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Photochemical production of ozone: a correlation study using GTE/CITE data

Poonam Narain
The University of Montana

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PHOTOCHEMICAL PRODUCTION OF OZONE: A CORRELATION
STUDY USING GTE/CITE DATA.

By
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BSc., University of Delhi, 1984

Presented in partial fulfillment of the requirement
for the degree of
Master of Science
University of Montana
1987

Approved by

Chairman, Board of Examiners

Dean, Graduate School

June 10, 1987

Date
Photochemical production of ozone: A correlation study, using GTE/CITE data.

Director: Ron Erickson

The purpose of this study was to look at correlations between the concentrations of ozone with both nitric oxide and carbon monoxide during

1) Daylight and night time hours.
2) When NO concentrations are greater than and less than 30pptv.
3) When air masses are coming from sea and from land.

The data used are ground-based measurement obtained from GTE/CITE in July 1983 Wallop Islands, Virginia. The data were averaged over a period of ten minutes. Spearman's rank correlations for various time lags were calculated between ozone and nitric oxide between, ozone and carbon monoxide. Confidence intervals for each of the correlations were calculated.

The analysis suggested that carbon monoxide and ozone are positively correlated without any time lag during the daytime when NO concentrations are greater than 30pptv. Nitric oxide and ozone showed very low correlations during the daytime provided the nitric oxide concentrations were lower than 30pptv.

The rest of the hypotheses could not be tested conclusively due to the lack of sufficient amount of data. Confirmation studies with the use of more complete data are needed to test the hypotheses.
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Acknowledgements

This thesis would not have possible without tremendous support and assistance from many people. I'm indebted to them all.

Special thanks to Dr. Robert C Harriss who not only supplied the research topic and ideas but also helped in obtaining data. I also wish to thank Joseph Drewery for sending the data. I'm deeply indebted to Ron Erickson who has been my academic and thesis advisor.

Thanks to you Dr. D Patterson for helping with the statistical analysis and Richard Lane for all the help with the computer.
Chapter 1

INTRODUCTION

Theory

Until the 1970's scientists accepted the view that ozone is transported from the stratosphere and destroyed at the earth's surface (Junge, 1962, 1963; Mohen et al., 1977; Danielson and Mohen, 1977). It is now recognized that reactive nitrogen compounds, in particular nitric oxide, play an important role in the photochemistry of the troposphere (Levy, 1972; Chameides, 1978; Crutzen, 1979; Logan et al., 1981). The proposed ozone formation reactions are similar to so-called smog chamber reactions (Heiklen et al., 1971) which mimic urban smog formation:

\[
\begin{align*}
\text{CO} + \text{HO} & \rightarrow \text{CO}_2 + \text{H} \quad (1) \\
\text{H} + \text{O}_2 + \text{M} & \rightarrow \text{HO}_2 + \text{M} \quad (2) \\
\text{HO}_2 + \text{NO} & \rightarrow \text{HO} + \text{NO}_2 \quad (3) \\
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O} \quad (4) \\
\text{O} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M} \quad (5)
\end{align*}
\]

NET REACTION: CO + O$_2$ + hv $\rightarrow$ O$_3$ + CO$_2$ (6)

Presence of NO allows competition with (3) because the efficiency of ozone production depends critically on the amount of NO in the atmosphere. A competing reaction to (3) is
Coupling this with (1),(2) and with reactions

$$\text{O}_2 + \text{hv} \rightarrow \text{O}_2 + \text{O}^1(\text{D}) \text{ wavelength } 320\text{nm}$$ \hspace{1cm} (8)

and

$$\text{O}^1(\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$$ \hspace{1cm} (9)

we obtain a net ozone destruction reaction:

$$\text{CO} + \text{H}_2 + 2\text{O}_3 + \text{hv} \rightarrow \text{CO}_2 + 2\text{O}_2 + 2\text{OH}$$ \hspace{1cm} (10)

The two crucial rate constants (3) and (7) have been measured often. The rate constant of (3) is sufficiently large so that \(\text{HO}_2\) reacts predominantly with NO rather than ozone in the troposphere, providing the NOx mixing ratio is 30pptv or more.

Despite the importance of these photochemical processes in understanding tropospheric chemistry, the global distribution of nitrogen oxides is not well characterized, chiefly because of the difficulty of obtaining reliable measurements at a level below 50pptv.

The primary objective of this study is to examine correlations between the concentrations of carbon monoxide and ozone as well as between nitric oxide and ozone concentrations using NASA's GTE/CITE data. We used this data for the following reasons:

1. Only a limited number of reported studies have used sufficiently sensitive and reliable instruments with measurement capabilities in low parts per trillion range. This data is of that kind (for further detail see

2. The data were collected in a coastal area relatively free of strong anthropogenic local sources but downwind of several large metropolitan areas. It is representative, therefore, of a number of non-urban areas of the Eastern United States for which little other data are available.

3. The data also includes measurements of air masses that have resided over the ocean for 24-48 hours.
Hypotheses Tested In This Study

If the smog chamber reactions are applicable to the background level chemistry of the troposphere, then the following trends should be seen in the environment:

1. Equations

\[
\begin{align*}
\text{HO}_2 + \text{NO} & \longrightarrow \text{HO} + \text{NO}_2 \quad (3) \\
\text{NO}_2 + \text{hv} & \longrightarrow \text{NO} + \text{O} \quad (4)
\end{align*}
\]

show that NO is used to convert HO2 back to HO and produce NO2, which then dissociates into NO and O, thus producing NO back. Therefore, during the daylight hours NO concentrations will be positively correlated with ozone with a time lag between the two gases' concentration peaks.

2. During the daylight hours, when NO concentrations are relatively high (>30pptv) ozone concentrations will be positively correlated with NO concentrations. The concentrations will be uncorrelated when concentrations of NO are low(< 30pptv). This hypothesis should hold because of the rate of reactions of (3) and (7), where

\[
\begin{align*}
\text{HO}_2 + \text{NO} & \longrightarrow \text{HO} + \text{NO}_2 \quad (3) \\
\text{HO}_2 + \text{O}_3 & \longrightarrow \text{HO} + 2\text{O}_2 \quad (7)
\end{align*}
\]

The rate constants of these two reactions have been measured many times (Chameides.,1978; Fishman.,1983; Chameides and Walker.,1973; Sieler and Fishman., 1981; Logan et al.,1981; Levine et al.,1984; Haagen-Smit.,1952; Mahlman and Levy II.,1980;) It has been found that if NO >
30pptv, then the rate of reaction of equation (3) is sufficiently fast to dominate reaction (7), which results in destruction of ozone.

3. During daylight hours, when concentrations of NO are greater than 30pptv, CO will be negatively correlated with ozone. This hypothesis is derived from reaction (6)

\[ \text{CO} + \text{O}_3 + \text{hv} \rightarrow \text{CO}_2 + \text{O}_3 \]  

(6)

where, CO concentrations increase and react with \( \text{O}_2 \) in presence of light to yield \( \text{CO}_2 \) and \( \text{O}_3 \), provided \( \text{NO} > 30\text{pptv} \). Also, as reaction (6) shows, there should be no lag time.

4. The hypotheses in 2 and 3 will hold most tightly when the \( \text{O}_3 \) concentrations are high, that is, when air masses come from land. This hypothesis should hold because the air from land should have had precursors of ozone.

5. On the days when air is returning from the sea, \( \text{O}_3 \) will track the \( \text{NO} \) concentrations that is, presence of ozone in high concentrations, will depend on the availability of \( \text{NO} \).
Chapter 2

MATERIAL, METHOD OF SELECTION AND ANALYSIS OF DATA

Material

The data used in this study are ground-based measurements obtained from the Chemical Instrumentation Test and Evaluation (CITE) program conducted as a part of NASA's Global Tropospheric Experiment (GTE) in July 1983 at Wallops Island, Virginia\(^1\) (Details can be found in papers by Hoell et al, 1985; Gregory et al, 1985; Carroll et al, 1985; Torress, 1985; Hoell et al, 1985b).

The statistical package “S” was used to create the plots and perform the data analysis. The reason for selecting “S” in favor of other available packages was that this is an interactive package with excellent graphic features.\(^2\)

NASA sent the data on a 9 track magnetic tape. The data was loaded on to the computer and appropriate data sets were selected.

\(^1\)The data can be obtained from NASA Langley, Hampton, VA 23365

\(^2\)I used “S” on UM’s VAX-785 computer under the Ultrix operating system.
Method and Data Analysis

As stated above, the primary objective of this study is to examine the correlations of between CO and O, and NO and O concentrations

(1) When concentrations of NO less than 30pptv.
(2) When concentrations of NO greater than 30pptv.
(3) When air masses were coming from the Atlantic Ocean.
(4) When air masses were coming from North America.
(5) During the day time.3
(6) During the nighttime.

Upon inspection, I found that the days of low NO mixing ratios were the same as the days when air masses were coming from the sea (Carroll et al, 1985). There were two such days, July 27th and 28th, 1983. However there was no CO data for these two days. I also found that the days of mixing ratios greater than or equal to 30pptv were the same as the days when the air masses were coming from North America. There were five such days, July 15th, 16th, 18th, 20th, 22nd.

There were data recordings of all three gases for the night of the 21st. Though CO and NO data sets for the complete night (4pm to 10am) were lacking, there were data available from 4pm to 11pm. There was complete data for O3

3I considered a “day” to be from 10am to 4pm because this is the time of day when photochemical processes can occur, and night from 4pm to 10am.
There were NO data recordings for the night of 27th only from 10.30pm to 10am and the night of 28th from 9pm to 12.10 am.

Averaging and Plotting the Data Sets:

Since, as received, the data for the three gases were not averaged over a common time period (CO, NO and O₃ were averaged over five, one and two minutes respectively), the data were averaged over a time period of 10 minutes and preliminary plots⁴ of the concentrations of gases versus time were made for each of the gases. A Tektonix 4051 graphics terminal and Tektronix 4611 thermal plotter were used for the graphics. Plots indicated that the averaging process (for 10 minutes period) did smooth noise from the data but preserved its general behaviour over time.

Calculating the Lag Time:

The lag time has been calculated in two ways in this study. One of the way lag time⁵ was estimated by looking at difference in the time between the peak of concentrations of gases on the same day. The formula used for calculating the lagₖ was

\[ \text{Lag}_k = \text{Peak time of Ozone} - \text{Peak time of NO or CO}. \]

---

⁴There are times during the day when the instruments were turned off, and the graphs show these gaps. For further detail see Gregory et al,1985; Hoell et al,1985; and Carroll et al,1985;

⁵Let's call the lag time estimated by the formula as lagₖ time.

⁶In calculating the lag time, if the NO and the CO peaked before O₃, the lag time is reported as a positive number in minutes and if the O₃ exhibited the peak before CO or NO the data set, then, the lag time reported as negative.
Another way of estimating the lagtime was used to calculate the correlations for various lagtimes and select the time corresponding to the best correlation.

Calculating correlations

The Spearman Rank correlation coefficients were calculated between the gases using various time lags (0, 10, 20, 60, 90 and 120 minutes for CO and 120, 150, 180, 210, 240, 270, 300, 330, 360 and 390 minutes for NO). This correlation coefficient was used because the ordinary Pearson product-moment correlation coefficient assesses only the degree of linear association between two variables. In certain situations (for example in this study) variable y may increase (or decrease) with an increase in x but not necessarily in linear fashion. When this happens the ordinary correlation coefficient will not depict the full extent of the relationship between the variables. The rank correlation coefficient, measures any monotonic association between y and x (Ott, 1984). Scatterplots for each of the correlations were also plotted.

To assess the precision of the correlations 95% confidence interval of each were calculated (Ott, 1984).
Chapter 3

RESULTS

Figures 1, 2, 3, 4 and 5 show how concentrations of the ozone, carbon monoxide, and nitric oxide changed with time during the daylight hours on July 15th, 16th, 18th, 20th and 22nd, 1983, respectively. On these days the concentrations of NO exceeded 30pptv and airmasses were coming from land.

Of the above figures 1a, 2a, 3a, 4a, and 5a, all show that NO peaks in the morning and 1c, 2c, 3c, 4c, and 5c demonstrate that O$_3$ peaks in the evening. The lag time between the peaks of NO and O$_3$ was calculated for each of the above stated days. These were 270, 170, 340, 570 and 470 minutes, respectively. Judging from the graphs, these don't appear to be good estimates of the true lag times ($t_{lag}$). Hence, Spearmans rank correlations were calculated between NO and O$_3$ for several different lag time (120, 150, 180, 210, 240, 270, 300, 330, 360, and 390 minutes). These correlations (Table 1) are negative initially, but progressively change to positive as the lag time increases, except on July 20th, 1983. Scatterplots\textsuperscript{7} (1d and 2d) do not show any well defined relationship but the scatterplots of 16th and 22nd show a linear relationship. The precision of the correlations can be assessed by the confidence intervals given in the parentheses below each correlation coefficient. As can be seen, high coefficients have narrow

\textsuperscript{7}The scatterplots of the highest correlation of each day are included in the report.
confidence intervals. But size of the confidence interval is also determined by the number of data points and the lengths of time for each NO recording, which in this case are 340, 170, 160, 290 and 350 minutes for the five days respectively.

The figures 1a, 2a, 3a, 4a, and 5a show concentrations change versus time in the case of O$_3$ and figures 1b, 2b, 3b, 4b and 5b show the CO mixing ratio change with time. These plots demonstrate that the O$_3$ tracks CO very closely. The lag time between the peaks of O$_3$ and CO (Table 2), are -30, 180, 260, 280, -40 minutes respectively. These again do not appear to be good estimates of the lag time. Again, correlations between CO and O$_3$ for several different lag times (0, 10, 20, 60, 90 and 120 minutes) were calculated. The correlations between CO and O$_3$ for the 15th, 20th and 22nd are high and positive and keep decreasing as lag time approaches 120 minutes. The scatterplots (1e, 4e and 5e) also show an almost linear relationship. The correlations on the 16th remain negative for the lag time periods and the scatterplot (Fig 2e) does not show any relationship. Correlations on the 18th start out negative at zero lag time and turn positive at lag time of 60 minutes. The scatterplot of the 18th (Figure 3e) does not show any relationship either. The confidence intervals given in the parentheses and looking at the time period for each CO data set available which in this case are 320, 230, 130, 290 and 490 minutes.

The night recordings of the O$_3$, CO and NO concentrations versus time are shown in figures 6, 7, and 8. The data for the 27th and 28th nights for CO is lacking; therefore, two of these graphs, 7 and 8, show only O$_3$ and NO plots. No relationship can be seen between O$_3$ and NO mixing ratios. The lag time between
the peaks of NO and O$_3$ were 170, 130, and 290 minutes respectively (Table 3). The rank correlations between NO and O$_3$ on the above stated days show no pattern either. The night of July 21st shows high positive correlations (0.32 to .97) and the scatterplot (Figure 6d) too shows a linear relationship but July 27th and 28th show low correlations (0.06 to 0.27 and -0.17 to 0.38 respectively), and so do the scatterplots 7d and 8d. The length of time for NO data recordings were 320, 260, and 200 minutes respectively.

Figures 6a and 6b show the plot of O$_3$ versus time, and CO versus time, respectively for July 21st. Table 4 gives the rank correlations between CO and O$_3$. These range from 0. 51 to 0.56 for zero lag period to 60 minutes, 0.27 for 90 minutes, and -0.27 for 120 minutes. Scatterplot for the highest correlation (Figure 6e) shows data in two clusters. The night of the 21st had CO data recordings for 310 minutes and a lag time between peaks of CO and O$_3$ of -70 minutes.

NO recordings versus time and O$_3$ versus time on the 28th and 29th day are shown in figures 9 and 10. The CO data for these two days is lacking. Table 5 show the correlations which again shows no pattern. They range from -0.40 to 0.20 for the 28th and 0.10 to 0.26 for the 29th and so do the scatterplots (Figure 9d and 10d). Lag period are between peaks -70 and zero minutes for the two days, respectively. NO data recordings were available for the time period of 250 and 310 minutes respectively.
### TABLE 1. Daytime correlations between ozone and nitric oxide

(>30pptv), when airmasses were coming from the land.

<table>
<thead>
<tr>
<th>Date</th>
<th>Time length for which NO data was available</th>
<th>Lag period for which correlations were calculated</th>
<th>Lag period calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>13th</td>
<td>340 mins</td>
<td>120, 150, 180, 210, 240</td>
<td>270 mins</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>170 mins</td>
</tr>
<tr>
<td>16th</td>
<td>170 mins</td>
<td>120, 150, 180, 210, 240</td>
<td>270 mins</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>170 mins</td>
</tr>
<tr>
<td>18th</td>
<td>160 mins</td>
<td>120, 150, 180, 210, 240</td>
<td>270 mins</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>340 mins</td>
</tr>
<tr>
<td>20th</td>
<td>290 mins</td>
<td>120, 150, 180, 210, 240</td>
<td>270 mins</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>570 mins</td>
</tr>
<tr>
<td>22nd</td>
<td>350 mins</td>
<td>120, 150, 180, 210, 240</td>
<td>270 mins</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>470 mins</td>
</tr>
</tbody>
</table>

* correlation coefficients

** confidence interval for the correlation.
TABLE 2. Daytime correlations between ozone and carbon monoxide (\( > 30 \text{ppmv} \)), when airmasses are coming from the land.

<table>
<thead>
<tr>
<th>Date</th>
<th>Time length for which CO data was available</th>
<th>Lag period for which correlations were calculated</th>
<th>Lag Period Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 1983</td>
<td>30 mins</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>15th</td>
<td>330 mins</td>
<td>.79</td>
<td>.84</td>
</tr>
<tr>
<td>16th</td>
<td>230 mins</td>
<td>-.39</td>
<td>-.52</td>
</tr>
<tr>
<td>18th</td>
<td>130 mins</td>
<td>-.39</td>
<td>-.39</td>
</tr>
<tr>
<td>20th</td>
<td>290 mins</td>
<td>.76</td>
<td>.62</td>
</tr>
<tr>
<td>22nd</td>
<td>490 mins</td>
<td>.94</td>
<td>.93</td>
</tr>
</tbody>
</table>

* correlation coefficients
** confidence interval for the correlation
TABLE 3. Nighttime correlations between ozone and nitric oxide

<table>
<thead>
<tr>
<th>Date</th>
<th>Time length for which NO data was available</th>
<th>Lag period for which correlations were calculated.</th>
<th>Lag Period calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>21st</td>
<td>320 mins</td>
<td>0.32 (-0.03, 0.06) 0.39 (0.04, 0.63) 0.82 (0.66, 0.90) 0.95 (0.89, 0.97) 0.97 (0.93, 0.99) 0.93 (0.86, 0.96) 0.88 (0.76, 0.92) 0.86 (0.73, 0.92) 0.86 (0.67, 0.91) 0.83 (0.74, 0.93)</td>
<td>170 mins</td>
</tr>
<tr>
<td>27th</td>
<td>260 mins</td>
<td>0.06 (-0.34, 0.43) 0.08 (-0.32, 0.44) 0.25 (-0.16, 0.57) 0.20 (-0.21, 0.54) 0.08 (-0.31, 0.45) 0.16 (-0.24, 0.51) 0.27 (-0.13, 0.59) 0.22 (-0.18, 0.55) 0.17 (-0.23, 0.52) 0.23 (-0.17, 0.56)</td>
<td>130 mins</td>
</tr>
<tr>
<td>28th</td>
<td>200 mins</td>
<td>0.17 (-0.57, 0.43) 0.35 (-0.21, 0.55) 0.03 (-0.36, 0.42) 0.38 (-0.30, 0.47) 0.11 (-0.42, 0.54) 0.35 (-0.10, 0.68) 0.03 (-0.41, 0.46) 0.28 (-0.18, 0.64) 0.06 (-0.48, 0.39) 0.00 (-0.43, 0.44)</td>
<td>290 mins</td>
</tr>
</tbody>
</table>

* correlation coefficients
** confidence interval for the correlation
TABLE 4. Nighttime correlations between ozone and carbon monoxide.

<table>
<thead>
<tr>
<th>Date</th>
<th>Time length for which CO data was available</th>
<th>Lag period for which correlations were calculated</th>
<th>Lag Period Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 1983</td>
<td>310 mins</td>
<td>0       10  20  60  90  120</td>
<td>210 mins</td>
</tr>
<tr>
<td>1st</td>
<td>.51  .54  .56</td>
<td>.56  .27  -.26</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(.18,.73) (.23,.75) (.25,.76)</td>
<td>(.25,.76) (-.09,.56) (-.56,.10)</td>
<td></td>
</tr>
</tbody>
</table>

* correlation coefficients
** confidence interval for the correlation
TABLE 5. Daytime correlations between ozone and nitric oxide (< 30pptv), when airmasses were coming from the sea.

<table>
<thead>
<tr>
<th>Date</th>
<th>Time length</th>
<th>Lag for which correlations were calculated</th>
<th>Lag period calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 1983</td>
<td>for which NO data was available</td>
<td></td>
<td></td>
</tr>
<tr>
<td>28th</td>
<td>250 mins</td>
<td>0.05</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-0.35, 0.43)</td>
<td>(-0.21, 0.55)</td>
</tr>
<tr>
<td>29th</td>
<td>200 mins</td>
<td>0.26</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-0.10, 0.56)</td>
<td>(-0.09, 0.57)</td>
</tr>
</tbody>
</table>

* correlation coefficients
** confidence interval for the correlation
Figure 1: July 15, 1983 (daytime)

Fig. 1a. Plot of ozone in ppb versus time.

Fig. 1b. Plot of carbon monoxide in ppb versus time.

Fig. 1c. Plot of nitric oxide in ppb versus time.

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Fig. 1d. Scatterplot of nitric oxide versus ozone with 360 minutes lag time.
Fig. 1e. Scatterplot of carbon monoxide versus ozone with 10 minutes lag time.
Figure 2: July 16, 1983 (daytime)

Fig 2a: Plot of ozone in ppm versus time

Fig 2b: Plot of nitric oxide in ppm versus time
Fig. 2d. Scatter plot of nitric oxide versus ozone with 180 minutes lag time.
Fig 2. Scatterplot of carbon monoxide versus ozone with 90 minutes lag time.
Figure 3: July 18, 1983 (daytime)

Fig. 3a. Plot of ozone in ppb versus time

Fig. 3b. Plot of carbon monoxide in ppb versus time

Fig. 3c. Plot of nitric oxide in ppb versus time

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Fig. 3d. Scatterplot of nitric oxide versus ozone with 360 minutes lag time.
Fig. 3e. Scatterplot of carbon monoxide versus ozone with 60 minutes lag time.
Figure 4: July 20, 1983 (daytime)

Fig 4a. Plot of ozone in ppb versus time.

Fig 4b. Plot of carbon monoxide in ppb versus time.

Fig 4c. Plot of nitric oxide in ppb versus time.

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Fig. 4d. Scatterplot of nitric oxide versus ozone with 390 minutes lag time.
Fig. 4a. Scatterplot of carbon monoxide versus ozone with 10 minutes lag time.
Fig 5a: Scatterplot of nitric oxide versus ozone with 390 minutes lag time.
Figure 6: July 21, 1983 (nighttime)

Fig. 6a. Plot of ozone in ppb versus time.

Fig. 6b. Plot of carbon monoxide in ppb versus time.

Fig. 6c. Plot of nitric oxide in pptv versus time.
Figure 7: July 27, 1983 (nighttime)

Fig. 7a. Plot of ozone in ppb versus time

Fig. 7b. Plot of nitric oxide in pptv versus time
Fig. 76: Scatterplot of nitric oxide versus ozone with 360 minutes lag time.
Figure 8: July 28, 1983 (nighttime)

Fig. 8a. Plot of ozone in ppb versus time

Fig. 8b. Plot of nitric oxide in pptv versus time

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Figure 9: July 28, 1983 (daytime)

**Fig. 9a. Plot of ozone in ppb versus time**

**Fig. 9b. Plot of nitric oxide in pptv versus time**
Figure 10: July 29, 1983 (daytime)

Fig.10a. Plot of ozone in ppb versus time

Fig.10b. Plot of nitric oxide in pptv versus time
Fig. 10c. Scatterplot of nitric oxide versus ozone with 150 minutes lag time.
Chapter 4

DISCUSSION AND CONCLUSIONS

There were sufficient data for ozone for all days of the study period but not for NO and CO. There were satisfactory daytime data for CO on July 15th, 20th and 22nd. The results and the graphs show (1a, 2a, 3a, 4a, 5a, 1b, 2b, 3b, 4b and 5b) that concentrations of CO and \( \text{O}_3 \) are positively correlated, provided the NO concentrations are greater than 30pptv. The correlations on July 16th and 18th are negative and do not exhibit the same trends as the rest of the days, probably because the CO data were available for these two days were of very short time periods. Also, the relationship between these two gases when NO concentrations are less than 30pptv could not be determined because of lack of CO data on July 27th, 28th and 29th, 1983.

Let us return to the reason behind the hypothesis that, CO should be negatively correlated to \( \text{O}_3 \) with no lag period. To simulate a smog chamber observations in the lower troposphere it would be essential to follow the air parcels and make measurements throughout the moving parcel at the ground-base level and perhaps at heights of 200, 400 and 600ft. Then the recordings at the originating place (lets call it place A) would simulate the initial concentrations of CO and \( \text{O}_3 \). Measurements at a later destination (lets call it B) would simulate final measurements in a smog chamber. The air parcel had a certain CO:O\(_3\) ratios when it started from place A (Figure 11). Early in the morning CO concentrations start to
build up since there are no photochemical reactions going on. By the time the air parcel reaches place B, photochemical processes have taken place in it. Therefore, by the time the air parcel gets to place B, it should have low CO concentrations and high O$_3$ concentrations, according to reaction series (1) to (5) and the net reaction (6). Therefore, according to smog chamber reactions we should see a negative correlation between concentrations of O$_3$ and CO with no lag period. In the results obtained from the study, CO and O$_3$ are positively correlated, with no time lag. This brings us to very interesting question. Why are CO and O$_3$ positively correlated and what factors are responsible for the positive correlations?

There can be four different answers to the question. (1) The data is not sufficient to draw any reliable conclusions, so this hypothesis should be tested again using more complete data sets. (2) Rate of production of CO was greater than the rate it was transformed to CO$_2$ to produce O$_3$. (3) HO mixing ratios may be a limitation in changing CO to CO$_2$. (equation (1)), therefore HO concentrations need to be measured and taken into consideration. (4) If the above three explanations are not valid then further chemical reactions may be occurring and need to be investigated.

The NO data sets of the 15th and 22nd were a complete set too (that is from about 10am to 4pm). But from the data set of July 20th it was obvious that the NO peak occurred before 10am; therefore the calculated correlations cannot be used to draw highly reliable conclusions about the NO and O$_3$ relationship. Nonetheless for initial lag periods (until 240 minutes) the correlations are negative and turn positive after 240 minutes.
Again the nighttime data for CO cannot be used to draw reliable conclusions, because there were recordings for only one night (July 21st). Though the nighttime correlations between the two gases were positive for the initial lag period, conclusions ought not be drawn from such a skimpy data set.

Nighttime data of NO show no pattern in the correlations calculated. Correlations on July 21st are very high for 180 minutes lag time to 390 minutes lag time. For the other two nights, the 27th and 28th, when the concentrations of NO < 30 pptv, there is no pattern. But conclusions cannot be drawn because there was not enough NO data to cover the whole night.

The daytime NO data for July 28th and 29th were almost complete. The correlations between NO and $O_3$ are low throughout and they demonstrate no trends over time, which means that NO > 30 pptv is necessary to produce ozone. But these data sets have two limitations, (1) The data before 10 am is not available, and (2) CO data for both the days is lacking.

My method of calculating lagtime seems to show no consistency with the correlations at the corresponding lag times, which probably means that a different method should be used. In my method a faulty peak may have thrown the lag time off. The method of finding a lag time to get the best correlation seems to be better because of the higher consistency of in the lagtime.

Lastly, lack of a sufficient quantity of data proved to be a serious impairment to the research efforts.

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8A complete day considered to be 360 minutes, July 28th and 29th had data for 330 and 290 minutes respectively.
Suggestions

To confirm the finding in this study that CO is positively correlated to O$_3$ with zero lag time, more complete data sets should be used in future studies and several other factors should be considered (for example NO$_2$, CH$_4$, light intensity, HO that according to smog chamber study lead to production of O$_3$).

A Look at the rate of CO production relative to the rate of CO transformation to CO$_2$ which also produces ozone at the originating site of the air parcel will help answer one of the questions raised in this study.

It would be highly beneficial to trace the back trajectories of the air parcels, and to follow and make measurements throughout the moving air parcel.

To test the rest of the hypotheses successfully, additional data of the mixing ratios of the three gases and the above mentioned variables are needed. Also, the back trajectories should be traced and a look at measurements along the path should be taken. Some other interesting hypothesis can be tested using the kind of data used in the study. In the 23 days plots of ozone versus time, it was observed that ozone had a regular pattern of peaking every afternoon except on some days when it broke away from the pattern. It would be interesting to consider all factors driving ozone concentrations and ask why it is constant on some days and variable on others. Also, why are CO and O$_3$ correlations better on somedays than others?
Fig. 11. Pictographic representation of how CO and O$_3$ concentrations will change when air parcel moves from place A to B.
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