

## RESEARCH ON SURFACE $O_3$ WITH METEOROLOGICAL CONDITIONS UNDER ATMOSPHERIC BACKGROUND CONDITIONS IN NORTHEAST CHINA\*

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### ABSTRACT

Surface  $O_3$  concentration and its precursors have been observed at Longfengshan station, Heilongjiang Province for a period of one year from August 13, 1994 to July 30, 1995. Relationship between surface  $O_3$  and the meteorological conditions during this period is analyzed in this study. Observation results show that diurnal variation of surface  $O_3$  follows a pattern of double-peaks with amplitude of 27–28 ppb under fine days in summer and autumn. Although the diurnal variation is small (14 ppb), it is still detectable when it is overcast. Diurnal variation of  $O_3$  is irregular under rainy days. Surface  $O_3$  concentration rises when wind speed starts to increase at 0800 BT (Beijing Time) from 0 to 6 m s<sup>-1</sup> in autumn, winter and summer. Relative high surface  $O_3$  concentration is noticed frequently when S, SSW, SW and WSW wind are encountered at the station during all seasons. At 0800 BT and 1400 BT the surface  $O_3$  concentration increases with the increase of global radiation accordingly during fine days in winter, spring and autumn. During fine days average peak of  $O_3$  concentration in summer is 20 ppb higher than that in winter while the average peak of global radiation in summer is almost twice as high as that in winter. The average surface  $O_3$  concentration under fine days in autumn at Longfengshan station is 14 ppb lower in comparison to the observation results from Lin'an station where Lin'an is at about the same longitude and lower latitude, with same environment, which is mainly caused by the difference of global radiation due to different latitudes in these two areas (difference of average peak global radiation about 100 W m<sup>-2</sup>).

**Key words:** surface  $O_3$  concentration, meteorological conditions

### 1. INTRODUCTION

Comprehensive observation of  $O_3$  concentration and its precursors has been carried out

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at Longfengshan regional station, Wuchang city, Heilongjiang Province for a period of one year starting from August 13, 1994. Observation items include surface O<sub>3</sub>, total O<sub>3</sub>, NO<sub>x</sub>, SO<sub>2</sub>, CO<sub>2</sub>, methane, CO, NMHC, aerosol, solar radiation and meteorological elements, among which surface O<sub>3</sub>, total O<sub>3</sub>, NO<sub>x</sub>, SO<sub>2</sub> and solar radiation (visible light, infrared, ultra-violet) were continuously monitored using instruments. The instruments used include Model 49 for O<sub>3</sub>, Model 43S for SO<sub>2</sub> and Model 42S for NO<sub>x</sub> made in TE Co., USA, pyranometers (295, 395, 695 nm) made in APPLIED Co., USA for solar radiation and Brewer O<sub>3</sub> spectrophotometer made in Canada for the total O<sub>3</sub>. All the instruments were calibrated before use on site. Surface O<sub>3</sub> measuring instrument was also calibrated during the observation process. Longfengshan station is one of the only three regional stations that administrated by the China Meteorological Administration for atmospheric background concentration, which is also included in the Global Atmospheric Watch (GAW) under WMO. The observation station is 50 km away from Wuchang City. The station is close to a water reservoir, and located on a small hill in Zhangguangcai Mountain region. The hill is covered by vast amount of pine trees. At the bottom of the hill is a large rice field. There are no major pollution sources nearby. In this study relationship between surface O<sub>3</sub> and meteorological conditions is established for the year.

## II. RESULTS AND DISCUSSION

### 1. *Surface O<sub>3</sub> under Different Weather Conditions*

Hourly average O<sub>3</sub> data were compiled from Longfengshan station in autumn under fine, overcast and rain days respectively. The observation periods concerned are 23, 10 and 13 days respectively. Data for cloudy day are not included as the weather condition was not available. Under fine days in autumn, the diurnal variation of surface O<sub>3</sub> shows a typical double-peak pattern: at about 0600 BT surface O<sub>3</sub> concentration reaches a minimum of 28.9 ppb. The concentration gradually increases after sunrise and reaches its maximum of 56.1 ppb at about 1700 BT, and then the O<sub>3</sub> concentration starts to decrease until midnight. After a small peak occurs before early morning, it starts to decrease again until sunrise. Its diurnal variation is 27.2 ppb; the maximum of surface O<sub>3</sub> concentration is almost twice as high as the minimum. Under overcast days, the diurnal variation of O<sub>3</sub> concentration is far from regularity than under fine days. However the variation is still detectable to a certain degree and is seen with the double-peak pattern as well. The minimum occurs 1–2 h later than that in fine days at 24.1 ppb. The maximum occurs 2 h earlier than that in fine days at 38 ppb. After the occurrence of the maximum, O<sub>3</sub> concentration starts to decrease irregularly until sunrise the next day. The diurnal variation under overcast days is 13.9 ppb only about half of that under fine days. The surface O<sub>3</sub> diurnal range is relatively low with minimum of 7.6 ppb under rainy days and diurnal variation changes irregularly very much, which probably relates with different occurrence time of the rain and intensity of the rain as can be seen from Fig. 1. Before 1100 BT the surface O<sub>3</sub> concentration under overcast days is even lower than that under rainy conditions. This phenomenon can also be explained by the variation of rain intensity and occurring time. In addition, less data have been collected for the rainy days.

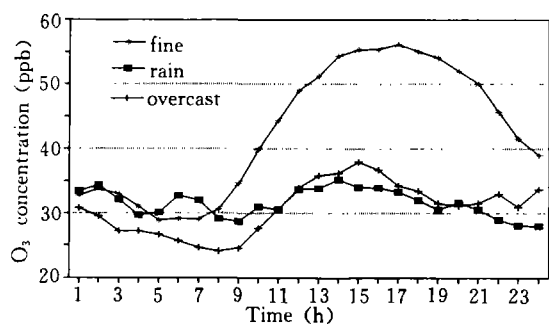


Fig. 1. Surface  $O_3$  concentration under different weather conditions in autumn (Longfengshan Sep. – Nov. 1994).

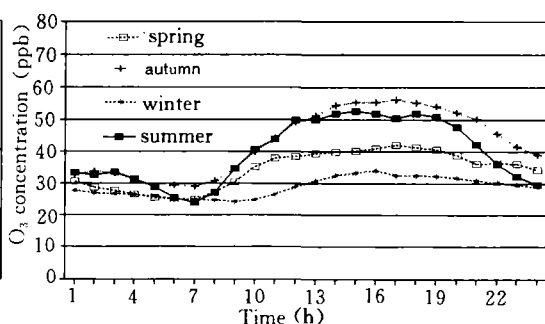


Fig. 2. Diurnal variation of surface  $O_3$  under fine days (Longfengshan station, Aug. 1994 – Jul. 1995).

Under fine days in other seasons, diurnal variation also shows a double-peak trend in summer (see Fig. 2). Its diurnal amplitude (28.7 ppb) is a little higher than that in autumn. Double peak trend can not be seen obviously during transition period from winter to spring. Diurnal amplitude reaches minimum in winter (only 9.7 ppb). Diurnal amplitude in spring is 17.2 ppb in between.  $O_3$  concentration in summer afternoons is slightly lower than that in autumn from diurnal variation trend. This is probably caused by higher  $NO_x$  concentration in autumn. Although diurnal variation amplitude is smaller in overcast days, diurnal variation still can be seen in other seasons. The maximum diurnal variation amplitude is 16.3, 8.8, 6.9 ppb in summer, winter and spring, respectively. In other seasons, noticeable precipitation including rain and snow is encountered, average diurnal variation of surface  $O_3$  concentration is irregular as in autumn. The diurnal variation is about 7–10 ppb.

The effect of precipitation on surface  $O_3$  is quite obvious and it can be seen easily from the variation of surface  $O_3$  concentration. There was continuously rain at 0700–2000 BT on May 9, 1995. The rainfall amount was 10.3 mm. Before the rain, the surface  $O_3$  concentration is above 50 ppb. It became lower after 0700 BT. There is 8.0 mm rainfall amount at 0100–1400 BT on Sept. 19, 1994. On that day, the hourly  $O_3$  concentration was

**Table 1.** Typical Diurnal Variation of Surface  $O_3$  Concentration under Rainy Days (Longfengshan Station August 1994–July 1995)

| time (BT)              | 0000 | 0100 | 0200 | 0300 | 0400 | 0500 | 0600 | 0700 | 0800 | 0900 | 1000 | 1100 |
|------------------------|------|------|------|------|------|------|------|------|------|------|------|------|
| 1995-05-09             | 46.5 | 52.0 | 51.8 | 53.5 | 54.8 | 54.2 | 51.2 | 50.1 | 41.6 | 40.4 | 36.0 | 35.7 |
| 1994-09-19             | 34.3 | 35.9 | 21.8 | 18.9 | 23.3 | 26.3 | 30.6 | 24.9 | 20.7 | 19.8 | 23.7 | 25.0 |
| Autumn 1994 rainy days | 33.5 | 34.3 | 32.1 | 29.7 | 30.1 | 32.7 | 32.0 | 29.2 | 28.8 | 31.1 | 30.6 | 33.7 |
| time (BT)              | 1200 | 1300 | 1400 | 1500 | 1600 | 1700 | 1800 | 1900 | 2000 | 2100 | 2200 | 2300 |
| 1995-05-09             | 35.9 | 37.3 | 39.8 | 39.4 | 30.0 | 26.7 | 24.8 | 24.9 | 23.7 | 22.0 | 23.5 | 24.4 |
| 1994-09-19             | 24.8 | 26.5 | 28.6 | 25.1 | 24.3 | 22.0 | 18.7 | 21.7 | 17.5 | 19.1 | 18.6 | 17.9 |
| Autumn 1994 rainy days | 33.9 | 35.2 | 34.1 | 34.0 | 33.3 | 32.0 | 30.6 | 31.7 | 30.6 | 29.0 | 28.1 | 28.0 |

lower by 10 ppb than what is derived from the average diurnal variation under rainy days in autumn (see Table 1). Similar phenomenon has been encountered in Lushan (Ding et al. 1991).

## 2. Wind

### (1) Wind speed

Average surface O<sub>3</sub> concentration has been compiled for four times at 0100, 0800, 1400 and 1900 BT under different wind speeds (see Table 2). Surface O<sub>3</sub> concentration rises with the increase of wind speed at many measurement times. This is typically demonstrated by the measurements obtained at 0800 BT in autumn. O<sub>3</sub> concentration increases by 2.7 ppb with the increase of wind speed by 1 m s<sup>-1</sup> under wind speed range from 0.1–1.0 m s<sup>-1</sup> to 5.1–6.0 m s<sup>-1</sup>. Similar trend presents at 1400 BT test results. Between 0100 and 1900 BT O<sub>3</sub> concentration varied slightly with the increase of wind speed. Surface O<sub>3</sub> concentration increases by about 1.6 ppb and 1.0 ppb respectively with wind speed increase by 1 m s<sup>-1</sup> when wind speed changed from 1.1–2.0 m s<sup>-1</sup> to 5.1–6.0 m s<sup>-1</sup>. The relationship between wind speed and O<sub>3</sub> concentration at 0100 BT in winter is opposite to each other. There is no obvious correlation between wind speed and surface O<sub>3</sub> concentration on other measurement times in winter. Surface O<sub>3</sub> concentration rises with the increase of wind speed at 0800 BT in spring. Surface O<sub>3</sub> concentration increases by 2 ppb with the increase of wind speed by 1 m s<sup>-1</sup> under wind speed range from 0.1–1.0 m s<sup>-1</sup> to 5.1–6.0 m s<sup>-1</sup>. O<sub>3</sub> concentration increases by about 5 ppb with increase of wind speed by 1 m s<sup>-1</sup> under wind speed range from 2.1–3.0 m s<sup>-1</sup> to 5.1–6.0 m s<sup>-1</sup> at 0100 BT except for the speed range of 0.1–1.0 m s<sup>-1</sup> and 1.1–2.0 m s<sup>-1</sup>. No strong correlation between wind speed and surface O<sub>3</sub> concentration is noticed at 1400 and 1900 BT. The surface O<sub>3</sub> concentration also increases with the increase of wind speed at 0800 BT in summer. Surface O<sub>3</sub> concentration increases by 3.8 ppb with the increase of wind speed by 1 m s<sup>-1</sup> under wind speed range from 0.1–1.0 m s<sup>-1</sup> to 5.1–6.0 m s<sup>-1</sup>. Surface O<sub>3</sub> concentration increases by 1.8 ppb with the increase of wind speed by 1 m s<sup>-1</sup> at 0100 BT when the O<sub>3</sub> variation is small. O<sub>3</sub> variation is irregular at 1400 and 1900 BT. However higher O<sub>3</sub> concentration presents at higher wind speed. For example, O<sub>3</sub> concentration is as high as 60.9 ppb at 1400 BT under wind speed range of 5.1–6.0 m s<sup>-1</sup>. The O<sub>3</sub> concentrations at 1900 BT are at 50.2 ppb and 51.8 ppb respectively under wind speed ranges of 4.1–5.0 m s<sup>-1</sup> and 5.1–6.0 m s<sup>-1</sup>.

Average surface O<sub>3</sub> concentration tends to increase with the increase of average diurnal wind speed all the year round, especially in autumn and in summer. Surface O<sub>3</sub> concentration increases by 5.1 ppb and 4.3 ppb respectively with wind speed increases by 1 m s<sup>-1</sup> under wind speed range from 0.1–1.0 m s<sup>-1</sup> to 5.1–6.0 m s<sup>-1</sup>. Similar trend is also observed in spring, but O<sub>3</sub> concentration increases only by 1 ppb.

**Table 2.** Average Surface O<sub>3</sub> Concentration with Different Wind Speed under Different Seasons and Times (Longfengshan, August 1994–July 1995)

| wind speed (m s <sup>-1</sup> ) |                     |                | 0.1–1.0        | 1.1–2.0 | 2.1–3.0 | 3.1–4.0 | 4.1–5.0 | 5.1–6.0 | 6.1–7.0 | 7.1–8.0 | 8.1–9.0 |
|---------------------------------|---------------------|----------------|----------------|---------|---------|---------|---------|---------|---------|---------|---------|
| Autumn<br>(Time BT)             | 0100                | O <sub>3</sub> | 36.1           | 30.6    | 30.7    | 33.4    | 35.9    | 37.0    | 47.9    | 57.2    | 61.3    |
|                                 |                     | No.            | 7              | 10      | 21      | 17      | 13      | 4       | 2       | 3       | 1       |
|                                 | 0800                | O <sub>3</sub> | 25.1           | 28.8    | 28.4    | 35.3    | 38.9    | 38.9    | 53.3    | 71.9    |         |
|                                 |                     | No.            | 5              | 10      | 25      | 14      | 12      | 2       | 2       | 3       |         |
|                                 | 1400                | O <sub>3</sub> | 38.8           | 44.9    | 49.4    | 43.7    | 52.7    | 49.7    | 44.5    | 59.6    | 62.1    |
|                                 |                     | No.            | 4              | 13      | 18      | 13      | 10      | 7       | 4       | 3       | 2       |
|                                 | 1900                | O <sub>3</sub> | 46.1           | 43.8    | 41.1    | 49.0    | 43.1    | 47.9    | 57.0    | 68.8    |         |
|                                 |                     | No.            | 4              | 20      | 12      | 15      | 14      | 3       | 3       | 2       |         |
|                                 | average             | O <sub>3</sub> | —              | 32.1    | 37.4    | 43.5    | 48.2    | 54.0    | 57.4    |         |         |
|                                 | No.                 |                | 32             | 17      | 13      | 6       | 2       | 2       |         |         |         |
| Winter<br>(Time BT)             | 0100                | O <sub>3</sub> | 30.7           | 30.8    | 28.4    | 27.0    | 26.6    | 28.9    | 20.7    |         |         |
|                                 |                     | No.            | 3              | 7       | 16      | 21      | 17      | 1       | 2       |         |         |
|                                 | 0800                | O <sub>3</sub> | 30.4           | 26.4    | 22.8    | 26.1    | 23.5    | 25.8    | 24.4    | 39.2    |         |
|                                 |                     | No.            | 4              | 17      | 11      | 17      | 11      | 5       | 2       | 1       |         |
|                                 | 1400                | O <sub>3</sub> | 36.1           | 33.4    | 34.7    | 34.0    | 34.3    | 36.3    | 34.0    | 27.0    | 32.2    |
|                                 |                     | No.            | 1              | 14      | 19      | 11      | 10      | 3       | 3       | 2       | 2       |
|                                 | 1900                | O <sub>3</sub> | 35.5           | 32.6    | 33.2    | 30.2    | 32.5    | 32.3    |         |         |         |
|                                 |                     | No.            | 4              | 6       | 16      | 21      | 12      | 5       |         |         |         |
|                                 | Spring<br>(Time BT) | 0100           | O <sub>3</sub> | 39.6    | 32.8    | 31.3    | 31.6    | 34.7    | 46.5    | 37.2    |         |
| No.                             |                     |                | 3              | 10      | 20      | 23      | 16      | 5       | 2       |         |         |
| 0800                            |                     | O <sub>3</sub> | 27.5           | 30.7    | 31.4    | 33.0    | 37.5    | 37.7    | 32.4    | 40.4    |         |
|                                 |                     | No.            | 14             | 16      | 14      | 16      | 7       | 11      | 2       | 4       |         |
| 1400                            |                     | O <sub>3</sub> | 39.9           | 43.6    | 36.8    | 42.5    | 46.7    | 39.9    | 39.9    | 41.5    | 57.5    |
|                                 |                     | No.            | 6              | 10      | 12      | 15      | 10      | 9       | 14      | 4       |         |
| 1900                            |                     | O <sub>3</sub> |                | 43.6    | 38.0    | 39.0    | 35.8    | 41.3    | 42.6    |         |         |
|                                 |                     | No.            |                | 18      | 22      | 17      | 10      | 12      | 4       |         |         |
| Summer<br>(Time BT)             |                     | 0100           | O <sub>3</sub> | 23.5    | 21.0    | 23.7    | 28.8    |         |         |         |         |
|                                 | No.                 |                | 2              | 9       | 19      | 10      |         |         |         |         |         |
|                                 | 0800                | O <sub>3</sub> | 25.3           | 30.2    | 27.6    | 30.7    | 38.5    | 44.4    |         |         |         |
|                                 |                     | No.            | 19             | 13      | 11      | 5       | 5       | 2       |         |         |         |
|                                 | 1400                | O <sub>3</sub> | 41.5           | 41.1    | 39.0    | 40.0    | 36.3    | 60.9    |         |         |         |
|                                 |                     | No.            | 6              | 13      | 20      | 10      | 3       | 3       |         |         |         |
|                                 | 1900                | O <sub>3</sub> | 32.9           | 36.3    | 38.0    | 33.9    | 50.2    | 51.8    |         |         |         |
|                                 |                     | No.            | 3              | 14      | 19      | 14      | 2       | 2       |         |         |         |

Except in winter, it is worth emphasizing that surface O<sub>3</sub> concentration increases by over 10 ppb with wind speed increase of 1 m s<sup>-1</sup> when wind speed is over 6.0 m s<sup>-1</sup> in autumn. Although the increase of O<sub>3</sub> concentration is not as high as that in autumn, clear evidence in spring shows that O<sub>3</sub> concentration rises with the increase of wind speed except for the measurements obtained at 0100 BT. In addition, relative high O<sub>3</sub> concentration is observed with 8 out of 15 measurements all the year round under low wind speed range of 0.1–1.0 m s<sup>-1</sup>. There is 50% probability of occurrence of high O<sub>3</sub> concentration under calm wind as can be seen from the following section —wind direction, indicating that

relative high surface  $O_3$  concentration occurs under conditions of calm and small wind. It is worthy of paying attention to this phenomenon, however this phenomenon is not very representative because of the limited number of observations.

Through the above analysis, we come to the conclusion that photochemical reaction rate increases with the increase of wind speed under condition of wind speed greater than  $1 \text{ m s}^{-1}$ . Especially when wind speed is over  $6 \text{ m s}^{-1}$ , there is a significant rise in photochemical reaction rate. It is observed at Lin'an regional station during PEM-WEAT-A experiment (August—November, 1991) that the surface  $O_3$  concentration did not increase obviously with the increase of wind speed over  $6 \text{ m s}^{-1}$  (Ding et al. 1995; Zhou et al. 1993). There is only about 100 days of records available during the period of this experiment. Meanwhile there are only few days of strong wind. So we need to do more detailed study before we are able to come to a definite conclusion.

Relationship of average diurnal wind speed with average diurnal surface  $O_3$  concentration is analysed at 0100 BT in autumn (see Fig. 3). It can be seen from the figure that most of the average diurnal wind speed peak values match with the peak values of the average diurnal surface  $O_3$  concentration. It is to be mentioned that during 290—310 Julian day, the three peaks of the average diurnal wind speed under wind speed greater than  $6 \text{ m s}^{-1}$  (which are the only three peaks available in autumn) are consistent with the three peaks of the average diurnal surface  $O_3$  concentration.

## (2) Wind direction

Wind direction with occurrence frequency less than 3 is not taken into consideration in our analysis. In autumn high  $O_3$  concentration mainly occurs under S, SSW and SW wind directions at 0100 BT (40.7, 43.0 and 43.5 ppb respectively), while at 0800 BT high  $O_3$  concentration occurs under SSW and WSW wind directions (49.3 ppb and 46 ppb). However at 1400 BT and 1900 BT, no high  $O_3$  concentration is noticed under any wind directions. In summer  $O_3$  concentration under SSW wind direction is higher than that under any other wind directions at 0100 BT (38.4 ppb); at 0800 BT high  $O_3$  concentration is observed under S, WSW and N wind directions (38.7, 42.3 and 42.1 ppb respectively). At 1400 BT high concentration is recorded under SSW, SW, WSW and SE wind directions

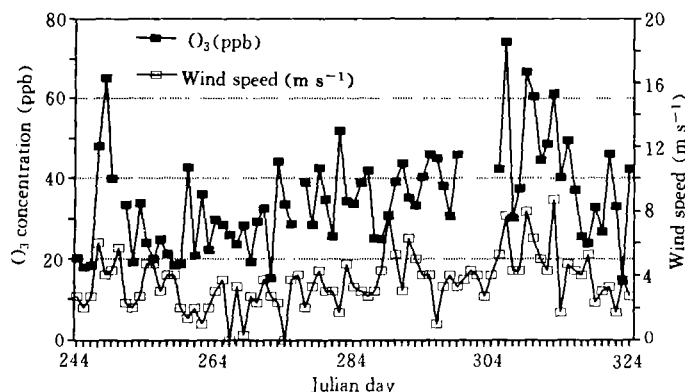


Fig. 3. Average diurnal wind speed in relation to average diurnal surface  $O_3$  concentration (Longfengshan station, September—November, 1995).

(48.6, 53.4, 58.4 and 50.6 ppb). At 1900 BT high O<sub>3</sub> concentration is encountered under SW and WSW wind directions (45.8 and 42.8 ppb). In spring at 0100 BT surface O<sub>3</sub> concentration is relatively high under SSW wind direction (39.4 ppb). At 1400 BT besides surface O<sub>3</sub> concentration is high under S, SSW, SW and WSW, the surface O<sub>3</sub> concentration is also higher under NE and SSE wind directions. At 0800 and 1900 BT, wind directions are not directly in relation with high O<sub>3</sub> concentration. In winter there is no clear relationship between wind directions and surface O<sub>3</sub> concentration (see Table 3). In conclusion surface O<sub>3</sub> transport mechanism exists under S and SW wind directions from the observations at Longfengshan station. Harbin lies at NW of Longfengshan station (about 250 km away). No high O<sub>3</sub> concentration is observed under that direction. It is obvious that NW wind has no significant effect on the surface O<sub>3</sub> concentration at Longfengshan regional station. Therefore we can infer that transport effect on O<sub>3</sub> concentration exists under S and SW directions at Longfengshan station.

**Table 3.** Surface O<sub>3</sub> Concentration in Different Wind Directions and Seasons (August 1994—July 1995, Longfengshan Station)

|                     |      |                | N    | NNE  | NE   | ENE  | E    | ESE  | SE   | SSE  | S    | WSW  | SW   | WSW  | W    | WNW  | NW   | NNW  | C    |
|---------------------|------|----------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| Autumn<br>(Time BT) | 0100 | O <sub>3</sub> | 38.9 | 23.5 | 31.8 | —    | 40.1 | 28.3 | 23.4 | 27.1 | 40.7 | 43.0 | 43.5 | 26.4 | 36.3 | 30.3 | 34.2 | 27.4 | 32.0 |
|                     |      | No.            | 1    | 1    | 1    | —    | 2    | 1    | 5    | 15   | 25   | 2    | 7    | 3    | 6    | 1    | 2    | 2    | 3    |
|                     | 0800 | O <sub>3</sub> | 15.9 | 25.9 | —    | —    | 26.9 | —    | 28.4 | 30.9 | 37.6 | 49.3 | 32.6 | 46.0 | 29.7 | 28.3 | 35.5 | —    | —    |
|                     |      | No.            | 3    | 1    | —    | —    | 1    | —    | 10   | 12   | 24   | 7    | 6    | 3    | 3    | 2    | 1    | —    | —    |
|                     | 1400 | O <sub>3</sub> | 49.5 | 63.8 | 32.9 | 63.1 | 60.4 | 47.8 | 50.3 | 57.4 | 48.7 | 50.1 | 52.8 | 48.2 | 43.0 | 50.4 | 38.4 | 47.7 | —    |
|                     |      | No.            | 5    | 1    | 2    | 1    | 1    | 1    | 1    | 1    | 15   | 5    | 11   | 2    | 7    | 9    | 8    | 6    | —    |
|                     | 1900 | O <sub>3</sub> | 51.3 | 51.7 | 44.1 | 47.4 | 47.5 | —    | 33.0 | 45.0 | 47.2 | 49.5 | 46.4 | 38.1 | 44.8 | 56.9 | 44.1 | 31.7 | —    |
|                     |      | No.            | 4    | 2    | 6    | 2    | 1    | —    | 3    | 4    | 19   | 4    | 12   | 2    | 6    | 1    | 7    | 3    | —    |
| Winter<br>(Time BT) | 0100 | O <sub>3</sub> | 31.9 | —    | —    | —    | 32.8 | 32.4 | —    | 32.6 | 28.5 | 27.5 | 25.1 | 25.8 | 22.9 | 26.6 | 29.0 | —    | —    |
|                     |      | No.            | 5    | —    | —    | —    | 1    | 1    | —    | 3    | 22   | 6    | 15   | 4    | 5    | 4    | 1    | —    | —    |
|                     | 0800 | O <sub>3</sub> | —    | —    | —    | —    | 33.9 | 31.0 | 27.6 | 27.7 | 26.8 | 25.7 | 21.3 | 29.2 | 20.1 | 27.8 | 27.5 | —    | —    |
|                     |      | No.            | —    | —    | —    | —    | 1    | 1    | 4    | 5    | 22   | 7    | 16   | 2    | 5    | 3    | 1    | —    | —    |
|                     | 1400 | O <sub>3</sub> | 31.3 | 33.6 | —    | —    | —    | —    | 36.4 | 31.7 | 31.8 | 33.3 | 41.1 | 34.8 | 32.3 | 37.6 | 35.4 | —    | —    |
|                     |      | No.            | 9    | 1    | —    | —    | —    | —    | 1    | 10   | 7    | 16   | 2    | 8    | 4    | 7    | 7    | —    | —    |
|                     | 1900 | O <sub>3</sub> | 33.3 | 32.7 | —    | 34.5 | —    | —    | 34.1 | 32.5 | 31.4 | 27.1 | 32.0 | 33.3 | 30.4 | 37.1 | 34.4 | 27.6 | 41.7 |
|                     |      | No.            | 4    | 2    | —    | 1    | —    | —    | 2    | 1    | 17   | 5    | 11   | 5    | 10   | 1    | 5    | 1    | 2    |
| Spring<br>(Time BT) | 0100 | O <sub>3</sub> | 24.9 | 30.7 | 32.2 | 32.7 | 41.1 | 36.3 | 36.8 | 35.2 | 35.1 | 39.4 | 30.3 | 30.6 | 27.8 | —    | 31.3 | 28.1 | 44.7 |
|                     |      | No.            | 3    | 1    | 2    | 1    | 1    | 3    | 1    | 11   | 21   | 14   | 7    | 3    | 6    | —    | 4    | 3    | 1    |
|                     | 0800 | O <sub>3</sub> | 24.9 | —    | 31.6 | —    | —    | 36.7 | 32.2 | 35.4 | 37.2 | 34.3 | 32.8 | 28.5 | 28.0 | 35.4 | 24.1 | 29.1 | 19.6 |
|                     |      | No.            | 3    | —    | 3    | —    | —    | 3    | 7    | 7    | 24   | 14   | 11   | 5    | 1    | 1    | 5    | 2    | 1    |
|                     | 1400 | O <sub>3</sub> | 37.2 | 36.1 | 51.1 | —    | —    | —    | 47.2 | 45.0 | 43.2 | 45.6 | 48.6 | 39.9 | 38.9 | 36.2 | 36.7 | —    | —    |
|                     |      | No.            | 7    | 3    | 2    | —    | —    | —    | 5    | 10   | 16   | 5    | 2    | 8    | 5    | 7    | 7    | —    | —    |
|                     | 1900 | O <sub>3</sub> | —    | —    | 39.9 | —    | 48.4 | 48.4 | 42.4 | 44.4 | 43.5 | 41.3 | 37.9 | 38.0 | 32.2 | 40.3 | 36.0 | 34.7 | —    |
|                     |      | No.            | —    | —    | 4    | —    | 2    | 1    | 3    | 1    | 19   | 9    | 7    | 5    | 6    | 7    | 11   | 9    | —    |
| Autumn<br>(Time BT) | 0100 | O <sub>3</sub> | 24.1 | 25.0 | 11.4 | —    | 26.3 | 23.4 | 27.4 | 19.1 | 25.0 | 38.4 | 22.7 | —    | —    | 13.2 | —    | 17.7 | —    |
|                     |      | No.            | 1    | 1    | 2    | —    | 1    | 1    | 4    | 11   | 11   | 5    | 1    | —    | —    | 1    | —    | 1    | —    |
|                     | 0800 | O <sub>3</sub> | 42.1 | —    | 20.5 | 22.6 | 13.1 | 27.2 | 23.5 | 29.3 | 38.7 | 33.0 | 22.0 | 42.3 | 17.9 | —    | 27.5 | 31.9 | 36.5 |
|                     |      | No.            | 2    | —    | 5    | 2    | 1    | 1    | 13   | 8    | 13   | 8    | 1    | 1    | 1    | —    | 1    | 1    | 2    |
|                     | 1400 | O <sub>3</sub> | 40.0 | 39.0 | 29.2 | 23.3 | 41.6 | 39.3 | 50.6 | —    | 39.1 | 48.6 | 53.4 | 58.3 | 40.6 | —    | 31.4 | 37.5 | —    |
|                     |      | No.            | 9    | 3    | 3    | 1    | 4    | 1    | 7    | —    | 11   | 6    | 4    | 2    | 6    | —    | 3    | 2    | —    |
|                     | 1900 | O <sub>3</sub> | 31.9 | —    | 26.9 | 40.8 | 33.9 | —    | 35.3 | 30.9 | 38.6 | 38.3 | 45.8 | 42.8 | 36.0 | 39.8 | 32.8 | 35.1 | 22.1 |
|                     |      | No.            | 3    | —    | 3    | 2    | 1    | —    | 3    | 2    | 15   | 4    | 7    | 2    | 1    | 2    | 5    | 7    | 1    |

3. Global Radiation

Average O<sub>3</sub> concentration is compiled under fine and cloudy days at every 100 W m<sup>-2</sup> interval of global radiation intensity. At 0800 and 1400 BT, O<sub>3</sub> concentrations are

consistent with global radiation intensity at the same time while O<sub>3</sub> concentrations at 1000 and 1600 BT are consistent with radiation intensity at 0800 and 1400 BT respectively. In autumn at 0800 BT O<sub>3</sub> concentration increases with the increase of global radiation intensity. Average O<sub>3</sub> concentration increases by 1 ppb when radiation intensity increases by about 100 W m<sup>-2</sup>. At 1000 BT, O<sub>3</sub> concentration shows clear increase with radiation intensity compared with that at 0800 BT and the amplitude of the increase is also higher (O<sub>3</sub> concentration increases by 2.5 ppb with every 100 W m<sup>-2</sup> of radiation intensity increase). At 1400 and 1600 BT, O<sub>3</sub> concentration increases by over 2 ppb every 100 W m<sup>-2</sup> rise of global radiation intensity except for the test results obtained at 100–200 W m<sup>-2</sup> radiation intensity group, due to lack of enough data. Furthermore clearer relationship between O<sub>3</sub> concentration at 1600 BT and radiation intensity at 1400 BT exists comparing the relationship between O<sub>3</sub> concentration at 1400 BT and radiation intensity at 1400 BT (see Fig. 4).

The relationship between O<sub>3</sub> concentration and global radiation is more consistent in winter than that in autumn. Every 100 W m<sup>-2</sup> rise in radiation intensity, O<sub>3</sub> concentration increases by 3.6 ppb at 0800 BT, by 3.2 ppb at 1000 BT, by 2.8 ppb at 1400 BT, by 3.5 ppb at 1600 BT. The relationship between surface O<sub>3</sub> concentration and global radiation is similar in winter and spring. Surface O<sub>3</sub> concentration increases with the rise in global radiation except for the radiation intensity of 601–700 W m<sup>-2</sup> at 1600 BT. At 0800 BT, surface O<sub>3</sub> concentration increases by 3.1 ppb every 100 W m<sup>-2</sup> rise in total radiation; by 2.9 ppb at 1000 BT; by 1.6 ppb at 1400 BT; by 2.1 ppb at 1600 BT. There are no enough data available under fine days in summer.

Through the above analysis we can see: (1) O<sub>3</sub> concentration in the afternoon is higher than that in the morning at 0800 BT by over 20 ppb under the same radiation intensity, which is probably the result of different photochemical reaction rate. Strong turbulence in the afternoon results in higher photochemical reaction rate. (2) The relationship between O<sub>3</sub> concentration and global radiation delayed 2 h is better than that between O<sub>3</sub> concentration and global radiation at the same time. Relationships between surface O<sub>3</sub> concentration and infrared and ultraviolet radiation are similar to what mentioned above.

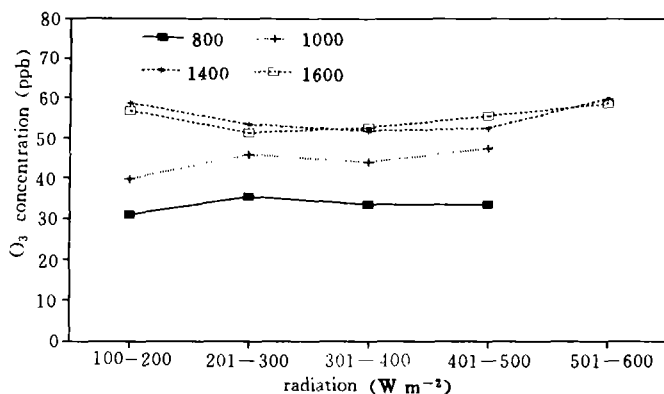


Fig. 4. Surface O<sub>3</sub> concentration versus global radiation intensity in different times (Longfengshan, September–November, 1994).

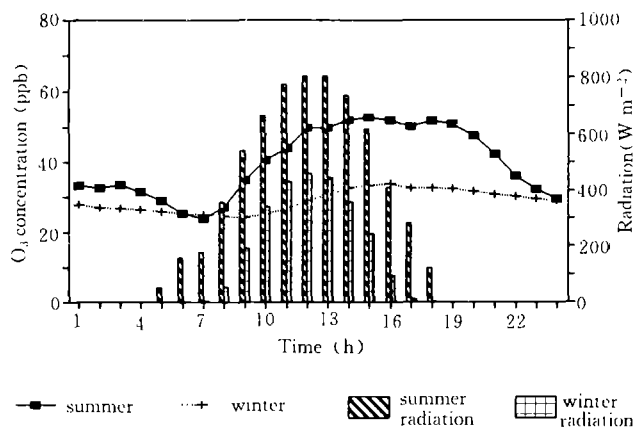


Fig. 5. Diurnal variation of surface  $O_3$  and global radiation in summer and winter (Longfengshan, August, 1994–July, 1995).

The relationship between surface  $O_3$  concentration and radiation also varies with seasons. Hourly average surface  $O_3$  concentration and corresponding radiation are shown in Fig. 5 under fine days in summer and winter. It can be seen from Fig. 5 that, average peak value of surface  $O_3$  concentration in summer is over 50 ppb while in winter lies over 30 ppb. The difference between summer and winter is about 20 ppb. Global radiation in summer is approximately  $800 W m^{-2}$ , while  $400-500 W m^{-2}$  in winter. The difference in global radiation between summer and winter is about one fold.

$O_3$  concentrations are compared between data collected under 5 fine days at every hour in autumn from Longfengshan station and Lin'an station. These two stations have similar environmental conditions with about same longitude (see Fig. 6). Both diurnal variations are very similar.

However average  $O_3$  concentration at Lin'an station is always higher than that at Longfengshan station. The difference is always around 6–24 ppb except for result obtained at 0800 BT. Right after sunrise, this difference is small and becomes bigger

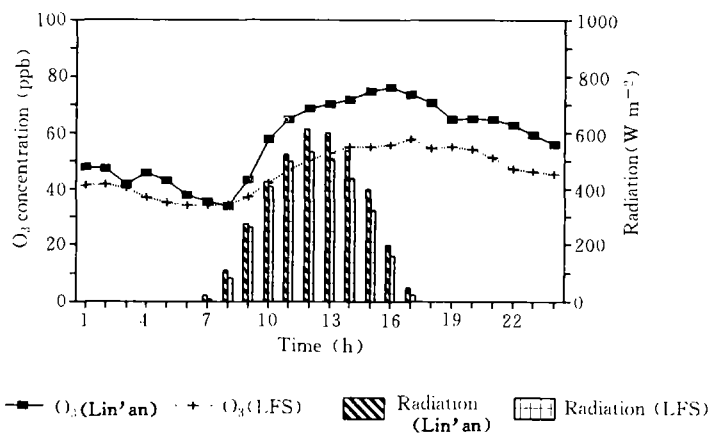


Fig. 6. Surface  $O_3$  and global radiation at south and north stations in autumn (September–November, 1994).

gradually after 1000 BT. The maximum difference occurs at 1500 BT. The average of the difference is about 11 ppb. This difference is mainly caused by the difference in global radiation due to different latitudes of these two stations (44°44'N at Longfengshan, 30°18'N at Lin'an): In the morning the global radiation at these two stations is about the same. However the difference gradually gets bigger after 1000 BT. The maximum difference occurs at 1200 BT ( $94 \text{ W m}^{-2}$ ) and then it becomes smaller until sunset.

#### 4. Temperature and Sunshine Time

Average daily temperature and its corresponding average daily O<sub>3</sub> concentration are compiled statistically. No straight relationship is seen from the data collected. Also there is no clear evidence to show the relationship between daily accumulated sunshine time and average daily O<sub>3</sub> concentration.

#### 5. Correlation Analysis

Table 4 shows the correlation coefficient of the average daily O<sub>3</sub> concentration and wind speed, temperature, SO<sub>2</sub>, NO<sub>x</sub>, accumulated daily global radiation and accumulated daily sunshine time. As the number of samples varies, we only lists critical correlation coefficient with 0.01 degrees of confidence of 40, 60, 70 and 90 samples. Between the average daily surface O<sub>3</sub> and the average daily wind speed and the average daily SO<sub>2</sub> there shows a strong correlation in all seasons except in winter. This is especially true in autumn. The average daily surface O<sub>3</sub> and the accumulated daily global radiation demonstrate a little correlation in winter and spring. There is a relatively obvious correlation between the average daily surface O<sub>3</sub> and the average daily temperature in spring. Therefore parameters other than the average daily wind speed and average daily SO<sub>2</sub> show no obvious correlation with the average daily O<sub>3</sub> concentration. Hence using only the average daily value of all the parameters concerned to study the relationship between the surface O<sub>3</sub> concentration and meteorological conditions is not adequate. A more detailed analysis needs to be carried out.

**Table 4.** Correlation Coefficient between O<sub>3</sub> and Other Parameters \*

|        |     | SO <sub>2</sub> | NO <sub>x</sub> | G     | V      | S     | T      |
|--------|-----|-----------------|-----------------|-------|--------|-------|--------|
| Spring | cc  | 0.333           | -0.159          | 0.312 | 0.339  | 0.201 | 0.584  |
|        | No. | 90              | 90              | 90    | 90     | 90    | 90     |
| Summer | cc  | 0.474           | 0.334           | 0.135 | 0.392  | 0.326 | 0.355  |
|        | No. | 60              | 60              | 60    | 60     | 60    | 60     |
| Autumn | cc  | 0.748           | -0.079          | 0.153 | 0.618  | 0.335 | -0.029 |
|        | No. | 72              | 44              | 72    | 72     | 72    | 72     |
| Winter | cc  | -0.183          | -0.132          | 0.461 | -0.308 | 0.222 | 0.303  |
|        | No. | 69              | 69              | 69    | 69     | 69    | 69     |

\* G global radiation ( $\text{MJ m}^{-2}$ ); V wind speed ( $\text{m s}^{-1}$ ); S sunshine time (h); T temperature ( $^{\circ}\text{C}$ ); cc correlation coefficient.  $f = 90$ ,  $\alpha = 0.01$ ,  $P = 0.2673$ ;  $f = 70$ ,  $\alpha = 0.01$ ,  $P = 0.3017$ ;  $f = 60$ ,  $\alpha = 0.01$ ,  $P = 0.3248$ ;  $f = 40$ ,  $\alpha = 0.01$ ,  $P = 0.3932$ , where  $f$  is the number of samples,  $\alpha$  degree of confidence,  $P$  critical correlation coefficient.

### III. CONCLUSIONS

(1) Diurnal variability of the surface  $O_3$  shows a double-peak pattern with daily amplitude of 27–28 ppb in summer and autumn under fine days. In overcast days diurnal variation of the surface  $O_3$  is noticeable, however its daily amplitude is relatively small (about 14 ppb). In rainy days the variation shows irregular change pattern and its daily amplitude is 7–10 ppb, which depends on the raining time and rainfall amount.

(2) At 0800 and 1400 BT in autumn, at 0100 and 0800 BT in spring, at 0100 and 0800 BT in summer, the surface  $O_3$  concentration increases with the increase of ground wind speed. When wind speed is greater than  $7 \text{ m s}^{-1}$  the surface  $O_3$  concentration increases rapidly.

(3) In most of the times while there are S, SSW, SW and WSW wind directions, the surface  $O_3$  is high in concentration. This is probably due to the transport effect in these directions.

(4) At 0800 BT under fine days in winter, spring and autumn, surface  $O_3$  concentration tends to increase with the increase of global radiation. This is even more obvious when comparing radiation at 0800 BT and 1400 BT with surface  $O_3$  at 1000 BT and 1600 BT respectively.

(5) The average peak value of surface  $O_3$  concentration under fine days in summer is higher than that in winter by about 20 ppb, while the average peak value of global radiation is almost twice as high as in winter.

(6) Comparing the average hourly surface  $O_3$  concentration during 5 fine days at Longfengshan station with that at Lin'an station, both are similar in longitude, the concentration in the former is always lower than that in the latter station by 6–24 ppb, except at 0800 BT. Its difference maximizes at 1500 BT and the average difference is 11 ppb. The main reason is due to the difference in global radiation (difference of about  $100 \text{ W m}^{-2}$ ) caused by different latitude of these two stations.

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