Evaluation of Gaseous Pollutants and Source-receptor Relationships for Reactive Nitrogen Deposition in East Asia

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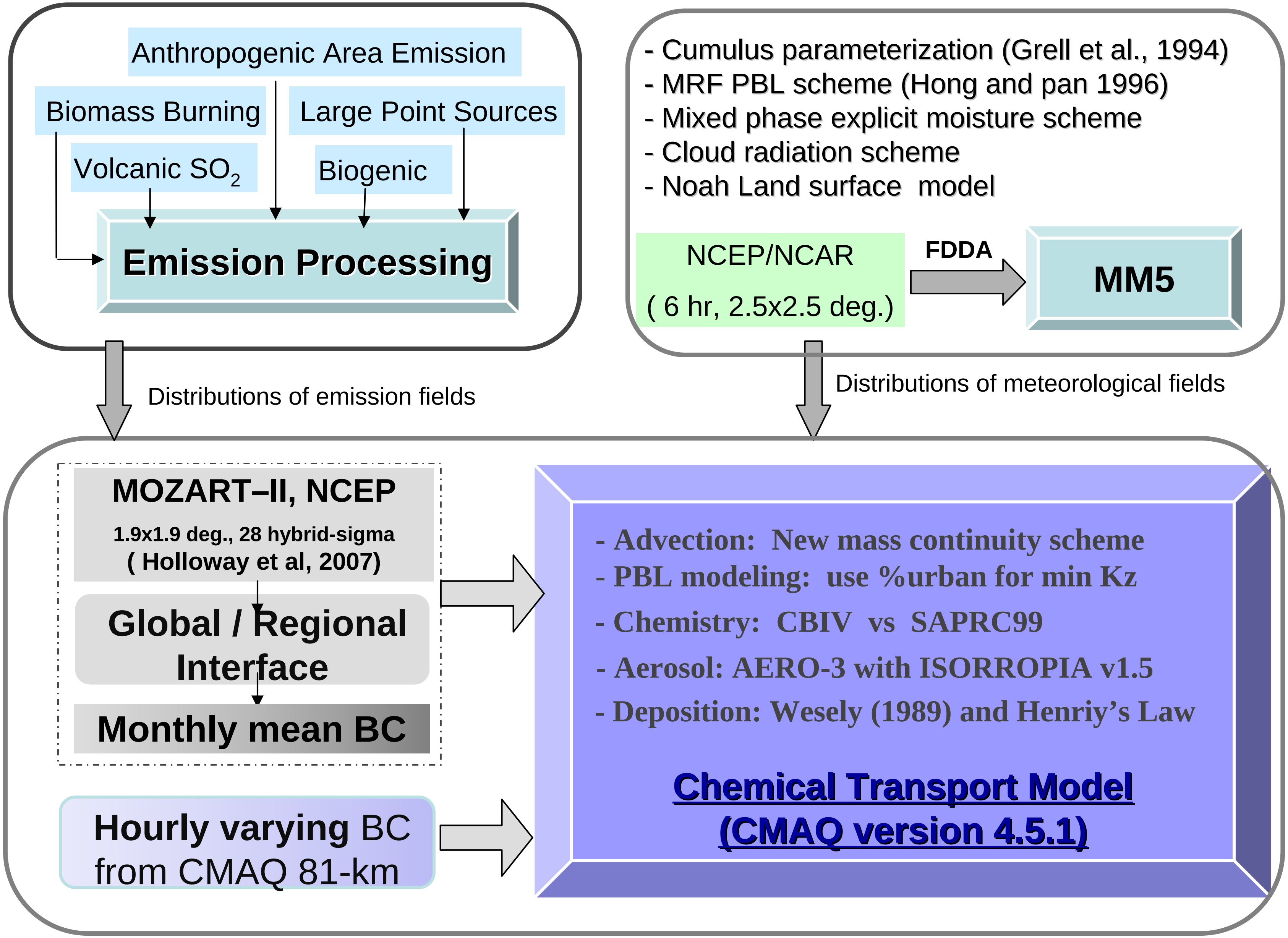
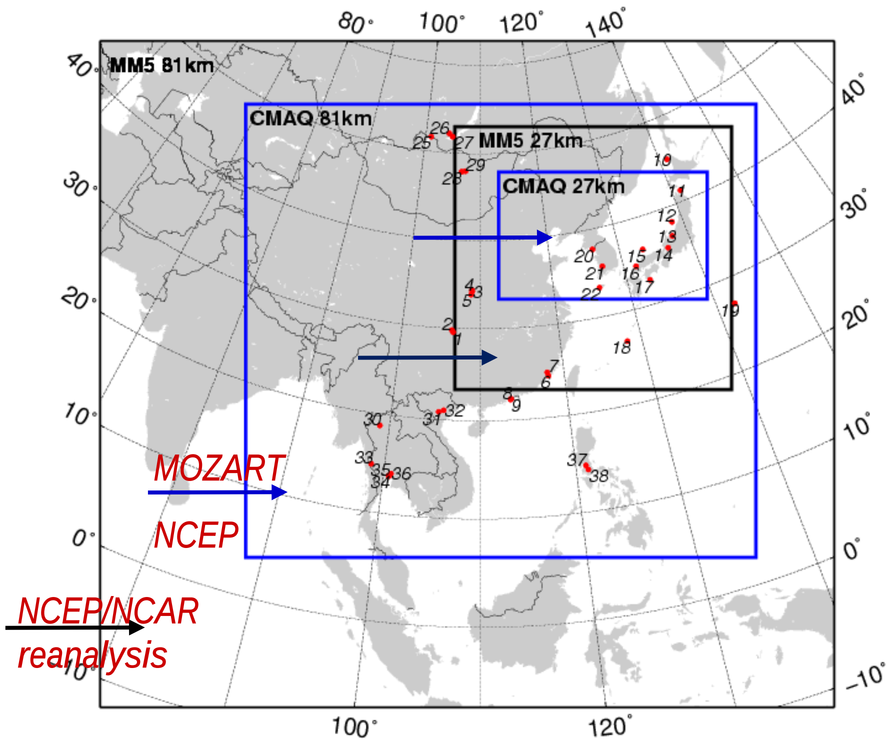
2.1 Model Components and its configuration



2.1 MODEL Description: Simulation Features in East Asia

❶ Horizontal Domains

-- Center: (110E, 25N), East Asia
-- Coarse grid: 81 km
-- One way nested fine grid: 27km



Locations of EANET monitoring sites are shown with labeling IDs

❷ Vertical Distribution

-- 23 sigma layers for meteorology
-- 8 sigma layers for Chemical Transport
-- Lowest : ~70m above ground
-- Highest : ~13 km above ground
-- Finer resolution in the lowest 1500 m

❸ Initial / Boundary Conditions

-- 2001 annual simulation with hourly time step is initialized on Dec 15th 2000 with standard concentration values

-- Lateral BC of CMAQ:
Coarse (81km): monthly mean BC extracted from MOZART-NCEP, including PAN and NH_4NO_3

Fine (27km) : hourly varying BC extracted from CMAQ 81-km output

--No upper O_3 BC employed in CMAQ

❹ Observation Data

-- Ground-based monitoring (EANET2002)
-- Satellite-borne NO_2 columns: Global Ozone Monitoring Experiment (GOME) (Ritcher et al., 2005, Nature)

Ⅲ 2. 2 Emissions: Sources and Characteristics of Emission Data

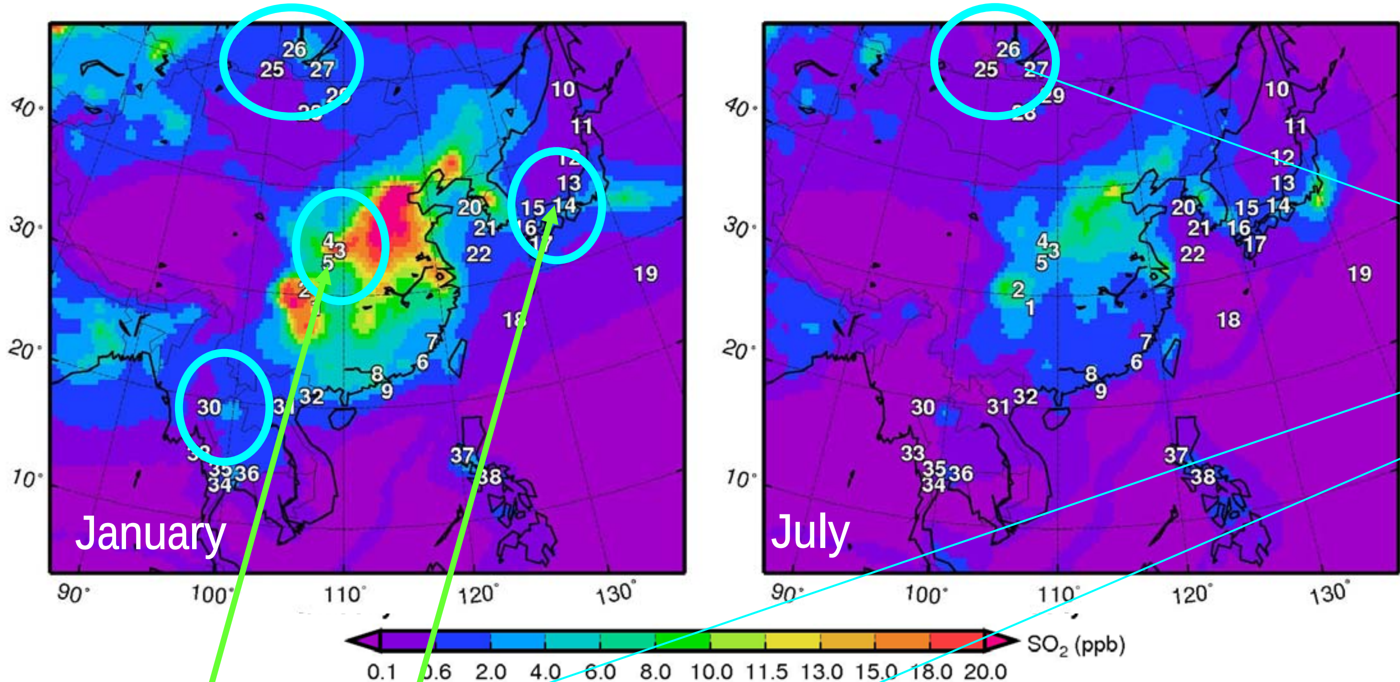
References	Source types (species)	Applied region (Resolution)	Temporal
MICS-Asia (Streets et al.,2003)	Anthropogenic area and Large Point Sources (SO_2, NO_x, NH_3, CO, BC, OC, PM_{10}, $PM_{2.5}$, VOCs)	All regions except Russian (0.5x0.5°)	Domestic heating and NH_3 / CH_4 emission from China only
GEIA (Martin et al.,2005a)	Anthropogenic area (NO$_x$, CO, and VOCs only)	Russian only (0.5x0.5°)	Seasonal
EDGAR FT2000 (Oliver et al.,2005)	Anthropogenic area (SO_2 and NH_3 only)	Russian only (1x1°)	Annual
GEIA (Martin et al.,2005b)	**Biomass burning** (SO_2, NO_x, NH_3, BC, OC, $PM_{2.5}$,VOCs)	All regions (0.5x0.5°)	Seasonal
GEIA POET (Grannier et al., 2005)	**Biogenic** (CO, NO, VOCs)	All regions (1x1°)	Seasonal
Kajino et al.,2004 Kazahaya et al.,2004	Volcanic (SO_2)	**Miyakejima volcano**	Seasonal
Fujita et al., 1992	Volcanic (SO_2)	**Other volcanoes**	Annual

※ No emissions of sea salt

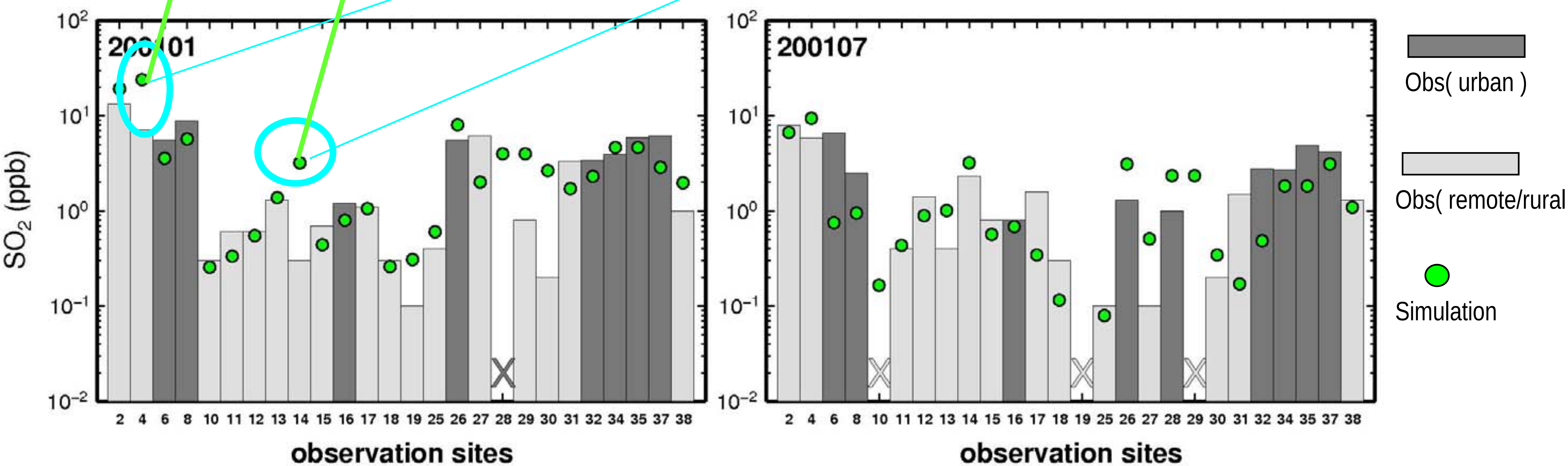
※ No emissions of soil dust

※ No emissions of lightening NOx

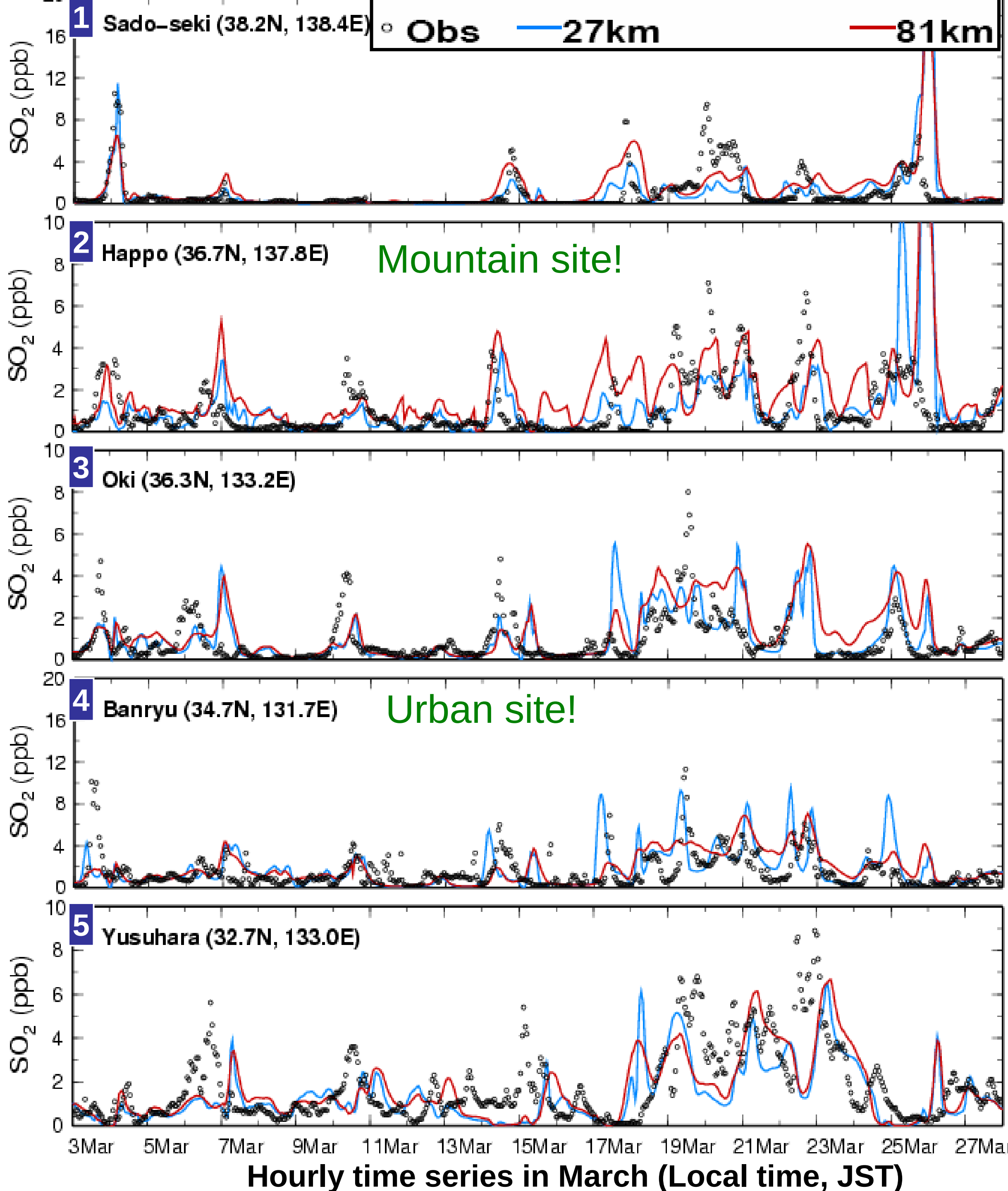
3.1 Seasonal variations of surface concentrations of SO_2

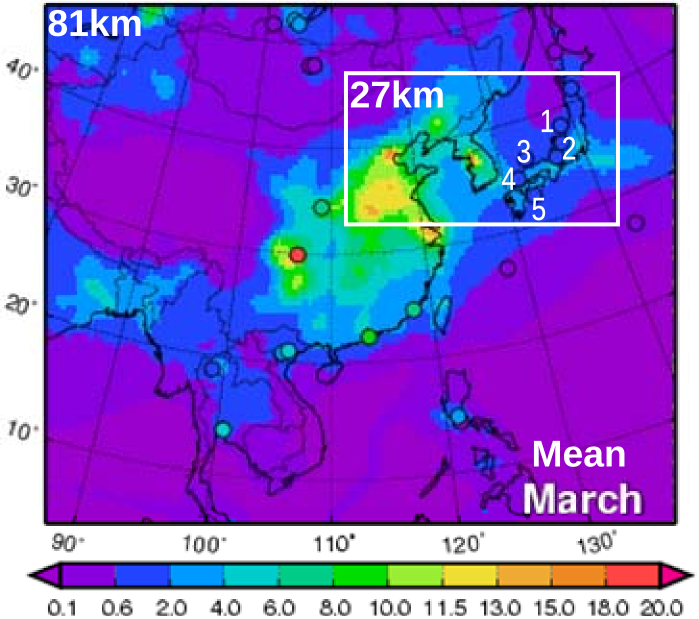


- General agreement in spatial and seasonal variation
- Russian sites: Emission seasonality
- Site 4(near Xi-an) and site 14 (central Japan) : topography and vertical mixing
- Site 30: uncertainty in Large Point Sources



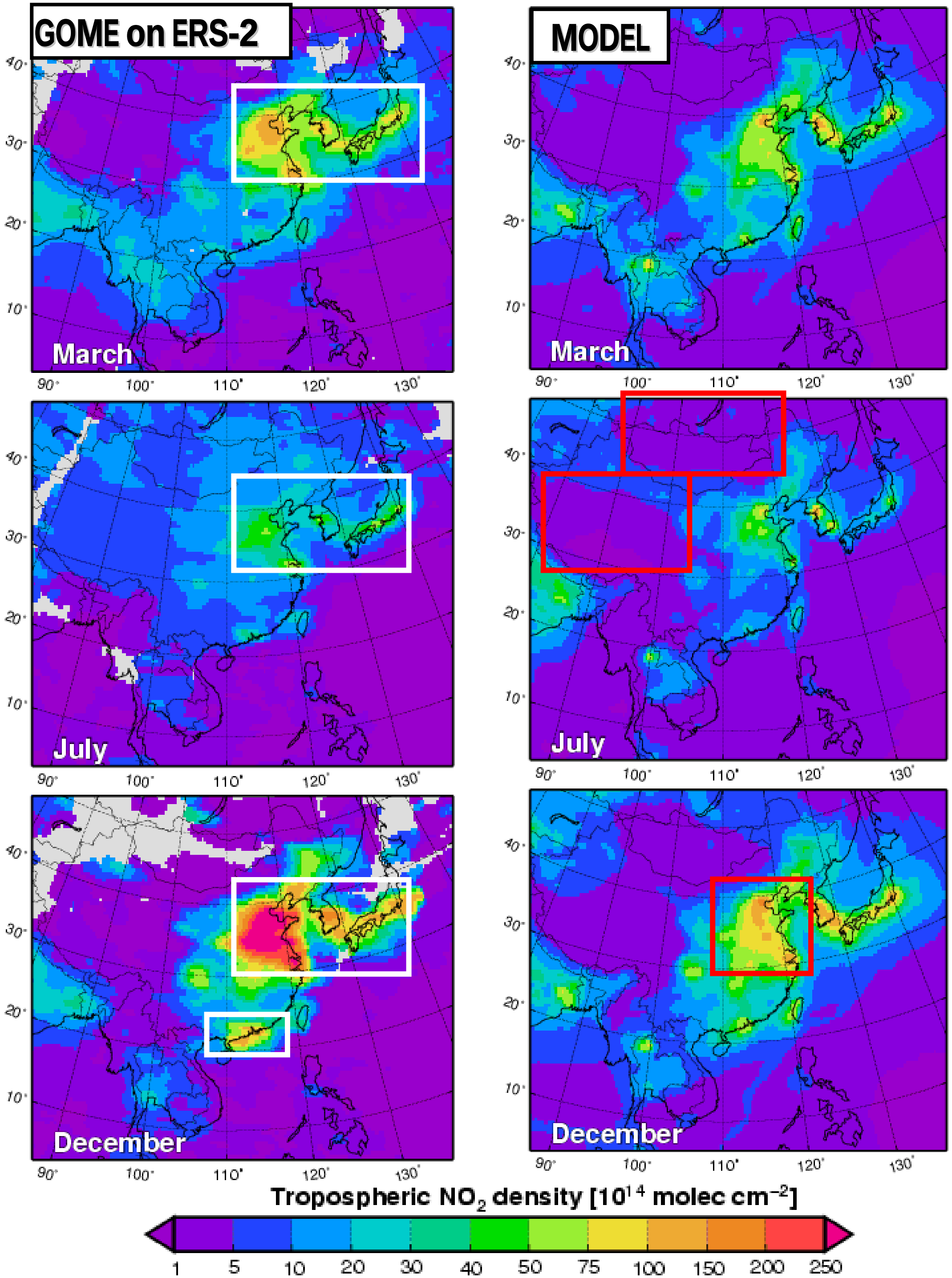
3.1 Hourly mixing ratios of SO_2





Note: the filled circles show the observed values

- Successfully reproduce the diurnal variations and magnitudes of SO_2
- The 27-km grid simulation captures the fine dynamic structure of SO_2 mixing ratios at Oki and Banryu
- Mountain Happo: local vertical mixing associated with topography
- Urban Banryu: sub-grid variation of SO_2 emissions and fine scale dispersion
- Short-term changes of met condition: large-scale observational data ingested in the global reanalysis in MM5



3.2 Tropospheric NO_2 column density

- **Calculate NO_2 column amount** from vertical resolved mixing ratio, temperature, and pressure

$$VCD = \sum_{l=1}^{8} \frac{P_l \times \Delta Z_l \times A \times [NO_2]_{ppm,l}}{Rg \times T_l \times 10^6 \times 10^4}$$

at 03:00 UTC (11:00 LT for China and 12:00 LT for Japan)

- Both **highlight** the areas of intense pollution in industrialized regions

- **Seasonal variations** of NO_x lifetime in PBL, meteorological conditions, and higher winter emissions

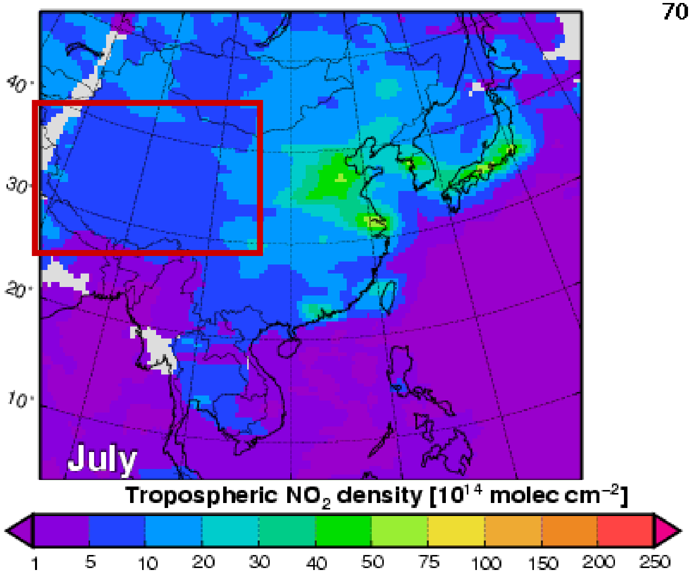
Summer: **soil-biogenic NO** emissions from **grassland/scrubland** in mid-latitudes

- Short lifetime → NO_2 abundance in PBL → **controlled by regional emissions, less by transport**

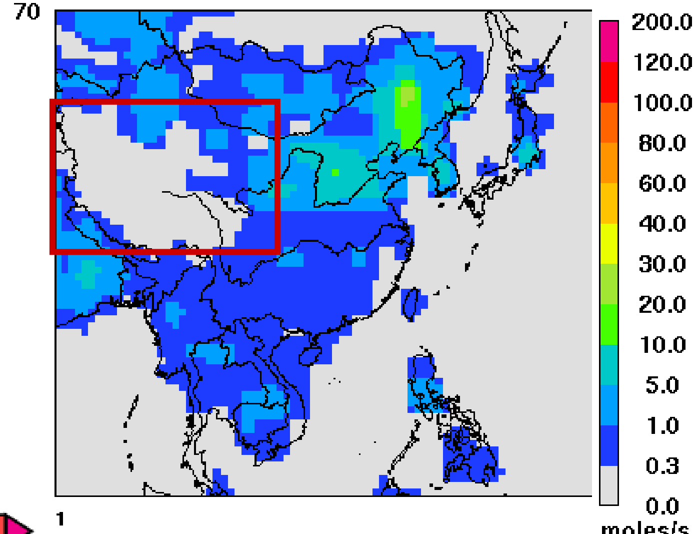
Spring/Winter: **anthropogenic emission** in central eastern China and Japan

3.2 Implication for uncertainty in soil-biogenic emission of NO

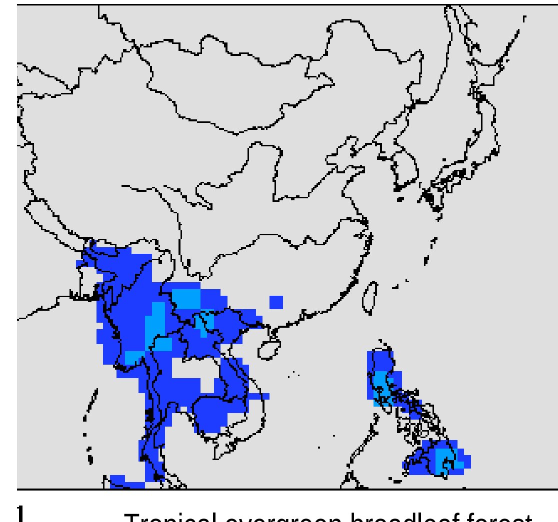
GOME NO2 columns



July NO



January NO



Tropical evergreen broadleaf forest in South East Asia

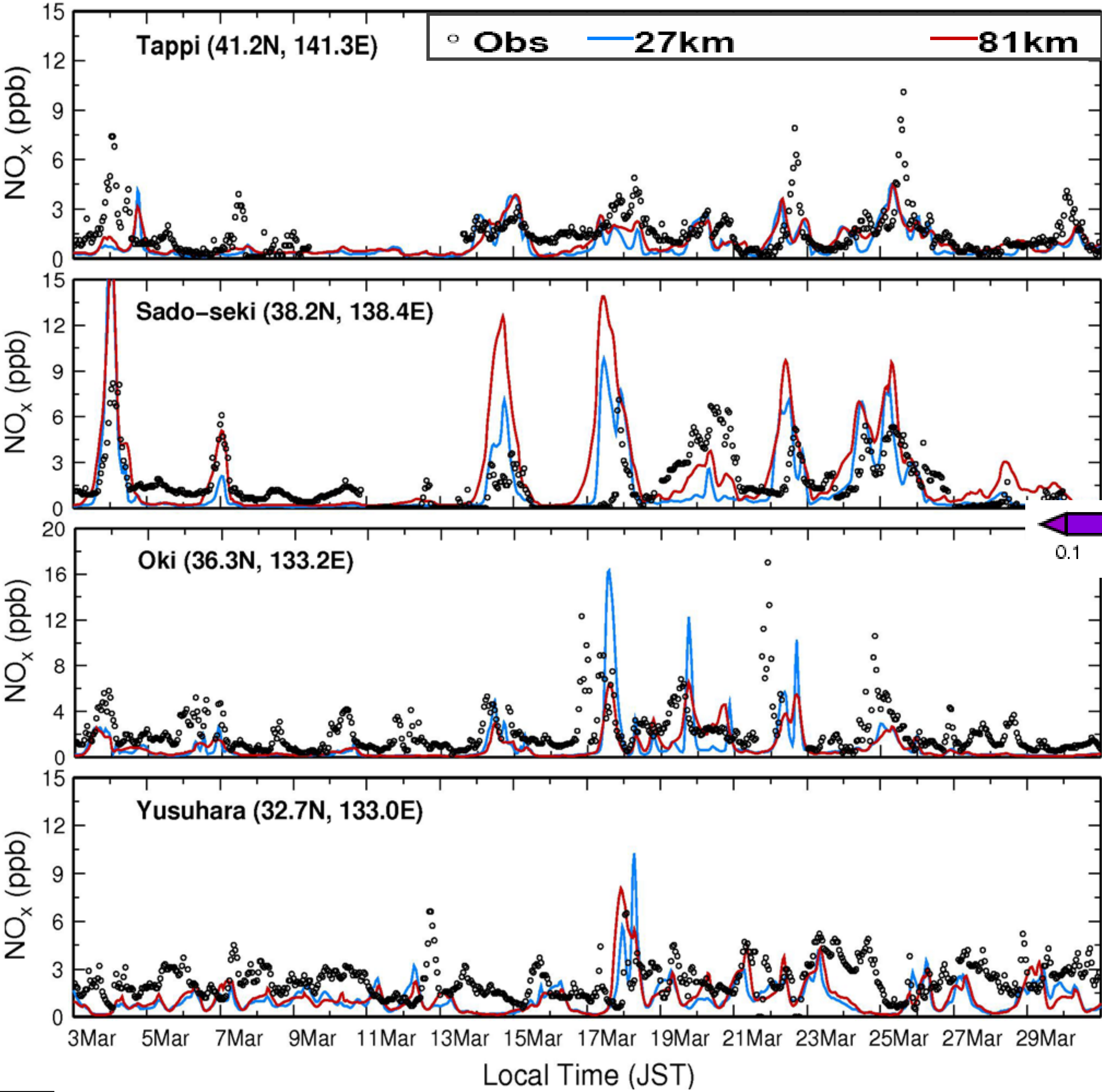
Large spatiotemporal variability of the microbial soil processes

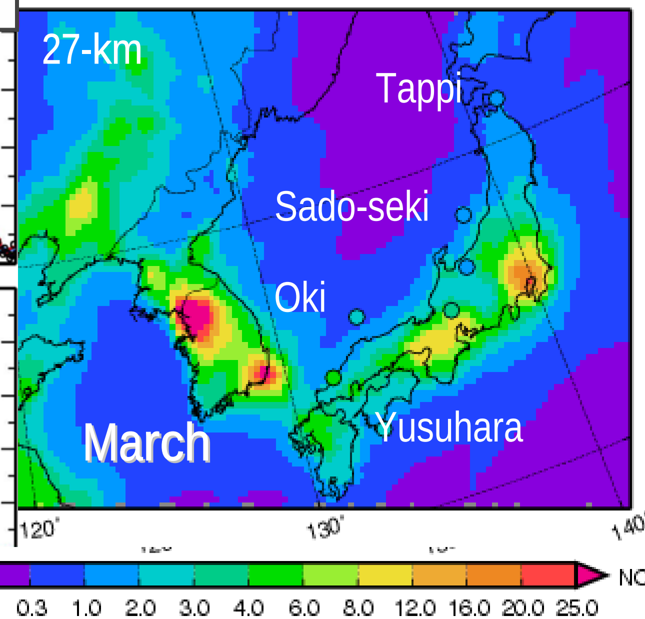
- Temperature, soil, and precipitation dependent
- Stimulation of N-fertilizer and biomass burning
- Biome-dependent canopy recapture
- Rain-induced pulsing (an increase of NOx measured after a shower of rain)

Main uncertainty of soil-biogenic NO estimates by Yienger and Levi (1995)

- Spring: the fraction of applied N-fertilizer released as NO (0.3% ~ 2.5%) and the timing of fertilizer application
- Summer: Exclude the possibility of rain-induced pulsing in arid-scrubland/desert regions (e.g. western China)

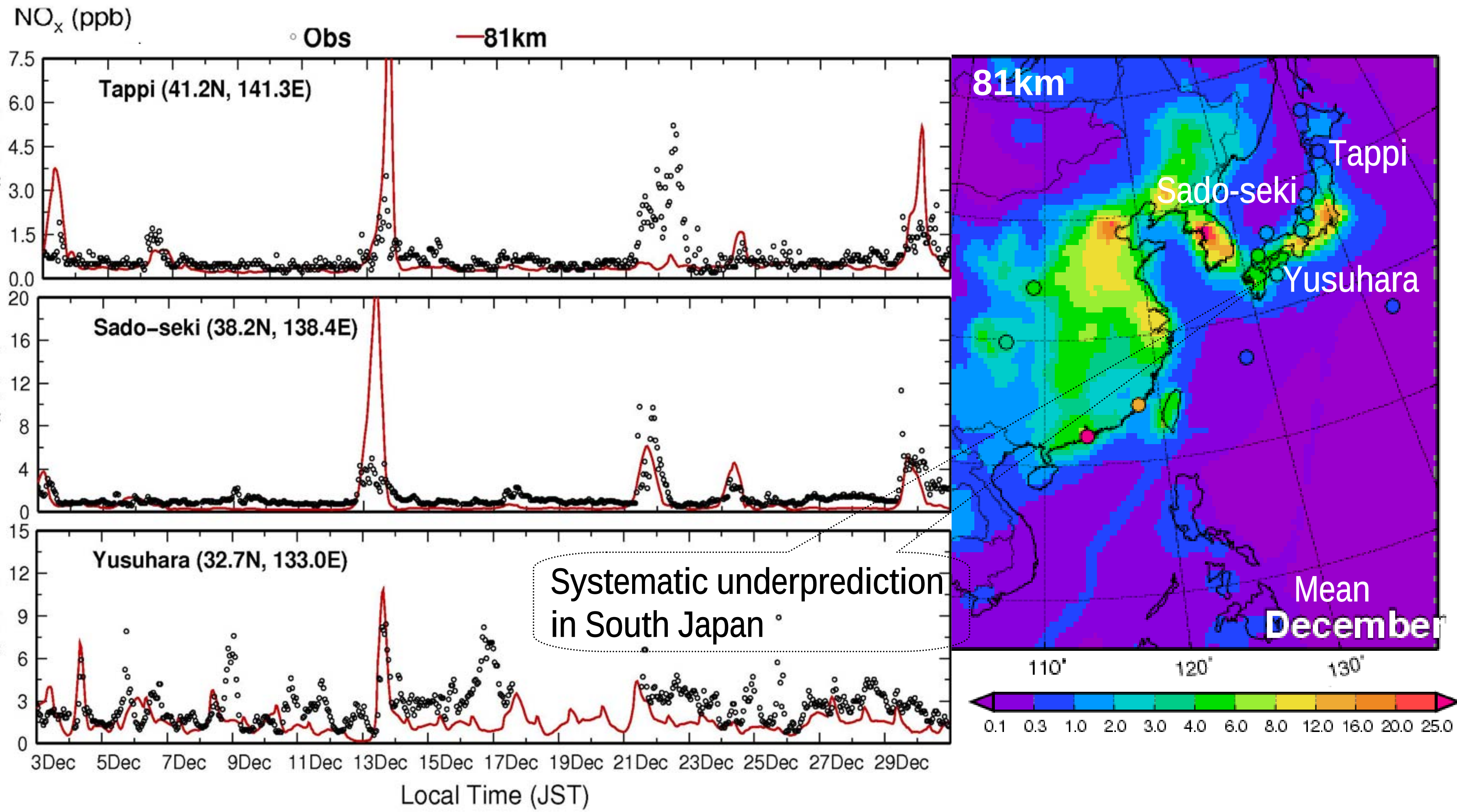
3.2 Hourly NO_x mixing ratios in March compared with ground-based monitoring





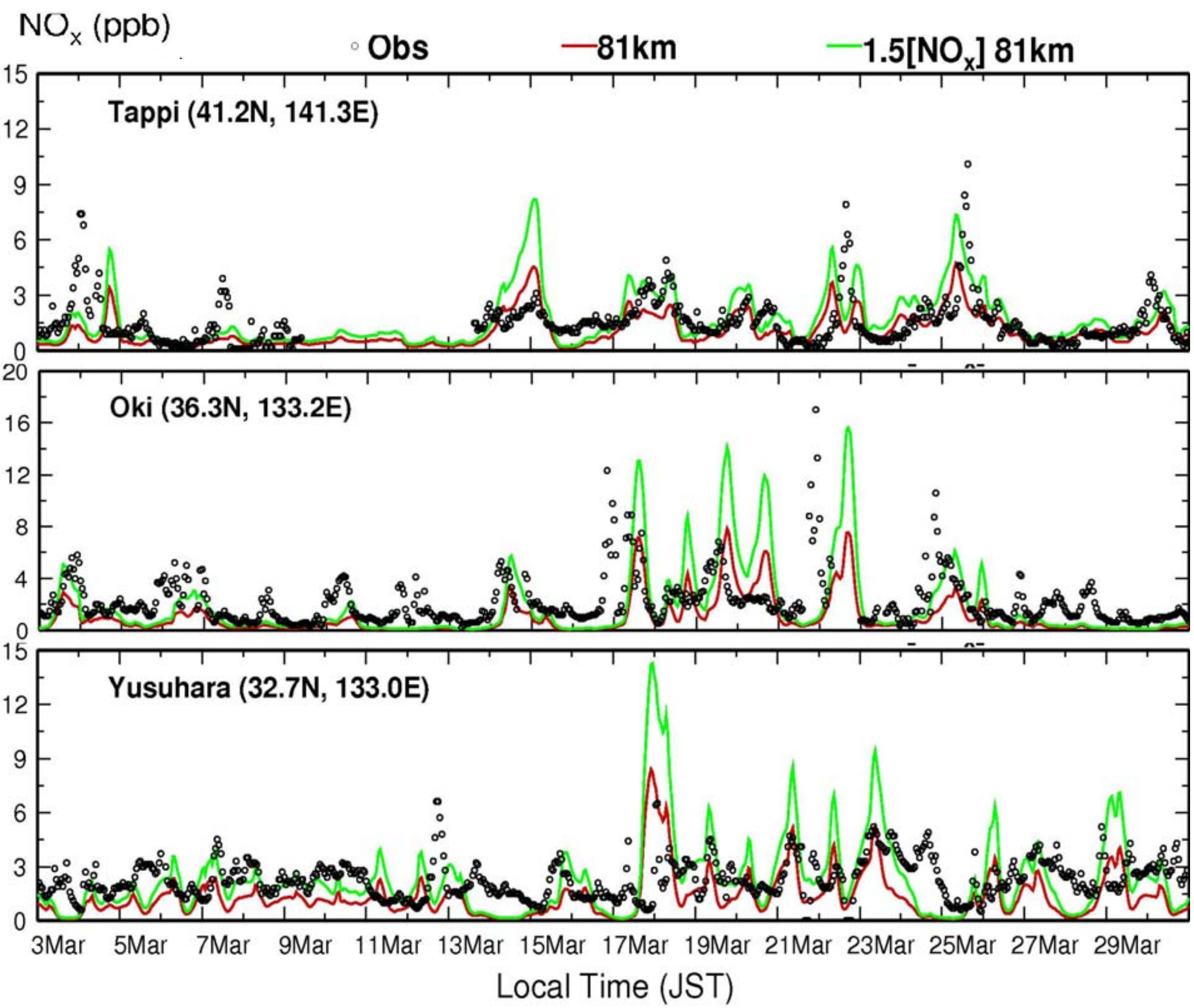
- North Japan: well reproduced both for magnitude and diurnal variation
- Southern Japan: Slightly under-prediction of NO_x mixing ratio
- Consistent with the underestimation of NO_2 column density
- EAGrid2000-Japan (Kannari et al, 2007) 10% > MICS-Asia

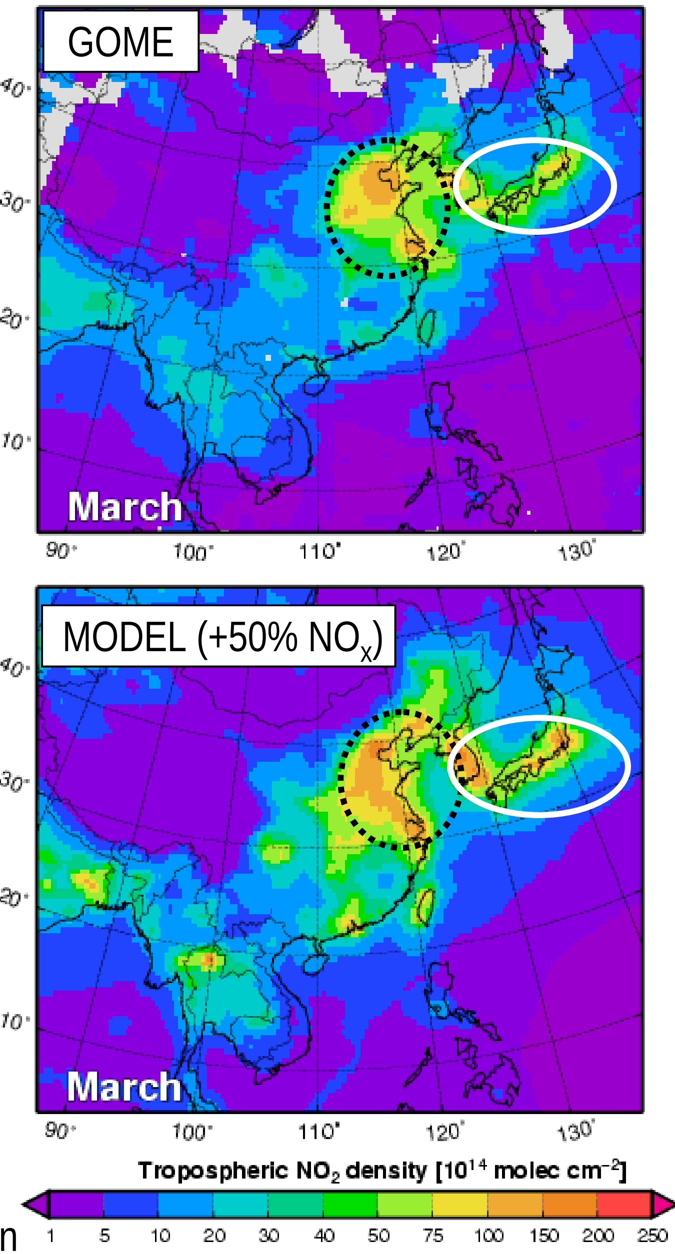
3.2 Hourly NO_x mixing ratios in December compared with ground-based monitoring



- A similar spatial pattern: -Better agreement in north Japan
  -Discrepancies in south Japan
- NOx predictions have larger uncertainty in central and south Japan than in northern Japan

3.2 Sensitivity simulation with NO_x emission increased by 50%

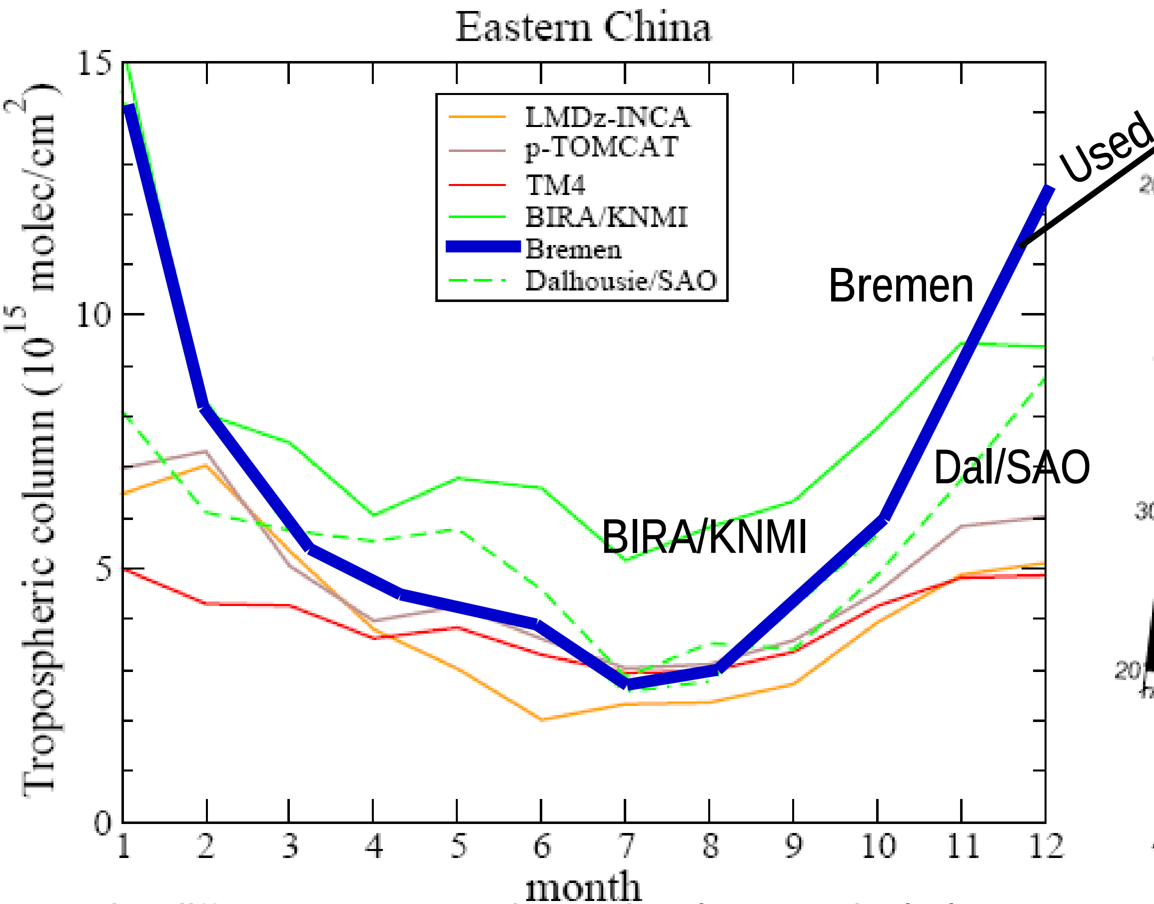


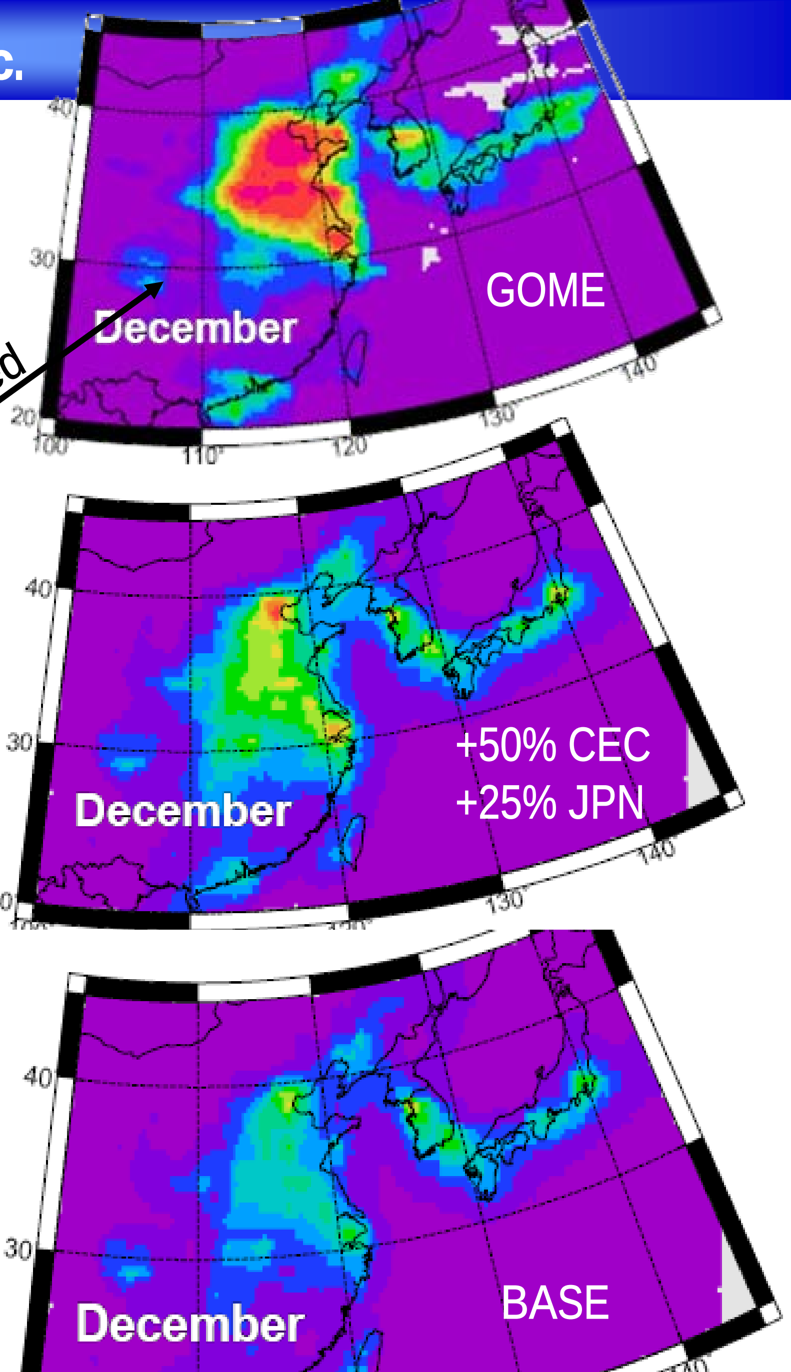


- **Evaluation with EANET**: +50% NOx emissions move the results in the right direction, but does not eliminate the problems
- **Evaluation with GOME**: +50% NOx emissions considerably improve over central eastern China, but overpredict the retrieval over south Korea and Japan

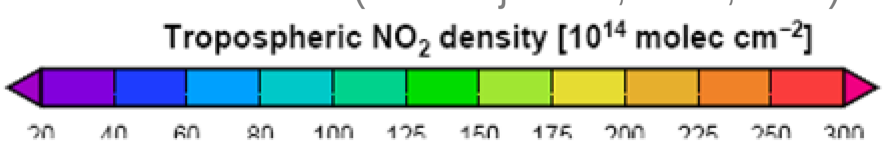
3.2 Sensitivity analysis of NO2 columns in Dec.

1. GOME NO2 errors: 40-60% for monthly averages over polluted regions (Richter et al, 2005, Nature)



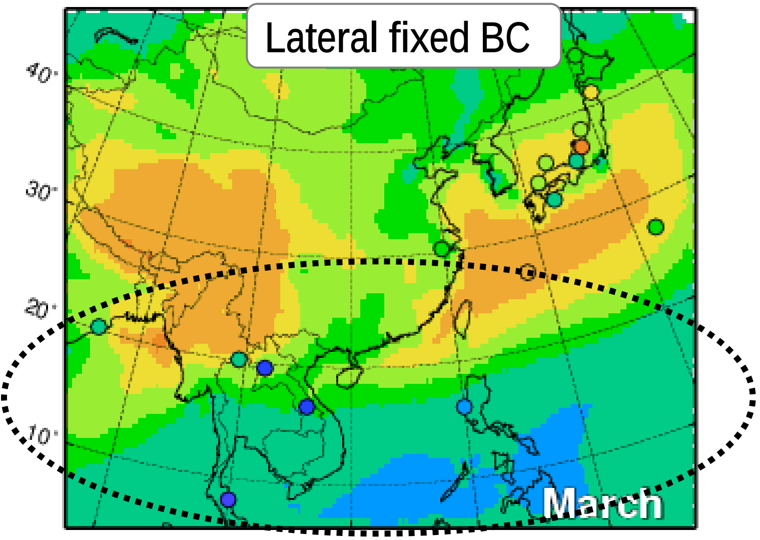


2. The differences among the retrieval are particularly pronounced in wintertime (van Noije et al, 2006, ACP)

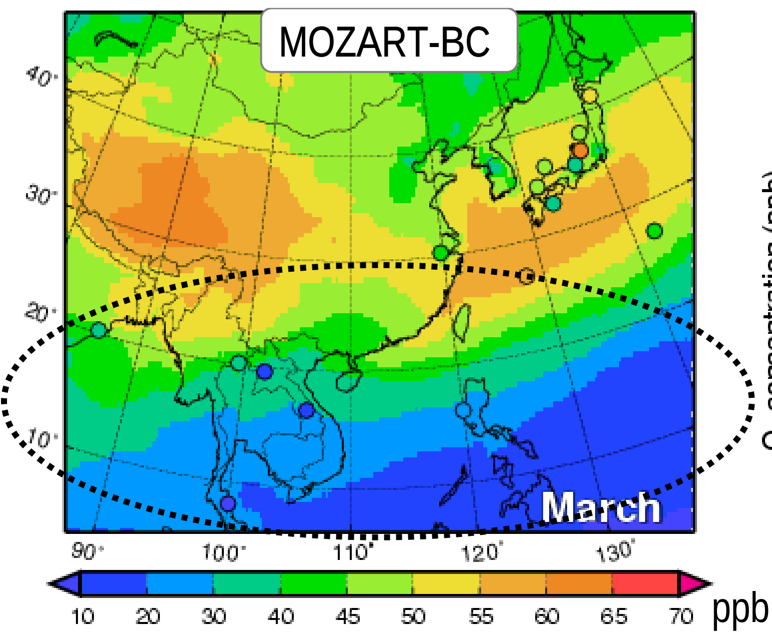


3.3 Sensitivity of O_3 boundary condition

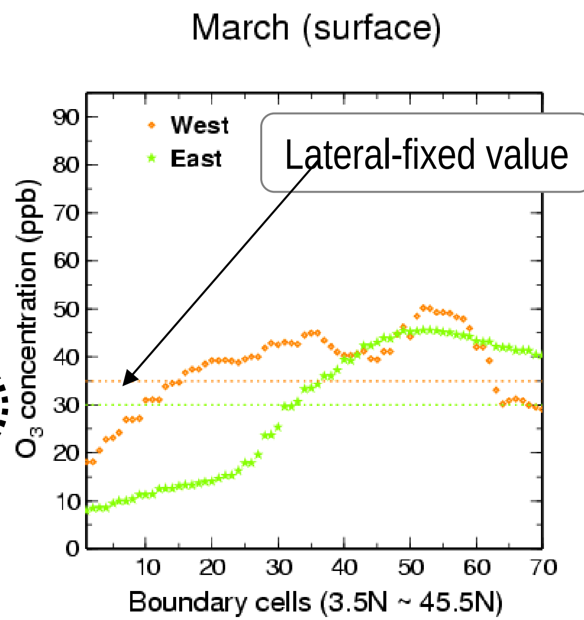
Simulated surface ozone

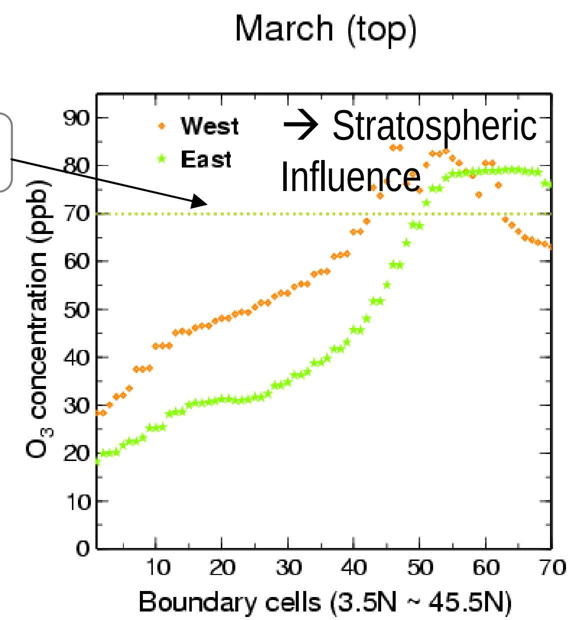


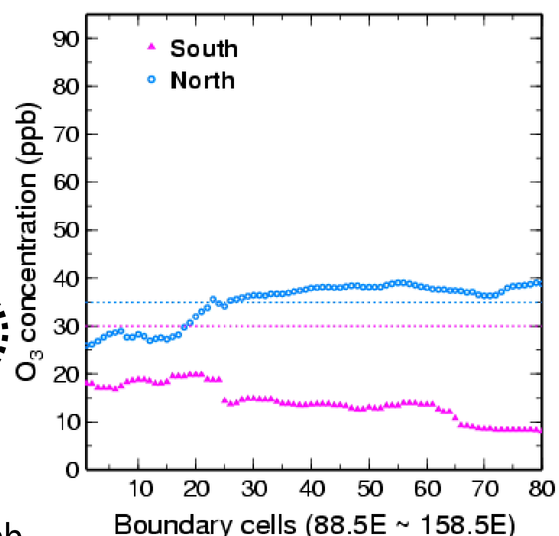
Note: the filled circles show the observed values

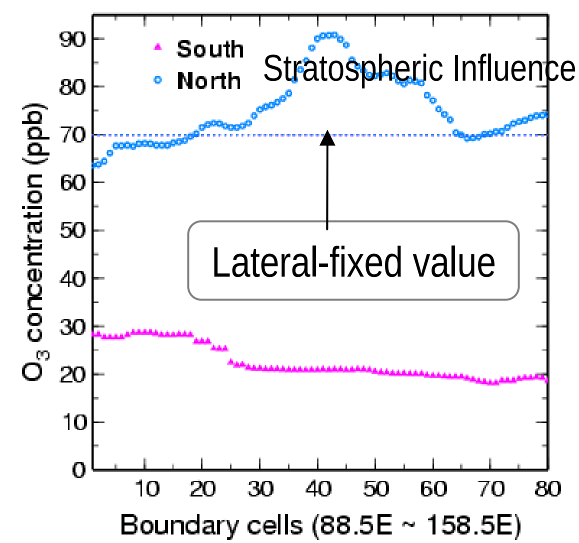


Ozone BC in the surface and model top

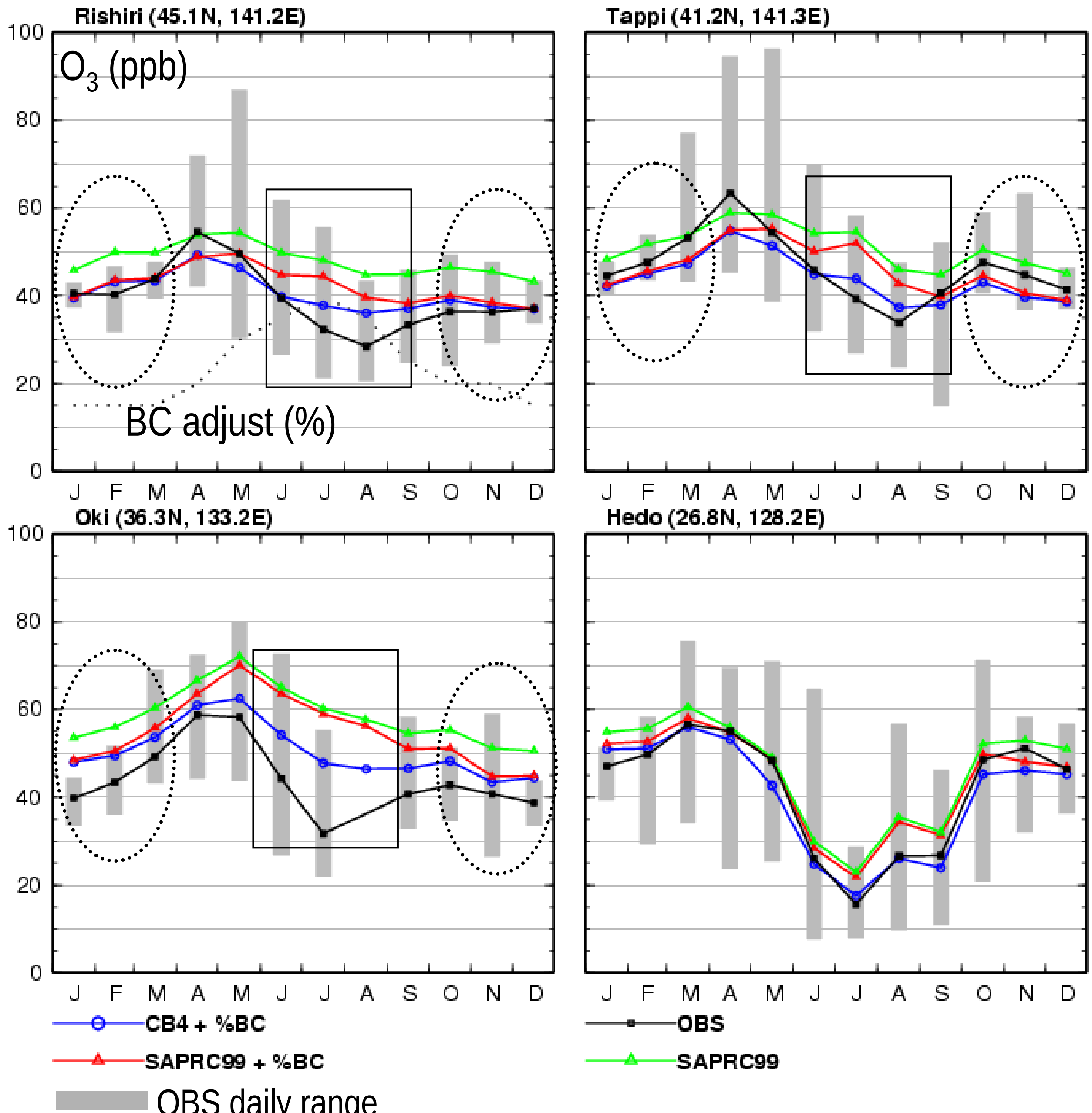






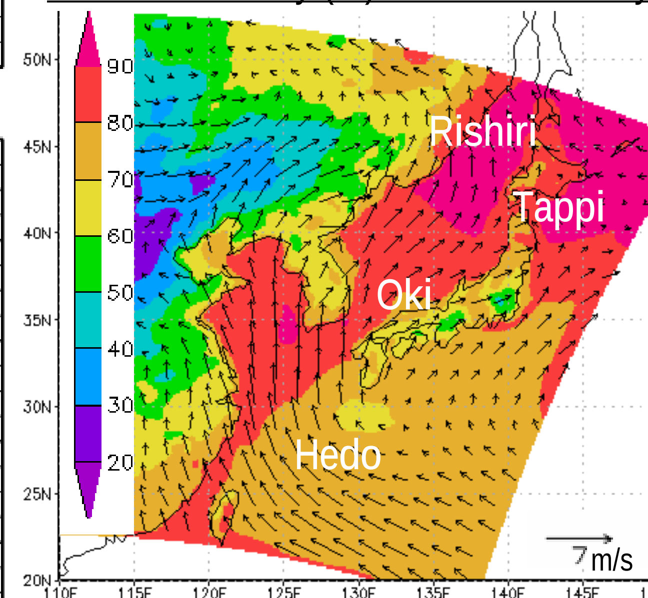


3.3 Seasonal cycle of surface O_3 (Sensitivity of BC and photochemistry)



- 1-2 month lifetime in winter → **influences of MOZART-derived BC in winter**
- **Spring maximum** from winter storage and stratospheric intrusion
- **Summer minimum** explained by the exchange of clean marine air mass

Relative humidity (%) and winds in July



- Oki: over-prediction of O_3 in summer by the SAPRC99 mechanism

3.3 Sensitivity of photochemistry to O_3 production in summer

❖SAPRC99: **more reactive** mechanism with a **more detailed** representation of HC classification

(R1) $OH + HC \xrightarrow{k} RO_2 + H2O$

ALK1~ALK5, OLE1/OLE2, ARO1/ARO2, HCHO/ CCHO/RCHO, ETHENE, TRP1, ISOPRENE

(R2) $RO_2 + NO \rightarrow NO_2 + RO$

(R3) $NO_2 + hv(< 420nm) \rightarrow O(3P) + NO$

(R4) $O(3P) + O_2 + M \rightarrow O_3 + M$

❖SAPRC99 produces **more PAN**, **less** HNO_3

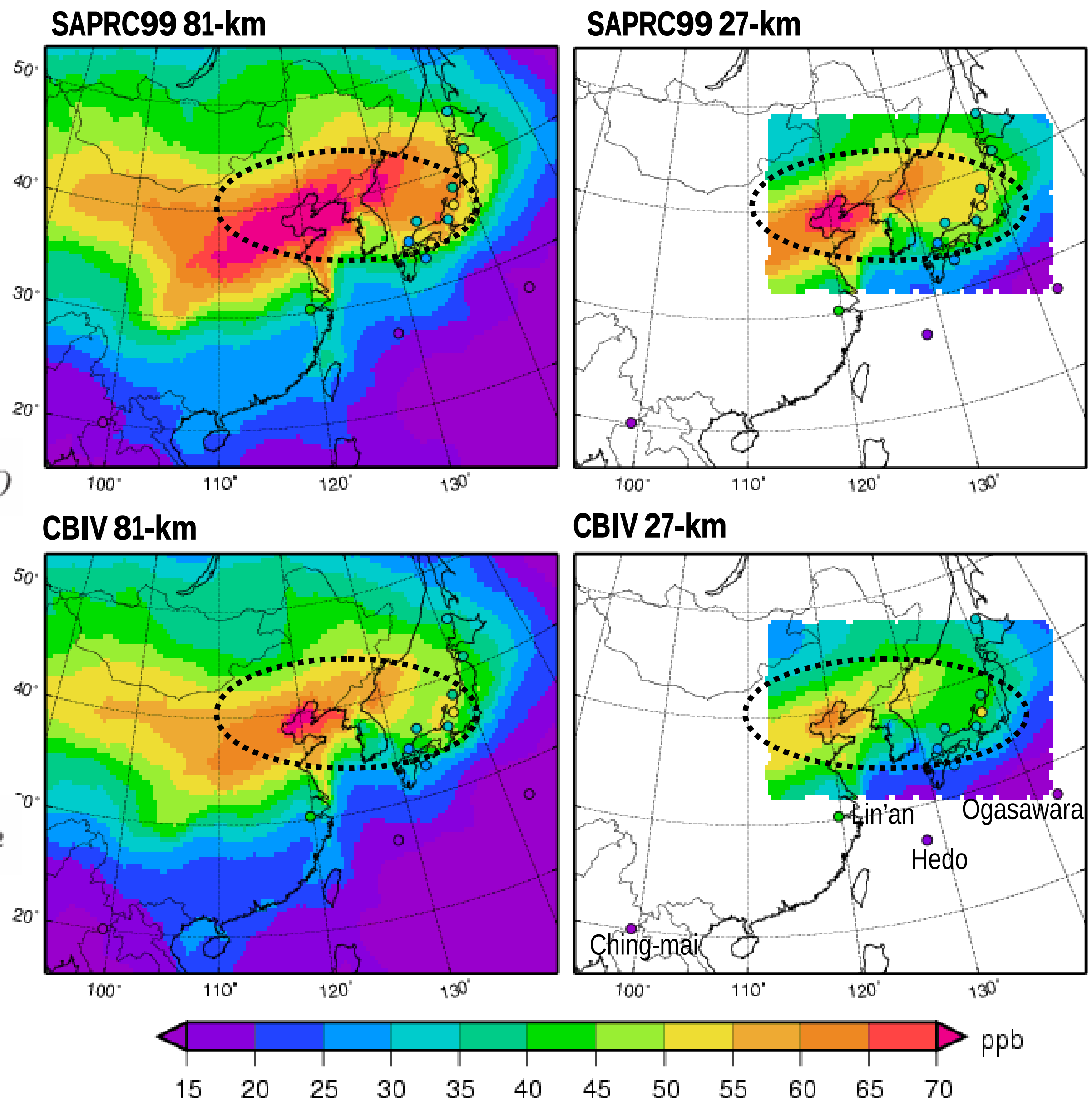
$NO_{2(g)} + OH_{(g)} \leftrightarrow HNO_{3(g)}$ —● Loss

NO_2 $CH_3C(O)OC \rightleftharpoons CH_3C(O)OONO_2$

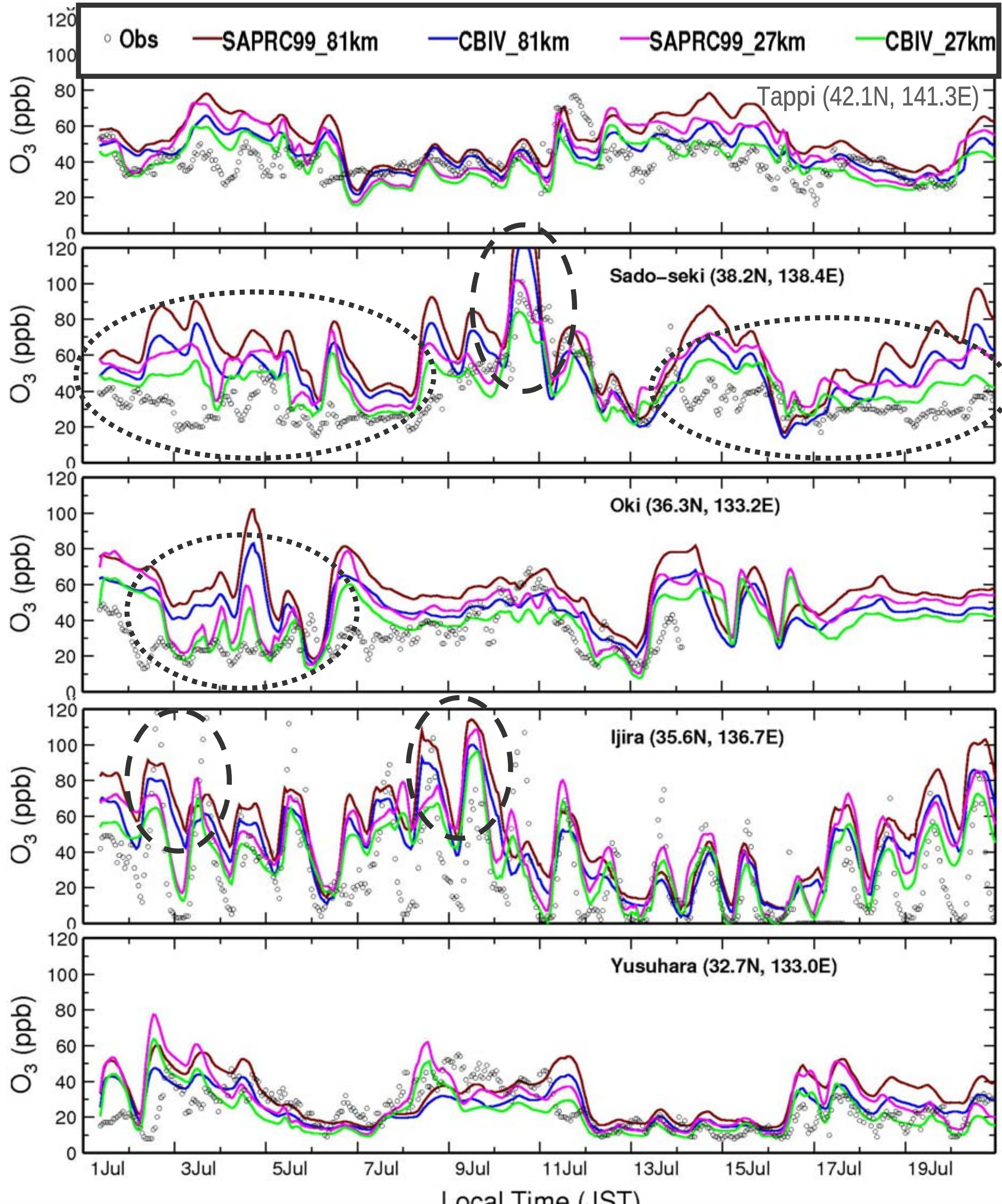
Thermo-decomposition

Reservoir

❖The **CBIV** (carbon-bond-IV) mechanism with the **27-km** grid spacing give the **best** agreements against EANET JPN monitoring sites.



Note: the filled circles show the observed value



3.3 Hourly time series of O_3 mixing ratios in July

Coarse-grid vs Fine-grid

- **Over-prediction** of the coarse simulations on **low ozone days**
- **Hourly varying BC** likely improve the find grid simulation

SAPRC vs CBIV

- High O_3 production efficiency of SAPRC99: **high O_3 at urban** area with a high quality of emission inventory
- CBIV: O_3 prediction at **regional scale** with the coarse grid spacing

3.3 Correlations of NO, NO_x and O_3 mixing ratios at the rural site Ijira

1. Net production of O_3 in a NOx rich env.

$$\begin{cases} OH + CO \rightarrow HO_2 + CO_2 \\ OH + VOCs \rightarrow RO_2 + H_2O \end{cases}$$

$$\begin{cases} HO_2 + NO \rightarrow NO_2 + OH \\ RO_2 + NO \rightarrow NO_2 + RO \end{cases}$$

$$\begin{cases} NO_2 + hv(< 420nm) \rightarrow O(3P) + NO \\ O(3P) + O_2 + M \rightarrow O_3 + M \end{cases}$$

2. NOx titration of O_3

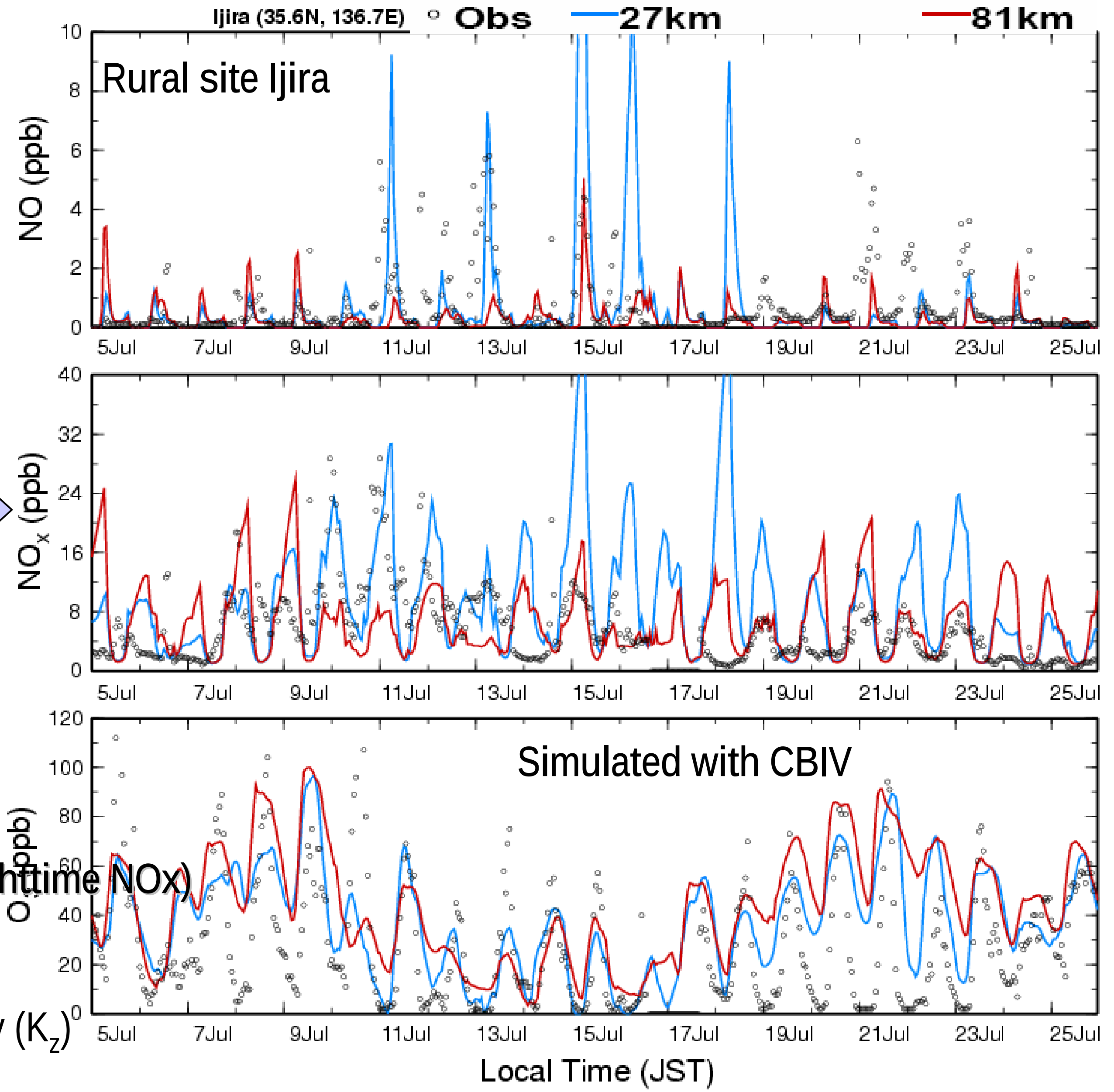
$$O_3 + NO \rightarrow NO_2 + O_2$$

--O_3 correlated negatively with NO and NO_x on most days

--VOC-limited O3 production

3. Overprediction of nighttime O_3 (caused underprediction of nighttime NOx)

-PBL modeling
-depth of first layer: 146m
-minimum vertical eddy diffusivity (K_z)
-local scale mixing



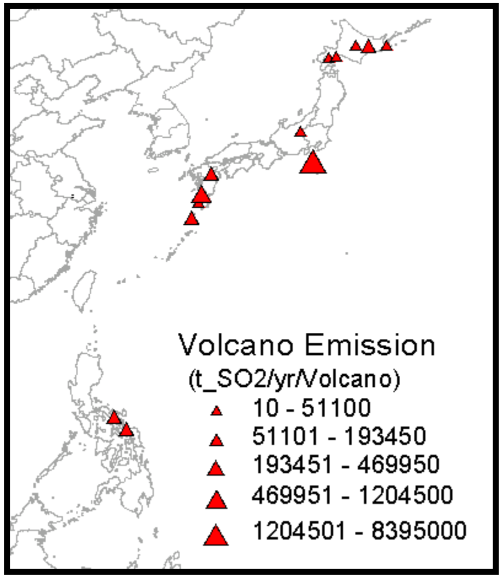
Contents

4.1 Source region attribution methodology: source division map

>> Division of emitter regions or groups of sources <<

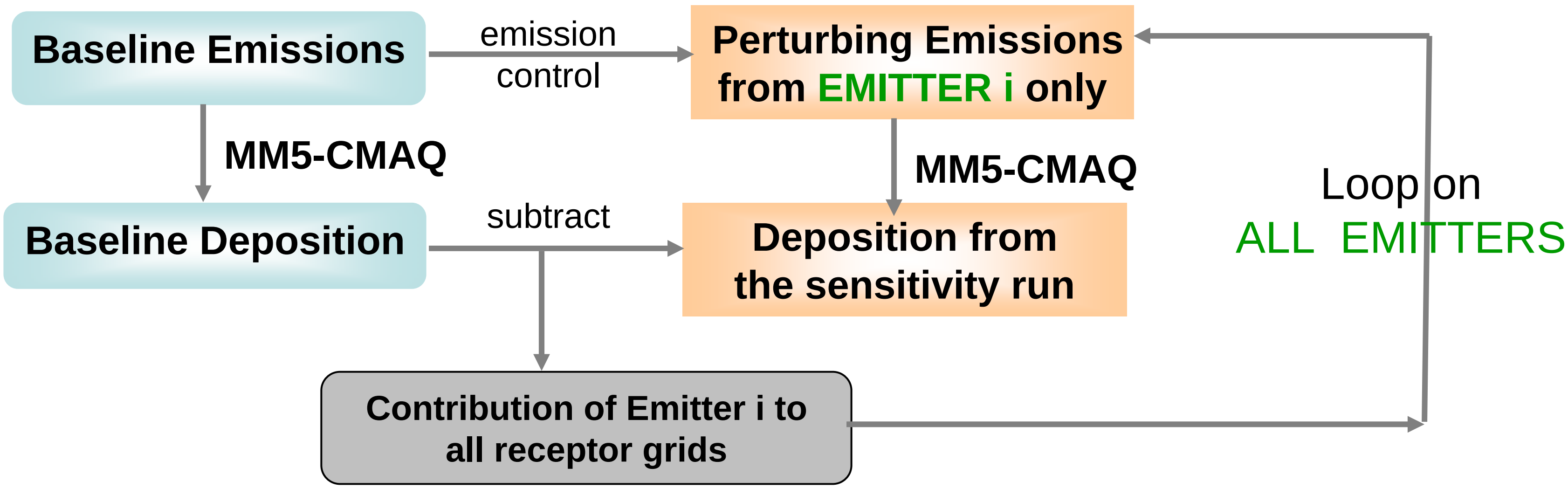
- Seven source regions in China
- Seven source regions in Southeast Asia
- SHIP: International shipping
- ICBC: Initial and boundary Condition (MOZART)
- Volcanoes

SO_2 emission from volcanoes



Sources:
http://www.cgrer.uiowa.edu/EMISSION_DATA/index_16.htm

4.1 Source region attribution methodology



Reactive Nitrogen [$NO_y = NO + NO_2 + NO_3 + 2N_2O_5 + HONO + HNO_4 + HNO_3 +$ Aerosol Nitrate + PAN(s) + other organic nitrates]

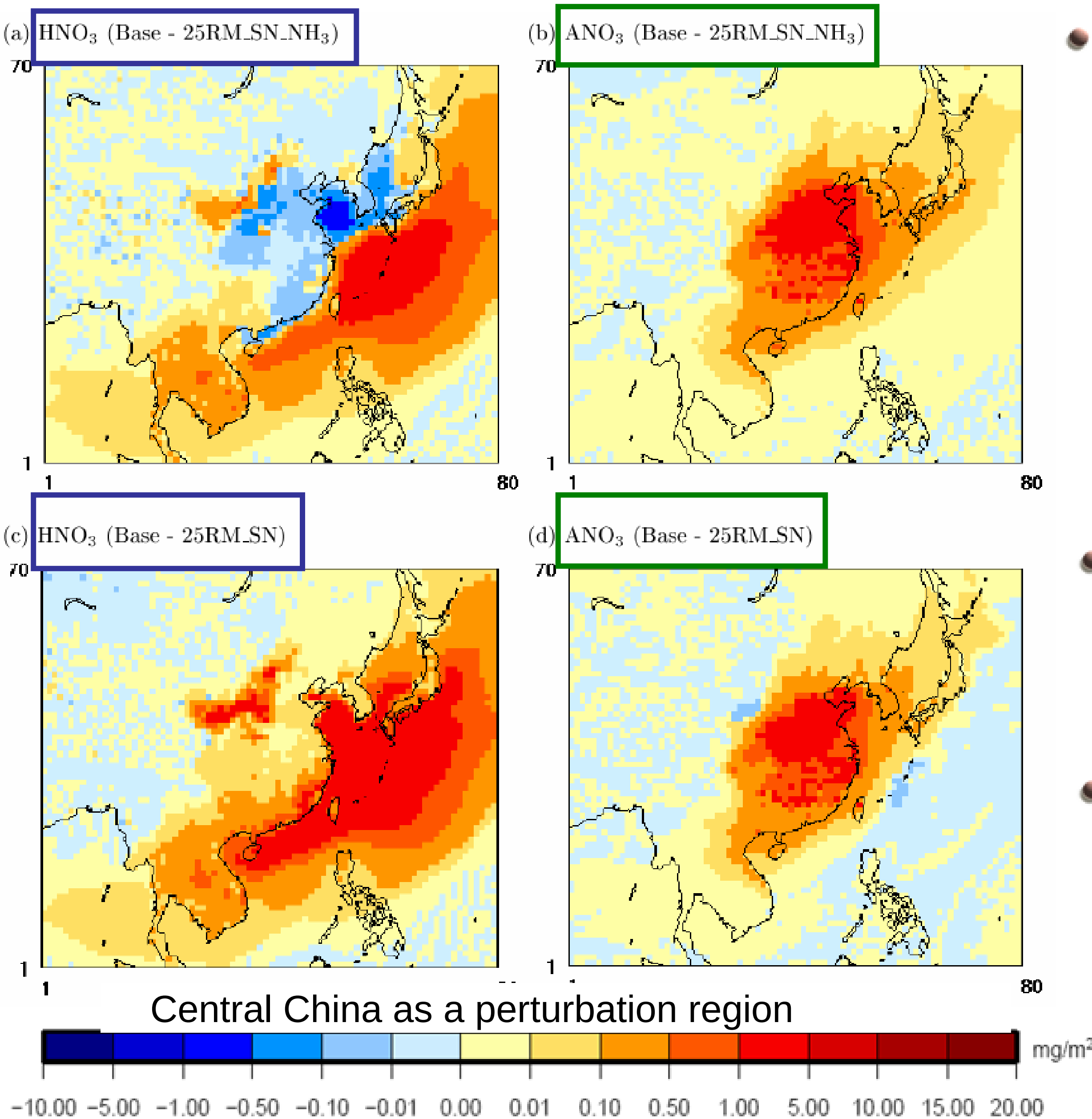
- **Nonlinearities** in atmospheric chemistry and deposition process in **Eulerian models**
- Three scenarios of emission reduction for each source region

1 100RM_SO_2_NO_x_NH_3 : a 100% reduction of SO_2, NO_x, and NH_3 simultaneously

2 25RM_SO_2_NO_x_NH_3 : a 25% reduction of SO_2, NO_x, and NH_3 simultaneously

3 25RM_SO_2_NO_x : a 25% reduction of SO_2 and NO_x simultaneously

- Propose a source region attribution methodology **applicable for reactive nitrogen**



Central China as a perturbation region

- **Thermodynamic equilibrium between gaseous HNO_3 and aerosol nitrate**

(R1) $NO_{2(g)} + OH_{(g)} \leftrightarrow HNO_{3(g)}$

(R2) $NO_{3(g)} + NO_{2(g)} \rightarrow N_2O_{5(g)}$

(R3) $N_2O_{5(g)} + H_2O_{(l)} \rightarrow 2HNO_{3(g)}$

(R4) $NH_4NO_{3(s)} \Leftrightarrow NH_{3(g)} + HNO_{3(g)}$

- **Atmospheric lifetime:**

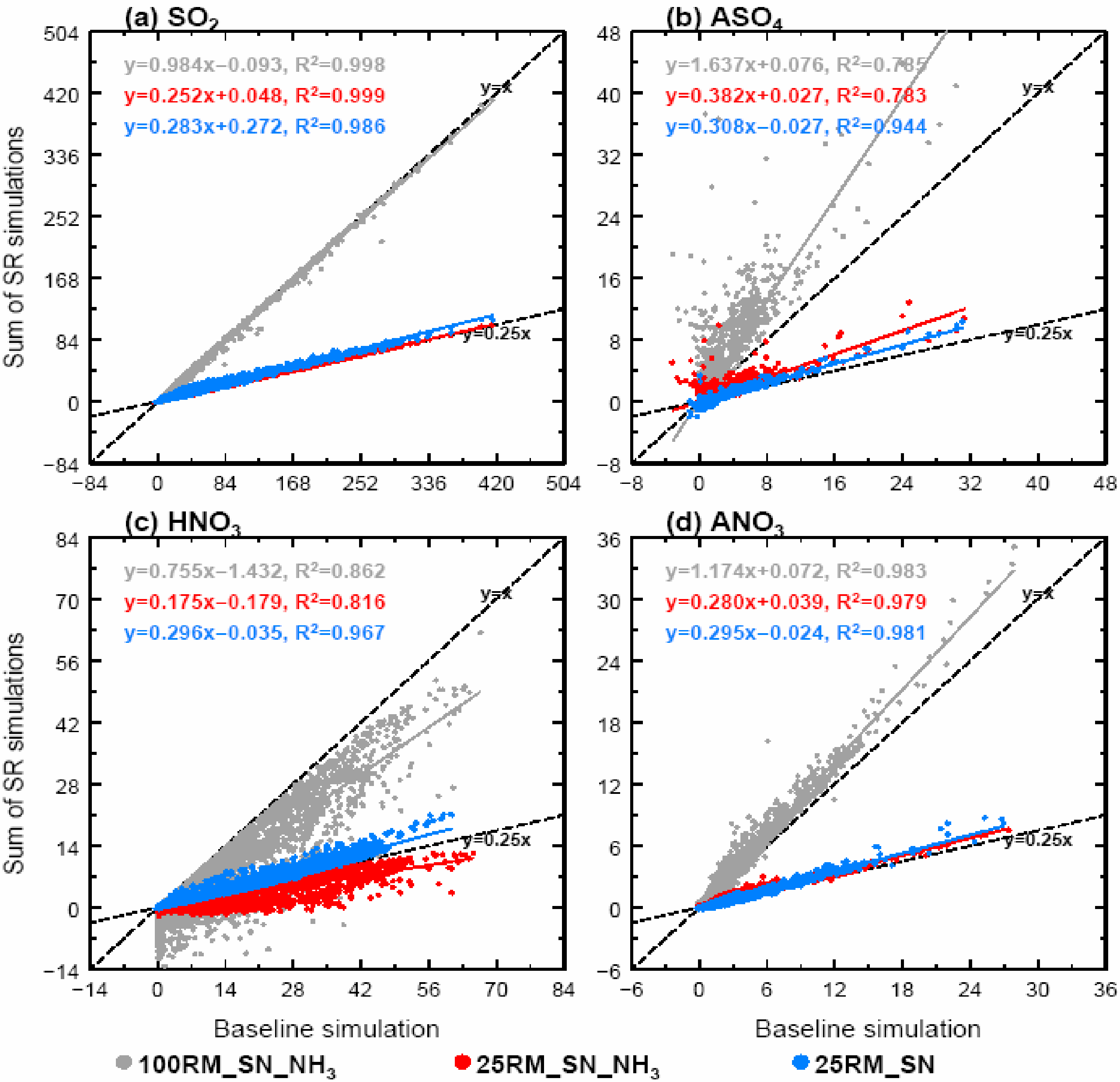
NH_4NO_3 > HNO_3

NH_4NO_3 > NH_3

- **For the reduction case of 25RM_SO_2_NO_x_NH_3**

A deficit in the availability of ammonia over Central China

4.1 Relationships of dry deposition between baseline simulation and sum of regional contributions due to emissions perturbation



Unit: mg/m^2/month (Jan)

- Deviations from linearity are largest when 100% reduction of SO_2, NO_x, and NH_3 from regional emissions

Reduction case ● 25RM_SN

- SO_2 emission reduction ↓

  → Ammonia ↑

  → HNO_3 dry deposition ↓

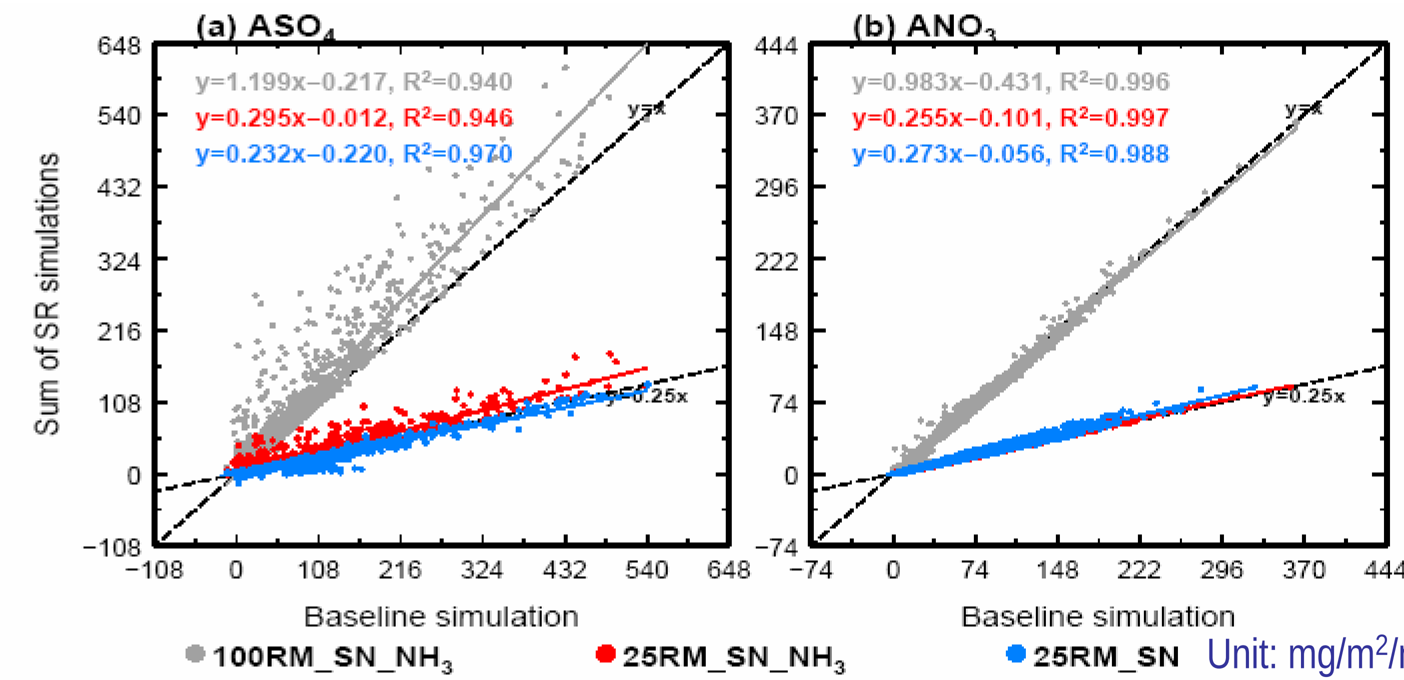
$$SO_{2(g)} + OH_{(g)} \rightarrow H_2SO_4 + HO_2$$

$$NH_3 + H_2SO_4 \Leftrightarrow (NH_4)HSO_4$$

$$NH_3 + (NH_4)HSO_4 \Leftrightarrow (NH_4)_2SO_4$$

$$NH_4NO_{3(s)} \Leftrightarrow NH_{3(g)} + HNO_{3(g)}$$

4.1 Relationships of wet deposition between baseline simulation and sum of regional contributions due to emissions perturbation



Unit: mg/m^2/month (Jan)

When 25% reduction of SO_2 and NO_x in combination

- **NO_x emission reduction** ↓

$$NO_{2(g)} + OH_{(g)} \leftrightarrow HNO_{3(g)}$$

→ OH radical ↑

$$SO_{2(g)} + OH_{(g)} \rightarrow H_2SO_4 + HO_2$$

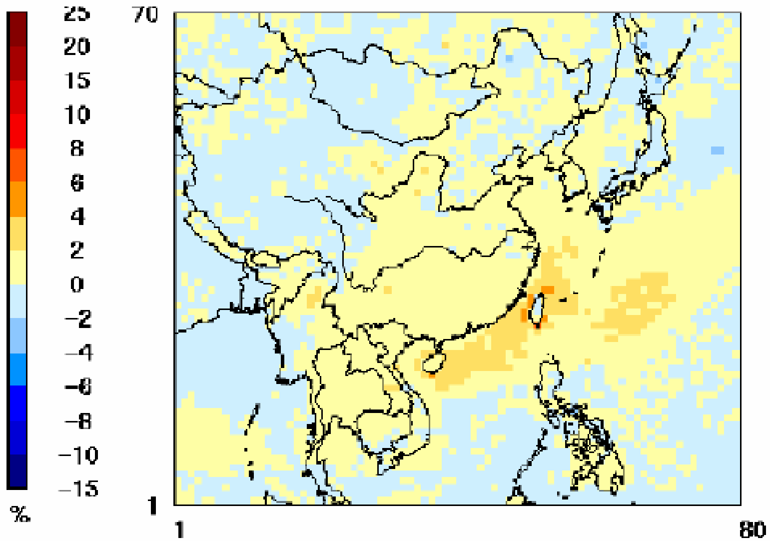
→ Sulfate deposition ↑

$$NH_3 + H_2SO_4 \Leftrightarrow (NH_4)HSO_4$$

$$NH_3 + (NH_4)HSO_4 \Leftrightarrow (NH_4)_2SO_4$$

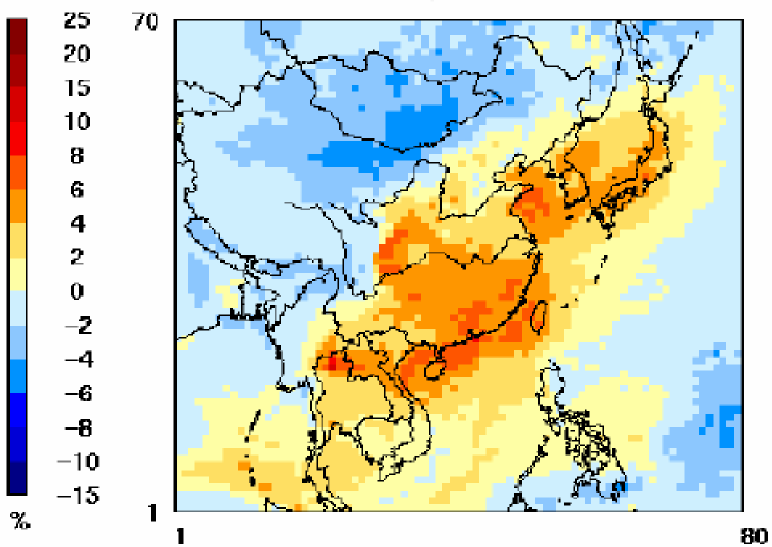
Departure from Linearity for 25RM_SO_2_NO_x

(a) TOXS (SumSR/Base - 25%)



Annual Averaged

(b) TOXN (SumSR/Base -25%)



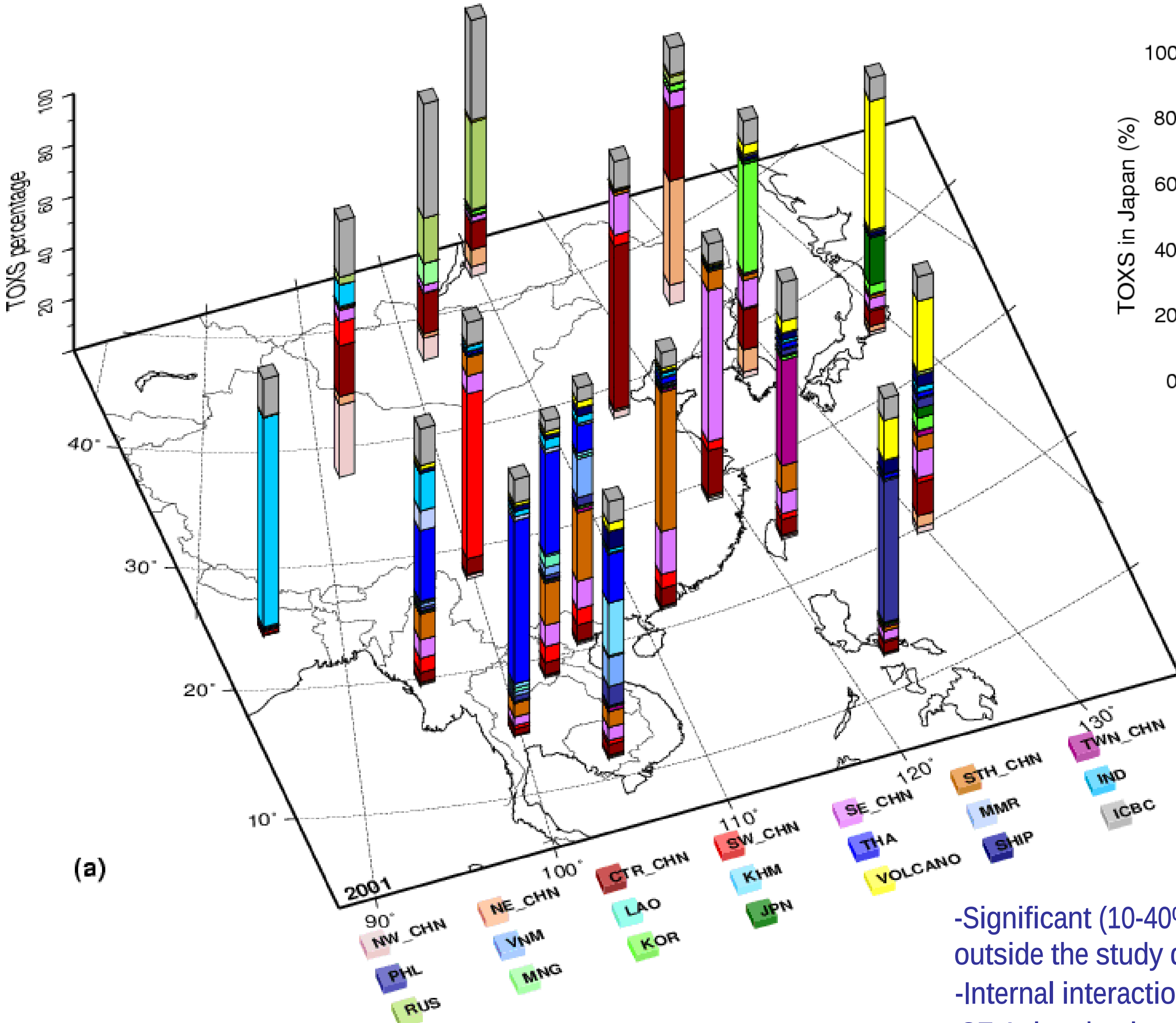
Findings:

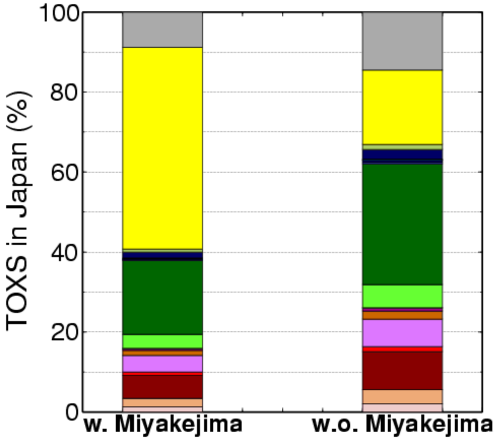
- Departure from linear behavior depend on the extent of emission perturbation
- The reduction of **ammonia** show the **largest non-linear effects** on the deposition of reactive nitrogen

Proposal: 25RM_SO_2_NO_x

- Departure from linearity at most areas are generally lower than 2% for sulfur, and lower than 5% for reactive nitrogen.
- **Realistic** increase/reduction of **combustion related** SO_2 and NO_x
- **Large enough** emission changes for **model response**

4.2 Results and Discussions: Source receptor relationships for sulfur in 2001





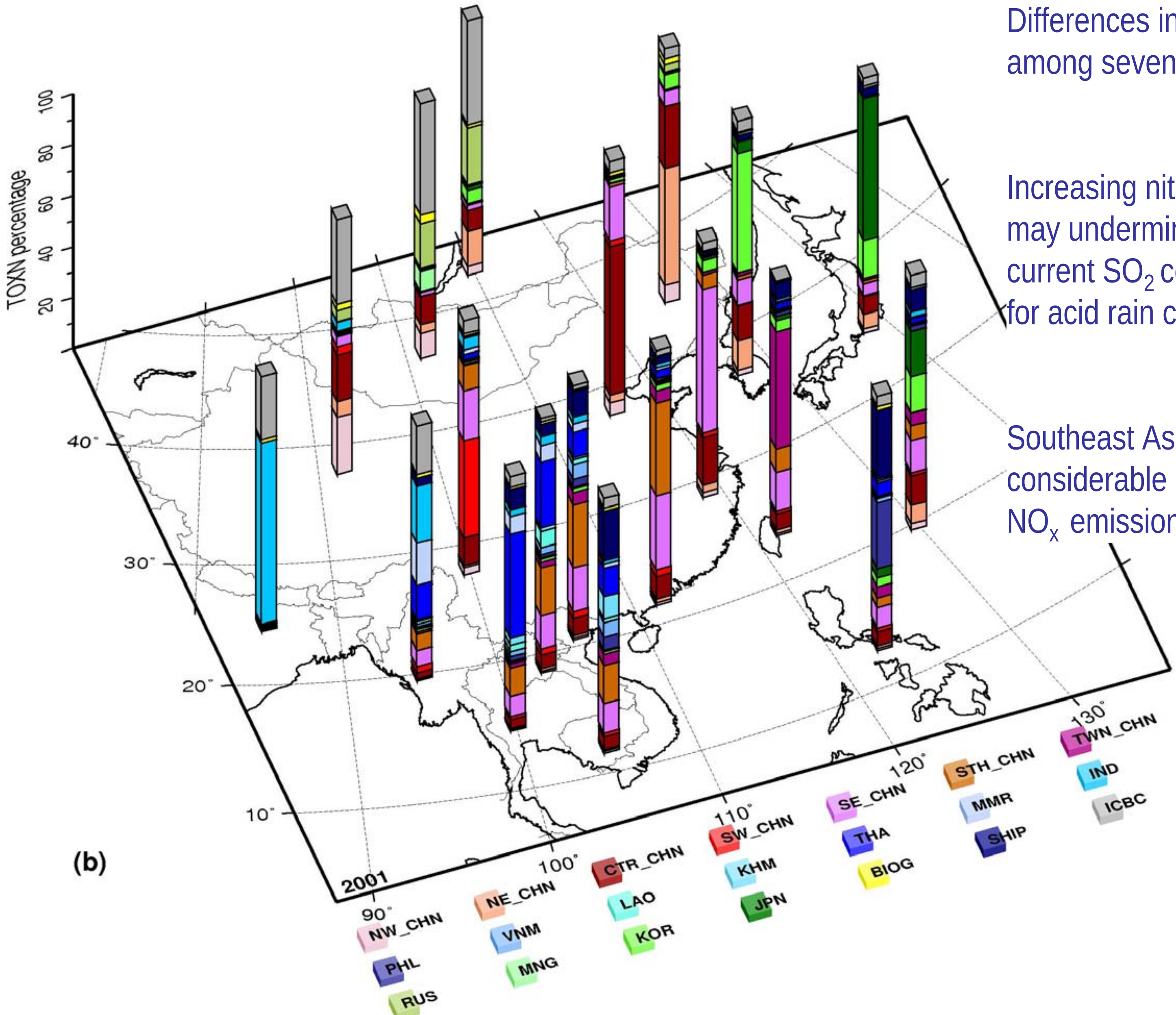
Sources of sulfur deposition in Japan (%) with and without Miyakejima

-Significant (10-40%) contribution from regions outside the study domain

-Internal interactions in China

-SE Asia: dominated by Thailand and South China

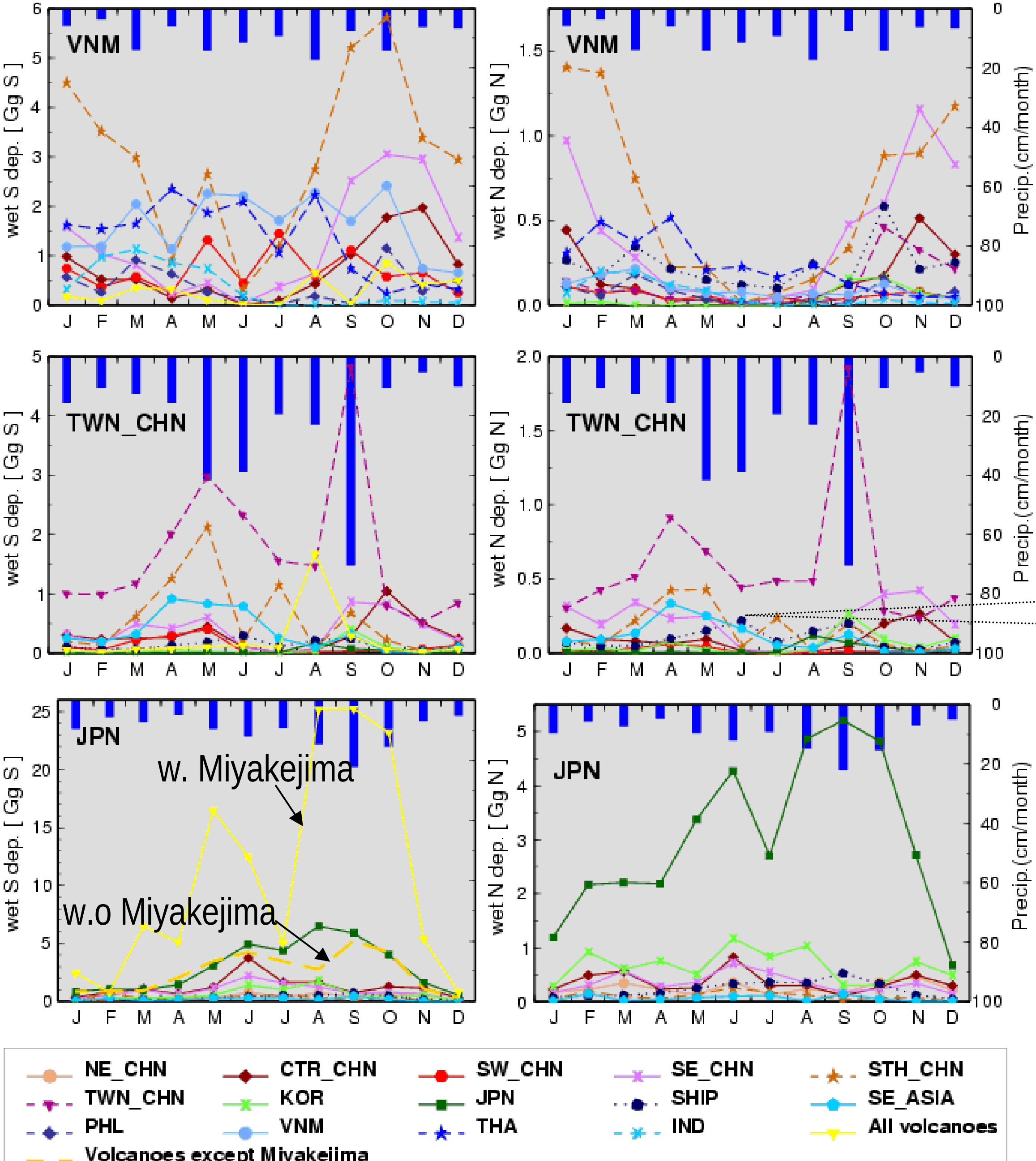
4.2 Results and discussions: source receptor relationships for reactive nitrogen in 2001



Differences in internal relationships among seven source regions of China

Increasing nitrate in rainwater may undermine the success of current SO_2 control strategies for acid rain controlling zone of China

Southeast Asia:
considerable contribution of NO_x emissions from international shipping



- Consider wet deposition alone
- Strong seasonal variation reflecting the Asian monsoon circulation

  wet scavenging + prevailing winds

- Maximum effects of long-range transport during the dry season
- Southeast Asia: Biomass burning sources and northeastward transport in spring time
- Sources of acid deposition in Japan

  -- Volcanic sources dominate total sulfur wet deposition in Japan

  -- High production of aerosol nitrate in central Japan

Sulfur sources over Japan (%)

References	Year	China	N-S Korea	Japan	Volcano
Huang et al.(1995)	1989	3.5	2[a]	93[b]	-
Ichikawa and Fujita (1995)	1990	(45)	(16)	(33)	20
Ichikawa et al.(1998)	1990	25.0	16	40	18
Ardnt et al.(1998)	1990	(17)	(14)	-	
Calori et al.(2001)	1997	36.0	12	-	
This study[c]	2001	15.4(31)	3.5(7)	18.4(37.2)	50.4

quoted values for anthropogenic sulfur only

[a]South Korea only
[b]Combined contribution from anthropogenic and volcanic sources in Japan
[c] Boundary contribution in this stusy is (8.9)17.8%

- JPN → a remarkable contribution of Miyakejima volcano in the year 2001
- JPN → a considerable inflow of sulfur compounds from regions outside of the study domain
- The results obtained in this study are more realistic

Sulfur sources over Vietnam (%)

References	Year	China	Vietnam	Thailand	Boundary	Shipping
Ardnt et al.(1998)	1990	40	36	19	-	-
Engardt et al.(2005)	2000	38[a]	41	7	9	1
This study[b]	2001	51.4	15.3	10.5	5.3	3.0

[a]Parts of Southern China only
[b] Other noticeable (⩾ 2.0%) contributors are IND (2.9%), PHL (3.3%), and volcano (2.5%)

- VNM→ more effects of long-range transport in Eulerian models as contrast to simple Lagrangian model

Source-receptor relationships of total reactive nitrogen in East Asia

Receptors →	Taiwan		N-S Korea		Japan		China	
Sources ↓	This study	ATMOS-N	This study	ATMOS-N	This study	ATMOS-N	This study	ATMOS-N
Taiwan	46.0	80	1.1	-	0.9	2	1.6	2
N-S Korea	4.2	-	46.9	61.5^a	14.9	15^a	2.6	1^a
Japan	1.8	1	4.6	2.5^b	55.7	65	0.5	-
China	34.1	18	39.1	36^b	20.6	18	79.7	90
SE Asia	6.6	-	0.6	-	0.6	-	4.0	-
Shipping	6.5	-	2.1	-	3.4	-	1.1	-
Boundary	0.6	-	4.3	-	2.7	-	8.1	-

a. Taken as combined contribution from emissions in South and North Korea

b. Taken as averaged contribution to deposition in South Korea and deposition in North Korea

Lagrangian ATMOS-N, Holloway et al, 2002

- Domestic emissions are the primary sources of nitrogen deposition in the receptors shown in the table
- This study shows more long-range transport effects from foreign sources by using a 3-D Eulerian model as contrast to the simple Lagrangian models

Conclusions

- The model successfully reproduces the magnitudes, daily, and diurnal variations of SO_2 mixing ratios especially with 27-km grid spacing. Main uncertainty of SO_2 predictions is caused by the representation of model topography and sub-grid variation of emissions in urban areas, which may not be resolved in the coarse 81-km grid resolution.

- Integrated analysis using satellite measurements and ground-based monitoring suggests that
  -- Soil-biogenic NO emission from grasslands/scrubland/desert in the middle-latitudes are likely underestimated during the wet season.
  -- Anthropogenic NO_x emissions in winter are likely under-estimated in by 50% over central eastern China and by 25% over Japan

- The photochemical production of O_3 in summer over central eastern China and central Japan is highly sensitive to the chemical mechanisms applied in CMAQ. The CBIV simulation with 27-km grid resolution gives the best agreement against observation data. The SAPRC99 simulation with 81-km grid resolution largely over-predicts the observed O_3 in central Japan especially on low ozone days .

- Reduction of ammonia emissions has significant non-linear effects on the thermodynamic equilibrium between nitric acid and aerosol nitrate. A source region attribution methodology is proposed perturbing SO_2 and NO_x for the calculation of source-receptor relationships for sulfur and reactive nitrogen.

Conclusions (continued)

- Sulfur inflows from regions outside the study domain are pronounced (10~40%) over different parts of Asia. Compared with previous studies using simple Lagrangian models, S/R relationships of reactive nitrogen derived in this study firstly using a complex 3-D Eulerian model, indicate higher influence from long-range transport. The estimated S/R relationships are believed to be more realistic since they include the global influences and internal interactions among different parts of China

Connections to MICS-Asia Phase II

- This study follows the general intercomparison framework of MICS-Asia Phase II, but the model evaluation provides additional information such as the use of GOME data to evaluate NOx emissions, the influence of hourly varying BC , and the photochemical sensitivity of ozone production.

- This study have estimated S/R relationships for sulfur and reactive nitrogen using the state-of-the-art 3-D Eulerian model. This provides an important connection between the focuses of MICS Phase I and Phase II. The analysis shows that the influence of aerosol chemistry to predicted S/R relationships is significant.

Thank you
for your attention!