ABSTRACT  Physical phenomenon of the relation among the ground level O₃, NOₓ 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 PM₁₀, NO₂, CO, O₃ and SO₂ 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, NO₂, NO, O₃ 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 NOₓ-VOC-O₃ sensitivity among these cities. Colombo, Kurunegala, Jaffna, Matara, Badulla, Pollonnaruwa, and Gampaha are the NOₓ-sensitive regime. While Rathnapura, Anuradhapura, Kandy and Nuwaraelliya are the VOC-sensitive regime. In the NOₓ-sensitive regime (with relatively low NOₓ and high VOC), O₃ increases with the increasing NOₓ and slightly changes in response to the increasing VOC levels. In the NOₓ-saturated or VOC-sensitive regime, O₃ decreases with increasing NOₓ level and increases with increasing VOC levels. In the immediate vicinity of very large emissions of NO, O₃ concentrations are depressed through the process of NOₓ titration. Mathematical relationships were developed to calculate the steady state ozone concentration (O₃ss) that gives the values for both NOₓ-sensitive regime and the VOC-sensitive regime. Establishment of these relationships are essential for Sri Lanka to develop the appropriate interventions for controlling O₃ pollution in each city.

KEY WORDS  Volatile Organic Compounds, Ozone, NOₓ-VOC-O₃ sensitivity, Urban environments, Sri Lanka

1. INTRODUCTION

Ozone (O₃) is produced in the troposphere as a result of a complex set of reactions that involve volatile organic compounds (VOCs) and oxides of nitrogen (NOₓ). The interaction among O₃, NOₓ and VOC are driven by the complex non-linear photochemistry (Atkinson and Arey, 2003; Atkinson, 2000). Many Studies have been investigated the relation among NOₓ, O₃ and VOC reactivity and NOₓ-VOC-O₃ 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 Baldazano, 2004; Sillman, 2003; Zaveri et al., 2003; Sillman, 2002; Sillman, 1999;
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 NOx-VOC-O3 sensitivity to certain measurable species which have different values to calculate this phenomenon, it will greatly help to reduce the O3 concentration in urban environments. However, there is relatively little research on this topic in Sri Lanka; hence, the comprehensive analysis of NOx-VOC-O3 sensitivity is an urgent need for effective ozone control in the country. Accurate understanding of the relation among O3, NOx 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 O3, NOx and VOC interactions has hindered in developing air quality modeling tools with sufficient accuracy. Consequently, development of interventions for the control of O3 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 NOx-VOC-O3 sensitivity in Sri Lankan cities by establishing pollutants interactions which subsequently assist in developing appropriate interventions for controlling O3 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 PM10, NO2, CO, O3 and SO2 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. PM10 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, NOx, NO2 were measured using Environnement S.A.- NO, NOx, NO2-AC32M by gas phase chemi-luminescence method. SO2 was measured using Environnement S.A.-AF22M, EN Series, UV Fluorescent sulfur dioxide analyzer by Pulse Fluorescent method. O3 was measured using Environnement S.A.-O3-42M, 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.](image-url)
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, NO2, NO and O3 pollutants, and the NOX-VOC-O3 sensitivity. The ambient real time air quality data of all air pollutants and meteorological parameters were presented in weekly basis for

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 | Days of data | PM10 | NO2 | SO2 | O3 |
|------|--------------|------|-----|-----|----|
|      |              | Hrly | Total days (%) | Total days (%) | Hrly | Total days (%) | Total days (%) |
|      |              | max  | exceed NAAQS 100 μgm⁻³ | exceed WHO 50 μgm⁻³ | max  | exceed NAAQS 100 μgm⁻³ | exceed WHO 40 μgm⁻³ |
| 1998 | 224          | 101  | (0.4) | (14.3) | 0.093 | (1.8) | (13.8) |
| 1999 | 350          | 132  | (2.6) | (14.3) | 0.076 | (3.8) | (14.3) |
| 2000 | 350          | 145  | (2.0) | (14.0) | 0.067 | (4.6) | (14.6) |
| 2001 | 91           | 103  | (1.1) | (12.1) | 0.082 | (7.1) | (16.3) |
| 2002 | 126          | 120  | (1.6) | (12.7) | 0.059 | (4.8) | (14.3) |
| 2003 | 189          | 119  | (1.6) | (14.3) | 0.056 | (5.1) | (12.1) |
| 2004 | 364          | 136  | (3.3) | (14.0) | 0.076 | (2.0) | (14.3) |
| 2005 | 357          | 126  | (2.8) | (13.7) | 0.076 | (3.1) | (14.3) |
| 2006 | 357          | 124  | (2.5) | (12.6) | 0.076 | (3.1) | (14.3) |
| 2007 | 280          | 132  | (2.5) | (12.1) | 0.064 | (1.6) | (14.3) |
| 2008 | 189          | 126  | (1.6) | (12.2) | 0.075 | (9.6) | (14.3) |

| Year | Days of data | CO | SO2 |
|------|--------------|----|-----|
|      |              | Hrly max | Total days (%) exceed NAAQS 1 hour 30 mgm⁻³ | Total days (%) exceed WHO 35 ppb (35,000 ppm)/40 mgm⁻³ | Hrly max | Total days (%) exceed NAAQS Annual-0.03 ppm/24 hour-0.14 ppm | Total days (%) exceed WHO 20 μg/m³ |
| 1998 | 224          | 2.508 | (0.0) | (0.0) | 0.099 | (0.0) | (0.0) |
| 1999 | 350          | 2.27  | (0.0) | (0.0) | 0.095 | (0.0) | (0.0) |
| 2000 | 343          | 2.94  | (0.0) | (0.0) | 0.166 | (0.6) | (0.6) |
| 2001 | 105          | 8.197 | (0.0) | (0.0) | 0.14  | (0.9) | (0.9) |
| 2002 | 140          | 5.536 | (0.0) | (0.0) | 0.116 | (0.0) | (0.0) |
| 2003 | 182          | 5.332 | (0.0) | (0.0) | 0.066 | (0.0) | (0.0) |
| 2004 | 364          | 8.108 | (0.0) | (0.0) | 0.067 | (0.0) | (0.0) |
| 2005 | 336          | 5.981 | (0.0) | (0.0) | 0.127 | (0.0) | (0.0) |
| 2006 | 329          | 2.289 | (0.0) | (0.0) | 0.135 | (0.0) | (0.0) |
| 2007 | 252          | 2.86  | (0.0) | (0.0) | 0.138 | (0.0) | (0.0) |
| 2008 | 161          | 2.31  | (0.0) | (0.0) | 0.084 | (0.0) | (0.0) |

| Year | Days of data | O3 | |
|------|--------------|----|-----|
|      |              | Hrly max | 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) |
| 2008 | 161          | 0.025 | (0.0) | (0.0) |
the detailed analysis. Validation (http://statisticalout
sourcingservices.com/Outlier2.pdf) was carried out for
the NOX-VOC-O3 sensitivity regimes developed using
ambient real time air quality monitoring data collected
weekly based on the same methodology in another
series of cities (e.g., Matara, Badulla, Pollonnaruwa, Gam-
paha, Kandy, Nuwaraelliya) for the above mentioned
pollutants and the trends were compared to confirm the
proposed NOX-VOC-O3 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 (O3ss) that gives the values for the NOX-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 PM10 level in Colombo
over the years have remained relatively within the 60 to
82 μg/m³ range with a slight decreasing trend from 2003
to 2008 (Fig. 2). These values, consistently exceeded
WHO latest guideline value of 50 μg/m³ for PM10. How-
ever, there is a slight decreasing trend of PM10 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 NOX 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/m³) and therefore CO is not a major air pollut-
ant in Sri Lanka. 24 hour average values of ambient SO2
level in Colombo over the years have remained relatively
within the 0.02 ppm to 0.08 ppm range with an incre-
sing trend from 2003 to 2008 (Fig. 5). USEPA Standard
for 24 hour SO2 is 0.014 ppm. Thus city of Colombo
was exposed to high SO2 pollution during this period.
Recognizing the importance of the problem, govern-
ment of Sri Lanka has proposed the fuel quality and air
quality improvement road map to reduce the SO2 emis-
sions. 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. Fur-
ther, 350 ppm sulfur diesel as auto diesel and 150 ppm
sulfur diesel as super diesel with effect from 2016. 24
hour average values of ambient O³ 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 O³ 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 O³, 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 (PM10-64 μgm⁻³, PM2.5-40 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 PM10 and PM2.5 (PM10-55 μgm⁻³, PM2.5-28 μgm⁻³, ppm where in both cases WHO guideline value has exceeded), high oxides of nitrogen both NO and NO₂ (NO-

| Pollutant/Parameters | Colombo | Anuradhapura | Jaffna | Rathnapura | Kurunagala | Standard/Guideline (WHO, 2006) |
|----------------------|---------|---------------|--------|------------|------------|--------------------------------|
| PM2.5 (μgm⁻³)        | 28      | 16            | 15     | 40         | 25         | PM2.5 SL Standard-50 μgm⁻³   |
|                      |         |               |        |            |            | PM2.5 WHO Guideline-25 μgm⁻³ |
| PM10 (μgm⁻³)         | 55      | 30            | 39     | 64         | 51         | PM10 SL Standard-100 μgm⁻³   |
|                      |         |               |        |            |            | PM10 WHO Guideline-50 μgm⁻³  |
| THC (ppm)            | 2.344   | 2.254         | 1.678  | 2.672      | 2.243      | No standard has been developed yet |
| CH₄ (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      |
| NO                   | 0.044   | 0.048         | 0.005  | 0.114      | 0.031      |
| NO₂                  | 0.026   | 0.005         | 0.011  | 0.011      | 0.011      |
| NOₓ                  | 0.070   | 0.053         | 0.016  | 0.125      | 0.042      |
| O₃                   | 0.005   | 0.007         | 0.017  | 0.013      | 0.003      |
| 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     |
0.044 ppm and NO₂-0.026 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 CH₄ (CH₄-1.828 ppm) concentration was observed. With the favorable temperature (28.4°C) in Anuradhapura, production of O₃ (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 NOₓ-VOC-O₃ sensitivity. In some conditions, the process of O₃ formation is controlled almost entirely by NOₓ and is largely independent of VOC (i.e., NOₓ-sensitive regime), while for other conditions O₃ production increases with increasing VOC and does not increase (or sometimes even decreases) with increasing NOₓ (i.e., VOC-sensitive regime). In the NOₓ-sensitive regime (with relatively low NOₓ and high VOC), O₃ increases with increasing NOₓ 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, NOₓ-sensitive regime occurs in Kurunegala and Jaffna as well. Further, it was observed the trend patterns of NO, NO₂ and NOₓ 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.
In the NOX saturated or VOC sensitive regime O3 decreases with increasing NOX 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 O3 concentration is seen in Fig. 4. However, with very high NO concentration, O3 concentration has reduced. This is due to the removal of O3 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 O3. Therefore, it is essential to reduce both pollutants NO and VOC simultaneously to mitigate formation of O3. Intermediate of this high O3 production and how the titration of produced O3 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 NOX-VOC-O3 sensitivity. Accordingly in Matara, Badulla, Pollonnaruwa, and Gampaha show the NOX-sensitive regime. In Kandy and Nuwaraeliya shows the VOC-sensitive regime as shown in Fig. 6.
3.5 Chemical Relationship

3.5.1 NOX-sensitive Regime

By considering the chemical reactions of NOX-O3 cycle, mathematical relationship could be developed to calculate O3ss in the NOX-sensitive regime as (Atkinson and Arey, 2003; Atkinson, 2000):

\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O (3P)} (\lambda < 420 \text{ nm}) \quad (R1) \]
\[ \text{O (3P)} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad (R2) \]
\[ \text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2 \quad (R3) \]

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 O3 concentration. The NOX sensitive steady state O3 concentration is proportional to the \([\text{NO}_2]/[\text{NO}]\) ratio and it is defined as:

\[ [\text{O}_3]_{\text{NOX sensitivity}} = \frac{j_{\text{NO}_2}[\text{NO}_2]}{k_{\text{NO} + \text{O}_3}[\text{NO}]} \]

where

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

k - depends on Temperature; 1 \(\Omega\) 0.4 ppm\(^{-1}\) s\(^{-1}\)

3.5.2 VOC-sensitive Regime

By considering the chemical reactions of NOX-VOC, split mathematical relationship could be developed to calculate O3ss in the VOC-sensitive regime. O3 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 NO2 (through reaction with HO2 or RO2 radicals), which also regenerates OH (see R6 and R7). NO2 is photolyed to generate atomic oxygen, which combines with O3 to create O3, as given in R8 and R9 (Sillman, 1999).

\[ \text{VOC} + \text{OH} \rightarrow \text{RO}_2 + \text{H}_2\text{O} \quad (R4) \]
\[ \text{CO} + \text{OH} \rightarrow \text{HO}_2 + \text{CO}_2 \quad (R5) \]
\[ \text{RO}_2 + \text{NO} \rightarrow \text{VOC} + \text{HO}_2 + \text{NO}_2 \quad (R6) \]
\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \quad (R7) \]
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.

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad \text{(R10)}
\]

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).

\[
\frac{d[\text{OH}]}{dt} = P_{\text{OH}} - \{\text{OH}\} \sum_{i} k_{i}[S_{i}] = 0
\]

\[
\frac{d[\text{HO}_2]}{dt} = P_{\text{HO}_2} - \{\text{HO}_2\} \sum_{j} k_{j}[S_{j}] - 2K_{\text{peroxid}}[\text{HO}_2]_{2} = 0
\]

\[
\frac{d[\text{RO}_2]}{dt} = P_{\text{RO}_2} - \{\text{HO}_2\} \sum_{j} k_{j}[S_{j}] - 2K_{\text{peroxid}}[\text{RO}_2]_{2} = 0
\]

where $P_{\text{OH}}$, $P_{\text{HO}_2}$, and $P_{\text{RO}_2}$ 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).

\[
\text{NO} + \text{HO}_2 \xrightarrow{k_1} \text{NO}_2 + \text{HO} \quad \text{(R11)}
\]

\[
\text{NO} + \text{RO}_2 \xrightarrow{k_2} \text{NO}_2 + \text{RO} \quad \text{(R12)}
\]
\[ k_1 = 8.5 \times 10^{-12}; \quad k_2 = 7.7 \times 10^{-12}; \quad \text{Rate constants at 298 K in cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ for bimolecular reactions and in s}^{-1} \text{ for photolysis reactions (Spirig et al., 2002).} \]

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;

\[
[O_{3}]_{ss} = [O_{3}]_{\text{NOX sensitivity}} + [O_{3}]_{\text{VOC sensitivity}}
\]

\[
[O_{3}]_{ss} = \frac{j_{NO}[NO]}{k_{NO+O_2}[NO]} + [NO](k_1[HO_2] + k_2[RO_2])
\]

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

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, Mataara, Badulla, Pollonnaruwa, and Gampaha show the NO\(_X\)-sensitive regime. In Rathnapura, Anuradhapura, Kandy and Nuwaraeliya 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 versa 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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