CHEMISTRY LETTERS, pp. 1037-1040, 1981.

SULFATE AND NITRATE CONCENTRATION IN AEROSOL ABOVE KANTO AREA

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The concentration of sulfate and nitrate in aerosol above Kanto area was measured by aircraft on 6 th and 7 th August 1980 as a survey of photochemical smog. The concentration variation of both ions coincided with that of ozone throughout the field observation. This phenomenon is explained that the formation mechanism of sulfate and nitrate is closely concerned with that of ozone formation. The transport of ozone, sulfate and nitrate is governed mainly by Sagami Bay sea breeze and Kashima Nada sea breeze.

Particulate sulfate and nitrate are major compound concerning photochemical air pollution by its adverse health effects. The concentration of sulfate was measured frequently at ground and above ground, by means of filter sampling subsequent wet chemical analysis[1,2,3,4,5], ion chromatographic analysis[6] and continuous in situ monitoring using flame photometry[7], but that of nitrate was not measured by high time resolution sampling above ground. Grosjean and Friedlander observed ozone and nitrate at ground on 25 th July 1973. For this day the maximum particulate nitrate and ozone concentrations occurred at the same time. Because of the high ozone concentration for that day, OH radical formation was probably high[8] leading to nitric acid production by reaction of $OH + NO_2 \longrightarrow HONO_2$.

We measured sulfate and nitrate concentration variation above Kanto area by as short as five minutes sampling and observed horizontal distribution of particulate sulfate and nitrate showing the peak concentration correspondence of both ions and ozone predicting the formation of both ions is same as that of ozone.

The sampling tube made of Teflon was extended at the head of the nose of the aircraft, Cessna 404. The flight speed of the aircraft was about 70 m/sec. High volume sequential sampler ca. 300 ℓ/min was equipped in the aircraft and the atmospheric aerosol was collected in every 5 minutes on to Fluoropore AF07P filter (Sumitomo Denko Co. LTD). The deposited area was cutted and water soluble sulfate and nitrate was extracted about 30 minutes by electrical shaker with 10 mℓ of eluent of ion chromatography. The concentration of both ions was analysed by ordinary ion chromatograph, (A Dionex Model 10 Ion Chromatograph, injecting loop: 0.1 mℓ, eluent: 0.003 M $NaHCO_3$, 0.0024 M Na_2CO_3, anion precolumn, anion separator column: 3 × 250 mm, anion suppressor column: 6 × 250 mm).

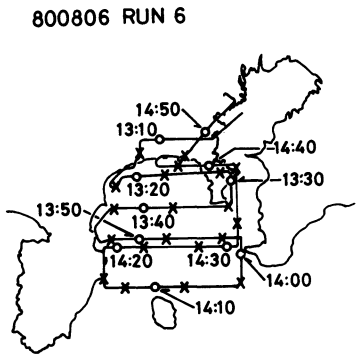

Fig. 1 Flight course map of Run 6.

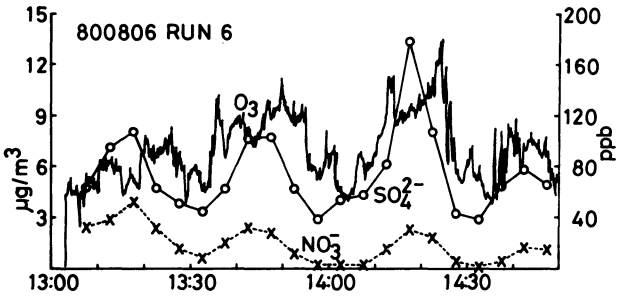

Fig. 2 Concentration variation of sulfate, nitrate and ozone of Run 6. Sulfate and nitrate in $\mu g/m^3$, and ozone in ppb.

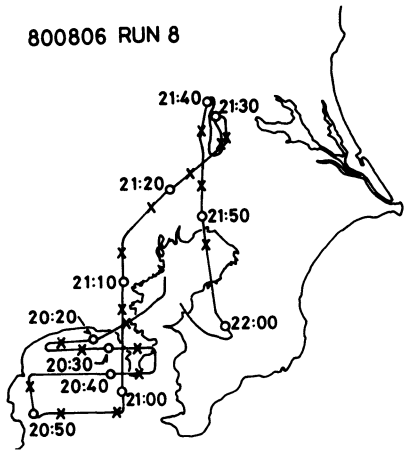

Fig. 3 Flight course map of Run 8.

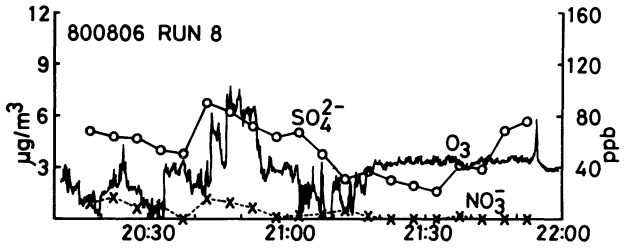

Fig. 4 Concentration variation of sulfate, nitrate and ozone of Run 8.

The error of sulfate and nitrate concentration determination may be caused by sampling loss of large particle by long sampling tube, unaccuracy of sampling flow rate, extraction efficiency of water soluble anion and error of analysis by ion chromatography. But these factor may not exceed 10 % as total error. Ozone was monitored by ethylene chemiluminescent detection and data acquisition system. The whole analysis system by aircraft is described elsewhere[9].

The field study was conducted on 6 th and 7 th August 1980. Five Runs (Run 6, 6 th 13:00 ∿ 15:00, Run 8, 6 th 20:00 ∿ 22:00, Run 10, 7 th 4:00 ∿ 6:00, Run 12, 7 th 10:00 ∿ 12:00, Run 14, 7 th 16:00 ∿ 18:20) are the flight of about 380 ∿ 430 m. But the height of flights (Run 6, 14:15 ∿ , Run 8, 21:45 ∿ 21:50, Run 10, 5:45 ∿ , Run 12, 11:24 ∿ , Run 14, 16:40 ∿ 17:10) was about 600 m above ground. Figures 1,3,5,7,9 show flight course and time, and mid point of 5 minutes sampling shown as × in the Kanto area map. Figures 2,4,6,8,10 show the concentration variation of sulfate, nitrate and ozone by the unit of $\mu g/m^3$ and ppb, respectively. In Run 6, 8 and 10, northeast wind is blowing mainly and in Run 12 and 14 southeast wind is blowing according to the pilot balloon observation. In Run 6, a northeast wind is blowing, so the flight course is taken above Sagami Bay as is shown in Fig. 1. The horizontal concentration variation of sulfate, nitrate and ozone is shown in Fig. 2. The time coincidence of concentration increase of sulfate, nitrate and ozone is very good showing peaks at 13:18, 13:45 and 14:20, at the east of Izu Peninsula. The northeast wind transported the pollutants southwestward, and accu-

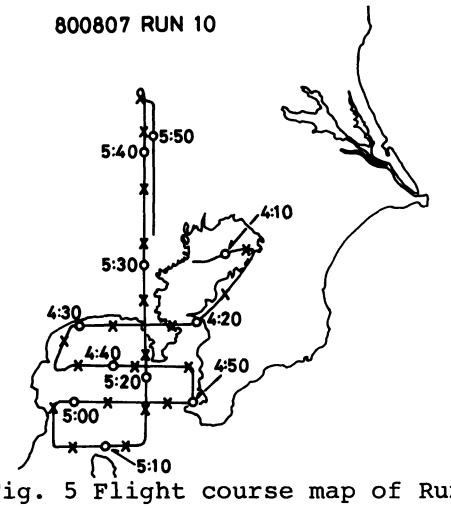

Fig. 5 Flight course map of Run 10.

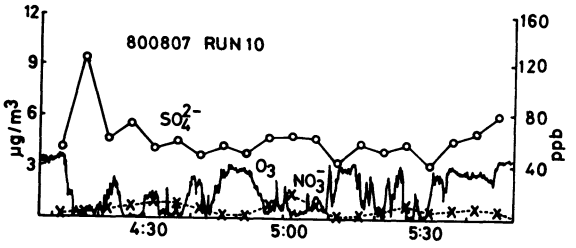

Fig. 6 Concentration variation of sulfate, nitrate and ozone of Run 10.

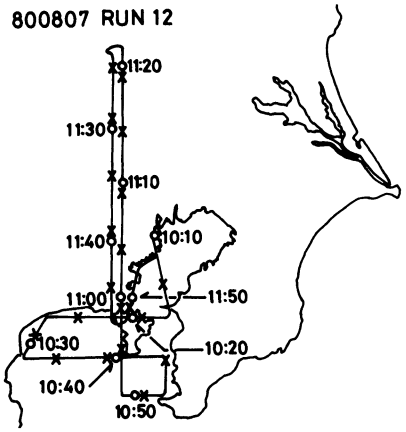

Fig. 7 Flight course map of Run 12.

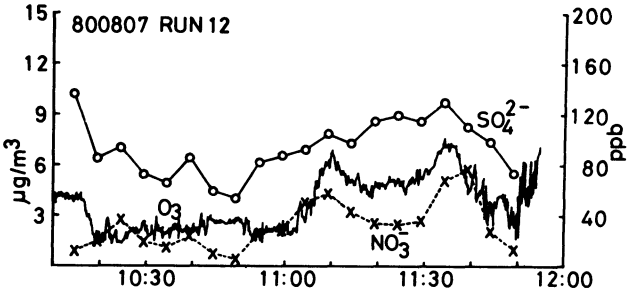

Fig. 8 Concentration variation of sulfate, nitrate and ozone of Run 12.

mulated sulfate, nitrate and ozone at the east of Izu Peninsula, because the mountains of Izu Peninsula acted as a wall to stop the transport of pollutants. In Run 8, as is shown in Figs. 3 and 4, the concentration of pollutants is decreased dramatically by removal of particulate matter and stopping of photochemical reaction. From 21:20, the concentration of ozone and nitrate were 40 ppb and 0 $\mu g/m^3$, respectively. In Run 10, the concentration of sulfate and nitrate was as low as about 5 $\mu g/m^3$ and 1 $\mu g/m^3$, respectively, showing no maxima throughout the flight course except 4:10 $\sim$ 4:20 as is seen in Fig. 6. The sulfate maximum at 4:17 is considered to be emitted particulate matter by Keiyo industrial area as a plume, because nitrate shows no maximum at this point. The concentration of sulfate and nitrate is averaged in night time by complete mixing of the air and the maxima of both ions in the east of Izu Peninsula are disappeared.

In Run 12, the ultraviolet radiation was increased a little and the photochemical reaction started showing ozone peak at 11:00 about 80 ppb and at 11:35 about 100 ppb above Tokyo Metropolitan area. Sulfate and nitrate also were increased at that point of ozone maxima showing about 9 $\mu g/m^3$ and 5 $\sim$ 6 $\mu g/m^3$, respectively. The time variation of sulfate, nitrate and ozone is closely correlated as shown in Fig. 8. These results suggest that the formation mechanism of sulfate and nitrate is resembled with that of ozone. Calvert et al.[10] exhibited the oxidation of sulfur dioxide by the way of $HO + SO_2 \longrightarrow HOSO_2$, $HO_2 + SO_2 \longrightarrow HO + SO_3$, $CH_3O_2 + SO_2 \longrightarrow CH_3O + SO_3$, $SO_3 + H_2O \longrightarrow H_2SO_4$. Gay and

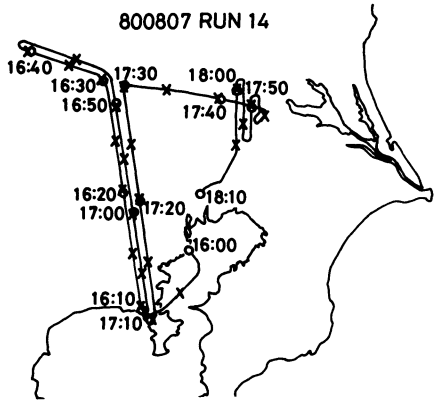

Fig. 9 Flight course map of Run 14.

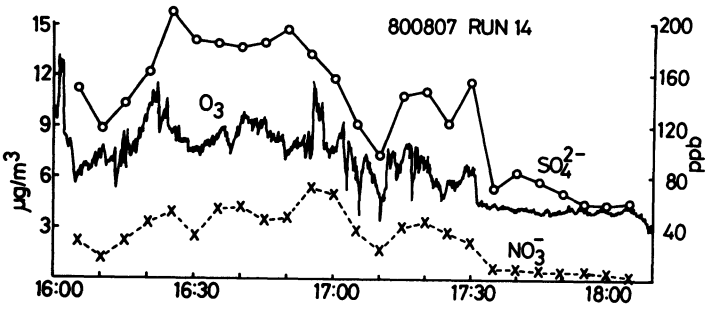

Fig. 10 Concentration variation of sulfate, nitrate and ozone of Run 14.

Bufalini[11] showed nitric acid formation by two ways, $OH + NO_2 \longrightarrow HONO_2$ and $N_2O_5 + 2H_2O \longrightarrow 2HNO_3$. The formation of sulfate and nitrate which proceed by these mechanisms is also considered above ground because the simultaneous increase of ozone, OH, HO_2 and CH_3O_2 is predicted by Graedel et al.[8] at photochemical smog episode.

In Run 14, ozone concentration was as high as 100 ppb from 16:20 to 17:00 as shown in Fig. 10. The sulfate and nitrate was increased at the same time about 14 $\mu g/m^3$ and 5 $\mu g/m^3$, respectively, showing the same coincidence of increase of ozone and both ions as is in Run 12. In this Run the pollutant maxima are transported northward as compared with Run 12 by the Sagami Bay sea breeze. From 17:30 the flight course was taken bound for east, then ozone, sulfate and nitrate was decreased dramatically as low as 50 ppb, 6 $\mu g/m^3$ and 1 $\mu g/m^3$, respectively. The clean sea breeze of Kashima Nada from east affects these concentration variation. From Run 12 and 14 it is seen that the sulfate and nitrate is transported from south to north by Sagami Bay sea breeze, and the concentration of both ions are high in Tokyo Metropolitan area, and moving to north in the afternoon to be highest in Saitama Prefecture. In Kanto area the ozone, sulfate and nitrate maxima is governed by two sea breezes mainly.

Acknowledgement The authors wish to express their thanks to Dr. Y. Ogawa and M. Suzuki in our Institute, K. Goi in the Saitama Institute of Environmental Pollution, Y. Aburamoto in the Toyama Environmental Center, and H. Kurita in the Nagano Research Institute for Health and Pollution for the cooperation of aircraft field study

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(Received May 15, 1981)