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Assessment of the BTEX concentrations and reactivity in a confined parking area in Rio de Janeiro, Brazil

Barbara Prestes de Castro [a], Gladson de Souza Machado [b], Glauco Favila Bauerfeldt [b], Julio Domingos Nunes Fortes [a], Eduardo Monteiro Martins [a, *]

[a] DESMA, Universidade do Estado do Rio de Janeiro, Brazil
[b] Laboratório de Cinética Química, Departamento de Química, Instituto de Ciências Exatas, UFRRJ, Pavilhão Roberto Alvahydo (PQ), sala 44. km 7, Rodovia Br 465, Seropédica, RJ 23890-000, Brazil

HIGHLIGHTS

- BTEX concentrations are reported at a confined parking area in Rio de Janeiro.
- Vehicle exhaust and evaporative emissions are considered as the source of BTEX.
- Distinct evaporation profiles and reactivity explain the observed rank and ratios.
- Possibility of ozone formation is evaluated on the basis of the MIR scale.

GRAPHICAL ABSTRACT

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ABSTRACT

In this work, the contribution of evaporative emissions from light passenger vehicles to the degradation of the air quality was investigated on the basis of the indoor quantification of the monoaromatic volatile compounds Benzene, Toluene, Ethylbenzene and Xylenes (BTEX), specifically, a confined shopping mall parking area in the northern zone of Rio de Janeiro, a site that represents the reality of the vehicular fleet of the Metropolitan Region of Rio de Janeiro. In order to evaluate the concentration of the BTEX compounds, samples were collected, by an active sampling system using charcoal cartridge as adsorbent. The samples were extracted with organic solvent and subsequently analyzed by gas chromatography-mass spectrometry (GCMS). The average results were 54.14 μg m^{-3} (benzene), 209.24 μg m^{-3} (toluene), 45.87 μg m^{-3} (ethylbenzene) and 118.93 μg m^{-3} (xylenes). These results are compared with results from the literature of vehicular emissions in confined spaces such as garages and tunnels. Possible correlations with emissions from moving vehicles, obtained from previous studies in a tunnel of large circulation and emissions obtained in other underground parkings, are also investigated. The results suggest different emission sources.

1. Introduction

The metropolitan region of Rio de Janeiro (RMRJ), Brazil, is the second greatest in the country, with approximately 12 million people, showing also the greatest population density and an

* Corresponding author.
E-mail address: edmmartins@gmail.com (E.M. Martins).

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approximate vehicle fleet of 2.5 million. Like in other cities, most of the pollutants emitted to the atmosphere are related to technology development and population growth and vehicular emissions may be the most important source of anthropogenic pollution in urban areas. In the RMRJ, light vehicles are mainly fueled up with gasoline, ethanol and compressed natural gas. Besides, flexible-fuel vehicles using mixtures of gasoline and ethanol of random compositions are also found in the RJRM (Machado et al., 2007; de Oliveira et al., 2007; Martins et al., 2007).

Fossil fuels are the main source of the monoaromatic organic compounds benzene, toluene, ethylbenzene and xylenes (BTEX). From the environmental point of view the BTEX play an important role as primary pollutants, being considered some of the main ozone precursors (Buczynska et al., 2009; Caselli et al., 2010), also contributing to possible serious health problems. Xylenes, toluene and ethylbenzene are also found as the major ozone precursors in Rio de Janeiro city on the bases of the Maximum Incremental Reactivity (MIR) scale (Machado et al., 2007). The MIR scale is calculated from the IR coefficient, defined as the number of ozone molecules formed from carbon atoms of volatile organic compounds (VOC), added to an initial VOC/NOx mixture. In that work, the MIR scale was estimated from charcoal cartridges measurements of VOC concentrations (Machado et al., 2007).

The measurement of VOC concentrations and the understanding of the emission patterns in confined sites, like parking areas, are important because: (1) these gaseous compounds can migrate to the external (outdoor) areas, playing a role in the ozone formation; (2) these monoaromatic organic compounds may seriously contribute to indoor air contamination up to the detriment of air quality; (3) parking areas are mainly visited by people which may be exposed to a toxic ambient for some minutes or (considering the working personnel) for several days (Batterman et al., 2006). Despite the importance and urgency of assessing the indoor air quality in confined areas, concerning the measurements of the BTEX concentrations, only few case studies are found in the literature (Batterman et al., 2006; Zhang et al., 2008; Hun et al., 2011). However, several case studies are available discussing the indoor BTEX concentrations at houses, offices, libraries, industries and other sites (Esplugues et al., 2010; Lü et al., 2010; Zhang et al., 2012; Hamidin et al., 2013).

In Brazil, the vehicular emission control is determined by the Control Program of Air Pollution by Vehicles (*Programa Controle da Poluição do Ar por Veículos Automotores*, PROCONVE) (CONAMA, 1986), which sets the maximum limits for atmospheric pollutant emission, obeying also a rigorous specific chronogram (Souza et al., 2013). However, there are no goals concerning the BTEX emission reduction and known organic pollutants expect aldehydes, are not considered. The monitoring of the main atmospheric pollutants concentrations in Brazilian cities is generally responsibility of the state environmental agencies and the monitored compounds are defined by the CONAMA 03/90 resolution (CONAMA, 1990). There is no continuous BTEX monitoring in the Rio de Janeiro city, besides academic specific studies. Machado et al. determined BTEX concentrations in a tunnel in Rio de Janeiro in samples collected using charcoal (Machado et al., 2007). Correa and Arbilla studied the BTEX concentrations in one of the main avenues in the city, the Presidente Vargas Avenue along two years (Corrêa and Arbilla, 2007). Corrêa et al. investigated the BTEX concentrations at which the gas station personnel were exposed (Corrêa et al., 2012).

In this work, the assessment of BTEX concentrations and reactivity in a confined site is the main goal. The underground shopping mall parking was chosen since the emission source in the site must be mainly due to light vehicles and the influence of meteorological aspects is negligible. Venting in the chosen site is artificial and spontaneous transport between internal and external air must also be considered negligible.

2. Material and methods

The site is located at the northern zone at Rio de Janeiro city, and shows an approximate area of 77.1 thousand m^2. The shopping center shows a flux of 2.5 million people per month and the number of vehicles in the peak hours is about 4000. Light vehicles represent *ca*. 98% of the fleet and diesel vehicles are also found as the remaining 2%. The shopping mall parking is divided into three sections, two of them being opened areas and one underground, the latter with 1000 m^2 area and artificial venting. The total number of vehicles in all parking area per month is nearly 500,000. Samples were collected in the underground parking area, from July (07/01/2010) to November (11/30/2010), one sample per day, and two days per week. The highest vehicular flux had been recorded at 17:00, therefore this time was chosen for starting the sampling. A total of 37 samples were collected. It was not possible, unfortunately, to collect samples inside the shopping mall. Low flow sampling pumps (SKC®, model PCXR4) were used, after flow calibration at 1.0 L min^{-1}. The pump was left 1.20 m off the ground. Charcoal sorbent tubes (SKC®, 100/50) were employed. Charcoal is an excellent absorbent for volatile organic compounds, showing a high active surface area and high thermal stability. The total sampling time, for all samples, was 2 h. The sampling procedure was based on NIOSH 1501 method (NIOSH, 1997), with slight modifications in order to improve recovery.

In the laboratory, charcoal was transferred to 1 mL vials and put into Petri plates with ice aiming to reduce loss by volatilization of lighter compounds. In the vials, 25 μL of a 50 μg mL^{-1} solution of ααα-trifluorotoluene and 1-cloro-4-fluorobenzene in dichloromethane (DCM) were added. These compounds were employed as internal standard and surrogate standard, respectively. Finally, 1 mL of DCM was added and the vials were sonicated for 15 min. After this time, samples were allowed to settle time enough for complete deposition of suspended charcoal in solution.

Analysis of BTEX were done using an Agilent Technologies gas-chromatography system (model: 6890 GC system), equipped with mass detector and a capillary column RTX VRX (20 m length, 0.28 mm diameter, and 0.25 μm film thickness, Restek®) and helium as the carrier gas, with flow rate of 1.0 mL min^{-1}. Measurements were carried out in the splitless mode and 1 μl sample was injected. The temperature of the column was first 40 °C for 3 min and then reached 80 °C with the ramp of 12 °C min^{-1}; 6 °C min^{-1} to 162 °C and 40 °C min^{-1} to 230 °C and remained at this temperature for 4 min. The injector temperature was 250 °C and the source and GC interface temperatures were 200 and 250 °C, respectively. The MS system was operated in scan mode with a mass range of 45–300 *m*/*z* and the ion source was operated in the electron ionization mode (EI: 70 eV).

The calibration was performed with standard BTEX mixture (SUPELCO®), diluted in DCM to concentrations ranging from 1 to 15 μg mL^{-1}, using 1.25 ng μl^{-1} ααα-trifluorotoluene as internal standard. The method quantification limit (MQL) was 1 μg mL^{-1} and method detection limit (MDL) was 0.1 μg mL^{-1}. MDL was determined from seven determinations (from different injections) of the lowest concentration standard, multiplying the standard deviation of the determined concentrations by the appropriate one-sided 99% t-Student factor.

3. Results

The recoveries of the 1-cloro-4-fluorobenzene surrogate standard are observed in the accepted range from 45 to 125%, except the sample #21, which was rejected. Considering the remaining 36