Spatio-temporal of surface ozone (O$_3$) variations at urban and suburban sites in Sarawak region of Malaysia

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Abstract. Sarawak Region of Malaysia is currently experiencing a high demand for capital needs such as transformation forest to plantations, economic development, and improving transportation systems. Those land cover changes will increase primary pollutant emissions and trigger surface O$_3$ formation. Surface O$_3$ is a secondary pollutant and a significant greenhouse gas contributing to climate change and declining air quality. In this study, variations in surface O$_3$ concentrations at urban and suburban sites in Sarawak were explored using the Malaysian Department of Environment data spanning a two-year cycle (2018-2019). The primary aim of this study is to ascertain the variation of surface O$_3$ concentrations reported at four monitoring stations in Sarawak, namely Kuching (SQ1) (Urban), Sibu (SQ2) (Suburban), Bintulu (SQ3) (Suburban), and Miri (SQ4) (Suburban). The study also analysed the relationship between O$_3$ distribution and nitrogen oxides (NO and NO$_2$). The findings showed that O$_3$ concentrations observed in the region during the study period were lower than the maximum permissible value of 100 ppbv suggested by the Malaysian Ambient Air Quality Standard (2020). SQ4 (Miri) at suburban sites recorded the highest average surface O$_3$ concentrations with an hourly average and daily maximum O$_3$ concentration of 15.7 and 89.5 ppbv, respectively. Temperatures, UV exposure, and wind speed all impact the concentration of surface O$_3$ in Sarawak. In all stations, concentrations of O$_3$ were inversely linked with NO, NO$_2$, and relative humidity (RH). This research will assist the relevant agency in forecast, monitor, and mitigate the level of O$_3$ in the ambient environment, especially in the Sarawak Region.

Keywords: Surface ozone, Ozone precursors, Nitrogen oxides, Urban, Suburban.

Track Name: Atmospheric Chemistry and Physics
1. Introduction

The surface ozone (O\textsubscript{3}) is one of the most important greenhouse gases (GHG), as it functions dually, depending on its elevation in the atmosphere\cite{1}. O\textsubscript{3} plays a vital role in the chemistry of both the stratosphere and troposphere. Tropospheric O\textsubscript{3} is an important component of the troposphere that impacts air quality, atmospheric oxidation capabilities, and climate change \cite{2}. Tropospheric O\textsubscript{3}, often referred to as surface O\textsubscript{3} is an atmospheric pollutant that negatively impacts human health, contributes to respiratory problems and lung disorders such as asthma, and has a detrimental influence on plants, the environment, and agricultural productivity \cite{3–7}.

Surface O\textsubscript{3} is a significant contributor to air pollution in urban areas across the world \cite{8}. The relationship between the production of O\textsubscript{3} in the presence of solar radiation and a complicated sequence of photochemical reactions involving two major O\textsubscript{3} precursors, nitrogen oxides NO\textsubscript{x} (NO\textsubscript{x} = NO + NO\textsubscript{2}) and hydrocarbons such as volatile organic compounds (VOCs) \cite{8,9}. The primary scientific concern associated with urban air pollution is these two main O\textsubscript{3} precursors \cite{8}. It has been discovered that levels of O\textsubscript{3} are spread over various locations in major cities, as well as in suburban and industrial regions in Malaysia, with a particular focus on the present condition of air quality, the sources of O\textsubscript{3}, and the long-term projections for the ambient air quality \cite{10–14}.

Consequently, it is imperative to locate and analyse surface O\textsubscript{3}. Understanding the conditions that result in its formation and the role of climatic variables such as solar radiation, temperature, and wind direction can assist in a thorough understanding of photochemical processes and the relationship between O\textsubscript{3} concentration and weather variables. Thus, this study aims to determine the variation in surface O\textsubscript{3} concentrations recorded at four urban and suburban monitoring sites in Sarawak. Then, the relationship between O\textsubscript{3} and its precursors, nitrogen oxides NO\textsubscript{x} (NO\textsubscript{x} = NO + NO\textsubscript{2}), and climatic variables is discussed, emphasising the challenges associated with ozone abatement.

2. Study Area and Methodology

2.1. Study area

The state of Sarawak is located on the northwest coast of Borneo and stretches throughout the whole length of the island and most of the South China Sea beaches. The state is 124,450 square kilometers in size. Its interior location has been recognised for the mountainous, dense rainforest that it encompasses; part of it is preserved as nature reserves. Figure 1 depicts the four monitoring stations within Sarawak's urban and suburban areas that were chosen for investigation.

2.2. Ozone and ozone precursors (NO, NO\textsubscript{2}, and NO\textsubscript{x})

The data source from the Department of Environment Malaysia (DOE) with measurements based on hourly concentrations of surface O\textsubscript{3} and oxides of nitrogen (NO, NO\textsubscript{2} and NO\textsubscript{x}) between the period of January 2018 until December 2019 were used. In addition to air pollutant parameters, the stations also recorded temperature, relative humidity, solar radiation (UVb), wind speed, and wind direction. Surface O\textsubscript{3} measurements from 2018 to 2019 were measured using Ozone Analyzer (Model 49i). The continuous measurements of NO, NO\textsubscript{2}, and NO\textsubscript{x} were measured using Oxides of Nitrogen Analyzer (Model 42i) via chemiluminescence technique. The AIO2-Meteorology Sensor was used to detect wind speed, wind direction, temperature, and relative humidity, while the Photovoltaic Pyranometer was used to monitor solar radiation (UVb). Pakar Scieno TW (PSTW), a DOE-assigned entity, calibrates and manages all instruments.
2.3. Statistical data analysis
Descriptive statistics are used to provide data in a clear and easy-to-understand format. It has a descriptive statistic table and a boxplot created with R programming. Collecting, filtering, organising, summarising, and presenting data is also part of statistical analysis. The missing values for the data collected during the study period were between 4.69% and 8.29%. (Table 1). Missing values in the study period are not considered in the computation of statistics.

2.4. Polar Annulus
This polar plot is used to depict the temporal features of a pollutant concentration as a function of wind direction. It can show the monthly fluctuations in the concentration of surface \(O_3\).

2.5. Diurnal Plot
It describes the characteristics, plot, and average of hourly values on a 24-hour scale. It may demonstrate the time series correlation and effect of \(O_3\) precursors on surface ozone concentrations and the changes on a 24-hour timeframe.

2.6. Kolmogorov-Smirnov Test and Spearman Correlation Analysis
The Kolmogorov-Smirnov test used to decide if a sample comes from a population with a specific distribution. Kolmogorov-Smirnov test can be performed to assess the normality assumption.
Meanwhile, Spearman's rank correlation is a nonparametric measure of rank correlation in statistics (statistical dependence between the rankings of two variables). It determines how well a monotonic
function can explain the relationship between two variables such as surface O\textsubscript{3} levels and their precursors and meteorological parameters.

3. Results and Discussion

3.1. Descriptive analysis

The descriptive statistics of hourly surface O\textsubscript{3} concentrations for urban and suburban sites from 2018 to 2019 are presented in Table 1. The hourly average concentrations of surface O\textsubscript{3} at the continuous air quality monitoring stations were recorded between 10.6 and 15.7 ppbv. SQ4 (Miri) at suburban sites recorded the highest average surface O\textsubscript{3} concentrations (\(M = 15.7 \text{ ppbv}, SD = 10.2\)). This was followed by suburban site SQ3, Bintulu (\(M = 14.1 \text{ ppbv}, SD = 10.6\)), urban sites SQ1, Kuching (\(M = 12.6 \text{ ppbv}, SD = 9.65\)) and suburban site SQ3, Sibu (\(M = 10.6 \text{ ppbv}, SD = 8.08\)). The median values were within \(\pm 2\) ppbv of the average O\textsubscript{3} concentration, whereas the standard deviation ranged between 8.08 and 10.6 ppbv for all sites. The maximum O\textsubscript{3} concentration fell within the range of 54.3 to 89.5 ppbv recorded by the four stations. The varying local emissions of O\textsubscript{3} precursors from motor vehicles and industrial activities are assumed to be the primary factor for the difference in long-term hourly O\textsubscript{3} concentrations across all stations [12].

Table 1. Descriptive statistics for surface O\textsubscript{3} concentration between 2018 to 2019 in Sarawak Region (ASL: Altitude base on above sea level; U: Urban site; SU: Suburban site, SD: Standard Deviation, M: Median).

| Location   | Latitude     | Longitude     | Altitude (ASL) (m) | Station-Characteristic | Missing value (%) | Hourly [O\textsubscript{3}] (ppbv) |
|------------|--------------|---------------|-------------------|------------------------|------------------|--------------------------------------|
|            |              |               |                   |                        |                  | Average    | SD        | M          | Max        |
| SQ1- Kaching | N 01° 33.734 | E 110° 23.331 | 7                 | Kaching-U              | 5.86             | 12.6       | 9.65      | 11.2       | 69.7       |
| SQ2- Sibu   | N 02° 18.864 | E 111° 49.915 | 9                 | Sibu-SU                | 8.29             | 10.6       | 8.08      | 8.96       | 54.3       |
| SQ3- Bintulu| N 03° 10.625 | E 113° 02.465 | 8                 | Bintulu-SU             | 6.19             | 14.1       | 10.6      | 12.6       | 71.9       |
| SQ4- Miri   | N 04° 25.481 | E 114° 00.746 | 6                 | Miri-SU                | 4.69             | 15.7       | 10.2      | 14.9       | 89.5       |

3.2. Boxplot of surface O\textsubscript{3} concentration

The box plot in Figure 2 depicts the hourly O\textsubscript{3} concentration at study locations i.e., SQ1, SQ2, SQ3, and SQ4, from 2018 to 2019. In 2019, both SQ3 and SQ4 had increased in O\textsubscript{3} concentrations, as shown in a plot. The reason is most likely due to the proximity of the SQ4 and SQ3 monitoring stations to crowded residential districts and industrial areas. Compared to prior years, for SQ1, SQ2, and SQ3, the median O\textsubscript{3} concentration in SQ4 is the highest (16.01 ppbv) in 2019. Overall, from 2018 to 2019, all urban (SQ1) and suburban (SQ2, SQ3, and SQ4) stations exhibit an elevation in O\textsubscript{3} concentration. As a result, the O\textsubscript{3} concentration increased marginally but remained below the Malaysian Ambient Air Quality criterion of 100 parts per billion (ppb) for hourly O\textsubscript{3} concentration [15]. The O\textsubscript{3} concentration boxplot appears to skew to the right across all stations and years. Any skewness in the data indicates that the distribution is not normal.
3.3. Monthly variations of surface \( O_3 \) concentrations (Polar Annulus by season)

The surface \( O_3 \) concentration was analysed using average hourly data for every month to identify the monthly variation of \( O_3 \) concentration. Figure 3 presented the polar annulus of surface \( O_3 \) concentration for SQ1, SQ2, SQ3, and SQ4 by wind direction. The monthly plots show that the \( O_3 \) concentration in SQ1 was higher in Aug-Sept, influenced by north-westerly, north-easterly, and south-easterly winds. The \( O_3 \) concentration in SQ2 was higher in mid-Aug to mid-Sept by south-westerly, westerly and north-westerly winds. Meanwhile, SQ3 exhibits higher \( O_3 \) concentration, particularly in June and July-Sept, dominated by north-westerly winds. Lastly, SQ4 explicitly the higher \( O_3 \) concentration in mid-July-Sept with wind direction from the westerly winds.

Sarawak experienced the southwest (SW) monsoon from May to September, which is associated with a relatively dry period before the monsoon wind shifts to wet weather, which is more visible in abrupt spikes in rainfall levels. The current temperature and solar radiation rise due to this occurrence, which increases the rate of \( O_3 \) generation.
3.4. Diurnal Fluctuation of Ozone and Its Precursor (NO, NO\textsubscript{2} and NO\textsubscript{x})

Figure 4 (a-d) compares the diurnal variation of surface \(\text{O}_3\) and its precursors, NO\textsubscript{2}, NO, and NO\textsubscript{x}. The diurnal plots of \(\text{O}_3\) concentration for SQ1 (a), SQ2 (b), SQ3 (c), and SQ4 (d) were plotted according to the average hourly data set from 2018 to 2019. During daytime hours, the \(\text{O}_3\) single peak was visible from all sites. \(\text{O}_3\)'s diurnal fluctuation in urban and suburban areas is the primary feature of peak concentrations in the afternoon at about 1:00 p.m. As seen in Figure 4(c) and 4(d), the surface \(\text{O}_3\) concentrations in suburban areas (SQ3 and SQ4) were higher than the mean concentration in urban areas (SQ1), and the maximum \(\text{O}_3\) concentrations began to rise by 8:00 a.m. The \(\text{O}_3\) peak occurred between 1:00 to 3:00 p.m. in suburban areas (SQ3 and SQ4), with mean peak values of 25.7 and 26.9 ppb, respectively, whereas suburban (SQ2) had the lowest mean peak value of 21.4 ppb.

Meanwhile, the \(\text{O}_3\) peak occurred at about 2:00 p.m. in the urban location (SQ1), with a mean peak value of 23.8 ppb. This daily trend corresponds to the previous findings [11]. The concentration of surface \(\text{O}_3\) was greatest during midday at SQ1 (Kuching) in the previous research, when the intensity of UVb was at its peak. The high \(\text{O}_3\) levels during the daytime may be attributed to incoming solar radiation, which encourages \(\text{O}_3\) creation via photochemical reactions in the lower troposphere. In
contrast, the low O\textsubscript{3} levels during the night and early morning hours may be related to a lack of photochemical reactions, leading to a catalytic cycle for ozone loss. Urbanisation, industry, high-speed propulsion, and atmospheric emissions of a wide variety of active chemicals such as carbon dioxide and aerosol are significant factors in increasing O\textsubscript{3} concentration. Suburban regions (SQ3 and SQ4) were bordered by new townships with dense residential areas, urban infrastructure, and a significant volume of traffic, which may account for the elevated O\textsubscript{3} concentrations in both regions.

The O\textsubscript{3} formation is highly dependent on the precursor concentration and exhibits a distinct hourly variation. The diurnal pattern of precursor concentrations in this urban and suburban research region exhibited comparable bimodality observed in earlier research \cite{11–13}. This bimodality is attributable to traffic emissions. The daily trends of each precursor pollutant (NO, NO\textsubscript{2}, and NO\textsubscript{x}) increased during the morning rush hours due to increasing traffic emissions and unstable atmospheric conditions. The resulting first peak of NO activity occurs between 7:00 to 9:00 a.m., and then it levels out and declines around 9:00 a.m., consistent with \cite{11,16}. As is typically the case in polluted urban areas, NO reacts with O\textsubscript{3} and enters a "NO\textsubscript{x} titrated state" \cite{17}. This explains why the O\textsubscript{3} precursor concentrations at midday were low due to their conversion to a variety of secondary pollutants, including O\textsubscript{3}, and the convective transmission of pollutants to higher elevations. The concentration of O\textsubscript{3} precursors started to rise again at 6:00 p.m. and gradually decreased after 11:00 p.m. However, as the diurnal plot indicated, it was unusual for SQ2; the second peak began early, approximately 1:00 p.m., with NO\textsubscript{x} reaching its highest level of the day at 6:00 p.m., before rapidly decreasing after 7:00 p.m.

3.5. Kolmogorov-Smirnov Test and Spearman Rank Correlation Analysis

Part of the initial step in data analysis was to verify the normality assumption. A graphical method such as boxplots and histogram were used to assess the normality assumption. Further testing of normality using the Kolmogorov-Smirnov test revealed that the data in this study did not follow a normal distribution (sig. < 0.05). Since this data did not meet the normality assumption, the correlation between O\textsubscript{3} and its precursors and other meteorological parameters were assessed using non-parametric correlation (Spearman rank correlation).

Overall, the Spearman Rank correlation results for both years demonstrated that O\textsubscript{3} concentrations in all urban and suburban sites studied were negatively correlated with NO, NO\textsubscript{2}, and RH. This conclusion is consistent with the fact that NO and NO\textsubscript{2} are known precursors of O\textsubscript{3}, implying an increase in O\textsubscript{3} concentration relates to a decrease in these pollutants' levels. The direct association between relative humidity and precipitation or moist conditions contributed to the negative correlation between O\textsubscript{3} and relative humidity. The direct relationship between relative humidity and precipitation or wet circumstances explains why O\textsubscript{3} and relative humidity negatively correlate. This is consistent with occurrence of the heavy rain and thunderstorms that occur between November and January during the Northeast (NE) monsoon \cite{18}, resulting increases low temperatures, solar radiation (UVb) and wind speeds \cite{14}. Increased relative humidity increased O\textsubscript{3} degradation due to reduced photochemical efficiency and influenced the chemistry between O\textsubscript{3} precursors. Additionally, there was a positive correlation between surface O\textsubscript{3} concentration and temperature, wind speed, wind direction, and solar radiation.
Figure 4. Diurnal variation of $O_3$ and its precursors.
4. Conclusion

Overall, the study demonstrates that all urban (SQ1) and suburban (SQ2, SQ3, and SQ4) stations show a rising level of $O_3$ from 2018 to 2019. However, the concentration of surface $O_3$ in the urban and suburban Sarawak region is still lower than the maximum permissible value of 100 ppbv suggested by the Malaysian Ambient Air Quality Standard (2020). SQ4, Miri at suburban sites recorded the highest average surface $O_3$ concentrations. Following that, suburban sites SQ3, Bintulu, urban sites SQ1, Kuching and suburban SQ2, Sibu. The concentration of surface $O_3$ in the Sarawak region is influenced by meteorological conditions, including temperature, UV radiation, and wind speed. During the SW monsoon season, the polar annulus has a greater $O_3$ level from July to September. The possibility that biomass burning may produce higher quantities of $O_3$ during the SW monsoon requires more study and analysis. This study implies that more research on surface $O_3$ and its precursors in Sarawak is necessary, particularly on surface $O_3$ to other $O_3$ precursors such as NOx and VOC control strategies to determine the most effective solutions for comprehensive $O_3$ abatement. While the previous study highlighted various observational tendencies, little emphasis was made on the mitigating implications of these results in Malaysia's Borneo area. It is crucial to maintain $O_3$ precursor concentrations to sustain the $O_3$ concentration at or below the maximum limit. The challenges associated with $O_3$ mitigation could be tackled through the development of strategies and enactment of regulations such as strict NOx emission limits for power plants and industrial combustion sources; enhanced vehicle inspection programmes in states; or the application of Internet of things technologies such as low-cost sensors to be installed in previously unmeasured urban and industrial areas.

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