PRELIMINARY STUDY OF VARIATION OF SO_2 AND AEROSOL PARTICLE BACKGROUND CONCENTRATIONS IN THE EASTERN CHINA

Luo Chao (罗 超), *Ding Guo'an* (丁国安), *Yang Dongzhen* (杨东贞), *Tang Jie* (汤 杰) and *Zhou Xiuji* (周秀骥)

Chinese Academy of Meteorological Sciences, Beijing 100081

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ABSTRACT

The average concentrations of sulphur dioxide, sulfate aerosol and TSP were about 8—10 ppb, 15.08 $\mu g\ m^{-3}$, and 241.40 $\mu g\ m^{-3}$ respectively, which were measured at the Lin'an regional background station during August—November, 1991. The higher concentrations of SO_2 and SO_4^{2-} maybe acidify the rainfall. It has a great influence upon the human health and ecosystem. The simulated results indicate that the distributions of SO_2 and SO_4^{2-} were determined by local emission sources. Average aerosol particle number density was $2.0 \times 10^4\ cm^{-3}$. It shows that social development and human activities strongly affect the atmospheric background level.

Key words: TSP, aerosol particle, background concentration

1. INTRODUCTION

SO_2 and SO_4^{2} particles are the main pollutants in the atmosphere. It is harmful to human health and the ecosystem, reduces visibility, and acidifies rainfall. From the recent studies (Charlson et al. 1992; Hofmann 1992; Keys et al. 1993) the sulfur aerosol particles not only influence the global climate change but also destroy the stratosphere ozone through heterogeneous reactions on the particle surface. The residence times of SO_2 and SO_4^{2-} in the atmosphere are longer; therefore they can transport a long distance. Study of the sulfur cycle becomes an important subject of the environmental and atmospheric sciences.

The NASA GTE / PEM–WEST A (Global Troposphere Experiment / Pacific Expedition Mission–West A) was conducted in the west region of the Pacific Ocean during the months of August through November, 1991. It was the first comprehensive study of tropospheric chemistry in the clean, remote area. Since cycles involving trace gases are chemically coupled, it is particularly important to measure a comprehensive set of species simultaneously. Such measurements not only enhance our knowledge of distribution of the species, but also serve to test and validate the models which simulate chemical reactions in the troposphere.

So far, representative data are relatively sparse in the West Pacific region, especially in China. During the PEM–WEST Phase A, collaborative measurements were conducted by the Chinese Academy of Meteorological Sciences and the Georgia Institute of Technology at Lin'an Regional Atmospheric Background Station of China. Chemical measurements include: O_3, NO, NO_x, HNO_3, NO_3^-, SO_2, SO_4^{2-}, aerosol particle size distribution, meteorological

parameters, etc. In this paper, we will present some measured and simulated results.

II. EXPERIMENT

The measurement site was located in a mountainous area (30°25′N, 119°70′E, 132 m above the sea level) in Lin'an County, Zhejiang Province which is on the coast of the Chinese Mainland. The site is a weather station, and is located 10 km east of the Lin'an Town that has a population of about 50 000, 53 km west of Hangzhou, the provincial capital that has a population of 1 million. About 210 km to the northeast of Hangzhou, is China's largest and most important industrial city, Shanghai. To the west of the monitoring site is mountainous, usually less developed and less populated regions. There are several small villages around the monitoring site within 2 km range. The measurement site was located on a small hill with a mean elevation of 132 m. Surrounding areas are moderately covered with newly planted pine trees. The area is far way off a highway and thus there was no automobile activity in the immediate vicinity of the site.

III. ANALYTICAL TECHNIQUE

Ozone was measured with a photometric ozone analyzer (Thermo Environment Inc. Model 49) with the measuring precision being of 1 ppbv. SO_2 was determined with a pulsed fluorescence SO_2 analyzer (Thermo Environment, Inc. Model 43A). The measurement precision is 0.1 ppb. Sulfates were collected by a filter in a high–volume sampler. The collected samples were extracted into a buffer solution and then analyzed with an ion chromatography. The flow rate of air sample was measured using a mass flow meter.

Aerosol particle size was measured by the particle size instrument (model CSASP–100) made by PMS company of USA.

IV. RESULTS AND DISCUSSIONS

1. *Characteristics of Surface SO_2 Variation*

Figure 1 shows the daily average variation of the surface SO_2 measured in Lin'an during August—November, 1991. It can be seen that the daily average SO_2 concentration was about 8 ppb before October, and 10 ppb after October. Because at Lin'an station, nearby biomass burning could be visually seen during the period of measuremen after October, the increase of SO_2 after October may be caused by biomass burning. The SO_2 concentration in the Lin'an background station was higher than in other remote areas such as Lushan Mountain of Jiangxi Province (about 0.15 ppb), and Baiyun Mountain of Guangdong Province (about 1.15 ppb), and annual average SO_2 in the eastern coast of USA (about 4—6 ppb). In the northwest part of China (Waliguan Mountain), the SO_2 concentration was below 0.1 ppb. The atmospheric background levels of some species in developed region of the eastern China are much higher than that in remote clean areas of the northeastern China. It means that the social development and human activities strongly influence the atmospheric background level.

The diurnal variation of SO_2 averaged from all the sunny and overcast days was shown in Fig. 2. From Fig. 2 it can be seen that SO_2 is higher in the daytime and lower in the nighttime. The lowest concentration of SO_2 occurs in the afternoon. With the sunset it begins to increase. This is because SO_2 is mainly oxidized by the $SO_2+OH^- \rightarrow SO_4^{2-}$, and $SO_2+RO_2 \rightarrow SO_4^{2-}$

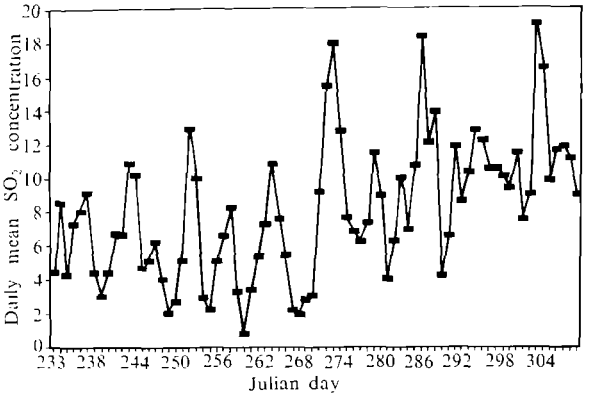

Fig. 1. The variation of daily mean SO_2 concentration.

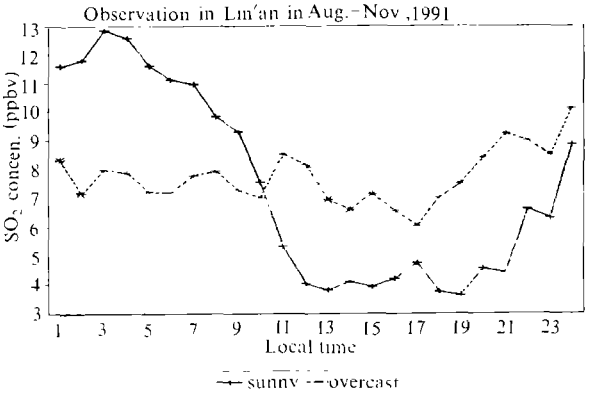

Fig. 2. The diurnal variations of SO_2 in sunny and overcast days.

reactions. In the sunny day afternoon, OH^- and RO_2 concentrations are the highest. With sunset the photochemical reactions cease, OH^- and RO_2 concentrations sharply decrease. Therefore SO_2 is higher in the daytime and lower in the nighttime. Figure 2 also shows that there is no SO_2 diurnal variation in the overcast days. In sunny days the vertical diffusion is stronger in the daytime. It also can cause SO_2 concentration to decrease in the daytime.

2. *Characteristics of* SO_4^{2-} *and TSP (Total Suspended Particles) Variation*

The variations of daily average SO_4^{2-} and TSP are shown in Fig. 3. The average concentrations of SO_4^{2-} and TSP are 15.08 $\mu g\ m^{-3}$ and 241.40 $\mu g\ m^{-3}$ respectively. The concentration of SO_4^{2-} is higher in Lin'an than in other remote clean areas, such as Lushan Mountain (about 6.11 $\mu g\ m^{-3}$), and also is higher than the annual average SO_4^{2-} concentration (10 $\mu g\ m^{-3}$) (NAPAP 1987). The original natural background SO_4^{2-} is about 2 $\mu g\ m^{-3}$. Now the

SO_4^{2-} concentration in the atmosphere is about five times as much as the natural background level due to human activities. The ratio of SO_4^{2-} to TSP is about 10%. The sizes of most SO_4^{2-} particles are less than 2 μm. The SO_4^{2-} pollutant is harmful to human health and the ecosystem, and also affects the global climate change. Energy in our country mainly comes from fossil fuel burning. Therefore SO_2 and SO_4^{2-} pollution is the main environmental problem.

3. *Theoretical Analysis*

In order to understand the variation and distribution of SO_2 and SO_4^{2-}, we used the three dimensional Eulerian regional air quality model to simulate the situation on October 2—5, 1991. The model system contains two major components: the dynamic and air quality models. Following Chang et al. (1987) the dynamic model is run off-line using the mesoscale meteorological model (MM4) and generates meteorological and physical variables that are used as input for the air quality model. The chemical mechanism of Stockwell (1986) was used and modified. The deposition rate and photolysis rate constants were calculated by the methods given by Chang et al. (1987). The model was divided into 15 unequally spaced vertical layers, and has a horizontal resolution of 60×60 km^2. The emission data used in the model were calculated according to the amounts of consumed energy using the method of Kato (1992). The scenario of SO_2 emission used in the model was shown in Fig. 4. Figures 5 and 6 are the surface distributions of SO_2 and SO_4^{2-} simulated by using above described model. Comparing Figs. 5 and 6 with Fig. 4, we can see that distributions of SO_2 and SO_4^{2-} concentrations are coincided basically with SO_2 emission. It means that surface SO_2 and SO_4^{2-} are determined by the local emission sources. SO_2 and SO_4^{2-} are higher in the eastern China than in a remote clean area such as the Waliguan Mountain. It means that human activities and industrial development are the dominated factor that influences the environment. The residence time of SO_4^{2-} is longer than that of SO_2, so the SO_4^{2-} pollution range is larger.

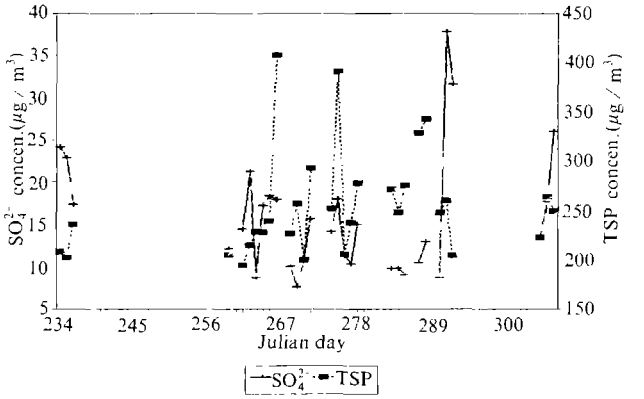

Fig. 3. The variations of daily mean SO_4^{2-} and TSP.

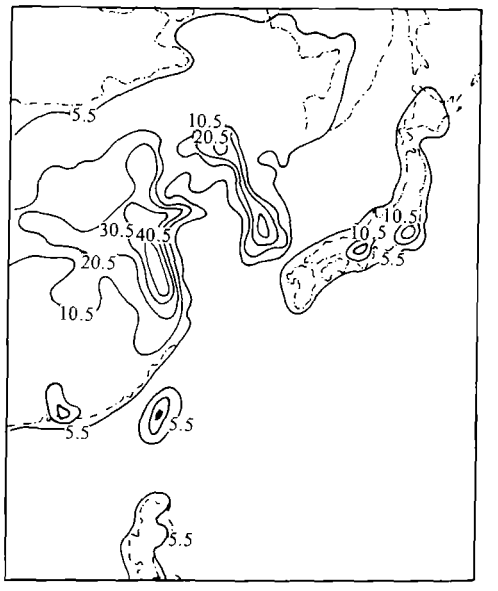

Fig. 4. The SO_2 emission used in the model.

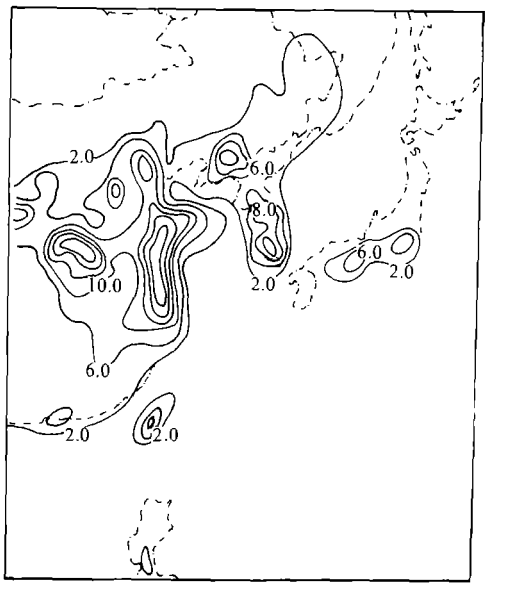

Fig. 5. The distribution of SO_2 (ppbv), averaged over 1—9 (GMT) on Oct. 5, 1991 on the surface layer.

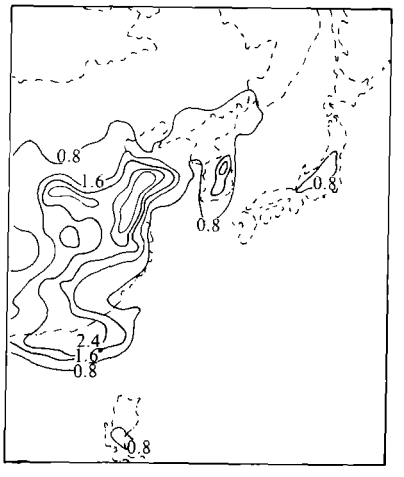

Fig. 6. The distribution of SO_4^{2-} (ppbv), averaged over 1—9 (GMT) on Oct. 5, 1991 on the surface layer.

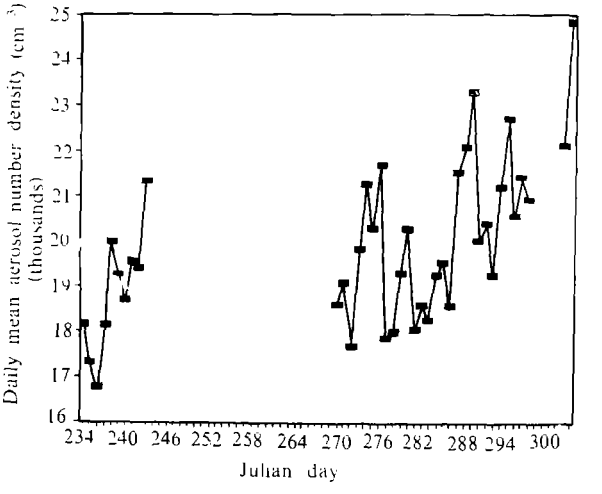

Fig. 7. The variation of daily mean aerosol particle density.

4. *Surface Aerosol Particle Variation and Its Relationship with Surface Ozone*

The daily average aerosol particle number density increased after October that is shown in Fig. 7. The trend of aerosol particle variation is same as that of SO_2. There is a good relationship between SO_2 and aerosol particle numbers that is shown in Fig. 8. The relationship means that SO_2 and SO_4^{2-} come from the same sources, and the SO_4^{2-} was produced by SO_2 oxidation. The average aerosol particle number density was 2.0×10^4 cm^{-3}. The concentration is higher for the clean area. The number of aerosol particles whose sizes are less than 2 μm is about

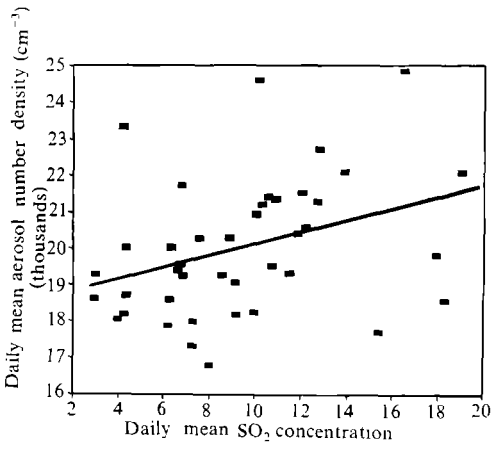

Fig. 8. The relationship between daily mean SO_2 and daily mean aerosol particle number density.

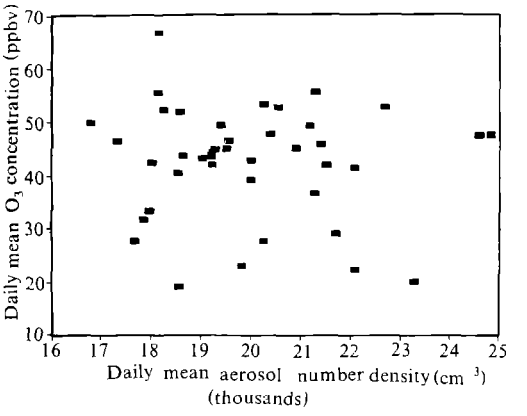

Fig. 9. The scatter plot of daily mean aerosol particle number density and daily mean O_3 concentration.

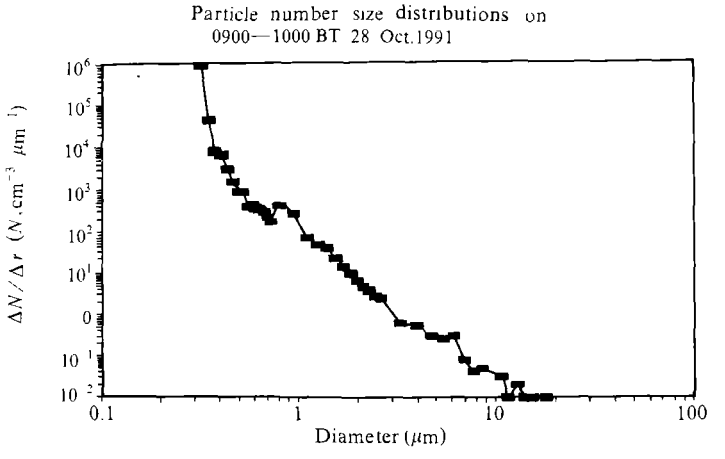

Fig. 10. The size distribution of aerosol particles.

98% of total number that is derived from Fig. 9. It is said that the heterogeneous reactions can occur in wet aerosol particle surface when $RH > 50\%$. This processes can destroy ozone. We analyzed the data of ozone and aerosol particle number density that are measured at the same time. The relative humidity was above 65% during the experiment. There is no obvious relation between ozone and aerosol particle concentrations that is shown in Fig. 10. The question is very complex, and should be thoroughly investigated and studied.

V. CONCLUSIONS

(1) The background concentrations of SO_2 and SO_4^{2-} in the middle latitude of the eastern China were 8—10 ppbv and 15.08 $\mu g\ m^{-3}$ respectively. The concentrations were higher in the clean area and can acidify the rainfall. It is harmful to human health and the ecosystem.

(2) From the simulated results by the model, it is shown that the local emission sources control the surface SO_2 and SO_4^{2-} concentrations and distributions. SO_4^{2-} is the secondary pollutant that is produced by SO_2 oxidation. The sizes of the most SO_4^{2-} particles are less than 2 μm. It has longer residence time and can hurt the ecosystem.

(3) The average particle number density was about 2×10^4 cm^3 in middle latitude of the eastern China in fall. The number of particles whose sizes are less than 2 μm is about 98% of the total number. The content of SO_4^{2-} in the aerosol particles is higher comparing with other constituents. There is a good relationship between SO_2 and SO_4^{2-}. There is no obvious relation between surface ozone and surface aerosol particle concentrations. This question is very complex, and should be thoroughly investigated and studied.

REFERENCES

Chang, J. S. et al. (1987), A three-dimensional Eulerian acid deposition model: Physical concepts and formulation, *J. Geophys. Res.*, **92:** 14681—14700.

Charlson, R. J. et al. (1992), Climate forcing by Anthropogenic aerosols, *Science*, **255:** 423—430.

Hofmann, D. J. et al. (1992), Observation and possible causes of new ozone depletion in Antarctica in 1991, *Nature*, **359:** 283—287.

Kato, N. et al. (1993), Anthropogenic emission of SO_2 and NO_x in Asia: Emission Inventories, *Atmos. Environ.*, **26:** 2997—3017.

Keys, J. G. et al. (1993), Evidence for heterogeneous reactions in the Antarctic autumn stratosphere, *Nature*, **361**, 49—51.

NAPAP (1987), The National Acid Precipitation Assessment Program III, 1987.

Stockwell, W. R. (1986), Homogeneous gas phase mechanism for use in a regional acid deposition model, *Atmos. Environ.*, **20:** 1615—1632.