

Pb pollution from leaded gasoline in South America in the context of a 2000-year metallurgical history

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Exploitation of the extensive polymetallic deposits of the Andean Altiplano in South America since precolonial times has caused substantial emissions of neurotoxic lead (Pb) into the atmosphere; however, its historical significance compared to recent Pb pollution from leaded gasoline is not yet resolved. We present a comprehensive Pb emission history for the last two millennia for South America, based on a continuous, high-resolution, ice core record from Illimani glacier. Illimani is the highest mountain of the eastern Bolivian Andes and is located at the northeastern margin of the Andean Altiplano. The ice core Pb deposition history revealed enhanced Pb enrichment factors (EFs) due to metallurgical processing for silver production during periods of the Tiwanaku/Wari culture (AD 450–950), the Inca empires (AD 1450–1532), colonial times (AD 1532–1900), and tin production at the beginning of the 20th century. After the 1960s, Pb EFs increased by a factor of 3 compared to the emission level from metal production, which we attribute to gasoline-related Pb emissions. Our results show that anthropogenic Pb pollution levels from road traffic in South America exceed those of any historical metallurgy in the last two millennia, even in regions with exceptional high local metallurgical activity.

INTRODUCTION

Lead (Pb) is highly neurotoxic, and in contrast to many other heavy metals including cobalt, copper, and zinc, it has no beneficial effects in humans even at low concentrations (1). The introduction of leaded gasoline in the 1920s initiated a period of unabated growth in the global emissions of Pb. Before the onset of leaded gasoline phase-out in the 1970s, atmospheric Pb levels increased dramatically. Worldwide Pb emissions from gasoline in AD 1983 is estimated at about 248,000 tons (2), which was reduced to ~90,000 tons in AD 1995 (3) after the implementation of environmental strategies through the introduction of low-leaded and unleaded gasoline. Apart from combustion of leaded gasoline, major sources of anthropogenic Pb emissions include mining, metallurgical processing, and coal burning (2). Long-term histories of Pb pollution in Eastern and Western Europe (4–6), North America (7, 8), and Asia (9–11) show evidence that, in these regions, the highest Pb emissions of the past 2000 years occurred in the second half of the 20th century. These studies suggest that emissions from metallurgy and coal combustion in the Northern Hemisphere, which significantly influenced atmospheric Pb concentrations [for example, during the Roman period (6, 12) and the first half of the 20th century (13)], are minor in relation to emissions caused by the intensified use of alkyl-lead in gasoline. There exist, however, no equivalent data for South America.

Emissions from leaded gasoline in South America are low compared to those in North America. In AD 1995, for example, about 13,000 tons of Pb was emitted from mobile sources in North America, but only ~6000 tons in South America (3). Despite this, the exploitation of the extensive polymetallic deposits of the Andean Altiplano in South America has caused substantial emissions of Pb into the atmosphere since precolonial times. Noticeable Pb pollution from metallurgical activities of the Inca era and even earlier cultures has been documented (14, 15). The Andes of South America are exceptionally

rich in mineral deposits and are considered to be the cradle of New World metallurgy (16–18). Bolivia and Peru dominated global silver production from the 16th to the 18th century. From the end of the 19th century onward, South America became an important world producer of nonferrous metals such as Sn, Sb, Zn, W, Ag, Au, Cu, Pb, and Cd. In 2013, the Andean countries Bolivia, Chile, and Peru held as much as ~40% of global silver and copper reserves (19). Although metallurgical processing is a dominant Pb source in South America, its historical significance compared to Pb pollution from leaded gasoline is not yet resolved. Sediment cores from lakes in Bolivia and Peru showed the influence of pre- and postcolonial metallurgy on atmospheric Pb concentrations. No recent increases resulting from industrialization and the use of leaded gasoline were detected in Pb records of Bolivian lake sediments from Laguna Lobato (14) and Taypi Chaka (15), pointing to rather local deposition histories. Pb maxima around AD 1950 and 1970 observed in Peruvian lake sediments from Laguna Chipian (20), Llamacocha (21), and Pirhuacocha (22) were attributed to extensive local mining activity. A 22,000-year ice core record of Pb enrichment factors (EFs) from Sajama, Bolivia (23), revealed a pronounced increase during the 19th and 20th centuries caused by human activity in South America. Data resolution of the record is, unfortunately, not sufficient to distinguish between metallurgical and gasoline-related Pb pollution. Pb EFs and concentration records obtained from Antarctic ice cores indicated a strong influence of gasoline-related emissions during the second half of the 20th century. Because Antarctica is affected by various source regions including South America, Africa, Oceania, and local sources, the individual sources cannot be resolved (24–29).

Here, we present the first comprehensive 2000-year Pb emission history for South America, based on a continuous, high-resolution ice core record from Illimani glacier, Bolivia. Complementary to local air pollution recorded in lake sediments, ice cores from mid-latitude glaciers provide information about more extended source areas. Nevado Illimani [6438 m above sea level (asl)] is the highest mountain of the eastern Bolivian Andes and is located at the northeastern margin of the Bolivian Altiplano (Fig. 1). The primary moisture source for precipitation at the Illimani is the tropical Atlantic Ocean via the Amazon basin

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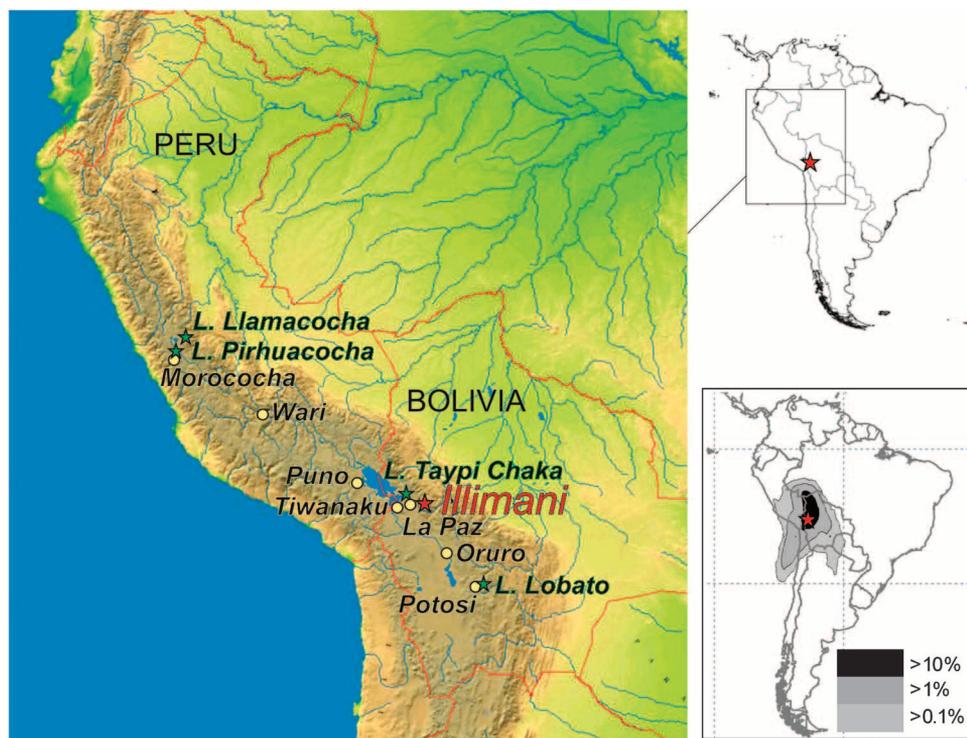


Fig. 1. Location of the drilling area and sites mentioned in the text. **Upper right:** Map of South America with the Illimani drilling site (red star). **Left:** Topographic map showing the mines, metallurgical and historical centers (yellow dots), and the Peruvian and Bolivian lake sediment sites (green stars) discussed in the text. The satellite image ©PlanetObserver was extracted from DVD-ROM “Der Große 3D-Globus 4.0 Premium,” #2008 United Soft Media Verlag GmbH. **Lower right:** Frequency plot of 5-day back trajectories for the Zongo valley close to the Illimani for the period 1989–1998 using HYSPLIT and the NCEP/NCAR reanalysis. Back trajectories were run every 6 hours.

[for example, see (30) based on 19-day back trajectories]. Occasionally, air masses from the Pacific reach the study site (Fig. 1). Thus, potential source regions of air pollution arriving at the Illimani include southern Peru, Bolivia, northern Chile, and northwestern parts of Brazil. Illimani is in close proximity to the extended polymetallic deposits of the Altiplano that have played a fundamental role in the economy of South America since precolonial times (14, 15). The Pb record allows us to evaluate the importance of gasoline-related Pb emissions compared to that from historical metallurgy in the Altiplano region.

RESULTS AND DISCUSSION

The 2000-year Pb concentration record from Illimani documents the history of South American Pb pollution from pre- and postcolonial metallurgical activities at the Altiplano, leaded gasoline, and local dust emissions (Fig. 2). The most prolonged Pb concentration maxima occurred during the periods AD 500–600, 1050–1350, and 1880–2000. The steepest rise of the Pb concentrations was observed at the end of the 19th century, parallel with industrialization in the Andes. The first two maxima were caused by deposition of soil dust as indicated by a strong enhancement of dust-related elements, such as Ce (Fig. 2). The period around AD 1050–1350 with increased dust deposition at the Illimani coincides with an exceptionally long period of low water

levels in nearby Lake Titicaca (31) (Fig. 2). Additional evidence for reduced precipitation and warmer conditions during the Medieval Climate Optimum is provided by the Quelccaya ice core accumulation record (32), the Illimani temperature reconstruction (33), and different proxies from peat bogs (34) and lake sediment cores (31, 35–40).

To trace the provenance of Pb pollution at the study site, we investigated variations in Pb isotopes. Temporal changes in Pb isotopes have been successfully used to differentiate between natural and anthropogenic Pb sources (4, 5, 41). The ice core records of the isotopic ratios $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ are presented in Fig. 2. In contrast to the mentioned studies, there are no significant changes in the ice core $^{206}\text{Pb}/^{207}\text{Pb}$ ratio during the entire period. This is due to a similar $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in local soils and ores in Bolivia (42) (Fig. 2). Likewise, the $^{208}\text{Pb}/^{207}\text{Pb}$ ratio does not show significant temporal variations, except after ~AD 1960, when the $^{208}\text{Pb}/^{207}\text{Pb}$ ratio was lower because of an input of non-local Pb primarily from leaded gasoline (see below). Thus, the Pb isotopic fingerprint during the period AD 0–1960 cannot be used to discriminate between Pb pollution from mining activities and natural soil dust input. To distinguish the anthropogenic signal from lithogenic Pb deposition, we calculated Pb EFs

based on local background composition (Fig. 3). Contrary to the Pb concentration records, Pb EFs are significantly enhanced during the period ~AD 450–950 and are close to background values during the Medieval Climate Optimum ~AD 1000–1400. A parallel increase of both EFs and Pb concentrations from the end of the 15th century until the 20th century points to a dominant anthropogenic Pb source during that time.

In the following sections, we will discuss the 2000-year Pb EF record with respect to Pb emissions from different civilizations during pre-Columbian archaeological cultural periods (Early Intermediate, ~AD 200–600; Middle Horizon, ~AD 600–1000; Late Intermediate, ~AD 1000–1450; Late Horizon, AD 1450–1532), colonial times (AD 1532–1900), and the industrial era.

Tiwanaku/Wari

The earliest anthropogenic Pb pollution detected from Pb EFs during the period ~AD 450–950 coincides with the expansion of the pre-Incan cultures Tiwanaku and Wari, who populated the Altiplano region and western parts of modern-day Peru, respectively, during the end of the Early Intermediate and Middle Horizon periods (43, 44). The most powerful ancient cities, Tiwanaku and Wari, were located less than 100 and ~700 km from the Illimani site, respectively (Fig. 1). Archaeological excavations and lake sediment records provided evidence that this early anthropogenic Pb maximum was caused by pre-Incan silver

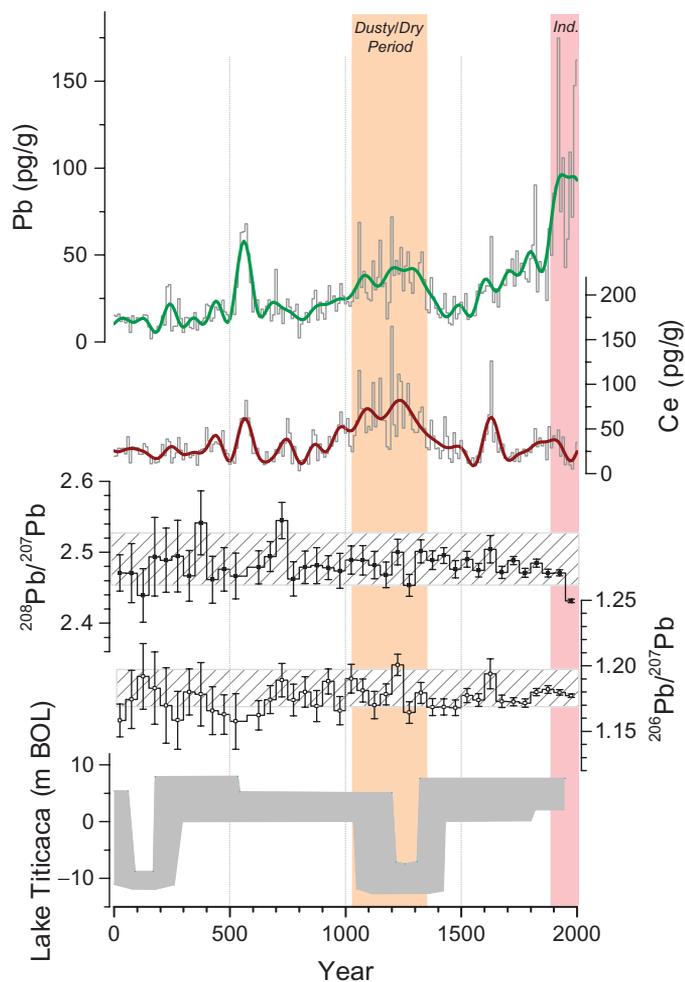


Fig. 2. Ice core records of Pb and Ce concentrations, Pb isotope ratios, and lake levels of the Lake Titicaca for the period AD 0–2000. Concentrations are shown as 10-year medians (gray lines) and 100-year low-pass filtered data (Pb, green bold line; Ce, brown bold line), whereas isotope ratios $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ are presented as 50-year means (\pm SE) together with the background range for Bolivia (local dust and soils + Porco and Cerro de Potosí mine tailings) (42) (hatched areas). Reconstructed lake levels of Lake Titicaca [meters below overflow level (BOL)] are from (31). The prolonged dusty/dry period during the Medieval Climate Optimum and the Industrial period (Ind.) are marked in orange and red, respectively.

refining (15, 45). During that time, a metallurgical center already existed at Huajje near Puno Bay, ~250 km from Illimani. Smelting debris and crucibles found at this site suggest the century-long application of a multistep silver extraction process including smelting of Pb, Ag-ore to silver-enriched Pb, and final purification of silver by selective oxidation of Pb (cupellation) (45). The productivity increased under the influence of the Tiwanaku culture, as measured by the number of artifacts found per cubic meter. There is evidence that, with the decline of the Tiwanaku in the region, the productivity decreased ca. AD 900–1000 (45). This was most likely related to a shortage of fuel resources surrounding the smelting and refining center or to warfare and raids caused by weakened centralized forces. Pb deposits in sediment cores from the nearby Laguna Taypi Chaka (15) and the more distant Laguna Llamacocha, 1000 km away (Peru) (21), confirmed the

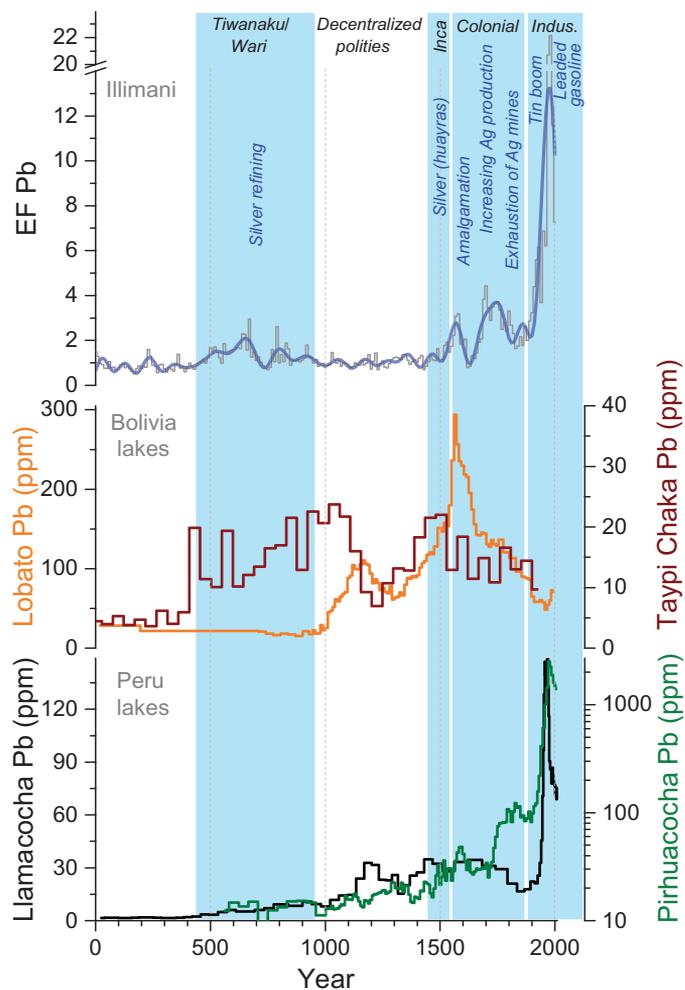


Fig. 3. Ice core Pb EF record compared to sediment core Pb concentrations from Bolivian and Peruvian lakes. Illimani Pb EF record (gray, 10-year medians; blue, 100-year low-pass filtered data) together with sediment core Pb concentrations from Laguna Lobato [orange, period AD 20–1995 (15)], Laguna Taypi Chaka [brown, period AD 4–1923 (15)], Laguna Llamacocha [black, period AD 25–2008 (21)], and Laguna Pirhuacocha [green, period AD 560–2005 (22)]. Periods of generalized Andean archaeological history together with causes of enhanced or reduced Pb deposition are marked in blue.

prevalence of silver-smelting technology from Tiwanaku and Wari cultures during the Middle Horizon period in the Andes (Fig. 3).

Decentralized polities

After ~AD 950, Pb EFs decreased to background levels, parallel with the nearly synchronous decline of the Tiwanaku and Wari empires (46, 47). Various hypotheses were proposed to explain the demise of the Middle Horizon civilizations, including ecological and climatical factors, such as a progressive drying of the climate devastating their sophisticated agriculture (38, 48), erupting conflicts with Wari or Huaracane people, or internal upheavals (46, 49). In particular, the question of whether a century-long drought may have played a crucial role is controversially discussed (46, 50–55). Our data support the occurrence of a prolonged dusty/dry period lasting for ~300 years (Fig. 2).

The decline of the Wari and Tiwanaku empires marked the end of the Middle Horizon and the beginning of the Late Intermediate period (LIP; ca. AD 1000–1450), which was characterized by decentralized polities until expansion of the Incas into the Altiplano starting ca. AD 1450. During the LIP, Pb EFs remained close to background. A rapid decline of Pb levels at the beginning of the LIP (~AD 1040), coinciding with the collapse of the Tiwanaku culture, was also observed in the Laguna Taypi Chaka sediments (14). However, other lake sediment data suggest a shift of metallurgical activities from the Titicaca basin to Cerro Rico, near Potosí in southern Bolivia, and Morococha in central Peru during the LIP (14, 15). Thus, whereas Pb concentrations at Laguna Taypi Chaka, close to Illimani and Titicaca basin, were low during the LIP, Pb levels at Laguna Lobato, close to Potosí and Laguna Llamacocha and Pirhuacocha in the Morococha mining region, increased during the time of decentralized polities (15, 21, 22). The LIP expansion of metallurgical knowledge into central Peru and southern Bolivia was interpreted as being due to a large, post-Middle Horizon diaspora initiated by the collapse of the Tiwanaku and Wari empires (15).

Incas

At the end of the 15th century, Illimani Pb EFs started to rise again coinciding with the expansion of the Inca Empire into the Altiplano from ~AD 1450. The Incas extracted high amounts of silver-enriched metal from ore with the use of small wind-driven furnaces (huayras or huayrachinas) (18, 56, 57) (Fig. 4). Huayras were easily and cheaply built from clay and well adapted to local resources, that is, the strong winds prevailing in the Altiplano and the scarce fuel supply (56, 58). Considered together with archaeological evidence (57), the Illimani Pb EF increase in the period AD 1450–1532 points to a continuous metallurgical technology application at the Altiplano in the Inca Empire until colonial influence. An indication of intensified smelting at Potosí after AD 1400 was also observed in sediment Pb records of Laguna Lobato and Taypi Chaka in Bolivia and Laguna Llamacocha and Pirhuacocha in Peru (14, 15) (Fig. 3).

Colonial period

Anthropogenic Pb continued to rise after the Hispanic conquest of Bolivia and Peru beginning in AD 1532. Intense Hispanic mining

and smelting followed an initial period of primary looting and melting down. Incan mines and metallurgical centers, for example, Porco near Potosí, were brought under Colonial control, and in AD 1545, the legendary silver mountain Cerro Rico at Potosí was discovered. During the first decades of the colonial period, silver extraction relied mainly on native operators who were familiar with the indigenous, pre-Columbian technology using huayras to melt silver-enriched Pb from Pb, Ag-ore (58). The maximal Pb enrichment during onset of colonization in the mid-16th century is comparable with that of the Tiwanaku culture (Fig. 3).

Although silver production in the Altiplano peaked at the end of the 16th century (59), anthropogenic Pb in the Illimani ice core decreased after AD 1570 (Fig. 3) with the introduction of the amalgamation process. At this time, easily exploitable and rich silver ore near the surface of the Cerro Rico was depleted. Poor-quality ore from deeper layers could not be extracted efficiently by fuel-demanding smelting in the flexible but low-capacity huayras. Instead, the “cold” amalgamation process based on mercury application, introduced in the Andes in AD 1572 (60), allowed extraction of tens of thousands of tons of silver from Cerro Rico with low fuel demand. Potosí thereby developed into the most important silver mine of the world. About 45,000 tons of mercury were consumed in Potosí during the colonial period, originating mainly from Huancavelica in Peru (60). Consistent with the Illimani record, a marked reduction of Pb emission to the atmosphere after the introduction of the amalgamation is also visible in sediments of Laguna Lobato close to Potosí (Fig. 3) (14).

After the mid-17th century and during the 18th century, Pb EFs were again at a high level. During that time, silver production at Cerro Rico peaked. Potosí was the world’s leading silver producer during the 16th and 17th centuries (59), and from AD 1500 through to 1800, Bolivia, Peru, and Mexico together accounted for >85% of the world silver production and trade (61). To keep up with the immense silver demand, new mineral deposits with high silver content outside of Potosí and Chuquisaca were exploited. The rich bonanza mine Laykakota at the northwestern Titicaca basin, about 250 km from Illimani, was discovered in AD 1657 (62). The high silver content of these ores probably allowed the reuse of the traditional smelting methods, resulting again in enhanced Pb emissions to the atmosphere. Further use of traditional smelting technologies, even after the introduction of refining by amalgamation, is also reported in Porco close to Potosí (58).

From the end of the 18th century until the mid-19th century, Pb EFs returned to lower levels. After around AD 1800, major silver mines around Potosí were depleted and silver mining became less profitable. The ore quality and accessibility strongly decreased, and silver market prices fell. By AD 1825, Cerro Rico was home to more than 5000 open mine shafts and adits (59). Many mines were abandoned, flooded, or caved in. Potosí’s population had fallen from ~160,000 during the silver boom in the 1600s to about 10,000 in the 1800s (59).

Industrial period

Parallel with the resurgence of the silver industry in Potosí around AD 1850–1873



Fig. 4. Colonial drawings of silver-smelting furnaces (huayras) in the Bolivian Andes. Left: Watercolor painting from the late 16th century showing three huayras with flames emerging from the orifices in the walls; two huayras smoke and are tended by individuals in indigenous ponchos and Spanish-style hats, from the *Atlas of Sea Charts*, courtesy of The Hispanic Society of America, New York. **Right:** After Barba 1640 [from (56)].

(59), Pb EFs started rising steeply into the 20th century. This increase in silver production was enabled by lower Hg prices allowing a draining and restart of many mines (59). From the end of the 19th century, however, the Bolivian silver industry lost its importance in relation to the tin industry. Tin started surpassing silver in economic importance from around AD 1900 (63). In the first half of the 20th century, Bolivia was one of the top three tin producers worldwide. Tin became the main export product of Bolivia. Between AD 1900 and 1966, an average of 66% of total exports (tons) were tin exports (64). Sn minerals in this region as cassiterite and teallite (65) contain Pb as a major or trace element, leading to the emission of Pb during metallurgy of Sn ores. A strong increase in Pb levels from the end of the 19th century onward was also observed at the Peruvian Laguna Llamacocha and Pirhuacocha, but not at the Bolivian Laguna Lobato close to Potosí or Laguna Taypi Chaka (Fig. 3). We relate this to a shift in the region of the metallurgical activities. Whereas the major silver-producing areas were Potosí and Chuquisaca in southern Bolivia, the main centers for tin production were in the more northern Bolivian provinces La Paz and Oruro (64). Tin production peaked between the 1920s and 1940s, corroborated by respective maxima in the Pb EFs (Fig. 5). Further evidence that the major anthropogenic Pb source in the first half of the 20th century was still local mining/metallurgical processing is provided by the records of Pb isotope ratios. Variations in the $^{208}\text{Pb}/^{207}\text{Pb}$ ratio are within the Bolivia background values from local ores and soils until the 1960s (Figs. 5 and 6).

Leaded gasoline

The most pronounced increase in the Pb EFs of the past 2000 years occurred during the 1960s parallel to the intensified use of leaded gasoline in South America (Figs. 3 and 5). Evidence that traffic-related emissions were responsible for the increased Pb EFs is provided by the Illimani ice core nitrate record (Fig. 5). We attribute the increase of the nitrate concentrations above background values from the 1960s onward to rising NO_x emissions from traffic, as suggested by the correlation with the elevated number of motor vehicles in Bolivia, Brazil, Chile, and Peru (Fig. 5, period 1928–1988). Although nitrate concentrations increased further during the 1980s, Pb EFs in the period AD 1985–1999 were a factor of 2 to 3 lower compared to AD 1965–1985 after the introduction of unleaded gasoline. The first country in South America initiating the phase-out of leaded gasoline was Brazil, moving toward alcohol fuels and unleaded gasoline from AD 1975 on, and achieving a total phase-out in 1991 (66). On the contrary, unleaded gasoline in Bolivia, Chile, and Peru was not introduced before AD 1990–1991, and leaded gasoline was still in use until 1995 (Bolivia), 2004 (Peru), and 2005 (Chile) (66). Thus, we relate the downward trend of the Pb EFs during the 1980s primarily to Pb reduction in Brazilian gasoline. With an average of 6.5 million motor vehicles during the period AD 1965–1985 (67), Brazil is expected to have dominated traffic-related Pb emissions in South America because the total number of cars in Bolivia, Chile, and Peru was only ~1 million.

A change of the Pb source is apparent in the Pb isotopic composition. The $^{208}\text{Pb}/^{207}\text{Pb}$ ratio decreased from the 1960s on, whereas the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio remained constant (Fig. 5). Thus, the latter isotopic ratio alone is not sufficient to trace changes in the Pb provenance in this region of South America. The three-isotope plot (Fig. 6) underlines that the Pb isotopic composition in the period AD 1850–1965 is indistinguishable from the Bolivia background range composed of local ores and soil dust. From the 1960s onward, the range of Illimani Pb isotopic composition is similar to that of ambient aerosols in

northern Chile, Argentina, and Brazil in the period AD 1994–1999 (68). During this time, leaded gasoline was still used in Chile and Argentina, whereas it was already phased out in Brazil. Accordingly, high aerosol Pb concentrations were observed in Santiago de Chile in AD 1994–1999, whereas concentration levels in Sao Paulo (Brazil) were one to two orders of magnitude lower (68). The similar isotopic range of the aerosols in this period indicates that Pb emissions from leaded gasoline in northern Chile and Argentina and industrial processes (mainly metallurgy) in Brazil in the 1990s cannot be distinguished isotopically, but have a different composition than the local soils and ores in Bolivia (Fig. 6).

During the second half of the 20th century, mining and metallurgical processing continued to be an important Pb source in South

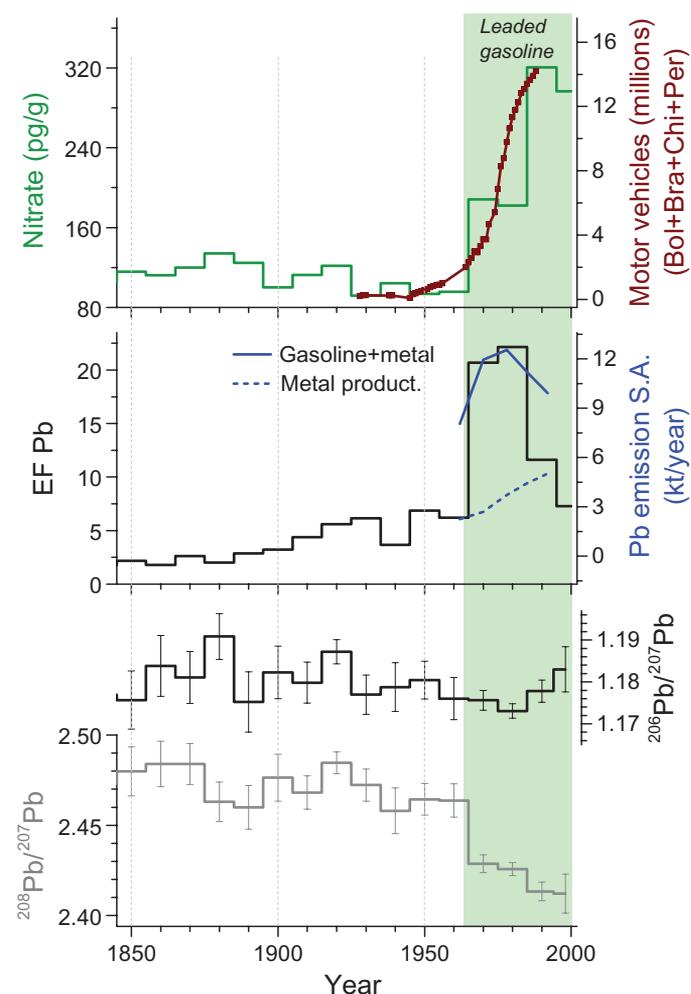


Fig. 5. Ice core records of nitrate concentrations, Pb EFs, and Pb isotope ratios for the period AD 1850–2000. Nitrate concentrations (10-year medians, green) and Pb EFs (10-year medians, black) are shown together with the number of motor vehicles in Bolivia (Bol), Brasilia (Bra), Chile (Chi), and Peru (Per) (67) (brown) and the estimated Pb emissions in South America (S.A.) (24) (blue solid line, emissions from gasoline and metal production; blue dashed line, emissions from metal production). The isotope ratios $^{206}\text{Pb}/^{207}\text{Pb}$ (black) and $^{208}\text{Pb}/^{207}\text{Pb}$ (gray) are presented as 10-year averages (\pm SE). The period of enhanced Pb pollution from leaded gasoline is marked in green.

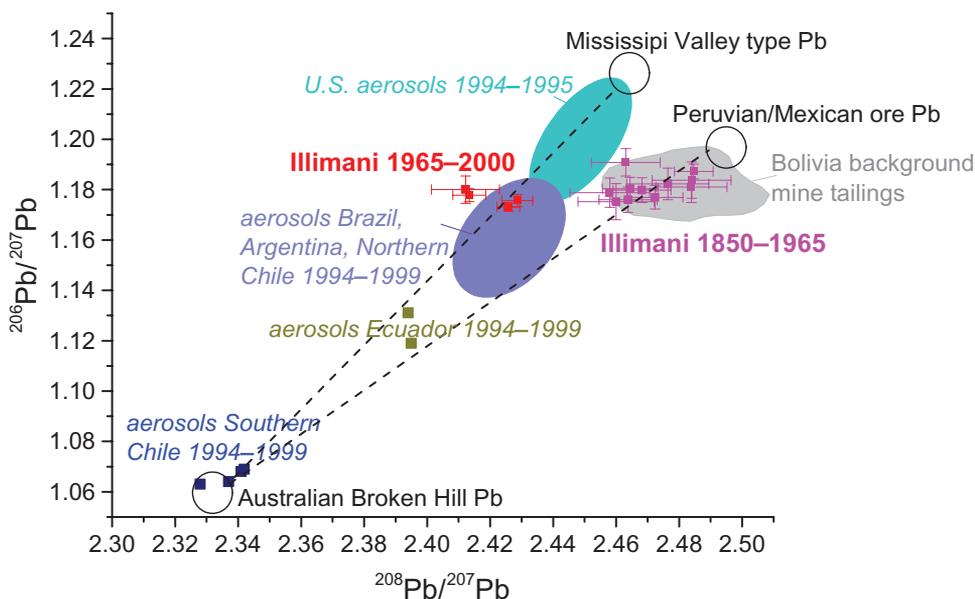


Fig. 6. Three-isotope plot of the Illimani Pb record for the period AD 1850–2000. Ice core values are given as 10-year averages (\pm SE) for the periods AD 1850–1965 (pink) and AD 1965–2000 (red). The gray range represents the isotopic composition of background soils and dust in Bolivia and Porco and Cerro de Potosí mine tailings (42). The Pb isotopic composition of aerosols from South America and the United States in the period AD 1994–1999 (68) is shown in blue and green, respectively. The three black circles mark areas typical for Australian Broken Hill Pb used in European gasoline, Mississippi Valley-type Pb used in U.S. gasoline, and the composition of Peruvian/Mexican ores (68).

America, dominated by Pb emissions from Cu and Ni production (24). Similarly to motorization, Cu and Ni production markedly increased after the 1960s (23). Quantitatively, emissions from metal production accounted for about one-third of the total Pb emissions during AD 1962–1999 (24). By scaling historical Pb emission estimates to the Illimani Pb EF record (Fig. 5), it becomes obvious that emissions from mining/metallurgical processing were responsible for the highest Pb EFs in the second half of the 20th century (EF \sim 7), which is unprecedented in the past 2000 years. The gasoline-related Pb emissions in 1965–1985 in South America resulted in a threefold increase in the Pb EFs (\sim 21) compared to the emission level from metal production. A similar contribution was observed in the Northern Hemisphere, where Pb emissions from road transport accounted for about 50 to 80% of the total Pb emissions between the 1960s and 1980s (5, 69, 70).

Our ice core-based anthropogenic Pb record for the Bolivian Andes allows putting recent gasoline-related emissions into a historical perspective. Even within the “cradle of New World metallurgy,” Pb pollution levels from leaded gasoline in South America exceed those of any historical metallurgy in the last two millennia.

MATERIALS AND METHODS

Ice core archive

The 138.7-m-long ice core investigated in this study is one of two parallel ice cores drilled on Nevado Illimani (16°37'S, 67°64'W, 6300 m asl) in a joint expedition of the Swiss Paul Scherrer Institut (PSI) and the French Institut de Recherche pour le Développement (IRD) in 1999. Low borehole temperatures, -7°C at 10-m depth and

-8.4°C near bedrock, and very few melt features (71) indicate well-preserved records of chemical signals. For ice core dating, a multiparameter approach was applied (33, 72). This included annual layer counting (ALC) for the upper 75 m as well as the use of known reference horizons like the tritium maximum (AD 1964) and volcanic eruptions (71). ALC dating was confirmed by ^{210}Pb dating for the most recent 100 years. This data set was complemented with ^{14}C ages (73, 74), resulting in a continuous age-depth scale through fitting with a two-parameter glacier flow model (75). From 134 m to bedrock of the core, dating was performed by linear interpolation between six additional ^{14}C dates (74). The oldest ice of the Illimani ice core has an age of 13,000 years, whereas the time scale covered by this study spans the last 2000 years (period AD 0–1996) corresponding to the upper 127.5 m of the ice core. Dating uncertainty of the ALC until about 1800 AD is estimated to ± 5 years between volcanic horizons and to ± 2 years in the vicinity of the volcanic time markers. From AD 1800 to 0, the uncertainty of the applied dating model is estimated to ± 20 years.

A mean annual net accumulation of 0.58 m water equivalent (76) allows for highly resolved records.

Sampling and analyses of Pb

Ice core sections with a length between 0.60 and 0.75 m and a diameter of 7.8 cm were sealed in polyethylene tubes in the field and transported to PSI in frozen conditions. In the -20°C cold room at PSI, inner sections with a diameter of 2.2 cm \times 2.2 cm were cut out of the cores to remove potential surface contamination. These inner sections were used for trace element analysis with continuous ice melting inductively coupled plasma-sector field-mass spectrometry (CIM-ICP-SF-MS) applying standard procedures (71, 77). The continuous ice melting device enables a final decontamination directly on the melting head by separating potentially contaminated melt water of the surface from melt water of the innermost part of the core (71, 77). Where continuous ice melting was not possible because of poor ice core quality, discrete samples were rinsed with ultrapure water (18 megohm cm quality, Milli-Q Element system, Millipore Inc.) in a class 100 clean bench to remove the outer ~ 0.3 cm. The decontaminated ice core sections were transferred into precleaned high-density polyethylene containers. Subsequently, these samples were acidified with ultrapure HNO_3 to yield a final concentration of 0.2 N HNO_3 .

Pb concentration and isotope (^{206}Pb , ^{207}Pb , ^{208}Pb) analysis was performed with CIM-ICP-SF-MS using Element 1 (Thermo Finnigan MAT) for the deepest ice core parts (34 to 138.7 m) and Element 2 (Thermo Scientific) for the upper 34 m. The melt water of the inner drain from the melting head was acidified to a final 0.2 N HNO_3 by addition of concentrated ultrapure HNO_3 to the capillary system via a syringe pump. The capillaries were connected to a microflow self-aspirating PFA

nebulizer of an APEX Q sample introduction system (Elemental Scientific Inc.). Discrete samples were introduced to the APEX system with an autosampler (221 XL, Gilson Inc. and ASX-260, Cetac, respectively). Details can be found elsewhere (71, 77). Concentrations were blank-corrected by subtracting the procedural blank and substituted with half the detection limit value (1 pg/g), if concentrations were below the detection limit. Sampling resolution varied from up to 150 samples per year in the last 50 years to two samples per decade in the deepest core sections (AD 0–100).

Calculation of enrichment factors

For the determination of changing mineral dust input to the Pb records, EFs were calculated. EFs are ratios of trace element concentrations to a lithogenic element like Sc, Al, Ti, Zr, or the rare earth elements (REEs), which are normalized to the same elemental ratios of a reference material such as the global upper continental crust (UCC) or the regional background. Pb EFs were calculated following the conventional equation:

$$EF(\text{Pb}) = \frac{([\text{Pb}]/[\text{X}]_{\text{sample}})}{([\text{Pb}]/[\text{X}]_{\text{background}})}$$

Cerium (Ce) was used as reference element X because Ce is highly correlated with Sc, La, and Nd ($r^2 = 0.79, 0.97, \text{ and } 0.96$, respectively, period 8000 BC–1997 AD), but can be measured with the ICP-SF-MS in the more sensitive low-resolution mode and has higher concentration levels than the other REEs. The average UCC [Pb]/[Ce] ratio is ~ 0.26 (78). Average values of the UCC are not necessarily representative of the drilling site owing to, for example, fractionation and altering processes during dust transport and a different analytical methodology for analyzing crustal element concentrations. Thus, we determined a site-specific natural background ratio for the regional dust from the ice core section BC 1500–100, when only negligible anthropogenic influence occurred. We used this local dust ratio of [Pb]/[Ce] = 0.59 instead of the average UCC ratio for calculating EFs.

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