Consistent histories of anthropogenic Western European air pollution preserved in different Alpine ice cores

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Abstract. Individual high-Alpine ice cores have been proven to contain a well preserved history of past anthropogenic air pollution in Western Europe. The question, how representative one ice core is with respect to the reconstruction of atmospheric
20 composition in the source region, has not been addressed so far. Here, we present the first study systematically comparing longer-term ice-core records (AD 1750-2015) of various anthropogenic compounds, such as major inorganic aerosol constituents (NH_4^+, NO_3^-, SO_4^{2-}), black carbon (BC), and trace species (Cd, F^-, Pb). Depending on the data availability for the different air pollutants, up to five ice cores from four high-Alpine sites located in the European Alps analysed by different laboratories were considered. Whereas absolute concentration levels can partly differ depending on the prevailing seasonal
25 distribution of accumulated precipitation, all seven investigated anthropogenic compounds are in excellent agreement between the various sites for their respective, species-dependent longer-term concentration trends. This is related to common source regions of air pollution impacting the less than 100 km distant four sites including Western European countries surrounding the Alps. For individual compounds, the Alpine ice-core composites developed in this study allowed us to precisely time the onset of pollution caused by industrialization in Western Europe. Extensive emissions from coal combustion and agriculture
30 lead to an exceeding of pre-industrial (AD 1750-1850) concentration levels already at the end of the 19th century for BC, Pb, $exSO_4^{2-}$ (non-dust, non-sea salt SO_4^{2-}) and NH_4^+, respectively. However, Cd, F^-, and NO_3^- concentrations started surpassing pre-industrial values only in the 20th century, predominantly due to pollution from zinc and aluminium smelters and traffic. The observed maxima of BC, Cd, F^-, Pb, and $exSO_4^{2-}$ concentrations in the 20th century and a significant decline afterwards, clearly reveal the efficiency of air pollution control measures such as desulphurisation of coal, the introduction of filters and
35 scrubbers in power plants and metal smelters, and the ban of leaded gasoline improving the air quality in Western Europe. In

contrast, NO_3^- and NH_4^+ concentration records show levels in the beginning of the 21th century, which are unprecedented in the context of the past 250 years, indicating that the introduced abatement measures to reduce these pollutants were insufficient to have a major effect at high altitudes in Western Europe. Only four ice-core composite records (BC, F^-, Pb, $exSO_4^{2-}$) of the seven investigated pollutants correspond well with modelled trends, suggesting inaccuracies of the emission estimates or an incomplete representation of chemical reaction mechanisms in the models for the other pollutants. Our results demonstrate that individual ice-core records from different sites in the European Alps generally provide a spatial representative signal of anthropogenic air pollution trends in Western European countries.

1 Introduction

High-alpine glaciers and polar ice sheets are invaluable archives of past air pollution and climate. Since direct measurements of the atmospheric composition are basically not available before the 1970s (WMO GAW, 2014), these natural archives are unique to put recent observations into a longer-term context and assess the anthropogenic impact in relation to natural changes in atmospheric constituents.

Ice-core records extending back to pre-industrial times were extracted from glaciers around the world, illustrating that various regions experienced distinct timing of anthropogenic emissions over the past ~150 years reflecting significant differences in industrialization and emission abatement. European, Greenland, and Devon Island ice-core records have been used to reconstruct the history of anthropogenic pollutants such as NH_4^+, NO_3^-, Pb, and SO_4^{2-} in Western Europe and North America, characterized by a substantial increase beginning already in the mid-19th century (Fischer et al., 1998; Schwikowski, 2004; Shotyk et al., 2005). Air pollutant levels above natural background in Eastern Europe appeared around 1930 based on ice-core records from the Altai and Caucasus, indicating a later onset of industrialization (Olivier et al., 2006; Eichler et al., 2014; Preunkert et al., 2019a). Concentrations of the majority of anthropogenic air pollutants in Western Europe, North America, and Eastern Europe peaked in the second half of the 20th century (Fischer et al., 1998; Schwikowski, 2004; Olivier et al., 2006). The subsequent downward trend is the consequence of changes in fuel type used (from coal to oil and gas), introduction of abatement measures, but also stagnation and downturn in industry after the political, social, and economic instability in the case of Eastern Europe (Eichler et al., 2012). On the contrary, anthropogenic emissions in Asia as reconstructed from Himalayan, Pamir, and Saint Elias Mountain ice-core records increased only after AD 1960-1970 and are still rising at the beginning of the 21th century, due to a later industrialisation in these regions (Duan et al., 2007; Osterberg et al., 2008; Zhao et al., 2011).

Ice-core drilling and analyses are very costly, demanding and time consuming processes, taking from months up to years. Thus, generally only one ice core is recovered at a time and replicates are rarely taken. It is assumed that one core is representative for emissions in a particular source region. However, there is a lack of evidence in literature, for which ice-core sites this assumption is actually valid. Only for Greenland ice cores a strong covariance in the trends of black carbon (BC), NO_3^-, Pb, and SO_4^{2-} records was observed between close-by sites (less than 100 km) and also for locations being 1000 km

apart (Fischer et al., 1998; Koch et al., 2011; Zdanowicz et al., 2018; Mcconnell et al., 2019). This finding indicates common source regions for the different Greenland sites, located in North America and Europe, characterised by a similar temporal evolution of anthropogenic emissions. In contrast, for other Arctic sites, such as the Saint Elias Mountains or Svalbard, significant differences in the anthropogenic trends of BC, NO_3^-, Pb, or SO_4^{2-} were detected among ice cores from close-by locations (Gross et al., 2012; Samyn et al., 2012; Beaudon et al., 2013; Osmont et al., 2018). Within the Saint Elias Mountains a distinct vertical profile of aerosol deposition was found. Ice cores from 5000 m above sea level (asl) documented long-range transported air pollution from East Asia, whereas those from 3000 m asl additionally recorded local emissions from North America (Gross et al., 2012). In Svalbard a west-east pollution gradient was detected, with ice cores from western parts reflecting rather boundary layer pollution, whereas those from eastern glaciers are more representative of free tropospheric conditions (Beaudon et al., 2013). Additionally, the latter study reports strong post-depositional melt-water induced disturbance of the ice-core records at the low-altitude Svalbard sites. Differences in SO_4^{2-}, Pb or Sb concentration trends have also been observed from two Himalayan ice cores (Mount Everest, Dasuopu, ~100 km distant) (Duan et al., 2007; Kaspari et al., 2009; Gabrielli et al., 2020). Although pollutants from South Asian regions are deposited at both sites, the ~900 m higher elevated Dasuopu probably receives a larger share of long-range transported air masses. Furthermore, in the Himalayas overwhelming natural dust deposition leads to an additional input of the compounds often strongly exceeding their anthropogenic impact (Sierra-Hernandez et al., 2018). For such locations an extensive dust correction is required, potentially producing higher uncertainties in the calculated anthropogenic trends. In conclusion, for many mountain ranges or glacier sites one ice core is not representative with respect to the reconstruction of atmospheric composition in a given source region.

This setting is different for the European Alps. Here, high-Alpine ice-core sites are within a short distance of less than 100 km, altitude differences are <500 m, and the signal of anthropogenic emissions in the ice-core records is overwhelming during industrial times. Individual ice cores from different high-altitude sites in the European Alps have been proven to contain well-preserved records of past Western European air pollution (e.g. (Schwikowski et al., 1999a; Schwikowski et al., 1999b; Eichler et al., 2000a; Fagerli et al., 2007; Preunkert and Legrand, 2013; Preunkert et al., 2019b). Generally, ice-core concentrations of anthropogenic major aerosol components and trace constituents increased dramatically during the last two centuries following the onset of industrialization (Schwikowski, 2004). Since the second half of the 20th century, concentrations for most of these species significantly declined as a result of the introduction of air pollution control measures in Western Europe. Two comparative studies indicate a good correspondence between NO_3^- and SO_4^{2-} records of summer concentrations at the Col Du Dôme site and annual concentrations from the 80 km distant Colle Gnifetti site in the period ~AD 1910-1995 (Preunkert et al., 2000; Preunkert et al., 2003; Wagenbach et al., 2012) and between the concentration trends of BC records from the Colle Gnifetti and 70 km distant Fiescherhorn site in the period ~AD 1750-2000 (Sigl et al., 2018), respectively. However, a systematic and more holistic investigation of pollution records from different ice cores to evaluate the spatial representativeness of single sites in the European Alps is still lacking.

Here we present the first study comparing longer-term records of anthropogenic pollution recovered from various European high-Alpine ice-core sites for the period AD 1750-2015. We focussed on pollutants, for which continuous records from at least

two of the four sites Colle Gnifetti, Fiescherhorn, Grenzgletscher (Swiss Alps) and Col du Dôme (French Alps) were available, i.e. the major inorganic aerosol species NH_4^+, NO_3^-, $exSO_4^{2-}$; BC, and the trace species Cd, F^-, Pb. This set of air pollutants analysed by different laboratories covers compounds of various emission characteristics and atmospheric chemistry. Among the seven considered pollutants, BC is the only one directly emitted to the atmosphere as primary aerosol from incomplete combustion processes. NH_4^+, NO_3^-, SO_4^{2-} are the dominant species and Cd, F^-, Pb minor species in secondary inorganic aerosols. These are formed in the atmosphere by chemical reactions involving a set of precursor compounds and condensation of vapours on pre-existing particles or by nucleation of new particles. NH_3, NOx, SO_2 emissions from agriculture and burning of fossil fuels associated with transportation and industry represent the main anthropogenic precursor compounds for the major inorganic aerosol species (Seinfeld and Pandis, 2016). Emissions of Cd(0) or CdO, HF, and PbBrCl from zinc and aluminium smelters and leaded gasoline, respectively, are predominant precursors for the anthropogenic trace species (Biggins and Harrison, 1979; Williams and Harrison, 1984; Abdul-Wahab and Alsubhi, 2019). Chemical reactions of these precursors in the atmosphere include oxidations, such as the formation of HNO_3, H_2SO_4, Cd(II) compounds from NOx, SO_2, Cd(0), respectively. Emitted precursors or atmospheric reaction products either directly form particles (such as H_2SO_4) or partition into particles by e.g. acid-base reactions (HNO_3, NH_3, HF) or by different reaction types (for Cd, Pb compounds) (see e.g. (Biggins and Harrison, 1979)). After an atmospheric lifetime in the order of a few days (Seinfeld and Pandis, 2016), wet (and dry) deposition lead to their removal from the atmosphere.

Ice-core records of the seven pollutants were systematically compared in terms of their concentration levels and the observed longer-term changes, allowing to test how representative a single ice core from the European Alps documents the pollution history in the source region. The pollution source regions for the four Alpine sites were determined using the state-of-the-art atmospheric aerosol transport model (FLEXPART). For the investigation of differences in absolute concentration levels at the four ice-core sites, the European-scale atmospheric chemical transport model (MATCH) was used to simulate concentrations of NH_4^+, NO_3^- and $exSO_4^{2-}$ in Alpine precipitation. In addition, we present Alpine composite records for the seven species and their evaluation using time of emergence (TOE) analyses, revealing the time at which Western European pollution levels first exceeded the natural variability of the pre-industrial period (AD 1750-1850) and allowing to place recent changes into a longer-term perspective. Finally, the ice-core composites of all pollutants were compared with available model estimates of either their emission history, atmospheric concentrations, or deposition data allowing to validate and constrain existing approaches for modelling the development of anthropogenic air pollution in Western Europe.

2 Methods

2.1 Study sites and ice-core archives

Longer-term ice-core data are available from four sites located in the Swiss and French Alps: Monte Rosa in the Valais Alps (Colle Gnifetti and Grenzgletscher), Fiescherhorn in the Bernese Alps (Fiescherhorn glacier) and Mont Blanc in the Auvergne-

Rhône-Alpes (Col du Dôme). These four Alpine sites are located within a ~100 by 100 km square. Their exact locations are shown in Figure 1 with details about the different ice cores being summarized in Table 1.

2.1.1 Colle Gnifetti (CG)

The Colle Gnifetti (4450-4470 m asl) is located in the Monte Rosa massif on the border between Switzerland and Italy in the Southern Alpine chain (Valais Alps). The Colle Gnifetti is a glacier saddle at the uppermost part of the Grenzgletscher between the summits Signalkuppe and Zumsteinspitze. Numerous firn and ice cores have been drilled there since 1976, revealing that this site is prone to wind erosion, preferentially removing parts or all of the winter snow cover (Wagenbach et al., 2012). The latter explains the low mean annual net accumulation rates of 0.2-0.5 m water equivalent (w.eq.) (Table 1) and the observation that older than 15000-year old ice was found at the bedrock (Jenk et al., 2009; Hoffmann et al., 2018). The dating of the different cores used in this study was achieved by combining a variety of dating methods such as annual layer counting using the seasonally varying signals of different parameters (e.g. NH_4^+ and $\delta^{18}O$), ^{210}Pb dating, the use of reference horizons (Saharan dust events, 1963 ^3H maximum from atmospheric nuclear tests, volcanic eruptions), application of ice flow models, and ^{14}C dating (Jenk et al., 2009; Sigl et al., 2018). In this study, we focus on the ice-core data covering the period AD 1750-2015, as detailed in Table 2.

2.1.2 Grenzgletscher (GG)

The Grenzgletscher was the main tributary of the Gornergletscher system in the Monte Rosa massif, until the strong retreat of the Gornergletscher separated them recently. A 125 m long ice core was drilled at 4200 m asl on the upper Grenzgletscher in October 1994 (Eichler et al., 2000b). The ice core covers the period AD 1937-1994 with a mean annual net accumulation rate of 2.7 m w.eq. (Table 1). This was established based on ^{210}Pb dating, annual layer counting, and detection of reference horizons, such as the Saharan dust layers in AD 1947, 1977, and 1990, as well as the ^{137}Cs maxima in AD 1986 and 1963 from the Chernobyl accident and atmospheric nuclear testing, respectively (Eichler et al., 2000b). Records of chemical species are partly disturbed for the period AD 1984-89, due to an inflow and percolation of meltwater causing partial leaching (Eichler et al., 2001). Thus, for this study only the undisturbed section covering the period AD 1937-1983 was considered.

2.1.3 Fiescherhorn (FH)

The Fieschergletscher in the Swiss Northern Alpine chain (Bernese Alps) has an extended plateau flanked by the mountains Grosses Fiescherhorn, Hinteres Fiescherhorn, and Kleines Fiescherhorn. A 150.5 m long ice core was drilled in 2002 at an altitude of 3900 m asl (Jenk et al., 2006). Dating was performed by annual layer counting, time markers such as Saharan dust events in AD 1947, 1977, 2000 and the 1912 Katmai volcanic layer, and ice flow modelling. The ice core covers the period from AD 1660 to 2002 and the mean annual net accumulation rate is 1.4 m w.eq. (Jenk, 2006; Jenk et al., 2006). Similar to the Grenzgletscher site, concentration records of selected chemical species were partly disturbed between AD 1989 and 1997 (Jenk, 2006), and we therefore restricted discussions to the period AD 1750-1988.

2.1.4 Col du Dôme (CDD)

165 The Col du Dôme is a glacier saddle at 4250 m asl between the Mont Blanc main summit and the Dôme de Goûter in the French Alps. Data used in this study are from three ice cores drilled in 1994 (126 m), 2004 (124 m), and 2012 (140 m). Ice-core sites are less than 20 m apart. Dating was performed by annual layer counting mainly based on the NH_4^+ concentrations (Preunkert et al., 2000), refined with reference horizons, such as the Saharan dust layers in 1936/37, 1947, and 1977, the 1963 ^3H maximum, and the ^{137}Cs maxima in 1954 and 1986. The mean annual net accumulation rate near the surface is 2.4 m w.eq.,

170 with a rather regular distribution of seasonal accumulation (Vincent et al., 1997). Due to changes in depositional processes upstream of the drilling site, winter layers at the CDD site were found to generally thin with depth relative to summer layers (Preunkert et al., 2000), resulting in a winter to summer accumulation ratio of 1 at the surface and of 0.4 in 1925 and to an absence of winter snow layers prior to 1890 (Legrand et al., 2020). To account for this, in the present study only data for the period AD 1890-2012 were considered.

175 **2.2 Sampling and analyses**

2.2.1 NH_4^+, NO_3^-, SO_4^{2-}, and F^-

The determination of the major ion concentrations (NH_4^+, NO_3^-, SO_4^{2-}, Ca^{2+}, Na^+) and of F^- in the CDD, CG15, CG93, FH, and GG cores on discrete samples was performed by Ion Chromatography (IC) with conductivity detection at the Paul Scherrer Institute (PSI) (Eichler et al., 2000a; Eichler et al., 2000b), the Institute for Environmental Physics, Heidelberg (IUP), and the

180 Laboratoire de Glaciologie et Géophysique de l'Environnement, Grenoble (LGGE) (Legrand et al., 1993; Preunkert et al., 2001a).

2.2.2 Pb and Cd

Pb and Cd concentrations were determined in discrete samples by Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS) at the PSI (CG95 core) (Schwikowski et al., 2004), by continuous flow analyses (CFA) with Inductively Coupled

185 Plasma Quadrupole Mass Spectrometry (ICP-QMS) at the University of Venice (CG03 core) (Gabrieli, 2008; Gabrieli and Barbante, 2014) and by CFA ICP-SFMS at the Desert Research Institute (DRI) (CDD cores) (Legrand et al., 2020). ICP-SFMS and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) at the University of Maine was used for the analyses of the CG13 core (More et al., 2017).

2.2.3 Black carbon - rBC and EC

190 Concentrations of atmospheric soot particles are determined with different analytical techniques. Depending on the method used, the non-organic carbon fraction of soot is denoted as BC or elemental carbon (EC). We here followed the notation recommended by (Petzold et al., 2013). After aerosolizing and drying of the aqueous sample in a jet nebulizer (APEX-Q, Elemental Scientific Inc., USA), concentrations of BC in the CG15 core were determined based on laser-induced

incandescence with a Single Particle Soot Photometer (SP2, Droplet Measurement Technologies) and are in the following

195   accordingly denoted as refractory black carbon (rBC) (Wendl et al., 2014; Sigl et al., 2018). Concentrations in the FH core were either measured by a thermal (Jenk et al., 2006) or thermal/optical technique (Cao et al., 2013) and thus here denoted as EC. For samples covering the period AD 1660-1940, EC was combusted to CO_2 for subsequent manometric quantification (Jenk et al., 2006), while it was quantified by a non-dispersive infrared (NDIR) detector (OC/EC analyzer, Sunset Laboratory Inc., USA) for the more recent samples (Cao et al., 2013).

200   **2.3 Data presentation, formation of composite records, time of emergence analyses**

The datasets for the four individual Alpine ice-core sites were compiled from values reported previously in the studies listed in Table 2. We here used data of the seven investigated species (BC, Cd, F$^-$, NH$_4^+$, NO$_3^-$, Pb, SO$_4^{2-}$) published before end of 2021. For SO$_4^{2-}$ the non-dust and non-sea salt contribution (exSO$_4^{2-}$) was calculated from the total SO$_4^{2-}$ accordingly to [exSO$_4^{2-}$] = [SO$_4^{2-}$]$_{total}$ − 0.12[Na$^+$] − 0.175 [Ca^{2+}], using Ca^{2+} and Na$^+$ as mineral dust and sea salt tracers, respectively

205   (Schwikowski et al., 1999b). ExSO$_4^{2-}$ thus represents the part of SO$_4^{2-}$, exclusively formed from the atmospheric oxidation of SO$_2$.

For all ice cores, annual averages were calculated similarly from these non-equidistant data as arithmetic mean of all data points in an annual layer. Then, based on these annual means, 10-year arithmetic concentration averages were calculated. 10-year averages were selected, since they showed to be most representative of pollutant emissions, smoothing out inter-annual

210   (short-term) fluctuations related to temperature dependent vertical transport to the high-alpine sites (see S1 and Fig. S1). Furthermore, they account for a lower temporal sampling resolution and increasing dating uncertainty with increasing depth, i.e. age (e.g. 10-25 years for the FH in the period 1750-1800). Averages represent mainly decadal means (e.g. 2000-2009), except for the most recent period (2010-2015).

Previous studies from CDD used a different procedure to calculate annual means. To account for the observed longer-term

215   trend in changing preservation of winter relative to summer snow (see section 2.1.4.), concentrations of winter and summer layers were averaged (Legrand et al., 2020) or winter and summer records investigated separately (Preunkert et al., 2001a; Preunkert et al., 2003; Preunkert and Legrand, 2013). Since for the other three study sites a disentangling of winter and summer layers was not possible especially for the pre-industrial periods with low data resolution, we accordingly formed arithmetic means of total annual layer data for all ice cores consistently as described above. In any case, for the 10-year means considered

220   in this study, CDD longer-term concentration trends for both averaging procedures were found to agree within the uncertainty envelopes for all investigated species (see S2 and Fig. S2).

Based on the 10-year average records obtained for each site, an ice-core composite record was formed for each species. For this, individual records were transformed into z-scores using the average and standard deviation of the common period AD 1910-1990. To obtain a sufficiently long overlapping period, the relatively short (< 50 years) GG records were not included.

225   The BC composite record consists of the FH EC and CG rBC records.

TOE analyses was applied to determine when the composite z-scores exceed the natural variability of the pre-industrial period for the first time. The TOE was defined as the year when the 10-yr-average composite z-scores first exceed (and remain above) the pre-industrial average z-scores (period AD 1750-1850) by at least two standard deviations determined from the variability in the pre-industrial 10-year averages (Lehner et al., 2017).

2.4 Source region of air pollutants using FLEXPART

The potential source regions of the pollutants deposited at the CDD, CG/GG, and FH sites were derived using the state-of-the-art Lagrangian particle dispersion model FLEXPART (version 10.4) (Stohl et al., 2005; Pisso et al., 2019). The model maps the emission sensitivity of sub-micrometre aerosol particles deposited at the three sites (Figure 1). The emission sensitivity in a certain grid cell represents the ratio of aerosol deposition at the respective study site (in $\mu g\ m^{-2}\ a^{-1}$) to emission of this aerosol in the grid cell (in $kg\ s^{-1}$) ("receptor/source" ratio). A detailed description of the calculation of the source-receptor relationship for deposited mass in FLEXPART is provided by Eckhardt et al. (2017). In the atmosphere over the Alps all species discussed in this study are predominantly present as sub-micrometre aerosols. The model was therefore run for SO_4^{2-} as a target species for dispersion of sub-micrometre aerosol. FLEXPART was run in its backward-in-time mode simulating dry and wet deposition (Eckhardt et al., 2017) for the period 2000 through 2009, while employing ERA5 re-analysis data at 0.5° x 0.5° horizontal and 1-hourly temporal resolution (137 vertical layers) (Hersbach et al., 2018) as the meteorological input. Particles were released continuously ($10^6/10^5$ per month for wet/dry deposition, respectively) and traced backward for 30 days. FLEXPART uses a statistic approach to calculate the mean residence time of all released particles in individual grid cells to derive the emission sensitivity. In order to compensate for model surface misrepresentation (the Alps are lower in the model than reality), wet deposition, which is highly sensitive to altitude, was calculated at the actual altitudes of the sites.

2.5 Modelling of air pollutant concentrations in precipitation

Two different versions of a European-scale atmospheric chemical transport model, MATCH (Robertson et al., 1999; Andersson et al., 2007; Theobald et al., 2019) were used to simulate concentrations of NH_4^+, NO_3^- and $exSO_4^{2-}$ in precipitation at the ice-core sites. To construct secular concentration trends in the period 1900-2020, we utilised a well-described set-up (50 km resolution) developed for the ECLAIRE project (MATCH-ECLAIRE). Details on this simulation, including input data, can be found in Engardt et al. (2017). The spatial distribution of $exSO_4^{2-}$ concentration during the 10-year periods 1970-1979 and 1990-1999 in the Alps were investigated using MATCH-ECLAIRE and for the more recent decade 1990-1999 also with the new, high-resolution set-up MATCH-BIODIV. The MATCH-BIODIV domain extends over most of Europe at 12 km resolution and the dataset covers the period 1987-2020. MATCH-BIODIV was forced by meteorological data generated by the regional climate model ALADIN with EC-EARTH on its boundaries under the influence of greenhouse gas emission scenario RCP8.5 (Belušić et al., 2020; Lind et al., 2022), and nitrogen and sulphur emissions from ECLIPSE V6b (Höglund-Isaksson et al., 2020). The output from the chemical transport model was finally averaged over the same 10-year periods as the ice-core data.

3 Results and Discussion

Average emission sensitivities during the period 2000-2009 derived with FLEXPART, indicate that in general the four ice-core sites CDD, CG, FH, and GG are most sensitive to emissions from the countries surrounding the Alps, i.e. Switzerland, France, Italy, Germany, Austria, Slovenia, and Spain, without substantial discrepancies between the four sites (Figure 1). A noticeable extension of the pollution source area into Spain is recognized for the westernmost CDD, and into larger parts of Germany for the northernmost FH site. To investigate, how representative ice-core records from the four sites are to document the pollution history in the identified source area we systematically compared a) concentration levels (section 3.1.) and b) longer-term variations in concentrations of BC, Cd, F$^-$, NH$_4^+$, NO$_3^-$, Pb, and exSO$_4^{2-}$ (section 3.2.).

3.1 Concentration levels

Absolute concentrations are very similar at CG, FH, and GG, whereas CDD concentrations are about a factor of 1.4 lower on average (1.1-1.7, Figure 2). Potential reasons for the lower concentrations at CDD are (1) a west-east gradient in the deposition of anthropogenic pollutants in the Alps, and/or (2) a relative higher amount of the cleaner winter snow at the CDD site.

(1) Increasing concentrations of NH$_4^+$, NO$_3^-$, and SO$_4^{2-}$ were observed along an Alpine west-east transect in winter snow samples for the period AD 1991-1993 (Nickus et al., 1997). The findings of this short-term study are supported by MATCH simulations using the MATCH-ECLAIRE set-up (50 km resolution, available for the period AD 1900-2020) which produced a factor of 2-3 difference between exSO$_4^{2-}$ concentration in precipitation at CDD and the other sites (Figure 3, Table 3). However, simulated concentrations are a factor of 6-8 higher than the ice-core values. Due to the rather low spatial resolution in MATCH-ECLAIRE, the mean heights of the grid cells including the drilling sites are between 1600 and 1800 m asl, far lower than the actual height of the sites (3900-4450 m asl). Generally, pollution concentrations in precipitation are higher at lower altitudes, where the emission sources are located. To test, whether the model output depends on the spatial resolution of the chemical transport model and its input (meteorology, emissions, topography etc.), we used data from MATCH-BIODIV with the higher spatial resolution of 12 km, providing concentrations in precipitation from 1987 on. Here, the mean height of the grid cells representing the ice-core sites span 2400 to 2700 m asl. As expected, exSO$_4^{2-}$ concentrations obtained from the MATCH-BIODIV dataset for the period AD 1990-1999 are significantly lower compared to MATCH-ECLAIRE, and are comparable to the ice-core concentrations (Figure 3, Table 3). Furthermore, the simulated concentrations using MATCH-BIODIV are similar at the four sites and the high-Alpine region in general (green region in Figure 3e) supporting the FLEXPART results that the same source regions of pollutants impact these high-Alpine sites (see 3.1.1.). Thus, based on the MATCH-BIODIV results we can exclude a high-Alpine west-east concentration gradient of anthropogenic pollutants to explain the lower concentrations at CDD.

(2) If not related to a west-east gradient, the lower concentrations observed at CDD could be explained by different conditions affecting snow deposition. In general, concentrations of anthropogenic pollutants at high elevation sites reveal a pronounced seasonal cycle due to a seasonality in the stability of the atmosphere. In summer, more intense radiation causes increased

290   convection and instability of the lower atmosphere, resulting in an expansion of the planetary boundary layer to the high elevations. During the colder months, mountain sites become decoupled from the boundary layer in the lower-altitude, stronger polluted areas, and encounter free tropospheric, cleaner, conditions. As an example, mean NH_4^+, NO_3^-, and SO_4^{2-} summer-to-winter concentration ratios of 14, 3.9, and 3.7, respectively, were observed at CDD during the period AD 1982-1991 (Preunkert et al., 2000). Thus, the mean annual concentrations at high-altitude sites strongly depend on the seasonality of accumulated

295   precipitation. At the CDD site in the western Alps, the distribution of precipitation is rather regular throughout the year (Vincent et al., 1997). This is different at the FH site in the northern Alps, revealing a precipitation maximum in summer due to convection. At the GG in the southern Alpine chain precipitation from tropical-maritime air masses during foehn situations leads to maxima in spring and autumn (Eichler et al., 2004). The CG site is prone to wind erosion, preferentially removing parts or all of the dry and lighter winter snow cover (see section 2.1.1.). For these reasons, the hypothesis that the lower ice-

300   core concentrations at the CDD compared to CG, FH and GG is related to a higher share of winter precipitation seems reasonable. The fact that mainly summer deposition is preserved at the CG is corroborated by the agreement in concentration levels of different major ions between summer CDD and annual CG accumulation layers (Preunkert et al., 2000; Preunkert et al., 2003; Wagenbach et al., 2012). Because of the preferential loss of the cleaner winter snow, higher annual average concentrations levels at CG are expected also compared to FH and GG. However, similar concentrations levels at all three

305   sites suggest that the loss of the cleaner winter snow at CG is compensated by the altitude concentration gradient (lower concentrations with increasing altitude) (Preunkert et al., 2001a).

Unfortunately, local differences in the seasonal distribution of precipitation and small-scale processes like wind erosion affecting its deposition on the glacier cannot be tested in the MATCH model due to its limitations in resolution.

3.2 Longer-term concentration variations

310   Generally, an excellent agreement in the 10-year ice-core longer-term concentration changes (trends) of all investigated pollutants is observed for the four sites CDD, CG, FH, and GG (Figure 2). This is confirmed by correlation analyses, revealing high correlation coefficients ($0.84 < r < 1.00$) between the respective pollutant records from the different ice cores (Figure 4). All correlations are significant at the 0.001 level. The observed trends are characteristic for the individual seven pollutants, reflecting differences in their respective emission sources, emission histories, the atmospheric chemistry of precursor species,

315   and compound specific implementation and efficiency of emission abatement measures. This is detailed in the following sections (3.2.1-3.2.3), including discussion of how representative the Western European pollution history is captured.

3.2.1 Trends in major inorganic aerosol species ($exSO_4^{2-}$, NO_3^-, NH_4^+)

Excess sulfate

The five alpine $exSO_4^{2-}$ records (CDD, CG15, CG93, FH, GG) consistently show low pre-industrial background levels (AD

320   1750-1850), increasing concentrations from the second half of the 19th century until the 1970s, and declining values afterwards

(Figure 2). In the pre-industrial period a significant proportion of the $exSO_4^{2-}$ originated from wood combustion for domestic heating (Schwikowski et al., 1999b). During the 1880s the Alpine composite $exSO_4^{2-}$ record indicates levels exceeding for the first time the variability of the pre-industrial values (Figure 5), denoting the onset of substantial anthropogenic SO_2 emissions from coal burning in Western Europe. In the following ~50 years FH concentrations are higher compared to the other sites Figure 2), which could reflect a stronger influence of SO_2 emissions from Germany that increased faster than in other Western European countries during that time (Hoesly et al., 2018). After ~1930 there is a consistent increasing trend at all sites, cumulating in maximum values in the 1970s. The majority of the anthropogenic SO_2 emissions during that time was from fossil fuel combustion in energy and transformation industries (stationary sources). Decreasing $exSO_4^{2-}$ concentrations from the 1980s on are the consequence of the implementation of air pollution control measures, such as the desulphurisation of coal, the use of low-sulphur fuels, and the introduction of filters and scrubbers in power plants.

The observed longer-term trend in the composite $exSO_4^{2-}$ record and modelled $exSO_4^{2-}$ concentrations in precipitation at the drilling sites agree exceptionally well during the period AD 1900-2020 (Figures 3 and 5). This finding confirms that European SO_2 emissions and the SO_2/SO_4^{2-} atmospheric chemistry are well described in the MATCH model. The pronounced maximum in the 1970s and the strong decline afterwards is reproduced on a regional, Western European level within the spatial model results (Figures 3b and 3c). The former is in accordance with the SO_2 emission peak in the main source regions (France, Germany, Italy, and Switzerland) during the 1970s (Hoesly et al., 2018). The Alpine ice-core composite record and model estimates of $exSO_4^{2-}$ consistently demonstrate that concentrations in the 2010s were again as low as in the first half of the 20th century, confirming the high efficiency of the introduced abatement measures in Western Europe.

Nitrate

Five NO_3^- records from CDD, CG15, CG93, FH, and GG are in excellent agreement, generally showing low pre-industrial background levels from 1750 to the mid of the 20th century, rising values until the 1980s and stabilization during the past decades (Figure 2). Major emission sources during the pre-industrial period included NOx emissions from natural soils, lightning, wild fires and anthropogenic activities such as biofuel combustion and agricultural waste burning (Preunkert et al., 2003; Hoesly et al., 2018). The strong NO_3^- increase in the second half of the 20th century reflects anthropogenic NOx emissions from high temperature combustion, pre-dominantly from the traffic and energy sector. The Alpine composite NO_3^- record exceeds the variability of the pre-industrial period for the first time during the 1930s (Figure 5), marking the onset of substantial anthropogenic NOx emissions to the atmosphere predominantly from motor vehicles in Western Europe. The delay of 50 years between TOE for $exSO_4^{2-}$ and NO_3^- potentially reflects the change of fossil fuel use over time in Western Europe; from coal burning during the first half of the 20th century to liquid/gaseous fuel burning during the second half of the 20th century.

Although air pollution control measures such as combustion catalysts have been widely implemented in recent decades in all Western European countries, no prominent decline in the ice-core NO_3^- concentrations is observed for the most recent years. During most of the 20th century, modelled concentrations in precipitation at the ice-core sites closely resemble the ice-core data (Figure 5). However, starting in the 1980s the composite NO_3^- record diverges from the model results and estimated NOx

emissions from Western European countries (Hoesly et al., 2018). All relevant European countries show a significant drop of
NOx emission estimates by roughly a factor of 2 between the 1980s and 2010s (Hoesly et al., 2018). Hypotheses for the
disagreement are potential uncertainties in NOx emissions estimates or model misrepresentation of the HNO_3/NO_3^- partitioning
between gas and particle phase and of the atmospheric chemistry. E.g. the formation of nitrate aerosols from HNO_3 is
depending on the presence of alkaline compounds (such as NH_3, or mineral dust). Still high recent NH_4^+ (NH_3) concentration
levels (though not predicted by the MATCH model, see below) could favor the formation of NH_4NO_3 aerosols. Nevertheless,
the still high Alpine composite NO_3^- concentrations beginning of the 21th century indicate that the so far introduced air pollution
control actions in Western Europe were still not sufficient to have a major effect on recent NO_3^- levels at high altitudes.

Ammonium

Overall the available five NH_4^+ records from CDD, CG15, CG93, FH, and GG agree well, consistently indicating low pre-
industrial values in the period AD 1750-1850, with a continuously increasing trend afterwards (Figure 2). The last ~30 years
of the records are characterized by the highest NH_4^+ concentrations, unprecedented during the last 250 years. The major
emission sources during pre-industrial times were biogenic and agricultural NH_3 emissions (Eichler et al., 2009). The observed
differences between the CG15, CG93, and FH concentration records during the first 150 years are not related to differences in
source regions, since the two CG cores are from the same site (Figure 2). This is most likely related to the fact that NH_4^+
measurements are prone to contamination from laboratory air (Legrand et al., 1984), which is especially problematic for the
very low pre-industrial levels being often below 30 ppb. Increasing NH_4^+ levels starting from the second half of the 19th century
were caused by rising anthropogenic NH_3 emissions from agriculture (bacterial decomposition of livestock wastes and fertiliser
applications) (Döscher et al., 1996; Hoesly et al., 2018). Based on the TOE analysis of the Alpine composite, the onset of these
extensive emissions in Western Europe started in the 1880s (Figure 5). Despite the partial introduction of agricultural emission
reduction measures in Western Europe since the end of 20th/beginning of the 21th century, such as NH_3 reductions in fertilizer
industry and livestock breeding (Giannakis et al., 2019; Liu et al., 2020; Liu et al., 2022), no corresponding decline in recent
NH_4^+ levels is observed in the ice-core records. Indeed, NH_3 emission reductions targeted for the past ~20 years based on
environmental policies were not achieved for many European countries (Giannakis et al., 2019). Observed slight decreasing
NH_3 emissions in some countries during this time could be in part related to different factors than air pollution control such as
the strong focus on animal welfare leading to declining livestock numbers (Kupper et al., 2015).

The observed longer-term trends in the Alpine composite NH_4^+ record and modelled concentrations in precipitation at the
drilling sites agree well during the period AD 1900-1980 (Figure 5). Similarly to NO_3^-, there is a strong deviation after 1980
with unprecedented high NH_4^+ ice-core concentrations, but decreasing simulated concentrations and emission estimates in the
source regions. Spain is the only country, with non-decreasing NH_3 emission estimates, whereas all other relevant Western
European source countries show a 10-35% decrease between the 1980s and 2010s. One hypothesis to explain the discrepancy
is that NH_3 emissions from soil amplified by increasing temperatures (Skjoth and Geels, 2013; Sutton et al., 2013) are not yet
considered in the used version of the MATCH model. Another hypothesis is the nonlinearity between NH_3 emissions and NH_4^+

deposition over the Alps not fully covered by the model. The conversion of gaseous NH_3 to aerosol-borne NH_4^+ strongly depends on the presence of acidic species (i.e. H_2SO_4, HNO_3) and the pH of the aerosol. Whereas the decreasing concentrations of SO_4^{2-} after the 1970s are well simulated by the MATCH (section 3.2.1.), the still high recent NO_3^- concentrations observed in the ice-core composite (section 3.2.2.), which also might cause enhanced NH_4^+ concentrations, are not reflected by them. Finally, also uncertain emission estimates can potentially contribute to the observed discrepancy. In any case, the still high Alpine composite NH_4^+ concentrations during the past decades clearly show that the introduced agricultural policies were not sufficient to create a significant downward trend in recent NH_4^+ levels at high altitudes in Western Europe.

In summary, concentration records of all three major inorganic aerosol species are highly correlated between the individual sites (Figure 4). Lowest correlation coefficients are observed for NH_4^+ ($0.86 < r < 0.99$), due to the stronger pre-industrial variability related to the potential contamination issue for NH_4^+. Highest correspondence is obtained between the different NO_3^- ($0.96 < r < 1.00$) and $exSO_4^{2-}$ records ($0.92 < r < 1.00$). These results demonstrate that longer-term changes in ice-core concentration records of major inorganic aerosol species from individual sites in the European Alps provide a spatial representative signal of anthropogenic pollution trends from Western European countries.

3.2.2 Trends in black carbon

The CG15 rBC record and FH EC record correspond well in their general trend (Figure 2). The difference in absolute concentrations of approximately a factor of 4 was expected, since thermo-optical methods to determine EC produce consistently higher values compared to methods utilizing the light-absorbing properties of BC (Currie et al., 2002; Bond et al., 2007; Lim et al., 2014; Sigl et al., 2018). The rBC and EC concentration trend is marked by low pre-industrial levels, an increase during the second half of the 19th century, maximum values in the beginning of the 20th century and subsequent decreasing levels. Pre-industrial rBC and EC sources are anthropogenic or natural biomass burning (Bond et al., 2007; Sigl et al., 2018). The significant increase of rBC and EC during the second half of the 19th century is concurrent with the rise in $exSO_4^{2-}$ concentrations and related to emissions from coal burning. The onset of substantial anthropogenic BC emissions from coal burning in Western Europe exceeding pre-industrial levels was during the 1870s, as determined with TOE of the Alpine composite (Figure 5). Coal burning emissions peaked in the first half of the 20th century. The still relatively high rBC and EC concentrations after the 1950s are due to emission from burning of other fossil fuels, such as petroleum (industrial sector and traffic) and domestic emissions (Sigl et al., 2018).

Modelled atmospheric BC mixing ratios at the FH site (FLEXPART model) (Fang et al., 2019) resemble Alpine ice-core concentrations exceptionally well during the past 150 years. The Alpine composite record together with modelled mixing ratios illustrate that BC pollution in Western Europe in the beginning of the 21th century was again as low as at the end of the 19th century demonstrating the effect of the substitution of coal with petroleum products (lower emission factors) and of the implemented air pollution control measures such as the requirement of filter systems and certified combustion efficiency and general regulations regarding firing.

420

3.2.3 Trends in trace species (Cd, Pb, F⁻)

Cadmium

The trends of the two Cd records from CG03 and CDD are in excellent agreement for the overlapping period AD 1890-2000
425 (Figure 2). Cd concentrations remain on a stable low level until the end of the 19th century, start to increase at the beginning of the 20th century and peak in the 1970s. Cd sources during the pre-industrial period are mineral dust and mining activities. Rising values from the beginning of the 20th century on are attributed to emissions from Zn and Cu smelters and coal burning. These extensive emissions are responsible for the exceeding of pre-industrial Alpine composite Cd levels since the 1900s (Figure 5). The major Cd source during the 20th century was growing emissions from Zn smelting followed by Cu smelting,
430 whereas emissions from coal combustion became less important towards the second half of the 20th century (Legrand et al., 2020). Decreasing Cd concentrations after the 1970s reflect the introduction of air pollution control measures, such as the implementation of filters to clean the vent gases of Zn and Cu smelters (Legrand et al., 2020).

We find a good correspondence in the trend between the Alpine composite Cd record and estimated Cd deposition until the 1960s (Figure 5). Past Cd deposition fluxes were calculated from emissions estimates in European countries weighted by the
435 FLEXPART emission sensitivities (combined emission scenarios (1) and (2) from (Legrand et al., 2020)). Whereas model estimates strongly decrease after the 1960s, ice-core Cd peaks in the 1970s, suggesting that the applied model emission reductions, considering the introduction of pollution control devices and other technological improvements, was too optimistic. However, the effectivity of the introduced abatement measures can clearly be detected in the ice-core records with similar Cd levels in the 1990s as in the 1920s.

440 **Lead**

Three Pb records from the CG (CG03, CG13, CG95) correspond exceptionally well, revealing low values until the end of the 19th century, with elevated levels at the beginning of the 20th century, strongly rising concentrations with a maximum in the 1970s, followed by a declining trend (Figure 2). This correspondence in trace element concentration records in the lower ppb range is remarkable, since the three CG cores were sampled and analysed in three different laboratories, using different
445 methods of analyses. The CDD Pb concentrations show a similar trend to the CG cores after AD 1940. The relative elevated Pb levels in the earlier period from around AD 1890-1940 observed in the CDD core still remain unexplained. Pb emissions during the pre-industrial period were mainly from soil dust and mining activities in Europe (Schwikowski et al., 2004). During the second half of the 19th century and first half of the 20th century, emissions from nonferrous metal production, iron and steel manufacturing, and coal combustion became dominant. The TOE analysis demonstrates that already from the 1870s on the

450   Alpine composite Pb record exceeds the pre-industrial Pb levels, related to these emissions (Figure 5). The increasing trend in Pb concentrations after the 1940s until the 1970s resulted from the use of lead additives in gasoline, whereas the subsequent decrease after the 1970s is related to the ban of leaded gasoline (Legrand et al., 2020).

Trends of the Alpine composite Pb record and the calculated Pb deposition based on emissions estimates in European countries weighted by the FLEXPART emission sensitivities (emission scenarios (1) and (2) from (Legrand et al., 2020)) agree

455   remarkably well (Figure 5). Ice-core records together with deposition estimates illustrate that, mainly as a result of the ban of leaded gasoline, Pb pollution in Western Europe in the beginning of the 21th century was reduced to pre-industrial values.

Fluoride

The F[-] concentration record from FH shows low values during the 18th and 19th century and increasing levels from the first half of the 20th century on. The three records from CDD, FH, and GG consistently reveal a significant rise during the 1930s-

460   1940s peaking in the 1960s and a strong drop afterwards (Figure 2). F[-] sources during the pre-industrial period are mainly soil dust emissions. In the 1930s the Alpine composite F[-] record exceeds for the first time the variability of the pre-industrial period (Figure 5), marking the onset of substantial F[-] emissions from aluminium smelters in Western Europe. Thus, from the 1930s to the 1980s the main contributor to anthropogenic F[-] changes at CDD, FH, and GG was HF emissions from the aluminium industry in France, Germany, and Switzerland, with the main smelters located in the Auvergne-Rhône-Alpes and in the Swiss

465   Rhone valley (Eichler et al., 2000a; Preunkert et al., 2001b). The emission of huge amounts of HF from this source caused severe ecological damage during the 1960s and 1970s (Eichler et al., 2000a). The strong drop of F[-] concentrations after the 1960s was the effect of installing waste-air purification system in aluminium smelters, such as cap systems equipped with Al_2O_3 filter to chemisorb HF (Preunkert et al., 2001b). During the 20th century, also coal burning contributed to anthropogenic F[-] changes, with a share of less than 30% (Preunkert et al., 2001b).

470   The Alpine composite F[-] record and HF emission estimates from the aluminium industry of France and Switzerland during the period AD 1920-1980 show comparable trends (Figure 5). Only in the 1990s the Alpine F[-] level is elevated compared to the emission estimates, pointing to an increasing share of other anthropogenic sources like cement and phosphate industrial processes (Preunkert et al., 2001b). However, the efficacy of the introduced abatement measures in Western Europe mainly for the aluminium industry, is well reflected in the ice-core records, revealing F[-] levels in the 1990s similar to the previously

475   lower levels in the 1950s.

Similar to the findings for the major ions and BC, also 10-year concentration records of all three trace species are highly correlated between the individual sites (Figure 4). Lower correlation coefficients are in part observed for Pb (0.84 < r < 0.98), related to the relative elevated CDD Pb levels in the period AD 1890-1940, whereas highest correspondence is obtained between the individual Cd and F[-] records (0.91 < r < 0.99). We conclude that also for trace elements, a single Alpine ice core

480   can be a representative archive of Western European air pollution trends.

4 Summary and Conclusion

Here we present the first study considering longer-term records (AD 1750-2015) of seven anthropogenic pollutants from four different high-Alpine ice-core sites in the European Alps (CDD, CG, FH, GG). The systematic comparison between ice-core records of BC, Cd, F^-, NH_4^+, NO_3^-, Pb, and $exSO_4^{2-}$ allowed addressing the question of how representative one ice core is with respect to the reconstruction of atmospheric composition in the source region.

High-Alpine ice-core sites have the advantage that they are located in less than 100 km distance, with altitude differences of < 500 m. Furthermore, the locations are either not affected by melting processes (CDD, CG) or melt-disturbed parts were removed before analyses (FH, GG). Emission sensitivities produced with the atmospheric aerosol transport model FLEXPART give evidence that the considered ice-core sites receive air masses from the same source region of pollutants, i.e. from Western European countries surrounding the Alps (Switzerland, France, Italy, Germany, Austria, Spain, and Slovenia).

In general, pollution concentration levels are similar at the three sites CG, FH, and GG. However, CDD concentrations of all studied species are on average about a factor of 1.4 (1.1-1.7) lower, most probably caused by a higher share of winter precipitation characterised by low concentrations. Thus, absolute pollution concentrations at the Alpine sites can vary depending on the prevailing seasonal distribution of accumulated precipitation, suggesting that they do not provide a spatial consistent signal.

In contrast, longer-term concentration variations of all investigated air pollutants feature a uniform timing in species-dependent anthropogenic impact at the four sites. Our results demonstrate that all ice-core records from the different sites in the European Alps provide a representative signal of anthropogenic pollution changes in Western European countries. Thus, in our study we show for the first time, how consistent this pollution history is recorded in different Alpine ice cores.

We were able to refine the history for different compounds by pinning down their onset of pollution, maxima, and recent changes. Based on the time of emergence analyses on the obtained Alpine ice-core composite records the onset of significant air pollution exceeding pre-industrial levels (AD 1750-1850) in Western Europe was pinpointed to the 1870s and 1880s for BC, $exSO_4^{2-}$, Pb, and NH_4^+, mainly caused by emissions from coal combustion and agriculture, respectively. Cd, F^-, and NO_3^- concentrations in the atmosphere predominantly from emissions of zinc and aluminium smelters and traffic, respectively, started surpassing pre-industrial values later; in the first half of the 20th century for Cd and F^-, and during the 1960s for NO_3^-.

Consistent pollutant-dependent maxima and recent changes at the four sites reveal a divers efficiency of implemented emission abatement measures. BC concentrations have a maximum in the first half of the 20th century, whereas those of Cd, $exSO_4^{2-}$, F^-, and Pb peak during the 1970s. Concentrations of all five pollutants significantly decrease afterwards, related to the desulphurisation of coal, the use of low-sulphur fuels, the introduction of filters and scrubbers in power plants and metal smelters, and the ban of leaded gasoline for improving the air quality in Western Europe. In contrast, the ice-core concentrations of the nitrogen species NO_3^- and NH_4^+ in the beginning of the 21th century are unprecedented in the context of the past 250 years, indicating that the introduced measures, such as denoxification of industrial and vehicle emissions or NH_3

reductions in fertilizer industry and livestock breeding were still not sufficient to have a major effect on reducing recent NO_3^- and NH_4^+ levels at high altitudes, respectively.

Ice-core records of four out of seven investigated pollutants (BC, F^-, Pb, $exSO_4^{2-}$) are in good correspondence with model trends of either their emission history, atmospheric concentrations, or deposition data. This is not the case for the recent, still high concentrations of NH_4^+ and NO_3^- and the Cd concentration maximum in the 1970s. Hypotheses for the disagreement are potential uncertainties of the emission estimates, or model misrepresentation of partitioning processes between the gas and particle phase (e.g. for NH_4^+ and NO_3^-) and of chemical reactions controlling the atmospheric lifetime. The fact that only four of seven pollutant records do agree with available model estimates, illustrates the necessity to include such ice core-based reconstructions for model constrain.

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Data availability

The data presented in this work are archived at the NOAA (National Oceanic and Atmospheric Administration) data center for paleoclimate (ice core sites): http://www.ncdc.noaa.gov/paleo/study/xxxxx.

Author contribution

AE, ML, and MS conceived the study and wrote the paper. AE, TMJ, and SP contributed to data analyses and interpretation. CA and ME performed the MATCH calculations. AP and SE performed the FLEXPART modelling. All authors contributed to manuscript preparation.

Competing interests

No competing interests are present.

540   References

Abdul-Wahab, S. and Alsubhi, Z.: Modeling and analysis of hydrogen fluoride pollution from an aluminum smelter located in Oman, Sustain. Cities Soc., 51, 10.1016/j.scs.2019.101802, 2019.

Andersson, C., Langner, J., and Bergstrom, R.: Interannual variation and trends in air pollution over Europe due to climate variability during 1958-2001 simulated with a regional CTM coupled to the ERA40 reanalysis, Tellus B, 59, 77-98, 10.1111/j.1600-0889.2006.00231.x, 2007.

Beaudon, E., Moore, J. C., Martma, T., Pohjola, V. A., van de Wal, R. S. W., Kohler, J., and Isaksson, E.: Lomonosovfonna and Holtedahlfonna ice cores reveal east west disparities of the Spitsbergen environment since AD 1700, J. Glaciol., 59, 1069-1083, 10.3189/2013JoG12J203, 2013.

Belušić, D., de Vries, H., Dobler, A., Landgren, O., Lind, P., Lindstedt, D., Pedersen, R. A., Sanchez-Perrino, J. C., Toivonen, E., van Ulft, B., Wang, F. X., Andrae, U., Batrak, Y., Kjellstrom, E., Lenderink, G., Nikulin, G., Pietikainen, J. P., Rodriguez-Camino, E., Samuelsson, P., van Meijgaard, E., and Wu, M. C.: HCLIM38: a flexible regional climate model applicable for different climate zones from coarse to convection-permitting scales, Geosci. Model Dev., 13, 1311-1333, 10.5194/gmd-13-1311-2020, 2020.

Biggins, P. D. E. and Harrison, R. M.: Atmospheric chemistry of automotive lead, Environ. Sci. Technol., 13, 558-565, 10.1021/es60153a017, 1979.

Bond, T. C., Bhardwaj, E., Dong, R., Jogani, R., Jung, S. K., Roden, C., Streets, D. G., and Trautmann, N. M.: Historical emissions of black and organic carbon aerosol from energy-related combustion, 1850-2000, Global Biogeochem. Cycles, 21, 10.1029/2006gb002840, 2007.

Cao, F., Zhang, Y. L., Szidat, S., Zapf, A., Wacker, L., and Schwikowski, M.: Microgram-level radiocarbon determination of carbonaceous particles in firn and ice samples: Pretreatment and OC/EC separation, Radiocarbon, 55, 383-390, 10.2458/azu_js_rc.55.16291, 2013.

Currie, L. A., Benner, B. A., Kessler, J. D., Klinedinst, D. B., Klouda, G. A., Marolf, J. V., Slater, J. F., Wise, S. A., Cachier, H., Cary, R., Chow, J. C., Watson, J., Druffel, E. R. M., Masiello, C. A., Eglinton, T. I., Pearson, A., Reddy, C. M., Gustafsson, O., Quinn, J. G., Hartmann, P. C., Hedges, J. I., Prentice, K. M., Kirchstetter, T. W., Novakov, T., Puxbaum, H., and Schmid, H.: A critical evaluation of interlaboratory data on total, elemental, and isotopic carbon in the carbonaceous particle reference material, NIST SRM 1649a, J. Res. Natl. Inst. Stan., 107, 279-298, 10.6028/jres.107.022, 2002.

Döscher, A., Gäggeler, H. W., Schotterer, U., and Schwikowski, M.: A historical record of ammonium concentrations from a glacier in the Alps, Geophys. Res. Lett., 23, 2741-2744, 10.1029/96gl02615, 1996.

Duan, K. Q., Thompson, L. G., Yao, T., Davis, M. E., and Mosley-Thompson, E.: A 1000 year history of atmospheric sulfate concentrations in southern Asia as recorded by a Himalayan ice core, Geophys. Res. Lett., 34, 10.1029/2006gl027456, 2007.

Eckhardt, S., Cassiani, M., Evangeliou, N., Sollum, E., Pisso, I., and Stohl, A.: Source-receptor matrix calculation for deposited mass with the Lagrangian particle dispersion model FLEXPART v10.2 in backward mode, Geosci. Model Dev., 10, 4605-4618, 10.5194/gmd-10-4605-2017, 2017.

Eichler, A., Schwikowski, M., and Gäggeler, H. W.: An Alpine ice-core record of anthropogenic HF and HCl emissions, Geophys. Res. Lett., 27, 3225-3228, 2000a.

Eichler, A., Schwikowski, M., Gäggeler, H. W., Furrer, V., Synal, H. A., Beer, J., Saurer, M., and Funk, M.: Glaciochemical dating of an ice core from upper Grenzgletscher (4200 m a.s.l.), J. Glaciol., 46, 507-515, 2000b.

Eichler, A., Schwikowski, M., and Gäggeler, H. W.: Meltwater-induced relocation of chemical species in Alpine firn, Tellus B, 53, 192-203, 2001.

Eichler, A., Schwikowski, M., Furger, M., Schotterer, U., and Gäggeler, H. W.: Sources and distribution of trace species in Alpine precipitation inferred from two 60-year ice core paleorecords, Atmos. Chem. Phys. Discuss., 4, 71–108, 10.5194/acpd-4-71-2004, 2004.

Eichler, A., Brütsch, S., Olivier, S., Papina, T., and Schwikowski, M.: A 750 year ice core record of past biogenic emissions from Siberian boreal forests, Geophys. Res. Lett., 36, L18813, 10.1029/2009gl038807, 2009.

Eichler, A., Tobler, L., Eyrikh, S., Gramlich, G., Malygina, N., Papina, T., and Schwikowski, M.: Three centuries of Eastern European and Altai lead emissions recorded in a Belukha ice core, Environ. Sci. Technol., 46, 4323-4330, 10.1021/es2039954, 2012.

Eichler, A., Tobler, L., Eyrikh, S., Malygina, N., Papina, T., and Schwikowski, M.: Ice-core based assessment of historical anthropogenic heavy metal (Cd, Cu, Sb, Zn) emissions in the Soviet Union, Environ. Sci. Technol., 48, 2635-2642, 10.1021/es404861n, 2014.

Engardt, M., Simpson, D., Schwikowski, M., and Granat, L.: Deposition of sulphur and nitrogen in Europe 1900-2050. Model calculations and comparison to historical observations, Tellus B, 69, 10.1080/16000889.2017.1328945, 2017.

Fagerli, H., Legrand, M., Preunkert, S., Vestreng, V., Simpson, D., and Cerqueira, M.: Modeling historical long-term trends of sulfate, ammonium, and elemental carbon over Europe: A comparison with ice core records in the Alps, J. Geophys. Res.-Atmos., 112, 10.1029/2006jd008044, 2007.

Fang, L., Cao, F., Henne, S., Szidat, S., Schwikowski, M., and Jenk, T. M.: Carbonaceous aerosol trends and sources from an Alpine ice core, Annual Report 2019, Laboratory of Environmental Chemistry, Paul Scherrer Institute, 2019.

Fischer, H., Wagenbach, D., and Kipfstuhl, J.: Sulfate and nitrate firn concentrations on the Greenland ice sheet - 2. Temporal anthropogenic deposition changes, J. Geophys. Res.-Atmos., 103, 21935-21942, 10.1029/98jd01886, 1998.

Gabrieli, J.: Trace elements and Polycyclic Aromatic Hydrocarbons (PAHs) in snow and ice sampled at Colle Gnifetti, Monte Rosa(4450 m), during the last 10,000 years: Environmental and climatic implications, Applied geology, Université Joseph-Fourier-Grenoble I, 2008.

595 Gabrieli, J. and Barbante, C.: The Alps in the age of the Anthropocene: the impact of human activities on the cryosphere recorded in the Colle Gnifetti glacier, Rend. Fis. Acc. Lincei, 25, 71-83, 10.1007/s12210-014-0292-2, 2014.

Gabrielli, P., Wegner, A., Sierra-Hernandez, M. R., Beaudon, E., Davis, M., Barker, J. D., and Thompson, L. G.: Early atmospheric contamination on the top of the Himalayas since the onset of the European Industrial Revolution, PNAS, 117, 3967-3973, 10.1073/pnas.1910485117, 2020.

600 Giannakis, E., Kushta, J., Bruggeman, A., and Lelieveld, J.: Costs and benefits of agricultural ammonia emission abatement options for compliance with European air quality regulations, Environ. Sci. Eur., 31, 10.1186/s12302-019-0275-0, 2019.

Gross, B. H., Kreutz, K. J., Osterberg, E. C., McConnell, J. R., Handley, M., Wake, C. P., and Yalcin, K.: Constraining recent lead pollution sources in the North Pacific using ice core stable lead isotopes, J. Geophys. Res.-Atmos., 117, 10.1029/2011jd017270, 2012.

Hersbach, H., Rosnay, P. d., Bell, B., Schepers, D., Simmons, A., Soci, C., Abdalla, S., Alonso-Balmaseda, M., Balsamo, G., Bechtold, P.,
605 Berrisford, P., Bidlot, J.-R., de Boisséson, E., Bonavita, M., Browne, P., Buizza, R., Dahlgren, P., Dee, D., Dragani, R., Diamantakis, M., Flemming, J., Forbes, R., Geer, A. J., Haiden, T., Hólm, E., Haimberger, L., Hogan, R., Horányi, A., Janiskova, M., Laloyaux, P., Lopez, P., Munoz-Sabater, J., Peubey, C., Radu, R., Richardson, D., Thépaut, J.-N., Vitart, F., Yang, X., Zsótér, E., and Zuo, H.: Operational global reanalysis: progress, future directions and synergies with NWP, 10.21957/tkic6g3wm, 2018.

Hoesly, R. M., Smith, S. J., Feng, L. Y., Klimont, Z., Janssens-Maenhout, G., Pitkanen, T., Seibert, J. J., Vu, L., Andres, R. J., Bolt, R. M.,
610 Bond, T. C., Dawidowski, L., Kholod, N., Kurokawa, J., Li, M., Liu, L., Lu, Z. F., Moura, M. C. P., O'Rourke, P. R., and Zhang, Q.: Historical (1750-2014) anthropogenic emissions of reactive gases and aerosols from the Community Emissions Data System (CEDS), Geosci. Model Dev., 11, 369-408, 10.5194/gmd-11-369-2018, 2018.

Hoffmann, H., Preunkert, S., Legrand, M., Leinfelder, D., Bohleber, P., Friedrich, R., and Wagenbach, D.: A new sample preparation system for micro-C-14 dating of glacier ice with a first application to a high Alpine ice core from Colle Gnifetti (Switzerland), Radiocarbon, 60,
615 517-533, 10.1017/rdc.2017.99, 2018.

Höglund-Isaksson, L., Gomez-Sanabria, A., Klimont, Z., Rafaj, P., and Schopp, W.: Technical potentials and costs for reducing global anthropogenic methane emissions in the 2050 timeframe -results from the GAINS model, Environmental Research Communications, 2, 10.1088/2515-7620/ab7457, 2020.

Jenk, T. M.: Ice core based reconstruction of past climate conditions and air pollution in the Alps using radiocarbon, Departement für Chemie
620 und Biochemie, Universität Bern, Bern, https://biblio.unibe.ch/download/eldiss/06jenk_tabs.pdf, 2006.

Jenk, T. M., Szidat, S., Schwikowski, M., Gäggeler, H. W., Brütsch, S., Wacker, L., Synal, H. A., and Saurer, M.: Radiocarbon analysis in an Alpine ice core: record of anthropogenic and biogenic contributions to carbonaceous aerosols in the past (1650-1940), Atmos. Chem. Phys., 6, 5381-5390, 2006.

Jenk, T. M., Szidat, S., Bolius, D., Sigl, M., Gäggeler, H. W., Wacker, L., Ruff, M., Barbante, C., Boutron, C. F., and Schwikowski, M.: A
625 novel radiocarbon dating technique applied to an ice core from the Alps indicating late Pleistocene ages, J. Geophys. Res.-Atmos., 114, 10.1029/2009jd011860, 2009.

Kaspari, S., Mayewski, P. A., Handley, M., Osterberg, E., Kang, S. C., Sneed, S., Hou, S. G., and Qin, D. H.: Recent increases in atmospheric concentrations of Bi, U, Cs, S and Ca from a 350-year Mount Everest ice core record, J. Geophys. Res.-Atmos., 114, 10.1029/2008jd011088, 2009.

630 Koch, D., Bauer, S. E., Del Genio, A., Faluvegi, G., McConnell, J. R., Menon, S., Miller, R. L., Rind, D., Ruedy, R., Schmidt, G. A., and Shindell, D.: Coupled Aerosol-Chemistry-Climate Twentieth-Century Transient Model Investigation: Trends in Short-Lived Species and Climate Responses, J. Clim., 24, 2693-2714, 10.1175/2011jcli3582.1, 2011.

Kupper, T., Bonjour, C., and Menzi, H.: Evolution of farm and manure management and their influence on ammonia emissions from agriculture in Switzerland between 1990 and 2010, Atmos. Environ., 103, 215-221, 10.1016/j.atmosenv.2014.12.024, 2015.

635 Legrand, M., de Angelis, M., and Delmas, R. J.: Ion chromatographic determination of common ions at ultratrace levels in antarctic snow and ice, Anal. Chim. Acta, 156, 181-192, 1984.

Legrand, M., de Angelis, M., and Maupetit, F.: Field investigation of major and minor ions along Summit (Central Greenland) ice cores by ion chromatography, J. Chromatogr., 640, 251-258, 1993.

Legrand, M., McConnell, J. R., Lestel, L., Preunkert, S., Arienzo, M., Chellman, N. J., Stohl, A., and Eckhardt, S.: Cadmium pollution from
640 Zinc-smelters up to fourfold higher than expected in Western Europe in the 1980s as revealed by Alpine ice, Geophys. Res. Lett., 47, 10.1029/2020gl087537, 2020.

Lehner, F., Deser, C., and Terray, L.: Toward a New Estimate of "Time of Emergence" of Anthropogenic Warming: Insights from Dynamical Adjustment and a Large Initial-Condition Model Ensemble, J. Clim., 30, 7739-7756, 10.1175/jcli-d-16-0792.1, 2017.

Lim, S., Fain, X., Zanatta, M., Cozic, J., Jaffrezo, J. L., Ginot, P., and Laj, P.: Refractory black carbon mass concentrations in snow and ice:
645 method evaluation and inter-comparison with elemental carbon measurement, Atmos. Meas. Tech., 7, 3307-3324, 10.5194/amt-7-3307-2014, 2014.

Lind, P., Belusic, D., Medus, E., Dobler, A., Pedersen, R. A., Wang, F. X., Matte, D., Kjellstrom, E., Landgren, O., Lindstedt, D., Christensen, O. B., and Christensen, J. H.: Climate change information over Fenno-Scandinavia produced with a convection-permitting climate model, Climate Dynamics, 10.1007/s00382-022-06589-3, 2022.

650   Liu, L., Zhang, X. Y., Xu, W., Liu, X. J., Li, Y., Wei, J., Gao, M., Bi, J., Lu, X. H., Wang, Z., and Wu, X. D.: Challenges for Global Sustainable Nitrogen Management in Agricultural Systems, J. Agric. Food. Chem., 68, 3354-3361, 10.1021/acs.jafc.0c00273, 2020.

Liu, L., Xu, W., Lu, X. K., Zhong, B. Q., Guo, Y. X., Lu, X., Zhao, Y. H., He, W., Wang, S. H., Zhang, X. Y., Liu, X. J., and Vitousek, P.: Exploring global changes in agricultural ammonia emissions and their contribution to nitrogen deposition since 1980, PNAS, 119, 10.1073/pnas.2121998119, 2022.

655   McConnell, J. R., Chellman, N. J., Wilson, A. I., Stohl, A., Arienzo, M. M., Eckhardt, S., Fritzsche, D., Kipfstuhl, S., Opel, T., Place, P. F., and Steffensen, J. P.: Pervasive Arctic lead pollution suggests substantial growth in medieval silver production modulated by plague, climate, and conflict, PNAS, 116, 14910-14915, 10.1073/pnas.1904515116, 2019.

More, A. F., Spaulding, N. E., Bohleber, P., Handley, M. J., Hoffmann, H., Korotkikh, E. V., Kurbatov, A. V., Loveluck, C. P., Sneed, S. B., McCormick, M., and Mayewski, P. A.: Next-generation ice core technology reveals true minimum natural levels of lead (Pb) in the

660   atmosphere: Insights from the Black Death, Geohealth, 1, 211-219, 10.1002/2017gh000064, 2017.

Nickus, U., Kuhn, M., Baltensperger, U., Delmas, R., Gäggeler, H., Kasper, A., KrompKolb, H., Maupetit, F., Novo, A., Pichlmayer, F., Preunkert, S., Puxbaum, H., Rossi, G., Schoner, W., Schwikowski, M., Seibert, P., Staudenger, M., Trockner, V., Wagenbach, D., and Winiwarter, W.: SNOSP: Ion deposition and concentration in high alpine snow packs, Tellus B, 49, 56-71, 1997.

Olivier, S., Blaser, C., Brütsch, S., Frolova, N., Gäggeler, H. W., Henderson, K. A., Palmer, A. S., Papina, T., and Schwikowski, M.:

665   Temporal variations of mineral dust, biogenic tracers, and anthropogenic species during the past two centuries from Belukha ice core, Siberian Altai, J. Geophys. Res.-Atmos., 111, 10.1029/2005jd005830, 2006.

Osmont, D., Wendl, I. A., Schmidely, L., Sigl, M., Vega, C. P., Isaksson, E., and Schwikowski, M.: An 800-year high-resolution black carbon ice core record from Lomonosovfonna, Svalbard, Atmos. Chem. Phys., 18, 12777-12795, 10.5194/acp-18-12777-2018, 2018.

Osterberg, E., Mayewski, P., Kreutz, K., Fisher, D., Handley, M., Sneed, S., Zdanowicz, C., Zheng, J., Demuth, M., Waskiewicz, M., and

670   Bourgeois, J.: Ice core record of rising lead pollution in the North Pacific atmosphere, Geophys. Res. Lett., 35, 10.1029/2007gl032680, 2008.

Petzold, A., Ogren, J. A., Fiebig, M., Laj, P., Li, S. M., Baltensperger, U., Holzer-Popp, T., Kinne, S., Pappalardo, G., Sugimoto, N., Wehrli, C., Wiedensohler, A., and Zhang, X. Y.: Recommendations for reporting "black carbon" measurements, Atmos. Chem. Phys., 13, 8365-8379, 10.5194/acp-13-8365-2013, 2013.

Pisso, I., Sollum, E., Grythe, H., Kristiansen, N. I., Cassiani, M., Eckhardt, S., Arnold, D., Morton, D., Thompson, R. L., Zwaaftink, C. D.

675   G., Evangeliou, N., Sodemann, H., Haimberger, L., Henne, S., Brunner, D., Burkhart, J. F., Fouilloux, A., Brioude, J., Philipp, A., Seibert, P., and Stohl, A.: The Lagrangian particle dispersion model FLEXPART version 10.4, Geosci. Model Dev., 12, 4955-4997, 10.5194/gmd-12-4955-2019, 2019.

Preunkert, S., Wagenbach, D., Legrand, M., and Vincent, C.: Col du Dome (Mt Blanc Massif, French Alps) suitability for ice-core studies in relation with past atmospheric chemistry over Europe, Tellus B, 51, 993-1012, 2000.

680   Preunkert, S., Legrand, M., and Wagenbach, D.: Sulfate trends in a Col du Dome (French Alps) ice core: A record of anthropogenic sulfate levels in the European midtroposphere over the twentieth century, J. Geophys. Res.-Atmos., 106, 31991-32004, 2001a.

Preunkert, S., Legrand, M., and Wagenbach, D.: Causes of enhanced fluoride levels in Alpine ice cores over the last 75 years: Implications for the atmospheric fluoride budget, J. Geophys. Res.-Atmos., 106, 12619-12632, 2001b.

Preunkert, S., Wagenbach, D., and Legrand, M.: A seasonally resolved alpine ice core record of nitrate: Comparison with anthropogenic

685   inventories and estimation of preindustrial emissions of NO in Europe, J. Geophys. Res.-Atmos., 108, 4681, 2003.

Preunkert, S. and Legrand, M.: Towards a quasi-complete reconstruction of past atmospheric aerosol load and composition (organic and inorganic) over Europe since 1920 inferred from Alpine ice cores, Clim. Past, 9, 1403-1416, 10.5194/cp-9-1403-2013, 2013.

Preunkert, S., Legrand, M., Kutuzov, S., Ginot, P., Mikhalenko, V., and Friedrich, R.: The Elbrus (Caucasus, Russia) ice core record - Part 1: reconstruction of past anthropogenic sulfur emissions in south-eastern Europe, Atmos. Chem. Phys., 19, 14119-14132, 10.5194/acp-19-

690   14119-2019, 2019a.

Preunkert, S., McConnell, J. R., Hoffmann, H., Legrand, M., Wilson, A. I., Eckhardt, S., Stohl, A., Chellman, N. J., Arienzo, M. M., and Friedrich, R.: Lead and Antimony in Basal Ice From Col du Dome (French Alps) Dated With Radiocarbon: A Record of Pollution During Antiquity, Geophys. Res. Lett., 46, 4953-4961, 10.1029/2019gl082641, 2019b.

Robertson, L., Langner, J., and Engardt, M.: An Eulerian limited-area atmospheric transport model, J. Appl. Meteorol., 38, 190-210,

695   10.1175/1520-0450(1999)038<0190:Aelaat>2.0.Co;2, 1999.

Samyn, D., Vega, C. P., Motoyama, H., and Pohjola, V. A.: Nitrate and Sulfate Anthropogenic Trends in the 20th Century from Five Svalbard Ice Cores, Arct. Antarct. Alp. Res., 44, 490-499, 10.1657/1938-4246-44.4.490, 2012.

Schwikowski, M., Brütsch, S., Gäggeler, H. W., and Schotterer, U.: A high-resolution air chemistry record from an Alpine ice core: Fiescherhorn glacier, Swiss Alps, J. Geophys. Res.-Atmos., 104, 13709-13719, 10.1029/1998jd100112, 1999a.

700   Schwikowski, M., Döscher, A., Gäggeler, H. W., and Schotterer, U.: Anthropogenic versus natural sources of atmospheric sulphate from an Alpine ice core, Tellus B, 51, 938-951, 10.3402/tellusb.v51i5.16506, 1999b.

Schwikowski, M.: Reconstruction of European Air Pollution from Alpine Ice Cores, in: Earth Paleoenvironments: Records Preserved in Mid- and Low-Latitude Glaciers, edited by: DeWayne Cecil, L., Green, J. R., and Thompson, L. G., Springer Netherlands, Dordrecht, 95-119, 10.1007/1-4020-2146-1_6, 2004.

705   Schwikowski, M., Barbante, C., Doering, T., Gaeggeler, H. W., Boutron, C., Schotterer, U., Tobler, L., Van De Velde, K. V., Ferrari, C., Cozzi, G., Rosman, K., and Cescon, P.: Post-17th-century changes of European lead emissions recorded in high-altitude alpine snow and ice, Environ. Sci. Technol., 38, 957-964, 10.1021/es034715o, 2004.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, John Wiley & Sons, Hoboken 2016.

710   Shotyk, W., Zheng, J. C., Krachler, M., Zdanowicz, C., Koerner, R., and Fisher, D.: Predominance of industrial Pb in recent snow (1994-2004) and ice (1842-1996) from Devon Island, Arctic Canada, Geophys. Res. Lett., 32, 10.1029/2005gl023860, 2005.

Sierra-Hernandez, M. R., Gabrielli, P., Beaudon, E., Wegner, A., and Thompson, L. G.: Atmospheric depositions of natural and anthropogenic trace elements on the Guliya ice cap (northwestern Tibetan Plateau) during the last 340 years, Atmos. Environ., 176, 91-102, 10.1016/j.atmosenv.2017.11.040, 2018.

715   Sigl, M., Abram, N. J., Gabrieli, J., Jenk, T. M., Osmont, D., and Schwikowski, M.: 19th century glacier retreat in the Alps preceded the emergence of industrial black carbon deposition on high-alpine glaciers, Cryosphere, 12, 3311-3331, 10.5194/tc-12-3311-2018, 2018.

Skjoth, C. A. and Geels, C.: The effect of climate and climate change on ammonia emissions in Europe, Atmos. Chem. Phys., 13, 117-128, 10.5194/acp-13-117-2013, 2013.

Stohl, A., Forster, C., Frank, A., Seibert, P., and Wotawa, G.: Technical note: The Lagrangian particle dispersion model FLEXPART version 720   6.2, Atmos. Chem. Phys., 5, 2461-2474, 10.5194/acp-5-2461-2005, 2005.

Sutton, M. A., Reis, S., Riddick, S. N., Dragosits, U., Nemitz, E., Theobald, M. R., Tang, Y. S., Braban, C. F., Vieno, M., Dore, A. J., Mitchell, R. F., Wanless, S., Daunt, F., Fowler, D., Blackall, T. D., Milford, C., Flechard, C. R., Loubet, B., Massad, R., Cellier, P., Personne, E., Coheur, P. F., Clarisse, L., Van Damme, M., Ngadi, Y., Clerbaux, C., Skjoth, C. A., Geels, C., Hertel, O., Kruit, R. J. W., Pinder, R. W., Bash, J. O., Walker, J. T., Simpson, D., Horvath, L., Misselbrook, T. H., Bleeker, A., Dentener, F., and de Vries, W.: Towards a climate-725   dependent paradigm of ammonia emission and deposition, Philos. Trans. R. Soc. London, Ser. B, 368, 10.1098/rstb.2013.0166, 2013.

Theobald, M. R., Vivanco, M. G., Aas, W., Andersson, C., Ciarelli, G., Couvidat, F., Cuvelier, K., Manders, A., Mircea, M., Pay, M. T., Tsyro, S., Adani, M., Bergstrom, R., Bessagnet, B., Briganti, G., Cappelletti, A., D'Isidoro, M., Fagerli, H., Mar, K., Otero, N., Raffort, V., Roustan, Y., Schaap, M., Wind, P., and Colette, A.: An evaluation of European nitrogen and sulfur wet deposition and their trends estimated by six chemistry transport models for the period 1990-2010, Atmos. Chem. Phys., 19, 379-405, 10.5194/acp-19-379-2019, 2019.

730   Vincent, C., Vallon, M., Pinglot, J. F., Funk, M., and Reynaud, L.: Snow accumulation and ice flow at Dome du Gouter (4300 m), Mont Blanc, French Alps, J. Glaciol., 43, 513-521, 10.3189/S0022143000035127, 1997.

Wagenbach, D., Bohleber, P., and Preunkert, S.: Cold, Alpine ice bodies revisited: What may we learn from their impurity and isotope content?, Geogr. Ann. A, 94A, 245-263, 10.1111/j.1468-0459.2012.00461.x, 2012.

Wendl, I. A., Menking, J. A., Farber, R., Gysel, M., Kaspari, S. D., Laborde, M. J. G., and Schwikowski, M.: Optimized method for black 735   carbon analysis in ice and snow using the Single Particle Soot Photometer, Atmos. Meas. Tech., 7, 2667-2681, 10.5194/amt-7-2667-2014, 2014.

Williams, C. R. and Harrison, R. M.: Cadmium in the atmosphere, Experientia, 40, 29-36, 10.1007/bf01959099, 1984.

WMO GAW: The Global Atmosphere Watch Programme 25 Years of Global Coordinated Atmospheric Composition Observations and Analyses. WMO-No. 1143, World Meteorological Organization, Geneva, 48 pp., ISBN 978-92-63-11143-2, 2014.

740   Zdanowicz, C. M., Proemse, B. C., Edwards, R., Wang, F. T., Hogan, C. M., Kinnard, C., and Fisher, D.: Historical black carbon deposition in the Canadian High Arctic: a > 250-year long ice-core record from Devon Island, Atmos. Chem. Phys., 18, 12345-12361, 10.5194/acp-18-12345-2018, 2018.

Zhao, H. B., Xu, B. Q., Yao, T. D., Tian, L. D., and Li, Z.: Records of sulfate and nitrate in an ice core from Mount Muztagata, Central Asia, J. Geophys. Res.-Atmos., 116, 10.1029/2011jd015735, 2011.

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Table 1: Details of the study sites from which the ice cores used in this study are recovered.

Study site	Country	Year of drilling	Abbreviation	Coordinates	Altitude m asl	Accumulation m w.eq./year	Reference
Colle Gnifetti	CH	1982 update 1995	CG95	45°53'33''N; 07°51'52''E	4450	0.33	Schwikowski et al. (1999b, 2004)
		1982 update 1993	CG93	45°55'43''N; 07°52'30.4''E	4470	0.22	Wagenbach et al. (2012)
		2003	CG03	45°55'50''N; 07°52'33''E	4455	0.46	Jenk et al. (2009); Sigl et al. (2018)
		update 2015	CG15				
		2013	CG13	45°55'44.2''N; 7°52'34.6''E	4450	0.22	Hoffmann et al. (2018)
Grenz-gletscher	CH	1994	GG	45°55'28''N; 07°52'3''E	4200	2.7	Eichler et al. (2000)
Fiescher-horn	CH	2002	FH	46°33'3''N; 08°04'0.4''E	3900	1.4	Jenk et al. (2006)
Col du Dôme	F	1994	CDD	45°50'28''N; 06°50'52''E	4250	2.4	Preunkert et al. (2000)
		2004					Legrand et al. (2013)
		2012					Legrand et al. (2018)

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Table 2: Origin of the datasets for the different ice cores from CDD, CG, FH, and GG.

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Species	CG	GG	FH	CDD
NH_4^+, NO_3^-, SO_4^{2-}	CG03A+CG15 (Sigl et al., 2018), CG93 (Wagenbach et al., 2012)	(Eichler et al., 2000b; Eichler et al., 2004)	Jenk (2006)	(Preunkert et al., 2001a; Preunkert et al., 2003; Fagerli et al., 2007)
EC, rBC	rBC CG03B+CG15 (Sigl et al., 2018)		EC (Sigl et al., 2018)	
F-		Eichler et al. (2000a)	Jenk (2006)	Preunkert et al. (2001b)
Pb	CG03 (Gabrieli and Barbante, 2014) CG13 (More et al., 2017) CG95 (Schwikowski et al., 2004)			Legrand et al. (2020)
Cd	CG03 (Gabrieli, 2008)			Legrand et al. (2020)

Table 3: ExSO$_4^{2-}$ concentrations for different 10-year periods derived from ice cores and the MATCH model (MATCH-ECLAIRE and MATCH-BIODIV datasets). Unit is ppb (corresponding to µg/l).

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exSO$_4^{2-}$ (ppb)	Ice core 1970-1979	MATCH-ECLAIRE 1970-1979	Ice core 1990-1999	MATCH-ECLAIRE 1990-1999	MATCH-BIODIV 1990-1999
CG	827	7258	524	4113	696
GG	876	7258		4113	696
FH	743	5189		2889	696
CDD	495	2310	336	1291	672

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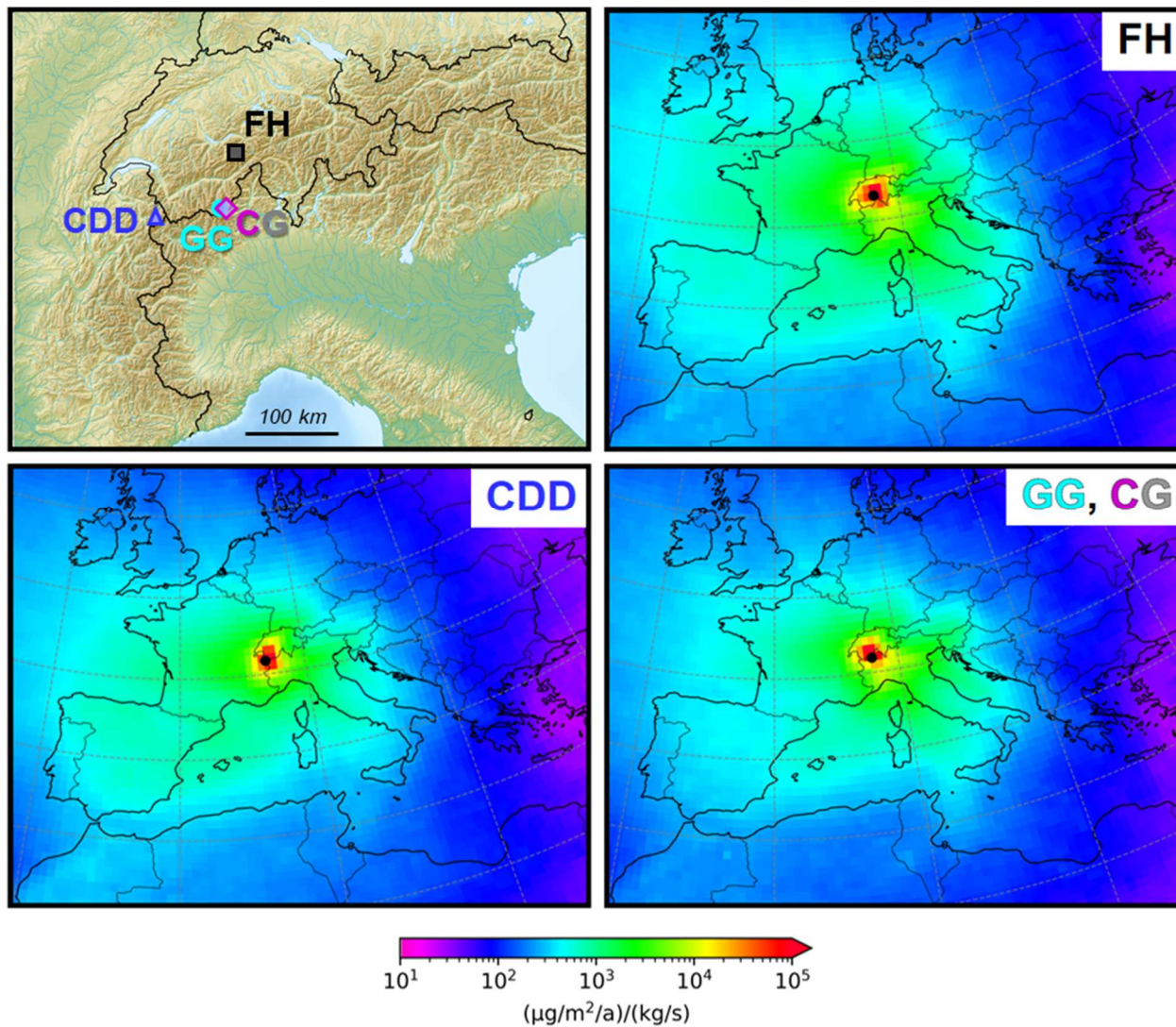


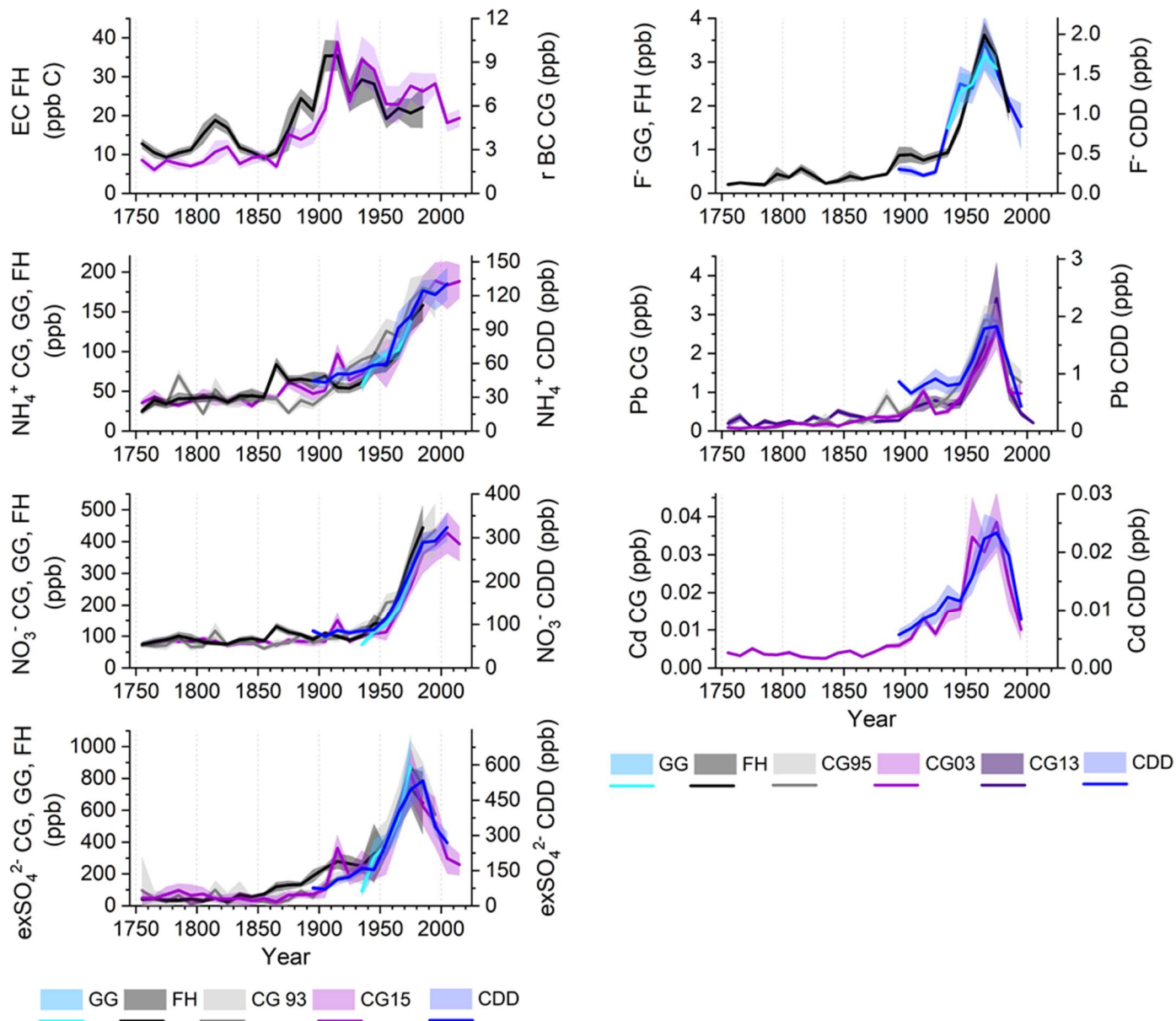
Figure 1: Topographic map of the European Alps (Credit Lencer/Pechristener, Alps location map borders, CC BY-SA 3.0, http://creativecommons.org/licenses/by-sa/3.0 or GFDL, http://www.gnu.org/copyleft/fdl.html, via Wikimedia Commons (2010), Date of
770 access: 23/06/2022) together with the four ice-core sites (upper left panel). Average SO_4^{2-} emission sensitivities (in µg m^{-2} a^{-1}/kg s^{-1}) at the FH, CDD and GG/CG site (black dots) based on FLEXPART model simulations (0.5x0.5°) for the period AD 2000-2009 (upper right and lower panels).

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Figure 2: Compilation of decadal ice-core concentration records (mean ±1 standard error) from the four ice-core sites (CDD, CG, FH, GG) for BC (EC and rBC), major inorganic aerosol species NH_4^+, NO_3^-, $exSO_4^{2-}$, and trace species F^-, Pb, Cd covering the time period 1750-2015.
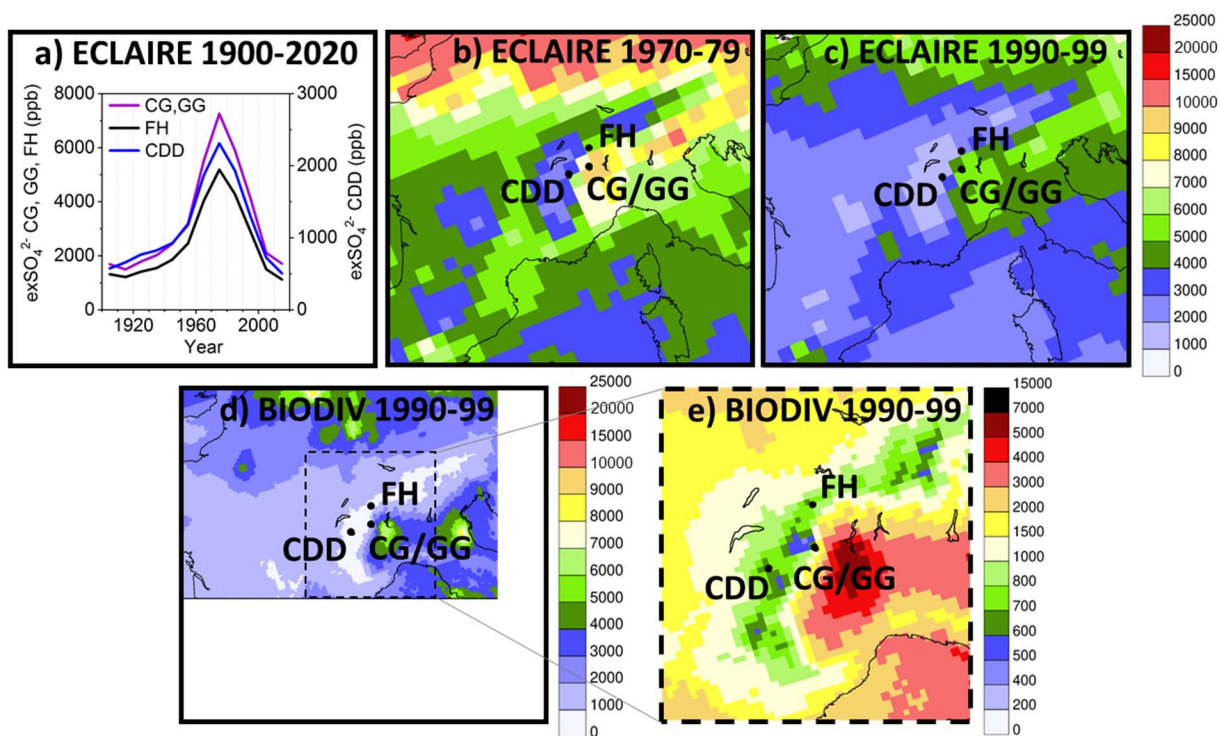
Figure 3: a) Modelled exSO$_4^{2-}$ concentration records at the four ice-core sites CDD, CG/GG and FH using the MATCH model (MATCH-ECLAIRE data set, period AD 1900-2020) and b-e) comparison of spatial exSO$_4^{2-}$ concentrations in precipitation at the surface (ppb) obtained by the MATCH model (b) MATCH-ECLAIRE data set AD 1970-1979, c) MATCH-ECLAIRE data set 1990-1999, d),e) MATCH-BIODIV data set 1990-1999). Note that color codes and covered area are identical for panels b)-d), whereas panel e) represents a magnified inset of panel d) with a different color code to illustrate variations in the high-Alpine regions.
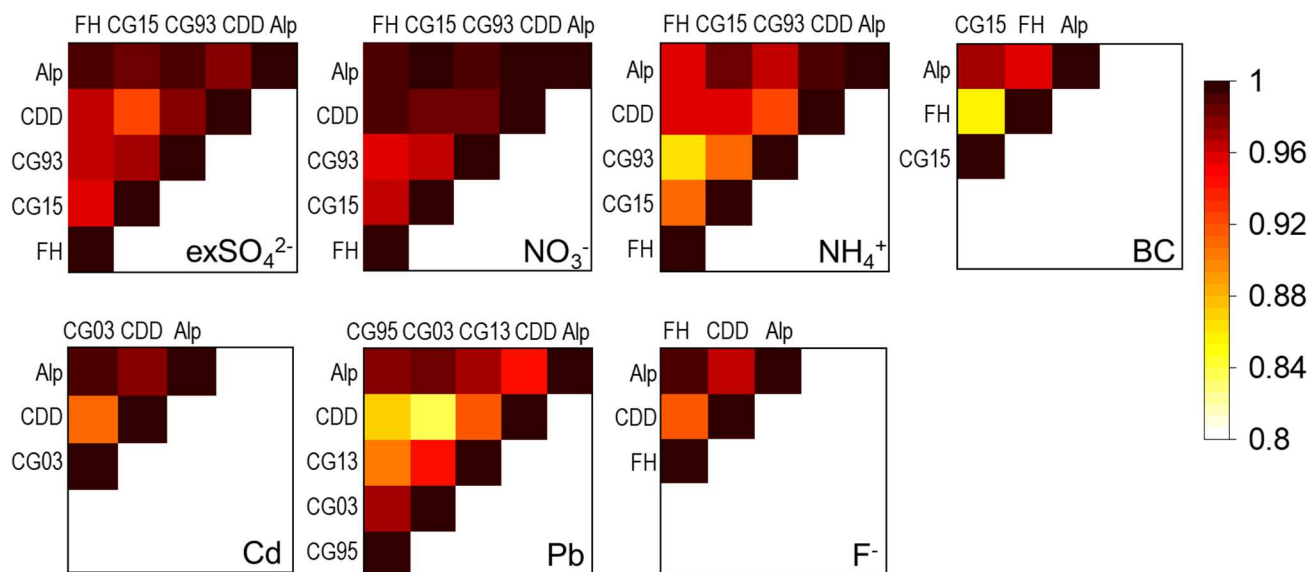
Figure 4: Correlation matrices showing the correlation coefficients r between 10-year concentration records from different ice cores and the Alpine composite (Alp) for individual pollutants $exSO_4^{2-}$, NO_3^-, NH_4^+, BC, Cd, Pb, and F^-.
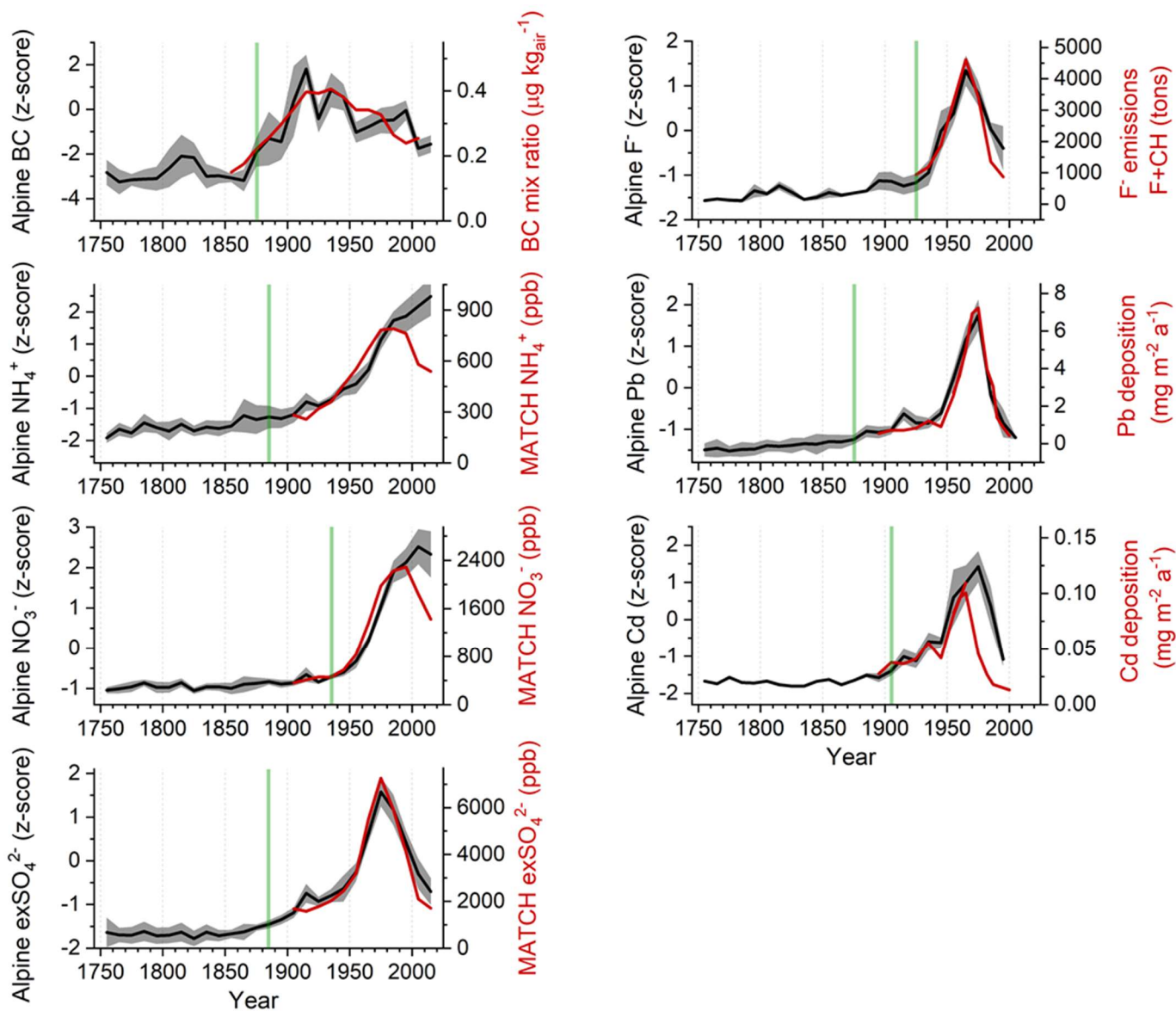
Figure 5: Compilation of decadal Alpine ice-core composite z-scores (mean ±1 standard error) based on longer-term concentration records of BC, major inorganic aerosol species NH_4^+, NO_3^-, $exSO_4^{2-}$, and trace species F^-, Pb, Cd from CDD, CG, and FH for the time period AD 1750-2015 (black/gray curves). The TOE (time of emergence, green line) is additionally shown together with modelled concentrations of NH_4^+, NO_3^-, $exSO_4^{2-}$(MATCH-ECLAIRE data set) (Engardt et al., 2017), estimated BC air mixing ratios (Fang et al., 2019), F^- emission estimates of France and Switzerland (Preunkert et al., 2001b), and Pb and Cd deposition estimates (Legrand et al., 2020) (red lines).

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