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Five years of formaldehyde and acetaldehyde monitoring in the Rio de Janeiro downtown area – Brazil

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ABSTRACT

The fuel matrix used in Brazil is unique around the world. The intensive use of hydrated ethanol, gasohol (gasoline with 25% v/v of ethanol), compressed natural gas (CNG), and biodiesel leads to a peculiar composition of the urban atmosphere. From 1998 to 2002 an increase in formaldehyde levels was observed and since then, a reduction. This work presents a monitoring campaign that was executed from March 2004 to February 2009 by sampling at early morning on every sunny Wednesday for a total of 183 samples. The results indicate a strong reduction in formaldehyde levels from 2004 (average of 135.8 $\mu g\,m^{-3}$ with SD 28.4 $\mu g\,m^{-3}$) to 2009 (average of 49.3 $\mu g\,m^{-3}$ with SD 27.4 $\mu g\,m^{-3}$). The levels of acetaldehyde showed a slight reduction from 2004 (average of 34.9 $\mu g\,m^{-3}$ with SD 8.0 $\mu g\,m^{-3}$) to 2009 (average of 26.8 $\mu g\,m^{-3}$ with SD 11.5 $\mu g\,m^{-3}$). Comparing the results with the concurrent evolution of the fleet and of fuel composition indicates that the observed formaldehyde levels could be associated with the increase in ethanol use and in CNG use by engines with improved technology over the first converted CNG engines. Modelling studies using the OZIPR trajectory model and the SAPRC chemical mechanism indicate that formaldehyde is the main ozone precursor in Rio de Janeiro and acetaldehyde is the forth one.

1. Introduction

The atmosphere of an urban area is strongly influenced by the composition of its vehicular fleet and the fuels used. Topographical and meteorological parameters also have some influence, but only on a minor scale when compared with the fleet and fuels.

In some parts of the world the search for renewable fuels is a highly active area of research and the predominant candidates being oxygenated fuels such as ethanol and biodiesel. This is driven by a new understanding of the global warming problem and the desire to reduce both the size of the carbon-based economy and the dependency on oil from the Middle East.

Toward accomplishing these goals, Brazil has a leading position with its inclusion of ethanol from sugarcane as automotive fuel in a hydrated form or blended with gasoline since the middle of the '70s. The use of biodiesel was 2% blended to diesel in 2005, 3% in March 2008, 4% in July 2009, and 5% in January 2010, with the prospective to reach 20% within the next five years. Stages of the evolution of the fuels used in Brazil are presented in Table 1 (Corrêa and Arbilla, 2003, 2006; US-EPA, 1987).

Fig. 1 shows fuel consumption in Brazil over the years, where is possible to see the increasing consumption of fossil and renewable fuels (ANP, 2006).

A feasible control strategy should be to use fuels with lower mass emissions and to reduce the emissions' reactivity, or both.

Some alternatives for reducing urban air pollution are reformulated gasoline, compressed natural gas (CNG), liquefied petroleum gas (LPG), alcohols, hydrogen, and electric vehicles. There is no agreed-upon definition of reformulated gasoline; however, the commonly expressed goal for the fuel is to reduce VOC emissions. Reformulated gasoline also has a lower vapour pressure, which reduces the evaporative emissions that can contribute nearly half of the total VOC emissions. It also exhibits a lower sulphur content, which improves catalyst operation, leading to a reduction of VOC, CO, and NOx emissions. The addition of oxygen-containing compounds into gasoline, such as ethers and alcohols is intended to counter the octane reduction by the reduced aromatic and olefin contents (Finlayson-Pitts and Pitts, 2000).

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Table 1
Events related to the use of fuels in Brazil.

Date	Event
1973	1st petrol crisis
1974	Brazil started to use ethanol
1977	Gasohol with 4.5% of ethanol
1979	Gasohol with 15% of ethanol
1980	2nd Petrol crisis
1983	90% of light automobiles sold with ethanol
1985	Gasoline with 22% of ethanol
1989	Price of gasoline equal to ethanol
1992	RIO 92: signature of climate change protocol
1990s	Gasoline with 20–25% of ethanol
1999	Light vehicles started to use CNG
2003	Flex fuel automobiles
2005	Biodiesel program authorises B2 (2%)
2007	3rd Petrol crisis
January 2008	B2 (2%)
March 2008	B3 from July 2008 (3%)
April 2008	Ethanol consumption equal to gasoline
September 2008	1.5 Million of light vehicles using CNG
July 2009	B4 (4%)
January 2010	B5 (5%)

In the USA, determination of the ambient concentrations of carbonyl compounds is a requirement of the 40 CFR, Part 58, Subpart E, enhanced ozone network monitoring programs (US-EPA, 1993). In Brazil, standard values for formaldehyde and acetaldehyde concentrations in ambient air have not been established and the state and local agencies have no monitoring programs. The only regulation is of the emissions values of aldehydes for all types of vehicles, using the dynamometric test, is the same as the FTP 75 (ABNT, 2005).

A concern regarding the use of alcohols in reformulated gasoline is that it can increase aldehydes concentrations in the atmosphere. Aldehydes are important constituents of atmospheric chemistry. They can be formed from the photochemical degradation of organic compounds and are emitted as primary pollutants mainly by diesel and CNG vehicles and by light vehicles (Martins and Arbilla, 2003). The three main degradation reactions of aldehydes in the atmosphere are via photolysis, OH radical reaction, and NO_3 radical reaction (to a lesser extent) as shown for formaldehyde and acetaldehyde, the main aldehydes in urban atmospheres (Seinfeld and Pandis, 2000; Martins et al., 2007, 2009):

$$HCHO + h\upsilon \rightarrow H^{\bullet} + HCO \quad (1)$$

$$HCHO + h\upsilon \rightarrow H_2 + CO \quad (2)$$

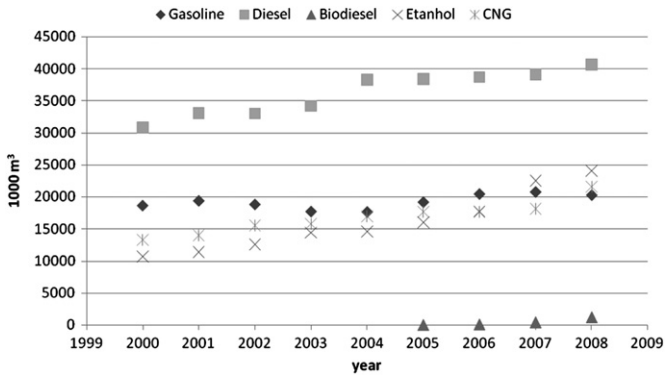

Fig. 1. Evolution of the use of fuels over the last nine years.

$$CH_3CHO + h\upsilon \rightarrow CH_4 + CO \quad (3)$$

$$CH_3CHO + h\upsilon \rightarrow CH_3^{\bullet} + HCO \quad (4)$$

$$HCHO + OH^{\bullet} \rightarrow HCO + H_2O \quad (5)$$

$$CH_3CHO + OH^{\bullet} \rightarrow CH_3CO + H_2O \quad (6)$$

The reactions with $OH^{\bullet}$ and photolysis also lead to secondary reactions with the hydroperoxyl radical ($HO_2^{\bullet}$) that forms from the produced hydrogen atom with an oxygen molecule. The reactions of the HCO and CH_3CO radicals with oxygen molecules lead to the formation of the hydroperoxyl and acyl peroxy radicals:

$$HCO + O_2 \rightarrow HO_2^{\bullet} + CO \quad (7)$$

$$CH_3CO + O_2 + M \rightarrow CH_3C(O)OO^{\bullet} + M \quad (8)$$

In summation, the formation of the acyl peroxy radical leads to the formation of peroxyacetyl nitrate (PAN), a powerful photochemical oxidant, by the reactions:

$$CH_3C(O)OO^{\bullet} + NO \rightarrow CH_3C(O)O^{\bullet} + NO_2 \quad (9)$$

$$CH_3C(O)O^{\bullet} \rightarrow CH_3^{\bullet} + CO_2 \quad (10)$$

$$CH_3C(O)O^{\bullet} + NO_2 + M \rightarrow CH_3C(O)OONO_2 + M \quad (11)$$

In contrast, the reaction products from formaldehyde in the atmosphere produce the $HO_2^{\bullet}$ radical, which drives the conversion of NO to NO_2 and the formation of O_3.

The reactions above show the importance of studying and monitoring the levels of formaldehyde and acetaldehyde in urban atmospheres.

In our past monitoring camping (Corrêa and Arbilla, 2003) we found an increase of the formaldehyde levels from 1998 to 2002, and this fact was attributed to the extensive use of CNG by engine with poor kits technologies.

In this study we attempt to correlate the atmospheric formaldehyde and acetaldehyde levels to the fuels used in Brazil and to their potential to form tropospheric ozone. The present study started a monitoring campaign from 2004 to 2009 for formaldehyde and acetaldehyde and tries to correlate the levels of these aldehydes with the evolution of the Brazilian fleet and fuels used.

2. Methodology

2.1. Site description

Samples were collected in the Rio de Janeiro downtown area, on Presidente Vargas Avenue. This is an important route in the city, which carries more than 120 thousand vehicles per day, including automobiles, motorcycles, trucks, and buses. Samples were collected next to an automatic air quality monitoring station (685978 E and 7465946 S) that also collects meteorological data (temperature, humidity, pressure, and solar flux) and criteria pollutants (nitrogen oxides, ozone, sulphur dioxide, carbon monoxide, total hydrocarbons, and particulate matter). All samples were collected on Wednesdays starting at 6:30 AM and finishing at 8:30 AM. The samples were collected on all sunny Wednesdays except on holidays and when rain was observed on the previous day. The location and site conditions were the same as described in previous works (Corrêa and Arbilla, 2003, 2005; Martins and Arbilla, 2003).

2.2. Sampling and analysis

All samples were collected over two hours at a flow rate of 1.0 L min^{-1}. The sampling system consisted of four main components: a battery pump (KNF UNMP850 KNDC or SKC PCXR4); a flow meter (Dwyer MMA-20 ranging from 0.2 to 1.2 L min^{-1}); silica cartridges coated with C18 (Sep-Pak Classic from Waters), impregnated with an acid solution of 2,4-dinitrophenilhydrazine (DNPH from Fluka), purified by double recrystalisation and checked by UV-HPLC; and an ozone scrubber (a silica cartridge filled with a saturated solution of potassium iodide and then dried). The interference from ozone is well explained by de Andrade et al. (1998), Possanzini and di Paolo (1997), Grosjean and Grosjean (1996), Grosjean et al. (1996) Miguel et al. (1995), and Pires and Carvalho (1998).

All the procedures for preparing cartridges and for sampling followed the US-EPA TO-11A methodology.

The aldehydes were trapped by reaction with DNPH in the cartridges forming the corresponding stable 2,4-dinitrophenylhydrazone derivatives. Hydrazone standards were prepared by dissolving a standard mixture purchased from Supelco (CARB Carbonyl-DNPH Mix 1) in acetonitrile.

The sampled material was eluted from the cartridges with 5 mL of acetonitrile into volumetric flasks and stocked in amber vials. An aliquot of 20 μL was analysed by UV-HPLC at 365 nm using a Perkin Elmer Series 200 instrument with an automated injector. A Whatman Partisil 10 ODS-1 column, 25 cm in length, internal diameter of 4.6 mm and particle size of 5.0 μm, and a mobile phase of 50% acetonitrile and 50% water were used in isocratic mode with a flow rate of 1.5 mL min^{-1}. A series of standards were used to obtain calibration curves for each aldehyde from 0.5 to 20 mg L^{-1}. Correlation coefficients were 0.99 or higher. Detection limits for both aldehydes were 0.2 mg L^{-1}.

2.3. Determination of criteria pollutants, meteorological parameters and organic volatile compound concentrations

Concentrations of volatile organic compounds (VOC) and criteria pollutants, as well as meteorological data, were obtained for use as input in an air quality model.

Data from INEA (Environment State Institute of Rio de Janeiro) automated air quality monitoring station were obtained in one-minute intervals and were averaged over one-hour periods. Concentrations of CO, NO_x, O_3, CH_4, SO_2, HCNM (non-methanic hydrocarbons) and PM_{10} were measured along with the temperature, air humidity and atmospheric pressure (INEA, 2009).

VOC sampling was performed over three days (June 12, 13 and 15, 2007) at two different times (9:00 AM. and 3:00 AM) using 1.8 L electropolished, stainless-steel, evacuated canisters. To collect each whole-air sample, a stainless-steel valve was slightly opened and the canister was filled to ambient pressure in about two minutes. The samples were analysed within three days as has been previously described (Martins et al., 2009).

The samples were analysed by Varian CP3800 gas-chromatography with flame ionisation detection (GC-FID) and a Varian Saturn 2000 mass spectrometry (GC–MS). The method followed the U.S. EPA guidelines (U.S. EPA Compendium TO-14 and TO-15 Method, 1997). Briefly, 200 mL aliquots of air from the canister samples were loaded on a cryo-trap (glass beads in 6" × 1/8" stainless-steel tubing) under liquid nitrogen (−180 °C), were desorbed from the cryo-trap at 200 °C, and were then injected onto the head of the GC column where the sample was cryo-focused at −50 °C. A DB-1 capillary column, 60 m long × 0.32 mm diameter × 1.0 μm film thickness was used. The temperature was held at −50 °C for 2 min, and raised from −50 °C to +200 °C at 6 °C min^{-1}. After leaving the capillary column, the sample was divided into two streams and was analysed simultaneously using the FID and MS detectors. The analyses were carried out using a Varian 3800 gas-chromatograph and a Saturn 2000 mass selective detector. The mass spectral libraries used for compound identification included the NIST Database. Quantitative analysis was performed using standard mixtures of alkanes (propane, butane, pentane and hexane from White Martins), alkenes (ethene, propene, butene, pentene and hexane from White Martins), aromatics (benzene, toluene, *o*-xylene and ethylbenzene from Scott Specialty), and a TO-14 standard mixture (Scott Specialty). Five standards (in the range 0.2–5.0 ppbv) were prepared, as recommended by the TO-14 Method. Detection limits (D.L.), in the range of 0.075–0.125 ppbv, were determined using the data from the calibration curve. Blank runs were performed before each sample analysis and all samples were run in duplicate. Results were validated when the difference was lower than 5%. Details of the monitoring campaign and the complete results will be published elsewhere. Results shown here are only used as inputs to the air quality model.

2.4. Air quality simulation

The impact of formaldehyde and acetaldehyde concentrations on air quality was evaluated using an empirical trajectory model implemented in OZIPR (Gery and Crouse, 1990, Tonnessen, 2000).

In this model a well-mixed box moves at the average wind speed along a trajectory through the urban area. As the box moves, its height increases because of the rise in the mixing height from the sun's heating. This rise results in a decrease in the concentrations of the species in the box. At the same time, fresh emissions are added through the bottom face of the box, increasing the concentrations of primary species. It was not possible to use a sophisticated urban airshed model, which requires very detailed information as input data, including the meteorology and emissions resolved in both time and space, which is not available for Rio de Janeiro. Therefore the use of a 3D airshed model would not have yielded meaningful results.

The photochemical model SAPRC (Carter, 1990; SAPRC, 2009) was used. This model has been extensively studied and validated and has been used both in our previous studies and in many simulations around the world.

In this study VOC were grouped according to their reactivity with the OH radical into a total of 12 different groups. The average concentration of each compound was determined using the experimental data obtained from the TO-14 U.S.-EPA methodology. The rate and stoichiometric coefficients were calculated as weighted averages of all the components within a species group. The descriptions of the groups are given in Table 2, along with the fractions associated with each one of them.

A more detailed description of the physical and chemical model is given in our previous works (Martins et al., 2002; Corrêa and Arbilla, 2003).

The model was used to describe a base case (*i.e.*, a representative scenario) that was considered as a reference for examining the effects of changing the input parameters (mainly formaldehyde and acetaldehyde levels) on the calculated ozone concentrations. The input data for the base case were selected to be relevant and representative of the Rio de Janeiro urban area. The initial concentrations (06:00 AM) used in the simulation were 1.10 and 0.15 ppm for CO and NOx, respectively, which were the mean experimental values obtained by the automatic monitoring station for June 2007. The VOC initial concentration was set as 0.90 ppm C following the TO-14A US-EPA results. The initial and maximum mixing heights were set as 600 m and 1600 m, respectively, which are typical values for Rio de Janeiro (Arbilla et al., 2002). The main

Table 2
Average composition of volatile organic compounds used for the simulation of the base case (units are ppbC and fractions sum to 1 ppbC in total).

Compound or group	Fraction on a ppm C basis
Alkanes 1 – $k_{OH} < 5.0 \times 10^2$ ppm^{-1} min^{-1}	0.020
Alkanes 2 (C_3–C_4) 5.0×10^2 ppm^{-1} min^{-1} $< k_{OH} < 2.5 \times 10^3$ ppm^{-1} min^{-1}	0.018
Alkanes 3 (C_5–C_7) 2.5×10^3 ppm^{-1} min^{-1} $< k_{OH} < 5.0 \times 10^3$ ppm^{-1} min^{-1}	0.037
Alkanes 4 (C_8–C_9) 5.0×10^3 ppm^{-1} min^{-1} $< k_{OH} < 1.0 \times 10^4$ ppm^{-1} min^{-1}	0.032
Alkanes 5 (C_{10}–C_{22}) $k_{OH} > 1.0 \times 10^4$ ppm^{-1} min^{-1}	0.148
Ethene	0.108
Olefins 1 – $k_{OH} < 7.0 \times 10^4$ ppm^{-1} min^{-1}	0.190
Olefins 2 – $k_{OH} > 7.0 \times 10^4$ ppm^{-1} min^{-1}	0.125
Aromatics 1 – $k_{OH} < 2.0 \times 10^4$ ppm^{-1} min^{-1}	0.226
Aromatics 2 – $k_{OH} > 7.0 \times 10^4$ ppm^{-1} min^{-1}	0.057
Formaldehyde	0.031
Acetaldehyde	0.008

effect of the mixing height is the dilution of gases. In this work, because the absolute values of CO emissions were also used as adjustable parameters, an error in the mixing height may be corrected by changing the emissions.

The VOC/NOx/CO emission ratios were calculated to be consistent with the most recent vehicle emission inventory for the city of Rio de Janeiro and the INEA emission inventory for the Metropolitan Region of Rio de Janeiro (Guimarães et al., 2009). On a mass basis, values of 0.243 and 0.210 for the VOC/CO and NOx/CO ratios, respectively, were used. These ratios were kept constant during the simulation, and because they depend on the characteristics of the vehicular fleet, they were considered as non-adjustable parameters. Absolute emission rates were adjusted to fit the measured ambient concentrations of CO (the average hourly values for the June 2007 period).

Hypothetical scenarios were constructed using the formaldehyde and acetaldehyde mean concentrations for each year and the ozone levels were calculated.

The base case was also used to develop the reactivity scale for the VOC mixture in the studied area. The reactivity of a mixture is the measure of the ozone amount formed from the photochemical reactions in a VOC and NOx mixture. It is the change in the reactivity of the mixture produced by an infinitesimally small change in the emissions of a component of the mixture. The component whose emissions are changed can be NOx, an individual VOC in the mixture, the VOC mixture as a whole, or some VOC that is not in the mixture. Mathematically, incremental reactivity (IR) is defined as the partial derivative of the reactivity with respect to a component of the mixture (Tonnessen, 2000).

Using the base case, an increase and decrease of 0.2% of total VOC for each main compound was applied and the ozone concentration was evaluated. Finally the positive and negative incremental reactivity were calculated as:

$$IR+ = \frac{[O_3]^{inc} - [O_3]^{base}}{0.002x[VOC_s]^{base}}$$

$$IR- = \frac{[O_3]^{inc} - [O_3]^{base}}{0.002x[VOC_s]^{base}}$$

The incremental reactivity was calculated as the average between the positive and negative IR for each VOC.

It is important to note that each change made in the individual VOC concentration leads to changes in all of the VOC' speciation, which is used to group the VOC by the SAPRC mechanism, so it is necessary to perform a new simulation for each change.

3. Results and discussion

A total of 183 samples were collected from March 2004 to February 2009. The experimental results are presented in Fig. 2 for formaldehyde and acetaldehyde. The data show a strong reduction (64%) in formaldehyde levels from 2004 (average of 135.8 mg m^{-3} with SD 28.4 mg m^{-3}) to 2009 (average of 49.3 mg m^{-3} with SD 27.4 mg m^{-3}). The levels of acetaldehyde showed a slight reduction (23%) from 2004 (average of 34.9 mg m^{-3} with SD 8.0 mg m^{-3}) to 2009 (average of 26.8 mg m^{-3} with SD 11.5 mg m^{-3}).

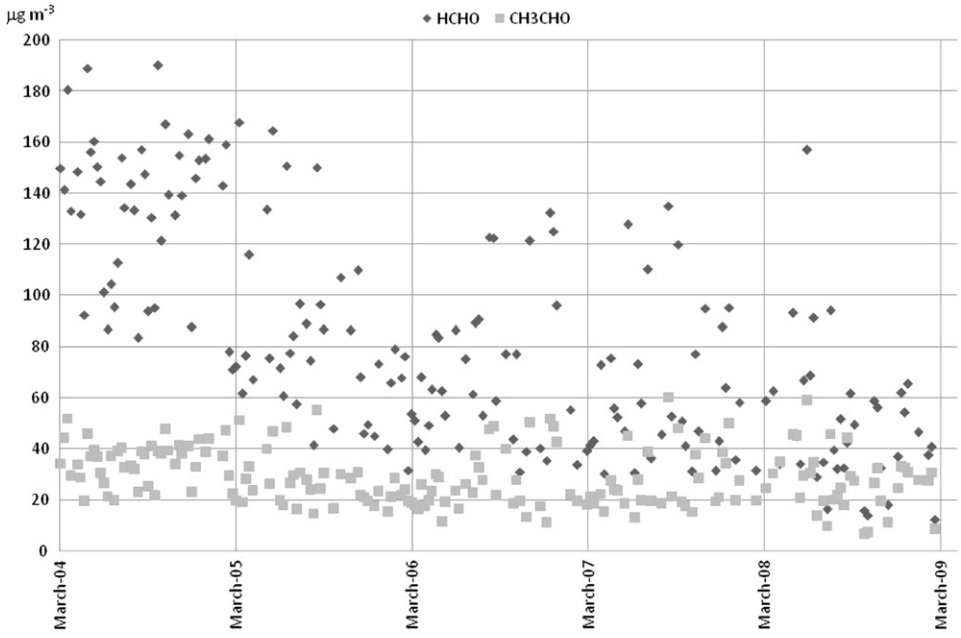

Fig. 2. Formaldehyde and acetaldehyde concentrations between 2004 and 2009 in the Rio de Janeiro downtown area.

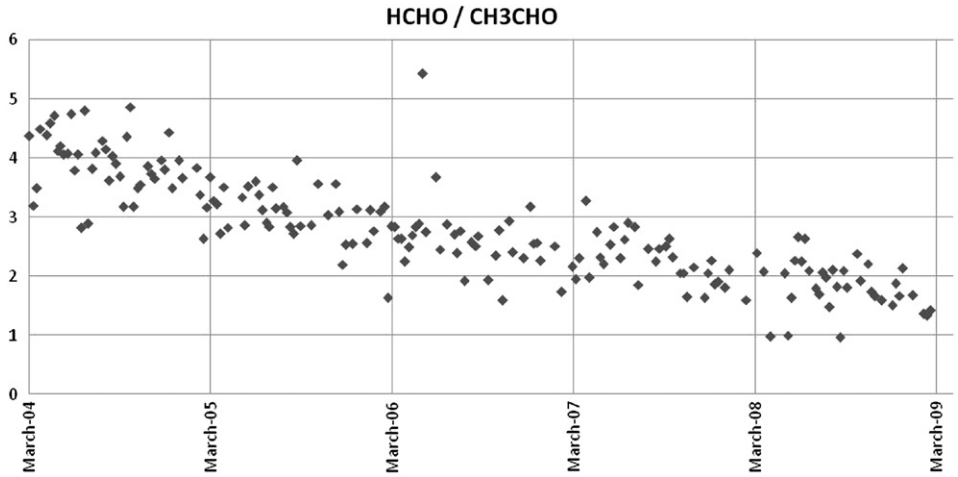

Fig. 3. Formaldehyde/acetaldehyde ratios for the period 2004–2009 in the Rio de Janeiro downtown area.

Formaldehyde/acetaldehyde ratios also show a clear decrease, as presented in Fig. 3. Both compounds have primary and secondary sources (Corrêa and Arbilla, 2003). Previous published results found that the main source of aldehydes in the early morning is by direct emission from vehicles and in the afternoon aldehydes are mainly formed from the photooxidation of volatile organic compounds (Arbilla et al., 2002). Since samples were collected in the early morning, the measured concentrations of formaldehyde and acetaldehyde may be mainly attributed to primary emissions. Differences in the patterns of formaldehyde and acetaldehyde concentrations may be the result of the changes in the fleet and the fuel use as described in the Introduction section.

Ozone concentrations were calculated using the base case scenario. Experimental and simulated results are shown in Table 3. Experimental meteorological and concentration data are the mean values for the period June-August 2007, which is the same month that the VOC samples were collected. Because the model was calibrated using experimental CO concentrations, results for this compound are also presented. As shown in Table 3, the calculated and experimental data for ozone concentrations are in reasonable agreement throughout the whole time period. Further adjustment was considered unnecessary because the mail goal of the simulation was to analyse the effect of the formaldehyde and acetaldehyde concentrations and not to exactly reproduce a particular day or scenario. Therefore, the constructed base case was considered to be representative of the average air quality of downtown Rio de Janeiro. The simulated ozone peak was obtained at 2:00 PM (24.6 $\mu g\,m^{-3}$).

Upon completion of the model adjustment, the contribution to ozone formation by formaldehyde and acetaldehyde was analysed by varying their concentrations within their mean values over the total period. Results are shown in Table 4. The ozone peaks that were calculated using the minimum, maximum and mean values for each year clearly show that a decrease in formaldehyde and acetaldehyde concentrations results in a decrease in ozone levels. In 2004, formaldehyde and acetaldehyde concentrations were in the range of 83.5–190.2 and 19.6–51.8 $\mu g\,m^{-3}$, respectively. Considering these experimental values, the calculated ozone concentrations peak was found to be in the range of 18.6–36.1 ppb in 2004. In 2008, the formaldehyde and acetaldehyde levels were 14.0–94.0 and 6.7–45.8 $\mu g\,m^{-3}$, respectively, leading to a calculated value for the ozone maximum of 11.7–21.8 ppb. Considering just the mean values, the experimental formaldehyde and acetaldehyde concentrations were measured to decrease from 76 to 41% from 2004 to 2009, respectively, while the calculated ozone peak concentrations were reduced by 56%. These results are dependent on the chemical mechanism, the conditions of the base case, solar flux, VOC mixture and NO_x concentrations. However, it is clear that under simulation conditions representative of Rio de Janeiro aldehydes, mainly formaldehyde, greatly contribute to the formation of ozone (Corrêa and Arbilla, 2003).

Calculated IR values for formaldehyde and acetaldehyde are shown in Fig. 4, respectively. As is already known, IR values depend on the base case conditions and on the chemical model. The results obtained here indicate that despite the reduction of the levels of

Table 3
Input meteorological parameters for the simulation of the base case (mean experimental values from June 2007). Experimental results (mean values for the period June 1–29) for CO and ozone were obtained at the monitoring station during 2007. Values in parentheses are the standard deviations.

Hour	Relative humidity (%)	Temperature (°C)	CO (ppm)		Ozone (ppb)	
			Experimental	Simulated	Experimental	Simulated
06:00	74.7	27.5	1.10 (0.06)	1.04	0.1 (0.01)	0.1
07:00	68.5	27.8	1.30 (0.07)	1.25	1.1 (0.06)	0.3
08:00	64.3	29.2	1.25 (0.06)	1.30	1.4 (0.07)	0.8
09:00	60.2	30.9	1.20 (0.06)	1.15	2.3 (0.12)	2.0
10:00	58.2	32.1	1.18 (0.06)	1.12	3.9 (0.20)	3.2
11:00	56.7	32.6	1.10 (0.06)	1.01	6.5 (0.33)	5.9
12:00	58.1	33.1	0.95 (0.05)	0.92	8.7 (0.53)	11.6
13:00	57.8	32.9	0.92 (0.05)	0.88	12.3 (0.62)	14.5
14:00	57.2	31.8	0.88 (0.04)	0.87	16.4 (0.82)	16.0
15:00	55.9	31.1	0.87 (0.04)	0.86	13.6 (0.68)	12.8
16:00	56.2	30.3	0.89 (0.05)	0.87	10.3 (0.52)	8.5
17:00	64.2	29.8	0.90 (0.05)	0.85	4.5 (0.23)	2.5
18:00	69.7	28.5	0.96 (0.05)	0.86	0.1 (0.01)	0.8

Table 4
Calculated ozone levels using the minimum, maximum and average value for formaldehyde and acetaldehyde experimental concentrations over the 2004–2009 period.

Year	Formaldehyde ($\mu g\,m^{-3}$)			Acetaldehyde ($\mu g\,m^{-3}$)			Ozone (ppb)		
	Mean	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.
2004	141.3	83.5	190.2	37.1	19.6	51.8	27.6	18.6	36.1
2005	77.8	41.5	167.8	27.4	14.7	48.4	18.4	14.6	30.3
2006	64.3	31.0	132.3	23.1	11.2	42.7	16.8	13.5	17.7
2007	52.6	30.3	127.9	21.8	13.2	60.2	15.9	13.5	27.9
2008	47.2	14.0	94.0	27.1	6.7	45.8	15.7	11.7	21.8
2009	39.2	12.4	46.5	27.7	8.8	30.7	15.0	11.7	15.8

formaldehyde and acetaldehyde levels these compounds still have great influence on the ozone formation for the Rio de Janeiro downtown area. Considering the IR values and the mean concentrations of the main compounds, formaldehyde is the main ozone precursor and acetaldehyde is the forth one. The high levels of acetaldehyde and formaldehyde in Rio de Janeiro and their importance as ozone precursors have been previously reported (Martins et al., 2009) and is mainly due to the use of ethanol and CNG.

One possible reason for the reduction of formaldehyde levels is the evolution of the CNG conversion kits technology. The light duty vehicle converted fleet is the main consumer of CNG (Melo et al., 2008). Engines were projected to use gasohol or hydrated ethanol and were converted to CNG use by kit installation. These kits were first available in the beginning of the decade with the first generation model and has evolved to the fifth generation kit used nowadays, as described in detailed by Melo et al. (2008).

- First Generation: mechanical kit conceived of originally for old vehicles with carburettors (US $1000). Emulators for fuel injectors and others sensors are necessary if installed in vehicles with fuel injection systems. In this case, emissions standards cannot be met.
- Second Generation: electronic kit conceived of originally for old vehicles with carburettors and some single-point electronic fuel injection systems (US $1500). The CNG injection is controlled by a stepper motor and a microprocessor module. The module receives the load and engine speed signals to control the stepper motor action. Because the oxygen sensor signal is not available on the electronic unit, strict emission standards cannot be attained with this kit. It is possible to install an oxygen sensor emulator to disable errors on the original vehicle module.
- Third Generation: electronic kit originally conceived of for vehicles with multi- or single-point electronic fuel injection systems and with a catalyst (US $2000). This kit employs an oxygen sensor signal (lambda sensor) to control the NG injection, so that the vehicle works near the stoichiometry air/fuel ratio. It is possible to achieve national standard L3 emission limits with this kit, after a proper kit tuning.
- Fourth Generation: electronic kit originally conceived of for vehicles with multi-point electronic fuel injection systems, with a catalyst and an intake plastic collector to avoid back-fire (US $2300). It features simultaneous multi-point NG injection system that can more easily attain current emission limits. All vehicles manufactured through 2006 use this kit.
- Fifth Generation: electronic kit originally conceived of for vehicles with multi-point electronic fuel injection systems, a catalyst and an intake plastic collector to avoid back-fire, (US $2500). It features sequential multi-point NG injection system that can attain future emission limits, mainly lower NOx. All vehicles manufactured through 2007 use this kit.

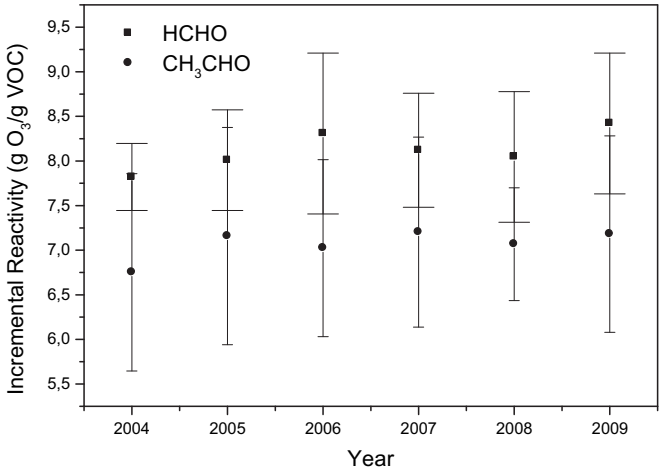

Fig. 4. Incremental reactivity for formaldehyde and acetaldehyde.

The Brazilian legislation in 2006 (CONAMA 291) indicated that CNG vehicular emissions must be lower than from using the original fuel. With these limits all first- and second-generation conversion kits were eliminated from the market.

From the scenarios presented regarding the fuel consumption, the fleet evolution, and the emissions pattern we conclude that the main reason for the reduction of the formaldehyde levels was the evolution of the conversion kit technology. At the onset of the decade the old kits were not capable of converting all methane to carbon dioxide. It was estimated by Corrêa and Arbilla (2003) that nearly 5% of the methane was not converted inside the engine and was converted by some mechanism to formaldehyde inside the three-way catalyst. With improved performance of the kits, formaldehyde emissions were reduced because of their improved methane combustion process.

Another reason for the reduction, both for formaldehyde and acetaldehyde, is the overall emissions reductions of the Brazilian fleet. The engines technology, the intensive use of three-way catalyst and a fuel with a better quality are the reasons for this emissions reduction (Corrêa and Arbilla, 2008).

4. Conclusions

The use of ethanol from sugarcane as automotive fuel since the mid-70s has lead to a well-documented increase in atmospheric acetaldehyde levels and to a high atmospheric acetaldehyde/formaldehyde ratio in comparison to the mean values in other countries. Since 1989, technological advances, such as electronic injection and catalyst converters, and reductions in gasoline prices have resulted in a decrease in these levels. Since 2000, the use of CNG was associated with an increase in formaldehyde levels. The results obtained in this work show that alongside the evolution of the conversion kit technology a further reduction in formaldehyde levels was observed. The Brazilian experience demonstrates how the impact of vehicular emissions can be reduced with the use of alternative fuels associated with technological development.

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