

Estimating Fugitive Emission Budget of Volatile Organic Carbon (VOC) in a Petroleum Refinery

B. P. S. Rao, F. Ansari, S. Ankam, A. Kumar, V. I. Pandit, P. Nema

Air Pollution Control Division, National Environmental Engineering Research Institute (NEERI), Nehru Marg, Nagpur 440 020, India

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The formation of ground level photochemical oxidants viz., ozone is a serious air pollution problem in a refinery. Ozone is not emitted directly but is formed from the photochemical interaction of Volatile Organic Carbon (VOCs) and Oxides of Nitrogen (NOx) in presence of sunlight. Different VOCs are emitted from refinery (Carter et. al., 1994). Fugitive VOCs emission are difficult to monitor accurately as the sources are diffused such as process vents, storage tanks, pumps, valves, rail, truck and marine loading and cleaning equipment leaks, sewers, solid waste disposal, equipment decommissioning and equipment cleaning and maintenance activities (Venkatesh et. al., 1998). At present, the refinery estimates total hydrocarbon losses by undertaking Leak Detection and Repair (LDAR) programme. The fugitive emission sources in the various units of refinery are numerous and are mostly inaccessible. Hence this technique needs exhaustive monitoring in and around such resources, may lead to omission of some sources leading to inaccurate emission estimation.

The present VOC monitoring technique would lead to identifying the possible sources of VOC emission which can be rigorously taken up for in depth studies. Different types of analyzers can be used to measure fugitive emissions. These analyzers operate on various principles but the three most common types are flame or photoionization, infrared absorption and combustion (Jeffrey H. Siegel et. al., 1998). Using portable instruments to analyze semi-volatile and volatile organic compounds in field is gaining popularity. Accurate and high speed measurements performed in the field can substantially reduce the cost-of analysis. Mini-RAE Plus is a programmable Photo Ionization Detector (PID) to measure volatile organic vapors in hazardous or industrial environments. It incorporates a sampling pump and data download capabilities for continuous toxic monitoring, site survey and leak detection. It can measure two classes of toxic gases viz., organic vapors and chlorinated compounds.

Volatile organic compounds are organic vapours having vapor pressure in the range of 0.1 to 380 mmHg. The sources of VOC emissions in a process industry are process vents, storage tanks, rail, truck and marine loading and cleaning, equipment leaks sewers, solid waste disposal, equipment decommissioning and equipment cleaning and maintenance activities are shown in Table 1. Major VOCs in a refinery are benzene, toluene, xylene, phenols, cresol, and cresylic acid as shown in Table 2. Fugitive emissions in a refinery are mostly volatile and semivolatile organic compounds. This paper details the method of sampling, analysis and fugitive emission estimation of VOC in and around different process units, tanks, truck loading, gantry area and treatment plants in a refinery.

Table 1. Hydrocarbon emission sources from a petroleum refinery

Source Category	Potential Emission Sources ^a		
	Process Point	Process Fugitive	Area Fugitive
Crude separation	O,J,L	F,H,M,N	I
Light hydrocarbon processing	O,G	F,H	I
Middle and heavy distillate processing	G,O,P,R	F,H	Q
Residual hydrocarbon processing	B,G,K,O,R	H	I
Auxiliary processes	G	F,H	I

a – Key to emission sources; B – vis breaker furnace; F – wastewater disposal (process drain, blow-down, cooling water); G – Flare, incinerator process heater, boiler; H – storage, transfer, and handling; I – pumps, valves, compressors, fittings etc.; J – absorber; K – process vent; L – distillation/fractionation; M – hot wells; N – steam ejectors; O – catalyst regeneration; P – evaporation; Q – catalytic cracker; R – stripper.

Table 2. Potential VOC for petroleum refining

Process Refining Operations	HAP Organic Vapour
Crude separation	Benzene, toluene, xylene, phenols, cresol, cresylic acid
Light Hydrocarbon processing	Benzene, toluene, xylene, mercaptans, nickel carbonyl, tetraethyl lead, cobalt carbonyl
Middle & Heavy distillate	Benzene, toluene, xylene, phenols, cresol, cresylic acid
Residual hydrocarbon proceeding	Benzene, toluene, xylene, phenols, cresylic acid
Auxiliary processing	Benzene, toluene, xylene, phenols, cresol

MATERIALS AND METHODS

The monitoring is carried out in a 13.7 MMTPA refinery which processes both indigenous as well as imported crude oils. The refinery manufactures petroleum products/petrochemical feedstock/specialty products like LPG, Naphtha, Motor Spirit, Superior Kerosene Oil (SKO), Aviation Turbine Fuel (ATF), High Speed Diesel (HSD), Light Diesel Oil (LDO), Xylene Feedstock, Benzene, Toluene, n-heptane, etc.

For area ground emission sources, the spatial distribution of conservative air pollutants is primarily dominated by the distribution of sources because the meteorology is the same for all sources and the accumulation of pollutants C_{max} occurs downwind of the greatest continuous area sources. Areas of homogenous landuse can thus be divided into uniform grid squares. The study area is divided into 50 x 50 m² grid squares. The sampling and monitoring is done in each grid for 15 min. The value entered portable PID in the instrument after 15 min. sampling is the average value. In this grid wise sampling area, the grid area for maximum background concentration is observed and this concentration is taken for further calculation.

The refinery area is considered to be having different area sources which are process units for crude separation, middle & heavy distillate processing, light hydrocarbon processing, residual hydrocarbon proceeding, storage tanks, effluent treatment plants,

truck loading areas and gantry areas. The unit areas considered have around 100m x 500 m of dimensions. These areas are separated from each other by a distance of around 100 to 500 m. The characteristics of the domain-complex as the sources may be put at certain height above ground level like flanges or any process vent from a equipment or may be from an oil spill over ground leak from a pump. A strip like area source of width x , that is normal to the wind vector is analyzed by an extension of the line source concept. As shown in Figure 2 if the cross wind dimension of the source is long enough to be considered of infinite extent then it may be divided into a series of infinite line sources of strength $Q_a dx^1$ per unit of length where Q_a ($\text{gmm}^{-2}\text{s}^{-1}$) is the area source strength then the concentration at the receptor located at $(x, 0)$ is expressed by

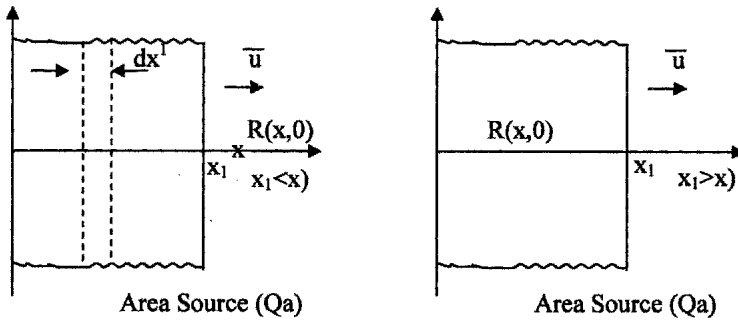


Figure 1. Cross section of a area source of VOC in a refinery

$$\bar{c} = \sqrt{\frac{2}{\pi}} \frac{Q_l}{\sigma_z \bar{u}} \text{ for infinite line as} \quad (1)$$

$$d\bar{c} = \sqrt{\frac{2}{\pi}} \frac{Q_a dx^1}{\bar{u} \sigma_z} \quad (2)$$

where σ_z is evaluated at the distance $x - x^1$ to integrate this relation we express σ_z as :

$$\sigma_z = b (x - x^1)^q \quad (3)$$

where values b and q are as per to the Pasquill dispersion class. The concentration at the receptor

$$\bar{c} = \sqrt{\frac{2}{\pi}} \frac{Q_a}{\bar{u} b} \int_0^x \frac{dx^1}{(x - x^1)^q} \quad (4)$$

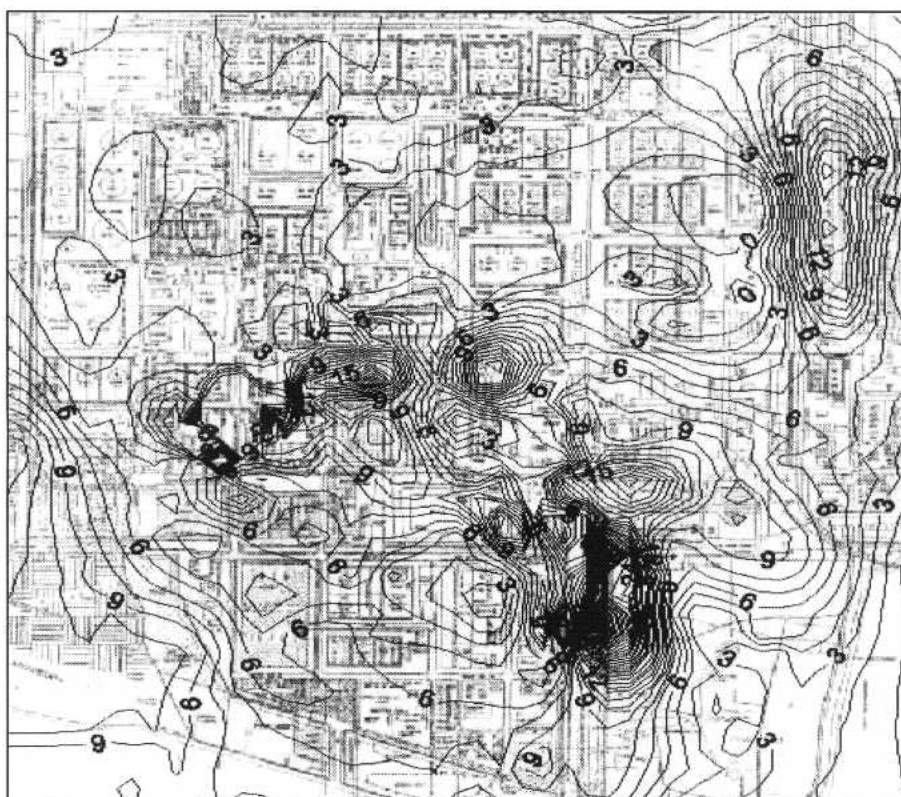
For $x_1 = x$ the receptor is located on the downwind edge interior to the area source

$$\bar{c} = \sqrt{\frac{2}{\pi}} \frac{Q_a x}{\bar{u} (1-q) \sigma_z(x)} \quad (5)$$

and

$$\sigma_z(x) = b x^q \quad (6)$$

Exact closed form solutions are not available for the case when the area source is finite in its crosswind dimension. In this case, the concentration at a receptor at a distance $x - x_1$ from the downwind edge of the finite source is given by the integral.



Legend : Pollutant : VOCs Unit : PPM Conc. Range : 1-40 PPM
 Period : June- Sept. 03 Average : 15 min.

Figure 2. : Ground level concentration contours of volatile organic carbons (VOCs) in refinery area

Table 3. Fugitive VOC emission contribution from different sources

Source Category	Emissions (Tonnes)	Percent Contribution
Crude separation	804	14.03
Heavy & Middle distillate processing	742	12.95
Light Hydrocarbon processing	806	14.07
Residual Hydrocarbon processing	84	1.47
Auxiliary Processing	22	0.38
Effluent Treatment Plant	1116	19.48
Truck Loading & Gantry	475	8.29
Storage Tanks	1680	29.32

Nomenclature

AU-I, II, III, IV, V : Atmospheric Unit	CRU: Catalytic Recovery Unit
PDF: Propane Dewaxing	DHDS: De Hydro Diesel esulphurization
FPU: Feed Preparation Unit	HCU: Hydro Cracker Unit
SRU: Sulphur Recovery Unit	FGH: Food Grade Hexane Unit
FCC: Fluidised Catalytic Cracking Unit	VBU: Vis Breaker Unit
CGP: Co Generation Plant	CETP: Combined Effluent Treatment Plant
VDU&BBU: Vacuum Distillation Unit & Bitumen Blowing Unit	
c - gas concentration, gm^{-3} ; Q_L - emission rate, $\text{gs}^{-1}\text{m}^{-1}$; σ - dispersion coefficient	
π - P_i ; u - velocity, ms^{-1} ; Q_a - emission rate, $\text{gs}^{-1}\text{m}^{-2}$;	
b, q - power law constants for calculation of dispersion coefficient	

Table 4. Fugitive VOC emissions in process units

S. No.	Process Units	Area m^2	Conc. PPM	Conc. gm/m^3	Gaussian model	
					Q_a $\text{Gm}/\text{m}^2.\text{s}$	Emissions Q Kg/A
1	AU-I	15600	11.3	3.08E-02	4.44E-04	218524.81
2	AU-II	15600	8.2	2.24E-02	3.22E-04	158575.53
3	AU-III	6032	25.3	6.90E-02	9.95E-04	189181.90
4	CRU	10125	8.6	2.34E-02	3.38E-04	107942.18
5	UDEX	5000	10	2.73E-02	3.93E-04	61982.31
6	AU-IV	3600	4.2	1.14E-02	1.65E-04	18743.45
7	AU-V	15500	11.4	3.11E-02	4.48E-04	219045.47
8	PDF	1500	18.2	4.96E-02	7.15E-04	33842.34
9	DHDS	6000	2.3	6.27E-03	9.04E-05	17107.12
10	H2-DHDS	6000	25.2	6.87E-02	9.91E-04	187434.49
11	FPU	6000	9.7	2.64E-02	3.81E-04	72147.40
12	HCU	16000	18.7	5.10E-02	7.35E-04	370902.11
13	SRU	20000	10	2.73E-02	3.93E-04	247929.22
14	BUTENE	4200	48.5	1.32E-01	1.91E-03	252515.91
15	MTBE	6000	9.3	2.54E-02	3.66E-04	69172.25
16	H2-HCU	4800	1.8	4.91E-03	7.08E-05	10710.54
17	N2-HCU	2400	0.6	1.64E-03	2.36E-05	1785.09
18	FGH	3000	8.9	2.43E-02	3.50E-04	33098.55
19	FPU-FCC	6000	4.8	1.31E-02	1.89E-04	35701.81
20	FCC	10944	3.4	9.27E-03	1.34E-04	46126.74
21	VDU&BBU	3600	6.1	1.66E-02	2.40E-04	27222.63
22	VBU	3600	11.6	3.16E-02	4.56E-04	51767.62
23	MEROX	2880	1.4	3.82E-03	5.50E-05	4998.25
24	CGP	4000	4.5	0.012267	0.000177	22313.63
25	CETP	90000	10	0.02726	0.000393	1115681.49
26	Truck Loading	10000	12	0.032712	0.000472	148757.53
27	Gantry	18000	14.6	0.0397996	0.000574	325779.00
28	Tanks	542220	2.5	0.006815	0.000098	1680402.272
Total						5729392

$$\bar{c} = \frac{Q_a}{\pi \bar{u}} \int_{y=-L/2}^{L/2} \int_{x^1=0}^{x_1} \exp \left[-\frac{(y-y^1)^2}{2\sigma_y^2} - \frac{H^2}{2\sigma_z^2} \right] \frac{1}{\sigma_y \sigma_z} dx^1 dy^1 \quad (7)$$

where $\sigma_y = \sigma_y (x - x^1)$ and $\sigma_z = \sigma_z (x - x^1)$

In fact we would expect the use of an infinite cross wind dimensions to be even a better approximation for the area source because the heaviest contribution at the receptor will always be received from the area close to its windward side. The concentration caused by the finite area source is then formulated.

$$\bar{c} = \sqrt{\frac{2}{\pi}} \frac{Q_a}{\bar{u}} \int_0^{x_1} \sigma_z^{-1} \exp \left(-\frac{H^2}{2\sigma_z^2} \right) dx^1 \quad (8)$$

The use of equation (8) in place of the exact integral equation (7) with less computational effort is referred to as the "narrow plume approximation. This equation is valid for an area source of arbitrary shape with an interior receptor where $x_1 = x$ and is interpreted as the distance from the receptor to the upwind edge of the source. Further more the upwind edge need not be normal to the wind because the heaviest contribution to the concentration at the receptor is from the portion of the area source that is immediately upwind often the height of the area source is just like for the infinite area source. Often the height of the area source is ground level, $H = 0$, in which case equation 8 can be integrated if a power law form for σ_z is employed. The result is same as equation 5 for infinite area source.

The equation used for emission calculation from finite area source is

$$Q_a = \sqrt{\frac{\pi}{2}} \frac{c u (1-q) \sigma_z(x)}{x} \quad (9)$$

RESULTS AND DISCUSSION

The monitored Ground Level VOCs concentration contour in refinery is shown in Figure 2. and around different process unit and offsites are shown in Table 4. The study was carried out in the month of Sept. 2003. The emissions from these sources using Gaussian model are calculated using equation 9 are shown in Table 4. The total emissions of fugitive VOCs in refinery works out to 5729 TPA and the percentage contribution different sources is shown in Table 3. Emission from different process unit and offsites are shown in figure 3.

The VOC emission factor for this refinery works out to be 0.46 KgT^{-1} of crude processed which is less than the World Bank guidelines of VOC emission i.e. 0.526 KgT^{-1} of crude processed. Major emission sources are storage tanks, effluent treatment plants, crude separation processes, light hydrocarbon processing units. These units are to be rigorously monitored for LDAR programme for reducing the VOC as well as hydrocarbon losses.

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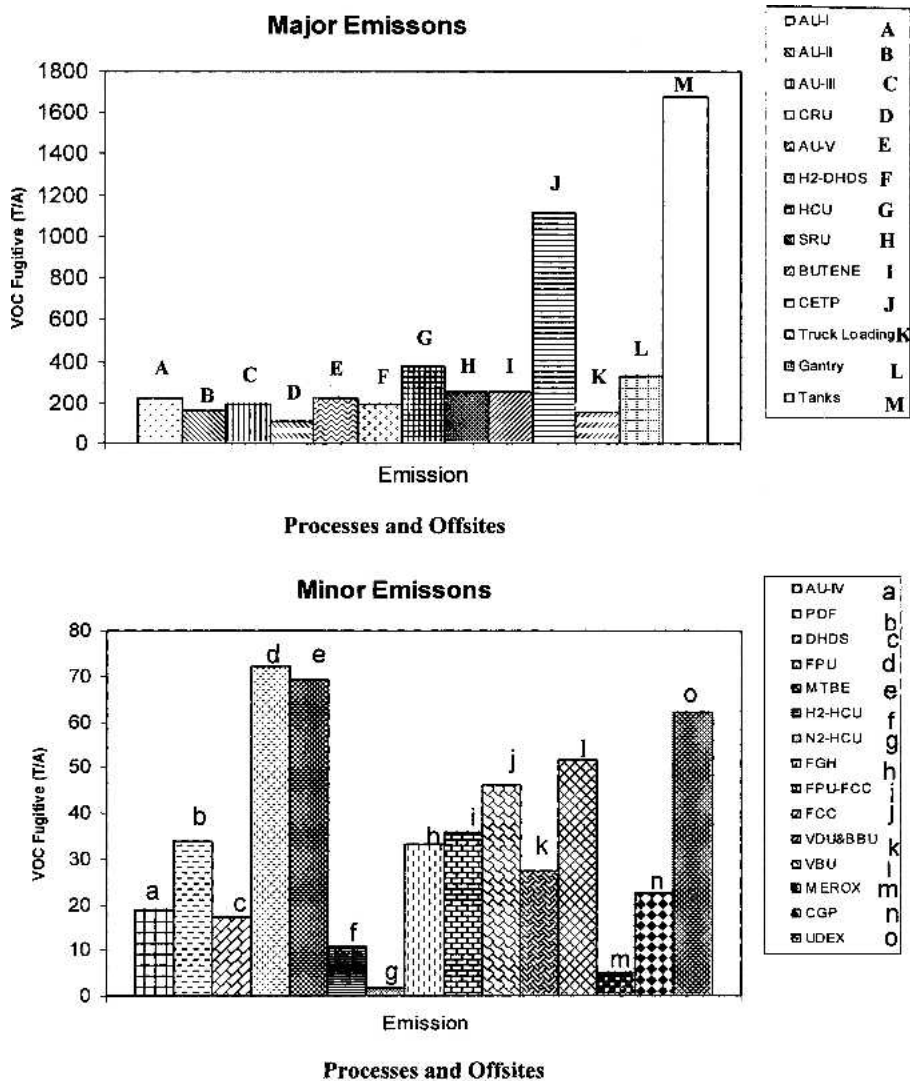


Figure 3. Emissions from different Processes units and offsites

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