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A 3500-Year Record of Hg and Pb Contamination in a Mediterranean Sedimentary Archive (The Pierre Blanche Lagoon, France)

F. Elbaz-Poulichet,*[,†] L. Dezileau,[‡] R. Freydier,[†] D. Cossa,[§] and P. Sabatier[‡,∥]

[†]Laboratoire Hydrosciences UMR 5569, CNRS, Universités Montpellier I & II, IRD, Place Eugène Bataillon, CC MSE, 34095 Montpellier cedex 5, France

[‡]Laboratoire Geosciences Montpellier UMR 5243, CNRS, Université Montpellier II, Place Eugène Bataillon, CC 60, 34095 Montpellier cedex 5, France

[§]IFREMER, Centre de Méditerranée, BP 330, 83507 La Seyne-sur-mer, France

[∥]Laboratoire des Environnements Dynamiques et des Territoires de Montagne UMR 5204, Université de Savoie, CISM, Campus Scientifique, 73376 Le Bourget du Lac cedex, France

Supporting Information

ABSTRACT: A sediment core encompassing 3500 years of continuous sedimentation has been collected from a coastal lagoon located on the southwestern French Mediterranean coast. Lead concentrations and stable isotopes show that the sediments have recorded the three major periods of Pb pollution: the Etruscan−Greek−Roman period (650 BC to AD 50), the medieval period (AD 650 to AD 1450), and the modern period (from around AD 1850 to the present). These periods were separated by low pollution periods during the Dark Ages (between AD 50 and 650) and during the 16th century. From the end of the 19th century to the 1960s, Pb pollution increased exponentially. Coal combustion was the major source of Pb in the lagoon in the second half of the 20th century. Both the decrease in coal consumption and the ban on leaded gasoline resulted in a decrease in Pb pollution by a factor of 1.5 between 1973 and 1995. From 1991, sewage treatment plants and incinerators could be the major source of Pb. The average baseline Hg concentration from 1525 BC to AD 900 was $0.017 \pm 0.003\ \mu g\ g^{-1}$ ($n = 54$). The Hg concentrations profile shows three major peaks: in AD 1150, AD 1660, and AD 1969, with the concentrations being respectively 8, 5, and 34 times higher than the baseline levels. The medieval peak (AD 1150) is attributed the medical use of Hg in the town of Montpellier and/or the burning of soil and vegetation. Noticeable Hg pollution was also detected during the 17th century in relation to gold and silver amalgamation in Europe. From the end of the 19th century, Hg concentrations increased exponentially until 1969. This modern pollution is attributed to the burning of coal.

INTRODUCTION

The history of atmospheric Pb pollution for 3000 years in Europe is well established by studies of Greenland and Arctic ice cores,[1,2] lake sediments,[3,4] and peat deposits.[5−7] The pollution reached a peak during the Roman period, about 2000 years ago. After a decline during the Dark Ages (AD 400−900), Pb deposition increased again during the Medieval period (around AD 1000). Beginning with the Industrial Revolution (from about AD 1850), the increase in atmospheric pollution was exponential until around AD 1970. Since then it has decreased.

For mercury, several studies of peat bog and lake sediments from northwestern Spain,[8] Greenland and Denmark,[6] the Swiss Jura,[9] and southern England[10] date atmospheric Hg pollution back to the Middle Ages. As for Pb, the studies show an increase of atmospheric Hg during the last two centuries that is generally related to coal combustion.

The influence of these long-term Pb and Hg emmissions on the pollution of the marine environment has not been closely studied, although this might contribute to a better understanding of present-day oceanic metal cycling. These historical inputs are expected to be high in the Mediterranean basin which hosts some of the oldest and largest metal mines in the world. The Iberian Pyrite Belt (Spain)[11] and the Hg mines of Almaden (Spain) were already exploited by the Romans. The history of Pb contamination in the Gulf of Lions over the last century has been reconstructed by Miralles et al.[12] Lead contamination in ancient Mediterranean harbors during the Bronze Age and Roman period has been reported.[13] In Alexandria harbor, anthropogenic Pb contamination was traced back to the Bronze Age (900 BC) and Roman period.[14] Lastly, Greco-Roman Pb was identified in Marseille harbor.[15] For Hg, data are scarcer than for Pb, and to our knowledge no long-term record of Hg contamination in marine environment has been published.

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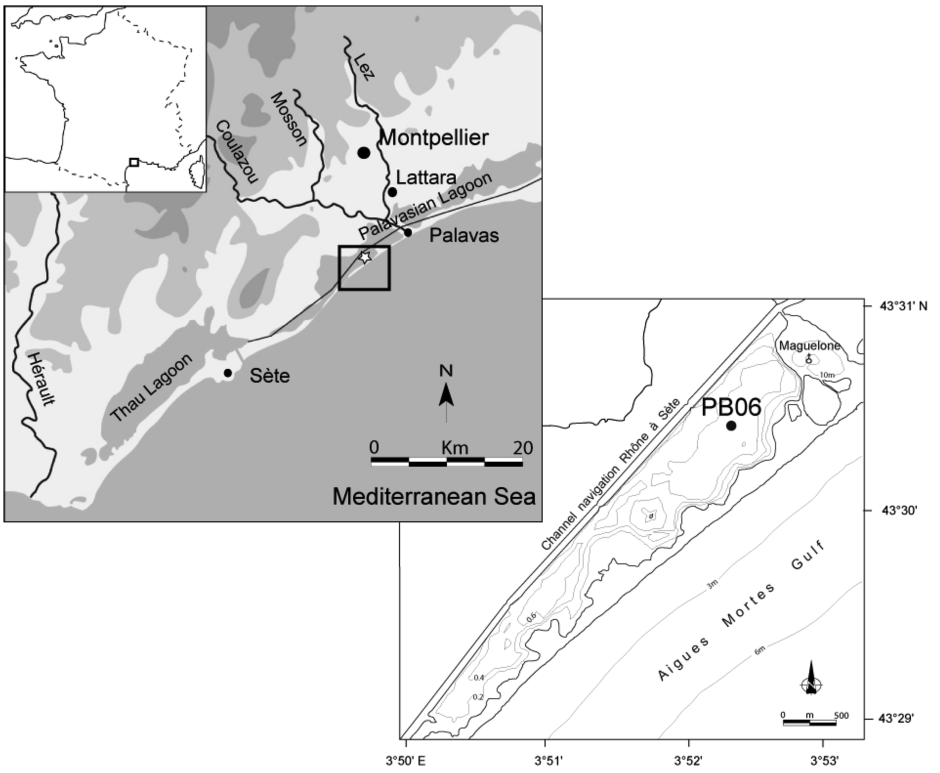

Figure 1. Map of the Pierre-Blanche Lagoon showing the location of the PB06 core.

To reconstruct the long-term history of Pb and Hg inputs into the Mediterranean coastal environment, the concentrations of these elements were measured in a sediment core collected in the Pierre Blanche lagoon (France). This lagoon is well suited to investigate the chronology of Pb and Hg inputs to sediments, because sufficient information is available on sedimentary conditions, rates of sedimentation, and paleostorm events.[16,17] The sediment analyzed in the present study encompassed 3500 years of continuous sedimentation from 1500 BC to AD 2006. The isotopic composition of Pb was used to better constrain the sources of Pb contamination.

MATERIALS AND METHODS

Description of the Pierre-Blanche Lagoon. The Pierre-Blanche (P-B) lagoon is part of the Palavasian lagoonal complex (Figure 1). It has a maximum water depth of approximately 1 m. The lagoon exchanges water with the Rhone-Sete Canal, built in the 18th century, and receives fresh water inputs from a 700 km^2 drainage basin, which includes those of the Lez and Mosson rivers. These two rivers drain the urbanized area of Montpellier (380 000 inhabitants with suburbs) and are the main sources of sediments to the lagoon, together with the landward transport of sand and silt materials during storm events.[17] The P-B lagoon suffers commonly from severe eutrophication.[18]

Complementary information on hydrology and soil occupation is given in the Supporting Information (SI).

Sample Collection. A 7.9-m-long piston core (PB06) was collected in the P-B lagoon (Figure 1) in March 2006 using the UWITEC coring platform. For this study, the sediments between the surface and a depth of 4 m were subsampled.

Chemical Analysis. Details for sample preparation and the chemical analysis are given in the SI. The Particulate Organic Carbon (POC) was analyzed according to ref 19. Aluminum, Pb concentrations, and Pb isotopes were determined after total digestion of the sediments using an ICP-MS, X Series II (Thermo Fisher Scientific), equipped with a CCT (Collision Cell Technology) chamber. Certified reference material from the Canadian National Research Council, i.e., MESS-3 (marine sediment), was used to check analytical accuracy and precision. Measured concentrations agree with recommended values to within ±5% (Al) and 2% (Pb). The precision was better than ±4%. For Pb isotope ratios, the external precision was assessed using eight individual measurements of MESS-3 reference. The following values were obtained: $^{206}Pb/^{207}Pb = 1.2353 \pm 0.0014$ (1σ), $^{208}Pb/^{207}Pb = 2.4964 \pm 0.0024$ (1σ), and $^{208}Pb/^{206}Pb = 2.0212 \pm 0.0033$ (1σ).

Total Hg concentrations in the sediment were determined using an automatic mercury analyzer (AMA-254, Altec) according to Cossa et al.[20]

Chronology frAmework. The chronology of core PB06 is based on ^{137}Cs and ^{210}Pb depth profiles and AMS ^{14}C dates. All details concerning the dating procedure, sedimentation rates, and fluxes for this core are given in Sabatier et al.[16] and in the SI. The sedimentation rates varies between 0.051 mm yr^{-1} and 0.268 mm yr^{-1}, with the highest values being measured between AD 1930 and AD 2006. Between AD 950 and AD 1000, the shift from a protected lagoonal environment to a closed lagoon changed the ^{14}C reservoir age, resulting in a relatively poor time resolution (around 100 yr) during this period. At the sediment surface, the excess ^{210}Pb profile indicated the presence of a 3.5-cm thick mixed layer related to bioturbation and resuspension. The time resolution was thus estimated at 10 yr for the last 100 years.

RESULTS

Lead Concentrations. The lead concentration data are listed in Table S1. Natural Pb is usually associated with the fine-grained

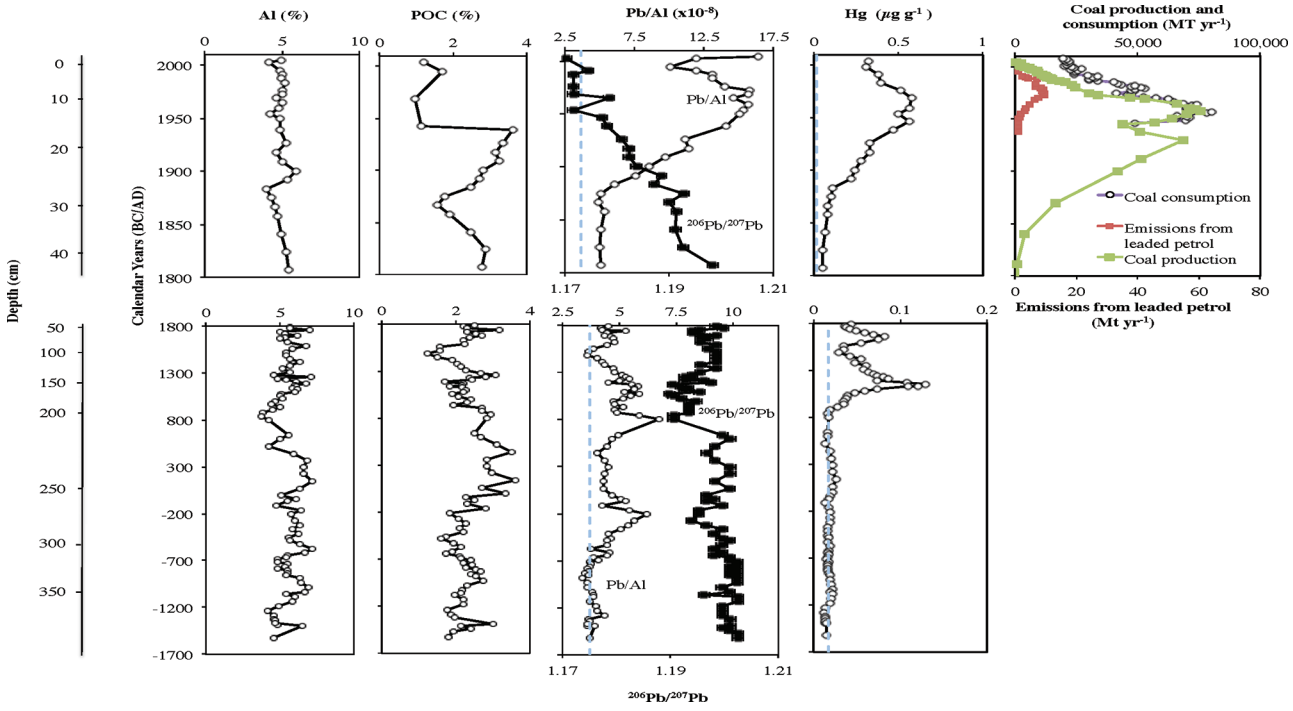

Figure 2. Al, POC, Pb/Al, $^{206}Pb/^{207}Pb$, and Hg concentrations in the sediment profile from the Pierre-Blanche lagoon. The dotted line is the local background concentration. The variations in coal production and coal consumption in France (data *Charbonnage de France*) and Pb emissions from leaded gasoline[57] are also shown.

fraction mainly constituted of organic matter and clay mineral on the alumino silicate fraction, for which Al is a good tracer. The affinity of natural Pb for this fraction in the Pierre-Blanche lagoon is reflected by the good correlation ($R = 0.92$) between Al and Pb in deep sediments (depth <320 cm, date <690 BC). To correct Pb concentrations for the dilution of this fraction by shell debris, normalization to Al, a common practice in marine geochemical studies,[21] was adopted.

The average local Pb/Al background ratio (depth <320, $n = 24$) was equal to $3.7 \times 10^{-8} \pm 0.2 \times 10^{-8}$. Higher Pb/Al ratios were generally observed between 310 and 250 cm depth (650 BC−AD 60), 220−107 cm depth (AD 650−1450), and between 9 and 10 cm depth (AD 1960−1972). The highest Pb/Al ratios, 16.4×10^{-8} and 15.8×10^{-8}, were found, respectively, in the 0.5-cm depth sample (AD 2004) and between 10 and 16 cm depth (AD 1959−1972). These values, higher by a factor of about 4 than the background ratio, are in the range of those reported in the surface sediments of the nearby Thau Lagoon.[22] Lower Pb/Al peaks (5.8×10^{-8}, 6.2×10^{-8}, 6.8×10^{-8}) were also found, respectively, at 150 cm (AD 1150), 205 cm (AD 800), and 274 cm depths (200 BC).

Isotopic Composition of Pb. The distribution of the $^{206}Pb/^{207}Pb$ ratios with depth mirror that of Pb/Al ratios, with the isotope ratios generally decreasing when the Pb/Al ratios increase (Figure 2). At depths >315 cm (prior to 650 BC), the average $^{206}Pb/^{207}Pb$ ratio was equal to 1.2011 ± 0.0015 ($n = 24$), a value which can be considered as the background level. The ratios decreased to a minimum of 1.1938 at a depth of 280 cm (280 BC). The layers comprised between depths of 107 and 205 cm exhibited values down to 1.1898. Above 50 cm (AD 1800), the $^{206}Pb/^{207}Pb$ ratios decreased sharply and leveled off at around 1.1728 ± 0.0028 between 14 cm depth (AD 1940) and the 1 cm depth (AD 2002).

Mercury Concentrations. The Hg concentrations are given in Table S1. Mercury, Al, and POC (Figure 2) were not found to be correlated in the P-B lagoon, and normalization of Hg concentrations to Al or POC, as proposed by various authors (e.g., refs 23 and 24) to minimize the variations related to changes in sedimentary clay and organic matter content, did not drastically modify the Hg profile. For depths >190 cm (i.e., prior to around AD 900), Hg concentrations were relatively low (mean = 0.017 ± 0.003 $\mu g\ g^{-1}$, $n = 54$) compared to crustal values,[25] and displayed minor variations. From 190 cm depth (~AD 900), concentrations increased sharply, peaking at 0.13 $\mu g\ g^{-1}$ at 153 cm depth (AD 1150). A second lower maximum (0.082 $\mu g\ g^{-1}$) was observed at 80 cm (~AD 1650). Above 30 cm depth, concentrations sharply increased, with a broad peak at 0.58 $\mu g\ g^{-1}$ being observed between 10 and 15 cm depth (AD 1945−1968).

DISCUSSION

History of Pb Contamination. The Al-normalized Pb concentration and the $^{206}Pb/^{207}Pb$ profiles (Figure 2) show that the P-B sediments have recorded the three major periods of Pb pollution in Europe outlined by Renberg:[26] the Etruscan−Greek−Roman period (650 BC to AD 50), the medieval period (AD 650 to 1450), and the modern period (from about AD 1850 to the present). These periods are separated by low pollution periods during the Dark Ages (between AD 50 and 650) and during the 16th century.

During the Etruscan−Greek−Roman period Pb isotopes (Figure 3) suggest a possible contamination of P-B sediments by Pb originating from the region of Murcia in Spain (Cartagena mines) in agreement with archeological studies[27] and the isotopic composition of Roman ingots found in the vicinity of the P-B lagoon.[28,29]

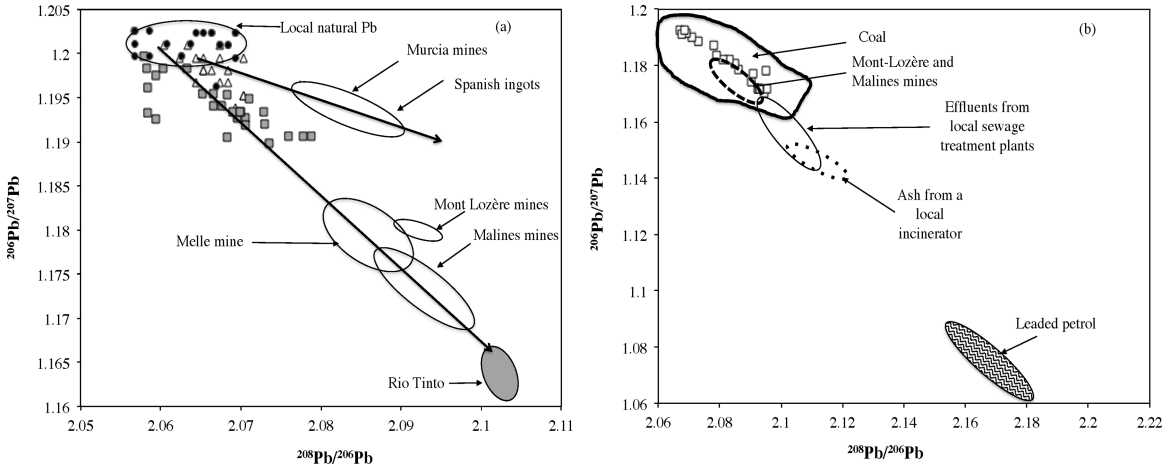

Figure 3. Plot of $^{206}Pb/^{207}Pb$ ratios vs $^{208}Pb/^{206}Pb$ ratios in preindustrial (before AD 1800) Pierre-Blanche sediments (a) and in modern sediments (after AD 1800) (b). Pre-650 BC samples: black circles; samples from the Etruscan−Greek−Roman period (650 BC to AD 50): triangles; medieval samples (AD 640 to 1450): full squares; modern samples (AD 1800 to 2002): open squares. Sources: Carthagena mine,[52] Spanish ingots,[28] Harz mineralization,[53] Mont Lozère mines,[54] Malines mines,[55] Melle mine,[56] Rio Tinto,[52] coal,[57,58] effluent from local sewage treatment plants,[34] ash from a local incinerator, and leaded gasoline.[35]

The medieval pollution comprises two pollution phases with a maximum Pb concentration around AD 800 and a second, lower peak around AD 1150. The studies in southern Europe have generally not detected a peak of Pb pollution before AD 1000[7,8,30] with the exception of Kylander et al.[31] in a high-resolution peat core in northwestern Spain. In that study, the peak of Pb pollution is observed around AD 900, which is consistent with the observations in the P-B lagoon, taking into account the great uncertainty (±100 yr) on dating due to variations of ^{14}C reservoir age in the P-B lagoon in the medieval period.[16]

During the medieval period the Pb isotope composition differs from that of the Estruscan−Greek−Roman period (Figure 3). It reflects inputs of mines from southern France. Several mines from the southern border of the Massif Central were very active during this period.[32] From AD 1250, the pollution starts to decrease in the P-B lagoon. The beginning of this decline coincides with the abandoning of the silver mines of southern France,[32] and continues with the economic crisis and the Black Plague, which affected the region during the 14th century. Concentrations remain around geochemical background levels until the middle of the 16th century. From the end of the 19th century the Pb concentrations increase whereas the isotope composition moves toward less radiogenic Pb sources, in agreement with other regional records.[26]

From the end of the 19th century, Pb concentrations increase exponentially and the $^{206}Pb/^{207}Pb$ ratios show a general decrease until 1950, indicating variations in the contamination sources. The isotope composition of Pb (Figure 3) indicates that the Pb in gasoline always represented a minor contribution to Pb in the P-B lagoon even in the 1970s, when its use reached maximum. The similarity between coal production and/or coal consumption in France and the Pb profile in the lagoon (Figure 2), suggests that the use of coal as the main source of energy largely contributed to Pb contamination of the P-B lagoon until the 1970s. Although the decline in coal consumption slowed contamination, the decrease in Pb concentrations did not occur until the phasing out of Pb additives to gasoline, which began in 1974 in several European countries including France. Between 1972 and 1995, the Pb concentrations decreased by a factor of 1.5 in relation to changes in the composition of gasoline. Similar results have been obtained in peat bogs from Denmark[6] and the Swiss Jura mountains.[33] However, unlike these studies, our data did not reveal an increase in $^{206}Pb/^{207}Pb$ as expected after the banning of Pb additives to gasoline.

More recent Pb sources to the lagoon include effluents of sewage treatment plants[34] and to a lesser extent those of regional incinerators.[35] The increase of Pb concentrations observed after 1991 may be related to an increased contribution of these sources.

History of Hg Contamination. Fitzgerald et al.[36] provided convincing evidence that Hg accumulating in lake sediments is not significantly affected by diagenetic processes. Furthermore, the histories of Hg deposition derived from dated sediment cores agree well with the known histories of inputs.[37] In oxic coastal sediments Hg is likely to be recycled prior to incorporation in the permanent sediment records; however, little postdepositional redistribution has been observed.[38,39] In addition, the P-B record shares some features with atmospheric deposition records in peat from NW Spain,[8] the Swiss Jura,[9] and in the Diss Mere lake (southern England).[10] All this pleads in favor of good preservation of the P-B Hg record. The Hg concentration profile (Figure 2) shows three major peaks: in AD 1150, in AD 1660, and between AD 1945 and AD 1969, with concentrations, respectively, 8, 5, and 34 times higher than the baseline level ($0.017 \pm 0.003\ \mu g\ g^{-1}$).

In the Middle Ages, significant Hg contamination is observed. As in other studies[8−10] this could be related to local inputs due to the widespread use of Hg salts as medication against the plague and leprosy.[40] At that time the town of Montpellier was famous for its Faculty of Medicine founded in AD 1150 and the use of Hg is attested by the discovery in the 19th century of metallic Hg and Hg salts in cellars of medieval houses.[41] However, as suggested by Givelet et al.,[42] deforestation and vegetation burning could also have contributed significantly to the medieval pollution of the P-B lagoon. These practices, which have been shown to mobilize the Hg currently stored in soils and vegetation and to increase the quantity of Hg in the water,[43,44] were widespread during the medieval period in Europe.[45]

Like lead, Hg contamination of the lagoon decreased during the 14th century, due to the deep economic depression. Mercury concentration increased again during the 16th century and peaked

in the middle of the 17th century. Similar observations in northwest Spain were attributed to the intense activity of the Almaden mine.[8] This period corresponds to the development of the Hg amalgamation process for the recovery of Ag and Au.[46] As a consequence, the production of the European Hg mines (Almaden in Spain and Idrija in Slovenia) nearly doubled between AD 1550 and AD 1650[47] in order to supply European and American Au and Ag mines. However, although increasing, European Hg production did not peak during the 17th century.[47] Therefore the peak of pollution observed in the P-B lagoon more probably reflects Hg uses. Mining activities in Central and South America, as well as in Eastern Europe, cannot account for the peak of contamination, because these activities did not result in global atmospheric contamination.[48] For this reason, the Hg peak observed in the P-B lagoon is attributed to the expansion of gold and silver amalgamation in Europe and in the vicinity of the study area, where many auriferous rivers were exploited during the 16th and 17th centuries, a period that is sometimes considered to be the golden age of gold-washing in France. In the 19th century this type of gold production decreased sharply, with most of the gold being obtained from gold mines.[49]

From the end of the 19th century until 1960 there was an exponential increase in the concentration of Hg. During the 20th century, the variations in Hg concentrations characterized by maximum concentrations between AD 1945 AD and 1969 AD and a decline from 1969 on well correlated with coal production and consumption in France (Figure 2). This correlation and the synchronicity of Hg and Pb enrichments, suggest that coal burning, which has been found to be the major source of atmospheric Hg deposited in peat bogs from remote areas in the second half of the 20th century,[6,9,50] was also the major source of Hg in the P-B lagoon.

This study shows that for at least 1000 years the P-B lagoon has received significant Hg inputs related to human activity. Other records in Mediterranean coastal areas would be necessary to define the respective importance of local and regional Hg sources, since this is fundamental for a better understanding of the Hg cycle in the Mediterranean Sea.

■ ASSOCIATED CONTENT

Supporting Information. Additional experimental details, data, and references. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: felbaz@univ-montp2.fr.

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