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Comparative Study of Automotive, Aircraft and Biogenic Emissions of Aldehydes and Aromatic Compounds

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Abstract Air samples were collected in three well characterized locations in the city of Rio de Janeiro, Brazil: downtown, the idle and taxi way areas of the national airport and an urban forest, where the main emissions are from vehicular, aircraft and biogenic sources, respectively. Aldehydes and BTEX concentrations show a characteristic profile which may be attributed to the emission sources. Formaldehyde/acetaldehyde ratios, in the early morning, were 1.39, 0.62 and 2.22 in downtown, airport and forest, respectively. Toluene/benzene ratios, for downtown, airport and forest areas, were 1.11, 1.82 and 1.06, respectively. The results show that the impact of the urban emissions on the forest is negligible as well as the impact of aircraft emissions over the urban area.

Keywords Vehicular emissions · Aircraft emissions · Biogenic emissions · Aldehydes · BTEX

Ozone, which is a secondary pollutant, is the major component of photochemical smog. The mechanisms of production of ground-level ozone have been the subject of considerable scientific studies (Filaysson Pitts and Pitts 2000). Ozone is generated through a complex series of chemical reactions, initiated by absorption of solar energy, in the presence of oxides of nitrogen (NOx) and volatile organic compounds (VOCs). VOCs can be either anthropogenic or biogenic in origin. In 2007, Theloke and Friedrich (2007) presented a compilation of VOCs species profiles for relevant anthropogenic emissions in Europe. Following their data for Germany in 1998, the emissions from vehicle sources contained about 41% alkanes, 27% aromatics, 16% alkenes and 9% of aldheydes. In Brazil, the contribution of aldheydes is higher due to the extensive use of ethanol, oxygenated gasolines (blended with ethanol) and compressed natural gas (Martins et al. 2007). The contribution of aircraft has been the subject of several studies. Literature results confirm that formaldehyde is one of the most dominant hydrocarbons during taxiing and idle operation (Herdon et al. 2006). Non-oxygenated VOCs concentrations were determined at the Zurich airport in 2004 (Schurmann et al. 2007), and typical benzene/toluene ratios of 1.6, during taxiing, were observed. Values well bellow 1 were determined during the ignition period. Aircraft emissions of non-oxygenated VOCs were dominated by high volatile and reactive alkenes. Regarding biogenic emissions, it has been recognized that a variety of VOCs are emitted into the atmosphere from vegetation (Kesselmeier and Staudt 1999). These organic compounds include isoprene, monoterpenes, sesquiterpenes, and a number of oxygenated compounds.

In this work, atmospheric levels of aldehydes and BTEX were determined for three well characterized locations where the emissions sources are clearly defined and nearly unique: vehicular (gasoline, ethanol, compressed natural gas and diesel), aircraft and biogenic emissions. The main goal of the work was to determine the levels of aldehydes and BTEX and the ratios formaldehyde/acetaldehyde and toluene/benzene for each place in order to characterize the emissions patterns of each source. The results may be also useful to assess the impact of the airport on the urban area as well as the impact of urban emissions on the forest.

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Formaldehyde and acetaldehyde were selected as the target compounds because formaldehyde is the main oxygenated VOC emitted both by plants and also by aircraft engine combustion. As discussed bellow, acetaldehyde is a characteristic compound of emissions from ethanol-fueled vehicles. BTEX were also selected because they are only emitted by anthropogenic sources. Due to their relative high stability, they can impact areas farther away from the emission sources, and may be used as an indicator of the impact of urban emissions on neighboring rural and forest areas. Moreover, all of these compounds are of health concern. All of them have been defined as hazardous by the 1990 amendments of the Clean Air Act (USEPA 1990). Benzene was classified as a Group A, human carcinogen. Acetaldehyde and formaldehyde were considered as probable human carcinogens (Group B). Toluene, ethylbenzene and xylenes were included in Group D, not classifiable as to human carcinogenicity. In Brazil, aldehydes emissions by vehicles are regulated by the environmental protection agencies while benzene and total aromatic compounds in gasoline are also controlled.

Materials and Methods

The samples were collected during 2007 and 2008 in three locations. The first point was Presidente Vargas Avenue in downtown Rio de Janeiro (Brazil), where the only significative emissions are due to light and heavy-duty vehicles. The avenue has a heavy traffic with diurnal fluxes (from Mondays to Fridays) between 6,000 and 8,000 vehicles h^{-1}, depending on the hour of the day. In downtown, only commercial administrative activities are developed. The industrial area of the city is more than 50 km apart and the industrial emissions plumes do not reach downtown. The second place was Santos Dumont National Airport, located in the city of Rio de Janeiro, by Guanabara Bay, at about 2 km from downtown. The airport serves about 4 million passengers $year^{-1}$ and has an average of about 70,000 landings and take-offs in a year. Vehicle emissions in that area are quite reduced and all samples were collected in the taxi and idle areas. During the sampling period, the prevailing wind was a steady 6 m s^{-1} at a slight angle across the runway. The prevailing winds are from the North and Northeast, in the morning, and from the South and Southeast, in the afternoon. The transport of pollutants from the city to the airport (west to east) is a minor contribution to overall pollutants. The third place was an isolated area inside Tijuca Forest, one of the largest urban forest of the world, in the Atlantic Rainforest, covering 39.51 km^2. The selected locations have no vehicular flux and a reduced circulation of visitors. This forest is home to hundreds of species of plants and wildlife and is surrounded by the city of Rio de Janeiro. The same methodology was used for sampling and analysis of all the samples.

Aldehydes were sampled and analyzed using a methodology based on the TO-11A (USEPA 1997). They were collected using C18 cartridges Sep-Pak Classic (Waters Corp. Ireland, part N° WAT051910) coated with 2,4-dinitrophenylhydrazine. Aldehydes collected by the cartridges were extracted using acetonitrile. The eluted solution was analyzed using an HPLC system (Agilent 1100 series, Agilent Technologies, Inc.) with a diode array UV–visible detector and a C18 Nucleosil 100-5 column (4 × 250 mm, 5 μm) (Agilent Technologies, Inc.). The mobile phase was poured water (A) × acetonitrile (B) at a linear gradient mode. The gradient program was as follows: 0-3 min, 45% (A); 3–5 min, 43% (A); 5–7 min, 30% (A); 7–20, 30% (A). The eluent flow rate was 1.5 mL min^{-1}, the column temperature was 38°C, and the volume of sample injected was 10 μL. The formaldehyde and acetaldehyde were quantified by external calibration curve of the authentic standard (TO11/IP6A Carbonyl DNPH Mix, Supelco, Bellefonte, PA, USA) and a minimum correlation factor of 0.999 was obtained for all compounds. The recovery efficiency was previously checked using spiked samples at three concentration levels. Values of >80 ± 10% were achieved for all compounds and samples.

BTEX were sampled and analyzed using a methodology based on EPA methods (USEPA 1988). They were sampled by drawing air through tubes containing two sections of activated coconut shell charcoal (SKC Inc., Eighty-Four. PA, USA, part no. 226-01). Charcoal beds in the sorbent tubes were transferred to 2 mL vials and extracted by adding 1.0 mL of dichloromethane with occasional agitation for 30 min. The samples were analyzed using a HP 5870 Series II GC with a FID detector. The column used was a CP SIL-8 CB fused silica capillary, 30 m × 0.25 mm i.d., 0.25 lm film thickness (Varian Inc., PA, USA). The oven temperature program was 38 (4 min) to 120°C at 6°C min^{-1} and 120 to 200°C at 35°C min^{-1} (hold 3 min), and the injector was heated at 250°C and the FID at 250°C. The carrier gas was He at a flow rate of 1 mL min^{-1}. BTEX was quantified by external calibration curve of the authentic standard (Wisconsin PVOC/GRO mixture, CHEM SERVICE Inc., West Chester, PA, USA) and a minimum correlation factor of 0.999 was obtained for all compounds.

The reproducibility of the results was checked through the analysis of duplicate samples for aldehydes and triplicate samples for BTEX, always with differences of less than 10%. Blank runs were performed before each sample analysis. Recoveries better than 75% were determined for all compounds using spiked samples.

Detection Limits (LD) were calculated using the equation: $LD = 3.3\sigma/S$, where σ is the standard deviation of the residual from the regression line and S is the slope of the regression equation of the calibration curve (Ribani et al. 2004). The calculated values for the carbonyl compounds were: 0.00978 ppb(v) for formaldehyde and 0.00163 ppb(v) for acetaldehyde. For BTEX, the values were: 0.317 μg m^{-3} for benzene, 0.173 μg m^{-3} for toluene, 0.0617 μg m^{-3} for *o*-xylene, 0.177 μg m^{-3} for *p*,*m*-xylene and 0.230 μg m^{-3} for etilbenzene.

Results and Discussion

Main concentrations of formaldehyde, acetaldehyde and BTEX are shown in Tables 1 and 2. Formaldehyde and acetaldehyde mixing ratios are clearly lower in the forest, mainly during the morning. Values determined in Presidente Vargas Avenue are similar to those previously obtained in many Brazilian cities (de Andrade et al. 2002). Levels determined in the Tijuca Forest are in the same range as those obtained in other forest and rural areas around the world and in some tropical sites in Brazil (de Andrade et al. 1998).

In the early morning, the ratios formaldehyde/acetaldehyde are similar for downtown and the airport area. In downtown the ratio is higher than 1. Similar values were obtained for several urban areas around the world once formaldehyde is almost always the predominant aldehyde emitted by automobiles powered by gasoline with and without catalytic converters (de Andrade et al. 1998). In the case of ethanol fueled vehicles, acetaldehyde emissions are, in general, significantly higher than formaldehyde. Brazil is the only country in the world where neat ethanol made from sugar cane, has been used, since the mid-1980s, as vehicle fuel. Ethanol is also added to gasoline as octane booster. Many literature reports, from the period 1985–1992, show formaldehyde/acetaldehyde ratios lower than 1 for Brazilian cities. In contrast, the average ratio in the last 10 years has begun to increase (Grosjean et al. 2002) due to the fleet turnover: older ethanol-fueled cars were replaced by newer vehicles that run on the gasoline-ethanol blend (gasohol) and, since 2003 by flexible-fuel vehicles (running on ethanol, gasohol or a mixture of both). Most new vehicles sold in Brazil since 1997 have continuous correction of fuel injection and catalytic converters to further reduce exhaust emissions.

Ratios determined in the airport are more than three times lower than those expected on the basis of the European Environmental Agency data for commercial aircraft (EEA 2001). The resulting ratio for Santos Dumont airport may be taken as an indicator of other emission sources than direct aircraft emissions, such as diesel ground support vehicles and, also, light-duty vehicles in the parking area and circulating in the vicinity of the airport. In the afternoon, formaldehyde concentrations in the idle and taxiway areas of the airport are lower than in the morning and acettaldehyde concentrations generally increase. This fact may be attributed to the variation on the number of

Table 1 Formaldehyde and acetaldehyde average levels and formaldehyde/acetaldehyde ratios determined in the three studied areas in Rio de Janeiro, in the period 2007–2008

Location	Early morning (8:00–10:00 h)			Early afternoon (12:00–14:00 h)		
	Formaldehyde	Acetaldehyde	Formaldehyde/ acetaldehyde	Formaldehyde	Acetaldehyde	Formadehyde/ acetaldehyde
Downtown (presidente vargas avenue) (N = 30)	7.93	5.12	1.55	6.88	4.94	1.39
Airport (N = 97)	6.60	4.09	1.61	4.26	6.82	0.62
Tijuca forest park (N = 40)	1.84	0.88	2.09	2.86	1.29	2.22

Units of ppb. N is the total number of samples collected in each place

Table 2 BTEX average concentrations and toluene/benzene ratios determined in the four studied areas in Rio de Janeiro, in the period 2007–2008

Location	Benzene	Toluene	o-xylene	m-and p-xylene	Etylbenzene	Toluene/benzene
Downtown (presidente vargas avenue) (N = 10)	4.37	4.84	1.43	4.89	2.06	1.11
Airport (N = 44)	9.36	16.96	4.68	7.55	5.23	1.82
Tijuca forest park (N = 15)	1.69*	1.79**	<LD	<LD	<LD	1.06

Units of μg m^{-3}. N is the total number of samples collected in each place

* Only 9 samples had a concentration >LD

** Only 1 sample had a concentration >LD landings and take-offs during the day. In the early morning (07:00–10:00 h), the aircraft traffic is very intense with four times more landings and take-offs than in the early afternoon. Consequently, the emissions during the morning are expected to be higher. This fact and the higher reactivity may lead to the reduction of formaldehyde levels. On the other hand, acetaldehyde levels may increase and remain nearly constant because of the lower reactivity of this compound, which favors its accumulation and the secondary formation through the reaction of other organic compounds emitted by aircraft. The different behaviour of formaldehyde/acetaldehyde ratios in downtown and in the airport may be due to differences in the photo-oxidation processes which form secondary aldehydes from other volatile organic compounds and also to the different diurnal pattern of contribution sources.

The different patterns for formaldehyde and acetaldehyde mixing ratios in the forest and in the urban area suggests that the carbonyl levels within the forest may be mainly due to biogenic emissions rather than to the impact of pollutants transported from the near city.

In urban areas, BTEX are mainly due to vehicles emissions (Yassaa et al. 2006). Due to their relative high stability, they can impact areas farther away from the emission sources, and may be used as an indicator of the impact of urban emissions in neighboring areas. However, the emission of aromatic compounds such as toluene has been reported for forest sites (Heiden et al. 1999).

The rate coefficients of BTEX-compounds with OH radicals cover a relative wide range, from the low reactivity of benzene (1.23×10^{-12} cm^3 molecule^{-1} s^{-1}) to *m*-xylene (23.6×10^{-12} cm^3 molecule^{-1} s^{-1}), which exhibits reaction rates comparable to those of alkenes. As discussed by Yassaa et al. (2006), the concentrations of alkylated benzenes in the atmosphere of urban environments often exceed those of benzene, and are related to the emissions ratios of the different sources, primarily automobile exhaust, gasoline evaporation, spillage and some industrial sources. In general, the benzene concentrations in rural sites are higher than toluene or other alkylated benzenes. Several authors have explained this phenomenon as a result of the accelerated atmospheric degradation of alkylated benzenes relative to benzene (Atkinson 1990; Clarkson et al. 1996).

Concentrations in all samples collected in downtown and in the airport were over the detection limit. Since the number of samples exceeding the BTEX detection limit was very small for the Tijuca Forest area, values reported for this area should be considered with caution.

Benzene and toluene concentrations inside Tijuca Forest are in the same range as values determined in a forest park in China (Yu et al. 2008). Xylenes and ethylbenzene were below their detection limit in all samples within the Tijuca Forest. Xylenes and ethylbenzene have no biogenic sources, and are more reactive than toluene and benzene through reaction with OH radicals during the daytime. In forest and rural sites, their concentrations may depend on transport, dilution, deposition and chemical removal. Since these compounds were not found within the park, it may be concluded that the influence of urban pollution on the air quality of the forest is very small.

In the urban area, toluene is the most abundant compound. The toluene/benzene ratio, calculated using mean concentration values, for downtown was 1.11. As noted by Gee and Sollars (1998), ambient air ratios in various cities around the word have been reported ranging from 4 to 2. The ratio determined in this work is rather low, as a consequence of the composition of Brazilian gasoline, which has relative high concentrations of benzene. For the airport area, the mean value is 1.82 and it probably reflects the composition of emissions during the engines ignition period, when the engines have not reached their final temperature. Values in the range 1.6–3.7 were determined by Schurmann et al. (2007) in the parking place of Zurich airport. For the forest area, the mean ratio was 1.05; this lower ratio may be attributed to the faster photochemical oxidation of toluene. This measure has previously been used as an indicator of the urban impact on suburban and rural areas (Yassaa et al. 2006).

In conclusion, formaldehyde/acetaldehyde ratios obtained in downtown reflect the use of catalytic converters and electronic injection in the Brazilian fleet as a consequence of the government control strategies to reduce acetaldheyde emissions due to the use of ethanol. The rather high benzene concentrations may be considered a consequence of the composition of Brazilian petroleum and the low reactivity of this compound. Results obtained in the national airport, located in a well ventilated area by the sea, show an insignificant impact of aircraft emissions and the input of other sources in the area. Tijuca forest remains as a basically non-impacted area, with aldehyde levels within the typical values of tropical forests, assessing the importance of urban forested areas as a source of non-polluted air and as a sink for urban emissions.

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