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

Anja Eichler[1,2], Michel Legrand[3,4], Theo M. Jenk[1,2], Susanne Preunkert[3], Camilla Andersson[5], Sabine Eckhardt[6], Magnuz Engardt[7], Andreas Plach[8], Margit Schwikowski[1,2,9]

[1] Laboratory of Environmental Chemistry, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland
[2] Oeschger Centre for Climate Change Research, University of Bern, CH-3012 Bern, Switzerland
[3] Institut des Géosciences de l'Environnement, Université Grenoble Alpes, Grenoble, France
[4] Laboratoire Interuniversitaire des Systèmes Atmosphériques, Université de Paris and Univ Paris Est Creteil, CNRS, LISA, F-75013, France
[5] Swedish Meteorological and Hydrological Institute, SE-60176 Norrköping, Sweden
[6] NILU - Norwegian Institute for Air Research, Kjeller, Norway
[7] Environment and Health Administration, SE-10420 Stockholm, Sweden
[8] Department of Meteorology and Geophysics, University of Vienna, Austria
[9] Department of Chemistry and Biochemistry, University of Bern, CH-3012 Bern, Switzerland

Correspondence to: Anja Eichler (anja.eichler@psi.ch)

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 composition in the source region, has not been addressed so far. Here, we present the first study systematically comparing long-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). Several ice cores from four high-Alpine sites located in the European Alps analysed by different laboratories for this set of air pollutants were used. All seven investigated anthropogenic compounds feature an excellent agreement in the species-dependent long-term concentration trends at the different sites. 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, i.e. Switzerland, France, Italy, Germany, Austria, Slovenia, and Spain. 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 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 scrubbers in power plants and metal smelters, and the ban of leaded gasoline improving the air quality in Western Europe. In contrast, the composite records of NO_3^- and NH_4^+ 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. Our results demonstrate that individual ice-core records from different sites in the European Alps provide a spatial representative signal of anthropogenic pollution

40   from Western European countries and are essential to constrain emission or deposition data of air pollutants in this region.

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

45   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,

50   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 cores from the Altai and Caucasus, indicating a later onset of industrialization (Olivier et al., 2006; Eichler et al., 2014; Preunkert et al., 2019). 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

55   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

60   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),

65   NO_3^-, Pb, and SO_4^{2-} records was observed between close-by sites (less than 100 km), but 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 Arctic sites in North America and Europe, and a similar temporal evolution of anthropogenic

emissions in these two source regions. 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

70   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

75   conditions (Beaudon et al., 2013). Additionally, 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 higher share of long-range transported air masses. Furthermore, in the Himalayas overwhelming

80   natural dust deposition leads to an additional input of the compounds often strongly exceeding their anthropogenic impact. 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,

85   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). Generally, ice-core concentrations of anthropogenic major aerosol components and trace constituents increased dramatically during the last two centuries following the onset of

90   industrialization (Schwikowski, 2004). Since the second half of the 20th century the majority of these species show a clear downward trend in concentrations 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., 2003; Wagenbach et al., 2012) and between the concentration trends of BC records from the Colle Gnifetti and 70 km distant

95   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 long-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

100   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

105   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

110   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, wet (and dry) deposition lead to their

115   removal from the atmosphere.

Our study first investigates with a state-of-the-art atmospheric aerosol transport model (FLEXPART), whether the four Alpine sites are influenced by emissions from the same source area in Western Europe. Subsequently, ice-core records of the seven pollutants are systematically compared, to test how representative one ice core from the European Alps is to document the pollution history in the deduced source area. For the investigation of differences in absolute concentration levels at the four

120   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). Finally, the ice-core composites of all pollutants were compared with available model estimates of either their emission history, atmospheric concentrations, or deposition data

125   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

Long-term ice-core data are available from four sites located in the Swiss and French Alps: Monte Rosa in the Valais Alps

130   (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
135   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 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
ice at bedrock is more than 15000 years old (Jenk et al., 2009). The dating of the different cores used in this study was achieved
140   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). 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)

145   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
150   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
155   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
160   (Jenk, 2006), and we therefore restricted discussions to the period AD 1750-1988.

2.1.4 Col du Dôme (CDD)

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
165 (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.. 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), and prior to 1890, no winter snow was preserved (Legrand et al., 2020). To account for this, only data for the period AD 1890-2012 were considered.

170 ## 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 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 Laboratoire de
175 Glaciologie et Geophysique 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 Plasma Quadrupole Mass Spectrometry (ICP-QMS) at the University of Venice (CG03 core) (Gabrieli, 2008; Gabrieli and
180 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

Concentrations of atmospheric soot particles are determined with different analytical techniques. Depending on the method
185 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 accordingly denoted as refractory black carbon (rBC) (Wendl et al., 2014; Sigl et al., 2018). Concentrations in the FH core
190 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).

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

195   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 the published data of the seven investigated species (BC, Cd, F^-, NH_4^+, NO_3^-, Pb, SO_4^{2-}). 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 (Schwikowski et al., 1999b). $ExSO_4^{2-}$ thus represents the part of SO_4^{2-}, exclusively formed from the atmospheric oxidation of SO_2.

200   Annual averages were calculated from these non-equidistant data as arithmetic mean of all data points in an annual layer for CG, FH, and GG. For CDD, annual averages were calculated as arithmetic mean of winter and summer concentrations, to account for the observed long-term trend in changing preservation of winter relative to summer snow (see section 2.1.4.).

Based on annual means, 10-year concentration averages were calculated, thereby averaging out any inter-annual fluctuations related to variations in vertical transport to the high altitudes and potential short-term variations in post-depositional processes.

205   Such 10-year averages should better reflect and be most representative of long-term changes in emissions of air pollutants. Averages represent mainly decadal means (e.g. 2000-2009), only for the most recent period a mean from 2010 through 2015 was formed.

Based on the 10-year average records obtained for each site, an ice-core composite record was formed for each species (Figure 4). For this, individual records were transformed into z-scores using the average and standard deviation of the common period

210   AD 1910-1990. To obtain a sufficiently long overlapping period, the relatively short (< 50 years) GG records were not included. A BC composite record was formed by averaging 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

215   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 site 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

220   a certain grid cell represents the ratio of aerosol deposition at the respective study site (in µg m^{-2} a^{-1}) to emission of this aerosol in the grid cell (in kg s^{-1}) ("receptor/source" ratio). Most species discussed in this study are mainly present in the atmosphere over the Alps 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

225 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

A European-scale atmospheric chemical transport model, MATCH (Robertson et al., 1999; Andersson et al., 2007; Theobald et al., 2019) was 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 coarser set-up (50 km resolution) developed for the ECLAIRE project (MATCH-ECLAIRE) (Engardt et al., 2017). Additionally, the spatial distribution of $exSO_4^{2-}$ concentration

235 during the 10-year periods 1970-1979 and 1990-1999 were investigated using MATCH-ECLAIRE and a new, high-resolution (12 km) set-up, MATCH-BIODIV. Both configurations of MATCH use recent estimates of European nitrogen and sulphur emissions for the simulated years. The meteorological data to drive the atmospheric chemical transport model are taken from climate simulations representing average conditions during the respective periods. 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

3.1 Overall comparison of pollutant records

3.1.1 Long-term trends

Generally, an excellent agreement in the ice-core long-term concentration trends of all investigated pollutants is observed for CDD, CG, FH, and GG (Figure 2). This is in line with the average emission sensitivities during the period 2000-2009 derived

245 with FLEXPART, indicating that in general the four sites 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.

The observed, characteristic differences between the concentration trends of the individual seven compounds reflect

250 dissimilarities in emission sources and atmospheric chemistry of their precursor species, and compound specific implementation and efficiency of emission abatement measures, as discussed in sections 3.2.-3.4.

3.1.2. Absolute concentration levels

Absolute concentrations are very similar at CG, FH, and GG, whereas CDD concentrations are about a factor of 2 lower on average (1.5-2.5, Figure 2). As discussed in the following, the lower concentrations at CDD could be explained by a west-east gradient in the deposition of anthropogenic pollutants in the Alps, and/or a higher amount of cleaner winter snow at the CDD site.

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) 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 a higher spatial resolution (12 km). Here, the mean height of the grid cells representing the ice-core sites span 2400 to 2700 m asl. Indeed, $exSO_4^{2-}$ concentrations obtained from the MATCH-BIODIV dataset 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 4 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.

The lower concentrations observed at CDD could be related to different snow deposition conditions. In general, concentrations of anthropogenic pollutants at high elevation sites reveal a pronounced seasonal cycle due to the seasonality of the stability of the atmosphere. In summer, more intense radiation causes increased 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 are 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 precipitation. At the FH site in the northern Alps, the precipitation maximum is in summer due to convective precipitation and the minimum is in winter. Precipitation at the CG and GG in the southern Alpine chain exhibits maxima in spring and autumn due to precipitation from tropical-maritime air masses during foehn situations and likewise a minimum in winter (Eichler et al., 2004). In addition, the CG site is prone to wind erosion, preferentially removing parts of the dry winter snow cover (see section 2.1.1.). This is different at the CDD site in the western Alps, where a more regular distribution of precipitation occurs throughout the year (Vincent et al., 1997). Thus, the hypothesis

285 that the lower ice-core concentrations at the CDD compared to the other three sites CG, FH and GG is related to a higher share of winter precipitation seems reasonable. Such small-scale processes like wind erosion or the locally varying seasonal precipitation distribution can unfortunately not be tested in the MATCH model due to limitations in resolution.

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

3.2.1. Excess sulfate

290 The five alpine $exSO_4^{2-}$ records (CDD, CG15, CG93, FH, GG) consistently show low pre-industrial background levels (AD 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 4), denoting the onset of substantial anthropogenic SO_2 emissions
295 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
300 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 long-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 4). 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
305 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.

310 #### 3.2.2. 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.,
315 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 4), 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

320   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 4). However, starting in the 1980s the composite NO_3^- record diverges from the model results and estimated NOx

325   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

330   levels (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.

3.2.3. Ammonium

Overall the available five NH_4^+ records from CDD, CG15, CG93, FH, and GG agree well, consistently indicating low pre-

335   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). The most likely cause is analytical uncertainty, since

340   NH_4^+ measurements are prone to contamination from laboratory air (Legrand et al., 1984). This 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 4). Despite the partial introduction of

345   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

350   air pollution control such as the strong focus on animal welfare leading to declining livestock numbers (Kupper et al., 2015).

The observed long-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 4). 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

355   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

360   depends on the presence of acidic species (i.e. H$_2$SO$_4$, 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

365   sufficient to create a significant downward trend in recent NH$_4^+$ levels at high altitudes in Western Europe.

3.3 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.,

370   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

375   coal burning in Western Europe exceeding pre-industrial levels was during the 1870s, as determined with TOE of the Alpine composite (Figure 4). 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

380   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.

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

3.4.1. Cadmium

The trends of the two Cd records from CG03 and CDD are in excellent agreement for the overlapping period AD 1890-2000 (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 4). The major Cd source during the 20th century was growing emissions from Zn smelting followed by Cu smelting, 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 4). Past Cd deposition fluxes were calculated from emissions estimates in European countries weighted by the 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.

3.4.2. 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 analyses methods. The CDD Pb concentrations show a similar trend after AD 1940. The 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 Alpine composite Pb record

exceeds the mean pre-industrial Pb levels, related to these emissions (Figure 4). 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 remarkably well (Figure 4). 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.

3.4.3. 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-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 4), 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 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).

The Alpine composite F[-] record and HF emission estimates from the aluminium industry of France, Germany, and Switzerland during the period AD 1920-1980 show comparable trends (Figure 4). Only in the 1990s the Alpine F[-] level is higher 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 lower levels in the 1950s.

4 Summary and Conclusion

Here we present the first study considering long-term records (AD 1750-2015) of anthropogenic pollutants from four different high-Alpine ice-core sites in the European Alps. 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. At the same time, recent changes of air pollutant concentrations were placed

into the long-term context and the onset of increased pollution levels caused by industrialization in Western Europe was
445   precisely timed.

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). 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
450   different sites in the European Alps provide a representative signal of anthropogenic pollution in Western European countries. For studying the representativeness, high-Alpine ice cores have the advantage that the sites are located in less than 100 km distance, with altitude differences of < 500 m. Furthermore, the different locations are either not affected by melting processes (CDD, CG) or melt-disturbed parts were removed before analyses (FH, GG).

The uniformity of the pollutant concentration trends does not hold fully for the magnitude in concentrations. Absolute
455   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 2 lower (1.5-2.5), most probably caused by a higher share of winter precipitation characterised by low concentrations.

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,
460   $exSO_4^{2-}$, 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^-.

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
465   the 1970s. Concentrations of all five pollutants significantly decreased afterwards. This clearly shows the efficiency of abatement measures such as 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 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 air pollution control measures, such as denoxification of industrial and
470   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
475   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. Our results demonstrate that the representative signals of anthropogenic pollution from Western European countries preserved in the ice-core records

from different sites in the European Alps are essential to constrain or complement emission and deposition estimates of air pollutants in this region.

Acknowledgements

Tinja Olenius (Swedish Meteorological and Hydrological Institute) is acknowledged for performing the MATCH-BIODIV simulations in the research project BioDiv-Support. Camilla Andersson and Tinja Olenius were funded through the 2017-2018 Belmont Forum and BiodivERsA joint call for research proposals, under the BiodivScen ERA-Net COFUND programme, and with the funding organisations AKA (Academy of Finland contract no 326328), ANR (ANR-18-EBI4-0007), BMBF (KFZ: 01LC1810A), FORMAS (contract no:s 2018-02434, 2018-02436, 2018-02437, 2018-02438) and MICINN (through APCIN: PCI2018-093149). We thank Jacobo Gabrielli for providing the Cd data from Colle Gnifetti.

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.

References

Abdul-Wahab, S. and Alsubhi, Z.: Modeling and analysis of hydrogen fluoride pollution from an aluminum smelter located in Oman, Sustainable Cities and Society, 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.

Biggins, P. D. E. and Harrison, R. M.: Atmospheric chemistry of automotive lead Environmental Science & Technology, 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.

515 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.

520 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, 525 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.

530 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 535 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 540 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.

545 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.

550 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, Environmental Sciences Europe, 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., 555 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, 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., 560 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.

Jenk, T. M.: Ice core based reconstruction of past climate conditions and air pollution in the Alps using radiocarbon, Departement für Chemie und Biochemie, Universität Bern, Bern, 2006.

565   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. Chemis.
        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
        novel radiocarbon dating technique applied to an ice core from the Alps indicating late Pleistocene ages, J. Geophys. Res.-Atmos., 114,
570   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.
        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
575   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.
        Legrand, M., de Angelis, M., and Delmas, R. J.: Ion chromatographic determination of common ions at ultratrace levels in antarctic snow
580   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
        Zinc-smelters up to fourfold higher than expected in Western Europe in the 1980s as revealed by Alpine ice, Geophys. Res. Lett., 47,
585   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:
        method evaluation and inter-comparison with elemental carbon measurement, Atmos. Meas. Tech., 7, 3307-3324, 10.5194/amt-7-3307-
590   2014, 2014.
        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,
595   10.1073/pnas.2121998119, 2022.
        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.
600   B., McCormick, M., and Mayewski, P. A.: Next-generation ice core technology reveals true minimum natural levels of lead (Pb) in the
        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.
605   Olivier, S., Blaser, C., Brütsch, S., Frolova, N., Gäggeler, H. W., Henderson, K. A., Palmer, A. S., Papina, T., and Schwikowski, M.:
        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. Chemis. Phys. , 18, 12777-12795, 10.5194/acp-18-12777-2018, 2018.
610   Osterberg, E., Mayewski, P., Kreutz, K., Fisher, D., Handley, M., Sneed, S., Zdanowicz, C., Zheng, J., Demuth, M., Waskiewicz, M., and
        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. Chemis. Phys. , 13, 8365-
        8379, 10.5194/acp-13-8365-2013, 2013.
615   Pisso, I., Sollum, E., Grythe, H., Kristiansen, N. I., Cassiani, M., Eckhardt, S., Arnold, D., Morton, D., Thompson, R. L., Zwaaftink, C. D.
        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
620   in relation with past atmospheric chemistry over Europe, Tellus B, 51, 993-1012, 2000.

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 inventories and estimation of preindustrial emissions of NO in Europe, J. Geophys. Res.-Atmos., 108, art. no.-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. Chemis. Phys. , 19, 14119-14132, 10.5194/acp-19-14119-2019, 2019.

Robertson, L., Langner, J., and Engardt, M.: An Eulerian limited-area atmospheric transport model, Journal of Applied Meteorology, 38, 190-210, 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.

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.

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.

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.

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. Chemis. 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 6.2, Atmos. Chemis. 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-dependent paradigm of ammonia emission and deposition, Philosophical Transactions of the Royal Society B-Biological Sciences, 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. Chemis. Phys. , 19, 379-405, 10.5194/acp-19-379-2019, 2019.

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 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.

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. Chemis. 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.

680

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

685

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)

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

Species	CG	GG	FH	CDD
NH_4^+, NO_3^-, SO_4^{2-}	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 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).

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	7257	524	4113	696
GG	876	7257		4113	696
FH	743	5188		2889	696
CDD	381	2311	285	1291	672

700
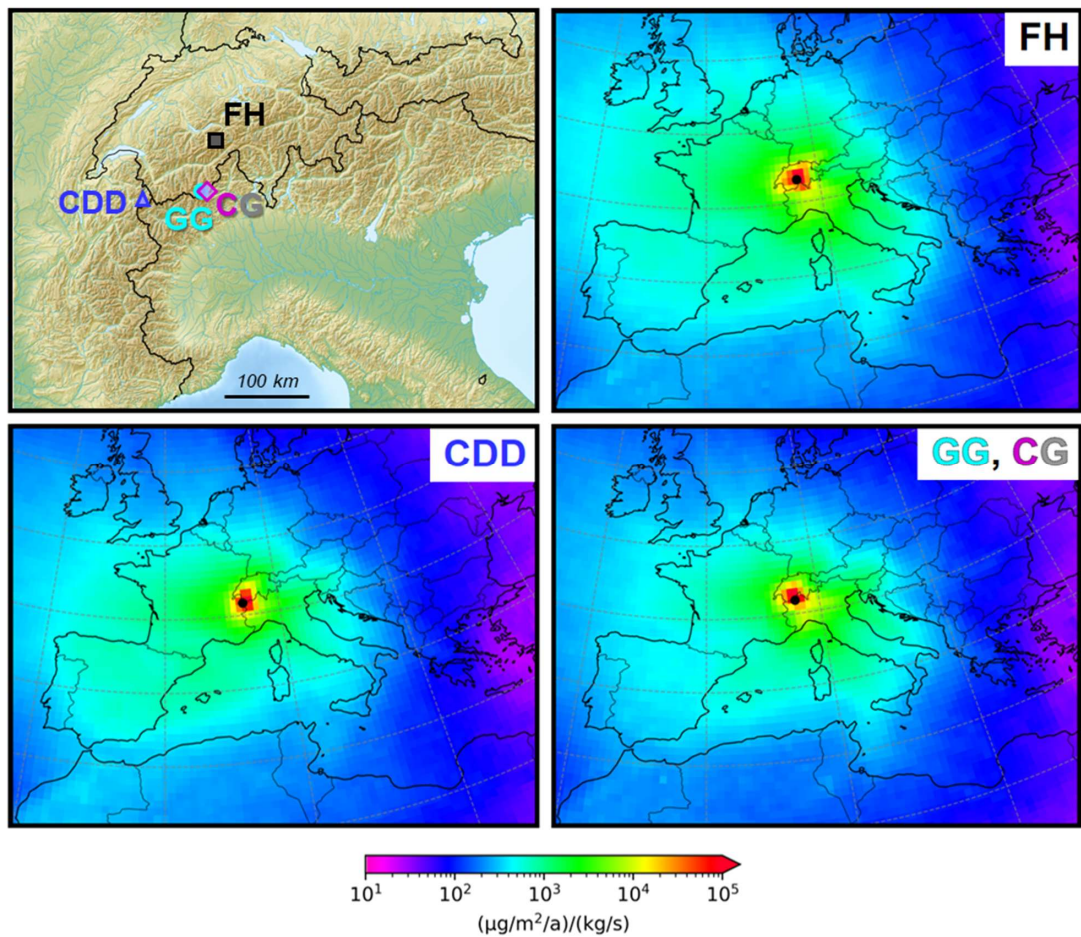
Figure 1: Topographic map of the European Alps (Credit Lencer/Pechristener, Alps location map borders, CC BY-SA 3.0,
705 http://creativecommons.org/licenses/by-sa/3.0 or GFDL, http://www.gnu.org/copyleft/fdl.html, via Wikimedia Commons (2010), Date of
access: 23/06/2022) together with the four ice-core sites (upper left panel). Average SO_4^{2-} emission sensitivities (in $\mu g\ m^{-2}\ a^{-1}/kg\ s^{-1}$) 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).

710
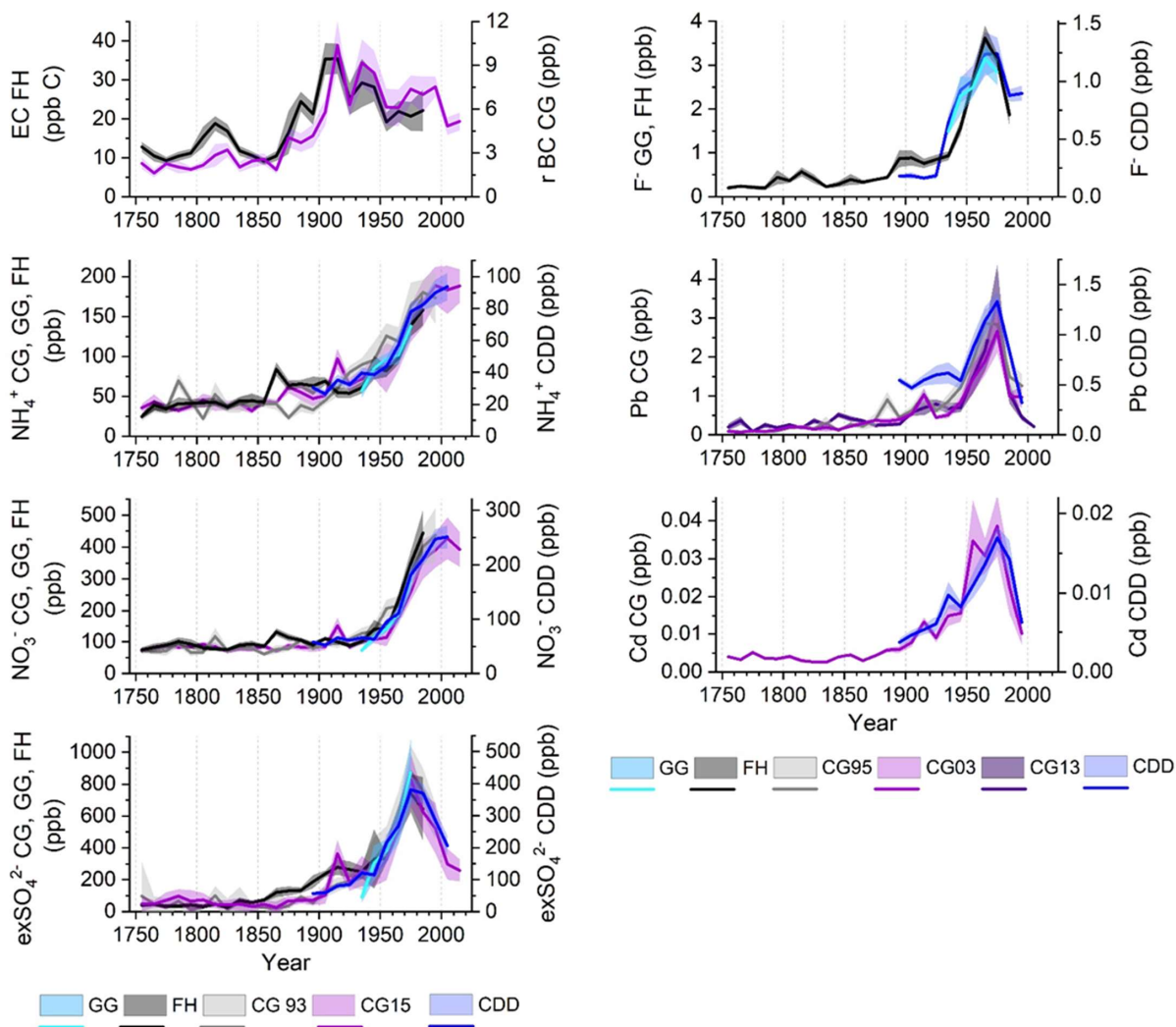
Figure 2: Compilation of decadal ice-core concentration records (mean ±1 standard error) from the four ice-core sites (CDD, CG, FH, GG) for BC (EC and rBC), major inorganic aerosol species NH₄⁺, NO₃⁻, exSO₄²⁻, and trace species F⁻, Pb, Cd covering the time period 1750-2015.

715

720
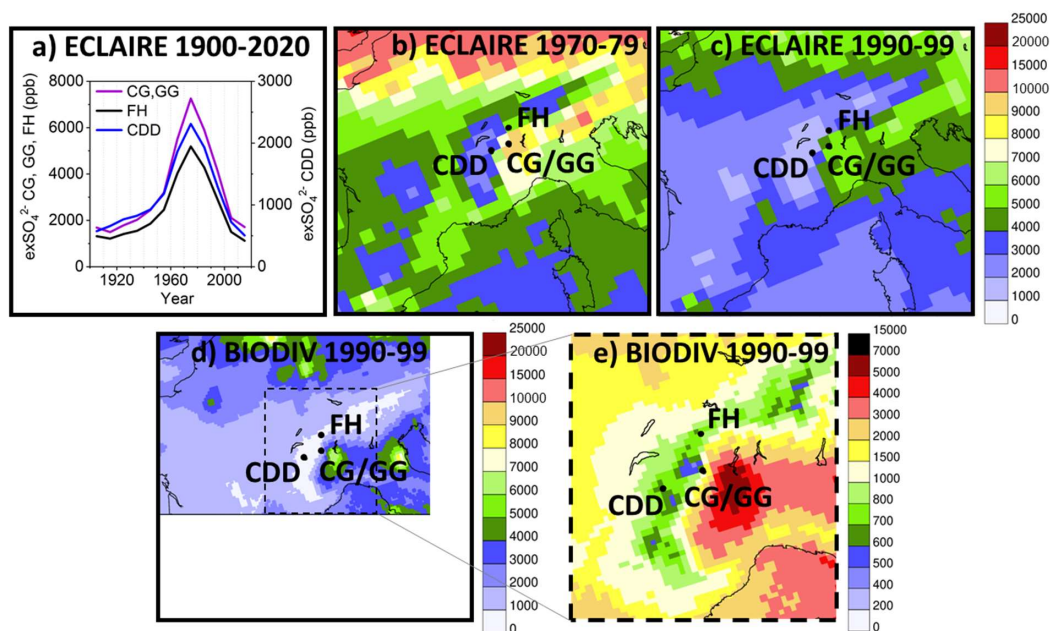
Figure 3: a) Modelled exSO$_4^{2-}$ concentration records at the four ice-core sites CDD, CG/GG and FH using the MATCH model (MATCH-ECLAIRE data set, period AD 1900-2020) and b-e) comparison of spatial exSO$_4^{2-}$ concentrations in precipitation at the surface (ppb)
725 obtained by the MATCH model (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.

730
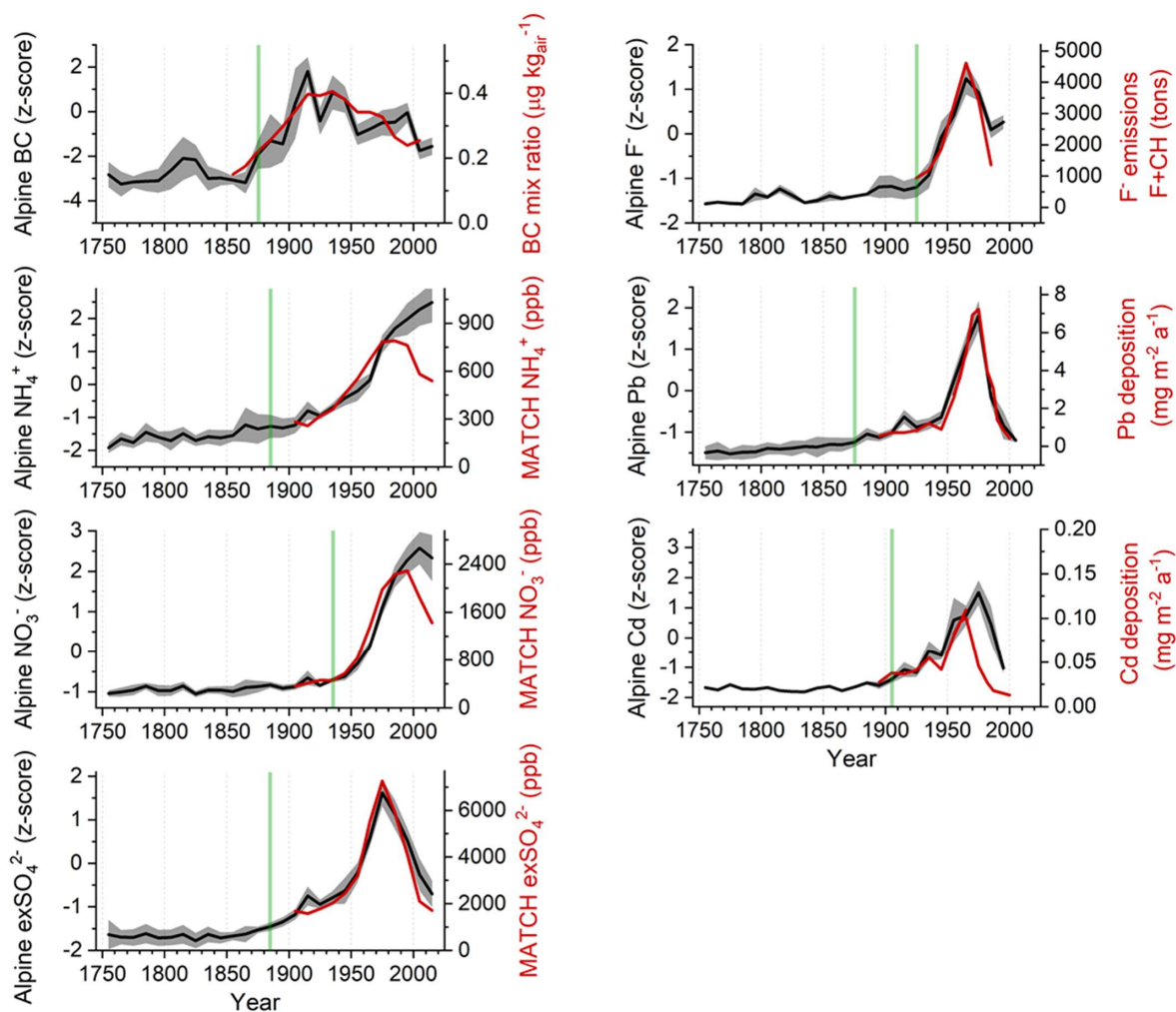
Figure 4: Compilation of decadal Alpine ice-core composite z-scores (mean ±1 standard error) based on long-term concentration records of BC, major inorganic aerosol species NH_4^+, NO_3^-, $exSO_4^{2-}$, and trace species F^-, Pb, Cd from CDD, CG, and FH for the time period AD 1750-2015 (black/gray curves). 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).

735