Updates to photolysis calculations in WRF-Chem and evaluation with measurements

Alma Hodzic, Young-Hee Ryu,

Stacy Walters, Sasha Madronich, Andrew Conley

National Center for Atmospheric Research
Atmospheric Chemistry Observations and Modeling

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Introduction

Photolysis: - chemical dissociation caused by absorption of solar radiation;
- an essential component of air quality models

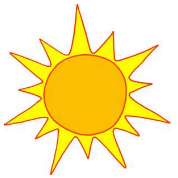
Example :

$O_3 + h\nu\ (\lambda < 340\ \text{nm}) \rightarrow O_2 + O(^1D)$ (J_{O1D}) source of OH in troposphere

$NO_2 + h\nu\ (\lambda < 420\ \text{nm}) \rightarrow NO + O(^3P)$ (J_{NO2}) source of O_3 in troposphere

Photolysis rates :

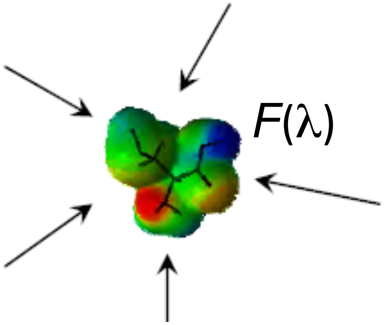
$$J\ (s^{-1}) = \int_\lambda F(\lambda)\ \sigma(\lambda)\ \phi(\lambda)\ d\lambda$$



$F(\lambda)$ = spectral actinic flux, quanta $cm^{-2}\ s^{-1}\ nm^{-1}$
$\propto$ probability of photon near molecule.

$\sigma(\lambda)$ = absorption cross section, $cm^2\ molec^{-1}$
$\propto$ probability that photon is absorbed.

$\phi(\lambda)$ = quantum yield, molec $quanta^{-1}$
$\propto$ probability that absorbed photon causes dissociation.



What do we need to know to predict photolysis reactions?

Compilations of Cross Sections & Quantum Yields

MPI-Mainz: http://www.atmosphere.mpg.de/enid/2295

NASA JPL: http://jpldataeval.jpl.nasa.gov/

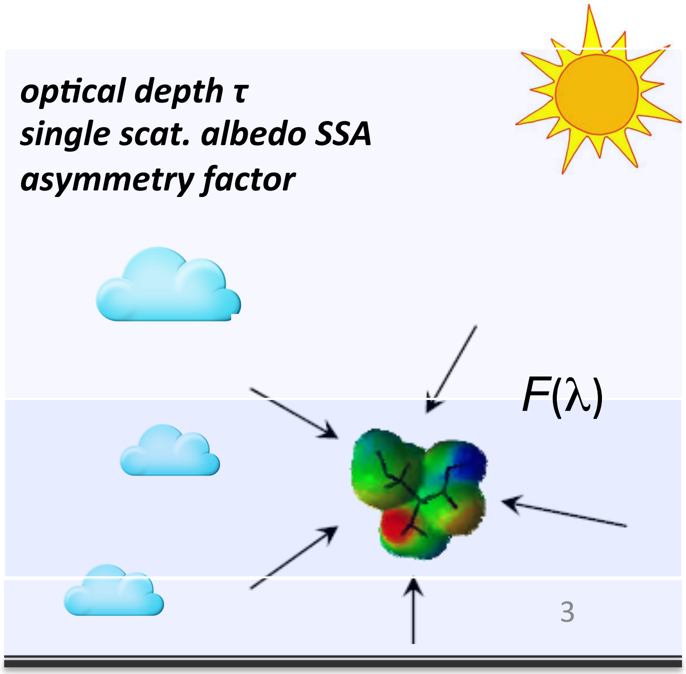
Actinic flux (F) is spherically integrated radiation (≠ irradiances on the surface)

$$F = \int_0^{\pi}\int_0^{2\pi} I(\theta,\varphi)\sin\theta \,\mathrm{d}\varphi\,\mathrm{d}\theta$$

(Watts m^{-2} or quanta s^{-1} cm^{-2})

Attenuations/enhancements of photolysis by:

- Molecules
  - Rayleigh scattering
  - Absorbing O_2, O_3, NO_2, SO_2
- Clouds (COD ~ 1-500) scattering
- Aerosols (AOD < 5) absorbing and scattering



Photolysis calculations in WRF-Chem : Current & updated

Several radiative transfer packages:

- phot_opt = 1 : TUV (140 λs, delta-Eddington)
- phot_opt = 2 : Fast-J (17 λs, 8-str Feautrier)
- phot_opt = 3 : F-TUV (17 λs, correction factor, delta-Eddington)

⇒ phot_opt = 4: updated TUV (140 λs, delta-Eddington – next release)

Limitations of current schemes & improvements :

- Cross sections & quantum yields data
  - are hard-coded and not up to date
  - ⇒ data are read from an input file wrf_tuv_xsqy.nc
  - ⇒ data are based on the latest version of the TUV model (V5.2, Jan 2016)

- Limited number of photolysis reactions
  - hard to add new reactions
  - ⇒ 109 photolysis reactions relevant for tropospheric and stratospheric chemistry (e.g. halogens chemistry)

List of available photolysis reactions in the updated TUV

*in mozart_mosaic_4bin

1	O2 -> O + O	(J_o2)
2	O3 -> O2 + O(1D)	(J_o1d)
3	O3 -> O2 + O(3P)	(J_o3p)
4	HO2 -> OH + O	
5	H2O2 -> 2 OH	(J_h2o2)
6	NO2 -> NO + O(3P)	(J_no2)
7	NO3 -> NO + O2	
8	NO3 -> NO2 + O(3P)	
9	N2O -> N2 + O(1D)	(J_n2o)
10	N2O5 -> NO3 + NO + O(3P)	
11	N2O5 -> NO3 + NO2	(J_n2o5b)
12	HNO2 -> OH + NO	
13	HNO3 -> OH + NO2	(J_hno3)
14	HNO4 -> HO2 + NO2	(J_hno4)
15	NO3-(aq) -> NO2(aq) + O-	
16	NO3-(aq) -> NO2-(aq) + O(3P)	
17	CH2O -> H + HCO	(J_ch2or)
18	CH2O -> H2 + CO	(J_ch2om)
19	CH3CHO -> CH3 + HCO	(J_ch3cho_a)
20	CH3CHO -> CH4 + CO	(J_ch3cho_b)
21	CH3CHO -> CH3CO + H	(J_ch3cho_c)
22	C2H5CHO -> C2H5 + HCO	
23	CH3OOH -> CH3O + OH	
24	HOCH2OOH -> HOCH2O. + OH	(J_pooh)
25	CH3ONO2 -> CH3O + NO2	
26	CH3(OONO2) -> CH3(OO) + NO2	
27	CH3CH2ONO2 -> CH3CH2O + NO2	
28	C2H5ONO2 -> C2H5O + NO2	
29	n-C3H7ONO2 -> C3H7O + NO2	
30	1-C4H9ONO2 -> 1-C4H9O + NO2	
31	2-C4H9ONO2 -> 2-C4H9O + NO2	
32	CH3CHONO2CH3 -> CH3CHOCH3 + NO2	
33	CH2(OH)CH2(ONO2) -> CH2(OH)CH2(O.) + NO2	
34	CH3COCH2(ONO2) -> CH3COCH2(O.) + NO2	
35	C(CH3)3(ONO2) -> C(CH3)3(O.) + NO2	
36	C(CH3)3(ONO) -> C(CH3)3(O) + NO	
37	CH3CO(OONO2) -> CH3CO(OO) + NO2	(J_pan_a)
38	CH3CO(OONO2) -> CH3CO(O) + NO3	(J_pan_b)
39	CH3CH2CO(OONO2) -> CH3CH2CO(OO) + NO2	
40	CH3CH2CO(OONO2) -> CH3CH2CO(O) + NO3	
41	CH2=CHCHO -> Products	
42	CH2=C(CH3)CHO -> Products	(J_macr)
43	CH3COCH=CH2 -> Products	(J_mvk)
44	HOCH2CHO -> CH2OH + HCO	(J_glyald_a)
45	HOCH2CHO -> CH3OH + CO	(J_glyald_b)
46	HOCH2CHO -> CH2CHO + OH	(J_glyald_c)
47	CH3COCH3 -> CH3CO + CH3	(J_ch3coch3)
48	CH3COCH2CH3 -> CH3CO + CH2CH3	(J_mek)
49	CH2(OH)COCH3 -> CH3CO + CH2(OH)	(J_hyac_a)
50	CH2(OH)COCH3 -> CH2(OH)CO + CH3	(J_hyac_b)
51	CHOCHO -> HCO + HCO	(J_gly_a)
52	CHOCHO -> H2 + 2CO	(J_gly_b)
53	CHOCHO -> CH2O + CO	(J_gly_c)
54	CH3COCHO -> CH3CO + HCO	(J_mgly)
55	CH3COCOCH3 -> Products	
56	CH3COOH -> CH3 + COOH	
57	CH3CO(OOH) -> Products	
58	CH3COCO(OH) -> Products	
59	(CH3)2NNO -> Products	
60	CF2O -> Products	

List of available photolysis reactions in the updated TUV

61	Cl2 -> Cl + Cl
62	ClO -> Cl + O(1D)
63	ClO -> Cl + O(3P)
64	ClOO -> Products
65	OClO -> Products
66	ClOOCl -> Cl + ClOO
67	HCl -> H + Cl
68	HOCl -> HO + Cl
69	NOCl -> NO + Cl
70	ClNO2 -> Cl + NO2
71	ClONO -> Cl + NO2
72	ClONO2 -> Cl + NO3
73	ClONO2 -> ClO + NO2
74	CCl4 -> Products
75	CH3OCl -> CH3O + Cl
76	CHCl3 -> Products
77	CH3Cl -> Products
78	CH3CCl3 -> Products
79	CCl2O -> Products
80	CClFO -> Products
81	CCl3F (CFC-11) -> Products
82	CCl2F2 (CFC-12) -> Products
83	CF2ClCFCl2 (CFC-113) -> Products
84	CF2ClCF2Cl (CFC-114) -> Products
85	CF3CF2Cl (CFC-115) -> Products
86	CHClF2 (HCFC-22) -> Products
87	CF3CHCl2 (HCFC-123) -> Products
88	CF3CHFCl (HCFC-124) -> Products
89	CH3CFCl2 (HCFC-141b) -> Products
90	CH3CF2Cl (HCFC-142b) -> Products
91	CF3CF2CHCl2 (HCFC-225ca) -> Products
92	CF2ClCF2CHFCl (HCFC-225cb) -> Products
93	Br2 -> Br + Br
94	BrO -> Br + O
95	HOBr -> OH + Br
96	BrNO -> Br + NO
97	BrONO -> Br + NO2
98	BrONO -> BrO + NO
99	BrNO2 -> Br + NO2
100	BrONO2 -> BrO + NO2
101	BrONO2 -> Br + NO3
102	BrCl -> Br + Cl
103	CH3Br -> Products
104	CHBr3 -> Products
105	CF2Br2 (Halon-1202) -> Products
106	CF2BrCl (Halon-1211) -> Products
107	CF3Br (Halon-1301) -> Products
108	CF2BrCF2Br (Halon-2402) -> Products
109	perfluoro 1-iodopropane -> products

Additional file in KPP/mechanisms/$mechanism/
$mechanism.tuv.jmap
Correspondence j_wrfchem with available j_tuv

Photolysis calculations in WRF-Chem : Current & updated

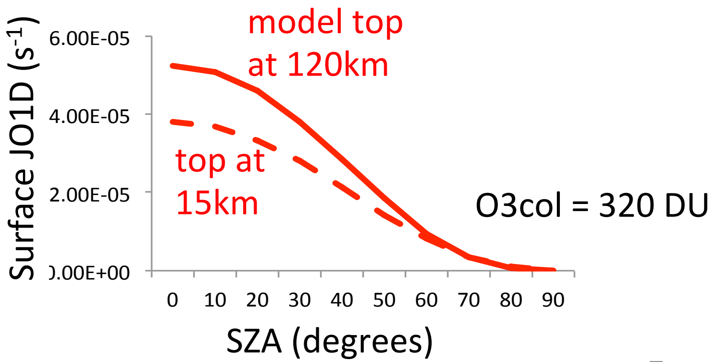
- Added routines in chem/
  - module_phot_tuv.F
  - module_subs_tuv.F

- Stratospheric ozone
  - f-TUV: climatology at the model top (input file exo_coldens.nc)
  - fast-J: specified value at the model top for the whole domain
  - TUV: specified value with extra levels above the model top
  - ⇒ Updated TUV: uses ozone climatology distributed from model top to 50km (extra levels above the model top, standard atmosphere)

- Aerosols: calculated in the optics driver

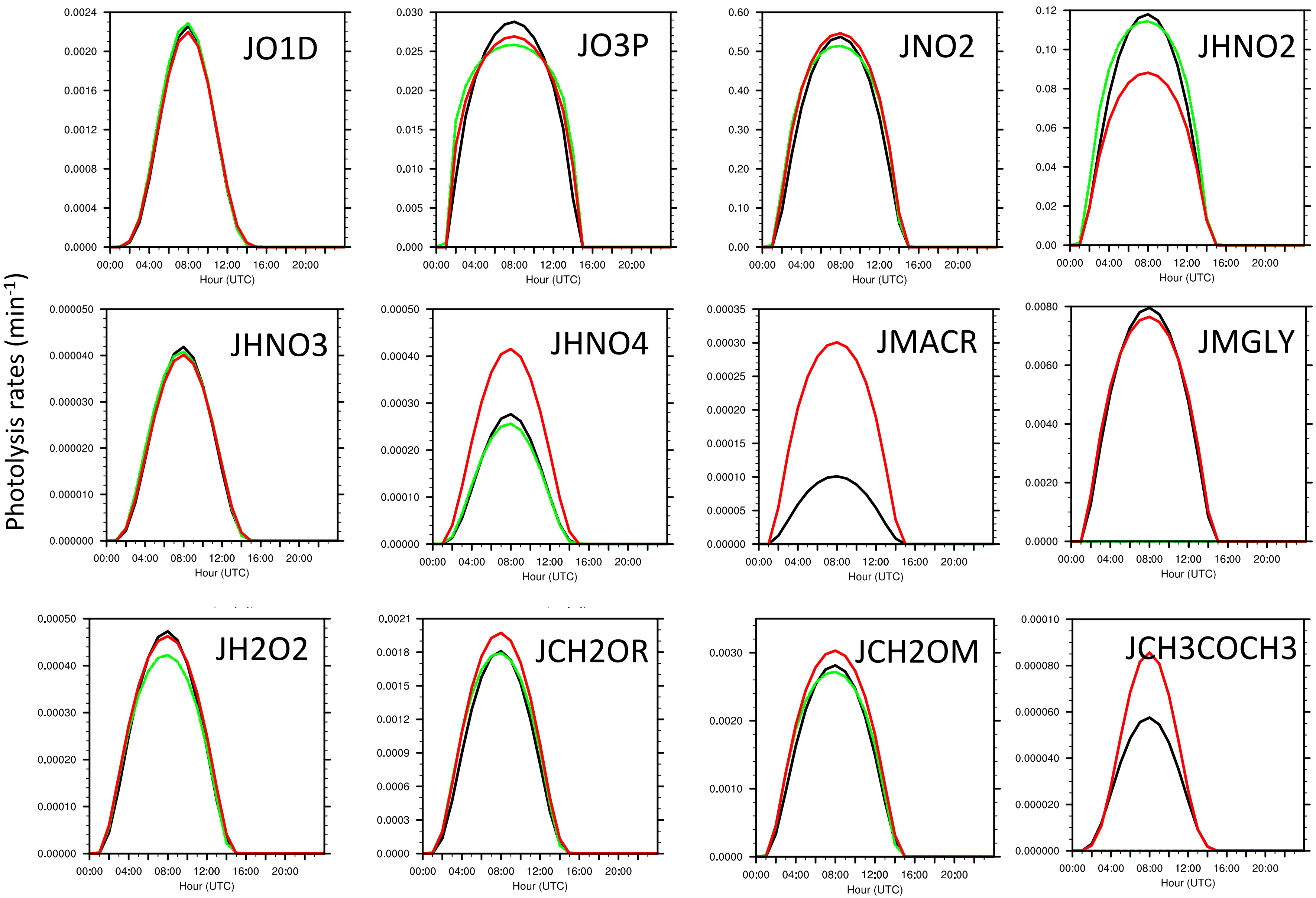
  Mixing rules for index of refraction;

  Different core-shell options



Comparison of diurnal profiles in clear sky conditions (Boulder)

Old TUV (phot_opt=1); New TUV (phot_opt=4); Fast-J (phot_opt=2)



Photolysis calculations in WRF-Chem

- Current treatment of clouds
  - Cloud optical properties are recalculated in photolysis scheme
  - Differ between schemes and from physics (e.g. RRTMG)
  - Sub-grid cloud overlap schemes

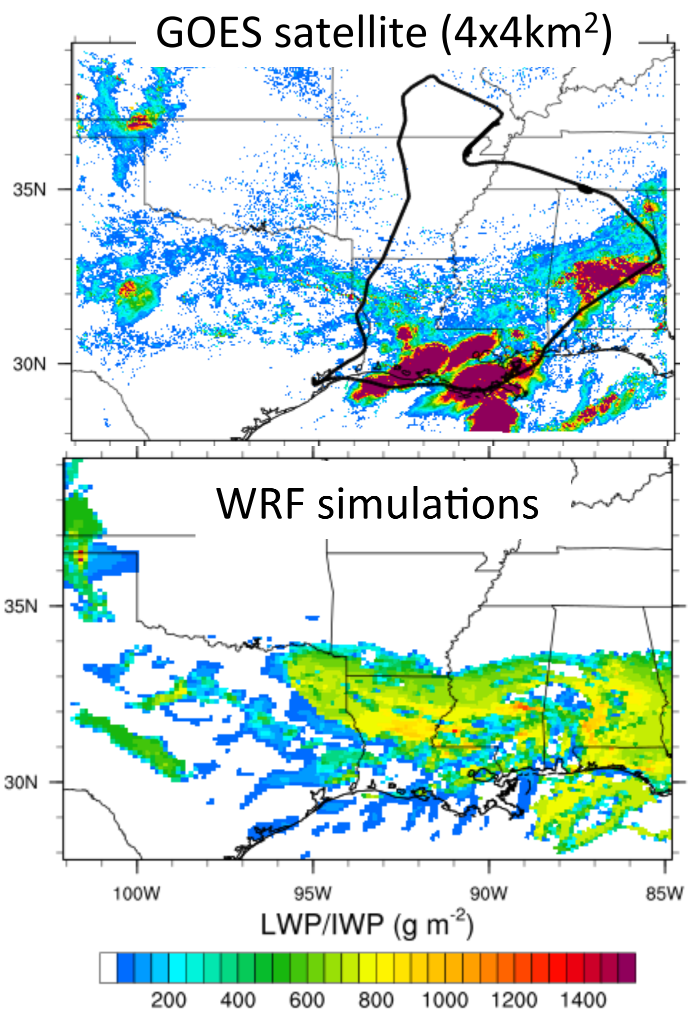
    e.g. f-TUV (max overlap if vertically contiguous, random otherwise)

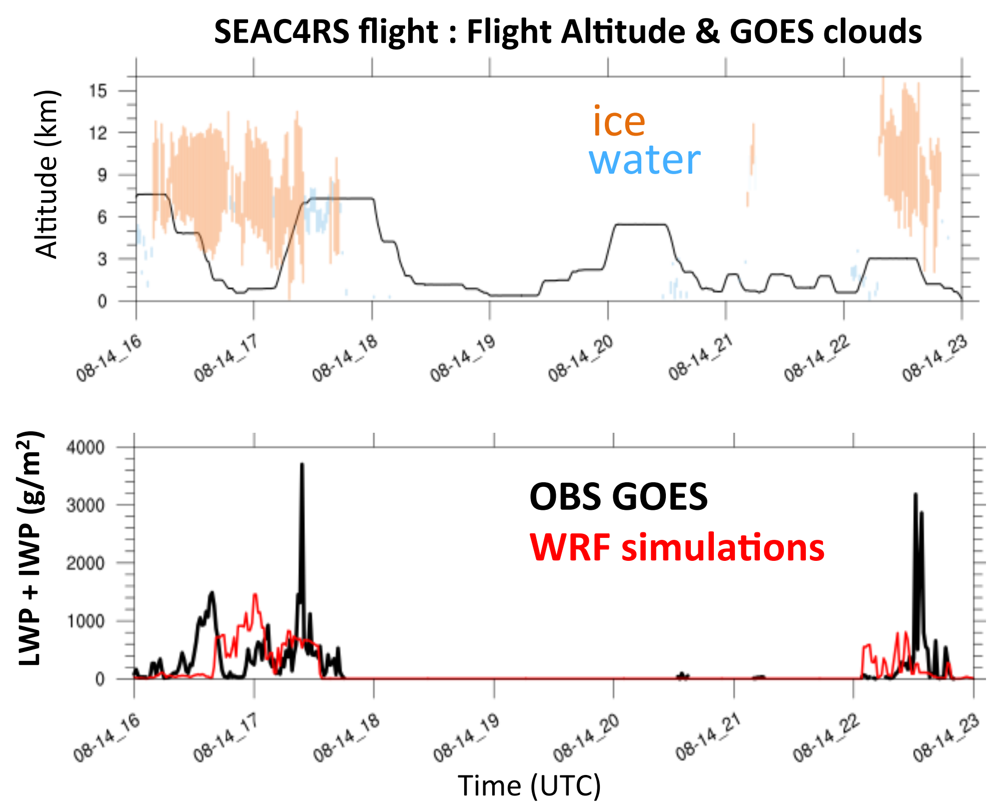
- Updated method 1 (phot_opt=4)
  - COD calculated from LWP/IWP and effective drop radius (Slingo 1989, similar to CAM radiation with SSA = 0.9999 and f_{assym} = 0.85)
  - Sub-grid cloud effects are represented as in Briegleb (1992) ($COD_{subgrid} = COD * FCLD^{3/2}$, equivalent to random overlap)

- Updated method 2 (phot_opt=4) uses RRTMG cloud vertical distribution
  - RRTMG adopts maximum-random overlap to distribute LWP/IWP randomly over wavelength bins based on cloud fraction.
  - Take COD that is averaged over the RRTMG wavelength bins.

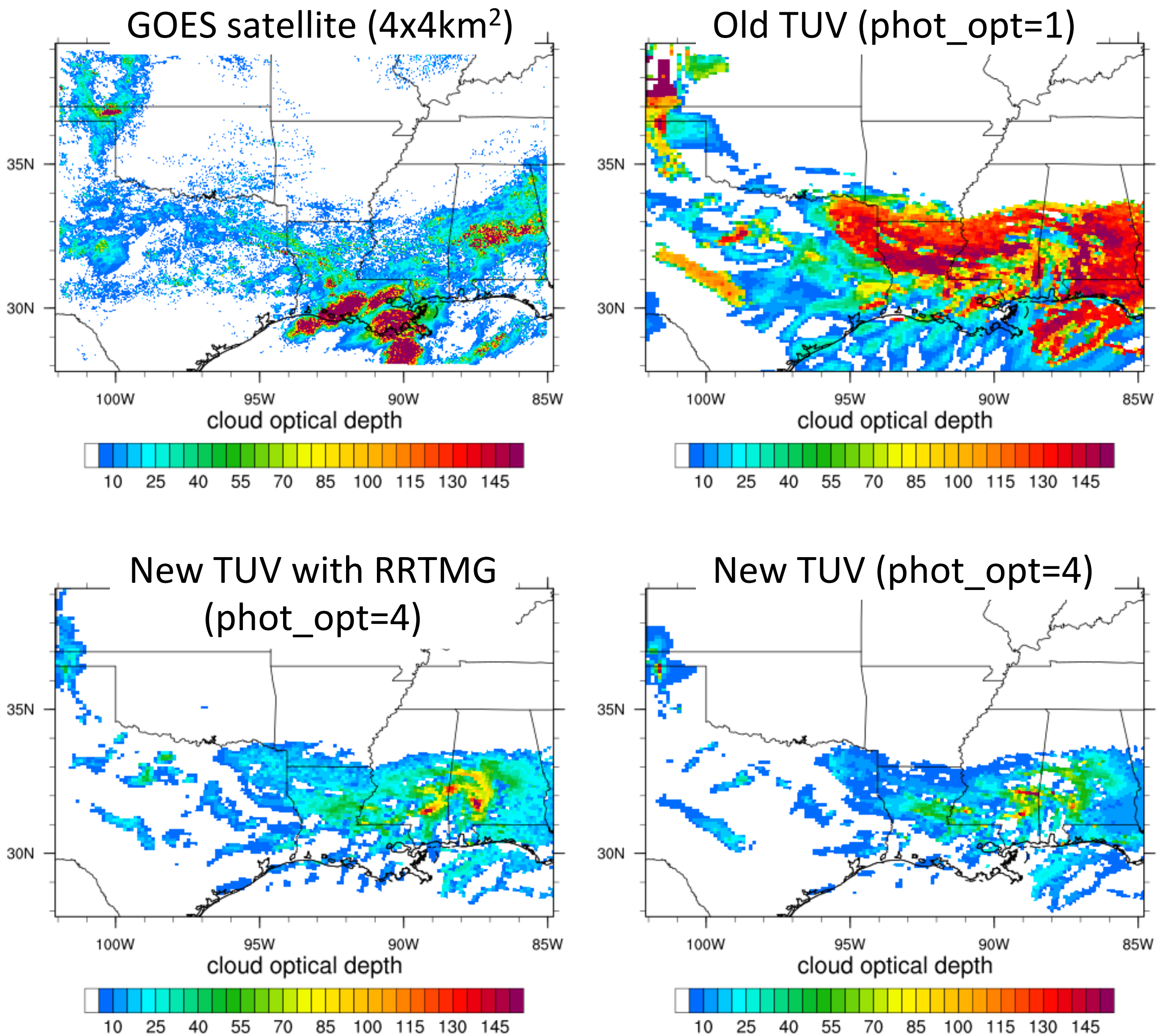
Comparison with SEAC4RS flight of 14 Aug. 2013

- WRF-Chem simulations : CONUS (12x12km^2) during summer 2013
- MOZART-MOSAIC chemistry
- Morrison microphysics + CU Grell

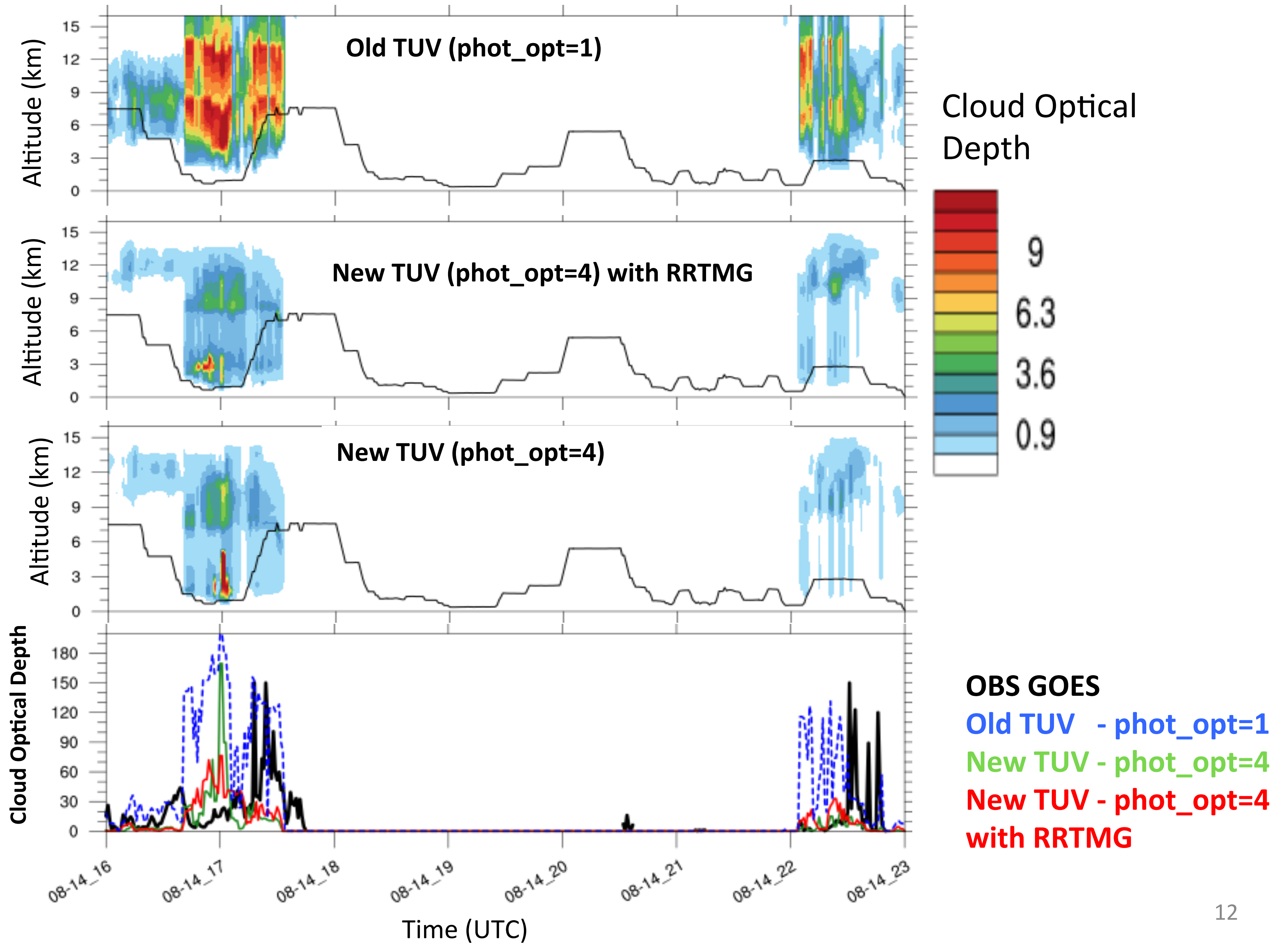




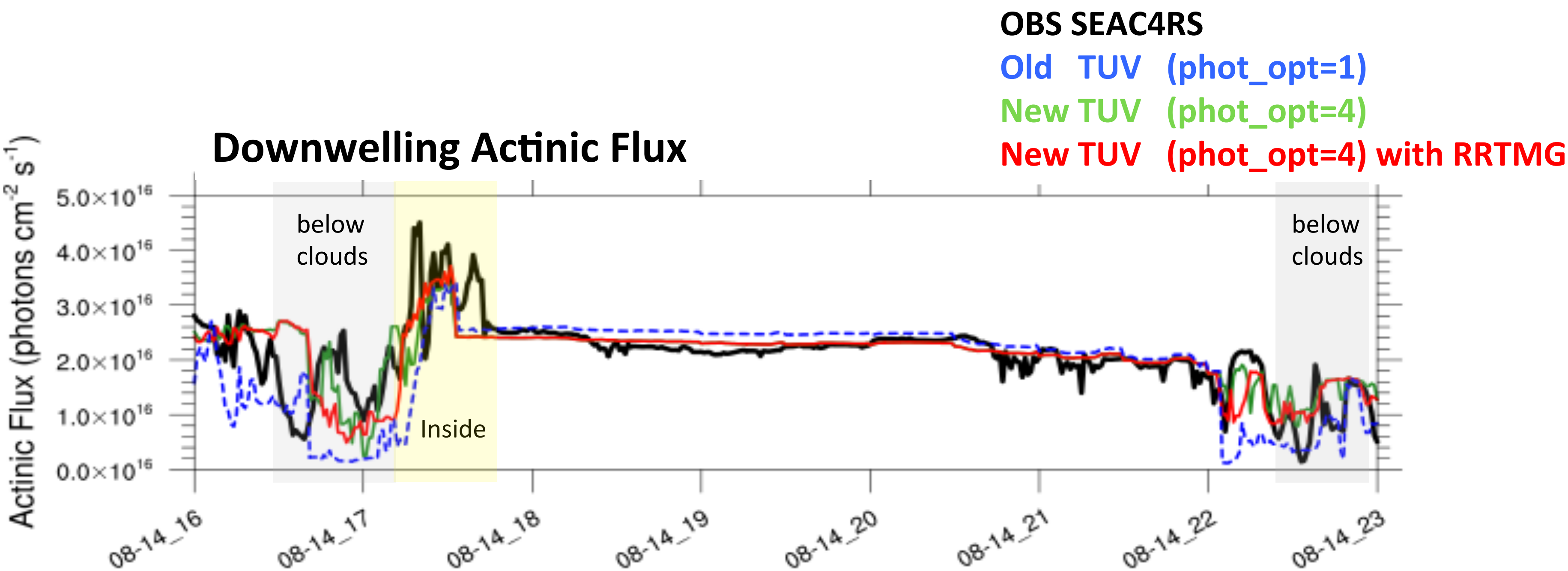
Effective cloud optical depths – 14 Aug. 2013 (18UTC)

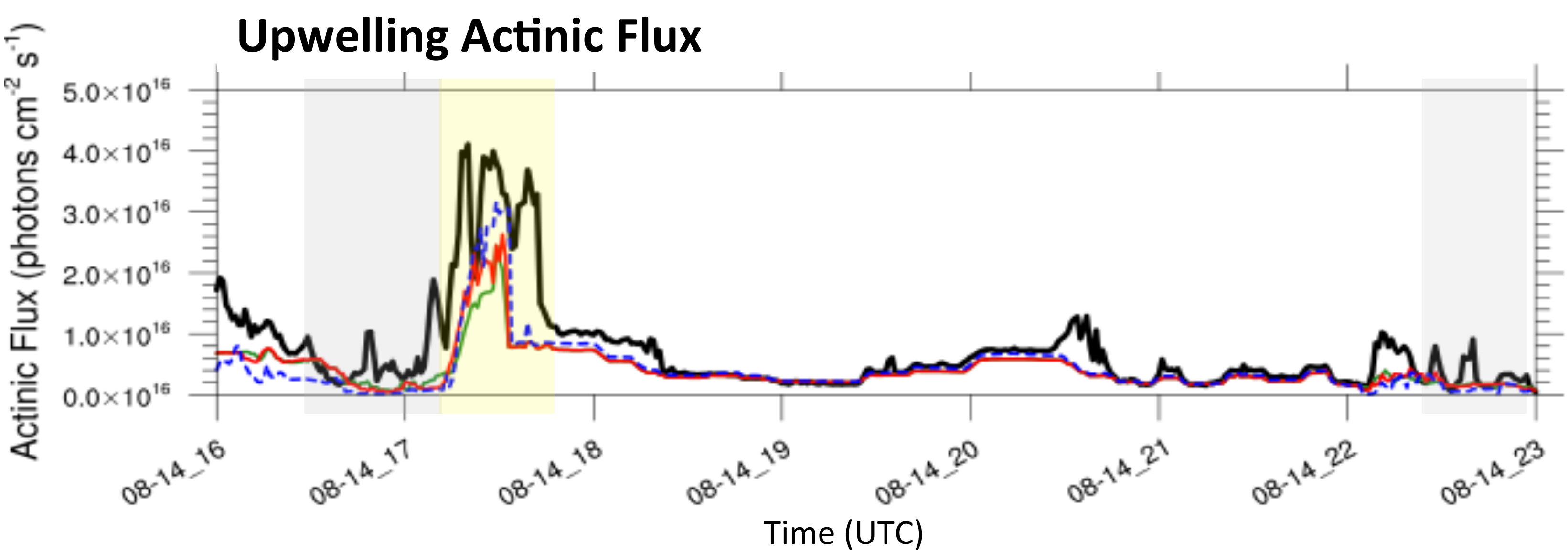


Comparison with SEAC4RS flight of 14 Aug. 2013

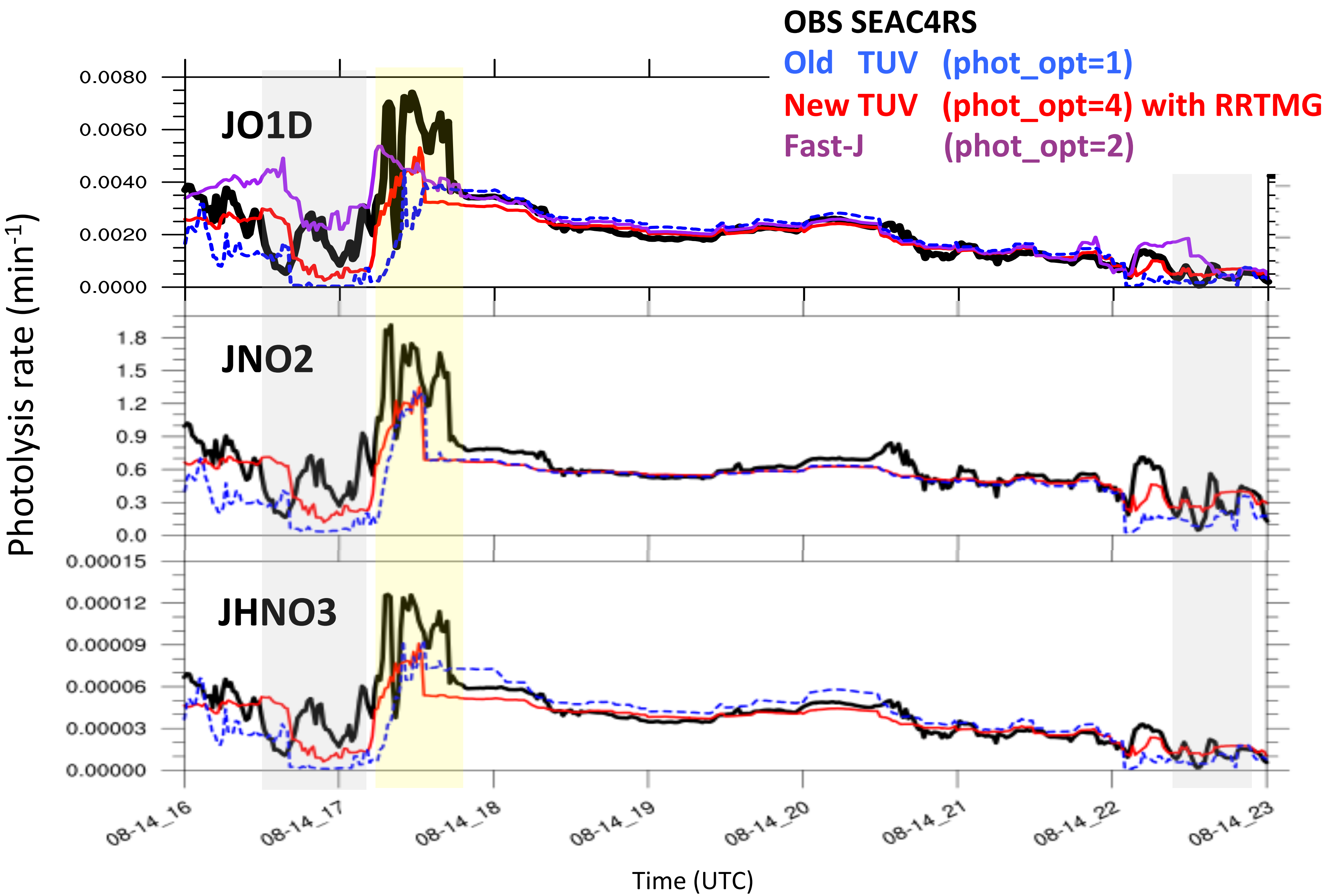


Comparison with SEAC4RS flight of 14 Aug. 2013

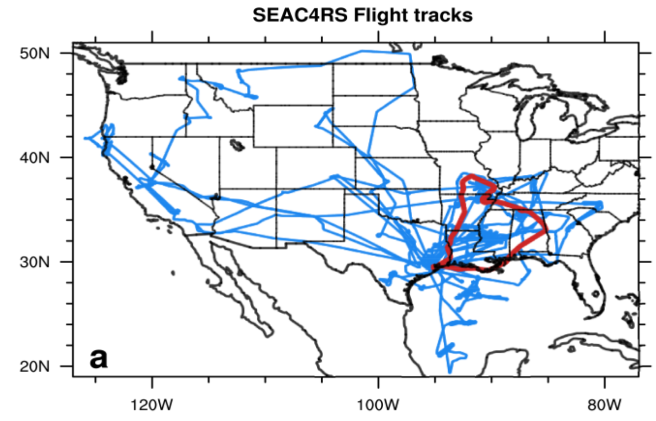




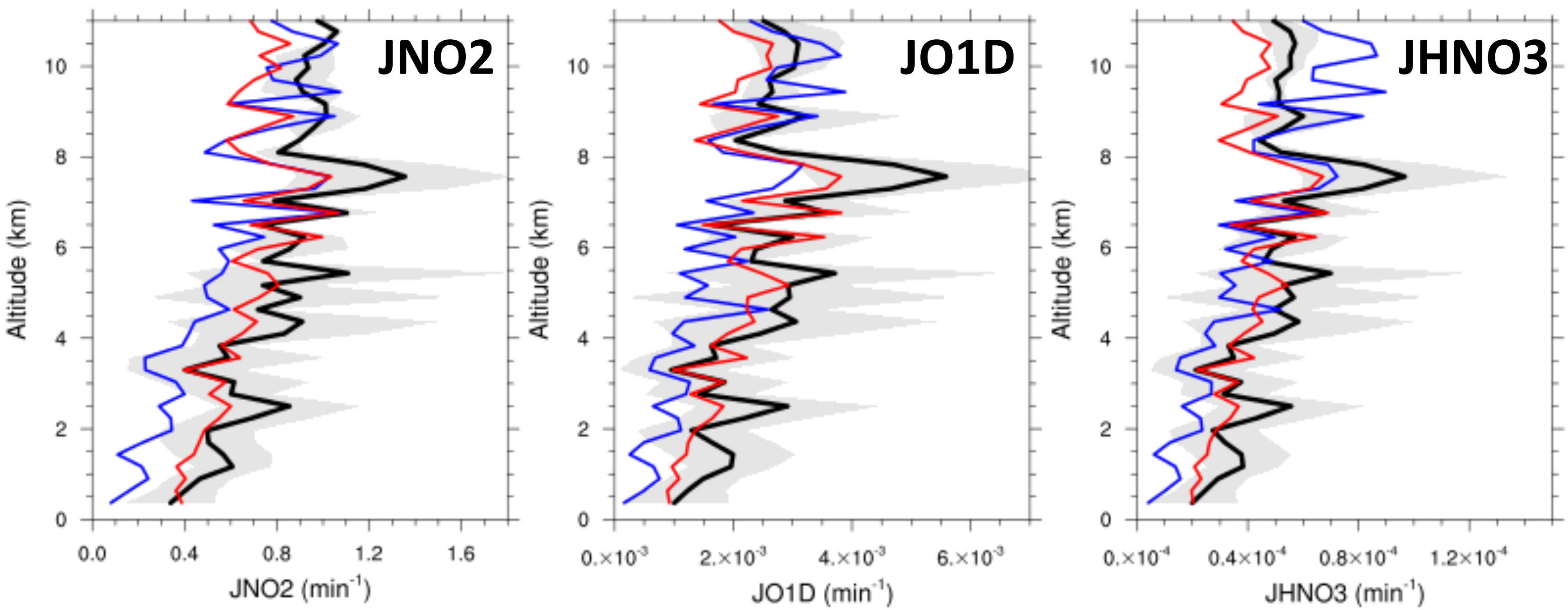
Comparison with SEAC4RS flight of 14 Aug. 2013



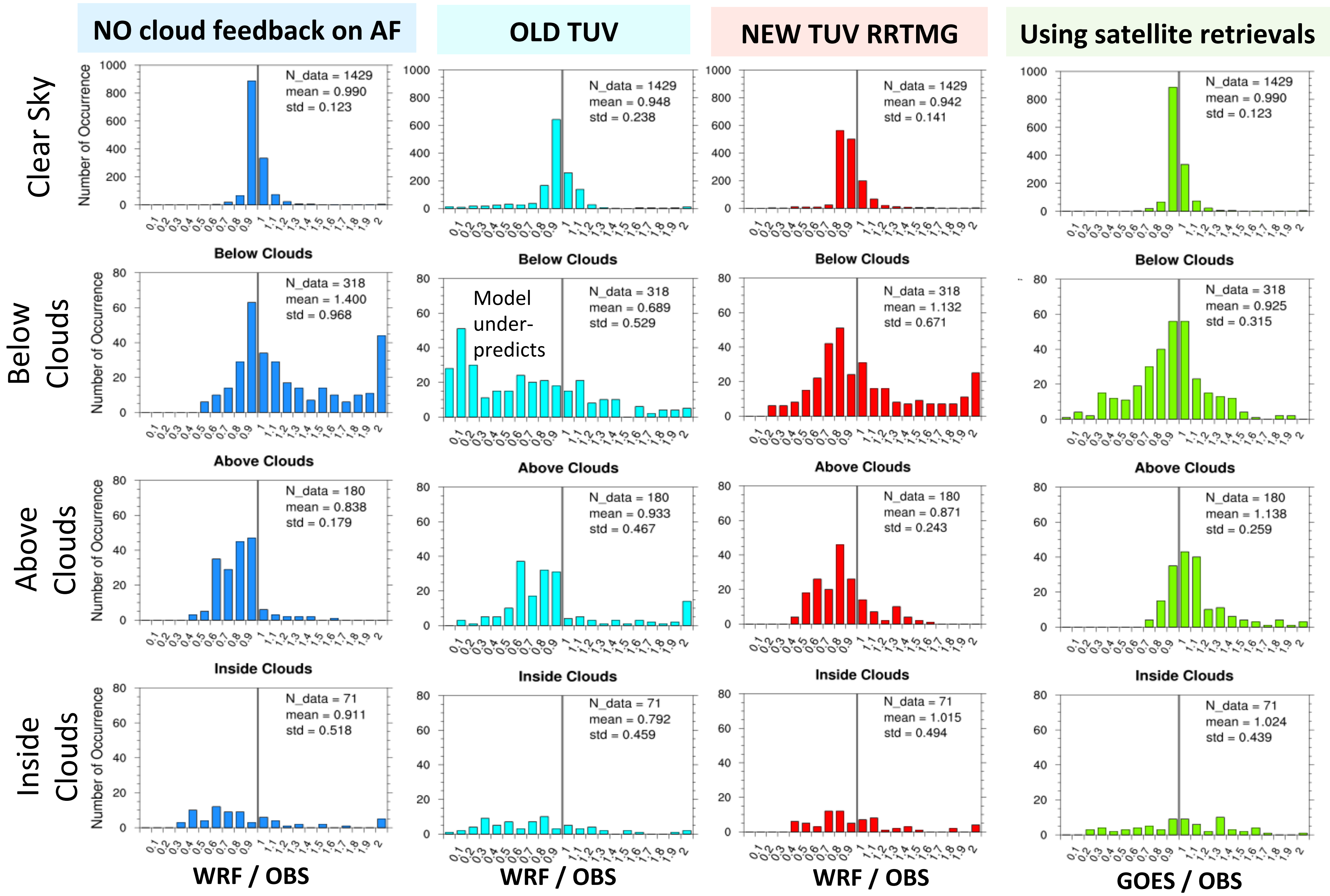
Comparison for all SEAC4RS flights



OBS SEAC4RS
Old TUV (phot_opt=1)
New TUV (phot_opt=4) with RRTMG



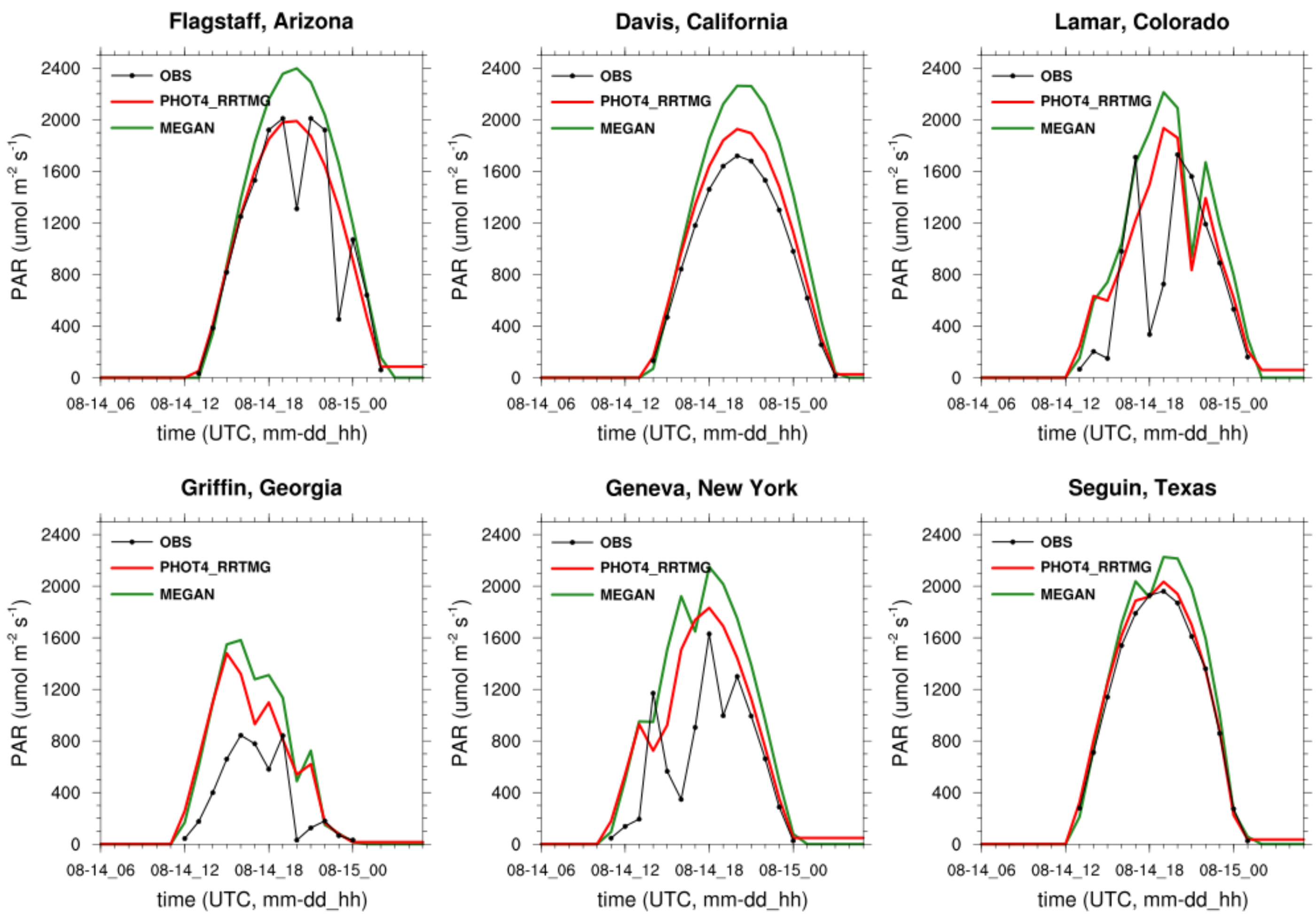
Ratio of WRF / OBS Actinic Flux for all SEAC4RS flights



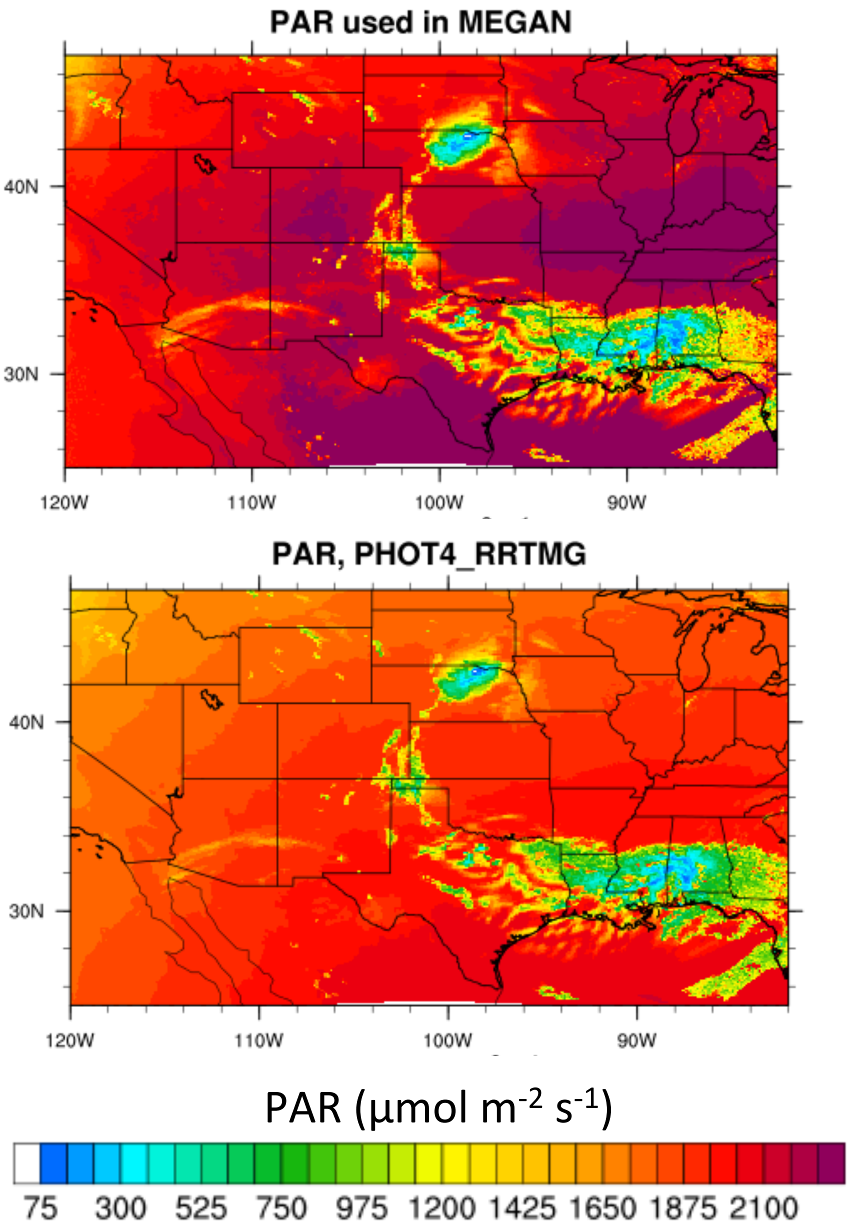
Comparison of PAR (Photosynthetically active radiation)

- **Observed PAR (USDA UV-B Monitoring Network over the US)**
- **WRF: used in MEGAN PAR = 4.766 * 0.5 * SWDOWN**
- **WRF: calculated from new TUV RRTMG phot_opt=4**

14 August 2013



PAR radiation – 14 August 2013



10-20% difference in simulated PAR between values used in the MEGAN model for biogenic VOC emissions, and those predicted by TUV.

=> Effect on BVOC emissions?

Conclusions and next steps

Updated TUV (phot_opt = 4):

- Offers a more flexible framework for updating quantum yields and cross sections and adding new photolysis reactions through KPP
- Provides computationally efficient treatment of the subgrid cloud effects
- Consistency between TUV radiation with RRTMG and MEGAN emissions
- Better agreement with observations in clear sky and cloudy conditions compared to old TUV (photolysis are less attenuated below clouds)
- Updates will be made available in the next major model release

Next Steps

- Evaluate the effect on ozone production caused by changes in both photolysis and PAR values.
- Seek improvements in photochemistry through data assimilation of actinic fluxes or better cloud fields.

Results of the offline TUV driven by GOES clouds