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Carbonyl compounds from urban activities and their associated cancer risks: The influence of seasonality on air quality (Fortaleza-Ce, Brazil)

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ABSTRACT

The main carbonyl compounds (CCs) were determined at gas stations for the first time in Fortaleza city, CE, Brazil, and the results were compared with other urban centers. The influence of seasonality on the production, distribution and balance of CCs, as well as the associated cancer risks, was also estimated. Formaldehyde was the most abundant carbonyl, followed by acetaldehyde, nonaldehyde, acrolein, butyraldehyde and benzaldehyde. The total CC concentration (Σ_{CC}) averages are less than most other studies in outdoor environments and gas stations. The Σ_{CCs} were higher in the dry period than in the wet period. It was observed that the insolation, cloud cover and precipitation should be influencing CCs distribution, while the ambient temperature should not. The study showed that the cancer risks associated with formaldehyde and

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acetaldehyde are 3.9 and 1.5 times higher, respectively, during the dry period than during the wet period. The cancer risk in the months of dry period of the year were observed to exceed the recommended exposure limit established by National Institute for Occupational Safety and Health (NIOSH).

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1. Introduction

Gas stations (GSs) are engaged in the activity of selling retail liquid fuels derived from petroleum, as well as ethanol and other automotive fuels. In their routine work, these facilities employ many workers and gas station attendants, who are exposed daily to many potentially dangerous fuel vapors, while lacking any personal protective equipment. According to the literature, activities and supplies associated with vehicles are major sources of emissions of volatile organic compounds (VOCs), which constitute a potential risk to users and attendants (Cruz-Nunes et al., 2003; Han et al., 2005). Professionals are thus occupationally exposed to elevated levels of hazardous substances, and the level of exposure is largely dependent on the type of combustion. Moreover, most GSs are avenues of high vehicular traffic, which further increases the risk of exposure (Woodruff et al., 2000).

Among these compounds, we highlight atmospheric carbonyl compounds (CCs), pollutants primary or secondary are produced directly from incomplete combustion of biomass, gasoline and diesel fuels (Zhang and Smith, 1999; Schauer et al., 2001; Correa et al., 2003; Correa and Arbilla, 2005) and formed as major reaction products in the atmospheric oxidation of many anthropogenic hydrocarbons and other volatile organic compounds (VOCs) (Carlier, 1986; Aschmann et al., 2001; Jo and Song, 2001; Lee et al., 2002). Natural sources also contribute to atmospheric concentrations of several carbonyls through biogenic emissions of some plants and photochemical oxidation of naturally emitted hydrocarbon precursors, e.g. isoprene (Grosjean et al., 1993; Müller et al., 2002; Wildt et al., 2003; Villanueva, 2004). Furthermore the carbonyls play a significant role in a formation of photochemical smog of peroxyacetyl nitrate (PAN), and of regional ozone. Photo-dissociation of aldehydes represents an important source of free radicals in the lower atmosphere (Atkinson, 1990; Grosjean, 1982; Duan et al., 2008).

These compounds, easily inhaled by users and attendants, are recognized as powerful depressants of human health, even at low concentrations (Buczynska et al., 2009). In particular, formaldehyde is classified as carcinogenic in humans, and others CCs are recognized as toxic (e.g., acrolein) (IARC, 1982; ACGIH, 2003). The literature also reports acute effects, such as irritation of the eyes and throat, headache, sickness, vomiting, dizziness, and memory loss, due to long-term or even low-dosage exposure to different levels of acetaldehyde and acrolein (IPCS/INCHEM, 1997; IARC, 2004; USEPA, 2005). Due to the harmful nature of these compounds, certain government agencies have established national and international levels for occupational maximum exposure to these compounds for an 8-h work day. According to NR-15, NIOSH and ACGIH, the permissible exposure limits for formaldehyde are $2300 \mu\text{g m}^{-3}$, $20 \mu\text{g m}^{-3}$, $370 \mu\text{g m}^{-3}$, respectively, and those for acetaldehyde are $140,000 \mu\text{g m}^{-3}$, $45,000 \mu\text{g m}^{-3}$, $32,400 \mu\text{g m}^{-3}$ (MTE-NR-15, 1978; NIOSH, 2003).

However, there are few studies of CC levels and risk assessment in places with CC sources, such as GSs (Som et al., 2008), especially in Latin America. Furthermore, hot climate regions are known to increase the fugacity of VOCs, thus increasing the health risk (Woodruff et al., 2000). Because GSs are outdoor places with abundant sources of hazardous substances, this study was designed to assess the CC levels, compare them to other outdoor environments and estimate their health risk. Due to the lack of work in warm climates, such as tropical and subtropical, we also evaluated the influence of the seasonality on the production, distribution and balance of CCs, as well as on the associated cancer risk. We think these results will be important in providing a useful baseline for future assessments of air quality, as well as contributing to politics related to the health protection of professionals engaged in similar activities or other outdoor activities in highly urbanized cities.

2. Experimental methods

2.1. Sampling site description

The study was conducted in three GSs (P1, P2 and P3) in Fortaleza city, Ceará state, Brazil (Fig. 1). Fortaleza city is localized on the Atlantic coast of Brazil in the Northeast region and contains approximately 3.5 million inhabitants distributed over a 313-km² area. Fortaleza is a tropical city with two well-defined seasons, the dry season (August–December) and the wet season (January–July), with temperatures ranging from 25 to 32 °C, an annual average wind speed of 3.53 m s⁻¹ and a total annual precipitation of 1200–1400 mm, averaging approximately 200 mm month⁻¹ during the wet season. Very little rain falls during the dry period between August and December (Gusev et al., 2004).

In 2012, the city reached the mark of 700,000 vehicles, of which approximately 74.9% use a mixture of gasoline and ethanol (gasohol), 10.5% are fueled with hydrated ethanol and 4.5% are diesel powered (Cavalcante et al., 2011). Flexible-fuel vehicles represent approximately 5.3% of the total fleet, and their number is rapidly increasing (Abrantes et al., 2009; Ministry of Cities, 2013).

Information on the three studied GSs is summarized in Table 1. The GSs are located on a fairly busy avenue (an average flow of 40,000 day⁻¹) and sell approximately 4000 l of fuel per day. The routine work schedule of attendants is 8 h a day for six days a week.

2.2. Reagents and solvents

All solvents and reagents used in this work were chromatography grade. The standards of CCs (Merck) and DNPHi (Aldrich) were purified by three rounds of recrystallization (Cavalcante et al., 2005, 2006; Sousa et al., 2011).

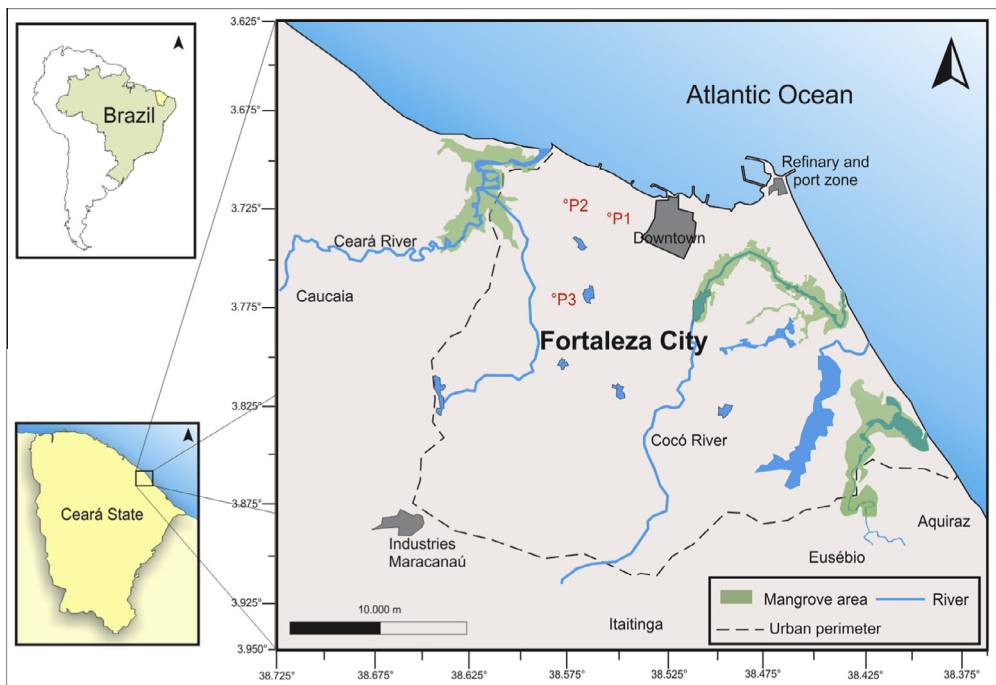


Fig. 1. Locations of the studied GSs in Fortaleza city.

Table 1

Characteristics of the gas stations in this study.

Characteristics	Gas Stations		
	Station 1 (P1)	Station 2 (P2)	Station 3 (P3)
Total number of employees	6	18	15
Number of female attendants	–	1	2
Area (m ²)	400	500	600
Number of pumps	4	6	6
Quantity of fuel sold (L day ⁻¹)	2726.4	5539.2	4377.6
Flow client in GSs (auto day ⁻¹)	58	69	42
Avenue flow (auto h ⁻¹)	4142	4970	3554

The 0.2% solution of 2,4-DNPHi was prepared by weighing 0.05 g of pure reagent in 15 mL of HPLC-grade acetonitrile, 9.75 mL of ultra-pure water and 0.25 mL of concentrated phosphoric acid (H₃PO₄), resulting in a final pH of approximately 2. A liquid–liquid extraction was then performed with 4 mL of HPLC-grade dichloromethane (Merck) to purify the solution (Cavalcante et al., 2005).

2.3. Chromatography method

To analyze the hydrazones eluted from the cartridges, a sampling model HPLC Shimadzu TA-20 reverse phase column type octadecylsilane (ODS)-C18 (25 cm × 4.6 mm, 5 μm) detector UV–VIS-diode array (model SPD-M20A) was used. The examined wavelength was 365 nm, the injection volume was 20 μL, and the system gradient mobile phase consisted of ACN/H₂O ratios of 70:30 (v/v) for 7 min, 77:23 (v/v) for 6 min and 70:30 (v/v) for 2 min at a flow of 1 mL min⁻¹. The analysis time for one sample injection was 15 min.

The quantification and identification of carbonyl compounds was carried out using a mixture of hydrazone standards (2,4-DNPHo – CCs). The identification of the hydrazones was based on retention time and absorption spectra. Calibration curves were prepared using 6 concentrations of standards (0.005–4 μg mL⁻¹), with a correlation coefficient (*R*²) greater than 0.998. The standards were injected at least three times, and the error between injections was at most 5%. The relative standard deviation (RSD) was less than 10%. The limit of detection for formaldehyde was 2.2 μg L⁻¹, acetaldehyde 4.4 μg L⁻¹, acrolein 2.3 μg L⁻¹, butyraldehyde 2.0 μg L⁻¹, benzaldehyde 1.5 μg L⁻¹ and nonaldehyde 3.5 μg L⁻¹.

2.4. Sampling and analysis

The CCs were collected by suctioning the air with the aid of a pump for 1 h of active sampling at a flow rate of 0.8–1.2 L min⁻¹, forcing the air to pass through two connected Sep-Pak C18 cartridges that were impregnated with an acid solution of 2,4-DNPHi (Cavalcante et al., 2005, 2006; Sousa et al., 2011). A calibration of the sampling pump was performed prior to each collection, and the error in the calculated variation of the flow was 2–7%. The system was mounted at a height equivalent to the breathing zone, approximately 1.50 m from the floor and far wall. Samples were collected in the morning during the months of September to December 2009 (dry season) and February to April 2010 (wet season), and totaled six replicates per week (*n* = 6). After collection, the cartridges were sealed, wrapped with aluminum foil, refrigerated and transported to the laboratory, where elution and chromatographic analyses were performed immediately to minimize the risk of interference.

The collection efficiency was determined for the two cartridges in series, and over 95% of the eluates were found in the first cartridge. The complete recovery of all compounds was observed. The RSDs were below 15%. The average background concentrations from samples were 0.45 and 1.56 mg cartridge⁻¹ for formaldehyde and acetaldehyde, respectively.

2.5. Evaluation of the cancer risk

The occupational exposure to the studied CCs over a lifetime was estimated by chronic daily intake (CDI) in accordance with the equation below. For the evaluation of the CDI, certain values have been assumed according to the USEPA (1997a,b) to facilitate the calculation of the parameters (Table 2). The application of these models eliminates the need for epidemiologic studies, which are time consuming and expensive (USEPA, 1992a, 1996b):

$$CDI = \frac{(CA * IR * ED * EF * L)}{(BW * ATL * NY)} \quad (1)$$

Cancer risk (CR) was estimated based on the CDI multiplied by the slope factor (SF) according to the Integrated Risk Information System (IRIS) (USEPA, 1992a, 1996b, 2004) (Eq. (2)). According to the IRIS, the slope factors (SF) for formaldehyde and acetaldehyde in this study are $0.0455 \text{ mg}^{-1} \text{ kg day}$ and $0.0077 \text{ mg}^{-1} \text{ kg day}$, respectively (USEPA, 1992a,b, 1996b, 2004).

$$CR = CDI * SF \quad (2)$$

2.6. Meteorological data

The insolation, precipitation, temperature and cloud coverage data were obtained from a conventional ground weather station of the National Institute of Meteorology, located at latitude $3^{\circ}45'S$, longitude $38^{\circ}33'W$ and altitude 19.53 m, inside the Fortaleza's urban area. The insolation data were measured hourly between 5 and 19 h (local time). The precipitation, temperature and cloud cover (scale ranging from 0 to 10) was observed three times a day: 9, 15 and 21 h, local time (12, 18, and 00 UTC respectively). However, in this work, only the 9 and 15 h observations were used. For the total daily rain measurements made at 9, 15 and 21 h were considered.

3. Results and discussion

3.1. Concentration of CCs in the air

In the present study, six carbonyls were measured in the ambient air at three GSs in Fortaleza city. Formaldehyde was the most abundant carbonyl, with a mean of $14.11 \mu\text{g m}^{-3}$, followed by acetaldehyde (mean: $9.52 \mu\text{g m}^{-3}$), nonaldehyde (mean: $2.12 \mu\text{g m}^{-3}$), acrolein (mean: $1.45 \mu\text{g m}^{-3}$), butyraldehyde (mean: $1.16 \mu\text{g m}^{-3}$) and benzaldehyde (mean: $0.45 \mu\text{g m}^{-3}$) (Fig. 2).

We compared our results to the majority of studies since 2005 that have investigated the major CCs in urban environments, such as outdoor public places, busy roads, tunnels, bus stations and gas stations in Brazil and on other continents. The average Σ_{CCs} are higher than those in most other studies on outdoor public places (Guangzhou, Elizabeth, Houston and Niteroi), with the exception of Rio Grande do Sul and Hangzhou (Table 3). In contrast, the average levels are less than those reported for a busy road in Kolkata, a tunnel in São Paulo and bus station in Salvador, but the levels are higher

Table 2
Description of the variables used in the estimation of CDI and cancer risk (CR).

Parameter	Description	Value	Unit
CA	Contaminant concentration	–	mg m^{-3}
IR	Inhalation rate, adult	1.02	$\text{m}^3 \text{h}^{-1}$
ED	Exposure duration, adult	40	h weeks^{-1}
EF	Exposure frequency	42	weeks year^{-1}
L	Length of exposure	30	year
BW	Body weight, man/woman	70/60	kg
ATL	Average lifetime of man/woman	69/72	year
NY	Number of days per year	365	days year^{-1}

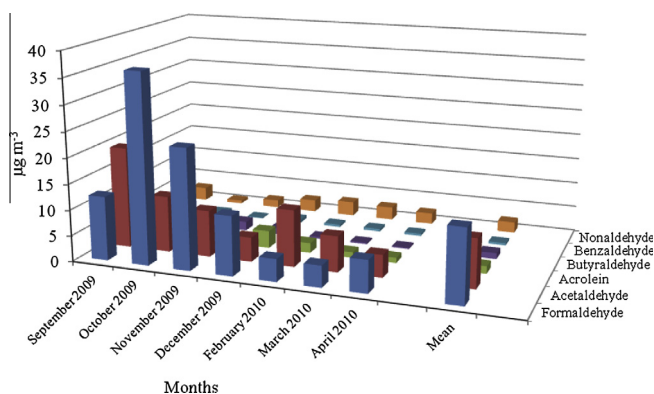


Fig. 2. Concentrations, Σ_{CCs} and means of carbonyl compounds in Fortaleza.

than those of a busy road in Beirut. Differently, the outdoor public places that may have primary and secondary sources of CCs, environments such as busy roads, tunnels and bus stations are known to have high concentrations of CCs because of the large quantity of vehicular emissions (Rodrigues et al., 2012). The rates of dispersion and degradation in these environments are much lower than the emission rate; thus, these areas are excellent locations to assess the primary emissions of various substances. According to Vasconcellos et al. (2005), tunnels are excellent for assessing the chemical composition of emissions coming from engine exhaust due to the absence of photochemical reactions. When compared to the levels reported by the few studies of gas stations, the Σ_{CCs} observed in Fortaleza are less than those reported by Som et al. (2008).

3.2. Seasonal distribution

The Σ_{CCs} were highest in October and lowest in April (Fig. 2). The Σ_{CC} average during the dry period was $37.65 \mu\text{g m}^{-3}$ higher than the average during the wet period ($16.36 \mu\text{g m}^{-3}$; Fig. 2). In the comparison of our data and the data of other studies, we consider the wet period to be winter and the dry period to be summer due to climatic similarities. The production of CCs can be influenced by seasonality because the Summer/Winter (S/W) ratio was observed to be > 1 for most of the studied CCs, except benzaldehyde and nonaldehyde (Fig. 3). According to Fig. 1S (supplementary material), during the studied period, the cloud cover was higher at 9 am than 15 pm, due to the semiarid rainfall characteristics in the Northeastern Brazilian region, which favors more abundant rainfall in the period of time between midnight and noon. In the days 20/03/2010 (79 Julian day) and 25/03/2010 (84 Julian day), the insolation was 2.1 and 0 respectively. It means that the sky was completely overcast (ten-tenths) or obscured during these two days. In the data series also highlight the day 12/12/2009 (Julian day 346) whose registered insolation value was 2.4 (Fig. 1S). This day presented sky with cloud cover between six tenths to eight-tenths but no precipitation was recorded. It can be explained because December is outside Fortaleza's rainy season (February to May). Considering the studies periods: 15/09/2009 (Julian day 258) to 28/12/2009 (Julian day 362) – dry season, and 02/02/2010 (Julian day 33) to 24/04/2010 (Julian day 114 – wet season, the insolation during dry season was approximately 19.4% higher than the wet period in Fortaleza. This result is in agreement to the solar radiation map (FUNCEME, 2011). Furthermore, considering that in average the cloud cover during wet season was 10% and 28% higher than the dry period in Fortaleza, for 9 h and 15 h observations respectively. The maximum precipitation registered during the dry season was 5.3 mm in December 01, 2009 (Julian Day: 335), and during the wet season was 40.0 mm in April 13, 2010 (Julian Day: 103) (Fig. 2S). According Fig. 2S the most significant rain falls at three different periods: first: 79, 82 and 84 Julian day; second: 100 and 103 Julian day; and third: 107 and 110 Julian day. These factors may be contributed too for the CCs formation during the dry period. In different way, the temperature, during

Table 3
Averages of the CC measurements in Brazil and other locations in $\mu\text{g}/\text{m}^3$.

Place	Formaldehyde	Acetaldehyde	Acrolein	Butyraldehyde	Benzaldehyde	Nonaldehyde	$\sum\text{CCs}^c$	Environment	References
Hangzhou, China	22.2	6.37	–	0.5	–	–	29.07	Outdoor in public place	MiliWeng et al. (2009)
Guangzhou, China	1.1	9.55	–	1.42	1.74	1.63	15.44	Outdoor in public place	Lü et al. (2010)
Elizabeth/Houston, USA	6.42	5.44	0.46	–	1.88	–	14.20	Outdoor in public place	Liu et al. (2006)
Niteroi, Brazil	3.22	6.53	–	1.09	3.75	0.80	15.39	Outdoor in public place	Ochs et al. (2011)
Rio Grande do Sul, Brazil	18.2	15.4	–	–	–	–	33.6	Outdoor in public place	Cavalcante et al. (2005)
Kolkata, India ^a	21.34	14.88	–	–	3.68	–	39.90	Busy road	Dutta et al. (2009)
Beirut, Lebanon ^b	5.6	3.4	–	–	–	–	9.00	Busy road	Moussa et al. (2006)
São Paulo, Brazil ^b	40.6	50.5	–	–	–	–	91.1	Tunnel	Vasconcellos et al. (2005)
Salvador, Brazil ^b	98.4	147.9	–	–	41.7	–	288.00	Bus Station	Rodrigues et al. (2012)
Kolkata, India	27.8	18.3	–	–	2.5	–	48.60	Gas stations	Som et al. (2008)
This study	14.11	9.52	1.45	1.16	0.45	2.12	28.81	Gas stations	

^a Average daily data.

^b converted by USEPA conversion (T = 25 °C, press = 1 ATM).

^c sum of averages.

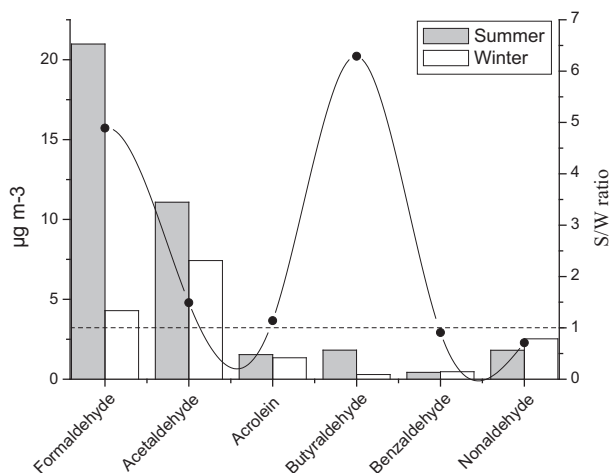


Fig. 3. Mean concentrations and Summer/Winter (S/W) ratio of carbonyl compounds in Fortaleza.

the dry period, it varies between 25.6 and 30.6 °C (average = 27.5 °C), and during the wet season between 25.2 and 32.4 °C (average = 28.4 °C) showing no significant variation in both periods.

Higher levels of CCs in the dry period relative to the wet period have also been observed by other studies in various locations around the world. Wang et al. (2007) report that the highest levels of formaldehyde occur in the summer due to higher photochemical production. In contrast, the temperature and relative humidity are lower in the winter, contributing to a reduction in the levels of CCs in Chinese cities. The production of formaldehyde and acetaldehyde in Greece through photochemical reactions are 2.5 times higher in the summer compared with winter, indicating that secondary sources are greater than primary sources during the period of maximum sunlight (Bakeas et al., 2003). In Rio de Janeiro, the highest levels of CCs were observed between the hours of 10 and 12 h due to the formation processes involving the photo-oxidation of hydrocarbons associated with the high solar radiation at this time. According to authors, this result indicates that vehicular emissions were not the primary and only source of these pollutants on the studied days (Ochs et al., 2011). Pang and Mu (2006) found that although the carbonyl photolysis rates in Beijing (China) were 1–2 orders of magnitude faster in summer than in winter, the measured carbonyl concentrations were still several times higher in summer than in winter. Therefore, the formation rates of carbonyl compounds through photo-oxidation of VOC must greatly exceed their photolysis rates in summer.

The formaldehyde/acetaldehyde ratio (F/A) in Fortaleza increased from 0.58 in the wet period to 1.89 in the dry period and featured an annual average of 1.23 (Fig. 3). According to Duane et al. (2002), high F/A ratio values indicate that the photo-oxidation of natural hydrocarbons, such as isoprene, produces more formaldehyde than acetaldehyde. The increase in the F/A ratio in Beijing (China) between winter and summer indicates that the photo-oxidation of natural hydrocarbons might play an important role in atmospheric carbonyl formation, especially in summer (Pang and Mu, 2006).

3.3. Assessment cancer risk (CR)

The estimate of cancer risk was evaluated using the CDI equation and the IRIS based on 30 years of occupational exposure to formaldehyde and acetaldehyde for men during the summer and winter periods (Fig. 4). Unfortunately, no studies of cancer risk that consider seasonality were found. Thus, we compare our data with the few cancer risk studies of outdoor environments.

The results show that the location P3 had the highest mean cancer risk associated with formaldehyde among the places studied, whereas P1 had the highest risk associated with acetaldehyde. In general,

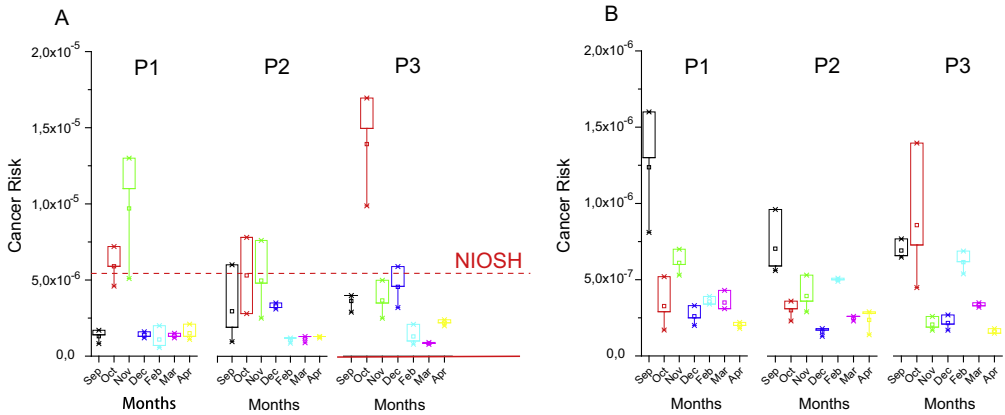


Fig. 4. Seasonal cancer risk estimates relative to the recommended exposure limit proposed by the NIOSH agency (A: formaldehyde e B: acetaldehyde).

the data show that the highest cancer risks are associated with the dry period of the year. On average, the cancer risks associated with formaldehyde and acetaldehyde during dry are 3.9 and 1.5 times higher, respectively, than those during the wet period. According to the literature, an increased risk of cancer is associated with increased radiation, which causes photo-oxidation of hydrocarbons and consequently increases the concentration of CCs (Pang and Mu, 2006). The results obtained during the summer exhibited a trend similar to those of other observed values. The absence of a pattern and the similarity in the values of risk during the winter season could be related to the low intensity of solar radiation and meteorological instability, which reduces the photolysis of hydrocarbons (Pang and Mu, 2006).

The probabilities of formaldehyde-related cancer for men after 30 years of exposure during the dry and wet seasons were above the limit established as safe by the USEPA (1992a,b), which is set at a limit of $1.0E^{-6}$ (1 case of cancer for every 1,000,000 individuals). Similar results were reported by Li et al. (2008) based on the study of the health risks of workers in Kolkata and China, respectively. The risks of cancer associated with 40 years of exposure to formaldehyde and acetaldehyde are $35.2E^{-6}$ and $4.03E^{-6}$, respectively. Dutta et al. (2009) evaluated the cancer risks associated with 15 years of exposure to formaldehyde and acetaldehyde in different sites in Kolkata, India. The observed risk values were $1.73E^{-5}$, $1.19E^{-5}$ and $2.14E^{-5}$ for formaldehyde and $2.14E^{-6}$, $1.25E^{-6}$ and $2.26E^{-6}$ for acetaldehyde.

We also estimated the cancer risk corresponding to the various recommended exposure limits proposed by NIOSH, OSHA, ACGIH and the Brazilian Standard regulatory (NR-15). As shown in Fig. 4, the levels of formaldehyde only had averages above the recommended exposure limit proposed by NIOSH in October and November in locations P1 and P2. The cancer risks are not dangerous based on the recommended exposure limits of the other agencies.

Although the cancer risk was calculated only for men, we observed a 4% increase in risk for women in the same scenario. This occurs when using linear risk model equation to assess health risk, as Cavalcante et al., (2005, 2006) and Sousa et al. (2011) reported.

4. Conclusion

The average Σ_{CCs} in Fortaleza are above most studies in outdoor public places and are below those reported by studies on busy roads, tunnels, and bus stations and by the few studies on gas stations. The Σ_{CCs} were highest in the dry period and lowest in the wet period. Seasonality was for the first time observed to have a large influence on the production, distribution and balance of CCs and on the associated cancer risks. The S/W ratio was greater than 1 for the most important CCs (formaldehyde,

acetaldehyde, acrolein and butyraldehyde), indicating that greater production of these compounds occurs during the dry period. During the study period, it was observed that the insolation, cloud cover and precipitation should be influencing CCs distribution, while the ambient temperature should not. The Σ_{CCs} and the F/A ratios during the dry period were two and three times higher, respectively, than those observed during the wet period.

The study showed that the cancer risks during dry period were 3.9 and 1.5 times higher than during the wet period for formaldehyde and acetaldehyde, respectively. The probabilities of cancer risk for men and women after 30 years of exposure during the dry and wet seasons were above the limits established as safe by the USEPA for formaldehyde. The cancer risk in the months of October and November (the dry period of the year) were observed to exceed the recommended exposure limit established by NIOSH.

Given the results observed during this research, technical solutions must be implemented to reduce occupational hazards to CCs in supply operations in fuel service stations (GSs) to protect the health of workers attendants, such as vapor recovery systems, filtration systems using activated carbon, biofilters systems can be installed in GSs to reduce these emissions, since some of these compounds are known to be carcinogenic.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.uclim.2015.03.004>.

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