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Volatile Aromatic Compounds in a Light-Duty Vehicle Tunnel in Rio de Janeiro, Brazil

M. C. S. Machado · J. C. S. Almeida · E. M. Martins · G. Arbilla

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The city of Rio de Janeiro represents the second largest running fleet in Brazil, roughly 1.9 million passenger cars and commercial vehicles. Presently, 73% of vehicles use gasohol (gasoline with 23% of ethanol), 13% use neat ethanol, 8.5% use compressed natural gas (CNG) and 3.5% diesel (DETRAN 2006).

According to the most recent available official emission approximately 76% of the total air pollution load of CO, SO_2, NO_x and PM-10 are direct contributions of the mobile sources. In the case of hydrocarbon gases and CO, 67% and 98%, respectively, come from vehicles (FEEMA 2004). Analysis performed in 1999, considering fueld sold by the main distributors in São Paulo (Brazil), showed that gasohol contains about 24.9% ethanol, 22.4 olefins, 12.2% aromatics and 0.37% benzene (Andrade et al. 2004).

Recently, emission factors measured in two road tunnels located in São Paulo, Brazil, were published (Martins et al. 2006a, b). The main goal of that work was determining the CO, NO_x and total volatile organic compounds (VOCs) emission factors. The main VOCs classes were aromatic, alkane and aldheyde compounds. Volatile aromatic compounds (VACs) accounted for approximately 30% of the VOCs mixture. These compounds are of great concern in urban air pollution as precursors for ozone formation and also because they are considered as carcinogen and mutation instigators (Hsieh et al. 1999).

Tunnel measurements represent the bulk emissions from a large number of vehicles under certain driving conditions (hot start). One of the main advantages of sampling inside an urban tunnel is the more realistic picture of the local fleet profile, given the absence or minimization of external perturbations, such as atmospheric scavenging processes, that may interfere by changing the profile of the local primary emissions. This is actually one of the main difficulties of assessing the atmospheric emissions in the open environment. It is worth to mention that the advantage of this type of study, as opposed to sampling emissions directly from a chassis dynamometer facility, for instance, is the adherence of the measured concentration levels to the emissions coming from the active fleet, given its current status and actual maintenance conditions.

In the present paper a different approach is presented. It focuses on the determination of VACs concentration and discusses the maximum ozone formation potential of the target compounds.

Materials and Methods

Sampling were collected in Rebouças Tunnel which links the North and South wards of the city. The tunnel has two main galleries, L1 (northwards) and L2 (southwards) with an approximate length each of 2,040 m, linking Humaitá to Cosme Velho. There are also two secondary galleries, R1 (northwards) and R2 (southwards), connecting Cosme

M. C. S. Machado
Analytical Solutions, Rio de Janeiro, RJ, Brazil

J. C. S. Almeida · E. M. Martins · G. Arbilla (✉)
Physical Chemistry Department, Federal University of Rio de Janeiro, CT, Building A, Room 408, 21949-900, Cidade Universitária, Rio de Janeiro, RJ, Brazil
e-mail: graciela@iq.ufrj.br

E. M. Martins
Laboratory of Developement of Bioprocess, Chemistry School, University of Rio de Janeiro, CT, Building E, Room E-121, 21949-900, Cidade Universitária, Rio de Janeiro, RJ, Brazil

Velho to Rio Comprido, with 772 m length each roughly. The tunnel cross section is 81 m^2 in both bores. A concrete wall separates the north-bound traffic from the south-bound traffic. Each gallery has three lanes. CO concentrations and the 1 h average traffic flow are currently monitored. The tunnel ventilation system is composed of 78 fans placed near the roof (Rebouças 2006). The daily traffic volume ranges from 180,000 to 190,000 vehicles day^{-1}. Light duty vehicles (LDV) represent roughly 95% of the local traffic, while diesel vehicles and motorcycles account for 2.8% and 2.2%, respectively (Moreira et al. 2006).

Aromatic compounds were sampled and analyzed using a methodology based on US-EPA methods (1998). Aromatic compounds were sampled by drawing air through tubes 7 cm long, 4 mm ID, containing 2 sections of activated coconut shell charcoal (main section 100 mg, second section 50 mg) separated by a 2 mm urethane foam (SKC Inc), during 1 h, at a flow rate of 1.0 L min^{-1}. The second section of tube was analyzed in order to detect breakthrough.

Charcoal beds in the sorbent tubes were transferred to 2 mL vials and extracted by adding 1.0 mL of CH_2Cl_2 with occasional agitation for 30 min. Bromofluorbenzene was added prior to extraction as internal standard. The samples were analyzed using a Trace GC coupled DSQ Quadrupole Mass Spectrometer (Thermo Finnigan). The column used was a DB–5 (5% phenyl-methyl-siloxane) – J&W Scientifics, 60 m long with 0.25 mm internal diameter and 0.25 μm thickness phase. Carrier gas was helium at 1 mL min^{-1} and 25 cm s^{-1} linear velocity. The injection mode was splitless with inlet temperature of 250°C. Temperature program was: 45°C, held for 2 min, 45–200°C at 6°C min^{-1}, held for 5 min. Mass spectrometer ionization was electronic impact and ion source, quadrupole and GC/MS interface temperatures were 230, 150 and 250°C, respectively.

The MS was run in selective ion monitoring mode. For each compound, two ions (one target and one qualifier) were monitored. Compounds were identified based on their relative retention times and ion ratios. Identified compounds were quantified using internal calibration procedure, with five levels of calibration as follows: 0.1; 1; 5; 25; 100 μg mL^{-1} in CH_2Cl_2, with 1 μg mL^{-1} of bromofluorbenzene in all solutions. All calibration solutions were purchased from Supelco. Correlation coefficients were evaluated and 0.99 was considered acceptable.

The reproducibility of the results was checked by analyzing duplicated samples and the difference was always below 10%. Blank runs were performed before each sample analyses. The uncertainties of the results were calculated, using the data of the calibration curves, as: benzene 18%, toluene 10%, ethylbenzene 21%, m, p-xylene 8% and o-xylene 12%.

Results and Discussion

Compounds were monitored in L1 gallery in two locations: station 1 (S1), roughly 500 m from the entrance, and station 2 (S2) about 1000 m apart from S1. A total of five samples were collected, in each location, in 20 October 2005 (at 11:00 am and 1:00 pm) and on 21 October 2005 (at 9:00 am, 11:00 am and 1:00 pm).

Traffic volume through the tunnel is currently counted. As shown in Fig. 1, the fleet profile is quite constant with time between 9:00 am and 8:00 pm. Also the vehicular flux during the two sampling days was very similar to mean values for 2005, showing that those days may be considered representative of the current conditions within the tunnel.

The mean concentrations (5 samples), maximum and minimum values and standard deviations of 14 VACs are summarized in Table 1. The mean mass contribution of each target compound and ratio compound/toluene are also shown.

As shown in Table 1, concentrations in S2 are about 2.4–2.7 higher than in S1. Also f-test shows that levels in the two locations are statistically different. These were the expected results for a one-way tunnel, where the vehicles enter one direction and the wind speed increases with the passing of cars, creating a piston effect. The entrance of the tunnel may be considered the upwind area and the exit of tunnel becomes downwind (Hsieh et al. 1999). Thus, higher concentrations may be expected in S2, 500 m from the exit of the tunnel.

The profiles of VACs were consistent in both stations, showing nearly the same mass composition. The most abundant species were toluene and xylenes. Although a direct comparison is not valid, since different fuels are used, the same major VACs were reported in other tunnels (Tsai et al. 1997; Chan et al. 1995; Sagebiel et al. 1995; Hsieh et al. 1999). They were also the most abundant VACs in São Paulo (Martins et al. 2006a, b). Benzene, toluene, ethylbenzene and xylenes represent 67.3% of the total VACs mixture.

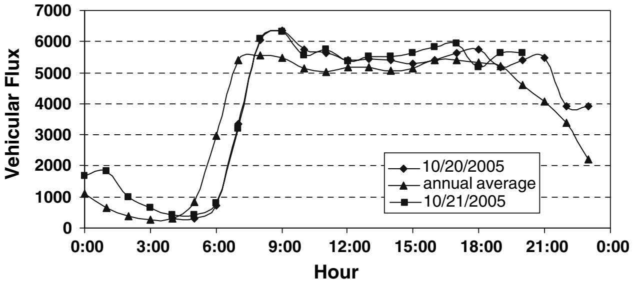

Fig. 1 Traffic volume for the monitoring campaign period and mean value for 2005 (vehicles per hour)

Table 1 Mean concentrations (N = 5)

Compound	Mean	Max	Min	Sd	Percentage of total	Ratio S1/S2	Compound/toluene	LOD	CR
Station 1									
Benzene	29	36	18	7	14.58	2.72	0.62	0.12	78
Toluene	46	59	28	11	23.45	2.56		0.15	91
Ethylbenzene	12	15	7	3	6.30	2.60	0.27	0.13	89
m-Xylene	27	36	17	6	13.80	2.61	0.59	0.11	85
p-Xylene	9	13	5	3	4.89	2.57	0.21	0.15	88
o-Xylene	8	11	5	2.0	4.24	2.68	0.18	0.15	85
Isopropylbenzene	2.3	3.0	1.3	0.7	1.15	2.61	0.05	0.21	79
n-Propylbenzene	7	9	4	2.0	3.33	2.55	0.14	0.22	80
1.3.5-Trimethylbenzene	17	23	9	5.0	8.53	2.65	0.36	0.20	78
1.2.4-Trimethylbenzene	34	46	19	10	17.28	2.51	0.74	0.19	82
Sec-butylbenzene	0.6	0.8	0.4	0.2	0.31	2.41	0.01	0.20	79
p-Isopropyltoluene	0.8	1	0.5	0.2	0.39	2.42	0.02	0.22	77
n-Butylbenzene	3	4	2	1	1.74	2.62	0.07	0.18	75
Total VACs	195.7								
Station 2									
Benzene	79	95	64	12	15.25		0.66	0.12	78
Toluene	120	141	89	19	23.14			0.15	91
Ethylbenzene	33	38	24	5	6.30		0.27	0.13	89
m-Xylene	72	93	49	17	13.86		0.60	0.11	85
p-Xylene	25	30	18	4	4.83		0.21	0.15	88
o-Xylene	23	26	16	4	4.37		0.19	0.15	85
Isopropylbenzene	6	7	4	1	1.16		0.05	0.21	79
n-Propylbenzene	17	21	12	3	3.28		0.14	0.22	80
1.3.5-Trimethylbenzene	45	53	32	8	8.70		0.38	0.20	78
1.2.4-Trimethylbenzene	86	106	65	15	16.71		0.72	0.19	82
Sec-butylbenzene	1.5	1.7	1.0	0.3	0.29		0.01	0.20	79
p-Isopropyltolue-ne	1.9	2.2	1.2	0.4	0.36		0.02	0.22	77
n-Butylbenzene	9	11	7	2	1.76		0.08	0.18	75
Total VACs	518.4								

Maximum (*Max*), minimum(*Min*) and standard deviations (*Sd*) of VACs in Stations 1 and 2 (units of µg m^{-3}). Mass composition (%), the ratio of concentrations in Stations 1 and 2 (S1/S2) and the concentration ratios compound/toluene are also shown. Limits of detection (LOD, ng m^{-3}) and compound recoveries (CR, %) are also reported

As previously noted (Bowmand and Seinfeld 1995) exhaust compositions differ from fuel composition in several aspects, mainly the generation of light olefins and carbonyls, depletion of paraffins and ethers and enrichment of benzene. Emissions are composed of unburned fuel, products of partial combustion and evaporative looses. Since 2002, the volume percentage of benzene and total aromatics in gasohol should be in the range 1.0–1.9% and 45–57%, respectively, according to the Brazilian legislation (ANP 2005). Results obtained in this work show that benzene account for 15% (in mass) of total VACs.

The benzene/tolune mass ratio is 0.62–0.66, quite similar to the value determined in São Paulo and to data for Mc Henry and Tuscarola Mountain Tunnels (Pierson et al. 1996). These values are rather high in comparison to reported ambient ratios for various cities around the world, which range from 0.25 to 0.50 (Martins et al. 2006a, b) and also the ratios determined in several tunnels in Taiwan (Hsieh et al. 1999; Hwa et al. 2002; Hsu et al. 2001) and Europe (Kristensson et al. 2004; Stemmler et al. 2005; Colberg et al. 2005). The benzene/toluene ratio determined in this work may be considered a characteristic value for the fuels used in Brazil and for the on-road tunnel emissions in Brazil. It worth noting that emission ratios depend on the fuel formulation, driving conditions, vehicle maintenance and traffic congestion. Emission factors of individual VACs were not calculated since data for CO, used as reference, and currently obtained by the tunnel control system are subject to a great uncertainty.

Table 2 Maximum ozone formation potentials calculated for the most abundant compounds in Station 2

Compound	MIR scale ($gO_3/gVOC$)	VACs concentrations ($\mu g/m^3$)	Weight percentage (weight %)	MIR × VACs concentration	Percentual reactivity
Benzene	0.42	79	16.4	33.2	1.3
Toluene	2.7	120	24.8	324	12.8
Ethylbenzene	2.7	33	6.8	89.1	3.5
m-Xylene	7.4	72	14.9	532.8	21.1
p-Xylene	7.4	25	5.2	185.1	7.3
o-Xylene	6.5	23	4.8	149.5	5.9
1.3.5-Trimethylbenzene	10.1	45	9.3	454.5	18.1
1.2.4-Trimethylbenzene	8.8	86	17.8	756.8	30
Total		483		2525.0	

As expected, the Spearman correlation matrix for the 14 compounds show a correlation factor higher than 0.9, confirming the existence of a unique emission source.

A rough estimation of the ozone formation potential of the target VACs was performed by calculating the maximum incremental reactivity (MIR) proposed by Carter (1994). Results are summarized in Table 2. The ozone formation potential was calculated by adding the weight MIR to VACs concentrations.

The importance of VACs to the formation of ozone depends on the reactivity of VACs and formation rate of radicals. As previously stated, the most abundant species were toluene and xylenes, while the major contribution to ozone formation is due to alkylbenzenes.

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