A 4,000 YEAR LAKE SEDIMENT RECORD OF ATMOSPHERIC LEAD POLLUTION FROM NORTHWESTERN SPAIN

by

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The Iberian Peninsula is rich in mineral resources that have been repeatedly exploited for hundreds, and sometimes thousands of years, leaving a legacy of metal pollution in the environment. This study presents a c. 4,000-year lake sediment record of atmospheric lead (Pb) deposition from Laguna Roya (42° 8'8.42"N, 6°47'38.95"E), a small glacial lake located in the Sierra Segundera of northwestern Spain. A chronological profile of Pb accumulation was reconstructed using the Pb concentration ([Pb]) and $^{206}Pb/^{207}Pb$ isotope ratios to elucidate the regional lead pollution history. Anthropogenic lead emissions are indicated after c. 500 BC, when $^{206}Pb/^{207}Pb$ ratios begin to decrease and [Pb] begins to increase. There is an abrupt maximum [Pb] peak (63 ppm), and minimum $^{206}Pb/^{207}Pb = 1.1760$ that occurs c. 15 BC, prior to the Roman occupation of the region. After the Fall of Rome (c. 550 AD), [Pb] decreases to 15 ppm. The $^{206}Pb/^{207}Pb$ increases to c. 1.1858 and remains relatively constant until just prior to the Industrial Revolution (c. 1820 AD) when atmospheric Pb deposition begins to steadily increase again. The [Pb] reaches a maximum (39 ppm) in 1972 AD and $^{206}Pb/^{207}Pb$ reaches a minimum (1.1688) in 1995 AD.

Source attribution of the anthropogenic Pb was estimated and compared to published lead isotope values of ores associated with mining sites throughout the Iberian Peninsula. It was found that the sources of atmospheric lead pollution prior to 1700 AD are ore deposits from the northwest of the peninsula. From 1700 AD until the mid-20th century the primary Pb emission sources are ores from the southwestern Iberian Pyrite Belt and the south-central Linares-La

Carolina mining districts. After 1960, leaded gasoline became a primary lead pollution source. It is estimated, that in 1972, 29% of the atmospheric Pb deposited in Laguna Roya was from leaded gasoline and 52% was from the southwestern and south-central ore fields. The Pb pollution record in Laguna Roya sediments not only illustrates the persistence and pervasiveness of lead pollution throughout history, but it also demonstrates how Pb concentrations and isotopic signatures in sediment archives reflect changes in both industrial activities, and trade relations throughout history.

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PREFACE

I dedicate this work to Boots, my study buddy.

1.0 INTRODUCTION

The Iberian Peninsula is rich in mineral resources and both archaeological and geochemical evidence of intensive mining activities date as far back as the Late Bronze Age (~3000 years BP) (Garcia-Alix et al., 2013). The largest ore deposits in this region are lead-rich massive sulfide deposits which are found along the southeastern, southwestern, northwestern and northern perimeter of the peninsula (Figure 1). Many of these deposits have been repeatedly exploited for hundreds, sometimes thousands of years and have resulted in the widespread accumulation of metal pollution in sediment archives. Laguna Roya is a high-altitude glacial lake (1608 m above sea level (asl)) located in the remote Sierra Segundera of Northwestern Spain (Figure 1). This is an ideal setting to investigate the history of atmospheric lead pollution, as there has been minimal human impact to the region and having a small catchment, Laguna Roya is isolated from any surficial anthropogenic contaminants (Hillman et al., 2017). The objective of this study is to reconstruct the regional lead accumulation history and, using lead isotopes, identify the sources of anthropogenic atmospheric lead pollution in an age-dated sediment core from Laguna Roya.

Lead (Pb), being one of the most widely used metals in human history, is a very useful geochemical tracer. It has four stable isotopes that exhibit highly varied abundances in geogenic materials: ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. Because of the small relative mass differences between these isotopes, they do not fractionate while undergoing physiochemical changes. Hence, lead deposits maintain the isotopic fingerprint of their original source (Miller et al., 2015). Furthermore, lead is relatively immobile once deposited and adsorbed to sediments and organic materials and this allows for accurate dating of depositional events within sediment archives (Gallon et al., 2004). Finally, in the past decades, analytical methods and technologies have improved enabling lead isotopes to be measured with high precision and accuracy (Miller et al., 2015). Thus, source apportionment of atmospheric Pb pollution can be estimated using ratios of lead's four stable isotopes ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208} Pb and isotopic fingerprinting techniques. This information can then be used, in combination with historical and archeological evidence, to reconstruct the mining and metallurgic history of a region.

1.1 A BRIEF HISTORY OF ENVIRONMENTAL LEAD POLLUTION

Most natural atmospheric lead comes from weathered and eroded crustal material but volcanic emissions, forest fires and sea spray can also play important roles (Klaminder et al., 2003). The global average deposition rate of lead from natural sources is estimated to be 0.6 ng/m^3 (Patterson, 1965). Archaeological evidence suggests that lead came into common use by the Early Bronze Age in the Near East and the Mediterranean, with Greece becoming a major center of production by the Late Bronze Age (Nriagu, 1983). Lead was one of the first metals to be used by ancient peoples, likely because it is malleable and ductile at room temperature, so it can be shaped using simple tools. Additionally, lead has a melting point of only 327ºC and therefore it is easy to smelt and cast without special furnaces or copious amounts of fuel. Thus, lead was used for many purposes throughout history. However, it was likely the processes involving intensive heating that contributed the largest quantities of lead emissions resulting in the widespread lead deposition found in natural archives.

Lead is not typically found in its native form and therefore it is believed that galena (PbS), which typically comprises approximately 86% lead, was the first and most common mineral smelted (Nriagu, 1983). It is thought that the first smelting methods were very crude, consisting basically of heating galena in a fire until the sulfur was burned off and the lead melted (Nriagu, 1983). Eventually, a metallurgic process that was used primarily to extract silver from argentiferous galena was developed (Nriagu, 1983). The extraction process known as cupellation, was developed as early as 4,000 B.C. in the regions of Anatolia and Persia (Nriagu, 1983). On the Iberian Peninsula, however, archaeological evidence of the widespread use of cupellation does not appear until the Phoenician occupation during the first millennium B.C. (Bartelhiem et al., 2012). Cupellation used molten lead to extract silver and sometimes gold from oxidizable ores using a carbonate cupel. The ore is heated along with lead to ~900ºC under oxidizing conditions so that the lead and any other base metal is oxidized (Nriagu, 1983). The oxidized metals are absorbed by the carbonate cupel, and the noble metals, including silver and gold separate from the lead and form a bead in the cupel. The basic principles of this method were used throughout the world and remained virtually unchanged until the beginning of the 19th century (Nriagu, 1983). The use of lead in the extraction of silver from ores is believed to be the primary source of anthropogenic lead emissions throughout history until the industrial revolution when lead began to be processed and used extensively for various industrial purposes (Settle and Patterson, 1980).

Dr. Clair C. Patterson (1922-1995) and colleagues are credited as being the first geochemists to recognize lead as a globally pervasive pollutant (Bindler, 2011). Through studies intended to quantify the global extent of lead pollution, Patterson and colleagues developed the main premises for the use of lead isotopes in tracing pollution in the environment (Bindler, 2011). They also put forth the understanding that lead and other metals persist for millennia and can travel long distances from their source through both the atmosphere and hydrosphere (Bindler, 2011). Lead aerosols from smelting and processing of lead-rich ore deposits are transported in the atmosphere far afield and can be detected in sediment archives by an increase in lead concentrations and deposition rates in addition to excursions to less radiogenic lead isotope values (Bindler, 2011).

Lead isotope studies of sediment archives relevant to this study including lake, peat, and marine cores from many regions throughout Europe, in addition to ice cores from Greenland, indicate three major lead pollution events (Bindler, 2011; Rosman et al., 1997; Hong et al., 1994; Zheng et al., 2007). The first major lead pollution event found in sediment archives occurs, at its peak, approximately 2000 years ago and is attributed to the extensive mining activities that occurred throughout the Roman Empire. Ore bodies from the Iberian Peninsula, were determined to be a dominant source of these lead deposits (Bindler, 2011). Lead was utilized on a large scale starting during the Roman era for both industrial and household applications (Nriagu, 1983). Lead was often alloyed with bronze or pewter and was used to make everything from sheathing for boat hulls, roofing, flashing, plumbing pipes, coins and ammunition (Nriagu, 1983). It was also used to make domestic items including kitchenware, dinnerware, utensils, jewelry, decorative and religious items. Hence, from the Roman period forward, lead was mined and traded as a commodity, and as such, transported from the various lead producing regions throughout the globe (Nriagu, 1983).

It is believed that global lead production at the height of the Roman Empire, was approximately 70 million kilograms per year (Settle and Patterson, 1980). After the fall of Rome there is little evidence for extensive, large scale mining operations involving lead until the Middle Ages c. AD 1000, when large silver mining operations were developed in the Harz region of Germany in addition to other sites throughout northern Europe (Bindler, 2011). This event is less prevalent in the sediment record compared to the lead pollution produced by Roman activities, but it is prominent in archives close to the mining sites in Northern Europe.

The primary source of atmospheric lead pollution prior to the late 19th century was from mining and metallurgical activities. After the onset of the Industrial Revolution, coal combustion became another significant source of atmospheric lead (Graney et al., 1995; Nriagu, 1983). The third, and most intensive lead pollution event in history however, began after the 1940s when the use of alkyl-lead additives in gasoline became standard the world over (Pacyna and Pacyna, 2000). This was truly a global pollution event, where increased deposition rates and concentrations of anthropogenic lead can be found even in the most remote locations. It was estimated in the late 1960s, that the global annual production of lead was about 270 million kilograms (Settle and Patterson, 1980). By the 1970s, the toxicity of these organolead compounds became well-known and leaded gasoline started to be phased out. Except for in a few countries, and for uses in limited applications, lead additives are no longer used in gasoline. Nevertheless, unleaded gasoline still contains around 10 to 15 mg Pb/liter as it is found naturally present in crude oil (Pacyna and Pacyna, 2000).

Presently, anthropogenic Pb emissions are about ten times greater than natural inputs, which is more than any other trace metal (Pacyna and Pacyna, 2000). Today, the most important sources of Pb emissions in the European Union (EU) are fossil fuel combustion, non-ferrous metal manufacturing, iron and steel production, waste disposal, and cement production (Pacyna and Pacyna, 2000). The primary advantage of using lead isotopes to investigate lead pollution history is in the ability to use source attribution methods to identify the anthropogenic lead emission sources and deposition history. This provides information regarding past lead emission sources that might otherwise be undocumented in addition to contributing to further understanding regarding the transport, pervasiveness and persistence of lead pollution.

1.2 LEAD ISOTOPE GEOCHEMISTRY

The four stable naturally-occurring isotopes of lead, along with their average crustal abundances are: ^{204}Pb (1.4%), ^{206}Pb (24.1%), ^{207}Pb (22.1%) and ^{208}Pb (52.4%). ^{204}Pb is primordial, so its abundance does not change through time. The radiogenic isotopes, ^{206}Pb, ^{207}Pb and ^{208}Pb are the end products of complex decay series that begin with ^{238}U (t½ = 4.47 x 109 years), ^{235}U (t½ = 7.04 x 108 years) and ^{232}Th (t½ = 1.4 x 1010 years) respectively. The Pb isotopic composition of a geogenic material therefore, depends on the initial composition of uranium and thorium in the source materials, in addition to the rate of the three independent decay chains and different geochemical behaviors of the parent elements. It follows that the isotopic signature of natural materials is the result of the elemental and isotopic composition of the source material at the time when the Pb was incorporated into host materials. The four stable isotopes of lead can be used as a powerful geochemical tracer because different lead-containing ore and mineral deposits, and the anthropogenic materials derived from them, have distinct isotope ratios or signatures. Also, the derived materials tend to have less radiogenic Pb isotopic signatures than crustal rocks or sediments (Bindler, 2011). This is because many ores and minerals exclude Th and U parent isotopes at the time of formation, and therefore the composition of the Pb that is incorporated into the material remains unchanged over time, whereas the lead in other crustal materials continue to evolve as the Th and U parent isotopes continue to decay (Komárek et al. 2007). Additionally, because lead is a heavy element, it has small relative mass differences between its isotopes and therefore they are not typically subject to mass dependent fractionation during physical and metallurgic processing, combustion or deposition (Komárek et al. 2007). Finally, recent analytical developments and defining of methods for the use of MC-ICP-MS have enabled rapid measurements of lead isotopes with a high degree of precision and accuracy further aiding in identification of sources, especially in cases when there are sources with similar isotopic signatures (Miller, et al., 2015).

Lead isotopic compositions are most often expressed as ratios and for natural materials the values typically range between 14.0-30.0 for ^{206}Pb/^{204}Pb, 15.0-17.0 for ^{207}Pb/^{204}Pb and 35.0-50.0 for ^{208}Pb/^{204}Pb (Doe, 1970). Normalization of the Pb isotope ratios using ^{204}Pb is used in this study because it enhances the variability in isotopic signatures caused by differences in the thorogenic and uranogenic parent isotope compositions of the original source material from which the ores formed (Komárek et al., 2008). Also, the ^{206}Pb/^{207}Pb ratio is plotted alongside the total leached, dry weight lead concentration [Pb] in this study because this is a well-established convention and the results can easily be compared to similar studies (Bindler, 2011). Lead ores, surface soils, and peat have ^{206}Pb/^{207}Pb ranges from 1.14–1.18 whereas parent material and older soils typically have ranges from ^{206}Pb/^{207}Pb= 1.3 to more than 2.0 (Bindler, 2011). Thus, the ^{206}Pb/^{207}Pb ratio is typically used to distinguish anthropogenic lead sources from natural sources.

1.3 SOURCE ATTRIBUTION USING LEAD ISOTOPES

A common method using isotopes to identify potential atmospheric lead endmembers requires that the natural background, or pre-pollution concentration and isotopic composition is determined. In the case of sediment cores, this is typically done by measuring the concentrations and isotope composition of sediment layers from pre-pollution times. Secondly, the anthropogenic source end member must have a homogeneous isotopic signature so that it might be identified (Stos-Gale and Gale, 2009). A variety of mixing equations that account for both the concentration and isotope ratios of the endmembers, have been derived. The following binary mixing equation effectively subtracts the background contribution from the measured sample to determine the isotope ratio of the anthropogenic lead source:

$$^{20x}Pb/^{20y}Pb_{anth} = (^{20x}Pb/^{20y}Pb_{s} * [Pb]_{s} - {}^{20x}Pb/^{20y}Pb_{B} * [Pb]_{B}) / ([Pb]_{s} - [Pb]_{B})$$

Where $^{20x}Pb/^{20y}Pb_{anth}$ is the isotope ratio of the anthropogenic source (any Pb isotope ratio can be substituted in this equation), $^{20x}Pb/^{20y}Pb_{s}$ is the measured isotope fraction of the sample and $^{20x}Pb/^{20y}Pb_{B}$ is the average background isotopic signature determined by measuring a sample from a sediment layer that dates to before the occurrence of anthropogenic lead pollution. $[Pb]_{s}$ is the leached lead concentration of the sample. $[Pb]_{B}$ is the leached concentration of the background, pre-pollution sample.

Another method to determine the isotopic ratio of the anthropogenic composition of lead in sediments is to use the relationship between concentration and isotopic composition. If the isotopic signatures of the sediment samples are the result of a binary mixture (consisting of a single anthropogenic source and the background composition), then the plot of $^{20x}Pb/^{20y}Pb$ vs.

$[Pb]^{-1}$ will plot as a straight-line (Faure, 1986; Hansmann and Köppel, 2000; Monna et al., 2000). The intercept at the y-axis then, represents the isotopic ratio of the contaminant source (Faure, 1986; Monna et al., 2000; Hansmann and Koppel, 2000; Gale and Stos-Gale, 1992). Hence, for environmental samples with isotopic compositions that approximate a normal distribution, the isotopic signature of an anthropogenic endmember can be approximated using a linear regression analysis by extrapolating a straight line from the Average Background end member through to the y-axis to determine the y-intercept (Faure, 1986; Hansmann and Köppel, 2000; Monna et al., 2000).

In the case of lake sediments and other environmental samples, there are likely multiple endmembers that contribute to the overall lead composition. The objective in this case, is to determine the primary end member. Hence, an ideal method of analysis will smooth out the variability in the data and identify the dominant trend. In this study, the anthropogenic end member is uncertain; however, there is likely a dominant pollution source that can be identified from a finite number of possibilities. Therefore, a linear regression statistical model that assumes a normal distribution of the data will be used to define a straight line between the endmembers.

2.0 THE GEOLOGY, MINING, AND MANUFACTURING HISTORY OF THE PRIMARY LEAD EMISSION SOURCES

2.1 INTRODUCTION

Archaeological studies have determined that lead-rich ore deposits around the coastal regions of southern Iberia have been mined for various minerals over 5000 years (Tornos et al., 2009). Throughout the rest of the peninsula, evidence of ancient mining operations dating at least as far back as the Roman occupation is commonly found. However, it is difficult to reconstruct the history of mining and metallurgy using only archaeological evidence because it was often destroyed by subsequent mining operations. Hence, geochemical analysis of local sediment records can be a valuable source of information. A brief overview of the Iberian peninsula's primary mining regions, including their mining history and the published Pb isotope values of ores (typically galena) from these regions, is given here as this background information is necessary for the interpretation of the Pb isotope profile of the Laguna Roya sediment core (Table 1. and Figure 1.).

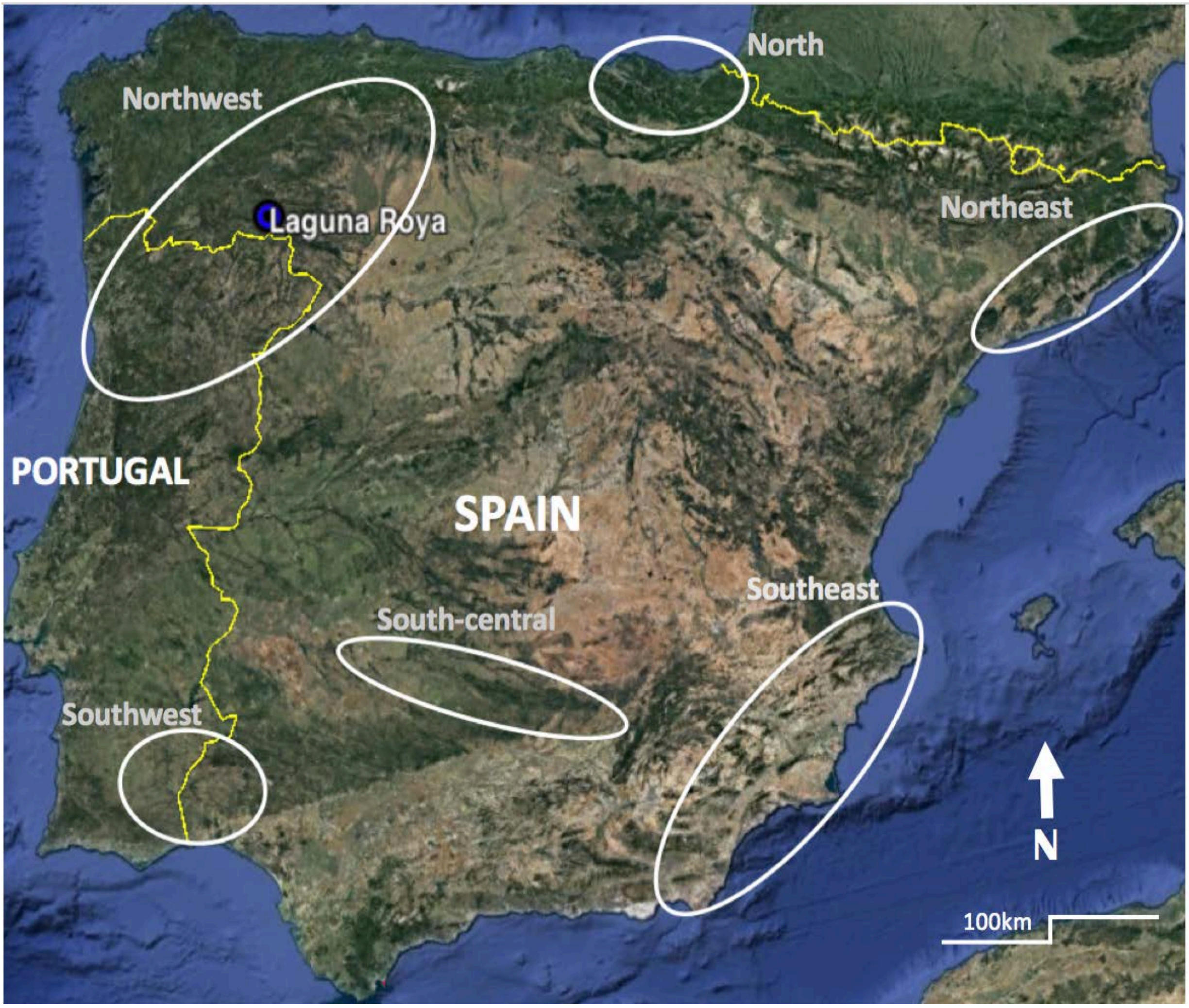


Figure 1. Map of Laguna Roya and the primary Iberian mining regions.

Most of the large-scale mining operations throughout the Iberian Peninsula are associated with massive hydrothermal sulfide deposits, such as the Iberian Pyrite Belt (IPB) in southwest Spain and southeastern Portugal, the Los Pedroches Batholith-Alcudia Valley in south-central Spain, the Basque-Cantabrian Basin in the north, and the Betic Cordillera in the southeast (Figure 1). Although these deposits are hundreds of kilometers from Laguna Roya, the intense heating (> 900 ºC) of large quantities of lead during smelting and cupellation processes would have volatilized large quantities of lead into the atmosphere. Having a residence time of roughly 7 days, lead particulates can be carried hundreds and even thousands of kilometers from their source (Pacyna, 1987). Hence, these sites are all considered possible sources of anthropogenic lead in the Laguna Roya sediments.

In the northwest of the peninsula, there are a variety of lead-bearing ore deposits that could potentially have been sources of atmospheric lead deposited into Laguna Roya sediments due to the proximity of mining operations to the lake. The northwest of the Iberian Peninsula is both geologically and historically complex. It includes both highly metamorphosed allochthonous and ophiolitic terrane and spans the Asturias gold mining region, Galicia-Tras-Os-Montes and the northern-western coast of the Central Iberian Zone (CIZ) (Spiering et al., 2000; Neiva et al., 2008). Laguna Roya is located at the border between the autonomous communities of Galicia and Castilla y Léon Spain and the district of Bragança, Portugal. This region shared a very different history than the south of the peninsula. Due to its remote location, it was not occupied by many of the invaders from the south including the Phoenicians, Carthaginians, Greeks and the Moors. The Romans only succeeded in conquering the north and northwestern regions of the peninsula after 19 BC, almost 200 years after their first invasion of a Carthaginian settlement in modern day Catalonia. It is well known that the northwest is rich in ruins of Roman-era mines but for the most part the mining and metallurgic history of this region is severely understudied.

The mining districts of Catalonian Coastal Ranges (CCR) of northeastern Spain is the final region included in this study. The Pb-rich ores in this area are found primarily in low-temperature hydrothermal vein deposits (Canals and Cardellach, 1997). The oldest evidence of metallurgic production in this region has been found in Phoenician archaeological sites dating back to the 8th century B.C. (Renzi et al., 2009). However, there are few published studies of the historical and archeological record of mining in this region. The primary importance of the Pb ores from this region lies with the fact that archeological studies have determined that the Phoenicians established sophisticated trade and production networks that transported lead from the CCR and the Betic Cordillera to mines in the IPB (Anguilano et al., 2010; Murillo-Barroso et al., 2016). Evidence suggests that this practice persisted, at least intermittently, until after the fall of Rome (Anguilano et al., 2010; Murillo-Barroso et al., 2016). Thus, it is important to consider that Laguna Roya sediments likely contain a mixture of Pb from different ore deposits both because they were transported in the atmosphere from different regions, and because Pb from different deposits was mixed on site during various metallurgic processes.

Isotopic provenancing of atmospheric lead pollution sources from the 20th century is more challenging due to both the global distribution and introduction of new lead-based products (Bindler, 2011). Additionally, coal, gasoline and other products containing lead typically have heterogeneous Pb isotope signatures. The northwest of Spain did not see industrialization until the mid 20th century (Álvarez-Iglesias et la., 2012). For example, coal did not appear as significant pollutant in the sediment record until c. 1930 (Álvarez-Iglesias et la., 2012). Leaded gasoline becomes a primary contributor of lead emissions after 1960. Because this intense pollution event has been relatively well documented and is characterized by uniquely low isotope values, this study will focus on source apportionment of this modern pollutant in the Laguna Roya sediment record (Bindler, 2011; Pacyna and Pacyna, 2000).

2.2 THE IBERIAN PYRITE BELT (IPB), SOUTHWESTERN SPAIN AND SOUTHEASTERN PORTUGAL

The IPB comprises the western part of the Sierra Morena in southwestern Spain and extends into southeastern Portugal (Figure 2). The IPB is one of the most remarkable ore provinces as it contains the largest known concentration of sulfides in the world (Tornos et al., 2009). It formed about 300 Ma during a period of intense submarine volcanism that precipitated hydrothermal fluids over a region that extends 250 km long and 30 km wide (Boulter, 1993; Van Geen et al., 1997). The Pb isotope values of galena samples sourced from throughout the IPB are relatively homogeneous (Table 1). However, the primary mineral that was mined in the IPB by the Phoenicians and Romans was argentiferous jarosite that often did not contain sufficient lead for the cupellation process used to recover the silver from the mineral (Anguilano et al., 2010; Murillo-Barroso et al., 2016). Therefore, according to archaeological evidence and lead isotope studies, lead was imported from the mining regions in the Betic Cordillera, the Catalonian Coastal Ranges and Linares-La Carolina district (Anguilano et al., 2010; Murillo-Barroso et al., 2016). This means that the isotopic signature of the lead pollution from the mining of silver in the IPB can reflect a mixture of the lead from both the local ores in addition to the lead imported and used in cupellation for extracting silver.

Mining in the IPB dates back as far as the third millennium B.C. The larger mines include Rio Tinto, Corta Largo, Tharsis, and Neves Corvo, that were worked primarily for copper, silver, gold and most recently for sulfur (Tornos et al., 2009; Morral, 1990; Van Geen et al., 1997). By the end of the Third Punic War in 146 B.C., when Carthage fell to the Romans, about 5 Mt of pyrite had been mined from the Rio Tinto (Pinedo, 1963; Van Geen et al., 1997).

After this region was conquered by Rome, mining in the Iberian pyrite belt for copper and silver continued at a large scale. Slag deposits indicate that about 25 Mt of sulfide ore was mined from the region through to the 4th century A.D. (Strauss et al., 1977; Van Geen et al., 1997). It is believed that most mining operations were abandoned after the fall of Rome, and large-scale mining in these regions did not reoccur until the mid-19th century when the deposits were mined for copper and sulfur. From the mid-19th century through the late 1970s, c. 250 Mt of sulfide ore was extracted from the IPB (Strauss et al., 1977). Small-scale mining operations continue in the IPB today (Tornos et al., 2009).

2.3 THE LOS PEDROCHES BATHOLITH - ALCUDIA VALLEY REGION, SOUTH-CENTRAL SPAIN

The mining sites in the Los Pedroches, Alcudia Valley, and Linares- La Carolina regions are associated primarily with the Los Pedroches Hercynian Batholith located in the eastern Sierra Morena, in south-central Spain (Figure 1; Santos Zaldegui et al., 2004). The batholith formed during the Hercynian orogeny c. 300 million years ago. This region, extends over 10,000 km^2 and is characterized by predominantly Pb-Zn bearing minerals that have likely been exploited since the Bronze Age. It was actively worked during Roman times, and there is evidence that smaller scale mining operations continued throughout the middle ages. Between the mid-19th century and the early 20th century, this region was one of the primary lead producers in the world (Santos Zaldegui et al., 2004). In the Alcudia Valley between 1866 and 1910, it is estimated that more than 30,000 t/yr of Pb ore was extracted, and at the turn of the 20th century, more than 40,000 t/yr was extracted from the Linares-La Carolina area (González Llana 1949; Santos

Zaldegui et al., 2004) Presently all mines in this region are inactive, the last mine closed in 1988 (Santos Zaldegui et al., 2004; Palero et al., 2003). The isotopic signatures of the ores group into four distinct fields (Table 1 and Figure 2). The Linares-La Carolina isotope field overlaps with the IPB isotope field and therefore specimens and deposits that have isotopic signatures in this range cannot be sourced to one or the other of these ore bodies through lead isotope studies alone.

2.4 THE BASQUE-CANTABRIAN BASIN, NORTHERN SPAIN

In northern Spain Zn-Pb deposits are associated with the Cinco Villas Massif, the Sierra Demanda and the Asturian Massif which are located along the margins of the Western Pyrenees and the Basque-Cantabrian basin (Figure 1; Águeda Villar and Salvador González, 2009). The Basque-Cantabrian Basin was formed by a rifting event that occurred during the Triassic, and resulted in the formation of the Bay of Biscay. As the extension progressed, hyrdorthermal fluids mobilized and infused and metasomatized overlying carbonates (Águeda Villar and Salvador González, 2009). The Zn-Pb and Fe mineralizations that occurred in the Basque-Cantabrian Basin, occurred with varied typology and include vein-like replacements, strata-bound, diapir, Mississippi Valley type and sedimentary exhalative (sedex) deposits (Águeda Villar and Salvador González, 2009). A lead isotope study of the massive sulfide deposits has determined that each of the three deposits define three relatively homogenous isotope fields (Table 1; Velasco et al., 1995).

There is evidence of Roman mining in this area but, there is no archaeological record of there being significant mining activity prior to, or after, the Roman occupation of the region

(Águeda Villar and Salvador González, 2009). The mineral deposits in this area were intensely mined from the 19th century to the mid-20th (Águeda Villar and Salvador González, 2009). For example, 4 million tons of Zn and 1 million tons of lead were extracted from the Reocín mining site since the mid 19th century to the present day (Águeda Villar and Salvador González, 2009). Hence, much of the archaeological record throughout the region was destroyed by recent mining activities.

2.5 SOUTHEASTERN IBERIAN PENINSULA

The Betic Cordillera is an orogenic fold belt that spans the southern coast of Spain (Figure 1). It formed during the collision between the African and Iberian plates from the late Mesozoic to the middle Cenozoic (Arribas and Tosdal, 1994). During the Miocene, the region experienced a period of crustal extension forming the Almeria- Cartagena Volcanic Belt (Arribas and Tosdal, 1994). Crustal thinning and volcanic activity resulted in the deposition of vast amounts of hydrothermal minerals (Arribas and Tosdal, 1994). The polymetallic deposits have a variety of mineralization typologies including strata-bound, vein and manto-type carbonate-hosted ores or, volcanic-hosted epithermal ores (Arribas and Tosdal, 1994). The NE-SW trending Au, Ag, Pb-Zn-Ag, Sn, Mn and Sb mineral rich volcanic belt extends over 150 x 25km (Gibbons and Moreno, 2012). The lead isotope studies conducted on the ores from the Betic Cordillera define four distinct isotope fields, however a comprehensive study relating geological units to all the isotope fields has yet to be undertaken (Table 1 and Figure 2).

This region has been extensively mined and occupied for millennia likely because the proximity of the mines to the Mediterranean Sea facilitated transport and trade (Trincherini, 2009). The lead-silver mines of Cartagena for example, were exploited by the Greeks and Carthaginians as early as the 500 BC, and in the 2nd and 1st c. B.C. by the Romans (Trincherini, 2009). It is believed that after the Roman era, there was only small-scale mining activity until the 19th century when intensive mining activities resumed (Conesa et al., 2007). In the 20th century, between 1940 and 1990 one third of the total reserves were extracted from the Almeria-Cartagena Volcanic Belt, an amount equivalent to the total ore extracted in the entire history of mining in the region (Conesa et al., 2007).

2.6 NORTHWESTERN IBERIAN PENINSULA

Laguna Roya is located in the northwest of the peninsula (Figure 1.). Hence, small-scale local metallurgic and mining activities that are not necessarily associated with Pb-rich ores are also considered as potential sources of lead emissions in this study. The oldest archeological evidence of gold mining in the northwest of the peninsula dates back about 4000 years, but iron working is not prevalent until after 500 BC (Sastre and Sánchez-Palencia, 2013). For the next few hundred years, the metal working skill becomes increasingly sophisticated including the development of the technology for smelting of bronzes, and the extraction of silver using cupellation. Nonetheless, the scale of such activities remained at a household, artisanal level until the Roman annexed the region in 19 BC (Sastre and Sánchez-Palencia, 2013; Reher et al., 2015). Thus, it is not expected that there will be significant local source of lead aerosols until after the Romans began industrial-scale mining operations in the region. Unfortunately, the mining history of the northwestern extent of the Iberian Peninsula, which includes the region of Galicia, and Asturia in Spain and northern Portugal is severely under-studied considering its richness in mineral resources and ancient mining sites. The following is an overview of information from the most recent studies, including a brief discussion of the published isotope data of the various ore deposits throughout this region (Table 1 and Figure 2).

Laguna Roya is situated in the Central Iberian Zone, a narrow anticlinorium that runs roughly north to south and is 10-65km in width. It separates the Galicia-Tras-Os- Montes, which extends westward to the coast and the Western Asturian and Cantabrian zones to the east (Neiva et al., 2008). These regions are known for their gold deposits that were extensively exploited by the Romans. So much so, that the landscape in some regions was completely transformed by their mining operations. The Las Médulas mine for instance, is located c. 35km north of Laguna Roya. It is believed to be the largest Roman gold mine and was exploited from the beginning of the 1st century AD to the about end of the 2nd century AD (Hillman et al. 2017; Perez-Garcia et al., 2000). The gold at Las Médulas was primarily from placer deposits that were mined using a technique called *ruinus montum*. This had a profound effect on the landscape such that 600 million cubic meters of earth were moved and hundreds of kilometers of canals were built (Perez-Garcia et al., 2000; Sánchez-Palencia and Suárez, 1985).

Another gold source exploited in this region were lode deposits including gold-bearing, arseno-pyrite quartz veins (Gomez-Fernandez et al., 2012; Hillman, 2017). The technique of fire-setting was used to extract gold from these deposits, where fires were burned against a rock face and rapidly quenched, causing the rock to shatter (Weisgerber and Willies, 2000; Pliny et al., 1855; Hillman et al., 2017). In both cases, lead from mining dust, or lead volatiles released from heating ore veins and country rock may have been sources of anthropogenic lead deposited in Laguna Roya. After the fall of Rome, it is uncertain what happened with the gold mining activities in the northwest. There is no strong evidence suggesting that this region was intensively mined again until the 19th century when modest mining activities resumed, focusing on gold-bearing arsenopyrite quartz until the early 20th century (Spiering et al., 2000).

The Galicia Tras-Os-Montes complex formed as the result of a collision between Gondwana and Laurentia and consists of allochthonous and ophiolitic terranes that include gold and polymetallic mineral deposits (Neiva et al., 2008). In the region now known as Bragança, Portugal there are Roman mines that are roughly 30 km to the southwest of Laguna Roya. Also, the scale and nature of mining activities in this region has yet to be thoroughly studied and therefore it is difficult to anticipate whether the mining activities in these regions were a significant source of lead pollution. Furthermore, this region is geologically very complex containing highly metamorphosed rocks and accreted terranes and therefore homogenous isotope fields may be difficult to define.

Lead sulfide deposits in the northwest are primarily found in the Aveiro district of Portugal. This formation was deposited by hydrothermal activity that occurred in association with a period of continental extension that formed submarine extensional basins along the northwestern margins of the Iberian Peninsula during the Mesozoic (Pais et al., 2012; Marques de Sá and Gomes, 2010). The Aveiro mining district is located about 200 km from Laguna Roya between the Douro and Vouga rivers. It is one of the largest deposits in the region being about 40 km long by 10 to 20 km wide (Braz Martins, 2010). Many mining sites are found in this region, including Malhada and Braçal which are known to have been important Roman lead mines (Braz Martins, 2010). The earliest registered mining concession in Portugal was granted for mining lead in Braçal in 1836. Braçal and Malhada mines were the sole lead mines in Portugal until around the turn of the century.

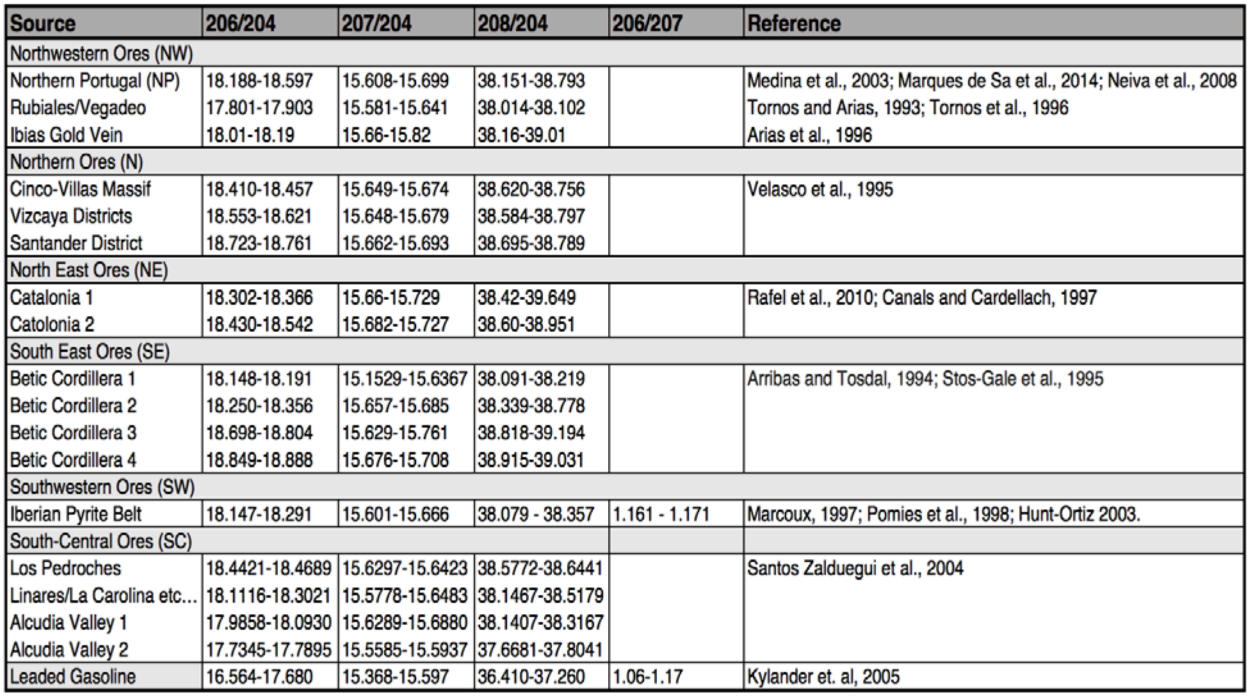
Like in Spain, Portugal saw an increase of mining activity from the mid-19th century to the mid-20th century (Marques de Sá and Gomes, 2010; Borg, F. and Hedlund, M., 2001; Braz Martins, 2010). The Aveiro region was most intensively mined at the beginning of the 20th century for minerals including antimony, lead, copper, iron, manganese and arsenopyrites (Braz Martins, 2010). The Aveiro mines processed an annual average of 900,000 tons of minerals between 1913-1915, c. 350,000 tons from 1944-1950 and c. 1,700,000 tons from 1950-1958 (Braz Martins, 2010). Production slowed after this time and the mines closed in 1972. Two additional lead mining regions are the Vagadeo and Rubiales formations located in the Western Asturian-Leonese Zone, both within ~75km of Laguna Roya. These deposits were mined intensively only during the latter half of the 20th century (Tornos and Arias, 1993; Tornos et al., 1996).

There is yet to be sufficient published lead isotope data of ore deposits in the northwestern Iberian Peninsula to establish well-defined isotope fields. The only published lead isotope study associated directly with a gold deposit in this region, is of the Ibias gold vein system (Table 1 and Figure 2, Arias et al., 1996). Hence, it is not possible to thoroughly evaluate the relationship of lead deposited in Laguna Roya sediments to gold mining activities. There are only a few isotope values measured at many of these sites and comprehensive lead isotope studies that document the stratigraphic units and exact location of the samples have yet to be undertaken. Nonetheless, the available data will be used to assess the possibility of a measurable contribution of lead emissions from regional mining operations to Laguna Roya.

2.7 CATALONIAN COASTAL RANGES (CCR)

The lead sulfide deposits in this region are associated with low temperature hydrothermal vein mineralizations that occurred in the fractures of basement and overlying rock (Canals and Cardellach, 1997). The veins are generally rich in fluorite, barite and sulfide metals and the variation in their compositions are closely related to the different strata they cut through. This region has been intensively mined throughout history, and for this reason there are significant gaps in the archaeological record as the evidence of prior mining activities is often destroyed. It is believed that this region was mined specifically for lead starting around the middle of the 7th century, and there is evidence that mining activities continued episodically through to the mid-20th century. Studies of metal artifacts have shown that trade in metals between the CCR, the

Table 1. Lead isotope ratio ranges of possible sources of atmospheric Pb emissions deposited in Laguna Roya.



Source	206/204	207/204	208/204	206/207	Reference
Northwestern Ores (NW)					
Northern Portugal (NP)	18.188-18.597	15.608-15.699	38.151-38.793		Medina et al., 2003; Marques de Sa et al., 2014; Neiva et al., 2008
Rubiales/Vegadeo	17.801-17.903	15.581-15.641	38.014-38.102		Tornos and Arias, 1993; Tornos et al., 1996
Ibias Gold Vein	18.01-18.19	15.66-15.82	38.16-39.01		Arias et al., 1996
Northern Ores (N)					
Cinco-Villas Massif	18.410-18.457	15.649-15.674	38.620-38.756		Velasco et al., 1995
Vizcaya Districts	18.553-18.621	15.648-15.679	38.584-38.797		
Santander District	18.723-18.761	15.662-15.693	38.695-38.789		
North East Ores (NE)					
Catalonia 1	18.302-18.366	15.66-15.729	38.42-39.649		Rafel et al., 2010; Canals and Cardellach, 1997
Catolonia 2	18.430-18.542	15.682-15.727	38.60-38.951		
South East Ores (SE)					
Betic Cordillera 1	18.148-18.191	15.1529-15.6367	38.091-38.219		Arribas and Tosdal, 1994; Stos-Gale et al., 1995
Betic Cordillera 2	18.250-18.356	15.657-15.685	38.339-38.778		
Betic Cordillera 3	18.698-18.804	15.629-15.761	38.818-39.194		
Betic Cordillera 4	18.849-18.888	15.676-15.708	38.915-39.031		
Southwestern Ores (SW)					
Iberian Pyrite Belt	18.147-18.291	15.601-15.666	38.079 - 38.357	1.161 - 1.171	Marcoux, 1997; Pomies et al., 1998; Hunt-Ortiz 2003.
South-Central Ores (SC)					
Los Pedroches	18.4421-18.4689	15.6297-15.6423	38.5772-38.6441		Santos Zalduegui et al., 2004
Linares/La Carolina etc...	18.1116-18.3021	15.5778-15.6483	38.1467-38.5179		
Alcudia Valley 1	17.9858-18.0930	15.6289-15.6880	38.1407-38.3167		
Alcudia Valley 2	17.7345-17.7895	15.5585-15.5937	37.6681-37.8041		
Leaded Gasoline	16.564-17.680	15.368-15.597	36.410-37.260	1.06-1.17	Kylander et. al, 2005

Betic Cordillera and the IPB was occurring as early as the Phoenician times. In particular, lead isotope studies have shown that lead from the CCR and the Betic Cordillera imported to the IPB for use in the extraction of silver from jarosite (Murillo-Barroso et al., 2016). The few lead isotope studies of the ores from the CCR have defined two isotope fields characteristic of this region (Table 1. and Figure 2.)

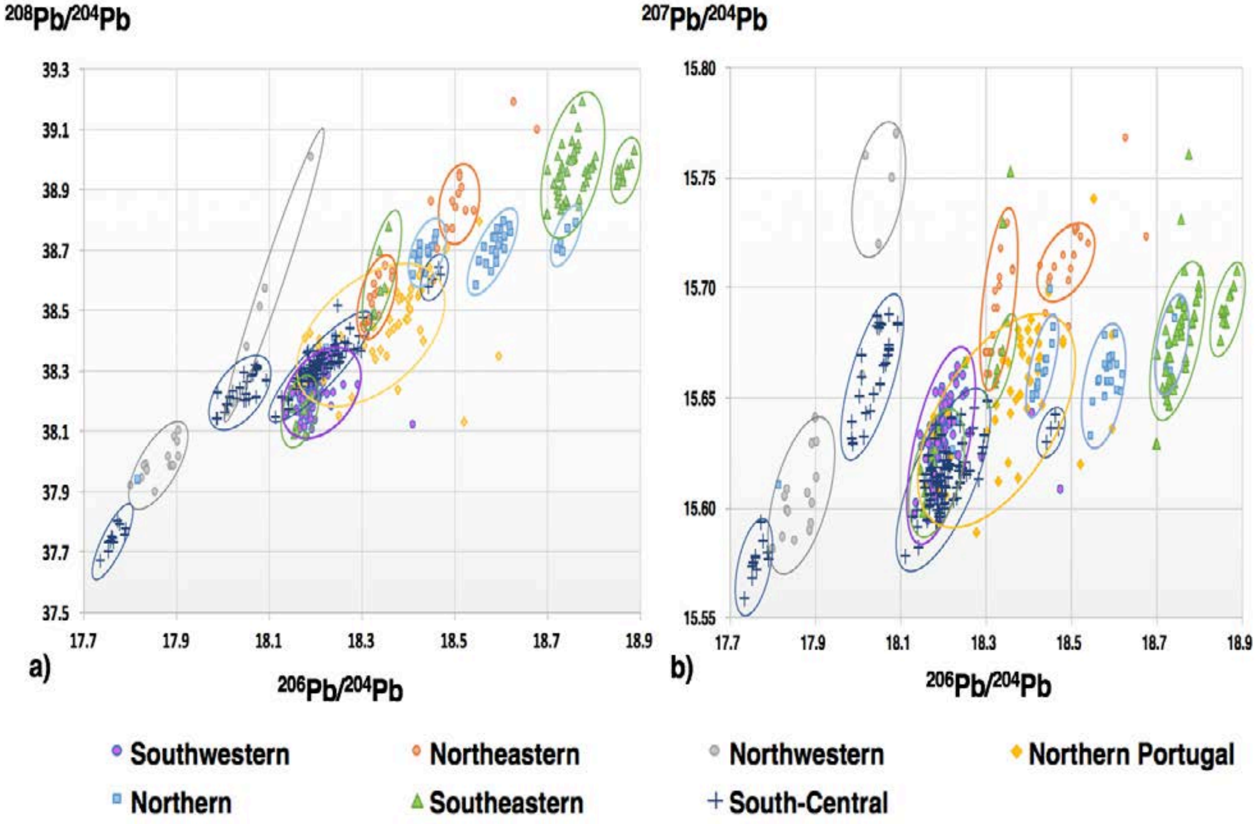


Figure 2. Isotope fields of ores from throughout the Iberian Peninsula.

2.8 TWENTIETH CENTURY LEAD POLLUTION SOURCES

During the early 20th century in Spain and Portugal many of the mining regions were being exploited at peak production (Conesa et al., 2007; Braz Martins, 2010; Águeda Villar and

Salvador González, 2009)). In the 1920s, it was found that adding alkyl lead to gasoline improved the performance of internal combustion engines by serving as an anti-knocking agent and octane enhancer. The lead to make these additives was sourced primarily from Broken Hill Mines in Australia and have characteristically low lead isotope ratio values $^{206/207}$Pb=f 1.04 (Bindler, 2011). Other sources of lead for gasoline additives came from ores deposits from throughout the globe, all with unique isotope signatures. In 1955 AD, non-ferrous metal manufacturing was the primary contributor of lead pollution in Spain, having emitted 733 tonnes, gasoline combustion contributed 583 tonnes of the total 1659.8 tonnes of Pb emitted that year (Figure 3; Pacyna and Pacyna, 2000). The dominant lead pollution source changed to leaded gasoline combustion after the 1960s, a period of economic prosperity in Spain, when both the auto and mining industry were thriving. Pacyna and Pacyna (2000) report an atmospheric lead pollution peak in 1975 AD, with a total of 6325.0 tonnes being released into the atmosphere. Gasoline combustion contributed 4724.0 tonnes, and non-ferrous metal manufacturing contributed 631.6 tonnes. After 1975, there is a significant decline in total atmospheric lead emissions. By 1995 AD the total atmospheric lead emissions had declined to 1826.0 tonnes with gasoline combustion contributing 900.0 tonnes, whereas non-ferrous mineral mining contributed 695.0 tonnes (Figure 3; Pacyna and Pacyna, 2000).

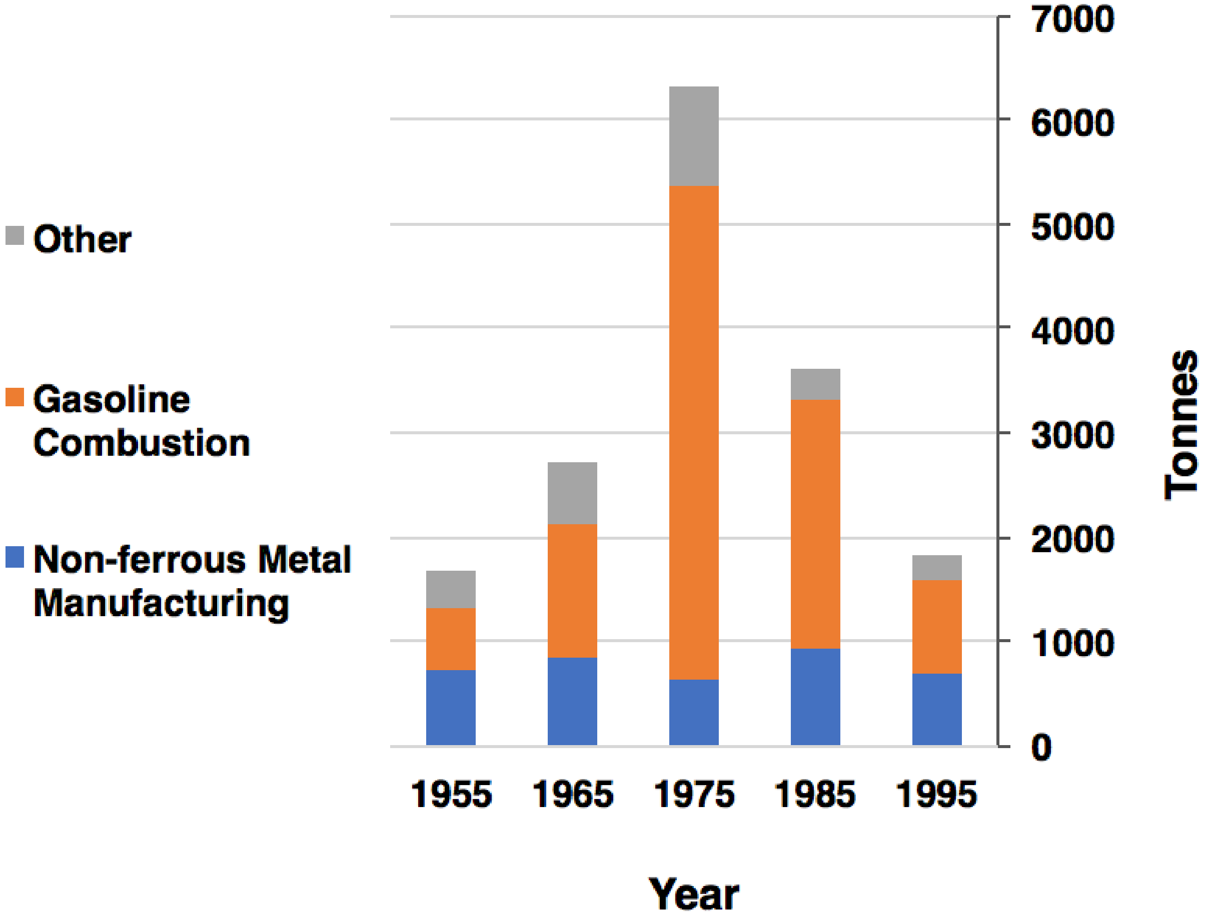


Figure 3. Primary atmospheric Pb emission sources in Spain between 1955-1995 (Pacyna and Pacyna, 2000).

3.0 METHODS

3.1 STUDY SITE

Laguna Roya (42° 8'8.42"N, 6°47'38.95"W, 1608m asl) is a small glacial lake situated on the plateau of the Sierra Segundera in the province of Zamora, Northwest Spain (Figure 1). This remote mountainous region is located within the Parque Natural Lago de Sanabria. The primary land use of this park has been the herding of sheep and cattle (Allen et al., 1996). This region marks the threshold between the Atlantic, Continental and Mediterranean climate zones (Muñoz Sobrino et al., 2013). The local climate is described as a cool temperate region, such that the lake freezes over in the winter and the summer water temperatures reach 20ºC (Allen et al., 1996 and Muñoz Sobrino et al., 2013). The closest local weather station, Presa Cárdena (c. 1600 m asl), reports temperatures ranging from -11 ºC to almost 30 ºC with the annual temperature average as c. 6 ºC (Muñoz Sobrino et al., 2013). Laguna Roya, having a small catchment area of c. 0.15 km^2, has a seasonally variable water level (Muñoz Sobrino et al., 2013). The surface area was measured on one occasion as c. 0.025 km^2 with its long axes being 296 m and 151 m (Allen et al., 1996). At the time the lake cores for this study were retrieved, the maximum water depth measured was 6.6 m at the approximate center of the lake (Hillman et al., 2017).

The lake basin and catchment are in the Ollo de Sapo formation, which consists of gneissic and granodiorite formations of Cambro-Ordivician age (492-486 Ma) (Jambrina-

Enríquez, 2014; Moreno, 2012). A water quality survey recorded a pH of 7.3, an alkalinity of 0.13 mEq/L and a conductivity of 19 µS/cm (Aldasoro et al., 1996). The lake basin was carved out by glaciers during the Pleistocene glaciation and the catchment area consists primarily of exposed bedrock with small depressions filled with acidic soil (Allen et al., 1996).

3.2 SEDIMENT CORE COLLECTION

The Laguna Roya sediment cores were collected over two days in June 2014 (Hillman et al., 2017). Using a light-weight percussion coring system, a 1.24-m surface core was collected from a water depth of 6.6 m with an intact sediment–water interface. Sample intervals of 0.5-cm were taken in the field from the upper 15 cm. Metal contamination was limited using plastic instruments and packaging. Ten overlapping drives were used to collect deeper sediments from the same location using a steel barrel Livingston corer. A composite record of 6.96 m was constructed by aligning drives using field notes, visible sedimentology, and geochemical profiles (Hillman et al., 2017).

3.3 GEOCHRONOLOGY OF LAKE SEDIMENT CORE

The age model for the Laguna Roya lake sediments is fully described by Hillman et al. (2017). A constant rate of supply (CRS), ^{210}Pb age model was used to date 11cm of the surface core (Appleby and Oldfield, 1983; Hillman et al., 2017). Radiocarbon dates were determined for sixteen wood, charcoal, and plant macrofossils samples that were first pretreated using a standard acid, alkali, acid procedure (Abbott and Stafford, 1996; Hillman et al., 2017). Radiocarbon was measured at the Keck Center for Accelerator Mass Spectrometry at the University of California Irvine, and calibrated using Calib 7.0 (Reimer et al., 2013; Hilllman et al., 2017). The age-depth model was then created by entering the calibrated dates into BACON code (Blaauw and Christen, 2011; Hillman et al., 2017).

3.4 LEAD CONCENTRATION ANALYSIS

Lead concentration and isotopic analysis were carried out at the Oregon State University (OSU) Keck Collaboratory, a Class 100 clean lab. Ultra-pure water ($\geq$18.2 MΩ cm), de-ionized and purified via reverse osmosis using a Milli-Q® system (Millipore, USA), was used to prepare all solutions and for all lab work. Prior to use, all labware was cleaned using successive washes with a ~2% Extran® 300 (EMD Millipore, USA) solution, analytical grade hydrochloric acid (HCl), and analytical grade nitric acid (HNO_3). HNO_3 and HCl reagents used in this study were purified in-house from concentrated reagent grade acid by sub-boiling acid distillation in a DST-1000 acid purification system (Savillex®, USA). Additionally, Optima™ grade Hydrobromic (HBr) acid from Fisher Scientific (USA) was another reagent used.

A dilute acid leach procedure was used to extract trace metals adsorbed onto particle surfaces (Graney et al., 1995). Dried sediment samples (~10mg) were weighed into clean 1.5 mL polypropylene centrifuge tubes and 1 mL of 1M HNO_3 was added. Samples were agitated for 12-24 hrs on a shaker table or tube rotator. Leachates were separated from sediment by centrifugation (13,000 rpm, 10 min) and the supernatant was transferred into a 5ml Savillex® vial. Samples were dried down on hot plates. 5ml of 1% HNO_3 was added to Savillex® and samples were refluxed on hot plate at 90ºC for 1 hr. Samples were then sonicated for 20 min. in preparation for concentration analysis. A Thermo XSERIES 2 (Thermo Scientific, Germany) inductively coupled plasma mass spectrometer (ICP-MS) was used for elemental analysis. The remaining 4 mL of solution was dried down on hot plates in preparation for anion exchange chromatography to isolate sample Pb.

For elemental concentration analysis, indium (In) was used as the internal standard. Samples, standards, and blanks were doped with a 100 ppm In solution (High Purity Standards) to a concentration of 1 ppb In. A 20 ppm Pb standard (High Purity Standards) was diluted and used to create a calibration curve at the beginning of each run, with additional standard checks taken in the middle and end of each run. Precision and accuracy of the measurements were determined through repeated analysis of the certified reference material International Atomic Energy Agency IAEA-SL-1 that was worked up and analyzed along with the samples and the 1 ppm Pb solution. Results of Pb concentration analysis are found in Table 2. The %Recovery of IAEA-SL-1 leached, dry weight concentration value for this study compared to the IAEA-SL-1 reference values was 67%, with 4% RSD (Table 3.)

3.5 LEAD ISOTOPE ANALYSIS

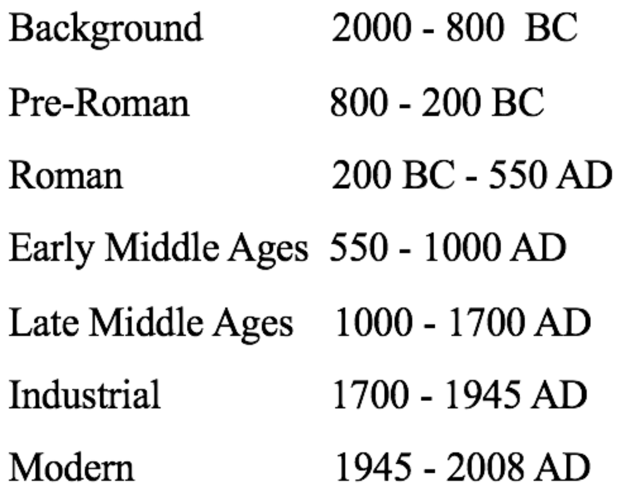
Sample Pb was isolated by anion exchange chromatography using the AG 1-X8 (100–200 mesh) resin (Bio-Rad Laboratories, Inc.), as previously described (Weis et al., 2006, Shiel et al., 2010). The dried samples are brought up in 1.8 mL of 0.5 M HBr and refluxed on a hot plate @100ºC for 1 hr. The samples are then sonicated for 20 min and then loaded onto the polypropylene microcolumns. The resin absorbs Pb while bulk elements are eluted. Lead is then recovered using 6 M HCl. Yield for Pb was ±6.75%. The eluate was then dried down and diluted with 3% HNO_3 in preparation for Pb isotope analysis.

A Nu Plasma (Nu Instruments, UK) multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) was used for isotopic analysis (Keck Collaboratory, OSU). Samples, standards, and blanks were introduced to the mass spectrometer through an CETAC Aridus II nebulizer. Pb analyses are comprised of 60 measurements (3 blocks of 20 × 10 s integrations with a 30 s ESA deflected baseline before each block). Samples were run following a modified sample-standard bracketing (SSB) measurement protocol, where the standard was run after every two samples (Weis et al., 2006; Shiel et al., 2010). A lead-free thallium spike (Alfa Aesar 13851, LOT: 792461QQ) with 205/203 Tl ratios of 2.3885 was added at a 4:1 [Pb]:[Tl] (16ppb:4ppb) ratio to each sample and standard. The Tl standard was used to correct for instrumental mass fractionation and ion signal intensities were measured for masses 202–208 (isotopes of Pb, Tl and Hg). The NIST SRM 981 common lead isotopic standard was used and Pb ratios were corrected within error of the triple spike Pb ratios of Galer and Abouchami (1998), depending on the level of instrumental mass bias drift using the ln–ln method or the SSB normalization method during the analytical session (White et al., 2000; Albarède and Beard, 2004). The accuracy of the analytical determinations was < +/- 0.2%. The isobaric Hg interference on ^{204}Pb was corrected by assuming natural abundances, ^{202}Hg/^{204}Hg=4.350 and monitoring ^{202}Hg (De Laeter et al., 2003). The external standard, IAEA-SL-1 was worked up and analyzed along with the samples (Table 4.).

4.0 RESULTS

4.1 PROFILE OF DOWNCORE TOTAL LEACHED LEAD CONCENTRATION AND 206-LEAD/207-LEAD ISOTOPE VALUES

The Laguna Roya Pb isotope and concentration record extends from 1943 BC to 2009 AD. The deposition of anthropogenic lead emissions is indicated after 500 BC when the $^{206}Pb/^{207}Pb$ value begins to decrease and the [Pb] begins to increase (Figure 4). The sediment record was classified into seven different phases according to apparent isotopic linear trends or clusters and are named according to historically significant eras to which they roughly coincide:



Background	2000 - 800 BC
Pre-Roman	800 - 200 BC
Roman	200 BC - 550 AD
Early Middle Ages	550 - 1000 AD
Late Middle Ages	1000 - 1700 AD
Industrial	1700 - 1945 AD
Modern	1945 - 2008 AD

Figure 4. Time periods used for reference in this study.

The overall trend, from c. 500 BC - 2009 AD to present-day shows variability and an overall increase in [Pb] (Figure 5). The ^{206}Pb/^{207}Pb isotopic signature also fluctuates and trends toward less radiogenic values during this time period. The [Pb] and ^{206}Pb/^{207}Pb are relatively consistent from 1943 BC to 952 BC and are used to calculate the leached, dry weight Average Background concentration, [Pb]$_B$ = 7 +/- 1 ppm, (n=4) and the Average Background isotope ratio, ^{206} Pb /^{207}Pb$_B$=1.1939 +/- 0.0001. During the Pre-Roman era (800 - 200 BC), the [Pb] ranges from 8.8 – 9.8 ppm, from c. 500 – 400 BC. From 400 BC – 200 BC, [Pb] increases rapidly and reaches [Pb] = 27.4 ppm by 246 BC. The ^{206}Pb/^{207}Pb begins to become notably less radiogenic, after c. 500 BC, decreasing from ^{206}Pb/^{207}Pb = 1.1902 to ^{206}Pb/^{207}Pb = 1.1800, by the end of the pre-Roman period. The maximum [Pb] (62.8 ppm) occurs at 15 BC during the Roman era (200 – 550 AD). The isotope ratios also rapidly decline during this period and reach a minimum of ^{206}Pb/^{207}Pb = 1.1759 in 15 BC . The end of the Roman era shows a more gradual decline in [Pb], decreasing to [Pb] = 14.21 ppm, and a gradual increase in isotope ratio where ^{206}Pb/^{207}Pb =1.1850 by the end of the Roman age. There is a relatively steady [Pb] and ^{206}Pb/^{207}Pb trend during the Early Middle Ages (550 – 1000 AD) with a [Pb] range of (13.0 – 16.6 ppm), and ^{206}Pb/^{207}Pb range of (1. 1858 – 1.186 3). Similarly, during the Late Middle Ages from 1000 – 1700 AD the [Pb] ranges from 13.20 – 15.74 ppm and ^{206}Pb/^{207}Pb from 1.1824 – 1.1852). The Industrial era (1700 - 1945 AD) shows a notable and consistent increase in [Pb] from (17.05 – 30.91 ppm) and ^{206}Pb/^{207}Pb increases from 1.1805 ppm to a maximum of 1.1740 ppm and then begins to decrease. The Modern period (1945 - 2009 AD) begins with a [Pb] = 38.51ppm peak in 1972, and declines steadily to 27.80 ppm in 2009. The ^{206}Pb/^{207}Pb, on the other hand, continues to decline to ^{206}Pb/^{207}Pb = 1.688 in 1995, and then slowly increases to ^{206}Pb/^{207}Pb = 1.1698 by 2009.

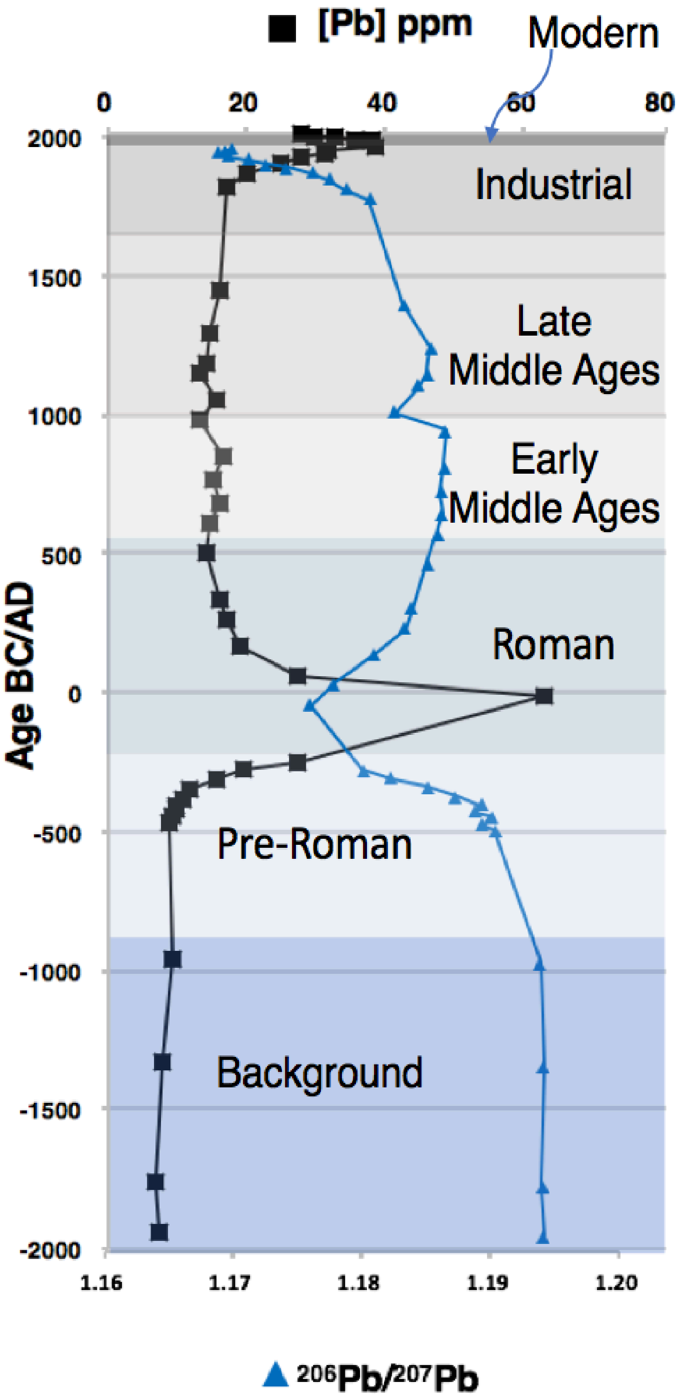


Figure 5. Downcore lead isotope and concentration profile of the Laguna Roya sediment core.

4.2 THREE-ISOTOPE PLOTS OF LAGUNA ROYA ISOTOPE DATA

Three-isotope plots using ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, ^{208}Pb/^{204}Pb are plotted as follows: ^{207}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb, ^{208}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb (Figure 6. (a and b)). The general trend of the three-isotope plots is that over time, the isotope ratios of the lake sediments decrease (become less radiogenic). The lead isotopes plot very close to a linear line with little deviation, defining a predominantly binary mixing line. The different temporal categories plot in clusters or in linear groups. The Background cluster is the most radiogenic and the isotope values of this group present in a tight cluster with a very narrow range of ^{208}Pb/^{204}Pb (38.8079 – 38.8034), ^{207}Pb/^{204}Pb (15.6881 –15.6851), ^{206}Pb/^{204}Pb (18.7249–18.7197). The Pre-Roman isotope ratios

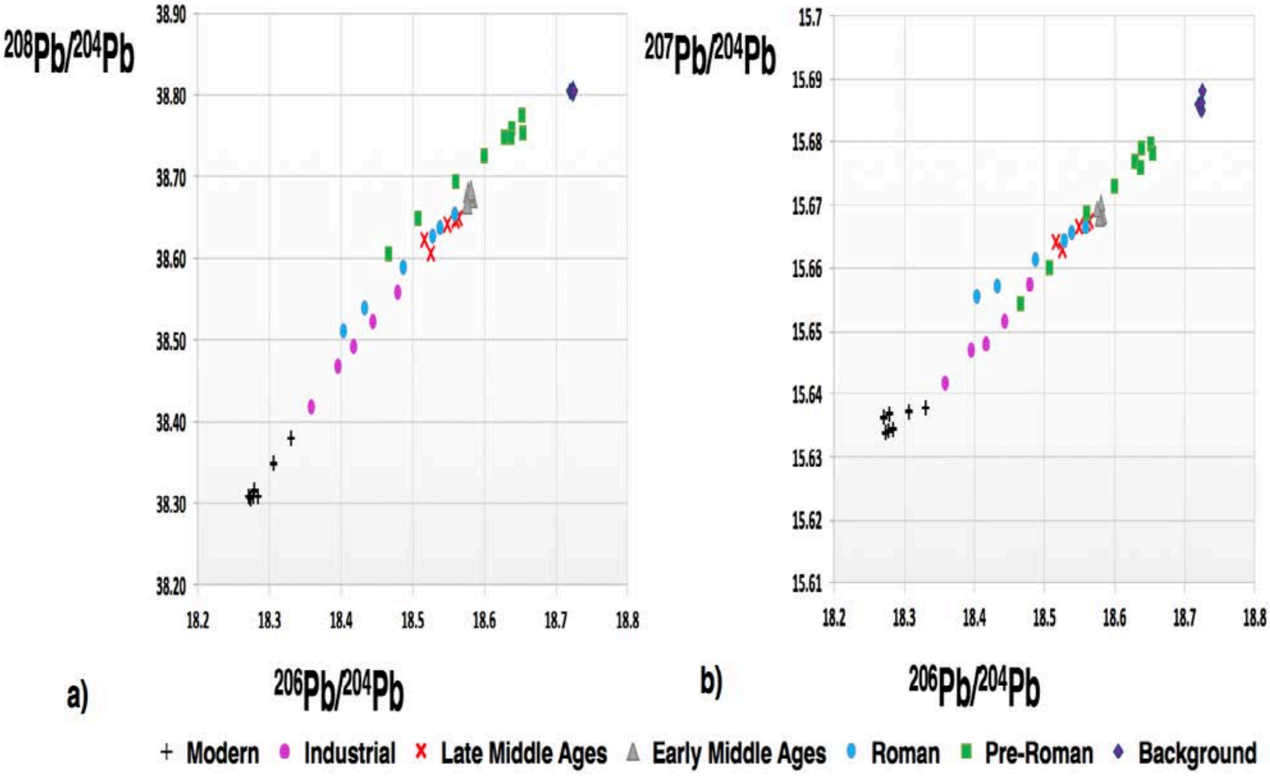


Figure 6. Three-Isotope Plots of Laguna Roya Lead Isotope Data.

form a small cluster and roughly a linear trend with values becoming less radiogenic over time: $^{208}Pb/^{204}Pb$ (38.6481-38.7734), $^{207}Pb/^{204}Pb$ (15.6540-15.6795), $^{206}Pb/^{204}Pb$ (18.4669-18.6546). The Roman isotope signatures. On the other hand, form close to a linear line, with isotope ratios becoming more radiogenic over time: $^{208}Pb/^{204}Pb$ (38.5100-38.6519), $^{207}Pb/^{204}Pb$ (15.6552-15.6664), $^{206}Pb/^{204}Pb$ (18.4045-18.5599). The Early Middle Ages data forms a small cluster with ratios: $^{208}Pb/^{204}Pb$ (38.6670-38.6836), $^{207}Pb/^{204}Pb$ (15.6681- 15.6703), $^{206}Pb/^{204}Pb$ (18.5754-18.5833). The Late Middle Ages isotope data, $^{208}Pb/^{204}Pb$ (38.6062-38.6501), $^{207}Pb/^{204}Pb$ (15.6630-15.6674), and $^{206}Pb/^{204}Pb$ (18.5159-18.5634), form a looser cluster with less radiogenic ratios than the Early Middle Ages data points. The isotope ratios for the Industrial era for the most part decrease over time, and exhibit a linear distribution with a relatively broad range $^{208}Pb/^{204}Pb$ (38.4198-38.5585), $^{207}Pb/^{204}Pb$ (15.6417-15.6575), $^{206}Pb/^{204}Pb$ (18.3588-18.4785). The Modern isotope values are clustered and have the least radiogenic values of the dataset: $^{208}Pb/^{204}Pb$ (38.3059-38.3799), $^{207}Pb/^{204}Pb$ (15.6337-15.6380), $^{206}Pb/^{204}Pb$ (18.2710-18.3299).

4.3 SOURCE ATTRIBUTION USING ISOTOPE RATIO VS. INVERSE CONCENTRATION PLOTS

Lead isotope ratios were plotted against the inverse of Pb concentration ($^{206}Pb/^{204}Pb$ vs. $[Pb]^{-1}$, $^{207}Pb/^{204}Pb$ vs. $[Pb]^{-1}$, $^{208}Pb/^{204}Pb$ vs. $[Pb]^{-1}$) and the data points approximate a linear relationship (Figure 7. (a-c)). Hence, a straight line is drawn through the data points from each defined time period (Figure 4.) in order to estimate the isotopic signature of the pollution sources (Section 1.3) The Average Background isotope values were calculated ($^{206}Pb/^{204}Pb$=18.723+/-0.002, $^{207}Pb/^{204}Pb$ = 15.686+/-0.001, $^{208}Pb/^{204}Pb$= 38.805+/-0.002) and are included with the analyses of the isotope values for each time period (Figure 7. (a-c)). A linear regression analysis using the Microsoft Excel® Linear Regression Tool was conducted for each data set. The slopes, R^2 values, y-intercepts, and standard errors of the y-intercept of each of the three lead isotope regression analyses are reported in Table 5. The y-intercept values that estimates the isotope value of the anthropogenic Pb endmember (AE) are also listed in Figure 7. (a-c).

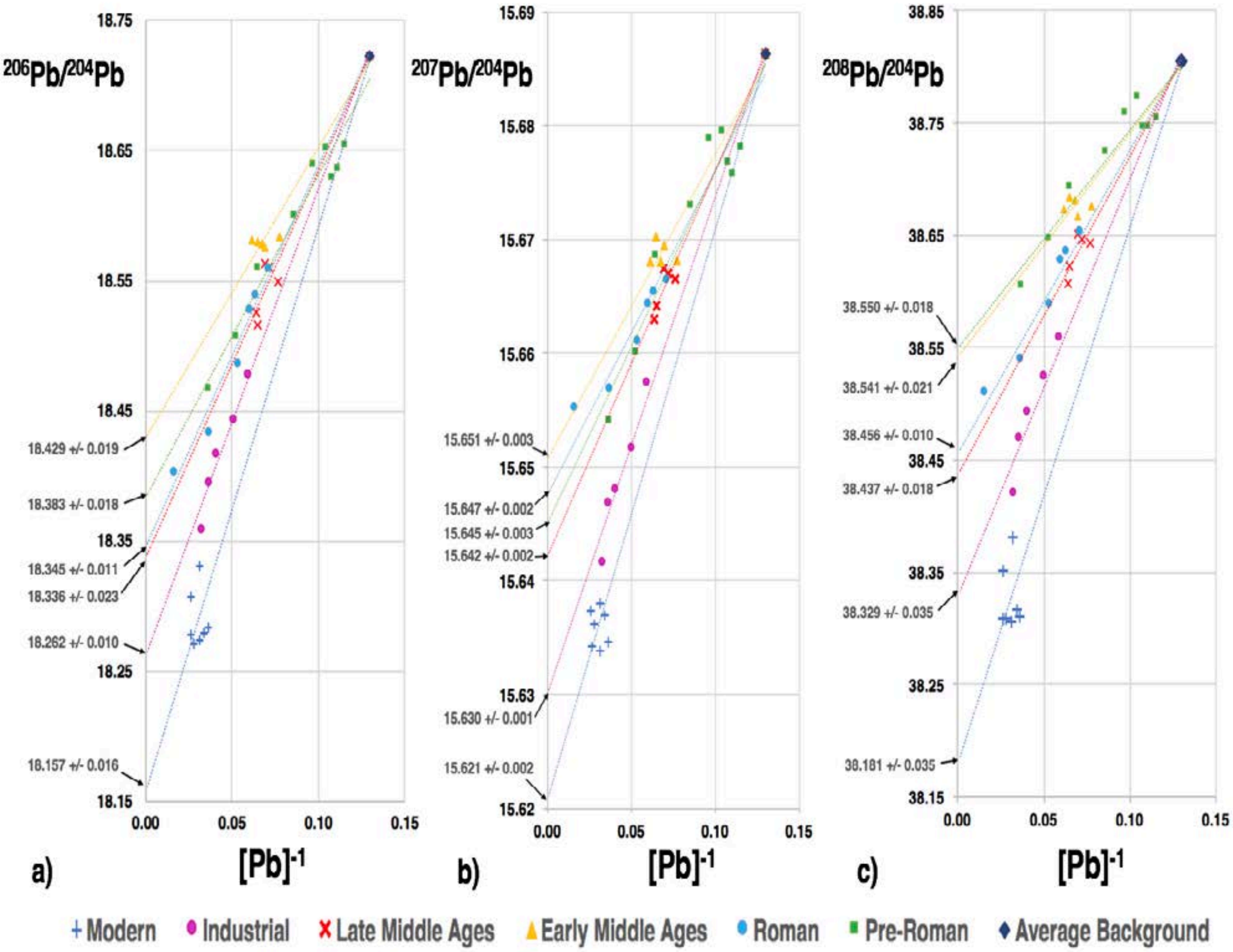


Figure 7. Lead isotope ratios plotted against inverse of concentration.

The AE values were then plotted onto three-isotope plots along with the ore isotope fields defined in Figure 2. Only those fields that mapped within the same isotope range as the AE data set were drawn (Table 1). The Pre-Roman, Roman, Early Middle Ages and Late Middle Ages AE estimates plot within the Northern Portugal (NP) isotope field on both the $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ plots (Figure 8). The Industrial era AE plots within the south-central (SC) and northern Portugal (NP) fields on both plots and on the periphery of southwestern (SW) on the $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ plot and within the SW field on the $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ plot. The Modern era AE plots on the least radiogenic periphery of the SW, SC, NP and southeastern (SE) fields.

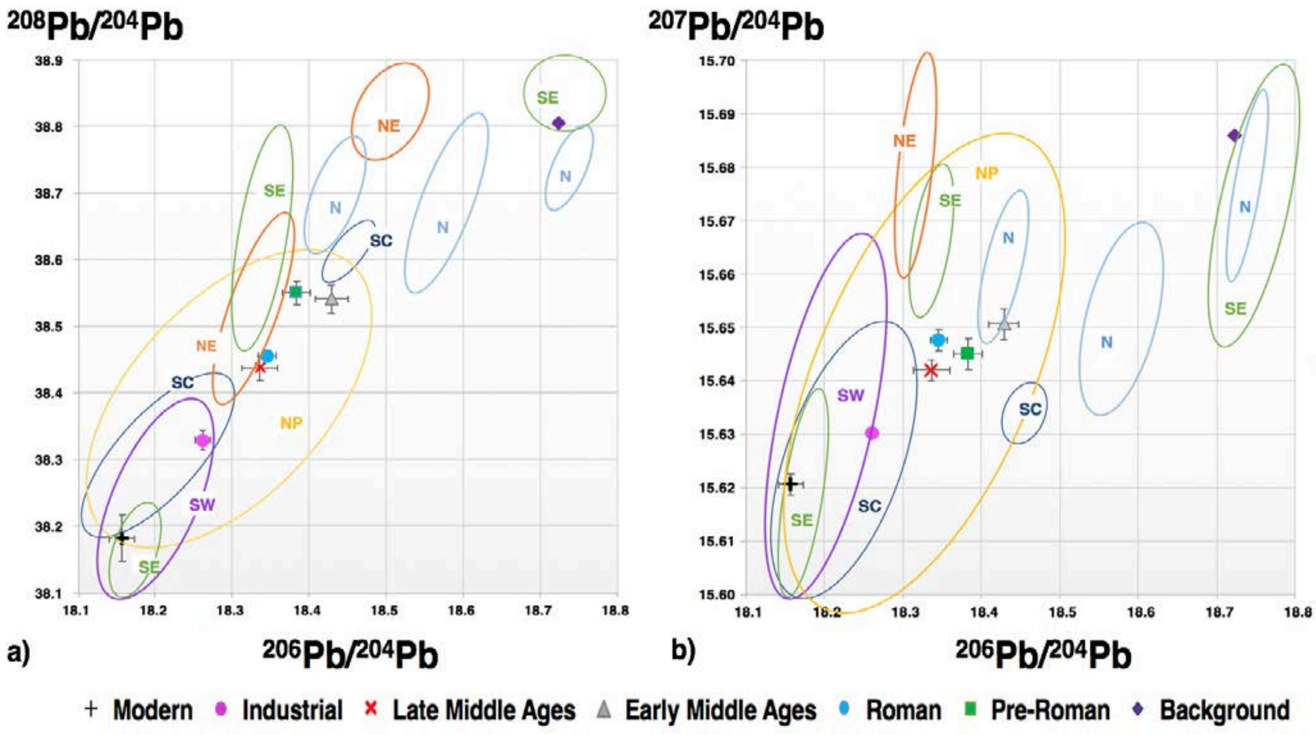


Figure 8. Estimated isotope ratios of the primary anthropogenic emission sources for each time period mapped onto Iberian ore isotope fields.

4.4 SOURCE APPORTIONMENT OF ANTHROPOGENIC ENDMEMBERS USING MIXING EQUATIONS

The $^{206}Pb/^{207}Pb$ for leaded gasoline ranges from 1.06–1.17, with an average of $^{206}Pb/^{207}Pb_{avg}=1.115$ (Table 1; Kylander M.E. et al., 2005). The contribution of leaded gasoline was estimated using the following mixing equation:

$$X_{sample}= \frac{(^{206}Pb/^{207}Pb)_{sample} - (^{206}Pb/^{207}Pb)_{background}}{(^{206}Pb/^{207}Pb)_{anth} - (^{206}Pb/^{207}Pb)_{background}}$$

Where European Leaded Gasoline $^{206}Pb/^{207}Pb_{anth}=1.115$, $^{206}Pb/^{207}Pb_{back} =1.19393$+/- 0.0001, $^{206}Pb/^{207}Pb_{sample}=1.170$. The sample dated to 1972 is used as this sediment layer had the highest [Pb]. The estimated contribution of leaded gasoline to the lead isotope composition in Laguna Roya sediments in 1972 is 29%.

Modifying the three-endmember mixing equation introduced in Section 1.8 to include the isotope ratios as a variable, the contribution of the lead from the SW/SC ore field can be estimated:

$$f_{LG}{}^{206}Pb/^{207}Pb_{LG} + f_{B}{}^{206}Pb/^{207}Pb_{B} + f_{SW}\,{}^{206}Pb/^{207}Pb_{SW} = {}^{206}Pb/^{207}Pb_{Sample}$$

Where f_{LG}= 0.29, f_{B}= 0.20, and f_{SW}= unknown, are the mass fractions of the leaded gasoline, background and southwestern ore respectively. The $^{206}Pb/^{207}Pb_{LG}=1.115$, $^{206}Pb/^{207}Pb_{B}=1.1939$, $^{206}Pb/^{207}Pb_{SW}=1.1658$ are the isotope ratios of the leaded gasoline, background and southwestern ore respectively. In this case, the values for SW ore field will be used since the Linares-La

Carolina SC isotope field closely overlaps with the SW field. The value of the lake sediment sample isotope ratio in 1972 is $^{206}Pb/^{207}Pb_{Sample}$ =1.1710. It is calculated that the 52% of the lead pollution in Laguna Roya in 1972 was from the SW mining region.

5.0 DISCUSSION

The two main goals of this study are to use the Pb concentration profile from the Laguna Roya age-dated sediment core to determine the timing of major pollution events and to use Pb isotopes to identify the primary sources of atmospheric lead pollution. This information can then be compared to archaeological and historical records. The lake sediments were leached using dilute HCl/HNO_3 and a method described by Graney et al. (1995). This method does not use hydrofluoric acid or stronger acids to digest sediments because this releases the geogenic metal fraction contained within the minerals of the sediments (Graney et al., 1995). The recovery was 67% of the IAEA-SL-1 reference recommended value (Table 3.). This is expected because this method is intended to capture the anthropogenic isotopic signature by releasing the lead adsorbed to sediment and organic matter, rather than to extract the total lead composition, which includes lead leached from the mineral structure of the sediment particles (Graney et al., 1995).

By plotting the downcore dry weight Pb concentration and isotopic composition as a function of time (Figure 5.), it can easily be determined that a dynamic lead pollution history was recorded in the Laguna Roya lake sediments. The lead isotope ratio $^{206}Pb/^{207}Pb$ is used to determine if the Pb source is anthropogenic because anthropogenic sources of Pb typically have less radiogenic isotopic signature (Section 1.2; Bindler, 2011). To estimate the isotopic signature of lead pollution that occurred during each time period (Figure 4.) the $^{208}Pb/^{204}$, $^{207}Pb/^{204}$ and $^{206}Pb/^{204}$ratios were each plotted against $[Pb]^{-1}$ (Figures 7a-c). The advantage of using this method is that the data can be displayed and other potential trends can be seen. When analyzing the data for each time period, tight clusters for example, might suggest a consistent lead source and rate of input, whereas linear trends might suggest changes in concentration, and deviations from this line might suggest an influx of a 3rd endmember source. The estimated anthropogenic endmember (AE) isotope values (Figure 7 (a-c)) are then compared to ore isotope fields (Figure 2 (a and b)) by plotting both data sets on three-isotope plots (Figure 8 (a and b)).

It is important to note that three-isotope plots are two dimensional representations of a three-dimensional plot. Therefore, to match an anthropogenic end member to a potential ore source it must overlap a field in *both* three isotope plots. The isotope fields were drawn by visual inspection to represent the densest regions defined by the published data sets. Only the ore isotope fields that fit within reasonable range of the lake sediment mixing line were plotted on the three-isotope plots (Figure 8. (a and b)). The ranges of the published isotopic values of ore bodies from the Southwest (SW), Southeast (SE), South-central (SC), North (N), and Northern Portugal (NP), North East (NE), and leaded gasoline can be found in Table 1. Ore fields that are considered ‘well defined’ have 30-50 measurements, and accurate provenancing requires well defined, homogeneous isotope fields (Stos–Gale and Gale, 2009). In this study, the SE, SC, and SW ore isotope fields are well-defined. As for the rest of the fields, the individual data points can be seen in Figure 2. The Northern Portugal field is heterogeneous and consists of a wide range of mineral deposits throughout the region. More lead isotope data needs to be collected from the mining regions in the northwestern, and other understudied regions to establish well defined isotope fields that can be confidently used in lead provenancing studies.

The leached dry weight concentration shows an unprecedented increase of Pb influx to Laguna Roya after c. 400 BC. The first detectible anthropogenic lead pollution in the lake sediments, indicated by a decrease in lead isotope ratios and an increase in concentration, occurs sometime after 500 BC (Figure 5). This coincides with the beginnings of the Late Iron-Age, when the local peoples developed the resources and technology to begin artisanal-scale mining and metallurgical activities (Sastre and Sánchez-Palencia, 2013; Reher et al., 2015) Also, the timing of this lead deposition coincides with the trend seen in many natural archive studies and is attributed to the beginnings of the widespread use of cupellation and the production of silver coinage (Settle and Patterson, 1980; Renberg et al, 2001).

The Romans conquered the northwestern regions of Iberia during the Cantabrian war (29-19 BC) and it is believed that they took over the mining operations in these regions shortly afterwards. Las Médulas, located c. 35km north of Laguna Roya, was one of the largest Roman gold mines that was exploited from the beginning of the 1st century AD to the about end of the 2nd century AD (Hillman et al. 2017; Perez-Garcia et al., 2000). Another Roman mining region is found in the vicinity of Bragança, Portugal, located only c. 30 km to the southwest of Laguna Roya. The lead pollution [Pb] in Laguna Roya reaches a maximum (62.8 ppm) at c. 15 BC (Figure 5), which may coincide with a period of intense local mining activities. Additionally, the Pre-Roman and Roman estimated sources fall well within the Northern Portugal isotope field in both three isotope plots (Figure 8 (a and b)). If this is the case, it is odd that the extensive Roman mining operations known to have occurred in the region during the 1st and 2nd centuries AD are not reflected in the sediment record. That is, the sediment record indicates a sharp decline in lead emissions by 66 AD, when the [Pb] drops to 27.3 ppm, and continues to rapidly decline to 19.0 ppm by 169 AD. This result is unexpected for the Pre-Roman and Roman data set as there is no indication of large-scale mining activities prior to the Roman conquest of the region. On the other hand, the Romans had been exploiting the lead-rich ore deposits throughout the south of the peninsula for up to 200 years. Thus, it is possible the lead deposited in Laguna Roya came from more distant sources and the isotope signature represents emissions from a relatively consistent mix of ores from remote sources. Still another possibility is that there is an offset in the age model of the sediment core.

Little is known about mining operations throughout the Iberian Peninsula after the Fall of Rome. The lead deposition in Laguna Roya subsequent to 550 AD, remains relatively constant, as is indicated by both the Pb isotopic ratios and concentration (Figure 5). Little archaeological evidence or documentation of mining events has survived from this time. Some researchers affirm however, that mining in the region continued at a small regional scale and that multiple mines and mints were in operation (Sánchez Pardo, 2013). The results from the linear regression analysis support this theory, plotting the Early and Late Middle Ages anthropogenic endmembers well into the NP isotope field.

There is a slight decrease in isotope values that occurs around 1052 AD which is coeval with similar excursions seen in multiple archive studies that are attributed to the mining operations in the Harz region in Germany, or other mining regions in northern Europe (Bindler, 2011; Renberg et al., 2001). The isotope values abruptly shift from $^{206}Pb/^{207}Pb = 1.1864$ in 987 AD to a local minimum in 1052 AD when $^{206}Pb/^{207}Pb$ decreases to 1.1824. The $^{206}Pb/^{207}Pb$ then increases back to 1.1850 by 1193 AD. This possibility infers that lead emissions travelled to Laguna Roya from the mining operations on the European mainland. Another event that is coincident with this small isotope excursion is the Medieval Climate Anomaly (MCA) which took place from 900-1300 AD. Paleoclimatology studies, using multiple proxies from lake and ocean sediment cores from the Iberian Peninsula, have determined that the climate in all but the northern reaches of the Iberian Peninsula experienced a dry and warm period with lower lake levels, and an influx of Saharan dust (Moreno et al., 2012). It follows that an extended warm and dry period could have resulted in an increase of dust and remobilization of lead particulates that may have been from previous mining operations. A final possibility is that this slight excursion was caused by local mining of an ore deposit with a less radiogenic Pb isotope signature than is typical of ores mined in the region.

The Industrial period saw a rebirth of the mining industry in the Iberian Peninsula with many of the old Roman mining sites being exploited again (Braz Martins, 2010; Santos Zalduegui et al., 2004; Tornos et al., 2009; Velasco et al., 1995). Major mining operations occurred in regions including the southwestern Iberian Pyrite Belt, the south-central Alcudia Valley and La Carolina-Linares. With improvements in technology, these sites were now profitable to mine and for the most part, large British mining companies operated these mines starting in the mid 19th century through to the 20th century (Vernon, 2003). The results of the regression analyses map the estimated anthropogenic lead pollution source to the SC Linares-La Carolina Field and SW regions. This estimate is reasonable, as it is in agreement with historical accounts and the SC and SW isotope fields are well defined.

Leaded Gasoline signatures are too broadly defined to effectively plot onto the three-isotope plots. Nevertheless, there is a substantial body of research dedicated to quantifying the contributions and timing of this lead pollution event (Section 2.8). Hence, source apportionment of lead from leaded gasoline can be estimate using a mixing equation and compared to published data (Section 1.3). The Modern isotope values plot to a region slightly less radiogenic than the SW and SC isotope fields. Studies accounting for the sources of atmospheric lead pollution indicate that the two primary sources of lead pollution after in 1955 are from leaded gasoline and non-ferrous mining. (Figure 3.; Pacyna and Pacyna, 2000). According to Pacyna and Pacyna (2000), the atmospheric lead contribution from leaded gasoline peaks at c. 75% by c. 1975 whereas non-ferrous metal manufacturing contributes 10% (Figure 3). The findings from this study are consistent with this study in that lead deposition in Laguna Roya sediments peaked in 1972 ([Pb]=38.5ppm). Using the mixing equations defined in Section 4.4, the estimated contribution of leaded gasoline to the lead isotope composition in Laguna Roya sediments in 1972 is 29%, and 52% was from ores from the SW and/or SC mining regions. Considering that Laguna Roya is a high elevation lake in a sparsely populated region of the peninsula, the estimates from this study for the lead contributions from mining and leaded gasoline during the Modern lead pollution maximum are possible, but further studies would be necessary to validate these estimations.

The linear regression estimate indicates that the primary source of lead is likely from the SW and/or SC ore fields. The lead isotope values for leaded gasoline are much less radiogenic than the lake sediment samples and plot far downfield. $^{206}\mathrm{Pb}^{/204}\mathrm{Pb}$=16.564-17.680, $^{207}\mathrm{Pb}^{/204}\mathrm{Pb}$=15.368-15.597, and $^{208}\mathrm{Pb}^{/204}\mathrm{Pb}$=36.410-37.260. However, the Modern AE plots in a less radiogenic region of the SW and SC fields suggesting that a that a 3rd end member, such as lead from leaded gasoline is contributing to the Pb pollution in the sediment record. Laguna Roya is in a remote region of Northwestern Spain so it is difficult to determine how this region is influenced by the trends indicated by lead emissions data.

One final consideration is that the highest concentrations of lead in Laguna Roya sediments occurred at c. 15 BC. The isotope values suggest that the source of atmospheric lead may be local, but evidence of industrial-scale mining in this region, prior to the Roman occupation, is yet to be found. Additionally, a record of intensive Roman mining operations in this area during the 1st and 2nd centuries is absent from the record. In contrast, the modern lead mining and emissions from leaded gasoline are believed to have been at least an order of magnitude larger than Roman mining activities, yet these remote sources are not reflected proportionately in the Laguna Roya sediment archive (Settle and Patterson, 1980; Strauss et al., 1977). There are likely additional factors at play affecting the deposition of lead in Laguna Roya, a high elevation lake. Possible variables may include changes in the climate and prevailing wind patterns, or in the technology by which lead is smelted or heated.

6.0 CONCLUSIONS

Comparing the downcore dry weight leached concentration to the $^{206}Pb/^{207}Pb$ in the Laguna Roya lead pollution sediment record, indicates that levels of atmospheric lead deposition in the past ~2,500 years, are unprecedented in the sediment record prior to this time. Anthropogenic sources of atmospheric lead pollution are detectible in Laguna Roya sediments after c. 500 BC, indicated an increase in [Pb] with less radiogenic $^{206}Pb/^{207}Pb$ isotope ratios. The Pb profile clearly responds to three major lead pollution events documented in multiple environmental archive studies from sites throughout Europe and various other sites throughout the northern hemisphere (Renberg et al., 2001). The major concentration and lead isotope excursion peaks in the Laguna Roya sediment record occur during the Roman (c. 15 BC), and Modern era (c. 1972 AD) with a minor excursion occurring in the Late Middle Ages (c.1050 AD). In the northwestern region of Spain, there is little archaeological evidence of major mining or metallurgic activities after the fall of Rome (c. 400 AD). Additionally, there is evidence of significant decline in mining operations during the Late Middle Ages, suggesting that the extraction of lead and cupellation activities were limited at these times (More et al., 2017). This is reflected in the sediment record by only slightly elevated, yet relatively steady Pb concentrations and isotope ratios. Considering the remote location of Laguna Roya, it is notable that the atmospheric lead deposition never returns to background levels. In other words, an important question to consider is: how much atmospheric lead deposition after a major pollution event is due to remobilization of lead adsorbed to dust particles? Also, how long would it take for the signal in surface sediments to return to background levels? These are important question to consider in Modern times since a major global lead deposition maximum has most recently occurred.

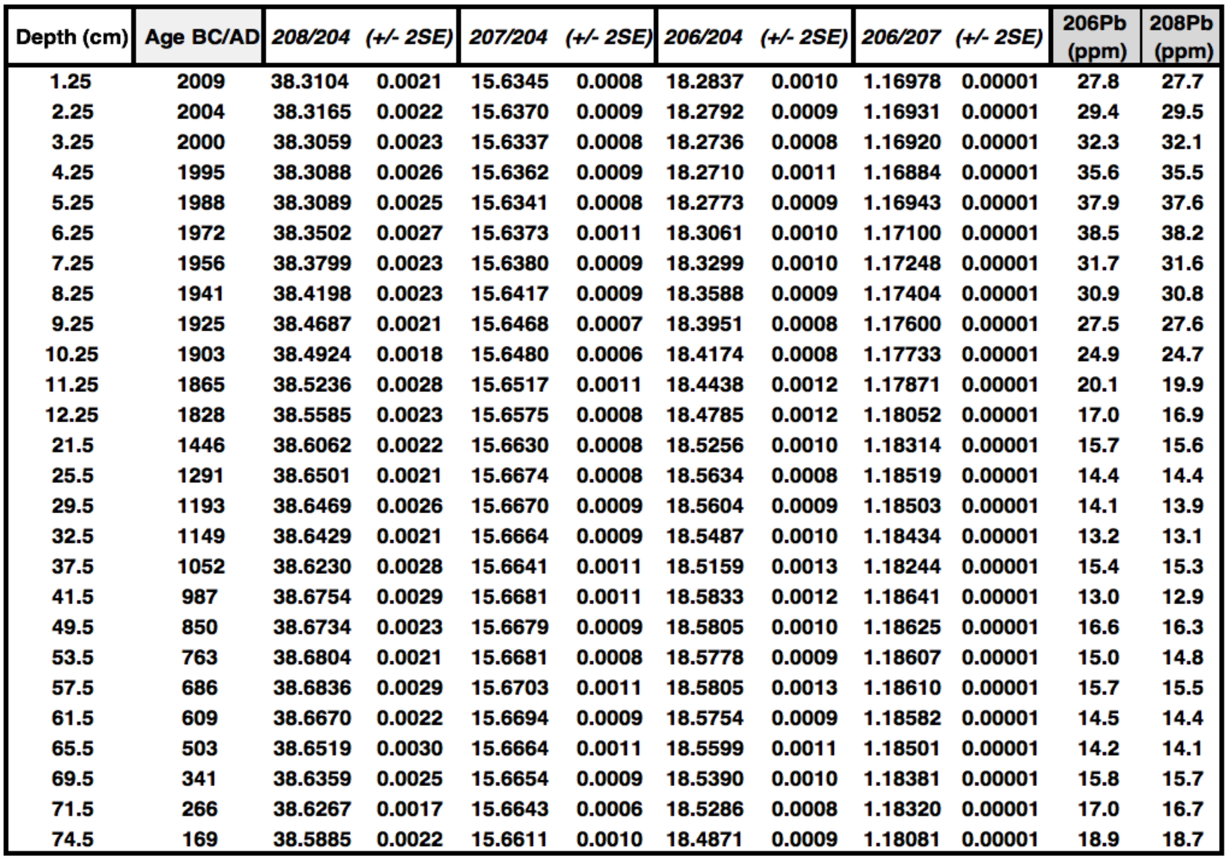
This study successfully estimated the primary sources of atmospheric lead pollution. The most likely pollution sources were identified as those from the lead-bearing ore deposits sources located in the northwest of the peninsula (northern Portugal) between c. 500 BC-1700 AD. After this time, c.1700-2009 AD, the lead-sulfide deposits from the southwestern and south-central regions became the primary sources of lead pollution in Laguna Roya. The Southwestern (Iberian Pyrite Belt) and South-central (Linares-La Carolina) ore isotope fields are well defined, enabling more certain identification. The Northern Portugal field, on the other hand, is not well defined. More work dedicated to documenting the precise locations, geological units and the Pb isotope values from historically important mining regions will contribute to the further success and certainty of source attribution studies.

Lead used in gasoline additives has a very broad isotopic signature range but its contribution to the Pb deposited in Laguna Roya can be accounted for using a mixing equation. The contribution of lead in the Laguna Roya sediments from leaded gasoline was calculated to be 29%. Whereas 52% of the lead pollution was attributed to the southwestern and south-central mining regions. Since antiquity, lead has been actively traded and transported for uses including the extraction and beneficiation of ores, and most recently, as an additive in gasoline. Hence, changes of Pb pollution concentrations and isotopic signatures in Laguna Roya sediments reflect changes in both industrial activities, and geopolitical relations throughout history.

APPENDIX A

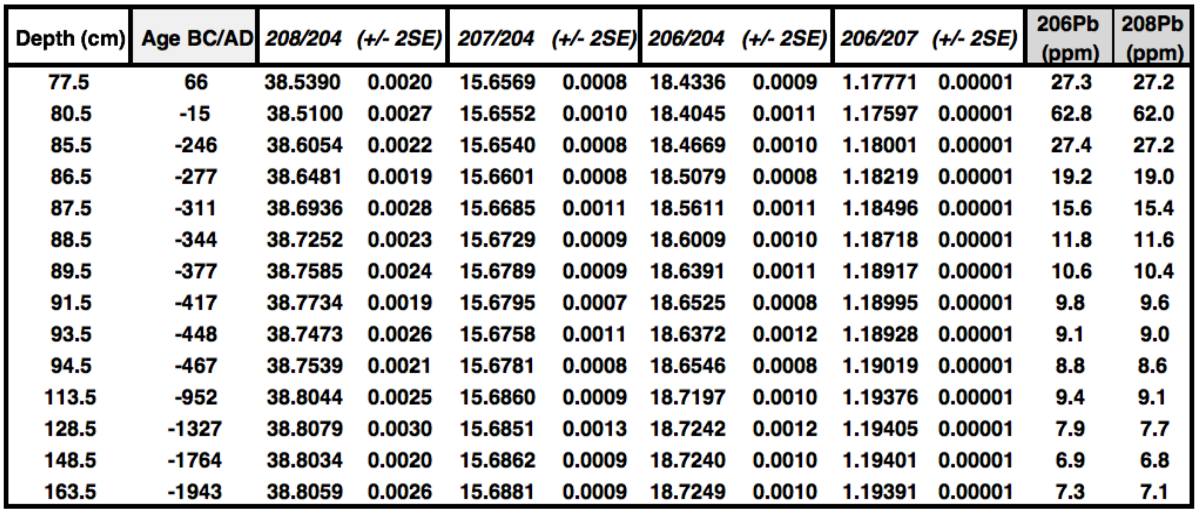
DATA TABLE

Table 2. Lead isotope ratios and dry weight concentrations according to sediment depth and modelled age for Laguna Roya.



Depth (cm)	Age BC/AD	*208/204*	*(+/- 2SE)*	*207/204*	*(+/- 2SE)*	*206/204*	*(+/- 2SE)*	*206/207*	*(+/- 2SE)*	206Pb (ppm)	208Pb (ppm)
1.25	2009	38.3104	0.0021	15.6345	0.0008	18.2837	0.0010	1.16978	0.00001	27.8	27.7
2.25	2004	38.3165	0.0022	15.6370	0.0009	18.2792	0.0009	1.16931	0.00001	29.4	29.5
3.25	2000	38.3059	0.0023	15.6337	0.0008	18.2736	0.0008	1.16920	0.00001	32.3	32.1
4.25	1995	38.3088	0.0026	15.6362	0.0009	18.2710	0.0011	1.16884	0.00001	35.6	35.5
5.25	1988	38.3089	0.0025	15.6341	0.0008	18.2773	0.0009	1.16943	0.00001	37.9	37.6
6.25	1972	38.3502	0.0027	15.6373	0.0011	18.3061	0.0010	1.17100	0.00001	38.5	38.2
7.25	1956	38.3799	0.0023	15.6380	0.0009	18.3299	0.0010	1.17248	0.00001	31.7	31.6
8.25	1941	38.4198	0.0023	15.6417	0.0009	18.3588	0.0009	1.17404	0.00001	30.9	30.8
9.25	1925	38.4687	0.0021	15.6468	0.0007	18.3951	0.0008	1.17600	0.00001	27.5	27.6
10.25	1903	38.4924	0.0018	15.6480	0.0006	18.4174	0.0008	1.17733	0.00001	24.9	24.7
11.25	1865	38.5236	0.0028	15.6517	0.0011	18.4438	0.0012	1.17871	0.00001	20.1	19.9
12.25	1828	38.5585	0.0023	15.6575	0.0008	18.4785	0.0012	1.18052	0.00001	17.0	16.9
21.5	1446	38.6062	0.0022	15.6630	0.0008	18.5256	0.0010	1.18314	0.00001	15.7	15.6
25.5	1291	38.6501	0.0021	15.6674	0.0008	18.5634	0.0008	1.18519	0.00001	14.4	14.4
29.5	1193	38.6469	0.0026	15.6670	0.0009	18.5604	0.0009	1.18503	0.00001	14.1	13.9
32.5	1149	38.6429	0.0021	15.6664	0.0009	18.5487	0.0010	1.18434	0.00001	13.2	13.1
37.5	1052	38.6230	0.0028	15.6641	0.0011	18.5159	0.0013	1.18244	0.00001	15.4	15.3
41.5	987	38.6754	0.0029	15.6681	0.0011	18.5833	0.0012	1.18641	0.00001	13.0	12.9
49.5	850	38.6734	0.0023	15.6679	0.0009	18.5805	0.0010	1.18625	0.00001	16.6	16.3
53.5	763	38.6804	0.0021	15.6681	0.0008	18.5778	0.0009	1.18607	0.00001	15.0	14.8
57.5	686	38.6836	0.0029	15.6703	0.0011	18.5805	0.0013	1.18610	0.00001	15.7	15.5
61.5	609	38.6670	0.0022	15.6694	0.0009	18.5754	0.0009	1.18582	0.00001	14.5	14.4
65.5	503	38.6519	0.0030	15.6664	0.0011	18.5599	0.0011	1.18501	0.00001	14.2	14.1
69.5	341	38.6359	0.0025	15.6654	0.0009	18.5390	0.0010	1.18381	0.00001	15.8	15.7
71.5	266	38.6267	0.0017	15.6643	0.0006	18.5286	0.0008	1.18320	0.00001	17.0	16.7
74.5	169	38.5885	0.0022	15.6611	0.0010	18.4871	0.0009	1.18081	0.00001	18.9	18.7

Table 2. (continued)

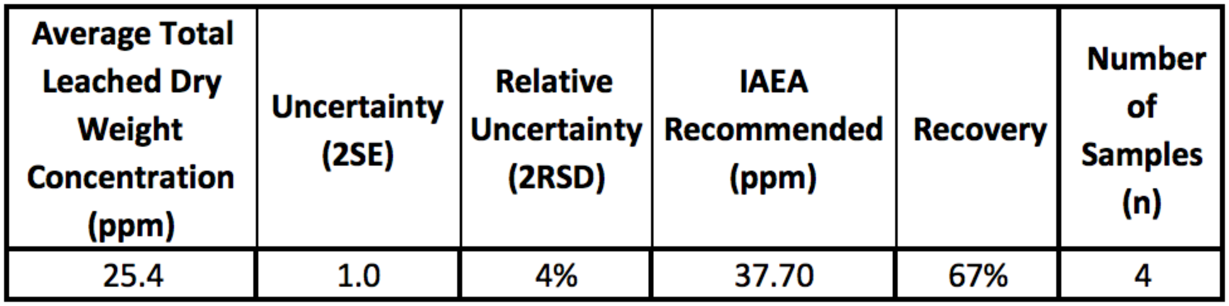


Depth (cm)	Age BC/AD	*208/204*	*(+/- 2SE)*	*207/204*	*(+/- 2SE)*	*206/204*	*(+/- 2SE)*	*206/207*	*(+/- 2SE)*	206Pb (ppm)	208Pb (ppm)
77.5	66	38.5390	0.0020	15.6569	0.0008	18.4336	0.0009	1.17771	0.00001	27.3	27.2
80.5	-15	38.5100	0.0027	15.6552	0.0010	18.4045	0.0011	1.17597	0.00001	62.8	62.0
85.5	-246	38.6054	0.0022	15.6540	0.0008	18.4669	0.0010	1.18001	0.00001	27.4	27.2
86.5	-277	38.6481	0.0019	15.6601	0.0008	18.5079	0.0008	1.18219	0.00001	19.2	19.0
87.5	-311	38.6936	0.0028	15.6685	0.0011	18.5611	0.0011	1.18496	0.00001	15.6	15.4
88.5	-344	38.7252	0.0023	15.6729	0.0009	18.6009	0.0010	1.18718	0.00001	11.8	11.6
89.5	-377	38.7585	0.0024	15.6789	0.0009	18.6391	0.0011	1.18917	0.00001	10.6	10.4
91.5	-417	38.7734	0.0019	15.6795	0.0007	18.6525	0.0008	1.18995	0.00001	9.8	9.6
93.5	-448	38.7473	0.0026	15.6758	0.0011	18.6372	0.0012	1.18928	0.00001	9.1	9.0
94.5	-467	38.7539	0.0021	15.6781	0.0008	18.6546	0.0008	1.19019	0.00001	8.8	8.6
113.5	-952	38.8044	0.0025	15.6860	0.0009	18.7197	0.0010	1.19376	0.00001	9.4	9.1
128.5	-1327	38.8079	0.0030	15.6851	0.0013	18.7242	0.0012	1.19405	0.00001	7.9	7.7
148.5	-1764	38.8034	0.0020	15.6862	0.0009	18.7240	0.0010	1.19401	0.00001	6.9	6.8
163.5	-1943	38.8059	0.0026	15.6881	0.0009	18.7249	0.0010	1.19391	0.00001	7.3	7.1

APPENDIX B

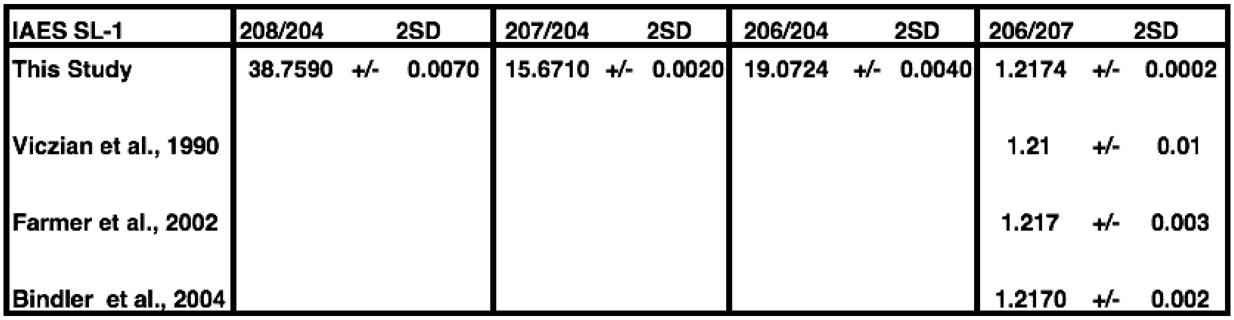
REFERENCE STANDARD TABLES

Table 3. IAEA-SL-1 external standard Pb abundances for this study compared to the reference value.



Average Total Leached Dry Weight Concentration (ppm)	Uncertainty (2SE)	Relative Uncertainty (2RSD)	IAEA Recommended (ppm)	Recovery	Number of Samples (n)
25.4	1.0	4%	37.70	67%	4

Table 4. Published lead isotope ratio values of IAEA-SL-1 reference standard compared to this study.

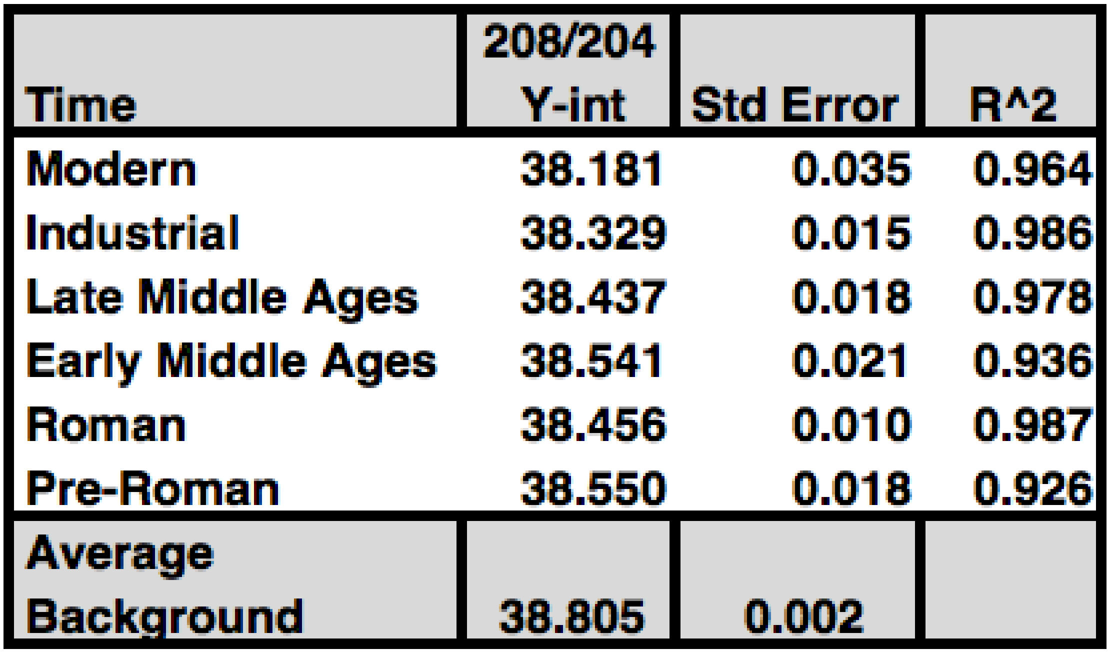


IAES SL-1	208/204		2SD	207/204		2SD	206/204		2SD	206/207		2SD
This Study	38.7590	+/-	0.0070	15.6710	+/-	0.0020	19.0724	+/-	0.0040	1.2174	+/-	0.0002
Viczian et al., 1990										1.21	+/-	0.01
Farmer et al., 2002										1.217	+/-	0.003
Bindler et al., 2004										1.2170	+/-	0.002

APPENDIX C

LINEAR REGRESSION ANALYSIS DATA

Table 5. Linear regression analysis of Pb isotope values and inverse concentration.



Time	208/204 Y-int	Std Error	R^2
Modern	38.181	0.035	0.964
Industrial	38.329	0.015	0.986
Late Middle Ages	38.437	0.018	0.978
Early Middle Ages	38.541	0.021	0.936
Roman	38.456	0.010	0.987
Pre-Roman	38.550	0.018	0.926
Average Background	38.805	0.002	

Table 5 (continued)

Time	207/204 Y-int	Std Error	R^2
Modern	15.621	0.002	0.981
Industrial	15.630	0.001	0.992
Late Middle Ages	15.642	0.002	0.982
Early Middle Ages	15.651	0.003	0.929
Roman	15.647	0.002	0.970
Pre-Roman	15.645	0.003	0.924
Average Background	15.686	0.001	

Time	206/204 Y-int	Std Error	R^2
Modern	18.157	0.016	0.973
Industrial	18.262	0.010	0.994
Late Middle Ages	18.336	0.023	0.966
Early Middle Ages	18.429	0.019	0.958
Roman	18.345	0.011	0.986
Pre-Roman	18.383	0.018	0.957
Average Background	18.723	0.002	

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