CHARACTERISTICS OF THE INTERACTIONS PATTERN OF SURFACE OZONE WITH ITS PRECURSORS IN MIE PREFECTURE OF JAPAN

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ABSTRACT

Surface ozone is a major cause of concern on urban air quality for the Mie Prefecture of Japan both in terms of annual ozone exceedance days and the potential effect on human and plant health. To characterize the interaction patterns between surface ozone and its precursors (nitrogen oxide and hydro carbon compounds (VOC)) has been statistically analyzed for four selected monitoring sites of different land habitats namely coastal-industrial (Yokkaichi), inland urban (Matsusaka), mountain-base urban (Nabari), and coastal resort city (Toba). Hourly raw ambient data on air criteria pollutants (1991-2001) of Air Quality Authority of Mie Prefecture were used to investigate the relationships of ozone with NO, NO_2, NOx, NO_2/NO and NMHC/NO_x and to determine the proportionate contribution of the precursors.

Despite relatively low concentrations of NO_x and NMHC, coastal sites experience relatively high ozone level than the inland urban sites indicating possible meteorological effects on the ozone movements and differences in ozone deposition rates. Both NO and NO_2 influences similarly on ozone process in all sites while significant influence of NMHC were found in the inland sites only. NO_2/NO ratio plays significant influence on ozone level of the inland sites particularly in the winter while the influence of NMHC/NO_x was insignificant in all sites indicating domination of NOx in ozone formation. Seasonal variations in interaction patterns show stronger relationships between ozone and precursors in the winter and weaker relationships in the summer indicating the possible meteorological effects.

Key word: Surface ozone, Ozone precursors (NO_x and NMHC), Interaction Patterns, Urban pollution, NO_2/NO ratio

1.0 INTRODUCTION

Surface level ozone is a cause of concern in East Asia including Japan as the trend of annual mean level of ozone as well as the ozone exceedance days are increasing over the past decade [1]. Surface level ozone formation is a complex process that are contributed, under favorable photochemical conditions, by the nitrogen oxide (NO_x) and volatile organic compounds (VOC) emitted from traffic vehicle, industrial activities, and household combustions (Health Canada, 2002; Lu and Wang, 2003). Studies show that intensity of ozone production depends on the availability of NO_2 and the favorable photochemical conditions. Availability of NO_2 again depends on the rate of transformation of NO_x and volatile organic compounds (VOC's) (Coopers, 2000). Ratio of NO_2 and NO plays a vital role in stabilizing the ozone level through production as well as destruction process [1,2,3] Saito et al. (2002) found that ozone production level could be related to the ratio of NO_x and non-methane hydrocarbon compound (NMHC) as NMHC could contribute in converting NO into NO_2 without consuming O_3. Cooper and Alley (2002) preferred to use NMHC as it contains the most reactive components of VOCs while methane component remains almost inert. The ratio of NO_2/NO at a certain location can be considered as an indicator of the potential of ozone production. Higher ratio of NO_2/NO indicates higher level of ozone production and low ratio indicates the higher potential for ozone destruction by NO. On the other hand, ratio of NMHC and NOx can influence the interaction patterns of ozone production process and could be used as indicator to control peak ozone level at a certain location [4].

This study aim to investigate the interaction patterns of ozone with its precursors through analyzing the pattern of NO_2/NO, NMHC/NO_x level, and correlations of ozone with its precursors.

2.0 STUDY METHODS

2.1 Description of the Areas under Study

Mie Prefecture is situated roughly in the middle of Japanese island chains with a population of about 1.9 million and land coverage of 5775 Sq. kilometer [5]. Northwestern part of the prefecture is covered with a mountain range whereas the south-eastern part is bounded by the Ise Bay as shown in the Figure 1. Major cities of the Mie prefecture could be divided based on several land habitat types namely Coastal-industrial: Yokkaichi, Suzuka, Tsu; Coastal: Toba, Owase; Inland urban: Matsusaka, Kameyama; Mountain-base urban: Nabari etc. Since the emissions of ozone precursors like NO_x (i.e. NO + NO_2) and VOC's (Methan and non-methane) depends on the industrial activities and traffic volume, we have chosen one city from each of the mentioned land habitat categories for investigation.

2.2 Physical and Chemical Transformation between Ozone and Precursors

Chemistry of ground level ozone goes through a complex process of production and destruction cycle. NO_2 is the compound responsible for the ozone formation by photo-dissociative process in the presence of sunlight where both nitric oxide (NO) and VOC contributes to NO_2 formations. Following chemical reactions are believed to be occurred in the process [2,3,4]:

(i) Motor vehicle and other combustions emits nitric oxide (NO)
(ii) $NO + O_3 \longrightarrow NO_2 + O\cdot$ ....R_1
(iii) NO_2 + Sunlight absorption ($h\upsilon$) ($\lambda < 4300$ Å) $\longrightarrow NO + O\cdot$ .... R_2
(iv) $O_2 (+M) + O\cdot \longrightarrow O_3 (+M)$ ....R_3

As the cycle of reactions (R_1 to R_3) continues, amount of ozone formation depends on the ratio of NO_2 and NO in the air and also on the availability of these two compounds. Volatile Organic Compound (VOC) contributes in the recycle of NO_2 required for ozone.

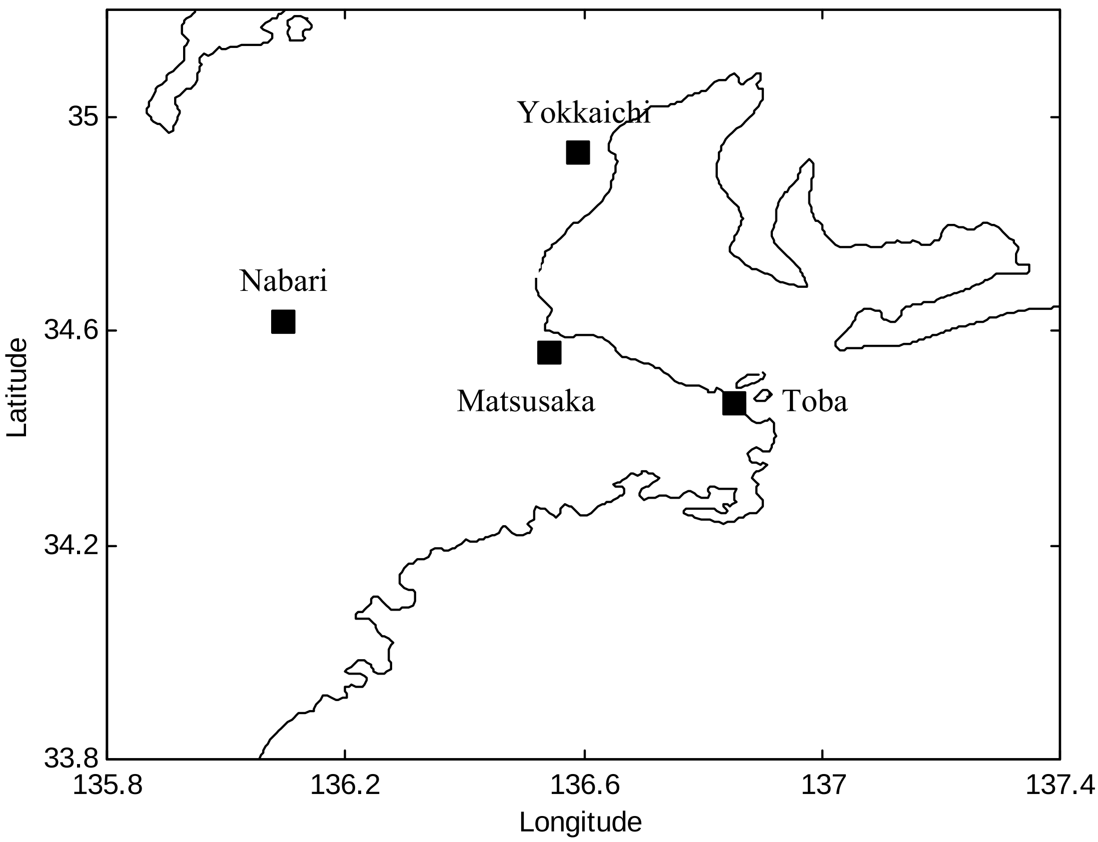


Figure 1: Maps showing Mie prefecture and the Approximate Locations of the Selected Monitoring Sites

(v) VOCs emitted from anthropogenic and biogenic sources reacts with hydroxyl radicals (HO•) undergoes following reaction process as below:

(vi) $RH + OH\cdot \longrightarrow R\cdot + H_2O$ …………………………………….. R_4

(vii) $R\cdot + O_2 (+M) \longrightarrow ROO\cdot + M$ …………… ………………………R_5

(viii) $ROO\cdot + NO \longrightarrow RO\cdot + NO_2$ ………………………………..R_6

(ix) $RO\cdot + O_2 (+M) \longrightarrow RCHO + HO_2\cdot$ ………………………...R_7

(x) $HO_2\cdot + NO \longrightarrow NO_2 + HO\cdot$ ……………………………….…R_8

As shown in the above reactions (R_4 to R_8), one VOC molecule could contribute two molecules of NO_2 upon availability of hydroxyl ions which may be found in the polluted atmosphere. While variations in the ratio of NO_2 and NO effects the stability in ozone level, variations in the ratio of VOC and NO_x could have influence on the quantity of ozone level.

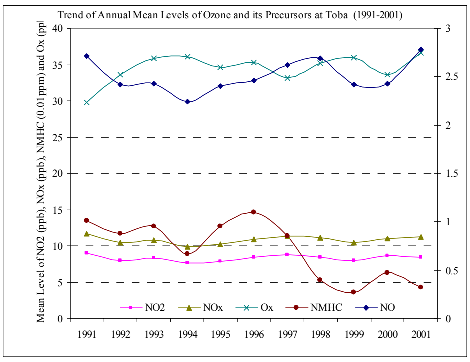
2.3 Data Gathering and Analysis

Air quality authority of Mie Prefecture, Japan was the source of all data provided as diurnal mean concentration. We received ambient data on all the criteria air pollutants including NO, NO_2, NO_x, CH_4, NMHC, THC, oxidant (Ox). Oxidant contains mainly ozone (95%) [1] and hence synonymously used the term O_3 instead of O_x. We have chosen data between the periods of 1991-2001. The raw data has been further analyzed statistically to derive aggregated diurnal, monthly, seasonal and annual values. Linear regression analysis of the aggregated values was done for interactive characteristics analysis between Ozone and NO_x and VOC's (mainly NMHC).

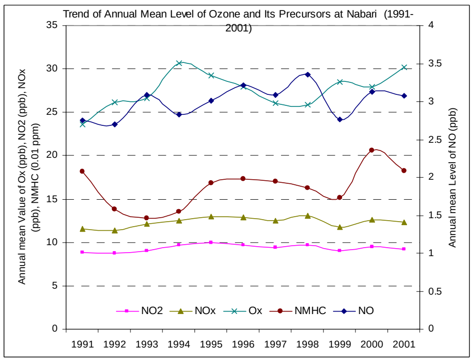
3.0 RESULTS AND DISCUSSION

3.1 Temporal Pattern of Ozone and its Precursors

Annual mean values of ozone and precursors pollutants have been plotted for the period of 1991-2001 to examine the pollution trend as shown in the Figure 2. Results show that amongst the selected sites, highest level of ozone and lowest level of NO, NO_2, NO_x, and NMHC existed in the coastal city of Toba. While lower level of ozone but highest level of precursors was found at the coastal-industrial city of Yokkaichi where industrial emissions contributes to the added level of precursors. Ozone and its precursors levels at the mountain-base urban town of Nabari follows the levels found at Toba. In the inland urban town of Matsusaka ozone level lies between the levels found at Toba and Nabari. Despite the decreasing trend in NOx and NMHC, ozone level has been found in increasing trend at both the coastal sites of Toba and Yokkaichi. While at Nabari and Matsusaka, both ozone and precursors levels were in increasing trend.



(a) Toba



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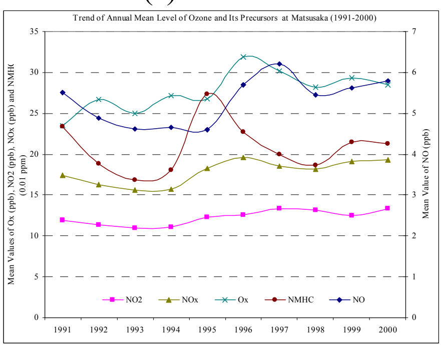
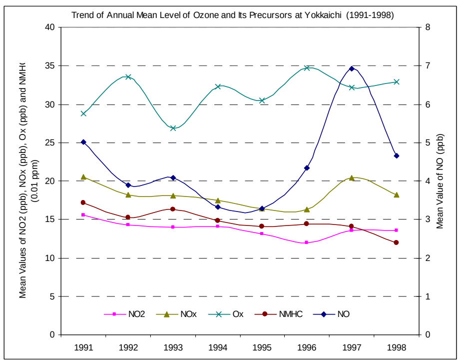


(b)Matsusaka



(d) Yokkaichi

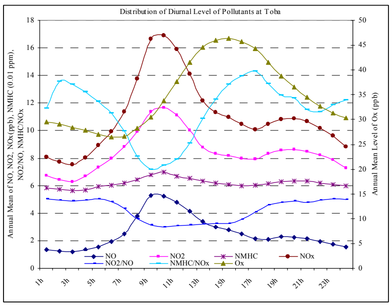
Figure 2: Trend of Annual Mean Level of Ozone and Its Precursors at Selected Stations for the period of 1991-2001

3.2 Interaction Patterns of Ozone and its Precursors

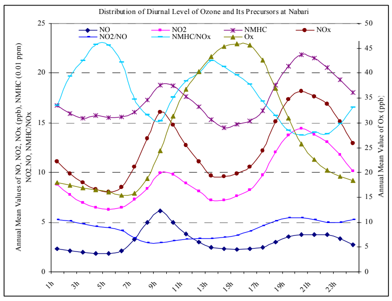
3.2.1 Diurnal Variations in Ozone and Precursors

Figure 3 shows the typical pattern of diurnal variations of ozone and precursors at the different land habitat sites. As regards to ozone level, an increase in day time and decrease in night were observed in all the sites of different land habitat types. Peak level of ozone also appeared almost at the same time of the day (15.00 hr) in all sites implying that ozone peak level reached due to local photochemical processes. However, decreasing rate of ozone level in the coastal site is lower than that of the inland sites. Peak level of NO, NO_2, NO_x and NMHC were found both in the morning and late afternoon contributed mainly by the traffic rush hours. However, at the Matsusaka and Nabari sites, distinct afternoon lean and late afternoon peak level for precursors were found at about 15:00 hr and 21:00 hrs respectively while such distinct patterns were not occurred at coastal sites like Toba and Yokkaichi. Peak level of NO was observed during the morning traffic rush hour at 09:00 hr while two NO_2 peaks were found both at the morning and afternoon traffic rush hours. Generally morning peak level of NO_2 occurred about 1 hr after the NO peak level and ozone peak level occurred about 3 hours after the NO_2 peak. This phenomenon (i.e. NO -> NO_2 -> Ox) was true for all the sites.

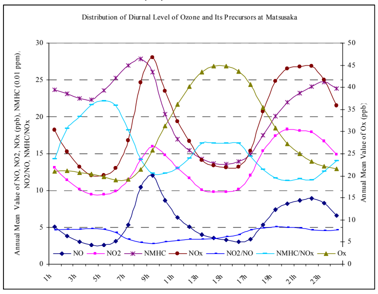
Diurnal variations of the ratio of NO_2 & NO follow a distinct pattern during the whole day and also show a relationship with the ozone variations. NO_2/NO ratio reaches at the minimum level during the morning traffic rush when maximum level of NO emitted from the traffic and photochemical process begins. However, the value of the ratio starts increasing along with the consumption of NO_2 due to its photochemical conversion into oxidants (O_x) as well as simultaneously less emission of NO from the traffic lean period (11:00 to 17:00 hr) of the day. As the ozone production level starts decreasing after the late afternoon, NO_2 level starts building up and the ratio reaches to the peak level at the late night (21:00 hr) and continue at that level till 06:00 hr considered to be due to two reasons: (a) emission of NO from the evening traffic rush and other industrial sources; (b) emitted NO undergoes through the catalytic reaction process (in the polluted atmosphere) with the already produced ozone to convert it again into NO_2. Similar to the NO_2/ NO, level of NMHC/NO_x also follows a distinct diurnal pattern and shows relationship with the level of ozone. Peak ozone level and the peak NMHC/NO_x ratio found to occur at the same time (about 15:00 hr) in both the coastal sites but in the other inland urban sites, second peak ratio was also found to occur early in the morning. Generally, ozone differential level could be positively related with the ratio of NMHC/ NO_x levels. However, the relative level of NMHC and NO_x differs according to the land habitat of the sites. Coastal sites particularly in Toba level of both NMHC and NOx are lower (maximum of diurnal mean: 70.0 and 16.90 ppb respectively) than that of the inland urban sites of Matsusaka (278.80 and 28.04 ppb respectively) and Nabari (219.0 and 18.21 ppb respectively). On the other hand, Yokkaichi, despite its location in the coast, shows relatively higher level of NO_x and NMHC contributed by the industrial emission in addition to the traffic.



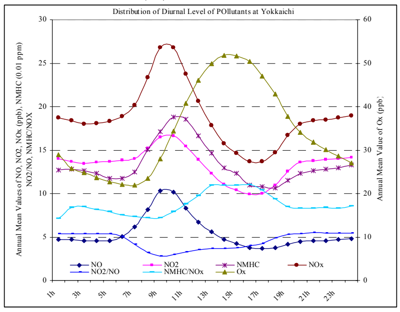
(a) Toba



(b) Nabari



(c) Matsusaka

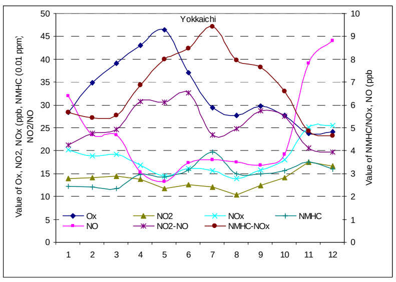


(d) Yokkaichi

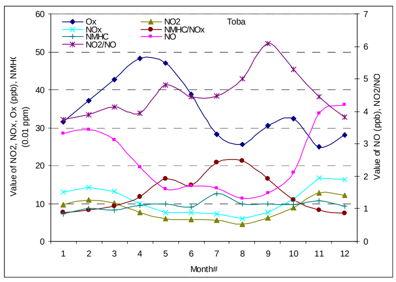
Figure 3: Diurnal Pattern of Annually Averaged Diurnal Level of Ozone and Its Precursors

3.2.2 Seasonal Variations in Ozone and Precursors

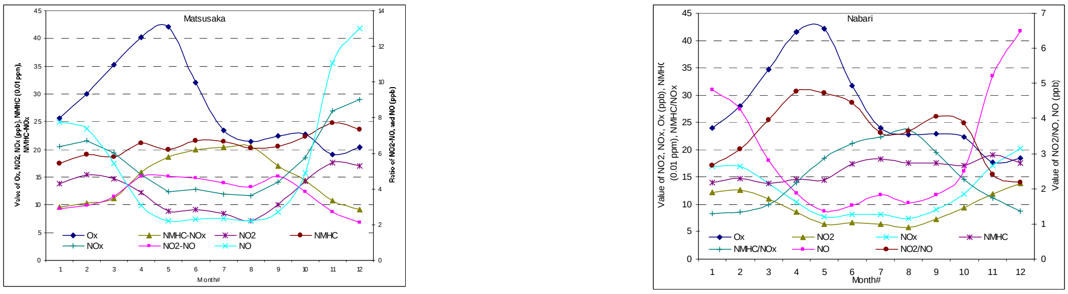
There are distinct seasonal variations in the interaction pattern between ozone and precursors as well as between the precursors themselves. In general, stronger correlations exist between the parameters in the winter compared to the summer in all the sites although the degree of such relationships differs between the sites. In the summer, NMHC/ NO_x ratio is higher in all the sites while the ratio is decreased to less than 50% during the winter. Higher NO_2/NO ratio were observed in both coastal and inland urban sites during the spring season and lower in the winter considered due to higher level of NO emissions from traffic and heating system. Maximum ozone level was observed during the spring seasons irrespective of the sites and maximum median level of ozone was observed in the coastal sites of Toba and Yokkaichi indicating lower rate ozone depositions in the sea side compared to the inland sites. Higher ratio of NMHC/NO_x during the summer and spring indicates higher contribution of NMHC from biogenic and anthropogenic sources in ozone production process. Significant correlations between NMHC and temperature indicate that higher temperature in summer may cause higher level of NMHC.



(a) Yokkaichi



(c) Toba



(b) Matsusaka (d) Nabari

Figure 4: Month wise distribution of Aggregated Daily Mean Values of Ozone and Precursors (NO, NO_2, NO_x, NMHC), NO_2/NO, and NMHHC/NO_x. (a) Yokkaichi, (b) Matsusaka, (c) Toba (d) Nabari

3.2.3 Regressions Analysis for Characterizing the Interaction Patterns

Interaction patterns between ozone and precursors as well as between the precursors themselves have been analyzed through linear regression analysis. Following sections presents coefficient of determinations (R^2) of the regression analysis of the aggregate daily mean level of ozone and its precursors for the period of 1991-2001 and its seasonal variations:

3.2.3.1 Interaction between Ozone and its Precursors

As regards to the correlations between ozone and its precursors, it was found that both NO and NO_2 influences with similar intensity in the ozone production and destruction process in both coastal and non-coastal sites and strength of such relationship ranges between $0.13< R^2<0.25$ as also evidenced from smaller ratio between NO_2 and NO (<6.0) and its small variations in all the sites. However, correlations between ozone and NO_2/NO shows that in Nabari, more than 50% of the of Ozone level variations could be explained by the variations in NO_2/NO indicating relative contribution of both NO_2 and NO in interaction process while there was very little influence on ozone process by the variations in NO_2/NO.

3.2.3.2 Interaction Pattern amongst Ozone Precursors

Strong correlations were found in all the sites between NO_x and NO (R^2 > 0.75) and between NO_x and NO_2 (R^2 >0.70) indicating similar influence of both NO and NO_2 on ozone production or destruction cycle (Ref. equation R_1 to R_3). Significant correlations also exists between NO_x and NMHC with relatively stronger coefficient of determinations in coastal-industrial and inland urban sites (Yokkaichi:R^2=0.44, Matsusaka:R^2 =0.52, and Nabari: R^2=0.32) compared to coastal site (Toba:R^2=0.13). Relatively lower concentration of NMHC and its decreasing trend in Toba seems to be responsible for the weaker correlations. Stronger correlations between NO_2 and NO at Toba (R^2= 0.75) also supports the dominant contribution of traffic through NO emissions.

3.2.3.3 Seasonal Relationship in Interaction Pattern amongst Ozone Precursors

Regression analysis of the daily mean values (1991-2001) of nitrogen oxides and non-methane hydrogen compounds (NMHC) has been done based on the different seasons and for sites of different land habitat types. Figure 4 shows the regression results between NO_x and NMHC with best line-fit for the winter and summer seasons. Amongst the land habitat types, both inland urban site of Matsusaka (winter: R^2=0.79, summer: R^2=0.35) and mountain-base urban site of Nabari show higher coefficient of determinations (winter: R^2=0.80, summer: R^2=0.39) than the coastal site of Toba (winter: R^2=0.38; summer: R^2=0.08) and coastal–industrial site of Yokkaichi (winter: R^2=0.65; summer: R^2=0.38) sites. In coastal sites both NO_x and NMHC concentration level are relatively low compare to the urban sites. In the coastal industrial site of Yokkaichi, NMHC level is generally low although NO_x level is high indicating the higher level of NO emissions from the industry and traffic of the area.

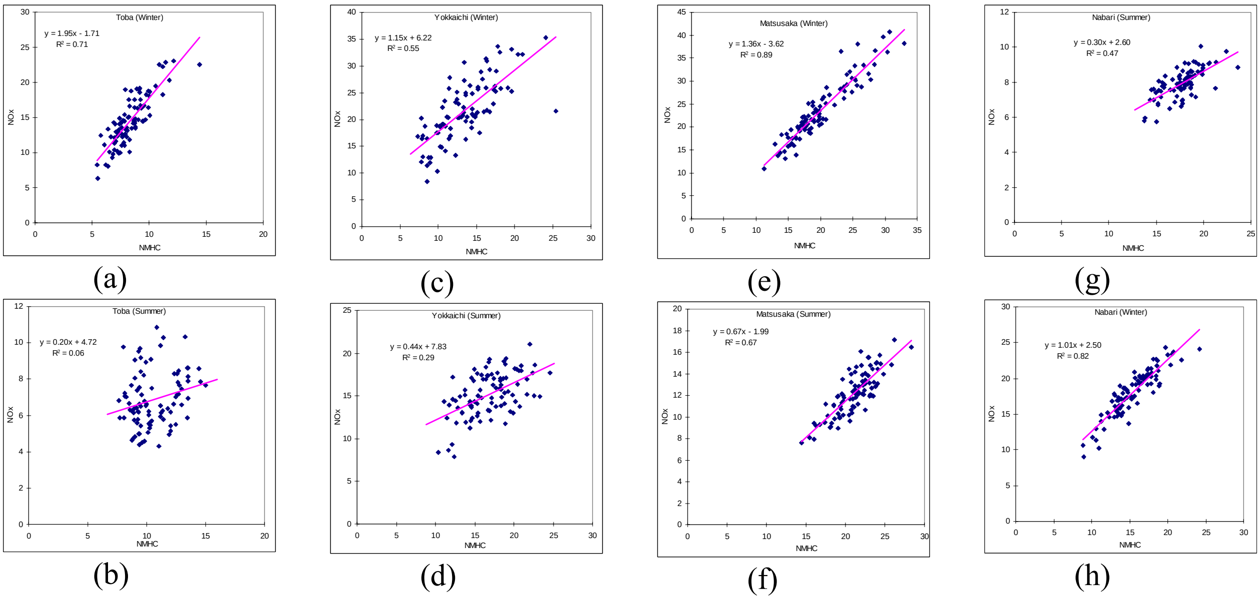


Figure 4: Regression Coefficients of Daily Averaged Data on NO_x, (ppb) and NMHC (0.01 ppm). (a)-(b): Coastal site-Toba, (c) & (d): Coastal-industrial site – Yokkaichi, (e) & (f): Inland urban site – Matsusaka, and (g) & (h): Mountain-base urban site – Nabari.

Regression coefficients between NOx and NO show significantly strong relationships in the coastal sites with slight variations in different seasons (R^2 >0.60) indicating that dominant sources of NO remains same all over the year. Significant relationship also exists in other two inland urban sites of Matsusaka and Nabari but there is a distinct variation in such relationship between different seasons: higher coefficient of determination (R^2 >0.60) in winter implying relative increase or decrease of both NO_2 and NO levels and lower coefficients in the summer (R^2 < 0.30) indicating disproportionate variations in the NO_x components perhaps due to NMHC contributions (Eqn. R_4 to R_8) as supported by relatively high correlations between NO_x and NMHC in the inland sites.

3.2.3.4 Seasonal Relationship in Interaction Pattern between Ozone and Precursors

As shown in the Figure 5, stronger correlations (winter: R^2>0.60 and summer: R^2 <0.50) between Ox and NO_2/NO were observed in the inland urban sites that indicates proportional contribution of both NO_2 and NO in ozone production as well as destruction process. While coastal sites experiences weaker correlations (R^2<0.26) which indicate the effects of meteorological factors in the ozone level in addition to the precursors. However, small ratio of NO_2/NO in all the sites (median range 2.45 to 5.0) indicates the similar dominant sources of precursors (e.g. traffic emissions).

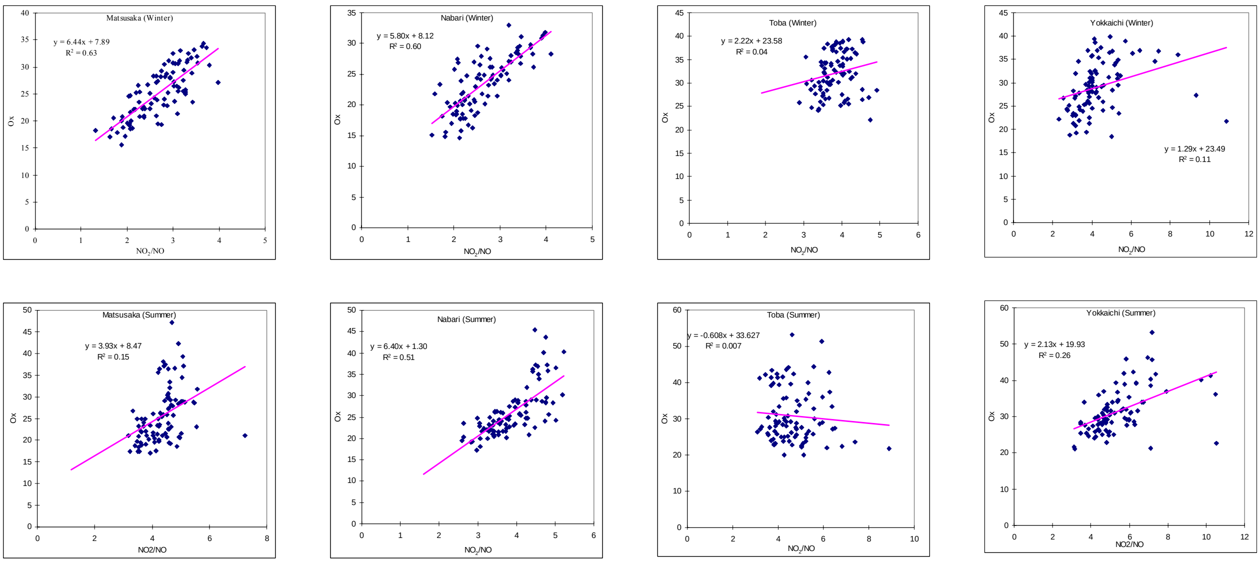


Figure 5: Seasonal Variations in Regression Coefficients of Daily Averaged Data on Ozone and NO_2/NO

3.2.3.5 Overall Interaction between Ozone and Precursors

Overall interaction pattern of ozone with different ozone precursors has been analyzed through linear regression analysis to investigate the significant precursors contributing to the ozone level according to the land habitats and seasonal variations. Results show that ozone precursors contributes relatively more strongly in winter (R^2 >0.50) compared to the summer (R^2 <0.30). Ozone level in the inland urban sites, are more influenced by the variations of NO_2 /NO, and NMHC/NO_x compare to the coastal sites. Influence of NMHC on the ozone level is dominant in Masusaka particularly in winter, spring and autumn. In the summer, there was negligible influence of NMHC on the ozone variations in all the sites. Relatively low wind speed and scattered wind directions in the region may reduce the influence of NMHCs [6]. In the coastal-industrial site of Yokkaichi, there was significant influence of NMHC and NMHC/NOx in all the seasons but ratio of NO_2 and NO influences during the summer and autumn.

4.0 CONCLUSION

Characteristics of interaction pattern of ozone (O_x) and precursors (NO, NO_2, NO_x, and NMHC) in four different land habitat sites of Mie prefecture, Japan has been discussed in this paper. The results show some interesting pattern in the distribution of ozone and its precursors in terms of the trend, variations in concentration levels in different sites and in different seasons. Ozone production/destruction process is mainly influenced by the interactions with NOx (i.e. NO, NO_2) in all the sites during all the seasons. Ozone production process in the inland urban sites (Matsusaka and Nabari) was influenced by the ratio NO_2/NO particularly in the winter. Variations in the ozone level were negligibly influenced by the ratio NMHC/NOx in all the sites except for Nabari. Ozone level at Nabari was significantly influence of the ratio NMHC/NOx during the winter perhaps due to mountainous topography. The study concludes that irrespective of the land habitats, ozone production processes in all the sites are mainly dominated by the NOx constituents (i.e. NO and NO_2).

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