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The Medieval Metal Industry Was the Cradle of Modern Large-Scale Atmospheric Lead Pollution in Northern Europe

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There is great concern for contamination of sensitive ecosystems in high latitudes by long-range transport of heavy metals and other pollutants derived from industrial areas in lower latitudes. Atmospheric pollution of heavy metals has a very long history, and since metals accumulate in the environment, understanding of present-day pollution conditions requires knowledge of past atmospheric deposition. We use analyses of lead concentrations and stable lead isotopes ($^{206}Pb/^{207}Pb$ ratios) of annually laminated sediments from four lakes in northern Sweden (∼65° N) to provide a decadal record of atmospheric lead pollution for the last 3000 years. There is a clear signal in the sediments of airborne pollution from Greek and Roman cultures 2000 years ago, followed by a period of "clean" conditions 400−900 A.D. From 900 A.D. there was a conspicuous, permanent increase in atmospheric lead pollution fallout. The sediments reveal peaks in atmospheric lead pollution at 1200 and 1530 A.D. comparable to present-day levels. These peaks match the history of metal production in Europe. This study indicates that the contemporary atmospheric pollution climate in northern Europe was established in Medieval time, rather than in the Industrial period. Atmospheric lead pollution deposition did not, when seen in a historical perspective, increase as much as usually assumed with the Industrial Revolution (1800 A.D.).

Introduction

In the late 1960s, severe problems of surface water acidification were discovered in Scandinavia. This acidification was largely caused by sulfur emissions from continental Europe and the U.K. and drew the attention to the existence of large south to north transport of air pollution (*1, 2*). Today, there is great concern for contamination of the Arctic environment by atmospheric emissions derived from lower latitudes (*3, 4*). There are several studies of ice cores from Greenland (*5*−*8*) and lake sediments and peat in Sweden (*9*−*11*) which indicate that large scale pollution of high latitudes by emissions from cultural centers in Europe has occurred for several thousand years, and there is also convincing evidence of early pollution from the British Isles (*12*) and continental Europe (*13*−*16*). Despite this evidence, the common opinion is still that large-scale atmospheric pollution is a problem that started with the Industrial Revolution in the 19th century and that concentrations observed in remote regions today represent the natural background values *(17, 18)*. This is a false picture, at least for lead and copper (*6*−*16*), but most likely for several other atmospheric pollutants, such as mercury (*19*). Lead is a suitable pollution indicator since it is easy to analyze, nonmobile in natural environmental archives such as lake sediments (*20, 21*), and is emitted from many different kind of sources, such as the mining and metal industry and fossil fuel burning, that produce a variety of additional airborne pollutants of which many are difficult to analyze.

Stable lead isotope analysis has been used in studies of environmental pollution to trace emission sources, particularly to assess spatial and temporal changes of recent lead pollution originating from lead smelters and industries and from the use of alkyl-lead in gasoline. The $^{206}Pb/^{207}Pb$ ratios reported in these investigations of atmospheric aerosols (*22*−*24*), snow (*25*), sediments (*26, 27*), and surface soils (*28, 29*) usually vary between 1.1 and 1.2. Recent lake sediment and peat deposits and surface soil horizons in Sweden have a similarly low isotope ratio, typically 1.15−1.18 (*11*). We have found, in contrast, that the natural $^{206}Pb/^{207}Pb$ ratios in unpolluted sediment, peat, and mineral soil horizons in Sweden are clearly higher (mean = 1.53 ± 0.08; range = 1.28−3.11; n = 50 sites) (*11*). The low ratios in recent sediments and surface soils are caused by deposition and accumulation of atmospheric lead pollution. The very large differences in isotope ratios between natural soil-derived lead in Sweden and atmospheric pollution lead make analysis of lead isotopes a powerful tool to detect the influx of pollution lead to the natural environment. For example, sulfide ores exploited in the Greek and Roman periods two millennia ago and in Medieval Europe had a lead isotope ratio of about 1.17 (1.174 ± 0.023), mean of all reported values in refs *8* and *30*−*32*.

There is no parallel to varved (annually laminated) lake sediments for retrospective analysis of atmospheric pollution history in continental areas, since varved sediments can be found in many regions, e.g. Fennoscandia, Central Europe, North America, and the logistics of core collection, sample handling, and core dating are quite simple. In these sediment deposits individual varves (years) are discernible, and absolute chronologies of past changes can be established by varve counting. High-resolution subsampling, even to an annual level, is possible from these unmixed sediments. In northern Sweden, several lakes with several thousand varves in an unbroken series extending to the present-day are found (*33*). Northern Fennoscandia has always been sparsely populated and was not exploited for minerals until a few hundred years ago. Therefore, there were few local emission sources for heavy metals in preindustrial time. The combination of varved lake sediments, large differences in stable lead isotope signatures between natural soil-derived lead and pollution lead, and the remote location in relation to old

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cultural centers in the old world makes lakes in northern Sweden useful for studies of large-scale atmospheric pollution history.

We combine concentration and stable lead isotope analyses of varved sediments from four lakes to differentiate between natural and pollution lead to study the detailed atmospheric pollution history of the last 3000 years in northern Sweden.

Materials and Methods

Grånästjärn, Kassjön, Koltjärn, and Norrtjärnsjön are small (11−23 ha), boreal forest lakes located in northern Sweden (between 63 and 65°N) (Figure 1). The four lakes are between 19 and 184 m above sea level and were isolated from the Baltic Sea between 2000 years ago (Norrtjärnsjön) and 8000 years ago (Grånästjärn). Currently, agriculture occurs in the catchment of each lake, but until the 19th century the anthropogenic impact was minute.

The sediments were collected in the deepest basin of each lake using a large Russian peat corer (length 1 m, diameter 8 cm) for deeper, consolidated sediments, and a freeze corer *(34)* for the less-consolidated recent sediments in Kassjön and Koltjärn. Lake sediments were freeze-dried, ground, and then homogenized before analysis. Approximately 0.5 g of dried sediment was first weighed and then digested in open Teflon vessels with $HNO_3 + HClO_4$ (10:1) for 2−5 h at < 130 °C. Determination of lead isotopes (^{206}Pb and ^{207}Pb) and lead concentrations were made using inductively coupled plasma-mass spectrometry (ICP-MS, Perkin-Elmer model ELAN 5000) (*35*). Calibration curves and isotope correction factors were made using the certified natural lead (isotopic) standard reference material SRM 981 (National Institute of Standards and Technology). Concentrations were verified against the certified multielement standard, SPEX ICPMS-2 (SPEX CertiPrep Certified Reference Materials). The relative standard error for analyses is ≤10% for lead concentration and ≤± 0.009 for $^{206}Pb/^{207}Pb$ isotope ratio; these values are determined from more than 50 analyses of four reference samples made of sediments from Kassjön and three other lakes, which have been digested and analyzed 16 times over a 5 year period. This total analytical error reflects all aspects of sample heterogeneity, sample handling and preparation, and acid digestion as well as ICP-MS analysis.

Pollution lead is calculated applying a simple mixing model:

$$Pb_{\text{pollution concn}} = \left(\frac{\text{Pb ratio}_{\text{sample}} - \text{Pb ratio}_{\text{background}}}{\text{Pb ratio}_{\text{pollution}} - \text{Pb ratio}_{\text{background}}}\right) \times Pb_{\text{sample concn}}$$

The model uses the background ratio from each lake, which is the mean isotope ratio of unpolluted sediments (old sediments in which the $^{206}Pb/^{207}Pb$ isotope ratio is high and stable). Furthermore, the model assumes that the $^{206}Pb/^{207}Pb$ ratio of pollutant lead was 1.17 (*8, 30−32*) up until 1900, that it declined linearly between 1900 and 1945 to 1.15, and was 1.15 thereafter. A value of 1.15 is selected as the average signature of modern pollution lead in Sweden based on lead isotope analyses of soil organic horizons (mor layers) and ombrotrophic peat bogs (*10, 11*) and atmospheric aerosols (*36*). The decline in the isotope ratio below 1.17 occurred as a result of the importation of Australian lead to Europe and the introduction of alkyl-lead in gasoline, which had characteristically low isotope ratios (*22, 24, 37*).

The chronology in the varved sediments was derived from counting varves from today and backward in time, and the estimated cumulative error is <±50 years for 2000 years. Contiguous 10 year samples were analyzed in Kassjön, and in Norrtjärnsjön contiguous 20 year samples were used. For the other two lakes noncontiguous samples were taken at irregularly selected intervals (20−40 years) to provide reasonable resolution.

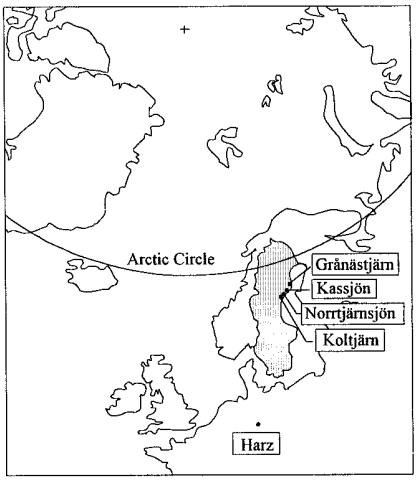

FIGURE 1. Location of studied lakes in Sweden. The distance between Koltjärn and Grånästjärn is about 220 km.

Results and Discussion

Early Lead Pollution. Analyses of radiocarbon-dated, non-laminated sediments, and peat bogs from southern Sweden have previously disclosed that the first signs of an influx of non-Swedish airborne lead date to 3500−4000 years ago (*10*). Some of this early influx of external lead may have been the result of increased long-range transport of soil dust from mainland Europe and the British Isles following forest clearance for agriculture. However, studies of Swedish bogs indicate this flux was not a significant source (*10, 11*) and that pollution-derived lead from metallurgy dominated from at least 2500−3000 years ago (*9, 10*). There was a small peak in airborne lead derived from Greek and Roman cultures occurring about 2000 years ago (*9*), and this early pollution peak is a well-established feature in paleoenvironmental studies of lake sediments and peat bogs in Europe (*9−16*) and the Greenland ice sheet (*5, 6, 8*).

In the varved sediments from northern Sweden, the three lakes with the longest analyzed records, Kassjön, Grånästjärn, and Koltjärn, show relatively stable $^{206}Pb/^{207}Pb$ isotope ratios in the period prior to about 500 B.C. The oldest sediments of these lakes as well as the oldest sediments from Norrtjärnsjön have high isotope values, between 1.45 and 1.55, which are typical for older lake sediments, basal peat layers, and deeper soil mineral horizons (C-horizon) in Sweden. At about 0 A.D., the peak of Greek and Roman air pollution is clearly signaled by a pronounced decline in the $^{206}Pb/^{207}Pb$ ratios in Grånästjärn and Koltjärn (Figure 2). It is not visible in Kassjön because of the relatively high natural lead concentration (~*20* $\mu g\ g^{-1}$ dry sediment) and a high annual influx of soil material from the catchment, which overwhelms the early pollution signal seen in the other lakes. In Norrtjärnsjön the analyzed sediment record only extends back to 800 A.D., and the isotope values from the sediment of that time cannot properly be considered the natural, background ratio; consequently, calculation of the pollution lead concentration using the oldest isotope values in this lake may under-represent the actual pollution contribution.

Following the decline of the Roman empire there was a long period of "clean" conditions between about 400 A.D. and 900 A.D. In Grånästjärn and Koltjärn this is indicated by an increase in the $^{206}Pb/^{207}Pb$ isotope ratios to nearly their background values.

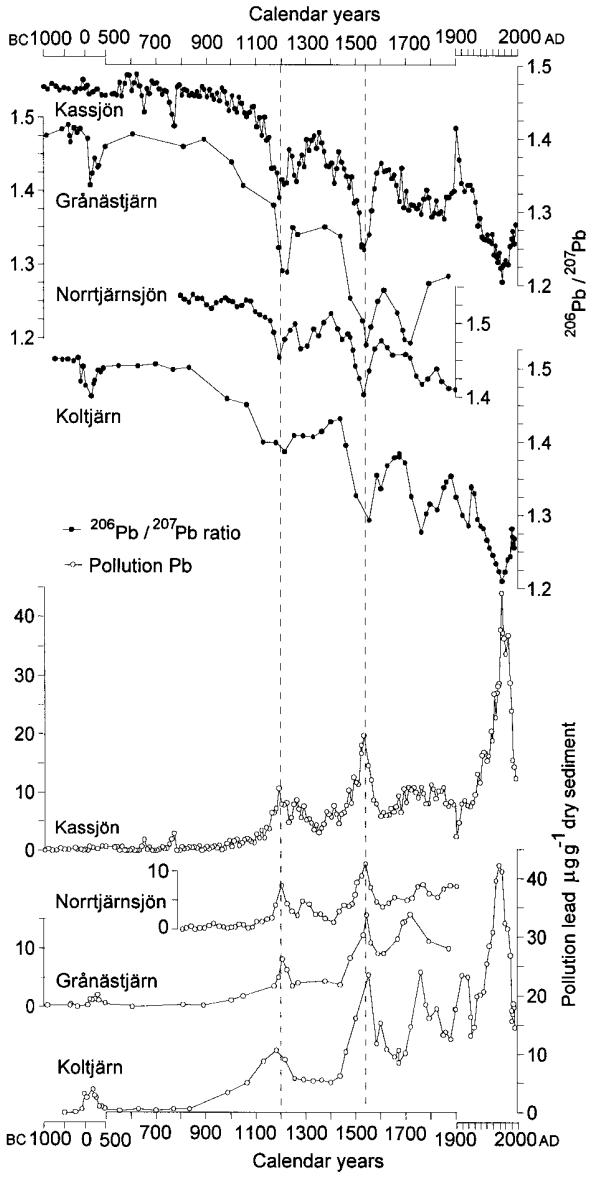

FIGURE 2. ^{206}Pb/^{207}Pb isotope ratios and pollution lead concentrations in sediment cores from four northern Swedish lakes with annually laminated sediments. Results are plotted on a calendar time-scale obtained by counting of the annual laminations (varves). In Norrtjärnsjön the time-scale must be considered a floating chronology because of a disturbance in the varve record in the near surface sediment, and, therefore here, the results are matched to the other lakes using the lead isotope curves. Note, scale changes on the time axis.

Medieval Period (900−1600 A.D.). From 900 to 1200 A.D. there was a large, conspicuous increase in the lead pollution level, reflected by rapid declines in lead isotope ratios in all four varved sediment records. In the high-resolution series (contiguous 10-year samples) from Kassjön there was an increasingly rapid decline from a lead isotope ratio of 1.46 at 900 A.D. to 1.32 at 1200 A.D., with a precipitous decline in the isotope ratio from 1.40 to 1.35 between 1150 and 1170 A.D. This sharp decline is also visible in the sediments of the other three lakes and signals a major increase in atmospheric lead pollution. In the four lakes the contribution of pollution lead increases from $<1\ \mu g\ g^{-1}$ dry sediment prior to 900 A.D. to nearly $10\ \mu g\ g^{-1}$ at 1200 A.D.

The period 900 to 1200 A.D. in Europe was one of both increasing population and economic growth that included an expansion of mining with the discovery of new ore deposits and the reopening of old mines. Metallurgy expanded in several regions, such as in present-day Austria, Czech Republic, Germany, Great Britain, and Poland (*38*, *39*). An important example are the mines in the German Harz mountains (e.g. Rammelsberg), which were established about 980 A.D. and soon became a major producer of silver. Silver was derived from argentiferous lead ores, and lead was also used in the refining processes of the silver (*40*−*42*). Local pollution of lead has been detected in peat bogs in the Harz region, which also show a peak around 1200 A.D. (*13*).

After 1200 A.D., there was a decline in the input of pollution lead to the lake sediments, indicated by the increases in the lead isotope ratio; in Kassjön the ratio increased from 1.34 to 1.40, corresponding to a 50% decline in pollution lead inputs to the sediments. According to historical sources (*38*), an economic decline began after 1200 A.D. and culminated during the Black Death about 1350 A.D., when 25% of the European population died (*43*). After 1400 A.D. lead isotope ratios resumed their decline, and pollution lead concentrations increased in conjunction with a new period of economic expansion that culminated in a minimum in the lead isotope ratios and a maximum in lead concentrations in the sediment records at 1530 A.D. Metal production in Europe reached its peak about 1530 A.D., after which mining and metal production declined as a result of increased exploitation of metal resources in the Americas (*38*, *39*, *44*). There is a remarkable consistency between the records of atmospheric pollution in the varved lake sediments in northern Sweden and the historical data on silver and lead production in Europe.

Modern Period (1600−1997 A.D.). After a minimum in atmospheric lead deposition around 1600 A.D., there is a new peak in the 18th century in the sediments. Thereafter, there is a tendency toward greater inconsistency in specific events as a consequence of the influence from more local lead emission sources and increased local disturbance, e.g. agricultural development, that affected the sediment records of the studied lakes. Although atmospheric lead deposition in northern Sweden increased with the Industrial Revolution, it is not, when seen in a historical perspective, as much as usually assumed. The major increase in lead pollution, to approximately 40 $\mu g\ g^{-1}$ in Kassjön and Koltjärn, did not occur until this century and particularly after the Second World War and the increased use of leaded gasoline (*45*). Reductions in lead emissions since the early 1970s have led to a drastic decline in pollution lead concentrations in the recent varved sediments to one-third the value of the 1970 peak.

In Kassjön and Koltjärn the concentrations of pollution lead in the sediments from the mid-1990s ($10-15\ \mu g\ g^{-1}$) are similar to the concentrations from 1200 A.D. ($10\ \mu g\ g^{-1}$) and less than the concentration peaks about 1530 A.D. ($20\ \mu g\ g^{-1}$). However, it is clear that even lead values from 1200 A.D. were well above the natural conditions. Estimates from ombrotrophic peat bogs in southern Sweden (*11*) as well as in Switzerland (*16*) indicate that the atmospheric lead deposition in the 13th century was 100 times larger than prior to the appearance of anthropogenic pollution 3500−4000 years ago.

Calculation of the total inventory of pollution lead in the varved sediment cores (μg Pb cm^{-2} of the lake bottom) from Kassjön and Koltjärn shows that about 50% of the accumulated atmospheric lead pollution deposited through time in northern Sweden was preindustrial (pre-1800 A.D.). This supports an earlier estimate from lakes in southern Sweden, based on lead concentration analyses only (*9*). Hence, from being virtually overlooked, the cumulative, preindustrial, atmospheric load of long-range transported

lead at high latitudes might obviously deserve more attention in environmental pollution contexts.

Evaluating Source Regions. In studies of Greenland ice (*8*) and ombrotrophic peat in a Swiss bog (*16*), which only contain lead derived from atmospheric deposition, identification of source regions for atmospheric contamination have been assessed using isotope signatures of the lead. Given that our lake sediments contain a catchment-derived lead fraction with high $^{206}Pb/^{207}Pb$ isotope ratios (1.3−2.0) and that the site-dependent ratio may naturally vary by >0.01, while the various lead ores exploited in the historical European mining regions differed in isotope ratios by <0.01, it is not possible to assess the contribution from the individual European source regions to contamination of the Swedish lake sediments using $^{206}Pb/^{207}Pb$ ratios. Therefore, to assess whether each of the different historical mining regions of Europe were viable emission sources for the Medieval lead pollution observed in Swedish sediments, we applied the Heavy Metals Eulerian Transport (HMET) model, which was developed at the Norwegian Meteorological Institute in Oslo to assess present-day, long-range trans-boundary heavy metal pollution in Europe.

The computational domain of the latest version of HMET (*46*), used for this study, covers all of Europe and a large portion of the Atlantic Ocean. The model domain and grid system consist of 1443 nodes located in the center of 150 km × 150 km grid squares at 60° N in Polar Stereographic Projection. Heavy metal emissions are estimated at each node, and they represent the sum of all sources within the corresponding grid square. Meteorological data, e.g. transport wind, precipitation and mixing height, are also assigned to each node. Detailed description of the model (*46*) and the preparation procedure of the meteorological data (*47*) are published elsewhere.

In our computations we have assumed that the 11-year period, 1985−1995, which is the basis for the HMET model, is long enough to represent the atmospheric transport and deposition of lead in the Medieval Period. We use the model to determine whether each of the most well-known historical mining regions of Europe at about 1200 A.D. (*38, 42*) could have contributed to the long-range transport of lead to the lakes in northern Sweden as well as to other Swedish sites. The model was run using known mining locations in England, Wales, Germany, Poland, Austria, and the Czech Republic. Since the emission rates for the selected historical sources are not known, we have assumed a lead emission rate of 1 ton per year for each region and run the model for an 11-year period.

The HMET model shows that each of the known historical mining regions would have been a viable source region for the lead pollution observed in the lake sediments in northern Sweden about 1200 A.D. If we further assume equal emissions from each of the source regions, then the relative importance of each of the mining regions as pollution sources to Sweden would have been the following: England > Germany > Wales > Poland > other regions. As an example, Figure 3 shows the Pb deposition pattern produced by the HMET model when the Harz region in Germany, where the Rammelsberg mines were established about 980 A.D., is incorporated as the emission source. More realistic source apportionment is difficult without detailed examination of lead production records, which exceeds the current scope of this project.

Need for Long-Term Perspectives. As demonstrated here, large-scale south to north transport of airborne lead, and likely also other pollutants, has been in progress for a very long time. Although the earliest origins of lead pollution have their roots in antiquity, the foundation of the contemporary atmospheric lead pollution regime in Europe was established in the Medieval period. If the current decline in pollution

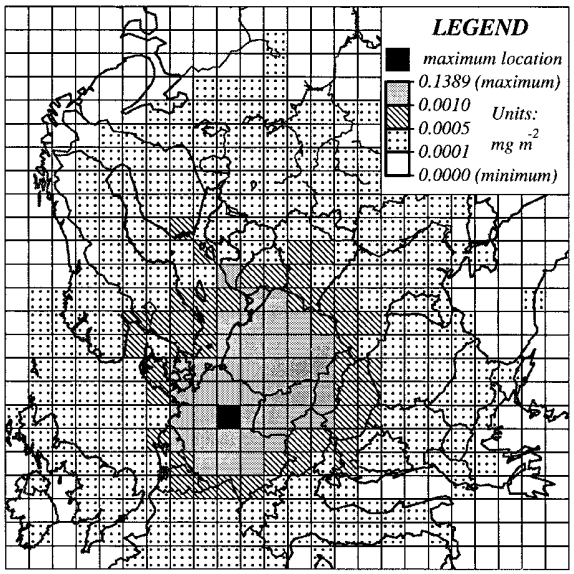

FIGURE 3. Results of calculations with the HMET model for atmospheric lead pollution transport in Europe using the Harz region, Germany, as emitter-grid. The Harz region was a major mining and metal production site about 1200 A.D. when lake sediments in Sweden show a significant Medieval peak in atmospheric lead pollution. The map shows estimated accumulated lead deposition per m^2 assuming an arbitrary lead emission of 11 tonnes per 11 years.

emissions continues, then the Industrial Period (ca. 1800 to today), with large emissions particularly from vehicles using leaded petrol in the 20th century, will represent only a short interval in the history of atmospheric lead pollution, although with higher pollution deposition levels than ever before.

Long prior to the Industrial Revolution, pollution lead became the totally dominant source of lead in the remote north Scandinavian environment, and the same must have applied to areas closer to the main sources in old cultural areas of Europe. It was hypothesized at least 20 years ago that a general increase of the lead concentration in the atmosphere of the Northern Hemisphere occurred as early as 2000 years ago (*39*). Given the widespread atmospheric lead pollution, it is impossible to find unpolluted reference areas in the present-day environment even in the most remote areas. However, environmental archives preserved in lake sediments, peat bogs, and glacial ice give us valuable insights into the natural, unpolluted environment and allow improved estimates of natural baseline values. Many environmental concerns, e.g. heavy metal pollution and lake acidification (*48*), must be viewed in a light of long-term changes in order to properly understand the current situation and to assist with establishing future goals.

Historically, fluctuations in lead deposition reflected trends in European economies. In contrast, declines in lead deposition since the early 1970s are largely the result of the successful implementation of stricter emission controls and large reductions in the use of alkyl-lead additives in petrol. The recent decline provides a positive example of how pollution regulations can lead to improvements in the environment.

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