SPATIAL AND SEASONAL DISTRIBUTION OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN THERMAL POWER PLANT REGION IN KUTAHYA, TURKEY

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ABSTRACT

In this study, Volatile Organic Compounds (VOCs) were sampled with Tenax TA passive sampling tubes to determine spatial and seasonal distribution in a thermal power plant region in Kütahya, Turkey. Two-week summer and winter sampling campaigns were performed in an area of approximately 130 km x 120 km, at 108 sampling points in both seasons.

46 VOCs were measured by the passive tubes and analyses of the samples were performed by using Thermal Desorber connected to Gas Chromatograph-Flame Ionization Detector (FID). Parameters such as method detection limit, recovery and repeatability were determined within the context of quality control studies. For the evaluation of the analyses results, some statistical values were calculated (mean, geometric mean, maximum, minimum, median, standard deviation) for 46 VOCs. Geometric mean values ($\mu g\ m^{-3}$) for winter and summer seasons ranged between 0.03-1.63 and 0.02-0.69, respectively. The highest standard deviation values were obtained as 0.57 (benzene), 0.76 (toluene), 0.59 (n-decane), 0.73 (n-undecane) and 0.84 (n-dodecane) for winter season and 0.89 (n-Decane), 1.25 (n-Hexane), 1.30 (n-Undecane), 1.38 (toluene) and 1.78 (n-Dodecane) for summer season.

According to the seasonal comparison results, concentration values of total VOCs in winter (14.44-27.35 $\mu g\ m^{-3}$) were found higher than summer values (6.77-25.74 $\mu g\ m^{-3}$) in industrial sampling points, except for a few points. Similar to the industrial points, winter values (7.67-39.75 $\mu g\ m^{-3}$) were higher than summer values (6.74-25.90 $\mu g\ m^{-3}$) in urban sampling points, For rural areas, there is no significant seasonal difference in VOC concentrations except some sampling points very near traffic-dense regions and settlements. The spatial and seasonal distributions of VOCs were visualized through pollution maps prepared by using Geographical Information System. When the spatial distribution of the pollutants was evaluated, higher VOC levels were measured at the points especially around power plants, city center and districts having both dense population and high traffic density.

Outdoor cancer risks for benzene were also calculated for each sampling point. Cancer risk values changed between $3.65.10^{-8}$-$2.2.10^{-5}$ for winter and $2.11.10^{-7}$-$1.32.10^{-5}$ for summer. Cancer risk limit value for benzene given by EPA is 1.10^{-6}. The risk values determined in this study exceeded the limit value at approximately >80% of the sampling points in both season.

Keywords: volatile organic compounds, passive sampling, seasonal and spatial distribution, cancer risk

1. Introduction

Volatile Organic Compounds (VOCs) are among the pollutants that have toxic and carcinogenic effects on human health. They also play an important role in the formation of pollutants such as ozone and PAN (Peroxyacetyl Nitrates) by the reactions with nitrogen oxides (NO_x) in the presence of sunlight. While the main anthropogenic sources of VOCs are solvent usage and internal combustion engines, VOCs are also emitted to the atmosphere from power plants in significant amounts. It has been reported that 37% of total anthropogenic emissions are released during power production processes (Fernández- Martinez *et al.*, 2001).

A total of 188 air pollutants have been identified as hazardous air pollutants by US Environmental Protection Agency (USEPA) and 149 of them are VOCs. EPA evaluates the effects of environmental pollutants on human health within the scope of the IRIS program (EPA-IRIS, 2015). Respiratory-induced cancer risk can be calculated by using unit risk factor and ambient concentrations. Several studies present in the literature about risk analysis of VOCs, but there are limited studies carried out in Turkey (Durmusoglu *et al.*, 2010, Scheepers *et al.*, 2010, Sofuoglu *et al.*, 2011).

When the national and international literature is examined, studies performed to determine the distribution of health risks in a large urban scale are not common. Health risk studies are usually based on measurements performed on a single (or a few) station or indoor measurements. In this study, VOC concentrations measured at 108 points in Kütahya by passive samplers and they were used to calculate risk values for two seasons (winter and summer).

Kütahya is among the cities which have air pollution problem in Turkey. Thermal power plants located in the borders of the city may negatively affect the urban air quality. Urban air pollution can cause a major threat to human health and the environment. Air quality measurement studies are very limited in Kütahya and so an extensive sampling study that covers all the province boundaries is needed to investigate the air quality of the city.

The objectives of this study are: (1) to determine spatial and seasonal distributions of VOCs in an area of 130 km*120 km, (2) to calculate cancer risks by using measured pollutant concentrations.

2. Materials and methods
2.1. Study area and sampling strategy
Passive sampling studies were carried out at 108 points in summer and winter seasons in thermal power plant region in Kütahya. Sampling area is 130 x 120 km^2. This area includes not only city center but also all city counties. The city has three thermal power plants. Seyitömer Power Plant is 20 km, Tunçbilek Power Plant is 50 km and Orhaneli Power Plant is 105 km far from the city. Prevailing wind direction is north-west and south-east. All the power plants are located in the north west of the city and poor quality coal with high ash content is used.

In order to investigate spatial distributions of the VOCs, sampling points were chosen considering source types (industry, traffic, heating etc.). While choosing the sampling points, other parameters such as topography of the city, transportation, security, wind direction, settlement regions were also taken into consideration. The sampling points were classified as industrial, rural and urban.

Samplings were carried out by using Tenax TA passive sampling tubes for 46 VOCs. Samples were collected during two-week period between 3-17 February 2014 for winter and 2-16 June 2014 for summer campaign. During each sampling period, the samplers were placed in the shelters to prevent the effects of some meteorological parameters such as wind, rain, snow, etc.

2.2. Preparation and analyses of the samples
Before each sampling campaign, Tenax TA sampling tubes were conditioned by using Markes TC-20 conditioning instrument by passing stream of nitrogen at 25 psi at 330°C for 30 min. Then, the tubes were capped with Swagelok end-caps and put in falcon tubes which contain silica gel and activated carbon. After the sampling was completed, all the samplers were brought to the laboratory in ice bags and stored at -18°C.

Analyses of the samples were performed by using Thermal Desorber (Markes, Unity 2) connected to Gas Chromatograph (Agilent, 6890) - Flame Ionization Detector (FID). The GC is equipped with Deans' Switch System which allows transfer of sample in two columns (Alumina Plot (HP-AL/S) and DB-1) having different polarities and columns are connected to two Flame Ionization Detectors. The GC oven was programmed to hold at 40°C for 5 min and ramped to 195°C at a rate of 5 °C min^{-1}, then again hold at 195°C for another 25 min. A six point (1-200 ppm) calibration was prepared and r^2 values were obtained between 0.9769-0.9999. Concentrations of the measured pollutants were calculated based on Fick's first law of diffusion.

2.3. Quality control/quality assurance (QC/QA) studies

For QA/QC studies, an intermediate calibration standard was used as a calibration check standard and analysed before every analysis batch. The concentration of the intermediate check standard did not change more than ± 15% of the calibration level concentration. CRS (certified reference standard) including 100 ng benzene, toluene and xylenes was analysed to check the analyses. The results obtained from the instrument were 92.43 ng, 106.24 ng and 96.11 ng, respectively. Instrumental detection limit was calculated by the analysis of the lowest calibration standard seven times and standard deviation of the measurements was multiplied by three. Detection limit values for 46 VOCs were between 0.110-0.988 ng.

2.4. Health risk assessment

Inhalation cancer risk values were determined for benzene by using the data from USEPA Integrated Risk Information System (EPA IRIS, 2015). Risk values were calculated by using Equation 1 given below for each sampling point and for both seasons.

$$\text{Cancer risk} = IUR * EC \qquad\qquad (1)$$

where *IUR* is unit risk $(\mu g\ m^{-3})^{-1}$ and *EC* is exposure concentration $(\mu g\ m^{-3})$.

3.   Results and discussion
3.1. Statistical evaluation of the results

Some statistical parameters (minimum, maximum, mean, geometric mean, standard deviation) were calculated for each VOC for both seasons. Geometric mean values were found between 0.02-1.63 $\mu g\ m^{-3}$ in winter season while they were in the range of 0.02-0.69 $\mu g\ m^{-3}$ in summer season. Standard deviations for some VOCs such as n-dodecane, toluene, n-undecane, benzene were much higher than the other compounds in winter. In summer, standard deviations of n-hexane, toluene, n-decane, n-undecane, n-dodecane were found higher than the other VOCs. Higher standard deviations of some VOCs indicate some specific sources of these pollutants.

3.2. Spatial and seasonal distributions of the measured VOCs

Spatial and seasonal distributions of the measured VOCs were determined by preparing pollution maps. Spatial and seasonal distribution maps for benzene were given as an example in Fig.1.
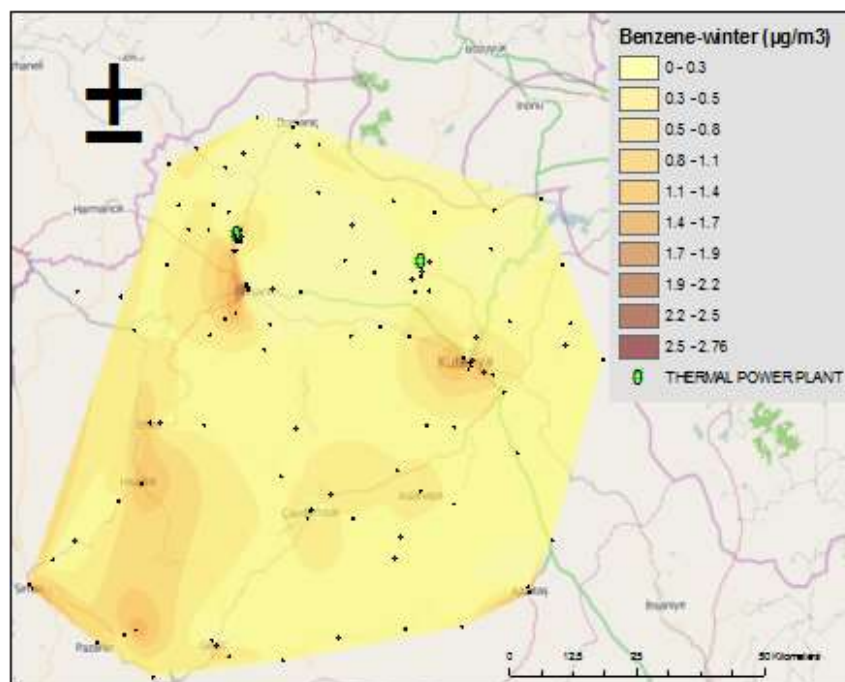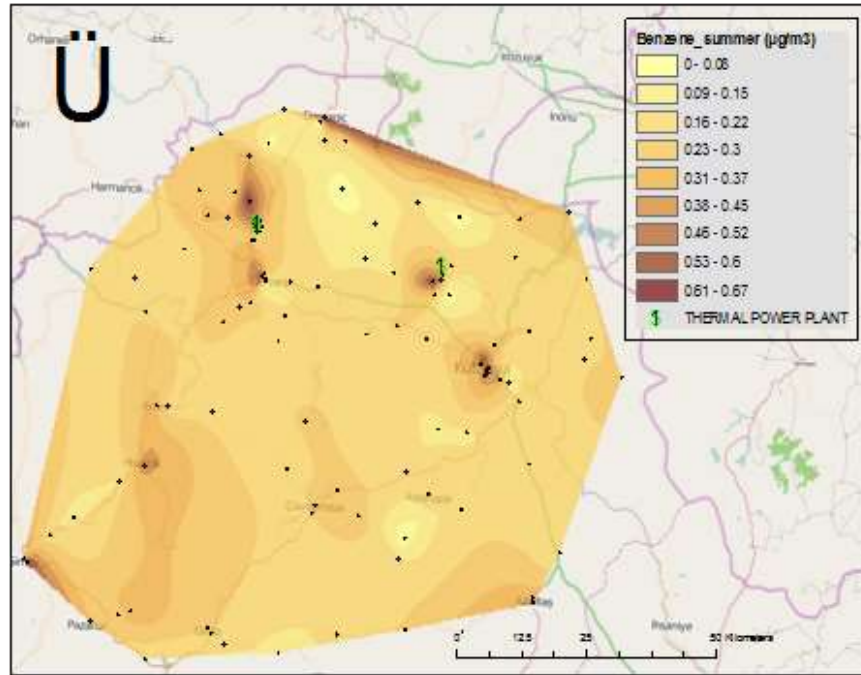
Figure 1: Distribution maps of benzene in winter and summer seasons

In winter, concentrations of total VOCs (14.44-27.35 µg m^{-3}) were found higher than summer season (6.77-25.74 µg m^{-3}) at industrial sampling points, except for a few ones. Similar to the industrial points, winter concentrations (7.67-39.75 µg m^{-3}) were higher than summer concentrations (6.74-25.90 µg m^{-3}) in urban sampling points. For rural areas, there is no significant seasonal difference in VOC concentrations except some sampling points which are very close to traffic-dense regions and settlements**.** In general, except for about 15 sampling points, total VOC concentrations measured in winter were higher. This may due to low mixing height, higher traffic density and heating activities in winter season.

3.3. Respirable cancer risk assessment
Cancer risks were calculated for all the sampling points and for both seasons by using benzene concentrations and unit risk factor taken from EPA IRIS which is 7.8*10^{-6} (µg   m^{-3})$^{-1}$ (EPA IRIS, 2015).

Estimated risk values were between 3.7*10^{-8} – 2.2*10^{-2} for winter and 2.12*10^{-7} –   5.36*10^{-6} for summer. Acceptable cancer risk value is expressed as 1*10^{-6} by USEPA (EPA, 2015). This acceptable risk value was exceeded at 86 sampling points in winter and at 103 sampling points in summer. WHO (World Health Organization) acceptable risk value is between 1*10^{-6} – 1*10^{-5} (Demirel *et al*, 2014). Most of the risk values calculated in this study were within the WHO limit. Risk values obtained for 17 sampling points in winter and for 4 sampling points in summer exceeded the WHO acceptable risk level.

Since the benzene concentrations were higher especially in the center of the city in both seasons, higher risk values were obtained from the points located in the center.

4.   Conclusions
In this study, seasonal and spatial distributions of 46 VOCs were determined by using passive sampling method at 108 sampling points in Kütahya, Turkey.

When the seasonal distributions were evaluated, concentrations of the most of the measured VOCs were found higher in winter season. According to the spatial evaluation, VOC concentrations obtained especially around thermal power plants, dense-traffic regions and settlements were measured in higher levels.

Cancer risks were estimated by using ambient concentrations of benzene. Although cancer risk values calculated for winter season were higher than summer values, the acceptable risk value set by EPA ($1*10^{-6}$) was exceeded at many of the sampling points in the summer. Also, risk values obtained in winter season at 17 sampling points and in summer season at only 4 sampling points were out of the acceptable risk level recommended by WHO ($1*10^{-6}$ – $1*10^{-5}$).

ACKNOWLEDGMENTS

REFERENCES

1. Demirel, G., Özden, Ö., Döğeroğlu, T. and Gaga, E.O (2014)., Personal Exposure of Primary School Children to BTEX, NO2 and Ozone in Eskişehir, Turkey: Relationship with Indoor/Outdoor Concentrations and Risk Assessment, Science of the Total Environment, **473–474**, 537–548.
2. Durmusoglu E., Taspınar F., and Karademır A. (2010), Health risk assessment of BTEX emissions in the landfill environment, Journal of Hazardous Materials, **176, 1-3,** 870-877.
3. EPA http://www.epa.gov/teach/chem_summ/BENZ_summary.pdf (2015).
4. EPA-IRIS http://www.epa.gov/iris/supdocs/0276index.html (2015).
5. Fernández-Martínez G., López-Mahía P., Muniategui-Lorenzo S., Prada-Rodríguez D., and Fernández- Fernández E. (2006), Spatial and temporal trends of volatile organic compounds (VOC) in rural area of northern Spain, Science of Total Environment, **370**, 157-167.
6. Sofuoglu S. C., Aslan G., Inal F. and Sofuoglu A., An assessment of indoor air concentrations and health risks of volatile organic compounds in three primary schools (2011)., International Journal of Hygiene and Environmental Health, **214**, **1,** 38-46.
7. Scheepers P. T. J., Konıngs J., Demırel G., Gaga E. O., Anzıon R., Peer P. G. M., Dogeroglu T., Ornektekın S. and Van Doorn W.(2005), Determination of exposure to benzene, toluene and xylenes in Turkish primary school children by analysis of breath and by environmental passive sampling, Science of the Total Environment, **408**, **20**, 4863-4870.