

# Global and Regional Impacts of HONO on the Chemical Composition of Clouds and Aerosols

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## Introduction

- HONO photolysis is an important source of the OH radical, the primary oxidant of the atmosphere, responsible for the removal of most reactive gases.
- Owing to the incomplete knowledge of HONO sources, realistic HONO mechanisms have not yet been implemented in global models.
- Recently, realistic simulation of HONO based on a HONO/NO<sub>x</sub> ratio of 0.02 was found to have a significant impact on the global budgets of HO<sub>x</sub> (OH+HO<sub>2</sub>) and secondary oxidation products, especially in winter (Elshorbany et al., 2012).
- Underestimation of sulphate aerosols has been reported by several studies, especially during winter, which was attributed to missing oxidation pathways.
- Enhanced H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> as a result of realistic HONO simulations may improve aerosol simulations in high NO<sub>x</sub> regions.

## Aim of the Work

- Investigate the impact of simulating realistic HONO levels on aerosol and cloud compositions under different conditions, both on regional and global scale.

## Modelling Approach

ECHAMv5.3.01/MESy v2.42 Atmospheric Chemistry (EMAC) model (Jöckel et al., 2005, 2006, 2010):

### Reference runs (Base\_#):

- Base\_S1:** Simulation Period: 2000-2001  
Resolution: T42L31MA (about 2.8°×2.8°)  
HONO chemistry: default setup, only HONO pss.
- Base\_S2:** as Base\_S1 except SCAV=EASY, no aqueous phase chemistry.
- Base\_S3:** as Base\_S1 except SO<sub>2</sub>+OH=DUMMY, no H<sub>2</sub>SO<sub>4</sub> production.

### Sensitivity runs (S\_#):

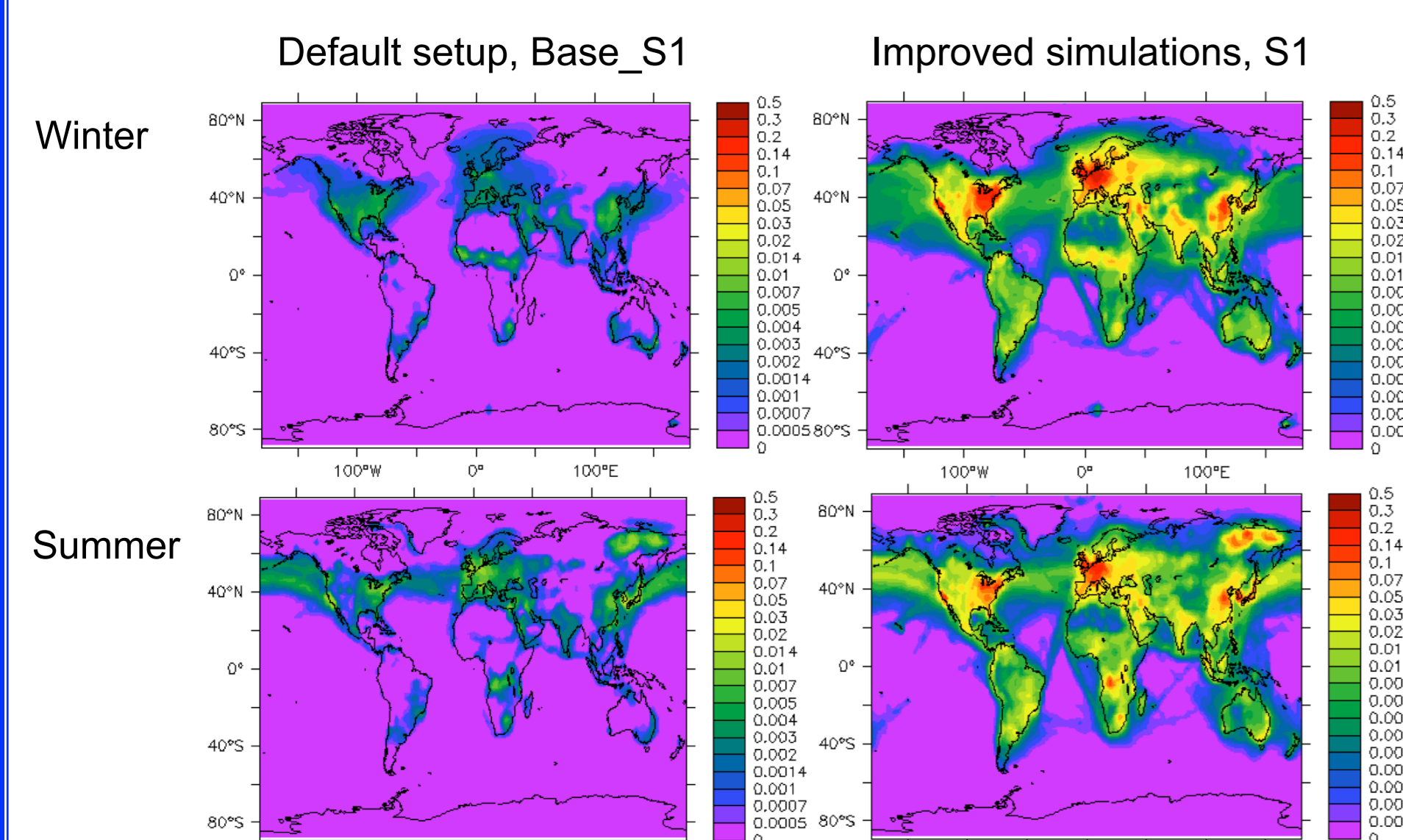
- S1:** as Base\_S1 except HONO: Iterative correction of HONO/NO<sub>x</sub> ratio=0.02 with integration time set to 1 min.
- S2:** as S1 except SCAV=EASY, no aqueous phase chemistry.
- S3:** as S1 except SO<sub>2</sub>+OH=DUMMY, no H<sub>2</sub>SO<sub>4</sub> production.

## Measurement Networks

The simulated aerosol concentrations are compared with:  
CASTNET (54 station): North America  
EMEP (81 station): Europe  
EANET (10 station): Asia

## Results and Discussion

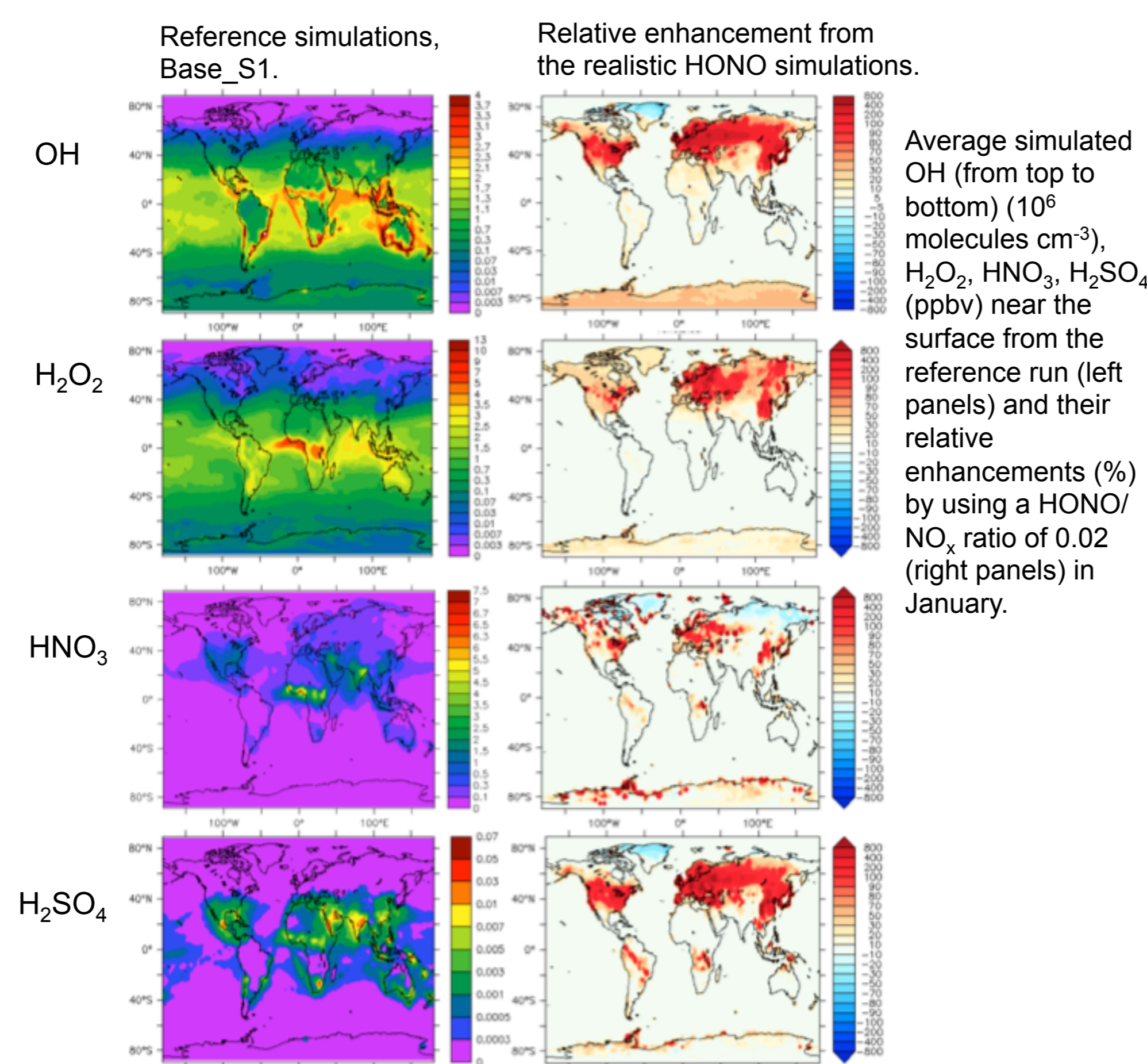
### Realistic HONO simulations



Simulated monthly average HONO mixing ratios (ppbv) from the reference run (Base\_S1, left) and the sensitivity run (S1, i.e., using a HONO/NO<sub>x</sub> ratio of 0.02) near the surface in January (upper panels) and July (lower panels).

- Simulated HONO levels are about tenfold higher than the base scenario, which considers the known gas phase formation (OH+NO→HONO) as a sole source of HONO, in agreement with previous measurement-modelling studies (Elshorbany et al., 2012).

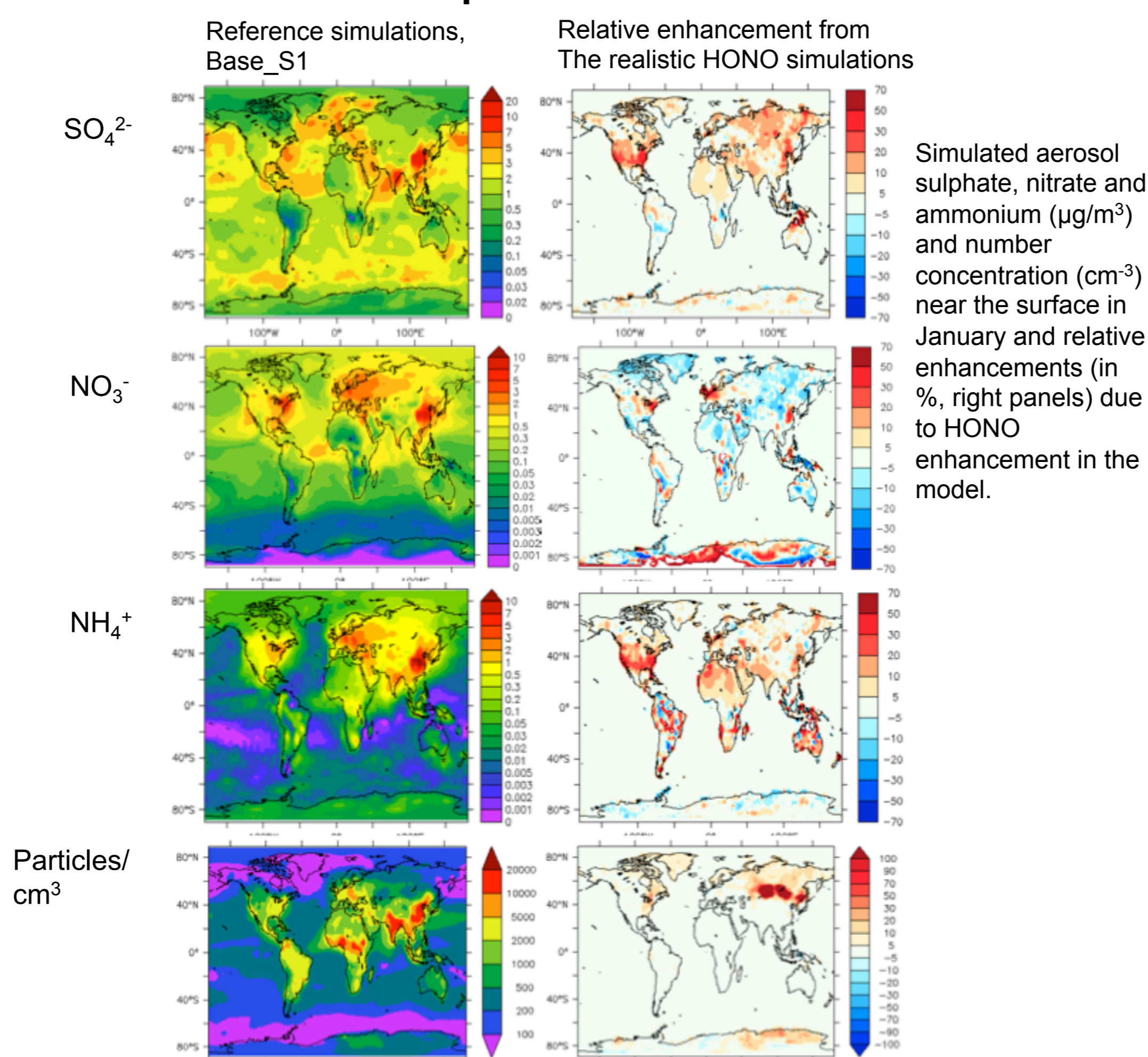
### HO<sub>x</sub> and secondary oxidation products



- HO<sub>x</sub>, H<sub>2</sub>O<sub>2</sub>, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> are enhanced in high NO<sub>x</sub> regions as a result of simulating realistic HONO levels, especially in winter, when other photolytic sources are of minor importance.

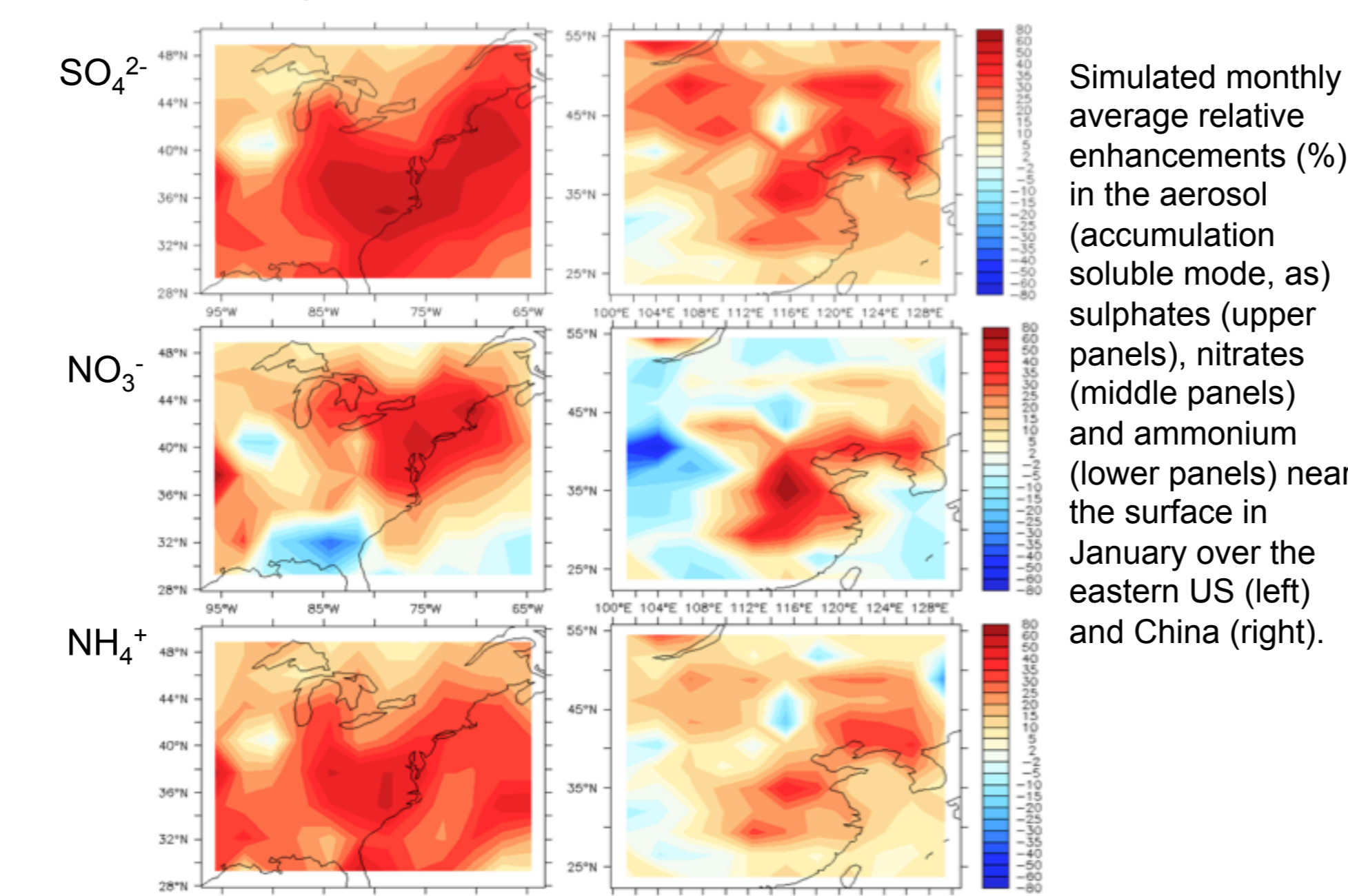
### Aerosol composition

#### Global Impact



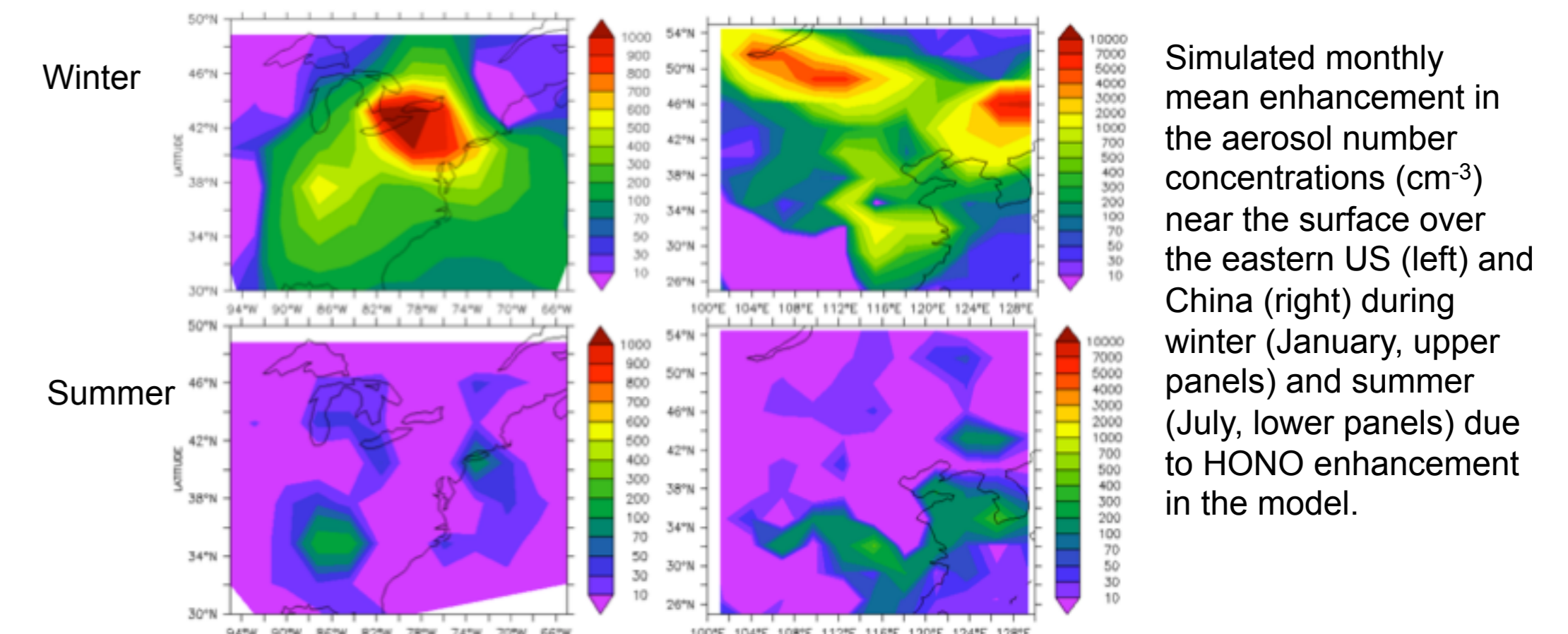
- Sulphates:** Enhanced in high NO<sub>x</sub>, high NH<sub>4</sub> regions and mainly due to enhanced OH+SO<sub>2</sub> reaction. H<sub>2</sub>O<sub>2</sub> oxidation of S(IV) did not contribute to enhanced SO<sub>4</sub><sup>2-</sup> (→ S(IV) limited conditions except in E. Asia).
- Nitrates:** Enhanced due to:
  - Enhanced HNO<sub>3</sub> in high NO<sub>x</sub>, high NH<sub>4</sub> regions.
  - Due to enhanced N<sub>2</sub>O<sub>5</sub> hydrolysis on sulphate aerosol particles in high NH<sub>4</sub><sup>+</sup> regions.
  - Enhanced SO<sub>4</sub><sup>2-</sup> in limited NH<sub>4</sub> regions may decrease NO<sub>3</sub><sup>-</sup> levels.
- Aerosol number concentrations:** Enhanced in high NO<sub>x</sub>, high NH<sub>4</sub> regions and mainly due to enhanced H<sub>2</sub>SO<sub>4</sub>.

### Regional Impact



- Sulphates:** In eastern US, sulphates are significantly enhanced with OH+SO<sub>2</sub>→H<sub>2</sub>SO<sub>4</sub> reaction being more important than H<sub>2</sub>O<sub>2</sub> oxidation of S(IV) as a result of realistic HONO simulations.
- Nitrates:** is enhanced in high NO<sub>x</sub>, high NH<sub>4</sub><sup>+</sup> regions but are reduced in NH<sub>4</sub><sup>+</sup> limited regions.

### Aerosol number concentrations



- Maximum relative enhancements are calculated during the winter season with an increase of 10<sup>4</sup> cm<sup>-3</sup> in eastern China, about one order of magnitude higher than that over the eastern US.

| aerosol mode  | run | aerosol number concentration |      |                            |      |
|---------------|-----|------------------------------|------|----------------------------|------|
|               |     | eastern US <sup>1</sup>      |      | eastern China <sup>2</sup> |      |
|               |     | cm <sup>-3</sup>             | % *  | cm <sup>-3</sup>           | % *  |
| total aerosol | S1  | 2032                         | 10   | 5520                       | 11   |
|               | S3  | 1956                         | -0.3 | 5438                       | -0.1 |
| ns            | S1  | 8.51                         | 681  | 10.4                       | 5131 |
|               | S3  | 7.59×10 <sup>-4</sup>        | 48   | 1.07×10 <sup>-3</sup>      | -37  |
| ks            | S1  | 552                          | 44   | 825                        | 31   |
|               | S3  | 358                          | 2    | 550                        | 1    |
| as            | S1  | 235                          | 27   | 567                        | 14   |
|               | S3  | 148                          | 1    | 369                        | 2    |
| cs            | S1  | 1.40                         | 0.6  | 2.61                       | -2   |
|               | S3  | 1.33                         | 0.2  | 2.70                       | -4   |
| ki            | S1  | 1235                         | -13  | 4075                       | -6   |
|               | S3  | 1448                         | -1   | 4472                       | -1   |
| ai            | S1  | 5.97×10 <sup>-3</sup>        | -38  | 33.9                       | 2    |
|               | S3  | 1.15×10 <sup>-1</sup>        | -2   | 39.1                       | 2    |
| ci            | S1  | 1.08×10 <sup>-3</sup>        | -30  | 2.74                       | 2    |
|               | S3  | 5.73×10 <sup>-3</sup>        | -1   | 3.10                       | 1    |

\*) Relative enhancement as a result of simulating realistic HONO levels (S1 run). Abbreviations "ns, ks, as and cs" refer to nucleation, Aitken, accumulation and coarse soluble aerosol modes, respectively, while "ki, ai and ci" refer to the corresponding insoluble modes. Data are averaged over the eastern 1) US (95-65°W, 30-50°N) and 2) China (100-130°E, 25-55°N).

### Aerosol number concentrations:

- Dominated by the ks and as modes (→ typical surface distribution).
- Mean relative enhancement over E. US and E. China is 10-11%.
- Enhancements are accompanied by Hydrophobic-to-Hydrophilic transformation related mainly to the enhanced condensation of gas phase H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> on aerosol particles.

### Comparison with Measurements

Summary of the comparison of the Base\_S1 and S1 model simulations to observations of aerosol concentrations during January-March 2001. OAM and MAM are the arithmetic mean of the observations and of the model, respectively, in µg m<sup>-3</sup>. MAM and OAM represent co-located measurements and model results (i.e., based on the locations of the observations).

| species                       | network | Nr. of stations | OAM  | MAM [µg m <sup>-3</sup> ] |      | MAM/OAM |      |
|-------------------------------|---------|-----------------|------|---------------------------|------|---------|------|
|                               |         |                 |      | base_S1                   | S1   | base_S1 | S1   |
| SO <sub>4</sub> <sup>2-</sup> | CASTNET | 53              | 3.17 | 2.57                      | 3.05 | 0.81    | 0.96 |
|                               | EMEP    | 80              | 2.00 | 2.95                      | 3.09 | 1.48    | 1.55 |
|                               | EANET   | 11              | 2.82 | 2.89                      | 3.13 | 1.03    | 1.11 |
| NO <sub>3</sub> <sup>-</sup>  | CASTNET | 53              | 1.27 | 1.81                      | 1.97 | 1.43    | 1.55 |
|                               | EMEP    | 27              | 1.75 | 2.24                      | 2.42 | 1.28    | 1.38 |
|                               | EANET   | 10              | 0.81 | 1.26                      | 1.14 | 1.55    | 1.41 |
| NH <sub>4</sub> <sup>+</sup>  | CASTNET | 53              | 1.26 | 1.23                      | 1.43 | 0.98    | 1.14 |
|                               | EMEP    | 21              | 1.00 | 1.43                      | 1.54 | 1.43    | 1.54 |
|                               | EANET   | 9               | 0.96 | 0.96                      | 1.02 | 1.01    | 1.07 |

- General increase in the Mean modelled/observed ratio.
- Simulating realistic HONO levels improve the sulphates modelled/observed ratios in eastern US.
- Nitrates modelled/observed ratios are improved in E. Asia.
- Ammonium are generally well simulated.

## Conclusion

### Simulating Realistic HONO levels lead to:

- Enhanced HO<sub>x</sub>, H<sub>2</sub>O<sub>2</sub>, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> in high NO<sub>x</sub> regions, especially in winter, when other photolytic sources are of minor importance.
- Enhanced sulphate aerosol mainly due to enhanced oxidation of SO<sub>2</sub> with OH. Though H<sub>2</sub>O<sub>2</sub> oxidation is the main source of sulphates, it did not contribute to enhanced SO<sub>4</sub><sup>2-</sup> due to the S(IV) limited conditions in most regions except in E. Asia.
- Enhanced Nitrates due to enhanced HNO<sub>3</sub>, in ammonia-rich regions.
- Enhanced aerosol number concentration accompanied with transformations from hydrophobic to hydrophilic. The enhancement of aerosol number and solubility implies potential impacts on the cloud nucleation properties and the particle lifetime.

## References

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