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## Trends of BTEX in the central urban area of Iran: A preliminary study of photochemical ozone pollution and health risk assessment

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## ABSTRACT

The Environmental Protection Agency (USEPA) has identified Benzene, Toluene, Ethylbenzene, and Xylene (BTEX) as hazardous air pollutants. In this study, BTEX sampling was conducted at 20 sites during summer 2015 and winter 2016 in Yazd. Concentrations of BTEX were analyzed using a gas chromatograph with a flame ionization detector (GC-FID). In addition, ozone formation potential (OFP) and the health risks of BTEX were calculated. Spatial mapping was accomplished using the Kriging method. The obtained concentrations of total BTEX ranged from 8 to 560  $\mu\text{g}/\text{m}^3$ . The highest average individual values belonged to toluene and xylene ( $38 \pm 42$  and  $41 \pm 45 \mu\text{g}/\text{m}^3$ , respectively). Seasonal variation showed a downward trend from summer to winter. The peak BTEX emissions occurred in the evenings, due to rush hour traffic and meteorological factors. Spatial analysis showed that the maximum levels of BTEX occurred on high traffic roads or near fuel stations. Significant correlation coefficients between benzene and other BTEX compounds revealed that BTEX were emitted from main sources including gasoline vehicles and stations. The mean ratio of toluene/benzene (T/B) in summer (1.8) was more than winter (1.4). The seasonal changes in T/B ratio possibly were attributed to photochemistry, meteorology, and emission aspects. The OFP values were  $720 \pm 729$  and  $375 \pm 319 \mu\text{g}/\text{m}^3$  in summer and winter, respectively. OFPs, ranked maximum to minimum, were as follows: xylene > toluene > ethylbenzene > benzene. Although the values of the non-cancer risk of BTEX were under permissible recommended level, a cancer risk still exists because of high values of airborne benzene.

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## 1. Introduction

The atmospheric pollutants, which have a major impact on the human health are increasing due to the population growth, increasing number of vehicles, and expansion of urbanization (da Silva et al., 2016; Fard et al., 2016). With the rapid increase of the vehicles and consumption of fossil fuels, a large amounts of hydrocarbons and nitrogen oxides (NOx) are released into the atmosphere (Atkinson, 2000). Volatile Organic Compounds (VOCs) are

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an important group of air pollutants. These compounds have both anthropogenic and biogenic sources. Anthropogenic emissions of VOCs in the urban atmosphere consist vehicular exhaust, gasoline evaporation, solvent usage, leakage from the Compressed Natural Gas (CNG) and Liquefied Petroleum Gas (LPG) stations, petroleum refining, air fresheners, tobacco smoke, dry cleaners, municipal solid waste, bio-decomposition of the waste in landfills, and industrial processes. Biogenic VOCs (BVOCs) mainly come from the vegetation (forests), and wetlands and contribute minimally in the urban pollution compared to anthropogenic emissions (Bauri et al., 2016; da Silva et al., 2016). The United States Environmental Protection Agency (USEPA) has considered VOCs such as benzene, toluene, ethylbenzene, and xylene isomers (BTEX) as the air toxicants or hazardous air pollutants (HAPs). HAPs are pollutants known for causing cancer or having other serious detrimental health effects (Presto et al., 2016).

Some VOCs are toxic (benzene and 1,3-butadiene) and many participate in complex photochemical reactions in the presence of sunlight and hydroxyl radicals. The photochemical reactions can generate tropospheric ozone, peroxyacetyl nitrate (PAN), and Secondary Organic Aerosol (SOA) (Bauri et al., 2016; Marć et al., 2016; Atkinson, 2000).

In the urban areas, BTEX is responsible more than 60% of non-methane VOCs and can be used as an indicator of the organic pollutants in traffic. The main sources of BTEX include the mobile and stationary, particularly fuel combustion, evaporation of fuels and solvents, and fuel leakage from tanks (Lee et al., 2002; Tsai et al., 2006).

Benzene is carcinogenic to humans; therefore, the World Health Organization (WHO) and the USEPA do not recommend any safe level of exposure for it. However, a threshold for ambient air benzene levels has been defined in many countries. The European Commission (EC) guideline value for the annual average benzene concentration in Europe was  $5 \mu\text{g}/\text{m}^3$  in 2000 (Su et al.), then decreased by  $1 \mu\text{g}/\text{m}^3$  every 12 months, starting in 2006, to finally reach zero by January 2010. However, as yet, this goal has not been achieved. In Asia, the recommended annual thresholds for the ambient air benzene are 3, 5, 5, 20, 1.7, and  $10 \mu\text{g}/\text{m}^3$ , respectively, for Japan, India, Korea, Nepal, Thailand, and Vietnam (Lan and Binh, 2012). However, to the best of our knowledge, there is no recommended threshold level for the ambient air benzene in China and Singapore (Frank De Leeuw, 2017; Lan and Binh, 2012). Toluene affects the central nervous system, and ethylbenzene causes brain disorders and eye irritations. Xylene can cause skin inflammation and respiratory problems (Esmaelnejad et al., 2015; Mosaddegh Mehrjerdi et al., 2014).

Nowadays, the use of unleaded gasoline, which is rich in aromatic organic compounds like as BTEX, is increasing in the world (Miri et al., 2017; Nikoonahad et al., 2017). Therefore, monitoring of hydrocarbons is important in the urban areas.

Studies showed that xylene and toluene, as well as butane and ethylene, can produce one-third of the photocatalytic ozone (Derwent et al., 1996). In a two-year study, Majumdar (Majumdar et al., 2011) measured the concentration of benzene and toluene as  $13\text{--}72 \mu\text{g}/\text{m}^3$  and  $21\text{--}83 \mu\text{g}/\text{m}^3$ , respectively, in Kolkata, India. Wang reported a daily average of BTX of  $17.5 \mu\text{g}/\text{m}^3$  in China (Wang et al., 2010), and Kerbach stated the mean concentration of BTEX in Algeria between 28 and  $99 \mu\text{g}/\text{m}^3$  (Kerbach et al., 2006). Based on studies in Iran, the average concentration of benzene and toluene was 63 and  $9 \mu\text{g}/\text{m}^3$ , respectively, in Tehran (Fazlzadeh et al., 2012) and the average concentration of BTEX in Ahvaz was  $8.61 \mu\text{g}/\text{m}^3$  (Rad et al., 2014).

The BTEX has been commonly measured to evaluate the air quality in the urban area (Hoque et al., 2008), rural area (Liu et al., 2015), residential and commercial area (Schneider et al., 2001),

industrial environments and gas stations (Esmaelnejad et al., 2015; Baltrėnas et al., 2011). The differences between the results of these studies are related to sampling and analysis methods. Sampling methods include active and passive ones (Pekey and Yilmaz, 2011), both of which have good accuracy. Passive sampling is based on the diffusion mechanism and adsorbent tubes are used in it. This method needs more sampling time (Lan and Binh, 2012). Active sampling performs with low velocity pumps and other sampling equipment such as a flow meter, which makes it an expensive method (Yurdakul et al., 2017). Sampling time in active approach could be set in short periods. In most studies, a gas chromatograph with a flame ionization detector (GC-FID) or mass detector (GC-MS) is used for analyzing the BTEX. Another method for measuring hourly or daily values of BTEX in the air is on-line gas chromatograph, which is installed in urban or industrial areas (Pekey and Yilmaz, 2011; Martin et al., 2010).

Ozone formation potential (OFP) is generally used to estimate the maximum ozone formation capacity from VOCs, especially BTEX in cities (Wang et al., 2016). It could be calculated using maximum incremental reactivity (MIR) described by Carter (1994). Due to the intrinsic chemical behavior of each species, OFP of different VOCs varies. Therefore, qualitative and quantitative characterization of VOCs, as ozone precursors in a region, can help to understand the ozone formation process as well as evaluation of the best strategy for management and control of VOCs (Galvão et al., 2016).

Alghamdi et al. revealed photocatalytic OFP from BTEX of  $260 \mu\text{g}/\text{m}^3$  in Jeddah, Saudi Arabia (Alghamdi et al., 2014). Fanizza et al. reported photocatalytic OFP from aromatic compounds of  $197 \mu\text{g}/\text{m}^3$  in Rome, Italy (Fanizza et al., 2011).

Yazd is an industrial city located in Iran's central tropical desert, and the number of vehicles is increasing with the expansion of the city. Therefore, the release of BTEX compounds is inevitable, which increases urban air pollution and detrimental effects on human health. The monitoring of BTEX concentration is necessary for predicting the ambient air quality, especially in the middle-east cities such as Yazd. To the best of our knowledge, the research regarding OFP from BTEX in Iran has not yet been reported in detail. Therefore, this study is aimed to monitor the spatial and temporal trends of BTEX concentrations in the ambient air, their ratios, and OFP in the central urban area of Iran, Yazd. In addition, assessing the health risk of BTEX and determining their sources can be useful for the assessment of environmental health criteria in this city.

## 2. Materials and methods

### 2.1. Study area and sampling sites

Yazd is one of the oldest cities in Iran, established more than 2000 years ago, remaining intact throughout the centuries. The city ( $31^\circ 88' \text{N}$ ,  $54^\circ 36' \text{E}$ ) is the capital of Yazd Province, which is located east of Isfahan and south of the Lut desert, in the center of Iran (Fig. 1). Yazd has an area of  $97 \text{ km}^2$  and a traffic network of approximately 240 km (Mahmoudi et al., 2014; Nejadkoorki et al., 2010). Industrial activities and local road traffic in the city and surrounding areas continue to grow.

The climate of Yazd is typical of a desert, with 300 sunny days per year and average annual precipitation of 50 mm. The absolute maximum and minimum air temperatures are  $44^\circ \text{C}$  and  $10.17^\circ \text{C}$ , respectively. June and July are the hottest months, with mean daily maximum temperature of  $38.4^\circ \text{C}$ . December and January are the coldest months, with temperatures in the range  $6\text{--}18^\circ \text{C}$  (Mokhtari et al., 2015).

The wind rose for the sampling period was drawn using meteorological data taken from the Iranian Meteorological Department

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