Modeling Investigation on Amines and Sea-salt Aerosol Interactions to Assess Their Potential Climate Impacts

Background Information

- Amines (derivatives of ammonium) are organic compounds emitted to the atmosphere from sources such as animal husbandry, biological marine activity, and biomass burning (Olenius et al., 2017)
  - Contribute to particle formation in the atmosphere, which is a dominant source of aerosols
- Sea salt aerosols are common, can serve as cloud condensation nuclei, (Murphy et al., 1998)
  - 50% of CCNs come from particle formation with vapors (Hills, 2013)
  - Important role in light scattering as a result, influencing global radiation balance and climate change
  - Can react with sulfuric acid to form hydrochloric acid, leaving them with a chloride deficiency
    - 2NaCl + H2SO4 = 2HCl (gas) + 1Na2SO4
- One pathway for particle formation with amines is acid neutralization ex. sulfuric acid to change aerosol properties (Ge et al, 2011)
- Amines are understudied, especially interactions w/organic compounds and usage in atmospheric models (Ge)

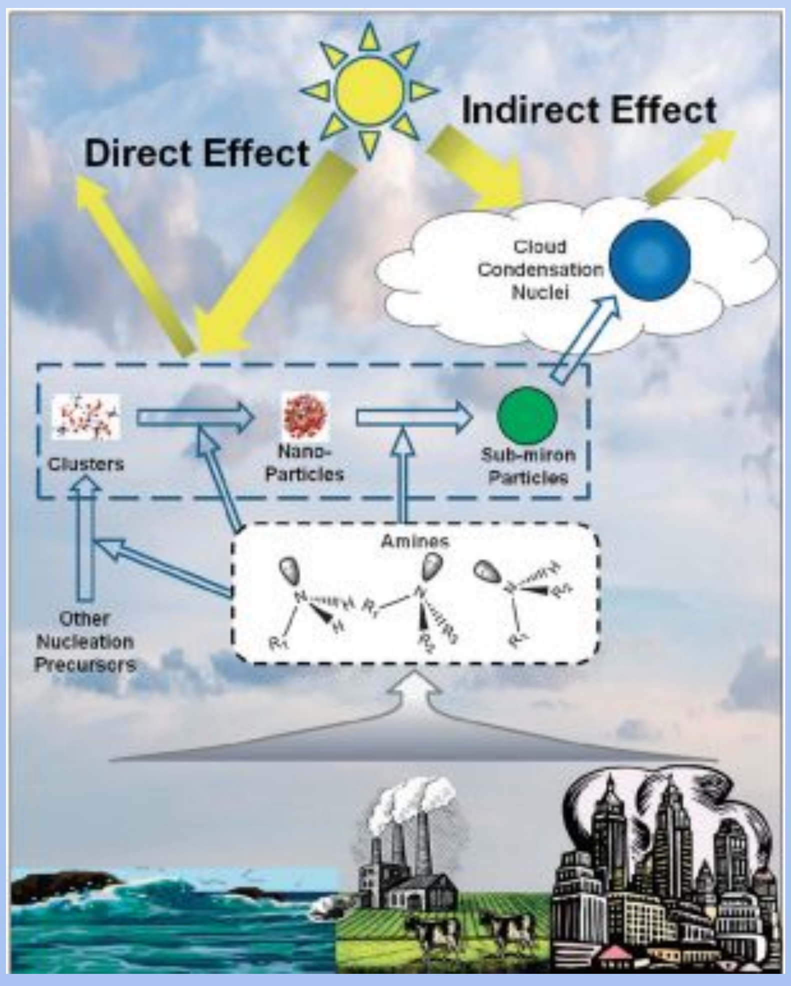


Fig 1. Diagram of amine emissions, interactions in the atmosphere

- E-AIM: Extended Aerosol Inorganics Model, models chemical systems at equilibrium with multiple phases (Clegg, Brimblecombe, Wexler, 2021)

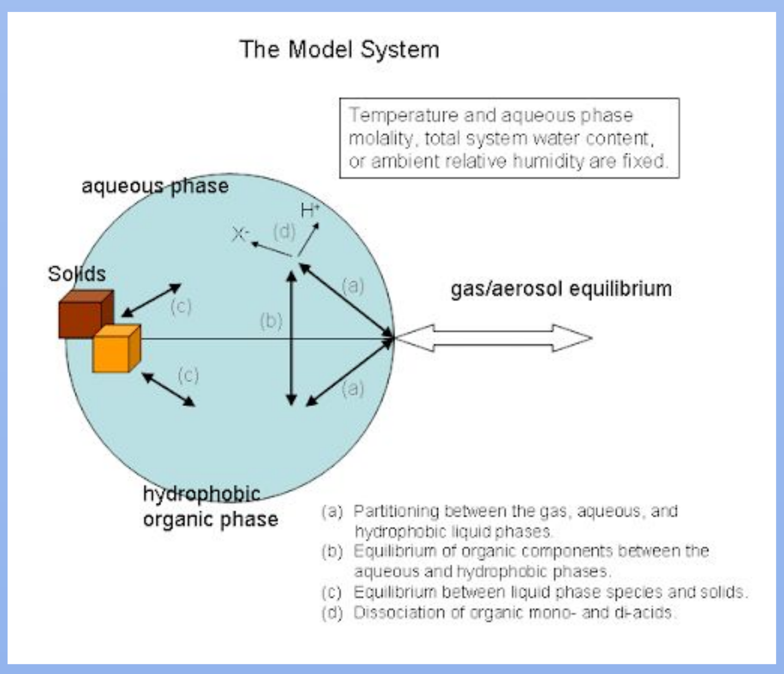
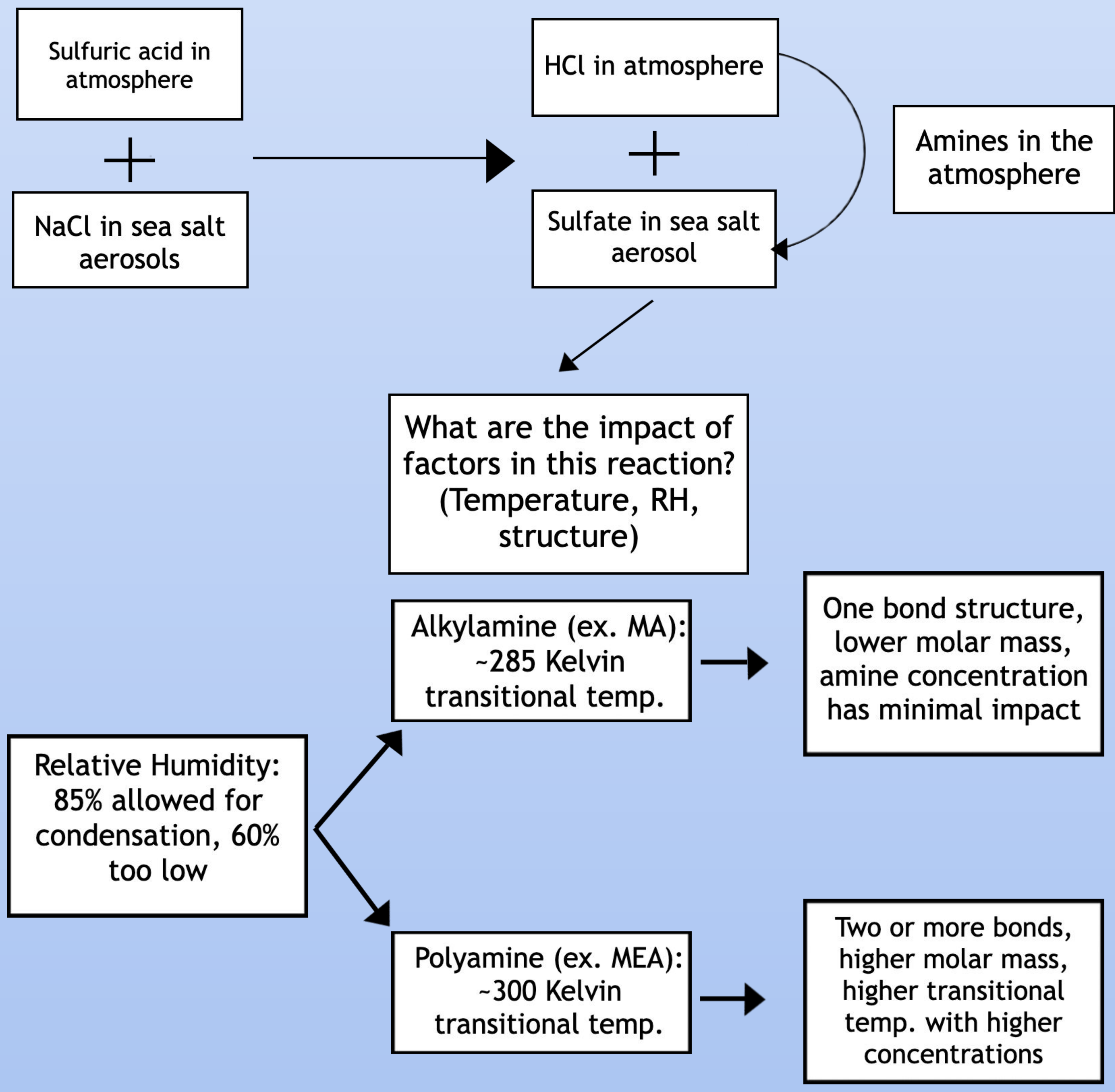


Fig 2. Visual of how E-AIM Model System functions, partitioning across aqueous, organic, gas, and solid phases

Purpose and Hypothesis

- Since hydrochloric acid (HCL) is more volatile than sulfuric acid and closely linked to sea salt aerosols, the purpose was to find out if amines will react with HCL to form amine chloride salt through acid neutralization?
  - Amine chlorides are solid, have no choice but to condense
  - Will amine chloride salts be volatile?
  - Will they condense onto the sea salt particles at low temperatures?
- Hypothesized that amines will react with HCL, the amine chloride will be volatile at room temperature, and will condense on sea salt aerosols at low temperatures.
  - Based on the fact that ammonium chloride is also volatile

Experimental Design



- IV: Temperature
- DV: HCL uptake, resultant properties (condensation, volatility)
- Control: Group of sea salt aerosol not exposed to any amine in the same temperature range (base scenario w/ammonia)
- Constants: Concentration of inorganic and organic compounds.
- Primary amines chosen
  - Ammonia: Base scenario
  - MA: Methylamine, one of the most common amines in the atmosphere (Lv, 2015)
  - DMA: Dimethylamine, another common amine, similar in structure to MA to compare results
  - MEA: Monoethanolamine emitted in high concentrations due to usage in post combustion CO2 capture at power plants (Tian, 2021), structurally different from MA
  - PiPz: Piperazine, rarer, but similar in structure to MEA
- Secondary amines studied: isobutanolamine, diethanolamine, trimethylamine
  - Provide more data to extract trends, validate hypotheses
- Simulations in E-AIM, 50 temperature intervals from 263.15-330K (14-134.33F)
  - 60 and 85% relative humidity
- Amine concentrations; 1E-10 to 1E-7 moles
- **Quantitative measure for condensation of the amine chloride**; 50%, or 1E-7 of HCl in gas phase (T50 or Tc for short)
  - Temperature at which the particle has condensed 50% of the HCl
- Compared physical properties of each amine to transitional temperature
  - Molar mass, basicity, vapor pressure, aqueous base hydrolysis constant
- Mentor: Guidance for experimental design, analysis

Results

	NH3	MA, DMA, TMA	MEA	PiPz	AMP	DEA
T50 (HCL, gas, 1E-7)	291.848	287.402	296.556	294.634	296.114	306.735
T50 (HCL, gas, 1E-8-10)	N/A	287.402	287.538	287.525	287.531	287.543

Fig 6. Table of transitional temperatures for amines, bottom row are averages with standard deviations of 0, 0.38, 0.2, 0.2, 0.21 respectively

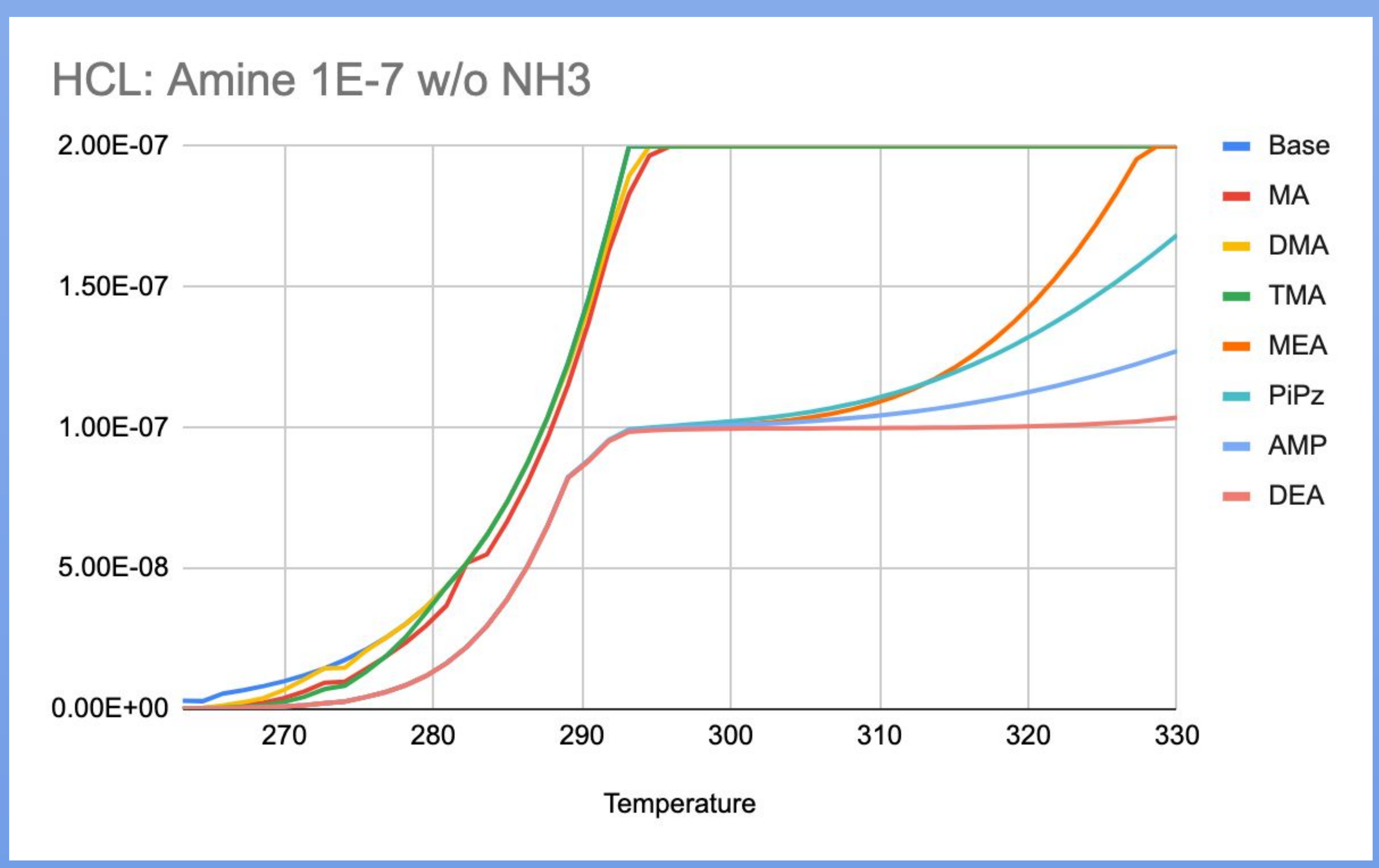


Fig 7. Amines at 1E-7, no NH3; MEA and PiPz are part of lower curves, base, MA, and DMA curves are higher

Results/Discussion

- Amines react with HCl to form amine chloride salts at 85% RH (possible over ocean)
  - Alkylamines condense at 285K
  - Polyamines condense at 300K
- Condensation depends highly on temperature
- MEA and PiPz require higher temperatures as concentrations increase, MA and DMA lower and more stable

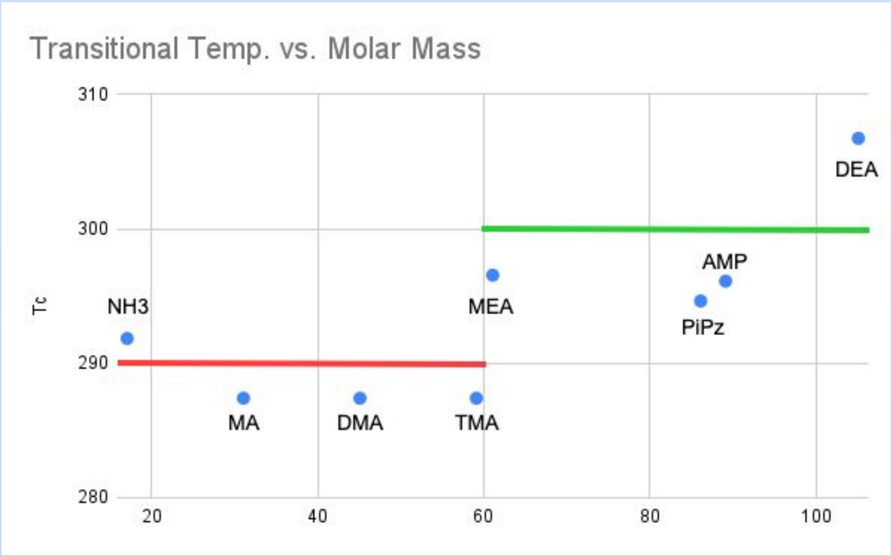


Fig 8 & 9. Transitional temp. w/molar mass, visual of molecular structures

- Molar mass show trends with temps, other physical properties didn't
  - Within polyamines, the higher the molar mass the higher the condensation temp
- Hypothesize that the structure of amines play a role
  - Polyamines (amines that can form 2 or more bonds) require higher transitional temperatures
  - Alkylamines (amines that can only form 1 bond) will have lower, more stable transitional temperatures

Continuations

- Study inorganic ions related to sea salt aerosols (nitrate, volatile)
  - Vary other experimental conditions; initial concentrations of ions etc.
- Physical properties and their true contribution
  - Unresolved with molar mass so far

Implications

- New mechanism for particle formation under acid neutralization,
  - Unexpected composition of condensation with HCl, sea salt aerosol, and amine chloride salts
- How emissions of industrial amines change composition and properties of sea salt aerosol
- Improve current atmospheric models
- Further knowledge on roles of amines and aerosols in light scattering, climate change, and human health
  - Toxic components in aerosols (industrial amines)

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