DIURNAL VARIATION OF HEALTH RISK LEVELS OF VOCs IN BURSA, A HEAVILY INDUSTRIALIZED CITY IN TURKEY

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ABSTRACT

Volatile organic compounds (VOCs) attracted attention as air pollutants due to their health effects, particularly with their potential to induce cancer. The estimated health risk of VOCs in Bursa atmosphere, which is one of the most heavily industrialize cities in Turkey, were diurnally investigated by measuring VOCs with 60 minute intervals using an online GC-FID. The sampling campaign was performed between September 14 and November 6, 2005. Risk were estimated for VOCs having potential chronic toxic effects (non-cancer risk) and cancer risks such as benzene, 1,3-butadiene, toluene, ethyl benzene, hexane, naphthalene, styrene, xylenes and tetrachloroethylene. The questionnaire was filled out by selected people living in Bursa to obtain time-activity pattern for health risk assessment. VOCs concentrations generated in the study, time-activity data corresponding to different inhalation rates and body weight data obtained from the questionnaires were used to calculate potential risk. Slope factor and RfD used for cancer risk and chronic toxic effects calculations were obtained from the USEPA (2014).

The mean cancer risks due to 1,3-butadiene and benzene inhalation were approximately 41 and 76 per-one-million population, which exceeded the U.S. EPA benchmark of 1 per one million. The lifetime chronic toxic effects were estimated for all 10 VOC and none of the VOCs exceeded the threshold value, which was 1. According to result of the source apportionment model (PMF) applied on the data set, traffic and industrial solvent emissions were the major sources of cancer risk and chronic toxic effects due to inhalation of VOCs in the Bursa airshed. Relative contributions of these two source groups were also changed diurnally. Furthermore, the risks showed well defined short- and long-term temporal variations. The most pronounced short-term variation was diurnal pattern with a morning and afternoon maxima. In addition to diurnal variations, both cancer risk and chronic toxic effects showed consistent weekend-weekday differences.

Keywords: Volatile organic compounds (VOCs), online measurements, diurnal variations, cancer risk, chronic toxic effects

1. Introduction

VOCs attracted attention as air pollutants due to their health effects, especially some VOCs such as 1,3-butadiene and benzene have potential to induce cancer. The potential health risks of other VOCs include a range of effects such as irritation of the eyes and respiratory tract and sensory, neurotoxic, and hepatotoxic disorders (Kumar *et al*., 2014). Accordingly, the measurement and calculation of health risk potential of VOCs in ambient atmospheres are essential, especially in crowded or heavily industrialized cities (Parra *et al*., 2006)

The previous studies have investigated the health concern of VOCs in indoor (Sofuoglu *et al*., 2011; Kumar *et al*., 2014; Peng et. al., 2013) and also outdoor environment (Thepanondh *et al*., 2011; Zhang *et al*., 2012; Pratt *et al*., 2000). The present study estimate the cancer and non-cancer due to inhalation of some VOCs measured in ambient air by the population living in this area. To our best knowledge this is the first report of diurnal pattern of the risk due to inhalation of VOCs. Moreover the obtained results were compared with the USEPA guideline given for cancer and non-cancer risk.

2. Material and method

2.1. Site Description and Sampling

An online GC-FID system was placed at the Bursa Hygiene Center (40.19ºN, 29.05ºE), which is located at the city center of the Bursa, which is one of the most heavily industrialize cities in Turkey, and on-site measurements were performed (Figure 1).

Ambient air samples were diurnally investigated by measuring VOCs with 60 minute intervals using an online gas chromatography with Flame Ionization Detectors. The sampling campaign was performed between September 14 and November 6, 2005 and 641 samples were collected. Extensive Quality Assurance/Quality Control (QA/QC) procedure was followed during the sampling campaign (Civan 2010; Yurdakul, 2014).

Figure 1: Sampling site

2.2. Health Risk Assessment

Risk was estimated for VOCs having potential chronic toxic effects (non-cancer risk) and cancer risks. Carcinogenic risk for the benzene and 1,3-butadiene have classified as carcinogen by the International Agency for Research on Cancer (IARC), was calculated based on the following equation:

$$R=I\times SF \qquad (1)$$

Where;

R: Estimated inhalation cancer risk from pollutant (unitless), I: contamination intake (mg $kg^{-1}day^{-1}$), SF=Unit risk or slope factor of dose-response curve (mg $kg^{-1}day^{-1})^{-1}$.

Chronic toxic risks (hazard ratios) for non-carcinogenic compounds such as benzene, 1,3-butadiene, toluene, ethylbenzene, hexane, naphthalene, styrene, xylenes and tetrachloroethylene were calculated by using benchmark concentrations (RfC, RfD, REL, etc.). Either pollutant concentration was divided by their corresponding Reference Concentration (RfC) or contamination intake rate value of pollutants was divided by Reference Dose (RfD) to derive a hazard ratio. Hazard ratio for each pollutant was calculated using the following formula:

$$HR=\frac{I}{RfD} \text{ or } \quad HR=\frac{C}{RfC} \qquad (2)$$

The following equation is advised by USEPA (2009) to estimate the life time contamination intake (I) via inhalation route for each compound for and lifetime cancer risk

$$I=\frac{C\times CU\times IR}{BW} \quad (3)$$

Where;

I: contamination intake (mg $kg^{-1}day^{-1}$), C (μgm^{-3}): concentration of chemical measured in personal sampling, IR: Inhalation rate (m^3day^{-1}), BW: Body weight (kg), CU conversion unit (10^{-3} mg μg^{-1})

Inhalation rate used for risk assessment was calculated by using the VOCs concentrations generated in the stud, body weights and activity data obtained from the questionnaires which were applied on the participants living in Bursa region (Civan, 2010). The questionnaire was filled out by selected people living in Bursa to obtain time-activity pattern for health risk assessment (Civan, 2010). The activity levels were categorized as light, moderate, or heavy according to the criteria developed by the U.S. EPA Office of Environmental Criteria and Assessment for the Ozone Criteria Document (USEPA, 1985). Slope factor and RfD used for cancer risk and chronic toxic effects calculations were obtained from the USEPA (2014).

3. Result and discussion

The statistic information about the cancer risk due to inhalation of benzene and 1,3-butadiene and also non-cancer risk calculated for selected VOCs such as benzene, 1,3-butadiene, toluene, ethylbenzene, hexane, naphthalene, styrene, xylenes and tetrachloroethylene are given in Table 1. The mean cancer risks due to exposed to 1,3-butadiene and benzene in Bursa airshed were approximately 41 and 76 per-one-million population, which exceeded the U.S. EPA benchmark of 1 per one million. The high value of standard deviations and the differences between minimum and maximum cancer risks indicate a high cancer risk which occurs at specific hours in a day. The mean and median non-cancer risk levels of all VOCs depicted in the table do not exceed benchmark level of “1”. The non-cancer risk were higher than the threshold (HQ = 1) for benzene and 1,3 butadiene at total of 56 and 4 hours out of 641 hours, respectively.

Table 1: Statistical values of the cancer and non-cancer risks due to inhalation of VOCs in Bursa atmosphere

	Mean	**Median**	**Standard Deviation**	**Min-Max**
Cancer Risk				
Benzene	7.6×10^{-5}	3.4×10^{-5}	9.8×10^{-5}	2.9×10^{-6} -7.08×10^{-4}
1,3-Butadiene	4.1×10^{-5}	2.6×10^{-5}	4.8×10^{-5}	2.8×10^{-6} - 3.28×10^{-4}
Non-cancer Risk				
Benzene	0.375	0.234	0.433	0.026-2.95
1,3-Butadiene	0.144	0.065	0.185	0.006-1.34
n-Hexane	0.004	0.004	0.004	0-0.02
Toluene	0.006	0.004	0.01	0-0.19
Tetrachloroethylene	0.006	0.004	0.004	0.001-0.026
Ethylbenzene	0.003	0.002	0.004	0-0.079
m+p-Xylene	0.037	0.025	0.063	0.001-1.13
Styrene	0.003	0.003	0.002	0-0.01
o-xylene	0.012	0.008	0.015	0.001-0.24
Naphthalene	0.305	0.281	0.152	0.049-1.55

Diurnal variations of cancer and non-cancer risks are given in Figure 2 and Figure 3. Diurnal pattern of the benzene and 1,3-butadiene risks had different diurnal profile. High risk of benzene were observed at morning (8:00-11:00), and evening (19:00-21:00) hours. Since the health risk is reflected in the concentrations of atmospheric pollutants, this diurnal pattern of risk is dictated by diurnal variations of pollutant source strengths. Usually, double peaks are reflective of the typical traffic pattern (Chang *et al.*, 2006) in diurnal profiles. With the increase in the traffic intensity, benzene risk level start to increase in the morning. After 10:00, benzene risk level started to decrease. Relatively low level of risk was observed between 12:00 and 18:00, most likely owing to decrease in the traffic density, lower level was observed in noon time as compared to morning and evening rush hours. The risk level then increased after 18:0 due to afternoon rush hour. This second peak which occurred between 18:00 and 21:00 was slightly later than we expected. It should be real, because a similar afternoon rush hour peak was also observed in earlier studies in Ankara (Kuntasal *et al*., 2005).

The risk of 1,3-butadiene had slightly different from the diurnal pattern of benzene risk. The people living in the area had more expose to risk due to inhalation of the 1,3-butadiene at evening (19:00-21:00) hours and just after midnight. The exhaust emissions appears to be the dominating source of 1,3-butadiene and benzene emissions based on the result of the source apportionment model (PMF) applied to the data set (Yurdakul, 2014). Nevertheless the diurnal concentration and hence cancer risk levels of these two compounds had different pattern. The atmospheric reactivities, the presence of the other VOCs and the sunlight affect the concentration level of these two hazardous pollutants. It should be also pointed out that the risk level of 1,3 butadiene and benzene exceeded the U.S. EPA benchmark of 1 per one million during whole sampling days.

The other important issue is to evaluate the risk for exposed people living in the city at weekend and weekday. The cancer and non-cancer risk levels were calculated for these data set showed statistically significant weekday to weekend variation at 90% of confidence level (p<0.1). Figure 4 depicted hourly average cancer and non-cancer risk levels calculated for week days and weekend days.

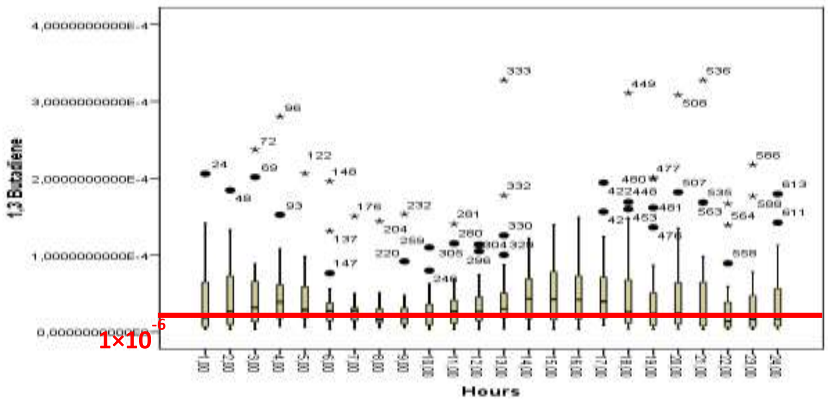

Figure 2: Diurnal variation of the carcinogenic risk level due to inhalation of 1,3-butadiene (Extreme values and outliers marked with star and round dot, respectively).

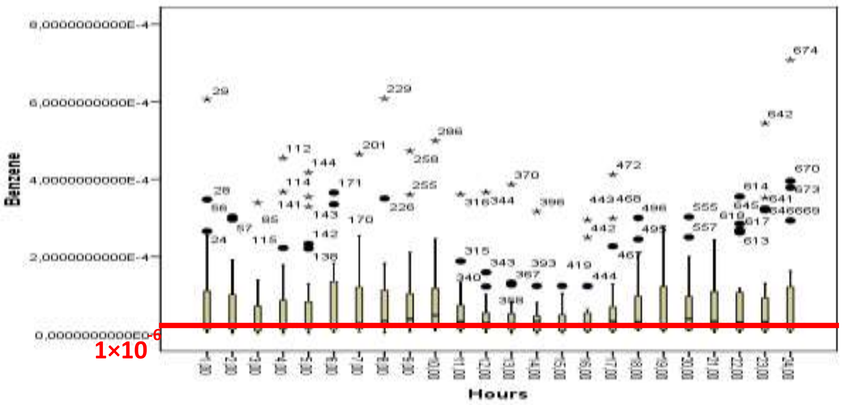

Figure 3: Diurnal variation of the carcinogenic risk level due to exposed of benzene in ambient air (Extreme values and outliers marked with star and round dot, respectively).

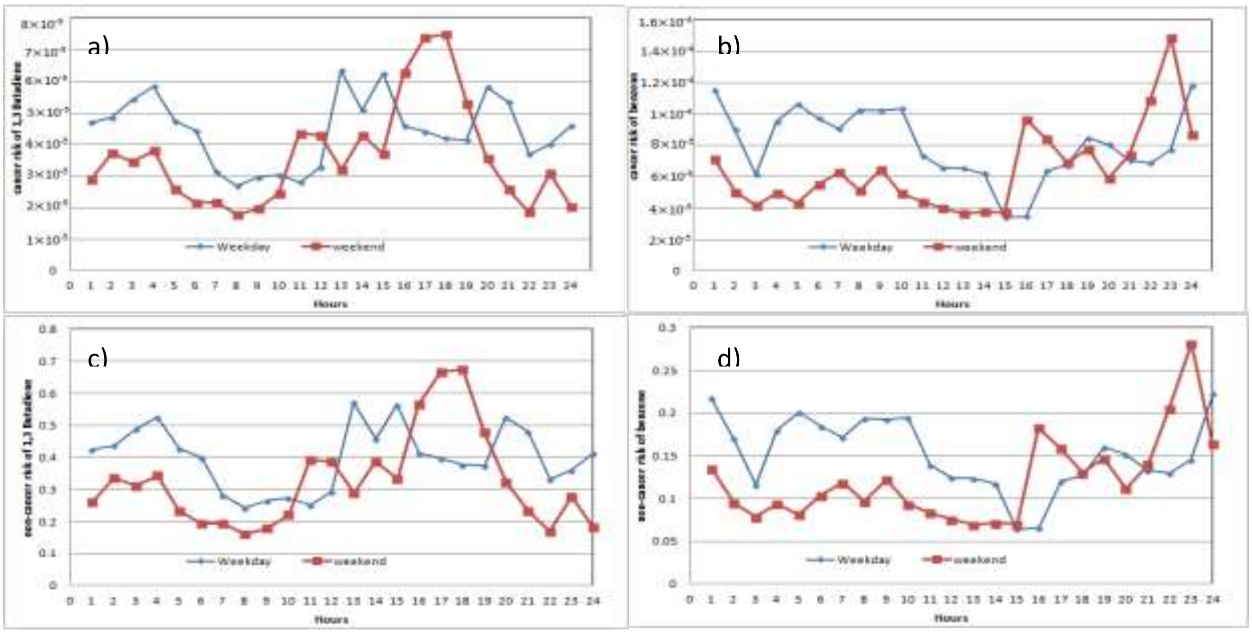

Figure 4: Hourly average week days and weekend days cancer risks levels for a) 1,3-butadiene, b) benzene and non-cancer risks levels for c) 1,3-butadiene, d) benzene.

The hourly average risk level estimated for the weekdays were higher than that of weekend days except for between 16:00 and 19:00 and at 15:00 and 21:00 for 1,3-butadiene and benzene. Concentrations of traffic related pollutants are often higher on weekdays than on weekends. Heavy-duty diesel truck activity and light duty passenger vehicle activity on highways have been found to be 70–80% and 10% lower on weekends, respectively (Marr and Harley, 2002). Therefore, in this study, a possible reason of the lower concentrations related with the traffic based organics on weekends is the reduction of traffic density in city center.

4. Conclusion

Mean cancer risks due to 1,3-butadiene and benzene inhalation were approximately 40 and 70 per-one-million population, which exceeded the U.S. EPA benchmark of 1 per one million. The lifetime chronic toxic effects were estimated for all 10 VOC and none of the VOCs exceeded the threshold value, which was “1”. According to PMF results applied on the data set, traffic and industrial solvent emissions were the major sources of cancer risk and chronic toxic effects due to VOCs inhalation in the Bursa airshed. Relative contributions of these two source groups changed diurnally. The calculated risks showed well defined short- and long-term temporal variations. The most pronounced short-term variation was diurnal pattern with a morning and afternoon maxima. In addition to diurnal variations, both cancer risk and chronic toxic effects showed also consistent weekend-weekday differences.

Potential cancer and non-cancer risk levels at Bursa, due to inhalation of benzene, 1,3-butadiene, toluene, ethyl benzene, hexane, naphthalene, styrene, xylenes and tetrachloroethylene were calculated using a hourly measured pollutants concentrations in ambient air and body weights and activity data obtained from the applied questionnaires. Hence calculated risk was probably to be underestimated mainly as only limited number of species was monitored and there were no indoor measurements that should be included in data set. Despite a possible underestimation, the estimated risks still exceeded the acceptable level, suggesting that the pollutants with health hazards in this region are worth further investigation. The source apportionment and estimated hourly lifetime cancer risk results presented in the paper can provide the guidance for future health risk managers to design the risk reduction strategy more effectively.

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