Parameterization of N_2O_5 Reaction Probabilities for Inclusion in CMAQ

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In partnership with the National Exposure Research Laboratory, U.S. Environmental Protection Agency

OBJECTIVES

- Develop a comprehensive parameterization for the heterogeneous reaction probability of N_2O_5, γ, as a function of temperature (T), relative humidity (RH), particle composition, and phase state, using:
  - all of the available laboratory measurements of γ on ammoniated sulfate and nitrate particles at tropospheric T and RH conditions; and
  - rigorous statistical methods (e.g., significance test of each independent variable, weighting of each data point by the measurement uncertainty, defining extrapolation limits).
- Consider the effects of
  - phase changes (i.e., crystallization and ice formation), such that γ on aqueous particles exceeds that on solid particles;
  - particle acidity, by comparing laboratory data on NH_4HSO_4 with data on $(NH_4)_2SO_4$; and
  - nitrate, by comparing our parameterizations on $(NH_4)_2SO_4$ and NH_4NO_3.
- Over a broad range of atmospherically-relevant conditions, compare our final parameterization with others that have been used in air quality models.
- Identify critical data gaps in the laboratory data that will be most valuable for future refinements of the γ parameterization.

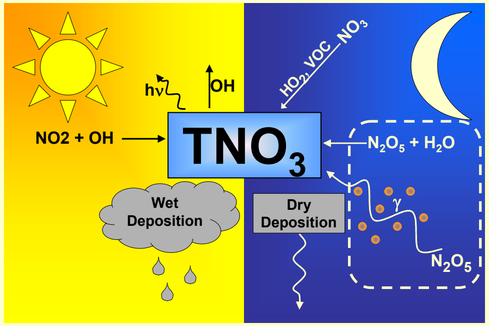

Figure 1. Total nitrate ($TNO_3 \equiv HNO_3 + NO_3^-$) formation and removal pathways.

LABORATORY DATA

We used all of the published laboratory measurements of γ on ammoniated sulfate and nitrate particles at T and RH conditions relevant to the troposphere. These data are documented by Mozurkewich and Calvert (1988), Hu and Abbatt (1997), Folkers (2001), Kane et al. (2001), Folkers et al. (2003), Hallquist et al. (2003), Badger et al. (2006). For brevity, these documents are referred to hereafter as MOZ88, HU97, FOL01, KAN01, FOL03, HAL03, and BAD06, respectively. A total of 78 data points are used to develop the regression models.

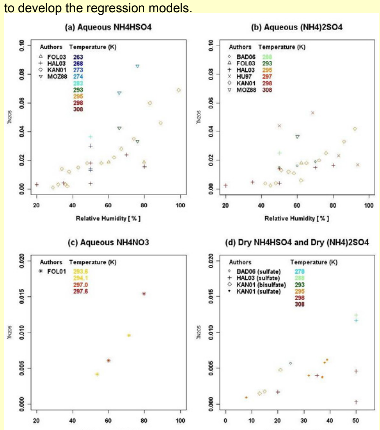

Figure 2. Laboratory measurements of γ used to develop the parameterizations.

PARAMETERIZATIONS

Using the laboratory data shown in Figure 2, we developed a parameterization for the heterogeneous reaction probability of N_2O_5 as a function of RH, T, particle composition, and phase state. For details on the development of these equations, please see the extended abstract. The final parameterization is summarized below with coefficients given in Table 1 and subscripts defined as follows:

1 = $NH_4HSO_{4\,(aq)}$
2 = $(NH_4)_2SO_{4\,(aq)}$
3 = $NH_4NO_{3\,(aq)}$
d = dry NH_4HSO_4 and $(NH_4)_2SO_4$

$$\gamma_i = \frac{1}{1+e^{-\lambda_i}} \quad i = 1, 2, 3, \mathrm{d}$$

where

$$\lambda_1 = \beta_{10} + \beta_{11}RH + \beta_{12}T_{287}$$
$$\lambda_2 = (\beta_{10} + \beta_{20}) + \beta_{11}RH + \beta_{12}T_{287}$$
$$\lambda_3 = \beta_{30} + \beta_{31}RH$$
$$\lambda_d = \beta_{d0} + \beta_{d1}RH + \beta_{d2}T_{293}$$

and

$$T_j = \begin{cases} T-j & T > j \\ 0 & T \le j \end{cases}$$

Constraints are applied to prevent extrapolations beyond the maximum laboratory measurement:

$$\gamma_1^* = \min(\gamma_1, 0.08585)$$
$$\gamma_2^* = \min(\gamma_2, 0.053)$$
$$\gamma_3^* = \min(\gamma_3, 0.0154)$$
$$\gamma_d^* = \min(\gamma_2, 0.0124)$$

For atmospheric applications:

$$\gamma_{ambient} = \begin{cases} \gamma_{d,mix} & RH < CRH \\ \gamma_{ice,mix} & RH > IRH \\ \gamma_{aq,mix} & otherwise \end{cases}$$

where

$$\gamma_{aq,mix} = \sum_{i=1}^{3} x_i \gamma_i^*$$
$$\gamma_{d,mix} = (x_1 + x_2)\gamma_d^* + x_3 \cdot \min(\gamma_d^*, \gamma_3^*)$$
$$\gamma_{ice,mix} = 0.02$$

and

$$x_1 = 1 - (x_2 + x_3)$$
$$x_2 = \max\left(0, \min\left(1 - x_3, \frac{A}{N+S} - 1\right)\right)$$
$$x_3 = \frac{N}{N+S}$$

A, *S*, and *N* are molar concentrations of NH_4^+, SO_4^{2-}, and NO_3^-, respectively.

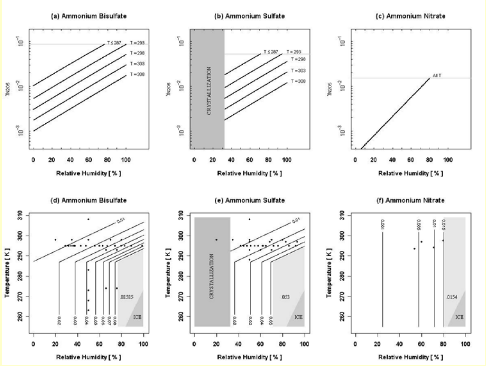

Figure 3. Parameterization of γ on aqueous particles as a function of RH and T. Discrete points in (d-f) show combinations of T and RH at which laboratory measurements were collected.

	Estimate	Std. Error	t value	Pr(>|t|)	
β_{10}	-4.559088	0.212216	-21.483	< 2e-16	***
β_{20}	-0.369769	0.10007	-3.695	0.000508	***
β_{11}	0.028593	0.003074	9.3	7.02E-13	***
β_{12}	-0.111201	0.016155	-6.883	5.86E-09	***
β_{30}	-8.107744	0.199409	-40.66	0.000604	***
β_{31}	0.049017	0.002901	16.89	0.003485	**
β_{d0}	-6.133764	0.1656	-37.04	9.62E-14	***
β_{d1}	0.03592	0.004328	8.3	2.57E-06	***
β_{d2}	-0.196879	0.028148	-6.994	1.45E-05	***

Significance Codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Table 1. Coefficients of the regression equations.

ATMOSPHERIC ESTIMATES of γ

WINTER (Jan – Feb, 2001)

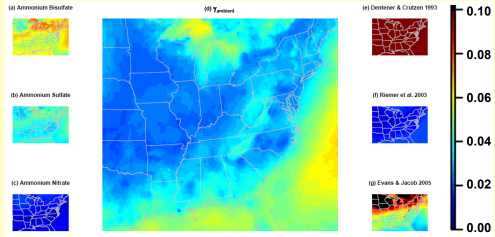

Figure 4. Average winter nighttime γ values at 75 – 150m above surface, comparing (a-d) our parameterizations with (e-g) those used in previous model applications.

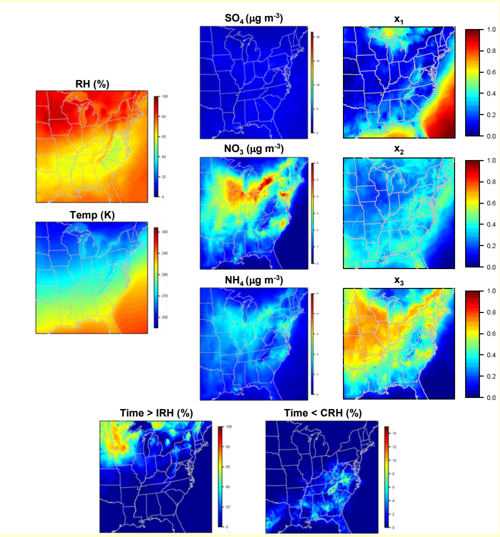

Figure 5. Input fields for Figure 4 calculations, from CMAQ v4.6 at 12km.

SUMMER (Jul – Aug, 2001)

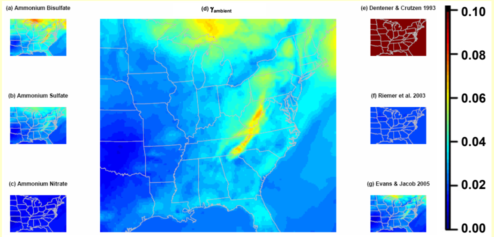

Figure 6. Average summer nighttime γ values at 75 – 150m above surface, comparing (a-d) our parameterizations with (e-g) those used in previous model applications.

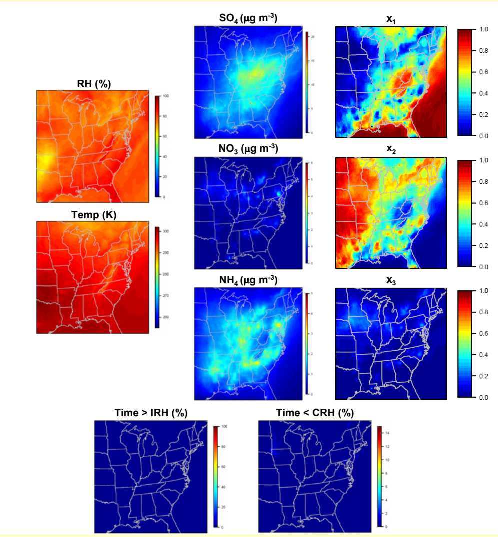

Figure 7. Input fields for Figure 6 calculations, from CMAQ v4.6 at 12km

CONCLUSIONS

- Developed a robust parameterization for γ as a function of T, RH, particle composition, and phase state, which can be incorporated into CMAQ.
- Parameterization reproduces 79% of the laboratory data within a factor of 2 and 53% within a factor of 1.25.
- Nitrate effect is quantified as only a factor of 1.4 – 4.4, rather than the factor of 10 proposed previously by Riemer et al. (2003).
- Parameterization captures the ~50% enhancement of γ on acidic NH_4HSO_4 particle surfaces relative to that on $(NH_4)_2SO_4$ surfaces.
- Parameterization of γ on aqueous particles exceeds that on solid particles. This is the first γ parameterization in which phase changes are considered explicitly.
- Our parameterization yields slightly larger values of γ than have been estimated during intensive summertime field campaigns (e.g., NEAQS, ICARTT).
- During winter, large differences between our parameterization and Evans & Jacob (2005) arise from different extrapolations of the available laboratory data into typical winter conditions.
- Future improvements to our γ parameterization will require laboratory measurements at the low-T and high-RH conditions typical of winter.

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DISCLAIMER. The research presented here was performed under the Memorandum of Understanding between the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Commerce's National Oceanic and Atmospheric Administration (NOAA) and under agreement number DW13921548. This work constitutes a contribution to the NOAA Air Quality Program. Although it has been reviewed by EPA and NOAA and approved for publication, it does not necessarily reflect their policies or views.