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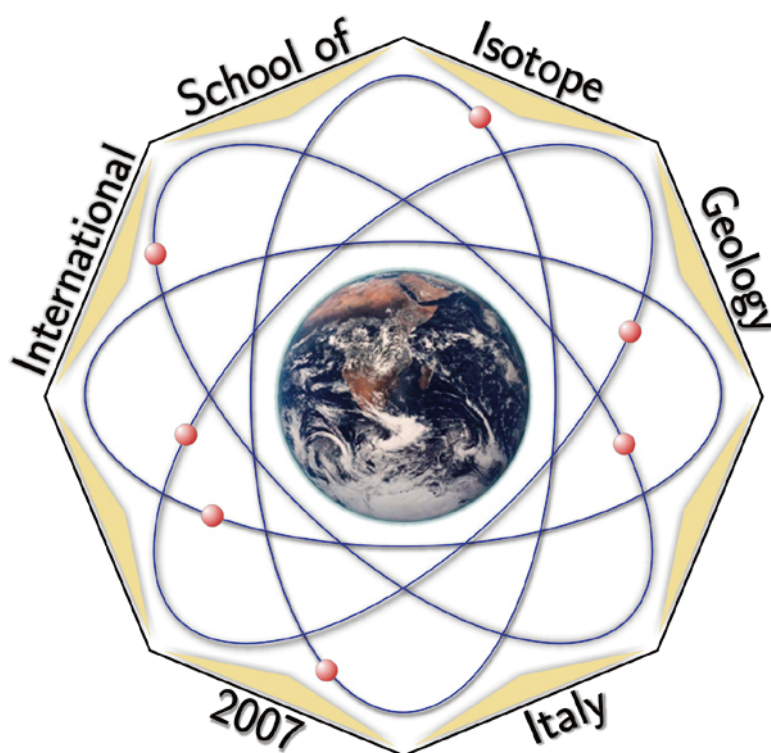
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HISTORICAL RECORDS OF ATMOSPHERIC Pb POLLUTION

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1. Pb AND HEALTH

LEAD (Pb) is a metallic element of atomic number 82, Group IVA of the Periodic Table (At. Wt. 207.2 g/mol). Lead is a heavy, ductile, soft gray solid, soluble in dilute nitric acid and insoluble in water, although dissolves slowly in water containing a weak acid.

Lead has long been recognised as a harmful environmental pollutant. There are many ways in which humans are exposed to lead: through air, drinking water, food, contaminated soil, deteriorating paint, and dust. Airborne lead enters the body when an individual breathes or swallows lead particles or dust once it has settled. Before it was known how harmful lead could be, it was used in paint, gasoline, water pipes, and many other products.

Lead affects practically all systems within the body. Lead at high levels (lead levels at or above 80 µg/dl of blood) can cause convulsions, coma, and even death. Lower levels of lead can cause adverse health effects on the central nervous system, kidney, and blood cells. Because of lead's importance as a cause of public health problems, a number of international organisations have issued advisory standards or enforceable regulations that set lead levels in different media. In the U.S., for example, the B.B.L. (blood lead level) of concern for lead exposure in children has been progressively lowered to 10 µg/dl; the amount of Pb allowed in workplace air cannot exceed 50 µg/m³ averaged over an 8-hour workday; the action level for lead in water delivered to users of public drinking water systems has been set to 15 µg/l; the amount of lead in paint intended for residential use has been limited to 0.06% (before 1955, much white house paint was 50% lead and 50% linseed oil).

2. ATMOSPHERIC Pb POLLUTION

Atmospheric pollution from fossil fuel combustion has increased dramatically during last century (e.g., Murozumi *et alii* 1969, Chow *et alii* 1975, Shirahata *et alii* 1980). The principal gaseous pollutants are CO₂, CO, SO₂ and a number of N-oxides. Fossil fuel burning also delivers a variety of particulate matter, such as smoke particles and ashes, to the atmosphere. Lead alkyls, in particular, added to gasoline since 1920s for their antiknock properties, are emitted in particulate form from car exhaust and their addition to the Earth's ecosystem has long been recognised (e.g., Chow and Johnstone 1965, Chow *et alii* 1975, Nriagu 1979, Schaule and Patterson 1981, Settle and

Patterson 1982, Boyle *et alii* 1986, Shen and Boyle 1987, Sturges and Barrie 1989). On a global scale about 85% of industrial Pb emissions are introduced into the atmosphere in the Northern Hemisphere (Schaule and Patterson 1981, Pacyna and Graedel 1995). This means that, given the characteristic time for interhemispheric exchange of about one year (Levin and Hessheimer 1996), and the mean residence time of Pb in the atmosphere of ~10 days (Settle and Patterson 1991), the Northern Hemisphere emissions have a negligible influence on the Southern Hemisphere.

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, and since 1980s most countries are phasing out leaded fuel replacing lead compounds with different additives (aromatic hydrocarbons, ethers and alcohol, usually ethanol or methanol). For the sake of clarity, unleaded gasoline does not mean Pb-free gasoline but gasoline containing < 0.013 g/l of Pb, as opposed to leaded gasoline which had > 0.5 g/l of Pb.

At present, the phase out of leaded gasoline in industrialised countries is near completion, although the incessant emission of anthropogenic lead into the environment will not stop, and will continue to overwhelm the very small amounts of Pb that occur naturally in the air. This is because i. the automobile traffic all over the world increases every year (including in developing countries where emission control is poor and unleaded gasoline is largely unavailable); ii. fuel containing lead may continue to be sold for off-road uses, including aircraft, racing cars, farm equipment, and marine engines until 2008; iii. mining activities, smelting, non-ferrous metal refining, waste incineration and coal burning are still active and represent the other major sources contributing to atmospheric Pb pollution. It is true, however, that Pb emissions to the atmosphere have been reduced in industrialised countries and several published estimates are available. For example, an E.U. programme to establish an inventory of emissions of air pollutants in Europe (CORINAIR) indicated a reduction of total lead emissions in Europe from 8.5 10⁴ tons in 1985 (75% from car exhaust) to some 3.2-5.4 10⁴ tons in 1990.

3. IDENTIFICATION OF ATMOSPHERIC Pb SOURCES

Aerosols represent a mixture of *natural* and *anthropogenic* airborne solid particles and liquid droplets. The pollutant anthropogenic component can have different

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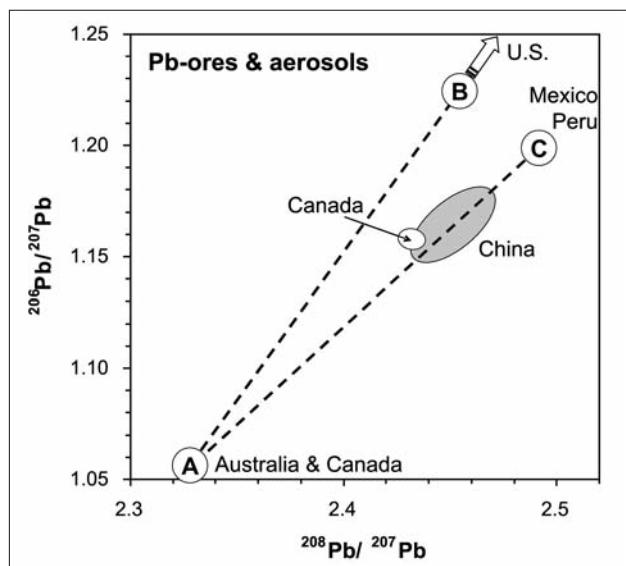


FIG. 1. The Pb isotope compositions of world-wide recent aerosols fall within the field defined by three end-members (Sources A, B, C), which correspond to the major Pb ores producer countries, *i.e.* China, Australia, United States, Peru, Mexico and Canada (redrawn from Bollhöfer and Rosman 2000, 2001).

sources and attempts to identify them have included the use of elemental ratios (Lowenthal *et alii* 1997). However, this approach can be distorted due to different physico-chemical removal processes for the elements, which change their relative abundances during transport. In contrast, Pb isotope abundances are not affected to any measurable extent by physical or chemical processes in terrestrial environments. Lead is commonly used in pollution studies because of, unlike other heavy metal pollutants, the effectiveness of stable Pb isotopes to distinguish between Pb sources, *i.e.* *natural vs anthropogenic*.

Lead is composed of 4 stable isotopes: ^{208}Pb , ^{207}Pb , ^{206}Pb , and ^{204}Pb . Of these four isotopes, only ^{204}Pb is non radiogenic. The others derive from the radioactive decay, through a series of intermediate daughters, of ^{232}Th (^{208}Pb), ^{235}U (^{207}Pb), and ^{238}U (^{206}Pb). The abundances of ^{208}Pb , ^{207}Pb , and ^{206}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 of the radioactive isotopes of Th and U, which vary from 14 Ga (^{232}Th) to 4.5 Ga (^{238}U) and 0.7 Ga (^{235}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.*, Dickin 1995). In general, upper crust rocks have more radiogenic Pb isotope composition than Pb ore bodies, and different ore bodies have different Pb isotope signature depending on their age and the time-averaged U/Th/Pb values of their source(s). This means that the isotopic composition of alkyllead, and consequently that of Pb oxides, Pb halides and organolead compounds emitted from burning of leaded gasoline, re-

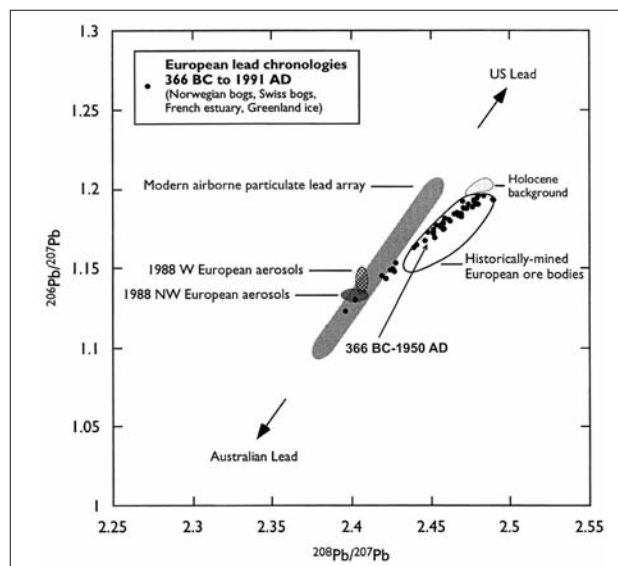


FIG. 2. Comparison of two millennia European Pb isotope record with possible sources of airborne Pb (from Dunlap *et alii* 1999).

flects the composition of the Pb ore(s) used in its production (Chow *et alii* 1975). This makes Pb isotopes an unique tool in environmental studies for tracing Pb emissions to the atmosphere due to human activities (*e.g.*, Shirahata *et alii* 1980; Maring *et alii* 1987; Sturges and Barrie 1987; Church *et alii* 1990; Erel *et alii* 1990; Hopper *et alii* 1991; Veron *et alii* 1992, 1994; Erel and Patterson 1994). However, multiple sources of industrial Pb and the fact that the Pb industry is becoming more and more a secondary commodity industry are adding further variety to the isotopic signatures that are appearing in the environment.

Given the predominant anthropogenic Pb emissions in the Northern Hemisphere, most of the studies on the Pb isotope fingerprinting technique have been concentrated over the Northern Hemisphere, although a few studies have been also focussed on the Southern Hemisphere, allowing a global assessment of the recent sources and pathway of atmospheric pollution (Maring *et alii* 1987; Sturges and Barrie 1987, 1989; Hopper *et alii* 1991; Flegal *et alii* 1993; Mukai *et alii* 1993; Rosman *et alii* 1994; Kober *et alii* 1999; Bollhöfer and Rosman 2000, 2001).

On a global scale (Bollhöfer and Rosman 2000, 2001), the recent Pb isotope composition of aerosols (from 1994 to 1999) is confined within three major end-members (FIG. 1), which correspond to the most important Pb producer countries (*i.e.*, China, Australia, United States, Peru, Mexico and Canada). Source A is typical for Australian and Canadian (British Columbia) type Pb ores with low $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$; source B characterises isotopic ratios which are similar to those measured in alkyllead available in the U.S. in the 1970s and the arrow (FIG. 1) points towards the composition of Mississippi valley type Pb ores; source C is typical of Pb ores from Peru and Mexico. The Pb isotope compositions of Pb ores from China and other

sectors of Canada, are aligned along those of source A and C. In countries where leaded gasoline is still marketed, automobile emissions generally determine the aerosol signature. However, as the phase out of leaded gasoline proceeds, the aerosol signature is expected to be dominated by local industrial sources and/or incursions from nearby or even distant regions. This means that time series analyses of the Pb isotope composition of aerosols are critical in determining variations of the sources of airborne Pb pollution to the environment.

4. HISTORICAL RECORDS OF ATMOSPHERIC Pb POLLUTION

4.1. Peat Bogs and Ice Core

Aside the present or the recent past, studies of the temporal trends of atmospheric pollution typically focus on the environmental archives preserved in peat bogs and ice cores. One disadvantage of these archives is their geographic distribution: peat bogs are most abundant in formerly glaciated regions, e.g., Scandinavia and Northern North America, while ice cores are restricted to high altitude and high latitude regions.

To mention a few studies, Dunlap *et alii* 1999 presented a synthesis of Pb isotopes in two millennia of European air analysing airborne particulate from ombrotrophic peat bogs in Southern Norway, and combining the data with previously reported measurements from France (Elbaz-Poulichet *et alii* 1984), Switzerland (Shotyk *et alii* 1996), and Greenland (Rosman *et alii* 1997) that cover different ranges of time. The integrated European record (FIG. 2) suggests human control of Pb in airborne particulates over the last 2,300 years. From 366 BC through the first half of the 20th century, Pb isotope compositions in European air plot within the range of compositions in European ore bodies. Since 1950, Pb isotope compositions shift within the array of Pb isotope compositions typical of gasoline from western industrial nations (a mixing line between U.S. and Australian lead in gasoline). Rosman *et alii* (2000) presented a two century record of Pb isotopes in high altitude Alpine snow and ice core drilled at Mont Blanc, France. The results (FIG. 3) reveal three isotopic groupings, associated with the periods pre-1923, 1923-1968 and 1969-1991. In the first group, the isotopic composition is consistent with local mining, smelting and coal burning, while in the second, motor vehicle exhaust emissions dominate. In the third group, motor vehicle emissions also dominate but the Pb is even less radiogenic and it is a clear consequence of the Italian Isotopic Lead Experiment (I.I.L.E.) when Australian Pb was exclusively used in gasoline in the Piedmont Region of North-West Italy.

4.2. Tree Rings and Bark Pockets

Another possibility to record local and global environmental pollution is offered by trees. The advantage is that trees are more geographically widespread, with

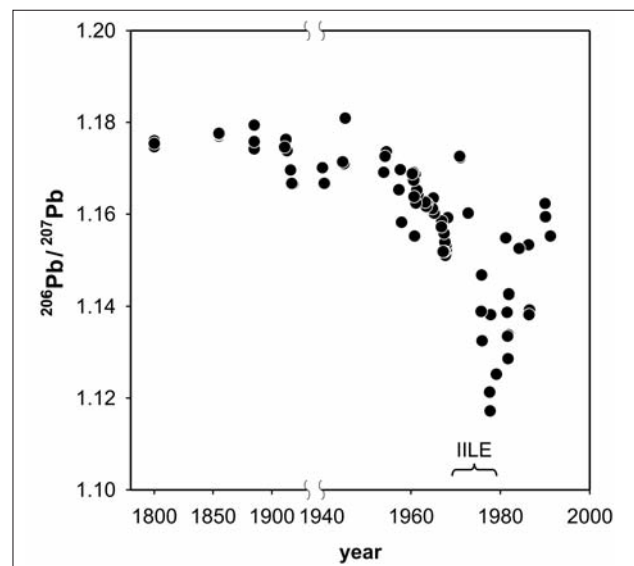


FIG. 3. Two century record of Pb isotopes in ice core drilled at Mt. Blanc (France - redrawn from Rosman *et alii* 2000).

some species being present across many ecological, geographical, as well as human-impact gradients. Sample collection for tree rings is also logistically much simpler and less costly than is the case for peat or ice. Besides their wide geographic presence, tree rings also offer a precise chronology reliably spanning at least the Industrial Period with a potential for far longer periods. Consequently, there is strong interest in dendrochemistry as a biomonitor tool to reconstruct temporal trends in atmospheric pollution. To provide a historical record, a proportion of the pollutants present in the environment must be accumulated and stored within the currently forming annual ring in a reproducible fashion. Trees may accumulate environmental pollutants directly from the atmosphere, by deposition on the leaves or bark, or indirectly following deposition on the soil and subsequent root uptake (Lepp 1975).

The use of annual rings as historical monitors has proved controversial, however, as it is unclear whether the relative concentration of heavy metals and the Pb isotope composition accurately reflects relative changes in the environment (Hagemeyer 1993, Nabais *et alii* 2001). This controversy may, in part, be due to the choice of tree species (Baes and Ragsdale 1981, Cutter and Guyette 1993) and to the fact that the Pb incorporated during the annual growth of tree rings is a mixture between a *natural* component, derived from rock weathering and root uptake, and an *anthropogenic* component derived from industrial Pb emission to the environment. Also, the studies questioning the use of tree rings as biomonitors of anthropogenic Pb emissions did not adopt the pre-treatment procedure, developed for radiocarbon analyses of wood (Kalin *et alii* 1995), to remove exchangeable Pb that may be mobile across tree ring boundaries.

In addition to tree rings, bark and bark pockets are another potentially robust biomonitor of airborne Pb pollution, as they accumulate Pb and other pollutants di-

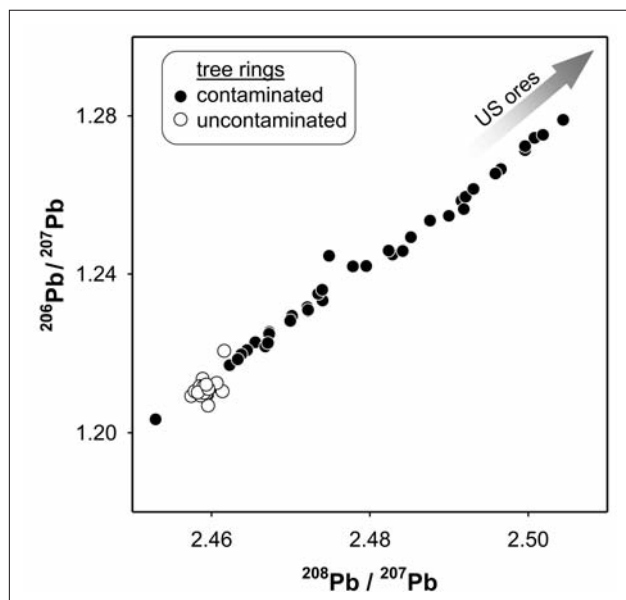


FIG. 4. $^{206}\text{Pb}/^{207}\text{Pb}$ of tree rings from seven baldcypress trees in both highly contaminated and relatively noncontaminated regions of Bayou Trepagnier (Southern Louisiana - redrawn from Marcantonio *et alii* 1998).

rectly from the atmosphere through dry and wet deposition (e.g., Lotschert and Kohm 1978). The relative position of the bark pockets with respect to the annual rings allows their age, *i.e.*, the date they were enclosed by the trunk, to be determined and provides a record of historical changes in pollution (Satake *et alii* 1996, Bellis *et alii* 2002).

4. 3. Case Studies

The following paragraphs deal with a number of case studies on the controversial results of using tree rings and tree barks as robust biomonitors of historical changes in environmental pollution.

Marcantonio *et alii* (1998) measured the Pb isotopic composition of tree rings from seven baldcypress trees in both highly contaminated and relatively noncontaminated regions of Bayou Trepagnier, a bayou in southern Louisiana that has had oil refinery effluent discharged into it over the past 70 years. The Pb isotope composition of tree rings suggests mixing between two sources of Pb (FIG. 4). One of the sources is derived from the highly polluted dredge spoils on the banks of the bayou and the other from the natural environment. The nature of the contaminant Pb is unique in that it is, isotopically, relatively homogeneous and extremely radiogenic, similar to ores of the Mississippi Valley ($^{206}\text{Pb}/^{207}\text{Pb} \sim 1.28$). The time series analysis provided by tree rings permitted also to establish that the oil refinery started to use the Pb ores from the Mississippi Valley prior to 1950, whilst the majority of U.S. industry did not begin using Pb derived from the Mississippi Valley ores until the 1970s.

Tommasini *et alii* 2000 determined Pb isotope composition of tree rings and urban aerosols in Firenze, Italy, to assess whether arboreal species could be used as

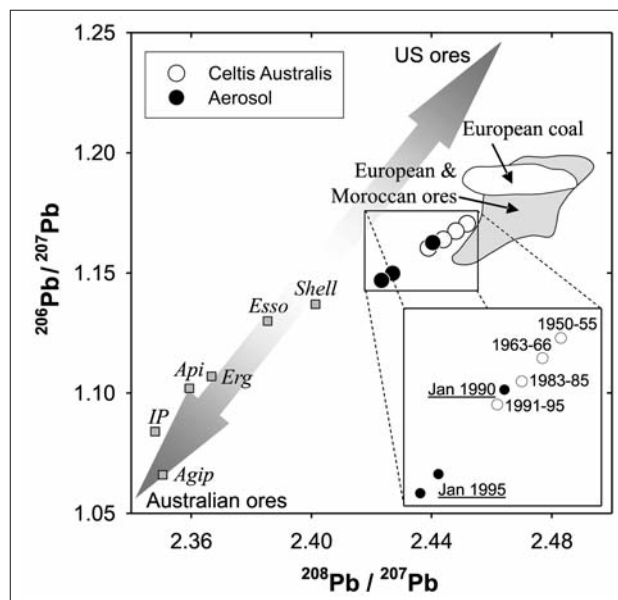


FIG. 5. Pb isotope composition of tree rings (*Celtis Australis*) and aerosols from Florence (Italy), with the potential sources of airborne Pb (gasoline data of the main Italian suppliers are from Dongarrà *et alii* 2003). Inset: Enlarged diagram with only tree rings and aerosols data, and their relative age (redrawn from Tommasini *et alii* 2000).

bio-geochemical tracers of the evolution of heavy metal pollution to the environment. The Pb isotope composition of tree rings from 1950 to 1995 is within the range of European aerosols and is linearly correlated with the temporal evolution of Pb isotopes measured in air particulates from Firenze (FIG. 5), with the younger samples having lower $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ than the older samples. Taken together, tree rings and aerosols define a mixing line between the Pb isotope composition of European and Moroccan Pb ores and European coal, and the Pb isotope composition of alkyllead from the major suppliers of gasoline in Italy, and indicate, as expected, an increasing contribution from car exhaust to airborne Pb pollution from 1950 to 1995. 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.

Bindler *et alii* 2004 studied the possibility to use tree rings as Pb pollution archives, comparing the results with other environmental media. They collected tree ring samples in Sweden covering an age range of 100-300 years. They compared the $^{206}\text{Pb}/^{207}\text{Pb}$ of tree rings with that of the soil profile along with temporal changes in the $^{206}\text{Pb}/^{207}\text{Pb}$ in peat and lake sediment deposits in Sweden. The mineral soils at each site are characterised by high $^{206}\text{Pb}/^{207}\text{Pb}$ (1.35), while the ratios in the O-horizon are low (1.14-1.16) and characterised by atmospheric lead pollution. The $^{206}\text{Pb}/^{207}\text{Pb}$ of the tree rings, typically 1.18-1.20, indicates a signifi-

cant (10–30%) contribution of Pb derived from the underlying mineral soil. While peat and lake sediment records show that the $^{206}\text{Pb}/^{207}\text{Pb}$ of atmospheric deposition has varied over time, with a pronounced trough between approximately 1930 and 1990, the tree rings show no similar trend, implying that the dendrochemical record is not useful in temporal studies of metal pollution.

Bellis *et alii* (2002) evaluated the historical records of Pb pollution in the annual growth rings and bark pockets of a 250-year-old *Quercus crispula* in Nikko, Japan. The annual rings record Pb concentrations from 0.01 to 0.1 ppm and there is no significant change in concentration with time (FIG. 6). In contrast, bark pocket samples dating from 1875 to the present show a progressive increase in Pb concentration with time, from approximately 0.1 to 10 ppm (FIG. 6), recording the historical increase in airborne Pb pollution accompanying the industrialisation of Japan, which was initiated by the opening of Japan's borders from 1854. Similarly, the Pb isotope composition of the bark pockets remain constant until 1964 ($^{206}\text{Pb}/^{207}\text{Pb} \sim 1.18$) and then gradually decrease to a present-day value of ~ 1.16 , indicating changes in the sources of Pb pollution. The data imply that bark pockets are more effective than annual rings for recording historical change in airborne Pb pollution.

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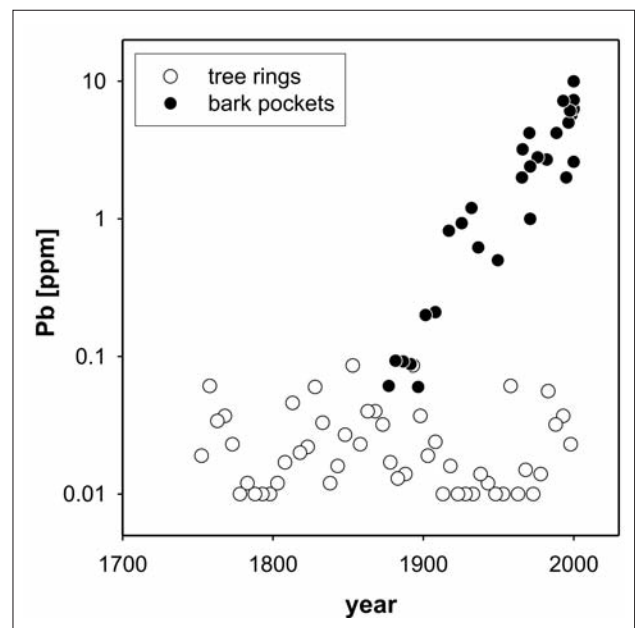


FIG. 6. Pb content in tree rings and bark pockets of *Quercus Crispula* from Nikko (Japan-redrawn from Bellis *et alii* 2002).

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