Introducing AMATI, a New Tool for Rapid Aerosol Thermodynamic Calculations on Large Field Datasets

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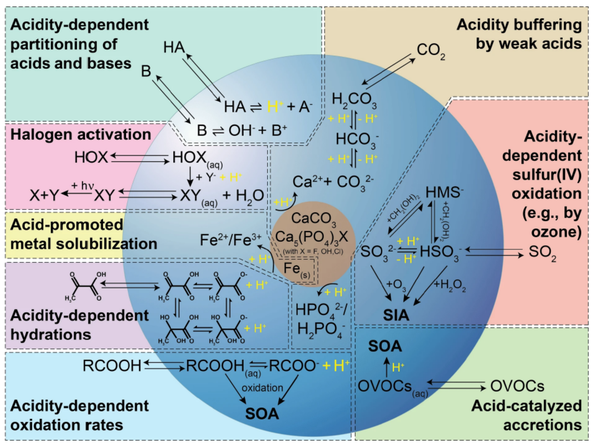
INTRODUCTION



Cartoon from the Tilgner et al (2021) review showing the many atmospheric processes that are influenced by particle acidity

- As several recently published reviews have highlighted (Pye et al, 2020, Tilgner et al, 2021), many studies over the past decade have shown the importance of aerosol acidity in controlling many atmospheric processes, involving both organic and inorganic chemistries.
- However, direct measurements of aerosol acidity outside the laboratory are still rare. Instead, thermodynamic models are used to infer a measure of acidity, aerosol pH from gas + particle phase field data.
- These models tend to be complex and many have not been designed / implemented originally with field data in mind, hence the barrier of entry to their effective (and error-free) use is high.
- Hence outside of some specific regions of high interest (such as Eastern China), there are fairly limited reports on aerosol acidity from field datasets.

- However, as Nault et al (2021) recently showed, global models do not represent acidity well, so increasing the breadth of observations in both space and time would provide muchneeded constraints on both global and regional processes.
- Based on our past work using the Extended Aerosol Inorganic Model (E-AIM) (Clegg et al, 1998; Wexler and Clegg, 2002; Friese and Ebel, 2010) to infer acidity in 10 field datasets, this poster presents our development work on a new, user-friendly tool to run E-AIM on field datasets, with a strong focus on users of the Aerodyne Aerosol Mass Spectrometer (Canagaratna et al, 2007).

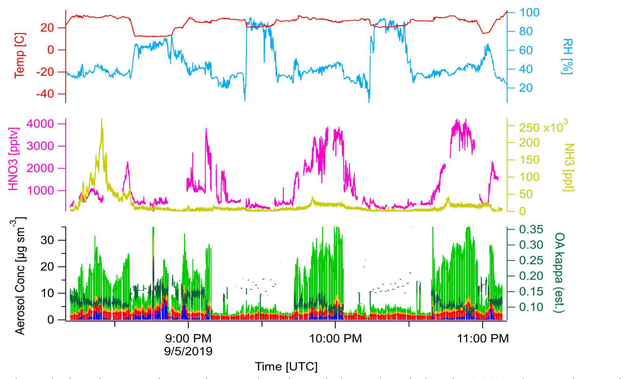
Design Goals

- Provide an easy way to run E-AIM inside Igor Pro (Wavemetrics, Lake Oswego, OR) that does not require any Fortran knowledge to process large datasets
- Provide a simplified set of E-AIM defaults geared towards calculating realistic pH and aerosol liquid water in ambient aerosol over a wide range of temperatures
- Provide a framework to explore the sensitivity to one input parameter iteratively. This can also then be used, as shown by Guo et al (2016) and Nault et al (2021), to model field datasets where one critical input is missing (e.g. ammonia)
- Allow expert users full access to all model options if needed
- Optimized for speed)

AMATI PANEL DESCRIPTION AND RESULTS

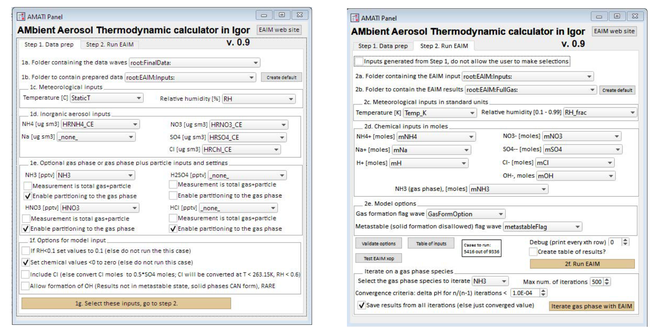
AMATI (AMbient Aerosol Thermodynamic calculator in Igor) is a software package for the Igor Pro analysis software designed to run a standalone version of the Extended Aerosol Inorganics Model (E-AIM) on large ambient datasets. Its main objective is the computation of aerosol water and pH. It is optimized for Aerodyne AMS data + CIMS gas inputs, but can take other inputs (e.g total nitrate and ammonium measurements from mist chamber IC instruments). It provides a variety of diagnostics and can explore the sensitivity to different inputs by an iterative approach

Example of AMS, soluble gases and Met input



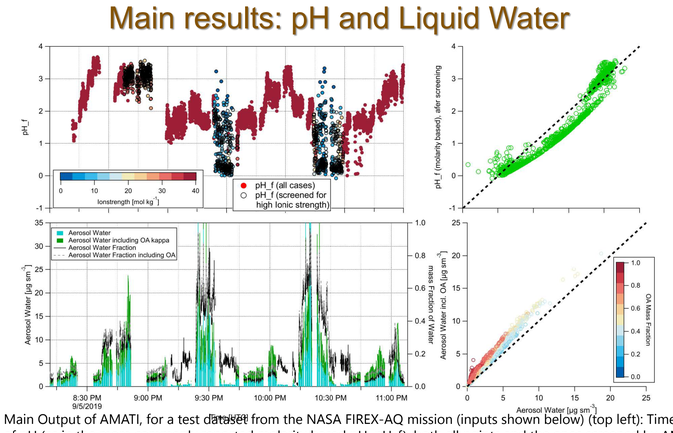
Inputs used to calculate the pH and aerosol water plots shown below, taken during the FIREX-AQ campaign on the NASA DC-8 flying over the LA Basin on Sep 5th, 2019, recorded at 1 Hz (about 9000 individual points). These were taken as is by AMATI, total computing time was 85 s..

Current version of the Igor Panel



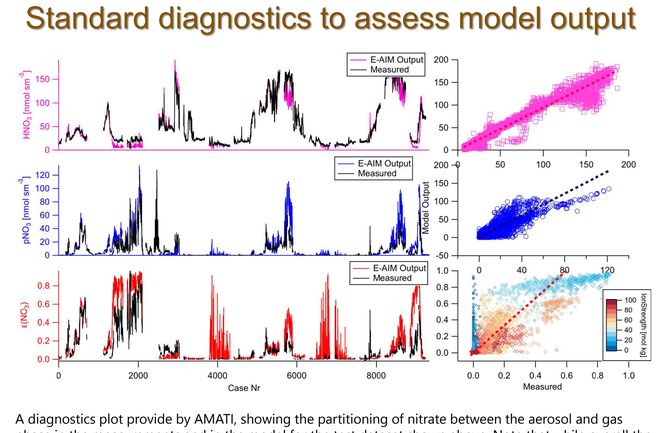
Current (pre-release) version of the AMATI panel, showing the input panel for measurements, the editable and consistency checked E-AIM model input in the second panel and the buttons to both run the model and explore iteratively the sensitivity to a particular input (see section to the left of this one)

Main results: pH and Liquid Water



Main Output of AMATI, for a test dataset from the NASA FIREX-AQ mission (inputs shown below) (top left): Timeseries of pH (as in the more commonly reported molarity based pH, pH_f), both all points and the ones screened by AMATI for highest model trustworthiness (which for aircraft datasets such as this one can be a large fraction) (top right) Correlation of pH_f vs the activity based pH, which is also calculated (bottom left) Timeseries of the inorganic aerosol water output from E-AIM Organic water (based on a simple O/C of OA parametrization of kappa) is included as well (bottom right): Total vs inorganic only liquid water, colored by dry OA fraction in the aerosol

Standard diagnostics to assess model output

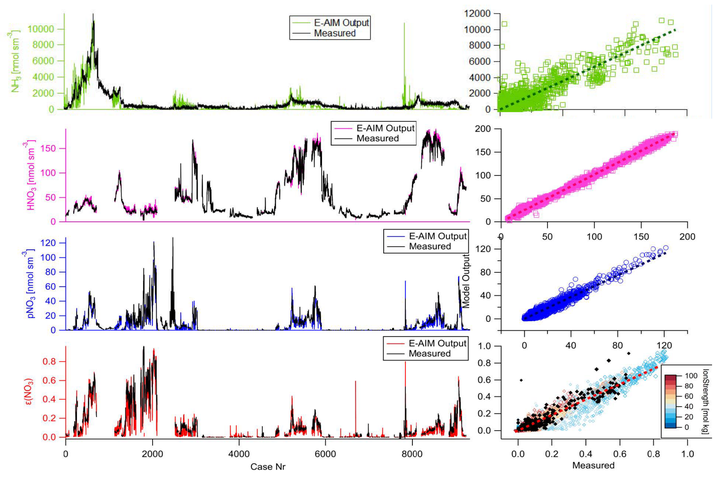


A diagnostics plot provide by AMATI, showing the partitioning of nitrate between the aerosol and gas phase in the measurements and in the model for the test dataset shown above. Note that while overall the concentrations agree, the partitioning ratio epsilon (particulate/total nitrate ratio) is poorly correlated. The model sensitivity was explored further by iterative approaches (see left panel), and it was found that modest adjustments to the ammonia concentration within instrumental uncertainties greatly improved the overall measurement/model agreement.

BUILD-IN FAST ITERATIVE ALGORITHM FOR MISSING INPUTS / SENSITIVITY ANALYSIS

Iterative approach to sensitivity analysis

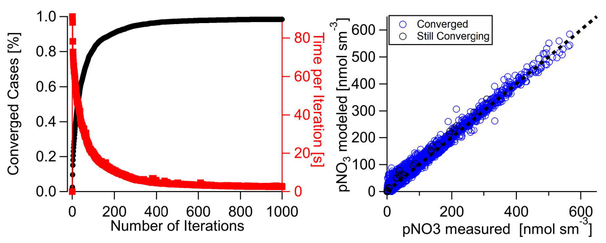
The highly non-linear nature of thermodynamic models makes evaluation of input errors challenging. One simple approach to this problem is to do iterative sensitivity analysis on a single input parameter while keeping all others constant. AMATI provides this as a standard feature. The model is run till a convergence criterion (by default a stable pH in the model, but this can be changed) is met. By iterating on a case by case basis, not only is computational time saved but a consistent convergence criteria can be applied to every case.



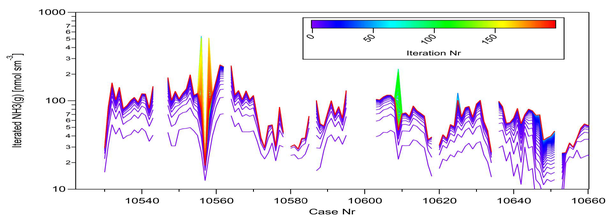
Exploration of the NH3 sensitivity for the FIREX-AQ LA test dataset shown in the main panel. After 500 iterations adjusting NH3, the model gets the nitrate partitioning almost spot on (black points show 60 points that did not converge after 500 iterations), while the change in ammonia is overall still within the measurement uncertainties, hence the rather poor partitioning in the model run with straight inputs is not indicative of any major problems with the model.

Estimating pH when inputs are missing

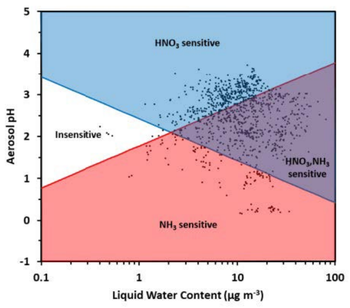
In addition to its usefulness for sensitivity analysis, the by far most important application for ambient datasets of the iterative approach is to still be able to run a thermodynamic model when data is missing (e.g. typically one of the gas inputs, ammonia or nitric acid). While this approach has its limitations, it does greatly expands the number of datasets that can potentially be analyzed with AMATI, since a full gas suite of measurements is often not available.



Example of an iterative approach to calculate pH for the KORUS-AQ campaign (Kim et al, 2021), where an ammonia measurement was missing. Under more acidic conditions, where the sensitivity to NH3 is higher, fast convergence is observed, while for more neutral conditions many iterations are needed..



Example of typical convergence behaviour for the (missing) ammonia concentration for subset of the NASA KORUS-AQ dataset. The spikes are caused by numerical noise close to the neutralization point but converge fairly quickly afterwards (see also ISORROPIA comparison)

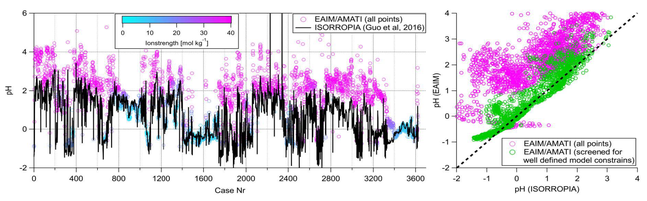


From Ibikunle et al, 2020: Sensitivity of pH to different gas inputs depending on total inorganic mass/total water contents as calculated by ISORROPIA. If e.g. ammonia measurements are missing, an iterative approach can be used to get consistent thermodynamic model output for moderately to very acidic conditions, but it will be underconstrained for near neutral conditions. Likewise, if nitric acid measurements are missing, an iterative approach will work wery well at near neutral conditions and rather poorly at very acidic conditions.

COMPARISONS WITH ISORROPIA (WINTER CAMPAIGN)

The ISORROPIA model (Fountoukis and Nenes, 2007) has often been used in the past for field datasets (e.g. Guo et al, 2015), in part due to its lower computing requirements compared to E-AIM. Furthermore, Guo et al (2016) pioneered the use of an iterative approach to approximate unmeasured ammonia to derive pH and used this for the data from the NSF WINTER campaign (see section on iterative approach for details). Here we show a comparison of the output of AMATI with the ISORROPIA-II data in Guo et al, (2016). Note that different thermodynamic models are not supposed to agree perfectly (see e.g. Pye et al, 2020 for an extended discussion), and hence these are provided mostly as a consistency check

pH Output Comparison



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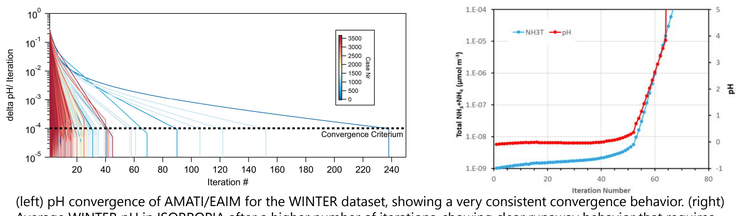
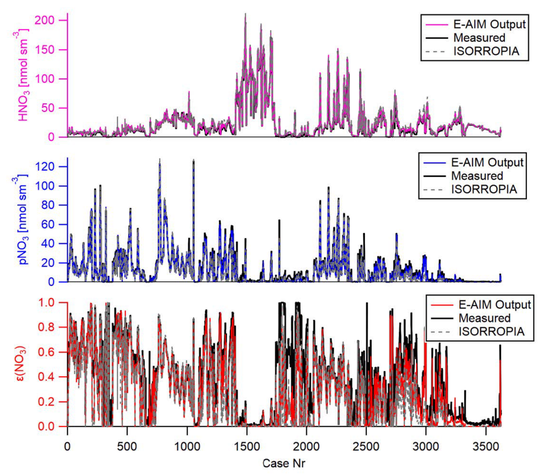
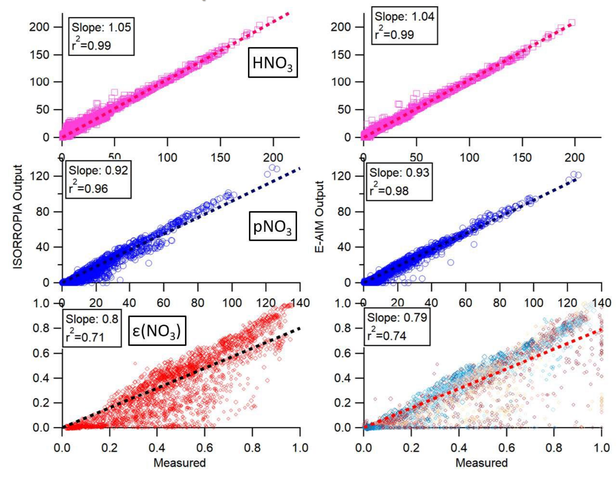
Convergence behavior AMATI vs ISORROPIA



(left) pH convergence of AMATI/EAIM for the WINTER dataset, showing a very consistent convergence behavior. (right) Average WINTER pH in ISORROPIA after a higher number of iterations, showing clear runaway behavior that requires additional constrains (Ibunkule et al, 2020). The reasons for the more consistent EAIM behavior (also observed for other datasets) is still under investigation, but is like related to (a) the exclusion of OH in the configuration used and (b) the higher fidelity and complexity of the E-AIM model.

Comparison of model outputs for volatile species





Summary and Outlook

- AMATI is intended to provide a simplified access to the E-AIM model (not unlike the E-AIM website) for researchers interested in applying it to large datasets. It requires Igor Pro running on a Windows PC.
- The implementation of the AMATI input panel and the iterative model run framework is largely concluded, work on more extended and user friendly diagnostics is ongoing.
- The use of parallelization is currently being explored. While AMATI performance for typical ground campaign datasets (e.g. 20k points) is fast (less than 3 min for full inputs, 10-200 min in iterative mode, depending on the type of data), for larger datasets (aircraft/multiyear ground) parallelization would have a clear benefit.
- AMATI is currently in early beta stage with a general release targeted for Fall 2022. If you are interested in using AMATI before that and would like to help us test it, please contact us.
- While not intended for the initial release next year, AMATI has the capability built in to model mixed organic/inorganic systems (Clegg and Seinfeld, 2006a and b). An implantation of AMATI where the concentrations of different PMF Factors can be assigned to specific model compounds (e.g. oxalate for LOOOA) is both possible and planned.

Acknowledgements

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