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On-road emissions of carbonyls from vehicles powered by biofuel blends in traffic tunnels in the Metropolitan Area of Sao Paulo, Brazil

Thiago Nogueira [a, *], Kely Ferreira de Souza [b], Adalgiza Fornaro [a], Maria de Fatima Andrade [a], Lilian Rothschild Franco de Carvalho [b]

[a] Department of Atmospheric Sciences, Institute of Astronomy, Geophysics and Atmospheric Sciences, University of São Paulo, São Paulo, Brazil
[b] Department of Fundamental Chemistry, Institute of Chemistry, University of São Paulo, São Paulo, Brazil

HIGHLIGHTS

- Formaldehyde (F) and acetaldehyde (A) were the most abundant carbonyl compounds.
- The F/A ratio from Brazilian light-duty vehicles ranged from 0.77 to 1.3, lower than that obtained in other countries.
- Heavy-duty vehicles emit F concentrations close to California's vehicles.

GRAPHICAL ABSTRACT

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ABSTRACT

On-road emissions of carbonyls from the current vehicle fleet of Brazil were determined in two experimental campaigns, conducted in traffic tunnels located in the Metropolitan Area of São Paulo (MASP), in southeastern Brazil. Among carbonyl species, formaldehyde and acetaldehyde were the most abundant in all sampling periods. In Brazil, heavy-duty vehicles (HDVs) run on a blend of 95% regular diesel/5% biodiesel from soy, whereas light-duty vehicles (LDVs) run on gasohol (75–80% gasoline/20–25% ethanol) or hydrous ethanol. We found that HDVs showed the highest overall carbonyl emissions, although LDVs were responsible for high emissions of acetaldehyde. In comparison with LDVs in California, which are powered by 90% gasoline/10% ethanol, LDVs in Brazil were found to emit 352% and 263% more formaldehyde and acetaldehyde.

1. Introduction

Carbonyls are a subset of volatile organic compounds (VOCs) that includes aldehydes and ketones. Many carbonyls are highly reactive in the atmosphere, contributing to the formation of ozone, peroxyacyl nitrates, and other photochemical air pollutants (Atkinson, 2000). Carbonyls are emitted by mobile and stationary sources, including indoor sources (Sawyer et al., 2000; Weschler et al., 1992), and are formed as major reaction products in the atmospheric oxidation of many hydrocarbons and other VOCs (Atkinson, 1997; Carter, 1990; Grosjean and Grosjean, 1997). Anthropogenic sources include industrial processes and waste

* Corresponding author. Department of Atmospheric Sciences, Institute of Astronomy, Geophysics and Atmospheric Sciences, University of São Paulo, Rua do Matão, 1226, CEP 05508-900, São Paulo, SP, Brazil.
E-mail address: thiago.nogueira@iag.usp.br (T. Nogueira).

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incineration, as well as the burning of wood, fuel, and forests. Fuel combustion is a well-known direct source of carbonyls, which are intermediate species created during fuel oxidation and emitted into the atmosphere when combustion is incomplete (McLaren et al., 1996; Siegl et al., 1999; Zhang and Smith, 1999). However, the impact of those emissions depends on the kind of fuel used, the presence of catalysts, and the traffic conditions (Guarieiro et al., 2009, 2008; Rodrigues et al., 2012; Zervas, 2008). Carbonyls present in motor vehicle exhaust, such as formaldehyde and acetaldehyde, have been identified as toxic air contaminants—defined as pollutants known or suspected to cause adverse health effects (Ban-Weiss et al., 2008; Garcia et al., 2011; Goldmacher and Thilly, 1983).

In vehicle emissions, formaldehyde is typically the most abundant carbonyl, although others, such as acetaldehyde, benzaldehyde, the sum of tolualdehyde isomers, and acetone, can be present at similar magnitudes (Wagner and Wyszynski, 1996). Although diesel engines are a minor source of hydrocarbon emissions, total carbonyl emissions per total distance traveled have been found to be higher for diesel engines than for gasoline engines (Ban-Weiss et al., 2008; Grosjean et al., 2001; Ho et al., 2007; Kristensson et al., 2004; Legreid et al., 2007; Schmid et al., 2001). A 2009 emissions inventory for California showed diesel engines to be the largest direct source of formaldehyde and acetaldehyde, accounting for 50% and 57% of the total anthropogenic emissions of those two pollutants, respectively (ARB-Almanac, 2009).

Studies conducted in various countries have monitored these compounds in the areas directly affected by vehicle emissions—along roadsides and within tunnels (Ban-Weiss et al., 2008; Grosjean et al., 2001; Ho et al., 2007; Kean et al., 2001; Kristensson et al., 2004; Legreid et al., 2007; Schmid et al., 2001). However, there are still few data for countries where there is large-scale use of ethanol and biodiesel as vehicle fuels, such as Brazil. In 2001 and 2004, respectively, Vasconcelos et al. (2005) and Martins et al. (2006) reported VOC emissions from light-duty and heavy-duty vehicles (LDVs and HDVs, respectively) in two distinct urban tunnels in one of the largest megacities in the world, within the most economically important region of Brazil—the Metropolitan Area of São Paulo (MASP). In other parts of Brazil, carbonyls emitted by HDVs running on diesel or a diesel/biodiesel blend have been measured at regional bus terminals (Pinto and Solci, 2007; Rodrigues et al., 2012). A few studies have also reported carbonyl concentrations for major urban centers, including São Paulo and Rio de Janeiro (Alvim et al., 2011; Correa et al., 2010, 2003; Martins et al., 2008; Nogueira et al., 2014; Rocha et al., 2008).

Large urban centers in Brazil can be considered ideal places to study the impact of carbonyls, because their production is greater during ethanol combustion (He et al., 2003; Niven, 2005). Some studies have shown that carbonyl emissions are significantly higher when diesel/biodiesel blends are used (Chai et al., 2013; Fontaras et al., 2010; Guarieiro et al., 2009, 2008). Brazil is the only place in the world where fuels with high ethanol contents have long been used, the objective being to decrease dependence on petroleum imports and improve urban air quality. In Brazil, anhydrous ethanol (maximum water content, 0.7%) is used as an anti-knock additive in regular gasoline, resulting in gasohol (20–25% ethanol/75–80% gasoline). In addition, hydrous ethanol (maximum water content, 7.4%) is also used as a fuel for LDVs. From 2008 to 2010, HDVs in Brazil ran on a blend of 98% diesel/2% soy biodiesel (B2), running on 95% diesel/5% soy biodiesel (B5) thereafter.

In urban areas of Brazil, vehicle emissions constitute the main source of certain air pollutants. Activity in the MASP, which had been primarily industrial, has become focused on the provision of consumer goods and services, making vehicles the main source of pollutant emissions (de Miranda et al., 2012). The more than 6 million passenger and commercial vehicles in the MASP are responsible for emitting 97% of all carbon monoxide (CO), 85% of all hydrocarbons, 82% of all nitrogen oxides, 36% of all sulfur dioxide, and 36% of all inhalable particulate matter (CETESB, 2012). The MASP vehicle fleet comprises LDVs (85%), HDVs (3%), and motorcycles (12%). Of the LDVs, approximately 55% run on gasohol, 5% run on hydrous ethanol, 38% are flex-fuel vehicles capable of burning gasohol or hydrous ethanol, and 2% run on diesel, whereas all of the HDVs run on B5 and all of the motorcycles run on gasohol (CETESB, 2013). Since 2003, significant changes have occurred in the Brazilian fleet, primarily due to the introduction of flex-fuel vehicles, with new catalysts and exhaust systems, and the mandatory addition of biodiesel to diesel since 2008. Anderson (2009) reviewed the available data on air quality and vehicle emissions in Brazil, focusing on pollutants whose concentrations might be affected by the combustion of large quantities of ethanol. The author reported that atmospheric concentrations of acetaldehyde and ethanol are much higher in Brazil than in other areas of the world, whereas those of aromatic compounds and carboxylic acids are lower. Salvo and Geiger (2014) reported that ambient tropospheric ozone concentrations in the MASP, the production of which is hydrocarbon-limited, decreased by approximately 20% between 2009 and 2011. Those authors suggested that this was attributable to the proportional increase (from 14% to 76%) in flex-fuel vehicles burning gasohol over that same period, which increased nitrogen oxide concentrations. These results are consistent with those of the modeling study conducted by Orlando (2010).

Prompted by stricter government-imposed regulations, the automobile industry has invested in technologies to reduce on-road emissions of pollutants. In 2011, to support the development of public policies aimed at decreasing total emissions, Brazil published its first national mobile-source emissions inventory (MMA, 2011), using emission factor (EF) data obtained from dynamometer tests of new vehicles. However, dynamometer testing is limited by the small numbers of vehicles that can be tested and by test cycles that do not fully represent real-world driving conditions (Dallmann et al., 2013). Therefore, large uncertainties remain in current inventories of on-road vehicle emissions. The rate of aging and deterioration of the EFs are generally underestimated in the calculation of EFs, potentially resulting in an underestimation of total emissions (Gallardo et al., 2012). As fuel composition and vehicle technology continue to evolve, it is important to characterize current on-road emissions of carbonyls, providing baseline data for comparison with those obtained in the future. To measure current carbonyl EFs and to evaluate the chemical composition from on-road vehicles, including vehicles running on gasohol, hydrous ethanol, or diesel/biodiesel blends, two experimental campaigns were performed in the MASP in 2011 (Brito et al., 2013; Pérez-Martínez et al., 2014).

In this study, we provide current carbonyl emission data for LDVs and HDVs powered by gasohol, hydrous ethanol, or a diesel/biodiesel blend in Brazil, compare the on-road emissions data with those reported for other countries, and compare the measured data with official estimated EF data from dynamometer tests of new vehicles in Brazil. In addition, we estimate on-road emissions of total aldehydes (formaldehyde + acetaldehyde) in the MASP, comparing our data with those obtained for other cities in Brazil and in California.

2. Experimental

2.1. Sampling

Carbonyls were sampled on weekdays in two roadway tunnels in the MASP: the Jânio Quadros Tunnel (JQT), which carries LDVs