BTEX profile and health risk at the largest bulk port in Latin America, Paranaguá Port

Hugo Sarmiento[1], Sanja Potgieter-Vermaak[2,3], Guilherme C. Borillo[1], Ana Flavia L. Godoi[1], Rodrigo A. Reis[4], Carlos I. Yamamoto[5], Theotonio Pauliquevis[6], Gabriela Polezer[1,7], Ricardo H.M. Godoi[1*]

*rhmgodoi@ufpr.br

1- Federal University of Parana, Water Resources and Environmental Engineering Department, Curitiba, Brazil.
2- Ecology & Environment Research Centre, Department of Natural Science, Manchester Metropolitan University, Manchester, M1 5GD, United Kingdom.
3- Molecular Science Institute, University of the Witwatersrand, Johannesburg, South Africa.
4- Department of Cell Biology, Federal University of Parana, Curitiba, Parana, Brazil.
5- Chemical Engineering Department, Federal University of Parana, Curitiba, Parana, Brazil.
6- Department of Environmental Sciences, Federal University of São Paulo, Diadema, Brazil.
7- Department of Technology, State University of Maringá, Umuarama, Paraná, Brazil

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ABSTRACT

Port-related activities have a detrimental impact on the air quality both at the point of source and for considerable distances beyond. These activities include, but are not limited to, heavy cargo traffic, onboard, and at-berth emissions. Due to differences in construction, operation, location, and policies at ports, the site-specific air pollution cocktail could result in different human health risks. Thus, monitoring and evaluating such emissions are essential to predict the risk to the community. Environmental agencies often monitor key pollutants ($PM_{2.5}$, PM_{10}, NO_2, SO_2), but the volatile organic carbons (VOC's) most often are not, due to its analytical challenging. This study intends to fill that gap and evaluate the VOC emissions caused by activities related to the port of Paranaguá - one of the largest bulk ports in Latin America - by characterizing BTEX concentrations at the Port and its surroundings. At seven different sites, passive samplers were used to measure the dispersion of BTEX concentrations throughout the port and around the city at weekly intervals from November 2018 to January 2019. The average and uncertainty of BTEX concentrations ($\mu g\ m^{-3}$) were 0.60 ± 0.43; 5.58 ± 3.80; 3.30 ± 2.41; 4.66 ± 3.67; and 2.82 ± 1.95 for Benzene, Toluene, Ethylbenzene, m-and p-Xylene, and o-Xylene, respectively. Relationships between Toluene and Benzene and health risk analysis were used to establish the potential effects of BTEX emissions on the population of the city of Paranaguá. Ratio analysis (T/B, B/T, m,p X/Et and m,p X/B) indicate that the BTEX levels are mainly from fresh emission sources and that photochemical ageing was at minimum. The cancer risk varied across the sampling trajectory, whereas Ethylbenzene represented a moderate cancer risk development for the exposed population in some of the locations. This study provided the necessary baseline data to support policymakers on how to change the circumstances of those currently at risk, putting in place a sustainable operation.

Keywords: Port air pollution, BTEX emission, Passive sampler, Thermal desorption CG-MS, Health risk, Air quality

1. INTRODUCTION

Maritime transport currently constitutes more than 90% of the global trade by value and is seen as a World Trade Vehicle (International Maritime Organization - IMO) (UNCTAD 2021). The activities at maritime ports increase anthropogenic emissions significantly and thus result in poor air quality, both on-site and in the surrounding areas (Super et al. 2017). Extensive road networks at and close to the port, supporting container transportation, further compound the situation due to heavy traffic. Cargo transport is the primary emission contributor, for which mainly diesel-driven trucks are used. It is, therefore, not surprising that some studies indicated that air pollution in areas close to ports is a potential public health problem (Corbett et al. 2007; Eyring et al. 2010; Viana et al. 2014; Debia et al. 2016; Rice et al. 2014;). Cargo handling activities in ports are also a substantial source of complex mixtures of particulate matter, volatile organic compounds (VOC's), nitrogen and sulfur oxides, and other ozone-depleting substances.

Previous studies reported on the adverse effect of port activities and maritime transport on air quality, alerting to increased levels of most pollutants on-site as well as in the surroundings (De Meyer et al. 2008; Viana et al. 2014; Gregoris et al. 2016; Burwell-Naney et al. 2017; Han et al. 2017; Kotrikla et al. 2017). Off-shore emissions are equally of concern with significant contributions to global anthropogenic NO_x and SO_2 emissions (Endresen et al. 2003; Eyring et al. 2005; Corbett et al. 2007; Butterfield and Quincey 2017; Hamid et al. 2020). Due to the myriad of factors influencing the air pollution cocktail, local-scale variation needs to be captured, as regional or city-specific air pollution monitoring will not provide the evidence required to inform decision-makers (Miller et al. 2011).

Apart from the significance of onboard and at-berth emissions, the determination and assessment of BTEX concentrations in harbors located near densely populated urban areas are of great importance due to its potential deleterious health effects on coastal communities. There are numerous BTEX sources in and around ports: diesel-operated vehicles (cars, trucks, cargo transport, ground vehicles) and other maritime activities (diesel operated cranes, in-berth ship emissions, for example). Diesel usage is of concern, as 40 components of diesel exhaust can be considered as potential causes of cancer in populations that live near sources of diesel emissions (California-Environmental Protection Agency).

To put that in context, according to the 2020 Maritime Transport Review (UNCTAD 2021), Brazil was ranked in the world's top 25 container port traffic countries in 2019 and was one of only two in Latin America in the top 25. Brazil shipped a total of US$ 209.8 billion worth of goods in 2020, which represented 6.8% of its overall Gross Domestic Product (GDP). Paranaguá is the largest and leading grain port in Latin America with 44 cargo vessels every 24 h and an average of 43,000 truck trips per month. FINDAPORT (2021) reports that the Port of Paranaguá handles containers, solid bulk, fractional cargo, passengers, refrigerated containers, and tankers.

The accelerated growth of maritime transport worldwide, specifically at Paranaguá, and the lack of local-scale monitoring motivated the aim of this research. To that end, local-scale BTEX monitoring was conducted by passive sampling using Radiello diffusion tubes. BTEX profiles from 7 sites, at and around the port are presented over nine weeks. The results could be fundamental to assess the impact of shipping emissions on the workers' health, residents, and the surrounding environment (radius of 13 km). It can feed forward into attaining sustainable operations at the port as well as provide evidence to policymakers at a local scale. In addition, this baseline study could serve as an example for ports worldwide.

2. MATERIAL AND METHODS

Due to the numerous advantages (low cost, easy deployment, replicates, no electricity required) that passive samplers offer, it was decided to use it for this study.

2.1 Sampling and Site Description

Sampling occurred across a nine-week window (21 November 2018 to 18 January 2019), during which the diffusion tubes were exposed for 7 days at a time, thus resulting in nine samples per site. Duplicate sets of Radiello passive samplers were placed at the 7 sites described and illustrated in Figures 1A and B, and Table 1.

Different criteria were considered for the selection of the BTEX collection points. Points A and B were chosen based on proximity to the port, and the remaining sampling stations are inland, and this selection was based on the prevailing wind direction.

Table 1. Geographical location and description of sampling point.

Point	Latitude S	Longitude O	Neighborhood characteristics	Traffic
A	25°30'19.02"	48°31'3.12"	Near Port	Ships, heavy duty vehicles
B	25°30'45.25"	48°30'49.12"	Near Port, Industries	Ships, heavy duty vehicles
C	25°31'25.04"	48°30'34.10"	Public transport	Bus, vehicles
D	25°31'35.69"	48°30'16.33"	No Traffic	Bikes
E	25°32'9.07"	48°31'52.31"	Intense Traffic	Heavy duty vehicles
F	25°32'36.52"	48°31'36.46"	Residential area	Bus
G	25°35'7.00"	48°33'53.25"	Residential area	Bus, vehicles

Figure 1A

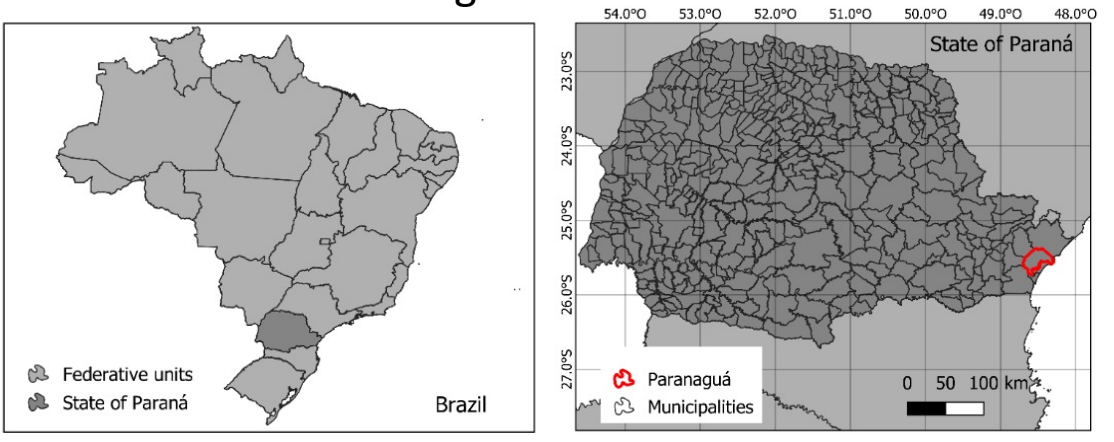

Figure 1B

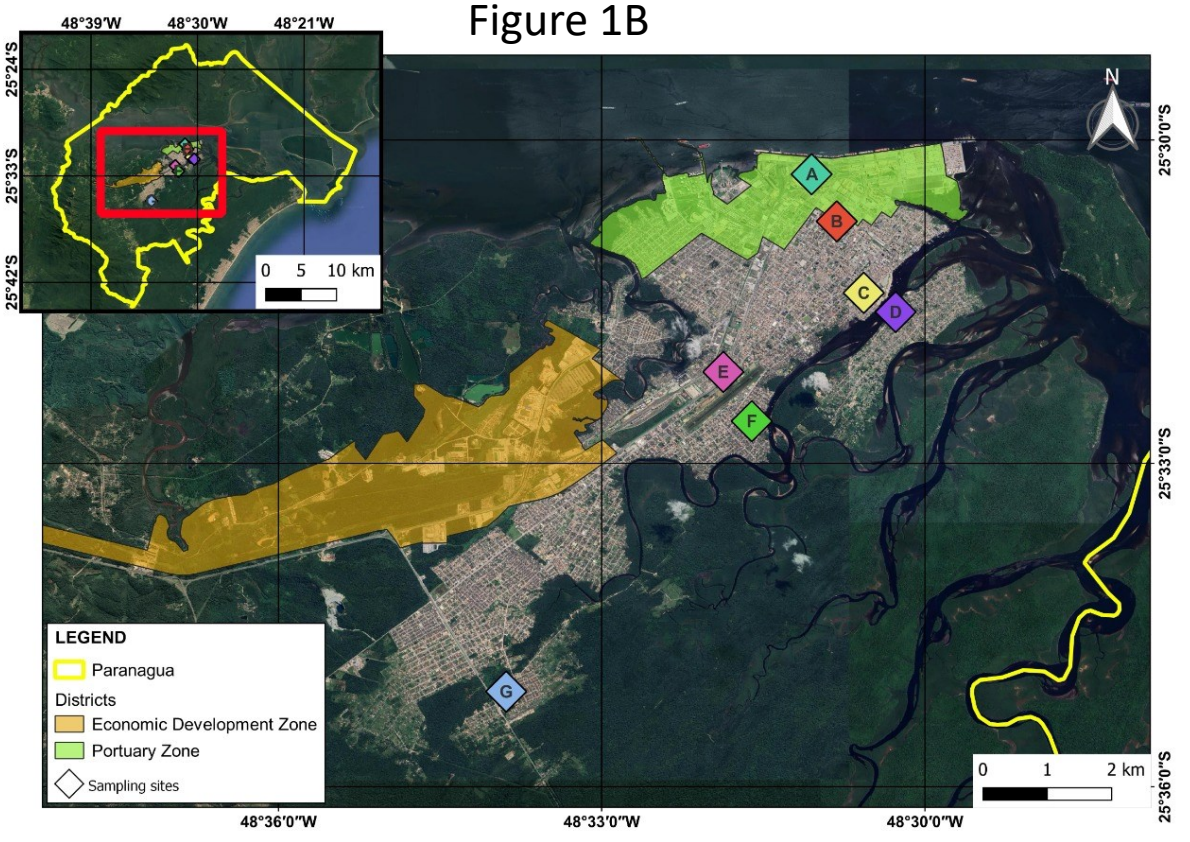

Fig. 1 Part A: City of Paranaguá, located in the state of Paraná, southern Brazil. Part B: Location of the seven sampling points for BTEX in Paranaguá, identified by letters in boxes. The following values correspond to the distance from each point to the port of Paranaguá: (A) 0.2 km; (B) 1.2 km; (C) 3.1 km; (D) 3.5 km; (E) 4.2 km; (F) 6.0 km and (G) 13.7 km.

Passive samplers were exposed for seven days, collected, sealed, and transported at 4°C to the laboratory, where the samples were extracted by thermal desorption and subsequently analysed by gas chromatography-mass spectrometry (GC-MS). In total, 59 samples were analysed across the 7 sites for the nine-week period.

2.2 BTEX desorption and analysis

The captured BTEX mixtures were thermally desorbed using the EPA TO-15 method (EPA 2018), following the conditions reported in Supplementary Table SM1. A Rxi 624 Sil MS-Restek column (95% dimethyl-polysiloxane, length of 30 m, i.d. 0.32 mm, and film thickness 1.8 µm) was used. A temperature program (provided in Supplementary Table SM2) was used, and the carrier gas flow was 1.2 ml min^{-1} (Helium).

For quality control purposes, the Brazilian Association of Technical Standards - Brazilian Technical Standard (ABNT NBR) ISO/IEC 17025 recommendations (ABNT 2017) were used to verify the method. The limits of detection (LOD), limits of quantification (LOQ), precision (%CV) and linearity are, respectively, for Benzene 0.5979; 19.73; 2.08 and 0.9948; for Toluene 0.5927; 19.56; 2.36 and 0.998, although for Ethyl benzene it is 0.5958; 19.49; 5.56 and 0.9980, for m+p Xylene it was 0.5958; 14.49; 7.27 and 0.9973, and finally o-xylene has values of 0.5958; 14.49; 6.79 and 0.9968.

Analytical calibration curves were obtained by injecting 1 µl of a pre-prepared multi-component standard solution (Sigma Aldrich 47993) into empty preconditioned cartridges (cleaned with a tube conditioner TC-20 Markes), done under a 50 ml min^{-1} nitrogen flow and followed by a purge. A 20 ml min^{-1} split was used. The system was cooled to -10°C to separate VOC's from water. Subsequent dilutions produced two sets of calibration standards (SET 1: 2 to 70 µg ml^{-1} (0 to 80 ng) and SET 2: 90 to 300 µg ml^{-1} (80 to 400 ng). For quality control purposes each concentration had three replicates. The samples were analyzed using the same conditions.

2.3 Data Analysis

2.3.1 BTEX concentration calculations in air

The BTEX sampling and analysis methodology was proposed by the passive sampling tube manufacturer Radiello in its application note E1 of 2006 for the determination of Volatile Organic Compounds (Radiello 2006).

The average concentration during the sampling period is calculated from the analyte mass, the sampling rate (which is temperature-dependent), and the exposure time. The average concentration C in µg m^{-3} throughout the exposure time is calculated according to the following equation (1).

$$C(\mu g\ m^{-3}) = \left(\frac{m(\mu g)}{Q_k(ml \cdot min^{-1}) \cdot t(min)}\right) \cdot 1000000 \left(\frac{\mu g}{g}\right) \quad (1)$$

Where m = analyte mass in μg, t = exposure time in minutes, and Q_k sampling rate at temperature K. The sampling rate, Q, recommended by the manufacturer was used. Sampling rate values at 298 K (25°C) and 1013 hPa were 27.8, 30.0, 25.7, 26.6, and 24.6 ml min^{-1} for Benzene, Toluene, Ethylbenzene, m-and p-Xylene, and o-Xylene, respectively.

Sampling rates were corrected for temperature variation from 298 K using equation (2).

$$Q_k = Q_{298K} * \left(\frac{K}{298K}\right)^{1.5} \quad (2)$$

Where Q_K = sampling rate at temperature K, Q_{298} = reference value at 298 K. The temperatures at each point were measured directly with electronic thermometers that were placed next to each passive sampler. The value 1.5 represents the temperature importance in passive sampling. Molecular diffusion coefficients increase with temperature, therefore increased sampling rates can be expected for diffusion samplers as temperature increases. For gases, the kinetic theory predicts that diffusion coefficients are proportional to $T^{1.5}$ (where T is absolute temperature), Górecki et al. 2002.

166 2.3.2 Toluene and Benzene Ratios

167 Toluene/Benzene ratio (T/B) was used to explore the relative abundance of traffic and non-traffic
168 sources. Depending on gasoline composition, T/B values from 2 to 3 indicate that traffic is the primary
169 source of pollution, while values smaller than 0.5 correspond predominantly to industrial sources (Garzón
170 et al. 2015). T/B ratios greater than 2 suggest the presence of additional Toluene sources, such as major
171 industrial emissions from fuel storage, oil refineries, handling losses, and oil leakage equipment.
172 (Beauregard 1993; Barletta et al. 2008; Gee and Sollars 1998; Na and Kim 2001; Giakoumi et al. 2009;
173 Zhang and Li 2016). In the present investigation, T/B ratios were determined to estimate the origin of
174 BTEX emissions.

175

176 2.3.3 Health Risk Analysis

177 For the estimation of non-carcinogenic effects, reference concentrations were reported in the
178 databases of the Federal Agency for Toxic Chemical Substances and Disease Registry of the U. S.
179 (ATSDR), and in the Integrated Risk Information System (IRIS) of the U.S. Environmental Agency (EPA)
180 were considered. To assess the health risk upon exposure to the concentration levels found for BTEX at the
181 sites, the non-carcinogenic hazard quotient HQ (equation 3) was calculated. An HQ smaller than or equal
182 to 1 indicates adverse effects are not likely to occur and can be considered negligible (ATSDR 2022).

183 $$HQ_i = \frac{C_i}{RfC_i} \quad (3)$$

184

185 where HQ_i is the hazard quotient for each compound, RfC_i the reference concentration ($\mu g\ m^{-3}$)
186 from which adverse effects would develop, and C_i is the average daily exposure concentration ($\mu g\ m^{-3}$).

187

188 EPA defines an RfC as "an estimate (with uncertainty spanning perhaps an order of magnitude) of
189 a continuous inhalation exposure to the human population (including sensitive subgroups) that is likely to
190 be without an appreciable risk of deleterious effects during a lifetime" (EPA 2002). That is, an RfC is a

concentration at which exposures would be allowed to occur with sufficient certainty, considering susceptibility and variability, that adverse outcomes would not result.

The cancer risk CR was calculated according to equation (4).

$$CR_i = C_i \times IUR_{Ai} \quad (4)$$

Where CR is cancer risk$_i$ for compound **i**, IUR_{Ai} is the inhalation unit cancer risk, equivalent to excess cancer risk from continued lifetime exposure (70 years) (EPA 2011) to 1 µg m^{-3} of a contaminant, and $C_{i\ is}$ the average daily exposure concentration (µg m^{-3}).

For carcinogenic effects, the calculation of the inhalation Unit Risk (IUR_{Ai}) was performed, prioritizing the data obtained from the World Health Organization (WHO) (Rumchev et al. 2007) and the California-Environmental Protection Agency (Cal-EPA). Inhalation Unit Risk (IUR_{Ai}) is calculated as the product of IUR_i xET x EF x ED/AT, where IUR_i is the risk value for the specific compound, for example IUR_i for Benzene is 2.2 10^{-6}; ET is Exposure time, EF is Exposure Frequency, ED is Exposure Duration and AT is average time in hours per exposure period.

Robson and Toscano (2007) and Sexton et al. (2007) classified excess risk> 10^{-4} as a definitive risk; values between 10^{-5} and 10^{-4} as a probable risk; and between 10^{-5} and 10^{-6} as a possible risk. The CR level corresponding to cancer risk of 10^{-6} is the target for the cancer endpoint.

Based on US EPA recommends (Means 1989), the exposure to the contaminant was calculated over a lifetime; therefore, the value AT of 70 years (or 25,500 days) was used. In this study, the risk was calculated for workers in the port with an average daily working time of 8 hours (ET) (except Sundays). Considering the 30 days of annual vacation, one can find the frequency of exposure (EF) for workers of 74 days (= 52 × (6/3)-30) (52 weeks for year, and 6/3 days for week). In addition, the working lifetime is assumed to be 20 years (ED).

2.3.4 Source Apportionment

To investigate whether the whole sampling network has a regional footprint or not, Analysis of Variance - ANOVA was used. Here we specifically refer to the region of Paranaguá where the study took place.

3. RESULTS AND DISCUSSION

3.1 Variation of BTEX in the Study Area

3.1.1 Average concentration levels

The average concentrations of BTEX for all collection points were, respectively, for Benzene 0.60 μg m^{-3} (0.008-1.354 μg m^{-3}), Toluene with 5.58 μg m^{-3} (0.18-11.98 μg m^{-3}), whereas Ethylbenzene has 3.30 μg m^{-3} (0.095-8.34 μg m^{-3}), m+p Xylene has 4, 66 μg m^{-3} (0.38-12.80 μg m^{-3}) and finally o-xylene has middle values of 2.90 μg m^{-3} (0.19-8.27 μg m^{-3}) are illustrated in Figure 3.

Toluene was, on average, the most dominant compound at all sites (5.58 μg m^{-3}) and for most weeks, corroborating the findings of Roukos et al. (2009), who reported on BTEX levels at the urban and industrial harbors of Dunkirk, France, as well as Prati et al. (2015) reporting on levels at the port of Naples. Le et al. (2022) in the port of Kaohsiung in Taiwan and Salvador et al. (2022) in the port next of Butuan Philippines, agree in stating that the most abundant species in the air in those regions is Toluene.

The average relative abundance for the sampling sites was in the order of Toluene>m,p-Xylene>Ethylbenzene>o-Xylene>Benzene, which is largely in agreement with the port of Long Beach (Toluene > m,p-Xylene > Benzene > Ethylbenzene > o-Xylene (Mason et al. 2011)), and with the port of Naples (Toluene > m,p-Xylene > Ethylbenzene > o-Xylene > Benzene (Prati et al. 2015)).

The high Toluene levels are not surprising as port activities lead to automotive exhaust fumes and emissions from handling, distributing and storage of petrol which are major contributors to atmospheric Toluene. In fact, Toluene levels would typically fluctuate proportional to the traffic density. Studies carried out by Baltrénas et al. (2011) show that airborne Toluene levels are generally higher in

urban areas heavily congested with traffic (21.4–98.1 ppbv or 80.5–368.9 μg m^{-3}), compared to outdoor air in less congested urban areas (1.95 ppbv or 7.3 μg m^{-3}).

Since m,p-Xylene has a shorter lifetime than Ethylbenzene and Benzene, high levels of this VOC's could be due to a point source. According to Nelson and Quigley (1983) and Miller et al. (2011) aged air masses containing VOC's from distant sources would be expected to have low m,p-Xylene/Ethylbenzene and m,p-Xylene/Benzene ratios, whereas fresh air from local emissions should have higher ratios.

The ratio of mean values of the m,p-Xylene/Ethylbenzene and m,p-Xylene/Benzene ratios observed in this study were 1.220 and 2.381, similar to those found by Cruz et al. (2020) in Salvador-Brazil and Jiang et al. (2017) in Orleans-France. The m,p-xylene/Benzene ratios obtained in the present study are higher than those observed in other urban areas, such as those reported by Bretón et al. (2017) and Mor et al. (2021) in Chandigarh India. These differences might be attributed to the presence of compounds with young photochemical age and fresh emission sources in the study area (Bretón et al. 2017).

3.1.2 Paranaguá compared to the Port of Naples and Long Beach

A comparison of our data to two other port studies wherein Radiello samplers were used to measure BTEX levels is illustrated in Figure 2. Apart from Toluene being the highest in concentration at all the ports as mentioned before, it is observed that Toluene and m,p-Xylene levels are much higher than Benzene, Ethylbenzene and o-xylene at the three ports (ranging from 17% – 93% higher for Toluene and 29% – 90% higher for m,p-Xylene). In addition, the Ethylbenzene and o-Xylene levels at Paranaguá are significantly higher than either Naples or Long Beach (on average 62% and 46% higher, respectively).

The physical description of the ports compared in terms of areas (Km^2), The cargo handled per year (Tons/year) in millions, and the cargo handled by containers (TEUs) per month, respectively, shows that the port of Long Beach has 13 Km^2, 78.2 Tons/Year and 771,735 TEUs, while Naples has an area of 2.66 Km^2, 25.0 Tons/Year and 500,000 TEUs, and Paranaguá has an area of 4.1 Km^2, 53, 2 Tons/year and 125,000 TEUs, being the largest area and the largest volume of cargo in the port of Long Beach.

Upon comparing the absolute concentration levels between the three ports (Figure 2), it becomes evident that Long Beach has a much lower BTEX profile overall (with a difference of between 61% and 94% in absolute concentrations). This is an interesting observation, given the greater volume of cargo arriving at the Port of Long Beach and could be due to the stringent policies in place at this port. Long Beach operates with electrical equipment and has a clear policy of non-admission of ships powered by high sulphur fuels and requiring all trucks to be new model trucks. On the other hand, the Port of Naples is one of the largest passenger ports in Europe and does not operate with electrical equipment.

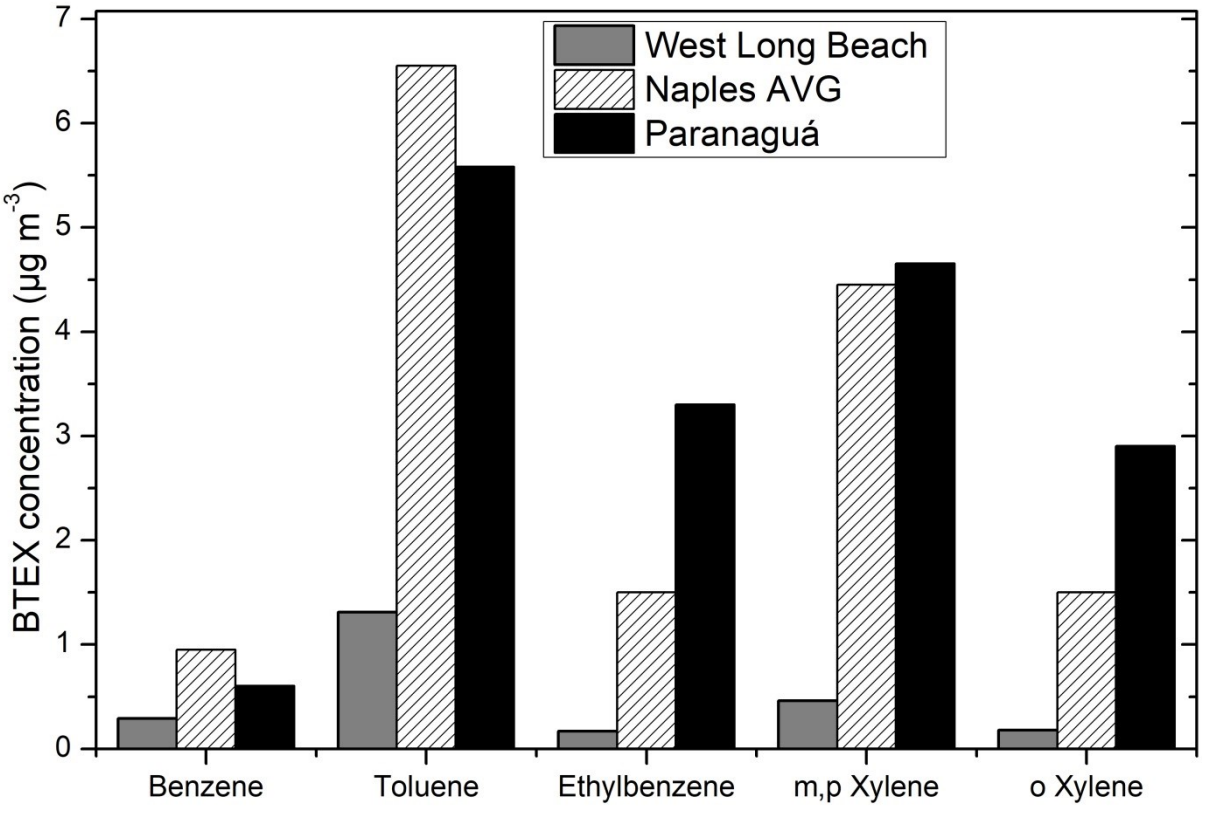

Fig. 2 Comparisons of the average BTEX concentrations at three different ports: Long Beach (USA), Naples (Italy) and Paranaguá (Brazil). All data compared here were obtained by Radiello diffusion tubes

282 3.1.3 Variation in BTEX levels within and between sampling points

283 Box and whisker plots were used to establish the degree of variation within and between sampling
284 points of the Paranaguá study. Figure 3 illustrates the data spread across all sampling points and for all
285 weeks.

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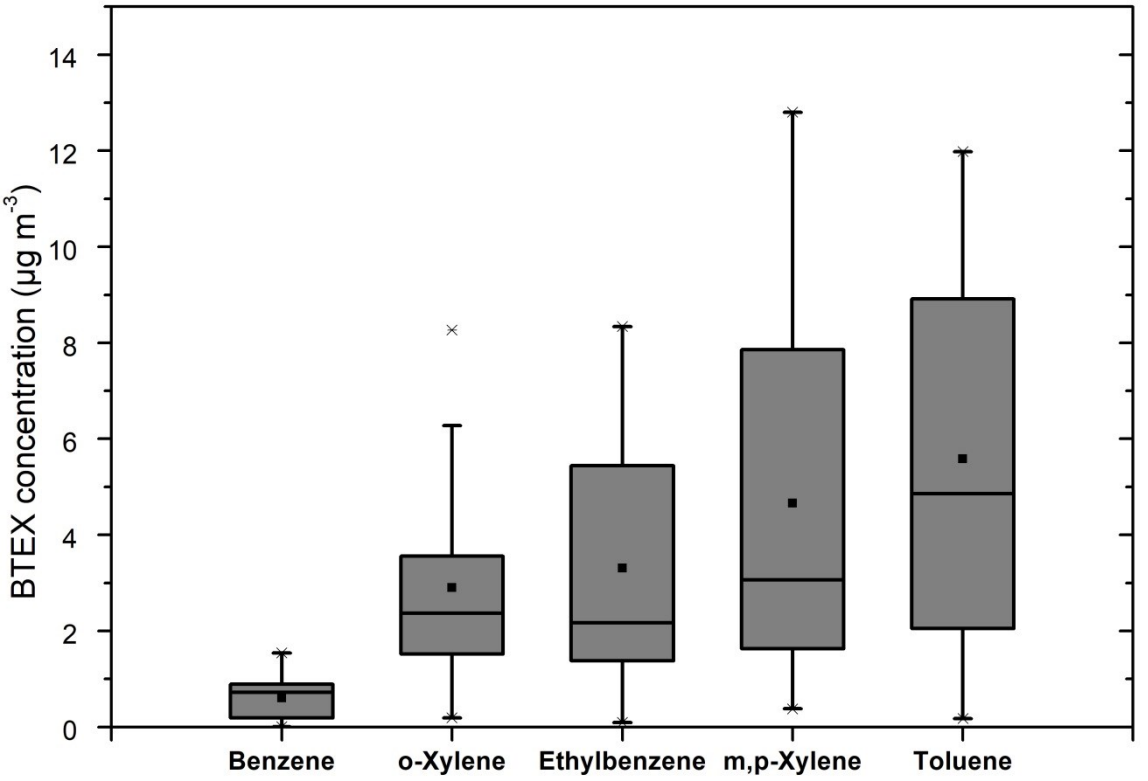

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288 **Fig. 3** Box and whisker plot of BTEX concentration levels obtained for each week at each sampling point

289

290 From the data in Figure 3, it is evident that Benzene shown the least variation across the sampling
291 weeks and between the sampling points. This could be indicative of a common source for Benzene during
292 the time period and/or be ascribed to the fact that Benzene's lifetime is, on average, 9.4 days, which
293 would cover the whole of the sampling week. The latter may therefore cause less fluctuation over time.
294 The common source is most likely gasoline/petrol as Benzene is a typical additive (up to 2%). Once again,

the Toluene levels are noticeably the highest of all BTEX. In Brazil the typical aromatic hydrocarbon content in standard gasoline varies from 26% to 35%, however in premium gasoline the range is from 28% to 48%, of which almost half corresponds to Toluene (13.7%). It is also evident that the concentration levels of BTEX differ in the spread as well as averages and median values. At the date of this study, the Residual Marine (RM) fuels used in ships are a complex mix of heavy hydrocarbons highly viscous and aromatic from petroleum (Thomas et al. 2019).

To determine if the average BTEX concentrations are significantly different between the sampling points the Friedman's test was performed. The result indicated that the ***p*** is less than 0.05 ($p<0.05$) (Supplementary Table SM3) which shows that with a significance level of 95% null hypotheses are rejected (Ho = the averages of BTEX concentrations are equal). It therefore indicates that the average concentrations between sites are different. This may be in part due to the shorter lifetimes of these VOC's.

Box and whisker plots are used to look at the variation of the data across the different sampling points (Boxplot in Supplementary Figure SM1) for which the interquartile ranges, medians, and means for the different sampling points are displayed in Table 2. The individual concentrations are provided in Supplementary Table SM4.

It is once again observed that the Benzene values vary the least (lowest IQR) at each sample point (similar to what the average over all sampling points showed) and that the average at each sampling point is within experimental error the same. It can be said that there is a slight increase in the IQR values for Benzene from sampling points A – G. It is noteworthy that the maximum concentration of Benzene (1.54 µg m^{-3}) did not exceed 5 µg m^{-3} (limit established by the European Union (EU) (EC 2008) at any of the seven sampling points.

The weak correlation (R^2=0.55, $p<0.05$) observed between Benzene and Toluene mean values further suggests that Benzene and Toluene are not always from the same emission source(s). The correlation between BTEX and Benzene is very weak (R^2 = 0.253, $p<0.05$) which leads to the understanding that Benzene may have a single source and that by a compendium of sources influences BTEX levels. This is in contrast to the findings of Bréton et al. (2017), where medium to strong correlations are reported for all

BTEX components at both sites and during both seasons investigated. Very strong correlations are observed for the Ethylbenzene and the Xylene family (R^2 = 0.972 and 0.961 respectively). The latter may be indicative of industrial activity as the main role player in the emissions of these compounds. This is further corroborated by the observation that the average concentrations of the Ethylbenzene and Xylene family at point G is much lower than at point F as it is predominantly influenced by vehicular activity, being furthest away from the port.

Table 2. Interquartile range (IQR) of BTEX in Paranaguá city

Sampling Point		**Concentration BTEX (μg m^{-3})**				
		Benzene	**Toluene**	**Ethylbenzene**	**m+p Xylene**	**o Xylene**
A	Average	0.67	3.16	1.14	1.20	1.01
	IQR	0.55	5.20	3.48	5.69	2.91
B	Average	0.52	4.35	3.42	4.40	2.37
	IQR	0.62	7.09	4.79	7.13	2.78
C	Average	0.36	5.26	2.13	3.70	1.90
	IQR	0.60	8.04	7.08	5.15	2.71
D	Average	0.84	5.39	3.02	4.42	2.03
	IQR	0.66	6.60	2.19	4.60	1.39
E	Average	0.67	5.55	4.32	5.37	3.44
	IQR	0.85	8.97	4.86	7.67	3.10
F	Average	0.87	5.59	5.37	7.86	4.87
	IQR	0.90	8.90	5.00	8.87	4.43
G	Average	0.91	7.42	1.92	2.85	1.88
	IQR	0.84	9.42	2.36	5.58	2.27

331 3.1.4 Temporal variation across the sites.

332 The meteorological station from which the data for this investigation was obtained is located
333 close to Point A. The temperature ranged from 15.5°C to 43.5°C, with an average of 25.3°C. Figures 4A
334 and B (WR-Plot/Lakes Environmental) illustrate the prevailing wind direction (red vectors) during the first
335 5- and the second 4-week periods. During the first five weeks the prevailing wind direction was from the
336 Southeast (Figure 4A), whereas from week six onwards, the wind direction changed to a north-eastern
337 direction (Figure 4B).
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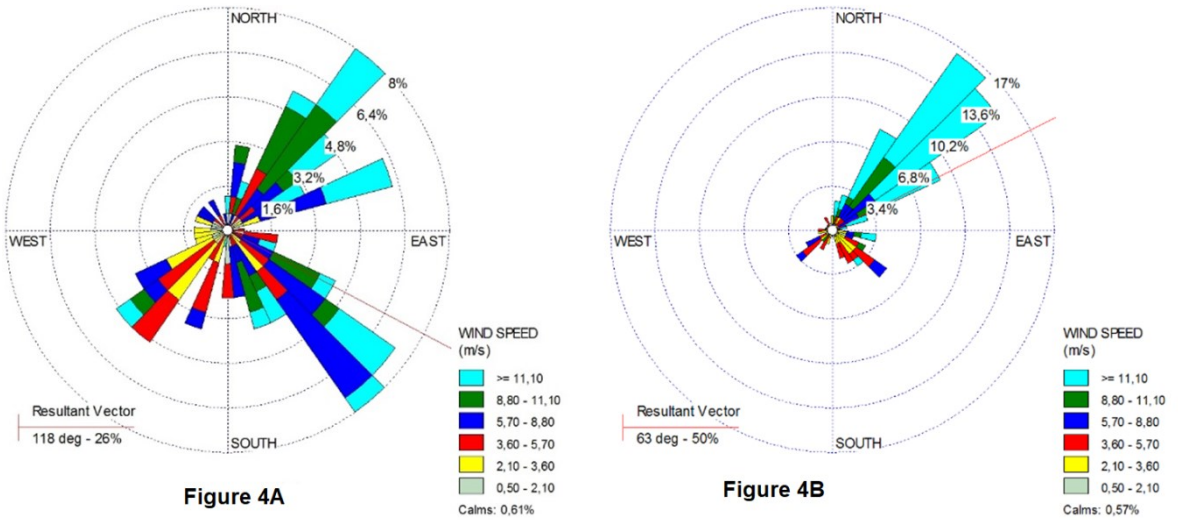

339

340 **Fig. 4** Wind Rose (WR-Plot) of Point A at Paranaguá city – week of 27 to December 4 (Figure 4A) and week of
341 January 1 to 7 (Figure 4B)
342

343 The variations in BTEX concentrations in the study period can be explained mainly by
344 phenomena associated with the influence of climatological factors such as wind speed (m s^{-1}) and direction.
345 The wind rose after the fifth week of the study shows a drastic change in wind direction, during which
346 winds from the southeast (126°) changes to winds from the northeast (63°) with frequencies above 50%
347 and speeds that generate high dispersion (frequencies higher than 17% for speeds greater than 11 m s^{-1})
348 (See Figure 4). This change in wind direction promotes that the emissions generated at the port and by

industries located in the vicinity of it, are dragged to the city of Paranaguá, with a consistent increase in concentrations by the pollutants emitted, as illustrated in Figure 5. This trend is not directly observed for Benzene, mainly due to the alight change in the vehicular flow, which is the main source of Benzene.

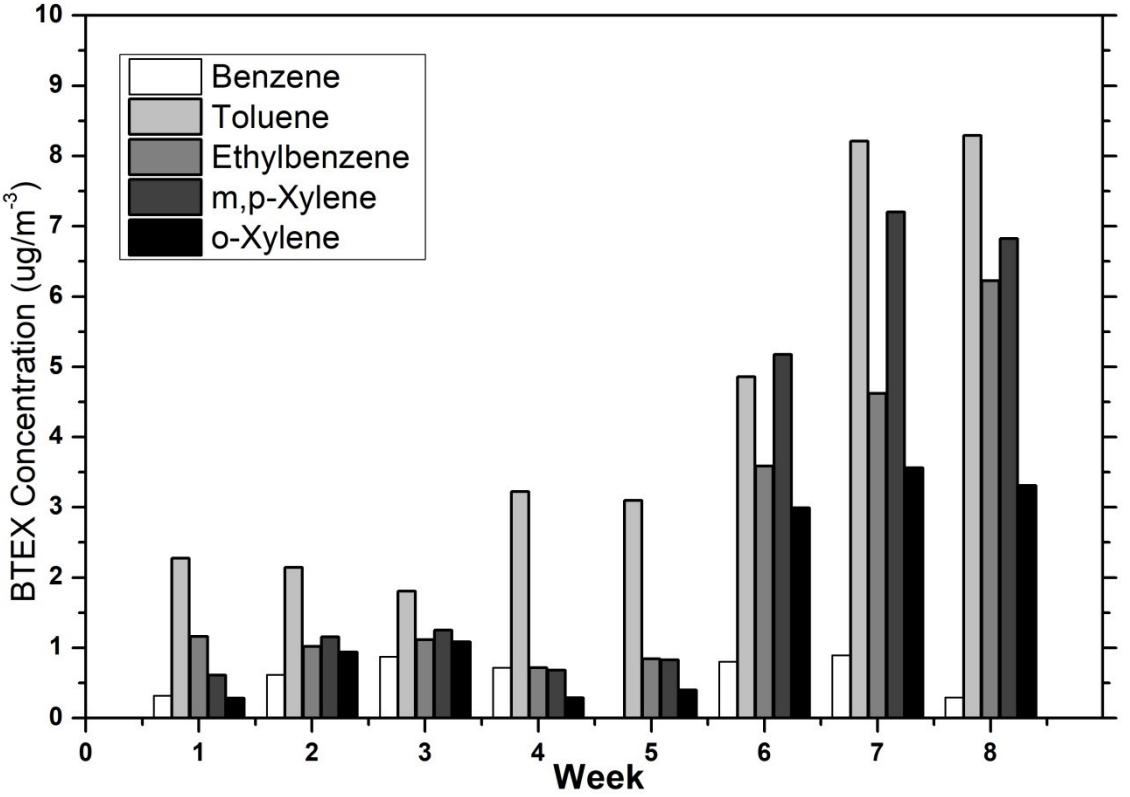

Fig. 5 Temporal variation of BTEX at point A for the study period

3.2 BTEX correlations and ratios in context.

3.2.1 T/B ratios

Ratio analyses are commonly used to identify sources and get a better understanding of the temporal and geographical variations. In general, Benzene and Toluene are highly correlated with vehicle traffic. Benzene, however, can mostly be solely ascribed to vehicular emissions as it is classified as a carcinogen and its use as a solvent is strictly controlled in contrast to Toluene. Therefore, T/B ratios in the

lower range (typically below 2) are normally indicative of vehicular emissions (Bretón et al. 2017). The T/B ratios and its variation across the sampling period are illustrated with box plots (See Supplementary Table SM5 for data), whereby Benzene values below the LoD for Benzene using Radiello tubes (0.05 μg m^{-3}) have been removed. (Figure 6)

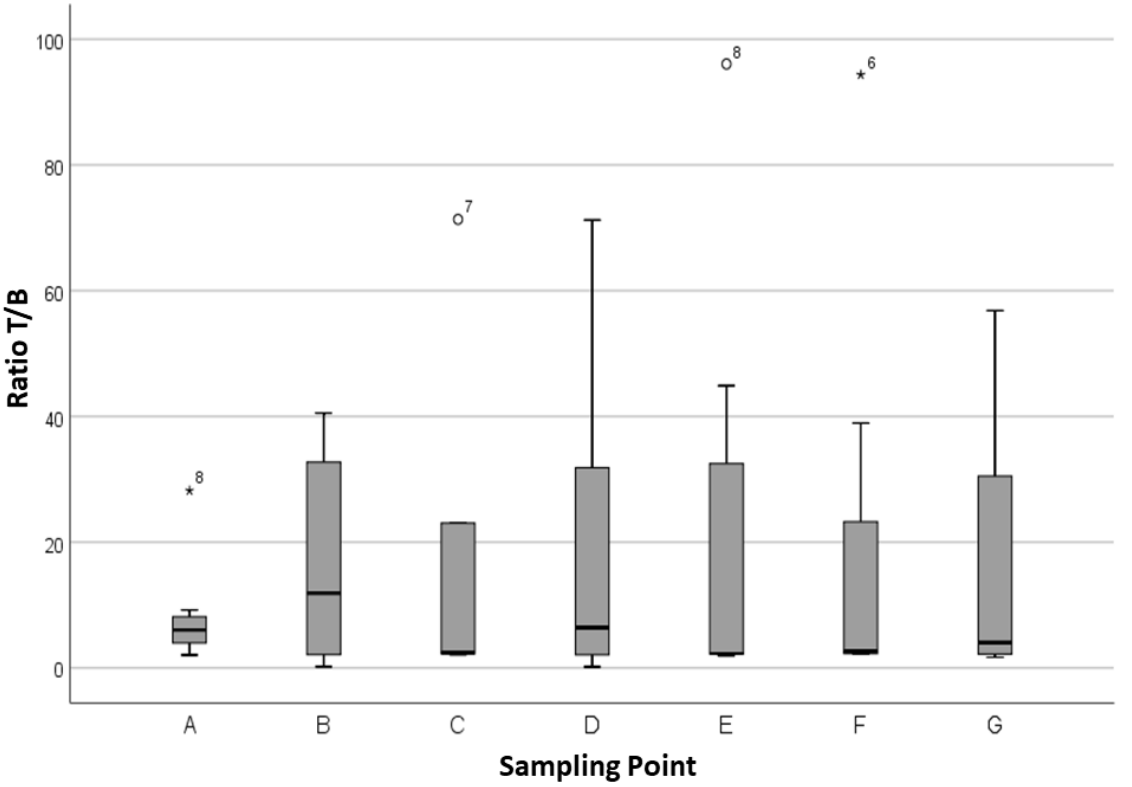

Fig. 6 Box and whisker plot of T/B ratios, calculated from the data obtained for each week at each sampling point.

Figure 6 indicates that the T/B ratios are, on average, much higher than 2. Gaston et al. (2013) reported the same tendency at the Port of Long Beach, where Toluene to Benzene ratios varied from 1.89 to a maximum of 6.1, indicating a photo-chemically unprocessed air mass. According to the author, air masses containing fresh urban emissions undergoing minimal photochemical processing typically have

Toluene/Benzene ratios ≥2. Lower values indicate more photochemically processed air masses as the more reactive Toluene is preferentially removed by reactions with the hydroxyl radical. It would, therefore, not be unreasonable to suggest that the air masses at the port are fresh emissions with minimal ageing, a conclusion which was also made earlier with regards to the m,p-Xylene to Ethylbenzene ratio being lower than 3.8 at all sampling points. Studies by Hartmann et al. (1997), Brocco et al. (1997), Monod et al. (2001), Barletta et al. (2005), Jiang et al. (2017) also report that T/B ratios are high in port cities because these areas are greatly affected by high levels of industrial emissions, with possible additional sources of Toluene.

It is evident that the T/B ratios at point A is the only site where the ratios were below 10 during all weeks, except for one of the weeks, as indicated by the outlier. For all other sites much higher values with significant variation were recorded and is indicative of the contribution of other sources to the Toluene levels. Especially at point G, it was expected that the T/B ratio would be in the traffic emission range, as the site is 13 km away from the port. However, a closer look at the data indicated that the T/B ratios during the first 4 weeks were, in general, in the range of 1.5 - 3 at points D, E, F, and G. During this time, the predominant wind direction was from the SE blowing toward the port, which would mean that a traffic signature from the surrounding area would prevail. This changes significantly from weeks 5 onwards, when the wind blows from the port towards point G, causing the T/B ratios to increase significantly.

3.2.2 Source apportionment BTEX

Both Pearson's and Spearman's correlation data (Supplementary Tables SM6 and SM7) indicate a negative correlation between the BTEX and Benzene. On the other hand, significant positive correlations are observed for BTEX. It again shows that the Benzene's sources are totally different from those of the BTEX, and that Toluene presents a significant contribution from different sources than vehicular gasoline sources.

ANOVA was employed to explore differences among stations. The question is whether the sampling network has one or more stations with a discrepant behavior or does it behave as a good

representation of the region. If the null hypothesis is rejected, at least one station would be subject to some critical local source that would be responsible for such a different behavior.

The results of the ANOVA test using the collection points as independent variables, show an F value for each BTEX of 0.49 (Benzene – p-Value 0.81); 0.40 (Toluene - p-Value 0.87), 1.82 (EthylBenzene - p-Value 0.11); 0.98 (m+p Xylene – p-Value 0.45) and 2.08 (the Xylene – p-Value 0.07). The ANOVA results show that p-values were relatively high, and the null hypothesis could not be rejected even for a significance level of 5%. It means that for this study, the variability between stations is not greater than the individual station variability, and the operational network behaves in a similar way, without any substantial source influencing stations in an individual perspective.

3.3 Health Risk Assessment

3.3.1 Non-carcinogenic effects

For the estimation of non-carcinogenic effects, reference concentrations, reported in the databases of the Federal Agency for Toxic Chemical Substances and Disease Registry of the U. S. (ATSDR), and in the Integrated Risk Information System (IRIS) of the U.S. Environmental Agency (EPA), were considered. All BTEX scored a Risk Quotient (HQ) below 1, indicating a low risk of non-carcinogenic health effects. The calculated HQ using all data were lower than 1 (Supplementary Figure SM2). Although we acknowledge that one could conclude that the total HQ values are similar across the site, it is interesting to observe that the points furthest away from the port present the highest risk. The maximum value of HQ recorded during the entire study corresponded to Benzene (0.1607) at point F (Supplementary Figure SM2 and Table SM8), and was below the reference value, this point being mainly influenced by the vehicular activity.

3.3.2 Carcinogenic effects

Benzene and Ethylbenzene may cause carcinogenic effects, and the risks associated with each one of the species at the different sampling points are displayed in Supplementary Figure SM3. Xiao et al.

426 (2018) reported on the importance of VOC emissions from marine shipping concerning the health impacts
427 on the workers and surrounding residents, as it is well known that VOC exposure could lead to mutagenic
428 and carcinogenic effects. Studies carried out at ports in China (Huang et al. 2018; Xiao et al. 2018) showed
429 that 50% to 78% of VOC's emitted by ships are Benzene and Toluene, respectively.

430 The criterion established by the EPA (EPA 2018) classifies Cancer Risk (CR) values between
431 10^{-5} and 10^{-6} as a possible risk to develop cancer. CR values $>10^{-5}$ (Red Line Figure SM3) are considered
432 a probable risk to develop cancer during a lifetime of exposure. To that end, Benzene can be considered as
433 low to possible risk at all the sampling points and Ethylbenzene as a possible risk at points D and G, and a
434 probable risk at points A, B, C, E, and F. This is in contrast to Bréton et al. (2017) who concluded that
435 populations living in the metropolitan area of Mérida, Yucatán, would be at definite risk of suffering from
436 cancer. In our investigation this is only the case at sampling points E and F.
437
438
439 **4. CONCLUSION**

440 The BTEX profile and levels at the Paranaguá Port were the same as the port of Naples, but both
441 differed significantly from the levels of BTEX at Long Beach port. This is an important finding as the port
442 of Long Beach has policies in place to mitigate emissions and therefore, despite the fact that it has a
443 significantly larger cargo volume, its BTEX emission level is much lower.

444 Benzene showed the lowest variation across the sampling sites and a poor correlation to BTEX
445 levels. In addition, it hardly varied across the sampling trajectory away from the port. Therefore, it can be
446 concluded that it is indicative of a common source for Benzene across the sites but different sources for
447 BTEX. The ratios analysis (T/B, B/T, m,p X/Et and m,p X/B) indicate that the BTEX levels are mainly
448 from fresh emission sources and that photochemical ageing was at minimum.

449 The non-carcinogenic risk was not significant for any of the pollutants as the HQ was below unity.
450 However, the carcinogenic risk varied across the sampling points from possible to a probable risk to contract

cancer during the lifetime of the ones exposed. This is a worrying finding as the points most at risk is closest to the city and residential areas.

This study provided the necessary baseline data to inform policymakers on how to change the circumstances of those currently at risk. Serious consideration should be given to the type of fuel used and fuel handling regulations, as well as the age of vehicles used at the port and in its surroundings. It is clear that large volumes of cargo can be handled without detrimental effects on human health, as is the case at Long Beach port, and further expansion and demand at Paranaguá can be met without an increasing risk, provided that policies are put in place for a sustainable operation.

DECLARATIONS

Ethical Approval

Not applicable

Consent to Participate

Not applicable

Consent to Publish

We affirm that the article has been studied and accepted by all listed authors. In addition, we affirm that all the authors mentioned in the article have been approved by all of us.

Authors Contributions

Hugo Sarmiento: Methodology, Investigation, Data Curation, Writing - Original Draft, Writing - Review & Editing. Sanja Potgieter-Vermaak: Conceptualization, Data Curation, Writing - Review & Editing, Visualization. Guilherme C. Borillo: Methodology, Investigation, Writing - Review & Editing. Ana Flavia L. Godoi: Resources, Writing - Review & Editing. Rodrigo A. Reis: Resources, Writing - Review & Editing Carlos I. Yamamoto: Resources, Writing - Review & Editing, Funding acquisition. Theotonio Pauliquevis:

Formal analysis, Writing - Review & Editing. Gabriela Polezer: Software, Writing - Review & Editing. Ricardo H.M. Godoi: Resources, Writing - Review & Editing, Funding acquisition.

Availability of data and materials

The data acquired or analyzed during this investigation are incorporated in this article.

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Statements & Declarations

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Competing Interests

The authors have no relevant financial or non-financial interests to disclose