Chapter 12
Air Pollution: Short-Lived Climate-Forced Ozone in Urban Areas of Kolkata

Anjali Srivastava and Dipanjali Mujumdar

Abstract The rapid growth in the economy as well as urban population brings us challenges to the venture of maintaining the clean urban air. Urban air quality is a cause of public concern, largely as a result of increased instances of smog and health problems. New pollutants are being increasingly recognised and point to sources, which are of inevitable use in day-to-day modern life. Air pollution sources have grown and so the pollutants. Many of these sources are indices of development. As ubiquitous components in the atmosphere, non-methane volatile organic compounds have received immense attention due to not only their adverse health effects on humans but also because of their role as the precursor of lower tropospheric ozone which eventually leads to urban photochemical smog.

Modern studies on atmospheric photochemistry indicate that ozone mixing ratios at ambient air depend on complex, non-linear, feedback control processes involving NOx and VOC precursor mixing ratio. Hence, control computation is required, adopting mathematical models that include the best representation of the non-linear chemistry as the basis.

12.1 Introduction

Cyclical variations in the Earth's orbit have been a cause of changes in the distribution of surface heating and natural variability. Climate change today is dominated by 'anthropogenic' factors, principally emissions of greenhouse gases. Fifty-five to sixty percent of anthropogenic radiative forcing is caused by carbon dioxide. The

---

A. Srivastava (✉)
National Environmental Engineering Research Institute, Mumbai Zonal Laboratory,
Worli, Mumbai 400 018, Maharastra, India
e-mail: anjali54@gmail.com

D. Mujumdar
National Environmental Engineering Research Institute, Kolkata Zonal Laboratory,
Kolkata 700107, West Bengal, India
e-mail: ds_mujumdar@neeri.res.in

remaining 40–45 % of radiative forcing is due to secondary reactions of pollutants in the atmosphere.

The secondary reactions of pollutants involve an array of pollutants such as methane, black carbon, tropospheric ozone and hydrofluorocarbons (HFCs). Collectively they are referred to as short-lived climate pollutants (SLCPs). These pollutants have short atmospheric lifetimes varying from days to a couple of decades. For slowing the rate of climate change over the next few decades and for protecting the vulnerable ecosystems and sensitive regions as well as sensitive human population, it is extremely important to reduce the SLCFs. These pollutants are more local/regional in nature than long-lived GHGs. Reducing SLCFs can lead to immediate climate benefits as the Earth's climate system responds quickly to reductions in these pollutants. Reducing SLCFs may be particularly beneficial for the protection of regions more sensitive to climate change like the Arctic and the Himalayan glaciers. The so-called climate tipping point may be deferred by slowing the rate of warming which will also be abetted by the reduction of SLFCs.

Non-methane volatile organic compounds (NMVOCs) and are precursors to ozone and are one of the SLCFs. NMVOCs, one group of precursors of ozone, lead to warming; where as on the other hand, NOx emissions lead to cooling. The overall effect of controls on ozone precursors varies on climate depending upon other meteorological factors. Tropospheric ozone (O_3) is of concern due to its adverse effects on both the environment and human health (Goldsmith and Nadel 1969; Krupa and Manning 1988). Breathing O_3 can trigger an array of health problems including coughing, throat irritation, congestion and even chest pain. It can worsen bronchitis, emphysema and asthma. Ground-level O_3 also can severely affect lung function and inflame the linings of the lungs (Roselle et al. 1991). Ozone does not essentially respond in a proportional manner to reductions in its precursor emissions (Finlayson-Pitts and Pitts 2000), and thus control of ground-level O_3 is difficult.

The present study focuses on the monitoring of ozone (hourly for 24 h) and its precursors non-methane VOCs (NMVOC) and carbonyls (24-hourly average), twice in every month in each of the 12 sites characterised by residential, industrial and traffic intersections and petrol pumps in the urban area of Kolkata along with VOCs, carbonyls and NOx. The probabilistic collocation method used by Tatang et al. (1997) was used to predict ozone concentrations for comparison with observed values.

12.2 Methodology

Ambient air was sampled at 12 sampling sites in the urban area of Kolkata using a low-volume sampler for the analysis of VOCs and carbonyls. The sampling locations can be characterised as residential, industrial and traffic intersections and petrol pump, three in each category (Fig. 12.1).

The detailed description of the study sites can be found in a previous publication (CPCB 2010). Samples were collected in three shifts for 24 h twice every month for
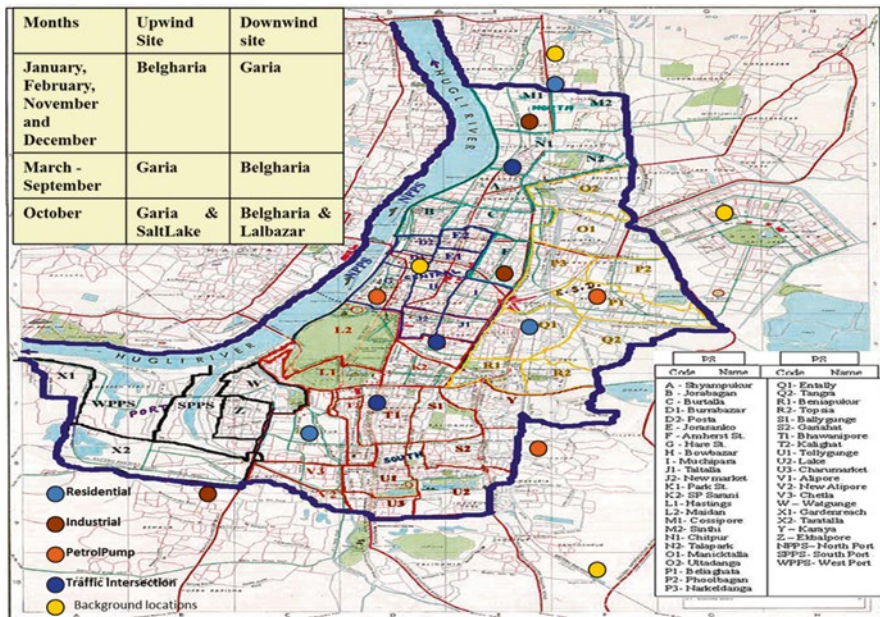
Months	Upwind Site	Downwind site
January, February, November and December	Belgharia	Garia
March – September	Garia	Belgharia
October	Garia & SaltLake	Belgharia & Lalbazar

Fig. 12.1 Sampling locations

NOx; VOC and aldehyde hourly ozone concentrations have been monitored using ambient O_3 monitor (Model No. APOA370) of HORIBA along with the other target pollutants.

VOCs were analysed using compendium method TO-17 and carbonyls were analysed using compendium method TO-11A.

Levels of VOCs in ambient air have been determined by adsorbing air drawn at a uniform flow rate through specially fabricated sorbent tubes with partly filled Chromosorb 106 and Carbopack™ B 60/80 mesh used as sorbents, followed by thermal desorption and its further detection on Varian GC-MS in accordance with TO-17 compendium of methods for the determination of toxic organic compounds (USEPA 1999). Sorbent cartridges were fabricated using glass tubes with a length of 15 cm with an internal diameter of 4 mm and external diameter of 6 mm and having a tapered nozzle on one end. A battery-operated air sampler (Model Polltech-PEM-LVAS2) was used to sample air at the rate of 50 ml per minute through the fabricated adsorption cartridge. Uniform flow rate was monitored using a rotameter. The monitoring was carried out from 12 noon to 6:00 pm, 6:00 pm to 6:00 am and 6:00 am to 12:00 noon. Breakthrough value was estimated by connecting two tubes in series, and it was considered that breakthrough occurred when the backup tube had a concentration of more than 5 % of the total concentration. At the end of the sampling period, the sorbent tubes were removed, capped tightly, sealed in plastic zip bags and stored at 4 °C. Blank cartridges were also stored in identical conditions.

Varian GC-MS (Model Saturn 3) with injection mode of sample introduction with DB 624 capillary column of 30 m length, 0.32 mm internal diameter and 1.8 microfilm was used. Helium gas with a flow rate of 1 ml per minute was used as carrier gas with a split ratio of 1:25; GC oven was programmed for a hold at 35 °C for 4 min and ramped to 210 °C. Thermal desorption of sorbent tube was carried out by slowly heating the tube up to 180 °C for 10 min and 100 μl of the desorbed gas was Injected and analysed by gas chromatography (GC).

The estimation of oxygenated VOCs (aldehydes and ketones) was done following USEPA TO-11 method where the air sample was passed through a cartridge filled with silica impregnated with an acidified solution of 2,4-dinitrophenylhydrazine (2,4-DNPH), producing hydrazone which itself was quantified using high-performance liquid chromatography (HPLC). The cartridges were kept away from direct sunlight by wrapping them with an aluminium foil, and they were dried in a vacuum desiccator for 15–24 h before being closed with two caps and stored in a refrigerator until use. To prevent any consumption of hydrazones by reaction with the ozone contained outdoor which may lead to an underestimation of aldehydes concentrations, an ozone scrubber was used before the DNPH cartridge in order to trap ozone.

The cartridges after sampling were eluted with about 2 mL of acetonitrile. The obtained extracted derivative solutions were then analysed by HPLC coupled to UV detection (Dionex ICS-3000). The solution obtained after extraction was injected by a 20 µl sample loop into a reversed-phase C-18 column ((Supelcosil™, Supelco), 25.0 cm length, 4.6 mm i.d.) and detected at a wavelength of 360 nm using gradient mobile phase consisting of 10 % THF in water and acetonitrile. The compounds were quantified against a five-point external calibration curve prepared using TO11/IP6A Carbonyl-DNPH Mix procured from Supelco.

NOx has been measured as NO_2 by modified Jacobs-Hochheiser method (Na-arsenite). In the method, the NO_2 from ambient air is absorbed in a solution of sodium hydroxide and sodium arsenite. Sulphur dioxide is the major interfering compound. The interference of sulphur dioxide is eliminated by converting it to sulphuric acid by the addition of hydrogen peroxide. The absorbed nitrogen dioxide is then reacted with sulphanilamide in the presence of phosphoric acid at a pH of less than 2 and then coupled with N-(1-naphthyl)ethylenediamine dihydrochloride. The absorbance of the highly coloured azo-dye is measured on a spectrophotometer at a wavelength of 540 nm. The detection range of the NO_2 concentration is 9–750 µg/m³. Calibration was carried out by plotting standard curve using high-purity sodium nitrite solution. Known concentration of sodium nitrite was determined intermittently to verify the validity of the calibration curve.

12.2.1   Quality Assurance and Quality Control

A linearity test has been carried out to determine the breakthrough volume by sampling a synthetic mixture of six components of VOC mix-15 for 20, 40 and 80 min at a rate of 100 ml/min. The linearity study indicated that breakthrough has not occurred at a sampling volume of 8,000 ml. Percentage accuracy for observation has

been determined as a relative difference of measured concentration and spiked concentration for each component. Also mean response factor and percent relative standard deviation for all target compounds have been calculated. Method detection limit (MDL) has been established by making seven replicated measurements of 0.002 μg. The standard deviation for these replicated concentrations multiplied by Student's t value for 99 % confidence for seven values gives the MDL. The MDL varied from 0.00076 μg for 1,2-dichlorobenzene to 0.0045 μg for butyl benzene.

12.3   Results and Discussions

A maximum number of 132, 130, 86 and 85 NMVOCs have been identified at residential locations followed by traffic intersections, industrial and petrol pumps, respectively. The percentage of hazardous air pollutants (HAPs) identified was highest at petrol pump followed by industrial, residential and traffic intersections, respectively (Table 12.1). In the present discussion, NMVOCs that do not include carbonyls are referred to as non-carbonyl VOCs.

12.3.1   Industrial Areas

Amongst the industrial areas, highest concentrations of total non-carbonyl VOC are observed at Behala (456.1 μg/m^3) during winter season. The minimum concentration of 47.3 μg/m^3 was observed at Cossipore during summer. The total non-carbonyl VOC concentration at Behala was higher as compared to Baithakkhana Bazar and Cossipore. At Baithakkhana Bazar, the total non-carbonyl VOCs ranged from 48.0 to 210.9 μg/m^3, while at Cossipore, it ranged from 47.3 to 282.5 μg/m^3, and at Behala, the minimum concentration observed was 83.4 μg/m^3 and a maximum of 456.1 μg/m^3 (Table 12.2).

Amongst the industrial areas, highest concentrations of carbonyls were observed at Baithakkhana Bazar (1,131.7 μg/m^3) during summer. A minimum concentration of 135 μg/m^3 was observed at Behala during summer. The carbonyl concentration at Baithakkhana Bazar was higher as compared to Behala and Cossipore. At Baithakkhana Bazar, carbonyls ranged from 461.6 to 1,131.7 μg/m^3, while at Cossipore, it ranged from 217.8 to 1,111.5 μg/m^3, and at Behala, the minimum concentration observed was 72.0 μg/m^3 and a maximum of 1,091.1 μg/m^3 (Table 12.3).

Table 12.1   Category-wise distribution of VOCs and HAPs identified

Category	No. of VOCs identified	No. of HAPs identified	% of HAPs identified
Industrial	86	28	32.56
Petrol pump	85	30	35.29
Residential	132	35	26.52
Traffic intersection	130	31	23.85

Table 12.2 Seasonal variation of total non-carbonyl VOCs observed at industrial locations

		1	2	3
Seasons	Sampling locations	12:00–6:00 pm	6:00 pm–6:00 am	6:00 am–12:00 noon
Summer	Baithakkhana Bazar	53.4	67.12	61.7
	Cossipore	55.7	72.3	47.3
	Behala	98.0	79.0	98.1
	Upwind	56	62	58
	Downwind	87	113	72
Monsoon	Baithakkhana Bazar	48.0	50.2	53.4
	Cossipore	64.6	77.3	66.5
	Behala	102.7	111.5	104.2
	Upwind	49	64	51
	Downwind	71	96	91
Post-monsoon	Baithakkhana Bazar	177.1	146.3	170.5
	Cossipore	158.8	209.3	194.3
	Behala	302.3	83.4	198.1
	Upwind	89	114	100.7
	Downwind	123	145	111
Winter	Baithakkhana Bazar	195.2	210.9	210.4
	Cossipore	236.1	282.5	234.4
	Behala	381.2	456.1	380.3
	Upwind	79	132	121
	Downwind	117	178	124

Table 12.3 Seasonal and diurnal variation of carbonyls observed at industrial locations

	Industrial	Baithakkhana Bazar	Cossipore	Behala	Upwind	Downwind
Summer	Shift 1	1131.7	723.4	426.9	315.9	564.8
	Shift 2	511.7	908.2	1091.1	357.4	1072.0
	Shift 3	1056.0	649.9	135.0	578.7	1537.0
Monsoon	Shift 1	529.0	676.3	928.1	379.5	900.6
	Shift 2	557.9	993.0	732.2	389.1	652.8
	Shift 3	627.6	545.5	475.7	121.5	385.5
Post-monsoon	Shift 1	727.4	599.1	555.3	623.0	382.1
	Shift 2	637.7	323.0	268.8	667.9	840.7
	Shift 3	712.5	373.1	398.3	374.7	777.9
Winter	Shift 1	1082.5	880.5	731.2	495.5	893.1
	Shift 2	461.6	217.8	345.2	483.9	1480.4
	Shift 3	645.2	1111.5	891.2	223.3	517.1

Table 12.4 Seasonal variation of non-carbonyl VOCs observed at petrol pumps

		1	2	3
Seasons	Sampling locations	12:00–6:00 pm	6:00 pm–6:00 am	6:00 am–12:00 noon
Summer	Beleghata	405.8	128.3	171.9
	Bose Pukur	141.0	459.4	136.3
	Theatre Road	221.0	319.8	276.1
	Upwind	56	62	58
	Downwind	87	113	72
Monsoon	Beleghata	212.0	187.6	307.6
	Bose Pukur	131.1	267.8	301.5
	Theatre Road	154.5	284.9	197.9
	Upwind	49	64	51
	Downwind	71	96	91
Post-monsoon	Beleghata	260.6	346.1	686.4
	Bose Pukur	297.2	561.9	294.1
	Theatre Road	500.2	689.0	499.0
	Upwind	89	114	100.7
	Downwind	123	145	111
Winter	Beleghata	753.9	1173.6	650.0
	Bose Pukur	395.3	518.2	306.2
	Theatre Road	621.0	741.7	633.5
	Upwind	79	132	121
	Downwind	117	178	124

12.3.2 Petrol Pumps

Table 12.4 gives the seasonal concentration of total non-carbonyl VOCs observed at Bose Pukur, Beleghata and Theatre Road petrol pumps. Maximum and minimum total non-carbonyl VOC concentrations have been observed at Beleghata petrol pump during winter and summer, respectively. At Bose Pukur petrol pump, the total non-carbonyl VOC concentrations ranged from 131.1 $\mu g/m^3$ during monsoon to 561.9 $\mu g/m^3$ during post-monsoon. At Beleghata petrol pump, a minimum concentration of 128.3 $\mu g/m^3$ during summer and a maximum concentration of 1,173.6 $\mu g/m^3$ during winter were observed. At Theatre Road petrol pump, a minimum concentration of 154.6 $\mu g/m^3$ during monsoon and a maximum concentration of 741.7 $\mu g/m^3$ during winter have been observed.

Amongst these three petrol pumps, the highest concentration of total carbonyls has been observed at Beleghata during monsoon (1,184.8 $\mu g/m^3$) and a minimum concentration at Bose Pukur petrol pump (130.7 $\mu g/m^3$) during post-monsoon. The concentration of total carbonyl was found higher at Beleghata as compared to the other two petrol pumps. The concentration of total carbonyls at Bose Pukur ranged from 130.7 to 1,015.4 $\mu g/m^3$. At Theatre Road, the minimum and maximum concentrations were 205.8 $\mu g/m^3$ and 688.8 $\mu g/m^3$, respectively (Table 12.5).

Table 12.5 Seasonal variation of carbonyls observed at petrol pumps

Petrol pump		Beleghata	Bose Pukur	Theatre Road	Upwind	Downwind
Summer	Shift 1	859.2	612.6	512.6	315.9	564.8
	Shift 2	394.1	834.5	417.0	357.4	1072.0
	Shift 3	302.0	616.0	380.4	578.7	1537.0
Monsoon	Shift 1	1184.8	856.8	578.9	379.5	900.6
	Shift 2	735.7	590.5	535.5	389.1	652.8
	Shift 3	597.6	477.7	205.8	121.5	385.5
Post-monsoon	Shift 1	609.1	236.0	381.6	623.0	382.1
	Shift 2	564.6	227.1	383.3	667.9	840.7
	Shift 3	522.1	130.7	291.1	374.7	777.9
Winter	Shift 1	1104.4	642.8	464.8	495.5	893.1
	Shift 2	959.3	1015.4	688.8	483.9	1480.4
	Shift 3	573.4	219.9	344.9	223.3	517.1

12.3.3   Residential Cum Commercial Areas

The total non-carbonyl VOC concentrations observed ranged from 43.0 μg/m^3 at Dunlop during monsoon to 546.1 μg/m^3 at Alipore during post-monsoon in residential cum commercial areas. At Alipore, the minimum concentration observed was 41.5 μg/m^3 during monsoon. Entally showed a minimum total non-carbonyl VOC concentration of 43.1 μg/m^3 during monsoon and a maximum concentration of 412.0 μg/m^3 during post-monsoon. The total non-carbonyl VOC concentration observed at Dunlop ranged from 43.0 μg/m^3 during monsoon to 84.8 μg/m^3 during winter. Seasonal and annual averages of total non-carbonyl VOCs at Alipore, Dunlop and Entally are presented in Table 12.6. In the case of carbonyls, the highest concentration was found at Entally (1,430.1 μg/m^3) during monsoon, while the lowest concentration was observed at Dunlop (177.4 μg/m^3) during post-monsoon. Entally showed a higher concentration of total carbonyls as compared to Alipore and Dunlop. At Entally and Dunlop, the concentration of total carbonyls varied from 189.3 to 1,430.1 μg/m^3 and 177.4 to 972.4 μg/m^3, respectively. The total carbonyl concentration range at Alipore was 246.6 to 781.4 μg/m^3 (Table 12.7).

12.3.4   Traffic Intersection

The total non-carbonyl VOC concentration at Rash Behari was observed to be in the range of 255.6 μg/m^3 during monsoon to 668.9 μg/m^3 during winter. At Shyam Bazar, which is located at the northern side of Kolkata, a minimum concentration of 177.6 μg/m^3 was observed during summer and a maximum concentration of 745.2 μg/m^3 was found during post-monsoon which was also the maximum observed concentration for all the traffic intersections (Table 12.8). At Park Street, a maximum concentration of 472.2 μg/m^3 was observed during summer and a minimum of 28.3 μg/m^3 during monsoon which was the lowest observed concentration for traffic intersections.

Table 12.6 Seasonal variation of total non-carbonyl VOCs observed at residential cum commercial locations

Seasons	Sampling locations	1 12:00–6:00 pm	2 6:00 pm–6:00 am	3 6:00 am–12:00 noon
Summer	Dunlop	56.4	61.3	60.0
	Entally	51.3	51.5	52.2
	Alipore	56.9	43.2	66.1
	Upwind	56	62	58
	Downwind	87	113	72
Monsoon	Dunlop	55.6	43.0	52.0
	Entally	74.7	43.1	75.7
	Alipore	44.3	49.7	41.5
	Upwind	49	64	51
	Downwind	71	96	91
Post-monsoon	Dunlop	77.7	51.9	45.0
	Entally	103.3	61.0	412.0
	Alipore	129.3	546.1	385.9
	Upwind	89	114	100.7
	Downwind	123	145	111
Winter	Dunlop	84.8	58.0	69.0
	Entally	85.6	55.6	45.5
	Alipore	107.0	140.0	98.0
	Upwind	79	132	121
	Downwind	117	178	124

Table 12.7 Seasonal variation of carbonyls observed at residential cum commercial locations

	Residential	Alipore	Dunlop	Entally	Upwind	Downwind
Summer	Shift 1	706.1	828.5	510.8	315.9	564.8
	Shift 2	453.1	384.1	496.6	357.4	1072.0
	Shift 3	554.8	483.4	794.2	578.7	1537.0
Monsoon	Shift 1	781.4	972.4	1430.1	379.5	900.6
	Shift 2	590.2	418.6	741.7	389.1	652.8
	Shift 3	451.2	594.6	382.3	121.5	385.5
Post-monsoon	Shift 1	483.7	481.8	669.0	623.0	382.1
	Shift 2	246.6	353.5	633.6	667.9	840.7
	Shift 3	429.6	177.4	189.3	374.7	777.9
Winter	Shift 1	374.6	614.9	671.5	495.5	893.1
	Shift 2	646.5	298.5	218.4	483.9	1480.4
	Shift 3	363.8	405.6	398.2	223.3	517.1

The highest concentration of carbonyls was found at Rash Behari during summer (1,985.4 µg/m³), while the lowest concentration was observed at Shyam Bazar (325.1 µg/m³) during post-monsoon. At Shyam Bazar and Park Street, the concentration ranges were found to be 325.1 to 1361.9 µg/m³ and 413.8 to 1680.3 µg/m³,

Table 12.8 Seasonal variation of total non-carbonyl VOCs observed at traffic intersections

		1	2	3
Seasons	Sampling locations	12:00–6:00 pm	6:00 pm–6:00 am	6:00 am–12:00 noon
Monsoon	Park Street	297.3	28.2	262.6
	Rash Behari	329.7	317.2	255.6
	Shyam Bazar	344.5	545.6	395.0
	Upwind	49	64	51
	Downwind	71	96	91
Post-monsoon	Park Street	257.3	404.5	244.9
	Rash Behari	465.3	373.3	312.1
	Shyam Bazar	485.8	557.3	745.2
	Upwind	89	114	100.7
	Downwind	123	145	111
Summer	Park Street	367.9	472.2	345.8
	Rash Behari	573.9	490.0	663.4
	Shyam Bazar	607.7	177.6	433.4
	Upwind	56	62	58
	Downwind	87	113	72
Winter	Park Street	401.8	467.0	379.0
	Rash Behari	488.0	668.9	350.5
	Shyam Bazar	535.8	364.3	450.0
	Upwind	79	132	121
	Downwind	117	178	124

Table 12.9 Seasonal variation of carbonyls observed at traffic intersections

Traffic intersection		Park Street	Rash Behari	Shyam Bazar	Upwind	Downwind
Summer	Shift 1	839.9	1985.4	1361.9	315.9	564.8
	Shift 2	547.3	419.5	480.5	357.4	1072.0
	Shift 3	1024.2	879.3	1310.8	578.7	1537.0
Monsoon	Shift 1	1687.1	815.3	1004.2	379.5	900.6
	Shift 2	635.1	675.6	1178.0	389.1	652.8
	Shift 3	442.6	1277.6	872.8	121.5	385.5
Post-monsoon	Shift 1	767.9	354.1	475.7	623.0	382.1
	Shift 2	413.8	606.1	325.1	667.9	840.7
	Shift 3	545.1	702.4	775.8	374.7	777.9
Winter	Shift 1	1112.0	1730.5	743.3	495.5	893.1
	Shift 2	599.5	755.7	1246.9	483.9	1480.4
	Shift 3	1680.3	1154.2	694.2	223.3	517.1

respectively. The concentration of total carbonyls at Rash Behari varied from 354.1 to 1985.4 $\mu g/m^3$ (Table 12.9).

In the urban air of Kolkata, high values of aldehydes have been observed (Tables 12.2, 12.3, 12.4, 12.5, 12.6, 12.7, 12.8, and 12.9). This may be due to the
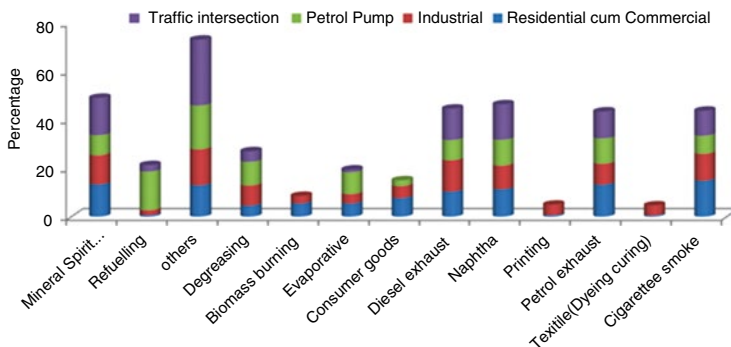
Fig. 12.2 Major sources of VOCs in ambient air

oxidation of VOCs. Source apportionment of VOCs using CMB 8 model shows that the major sources of VOCs in ambient air are petrol and diesel exhaust, combustion of naphtha and mineral spirit and cigarette smoke (Fig. 12.2).

Contributions of different sources at each category of location are shown in Fig. 12.3.

It is observed that the average level of NO_2 is quite low in all Kolkata air. The level is consistently lower than 80 μg/m^3 which is the permissible limit of NO_2 (24-h average) (National Ambient Air Quality Standards, CPCB 2009). Figures 12.4, 12.5, 12.6, and 12.7 depict the seasonal as well as diurnal distribution of NO_2 concentration in different categories of sites.

Percentile distribution of hourly concentration of ozone (Figs. 12.8, 12.9, 12.10, and 12.11) shows that from November to May, 95 percentile values crossed 100 μg/m^3 at residential areas. At industrial locations except Behala, 100 μg/m^3 was never exceeded. At Behala, this concentration exceeded 5 % times from July and December to March. At traffic intersections, only at Rash Behari, crossing the month of February, violation from the standard of 100 μg/m3 was observed 5 % times. At all petrol pumps, ozone concentrations exceeded 100 μg/m^3 5 % times in the month of July.

VOC/NO_2 ratios observed in Kolkata are primarily high, indicating NO_2-sensitive conditions. A high rate of VOC emissions (due to local activity like biomass burning, roadside cooking, etc.) increases the ratio of VOC to NO_2 and makes NO_2-sensitive conditions more likely.

Instantaneous photochemical ozone P(O_3) formation can be computed as the O_3 production rate is a function of NO_2 concentration. The chemical production rate of ozone is defined as

$$P(O_3) = \frac{d(Ox)}{dt} \tag{12.1}$$

where
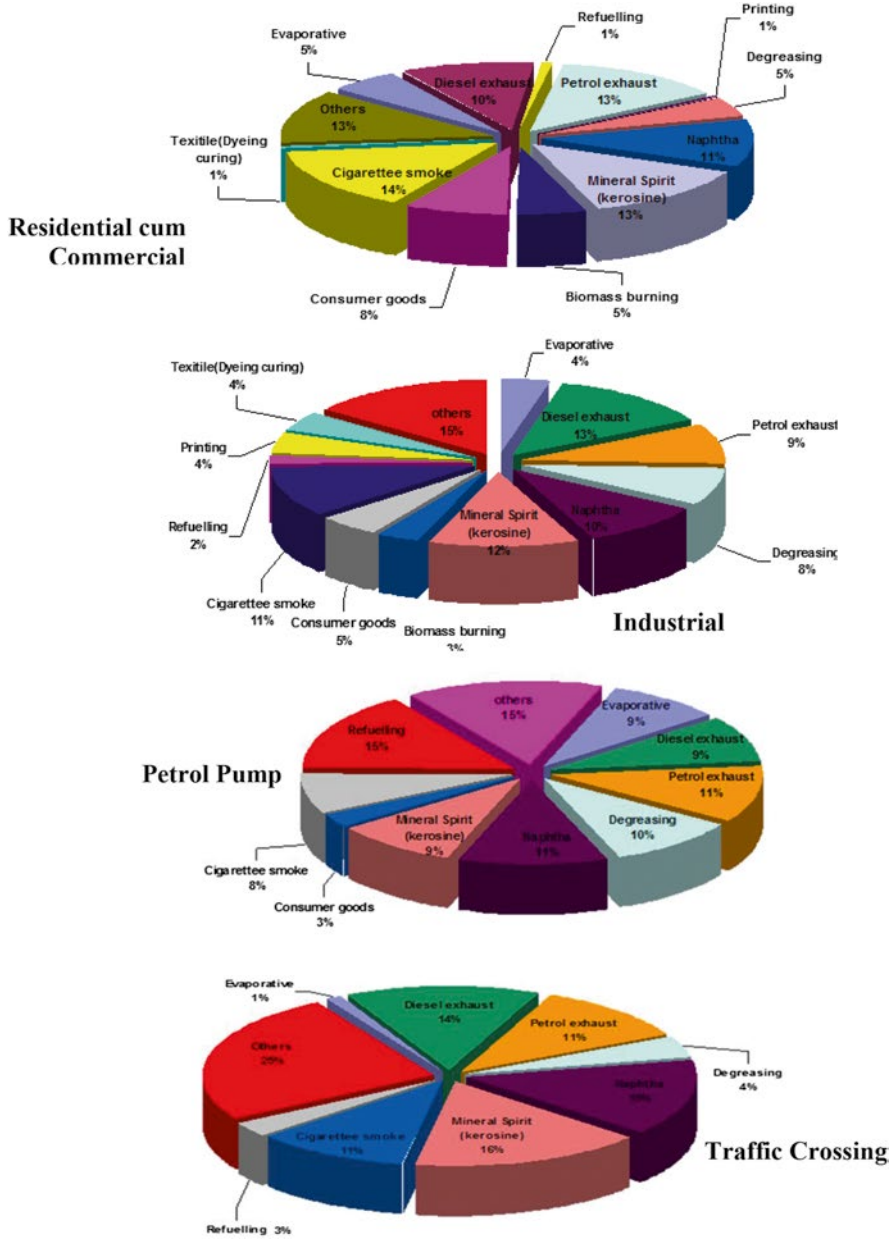
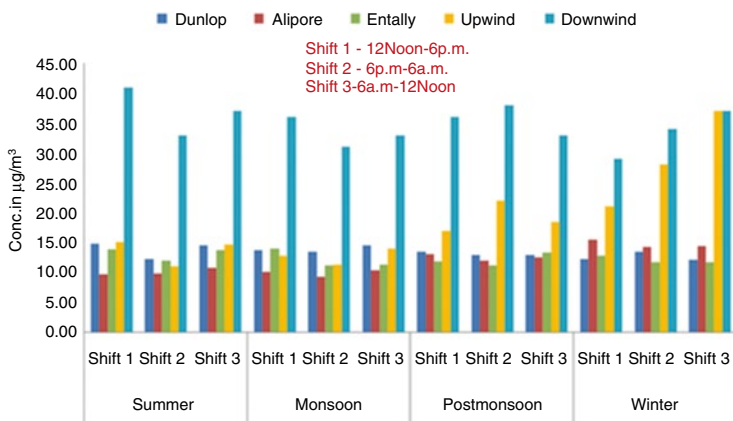**Fig. 12.3** Contribution of sources of VOCs at different categories of locations

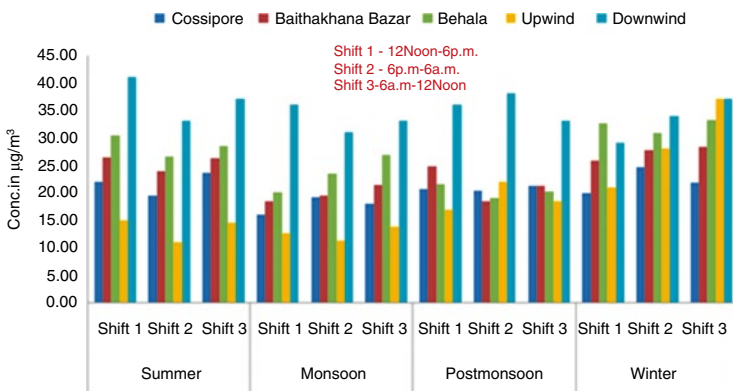**Fig. 12.4** Diurnal distribution of NO$_2$ in residential cum commercial location

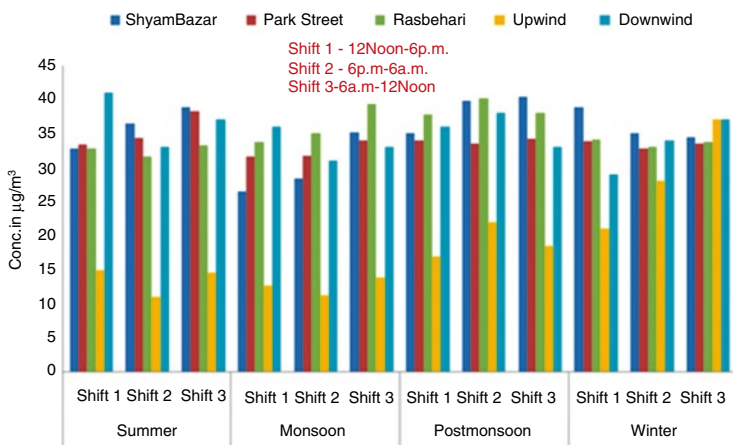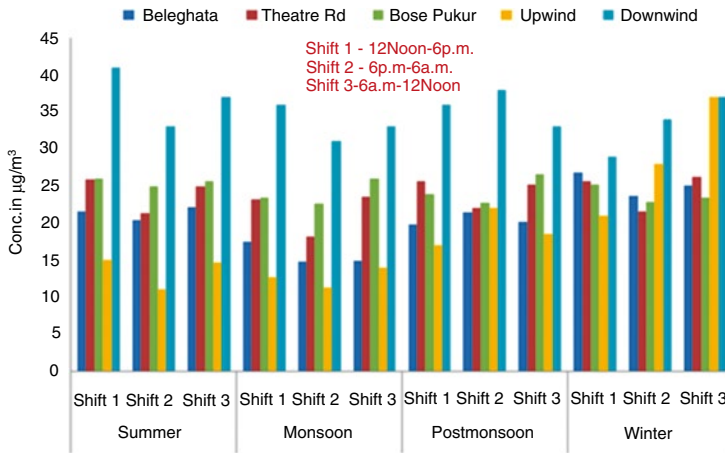**Fig. 12.5** Diurnal distribution of NO$_2$ in industrial location

Fig. 12.6 Diurnal distribution of NO$_2$ in traffic intersection

**Fig. 12.7** Diurnal distribution of NO_2 in petrol pumps

$$Ox = O(1D) + O_3 + NO_2 \qquad (12.2)$$

During daytime, NO_2 can be reasonably assumed to achieve a steady state so that $d(Ox) = d(O_3)/dt$. It is commonly believed that the O_3 production rate increases at low NO_2 until a maximum is reached and then decreases at high NO_2. Figure 12.12 shows a similar behaviour for urban air of Kolkata. Negative values of P (O_3) have been observed from 6:00 pm to 6:00 am during all seasons. This behaviour occurs because high NO_2 promotes removal of OH radicals by reaction with NO_2 and hence reduces photochemical O_3 formation. In addition to NO_2, P(O_3) is also dependent on VOC reactivity, sunlight and radical precursors.

The upper-limit kinetic and mechanistic reactivities are used to obtain an estimate of the incremental reactivity in the MIR scale. The incremental reactivities obtained by multiplying the kinetic and mechanistic reactivities derived is in units of moles of ozone formed per mole VOC emitted, but for regulatory applications, the appropriate units are grams of O_3 per gram VOC. This conversion is done by multiplying the ratio of the molecular weight of O_3 to the molecular weight of the VOC. Therefore,

$$\frac{\text{Upper Limit MIR}}{(gm\, O_3 / gm\, VOC)} = \frac{\text{Upper Limit}}{\text{Kinetic Reactivity}} * \frac{\text{Upper Limit Mechanistic}}{\text{Reactivity}(mol\, O_3 / mol\, VOC)} * \frac{48(gm\, O_3 / mol\, O_3)}{Mwt^{voc}(gm / mol)}$$

$$(12.3)$$

For regulatory or life cycle impact assessment applications where NO_2 impacts need to be evaluated using the same scale as VOC impacts, and where the MIR scale is used for evaluating VOC impacts, the NO_2 impacts used should be those derived for the NMIR scale. For the SAPRC-07 reactivity scale given by Carter (2007, 2010), the NMIR values of 25.37, 17.24 and 15.85 g O_3 per gram compound for NO, NO_2
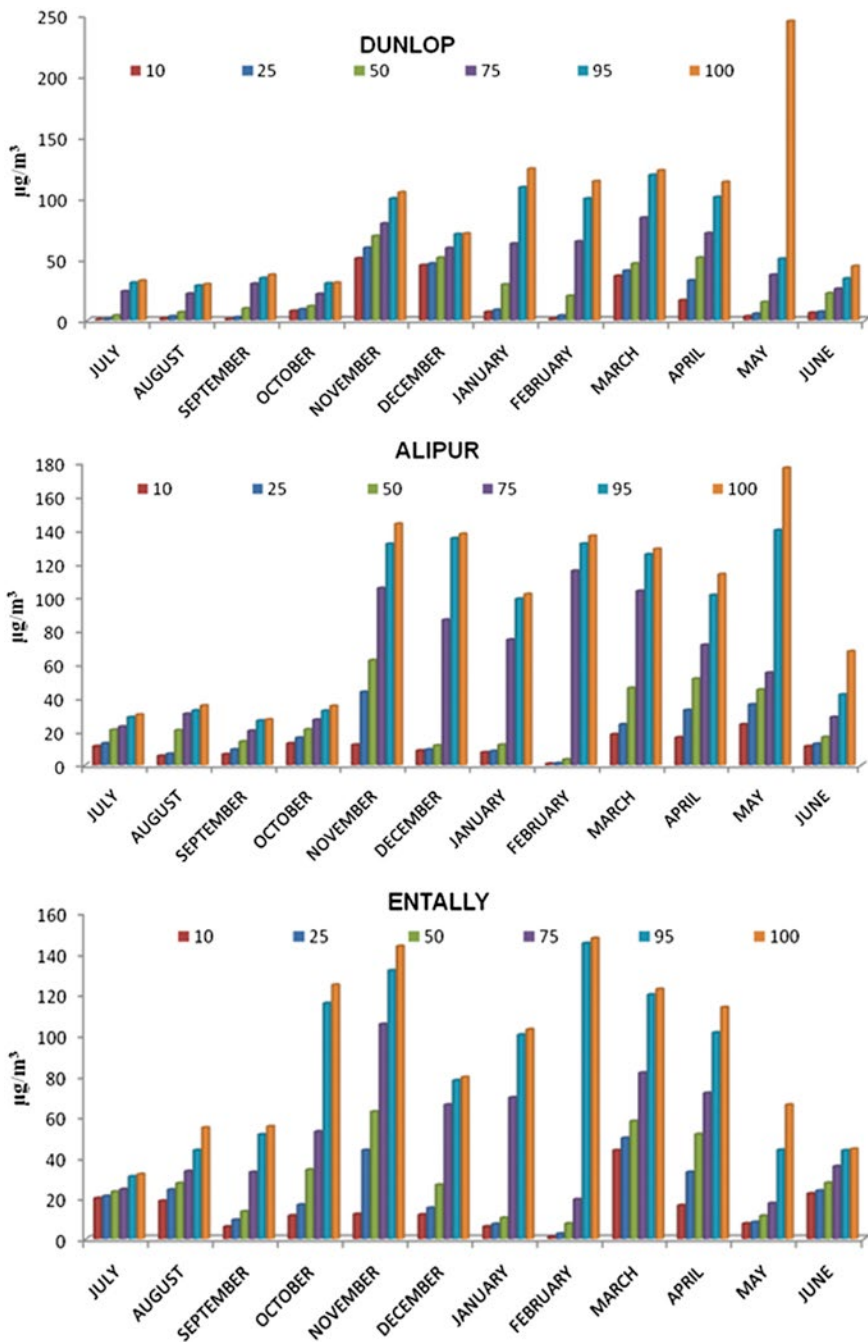
Fig. 12.8 Percentile distribution of hourly concentration of ozone (residential cum commercial locations)
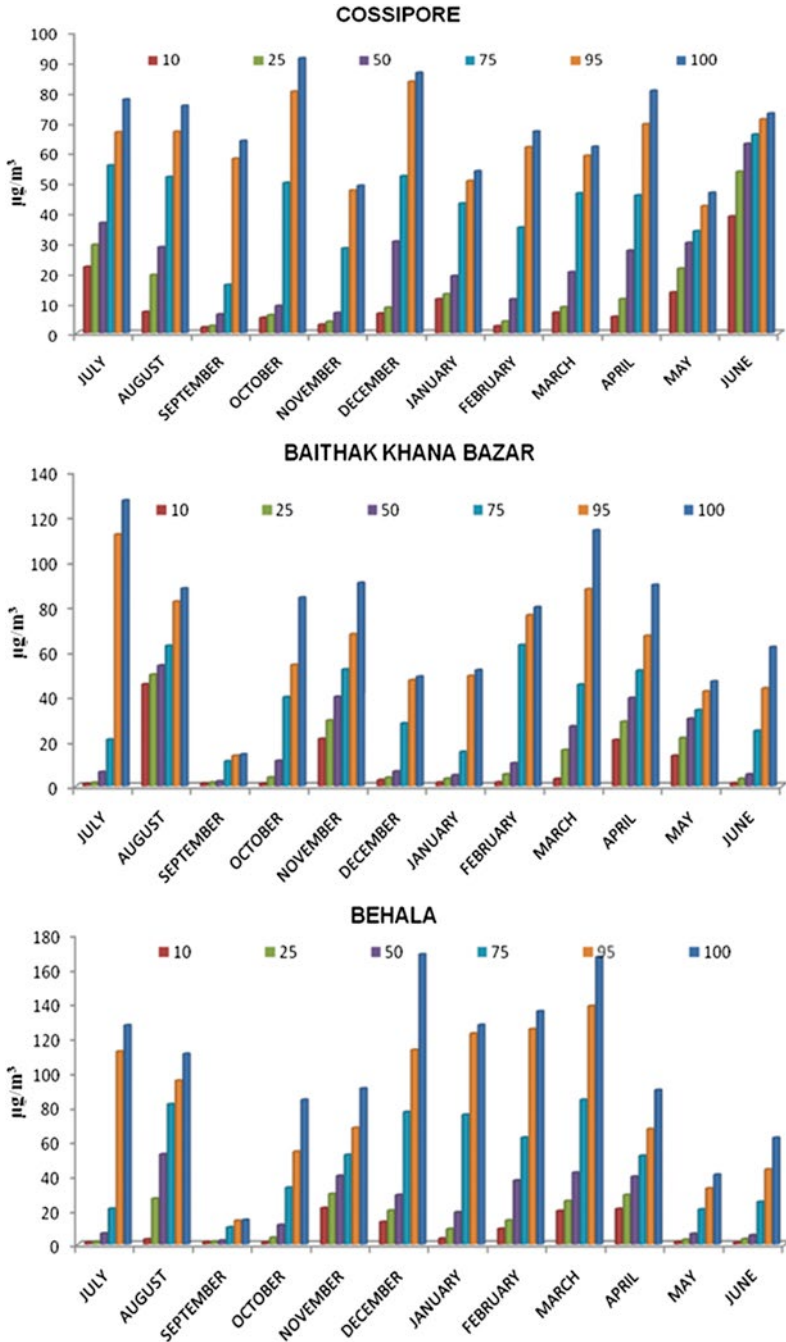
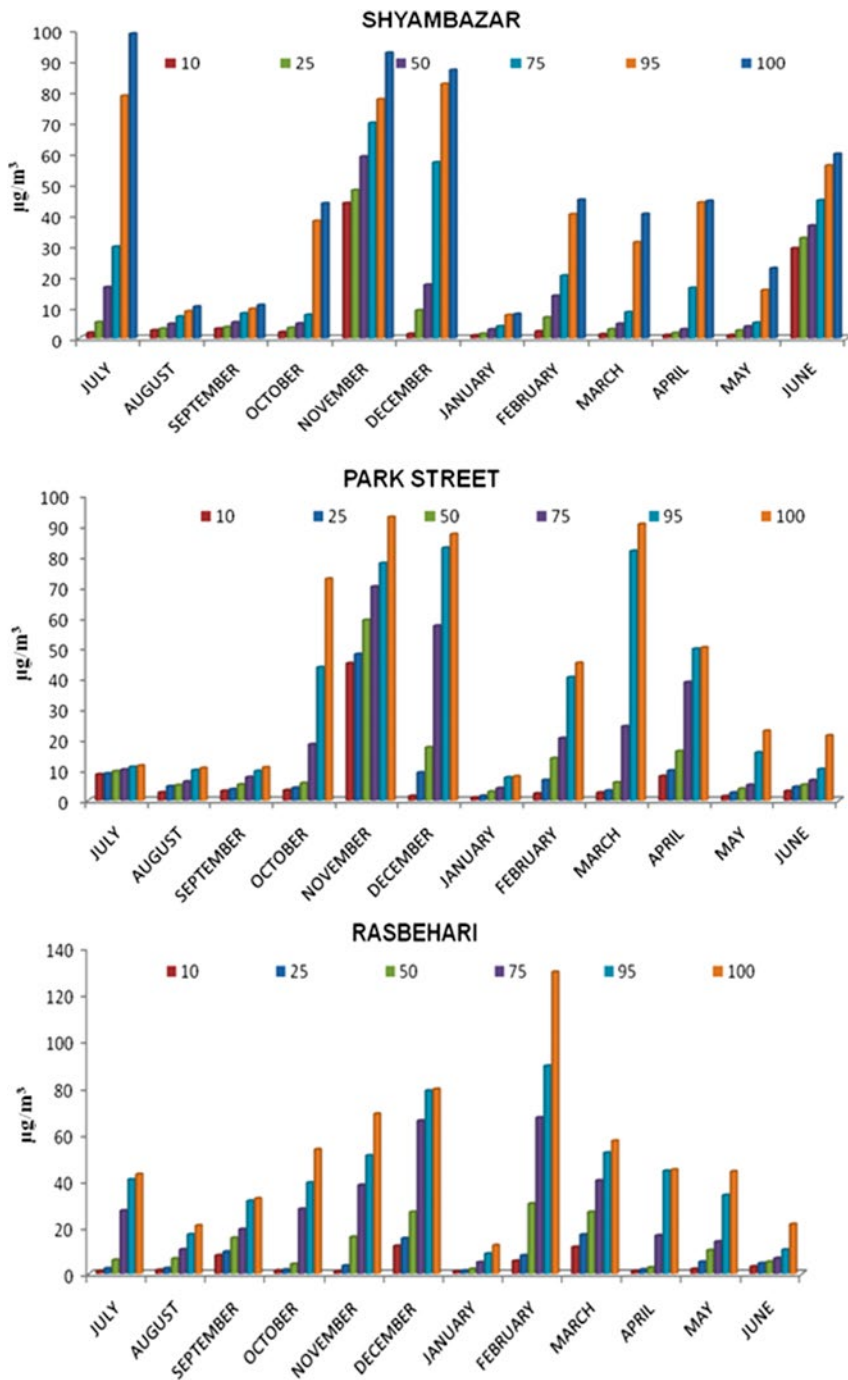**Fig. 12.9** Percentile distribution of hourly concentration of ozone (industrial locations)

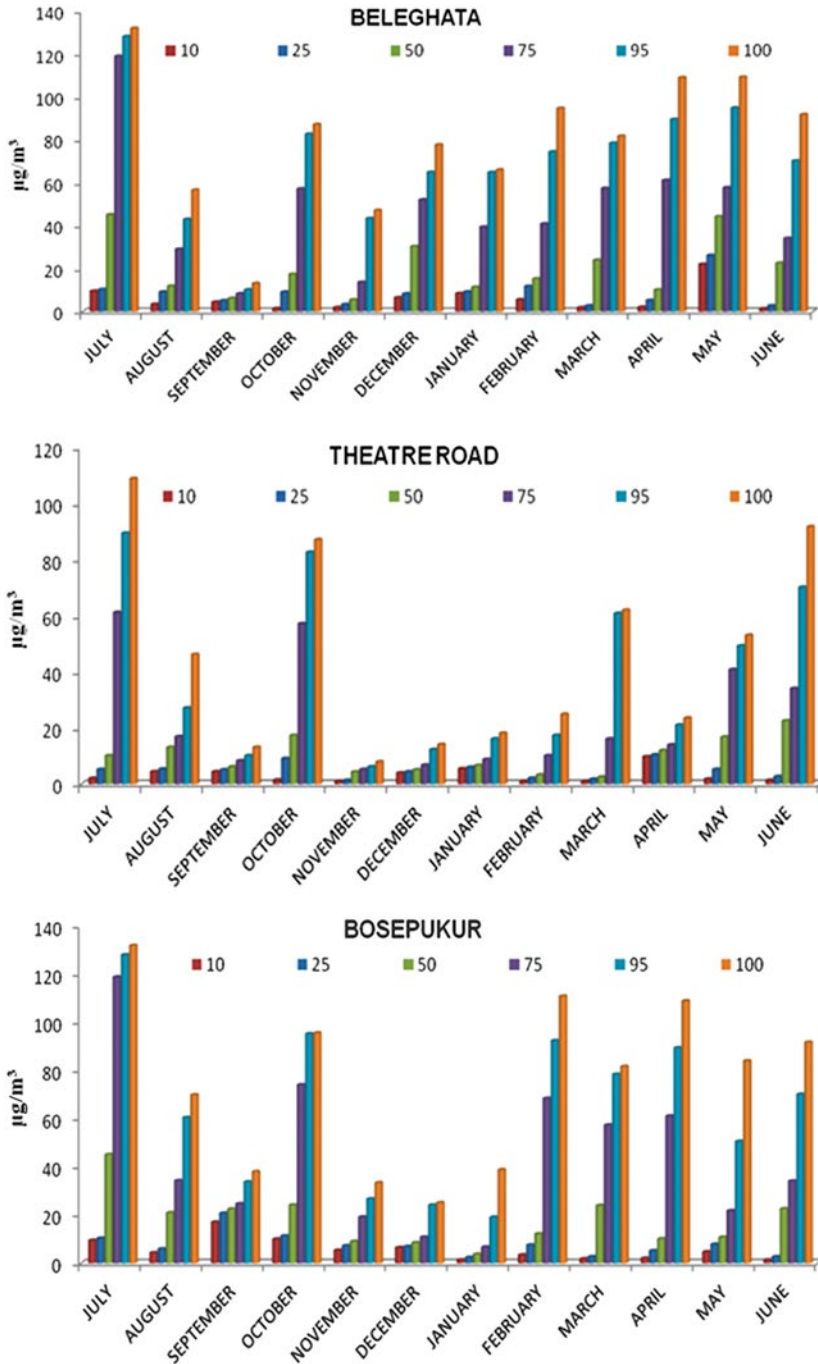**Fig. 12.10** Percentile distribution of hourly concentration of ozone (traffic crossings)

Fig. 12.11 Percentile distribution of hourly concentration of ozone (petrol pumps)
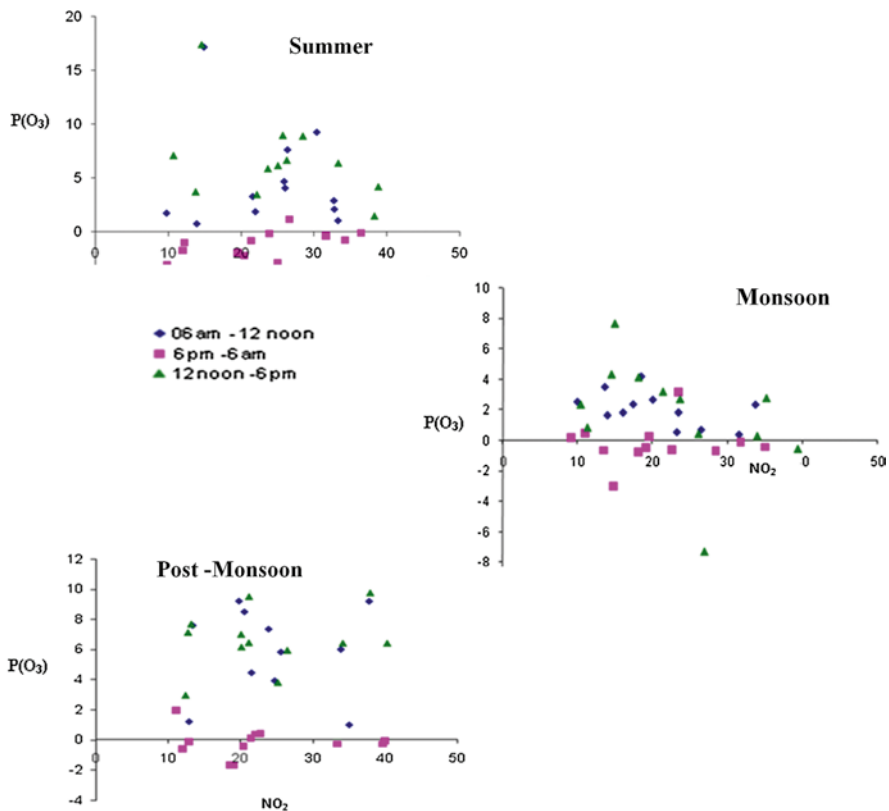
Fig. 12.12 Instantaneous ozone production in Kolkata with respect to NO_2 (seasonal variation)

and HONO, respectively, are to be added to the MIR values given for the VOCs. Table 12.10 shows the ozone formation by VOCs observed using MIR values given by SAPRC-07.

A strong correlation between ozone, NO_2 and total VOCs (i.e. carbonyl and non-carbonyl VOCs) is observed.

12.3.5 Probabilistic Collocation Method (PCM)

The probabilistic collocation method was used to predict ozone concentrations. The probabilistic collocation method used by Tatang et al. (1997) is one of the several mathematical techniques which can be used for parameterisation. Given a set of k input parameters xj used to drive a model, $\{x_1, x_2, \ldots, xk\}$, there are M output responses yj predicted by the model that are functions of the xj values:

Table 12.10 Instantaneous ozone formation by VOCs using MIR values

Compound	MIR	6:00 pm–6:00 am	12:00 noon–6:00 pm	6:00 am–12:00 noon
Toluene	5.2	5.51E-02	1.17E+03	5.55E-02
4-Isopropyltoluene	7	3.94E-02	6.92E+02	6.18E-02
1,3,5-Trimethylbenzene	13.9	3.35E-02	1.27E+02	4.32E-02
p-Xylene	5.69	1.09E-02	4.68E+01	1.06E-02
Ethylbenzene	2.93	9.38E-03	6.59E+01	8.98E-03
Styrene	1.95	5.28E-03	5.18E+01	1.05E-02
Naphthalene	3.24	3.67E-03	1.81E+01	3.23E-03
n-Propylbenzene	1.95	1.90E-03	2.86E+00	4.21E-03
Benzene	0.8	1.79E-03	3.18E+00	1.36E-03
Benzene, 1,3-dimethyl-	7	1.04E-03	3.08E-01	9.63E-04
Benzene, 1,2,4-trimethyl-	11.44	9.89E-04	2.46E-01	1.36E-03
Isopropylbenzene	2.43	5.59E-04	2.41E-01	6.33E-04
Benzene, propyl-	8	4.20E-04	2.60E-02	5.12E-04
Benzene, butyl-	8	3.21E-04	1.67E-02	4.06E-04
1-Propene, 1,3-dichloro-,	8	2.74E-04	3.23E+02	3.00E+00
Benzene, 1,2,3,4-tetramethyl	9.01	1.93E-04	5.05E-03	2.18E-04
Ethene, 1,1-dichloro-	1.69	4.24E-05	9.13E-04	3.30E-05
o-Xylene	7.44	2.01E-05	6.01E-05	3.50E-05
m-Xylene	9.52	1.35E-05	2.47E-05	2.07E-05
p-Isopropyltoluene	7	8.90E-06	1.36E-05	6.76E-06
Methylene chloride	0.04	5.30E-06	6.39E-04	4.27E-06
Ethane 1,1-dichloro	0.07	1.24E-06	2.74E-05	1.67E-06
Chloroform	0.02	7.28E-07	3.05E-05	5.85E-07
Ethane, 1,2-dibromo-	0.1	2.44E-07	1.38E-06	4.18E-07
Ethane, 1,1,1-trichloro-	0.005	3.62E-08	4.88E-07	5.40E-08

$$\{y_1, y_2, \ldots, y_M\} = f\left(\{x_1, x_2, \ldots, x_k\}\right) \tag{12.4}$$

where y_j are the physical concentrations, mass fluxes and deposition fluxes of species that are approximated. Since there is a range of possible values which each input parameter can take, it is important to treat the input variables as being independent of each other with their statistics defined by their probability distribution function (PDF) over this range. All of the input variables are considered random; thus, the output variables also are considered random variables. This is explained in more detail in Cohen and Prinn (2009).

The smallest possible set of input variables capturing the effects of urban chemical and physical processing must be derived in order to form a reduced-form model which is as compact as possible. This set of inputs need to be flexible enough to be applicable to the many variations of the properties of urban areas. The variables need to span the differences in geography, location, time of the year, atmospheric temperature, cloudiness, amount and type of precipitation, vertical motion, time tendency of emissions, spatial tendency of emissions, the amount of each type of

Table 12.11 Descriptions of the input variable PDFs used

Input variable	Type of PDF#	Kolkata urban area
Day of the year (days)	Uniform	1
	(a,b)	365
Geographic latitude of urban area (°+90)	Beta	2.554
	(p,q,a,b)	2.131
		78.4
		125.4
Temporal weight	Uniform	0.00
	(a,b)	1.00
Spatial distance (Km)	Uniform	21.6
	(a,b)	93.2
Daily Average:	Beta	8.483
Surface temperature [° K]	(p,q,a,b)	2.810
		267.4
		309.4
Diurnal	Beta	1.741
Temperature [° K]	(p,q,a,b)	1.976
		5.318
		18.76
TVOC [ton/day]	Fixed (S)	0.2089
NOx [ton/day]	Fixed (S)	0.2511
Boundary values		
Ozone [ppb]	Lognormal	70.11
	(m,σ)	1.099
NOx [ppt]	Lognormal	19.22
	(m,σ)	1.595
TVOC [ppt]	Lognormal	472.98
	(m,σ)	2.534
Carbonyls [ppt]	Lognormal	502.65
	(m,σ)	3.015

See Eqs. 12.5, 12.6, 12.7, and 12.8 for PDF formulas and parameters

emitted species and the upwind concentrations of species of interest as a function of space and time.

These input variable PDFs are defined and described in Table 12.11 using the following formulas:

$$\text{Uniform}\,(a \le x \le b): f(x) = 1/(b-a) \tag{12.5}$$

$$\text{Beta}\,(a \le x \le b; p,q > 0): \mathbf{f}(x) = \left[(x-a)p - 1(b-x)q - 1\right]/ \\ \left[\left(\int 01tp - 1(1-t)q - 1\mathbf{d}t\right)(b-a)p + q - 1\right] \tag{12.6}$$

$$\text{Lognormal}(x, m, \sigma > 0): \mathbf{f}(x) = \exp\left(-\left(\ln(x/m)\right)2/\left(2\sigma2\right)\right)/\left(x\sigma\sqrt{(2\pi)}\right) \qquad (12.7)$$

$$\text{Fixed}: f(x) = xS \qquad (12.8)$$

where a, b, p, q, m, σ and S are the parameters, and x is the input value, which in the case of the fixed equation is the emissions of the appropriate parent species (either CO or BC). The first set of input variables in Table 12.11 are for the time, location, emission spatial distribution and temperatures as discussed later. The second set of input variables are fluxes for those species that are directly emitted in the urban area. The directly emitted species considered here are NOx (95 % emitted as NO and 5 % emitted as NO_2) and VOCs.

The other set of input variables in Table 12.11 are the mole fractions of trace species along the boundaries (the four sides and the top) of the urban area that impact the chemical and physical processing inside the urban area. The trace species considered in this analysis are NOx, O_3, TVOCs (represented by toluene, xylene and chloroform) and carbonyls. These concentration data were fitted by lognormal probability distribution functions, as given in Figs. 12.13, 12.14, 12.15, and 12.16.

The first two variables are the day of the year and the latitude of the urban region. These are both needed for computing the ultraviolet radiative flux. A uniform variable has been assigned, from 1 to 365, for the day of the year. A beta fit of the distribution of latitudes of urban area has been assumed, with an assumption that the whole urban area is of equal importance.

The daily average temperature and the daily diurnal temperature, at the surface of the urban area, are the other inputs. The atmospheric temperature in the urban area and its range are important variables for determining the rates of many chemical reactions, Henry's law partitioning, gas/aerosol phase partitioning, the state of water in the urban atmosphere and the state and amount of precipitation. For the purposes of determining their global distribution, historical temperature data (Jones et al. 1999) has been weighted by the beta PDF of latitude for the urban area and the
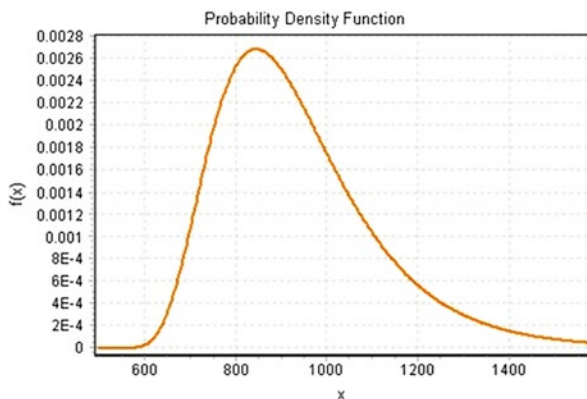

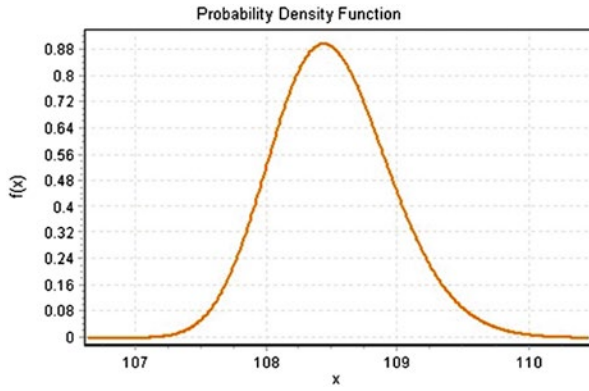**Fig. 12.13** Lognormal probability distribution function of carbonyls

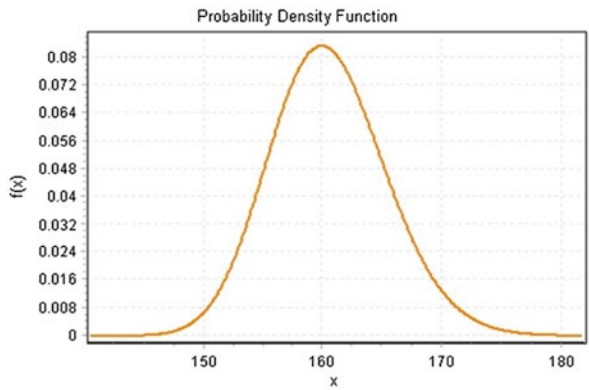**Fig. 12.14** Lognormal probability distribution function of NOx

Fig. 12.15 Lognormal probability distribution function of ozone
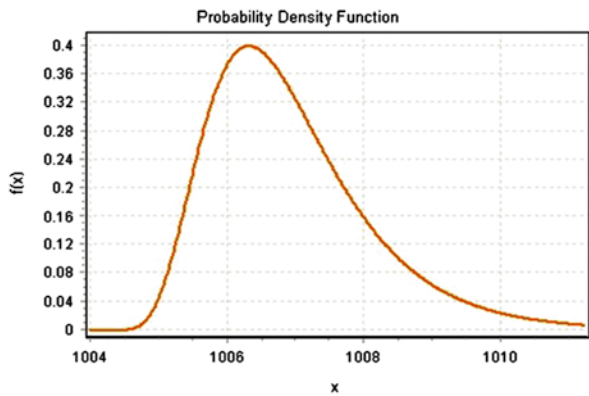

Fig. 12.16 Lognormal probability distribution function of total non-carbonyl VOC

resulting data fitted by a beta function. The average 16 temperatures of each vertical layer above the surface is computed assuming a linear decline with height with standard linear lapse rate of 6.5 K/km. The spatial and temporal deviations from these layer averages in the temperature of each grid box of the urban domain are taken from the meteorology chosen for that particular urban region.

The last physical input is rainfall (and the associated cloudiness), which impacts the radiative fluxes, the uptake of soluble gases and the removal rate of aerosols. After extensive testing, it has been found that treating these inputs as separate variables using the PCM approach does not yield reasonable results, due to the extremely non-linear impact these variables have on the system. Therefore, separate metamodels were formed for each of the four meteorological conditions. It is commonly found that emissions in urban areas have a time profile which is doubly peaked, with the peaks occurring around the times of the morning and evening rush hours.

The first variable thus represents the temporal distribution of emissions, which mimics transportation and habitation patterns of the people.

To account for this, an input variable (wt) is defined that is uniformly distributed from 0 to 1 and is the weight given to this double-peaked temporal emissions spectrum when it is linearly added to a time-invariant emissions profile. Therefore, for any given value of wt, the weights assigned to the double-peaked distribution is wt and the weight assigned to the time-invariant emissions distribution is 1-wt (Yang et al. 2005). A second input variable relates to the spatial distribution of emissions in the urban region. Such a distribution must consider that urban areas vary greatly in terms of their density of people, activity and thus emissions. In general, different emitted species come from different sources, which themselves may be distributed independently from one another in many cases. However, since most emissions are related to the population in the urban centres, the emissions of both VOC and NOx are considered to be spatially correlated. These spatial distributions are fitted by a two-dimensional Gaussian function whose standard diameter has a uniform distribution.

Another input is required to simulate whether VOC emissions consist of a larger fraction of light hydrocarbons.

To address the issue of the impacts of the circulation, water content and temperature on the processing in urban areas, three different realistic sets of meteorology have been used to drive the urban modeling system. The widely different cases are considered to represent different seasons and to numerically analyse the impact of adopting different types of realistic meteorology.

12.3.6 Concentrations, Mass Fluxes and Deposition

The results for the urban concentrations for ozone, formaldehyde, acetaldehyde, toluene and xylene species are given in Figs. 12.17, 12.18, 12.19, 12.20, and 12.21.

The regions of higher mole fractions must have a larger net chemical production (production minus loss) of the species. Conversely, regions with lower mole
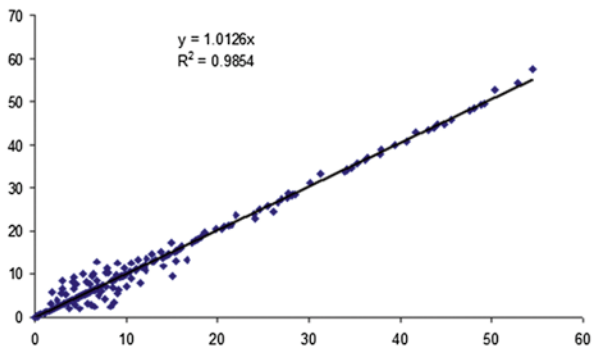
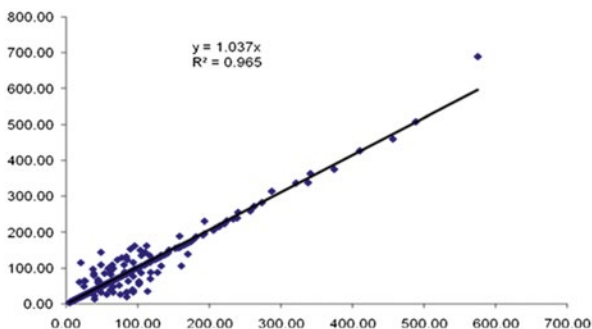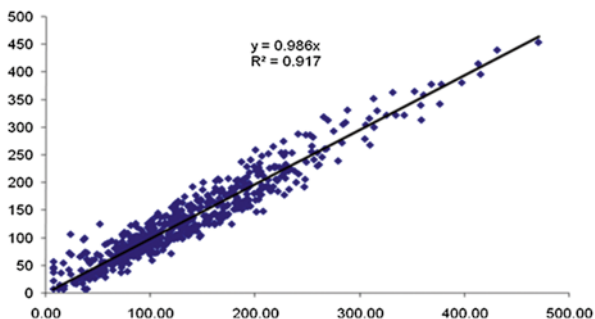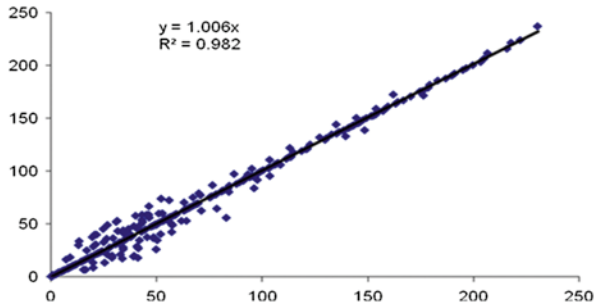**Fig. 12.17** Observed and predicted concentration of ozone

Fig. 12.18 Observed and predicted concentration of formaldehyde

Fig. 12.19 Observed and predicted concentration of acetaldehyde. X-axis, observed concentration, y-axis predicted concentration


fractions must have a more smaller or negative net chemical production of the species. Also, if the mole fraction remains constant across different regions, then this means that there is negligible net chemical production.

When looking at the metamodel results for the mass fluxes, emissions, chemical production or loss and the deposition, it is straightforward to determine whether the urban area is a net importer or exporter of the species of interest. For a species to have a mass flux which is not equal to its emissions, there must be a net amount of

Fig. 12.20 Observed and predicted concentration of toluene
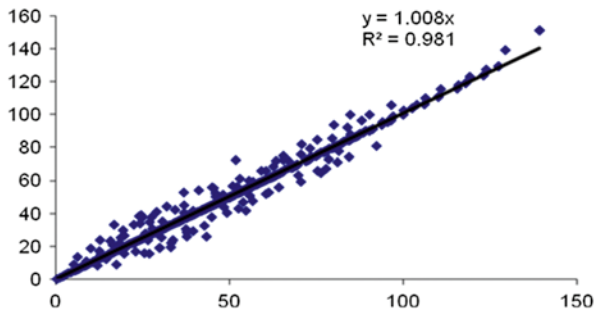
Fig. 12.21 Observed and predicted concentration of xylene. X-axis observed concentration, y-axis predicted concentration

chemical processing, deposition or convergence or divergence in the continuity equation. A convenient parameter is the ratio of the export flux to the emissions:

$$\text{Flux}\,/\,\text{Emiss}= \left(\text{Emiss}+\text{Chem}-\text{Dep}\right)/\,\text{Emiss}=1+\text{Chem}\,/\,\text{Emiss}-\text{Dep}\,/\,\text{Emiss} \qquad (12.9)$$

Here the Flux is the net mass flux [g/day] through the boundaries of the urban region, Emiss is the emissions [g/day] into the urban area, Chem is the net chemical production [g/day] within the urban region and Dep is the deposition [g/day] to the surface of the urban region.

Using this, if the mass flux is positive and larger than the emissions, then the in situ chemical net production must be larger than the in situ depositional losses. Conversely, if a species has a mass flux which is positive but smaller than its emissions, its losses due to deposition must be greater than its net chemical production. Furthermore, for a species to have a mass flux which is negative (a net flux into the region), the in situ net chemical loss must be so large as to consume not only all of the emissions but also some of the species mass transported through the boundaries into the urban area.

If *Xi* is the value computed by the metamodel, *Xip* is the value computed by the CAMx model and n is the number of points analysed, we have

$$\text{Normalized RMS} = \sqrt{\left(\Sigma i = 1, n\left(X_{ip} - X_i\right)2 / n\right)} / \sqrt{\left(\Sigma j = 1, nX_i^2 / n\right)} \qquad (12.10)$$

The RMS error gives a measure of the absolute magnitude of the error.

Normalised fractional RMS errors for species concentrations using CAMx model

Species	Summer	Monsoon	Winter
Ozone	1.38E-01	2.68E-01	1.46E-01
Formaldehyde	2.98E-01	3.75E-01	3.01E-01
Acetaldehyde	1.36E-01	3.69E-01	3.76E-01
Toluene	7.94E-01	0.89E-01	8.15E-01
Xylene	3.57E-01	9.67E-01	4.15E-01

12.4   Conclusions

VOCs in the urban airshed of Kolkata are contributed mainly due to fuel burning. It is observed that benzene levels are below the recent standard prescribed by CPCB. Vehicle-related sources typically contribute the largest to ambient VOCs. Naphtha and mineral oil combustion as major sources indicate rampant adulteration of fuel. High levels of chloroform may be due to the liberal use of bleaching powder in fish markets. Odabasi (2008) has shown that concentrations of chloroform (8–52 times) and carbon tetrachloride (1–1,170 times) significantly increase above baseline quantities in the household with the use of bleach-containing products.

Observed high levels of acrolein, formaldehyde and acetone may be due to cigarette smoke. This fact corroborates with the fact that the percentage of the smoking population is highest in Kolkata in India. High levels of observed formaldehyde and other carbonyls confirm cigarette smoke as a source besides the atmospheric chemistry.

Kolkata urban airshed can be considered to be NOx sensitive based on the VOC/NOx ratio.

Location	Percentage of population smoking (age 15–49)		
	Men	Women	Total
India	33.3	1.6	34.9
Kolkata	50.0	0.1	50.1
Chennai	30.5	0.1	30.6
Mumbai	22.1	0.1	22.2
Hyderabad	21.9	0.1	22.0

Source: National Family Health Survey (NFHS-3), 2005–2006, by the International Institute of Population Sciences, Deonar, Mumbai

It is currently established that ozone is a secondary pollutant formed by reactions of NOx and VOC, known as ozone precursors. So it is widely accepted that control strategies targeting ozone attainment must necessarily be based upon the control of its precursors. As the science of atmospheric photochemistry evolved, it became clear that complex, non-linear, feedback control processes relate NOx and VOC precursor mixing ratios to ozone mixing ratios. This fact led regulators to adopt mathematical models that include the best representation of the non-linear chemistry as the basis of needed control computations.

The amount of ozone attributable to each reaction species is estimated using MIR scales developed by Carter and SAPRC-07. Control strategies derived from the isopleths generated under the constraint of constant VOC/NOx ratio, for an upwind location, often do not reflect the conditions in downwind areas, where the VOC/NOx ratio is different. Mathematical model provides useful information and may be used to explain the main aspects of air pollution, but it requires detailed meteorological and kinetics of tropospheric chemical reaction data as inputs.

Note: Figures 12.2, 12.3, 12.4, 12.5, 12.6, 12.7, 12.8, 12.9, 12.10, 12.11, 12.12, 12.13, 12.14, 12.15, 12.16, 12.17, 12.18, 12.19, 12.20, and 12.21 have been developed by the authors from data generated at the institute.

References

Carter WPL (2007) Development of the SAPRC-07 chemical mechanism and updated ozone reactivity scales, Final report to the California Air Resources Board Contract No. 03-318. August. (www.cert.ucr.edu/~carter/SAPRC)

Carter WPL (2010) Development of a condensed SAPRC-07 chemical mechanism. Atmos Environ 44(40):5336–5345

Cohen J, Prinn R (2009) Development of a fast and detailed model of urban-scale chemical and physical processing. MIT Joint Program on the Science and Policy of Global Change Report no. 181

CPCB (2009) National ambient air quality standards. cpcb.nic.in/National_Ambient_Air_Quality_Standards.php

CPCB (2010) Study of urban air quality in Kolkata for source identification and estimation of ozone, carbonyls, NOx and VOC emissions. Control of Urban Pollution Series: CUPS/72/20010-11. Central Pollution Control Board (Ministry of Environment & Forests) August, 2010

Finlayson-Pitts BJ, Pitts JN (2000) In chemistry of the upper and lower atmosphere. Academic, New York

Goldsmith JR, Nadel JA (1969) Experimental exposure of human subjects to ozone. J Air Pollut Control Assoc 19(5):329–330

Jones PD, New M, Parker DE, Martin S, Rigor IG (1999) Surface air temperature and its changes over the past 150 years. Rev Geophys 37(2):173–199

Krupa SV, Manning WJ (1988) Atmospheric ozone: formation and effects on vegetation. Environ Pollut 50:101–137

Odabasi M (2008) Halogenated volatile organic compounds from the use of chlorine-bleach- containing household products. Environ Sci Technol 42:1445–1451

Roselle SJ, Pierce TE, Schere KL (1991) The sensitivity of regional ozone modelling to biogenic hydrocarbons. J Geophys Res 96:7371–7394

Tatang MA, Pan WW, Prinn RG, McRae GJ (1997) An efficient method for parametric uncertainty analysis of numerical geophysical models. J Geophys Res Atmos 102(D18):21925–21932

USEPA- Compendium Method TO-17 (1999) epa.gov/ttn/amtic/files/ambient/airtox/to-17r.pdf

Yang KL, Ting CC, Wang JL, Wingenter OW, Chan CC (2005) Diurnal and seasonal cycles of ozone precursors observed from continuous measurement at an urban site, in Taiwan. Atmos Environ 39(18):3221–3230