



A novel firn/ice-core melter system for semi-continuous extraction of PAHs and continuous ICP-QMS trace element analysis

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A new melting device for on-line decontamination and continuous analysis of firn/ice cores was used to analyse an alpine firn/ice core drilled at Colle Gnifetti (M. Rosa, 4450 m a.s.l.), covering a time period of 10,000 years. Melt water from inner part of ice core section was pumped to an ICP-QMS and a conductivity micro-cell for trace elements and continuous conductivity measurements, respectively. Melt water from the outer section was extracted on-line by solid-phase cartridges for semi-continuous Polycyclic Aromatic Hydrocarbons (PAHs) analysis. High resolution profiles of 24 elements were obtained. Pronounced seasonal variations were observed for both crustal (eg. Mg, Al) and anthropogenically enriched (eg. Cd, Pb) elements, with higher concentrations during summer. While the long-term profiles of crustal trace elements didn't show significant variations, for anthropogenic enriched metals a widespread increase is reported from 18th century, reflecting changing emissions.

Very few works regarding PAHs determination in snow and ice samples are present in the literature. As for polar environments, PAHs have only been sampled and analyzed in shallow Greenland snow. To our knowledge, no PAHs profiles have been published for firn/ice in the Alps. The concentrations of 12 PAHs were determined by HPLC-FD, obtaining detailed profiles for the last three centuries.

Before 1875 the PAHs levels were very low: the pre-1750's PAHs concentrations were assumed to be the background level. Σ PAHs in the 1945-1955 ten-years period were 10 times higher than background values with Σ PAHs* (heaviest compounds) about 40-50 times higher. From 1900, PAHs concentrations increased exponentially, reaching a maximum in 1920. From the mid-1930s PAHs rapidly doubled reaching maximum concentrations from 1940 to 1950. Concentrations of the heaviest Σ PAHs* decreased by a factor 5 from 1950 to 1975 while for total Σ PAHs the concentrations halved. From 1975 to 2003, Σ PAHs rose again to almost 1910 values. If the general PAHs trends are strongly correlated with anthropogenic emission variation, the fine shape of the profile can be influenced by several other parameters. This trend does not seem to be completed and further increases may occur in coming years. The PAHs pattern is normally dominated by phenanthrene, fluoranthene and pyrene, which represent 60-80% of the total. The different behaviour of light and heavy PAH profiles reflects the chemical features of single compounds. For light compounds, which are relatively volatile, climatic variables affecting transport and deposition processes may influence concentrations more than anthropogenic emissions.