Yale-NUIST Center on Atmospheric Environment

IMPACT OF ENTRAINMENT ON OZONE IN THE ATMOSPHERIC BOUNDARY LAYER

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OUTLINE

1. Background
2. Method
3. Results & Discussion
4. Conclusions
5. Future Work

MOTIVATION

O_3 > 80ppbv

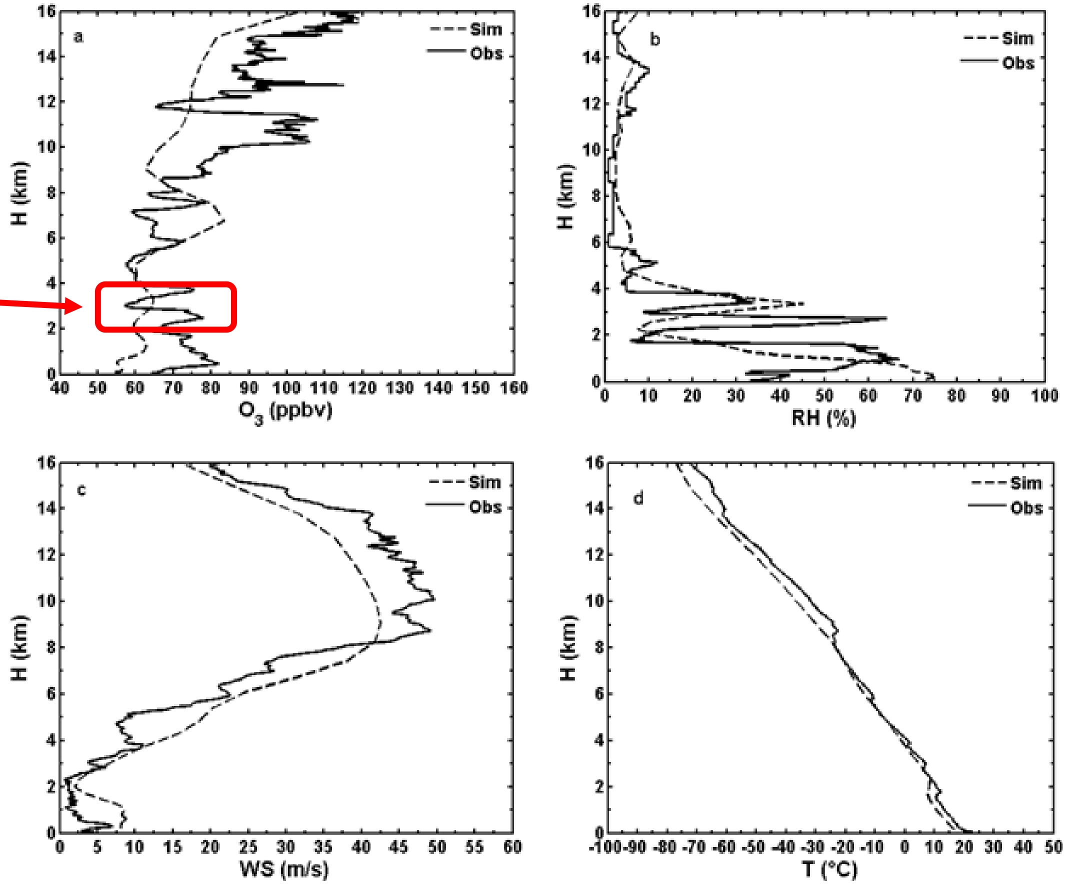


Fig.1. Vertical profiles of O_3、RH、WS and T observed in Hong Kong .

(*from KaiHui*)

Question: How does the high O_3 at the 2-4 layer influence O_3 in the atmospheric boundary layer? How much?

BACKGROUND

Surface ozone (O_3)

- Ozone is produced through a series of complicated chemical reactions involving NOx , VOCs and solar ultraviolet radiation (secondary pollutant);
- High levels of O_3 are harmful to human health, vegetation ecosystems, and crop yields;
- Important greenhouse gas;
- One of the major sources of hydrogen radicals.

BACKGROUND

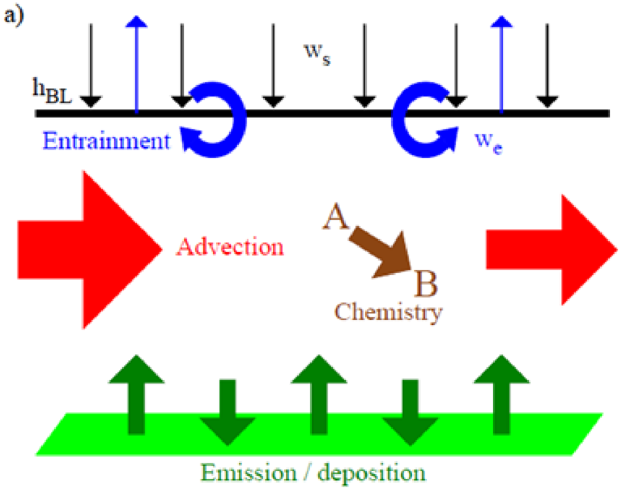


Fig.2. Schematic overview of the different terms that affect the evolution of ozone. (Ouwersloot et al.,2012)

Three major sources of O_3 in the atmospheric boundary layer (ABL)

— Local production via photochemical reactions

e.g., Penkett and Brice, (1986) , Dickerson et al., (1995), Li et al.,(2002)

— Regional transport

e.g., Zheng Yongguang et al.， 2005； Oltmans et al.， 2004

— Vertical transport from upper levels (entrainment)

As showed previously, the enhanced O_3 from upper levels (like from stratosphere) (e.g., Danielsen et al., 1968; Logan et al., 1985; Levye et al. (1985); Moody et al.(1995); Oltmans et al., 2004) may impose important impact on O_3 in the ABL.

As compared to chemical reactions and horizontal transport, the impact of entrainment on ozone in the ABL is not well quantified.

BACKGROUND

Entrainment

- ❖ **Transition area between ABL(turbulent area) and free atmosphere(without turbulent)**
- ❖ **Essential to the development and evolution of ABL**
- ❖ **Very limited observations**
- ❖ **An important passage of matter and energy exchange between the ABL and the free atmosphere, and has an important impact on the heat, water vapor, CO_2 and O_3 in the ABL.**

As compared to heat, water vapor, and CO_2, the study of impact of entrainment on O_3 om the ABL is very limited.

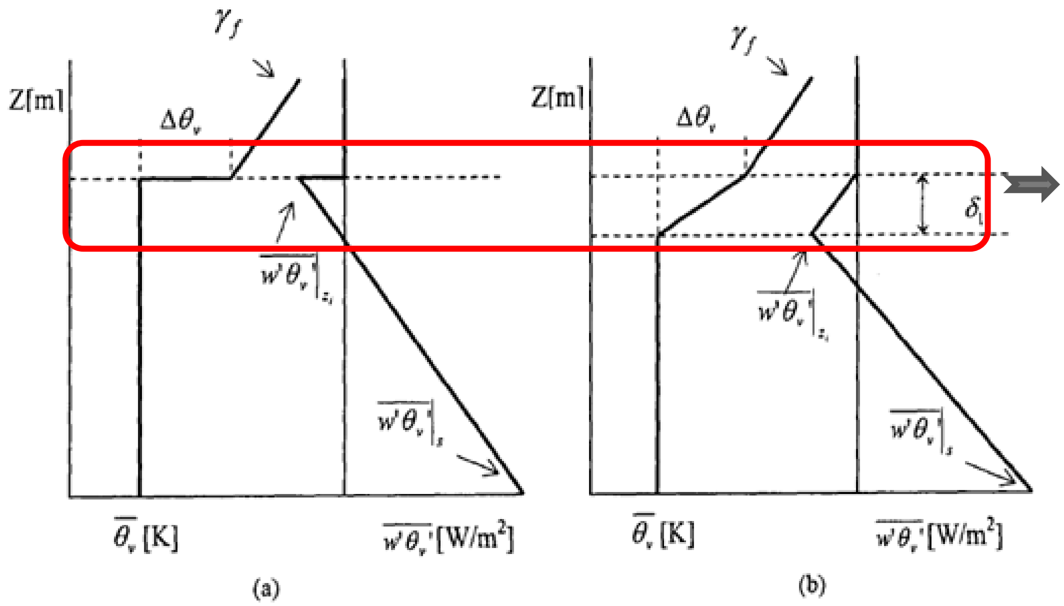
OBJECTIVES

- **To simulate diurnal variation of O_3 in the atmospheric boundary layer with an atmospheric boundary layer chemistry model (CLASS model).**
- **To quantify the relative contributions of entrainment and local chemical production to O_3 in the ABL under different jump conditions.**
- **To quantify the relative contributions of entrainment and local chemical reaction to O_3 in the ABL under different emission (i.e., NO_x and VOCs) conditions.**

METHOD

Chemistry Land-surface Atmosphere Soil Slab (CLASS) Model

1. Representation of boundary layer dynamics



Don't consider the aerosol optical depth(AOD)

Fig.3. Sketch of the profiles of virtual potential temperature and heat flux in a zero-order and first-order jump model

METHOD

$$\langle\phi\rangle = \frac{1}{h}\int_{s}^{h}\phi(z)\,\mathrm{d}z, \qquad (1)$$

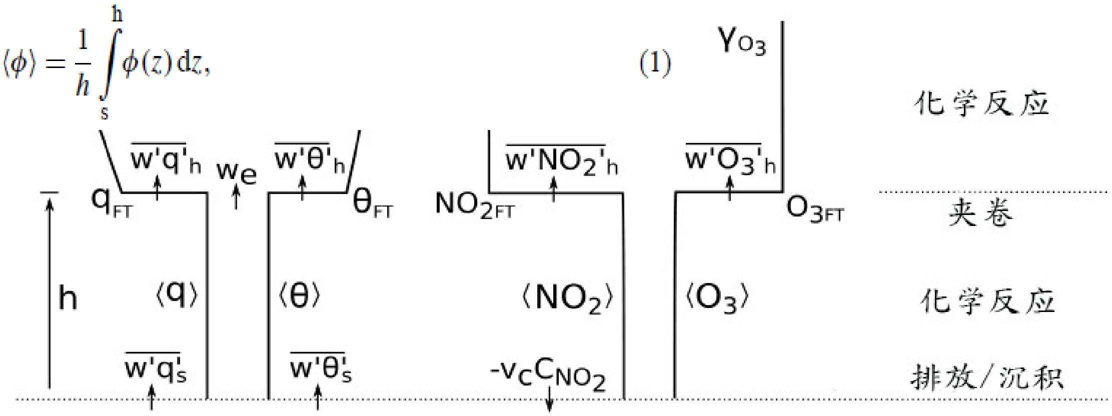


Fig.4. Conceptual representation of the vertical profiles of specific humidity (q), potential temperature(θ)and, as an example, nitrogen dioxide(NO2)and ozone(O3).

The governing equation of <Ø> are derived from 1-D Reynolds averaged Navier-Stokes equation

$$\frac{\partial\langle\phi\rangle}{\partial t} = \boxed{\frac{\overline{w'\phi'}_s - \overline{w'\phi'}_h}{h}} + \boxed{S_\phi.} \qquad (2)$$

(1)

dynamics chemistry

$\emptyset = \{\theta, q, S\}$; “s” and “h” denote the surface and mixed-layer height; $\overline{w'\emptyset'}$ denotes a turbulent flux at the surface(s) and the entrainment zone(h); $S_\emptyset$ contains additional source and sink terms

METHOD: CLASS/CHEMISTRY

Table 1. Chemical reaction scheme used in numerical experiment(CLASS)

Name	Chemical equation			Reaction rate constant
R1	$O_3 + h\nu$	$\rightarrow$	$O^{1D} + O_2$	$3.83 \times 10^{-5} \cdot e^{-\frac{0.575}{\cos(\chi)}}$
R2	$O^{1D} + H_2O$	$\rightarrow$	$2\ OH$	$1.63 \times 10^{-10} \cdot e^{\frac{60}{T}}$
R3	$O^{1D} + N_2$	$\rightarrow$	$O_3 + REST$	$2.15 \times 10^{-11} \cdot e^{\frac{110}{T}}$
R4	$O^{1D} + O_2$	$\rightarrow$	O_3	$3.30 \times 10^{-11} \cdot e^{\frac{55}{T}}$
R5	$NO_2 + h\nu$	$\rightarrow$	$NO + O_3 + REST$	$1.67 \times 10^{-2} \cdot e^{-\frac{0.575}{\cos(\chi)}}$
R6	$CH_2O + h\nu$	$\rightarrow$	$HO_2 + REST$	$1.47 \times 10^{-4} \cdot e^{-\frac{0.575}{\cos(\chi)}}$
R7	$OH + CO$	$\rightarrow$	$HO_2 + CO_2 + REST$	2.40×10^{-13}
R8	$OH + CH_4$	$\rightarrow$	$CH_3O_2 + REST$	$2.45 \times 10^{-12} \cdot e^{\frac{-1775}{T}}$
R9	$OH + C_5H_8$	$\rightarrow$	RO_2	1.00×10^{-10}
R10	$OH + MVK$	$\rightarrow$	$HO_2 + CH_2O + REST$	2.40×10^{-11}
R11	$HO_2 + NO$	$\rightarrow$	$OH + NO_2$	$3.50 \times 10^{-12} \cdot e^{\frac{250}{T}}$
R12	$CH_3O_2 + NO$	$\rightarrow$	$HO_2 + NO_2 + CH_2O + REST$	$2.80 \times 10^{-12} \cdot e^{\frac{300}{T}}$
R13	$RO_2 + NO$	$\rightarrow$	$HO_2 + NO_2 + CH_2O + MVK$	1.00×10^{-11}
R14	$OH + CH_2O$	$\rightarrow$	$HO_2 + REST$	$5.50 \times 10^{-12} \cdot e^{\frac{125}{T}}$
R15	$2\ HO_2$	$\rightarrow$	$H_2O_2 + O_2$	k^1
R16	$CH_3O_2 + HO_2$	$\rightarrow$	$REST$	$4.10 \times 10^{-13} \cdot e^{\frac{750}{T}}$
R17	$RO_2 + HO_2$	$\rightarrow$	$REST$	1.50×10^{-11}
R18	$OH + NO_2$	$\rightarrow$	HNO_3	$3.50 \times 10^{-12} \cdot e^{\frac{340}{T}}$
R19	$NO + O_3$	$\rightarrow$	$NO_2 + O_2$	$3.00 \times 10^{-12} \cdot e^{-\frac{1500}{T}}$
R20	$OH + HO_2$	$\rightarrow$	$H_2O + O_2$	$4.80 \times 10^{-11} \cdot e^{\frac{250}{T}}$
R21	$OH + H_2O_2$	$\rightarrow$	$H_2O + HO_2$	$2.90 \times 10^{-12} \cdot e^{\frac{-160}{T}}$
R22	$NO + NO_3$	$\rightarrow$	$2\ NO_2$	$1.80 \times 10^{-11} \cdot e^{\frac{110}{T}}$
R23	$NO_2 + O_3$	$\rightarrow$	$NO_3 + O_2$	$1.40 \times 10^{-13} \cdot e^{\frac{-2470}{T}}$
R24	$NO_2 + NO_3$	$\rightarrow$	N_2O_5	k^2
R25	N_2O_5	$\rightarrow$	$NO_2 + NO_3$	k^3
R26	$N_2O_5 + H_2O$	$\rightarrow$	$2\ HNO_3$	2.50×10^{-22}
R27	$N_2O_5 + 2\ H_2O$	$\rightarrow$	$2\ HNO_3 + H_2O$	1.80×10^{-39}
R28	$HO_2 + O_3$	$\rightarrow$	$OH + 2\ O_2$	$2.03 \times 10^{-16} \cdot \left(\frac{T}{300}\right)^{4.57} \cdot e^{\frac{693}{T}}$

[1] $k = (k_1 + k_2) \cdot (1 + k_3),\ k_1 = 2.2 \times 10^{-13} \cdot e^{\frac{600}{T}},\ k_2 = 1.9 \times 10^{-33} \cdot e^{\frac{980}{T}} \cdot c_{air},\ k_3 = 1 + 1.4 \times 10^{-21} \cdot e^{\frac{2200}{T}} \cdot c_{H_2O},$

[2] $k = 0.35 \cdot (k_1 \cdot k_2) / (k_1 + k_2),\ k_1 = 3.6 \times 10^{-30} \cdot \left(\frac{T}{300}\right)^{-4.1} \cdot c_{air},\ k_2 = 1.9 \times 10^{-12} \cdot \left(\frac{T}{300}\right)^{0.2},$

[2] $k = 0.35 \cdot (k_1 \cdot k_2) / (k_1 + k_2),\ k_1 = 1.3 \times 10^{-3} \cdot \left(\frac{T}{300}\right)^{-3.5} \cdot e^{\frac{-11000}{T}} \cdot c_{air},\ k_2 = 9.7 \times 10^{14} \cdot \left(\frac{T}{300}\right)^{0.1} \cdot e^{\frac{-11080}{T}}.$

METHOD: OBS. SITE

Fig.5. Location of TAP MUN in Hong Kong

RESULTS & DISCUSSION

Table 2. Prescribed Met ICs used for the numerical experiment

属性	值
1. 初始混合层高度 h[m]	200
2. 水平速度散度 $\nabla \times V_h\,[s^{-1}]$	5×10^{-6}
3. 地转风 $U_g, V_g\,[ms^{-1}]$	(0,0)
4. 地表感热通量 $\overline{w'\theta_s'}[Kms^{-1}]$	$0.1\sin(\pi t/t_d)$
5. 夹卷/地表热通量比率 $\beta = -\overline{w'\theta_h'}/\overline{w'\theta_s'}[-]$	0.2
6. 初始混合层位温 $<\theta>$ [K]	288
7. 初始自由对流层位温 θ_{FT} [K]	289
8. 自由大气位温递减率 γ_θ [Km^{-1}]	0.006
9. 地表潜热通量 $\overline{w'q_s'}$[gkg^{-1} ms^{-1}]	$0.03\sin(\pi t/t_d)$
10. 初始混合层比湿 $<q>$[gkg^{-1}]	5.3
11. 初始自由对流层比湿 q_{FT}[gkg^{-1}]	4.5
12. 自由对流层比湿递减率 γ_q [gkg^{-1}m^{-1}]	-0.0012

Table 3 Prescribed chemical species (ppbv) and surface fluxes (emission, ppbv m s^{-1})

	O_3	NO	NO_2	CH_4	ISO	CO	H_2O_2	MVK
<S> [ppb]	46	0	6	1724	2	100	0.1	1.3
S_{FT} [ppb]	15	0.5	0	1724	0	100	0.1	1.3
$\overline{w's'}$[μgm^{-2}s^{-1}]	0	0.004	a	0	b	0	0	0

a NO_2 的沉降通量用$-v_c C_{NO2}$计算，其中 v_c=0.015ms^{-1}

b $\overline{w'ISO'}=0.05\sin(\pi t/t_d)$

RESULTS & DISCUSSION

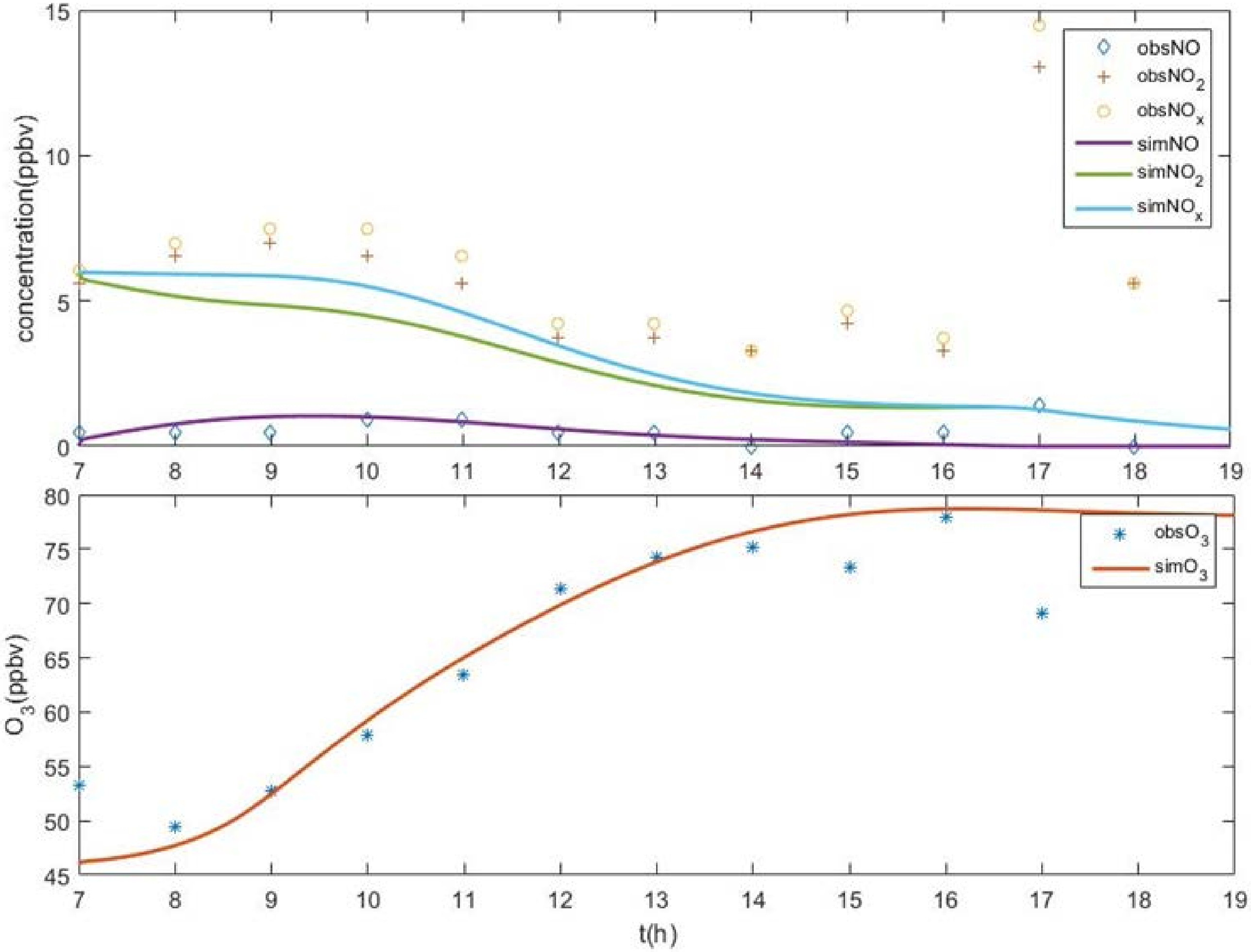


Fig.6. Comparison of simulated with observed NO,NO_2,NOx and O_3 at Tap Mun on Mar. 6, 2013

RESULTS & DISCUSSION

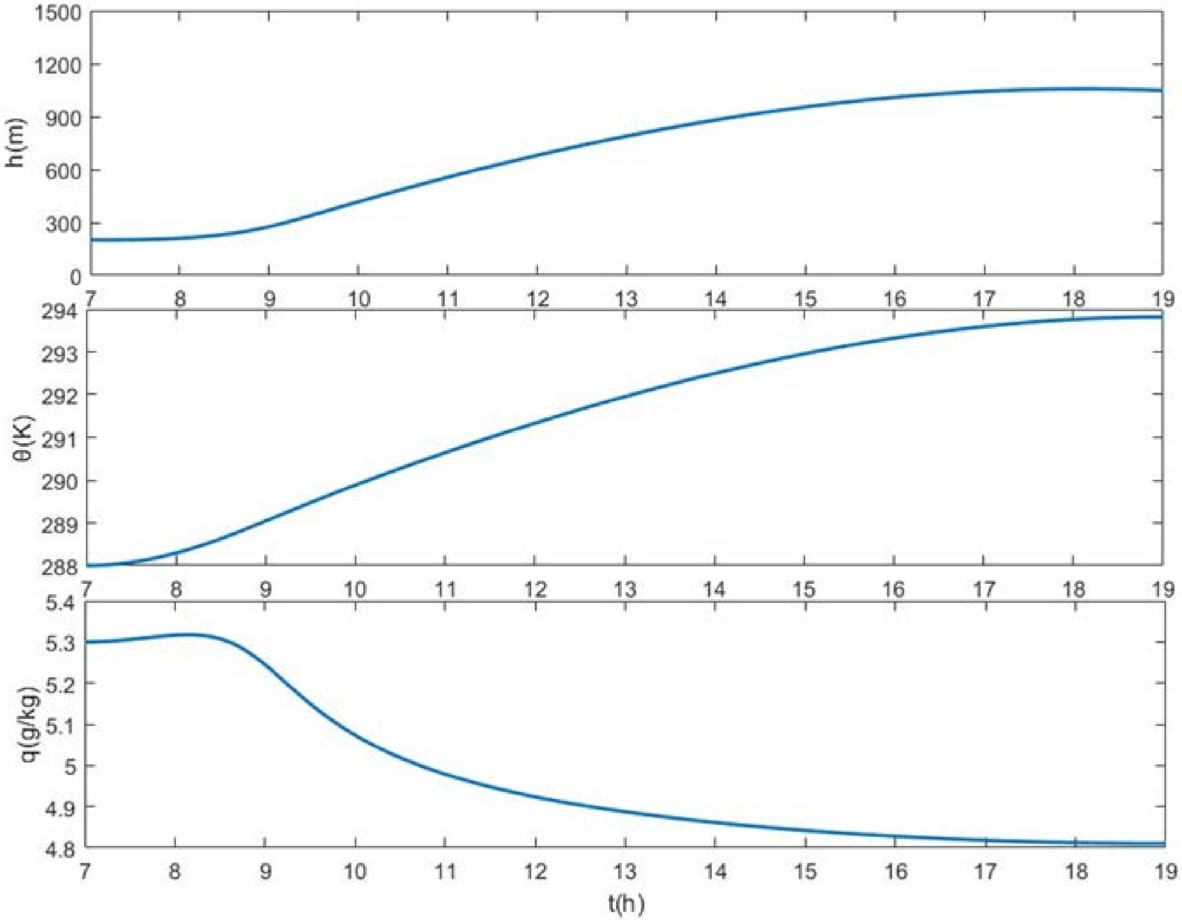


Fig.7. The PBL height(h), potential temperature (θ), and specific humidity (q) predicted by CLASS.

RESULTS & DISCUSSION

Case 1	Initial O_3 [ppb]	ΔO_3[ppb]
Control	46	0
Physics	46	15

Chem: 19 ppbv (65-46)
Phy: 13ppbv (78-65)

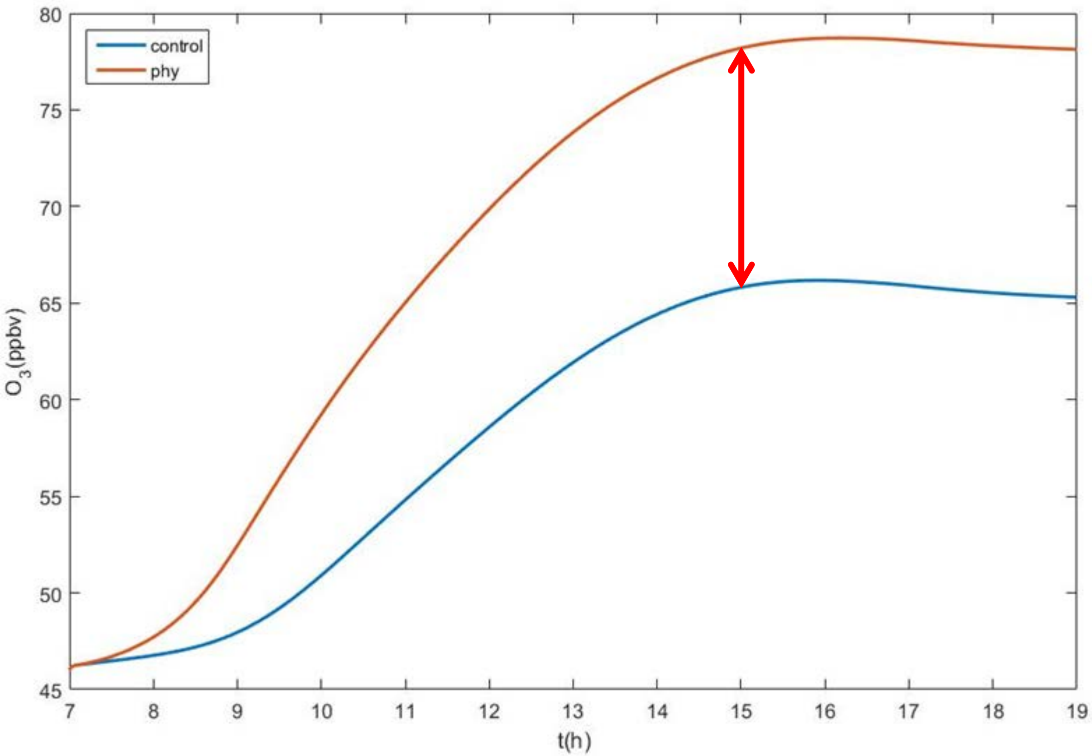


Fig.8. Time evolution of the O3 mixing ratio obtained with the mixed layer model with and without chemical reactions

RESULTS & DISCUSSION

Case 2	Initial O_3 [ppb]	ΔO_3[ppb]
Physics1	46	0
Physics2	46	5
Physics3	46	10
Physics4	46	15
Physics5	46	20
Physics6	46	25

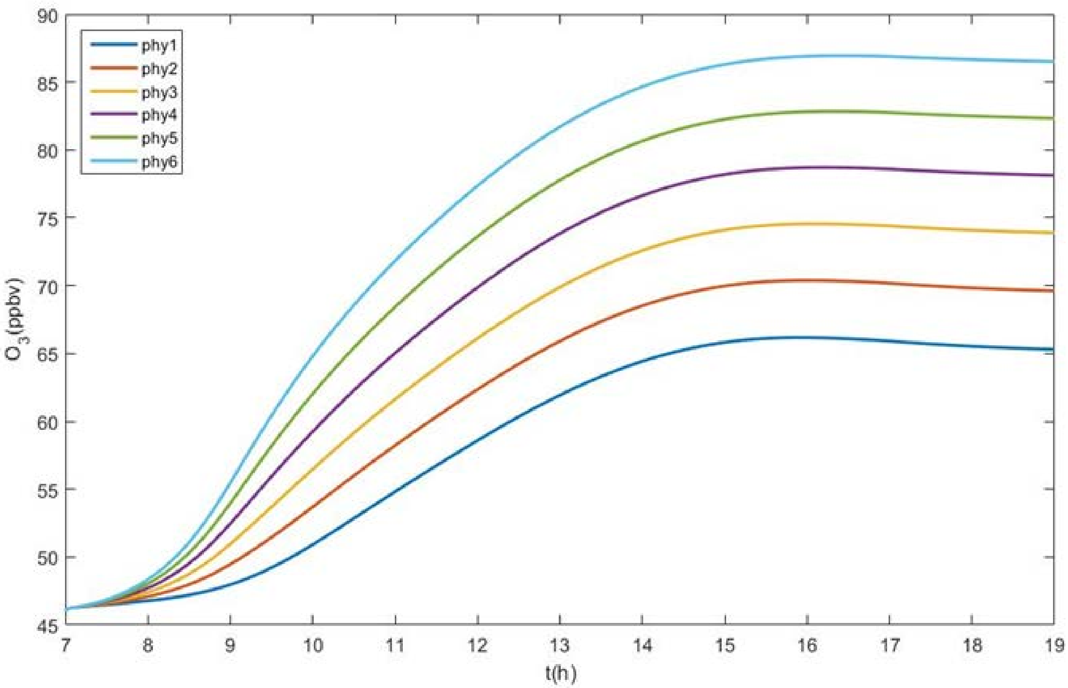


Fig.9. The CLASS-simulated O_3 at different O_3 jumps.

RESULTS & DISCUSSION

Table 5. CLASS-simulated peak O_3 at different O_3 jumps

Case	O_3 jump (ppb)	Simulated O_3 peak (ppb)
Physics1	0	66
Physics2	5	70
Physics3	10	74
Physics4	15	78
Physics5	20	82
Physics6	25	86

Every 5-ppb O_3 jump causes about 4-ppb increase of O_3 in the ABL

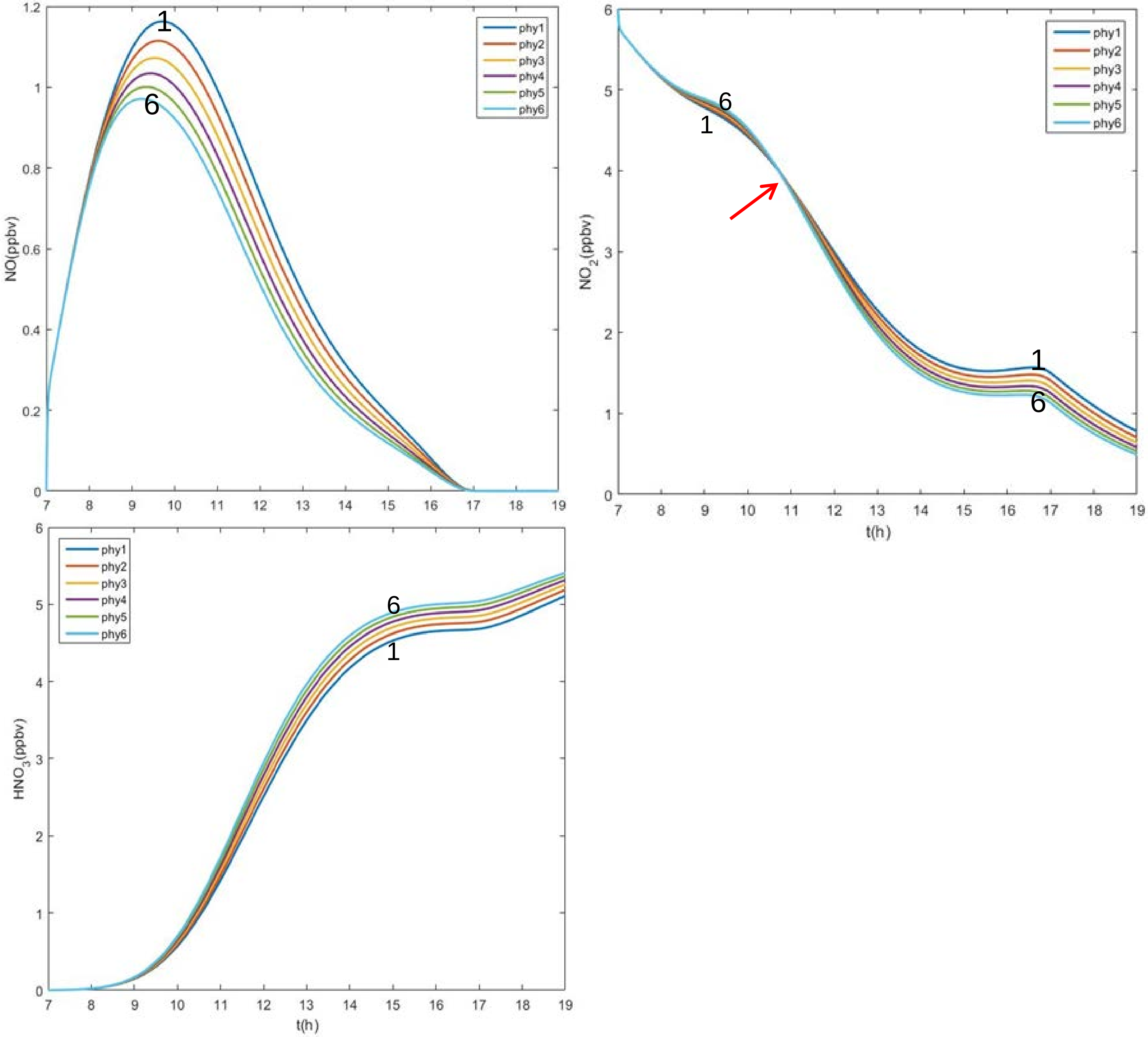


Fig.10. NO,NO_2 and HNO_3 simulated by CLASS model with different O_3 jumps

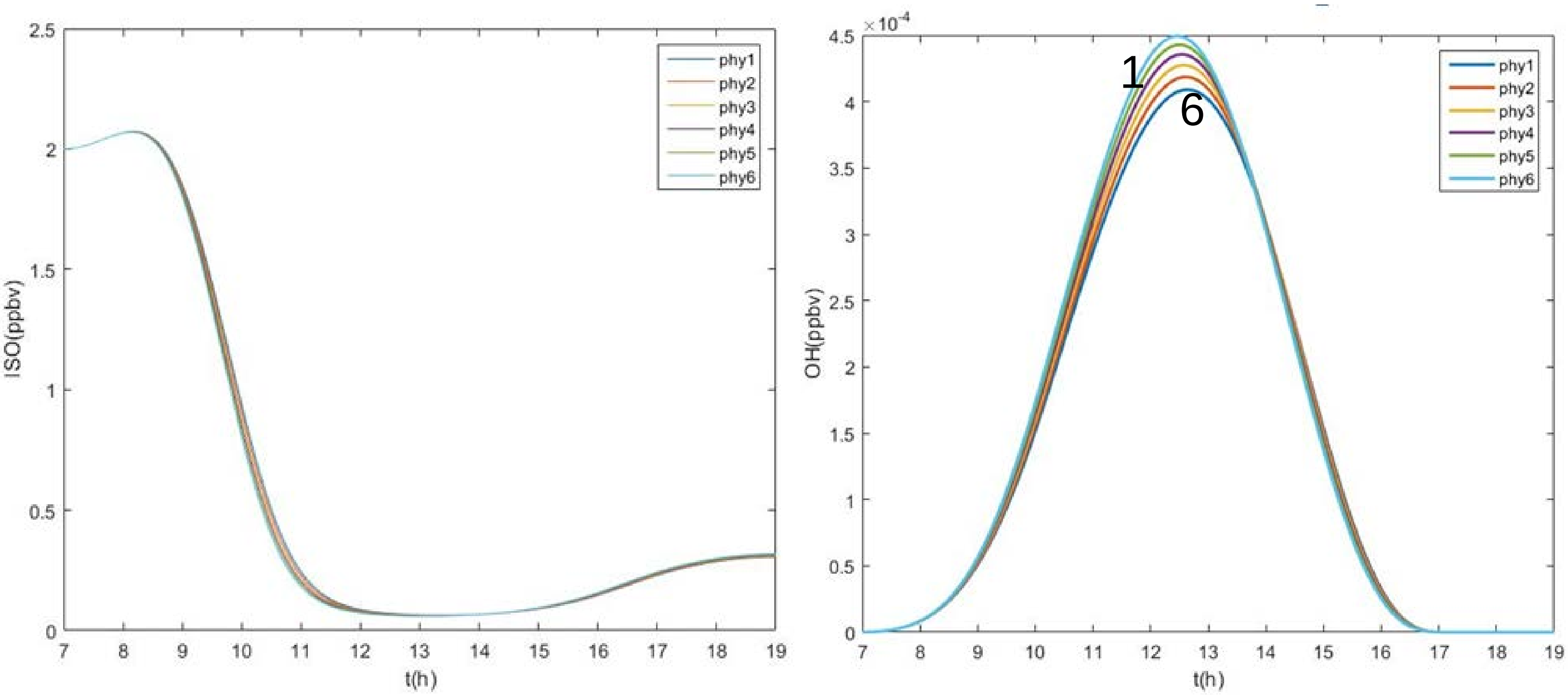


Fig.11. Similar to Figure 10 but for Isoprene and OH radicals

RESULTS & DISCUSSION

Impact of different emissions (i.e., NO_x and VOCs) conditions

EKMA: emipirical kinetic modeling approach

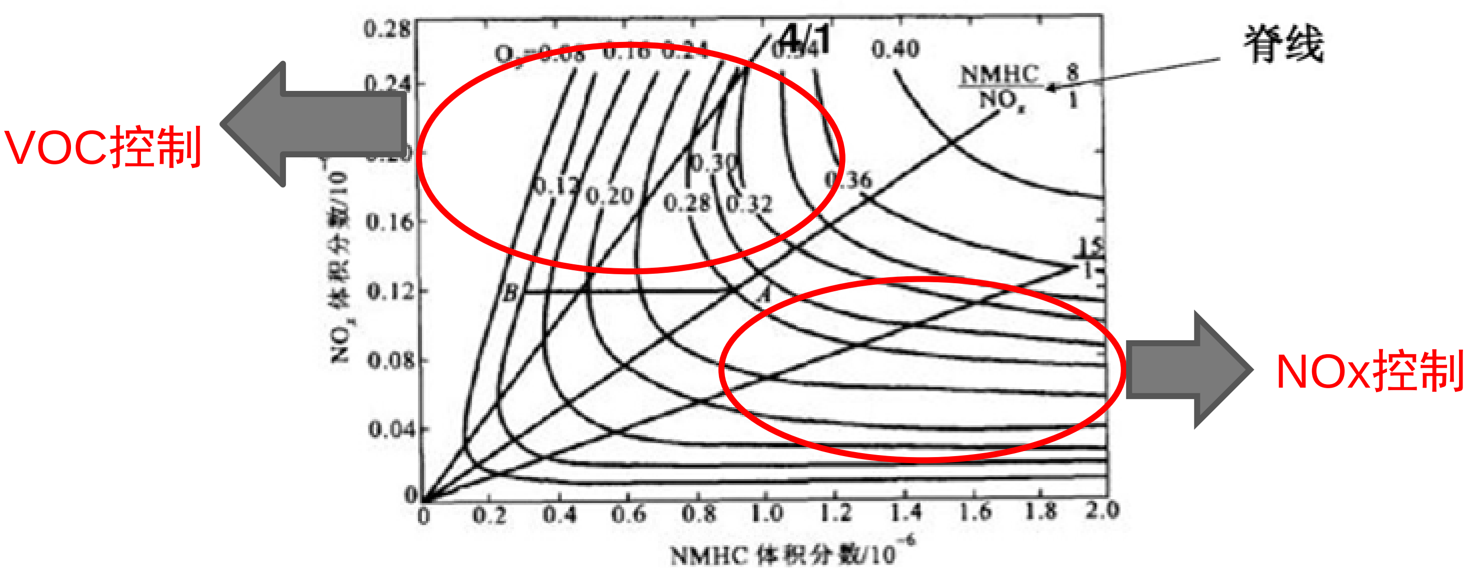


Fig.12. EKMA (Empirical Kinetic Modeling Approach) plot

RESULTS & DISCUSSION

	O_3	NO	NO_2	CH_4	ISO	CO	H_2O_2	MVK
<S> [ppb]	46	0	6	1724	60	100	0.1	1.3
S_{FT} [ppb]	15	0.5	0	1724	0	100	0.1	1.3
$\overline{w's'}$[$\mu g m^{-2} s^{-1}$]	0	0.004	a	0	b	0	0	0

a NO_2 的沉降通量用$-v_c C_{NO2}$计算，其中 v_c=0.015ms^{-1}

b $\overline{w'ISO'}$=0.05sin($\pi t/t_d$)

VOC控制（塔门）：VOCs/NOx= 0.55<8
NOx控制：ISO变成60ppb，VOCs/NOx>8

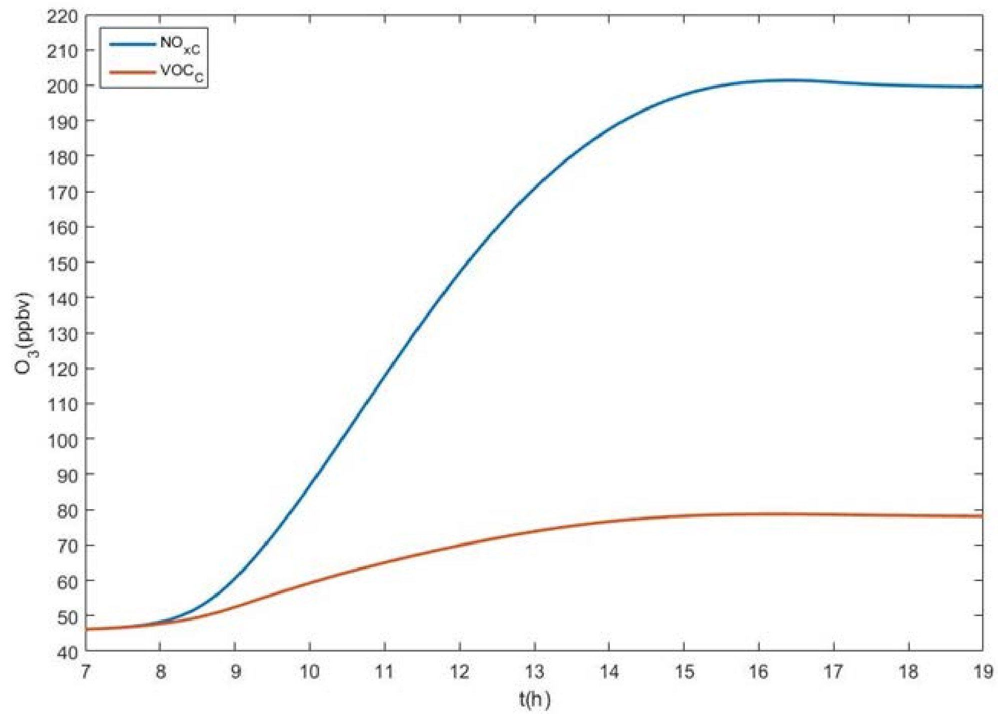


Fig.13. CLASS-simulated O_3 for different VOCs/NOx

RESULTS & DISCUSSION

	1	2	3
ΔO_3(ppbv)	10	15	20

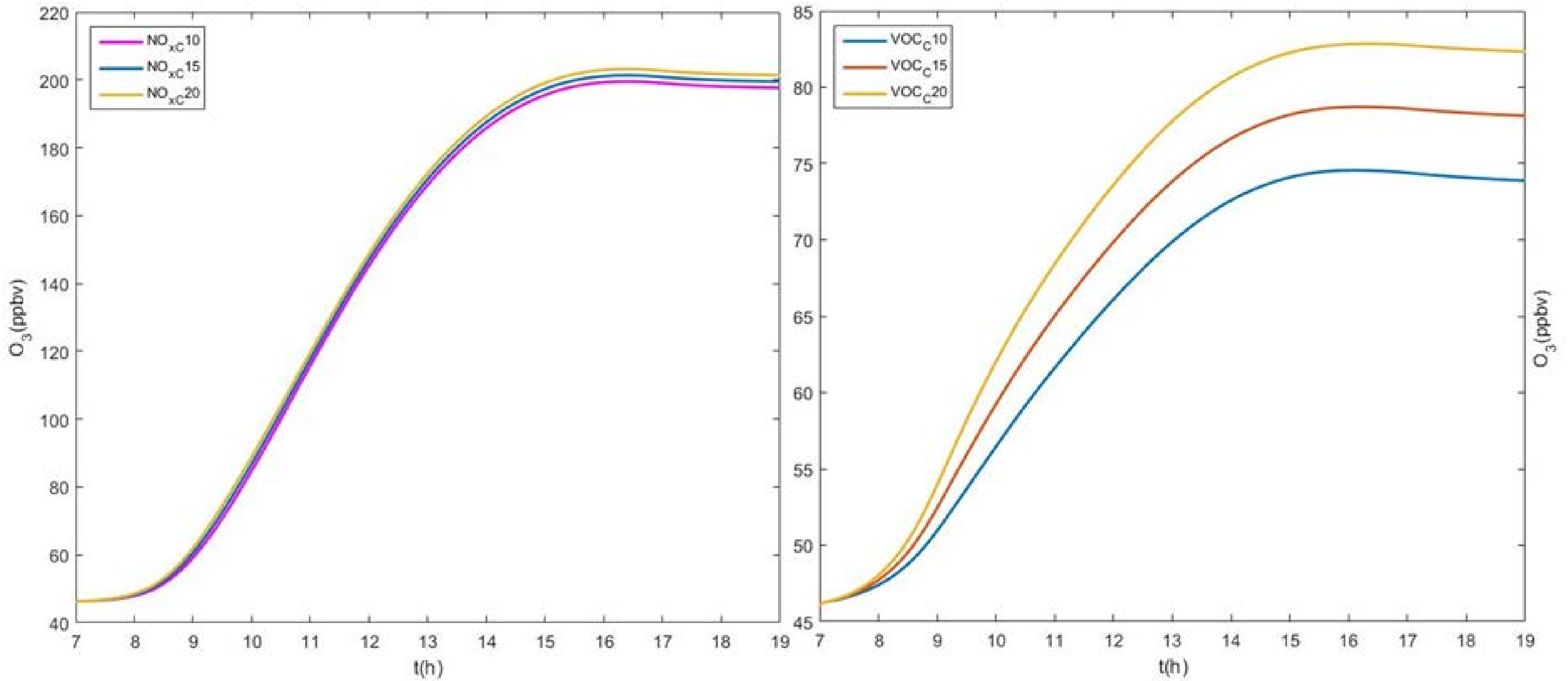


Fig.14. CLASS-simulated O_3 for different VOCs/NOx and O3 jump

RESULTS & DISCUSSION

Table 6. under different NO and ISO surface flux

species	control	case1	case2	case3	case4
NO flux (ppbv)	0.004	0.005	0.006	0.004	0.004
ISO flux (ppbv)	0.05	0.05	0.05	0.06	0.07

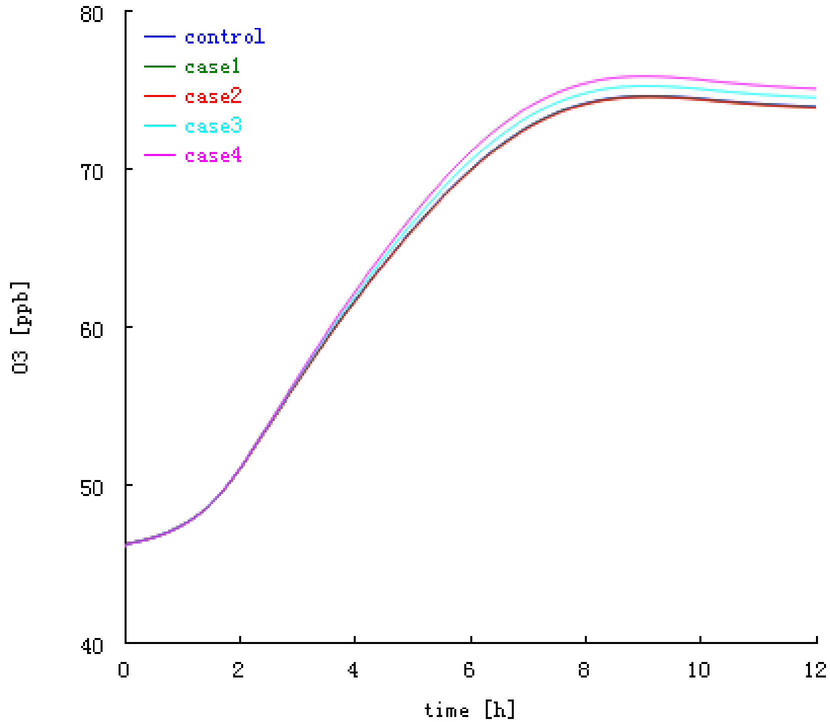


Fig.15. CLASS-simulated O_3 under different NO and ISO

CONCLUSIONS

❖ The impact of entrainment on O3 in the ABL is quantified by the CLASS model successfully.

❖ The entrainment plays a competitive role in the change of O3 in the ABL as compared to the local chemical reactions.

❖ The impact of entrainment on the O3 in the ABL is highly associated with O3 jumps.

❖ The relative contributions of entrainment versus chemical reactions to O3 in the ABL is also related to the emissions especially to the ratios of NOx/VOC.

NEXT STEPS

- Refine the simulations and experiments
- Complete statistical evaluations of the CLASS simulations.
- Developing one or two manuscript(s)

THANK YOU FOR YOUR ATTENTION！