JRHS
Journal of Research in Health Sciences
journal homepage: www.umsha.ac.ir/jrhs

Original Article

Investigation of Qualitative and Quantitative of Volatile Organic Compounds of Ambient Air in the Mahshahr Petrochemical Complex In 2009

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ARTICLE INFORMATION

Article history:
***Received**: 02 February 2013*
***Revised**: 27 February 2013*
***Accepted:** 04 March 2013*
***Available online:** 10 March 2013*

Keywords:
Volatile organic compounds
Air sampling
Petrochemical
Iran

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ABSTRACT

Background: Volatile organic compounds (VOCs) are human-made chemicals widely spread in the environment and produced by petrochemical industries and petroleum refineries. The aim of this research was to evaluate the distribution of VOCs in the ambient air of Mahshahr Petrochemical Complex, Iran.

Methods: This study was a cross-sectional research performed in 2009. We used the method numbered 1501, 1500, 2000, 1003, 1005, 1010, 2555, 1300 and 1400 of the National Institute of Occupational Safety and Health (NIOSH) for the sampling and analysis of compounds in the air. A total of 204 samples were analyzed using Gas Chromatography-Mass Spectrometry (GC-MS) and a Gas Chromatography-Flame Ionization Detector (GC-FID).

Results: The mean of concentrations of the pollutants in the winter is less than in summer and a strong variation occurred among the sampling site, attributed to the change in meteorology. The results indicated high concentrations of benzene in most factories. In addition, a significant difference occurred between the concentrations of the compounds in the ambient air inside and outside the factories in both seasons ($P<0.050$).

Conclusion: It seems that the atmospheric conditions of the workplace affect the spreading of the pollutants, causing the concentration of the pollutants in the summer to be higher than in the winter. In addition, the frequent prevailing wind speed in the region plays a major role in the distribution of the pollutants from Mahshahr Petrochemical factories.

Citation: Maghsoodi Moghadam R, Bahrami A, Ghorbani F, Mahjub H, Malaki D. Investigation of Qualitative and Quantitative of Volatile Organic Compounds of Ambient Air in the Mahshahr Petrochemical Complex In 2009. J Res Health Sci. 2013; 13(1): 69-74.

Introduction

The Petrochemical Economic Zone of Mahshahr is located in southwestern Iran, along the Persian Gulf, and is a center for producing chemical compounds. The petrochemical operation, which is in general big industrial installations, is associated with the emission of various substances into the atmosphere, originating primarily from the production processes, storage tanks, transport pipelines, and waste areas[1-3]. Volatile Organic compounds which are emitted and diffused in vast quantities in ozone and other photochemical compounds, play a principle role in physicochemical processes of the atmosphere[2,3,5-7].Several effects of volatile organic compounds (VOCs) are recognized such as their contribution to stratospheric ozone depletion, toxic and carcinogenic human health effects, and enhancement of the global greenhouse effect among these VOCs. Benzene has been shown to cause cancer in both animals and humans, and therefore is currently classified by the Environmental Protection Agency (EPA), ACGIH, and the International Agency for Research on Cancer (IARC) as a human carcinogen[3,4,5,7,8]. Once VOCs are emitted into the atmosphere, they cause not only pollution problem on local scale but also play an important role on regional scale like acid rain, photochemical ozone formation initiated by the reaction with OH radicals in the troposphere in the presence of nitrogen oxides and sunlight[2,8-11].

There are few studies reported VOC levels in petrochemical of Iran cities so far. In this study, field measurements of selected atmospheric VOCs were performed at selected eleven locations. The aim of the study was to determine the atmospheric pollution levels of aliphatic and aromatic VOCs. The present study is an attempt to envisage and investigate the impact of the presence of petrochemical storage facilities on local air quality and associated health risk to the local population. Characterization of the VOCs in terms of their concentration in ambient air at different locations was carried out. The seasonal and spatial variations of ambient volatile organic compounds were analyzed.

Methods

Ambient air quality samples were collected during the period of January to June 2009. Sampling was carried out by active pump sampling using the method numbers 1501, 1500, 2000, 1003, 1005, 1010, 2555, 1300, 1400 (NIOSH) for sampling and analysis of compounds in air and method number 2123 OSHA was used to determine morpholine. A total of 204 samples were collected during the campaign. Air samples at each of the 13 sampling sites which were Amir-e Kabir, Fanavaran, Tondgooyan, Razi, Terminals reservoirs, Bu-Ali Sina, Marun, export jetty, Karun, Khuzestan, Imam Khomeini, Fajr, and Shimi-baft were collected.

The charcoal desorbtion tube (from SKC, USA) connected to a small pump were used to obtain samples from volatile organic compounds, chlorobenzene, halogenated compounds, epichlorohydrin and iso-propanol. The silicagel was used to obtain samples from methanol, methyl ethyl ketone and morpholine. The pumps were operated at 100-200 ml/min flow rate with duration of sampling 1-6 hours. The compounds were extracted from charcoal with carbon disulfide and different solution from silicagel based on method. After samples were taken, transferred by ice-bag and analyzed immediately, some of samples were stored in refrigerator for few days in 4-10ºC. Samples were transported to the laboratory and the external calibration standard mixture of 20 VOCs was obtained in laboratory.

The calibration standards were prepared by diluting the stock standard mixtures of 20 VOCs. Then, the working standard in parts per billion levels from 5 to 800µg/ml was prepared from the standard concentrations. Samples were analyzed with a Varian 3800 GC equipped with a Saturn 2200 ion trap MS. The mean of temperature and relative humidity were 16ºC and 46% at winter and were 41ºC and 16% at summer. The solutions (99%) were used from Merck (Darmstadt, Germany).

The quantitative of samples were determined by GC (Unicam , Model 4600) equipped with FID The column was packed (1.5m×4mm i.d. Glass Column packed with 10% peg 20M on chromosorb W). The temperature was programmed for 50 °C hold for 2 min and ramped to 90 °C at 6 °C min^{-1} rate and increase to 180 at 4 °C min^{-1} rate with 2 min hold at 160 °C and the qualitative the samples was done by Gas Chromatography-Mass Spectrometry (Varian, Model CP-3800). Separation of hydrocarbons was achieved by a capillary column (25m×0.22mm ID BP10) The temperature was programmed for 30 °C hold for 4 min and ramped to 180 °C at 4 °C min^{-1} rate with 4 min hold at 180 °C. Helium was used as a carrier gas with flow rate of 1 mL min^{-1} and split ratio of 1:10. Figure 1 shows chromatogram of compounds analysis with GC/MS.

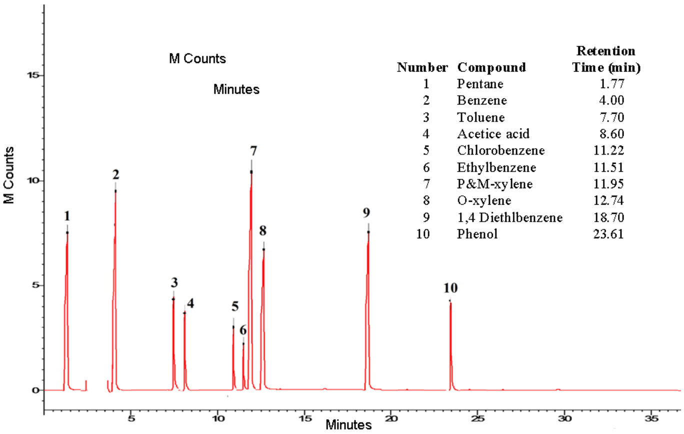

Figure 1: Chromatogram of compounds analysis with GC/MS

The data were analyzed by using the statistical package for social science (SPSS). Comparison between the mean of pollutants concentration in personal samples and different site was performed by one way ANOVA test.

Results

The results include quantitative and qualitative assessments of the samples collected from the petrochemical units in both summer and winter. Accordingly most of the samples had benzene, toluene, ethyl benzene and xylene (BTEX) compounds. The results of the qualitative investigation showed that 80% of the samples contained p/m-xylene, 75% toluene, 71% o-xylen, 69% benzene, 55% ethylbenzene, and 18% p-diethylbenzene. Table 1 summarizes the qualitative analyses of compounds in each of the factories at Bandar-e Mahshahr Petrochemical in both winter and summer. Benzene was a major pollutant in all of the samples, and xylene (Para, Ortho, and Meta) was identified within all of the petrochemical units, whereas carbon tetrachloride and epichlorohydrin pollutants were not indicated within any of the petrochemical units in the winter. Bandar-e Imam Khomeini and Shimi-baft contained the highest (19) and lowest (5) number of samples, respectively.

According to the data, 10 compounds from among those assessed namely, benzene, ethylbenzene, *p*-Diethylbenzene, toluene, *p, m* & *o*-Xylene, Pentane, Phenol, and chlorobenzene were identified together within three sampling locations (Table 2).

Significant differences in data occurred in terms of winter and summer; in most locations, the concentration of the pollutants was greater in summer than in winter

(Figure 2). Comparing the concentrations of each pollutant with the recommended standard level shows that the concentrations of benzene in the ambient air of factories and most of personal samples were higher than the standard level recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) (TWA=0.5ppm). The mean concentrations of personal samples of benzene at the loading site of bu-Ali Sina in the winter and summer were 37.03ppm and 43ppm respectively, which was more than other factories; the concentration of other pollutants was below the standard level recommended by ACGIH and ITCOH. No significant differences occurred between the mean concentrations of benzene inside and outside the factories; the differences were also non-significant for other pollutants between personal samples in summer and winter seasons (P>0.05).

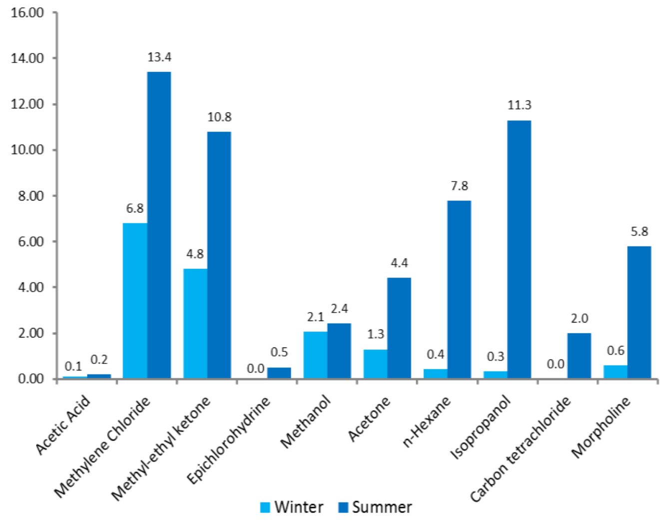

Figure 2: The mean concentrations of the compounds from the respiratory air of the staff of all the production factories, 2009

Table 1: Identified compounds in each petrochemical factories at Mahshar Area

Petrochemical factories	Identified compounds
Amir-e Kabir	BTEX compounds, Epicholorehydrin, N-hexane
Terminal reservoirs	Phenol, Acetic acid, Methyl ethyl kethone, Acetone, BTEX compounds, Epicholorehydrin, Methylenel
Export jetty	Pentane, BTEX compounds, Diethyl benzene
Fanavaran	Morpholine, Methanol, BTEX compounds
Tondgooyan	Phenol, Acetic acid, BTEX compounds, Pentane diethyl benzene
Razi	BTEX compounds, Pentane
Bu-Ali Sina	BTEX compounds, Ddiethyl benzene
Marun	Phenol, Acetic acid, BTEX compounds, Pentane diethyl benzene
Karun	Carbon tetrachloride, Pentane, BTEX compounds, Methylenel
Khuzestan	Isopropanol, BTEX compounds, Methylenel
Imam Khomeini	Isopropanol, Morpholine, BTEX compounds, Methyl ethyl kethone, Acetone, Methylenel, Pentane, N-hexane, Diethyl benzene
Fajr	BTEX compounds, Diethyl benzene
Shimi-baft	BX compounds, Methanol

Table 2: The mean concentration (ppm) of pollutants in ambient air of different factories Bandar-e Mahshahr Petrochemical during winter, and summer 2009

	Winter			Summer			
Pollutants	**Number**	**Mean**	**SD**	**Number**	**Mean**	**SD**	***P* value**
Benzene							
Inside unit	18	0.15	0.14	18	0.48	1.10	0.163
Outside unit	17	0.06	0.16	17	0.17	0.23	0.244
Personal	27	1.63	7.15	27	2.00	8.30	0.867
Ethylbenzene							
Inside unit	13	0.02	0.03	13	0.13	0.30	0.010
Outside unit	10	0.01	0.00	10	0.03	0.03	0.004
Personal	26	0.13	0.41	26	0.16	0.59	0.743
Toluene							
Inside unit	21	0.11	0.28	21	0.27	0.50	0.103
Outside unit	17	0.02	0.01	17	0.22	0.12	0.001
Personal	29	0.13	0.34	29	0.19	0.35	0.798
m/p-Xylene							
Inside unit	21	0.041	0.08	21	0.27	0.65	0.004
Outside unit	21	0.01	0.02	21	0.07	0.12	0.004
Personal	30	0.63	2.72	30	0.54	2.38	0.317
o-Xylene							
Inside unit	18	0.02	0.03	18	0.11	0.25	0.013
Outside unit	17	0.01	0.01	17	0.01	0.02	0.001
Personal	29	0.20	0.81	29	0.19	0.72	0.800

As shown in Table 3, a significance difference occurred between the mean concentration of ambient air inside and outside of factories in each season ($P<0.050$). More pollutants existed in the ambient air inside the factories than outside the factories. The concentration of personnel exposure was also more than ambient air. The greatest concentration of pollutants in petrochemical factories occurred in those located in the east and southeast while the least concentration occurred in those located in the northwestern and western parts of the region.

Table 3: The mean concentrations of the pollutants in ambient air inside and outside the production factories in Bandar-e Mahshahr Petrochemical Complex

	Outside		Inside		
Analyte	**Mean**	**SD**	**Mean**	**SD**	***P* value**
Benzene	0.0012	0.0020	0.0032	0.0083	0.046
Ethylbenzene	0.0015	0.0020	0.0075	0.0022	0.032
Toluene	0.0020	0.0040	0.0070	0.0010	0.003
m/p-Xylene	0.0016	0.0047	0.0037	0.0088	0.005
o-Xylene	0.0010	0.0016	0.0062	0.0018	0.009
P-Diethylbenzene	0.0011	0.0097	0.0097	0.0080	0.149
Pentane	0.0015	0.0028	0.0080	0.0018	0.240
Phenol	0.0018	0.0017	0.0014	0.0027	0.022
Chlorobenzene	0.0040	0.0030	0.0016	0.0014	0.000

Discussion

The main reason for the distribution of pollutants from petrochemical factories to the ambient air depends on the process activities. The petrochemical industries in the studies location include industries such as petrochemical refining and storage, polypropylene, paints, and solvent. In some factories, leakage takes place from the reservoirs, transferring pipes, and installations. The concentration of pollutants ultimately goes beyond the recommended standard level.

Benzene is the primary compound of the aromatic compounds, along with its derivations, and is widely consumed either as the primary or produced material in petrochemical units. Thus, not surprisingly, it was recognized in most of the samples. P&m-xylene and O-xylene are the most frequently observed compounds in the majority of the samples collected and the common pollutant compounds in the entire complex.

In order to diagnose the status of VOC pollution in the study area, ambient VOC data measured in this study were compared with those taken from various locations around the world. As most of the previous studies focused on the distribution of aromatic VOCs, the data for non-aromatic VOCs were in general scarcely available, e.g., only in few studies. If the magnitude of VOC data is compared by their mean concentration values, the results obtained at roadside area or under the industrial influence exhibit the highest levels (e.g., 0.04-9.53 (styrene), 1.06-37.0 (toluene), and 0.07-6.43 (xylene)). These VOC concentration data are easily differentiated from those of urban and rural land areas (e.g. 0.01-0.11 (styrene), 0.15-0.74 (toluene), and 0.11-0.42 (xylene)) [12, 13]. The combined effects between different levels of source activities and the surrounding environmental conditions should be considered simultaneously to explain differences in the VOC distribution in each study site.

If the compiled VOC data are compared between regions, the concentrations of most VOCs in industrial areas are generally higher in Asia including Australia than in America and European countries. In fact, air quality in most western countries have improved dramatically over the past decades as a consequence of more rigorous legal regulations and the adoption of less-polluting and environment friendly technologies. Comparison of toluene (and xylene) values shows that the results of Mahshar Petrochemical area are quite similar to those of several cities in Asia, particularly with the Ren-Wu industrial area at Taiwan[14]. However, the results of Mahshar Petrochemical are noticeably large compared to other Asian industrial areas like Japan, India, and Thailand as well as other cities in Korea such as Ulsan. It is thus speculated that the effect of fugitive emissions should be prominent in the study area, as its VOC pollution should be governed by a number of complicated factors and processes.

In terms of the magnitude of concentration data, benzene was observed as the most dominant among all target species in this study. For example, the average concentration of toluene (16.1 ppb) was higher by approximately 5 times than the next highest mean of xylene (3.32 ppb), although the release of toluene generally occurs via its common use as solvents, is another reason [15].

The results indicated that the concentration of VOC pollutants were greater during summer than in winter. It was reported in a similar study that the concentration of VOCs, especially those studied herein, was lower in cold seasons in petrochemical complexes [11, 18]. Increased temperatures (to 16-41ºC) cause evaporation and emit pollutants from the surface of reservoirs, transfer pipes, and the installations to the atmosphere. As a result, the concentration of pollutants is higher in summer than in winter. According to a study made at a roadside area in Korea, aromatic VOCs (i.e., toluene, xylene, etc.) showed their peak occurrences during the summer, while reaching the minimum during fall or winter[16] .Similar to such finding, the concentrations of most VOCs (i.e., benzene, toluene, ethyl benzene, xylene, etc.) measured near a main roadside in Hong Kong were higher in summer than in winter [17]. A line of evidence thus suggests that many aromatic VOCs can exhibit enhanced concentrations during warmer seasons probably due to their elevated evaporation capacities in the summer.

The lower humidity in summer than in winter when collecting samples resulted in better absorption of the pollutants by the sorbent tubes. Note that the total VOC concentrations in a petrochemical complex and an oil refinery generally increased with temperature, as the temperature can exert direct influences on their evaporative emissions[18]. Likewise, in another study conducted inside public buses in Pamplona, Northern Spain, VOCs exhibited strong correlations with temperature (P<0.050) [19,13]. The majority of VOCs were significantly correlated with temperature (positive) in Belgrade, the capital and largest city of Serbia

The results indicated that concentrations of compounds in samples obtained from the Bandar-e Imam Khomeini Petrochemical Factory were more than from other factories. This factory is spread over a vast area and has a higher production level than other factories. The Imam Khomeini Petrochemical Factory in the southeast Mahshaher Petrochemical region registered higher levels of pollutants as well. This is likely due to the prevailing winds from the northwest and west to the south and southeast. Meanwhile, the Shimi-baft factory registered fewer pollutants than other factories. This factory is in the northern Mahshaher Petrochemical region and is smaller than other factories. Other companies in the west and northwest have lower concentrations of pollutants. The lowest concentration of pollutants occurred in Amir-e Kabir, Karun, Marun, and Fanavaran units in the west and northwest.

Indoor concentrations typically exceeded outdoor levels by 2 to 5 times; indoor levels can be increased by low ventilation, high temperatures, and high humidity. Personal exposures can also increase sharply due to low distance from sources of pollutants.

Conclusion

Benzene the primary compound of the aromatic compounds, along with its derivations is widely used in petrochemical units and showed much higher concentrations than other compounds. Comparing the concentrations of the pollutants and the recommended standard levels indicated that benzene and epichlorohydrin were higher than the standard levels within the ambient air both inside and outside the units and within the respiratory air of the staff. The workplace's atmospheric conditions are effective in spreading pollutants, causing the concentration of pollutants to be higher in the summer than in the winter. As the direction of the frequent and prevailing winds is mainly from the west or southwest to the east and southeast of the region, the highest concentration of pollutants occurred in factories located in either the eastern or southeastern parts of the petrochemical complex.

Acknowledgments

The authors would like to acknowledge Vice-Chancellor of Research and Technology, Hamadan University of Medical Sciences for approval of this study.

Conflict of interest statement

The authors have no conflict of interest to declare.

Funding

This study was funded by Mahshahr Special Economic Zone, at state of Khozestan, Islamic Republic of Iran.

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