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Formaldehyde and acetaldehyde in a high traffic street of Rio de Janeiro, Brazil

Sérgio M. Corrêa^{a,b}, Eduardo M. Martins^a, Graciela Arbilla^{a,*}

^a Departamento de Físico-química, Universidade Federal do Rio de Janeiro, Instituto de Química, Sala 408, Ilha do Fundão, 21949-900 Rio de Janeiro, Brazil

^b Universidade do Estado do Rio de Janeiro, Campus Regional de Resende 27523-000 Resende, Brazil

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Abstract

The data for formaldehyde and acetaldehyde levels in ambient air of the city of Rio de Janeiro, obtained in the period from 4 December 1998 to 17 January 2001 is presented. A total of 28 samples were collected at a downtown area, where emissions may be mainly attributed to the vehicular fleet. Values between 1.52 and 54.31 ppb for formaldehyde and between 2.36 and 45.60 ppb for acetaldehyde were obtained. The high acetaldehyde/formaldehyde ratios (0.76 to 1.61) are a consequence of the use of oxygenated fuels. Brazilian cities are unique in that the vehicles use hydrated ethanol (over 4 million of light duty vehicles), gasohol (a mixture with gasoline and 24% v/v of ethanol) and diesel fuels. The analysis of vehicle exhaust and model simulations of the air quality in August and December 1999, confirmed that the high levels of acetaldehyde could be attributed to direct emissions of the vehicular fleet and to the photochemical initiated oxidation of organic compounds.

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1. Introduction

Air quality in urban atmospheres depends on several related factors: primary pollutants' emissions, secondary pollutants' formation and consumption, geographical and meteorological factors. Formaldehyde and acetaldehyde are the two most abundant aldehydes in ambient air and may be considered as both primary and secondary pollutants. Their sources include natural and anthropogenic emissions, mainly automobile exhaust, as well as the photochemical oxidation of volatile organic compounds. Both formaldehyde and acetaldehyde are of great significance to atmospheric chemistry due to the strong influence that these species have on the formation of nitric acid, peroxyacetyl nitrate

(PAN) and other smog components (de Andrade et al., 1998).

In the United States, the determination of ambient concentrations of carbonyl compounds is a requirement of 40 CFR, Part 58, Subpart E, enhanced ozone network monitoring programs (US-EPA, 1993). In Brazil standards values for formaldehyde and acetaldehyde concentrations have not been established and the States and local agencies have no monitoring programs.

Literature results show that, in metropolitan areas, formaldehyde is almost always the predominant aldehyde emitted by automobiles and the acetaldehyde/formaldehyde ratio is always lesser than unit. In contrast, experimental results for Brazilian cities showed acetaldehyde/formaldehyde ratios equal or higher than unit. This behavior was attributed to the use of hydrated ethanol and gasohol (gasoline with 24% of ethanol) as fuels (Nguyen et al., 2001; Grosjean et al., 1990; Tanner et al., 1988). In spite of its importance to air quality,

*Corresponding author. Tel.: +55-21-2562-7755; fax: +55-21-2562-7265.

E-mail address: graciela@iq.ufrj.br (G. Arbilla).

experimental data for Rio de Janeiro are rather sparse and mostly outdated (Martins, 2001).

The present work is concerned with the determination of formaldehyde and acetaldehyde from December 1998 to January 2001 in downtown Rio de Janeiro, where pollution can be clearly attributed to vehicular emissions.

2. Experimental methods

2.1. Sampling site description

The metropolitan area of Rio de Janeiro, located on the Atlantic coast of Brazil, has about 6 million inhabitants distributed over an area of 1255 km². The climate is tropical, hot and humid type, with local variations, due to the altitude differences, vegetation and proximity of the Atlantic Ocean and the Guanabara Bay. The annual average temperature is 22°C, with elevated daily averages in the summer (between 30°C and 32°C); rainfall varies between 1200 and 1800 mm².

The main source of pollution in the central area of the city is the vehicular fleet fueled with gasohol (gasoline with 24% v/v of ethyl alcohol), ethanol, diesel and, in minor extent, natural gas.

All the samples were collected at President Vargas Avenue, a heavy traffic avenue in downtown. Presidente Vargas Avenue carries fourteen lanes of traffic, seven in each direction. The exhaust at this avenue are representative of downtown vehicle fleet's, because the traffic includes light duty vehicles which uses ethanol (17.5%) and gasohol (66.0%) as well as diesel fueled heavy duty vehicles (16.5%), with diurnal fluxes (from Mondays to Fridays) between 6000 and 8000 vehicles/h, depending on the hour of the day (Campos et al., 1999). All the samples were collected in sunny days with a clear sky.

The samples were collected at 1.5 m above ground, beside an air quality automatic monitoring station (22°54'S and 43°10'W), which measures criteria pollutants (ozone, sulfur dioxide, nitrogen oxides, carbon monoxide, total hydrocarbons and particulate matter). Meteorological variables as direction and speed of the wind, temperature, humidity and atmospheric pressure are also monitored. Others parameters, required for photochemical modeling, such as solar radiation and mixing height were obtained at IAG-USP home page (<http://www.naster.iag.usp.br>).

2.2. Materials

Aldehydes were sampled using C₁₈ resin cartridges (Sep-Pak Classic from Waters) coated with 2,4-dinitrophenylhydrazine (DNPH). DNPH was purified by recrystallization and checked by high-performance liquid chromatography (HPLC). The aldehydes were trapped

by making them react with DNPH in the cartridges to form the corresponding stable 2,4-dinitrophenylhydrazone derivatives.

The hydrazone standards were prepared by adding a molar excess of the carbonyl compound to the saturated solution of DNPH. The formed precipitate was washed with 2N HCl and later with water and allowed to dry in an amber desiccator under vacuum for 48 h. Starting from 100 mg of the hydrazone a solution of 100 ppm was prepared, diluted with acetonitrile and stocked in a dark flask in a refrigerator.

As related by several authors (de Andrade et al., 1998; Possanzini and Di Paolo, 1997; Grosjean and Grosjean, 1996; Grosjean et al., 1996; Miguel et al., 1995; Pires and Carvalho, 1998), ozone represents a serious interference in the carbonyl compounds sampling when cartridges impregnated with DNPH are used. This influence is more pronounced for compounds with more than four carbon atoms. Ozone interference occurs in three ways:

- Ozone reacts with DNPH of the cartridge making it unavailable for derivating carbonyl compounds;
- ozone degrades the hydrazones formed during the sampling (mainly high molecular weight and unsaturated species) and
- these derived, degraded compounds can coelute with the target hydrazones during the analysis.

The extent of ozone interference will depend on the duration of the sampling and on the concentration of ozone. Carbonyl compound losses have been estimated to be > 48% for a concentration of 120 ppb of ozone for an hour of sampling (Beasley et al., 1980).

In this work a denuder scrubber with potassium iodide as the scrubber agent was used.

2.3. Sampling procedure

The sampling system contained a pump provided with a battery, a flow meter, the cartridge with C₁₈ resin impregnated with DNPH, the ozone scrubber and tygon tubes. The sampling system was run for 2 h at the flow rate of 1.0 l/min.

2.4. Analytical method

The sampled material was eluted from the cartridges by washing with 4 ml of acetonitrile. The liquid was collected in amber vials and weighed to obtain the solution volume. An aliquot of 25 µl of this solution was injected in a Rheodine injector model 7125 with a sampling loop of 20 µl. A Varian Chrompack C₁₈ column, with particle size of 5 µm with 25 cm of length, and a GBC UV-VIS detector model LC1210 at 365 nm were used. A series of standards of 2 up 15 mg/l were used to obtain the calibration curve for each

composition. In general, a minimum correlation coefficient of 0.999 was considered acceptable.

3. Results and discussion

A total of 28 samples were collected from 1998 to 2001. Results are presented in Table 1 and in Fig. 1. In Fig. 1, samples taken on the same day are presented as a mean value for the date.

The data in Table 1 and Fig. 1 show only results for formaldehyde and acetaldehyde, though other carbonyls compounds were also identified. Acrolein, acetone, benzaldehyde, crotonaldehyde and propionaldehyde were also quantified, but these data will be reported elsewhere.

Values found for formaldehyde mixing ratios do not differ very much from data reported in other cities, both in Brazil and other countries. As in previous reports, the values found for Brazilian cities are higher than the ones measured elsewhere in the world. As reported by

Grosjean et al. (1990, 1996), the average acetaldehyde/formaldehyde ratio for 250 samples taken in urban areas of the USA was found to be 0.44. The ratio for 350 samples for European urban areas was 0.33. In most reports of Brazilian cities, encountered in the literature, this ratio is equal or > 1 . Similar results were obtained in this work for Rio de Janeiro and in a recent report of the city of São Paulo (Nguyen et al., 2001).

As previously described, these high values for acetaldehyde may be attributed to the composition of fuels used by the vehicular fleet of Brazilian cities. The incomplete combustion of ethanol results in the acetaldehyde emission in larger scale than formaldehyde, both in cars powered by hydrated ethanol and in cars powered by gasohol. However, there is no correlation between acetaldehyde and primary pollutants concentrations, as illustrated in Table 2 for the period 2–6 August 1999. Also CO peak is always obtained earlier than acetaldehyde maximum. As it will be discussed later, these data suggest that acetaldehyde is both a primary and a secondary pollutant.

To confirm these hypotheses, measurements were performed in the exhaust of three cars powered by ethanol and three cars moved by gasohol. The ethanol powered cars were a 1992 Fiat Uno Mille, a 1995 Volkswagen Logus and a 1994 Ford Verona. These cars, rather old, are representative of Rio de Janeiro ethanol fleet where ethanol use is being reduced. The gasohol powered cars were a 1996 Fiat Uno Mille, a 1997 Fiat Uno Mille and a 2000 Fiat Siena. These vehicles represent typical cars in the Rio de Janeiro light duty vehicular fleet. Since carbonyls concentration in the exhaust is higher than in ambient air, some modifications were introduced in the sampling methodology. The first modification was the impregnation of the cartridges with the saturated solution of DNPH diluted just 5 times with acetonitrile to increase the retention capacity of the carbonyls on the cartridge. Air was sampled using a 10 l bag of black Tedlar placed directly at the exhaust pipe with the cars' gearshift in neutral and with the engine at 800 rpm. The air contained in this bag was then immediately sampled at a flow rate of 1.0 ml/min with two cartridges in series and with the ozone scrubber. The cartridges were eluted with acetonitrile and then analyzed. Since de exhaust gas contains high concentrations of water vapor, which condenses in the bag and dissolve aldehydes, the measured concentrations are a lower limit. The second cartridge did not indicate the presence of carbonyls showing the efficiency of the collection system. A new calibration curve with more concentrated standards was determined. The average results for automobiles are shown in Fig. 2. Results for pure gasoline were not obtained because it is not in use in Brazil.

Clearly, the results in Fig. 2 may be considered a rough estimate of the composition of the exhaust since a

Table 1
Experimental acetaldehyde and formaldehyde concentrations obtained in Rio de Janeiro for the period December 1998–January 2001

Sample	Date	Period	HCHO (ppb)	CH ₃ CHO (ppb)
1	4/12/1998	8:00–10:00 h	10.40	8.45
2	4/12/1998	10:00–12:00 h	19.27	22.02
3	4/12/1998	12:00–14:00 h	26.41	28.05
4	4/12/1998	14:00–16:00 h	21.77	26.43
5	2/8/1999	8:00–10:00 h	4.72	4.96
6	2/8/1999	10:00–12:00 h	5.07	5.36
7	2/8/1999	12:00–14:00 h	4.34	4.38
8	3/8/1999	8:00–10:00 h	4.20	6.18
9	3/8/1999	10:00–12:00 h	3.84	4.70
10	3/8/1999	12:00–14:00 h	4.25	6.32
11	4/8/1999	8:00–10:00 h	1.70	2.80
12	4/8/1999	10:00–12:00 h	2.04	3.14
13	4/8/1999	12:00–14:00 h	1.52	2.36
14	5/8/1999	8:00–10:00 h	2.02	2.66
15	5/8/1999	10:00–12:00 h	3.04	4.11
16	5/8/1999	12:00–14:00 h	2.21	3.72
17	6/8/1999	8:00–10:00 h	5.18	8.37
18	6/8/1999	10:00–12:00 h	3.92	8.70
19	6/8/1999	12:00–14:00 h	2.95	5.56
20	14/8/2000	6:00–9:00 h	8.88	7.13
21	15/8/2000	6:00–9:00 h	10.24	8.46
22	16/8/2000	6:00–9:00 h	10.47	9.60
23	18/10/2000	8:00–10:00 h	10.70	8.39
24	14/11/2000	8:00–10:00 h	30.47	30.52
25	14/11/2000	10:00–12:00 h	30.15	27.87
26	17/1/2001	8:00–10:00 h	47.19	38.96
27	17/1/2001	10:00–12:00 h	54.31	45.60
28	17/1/2001	12:00–14:00 h	52.09	39.40

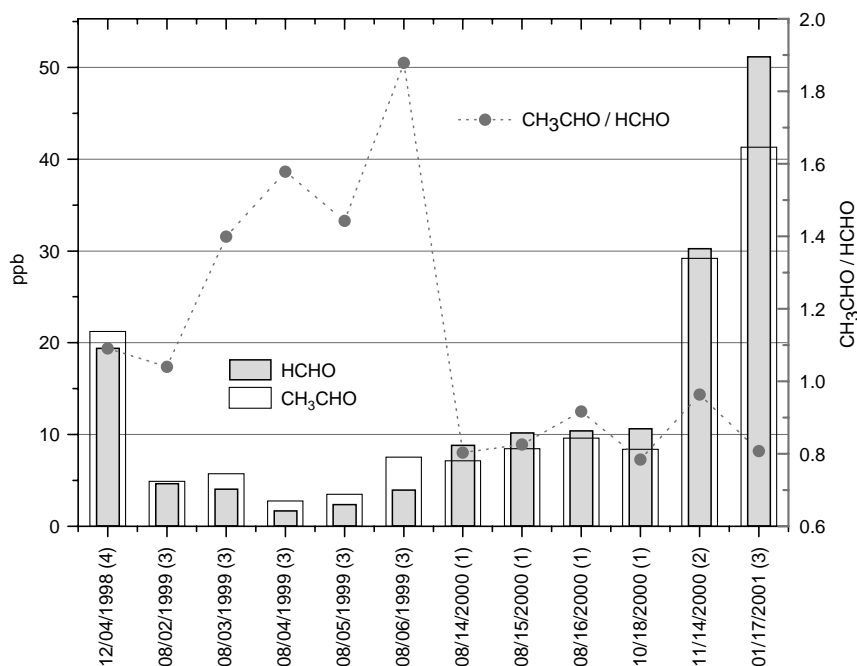


Fig. 1. Acetaldehyde and formaldehyde concentrations (ppb) obtained in Rio de Janeiro for the period December 1998–January 2001 (left vertical axis). Also acetaldehyde/formaldehyde ratios (in a ppb basis) are show (right vertical axis). The number in parenthesis is the number of samples taken each day.

Table 2

Experimental results, for the period 2/8/1999 to 6/8/1999, for formaldehyde (ppb), acetaldehyde (ppb), CO (ppm) and total NO_x (ppb). Concentrations are mean values for each time period. CO and NO_x concentrations were obtained by FEEMA monitoring station

Date	Period	HCHO (ppb)	CH ₃ CHO (ppb)	CO (ppm)	NO _x (ppb)
2/8/1999	8:00–10:00 h	4.72	4.96	0.55	74.0
2/8/1999	10:00–12:00 h	5.07	5.36	1.25	73.0
2/8/1999	12:00–14:00 h	4.34	4.38	1.10	62.5
3/8/1999	8:00–10:00 h	4.20	6.18	3.00	149.5
3/8/1999	10:00–12:00 h	3.84	4.70	1.90	72.0
3/8/1999	12:00–14:00 h	4.25	6.32	1.25	44.5
4/8/1999	8:00–10:00 h	1.70	2.80	4.50	159.0
4/8/1999	10:00–12:00 h	2.04	3.14	2.35	96.5
4/8/1999	12:00–14:00 h	1.52	2.36	2.05	115.5
5/8/1999	8:00–10:00 h	2.02	2.66	2.30	175.0
5/8/1999	10:00–12:00 h	3.04	4.11	1.5	148.0
5/8/1999	12:00–14:00 h	2.21	3.72	0.45	43.0
6/8/1999	8:00–10:00 h	5.18	8.37	1.65	133.5
6/8/1999	10:00–12:00 h	3.92	8.70	2.1	142.5
6/8/1999	12:00–14:00 h	2.95	5.56	0.95	71.5

dynamometer was not used and the driving schedule recommended by US-EPA was not followed, because they were not within the scope of this work. Nevertheless, it is clear that acetaldehyde emissions from ethanol and gasohol are significantly higher than formaldehyde ones, affecting the hydrocarbon mixture in urban atmosphere. Similar acetaldehyde/formaldehyde

ratios were obtained by Miguel and de Andrade (1990) for two typical Brazilian ethanol-fueled vehicles. In a recent article published by Schifter et al. (2001a) emissions from MTBE (5 vol%)-and ethanol (3,6,10 vol%)-gasoline blends were also evaluated. The authors found a considerable increase of acetaldehyde emissions (80–104%) regardless of the emission control

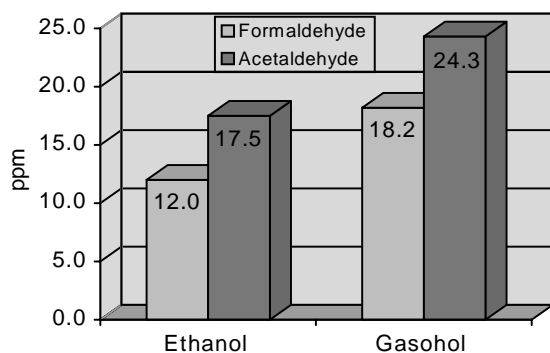


Fig. 2. Acetaldehyde and formaldehyde concentrations (ppm) determined in car exhaust.

technology in the fleet. An extra source of both, acetaldehyde and formaldehyde is the OH radical reaction of volatile organic compounds (VOC). Finally, both compounds can undergo photolysis and oxidation by OH radical. The main reaction path for acetaldehyde is hydrogen abstraction by OH radical leading to the formation of radicals which may be further oxidized to formaldehyde or may form peroxyacetyl nitrate. In hot urban systems, with high NO concentrations, the formed PAN can decompose to form formaldehyde again (Gaffney and Marley, 2001; Schifter et al., 2001b).

Previously published works show an acetaldehyde/formaldehyde ratio of 0.3–1.2 for Rio de Janeiro in 1985 (Tanner et al., 1988), 0.8–3.4 for São Paulo in 1988 (Grosjean et al., 1990) and 1.61–3.84 for Salvador in 1988 (Grosjean et al., 1990). In 1992, de Andrade et al. determined values between 0.37 and 1.67 in Salvador (de Andrade et al., 1998). In 1998, an average ratio of 1.1 was obtained for São Paulo (Nguyen et al., 2001). Our data, between 0.76 and 1.61, are, in general, lower than the ratios in the 1980s. These results are also a consequence of fuel use: in 1989 about 50% of light duty vehicles in Brazil used hydrated ethanol. In 1995, about 29% of vehicles used ethanol. Nowadays only about 20% of vehicles run on ethanol in Rio de Janeiro, 17% in Porto Alegre and 28% in São Paulo (CETESB, 2001; Nguyen et al., 2001; Campos et al., 1999).

Some air quality simulations were also performed in order to obtain a qualitatively description of the system and help the interpretation of the experimental results. A trajectory model, implemented in OZIPR code (Gery and Crouse, 1990) was used. In this model a well-mixed box is moved at average wind speed along a trajectory through the urban area. As the box moves, its height increases due to the mixing height rise 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 of the box increasing the concentrations of primary species.

The photochemical model SPRAC (Carter, 1990) was used. This model has been extensively studied and validated and has been used in many computer simulations of urban air quality in the United States and elsewhere. Reactions of ethanol were included and stoichiometric coefficients and rate constants were recalculated for a VOC mixture characteristic of Brazilian cities. Also, reaction rate coefficients were updated by Martins (Martins, 2001). The VOC/NO_x/CO emission ratios were calculated in consistence with the vehicle emission inventory for Rio de Janeiro City and the local vehicle flux (VOC/CO=0.173 and NO_x/CO=0.157, both on mass basis) (Campos et al., 1999). Other details about the model can be found elsewhere (Martins et al., 2002). The model was calibrated using experimental CO concentrations obtained in the same local of the aldehydes sampling, during August and December 1999. Initial concentrations and the meteorological data from the monitoring station and emission inventory data from literature were used. An acetaldehyde/formaldehyde emission ratio of 1.0 was used (Martins, 2001; Martins et al., 2002).

As an example, experimental and simulated results for December 1999 are shown in Table 3. Experimental data were collected by FEEMA (FEEMA, 1999), at the monitoring station, between 1 December and 29 December 1999. For December, the simulation indicated an ozone peak at 3:00 PM (22.98 ppb), which is in good agreement with experimental results for December 1999 that show maximum ozone mixing ratios between 5.0 and 35.0 ppb, peaking at about 2:00 PM, and with a mean maximum value of 19.1 ppb. Similarly, for August, a maximum ozone mixing ratio was obtained at 2:46 PM (15.29 ppb) in good agreement with experimental data.

Calculated acetaldehyde and formaldehyde peaks were centered between 10:00 and 12:00 AM, depending on the modeling conditions, in good agreement with experimental results. Both, experimental and calculated, formaldehyde and acetaldehyde peaks were obtained after the CO maximum (about 9:00 AM), which coincides with the peak automobile traffic. Further, the aldehyde's maximum value were obtained prior to the ozone peak (at about 3:00 PM). This fact may be interpreted as an indication of both primary and secondary sources of aldehydes in Rio de Janeiro ambient air. (Table 4).

Also, as a general trend, concentrations are higher in the summer than in the winter, which may be interpreted as a consequence of photochemical formation of both, acetaldehyde and formaldehyde, through the photochemical oxidation of volatile organic compounds. The acetaldehyde/formaldehyde ratio is higher in the winter suggesting a slower photochemical decomposition and oxidation of acetaldehyde leading to formaldehyde.

Table 3

Input meteorological parameters for the simulation of the base case (mean experimental values for December 1999). Experimental results (mean values for the period December 1–29) for CO and ozone obtained at the monitoring station in the year of 1999. Values in parentheses are the standard deviations. Simulated results were calculated for 21 December 1999

Hour	Relative humidity (%)	Temperature (°C)	CO (ppm)		Ozone (ppb)	
			Experimental	Simulated	Experimental	Simulated
8:00	69.18	24.74	1.66 (0.69)	1.70	0.12 (0.34)	0
9:00	65.13	25.72	2.31 (0.88)	2.23	0.60 (1.05)	2.64
10:00	63.46	26.76	2.21 (0.97)	2.21	3.60 (5.19)	4.08
11:00	60.80	27.54	1.90 (0.88)	2.09	9.87 (11.24)	7.43
12:00	57.12	28.65	1.76 (0.81)	1.81	13.94 (12.73)	10.26
13:00	54.56	29.16	1.52 (0.70)	1.62	17.75 (17.26)	14.98
14:00	51.93	29.50	1.13 (0.46)	1.22	19.10 (13.68)	20.78
15:00	51.46	29.54	1.11 (0.51)	1.23	15.00 (10.45)	22.98
16:00	50.81	29.17	0.89 (0.28)	1.24	13.25 (6.41)	22.14

Table 4

Acetaldehyde and formaldehyde concentrations, for 21 December 1999, calculated using the OZIPR model and the conditions of Table 3 (see text for details)

Hour	Acetaldehyde (ppb)	Formaldehyde (ppb)	Acetaldehyde/formaldehyde ratio
8:00	5.60	5.60	1.00
9:00	11.41	9.37	1.21
10:00	16.1	11.87	1.40
11:00	21.65	14.59	1.48
12:00	20.61	14.52	1.42
13:00	20.30	14.78	1.37
14:00	14.36	11.10	1.29
15:00	14.79	11.98	1.23
16:00	14.81	12.57	1.17

Simulated results gave acetaldehyde/formaldehyde ratios higher than 1.0 for both scenarios with a maximum value between 1.40 and 1.45, located between 11:00 AM and 1:00 PM. This ratio peaks earlier in the summer than in the winter and depends on the effective solar flux and the vehicular emissions, which again, confirms that the aldehydes have primary and secondary sources. Computed results, which will be published later (Martins, 2001), confirm that the main source of aldehydes, in the morning, is the direct emission by vehicles, while in the afternoon, aldehydes are mainly formed by photooxidation of volatile organic compounds. The combined effect is the lack of correlation between CO and aldehydes concentrations.

The results showed that, using simulation conditions representative of the Rio de Janeiro summer period, aldehydes, mainly formaldehyde, have a significant contribution to the formation of ozone (Martins et al., 2002). Different ranking scales of photochemical reactivity have been proposed (Carter, 1990). In a kinetic scale the rate of consumption of OH radicals is usually considered. Simulation results for 3:00 PM show that

carbon monoxide, acetaldehyde, formaldehyde and propene are the most reactive species. The amount of ozone attributable to each reaction species can also be estimated. Examining ozone formation after an increase of 1 ppb in the mixing ratio of individual volatile organic compounds, the most productive species are found to be higher aromatics, xylenes, higher alkenes, formaldehyde and propene. The high formaldehyde efficiency is not only due to the direct reactions of HCHO but mainly to the improvement of the ozone-forming capability of the entire mixture (i.e. the reaction of the free radical species).

4. Conclusions

Experimental data for Rio de Janeiro City show relatively high ambient levels of acetaldehyde and acetaldehyde/formaldehyde ratios higher than those measured elsewhere in the world. These results are in good agreement with literature data and may be

explained by the use of alcohol-based fuels for automobiles.

Both, experimental and calculated results show that there are primary and secondary sources of aldehydes in Rio de Janeiro ambient air. The acetaldehyde/formaldehyde ratio changes depending upon the solar flux, vehicular emissions and temperature. Aldehydes concentrations also affect the rate of ozone formation and OH radical consumption.

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