

Ambient Air Quality Monitoring in Terms of Volatile Organic Compounds (VOCs) Occupational Health Exposure at Petroleum Refinery

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Abstract- Study of ambient air quality data of volatile organic compounds (VOCs) in the atmosphere is of growing importance due to the inclusion of these parameters in the new notification November 2009 by MoEF, India and in view of health impacts of VOCs, their occupational exposures at workplace. Measurements were carried out for 8 hours to generate the database regarding exposures of the workers and the village inhabitants. The samples were adsorbed on activated charcoal tubes and subsequently desorbed using thermal desorption unit and analyzed by GC/FID system. The 8-hour Time Weighted Average (TWA) of Total BTEX inside refinery, at boundary walls and in nearby villages around the refinery varies in the range of 21.61–56.67 $\mu\text{g}/\text{m}^3$, 5.03–16.88 $\mu\text{g}/\text{m}^3$ and 3.69–7.91 $\mu\text{g}/\text{m}^3$ respectively. The decrease in 8-hour TWA and concentration ratios of BTEX at boundary walls and nearby villages indicate that the exposure of these aromatic compounds on the nearby village inhabitants is negligible. The study also reports fugitive emissions data of VOCs near major activities in the refinery. Specific guidelines were needed to combat these uncontrolled fugitive emissions of Total VOCs at petroleum refineries.

Keywords- BTEX; 8-hour TWA; Occupational Exposure; Boundary Walls; Villages Inhabitants

I. INTRODUCTION

The content of volatile organic compounds (VOCs) in air is considered as a fundamental parameter for assessing the quality of the atmosphere because some compounds are acting as precursors of photochemical smog formation whereas others represent potential threats to human health [1]. In addition to this, some specific components can contribute to global change, by depleting the stratospheric ozone (such as chlorofluorocarbons) and/or to the radiative forcing of the earth (such as methane, chlorofluorocarbons and dimethylsulphide) [2]. Several VOCs are involved in stratospheric ozone depletion, toxic and carcinogenic effects on human health and acceleration of the global greenhouse effect [3-4].

Oil refineries are complex process plants, which convert crude oil into variety of products. Refining operation is associated with the emission of various volatile organic compounds (VOCs) into the atmosphere, mainly originating from production processes, storage tanks, distribution terminals and wastewater treatment areas [5]. The transportation, distribution and marketing of refined products involve many distinct operations, each of which represents a potential source of evaporation, loss and occupational exposure problem for the workers.

The fugitive emissions from oil refineries add millions of pounds of harmful pollutants to the atmosphere each year, including over 80 million pounds of volatile organic compounds (VOCs) and over 15 million pounds of toxic pollutants [6]. But there is a lack of data on exposure to these fugitive emissions. The atmospheric behavior of VOCs is governed to a large extent by their life time. In the process of long-range transport, BTEX are among other VOCs that react with other pollutants such as NO_x and produce secondary pollutants with different reaction rates [7-8]. The wide range of VOCs released at petroleum refineries may have significant impacts on health of the workers depending on the levels of exposure. Assessment of human exposure to a complex array of such volatile compounds is a key factor in quantifying the relationship between environmental factors and human diseases.

At present, the database for Ambient Air Quality in and around an oil refinery regarding exposures of the workers and the village inhabitants is rather sparse in the international literature. In general, a main problem in linking the environmental pollution to health effects is the current lack of data about the actual exposure to hazardous pollutants [9]. This study compiles estimates of population exposures and risk associated with current ambient levels of VOCs inside the factory (process units, distribution terminals and wastewater treatment plant), near boundary walls and at some nearby villages outside the factory. The fugitive emissions of Total VOCs were also monitored near major activities inside oil refinery to have first-hand information on status of these uncontrolled emissions.

II. MATERIALS AND METHODS

A. Study Area

The oil refinery site is located in the coastal belt and bounded by 12°58'–13°01'N latitude and 74°50'–74°52'E longitude. The refinery site is situated in a complex terrain with ground elevations varying from about 10 m to 75 m from mean sea level.

All process units are located in upper plateau, while the storage facilities, township etc. are located in lower plateau.

The study area falls in coastal midland having dry sub-humid & per-humid agro-climatic conditions. This area is expected to be under the influence of coastal weather having moderate winds with diurnal variations as well as seasonal variations. As per the climatological tables, the mean ambient temperature in project area varies from 21.1°C (December) to 36.1°C (March) with the extremities of 15.9°C (November 1974) and 39.0°C (March 1980). The relative humidity has been recorded in the range 56%–93%. The average annual rainfall in this region recorded is 3965 mm with the variation from 2952 mm to 5879 mm per year; out of which major component occurs during May–November months. The monthly mean wind speed in this region has been recorded in the range 5.3–8.0 km/h. The predominant wind directions are East in morning hours and W, NW directions in the evening hours in most of the year. The ambient air quality status in nearby area of refinery site is expected to vary due to typical local topographical features, industrial and automobile emissions at varied elevations apart from domestic emissions.

B. Experiment

Battery operated, portable, fire proof, Organic Vapor samplers were installed in the refinery for the purpose of continuous 8-hour VOCs monitoring. The sampling locations inside the refinery and boundary walls are shown in Fig. 1 while sampling locations in nearby villages are shown in Fig. 2. Monitoring was carried out during 8 hours working period (08.00–16.00 hrs) in the day time so as to obtain OSHA exposure limit of 8-hour Time Weighted Average (TWA) at each location.

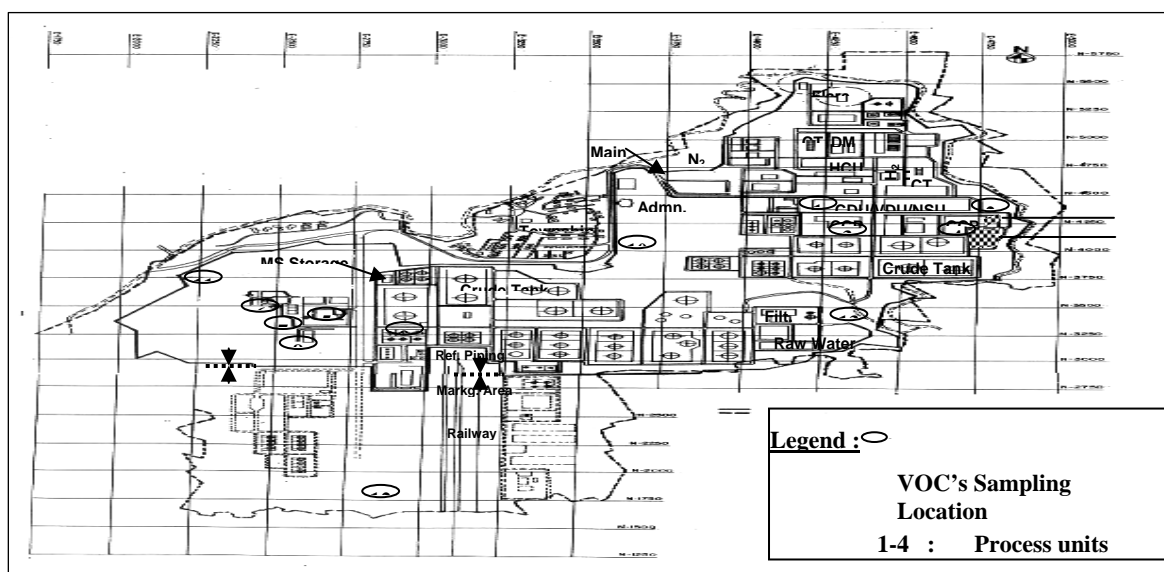


Fig. 1 Monitoring locations inside refinery and at boundary walls

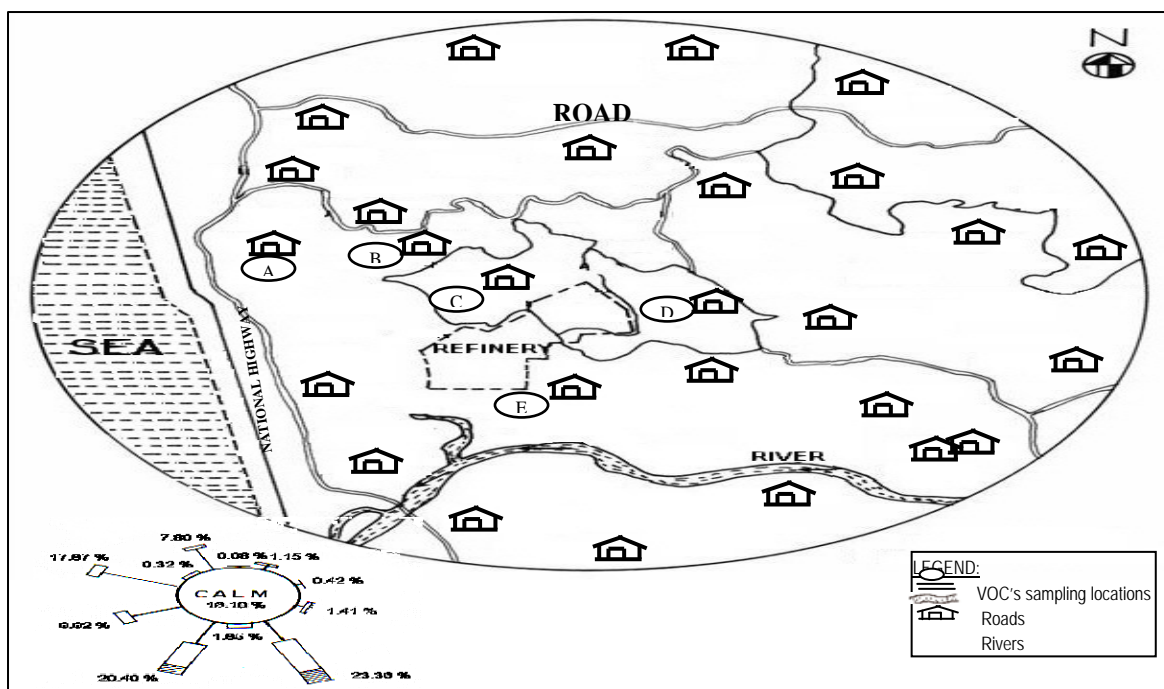


Figure 2 Monitoring locations in nearby villages along with wind rose diagram

The sampling system consisted of pump, flow regulator, tubing and charcoal tube prepared as per the ASTM: D 3686–95 Method [14]. Analytical grade activated carbon was heated at 200°C for 12 hrs and cooled in vacuum desiccator. About 400 mg of preheated activated carbon was filled in the adsorption tube with glass wool plugs on either side of the sorption tubes. The sampling system was assembled at the location where sampling was to be carried out. The charcoal tube was inserted into the sampling line, placing the backup section nearest to the pump. The pump was turned on and a known volume of the air was passed through a specially designed activated charcoal tube for large loading of volatile organic compounds, at a flow rate of 50 ml/min. Uniform flow rate was maintained using a Rota meter. The sampling was repeated at all stations to collect sufficient data from each station, so that a representative result of that location was obtained. The samples were collected at an approximate distance of 1 m away from the probable sources and in downwind direction. At the end of the sampling period the flow rate was rechecked, the pump was turned off, and all the pertinent information was recorded on the field data sheet. The sample tubes were sealed with the caps and the tubes were labeled with the appropriate identification information [8]. The sampling tubes were stored in refrigeration before thermal desorption and subsequent analysis using gas chromatography with Flame Ionization Detector.

C. Instrumentation

The flow rate of the battery operated low volume sampler was adjusted to 50 ml/min. The flow meter was calibrated using soap bubble meter [15]. The sampling VOC tubes were assembled in a thermal desorption unit developed in the institute. Desorption from sorbent tubes was carried out by heating at 180°C for 20 minutes. Two tubes were connected in series to check the occurrence of the breakthrough. At none of the locations breakthrough was observed.

A Perkin Elmer Clarus 500 Gas-Chromatograph system was employed for the determination of analytes present in unknown sample using Flame Ionization Detector. The GC oven was programmed with a hold of 1 minute at 50°C and subsequently 50°C to 170°C @ 8°C/min. The injector temperature was kept at 200°C. The detector was maintained at 300°C. The flow was adjusted to 0.5 mL/min. The sample was allowed to run for the above set condition of GC. 100 µl of the vapors were taken out in a syringe and injected in the GC. One by one each unknown sample tube was thermally desorbed and allowed to run in GC. The corresponding plots were recorded and stored by giving a specific file name in attached computer. These plots were overlaid and compared with standard VOCs 13 mix plot to determine the concentration of unknown samples.

Separation was performed on Varian Chrompack Capillary column WCOT Fused Silica (30 m long, 0.25 mm ID) CP–624 [6]. Hydrogen (Ultra pure 99.99% with less than one ppm each of water, oxygen, and total hydrocarbons) was employed as a carrier gas. The detector was programmed to scan over a wide range of VOCs [8].

A portable online digital VOC monitor (Photovac 2020 PRO) with Photo Ionization Detector (PID) Sensor was used for conducting fugitive air quality survey within refinery premises. The Operating Temperature Range was 0°C to 40°C while Operating Concentration Range was 0.1–2,000 ppm (Isobutylene equivalent). The instrument was calibrated with isobutylene standard prior to the start of survey at refinery.

D. Reagents and Standards

A Reference Standard Mix 2 of Volatile Organic Compounds was obtained from Supelco, USA. The Mix contains 13 volatile compounds. These were impregnated into the charcoal tubes and thermally desorbed. 100 µl of the sample was injected into the GC and multipoint calibration curves for 13 compounds were prepared. A chromatogram of the separated compounds is illustrated in Fig. 3. Using the calibration curve, the value of unknown analyte was determined.

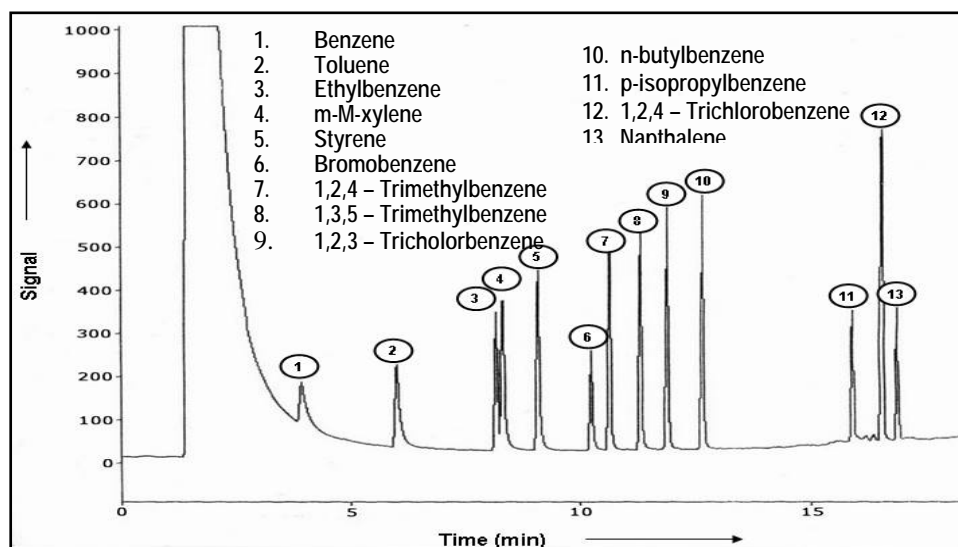


Fig. 3 Separation and identification of VOC's by gas-chromatography

E. QA/QC

QA/QC in the analysis of target VOCs compounds involved the assessment of the reproducibility, recovery results and established detection limits of the analysis method. Table I summarizes VOCs compounds with their RT, Recovery yield, Method Detection Limits and Relative Standard Deviation. The MDL ranged from 0.2–0.5 mg/m³ for the target VOCs. Duplicate samples were used at each location in order to test the precision of the sampling and analysis techniques. The concentrations of VOCs measured at each duplicate sample set were in excellent agreement with a relative standard deviation of less than 20 % (Table I).

TABLE I LIST OF VOCs COMPOUNDS WITH THEIR RT, RECOVERY YIELD, METHOD DETECTION LIMITS AND RELATIVE STANDARD DEVIATION

VOCs	RT	Recovery (%)	MDL (mg/m ³)	Precision (RSD) (%)
Benzene	3.92	96.3	0.3	12
Toluene	5.99	96.8	0.4	15
Ethylbenzene	8.16	97.4	0.3	13
m-xylene	8.33	97.8	0.3	14
Styrene	9.10	96.9	0.4	12
Bromobenzene	10.25	98.2	0.2	10
1,2,4-Trimethylbenzene	10.64	97.5	0.5	14
1,3,5-Trimethylbenzene	11.32	96.4	0.3	13
1,2,3-Trichlorobenzene	11.90	97.7	0.2	13
n-Butylbenzene	12.66	97.2	0.3	12
p-Isopropylbenzene	15.91	96.6	0.3	15
1,2,4-Trichlorobenzene	16.54	96.5	0.4	11
Napthalaene	16.87	97.8	0.2	10

III. RESULTS AND DISCUSSION

The ambient BTEX concentrations were determined inside the refinery, near boundary walls and in nearby villages. The distance and direction of the measurement points (within the villages) from the refinery and the national road are depicted in Table II. Total 13 VOCs viz, Benzene, Toluene, Ethyl benzene, m-xylene, Styrene, Bromobenzene, 1,2,4-Trimethylbenzene, 1,3,5-Trimethyl benzene, 1,2,3-Trichlorobenzene, n-butyl benzene, p-Isopropylbenzene, 1,2,4-Trichlorobenzene, Napthalaene etc. are identified in the sampled air for this study. Half of the VOCs are classified as Hazardous Air Pollutants in USEPA Air Toxic Programme (Table III). It is observed that benzene, toluene, ethyl benzene and m-xylenes have been identified and quantified in all the samples at all the locations. While the other VOCs are identified at some of the locations, but their concentrations are negligible. Thus, concentrations of VOCs were reported in terms of Total BTEX (Total Benzene, Toluene, Ethylbenzene and m-xylene).

TABLE II DETAILS OF MONITORING LOCATIONS IN THE NEARBY VILLAGES

Sr. No.	Monitoring Location	Direction	Distance (Km)	
			From the Refinery	From National Highway
1.	A	NNW	2.9	1.2
2.	B	NNW	2.5	1.8
3.	C	NNW	1.5	2.1
4.	D	ESE	1.8	3.5
5.	E	SSE	2.1	2.8

TABLE III LIST OF IDENTIFIED VOCs AT MONITOR SITES

Sampling Locations	Volatile organic Compounds												
	Benzene (Cas No. 71432)	Toluene (Cas No. 108883)	Ethyl Benzene (Cas No. 100414)	m-Xylene (Cas No. 108383)	Styrene (Cas No. 100425)	Bromo benzene (Cas No. 108861)	1,2,4-TMB (Cas No. 95636)	1,3,5- TMB (Cas No. 108678)	1,2,3-TCB (Cas No. 87616)	n-BB (Cas No. 104518)	P-IPB (Cas No. 100185)	1,2,4-TCB (Cas No. 120821)	Naphthalene (Cas No. 91203)
INSIDE REFINERY													
Process Units													
CDU-VDU-I	√#*	√#*	√#*	√#*						√	√		
CDU-VDU-II	√#*	√#*	√#*	√#*						√	√		
CCR-I	√#*	√#*	√#*	√#*	√				√	√	√	√*	√*
CCR-II	√#*	√#*	√#*	√#*	√				√	√	√	√*	√*
Wastewater Treatment Plant													
IRS-I (ETP-I)	√#*	√#*	√#*	√#*	√				√	√		√*	
IRS-II (ETP-II)	√#*	√#*	√#*	√#*	√				√	√		√*	
Sludge PIT	√#*	√#*	√#*	√#*						√			
Distribution Terminal													
High speed diesel loading area	√#*	√#*	√#*	√#*						√		√*	√*
Motor spirit loading area	√#*	√#*	√#*	√#*					√	√		√*	√*
Naphtha loading area	√#*	√#*	√#*	√#*	√								
BOUNDARY WALLS													
Near colony gate	√#*	√#*	√#*	√#*		√	√	√		√	√		√*
Near cargo gate	√#*	√#*	√#*	√#*	√	√	√	√	√	√	√	√*	√*
Near south boundary wall	√#*	√#*	√#*	√#*							√		
Near D-gate	√#*	√#*	√#*	√#*				√	√		√	√*	
NEARBY VILLAGES													
Location-A	√#*	√#*	√#*	√#*							√		
Location-B	√#*	√#*	√#*	√#*	√			√	√		√	√	
Location-C	√#*	√#*	√#*	√#*	√	√	√	√			√		
Location-D	√#*	√#*	√#*	√#*					√		√	√	
Location-E	√#*	√#*	√#*	√#*	√								

(TMB-Trimethylbenzene, TCB, 1,2,3-Trichlorobenzene, n-BB- n-butyl benzene, P-IPB-Para-isopropylbenzene, √ = VOC identified, # = VOC quantified, * = VOC enlisted in

A. Meteorological Conditions

Climatological Tables of Observatories in India, published by India Meteorological Department (IMD), were used to obtain climatological normals corresponding to study area for post monsoon season, 2009. The 24 hourly wind rising at refinery site shows predominant winds primarily from SSE, SSW directions as well as from WNW, WSW & NNW directions with significant occurrence of wind speed in the range 1–10 kmph (Fig. 2). The wind speed and direction had an influence on the distribution of concentrations of BTEX. The average calm condition was 18.10 % of time during study period.

B. Concentrations of BTEX Inside Refinery

The minimum, maximum and average concentration of benzene, toluene, ethyl benzene m-xylene and Total BTEX along with their standard deviation were given in Table IV. The location chosen included the crude distillation and vacuum distillation unit, catalytic converter and reformat unit, inlet recovery sumps (IRS–I, IRS–II), sludge pit, naphtha loading area, motor spirit and high speed diesel filling area. The VOCs monitored at this location indicated the presence of vapors of VOCs like BTEX, Styrene, bromobenzene, substituted benzene, n-butyl benzene, p-isopropyl benzene and naphthalene (Table III). The occupational exposure varies and depends on the volatility of the compounds. However, such data are required for workers' safety and health protection.

TABLE IV CONCENTRATION OF BTEX INSIDE THE REFINERY

Units: $\mu\text{g}/\text{m}^3$		Average. : 8 hrs.				
Sr. No.	Monitoring Location	Benzene	Toluene	Ethyl benzene	m-xylene	Total BTEX
		Average \pm Standard Deviation (Range)				
Process Units						
1.	CDU-VDU-I	17.21 \pm 10.76 (6.39-34.48)	13.87 \pm 8.46 (8.46-28.68)	6.67 \pm 5.10 (3.46-15.48)	5.08 \pm 4.19 (2.46-12.26)	42.83 \pm 7.81 (30.59-49.58)
2.	CDU-VDU-II	16.29 \pm 10.10 (5.02-32.42)	14.95 \pm 10.59 (5.46-32.56)	8.33 \pm 4.06 (4.23-14.48)	6.55 \pm 3.27 (3.20-11.20)	46.12 \pm 14.79 (23.17-59.62)
3.	CCR-I	12.20 \pm 5.83 (5.80-21.60)	9.94 \pm 4.46 (5.40-17.20)	8.92 \pm 4.20 (4.20-14.80)	6.05 \pm 2.73 (2.80-9.87)	37.11 \pm 13.37 (22.80-54.10)
4.	CCR-II	10.10 \pm 5.72 (4.40-18.40)	9.68 \pm 4.02 (4.10-14.20)	9.40 \pm 4.51 (3.80-15.10)	5.36 \pm 2.02 (2.40-7.82)	34.54 \pm 12.22 (23.40-48.70)
Mean		14.0	12.1	8.3	5.8	40.2
Wastewater Treatment Plant						
5.	IRS-I	20.82 \pm 12.81 (4.15-37.19)	13.09 \pm 6.19 (4.26-18.76)	8.77 \pm 3.26 (3.44-12.10)	4.43 \pm 1.29 (2.38-5.86)	47.12 \pm 13.76 (29.11-66.75)
6.	IRS-II	14.52 \pm 9.64 (3.85-29.42)	5.98 \pm 2.39 (3.28-9.42)	5.48 \pm 1.62 (3.22-7.48)	3.70 \pm 0.79 (2.40-4.45)	29.68 \pm 12.85 (17.09-50.77)
7.	Sludge PIT	9.96 \pm 4.66 (3.26-15.24)	5.36 \pm 1.77 (3.16-7.80)	3.53 \pm 1.20 (2.14-5.10)	2.77 \pm 0.84 (1.60-3.86)	21.61 \pm 2.33 (19.26-25.30)
Mean		15.1	8.1	5.9	3.6	32.8
Distribution Terminal						
8.	High Speed diesel loading area	20.86 \pm 14.35 (12.38-46.28)	15.46 \pm 6.73 (11.18-27.16)	11.77 \pm 2.91 (8.68-15.88)	6.17 \pm 3.54 (3.48-11.72)	54.26 \pm 11.34 (43.66-70.87)
9.	Motor Spirit loading area	15.51 \pm 8.91 (9.46-31.23)	10.60 \pm 2.34 (8.52-14.38)	9.78 \pm 2.57 (7.24-13.72)	6.31 \pm 1.61 (4.24-8.22)	42.20 \pm 11.10 (33.63-61.47)
10.	Naphtha loading area	24.58 \pm 16.81 (14.16-54.22)	14.64 \pm 6.51 (10.36-26.14)	11.36 \pm 3.72 (8.12-17.38)	8.10 \pm 3.97 (4.68-14.76)	56.67 \pm 15.34 (40.42-81.71)
Mean		20.3	13.6	11.0	6.9	51.0

C. Process Units

Oil refining involves physical separation, chemical conversion, treating processes apart from storage and handling of feed stock, intermediates as well as marketable products along with associated auxiliary activities. During process operations leaks result in releasing emissions of volatile organic compounds. It is essential to assess VOCs exposure of the workers at these locations. The sampling site–1 and 2 were located inside the CDU/VDU process plant and show relatively higher concentrations of Total BTEX (42.83 $\mu\text{g}/\text{m}^3$ and 46.13 $\mu\text{g}/\text{m}^3$ respectively). Several compressor pumps, reflux pumps and operators cabin were near to these sites.

Further, in the catalytic cracking and reformat unit (sampling site–3 and 4) the Total BTEX concentrations were observed as 37.11 $\mu\text{g}/\text{m}^3$ and 34.54 $\mu\text{g}/\text{m}^3$ respectively. The 8 hourly mean concentrations of benzene, toluene, ethyl benzene, m-xylene

and Total BTEX at all the process units together were observed as 14.0 $\mu\text{g}/\text{m}^3$; 12.1 $\mu\text{g}/\text{m}^3$; 8.3 $\mu\text{g}/\text{m}^3$; 5.8 $\mu\text{g}/\text{m}^3$ and 40.2 $\mu\text{g}/\text{m}^3$ respectively (Table IV).

D. Wastewater Treatment Plant

Petroleum refineries do not like salts in their feedstock since these corrode and foul process equipment. The first refining step is desalting where a hot water wash extracts the salts. If feedstock contains aromatics then some will be in the desalter effluent and this is a major source of refinery wastewater containing VOCs [16]. At several refineries the desalter effluent flow has been as high as 50% of the total wastewater flow and over 70% of total BTEX discharge. The environmental community is concerning about releases of VOCs and HAPs (Hazardous Air Pollutants) to rivers and streams, to groundwater sources, as well as to the atmosphere.

Among sampling site-5, 6 and 7 which are located near the IRS-I, IRS-II and near sludge pit area, a very high Total BTEX (47.12 $\mu\text{g}/\text{m}^3$) was observed near IRS-I. These may be due to a number of petroleum products storage tanks located nearby the IRS-I. The Total BTEX observed near IRS-II and sludge pit were 29.68 $\mu\text{g}/\text{m}^3$ and 21.61 $\mu\text{g}/\text{m}^3$ respectively (Table IV). Generation of vapors due to evaporation in the sludge pit contributes to the concentrations of BTEX and other compounds at this location.

The 8 hourly mean concentrations of benzene, toluene, ethyl benzene, m-xylene and Total BTEX at the water treatment plant were observed as 15.1 $\mu\text{g}/\text{m}^3$; 8.1 $\mu\text{g}/\text{m}^3$; 5.9 $\mu\text{g}/\text{m}^3$; 3.6 $\mu\text{g}/\text{m}^3$ and 32.8 $\mu\text{g}/\text{m}^3$ respectively (Table IV). The maximum Total BTEX concentration observed was comparatively higher than the other monitored sites. These were in conformity with those reported earlier [12].

E. Distribution Terminals

The products of the refinery fall into three major categories: fuels (liquefied petroleum gas [LPG], motor spirit [MS], high speed diesel [HSD], light diesel oil [LDO], superior kerosene [SK]), finished non-fuel products (naphtha, solvents, lubricating oils, greases, petroleum wax, petroleum coke) and chemical industry feedstock (naphtha, benzene, toluene and m-xylene). The different operation involved in the transportation of these products represents a potential source of evaporation loss. The range of adverse effects due to these compounds includes cancer and a number of other chronic disorders, e.g., aplastic anemia, pancytopenia, pulmonary (lung), structural changes, and a number of acute health disorders, like, dyspnea (difficulty in breathing), upper respiratory tract irritation with cough, conjunctivitis, neurotoxic effects (e.g., visual blurring, tremors, delirium, unconsciousness, coma, convulsions) [8].

The tank lorry is loaded with petroleum liquid at distribution terminals inside the refinery area. About 30 minutes are required for loading each of the tankers. A separate barrel filling facilities for petrol, diesel and kerosene along with naphtha loading is available. Battery operated samplers were installed at the top of the tanker loading platform. Daily 30-35 tankers were filled at each facility. Most of the VOCs are released into the atmosphere during filling of the tankers, barrels and wagons. Besides BTEX, the emission of substituted benzenes, such as 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene and n-butylbenzene has also been identified. Polyaromatic compounds like naphthalene were also observed during loading of HSD and MS. Naphthalene is a part of light oil fractions and gets released into the atmosphere during handling of petroleum liquids [8]. Styrene was also identified during the loading operations of naphtha. A higher Total BTEX concentration at distribution terminal was observed at naphtha loading area (56.67 $\mu\text{g}/\text{m}^3$) followed by HSD loading area (54.26 $\mu\text{g}/\text{m}^3$) and MS loading area (42.20 $\mu\text{g}/\text{m}^3$). The 8 hourly mean concentrations of benzene, toluene, ethyl benzene and m-xylene and Total BTEX at distribution terminal were observed as 20.3 $\mu\text{g}/\text{m}^3$; 13.6 $\mu\text{g}/\text{m}^3$; 11.0 $\mu\text{g}/\text{m}^3$; 6.9 $\mu\text{g}/\text{m}^3$ and 51.0 $\mu\text{g}/\text{m}^3$ respectively (Table IV).

Overall, the major activities are taking place at the distribution terminals. The high concentrations of BTEX at these locations clearly indicate the evaporative loss of liquids while filling of Tank, Lorries and rail Wagons. Pandya et al^[11], reported much higher concentrations of BTEX at refinery process units and its offsite facilities like wastewater treatment plant and distribution terminal.

F. Concentrations of BTEX at Boundary Walls

The concentrations of VOCs at boundary walls were monitored at four locations along the periphery of the refinery to determine VOCs levels away from the source and its impacts on the nearby village inhabitants. BTEX were observed at all the locations. Styrene, bromobenzene, substituted benzene, n-butyl benzene, p-isopropyl benzene and naphthalene were also identified at the boundary walls. The results of measurements were summarized in Table V. The concentrations of Total BTEX near south boundary wall (5.08 $\mu\text{g}/\text{m}^3$) and near D-gate (5.03 $\mu\text{g}/\text{m}^3$) were negligible. At Cargo-gate (16.88 $\mu\text{g}/\text{m}^3$) and colony-gate (16.16 $\mu\text{g}/\text{m}^3$) higher Total BTEX concentrations were observed. These may be due to the excessive vehicular movements, as it is the main entrance for the refinery. The 8 hourly mean concentrations of benzene, toluene, ethyl benzene and m-xylene and Total BTEX at all the boundary walls together were observed as 4.4 $\mu\text{g}/\text{m}^3$; 3.3 $\mu\text{g}/\text{m}^3$; 2.2 $\mu\text{g}/\text{m}^3$; 1.0 $\mu\text{g}/\text{m}^3$ and 10.8 $\mu\text{g}/\text{m}^3$ respectively (Table V).

TABLE V CONCENTRATION OF BTEX AT BOUNDARY WALLS

Units: $\mu\text{g}/\text{m}^3$		Average. : 8 hrs.				
Sr. No.	Monitoring Location	Benzene	Toluene	Ethyl benzene	m-xylene	Total BTEX
		Average \pm Standard Deviation (Range)				
1.	Near colony gate	6.74 \pm 2.64 (2.78-9.22)	5.36 \pm 2.72 (0.54-6.92)	2.94 \pm 1.36 (0.52-3.78)	1.12 \pm 0.80 (0.22-2.36)	16.16 \pm 2.65 (12.41-19.83)
2.	Near cargo gate	6.87 \pm 2.41 (2.86-9.14)	5.21 \pm 2.66 (0.48-6.64)	3.23 \pm 1.56 (0.52-4.38)	1.58 \pm 0.90 (0.21-2.28)	16.88 \pm 4.58 (9.22-21.05)
3.	Near south boundary wall	1.91 \pm 1.07 (0.28-2.78)	1.23 \pm 0.68 (0.14-1.87)	1.45 \pm 0.72 (0.19-1.96)	0.49 \pm 0.30 (0.08-0.82)	5.08 \pm 0.79 (4.42-6.37)
4.	Near D-gate	2.07 \pm 1.23 (0.36-3.72)	1.20 \pm 0.73 (0.28-2.22)	1.14 \pm 0.57 (0.16-1.62)	0.62 \pm 0.33 (0.08-0.94)	5.03 \pm 1.05 (3.53-6.43)
Mean		4.4	3.3	2.2	1.0	10.8

G. Concentration of BTEX at Some Nearby Villages

The sampling locations in the nearby villages were identified primarily based on regional climatological data during study period, to evaluate the regional background as well as the distribution of maximum impact in downwind directions and also the existing inhabited areas. Measurements were carried out at five locations namely A, B, C, D, and E. Besides BTEX, these locations also indicated the presence of Bromobenzene, Substituted benzene and p-Isopropyl benzene (Table III).

The ambient concentrations of BTEX recorded at the sampling locations A–E were summarized in Table VI. At Location A ($7.91\mu\text{g}/\text{m}^3$), the highest Total BTEX concentration was observed followed by Location B ($7.04\mu\text{g}/\text{m}^3$) and Location C ($5.94\mu\text{g}/\text{m}^3$). High concentrations at these sites are due to its proximity to nearby highway. About 10,000 vehicles are playing daily on this road. Further these locations are situated in the downwind directions which indicate dispersion conditions arising in the refinery. Similar trend was also recorded for benzene and toluene in the study of Lin et. Al [12]. The minimum Total BTEX concentration was observed at Location D ($3.82\mu\text{g}/\text{m}^3$) and Location E ($3.69\mu\text{g}/\text{m}^3$) which are located 1.8 and 2.1 km away from the refinery site and in the ESE and SSE directions respectively. The 8 hourly mean concentrations of benzene, toluene, ethyl benzene and m-xylene and Total BTEX at all the villages together were observed as $2.2\mu\text{g}/\text{m}^3$; $1.6\mu\text{g}/\text{m}^3$; $1.3\mu\text{g}/\text{m}^3$; $0.6\mu\text{g}/\text{m}^3$ and 5.7 respectively (Table VI).

TABLE VI CONCENTRATION OF BTEX AT NEARBY VILLAGES

Units: $\mu\text{g}/\text{m}^3$		Average. : 8 hrs.				
Sr. No.	Monitoring Location	Benzene	Toluene	Ethyl benzene	m-xylene	Total BTEX
		Average \pm Standard Deviation (Range)				
1.	A	3.07 \pm 1.57	1.87 \pm 0.89	1.89 \pm 0.83	1.08 \pm 0.60	7.91 \pm 3.10
		(0.41-4.32)	(0.34-2.56)	(0.42-2.37)	(0.12-1.62)	(8.69-10.35)
2.	B	2.83 \pm 1.53	1.88 \pm 1.00	1.42 \pm 0.76	0.82 \pm 0.47	7.04 \pm 3.12
		(0.36-4.14)	(0.28-2.72)	(0.21-2.09)	(0.08-1.20)	(2.01-9.65)
3.	C	2.16 \pm 1.07	1.74 \pm 0.86	1.55 \pm 0.67	0.49 \pm 0.25	5.94 \pm 1.21
		(0.31-2.86)	(0.26-2.34)	(0.38-2.05)	(0.06-0.68)	(4.88-7.42)
4.	D	1.43 \pm 0.67	1.13 \pm 0.59	0.91 \pm 0.44	0.35 \pm 0.16	3.82 \pm 1.18
		(0.24-1.86)	(0.20-1.62)	(0.13-1.19)	(0.08-0.49)	(2.50-5.00)
5.	E	1.33 \pm 0.64	1.18 \pm 0.50	0.88 \pm 0.45	0.30 \pm 0.14	3.69 \pm 0.95
		(0.19-1.69)	(0.28-1.47)	(0.09-1.19)	(0.06-0.42)	(2.43-4.55)
Mean		2.2	1.6	1.3	0.6	5.7

The levels of benzene, toluene, ethyl benzene and m-xylene and Total BTEX decrease at boundary walls and nearby villages as shown in Fig. 4 and Fig. 5. Benzene is considered to be the most toxic chemical in this group of VOC and its carcinogenic effects have been widely accepted [4]. Toluene was the most abundant volatile compound found near the automatic filling terminal [17]. It has been observed that chemical removal of toluene in ambient air is much higher than benzene due to important reaction rates with OH radicals [18]. Ethyl benzene is an aromatic hydrocarbon and smells like gasoline. It is also a constituent of asphalt and naptha. It is present in the air during evaporative emissions from the process plants such as crude distillation and reforming units and from gasoline containers. M-xylene are present in gasoline fuels.

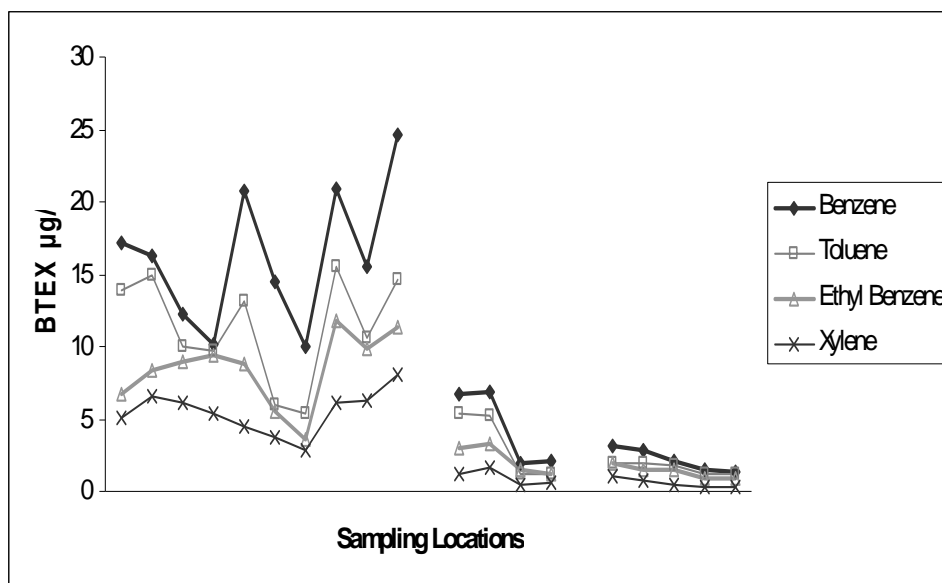


Fig. 4 Variation of Benzene, Toluene, Ethyl benzene and m-xylene at monitoring locations

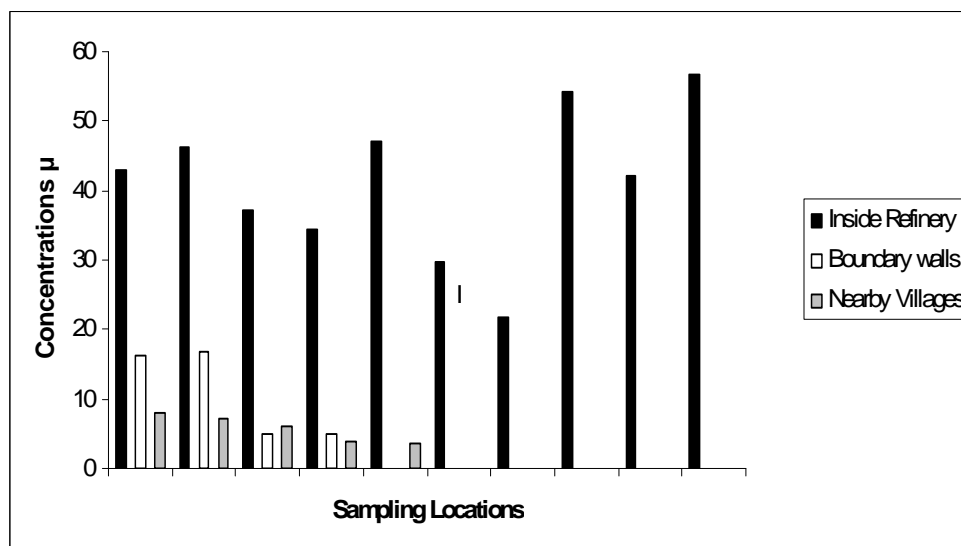


Fig. 5 Variation of Total BTEX at monitoring locations

The ratio of benzene/toluene (B/T), benzene/ethyl benzene (B/EB) and benzene/m-xylene (B/m-X) was calculated for all the villages, to find out the impact due to BTEX. The ratio of benzene to toluene, benzene to ethyl benzene and benzene to m-xylene inside the refinery averaged to 1.50, 2.03 and 3.09 respectively. These ratios are decreased as one measured these compounds at boundary walls and outside the refinery as shown in Table VII. The lower ratios away from the sources indicate the high volatility of chemicals and subsequent low residence time of these chemicals in the atmosphere. Time Weighted Average (TWA) Threshold Limit values (TLVs) of BTEX along with risk levels as given by American Conference of Governmental Industrial Hygienists (ACGIH) and Occupational Safety and Health Administration (OSHA) are given in Table VIII. It has been observed that the levels of benzene, toluene, ethyl benzene and m-xylene were well within the ACGIH and OSHA TLVs. As per the National Ambient Air Quality Standards in India, only the annual limit for Benzene ($5 \mu\text{g}/\text{m}^3$) is prescribed (Table VIII) [19]. No regulatory standards for other VOCs are developed in India. The 8-hour TWA concentration of benzene was exceeding the annual limits inside the refinery and near colony gate & cargo gate. While, the 8-hour TWA concentration of benzene was well within the prescribed annual limits at nearby villages and south boundary wall & D-gate.

TABLE VII BENZENE TO TOLUENE AND OTHER COMPOUND RATIOS

Sr. No.	Ratio	Inside Refinery	Boundary Walls	Nearby Villages
1	Benzene/Toluene	1.50	1.44	1.36
2	Benzene/Ethyl benzene	2.03	1.89	1.62
3	Benzene/m-xylene	3.09	2.68	1.33

TABLE VIII THRESHOLD LIMITS AND RISK LEVELS OF BTEX

VOCs	Exposure limits in Air					RFC	RFD
	ACGIH-TLV		OSHA-TLV		NAAQS		
	TWA ppm	STEL ppm	TWA ppm	STEL ppm	Annual $\mu\text{g}/\text{m}^3$		
Benzene	0.5	2.5	1	5	5	No safe level Group A Carcinogenic	No safe level Confirmed Carcinogen effects on humans
Toluene	50	NE	200	300	NE	Group D Carcinogen $0.4 \text{ mg}/\text{m}^3$	0.2 mg/kg/day
Ethyl benzene	100	NE	100	125	NE	Group D Carcinogen $1 \text{ mg}/\text{m}^3$	Group D Carcinogen 1 E-1 mg/kg/day
m-xylene	100	150	100	150	NE	Group D Carcinogen $0.1 \text{ mg}/\text{m}^3$	Group D Carcinogen 0.2 mg/kg/day

TWA: Time weighted average concentration for a normal 8-hour workday or 40- hour workweek to which nearly all workers may be repeatedly exposed

ACGIH: American Conference of Governmental Industrial Hygienists – www.acgih.org

OSHA : Occupational Safety and Health Administration – www.osha.gov

NAAQS : National Ambient Air Quality Standards

NE : Not Established

RFC : Provisional Reference Concentration that is likely to be without appreciable risk of deleterious non cancer effects during a life time

RFD : Provisional Reference dose

Group A : Confirmed Carcinogenic effect on humans by all routes of exposure

Group D : Not classified as to human carcinogenicity

H. Fugitive Emissions

The uncontrolled evaporation losses in the form of process escapes; minor leaks from flanges valves, pumps etc.; spillages from sample collection, loading/unloading facilities at petroleum refineries are categorized as fugitive emissions. The fugitive emissions not only cause air pollution problem at purely local level, especially work environment within the project premises, but also result in considerable material loss. It depends on various factors like housekeeping, preventive maintenance of the rotating equipment, day-to-day operation practices, the operational life of the individual units etc. Among the various potential fugitive emission sources at refineries, the crude oil, petroleum products and intermediates storage tanks, valves etc. are considered to be major in view of continuous evaporation/breathing and working losses.

All individual activities at the refinery have been broadly categorized into limited groups of operations like process units, material storage & loading, wastewater treatment facilities etc. for the convenience practical approach. Accordingly VOCs are monitored near individual process units, at the flanges/valves of pumps of product outlets, near Naphtha truck loading facility, Effluent Treatment Plant (ETP), sludge pit, cooling towers, Flare, crude oil tanks, product tanks and LPG Spheres etc. The Fugitive VOCs emission results at major activity are presented in Table 9. The fugitive VOCs emission results indicate that the VOCs are detectable at (very close to) the flanges/valves (CDU units) and product pumps. However, beyond 1 m distance from the flanges/valves, they were not detectable. Products storage tanks and few units of effluent treatment plants were major contributors of the VOC emissions as per the observations (Table 9).

TABLE IX FUGITIVE EMISSIONS OF TVOCs OBSERVED AT REFINERY

Sr. No.	Major Activities	TVOCs (mg/m^3)	
		Range (Instant Obs.)	Average* (5 min)
1.	Valves - CDU II Unit	0 - 94.9	5.2
2.	Near CDU/VDU stack	0 - 60.8	13.0
	Product outlets		
3.	a) Valves at pumps	0 - 64.3	1.3
	b) Naphtha truck loading gantry	0-106.0	21.4
	c) LPG sampling point	BDL	BDL
	Effluent treatment plant		
4.	a) Inlet sump of ETP I	0 - 38.0	1.9
	b) Inlet sump of ETP II	0 - 18.7	2.6
	c) Equalization tank	0 - 20.0	3.6
5.	Crude oil tanks	4.3 - 501.0	62.5
	Products storage		
6.	a) MS Tanks	0 -124.0	17.1
	b) Naphtha Tanks	0 -164.0	38.9

BDL: Below Detection Limit :< 0.1ppm * Screening Value in ppmv

IV. CONCLUSIONS

The present study is carried out for the measurements of VOCs at an oil refinery with 12.5 Million Metric Tonne Per Annum capacity, including process units, distribution terminals and wastewater treatment plant as well as factory boundary and nearby villages. The paper reports potential valuable insight on the air quality in and around an oil refinery regarding expo-

tures of the workers and nearby village inhabitants, which is rather sparse in the international literature. It is found that the 8-hour TWA concentration of BTEX in ambient and workplace environment is quite low and it is not exceeding the threshold limits (Table VIII). The BTEX concentrations go on decreasing from the source to the boundary walls and the impact on the nearby villages is negligible.

Because of their health and environmental effects, many of the VOCs are enlisted in the USEPA Hazardous Air Pollutants list. The monitoring and assessment of VOCs are thus required to be carried out for oil refineries and regulatory standards should be developed for individual VOCs. Keeping in view the environmental concern and importance of fugitive VOC emissions, specific guidelines will be needed to combat even minor sources of environmental pollution at petroleum refineries.

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REFERENCES

- [1] MacKenzie, A.R., Harrison, R.M., Colbeck, I., Hewitt, C.N. The role of biogenic hydrocarbons in the production of ozone in urban plumes in southeast England. *Atmos. Environ.* Vol. 25A, iss. 2, pp. 351-359., 1991
- [2] Brancalonia, E., Scovantib, M., Frattonia, M., Mabiliaa, R., Ciccioli, P. Novel family of multi-layer cartridges filled with a new carbon adsorbent for the quantitative determination of volatile organic compounds in the atmosphere. *J. Chromatogr. A.* vol. 845, iss. 1-2, 317-328, 1999.
- [3] Dewulf, J., Jagenhove, H.V. Anthropogenic volatile organic compounds in ambient air and natural waters: a review on recent developments of analytical methodology, performance and interpretation of field measurements. *J. Chromatogr. A.* 1999, 843(1-3), 163-177.
- [4] Harrison, R.M. Setting health-based air quality standards, In: *Air Pollution and health, Issues in Environmental Sciences and Technology*, 10 (Cambridge: The Royal Society of Chemistry), pp. 57-73. 1998
- [5] Kalabokas, P.D., Hatziaianestris, J., Bartzis, J.G., Papagiannakopoulos, P. Atmospheric concentrations of saturated and aromatic hydrocarbons around a Greek refinery. *Atmos. Environ.* Vol. 3, iss. 14, pp. 2545-2555. 2000
- [6] Waxman, H.A. Oil refineries fail to report millions of pounds of harmful emissions. Minority Staff Special Investigations Division, Committee on government Reform U.S. House of representatives, 1999.
- [7] Atkinson, R. Atmospheric chemistry of VOCs and NOx. *Atmos. Environ.* Vol. 34, iss. 12-14, pp. 2063-2101. 2000
- [8] Pandya, G.H. Concentration of volatile organic compounds (VOCs) at an oil refinery. *International J. Environ. Studies*, vol. 6, iss. 3, pp. 337-351. 2006
- [9] Garriazo, C., Pelliccioni, A., Filipo D., Sallusti, F., Cecinato, A. Monitoring & analysis of volatile organic compounds around an oil refinery. *Water, Air & Soil Poll.* Vol. 16, 7, iss. 1-4, pp. 17-38. 2005
- [10] Park, K.H., Jo, W.K. Personal volatile organic compound (VOC) exposure of children attending elementary schools adjacent to industrial complex. *Atmos. Environ.*, vol. 38, iss. 9, pp. 1303-1312. 2004
- [11] Pandya, G.H., Kondawar, V.K., Gavane, A.G. An integrated investigation of volatile organic compounds emission in the atmosphere from refinery and its offsite facilities. *Indian J. Chem. Tech.* vol. 14, iss. 3, pp. 283-291. 2007
- [12] Lin, T.Y., Sree, U., Tseng, S.H., Chiu, K.H., Wu, C.H., Lo, J.G. Volatile organic compound concentrations in ambient air of Kaohsiung petroleum refinery in Taiwan. *Atmos. Environ.* Vol. 38, iss. 25, pp. 4111-4122. 2004
- [13] Chambers, A.K., Strosher, Wootton, T., Moncrieff, J., McCready, P. Direct Measurement of Fugitive Emissions of Hydrocarbons from a Refinery. *J. Air & Waste Manag. Assoc.* Vol. 58, iss. 8, pp. 1047-1056. 2008
- [14] American Standards for Testing and Materials, In: *Method D3686-95. Standard Practice for sampling Atmosphere to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption method)*, Annual book of ASTM Standards, 2000, 188.
- [15] Pandya, G.H.. A simple air flow calibrator for gaseous sampling. *Indian J. Environ. Health*. vol. 30, iss 3, pp. 168-172. 1998
- [16] Worral, M., Zuber, I. Control VOCs in Refinery Wastewater paper presented at the process Optimization Conference, Houston, 1998.
- [17] Bond, A.E., Thompson, V.L., Ortman, G.C. Self service station vehicle refueling exposure study. In: *Proceeding of the EPA/APCA Symposium on Measurement of Toxic Air Pollutants Pittsburgh, PA: Air Pollution control Association*, pp. 458-66. 1986
- [18] Field, R.A., Goldstone, M.E., Lester, J.N., Perry, R. The sources and behavior of tropospheric anthropogenic volatile hydrocarbons. *Atmos. Environ.* Vol. 26 A, iss. 16, pp. 2983-2996. 1992
- [19] National Ambient Air Quality Standards, Central Pollution Control Board, New Delhi, India. 2009.