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The Kinetic Approach of NO_x Photoreaction Related to Ground Measurement of Solar Radiation in Estimates of Surface Ozone Concentration

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Abstract : Surface ozone is a secondary pollutant produced by the collision of oxygen molecules with *oxy*-radicals as a result of the photoreaction of nitrogen oxide. Excessive levels of this pollutant cause negative impacts on the environment. Moreover, understanding the formation kinetics and precursors are important for air quality management. This study aims to determine the surface ozone reaction kinetics of formation phase dominant factors (NO_x precursors and influx radiation) in urban areas. These kinetics are based on the recorded measurements of global radiation, remaining NO_x and ozone concentration at ground level from air quality monitoring. These data are then categorised for rainy and dry seasons. Each data category was analysed according to daily pattern and daily maximum value. The relationship and kinetic constants of concerned parameters were determined. The ozone concentration is proportional by factor *k* to the influx radiation and conversely to the remaining nitrogen dioxide in the first-order photoreaction. This relationship is linear with R^2 greater than 0.9 during both rainy and dry seasons. The value of kinetic constant *k* is equal to 1.1044 for rainy seasons and to 0.8416 for dry seasons. It shows the factor of influx radiation and remaining [NO_x] in an atmosphere with a dominant rainy as compared to dry season.
Keywords: Air quality, Photochemical kinetics, Atmospheric oxidation, Influx radiation, Urban.

Introduction

Regardless of the importance of other aspects in an urban environment, air pollution is one of the most common problems faced by major cities in developing countries. This problem stems from the fact that many standard parameters measuring the concentrations of air pollutants are frequently violated, such as ozone (O_3), nitrogen dioxide (NO_2), sulphur dioxide (SO_2), and dust[1]. Increasing air pollutant levels can affect the shift toward radiation equilibrium and particulate stability, with effects on radiative properties[2] and environmental health. High ozone concentration in the surface atmosphere is injurious to life and plants, materials, as well as serious consequences of the health of the human respiratory system, mainly when ambient concentrations are over acceptable levels[3].

Surface zone is not directly emitted from sources because it is a secondary air pollutant. This pollutant results from the oxidation of organic compounds (e.g., methane and other volatile organics) and nitrogen oxides (NOx) in the presence of photon radiation[4]. During daylight, the photon energy is used by nitrogen dioxide

molecules (NO_2) to initiate radical nitric oxide (NO) and *oxy*-radical (O). This *oxy*-radical thus combines with oxygen (O_2) to form ozone (O_3)[5].

Concentration of ozone may accumulate in atmosphere as result of formation, transport, destruction, and deposition[6]. Resources of ozone formation are the photochemical reaction from its precursors, which is distributed throughout the stratosphere, and transport from any distant source[7]. This may vary in time and space due to their moving in transport and dispersion pattern follow the wind direction and speed[8]. In contrast, ozone is eliminated from the surface by photochemical and removal processes[9]. This indicates that surface ozone is closely influenced by an influx of local radiation.

Recently, de Souza develop an artificial neural network (ANN) method to estimate the level concentration of surface ozone by season of climate data[10]. Other researchers have found that the ozone concentration is altered according to nitrogen oxide's characteristics, solar radiation, the direction of wind from potential sources[11], and changing climate patterns, mainly related to extreme temperatures during the summer season[12]. The surface ozone concentration varies, with a maximum value at around mid-day and a minimum in the morning[3]. This study is an urban air quality data analysis, especially for the kinetic of surface ozone due to its precursor availability and influx of measured solar radiation. The intention of this study is to develop the kinetic constants of surface ozone patterns in urban areas as related to the radiative cycle and NO_2 as its precursor.

Materials and Methods

The estimation of surface ozone concentration, related to measured global radiation (GRAD) and NO_2 concentration as its precursor in photoreaction, are approached by using: 1) the pattern that describes the concentration changes related to radiation intensity, in daily and monthly cycle during both rainy and dry seasons, 2) mathematical relationship of concerned parameters that is analysed in regression pattern or in the kinetic form of overall reaction that occurs. The entire analysis was conducted based on hourly data monitoring of urban air quality. The parameters studied are expressed as ozone concentration ($\mu g.m^{-3}$), NO_2 concentration ($\mu g.^{m-3}$), and global radiation ($watt.^{m-2}$). All of approaching estimation are verified with data in tropical country monitoring (case of Surabaya, Indonesia at the latitude (λ) = - 7.23, longitude = 112.74, an average altitude is 5–10 m from the sea level and in year of 2010).

Moreover, all of the data are classified by rainy and dry seasons. For this purpose, the hourly data were selected by normality pattern from the data collected in January, February, and March for the rainy season and the data collected in June, July, and August for the dry season. The daily pattern and daily maximum value are analysed from both season categories. Furthermore, changes in ozone concentration and NO_2 as related to the GRAD are characterised from this pattern. These changes are then used to determine the mathematical relationship of concerned parameters and to approximate the kinetics involved. Result of this mathematic and kinetics expressions use to describe and estimate the surface ozone level change in time for known remaining NO_2 and GRAD data.

Results and Discussion

Photoreaction kinetics for the prediction of ozone formation

NO_2 is a primary pollutant emitted from its sources, mainly due to the fossil fuel consumption associated with urban activity, i.e. transportation, industry, and domestic. Any change of atmospheric NO_2 concentration is a consequence of such activity. In general, the industrial and domestic activities operate almost continuously, with uniform loads daily. Conversely, the transportation activities have specific cycle pattern. In assumption a constant load from the other sources, the NO_x and other pollutant concentration change in urban area are mainly due to transportation activities[13]. It can be estimate in proportion to the number of passenger car units (PCU) per time, vehicle emission factor, and fuel consumption[13, 14]. There are highest loads during peak times in morning and evening in every day[14]. According to this pattern, the increasing NO_2 concentration is in line with peak activity, mainly due to the transportation load, as shown in Fig 1.

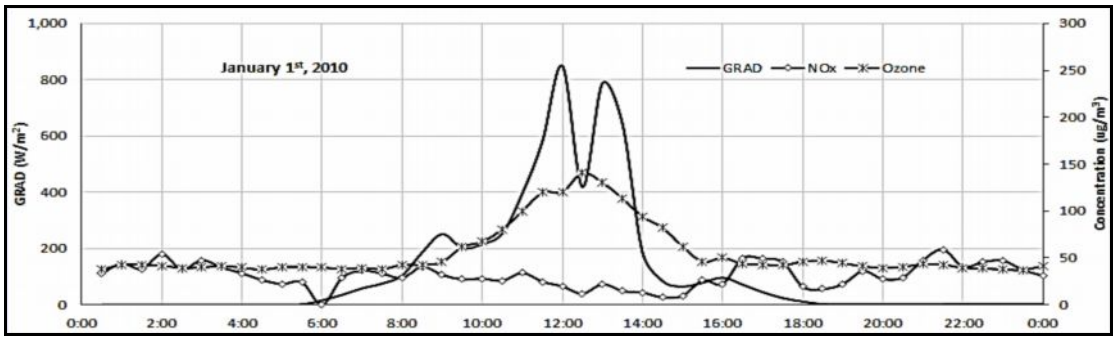

Figure 1. The resume data of surface ozone, NO_2, and GRAD (one cycle)

During the daylight, NO_2 concentration decreases as influx solar radiation increases, and more surface ozone is formed by photoreaction. It is reasonably obvious because NO_2 is a precursor in the formation of ozone as part of the surface photoreaction. When the radiation intensity is sufficient to initiate radical reaction, the photoreaction starting immediately for NO_2 to produce NO and O radicals. This process is faster as the intensity is greater, ready for midday. Consequently, the concentration of NO_2 will decrease as NO molecules increase. This is an initiation process of the radical photoreaction.

$$NO_2 \; | \; h\nu \; \rangle \; NO \; | \; O \qquad 1$$

The next process is simultaneous: the O radicals react with free O_2 molecules in the atmosphere to produce ozone molecules. This is a propagation process. More O radicals are formed in the initiation process; more ozone is produced in this reaction. However, the ozone formed may split to O_2 and O again. This latter reaction has a slower reversal rate than the rate of its initial formation.

$$O + O_2 \longrightarrow O_3 \qquad 2$$

$$O_3 \longrightarrow O_2 + O \qquad 3$$

In line with the decreasing of solar intensity (after 12.30 pm, see Fig 1.) the reaction 1 is slowing down, yield slower propagation process. In this reaction, due to the accumulation of ozone has been high, the reverse reaction (ozone depletion process) occurs more quickly. The evidence for this assertion comprises reduced concentrations of ozone and the rise of NO_2 concentrations again. Ozone that has been depleted into O_2 and O can re-join NO to reform NO_2. This process is called a termination.

$$O \; | \; NO \; \rangle \; NO_2 \qquad 4$$

All of the above reactions may be divided in two categories, namely, the reactions of ozone formation and the reactions of ozone depletion. Furthermore, it was analysed from surface ozone cycle, its concentration changes in cycle with three dominant phases. Phase 1 is an increasing or formation phase up to maximum level; Phase 2 is a decreasing or destruction phase up to minimum level; Phase 3 is a steady phase at minimum level with no photoreaction. These phases are illustrated simpler in Fig. 2. The variation of ozone concentration strongly depend on the influx radiation and precursor that are present (i.e., NO_2).

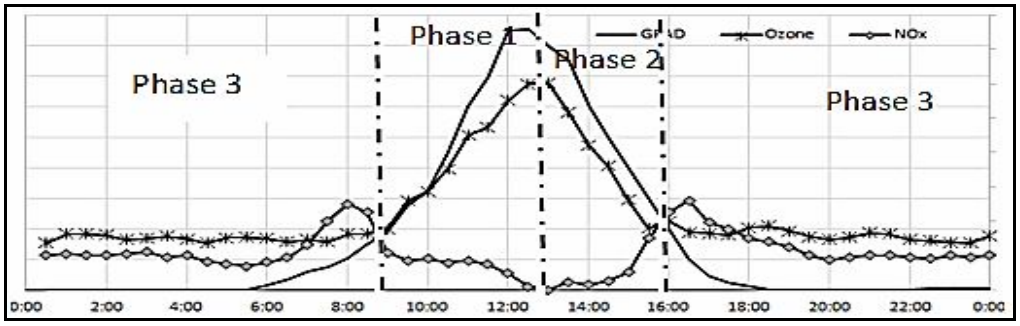

Figure 2. Simplification phase description of one daily surface ozone cycle

In environmental concern, the reaction of ozone formation is more interest in pollutant management. This reaction will give information on how to decrease it. To achieve that goal, a deeper analysis of the kinetics will be needed. In any simplification reason, some environmental phenomena can be conducted in mathematical model[15].

Below is a simplification of the reaction kinetics based on all reactions presented previously. Mechanism of formation can be written from reaction 1 and reaction 2. The kinetics for those reactions can be written as follows:

$$\frac{d[O]}{dt} = k_1[NO_2]hv \quad k_2[O][O_2] \qquad \text{Eq.1}$$

$$\frac{d[O_x]}{dt} - k_2[O][O_2] \qquad \text{Eq.2}$$

Radiation intensity is varies during the formation reaction, and useful to include it parameter as a variable in calculation as the assumed reactants. For steady state, the change in [O] is zero. The rearrangement of Eq. (1) yields:

$$k_1[NO_2]hv - k_2[O][O_2] - 0 \qquad \text{Eq.3}$$

$$[O] = \frac{k_1[NO_2]hv}{k_2[O_2]} \qquad \text{Eq.4}$$

By substituting Eq. (4) into Eq. (2) we obtain the first order reaction:

$$\frac{d[O_3]}{dt} = k_2 \frac{k_1[NO_2]hv}{k_2[O_2]}[O_2] = k_1[NO_2]hv \qquad \text{Eq.5}$$

From Eq. (5), it appears that the formation of photochemical reactions is only influenced by the initial concentration of NO_2 and radiation intensity. By solving the last equation, we get the relationship $[O_3]$ with $[NO_2]$ and *hv*, such as the following:

$$\int d[O_3] = k_1[NO_2]hv \int dt \qquad \text{Eq.6}$$

$$[O_3]_t - [O_3]_0 + k_1[NO_2]hv.t \qquad \text{Eq.7}$$

Eq. (7) specifically applies in the reactor, where there are no external changes during the reaction in terms of the reactants and the intensity of the radiation. Value of $[NO_2]$ in the last equation is a initial $[NO_2]$. It must be converted to the remaining $[NO_2]$. In that reaction system, the initial $[NO_2]$ is conversely related to the remaining $[NO_2]$ using this formula:

$$[NO_2] = \frac{k_i}{[NO_x]_r} \qquad \text{Eq.8}$$

In regards with natural reaction system in urban atmosphere, the reaction occurs with varied reactants and intensity, therefore we use the Eq. (8) and assume $[O_3]_0 - 0$, and thus the Eq. (7) should be modified to be:

$$[O_3]_t = [O_3]_0 \mid k_1 k_i \frac{hv_t}{[NO_x]_r} = k \frac{hv_t}{[NO_x]_r} \qquad \text{Eq.9}$$

The reaction is assumed to be independent from the set reaction, the earlier or the later (no accumulation), with *k* as the overall reaction constant. In that equation, *hv* is expressed by the measured GRAD.

Profile of the surface ozone and application of the kinetics

Based on the data presented in Fig. 1, the surface ozone concentration varies according to the daily cycle pattern. Right after sunrise, the ozone concentration increases progressively because of the photoreactions in the presence of an influx of solar radiation. The maximum concentration of ozone occurred roughly on mid-day which corresponds to the maximum of solar radiation influxes. Later, the decrease in ozone concentration was recorded until the minimum level at sunset. This minimum concentration occurred throughout the night until sunrise the next day.

For case of this study, based on recapitulation of analysed data (see Fig. 1 and Fig. 2), the ozone daily cycle phases describes as below:

1. Phase 1 (the surface ozone formation phase) begins at around 08:30 local time and continues up to around mid-day (12:30 or 13:00 local time). During this phase, the surface ozone concentration rises up from about 30–40 $\mu g.m^{-3}$ to the average maximum value, which is about 110 $\mu g.m^{-3}$ during the rainy season and about 90 $\mu g.m^{-3}$ during the dry season.
2. Phase 2 or surface ozone destruction phase occurs after mid-day until around 16:00 or 17:00 local time. During this phase, the concentration of ozone decreases to a minimum level at 30–40 $\mu g.m^{-3}$.
3. Phase 3 or steady phase in minimum level ozone occurs in the night time until sunrise the next day. During this phase, the concentration is relatively constant at the minimum level.

In seasonal analysis, the level of surface ozone appears to have no big difference for rainy and dry season. Average maximum concentration during the rainy season is about 108 $\mu g.m^{-3}$; during the dry season, the concentration is 96 $\mu g.m^{-3}$, as shown in Fig. 3.

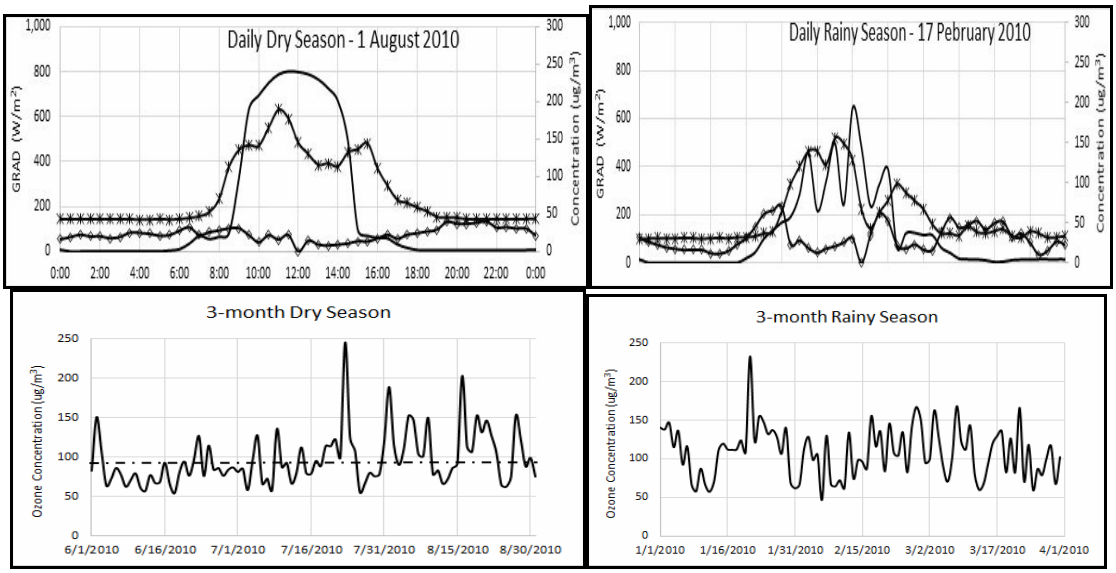

Figure 3. The profile of GRAD, NO_2, surface ozone (up) and average of maximum seasonal ozone concentration (down) in dry and rainy season

The average maximum concentration of surface ozone during the rainy season is higher because the influx of solar intensity is higher during this season. During January–March (rainy), GRAD value is higher than in June–August (dry), as seen in Fig. 4, with relatively same atmospheric clearness indexes (*CI*). So, the photoreaction in rainy season is higher than in dry season. The *CI* value can be interpreted as daily pollutant accumulation during minimum cloud covering[16].

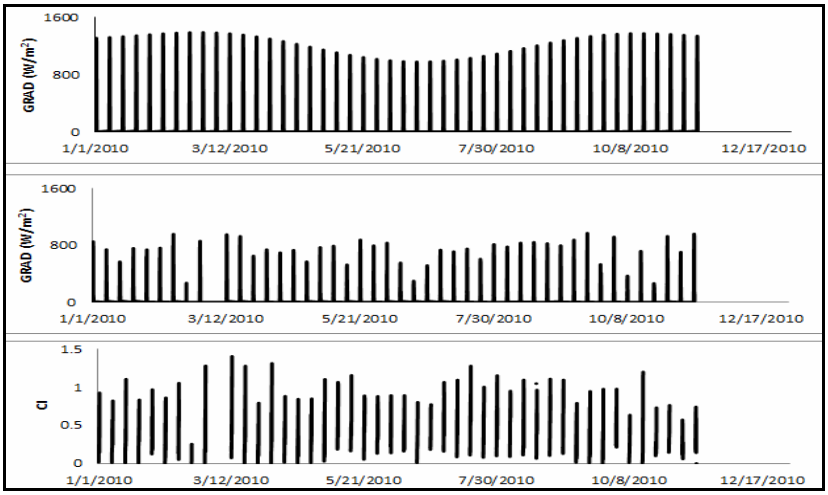

Figure 4. Estimated solar influx radiation (top), data observation (middle) and atmosphere clearness index (bottom) in Surabaya 2010[16]

The other interesting fact is the NO_2 pattern. Observed data shows the changes of NO_2 value differ with surface ozone pattern in daily cycle. It shows at ending and beginning of phase 3, the concentration of NO_2 is the highest and at transition phase 1 to phase 2 the concentration of NO_2 is lowest. It is contrary with surface ozone pattern. In overall, the pattern of ozone, NO_2 and GRAD based on the maximum data analysed is shown in Fig. 5. This figure shows the complexity of the relationship among parameters, which necessitates the use of kinetic theory for analysis approaches.

For surface ozone formation (phase 1) analysis, applying Eq. (9) for two seasonal average recorded data yielded the good confidence. Result of that application is presented below. First, all of the data (presented in Fig. 5) were analysed to yield the average value of each parameter in both seasons. Then the value of $h\nu/[NO_2]$ is calculated from them. This average value is shown in Table 1.

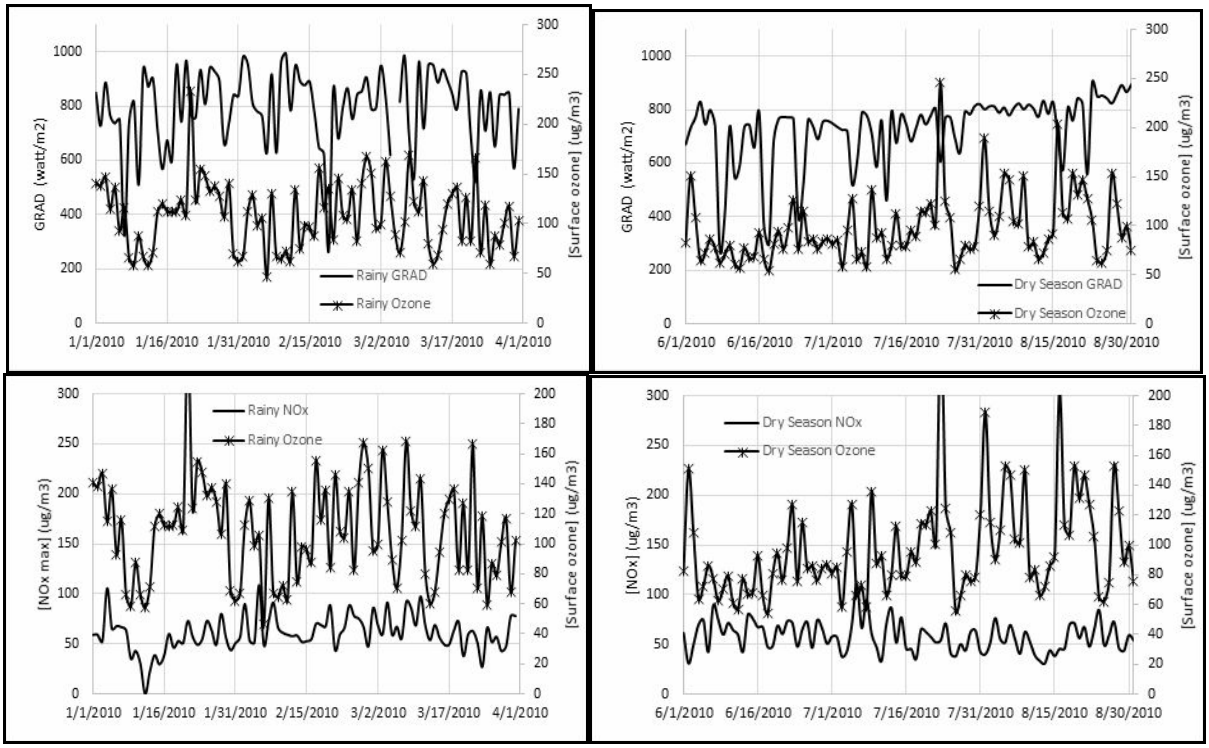

Figure 5. The pattern of ozone, NO_2, and GRAD in maximum data

Table 1. The average seasonal GRAD, remained NO_2, and O_3 formed in formation phase

time	3 month Drought Seasonal (Jun – Aug. 2010)				3 month Rainy Seasonal (Jan -Mar 2010)			
	GRAD (watt/m^2)	$[NO_2]_r$ (µg/m^3)	$[O_3]$ formed (µg/m^3)	$\frac{h\nu}{[NO_2]}$	GRAD (watt/m^2)	$[NO_2]_r$ (µg/m^3)	$[O_3]$ formed (µg/m^3)	$\frac{h\nu}{[NO_2]}$
8:00	101.6	42.6	45.8	2.4	209.8	36.9	50.4	5.7
8:30	127.6	33.2	53.6	3.8	320.8	29.7	58.1	10.8
9:00	292.8	25.3	63.0	11.6	404.1	23.0	65.4	17.6
9:30	450.2	20.1	72.0	22.4	504.4	19.3	73.0	26.2
10:00	502.1	16.3	78.3	30.7	549.2	17.4	80.0	31.6
10:30	555.9	15.1	81.9	36.9	536.9	16.6	84.3	32.4
11:00	603.2	14.0	83.4	43.0	605.4	16.2	83.7	37.3
11:30	606.0	13.6	84.8	44.6	559.7	16.0	84.5	35.0
12:00	632.3	13.4	85.4	47.1	571.0	15.7	85.0	36.3
12:30	628.4	12.2	84.1	51.6	506.3	15.0	82.4	33.8

According to Eq. (9), the parameters $[O_3]_t$ and $\frac{h\nu_t}{[NO_x]_T}$ produce linear association with *k* as slope (overall kinetic constant). Using the data presented in Table 1 for graphical analysis and linear regression, we obtained a good linear relationship for both parameters, as seen in Fig. 6.

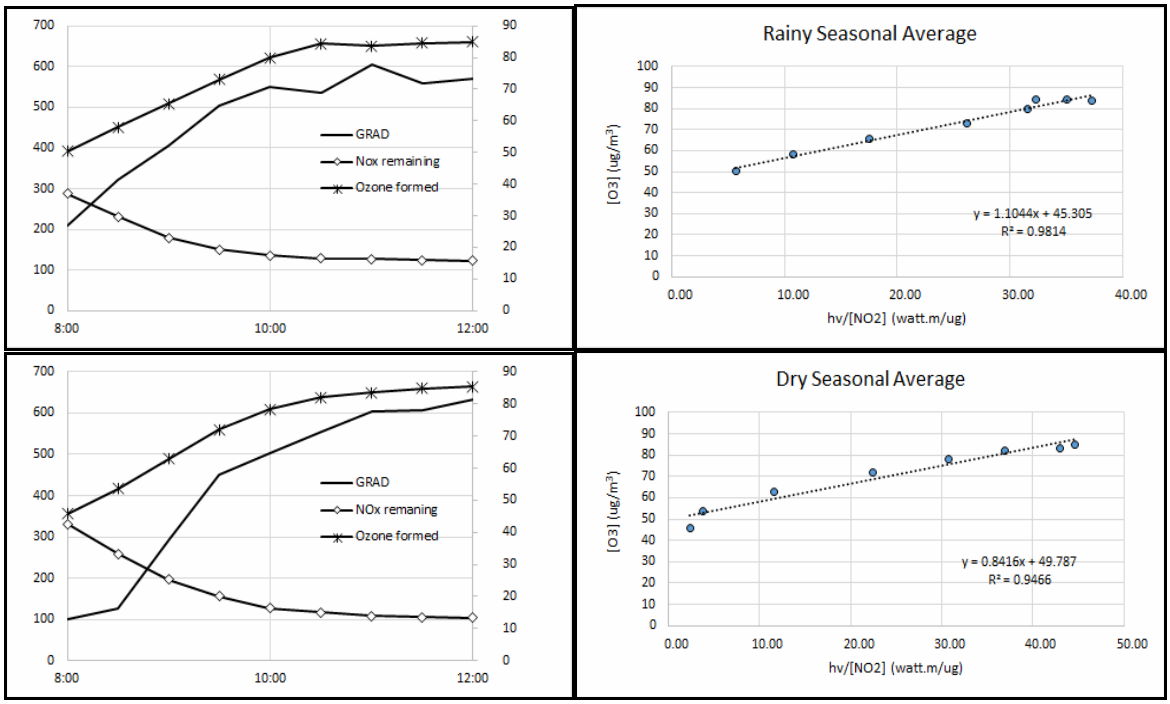

Figure 6. Trend of averages GRAD, NOx, ozone and $[O_3]$ - $\frac{h\nu_t}{[NO_x]_T}$ regression in rainy season (top) and dry season (bottom)

It relationship is described in linear regression with $R^2 > 0.9$ on both rainy and dry seasons. The value of kinetic constant *k* is equal to 1.1044 for rainy, and 0.8416 in µg^{2}m^{-1} unit for dry season as see in Fig. 6. Slope *k* for rainy season is greater than in dry season. It means that the factor of $\frac{h\nu_t}{[NO_x]_T}$ is more dominant in rainy season than in dry season.

Conclusion

The characterisation of surface ozone concentration, yielded a pattern of ozone concentration changes influenced by the remaining [NO_2] and the influx of solar radiation. This pattern also describes formation, depletion, and steady phase as dominant phase in surface ozone daily cycle. In seasonal analysis, it is shown that the surface ozone concentration in rainy is higher than its concentration in dry season. The mathematical relationship and kinetics analysis of the parameters involved have produced a linear equation with which to estimate ozone concentration using GRAD and remaining NO_2 data. The relationship is described in linear regression with $R^2 > 0.9$ on both rainy and dry seasons. The value of slope *k* for rainy season is greater than in dry season, meaning that the factor of $\frac{h\nu_r}{[NO_2]_r}$ is more dominant in rainy season as compared with in dry season.

Acknowledgements

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