Supplement of The Cryosphere, 17, 2119–2137, 2023
https://doi.org/10.5194/tc-17-2119-2023-supplement

The Cryosphere
Open Access

Supplement of

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

Anja Eichler et al.

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

S1. Selection of the averaging period

To select an adequate averaging period, we investigated the influence of different averaging windows on the CG15 $exSO_4^{2-}$ record in the period 1920-2015 (Fig. S1). Fig. S1a illustrates that annual $exSO_4^{2-}$ maxima/minima are in part synchronous with $\delta^{18}O$ maxima/minima. Since $\delta^{18}O$ is a temperature proxy (Bohleber et al., 2013), this reflects a stronger/weaker vertical transport of pollutants from their source regions at lower elevations to the high-altitudes sites during warmer/colder summers. This is still partially visible in the 5-year means (Fig. S1b), e.g. the temperature ($\delta^{18}O$) maximum in the period 1970-75 lead to an amplification of the $exSO_4^{2-}$ concentration at CG compared to what is expected based on the SO_2 emission history (Fig. S1e). This modulation of the ice-core record by year-to-year variability of vertical transport/atmospheric stability also produces a larger variability compared to the modelled concentrations for the annual and 5-year means (Fig. S1d,e), but not for the 10-year averages. The MATCH-ECLAIRE model does not have sufficient resolution to resolve the small-scale vertical transport.

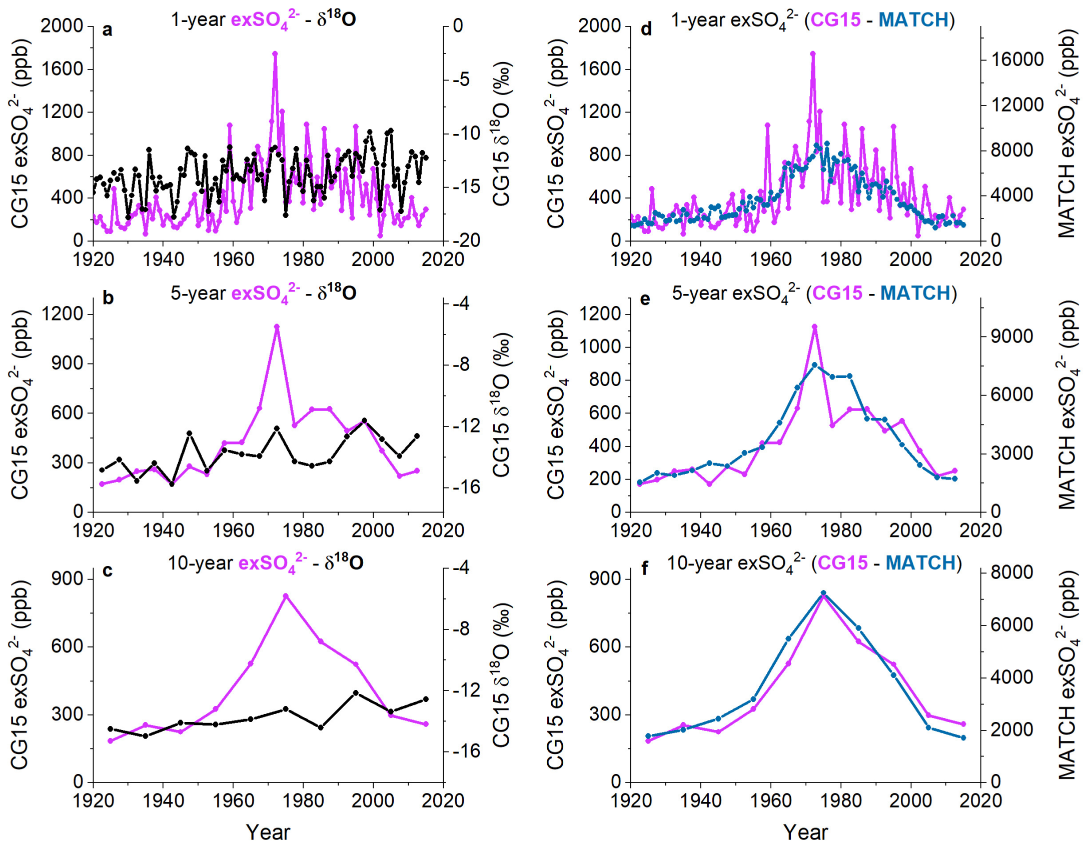

Fig. S1: Comparison of CG15 $exSO_4^{2-}$ concentrations (pink) with CG15 $\delta^{18}O$ records (panels a-c, black) and with modelled $exSO_4^{2-}$ concentrations (MATCH-ECLAIRE) (panels d-f, turquis) in the period 1920-2015 using different averaging periods (a,d – 1-year, b,e – 5 year, c,f – 10 year).

Thus, ice-core 10-year averages are representative for changing pollutant emissions, smoothing out the inter-annual (short-term) fluctuations related to temperature dependent vertical pollutant transport to the high-alpine sites. 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).

S2. Comparison of two different averaging procedures for the CDD core

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). Thus, to avoid a bias of annual averaged concentrations towards summer values with depth, but also to take advantage from the seasonal resolution when beneficial, in previous studies CDD ice-core concentration trends were investigated either on a seasonal basis (winter and summer) or using annual arithmetic means of the respective winter and summer level for each year (see e.g. Preunkert et al., 2001; Preunkert et al., 2003; Preunkert and Legrand, 2013, Legrand et al., 2020). Since for the other Alpine sites investigated in this study data resolution in the pre-industrial period is too low to disentangle winter and summer layers, we tested if CDD arithmetic means of total annual layer data were different than respective winter/summer averages. We found that for the 10-year means considered in this study CDD longer-term concentration trends for all investigated species agree within the uncertainty envelopes between the two averaging procedures (see Figure S2). Thus, for the discussion of longer-term concentration changes (section 3.2.), correlation analyses (Figure 4) and the formation of Alpine z-scores (Figure 5), the used averaging procedure does not matter.

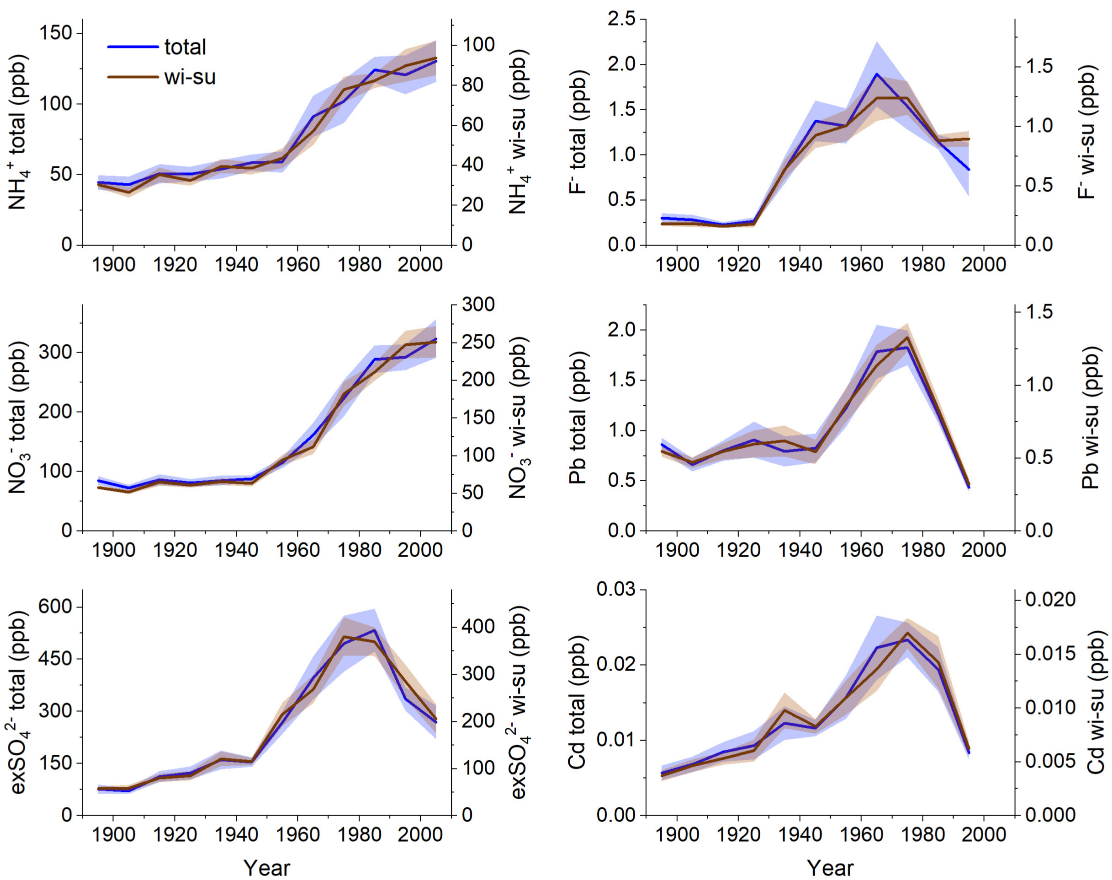

Fig. S2: 10-year averages (±standard error) of CDD NH_4^+, NO_3^-, $exSO_4^{2-}$, F^-, Pb, and Cd concentrations based on annual concentrations calculated as the arithmetic mean of data from total annual layers (total, blue lines, left scales) and arithmetic mean of winter and summer (wi-su, brown lines, right scales).

Whereas relative concentration trends agree, absolute concentrations are factor 1.3-1.5 lower for the winter/summer averages compared to the total annual layer means (Figure S2). This is related to a higher share of cleaner winter precipitation considered in the winter/summer averages. As mentioned above, since the calculation of winter/summer averages was only possible for the CDD site, the comparison of concentration values between all sites is consistently presented in this study based on the averages of total annual layers.

References

Bohleber, P., Wagenbach, D., Schöner, W., & Böhm, R. To what extent do water isotope records from low accumulation Alpine ice cores reproduce instrumental temperature series? Tellus B: Chemical and Physical Meteorology, 65(1), DOI: 10.3402/tellusb.v65i0.20148, 2013.

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, 10.1029/2020gl087537, 2020.

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.

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, 2001.

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, 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.