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Volatile Organic Compounds in a Residential and Commercial Urban Area with a Diesel, Compressed Natural Gas and Oxygenated Gasoline Vehicular Fleet

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Abstract Air samples were collected in a typical residential and commercial area in Rio de Janeiro, Brazil, where buses and trucks use diesel and light duty vehicles use compressed natural gas, ethanol, and gasohol (gasoline blended with ethanol) as fuel. A total of 66 C_3–C_{12} volatile organic compounds (VOCs) were identified. The most abundant compounds, on a mass concentration basis, included propane, isobutane, i-pentane, *m*,*p*-xylene, 1,3,5-trimethylbenzene, toluene, styrene, ethylbenzene, isopropylbenzene, *o*-xylene and 1,2,4-trimethylbenzene. Two VOCs photochemical reactivity rankings are presented: one involves reaction with OH and the other involves production of ozone.

Keywords Vehicular emissions · VOCs reactivities · Urban pollution

Volatile organic compounds (VOCs) are emitted from anthropogenic sources, such as vehicles and industries and also from biogenic sources. In urban environments the emission of C_2–C_4 hydrocarbons (HC) from motor vehicles has been recognized as the main contribution to total HC inputs (Na et al. 2003). A detailed emission inventory and a explicit chemical mechanism were used to describe photochemical ozone formation in the United Kingdom and North West Europe (Derwent et al. 2007).

VOCs play an important role in atmospheric chemistry (Carter 1990). The reactions of VOC with hydroxyl radical, OH, lead to the enhancing of the NO oxidation to NO_2. In turn, NO_2 is photolyzed to form ozone by combining with atmospheric oxygen (Carter 1994; Grosjean et al. 1998a, b; Finlaysson-Pitts and Pitts 2000). These reactions also lead to other gas-phase photochemical oxidants including peroxyacyl nitrates, carbonyls, carboxylic acid and secondary aerosols (Finlaysson-Pitts and Pitts 2000). Beside their role in urban atmospheric chemistry, VOCs have received attention for their possible adverse health effects (e.g. benzene, 1,3-butadiene and chlorinated hydrocarbons) (Jo and Song 2001).

Alkenes and alkynes, mainly ethane and ethyne, are characteristic products of internal combustion engines, while saturated C_5–C_8 hydrocarbons are generally associated with unburned vehicular emissions (Mayrsohn and Crabtree 1976). Alkanes are characteristic of gasoline evaporation and natural gas leakage (Blake and Rowland1995; Chen et al. 2001; Barletta et al. 2002) while aromatic hydrocarbons come both from fuel combustion and evaporation of fuels and solvents (Barletta et al. 2005).

Many studies of VOCs composition in urban areas have been carried out around the world (see for example, Grosjean et al. 1998a, b; Sharma et al. 2000; Barletta et al. 2002; Chan et al. 2002; Na et al. 2003; Chan et al. 2003; Barletta et al. 2005; Guo et al. 2007; Qin et al. 2007).

In Brazil 75% of the population lives in cities, while in Rio de Janeiro, this figure gets to 95%. Thus, urban

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pollution is of major concern. According to regulatory agencies, in the Metropolitan Region of Rio de Janeiro (MRRJ), 77% of the emissions of total pollutants and 98% of total carbon monoxide are due to vehicles (FEEMA 2007). Literature data suggest that urban atmosphere composition is closely related to the use of vehicular fuels (Miguel 1991). In the MRRJ, the total number of vehicles increased from 1,570,000 in January 2001 to 1,890,000 in January 2005. In 2004–2005, 73% of vehicles used gasohol (gasoline with 24% of ethanol), 13% used neat ethanol, 8.5% used compressed natural gas (CNG) and 3.5% diesel (DETRAN 2008). These figures were slightly changed in the last years. In January 2008, the total fleet was about 2 million vehicles, with 61%, 11% and 8.7% of vehicles using gasohol, neat ethanol and CNG, respectively. Many of the new cars can alternatively use gasohol or ethanol (10%) and gasohol, ethanol or CNG (2%) (DETRAN 2008).

Few works have been published for Brazilian cities so far (Grosjean et al. 1998a, b; Gatti et al. 2006; Vivanco and Andrade 2006). Also, unpublished data were obtained for Rio de Janeiro downtown. In this study the composition and reactivity of VOCs in the atmosphere of Tijuca, a typical residential and commercial area in Rio de Janeiro, are presented.

Materials and Methods

The city of Rio de Janeiro has about 6 million inhabitants distributed over a 1224.6 km^2 area. The city is located on the Atlantic coast of Brazil (latitude, 22°45′ 05″ S, North city limit, and 23°04′ 10″ S, South city limit, and longitude, 43°06′ 30″ W, East city limit, and 43°47′ 40″ W, West city limit). The climate is tropical, hot and humid, with local variations due to the proximity to the Atlantic Ocean, Guanabara Bay and Tijuca National Park, one of the biggest urban forests in the world. The annual average temperature is 23.7°C, and annual rainfalls are about 1200 mm. Tijuca District is located at about 2 km from the Tijuca National Park and the Tijuca Massive. The region has an area of 10 km^2 and a population of about 160,000 inhabitants.

All samples were collected at Saens Peña Square (22°55′ 48″ S, 43°13′ 64″ W), a commercial central area of Tijuca District with a high flux of vehicles, mainly light duty vehicles which use ethanol, 14.6%, gasohol, 78% and CNG 7.4%. Depending on the time of day, buses represent 7–20% of the total fleet. Also, a terminal subway station with about 80,000 passengers/day is located at this square. No industrial activities are developed in the area. Due to the proximity of the Tijuca Massive, the region is poorly ventilated. Emissions may be mainly attributed to vehicular sources. Samples were collected at 1.5 m above the ground.

Sampling was performed in 4 days (March 26, 29 and 30 and May 17 of 2004 at three different times (9:00 a.m., 11:00 a.m. and 1:00 p.m.). 1.8 L electropolished, stainless-steel, evacuated canisters were used for sampling. To collect each whole air sample, a stainless-steel valve was slightly opened and the canister was filled to ambient pressure in about 2 min. The samples were analyzed within 3 days.

Gas chromatography with flame ionization detection (GC-FID) and gas chromatography–mass spectrometry (CG–MS) were used to analyse the samples. The method follows U.S. EPA guidelines (U.S. EPA Compendium TO-14 Method 1997). Briefly, 100 mL aliquots of air from the canister samples were loaded on a cryo-trap (glass beads in 6″ × 1/8″ stainless-steel tubing) in liquid nitrogen ($T = -180°C$), desorbed from the cryo-trap at ca. 400°C and 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 in two and analyzed simultaneously using 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 Data Base. Quantitative analysis was performed using standard mixtures of alkanes (propane, butane, pentane and hexane) (White Martins), alkenes (ethene, propene, butene, pentene and hexene) (White Martins), aromatics (benzene, toluene, *o*-xylene and ethylbenzene) (Scott Specialty) and a TO-14 standard mixture (Scott Specialty). Cylinders contained approximately 1 ppmv of each of the target compounds. Five standards (in the range 0.2–5.0 ppbv) were prepared, as recommended in TO-14 Method. Detection limits (D.L.) were determined using the data of the calibration curve (Ribani et al. 2004). All values were in the range 0.075–0.125 ppbv. The performance of the chromatographic system was audited using a TO-14 standard mixture. After analysis, results were converted to mass units. All samples were run by duplicate and the difference was lower than 5%. Blank runs were also performed before each sample analysis.

Results and Discussion

Results for the sampling site are shown in Table 1. Each hour values are the average of four samples run by duplicate. A total of 66 C_3–C_{12} VOCs were identified. In general, alkanes in the range C_8–C_{12}, C_5–C_6 alkenes, cycloalkanes and cycloalkenes were under the detection limit.

Total VOCs concentrations of the determined compounds were 46.3, 45.9 and 26.7 ppbC at 9:00 a.m., 11:00 a.m. and 1:00 p.m., respectively. In mass units these values are: 220.5, 229.5 and 133.8 μg m^{-3}, respectively.

In mass units, the main compounds determined at 9:00 a.m, in order of decreasing concentrations were propane, isobutane, 2-methyl butane, *m*,*p*-xylene, 1,3,5-trymethyl benzene, toluene, styrene, ethylbenzene, isopropylbenzene, *o*-xylene and 1,2,4-trimethylbenzene. Methane and C_2 compounds were not quantified because of the experimental set up. On a ppbC basis, aromatics, alkanes and alkenes represent 44.3%, 39.8% and 12.0%, respectively. The distribution of compounds was rather different at 11:00 a.m. and 13:00 p.m. On a ppbC basis the five more abundant compounds determined at 11:00 a.m. were 2-methyl-butane, toluene, 2-butene, isobutane and n-butane. At 13:00 p.m., the total VOC concentration was significantly lower. This result may be due to several reasons: vehicular flux is significatively lower during the afternoon, meteorological data show that, in general wind speed and pollutant dispersion are higher in the afternoon and reactive VOCs are highly vulnerable to reaction with OH radical. These results are in good agreement with data obtained for Porto Alegre (Brazil) by Grosjean et al. (1998b). Unpublished results indicate that the main composition of gasoline exhaust in Brazil is about 44.7% aromatics, 24.5% alkanes and 20.2% alkenes, confirming that the main emission source in this area is the vehicular fleet.

The relative reactivity of individual VOCs at 9:00 a.m. was evaluated using reactivity scales. Different ranking scales of photochemical reactivity may be built. In a kinetic scale, the reaction with OH is evaluated by multiplying the reactive species concentration by the corresponding specific OH reaction rate coefficient. This is portrayed by the second entry in Table 2 and is indicative of the efficiency of OH removal by the reactive species, leading to carbonyls and radicals. Another approach is the ranking of organic compounds in terms of their potential for ozone production. The ozone-forming potential may be treated in terms of the incremental reactivity (IR) which is the product of the kinetic and the mechanistic reactivities and is defined as the number of molecules the ozone formed per VOC carbon atom added to an initial atmospheric reaction mixture of VOCs and NOx. The peak IR value of a VOC is known as its Maximum Incremental Reactivity (MIR). The MIR scale was developed by Carter (1994) and MIR coefficients are reported in grams of ozone per gram of VOC added. The products of the MIR coefficients and the compound concentrations are shown in the last entry of Table 2 and indicate how much the compound contributes to ozone formation in the air mass. It is important to note that IR coefficients depend on the VOC/NOx ratio and, for this reason, results presented in this work are only indicative values and more precise ones should be evaluated for the particular case of Rio de Janeiro. In this work the upper limit MIR, estimated by Carter (1994) using the SAPRC-99 mechanism were used.

Although propane and isobutane are the most abundant compounds in a concentration (ppbC units) basis, they are

Table 1 Compounds identified in canister samples collected in Tijuca, Rio de Janeiro

	09:00 a.m.	11:00 a.m.	01:00 p.m.
Alkanes			
Propane	29.1	5.1	N.D.
Butane	<D.L.	14.2	8.7[a]
Pentane	N.D.	12.7	15.1
Hexane	5.5	6.0	2.8
Heptane	5.1	3.1	<D.L.
Nonane	1.7	1.2	<D.L.
Isobutane	20.5	15.1	8.2
2-Methyl-butane	19.3	21.9	8.7
2-Methyl-pentane	7.8	4.9	0.8
3-Methyl-pentane	1.4	1.6	<D.L.
3-Methyl-hexane	0.9	0.3	N.D.
3-Ethyl-hexane	1.1	1.5	<D.L.
Alkenes			
Propene	6.6	8.7	N.D.
Butene	2.9	15.4	N.D.
Isobutene	2.6	0.9	<D.L.
Methyl butene	2.5	4.7	0.1
Styrene	13.5[a]	12.7	N.D.
1,3-Pentadiene	N.D.	0.7	3.0
Aromatic compounds			
Benzene	6.6	4.8	1.5
Toluene	14.9	15.6	10.8
Ethylbenzene	11.2	10.6	2.4
m,*p*-Xylene	16.1	11.9	6.3
o-Xylene	8.2	5.0	5.1
1-Ethyl-2-methyl-benzene	N.D.	<D.L.	8.5
1-Ethyl-3-methyl-benzene	5.8	7.1	6.0
1-Ethyl 4-methyl-benzene	N.D.	N.D.	9.1[a]
Isopropyl-benzene	10.5	13.3	12.4[a]
1,3,5-Trimethyl-benzene	15.9	9.9	8.7
1,2,4-Trimethyl-benzene	7.9	7.2	8.4
1,x-Diethyl-benzene	5.8	2.2	N.D.
Cycloalkanes			
Ethyl-cyclopropane	0.2	N.D.	N.D.
1,y-Dimethyl-cyclopropane	5.4	N.D.	0.6
1,x-Dimethyl-cyclopropane	<L.D.	6.3	N.D.
Cyclohexane	N.D.	1.9	N.D.
Methyl-cyclopentane	2.0	3.5	<D.L.
Methyl-cyclohexane	1.4	0.1	<D.L.

Table 1 continued

	09:00 a.m.	11:00 a.m.	01:00 p.m.
Other compounds			
1-Chloro-2-methyl-propane	N.D.	N.D.	3.9
Trichlorofluoromethane	N.D.	N.D.	3.4

Each value is the average of four samples run by duplicate. Concentrations are reported in µg m^{-3}

Octane, decane, undecane, dodecane, 2,5-dimethyl-hexane, 2-methyl-nonane, 1-pentene, 1-hexene, 2-methyl-1-pentene, 3-methyl-hexene, acetone, 2-methyl-propanol, n-butanal, 3-methyl-butanal, methyl-isobutyl-ketone, hexanal, octanal, dimethyl-cyclopentane, dimethyl-cyclohexano, cyclopentene, methylcyclo-pentene, 1-3-cyclopentene, naphthalene and limonene were under their detection limits in all samples. Reported butane concentrations are for the integrated value of all isomers

<D.L. under detection limit, *N.D.* not found in those samples

[a] Determined in only one sample

not the major contributors to ozone production and to OH removal. Ranking with respect to ozone production yields, in general, results which are substantially different from those for reaction with OH. Anyway, styrene, trimethylbenzene, propene and *m*,*p*-xylene are the top-ranking compounds. Using the MIR scale, the top compounds are styrene, *m*,*p*-xylene and 1,3,5 trimethylbenzene.

CO concentrations determined, at 9:00 a.m., in the monitoring station where samples were collected, ranged from 0.25 to 2.0 ppm during the sampling period. Using the OH scale, values between 1.29 and 10.33 are obtained for CO. Considering the MIR scale values between 128.8 and 1030.4 are obtained. Theses values indicate that, in spite of its low rate coefficient (k_{OH}), CO has an important role in the removing of OH radicals and in the ozone production due to its relatively high concentration.

In the same period and location, formaldehyde and acetaldehyde concentrations were determined (Martins et al. 2007). Mean concentrations of formaldehyde and acetaldehyde were 151 and 30 ppb, respectively. Using the k_{OH} values, 2.5×10^{-11} and 2.1×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for formaldehyde and acetaldehyde, respectively, OH removals of 92.86 and 15.50 are obtained. Theses values are 24 and 4 times higher than those calculated for styrene. Using the MIR coefficients (15.81 and 21.36 for formaldehyde and acetaldehyde, respectively) the values 2929.23 and 1155.80 are calculated. These values are 18 and 7 times higher than those obtained for styrene.

The high concentrations of aldehydes and the high formaldehyde/acetaldehyde ratios were attributed to extensive use of compressed natural gas (80%–90% methane) that is catalytically converted to formaldehyde in the exhaust pipe (Corrêa and Arbilla 2005; Martins et al. 2007). Ethanol-powered vehicles also contribute to aldehyde emissions, mainly of acetaldehyde which is formed by the reactions of ethanol with OH. These VOCs data confirm that in this scenario the most significant sources of ozone are formaldehyde and acetaldehyde and contribution of other organic compounds is not significant. In fact, oxygenated compounds account for about 80% of the VOCs mixture (in a ppbC basis). The contribution of aromatic compounds may be explained as a consequence of the composition of Brazilian gasoline which is rich is this type of compound.

The relative low levels of VOCs in comparison with previously determined values for formaldehyde and acetaldehyde and with data for other urban areas are probably due to the extensive use of alternative fuels (ethanol and

Table 2 Relative reactivity of main VOCs

Compound	k_{OH} cm^3 $molecule^{-1}$ s^{-1}	Cc × k_{OH}	MIR	MIR × Cm
m,*p*-Xylene	2.4×10^{-11}	1.18	15.15	131.65
1,3,5-Trimethylbenzene	5.8×10^{-11}	2.57	13.48	123.7
Propene	3.1×10^{-11}	1.68	23.87	90.42
o-Xylene	2.4×10^{-11}	0.59	14.55	63.20
Toluene	5.9×10^{-11}	0.30	12.07	94.48
1,2,4-Trimethylbenzene	3.3×10^{-11}	0.07	13.94	61.68
Isobutane	2.2×10^{-12}	0.22	3.62	35.27
Styrene	6.6×10^{-11}	3.90	16.13	164.98
Ethylbenzene	7.1×10^{-12}	0.24	11.53	70.11
Butene	3.6×10^{-11}	0.71	23.92	43.91
Isobutene	5.8×10^{-11}	1.0	23.95	38.47
Methyl butene	3.7×10^{-11}	0.05	23.92	34.29
Isopropylbenzene	6.5×10^{-12}	0.27	9.71	79.14
Propane	1.1×10^{-12}	0.26	2.61	45.66

Cc Concentrations in molecule cm^{-1}, *Cm* concentration in µg m^{-3}

compressed natural gas). Aromatic compounds represent the most abundant group in good agreement with gasoline composition in Brazil.

This is, to our knowledge, the first study of NMCHs composition for Rio de Janeiro. This data may be useful as an input to photochemical models (ozone formation) and other air quality and fuel policy related studies of air pollution control in Brazil. Brazilian government policies to reduce emissions were effective in the reduction of particulate matter and CO levels. Also national legislation was effective in the reduction of aldehydes from new ethanol and gasohol cars. On the other way no legislation is available for the control of aldehydes atmospheric levels and formaldehyde emissions from CNG vehicles. This fact leads to unusual high concentrations of aldehydes, mainly formaldehyde, which are important ozone precursors. Many studies have focused the emissions of criteria pollutants but very little is known about VOCs emissions. The results of this study may contribute to the knowledge of ozone precursors in this kind of atmosphere. These data may be used as a guideline to other countries which are planning to introduce alternative fuels such as CNG or renewable sources such ethanol and ethanol-blended gasoline.

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