Atmósfera 29(3), 197-207 (2016)
doi: 10.20937/ATM.2016.29.03.02

Isoprene, benzene and toluene levels at the major landmarks of Rio de Janeiro during the 2014 FIFA World Cup

ELAINE CESAR SOUZA, RAFAEL LOPES OLIVEIRA and GRACIELA ARBILLA
Instituto de Química, Universidade Federal do Rio de Janeiro, Av. Athos da Silveira Ramos, 149, Rio de Janeiro - RJ, 21941-909, Brasil
Corresponding author: Graciela Arbilla; email: graciela@iq.ufrj.br

Received: December 15, 2015; accepted: May 31, 2016

RESUMEN

Se recolectaron muestras de aire en los días anteriores al Campeonato Mundial de Futbol FIFA 2014 y durante la celebración de éste, en los principales puntos turísticos de Río de Janeiro, Brasil. Las muestras fueron recolectadas y analizadas siguiendo el método TO-15 de la US-EPA. El isopreno fue seleccionado como indicador de las emisiones biogénicas, y el benceno y el tolueno como indicadores de las emisiones vehiculares primarias. Se encontraron concentraciones de isopreno, benceno y tolueno en los intervalos 0.39 a 2.32 μg m^{-3}, 2.27 a 10.16 μg m^{-3}, y 5.21 a 21.83 μg m^{-3}, respectivamente. También se calcularon las reactividades cinéticas y mecánicas de estos compuestos para estimar su contribución a la formación de oxidantes atmosféricos. Las concentraciones de benceno y tolueno muestran que las emisiones urbanas impactan de manera considerable las áreas verdes de la ciudad. Los niveles de isopreno son similares a los encontrados previamente en otras regiones con vegetación.

ABSTRACT

Air samples were collected in the days before and during the 2014 FIFA World Cup at the major landmarks of Rio de Janeiro, Brazil. Samples were collected and analysed following Method TO-15 (US-EPA). Isoprene was selected as a marker of biogenic emissions, and benzene and toluene were selected as markers of anthropogenic emissions, primarily vehicular emissions. The isoprene, benzene, and toluene concentrations ranged from 0.39 to 2.32 μg m^{-3}, 2.27 to 10.16 μg m^{-3}, and 5.21 to 21.83 μg m^{-3}, respectively. The kinetic and mechanistic reactivities of these compounds were also calculated to estimate the actual contribution of these compounds to atmospheric oxidant formation. The benzene and toluene concentrations indicated that greener areas of the city are strongly affected by urban emissions. Levels of isoprene were similar to those previously determined in other areas with vegetation.

Keywords: Isoprene, benzene, toluene, 2014 FIFA World Cup, air quality.

1. Introduction

Aromatic compounds are mainly emitted by anthropogenic sources. In urban areas they are mainly due to vehicular emissions. As well as other volatile organic compounds, they play a central role in tropospheric chemistry and photochemical air pollution (Atkinson, 2000). Their negative impact on environmental and public health are also of general concern (Liu *et al.*, 2009). Biogenic volatile organic compounds are also emitted by vegetation. Diverse factors influence the emission of biogenic compounds such as light and temperature and their atmospheric concentrations depend on emission factors, meteorology, deposition rates and transport (Kesselmeier and Staudt, 1999).

Rio de Janeiro is the second largest city in Brazil and is home to 6 320 446 inhabitants (IBGE, 2015). It is one of the most visited cities in the Southern

Hemisphere, and it is known for its natural settings, beaches, music and events. Rio de Janeiro's Maracanã stadium held the finals of the 2014 FIFA World Cup, the 2013 FIFA Confederations Cup and both the opening and closing ceremonies of the XV Pan American Games. The city also hosted the 2011 World Military Games and the World Youth Day in 2013. During the 2014 FIFA World Cup, the city hosted 886 000 tourists (471 000 from other countries and 415 000 from Brazil), who spent approximately nine days in the city. A total of 580 000 spectators attended the seven football matches that were held at Maracanã stadium, and 814 000 people participated in the FIFA Fan Fest in Copacabana (Portal da Copa, 2014). These tourists spent an average of R$639/day each in the city, including expenditures for meals, accommodations, travel and leisure; thus, these visitors as a whole injected more than R$4.7 billion into the economy (Portal da Copa, 2014). Rio de Janeiro will host the 2016 Summer Olympics and the 2016 Summer Paralympic Games, which will be the first time a South American and Portuguese-speaking nation has hosted this event and will be the third time the Olympics have been held in a Southern Hemisphere city (Rio 2016, 2015). These major events have provided a unique opportunity to hasten needed infrastructure investments in the city. During these major events, the eyes of the world will be on Rio de Janeiro and its transportation, security, education and environmental quality, the latter of which is discussed in both Brazil and other countries.

In this work, the concentrations of three selected compounds were determined in the most visited locations within the city during the 2014 FIFA World Cup (June 12, 2014 to July 13, 2014). Isoprene (2-methyl-1,3-butadiene) was selected as a marker of biogenic emissions, and benzene and toluene were selected as markers of anthropogenic emissions, primarily vehicular emissions. To the best of our knowledge, isoprene concentrations have never been reported for the Tijuca Forest and the greener areas of the city of Rio de Janeiro. The kinetic and mechanistic reactivities of these compounds were also calculated to estimate the actual contribution of these compounds to atmospheric oxidant formation.

2. Experimental

2.1 Sampling sites

Air samples were collected in the days before and during the 2014 FIFA World Cup at the major landmarks in Rio de Janeiro. A map of the city with the sampling locations highlighted is presented in Figure 1 and the coordinates of the sampling locations and the sampling dates are listed in Table I. All sampling was performed in duplicate using 1.8 L canisters at a height of approximately 1.5 m, as described below.

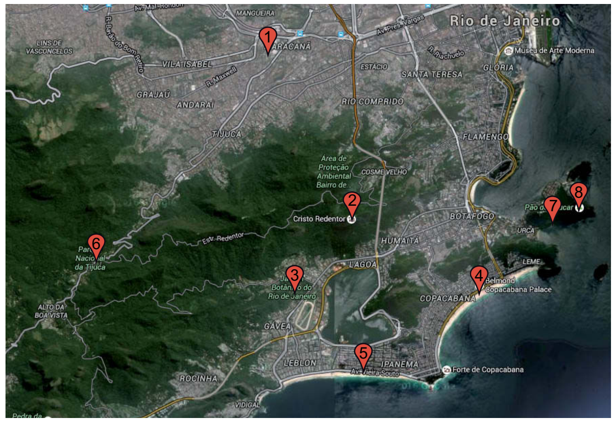

Fig. 1. Map of Rio de Janeiro showing the sampling locations: (1) Maracanã stadium; (2) Corcovado; (3) Botanical Garden; (4) Copacabana; (5) Ipanema; (6) Tijuca forest; (7) Claudio Coutinho trail; (8) Sugarloaf mountain (top). Source: Google Maps.

2.1.1 Copacabana

Copacabana is a neighbourhood located in the south zone of Rio de Janeiro. It is known for its 4.15 km beach located on the Atlantic shore (Rio Guide, 2015). According to the Instituto Brasileiro de Geografia e Estatística (Brazilian Institute of Geography and Statistics, IBGE), 160 000 people live in Copacabana, and 44 000 or 27.5% of them are 60 years old or over (IBGE, 2015). Hotels, restaurants, bars, nightclubs and residential buildings dot the famous promenade between the ocean and Atlantic Avenue, which is built of black and white Portuguese pavement. Samples were collected in the promenade before the World Cup opening (June 8) and during the event (June 29) in front of the Copacabana Palace Hotel (Post 7), one of the most frequented places in Copacabana. On both days, only one line of Atlantic Avenue was open to traffic. On June 29, many tourists were attending the TV exhibition of the FIFA Fan Fest.

2.1.2 Ipanema

Ipanema is also a neighbourhood located in the south zone of Rio de Janeiro, between Arpoador and

Table I. Sampling sites and dates.

Location	Latitude (ºS)	Longitude (ºW)	Date	T (°C)	Sampling time (LT)	Football game at Rio de Janeiro
Copacabana beach	22.96796	43.17889	06/08/2014	30	15:03 and 15:10	—
Copacabana beach	22.96771	43.17862	06/29/2014	35	14:41 and 14:48	Round of 16
Ipanema beach	22.98627	43.20741	06/08/2014	30	16:00 and 16:05	—
Ipanema beach	22.98663	43.20749	06/29/2014	29	15:40 and 15:47	Round of 16
Sugarloaf mountain	22.94939	43.15642	05/03/2014	22	14:30 and 14:37	—
Sugarloaf mountain	22.94931	43.15635	07/05/2014	32	13:40 and 13:48	Quarterfinals
Claudio Coutinho trail	22.95254	43.16084	05/03/2014	30	13:31 and 13:36	—
Claudio Coutinho trail	22.95258	43.16092	07/05/2014	26	12:31 and 12:38	Quarterfinals
Corcovado	22.95177	43.21018	05/04/2014	32	14:00 and 14:05	—
Corcovado	22.95185	43.21019	07/06/2014	32	13:38 and 13:45	—
Botanical Garden	22.96865	43.22451	06/08/2014	30	13:21 and 13:26	—
Botanical Garden	22.9687	43.22539	06/29/2014	32	13:28 and 13:35	Round of 16
Tijuca forest	22.96736	43.28528	06/22/2014	22	12:03 and 12:08	Group matches
Tijuca forest	22.96137	43.27344	06/22/2014	22	13:15 and 13:20	Group matches
Tijuca forest	22.96119	43.27343	06/29/2014	25	12:50 and 12:55	Round of 16
Maracanã stadium	22.91325	43.22784	06/08/2014	33	12:29 and 12:34	—
Maracanã stadium	22.91325	43.22784	06/12/2014	29	12:25 and 12:30	Group matches
Maracanã stadium	22.91325	43.22784	06/15/2014	27	12:20 and 12:25	Group matches
Maracanã stadium	22.91325	43.22784	08/18/2014	28	12:50 and 12:55	Group matches
Maracanã stadium	22.91379	43.22928	06/25/2014	29	11:05 and 11:10	Group matches

Leblon. Ipanema is famous for its social and cultural life. Every Sunday, the roadway closest to the beach (2 km) is closed to motor vehicles, and people ride bikes, roller skate, skateboard, and walk along the ocean (Rio Guide, 2015). Sampling was performed in Post 9, near a hotel located in Vieira Souto avenue and Farme de Amoedo street, directly in front of the beach. The area is always crowded, and it is considered one of the most beautiful urban beaches in the world and an icon of the city. During the first sampling date (June 8), many people were in the surrounding area because the Netherlands national football team was staying at the hotel. During the second sampling date (June 29), many tourists were visiting the area.

2.1.3 Sugarloaf mountain

Sugarloaf mountain is a 396 m peak situated in Rio de Janeiro at the entrance of Guanabara Bay on a peninsula that protrudes into the Atlantic Ocean. Sugarloaf is a natural, historic and tourist landmark. It consists in a single massive block of granite-derived stone that has been moulded by atmospheric pressure and temperature over a period of 600 million years. It has very little vegetation on its slopes but is surrounded by tropical vegetation in remnants of the Atlantic forest, containing native species that are extinct in other areas of the Brazilian coast (Rio Guide, 2015; Bondinho, 2015). The hill is accessible via cable car. In the first leg, the cable car travels approximately 575 m from Praia Vermelha to a height of 220 m above sea level; the second leg covers 750 m to reach the top. Between June 12 and July 13, 174 830 tourists visited the Sugarloaf mountain, with a mean of 5500 visitors and peaks of 8000 tourists on some days (Portal da Copa, 2014; RJ, 2014). Samples were collected on the Claudio Coutinho trail between the beach and the Sugarloaf mountain and on top of the hill (May 3 and July 5).

2.1.4 Corcovado

The statue of Corcovado (Christ the Redeemer) is the largest and most famous Art Deco sculpture in the world. It is located in the Tijuca National Park at an altitude of 710 m and gives a sweeping panorama of the sea and mountains, a world-famous vista. The mountain is crowned by the statue of Christ the Redeemer, which is 30 m high with an 8 m pedestal, and a chapel to honour our Lady of Aparecida, the patron saint of Brazil (Rio Guide, 2015). In 2007, it was selected by more than 100 million votes as one of the Official New 7 Wonders of the World to represent our global heritage (New 7, 2015). During the World Cup, 295 917 tourists visited the Corcovado, with a daily mean of 5000 people and a maximum of 12 000 people (Portal da Copa, 2014). Samples were collected at the top of Corcovado on May 4 and July 6.

2.1.5 Botanical Garden

The Botanical Garden is considered to be one of the most important gardens in the world. The 1.40-km^2 park lies at the foot of Corcovado mountain, far below the right arm of the statue of Christ the Redeemer, and contains more than 8000 different species of tropical and subtropical plants and trees, including 900 varieties of palm trees. The park is protected by the Patrimônio Histórico e Artístico Nacional (National Historical and Artistic Heritage) and was designated as a biosphere reserve (live museum) by UNESCO in 1992 (Rio Guide, 2015). Samples were collected on June 6 and June 29 in sector 9, an area with Bengal bamboo trees, at approximately 100 m from Frei Leandro Lake and Alea Barbosa Rodrigues (the main street with imperial palms). Bengal bamboos (*Bambusa multiplex*) are approximately 8 m tall, and the area is clear and sunny. According to the administration of the Botanical Garden, 727 389 people visited the park in 2014. During the 2014 FIFA World Cup, the Botanical Garden received approximately 50 000 visitors, approximately the same number of visitors as in the same period of 2015.

2.1.6 Tijuca forest

The Tijuca National Park, with approximately two million visitors per year, is one of the largest urban forests in the world, covering 39.51 km^2. It is home to hundreds of species of plants and wildlife found only in the Atlantic rainforest, many of which are threatened by extinction. The park is divided into four sectors: Tijuca Forest, Serra da Carioca, Pedra Bonita/Pedra da Gávea, and Pretos Forros/Covanca. The Tijuca Forest, the largest urban reforested area in the world sector is home to Tijuca Peak (1021 m), Papagaio Peak (987 m) and the Taunay Waterfall (Rio Guide, 2015). The peaks form a natural barrier to air circulation that results in heavy rains of more than 2000 mm year^{-1}. This preserved portion of the Atlantic forest area is highly sought after by locals and tourists for sports, walking and bike hires. The forest is located in the middle of Rio de Janeiro, dividing the city into northern and southern regions (Pougy *et al*., 2014; Azevedo *et al*., 1999; Custódio *et al*., 2010).

In this work, samples were collected at the park entrance (372 masl) in a residential area with a high circulation of people, a small restaurant and a bus stop and at the Excelsior's pathway, a trail in a rather isolated area inside the forest at an altitude of approximately 550 m that is only accessible by foot. The area inside the forest was sunless and humid. On June 22, samples were collected at the entrance of the park (Afonso Viseu square) and at Excelsior's pathway. On June 29, samples were collected at Afonso Viseu square.

2.1.7 Maracanã stadium

Maracanã stadium, officially called Estádio Mário Filho, with a capacity of 79 000 seats (Maracanã, 2015), hosted a total of seven matches during the 2014 World Cup, including one quarterfinal and the final. Samples were collected near the statue of Bellini at the entrance to Maracanã on June 8, 12, and 15. On June 8, many tourists visited this location, and Maracanã avenue was open to regular traffic. On June 12 (the opening of the World Cup in the city of São Paulo), many tourists and regular traffic were also present. On June 15, the first match in Rio de Janeiro, the vicinity of the stadium and the neighbourhood were crowded with heavy traffic. On June 18 and 25, sampling was performed approximately 50 m from the entrance because access was closed to the general public. The area was crowded, and Maracanã avenue was closed to traffic.

2.2 Sampling and analysis

Samples were collected at a standard sampling height of 1.5 m using 1.8 L stainless steel canisters (RM Environmental System) with Swagelok diaphragm valves. The canisters were cleaned per the recommended procedures outlined in Method TO-15 (US-EPA, 2015), using a Teledyne Hasting Instruments cleaning system (model Omega CN9000A). Briefly, all canisters were evacuated to 5 mTorr at 120 ºC and maintained under vacuum for 60 min; the canisters were then filled with humidified (50% relative humidity) He to 30 psig. This cycle was completed two additional times for a total of three cycles, and then three additional cycles were completed with dry He. The canisters were then evacuated to < 5 mTorr. Grab samples were collected using the sub-atmospheric method with the evacuated canisters. When the canisters were opened to the atmosphere containing the VOCs to be sampled, the differential pressure caused the sample to flow into the canister (duration of 2 to 3 min).

Canister samples were analysed on a GC/MS/TD system (Agilent, model GC 5975C, CG/EM 7890A and Markes CIA Advanced). Samples were transferred and analysed according to the TO-15 method. In the analysis of a sample, 500 ml of the air sample were directed from the canister (flow rate of 20 ml min^{-1}) through a Nafion dryer trap to reduce the water vapour content below any threshold affecting the proper operation of the analytical system. It was then directed through a cold trap containing carbon molecular sieves (Markes U-T3ATX-2S) at –10 ºC. After completion of the drying and concentration steps, the VOCs were thermally desorbed (300 ºC) and then released onto the gas chromatographic column for separation (60 m × 0.32 mm × 1.80 µm DB-624 column, Agilent catalogue number 123-1364). The carrier gas was He at a constant flow rate of 3.5 ml min^{-1}. The oven temperature programme was as follows: 25 ºC for 5 min, from 25 ºC to 50 ºC at 0.8 ºC min^{-1}, 50 ºC to 250 ºC at 5 ºC min^{-1}, and then 250 ºC for 3 min. The injector temperature was 190 ºC, and split injection mode was used. The detection and identification of each compound was achieved by selective ion monitoring (SIM) of the most abundant ions: isoprene at *m/z* 67, 68, 53; toluene at *m/z* 91, 92, 65; and benzene at *m/z* 78, 77, 51. Quantification was carried out on the basis of two external calibration curves constructed using two standard reference mixtures that covered the entire concentration range of the ambient samples (57 compounds, Restek, 20-60 ppbC, p/n 34445; and 57 compounds, Supelco, 100 ppb, p/n P400947). The calculated correlation coefficients of the linear fits were greater than 0.99. For isoprene, the concentration range of the calibration curve was 0.26-5.22 mg m^{-3} and the correlation coefficient was 0.993. For benzene, the concentration ranges for the two calibration curves were 0.37-7.44 and 5.10-63.80 mg m^{-3}, and the correlation coefficients were 0.996 for both curves. For toluene, the concentration ranges for the two calibration curves were 0.50-10.10 and 7.22-90.30 mg m^{-3}, and the correlation coefficients were 0.991 and 0.997, respectively. All of the samples were measured in duplicate, and a difference of less than 25% was considered acceptable, as stated in the TO-15 method. The limits of detection (LOD) and quantification (LOQ), calculated using the standard deviation of the noise, were 0.2 ng and 0.6 ng, respectively, for the three compounds. Blank canisters were generated by pressurizing clean canisters with He. Canisters were considered clean if less than 0.2 ng of each target compound were detected. Samples were analysed within 30 days of the sampling date.

3. Results and discussion

3.1 Concentrations

Samples were collected in the days before and during the FIFA World Cup, specifically, from May 3, 2014 to July 6, 2014 and between 13:00 and 15:00 LT. All days were sunny, with temperatures between 25 ºC and 32 ºC at the sampling hour.

The mean concentrations at each location and the number of samples are presented in Table II. For individual samples, the isoprene concentrations ranged from 0.39 µg m^{-3} (Maracanã) to 2.32 µg m^{-3} (Botanical Garden). The benzene concentrations were between 2.27 µg m^{-3} (Maracanã) and 10.16 µg m^{-3} (Claudio Coutinho trail). Finally, the toluene concentrations ranged from 5.21 µg m^{-3} (Maracanã) to 21.83 µg m^{-3} (Claudio Coutinho trail).

The benzene and toluene concentrations were lower in the Maracanã area, primarily in the last three days. These lower concentrations are likely attributable to the restriction of vehicular travel near the stadium during those days. The highest concentrations were detected at the Claudio Coutinho trail leading to the Morro da Urca and Sugarloaf mountains, likely because of the emissions from ships entering Guanabara Bay. Ipanema, Copacabana and the Botanical Garden showed similar concentrations, as expected considering that the three locations are in the south area of the city, where the main emission source is vehicular traffic.

The isoprene concentrations were lower in Ipanema, Copacabana and Maracanã, which are typical urban areas. The lower levels on the top of Corcovado and Sugarloaf mountains than at the Claudio Coutinho trail, may be due to the circulation of air and dispersion of isoprene at higher altitudes. At sea level typical wind speeds in the costal area are 4-9 km h^{-1} (ICEA, 2016), while on the top of Corcovado are 10-15 km h^{-1} (Meteoblue, 2016). The highest isoprene concentrations were detected

Table II. Concentrations of isoprene, benzene and toluene in µg m^{-3} (each value was determined in duplicate), mean concentrations at each studied location, and values obtained worldwide using canisters, cartridge sampling and continuous monitoring.

Location	Date	Method	Concentration / µg m^{-3}						Benzene/ toluene ratio (w/w)	N	Reference
			Isoprene	SD	Benzene	SD	Toluene	SD			
Rio de Janeiro											
Copacabana beach	June 2014	TO-15	0.55	0.06	4.7	0.2	10.6	0.9	0.44	8	This work
Corcovado	July 2014	TO-15	0.69	0.05	4.9	0.5	10.0	0.4	0.49	4	This work
Tijuca forest	June 2014	TO-15	0.64	0.03	4.7	0.1	10.3	0.3	0.46	12	This work
Ipanema beach	June 2014	TO-15	0.66	0.05	4.9	0.5	11.4	2.0	0.43	8	This work
Botanical Garden	June 2014	TO-15	1.9	0.2	4.6	0.1	10.2	0.3	0.45	8	This work
Maracanã stadium	June 2014	TO-15	0.6	0.2	3.8	0.4	9.7	0.8	0.39	18	This work
Sugarloaf mountain	May 2014	TO-15	1.1	0.2	4.7	0.4	9.5	0.5	0.49	7	This work
Claudio Coutinho trail	May 2014	TO-15	1.1	0.2	7.4	0.2	15.9	0.5	0.47	6	This work
Oswaldo Cruz Institute	Apr-Dec 2002	TO-1 and TO-2	ND	–	1.9	NI	9.0	NI	0.21	13	Rodrigues *et al*. (2007)
Saens Peña square	Mar/2002-Feb 2003	TO-1 and TO-2	ND	–	1.1	NI	4.8	NI	0.23	30	Martins *et al*. (2007)
President Vargas avenue	2004-2005	TO-1 and TO-2	ND	–	4.8-40.7	8.2	9.1-37.5	6.6	0.53-1.0	94	Corrêa and Arbilla (2007)
Tijuca forest (entrance of the park)	Mar-Aug 2008	TO-2	ND	–	2.6	2.6	2.7	2.7	0.96		Custódio *et al*. (2010)
Tijuca forest (leisure area)	Mar-Aug 2008	TO-2	ND	–	1.6	1.6	1.5	1.5	1.11		Custódio *et al*. (2010)
Tijuca forest (Bandeira peak)	Mar-Aug 2008	TO-2	ND	–	1.7	1.7	1.8	1.8	0.94	60	Custódio *et al*. (2010)
Gas stations	2008-2009	TO-1 and TO-1A	ND	–	29.7	19.7	47.7	27.4	0.63	49	Corrêa *et al*. (2012)
Rio de Janeiro/RJ	2012	TO-15	1.39	2.41	7.90	6.81	12.05	9.34	0.65	16	Martins *et al*. (2015)
Other cities in Brazil											
São Paulo/SP	2003	TO-17	ND	–	8.6	4.4	28.2	12.7	0.30	14	Martins *et al*. (2008)
Curitiba/PR	Jul 2008-Sept 2008	TO-1 and TO-2	ND	–	3.9-6.1	NI	6.5-7.2	NI	0.59-0.83	12	Godoi *et al*. (2010)
Curitiba/PR	2009 – 2011	TO-1 and TO-2	ND	–	1.8	0.58	4.2	2.8	0.43	NI	Godoi *et al*. (2013)
Other cities around the world											
Hong Kong (roadside)	1998	Sorbent tubes	ND	–	26.7	33.0	77.2	74.4	0.35	36	Chan *et al*. (2002)
Perth (Australia)	2000	TO-15	ND	–	5.7	4.4	18.4	18.8	0.31	NI	Hinwood *et al*. (2006)
Industrial parks (southern Taiwan)	2003-2004	NIOSH-1615	ND	–	6.6	3.7	22.8	16.5	0.29	129	Hsieh *et al*. (2006)
Antwerp (Belgium)	2005	TO-1 and TO-2	ND	–	2.1	0.7	9.5	2.9	0.26	NI	Buczynska *et al*. (2009)
Beijing (China)	2006	TO-15	3.55	NI	8.37	NI	14.41	NI	0.58	NI	Duan *et al*. (2008)
Beijing (China)	2008	TO-1 and TO-2	ND	–	3.72	3.03	6.94	7.86	0.54	982	Liu *et al*. (2009)
Bogota, southwest (Colombia)	2008-2009	Continuous monitoring	1.5	1.1	4.6	3.6	ND	ND	–	NI	Franco *et al*. (2015)
Mexico City (Mexico)	2011-2012	TO-14A / TO-15	ND	–	20.4	NI	97.9	NI	0.21	NI	Garzón *et al*. (2015)
Bogota, southwest (Colombia)	2008-2009	Continuous monitoring	1.5	1.1	4.6	3.6	ND	ND	–	NI	Franco *et al*. (2015)

N: number of samples; ND: non-determined; NI: non-informed.

at the Botanical Garden, where the levels were even higher than those in the Tijuca forest. This latter result is attributed to the distribution of vegetation at the Garden, which allows incoming solar radiation to reach the ground. Conversely, the Tijuca forest is colder, sunless and humid. A thermal gradient of 0.4 ºC/100 m was calculated for temperature variation with altitude (80 to 1021 m) within the Forest (Freitas *et al*., 2006). Literature data have shown that increases in light and temperature trigger the production and release of isoprene and that isoprene emissions decrease significantly with shading. Emission factors are also highly variable among species (Kesselmeier and Staudt, 1999). Also, the Tijuca forest is a secondary Atlantic rainforest (Mata Atlântica) with species that are quite different from those at the Botanical Garden, which is home to tropical and subtropical plants and trees.

The number of samples was not sufficient to clearly assess the impact of the World Cup event on the air quality. The obtained results show that for Ipanema, Copacabana and the greener areas, the difference in concentrations before and during the event is smaller than the variation in concentrations due to meteorological factors and the experimental uncertainties of the analytical method. In the Maracanã area, benzene and toluene concentrations were approximately 2 and 3 times higher, respectively, before the event than during the event. As previously noted, this difference may be due to the restriction of vehicular traffic during the World Cup. This finding suggests that light and heavy traffic are the main emission sources, whereas other events, such as shows and fireworks, and the increase in the number of visitors do not affect the air quality in a noticeable way. The 2016 Olympic Games will be a good opportunity to further examine these conclusions. Sixteen new monitoring stations were installed by the Instituto Estadual do Ambiente (State Environmental Institute, INEA) in locations where the games are to be held, as part of the "environmental commitment" signed by the government and the Brazilian Olympic Committee. The authorities have considered the possibility of making changes such as diverting bus routes, temporarily closing nearby gasoline stations and altering the operating hours of factories if air pollution is detected. To cut city traffic during the period of the Games, school holidays will take place in August rather than the traditional month of July and will also last longer than usual. Meanwhile, city authorities and industry associations have said they will be encouraging employees to work from home; the target is for each company to reduce commuting traffic by 30% during the Games (Rio 2016, 2015).

Data obtained at other locations are also shown in Table II for comparison. These results were obtained under a variety of conditions using different sampling and analytical methods under different meteorological and climatic conditions. Nevertheless, the concentrations are of the same order of magnitude as those determined at other locations in Rio de Janeiro, Brazil, and in other countries with developed or emerging economies and lower than typical values for some industrial and urban areas of developing countries in Asia (Chan *et al*., 2002). They are also in agreement with the results recently reported by Martins *et al.* (2015) using the same method. A benzene/toluene ratio of around 0.5 (w/w) has been reported as characteristic of vehicular emissions (Duan *et al*., 2008). The benzene/toluene ratios obtained in this study ranged from 0.39 to 0.49 and were similar at all locations, suggesting that both compounds have a common emission source, i.e., vehicular emissions that are transported from the city to greener areas (Tijuca forest, Corcovado and Sugarloaf mountain).

Mean concentration values are higher than those determined by Liu *et al.* (2009) during the Olympic Games in an urban area of Beijing. Benzene is carcinogenic and accounts for 68% of the cancer risk from all vehicle related pollutants (Chan *et al.*, 2002). The Ambient Air Quality and Cleaner Air for Europe limit value (EC, 2008), to be attained until January 2010, was specified as 5 mg m^{-3}, to protect human health. Mean values determined in this work are slightly under this limit value, except for the Claudio Coutinho trail, which is an important leisure area next to the place were the sailing Olympic competitions will be held. Except for Maracanã, the studied locations are in the south area of the city characterized by a higher standard of living and a better air quality. As shown in Table II, Martins *et al*. (2015) determined a mean benzene concentration of 7.9 mg m^{-3} in several streets of the north area of the city, indicating a severe air quality deterioration and risk for visitors and permanent residents.

Results obtained in this study also show that the greener areas are strongly affected by urban emissions, even the top of the Corcovado and Sugarloaf mountains, and the Tijuca forest, which are expected to be cleaner areas for leisure and athletics. The transport of pollutants from downtown and the northern, industrialized region of the metropolitan Area of Rio de Janeiro clearly impacts the air quality of these regions and may affect the life of local plants and animals.

3.2 Reactivity study

The atmospheric roles of isoprene, toluene and benzene were evaluated in terms of their reactivities towards hydroxyl radicals (OH) and roles in the formation of ozone. As thoroughly described by Atkinson (2000), in the troposphere VOCs are removed by the physical processes of wet and dry deposition and are transformed by the chemical processes of photolysis and reaction with hydroxyl (OH) radicals, nitrate (NO_3) radicals and O_3. Isoprene, as well as other alkenes, and aromatic compounds such as benzene and the alkyl-substituted benzenes react with both OH and NO_3 radicals, and the OH radical reactions dominate tropospheric removal during daytime hours.

Two reactivity scales were used in this work: kinetic and mechanistic. The kinetic reactivity was evaluated as the product of mean concentrations of each VOC and the rate coefficient (k_{OH}) for the reaction of the target compound with OH radicals, using literature k_{OH} values of 1.01×10^{-10}, 6×10^{-12} and 1.2×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for isoprene, toluene and benzene, respectively. This scale is based on the fact that attack of VOCs, such as those studied in this work, by OH radicals is responsible for the majority of VOC consumption, and this process leads to the production of the free radicals (HO_2, RO_2) that oxidize NO to NO_2, which, in turn, leads to ozone formation. These values are related to the reaction rate and to the lifetime of the VOCs in the atmosphere. Also lifetimes were calculated as $1/([OH] \times k_{OH})$, were [OH] is the 12-h daytime average OH radical concentration of 2.0×10^6 molecules cm^{-3}. The mechanistic reactivity reflects the oxidation process and is a measure of the ozone-forming potential of the target VOC, which depends not only on the k_{OH} values but also on the reaction mechanism. The mechanistic reactivity (ozone-forming potential) can be expressed as the incremental reactivity (IR), which is defined as the number of molecules of ozone formed per VOC carbon atom added to an initial atmospheric reaction mixture of VOCs and NO_x. The maximum incremental reactivity (MIR) coefficients proposed by Carter (2010) in units of grams of formed O_3 per gram of VOC added are typically used. In this work, the mechanistic reactivity was calculated as the product of the concentration (μg m^{-3}) and the MIR coefficient (dimensionless). It is worth mentioning that MIR coefficients were calculated for typical urban conditions with high NO_x concentrations. In fact, the production of ozone from isoprene and other VOCs only occurs in the presence of nitrogen oxides through the conversion of NO to NO_2.

The kinetic and mechanistic reactivities for the three compounds are displayed in Tables III and IV, respectively.

Although the mass contribution of isoprene is low in comparison to the other compounds, its OH-reactivity is about ten times the benzene OH-reactivity

Table III. Kinetic reactivities for isoprene, toluene and benzene at the studied locations. Values (s^{-1}) were evaluated as the product of the concentrations and the rate coefficient (k_{OH}) for the reaction of the target compound with OH radical.

Location		Isoprene kinetic reactivity	Benzene kinetic reactivity	Toluene kinetic ractivity
Urban areas	Copacabana Beach	0.49	0.04	0.42
	Ipanema beach	0.59	0.05	0.45
	Claudio Coutinho trail	0.96	0.07	0.62
	Maracanã stadium	0.57	0.03	0.38
Green areas	Corcovado	0.62	0.05	0.39
	Sugarloaf mountain	1.02	0.05	0.37
	Tijuca forest	0.57	0.04	0.40
Botanical Garden		1.73	0.04	0.40

Table IV. Mechanistic reactivities for isoprene, toluene and benzene at the studied locations (in units of μg m^{-3}). Values were calculated as the product of the mean concentration (μg m^{-3}) and the maximum incremental reactivity (MIR) coefficient, which is dimensionless.

Location		Isoprene	Benzene	Toluene
Urban areas	Copacabana beach	5.8	3.4	42.5
	Ipanema beach	7.0	3.6	45.8
	Claudio Coutinho trail	11.5	5.4	63.4
	Maracanã stadium	6.8	2.7	38.8
Green areas	Corcovado	7.3	3.5	40.2
	Sugarloaf mountain	12.1	3.4	38.2
	Tijuca forest	6.8	3.4	41.3
Botanical Garden		20.6	3.3	40.9

and of the same order of the toluene reactivity. These results were expected because the rate coefficient k_{OH} for isoprene is 84 and 17 times greater than those of benzene and toluene, respectively. The lifetimes of these compounds, considering a 12-h daytime average OH radical concentration of 2.0×10^6 molecule cm^{-3}, were 3 h, 2 days and 10 days for isoprene, toluene and benzene, respectively. For this reason, benzene and toluene can be transported from the urban areas to the forest and remote areas. Climatological evaluations of the wind patterns for Rio de Janeiro revealed a higher frequency of south-southeast to north-northwest winds in virtually every month of the year (Azevedo *et al.*, 1999). The incoming air masses from the Atlantic Ocean transport pollutants from the city to the north and the mountains of the Tijuca forest, with peaks at 800-1000 m altitude (Azevedo *et al.*, 1999; Cústodio *et al.*, 2010). Therefore, as previously discussed, the Tijuca forest, a national park, is likely severely impacted by urban emissions.

The mechanistic reactivities ranged from 5.8 μg m^{-3} (Copacabana) to 20.6 μg m^{-3} (Botanical Garden) for isoprene, 2.7 μg m^{-3} (Maracanã) to 3.6 μg m^{-3} (Ipanema) for benzene, and 38.2 μg m^{-3} (Sugarloaf mountain) to 63.4 μg m^{-3} (Claudio Coutinho trail) for toluene. These values represent the quantity of ozone, in μg m^{-3}, that can form from the target compounds under typical conditions. In the present conditions toluene is the most effective compound to form ozone.

To the best of our knowledge, this is the first report of the atmospheric kinetic and mechanistic reactivities for the city of Rio de Janeiro showing the importance of isoprene as an ozone precursor.

4. Conclusions

Benzene and toluene concentrations indicated that the greener areas of the city were strongly affected by urban emissions due to the transport of pollutants. The levels of these compounds in all of the studied areas were similar to those of other urban areas around the world and higher than those determined in an urban area of Beijing during the Olympic Games. Samples were collected in the major landmarks of the city, which are in the south area of Rio de Janeiro. This area is characterized by a higher air quality, which suggests that permanent residents and some visitors in the north and west areas may be exposed to severe air quality deterioration and health risks. The levels of isoprene were similar to those previously determined in areas with vegetation. The data from the Botanical Garden suggest that this area should be studied further. Despite the important roles of tropical and subtropical ecosystems in atmospheric processes, global carbon sequestration and VOC emission levels, available data on the exchange of VOCs in these regions remain scarce. Notably, this work is the first report on isoprene concentrations in the Tijuca forest and the greener areas of Rio de Janeiro.

Certainly it would have been important to collect more air samples within the canisters. Unfortunately, it was not possible because of the police control during the World Cup. In locations such as Corcovado, Sugarloaf and mainly the Maracanã area, it was very difficult to get the samples because on some days we were not allowed to go into those places with the sampling Due to the reduced number of samples it was not possible to perform a statistical analysis. In view of the upcoming

Olympic Games, this study could be quite valuable for planning the exhaustive monitoring campaign which will be conducted in 2016.

Acknowledgments

The authors acknowledge financial support from FAPERJ, CAPES and CNPq (CNPq Proc. 490252/2011-7). ECCS and GA also acknowledge CNPq for doctoral and researcher scholarships, respectively.

References

Atkinson R., 2000. Atmospheric chemistry of VOCs and NOx. *Atmos. Environ.* **34**, 2063-2101, doi: 10.1016/S1352-2310(99)00460-4.

Azevedo D. de A., L. S. Moreira and D. S. de Siqueira, 1999. Composition of extractable organic matter in aerosols from urban areas of Rio de Janeiro city, Brazil - occurrence and origin. *Atmos. Environ*. **33**, 4987-5001, doi: 10.5094/APR.2014.011.

Bondinho, 2015. Bondinho 100 anos. Available at: http://www.bondinho.com.br (last accessed on December 14, 2015).

Buczynska A. J., V. Kontozova-Deutshc, L. Bencs, I. Naveau, E. Roekens and R. V. Grieken, 2009. Atmospheric BTEX-Concentrations in an area with intensive street traffic. *Atmos. Environ.* **43**, 311-318, doi: 10.1016/j.atmosenv.2008.09.071.

Carter W. P. L., 2010. Development of the SAPRC-07 chemical mechanism. *Atmos. Environ.* **44**, 5324-5335, doi: 10.1016/j.atmosenv.2010.01.026.

Chan C. Y., L. Y. Chan, X. M. Wang, Y. M. Liu, S. C. Lee, S. C. Zou, G. Y. Sheng and J. M. Fu, 2002. Volatile organic compounds in roadside microenvironments of metropolitan Hong Kong. *Atmos. Environ*. **36**, 2339-2047, doi: 10.1016/S1352-2310(02)00097-3.

Corrêa S. M. and G. Arbilla, 2007. A two-year monitoring program of aromatic hydrocarbons in Rio de Janeiro downtown area. *J. Braz. Chem. Soc*. **18**, 539-543, http://dx.doi.org/10.1590/S0103-50532007000300007.

Corrêa S. M., G. Arbilla, M. R. C. Marques and K. M. G. Oliveira, 2012. The impact of BTEX emissions from gas stations into the atmosphere. *Atmos. Poll. Res.* **3**, 163-169, doi: 10.5094/APR.2012.016.

Custódio D., C. S. Guimaraes, L. Varandas and G. Arbilla, 2010. Pattern of volatile aldehydes and aromatic hydrocarbons in the largest urban rainforest in the Americas. *Chemosphere* **79**, 1064-1069, doi: 10.1016/j.chemosphere.2010.03.028.

Duan J., J. Tan, L. Yang, S. Wu, and J. Hao, 2008. Concentration, sources and ozone formation potential of volatile organic compounds (VOCs) during ozone episode in Beijing. *Atmos. Res.* **88**, 25-35, doi: 10.1016/j.atmosres.2007.09.004.

EC, 2008. CAFE Directive 2008/50/EC. European Commission. Available in: http://www.ec.europa.eu (last accessed on April 28, 2016).

US-EPA, 2015. *Compendium of methods for the determination of toxic organic compounds in ambient air.* 2nd ed. Compendium method TO-15, determination of volatile organic compounds (VOCs) in air collected in specially-prepared canisters and analyzed by gas chromatography/mass spectrometry (GC/MS*)*. U.S. Environmental Protection Agency Cincinnati, OH, 67 pp. Available at: http:// www.epa.gov/ttnamti1/files/ambient/airtox/to-15r.pdf (last accessed on December 14, 2015).

Franco J. F., J. Pacheco, L. C. Belalcázar and E. Behrentz, 2015. Characterization and source identification of VOC species in Bogotá, Colombia. *Atmósfera* 28, 1-11.

Freitas S. R., Neves, C. and Chernicharo, P., 2006. Tijuca National Park: two pioneering restorationist initiatives in Atlantic forest in southeastern Brazil. *Braz. J. Biol.* **66**, 975-982, http://dx.doi.org/10.1590/S1519-69842006000600004.

Garzón J. P., J. I. Huertas, M. Magaña, M. E. Huertas, B. Cárdenas, T. Watanabe, T. Maeda, S. Wakamatsu and S. Blanco, 2015. Volatile organic compounds in the atmosphere of Mexico City. *Atmos. Environ.* **119**, 415-429, doi: 10.1016/j.atmosenv.2015.08.014.

Godoi A. F. L., R. H. M. Godoi, R. Azevedo and L. T. Maranho, L. T., 2010. Poluição e a densidade de vegetação: BTEX em algumas áreas públicas de Curitiba - PR, Brasil. *Quim. Nova* **33**, 827-833, http://dx.doi.org/10.1590/S0100-40422010000400012.

Godoi R. H. M., A. F. L. Godoi, S. J. G. Junior, S. L. Paralovo, G. C. Borillo, C. G. G. Barbosa, M. G. Arantes, R. C. Charello, N. A. R. Filho, M. T. Grassi, C. I. Yamamoto, S. Potgieter-Wermaak, G. G. Rotondo, K. de Wael and R. V. Grieken, 2013. Healthy environment - indoor air quality of Brazilian elementary schools nearby petrochemical industry. *Sci. Total Environ*. **463**, 639-646, doi: 10.1016/j.scitotenv.2013.06.043.

Hinwood A. L., H. N. Berko, D. Farrar, I. E. Galbally and I. A. Weeks, 2006. Volatile organic compounds in selected micro-environments. *Chemosphere* **63**, 421-429, doi: 10.1016/j.chemosphere.2005.08.038.

Hsieh L., H. Yang, H. and H. Chen, 2006. Ambient BTEX and MTBE in the neighborhoods of different industrial parks in Southern Taiwan. *J. Hazard Mater.* **128**, 106-115.

ICEA, 2016. Instituto de Controle do Espaço Aéreo. Available at: http://www.icea.gov.br/novo/ (last accessed on May 4, 2016).

IBGE, 2015. Instituto Brasileiro de Geografia e Estatística. Available at: http://www.ibge.gov.br (last accessed on December 14, 2015).

Kesselmeier J. and M. Staudt, 1999. Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology. *J. Atmos. Chem*. **33**, 23-88, doi: 10.1023/A:1006127516791.

Liu J., Y. Mu, Y. Za, Z. Zhang, X. Wang, Y. Liu and Z. Sun, 2009. Atmospheric levels of BTEX compounds during the 2008 Olympic Games in the urban area of Beijing. *Sci. Total Environ.* **408**, 109-116, doi: 10.1016/j.scitotenv.2009.09.026.

Maracanã, 2015. The stadium guide. Available at: http://www.stadiumguide.com/maracana/ (last accessed on December 14, 2015).

Martins E. M., G. F. Bauerfeldt, M. de Paula and G. Arbilla, 2007. Atmospheric levels of aldehydes and BTEX and their relationship with vehicular fleet changes in Rio de Janeiro urban area. *Chemosphere* **67**, 2096-2103, doi:10.1016/j.chemosphere.2006.09.088.

Martins L. D., M. F. Andrade, R. Y. Youne, E. L. Albuquerque, E. Tomaz and P. C. Vasconcellos, 2008. Ambiental volatile organic compounds in the megacity of São Paulo. *Quim. Nova* **31**, 2009-2013, http://dx.doi.org/10.1590/S0100-40422008000800018.

Martins E. M., A. C. L. Nunes, and S. M. Corrêa, 2015. Understanding ozone concentrations during weekdays and weekends in the urban area of the city of Rio de Janeiro. *J. Braz. Chem. Soc.* **26**, 1967-1975, http://dx.doi.org/10.5935/0103-5053.20150175.

Meteoblue, 2016. Tempo Morro do Corcovado. Available at: www.meteoblue.com (last accessed on May 4, 2016).

New 7, 2015. New seven wonders of the world. Available at: http://world.new7wonders.com/new7wonders-of-the-world-page/new7wonders-of-the-world/ (last accessed on December 14, 2015).

Portal da Copa, 2014. Available at http://copa2014.gov.br (last accessed on October 15, 2014).

Pougy N., E. Martins, M. Verdi, J. A. de Oliveira, D. Maurenza, R. Amaro R. and G. Martinelli, 2014. Urban forests and the conservation of threatened plant species: The case of the Tijuca National Park, Brazil. *Nat. Conservação* **12**, 170-173, doi:10.1016/j.ncon.2014.09.007.

Rio 2016, 2015. Available at: http://www.rio2016.com.br (last accessed on December 14, 2015).

Rio Guide, 2015. Guia do Rio. Available at: http://www.rioguiaoficial.com.br (last accessed on December 14, 2015).

RJ, 2014. Prefeitura do Rio de Janeiro. Available at: http://www.rio.rj.gov.br/web/riotur (last accessed on October 14, 2014).

Rodrigues F., I. Milas, E. M. Martins, G. Arbilla, G. F. Bauerfeldt and M. de Paula, 2007. Experimental and theoretical study of the air quality in a suburban industrial-residential area in Rio de Janeiro, Brazil. *J. Braz. Chem. Soc.* **18**, 342-351, http://dx.doi.org/10.1590/S0103-50532007000200015.