Addressing the role of major chemical uncertainties on top-down NOx and VOC emission estimates

PRESCRIBE WORKSHOP

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- Inverse modeling adjusts emission fluxes in a model to match the observations – Main assumption : Uncertainties in bottom-up emissions larger than uncertainties in the data and in the model
- Recent studies point to flaws in the current mechanisms regarding the representation of NOx and VOC chemistry in models ☹

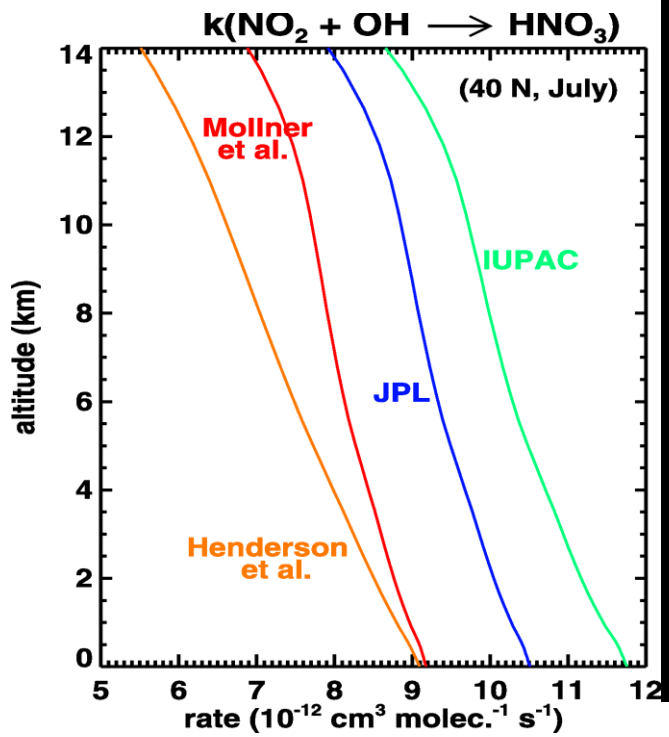
QUESTIONS THAT WE ADDRESS :

- Sinks of tropospheric NOx : how well are they known?
- How are affected top-down NOx emissions based on satellite NO_2 retrievals?
- Can independent data help to reduce the overall uncertainty?
- How well OH radicals are represented in models?
- Oxidation of isoprene : what are the latest developments?
- What is the impact of OH recycling on top-down VOC estimates ?
- Other uncertainties?

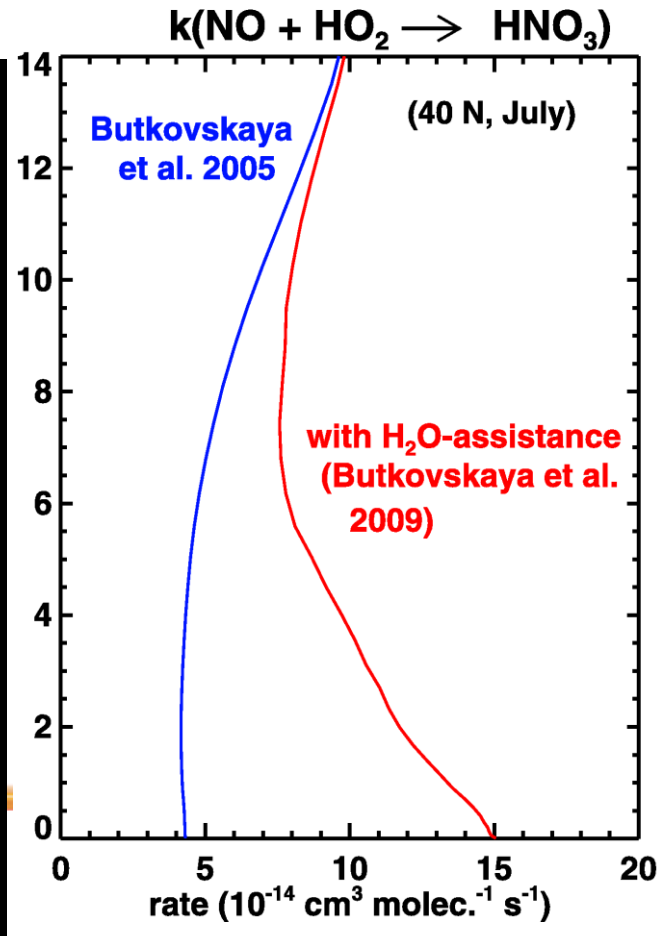
Sinks of tropospheric NOx : how well are they known?

THE MAIN NOx SINK:
$NO_2 + OH \rightarrow HNO_3$

A POTENTIALLY IMPORTANT SINK:
$NO + HO_2 \rightarrow HNO_3$



- Minor channel (≤0.5% in dry conditions), but faster with $HO_2 \cdot H_2O$ complex (Butkovskaya et al., 2005, 2009)
- x2-3 increase of *k* below 4 km



THE DOMINANT NIGHTTIME NOx SINK : N_2O_5 +H_2O ON AQUEOUS AEROSOLS

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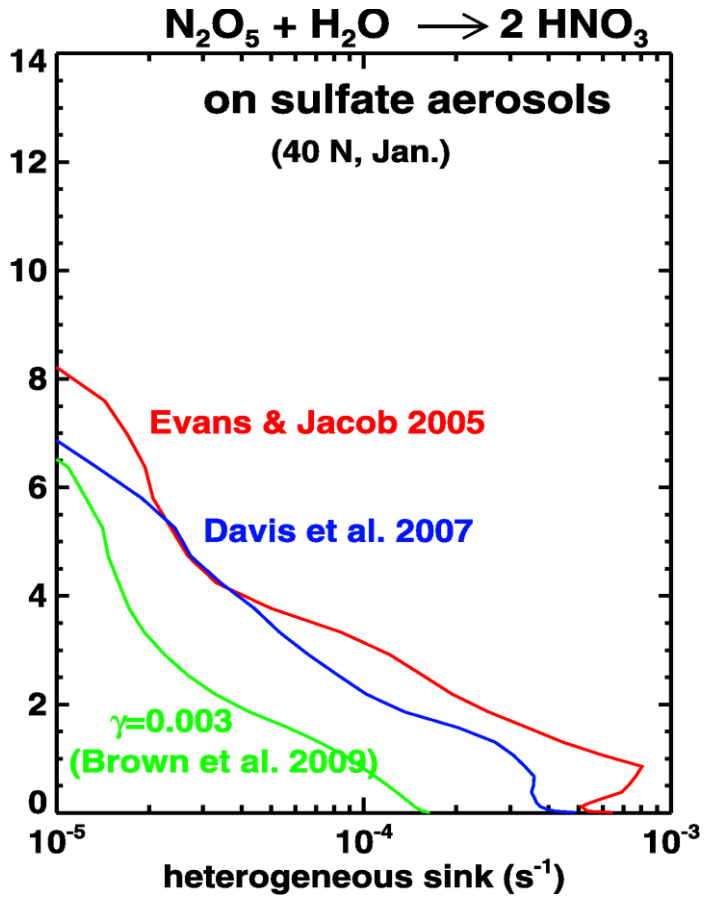


OTHER SINKS

-
-
-
-

→ 18% of global NOx sink

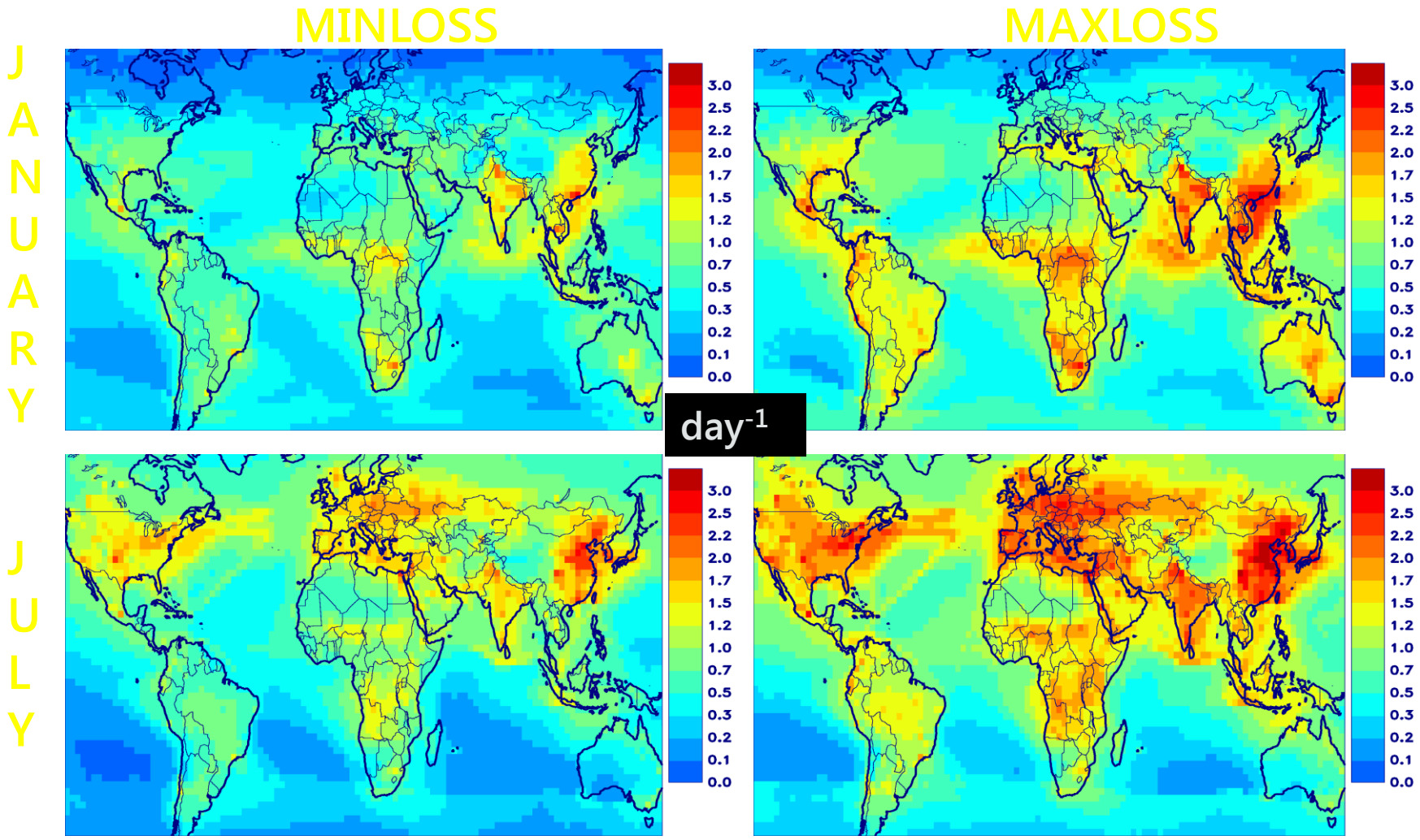
BETWEEN TWO REALISTIC SCENARIOS

	MINIMUM LOSS	MAXIMUM LOSS
NO_2+OH	Henderson et al. (2012)	Sander et al. (2011)
NO+HO_2→ HNO_3	Ignored	Butkovskaya et al. (2009)
γ_{N2O5}	Brown et al. (2009)	Davis et al. (2008)
Isoprene chemistry	MIM2 (Taraborrelli et al. 2009)	MIM2+ (Lelieveld et al. 2008)

MODELING TOOL : IMAGESv2 GLOBAL CTM

- & seasonal variations considered for all emission categories

NO_x SINK RATES



- ✓ Spectacular increase in the loss rate over tropical regions mostly due to $NO+HO_2 \rightarrow HNO_3$
- ✓ In mid-latitudes the loss is more important in July due to radiation
- ✓ The major sink is NO_2+OH → distributions reflect boundary layer OH

How are affected top-down NOx emissions based on satellite NO_2 retrievals?

- (DOMINO v2.0, www.temis.nl)
-

SEARCH FOR EMISSION PARAMETERS THAT MINIMIZE THE COST FUNCTION

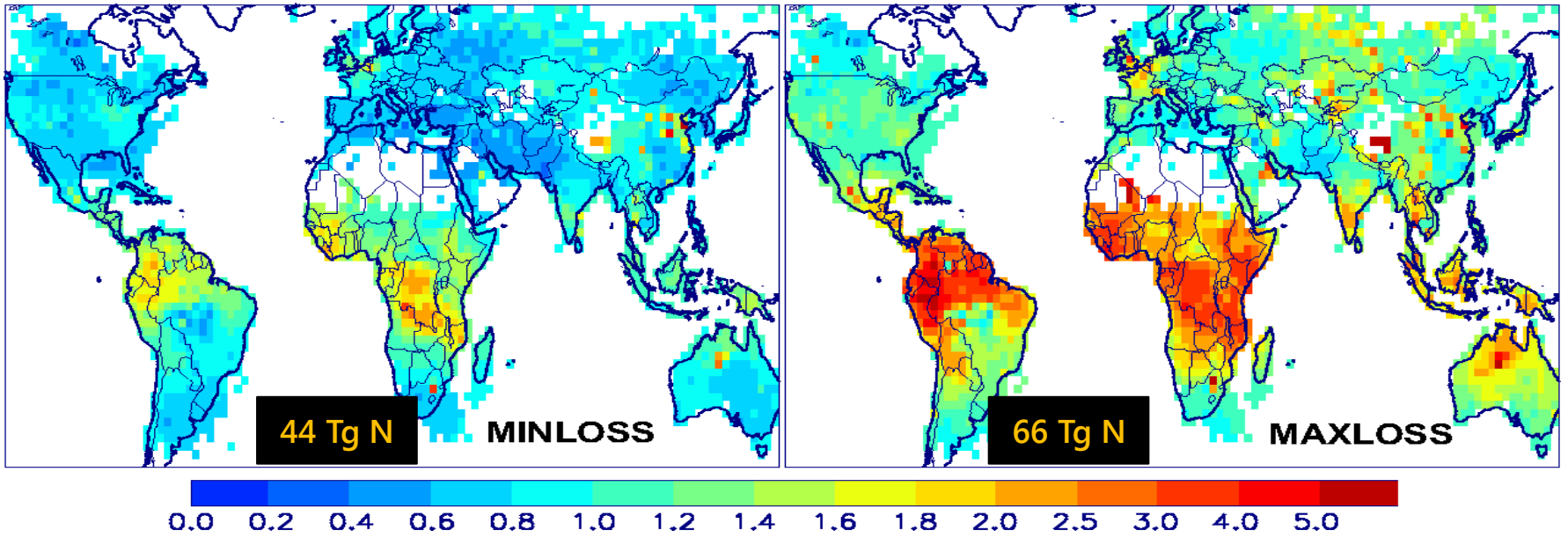
$$J(f)=\tfrac{1}{2}\Sigma_i\,(H_i(f)-y_i)^T\,E^{-1}(H_i(f)-y_i)+\tfrac{1}{2}\,(f-f_B)^T B^{-1}(f-f_B)$$

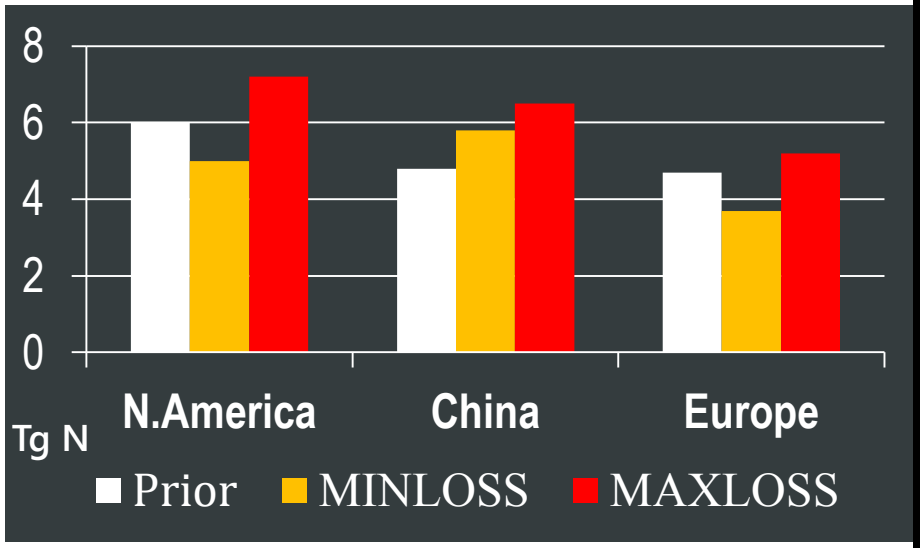
- f: control variables vector
- $H_i(f)$: model operator
- y_i: observations
- E: error covariance matrix of f's and observations
- f_B: 1st guess values of the control variables

Solve using the adjoint model technique (Stavrakou et al. 2006, 2008,2009)

✓ **Perform inversion at 2°x2.5° for 2007**

NOx ANNUAL EMISSION UPDATES IN 2007

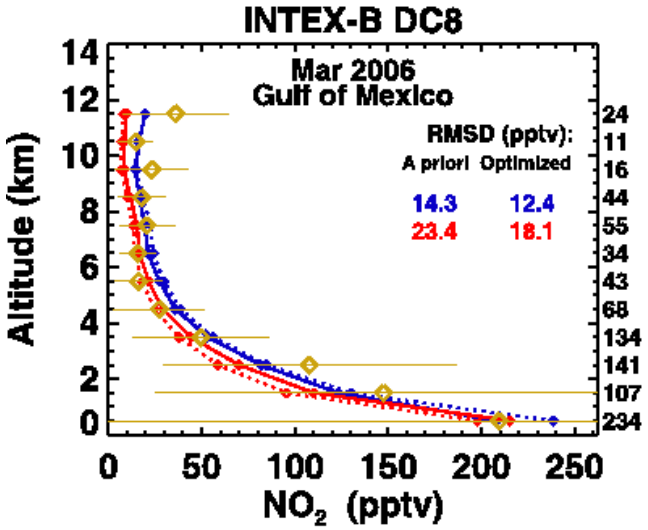


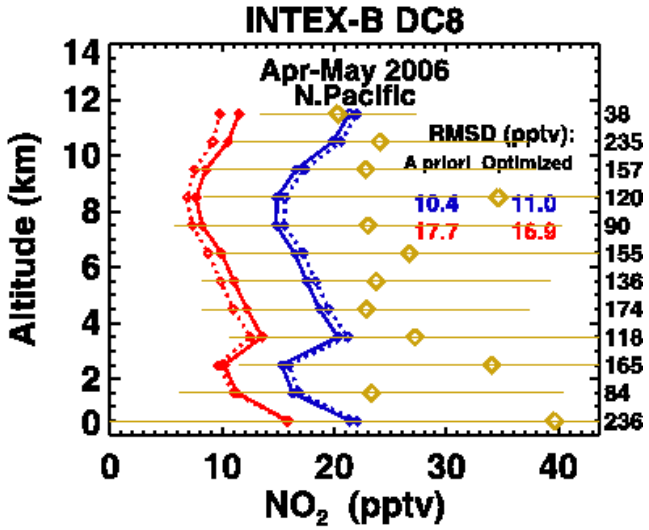


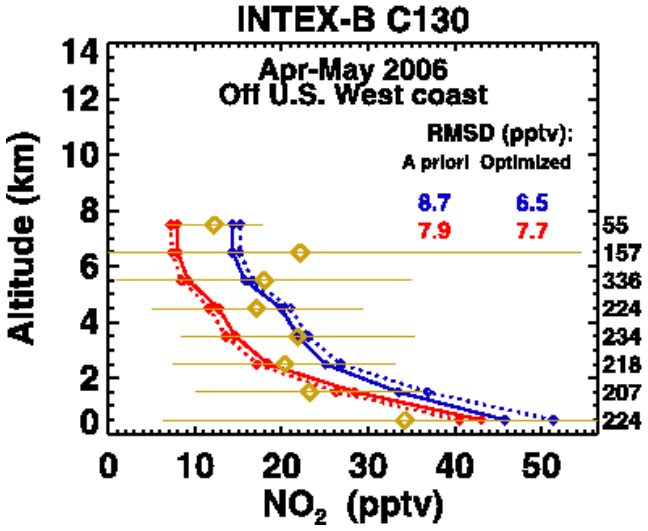
- ✓ **Major differences : 50% higher emission in MAXLOSS**
- ✓ Largest discrepancies in natural emissions
- ✓ Significant differences also in anthropogenic emissions, estimates in China consistently higher than the a priori
- ✓ MAXLOSS : 1/5 of NOx source is removed via $NO+HO_2 \rightarrow HNO_3$

Can independent data help to reduce the overall uncertainty?

1 → COMPARISON TO AIRBORNE MEASUREMENTS







A priori model, MINLOSS

A priori model, MAXLOSS

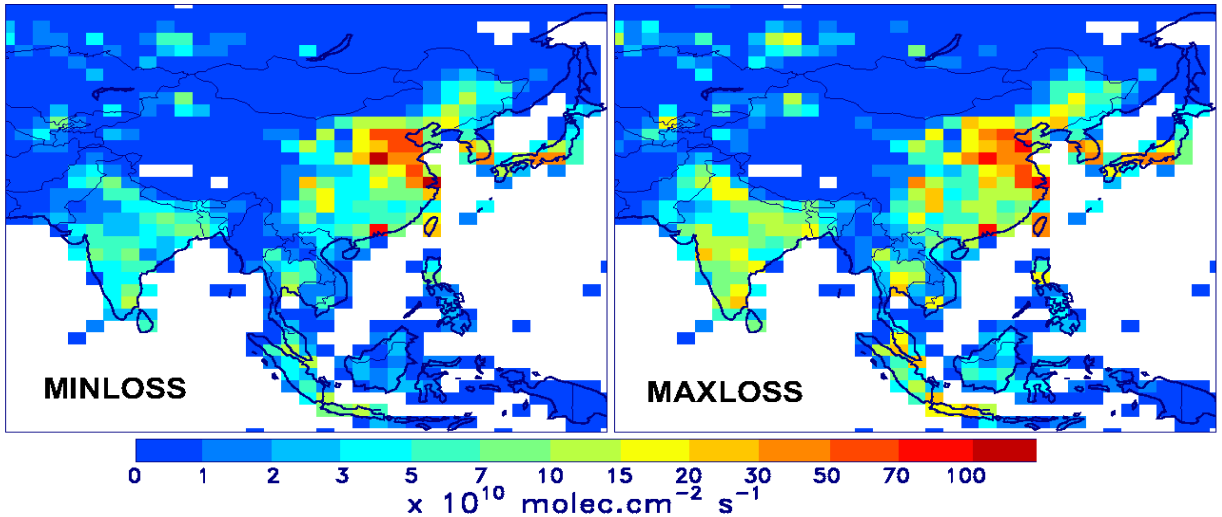
Optimized model, MINLOSS

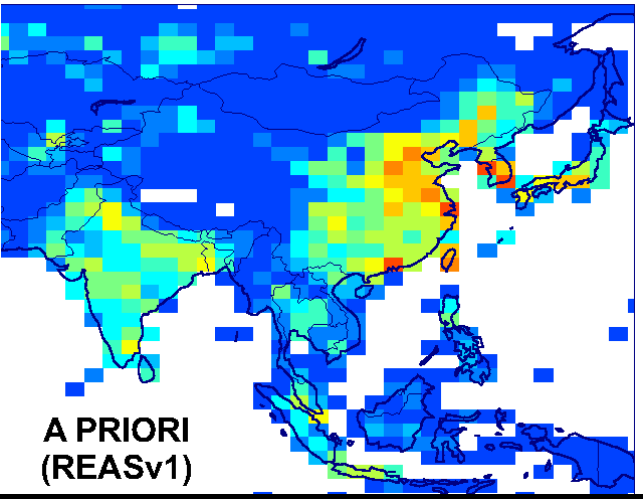
Optimized model, MAXLOSS

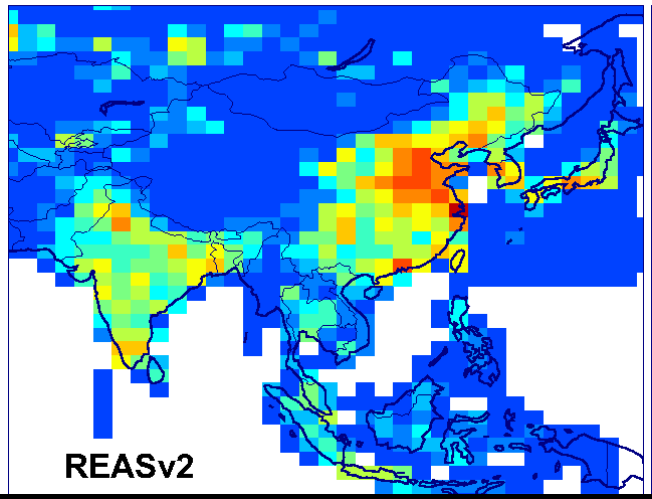
NO_2 measurements, adjusted for MPN & HNO_4 interferences following Browne et al., 2011

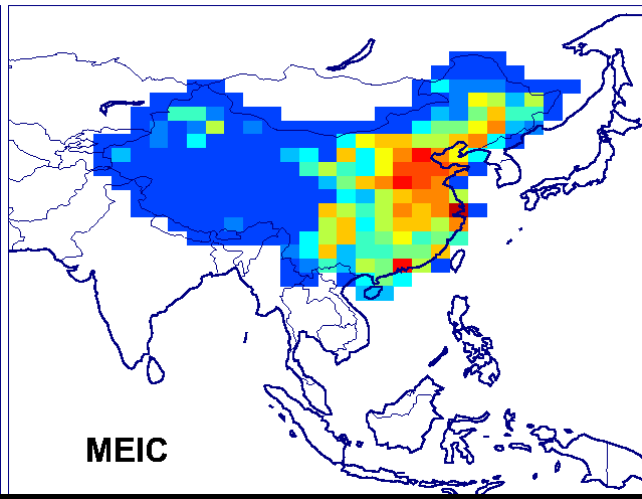
- ✓ MINLOSS provides a better match with observations both over land and ocean

2 → COMPARISON TO REASV2 AND MEIC INVENTORIES

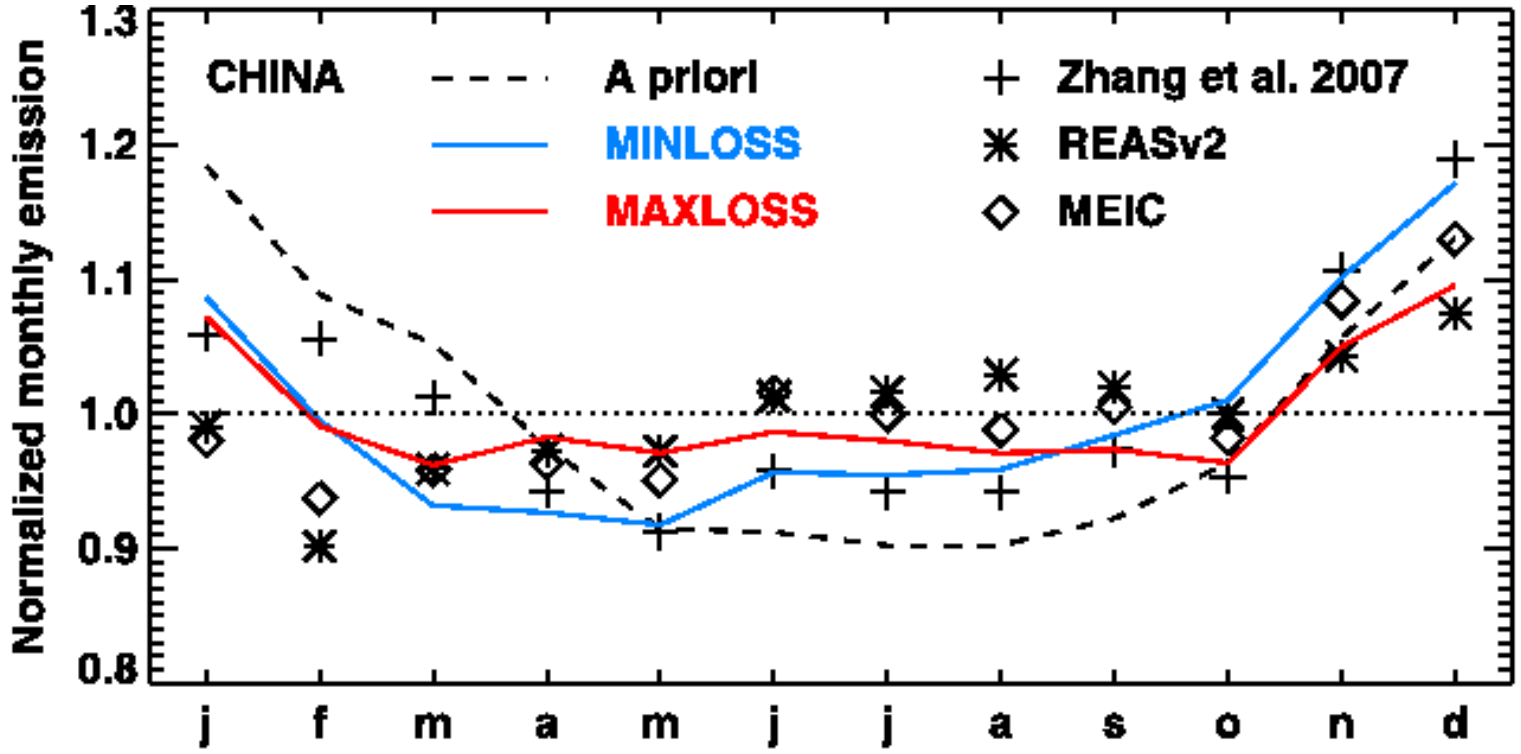




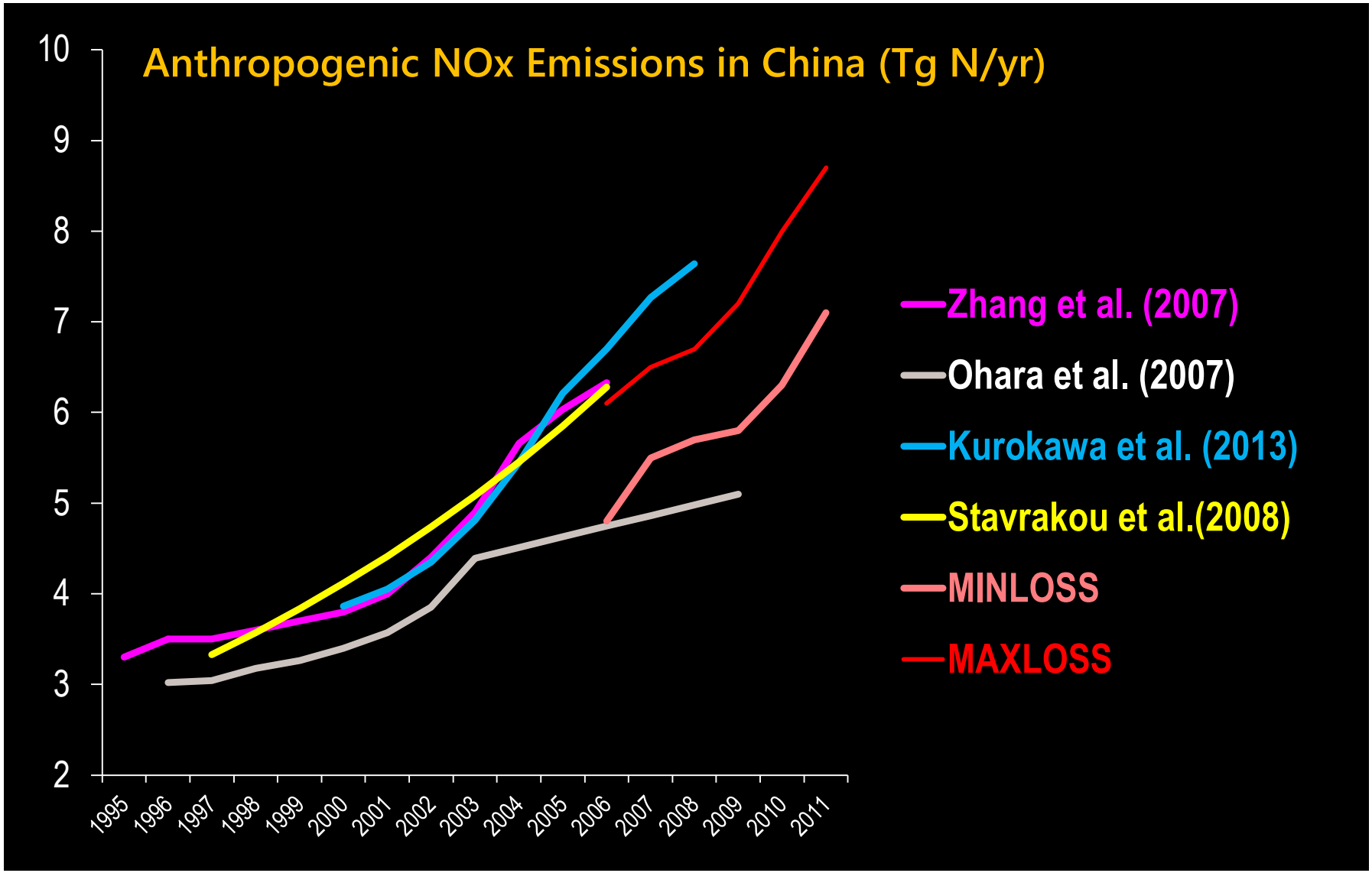




- ✓ MAXLOSS realizes the best match with both inventories
- ✓ Total emission is underestimated by both inversions
- ✓ Correlation is higher for MAXLOSS (0.90-0.92), 0.85-0.88 for MINLOSS
- ✓ REASv2 : 7.2 Tg N, MEIC : 7.6 Tg N, MAXLOSS : 6.5 Tg N, MINLOSS : 5.8 Tg N



- Both inversions modify the seasonality of anthropogenic emissions
- MAXLOSS seasonality is in remarkably good agreement with the recent bottom-up inventories
- The a priori seasonality – too high in late winter, too low in summer – is not supported by OMI observations


Anthropogenic NOx Emissions in China (Tg N/yr)
10
9
8
7
6
5
4
3
2
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
Zhang et al. (2007)
Ohara et al. (2007)
Kurokawa et al. (2013)
Stavrakou et al.(2008)
MINLOSS
MAXLOSS

- Support from comparisons with independent data, but evidence favoring one or the other assumption is still partial

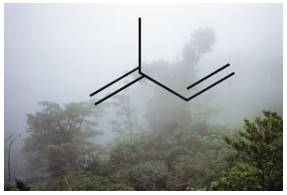
- Neither scenario improves the agreement with ALL independent datasets

- Comparisons to SCIAMACHY and aircraft measurements point to MINLOSS as the most likely, BUT opposite conclusions are drawn from top-down estimates in China

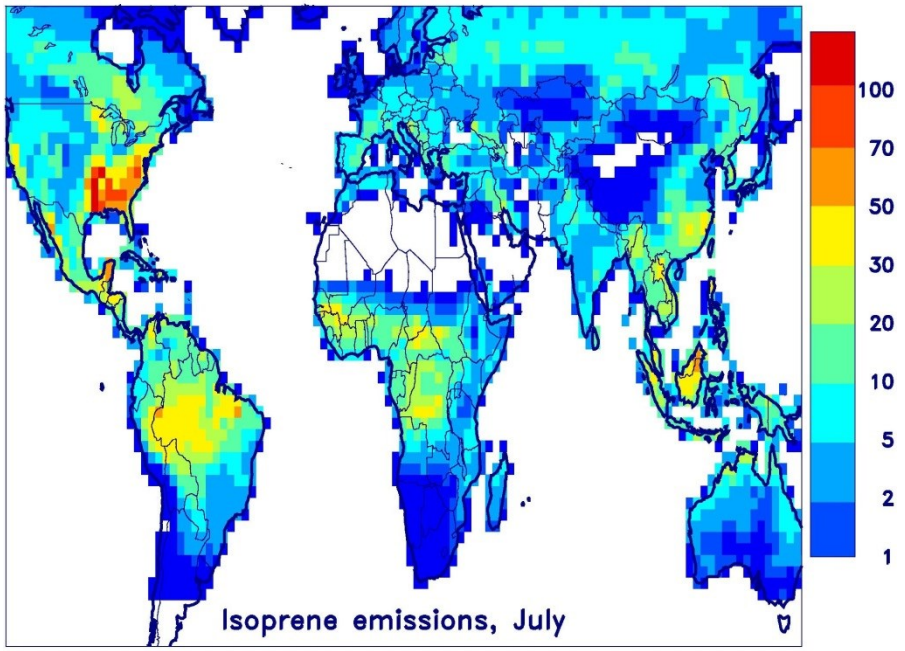
- Ideas? Organic nitrate formation dominates instantaneous NOx sink in rural sites, underestimated OH levels in large Chinese cities, HONO formation → unknown mechanisms !

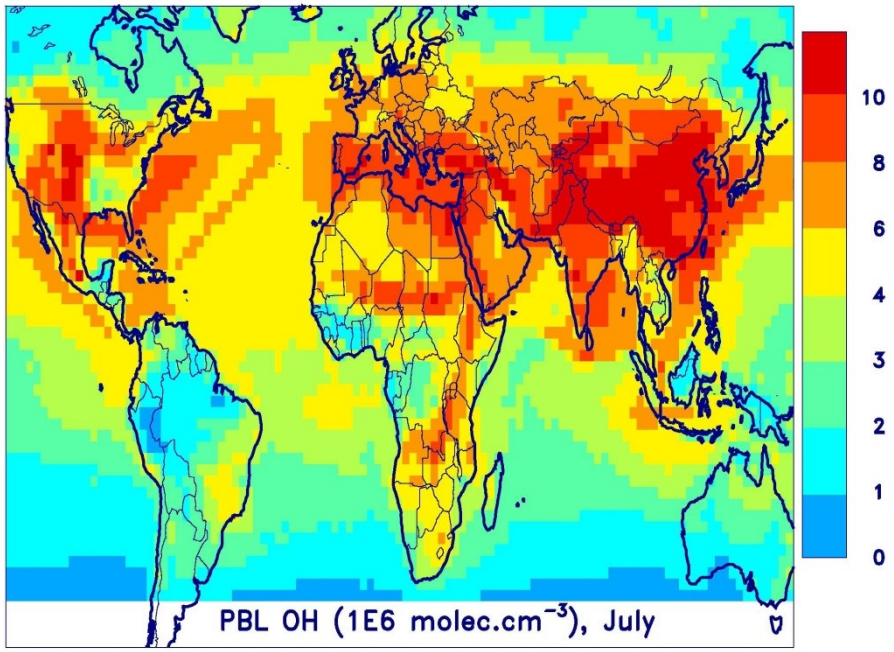
Stavrakou, T. et al., Atmos. Chem. Phys. Discuss., 2013

How well OH radicals are represented in models?



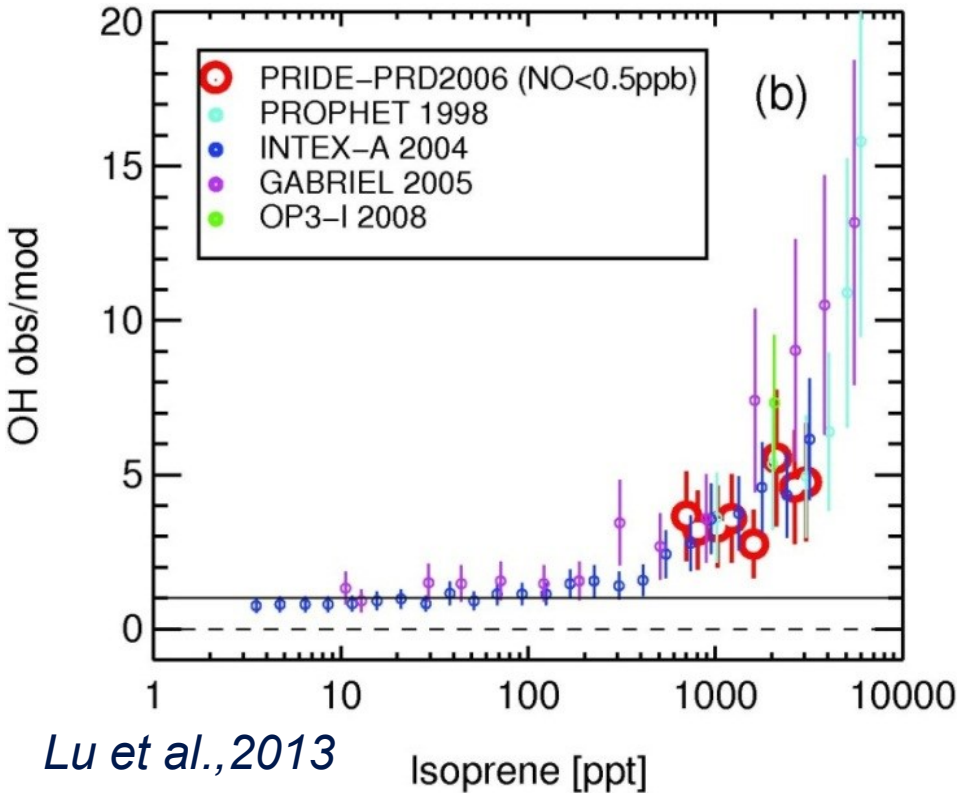
Traditional view : Isoprene depletes OH, especially at remote (low-NOx) locations and decreases the oxidizing capacity of the atmosphere



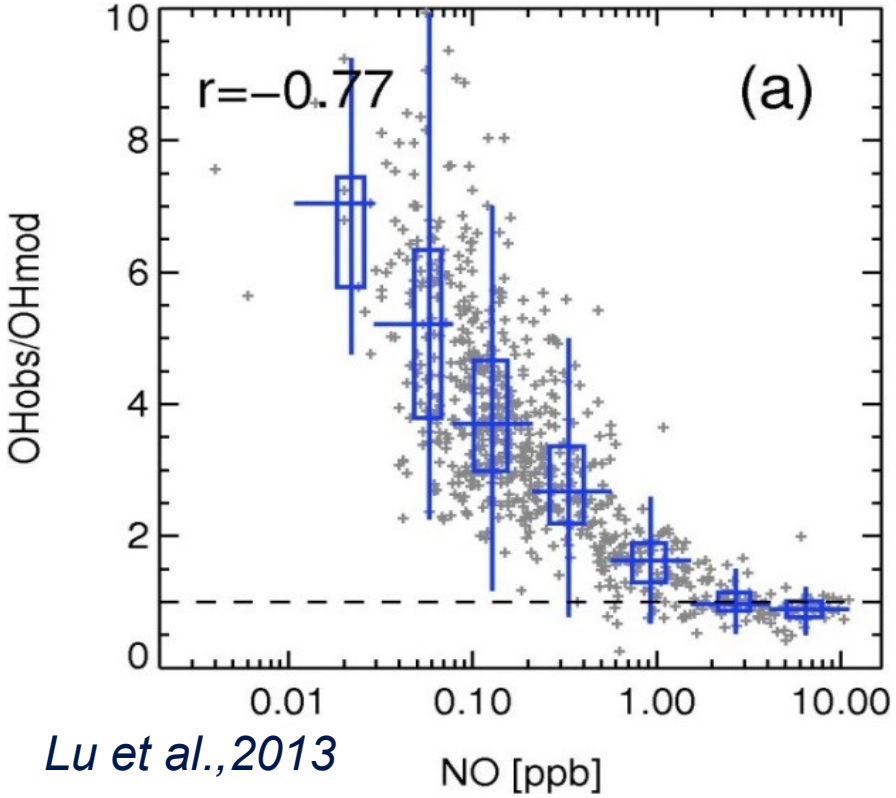


- BUT observations show that OH is severely underestimated by CTMs

Modelled and observed OH



Lu et al.,2013



Lu et al.,2013

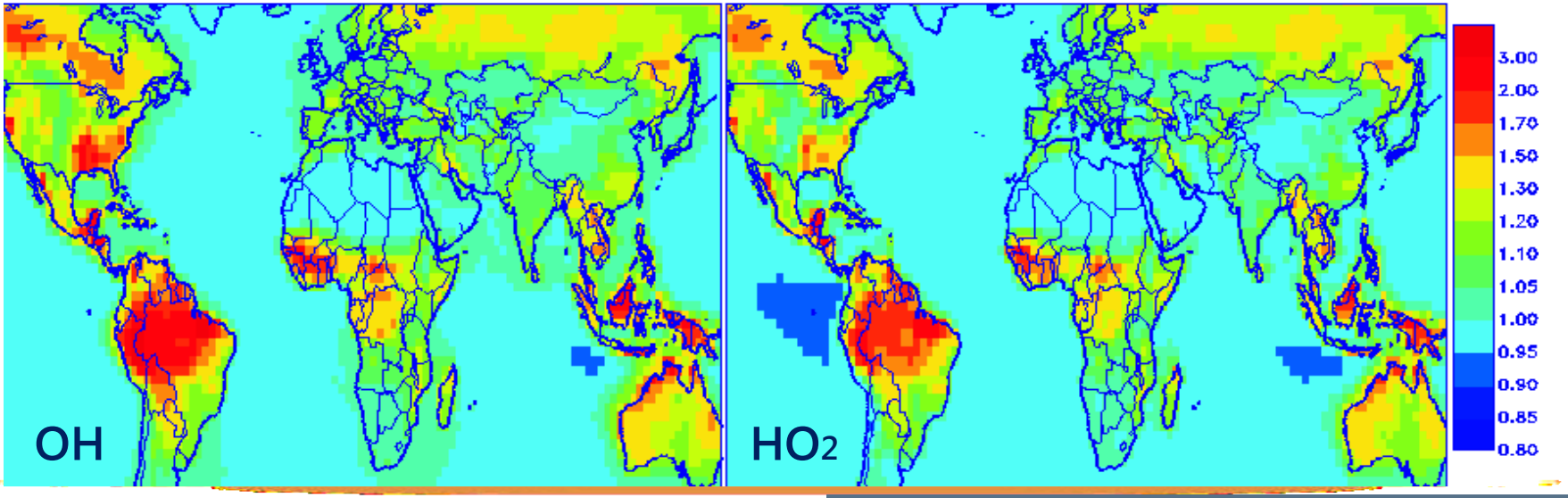
- Model underprediction increases for increasing isoprene concentrations and decreasing NO levels
- Isoprene oxidation recycles much more OH than predicted by current oxidation mechanisms, especially at low/moderate NOx

Enhance OH formation in isoprene oxidation? Recycling !

Leuven

Isoprene Mechanism" (LIM0)

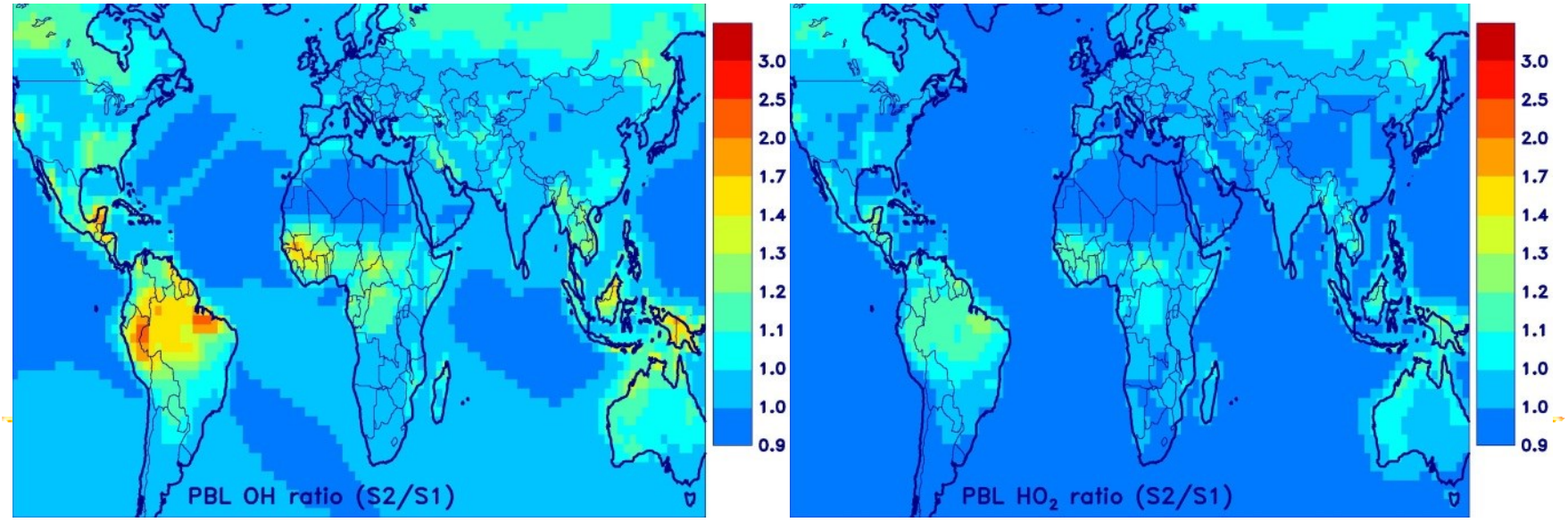
- Fast isomerisation of the Z-δ-OH-hydroxy-isoprenyl-peroxy radicals by 1,6-H shift, yielding hydroperoxy-methyl-butenals, "HPALDs" which photolyse rapidly to yield several OH (Peeters and Muller, 2010)
- Implemented LIM0 in IMAGESv2 CTM (Stavrakou et al. 2010)



Lelieveld et al., Nature, 2008
Peeters et al., Phys. Chem. Chem. Phys., 2009
Peeters, J., and J.-F. Müller, Phys. Chem. Chem. Phys., 2010
Stavrakou, T., J. Peeters, and J.-F. Müller,, Atmos. Chem. Phys., 2010

Oxidation of isoprene : what are the latest developments?

- LIM0 was upgraded in light of theoretical findings & recent literature → *LIM1* (Peeters et al. in preparation)
- Compared to LIM0 :
  - lower isomerisation yield but secondary chemistry generates more OH, while keeping [HO2] down
  - Several mechanisms and crucial rates remain uncertain, require refined theoretical quantifications and/or experimental verification



What is the impact of OH recycling on top-down VOC estimates ?

-
-
  -

Impact of OH uncertainty on the HCHO columns & top-down estimates

- Tropospheric HCHO columns from GOME-2 (De Smedt et al. 2012, http://h2co.aeronomie.be)
- Monthly averaged columns accounting for the sampling times of observations at each location
- 2 global-scale inversions either using MIM2+ mechanism, or LIM1 *(preliminary!)*

HCHO yield from isoprene : KPP box calculations

Isoprene mechanism	0.1 ppb NOx		1 ppb NOx	
Duration	*1 day*	*10 days*	*1 day*	*10 days*
MIM2+	1.6	2.1	2.5	2.5
LIM1	1.5	1.9	2.2	2.3

- MIM2+ yields are higher, low NOx : by 8% - 12%, high NOx : by 10%

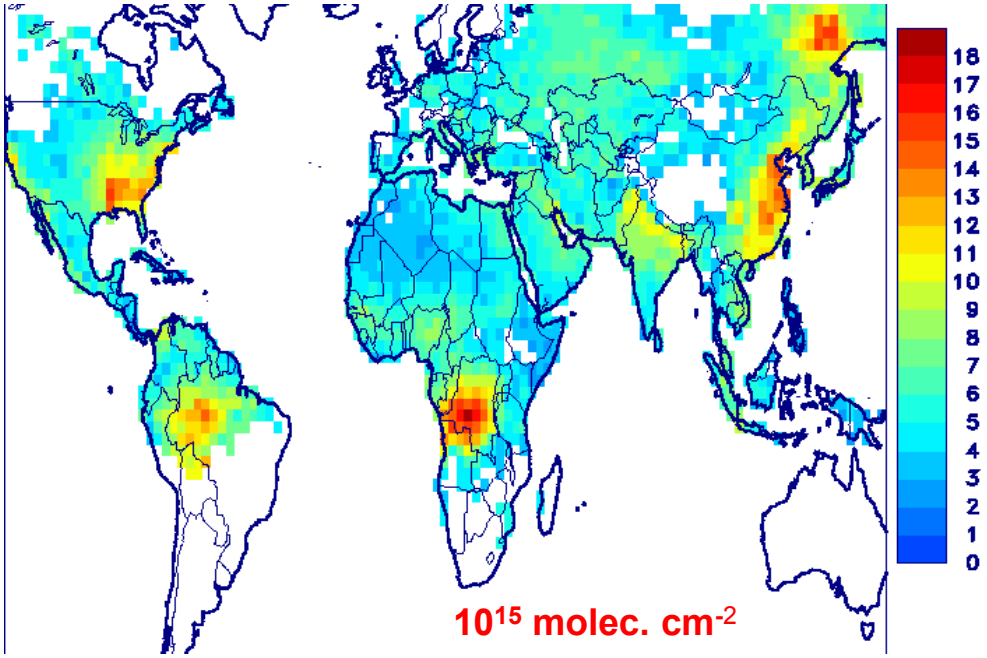
- Input in IMAGESv2 : REASv2, GFEDv3, MEGANv2011

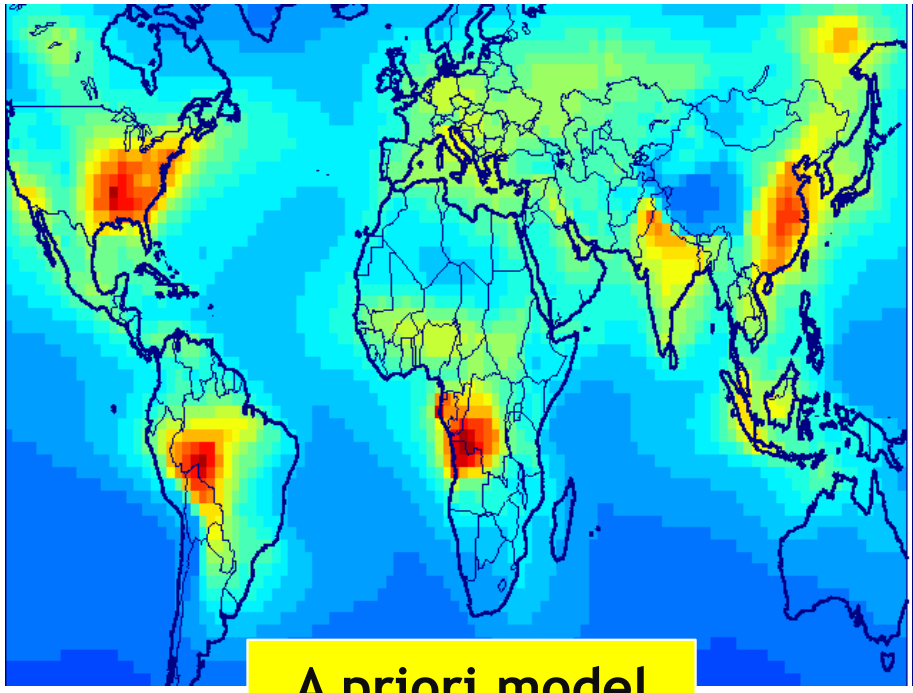
Biogenic JJA emissions (Tg)		
Inversion	MIM2+	LIM1
Global	66	70
China	3.8	4.1
N. America	11.1	12.4

- LIM1 inversion yields by 6% higher emissions globally, by 8% in China, by 12% in N. America

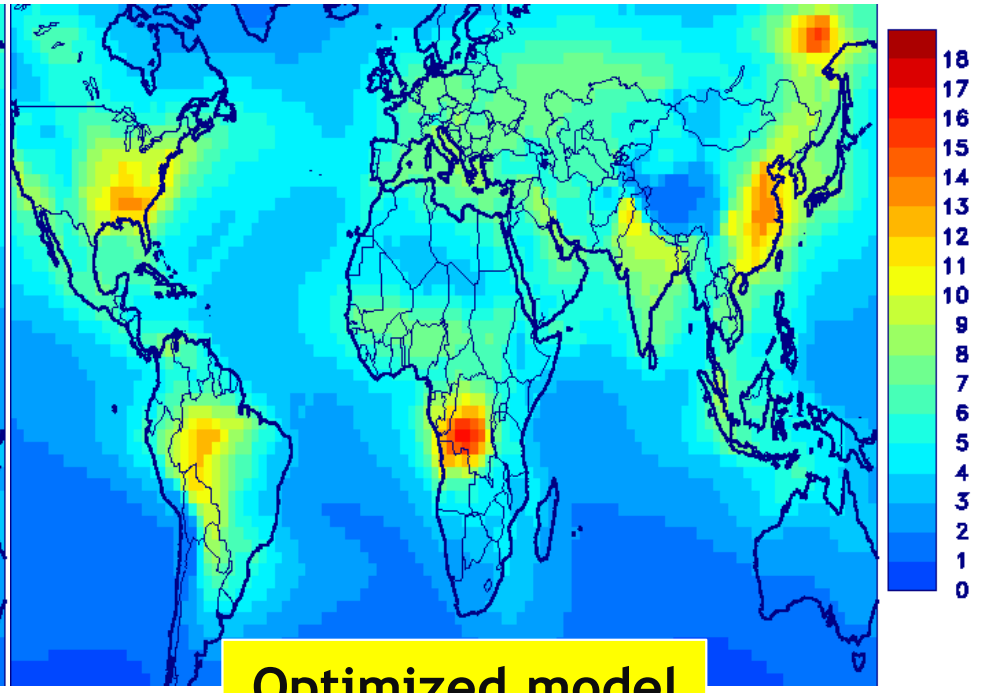
→ Not much difference!

GOME-2
HCHO
July
2008





A priori model



Optimized model

GOME-2

June

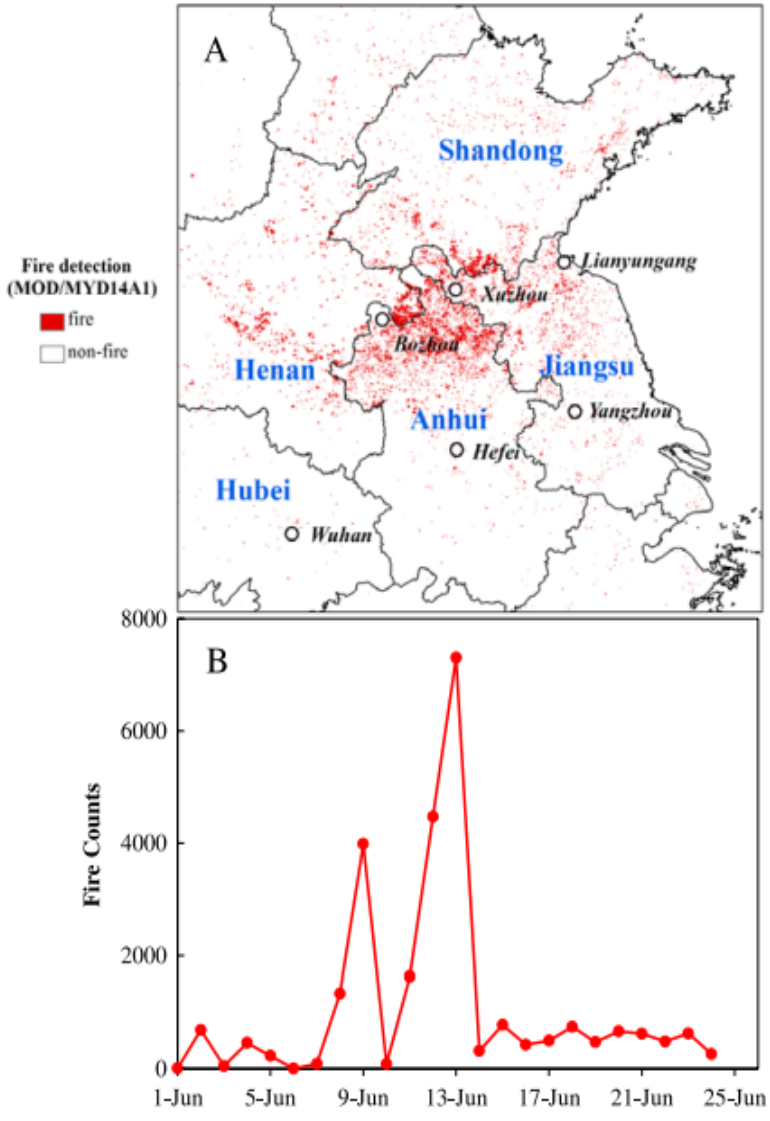
10^{15} molec. cm^{-2}

Prior

Optimized

18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0

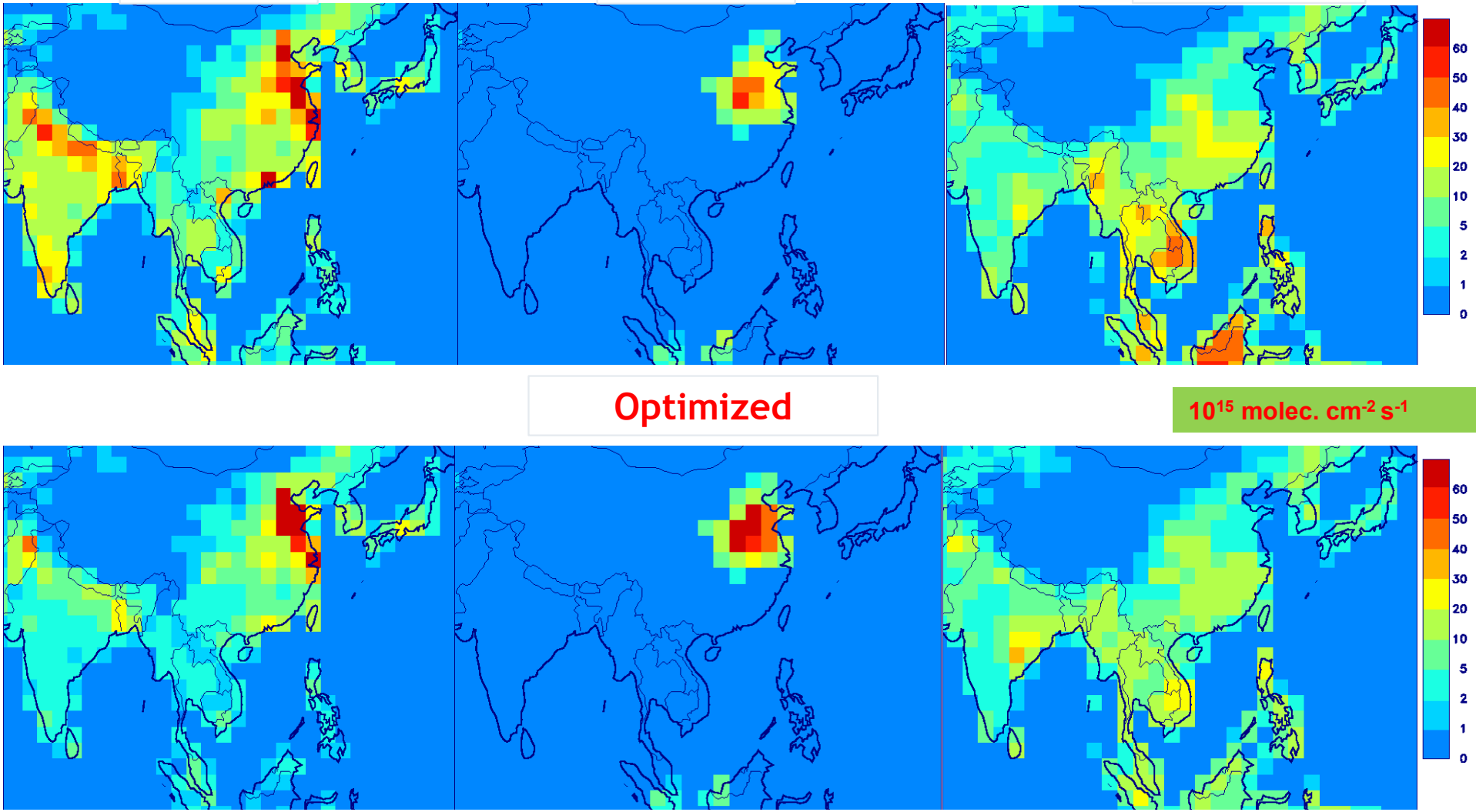
Other uncertainties?



Combine crop maps with harvest season burning from *Huang et al. (2012)*

June 2008

REASv2 | Fires | Isoprene



Optimized

10^{15} molec. cm^{-2} s^{-1}

- Doubling of anthrop. emissions in Beijing and surrounding provinces, strong decrease in South China, decreased isoprene in South China and Indonesia – in agreement with flux measurements in tropical rainforests

- June's harvest burning patterns explain a major part of the correlation in central and south China Plain, but cannot explain the high HCHO columns around Beijing region – other sources present? Correct a priori information is essential
- Inherent difficulty to infer anthropogenic VOCs from HCHO inversion : thousands of VOCs with different reactivities → Chemistry matters!
- Effort to improve the a priori model (sources-chemistry, etc.) – inversions cannot repair missing or misrepresented sources/processes

THANK YOU FOR YOUR ATTENTION

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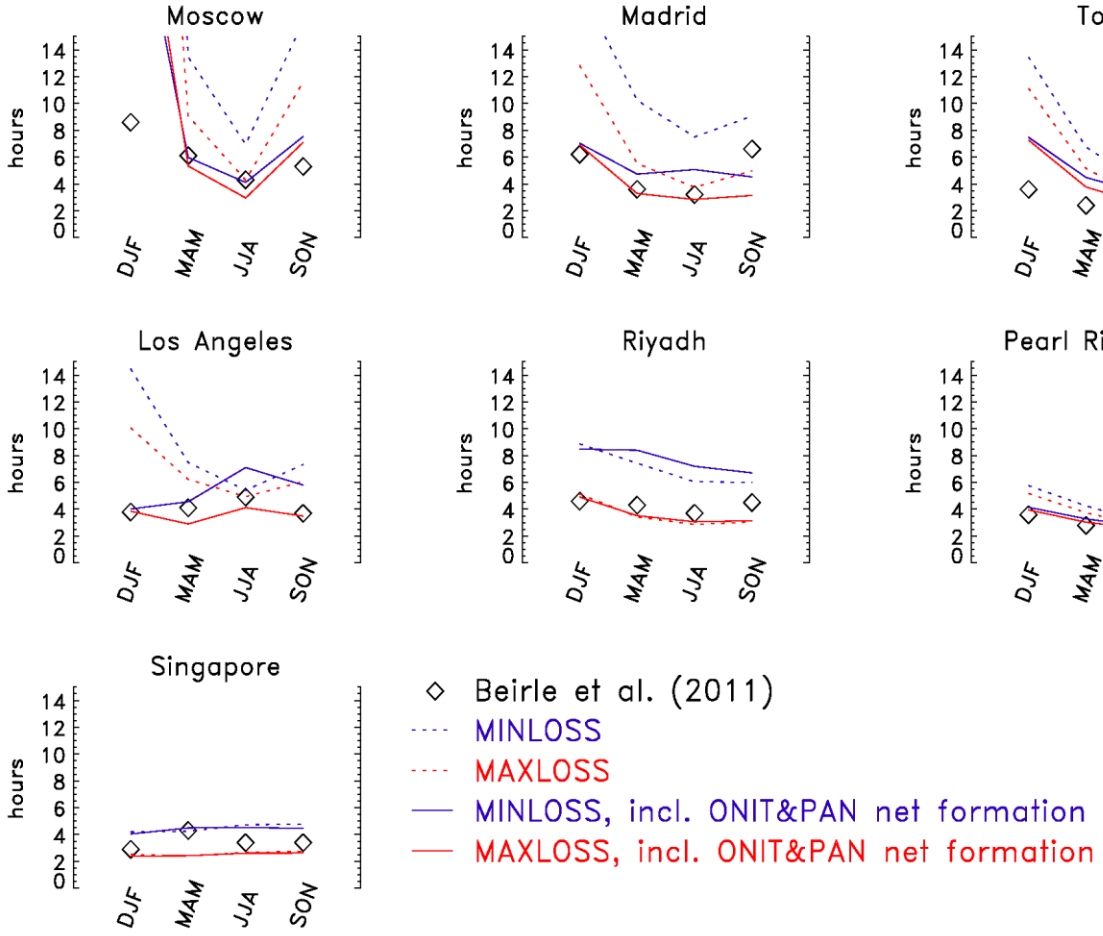
SPARE SLIDES

NO_X DAYTIME LIFETIMES OVER MEGACITIES



- ✓ Calculate the lifetime : (1) ONIT&PAN are not a NOx sink (dotted lines) , (2) ONIT&PAN are formed in the grid cell & exported (solid lines)
- ✓ Very satisfactory agreement for most of the cities, but discrepancy for Moscow in winter, to a lesser extent for Tokyo