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Systematic Literature Review on Ozone Dispersion Correlated with Diurnal Concentration Pattern in Urban and Rural Areas

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ABSTRACT

Ground level ozone is known to exhibit a strong daily variation of concentration leading to long-range transport of air pollutants from urban to rural areas. Moreover, the characteristics of O_3 relationship between urban, suburban, and rural sites can be explained by O_3 photochemical chemistry and meteorological dispersions as indicated by the different result of O_3 diurnal pattern. However, little is known about the global phenomenon of diurnal concentration of ozone, meteorological dispersion such as long-range transport, and their correlation with ozone precursors, especially in urban and rural areas. This paper attempt to compare the difference between daily ozone fluctuations in both sites and assess some factors that cause long-range ozone transport from urban and rural areas both in subtropical and tropical areas for global scale. Using systematic literature review analysis with the PRISMA method, it examined 43 peer-reviewed articles published between 2010 and 2022 globally meeting the inclusion criteria. The result showed that the fluctuation patterns of daytime ozone in urban and rural areas are different to those in tropical and subtropical regions, depending on latitude. This was primarily due to the influence of solar radiation and the presence of precursors. Conversely, a slight decrease in ozone rate at night occurs because the precursor was accumulated by the shutdown of photochemical ozone production. Some precursors of ozone from other regions can be transported and accumulated from the long-range transport process in other locations. This paper serves as an initial guideline to analysing the pattern of ozone concentration in urban and rural areas and the factors that influence it.

KEYWORDS
air pollutant, dispersion pattern, long-range transport, rural, urban

INTRODUCTION

Ground Level Ozone (GLO) or surface ozone, is a secondary pollutant generated from a complex chain of photochemical reaction involving its gas precursor, consisting of oxides of nitrogen (NO_x = NO + NO_2), Volatile Organic Compound (VOCs) and Carbon Monoxide (CO). The diurnal variation of ozone production in urban and rural areas depending on its precursor, wind direction, and long-range transport has been studied globally by applying direct measurement and chemistry modelling for air quality analysis. Some variations of diurnal ozone pattern in tropical and subtropical areas are influenced by many factors such as radiation, geographic location (longitude and latitude), precursors, and emission sources (Sillman, 1999; Huang et al., 2018). Air in the troposphere has relatively low ozone concentrations, except in highly polluted urban environments. Even polluted regions are relatively low when compared to stratospheric levels. As this "clean ozone area", air moves slowly upward in the tropical stratosphere.

Table 1. Keyword for literature review.

Category	Keyword
Population	*ozone* OR O_3 AND NO_x* OR NO OR NO_2*
Intervention	*diurnal fluctuation* OR transport* OR long-range transport*
Comparison	*urban* OR suburban* OR rural* AND tropical* OR tropic OR subtropical**
Output	*ozone diurnal fluctuation* OR ozone urban area* OR ozone suburban area* OR ozone rural area* OR NOx-regime* OR NOx-limited regime OR ozone contribution* OR air dispersion* OR ozone long-range transport**

Tropospheric Ozone (O_3) is formed by complex non-linear photochemical reactions between O_3 precursors: methane, carbon monoxide, volatile organic compounds (VOCs), and nitrogen oxides with reaction: NOx = NO + NO_2 (Sillman, 1999). A non-linear relationship between NOx and O_3 occurs mainly in urban areas. It is primarily caused by the lessened titration effect of NO in urban areas, where the O_3 photochemical chemistry is mostly VOC-sensitive (Paoletti et al., 2014; Simon et al., 2015; Sicard et al., 2016; Li et al., 2016). In addition, an essential process of ozone removal is associated with directly emitted NO. This process, referred to as NOx titration, occurs because freshly emitted NO (typically, 90% or more of total NOx emitted) reacts rapidly with O_3 to produce NO_2. In situations with significant ozone production that includes most urban and polluted rural areas during meteorological conditions favorable to ozone formation), this removal of O_3 is small compared to the ozone production rate. The process of NOx titration can only remove at most one O_3 per emitted NO (up to 1.5 O_3 per NOx at night), whereas the process of ozone formation typically produces four or more O_3 per emitting NOx (Al-Qasimy, 2017).

Apart from emissions of O_3 precursors, meteo rological factors are also important in affecting O_3 levels both directly and indirectly. Meteorological factors can directly impact the formation of O_3 because the reactions are sensitive to the changes in sunlight and temperature (Xie et al., 2016; Wang et al., 2017). Meteorological factors such as wind speed, surface pressure, and precipitation also impact the accumulation, dilution, and deposition of O_3 (Tong et al., 2017). The prevailing wind direction that changes with the season is closely related to air pollutant transport from near and distant areas (Wang et al., 2001; Xie et al., 2016; Wang et al., 2017). The relationship between air pollutants and meteorological factors varies significantly by geographical location and season (Wang et al, 2019).

The characteristics of O_3 at urban, suburban, and rural sites depend on the O_3 photochemical sensitivity of the region. While mostly in many parts, rural areas have been strongly affected by ozone from long-range transportation from surrounding urban and suburban areas. However, to this date, the publication of the review paper needs to more summaries the phenomenon of the global diurnal pattern of ozone in tropical and subtropical regions and its correlation with meteorological aspects such as dispersion and long-range transport. Identifying the current situation of diurnal fluctuation of O_3 pattern in various areas with different latitude and longitude located both at urban and rural areas will help determine the controlling presence of precursors related to the O_3 production rate, which is critical for O_3 control and management. Based on these issues, objectives of the research are to compare the difference between the diurnal ozone fluctuation in urban and rural areas located in both tropical and subtropical regions and to assess some factors that cause long-range ozone transport from urban and rural areas based on meteorological factors.

RESEARCH METHODS

Literature Search and Selection Criteria

The method used in this study was a systematic literature review (SLRs). It was a way of synthesizing scientific evidence to answer a particular research question in a way that was transparent and reproducible while seeking to include all published evidence on the topic and appraising the quality of this evidence (Petticrew, 2001; Liberati et al., 2009; Lame, 2019). By using SLRs, this study systematically examined the different fluctuation patterns of ozone production in urban and rural areas located in tropical and subtropical regions correlated with a diurnal dispersion pattern. Another primary effect that influenced the long-range transport of ozone has also been assessed to understand the influence of meteorological factors on ozone formation in a specific region. Some applications, such as Publish or Perish, and Zotero combined with Mendeley, were used to collect and select literature publications.

Following PRISMA (Preferred Reporting Items for Systematic Reviews and Meta-Analyses) guidelines, we used predefined eligibility criteria to search the database of Scopus and Web of Science for peer-reviewed published literature investigating the nexus between ozone production, di urnal dispersion pattern,
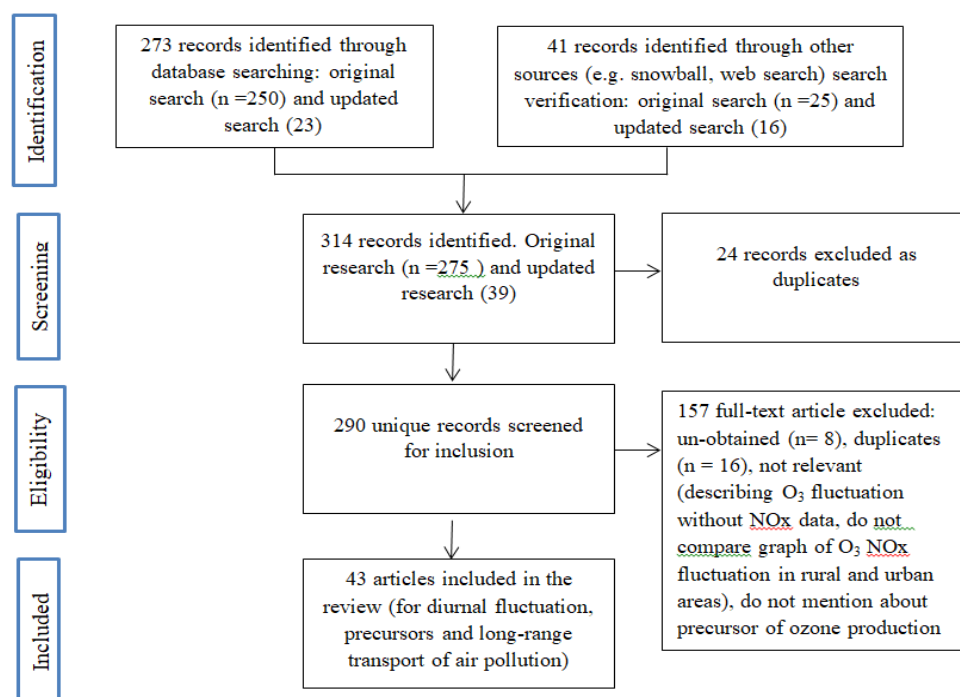
Figure 1. Flowchart of PRISMA (Preferred Reporting Items for Systematic Reviews and Meta-Analyses).

and long-range transport globally. Identifying keywords in (Table 1) was conducted before collected literature review. The keywords were arranged based on the PICO method (Population, Intervention, Comparison, Outcome). This method can be used as a good step for research based on systematic literature review (Cooke et al., 2012).

Data Extraction

After applying the search engines and keywords, we found 273 relevant papers. To identify which articles should be included or excluded in this paper, the following criteria were applied:

1. Duplicate works of literature were deleted.
2. Studies that described diurnal ozone fluctuation in urban and rural in the range publication year from 2011 to 2022 were included. While observational studies independently observed diurnal patterns of urban only or rural only, and works of literature that describe O_3 fluctuation in urban and rural without observing NOx fluctuation were excluded.
3. Publications involving meteorological aspects that do not include long-range transport of air pollution were excluded.
4. Taking relevant pictures (Figures 2-6) from reviewed papers as literature to describe O_3 phenomenon, both fluctuation and long-range transport, in subtropical and tropical regions.

After screening the titles and abstracts of the reviewed papers, the content was screened based on the relevance and focus of the representation presented in the study. If the study was still relevant and describes diurnal fluctuations and long-range ozone transport, then the paper can be used in the literature review. Relevant articles were articles that include discussions following the author's objectives. Then, the selected papers were extracted to obtain more detailed information.

According to these criteria, the regional studies in tropical and subtropical areas described diurnal fluctuation, and long-range transport of ozone was included. We examined all 273 of the included papers and further checked each paper's listed reference to ensured that every related paper was addressed.

Table 2. Studies of diurnal variations of ozone in urban, suburban and rural areas for tropical areas.

Author	Location	Period	Urban	Suburban	Rural
Hasanah, 2018	Bogor, Indonesia	2016-2018	–	√	√
Huang et al., 2018	Shenzhen, China	2011-2017	√	√	√
Shith et al., 2021	Malaysia	2013-2015	√	√	√
Diaz et al., 2022	Guadalajara, Mexico	1996-2019	√	–	√

Table 3. Studies of diurnal variations of ozone in urban, suburban and rural areas for subtropical areas.

Author	Location (Period)	Period	Urban	Suburban	Rural
Khuriganova, et al., 2016	Siberia, Russia	2013-2014	√	−	√
Saini et al., 2014	Agra, India	2012	√	−	√
Hassan et al., 2013	Jeddah, Saudi Arabia	2011-2012	√	−	√
Tong et al., 2016	Ningbo, China	2012-2015	√	√	√
Tyagi et al., 2016	NCR of Delhi, India	2014	√	√	−
Amit Kumar et al., (2014)	Delhi, India	2013-2014	√	−	√
Cheng et al., 2019	Beijing, China	2006-2017	√	−	√
Hamdun et al., 2015	Tanzania	2012-2015	√	√	√
Wang et al., 2020	Hangzhou,	2019-2020	√	−	√
Im et al., 2013	Istanbul, Turkey	2017	√	√	√
Betancourt-Odio et al., 2021	Madrid, Spain	2011-2018	√	√	√
Mitchell et al., 2021	Nova Scotia, Canada	2017	√	√	√
Nishant, 2011	Kannur, India	2009-2010	√	−	√
Xu et al., 2011	China	2007	√	√	√
Mahidin et al., 2021	Sarawak, Malaysia	2018-2019	√	√	−
Zong et al., (2017)	Ji'nan, Yucheng China	2013	√	√	√

There were 43 publications included in this study with restricted criteria that the study should describe the precise time of ozone and its precursor concentration peak in daytime or night time, the comparison of two or more places with different characteristics (urban, suburban, and rural), and the seasonal patterns of ozone and its precursors. We also cited the relevant graph (Figures 2-5) as the representation to describe O_3 diurnal fluctuation in tropical and subtropical areas. For long-range transport of O_3 review, the impact of long-distance transport at the high O_3 concentration was observed by in situ measurement. For clusters of long-range transport categorized by high O_3 concentrations come from urban rural, urban to rural, also other factors such as regional or local transport that have caused ozone accumulation in a specific site. A flowchart that illustrates the detailed procedures applied for article identifications was presented in Figure 1.

RESULTS AND DISCUSSION

This systematic literature review examined diurnal ozone fluctuation from 21 publications globally. From the urban and rural site observations, some factors which have influenced the diurnal fluctuation of ozone concentration emerged, such as various sources of emission and geographical conditions such as latitude and topography, which influence acceptance of solar radiation. Besides, the influence of meteorological conditions such as wind speed and long-range transport has impacted the dynamic of ozone concentration daily (Proietti et al., 2020). There are 21 studies that qualify for diurnal variations of ozone in urban and rural areas. From these studies, there are 4 studies in tropical areas and 17 studies in subtropical areas. The details of the studies included the location of observation (urban, suburban, and rural) areas are presented in Table 1 and 2.

Diurnal Variations of Ozone in Tropical Areas

Tropical areas in this study referred to areas surrounding the equator that receive sunlight which is more direct than the rest of Earth and are generally more hot and wet as they are not affected as much by the solar seasons. Ozone is created in this tropical region because it is here that the sun, positioned high overhead during the day all year long, is most intense. There is enough of the necessary energetic UV light to split apart molecular oxygen and O_2 and form ozone. It typically takes more than six months for air at 16 km (near the tropical tropopause) to rise to about 27 km (Toihir et al., 2018).

Overall, there are four studies from Hasanah et al., (2018), Huang et al., (2018), Shith et al., (2021), and Diaz-Torres et al., (2022) that met the criteria, in which three studies discussed diurnal fluctuation of ozone in the urban area, four studies in rural areas, and three studies in suburban area conditions. Based on those studies, ozone diurnal fluctuation in tropical areas had a similar pattern, which increases as high intensity of radiation and decreases as low intensity of radiation.
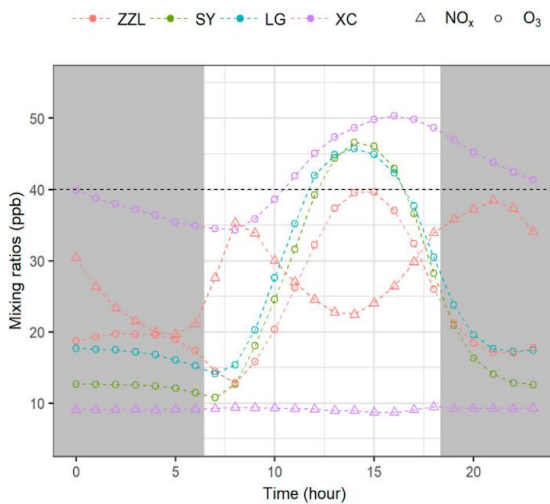
Figure 2. Comparison of Zhuzilin (ZZL), Shiyan (SY), Longgang (LG), and Xichong (XC) sites consist of urban, suburban, and rural sites towards O_3 and NOx concentration (Under author permission, Huang et al., 2018).

The increased of ozone concentration in urban areas occurs earlier than in suburban and rural areas due to long transport of ozone and its precursors causing ozone accumulation in rural areas. The increasing of ozone concentration in urban areas occurred earlier due to direct emissions from several sources, such as automobiles exhausted and factories, while the accumulation of ozone emissions in the rural which was inclining due to the long-range transport phenomenon of ozone and its precursors for ozone accumulation particularly to the rural areas.

The ozone concentration in rural areas is also generally higher than in urban areas (Figure 2). Ozone concentration in urban areas could increase higher than in rural areas in the daytime, as increasing diurnal radiation. However, when ozone concentration starts decreasing, it is higher than in rural areas, so that urban areas have much lower ozone concentrations than rural areas at night. In addition, the synchronous decrease of O_3 in the morning is mainly caused by the titration effect of NO, which is a dominant reaction when sunlight is limited for O_3 production. Then, O_3 increases rapidly and reaches its daily maximum values when the precursors' concentration tends to be the same at the same period. Also, during the daytime titration effect is normally balanced by photolysis of NO_2 to produce abundant ozone. This phenomenon is evidence for photochemical ozone formation from precursors NOx and VOCs (Hasanah, 2018; Huang et al., 2018; Shith et al., 2021).

Regarding ozone in the tropical region, it is interesting to regard the characteristics of tropospheric O_3 in tropical areas. It consisted of: i) intense photochemistry due to high UV radiation and humidity, ii) large active natural sources of CO and other O_3 precursors through biomass burning (Ziemke et al., 2009), biogenic (Aghedo et al., 2007), and lighting emissions (Sauvage et al., 2007b, c), iii) increasing anthropogenic emission due to rapid industrialization (Granier et al., 2011; Duncan et al., 2016, iv) large net ozone production potential because deep convection can transport surface emissions to higher altitudes, where their lifetime is increased due to lack of surface deposition and dilution with unpolluted background (Pickering et al., 1995) and (v) dynamic processes capable of redistributing chemical species in a regional and global scale (Zhang et al., 2016). Thus, the tropics are a region where O_3 production is favored (Tsivlidou et al., 2022).

However, there were several reasons for low O_3 concentration in tropical areas: First, it was mainly because from winter until spring, there was an O_3 transport and accumulation phenomenon from tropical areas to the high latitude region (subtropical area) or Southern Hemisphere (Toihir et al., 2018). This phenomenon was a result of Brewer–Dobson circulation on a regional (air mass transport from the tropics to subtropics) and global scale (from summer hemisphere to winter hemisphere) (Holton et al., 1995; Fioletov, 2008). In addition, ozone transport from the tropical to extratropical regions is the most dominant process during winter (Portafaix, 2003). It constitutes the principal reason for the observed annual maximum over the area 20–30° S. The second reason that caused a low-tropospheric O_3 in the tropical region is that a zonal wave-one observed on tropical tropospheric O_3 (Thompson et al., 2003a).
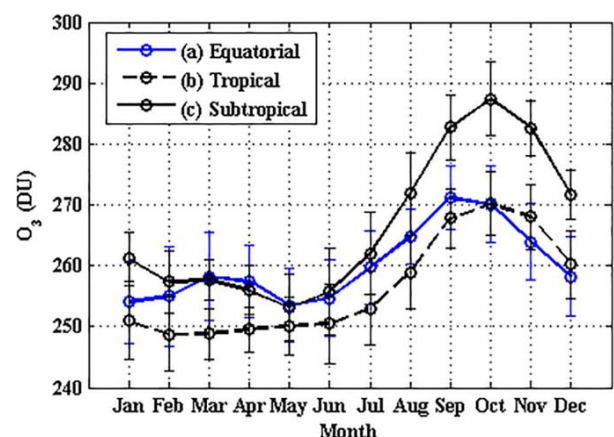
Figure 3. Seasonal variations of total ozone over three different regions: (a) equatorial, (b) tropical, (c) subtropical regions. Error bars represent ±1σ (Under author permission, Toihir et al., 2018).
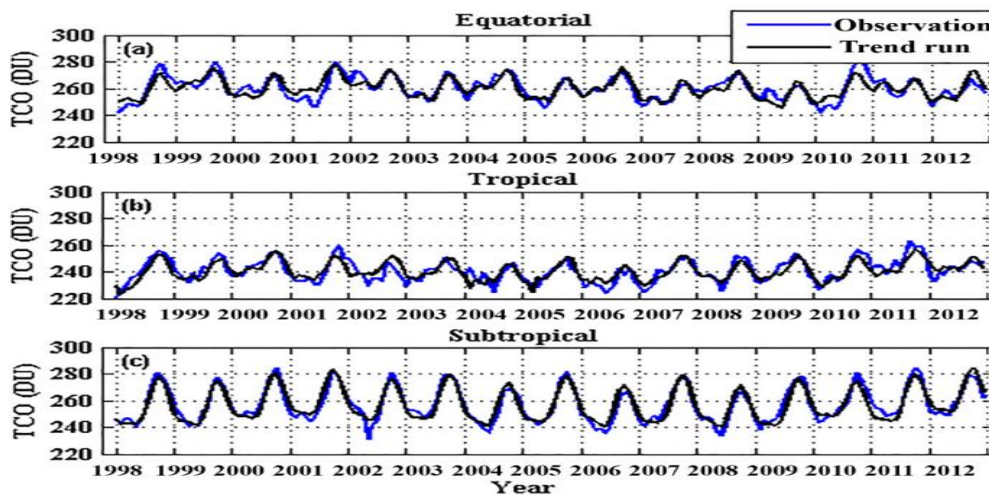
Figure 4. Monthly mean total ozone values (blue) over (a) the equatorial, (b) tropical, (c) and subtropical regions. The black lines represent TCO values by ditorRun (Under author permission, Toihir et al., 2018).

Moreover, ozone levels decline during late spring and summer was explained by a decrease in ozone transport coupled with ozone photochemical loss (Fioletov, 2008). However, the observation of maximum ozone in September over the equatorial region but 1 month later over the subtropics may be explained by a delay in ozone transport between the two regions (Figure 3). Figure 4 illustrated the curve of the seasonal distribution of TCO was attributed to the time evolution of monthly mean total ozone values (blue) over the equatorial (a) the equatorial, (b) tropical, (c) and subtropical regions. While considering the process of formation and transport of ozone as described above, TCO annual records in tropical regions should be higher than those recorded over equatorial regions. However, it was important to note that both sites (Samoa and Fiji, in the 10–20° latitude range) are in the Pacific Ocean. The low TCO quantity observed in the Pacific is due to low tropospheric ozone levels over the region due to a zonal Wave-One observed on tropical tropospheric ozone (Thompson et al., 2003a, 2003b).

Diurnal Variations of Ozone in Subtropical Areas

The subtropical areas were geographical and climate zones located north and south of the tropics. This area is often characterised by hot summers and mild winters with infrequent frost. Sixteen studies about ozone diurnal fluctuation in suburban areas located in subtropical areas. All studies discuss urban areas, while the others of nine studies discuss suburban regions, and fourteen studies examine rural areas. Based on those studies, the daily ozone fluctuations in subtropical regions were like the tropical areas, as increasing the high intensity of sunlight radiation and decreasing the low intensity of radiation. The ozone fluctuation patterns occur in rural, suburban, and urban areas and are likely caused by local photochemical

production (Nishant and Kumar, 2011; Xu et al., 2011; Hassan et al., 2013; Kumar et al., 2014; Hamidun et al., 2015; Saini et al., 2015; Khuriganova et al., 2016; Tong et al., 2016; Tyagi et al., 2016; Im et al., 2017; Zong et al., 2017; Cheng et al., 2019; Wang et al., 2020; Betancourt-Odio et al., 2021; Mitchell et al., 2021Mahidin et al., 2021).

In addition, another factor that emerged in the subtropical regions was an increasing ozone concentration in urban sites that occured earlier than in suburban and rural areas. Some studies had identified that ozone concentration in subtropical urban areas rose earlier than in rural regions (Nishant and Kumar, 2011; Xu et al., 2011; Hassan et al., 2013; Tong et al., 2016; Mitchell et al., 2021; Mahidin et al., 2021). In contrast, others identified the inverse resulted that increasing ozone concentration in rural areas occured initially (Im et al., 2017). Interestingly, some publications revealed ozone concentration in urban and rural regions started to rise at a similar time (Kumar et al., 2014; Hamidun et al., 2015; Cheng et al., 2019; Tyagi et al., 2016). In addition, some publications revealed that peak O_3 in urban and rural regions occured at mid-day, precisely at around 2pm to 4pm (Hassan et al., 2013; Kumar, 2014; Saini et al., 2015; Khuriganova et al., 2016; Tong et al., 2016; Tyagi et al., 2016; Cheng et al., 2019). The urban sites offer high NOx emissions due to heavy vehicle traffic during the morning rush hour, while a strong inverse relationship between NOx and O_3 had also emerged. The concentration of NOx was high while O_3 was considerably low in the morning (Nishant, 2011; Xu et al., 2011; Hassan et al., 2013; Amit-Kumar et al., 2014; Khuriganova et al., 2016; Saini et al., 2015; Tong et al., 2016; Wang et al., 2020; Mahidin et al., 2021; Zong et al., 2017). However, photochemical dominated at the mid-day (Nishant and Kumar, 2011; Xu et al., 2011;

Hassan et al., 2013; Kumar, 2014; Saini et al., 2015; Khuriganova et al., 2016; Tong et al., 2016; Tyagi et al., 2016; Im et al., 2017; Hasanah et al., 2018; Huang et al., 2018; Cheng et al., 2019; Wang et al., 2020; Betancourt-Odio, 2021; Mahidin et al., 2021; Shith et al., 2021; Diaz et al., 2022).

The mid-day peak and low night-time concentrations of O_3 are typical characteristics of the diurnal cycle of ozone. At night-time, the reduction in O_3 level was mainly due to the decrease of solar radiation, which would lower the level of photochemical production (Nishant and Kumar, 2011; Xu et al., 2011; Hassan et al., 2013; Saini et al., 2015; Khuriganova et al., 2016; Zong et al., 2017; Mahidin et al., 2021; Mitchell et al., 2021). Finally, during night, the NOx and O_3 maintained balance quickly, there was no solar radiation, and both the source emission and dilution effects decreased significantly. Moreover, an anomaly of the ozone peak pattern occurred at Halifax, caused by sea breeze and latitude. Mitchel et al., (2021) report that the peak of ozone concentration did not appear at the mid-day. Instead, ozone remains stable, starting from 12-9pm, while it dramatically drops at 8am. This anomaly happened because the sea-breeze effect facilitates the dispersion of pollutants throughout the day and limits ozone titration of NOx in the afternoon, even though the peak of ozone concentration in urban areas was comparably lower than in rural sites. Figure 5 manifested the relationship between ozone and NOx, diurnal variation of NOx and ozone are plotted for Halifax (urban core), Lake Major (suburban), and Aylesford (remote background) in 2017 (Mitchell et al., 2021). The downtown Halifax station was subject to high NOx emissions due to heavy vehicle traffic during the morning rush hour. It corresponded to a strong inverse relationship between NOx and O_3, driven by NO titration of O_3 during this time. Although the urban centre of Halifax also experiences a pronounced afternoon rush hour, the build-up of NOx was limited by active boundary layer mixing and, at times, the sea breeze effect.

Moreover, a significant influence of diurnal ozone fluctuation assumed by BVOC (Biogenic Volatile Organic Compound) had been identified in urban areas of China (Nishant and Kumar, 2011). After analysis, it was determined that the concentration of Biogenic VOC in rural areas was smaller (1.59 ppb) than in urban areas (4.18 ppb). Isoprene is a metropolitan area that is primarily biogenic rather than anthropogenic in summertime Beijing. The deciduous and coniferous tree can release a substantial amount of isoprene and monoterpene in urban area Baolian (BL). In contrast, there were only a few biogenic VOC sources in rural areas because it was surrounded by fruit and crops with less emission from isoprene and monoterpene. Besides BVOC, Xu et al., (2011) also tried to analyse another factor that caused a high concentration of O_3 in rural areas. Precisely, by investigating chemical characteristics of air masses from different regions, segregating this bulk based on diurnal variation and wind direction then assess the effect of pollutant transport at some downwind side of rural areas of Shandong, China.

Analysis of Precursors that Influence Diurnal Fluctuation of Ozone in Rural and Urban

The daily ozone concentration was controlled primarily by the patterns of radiation and by the precursors. These precursors of ozone are primarily pollutants emitted by different processes such as combustion (anthropogenic and natural) and biogenic (from vegetation sources). As the ozone precursors, chemical compounds, such as carbon monoxide (CO), methane (CH_4), Volatile Organic Compound (VOCs) and nitrogen oxide (NOx), which in the presence of solar radiation can react with other chemical compounds to form ozone, mainly in the troposphere. Based on 21 review papers which unravel the diurnal dynamic of ozone concentration in urban and rural areas, 18 articles agree that maximum O_3 production occured at noon in tropical and subtropical urban sites (Nishant and Kumar, 2011; Xu et al., 2011; Hassan et al., 2013; Kumar, 2014; Saini et al., 2015; Khuriganova et al., 2016; Tong et al., 2016; Tyagi et al., 2016; Im et al., 2017; Hasanah et al., 2018; Huang et al., 2018; Cheng et al., 2019; Betancourt-Odio, 2021; Mahidin et al., 2021; Shith et al., 2021; Diaz et al., 2022). The ozone concentration in the urban area was also higher than at the rural site in the mid-daytime. However, the rest two papers had showed the inverse result (Wang et al., 2020; Mitchell et al., 2021). Moreover, as the precursor, NOx had demonstrated an inverse relationship with ozone concentration, accounting for a higher concentration in urban areas and a lower concentration in rural areas.

Generally, all articles agree that levels of precursors (NOx) strongly influence the shape and amplitude of ozone cycles. In the highly urbanised environment, the primary sources of NOx were traffic and vehicular emission. For example, Schuch, (2019) unravelled that vehicles were the most critical source of ozone precursors in the São Paulo, Brazil, urban area. Several articles also explicitly revealed that the primary precursor of ozone in urban areas was NOx (Nishant and Kumar, 2011; Ibrahim Hassan et al., 2013; Im et al., 2013; Kumar, 2014; Amit Kumar et al., 2014; Tong et al., 2017; Torres et al., 2017; Cheng et al., 2019; Al-Qassimy and Al-Saleem 2019; Shith et al., 2021). A large amount of NO can be found in car exhaust gases. NO had a very short lifespan of only a couple of minutes and was
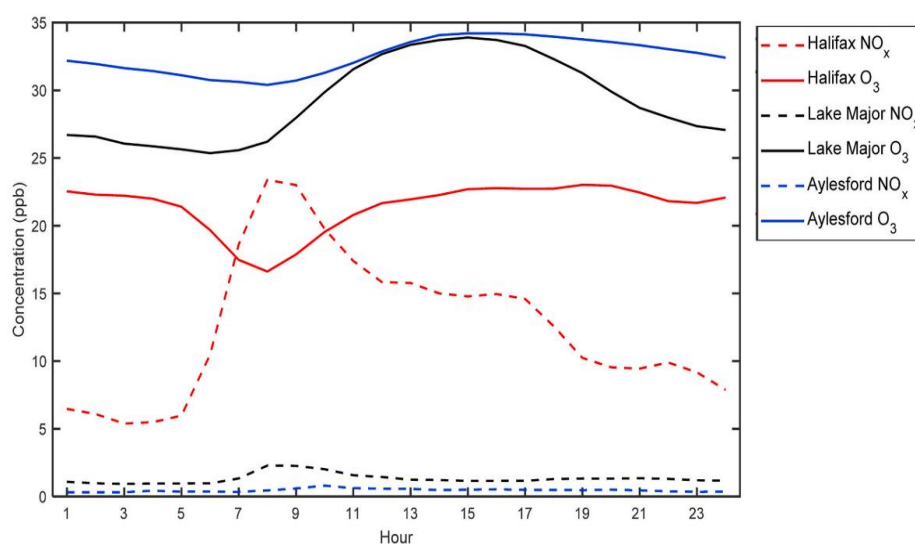
Figure 5. Diurnal Fluctuation of hourly NOx and O_3 at Halifax (urban core), Lake Major (suburban) and Aylesford (remote background) in 2017 (Under author permission, Mitchell et al., 2021).

immediately converted or oxidised into NO_2. It had a longer lifespan than NO of hours to even days, allowing it to be transported over larger distances by wind, from the urban to more rural areas, because there is less ozone in the towns than in the countryside (Al-Qassimy and Al-Saleem, 2019). Moreover, for the vehicle as emission sources, it had been assessed that heavy duty vehicles and light duty vehicles contribute to high NOx concentration, and motorcycles contribute to high non-methane hydrocarbons (NMHC). Interestingly, NMVOC was one of the major precursors of forming ozone involving photochemical reactions (Schuch, 2019).

Wang et al., (2020) explained the dynamic of ozone fluctuation during the lockdown period in several observation sites in Hangzhou Province, China, caused by reduction of pollutant concentration. The results showed that city lockdown decreased $PM_{2.5}$, PM_{10}, CO, and NO_2 concentrations at urban and rural locations. The decline of ozone precursor, NO_2, was explained by the reduced traffic emissions in the urban areas and by lower regional transport in rural areas during the lockdown. Paradoxically, reducing nitrogen oxide levels had increased O_3 concentrations by 145%, from 24.6 to 60.6 μgm^{-3} in the urban area and from 42.0 to 62.9 μgm^{-3} in the rural area. This finding was explained by the weakening of the chemical titration of O_3 by NO due to reductions of NOx new emissions during the non-photochemical reaction period from 8 pm to 6 am. Another reason was due to loss of HO_2 uptake from reduction of PM2.5 which led to O_3 formation (Li et al., 2021).

Besides NOx, Carbon Monoxide and Volatile Organic Compound was another ozone precursor that highly influences the ozone diurnal fluctuation in the atmosphere. Carbon monoxide, which was mainly emitted from transportation exhaust, was also known

as an ozone precursor, and was considered one of the major contributors to ozone formation in Brazil and New Delhi urban areas, respectively. Torres et al., (2017), Saini et al., (2014), and Im et al., (2013) also revealed that the primary ozone precursor in the city was not only NO, but also CO (Carbon dioxide) emission. The condition is getting exacerbated since combinations of CO at boundary layer process, chemistry and anthropogenic emissions occurred. Moreover, Mitchell, (2021) revealed that in the Halifax urban area, the ozone precursors considered are nitrogen oxides (NOx) and volatile organic compounds (VOC). At the same time, Xu et al., (2011) unravelled that besides NOx, aromatics VOC from industrial areas is known to dominate Ozone Formation Potential at both urban and rural sites. Within the industrial area, measured VOC concentration was dominated by halogenated hydrocarbons, and alkene was the highest contributor to ozone formation (Pinthong et al., 2022).

Aligning to this situation, Calfapietra et al., (2013) revealed that BVOC was also presented in urban areas due to emission of isoprene by city trees alongside sidewalks and from forests at city park at San Paulo, Brazil. However, in rural areas, O_3 precursors are typically due to high levels of biogenic hydrocarbons (BVOCs) which are emitted by forest or other vegetation (Yan Liu et al., 2018; Betancourt Odio et al., 2021). Based on the sensitivity modelling analysis, Zong et al., (2017) revealed that the main precursors for ozone in this area were dominated by isoprene in the NCP rural area of China. This BVOC caused intense local biogenic emissions in rural site. Combined with transport polluted plumes from urban areas, these biogenic VOCs played a significant role in O_3 formation by causing the severe O_3 pollution in rural atmospheres of the NCP and other polluted regions of China.

Table 4. Types of long-range transport phenomenon.

No	Publication	First Cluster	Second Cluster	Third Cluster	Fourth Cluster
1	Azevedeo et al., 2011	–	√	–	√
2	Betancourt-Odio et al., (2021)	–	–	√	–
3	Chatani et al., (2020)	√	–	–	–
4	Cheng et al., (2019)	–	√	–	–
5	Edwards et al., (2012)	–	√	–	–
6	Fernández-Guisuraga et al., (2016)	–	–	√	√
7	Fine et al., (2015)	–	–	√	√
8	Glavas et al., (2011)	–	–	–	√
9	Hasanah (2018)	–	√	√	–
10	Im et al., (2013)	–	–	√	√
11	Lai and Brimblecombe (2021)	–	√	–	–
12	Li et al., (2021)	√	–	–	–
13	Lien and Hung (2021)	–	–	–	√
14	Mithcell et al., (2021)	√	√	–	–
15	Ryoo et al., (2017)	–	–	–	√
16	Saini et al., (2014)	–	–	–	√
17	Squizzato et al., (2021)	√	–	–	–
18	Tong et al., (2016)	–	√	–	–
19	Xu et al., (2011)	–	–	√	–
20	Yadav et al., (2016)	√	–	–	√

Long-Range Transport Influence for Ozone Production

Air emissions from anthropogenic activities in one area can come from other areas, even over great distances. Evidence of the transport of air emissions from distant areas continued to emerge after the Second World War when the nature of air pollution in urban areas began to change due to the population shift from rural to urban areas (CEC 1997). Atmospheric chemistry will change when favourable meteorological conditions (warm air temperatures and intense sunlight) increase ozone concentrations and the total air emissions mix. High ozone concentrations in rural areas far from precursor sources can only be explained by the transport of pollution over hundreds of kilometres. A significant factor contributing to the high regional level ozone concentrations generated in the precursor emission source areas was the meteorological wind field. Ozone tended to remain in or near the region where it was formed when an area was in relatively light wind conditions.

In terms of analysis of long-range transport, there were four different clusters to depict the pollutant source and impact from a specific site. Furthermore, several publications fall into more than one cluster. The first cluster were some publications that conclude high ozone accumulation in urban areas comes from long-range transport. The second cluster are publications specifically mentioning that ozone accumulation in rural areas comes from a long-range transport process. The third cluster was that some publications had

successfully revealed that there was a long-transport phenomenon of ozone from urban to rural areas. The last cluster reveals some other factors such as regional or local transport had caused accumulation of ozone in specific sites.

The first cluster was a group of publications that discuss the phenomenon of long-distance transportation from urban to rural areas, one of which was disclosed by Mitchell et al., (2021) which discovered the phenomenon of long-distance transportation from the north-eastern US region, which was a densely populated and industrial area known as a source of ozone precursors and ozone pollution, to Nova Scotia. These regional transport pollution days were continuously in progress, causing Nova Scotia to experience statistically significant decreasing ozone concentration influenced by net decreasing transboundary pollution sources that accumulated in Aylesford rural areas.

The second cluster was the phenomenon of long-range transport in rural areas where one of them was revealed by Edward, (2012) who found a high concentration of ozone in the Parsons area (a rural area in the state of West Virginia), which may be caused by the transport of ozone and remote precursors. The western air current carries many components including high concentrations of sulfuric, nitric, and acids from the Midwestern and Ohio River Valleys. Another publication included in this second cluster was by Tong et al., (2016) who revealed high levels of O_3 in Lake Dong-qian (DQL) and the Ningbo urban environment

observation and research station (NUEORS), which were the two non-urban areas, which are higher when compared to urban areas. Much higher wind speeds at DQL and NUEORS result in the background transport of pollutants to these non-urban locations.

While the third cluster revealed that high accumulation of O_3 comes from the long-transport phenomenon of ozone from urban to rural areas. One of them was the publication by Xu et al., (2011) who revealed that the impact of urban plume on ozone pollution in downwind rural areas can transport not only O_3 but it was precursors. The primary precursor, Carbon Monoxide (CO), will lead to more photochemical O_3 production when mixed with the background atmosphere in the downwind rural area. Another publication by Betancourt-Odio et al., (2021) found that the average daily O_3 level ($\mu g/m^3$) tended to be higher at stations far away from urban sites in the Spanish Community of Madrid (CM) and located in rural areas such as El Atazar, Orusco Tajuña, San Martin. de Valdeiglesias, Villarejo de Salvanés and Guadalix Sierra Norte. Betancourt-Odio et al., (2021) suspect that meteorological characteristics and gas circulation favour the rapid migration of gases from urban to rural areas.

The last cluster was related to long-range transport processes from another region. Lien and Hung, (2021) analysed another meteorological factor that influences maximum ozone increase by sea-breeze convergence, which leads to maximum ozone increase in the coastal Taiwan area during the accumulation via the local transport process. The transport causes the noontime O_3 time lag under pseudo-steady state conditions. Factors driving O_3 production through photo-oxidation process include the availability of intense solar radiation and local air transport since the recirculation of air over Istanbul contains a high-pressure system leading to accumulated ozone levels.

In addition, Ryoo et al., 2017 revealed a relationship between increased O_3 concentrations off the coast of California (CA) and pollutant sources in North Asia. Local sources and stratospheric intrusion can only partially explain the high O_3 at this location. Back trajectory analysis was used to determine the impact of long-distance transport at the high O_3 concentrations observed by in situ measurements of O_3 were performed as part of the Alpha Jet Atmospheric experiment (AJAX) on the California Coast. Factors causing convective events so that the polluted air parcel rises into the free troposphere are Low outgoing longwave radiation (< 190 W/m) was also found in North Asia and the Western Pacific and atmospheric chemistry mechanisms by Peroxyacyl Nitrates (PANs) which is an important reservoir of atmospheric

nitrogen, modulating reactive nitrogen cycle and ozone (O_3) formation.
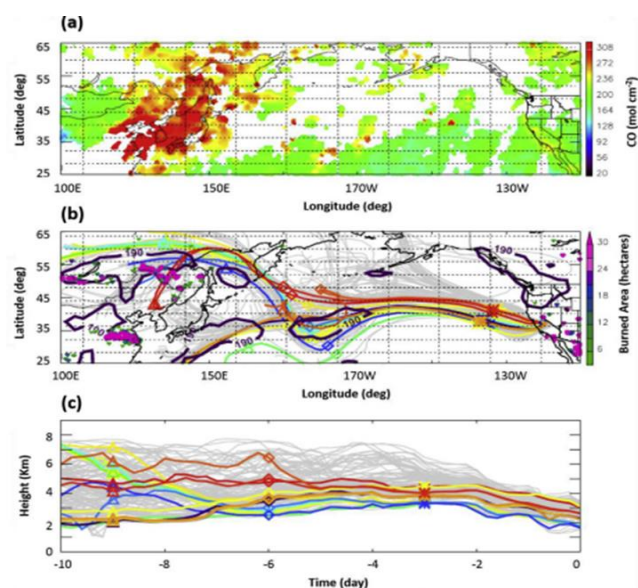
Figure 6. The impact of long-distance transport at the high O_3 concentrations observed by in situ measurements of O_3 on the California Coast (Under author permission, Ryoo, 2016).

CONCLUSIONS

Even though most publications report that ozone emerges earlier in urban rather than rural areas, in fact, mean ozone concentrations in urban (polluted) areas were significantly lower (about two-times) than in rural and suburban areas. It is attributed to the increased consumption of ozone for oxidation of other air pollutants, transport of air pollution from urban to rural, and the titration effect in highly polluted areas. Regarding the diurnal fluctuation, both tropical and subtropical areas had a similar pattern of ozone concentration, highest at afternoon and lowest at early morning. This is affected by precursor concentrations and radiation that increase in the afternoon. Geographical factors can also influence ozone concentration.

Areas with higher elevation had higher ozone concentrations, also coastal areas had a unique pattern of ozone and it was precursors because of sea-breeze effect. Moreover, the long-range transport from urban to rural areas can cause high ozone concentrations even though the area was not a source of pollution. This happened because the air mass carries ozone and its precursors to the village. This long-range transport phenomenon was inseparable from local meteorological conditions such as differences in solar radiation reception, air temperature, rainfall, and humidity. Another factor that played a role in long-range transport was the geographical condition of an

area that causes local phenomena such as sea breezes-land breezes, and winds in mountainous areas.

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