SUPPORTING INFORMATION

Post 17th-Century Changes of European PAH Emissions Recorded in High-Altitude Alpine Snow and Ice

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Supporting information consists of:

- 8 pages;
- 2 figures;
- 4 tables.

SI - 1. Sample location and dating

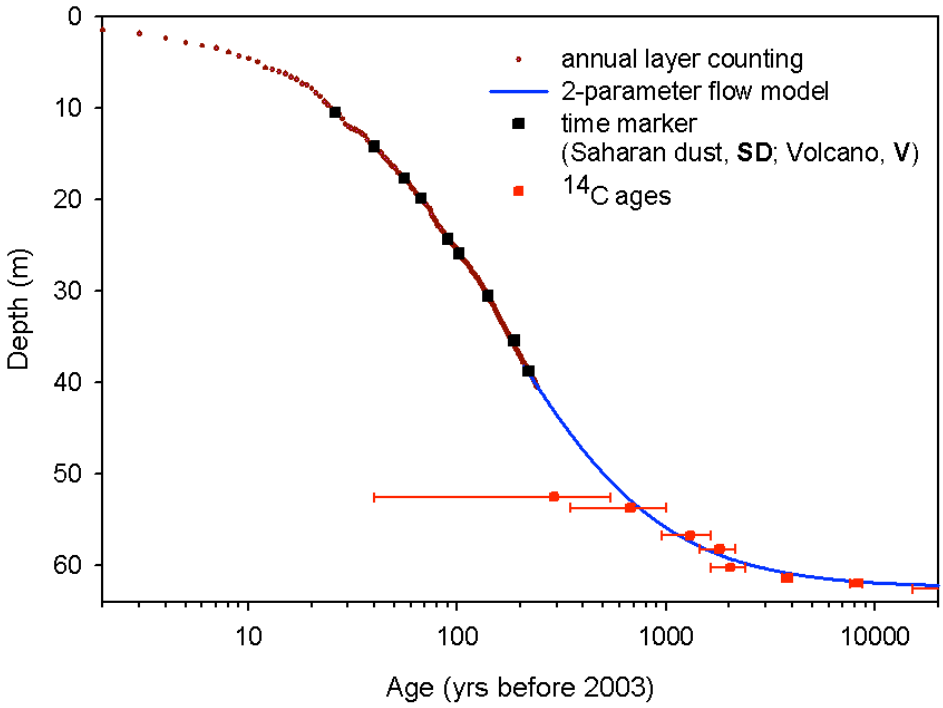
Figure 1. Map of the Alps showing the position of Monte Rosa, on the Swiss-Italian border.

Colle Gnifetti is the uppermost part of the accumulation area of Grenzgletscher, forming a saddle between Zumsteinspitze and Punta Gnifetti of Monte Rosa, at an altitude of 4400-4550 m a.s.l.

The potential of the glacier on Colle Gnifetti as a climate archive was recognized early as the first ice cores were drilled in 1976 and 1977 (Oeschger et al., 1977) and until now ten cores have been collected. A short overview of the drilling history at Colle Gnifetti has been provided by Bolius (2006). The measured annual accumulation on Colle Gnifetti ranges between 0.2 and 1.1 m weq/yr, depending on the annual wind strength. For this reason, Colle Gnifetti conserves the accumulation history over a long time period and is an appropriate site for obtaining a climate archive. The 2003 cores were drilled at two sites where the thickness of ice older than 500 years was greatest (>14 m) according to ice flow modelling.

The dating has been performed combining several horizons obtained from annual layer counting (back to 1766 AD), Saharan dust strata (1977, 1947, 1936 1901 AD), volcanic eruptions (Katmai, 1911 AD; Laki, 1783 AD), tritium horizon (1963 AD) and radiocarbon measurements (*Sigl et al., 2009*).

Fig. 2 Reference horizons and estimation of the age by a 2-parameter flow model.



SI - 2. Melter system

The melting system is hosted in a -20°C vertical freezer and consists of a melting head made of high purity Nickel-270. The temperature of the melting head was maintained at 30°C using an electrical heater coupled with a thermocouple. Nickel was used because of its good thermal conductivity and it's availability in a pure form; in addition Nickel is also used for skimmer cones on the ICP-MS instruments, hence its measurement is already compromised at low concentration levels. The melting head consisted of two concentric sections, the inner comprising a circle of 21 mm diameter, corresponding to about 34% of the total 32x32 mm cross-section (Figure 3).

The sample collected from the inner channel was split in a PTFE T-junction (Figure 4). The first aliquot was pumped to a debubbler device and then, after on-line acidification and internal standard addition, to a quadrupole ICP-MS (Agilent 7500; Agilent Technologies, Tokyo, Japan) was collected in low-density polyethylene bottles (LDPE) bottles for discontinuous sampling. Highly resolved profiles of 24 trace elements as well as total ionic load were recorded with a resolution better than 1 cm. The high frequency profiles allowed sub-annual resolution to be obtained; seasonal variations in the occurrence of trace elements was also used to match the dating.

The spatial resolution of sampling varied depending on the amount of sample needed for further analysis and ranged from 10 to 30 cm, corresponding to a minimum of 6 (for firn sections) to a maximum of 30 mL of meltwater.

Fig.3 Schematic of the Ni melting head. The geometry of the melting surface was carefully designed to reduce the risk of melt water crossover from the external to the internal part.

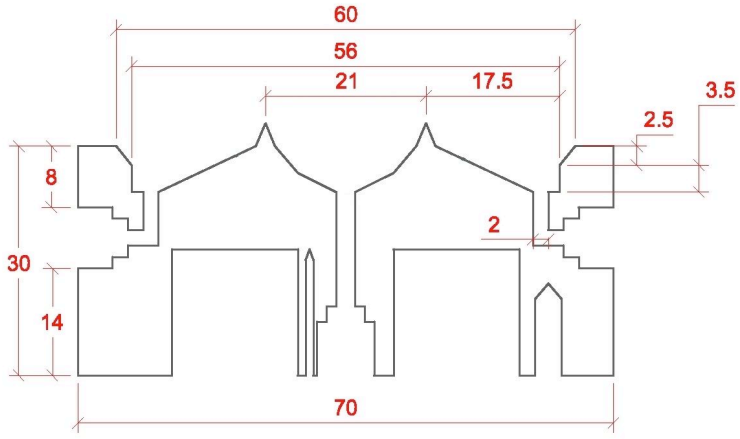
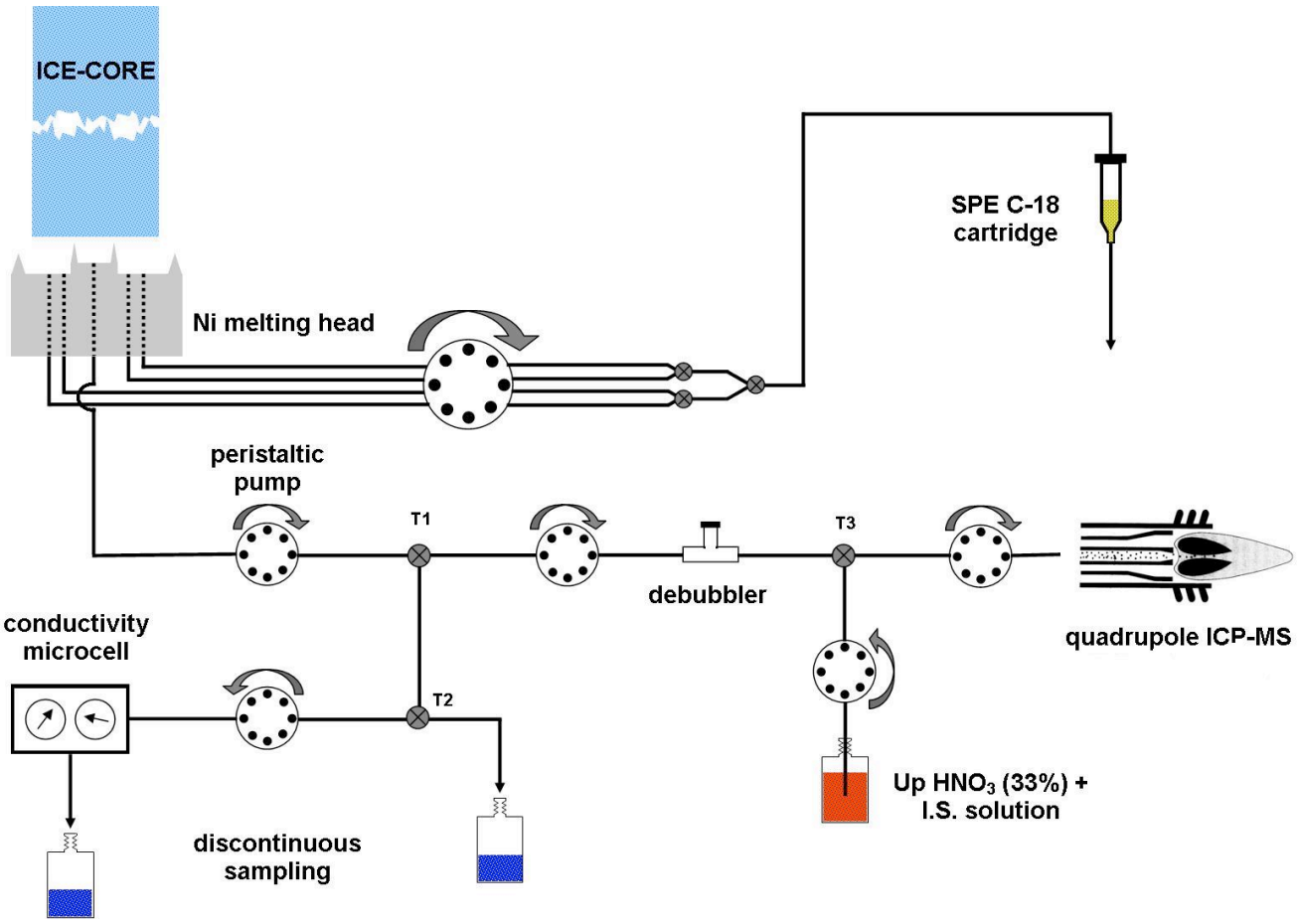


Fig. 3 Schematic of the melting system and continuous flow analysis. Melted water from the inner part of each ice core section was pumped to an Inductively Coupled Plasma Quadrupole Mass Spectrometer (ICP-QMS) and a conductivity micro-cell for continuous measurements of trace element concentrations and conductivity, respectively. Discrete samples were also collected. Melted water from the outer section was extracted on-line by solid-phase cartridges for semi-continuous Polycyclic Aromatic Hydrocarbons (PAH) analysis.



SI - 3. Reproducibility test results

Table 1. Reproducibility for two replicates of parallel sub-sections of Monte Rosa ice.

Compound	*Section 61 (ng/kg)*			*Section 31 (ng/kg)*		
	First replicate	*Second replicate*	*Difference (%)*	*First replicate*	*Second replicate*	*Difference (%)*
Phe	14.7	14.8	1.0	11.4	12.4	7.7
Ant	0.56	0.39	30	0.50	0.43	14
Fla	4.6	4.1	11	2.9	3.2	9.4
Pyr	2.5	2.3	7.6	2.3	2.4	4.6
BaA	< d.l.	< d.l.	-	< d.l.	< d.l.	-
Chr	1.7	1.6	3.6	1.6	1.9	17
BbF	1.9	1.7	12	1.2	1.2	3.9
BkF	0.91	0.84	7.7	0.69	0.64	7.3
BaP	0.89	0.80	10	0.62	0.59	4.8
dBA	0.058	0.084	31	0.11	0.15	29
BghiP	1.3	1.7	21	1.5	1.1	26
InP	1.5	1.2	21	0.86	0.82	5.0

SI - 4. PAH concentration

Table 2. Averaged concentrations of individual PAH, ΣPAH and ΣPAH (heaviest compounds with more than 4 aromatic rings) in selected time windows (10 year averages from 1860 to 1930, 5 year averages from 1930 to 2000)*

	Concentrations (ng/kg)												
	Phe	Ant	Fla	Pyr	Cri	BbF	BkF	BaP	dBP	BghiP	InP	Σ PAH	Σ PAH *
2003 - 2000	7.9	0.18	1.8	0.89	0.55	0.26	0.22	0.13	0.013	0.49	0.31	13	1.4
2000 - 1995	5.9	0.10	1.3	0.66	0.74	0.48	0.29	0.13	0.037	0.68	0.28	11	1.9
1995 - 1990	5.1	0.16	1.3	0.83	0.53	0.28	0.18	0.13	0.007	0.37	0.23	9.1	1.2
1990 - 1985	5.2	0.22	1.1	0.86	0.44	0.27	0.15	0.13	0.003	0.52	0.19	9.1	1.3
1985 - 1980	4.3	0.19	0.88	0.91	0.41	0.31	0.18	0.16	0.010	0.43	0.21	8.0	1.3
1980 - 1975	4.1	0.18	0.86	0.83	0.43	0.30	0.22	0.15	0.014	0.35	0.21	7.7	1.3
1975 - 1970	4.3	0.17	1.4	0.99	0.73	0.63	0.35	0.26	0.028	0.60	0.42	9.9	2.3
1970 - 1965	5.3	0.26	2.0	1.5	0.88	0.97	0.41	0.37	0.053	1.7	0.58	14	4.1
1965 - 1960	4.5	0.16	1.4	1.3	0.87	0.70	0.30	0.22	0.020	1.0	0.39	11	2.7
1960 - 1955	5.4	0.22	2.7	2.0	1.5	1.5	0.59	0.51	0.068	1.2	0.90	17	4.8
1955 - 1950	5.0	0.22	2.8	2.1	1.5	1.5	0.63	0.77	0.080	1.4	1.1	17	5.4
1950 - 1945	5.6	0.28	3.5	2.5	1.7	1.7	0.73	0.82	0.085	1.4	1.2	20	5.9
1945 - 1940	7.2	0.31	4.0	2.7	1.7	1.7	0.75	0.71	0.098	1.3	1.1	22	5.7
1940 - 1935	7.3	0.32	3.7	2.4	1.5	1.6	0.68	0.66	0.098	1.2	1.0	21	5.3
1935 - 1930	6.4	0.18	2.2	1.3	0.75	0.82	0.37	0.34	0.053	0.88	0.53	14	3.0
1930 - 1920	5.8	0.17	2.7	1.6	1.1	1.3	0.57	0.59	0.076	1.1	0.91	16	4.5
1920 - 1910	4.7	0.17	2.5	1.7	1.1	1.3	0.60	0.63	0.059	0.93	0.97	15	4.5
1910 - 1900	2.8	0.12	0.78	0.48	0.18	0.17	0.12	0.08	< d.l.	0.13	0.10	5.0	0.60
1900 - 1890	1.3	0.06	0.39	0.23	0.02	0.06	0.05	0.04	< d.l.	0.05	0.03	2.2	0.23
1890 - 1880	1.3	0.07	0.29	0.14	0.01	0.05	0.04	0.03	< d.l.	0.04	0.02	2.0	0.17
1880 - 1870	1.4	0.07	0.28	0.12	0.01	0.03	0.03	0.03	< d.l.	0.04	0.01	2.0	0.13
1870 - 1860	1.4	0.06	0.30	0.16	0.02	0.02	0.02	0.02	< d.l.	< d.l.	< d.l.	2.0	0.08

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