isotope composition to monitor the evolution of heavy metal pollution in urban areas. Moreover, the data establish that Pb isotopes in arboreal species can potentially be used to trace the temporal variations of air mass trajectories in the troposphere as is the case for surface ocean waters and ice cores (e.g., Rosman et al., 1993; Véron et al., 1993, 1994; Hamelin et al., 1997).

The difference between the Pb isotope record of tree rings and air particulates is that the former represent yearly averages, whilst the latter are single-day measurements. With this limitation in mind, the variation in Pb uptake by the *C. Australis* between 1950 and 1995, exhibits a progressive increase of  $^{207}\text{Pb}/^{206}\text{Pb}$  and a concomitant decrease of  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{207}\text{Pb}$ . This variation is correlated with the temporal change of atmospheric Pb isotopes measured in air particulates (Fig. 4). A detailed assessment of the origin of the evolution of the Pb isotope signature (tree rings and air particulates) is beyond the scope of the paper, owing to the limited number of samples analysed, but some general comments can be made. The shift in Pb isotope signature of tree rings and aerosols is consistent with the trend observed in ombrotrophic peat bogs from Switzerland (Shotyk et al., 1996) and Norway (Dunlap et al., 1999), although the absolute values are different (Fig. 4). Ombrotrophic bogs are hydrologically isolated from the influence of local groundwaters and surface waters and have negligible interaction with their substrate (Livett et al., 1979; Shotyk, 1988). They represent, therefore, excellent traps of long-term atmospheric heavy metal deposition (Shotyk et al., 1996; Dunlap et al., 1999). The shift in Pb isotope signature observed in peat bogs during the 19th and 20th centuries was successively caused by Pb ore smelting and Pb alkyls added to gasoline (Shotyk et al., 1996; Dunlap et al., 1999). The Pb isotope record in tree rings is consistent with this

explanation, although the time span of the present data is restricted to the second half of the 20th century.

The difference in absolute values between peat bogs and tree rings and air particulates from Firenze (Fig. 4) could be due to a number of reasons. For example, (i) the peat bogs are located in remote areas and their Pb isotope record represents European averages of airborne Pb (Dunlap et al., 1999), whilst tree rings and air particulates represent a local record; (ii) the peat bogs have negligible vertical downward migration of Pb (Shotyk et al., 1996), whilst tree rings can possibly record a time-integrated *industrial* Pb emission.

The latter reason, in particular, could explain why the increase/decrease of Pb isotopes in tree rings is less steep than in peat bogs (Fig. 4), and would indicate

that the main source of Pb to the *C. Australis* is the soil. The *industrial* Pb content of urban soils overwhelms the *natural* Pb content from rock weathering (e.g., Lagerwerff and Specht, 1970; Rolfe and Jennet, 1975; Thornton, 1991; Paterson et al., 1996; Kelly et al., 1996), and provides us with a record of time-integrated Pb load due to human activities. This means that the Pb uptake by the *C. Australis* could represent a mixture between *industrial* Pb from ore smelting (and possibly coal burning and power plant given the location of the sampling site in an urban area), and a progressively increasing amount of *industrial* Pb from car exhaust which started to accumulate in the soil with the introduction of leaded gasoline.

Finally, the different Pb isotope signature for 1990 and 1995 air particulates demonstrates a change in the

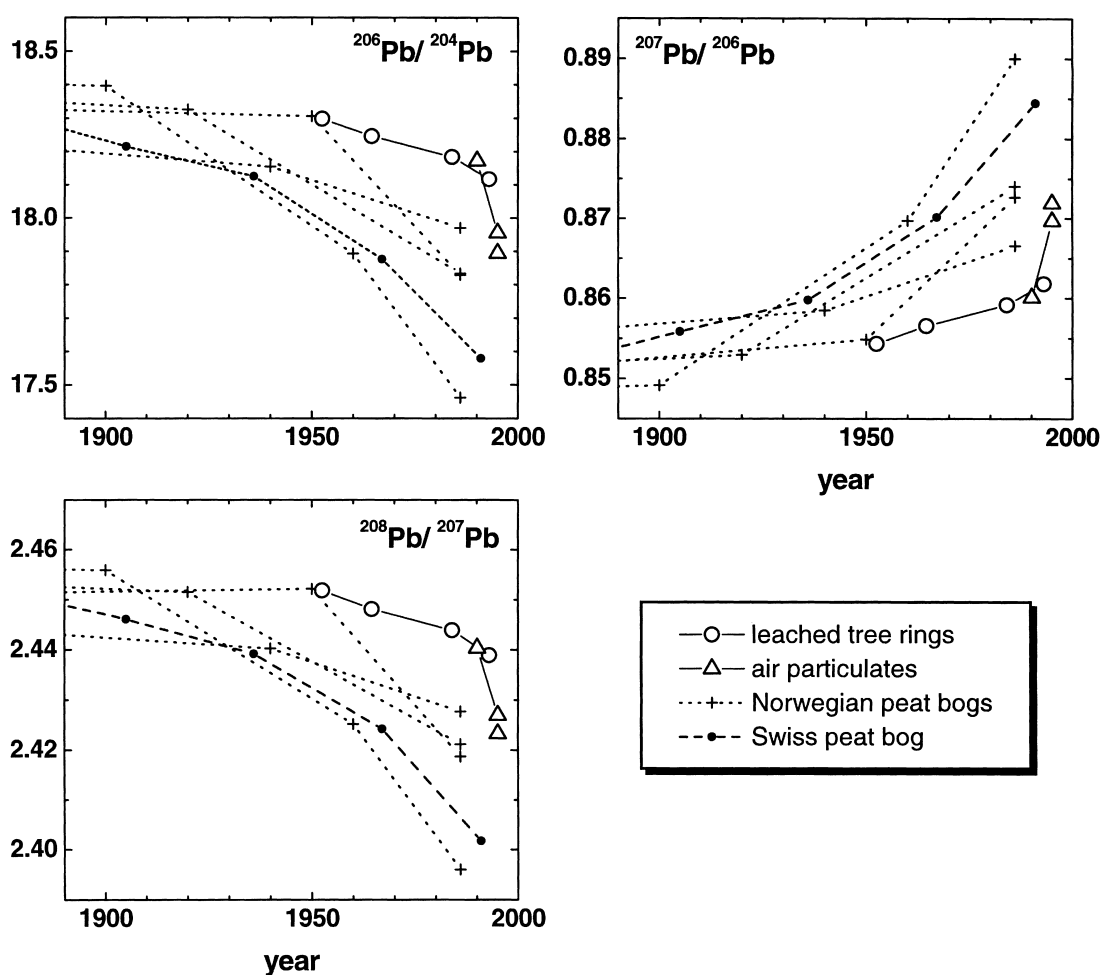


Fig. 4. Temporal variation of Pb isotopes in the tree rings of the *C. Australis* and air particulates. The coherent trend exhibited by the tree rings implies that the Pb isotope signature of the urban air of Firenze can be traced back to 1950, even though collection of air samples only started in 1990. The airborne Pb isotope signature measured in ombrotrophic peat bogs from Norway (Dunlap et al., 1999) and Switzerland (Shotyk et al., 1996) during the 20th century is reported for reference. Errors ( $2\sigma$ ) within symbol size.

anthropogenic Pb emission from car exhaust to the urban air of Firenze. Similar changes have been documented in other case studies (e.g., Shirahata et al., 1980; Erel and Patterson, 1994; Erel et al., 1997). The diagrams in Fig. 4 also reveal that the Pb ores used for the production of Pb alkyls and emitted from car exhaust in the city of Firenze (air particulates of 1990 and 1995), are different from the average European airborne Pb recorded by the Swiss and Norwegian peat bogs during the same time span. Providing evidence of the switch in Pb ore consumption is, however, difficult because despite the knowledge of the major Pb producing countries (USA, Australia, Canada, former USSR, China, Peru and Mexico) (Crowson, 1984; Craig et al., 1996; Michel et al., 1998), the source of Pb used in the production of gasoline additives at different times by various companies is not readily available, and is often considered confidential by commercial consumers (Hopper et al., 1991; Graney et al., 1995). This is a misfortune for geochemists, because if this information were available, Pb isotopes in aerosols could readily trace the temporal change of industrial Pb, given the unique isotopic signature of each mining district from which Pb is extracted for industrial use. For example, the  $^{207}\text{Pb}/^{206}\text{Pb}$  in the USA urban air changed from ca 0.88 in the 1960s to ca 0.82 in the 1980s due to a shift in the major use of Pb produced from the anomalously radiogenic ores of the Mississippi Valley (Shirahata et al., 1980; Sturges and Barrie, 1987; Erel and Patterson, 1994).

The important conclusion is that the data reported here establish that the Pb isotope composition of tree rings can be a powerful bio-geochemical tracer for monitoring heavy metal pollution history of urban areas. In addition to temporal tracers, tree rings could also be used as bio-geochemical tracers to map the extent of environmental pollution due to anthropogenic emissions by the different countries. In other words, the Pb isotope record preserved in tree rings, when combined with records of land development, Pb ore sources, and industrial Pb consumption, can be used for quantitative estimates of the pollution history of a given region, and provide a substantial contribution to environmental studies.

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