Atmospheric Pollution Research 5 (2014) 404-410

Atmospheric Pollution Research

www.atmospolres.com

Carbonyl concentrations from sites affected by emission from different fuels and vehicles

Jurandir Pereira Pinto [1], Leila Droprinchinski Martins [2], Carlos Roberto da Silva Junior [1], Fabio Cal Sabino [1], Ismael Rodrigues Amador [1], Maria Cristina Solci [1,3]

[1] *Universidade Estadual de Londrina, Celso Garcia Road, 86051–990, Londrina, Brazil*
[2] *Federal Technological University of Parana – Pioneiros Avenue, 3131, 86036–370, Londrina, Brazil*
[3] *INCT de Energia e Ambiente, UFBA, 40170–290, Salvador, BA, Brazil*

ABSTRACT

Concentrations of carbonyl compounds were evaluated on places impacted by emissions from different fuels and vehicles. In order to evaluate the concentrations, four campaigns during the winter and summer of 2011 and 2012 were performed, inside a covered parking area in a commercial establishment where mainly gasohol and ethanol vehicles are in circulation. Also, measurements were done inside a semi–closed bus station, which is the direct source of emissions from heavy duty vehicles (i.e. buses) burning B3–diesel (3% biodiesel and 97% diesel). The results indicated that acetaldehyde is the main aldehyde emitted by light vehicles due to large use of ethanol in Brazil by these vehicles. In addition, the concentrations found in the bus station revealed that B3–diesel fuel increases the emissions of carbonyl compounds and that of acetaldehyde when compared with results from B0–diesel at same bus station. Possible impacts of changing diesel to B3–diesel indicate an increase of ozone formation. In terms of health, a lower impact was estimated considering only the changes in formaldehyde concentrations.

Keywords: *Carbonyl compounds, fuels, vehicular emissions, ozone formation, health effects*

Corresponding Author:
Leila Droprinchinski Martins
☎ : *+55-43-3315-6100*
🖷 : *+55-43-3315-6121*
✉ : *leilamartins@utfpr.edu.br*

Article History:
Received: 22 October 2013
Revised: 10 February 2014
Accepted: 10 February 2014

doi: 10.5094/APR.2014.047

1. Introduction

Combustion processes generate pollutants in gaseous and particulate phases that have primary and secondary impacts on air quality, human health and climate (e.g. Marley et al., 2009; Gurjar et al., 2010). Emissions from regulated pollutants from vehicles burning traditional fuels are already well established. However, there is a current need for the study of non–regulated emissions and measurement of environmental concentrations of pollutants. Brazil is setting limits for new light and heavy–duty vehicle emissions, which are 2 g km^{-1} for carbon monoxide (CO), 0.02 g km^{-1} for total aldehydes and 0.05 g km^{-1} for non–methane hydrocarbons (NMHCs), nitrogen oxides (NO_X) and suspended particulate matter (PM_{10}). Since 2012, diesel (S50) with low sulfur content (50 ppm) is available in Brazil and, in 2013, diesel (S10–10 ppm of sulfur) is also available (CETESB, 2013).

There are certain emissions (unregulated) that should be considered to ascertain the impact of blended fuels on air quality, such as acetaldehyde, formaldehyde, propionaldehyde, acrolein and fine particulates (Merritt et al., 2005; Bunger et al., 2007). Additionally, unburned ethanol emissions (evaporative and exhaust processes) are important, mainly because it affects the ozone formation by oxidation and is an important secondary source of carbonyl compounds such as acetaldehyde in Brazil (Jacobson, 2007; Martins and Andrade, 2008).

In urban areas, the impact of vehicular emissions on atmosphere depends, among other factors, on the fuel composition and technology used in the construction of the engines (Kumari et al., 2011). Brazil has comprehensive experience with ethanol and ethanol in blends with gasoline, due to a governmental program started in 1975, which encouraged the production and use of ethanol as an alternative fuel. Brazil is the only country in the world where pure hydrated ethanol and a blend of gasoline with ethanol (20–25% mixture of anhydrous ethanol by volume) named gasohol are used throughout the country. Overall, there is growing interest in the use of alternative and "cleaner" energies such as ethanol and other biofuels in order to reduce the dependence on finite reserves of oil and to improve the air quality (Pinto and Solci, 2007).

Studies show that gasohol mix used in gasoline engine reduces HC, CO and NO_X emissions. However, carbonyl compounds can be formed during the use of gasoline and ethanol (Graham et al., 2008; Lopez–Aparicio and Hak, 2013). Research on air pollutant emissions from a gasoline engine showed that emissions of acetaldehyde increase with fuel containing ethanol. Measurements carried out directly from the exhaust of vehicles with gasoline/ ethanol engines showed that emissions of total carbonyl compounds were 3.0 to 61.7% higher than gasoline engines (Anderson, 2009; Yang et al., 2012).

The use of biofuels can interfere in size distribution of emitted particles as well as their chemical composition. There are concerns that the addition of biofuels to petroleum fuel or the use of pure biofuels will change particle size distribution (Zhang et al., 2009; Dutcher et al., 2011).

Carbonyl compounds are directly emitted into the atmosphere by anthropogenic and biogenic sources. The main anthropogenic sources are the combustion processes using fossil fuels and biofuels. Photochemical oxidation of hydrocarbons and other organic compounds is also a secondary important source for these compounds (Guarieiro and Guarieiro, 2013).

Taking into account important concerns of carbonyls on atmospheric chemistry and their negative impact on human health, the level of carbonyls and their diurnal variability can be an effective indicator, reflecting the status of local air pollution. The correlation between major aldehydes emitted by vehicles and fuel composition is an approach to infer the level of pollution of these compounds in sites impacted by these sources, which are still relatively scarce (Pang et al., 2008; Rodrigues et al., 2012).

The toxic effects that are most commonly observed on human health by some carbonyls are irritation of skin, eyes and nasopharyngeal membranes (Wang et al., 2007). Formaldehyde, which is more serious and usually the most abundant carbonyl in the air, is also the one that causes most concern because of its classification as carcinogenic to humans by IARC (IARC, 2006; Swenberg et al., 2013). Epidemiological studies suggest a causal relationship between exposure to formaldehyde and occurrence of nasopharyngeal cancer. McGwin et al. (2010) performed a review concerning the effects of formaldehyde on children's health. The results of that systematic review suggest that there is a positive association between formaldehyde levels and childhood asthma.

There is an annual increase in the number of flex vehicles using ethanol and/or gasohol in Brazil and around the world. Although there are some studies (e.g., Pinto and Solci, 2007; Martins et al., 2012; Lopez–Aparicio and Hak, 2013), there are still a few in the literature dealing with identifying and quantifying the emissions of unregulated pollutants from flex vehicles in real operation.

Similar to tunnels (Chen et al., 2003; Ho et al., 2004) or toll facilities (Sapkota and Buckley, 2003), parking lots and bus station facilities potentially provide a laboratory for evaluating vehicle emissions reflecting real–world conditions because of their closed character and restricted ventilation, lack of sunlight, specific emission sources and meteorological conditions. Parking lots and bus stations are microenvironments where high levels of air pollutants emitted from vehicular sources can occur (Batterman et al., 2006; Kim et al., 2007).

In order to investigate the profile originating from a primary source of light vehicles mainly fueled with flex fuels, carbonyl compounds were collected at a commercial parking lot that was exclusively affected by emissions from light–duty vehicles. In addition, concentration of carbonyl compounds were measured in a bus station exposed to 3% of biodiesel and 97% diesel (referred here as B3–diesel) buses and results are discussed herein. The possible impacts on ozone formation and health were also addressed.

2. Experimental

2.1. Description of the sampling site

The study site was a covered parking lot in a commercial establishment (supermarket) with a capacity of approximately 450 vehicles for light–vehicles located in the western side of Londrina, Brazil. The parking lot was selected due to local characteristics presented: semi–closed place; circulation of vehicles burning ethanol and gasohol, security and facilities to collect the samples. The building is surrounded by two large avenues that can still be external sources of pollutants, and also relatively close to food industries. The location of sampling point inside the parking lot was chosen to minimize the possible external influences.

The parking lot was designed to have one–way traffic. Access is controlled by numbered cards that the conductor receives when entering the parking lot, including a brief stop followed by acceleration. Even under of heavy traffic conditions, vehicles move slowly at free flow (around 20 km h^{-1}) without having to wait in line. The sampling was carried out in a single location 50 meters from the main entrance of the parking lot.

The other site, which is a bus station, is located in Londrina downtown area at 23.308°S and 51.161°W. About 100 000 people travel through this bus station on workdays. The bus station is a two–storey building and the samples were collected on the ground floor. This place is semi–closed with little air circulation and the buses speed is around 20 km h^{-1}. More details about the site are presented in Martins et al. (2012). Figure 1 show the locations of the both sites, the parking lot and the bus station.

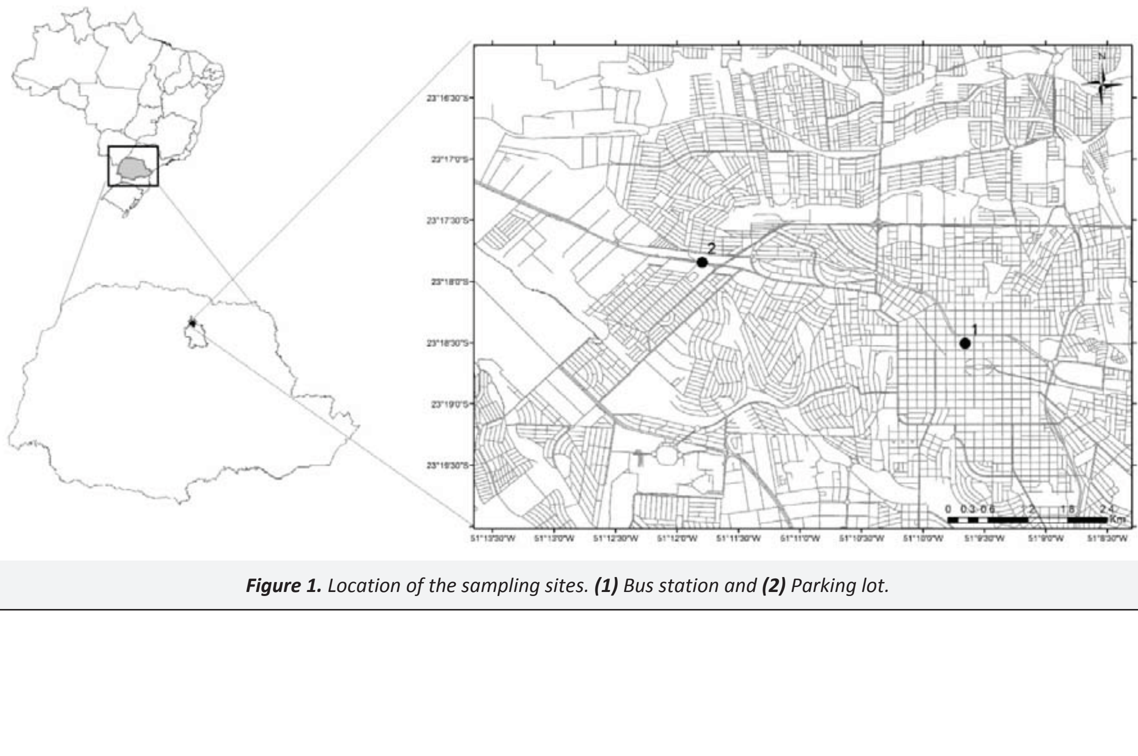

Figure 1. *Location of the sampling sites.* ***(1)*** *Bus station and* ***(2)*** *Parking lot.*