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13C as tracer for sources and processing of carbonaceous aerosols – a comprehensive study at urban, coastal, and forest sites in Eastern Europe

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The stable carbon isotopes 12C and 13C can be used to get information about sources and processing of carbonaceous aerosol. In Eastern Europe fossil fuel sources have a δ 13C values in a range of -28 ‰ which is depleted compared to aerosol produced by biofuel burning with δ 13C values of on average -25 ‰ secondary organic aerosol (SOA) from VOC precursors emitted by fossil fuel or biomass burning is likely depleted with respect to the precursors, since the oxidation reactions are usually not complete. On the other hand photochemical aging of organic aerosol, leads to a net loss of organic carbon from the particles and therefore to a gradual enrichment in 13C of the remaining aerosol phase. The isotope signature of other sources, such as biogenic secondary aerosol is not very well known.

We compare stable carbon isotope ratios of carbonaceous aerosol during summer and winter at three different sites: A city, a costal, and a remote forest site in Lithuania. In winter both PM2.5 (particulate matter with diameters < $2.5 \mu m$) and size resolved samples were available, and in summer PM2.5 samples. Stable carbon isotope ratios were measured for organic carbon (OC) in different volatility fractions and for total carbon (TC).

During winter-time in Lithuania we expect photochemistry and biogenic emissions to be of minor importance. The main sources of aerosol carbon should be fossil fuel and biomass combustion. Our results show that generally fossil sources are associated with smaller particles and the more volatile carbon fractions, whereas biomass burning sources are associated with larger particles and less volatile carbon fractions. At the coastal site, we identified an additional source as shipping emissions, probably from a nearby harbour, which have a strongly depleted isotope signature with $\delta 13$ C values between -29 to -30 %. The coastal site shows evidence of stronger SOA formation compared to the urban site, whereas the very low (OC) concentrations at the forest site show evidence of photochemical aging.

In summer $\delta 13C$ of OC and TC is depleted by roughly 3 %0 compared to winter, reflecting the missing biomass burning source and stronger contribution of SOA, both at the urban and the coastal site. At the forest site the most depleted isotope signatures are associated with the lowest aerosol concentrations and more enriched signatures with higher aerosol concentrations, probably associated with long-range transport. This will be further explored and might lead to an isotopic source signature for biogenic SOA for the first time.