doi.org/10.22498/pages.31.2.94

Exploring new molecular universes: How non-target screening analysis can open new perspectives in ice-core science

François Burgay

Ice cores are unique environmental archives for reconstructing the Earth's past climate. Each sample can contain thousands of different molecules, which, thanks to technological advances, can now be identified to gain a broader understanding of the Earth's system.

The organic challenge

Over the last decades, analytical chemistry applied to ice cores has developed rapidly. Among the most significant innovations, there are those related to the study of elements, which until the beginning of the 21st century was extremely challenging due to their very low concentration in ice, well below the detection limit of the analytical instrumentation. Until the mid-1990s, only a few elements could be analyzed simultaneously, and the analysis of a single sample could take several hours (Barbante et al. 1997). Today, an entire ice core can be continuously analyzed for virtually the entire periodic table of elements (Erhardt et al. 2019). The same applies for organic compounds, such as pollutants or wildfire tracers that are now routinely analyzed at extremely low concentrations (Vecchiato et al. 2020; Zennaro et al. 2014). The possibility to detect and quantify organics in ice samples has opened up new opportunities, such as investigating the anthropogenic perturbation of the environment, or allowing a deeper understanding of specific environmental processes. For example, whereas common inorganic proxies for wildfires, such as ammonium, only give us information about the occurrence of a biomass-burning event (Legrand et al. 2016), organic compounds, like methoxyphenols, can also tell us the type of vegetation that burned (e.g. grasses, conifers; Müller-Tautges et al. 2016).

However, the number of organic compounds that are usually measured only represents a small fraction of the overall organic burden, meaning that the identity of the large majority of the molecules remains unknown. Indeed, most of the analytical methodologies applied so far to ice cores are defined as targeted, meaning that only specific compounds are investigated. To put this into perspective, there are more than 60 million molecules recorded in the Chemical Abstracts Service (cas.org), while less than a hundred are routinely analyzed. These compounds are typically anthropogenic markers, terrestrial and marine biomarkers and biomass burning tracers (Giorio et al. 2018). If we step outside ice-core science for a moment, we can say that the approaches adopted so far are similar to those of a person walking through a meadow with a metal detector. What that person will find are pieces of metal, but they will not see, for example, fragments of plastic or the living beings that inhabit the meadow itself. Not seeing them does not mean that they do not exist, but they are simply invisible to the eye. Coming back to analytical chemistry: target methods, although essential, give us only a partial view of the chemical space. How, then, to proceed?

Non-target screening analysis

The development of high-resolution mass spectrometers (HRMS) unlocks the possibility of exploring what was previously invisible, by simultaneously detecting up to thousands of different molecules from a single sample by providing their exact mass (Fig. 1). The application of HRMS to environmental samples is a fast-growing research field. Methods have been successfully applied to freshwater, aerosol, soil and sediment samples (e.g. Ma et al. 2022). Generally, two approaches are followed: non-target screening (NTS) and suspect screening (SUS). The former refers to the identification in a mass spectrum of those masses that are particularly relevant according to specifically defined criteria (e.g. intensity, occurrence), followed by a characterization and confirmation using reference standards. The latter refers to a slightly different approach that involves the screening of a mass spectrum for specific masses related to a defined list of molecules, followed by a characterization through ion fragmentation and comparison with reference standards.

Despite being widely used in several different environmental matrices, NTS applied to ice cores is still in its infancy, meaning that, to date, the information we can get from ice cores is still under investigation. However, results obtained from the analysis of a single sample from the Belukha ice core (Siberian Altai, 4072 masl) highlight the great potential of the application of NTS (Burgay et al. 2023). Indeed, up to 313 different compounds have been detected, the majority of which (80%)

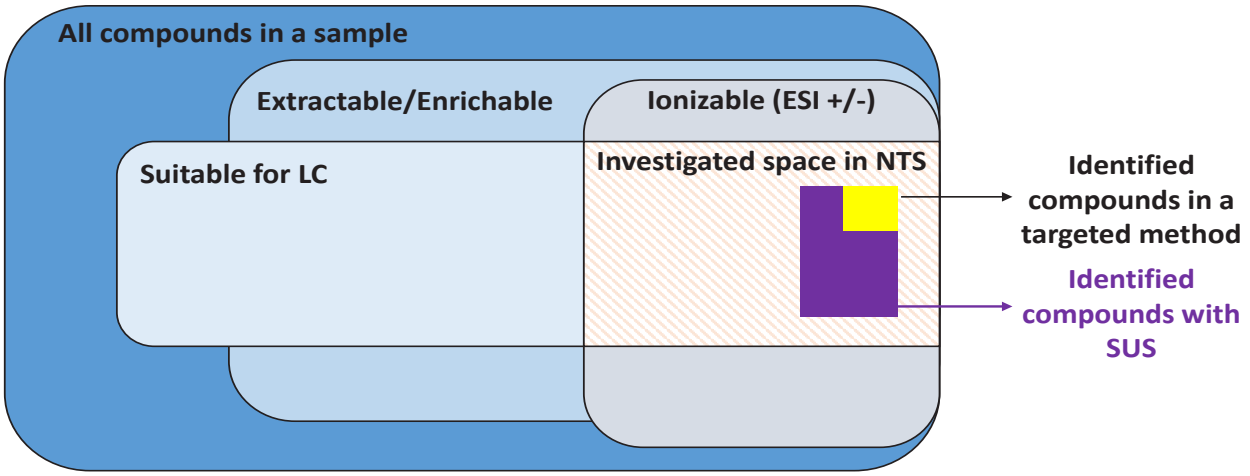

Figure 1: Example of the application of non-target screening (NTS, dashed orange rectangle) and suspect screening (SUS, purple rectangle) approaches when coupled to liquid chromatography (LC). These approaches enable the possibility to investigate a wider chemical space than standard target methodologies (yellow rectangle).

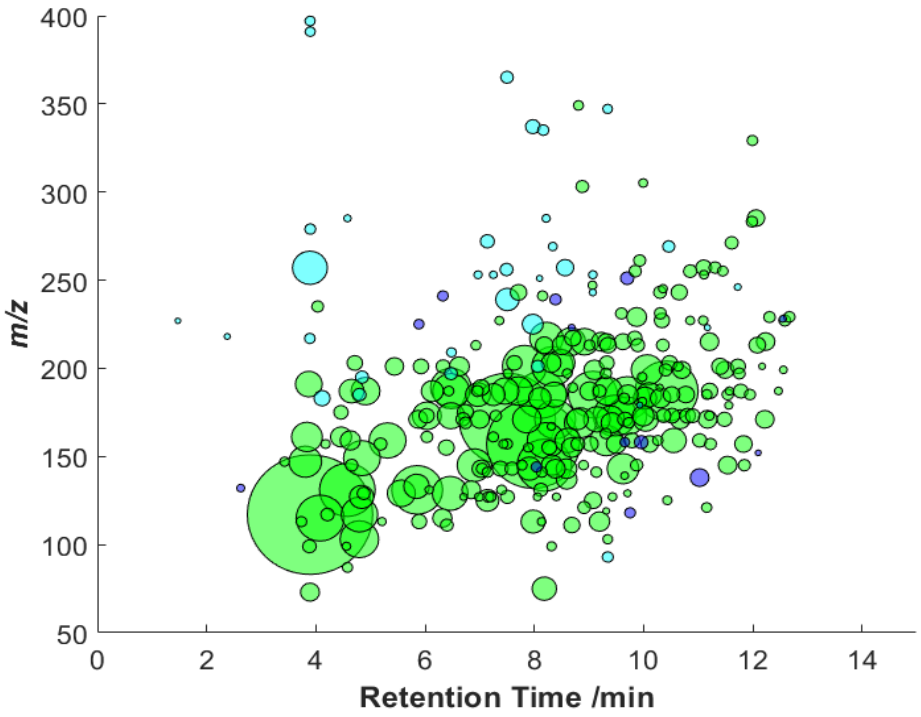

Figure 2: Mass-to-charge (m/z) ratios plotted against the retention time. The size of the circles is proportional to the area of the molecular ions. Green circles refer to compounds consisting of carbon, hydrogen and oxygen atoms. Purple circles refer to compounds that also have nitrogen in their structure. Light blue circles refer to compounds defined as "other", which contain other heteroatoms. Figure from Burgay et al. (2023) under CC-BY 4.0.

consist of carbon, hydrogen and oxygen. In addition, 7% of the molecules also contain nitrogen in their structure, while the remaining 13% contain other heteroatoms (Fig. 2). Focusing only on the most intense peaks, several carboxylic acids (e.g. succinic acid, glutaric acid, levulinic acid) and biomass burning tracers (e.g. *p*-hydroxybenzoic acid) were characterized.

Potentialities, challenges and future work

When applied to an entire ice-core record, the developed NTS workflow will allow scientists to understand how anthropogenic pollution has altered the aerosol molecular composition, and how the oxidative capacity of the atmosphere has changed between the pre-industrial and industrial periods. Additionally, NTS methods can be exploited for the identification of novel molecular proxies that can overcome limitations of existing proxies. For example, commonly used marine productivity proxies, such as methanesulphonic acid, may suffer from migration within the ice column, thus potentially compromising the reliability of paleoclimate reconstructions (Osman et al. 2017). However, phytoplankton also emits isoprene compounds, which can be oxidized in the atmosphere to secondary organic aerosol species (Hu et al. 2022) that are, in turn, deposited on the snow. Identifying these products using an NTS approach could provide unprecedented opportunities to test their suitability as reliable proxies for marine productivity.

Unfortunately, NTS methods are not universal. In other words, they allow the identification of hundreds or even thousands of new molecules, but many more may still be present in the ice-core samples. Coming back to the previous metaphor: NTS allows us to observe other materials as well, not just metal. However, others still remain invisible to the eye. This is due to their different chemical (polar/non-polar) and physical (volatile/non-volatile) properties. For this reason, there are no methods or instruments that can cover this wide range of molecular heterogeneity. Continuous methodological development based on well-constrained scientific questions is, therefore, essential to fully exploit the potential of NTS for comprehensive ice-core reconstructions. To date, the few available NTS ice-core methods are optimized for the detection of polar substances, i.e. those that are easily ionizable by electrospray ionization and compatible with liquid chromatography (Burgay et al. 2023; Vogel et al. 2019). However, future developments should also focus on the identification of non-polar and/or volatile substances relying on other ionization techniques and instruments.

A further challenge is the characterization of the identified molecules. We have seen that the application of HRMS provide the exact mass of the compounds, making it possible to unambiguously define their molecular formula. However, there may be many compounds with the same molecular formula, but different structure, known as isomers. This highlights the need for additional efforts to uniquely characterize a compound, for example by comparing the fragmentation spectra and retention time of the unknowns with those of reference standards. However, standards do not exist for all molecules, especially for those formed after reactions in the atmosphere, which are of particular interest to ice-core scientists. To fill this knowledge gap, a novel approach known as aerosolomics has been recently developed (Thoma et al. 2022). In brief, chamber experiments have been carried out to determine the oxidation products of specific precursors, such as terpenes, i.e. biogenic-derived molecules. When applied to environmental samples, this strategy would link the detected oxidation products to their respective precursors, assessing their oxidative pathways. For ice-core studies, this approach can shed light on past changes of the different oxidative pathways of terpenes, as well as on the temporal evolution of the source's strength.

As with any new scientific adventure, the difficulties and unknowns are many. However, the rewards of exploring a mysterious universe of molecules can be great. We are only at the beginning of this exciting journey, and there is much to discover.

AFFILIATION

Laboratory of Environmental Chemistry, Paul Scherrer Institute, Villigen, Switzerland

CONTACT

François Burgay: francois.burgay@psi.ch

REFERENCES

Barbante C et al. (1997) Int J Environ Anal Chem 68(4): 457-477

Burgay F et al. (2023) Anal Chem 95(30): 11456-11466

Erhardt T et al. (2019) Environ Sci Technol 53(22): 13275-13283

Giorio C et al. (2018) Quat Sci Rev 183: 1-22

Hu C et al. (2022) Sci Total Environ 853: 158645

Legrand M et al. (2016) Clim Past 12: 2033-2059

Ma J et al. (2022) Environ Sci Technol 56(11): 7017-7028

Müller-Tautges C et al. (2016) Atmos Chem Phys 16: 1029-1043

Osman M et al. (2017) The Cryosphere 11: 2439-2462

Thoma M et al. (2022) Atmos Meas Tech 15(23): 7137-7154

Vecchiato M et al. (2020) Sci Rep 10: 1-10

Vogel A et al. (2019) Environ Sci Technol 53: 12565-12575

Zennaro P et al. (2014) Clim Past 10: 1905-1924