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Exposure to Volatile Organic Compounds in an Ethanol and Gasoline Service Station

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Abstract The present study was conducted to determine the VOCs concentrations in a service station located in a residential and commercial area in the city of Rio de Janeiro. This is, to our knowledge, the first published determination in Brazil, where both ethanol and ethanol-blended gasoline are used. Electro polished, stainless steel, evacuated canisters were used for sampling. The analysis was performed by gaschromatography with flame ionization detection (CG-FID) and by gas chromatography–mass spectrometry (CG–MS). A total of 80 and 56 compounds were determined in samples collected at the service station and control location, respectively. The most abundant compounds at the service station were in order of decreasing concentration (units: µg m^{-3}): 2-methylbutane (1,715.7), 2-methylbut-1-ene (1,043.2), isobutene (758.8), 2-methylprop-1-ene (703.7), 2-methylpentane (492.1), pentadi-1,3-ene (189.7), toluene (157.0), benzene (144.5), but-2-ene (126.3) and *m*,*p*-xylene (123.2). A mean concentration of 144.5 µg m^{-3} was determined for benzene, this value is about ten times the concentration determined in the control location in this work and about 70 times the value determined in other locations of Rio de Janeiro using charcoal cartridges for the sampling. The mean benzene/toluene ratios are 0.92 and 0.31 in the service station and control location, respectively. Since in Brazil service station workers are employed to fill customer's cars (self-service is not commonly used) the possible risk of cancer of these workers should be evaluated in a future study.

Keywords Service station emissions · Volatile organic compounds · Evaporative emissions · Benzene

Mage et al. (1996) have indicated that motor vehicle traffic is a major source of air pollution in metropolis. In Brazil, 75% of the population lives in cities, furthermore, in the state of the Rio de Janeiro, this figure rises to 95%. According to regulatory agencies, in the Metropolitan Area of Rio de Janeiro (RJMR) 77% of the emissions of total pollutants and 99% of total carbon monoxide are due to mobile sources (FEEMA 2004). The city of Rio de Janeiro has a population of 6,094,183 habitants distributed over an area of 1,182 km^2 (IBGE 2005). In the city of Rio de Janeiro the total number of vehicles increased from 1,570,000 in January 2001 to 1,940,000 in January 2006. Presently, about 88% are light-duty vehicles, which use gasohol (gasoline with 24% of ethanol), 69.2%, net ethanol, 12.4%, and compressed natural gas (CNG), 11.1% (DETRAN 2006). Storage and distribution of gasoline may be an important source of volatile organic compounds (VOCs) emissions (Cruz-Núñes et al. 2003). In 2005, 1,741,237 m^3 of gasohol were sold in about 1,100 service stations in the city. Also, 180,260 m^3 of ethanol and 2,176,483 m^3 of diesel were sold (ANP 2005a).

Several studies discussed the occupational exposure to VOCs from gasoline emissions (Hartle and Young 1977; Kearney and Duham 1986; Jo and Song 2001; Lynge et al. 1997; Romieu et al. 1999) and the non-occupational

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exposure to VOCs from evaporative and exhaust emissions (Wallace 1989; Chan et al. 1991; Weisel et al. 1992; Jo and Park 1999). In many of these studies, the target VOCs are benzene, toluene, ethylbenzene, *o*-xylene and *p*-xylene because of their toxicity and because they are considered tailpipe and gasoline vapor emission markers (Jo and Song 2001). Since 2002, the volume percentage of benzene and total aromatics in gasohol should be in the range of 1.0%–1.9% and 45%–57%, respectively, according to the Brazilian legislation (ANP 2005b). The present study was conducted to determine the VOCs concentrations in a service station in the city of Rio de Janeiro. This is, to our knowledge, the first published determination in Brazil, where both ethanol and ethanol-blended gasoline are used.

Materials and Methods

The samples were collected on 9th June 2004 in a service station located in Flamengo District, a residential and commercial area in the city of Rio de Janeiro. The service station has five gasohol pumps and sold approximately 3.0 m^3 of gasohol per hour during the sampling period. A total of six samples were collected beside the pumps and other two samples were collected at 200 m from the service station at a location with the same vehicular flux than the station.

About 1.8 L electro polished, 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 canisters were then shipped to Instituto de Pesquisas Energéticas e Nucleares (IPEN) and analyzed within 3 days.

The analysis was performed by gas-chromatography with flame ionization detection (CG-FID) and by gas chromatography–mass spectrometry (CG–MS). The method follows US EPA guidelines (U.S. EPA 1999). Briefly, 100 mL aliquots of air from the canister samples were loaded on a cryo-trap (glass beads in 6″ and 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. The column was a DB-1 capillary column, 60 m long and 0.32 mm diameter and 1.0 µm film thickness. 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 the FID and the MS detectors. The analyses were carried out using a Varian 3800 gas-chromatography and a Saturn 2000 mass selective detector. The mass spectral libraries used for compound identification include the NIST Data Base (1998). 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). Other compounds were quantified using analogs compounds. All samples were run in duplicate and the difference was lower than 5%. Blank runs were also performed before each sample analysis.

Results and Discussion

A total of 80 and 56 compounds were determined in samples collected at the service station and control location, respectively. Compounds determined at the service station, with average concentrations higher than 12.0 µg m^{-3} are listed in Table 1. Reported values are the arithmetic means of six samples. Compounds with average concentrations lower than 12.0 µg m^{-3} are reported in the footnote of Table 1. In this table, concentrations determined at the control location and the ratios average concentration at the service station to average concentration at the control location are also shown.

Some compounds were identified in only one of the six samples: hexane (34.4 µg m^{-3}), nonane (7.6 µg m^{-3}), dodecane (4.6 µg m^{-3}), 2,6-dimethylhexane (0.2 µg m^{-3}), 3,4-dimethylhexane (504.7 µg m^{-3}), 2,6-dimethylheptane (2.4 µg m^{-3}), 2-methylnonane (0.1 µg m^{-3}), 3-methylnonane (2.9 µg m^{-3}), 4-methylnonane (3.1 µg m^{-3}), 2,6-dimethyloctane (0.18 µg m^{-3}), hex–2-ene (4.8 µg m^{-3}), hept–1-ene (3.5 µg m^{-3}), hept-2-ene (5.7 µg m^{-3}), oct-1-ene (14.3 µg m^{-3}), heptadi-3,4-ene (0.3 µg m^{-3}), 2-methylbut-2-ene (366.9 µg m^{-3}), 1-methylpent-2-ene (8.8 µg m^{-3}), 3-methylpent-1-ene (8.8 µg m^{-3}), 2,3-dimethylpent-2-ene (5.8 µg m^{-3}), 5,5-dimethylhexadi-1,3-ene (0.6 µg m^{-3}), 2-ethylpent-2-ene (0.5 µg m^{-3}), 2-ethylbut-1-ene (82.8 µg m^{-3}), styrene (1.5 µg m^{-3}), 2,4,1-dimethylethylbenzene (3.0 µg m^{-3}), 1,3-methylpropylbenzene (60.7 µg m^{-3}), 1,2,3,4-tetramethylbenzene (22.2 µg m^{-3}), 1,2,4,5-tetramethylbenzene (62.6 µg m^{-3}).

The two xylene isomers, *m*-xylene and *p*-xylene, coeluted. The most abundant compounds at the service station were in order of decreasing concentration (units: µg m^{-3}): 2-methylbutane (1,715.7), 2-methylbut–1-ene (1,043.2), isobutane (758.8), 2-methylprop-1-ene (703.7), 2-methylpentane (492.1), pentadi-1,3-ene (189.7), toluene (157.0), benzene (144.5), but-2-ene (126.3) and *m,p*-xylene (123.2).

In Figs. 1a, b the distribution of the main groups is shown. Clearly, the gas mixture collected in the service station, is richer in alkanes, mainly 2,2-dimethylbutane (149.5 times), 2,3-dimethylbutane (48.1 times), 2-methylbutane (29.2 times) and 2,3-dimethylpentane (23.6 times).

Table 1 Average concentrations (in µg m^{-3}) for the main volatile organic compounds determined in the service station and in the control location

Compounds	Service station (SE)	Control	Ratio (SE/control)
Alkanes			
2-Methylbutane	1,715.7	58.9	29.2
Isobutene	758.8	85.6	8.9
2-Methylpentane	492.1	24.7	19.9
Heptane	72.2	8.0	9.0
2,3-Dimethylbutane	69.9	1.5	48.1
3-Methylhexane	65.0	5.2	12.4
2,4-Dimethylheptane	26.8		
2,3-Dimethylpentane	25.9	1.1	23.6
2,2-Dimethylbutane	19.5	0.1	149.5
2,4-Dimethylpentane	16.7		
2,5-Dimethylhexane	14.8	1.5	9.8
Others[a]	19.9	6.8	
Alkenes			
2-Methylbut-1-ene	1,043.2	81.1	12.9
2-Methylprop-1-ene	703.7	12.0	58.5
Pentadi-1,3-ene	189.7		
But-2-ene	126.3	10.0	12.6
3-Methylpent-2-ene	104.7	1.0	107.9
2,3-Dimethylbut-2-ene	89.4		
Hex-3-ene	50.8	1.1	46.1
2-Methylpent-1-ene	44.2	1.7	25.9
3-Methylhex-2-ene	31.3	1.0	29.9
Others[b]	10.9	20.5	0.5
Aromatic hydrocarbons			
Toluene	157.0	45.1	3.5
Benzene	144.5	13.9	10.4
p,*m*-Xylene	123.2	31.4	3.9
1,2,4-Trimethylbenzene	56.0	8.6	6.5
o-Xylene	46.7	11.6	4.0
1,2-Ethylmethylbenzene	44.2	10.2	4.3
Ethylbenzene	35.8	11.4	3.2
1,2,3-Trimethylbenzene	32.1	11.2	2.9
2-Ethyl-1,4-dimethylbenzene	27.9	3.7	7.6
1,3-Ethylmethylbenzene	26.3	4.3	6.2
1-Ethylmethylbenzene	25.4	4.5	5.7
1,4-Methyl (1-methylethyl)benzene	21.7		
Propylbenzene	18.0	0.4	47.3
1-Butenylbenzene	17.4		
4-Ethyl-1,2-dimethylbenzene	17.3	1.3	13.1
1,4-Methyl (1-ethylpropyl)benzene	17.0		
Tert-butylbenzene	16.9	1.3	13.1
Others[c]	21.6	4.4	

[a] Decane (5.8), 2-methyloctane (1.3), 4-methyloctane (1.9), undecane (2.3); 3-ethylhexane (8.6)

[b] 3,4-Dimethylpent-1-1-ene (0.4), hexadi-1,4-ene (5.6), oct-2-ene (0.1), 2-methylhex-3-ene (3.9), 3-methylhex-3-ene (0.8), 2-methylhexadi-2,4-ene (0.09)

[c] Cyclopropylbenzene (9.6), 1,3,5-trimethylbenzene (12.0)

The distribution of individual compounds in the main groups is also shown in Fig. 1. The main three alkanes are 2-methylbutane, isobutane and 2-methylpentane in both, the service station and the control location.

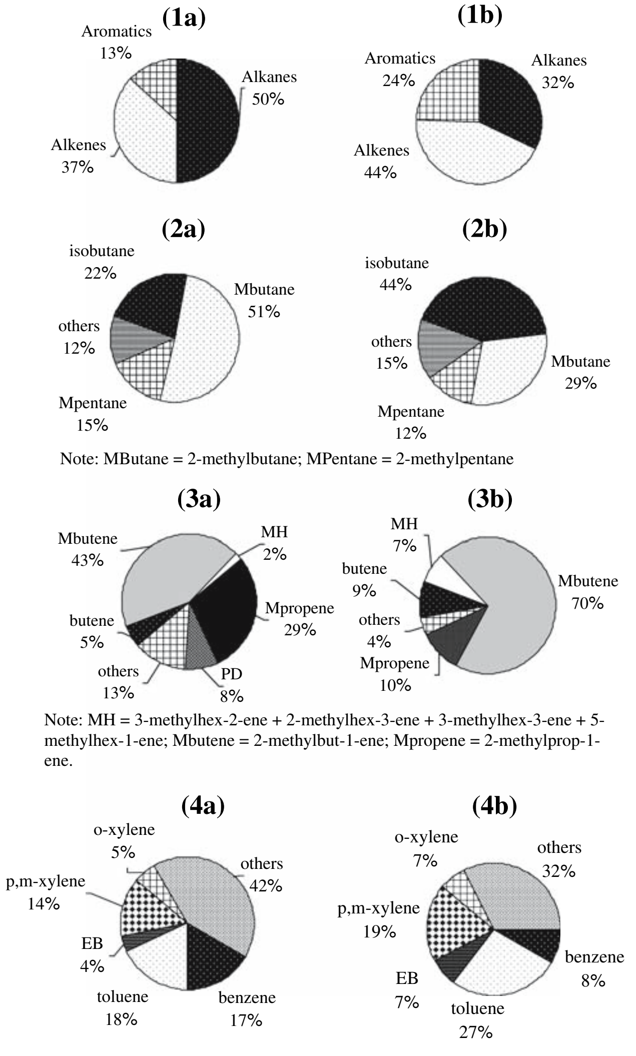
The most abundant alkene, at the control location, is 2-methylbut-1-ene (70%) while at the service station, 2-methylbut-1-ene, 2-methylprop-1-ene and pentadi-1,3-ene contribute with 80% to the gaseous mixture.

The distribution of aromatics is also different in both locations, with a higher percentage of benzene in the service station.

In Fig. 2, the concentration of main compounds is displayed as a function of the boiling point. Data adjust to a third order polynomial ($C = 603.9 - 11.4\mathrm{BP} + 0.07\mathrm{BP}^2 - 1.6 \times 10^{-9}\mathrm{BP}^3$) with $R^2 = 0.74$. This fact may explain the differences in VOCs distribution within the groups, since evaporative emissions should be more important in storage, distribution and refilling of fuels.

A mean concentration of 144.5 µg m^{-3} was determined for benzene, this value is about ten times the concentration determined in the control location in this work and about 70 times the value determined in other locations of Rio de Janeiro using charcoal cartridges for the sampling (Martins et al. 2007a, b). It should be noted that gasoline pumps in Brazil do not have vapor recovery and the samplings were short-time measurements (1–2 min). The value obtained in this work is in the same range than those reported by Lynge et al. (1977) for Nordic countries and by Romieu et al. (1999) for Mexico City. Anyway, it should be noted that the other studies were not conducted in gasohol service stations. More samples should be collected in a further work in order to assess the differences due to the use of ethanol and ethanol-blended fuel.

The mean benzene/toluene ratios are 0.92 and 0.31 in the service station and control location, respectively. Ambient ratios in various cities around the world have been



Note: MButane = 2-methylbutane; MPentane = 2-methylpentane

Note: MH = 3-methylhex-2-ene + 2-methylhex-3-ene + 3-methylhex-3-ene + 5-methylhex-1-ene; Mbutene = 2-methylbut-1-ene; Mpropene = 2-methylprop-1-ene.

Fig. 1 Distribution of VOCs (*1*), alkanes (*2*), alkenes (*3*) and aromatics (*4*) for samples collected at the service station (**a**) and the control location (**b**)

reported ranging from 0.25 to 0.50 (Martins et al. 2007b). The higher ratio determined in this work is also a clear indication of the important contribution of evaporative emissions in the service station.

Elevated concentrations were also determined for benzene derivates. For toluene, ethylbenzene and xylenes, concentrations at the service station are about three times the values obtained at the control location.

To our knowledge, no studies have been conducted in order to avaliate the incidence of leukemia in Rio de Janeiro and the correlation between benzene exposure and the incidence of cancer.

Since in Brazil service station workers are employed to fill customer's cars (self-service is not commonly used) the possible risk of cancer of these workers should be evaluated in a future study.

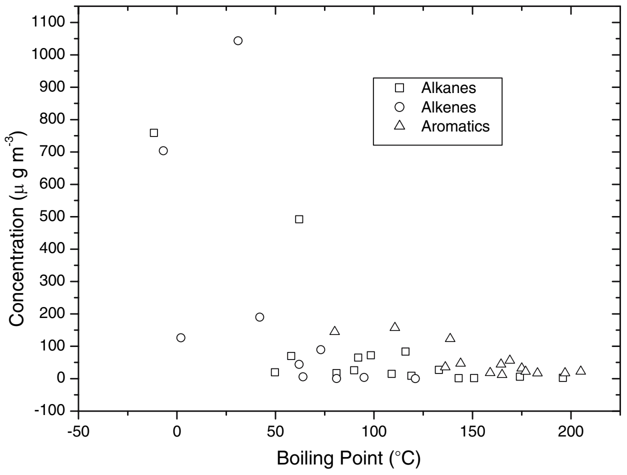


Fig. 2 VOCs average concentration in the service station as function of the boiling point of each compound

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