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► **To cite this version:**

Michel Legrand, Joe McConnell, L. Lestel, Susanne Preunkert, Monica Arienzo, et al.. Cadmium Pollution From Zinc-Smelting up to Fourfold Higher Than Expected in Western Europe in the 1980s as Revealed by Alpine Ice. *Geophysical Research Letters*, 2020, 47 (10), 10.1029/2020GL087537. hal-03039001

HAL Id: hal-03039001

<https://hal.science/hal-03039001>

Submitted on 11 Dec 2020

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Cadmium pollution from zinc-smelters up to four-fold higher than expected in western Europe in the 1980s as revealed by alpine ice

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Key Points:

- First evaluation of past cadmium and lead anthropogenic emissions in Europe by using 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

25 **Abstract**

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

37 **Plain Language Summary**

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

53 **1 Introduction**

54 The atmospheric concentrations and deposition of heavy metals have increased since pre-
55 industrial times because of human activities, sometimes causing adverse health effects in humans
56 as well as wildlife and the environment (Nriagu, 1990). Among toxic metals, cadmium (Cd), lead
57 (Pb), and mercury (Hg) were identified by international conventions as priority contaminants
58 (Vestreng et al., 2006). Based on statistical information and emission factors (EFs) estimated for
59 relevant emission source categories (fossil fuel and ore consumption, production of various types
60 of industrial goods), global anthropogenic emissions were calculated for 1983 and the mid-1990s
61 (Ngjaru & Pacyna, 1988; Pacyna & Pacyna, 2001). At the scale of Europe, several studies
62 estimated anthropogenic emissions every 5 to 10 years from 1955 to 2000 (Olendrzynski et al.,
63 1996; Pacyna & Pacyna, 1999; Pacyna et al., 2009), but little is known prior to 1955. Air and
64 precipitation monitoring, available in Europe since 1990 for Pb and Cd (Pacyna et al., 2009),
65 permit evaluation of post-1990 declines in emissions. However, no direct atmospheric
66 observations are available either for the 1965-1975 period thought to correspond to peak
67 emissions (Pacyna et al., 2009) or to evaluate expected decreases following implementation of
68 various policies in Europe to reduce emissions. Moreover, no inventories exist for Europe from

69 1955 back to the onset of the industrial period (~1850). Evaluation of anthropogenic
70 perturbations also requires understanding of natural sources, and estimates developed through
71 extrapolation of sparse datasets have large uncertainties (e.g., a factor of 20 for Pb and Cd
72 (Nriagu, 1979)). In its 2015 status report, the European Monitoring and Evaluation Programme
73 (EMEP) concluded that uncertainties in available emission data are still significant for recent
74 decades and there is a need to better quantify the contributions of anthropogenic versus natural
75 sources at remote sites to develop further strategies for emission reductions (Ilyin et al., 2015).

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

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

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

103 **2 Materials and Methods**

104 **2.1 Ice-core material and Dating**

105 Chemical measurements were made on two ice-cores extracted at Col du Dome (4,250 m
106 above sea level, French Alps). Melting of surface snow occasionally occur at the site, however,
107 the thickness of the infiltration ice layers does not exceed 0.2 m, which is small compared to the
108 annual layer thickness of 1.25 to 4.35 meters water equivalent (Preunkert et al., 2000). The C10
109 core (126 m long) was drilled in 1994 and the CDM core (140 m long), extracted less than 20 m
110 away from the C10, was drilled in 2012. Initially allocated to the study of metals, halogens, and
111 organic carbon, the analysis were restricted to the ice portion of the core to avoid potential

112 contamination of porous firn portion of the core by organics (Legrand et al., 2013) and loss of
113 iodine from the firn after core extraction (Legrand et al., 2018). In addition to analyzing the ice
114 portion of the C10 core (55.0 m to 125.7 m depth), we extended the time period to span the years
115 between 1983-2000 (i.e., 46.1 to 78.0 m depth) in the CDM core.

116 The upper sections of both cores were dated by annual layer counting primarily using
117 pronounced seasonal variations in ammonium concentrations (summer to winter ratio exceeded
118 10, Fig. S1). Winter layers generally thin with depth relative to summer layers because of
119 changes in depositional processes upstream of the CDD drilling site, although we were able to
120 identify winter layers for annual layer counting back to 1890. However, many of these winter
121 ammonium minima were too thin to reliably determine winter concentrations of Pb, Cd, and Zn
122 so prior to 1930, only five winter values were calculated (Fig. 1). Note also that during the
123 1960s, samples corresponding to full winter (based on ammonium values) were rather sparse and
124 eight winter values were not calculated. The resulting chronology was assigned an age of 1890 at
125 118.3 m (Legrand et al., 2018). Prior to 1890, no winter snow was preserved, but the age of the 7
126 lowest meters (below 118.3 m depth) of the C10 core were estimated to cover at least the period
127 1830-1890 (i.e., prior to the onset of the pre-industrial period in ~1850) (Text S1). Past summer
128 trends including during the pre-industrial time period are thus better documented so in the
129 following we evaluate and discuss mainly summer trends.

130 2.2 Measurements of metals and comparison with previous studies

131 CDD ice-cores were analyzed for a broad range of elements using the continuous flow
132 ice-core analytical system at the Desert Research Institute (DRI) Ultra Trace Chemistry
133 Laboratory (McConnell et al., 2019). Longitudinal samples (3.3×3.3 cm cross section) were
134 melted sequentially on a heated ceramic melter head and the meltwater stream split into three
135 regions by ridges engraved in the melter head. Pb, Cd, Zn, and co-analyzed species such as
136 cerium (Ce) were measured in the meltwater from the innermost ring (10% of the sample
137 volume) using two high-resolution inductively coupled plasma-mass spectrometers (HR-ICP-
138 MS) operating in parallel. The detection limits, defined as 3 times the standard deviation of the
139 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
140 Ce. Our new CDD measurements are in excellent agreement with previously-published, discrete
141 measurements performed on CDD ice-cores (Table S1). Comparison with those previously
142 obtained at CG indicates slightly higher values at CG than at CDD, likely due to less winter
143 snow preservation at CG than at CDD (Wagenbach et al., 2012).

144 2.3 The crustal fraction of Zn, Cd, and Pb

145 Many metals are naturally emitted within the atmosphere along with soil and desert dust
146 particles. The crustal contribution to each metal can be estimated from Ce measurements using
147 the “mean sediment” metal-to-Ce ratio (Bowen, 1966). Measurement of total concentrations of
148 Ce that is part of relatively insoluble dust is, however, influenced by acidification times because
149 Ce remains in the particle phase longer than other elements associated with pollution that are
150 adsorbed onto small particles and are readily washed from the outside of the particles during on-
151 line acidification of the continuous analytical system. Previous assessment of measurement
152 recovery during continuous measurements with the DRI system indicated that recovery was 100
153 % and 60% for Pb and Ce, respectively (McConnell et al., 2018). We assume a similarly high
154 recovery for Zn and Cd since they are also mainly associated with pollution.

155 Since the metal/Ce ratio can deviate from the “mean sediment” value and so result in an
156 incorrect determination of the crustal component, we used an alternative approach to estimate
157 site-specific metal/Ce ratios using ice samples containing relatively high dust or low
158 anthropogenic contributions. First, in ice samples deposited over the recent decades we used
159 alkalinity to select samples containing high Saharan dust concentrations (Wagenbach et al.,
160 1996). Second, we assumed that non-crustal contributions were negligible in some samples
161 deposited during pre-industrial time. Using both approaches, relationships between the metals
162 and Ce in dust-dominated CDD samples suggest site-specific crustal ratios of 1.9 for Zn/Ce, 0.02
163 for Cd/Ce, and ~0.4 for Pb/Ce (Fig. S3, Text S2). After correcting the Ce concentrations for the
164 60% under-recovery, these site-specific crustal ratios are 1.12 for Zn compared to 1.15 in mean
165 sediment, 0.012 instead of 0.002 for Cd, and 0.23 (i.e., similar to the mean sediment value) for
166 Pb.

167 2.4 FLEXPART and metal deposition fluxes at CDD

168 To compare the CDD ice-core summer trends with estimated past emissions in relevant
169 countries we used the Lagrangian particle dispersion model FLEXPART by applying a recent
170 development that allows running the model backward in time for dry and wet deposition (Stohl
171 et al., 2005; Eckhardt et al., 2017). The model maps the sensitivity of deposition at the CDD site
172 to emission flux. The model was run in backward mode at monthly intervals for the period 1901
173 through 1999, and particles were traced backward for 30 days. As meteorological input to
174 FLEXPART, we used the recently completed coupled climate reanalysis for the 20th century
175 (CERA-20C) (Laloyaux et al., 2018) performed at the European Centre for Medium Range
176 Weather Forecasts at a resolution of 2° x 2° and every six hours. As metal aerosol produced by
177 pollution consists of fine particles (diameter range of 0.5-1.2 µm, Nriagu, 1990) the model was
178 run for 0.4 µm diameter aerosol. Average summer emission sensitivity reported in Fig. S4 were
179 used to calculate summer deposition at CDD. Changing the aerosol size from 0.4 µm to 1 µm
180 leads to a decrease by 30% of emission sensitivities in the countries surrounding the Alps (Fig.
181 S5) and the calculated depositions at CDD are similarly reduced but the long-term temporal
182 trends remain essentially identical.

183 2.5 Past emissions in Europe

184 Past anthropogenic emissions of Pb, Cd, and Zn already were estimated for individual
185 European countries (Olendrzynski et al., 1996; Pacyna & Pacyna, 1999; Pacyna et al., 2009) for
186 the 1955-2000 time period, based on statistical data, EF values, and their changes over time.
187 While accurate information is available from European national authorities to quantify the
188 reduction of Pb additive in gasoline, there is much more uncertainty associated with the decrease
189 of EFs for non-ferrous smelters as well as the iron and steel industry during the 1980s (Pacyna
190 1991). The smelting-related EFs are assumed to have decreased with the progressive installation
191 of electrostatic precipitators and filters in the mid-1970s, initial flue gas desulfurization (FGD)
192 installations in the mid-1980s, and further deployment of FGD in the 1990s. EFs proposed for
193 the 1950s and 1960s (Table S2) are estimated to have decreased in the 1980s by a factor of 3 for
194 non-ferrous smelters and a factor of 5 for iron and steel manufacturing (Pacyna, 1991). For Cd
195 emissions from Zn smelters, an EF value of 1500 g per ton of zinc produced has been proposed
196 as an upper limit. When using the imperial smelter furnace (ISF) process, EF drops to 50 g per
197 ton of zinc produced. We have limited information on the use of this technique in various
198 European countries over the recent past. Since 1986, ~33% of production in France and 20% in

199 Germany used ISF, whereas ISF was not used either in Spain or in Belgium (Minemet, 1986). In
200 our calculations we therefore have applied an average EF value of 1200 g of Cd per tons of zinc
201 produced.

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

220 **3 Results and Discussions**

221 **3.1 High-resolution alpine ice record of pollution by lead, cadmium, and zinc**

222 Sub-annually resolved measurements of Pb, Cd, and Zn in alpine ice provide complete
223 emission records over the 20th century. To isolate variations in the ice record caused by
224 anthropogenic emissions, we subtracted crustal contributions determined using cerium
225 (McConnell and Edwards, 2008). Such corrections account for an increase of the crustal material
226 deposited at CDD, particularly after 1960 (Preunkert & Legrand, 2013). On average between
227 1890 and 2000, the crustal contributions comprised of the total 1% for Pb, 6% for Cd, and 9%
228 for Zn.

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

240 The summer pre-industrial values, are close to 0.001 ng g⁻¹ for ncCd and 0.080 ng g⁻¹ for
241 ncZn (prior to ~1875), and 0.025 ng g⁻¹ for ncPb (pre- and post-Roman period) (Table S3). The

242 three times higher pre-industrial level of ncZn compared to ncPb is very consistent with
243 estimates of global natural emissions of non-crustal Zn (26 ktons a⁻¹) and Pb (8 ktons a⁻¹)
244 (Ngiaru, 1979). Global natural emissions of non-crustal Cd are far lower (1.1 ktons a⁻¹) (Ngiaru,
245 1979). The difference by a factor of ~25 in global natural emissions of ncZn and ncCd is lower,
246 however, than the difference in ice pre-industrial levels (a factor of 80). Since natural non-crustal
247 emissions of Cd are dominated by volcanic emissions (0.8 ktons a⁻¹ out of a total of 1.1 ktons a⁻¹)
248 ¹), it is possible that while Cd volcanic emissions are dominant at a global scale, they have a
249 weaker impact on Europe.

250 The ncPb summer levels that already largely exceeded its pre-industrial ice level (< 0.1
251 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
252 ng g⁻¹ in 1950 (Fig. 1). After 1950, summertime ncPb levels rapidly increased to a maximum of
253 ~2.6 ng g⁻¹ at the beginning of the 1970s, after which levels sharply decreased over the following
254 three decades, the level in 2000 (~0.5 ng g⁻¹) being almost half of those observed at the
255 beginning of the 20th century. The long-term trends of ncCd and ncZn are similar, but differ from
256 ncPb, with a smaller relative increase above the pre-industrial background (0.001 ng g⁻¹ to 0.005
257 ng g⁻¹ for ncCd) at the beginning of the century, and a less marked decrease after the 1970s, with
258 levels remaining higher (~0.008 ng g⁻¹ for ncCd) in 2000 than at the beginning of the century.
259 Note that decreased preservation of winter snow in the 1960s (section 2.1) resulted in maximum
260 M-yr values in ~1965 for all three species, in contrast with the maximum M-W/S means (similar
261 to summer means) for ncPb and ncCd that indicate maxima in ~1975 and ~1980, respectively
262 (Fig. S5).

263 3.2 Past emissions of Pb, Cd, and Zn in European countries and deposition at CDD

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

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

278 The second scenario estimates depositional fluxes back to 1850 (Fig. 2; blue triangles
279 denoted Scenario [2]) using statistical data of relevant source categories for Pb, Cd, and Zn
280 emissions including smelters (lead, zinc, and copper), pig iron and steel manufacturing, and coal
281 consumption available since 1850. For these source categories, we have used the same EFs as for
282 1955-1970 (Table S2). For Pb emissions, we also considered lead mining and gasoline
283 consumption. Since Pb emissions from leaded gasoline are accurately known based on applied
284 regulations in each European country, we used the Pb emissions from leaded gasoline calculated
285 for each country for 1955 (i.e., the same as in Scenario [1]).

286 The third scenario also calculates metal deposition for 1970 to 2000 using statistical
 287 emissions data from Scenario [1], but uses pre-emissions-control EFs (i.e. does not account for
 288 reduction in EFs associated with emissions regulation since 1970) (Fig. 2; Emissions Scenario
 289 [3]). As in scenarios [1] and [2], we used the Pb emissions from gasoline calculated for each
 290 country in (Pacyna & Pacyna, 1999; Pacyna et al., 2009). As seen in Fig. 2, for recent decades
 291 the three emissions scenarios are consistent for lead, as the three scenarios all use the same
 292 leaded gasoline emissions estimates. For Zn and Cd, a good agreement between scenario [1] and
 293 [2] is observed from 1955 to 1970 as expected. The large difference between scenario [1] and [3]
 294 after 1970 is due to the difference in EFs, and shows how reduced EFs from non-ferrous smelters
 295 (Pb, Zn, and Cu) as well as iron and steel industry after 1970 counteracted increased productions
 296 from most source categories (except coal consumption that decreased by a factor of 2 from 1965
 297 to 2000).

298 The estimated deposition of anthropogenic Pb, Cd, and Zn at CDD partitioned by source
 299 at the beginning of the 20th century and in 1955 to 1970 are detailed in Fig. S6. For
 300 anthropogenic Pb, the main emissions were Zn and Pb smelting at the beginning of the 20th
 301 century, and leaded gasoline in the 1960s and 1970s. At the start of the 20th century, Pb
 302 deposition from Zn smelting was approximately evenly split between FR, BE, and W-DE, as the
 303 ~3-4 times lower Zn production in FR compared to BE and W-DE was compensated for by its
 304 much higher emissions sensitivity (Table S4). Contributions from Pb smelting were dominated
 305 by ES, with lesser contributions from W-DE and FR. In 1955 to 1970, Pb deposition from leaded
 306 gasoline emissions was primarily sourced from FR, followed by IT. For anthropogenic Zn and
 307 Cd, Zn smelting dominated emissions since 1890 (Fig. S6), though country-specific
 308 contributions evolved over the 20th century. Zn smelting contributions to both Zn and Cd
 309 deposition were evenly split between FR, BE, and W-DE at the beginning of the 20th century, but
 310 dominated by FR from 1955 to 1970 (Table S4). BE followed by FR became the largest Zn
 311 producers over recent decades.

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

319 3.3 The 1890-2000 lead and cadmium pollution

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

324 We begin the comparison between ice-core trends and past emissions for the most recent
 325 time-period over which more information on emissions are available. The ncPb summer ice trend
 326 shows a rapid increase of lead pollution over the second half of the 20th century that reached a
 327 maximum in ~ 1975 before subsequently decreasing by a factor of 6 by 2000 (Fig. 2a). The
 328 changes observed in the CDD ice-core are consistent with estimates of past anthropogenic Pb
 329 deposition at CDD that were dominated by leaded gasoline emissions (almost 70% in 1965),

330 with smaller contributions from non-ferrous smelters (~15% in 1965), pig iron and steel (10%,
331 mainly from pig iron), and coal (4%) (Fig. S6). The post-1975 ncPb decrease is attributed to the
332 reduction of Pb additives to gasoline that reduced gasoline-derived Pb emissions despite the
333 continuous growth of gasoline consumption. Using the same leaded gasoline emissions, the two
334 estimates of Pb deposition (triangles and squares in Fig. 2) agree well during the rapid increases
335 of emissions related to leaded gasoline. As leaded gasoline emissions declined during the mid-
336 1990s, calculations assuming pre-emissions control EFs for non-ferrous smelters and pig iron
337 production (Scenario [3] in Fig. 2) clearly overestimated the contribution of emissions from these
338 two sources at that time.

339 The ice-core ncCd trend indicates a steady increase from 1950 until the 1980s (Fig. 2b),
340 whereas past deposition calculated using Scenario [1] indicates a maximum in the mid-1960s
341 followed by a rapid decrease to 2000. Similarly, the ice-core ncZn peaks in the mid-1970s,
342 whereas calculated emissions peak in the mid-1960s. The 10-15 yr delay between the peak Cd
343 and Zn emissions in Scenario [1] and the ice-core data are likely a result of poorly constrained
344 EFs for Zn smelting, the dominant emissions source for both metals, compared to the much
345 better quantified decrease of Pb additives used in gasoline. Fig. 2 suggests that the EFs from Zn
346 smelters may have only decreased by a factor of 2 instead of 4-5 from ~1970 to 1980, a factor of
347 5 instead of 10 from ~1970 to 2000.

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

352 The calculated deposition fluxes at CDD indicate an increase by a factor of ~3 from 1890
353 to 1950 for anthropogenic Pb, Cd, and Zn (Fig. 2). This increase is comparable to the observed
354 increases of ncZn and ncCd ice concentrations (a factor of 3 and 2.2 from 1890 to 1950,
355 respectively), but is larger than the observed increase of ~1.5 for ncPb ice concentrations. At the
356 beginning of the 20th century, Pb emissions were dominated by Pb mining and smelting (42% of
357 total), and both Zn and Cd emissions were dominated by Zn smelters (Fig. S6). The difference
358 between the estimated Pb deposition and ncPb ice-core concentrations suggest that the EFs used
359 at the beginning of the 20th century underestimate emissions by a factor of 2-3 with respect to the
360 1955 value.

361 At the beginning of the industrial period, the statistics indicate a more rapid increase of
362 emissions for Zn and Cd (a factor of 3 from 1860 to 1885) than for Pb (a factor of 1.7), likely a
363 result of significant Pb production in Spain in the mid-19th century (Table S4). The larger
364 anthropogenic emissions of Pb compared to Cd and Zn at the very beginning of the industrial era
365 are partly reflected in ice, with ncCd and ncZn concentrations near their pre-industrial (1700 to
366 1835) values in 1875, whereas ncPb were already 20 times above its pre-industrial baseline at
367 that time (Table S3).

368 **5 Conclusions**

369 Continuous chemical measurements in alpine ice-cores were used to document
370 preindustrial and year-by-year, 1890 to 2000 summer Cd and Pb pollution in western Europe,
371 with ancillary measurements of Zn and Ce used for source apportionment. For the first time,
372 alpine ice-core trends were evaluated in detail using new pollution estimates for the region based

373 on country-specific emissions derived from updated source-category statistics, as well as state-
374 of-the-art atmospheric aerosol transport and deposition modeling. Comparisons with existing
375 pollution reconstructions back to 1955 show that while Pb pollution largely from leaded gasoline
376 was similar to estimates, Cd pollution primarily from Zn smelter emissions was up to four-fold
377 higher between the mid-1970s and 2000. In addition, peak Cd pollution occurred in the early-
378 1980s (i.e., almost coinciding with the Pb maximum) rather than the mid-1960s as previously
379 thought. It is suggested that previous reconstructions of Cd pollution assumed overly optimistic
380 emissions reductions from the introduction of pollution control devices and other technological
381 improvements particularly between 1965 and 1980. This finding has implications for the impact
382 of Cd pollution throughout ecosystems, which is sensitive to the concentration in the
383 environment and also the duration of exposure.

384

385 **Acknowledgments, Samples, and Data**

386 The ice-core drilling operations at CDD were supported by the European Community via ENV4-
387 CT97 (ALPCLIM) contract and the Region Rhône-Alpes. The LEFE-CHAT (CNRS) program
388 entitled “Evolution séculaire de la charge et composition de l'aérosol organique au dessus de
389 l'Europe (ESCCARGO)” provided funding for analysis in France with the support of ADEME
390 (Agence de l'Environnement et de la Maîtrise de l'Energie). NSF grant 1925417 to JRM provided
391 partial support for the analyses and interpretation at DRI. We thank colleagues who participated
392 in the drilling campaigns at CDD. We thank the two anonymous reviewers for their very useful
393 comments, which improved the quality of the manuscript.

394 Ice-core data are available at NCEI (National Centers for Environmental Information) data base
395 (<https://www.ncdc.noaa.gov/paleo/study/29492>).

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497

498

499 **Figure Captions:**

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

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

513

Figure 1.

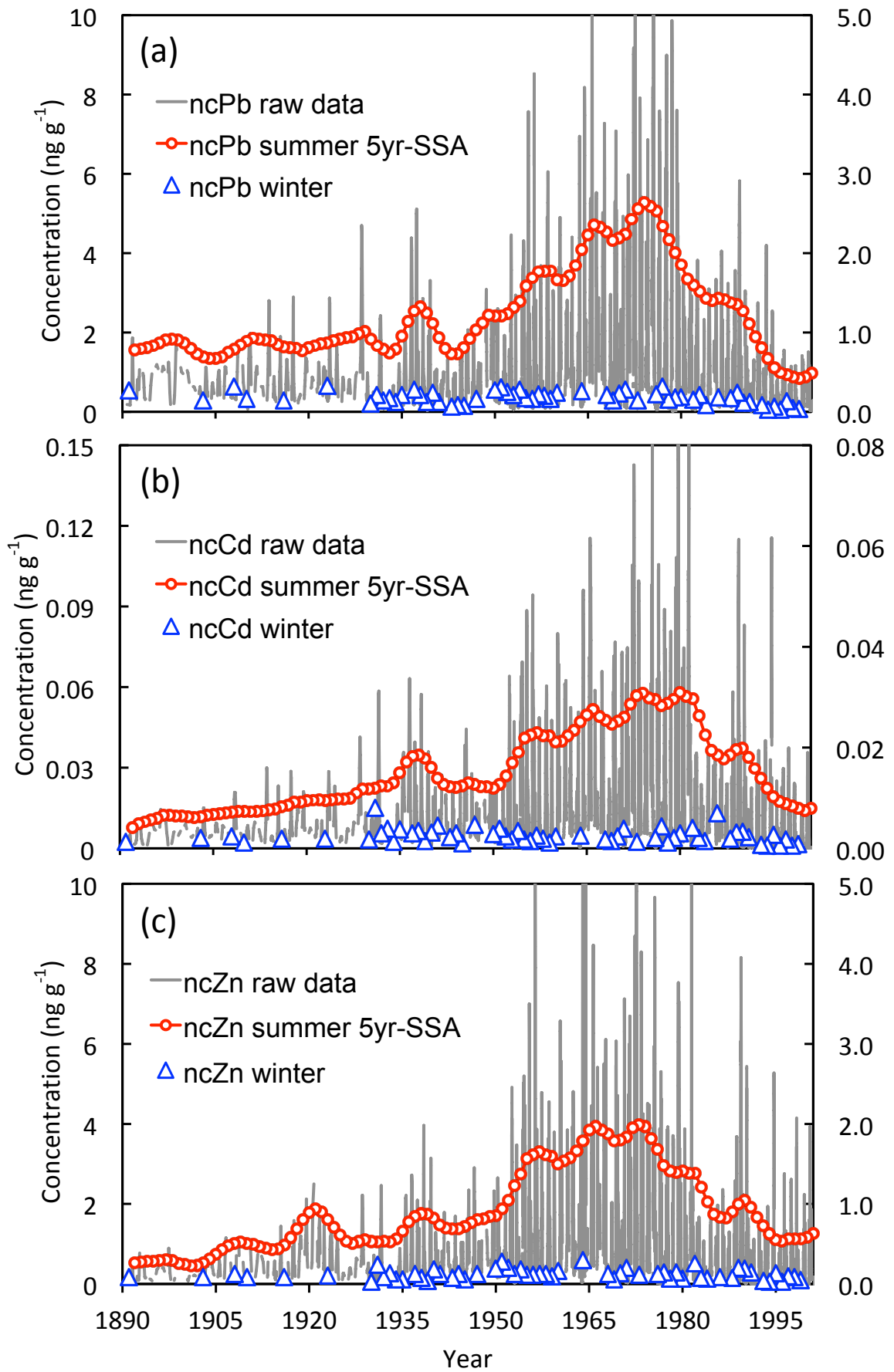


Figure 2.

