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Trace analysis of organic aerosol markers and lignin in samples from Alpine ice core Colle Gnifetti covering the 20th century using UHPLC-HRMS

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Ice cores are valuable climate archives preserving organic compounds from atmospheric aerosols over long time ranges. Different approaches of dating are available like annual layer counting, radioactive decay and stratigraphic markers like tephra from volcanic eruption. In combination, they enable accurate dating back to 800,000 years. Secondary organic aerosols (SOA) are formed in the atmosphere by condensation of oxidized highly volatile organic compounds and their chemical profile is highly complex due to the variety of emission sources and reactions in the atmosphere.

Well-known SOA markers include pinic acid, pinonic acid or terebic acid from monoterpene oxidation. Another class of important atmospheric markers are biomass burning products. During combustion of cellulose levoglucosan, an anhydrosugar is formed while the combustion of lignin results in the formation of phenolic compounds like vanillic acid, cinnamic acid, or p-hydroxybenzoic acid. While the lignin burning products provide important information on paleo-fire history, intact polymeric lignin offers a deeper insight into the type and abundance of vegetation. By alkaline oxidation, the polymeric lignin is degraded into the lignin oxidation products (LOP) and the ratios of these products are related to wooden and non-wooden, as well as angiosperm and gymnosperm vegetation.

In this work, an analytical approach is presented covering a variety of SOA markers, biomass burning markers, and polymeric lignin, using UHPLC-HRMS and an elaborate sample preparation procedure. The method was applied to samples from Colle Gnifetti in the Swiss-Italian Alps, a part of Grenzgletscher, covering the time between 1920 and 1994. We present first data on polymeric lignin in ice core samples and an examination of correlations with known organic proxies to emphasize the relevance of lignin not only in climate archives like speleothems and sediments but also in ice core samples.