

Insights into fossil vs. non-fossil SOA from online TOT-¹⁴C analysis

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Radiocarbon (¹⁴C) measurements with accelerator mass spectrometry can apportion emissions of carbonaceous aerosols into fossil and non-fossil sources (Szidat, 2009). This speciation relies on the principle that ¹⁴C is extinct in fossil substances, whereas it is on the contemporary level for modern materials. The technique constitutes an unambiguous tool, since the intrinsic ¹⁴C of the aerosol will not be affected by complex chemical transformations in atmosphere, such as it occurs for the formation of secondary organic aerosol (SOA) (Zotter et al., 2014). Our laboratory developed a separation method for the direct determination of ¹⁴C in organic carbon (OC) and elemental carbon (EC) using a thermal-optical transmittance (TOT) protocol with a Sunset OC/EC analyzer (Zhang et al., 2012).

Although this procedure is very helpful for emission apportionment of OC and EC, it cannot provide information on sources of sub-fractions, such as OC of different chemical stability or volatility, which are of large importance for the study of fossil vs. non-fossil precursors of secondary organic aerosol (SOA). As peaks of sub-fractions separated with a modified thermal ramp of the Sunset OC/EC analyzer appear too close to each other, an interface was required that injects the carbon dioxide in real-time mode into the ¹⁴C accelerator mass spectrometer (Figure 1). This setup allows online radiocarbon analysis of the carbon dioxide evolving from the TOT instrument (Agrios et al., 2015).

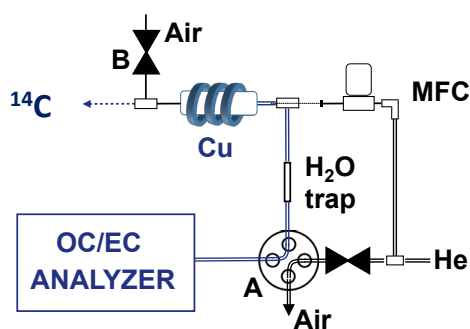


Figure 1. The technical scheme for continuous-flow online TOT-¹⁴C measurements (Agrios et al., 2015).

Figure 2 presents the real-time radiocarbon analysis of an aerosol filter from an urban background site in Zurich during winter to demonstrate the potential of the performance of the interface (Agrios et al., 2016).

In this analysis, OC was further split thermally into four fractions. The semi-volatility OC fraction (evolving at 200 °C in pure oxygen) is characterized by a lower ¹⁴C value with an increasing trend towards the lower volatility OC fractions at 260-375 °C, which in turn do not show any significant ¹⁴C trend with temperature. This indicates that the OC with the highest volatility originates from more pronounced fossil sources than the lower volatility OC.

A similar behaviour was observed earlier by comparison of ¹⁴C measurements of total OC with aerosol mass spectrometry for Los Angeles (Zotter et al., 2014). Here, the semivolatile oxygenated organic aerosol associated with fresh SOA showed a substantially more fossil signal than the low-volatility oxygenated organic aerosol from the regional background. Online TOT-¹⁴C analysis is advantageous compared to the previous method, as it allows even the study of sub-fractions of OC. Therefore, it may become a new analytical tool to apportion fossil and non-fossil precursor gases of fresh and altered SOA in combination with other techniques like aerosol mass spectrometry.

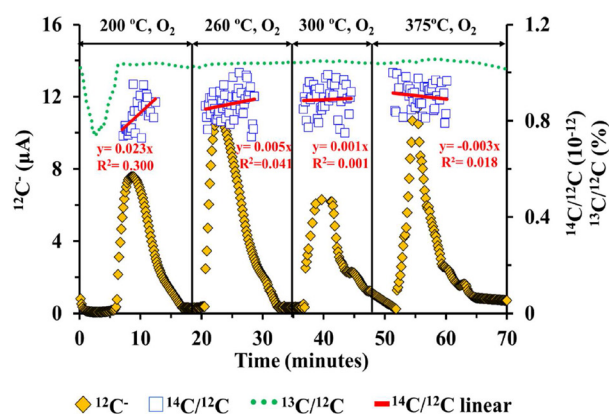


Figure 2. Continuous-flow TOT-¹⁴C analysis of OC sub-fractions evolving at 200, 260, 300 and 375 °C for an urban background aerosol from Zurich for 28/01/2009 (Agrios et al., 2016).

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