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Impact of Aerosol Radiation Effect on Surface Ozone during Heavy Haze Events

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Outline

- Introduction
- Data and models
- Results and discussion
- Summary and conclusions

Introduction

- High surface O_3 is a pollutant (air quality); tropospheric O_3 is major precursor of OH radicals (atmospheric chemistry); tropospheric O_3 is one of the greenhouse gases (climate change).
- Tropospheric O_3 is formed through photochemical reactions associated with NO_x and VOC. Ultraviolet (UV) radiation plays a critical role in O_3 formation.

Introduction (cont.)

- Aerosol may significantly reduce surface-reaching UV radiation. Previous studies have showed that aerosols have important impacts on surface UV and then surface O_3 concentrations, but the aerosol concentrations in those studies are not as high as observed in China. It is still not clear how surface O_3 will change with aerosol during heavy haze events.
- Scientific question: Will surface O_3 formation change from one state to another when aerosols reach extremely high concentrations?

Introduction: O_3 chemistry

- Photolysis reaction of NO_2

$$NO_2 + hv(\lambda < 430nm) \rightarrow NO + O(^3P) \quad (1.1)$$

$$O(^3P) + O_2 \rightarrow O_3 \quad (1.2)$$

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (1.3)$$

Note: The reactions (1.1-1.3) is a zero cycle when no other substances are involved in . This means thatO_3 is not increased.

- However, when other species (e.g., No_x and VOCs), they react with OH radicals to generate NO_2 which are given as follows

$$O_3 + hv(\lambda < 330nm) \rightarrow O_2 + O(^1D) \quad (1.4)$$

$$O(^1D) + H_2O \rightarrow 2OH \quad (1.5)$$

$$VOCs + OH + O_2 \rightarrow RO_2 + H_2O \quad (1.6)$$

$$RO_2 + NO \rightarrow RO + NO_2 \quad (1.7)$$

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

Data and Models

Observational Stations	Time period	Data availability
Shang Hai (Pu Dong)	Dec.1-10, 2013	PM_{10}、NO_2、O_3、UV、O_3 column content (OMI) AOD (Modis) and meteorological data
China (1423 stations)	2013-2015	PM_{10}、NO_2、O_3 and meteorological data

Models

- NCAR TUV

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

- NCAR MM

NCAR Master Mechanism (MM) Model is a chemistry box model that includes a detailed and flexible chemical scheme

TUV Model

- **Inputs**
  - **Basic information:** longitude, latitude, date, time, wavelength and height;
  - **Surface observations:** surface albedo, air pressure, and ozone column content ;
  - **Aerosols:** aerosol optical depth, single scattering albedo, and asymmetric factor. (ignore cloud effect in this study)
- **Outputs**
  - UV irradiance, actinic flux, and photolysis rate, etc.

MM Model

- **Inputs**
  - PBL Height
  - Background concentrations (O_3,NO_x,H_2O,CO,VOC,etc.)
  - Initial concentration (O_3,NO_x, VOC,etc.)
  - Emissions (No_x and VOC, etc.)
- **Outputs**
  - Time variations of ozone concentration and reaction rates

Results: Obs. time series of met and chemical species (Dec. 2013, Shanghai)

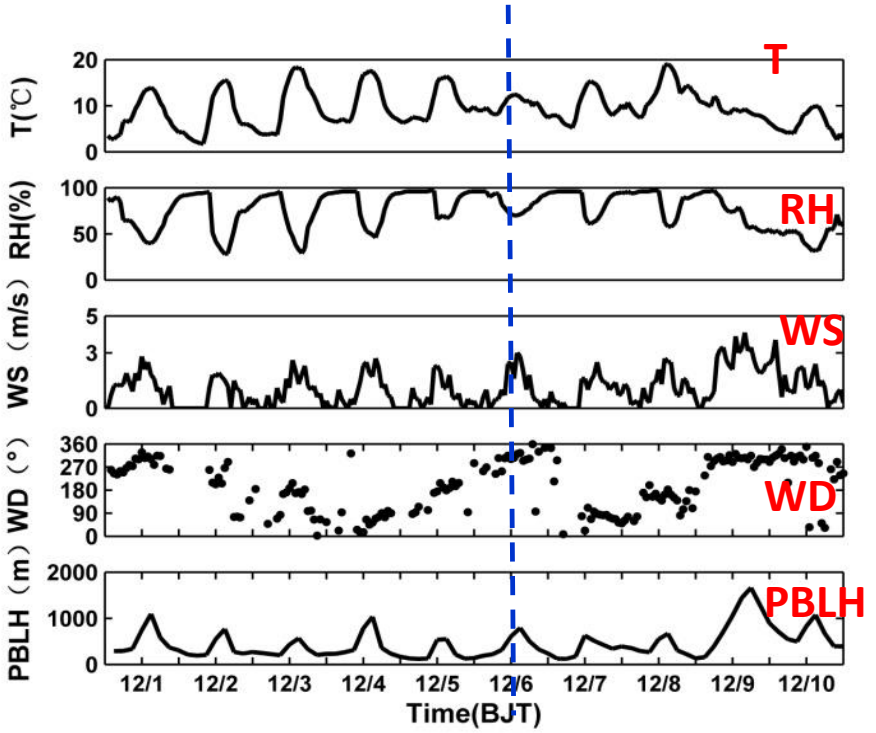


Fig.1 Time series of temperature, wind speed, wind direction, and relative humidity observed in Shanghai during Dec1-10, 2013

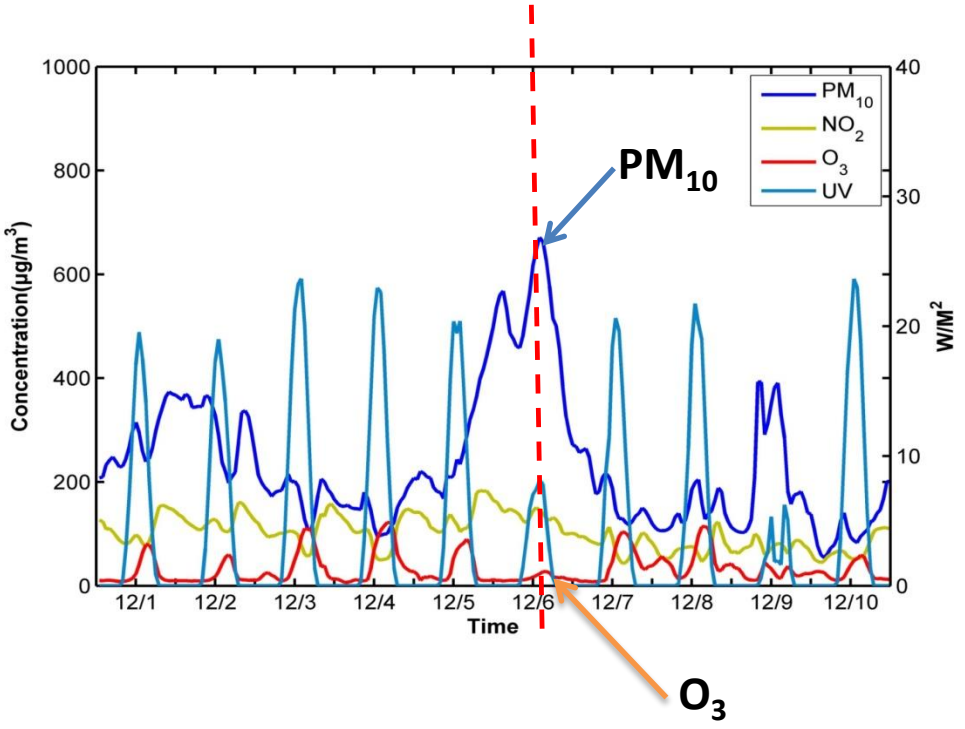
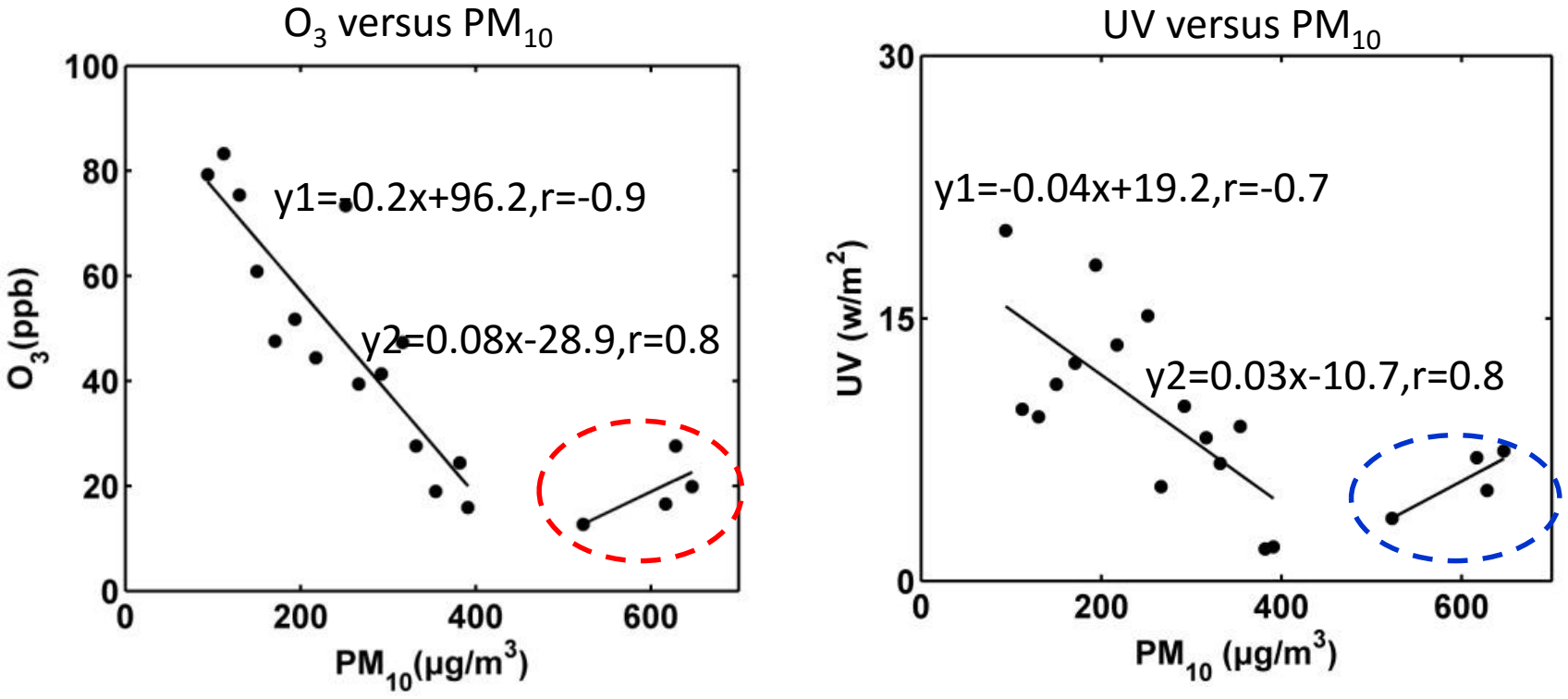


Fig.2 Time series of observed PM_{10}, NO_2, O_3 and UV in Shanghai during Dec1-10, 2013

Results: Impact of aerosol concentrations on UV and O_3 (Shanghai, Dec. 2013)



（a） （b）

Fig.3 Correlation of O_3 with PM_{10} (a) and UV with PM_{10} (b) observed at Shanghai Pudong station during 9:00-17:00 BJT During Dec. 1-10, 2013

1) O_3 was decreased with increasing PM_{10} when PM_{10} is lower than $400\mu gm^{-3}$
2) O_3 was increased slightly with increasing PM_{10}, indicating weak photochemical reactions on Dec. 6, 2013.

Comparisons between Dec. 4 and Dec. 6

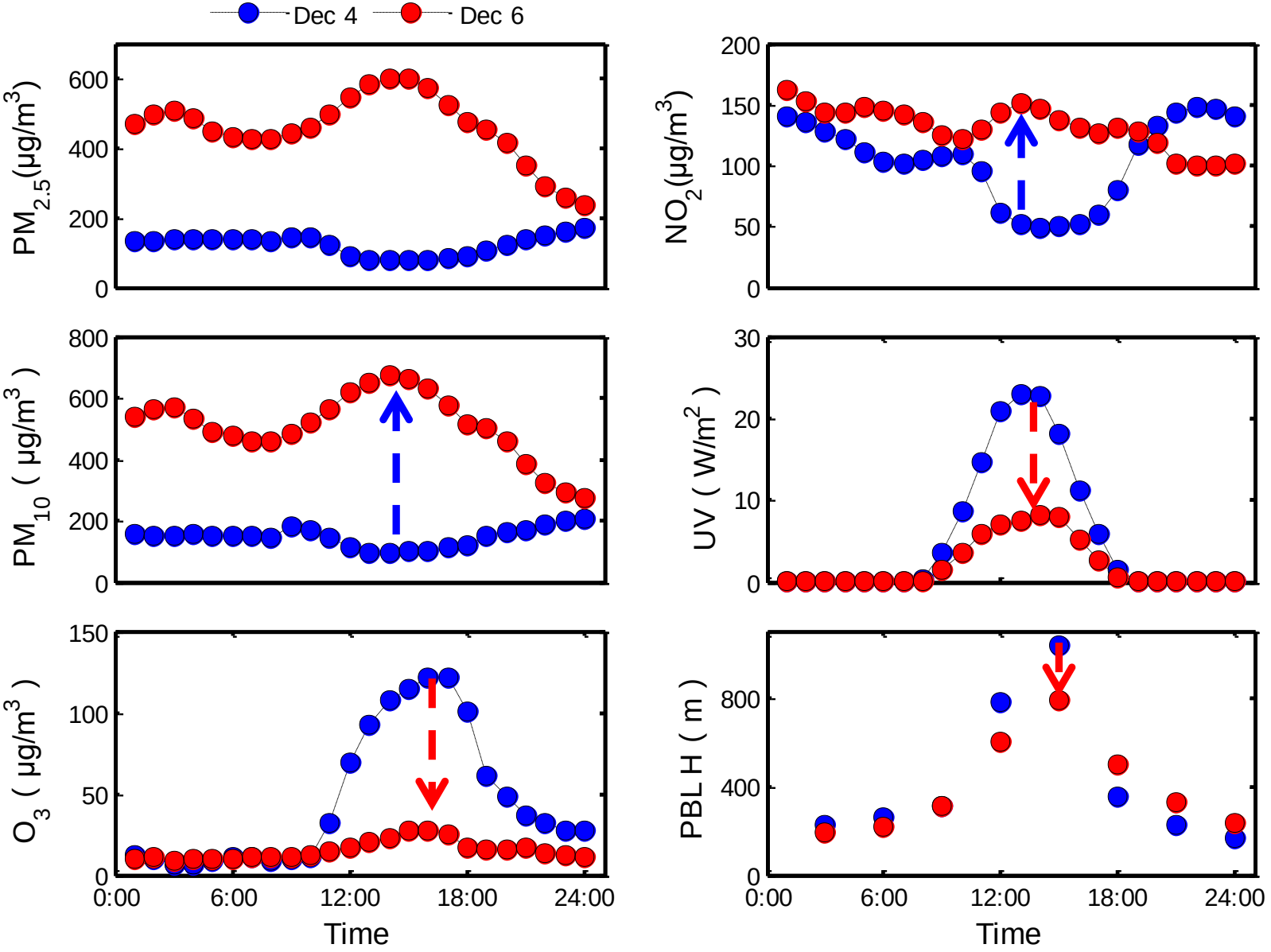


Fig.4 diurnal pattern of O_3, PM_{10}, NO_2 PBL between Dec.4 and Dec. 6th

Table.1 The rate change of $PM_{2.5}$, UV, O_3, NO_2 and PBLH from 11 am to 14 pm on Dec. 4 and Dec.6,2013

	Hourly change						Maximum	
	Dec. 4			Dec. 6			Dec. 4	Dec. 6
	12 BJT	13 BJT	14 BJT	12 BJT	13 BJT	14 BJT		
$PM_{2.5}$ ($\mu g/m^3$)	11.5	1.9	1.0	39.1	20.3	0.1	91.0	602.3
UV (W/m^2)	2.2	0.32	4.5	0.39	0.65	0.22	22.96	8.08
O_3 ($\mu g/m^3$)	22.8	15.1	8.1	3.3	2.9	4.2	115.1	27
NO_2 ($\mu g/m^3$)	10.6	1.8	1.5	6.8	4.9	7.9	62	150.7
PBL (m)			251			183	1032	778

Impact of T and RH on O_3 (Shanghai, Dec. 2013)

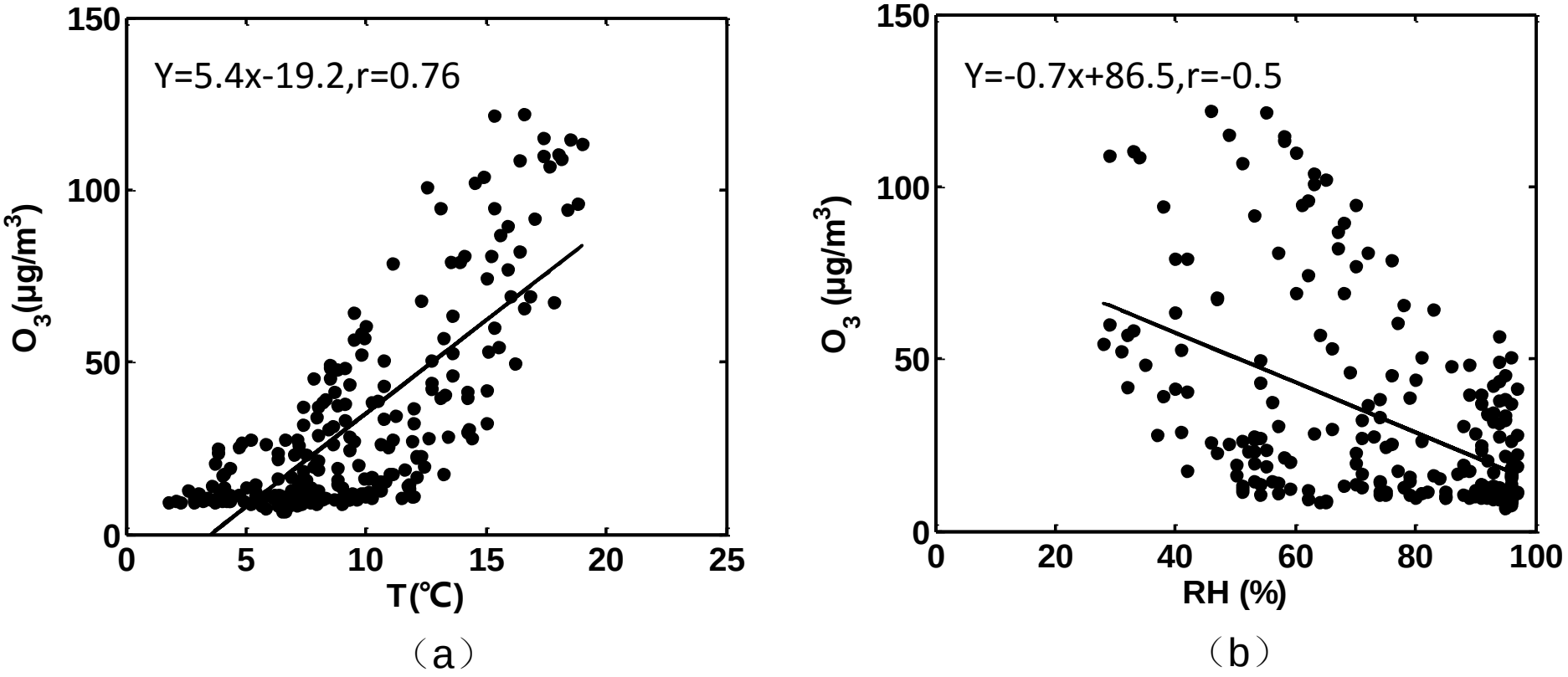
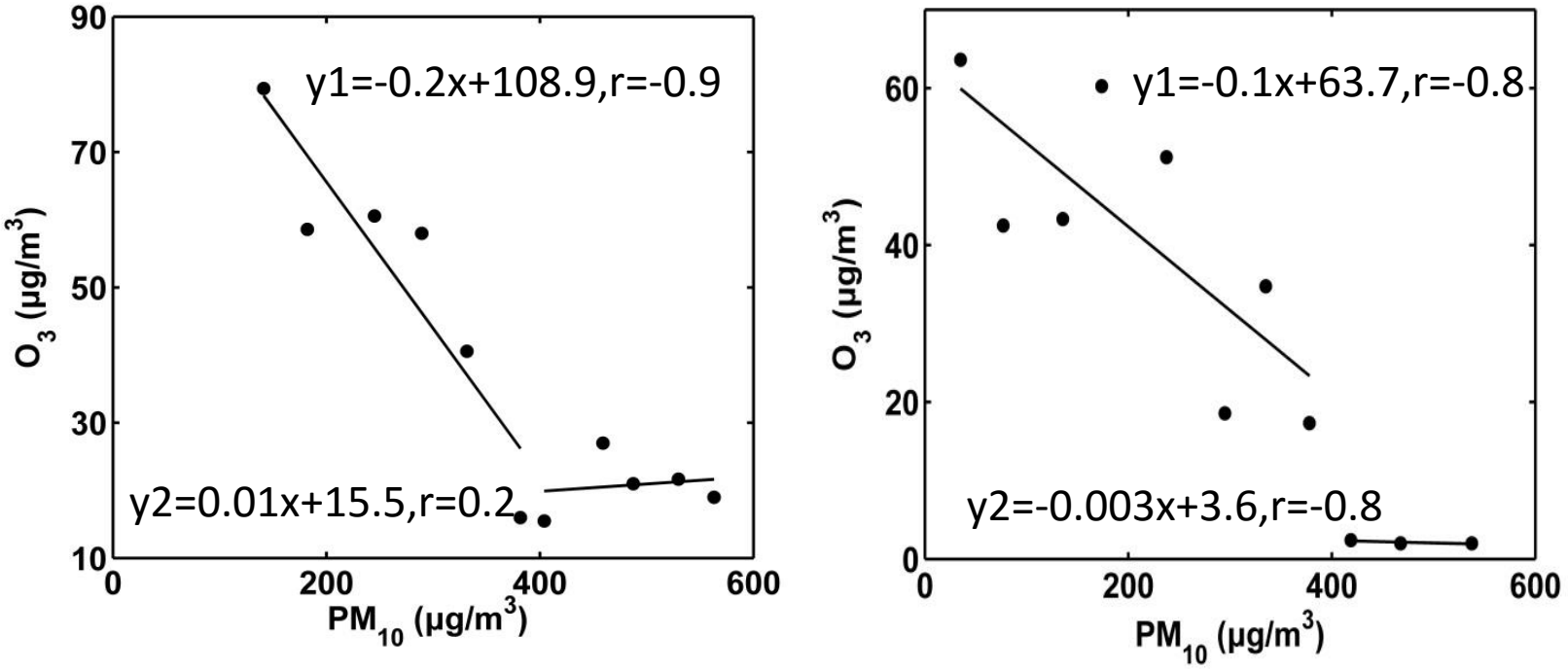


Fig.5 Correlation of O_3 with (a) temperature and (b) RH observed at Shanghai

Similar results at other sites



(a) (b)

Fig.6 Correlation of O_3 with PM_{10} observed at (a) Kunshan and O_3 with PM_{10} observed at (b) Beijing

Evaluation at more sites

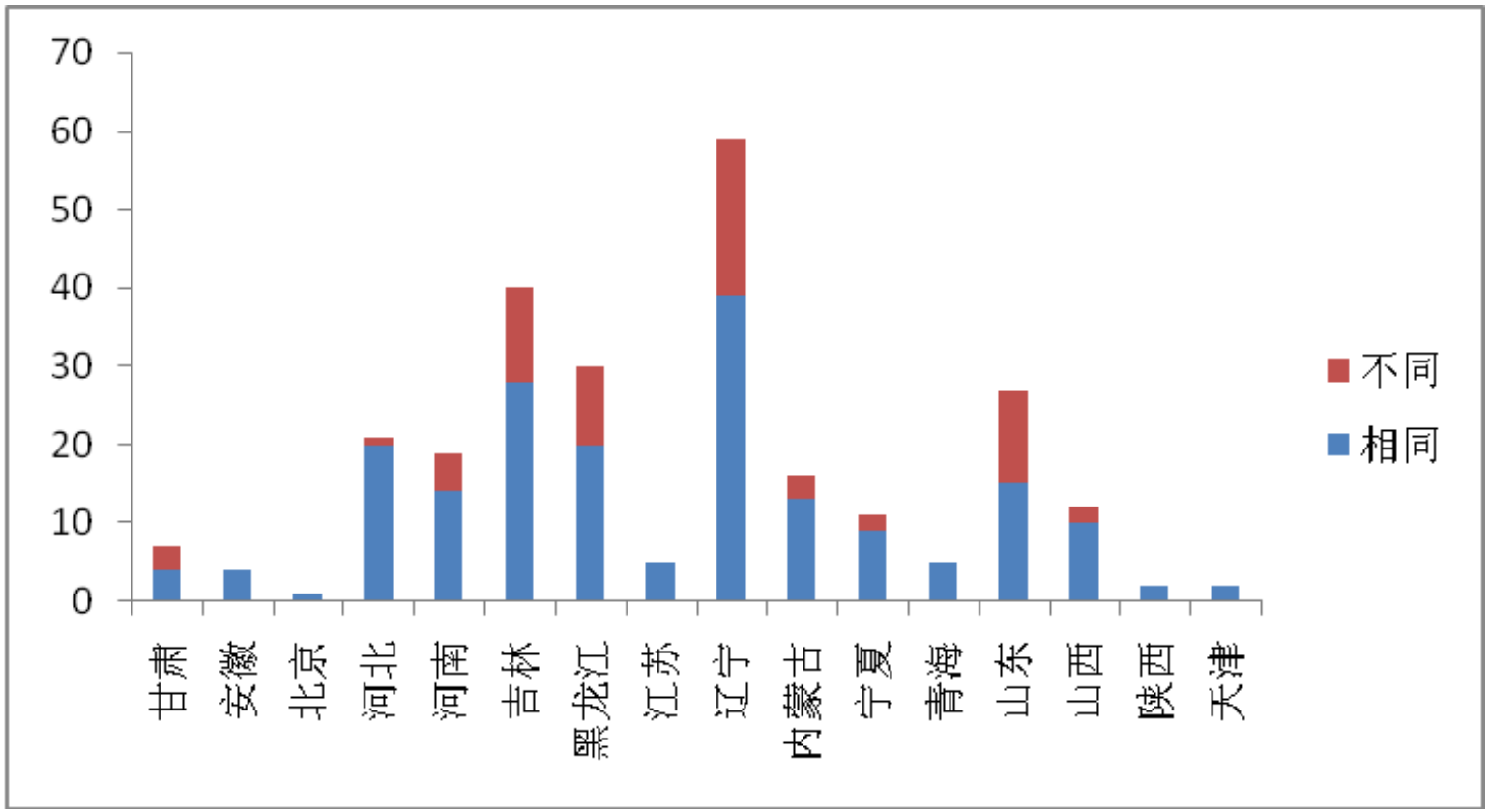


Fig.7 Site numbers with similar and different relationship of O_3-PM_{10} in China

Possible reasons: O_3 is decreased with increasing AOD (or PM_{10} or $PM_{2.5}$) when local photochemical reaction is dominant. However, when O_3 is increased with increasing AOD when regional tranpsort is domimant.

Impact of AOD on UV (TUV modeling results)

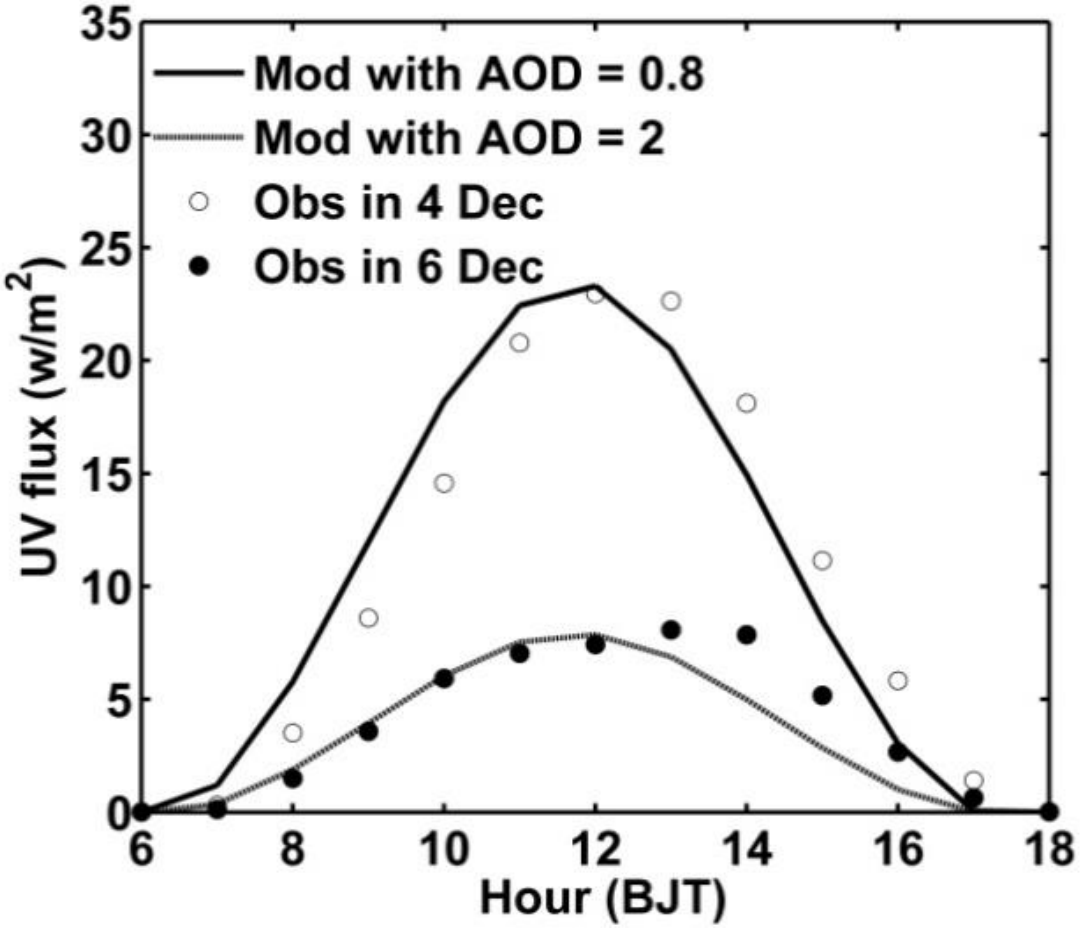


Fig.8 Sensitivity of UV to AOD in Shanghai on December 6th, 2013

Impact of AOD and SSA on UV (TUV modeling results)

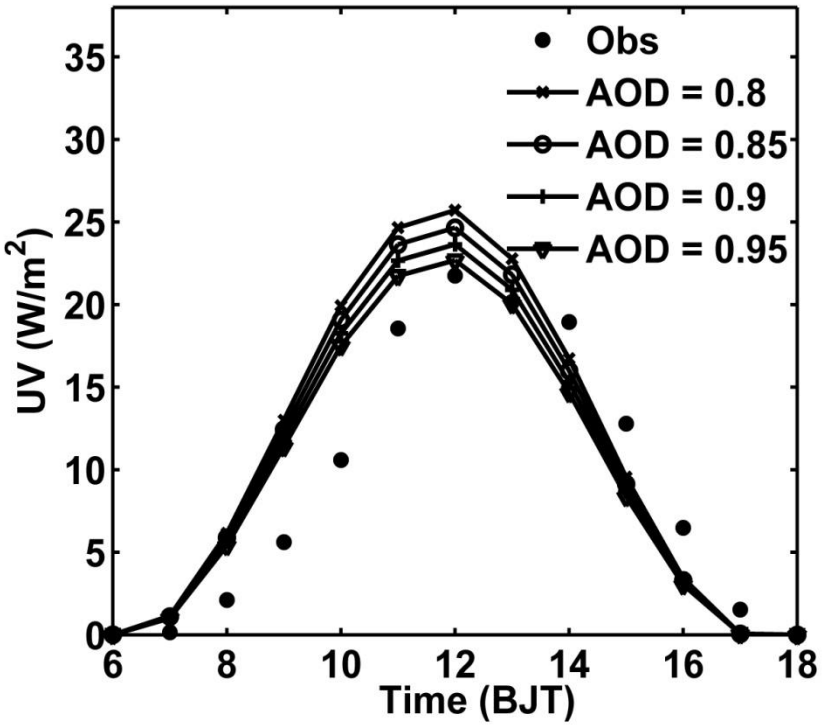


Fig.9 Sensitivity of UV to AOD in Shanghai on December 6th, 2013

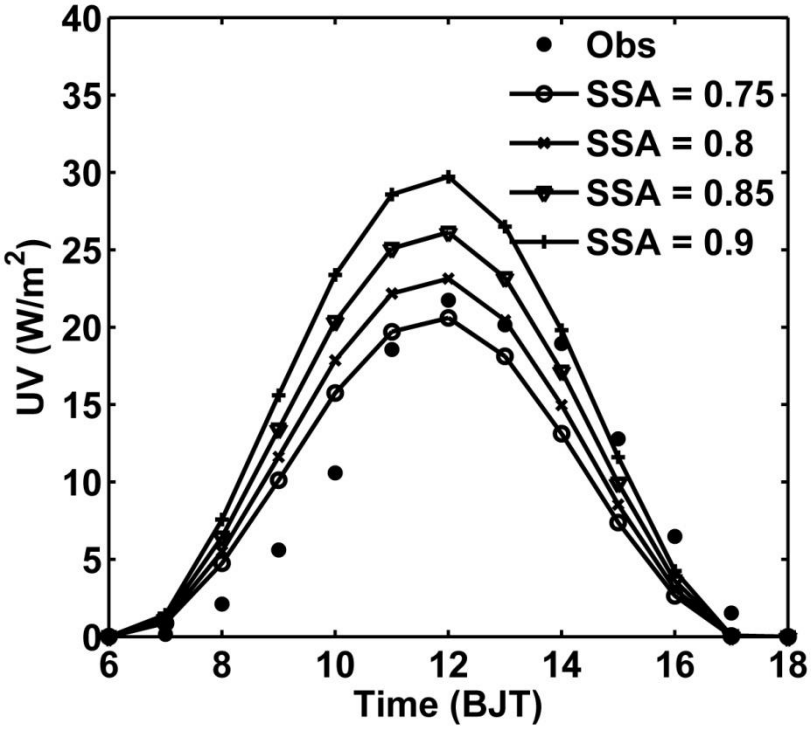


Fig.10 Sensitivity of UV to SSA in Shanghai on December 6th, 2013

Impact of AOD on O_3 (MM modeling results)

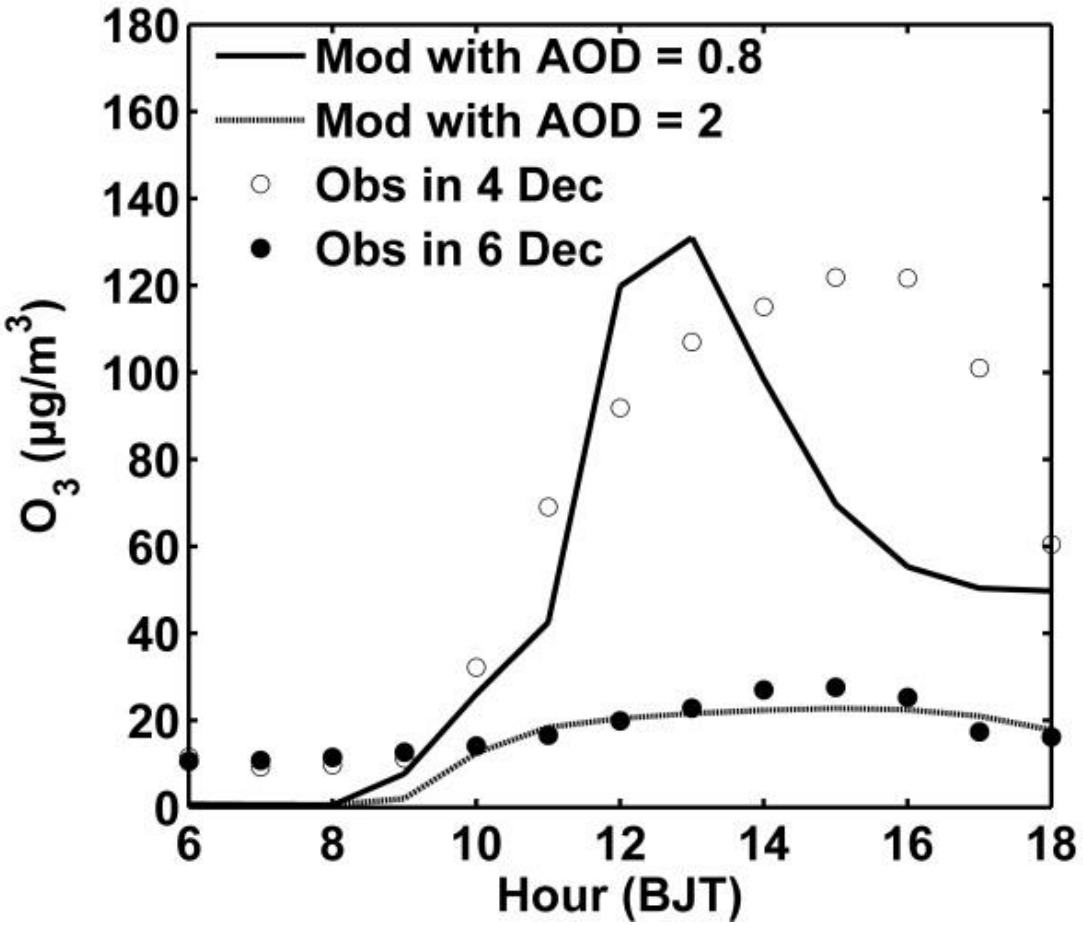


Fig. 11 The calculated ozone concentrations (solid lines) and observed concentrations during (point) during the two periods.

Impact of AOD on O_3 (MM modeling results, cont.)

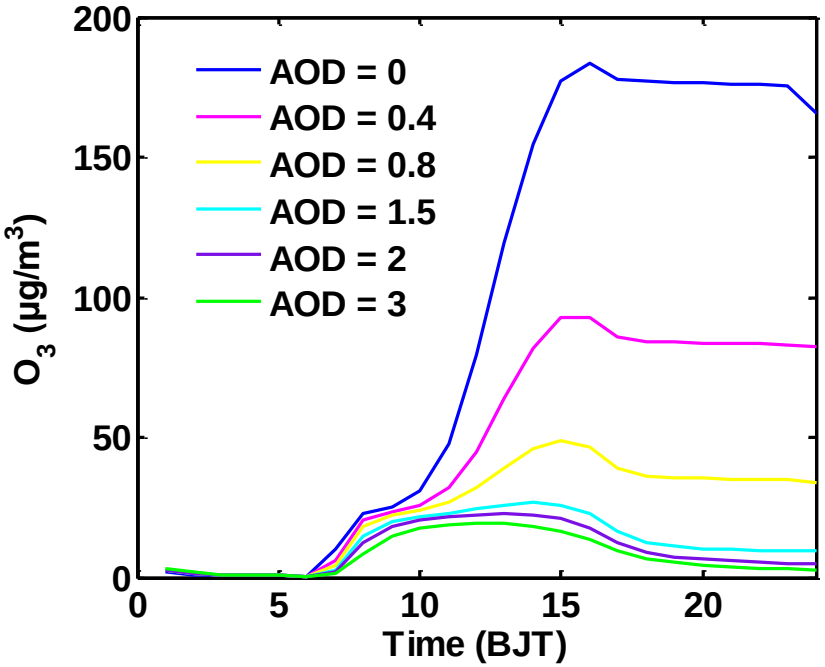


Fig.12 Diurnal variation of O_3 calculated under different AOD

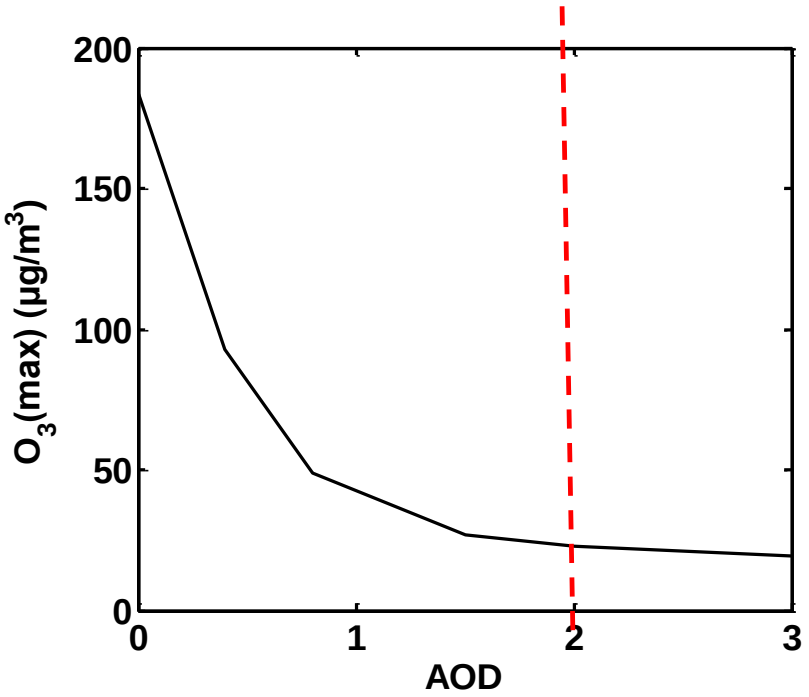


Fig.13 Daily maximum variation of ozone calculated under different AOD

Impact of SSA on O_3 (MM modeling results)

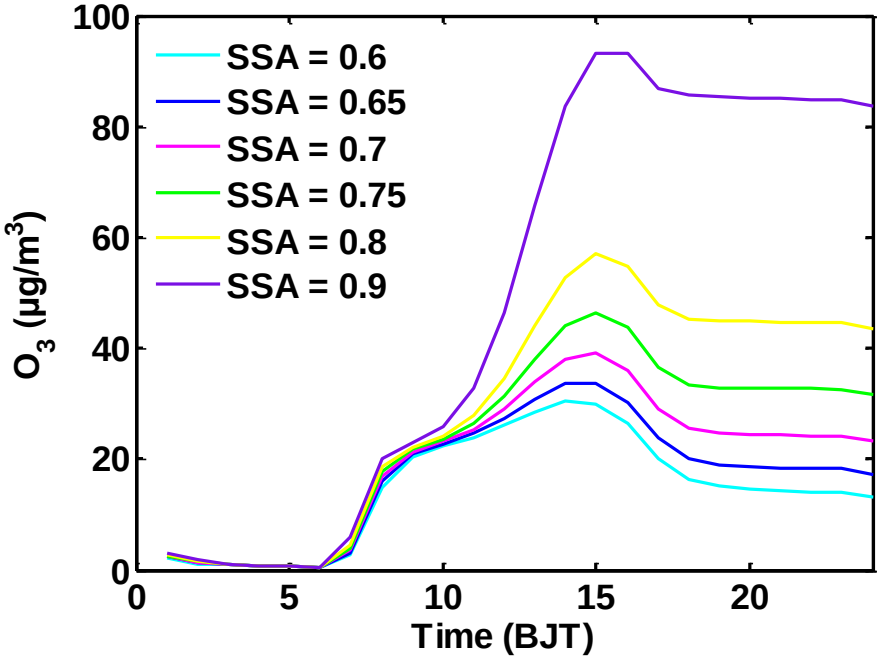


Fig.14 Diurnal variation of O3 calculated under different SSA

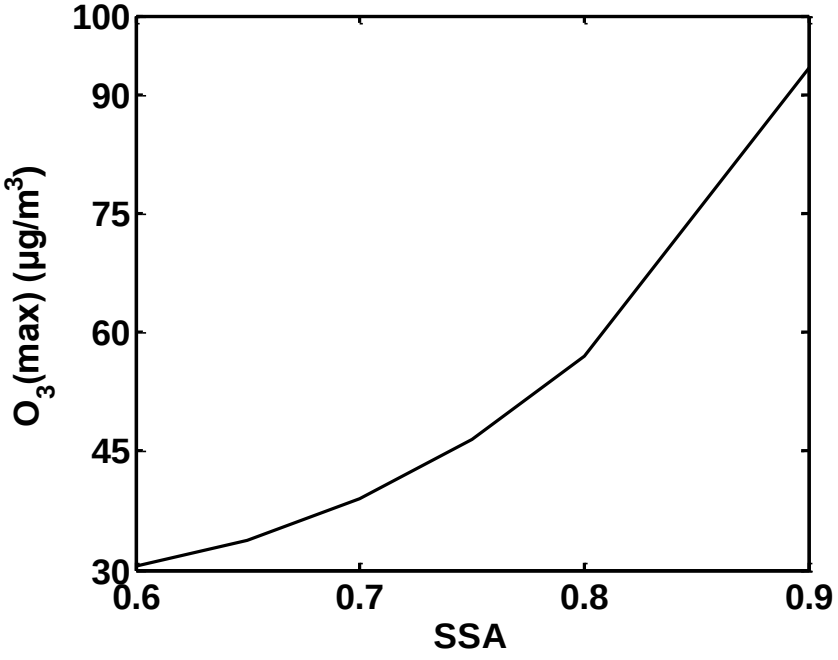


Fig.15 Daily maximum variation of ozone calculated under different SSA

Summary and conclusions

- Surface-reaching ultraviolet (UV) radiation is attenuated by aerosols greatly. This leads to significant reduction of surface O_3.
- O_3 concentrations are decreased with increasing aerosols (.e.g, PM_{10} or AOD) when PM_{10} is less than 400 $\mu g/m^3$, but is increased slightly when PM_{10} is greater than 400 $\mu g/m^3$ during a heavy haze event (.e.g., the case on Dec. 6th in Shanghai).
- Observational analyses confirm that more than 70% of sites support this finding and the rest doesn't. The former case is closely associated with the cases that local photochemical reactions play a dominant role in the O_3 enhancement whereas the latter is related to the regional transport.

- The modeling results indicate that ozone concentrations are increased with decreasing AOD and increasing SSA. The ozone concentration tends to reach a constant when AOD is higher than 2.0.

Thank you