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Article

Determination of CO_2, CH_4 and N_2O: a Case Study for the City of Rio de Janeiro Using a New Sampling Method

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A new sampling method using polypropylene syringes and chemical analysis by gas chromatography was proposed and applied to determine CO_2, CH_4 and N_2O. The samples' stability was evaluated and compared with the stability of the samples in stainless steel canisters and Tedlar® bags. This methodology was applied to a case study in the urban area of the city of Rio de Janeiro, Brazil. In 2012, annual averages of 507.6 ± 13.2 µmol mol^{-1} for CO_2, 1.95 ± 0.06 µmol mol^{-1} for CH_4 and 325.3 ± 3.4 nmol mol^{-1} for N_2O were obtained. The results for CO_2 and CH_4 showed peak values in the warmer months and lower values in winter. This CO_2 behavior is the opposite of that observed in studies performed in many other cities around the world and may be climate-related. CH_4 and N_2O inputs are probably due to the evaporation of liquid and solid waste both from landfill sites located within the city boundaries and from polluted rivers and canals. Additionally, other anthropogenic sources may be considered, such as the release of CH_4 by the gas fuel network of the urban area and the emissions due to the use of compressed natural gas by light vehicles.

Keywords: urban atmosphere, greenhouse gas, carbon dioxide, methane, sampling

Introduction

According to the National Oceanic and Atmospheric Administration (NOAA), the highest globally averaged temperature for land and ocean surfaces since records began in 1880 was measured in 2014.[1] Additionally, in 2014, for the first time since carbon dioxide has been measured at Mauna Loa Observatory, Hawaii, its peak levels surpassed 400 µmol mol^{-1} during three consecutive months in the atmosphere.[2]

The highest carbon dioxide global average concentration was 398.83 µmol mol^{-1} in May 2014, according to NOAA.[2] Although this value has not yet reached 400 µmol mol^{-1}, these global concentrations of the main greenhouse gases (GHG) represent the highest historical values.

Carbon dioxide (CO_2) is the most important anthropogenic greenhouse gas in the atmosphere;[3] however, two other gases, i.e., methane (CH_4) and nitrous oxide (N_2O), are important, and they are all closely related to anthropogenic activities, such as fossil fuel combustion, agriculture, biomass burning and waste management.

Brazil is the largest country in Latin America. It is the world's fifth largest country by both geographical area and population.[4] It is considered part of the BRICS (Brazil, Russia, India, China and South Africa) group of countries, which are similar in terms of area, large populations and growing economies and, together, are responsible for 18% of the world's gross domestic product (GDP).[5]

The BRICS group emits an average of 4.5 metric tons *per* capita of CO_2, whereas the entire world, including the developed countries, emits an average level of 4.9 metrics tons *per* capita, according to the World Bank.[6] This points the need for the effective monitoring of GHG emissions in these countries.

Many studies have been published involving the measurement of GHG that originate from different sources, including stationary sources, mobile sources and ambient air. For example, GHG measurements have been included in studies involving emissions from human activities in the soil,[7-11] ships,[12,13] hydroelectric reservoirs,[14] vehicles[15-17] and thermoelectric power plants.[18] However, to our knowledge, the available literature contains no information on the variation in GHG concentrations in Rio de Janeiro and other Brazilian cities, despite their high level of urbanization and economical activities. The annual emissions of CO_2, CH_4 and N_2O in Rio de Janeiro have been estimated as 8,734 Gg, 112,616 t and 800 t, respectively.[19] The total emissions was calculated

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as 11,352 Gg CO_2, which means that the CH_4 and N_2O contribution to GHG is approximately 25%.[19]

A variety of methods for determining trace gases in the atmosphere has been developed. Discontinuous methods can be performed, without pre-concentration, by using stainless steel canisters or Tedlar® bags to collect air samples and for further chromatographic analysis.[20]

The collection of ambient air samples in canisters is common practice, and it is mainly done for the determination of volatile organic compounds (VOCs) in the atmosphere.[21,22] These canisters have advantages such as inertness, ruggedness, reuse and durability. Despite the high collection efficiency, there are some disadvantages when it is necessary to collect multiple samples at different sampling points, such as the high costs and greater difficulties in transporting the samples.

In most of the published studies regarding the measurement of GHG in ambient air from stationary and mobile sources, online analysis methods are employed, such as chromatographic and spectroscopic techniques.[23-25] Commercial analyzers, which have the advantage of providing continuous measurements, are available for automatic GHG monitoring. The high cost of these instruments and the installation requirements are their main disadvantages.

GHG are not currently monitored in Brazilian cities. To our knowledge, there are no data for Rio de Janeiro, which is the second largest city in Brazil. The following investigation was conducted to evaluate the efficacy of low-cost polypropylene (PP) syringes for the sampling and storage of CO_2, CH_4 and N_2O. The method was applied in a study case in Rio de Janeiro to evaluate the concentration of these three compounds at representative locations to determine the hourly concentrations over a typical day and seasonal variations throughout one year.

Experimental

Sampling media

In this experiment, 6.0 L internally electropolished (Restek SUMMA® coating) stainless steel canisters, 3.0 L Tedlar® bags (SKC), and 100 mL medical graduate PP syringes with Luer caps were used. The syringes' features include easy handling and transportation and a very low cost *per* unit. These types of syringes are also used in medical procedures and contain a PP body and rubber plunger. PP syringes might be a suitable substitute when continuous measurements are not available or when sampling with other well-developed sampling media, such as canisters and Tedlar® bags, cannot be implemented due to the related costs or difficult-to-reach sampling locations. For a blank test, each sampling material was filled with 99.999% synthetic air provided by Linde Gas.

Chemical analyses

The samples were analyzed by gas chromatography with multiple detectors. Chemical analyses were performed using an Agilent 7890A Gas Chromatograph with three detectors: a thermal conductivity detector (TCD) to measure CO_2 at high levels as well as molecular oxygen and nitrogen, an electron capture detector (ECD) to measure N_2O and a flame ionization detector (FID) to measure CH_4 and CO_2 at low levels.

The chromatography system used two separated channels with 1/8" packed columns (HayeSep Q80/100). The first channel had two valves for the TCD and FID, which were organized in series to measure CO_2 by using a methanizer to convert CO_2 to CH_4. The other channel, which also had two valves, was used to measure N_2O on the micro ECD. Two pre-columns were used to retain heavier compounds and to purge oxygen and water through the vent.

The system used a 1.0 mL sampling loop, and the columns, valves, FID, ECD and TCD were operated at 60 °C, 100 °C, 250 °C, 350 °C and 200 °C, respectively. Helium 5.0 was used as the mobile phase at a flow rate of 21 mL min^{-1}. Quantification was performed using triplicate external calibration curves and three standard reference GHG mixtures provided by Linde Gas. The certified concentrations for CO_2, CH_4 and N_2O were 351 ± 7; 1.510 ± 0.075 and 0.250 ± 0.012 μmol mol^{-1}, respectively, according to the standard number 2040/11; 401 ± 7, 1.760 ± 0.088 and 0.300 ± 0.015 μmol mol^{-1}, respectively, according to the standard number 041/11; and 451 ± 9; 2.010 ± 0.100 and 0.350 ± 0.017 μmol mol^{-1}, respectively, according to the standard number 04/11. The determination coefficients (R^2) for the triplicate calibration curves were higher than 0.99 for CO_2 and CH_4 and 0.98 for N_2O.

Stability tests

First, a stability test was performed comparing the most common sampling methods (stainless steel canisters and Tedlar® bags) with the new proposed method (PP syringes) by checking the sample stability for 10 days of a certified standard mixture containing CO_2 (401 ± 7 μmol mol^{-1}), CH_4 (1.760 ± 0.088 μmol mol^{-1}) and N_2O (300 ± 15 nmol mol^{-1}) in synthetic air, supplied by Linde Gas (Linde, certificate number 2041/11).

Then, to verify the interaction of the GHGs with other gases and their stabilities, control atmospheres were prepared with different concentrations, stored in the three sampling medias for 10 days, and compared with the initial concentrations.

The control atmospheres were prepared inside 10 L black Tedlar® bags using 99.999% nitrogen as the dilution gas. The others gases (CO_2, CH_4, N_2O, CO, NO and NO_2) were supplied by Linde Gas.

A Sierra Mass Flow controller was used in the dilution process. The GHG were determined by gas chromatography, as previously described, and CO, NO, and NO_2 were determined using Thermo Scientific analyzers (models 48i for CO and 42i for NO and NO_2). Water content was controlled by injection, using a syringe at 20 °C and 101 kPa. The composition of the control atmospheres is shown in Table 1. The selected values for GHG concentrations were in the same range as those expected for the atmospheric samples.

Ambient air collection

PP syringes were used to collect ambient air samples in Rio de Janeiro. The city has a population of 6,453,682[26] and contains 2,451,155 vehicles[27] in an area of 1,224 km^2. Air circulation is greatly affected by topographical conditions; the Tijuca Forest, a mountainous rainforest area, forms a natural barrier to air circulation and divides the city into northern and southern sections.[28] As described below, all of the samples were collected in the northern area of the city in locations that are strongly affected by vehicle emissions.

No samples were collected during rainy days or days with atypical anthropogenic emissions. The distance from the sampling positions to obstacles was at least twice the height of the obstacle, and the surrounding environment was free of interference from obstacles. Sampling was performed at a height of approximately 1.5 m above the ground, and the syringe was rinsed five times with the same ambient air before sampling. A 0.2 µm fiberglass filter was linked to the syringe to prevent the entry of particulate matter, which could damage the chromatographic system. The duration of the sampling for one syringe was approximately 10 seconds. After sampling, the syringes were sealed with Luer caps, protected from light with aluminium foil and stored at room temperature.

Initially, 3 samples were collected in 2011 at different times in each of seven districts in the city, as described in Table 2. The sampling locations were mainly residential areas with intense vehicular traffic and commercial activity that are representative of the city. A map of the city indicating the sampling locations is shown in the Supplementary Information section, Figure S1. The exact localization of each sampling point is shown in the Supplementary Information section, Table S1. A brief description of each location is presented in Table 2. Data collected during the sampling period at three monitoring stations of the Environmental Municipal Secretary (SMAC) showed a predominance of weak winds (0-4 km h^{-1}) in the southeast and northwest directions and ambient temperatures between 20 and 35 °C. The mixing height profiles were measured using radiosondes at Rio de Janeiro International Airport, which is located approximately 10-15 km from the sampling sites.[29] At 10:00 a.m. on each day, the mixing heights were 388-858 m, as detailed in Table S1. Other meteorological data are presented in Table S2.

Later, to check the evolution of the hourly concentrations, 12 samples were collected during the period from 6:00 a.m. to 6:00 p.m. on January 3, 2012, at the Maracanã Campus of the Rio de Janeiro State University, where an automatic air quality monitoring station was located. The mixing height at 10:00 a.m. was 290 m. Meteorological and criteria pollutants concentration data were collected at the station.

Table 1. Composition of the control atmospheres used for the stability tests in µmol mol^{-1}; CO_2, CH_4 and N_2O concentrations were determined by gas chromatography at the conditions described in the text

Atmosphere	CO_2 / (µmol mol^{-1})	CH_4 / (µmol mol^{-1})	N_2O / (µmol mol^{-1})	CO / (µmol mol^{-1})	NO / (µmol mol^{-1})	NO_2 / (µmol mol^{-1})	H_2O / (µmol mol^{-1})
ATM 1	351	1.56	0.252	0.555	0.052	0.049	9.351
ATM 2	351	1.56	0.253	1.04	0.114	0.100	14.097
ATM 3	353	1.49	0.255	2.00	0.198	0.201	18.902
ATM 4	401	1.76	0.303	0.510	0.051	0.045	9.358
ATM 5	401	1.76	0.303	1.07	0.112	0.104	14.103
ATM 6	401	1.76	0.303	1.96	0.190	0.197	18.893
ATM 7	457	2.01	0.349	0.570	0.050	0.045	9.344
ATM 8	455	2.09	0.349	1.10	0.110	0.101	14.101
ATM 9	455	2.02	0.345	1.99	0.191	0.202	18.900

Table 2. Description of sampling districts in Rio de Janeiro

District	Population (inhabitants)[26]	Main streets (St.), avenues (Av.) and roadways	Site description
Bonsucesso	18,711	Brasil Av., Linha Vermelha, Linha Amarela, Teixeira de Castro Av., Dona Isabel St. and Leopoldo Bulhões St.	residential area with high commercial and medium industrial activity; public transport by bus and train
Cidade Nova	5,466	Presidente Vargas Av., Av. Paulo de Frontin, Av. Trinta e Um de Março, Av. Salvador de Sá, Frei Caneca St. and Júlio do Carmo St.	low commercial and industrial activities; public transport by bus and subway; heavy traffic
Maracanã	25,256	Presidente Castelo Branco Av., Maracanã Av., São Francisco Xavier St., Mariz e Barros St. and General Canabarro St.	low commercial and industrial activities; the area is home of the Maracanã stadium and two university campus; public transport by bus and subway; heavy traffic; samples were taken at the Rio de Janeiro state university
Méier	49,828	Linha Amarela, Dias da Cruz St., Vinte Quatro de Maio St., Arquias Cordeiro St., Getúlio Stand Hemengarda St.	high commercial activity; low industrial activity. transport by bus and train
Penha	78,678	Brasil Av., Lobo Júnior Av., Brás de Pina Av., Ibiapina St. and Leopoldina Rego St.	medium commercial and industrial activities; transport by bus
São Cristóvão	26,510	Brasil Av., Linha Vermelha, Pedro II Av., Francisco Bicalho Av., São Luiz Gonzaga St., São Januário St. and Campo de São Cristóvão St.	medium commercial activity and high industrial activity; public transport by bus and subway; heavy traffic
Tijuca	163,805	Maracanã Av., Conde de Bonfim St., Uruguai St., São Miguel St., General Rocca St., São Francisco Xavier St. and Hadock Lobo St.	residential area with high commercial and medium industrial activity; public transport by bus and subway; heavy traffic; samples were taken at the Saenz Pena square

The minimum temperature was 20 °C at 6:00 a.m., and the maximum temperature was 30 °C at midday. Wind was from the southeast direction and was weak (approximately 1.5 km h^{-1}).

Finally, 38 samples were collected at Maracanã Campus of the Rio de Janeiro State University during the year of 2012. Samples were always collected in triplicate on Mondays at 1:00 p.m. Samples were collected at a height of 70 m to avoid the possible contribution of local sources of GHG. Additionally, no samples were taken on rainy days or holidays (14 days).

Statistical analysis

The experimental data were analyzed using Statistica 7.0 (Statsoft) to define descriptive statistics before extended analyses. A multivariate statistical analysis was performed that included linear correlation analysis (Pearson coefficients) and principal component analysis (PCA). Both calculations were achieved using the individual experimental values for each sample and sampling site.

Results and Discussion

A typical chromatogram for the GHG standard, in which the three detectors operated simultaneously, is shown in the Supplementary Information section, Figure S2.

The results for the stability test performed with the GHG standard are shown in Table 3. The values for the three sampling media are the arithmetic means and standard deviations for six results obtained over 10 days of storage.

These results show that the stability of GHG samples is similar in the syringes to that found in the more usual sampling devices (stainless steel canisters and Tedlar® bags). The difference between the initial value and the mean value is always less than 3%, which suggests that syringes are an effective sample storage approach.[30] For volatile organic compounds, a difference less than 25% is considered satisfactory.[22]

The results for the stability test of GHG in the control atmospheres (Table 1) are shown in Table 4. The values are the mean concentrations for three replicate determinations of samples after 10 days of storage and the deviations from the initial value.

Considering the mean values and concentrations of the standard mixture and the uncertainties from the manufacturer (1.75% for CO_2, 5.11% for CH_4 and 5.00% for N_2O), it can be concluded that all of the sample media evaluated were effective in storing GHG for a period of 10 days under different concentration conditions.

No effect was observed in the presence of different levels of CO_2, CH_4, N_2O, CO, NO and NO_2. However, in the mixtures with higher water content, which was equivalent to a relative humidity of 80%, a reduction in N_2O value

Table 3. Mean concentration and standard deviation values of CO_2, CH_4 and N_2O in three sampling media along 10 days of storage at ambient temperature protected from light

	Mean concentration value			Standard deviation / %		
	CO_2 / (μmol mol^{-1})	CH_4 / (μmol mol^{-1})	N_2O / (nmol mol^{-1})	CO_2	CH_4	N_2O
Initial value[a]	401	1.76	300	–	–	–
Canister	402.83	1.72	302.47	0.10	0.45	0.23
Tedlar bag	403.55	1.71	300.69	0.15	0.28	1.01
PP[b] syringe	402.31	1.72	304.18	0.13	0.80	0.45

[a] Initial concentration value for each gas in the standard gas (Linde Gases number 2041/11); [b] PP: polypropylene.

Table 4. Mean concentrations of CO_2, CH_4 and N_2O in the control atmospheres and deviations from the initial value for three replicate determinations of samples after 10 days of storage

Sampling media	Average concentration / (μmol mol^{-1})			Deviation / %		
	CO_2	CH_4	N_2O	CO_2	CH_4	N_2O
atmosphere 1						
Canister	354	1.51	0.252	0.85	−3.2	0.0
Tedlar bag	353	1.52	0.251	0.85	−2.6	−0.40
PP[a] syringe	351	1.52	0.254	0.00	−2.6	0.79
atmosphere 2						
Canister	350	1.53	0.252	−0.28	−1.9	−0.39
Tedlar bag	352	1.53	0.254	−0.57	−1.9	0.39
PP[a] syringe	352	1.52	0.255	−0.57	−2.6	0.79
atmosphere 3						
Canister	350	1.50	0.218	−0.85	0.67	−14.5
Tedlar bag	350	1.49	0.217	−0.85	0.00	−14.9
PP[a] syringe	349	1.52	0.215	−1.1	2.2	−15.7
atmosphere 4						
Canister	403	1.72	0.302	0.50	−2.3	−0.33
Tedlar bag	404	1.72	0.301	0.75	−2.3	−0.66
PP[a] syringe	402	1.72	0.304	0.25	−2.3	0.33
atmosphere 5						
Canister	401	1.70	0.305	0.00	−3.4	0.65
Tedlar bag	402	1.72	0.301	0.25	−2.3	−0.66
PP[a] syringe	402	1.71	0.305	0.25	−2.8	0.65
atmosphere 6						
Canister	401	1.73	0.248	0.00	−1.7	−18.1
Tedlar bag	402	1.74	0.257	0.25	−1.1	−15.2
PP[a] syringe	402	1.73	0.254	0.25	−1.7	−16.2
atmosphere 7						
Canister	451	2.01	0.351	−1.31	0.00	0.57
Tedlar bag	451	2.02	0.351	−1.31	0.50	0.57
PP[a] syringe	450	2.02	0.355	−1.56	0.50	1.72
atmosphere 8						
Canister	451	2.04	0.351	−0.88	−2.4	0.57
Tedlar bag	452	2.04	0.350	−0.66	−2.4	0.28
PP[a] syringe	452	2.01	0.350	−0.66	−3.8	0.28
atmosphere 9						
Canister	452	2.01	0.311	−0.66	−0.49	−9.85
Tedlar bag	452	2.03	0.319	−0.66	0.49	−7.54
PP[a] syringe	451	2.04	0.313	−0.88	0.99	−9.27

[a] PP: polypropylene.

was observed. In the ATM 6 mixture, a reduction of 18.1, 15.2 and 16.2% was observed for the canister, Tedlar® bag (14.33%) and PP syringe, respectively. This may be explained by possible water condensation on the inner wall and the partial solubilization of N_2O.

After the calibration procedure, samples were collected at seven locations in Rio de Janeiro at three different hours of the day. The mean concentrations are shown in Table 5.

Table 5. Concentrations of CO_2, CH_4 and N_2O in seven districts of Rio de Janeiro. Samples were collected using syringes, as described in the text

Date	Hour	District	Concentration / (μmol mol^{-1})		
			CO_2	CH_4	N_2O
2011/10/28	06:30 a.m.	Bonsucesso	577	1.86	0.341
	12:00 a.m.		575	1.83	0.351
	04:00 p.m.		602	1.94	0.361
2011/11/25	07:25 a.m.	Cidade Nova	ND[a]	ND[a]	ND[a]
	01:40 p.m.		528	2.07	0.330
	04:15 p.m.		484	2.38	0.292
2011/11/25	07:45 a.m.	Maracanã	481	2.26	0.288
	01:15 p.m.		475	2.18	0.290
	04:30 p.m.		515	2.01	0.330
2011/10/27	06:45 a.m.	Méier	603	1.94	0.354
	01:00 p.m.		607	1.94	0.362
	04:45 p.m.		609	1.93	0.357
2011/11/25	06:40 a.m.	Penha	525	1.97	0.330
	01:00 p.m.		484	2.44	0.288
	05:00 p.m.		526	2.00	0.319
2011/11/25	07:45 a.m.	São Cristóvão	526	2.01	0.327
	01:25 p.m.		527	1.98	0.327
	04:15 p.m.		512	2.03	0.325
2011/11/25	07:05 a.m.	Tijuca	524	2.00	0.327
	02:00 p.m.		523	2.02	0.468
	04:00 p.m.		522	1.96	0.324

[a]ND = not determined.

The CO_2 concentrations were higher than 400 μmol mol^{-1} for all samples. The reported values, which were between 475 and 609 μmol mol^{-1}, are typical of urban areas, as previously determined in many other places throughout the world. The persistence of CO_2 over urban areas as a result of anthropogenic contribution to the CO_2 budget has been reported in many cities and is known as the urban dome. The typical concentrations of CO_2 in urban areas are between 350 and 600 μmol mol^{-1} and depend on meteorological parameters and urban agglomeration.[31,32] In this work, samples were collected in the spring (October and November) in residential areas that are highly affected by vehicle emissions, which were expected to be the main source of CO_2.[33]

As shown in Table 5 and in the Supplementary Information section, Figure S3, when the sample locations are compared, higher levels of CO_2 can be observed in two districts, Bonsucesso and Méier, which is probably due to the preferential dispersion of pollutants affected by the topography of these districts and a higher local anthropogenic contribution related to intense commercial activity, high vehicular flux and traffic jams.

According to literature data, the typical concentrations of CH_4 in urban areas are between 1.70 and 2.50 μmol mol^{-1} and are influenced by meteorological parameters and urban agglomeration. The most significant sources of methane come from the anaerobic decomposition of organic matter.[3] The values obtained in this work were in the range of 1.83-2.44 μmol mol^{-1}, which is in good agreement with the reported values for other urban centers. As shown in Table 5 and in the Supplementary Information section, Figure S4, the higher values were obtained in the Penha, Maracanã and Cidade Nova Districts, and they may be attributed to the proximity of polluted rivers with a high organic matter content. The available emission inventories for the city attribute approximately 90-95% of the total CH_4 emissions to the disposal of residential, commercial and industrial solid waste in sanitary landfills and to untreated liquid waste.[33]

As shown in Table 5 and in the Supplementary Information section, Figure S5, N_2O concentrations were in the range of 292-360 nmol mol^{-1}, except for one atypical value (468 nmol mol^{-1}). The anthropogenic contribution of N_2O is mainly related to the disposal of solid and liquid waste.[33]

Diurnal variations in the concentrations were also observed, as shown in Figure 1. For CO_2, the concentrations varied between 490 and 616 μmol mol^{-1}. The results indicate that for this compound, higher values were observed in the morning and evening hours, which indicates the effect of the rush hours, and the lowest values were obtained at midday, as previously observed in other cities.[34] The methane concentrations varied between 1.50 and 1.77 μmol mol^{-1}, which is in the same range as the natural levels (1.65 μmol mol^{-1}). A slight diurnal variation due to the boundary layer height and potential photochemical decay was observed. These effects are probably compensated by methane release through evaporation, which, in turn, depends on temperature. N_2O concentrations varied between 335 and 349 nmol mol^{-1}, with a slight decrease near midday that was probably due to the superposition of two effects: the dilution effect of the boundary layer height and the increase of emissions through the evaporative process.

Correlation coefficients were calculated between CO_2, CH_4 and N_2O and the criteria pollutants' concentrations, which were determined at the monitoring station. The CO_2 concentrations showed correlation coefficients over the 0.6 threshold with all of the primary pollutants, CO (0.84), NO_x (0.91) and inhalable particulate matter (0.66). Because the main emission source in the studied area of the criteria pollutants are vehicles, it could be assumed that this is also the main source of CO_2 and that anthropogenic emissions are the primary source of the urban CO_2 dome. The correlation of CH_4 with the criteria pollutants was poor except for with NO_x (0.60). N_2O showed correlations with CO (0.74) and NO_x (0.78).

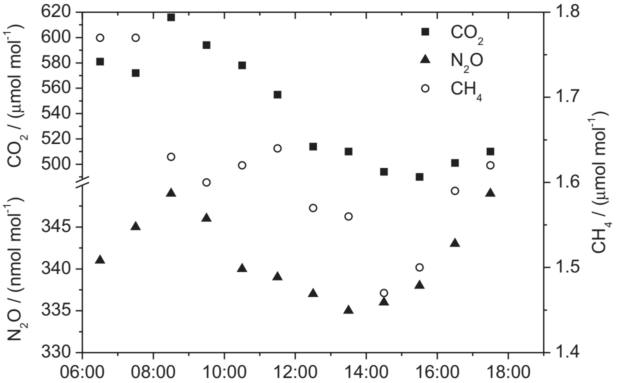

Figure 1. Concentrations of CO_2, CH_4, and N_2O on January 3, 2012, at the Maracanã Campus of the Rio de Janeiro State University (UERJ).

Figure 2 shows the results of samples collected from January to December 2012 at the Maracanã campus of Rio de Janeiro State University (UERJ). GHG have seasonal variations, which are called annual cycles, as previously reported by several authors.[35-38] These annual cycles vary according to geographical location, altitude and meteorological conditions. Correlation coefficients were calculated between our data and the meteorological data (temperature, relative humidity and wind speed). These correlations were poor, and the analysis of regression coefficients showed that all of the values were lower than the 0.6 threshold. The highest value was observed for the CO_2-temperature correlation (0.46). A high correlation was observed for CO_2 and CH_4 (0.85), which may be due to a common source or to an indirect correlation with another parameter, such as the mixed layer height. This correlation suggests that anthropogenic activities, particularly vehicle traffic, are an important source of methane in the urban atmosphere.[34] PCA analysis highlighted three principal components, P1 (CO_2, CH_4 and temperature), P2 (relative humidity) and P3 (N_2O), which account for 82% of the total variance.

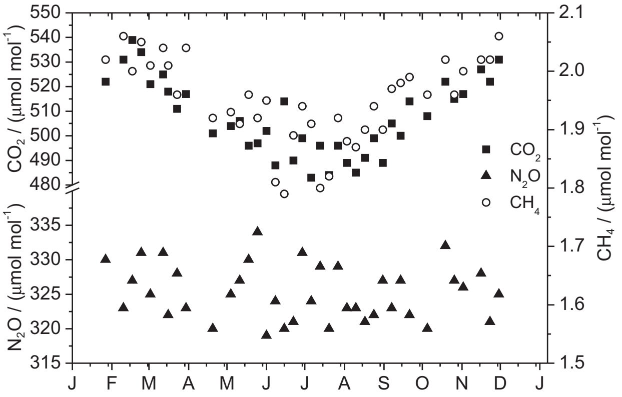

Figure 2. Concentrations of CO_2, CH_4, and N_2O in 2012 at the Maracanã of the Rio de Janeiro State University. Samples were collected at a height of 70 m.

The results in Figure 2 indicate strong seasonal variations of CO_2 and CH_4, with peak values in the warmer months and lower values in winter and with averages of 507.6 ± 13.2 µmol mol^{-1} for CO_2, 1.95 ± 0.06 µmol mol^{-1} for CH_4 and 325.3 ± 3.4 nmol mol^{-1} for N_2O. The values for N_2O were not related to the seasons, with an average standard deviation of 1.0%.

This CO_2 behavior was the opposite of that observed in studies performed in many other cities around the world. In general, for CO_2, the largest values were recorded in autumn, at the end of the biological cycle of plants, and during the winter, and the CH_4 concentrations showed a seasonal variation, with maxima in the summer and minima in the autumn and spring.[34] The observed behavior in Rio de Janeiro may be related to the climatic and geographical characteristics. The city has a tropical wet and dry/savanna climate, with a pronounced dry season in the low-sun months, no cold season and a wet season (October-March) during the high-sun months. The city surrounds Tijuca National Park (TNP), a secondary rainforest, which occupies 32 km^2 (3.5% of the area of Rio de Janeiro), and is home to hundreds of species of plants and wildlife, of which many are threatened by extinction and are found only in the Atlantic Rainforest.[39] The concentrations of CO_2 and CH_4 were higher during the high-sun months (November-March). The annual CO_2 cycle with the highest values in summer and the lowest values in winter may reflect the high increase in energy consumption, especially that generated by thermo-electrical units, related to the use of refrigeration systems and the increase in tourism in the city. It may also be related to the growth and decay of vegetation in TNP, which is surrounded by the city. The TNP vegetation is characterized by large trees, palms, ferns, epiphytes and lianas. The more frequent plant families are Leguminosae, Sapotaceae, Bombacaceae, Lecythidaceae, Mraceae and Melastomataceae.[40] To our knowledge, no studies about CO_2 sequestration have been conducted for this forest.

As discussed in the literature, the global estimates of atmospheric CO_2 exchange indicate that the tropics are near equilibrium or are a source with respect to carbon, though there remain considerable uncertainties as to the contribution of different processes.[41]

Regarding CH_4, the variations may be related to the input from evaporation of liquid and solid waste from landfill sites located within the city boundaries and from polluted rivers and canals. Additionally, other anthropogenic activities that may be considered are the release of methane by the gas fuel network of the urban area and emissions due to the use of compressed natural gas in taxis and light vehicles.[42,43]

The mean concentration values for each compound, calculated as the arithmetic mean of data obtained from January to December 2012, and the concentrations from the pre-industrial period and global values are shown in Table 6.[44] The pre-industrial global-scale trace-gas concentrations from prior to 1750 are assumed to be practically uninfluenced by human activities such as increasingly specialized agriculture, land clearing, and combustion of fossil fuels. Recent tropospheric concentrations of most gases tend to vary systematically over the course of a year, and the global values given in Table 6 represent averages over a specific 12-month period for all gases (the year of 2013 for CO_2 and 2012 for CH_4 and N_2O).

Table 6. CO_2, CH_4 and N_2O tropospheric concentrations in the pre-industrial period (pre-1750), average global data and values determined in Rio de Janeiro (annual averages)

GHG	Pre-1750 / (μmol mol^{-1})	Recent values[a] / (μmol mol^{-1})	Rio de Janeiro / (μmol mol^{-1})
CO_2	280	395.4	507.6
CH_4	0.70	1.893/1.762	1.95
N_2O	0.270	0.326/0.324	0.325

[a] Averages over a specific 12-month period for all gases (the year of 2013 for CO_2 and 2012 for CH_4 and N_2O).[44]

Comparing the data in Table 6, it can be observed that in Rio de Janeiro, the concentration of CO_2, the main compound responsible for the greenhouse effect, is 30% higher than the mean global value, thus confirming the presence of a CO_2 dome over the studied urban area. For CH_4 and N_2O, the values obtained in this work are, respectively, 11.5 and 1% higher than the global concentrations. Values reported in this work should be considered with caution because samplings were always made at noontime on non-rainy workdays and were thus not obtained in the conditions of global values and are not representative of diurnal and weekly variations. However, they do indicate a contribution of urban emissions to CO_2 and CH_4 levels.

Conclusions

The proposed method of sampling provided good results, lower costs and easier implementation in comparison to other sampling devices. It seems to be a good alternative for investigating the CO_2, CH_4 and N_2O concentrations in cities where global monitoring is not performed, such as Brazilian and other Latin American cities.

In the studied urban area in Rio de Janeiro, the concentration of CO_2, which is the main compound responsible for the greenhouse effect, is 30% higher than the mean global value, confirming the presence of a CO_2 dome over the studied urban area. The results for CO_2 and CH_4 show peak values in the warmer months and lower values in winter. This CO_2 behavior is the opposite to that observed in studies performed in many other cities around the world and may reflect the summer increase in energy use due to the higher temperatures and the vegetation cycle in the rainforest, which is part of the urban area. These particular characteristics suggest that further study of the role of the urban rainforest, wetlands and rivers in the air quality of the city may be significant and that the carbon cycle of the vegetation in the rain forest should be studied.

Supplementary Information

Supplementary Information (Tables S1 and S2 and Figures S1-S5) is available free of charge at http://jbcs.sbq.org.br as PDF file.

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