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NO_X-VOC-O_3 Sensitivity in Urban Environments of Sri Lanka

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ABSTRACT Physical phenomenon of the relation among the ground level O_3, NO_X and VOC governed by complex nonlinear photochemistry in urban environments is explained in detail using the ambient pollutant concentration data of eleven cities in Sri Lanka. The time-series analysis was conducted using the 24-hour average ambient concentrations of PM_{10}, NO_2, CO, O_3 and SO_2 air pollutants obtained from fixed air pollution monitoring station located in Colombo since 2008. Further analysis was carried out from the mobile air pollution monitoring station for eleven cities. The hourly averaged ambient real time air quality data i.e. VOC, NO_2, NO, O_3 pollutants and the corresponding meteorological parameters were analyzed and presented in weekly results for the base year 2013, 2014 and 2015. It was identified that there exist two regimes of NO_X-VOC-O_3 sensitivity among these cities. Colombo, Kurunegala, Jaffna, Matara, Badulla, Pollonnaruwa, and Gampaha are the NO_X-sensitive regime. While Rathnapura, Anuradhapura, Kandy and Nuwaraelliya are the VOC-sensitive regime. In the NO_X-sensitive regime (with relatively low NO_X and high VOC), O_3 increases with the increasing NO_X and slightly changes in response to the increasing VOC levels. In the NO_X-saturated or VOC-sensitive regime, O_3 decreases with increasing NO_X level and increases with increasing VOC levels. In the immediate vicinity of very large emissions of NO, O_3 concentrations are depressed through the process of NO_X titration. Mathematical relationships were developed to calculate the steady state ozone concentration (O_{3ss}) that gives the values for both NO_X-sensitive regime and the VOC-sensitive regime. Establishment of these relationships are essential for Sri Lanka to develop the appropriate interventions for controlling O_3 pollution in each city.

KEY WORDS Volatile Organic Compounds, Ozone, NO_X-VOC-O_3 sensitivity, Urban environments, Sri Lanka

1. INTRODUCTION

Ozone (O_3) is produced in the troposphere as a result of a complex set of reactions that involve volatile organic compounds (VOCs) and oxides of nitrogen (NO_X). The interaction among O_3, NO_X and VOC are driven by the complex nonlinear photochemistry (Atkinson and Arey, 2003; Atkinson, 2000). Many Studies have been investigated the relation among NO_X, O_3 and VOC reactivity and NO_X-VOC-O_3 sensitivity (Simon *et al.*, 2015; Kim *et al.*, 2012; Kim *et al.*, 2011; Shao *et al.*, 2009; Geng *et al.*, 2008; Murphy *et al.*, 2007; Stein *et al.*, 2005; Jiménez and Baldasano, 2004; Sillman, 2003; Zaveri *et al.*, 2003; Sillman, 2002; Sillman, 1999;

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Jiang *et al.,* 1997). In urban areas this can be affect the design of control strategies to reduce ambient ozone levels. If we were able to introduce a NO_X-VOC-O_3 sensitivity to certain measurable species which have different values to calculate this phenomenon, it will greatly help to reduce the O_3 concentration in urban environments. However, there is relatively little research on this topic in Sri Lanka; hence, the comprehensive analysis of NO_X-VOC-O_3 sensitivity is an urgent need for effective ozone control in the country. Accurate understanding of the relation among O_3, NO_X and VOC is especially important because it suggests the possible role for developing national air quality management plan. Lack of clear understanding on physical phenomenon among O_3, NO_X and VOC interactions has hindered in developing air quality modeling tools with sufficient accuracy. Consequently, development of interventions for the control of O_3 has become a challenging task for the policy makers and regulatory agencies in Sri Lanka. The objectives of this research are to identify (1) the influential parameters and (2) the governing mechanisms of NO_X-VOC-O_3 sensitivity in Sri Lankan cities by establishing pollutants interactions which subsequently assist in developing appropriate interventions for controlling O_3 in a particular city in Sri Lanka.

2. RESEARCH METHODOLOGY

In this research, the time-series analysis was conducted using the 24-hour average ambient concentrations of PM_{10}, NO_2, CO, O_3 and SO_2 air pollutants obtained from fixed air pollution monitoring station located at Fort, Colombo from 1998 to 2008 according to the data availability. Additional analysis was carried out using the data in 2013, 2014 and 2015 which were collected from the mobile air pollution monitoring station for eleven cities in Sri Lanka. Equipment's of the monitoring unit belongs to CEA, Sri Lanka, was used for the ambient air quality monitoring measurements. PM_{10} was measured using Environnement S.A.-PM101M Particulate monitor by Beta attenuation method. CO was measured using Environnement S.A.-CO12M Gas filter correlation carbon monoxide analyzer, EN series using the non-dispersive infrared spectroscopy. NO, NO_X, NO_2 were measured using Environnement S.A.- NO, NO_X, NO_2-AC32M by gas phase chemi-luminescence method. SO_2 was measured using Environnement S.A.-AF22M, EN Series, UV Fluorescent sulfur dioxide analyzer by Pulse Fluorescent method. O_3 was measured using Environnement S.A.-O_3-42M, UV Photometric ozone analyzer, EN series using ultra violet photometric method. Non-

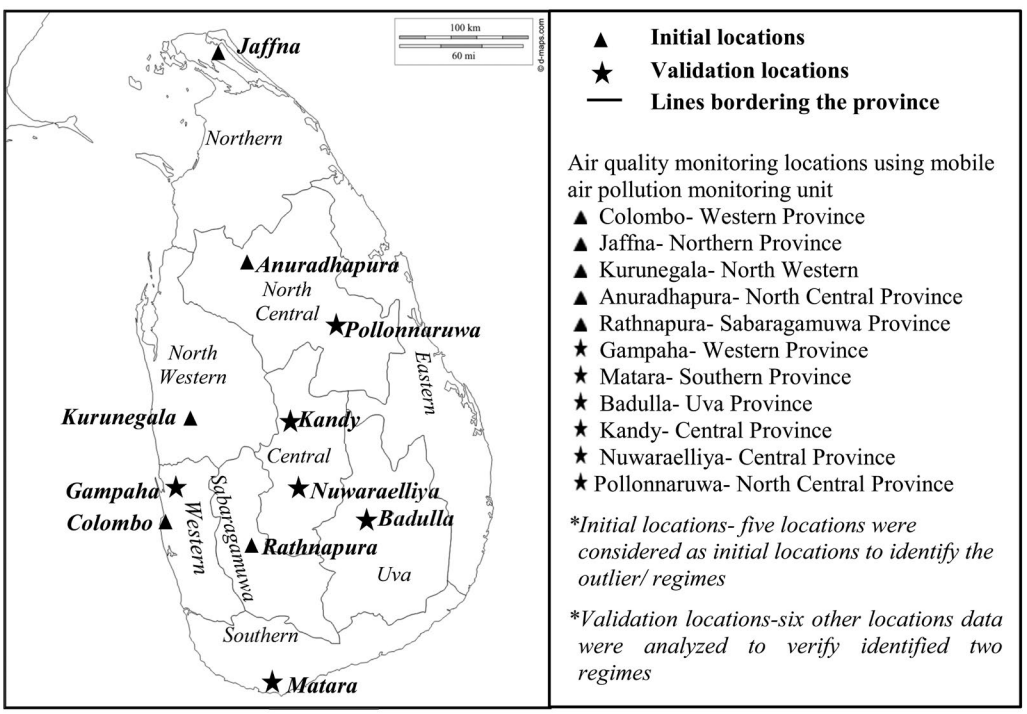


Fig. 1. The eleven air quality monitoring locations of this research in Sri Lanka.

Table 1. Results of the 1998 to 2008 for the pollutant exceedance of the national standards and the WHO guideline values in Sri Lanka.

Year	PM_{10}				NO_2			
	Days of data	Hourly maximum (μgm^{-3})	Total days (%) exceed NAAQS 100 μgm^{-3}	Total days (%) exceed WHO 50 μgm^{-3}	Days of data	Hourly maximum (ppb)	Total days (%) exceed NAAQS 100 μgm^{-3} 0.0494 ppm	Total days (%) exceed WHO 40 μgm^{-3} (0.0197 ppm)
1998	224	101	1 (0.4)	32 (14.3)	224	0.093	4 (1.8)	31 (13.8)
1999	350	132	9 (2.6)	50 (14.3)	343	0.076	13 (3.8)	49 (14.3)
2000	350	145	7 (2.0)	49 (14.0)	350	0.067	16 (4.6)	51 (14.6)
2001	91	103	1 (1.1)	11 (12.1)	112	0.082	8 (7.1)	16 (14.3)
2002	126	120	2 (1.6)	16 (12.7)	147	0.059	7 (4.8)	21 (14.3)
2003	189	119	3 (1.6)	27 (14.3)	203	0.046	0 (0.0)	24 (11.8)
2004	364	136	12 (3.3)	51 (14.0)	371	0.056	5 (1.3)	45 (12.1)
2005	357	126	10 (2.8)	49 (13.7)	343	0.076	7 (2.0)	49 (14.3)
2006	357	124	9 (2.5)	45 (12.6)	357	0.076	11 (3.1)	48 (14.3)
2007	280	132	7 (2.5)	34 (12.1)	182	0.064	3 (1.6)	26 (14.3)
2008	189	126	3 (1.6)	23 (12.2)	140	0.075	9 (6.4)	20 (14.3)

Year	CO				SO_2			
	Days of data	Hourly maximum (ppb)	Total days (%) exceed NAAQS I-hour 30 mgm^{-3}	Total days (%) exceed WHO 35 ppb (35,000 ppm)/ 40 mgm^{-3}	Days of data	Hourly maximum (ppb)	Total days (%) exceed NAAQS Annual-0.03 ppm/ 24 hour-0.14 ppm	Total days (%) exceed WHO 20 $\mu g/m^3$
1998	224	2.508	0 (0.0)	0 (0.0)	224	0.099	0 (0.0)	0 (0.0)
1999	350	2.27	0 (0.0)	0 (0.0)	350	0.095	0 (0.0)	0 (0.0)
2000	343	2.94	0 (0.0)	0 (0.0)	350	0.166	2 (0.6)	2 (0.6)
2001	105	8.197	0 (0.0)	0 (0.0)	112	0.14	1 (0.9)	1 (0.9)
2002	140	5.536	0 (0.0)	0 (0.0)	133	0.116	0 (0.0)	0 (0.0)
2003	182	5.332	0 (0.0)	0 (0.0)	203	0.066	0 (0.0)	0 (0.0)
2004	364	8.108	0 (0.0)	0 (0.0)	343	0.067	0 (0.0)	0 (0.0)
2005	336	5.981	0 (0.0)	0 (0.0)	308	0.127	0 (0.0)	0 (0.0)
2006	329	2.289	0 (0.0)	0 (0.0)	357	0.135	0 (0.0)	0 (0.0)
2007	252	2.86	0 (0.0)	0 (0.0)	259	0.138	0 (0.0)	0 (0.0)
2008	161	2.31	0 (0.0)	0 (0.0)	77	0.084	0 (0.0)	0 (0.0)

Year	O_3			
	Days of data	Hourly maximum (ppb)	Total days (%) exceed NAAQS 1 hour 200 μgm^{-3} (0.0946 ppm)	Total days (%) exceed WHO 1 hour-0.12 ppm 8 hour-0.08 ppm
2007	175	0.011	0 (0.0)	0 (0.0)
2008	161	0.025	0 (0.0)	0 (0.0)

methane and methane hydrocarbons were measured using Environnement S.A.-HC51M, FID hydrocarbon analyzer by flame ionization method. Environnement S.A,-MGC 101 computerized multi gas calibrator is also available and equipment's are kept in 20°C temperature. The data in five out of eleven cities were selected for identification of major trend patterns as initial analysis, while the data of remaining cities were used for validation of the two regimes (Fig. 1). The locations of the mobile air pollution monitoring stations considered for the initial analysis are resided in the cities of Jaffna, Anuradhapura, Colombo, Rathnapura and Kurunegala (Table 1) covering five different provinces in the country. The 24-hour average data of various pollutants and meteorological parameters at these five different locations were compared with each other to assess air pollution status in different cities. Further similarities and differences of the trend patterns were analyzed to develop the inter-relationships of VOC, NO_2, NO and O_3 pollutants, and the NO_X-VOC-O_3 sensitivity. The ambient real time air quality data of all air pollutants and meteorological parameters were presented in weekly basis for

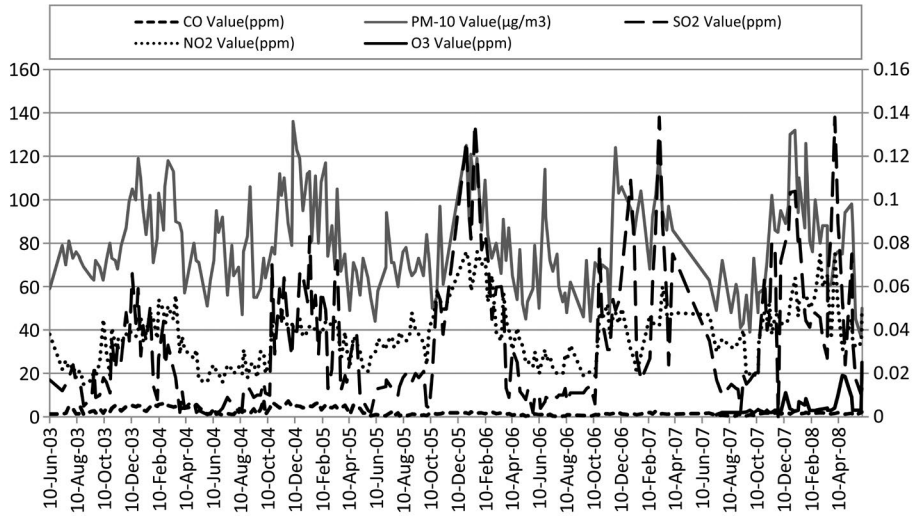


Fig. 2. PM_{10}, NO_2, CO, SO_2 and O_3 24 hour average values from 2003 to 2008 at Colombo Fort Air Pollution Monitoring Station. *Concentrations of O_3 and SO_2 are shown in secondary axis.

the detailed analysis. Validation (http://statisticaloutsourcingservices.com/Outlier2.pdf) was carried out for the NO_X-VOC-O_3 sensitivity regimes developed using ambient real time air quality monitoring data collected in weekly based on the same methodology in another series of cities (e.g., Matara, Badulla, Pollonnaruwa, Gampaha, Kandy, Nuwaraelliya) for the above mentioned pollutants and the trends were compared to confirm the proposed NO_X-VOC-O_3 sensitivity for Sri Lankan cities. Physical phenomenon was developed that explains the chemical reactions of the two regimes. Mathematical relationship was developed to calculate the steady state ozone (O_{3ss}) that gives the values for the NO_X-sensitive regime and the VOC-sensitive regime.

3. RESULTS AND DISCUSSION

3.1 Ambient Air Pollution Status in Sri Lanka

24 hour averages of ambient PM_{10} level in Colombo over the years have remained relatively within the 60 to 82 µg/m^3 range with a slight decreasing trend from 2003 to 2008 (Fig. 2). These values, consistently exceeded WHO latest guideline value of 50 µg/m^3 for PM_{10}. However, there is a slight decreasing trend of PM_{10} from 2003 to 2008 (Fig. 2) and considerable decreasing trend since 2008 (CEA, 2017). This could be due to the introduction of vehicle emission testing program and promotion of tax concession on newer cleaner vehicles. 24 hour averages values of ambient NO_2 level in Colombo over the years have remained relatively within the 0.030 ppm to 0.050 ppm range with a slight decreasing trend from 2003 to 2008 (Fig. 2). High pollutant concentration was observed during the months of December to April having dry weather conditions. On the other hand, low pollutant concentration was observed during the months of June to September having wet weather conditions. 24 hour average values of ambient CO level in Colombo over the years have remained relatively within the 1 ppm to 2 ppm range with a remarkable decreasing trend from 2005 to 2008 (Fig. 2). USEPA Standard for CO is 9 ppm (10 mg/m^3) and therefore CO is not a major air pollutant in Sri Lanka. 24 hour average values of ambient SO_2 level in Colombo over the years have remained relatively within the 0.02 ppm to 0.08 ppm range with an increasing trend from 2003 to 2008 (Fig. 5). USEPA Standard for 24 hour SO_2 is 0.014 ppm. Thus city of Colombo was exposed to high SO_2 pollution during this period.

Recognizing the importance of the problem, government of Sri Lanka has proposed the fuel quality and air quality improvement road map to reduce the SO_2 emissions. This will enhance the quality of fossil fuels for managing air quality in Sri Lanka. From this road map it had introduced high quality fuels in the country as follows; 500 ppm sulfur diesel as auto diesel distributed island-wide with effect from 1st of January 2014. Further, 350 ppm sulfur diesel as auto diesel and 150 ppm sulfur diesel as super diesel with effect from 2016. 24

Table 2. Comparison of 24-hour average values of pollutants at five locations.

Pollutant/Parameters	Colombo	Anuradhapura	Jaffna	Rathnapura	Kurunagala	Standard/Guideline (WHO, 2006)
$PM_{2.5}$ (μgm^{-3})	28	16	15	40	25	$PM_{2.5}$ SL Standard-50 μgm^{-3} $PM_{2.5}$ WHO Guideline-25 μgm^{-3}
PM_{10} (μgm^{-3})	55	30	39	64	51	PM_{10} SL Standard-100 μgm^{-3} PM_{10} WHO Guideline-50 μgm^{-3}
THC (ppm)	2.344	2.254	1.678	2.672	2.243	No standard has been developed yet
CH_4 (ppm)	1.674	1.828	1.259	1.675	1.440	
NMHC (ppm)	0.669	0.426	0.419	0.997	0.803	
CO (ppm)	0.769	0.556	0.503	1.017	0.747	CO I-hour SL Standard-30 mgm^{-3} CO 1-hour USEPA Standard-35 ppb (35,000 ppm)/40 mgm^{-3}
NO	0.044	0.048	0.005	0.114	0.031	NO_2 SL Standard-100 μgm^{-3} (0.0494 ppm) NO_2 WHO Guideline-40 μgm^{-3} (0.0197 ppm)
NO_2	0.026	0.005	0.011	0.011	0.011	
NO_X	0.070	0.053	0.016	0.125	0.042	
O_3	0.005	0.007	0.017	0.013	0.003	O_3 1-hour SL Standard-200 μgm^{-3} (0.0946 ppm) O_3 1-hour USEPA Standard-0.12 ppm
Temperature (°C)	28.21	26.05	28.62	26.95	27.02	
Relative-Humidity (%)	76.43	82.67	77.08	73.25	75.94	
Wind speed (m/s)	0.694	0.328	1.908	0.620	0.953	
Wind direction (degree)	223.64	109.82	157.70	232.89	180.35	

hour average values of ambient O_3 level in Colombo from July 2007 to June 2008 one year period shows that moderate peaks in December and January and prominent high peaks in April and June (Fig. 2). This also could be explained as a results of dry weather condition during these four months. Table 1 shows the results of the 1998 to 2008 for the above five pollutant exceedance of the Sri Lankan national standards and the WHO guideline values.

3.2 The Seasonal Variation of Ozone

Surface ozone over the continents has a marked seasonal cycle (Zvyagintsev, 2004). A number of studies have been investigated on seasonal variation as explained below. Historically, high ground-level ozone has been reported in urban areas during hot, stagnant summer weather. According to the latest research findings, maximum can occur in winter/early spring (Almadov *et al.*, 2015; Oltmans *et al.*, 2008; Oltmans *et al.*, 2006; Gros *et al.*, 1998), in spring, or in spring/summer (Ahammed *et al.*, 2006; Felipe-Sotelo *et al.*, 2006). A complex interaction of photochemical and dynamic processes controls the key features of surface ozone variations (Lelieveld and Dentener, 2000) and the shape of the seasonal cycle (Monks, 2000; Oltmans and Levy, 1992). The lifetime of O_3 in the lower troposphere varies from 4–5 days to 1–2 weeks depending on season (Wang *et al.*, 2011). Due to the limited data available on O_3, local variation can't be explained in detail.

3.3 Air Quality Monitoring Data in Five Sites

Table 2 shows the comparison of 24-hour average values of pollutant at five different locations in Sri Lanka. It shows that high level of air pollutants have shown in different location base on the pollutant source. Due to the industrial air pollution at Rathnapura highest particulate pollution (PM_{10}-64 μgm^{-3}, $PM_{2.5}$-40 μgm^{-3}, ppm where in both cases WHO guideline value has exceeded), high oxides of nitrogen (0.125 ppm), and high non-methane hydrocarbon (NMHC-0.997 ppm) was observed. Colombo has high air pollutant levels mainly coming from vehicular emission (Perera *et al.*, 2018). In Colombo high particulate pollution was observed for both PM_{10} and $PM_{2.5}$ (PM_{10}-55 μgm^{-3}, $PM_{2.5}$-28 μgm^{-3}, ppm where in both cases WHO guideline value has exceeded), high oxides of nitrogen both NO and NO_2 (NO-

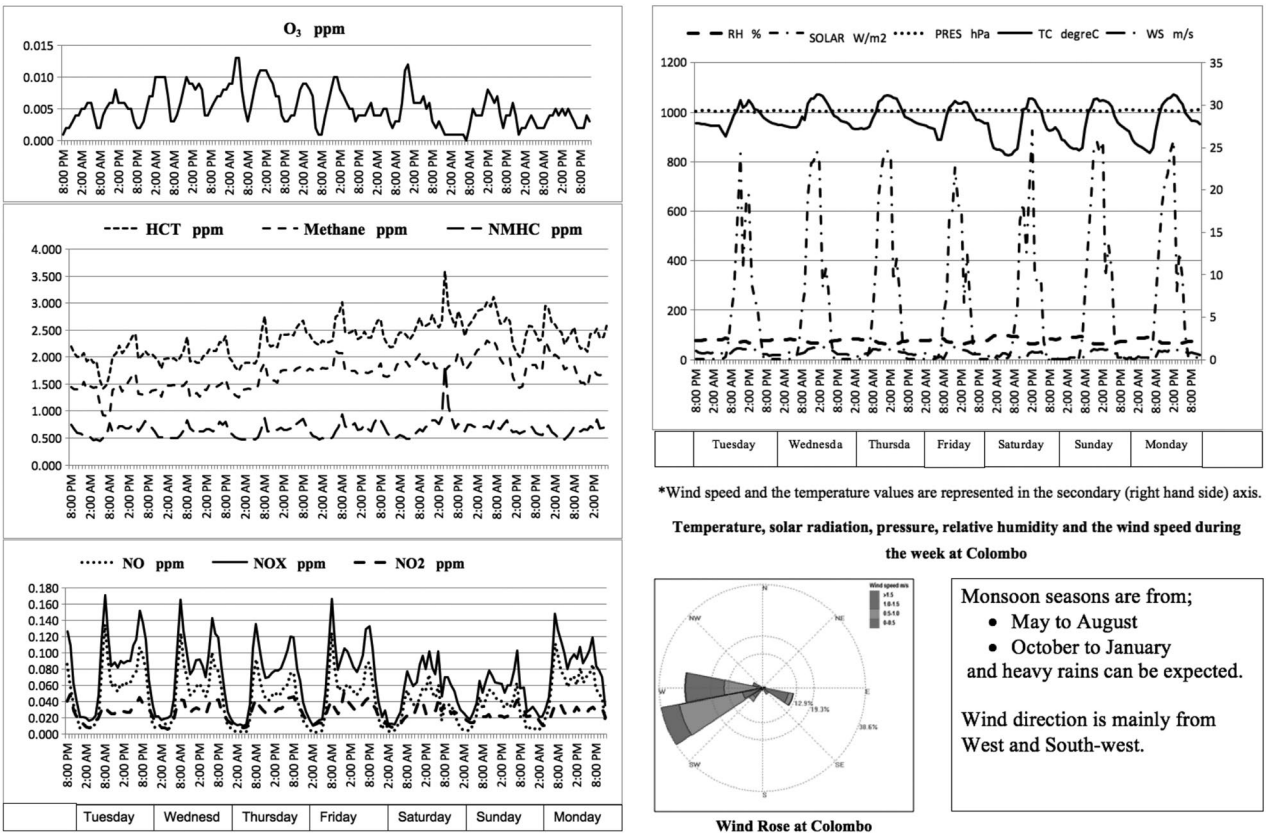


Fig. 3. NO_X-sensitive regime in Colombo.

0.044 ppm and NO_2-0.026 ppm), and high non-methane hydrocarbon (NMHC-0.669 ppm) was observed. Jaffna and Anuradhapura have comparatively low air pollutant concentration. At Anuradhapura having higher Paddy fields high CH_4 (CH_4-1.828 ppm) concentration was observed. With the favorable temperature (28.4°C) in Anuradhapura, production of O_3 (0.017 ppm) was also higher. Low concentration of pollutant at Jaffna could be due to the high sea breeze in the area.

3.4 Physical Phenomenon

Data signifies that two concepts exist for NO_X-VOC-O_3 sensitivity. In some conditions, the process of O_3 formation is controlled almost entirely by NO_X and is largely independent of VOC (i.e., NO_X-sensitive regime), while for other conditions O_3 production increases with increasing VOC and does not increase (or sometimes even decreases) with increasing NO_X (i.e., VOC-sensitive regime). In the NO_X-sensitive regime (with relatively low NO_X and high VOC), O_3 increases with increasing NO_X and changes little in response to increasing VOC. As an example, Fig. 3 shows that this phenomenon occurs in Colombo. The city is located in the wet zone. The average high temperature is around 31°C from March to April. Instruments are located down wind. At the Colombo site, wind direction is mainly from West and Southwest. Similarly, NO_X-sensitive regime occurs in Kurunegala and Jaffna as well. Further, it was observed the trend patterns of NO, NO_2 and NO_X in these cities in Sri Lanka. These cities are with high traffic congestion and witnessed trends are probably due to traffic related emissions (Perera *et al.*, 2010; Perera and Emmanuel, 2005). The Sri Lanka vehicle emission testing program (SLVET) was established in 2008. Sri Lanka has attempt to reduce air pollution by vehicle emission reduction methods including promotion of cleaner fuels and technologies (such as shifting to electric vehicles, fixing catalytic converters at the exhausts line), tax concession of importing newer and cleaner vehicles, i.e. 25% on electric vehicles and 50% on hybrid vehicles (MOF, 2010; Perera and Jayaweera, 2008), reduction of traffic by transport demand management, etc.

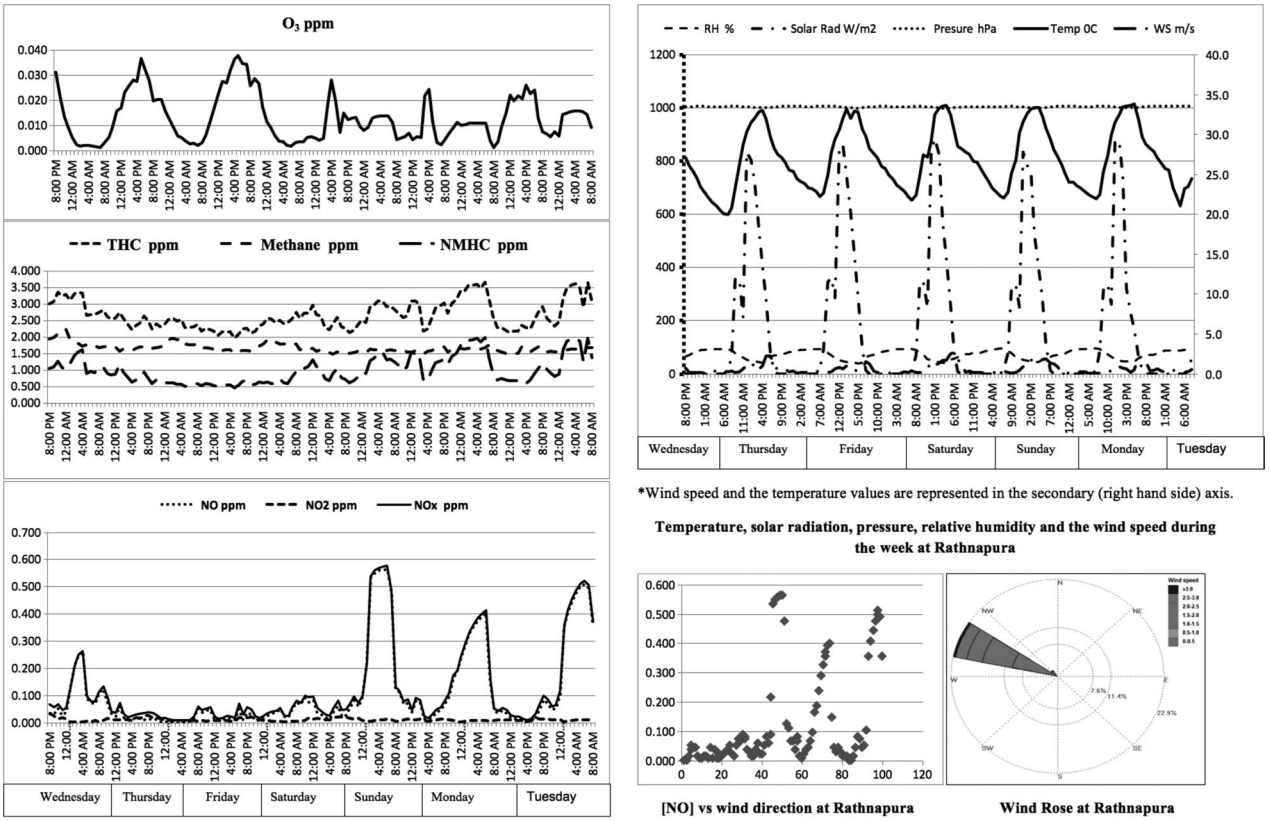
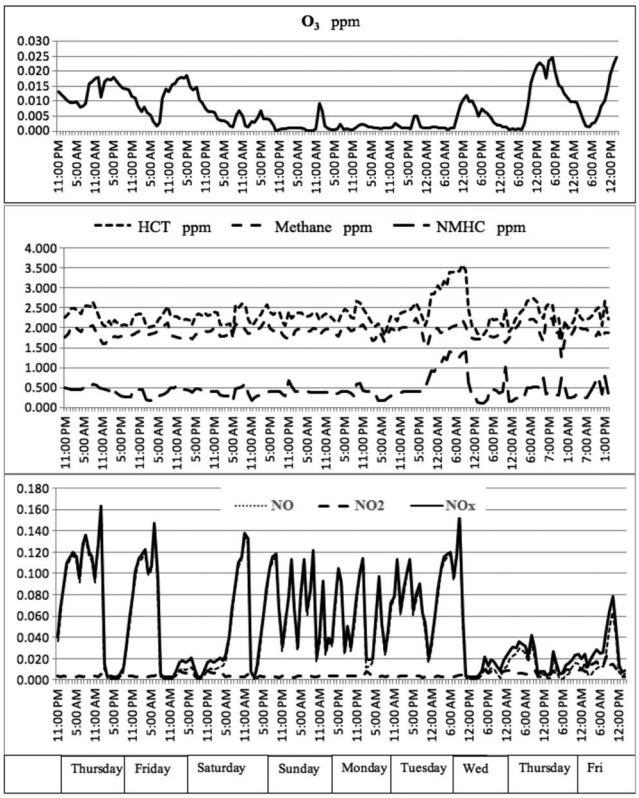
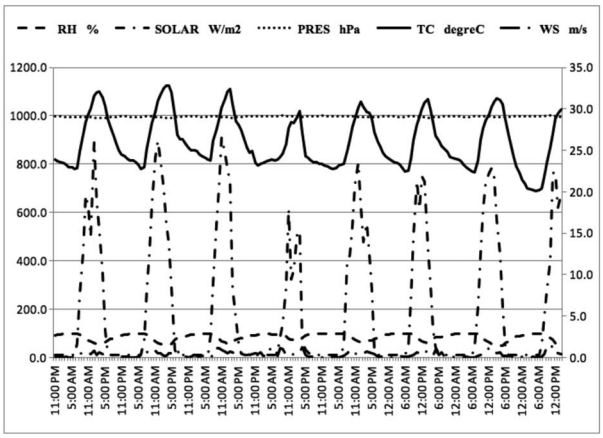


Fig. 4. NO_X-saturated or VOC-sensitive regime in Ratnapura.

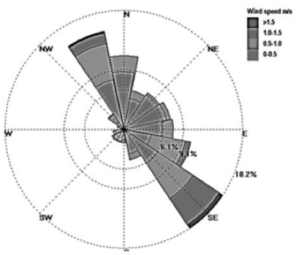
In the NO_X saturated or VOC sensitive regime O_3 decreases with increasing NO_X and increases with increasing VOC, which is predominant in city of Rathnapura (Fig. 4). NO concentration vs wind direction at the Rathnapura location shown that the source or the industry may placed in 60° to 80° direction Rathnapura is located in the wet zone. The town receives rainfall mainly from south-western monsoons from May to September. The average temperature varies from 24 to 35°C, and there are high humidity levels. At the Rathnapura site, wind direction is mainly from North West directions. In the presence of low NO concentration, marked O_3 concentration is seen in Fig. 4. However, with very high NO concentration, O_3 concentration has reduced. This is due to the removal of O_3 through reaction with NO as described in the introduction section. Further NO concentration vs wind direction at Rathnapura shows that pollutants are coming from the direction of 60–80° implying that a point emission source such as industry is located in that particular direction. Further, high peaks of NO concentration were observed when the industrial actions are involved. This type of condition needs to handle carefully as reduction in NO concentration may result in high production of O_3. Therefore, it is essential to reduce both pollutants NO and VOC simultaneously to mitigate formation of O_3. Intermediate of this high O_3 production and how the titration of produced O_3 concentration suddenly reduced could be clearly showed in Fig. 5 at the Anuradhapura site. Anuradhapura is usually hot and humid throughout the year and the average temperature remains 25–30°C. The town receives rainfall mainly from Southwest monsoon season begins in mid-May to October. At the Anuradhapura site, wind direction is mainly from North west and South east. The large thermal power plant such as Norocholai Coal Power plant, Kelanitissa Oil Power plant, Sapugaskanda Oil Power plan are away from the measurement sites. Accordingly, effects of power plant emissions could be excluded in the present study. Further, validation results confirm the two regimes of NO_X-VOC-O_3 sensitivity. Accordingly in Matara, Badulla, Pollonnaruwa, and Gampaha show the NO_X-sensitive regime. In Kandy and Nuwaraelliya shows the VOC-sensitive regime as shown in Fig. 6.





*Wind speed and the temperature values are represented in the secondary (right hand side) axis.

Temperature, solar radiation, pressure, relative humidity and the wind speed during the week at Anuradhapura.



Southwest monsoon season begins in mid-May to October.

April is the warmest month of the year in Anuradhapura.

Wind direction is mainly from North west and South east.

Hot and humid throughout the year.

Fig. 5. Intermediate of NO_X-sensitive regime and VOC-sensitive regime in Anuradhapura.

3.5 Chemical Relationship

3.5.1 NO_X-sensitive Regime

By considering the chemical reactions of NO_X-O_3 cycle, mathematical relationship could be developed to calculate O_{3ss} in the NO_X-sensitive regime as (Atkinson and Arey, 2003; Atkinson, 2000):

$$NO_2 + h\nu \rightarrow NO + O(3P) (\lambda < 420\,nm) \quad (R1)$$

$$O(3P) + O_2 + M \rightarrow O_3 + M \quad (R2)$$

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

Since the inter conversion between these species is so fast, a steady state is reached within a few minutes. This photo stationary state relation determines the O_3 concentration. The NO_X sensitive steady state O_3 concentration is proportional to the $[NO_2]/[NO]$ ratio and it is defined as:

$$[O_3]_{NO_X\ sensitivity} = \frac{j_{NO_2}[NO_2]}{k_{NO+O_3}[NO]}$$

where

k - depends on Temperature; Ω 0.4 $ppm^{-1}\ s^{-1}$

j - depends on solar radiation; at night = 0; at full sunlight = 0.4 min^{-1} (Atkinson and Arey, 2003)

3.5.2 VOC-sensitive Regime

By considering the chemical reactions of NO_X-VOC, split mathematical relationship could be developed to calculate O_{3ss} in the VOC-sensitive regime. O_3 formation occurs through the following sequence of reactions. The sequence is almost always initiated by the reaction of various VOC or CO with the OH radical (R4 and R5). This is followed by the conversion of NO to NO_2 (through reaction with HO_2 or RO_2 radicals), which also regenerates OH (see R6 and R7). NO_2 is photolyed to generate atomic oxygen, which combines with O_2 to create O_3, as given in R8 and R9 (Sillman, 1999).

$$VOC + OH \xrightarrow{O_2} RO_2 + H_2O \quad (R4)$$

$$CO + OH \xrightarrow{O_2} HO_2 + CO_2 \quad (R5)$$

$$RO_2 + NO \xrightarrow{O_2} VOC + HO_2 + NO_2 \quad (R6)$$

$$HO_2 + NO \rightarrow OH + NO_2 \quad (R7)$$

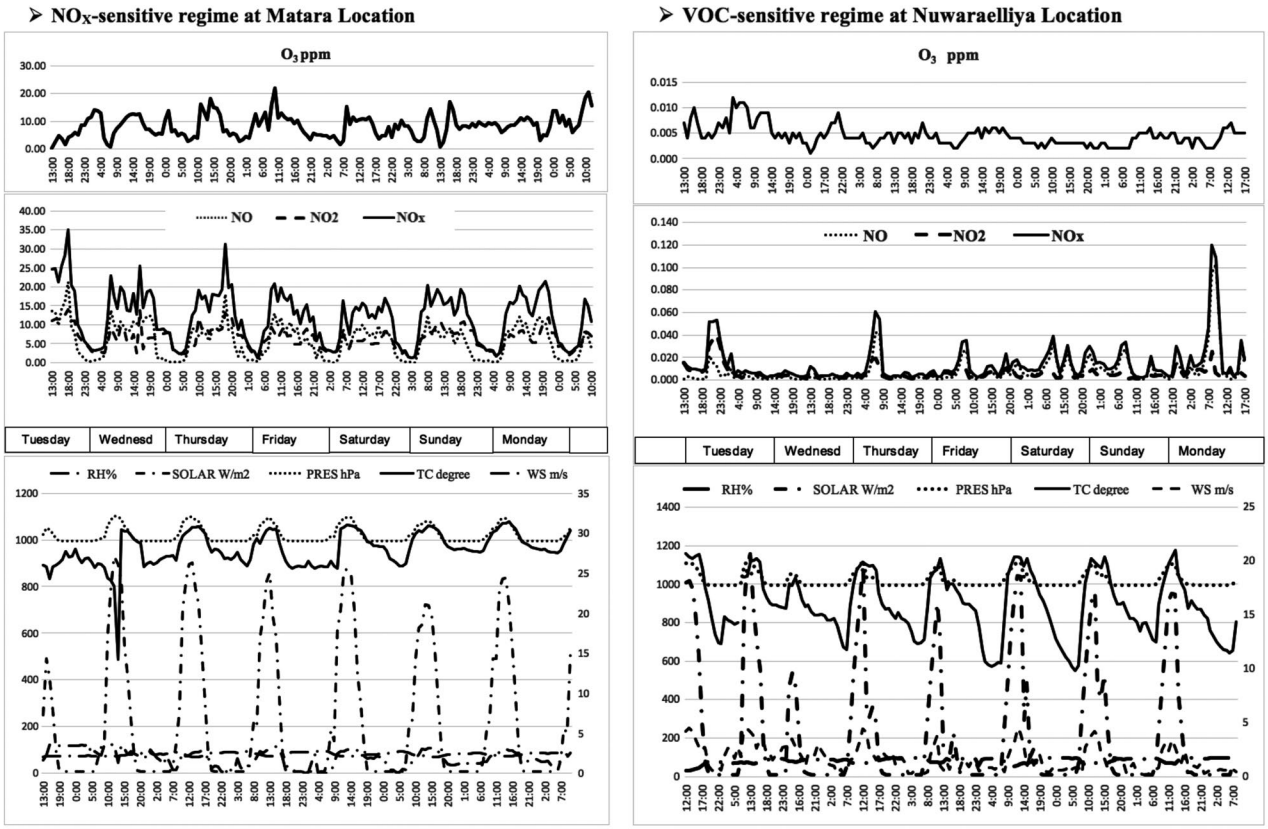


Fig. 6. Validation of NO_X-sensitive and VOC-sensitive regime in other cities.

$$NO_2 \xrightarrow{\text{sunlight}} NO + O \quad (R8)$$

$$O + O_2 + M \longrightarrow O_3 + M \quad (R9)$$

Here, RO_2 represents any of a number of chains of organics with an O_2 attached (replacing H in the original chain). This reacts with NO (R6) and H (which combines with O_2 to form HO_2). The rate of ozone formation is controlled primarily by the rate of the initial reaction of VOC with OH.

At the nighttime and in the immediate vicinity of very large emissions of NO, O_3 concentrations are depressed through the process of NO_X titration (Sillman, 1999; Gillani and Pleim, 1996). This consists of removal of O_3 through reaction with NO as given in R10.

$$NO + O_3 \longrightarrow NO_2 + O_2 \quad (R10)$$

Concentrations of odd-H radicals (odd hydrogen = $OH + HO_2 + RO_2$, whereas RO_2 stands for any organic peroxy radicals) were estimated with a radical steady state approximation (SSA) (Spirig *et al.*, 2002; Staffelbach *et al.*, 1997).

$$\frac{d[OH]}{dt} = P_{OH} - [OH]\sum_i K_i[S_i] = 0$$

$$\frac{d[HO_2]}{dt} = P_{HO_2} - [HO_2]\sum_j K_j[S_j] - 2K_{peroxid}[HO_2]^2 = 0$$

$$\frac{d[RO_2]}{dt} = P_{RO_2} - [HO_2]\sum_{j^1} K_{j^1}[S_{j^1}] - 2K_{o_{peroxid}}[RO_2]^2 = 0$$

where P_{OH}, P_{HO_2}, and P_{RO_2} are the production rates of OH, HO_2, and RO_2, respectively. S_i, S_j, and S_j' denote (radical or nonradical) species that act as reaction partners in sink reactions of OH, HO_2, and RO_2, respectively. R11 and R12 reactions have k_1 and k_2 Reaction Rate Constants which are available in literature (Spirig *et al.*, 2002; Staffelbach *et al.*, 1997).

$$NO + HO_2 \xrightarrow{k_1} NO_2 + HO \quad (R11)$$

$$NO + RO_2 \xrightarrow{k_2} NO_2 + RO \quad (R12)$$

$k_1 = 8.5 \times 10^{-12}$; $k_2 = 7.7 \times 10^{-12}$; Rate constants at 298 K in cm^3 $molecule^{-1}$ s^{-1} for bimolecular reactions and in s^{-1} for photolysis reactions (Spirig *et al.*, 2002).

Since subsequent NO_2 photolysis and the reaction of O (3P) atoms with oxygen are reasonably fast. With the peroxy radical concentrations obtained from the steady state approximation (SSA), (O_{3ss}) in the VOC-sensitive regime is thus calculated as;

$$[O_3]_{\text{VOC sensitivity}} = [NO](k_1[HO_2] + k_2[RO_2])$$

Therefore, steady state Ozone concentration (O_{3ss}) in both regimes could be calculated as below;

$$[O_3]_{ss} = [O_3]_{NO_X \text{ sensitivity}} + [O_3]_{\text{VOC sensitivity}}$$

$$[O_3]_{ss} = \frac{j_{NO_2}[NO_2]}{k_{NO+O_3}[NO]} + [NO](k_1[HO_2] + k_2[RO_2])$$

$$= \frac{0.4\,\text{min}^{-1}[NO_2]}{24\,\text{ppm}^{-1}\,\text{min}^{-1}[NO_2]} + [NO]\{(8.5 \times 10^{-12}[HO_2] + 7.7 \times 10^{-12}[RO_2]\}$$

In the ambient air hydrocarbon concentrations are equal to the volatile organic compounds concentration. As all ambient hydrocarbon are volatile. Therefore; $[RO_2]$ concentration could be replaced by the measured NMHC.

4. CONCLUSION

There exist two regimes of NO_X-VOC-O_3 sensitivity in Sri Lankan cities. Accordingly in Colombo, Kurunegala, Jaffna, Matara, Badulla, Pollonnaruwa, and Gampaha show the NO_X-sensitive regime. In Rathnapura, Anuradhapura, Kandy and Nuwaraelliya shows the VOC-sensitive regime. The developed mathematical relationship could calculate the steady state ozone (O_{3ss}). Further by identification of the regime type it will provide whether it is essential to reduce both pollutants NO and VOC simultaneously or vise vasa and the quantification of pollutants. Establishment of these relationships will assist in developing appropriate interventions to control O_3 in a particular city.

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