Research Article

Gaseous pollutants over different sites in a metropolitan region (Pune) over India

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Abstract
The various gaseous pollutants (ozone, nitrogen oxides, carbon monoxide and Volatile Organic Compounds) were measured at 9 different micro—environments (i.e. Urban area, semi urban area, industrial area, residential area, agricultural area, etc.) over Pune city in the year 2017 (January–December). The urban area had the highest concentration of ozone (during Mar to May), attributed mainly due to the high concentration of the precursor gases like nitrogen oxide (NO_x) and carbon monoxide (CO). The diurnal patterns of CO and NO_x show inverse relation with Ozone at all the locations indicating that during ozone production these gases are utilized. However, NO_x at the urban locations is found to be high even during the day when generally the ozone concentrations were high. The airport area of the city showed higher concentration of Ozone after 12 am (early morning hours). VOC's such as benzene, toluene, ethylbenzene and xylenes are also found to play a role in the formation of the tropospheric ozone. The maximum increment reactivity of different VOCs enables in determining the ozone forming potential at each of our locations. Toluene is found to have the highest ozone forming potential amongst the VOCs in most of the locations. The distribution of pollutants and its potential sources over this Metropolitan region is illustrated in detail in this paper.

Keywords Air pollution · Nitrogen oxides · Tropospheric ozone · Volatile organic compounds · Metropolitan region

1 Introduction

In urban environments, the air pollution is on increase due to anthropogenic emissions from various sources. The ever growing atmospheric trace gas concentration is one of the challenging issues in industrial and urban environments [1, 2]. India which is a fast developing nation, with its rapid urbanization and industrialization is a region exposed to vast levels of pollutants. Gaseous pollutants like Nitrous Oxides, volatile organic compounds (VOCs), Tropospheric Ozone, Carbon monoxide are some of the many pollutants emitted in the atmosphere which cause air pollution. Ozone at ground level acts as a strong oxidant and thus is detrimental to human health and vegetation [3]. The trace gases not only have an impact on the air quality of a particular environment but also play a role in modulating the earth's climate by modifying the radiation and energy balance of the earth's atmosphere [4–6]. Due to industrialization, urban developments and transport, gases such as Carbon Monoxide, Nitrous Oxides, Methane, VOCs are emitted which are chemically involved in producing tropospheric ozone. Ozone in troposphere also occurs by transport of air from the stratosphere [4, 5, 7]. The ozone concentration in tropical countries is also contributed from biomass burning especially forest fires [8–10]. Ozone is a greenhouse gas and its increasing concentrations results in warming of the troposphere and thus inducing climate change in the long run [11–13]. Due to the anthropogenic emissions as well as natural

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sources like lightning and vegetation the contribution of NO_x, CO and VOCs are increasing in urban as well as rural areas. To understand the long term effects of Ozone (O_3) and its precursor gases on the ambient air quality of a locality it is necessary to undertake studies about these gases. O_3 is a chemically complex gas and thus it is essential to study what are the governing factors causing an increase or decrease in the levels of this gas. To understand the variability of O_3 in a region it is essential to study the various gaseous species which are involved in the production of this gaseous pollutant. In urban locations the emissions from transport sector and industries is a major contributor to the NO_x concentrations [14]. In urban areas a group of aromatic VOCs like benzene, toulene, ethylbenzene, xylenes (BTEX) contribute to 60% of the non-methane VOCs [15] and these VOCs also react with nitrates to form secondary organic aerosols. The presence of VOCs in urban air is mainly attributed to man-made factors viz. use of mechanical vehicles equipped with gasoline or diesel engines [16]. Carbon Monoxide (CO) also forms a part of the precursor gas of tropospheric ozone. The major anthropogenic sources of CO include motor vehicles exhaust, industrial activities, heating and incinerators. CO reacts with water vapour producing OH radical and in the presence of UV radiation leads to the formation of Ozone in the presence of sufficient NO_x. Thus it is necessary to study all the precursor gases which are chemically involved in producing tropospheric Ozone. Elevated levels of VOCs and NO_x have led to an approximate doubling of Ozone in the lower troposphere over the past of couple of centuries, making tropospheric ozone the third most important anthropogenic greenhouse gas after CO_2 and methane.

This study is carried over the Pune Metropolitan Region using the observational network of the system of air quality and weather forecasting and research (SAFAR), which was established in Pune in the year 2013. For the forecasting of Air Quality, a very high resolution emission inventory (1.67 km × 1.67 km) was developed for a domain of 50 km × 50 km for Pune Metropolitan Region. This emission inventory was developed for various pollutants like PM_{10}, $PM_{2.5}$, BC, OC, CO, NOx, and VOCs over Pune Metropolitan region. Based on the emission inventory conducted, various emission hotspots and sources were identified and thus different strategic locations within the city were chosen where the continuous monitoring of the various pollutants is carried out. For the continuous measurements of the various species air quality monitoring stations (AQMS) are setup with different analyzers. This study is carried out to assess the variability of the gaseous pollutants within Pune Metropolitan Region at different locations for the year 2017.

2 Observational site, general meteorology and data

Pune (18.52° N 73.85° E) is a metro city in the state of Maharashtra in the western part of India situated in the Western Ghats of Sahyadris. It is located at an altitude of 598 m above sea level. The observations were carried out over different environments within the city of Pune as shown in Fig. 1. Each of the observational sites has different environments and thus different micro environments of the city are covered. Pune is a fast developing urban city, with a growing Information Technology hub, number of industries and many private vehicles owing to an increase in the transport sector. Due to these reasons it is essential to investigate the gaseous pollutants affecting the air quality of the city. Owing to a rise in the vehicles in Pune the emissions from transport sector are on the rise and thus contributing to O_3 precursors like CO, NO_x etc. There have been many studies where the ambient trace gases have been monitored for many Indian cities including Pune [17]. All of these studies pertained to observations taken at a single location representing the whole city. In our study we have undertaken observations at various locations within Pune city thus enabling to capture different type of areas of the city. The different observational sites in Pune city include an industrial area, traffic junctions, residential area, background (green environment), pilgrim site, urban site and agricultural area. These sites are spread out all throughout the Pune Metropolitan Region (PMR) including the twin township of Pimpri Chinchwad. The different observational sites are viz. Pashan (background area), Shivajinagar (core city area), Lohegaon (airport), Alandi (pilgrim area), Katraj (urban area), Hadapsar (urban complex), Bhosari (industrial area), Nigdi (residential area), Manjri (sugar industry). Each of these sites will hereafter be addressed as S1(Pashan), S2(Shivajinagar), S3(Lohegaon), S4(Alandi), S5(Katraj), S6(Hadapsar), S7(Bhosari), S8(Nigdi) and S9(Manjri).

For the measurement of various pollutants, the AQMS which have been set up at each of the locations mentioned above have online analyzers for measuring each of the pollutants. Each of the observational sites is also equipped with an automatic weather station (AWS) with the help of which the various meteorological parameters are obtained. All the analyzers are US-EPA approved. The ozone analyzer (model O342M) used to detect the gaseous ozone uses the principle of Ozone detection by absorption in Ultraviolet light and it is a continuous Ozone monitoring instrument. Its minimum detectable limit is 1 ppb and the measurement range is 0.1–10 ppm. Carbon Monoxide monitoring is done by

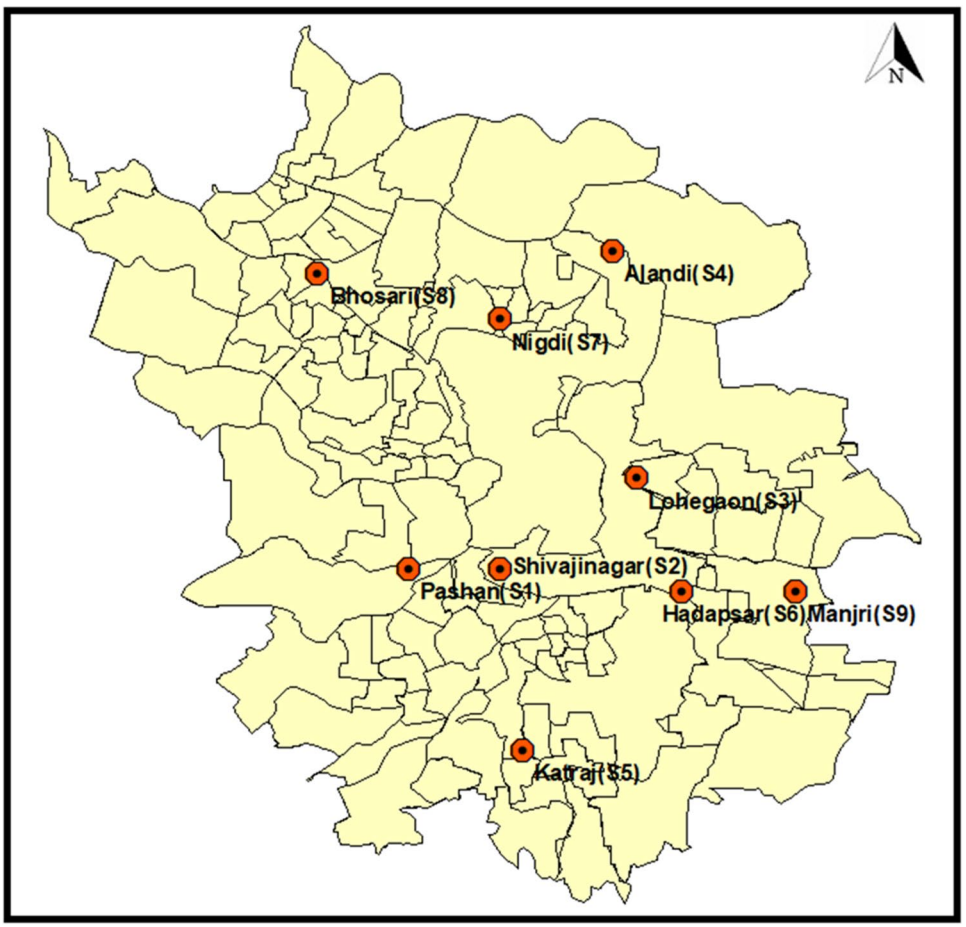

Fig. 1 Map showing the different micro-environments in Pune

the CO analyzer (Model CO12M) which uses the principle of absorption in the infrared region according to the Beer-Lambert law and it is suitable for measuring low concentrations in ambient air. The maximum detection limit is up to 200 ppm and the minimum detectable limit is 0.05 ppm. The instrument used to monitor the VOCs (Model VOC72M) is based on gas chromatography coupled with photo-ionization detection. This detector detects the VOCs viz. Benzene, Toulene, MP-Xylene and O-Xylene. The lower detectable limit is 0.05 µg/m^3 and maximum up to 1000 µg/m^3 can be detected. To monitor Nitrogen oxides the detector (Model AC32M) used is designed to monitor low concentrations in ambient air. It uses the principle of chemiluminescence i.e. NO emits light in presence of highly oxidizing ozone molecules. Here first NO and NO_x are detected and the difference of the two give NO_2. The minimum detectable limit is 0.4 ppb and the maximum detection limit is 50 ppm.

2.1 Meteorological background

Pune is located on the leeward side of the Western Ghats and has a fair weather. It experiences a normal monsoon and not very heavy rains as it is on the leeward side of the Western Ghats. During winter season the minimum temperatures in this city drop down and thus increasing the level of the pollutants as the low temperature reduces vertical mixing and thus lowers the mixing layer height thereby trapping the pollutants in the atmosphere. Each of our observational sites is spread out at different locations and thus the micro meteorology plays an important role.

The wind direction and wind speed for each of these observational sites is depicted through the windrose diagram in Fig. 2. It is observed that each of these locations have different mean wind speeds. The highest mean wind speed is observed at the site S3 which reaches up to 4.5 m/s. At sites S4, S7, S8 and S9 the mean wind speed attains a maximum of 3.2–3.6 m/s. Exceptionally low wind speeds are observed at site S6 where the mean wind speeds reach a maximum of only 0.7 m/s. Low wind speeds indicate that there will be low dispersion of pollutants from the atmosphere. All these observational sites have different wind directions all throughout the year and they are different for each of the sites. Thus, the city of Pune does not show very high wind speeds in the year 2017. Each of the observational sites differs in their wind

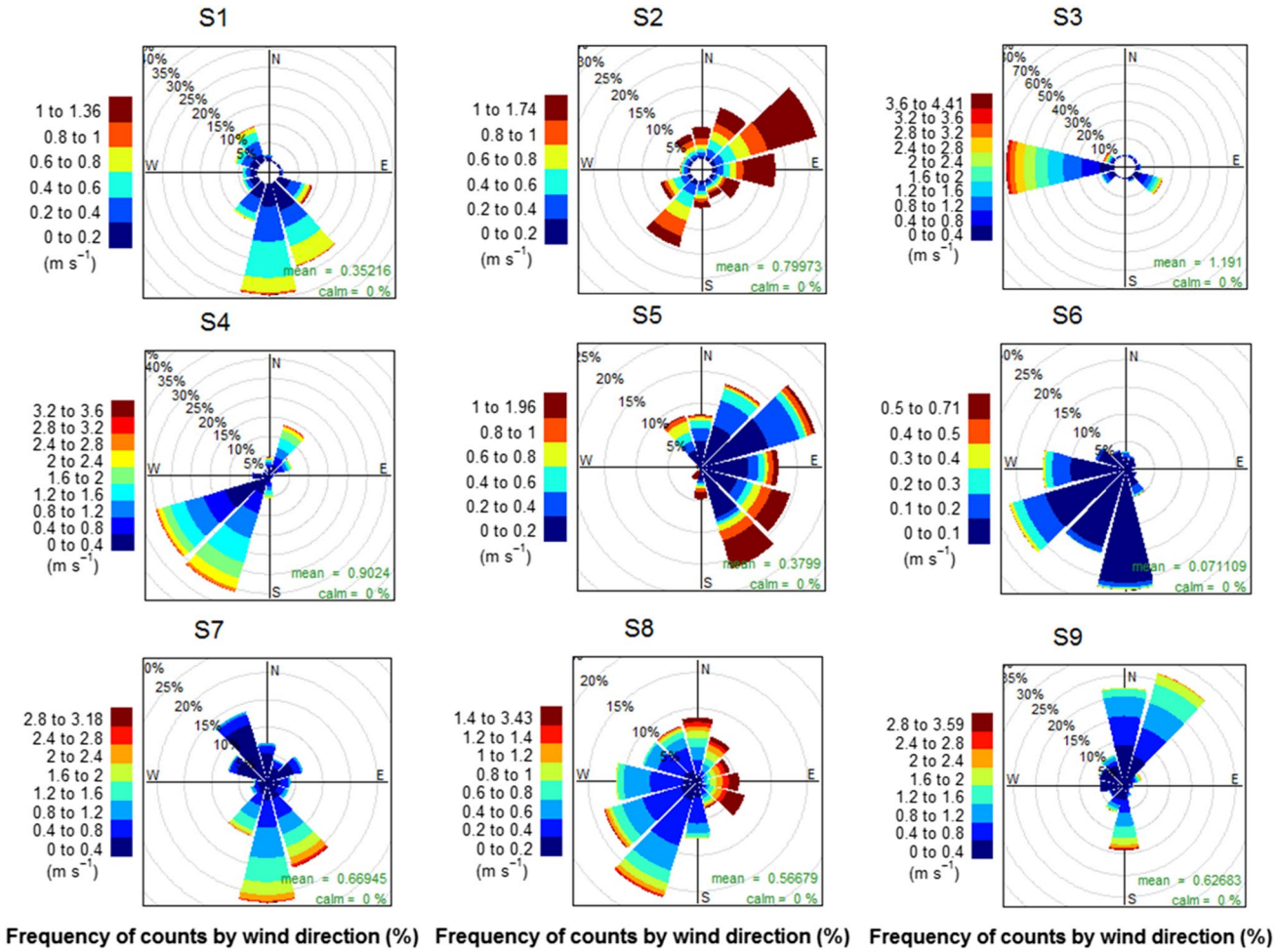

Fig. 2 Wind rose showing the wind speed and wind direction

speeds and wind directions indicating the importance of the micro meteorology.

Generally, Pune experiences higher temperatures in the summer season and in the winter season on some occasions low minimum temperatures are observed. While observing the minimum and maximum temperatures (Fig. 3) at the different sites in Pune in the year 2017, there are some daily variations observed amongst the sites (Fig. 4).

3 Results and discussion

3.1 Monthly variability of CO

The eight hourly mean concentration of CO at different environments in Pune for the duration of Jan 2017 to Dec 2017 is shown in Fig. 5. The highest concentration observed was around 2.8–3 ppm at few sites. Only certain peaks of high-level concentration were observed but no significant long periods of high concentration were observed. It is observed that during Jun to Sept the CO concentrations were particularly lower than the other months. However, at site S4 and S8 the concentration shows a higher value of about 2.5 ppm. At site S9 the CO concentrations observed did not vary much and it was in the range of 0.5–1.5 ppm throughout the year.

The diurnal variability of CO is depicted in Fig. 6. It can be observed that, each of the locations has different patterns, however generally at most locations the concentration was found to peak at 9 h. At site S1, the month of Feb had the highest concentration of CO, which was around 1.3 ppm. During Feb and Mar distinguished diurnal variability was observed as compared to other months. The CO concentration showed a peak at 9–10 h in all months (except for Jun to Sept). In the month of Aug, there was no diurnal variability observed and the concentration remained very low. At site S2 the concentration of CO was high almost all throughout the month of Aug with the concentration peaking between

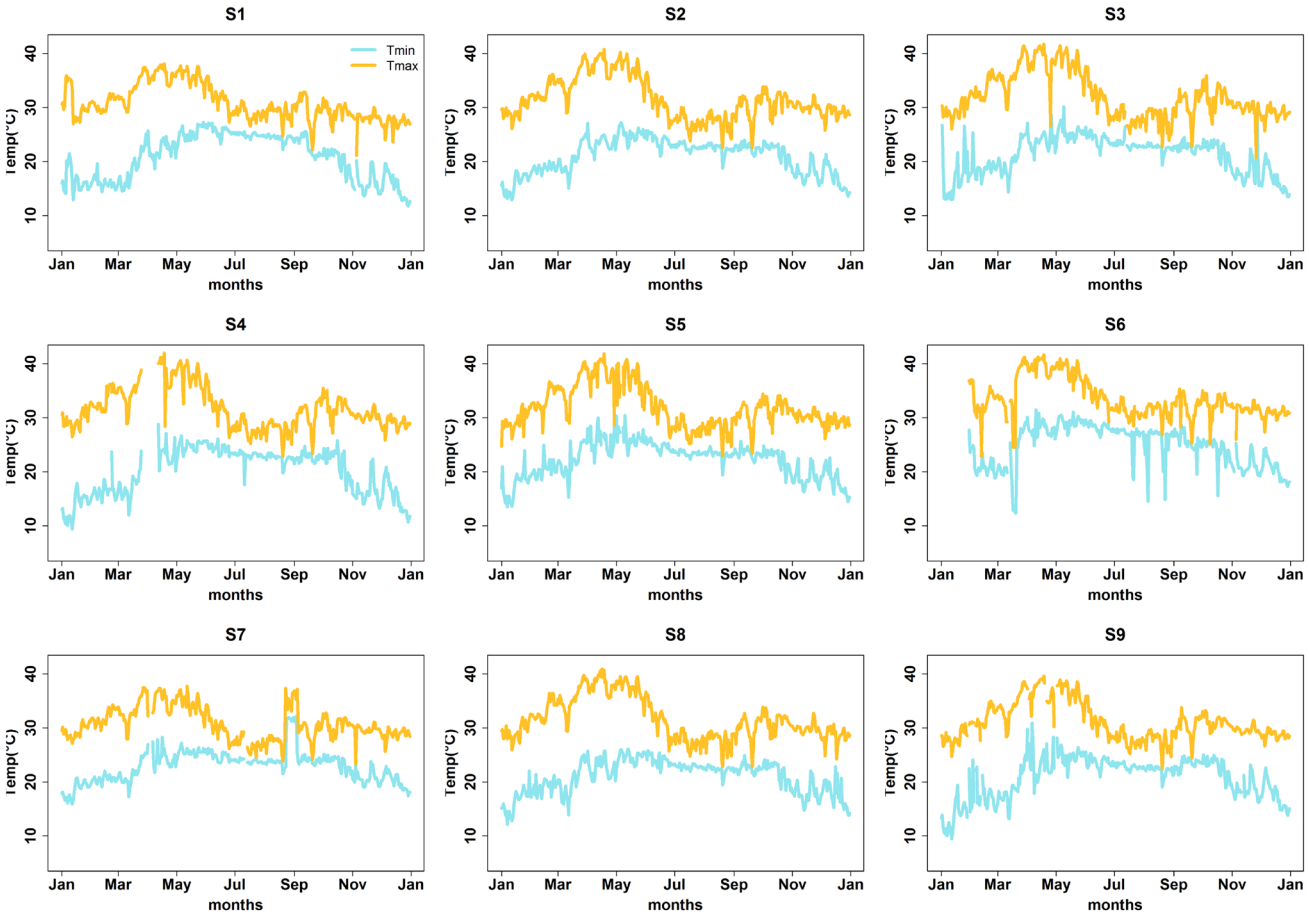

Fig. 3 Daily minimum and maximum temperature

9 and 11 h. However, in Oct and Nov a night time peak was also observed at this location and the concentration was 2.1 ppm. S2 is a traffic junction and owing to high vehicular emission CO concentration is higher almost all throughout the year. S3 is the location which had the highest concentration as compared to the other sites. S3 has the influence of aircrafts and also of other vehicles which ply on the road as it is in the proximity of the city's airport and thus has higher emissions. In the month of Jun, the concentrations were low in all locations, however, at S3 site the concentrations were found to be around 2.5–2.7 ppm during 5–9 h. The month of Dec had high concentration and the concentration was found to have 3 peaks (at 5 h, then between 11 and 13 h and again at midnight). Even at site S4, Dec showed the highest level of CO concentration with peak concentration of 1.8–2 ppm at 9–10 h. In the month of Dec, the temperatures are lower and the wind speed is low thus accounting for higher concentration. Here, even in the month of Aug, high concentration was observed as opposed to other locations. S4 being a pilgrim site has temples located around it and therefore during certain festivities people flock to this location thereby causing increase in emissions. At location S5 the CO concentration was 3.5 ppm, which was highest in Feb and two prominent peaks were observed at 10 h and 22 h in this month. At this site even in the month of Sept, diurnal variability was observed. At site S6 it is observed that the concentrations were highest in Jan and Dec. A peculiar observation here is that in the month of Nov the CO concentration was only 0.5–0.8 ppm whereas generally in Nov the concentration was higher at almost all sites. In the month of Jan and Mar, proper diurnal variability was visible at site S7 with a peak in the concentration at 9 h. However, it is in the month of May that the concentration was highest amongst all the other months, but there was no or little diurnal variability observed. S8 site does not show any strong diurnal variability and it is observed that the concentration is higher in Aug. Being a residential site here the sources of emission of CO is not that high. CO concentration was the lowest at site S9 and again there is no strong diurnal variability observed.

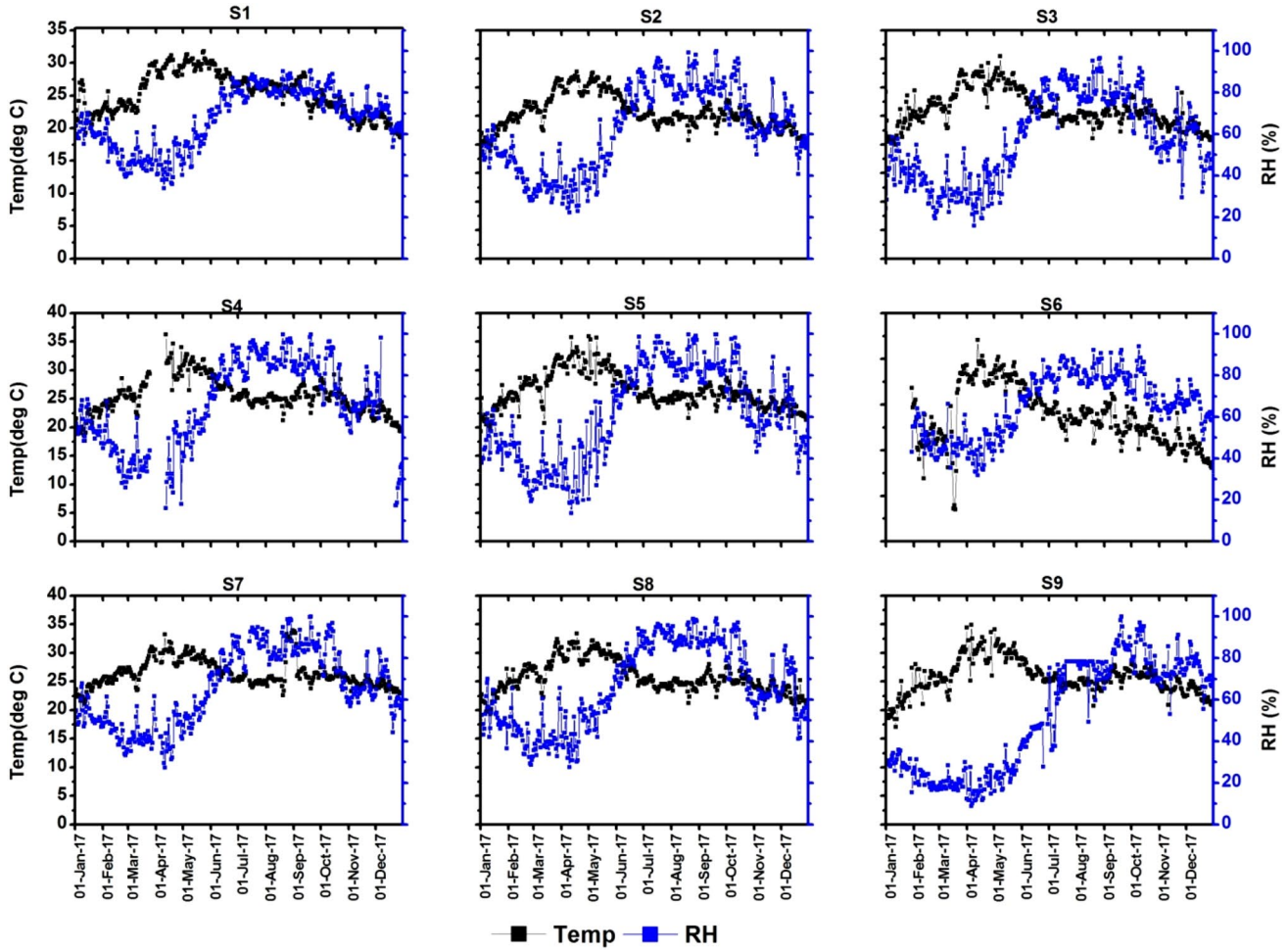

Fig. 4 Daily average temperature and relative humidity

3.2 Variability in NO_x, NO and NO_2

The diurnal variability of NO_x, NO_2 and NO for each month in the year 2017 is depicted in Figs. 7, 8 and 9 respectively. It is observed that moreover these three gases follow a similar pattern. The highest NO_x concentration was observed at sites S3, S2 and S6 respectively which are mainly areas dominated with heavy transport. Site S3 being an airport site and as there are many vehicles plying in the region mainly the emissions are from transport sector thus contributing to the NO_x concentrations. S2 is a major traffic area in the city and thus the NO_x concentrations are higher and S6 is an urban complex and thus the anthropogenic activities (mainly due to transport sector) are higher here due to which NO_x concentration is higher. The total vehicle density in Pune Municipal corporation region was about 2.3 crores in 2012 and site S6 had the second largest number of vehicles on road according to the survey [18]. The highest concentration at location S1 was observed in Oct during 17–19 h. At site S2, diurnal variability of NO_x showed peaks at midnight, 9 h and again in the evening at 19 h which can be attributed to the rush hours of traffic in the morning and evening. Another reason could be associated with the boundary layer, after sunrise the nocturnal boundary layer breaks, lifting up the concentration and thus giving a sharp peak in the morning. The evening peak can be attributed to the decadence of the local boundary layer [19, 20]. The concentration was highest in the month of Feb (165 ppb) and was lowest in Aug and Sep. At S3 it is observed that from Jan to Mar significant diurnal variability is observed with a prominent peak around 9 h. Except for Nov and Dec all other months showed a diurnal variability, however not as significant as seen in the initial months of the year. Site S4 also showed a similar pattern like S3 with significant diurnal variability in the months Jan to Mar and Nov–Dec. Site S5 showed high concentration in the month of Apr and May and at this site the peaks are observed during 13–14 h and 17–18 h and no typical morning peak was

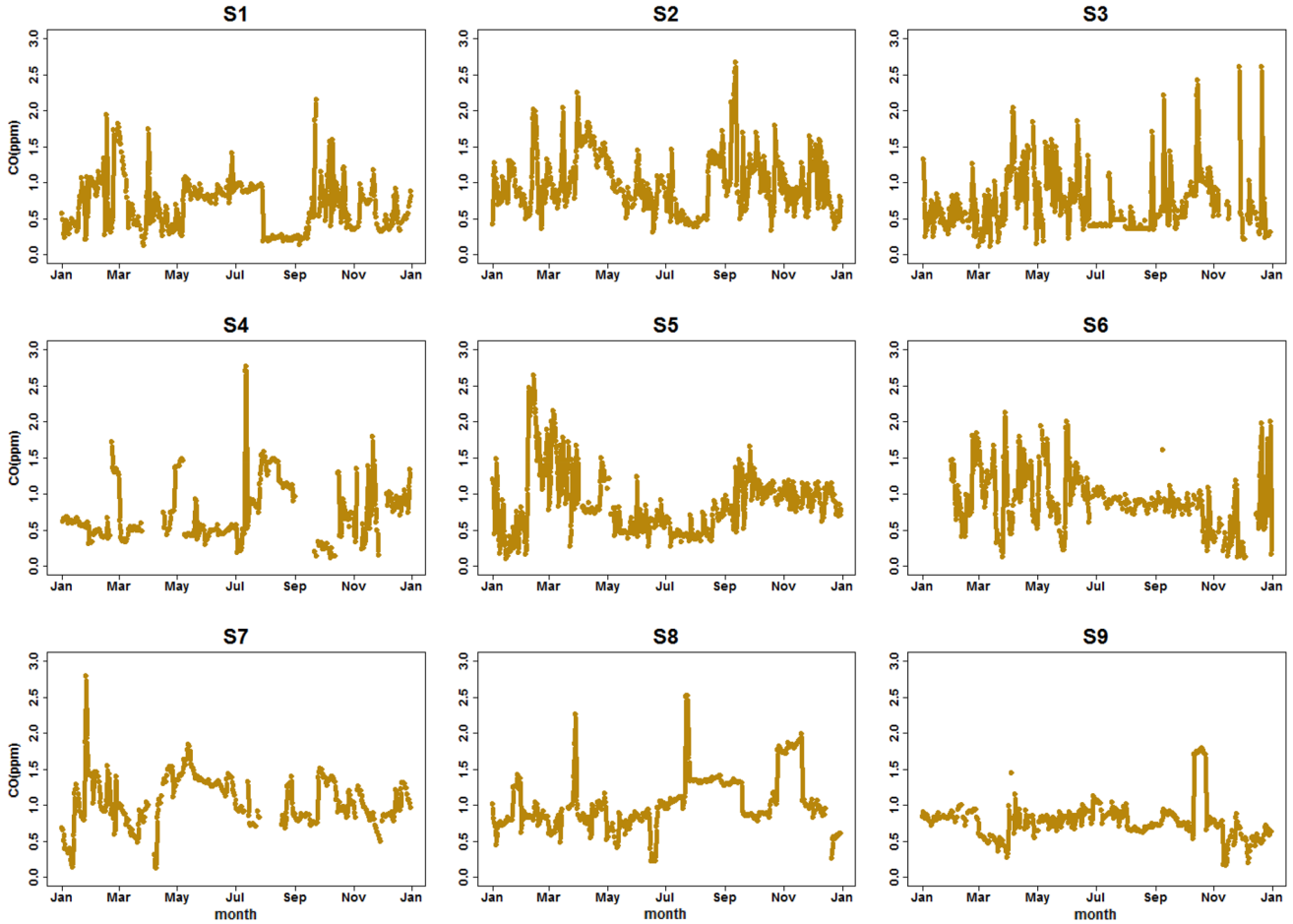

Fig. 5 Daily mean 8 h CO concentrations

observed. Site S6 does not show the typical diurnal pattern and showed many peaks during Jan with the highest concentration about 130 ppb. However in Feb and Mar the concentration peaks around 10–11 h which was the normal morning peak observed at other locations. There was no specific NO_x diurnal variability observed at site S7 except in the months Nov and Dec. At site S8 the diurnal variability in NO_x was observed in the month of Feb, Nov and Dec. Site S9 does not show any significant diurnal variability in most of the months except for the months Jan and Feb.

The highest concentration of NO_2 and NO was observed at sites S6, S2 and S3. Like NO_x diurnal variability of NO_2 and NO showed a similar pattern with a peak concentration in the morning time (9–11 h). The sites S1 and S9 show no diurnal variability of NO_2 all throughout the year, S1 being a background clean site has not many emission sources and thus there are no specific peaks observed. At the other sites a prominent diurnal variability was visible generally during the months Jan to Mar and Nov to Dec. Diurnal variability of NO at site S4 showed a peak in the concentration in the month of Apr along with the other months mentioned above at night time (20–21 h).

3.3 Monthly and diurnal variation of ozone

The eight hours (10–18 h) average O_3 concentrations during the period, from Jan 2017 to Dec 2017 are shown in Fig. 10. It is observed that the daily concentrations have lower values in the months from Jun to Sept. At the site S1 the O_3 concentration does not show any strong variability from Jan to Apr. Higher concentration was observed in the month of May and Nov and the highest concentration was observed to be 70 ± 15 ppb. As CO and nitrogen oxide concentration are lower at S1, the ozone production will be lower. At site S2 high concentration of about 70 ± 9 ppb was observed during Feb and Mar. At the site S2 no significant increase in the O_3 concentrations was observed after the monsoon months same as in site S1. Site S3 had the highest concentration of 86 ppb in the month of Feb for the first few days after which the concentration was found to decrease. Even in the month of Jun we could observe

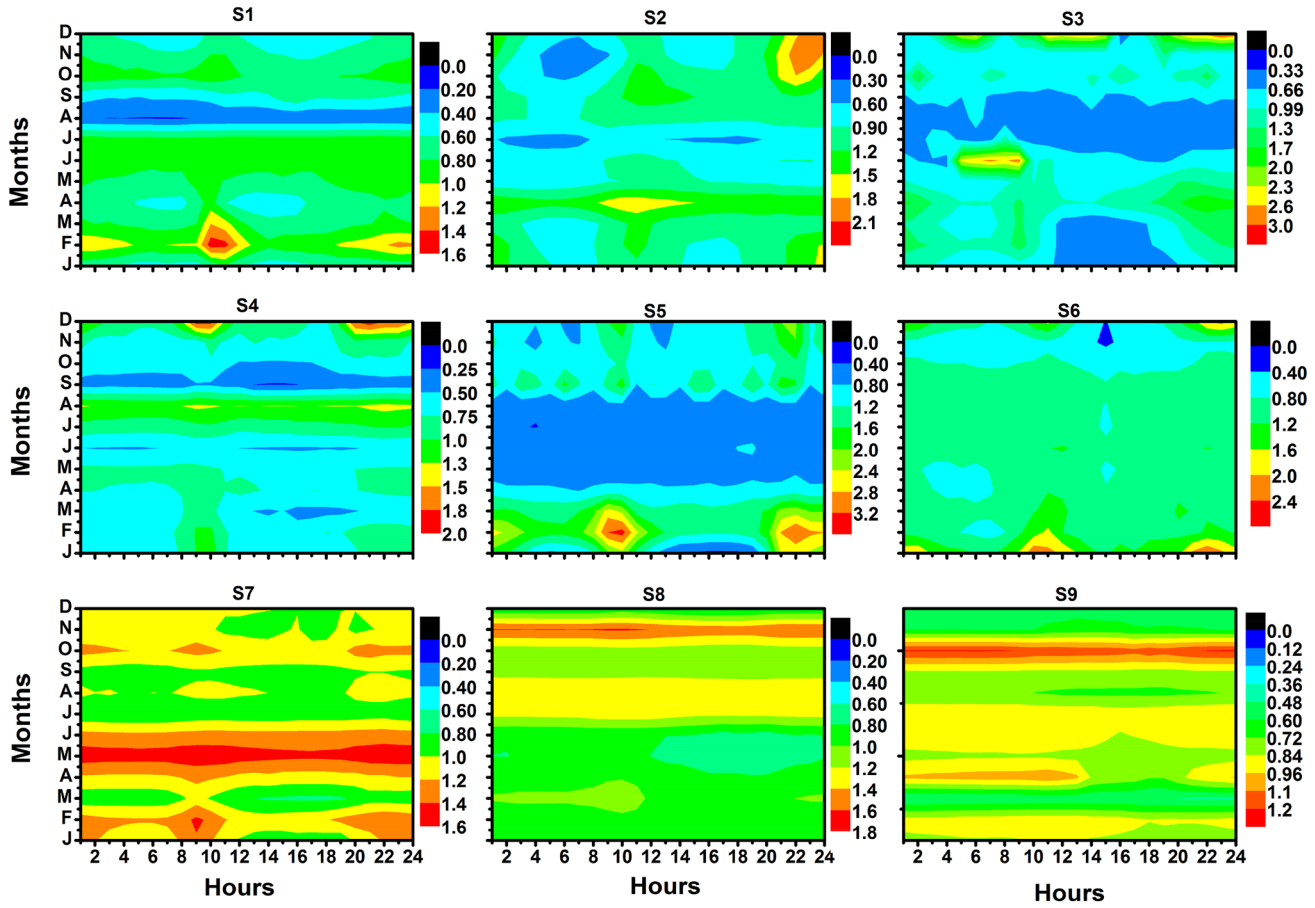

Fig. 6 Diurnal variability of CO from Jan 2017 to Dec 2017

high O_3 concentrations at site S3. S3 being located close to the city airport is in the proximity of the emissions of ozone precursor gases. At the site S4 the O_3 concentrations varied between 35 and 50 ppb from Jan to May and then further decreased during Jun to Aug. From mid-Oct the concentration was found to increase and attained a maximum of 70 ppb in Nov and Dec. The site S5 showed the highest concentration amongst all the other sites in the month of Sep and has the maximum concentration of 92 ppb. This is an urban site and hence the precursor gases of O_3 are higher which further build up the concentration of O_3. Generally the site S5 has higher O_3 concentration from Apr to Jun as compared to all the other sites and then there is a significant dip in the O_3 levels thereafter. In this location the O_3 concentration was higher during the summer months of Apr to May than the concentration in the months Nov to Dec. S6 is the location where the concentration was lowest as compared to all the other stations and the values ranged between 10 and 45 ppb. Locations S7 and S8 had a similar pattern with concentrations peaking to about 65–70 ppb, however at different periods (viz. at S7 in Mar and in S8 during Feb and Nov). At S9 the concentrations were generally in the range 10–40 ppb with only a peak observed in the month of Jun. It can be observed that O_3 concentrations were generally higher during the months Feb to Jun at some locations and at some during Nov and Dec. As the Ozone Production is basically dependent on its precursor gases and sunlight; these play a major role in the variations amongst each of the locations. Ozone which is a secondary pollutant has various precursor gases which affect its formation in the atmosphere. In this study it is observed that in different locations in Pune the ozone formation is dependent on the various gases like CO, NO_x, NO_2 and VOCS.

Diurnal variation of Ozone is shown in Fig. 11 Ozone is typically produced in the atmosphere in the presence of sunlight due to the chemical reactions between Nitrogen oxides, VOCs, CO etc. Thus, generally the daytime concentration of O_3 is higher as compared to other times of the day. The diurnal variability of O_3 for the time period Jan 2017 to Dec 2017 is shown in Fig. 6 at the various sites in Pune. On a whole the diurnal variability shows higher concentration between 12 and 18 h. Generally, the diurnal concentrations are higher in the months of Mar to

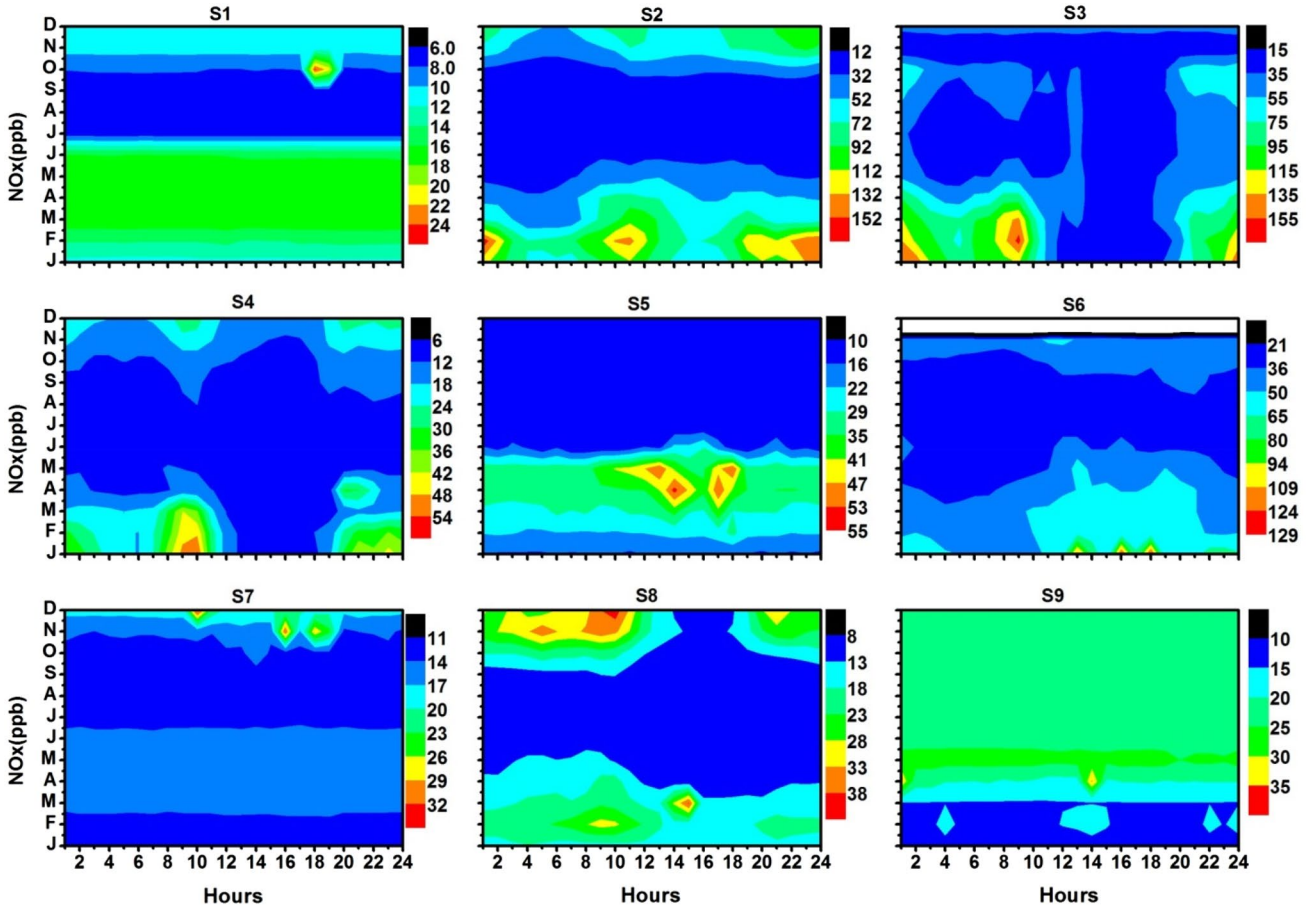

Fig. 7 Diurnal variability of NO_x from Jan 2017 to Dec 2017

May and at some locations during Nov and Dec. At site S1 the high concentration was observed between 16 and 17 h in the month of Mar and Apr and the concentration was observed to be about 60 ppb. In the month of Nov higher concentration was observed (66–68 ppb) during 13–15 h. In the months Jun to Sept the O_3 concentration does not show any variability with the evolution of the day and it is about 10–20 ppb. At S2 the highest concentration (57 ppb) is observed in the month of Mar during 16to 17 h (slight variability also was observed during Jun-Sept periods also), Oct and Nov also followed a similar pattern like Mar. The site S3 had the highest concentration of O_3 as compared to all the other sites. At this location a peculiarity is observed and that is in Feb and Mar the ozone concentrations showed a night time high and a decrease during the day. The highest concentration was observed during 8–11 h and it was 80–83 ppb in Feb. During Jun to Oct there was no significant diurnal variability observed at this site owing to the monsoon season. S4 has highest O_3 concentration of 60–70 ppb in Nov and Dec during 12–17 h. The site S5 showed high concentration in the month of May (between 10 and 19 h), which was not as in the case at the other sites. Even at site S6 May month had the highest concentration between 16 and 19 h. From Oct to Dec the well-defined diurnal pattern of O_3 is observed at this site. Generally, the diurnal pattern of ozone i.e. an increase with the evolution of the day and decrease during the night hours is observed. But each of the location has different timings when the peak is observed. Only S3 showed slightly different feature of early morning high concentration of Ozone.

The diurnal average for the whole year of 2017 for both NO_x and O_3 is shown in Fig. 12. When the average of Ozone and NO_x for the whole year is plotted against each other it showed an inverse correlation. It is seen that at sites S2, S3, S4, S7 and S8, the peak in the NO_x concentration was present at 9 h. Sites S2, S3, S4 and S8 showed proper inverse relation between Ozone and NO_x i.e. during the day time when the O_3 concentration increases, the NO_x concentration decreases. The Ozone concentration showed peak during 12–18 h at all the locations. At site S1, NO_x did not show any particular variability except for a peak at 17 h. At location S5, S6 and S7 this inverse relation is not observed between the two gaseous pollutants and NO_x shows peaks

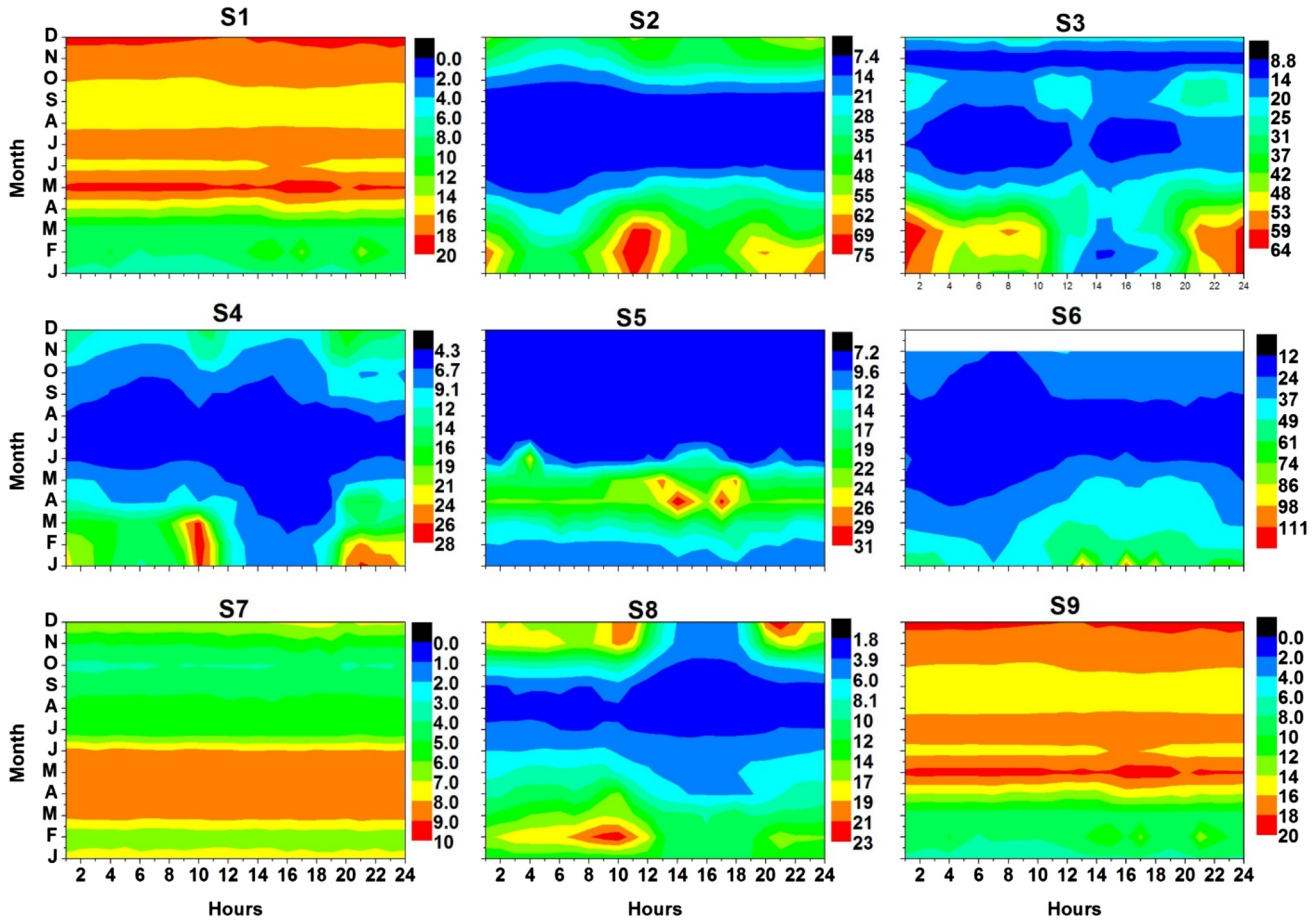

Fig. 8 Diurnal variability of NO_2 from Jan 2017 to Dec 2017

even during the day time. Though the locations are in close proximity to each other due to difference in the emissions at each location the pollutant concentrations vary. Ozone production is dominated by the following reactions

$$NO_2 + h\nu \rightarrow NO + O \quad \text{(R1)}$$

$$O + O_2 + M \rightarrow O_3 + M \quad \text{(R2)}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad \text{(R3)}$$

Nitrogen Dioxide provides the molecular Oxygen needed for producing Ozone in the troposphere. Along with this CO and VOCSs also play a role in the formation of Ozone. NO_x and VOCs combine in the presence of sunlight to form tropospheric ozone. Ozone has high accumulation rate when the photolysis rate of NO_2 is higher than that of NO during nighttime [21]. The mean NO concentration is lower when the Ozone concentration is high at site S3 and this contributes to reduction of NO titration rates and thus affects the O_3 removal rates during the night hours and thus O_3 remains in the atmosphere. Therefore site S3 has higher O_3 at night time (observed in Fig. 11). Low NO_x concentrations also play a role in the removal of O_3 during the night allowing O_3 to stay in the atmosphere [22]. It is observed that the NO_x concentrations are not very low but are lower when the O_3 concentrations are higher.

3.4 Variability of VOCs

The different VOCs at each of the locations are depicted in the Fig. 13. The daily mean values of the VOCs are plotted in this figure and it can be seen that each of the VOCs have different levels of concentrations at different locations. The site S6 has the highest concentration of benzene with the concentration reaching about 35 μg/m^3. It was observed that this location has many outliers as compared to other locations whereas most of the locations had lower concentrations varying between 5 and 20 μg/m^3. The ethyl benzene concentrations showed that all the sites show low concentrations except for site S2; here the concentration varies from 10 to 80 μg/m^3. Xylenes had highest concentration at site S6 and S2 and all other locations have comparatively

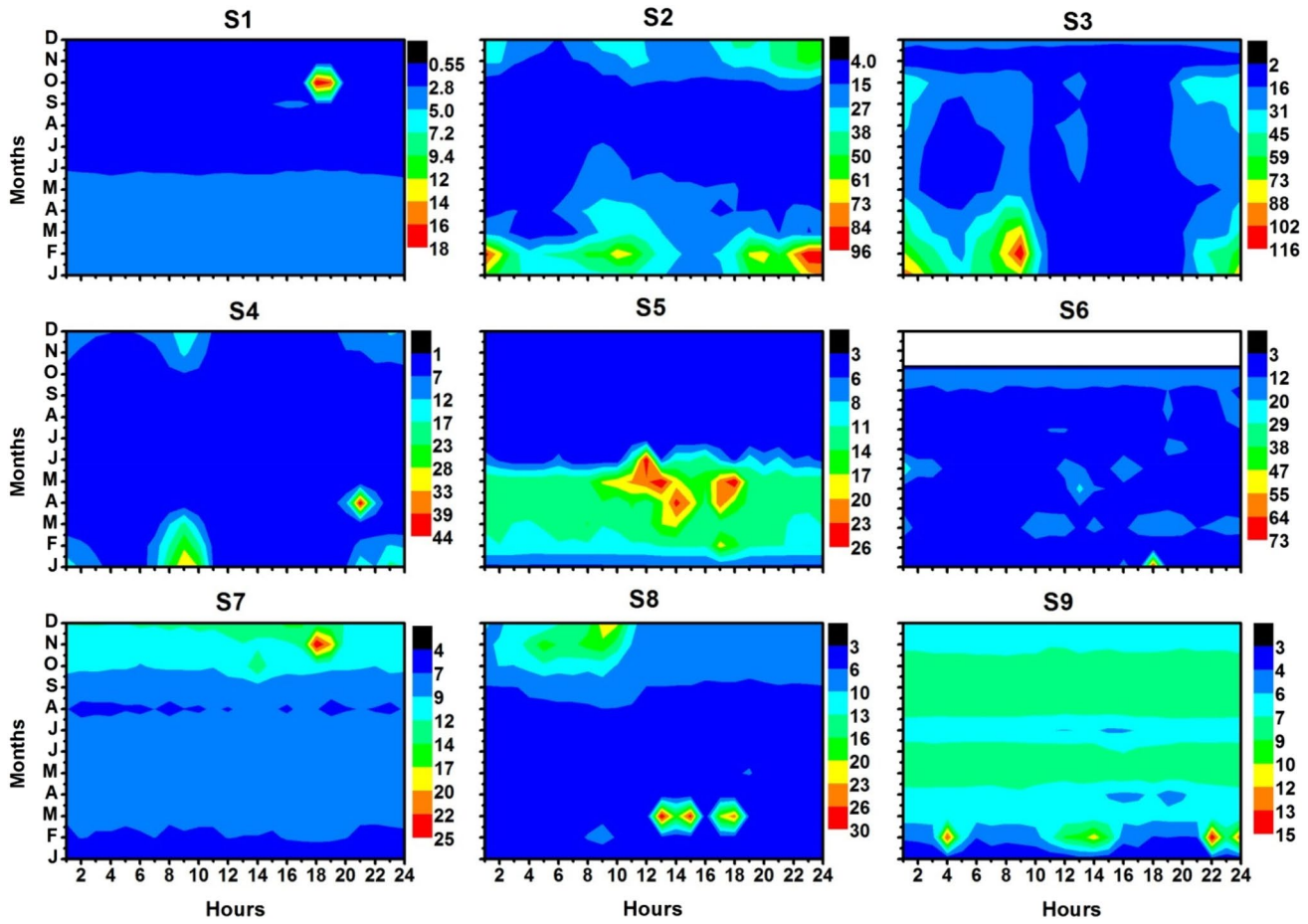

Fig. 9 Diurnal variability of NO from Jan 2017 to Dec 2017

low concentrations. Toluene has the highest magnitude amongst all the VOCs that are measured and its highest concentration is observed to be at site S6 (approximately 100 µg/m^3).

The monthly variability of BTEX is shown in Fig. 14 at the different locations in Pune. It can be observed that site S1 has the lowest magnitude of the different VOCs as compared to the other site as this is a location with low anthropogenic emissions. At site S1 Toluene is the VOC with highest concentration and it shows a high concentration in the month of August and again there is an increase in Nov and Dec. At All locations (except for site S2), toluene was the leading VOC present. But at site S2, Ethyl benzene is found to have the highest concentration and it shows higher concentrations in Jan and from Sept to Dec. At the remaining sites toluene has highest concentration and generally it shows a peak after Oct. At all locations apart from S2 ethyl benzene has the lowest concentration. The maximum concentration of Toluene is observed at site S6 in the month of Nov (60 µg/m^3).

3.5 Inter correlation between the different VOCs

The inter correlation between various VOCs enables to determine whether the VOCs have a single source of emission or different sources. A good correlation between the various species indicates that their source of emission was the same. The inter species correlation values are shown in Table 1. It is observed that site S2 has high correlation value of 0.9 or more (at 95% significance) amongst all the different species indicating that all the VOCs have the same source of emission. S2 being a heavy traffic junction the main source of emissions is vehicular emissions and thus all the VOCs have the same source. According to the Emission Inventory report [18] of Pune Metropolitan region the vehicle density on various roads were taken and the road close to site S2 (University road) had highest number of two wheelers and four wheelers (2.65 lakhs). Benzene is mainly having its source from vehicular emissions and a good correlation of it with other species indicates that those VOCs also originate from the same source.

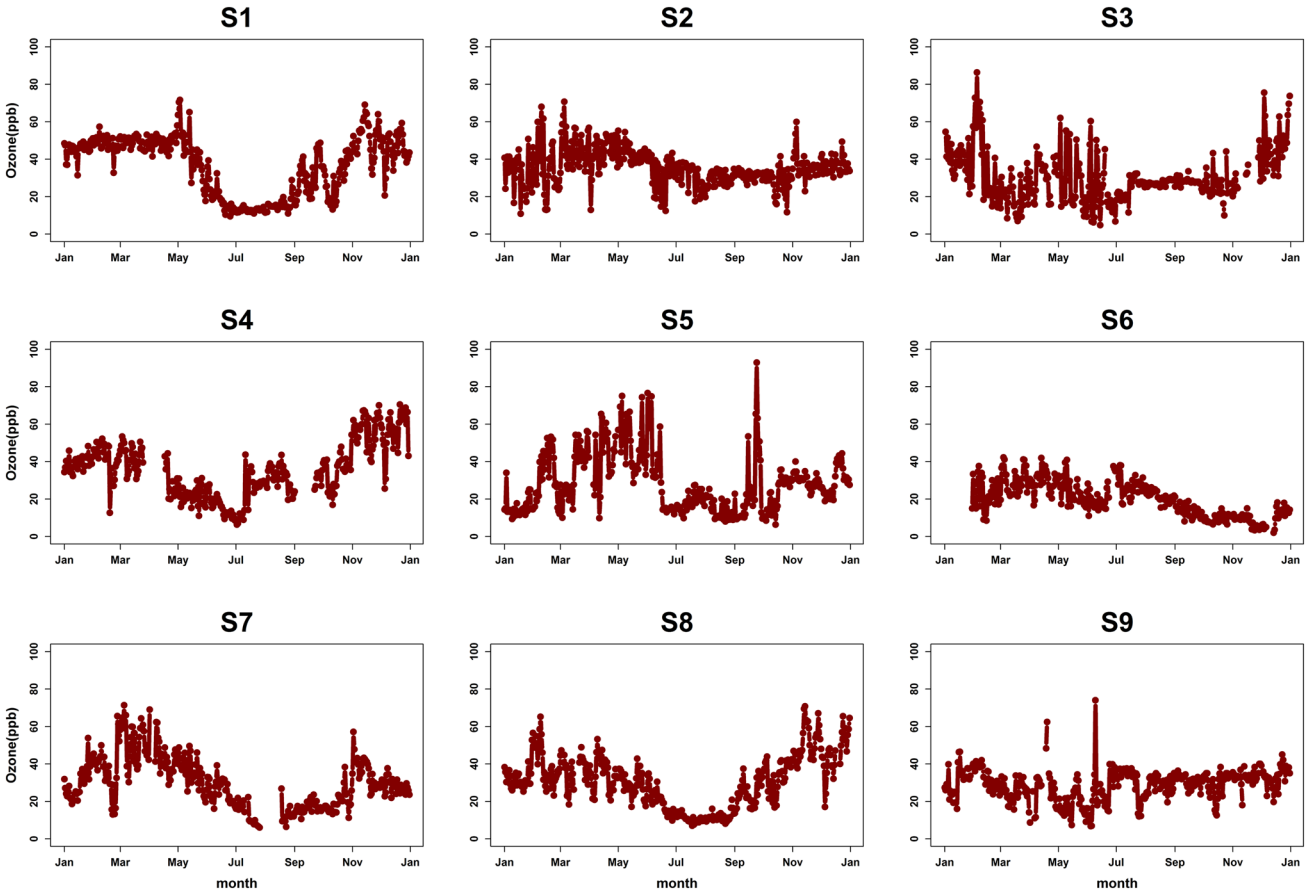

Fig. 10 Daily mean 8 h ozone concentrations at the 9 locations

Benzene has a high correlation with mp-xylene of 0.7–0.8 at sites S1, S6 and S8 and with ethyl benzene at site S4 and with toluene at sites S4, S5, S8 and S9. Only at site S3 benzene has low correlation ($r < 0.5$) with the other species indicating that they do not have the same vehicular emissions as their source. At site S9 ethyl benzene has a high correlation($r = 0.9$) with all the other species of VOCs.

The VOCs can be ranked on the basis of their role in photochemical smog formation including production of tropospheric Ozone [15, 23]. The Maximum Increment Reactivity (MIR) given by Carter is popular in assessing the potential of the different VOCs in the formation of Ozone. The MIR is a unitless coefficient used in a relatively NO_x rich environment to determine how much a specific VOC may contribute in forming Ozone. The MIR coefficients for each of the VOCs and their formation potential are given in Table 2. According to the MIR scales each of the locations has different VOC which is the major contributor in the formation of ozone. Toluene has the highest Ozone forming potential at locations S1, S3, S4, S5, S7, S8 and S9. At location S2 o-xylene has the highest ozone forming potential and it is only at this location that this VOC has the highest ozone forming potential. S6 location shows that mp-xylenes have the highest ozone forming potential. The VOCs are very high at the locations which have heavy traffic density.

4 Conclusions

This study reports variation of gaseous pollutants over different in Environments over Pune.

- It is observed that the concentration of Ozone is highest at the airport site (S3) as compared to all other sites. This is also the only location with the peculiar diurnal variability in the month of Feb.
- The urban complex (S5) also shows higher concentration of Ozone as compared to other locations.
- The concentrations of Ozone are considerably lower at the site S6 which is an area close to a roadside with residential and urban complexes around it.

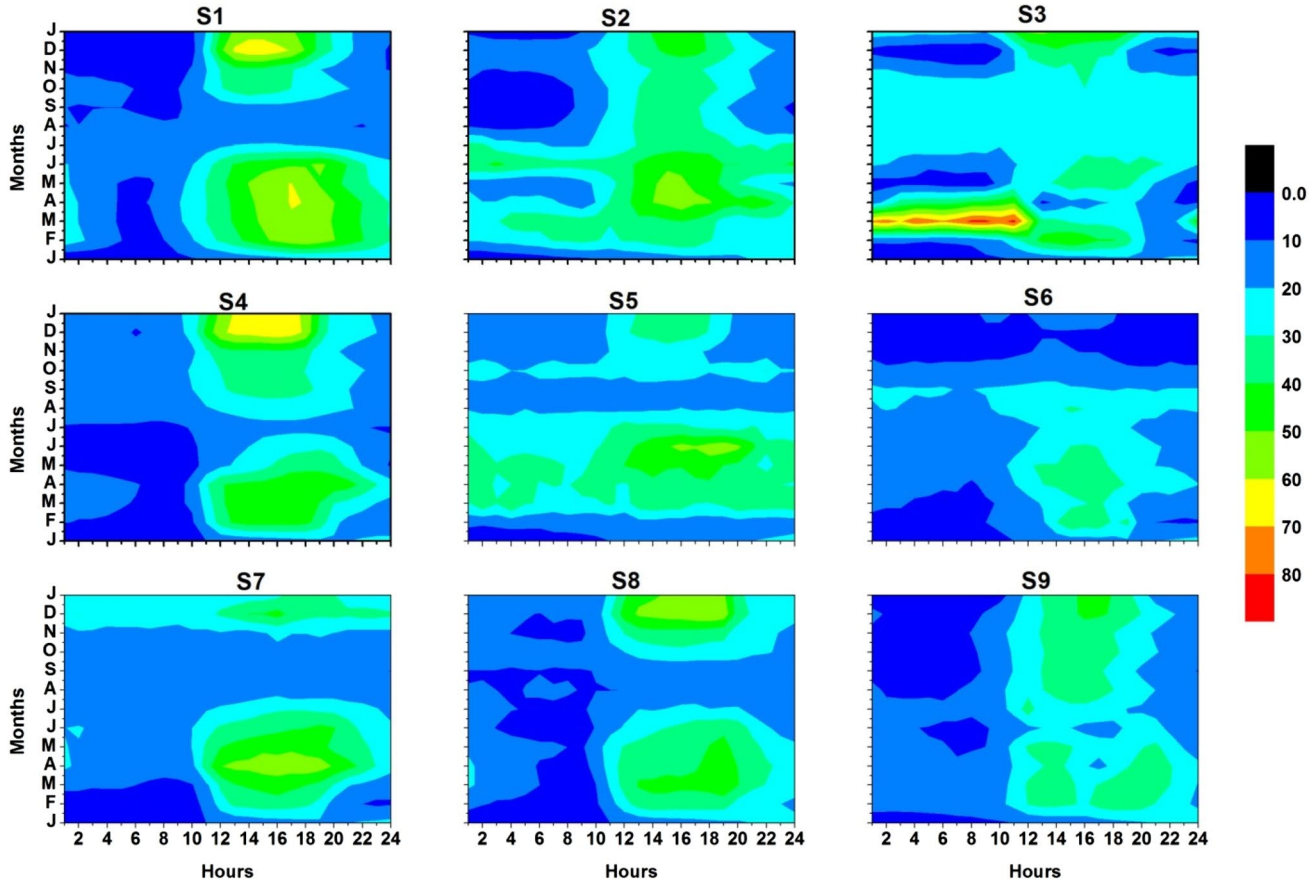

Fig. 11 Diurnal variability of ozone from Jan 2017 to Dec 2017

- The CO concentrations are highest at the airport site and it is lowest at the location (S7) which is the area in the proximity of industries.
- The NO_x and NO concentrations are highest at S3 and S2 locations where the emissions are mainly due to transport sector, whereas NO_2 concentrations are found to be high at site S6 in the month of Jan.
- The major emission sources of these pollutants come from the transport sector followed by industries. The emission inventory report of PMR [18] stated that the transport sector emissions were highest for all the pollutants discussed in this paper.
- As most of the locations have shown the presence of NOx, these locations are NO_x rich environments and thus the VOCs contributing to the formation of Ozone are analyzed. Toluene is observed to have the highest ozone forming potential at almost all stations except for S2 and S6 locations where xylenes have high ozone forming potential.

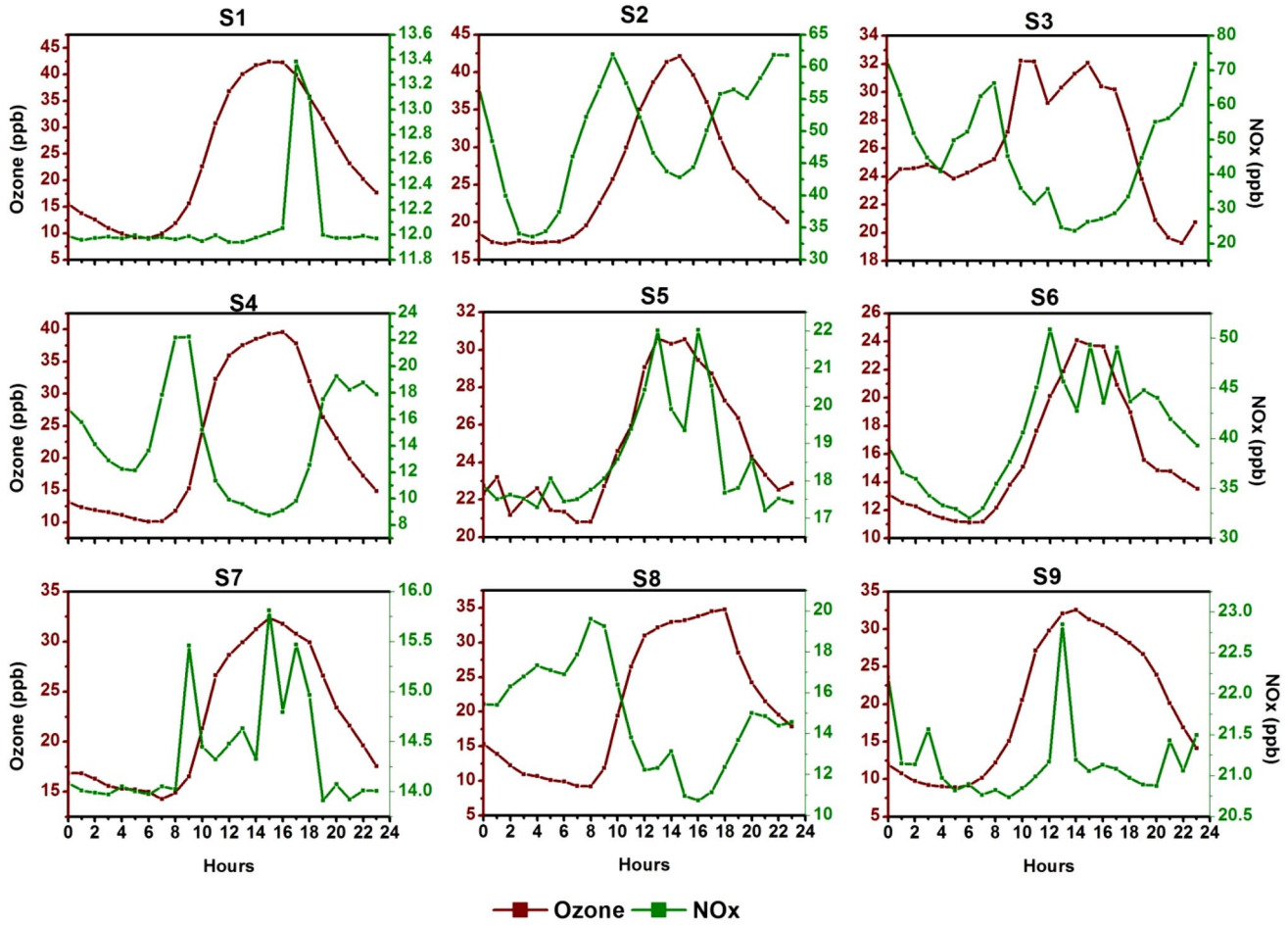

Fig. 12 Diurnal variability of NO_x and O_3 during the year 2017

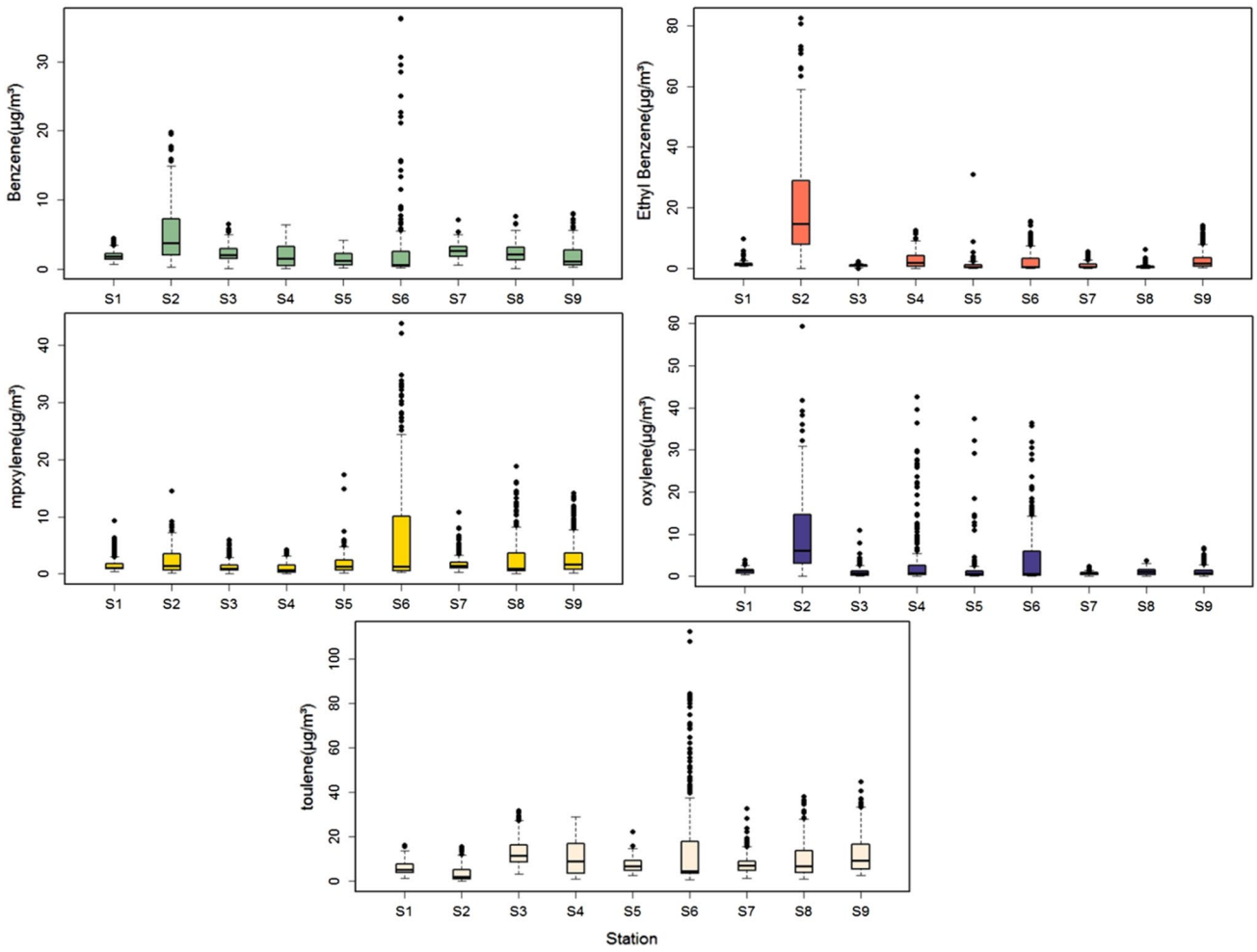

Fig. 13 VOCs at the different locations for the period Jan 2017 to Dec 2017

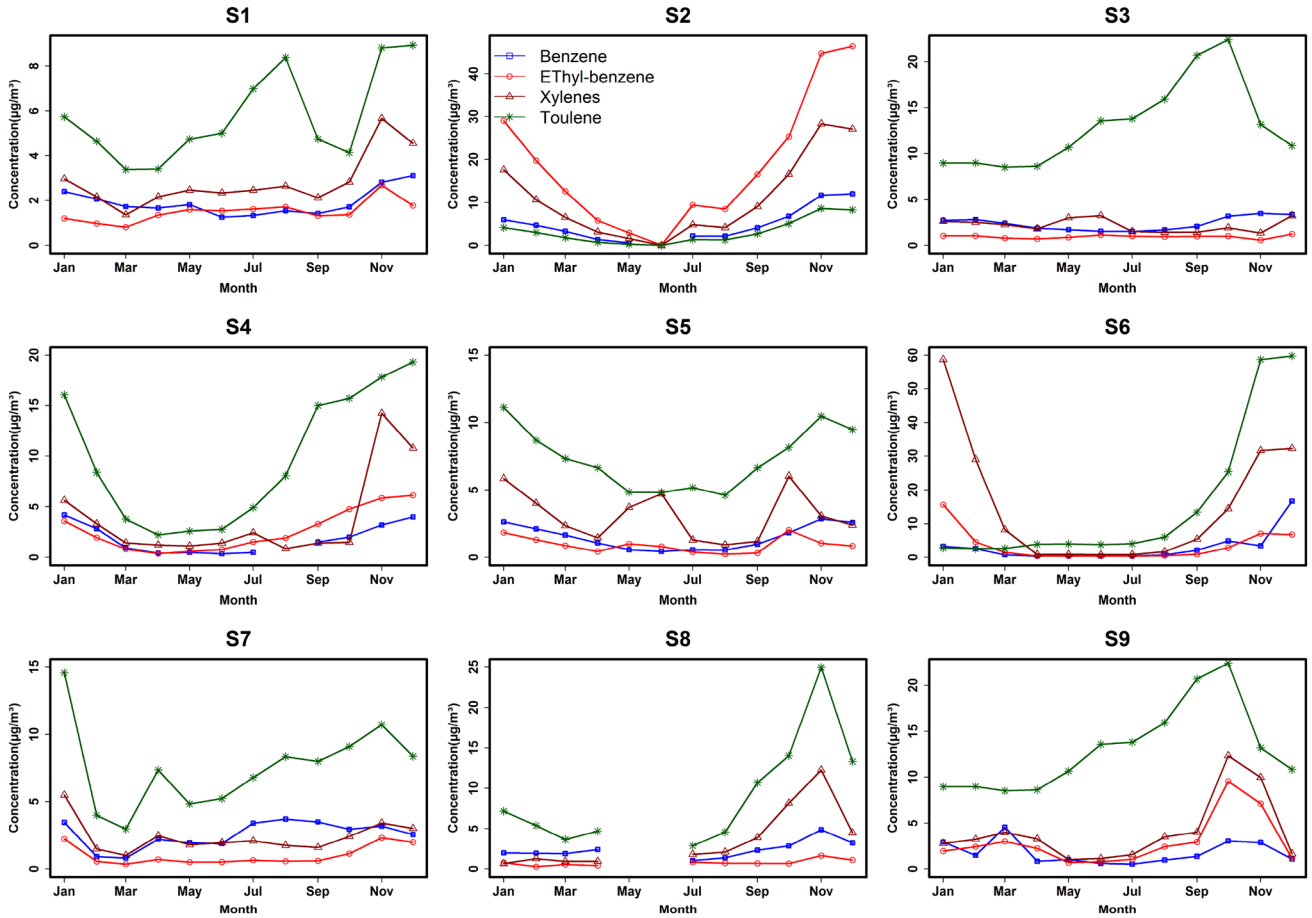

Fig. 14 Monthly variation of VOCs

Table 1 Correlation coefficient (r) at 95% significance between the different VOC species

	Benzene	Ethyl-benzene	MP-xylene	O-xylene	Toulene
S1					
Benzene	**1**				
Ethyl-benzene	**0.402**	**1**			
MP-xylene	**0.813**	**0.74**	**1**		
O-xylene	**0.47**	**0.815**	**0.66**	**1**	
Toluene	**0.59**	**0.52**	**0.61**	**0.69**	**1**
S2					
Benzene	**1**				
Ethyl-benzene	**0.98**	**1**			
MP-xylene	**0.94**	**0.939**	**1**		
O-xylene	**0.96**	**0.975**	**0.969**	**1**	
Toluene	**0.978**	**0.966**	**0.968**	**0.967**	**1**
S3					
Benzene	**1**				
Ethyl-benzene	**0.454**	**1**			
MP-xylene	**0.54**	**0.54**	**1**		
O-xylene	0.04	**0.26**	**0.233**	**1**	
Toluene	**0.34**	**0.44**	−0.07	**0.239**	**1**
S4					
Benzene	**1**				
Ethyl-benzene	**0.758**	**1**			
MP-xylene	**0.263**	−0.045	**1**		
O-xylene	**0.42**	**0.502**	−**0.16**	**1**	
Toluene	**0.84**	**0.905**	0.006	**0.456**	**1**
S5					
Benzene	**1**				
Ethyl-benzene	**0.288**	**1**			
MP-xylene	**0.47**	**0.454**	**1**		
O-xylene	0.15	**0.562**	**0.495**	**1**	
Toluene	**0.903**	**0.257**	**0.568**	0.13	**1**
S6					
Benzene	**1**				
Ethyl-benzene	**0.64**	**1**			
MP-xylene	**0.678**	**0.968**	**1**		
O-xylene	**0.392**	**0.811**	**0.743**	**1**	
Toluene	**0.67**	**0.805**	**0.88**	**0.364**	**1**
S7					
Benzene	**1**				
Ethyl-benzene	**0.484**	**1**			
MP-xylene	**0.466**	**0.77**	**1**		
O-xylene	**0.495**	**0.85**	**0.535**	**1**	
Toluene	**0.69**	**0.786**	**0.82**	**0.64**	**1**
S8					
Benzene	**1**				
Ethyl-benzene	**0.5**	**1**			
MP-xylene	**0.73**	**0.375**	**1**		
O-xylene	**0.59**	**0.577**	**0.689**	**1**	
Toluene	**0.875**	**0.506**	**0.904**	**0.699**	**1**
S9					
Benzene	**1**				
Ethyl-benzene	**0.608**	**1**			

Table 1 (continued)

	Benzene	Ethyl-benzene	MP-xylene	O-xylene	Toulene
MP-xylene	**0.612**	**0.996**	**1**		
O-xylene	**0.531**	**0.914**	**0.91**	**1**	
Toluene	**0.665**	**0.91**	**0.91**	**0.78**	**1**

The significant values are represented in bold

Table 2 Maximum increment reactivity of the different VOCs

	Benzene	Toluene	Ethyl-benzene	MP-xylene	O-xylene
MIR	0.42	2.7	2.7	8.2	6.5
S1*	0.80	15.50	4.04	12.76	8.17
S2*	2.10	8.39	49.71	18.19	62.12
S3*	0.99	35.17	2.55	10.04	6.30
S4*	0.78	26.27	7.13	7.72	18.50
S5*	0.63	19.78	2.51	14.43	8.63
S6*	1.26	42.09	9.32	69.20	45.25
S7*	1.07	20.32	2.73	14.01	4.35
S8*	1.00	24.67	2.07	20.71	7.30
S9*	0.75	33.80	7.95	24.21	7.10

*MIR × VOC concentration (in $\mu g/m^3$)

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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