Comparing the ISORROPIA and EQSAM Aerosol Thermodynamic Options in CAMx

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INTRODUCTION

Atmospheric particulate matter (PM) is a complex mixture of inorganic ions, carbonaceous material, crustal elements, trace metals and water. The inorganic components, which are mainly comprised of sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), sodium (Na^+) and chloride (Cl^-), are important contributors to $PM_{2.5}$ mass globally. Atmospheric PM models typically assume thermodynamic equilibrium to determine partitioning of volatile inorganic components such as NO_3^- and NH_4^+ between the gas and aerosol phases. Among a variety of thermodynamic equilibrium models developed so far, we considered two models in this study:

ISORROPIA

(Nenes *et al.*, 1998; Fountoukis and Nenes, 2007)

- Widely used by regional and global chemical transport models because of its numerical efficiency
- Reduces computational costs by dividing the relative humidity (RH) and composition space into subdomains that minimize the number of equations to be solved
- Iterative solution algorithm for activity coefficients adds to computational cost

EQSAM4clim

(Metzger *et al.*, 2012; 2016)

- Based on a single solute coefficient approach that efficiently parameterizes single solution hygroscopic growth accounting for aerosol water uptake from the deliquescence RH up to supersaturation; extended to treat water uptake for multi-component mixtures
- Analytically solves the gas-aerosol partitioning and the mixed solution water uptake eliminating the need for iterations

The Comprehensive Air quality Model with extensions (CAMx[1]) has been employing ISORROPIA for inorganic aerosol thermodynamic calculations. In this study, we implemented EQSAM4clim in CAMx as an alternative to ISORROPIA, and evaluated model predictions of inorganic $PM_{2.5}$ components and model responses to emission changes by the two models over a continental US modeling domain.

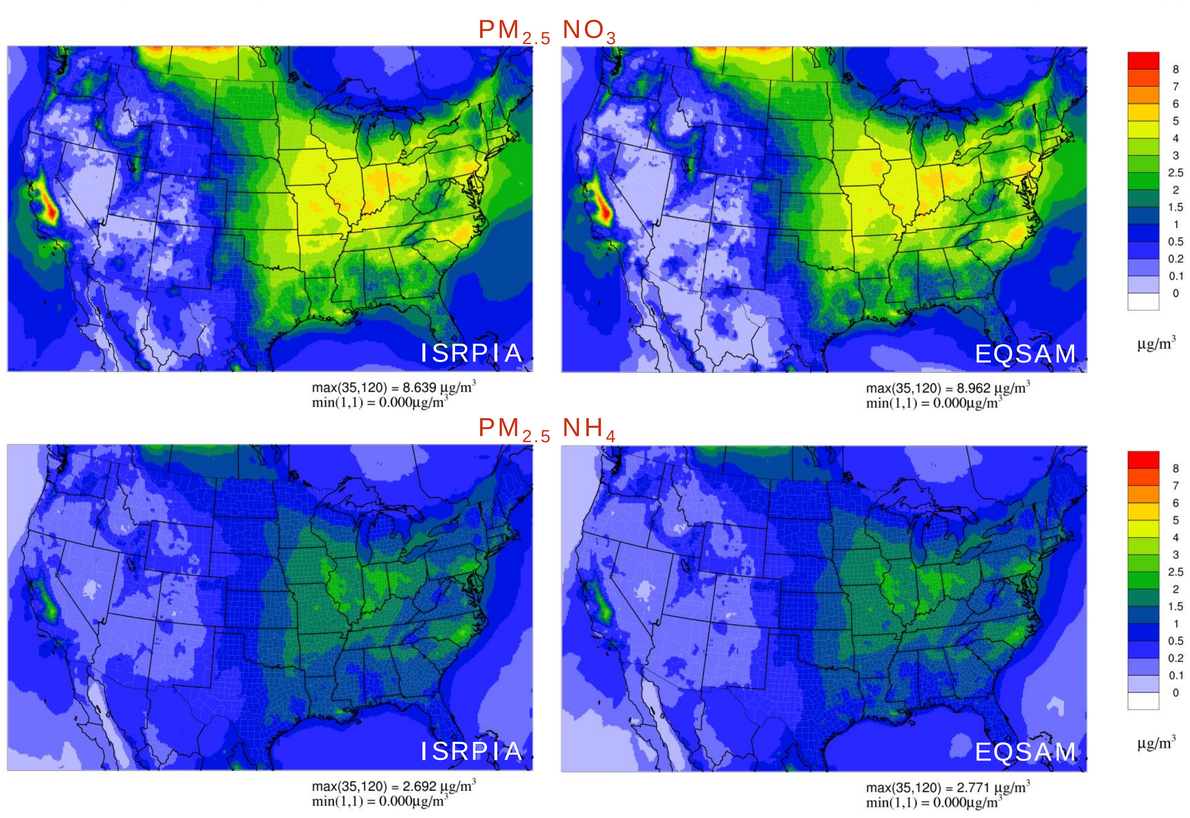
MODELING PLATFORM

- Month-long episodes (Jan & Jul) from a US EPA's 2011 database
- 12-km US modeling domain
- CB6r4 chemistry mechanism
- Both ISORROPIA and EQSAM solve SO_4-NO_3-NH_4-Na-Cl-H_2O system assuming metastable aerosols

[1] www.camx.com

MODEL PREDICTION OF $PM_{2.5}$ COMPONENTS

Monthly Average Concentrations of Nitrate and Ammonium (January)

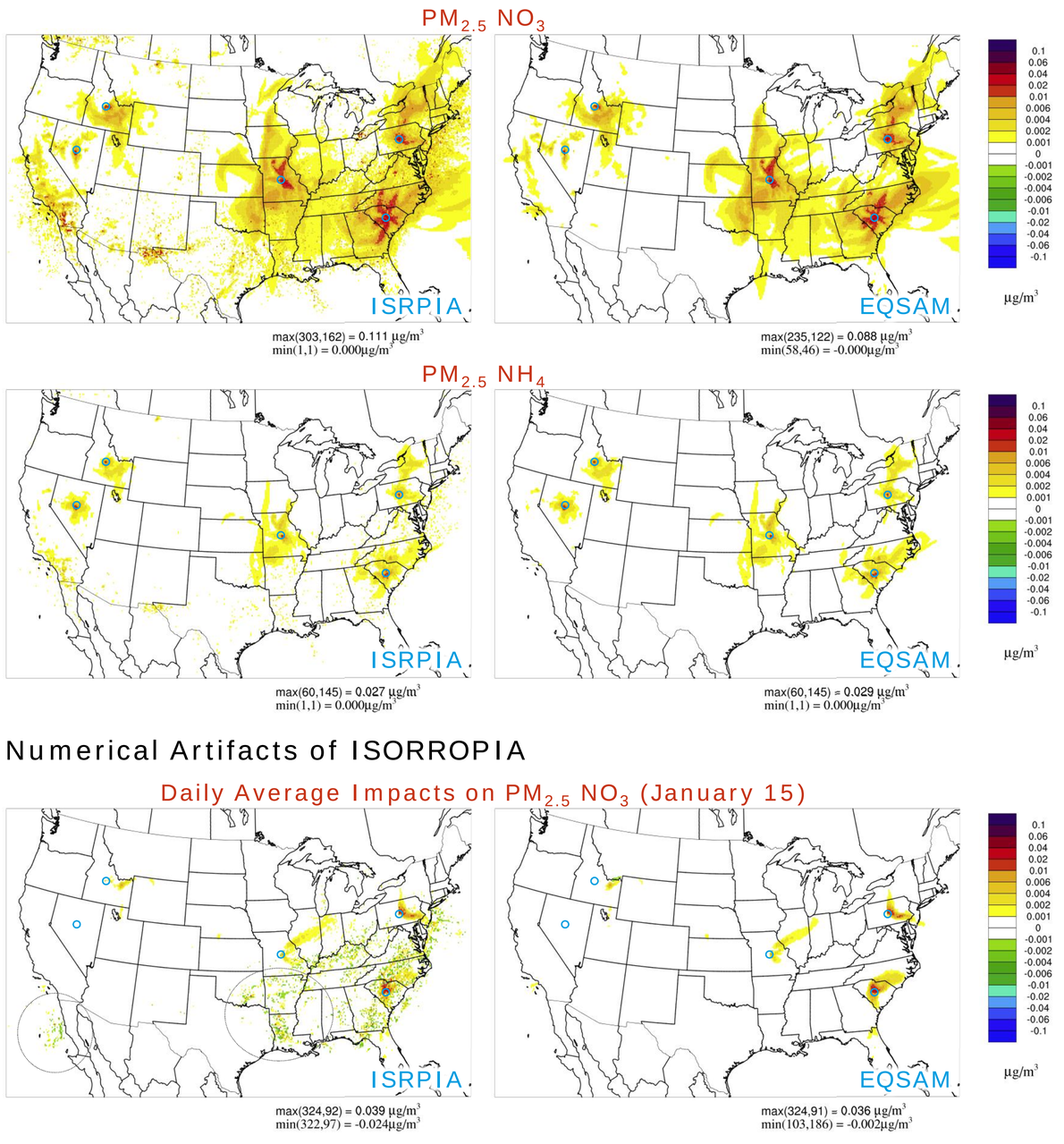


Model Performance Statistics (January)

Network	Species	NMB (%)		NME (%)		R	
		ISRPIA	EQSAM	ISRPIA	EQSAM	ISRPIA	EQSAM
CSN	NO_3^-	3.1	1.4	51.4	50.0	0.50	0.51
	NH_4^+	-7.5	-9.7	40.6	39.4	0.63	0.65
	Cl^-	79.0	-12.9	169	115	0.14	0.15
IMPROVE	NO_3^-	43.6	34.3	86.9	82.2	0.69	0.70
	NH_4^+	7.6	3.7	45.0	43.7	0.82	0.82
	Cl^-	60.9	-29.3	192	124	0.29	0.28

MODEL PREDICTION OF NEW SOURCE IMPACT

Maximum Impacts on 24-h Nitrate and Ammonium (January)



Numerical Artifacts of ISORROPIA

Daily Average Impacts on $PM_{2.5}$ NO_3 (January 15)

SUMMARY

- A computationally efficient thermodynamic equilibrium model, EQSAM4clim was implemented in CAMx and compared with ISORROPIA.
- Both models' results are sufficiently similar that either could reasonably be selected.
- Advantages of using EQSAM are that it runs faster (in our test, EQSAM reduced the overall CAMx runtime by 4% (January) to 7% (July)) and is free of numerical artifacts.

Monthly Average Predictions

- In January, both ISORROPIA and EQSAM agree fairly well in predicting spatial distributions and peak magnitudes of NO_3 and NH_4.
- In July, EQSAM tends to predict lower NO_3 than ISORROPIA.
- Both models assume a negligible vapor pressure of H_2SO_4, essentially driving all H_2SO_4 into the particle phase.

Model Performance

- Evaluated against the EPA's CSN (urban/suburban) and IMPROVE (rural) ambient measurement data.
- Both models show relatively good NH_4 performance while somewhat overestimating NO_3 in rural sites.
- For Cl, ISORROPIA shows overprediction biases while EQSAM tends to underpredict.

New Source Impact

- Tested by adding 5 hypothetical sources in Nevada, Idaho, Missouri, Pennsylvania & S. Carolina.
- Max impacts in January: (µg/m³)

Source	NO_3		NH_4	
	ISRPIA	EQSAM	ISRPIA	EQSAM
NV	0.05	0.04	0.03	0.03
ID	0.02	0.02	0.01	0.01
MO	0.04	0.09	0.03	0.03
PA	0.05	0.06	0.02	0.02
SC	0.05	0.05	0.02	0.02

- ISORROPIA responses often show numerical artifacts for small emission changes but EQSAM does not.

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