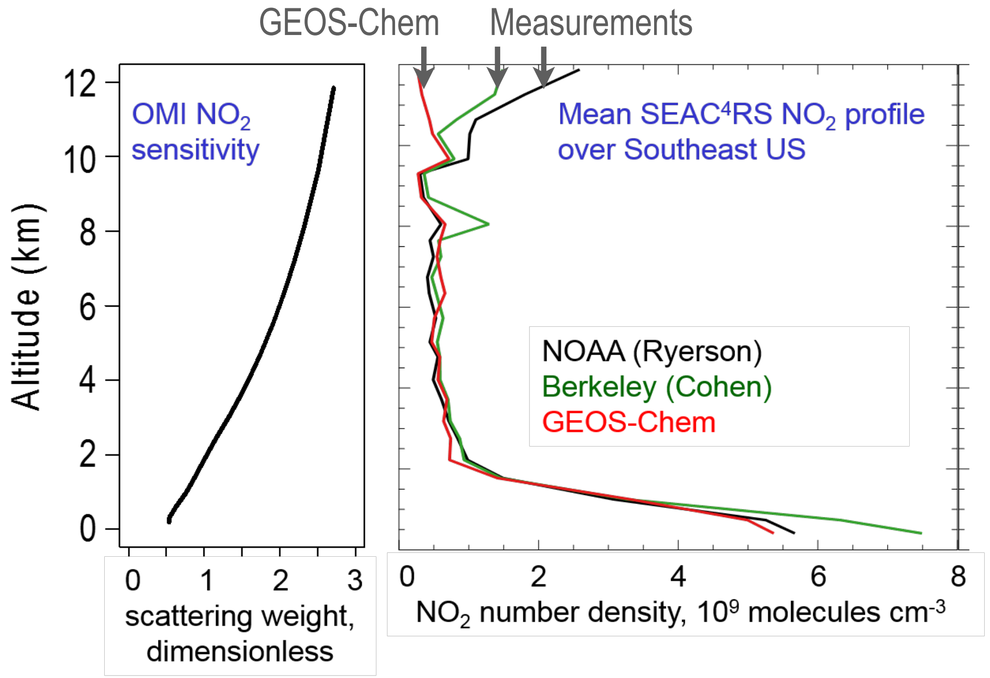
NO_x in the free troposphere:

Importance for tropospheric oxidants and interpretation of satellite NO_2 data

Viral Shah, D. J. Jacob, L. N. Lamsal, S. A. Strode, S. D. Steenrod, K. F. Boersma, S. D. Eastham, T. M. Fritz, C. Thompson, J. Peischl, I. Pollack, T. Ryerson, B. A. Nault, R. C. Cohen, S. T. Andersen, L. Carpenter, M.J. Evans

Satellite NO_2 retrievals need a priori NO_2 vertical profiles, but these are uncertain in UT

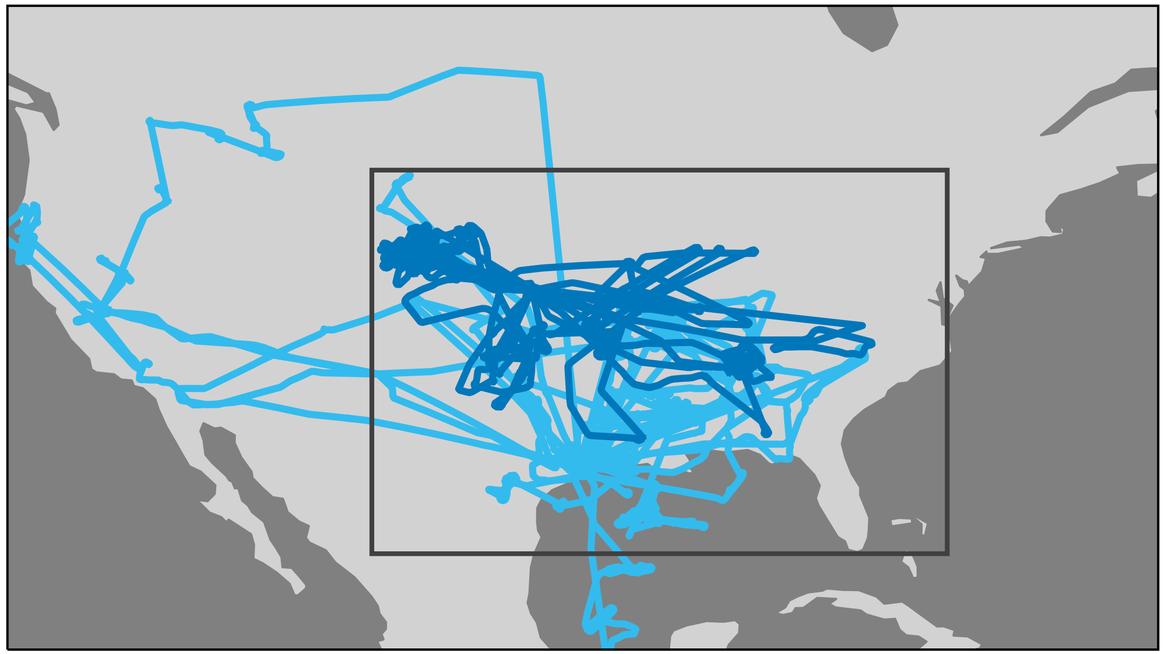


(Travis et al. 2016)

Background NO_2 also affects the interpretation of trends in satellite data

Understanding the NO_2 background using aircraft measurements & GEOS-Chem

SEAC⁴RS (Aug-Sept 2013)
DC3 (May-June 2012)

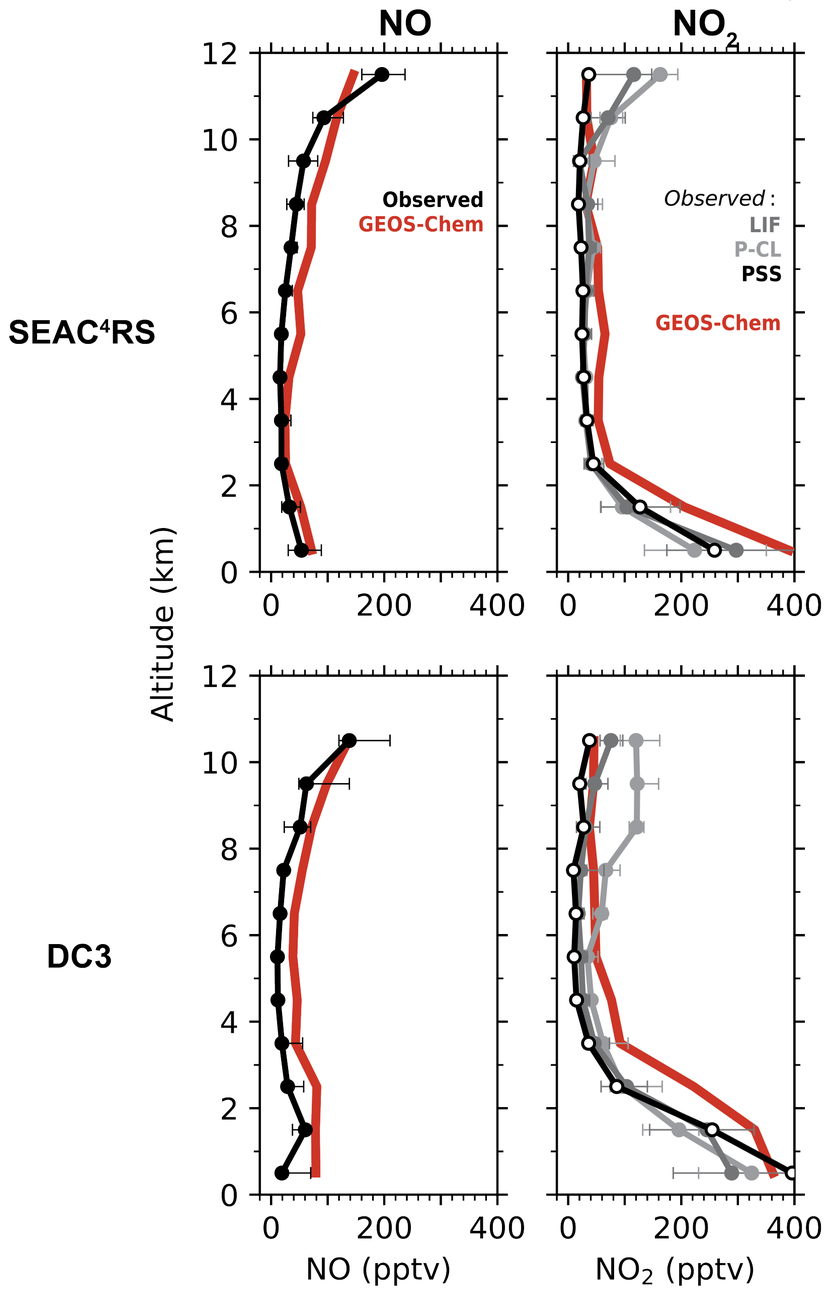


ATom
(Feb, May, Aug, Nov; 2016-18)

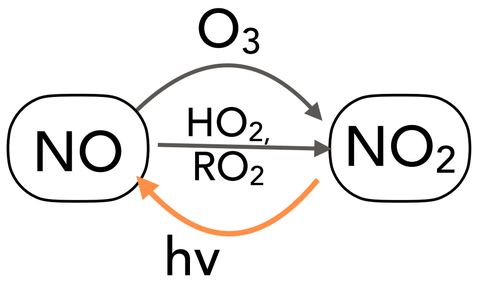
NOx measurements:
LIF NO_2 (Berkeley)
SEAC⁴RS and DC3
P-CL NO and NO_2 (NOAA)
ATom, SEAC⁴RS and DC3

GEOS-Chem
version 12.9; no SSA debromination

Error in the model NO/NO_2 ratio in the upper troposphere



GEOS-Chem consistent with NO and NO_2 concentrations derived from NO measurements and photochemical steady state (PSS):

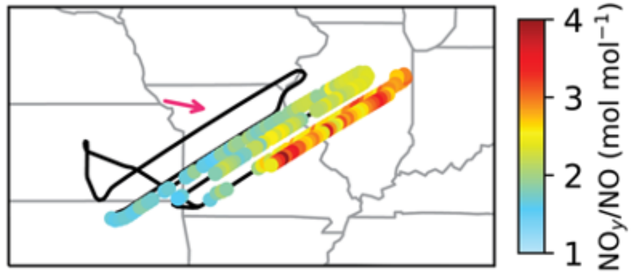


Issues with either NO-NO_2 chemistry or NO_2 measurements?

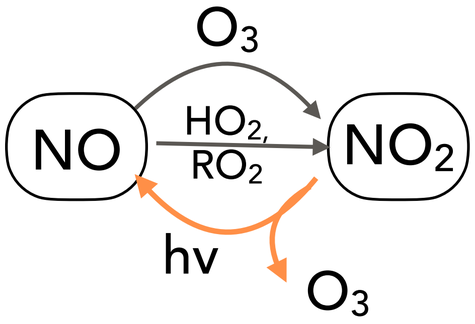
(Silvern et al. 2018)

Investigating free tropospheric NO_2 on a DC3 flight

Flight sampled outflow from a thunderstorm

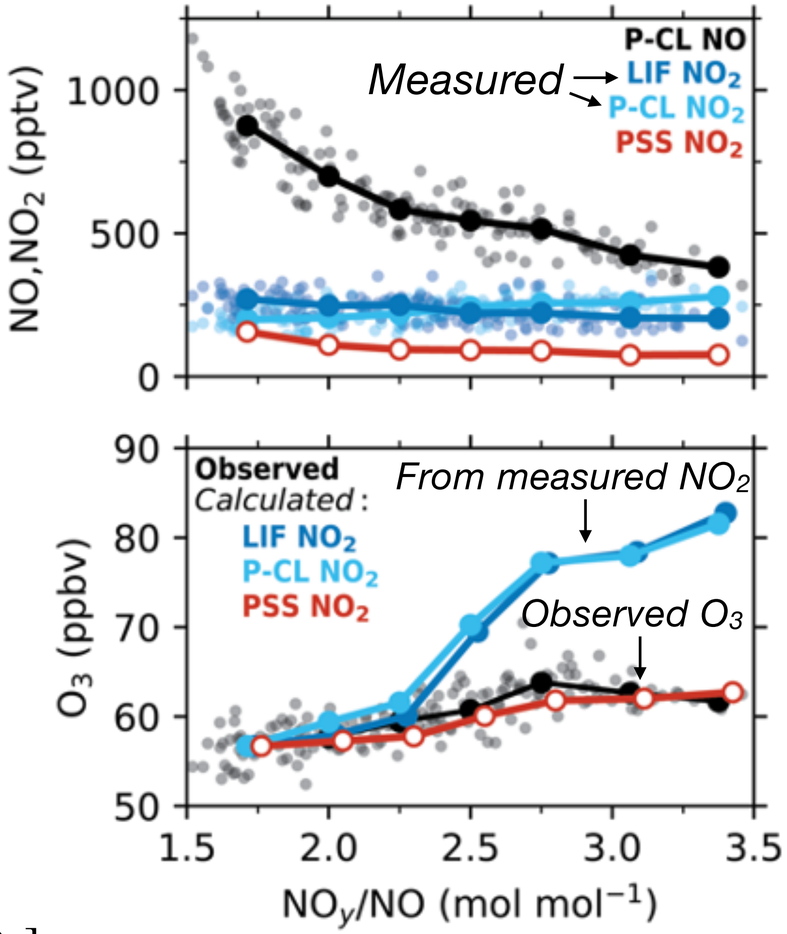


NOy/NO ratio used as a proxy for photochemical age



$$P(O_3) = J_{NO_2}[NO_2] - k_{NO+O_3}[NO][O_3]$$

$L(O_3)$ by photolysis and rxn with HO_2



Large decrease in measured NO, but not in measured NO_2

Ozone production calculated from measured NO_2 exceeds observations

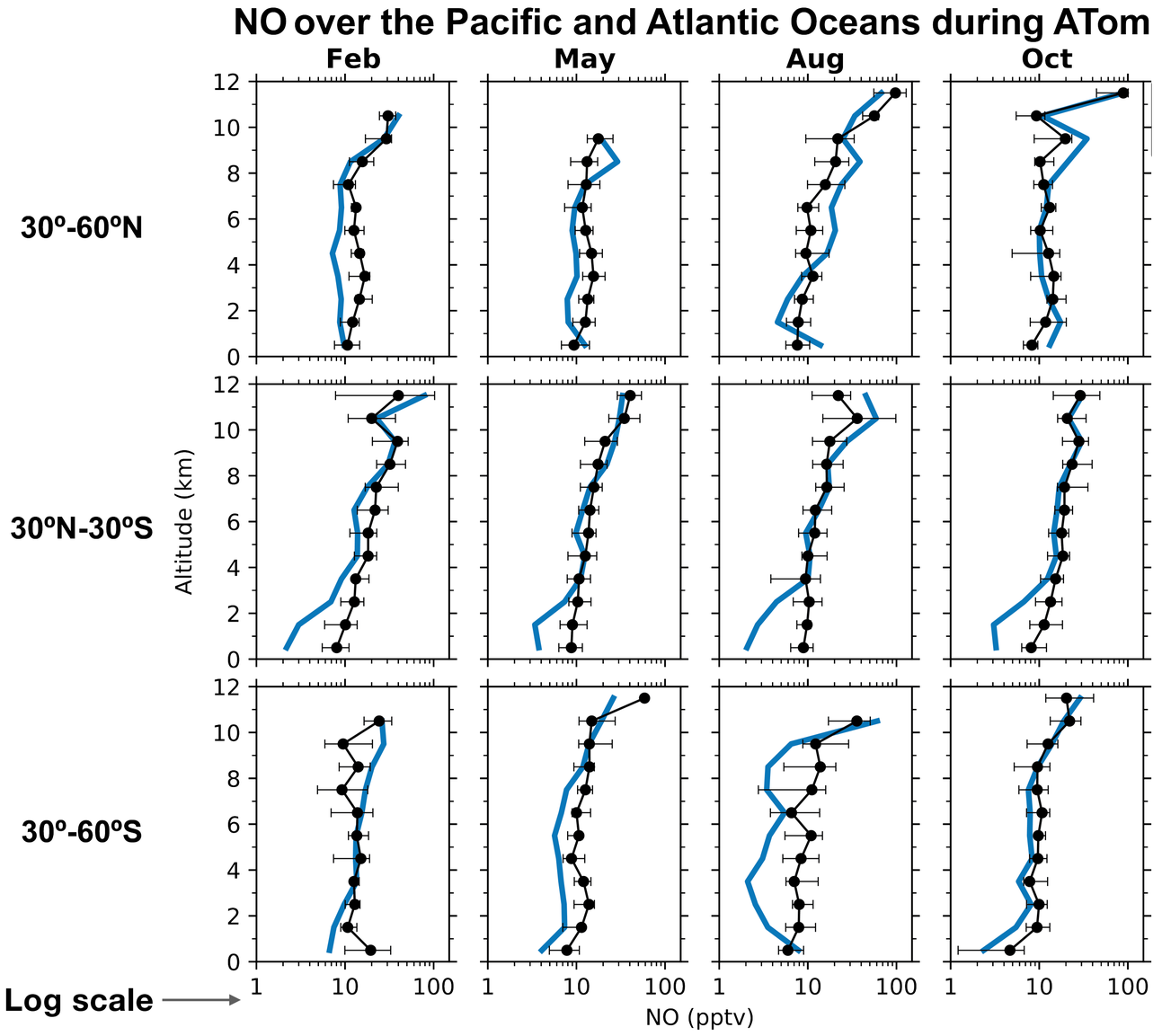
PSS NO_2 consistent with ozone observations

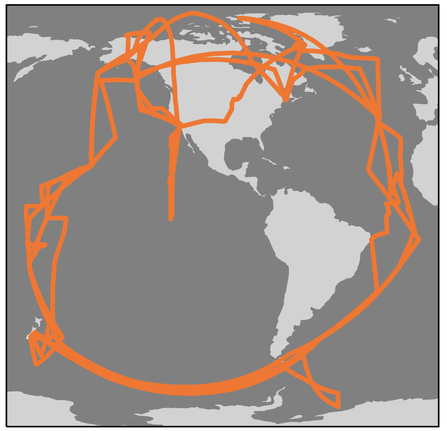
NO_2 measurements biased high in the UT

(likely interference from HNO_4 and organic nitrates)

NO measurements+PSS sufficiently reliable

ATom: GEOS-Chem underestimates NO in the lower troposphere





GEOS-Chem OK in the upper troposphere, lightning emissions OK

GEOS-Chem HNO_3 and PAN largely consistent with ATom observations

(Travis et al. 2020; Zhai et al. *in prep*)

Particle nitrate photolysis could supply additional NO_x over the oceans

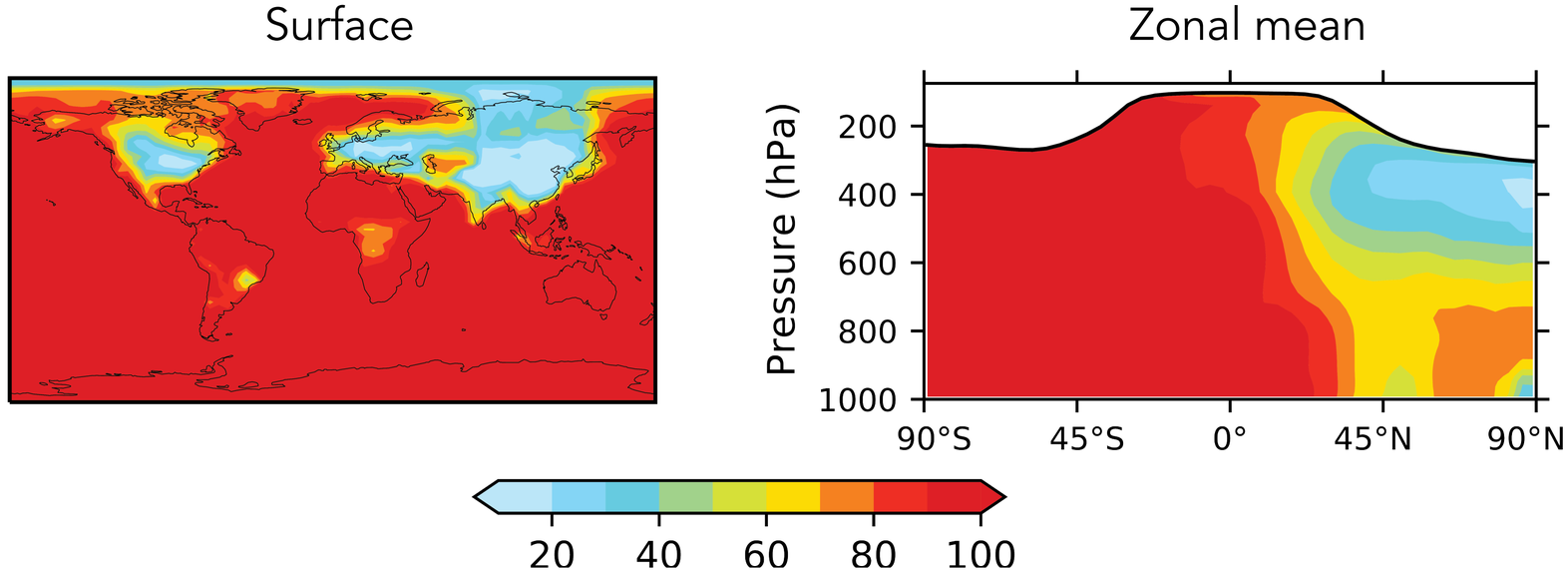
$$pNO_3^- + h\nu \rightarrow HONO + NO_2 \qquad \text{EF: } j(pNO_3^-) \,/\, j(HNO_3)$$

Implemented in GEOS-Chem by Kasibhatla et al. (2018)

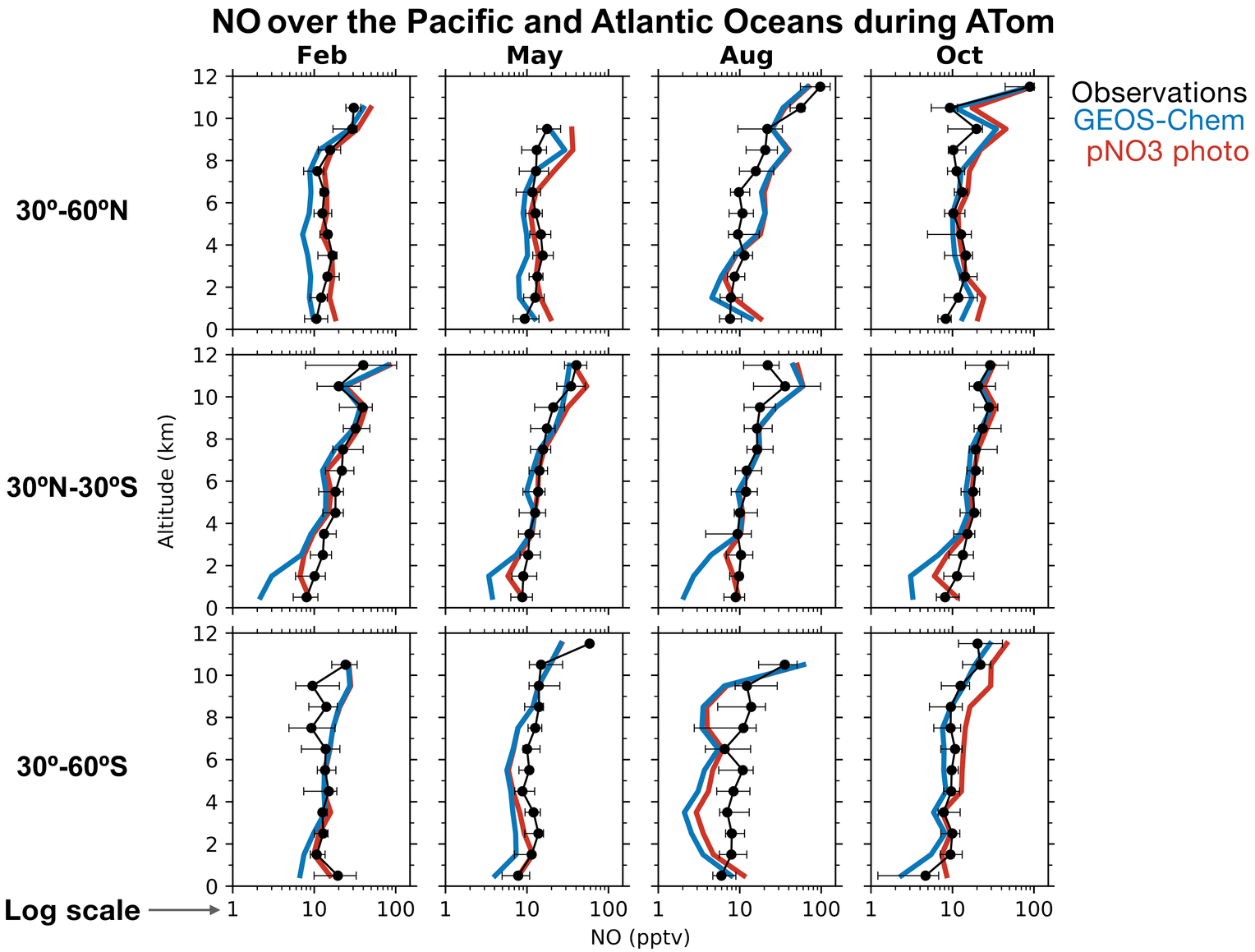
Modified EF in GEOS-Chem

Coarse mode pNO_3
EF=100

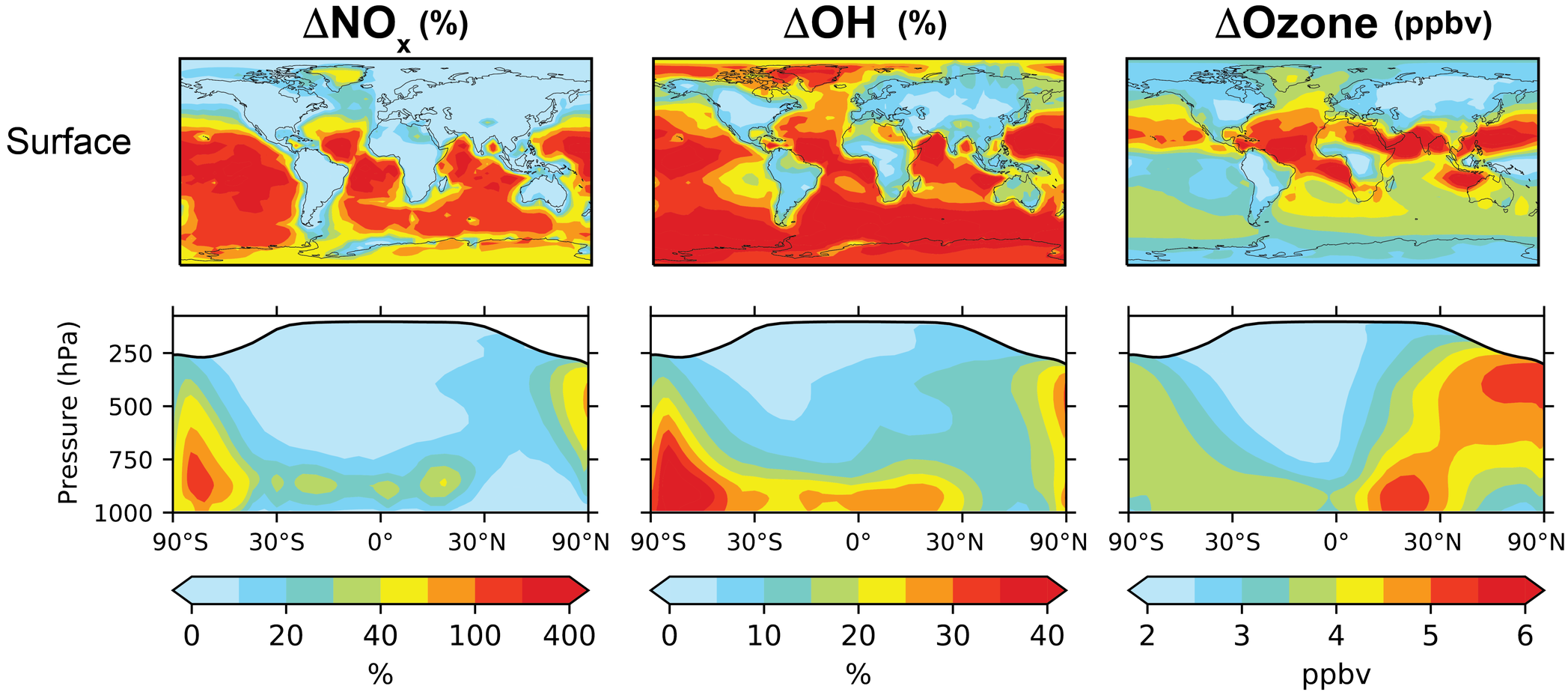
Fine pNO_3
EF: 10 → 100; increases with SSA/pNO_3 ratio



pNO_3 photolysis largely corrects the NO underestimate



pNO_3 photolysis increases global OH and ozone

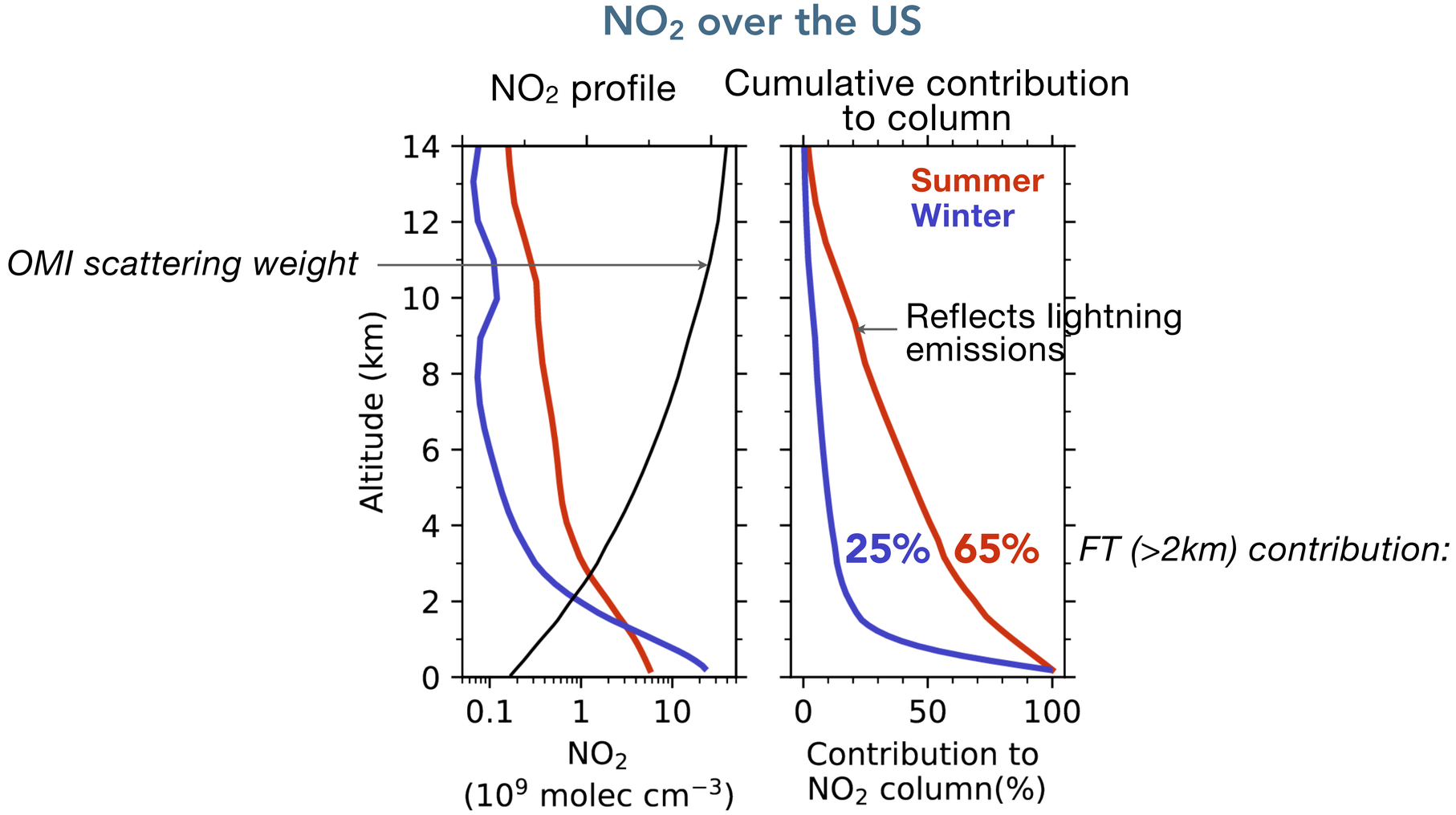


Global increase: 10%; mostly in MBL, smaller increase in northern midlats

Global increase: 19%; due to higher NOx, and more HONO production

Global increase: 10%; ~5ppb increase in FT in northern extratropics; improves simulation compared to obs

Large background NO_2 in FT in summer - weak relationship between NO_x emissions & satellite NO_2 data



CONCLUSIONS

1. NO_2 measurements in free troposphere are biased high, GEOS-Chem consistent with NO measurements & NO_2 from photochemical steady state in SEAC^{4}RS and DC3.

2. pNO_3 photolysis is an important source of NO_x over the oceans, explains ATom NO observations in the lower troposphere

3. pNO_3 photolysis increases GEOS-Chem OH and ozone; brings model ozone closer to observations

4. Free tropospheric background NO_2 contributes 65% of NO_2 columns over the US in summer