

Fossil Sources of PM_{2.5} Aerosol Carbon based on ¹⁴C Measurements

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Summary

Significant portions of PM_{2.5} mass consists of organic and elemental carbonaceous material. In the southeastern United States typically 1/3 of the FRM-measured fine mass consists of organic carbon and, in urban areas, of the order of 10% consists of elemental carbon. The organic portion of this carbonaceous is a complex mixture of primary compounds and secondary materials formed in situ from primary emissions. Both primary and secondary constituents derive from a variety of sources which are dynamically changing in time and space. Source characterization has been hampered by this complexity, and further constrained by lack of knowledge of secondary formations processes and tactically by the expense of identifying and analyzing for tracers of specific emissions sources. One underutilized way of addressing these shortcomings is through the measurement of the ¹⁴C content of organic aerosol particles. Based on the two-source model, organic aerosol carbon may consist of "modern" or recently formed carbonaceous material in equilibrium with current concentrations of atmospheric ¹⁴CO₂ which has formed from the interaction of cosmic rays with atmospheric nitrogen. The second source of aerosol carbon is derived from fossil carbon whose age much exceeds the half-life of ¹⁴C (*ca.* 5800 y) hence contains essentially no ¹⁴C. By measuring the ¹⁴C content of ambient aerosols, along with the ¹³C/¹²C isotopic ratio to correct for fractionation processes, the fraction of modern carbon (*f_m*) in aerosol samples can be determined, and the fraction derived from fossil fuel combustion determined as 1-*f_m*.

Measurements have now been made of the ¹⁴C content of PM₁₀ samples collected at TVA's enhanced monitoring facility at Look Rock, TN, during three seasons: spring of 2000, summers of 2000 and 2001, and fall, 2001. Results from the first three of these periods, calculated as the fraction of fossil carbon, are reported here. Variable fossil carbon fractions were observed during the spring season, decreasing from about 45% in mid-April to about 10% in mid-May at about the same time frame as the leaves of the predominantly mixed deciduous forest surrounding the sampling site emerged. Relatively constant fractions of 60±10% fossil carbon were observed during the late summer period (mid-August to early September) in 2000. This occurred during a period in which the fine mass and organic carbon concentrations were generally decreasing from >20 µg/m³ to levels near the annual average of about 12 µg/m³.

Recently acquired data for the summer, 2001, period, which included the entire month of July, showed a different pattern, with the fraction of fossil carbon varying from 12 to 27 %. This sampling period exhibited widely varying fine mass concentrations from <10 to as high as 40 $\mu\text{g}/\text{m}^3$ (based on TEOM continuous monitoring of $\text{PM}_{2.5}$ mass). The reasons for this wide variation in fraction of fossil carbon from season to season and summer to summer is not yet clear.

The relation of observed fractions of fossil carbon to controllable anthropogenic organic carbon sources is complex. Products of fossil fuel combustion, largely from mobile sources (gasoline- and diesel-powered vehicles), clearly comprise in the large part the fossil-derived organic carbon in ambient aerosols. There is a major contribution to the "modern" organic carbon from natural emissions of trees and other plant life which are converted by photochemical oxidation to non-volatile products, and some contribution from resuspended plant detritus. However, there are also contributions to "modern" aerosol organic carbon from wood-burning and the burning of agricultural wastes which are anthropogenically derived hence also potentially controllable sources. Wood burning contributions to "modern" carbon is complicated by the residual radiocarbon derived from thermonuclear bomb tests in the mid-twentieth century, since combusted wood can be several decades old. Large seasonal variations in these sources are also expected. Even with these complexities in interpreting fraction of fossil carbon data, we suggest that the observed fractions of modern carbon are lower limits to the fraction of fine organic carbon in atmospheric aerosols which could be targeted for emissions reductions. Since organic carbon fractions of fine mass average $\frac{1}{3}$ or more of the $\text{PM}_{2.5}$ mass, organic carbon aerosols are a legitimate target for any necessary future control strategies.