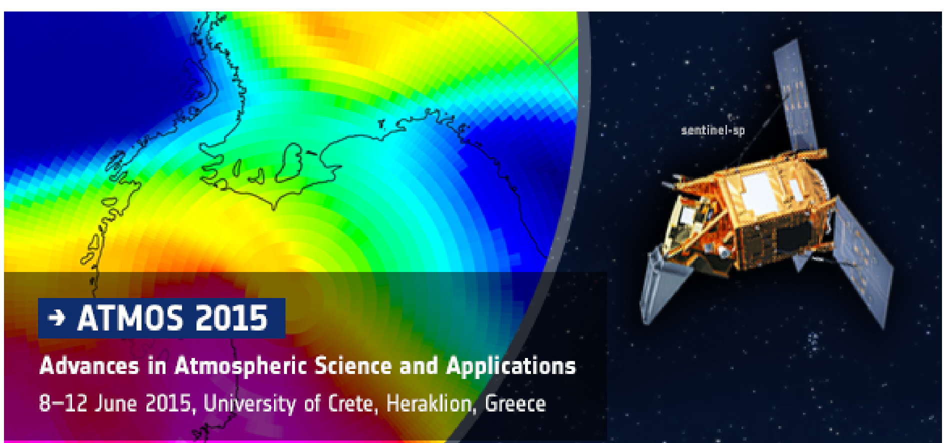
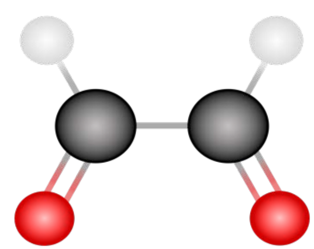
Revising the budget of glyoxal using OMI vertical columns

J.-F. Müller, T. Stavrakou, C. Lerot, I. De Smedt, M. Van Roozendael

Belgian Institute for Space Aeronomy (BIRA-IASB)



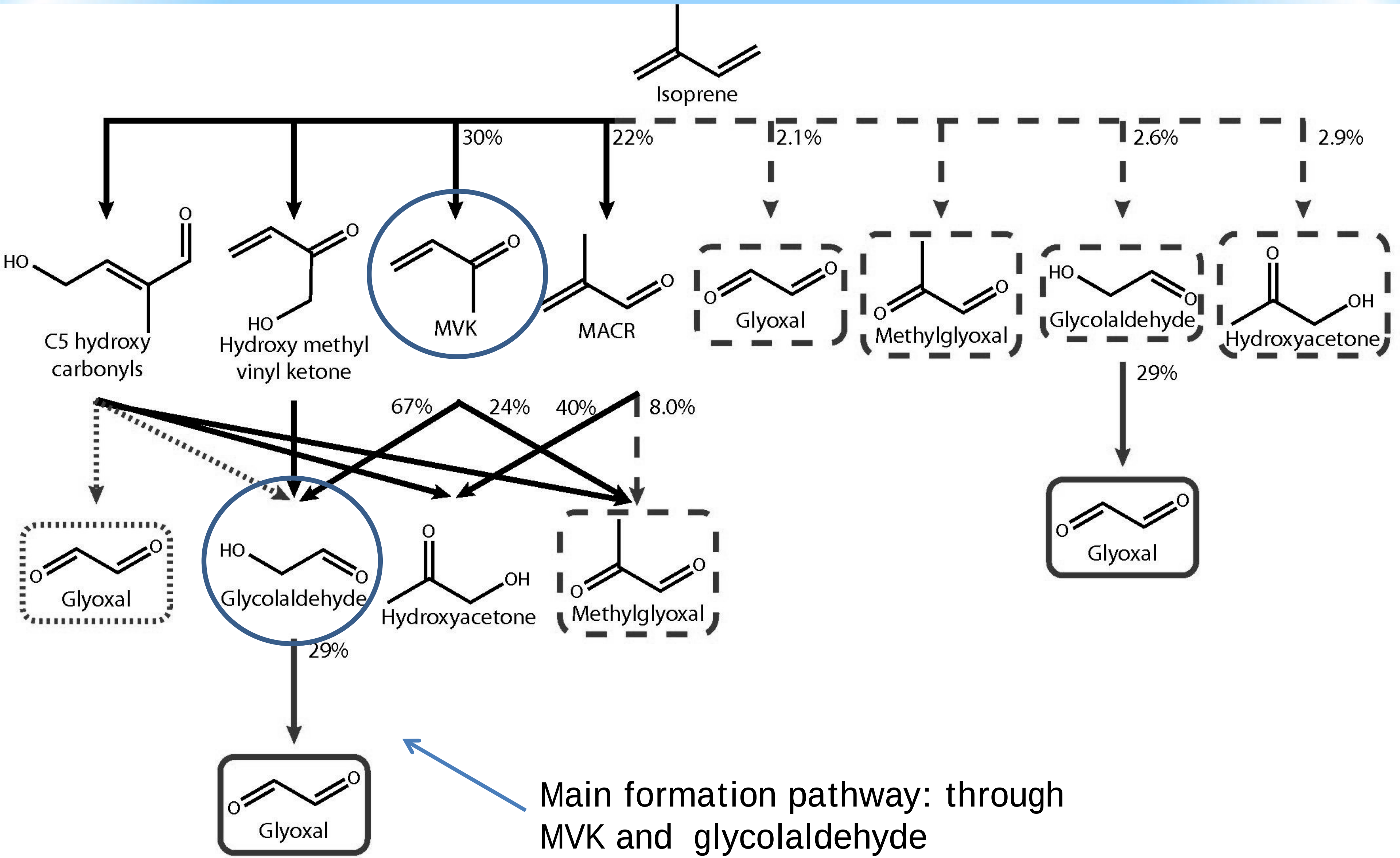


Why (should anyone be interested in) glyoxal?

- Short-lived product from the oxidation of many (but not all) VOCs, which are key players in smog formation & air quality
- Isoprene likely the most important precursor (as for HCHO)
- Soluble in water where it can react or oligomerize ➔ important precursor of particulate matter due to uptake by clouds & aerosols
- Very sparse in situ measurements/poor understanding of glyoxal budget ➔ a lot can be learned from satellite data
- First satellite observations (SCIAMACHY) pointed to large additional sources over land & ocean (Myriokefalitakis et al., 2008; Fu et al., 2007; Stavrakou et al., 2009; Liu et al., 2012)
- However our knowledge of chemical mechanisms has dramatically improved + we now have many more observations including new satellite datasets

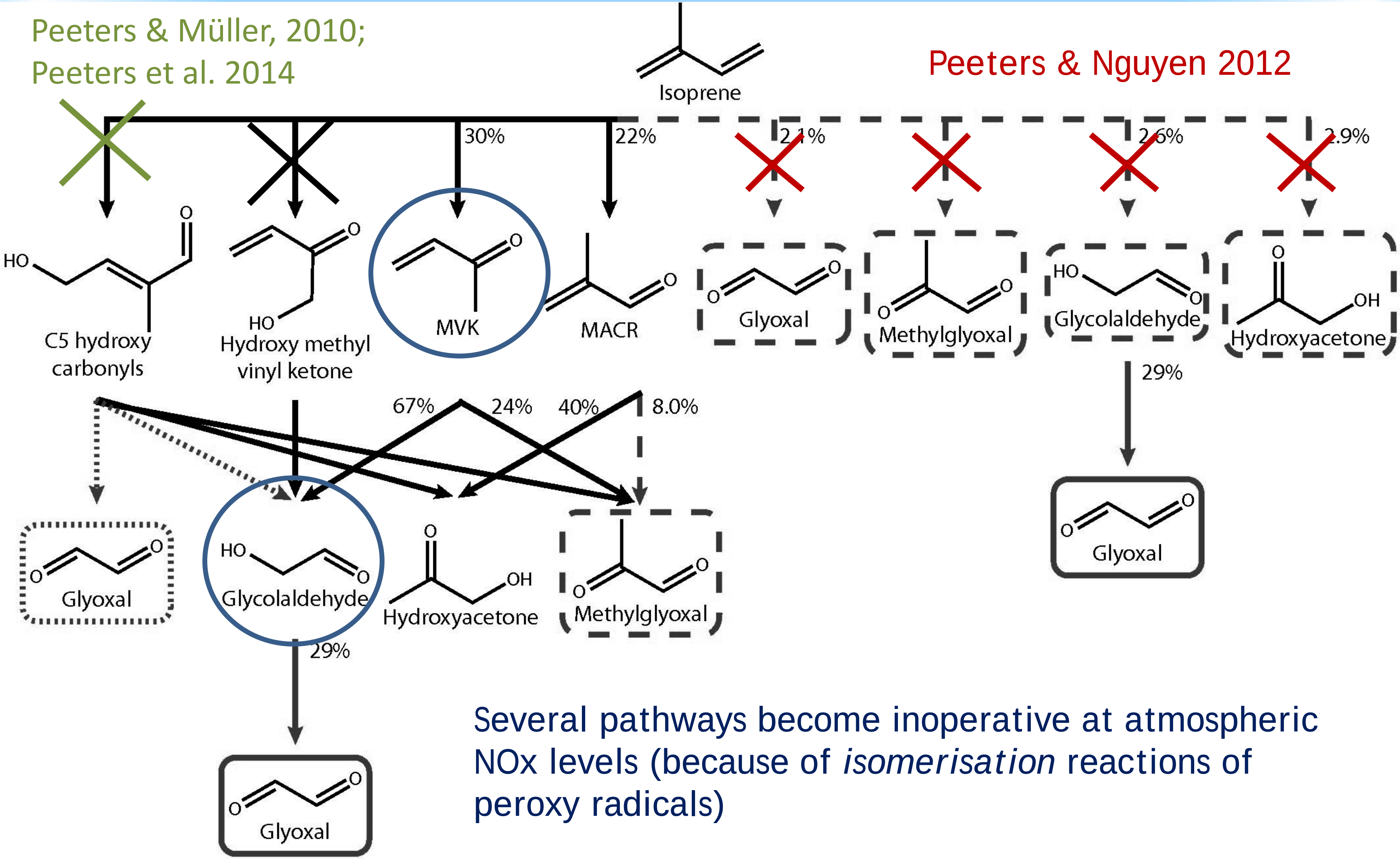
Pathways to glyoxal from isoprene + OH

Galloway et al. (ACP2011) : very high NOx levels



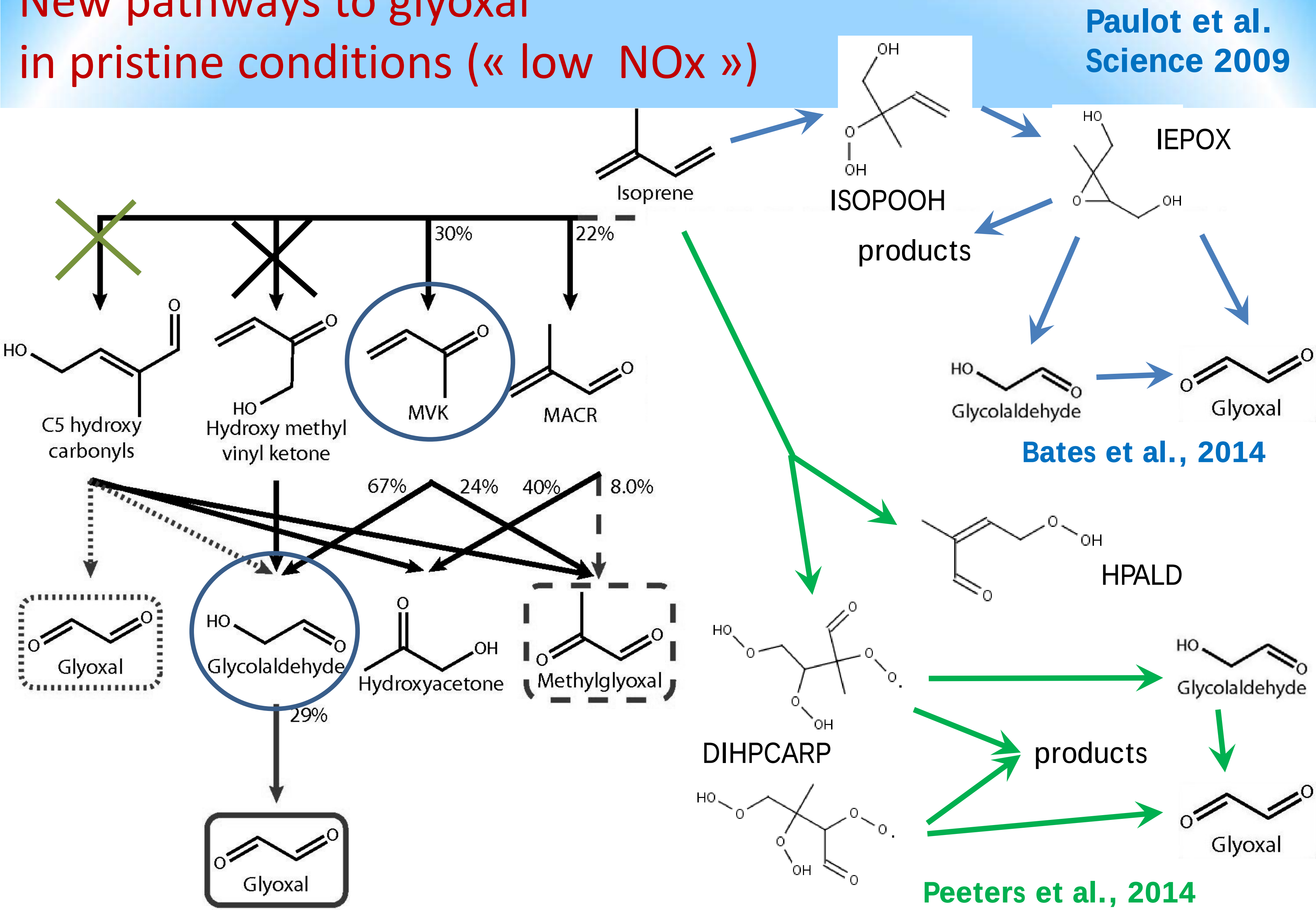
Main formation pathway: through MVK and glycolaldehyde

Pathways to glyoxal from isoprene + OH in atmospheric conditions

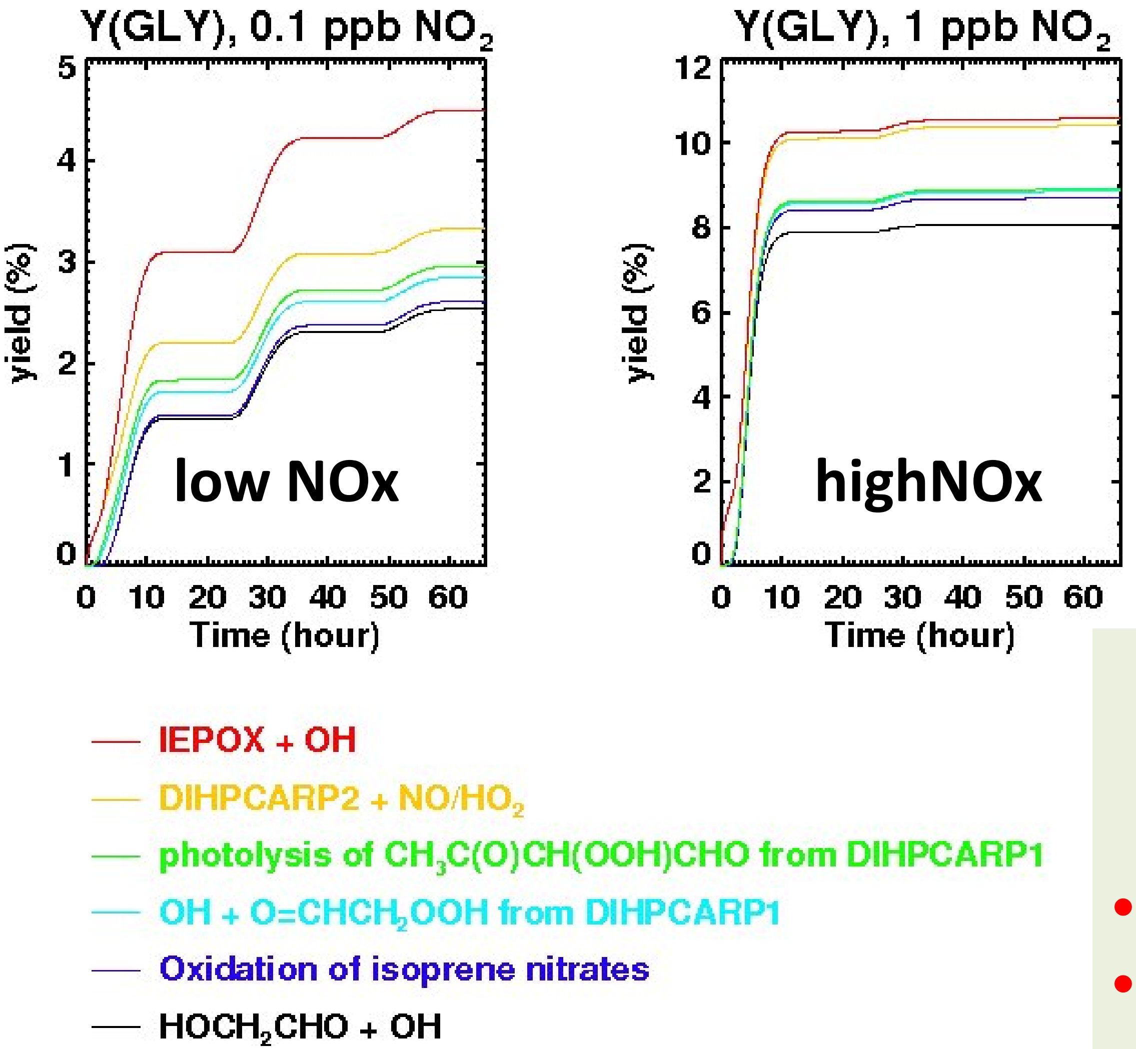


Several pathways become inoperative at atmospheric NOx levels (because of *isomerisation* reactions of peroxy radicals)

New pathways to glyoxal in pristine conditions (« low NOx »)



Quantifying the pathways to glyoxal from isoprene: box model simulations



Sensitivity calculations to determine impact of uncertainties on

- isomerisation rates
- OH-reaction rates
- photolysis rates
- unexplored pathways

Definition of 3 model setups:

- **STANDARD: best estimate**
- **MINGLY : lowest yield**
- **MAXGLY: highest yield**

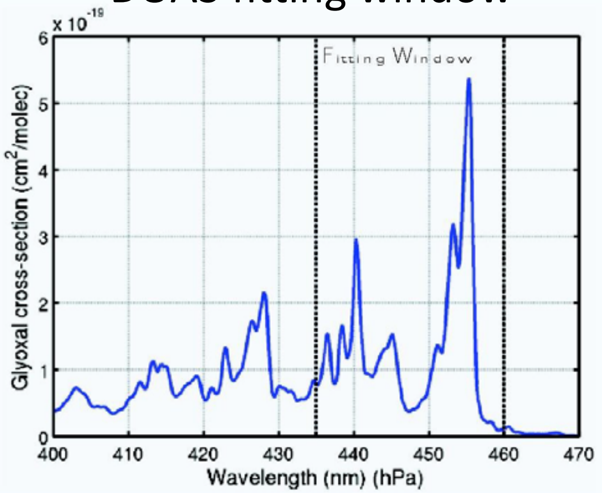
Glyoxal columns from OMI/Aura

(Lerot et al., EGU 2015; see also Lerot et al., ACP 2010)

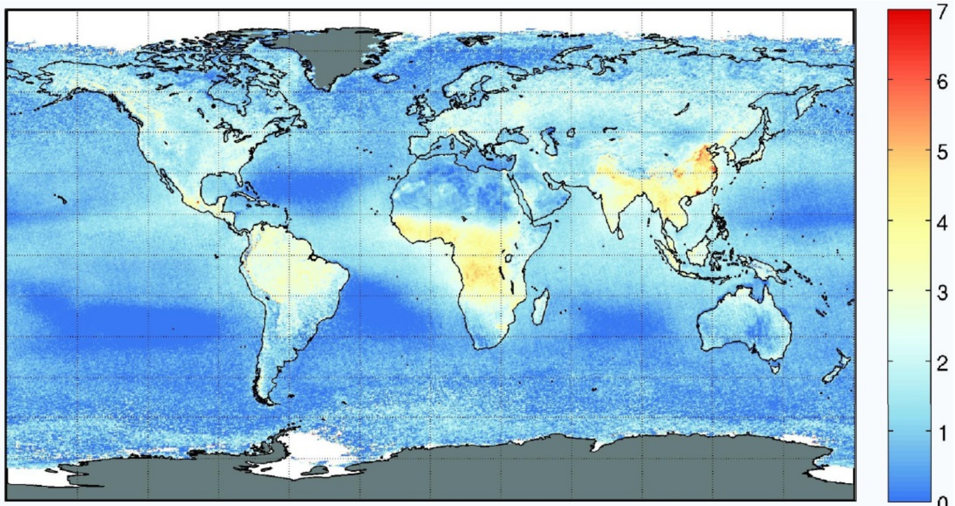
DOAS fitted parameters

Cross-sections pre-convolved using the (row-dependent) slit functions	
CHOCHO	Volkamer et al. (2005)
Ozone	Brion et al. (1998)
NO_2	Vandaele et al. (1996) – Two temperatures as recommended by Alvarado et al. (2014) and Miller et al. (2014)
O2-O2	Thalman et al. (2013)
H_2O (vapor)	HITEMP 2010 (Rothman et al., 2010)
Ring	Pseudo-absorber cross-section (Chance and Spurr, 1997)
Liquid water + VRS	Pope et al. (1997) + residual cross-section measured by Peters et al. (2014)
Other parameters:	Second-degree polynomial, Linear intensity offset, Doppler-shift

DOAS fitting window



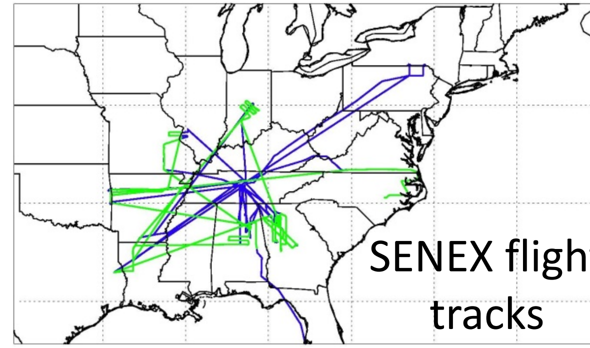
OMI CHOCHO column – 2005-2013
(10^{14} molec. cm^{-2})

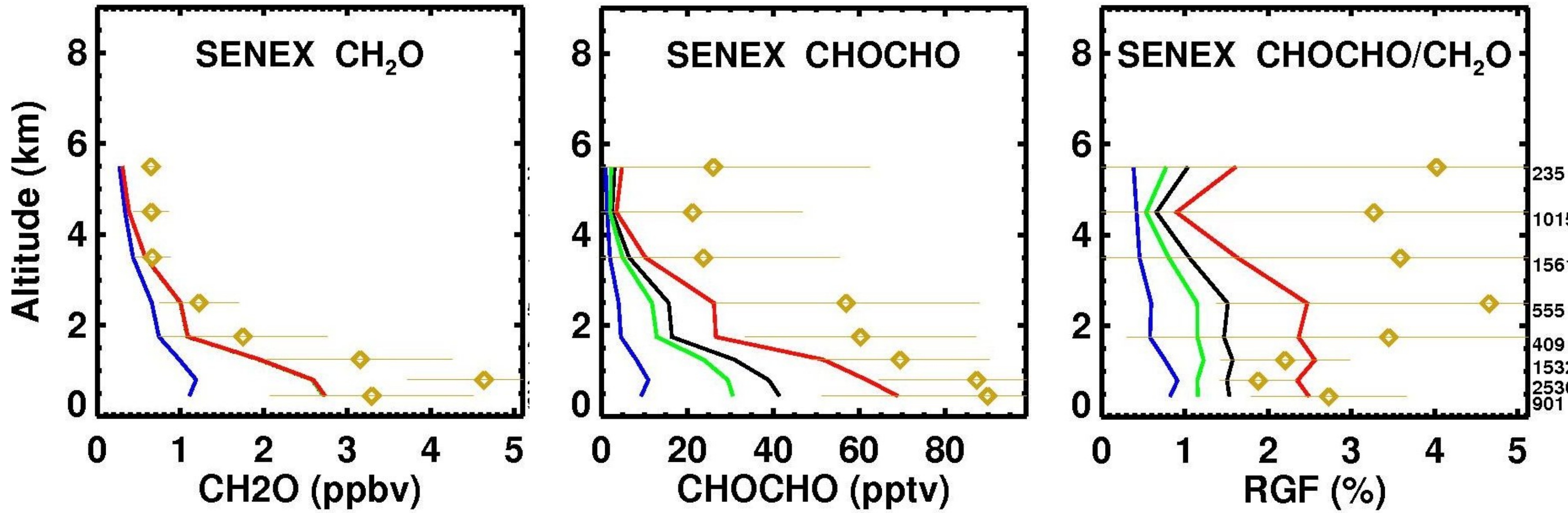


- liquid water : predetermined in wider window (405-490 nm)
- normalization: based on Pacific sector
- AMF : combine weighting functions computed with LIDORT with a priori profiles from IMAGESv2 and field data (TORERO)
- no cloud correction, use only CF<0.2

SENEX campaign June-July 2013

(14-17 LT)





standard IMAGESv2 model run

no isoprene

MINGLY

MAXGLY

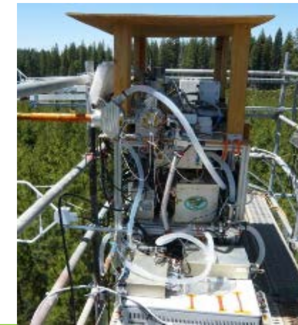
CH_2O data : FI-LIF (NASA)
CHOCHO : Cavity enhanced spectrometer (NOAA)

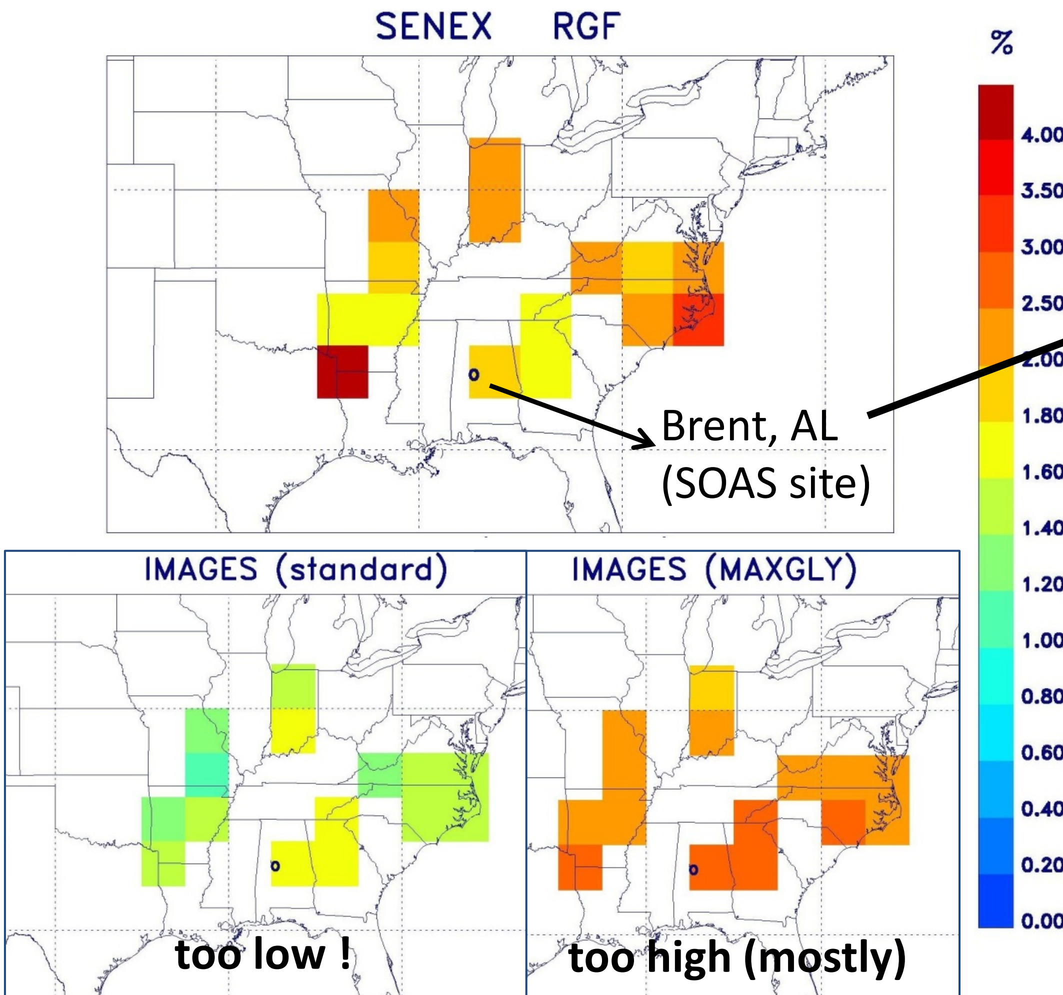
(Courtesy of F. Keutsch, Harvard)

SENEX
June-July 2013

RGF = CHOCHO / CH_2O

SOAS
Southern Oxidant & Aerosol Study





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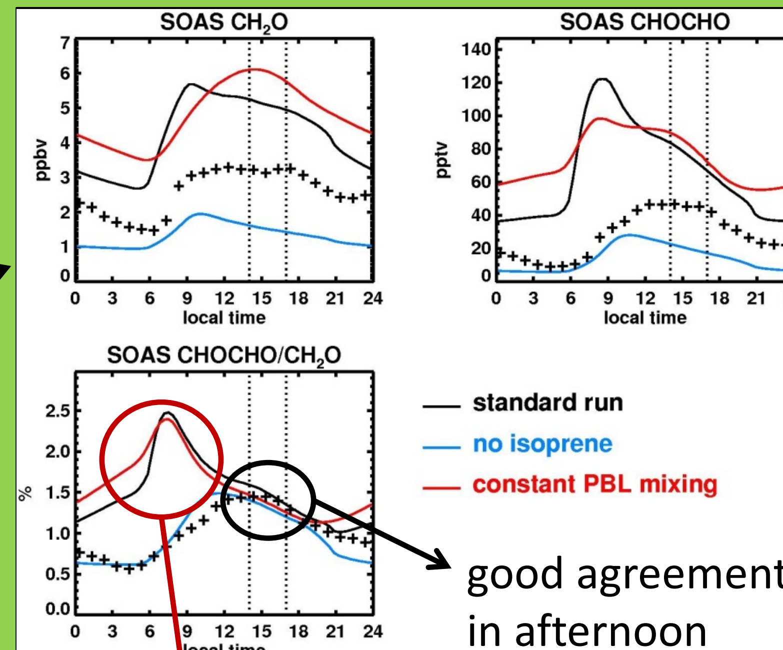
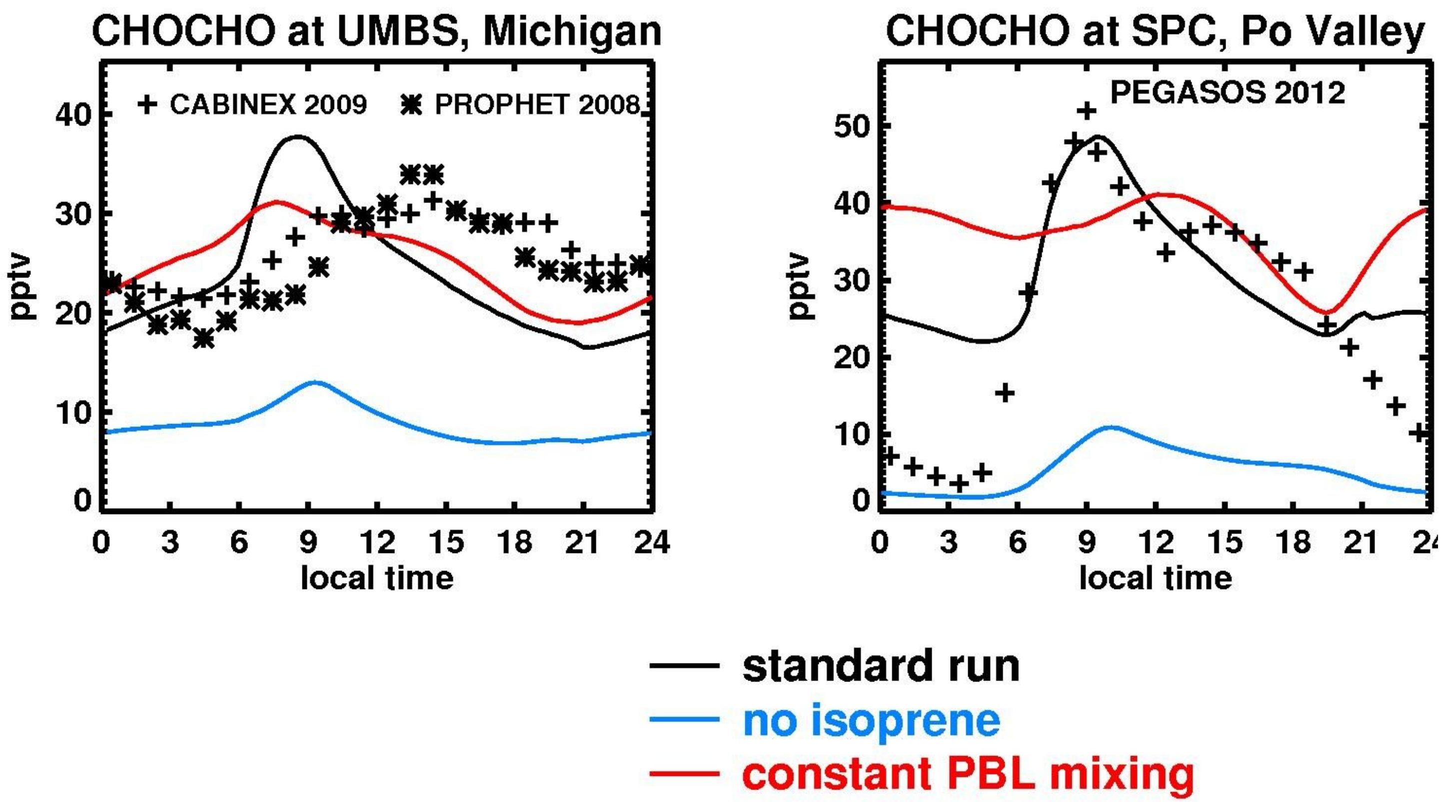


unrealistic **morning peak**

CH_2O data : FI-LIF (U.Wisconsin)
CHOCHO : LIP (U.Wisconsin)

(Data courtesy of F. Keutsch)

Glyoxal morning peak: is it real?



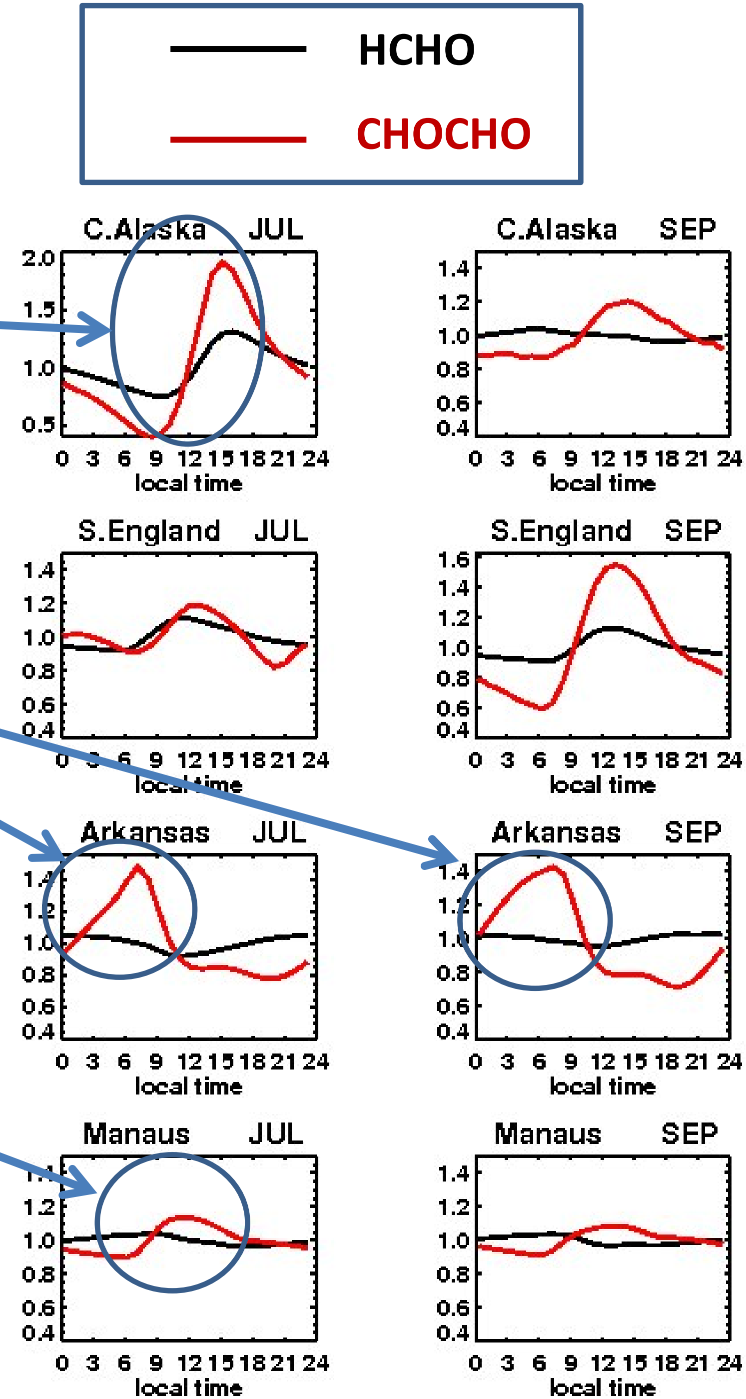
CHOCHO data: LIP (U. Wisconsin)
(data courtesy of F. Keutsch)

Modelled diurnal cycles of HCHO and CHOCHO columns

biomass burning area:
stronger variation for CHOCHO
due to primary emission

morning peak in high-isoprene, « high NOx » areas…

…but not in high-isoprene, low-NOx areas

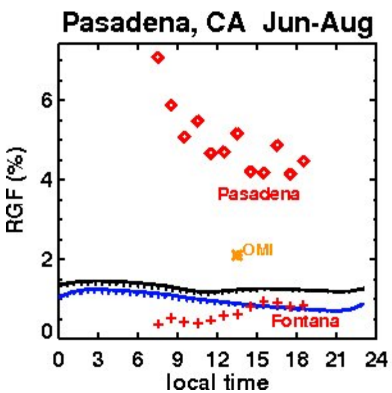


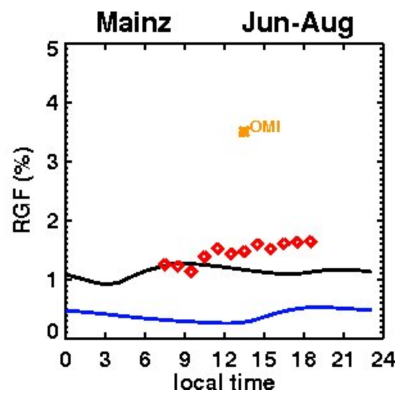
role of ISOP + NO_3 ?!

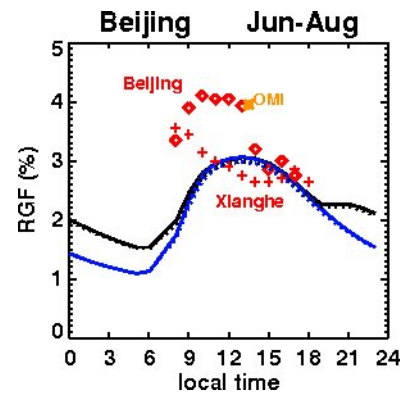
Comparison with MAX-DOAS data for RGF = CHOCHO/HCHO

(data from Ortega et al. & Hendrick et al.)

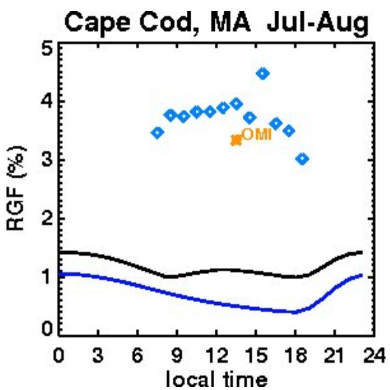
Urban

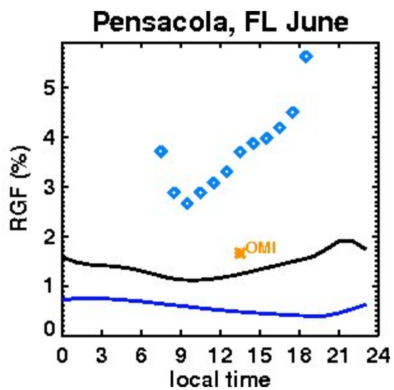






Coastal

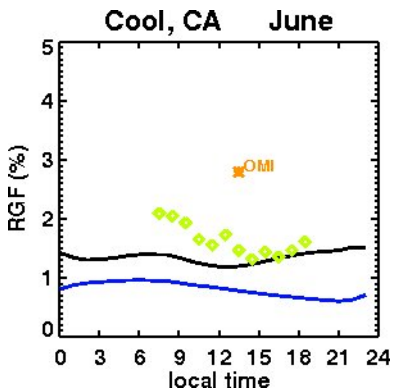


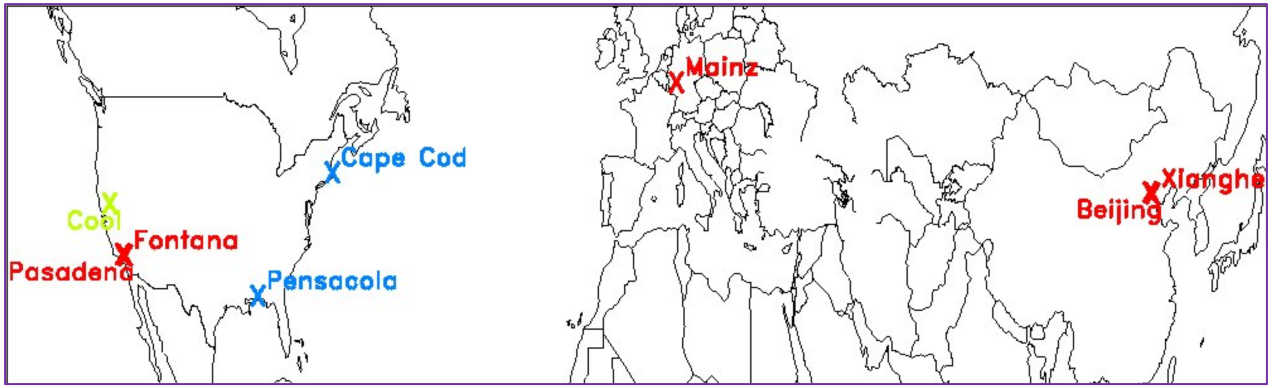


standard run

no isoprene

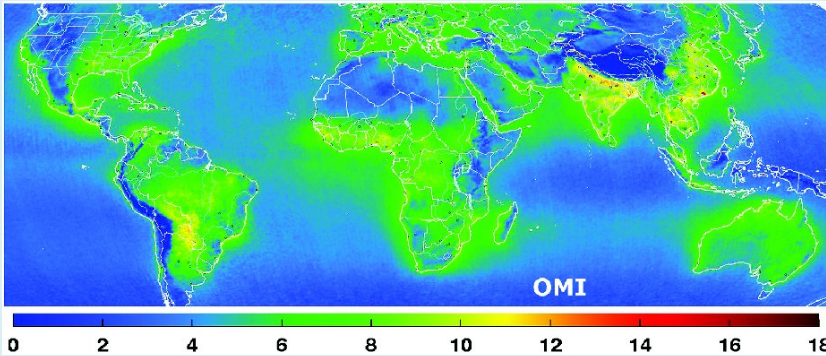
Rural





RGF : model vs. OMI data

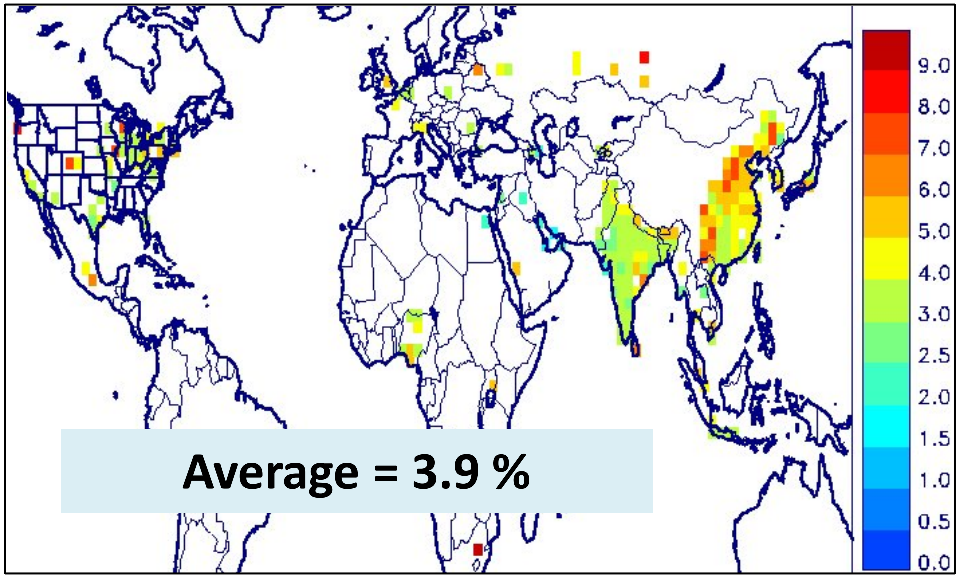
- IMAGESv2
  - anthropogenic VOC emissions: RETRO + REASv2 ; aromatic emissions x 4 over China
  - isoprene and biomass burning emissions : optimized using OMI CH_2O column data (e.g. Stavrakou et al. ACPD 2015)
- OMI CH_2O : De Smedt et al. 2015



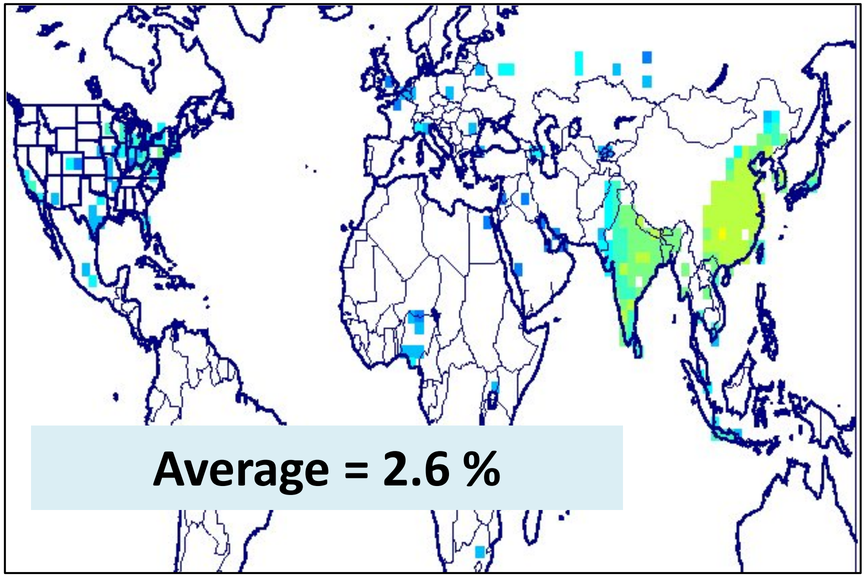
- Simulations:
  - STANDARD : standard mechanism, Andreae &Merlet EFs
  - AKAGI : Akagi et al. emission factors for biomass burning
  - MAXGLY : maximization of glyoxal yield from isoprene

WHERE ANTHROPOGENIC EMISSIONS ARE LARGELY DOMINANT:

OMI RGF



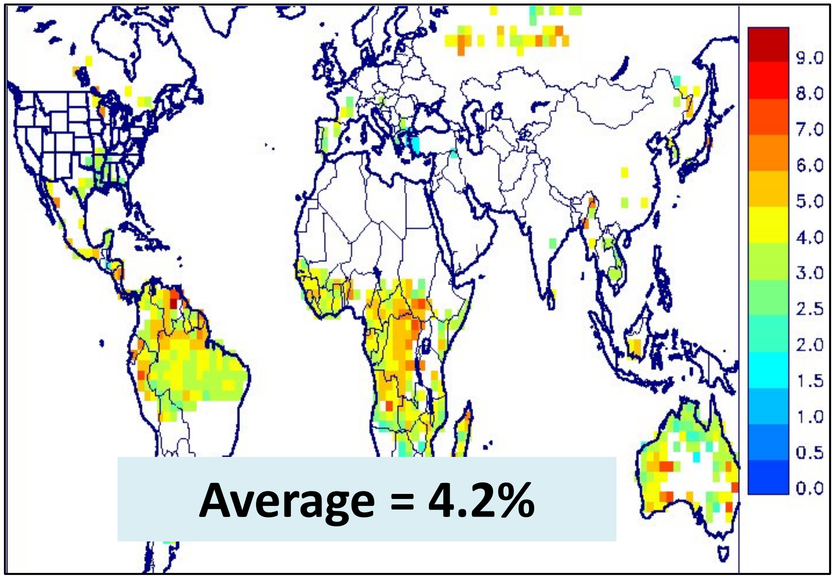
IMAGESv2 RGF



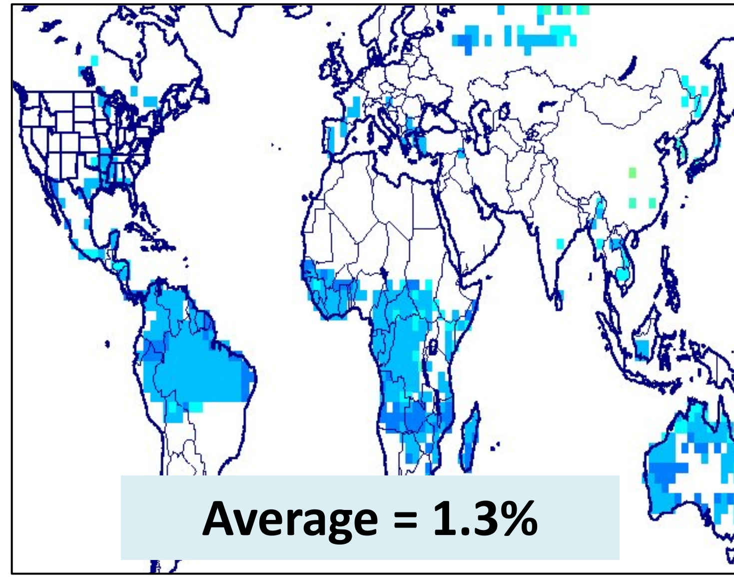
discrepancy largest over Europe and U.S.

WHERE ISOPRENE IS LARGELY DOMINANT :

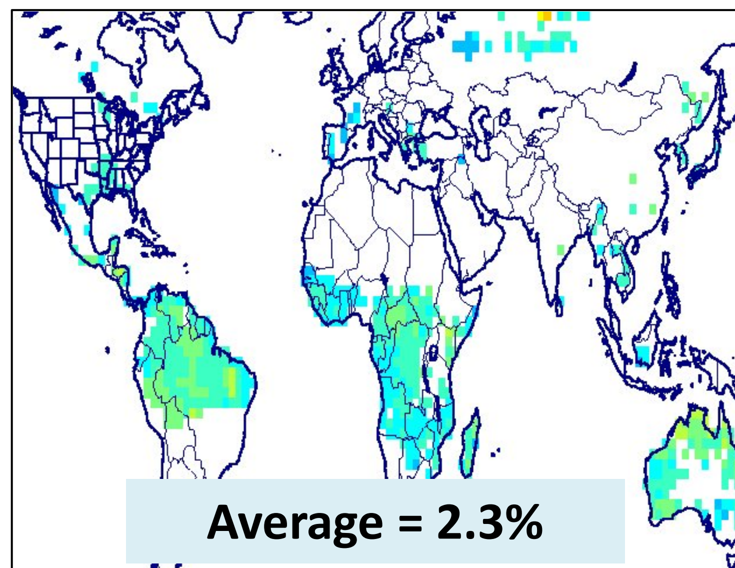
OMI RGF



STANDARD



MAXGLY



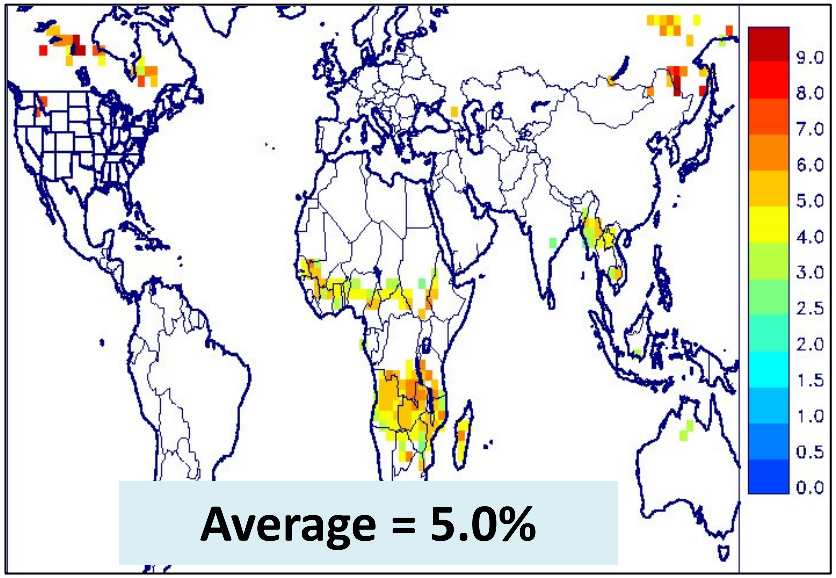
OMI : RGF largest in remote (low-NOx) areas (4.3 vs 3.8%)

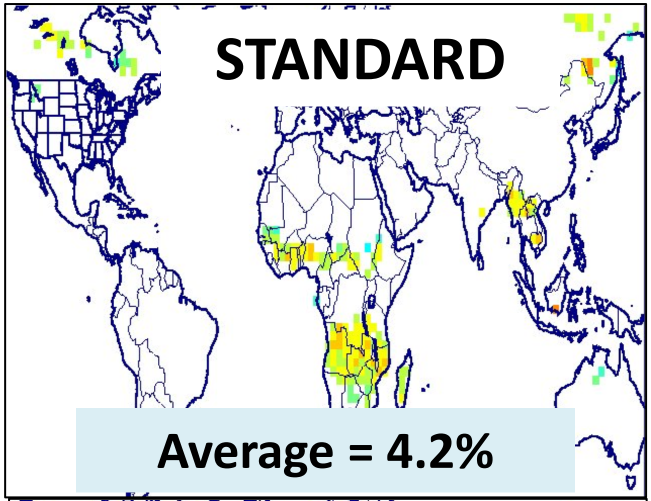
STD: RGF largest in high-NOx areas (1.62 vs 1.25)

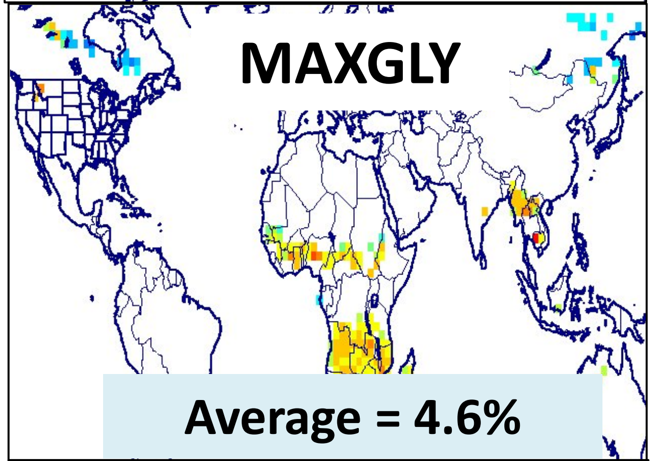
MAXGLY : no clear NOx dependence

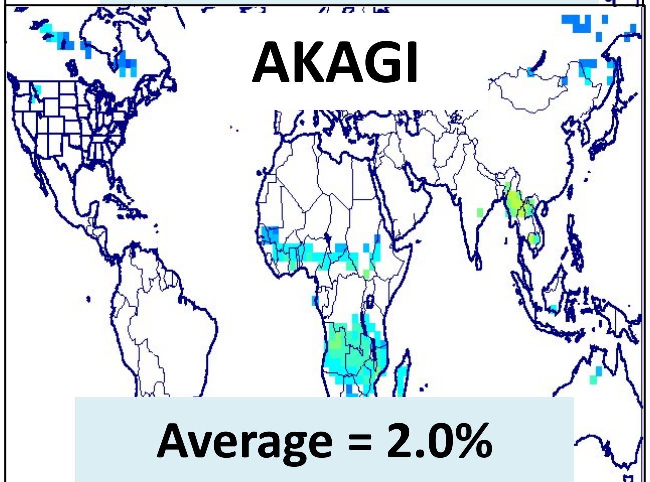
WHERE BIOMASS BURNING IS LARGELY DOMINANT :

OMI RGF









good agreement in most areas **when including primary CHOCHO emissions** (Andreae&Merlet)

CONCLUSIONS

Still many mysteries associated to that compound… but:

- RGF *not* an unambiguous indicator for the origin (biogenic or anthropogenic or pyrogenic) of glyoxal
- OMI data suggest missing sources of glyoxal (both biogenic and anthropogenic), probably not from isoprene
- In situ data also points to (smaller) model underestimations
- NOx-dependence of RGF ➔ ISOP + NO_3 is probably too large a source of glyoxal in the model ➔need to revisit the oxidation mechanism
- Vertical profile issue (SENEX, also TORERO) ➔ glyoxal source in FT (?) ➔ aerosol heterogeneous oxidation best candidate for missing VOC?
- Primary glyoxal emission from fires well supported by OMI data