Photochemical pollution in Lanzhou, China
— A case study

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Abstract– The photochemical air pollution in Xigu district of Lanzhou city, Gansu Province was studied during a period of 1981-1984. The extremely high NMHC/NO_X ratio and ozone level elevation after rain have been noticed. A series of outdoor and indoor reaction chamber simulation experiments conducted in order to understand the specific conditions. The ozone formation under NMHC/NO_X condition and the possible reason for high ozone concentration after rain are discussed.
Keywords: photochemical smog; ozone; air pollution.

INTRODUCTION

Since 1974, eye irritation, vegetative damage and poor visibility associated with photochemical pollution have been observed frequently in summer and fall at Xigu district of Lanzhou city (Gansu Provincial Environmental Protection Research Institute, 1984.)

Xigu district is located in a river valley basin on the northwest plateau of China, 1570m above sea level, and is an important petrochemical industrial district in China. More than one hundred industrial facilities are all present in the approximate 70km^2 area, leading to sustantial emissions of primary air pollutants. The yearly average climatological patterns of this region are: relative humidity 58%; temperature 9.3°C; hours of sunlight 2446.4; wind speed 0.94m/s; probability of calm conditions 62% and frequency of inversion 85%. Horizontal and vertical convection are often suppressed and the accumulation of air polutants and active chemical reactions are expected in this areas.

The results presented here included three years of field measurements in the summer for a variety of atmospheric trace gases [NO, NO_X, O_3 and general oxidant, SO_2, peroxyl acetylnitrate (PAN), non-methane hydrocarbons (NMHC), specific hydrocarbons (C_1–C_5)] and aerosols (mass and number concentration, size distribution and ionic compositions) in 14 sites inculding those upwind and downwind. Coordinated with these measurements, meteorological observations of solar radiation (total and UV radiations), temperatures, humidity, wind profiles, surface wind fields and atmospheric stability were gathered at several sites.

The results showed that Xigu district is a photochemically active area, with high ozone concentration (>100ppb), O_3 and NO_X time profiles, typical of a polluted urban environment and vigorous formation of secondary aerosols in the range of 0.01-0.1μ at noon time. Extensive downwind transport of ozone and other pollutants to nearby areas was also observed.

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Based on the data collected in three summers, two interesting phenomena have been notticed. One was the extremely high ambient concentration of NMHC, leading to a very high NMHC/NO$_X$ ration (76-224) which was rarely observed in other well-known photochemical smog polluted area, such as Los Angeles or Tokyo. Another unique phenomenon was that the ozone concentration increased greatly, on the first sunny day after rain, which we found regularly during the summer experiment periods from 1981 to 1983. In order to fully understand the specific conditions associated with ozone formation in this area, a series of outdoor and indoor reaction chamber simulation studies were conducted. The results of these experiments will be specifically examined in the next part of this report.

In addition, an Eulerian Air Quality Simulation Model developed by MacCracken *et al.* (MacCracken, 1978) has been used, so as to carry out source-receptor assessment studies and describing the spatial and temporal distributions of pollutants resulting from known source emissions. The model uses changing meteorology and detailed source emission patterns to generate surface and vertical average pollutant concentrations with grid resolutions of 2.5 km. It treats atmospheric photochemistry using 18 species and 32 reaction chemical mechanisms suggested by Whitten (Whitten, 1980). Seven representative days were selected from both high and low-pollution periods for comparison by model simulations. The results indicated resonable agreement and the potential for future application.

Due to the importance of estabilishing a reasonable control strategy for reducing the potential for the formation of ozone, this report concentrates on the examination of ozone formation under high NMHC/NO$_X$ ratio condition and the explanation of high ozone concentration after rain events.

EXPERIMENTAL METHODS

Several laboratory simulation experiments were performed using the indoor reaction chamber at peking University (Tang Xiaoyan, 1982). The wall decay rate of O$_3$ (ppm level) observed in the chamber was 1.2-$2.0 \times 10^{-5} \mathrm{s}^{-1}$. The NO$_2$ photolysis rate constant (k_1) value for all runs was 0.10-0.12 min^{-1}.

For the outdoor irradiation experiments, two 2m^3 FEP film bags were used. The two bags sit on the top of a three story buliding in the center of the Xigu district. The experiments were performed on sunny days during Aug.15–Sep.20, 1983. Both bags were filled in the morning (before sunrise) with ambient air. One bad was left unadulterated and served as a control. In the other bag, either nitrogen oxides were added, or aerosols were removed, or the soluble agents were washed out in order to assess the effects on ozone formation. O$_3$, NO$_X$, SO$_2$ were measured in each bag for 5 minutes every half hour untill 17:00 sundown by using GSH–20–Chemiluminescent Ozone Analyzer (China, Beijing Co.) calibrated by Teco49 PSO$_3$ Calibrator, Teco14 B/E NO$_X$ Analyzer and Teco43 Pulsed Fluorescent SO$_2$ Analyzer, respectively.

RESULTS AND DISCUSSION

The ozone precursor relationships for high NMHC/NO$_X$ ratio

Table 1 and 2 listed the average data of NMHC, NO$_X$ concentrations and NMHC/NO$_X$ ratio from 1981-1983 in the summer time, and mean value of the 0700-1000 hr NMHC/NO$_X$ ratio in several representative sites, respectively. It is indicated that both summer average NMHC/NO$_X$ ratio and average over 0700-1000 hr ratio were unusually high.

To examine the effect of increased NO$_X$ on ozone formation at such a large NMHC/NO$_X$ ratio, NO$_X$ addition experiments were conducted in the in-situ outdoor smog chambers. It was shown that a small increase of NO$_X$ in the ambient air will obviously elevate the peak value of ozone as well as the ozone formation rate. Fig. 1 shows the comparison between the results using two bags.

Table 1   Summer average NMHC, NO_X concentrations and their ratio

	1981	1982	1983
NMHC, ppmC	2.68	2.92	4.16
NO_X, ppm	0.035	0.019	0.017
NMHC/NO_X	76	153	224

Table 2   Average over 0700-1000 hr NMHC/NOx ratio in the summer time, 1982

	NMHC, ppmC		NOx, ppm		NMHC/NOx
	N*	mean conc.	N*	mean conc.	
District Center	15	2.9	20	0.026	111
Industrial Area	15	5.1	20	0.010	510
Mountain Side	16	3.0	20	0.016	206
Residential Area	16	3.8	20	0.014	271

*Numer of samples
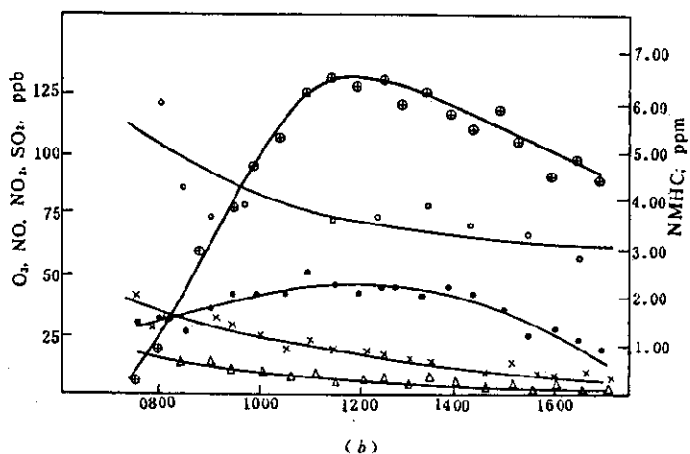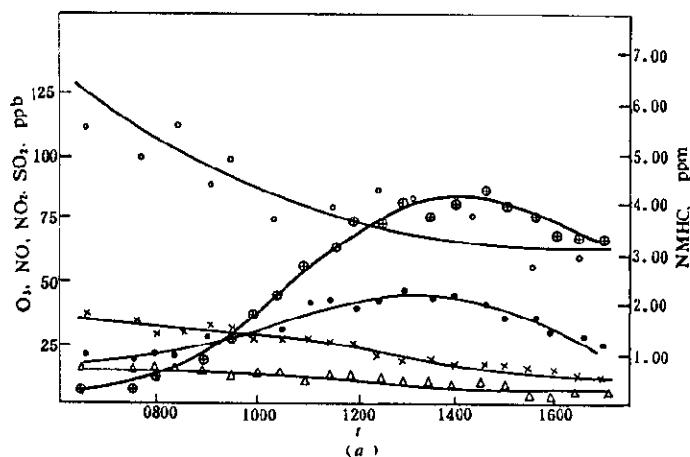
Fig.1 Time profile of the simulation of outdoor chamber runs on Setp. 13, 198?
(a) Unadulterated ambient air, (b) ambient air with NO_2 addition
⊕O_3 ○NMHC   ●NO_2 × SO_2

For reference, the indoor reaction chamber experiments with different NMHC/NO$_X$ ratios were studied. The NMHC used was a mixture of ethylene, propylene, propane, isobutane and *n*-butane with mixing ratio of 1.0, 1.9, 2.2, 1.0 and 0.3, respectively. This mixture approximates the organic components of the ambient air in Xigu district. The indoor experiments showed the same ozone elevation tendency in higher NOx concentration runs with the captive-air experiments. Table 3 lists the results of ozone formation with the change in NOx concentration obtained in both indoor and outdoor chambers while leaving hydrocarbon concentration almost unchanged.

Table 3 O_3 maximum concentration under high NMHC/NOx ratio

		[NMHC]$_o$, ppmc	[NOx]$_o$, ppm	[NMHC]$_o$ (NOx)$_0$	[O$_3$]$_{max}$, ppm
Outdoor Chamber	83, 8, 19	2.7	0.025	108	0.09
		1.5	0.040	38	0.27
	83, 9, 13	6.0	0.045	133	0.084
		5.6	0.060	93	0.135
Indoor Chamber	Group I	5.90	0.053	112	0.140
		7.57	0.124	61	0.221
	Group II	36.21	0.078	464	0.051
		37.09	0.140	265	0.121

These experimental results agree well with prediction of the EKMA model (Dimitriades, 1977 and USEPA, 1982), which was a method recommended by USEPA to predict the relationship between ozone and its precursors. According to EKMA, peak ozone concentration is protional to the NOx concentration when the NMHC/NOx ratio is > -8. Each pair of smog chamber run showed that NOx concentration is directly proportional to O_3 generation under approximate equal concentration of NMHC. These experiments offered evidence of the role of NOx in ozone formation, it supports the idea that a light increase in NOx emissions in this area is apt to cause elevated mid-day summer ozone concentration in ambient air.

The ozone level elevation after rain

Fig. 2 shows the observed ozone level elevation at the first sunny day after rain during the summer experiment periods in 1981-1983. This phenomenon could be sustained for several days.

It was known that the ozone elevation in the summer daytime is mainly caused by photo-chemical reactions in the atmosphere. But the detailed mechanism which promotes the ozone formation or accumulation is still subjects of both chemical and physical interests.

Possible explanations might include: (1) the increased intensity of UV radiation after rain, leading to strengthend photochemical reaction; (2) the effect of relative humidity; (3) the removal of soluble reductants from the air by rain; (4) the removal of aerosols by rain and a lowering of heterogeneous reactions; (5) different meteorological conditions after and before rain and (6) other factors which increase free radical concentration in the air after rain. To test some of these possibilities, several reactor chamber studies were conducted.

A pair of outdoor chamber exposure experiments were used to test the effect of aerosols on ozone formation. A bag containing ambient air, from which aerosols were removed by filtration before filling, gave the same ozone time profile as a bag without removal of aerosols (Fig. 3), indicating that aerosol is not the major factor causing the ozone elevation after rain.

Other indoor chamber experiments were conducted to examine the effect of water vapor. The results show that the generalized maximum ozone has a linear relationship with water vapor concentration in the NOx-C_2H_4/C_3H_6 - H_2O system. The [O$_3$]$_{max}$ / [O$_3$]$_{ps}$ [NMHC]$_o$ was used to compensate for the difference caused by the variable initial concentration of NMHC (0.7- 2.5 ppm). [O$_3$]$_{ps}$ is the steady state concentration of ozone. The same linear relationship
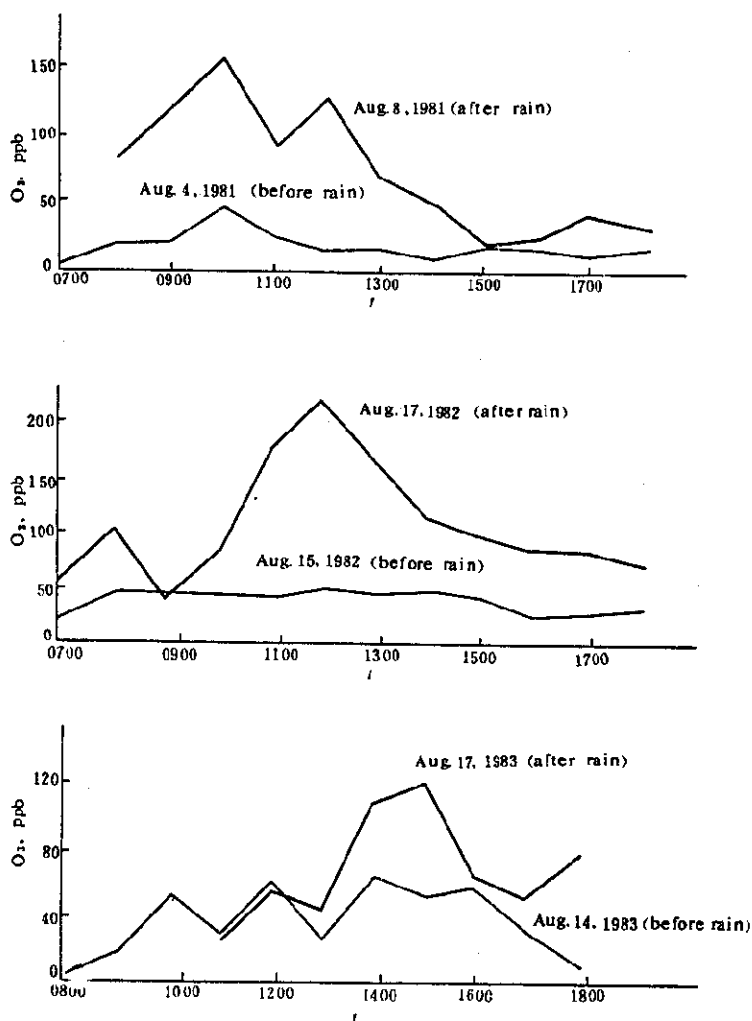
Fig.2 Comparison of ozone levels before and after rain in summer

could be observed in the ozone maximum formation rate curve with water vapor concentration. Both O_3 maximum value and O_3 maximum formation rate per unit NMHC vary inversely with water vapor concentration. If the H_2O concentration effect on ozone concentration observed in the chamber is representative of atmospheric conditions, the elevated ozone level after rain can not be explained by the effect of water vapor.

Gaseous NH_3 is emitted from a fertilizer factory in the Xigu district and was observed in the ambient air. As a gaseous soluble reductant, the system C_3H_6-NO_X-NH_3-Air was studied and compared with the system without NH_3. Results indicate that lowering NH_3 concentration by 300 ppb did not influence the ozone formation, so that the washout of NH_3 from air by rain will not contribute to the ozone elevation. Outdoor chamber tests after washout of soluble agents from the air further support this conclusion.

According to the weather analysis, a high level through and cold air activity was the major summer weather system in the Lanshou city area. Before the cold air mass arrived,
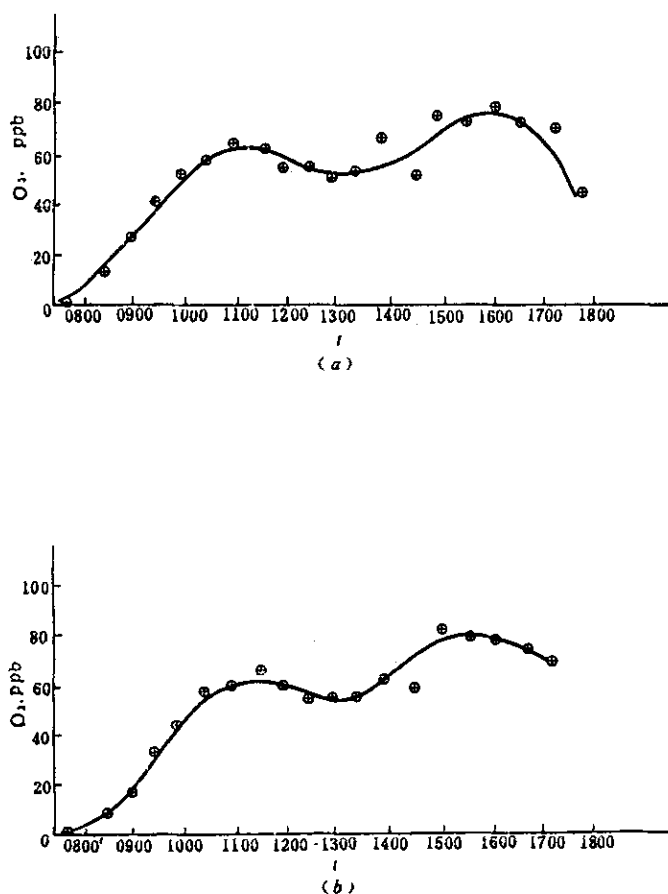
Fig.3 Comparison of the osone generating ambient air with and without aerosols
(a) ambient air (b) ambient air without aerosols

Lanzhou city was located in the southwest air flow in front of the high level trough. In this case, poor atmosphere stability and strong wind speed did not favor pollutant accumulation. In the opposite situation when the cold front passed through, this area was located in the ground high pressure after the high level trough, with stable atmosphere, weak wind and sunny sky conductive to photochemical reaction and accmulation of primary and secondary air pollutants. Aug. 17, 1982 and Aug. 18, 1983 were typical of such conditions.

From these results, it appears that the meteorological factors indeed contributed to the high ozone levels after rain. Further studies are needed to fully understand any possible contribution from atmospheric chemistry.

Based on the above results, it is concluded that osone formation is highly sensitive to NOx in Xigu district atmosphere. Additional emissions of NOx should not be permitted, if the high ratio of NMHC/NOx is not changed. In the Xigu district, it would be difficult to reduce NOx and NMHC emissions and since osone level is closely related to the meteorological conditions in this region, the control strategies must consider both meteorological and pollution problems.

REFERENCES

Dimitriades, B., Environ. Sci. Technol., 1977, 11:80

Gansu Provincial Environ. Protection Res. Institute, Environ. Sci. (in Chinese), 1984, 5:24
MacCracken, M. C. *et al.*, J. Appl. Meteor., 1978, 17:254
Tang Xiaoyan *et al.*, Environ. Sci. Technol., 1980, 14:690
USEPA, Guideline for Use of City-Specific EKMA in Preparing Ozone SIPS, Report of USEPA,
    No. EPA-450/4-80-027, Research Triangle Park, NK, March 1982
Whitten, G. Z. *et al.*, Environ. Sci Technol., 1980, 14:690.