A comparison of water uptake by aerosols using two thermodynamic models

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1. Introduction

The water uptake by hygroscopic aerosols can significantly alter aerosol size, optical properties and direct radiative forcing. Here we compare the uptake of water by aerosols in EQSAM3[3] with the results of the thermodynamic module EQUISOLV II[2] currently used in our global chemical transport model[1].

2. Model Descriptions

EQSAM3: solves the gas/liquid/solid partitioning analytically based on components' solubility.

EQUISOLV II: solves the gas/liquid/solid partitioning iteratively by using prescribed deliquescent relative humidity (DRH), Multicomponent deliquescent relative humidity (MDRH), water activity data and empirical formulation of activity coefficients.

3. Case Study Results

Initial composition: Sulfate condition	Case No.	TNH_3/TH_2SO_4 mole ratio	TNO_3/TH_2SO_4 mole ratio	$TNaCl/TH_2SO_4$ mole ratio	TK/TH_2SO_4 mole ratio	TCa/TH_2SO_4 mole ratio	TMg/TH_2SO_4 mole ratio
Sulfate Rich	1	0.5	1.0	0	0	0	0
	2	1.0	1.0	0	0	0	0
	3	1.5	0.33	0	0	0	0
	4	1.5	3.0	0	0	0	0
	5	0.5	1.0	0.5	0	0	0
	6	1.0	1.0	0.5	0	0	0
	7	0.5	1.0	0.5	0.04	0.02	0.01
	8	1.0	1.0	0.5	0.04	0.02	0.01
	9	1.5	0.33	0	0.04	0.02	0.01
	10	1.5	3.0	0	0.04	0.02	0.01
Sulfate Neutral	11	2.0	1.0	0	0	0	0
	12	1.5	0.33	0.5	0	0	0
	13	1.5	3.0	0.5	0	0	0
	14	1.5	0.33	0.4	0.04	0.02	0.01
	15	1.5	3.0	0.4	0.04	0.02	0.01
Sulfate Poor	16	2.0	1.0	0.5	0	0	0
	17	2.0	3.0	0.5	0	0	0
	18	1.5	1.0	2.0	0	0	0
	19	2.0	1.0	0.5	0.04	0.02	0.01
	20	1.5	1.0	2.0	0.04	0.02	0.01

[H2SO4] = 20 ug/m³ T = 298.15 K RH = 10, 20, 30, 40, 50, 60, 70, 80, 90, 95

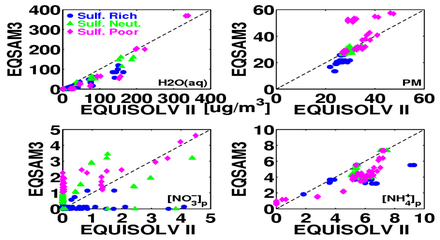


Fig. 1. Scatter plots of aerosol water, total particulate matter, particulate NO_3^- and particulate NH_4^+ predicted from EQSAM3 and EQUISOLV II based on 20 cases at the temperature 298.15K.

- EQSAM3 underestimates total particulate matter by about 2% at RH=30% and 9% at RH=80% and aerosol water by about 45% at RH=80% averaged for all 20 cases.
- The prediction of different solids in the aerosol phase between EQSAM3 and EQUISOLV II and the missing letovicite in EQSAM3 may lead to the discrepancy in the prediction of the total particulate matter together with aerosol water.

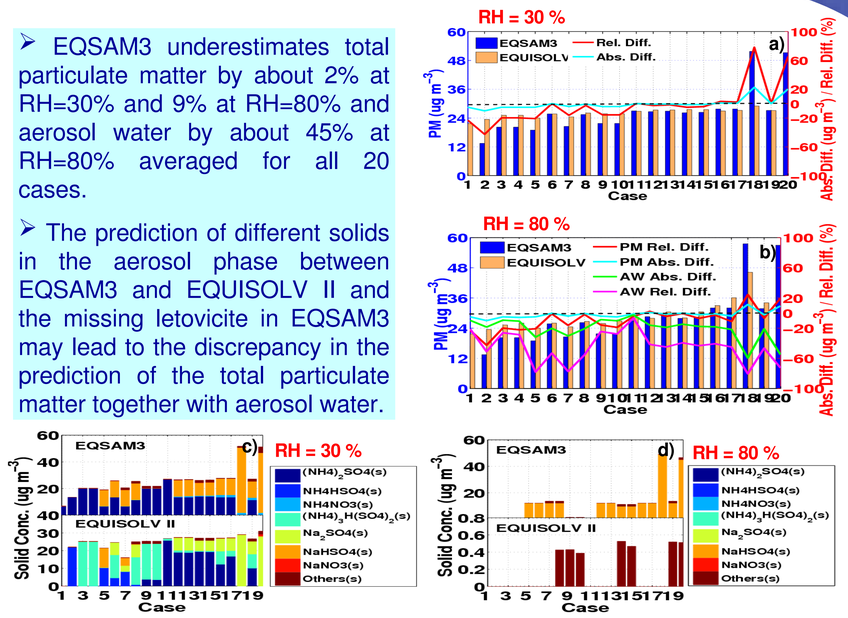


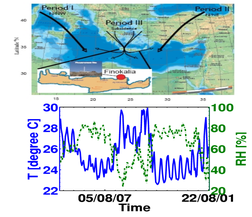
Fig. 2. (a, b) Total particulate matter and calculated absolute/relative difference of particulate matter and aerosol water between EQSAM3 and EQUISOLV II at RH 30% and 80%; (c, d) Major solid predicted by EQSAM3 and EQUISOLV II at RH 30% and 80%.

Compared with EQUISOLV II, EQSAM3:

- underestimates aerosol water and $[NH_4^+]_p$ for almost all cases in all three sulfate regimes and underestimates $[NO3^-]_p$ for almost cases in both sulfate poor and sulfate neutral regimes. $[NO3^-]_p$ is overestimated in the sulfate rich regime.
- predicts a similar amount of total particulate matter in the sulfate rich and sulfate neutral regimes and shows some overestimates in the sulfate poor regime.

4. Comparison during MINOS campaign

MINOS: Over the Eastern Mediterranean in July and August 2001. This region is characterized by a high solar intensity and humid marine air along with polluted air from Europe.



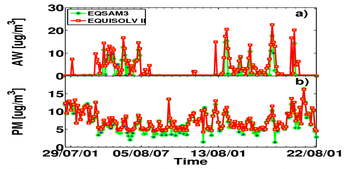


Fig. 3. Time series of aerosol water, total particulate matter from EQSAM3 and EQUISOLV II.

The prediction of aerosol water and particulate matter from EQSAM3 and EQUISOLV II during MINOS campaign agrees well.

- Both models show larger bias in the prediction of $[NO3^-]_p$ at lower temperature, higher relative humidities, higher $[SO4^{2-}]$ and higher molar ratio of TNH4/TSO4.
- EQSAM3 always overestimates while EQUISOLV II almost always underestimates $[NO3^-]_p$.
- EQSAM3 has a larger bias in $[NO3^-]_p$ at the higher temperature and lower relative humidity than does EQUISOLV II.

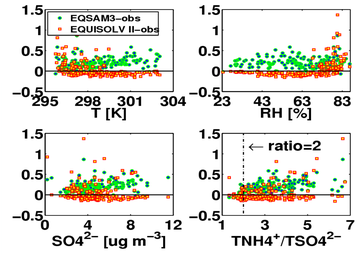


Fig. 4. Difference in the prediction of $[NO3^-]$ between models and observations as a function of temperature, relative humidity, $[SO4^{2-}]$ and molar ratio of TNH4/TSO4.

5. Global Off-line Calculations

Data: aerosol field from Umich-IMPACT-Nitrate model output[1]

- EQSAM3 overestimates the aerosol growth factor over land areas and underestimates the growth factor over the ocean.
- The discrepancy over the Sahara region is consistent with the model performance under the low relative humidities and high temperatures.
- The discrepancy over the ocean might be explained by the difference of the partitioning between HNO3/NO3- and NH3/NH4+ in the two models.

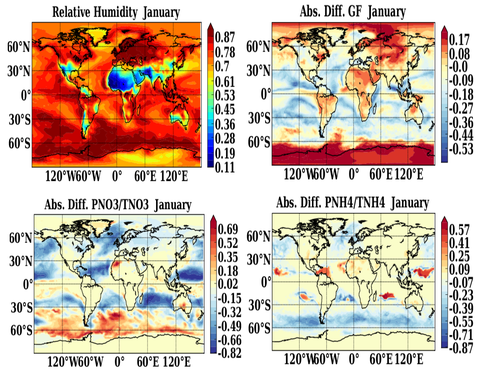


Fig. 5. Global distribution of relative humidity, absolute difference of growth factor and molar ratio of PNO3/TNO3 and PNH4/TNH4 in January.

6. Summary and Future Work

- For 200 arbitrary test cases, EQSAM3 predicts lower aerosol water than that of EQUISOLV II which might be due to the different chemical compounds predicted in the two models and the missing letovicite in EQSAM3.
- EQUISOLV II is in better agreement with the observations during the MINOS campaign.
- The discrepancy between the two models over land areas might be ascribed to the different model performance under the low RH and higher temperatures while that over the ocean might be due to the different partition between gas/solid/liquid.
- A recent EQSAM3e with some improvements is to be compared in near future.

Reference:

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