

Source apportionment of carbonaceous aerosol in Sao Paulo using ^{13}C and ^{14}C measurements

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The Metropolitan Area of Sao Paulo is affected by high aerosol concentrations, which contain a large fraction of organic material. Up to date, not much is known about the composition and origin of the organic aerosol in this city. We present the first source apportionment of the carbonaceous aerosol fraction in Sao Paulo, using stable (^{13}C) and radioactive carbon isotopes (^{14}C). ^{14}C provides a clear-cut distinction between fossil sources, which contain no ^{14}C , and contemporary sources such as biofuels, biomass burning, or biogenic sources, which contain a typical contemporary $^{14}\text{C}/^{12}\text{C}$ ratio. ^{13}C can be used to distinguish C3 plants, such as maize and sugarcane, from C4 plants. This can help to identify a possible impact of sugarcane field burning in the rural areas of Sao Paulo State on the aerosol carbon in the city.

In the first part of the study, we compare two tunnel studies: Tunnel 1 is frequented only by light duty vehicles, which run mainly on mixtures of gasoline with ethanol (gasohol, 25% ethanol and 85% gasoline) or hydrated ethanol (5% water and 95% ethanol). Tunnel 2 contains a significant fraction of heavy-duty diesel vehicles, and therefore the fraction of biofuels in the average fleet is lower. Comparison of ^{14}C in organic and elemental carbon (OC and EC) shows that in both tunnels there is no significant contribution of biofuels to EC. Combusting ethanol-gasoline fuels in a vehicle engine does apparently not result in significant EC formation from ethanol. Biofuels contribute around 45% to OC in Tunnel 1 and only 20% in Tunnel 2, reflecting a strong impact of diesel vehicles in Tunnel 2.

In the second part of the study we conduct a source apportionment of ambient aerosol carbon collected in a field study during winter (July-August) 2012. Ambient EC has two main sources, vehicular emissions and biomass burning. We estimate a contribution of vehicular sources to EC of roughly 90% during weekdays and 80% during weekends, using the ^{14}C values measured in the tunnel studies. The absolute concentration of biomass burning EC is roughly $0.5 \mu\text{g}/\text{m}^3$ both during weekend and weekdays, whereas vehicular EC concentrations almost double during weekdays, increasing from 1.8 to $3.7 \mu\text{g}/\text{m}^3$ on average. OC concentrations are dominated by secondary carbon from vehicular emissions, both on weekdays and during weekends, however primary OC from biomass burning and contemporary secondary OC (from both biogenic and biomass burning emissions) are important fractions as well. Overall, primary biomass burning contributes between 10 and 30% to the carbonaceous aerosol in Sao Paulo. ^{13}C measurements indicate that sugarcane burning could account for up to 15% of OC in the Sao Paulo metropolitan area.