Impact of aerosols on surface ozone during a heavy haze event

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Outline

- Introduction and objectives
- Data and TUV model
- Results and discussion
- Summary and conclusions
- On-going work

Introduction

- Tropospheric O₃ is generated through a series of complex photochemical reactions involving nitrogen oxides (NO_x) and volatile organic compounds (VOCs) and solar radiations (i.e., Ultraviolet radiation).
- High concentrations of surface ozone have detrimental impacts on human health and ecosystem.
- Surface O₃ concentrations are dependent on not only its precursors (NO_x and VOCs), but also UV radiation. UV represents the par of solar radiation with wavelength range of 100–400 nm, composes 8.73% of the solar spectrum at the top of the atmosphere.
- Aerosols have important impacts on UV radiation. Solar radiation can be significantly attenuated due to aerosols' absorption and back-scattering before reaching surface.

Introduction (cont.)

- The impact of aerosol on solar radiation reaching surface is closely associated with aerosol optical properties which include the aerosol optical depth (AOD), the single-scattering albedo (SSA), and the asymmetry factor. The values of these parameters are dependent on aerosol concentrations.
- Thus it is important to assess the importance of aerosol on surface ozone.

Introduction: O₃ chemistry

Photolysis reaction of NO₂

$$NO_{2} + hv(\lambda < 430nm) \rightarrow NO + O(^{3}P) (1.1)$$

$$O(^{3}P) + O_{2} \rightarrow O_{3} (1.2)$$

$$O_{3} + NO \rightarrow NO_{2} + O_{2} (1.3)$$

Note: The reactions (1.1-1.3) is a zero cycle when no other substances are involved in . This means that O_3 is not increased.

 However, when other species (e.g., No_x and VOCs), they react with OH radicals to generate NO₂ which are given as follows

| $\mathcal{O}_3 + h v (\lambda < 330 nm) \rightarrow \mathcal{O}_2 + \mathcal{O}({}^1D)$ | (1.4) |
|-----------------------------------------------------------------------------------------|-------|
| $O(^1D) + H_2O \rightarrow 2OH$ | (1.5) |
| $VOCs + OH + O_2 \rightarrow RO_2 + H_2O$ | (1.6) |
| $RO_2 + NO \rightarrow RO + NO_2$ | (1.7) |

- When NO₂ generated through reactions (1.4-1.7) exceeds the consumed amount (reactions 1.1-1.3), O₃ is accumulated !
- It can be seen that UV is important to photolysis reaction of NO_2 and then O_3 formation.

Scientific questions and objectives

- Previous studies have showed that aerosols have important impact on surface ozone concentrations. But in these studies, aerosol concentrations are not as high as observed in China. It is still not clear that at what levels of aerosols, surface ozone experiences a significant change from one state to another.
- Specific questions: (1) How does surface ozone change with aerosol at high aerosol concentrations (e.g., PM_{2.5} or PM₁₀)? (2) At what concentrations of aerosol does ozone formation will be suspended or shut down?

Data and TUV model



Fig.1 Study sites

Data and TUV Model (cont.)

| Stations | Time period | Data availabitliy |
|------------------------------------------------------------------|----------------|----------------------------------------------------------------------------------|
| Shang Hai (Pu Dong) | Dec.1-10, 2013 | PM_{10} , NO_2 , O_3 , UV_3 O_3 column content (OMI) AOD (Modis) |
| Kun Shan (Zhen Chuan Middle School and Jing He Shui Chang) | 2011-2014 | PM ₁₀ , NO ₂ , O ₃ |

Data and TUV Model (cont.)

Tropospheric Ultraviolet and Visible Radiation Model

 TUV model was originally developed by USA National Center for Atmospheric Research (Madronieh and Floeke, 1999) for the calculation of ultraviolet and visible light radiations.

Data and TUV Model (cont.)

- Inputs
- Basic information: longitude, latitude, date, time, wavelength and height;
- Surface observations: surface albedo, air pressure, and ozone column content;
- Cloud and aerosols: aerosol optical depth, single scattering albedo, and asymmetric factor.

Outputs

- UV irradiance, actinic flux and photolysis rate, etc.

A heavy haze event on Dec. 1-10, 2013 in Shanghai and surrounding region

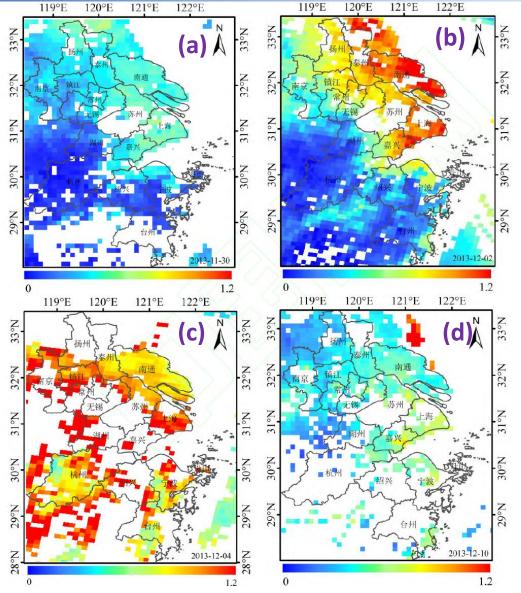


Fig.2 MODIS derived AOD in Yangtze River Delta (a. Nov.30, b.Dec.2, c. Dec.4, d. Dec.10 2013) (*Wang J.2014*)

This is a heavy haze event. It is obvious that AOD was increased significantly during the event.

Preliminary results: observed time series

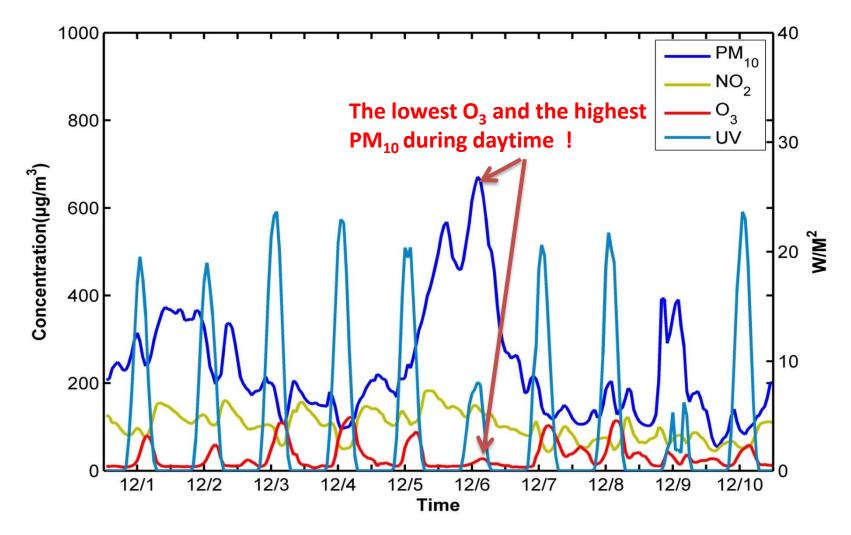


Fig.3 Time series of observed PM₁₀, NO₂, O₃ and UV in Shanghai during Dec1-10, 2013

Preliminary results: O₃ vs. PM₁₀

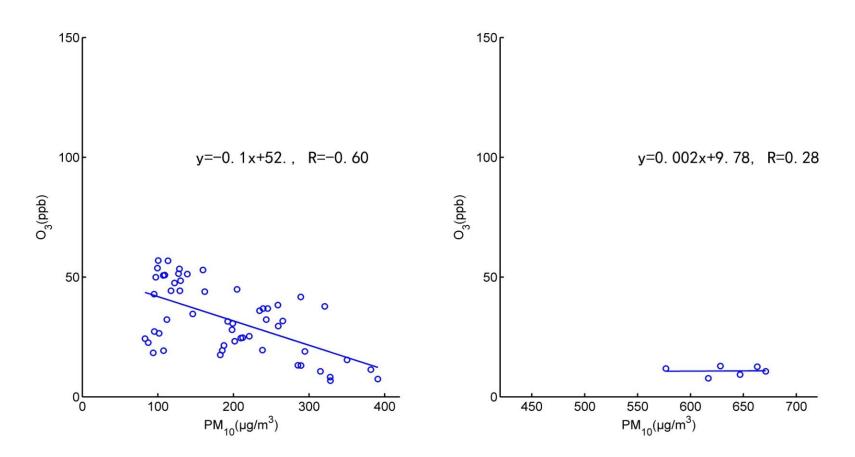


Fig.4 Correlation of and O_3 with PM₁₀ in Shanghai during Dec.1-10, 2013

Preliminary results: O₃ vs. PM₁₀ (Kunshan/ZC)

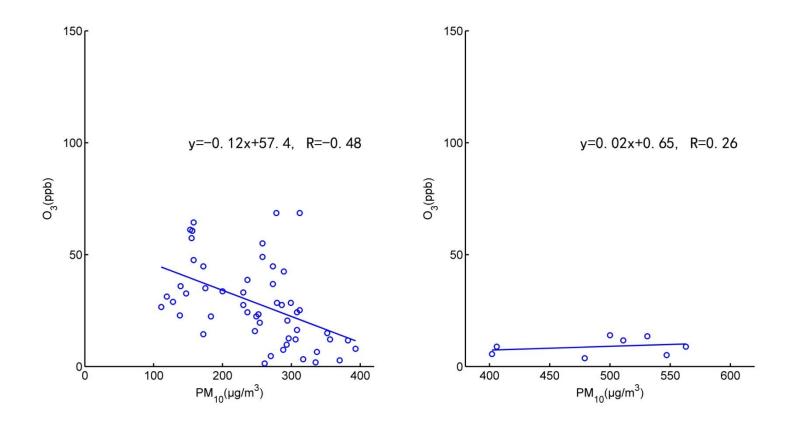


Fig.5 Correlation of O₃ with PM₁₀ observed Kunshan ZC site during Dec.1-10, 2013

Preliminary results: O₃ vs. PM₁₀ (Kunshan/SC)

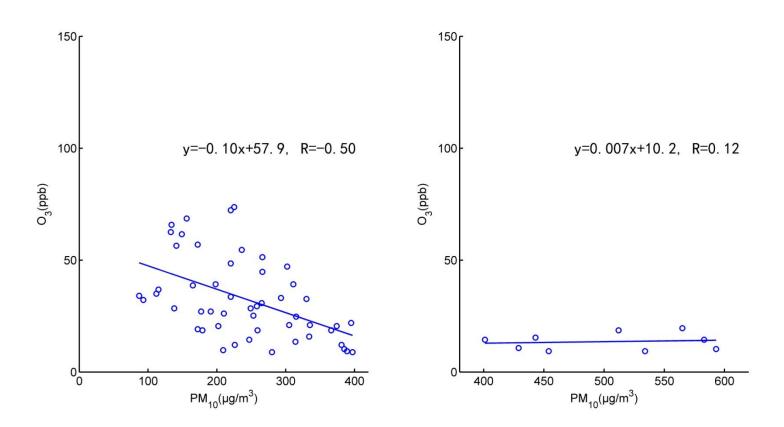


Fig. 6 Correlation of O₃ with PM₁₀ observed Kunshan SC site during Dec.1-10, 2013

Preliminary results: UV vs. PM₁₀

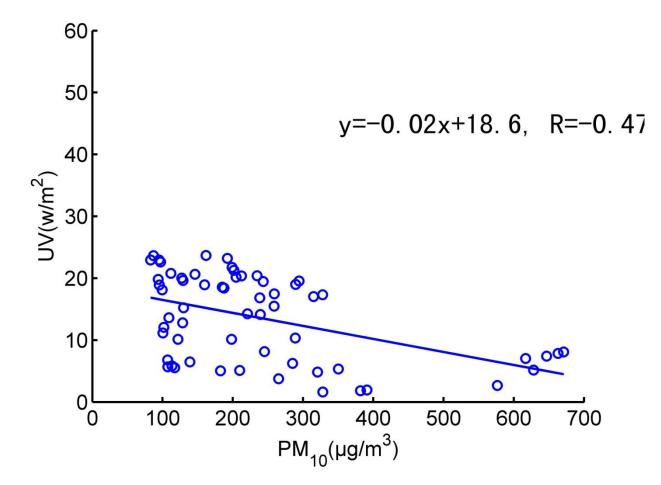


Fig.9 Correlation of UV with PM₁₀ observed in Shanghai during the same period

Preliminary results: O₃ vs. UV

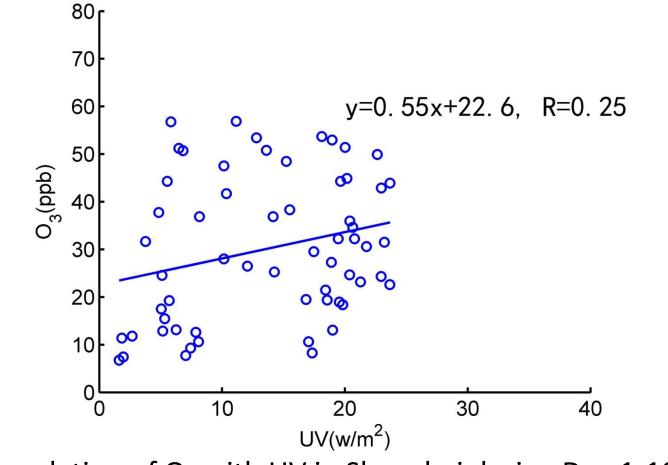
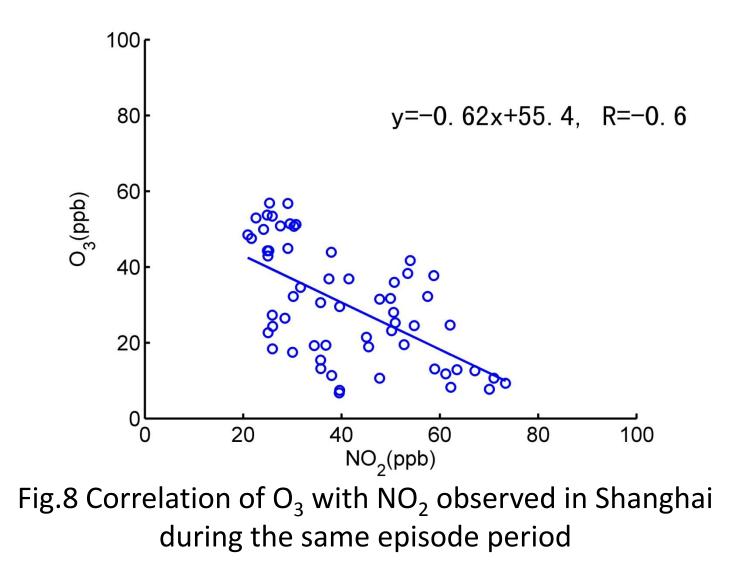


Fig.7 Correlation of O_3 with UV in Shanghai during Dec.1-10, 2013

Preliminary results: O₃ vs. NO₂



Preliminary results: observed met variables

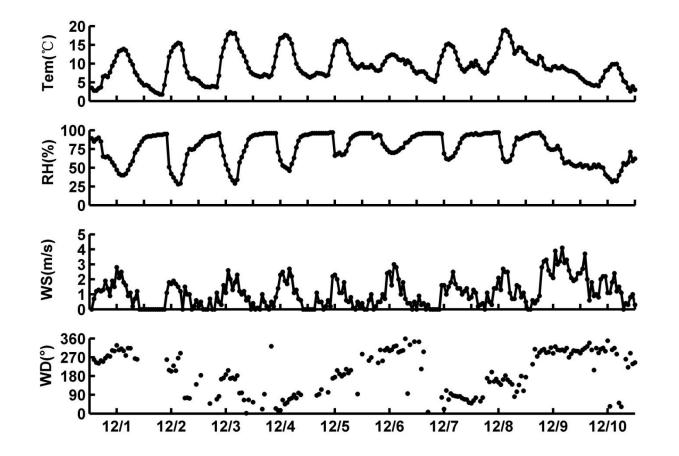


Fig.10 Time series of temperature, wind speed, wind direction, and relative humidity observed in Shanghai during Dec1-10, 2013¹⁹

Preliminary results: O₃ vs. T

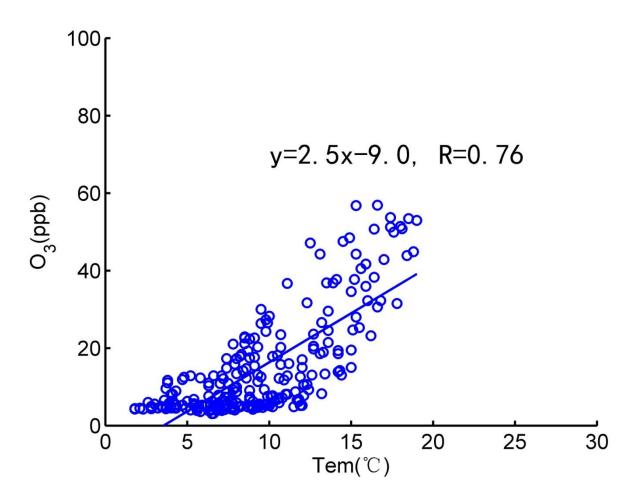


Fig.11 Correlation of and O₃ with temperature observed in Shanghai during Dec.1-10, 2013

Preliminary results: O₃ vs. RH

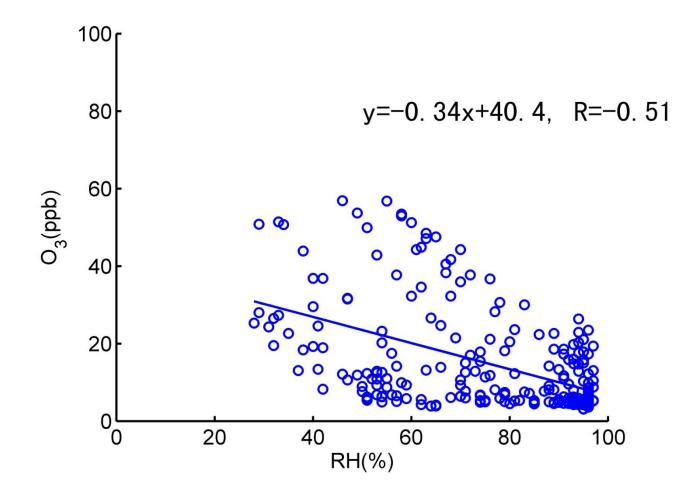


Fig.12 Similar to Fig.9 but for O₃ with relative humidity

TUV modeling results: Impact of NO₂ on UV

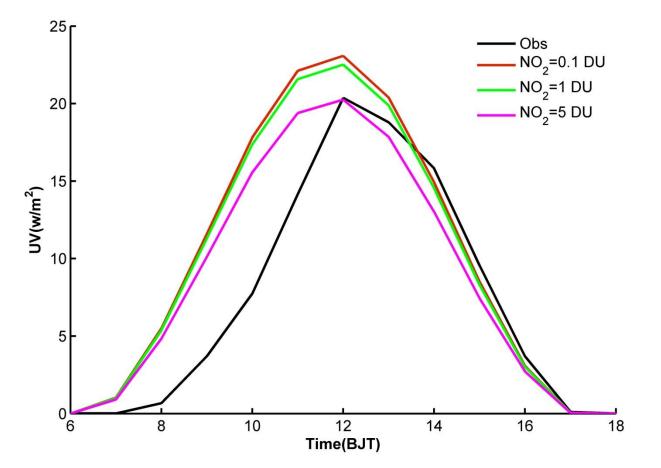


Fig.13 Simulated UV with TUV model as compared to observations at different NO₂ values (ozone column is assumed as 249.45 DU, AOD is 0.926 and SSA is 0.8 on Dec 8, 2013). ²²

TUV modeling results: Impact of SSA on UV

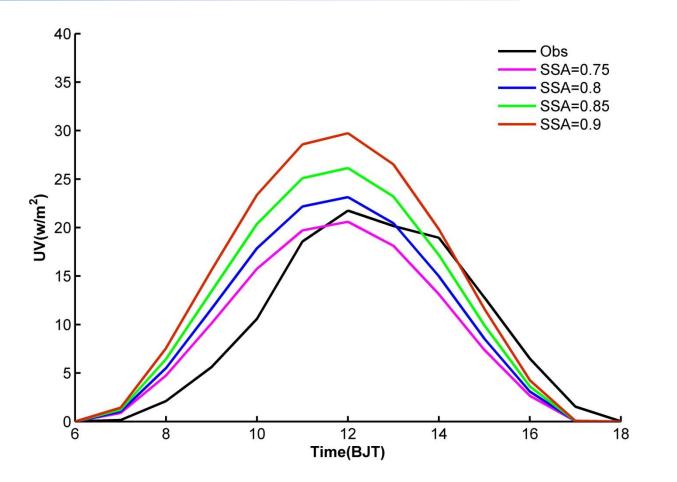


Fig.14 Simulated UV with TUV model as compared to observations at different SSA values (ozone column is assumed as 249.45 DU and AOD is 0.926 on Dec 8, 2013).

TUV modeling results: Impact of AOD on UV

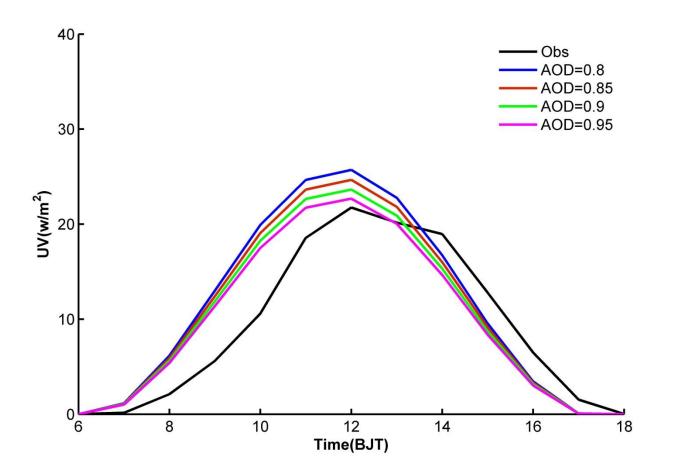


Fig.15 Simulated UV with TUV model as compared to observations at different AOD values (ozone column is assumed as 249.45 DU and on Dec 8, 2013 AOD is 0.926).

Summary and conclusions

- The observational analyses confirm the findings of previous studies that O₃ was decreased with increasing PM_{2.5} and PM₁₀. But we found that the photochemical formation of O₃ was suspended when PM₁₀ reached 400 µg/m³ and above.
- The prevailing wind direction is southwestly wind during the episode. Weak wind, the relative humidity is basically less than 80%, higher temperature and lower humidity are favorable for ozone formation.

Summary and conclusions (cont.)

- Photolysis rates of NO₂ are highly dependent on the surface-reaching UV radiation. The TUV mode simulations show that surface-reaching UV is decreased when AOD is increased or SSA is decreased.
- TUV model studies show that the simulated UV shows good agreement with observations when SSA equals to 0.8 and AOD is 0.926. This (0.8 of SSA) indicates that aerosol has strong absorption in this region.

On-going work

• Using the NCAR MM model to quantify the impact of aerosol on ozone formation and the ozone maximum concentrations.

Thank you