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

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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*

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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.*

2.2. Sampling and analysis procedures

A total of four campaigns were performed at the supermarket parking lot in winter (June) and summer (December), 2011 and 2012. The measurements were conducted continuously for eight to ten days inside the parking lot, especially on the first campaign with intervals of twenty–four hours continually starting at 9 am, and close to entrance. The next three periods of sampling occurred at 12–hour intervals (9 am to 9 pm) inside the parking lot. All samplings were conducted at approximately 1.8 meters from the ground. At the bus station, air samples were collected for 14 consecutive days, on both workdays and weekdays during winter, 2008. The air samples for carbonyl compounds were collected over twenty–four–hour periods starting at 9 am.

For both sites, carbonyl compounds were sampled by using a cartridge (Sep–Pak–C_{18} DNPH–Silica; Waters, Milford, MA, USA) at 60 L h^{-1}. Environmental air was filtered using ozone scrubber filters containing potassium iodide to avoid artifact formation on samples. All cartridges were previously prepared and the preparation procedure, purification of 2,4–DNPH acid, is described in Pinto and Solci (2007).

After sampling, each cartridge was immediately wrapped with PTFE tape and placed into a bag, transported to the laboratory, and the elution of the sample was performed. The hydrazones formed in each cartridge were eluted by using acetonitrile until completion to 2.0 mL and then, stored under refrigeration at 4 °C until analysis. Carbonyl samples were either analyzed immediately after collection or remained under refrigeration for a maximum of one day of storage, until analysis. The samples from the parking lot were analyzed using a High Performance Liquid Chromatography (HPLC) system DIONEX model ULTIMATE 3000, with 20 µL auto–sampling. The hydrazones were separated in the following conditions: a Metasil ODS Metachem column (250x4.6 mm x 5.0 µm); temperature at 35 °C; gradient mobile phase of acetonitrile aqueous solution: 0–7 min at 60%, 7–9 min at 70 %, 9–12 min 90%, and 12–15 min at 60%, mobile flow rate of 1.0 mL min^{-1}. A photodiode array detector was used and set at 365 nm.

Measurements performed in winter 2008 inside the bus station in the same city were analyzed and are presented. The sampling and extraction procedures were the same for both sites, as well as the carbonyls investigated and methodology used to calculate the detection and quantification limits. Carbonyl analyses of the samples from the bus station were performed in Federal University of Bahia using a high–performance liquid chromatography (HPLC) system (Agilent 1100, USA) coupled with a DAD detector set at 365 nm. The analytical conditions were as follows: a C–18 x–Terra MS column (5 µm, 2.1 mm x 250 mm); gradient mobile phase: 0–25 min from 65% to 40% of A phase (deionized water) and from 35% to 60% of B phase (acetonitrile), between 25–30 min, the mobile portion of phase A went to 0%, and at 40 min, the initial conditions of 65% A–phase and 35% B–phase were regenerated, until the end of the running time, which lasted for 47 min. The mobile phase flow rate was 0.25 mL min^{-1} and the injection volume was 10 µL (Rodrigues et al., 2012).

A standard solution containing carbonyl derivatives from formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde butyraldehyde, benzaldehyde, isovaleraldeyde, pentanal, *o*–tolualdehyde, *m*–tolualdehyde, *p*–tolualdehyde, hexanal, 2,5–dimethylbenzaldehyde (TO11/IP–6A, No. 47285–U, Supelco Analytical, USA) was used to identify carbonyls in all samples. Quantification was performed using the external calibration method.

The detection limit (DL) was calculated considering the blanks and $DL=3\sigma_s/a$ where σ_s is the standard deviation and a is the angular coefficient from the analytical curve, adjusted to the sampling time and flow rate used during the collection of samples. For analytes not detected in blank cartridges, DL was considered as $DL=3\sigma_s$, which is the standard deviation of noise baseline in the chromatogram. The quantification limit (QL) was calculated as $QL=10\sigma_s/a$.

The DL and QL from the samples from the parking lot (light–duty vehicles) were 0.36±0.06 µg mL^{-1} and 1.20±0.21 µg mL^{-1} for formaldehyde and 0.81±0.06 µg mL^{-1} and 2.70±0.19 µg mL^{-1} for acetaldehyde. For other carbonyls, DL ranged from 0.05±0.003 µg mL^{-1} to 0.08±0.006 µg mL^{-1} and QL from 0.09±0.02 µg mL^{-1} to 0.24±0.08 µg mL^{-1}. The DL and QL for samples from the bus station (diesel buses) were 0.02 µg mL^{-1} and 0.07 µg mL^{-1} for formaldehyde and 0.01 µg mL^{-1} and 0.02 µg mL^{-1} for acetaldehyde. For other carbonyls, DL ranged from 0.02 µg mL^{-1} to 0.06 µg mL^{-1} and QL from 0.05 µg mL^{-1} to 0.2 µg mL^{-1}.

3. Results and Discussion

Table 1 presents the average carbonyl concentrations from 2011 and 2012 winter and summer inside the parking lot. Formaldehyde and acetaldehyde were the compounds with the highest concentrations in both the parking lot and the bus station, considering the carbonyls analyzed. Formaldehyde and acetaldehyde represent 86.3% and 93.8% of carbonyls analyzed in winter and summer, respectively. The average concentration found for formaldehyde was 4.70 µg m^{-3}, and for acetaldehyde, 10.73 µg m^{-3} in the winter period, and for summer, it was of 9.46 µg m^{-3}, and 33.64 µg m^{-3}, respectively, for formaldehyde and acetaldehyde. The other compounds analyzed, pentanal, *o,m,p*–tolualdehyde, hexaldehyde and 2,5–Dimethylbenzaldehyde, were below the quantification limit.

Table 1. *Carbonyl compounds in winter and summer periods of 2011 and 2012 at parking lot*

Carbonyl Compounds (µg m^{-3})	Winter		Summer	
	Min - Max	Average ± SD[a]	Min - Max	Average ± SD[a]
Formaldehyde	2.36 – 6.80	4.70 ± 1.62	3.59 – 16.01	9.46 ± 4.33
Acetaldehyde	4.91 – 16.77	10.73 ± 4.52	15.23 – 56.35	33.64 ± 13.67
Acetone	0.44 – 2.52	1.46 ± 0.72	1.26 – 3.88	2.84 ± 0.75

[a] *SD: Standard deviation.*

Figure 2 shows daily concentrations of formaldehyde and acetaldehyde for the winter campaigns.

Acetaldehyde concentrations were the highest in all campaigns, which corresponds to 60% and 73.2% of overall compounds analyzed, respectively. The higher carbonyl concentrations on Tuesdays can be attributed to the higher traffic on these sales days. On the average, the lowest carbonyl concentrations were observed on Mondays, and this can be associated with the lower flow of consumers in that weekday. For summer campaigns, daily concentrations of formaldehyde and acetaldehyde are presented in Figure 3.

During the summer campaigns, Tuesdays also presented the highest concentrations of acetaldehyde associated with the increase in the flow of vehicles. Another behavior observed is that on Saturdays and Sundays during the summer campaigns, there was an increase in acetaldehyde as a result of a greater flow of consumers and consequentially vehicles, due to the holiday season in December. In Brazil, sales increase at the end of the year, especially that of foods.

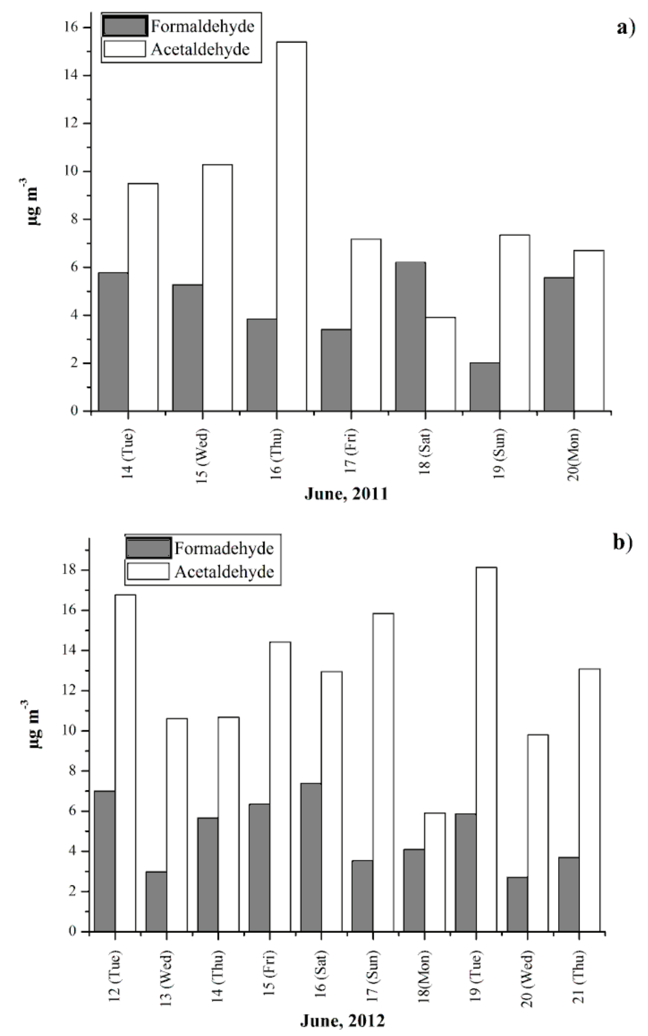

Figure 2. *Formaldehyde and acetaldehyde concentrations in winter campaigns at the parking lot.*

Figure 4 presents the ratio of formaldehyde/acetaldehyde (F/A) for all campaigns performed in the parking lot. The average ratio were 0.65±0.46, 0.35±0.13, 0.40±0.15, and 0.26±0.13, respectively for first, second, third, and fourth campaigns, respectively. As expected, the contribution of acetaldehyde is higher than formaldehyde due to the mixture of fuel burned by light vehicles, which consists of gasohol and ethanol. The mixture of ethanol in gasoline and the possibility of flex–fuel vehicles burning either gasohol or pure ethanol increase the emission and consequently the concentration of acetaldehyde. Saturday on the first campaign showed the highest ratio (F/A), which could be an external influence at that day, because on the first campaign the sampling was performed close to the entrance. However, any different behavior was not observed when compared to other days of the first campaign.

Table 2 shows a comparison of two major aldehydes, formaldehyde and acetaldehyde concentrations measured in the parking lot and the bus station. It is important to note that the parking lot had mainly light–duty vehicles burning gasohol and ethanol and, at the bus station, only buses run in real operation conditions, burning B3–diesel.

As pointed out in some studies (Correa and Arbilla, 2008; Liu et al., 2009; Rodrigues et al., 2012), biodiesel increases the emission of carbonyl compounds. Acetaldehyde presented the highest concentration in both sites, even at the bus station site, where, as expected, higher concentrations of formaldehyde were found, which could be attributed to biodiesel in the diesel. Comparing the F/A ratio in the parking lot and the bus station, similar values of 0.32 (average for all seasons) and 0.27, respectively, were found, meaning that for both types of fuels and vehicles, the emission of acetaldehyde is more pronounced. Concentration magnitudes found of F+A were similar for light and heavy vehicles on winter, but at the bus station (B3–diesel), the concentration of other carbonyls (acetone, *m+p*–tolualdehyde, etc.) was higher with a significant contribution to total carbonyl compounds measured.

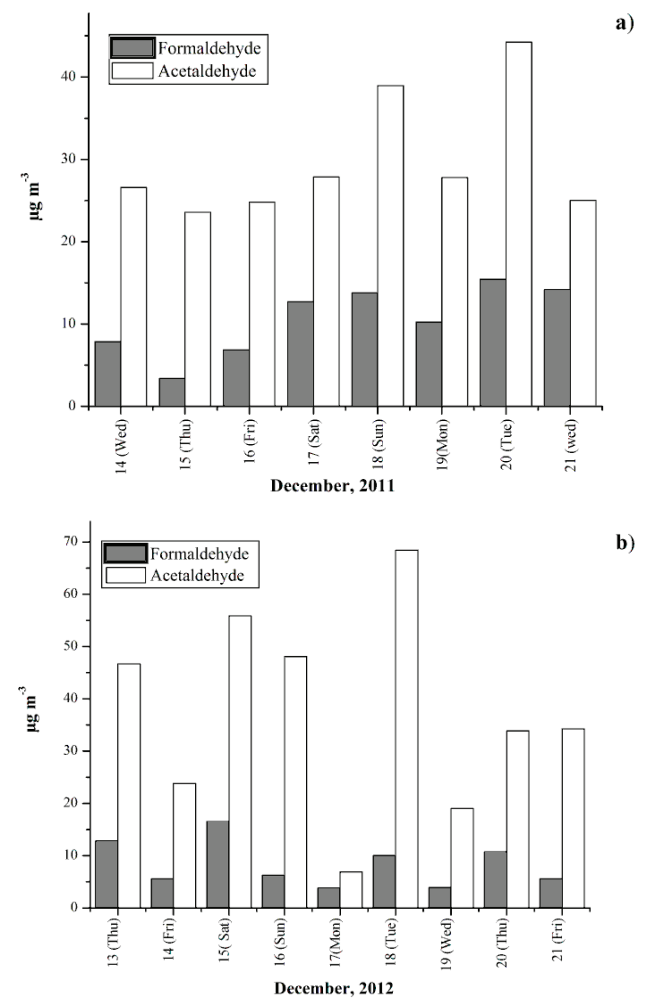

Figure 3. *Formaldehyde and acetaldehyde concentrations in summer campaigns at the parking lot.*

Analyzing the results obtained by Liu et al. (2009), who performed carbonyl measurements of different biodiesel blends, the F/A ratio for B10–diesel (33% engine load) is 0.26 and for B0–diesel (diesel without biodiesel), 1.38 (10% engine load). In addition, in a study performed by Pinto and Solci (2007) at the same bus station in 2002, when Brazil had only B0–diesel, the F/A ratio found in summer was 6.3, with an average of 9.2 µg m^{-3} for F+A. On the other hand, this study found an average of 14.59 µg m^{-3} when B3–diesel was used. Therefore, biodiesel increases the emissions of aldehydes and acetaldehyde.

In order to infer about possible consequences in change of fuel on human health and atmospheric chemistry associated with the change in emissions of formaldehyde and acetaldehyde, the ozone formation potential was calculated for the concentrations of two major aldehydes measured. Additionally, the variation of mortality for both scenarios B0–diesel and B3–diesel was considered.

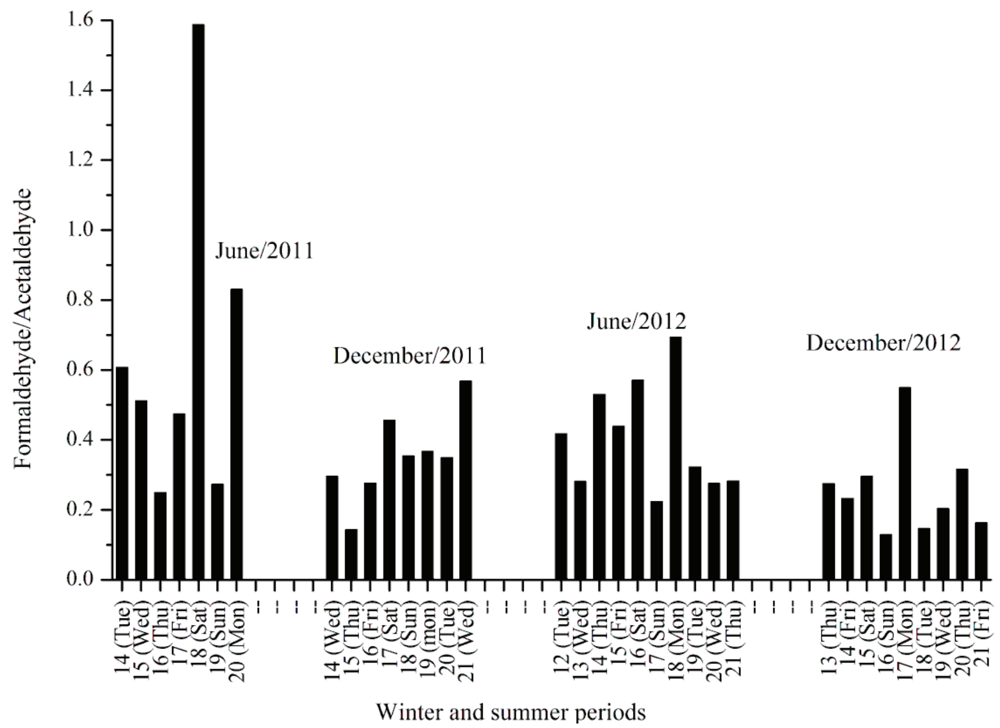

Figure 4. *Formaldehyde/Acetaldehyde ratios for winter and summer campaigns at the parking lot.*

Table 2. *Comparison of two major aldehydes, formaldehyde and acetaldehyde concentrations measured in the parking lot and the bus station*

Carbonyl Compounds ($\mu g\ m^{-3}$)	Parking Lot – Light Vehicles (Gasohol/Ethanol)		Bus Station – Heavy Vehicles (B3–diesel)
	Winter Average	Summer Average	Winter Average
Formaldehyde	4.70±1.62	9.46±4.33	3.14±0.55
Acetaldehyde	10.73±4.52	33.64±13.67	11.45±2.59
Formaldehyde+Acetaldehyde	15.43	43.10	14.59
Formaldehyde/Acetaldehyde	0.44	0.28	0.27
Others carbonyls	2.45±1.21	2.84±0.75	12.48±5.02

Table 3 shows ozone formation potentials for formaldehyde and acetaldehyde measured at the parking lot impacted by light vehicles burning gasohol and ethanol. Maximum Incremental Reactivity (MIR) scale proposed by Carter was used to estimate the individual contribution of volatile organic compounds in ozone production. The updated ozone reactivity MIR scale was used in this application (Carter, 1994; Carter, 2009).

Considering that the concentrations of major carbonyls were measured in summer from light vehicles (gasohol and ethanol), when comparing with other fuels and vehicles, the formation of ozone in terms of MIR was also the highest. By analyzing MIR for all fuels and vehicles, it was observed that B3–diesel increases MIR when compared to B0–diesel. Additionally, the MIR–F/MIR–A ratio is 0.63 and 0.41 for light vehicles in winter and summer, respectively. For heavy vehicles (buses), MIR–F/MIR–A ratio is 0.40 and 9.18. Therefore, considering the carbonyls measured, B3–diesel contributes more towards ozone formation than B0–diesel.

The odds ratio (*OR*) obtained from McGwin et al. (2010) for asthma in children and those obtained by Zhai et al. (2013) for adults and children in an indoor study were used to evaluate the potential health impact considering the change in formaldehyde concentrations in B0–diesel and B3–diesel scenarios. The *OR* values applied were 1.17 (95% CI – random effects model) for mortality by asthma in children, 2.603 for adults, and 4.250 for children for general respiratory diseases (morbidity). An equation adapted from Fang et al. (2013) was used to indicate a positive or negative contribution for mortality and morbidity due to formaldehyde concentration changes in B0–diesel and B3–diesel (Δ_{mor}) scenarios. The equation is $\Delta_{mor}=(1-e^{-OR \times \Delta x})$, where Δ_x is the variation of formaldehyde concentration in B0–diesel and B3–diesel, and *OR* is the odds ratio, which is a measure of the association between an exposure and an outcome (McGwin et al. 2010; Zhai et al. 2013).

The Δ_{mor} is expressed as negative or positive contribution considering B0–diesel and B3–diesel scenarios are presented in Table 4 for asthma and general respiratory diseases for children and adults. Negative Δ_{mor} means a decrease in morbidity or mortality and a positive Δ_{mor} means an increase in mortality or morbidity. Δ_{mor} multiplied by population number and mortality/ morbidity rate results in the estimated change in premature mortalities or morbidities associated with changes in formaldehyde concentrations in B0–diesel to B3–diesel or vice–versa.

Considering the changes in formaldehyde concentrations measured from B0–diesel and B3–diesel fuel, and the approach used to estimate the possible contributions of the change, a negative contribution was found in children mortality by asthma, all respiratory diseases in children and adults associate with the reduction of formaldehyde concentration in B3–diesel scenario. On the other hand, if B3–diesel was replaced by B0–diesel, a positive contribution is found, which means an increase in respiratory morbidity and mortality.

Table 3. *Ozone formation potentials for formaldehyde and acetaldehyde for different fuels and vehicles*

Compounds	MIR Scale, Ozone Formation Potential (μg O_3 m^{-3})			
	Light Vehicles (Gasohol/Ethanol) Winter	Light Vehicles (Gasohol/Ethanol) Summer	Heavy Vehicles (B3–diesel) Winter	Heavy Vehicles (B0–diesel) [a] Summer
Formaldehyde	44.46	89.49	29.01	73.37
Acetaldehyde	70.17	220.01	72.60	7.99
F+A	146.63	309.50	101.61	81.36

[a] *Pinto and Solci (2007)*

Table 4. *Positive or negative contribution for mortality and morbidity associated with changes in formaldehyde concentrations*

Disease/Age	Δ_{mor} (B0–diesel to B3–diesel)	Δ_{mor} (B3–diesel to B0–diesel)
Asthma/children (mortality, random–effects)	Negative	Positive
Respiratory/children (morbidity)	Negative	Positive
Respiratory/adults (morbidity)	Negative	Positive

Studies concerning acetaldehyde human effects are scarce and it is considered a probable human carcinogen (group B2). Based on results from modeling studies, Environmental Protection Agency estimated that breathing air containing 5.0 μg m^{-3} would result in not greater than a one–in–a–hundred thousand increased probability of developing cancer (U.S. EPA, 2013). Based on tests, Liu et al. (2009) found a severe acute toxicity and cytotoxicity for B10–diesel, indicating that the gaseous emissions from the biodiesel blend had more adverse health effects than those from diesel.

4. Conclusions

Formaldehyde and acetaldehyde presented the highest concentrations from both light and heavy vehicles in real operation conditions burning gasohol, ethanol and B3–diesel. Acetaldehyde concentrations were the highest in all campaigns, corresponding to 60.0%, 73.2% and 42.3% of overall carbonyl compounds analyzed in the parking lot (winter and summer) and bus station, respectively. Biodiesel increases the emissions of aldehydes and acetaldehyde. The possible impacts of this change in terms of ozone formation indicate a negative effect of the change from B0–diesel to B3–diesel. In terms of health, considering only changes in formaldehyde, a beneficial effect was found. However, the increase in other carbonyls by B3–diesel was not estimated and should be considered in future works.

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References

Anderson, L.G., 2009. Ethanol fuel use in Brazil: Air quality impacts. *Energy & Environmental Science* 2, 1015–1037.

Batterman, S., Hatzivasilis, G., Jia, C., 2006. Concentrations and emissions of gasoline and other vapors from residential vehicle garages. *Atmospheric Environment* 40, 1828–1844.

Bunger, J., Krahl, J., Munack, A., Ruschel, Y., Schroder, O., Emmert, B., Westphal, G., Muller, M., Hallier, E., Bruning, T., 2007. Strong mutagenic effects of diesel engine emissions using vegetable oil as fuel. *Archives of Toxicology* 81, 599–603.

Carter, W.P.L., 2009. Updated Maximum Incremental Reactivity Scale and Hydrocarbon Bin Reactivities for Regulatory Applications, California Air Resources Board Contract 07–339, California, 61 pages.

Carter, W.P.L., 1994. Development of ozone reactivity scales for volatile organic compounds. *Journal of the Air & Waste Management Association* 44, 881–899.

CETESB (Environmental Protection Agency), 2013. Qualidade do ar no Estado de Sao Paulo 2012, http://www.cetesb.sp.gov.br/ar/qualidade–do–ar/31–publicacoes–e–relatorios, accessed in February 2014 (in Portuguese).

Chen, K.S., Lai, C.H., Ho, Y.T., 2003. Source profiles and ozone formation potentials of volatile organic compounds in three traffic tunnels in Kaohsiung, Taiwan. *Journal of the Air & Waste Management Association* 53, 102–112.

Correa, S.M., Arbilla, G., 2008. Carbonyl emissions in diesel and biodiesel exhaust. *Atmospheric Environment* 42, 769–775.

Dutcher, D.D., Stolzenburg, M.R., Thompson, S.L., Medrano, J.M., Gross, D.S., Kittelson, D.B., McMurry, P.H., 2011. Emissions from ethanol–gasoline blends: A single particle perspective. *Atmosphere* 2, 182–200.

Fang, Y., Mauzerall, D., Liu, J., Fiore, A., Horowitz, L., 2013. Impacts of 21st century climate change on global air pollution–related premature mortality. *Climatic Change* 121, 239–253.

Graham, L.A., Belisle, S.L., Baas, C.–L., 2008. Emissions from light duty gasoline vehicles operating on low blend ethanol gasoline and E85. *Atmospheric Environment* 42, 4498–4516.

Guarieiro, L.L.N., Guarieiro, A.L.N., 2013. Vehicle emissions: What will change with use of biofuel, in *Biofuels – Economy, Environment and Sustainability*, edited by Fang, Z., pp. 359–386.

Gurjar, B.R., Jain, A., Sharma, A., Agarwal, A., Gupta, P., Nagpure, A.S., Lelieveld, J., 2010. Human health risks in megacities due to air pollution. *Atmospheric Environment* 44, 4606–4613.

Ho, K.F., Lee, S.C., Guo, H., Tsai, W.Y., 2004. Seasonal and diurnal variations of volatile organic compounds (VOCs) in the atmosphere of Hong Kong. *Science of the Total Environment* 322, 155–166.

IARC (International Agency for Research on Cancer), 2006. Formaldehyde, 2-Butoxyethanol and 1-tert-Butoxypropan-2-ol. *IARC Monographs on the Evaluation of Carcinogenic Risks to Human* 88, 1-287.

Jacobson, M.Z., 2007. Effects of ethanol (E85) versus gasoline vehicles on cancer and mortality in the United States. *Environmental Science & Technology* 41, 4150–4157.

Kim, S.R., Dominici, F., Buckley, T.J., 2007. Concentrations of vehicle–related air pollutants in an urban parking garage. *Environmental Research* 105, 291–299.

Kumari, R., Attri, A.K., Gurjar, B.R., 2011. Impact of CNG on emissions of PAHs and PCDDs/Fs from the road transport in Delhi. *Atmospheric Pollution Research* 2, 394–399.

Liu, Y.–Y., Lin, T.–C., Wang, Y.–J., Ho, W.–L., 2009. Carbonyl compounds and toxicity assessments of emissions from a diesel engine running on biodiesels. *Journal of the Air & Waste Management Association* 59, 163–171.

Lopez–Aparicio, S., Hak, C., 2013. Evaluation of the use of bioethanol fuelled buses based on ambient air pollution screening and on–road measurements. *Science of the Total Environment* 452–453, 40–49.

Marley, N.A., Gaffney, J.S., Tackett, M., Sturchio, N.C., Heraty, L., Martinez, N., Hardy, K.D., Marchany–Rivera, A., Guilderson, T., MacMillan, A., Steelman, K., 2009. The impact of biogenic carbon sources on aerosol absorption in Mexico City. *Atmospheric Chemistry and Physics* 9, 1537–1549.

Martins, L.D., Andrade, M.F., 2008. Emission scenario assessment of gasohol reformulation proposals and ethanol use in the metropolitan area of Sao Paulo. *The Open Atmospheric Science Journal* 2, 166–175.

Martins, L.D., da Silva Junior, C.R., Solci, M.C., Pinto, J.P., Souza, D.Z., Vasconcellos, P., Guarieiro, A.L., Guarieiro, L.L., Sousa, E.T., de Andrade, J.B., 2012. Particle emission from heavy–duty engine fuelled with blended diesel and biodiesel. *Environmental Monitoring and Assessment* 184, 2663–2676.

Mc Gwin, G., Lienert, J., Kennedy, J.I., 2010. Formaldehyde exposure and asthma in children: A systematic review. *Environmental Health Perspectives* 118, 313–317.

Merritt, P.M., Ulmet, V., McCormick, R.L., Mitchell, W.E., Baumgard, K.J., 2005. Regulated and Unregulated Exhaust Emissions Comparison for Three Tier II Non–Road Diesel Engines Operating on Ethanol–Diesel Blends, SAE Technical Paper 2005–01–2193, Rio de Janiero, Brazil, 12 pages.

Pang, X., Mu, Y., Yuan, J., He, H., 2008. Carbonyls emission from ethanol–blended gasoline and biodiesel–ethanol–diesel used in engines. *Atmospheric Environment* 42, 1349–1358.

Pinto, J.P., Solci, M.C., 2007. Comparison of rural and urban atmospheric aldehydes in Londrina, Brazil. *Journal of the Brazilian Chemical Society* 18, 928–936.

Rodrigues, M.C., Guarieiro, L.L.N., Cardoso, M.P., Carvalho, L.S., da Rocha, G.O., de Andrade, J.B., 2012. Acetaldehyde and formaldehyde concentrations from sites impacted by heavy–duty diesel vehicles and their correlation with the fuel composition: Diesel and diesel/biodiesel blends. *Fuel* 92, 258–263.

Sapkota, A., Buckley, T.J., 2003. The mobile source effect on curbside 1,3–butadiene, benzene, and particle–bound polycyclic aromatic hydrocarbons assessed at a tollbooth. *Journal of the Air & Waste Management Association* 53, 740–748.

Swenberg, J.A., Moeller, B.C., Lu, K., Rager, J.E., Fry, R.C., Starr, T.B., 2013. Formaldehyde carcinogenicity research: 30 years and counting for mode of action, epidemiology, and cancer risk assessment. *Toxicologic Pathology* 41, 181–189.

U.S. EPA (U.S. Environmental Protection Agency), 2013. Acetaldehyde, http://www.epa.gov/ttnatw01/hlthef/acetalde.html, accessed in December 2013.

Wang, B., Lee, S.C., Ho, K.F., 2007. Characteristics of carbonyls: Concentrations and source strengths for indoor and outdoor residential microenvironments in China. *Atmospheric Environment* 41, 2851–2861.

Yang, H.H., Liu, T.C., Chang, C.F., Lee, E., 2012. Effects of ethanol–blended gasoline on emissions of regulated air pollutants and carbonyls from motorcycles. *Applied Energy* 89, 281–286.

Zhai, L., Zhao, J., Xu, B., Deng, Y., Xu, Z., 2013. Influence of indoor formaldehyde pollution on respiratory system health in the urban area of Shenyang, China. *African Health Sciences* 13, 137–143.

Zhang, X.S., Zhao, H., Hu, Z.J., Wu, Z.J., Li, L.G., 2009. Effect of biodiesel on the particle size distribution in the exhaust of common–rail diesel engine and the mechanism of nanoparticle formation. *Science in China Series E–Technological Sciences* 52, 2773–2778.