Temporal Analysis of Ozone and Nitrogen Oxides Fluctuations at Pasir Gudang, Malaysia

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Abstract. Ozone (O3) and nitrogen oxides (NOx) are closely related in the atmosphere. In ambient air, these pollutants always fluctuated depending on their emission sources and meteorological influences. The paper is aims to gain insight understanding of the monthly temporal variation of O3 and NOx concentrations to enable proper control strategies against these pollutants. One-year monitoring records from 1st January to 31st December 2009 of O3 and NOx at Pasir Gudang, were obtained from Department of Environmental Malaysia. Temporal analysis of O3 and NOx concentration fluctuation during annual and monthly were assessed using time series and scatter plots. The annual variations of O3 concentrations were negatively correlated with annual variation of NO and NO2 concentrations. Results suggest that O3 concentration are higher than NO and NO2 especially in May 2009. However, zero exceedences were recorded in the studied period for all pollutants against the Malaysia Ambient Air Quality Guidelines.

Introduction

Ozone (O3) and nitrogen oxides (NOx) are important compounds in atmospheric chemistry. At the ground level, ozone is one of the significant air pollutants and always relates with degrading air quality especially in urban areas. High ozone levels can potentially affected human health, plant species, various natural materials, and manufactured goods [1]. Ground level O3 is produced by series of chemical reaction of the main precursors (NOx and VOCs) that were anthropogenic emitted in the ambient air with ultraviolet radiation that act as catalyst to the reactions [2].

NOx is produced when fuel is burned at high temperature and the primary sources of NOx are any human activities, which associated with burning fuels. The main sources of NOx came from fossil fuel combustion from either industrial and vehicular, biomass burning, microbial activity in soils, and lightning [2]. In the presence of sunlight, NO is generated by photolysis of NO2 but it will oxidized by O3 to regenerated NO2 [1,3]. Photolysis of NO2 created atom O that will react with molecule O2 that already existed in the atmosphere to create O3. The destruction of O3 will happen when it is reacted with NO to produce NO2. Ghazali [1] regarded the NO2 photolysis and NO titrations are the main chemical reactions that controlling the formations and destruction of the ground level ozone. These reactions also directly influence by meteorological variability such as temperature, solar radiation, wind speed and direction as well as the availability of the precursors sources [2, 3, 4].

Reduction in NOx emission will tremendously effected the O3 concentration vice versa. As levels of O3 and NOx are inextricably linked, any changes in O3 levels may indicated the effectiveness of local NOx emissions control [3]. The selection of Pasir Gudang is made based on the growth of the area regarding the populations, traffic density, shipping and industrial activities. Majority of air pollution studies in Malaysia focusing in Klang Valley [1, 4, 5]. It is therefore necessary to gain insight into the O3 and NOx relationship in the atmosphere at Southern region of Peninsular Malaysia. The paper, the fluctuational behavior of ozone O3 and NOx were analyzed temporally during annual and monthly. The rest of the temporal analysis is reported elsewhere.
Site description

The dispersion and dilution of air pollution are directly influenced by local attribution such as meteorological condition as well as the location of the monitoring stations. The monitoring station was established at Sekolah Menengah Kebangsaan Pasir Gudang, Pasir Gudang (Fig. 1). Pasir Gudang was located at Johor, which is the southern state of Peninsular Malaysia. The monitoring station was established and operated by Department of Environmental, Malaysia to monitor any significant changes in the ambient air quality. Pasir Gudang is one of the Johor’s districts infamous with Pasir Gudang’s Port. The major industries that were governing Pasir Gudang economy were transportation and logistics, shipyard industries, petrochemical industries and oil palm storage and distribution. Pasir Gudang Port was the third busiest port in Malaysia after Klang Port and Penang Port. In 2010, Pasir Gudang Port handled about 28 million tons of cargo and received nearly 5000 international and local ships [6]. Malaysia Statistical Department (2010) reported that during 2010 census the number of Pasir Gudang populations is approximately 43,000 persons. The growth of the town indirectly degrading the air quality status at Pasir Gudang due increasing anthropogenic emissions. Climatically, Pasir Gudang as the rest of Johor state experienced tropical monsoon with uniform temperature throughout the year an average temperature is ranging from 24°C to 32°C [7].

O<sub>3</sub> and NO<sub>x</sub> monitoring records and measurement techniques

One year hourly continuously monitoring records of O<sub>3</sub>, NO, and NO<sub>2</sub> were obtained from Department of Environmental Malaysia (DoE) from 1<sup>st</sup> January to 31<sup>st</sup> December 2009. The record is regularly subjected to standard quality control processes and quality assurance procedures by the DoE [8], the quality controlled procedures were followed the international standards outlined by United State Environmental Protection Agency (USEPA) [11]. Hourly O<sub>3</sub> concentrations monitoring samples were collected using UV Absorption Ozone Analyzer Model 400A which is a microprocessor controlled analyzer [8] based on the Beer-Lambert law in order to measure law ranges of O<sub>3</sub> the ambient air or gaseous media [1]. Ambient O<sub>3</sub> molecule were detected based on internal electronic resonance of O<sub>3</sub> molecule using absorption of 254 nm UV light that were emitted from internal mercury lamp [9]. Samples of hourly and daily NO<sub>x</sub> (NO, NO<sub>2</sub>) concentrations were collected using chemiluminescent NO/NO<sub>2</sub>/NO<sub>x</sub> Analyzer Model 200A which is an EPA approved method. Ghazali [1] reported that, the analyzer were applying the chemiluminescent detection principle to detect the NO<sub>x</sub> concentration in the ambient air coupled with microprocessor technology to enhance the pollutants monitoring ability. The usage of microprocessor technologies in the analyzer provides sensitivity, stability and ease to be use in a continuous monitoring environment [10].
Temporal analysis of annual and monthly fluctuations of O$_3$ and NO$_x$ concentrations

It is unarguable that NO and NO$_2$ plays the most significant role in formations and destructions of O$_3$ at ground level [1,2, 3]. Fig. 2 showed the scatter plots of daily average of O$_3$ variations against NO and NO$_2$ concentrations. Since, NO$_2$ and NO concentrations acts as the precursors to O$_3$, it is expected that O$_3$ variations to be negatively correlated with variations in NO$_2$ and NO concentrations. Weak correlations coefficients ($R^2$) is obtained from O$_3$ and NO$_2$ (-0.364), while for the relationship between O$_3$ and NO is slightly higher at -0.424. During the photochemical reactions of O$_3$ formations, molecule of NO$_2$ is react with solar radiation produced atom of oxygen, which is later reacted with oxygen molecule producing O$_3$ molecule [1, 3]. Meanwhile, reactions between O$_3$ and NO will destroying O$_3$ and reproducing NO$_2$. The inter-convension between O$_3$, NO$_2$ and NO is can be well illustrated by diurnal plot (24 hour), however, the result is presented elsewhere.

Fig 2 Scatter plots of O$_3$ variations against NO$_2$ and NO concentrations

Annual maximum concentrations of O$_3$, NO and NO$_2$ in Pasir Gudang are analyzed using time series plots as shown in Fig. 3. The results suggested that O$_3$, NO and NO$_2$ were fluctuated throughout the year and relatively high concentrations were observed during second and third quarter of the year (April- September). Figuratively, Pasir Gudang experienced more severe NO pollutions compared to O$_3$ and NO$_2$ pollutions. Han [3] reported that vehicular emissions is the main contributors towards NO pollution and it is reported by Ministry of Transport Malaysia [6] the total number of registered vehicle in Johor is approximately 2.7 million in year 2010. Noticeably, all pollutants were at minimal concentrations during the early and the end of the year compared to during the mid of the year. Several distinct peaks of O$_3$ concentrations were observed throughout the year especially during March to May, which is coincided with increasing trends in NO and NO$_2$ concentrations. However, these peaks concentrations not rise beyond MAAQG levels of 100 ppb for O$_3$ and 170 ppb for NO and NO$_2$ for 1-hor averaging period. The means of maximum concentrations of O$_3$, NO$_2$ and NO in Pasir Gudang in 2009 are 36.13 ppb, 24.80 ppb and 50.96, respectively.
Fig. 3 Time series plot of daily average O$_3$, NO, and NO$_2$ concentrations

Fig. 4 Monthly temporal variations concentrations of O$_3$, NO, and NO$_2$; a) average; b) maximum

Fig. 4 illustrated the plot of monthly average and maximum of O$_3$ and NO$_x$ concentrations in 2009. From the average plot, January recorded the highest in O$_3$ concentration (23 ppb) followed by February (16.2 ppb). However, the highest average concentrations for NO and NO$_2$ were recorded on July and October with 17.4 ppb and 15.22 ppb, respectively. Results also exhibits that, the lowest monthly average concentration recorded on November for O$_3$ (11.8 ppb) and on December for both NO (5.42 ppb) and NO$_2$ (7.6 ppb) concentration. Meanwhile, based on Fig. 4(b) the highest maximum concentrations of O$_3$, NO$_2$ and NO is all recorded on May with 91 ppb, 63 ppb and 169 ppb, respectively. It is also observed, lower maximum concentration of all pollutants during December and January which most probably induced by monsoonal effect. According to Toh [11], there are two major monsoonal period occurs in Malaysia which are North East Monsoon (November to March) and South west Monsoon (June to September) accompanied by two inter-monsoon periods. Heavy rainfall, which always associated with North East Monsoon, may contribute to the reductions of the O$_3$ and NO$_x$ concentrations in the atmosphere. Increasing in intensity of the rainfall will be promoting wet deposition of air pollution molecule in ambient air, thus reducing the pollution concentration [3, 11]. All pollutant especially ozone shall have scouring effect due to rainfall and PM$_{10}$ will be effected by wet deposition. Scavenging of air pollutants in ambient air also can be triggered by chemical reactions such as NO titration as well as dispersion and transport of the pollutants by winds [2, 3, 4, 11].

**Conclusion**

The result demonstrated that NO is more prominent air pollutant in Pasir Gudang compared to O$_3$ and NO$_2$. However, since O$_3$ formation was controlled by NO$_x$ concentration, O$_3$ can also plays significant role towards air pollution status in Pasir Gudang. This study proved that, annual
variations in O\textsubscript{3} concentration is negatively correlated with annual NO\textsubscript{2} and NO. Even though, there are several spikes were observed on the pollution annual time series plots, there are zero exceedences of the guidelines limit were recorded. The maximum monthly O\textsubscript{3} concentration with 91 ppb is observed on May 2009, while the monthly maximum of NO and NO\textsubscript{2} concentrations are 169 ppb and 63 ppb, respectively. Heavy rainfall that is associated with North East Monsoon during November to March every year promoting pollutants scouring effect, hence O\textsubscript{3} and NO\textsubscript{x} concentrations during the periods is significantly lower than the rest of the year.

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