Monitoring and Assessment of Volatile Organic Compounds in Ambient Air in the Vicinity of Industrial Area – A case study

工業地帯周辺における大気中揮発性有機化合物のモニタリングと評価～事例研究

環境リスクマネジメント専攻　責任指導教員：益永　茂樹
Vasu Tiwari（テワリ　ワス）

ABSTRACT

Urban ambient air concentrations of 39 aromatic (including benzene, toluene and xylenes) and aliphatic volatile organic compounds (VOCs) were measured in Yokohama city. Yokohama city was selected as a case study to assess the amount of VOC released from Industrial area, to characterize the ambient air quality with respect to VOC as well as to know the impact of petrochemical storage facilities on local air quality. For this purpose, ambient air samples were collected (from June 2007 to November 2008) at six selected locations, which are designated as industrial, residential or commercial areas. To find out the diurnal variations of VOC, hourly night time sampling was carried out for 3 nights at one of the industrial location (Shiohama). Samples were analyzed using gas chromatographic system (GC-FID). Results show strong variation between day and night time concentrations and among the seasons. Aliphatic fractions were most abundant suggesting petrochemical storage facilities as the major source of atmospheric hydrocarbons. Monitored results were compared with simulated model results (using METI-LIS software and PRTR data). A screening level (tier -1) health risk assessment was conducted results show that residents at any of the locations are not being exposed to airborne concentrations of VOCs at an unacceptable level via inhalation that may pose unacceptable risks to their health.

1. Introduction

The importance of organic compounds produced due to anthropogenic activities into the atmosphere was recognized about 50 years ago by Haagen-Smit in his studies of Los Angeles' smog (Derwent, 1995). Benzene, toluene, ethyl benzene and xylene are the most typical components of VOC pollution in air (Chattopadhyay et al., 1997). Several effects of VOCs are recognized such as their contribution to stratospheric ozone depletion, toxic and carcinogenic human health effects and enhancement of the global greenhouse effect (Cetin et al., 2003). Petroleum refineries and petrochemical storage facilities are generally large installations. Their operation is associated with the emission of various hydrocarbons into the atmosphere, mainly originated from the production processes, the storage tanks and the waste areas (Kalabokas et al., 2001). Studies on long-term monitoring of toxic pollutants from industrial facilities confirm a significant exposure for inhabitants of these areas (Suleimanov, 1997). The present study is an attempt to envisage and investigate the impact of presence of petrochemical storage facilities on local air quality and associated health risk to the local population.

2. Materials and Methods

Sampling was carried out by active grab sampling method, using a hand operated pump. Air samples at each of the six sampling sites (Negishi, Honmoku, Shiohama – industrial; Minezawa, Tsurumi – residential; Sakuragicho - commercial) were collected in 10 L flek polyester bags and analyzed by GC (Hewlett-Packard 5890 series II) equipped with FID. The external calibration standard mixture of 38 VOCs was purchased from Spelco, Japan and was used for calibration. The calibration standards were prepared by diluting the stock standard mixtures of 38 VOCs, to 20 ppb level. And then the working standard in ppb level was prepared from the standard concentrations. The analytical column was a 30 m X 0.33 mm (HP-5) and total chromatopack-software. The temperature was programmed for 50^{o}C hold for 4 min and ramped to 250^{o}C at 10^{o}C min^{-1} rate with 10 min hold at 250^{o}C. Nitrogen was used as a carrier gas with flow rate of 1 mL min^{-1} and split ratio of 1:10. Quality assurance and quality control (QA/QC) measures include laboratory and field blanks during each sampling round. The concentrations were below detection limit in blanks. The coefficient of variation for aliphatic and aromatic hydrocarbons were observed to be well below five percent (<5%). Slightly higher percentage of coefficient of variation was observed (5.5 – 5.98%) for 1,2,4-trimethyl benzene and 1,3,5-trimethyl benzene.

3. Results

Among aliphatic hydrocarbons, propane, iso-butane, n-butane, n-pentane iso-pentane and ethylene were found to be abundant at industrial locations. The minimum levels of VOCs were detected at residential site (Minezawa). The mean concentration of benzene (considering all six locations) was 2.79 μg/m^3. Exposure to VOCs vary with location since, the distribution of population is not equal at industrial and residential areas. At Shiohama during night, the observed ambient concentrations increased at midnight (11:00 pm – 1:00 am). High concentrations of benzene (8 μg/m^3), and *m*- & *p*-xylenes (10.8 μg/m^3) were observed at this time. These high concentrations can be attributed to the calm atmospheric conditions and lack of photochemical activity.

4. Discussions

It was observed that our monitored concentrations were relatively high when compared to the results of the model (METI-LIS) concentrations which were attributed industrial operational pattern change, unknown and other sources, industries those may not be representing to the PRTR data listing. The major source of n-butane in the urban atmosphere is gasoline evaporative emission and is a tracer of gasoline use. At industrial sites, it was in the range of 3.5 – 6 ppb. Propane comes into the ambient air from LPG and natural gas usage besides oil and gas production. The observed high concentration of propane at the industrial location Shiohama was 24.7 ppb. The high concentration of Toluene at Shiohama can be justified by the petrochemical industrial activities at this site.

The non-carcinogenic hazard estimate results show that the hazard quotients (HQs) for chronic, intermediate and acute non-cancer hazard estimates of BTEX were less than one and well within the limits indicating no considerable non-carcinogenic risk due to the exposure. This provides a "snapshot" in time for characterizing health risks from exposure to selected VOCs and it does not take into account the potential increase in emissions over time, as a result of anticipated increase in industrial development activities. The ranking of BTEX with respect to the ozone formation potential using Carter's maximum incremental reactivity (MIR) show that, *m*- & *p*-xylenes were the most dominant contributors to ozone formation among BTEX toluene was the second largest contributor followed by ethyl benzene. A good correlation between and among the species indicate that their primary source of origin is similar. Indeed, a good mutual correlation was observed between ethyl benzene and xylenes ($r > 0.81$) indicating that they might possibly originate from gasoline source (Baladsano et al., 1998).

5. Conclusion

A comparison of our monitored results with that of model results using METI-LIS model was done. Estimated results show low concentrations from a point source than the monitored concentrations. It indicates the existence of several other sources that contribute to the ambient air such as vehicles, non reported small industries. The predominant winds blow from SW in Yokohama city. The location of monitoring point with respect to the point source falls in the up wind direction of the point sources which is why our estimated ambient concentrations are low. To get a better understanding of VOC dispersion with respect to time and wind direction we propose multiple and continuous monitoring points must be selected around the point source.

Acknowledgments

This study was carried out under the funding support of Japanese Government Scholarship Program (Monbukagakusho). The author would like to thank Ministry of Education, Culture, Sports, Science and Technology (MEXT), Government of Japan.

References

[1] Atkinson R (1997) Gas-phase tropospheric chemistry of volatile organic compounds 1. Alkanes and alkenes. J Phy and Chem reference Data 26:215-90.

[2] Kalabokas PD, Hatzianestis J, Bartzis JG, Papagianna kopoulos P (2001) Atmospheric concentrations of saturated and aromatic hydrocarbons around a Greek oil refinery. Atmospheric Environment 35:2545-2555.

[3] Khillare PS, Hoque RR, Agarwal T, Shridhar V, Balachandran S (2008) Spatial and temporal variation of BTEX in the urban atmosphere of Delhi, India. Science of the Total Environment 392:30-40.