

## Acetaldehyde and formaldehyde concentrations from sites impacted by heavy-duty diesel vehicles and their correlation with the fuel composition: Diesel and diesel/biodiesel blends

Marina C. Rodrigues<sup>a,c</sup>, Lílian L.N. Guarieiro<sup>a,c,d</sup>, Manuela P. Cardoso<sup>a,c</sup>, Luiz Souza Carvalho<sup>a</sup>, Gisele O. da Rocha<sup>a,b,c</sup>, Jailson B. de Andrade<sup>a,b,c,\*</sup>

<sup>a</sup> Universidade Federal da Bahia (UFBA), Instituto de Química, 40170-115, Salvador, BA, Brazil

<sup>b</sup> Centro Interdisciplinar de Energia e Ambiente – CIEnAm, UFBA, 40170-115 Salvador, BA, Brazil

<sup>c</sup> INCT de Energia e Ambiente, UFBA, 40170-115 Salvador, BA, Brazil

<sup>d</sup> SENAI-CIMATEC, 41650-010 Salvador, BA, Brazil

### ARTICLE INFO

#### Article history:

Received 5 April 2011

Received in revised form 7 July 2011

Accepted 14 July 2011

Available online 31 July 2011

#### Keywords:

Carbonyl compounds

Vehicular exhaust

Diesel

Biodiesel

Diesel engine

### ABSTRACT

The increasing of both industrialization and motorization of the world has led to a sharp rise in the demand for fossil fuels. Concern about the environmental impact caused by burning of these fuels has involved researchers that became engaged in assessing the damages of pollution not only to environment, but also to human health. In this study, carbonyl compounds (CC) were measured in vapor samples from a place impacted by heavy-duty vehicles (Bus Station) fuelled with diesel/biodiesel fuel blend (B5) in Salvador, Brazil. Among them, formaldehyde, acetaldehyde and propanone were the most abundant quantified compounds. Concentration levels (ppbV) for major CC detected during the sampling period ranged from 28.45 to 287.3 (formaldehyde), 24.91 to 171.3 (acetaldehyde) and 5.835 to 72.29 (propanone). The obtained data in this site was compared to formaldehyde and acetaldehyde concentrations found in other sites impacted by heavy-duty vehicles fuelled with pure diesel and diesel/biodiesel blends. All data were used to make a possible correlation with formaldehyde/acetaldehyde ratio and the relationship with the kind of fuel used by these vehicles. PCA was used to verify possible grouping among 19 sites impacted by heavy-duty vehicles and showed two major groups, one characterized by being strongly impacted and the other with a low contribution of heavy-duty vehicles. Thus, the addition of higher concentrations of biodiesel to diesel showed an improvement in the carbonyl concentration profile at places with high circulation of heavy-duty vehicles, which had similar profile to those found for sites less impacted by these kind of vehicles.

Published by Elsevier Ltd. Open access under the [Elsevier OA license](#).

### 1. Introduction

Carbonyl compounds (CC) are ubiquitous components in the atmosphere, which have received great attention due to their potential adverse health effects on humans and to their important role in atmospheric chemistry. Carbonyls are emitted either directly from incomplete combustion of fossil fuel such as exhausts of motor vehicles and biomass burning or formed indirectly by atmospheric photo-oxidation of volatile organic compounds (VOCs) emitted from anthropic and/or natural sources [1,2]. The spontaneous burning of forests is the main natural source of carbonyls, with the issuance of aliphatic, aromatic, cyclic aldehydes as well as others compounds [3]. However, natural sources contribute to atmo-

spheric concentrations of several carbonyls through biogenic emissions of some plants [4] and photochemical oxidation of naturally emitted hydrocarbon precursors [1]. Among anthropogenic sources, it includes industrial processes, waste incineration, wood, fuel, and forest burnings. Burning of fossil fuels has become the main source of carbonyls in urban areas, but these emissions depend on the kind of fuel used, the use of catalysts and the traffic conditions [5–7].

Several studies have been conducted using either biomass and vegetable oils by themselves or added to fossil diesel in order to assess them as possible partial and/or total substitutes to pure diesel as combustibles. Indeed, using of biodiesel has traditionally been motivated by factors such as their enhancing effect on the fuel's cetane number, its capacity to reduce both exhaust emissions of some pollutants and the dependence on imported oil as well as supporting of agricultural subsidies in certain regions [8]. In comparison, biodiesel can produce 4.5 units of energy against every unit of fossil energy needed to produce biodiesel [9]. However, there

\* Corresponding author at: Instituto de Química, Universidade Federal da Bahia, Campus Universitário de Ondina, 40170-115 Salvador, Bahia, Brazil. Tel./fax: +55 71 3283 6821.

E-mail address: [jailsong@ufba.br](mailto:jailsong@ufba.br) (J.B. de Andrade).

are some technical problems associated with the use of biodiesel fuels. Burning of them has shown an increase in nitrogen oxide (NO<sub>x</sub>) exhaust emissions (which has strict environmental regulations), relatively poor low temperature and flow properties compared to diesel [10,11], and low oxidation stability of biodiesel [12]. Despite these challenges, the addition of biodiesel in diesel fuel is already established in many countries such as Brazil, where it has been regulated the use of 5% biodiesel added to diesel (B5).

Taking into account important concerns of CC for atmospheric chemistry and their negative impact on human health, the levels of carbonyls and their diurnal variability, can be an effective indicator reflecting the status of local air pollution. Studies on CC in Brazilian atmosphere and other part of the world have rarely been reported [3,13,14]. In this sense, correlations between major aldehydes emitted by heavy-duty vehicles and the level of pollution of these compounds in sites impacted by this source are still relatively scarce.

The most observed toxic effects to human health of some CC are irritation of skin, of eyes and nasopharyngeal membranes [15]. More seriously, formaldehyde, which is usually the most abundant carbonyl in the air, is also the one of more concern because it is classified as carcinogenic to humans by the International Agency for Research on Cancer (IARC) [16]. Epidemiological studies suggest a causal relationship between exposure to formaldehyde and occurrence of nasopharyngeal cancer, although this conclusion is based in a small number of observed and expected cases in the studies [16].

The aim of this study was to measure CC in vapor samples from a site impacted by heavy-duty vehicles (Bus Station) fuelled with diesel/biodiesel fuel blend (B5) in Salvador, Brazil. The obtained data in this site was compared to formaldehyde and acetaldehyde concentrations found in other sites impacted by heavy-duty vehicles fuelled with pure diesel and diesel/biodiesel blends. All found data were used to make a possible correlation between formaldehyde/acetaldehyde ratio and the kind of fuel used (diesel or diesel/biodiesel blends) by heavy-duty vehicles.

## 2. Experimental

### 2.1. Description of sampling site

Sampling site of this study was Lapa bus station (12°58'59.54" S, 38°30'39.25" W, altitude 52 m above sea level), the largest bus terminal in Salvador city, Brazil. The bus station was inaugurated in 1982 and currently receives more than seventy urban lines of buses, being part of the daily routine of about 460,000 passengers. The station consists of an underground floor, a ground floor and a top floor, where they run shops, cafes and local administration, with a total area of 150,000 m<sup>2</sup>. Nowadays, the predominant traffic is diesel/biodiesel (95/5% v/v – B5) fueled buses. The bus station can raise about 330 buses circulating per hour on weekdays.

The sampling site selection took into account the place where the buses came and went frequently and there were many passengers waiting for it. The underground floor of the bus station was chosen as the monitoring site among the three floors because it does not have an appropriate air exhaust system, and it is partially closed with no wind circulation and no sunlight. Observing these characteristics, we interpret that photochemical reactions were not such a relevant source of CC for the site and it is therefore not taken into consideration in this study.

### 2.2. Carbonyl sampling and analysis at Lapa bus station

In the present study, samples were collected in Lapa bus station in one week from May 6th to May 12th, 2010. The sampling system was set at 1.7 m above the ground level in the underground floor on the side where the buses were going through a way. Vapor

phase carbonyl samples were collected by drawing the air with a sampling pump at a flow rate of 0.2 L min<sup>-1</sup> through a C18 coated-cartridge Sep-Pak Silica Gel Cartridge (Waters-Millipore, USA) impregnated with acid solution of 2,4-dinitrophenylhydrazine (2,4-DNPH). A detailed account of preparation, purification of the acid 2,4-DNPH solution and sampling procedure is described elsewhere [17]. At each sampling time a cellulose filter impregnated with 5% potassium iodide (KI) solution was upstream connected to two-coated cartridges in series in order to prevent the interference of ozone. The samples were collected for 15 min each time during morning (7 am), afternoon (1 pm) and evening (7 pm) time (Salvador time, GMT – 3 h). The whole sampling campaign had 42 carbonyls real samples with 10 field blanks.

After sampling, each cartridge was immediately wrapped with PTFE tapes, resealed in a Teflon bag and transported back to the laboratory. The hydrazones formed by reaction between carbonyls and DNPH were slowly eluted from the sampled cartridges with 5 mL of acetonitrile into amber bottles and stored under refrigeration at 4 °C until analysis. The CC samples were either analyzed immediately after collection or remained under refrigeration at maximum of one day of storage, until analysis.

The carbonyl extracts were separated and quantified by using a High Performance Liquid Chromatograph (HPLC) system (Agilent 1100, USA) coupled with a DAD detector set to 365 nm. The analytical conditions were as follows: a C-18 x-Terra MS column (5 mm, 2.1 mm × 250 mm); gradient mobile phase: 0–25 min from 65% to 40% of A phase (deionised water) and from 35% to 60% of B phase (acetonitrile), 25–30 min the proportion of mobile A phase went to 0%, and at 40 min, the initial conditions of 65% of A phase and 35% of B phase were regenerated, until the end of the running time, which lasted for 47 min. Mobile phase flow rate was 0.250 mL min<sup>-1</sup> and the injection volume was 10 µL.

Authentic standard solution containing carbonyl derivatives of formaldehyde, acetaldehyde, propanone, propanaldehyde, crotonaldehyde and benzaldehyde hydrazones (TO11/IP-6A Aldehyde/Ketone-DNPH Mix, Supelco<sup>®</sup> Analytical, USA) was used to identify carbonyls in all samples. The quantification of the identified compounds was carried out by using analytical curves made from seven levels of external standard concentrations, ranging from 5 to 250 µg L<sup>-1</sup>, for each carbonyl. The limit of detection (LOD) was considered as 3  $\times$  (s/a), where "s" is the standard deviation of linear coefficient from analytical curve and "a" is the angular coefficient from analytical curve, adjusted to the sampling time and flow rate used during collection of samples. The LOD were (ppbV): 1.49 (formaldehyde), 3.65 (acetaldehyde), 1.66 (acetone), 6.19 (propanaldehyde), 4.53 (crotonaldehyde), 2.43 (benzaldehyde).

### 2.3. CC data and their correlation with other sites

The CC data collection from other possible sites polluted by heavy-duty vehicles was done through a search of studies that had available CC concentration data, specifically formaldehyde and acetaldehyde concentrations. The selected sites for CC data collection were: bus stations, urban sites, tunnel and roadside; it was also carried out a search for CC concentration data from stationary diesel engine experiments using pure diesel and fuel blends of diesel/biodiesel. To enhance the interpretation of the obtained data was used the technique of Principal Components Analysis (PCA). The evaluated variables were formaldehyde and acetaldehyde concentration and the formaldehyde/acetaldehyde ratio (C1/C2) for different sites.

## 3. Results and discussion

In this study, six CC were measured/identified in the vapor phase in the atmosphere of Lapa bus station, namely formaldehyde,

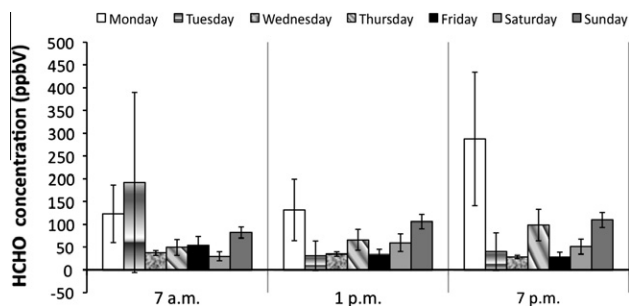
acetaldehyde, propanone, propanaldehyde, crotonaldehyde and benzaldehyde (Table 1). Among them, formaldehyde, acetaldehyde and propanone were the most abundant quantified compounds. The concentration (ppbV) of the major CC detected during the sampling period ranged from 28.45 to 287.3 (formaldehyde), 24.91 to 171.3 (acetaldehyde) and 5.835 to 72.29 (propanone). However, propanone was only quantified from Tuesday to Thursday (May 11th to 12th, 2010). The mean concentrations (ppbV) of the major CC detected during the sampling period were 79.8, 82.2 and 38.8 for formaldehyde, acetaldehyde and propanone, respectively.

During sampling, bus emissions were the main source of CC, since buses fuelled with B5 were the only vehicles passing throughout the Lapa bus station. Thus, the Figs. 1 and 2 show formaldehyde and acetaldehyde concentrations, respectively, obtained during one week in the Lapa station. In general, it was observed that formaldehyde emission was more significant on Monday. The error bars in both figures represent the relative standard deviation (RSD) of the CC emissions obtained in the three selected sampling times, for each day. The RSD (%) for formaldehyde and acetaldehyde ranged from 13.14 to 102.8 and 7.342 to 101.8, respectively. In this manner, it could be noted that there is a large

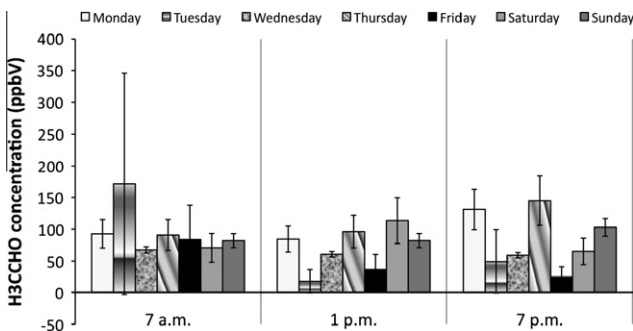
**Table 1**  
Average concentrations (ppbV) of carbonyl compounds in Lapa bus station.

Compounds	Morning	Afternoon	Evening	RSD <sup>a</sup>	Range
Formaldehyde	81.1	66.1	92.0	16	66.1–92.0
Acetaldehyde	94.1	70.2	82.3	14	70.2–94.1
Propanone	21.3	38.4	63.8	52	21.3–63.8
Propanaldehyde	3.51	12.9	11.1	54	3.5–12.9
Crotonaldehyde	–	0.97	1.23	15	0.97–1.23
Benzaldehyde	2.77	4.99	1.83	0.51	1.83–4.99

<sup>a</sup> RSD – Relative standard deviation (%).



**Fig. 1.** Formaldehyde concentrations obtained for each sampling day (6–12th May 2010), error bars are the relative standard deviation – RSD.



**Fig. 2.** Acetaldehyde concentrations obtained for each sampling day (6–12th May 2010), error bars are the relative standard deviation – RSD.

**Table 2**

Carbonyl compounds concentrations (ppbV) in two different periods at Lapa bus station.

Compounds	Formaldehyde			Acetaldehyde		
	Av. <sup>b</sup>	Min. <sup>c</sup>	Max. <sup>d</sup>	Av.	Min.	Max.
1997 [12]	52	31	76	12	9	16
2010 <sup>a</sup>	79.8	28.5	287.3	82.2	24.9	171.3
2010 <sup>a</sup> /1997 ratio	1.53	0.92	3.78	6.89	2.83	10.70

<sup>a</sup> This study.

<sup>b</sup> Av. = average.

<sup>c</sup> Min. = minimum.

<sup>d</sup> Max. = maximum.

variation of formaldehyde emission during both days on Monday and on Tuesday (Fig. 1), and a large variation on acetaldehyde emission on Tuesday. It probably could occur due to the fact that these weekdays are the beginning of the working time and consequently it could cause a higher rate of buses and people circulating at Lapa station. Among other weekdays, it was observed lower RSD, thus the formaldehyde and acetaldehyde emission concentrations all day long could be considered less variable.

In 1997, de Andrade et al. [13] reported data of formaldehyde and acetaldehyde concentrations from Lapa bus station. Higher concentrations of these aldehydes were observed in this present study compared to the results of de Andrade et al. [13], 13 years ago (Table 2). The average formaldehyde and acetaldehyde concentrations increased approximately 1.5 and 7 times, respectively, between the two sampling periods can be explained by the increase of the vehicle fleet currently circulating in Lapa bus station. In 1997, the vehicle fleet at Lapa bus station was 150 buses per hour; while in 2010 were over 330 buses per hour. In this manner, an increase of twice in vehicle fleet circulating in Lapa station, can reflect a raise of both formaldehyde and acetaldehyde emission concentrations in that site. Other possible factor that could cause a raise of CC concentration in this site is the change of fuel used in vehicles. In 1997, the buses were fuelled with pure diesel and nowadays they are fuelled with B5 fuel blend.

In recent years, many studies have been conducted about the CC emitted from diesel engines in the burning of diesel and diesel/biodiesel blends. Several researchers have also evaluated the concentration of these compounds in the urban atmosphere and their relationship with the formation of secondary compounds, mainly ozone. These studies have concluded that the addition of biodiesel to diesel increases the total CC emission and among them, acetaldehyde is the compound emitted in higher concentration, but the increase of biodiesel percentage added to diesel fuel can cause a greater rise in formaldehyde emission than acetaldehyde emissions [5,18–20]. Also, some characteristics as the quality of biodiesel regarding the fatty acid profile and purity level play a role on certain carbonyl emissions [21].

In 2005, the Brazilian government has established the addition of 2% biodiesel to diesel (B2), in 2008 it was raised to 3% (B3), in 2009 it was again increased to 4% (B4), and finally today the 5% of biodiesel added to diesel (B5) is compulsory. Furthermore, a study about CC concentration performed in Brazil (in the downtown of Rio de Janeiro city, site also strongly impacted by heavy-duty vehicles), for the period of 2004–2009, concluded that there was a higher reduction of formaldehyde than acetaldehyde concentration in that site, where the 2004/2009 concentration ratios were 2.77 (formaldehyde) and 1.30 (acetaldehyde) [22]. However, for this period in Brazil, together to incorporation of diesel/biodiesel blend, there was an increase of vehicles fuelled with ethanol, which also can cause an increase in CC emissions. In this scenario, one can conclude that the increase in the CC emission with the

addition of biodiesel to diesel can reflect in a “false positive” of CC atmospheric concentrations from diesel engines, since studies point to the fact that reduction of formaldehyde and acetaldehyde levels still are of concern for ozone formation.

Recently, Guarieiro et al. [5] evaluated CC directly emitted from diesel engines using pure diesel fuel and diesel/biodiesel blends in different ratios (Table 3). The results showed a relationship between formaldehyde/acetaldehyde (C1/C2) ratio of 0.24 for diesel fuel, 0.33 for diesel/biodiesel (B5) and 0.45 for pure biodiesel, e.g. acetaldehyde emission concentration was considerably higher than formaldehyde and the addition of biodiesel to diesel can bring an increase in this ratio, when compared to that found by de Andrade et al. [13]. However, when we analyze the concentration of formaldehyde and acetaldehyde in different environments, which have contribution of many sources, mainly those impacted by vehicular emissions, the C1/C2 ratios can be different and it will directly depend of kind of pollutant sources.

In order to improve the discussion about formaldehyde and acetaldehyde concentration from heavy-duty vehicles and their

relationship with kind of fuel used by these vehicles a study was done using data of different sites impacted by these vehicles. It was observed significant differences of C1/C2 ratio in sites hardly impacted by vehicular emissions (Table 3), which can be attributed to the kind of vehicles, fuel composition, the conductor manner of driving, pollutant sources as well as the photochemical reactions into the atmosphere, among other factors. In the case of diesel engine contributions, among found data of C1/C2 ratio, it is not clear that the relationship between the kind of fuel used by heavy-duty vehicle and C1/C2 ratio in all sites. However, in order to verify possible grouping of obtained data (Table 3) about C1/C2 ratio was used the techniques of PCA.

The graph of scores and loadings (PC1 × PC2) for the dataset (Fig. 3) illustrates the division of the sites into two groups (named here “a” and “b”) based on three variables (formaldehyde and acetaldehyde concentration and C1/C2 ratio) for 29 cases (Table 3) from data collection of sites. The present codes in Fig. 3 correspond to the sites described in Table 3. PCA showed that the first principal component (PC1) explains 59.5% of total variance being

**Table 3**  
Comparison of HCHO and H<sub>3</sub>CCHO levels and C1/C2 ratio among different studies.<sup>i</sup>

Sites	Code <sup>a</sup>	Fuel <sup>b</sup>	[HCHO] <sub>av</sub>	[H3CCHO] <sub>av</sub>	C1/C2 ratio
<i>Bus stations</i>					
Salvador, Brazil 2010 (ppbV) <sup>c</sup>	BT1 (B5)	B5	80	82	0.95
Salvador, Brazil 1997 (ppbV) [13]	BT2	D	52	12	4.40
Guangzhou, China (μg m <sup>-3</sup> ) [23]	BT3	D	67	23	2.91
Salvador, Brazil 1995 (μg m <sup>-3</sup> ) [24]	BT4	D	23	10	2.26
<i>Urban centers</i>					
Commercial mall parking, Salvador, Brazil (ppbV) [13]	UC1	D	8	13	0.66
Business building parking lot, Salvador, Brazil (ppbV) [13]	UC2	D	44	69	0.65
Downtown area, Guangzhou, China (μg m <sup>-3</sup> ) [23]	UC3	D	12	10	1.20
Downtown area Rio de Janeiro, Brazil (mg m <sup>-3</sup> ) [15]	UC5	D	141	37	3.81
	UC6 (B2)	B2	78	27	2.89
	UC7 (B3)	B3	47	27	1.74
	UC4 (B4)	B4	39	28	1.39
Northern part, Kaohsiung, Taiwan (mg m <sup>-3</sup> ) [15]	UC8	D	18	15	1.20
<i>Tunnel sites</i>					
Salvador, Brazil (ppbV) [13] <sup>d</sup>	T1	D	80	72	1.11
Hong Kong (μg m <sup>-3</sup> ) [22] <sup>e</sup>	T2	D	23	7	3.31
Salvador, Brazil (μg m <sup>-3</sup> ) [24]	T3	D	98	129	0.76
São Paulo, Brazil (ppbV) [25] <sup>f</sup>	T4	D	33	28	0.95
<i>Roadside sites</i>					
Hong Kong (mg m <sup>-3</sup> ) [26]	R1	D	5	4	1.25
Rio de Janeiro, Brazil (μg m <sup>-3</sup> ) [27]	R2	D	18	23	0.78
<i>Stationary diesel engine</i>					
DDI engine (ppm) [28]	S1	D	10	3	3.33
Agrale_engine, model M85 (ppmV) [6] <sup>g</sup>	S2	D	4	13	0.33
	S3 (B2)	B2	6	11	0.56
	S4 (B5)	B5	3	13	0.22
	S5 (B10)	B10	6	12	0.48
	S6 (B20)	B20	4	8	0.51
	S7 (B50)	B50	3	2	1.28
	S8 (B75)	B75	5	8	0.60
	S9 (B100)	B100	5	8	0.63
Cummins-4B (mg m <sup>-3</sup> ) [29] <sup>h</sup>	S10	D	2	4	0.5
EURO 2 IVECO 8360.46R (mg/kWh) [30]	S11	D	43	16	2.69
Cummins-4B (mg m <sup>-3</sup> ) [31] <sup>h</sup>	S12	D	5	2	2.50

<sup>a</sup> Code used in PCA graphic.

<sup>b</sup> Fuel used only in diesel engine.

<sup>c</sup> This study.

<sup>d</sup> Heavy-duty vehicles were 18%.

<sup>e</sup> Heavy-duty vehicles were 46%.

<sup>f</sup> Heavy-duty vehicles ranged from 12% to 14%.

<sup>g</sup> Data for 1800 rpm without load, samples were collected by direct emission.

<sup>h</sup> Data for 2800 rpm and full load.

<sup>i</sup> av = average; D = pure diesel; BX = fuel blends of diesel and biodiesel, “X” means amount of biodiesel (%) added to diesel.

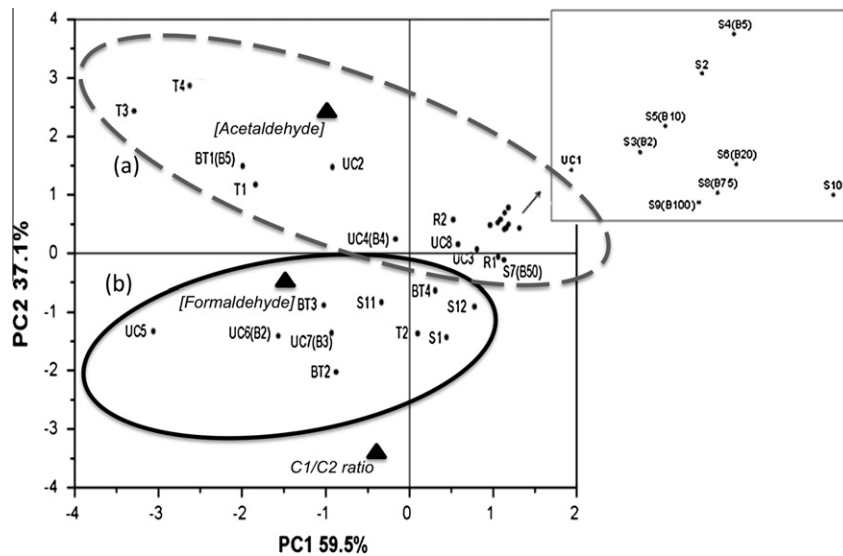


Fig. 3. Scores of the factors in the main components 1 and 2 obtained from acetaldehyde and formaldehyde concentration and C1/C2 ratio of different sites impacted by heavy-duty vehicles.

followed by the second (PC2) and third principal (PC3) components, whose explain 37.1% and 3.4% of the variance, respectively. Thus, PC1 and PC2 describe 96.6% of the total variance and the third principal component had low contribution.

In PC2, it could be noted two different groups where in *group b* there are sites more impacted by heavy-duty vehicles while *group a* is constituted by data from sites less impacted by these vehicles. Thus, about Tunnel sites, “T1” and “T2” sites were grouping in *group a* and *group b*, respectively. It can be occurring because 48% of vehicles that went through the T2 were heavy-duty vehicles, whereas in the “T1” site this percentage was only 18%. This tendency can be noted for “T4” site, which had heavy-duty vehicles ranged from 12% to 14%. Among Urban Center sites, those more impacted by heavy-duty vehicles (UC5, UC6 (B2) and UC7 (B3)) were grouped in *group b*. It is interesting to mention that for the same site there were obtained different values for variable data and the difference can be attributed to the kind of fuel used in diesel engines. So, when it was used diesel/biodiesel fuel blends up to 3% of biodiesel, the sites were located at *group b*, and when using biodiesel percentage higher than 3% added to diesel, located the site at *group a* (UC4 (B4)). The same tendency was observed to bus station sites, which showed, for the same site, a positioning of “BT2” (buses used pure diesel as fuel) in *group b* and “BT1 (B5)” (buses filled with B5) in *group a*.

However, data from stationary diesel engine experiments showed that is important the information about the test conditions. Those tests that used lower conditions of load and rotation were located at *group a*, and tests that used full load and higher rotation were located at *group b*, independently of the kind of fuel used in the tests. Thus, it was observed that some data from stationary diesel engine (test with 1800 rpm without load) were grouped together and very close to each another (S2–S9 (B100)). The data from roadside were located at *group a*, possibly by lower rate of heavy-duty vehicles in this sites when compared those site with higher rate.

Despite the fact not being possible to observe a clear relationship between the kind of fuel used by heavy-duty vehicles and the CC concentrations (formaldehyde, acetaldehyde) and their ratio (C1/C2) individually in different sites, the PCA technique could group these values and show certain correlation. Therefore, the variables formaldehyde concentration and C1/C2 ratio have a negative contribution for PC2 and acetaldehyde concentration

has a positive contribution. In other words, it can be possible to separate sites impacted by heavy-duty vehicles that use different kind of diesel/biodiesel fuel blends through CC data emissions. The higher formaldehyde concentration and lower acetaldehyde concentration can characterize sites impacted by heavy-duty vehicles that use biofuels blends or sites slightly impacted by these kinds of vehicles.

Concerns about public health show that formaldehyde has been classified by the EPA Group as B1, probable human carcinogen of medium carcinogenic hazard [32] and acetaldehyde has been classified as B2, probable human carcinogen of low carcinogenic hazard [33]. According to the American Conference of Governmental and Industrial Hygienists (ACGIH) there is a threshold limit value (TLV) of exposure to formaldehyde of 0.3 ppm, which should not be exceeded at any time [34]. However, the Occupational Safety and Health Administration (OSHA) [35] has set a permissible exposure limit for formaldehyde of 0.75 ppm for an 8-h workday. Thus, through the obtained results in this study, it is clear that the atmospheric air pollution in Lapa bus station has considerably increased, mainly because of the vehicular fleet that circulates nowadays. The formaldehyde maximum concentration found in this study is about 0.29 ppm, which is very close to the maximum of exposure permitted by ACGIH, which might probably aggravate the situation of people who work or utilize the facilities of the station. However, since the aim of our study was not to assess health effects by CC emissions we are not able to affirm that the air quality found in Lapa bus station is unsatisfactory for human beings. For that, it is necessary to perform wider and longer studies.

#### 4. Conclusion

Throughout this study, it was observed a relationship between the type of fuel used in heavy vehicles and the concentration of formaldehyde and acetaldehyde found in site impacted by these vehicles. Two major groups were observed by using PCA. One group was characterized of being strongly impacted by heavy duty vehicles and the other with a low contribution of these vehicles. Thus, the addition of concentrations higher than 3% of biodiesel to diesel showed an improvement in the carbonyl concentration profile of these places with high flow of heavy-duty vehicles. The use of these biofuels showed profile similar to those found for sites less impacted by these vehicles.

## Acknowledgements

The authors wish to thank Prof. Dr. Rinaldo Mota de Jesus (DCET/UESC) for his valuable help with the PCA analysis and the Lapa Bus Station Management for providing sampling conditions. Also we acknowledge the Brazilian agencies that have funded this work: CNPq, FAPESB, CAPES, FINEP, ANEEL, PRONEX, and INCT for Energy & Environment.

## References

- [1] Grosjean D, Grosjean E, Moreira LFR. Speciated ambient carbonyls in Rio de Janeiro, Brazil. *Environ Sci Technol* 2002;36:1389–95.
- [2] Kim KH, Hong YJ, Pal R, Jeon EC, Koo YS, Sunwoo Y. Investigation of carbonyl compounds in air from various industrial emission sources. *Chemosphere* 2008;70:807–20.
- [3] de Andrade MVAS, Pinheiro HLC, Pereira PAP, de Andrade JB. Compostos carbonílicos atmosféricos: fontes, reatividade níveis de concentração e efeitos toxicológicos. *Química Nova* 2002;25:1117–31.
- [4] Villanueva-Feirero I, Popp CJ, Martin RS. Biogenic emissions and ambient concentrations of hydrocarbons, carbonyl compounds and organic acids from ponderosa pine and cottonwood trees at rural and forested sites in Central New Mexico. *Atmos Environ* 2004;38:249–60.
- [5] Guarieiro LLN, Pereira PAP, Torres EA, da Rocha GO, de Andrade JB. Carbonyl compounds emitted by a diesel engine filled with diesel and biodiesel–diesel blends: sampling optimization and emissions profile. *Atmos Environ* 2008;42:8211–8.
- [6] Guarieiro LLN, de Souza AF, Torres EA, de Andrade JB. Emission profile of 18 carbonyl compounds, CO, CO<sub>2</sub> and NO<sub>x</sub> emitted by a diesel engine fuelled with diesel and ternary blends containing diesel, ethanol and biodiesel or vegetable oils. *Atmos Environ* 2009;43:2754–61.
- [7] Zervas E. Regulated and non-regulated pollutants emitted from two aliphatic and a commercial diesel fuel. *Fuel* 2008;87:1141–7.
- [8] Ribeiro NM, Pinto AC, Quintella CM, da Rocha GO, Teixeira LSG, Guarieiro LLN, et al. The role of additives for diesel and diesel blended (ethanol or biodiesel) fuels: a review. *Energy Fuels* 2007;21:2433–45.
- [9] McCarthy P, Rasul MG, Moazzem S. Analysis and comparison of performance and emissions of an internal combustion engine fuelled with petroleum diesel and different bio-diesels. *Fuel* 2011;90:2147–57.
- [10] Randazzo ML, Sodr e JR. Exhaust emissions from a diesel powered vehicle fuelled by soybean biodiesel blends (B3–B20) with ethanol as an additive (B20E2–B20E5). *Fuel* 2011;90:98–103.
- [11] Wadumesthrige K, Ara M, Salley SO, Simon Ng KY. Investigation of lubricity characteristics of biodiesel in petroleum and synthetic fuel. *Energy Fuels* 2009;23:2229–34.
- [12] McCormick RL, Westbrook SR. Storage stability of biodiesel and biodiesel blends. *Energy Fuels* 2010;24:690–8.
- [13] de Andrade JB, Andrade MV, Pinheiro HLC. Atmospheric levels of formaldehyde and acetaldehyde and their relationship with the vehicular fleet composition in Salvador-Bahia, Brazil. *J Brazilian Chem Soc* 1998;9:219–23.
- [14] Ho KF, Ho SSH, Cheng Y, Lee SC, Yu JZ. Real-world emission factors of fifteen carbonyl compounds measured in a Hong Kong tunnel. *Atmos Environ* 2007;41:1747–58.
- [15] Wang B, Lee SC, Ho KF. Characteristics of carbonyls: concentrations and source strengths for indoor and outdoor residential microenvironments in China. *Atmos Environ* 2007;41:2851–61.
- [16] IARC, World Health Organization. International Agency for Research on Cancer. Summary of data reported and evaluation, vol. 88; 2006. p. 2–3. <<http://www.inchem.org/documents/iarc/vol88/volume88.pdf>>.
- [17] de Andrade JB, Reis JON, Rebouças MV, Pinheiro HLC, de Andrade MV. Determination of formaldehyde and acetaldehyde in drinking water and alcoholic beverages by high performance liquid chromatography (HPLC). *Química Anal* 1996;15:144–7.
- [18] Corr ea SM, Arbillia G. Carbonyl emissions in diesel and biodiesel exhaust. *Atmos Environ* 2008;42:769–75.
- [19] He C, Ge Y, Tan J, You K, Han X, Wang J, et al. Comparison of carbonyl compounds emissions from diesel engine fueled with biodiesel and diesel. *Atmos Environ* 2009;43:3657–61.
- [20] Karavalakis G, Boutsika V, Stournas S, Bakeas E. Biodiesel emissions profile in modern diesel vehicles. Part 2: Effect of biodiesel origin on carbonyl, PAH, nitro-PAH and oxy-PAH emissions. *Sci Total Environ* 2011;409:738–47.
- [21] Fontaras G, Karavalakis G, Kousoulidou M, Tzankiozis T, Ntziachristos L, Bakeas E, et al. Effects of biodiesel on passenger car fuel consumption, regulated and non-regulated pollutant emissions over legislated and real-world driving cycles. *Fuel* 2009;88:1608–17.
- [22] Corr ea SM, Arbillia G, Martins EM, Quit erio SL, Guimar es CS, Gatti LV. Five years of formaldehyde and acetaldehyde monitoring in the Rio de Janeiro downtown area – Brazil. *Atmos Environ* 2011;44:2302–8.
- [23] Feng Y, Wen S, Chen Y, Wang X, Lu H, Bi X, et al. Ambient levels of carbonyl compounds and their sources in Guangzhou, China. *Atmos Environ* 2005;39:1789–800.
- [24] de Andrade JB, Andrade MV, Pinheiro HLC. The formaldehyde and acetaldehyde content of atmospheric aerosol. *J Brazilian Chem Soc* 1995;6:287–90.
- [25] Vasconcellos PC, Carvalho LRF, Pool CS. Volatile organic compounds inside urban tunnels of S o Paulo City, Brazil. *J Brazilian Chem Soc* 2005;16:210–1216.
- [26] Ho KF, Lee SC, Tsai WY. Carbonyl compounds in the roadside environment of Hong Kong. *J Hazard Mater* 2006;133:24–9.
- [27] Corr ea SM, Martins EM, Arbillia G. Formaldehyde and acetaldehyde in a high traffic street of Rio de Janeiro, Brazil. *Atmos Environ* 2003;37:23–9.
- [28] Roy MM. HPLC analysis of aldehydes in automobile exhaust gas: comparison of exhaust odor and irritation in different types of gasoline and diesel engines. *Energy Convers Manag* 2008;49:1111–8.
- [29] Pang X, Shi X, Mu Y, He H, Shuai S, Chen H, et al. Characteristics of carbonyl compounds emission from a diesel-engine using biodiesel–ethanol–diesel as fuel. *Atmos Environ* 2006;40:7057–65.
- [30] Turrio-Baldassarri L, Battistelli CL, Conti L, Crebelli R, de Berardis B, Iamiceli AL, et al. Emission comparison of urban bus engine fueled with diesel oil and ‘biodiesel’ blend. *Sci Total Environ* 2004;327:147–62.
- [31] Shi X, Pang X, Mu Y, He H, Shuai S, Wang J, et al. Emission reduction potential of using ethanol–biodiesel–diesel fuel blend on a heavy-duty diesel engine. *Atmos Environ* 2006;40:2567–74.
- [32] US Environmental Protection Agency (US EPA). Integrated risk information system (IRIS) on formaldehyde. On-line IRIS, CASRN 50-00-0. 1991
- [33] US Environmental Protection Agency (US EPA). Integrated risk information system (IRIS) on acetaldehyde. On-line IRIS, CASRN 75-07-0. 1991.
- [34] American Conference of Governmental Industrial Hygienists (ACGIH). Threshold limit values for chemical substances and physical agents. Cincinnati; 1993.
- [35] Occupational Safety & Health Administration (OSHA). Chemical sampling information (CSI) formaldehyde. <[www.osha.gov/dts/chemicalsampling/data/CH\\_242600.html](http://www.osha.gov/dts/chemicalsampling/data/CH_242600.html)>.