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**Key Points:**

- Alpine ice core data indicate thallium pollution in western Europe since ~1850
- Emissions from growing cement production after World War II contributed little to European thallium pollution
- Anthropogenic thallium emissions in western Europe were dominated by coal burning throughout the 20th century

**Supporting Information:**

Supporting Information may be found in the online version of this article.

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# Thallium Pollution in Europe Over the Twentieth Century Recorded in Alpine Ice: Contributions From Coal Burning and Cement Production

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**Abstract** Emission inventories indicate that thallium, a highly toxic metal, is emitted during coal burning and cement production. These estimates have been established only for the 1980s and 1990s but up to now they have not been compared to long-term observations. Here we used alpine ice cores to document thallium pollution over Europe since ~1850. Ice-core thallium concentrations increased from 1890 to 1910, and decreased after 1965 to concentrations that were half 1890 levels. Comparison of ice-core trends, estimated past emissions, and state-of-the-art atmospheric aerosol transport modeling suggest that coal burning was responsible for thallium pollution in Europe, particularly from 1920 to 1965 because of high coal consumption at that time. The subsequent decline resulted from decreased coal consumption and reduced emissions following technological improvements. The ice-core data suggest that the rapid growth of cement production that took place in Europe after 1950 had a limited impact on thallium pollution.

**Plain Language Summary** Although less prevalent in the environment than toxic metals such as lead and cadmium, thallium is a highly toxic metal even at very low levels. Because reliable measurements are difficult at such low concentrations, thallium pollution is far less documented than other toxic metals. Cement production originally was estimated to be the primary source of thallium pollution at the global scale, but it was later recognized that coal burning was likely the main source. These previous estimates refer to the recent decades but no longer-term inventories were available. Furthermore, no inventories were established at the scale of the European continent. Detailed measurements in Alpine ice cores show that thallium pollution after the late 19th century primarily was the result of coal burning in western Europe, and was largest between 1920 and 1965 as expected from coal consumption records. The rapid growth of cement production that took place after World War II had only limited impact on thallium pollution in Europe.

## 1. Introduction

Previous studies on trace metal emissions and their changes over the past have focused on some 15 species, with special efforts on the most harmful such as lead (Pb), cadmium (Cd), and mercury (Hg) (Pacyna & Pacyna, 2001). Although toxic even at low concentrations and with the ability to bioaccumulate (Karbowska, 2016; Peter & Viraraghavan, 2005), thallium (Tl) is far less documented in emission inventories than other metals. Coal burning and cement production were identified as main anthropogenic Tl sources (Antón et al., 2013). Although a few quantifications of these sources have been proposed (e.g., Ewers, 1988), the first estimates of anthropogenic sources suggested that at the global scale, ~5 kilotonnes (kt) of Tl were emitted in 1983 primarily from cement production (Nriagu & Pacyna, 1988). Partly because of an overestimation of the emission factor (EF) previously used to compute emissions from cement production for 1983, this worldwide estimate was reduced to 1.8 kt for 1995 and attributed largely to coal burning (Pacyna & Pacyna, 2001). No emission inventories are available for years prior to 1983 and no inventories have been developed specifically for Europe. Thallium records also are very scarce with respect to past trends in environmental archives such as ice-cores and peat bogs, partly because of analytical difficulties in measuring very low concentrations (e.g., a few pg $g^{-1}$ or less in ice). In Greenland ice, McConnell & Edwards (2008) reported a threefold increase of Tl from pre-industrial (PI) times to the onset of

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the 20th century, with attribution of early 20th century increases to coal burning in the USA and Europe based largely on covariance with black carbon and sulfur concentrations in the ice. Chellman et al. (2017) reported similar Tl trends in an ice-core from a mid-latitude glacier located in North America (Upper Fremont Glacier, Wyoming). At Mount Everest (Himalaya), two thallium records were extracted (Gabrielli et al., 2020; Kaspari et al., 2009). Kaspari et al. (2009) reported a very slight increase of Tl concentrations (from 1.4 pg $g^{-1}$ between 1800 and 1950 to 1.9 pg $g^{-1}$ between 1970 and 2002) that was not discussed in terms of anthropogenic source apportionment. Atmospheric Tl deposition also was recorded in a Swiss peat bog core, showing an increase of enrichment factors with respect to the crustal composition starting during the middle of the 19th century and reaching high enrichments (above 5) at the beginning of the 20th century (Shotyk & Krachler, 2004). Among other metals, molybdenum (Mo) also was proposed to be emitted largely by European coal burning (J. M. Pacyna et al., 1984), but based on an Alpine ice-core record covering the 20th century, Arienzo et al. (2021) concluded that Mo emissions from metallurgy exceeded those from coal burning in western Europe.

Here we present a seasonally resolved ice-core record of Tl deposition extracted from the Col du Dôme (CDD) glacier close to the Mont Blanc summit. Our main goal was to examine natural sources in Europe during the PI period and the importance of coal burning with respect to other anthropogenic emissions during and after industrialization. This was accomplished by comparing the long-term ice-core records to anthropogenic emission estimates and using simulations from state-of-the-art FLEXPART atmospheric transport and deposition model.

## 2. Materials and Methods

### 2.1. Ice-Core Material and Dating

We investigated long-term trends of Tl over the 20th century using chemical analysis of ice-cores extracted at the Col du Dome site (45.8°N, 6.8°E, 4250 m above sea level) located near the Mont Blanc summit in the French Alps. More details on the ice-cores extracted from CDD are given in Text S1 in Supporting Information S1. The upper sections of cores were dated by annual layer counting primarily using pronounced seasonal variations in ammonium concentrations (Figure S1 in Supporting Information S1). As detailed in Legrand et al. (2018), Legrand et al. (2020) and Arienzo et al. (2021), a composite continuous (1890–2000) record was obtained from these ice-cores with a dating error typically ranging from 1 year in the upper layers to 5 years prior to 1930 (Text S1 in Supporting Information S1). Winter layers thin with depth relative to summer layers because of a lack of preservation of blowing winter snow upstream of the CDD drilling site. From 1891 to 1929 many of the winter ammonium minima used to define a winter layer were too thin to determine reliably winter concentrations of Tl, and only six winter values were calculated (Figure 1a). These six winter concentrations likely represent upper limits and so should be interpreted with caution. Although no winter snow was preserved prior to 1890, the age from 125 to 123 m depth of the C10 core was estimated by Legrand et al. (2020) to span the period from ~1850 to 1890, representing mostly summertime concentrations. Finally, we also analyzed basal ice of the CDD glacier previously dated using $^{14}C$ analysis of particulate organic carbon (Preunkert et al., 2019) to correspond to the 1st millennium, thereby establishing summer concentrations of Tl as far back as antiquity (Table S1 in Supporting Information S1).

In contrast to the summer record, the winter record is far less documented with (a) 52 winter values (instead of 72 for summer) between 1930 and 2000, (b) only 6 winter values from 1891 to 1929, and (c) virtually unknown PI winter concentrations. In the following sections we therefore focus on the summer trend and only briefly discuss winter values.

### 2.2. Analysis in CDD Ice

The CDD ice-cores were analyzed using the continuous ice-core analytical system at the Desert Research Institute (DRI) Ultra Trace Chemistry Laboratory. Working conditions were described in Maselli et al. (2017) and McConnell et al. (2019). Longitudinal core samples (section of 3.3 × 3.3 cm) were melted sequentially, with the meltwater stream split into three regions. Tl and co-analyzed cerium (Ce) species were measured in the meltwater from the innermost ring (10% of the sample cross section) using two inductively coupled plasma mass spectrometers operating in parallel. As in other heavy metal studies (e.g., McConnell and Edwards, 2008; McConnell et al., 2018), ~5 mm at the ends of each longitudinal sample were removed using a clean ceramic blade. The measurement uncertainties were estimated by looking at the Relative Standard Deviations (RSDs)

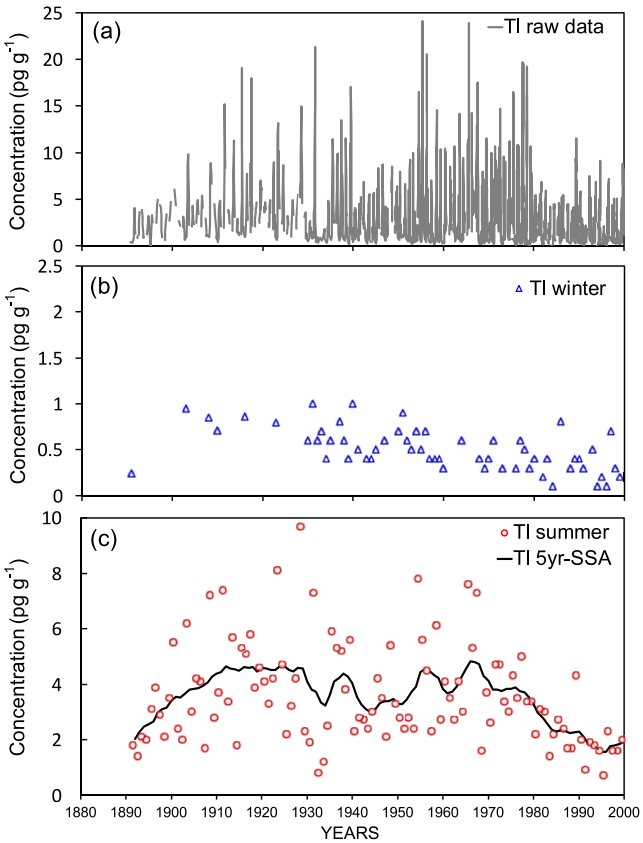


**Figure 1.** The 1890–2000 Col du Dôme ice records of thallium: (a): the high-resolution continuous measurements, (b) the half-year winter values, and (c) the half-year summer values. The black line refers to the first component of singular spectrum analysis with a 5-year time window.

during check standards that we introduce routinely during the continuous analyses. For the CDD measurements of Tl, these RSDs were 1%–2%. The detection limits were determined as three times the standard deviation of the blank (0.02 pg $g^{-1}$ for Tl, and 0.03 pg $g^{-1}$ for Ce). More details on HR-ICP-MS instruments (calibration, accuracy, detection limits) can be found in McConnell & Edwards (2008) and McConnell et al. (2017).

Ranging between 1 and 3 pg $g^{-1}$ (Table S2 in Supporting Information S1), the Tl concentrations in CDD ice are very similar to those observed at other non-polar sites and are 5–10 times higher than in Greenland. Such higher concentrations at non-polar sites compared to Greenland previously were observed for other anthropogenic trace metals (e.g., Preunkert et al. (2019) for Pb) reflecting the proximity of man-made emissions.

### 2.3. FLEXPART Model Simulations

Similar to the approach applied in Legrand et al. (2020) and Arienzo et al. (2021), the CDD ice-core long-term trends were compared to estimated past emissions from relevant European countries. To account for the effects of atmospheric transport and deposition, we used backward simulations of the Lagrangian particle dispersion model FLEXPART to estimate emission sensitivities at CDD for both dry and wet deposition (Eckhardt et al., 2017; Stohl et al., 2005). The emission sensitivity represents a source-receptor relationship that maps the sensitivity of the deposition at the site (receptor) to an emission flux (source). The model (version 10.4, Pisso et al. (2019)) was run at monthly intervals for the 1901–1999 time period, and particles were traced backward for 30 days. FLEXPART calculations were made by using the 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° × 2° and with 91 vertical layers (of which 27 are located below 5000 m asl), and every six hours. As metal aerosol consists of submicron particles (Davison et al., 1974; Nriagu, 1990; Querol et al., 1995), the model was run for 0.4 μm diameter aerosol. A map of average summer emission sensitivities for the CDD site is shown in Figure S2a in Supporting Information S1. These values were averaged for each country to calculate the expected deposition fluxes at the CDD site from European emissions. This was done by weighting emissions from each country by its emission sensitivity and summed.

As the Alpine topography is not well resolved in the CERA-20C data set, as discussed in Section 5, additional simulations were done for the years 2000–2009 with the more recent ERA-5 reanalysis which has a much higher resolution (0.5° × 0.5° and 137 vertical layers, of which 41 are located below 5000 m asl) (Hersbach et al., 2020).

## 3. Ice-Core Data

In addition to the overall Tl trend, the CDD ice record exhibits significant year-to-year variability (Figure 1). Simulations made with the EMEP (European Monitoring and Evaluation Programme) transport-chemistry model previously have shown that the overall trend of ammonium in summer CDD ice is well reproduced by the model, with year-to-year meteorological variability modulating the concentrations to within a factor 2–3 (Fagerli et al., 2007). As seen in Figure S3 in Supporting Information S1, it is also generally the case with Tl with high (low) concentrations in summer corresponding with high (low) ammonium concentrations. To minimize the impact of this year-to-year variability on the long-term trend we calculated the summer ice record using the first component of singular spectrum analysis with a 5-year time window (Figure 1c).

As for many other metals, Tl is emitted to the atmosphere along with terrigenous particles. Anthropogenic Ce sources remained far lower than crustal emissions in Europe (Arienzo et al., 2021), and as conducted in previous ice-core studies from Greenland and several high-elevation mid-latitude glaciers (Eichler et al., 2015, 2017; McConnell et al., 2018), we first used Ce and the "mean sediment" Tl-to-Ce ratio (Bowen, 1966) to estimate the

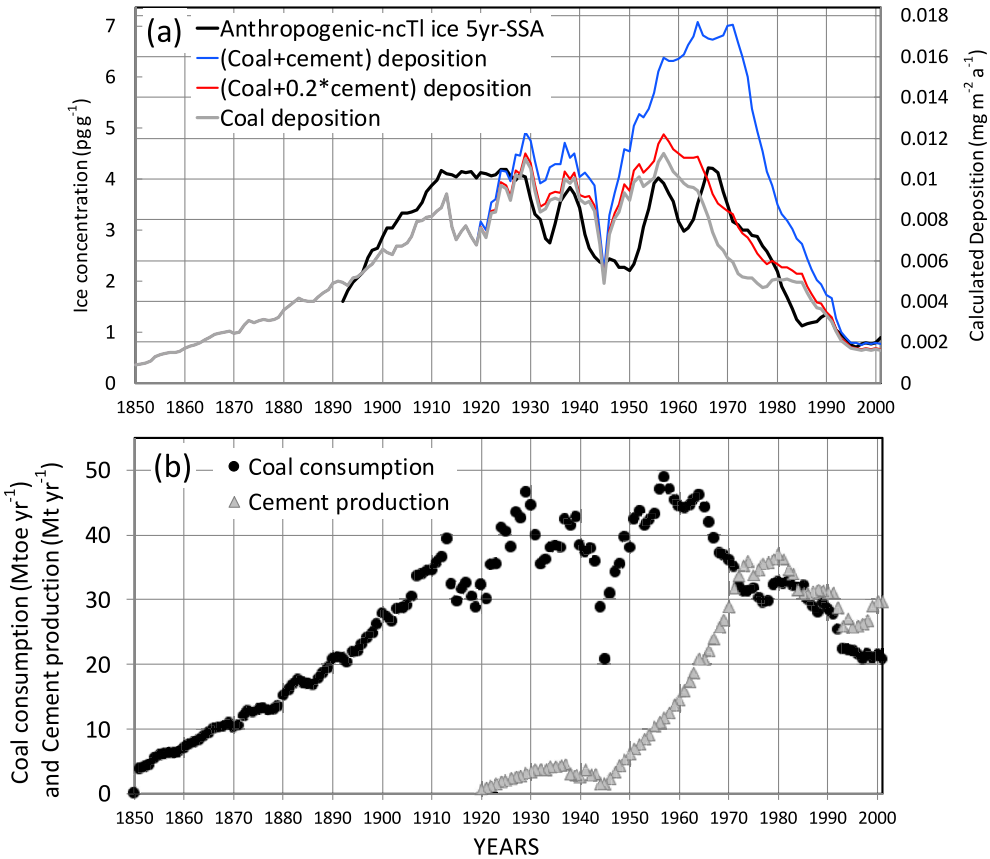


**Figure 2.** (a): Summer ice-core trends of non-crustal thallium concentrations (black line: 5years-SSA) from which the pre-industrial value of 0.30 pg $g^{-1}$ (Table S1 in Supporting Information S1) was subtracted, and deposition fluxes at Col du Dôme calculated by FLEXPART using estimated past anthropogenic emissions related to coal burning (gray line) and coal burning plus cement production (blue line). The red line represents deposition fluxes calculated when considering emissions from coal-burning plus 20% of cement production (Section 6.2). (b): Annual coal consumption (black circles) and cement production (gray triangles) from European countries (Section 4) scaled by emissions sensitivities estimated from FLEXPART simulations.

crustal contribution. The anthropogenic Tl fraction was determined by subtracting the crustal contribution from the total measured concentrations. However, the Tl-to-Ce ratio of dust reaching the CDD site may deviate from the "mean sediment" value, so we instead used an alternative approach to estimate the site-specific Tl-to-Ce ratio using ice CDD samples containing relatively high dust or low anthropogenic contributions (Text S2 in Supporting Information S1). The observed relationships between Tl and Ce in CDD ice samples suggest a site-specific crustal ratio of 0.0065 for Tl/Ce, compared to 0.0114 in mean sediments (Figure S4 in Supporting Information S1). In summer, the crustal contribution of Tl is close to 10% of the total prior to 1980 and was enhanced to 30% of the total between 1980 and 2000. This change resulted from decreasing Tl pollution (Figure 2c) and increasing dust input as revealed by the doubling of Ce concentrations (from 40 prior to 1980 to 80 pg $g^{-1}$ after 1980, Arienzo et al., 2021). This recent Ce change was due mainly to enhancement of dust deposited at CDD during the last decades of the 20th century, as shown in previous studies (Arienzo et al., 2021; De Angelis & Gaudichet, 1991; Preunkert & Legrand, 2013).

## 4. Past Anthropogenic Emissions in Europe

To compare ice-core trends and past deposition fluxes at CDD calculated using FLEXPART emission sensitivities from estimated 1890–2000 emissions, we calculated past emissions using statistics of relevant sources categories in Europe. We used annual coal consumption statistics from Mitchell (1975) for the period prior to 1975,

and from British Petroleum (British Petroleum, 2020) for 1975–2000. For cement production, we used statistical data from Lacoste (1957) for 1920–1950, as well as U.S. Geological Survey statistics (n.d.) for 1950–2000.

Tl emissions were calculated using estimated EFs reported in Table S3 in Supporting Information S1. A worldwide averaged EF of 0.5 g of Tl per tonne of coal burned was proposed by Pacyna & Pacyna (2001) for 1995, and an EF of 1 g of Tl per tonne of coal burned by Nriagu and Pacyna (1988) for 1980–1985. The EF decrease of coal burning from 1995 to 1980 is lower than those reported for non-ferrous smelters (Pacyna, 1991), likely because Tl is very volatile and less efficiently removed by pollution control equipment intended to reduce emissions. Furthermore, EFs from coal burning between 1950 and 1980 (Table S3 in Supporting Information S1) were scaled down to those proposed by Pacyna (1991) for Pb emissions from coal burning.

An estimated zero to 1.56 g of Cd and Tl combined per tonne of cement produced was emitted in 2005 in Europe ($0.045 \pm 0.14$ g per tonne, Schorcht et al., 2013), with most of values between zero and 0.05 g (mean value of ~0.02 g) per tonne. Assuming that these emissions were 50% higher in 1995 (Pacyna et al., 2009) and considering that Tl accounts for 80% of the Cd and Tl combined emissions (Schorcht et al., 2013), we estimated an EF of 0.025 g of Tl per tonne of produced cement in 1995. To account for past EF changes due to the progressive installation of electrostatic precipitators and filters in the mid-1970s, initial flue gas desulphurization installations in the mid-1980s, and further deployment of flue gas desulphurization in the 1990s, we scaled the 1995 EF Tl value to past EFs of Pb from iron and steel production proposed by Pacyna (1991) (Table S3 in Supporting Information S1).

Since we focused on summer changes, we have assumed that emissions from coal burning were about double in winter compared to summer in most European countries (except in the south) (Fagerli et al., 2007), whereas emissions from industrial processes like cement production were assumed to be constant throughout the year.

## 5. Comparison of Deposition Fluxes Calculated by FLEXPART and Derived From Ice-Core Concentrations

To evaluate the quality of estimates of past anthropogenic emissions, previous CDD ice-core studies compared ice-core trends with past deposition fluxes at the CDD site calculated by FLEXPART (CERA-20C) using estimates of past anthropogenic emissions from Europe (Arienzo et al., 2021; Legrand et al., 2020). This approach is based on assumption that CDD ice-concentration changes are mainly associated with changes of depositional fluxes, both being influenced by changes of emissions and transport pathways. Since variations of precipitation in the Alps do not show significant trends after 1901 (Masson & Frei, 2016), it can be assumed that conditions of snow deposition at CDD did not change significantly over the 20th century. Information on past precipitation at CDD cannot be derived from the ice-core records because the ice-core annual layer ice thickness is affected by wind-driven accumulation or erosion and therefore is not consistently representative of past precipitation.

The prior approach that only compares relative changes over the past, however, does not directly assess how well simulated deposition fluxes, calculated from known emissions sources coupled with FLEXPART modeling, agrees with observed ice core fluxes. The FLEXPART-based approach would reflect uncertainties in past emissions and/or model biases including the coarse resolution of the CERA-20C model ($220 \times 155$ km for the CDD grid cell) that poorly resolves Alpine orography (mean elevation of the CDD grid cell is only 1,166 m). Observed CDD deposition fluxes were calculated by multiplying ice-core concentrations by precipitation rates (assumed to be unchanged over the past). The precipitation rate at the high-elevation CDD site is not monitored but estimates can be made from observations made at lower elevations in the Mt Blanc area. Located at 1,035 m elevation near the Mt Blanc, the Chamonix station experiences an annual precipitation of ~1.25 m with similar amount in summer and winter (//fr.climate-data.org/europe/france/rhone-alpes/chamonix-mont-blanc-66184/) for instance, a slightly higher precipitation rate being expected at CDD.

Consideration of other pollutants with well-known anthropogenic emissions histories might allow evaluation of the bias in FLEXPART-simulated deposition with respect to the grid size. As shown by Legrand et al. (2020), the well-marked increase of Pb in CDD ice between 1950 and 1975, and the subsequent rapid decrease toward the late 1990s, are very consistent with changes in well-documented Pb emissions from leaded gasoline that dominated the Pb anthropogenic budget after 1950 in Europe. Assuming a 50% higher precipitation rate at CDD with respect to Chamonix (i.e., 0.95 m in summer), a Pb concentration of 3.6 ng $g^{-1}$ in summer CDD ice (left scale in

Figure S5 in Supporting Information S1) would correspond to a summer deposition flux of 3.4 mg $m^{-2}$ instead of 9 mg $m^{-2}$ as simulated by FLEXPART (right scale in Figure S5 in Supporting Information S1). This suggests that deposition fluxes calculated by FLEXPART overestimates observed fluxes by almost a factor of 3. This bias could be related to the coarse resolution of the model that would overestimate pollution by including the polluted lower atmosphere that is not representative of the CDD site. We investigated this by comparing simulations made for the years 2000–2009 with the CERA-20C version (Figure S2b in Supporting Information S1) and the higher-resolution ERA-5 data set (Figure S2c in Supporting Information S1). Although lower by a factor of 1.3, the deposition fluxes calculated with ERA-5 still overestimate the ice-core fluxes by a factor 2, likely because the Alpine orography is still not well resolved in the ERA-5 data set (the mean elevation of the CDD grid cell is 1750 m asl). A lower limit for the simulated deposition flux was derived using the ERA-5 data set and calculating deposition at the actual elevation of the CDD site (4450 m asl, i.e., 2700 m above the model surface). As shown in Figure S2d in Supporting Information S1, the emission sensitivities calculated with the ERA-5 version at the true elevation are a factor of 5 lower compared to those calculated with CERA-20C at the CDD location model surface. These different simulations clearly indicate systematic uncertainties in Pb deposition fluxes are related to the poorly resolved Alpine topography and suggests that underestimation of the Pb deposition fluxes by the CERA-20C FLEXPART simulations (almost a factor of 3) is due mainly to grid size.

We can assume that most metals emitted by anthropogenic activities have a similar behavior (size distribution, hygroscopicity) with respect to deposition. Therefore, the relationship between Pb ice-concentrations and CERA-20C FLEXPART Pb deposition fluxes at CDD can be used to evaluate the quality of estimated emissions of other trace metals such as Tl whose emissions generally are far less constrained.

## 6. Trend of Thallium

### 6.1. Pre-Industrial Thallium Levels

The summer PI level of Tl is of 0.5 pg $g^{-1}$ of which a half is of non-crustal origin (Table S2 in Supporting Information S1). Natural sources of Tl may include vegetation emissions and biomass burning since Tl is present in plants (Karbowska, 2016). With a natural Tl content in plants of 0.05 μg $g^{-1}$ (Krasnodebska Ostroga & Golimowski, 2008), this biogenic source would remain, however, rather weak. Considering a primary aerosol emission by vegetation of some 50 Tg per year (Kiehl & Rodhe, 1995), we indeed estimate a global continental biogenic emission of Tl in the range of 2.5 tonnes per year, so a relatively minor source. Biomass burning was estimated to emit some 15 Tg per year of particulate organic matter during the PI (Ito & Penner, 2005), and so also would represent a minor Tl source.

Volcanoes emit various trace metals including Tl (Edmonds et al., 2018). Mount Etna continuously emits large amounts of metals and is located in Sicily where the emission sensitivity at the CDD site is less than 1000 (μg $m^{-2}$ $a^{-1}$)/(kg $s^{-1}$) (i.e., <10% of the average value for France, Figure S2a in Supporting Information S1). Under quiescent conditions, the Etna volcano emits some 25–40 tonnes of Tl per year (Calabrese et al., 2011; Gauthier & Le Cloarec, 1998) so the Mount Etna volcano is thus an important nearby natural source of atmospheric Tl with a contribution relative to the global volcanic budget of 1.6% during quiescent periods and 13% during eruptive periods. Using the FLEXPART emission sensitivity for Sicily of 760 (μg $m^{-2}$ $a^{-1}$)/(kg $s^{-1}$) Figure S2a in Supporting Information S1), the estimated Tl deposition fluxes at CDD related to Etna emissions under quiescent conditions would be 0.38 μg $m^{-2}$ in summer corresponding to a summer ice concentration of 0.15 pg $g^{-1}$ compared to the PI level of 0.25 pg $g^{-1}$. It is therefore possible that passive emissions from Mount Etna account for much of the Tl in summer CDD PI ice. Interestingly, the Tl emissions of Mount Etna during eruptive phases are 8 times higher than during non-eruptive periods, leading to an expected summer deposition close to 1 pg $g^{-1}$ following a 6-month eruption. Given the inter-annual variability of summer Tl ice concentrations (Figure 1a), however, it would be difficult to identify past eruptions of Mount Etna using CDD ice records at least during the 20th century when anthropogenic sources dominated (Section 6.2). In conclusion, even though it is located ∼1200 km from the Alps, Mount Etna was probably a significant source, in addition to crustal emissions, of Tl deposited over western Europe during pre-industrial times.

### 6.2. Thallium Pollution in Summer

Summer ncTl levels close to 2 pg $g^{-1}$ in CDD ice in the early 1890s already were nearly 10 times higher than the 0.30 pg $g^{-1}$ observed in PI samples (Figure 2a), with a rapid increase to 4 pg $g^{-1}$ between 1910 and 1930. This increase by a factor of ∼20 relative to PI concentrations persisted until the early 1970s except between 1940 and 1955, possibly reflecting lower anthropogenic emissions during and following World War II. After 1970, ncTl levels gradually decreased to 1 pg $g^{-1}$ in the 1990s, equivalent to half the levels of the 1890s but still well above PI concentrations.

Prior to 1930, cement production in Europe was limited and anthropogenic Tl emissions mainly resulted from coal combustion estimated to be ∼40 Mt of oil equivalent per year (Figure 2b). Annual cement production in Europe was ∼2 Mt between 1920 and 1930, much lower than the reported 34 Mt between 1970 and 1980 (Figure 2b). Conversely, coal consumption increased by a factor of seven between 1850 and 1890, and by a factor of 14 from 1850 to 1930 (Figure 2b). Though ice layers deposited prior to 1850 are not well dated in the CDD record, the increase of Tl concentrations from 1850 to 1890 of ∼1.75 pg $g^{-1}$ compared to ∼2.0 pg $g^{-1}$ from 1890 to 1920 is consistent with coal burning statistics.

Whereas the observed 1890–1920 increase in ncTl concentration followed by a plateau until 1960 (Figure 2a) is qualitatively well reproduced by FLEXPART-based estimates, the simulated depositional fluxes using an EF value of 0.5 g of Tl per tonne of burned coal are approximately three times higher than expected (0.012 mg $m^{-2}$ in 1890 and 0.025 mg $m^{-2}$ in 1930) compared to similar evaluation of Pb emissions and deposition at CDD (Figure S4 in Supporting Information S1). Using instead an EF value of 0.2 g of Tl per tonne of burned coal, the FLEXPART-simulated flux increased by 0.005 mg $m^{-2}$ from 1890 (0.005 mg $m^{-2}$) to 1930 (0.01 mg $m^{-2}$) for a corresponding increase of ice ncTl concentration of 2 pg $g^{-1}$ (Figure 2a), in better agreement with similar simulations of Pb deposition. That Tl EFs for coal burning are different in Europe (0.2 g per tonne of burned coal) compared to the world average value (0.5 g per tonne of burned coal) is not surprising since, in addition to inherent uncertainties in estimating EFs, the Tl content of coal itself is highly variable. Insufficient data on the Tl content of different coal deposits (e.g., estimated to range from <0.2 to 1 ppm (Swaine, 1990)), however, preclude determination of coal provenance from the ice-core records and emissions statistics.

Concentrations of ncTl persisted at high levels (between 2.5 and 4 pg $g^{-1}$) in CDD ice from 1920 to the mid-1960s, except during the 1940s (Figure 2a). Whereas at the beginning of the period, coal combustion was the dominant source of pollution with annual consumption of 40–50 Mt of oil equivalent per year, the demand for cement grew rapidly after World War II and reached a maximum in the late 1970s (Figure 2b). Depositional fluxes from coal burning and cement production calculated with the FLEXPART simulations (blue curve in Figure 2a) clearly indicate an overestimation from cement production, particularly in the late 1960s. That is likely due to over-enhancement of the cement production EFs we made for years prior to 1995 (Table S3 in Supporting Information S1). As detailed in Section 4, these past values of Tl EFs were scaled on past Pb EFs from iron and steel production proposed by Pacyna (1991). It was later recognized that these past EFs were significantly overestimated (Pacyna & Pacyna, 2001). Furthermore, it is likely that emission reductions from pollution control devices intended mainly for other metal pollutants were far less efficient for Tl because of its high volatility. Reducing the increase of EFs for cement for years prior to 1995 by a factor of ∼5, results in much better agreement between the FLEXPART-simulated depositional fluxes and ice core records (red line in Figure 2a) between 1955 and 1985 when emissions from cement production were highest. From that, we conclude that whereas the cement production contributed up to 20%–30% of Tl pollution during the period 1967–1977, coal burning represented the main source of thallium pollution in Europe observed in the CDD summer record through most the 20th century.

The post-1970 decrease of ncTl concentrations in CDD summer ice by a factor of 4 is consistent with the decrease of calculated depositional fluxes, and driven mainly by the factor of two decrease in both coal consumption (Figure 2b) and EFs (Table S3 in Supporting Information S1), as well as smaller declines in emissions from cement production resulting from lower EFs after 1980 (Table S3 in Supporting Information S1) even though cement production remained high (30 Mt, Figure 2b) between 1970 and 2000.

### 6.3. Thallium Pollution in Winter

Weaker vertical atmospheric transport between the polluted boundary layer and high-elevation alpine regions meant that pollution reaching the CDD site was less directly connected to surface pollution sources than during

summer (Figure 1). Furthermore, as discussed in Section 2.1, the record of wintertime pollution is far less complete at CDD because of wind-driven losses of winter layers upstream of the ice-core site. This is especially true before 1930 when winter concentrations are probably not representative. After 1930, winter concentrations of ncTl decreased from 0.5 pg $g^{-1}$ between 1930 and 1950 to 0.25 pg $g^{-1}$ between 1980 and 2000 (Figure 1a). This 1930–2000 winter trend was similar to the summer trend but the strong lack of winter data between 1960 and 1970 (Figure 1a) precludes further comparisons. As discussed in Section 4, we expect the contribution of coal burning to be even more dominant in winter than in summer because of greater coal consumption. Our summer-based finding that coal burning was the main source of Tl pollution in Europe likely also applies during winter.

## 7. Conclusions

Chemical measurements in Alpine ice-cores were used to document preindustrial levels and Tl pollution in western Europe after 1850, and used to derive estimates of Tl emissions from coal burning and cement production thought to be the two major anthropogenic sources. Our analysis indicates that coal burning was the major source of Tl pollution, with the most pronounced impact from prior to 1890 through 1965. Coal-related pollution subsequently decreased because of lower coal consumption and introduction of pollution controls and technological improvements to reduce emissions. The contribution, if any, from cement production that grew strongly in Europe after World War II was low and probably limited to the period 1960–1985. As a result, Tl pollution in the Alps during the 1990s was only 20% and 50% of levels during the 1970s and 1890s, respectively. Our study suggests that Tl is an ideal tracer for identifying coal-related pollution in ice-core and other proxy records, at least in Europe. In addition to terrigenous dust, it is likely that quiescent volcanic emissions from Mount Etna (Sicily) constitute a significant natural source of atmospheric thallium over western Europe.

## Data Availability Statement

Ice core data are available at NCEI (National Centers for Environmental Information) data base (https://doi.org/10.25921/04v7-rj29). Input files for flex_extract and FLEXPART, especially the SPECIES file defining the properties of the simulated tracer are available at https://doi.org/10.25365/phaidra.340.

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## References

Antón, M. A. L., Spears, D. A., Somoano, M. D., & Tarazona, M. R. M. (2013). Thallium in coal: Analysis and environmental implications. *Fuel*, *105*, 13–18. https://doi.org/10.1016/j.fuel.2012.08.004

Arienzo, M. M., Legrand, M., Preunkert, S., Stohl, A., Chellman, N., Eckhardt, S., et al. (2021). Alpine ice-core evidence of a large increase in vanadium and molybdenum pollution in western Europe during the 20th century. *Journal of Geophysical Research: Atmospheres*, *126*(4), e2020JD033211. https://doi.org/10.1029/2020JD033211

Bowen, H. (1966). *Trace elements in biochemistry*. Academic Press.

British Petroleum. (2020). Energy charting tool—app, database visited in August 2021. Retrieved from https://www.bp.com/en/global/corporate/energy-economics/energy-charting-tool-desktop.html

Calabrese, S., Aiuppa, A., Allard, P., Bagnato, E., Bellomo, S., Brusca, L., et al. (2011). Atmospheric sources and sinks of volcanogenic elements in a basaltic volcano (Etna, Italy). *Geochimica et Cosmochimica Acta*, *75*(23), 7401–7425. https://doi.org/10.1016/j.gca.2011.09.040

Chellman, N., McConnell, J. R., Arienzo, M., Pederson, G. T., Aarons, S. M., & Csank, A. (2017). Reassessment of the Upper Fremont Glacier ice-core chronologies by synchronizing of ice-core-water isotopes to a nearby tree-ring chronology. *Environmental Science and Technology*, *51*(8), 4230–4238. https://doi.org/10.1021/acs.est.6b06574

Davison, R. L., Natusch, D. F. S., Wallace, J. R., & Evans, C. A. (1974). Trace elements in fly ash, dependence of concentrations on particle size. *Environmental Science and Technology*, *8*(13), 1107–1113. https://doi.org/10.1021/es60098a003

De Angelis, M., & Gaudichet, A. (1991). Saharan dust deposition over Mont Blanc (French Alps) during the last 30 years. *Tellus B: Chemical and Physical Meteorology*, *43*(1), 61–75. https://doi.org/10.3402/tellusb.v43i1.15246

Eckhardt, S., Cassiani, M., Evangeliou, N., Sollum, E., Pisso, I., & Stohl, A. (2017). Source-receptor matrix calculation for deposited mass with the Lagrangian particle dispersion model FLEXPART v10.2 in backward mode. *Geoscientific Model Development*, *10*(12), 4605–4618. https://doi.org/10.5194/gmd-10-4605-2017

Edmonds, M., Mather, T. A., & Liu, E. J. (2018). A distinct metal fingerprint in arc volcanic emissions. *Nature Geoscience*, *11*(10), 790–794. https://doi.org/10.1038/s41561-018-0214-5

Eichler, A., Gramlich, G., Kellerhals, T., Tobler, L., Rehren, T., & Schwikowski, M. (2017). Ice-core evidence of earliest extensive copper metallurgy in the Andes 2700 years ago. *Scientific Reports*, *7*(1), 41855. https://doi.org/10.1038/srep41855

Eichler, A., Gramlich, G., Kellerhals, T., Tobler, L., & Schwikowski, M. (2015). Pb pollution from leaded gasoline in South America in the context of a 2000-year metallurgical history. *Science Advances*, *1*(2), e1400196. https://doi.org/10.1126/sciadv.1400196

Ewers, U. (1988). Environmental exposure to thallium. *Science of the Total Environment*, *71*(3), 285–292. https://doi.org/10.1016/0048-9697(88)90199-4

Fagerli, H., Legrand, M., Preunkert, S., Vestreng, V., Simpson, D., & Cerqueira, M. (2007). Modeling historical long-term trends of sulfate, ammonium, and elemental carbon over Europe: A comparison with ice core records in the Alps. *Journal of Geophysical Research*, *112*(D23), D23S13. https://doi.org/10.1029/2006JD008044

Gabrielli, P., Wegner, A., Sierra-Hernández, R., Beaudon, E., Davis, M., Barkera, J. D., & Thompson, J. G. (2020). Early atmospheric contamination on the top of the Himalayas since the onset of the European Industrial Revolution. *Proceedings of the National Academy of Sciences of the United States of America*, *117*(8), 3967–3973. https://doi.org/10.1073/pnas.1910485117

Gauthier, J.-P., & Le Cloarec, M.-F. (1998). Variability of alkali and heavy metal fluxes released by Mt. Etna volcano, Sicily, between 1991 and 1995. *Journal of Volcanology and Geothermal Research*, *81*(3–4), 311–326. https://doi.org/10.1016/S0377-0273(98)00002-X

Hersbach, H., Bell, B., Berrisford, P., Hirahara, S., Horanyi, A., Munoz-Sabater, J., et al. (2020). The ERA5 global reanalysis. *Quarterly Journal of the Royal Meteorological Society*, *146*(730), 1999–2049. https://doi.org/10.1002/qj.3803

Ito, A., & Penner, J. E. (2005). Historical emissions of carbonaceous aerosols from biomass and fossil fuel burning for the period 1870-2000. *Global Biogeochemical Cycles*, *19*(2), B2028. https://doi.org/10.1029/2004GB002374

Karbowska, B. (2016). Presence of thallium in the environment: Sources of contaminations, distribution and monitoring methods. *Environmental Monitoring and Assessment*, *188*(11), 640. https://doi.org/10.1007/s10661-016-5647-y

Kaspari, S., Mayewski, P. A., Handley, M., Osterberg, E., Kang, S., Sneed, S., et al. (2009). Recent increases in atmospheric concentrations of Bi, U, Cs, S and Ca from a 350-year Mount Everest ice core record. *Journal of Geophysical Research*, *114*(D4), D04302. https://doi.org/10.1029/2008JD011088

Kiehl, J. T., & Rodhe, H. (1995). Modeling geographical and seasonal forcing due to aerosols. In R. J. Charlson & J. Heintzenberg (Eds.), *Aerosol forcing of climate* (pp. 281–296). Wiley.

Krasnodębska Ostręga, B., & Golimowski, J. (2008). Zielona gałązka, która truje—Thallus. *Analityka: nauka i praktyka*, *1*, 46–50.

Lacoste, Y. (1957). L'industrie du ciment. *Annales de Géographie*, *357*, 411–435. https://doi.org/10.3406/geo.1957.18305

Laloyaux, P., de Boisseson, E., Balmaseda, M., Bidlot, J., Broennimann, S., Buizza, R., et al. (2018). CERA-20C: A coupled reanalysis of the twentieth century. *Journal of Advances in Modeling Earth Systems*, *10*(5), 1172–1195. https://doi.org/10.1029/2018MS001273

Legrand, M., McConnell, J. R., Lestel, L., Preunkert, S., Arienzo, M., Chellman, N. J., et al. (2020). Cadmium pollution from zinc-smelters up to fourfold higher than expected in Western Europe in the 1980s as revealed by alpine ice. *Geophysical Research Letters*, *47*(10), e2020GL087537. https://doi.org/10.1029/2020GL087537

Legrand, M., McConnell, J. R., Preunkert, S., Arienzo, M., Chellman, N., Gleason, K., et al. (2018). Alpine ice evidence of a three-fold increase in atmospheric iodine deposition since 1950 in Europe due to increasing oceanic emissions. *Proceedings of the National Academy of Sciences of the United States of America*, *115*(48), 12136–12141. https://doi.org/10.1073/pnas.1809867115

Maselli, O. J., Chellman, N. J., Grieman, M., Layman, L., McConnell, J. R., Pasteris, D., et al. (2017). Sea ice and pollution-modulated changes in Greenland ice core methanesulfonate and bromine. *Climate of the Past*, *13*(1), 39–59. https://doi.org/10.5194/cp-13-39-2017

Masson, D., & Frei, C. (2016). Long-term variations and trends of mesoscale precipitation in the Alps: Recalculation and update for 1901–2008. *International Journal of Climatology*, *36*(1), 492–500. https://doi.org/10.1002/joc.4343

McConnell, J. R., Burke, A., Dunbar, N. W., Köhler, P., Thomas, J. L., Arienzo, M. M., et al. (2017). Synchronous volcanic eruptions & abrupt climate change ~17.7ka plausibly linked by stratospheric ozone depletion. *Proceedings of the National Academy of Sciences of the United States of America*. https://doi.org/10.1073/pnas.1705595114

McConnell, J. R., Chellman, N. J., Wilson, A. I., Stohl, A., Arienzo, M. M., Eckhardt, S., et al. (2019). Pervasive Arctic lead pollution suggests substantial growth in medieval silver production modulated by plague, climate, and conflict. *Proceedings of the National Academy of Sciences of the United States of America*, *116*(30), 14910–14915. https://doi.org/10.1073/pnas.1904515116

McConnell, J. R., & Edwards, R. (2008). Coal burning leaves toxic heavy metal legacy in the Arctic. *Proceedings of the National Academy of Sciences of the United States of America*, *105*(34), 12140–12144. https://doi.org/10.1073/pnas.0803564105

McConnell, J. R., Wilson, A. I., Stohl, A., Arienzo, M. M., Chellman, N. J., Eckhardt, S., et al. (2018). Lead pollution recorded in Greenland ice indicates European emissions tracked plagues, wars, and imperial expansion during antiquity. *Proceedings of the National Academy of Sciences of the United States of America*, *115*(22), 5726–5731. https://doi.org/10.1073/pnas.1721818115

Mitchell, B. (1975). *European historical statistics, 1750–1970*. Palgrave Macmillan UK. https://doi.org/10.1007/978-1-349-01088-2

Nriagu, J. O. (1990). The rise and fall of leaded gasoline. *Science of the Total Environment*, *92*, 13–28. https://doi.org/10.1016/0048-9697(90)90318-O

Nriagu, J. O., & Pacyna, J. M. (1988). Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature*, *333*(6169), 134–139. https://doi.org/10.1038/333134a0

Pacyna, J. (1991). *Emission factors of atmospheric Cd, Pb and Zn for major source categories in Europe during 1950–1985*, Norwegian Institute for Air Research, Technical Report NILU-OR-30/91, 34

Pacyna, J. M., & Pacyna, E. G. (2001). An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. *Environmental Reviews*, *9*(4), 269–298. https://doi.org/10.1139/a01-012

Pacyna, J. M., Pacyna, E. G., & Aas, W. (2009). Changes of emissions and atmospheric deposition of mercury, lead, and cadmium. *Atmospheric Environment*, *43*(1), 117–127. https://doi.org/10.1016/j.atmosenv.2008.09.066

Pacyna, J. M., Semb, A., & Hanssen, J. E. (1984). Emission and long-range transport of trace elements in Europe. *Tellus*, *36B*(3), 163–178. https://doi.org/10.3402/tellusb.v36i3.14886

Peter, A. L. J., & Viraraghavan, T. (2005). Thallium: A review of public health and environmental concerns. *Environment International*, *31*(4), 493–501. https://doi.org/10.1016/j.envint.2004.09.003

Pisso, I., Sollum, E., Grythe, H., Kristiansen, N. I., Cassiani, M., Eckhardt, S., et al. (2019). The Lagrangian particle dispersion model FLEXPART version 10.4. *Geoscientific Model Developent*, *12*, 4955–4997. https://doi.org/10.5194/gmd-12-4955-2019

Preunkert, S., & Legrand, M. (2013). Towards a quasi-complete reconstruction of past atmospheric aerosol load and composition (organic and inorganic) over Europe since 1920 inferred from alpine ice cores. *Climate of the Past*, *9*(4), 1403–1416. https://doi.org/10.5194/cp-9-1403-2013

Preunkert, S., McConnell, J. R., Hoffmann, H., Legrand, M., Wilson, A. I., Eckhardt, S., et al. (2019). Lead and antimony in basal ice from Col du Dome (French Alps) dated with radiocarbon: A record of pollution during antiquity. *Geophysical Research Letters*, *46*(9), 4953–4961. https://doi.org/10.1029/2019GL082641

Querol, X., Fernandez-Turiel, J. L., & Lopez-Soler, A. (1995). Trace elements in coal and their behaviour during combustion in a large power station. *Fuel*, *74*(3), 331–343. https://doi.org/10.1016/0016-2361(95)93464-o

Schorcht, F., Kourti, I., Scalet, B. M., Roudier, S., & Sancho, L. D. (2013). Best available techniques (BAT) reference document for the production of cement, lime, and magnesium oxide. *European Commission Joint Research Centre Institute for Prospective Technological Studies, Luxembourg*, 506. https://doi.org/10.2788/12850

Shotyk, W., & Krachler, M. (2004). Atmospheric deposition of silver and thallium since 12370 $^{14}$C years BP recorded by a Swiss peat bog profile, and comparison with lead and cadmium. *Journal of Environmental Monitoring*, *6*(5), 427–433. https://doi.org/10.1039/B315084B

Stohl, A., Forster, C., Frank, A., Seibert, P., & Wotawa, G. (2005). Technical note: The Lagrangian particle dispersion model FLEXPART version 6.2. *Atmospheric Chemistry and Physics*, *5*(9), 2461–2474. https://doi.org/10.5194/acp-5-2461-2005

Swaine, D. J. (1990). *Trace elements in coal*. Butherworths.

U.S. Geological Survey statistics. (n.d.). National minerals information center. Retrieved from https://www.usgs.gov/centers/nmic/minerals-year-bookmetals-and-minerals,%20database%20visited%20in August 2021.

## References From the Supporting Information

Preunkert, S., Legrand, M., & Wagenbach, D. (2001). Causes of enhanced fluoride levels in Alpine ice cores over the last 75 years: Implications for the atmospheric fluoride budget. *Journal of Geophysical Research: Atmospheres*, *106*, 12619–12632. https://doi.org/10.1029/2000JD900755

Preunkert, S., Wagenbach, D., Legrand, M., & Vincent, C. (2000). Col du Dome (Mt Blanc Massif, French Alps) suitability for ice-core studies in relation with past atmospheric chemistry over Europe. *Tellus Series B: Chemical and Physical Meteorology*, *52*(3), 993–1012. https://doi.org/10.3402/tellusb.v52i3.17081

Wagenbach, D., Preunkert, S., Schäfer, J., Jung, W., & Tomadin, L. (1996). Northward transport of Saharan dust recorded in a deep alpine ice core. In S. Guerzoni & R. Chester (Eds.), *The impact of desert dust across the Mediterranean* (pp. 291–300). Kluwer Academic Publishers. https://doi.org/10.1007/978-94-017-3354-0_29