Biofuel and fossil fuel contribution to carbonaceous aerosol from vehicular emissions in Sao Paulo, Brazil

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Sao Paulo city has been the focus of several studies that investigated the impact of vehicular emissions on the concentration and composition of particulate matter. The main goal of this work was to study fine particulate matter ($PM_{2.5}$) originated from vehicular emissions, focusing on the distinction between emissions from light duty vehicles (LDV) and heavy duty vehicles (HDV), using stable (^{13}C) and radioactive carbon isotopes (^{14}C).

Vehicular emissions have a big impact on air quality and are the main source of PM2.5 in Sao Paulo city (Cetesb, 2014). The current vehicular fleet runs on different types of fuel: diesel (5% of biodiesel), hydrated ethanol, gasohol (gasoline with 25% of ethanol) and flex fuel (any proportion of gasohol and ethanol). The vehicular fleet is composed of 85% of LDV (mainly flex fuel vehicles), 3% of HDV, which run on diesel, and 12% motorcycles. The distinction between contributions from LDV and HDV to carbonaceous aerosol (organic, OC, and elemental carbon, EC) is still an open question.

Two tunnel campaigns were performed in Sao Paulo city: Tunnel 1 (T1) is frequented only by LDV, and Tunnel 2 (T2) contains a significant fraction HDV, and therefore the fraction of biofuels in the average fleet is lower. In order to distinguish the contribution from HDV and LDV, different measurements were performed: ^{14}C (distinction between fossil and contemporary sources), ^{13}C (distinction of C3 plants from C4 plants, such as sugarcane - feedstock for ethanol), and OC / EC concentration.

Table 1 shows average OC and EC concentrations measured in both tunnels. T2 had significantly higher EC and OC concentrations than T1 due to higher HDV emissions and also due to the higher amount of vehicles. The main difference between the tunnels was the OC/EC ratio. A ratio around 1.5 is observed for T1, where the OC emissions are higher due to the combustion of mainly gasohol and ethanol, and the emission of EC is lower than in the T2, which is more impacted by HDV. In T2, the OC/EC ratio was approximately 0.5.

$F^{14}C$ measured on OC and EC is also presented in Table 1. The fraction of HDV is much higher in T2 than in T1, which explains the lower $F^{14}C$ (OC) values in T2. Notably, EC emissions mostly originate from fossil fuels ($F^{14}C=0$), even in the T1, where a high number of FFV is expected. Fig 1 presents the relative contributions biofuels and fossil fuels to OC and EC. Fossil fuel presented large contributions to OC and EC concentrations, due to fossil fuels.

Table 1.: OC and EC average concentrations and $F^{14}C$ values for OC and EC for each campaign

Campaign	OC		EC	
	OC (μg/m³)	$F^{14}C$	EC (μg/m³)	$F^{14}C$
T1	14.3	0.46	9.2	0.04
T2	61.5	0.19	121	0.04

Biofuel burning represented 45% of OC measured in T1, however this contribution was lower in T2 (18%), where HDV represented 30% of vehicular fleet. The low values of EC from biofuel (EC_b) and high values of EC from fossil fuel (EC_f) confirm that fossil fuel burning is the main source for EC in the tunnels. A slight enrichment of ^{13}C in OC is observed in T1, but not as much as could be expected, if significant higher amounts of OC was produced from burning of ethanol.

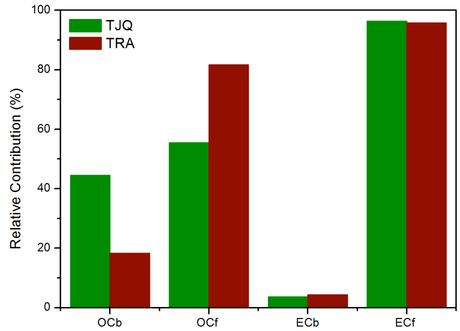

Figure 1: Relative contributions (in %) of biofuel (b) and fossil fuel (f) burning to the total carbon for T1 (green) and T2 (red)

In conclusion, comparison of ^{14}C in OC and EC shows that in both tunnels there is no significant contribution of biofuels to EC. Combustion of ethanol-gasoline fuels in a vehicle engine does not apparently result in significant EC formation from ethanol. Biofuels contribute around 45% to OC in TJQ an only 20% in TRA, reflecting a strong impact of HDV.

Cetesb: *Relatório de Qualidade do Ar no Estado de São Paulo 2013*. 110 [online] Available from: http://ar.cetesb.sp.gov.br/publicacoes-relatorios/, 2014.