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Key Points:

- First evaluation of past cadmium and lead anthropogenic emissions in Europe by alpine ice records and model simulations over the Alps
- Maximum of cadmium pollution in Europe in 1980 instead of 1965 due to less efficient reduction of emissions than predicted
- Maximum pollution by cadmium from zinc smelters and by lead from leaded gasoline in the late 1970s in Europe

Supporting Information:

- Supporting Information S1

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Cadmium Pollution From Zinc-Smelters up to Fourfold Higher Than Expected in Western Europe in the 1980s as Revealed by Alpine Ice

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Abstract Estimates of past emission inventories suggest that toxic heavy metal pollution in Europe was highest in the mid-1970s for lead and in the mid-1960s for cadmium, but these previous estimates have not been compared to observations. Here, alpine ice-cores were used to document cadmium and lead pollution in western Europe between 1890 and 2000. The ice-core trends show that while lead pollution largely from leaded gasoline reached a maximum in ~1975 as expected, cadmium pollution primarily from zinc smelters peaked in the early-1980s rather than in ~1965 and was up to fourfold higher than estimated after 1975. Comparisons between ice-core trends, estimated past emissions, and state-of-the-art atmospheric aerosol transport and deposition modeling suggest that the estimated decreases in cadmium emissions after 1970 were based on overly optimistic emissions reductions from the introduction of pollution control devices and other technological improvements.

Plain Language Summary Cadmium and lead are among the most toxic heavy-metal pollutants and identified by international conventions as priority contaminants for emissions reduction. Anthropogenic emissions in Europe previously estimated from commodity production statistics are uncertain; comparison with long-term pollution records extracted from well-dated ice cores provides a means of evaluating these estimates. Alpine ice-core records spanning 1890 to 2000 show that lead pollution, mainly related to leaded gasoline use since the mid-20th century, reached a maximum in the mid-1970s as predicted by estimated past emissions. Surprisingly, however, cadmium levels primarily arising from zinc smelter emissions were up to fourfold higher than expected and decreased only after 1980, suggesting that previous reconstructions of past cadmium pollution had assumed overly optimistic emissions reductions from the introduction of pollution control devices and other technological improvements particularly after 1975. Contrary to previous emissions estimates, these new alpine ice-core records show that western European pollution maxima for these two toxic metals coincided in the 1970s. This finding is important in terms of impact of Cd pollution on organisms that depends on concentration in the environment but also duration of exposure.

1. Introduction

The atmospheric concentrations and deposition of heavy metals have increased since pre-industrial times because of human activities, sometimes causing adverse health effects in humans as well as wildlife and the environment (Nriagu, 1990). Among toxic metals, cadmium (Cd), lead (Pb), and mercury (Hg) were identified by international conventions as priority contaminants (Vestreng et al., 2006). Based on statistical information and emission factors (EFs) estimated for relevant emission source categories (fossil fuel and ore consumption, production of various types of industrial goods), global anthropogenic emissions were calculated for 1983 and the mid-1990s (Nriagu & Pacyna, 1988; Pacyna & Pacyna, 2001). At the scale of Europe, several studies estimated anthropogenic emissions every 5 to 10 years from 1955 to 2000 (Olendrzyński et al., 1996; Pacyna & Pacyna, 1999; Pacyna et al., 2009), but little is known prior to 1955. Air and precipitation monitoring, available in Europe since 1990 for Pb and Cd (Pacyna et al., 2009), permit evaluation of post-1990 declines in emissions. However, no direct atmospheric observations are available either for the

1965–1975 period thought to correspond to peak emissions (Pacyna et al., 2009) or to evaluate expected decreases following implementation of various policies in Europe to reduce emissions. Moreover, no inventories exist for Europe from 1955 back to the onset of the industrial period (~1850). Evaluation of anthropogenic perturbations also requires understanding of natural sources and estimates developed through extrapolation of sparse data sets have large uncertainties (e.g., a factor of 20 for Pb and Cd, Nriagu, 1979). In its 2015 status report, the European Monitoring and Evaluation Programme (EMEP) concluded that uncertainties in available emission data are still significant for recent decades, and there is a need to better quantify the contributions of anthropogenic versus natural sources at remote sites to develop further strategies for emission reductions (Ilyin et al., 2015).

Except for Hg that is poorly scavenged from the atmosphere by precipitation, well-dated ice-cores have been studied to evaluate past deposition of numerous metals and thus can help to reduce emissions uncertainties. Records from Greenland ice-cores documented past pollution from growing anthropogenic emissions of Pb and Cd from industrialized regions of the Northern Hemisphere, particularly North America (McConnell & Edwards, 2008). More intimately connected to European emissions, alpine ice records have been used to evaluate several aspects of pollution over Europe, with most studies conducted at Colle Gnifetti (Monte Rosa, CG) (Schwikowski, 2004; Wagenbach et al., 1988, 2012) and Col du Dome (Mont Blanc, CDD) (Preunkert & Legrand, 2013).

The longest alpine ice-core records have been obtained at CG due to low snow accumulation rate, with continuous profiles of Pb and Cd extending back to the Middle Ages (Gabrieli, 2008; Gabrieli & Barbante, 2014; Schwikowski et al., 2004). These records identified a large increase of pollution between ~1960 and 1980 and a subsequent recent (1980 to 1995) decrease. Given the larger pollution deposition in summer relative to winter (a factor of 5 to 10, Preunkert et al., 2002) when vertical atmospheric mixing is strong, accurate interpretation of ice records extracted from a low snow accumulation site is limited by large uncertainties in the seasonal variations in snow deposition and/or preservation affected by preferential wind scouring of winter snowfall. At CDD, winter snow scouring occurs, but the high snow accumulation rate at the site enables distinguishing between summer and winter layers in the ice dating back to the past century (Wagenbach et al., 2012). Prior to this study, no seasonally resolved ice records of metals have been reported from the CDD site.

We developed a seasonally resolved continuous ice-core record of Pb, Cd, and Zn concentrations spanning the 20th century from ice-cores extracted at CDD. We targeted the toxic heavy metals Pb and Cd, as well as Zn as an indicator of emissions from zinc-smelters, which also are prominent sources of Cd emissions. We interpreted these ice-core records in the context of reported European emissions and statistics of various source categories together with state-of-the-art FLEXPART atmospheric transport and deposition modeling.

2. Materials and Methods

2.1. Ice-Core Material and Dating

Chemical measurements were made on two ice-cores extracted at Col du Dome (4,250 m above sea level, French Alps). Melting of surface snow occasionally occur at the site; however, the thickness of the infiltration ice layers does not exceed 0.2 m, which is small compared to the annual layer thickness of 1.25 to 4.35 m water equivalent (Preunkert et al., 2000). The C10 core (126 m long) was drilled in 1994, and the CDM core (140 m long), extracted less than 20 m away from the C10, was drilled in 2012. Initially allocated to the study of metals, halogens, and organic carbon, the analysis were restricted to the ice portion of the core to avoid potential contamination of porous firn portion of the core by organics (Legrand et al., 2013) and loss of iodine from the firn after core extraction (Legrand et al., 2018). In addition to analyzing the ice portion of the C10 core (55.0 to 125.7 m depth), we extended the time period to span the years between 1983–2000 (i.e., 46.1 to 78.0 m depth) in the CDM core.

The upper sections of both cores were dated by annual layer counting primarily using pronounced seasonal variations in ammonium concentrations (summer to winter ratio exceeded 10, supporting information Figure S1). Winter layers generally thin with depth relative to summer layers because of changes in depositional processes upstream of the CDD drilling site, although we were able to identify winter layers for annual layer counting back to 1890. However, many of these winter ammonium minima were too thin to reliably

determine winter concentrations of Pb, Cd, and Zn, so prior to 1930, only five winter values were calculated (Figure 1). Note also that during the 1960s, samples corresponding to full winter (based on ammonium values) were rather sparse, and eight winter values were not calculated. The resulting chronology was assigned an age of 1890 at 118.3 m (Legrand et al., 2018). Prior to 1890, no winter snow was preserved, but the age of the 7 lowest meters (below 118.3 m depth) of the C10 core were estimated to cover at least the period 1830–1890 (i.e., prior to the onset of the pre-industrial period in ~1850) (Text S1). Past summer trends including during the pre-industrial time period are thus better documented, so in the following we evaluate and discuss mainly summer trends.

2.2. Measurements of Metals and Comparison With Previous Studies

CDD ice-cores were analyzed for a broad range of elements using the continuous flow ice-core analytical system at the Desert Research Institute (DRI) Ultra Trace Chemistry Laboratory (McConnell et al., 2019). Longitudinal samples (3.3×3.3 cm cross section) were melted sequentially on a heated ceramic melter head and the meltwater stream split into three regions by ridges engraved in the melter head. Pb, Cd, Zn, and co-analyzed species such as cerium (Ce) were measured in the meltwater from the innermost ring (10% of the sample volume) using two high-resolution inductively coupled plasma-mass spectrometers (HR-ICP-MS) operating in parallel. The detection limits, defined as three times the standard deviation of the blank, were 0.0004 ng g^{-1} for Pb, 0.0001 ng g^{-1} for Cd, 0.009 ng g^{-1} for Zn, and 0.0003 ng g^{-1} for Ce. Our new CDD measurements are in excellent agreement with previously published, discrete measurements performed on CDD ice-cores (Table S1). Comparison with those previously obtained at CG indicates slightly higher values at CG than at CDD, likely due to less winter snow preservation at CG than at CDD (Wagenbach et al., 2012).

2.3. The Crustal Fraction of Zn, Cd, and Pb

Many metals are naturally emitted within the atmosphere along with soil and desert dust particles. The crustal contribution to each metal can be estimated from Ce measurements using the “mean sediment” metal-to-Ce ratio (Bowen, 1966). Measurement of total concentrations of Ce that is part of relatively insoluble dust is, however, influenced by acidification times because Ce remains in the particle phase longer than other elements associated with pollution that are adsorbed onto small particles and are readily washed from the outside of the particles during on-line acidification of the continuous analytical system. Previous assessment of measurement recovery during continuous measurements with the DRI system indicated that recovery was 100% and 60% for Pb and Ce, respectively (McConnell et al., 2018). We assume a similarly high recovery for Zn and Cd since they are also mainly associated with pollution.

Since the metal/Ce ratio can deviate from the “mean sediment” value and so result in an incorrect determination of the crustal component, we used an alternative approach to estimate site-specific metal/Ce ratios using ice samples containing relatively high dust or low anthropogenic contributions. First, in ice samples deposited over the recent decades we used alkalinity to select samples containing high Saharan dust concentrations (Wagenbach et al., 1996). Second, we assumed that non-crustal contributions were negligible in some samples deposited during pre-industrial time. Using both approaches, relationships between the metals and Ce in dust-dominated CDD samples suggest site-specific crustal ratios of 1.9 for Zn/Ce, 0.02 for Cd/Ce, and ~0.4 for Pb/Ce (Figure S3, Text S2). After correcting the Ce concentrations for the 60% under-recovery, these site-specific crustal ratios are 1.12 for Zn compared to 1.15 in mean sediment, 0.012 instead of 0.002 for Cd, and 0.23 (i.e., similar to the mean sediment value) for Pb.

2.4. FLEXPART and Metal Deposition Fluxes at CDD

To compare the CDD ice-core summer trends with estimated past emissions in relevant countries we used the Lagrangian particle dispersion model FLEXPART by applying a recent development that allows running the model backward in time for dry and wet deposition (Eckhardt et al., 2017; Stohl et al., 2005). The model maps the sensitivity of deposition at the CDD site to emission flux. The model was run in backward mode at monthly intervals for the period 1901 through 1999, and particles were traced backward for 30 days. As meteorological input to FLEXPART, we used the recently completed coupled climate reanalysis for the 20th century (CERA-20C) (Laloyaux et al., 2018) performed at the European Centre for Medium Range Weather Forecasts at a resolution of $2^\circ \times 2^\circ$ and every 6 hr. As metal aerosol produced by pollution consists of fine particles (diameter range of $0.5\text{--}1.2 \mu\text{m}$, Nriagu, 1990) the model was run for $0.4 \mu\text{m}$ diameter aerosol.

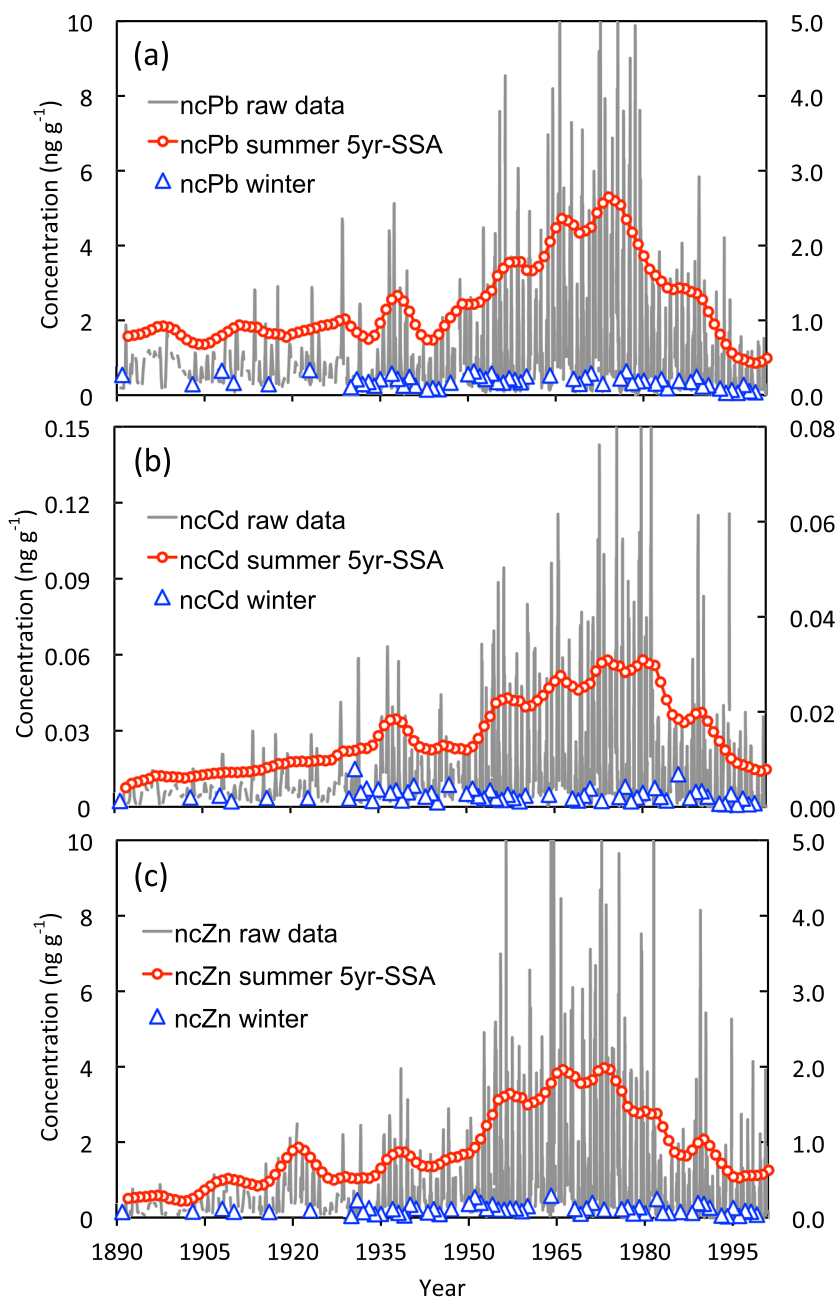


Figure 1. The 1890–2000 CDD ice records of non-crustal lead (a), cadmium (b), and zinc (c). The gray lines refer to raw data (left scales). The red curves and blue symbols are the smoothed summer profiles (first component of single spectra analysis with a 5-year time window, 5 year SSA) and winter values, respectively (right scales).

Average summer emission sensitivity reported in Figure S4 was used to calculate summer deposition at CDD. Changing the aerosol size from $0.4 \mu\text{m}$ to $1 \mu\text{m}$ leads to a decrease by 30% of emission sensitivities in the countries surrounding the Alps (Figure S5), and the calculated depositions at CDD are similarly reduced, but the long-term temporal trends remain essentially identical.

2.5. Past Emissions in Europe

Past anthropogenic emissions of Pb, Cd, and Zn already were estimated for individual European countries (Olendrzyński et al., 1996; Pacyna & Pacyna, 1999; Pacyna et al., 2009) for the 1955–2000 time period, based on statistical data, EF values, and their changes over time. While accurate information is available from

European national authorities to quantify the reduction of Pb additive in gasoline, there is much more uncertainty associated with the decrease of EFs for non-ferrous smelters as well as the iron and steel industry during the 1980s (Pacyna, 1991). The smelting-related EFs are assumed to have decreased with the progressive installation of electrostatic precipitators and filters in the mid-1970s, initial flue gas desulfurization (FGD) installations in the mid-1980s, and further deployment of FGD in the 1990s. EFs proposed for the 1950s and 1960s (Table S2) are estimated to have decreased in the 1980s by a factor of 3 for non-ferrous smelters and a factor of 5 for iron and steel manufacturing (Pacyna, 1991). For Cd emissions from Zn smelters, an EF value of 1,500 g per ton of zinc produced has been proposed as an upper limit. When using the imperial smelter furnace (ISF) process, EF drops to 50 g per ton of zinc produced. We have limited information on the use of this technique in various European countries over the recent past. Since 1986, ~33% of production in France and 20% in Germany used ISF, whereas ISF was not used either in Spain or in Belgium (Minemet, 1986). In our calculations we therefore have applied an average EF value of 1,200 g of Cd per tons of zinc produced.

To extend the reconstruction prior to 1955 and discuss some discrepancies between ice-core trends and past deposition at CDD calculated by FLEXPART from estimated 1955–2000 emissions, we calculated past emissions using statistics of relevant sources categories in European countries. We used annual coal consumption, as well as pig iron and steel production statistics available prior to 1975 (Mitchell, 1975). For the 1975–2000 period, we used coal consumption from British Petroleum (<http://tools.bp.com/energy-charting-tool>). For non-ferrous metallurgy (primary and secondary productions from Zn, Pb and Cu smelters, Pb mining), as well as pig iron and steel production, we used statistical data from (Schmitz, 1979). For the more recent years we used data from Minéraux et métaux statistiques and U.S. Geological Survey statistics (n.d.). We have assumed EF values reported for prior to 1970 as detailed in Table S2. For Pb, statistical data on leaded gasoline emissions derived from Pacyna et al. (2009) and Pacyna and Pacyna (1999) were used here since the past amount of lead additive is fairly well documented for each country. For leaded gasoline emissions prior to 1955, we scaled down emissions from the different countries reported in Pacyna et al. (2009) using statistical data on oil consumption from Mitchell (1975). Since we focused on summer changes, we have considered the seasonality of emissions from coal burning that are about double in winter compared to summer in most European countries (except in the south), whereas emissions from all other sources can be assumed to be constant throughout the year (Fagerli et al., 2007).

3. Results and Discussions

3.1. High-Resolution Alpine Ice Record of Pollution by Lead, Cadmium, and Zinc

Sub-annually resolved measurements of Pb, Cd, and Zn in alpine ice provide complete emission records over the 20th century. To isolate variations in the ice record caused by anthropogenic emissions, we subtracted crustal contributions determined using cerium (McConnell & Edwards, 2008). Such corrections account for an increase of the crustal material deposited at CDD, particularly after 1960 (Preunkert & Legrand, 2013). On average between 1890 and 2000, the crustal contributions comprised the total 1% for Pb, 6% for Cd, and 9% for Zn.

The quasi-continuous (1890–2000) records of non-crustal Pb (ncPb), Cd (ncCd), and Zn (ncZn) are reported in Figure 1 together with mean summer and winter levels. The use of annual mean (M-yr) ice concentrations, as commonly done in previous studies of metals in alpine ice-cores, may bias the atmospheric signal because of year-to-year changes in winter relative to summer snow deposition and preservation. This is particularly true for metals that exhibit pronounced seasonal contrast (typical summer to winter ratios are 5 to 10, Figure S1). To avoid the potential bias of using averaged M-yr concentrations, ice-core trends can be compared to past emissions on a seasonal basis (summer and winter) or using annual arithmetic means calculated using the respective summer and winter level in each year (M-W/S). As seen in section 2.1, past summer trends including during the pre-industrial are better documented, and in the following we evaluate and discuss mainly summer trends.

The summer pre-industrial values are close to 0.001 ng g^{-1} for ncCd and 0.080 ng g^{-1} for ncZn (prior to ~1875) and 0.025 ng g^{-1} for ncPb (pre- and post-Roman period) (Table S3). The three times higher pre-industrial level of ncZn compared to ncPb is very consistent with estimates of global natural emissions of non-crustal Zn (26 kt ons a^{-1}) and Pb (8 kt ons a^{-1}) (Nriagu, 1979). Global natural emissions of non-crustal Cd

are far lower (1.1 ktons a^{-1}) (Nriagu, 1979). The difference by a factor of ~ 25 in global natural emissions of ncZn and ncCd is lower, however, than the difference in ice pre-industrial levels (a factor of 80). Since natural non-crustal emissions of Cd are dominated by volcanic emissions (0.8 ktons a^{-1} out of a total of 1.1 ktons a^{-1}), it is possible that while Cd volcanic emissions are dominant at a global scale, they have a weaker impact on Europe.

The ncPb summer levels that already largely exceeded its pre-industrial ice level ($<0.1 \text{ ng g}^{-1}$, Table S3) at the beginning of the 20th century slightly rose from 0.8 ng g^{-1} in 1890 to 1.2 ng g^{-1} in 1950 (Figure 1). After 1950, summertime ncPb levels rapidly increased to a maximum of $\sim 2.6 \text{ ng g}^{-1}$ at the beginning of the 1970s, after which levels sharply decreased over the following three decades, the level in 2000 ($\sim 0.5 \text{ ng g}^{-1}$) being almost half of those observed at the beginning of the 20th century. The long-term trends of ncCd and ncZn are similar but differ from ncPb, with a smaller relative increase above the pre-industrial background (0.001 to 0.005 ng g^{-1} for ncCd) at the beginning of the century, and a less marked decrease after the 1970s, with levels remaining higher ($\sim 0.008 \text{ ng g}^{-1}$ for ncCd) in 2000 than at the beginning of the century. Note that decreased preservation of winter snow in the 1960s (section 2.1) resulted in maximum M-yr values in ~ 1965 for all three species, in contrast with the maximum M-W/S means (similar to summer means) for ncPb and ncCd that indicate maxima in ~ 1975 and ~ 1980 , respectively (Figure S5).

3.2. Past Emissions of Pb, Cd, and Zn in European Countries and Deposition at CDD

Past metal deposition fluxes at CDD were calculated from estimated past emissions in European countries that were weighted by the emission sensitivities (averaged for each country) of the site calculated by the Lagrangian particle dispersion model FLEXPART. Average summer emission sensitivities calculated by FLEXPART (Figure S4) indicate that CDD is most sensitive to emissions originating from countries surrounding the Alps, in decreasing order Switzerland (CH), France (FR), Italy (IT), Spain (ES), ex West Germany (W-DE), Belgium (BE), and United Kingdom (UK).

Three emissions scenarios were used to estimate past depositional fluxes at CDD by scaling emission estimates for each country by the country's average FLEXPART emissions sensitivity. The first scenario estimates fluxes for recent decades using previously published country-specific metal emissions from 1955 to the 1980s (Olendrzyński et al., 1996; Pacyna & Pacyna, 1999) and for 2000 (Pacyna et al., 2009) on the basis of statistical data and considering successive reductions of emission factors (EFs) beginning in the 1970s (Figure 2; red squares denoted Scenario [1]).

The second scenario estimates depositional fluxes back to 1850 (Figure 2; blue triangles denoted Scenario [2]) using statistical data of relevant source categories for Pb, Cd, and Zn emissions including smelters (lead, zinc, and copper), pig iron and steel manufacturing, and coal consumption available since 1850. For these source categories, we have used the same EFs as for 1955–1970 (Table S2). For Pb emissions, we also considered lead mining and gasoline consumption. Since Pb emissions from leaded gasoline are accurately known based on applied regulations in each European country, we used the Pb emissions from leaded gasoline calculated for each country for 1955 (i.e., the same as in Scenario [1]).

The third scenario also calculates metal deposition for 1970 to 2000 using statistical emissions data from Scenario [1] but uses pre-emissions-control EFs (i.e., does not account for reduction in EFs associated with emissions regulation since 1970) (Figure 2; Emissions Scenario [3]). As in Scenarios [1] and [2], we used the Pb emissions from gasoline calculated for each country in Pacyna et al. (2009) and Pacyna and Pacyna (1999). As seen in Figure 2, for recent decades the three emissions scenarios are consistent for lead, as the three scenarios all use the same leaded gasoline emissions estimates. For Zn and Cd, a good agreement between Scenarios [1] and [2] is observed from 1955 to 1970 as expected. The large difference between Scenarios [1] and [3] after 1970 is due to the difference in EFs and shows how reduced EFs from non-ferrous smelters (Pb, Zn, and Cu) as well as iron and steel industry after 1970 counteracted increased productions from most source categories (except coal consumption that decreased by a factor of 2 from 1965 to 2000).

The estimated deposition of anthropogenic Pb, Cd, and Zn at CDD partitioned by source at the beginning of the 20th century and in 1955 to 1970 are detailed in Figure S6. For anthropogenic Pb, the main emissions were Zn and Pb smelting at the beginning of the 20th century and leaded gasoline in the 1960s and 1970s. At the start of the 20th century, Pb deposition from Zn smelting was approximately evenly split between

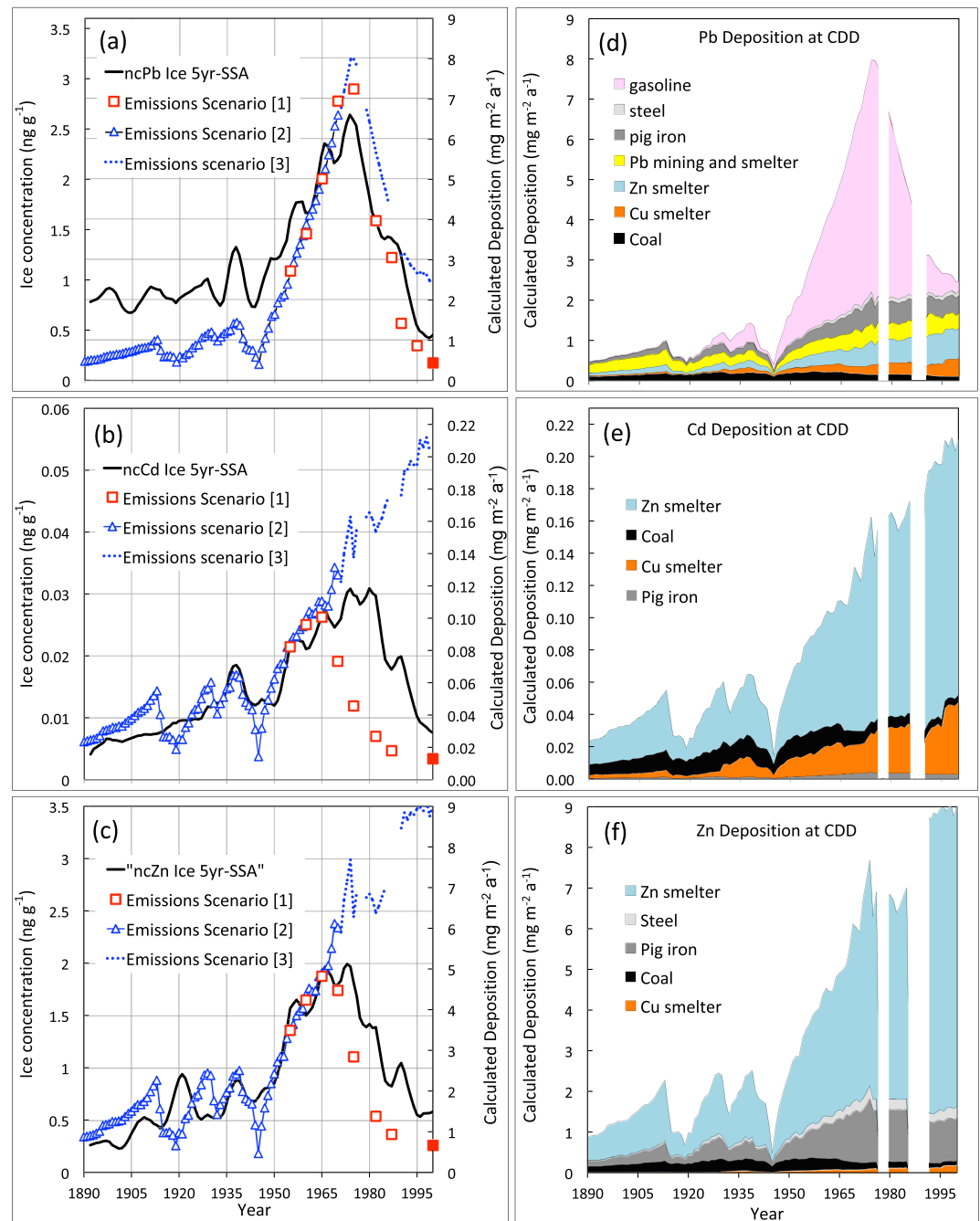


Figure 2. (a–c) Summer ice-core trends of non-crustal concentrations (black lines: 5 year SSA) and anthropogenic deposition fluxes at CDD calculated using FLEXPART simulations and estimated past anthropogenic emissions from 1890 to 2000. Red squares and blue triangles refer to deposition fluxes obtained by using 1955–2000 emissions (see section 2.5), and 1890–1970 statistical data with EFs for prior to 1970 (except for coal, Table S2), respectively. The dashed blue line is calculated deposition after 1970 keeping the same EFs for non-ferrous and ferrous metallurgy as before 1970. (d–f) Estimated summer deposition fluxes since 1890 related to the different source categories and applying assumptions made for Scenario [3] (see section 3.2). Blanks in the 1975–1979 and 1985–1991 years denote lack of statistical data.

FR, BE, and W-DE, as the ~3–4 times lower Zn production in FR compared to BE and W-DE was compensated for by its much higher emissions sensitivity (Table S4). Contributions from Pb smelting were dominated by ES, with lesser contributions from W-DE and FR. In 1955 to 1970, Pb deposition from

leaded gasoline emissions was primarily sourced from FR, followed by IT. For anthropogenic Zn and Cd, Zn smelting dominated emissions since 1890 (Figure S6), though country-specific contributions evolved over the 20th century. Zn smelting contributions to both Zn and Cd deposition were evenly split between FR, BE, and W-DE at the beginning of the 20th century but dominated by FR from 1955 to 1970 (Table S4). BE followed by FR became the largest Zn producers over recent decades.

It is not possible to directly compare calculated FLEXPART deposition fluxes to ice-core concentrations because of uncertainties associated with precipitation rates simulated by the coarse-resolution model (220 km \times 155 km for the CDD grid cell), partly related to the fact that the alpine orography is not well resolved, and because the annual layer ice thicknesses, which decrease with depth due to ice thinning, do not directly represent past precipitation rates. Nevertheless, relative changes of ice concentrations should be related to past changes in emissions and EFs.

3.3. The 1890–2000 Lead and Cadmium Pollution

It is first interesting to note that the calculated deposition of ncPb and ncZn ($\sim 5 \text{ mg m}^{-2} \text{ a}^{-1}$ in 1965) is ~ 50 –70 times higher than ncCd deposition ($\sim 0.1 \text{ mg m}^{-2} \text{ a}^{-1}$ in 1965), consistent with the ~ 70 times higher measured ice concentrations of ncPb and ncZn ($\sim 2 \text{ ng g}^{-1}$ in 1965) relative to ncCd ($\sim 0.3 \text{ ng g}^{-1}$) (Figure 2).

We begin the comparison between ice-core trends and past emissions for the most recent time-period over which more information on emissions are available. The ncPb summer ice trend shows a rapid increase of lead pollution over the second half of the 20th century that reached a maximum in ~ 1975 before subsequently decreasing by a factor of 6 by 2000 (Figure 2a). The changes observed in the CDD ice-core are consistent with estimates of past anthropogenic Pb deposition at CDD that were dominated by leaded gasoline emissions (almost 70% in 1965), with smaller contributions from non-ferrous smelters ($\sim 15\%$ in 1965), pig iron and steel (10%, mainly from pig iron), and coal (4%) (Figure S6). The post-1975 ncPb decrease is attributed to the reduction of Pb additives to gasoline that reduced gasoline-derived Pb emissions despite the continuous growth of gasoline consumption. Using the same leaded gasoline emissions, the two estimates of Pb deposition (triangles and squares in Figure 2) agree well during the rapid increases of emissions related to leaded gasoline. As leaded gasoline emissions declined during the mid-1990s, calculations assuming pre-emissions control EFs for non-ferrous smelters and pig iron production (Scenario [3] in Figure 2) clearly overestimated the contribution of emissions from these two sources at that time.

The ice-core ncCd trend indicates a steady increase from 1950 until the 1980s (Figure 2b), whereas past deposition calculated using Scenario [1] indicates a maximum in the mid-1960s followed by a rapid decrease to 2000. Similarly, the ice-core ncZn peaks in the mid-1970s, whereas calculated emissions peak in the mid-1960s. The 10–15 year delay between the peak Cd and Zn emissions in Scenario [1], and the ice-core data are likely a result of poorly constrained EFs for Zn smelting, the dominant emissions source for both metals, compared to the much better quantified decrease of Pb additives used in gasoline. Figure 2 suggests that the EFs from Zn smelters may have only decreased by a factor of 2 instead of 4–5 from ~ 1970 to 1980, a factor of 5 instead of 10 from ~ 1970 to 2000.

In conclusion, the observed changes of Pb, Cd, and Zn at CDD over recent decades indicate that the decrease of ice concentrations of Cd (consistent with Zn) is less than expected based on previous estimates of decreasing emissions factors after 1970, in particular from non-ferrous metal smelting.

The calculated deposition fluxes at CDD indicate an increase by a factor of ~ 3 from 1890 to 1950 for anthropogenic Pb, Cd, and Zn (Figure 2). This increase is comparable to the observed increases of ncZn and ncCd ice concentrations (a factor of 3 and 2.2 from 1890 to 1950, respectively) but is larger than the observed increase of ~ 1.5 for ncPb ice concentrations. At the beginning of the 20th century, Pb emissions were dominated by Pb mining and smelting (42% of total), and both Zn and Cd emissions were dominated by Zn smelters (Figure S6). The difference between the estimated Pb deposition and ncPb ice-core concentrations suggest that the EFs used at the beginning of the 20th century underestimate emissions by a factor of 2–3 with respect to the 1955 value.

At the beginning of the industrial period, the statistics indicate a more rapid increase of emissions for Zn and Cd (a factor of 3 from 1860 to 1885) than for Pb (a factor of 1.7), likely a result of significant Pb production in Spain in the mid-19th century (Table S4). The larger anthropogenic emissions of Pb compared to Cd and Zn

at the very beginning of the industrial era are partly reflected in ice, with ncCd and ncZn concentrations near their pre-industrial (1700 to 1835) values in 1875, whereas ncPb were already 20 times above its pre-industrial baseline at that time (Table S3).

4. Conclusions

Continuous chemical measurements in alpine ice-cores were used to document preindustrial and year-by-year, 1890 to 2000 summer Cd and Pb pollution in western Europe, with ancillary measurements of Zn and Ce used for source apportionment. For the first time, alpine ice-core trends were evaluated in detail using new pollution estimates for the region based on country-specific emissions derived from updated source-category statistics, as well as state-of-the-art atmospheric aerosol transport and deposition modeling. Comparisons with existing pollution reconstructions back to 1955 show that while Pb pollution largely from leaded gasoline was similar to estimates, Cd pollution primarily from Zn smelter emissions was up to four-fold higher between the mid-1970s and 2000. In addition, peak Cd pollution occurred in the early-1980s (i.e., almost coinciding with the Pb maximum) rather than the mid-1960s as previously thought. It is suggested that previous reconstructions of Cd pollution assumed overly optimistic emissions reductions from the introduction of pollution control devices and other technological improvements particularly between 1965 and 1980. This finding has implications for the impact of Cd pollution throughout ecosystems, which is sensitive to the concentration in the environment and also the duration of exposure.

Acknowledgments

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