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Assessment of source contribution to ambient air quality through comprehensive emission inventory, long-term monitoring and deterministic modeling

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Abstract

In the present study, air pollution monitoring was carried out in Chennai city continuously for more than 3 decades from 1978 to 2016 and air quality trends are established for planning mitigation measures. An extensive air pollution monitoring network consisting of 19 sampling locations covering traffic corridors and intersections, residential, commercial and industrial areas was operated to monitor dust and gaseous pollutants, toxic trace metals, polycyclic aromatic hydrocarbons (PAHs) and other criteria pollutants. Comprehensive emission inventory indicated contribution of pollution load is mainly from transport (80%) followed by domestic (13%), industry (4%), commercial activities (2%) and power back generators (1%). The air pollutant concentrations were high during day time in winter season at traffic corridors, intersections and industrial areas. The monitoring data indicated PM_{10}, $PM_{2.5}$ and PAHs concentrations were exceeding the limits due to vehicular emissions, road condition (paved and unpaved), construction, industrial and commercial activities. Carbon monoxide and hydrocarbon concentrations were high during traffic peak hours and near road corridors where traffic congestion is high. GM, ATDL and ISCST3 models were employed to assess the contribution of air pollutants from transport, domestic and industry sector, respectively. Performance evaluation of models was also carried out by comparing monitored and model-predicted concentration to assess model prediction accuracy.

Introduction

Air pollution problem is the main issue in developing countries like India. Most of the cities worldwide have witnessed serious air pollution problems mainly due to increasing population, industrialization and automobile pollution (Mathew et al. 2015; Kumar et al. 2016). As a result, air pollution in the cities resulted in serious threat to the environment,

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people's life and health causing respiratory illness, cancer and other serious disorders (Abidin et al. 2014; Buonanno et al. 2013). Hence, for proper air pollution management program, assessment of air pollutants from various sources and analyzing their impact on air quality becomes the crucial step in planning mitigation strategies for reducing air pollution in the city (Gu et al. 2014; Panepinto et al. 2014).

The major sources of air pollution in Chennai city are automobiles, industries, commercial and household activities. Monitoring and modeling of air pollutants emanating from various sources on long-term basis helps to understand the distribution of air pollutants with reference to space and time. In this paper, the concentration of various gaseous pollutants, viz., sulfur dioxide (SO_2), nitrogen dioxide (NO_2), hydrogen sulfide (H_2S), ammonia (NH_3), carbon monoxide (CO), hydrocarbon (HC), volatile organic compounds (VOC), and dust pollutants, viz., total suspended particular matter (TSPM), respirable suspended particular matter (PM_{10}) and fine respirable suspended particular matter

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($PM_{2.5}$), in the ambient air in Chennai city was monitored on long-term basis. In addition, comprehensive emission inventory, monitoring of meteorological conditions and air quality and modeling were also carried out to assess the contribution from different sources on air quality in the city (Bhanarkar et al. 2005).

In order to establish long-term air quality status in 4 metropolitan cities, viz., Chennai, Delhi, Kolkata and Mumbai, and two other urban cities, viz., Hyderabad and Nagpur, CSIR-NEERI has been operating National Ambient Air Quality Monitoring Network (NAAQMN) for more than 3 decades (1978–2012). In this connection, CSIR-NEERI, Chennai, has been operating NAAQMN in select locations in Chennai city from 1978 onward covering the parameters dust (PM_{10}, $PM_{2.5}$), gaseous (CO, HC, SO_2, NO_2, H_2S and NH_3) and trace metals (Cd, Zn, Ni, Fe, Pb and Cr) in ambient air to understand cross-sectional variation of these pollutants in spatial and temporal variation.

Study area

Chennai is the 4th largest metropolitan city in India, encompassing an area of 176 km^2 with a population of 46.81 lakhs and density of 26,902 per km^2. It lies between latitude of 12°50′49″N and 13°17′24′N and longitude of 79°59′53″E and 80°20′12″E and is situated on the coromandel coast in South India on a flat coastal plain terrain. It is a main conveyance center for road, rail, air and sea routes connecting cities. A number of medium- and small-scale industrial developments were established in the last 3 decades. Also, Chennai city is emerging as a main export center in South East Asia. In addition, Chennai metropolitan area (CMA) extends over 1189 km^2 and includes Chennai city, 16 municipalities, 20 town panchayats and 214 villages in Thiruvallur and Kancheepuram districts.

Materials and methods

Emission inventory

Emission inventory was carried out to assess the contribution of different sources on the air quality. It is used as an important data in air pollution modeling exercise. Emission inventory for Chennai city is made for different air pollutants (CO, HC, NO_2, SO_2, TSPM and Pb) by grouping the emission sources into three broad categories: industrial, transport, domestic and commercial sectors. The details of these sources were collected in the field to quantify the source emissions and their characteristics, and these data were used for monitoring and modeling purpose.

Industry

Industries are the major source of revenue for India, especially for a metropolitan city like Chennai. The major industries operating in and around Chennai city are broadly classified as: Chennai port trust, thermal power plants, petroleum refinery, petroleum complex, pharmaceutical, rubber, paint and additive industries, etc. A comprehensive emission inventory was carried out to assess the pollution load from various types of industries in the city. For this purpose, necessary data like type, location, capacity, production details, raw materials and emission details were collected for each industry. Based on the emission inventory, the pollution loads from different types of industries were estimated for Chennai city.

Transport sector

Automobiles plying in the city are the main cause of air pollution and mainly contribute CO, HCs, NO_x and dust. Field survey was carried out at major traffic junctions in the city to assess the vehicle count and composition to quantify pollution load from transport sector. Also, data on the total registered automobiles and fuel consumption in the city were collected to assess the pollution load from the transport sector. The vehicles were categorized as two and three wheelers, cars, light commercial vehicles (LCVs), heavy vehicles (buses, lorries, trucks and road rollers) for this purpose, and pollution loads were estimated using the appropriate vehicle-type emission factors (Sivacoumar and Thanasekaran 2000).

Domestic sector

Household burnings from residential sector in the city also contribute significantly toward air pollution (Liao et al. 2015). A field survey was carried out to assess the emissions from household burning in the Chennai city covering high-, middle- and low-income categories. The collected data include number of people, fuel type and consumption, source of supply, availability and cost. Based on these data, emissions were estimated. The major fuels used for household burning in the domestic sector in the city include liquefied petroleum gas (LPG), kerosene, coal and firewood. The fuel consumption in the city is influenced by fuel availability, transport services and income of the people.

Meteorology

The concentration of air pollutants in the atmosphere is influenced by the magnitude of the emissions from various air polluting sources and the assimilative capacity of the atmosphere to disperse the air pollutants in the atmosphere. The prevailing micrometeorological conditions in the region

play a crucial role in pollutant dispersion in the atmosphere, and collection of these data is an important step in the air pollution study.

Weather station

An automatic weather system was kept in the field to monitor the micrometeorological conditions continuously during the study period. Principal meteorological variables, viz., wind speed, wind direction, temperature, humidity, pressure, solar radiation and rainfall, were recorded continuously for every 1-h interval during the study period to fix the sampling locations for air quality monitoring program. The wind rose was drawn using the observed meteorological data to assess the predominant wind direction and wind speed for all the 12 months in a year.

Selection of air sampling location

Selection of air sampling stations is mainly influenced by the terrain conditions and the prevailing wind pattern of the region. In this study, a monitoring network consisting of 19 sampling locations covering residential, transport, corridor and intersections, commercial and industrial areas was operated to monitor dust and gaseous pollutants, toxic trace metals, polycyclic aromatic hydrocarbons (PAHs) and other criteria pollutants (Figure 1).

In addition, toxic trace metals—chromium (Cr), nickel (Ni), cadmium (Cd), lead (Pb), iron (Fe) and zinc (Zn), and polycyclic aromatic hydrocarbons (PAHs)—fluoranthene (Fl), pyrene (Py), benzo (a) anthracene, benzo (b) fluoranthene [B(b)F] and benzo (a) pyrene [B(a)P] in PM_{10} ($<10\mu$) fractions—were also monitored because of their health implications and importance in formulating city-specific air resource management strategies (ARMS) (NEERI 2011). Pollutants were analyzed and reported for 24 h for comparison with standards to assess the air quality status of these locations (CPCB 2009).

Air sampling and measurement techniques

The air samples were collected at selected areas throughout the year, and concentrations of pollutants were estimated by chemical analysis in the laboratory. The details of the pollutant-specific sampling and/or analytical procedures for the determination of gaseous, dust, toxic pollutants, their sources and effects are summarized in Table 1.

Gravimetric method

Particulates were determined using gravimetric method. Sampling instruments such as high-volume sampler (HVS) (Envirotech Inst, APM 430 for TSPM) and respirable dust sampler (RDS) (Envirotech Inst, APM 460NL for PM_{10} and APM 550EL for $PM_{2.5}$) were employed to measure the particulates in ambient air. The particulates were collected on Whatman GF/A glass fiber filter paper using samplers operating at a flow rate of 1.0–1.3 m^3/min. Dust measurement was taken at regular intervals, and the values were reported on a 24-hourly basis to compare with national limits (CPCB 2009). The dust concentration was estimated by the weight difference of the filter paper prior to and after the sampling as per standard method (BIS 1999a) for TSPM and (BIS 2006a) for RSPM.

Analytical techniques

Primary gaseous pollutants were determined using colorimetric techniques where the ambient air is bubbled through the respective absorbing solutions and samples were analyzed for every 1 h by adding the respective reagents and measuring the percentage transmission using spectrophotometer. Sulfur dioxide (SO_2) in the ambient air was analyzed as per standard improved West and Gaeke method (BIS 2001) and nitrogen dioxide (NO_2) by modified Jacob and Hochheiser method (BIS 2006b).

Hydrogen sulfide (H_2S) was determined by methylene blue method, based on the reaction under suitable conditions, between N, N-dimethyl-P-phenylenediamine sulfate (dye), ferric chloride and sulfamic acid, resulting in the formation of methylene blue and measuring the absorbance at 670 nm. Ammonia (NH_3) in the atmosphere was measured by Nesslerization method where air passes through a dilute solution of sulfuric acid to form ammonium sulfate and was analyzed colorimetrically by reaction with Nessler's reagent and measuring the absorbance at 420 nm with 1-cm light path.

Instrumental methods

Carbon monoxide (CO) was measured in ambient air (hourly measurement) by standard method, non-dispersive infrared (NDIR) absorption spectroscopy (BIS 1999b), whereas HC/VOC was measured in low detection range of ppb in ambient air using flame ionization detector (FID) in a GC (BIS 2006c). Monitoring location was chosen in such a way to assess the pollutant contribution from traffic corridors as well as industries and other sources.

In addition, toxic trace metals were also analyzed by inductively coupled plasma atomic emission spectrophotometer (ICP-AES technique) (BIS 2004a). Sample of exposed PM_{10} filter paper was digested in nitric acid (using microwave digester) and analyzed for the metal constituents by ICP-AES method.

Polyaromatic hydrocarbons (PAHs) were analyzed by collecting air particulates on a fine particle (glass fiber) filter
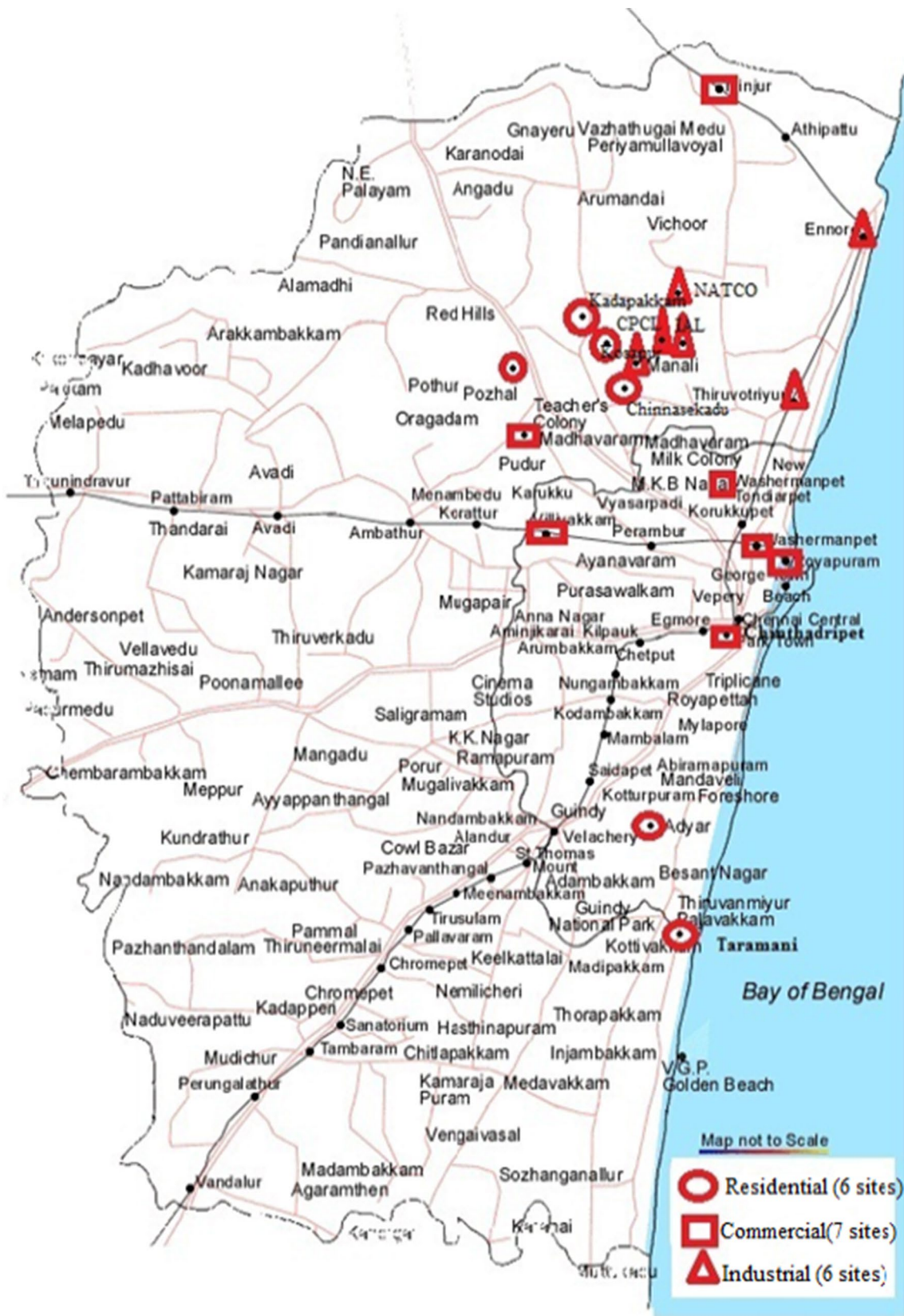
Fig. 1 Study area map

Table 1 Techniques used for ambient air quality monitoring

Pollutant		Techniques/analytical method and absorbance–wavelength, nm	Min. detectable limit, ($\mu g/m^3$)	Indian standards, (averaging period)	Sources	Environment and health effects
Particulate matter	TSPM, $\mu g/m^3$	Gravimetric (high-volume sampler)	5	200 (24 h)	Burning of diesel in vehicles, fossil fuels, application of fertilizers and pesticides, construction activities, industrial process, viz., steel making, mining, incineration, agricultural burning and operation of fire places and woodstoves	Produces haze, smoke and ash. Causes respiratory and cardiovascular illness and lung damage
	PM_{10}, (size less than 10 μm), $\mu g/m^3$	Gravimetric (respirable dust sampler)	5	100 (24 h)		
	$PM_{2.5}$, (size less than 2.5 μm), $\mu g/m^3$	Gravimetric (respirable dust sampler)	5	60 (24 h)		
Sulfur Dioxide (SO_2), $\mu g/m^3$		Colorimetric (improved West and Gaeke method), 560 nm	4	80 (24 h)	Oil, coal combustion in power stations, burning of fossil fuels, smelting and refining, open burning	Causes smog and acid rain affects plants and trees, causes irritation to eyes, nose and throat, causes lung problems including breathing problem and permanent damage to lungs
Nitrogen dioxide (NO_2), $\mu g/m^3$		Colorimetric (modified Jacob and Hochheiser method), 540 nm	9	80 (24 h)	Burning of fuels including gasoline and coal, combustion of fossil fuels in power plants, the use of fertilizers, bacterial oxidation of ammonia in soil	Photochemical smog, haze and acid rain, respiratory illness
Hydrogen sulfide (H_2S), $\mu g/m^3$		Colorimetric (methylene blue method), 670 nm	1	–	Pulp and paper manufacturing, metallurgical material handling, blast and steel furnaces, decaying vegetation and animal material, volcanic discharges, coal pits and sewers	Exposure to low concentrations causes headache, nausea, collapse, coma and may lead to death due to respiratory failure
Ammonia (NH_3), $\mu g/m^3$		Colorimetric (Nesslerization method), 420 nm	5	400 (24 h)	Inorganic chemicals and fertilizer manufacturing	Irritation to eyes, throat and affects respiratory system, highly corrosive in nature
Carbon monoxide (CO), mg/m^3		Non-dispersive infrared (NDIR) spectroscopy	1	4 (1 hourly)	Oil, coal, petrol and diesel fuel combustion	Photochemical smog reduces oxygen-carrying capacity in blood, causes headache, drowsiness and fatal at higher concentration
HC/VOC's benzene (C_6H_6), $\mu g/m^3$		GC-based continuous analyzer technique	1	5 (annual average)	Automobile emissions particularly two/three wheelers utilizing two-stroke engines, burning fuel, such as gasoline, wood, coal, natural gas and from solvents, paints, glues	VOC, especially benzene, causes carcinogenic effects on lung tissues, indirect effects on eyes, nose and throat irritation due to formation of smog
Lead (Pb), $\mu g/m^3$		Inductively coupled plasma (ICP)-atomic emission spectrometry after sampling on EPM 2000 or equivalent filter paper	0.002	1 (24 h)	Leaded petrol in cars, paints, smelters	Neural issues in children, digestive problems and some lead containing substances causes cancer

Table 1 (continued)

Pollutant	Techniques/analytical method and absorbance–wavelength, nm	Min. detectable limit, ($\mu g/m^3$)	Indian standards, (averaging period)	Sources	Environment and health effects
Arsenic (As), ng/m³	AAS/ICP method after sampling on EPM 2000 or equivalent filter paper	1	6 (annual average)	Use of inorganic pesticides in agriculture, metal refining, burning of coal, also present in tobacco	Poisonous and leads to loss of weight and appetite accompanied with gastrointestinal disorders, also causes cancer in lung and skin
Nickel (Ni), ng/m³	AAS/ICP method after sampling on EPM 2000 or equivalent filter paper	1	20 (annual average)	Used in petrochemical and electrical industries, household appliances	Inorganic nickel is carcinogenic in human
Benzo (a) pyrene [B(a)P] particulate phase only, ng/m³	Solvent extraction followed by HPLC/GC analysis	0.01	1 (annual average)	Coal production, vehicle disposal, wood burning, forest and agriculture burning, tire degradation, municipal incineration, petroleum refining and coal furnace	High concentrations are linked to carcinogenic or co-carcinogenic risk, Causes potential effects on reproduction and immunity reduction

using air samplers and subsequent analysis by gas chromatography (GC) using flame ionization detector (FID) (BIS 2004b).

Quality assurance in air quality monitoring program

The quality of data generated during air quality monitoring program needs to be accurate and reliable, if the data are to be used for decision-making purpose and applied for planning control strategies for air pollution problems. Quality assurance for the monitored data is primarily carried out by proper calibration of all the instruments used in the field and laboratory by comparing with the standards.

Data collection, handling and analysis

Diurnal variation

Gaseous pollutants, viz., SO_2, NO_2, H_2S, NH_3, CO, HCs, and dust pollutants, viz., TSPM, PM_{10}, and $PM_{2.5}$ concentrations, were monitored for every 1 h, and diurnal variation of these pollutants was estimated for each month in the year. The other pollutants, viz., toxic trace metals and PAHs, do not show much variation, and hence, diurnal studies were not carried out for those pollutants.

Trend analysis and seasonal variation

Trend analysis is used to measure the monthly, seasonal and yearly trends of pollutants in the city. In this study, gaseous, dust pollutants, toxic trace metals and PAHs were monitored continuously for 24 h in each month. The air quality trends and seasonwise variations were analyzed accordingly to assess the long-term air quality trends.

Spatial analysis

Spatial analysis plays a crucial role in assessing the cross-sectional variation of pollutants. Methodically designed 19 sampling locations as explained in "Selection of air sampling location" section were employed to assess the spatial and temporal variation of pollutants.

Long-term air quality trend for Chennai city

CSIR-NEERI has been operating a national ambient air quality monitoring network in selected Indian urban cities particularly in Chennai for more than 3 decades since 1978. This long-term air quality database is highly useful in assessing the air quality trends in the city to facilitate the policy decisions for mitigating air pollution problems.

Air pollution modeling using ISCST3, GM and ATDL models

Meteorology plays an important role by dispersing the pollutant in the horizontal and vertical direction of the atmosphere. Modeling was carried out to assess the contribution of air pollutants from industry, transport and domestic sectors. For modeling industrial emissions Industrial Source Complex Short Term, ISCST3 (USEPA 1995) model was identified. The Air Turbulence and Diffusion Laboratory (ATDL) model was applied for modeling domestic sources considering these sources as area sources releasing emissions from near to ground surface (Briggs 1973). The General Motors (GM) model was employed for modeling of vehicular emissions, since these sources are mobile in nature and considered as line source for modeling purpose (General Motors 1985).

The selected models were employed to predict CO, HC, SO_2, NO_2 and SPM concentrations in Chennai city with a grid size of 100 m × 100 m covering the entire city.

Assessment of models performance

Assessment of models performance was done by comparing the monitored data (O_i) with model predictions (P_i) to assess its accuracy and error involved while modeling (Sivacoumar et al. 1999; Sivacoumar and Thanasekaran 1999). The parameters used are observed and predicted mean ($\bar{O}, \bar{P}$), standard deviation (σ_o and σ_p), variance of the difference, fractional bias (FB), mean fractional bias (MFB), mean fractional error (MFE), correlation coefficient γ, regression constant and coefficient and difference measures index of agreement 'd' and the total and mean square error (MSE) and its components, the mean systematic error (MSE_S) and mean unsystematic error (MSE_U). These statistical parameters along with target and model efficiency score (MES) were calculated to assess the model performance based on monitored air quality data collected from 19 monitoring locations in Chennai city.

Health assessment

Health assessment of people exposed to air pollution included general clinical, pulmonary function and blood sample test (Sivacoumar et al. 2006). The general test included questionnaire and a physical test. Pulmonary function test was performed using a portable data logging spirometer according to the procedure of the American Thoracic Society (ATS 1991). The blood samples were analyzed for white blood cells and eosinophil count to assess dust exposure levels on the people.

Results and discussion

Emission inventory

Industry

About 2800 industries operating in the study area are broadly classified into 3 categories, viz., red (highly polluting), orange (medium polluting) and green (less polluting) considering their pollution potential (CMDA 2016). They constitute about 51% (red), 34% (orange) and 15% (green), respectively. The red, orange and green category industries were further subdivided into large-, medium- and small-scale industries based on their production capacity and fuel consumption pattern. Red category industries comprised of large (11%)-, medium (10%)- and small (79%)-scale industries; orange category industries comprised of large (5%)-, medium (26%)- and small (69%)-scale industries; green category industry comprised of large (1%)-, medium (19%)- and small (80%)-scale industries, respectively, indicating that the industry sector in Chennai city is mostly dominated by small-scale industries considering the history and development pattern of the city with limited availability of land along the coastal areas. The city is generally bustling with transport, commercial and port-related activities rather than industrial activities.

The data of industries in Chennai city along with raw material, products, emissions and their characteristics are given in Table 2. Specific information on stack characteristics, viz., height, radius and flue gas temperature, velocity and concentration, was also gathered in the field to quantify the pollution load from the industry sources and is used for modeling. The pollutant contribution from the industry sector is about 21.275 MT/day.

Transport sector

The total vehicle pollution load from different categories of vehicles in the transport sector is 1637 MT/day. The major air pollutants are CO (65%) followed by HC (30%), NO_2 (4.2%), SO_2 (0.6%), TSPM (0.09%) and Pb (0.03%). Two wheelers significantly contribute toward total pollution load (60%) among all categories of vehicles followed by cars and taxis (28%), three wheelers (7%), lorry

Table 2 Emission inventory for industry in the study area

S. no.	Name/type of the industry	Raw material used	Products	Sources of emission	Pollution load, MT/day			
					SO_2	NO_2	TSPM	HC
1.	Petroleum industries	Crude oil, coal	Petrol, LPG, naphtha, motor spirit, kerosene, diesel oil, wax, sulfur, aviation turbine fuel, lube base oil, hexane, propylene and poly-butyne.	Stacks emission, fugitive emission, emission from storage yard, vehicle movement, leaks from joints and valves, construction activities	4.34	1.55	0.44	0.041
2.	Thermal power plant	Bituminous coal	Power generation (capacity 450 MW)	Stacks emission, fugitive emission, vehicle movement	1.210	2.823	0.121	0.027
3.	Fertilizer industries	Naphtha, Natural gas, CO_2	Chemical and biofertilizers, agro-chemicals	Stacks emission, fugitive emission, vehicle movement, emission from storage yard	0.961	2.192	0.098	0.021
4.	Petro chemical industries	Ethylene oxide, propylene oxide Butane	Propylene oxide, propylene glycol and polyols Isobutylene	Stacks emission, fugitive emission, vehicle movement, construction activities	0.323	0.852	0.033	0.008
5.	Petro products industries	Crude oil, coal, HSD	Alkyl benzene, HCL, epichlorohydrin, caustic soda, ammonium chloride	Stacks emission, fugitive emission, vehicle movement, construction activities	0.189	0.421	0.016	0.004
6.	Fiber industries	Polyester	Synthetic polyester nylon	Stacks emission, fugitive emission	0.245	0.569	0.028	0.005
7.	Polymer industries	Polymer	Polyethylene terephthalate (PET), polybutylene terephthalate (PBT),etc.	Stacks emission vehicle movement	0.096	0.225	0.009	0.002
8.	Grease and lubricant industries	Crude oil, synthetic oils, LDO	Industrial greases and lubricants, performance chemicals	Stacks emission, vehicle movement, fugitive emission	0.126	0.322	0.015	0.003
9.	Indian additives industries	Crude oil, synthetic oils	Lubricant	Stacks emission, vehicle movement, fugitive emission	0.163	0.365	0.019	0.004
10.	Organic industries	Cytotoxic and bio-technology-based medicines	Medicines 9.5 kg/month	Stacks emission, vehicle movement, fugitive emission, leaks from joints and valves	0.129	0.321	0.014	0.003
11.	Rubber industries	Rubber	Tyres	Stacks emission, vehicle movement, fugitive emission, leaks from joints and valves	0.886	1.956	0.088	0.012
Total emissions					8.668	11.596	0.881	0.130

and trucks (2%), buses (2%), LCV (1%) and road rollers (0.001%). The percent contribution of pollutants by various types of vehicles categorywise is given in Table 3.

Domestic sector

The population pattern in Chennai city is a mixture of urban and suburban area. Field data represented most of the emissions from residential burning were during morning 06:00–10:00 h and evening 18:00–22:00 h. The contribution of total pollution load from different categories of fuels was fire wood (60.1%), followed by crop residues (20.1%), dung cake (8.95%), kerosene (5.6%), coke (4.4%) and LPG (0.89%), respectively. The estimated pollution load from domestic sector was 257 MT/day. The major air pollutants are CO (46.1%) followed by HC (43.8%), TSP (6.6%), NO_2 (2.3%) and SO_2 (1.2%). Based on the

Table 3 Total emissions from transport sector in Chennai city

S. no.	Vehicle type	Composition, %	Growth rate, % (1990–2013)	Fuel consumption, KL/day	Pollutant emission[a], %					
					CO	HC	NO$_2$	SO$_2$	Pb	TSPM
1.	Two wheelers	78.79	26.67	710.3	36.9	23.1	–	0.1	0.01	–
2.	Cars	16.00	20.62	478.5	23	3.4	1.5	0.1	0.01	–
3.	Three wheelers	2.08	71.94	71.7	4	2.5	–	0.009	0.002	–
4.	Buses	0.29	21.46	584.8	0.6	0.2	1.1	0.2	–	0.04
5.	Lorries and trucks	1.37	18.73	688.8	0.6	0.2	1.2	0.2	–	0.04
6.	Light commercial vehicles	1.56	29.44	458.6	0.3	0.1	0.5	0.1	–	0.02
7.	Road rollers	0.01	8.5	0.54	0.0003	0.0001	0.0007	0.0001	–	0.00002

[a]Total pollution load = 1636.73 MT/day

comprehensive emission inventory survey carried out and the data presented in Tables 1, 2 3 and Table SM1, it can be concluded that the major contribution of pollution load in the city is mainly from the transport sector (80%) followed by domestic sector (13%), industry (4%), commercial activities (2%) and power back generators (1%).

Meteorology

Weather station

The wind speed and direction were plotted in the form of annual wind rose as shown in Fig. SM1. The annual wind rose pattern implied that the predominant wind direction was from NE (15.4%) followed by NEE (9.6%), SEE (7.9%), SSE (7.8%), SSW (7.7%), SWW (7.6%), NWW (7.5%), NNW (7.4%), SW (5.8%), NNE (4.1%), SE (4.0%), W (3.8%), NW (3.7%), E (2.0%) and S (1.9%). The most prevailing wind speed was in the range 1–5 kmph (46.2%) followed by 10–15 kmph (23.1%), 5–10 kmph (19.2%) and 15–20 kmph (7.7%).

The calm condition (< 1 kmph) observed during the study period was about 3.8% with mean speed of 6.1 kmph. The average temperature recorded during the study period varied from 20.7 to 33.7 °C with a maximum temperature of 42 °C in the month of May. The average humidity (%) varied from 64.5 to 83.21%.

Diurnal variation

The diurnal concentration of air pollutants for residential area during the year 2010 is shown in Figs. 2, 3 and 4. Similarly, the diurnal variation graphs were drawn for commercial and industrial areas. The results from diurnal studies indicated that the peak concentrations of SO$_2$ occur in the day time mainly due to emissions from industries, domestic

burning and commercial activities in the morning hours. The peak concentrations of NO$_2$ occur during noon hours due to emissions from automobiles plying in the traffic corridors, industries, domestic and commercial activities. H$_2$S occurs in the night hours mainly due to emissions from pits, sewers and also industrial processes; peak values of NH$_3$ occur during evening and night hours without much variation throughout the day. NH$_3$ emissions are mostly from industries. Since the atmospheric dispersion/dilution is high during daytime and less in the night time, high concentration of ammonia was observed in the evening and night hours.

The high concentration of SPM and PM$_{10}$ occurred mostly during the day hours mainly due to continuous vehicular movement, re-suspension of dust on the roads, incineration activities and construction and industrial activities in the day time. The CO and HC concentrations were high in peak traffic hours (morning and evening) mainly due to vehicular activities and industrial emissions. In particular, a high concentration of CO and HC was observed near traffic corridors and the concentrations drop rapidly away from the road. (After 100 m from the road, the concentrations were within the limits.)

Air quality trends

Gaseous and dust pollutants

The air quality trend of gaseous and dust pollutants for traffic corridors and intersections, residential, commercial and industrial areas is shown in Fig. 5. The results indicated that the peak values of all pollutants (gaseous and dust) except NH$_3$ occurred in the month of January and December and generally exhibited decreasing trend from February to November. Also, the air quality trends for SO$_2$, NO$_2$ and H$_2$S showed not much variation throughout the year, whereas the trend of NH$_3$ showed variable peaks due to difference in
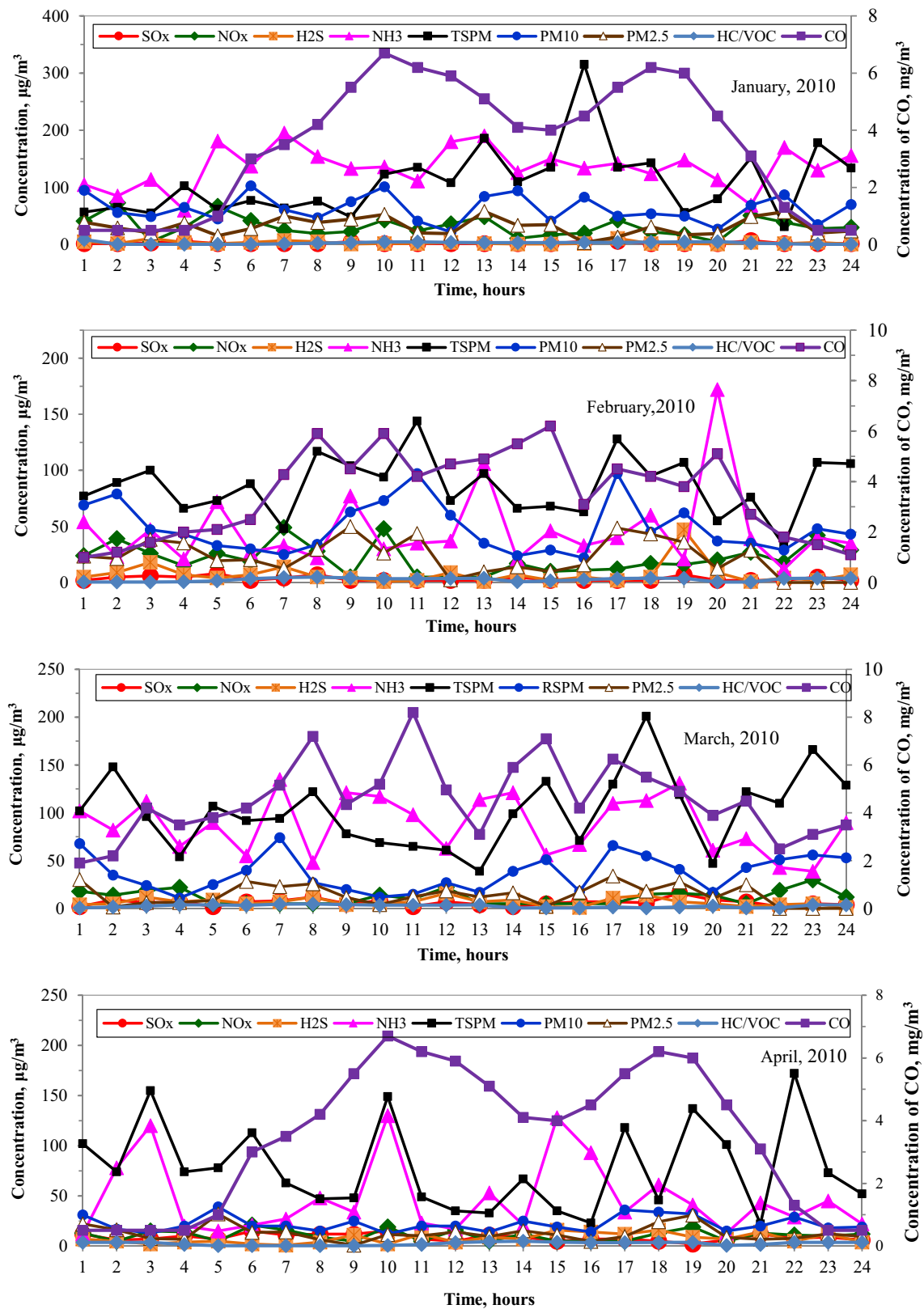
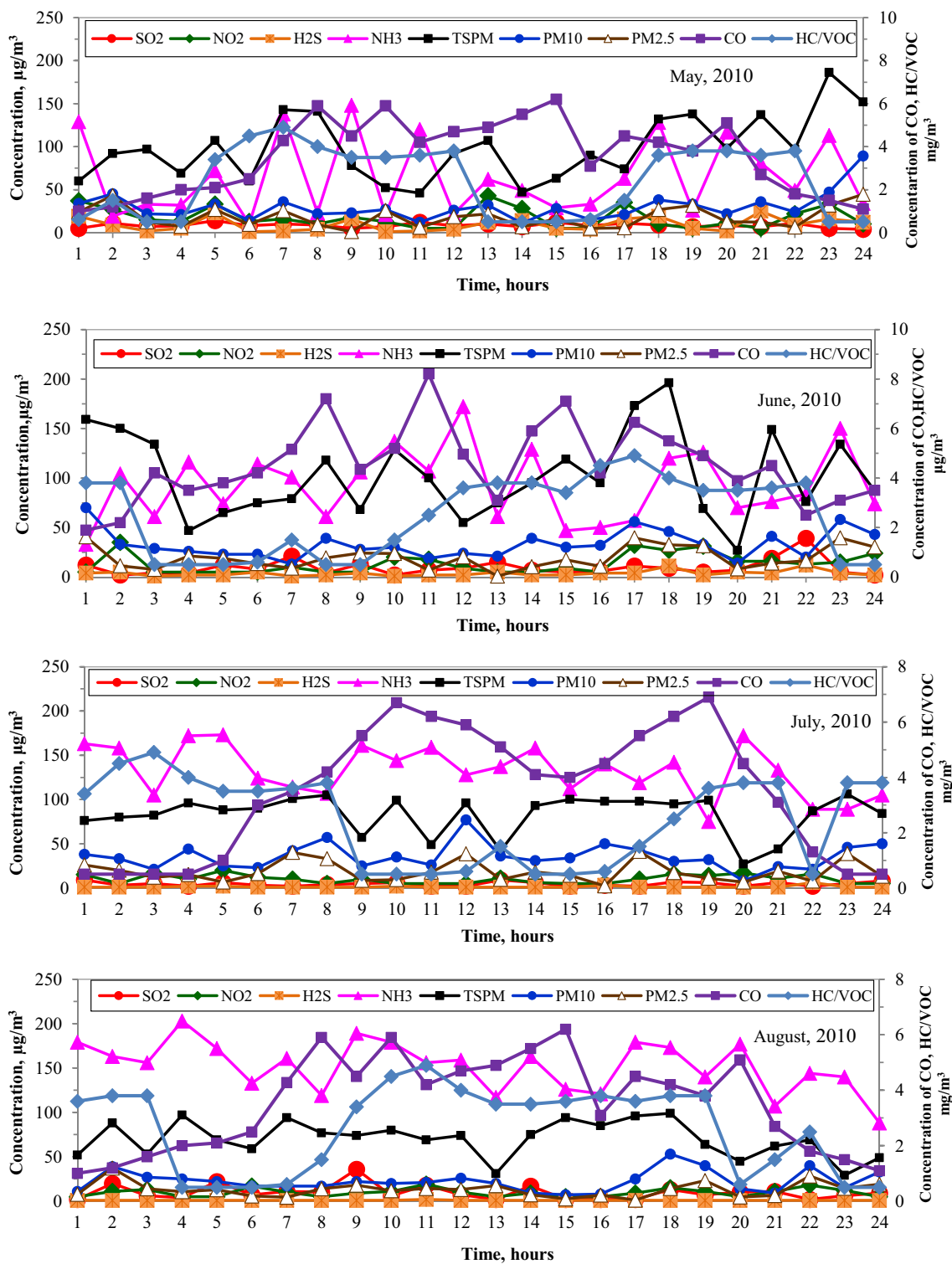**Fig. 2** Diurnal variation of air pollutants: residential site (January–April 2010)

Fig. 3 Diurnal variation of air pollutants: residential site (May–August 2010)

the atmospheric dispersion conditions, even though NH₃ is emitted mostly from industries.

Similarly, the peak concentration of dust pollutants, viz., TSPM, PM₁₀ and PM₂.₅, occurred in the month of January

and December, and the trends showed variable peaks mainly due to variation in atmospheric conditions, continuous vehicular movement in day time and industrial activities. Also, PM₁₀/TSPM ratio varied from 0.28 to 0.78 and was
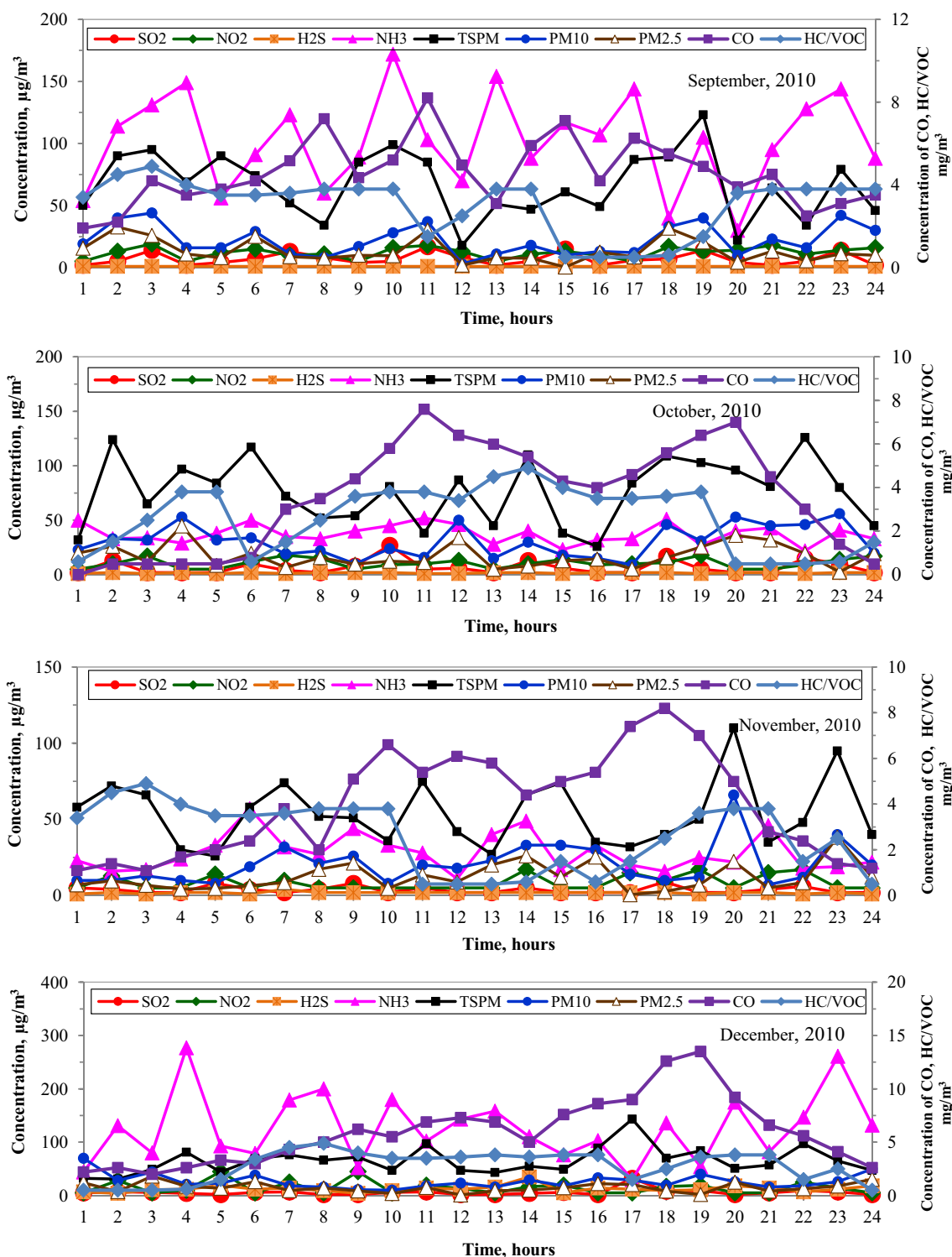
Fig. 4 Diurnal variation of air pollutants: residential site (September–December 2010)

high in the month of January. Thus, both the gaseous and dust pollutants were high in the winter season as compared to other seasons. The concentration of all gaseous pollutants was within limits except dust pollutants (TSPM and PM_{10}).

Toxic trace metals

Among the toxic trace metals, the concentration of cadmium and chromium was below the detectable limit. The peak
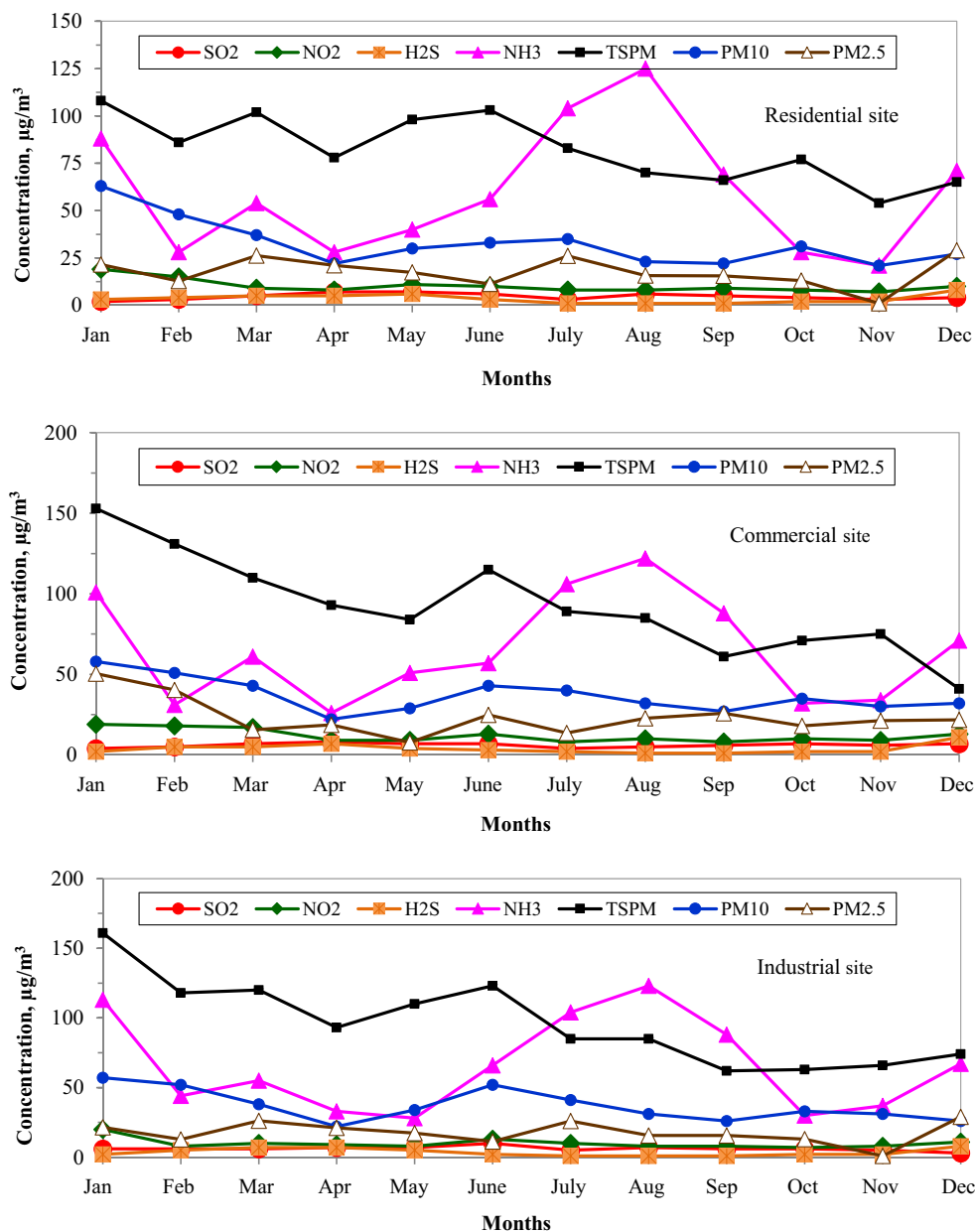
Fig. 5 Monthly air quality trends in Chennai city: 2010

concentrations of zinc and nickel, iron and lead occurred in the months of December and January, respectively (Fig. SM2). The trend of zinc showed variable peaks, whereas the other pollutants did not exhibit much variation. Toxic trace metals exhibited neither seasonal nor yearly trends which indicated that these concentrations are localized ones. Also, the concentrations of all these toxic pollutants were within limits. The concentration of zinc was higher when compared to nickel, iron and lead. The peak concentrations of toxic trace metals occurred during winter.

Polycyclic aromatic hydrocarbons

The monthly concentration levels of benzo-azo pyrene and its isomer in the respirable dust fractions varied from 15 to 42 ng/m^3 (Fig. SM3). The peak concentration of benz (a) anthracene and benz (b) fluoranthene occurred in the month of January, whereas for benz (a) pyrene it occurred in the month of September. The PAH concentrations observed here were associated with the inhalable fractions (< 10 µm), which are the cause for health issues and were

higher in winter season. This is due to low temperature, less solar intensity and variation of emissions during winter season (Karar and Gupta 2006; Hong et al. 2007).

Since the data consist of benzo-azo pyrene along with its isomers, the annual average concentration was higher than the permissible limit of 1 ng/m^3. The higher concentration of PAHs poses health issues due to their carcinogenic or co-carcinogenic nature (Bostrom et al. 2002) and their influence on reproduction and immunity (US-ATSDR 1995: Marr et al. 2004; Sharma et al. 2007).

Thus monitoring studies indicated that particulate pollutants and PAHs concentrations were above the limits and pollutant concentrations were high during winter season. This is because of less atmospheric dispersion condition in winter season which in turn causes more accumulation of pollutants. Air pollutants were less in monsoon season due to 'wash-out phenomena' by monsoon rains (Ravindra et al. 2003). Particulate matter concentrations were high in all the locations due to suspension of fine particles in ambient air because of vehicular movements, road dusts, commercial activities and industrial emissions.

Spatial variation of air pollutants

Air pollutants were generally high in major traffic corridors and traffic intersections, industrial areas followed by commercial and residential areas. The annual average concentration of air pollutants in Chennai city showed that the concentration of NO_2, PM_{10}, $PM_{2.5}$ and HC was higher in commercial area due to road traffic emissions, re-suspension of dust particles and construction activities, whereas CO, NH_3 and TSPM were higher in industrial area mainly due to emissions from industries and vehicular activities (Fig. SM4). Other pollutants, viz., SO_2, H_2S, PM_{10} and $PM_{2.5}$, were higher in both industrial and commercial areas due to emissions from industries and commercial activities. The concentrations of CO and HC were high in locations near traffic corridors where traffic congestion is high. The annual average and percentile concentrations of gaseous and dust pollutants are given in Table 4.

Long-term air quality trend for Chennai city (1978–2013)

Residential area

The trends of air pollutants over the year 1978–2012 are plotted in the form of trend graphs as shown in Fig. 6. The concentration of SO_2, NO_2 and H_2S showed not much variation over the years. The concentration of NH_3 showed slight variation from 1978 to 2008, and an increase in NH_3 concentration was observed from 2008 with peak concentration of

Table 4 Ambient air quality status in the study area, μg/m^3

Site	Pollutants	Min.	Max.	Mean		SD	Percentiles						Standard
				AM	GM		10	25	50	75	95	98	
Residential	SO_2	2	20	5	4	3	2	3	4	5	10	15	80
	NO_2	4	48	10	9	7	5	5	8	12	20	32	80
	H_2S	1	19	3	3	3	1	2	2	5	9	12	–
	NH_3	7	172	59	45	42	14	21	44	95	142	149	400
	TSPM	29	158	82	78	28	49	62	77	101	132	147	200
	PM_{10}	5	95	32	29	16	17	21	29	37	67	74	100
	$PM_{2.5}$	5	29	17	14	8	7	10	14	18	24	27	60
Commercial	SO_2	1	25	6	5	4	2	3	6	8	13	17	80
	NO_2	5	43	12	10	7	5	6	9	14	26	27	80
	H_2S	1	19	4	4	3	1	1	2	5	10	15	–
	NH_3	4	167	64	47	47	15	28	44	101	155	159	400
	TSPM	5	204	90	73	43	41	70	86	114	168	179	200
	PM_{10}	5	87	37	33	16	20	23	37	44	64	77	100
	$PM_{2.5}$	8	50	23	12	21	12	7	10	15	30	35	60
Industrial	SO_2	2	22	6	5	4	3	3	5	7	15	17	80
	NO_2	3	29	10	9	5	5	6	8	11	21	25	80
	H_2S	1	17	4	4	2	1	1	2	4	13	15	–
	NH_3	8	175	66	47	49	14	26	53	103	145	170	400
	TSPM	24	258	97	89	41	52	73	90	116	164	207	200
	PM_{10}	14	107	37	33	17	19	24	33	46	64	79	100
	$PM_{2.5}$	10	50	23	21	11	11	14	21	28	41	46	60

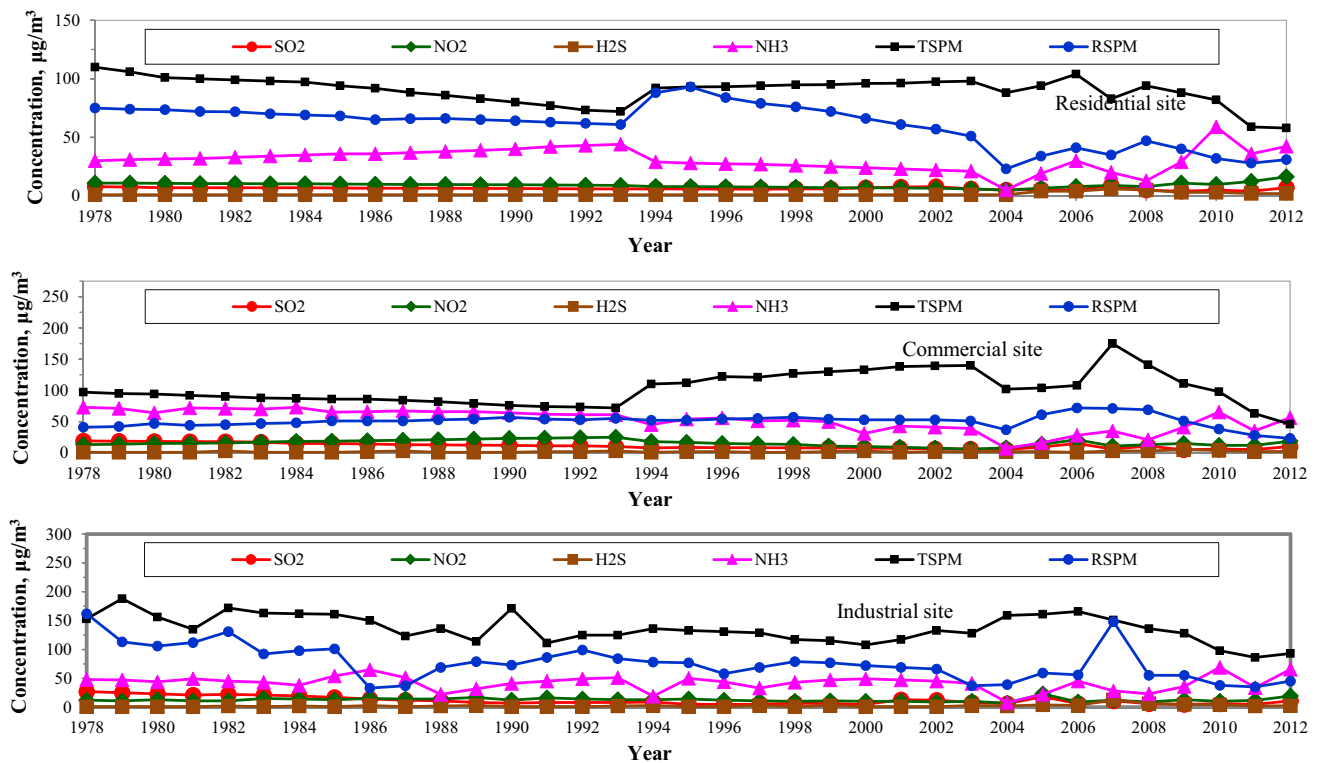**Fig. 6** Annual air quality trends in Chennai city: 1978–2012

59 μg/m³ in 2010. The concentration of RSPM and TSPM showed decreasing trend from 1978 to 1993, exhibiting an upward trend during 1994–2003 followed by decreasing trend during 2004–2012.

Commercial area

The concentration of SO_2, NO_2 and H_2S showed not much variation as in residential area. Similarly, the concentration of NH_3 showed not much variation during 1978–2003, with decrease in concentration during 2004–2006. The concentration of TSPM showed a decrease in trend from 1978 to 1993, with an upward trend during 1994–2010 followed by decreasing trend during 2011–2012, whereas RSPM followed more or less the same trend as TSPM.

Industrial area

The concentration of SO_2, NO_2 and H_2S in the industrial area also showed not much variation as in the case of other areas. Also, the concentration of NH_3 showed not much variation and dust pollutants (TSPM and RSPM) showed oscillating trend.

Thus, the air quality trends showed that the concentrations of SO_2 and NO_2 were gradually decreasing over the years which are due to improvement in quality of fuel in transport sector and implementation of desulfurization plants in industries where coal is used as raw material. The concentrations of ammonia and dust pollutants (SPM) showed variable peaks and were within the limits. Hence, proper laying of roads and dust suppression measures are to be taken to control the transport of dust which is a serious health hazard causing respiratory illness.

Air pollution modeling using ISCST3, GM and ATDL models

The modeling was carried out using source information (number, nature, type and dimensions), emission rates, meteorological conditions and source-receptor geometry to assess the contribution from different sources in the city. These models provide an estimation of air pollutants at required locations. In this work, modeling was done for 24-hourly basis covering entire Chennai city and its surrounding areas. The ground-level concentrations (GLCs) of all the pollutants

were predicted in a grid size of 100 m × 100 m covering entire Chennai city to assess the concentration gradient of pollutants in fine resolution.

The model-predicted concentrations of SPM varied from 53 to 85 µg/m^3 with the mean value of 55 µg/m^3 and the peak concentration occurring at Washermanpet location (Fig. SM5). The concentrations of SO$_2$ varied from 2 to 15 µg/m^3 with the average value of 8 µg/m^3 and the peak value occurring at Kosapur location. The concentration of NO$_2$ varied from 4 to 21 µg/m^3 with the mean value of 10 µg/m^3 and peak concentration occurring at Thiruvottriyur location. Modeling indicated air pollution contribution from transport, domestic and commercial and industry sectors is about 75%, 15% and 10%, respectively.

Model performance evaluation

Model performance evaluation was carried out by comparing measured and model-predicted concentrations at 19 locations using statistical analysis. The summary of the statistical analysis showed that the difference in observed and predicted means was least for NO$_2$ (0.3 µg/m^3) and maximum for SPM (2.7 µg/m^3) (Table SM2). Index of agreement 'd' indicating the accuracy of the model was 86%, 70% and 61% for SO$_2$, NO$_2$ and SPM, respectively (Fig. SM5). The RMSE indicated that the error was minimum for NO$_2$ (3.2 µg/m^3) followed by SO$_2$ (3.6 µg/m^3) and SPM (17.2 µg/m^3), respectively.

Health assessment

Clinical examination consisting of a physical evaluation followed by questionnaire was performed for people living near/working in the industries, traffic junction and commercial areas to determine the ill effects of pollutants. It was observed that all the people were found to be normal in physical examination, and 1/20 of the people suffered from respiratory illness and had frequent cough and breathing trouble. Pulmonary function tests were performed by using spirograms value (flow volume loop). About 5% of the people had abnormal spirogram which indicated dust obstruction in the respiratory tract. In addition, an increase in eosinophil count was also observed in most of the people.

Also, blood sample test was performed for these people to analyze the hemoglobin, total blood count and differential white blood count. Hemoglobin level was found to be normal, and eosinophil count was high among most of the people (60%) residing near traffic corridor and major

intersections. Thus, respiratory illness and high eosinophil count were observed among the people working in industries and living in and around the industries and traffic corridors.

Conclusion

Comprehensive emission inventory survey was carried out for Chennai city and its surroundings to assess the contribution from different sources on the air quality. Results of emission inventory and AAQM studies showed that the transport sector in Chennai city contributes to the significant level of air pollution followed by domestic and industrial sector.

The ambient air quality database collected through extensive monitoring studies indicated that dust concentrations and its associated PAHs were consistently high and exceeding the limits, whereas gaseous pollutants were within limits. Benzene concentrations were high near the industries and traffic intersections. CO and HC concentrations were exceeding the limits near the traffic corridors (< 10 m from road), and concentration gradient dropped drastically away from the road (> 10 m from road). Diurnal variation indicated that pollutants were generally high during day time except for ammonia and H$_2$S which occur during evening and night hours. This is because the ammonia emissions are mainly from industries and exhibit not much variation throughout the day. Since atmospheric dispersion/dilution is high during daytime and very less during night time, high concentration of ammonia was observed during evening and night hours. The concentration of H$_2$S is high in the night time due to emission from pits, sewers and industries. Also, the seasonal variation studies indicated that the peak values of all the air pollutants occurred either in the month of December or January (winter season) and are considerably low in the month of May (summer season). This is mainly because in summer the atmosphere is unstable due to increased solar radiation, wind speed and mixing height, causing high dispersion of pollutants. In winter, stable atmospheric condition and low-temperature cause decrease in mixing height leading to accumulation of air pollutants in the atmosphere.

In general, SO$_2$, NO$_2$ and H$_2$S trends indicated not much variation, whereas the trend of NH$_3$, TSPM, PM$_{10}$ and PM$_{2.5}$ showed variable peaks due to variable dispersion conditions and emissions. The spatial analysis of concentration of pollutants showed that the pollutant concentrations were higher in industrial areas due to traffic and

commercial activities. Thus, monitoring studies indicated that particulate pollutants and associated PAHs were above the NAAQ standards.

The long-term air quality data (1978–2012) for Chennai city indicated that the concentration of all gaseous and dust pollutants showed gradual decrease in trend from the year 1978 due to stringent emission and ambient air quality norms, supply of unleaded petrol and diesel in transport sector, shifting of fuel mix from fossil fuels (fire wood, crop residue and dung cake) to LPG and electric stove in the domestic sector, desulfurization of coal and petroleum products in industries.

The modeling indicated the contribution (%) from transport, domestic and commercial and industry is about 75%, 15% and 10%, respectively. Performance evaluation of models indicated the employed models prediction was good with least error. Health assessment survey carried out among the people indicated the air pollutants exposure levels producing a significant impact on the people's health in the city residing near to traffic corridors and major intersection and industrial areas.

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