

Ozone and related gaseous pollutants in the boundary layer of eastern China: Overview of the recent measurements at a rural site

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Abstract. We present a summary of the latest measurements of ozone (O_3) and primary air pollutants at a rural/agricultural site in the fast developing Yangtze Delta region of China. The results of this study show elevated levels of primary pollutants (CO , SO_2 and NO_x^*), which are about 1-5 times of those typically found in rural areas of North America and Europe. O_3 pollution events are frequently observed. CO and SO_2 levels are particularly high, resulting from the unique energy-use pattern in China. O_3 shows strong positive correlation with NO_x^* and CO during periods of high photochemical activity. The O_3 - NO_x^* slope is comparable to the result from rural North America, but the O_3 - CO slope is substantially smaller for the Chinese site. With the anticipation of rapid changes of atmospheric composition in China, long-term measurements of key air pollutants will be necessary for documenting their trends and for studying their environmental impacts.

1. Introduction

China and many other East Asian countries have experienced phenomenal economic growth in the past two decades. The economic expansion has resulted in increasing consumption of fossil fuels, leading to increasing emissions of the major air pollutants into the atmosphere [Galloway *et al.*, 1989; Kato and Akimoto, 1994; Aardenne *et al.*, 1999; Streets and Waldhoff, 2000]. Between 1990 and 1995, emissions in China increased by 9%, 26%, and 16% for SO_2 , NO_x and CO , reaching 25.2, 12, and 115 mt (1 mt = 10^{12} g or 1 Tg) in 1995, respectively [Streets and Waldhoff, 2000]. The large emissions of SO_2 have resulted in acidic deposition over the southern part of China [Wang and Wang, 1995]. Recent studies have suggested that rural ozone and aerosol levels in eastern China may be high enough to cause significant reduction of crop yields [Chameides *et al.*, 1999a, 1999b]. Other studies have shown that emissions from China and East Asia may have significant effects on tropospheric chemistry and the biogeochemical cycles of the remote Pacific [e.g., Crawford *et al.*, 1997; Elliott *et al.*, 1997]. There are also studies to suggest that Asian emissions can make their way across the Pacific Ocean and affect the air quality of the western United States [Jaffe *et al.*, 1999; Jacob *et al.*, 1999]. So far, field measurements of key air pollutants in eastern China have been comparatively sparse, especially in rural locations. Such studies are needed to provide data to elucidate atmospheric processes on the Chinese sub-continent, to reconcile emission

inventories, and to constrain regional chemical transport models. The first sizable measurement study was conducted in 1994 in several rural areas of eastern China [Peng *et al.*, 1997; Luo *et al.*, 2000]. In 1999, as a cooperative effort with the China-MAP project (The Yangtze Delta of China as an Evolving Metro-Agro-Plex), a field campaign was carried out in the Yangtze Delta region. During this experiment, the authors measured O_3 , CO , SO_2 , and NO_x^* at a typical rural/agricultural site for over a 1-year period. This report gives an overview of the measurements.

2. Experimental

The study was conducted at the Linan Baseline Air Pollution Monitoring Station ($30^{\circ}25'N$, $119^{\circ}44'E$, 132 m) situated on the southern edge of the Yangtze Delta plain of China (Figure 1). The station is 53 km west and 210 km southwest of the major population centers of Hangzhou and Shanghai, respectively, with the Linan township (population: ~50,000) 10 km to the south. To the west and further south are sparsely populated and less developed mountainous regions. The site is surrounded by hills planted in pines, mixed deciduous trees, and bamboo, as well as crop fields of various sizes in the valleys between the hills. Small villages are scattered around the station within a distance of a few kilometers. This land-use pattern is typical in the rural part of eastern China. Thus our measurements are believed to be representative for a large region, as opposed to isolated emission 'hot' spots. Indeed, a comparison of the data from the

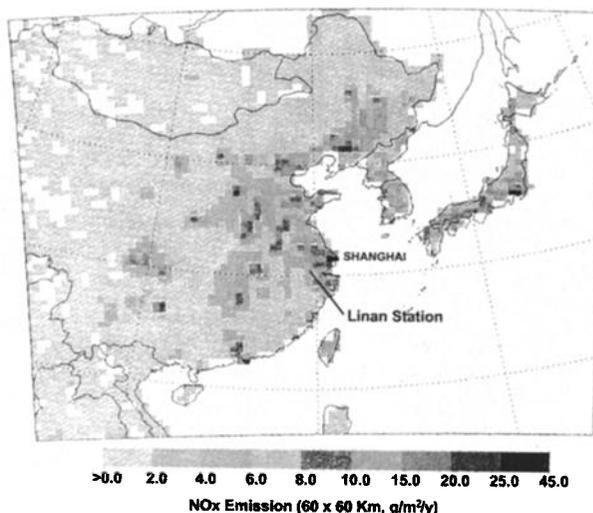


Figure 1. 60 km x 60 km grided map of NO_x emission [Luo *et al.*, 2000] showing the location of the Linan measurement site.

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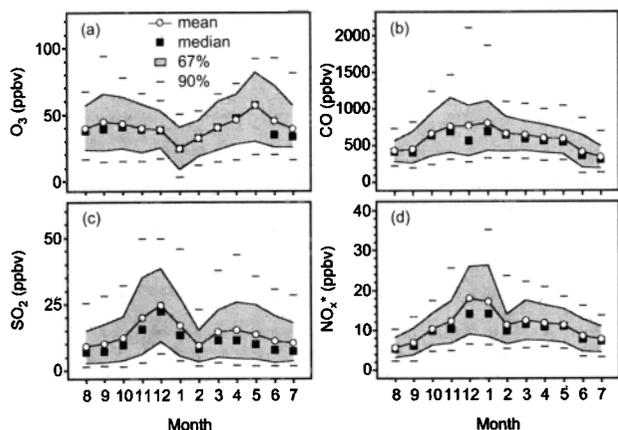


Figure 2. Monthly variations of the concentrations of: (a) O₃, (b) CO, (c) SO₂, and (d) NO_x* from August 1999 to July 2000. Daytime (08:00-19:59) data are used for O₃.

Linan site with those concurrently obtained at several other non-urban sites situated 100 to 300 km apart shows that the levels of the primary pollutants at Linan are either comparable or lower. It should be noted, however, that due to the large population in rural eastern China, human activities (and thus emissions) are more intense than in the rural/agricultural regions in the western countries. This is reflected in the ambient chemical data obtained from this study.

Measurement instruments were housed in a semi temperature-controlled laboratory. Ambient air samples were drawn through a PFA Teflon tube (OD: 12.7 mm; ID: 9.55 mm; length: 8.5 m) which was connected to a PFA manifold. A bypass pump drew air at a rate of 15 liters per minute. With four analyzers, the residence time of sampled air in the tube and the manifold was less than 2 seconds. An in-line Teflon filter (Fluoroware Inc., Chaska, Minnesota) was placed upstream of each analyzer to prevent particles from entering into the analyzer. The inlet of the sample line was located 5 m above the rooftop of the laboratory.

O₃ was measured using with a commercial UV photometric instrument (Thermo Environmental Instruments, Inc. (TEI), model 49) which had a detection limit of 2 ppbv and a 2-sigma (2-σ) precision of 2 ppbv for a 2-minute average.

SO₂ was measured by a pulsed UV fluorescence (TEI, model 43S), with a detection limit of 0.06 ppbv and 2-σ precision of 3% for ambient levels of 10 ppbv (2-minute average). The uncertainty was estimated to be about 9%.

CO was measured with a gas filter correlation, nondispersive infrared analyzer (Advanced Pollution Instrumentation, Inc., model 300) with a heated catalytic scrubber (as purchase) to convert CO to CO₂ for baseline determination. Our tests showed that water vapor was able to pass through the converter near 100%, although it could take a few minutes for the signal to reach an equilibrium. In our study the analyzer was zeroed every two hours, each lasting 12 minutes. The last two-minute data from each zeroing was taken as the baseline and was automatically subtracted from the signals. The detection limit was 30 ppbv for a 2-minute average. The 2-σ precision was about 1% for a level of 500 ppbv (2-minute average) and the overall uncertainty was estimated to be 10%. The *in situ* CO data were compared with those from the analyses of 16 canister samples taken at the site between October 26 and November 2, 1999 and analyzed at the University of California-Irvine using the gas chromatographic methods. The two sets of CO data correlate very well in the observed range of 350-1065 ppbv ($[\text{CO}]_{in\ situ} = 0.92[\text{CO}]_{canister} +$

20; $r^2 = 0.97$). The *in situ* data are slightly lower than the canister results.

NO was detected with a chemiluminescence analyzer (TEI, model 42S) with a detection limit of 0.05 ppbv. The 2-σ precision of this instrument was 4% (for NO=10 ppbv) and the uncertainty was about 10%. NO₂ was converted to NO by a hot molybdenum oxide maintained at 325°C with the NO subsequently measured by the chemiluminescence detector. This technique is known to convert not only NO₂ but also other reactive nitrogen species such as peroxyacetyl nitrate anhydride (PAN), aerosol nitrates and nitric acid. In our experiment, aerosol nitrate was most likely collected on the in-line Teflon filter (which was replaced normally every 10 days). Nitric acid was believed to have passed the PFA sample line [Neuman *et al.*, 1999] during the short residence time, but some could be absorbed by aerosols collected on the filter. The "NO_x" measured in this study is thus an approximate summation of NO, NO₂, PAN, organic nitrates, and nitric acid, hereafter referred to as NO_x*. The afternoon NO_x* levels were found to approach NO_y at several rural sites in eastern United States, with aerosol nitrate contributing less than 10% to total NO_y [Parrish *et al.*, 1993a]. It is possible that particulate nitrate has a larger contribution to NO_y in China due to the higher loading of particles (which can absorb and react with gas-phase nitric acid).

The analyzers were checked every 5-9 hours by injecting scrubbed ambient air (TEI, model 111) and a span gas mixture. A NIST traceable standard (Scott-Marrin Inc., California) containing 100.5 ppmv CO (± 2%), 11.28 ppmv SO₂ (± 5%), and 11.28 ppmv NO (± 5%) was diluted using a custom-made calibrator. The span gas and zero air were introduced to the analyzers through the in-line particulate filter to account for possible losses of measured gas during normal measurement cycles. The O₃ analyzer was spanned using an internal ozonator in the analyzer. The multi-point calibrations were performed at approximately 3-month intervals by our own personnel making the journey to the site. Local observatory staff carried out daily inspection of the instruments and replaced the in-line filters. A data logger (Environmental Systems Corporation, model 8816) was used to control the automatic zero/span and to acquire data. One-minute averaged data were stored in the data logger and hourly-averaged values are presented in this paper.

3. Results and Discussion

3.1. Seasonal and Diurnal Cycles

Monthly variations of the measured gases are shown in Figure 2 for the August 1999 to July 2000 period. For ozone, daytime (08:00-19:59) data were chosen while for others all of the 24 hourly values were included. Monthly mean O₃

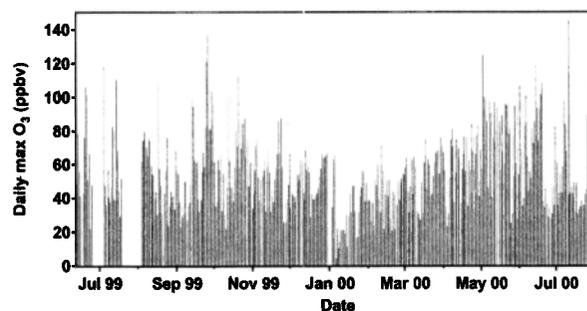


Figure 3. Time series of O₃ daily maximum concentrations from June 11, 1999 to July 31, 2000.

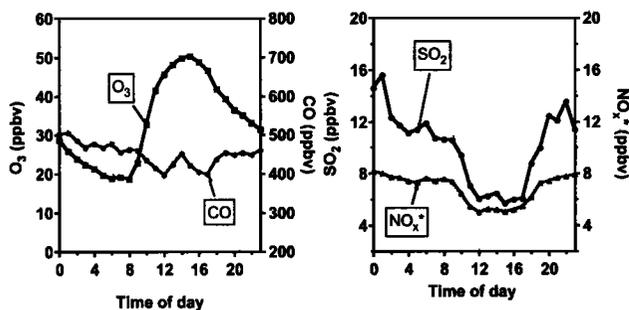


Figure 4. Average diurnal variations of O_3 , CO, SO_2 , and NO_x^* in September 1999.

concentrations show a maximum in May (57 ppbv) and a lowest value in January. This seasonal trend is similar to those observed in rural areas of the United States and Europe [e.g., Logan, 1989] except that O_3 from this study shows a sharper drop in July and August, which is attributable to the Asian monsoon circulation. (The Asian monsoon brings in maritime air masses and unstable rainy weather to the region in summer.) Although monthly averaged O_3 is relatively low compared to autumn, several extremely high O_3 episodes occurred in summer, as indicated in the daily maximum 1-h concentrations (Figure 3). Hourly values of 137 and 145 ppbv were observed in September 1999 and July 2000, respectively. The trend of monthly mean O_3 in 1999-2000 is different from that measured at the same site in 1994-1995, which showed an autumn maximum [Chameides et al., 1999a]. This difference may be due to year-to-year alternation in the meteorological conditions.

The primary pollutants (CO, SO_2 , and NO_x) are high in winter and low in summer. The observed winter peaks are believed to be due to a higher energy demand (for heating), slower chemical destruction rates, and weaker vertical mixing, as well as the transport of urban/industrial emissions from the Shanghai metropolitan area (by prevailing northeasterly winds) in winter. Monthly mean CO concentrations range from 340 ppbv (in July) to 808 ppbv (in January), which is approximately twice or more of the levels in the rural United States and western Europe [Parrish et al., 1991; Hallock - Waters et al., 1999; Holloway et al., 2000]. SO_2 monthly concentration increases from 9.0 ppbv (in July) to 24.8 ppbv (in December). These concentrations are equivalent to the levels in polluted regions of the West [Brasseur et al., 1999] and are about 5 times or more of the reported values in agricultural/forest regions of the southeastern United States [Klemmen et al., 1994; Buhr et al., 1995]. NO_x^* varies from 5.6 ppbv (August) to 17.9 ppbv (December). The summertime NO_x^* concentrations are comparable to those observed at Scotia and Bondville, two relatively polluted rural sites in eastern United States [Parrish et al., 1993a]. Besides the elevated concentrations, there is a large variability in the data, indicating a highly dynamic nature of the air masses impacting the site. The data reveal a characteristic on emissions in China, namely, that SO_2 and CO are much more abundant (relative to NO_x) than in the West, which can be attributed to the use of higher sulfur-content coal and less efficient combustion from domestic burning of biofuel, respectively.

Diurnal cycles are shown in Figure 4 for September 1999. O_3 has a typical rural profile showing a broad daytime maximum (~50 ppbv) and reduced levels (20-30 ppbv) at night. The primary pollutants have higher nighttime concentrations presumably due to continuous emissions at night and daytime chemical conversion and vertical dilution after the breakup of

the nocturnal boundary layer. It is very interesting to see that SO_2 concentration dropped more quickly than that of NO_x^* during the daytime, suggesting downward mixing of NO_x (or NO_y)-rich air masses and/or SO_2 being removed at a faster rate. The latter would be particularly interesting since it is normally thought that NO_x is removed more quickly.

3.2. The Relationships of O_3 with Other Trace Gases

The correlations of O_3 with NO_x^* and CO are shown in Figure 5 for the photochemically active afternoon hours (13:00-17:00) in four seasons. The result indicates that summertime afternoon O_3 concentrations are strongly correlated with NO_x^* (and CO as well) with a few exceptions which are mostly associated with rainy/cloudy days. If the measured NO_x^* were taken as a surrogate of commonly used NO_2 ($NO_2 = NO_x - NO$), then the slope ($\Delta[O_3]/\Delta[NO_x^*] \approx 8$) would suggest that about eight O_3 molecules are produced with one NO_x oxidized, which is similar to result from rural Germany [Volz-Thomas et al., 1993] and the rural United States [e.g., Trainer et al., 1993]. The intercept in the O_3 - NO_x^* correlation implies the summertime background O_3 of about 16 ppbv in eastern China. The overall O_3 - NO_x^* correlation deteriorates in autumn/spring and becomes negative in winter, presumably due to a decreasing photochemical production from summer to winter. The O_3 -CO correlation has a similar seasonal dependence. As a result of high CO concentrations, summer $\Delta[O_3]/\Delta[CO]$ is about 0.1 for this eastern China site, much smaller than that found in North America (~0.3) [Parrish et al., 1993b]. The low O_3 /CO ratios may be used as indications of rural air mass from eastern China.

4. Conclusions

The measurements from this rural/agricultural site in eastern China show elevated concentrations of CO, SO_2 , and NO_x^* , with ozone pollution frequently impacting the site. Given that

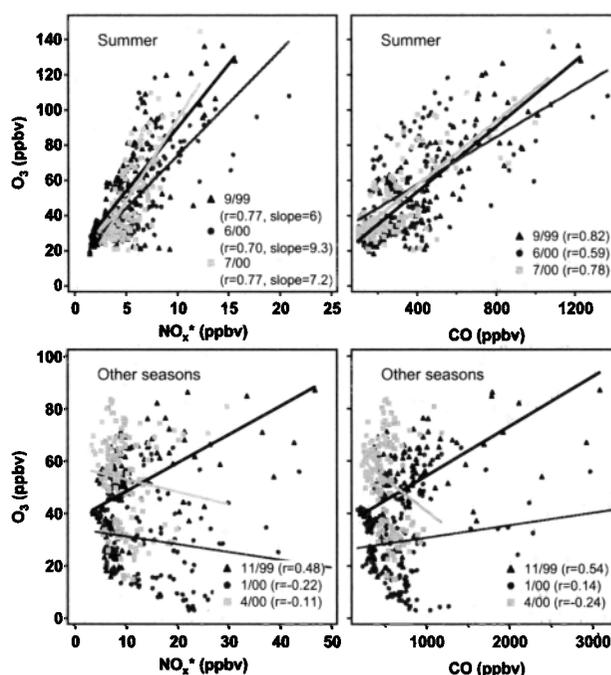


Figure 5. Correlation of afternoon (13:00-17:00) concentrations of O_3 with NO_x^* and CO in summer (September 1999, June and July 2000) and other seasons (November 1999, January and April 2000).

the measurements were conducted in a setting reflecting a typical land-use pattern, the observed concentrations are likely to represent the situation for a large portion of eastern China. Consequently the ecological impacts of the high air pollution levels may be widespread. Indeed, acid rain (for which SO₂ was found to be the most important precursor [Wang and Wang, 1995]) has already been recognized as a regional-scale environmental problem in China. The results from this study indicate that at present rural air masses are characterized by high CO and SO₂. However, in view of the likely stabilization/reduction in SO₂ and CO emissions by planned control measures and a projected continuing upward trend in NO_x emissions [Streets and Waldhoff, 2000; Streets et al., 2000], the atmospheric composition of chemically active gases in China is likely to change in the coming years. Such changes may have important implications for the regional atmospheric chemistry. For example, our study suggests that photochemically produced ozone is linearly dependent on NO_x. Thus increasing NO_x may cause more serious ozone pollution in eastern China. Control efforts for CO and SO₂ are also likely to reduce the levels of atmospheric particles (CO and particulate are co-pollutants from the burning of biomass and biofuel, and SO₂ is the dominant gaseous precursor to sulfate). A reduced loading of atmospheric aerosols, however, may allow more solar radiation to reach the earth's surface and result in a smaller loss of reactive gases on aerosol surfaces. Both effects would lead to higher ozone concentrations in the atmosphere in China. It is therefore of critical importance to monitor, on a long-term basis, chemically and radiatively important trace gases and aerosols so that their environmental implications can be reliably assessed. In this regard, The measurements from this study may serve as a baseline against which further changes can be compared and evaluated.

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