The fossil fraction of carbon in PM2.5: Variations on seasonal and diurnal time scales

U. Dusek[1], M. Monaco[1], A. Kappetijn[1], H. A. J. Meijer[2], S. Szidat[3], and T. Röckmann[1]

[1]IMAU, Utrecht University, Utrecht, the Netherlands
[2]Center for Isotope Research, Groningen University, Groningen, the Netherlands
[3]Department of Chemistry and Biochemistry, University of Berne, 3012, Switzerland

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Presenting author email: u.dusekt@uu.nl

Measurement of the radioactive carbon isotope ^{14}C in aerosols can provide a direct estimate of the contribution of fossil fuel sources to aerosol carbon (e.g. Szidat et al., 2007). In aerosol science, measurements of $^{14}C/^{12}C$ ratios are usually reported as fraction modern ($F^{14}C$). The radiocarbon signature gives a clear distinction between 'modern' carbon sources ($F^{14}C$ around 1.1-1.2 for biomass burning and around 1.05 for biogenic secondary organic aerosol) and 'fossil' carbon sources ($F^{14}C$ =0 for primary and secondary formation from fossil fuel combustion). Due to the high cost of ^{14}C analyses very few long-term studies have been conducted to date. The data that will be presented offer a unique insight into the seasonal variation of source contributions to the carbonaceous aerosol in a highly industrialized region.

High volume filter samples of PM2.5 have been collected roughly twice per month from February 2011 – July 2012 at Cabauw, a rural location in the Netherlands surrounded by major urban centers and highways. This site is representative of regional background aerosol contamination in the Netherlands. We report measurements of $F^{14}C$ for total carbon (TC), organic carbon (OC), water insoluble OC (WIOC) and thermally refractory carbon (RC) as a proxy for elemental carbon.

The fraction modern of OC lies between 0.65 - 1 and shows only a moderate seasonal variation, with highest values in the spring and lowest values in the summer. EC is generally dominated by fossil carbon, but shows a distinct seasonal variation with higher contribution of modern sources from November – Mai. This contribution is normally attributed to wood combustion, see Figure 1, but this is questionable for the filter samples taken in spring. The modern contribution is low when air masses arrive from the ocean and high for air masses with European continental origin, pointing to a main source outside the Netherlands. Water soluble organic carbon is dominated by modern sources throughout the year.

For TC concentrations between 1.2 and 8 $\mu g/m^3$, $f_m(TC)$ increases with TC concentration. A Keeling plot implies that synoptic scale variation in $f_m(TC)$ are mainly due to a modern source, imposed on a regional background with a relatively high contribution from fossil sources. TC concentrations > 8 $\mu g/m^3$ are associated with pollution events and can have much higher fossil contributions.

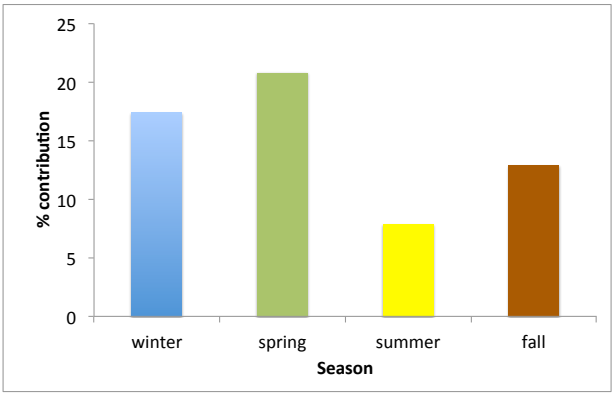

Figure 1. Contribution of biomass burning to refractory carbon in different seasons. Up to approximately 5% can be explained by not ideal separation of OC and RC

Measurements of diurnal variations in $F^{14}C$ can give an indication of the importance of regional emissions, such as traffic, or SOA production from biogenic emissions. For selected time periods during spring and summer 2012, we took separate day and night filter samples that were analyzed for ^{14}C in TC, OC, WIOC, and RC. In all carbon fractions the fossil contribution was higher in day time than in night time. This is consistent with the traffic density in the region, which is higher during day time (7 am to 7 pm) than during night time. Contrary to the synoptic scale variation dominated by modern carbon, the shorter term variations in the regional aerosol seem dominated by fossil sources. Condensation of semi-volatile carbon in the cooler night time might contribute to this trend.

Using a simple model, the contributions of fossil emissions, biomass burning, and biogenic emissions will be estimated for all carbon fractions. The seasonal variation in the source contributions will be presented and discussed.

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Szidat, S., Prevot, A. S. H., Sandradewi, J., Alfarra, M. R., Synal, H.-A., Wacker, L., and Baltensperger, U., (2007) *Geophys. Res. Lett.,* **34**, L05820, doi:10.1029/2006GL028325.