

Research Article

Measurements on Stationary Source Emissions and Assessing Impact on Ambient Air Quality around Two Indian Refineries

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ABSTRACT Emissions of particulate matter (PM), SO₂ and NO₂ from stationary sources and their concentration along with benzene and CO in ambient air around two Indian refineries were studied. Prediction of ground level concentration (GLC) of SO₂, NO₂ and PM was made by dispersion modeling. In Refinery 1, highest SO₂ emission (646 mg Nm⁻³) were detected in Sulphur Recovery Unit while NO_x emissions ranged from 57.8 to 445.0 mg Nm⁻³, respectively from various units. In Refinery 2, highest SO₂ emission (935 mg Nm⁻³) was observed from Utility Boiler while NO₂ emissions ranged from 13 to 235 mg Nm⁻³. Above emissions were within the stipulated emission standards prescribed by Central Pollution Control Board of India. Further, ambient concentrations of the above in the vicinity of these refineries were below their prescribed national ambient air quality standards. Air quality in terms of air quality index (AQI) was moderate or good at the study sites. Dispersion modelling exercise indicated that the observed GLC of SO₂ and NO₂ could be reasonably predicted by ISC-AERMOD model for both refineries while there was moderate to substantial difference between observed and modeled PM values due to presence of several sources of particulate emissions in the region that could not be considered in the model.

KEY WORDS Air pollution, Dispersion modeling, Ground level concentration, ISC-AERMOD, Stack emission

1. INTRODUCTION

Petroleum refineries are well-known sources of a wide variety of air pollutants. India is one of the major consumers of petroleum products in the world and was the 4th largest consumer of oil and petroleum products after USA, China, and Japan in 2011 (USEIA, 2013) and its demand was forecasted to rise further (IBEF, 2017). India's current refining capacity is 230 million metric tonnes per annum (MMPTA), including the just commissioned 15 MMPTA refinery at Paradip (IBEF, 2017). The public sector accounts for 66% (150 million metric tonnes) of the total refining capacity while the private sector accounts for the rest 34% or 80 million metric tonnes. Currently, there are 22 petroleum refineries operating across India (PPAC, 2018), some of which are located in populated areas, making the issue of air pollution from these refineries significant.

Refineries emit various inorganic and organic compounds into the atmosphere (Al-Hamad and Khan, 2008; Cetin *et al.*, 2003). Factors like process energy consumption, crude feed quality, types of refined products, fuels combusted for process energy generation, etc. govern the emissions (Karras, 2010). Gaseous sulfur compounds are the most important air pollutants generated in petroleum refineries, sulfur dioxide (SO₂) being the major one (USEPA, 1995; CPCB, 1981a), the others being oxides of nitrogen (NO_x) and volatile organic compounds (VOCs) (Cetin *et al.*, 2003). VOC emissions from petroleum refineries may be substantial, however these are mostly released as fugitive emissions. Fluid Catalytic Cracking (FCC) unit is the major contributor to SO₂ and particulate matter (PM) emissions (Yateem *et al.*, 2011). Refinery emits SO₂, NO_x and PM in the range of 30–6,000, 60–700 and 10–3,000 tonnes per million tonne of crude processed (Srivastava *et al.*, 2010). The general range of SO₂ and nitrogen oxides (NO_x) emissions are reported to be 0.143–0.892, 0.010–0.8 kg t⁻¹ in Indian refineries (Srivastava *et al.*, 2010). Some studies have reported 5–6 times higher SO₂ concentrations in ambient air over workplaces in refineries in India and other countries (Shie, 2013; Rao *et al.*, 2012). As per some reports, SO₂, nitrogen dioxide (NO₂) and BTEX concentrations exhibited diurnal as well as seasonal variations around refineries (Rao *et al.*, 2007; Chiu *et al.*, 2005; Lin *et al.*, 2004; Pimpisut *et al.*, 2003). Chiu *et al.* (2005) reported higher concentrations of ambient SO₂ and NO₂ during daytime. Day and night time values, recorded by Lin *et al.* (2004) were 123 and 154 ppbv for benzene, 137 and 139 ppbv for toluene, 1.7 and 2.3 ppbv for ethylbenzene and 4.1 and 4.7 ppbv for p-xylene, respectively.

Attrition of cold makeup catalyst, charging and operating conditions are mostly responsible for particulate emissions in a refinery (Yateem *et al.*, 2011). Sánchez de la Campa *et al.* (2011) reported emissions of fine and metalliferous particulate emissions from the oil refinery complex in San Roque. Particulates are mostly carbonaceous in nature or sometimes fine metalliferous that are mostly partitioned into < 0.33 µm, whereas emissions from production of purified terephthalic acid (PTA) were coarser.

Emissions from petroleum refinery are important as they have adverse impacts on local ecosystems (Al-Jahdali and Bin Bisher, 2008; Korte and Boedefeld, 1978) and health (Simonsen *et al.*, 2010; Smargiassi *et al.*, 2009;

Barberino *et al.*, 2005; Tasi *et al.*, 2003; Luginaah *et al.*, 2000; Yang *et al.*, 2000; Bertazzi *et al.*, 1989). Various international organizations and national pollution control authorities have imposed ambient air quality and emission standards for petroleum refineries (World Bank, 1998; USEPA, 1997; CPCB, 1985, 1981b). Ministry of Environment, Forest and Climate Change (MoEFCC), India, erstwhile Ministry of Environment and Forest (MoEF), has promulgated emission standards for Indian petroleum refineries (MoEF, 2008).

Information on particulate and gaseous emissions from petroleum refinery in India is very limited. Estimating emissions from stationary sources & likely impacts on local and regional air quality is important for understanding environmental sustainability around petroleum refineries and information and updates on the same are therefore important. In this paper, we report stationary source emissions along with observed and predicted ambient air quality around two Indian refineries that are situated in two very distant geographical regions and surroundings. We have also presented dispersion modeling of stationary source emissions as a tool for predicting concentration of air pollutants at ground level. The present work would improve the common understanding of the source emissions from refineries and their likely effects on regional ambient air quality.

2. RESEARCH METHODS

2.1 The Refineries

Two refineries (designated as Refinery 1 and Refinery 2) were selected for stationary source and air quality monitoring assignment. The two refineries selected are situated at different corners of India and also in different landuse pattern; one is located inland whereas the other is located at a coastal area. These refineries were chosen to understand emission patterns from refineries of different capacities and also to evaluate effects on ambient air quality in two different geographical areas and meteorological regimes. Refinery 1 is located in North Eastern part of India at Numaligarh in Assam, having a crude oil refining capacity of 3.0 MMTPA at the time of study. Superior kerosene oil (SKO), high speed diesel (HSD) and Aviation Turbine Fuel (ATF) are produced by Hydrocracker Technology for producing low sulphur products. Internally produced naphtha is used as fuel in the hydrogen generation unit (H₂U) and a fuel in captive

power plant. Other products included Liquefied Petroleum Gas (LPG), Petroleum Coke, Paraffin Wax and Sulphur. Low NO_x burners are in place to minimize NO_x generation from furnaces. There are two gas turbine generators (GTGs) with Heat Recovery Steam Generators (HRSGs), each having rated capacity of 30 MW.

Refinery 2 is located in the coastal area of Kochi in Kerala, situated in Southern part of India, that refined about 9.5 MMTPA crude oil at the time of study. This refinery has state of the art crude distillation unit and secondary processing units. Products from this refinery include LPG, Naphtha, Aviation Turbine Fuel, Kerosene, High Speed Diesel, Fuel Oils, Motor Spirit and Asphalt. Other products included Benzene, Toluene, Propylene, Poly Iso Butene, Bitumen and Sulphur.

2.2 Reconnaissance

Reconnaissance was conducted in the selected refineries for collection of secondary data on processes (Table 1), raw material consumption and environment management for planning on source emission and ambient air quality monitoring. Emission standards for particulates, SO_2 and NO_x prescribed by the State Pollution Control Boards in their 'consent to operate' letter to the industry were collected and studied.

2.3 Stationary Source Emission Monitoring

The method prescribed by Bureau of Indian Standards (IS: 11255, Part 1 and 3-1985) was used for stationary source emission monitoring and determination of stack gas flow rate and concentration of analytes (BIS, 1985). Stationary source monitoring for particulate matter (PM) estimation was carried out under isokinetic flow conditions for a period ranging from 1–2 h under normal plant operations. A thermocouple sensor attached to a pyrometer and a modified "S-type" Pitot tube fabricated from SS 304 in conjunction with a stack monitoring kit (Model VSS-1) was used to estimate temperature of flue gas and differential flue gas pressure, respectively, from which flue gas velocity and flow-rate were calculated. A dry gas meter was used to record total volume of gas sampled. Particulate matter present in stack gas was collected in glass fibre thimble filters (19×90 mm; Whatman) capable of collecting particulates down to $0.3 \mu\text{m}$ and withstanding temperature up to 600°C . The thimble filters were conditioned at 50°C and 10% relative humidity (RH) in an oven followed by its storage in a humidity controlled desiccator before initial weighing.

The same conditioning was also applied to the thimble filters after sampling and before final weighing. PM concentration in stack gas (mg Nm^{-3}) was estimated as gain in thimble weight against normalized volume (Nm^3) of sampled stack gas.

A USEPA certified flue gas analyzer (Model Testo 350, Testo GMBH, Germany) fitted with electrochemical sensors was used for monitoring of O_2 , SO_2 , nitric oxide (NO), NO_2 and carbon monoxide (CO) in the stack gas. This analyzer was calibrated with standard certified concentrations of CO, SO_2 , NO and NO_2 and was zero-calibrated with fresh air just before sampling, as per standard usage protocol. The fuel cell sensors deployed in the analyzer for SO_2 and NO_2 analysis, slowly and steadily decline in their output with time and therefore, must be recalibrated for a new zero at a pollution free ambient condition before they are used (Powrtech Solutions, Inc., <https://www.powrtechsolutions.com/page/testo.htm>; accessed on 25.2.2019). Subsequently, concentrations of PM, CO, SO_2 , NO and NO_x measured in stack gas (mg Nm^{-3}) were first corrected to 6% carbon dioxide (CO_2) concentration and then integrated with stack gas flow rate ($\text{Nm}^3 \text{h}^{-1}$) to estimate their emission rates (kg h^{-1}) and emission load (MT y^{-1}), considering continuous operation throughout the year.

2.4 Ambient Air Quality Monitoring

Ambient air monitoring (24-hourly) for a three-week period was conducted during the month of February for Refinery 1 and September for Refinery 2 at various locations around the refineries selected as per ASTM guidelines (ASTM, 2005). The locations of ambient air quality stations with respect to the refineries are depicted in Fig. 1. Fine Particulate Samplers (Model APM 550, Envirotech, Delhi, India) were used for monitoring PM_{10} in ambient air. Ambient air enters APM 550 through an omnidirectional inlet designed to give aerodynamic cut-point for particles larger than 10 microns. The samplers were run at 16.7 LPM flow rate without Wins Impactor for PM_{10} sampling. Calibration of flow rate of the instrument was undertaken by a Low Flow Calibrator (Model: APM-523, Envirotech) calibrated within 10–20 LPM flow range with error range of -0.4 – 8.20% full scale and expanded uncertainty ($k=2$) of $+1.05\%$ with traceability to FCRI, Palakkad. The combined (and expanded) uncertainty associated to atmospheric particulate measurements depends on uncertainty components (standard deviations) of relevant mea-

Table 1. Summary of various operations in the selected refineries.

Process units	Unit summary
Crude Distillation Unit (CDU)	Crude oil is preheated to a temperature of 360–385°C in an atmospheric furnace and introduced in a crude distillation column wherefrom oil, kerosene and heavy naphtha are obtained.
Vacuum distillation unit (VDU)	A vacuum heater heats up hot reduced crude oil from CDU, then introduced in a VDU wherefrom vacuum diesel, vacuum gas oil (VGO) and vacuum residue (VR) are obtained.
Delayed Coking Unit (DCU)	Residue from VDU is heated to 502°C in a coker furnace and then it undergoes cracking and polymerization in a coke chamber, forming raw petroleum coke (RPC), which is then processed at coke calcination unit.
Coke Calcination Unit (CCU)	RPC is put through a screen, crushed and then stored in RPC silos or introduced to a rotary kiln where it is dried, heated to 1,250–1,350°C to drive off moisture while hydrocarbons and other volatile matter are burnt off.
Hydrogen Generation Unit (H ₂ U)	Naphtha undergoes desulphurization by hydrogenation and adsorption on S adsorber. It then enters reforming section to get converted to synthetic gases like H ₂ , CO and CO ₂ . CO is converted to CO ₂ in shift conversion section and finally mixed gas is purified in gas purification section (PSA) to recover 99.9% pure H ₂ .
Hydrocracker Unit (HCU)	The feeds to this unit are vacuum gas oil coming from VDU/CDU and coker distillates from CDU which are heated to a desired temperature and partially cracked on catalyst bed in presence of H ₂ coming from H ₂ U.
Naphtha Hydrotreater/Hydro Desulphurisation (NHDT/NHDS) Unit	This unit desulfurize naphtha obtained from crude distillation by using hydrogen (Hydrodesulfurization) which is necessary before sending naphtha to the Catalytic Reforming Unit.
Catalytic Reforming Unit (CRU)	This unit converts naphtha-boiling range molecules into higher-octane products which have higher aromatics, olefins and cyclic hydrocarbons.
Isomerization Unit (IU)	This unit produces higher-octane molecules from linear molecules to blend with gasoline or introduced to alkylation units.
Sulphur Recovery Unit (SRU)	This unit recovers sulphur from H ₂ S-rich gas from sour-water-stripping unit and acid-gas coming from amine regeneration unit.
Vis Breaker Unit (VBU)	Biturox Unit produces Bitumen from Vacuum Residue (VR) obtained from VDU. Furnace Oil (FO) can also made from VR by feeding the later to a VBU.
Fluid Catalytic Cracking Unit (FCCU)	FCC unit processes VGO whereby heavier molecules are converted to LPG, Gasoline, and Diesel.
Diesel Hydro Desulphurisation (DHDS) Unit	This unit converts S in presence of H ₂ to produce H ₂ S to reduce S level in HSD.
Kerosene Hydro Desulphurisation (KHDS) Unit	Aviation Turbine Fuel (ATF) and Mineral Turpentine Oil (MTO) are produced from Kerosene obtained from crude distillation by treating in a MEROX unit or KHDS.
Hydrotreater Unit (HDS)	This process is used for selective hydrogen addition to olefins & aromatics in order to saturate them. Another important purpose is S & N compounds removal present in feedstock by selective hydrogenation.
Captive Power Production	
Utility Boiler (UB)	It is a single-burner boiler, generating steam for running generator.
Heat Recovery Steam Generator (HRSG)	The unit drives a generator with the help of steam generated by circulating water through the exit of utility boiler to capture the waste heat coming out of from boiler. It consists of a steam turbine.

surements viz. flow rate, time, mass, temperature, pressure, etc. Calibration for size is also critical. Therefore, uncertainties in impactor designing can be further added as one of the components of uncertainties (Aggarwal *et*

al., 2013). Thermoelectrically cooled gaseous samplers (Model VTG II) were used to sample SO₂ and NO₂ by IS 5182 (Part 2): 2001 Method (BIS, 2001) and IS 5182 (Part 6): 2006 Method (BIS, 2006), respectively. The



Fig. 1. Maps of study areas with marked refinery boundaries and ambient air quality monitoring stations (N1–N4) around Refinery 1 and (K1–K6) around Refinery 2.

temporary ambient air quality monitoring stations were established with assured power supply, round the clock vigilance and facility for periodic sample collection. SO_2 and NO_2 were sampled at 1 LPM flow rate in impingers filled with designated absorbing media for SO_2 or NO_2 . The IS 5182 Method (Part 2)-2001 (BIS, 2001) was used for SO_2 sampling and analysis. The impingers were calibrated by pipetting 35 mL absorbing reagent in 5 mL

calibrated pipette and checking correctness of markings on the impingers. Sampling for SO_2 was undertaken for 24 hours continuously. This method allowed estimation of SO_2 in the range of 25 to 1,050 $\mu\text{g m}^{-3}$ and concentrations $< 25 \mu\text{g m}^{-3}$ were measured by withdrawing higher air volumes. Likely NO_x interference was reduced by adding 1 mL of 0.06% sulphamic acid while ozone (O_3) was allowed to get decomposed by making the solution

to stand for some time. Interference of trace metals was minimized by addition of 0.01% ethylene diamine tetra acetic acid (EDTA) to the absorbing solution before sampling. Calibration curve was drawn with the help of serial dilution of stock sulphite solution.

Measurement of NO₂ was undertaken by sampling for 24 hours continuously following IS Method 5182 (Part 6): 2006 (BIS, 2006). The range of the method is reported to be 6 to 750 µg NO₂ m⁻³ (0.003 to 0.4 ppm) while the analysis range is 0.04 to 2.0 µg NO₂ mL⁻¹. Under 50 mL absorbing reagent, sampling rate of 200 cm³ min⁻¹ for 24 h and absorption efficiency of 82%, method range is reported to be 6 to 420 µg NO₂ m⁻³ (0.003 to 0.22 ppm). NO₂ concentrations (420 to 750 µg NO₂ m⁻³) (0.22 to 0.4 ppm) are measured accurately by 1 : 1 dilution of sample. The positive and negative interferences of nitric oxide (NO) and CO₂ are low and therefore no correction was applied. Potential interference from SO₂ is minimized by letting SO₂ convert to SO₄⁼ by adding hydrogen peroxide. In this method, reported intra-laboratory standard deviation was reported to be 8 µg m⁻³ (0.004 ppm) while inter-laboratory standard deviation was 11 µg m⁻³ (0.006 ppm) over a range of 50–300 µg NO m⁻³ (0.027 to 1.16 ppm) (BIS, 2006).

On the other hand, CO was sampled in Tedlar Bags (SKC Inc., USA) passively through portable air sampling pumps and were analyzed ex situ in a CO analyzer (Model CO11, Environmental SA, France). Stability of CO in Tedlar Bags is reported to be good and Tedlar bags have been used earlier by various researchers to sample CO (Johnson, 2009; Chudchawal *et al.*, 2000). SKC Tedlar bags are reported to have CO recovery rate of 90% within 48 hours after collection (Coyne *et al.*, 2011). USEPA recommends Tedlar bags for determination of CO emissions from stationary sources in Method 10A (<http://www.caslab.com/EPA-Methods/PDF/m-10a.pdf>; accessed on 26.2.2019) and 10B (<https://19january2017snapshot.epa.gov/sites/production/files/2016-06/documents/m-10b.pdf>; accessed on 26.2.2019). Standard recommendation for calibration by the manufacturer was followed and instrument calibration was done by two-point calibration process by zero air and a NIST traceable certified 100 ppm CO (Chemtron Laboratory, Mumbai, India). A suitable calibration coefficient was applied for correction of the obtained sample CO values. The instrument noise was 0.05 ppm and it had a lower detectable limit of 0.1 ppm CO (i.e. 100 ppb) and so anything below this concentration is reported as

below detectable limit (BDL). This family of instrument complies with ISO 4224 and EN 14626:2005 standards, EPA, automatic reference method RFCA-206-147 in United States, TÜV No. 936/21206773/B, according to EN 14626. As per TÜV-Report (TÜV, 2008), the combined standard uncertainty and actual expanded uncertainty of CO analyzer (CO12M) in measuring CO had been found to be 0.1490–0.4433 µmol mol⁻¹ and 7.11–10.29% which were good enough to fulfil the requirements of European Standard EN 14626.

Benzene was analyzed in a BTEX analyzer (Model VOC72M). This agreed with EN 14662-3 standard for measurement of benzene based on chromatographic separation of compounds in conjunction with photo-ionization detector (PID) (10.6 eV) (Environnement SA, http://www.hnunordion.fi/environnement/netissa/VOC72M_HNU.pdf; accessed on 25.11.2018). It is TUV Compliant following EN 14662-3. Sampling is done in a sorbent trap at a flow about 12 mL min⁻¹ that corresponds to a 165 mL sample volume in a 15-minute cycle. After sampling cycle, the trap is quickly heated to 35 to 380°C within 2 seconds to thermally desorb benzene and elute the same into GC column. Optimal separation in column is achieved by following a multi-ramp thermal cycle from 25°C to 160°C for flushing all the heavy compounds. The GC column is a stainless steel made (15 m × 0.25 mm × 1 µm, apolar). Measuring range of this instrument is maximum 1,000 µg m⁻³ with a lower detectable limit of ≤ 0.05 µg m⁻³ benzene and measuring noise of ≤ 0.025 µg m⁻³ at 0.5 µg m⁻³ benzene.

To record the prevailing meteorological conditions in the areas under study, meteorological data was collected from a portable meteorological station erected at a height of at least 10 meters at each refinery. Collection of meteorological data was carried out simultaneously with ambient air monitoring and windrose diagrams were prepared to understand and demarcate the zone (direction) of possible maximum pollutant concentrations during the study period. The study area maps are presented in Fig. 1.

2.5 Air Quality Modelling

USEPA's Industrial Source Complex Short Term (ISCST3) Model (used by ISC-AERMOD software) that is based on Gaussian plume dispersion and suitable for single or multiple emission sources, was applied for predicting average 24-hourly ground-level concentration (GLC) as influenced by stationary source emissions

(Cimorelli *et al.*, 1998). Earlier ISC3 model has been used in several studies to predict concentration of pollutants (Bhanarkar *et al.*, 2010; Bhanarkar *et al.*, 2005; Bhanarkar *et al.*, 2003; Abdul-Wahab *et al.*, 2002). Wind-speed and directions, two critical model input parameters, were recorded and processed according to the model requirement. The atmospheric stability classes were computed by using Turner's classification (Hanna *et al.*, 1982). By incorporating physical characteristics of emission source, emission rates, wind speed, wind direction, ambient temperature, stability classes and mixing height as inputs, dispersion modelling was carried out for predicting GLCs of pollutants within 5-km radius around the plant in winter. GLCs of SO₂ and NO₂ were modeled from their respective emissions from stacks by using ISC3 model and concentration contours over the study area were generated in order to identify the areas of concern. We have undertaken dispersion modeling by considering PM emissions from stacks, but in principle, we could consider PM primarily as PM₁₀, as refinery units are run on oil/ gas that are known to produce fine particles (Sánchez de la Campa *et al.*, 2011; Kulkarni *et al.*, 2007).

3. RESULTS AND DISCUSSION

3.1 Stationary Source Emission Assessment

In Refinery 1, the total emission load of PM, SO₂ and NO_x were found to range from 87.9–221.2 MT y⁻¹ (UB

and HRSG), 1.2–111.4 MT y⁻¹ (H2U and SRU) and 14.3–2033.9 MT y⁻¹ (SRU and HRSG), respectively. PM concentration in flue gas ranged from 48.4 to 144.9 mg Nm⁻³, the highest being from the utility boiler, but the emission load was highest (221.2 MT y⁻¹) in HRSG, followed by CCU (156.1 MT y⁻¹) and the lowest load was obtained from UB (87.9 MT y⁻¹) (Table 2). SO₂ was detected in the stack gas from all units, sulphur being a constituent in major raw materials. Highest SO₂ concentration and emission load were detected in SRU (646 mg Nm⁻³ and 111.4 MT y⁻¹, respectively) followed by UB (83.8 mg Nm⁻³ and 50.9 MT y⁻¹, respectively). Concentration of NO₂ was substantial in stack gas from all units, ranging from 57.8 to 445 mg Nm⁻³ corresponding to emissions of 24.3 and 2,034 MT y⁻¹, respectively. In CDU, concentration and emissions of CO were 6.07 mg Nm⁻³ and 5 MT y⁻¹, respectively. Concentration of PM, SO₂, NO₂ were well within the emission standards of MoEFCC in India.

In Refinery 2, the total emission load of PM, SO₂ and NO_x were found to range from 2.61–119.8 MT y⁻¹ (DHX 11 and COB), 9.65–656.3 MT y⁻¹ (DHX 11 and UB7) and 3.39–146.5 MT y⁻¹ (DHX 11 and CPP), respectively. The concentration of particulate matter in the stack gas was in the range of 8–99 mg Nm⁻³ and the emission load ranged from 2.6 to 119 MT y⁻¹ (Table 3). SO₂ emission was highest in UB 8/9 (935 mg Nm⁻³) and lowest in DHX11 (37 mg Nm⁻³) while NO_x concentration in stack gas ranged from 13 mg Nm⁻³ in DHX 11 to 235 mg Nm⁻³ in UB6, respectively. CO concen-

Table 2. Emissions of particulates and gases from stationary sources in Refinery 1.

Process/Unit	Fuel type	Fuel quantity (MT h ⁻¹)	Concentration (mg Nm ⁻³)			Emission load (MT y ⁻¹)		
			PM	SO ₂	NO _x	PM	SO ₂	NO _x
CDU	FO + FG	5.65 (including VDU)	ND	59	249	–	48.6	206.6
DCU	FO + FG	2.4	ND	45	227	ND	33.5	170.4
H2U	Naphtha	3.6	ND	3	58	ND	1.2	24.3
HCU1	FO + FG	2.2 (including HCU2)	ND	3	303	ND	2.9	322.3
HCU2	FG		ND	14	235	ND	15.1	252.4
HCU3	FO + FG	0.06	ND	50	217	ND	45.2	194.7
SRU	–	--	ND	646	83	ND	111.4	14.3
CCU	FO + FG	8.6	75.9	6	209	156.1	12.5	430.6
UB	FO + Naphtha	1.07	144.9	84	321	87.9	50.9	194.9
HRSG	Naphtha		48.4	7	445	221.2	31.9	2033.9
NHDT + CRU	FG		ND	6	105	ND	4.6	86.8

ND: Not determined (In many units, PM is not generated and hence not measured)

FO: Fuel Oil; FG: Fuel gas

Crude Distillation Unit (CDU); Delayed Coking Unit (DCU); Coke Calcination Unit (CCU); Hydrogen Generation Unit (H₂U); Hydrocracker Unit (HCU); Naphtha Hydrotreater/Hydro Desulphurisation Unit (NHDT/NHDS); Catalytic Reforming Unit (CRU); Sulphur Recovery Unit (SRU); Heat Recovery Steam Generator (HRSG)

Table 3. Emissions of particulates and gases from stationary sources in Refinery 2.

Process/Unit	Fuel type	Fuel quantity (MT h ⁻¹)	Concentration (mg Nm ⁻³)			Emission (MT y ⁻¹)		
			PM	SO ₂	NO _x	PM	SO ₂	NO _x
RH1	FO and FG	1.6	14	315	71	5.36	120.66	27.19
HH2	-do-	0.3	16	139	28	3.37	29.29	5.90
HH1	-do-	1.2	17	388	32	3.11	70.96	5.85
KH1	-do-	0.85	95	545	90	16.48	94.57	15.61
CH1	-do-	6.2	22	361	86	27.24	447.03	106.49
CH22	-do-	2.5	47	180	66	7.65	29.29	10.74
CH21	-do-	4.05	23	297	90	30.95	399.64	121.10
CH223	-do-	1.9	99	316	73	39.29	125.40	28.97
UB 8/9	-do-	6.0	43	935	199	12.55	272.91	58.08
DHX 11	-do-	5.0	10	37	13	2.61	9.65	3.39
SRU	-do-	0.13	42	734	86	4.74	82.84	9.71
CPP	-do-	5.8	8	173	70	16.74	362.08	146.51
UB 10	-do-	5.0	52	681	186	25.40	332.68	90.86
UB6	-do-	2.0	18	655	235	8.23	299.49	107.45
COB	-do-	2.55	93	121	62	119.80	155.87	79.87
UB7	-do-	4.8	72	563	70	83.94	656.33	81.60
UB 4/5	-do-	3.5	13	905	58	4.69	326.52	20.93
DDH1	-do-	0.85	22	285	85	5.32	68.93	20.56

RH1: Reformer charge heater (CDU1); HH1: Naptha splitter 2 heater/NHDS charge heater (NHDS); HH2: NHDS Stripper Reboiler (NHDS); KH1: Kerosene Unit Charge heater (KHDS); CH1, CH21, CH22: Crude charge heaters (CDU1, CDU2, CDU2); CH223: Vacuum heater (CDU); UB4/5, UB6, UB7, UB8/9: Utility boiler; DHX11: DHDS Unit (DHDS); CPP: PIB Heater; SRU: Sulphur Recovery Unit (SRU); UB10: HRSG; COB: FCC Charge heater (FCC); DDH1: Reformer charge heater (DHDS)

tration was 1–46 mg Nm⁻³. Concentration of PM, SO₂ and NO_x were also well within the emission standards of MoEFCC. An overview of emissions from refineries around the world indicated that emission loads of most of the air pollutants observed in this work were comparable or lower than that found in some other European, Canadian and Asian refineries (Table 4). High SO₂ emissions in Refinery 2 as compared to Refinery 1 might be due to use of high sulphur fuel oil as well as high amount of crude processing/ higher production capacity of Refinery 2 as compared to Refinery 1. High emissions levels of SO₂ have been reported by Rao *et al.* (2006) in 2004 at Gujarat Refinery in India with crude oil processing capacity of 13.5 MMTPA. Karbassi *et al.* (2008) also reported high SO₂ emissions at Tabriz oil refinery which used liquid fuels containing high sulphur.

3.2 Ambient Air Quality

The windrose diagram prepared for Refinery 1 indicated that prevailing wind direction was from North and Northeast direction, with the wind speed prevailing within a range of 2–5 m s⁻¹ (Fig. 1). Winds from other directions were also observed on a few occasions with a predominance of North-Western direction. Calm condition was significantly prevalent, in 44% cases. The 24-

hourly average levels of SO₂, NO₂, CO, benzene and PM₁₀ around the Refinery 1 prevailed within the limits promulgated in National Ambient Air Quality Standards (NAAQS) (CPCB, 2018a). Due to wind effect, higher concentration of pollutants are observed at sites located in downwind directions. SO₂ levels were always found to be low, while very low concentrations of NO₂ were found at one station (Table 5). On the other hand, CO was detected at all the locations. Benzene was detected at a few locations but was persistently low in concentration, ranging from 0.17 to 0.31 µg m⁻³. Maximum PM₁₀ concentration was 65 µg m⁻³ at location N1 followed by 53 µg m⁻³ at N4.

As per the windrose diagram for Refinery 2, the prevailing wind direction was from West-South West with wind speed mostly falling in the range of 0.5–2.1 m s⁻¹ (Fig. 1). Wind from the North-Western direction was also conspicuous. Higher wind speed of 2.1–3.6 m s⁻¹ were observed on a few occasions. Weather Conditions prevailing near the refineries during the month of monitoring showed substantial day-to-day variability in relative humidity, especially in the minima, while temperature and pressure variability were comparatively lower. As the monitoring exercises were undertaken during February in Refinery 1 and September in Refinery 2,

Table 4. Review of particulate and gaseous emissions and ambient air quality near refineries around the globe.

Refinery-City	Country	Year of study	Production/ crude processed (MT y ⁻¹)	Emissions (MT y ⁻¹ , unless specified)					Ambient air quality (µg m ⁻³ , unless specified)					Ref
				PM	SO ₂	NO _x	CO	HC/ VOC*	PM ₁₀	SO ₂	NO ₂	CO	HC/ VOC	
Gela Refinery-Sicily	Italy	1996	5320000	610	68000	7200	850	2050*	-	-	-	-	-	Bevilacqua and Braglia (2002)
Livorno Refinery	Italy	1996	4500000	155	13000	2000	152	170*	-	-	-	-	-	-do-
Priolo Refinery-Augusta	Italy	1996	8350000	480	17500	6400	380	2390*	-	-	-	-	-	-do-
Sannazzano Refinery-Padania	Italy	1996	8180000	440	4850	5200	430	2200*	-	-	-	-	-	-do-
Taranto Refinery	Italy	1996	3970000	440	8000	2250	305	1000*	-	-	-	-	-	-do-
Kaohsiung Refinery, Kaohsiung	Taiwan	2001	-	-	-	-	-	-	-	77 [#]	53 [#]	-	79 ^{+#} (benzene)	Chiu <i>et al.</i> (2005)
North Atlantic Refinery, Newfoundland	Canada	1998	-	-	23680	-	-	-	-	4.2-8.8	-	-	-	Fisher <i>et al.</i> (2003)
Corinth Refinery, Agioi Theodori, Corinthia	Greece	-	4750000	-	-	-	-	-	-	-	-	-	0.81 ⁺ (benzene)	Kalabokas <i>et al.</i> (2001)
Tabriz oil refinery-Tabriz	Iran	2004	408192	-	10963	6150	-	-	-	-	-	-	-	[62] Karbassi <i>et al.</i> (2008)
Mina Al-Fahal Refinery	Oman	-	39836289	-	315.0*	-	-	-	-	64.49	-	-	-	Abdul-Wahab <i>et al.</i> (2002)
Gujarat Refinery	India	2003	13500000	-	8203.7*	-	-	-	45-91	4-28	-	-	-	Rao <i>et al.</i> (2006), Rao <i>et al.</i> (2008)
Digboi Refinery	India	2003	650000	-	-	-	-	-	-	-	-	-	13.6-159.2 (benzene)	Pandya <i>et al.</i> (2006), Rao <i>et al.</i> (2007)
Chevron Burnaby Refinery	British Columbia	1998-2000	-	10.3-13.5	0.0021-0.0052 ⁺⁺	0.012-0.028 ⁺⁺	-	-	10.3-13.5	0.029-0.288	0.073-0.081	0.71-1.17 [§]	-	Kennedy <i>et al.</i> (2002)
Naphtha Cracking Complex	Taiwan	2009	450000 barrels day ⁻¹	-	6216	-	-	-	-	0.226-0.849	-	-	-	Shie <i>et al.</i> (2013)
Refinery, Montreal	Canada	-	-	-	-	-	-	-	-	4.4-6.9	-	-	-	Smargiassi <i>et al.</i> (2009)
Falconara	Italy	-	3900000	-	-	-	-	-	-	17.0	38.7	-	1.7 (benzene)	De Santis <i>et al.</i> (2004)
Refinery 1	India	2007	2568000	465.2	357.8	3931.2	5.0	0.0	38-65	3-8	3-9	0-525	-	This study
Refinery 2	India	2009	7680000	417.5	3884.2	940.8	88.1	0.0	46-79	3	4-7	130-501	-	This study

[#] day time concentration; ⁺⁺ ppm; ⁺ ppb; [§] avg. of 8-hourly maximum values in ppm; *estimated value considering 24 × 7 × 365 operation

average temperature difference between the refineries was about 4–5°C while temperature in Refinery 1 showed a slightly increasing trend due to approaching summer. In general, slightly higher concentration of pollutants are observed at sites located in downwind directions. Around Refinery 2 also, 24-hourly average levels of SO₂, NO₂, CO, benzene and PM₁₀ prevailed within the limits prescribed as NAAQS. In general, higher concentration of pollutants are observed at sites located in downwind directions. SO₂ levels were persistently low, while very low concentrations of NO₂ were found at a few stations (Table 5). Low ambient concentrations of SO₂ and NO₂ could be due to the location of refineries

in open land with almost no blockade that promoted good dispersion and dilution of pollutants. Also, negligible presence of polluting industries in the vicinity and low vehicular traffic ensured low levels of ambient SO₂ and NO₂. Low ambient levels of SO₂ and NO₂ have been reported by Central Pollution Control Board (CPCB) in 2008 and 2010 at a few cities and towns of India (<http://cpcb.nic.in/openpdffile.php?id=UmVwb3J0RmlsZX MvTmV3SXRLbV8xNDdfcmVwb3J0LTlwMDgucGRm; http://cpcb.nic.in/openpdffile.php?id=UHVibGljYXRpb25GaWxlLzYyOF8xNDU3NTA1MzkkX1B1Ym xpY2F0aW9uXzUyMF9OQUFRU1RjLnBkZg; both accessed on 22.2.2019>). CO and benzene were detected at all the locations but were low in concentration. However, benzene concentrations were found to be generally higher in this refinery than Refinery 1. Maximum PM₁₀ concentration was to the tune of 69 µg m⁻³ at site K3 followed by 61 µg m⁻³ in site K1. Observed ambient air quality in our study and ambient air quality around other petroleum refineries in several other countries was found to be comparable (Table 4).

Ambient concentration of PM₁₀, SO₂ and CO were converted to respective air quality indices (AQI) as per USEPA's concentration-AQI conversion principles and formulae (AirNow, 2018). It was noted that while AQI of CO never entered the zones of concern at any site and were always good, AQI of PM₁₀ were moderate at two sites, the rest being good (Table 6). In case of SO₂, no AQI could be calculated as SO₂ concentration values were outside the calculable range. AQI for NO₂ could

Table 5. Concentration of select criteria pollutants in ambient air.

Site code	PM ₁₀ (µg m ⁻³)	SO ₂ (µg m ⁻³)	NO ₂ (µg m ⁻³)	CO (µg m ⁻³)	Benzene (µg m ⁻³)
Refinery 1					
N1	65	5.0	9.0	171	ND ^a
N2	38	3.0	5.0	170	ND
N3	53	5.0	3.0	525	0.31
N4	53	8.0	5.0	430	0.17
Refinery 2					
K1	61	3.0	6.0	256	0.9
K2	52	3.4	5.2	388	1.2
K3	69	3.2	4.4	246	2.8
K4	51	3.4	4.0	380	4.4
K5	54	5.0	4.0	250	6.4
K6	46	3.0	4.0	501	1.6

ND: Not detected [^aLDL for Benzene = 0.05 µg m⁻³ benzene]
All the values are averages of 5 days.

Table 6. Conversion of ambient concentration to Air Quality Index (AQI).

Site code	USEPA ^a			CPCB ^b	
	AQI (PM ₁₀)	AQI (SO ₂)	AQI (CO)	AQI	Sub-index
Refinery 1					
N1	56 (moderate)	–	2 (good)	65 (satisfactory)	65 (PM ₁₀), 6 (SO ₂), 11 (NO ₂), 9 (CO)
N2	35 (good)	–	2 (good)	38 (satisfactory)	38 (PM ₁₀), 4 (SO ₂), 6 (NO ₂), 9 (CO)
N3	49 (good)	–	5 (good)	53 (satisfactory)	53 (PM ₁₀), 6 (SO ₂), 4 (NO ₂), 26 (CO)
N4	49 (good)	–	4 (good)	53 (satisfactory)	53 (PM ₁₀), 6 (SO ₂), 10 (NO ₂), 22 (CO)
Refinery 2					
K1	53 (moderate)	–	2 (good)	61 (satisfactory)	61 (PM ₁₀), 4 (SO ₂), 8 (NO ₂), 13 (CO)
K2	47 (good)	–	4 (good)	52 (satisfactory)	38 (PM ₁₀), 4 (SO ₂), 6 (NO ₂), 9 (CO)
K3	57 (moderate)	–	2 (good)	69 (satisfactory)	69 (PM ₁₀), 4 (SO ₂), 6 (NO ₂), 12 (CO)
K4	46 (good)	–	4 (good)	51 (satisfactory)	51 (PM ₁₀), 4 (SO ₂), 5 (NO ₂), 19 (CO)
K5	49 (good)	–	2 (good)	54 (satisfactory)	54 (PM ₁₀), 6 (SO ₂), 5 (NO ₂), 13 (CO)
K6	42 (good)	–	5 (good)	46 (satisfactory)	46 (PM ₁₀), 4 (SO ₂), 5 (NO ₂), 25 (CO)

N.B.: Missing values indicate 'out of range' returned by the calculator.

^aSource: USEPA (<https://www.airnow.gov/index.cfm?action=airnow.calculator>) [59]

^bSource: CPCB (<http://cpcb.nic.in/national-air-quality-index/>) [60]

not be calculated as the required 1-h average NO₂ concentration data needed for AQI calculation were not available. Further, AQI was also developed as per the formula AQI used by Central Pollution Control Board (CPCB) of India (CPCB, 2018b) (Table 6). Since all the eight pollutants included in AQI calculation was not monitored, AQI was calculated based on concentration of minimum necessary three pollutants amongst which one should be either PM_{2.5} or PM₁₀. Sub-indices were also generated for each pollutant to evaluate air quality status for that particular pollutant. The pollutant-wise calculated sub-index values for PM₁₀ ranged from 38–65 and 38–69 for refinery 1 and refinery 2 respectively. However, CO showed sub-index values varying between 9–26 and 9–25, respectively, for refinery 1 and refinery 2. Similarly, the sub-index values for NO₂ ranged from 6–11 and from 5–8, respectively, for refinery 1 and refinery 2, whereas for SO₂, it ranged from 4–6 for both the refineries. From the above calculations, it became apparent that AQI had never been poor under any circumstances at the selected sites, indicating no risk of significant health impacts to inhabitants residing near these refineries. Considering that clean burning fuels were used in these refineries and low PM concentration were obtained in stack gas from various units, AQI of all air quality monitoring stations in both the refineries were found to be satisfactory. Analysis of particulate-bound SO₄²⁻ and NO₃⁻ in filters containing either ambient particulates or stack gas particulates was not deemed crucial for drawing important conclusions. Hence, this aspect was kept out of scope of this work.

3.3 Dispersion Modeling

Air quality modeling exercise undertaken by ISCST 3 Model (used by ISC-AERMOD software) with the stationary source emission data of Refinery 1 revealed that major dispersion of PM, SO₂ and NO₂ occurred in southwest and northeast directions due to predominant winds patterns. However, the impact of refinery emissions was not significant and ambient air quality levels of these pollutants did not exceed NAAQS. The maximum modeled GLC of PM, SO₂ and NO₂ were 2.4, 2.6 and 14.9 µg m⁻³, respectively (Table 7). The isopleths of predicted concentrations for SO₂ in Refinery 1 are presented in Fig. 2a. In Refinery 2, predicted air quality generated by the model indicates that the maximum GLCs of PM, SO₂ and NO₂ were 2.1, 17.1 and 4.9 µg m⁻³, respectively (Table 6), which are lower than NAAQS and

Table 7. Summary of actual and predicted 24-hrly concentration of select criteria ambient air pollutants *vis a vis* regulatory standards.

24-hrly concentration	PM ₁₀ (µg m ⁻³)	SO ₂ (µg m ⁻³)	NO ₂ (µg m ⁻³)	CO (µg m ⁻³)	Benzene (µg m ⁻³)
Refinery 1					
Observed value	38–65	3–8	3–9	170–525	0–0.31
Modelled value	2.4*	2.6	14.9	NC	NC
CPCB standard	100	80	80	2 [#]	5 [§]
Refinery 2					
Observed value	46–69	3–5	4–6	246–501	0.9–6.4
Modelled value	2.1*	17.1	4.9	NC	NC
CPCB standard	100	80	80	2 [#]	5 [§]

*Particulate Matter (PM) concentration

[#]8-hourly avg. in mg m⁻³

**24-hourly avg.

[§]Annual avg.

NC - Modeling not conducted

occurred primarily in the eastern direction. The isopleths of predicted concentrations for SO₂ in Refinery 2 are presented in Fig. 2b. Maximum GLCs of these pollutants was observed within 3–4 km in eastern direction.

Low to moderate difference was observed between observed and modeled GLCs of the air pollutants which has been earlier reported by other researchers also (Abdul-Wahab *et al.*, 2002). The observed concentration of PM₁₀ in ambient air was found to be similar (Table 7) in both refineries as the total emission of PM from all stacks were similar in both. The concentrations for PM₁₀ in ambient air are higher than predicted values due to presence of other sources of particulates like vehicular emissions in nearby roads, fugitive dust emissions from nearby agricultural fields and road construction activities, emissions from other stationary sources that included small workshops and emissions from household biomass burning which were not considered by the model. The modelled values of PM by ISCST3 was also similar (2 and 3 µg m⁻³, respectively), that depended on the stack PM emissions and hence validated. Though the emission of SO₂ was much more in Refinery 2 than Refinery 1, the ambient concentration of SO₂ was similar in both, probably because of higher conversion of SO₂ into sulphate in the ambient air of Refinery 2, which is situated near sea shore. Conversion of SO₂ to sulphate on sea salt in atmosphere is reported (Alexander *et al.*, 2005) and hence, a predominance of this reaction might have played an active role in high conversion of emitted SO₂ near Refinery 2.

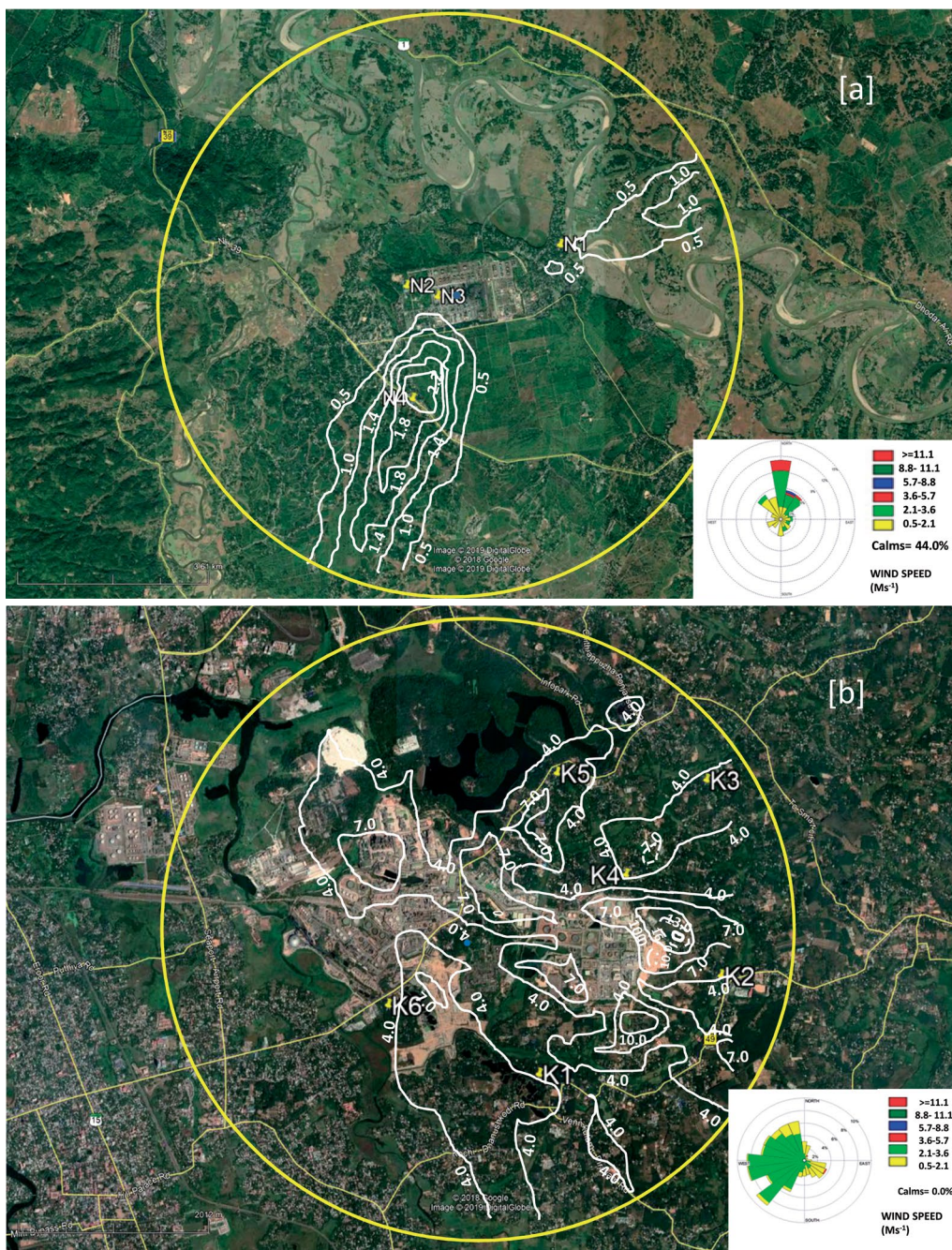


Fig. 2. Isopleths and windroses superimposed on maps showing predicted GLCs ($\mu\text{g m}^{-3}$) of SO_2 in (a) Refinery 1 (b) Refinery 2 and wind patterns, respectively [circles are of 5 km radius around the centres of refineries].

4. SUMMARY AND CONCLUSION

The results indicated that though SO_2 and NO_x were the major air pollutants released by the stationary sources in the refineries, ground level concentrations of SO_2 , NO_2 and PM did not exceed NAAQS followed in India.

Air quality in terms of AQI values was never poor under any circumstances at the selected sites. These refineries are located in non-industrial zones and hence no other industrial emission was present to further deteriorate ambient air quality. Observed GLCs of SO_2 , NO_2 and PM were predicted to a reasonable degree of accuracy

from the stack emissions by the model ISCST3 (used by ISC-AERMOD software), which was authenticated by the measured levels in ambient air.

Refineries are major sources of SO₂ and PM (Yateem *et al.*, 2011) that includes fine, deeply inhalable metalliferous atmospheric PM with high degree of chemical and size variation, along with hydrocarbons, VOCs, CO₂ etc. causing proximal and distal contamination in the long run and posing health risk to the inhabitants (Sánchez de la Campa, 2011; Holmgren and Sternhufvu, 2008; Karabassi *et al.*, 2008; Lin *et al.*, 2004; Cetin *et al.*, 2003). Considering these, further study is needed to focus on size distribution and chemical composition of particulate-bound metals and VOCs emanating from stationary sources in refineries to assess human health risk.

Although air quality in terms of SO₂, NO₂ and PM in the surrounding area of both the refineries did not exceed NAAQS and the AQI had never been poor, in order to maintain better air quality, low-sulphur fuels should be used in heaters and boilers of these refineries. Efficiency of SRU system should be monitored regularly to control SO₂ emissions to meet Indian emission standards specified by MOEF. Low NO_x burners should be used in all heaters and boilers to control emissions of NO_x from these refineries.

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