

Organic tracers in ice: Untapped potential for specific biomarkers of past environment

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Organic compounds in ice cores are valuable tracers of past terrestrial and marine biospheres. Analytical challenges have previously prevented quantification of these compounds, but recent breakthroughs have allowed us to measure and better understand biogenic processes and past atmospheric circulation.

Organic tracers in the cryosphere

Important paleoclimatic information can be yielded from the analysis of organic impurities in ice cores. Organic compounds contribute up to 90% of total fine aerosol particle mass. Thus, they contain large amounts of information about the sources and transport patterns of aerosols (Kanakidou et al. 2005). Organic particles and microorganisms can be cloud condensation and ice-nucleating particles, which means they can easily end up being deposited as snow. Additionally, wet precipitation is an efficient scavenger of organic particles from the atmosphere. Ice cores serve as an archive of the past atmosphere since they contain traces of organic aerosol particles and dissolved organic matter. Despite this, very few organic compounds have been successfully quantified in ice cores. Biomass burning tracers, such as levoglucosan and vanillic acid, and the sea-ice proxy methanesulfonic acid, are examples of organic compounds which have been successfully quantified in ice cores.

Challenges with quantification of organic compounds in ice

The greatest challenge with quantification of organic compounds in ice cores is their low concentrations. The total organic carbon content in ice cores from Antarctica has been measured in several ice cores to be between 5 and 900 ppb carbon (Federer et al. 2008; Legrand et al. 2013), which results in individual compounds being found at ppb or ppt levels. Most analyses of organic compounds in ice cores, therefore, require preconcentration steps. Ice cores are cut into discrete samples and the exposed outside is removed with a knife before the ice is melted and often preconcentrated. Preconcentration is the process of increasing the concentration of target compounds in a sample, either by collecting the target compounds from the solution, or by evaporating the solvent from the mixture. Preconcentration improves detection, but often part of the target compound is lost in the process. The amount of initial substance preserved after the preconcentration

steps is referred to as the “recovery rate”. Preconcentration methods used for organic compounds in ice have reported recovery rates upwards of 80% (King et al. 2019; Müller-Tautges et al. 2014). However, with discrete ice-core samples, the spatial resolution is limited as these methods often require high sample volumes. A measurement of the recovery rate of each compound measured is also necessary for proper quantification. Additionally, the process is labor intensive and the repeated cutting of the ice cores risks sample losses.

Preunkert et al. (2011) found that lab air could be a significant source of organic carbon contamination in their melted ice samples due to the dissolution of atmospheric traces of formic and acetic acids. These authors found a rapid increase in dissolved organic carbon (DOC) in open bottles of ultrapure water left in a clean room and in a “general purpose” room. The general purpose room had a contamination increase two orders of magnitude higher than in the clean room. Even a closed bottle in the general purpose room was found with a 25 ppb carbon DOC increase per hour, but this was much lower than the approximate 3000 ppb carbon DOC increase per hour observed in the open bottle, in the same location. This demonstrates that great care is needed to limit contamination of samples, especially after cutting and melting discrete samples of ice. One way of preventing this issue is by omitting the sample preparation steps altogether. This can be done using continuous methods, rather than discrete samples.

Continuous sampling and measurements of ice cores

Continuous flow analysis (CFA) has become one of the standard methods of ice-core analysis since it was developed in the 1990s (Fuhrer et al. 1993; Sigg et al. 1994). In CFA, sticks of ice are melted from the bottom, and the meltwater is continuously pumped into instruments for analysis. The sample experiences little to no contact with air, and is directly analyzed a few seconds after melting (Fig. 1). The melthead is often shaped so only the innermost section of ice is directed to the most sensitive analyses. The outermost ice is used for analyses less prone to contamination, such as stable water isotopes ($\delta^{18}\text{O}$ and δD). CFA reduces several of the issues related to analyzing organic

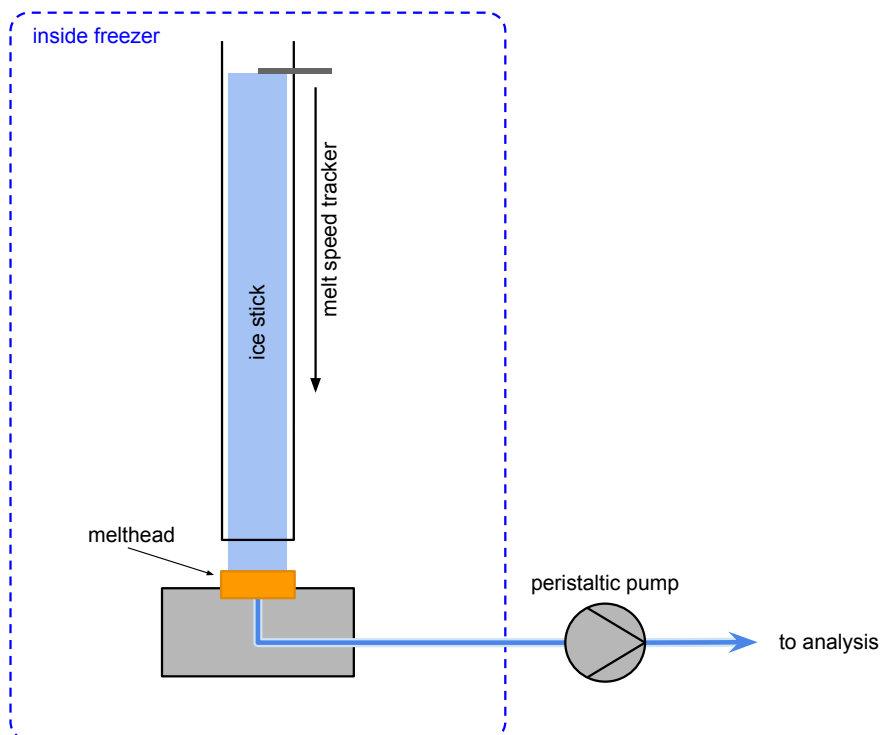


Figure 1: Continuous flow analysis (CFA) melting system. Ice cores are cut into sticks, which are placed on the melthead. The melt speed is regulated through the temperature of the melthead. Peristaltic pumps direct meltwater from the melthead to instruments for analysis.

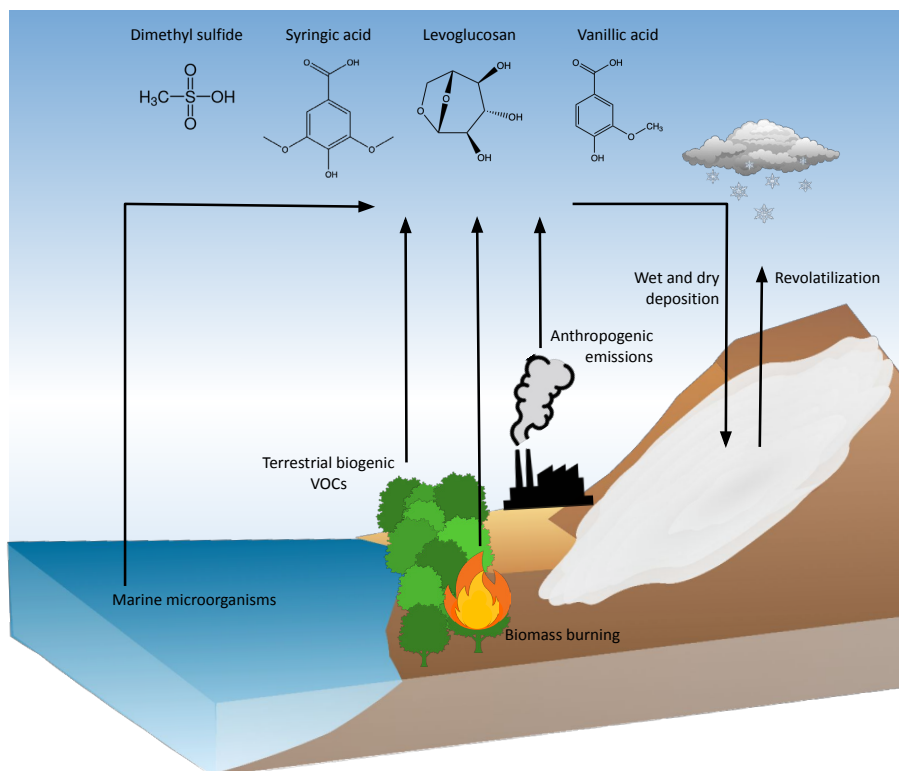


Figure 2: Schematic of transport pathways from sources such as marine microorganisms, terrestrial vegetation, wildfires, and anthropogenic emissions to glaciers and ice sheets. The organic compounds can be deposited as dry or wet deposition, and after deposition, compounds can be chemically or biologically degraded or revolatilized to the atmosphere.

compounds, such as airborne contamination and sample losses from cutting the ice. The drawback is that contamination can stem from the tubing, and signals may be dispersed in the tubing due to diffusion processes (Rasmussen et al. 2005).

The greatest challenge still is that very few methods are able to detect compounds at the low concentrations found in ice cores with high time resolution. Shi et al. (2019) measured discrete surface-snow samples in Antarctica, and observed mean concentrations of vanillic acid and syringic acid of 5.74×10^{-2} pg/mL and 3.84×10^{-2} pg/mL, respectively ($1 \text{ pg} = 10^{-12} \text{ g}$).

Barbaro et al. (2022) recently coupled a CFA melter to a fast liquid chromatography tandem mass spectrometer (FLC-MS/MS). They quantified vanillic and syringic acids, and recently also levoglucosan in alpine ice cores. The method uses two liquid chromatography columns in parallel, allowing one column to be in use while the other is flushed and prepared for the next sample. This results in fast measurements with a spatial resolution of 1 cm. The methods' limit of detection (LOD) was 3.6 pg/mL and 4.8 pg/mL for vanillic acid and syringic acid, respectively (Barbaro et al. 2022). Comparing the LOD of this method to the concentrations found in Antarctic snow shows that current methods involving CFA are not yet able to quantify organic compounds in Antarctica, but can be useful in areas with higher concentrations of organic trace components, such as continental glaciers.

Factors influencing observed organic components in ice

Measurements of organic compounds in ice have given us insight into biomass

burning, sea-ice extent in the Antarctic, and anthropogenic pollution in the past (Fig. 2). Continental glaciers can yield more local information, while ice cores drilled on ice sheets in Antarctica or Greenland can serve as atmospheric background pollution levels.

Shi et al. (2019) found higher levels of levoglucosan and syringic acid near the Antarctic coast compared to further inland. They found no trend with distance from the coast for vanillic acid. Since the compounds have the same sources and similar chemical structures, it is expected that levoglucosan and syringic acid are more sensitive to oxidation and are consequently depleted more rapidly in the atmosphere than vanillic acid. The oxidation of compounds must, therefore, be taken into consideration when interpreting measurements from ice cores. Industrial and fossil-fuel-related emissions have increased the oxidative potential of the atmosphere (Lelieveld and Dentener 2000), which could disproportionately deplete the signal of organic compounds in recent centuries of ice-core chronologies. For older sections of ice, post-depositional effects, such as chemical and microbial degradation, UV-induced degradation in the surface snow, and revolatilization of compounds, must be considered. These post-depositional effects are not currently well understood, but could have differing effects on the levels of organic compounds in different layers of ice.

Conclusion

Organic compounds remain largely unexplored in ice cores, mainly due to difficulties with contamination and not having sensitive-enough methods. Recent developments have allowed continuous measurements of organic biomass burning tracers in alpine ice cores, and high-resolution measurements

of discrete ice samples from Antarctica. Methods are being improved to increase both the number of organic analytes being measured in one core, and the temporal resolution of the ice-core chronology. By analyzing fatty acids, terpenes, phenolic acids, and other components, we gain insight into the terrestrial and marine biospheres of the past, as well as anthropogenic impact on atmospheric chemistry. Developing analysis methods further will allow us to unveil more of these processes, and better understand the biogenic processes and atmospheric circulation in the past.

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