NO_2 VERTICAL PROFILES OVER SOUTH KOREA AND THEIR RELATION TO OXIDANT CHEMISTRY:

IMPLICATIONS FOR GEOSTATIONARY SATELLITE RETRIEVALS

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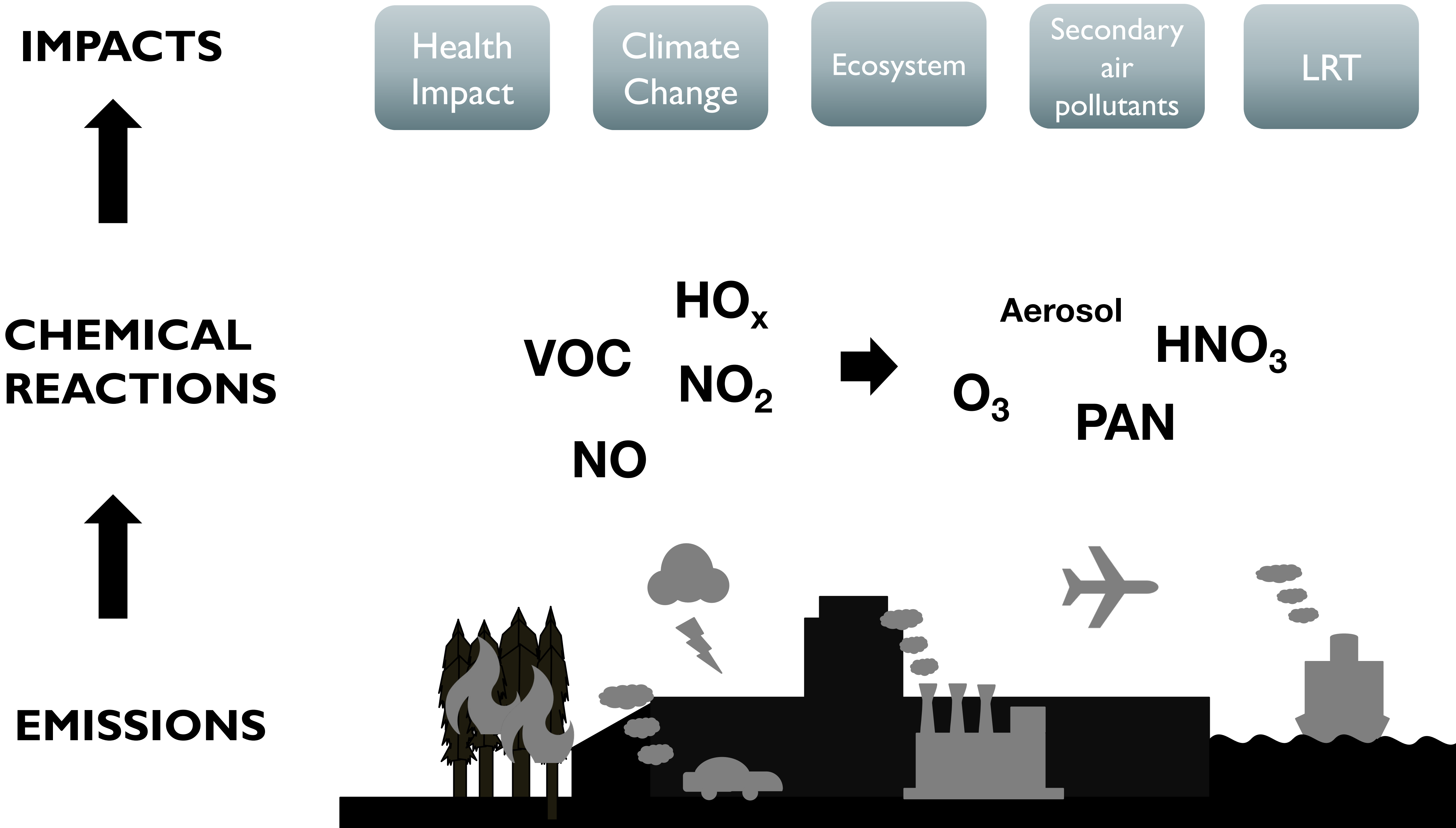
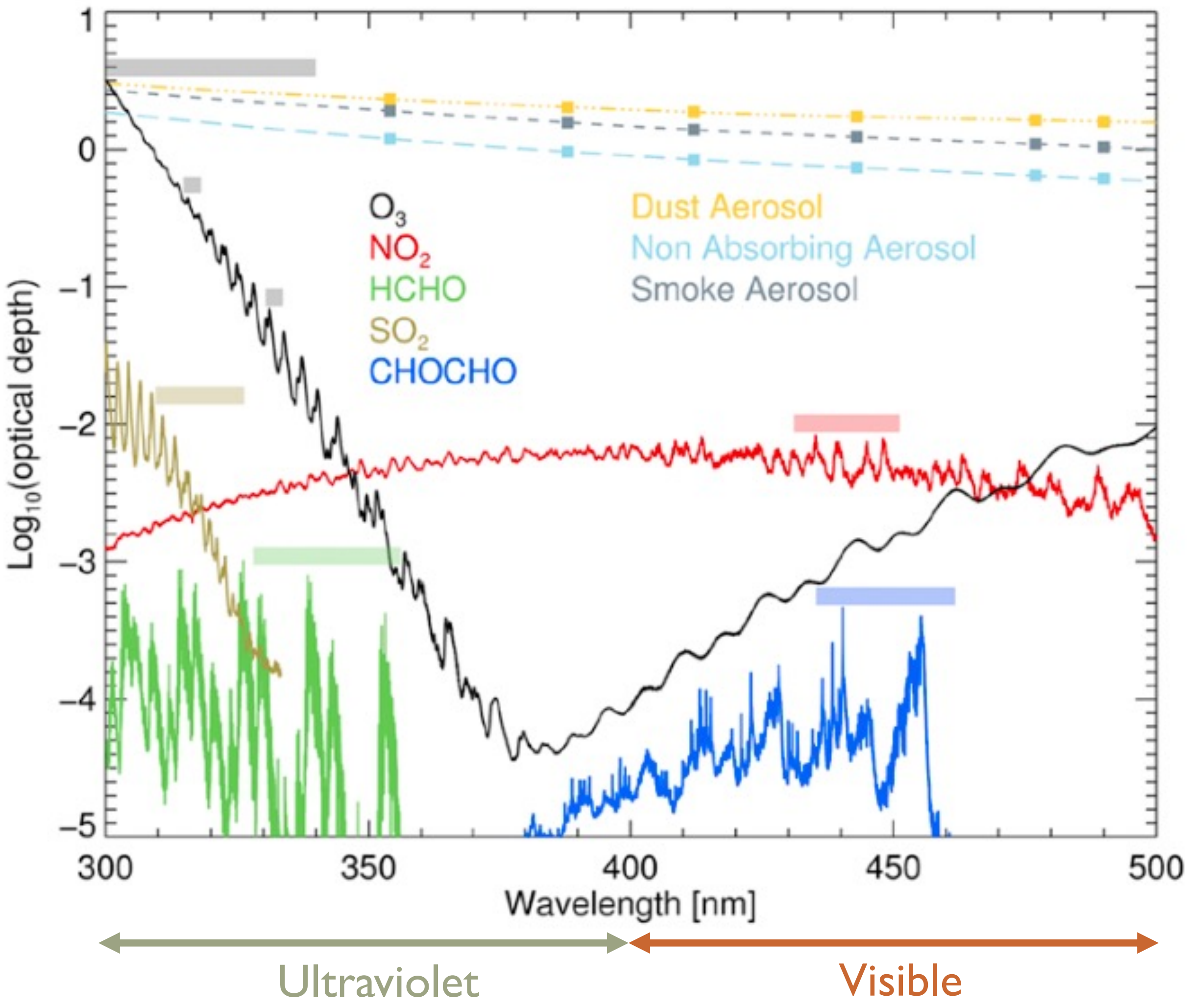
Jan. 27th, 2023


IMPACTS
Health Impact
Climate Change
Ecosystem
Secondary air pollutants
LRT
CHEMICAL REACTIONS
HO_x
VOC
NO_2
NO
Aerosol
HNO_3
O_3
PAN
EMISSIONS

NO_2 absorbs radiation in the UV-vis regions



Optical depth spectra in the GEMS spectral range [Fig. from Kim et al., 2020]

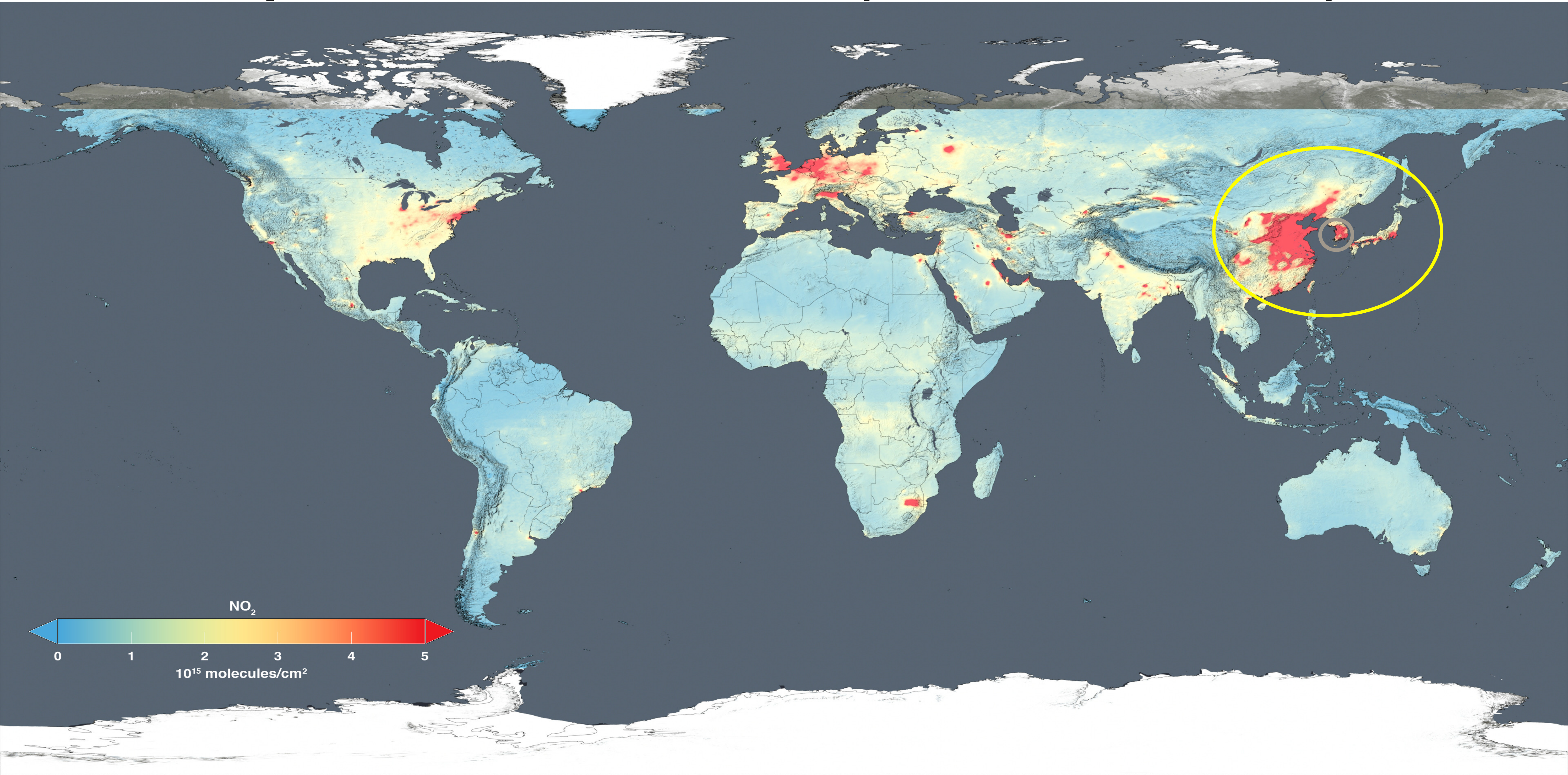
Line

Vertical optical depth

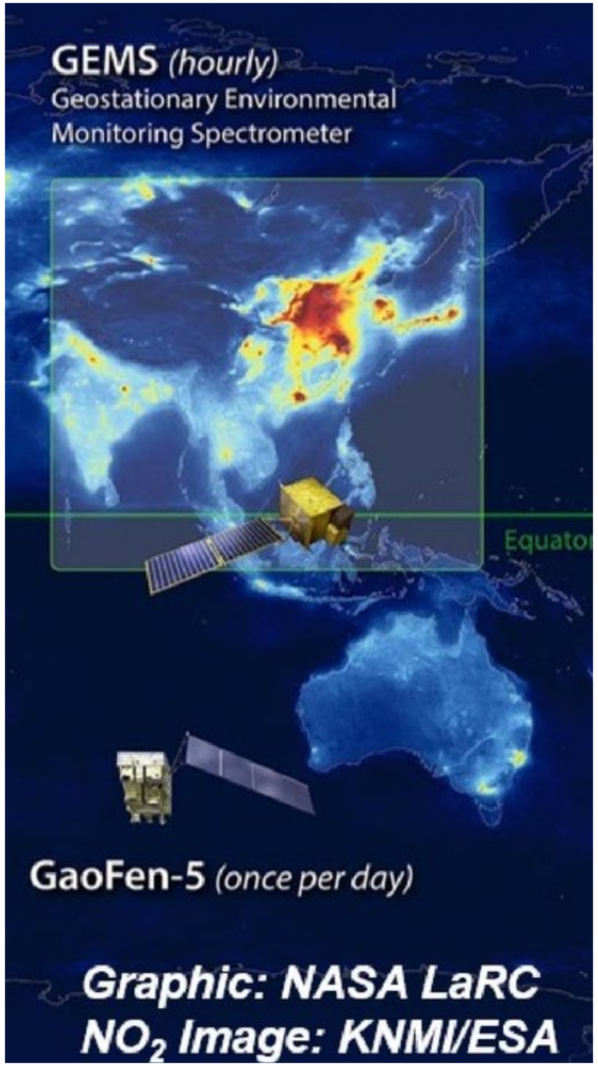
Horizontal Bar

Fitting window used for GEMS retrieval

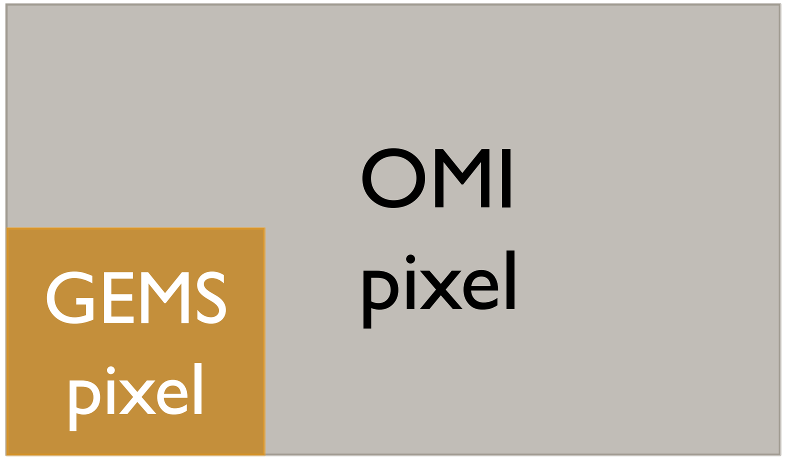
Global map of NO_2 concentration (OMI satellite, 2014)



Geostationary satellites allow for studying the diurnal variation of NO_2 from the space

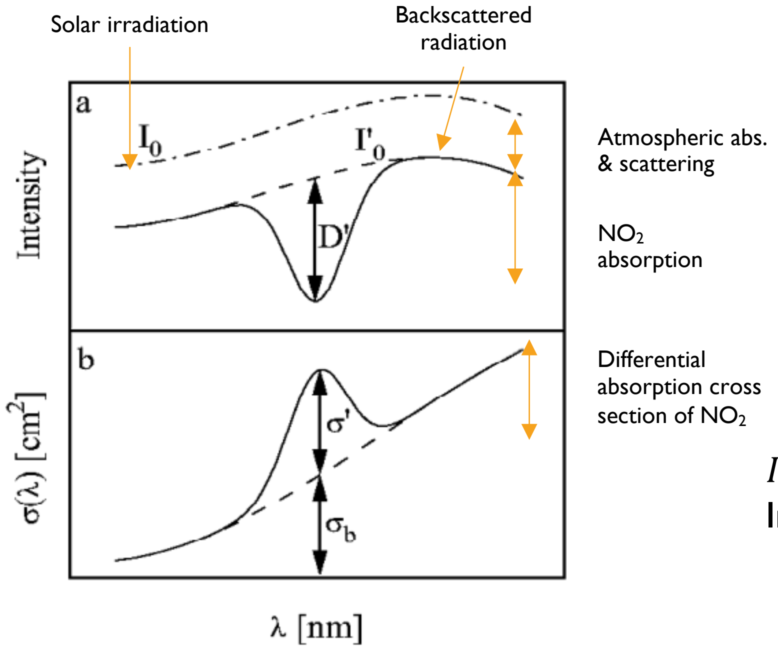


	OMI	GEMS
Spatial resolution	14 x 24 km	7 km x 8 km
Temporal resolution	Daily	1 hour
Wavelength for NO_2	402 – 465 nm	432 – 450 nm



Overview of monitoring NO_2 from space (Solar backscatter retrieval)

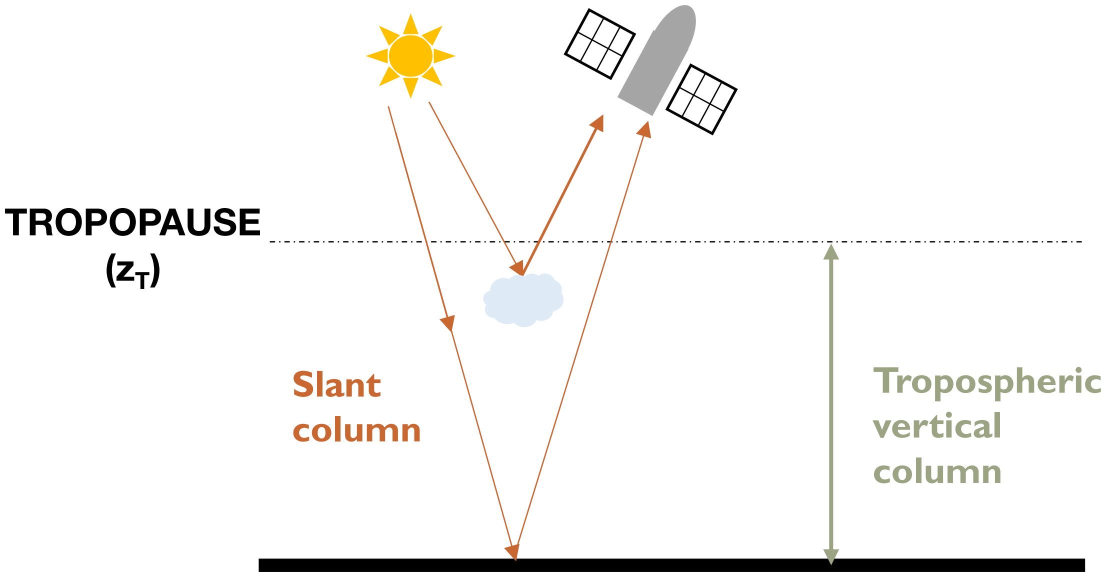
1. Convert radiance to slant column (SC)
2. Remove stratospheric portion from SC
3. Convert tropospheric SC to vertical column (VC)



Beer-Lambert law

$$SC = \frac{1}{\sigma'} \ln\left(\frac{I_{B0}}{I_B}\right)$$

I_B: Backscattered intensity In the presence of absorber



$$VC = \frac{SC}{AMF}$$

AMF (Air Mass Factor): A correction factor for light slant path to vertical path

Air Mass Factor (AMF) depends on 3 quantities

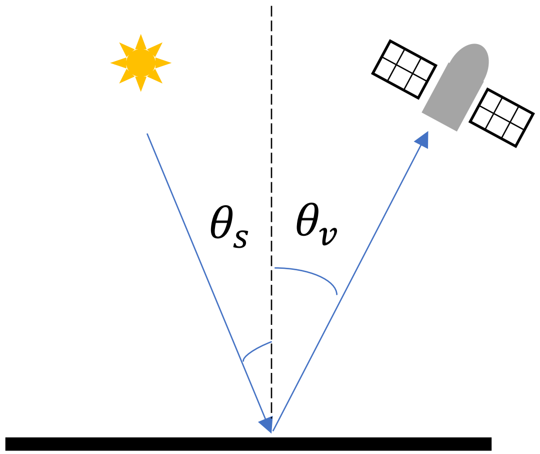
$$\mathrm{AMF} = \mathrm{AMF_G} \int^{z_T} w(z) S(z) \mathrm{dz}$$

Key assumption:
Species of interest is optically thin

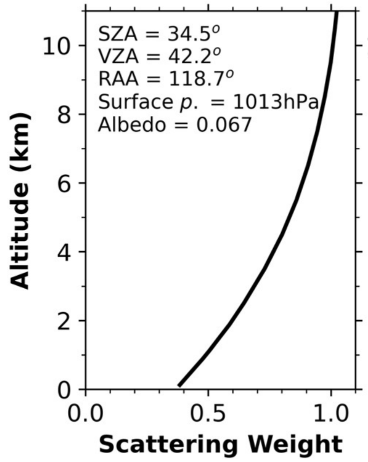
$\int_0^{z_T} w(z) S(z) \mathrm{dz}$: Scattering correction factor

Vie

Solar zenith angle (SZA; θ_s)
Satellite viewing angle (VZA; θ_v)



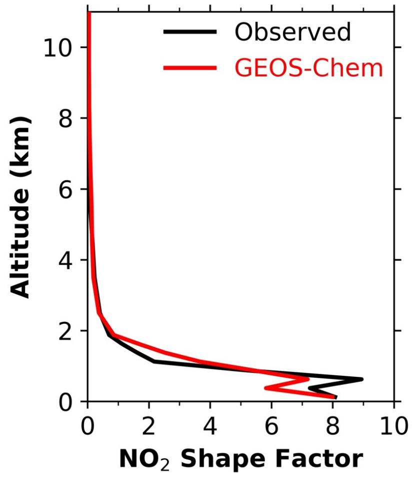
Captures where the satellite is sensitive to (from RTM)



Scattering weight vs. altitude

RTM: Radiative Transfer Model
RAA: Relative Azimuth Angle

Vertical distribution of NO_2 (from CTM like GEOS-Chem)



NO_2 shape factor vs. altitude

CTM: Chemical Transport Model

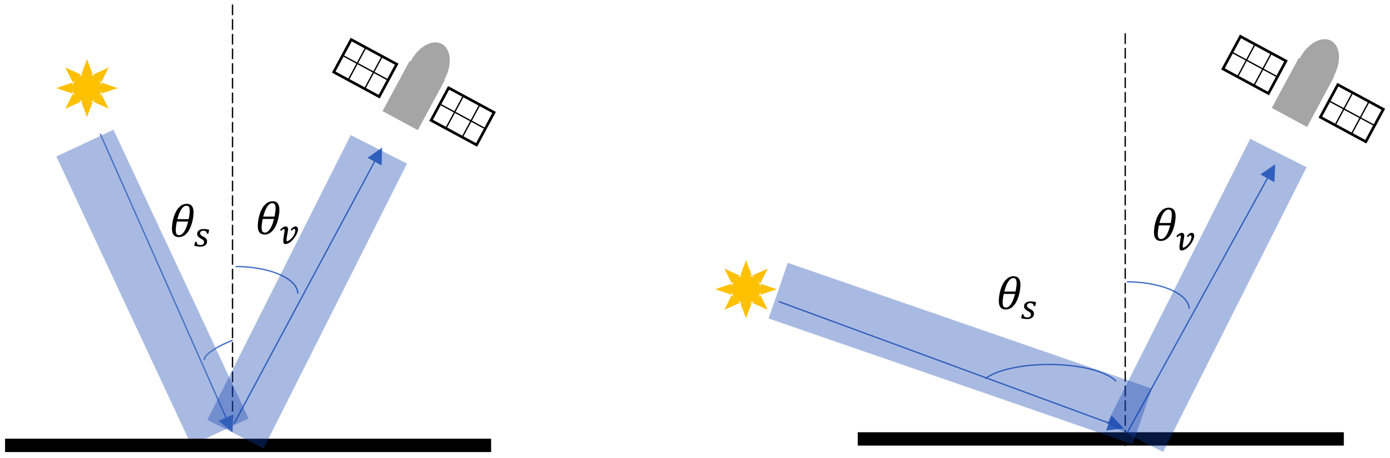
Geometric AMF (AMF_G) represents the length of the light path

$$\mathrm{AMF} = \mathbf{AMF_G} \int_0^{z_T} w(z) S(z) dz$$

$$\mathrm{AMF_G} = \sec\theta_s + \sec\theta_v$$

SZA; θ_s
VZA; θ_v

- AMF_G is AMF in the absence of atmospheric scattering
- Since θ_v is fixed for GEMS, $AMF_G = f(\theta_s)$

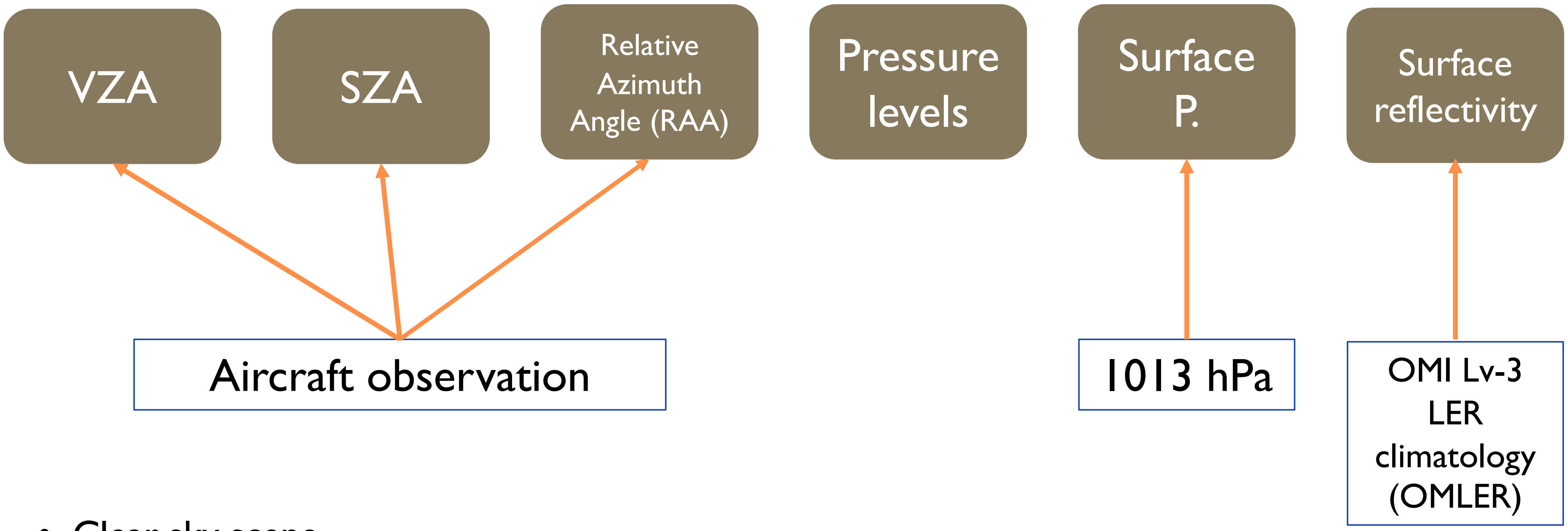


Longer light path as θ_s increases -> higher AMF_G

OMI TOMRAD look-up table (LUT) is used for scattering weight

$$\mathrm{AMF} = \mathrm{AMF_G} \int_0^{z_T} \boldsymbol{w}(\boldsymbol{z}) S(z)\mathrm{d}z$$

LUT is a function of 6 variables



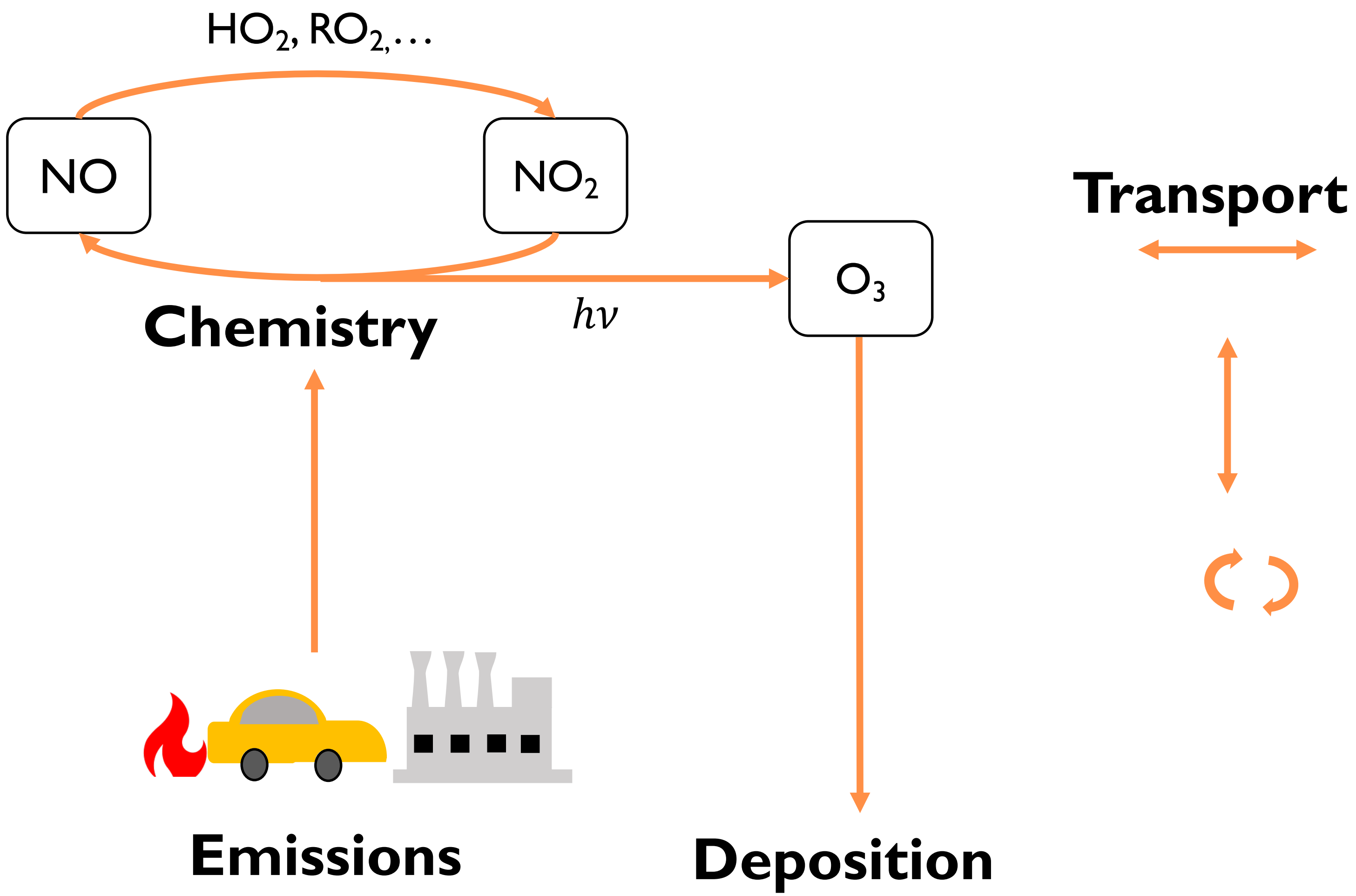
- Clear-sky scene
- OMI NO_2 (402 – 465 nm) vs. GEMS NO_2 (432 – 450 nm)

NASA SP v2 [Bucsela et al., 2013]

Schematic of Chemical Transport Model (CTM)

$$\mathrm{AMF} = \mathrm{AMF_G} \int_0^{z_T} w(z)\boldsymbol{S}(\boldsymbol{z})\,\mathrm{d}z$$

~913 chemical reactions in GEOS-Chem!



GEOS-Chem equations and structures

Solve continuity equations for chemical species concentrations n = $(n_i, \dots n_k)^\top$

$$\boxed{\frac{\partial n_i}{\partial t}} = \boxed{-\nabla \cdot (n_i \mathbf{U})} + \boxed{P_i(\mathbf{n}) - L_i(\mathbf{n})}$$

Local trend in concentration

Transport terms:

- Advection
- Convection
- PBL mixing

Chemical terms:

- Emissions
- Deposition
- Chemistry
- Aerosol microphysics

GEOS-Chem transport can be either:

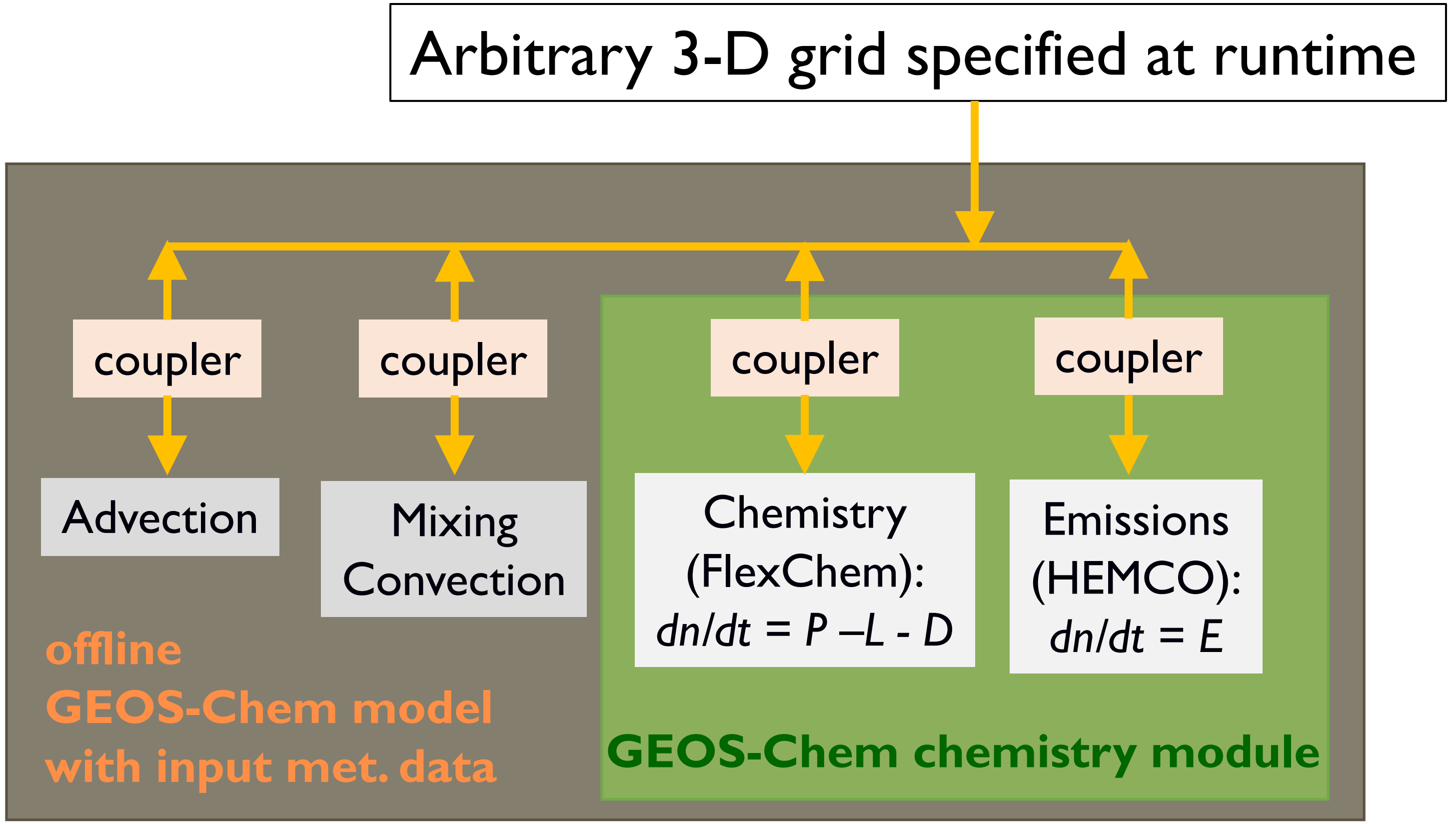
- **Offline** with its own modules
  - GEOS-FP, MERRA-2
- **Online** with the parent meteorological model providing the transport
  - GEOS, WRF, ESM, CESM

GEOS-Chem chemical module:

- Solve local d**n**/dt = **P(n) – L(n)** on grid-independent 1-D column

[Adopted from D. Jacob's pptx]

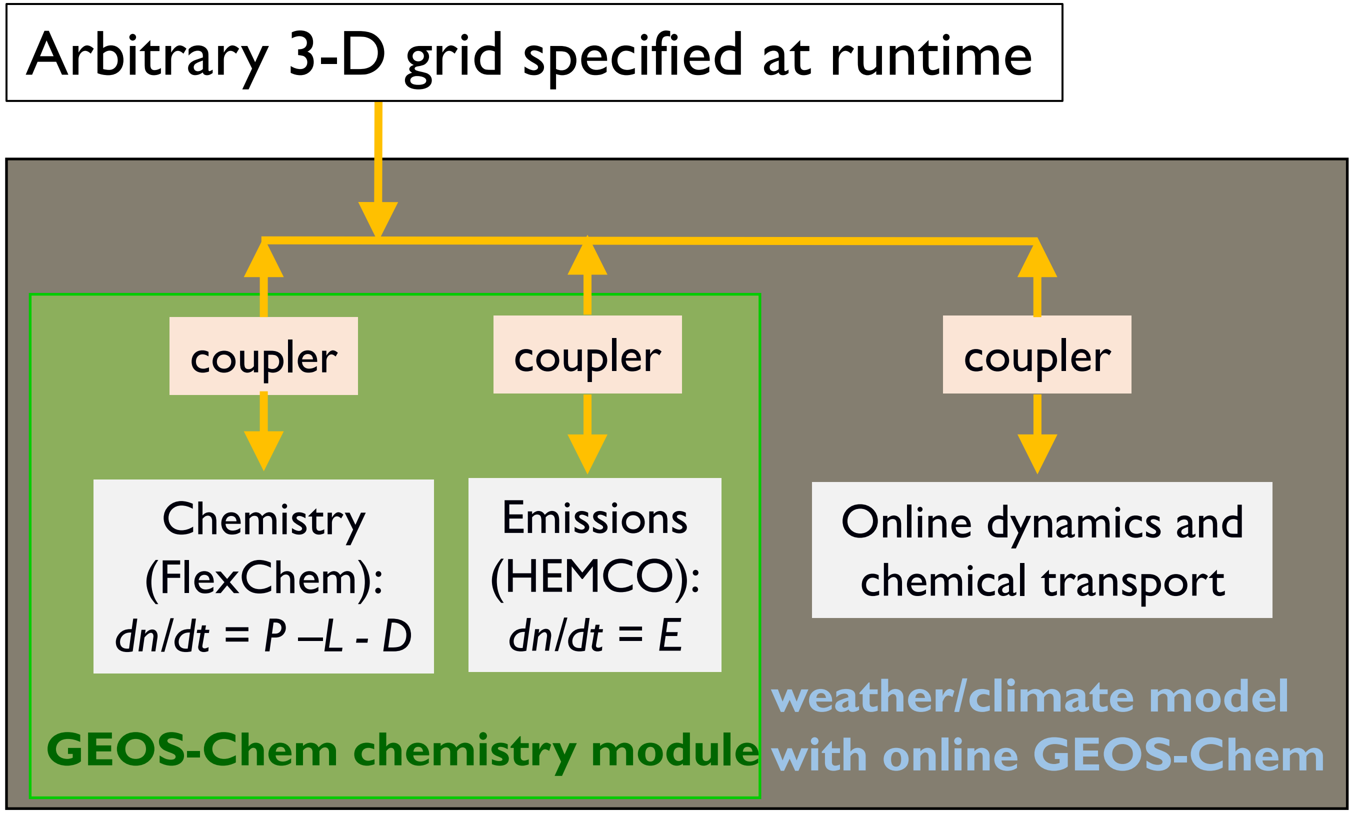
GEOS-Chem can run as offline (decoupled from dynamics)



- Archived meteorological data from NASA GEOS
  - GEOS-FP (0.25°x0.3125° operational, c720 custom)
  - MERRA-2 (0.5°x0.625°), soon MERRA-IT (c180)
  - GISS paleo and future-climate data
- Offline transport scheme used by the CTM

[Adopted from D. Jacob's pptx; Hu et al., 2018]

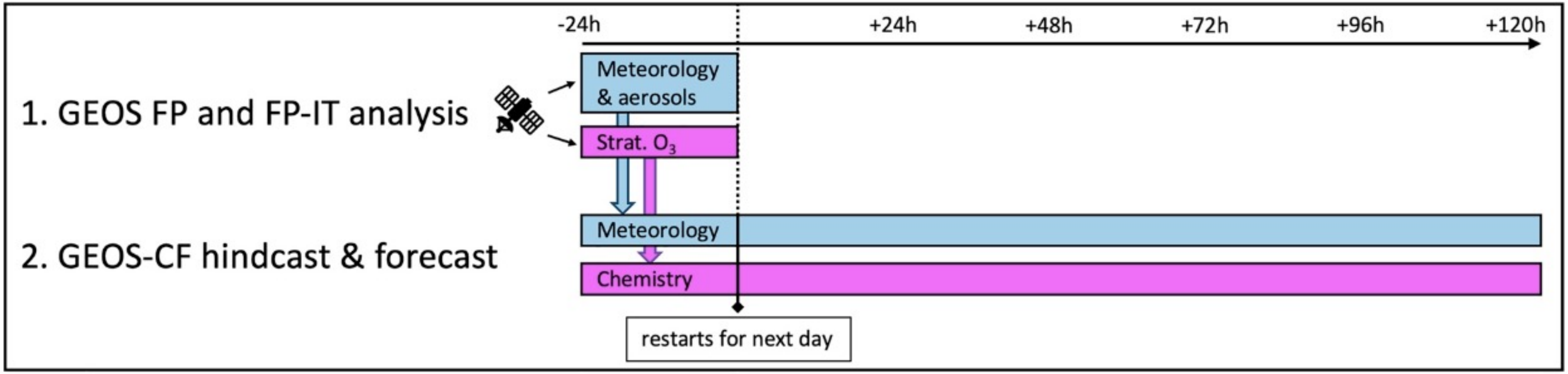
GEOS-Chem can run online (coupled to dynamics)



- Used for weather/climate applications in GEOS Earth System Model (ESM), NCAR CESM, WRF
- Meteorology **and** transport of species are calculated directly within ESM

[Adopted from D. Jacob's pptx; Hu et al., 2018]

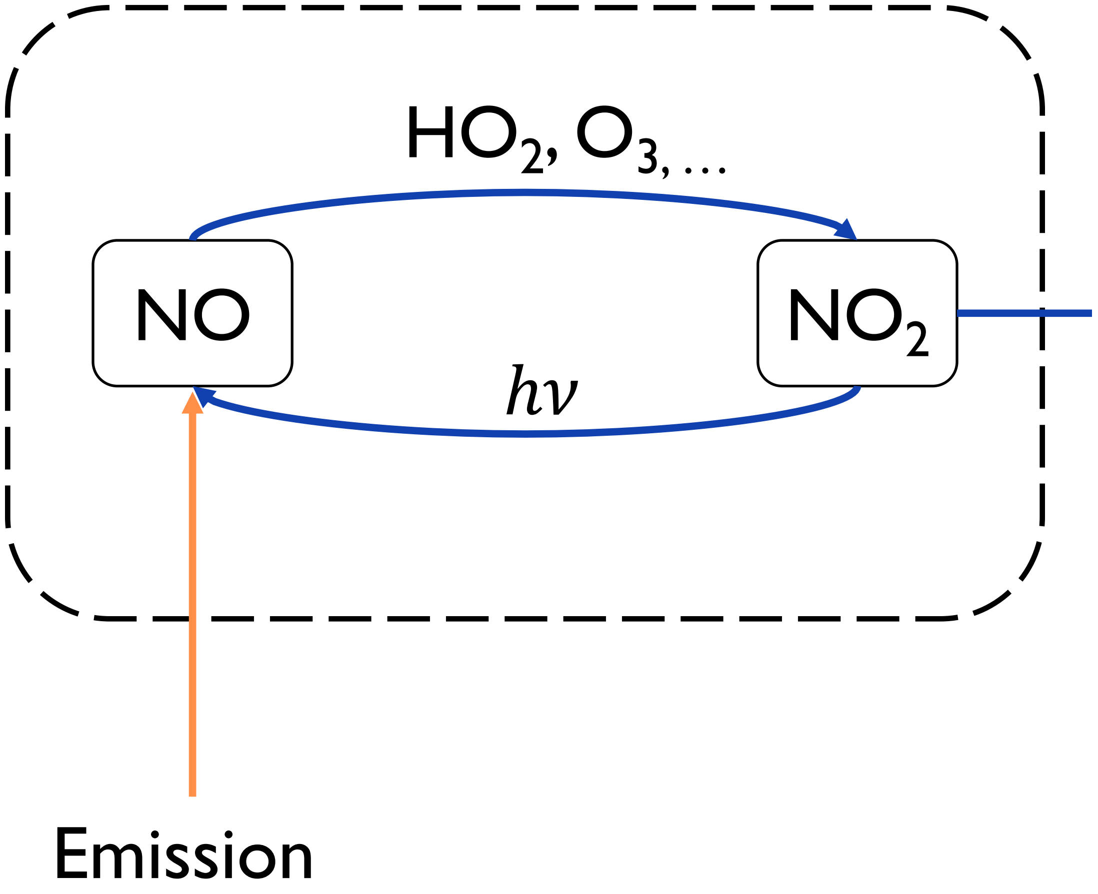
GEOS-CF used for TEMPO is GEOS-Chem running online (meteorology coupled to chemistry)



GEOS-CF schematics [Fig. from Keller et al., 2021]

- GEOS-CF allows for global chemical analyses and forecasts of air quality (up to 5 days)
- Near real-time estimates of key species (O_3, CO, NO_2, SO_2, and $PM_{2.5}$)

NO_2 concentrations are controlled by oxidant chemistry

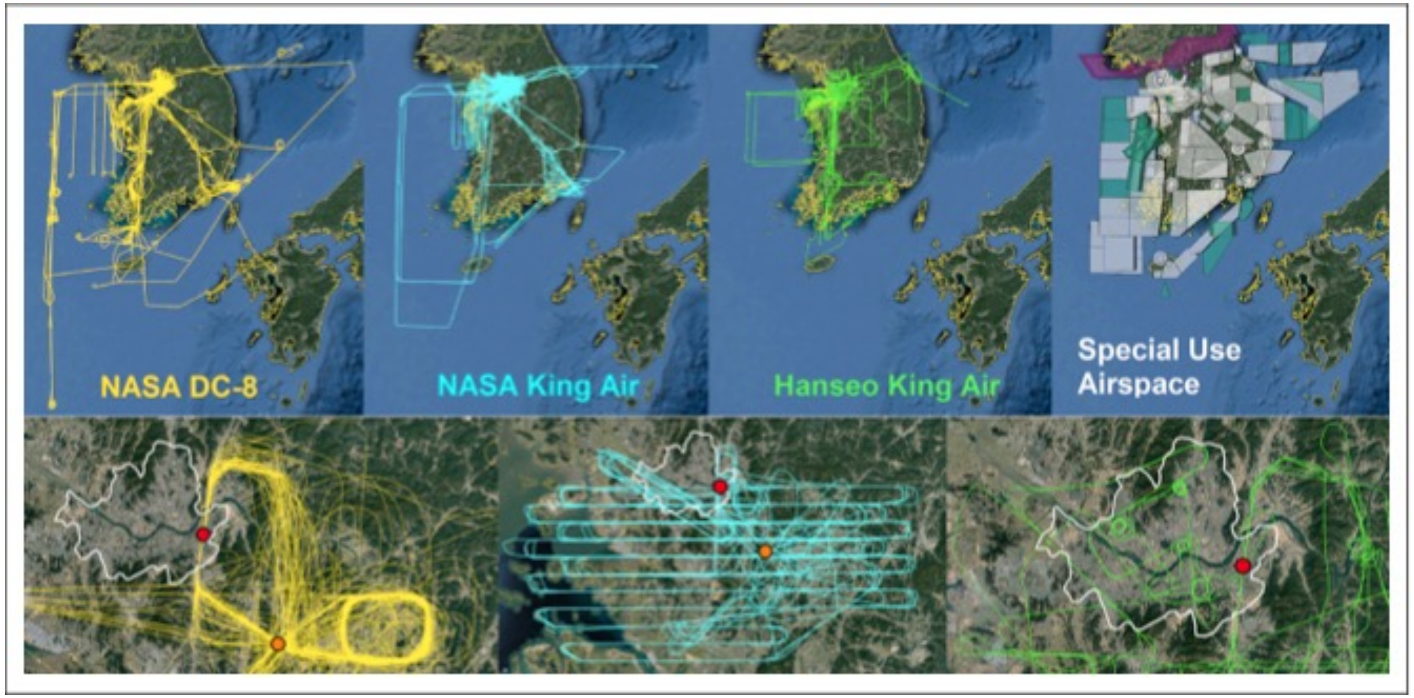


$$\mathrm{PSS} = \frac{[NO]}{[NO_2]} = f([O_3],[HO_2],\ldots)$$

PSS: Photostationary Steady State

Deposition

KORUS-AQ campaign offers observational constraint for chemical species

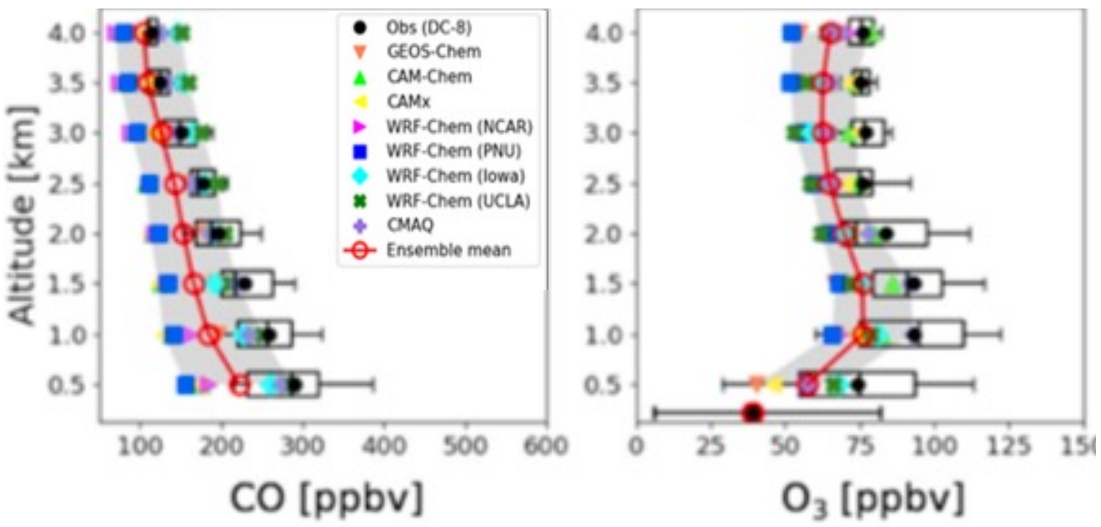


[Source: Crawford et al., 2021]

NASA DC-8	• **Trace gases** • **Aerosol composition** • **Actinic flux** • **AOD**
Hanseo King Air	Key subset of trace gases (NO_2, SO_2, CO, CH_2O, CH_4, CO_2, H_2O)
NASA King Air	• Remote sensing of NO_2 ,CH_2O, SO_2, and O_3 • ~ geostationary satellites

KORUS-AQ allowed evaluation of an ensemble of models [Park et al., 2021]

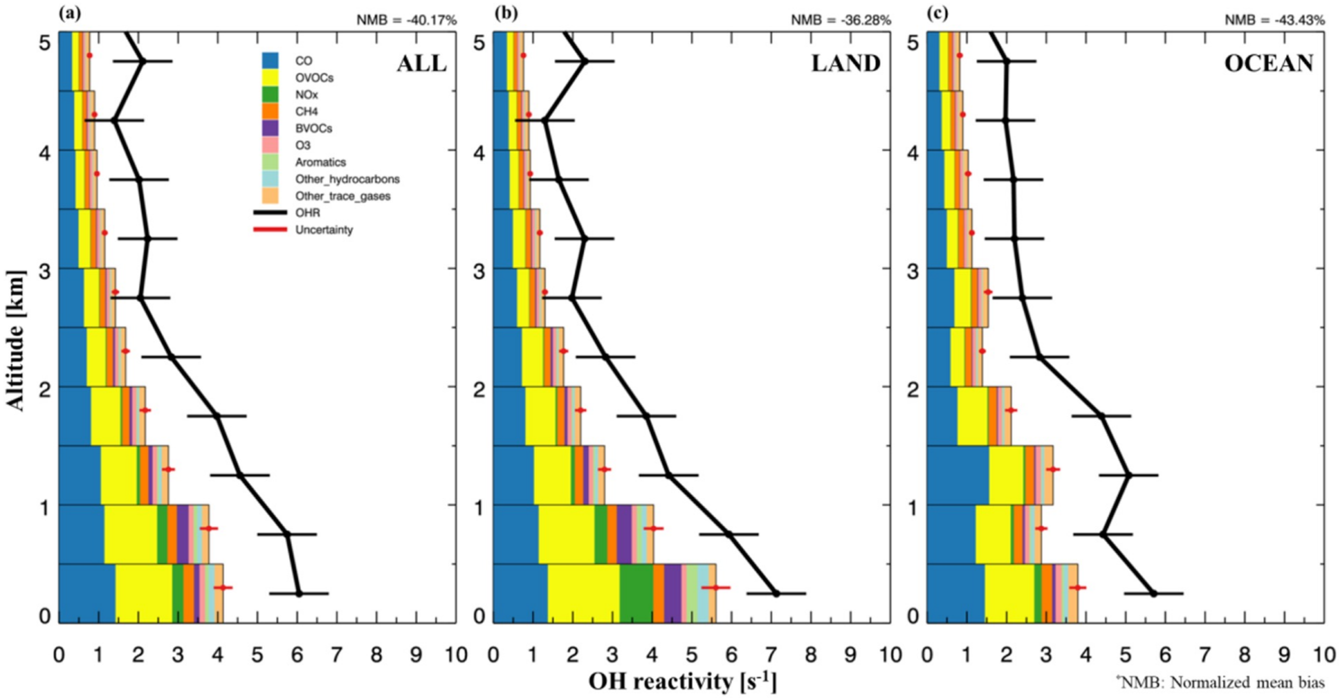
Blocking patterns (June 1 – 10)



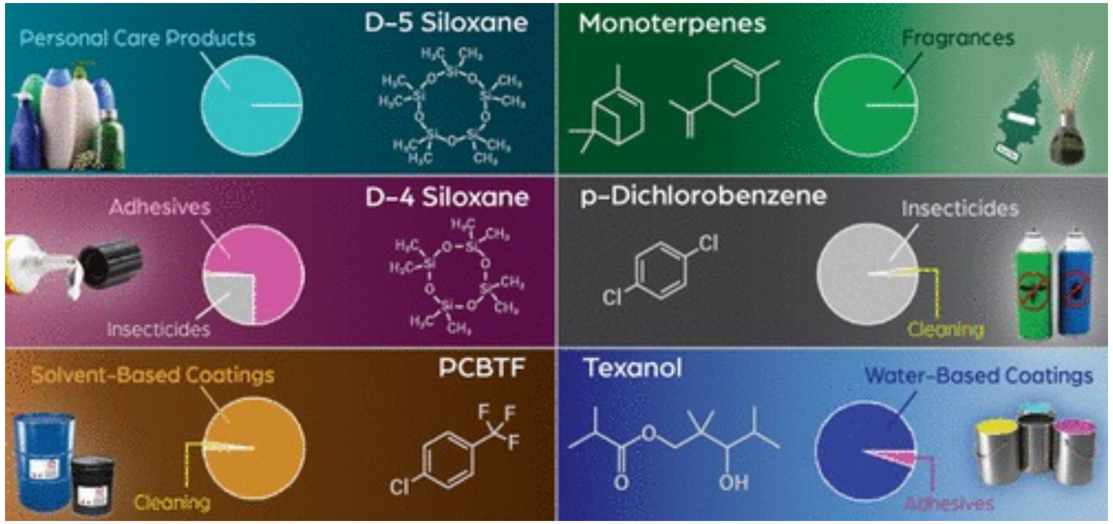
- Models showed systematic low biases of O_3 and CO at all altitudes
- Missing source of CO
- O_3 – low stratospheric O_3 influx? Nitrate photolysis?

KORUS-AQ vs. model points out the missing source VOCs via underestimate in OH reactivity (OHR)

OHR: Measure total trace-gas loading $(\frac{1}{\tau_{OH}})$



[Fig. from Kim et al., 2022]



[Fig. from Gkatzelis et al., 2022]

KORUS-AQ aircraft observation is used to evaluate model's capability in simulating chemical species and NO_2 AMF

GEOS-Chem

Standard Model

v13.3.4

0.25° × 0.3215°

No nitrate aerosol photolysis

No HNO_3 uptake by PMC

No VCP emission

CO boundary condition not scaled up

γ_{HO_2} = 0.2

GEOS-Chem

Modified Model

GEOS-Chem

0.25° × 0.3215°

With nitrate aerosol photolysis

With HNO_3 uptake by PMC

With VCP emission

CO boundary condition ×1.5

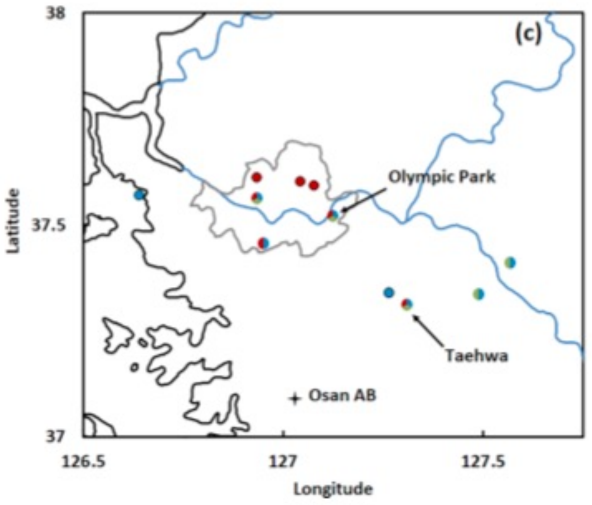
γ_{HO_2} = 0.1

PMC: Coarse PM
VCP: Volatile Chemical Product
γ_{HO_2}: HO_2 uptake coefficient

KORUS-AQ

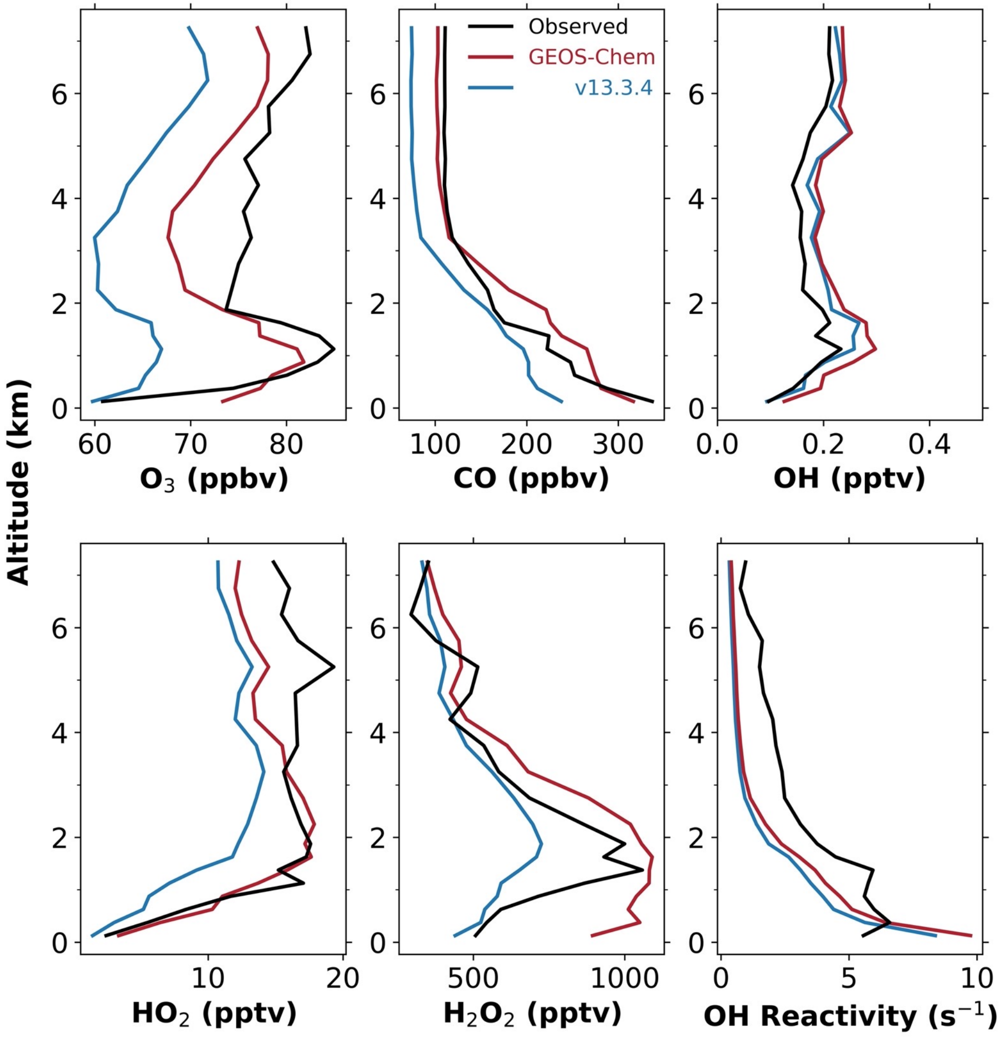
May – June 2016

Aircraft Observation



[Crawford et al. 2021]

GEOS-Chem is successful in simulating key species that drives NO_2 formation & oxidant chemistry



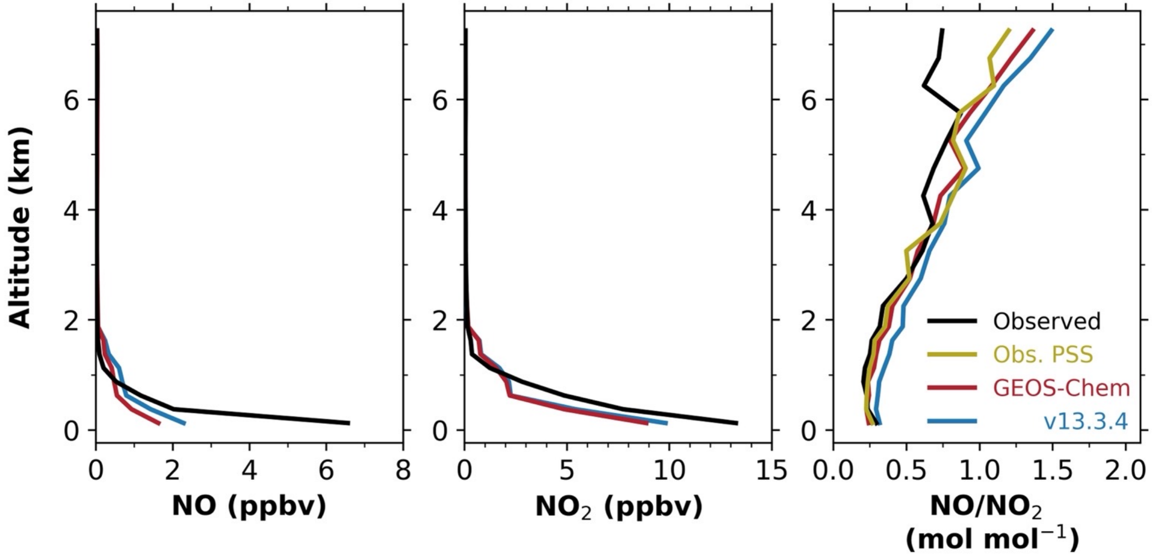
Median vertical profiles

O_3 and HO_2 are key driver species for forming NO_2

O_3 underestimation was significant issue in standard GEOS-Chem (Park et al., 2021)

Instruments/PIs	
Chemiluminescence:	A. Weinheimer
DACOM:	D. Glenn
ATHOS:	W. Brune
CIT-CIMS:	P. Wennberg

GEOS-Chem successfully simulates NO, NO_2, and NO/NO_2



Median vertical profiles

Instruments/PIs	
Chemiluminescence:	A. Weinheimer
TD-LIF:	R. Cohen

$$\left(\frac{[NO]}{[NO_2]}\right)_{PSS} \textbf{ Equation}$$

$$\frac{j_{NO_2}}{k_{O_3+NO}[O_3] + k_{HO_2+NO}[HO_2] + k_{BrO+NO}[BrO] + k_{RO_2+NO}[RO_2]}$$

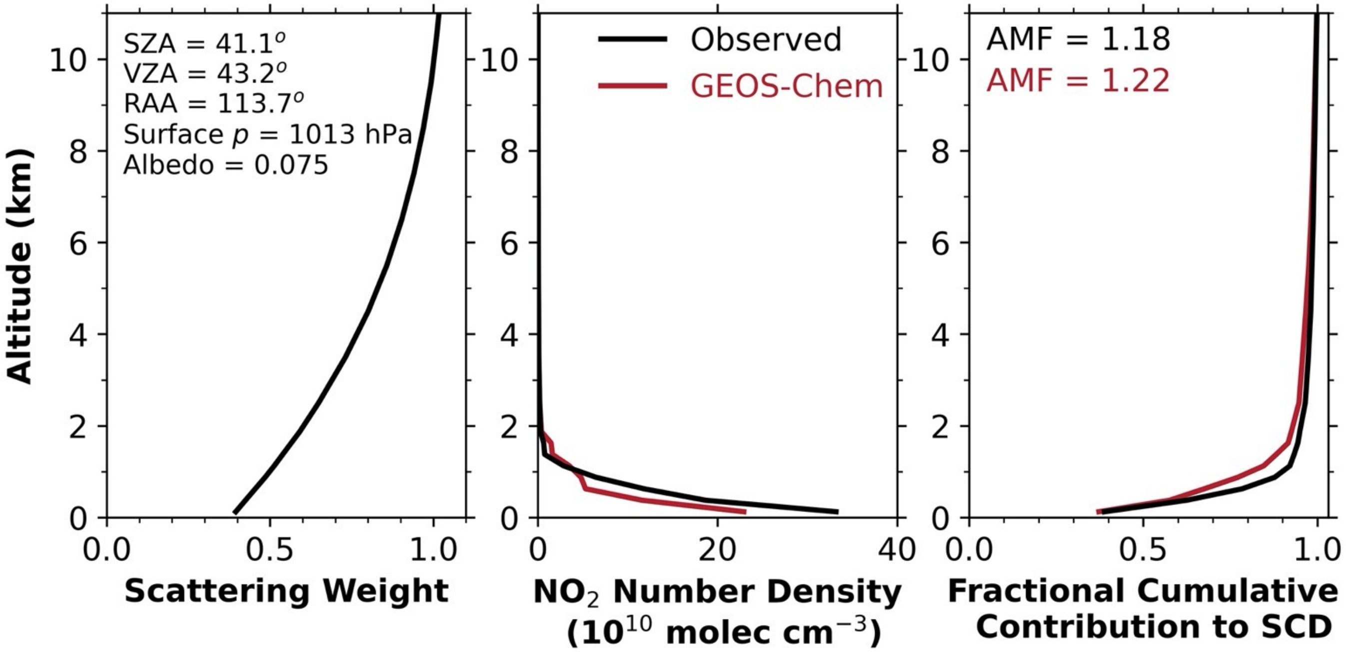
Observed

GEOS-Chem
(<4%)

NO/NO_2 observation departs from the model above 5km (TD-LIF NO_2 positive interference)

Photostationary Steady State (PSS) is more reliable & updated model is in closer agreement with PSS

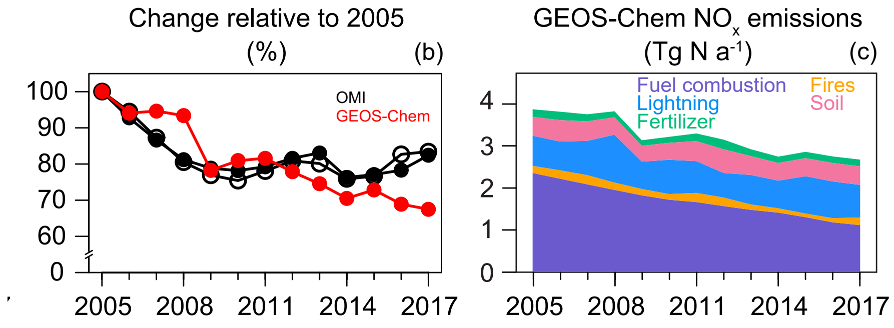
Over South Korea, NO_2 columns are mainly (80%) contained within planetary boundary layer (PBL; z ≤ 2 km)



SZA: Solar Zenith Angle
VZA: Viewing Zenith Angle
RAA: Relative Azimuth Angle
SCD: Slant Column Density (Same as SC)

Reflects highly polluted condition

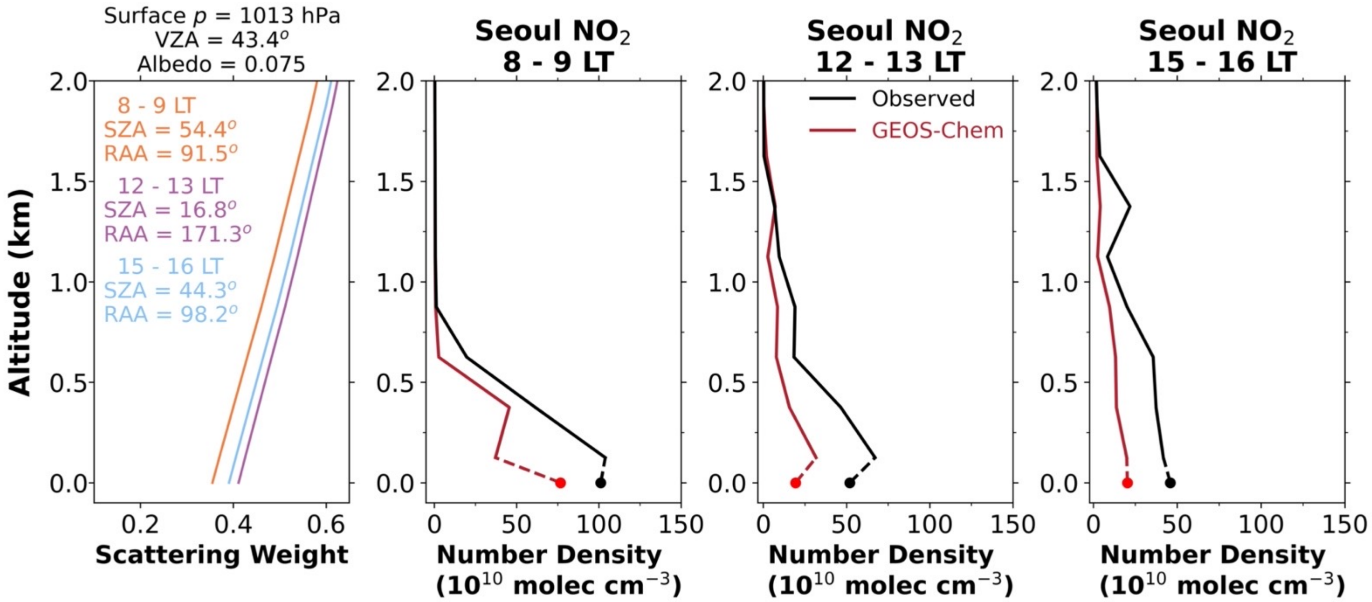
Over the U.S., only 20 – 35% of the column is contained within PBL (Travis et al. 2016)



[Fig. from Silvern et al., 2019]

- NO_2 column: Bottom-up estimate << Top-down estimate
- Higher contribution of NO_2 from FT background in the U.S.

Accounting for diurnal variation of scattering correction factor is critical



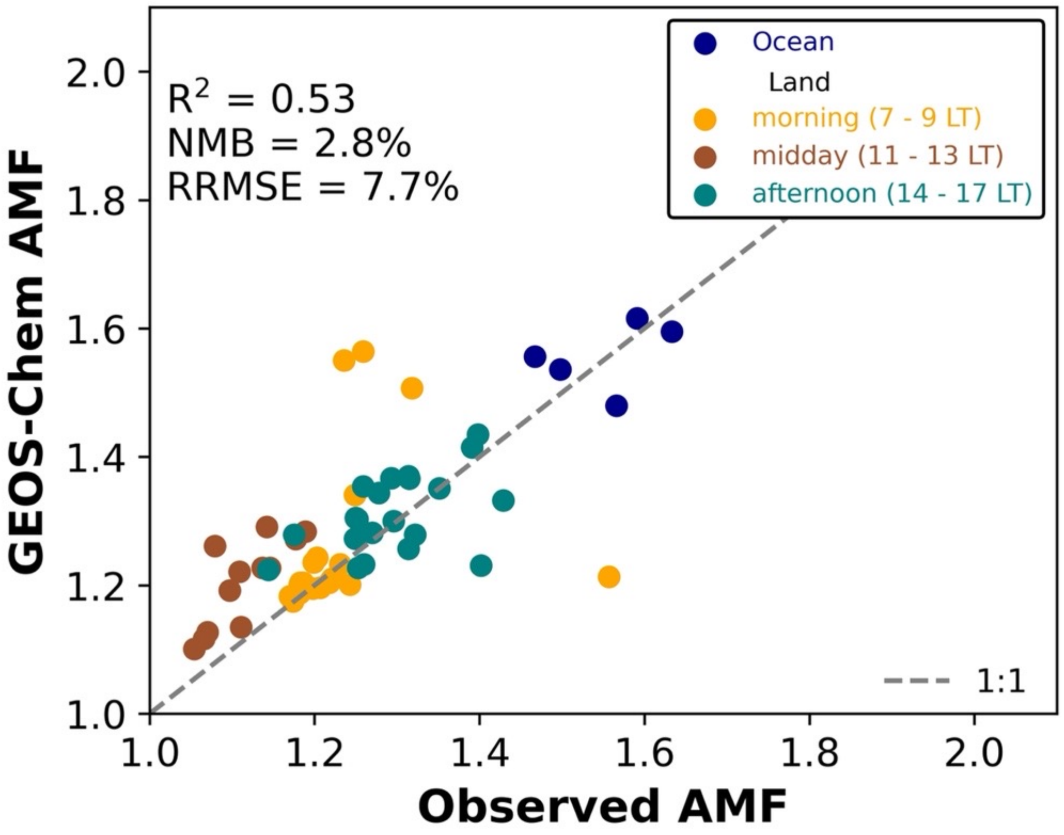
Time of day	AMF_G	$\int_0^{z_T} w(z)S(z)dz$	AMF
8-9 AM	3.09	0.38 (0.39)	1.19 (1.20)
12-1 PM	2.42	0.46 (0.47)	1.11 (1.14)
3-4 PM	2.77	0.46 (0.46)	1.26 (1.27)

Column's diurnal variation (22%) is much smaller than that of surface (87%) [Crawford et al. 2021]

Solar zenith effect (24%) and scattering correction factor (18%) offset each other

Diurnal variation in AMF (14%) is comparable to that of column (22%)

GEOS-Chem can capture the variability of observed AMF



Observed AMF shows high variability (1.05 – 1.63)

Ocean vs. land, and the time-of-day drive observed variability

Timing of the mixed layer growth in the morning is the largest contributor to the model error

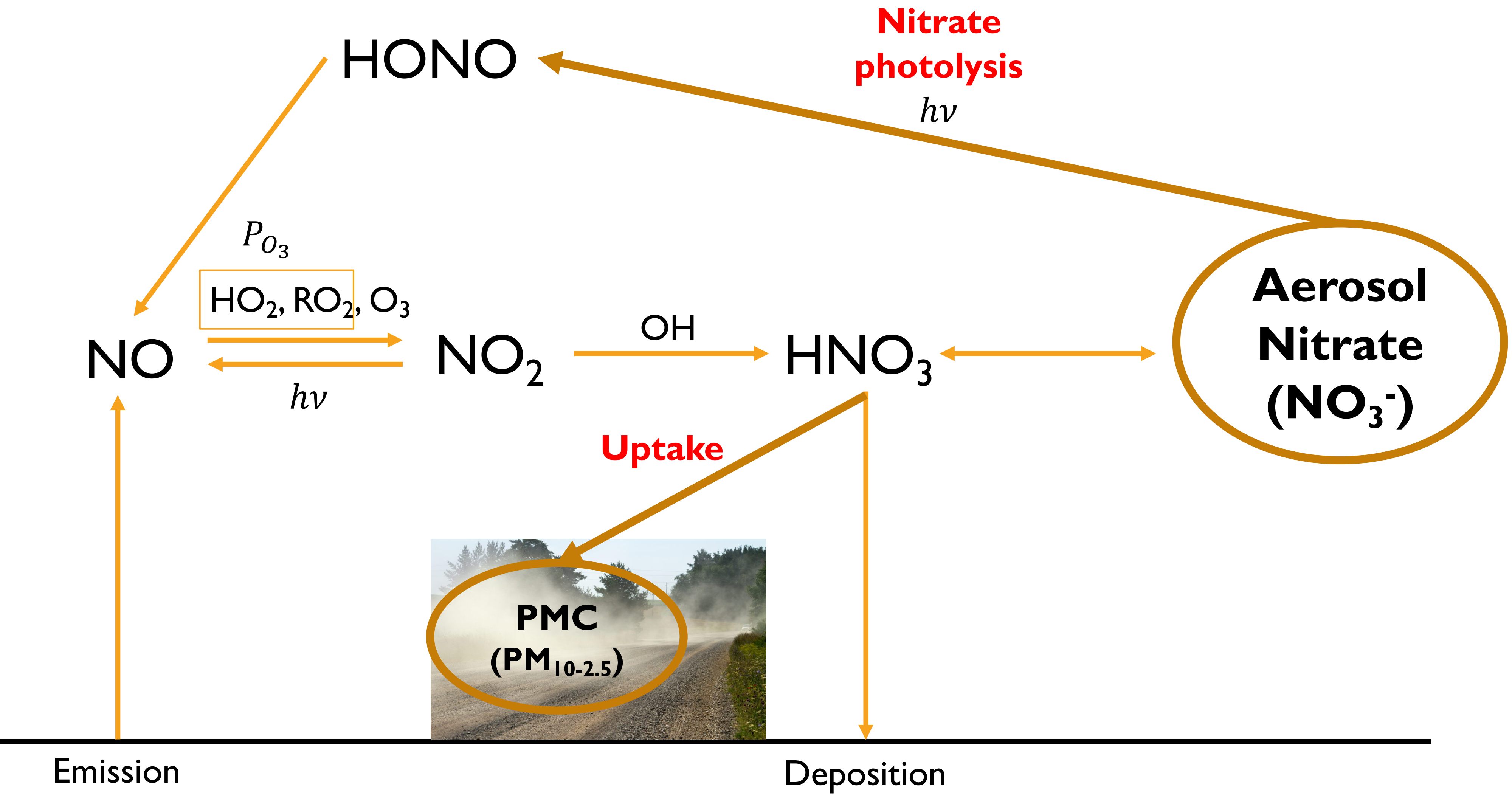
Takeaways

Accurate accounting of oxidant chemistry is important for modeling the shape factor that is used in the GEMS NO_2 retrieval

Accurate accounting for the diurnal variation in AMF is critical in interpretating the diurnal variation in NO_2 columns

GEOS-Chem can provide AMFs for GEMS retrieval with relatively low error (NMB: 2.8%, RRMSE = 7.7%)

Why did we make such modifications? (pt. 1)



Nitrate Photolysis
[Shah et al., 2022]

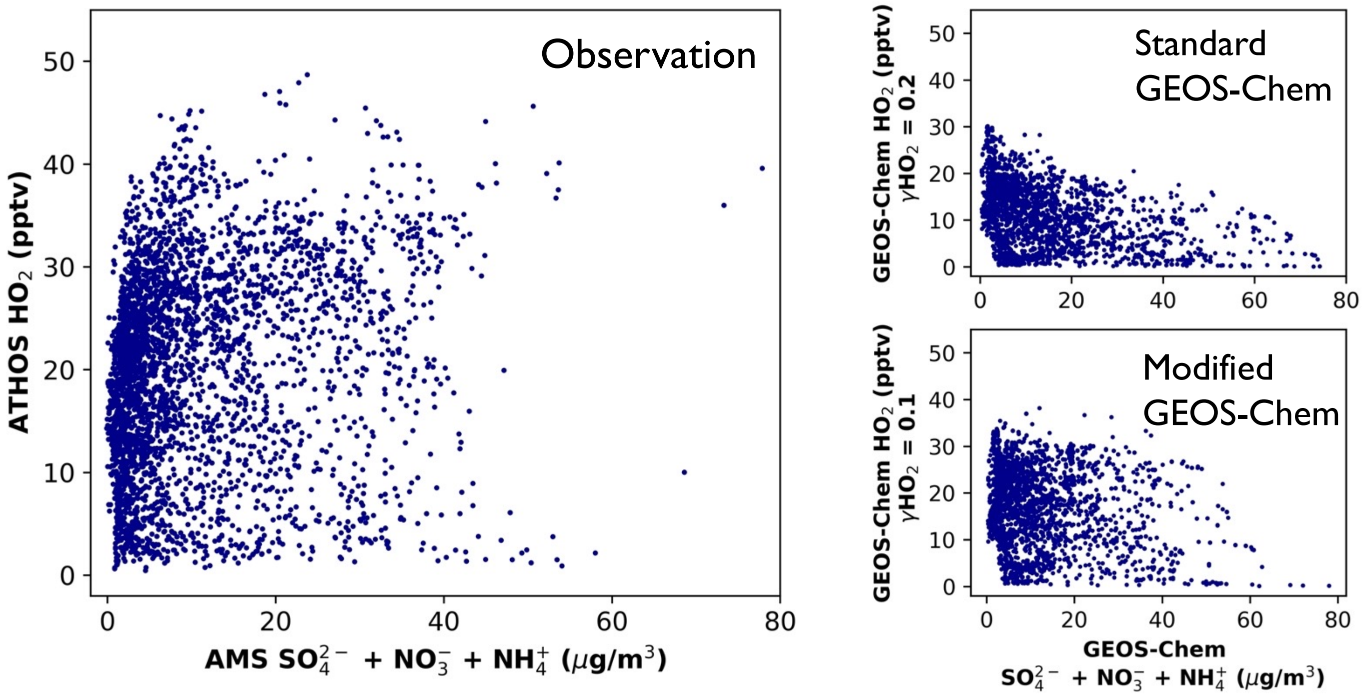
Reduces low model biases of O_3 & NO_x
[Kasibhatla et al. 2018]

PMC uptake of HNO_3
[Zhai, n.d]

Reduces high model bias of NO_3^- & HNO_3
[Travis et al. 2022]

Why did we make such modifications? (pt. 2)

	Observation	Updated GEOS-Chem	Standard GEOS-Chem
calculated OHR (s^{-1})	6.59	4.38	3.85



VCP Emission
[Bates, n.d.]

Reduces low model bias of OH reactivity (OHR) & CH_2O

γ_{HO_2} = 0.1
[Yang et al., 2023]

Reduces low model bias of HO_2

CO BC ×1.5
[Yang et al., 2023]

Fixes model low bias of CO
[Gaubert et al. 2020; Park et al. 2021]