

13C measurements on organic aerosol – ambient samples versus source studies

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The stable carbon isotopes ¹²C and ¹³C can be used to get information about sources and processing of organic aerosol (OA). We developed and tested a method to measure $\delta^{13}\text{C}$ values of OA collected on filter samples in different volatility classes. These filter samples are introduced into an oven, where organic compounds are thermally desorbed in He at different temperatures. The compounds released at each temperature step are oxidized to CO₂ using a platinum catalyst at 550 °C. The CO₂ is then passed on to an isotope ratio mass spectrometer (IRMS) to measure $\delta^{13}\text{C}$ ratios. With a similar setup the chemical composition at each temperature step can be determined using a Proton Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS).

System evaluation with controlled test compounds showed that organic compounds usually start evaporating from the filter when their melting point is reached. Isotopic fractionation occurs only if one temperature step is within a few degrees of the melting point of the substance, so that the substance only partially evaporates. However, this effect should be limited in an ambient sample containing thousands of individual chemical compounds. $\delta^{13}\text{C}$ values of aerosol filter samples do not depend on the sample amount used, i.e. the system shows good linearity. The reproducibility depends somewhat on the sample amount and is usually $< \pm 0.3 \text{ ‰}$ for oven temperatures up to 200 °C and $< \pm 0.5 \text{ ‰}$ for oven temperatures greater than 200 °C.

We analysed aerosol samples collected in a tunnel in Brazil (vehicular emissions), laboratory generated secondary organic aerosol (SOA) from alpha-pinene ozonolysis, and ambient filter samples from a regional site in the Netherlands and an urban site in Belgium. First results indicate that the SOA produced in our experiments is slightly enriched in $\delta^{13}\text{C}$ compared to the precursor alpha-pinene. It is also more volatile than organic aerosol from ambient or tunnel filters. The $\delta^{13}\text{C}$ ratios of SOA and vehicular emissions do not change strongly with oven temperature, i.e. the more refractory organic compounds have similar isotopic composition as the more volatile compounds.

This is in contrast to many ambient organic aerosol samples, where the more volatile compounds evaporating below 200°C are often depleted with respect to the refractory compounds (see Figure 1).

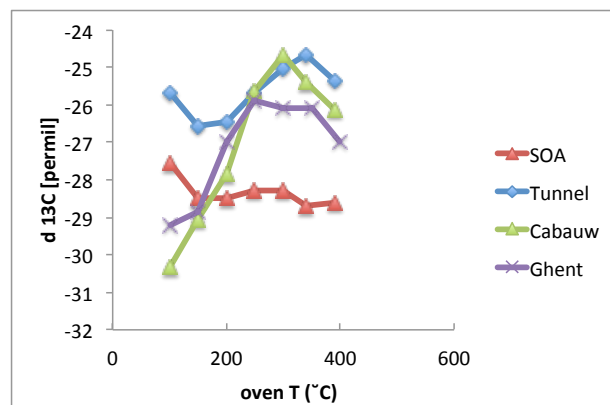


Figure 1. $\delta^{13}\text{C}$ of organic compounds released at a given oven temperature for aerosol filter samples taken in a tunnel in Brazil, SOA produced from alpha-pinene ozonolysis compared with typical ambient samples taken in the polluted regional background location of Cabauw, and the urban area of Ghent

Measurements at the Cabauw site show interesting differences between $\delta^{13}\text{C}$ measured in polluted air masses and relatively clean air with marine air mass origin. In polluted, continental air masses $\delta^{13}\text{C}$ is only weakly dependent on oven temperature, similar to the tunnel samples. In air masses with marine origin, organic compounds evaporating at low temperatures are strongly depleted in ¹³C, see figure 1.

Possible reasons for the difference between source profiles and ambient samples (mixture of sources vs. the role of heterogeneous oxidation in the ambient filter samples vs. sampling artefacts) will be discussed and related to the chemical composition of the aerosol.