Effect of ozone precursors on surface ozone variations in GAW Kototabang and Cibeureum

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Abstract. Ozone composition is widely distributed in the troposphere. Surface ozone, known as a secondary pollutant, is a by-product of burning fossil fuels. Increasing the concentration of GHG (CO₂, CH₄, and CO) as precursors can affect the surface ozone concentration. This study aims to determine the type of precursor that affects the concentration of surface ozone and also to determine the impact of surface ozone and its precursors in rural and remote areas. In general, surface ozone concentrations in both Kototabang and Cibeureum begin to increase at 08 – 09 WIB, following the increase in solar radiation intensity, and decrease at 18 – 19 WIB. This pattern is because surface ozone is a secondary pollutant formed by photochemical reactions, in which the photochemical reactions are triggered by energy from solar radiation. The correlation of the surface ozone concentration with CO₂, CH₄ and CO in the Cibeureum was -0.17, 0.31, and 0.40. The correlation values of surface ozone concentration with CO₂, CH₄ and CO in the Cibeureum area are 0.09, 0.45, and 0.48. The highest correlation is shown by a CO correlation of 0.40. Moreover, the highest correlation is shown by a CO correlation of 0.48. The results in this study indicate the effect of each precursor on surface ozone concentration and the accompanying processes.

Keyword: surface ozone, precursors, GHG, ozone

1. Introduction
Ozone composition is widely distributed in the troposphere, many factors can affect change in the composition. Surface ozone, known as a secondary pollutant, is a by-product of burning fossil fuels, including nitrogen oxides (NOx) and Volatile Organic Compounds (VOC) that react by being exposed to ultraviolet radiation from the sun [1]. Surface ozone depends much on meteorological conditions and the effects of climate change. The concentration of surface ozone is affected by the biogenic processes, chemical, natural precursor emissions, kinetics, deposition, also ozone deployment, and its precursor. Meteorological factors play a role in the biogenic activities of plants and microbes that affect the emission of ozone precursors [2]. Ozone has the potential to damage plants and human health, and vegetation through various mechanisms [3].

Ozone is a gas that can damage the lungs, mucous membranes of the eyes, skin, and also affect nerve function and give symptoms of tiredness, dizziness, and vomiting. Chronic exposure can cause bronchial irritation and cause bronchitis (Mukono, 2005). Research conducted by Aisyah in 2018 stated that the relationship between ozone and Acute Respiratory Infections (ARI) in pekabaru showed a strong relationship, ozone concentration affected the number of ARI cases by 26.4% [4].

Research conducted by Sham Lal in 1999 stated that the increase in ozone concentration during the day in urban areas is caused by the photooxidation of precursor gases such as CO, CH₄, and NMHCs.
CO and CH$_4$ gases are greenhouse gases in the atmosphere which are produced from various human activities. These gases build up in the air, cause the increase of the concentration over time [5]. Another precursor which often affects surface ozone formation is Carbon monoxide (CO). CO and ozone are two primary species in the photochemistry system in the lower (surface) troposphere. Around 70% of oxidant chemistry in the atmosphere reacts with CO [6]. Ozone precursors, especially carbon monoxide, hydrocarbons, and nitrogen oxides derived from nature and human activities, affect the concentration of tropospheric ozone in the atmosphere. This study was conducted to determine the type of precursor that affects the concentration of surface ozone and also to determine the impact of surface ozone and its precursors in rural and remote areas.

2. Methods

2.1 Site Description

![Locations of the observation surface Ozone and Its precursor](image)

The research was conducted at GAW Kototabang (representation of remote area) and Cibereum Air quality monitoring station (representation of rural area). Bukit Kototabang is located on the island of Sumatra, Indonesia (0°12'07" S – 100°19'05"E). The station is situated in a remote elevated area (865 m a.s.l). Cibereum Air quality monitoring station is located in West Java, Indonesia (06 ° 42'64 ''S – 106 ° 57'01 " E), the station is situated in a remote elevated area (1160 m a.s.l). GAW Bukit Kototabang and Cibereum stations are located in the Equatorial region, with a tropical climate and has two seasons, rainy and dry seasons.

2.2 Data

The data used in this study were generated from automatic equipment at the GAW Bukit Kototabang station and Cibereum air quality monitoring station. Series of data used is daily data from February 2019 – December 2020. Ozone surface is measured by using Ozone Analyzer Thermo 49iQ Series. Measurement/monitoring of surface ozone at GAW Bukit Kototabang station is done by using ozone analyzer 49iQ Series. The 49iQ operates on the principle that ozone (O$_3$) molecules absorb UV light at a wavelength of 254 nm. The degree to which the UV light is absorbed is directly related to the ozone concentration as described by the Beer-Lambert Law:

$$ I = I_o \ exp\left(\frac{-KL\cdot C}{L}\right) $$

Where:

- $K$ = molecular absorption coefficient, 308 cm$^{-1}$ (at 0°C and 1 atmosphere)
- $L$ = length of cell, 38 cm
- $C$ = ozone concentration in parts per million (ppm)
- $I$ = UV light intensity of sample with ozone (sample gas)
\( Io = \) UV light intensity of sample without ozone (reference gas)

Greenhouse data used at Kototabang and Cibeureum are obtained using Picarro G2401, with working principle using wavelength-scanned cavity ringdown spectrophotometry (WS-CRDS). The data obtained from the Picarro G2401 is near real-time with 5-second data resolution, then converted into hourly, daily and monthly data. Air samples were taken from an altitude of 32 meters from the ground.

2.3. Methodology

The concentration of air quality parameters data gained from the measurement using automatic equipment is analyzed on a daily basis and time series, and then correlation analysis is done to determine the closeness of relation/effect of surface ozone on its precursor. To analyze the relationship between surface ozone and its precursor, the researcher used Pearson correlation that is stated in the correlation coefficient value. The correlation coefficient value is more substantial if it approaches \( +1 \) and weaker if it approaches \( 0 \) \([7]\). Pearson correlation is a simple correlation that involves only one dependent and independent variable. The correlation coefficient value can be interpreted in table III.1 below.

| No | Interval     | Classification |
|----|--------------|----------------|
| 1  | 0.00 – 0.19  | Very low       |
| 2  | 0.20 – 0.39  | Low            |
| 3  | 0.40 – 0.59  | Moderate       |
| 4  | 0.60 – 0.79  | High           |
| 5  | 0.80 – 1.00  | Very High      |

3. Result and Discussion

3.1. Diurnal Characteristics of Surface Ozone

Ozone concentration in Cibeureum region in all-season ranges between 14.25-27.1 ppb, in dry season ranges between 15.8 ppb and 12.2-22.6 ppb in the rainy season. In all seasons, ozone concentration at Bukit Kototabang is lower than Cibeureum, which ranges between 8.25-17.85 ppb. So does in the dry and wet season, concentration in Kototabang is lower than ozone concentration measured in Cibeureum. In the dry season the concentration in Bukit Kototabang Area ranges from 6.5-16.5 ppb and in rainy season ranges between 10.52-19.94.

![Figure 2: Diurnal variation of ozone concentration](image-url)
According to the diurnal concentration of surface ozone in Cibeureum and Bukit Kototabang appeared that surface ozone concentration started to increase in the same time, which was at 08-09 local time, and decreasing on 18-19 local time. The intensity of surface ozone base on the intensity of solar radiation, this suitability is due to troposphere ozone is a secondary pollutant formed from photochemistry reaction which this photochemistry reaction occurred in the presence of solar radiation energy. Surface ozone is well known as a secondary pollutant. Its reaction depends on the concentration of Carbon Monoxides (CO), and Nitrogen Oxides (NO) with solar radiation during the day, which produces CO₂ and O₃.[8]

The photooxidation of precursor gases during the day causes the reduction of ozone. This can be seen on scatter plot relation between surface ozone with the UV radiation (Fig 4.) where the correlation value produced was 0.73 with the coefficient of determination of 0.054.

Figure 2. shows that ozone concentration in Cibeureum in the dry season is higher than in the rainy season, while ozone concentration in Kototabang is higher in the rainy season. This difference in diurnal concentration due to these two regions have different rain pattern. Diurnal ozone concentration in all-seasons measured in Cibeureum is higher than in Kototabang, and this was due to characteristics and sources of emissions in the area.
3.2. Trend and correlations Ozone and its precursors

![Ozone and CO2 concentration at Cibereum](image1)

![Relationship between O3 and CO2 at Cibereum](image2)

![Ozone and Methane (CH4) concentration at Cibereum](image3)

![Relationship between O3 and CH4 at Kototabang](image4)

![Ozone (O3) and Carbon Monoxide (CO) concentration at Cibereum](image5)

![Relationship between O3 and CO at Cibereum](image6)

**Figure 5.** Ozone concentrations and Its precursors (daily averages) measured from February 2019 to December 2020 at Cibereum

| Year | Cibereum | Bukit Kototabang |
|------|----------|------------------|
|      | O3 (ppb) | CO2 (ppm) | CH4 (ppm) | CO (ppb) | O3 (ppb) | CO2 (ppm) | CH4 (ppm) | CO (ppb) |
| **Maximum** | 2019 | 57.51 | 428.45 | 2.07 | 505.82 | 44.40 | 434.85 | 2.04 | 673.55 |
|       | 2020 | 34.12 | 439.20 | 2.02 | 565.75 | 29.96 | 447.45 | 2.05 | 284.05 |
| **Minimum** | 2019 | 4.52 | 311.02 | 1.82 | 101.03 | 3.45 | 409.00 | 1.83 | 69.49 |
|       | 2020 | 5.53 | 380.25 | 1.84 | 97.71 | 3.88 | 408.70 | 1.85 | 69.35 |
| **Average** | 2019 | 20.47 | 414.57 | 1.92 | 296.46 | 11.70 | 419.02 | 1.91 | 190.76 |
|       | 2020 | 16.59 | 416.05 | 1.92 | 208.21 | 12.86 | 420.21 | 1.92 | 132.27 |
Based on the correlation between surface ozone and CO, CH₄, and CO in Cibeureum, the highest correlation occurs in CO with a positive value (0.4), which means it has a moderate category. Similar to the correlation between CO and surface ozone, the correlation between surface ozone and CH₄/CO₂ is in the moderate category with a value of 0.45. Correlation between CO₂ with surface ozone has a shallow level, with a correlation value of 0.09, this relation due to Surface ozone (O₃) is a secondary pollutant produced from photochemistry oxidation of Nox with the abundance of carbon monoxides (CO), methane (CH₄) and non-methane hydrocarbons [9].

![Relationship between O₃ and CO at Kototabang](image1)

![Relationship between O₃ and CH₄ at Kototabang](image2)

![Relationship between O₃ and CO at Kototabang](image3)

Figure 6. Ozone concentrations (daily averages) and the relationship between Ozone and Its precursors measured From February 2019 to December 2020 at Bukit Kototabang

The relationship between surface ozone and CO₂ has a tendency very low correlation but has a positive tendency with CO and CH₄. In Fig 5, the increasing of CO concentration has an identical pattern with surface ozone concentration in Cibeureum and Bukit Kototabang. Based on the correlation result between surface ozone with CO₂, CH₄, and CO in Bukit Kototabang, the highest correlation value is found on the surface ozone and CO with the correlation value of 0.40 a pretty Moderate level. Correlation between CH₄ and surface ozone has a low level, which is in the value of 0.31. The relationship level from these two precursors is due to surface ozone (O₃) is a secondary pollutant
produced from photochemistry oxidation of Nox with the abundance of carbon monoxides (CO), methane (CH$_4$), and non-methane hydrocarbons [9]. Ozone concentration is still affected by other parameters such as meteorological parameters like temperatures, wind velocity and direction, and other ozone precursors. NO2/NO ratio is another factor that affects Ozone concentration [10].

Based on the correlation value in Bukit Kototabang and Cibeureum, the difference due to emission source and characteristics in both regions. The correlation between CO$_2$ and CH$_4$ in Cibereum is higher than in Kototabang, and this happens because the Cibeureum region is a rural area which is an area with relatively high farming and agricultural activities, as we all know, CH$_4$ is a greenhouse gas produced from such activities, aside from that, Cibeureum region is close to tourism sector where many vehicles often pass by which produces carbon emission, so it affects the CO concentration measured in that area, which we all know that CO gas is a result of incomplete combustion of fossil fuels used by motorized vehicles.

**Figure 7.** Ozone concentrations (daily averages) and the relationship between Ozone and Its precursors measured From February 2019 to December 2020 at Bukit Kototabang
3.3. Seasonal Variation in Ozone

Figure 8. Surface ozone seasonal Comparison

Figure 8 presents monthly variations of surface ozone at GAW Bukit Kototabang and Cibeureum station during 2020. Although both stations represent the rural and remote areas, seasonal variation patterns of ozone at GAW Bukit Kototabang and Cibeureum are entirely different. Compared to Bukit Kototabang, surface ozone concentrations in Cibeureum shows higher levels throughout June to November. GAW Bukit Kototabang and Cibeureum have different rainfall patterns. Factors that can affect ozone concentration apart from solar radiation are meteorological parameters, such as rainfall and wind direction. Surface ozone and its precursors are transported and accumulated by photochemical production [11,12,13,14,15]. However, there are still many debates on whether anthropogenic pollution or stratospheric intrusion plays a more dominant role [16,17,18,11,13]. Surface ozone at dry season showed a peak in a yearly cycle in Cibeureum, but no specific peak showed in GAW Bukit Kototabang.

4. Conclusion
1. Methane and carbon monoxide are precursors to background surface ozone, and their growth since pre-industrial times has contributed to an increase in ozone globally. Future changes in methane emissions are expected to affect ground-level ozone concentrations, including in polluted regions.
2. Anthropogenic methane has long been recognized to contribute to tropospheric ozone (in the presence of NOx). Because methane is long-lived and well-mixed in the troposphere, it affects the tropospheric ozone background, including surface air.
3. The precursors that most influenced the formation of surface ozone in the Kototabang and Cibeureum areas are Carbon Monoxide (CO) and Methane (CH₄).
4. Surface ozone concentration in GAW Bukit Kototabang higher than Cibeureum due to differences in characteristics and sources of emissions.

5. Recommendation
1. Further research on investigate the impact of global change (climate change and future emissions) on precursors ozone’s lifetime.
2. Further research on the methane - ozone relationship (through changes in NOx and OH)
3. Further research on understanding of effects of changes in methane on aerosols (for air quality and climate), and on stratospheric ozone (including any feedbacks to tropospheric ozone).
4. Future research should validate the surface ozone concentration response to methane through multi-model intercomparisons and observations.
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