https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

Atmospheric Measurement Techniques Discussions

Aerosol pH Indicator and Organosulfate Detectability from Aerosol Mass Spectrometry Measurements

Melinda K. Schueneman[1], Benjamin A. Nault[1], Pedro Campuzano-Jost[1], Duseong S. Jo[1,2], Douglas A. Day[1], Jason C. Schroder[1,*], Brett B. Palm[1], Alma Hodzic[2], Jack E. Dibb[3], and Jose L. Jimenez[1]

[1] Department of Chemistry, and Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, CO, USA
[2] Atmospheric Chemistry Observations and Modeling, National Center for Atmospheric Research, Boulder, CO 80301, USA
[3] Earth Systems Research Center, Institute for the Study of Earth, Oceans, and Space, University of New Hampshire, USA

* Now at: Air Pollution Control Division, Colorado Department of Public Health and the Environment, Denver, CO, USA

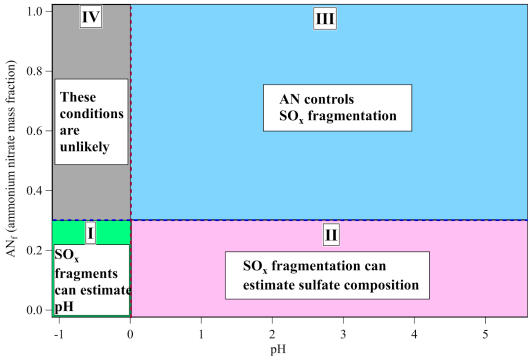
Correspondence: jose.jimenez@colorado.edu

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

Atmospheric Measurement Techniques Discussions

Abstract

Aerosol sulfate is a major component of submicron particulate matter (PM_1). Sulfate can be present as inorganic (mainly ammonium sulfate, AS) or organic sulfate (OS). Although OS are thought to be a smaller fraction of total sulfate in most cases, recent literature argues that this may not be the case in more polluted environments. Aerodyne Aerosol Mass Spectrometers (AMS) measure total submicron sulfate, but it has been difficult to apportion AS vs. OS as the detected ion fragments are similar. Recently, two new methods have been proposed to quantify OS separately from AS with AMS data. We use observations collected during several airborne field campaigns covering a wide range of sources and airmass ages (spanning the continental US, marine remote troposphere, and Korea) and targeted laboratory experiments to investigate the performance and validity of the proposed OS methods. Four chemical regimes are defined to categorize the factors impacting sulfate fragmentation (Fig. shown in abstract). In polluted areas with high ammonium nitrate concentrations and in remote areas with high aerosol acidity, the decomposition and fragmentation of sulfate in the AMS is influenced by multiple complex effects, and estimation of OS does not seem possible with current methods. In regions with lower acidity (pH>0) and ammonium nitrate (fraction<0.3), the proposed OS methods might be more reliable, although application of these methods often produced nonsensical results. However, the fragmentation of ambient neutralized sulfate varies somewhat within studies, adding uncertainty, possibly due to variations in the effect of organics. Under highly acidic conditions, sulfate fragment ratios show a clear relationship with acidity (pH and ammonium balance). The measured ammonium balance (and to a lesser extent, the $H_ySO_x^+/SO_x^+$ AMS ratio) is a promising indicator for rapid estimation of aerosol pH < 0, including when gas-phase NH_3 and HNO_3 are not available. These results allow an improved understanding of important intensive properties of ambient aerosols.



https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

Introduction

PM_1, or submicron aerosols, have important impacts on visibility, climate, and environmental and human health (Dockery et al., 1996; Lighty et al., 2000; Lohmann et al., 2004; IPCC, 2013). In order to quantify the impacts of PM_1, and their evolution with changes in emissions, chemistry, and climate, PM_1 sources, chemistry, and composition must be understood. Field measurements are critical to that goal, and one tool used extensively in field studies since the early 2000s is the Aerodyne Aerosol Mass Spectrometer (AMS) and more recently its simplified version, the Aerosol Chemical Speciation Monitor (ACSM) (Jayne et al., 2000; DeCarlo et al., 2006; Canagaratna et al., 2007; Ng et al., 2011a)). The AMS typically quantifies the chemical composition and size distribution of sulfate, nitrate, organic aerosol (OA), ammonium, and chloride (Jayne et al., 2000; DeCarlo et al., 2006; Canagaratna et al., 2007; Jimenez et al., 2009)

Within the AMS, particles are vaporized, leading to some thermal decomposition (e.g., (Docherty et al., 2015) and then ionized via 70 eV electron ionization, which leads to substantial fragmentation of the molecular ions. Despite or perhaps because of the substantial (and reproducible) decomposition and fragmentation, the relative signals of different AMS fragments have been found to be indicative of different chemical species in the aerosol. These include the presence of inorganic vs. organic nitrates (Farmer et al., 2010; Fry et al., 2013), and of several source and composition characteristics of organic aerosols (Alfarra et al., 2004; Zhang et al., 2004a; Cubison et al., 2011; Ng et al., 2011b; Hu et al., 2015). In contrast to nitrates, deconvolving inorganic vs. organic sulfates is thought to be more difficult, as the fragmentation pattern for one atmospherically relevant organosulfate (OS) was similar to those of inorganic

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

sulfates (mainly ammonium-sulfate salts, AS) in an early study, with minimal C-S-containing fragments (Farmer et al., 2010). Until recently, most studies have shown that the OS molar fraction (OS_f = OS / (AS + OS), calculated using only the sulfate moiety of the molecules) typically makes a small (~1-10%) contribution to total sulfate in PM_1 (e.g. (Tolocka and Turpin, 2012; Hu et al., 2015; Liao et al., 2015; Riva et al., 2016, 2019a)). However, for biogenic areas OS_f is predicted to increase substantially in the future (Riva et al., 2019b). Another important recent subject of debate is the missing sulfate production in haze events in China (Wang et al., 2014; Zheng et al., 2014; Li et al., 2017), which some studies have attributed to a major contribution of OS (e.g., (Song et al., 2019)). It is also important to quantify OS in order to understand the chemistry of aerosol formation and aging (Surratt et al., 2007, 2008; Song et al., 2019), which impacts the ability to understand how sulfate may influence various PM_1 properties and processes (e.g., gas uptake, aqueous reactions). Finally, accurate AS concentrations are needed to quantify the inorganic:organic ratio (to predict the hygroscopicity of PM_1, which impacts satellite and model interpretation) and to estimate aerosol pH and liquid water content from thermodynamic models, as it is currently still not possible to measure the aerosol pH in the field in-situ (Hennigan et al., 2015; Guo et al., 2016; Craig et al., 2018; Pye et al., 2019).

Recent AMS work has attempted to quantify OS_f from the measured individual sulfate ion signals. The vaporization and ionization of AS and OS in the AMS produces almost exclusively "inorganic" ion fragments, the major ones quantified being SO^+, SO_2^+, SO_3^+, HSO_3^+, and $H_2SO_4^+$ (Farmer et al., 2010). Note that these are the ions detected in the AMS (following ionization/decomposition), and not the ions present in the aerosols (discussed in Sect. 3.2 and shown in Fig. 2C). However, recent laboratory studies with many OS standards have found

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

reproducible differences in the fragmentation of AS vs OS (Chen et al., 2019). That study proposed a method using the unique AS ion fragments ($H_2SO_4^+$ and HSO_3^+) divided by the total sulfate signal ($H_2SO_4^+$ +HSO_3^++SO_3^++SO_2^++SO^+) to apportion OS, AS, and methylsulfonic acid (MSA, an organosulfur compound, but not an organosulfate) in field datasets. It is important to note that MSA can be directly measured with the (HR-)AMS (Phinney et al., 2006; Zorn et al., 2008; Huang et al., 2017; Hodshire et al., 2019), so quantification of MSA with the method in Chen et al. is not necessary. From this method, an average OS mass concentration (C_{OS}) of 0.12 µg m^{-3} was estimated for the SOAS ground campaign in rural Alabama (Carlton et al., 2018), with OS_f ~ 4% (Chen et al., 2019). That estimate is consistent with others for that site and region (Hu et al., 2015; Liao et al., 2015). An alternative method to estimate OS_f based on the same principle was proposed by Song et al. (2019) using the observed AMS $SO^+/H_ySO_x^+$ and $SO_2^+/H_ySO_x^+$. These authors reported OS_f~17%±7% (which corresponds to [OS] ~ 5-10 µg m^{-3}) during winter haze episodes in China, based on their method. A recent study (Dovrou et al., 2019) investigated mixtures of sodium sulfate and sodium hydroxymethanesulfonate (HMS); however, they found that HMS cannot be distinguished from AMS ions alone, due to the complex ambient aerosol mixture containing organic sulfates, and inorganic sulfates, which all, in part, produce the same sulfate fragments as HMS.

Another important and related analytical challenge is online quantification or estimation of ambient aerosol acidity from real-time measurements, e.g. during field campaigns. So far, online aerosol pH measurements have only been performed in the laboratory (Rindelaub et al., 2016; Craig et al., 2018). Aerosol acidity is important because it impacts human health by decreasing lung function (Raizenne et al., 1996), and strongly impacts the equilibria and kinetics

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

of a very large number of atmospheric physical and chemical processes (Jang et al., 2002; Meskhidze et al., 2003; Anon, 2007; Thornton et al., 2008; Bertram and Thornton, 2009; Gaston et al., 2014; Ackendorf et al., 2017; Guo et al., 2017; Losey et al., 2018). In addition, the deposition of acidic particles leads to damage to terrestrial and freshwater ecosystems, i.e. "acid rain" or more properly acid deposition (Schindler, 1988; Johnson et al., 2008). Currently, the state-of-the art technique to quantify aerosol acidity for field data is to run an inorganic aerosol thermodynamic model that includes the measured particle and gas inorganic concentrations, as well as temperature and humidity. The Extended Aerosol Inorganics Model (E-AIM) (Clegg et al., 1998a, 2003; Wexler and Clegg, 2002) is generally considered as the reference model (Pye et al., 2019). ISORROPIA-II (Nenes et al., 1999; Fountoukis and Nenes, 2007) is a faster model utilizing look-up tables to calculate aerosol liquid water content (and thus is frequently used as part of chemical transport models) at the expense of some accuracy at different RH levels (Pye et al., 2019). In general, these thermodynamic models are thought to perform best for pH estimation when gas-phase measurements of NH_3 and/or HNO_3 are used in the calculations, and to perform less well when run only with aerosol measurements (Guo et al., 2015; Hennigan et al., 2015; Song et al., 2018).

There has been an ongoing debate about the potential relationship between the inorganic cation/anion charge ratio (commonly referred to as "ammonium balance", see Eq. (4)) and aerosol acidity. Ammonia gas and its particle phase equivalent (ammonium) are the dominant bases in the atmosphere (Dentener and Crutzen, 1994). As the most important base in PM_1, a deficit of NH_4^+ vs. dominant PM_1 anions, SO_4^{2-} and NO_3^- (Jimenez et al., 2009), is indicative of the concentration of H^+, since the particles are (nearly) electrically neutral. Thus, in the absence

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

of substantial non-volatile cations (e.g. Na^+, K^+) ammonium balance is an indicator of aerosol acidity. Ammonium balance has been shown to correlate well with pH under certain conditions, specifically, when using daily averaged temperature and relative humidity (Zhang et al., 2007a), but has been criticized as being a poor surrogate of pH under other conditions (Hennigan et al., 2015). In particular, ammonium balance can be a poor surrogate of pH because changes in T and RH impact the aerosol liquid water in the diurnal cycle (Zhang et al., 2007a). This is especially important in the boundary layer where almost all past pH quantification has been carried out (Pye et al., 2019), compared to the lower diurnal variance of T and RH in the free and upper troposphere. Many field studies do not include measurements of NH_3 or HNO_3, sticky species present at low concentrations and thus not routinely measured, limiting the ability to calculate aerosol pH (Hennigan et al., 2015). A more direct estimate of aerosol acidity using only ambient particle data is highly desirable.

Here, we analyze sulfate ion fragment data from laboratory and ambient AMS observations, spanning multiple aircraft campaigns with a routinely calibrated AMS response to AS, and across a wide range of chemical and meteorological environments. We use this large dataset to test the applicability of recently published methods to partition AS and OS. We investigate the feasibility of estimating pH based on AMS data; as well as the regions of chemical space where the different estimation methods may work. Finally, we provide a physical interpretation for sulfate fragmentation in the AMS.

2 Methods

2.1 Airborne Campaigns

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

Sulfate fragmentation data was obtained using an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (AMS) (Aerodyne Research Inc., Billerica, MA, USA; (DeCarlo et al., 2006)). The ambient data used here are from aircraft observations from the following campaigns (Table 1): DC3 (Barth et al., 2015), SEAC^{4}RS (Toon et al., 2016), WINTER (Schroder et al., 2018), KORUS-AQ (Nault et al., 2018), and ATom-1 and ATom-2 (Guo et al., 2020; Hodzic et al., 2020)). Flight paths for all six campaigns are shown in Fig. S1. These campaigns span polluted urban, partially polluted biogenic, biomass burning smoke, rural, and remote regions of the atmosphere. DC3 sampled continental / rural conditions with diffuse pollution and some biomass burning events. WINTER and KORUS-AQ were airborne campaigns that focused on urbanized regions (although from different regions and times of year (Table 1)); therefore, the campaigns had appreciable mass concentrations of ammonium nitrate due to anthropogenic emissions of NO_x and the subsequent production of HNO_3 that partitions into the aerosol with ammonia (Seinfeld and Pandis, 2006). SEAC^{4}RS focused on regional background chemistry of the continental United States, which included impacts from biomass burning, biogenic, and pollution emissions, and upper tropospheric chemistry impacted by convection. Finally, ATom-1 and ATom-2 sampled the remote Pacific and Atlantic basins with continuous full vertical profiling, in order to study the composition of the remote marine atmosphere, impacted by long range transported chemical species and marine emissions, and far from anthropogenic sources. Not all campaigns are usable for all the analyses in this paper, depending on the quality and completeness of the data. Table 1 indicates which campaigns were usable for each analysis.

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

2.2 High-Resolution Time-of-Flight Aerosol Mass Spectrometer

The highly customized University of Colorado-Boulder aircraft AMS was used in all campaigns and has been described elsewhere (DeCarlo et al., 2008; Dunlea et al., 2009; Nault et al., 2018; Schroder et al., 2018; Guo et al., 2020), so only details relevant to this study are summarized here. Ambient air is drawn through a National Center for Atmospheric Research (NCAR) High-Performance Instrumented Airborne Platform for Environmental Research Modular Inlet (HIMIL: (Stith et al., 2009)) with a constant standard flow rate of 9 L min^{-1}, and all data is reported at a constant standard temperature (T = 273 K) and pressure (P = 1013 hPa). The sampled air enters a pressure controlled inlet (Bahreini et al., 2008) and is then introduced into an aerodynamic focusing lens (Liu et al., 1995; Zhang et al., 2004b). Particles then impact onto an inverted cone porous tungsten "standard" vaporizer, operated at ~ 600 °C under high vacuum. The standard vaporizer is used in this study. A "capture vaporizer" has been recently demonstrated, it leads to more thermal decomposition while still retaining similar (although noisier) fragment information (Hu et al., 2017a; Zheng et al., 2020), but it is not used here. Non-refractory species, those that evaporate in less than a few seconds (such as sulfate, nitrate, ammonium, and organic material), are subsequently ionized by 70 eV electrons. Some refractory and semi-refractory species such as sea-salt, lead and potassium can be detected by the AMS in some cases (Lee et al., 2010; Salcedo et al., 2010; Ovadnevaite et al., 2012; Hodzic et al., 2020)). A cryopump reduces background in the ionizer by orders of magnitude during the flights, leading to low detection limits, in particular for NH_4, which is critical for acidity quantification in the remote troposphere. Data was taken at 1 Hz, but was processed at both 1 Hz and 1 minute resolution, and the latter product is primarily used here due to higher signal-to-noise ratios. The

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

one minute datasets were further filtered by removing points where the sulfate signal was below three times its detection limit. Detection limits were estimated continuously via the methods of Drewnick et al. (2009), and confirmed with frequent in-flight filter blanks. For the laboratory studies, everything was kept the same as on the aircraft other than no use of the HIMIL aircraft inlet. Data was processed and analyzed with the standard Squirrel and PIKA ToF-AMS data analysis software packages within Igor Pro 7 (Wavemetrics) (DeCarlo et al., 2006; Sueper, 2018).

One important parameter for AMS quantification is collection efficiency (CE). CE is the probability that a particle entering the AMS is detected. It is affected by several particle properties (Huffman et al., 2005), the most important being particle bounce off the vaporizer without detection (Middlebrook et al., 2012). Bounce is controlled by particle phase (Quinn et al., 2006; Matthew et al., 2008), and is estimated for ambient particles based on their ammonium balance (acidity) and ammonium nitrate content (Middlebrook et al., 2012). This parameterization performs well for ambient particles (Middlebrook et al., 2012; Hu et al., 2017a, 2020; Guo et al., 2020). Still, potential variability in CE that is not perfectly captured by the parameterization contributes a major fraction of the AMS uncertainty for ambient particle analysis (Bahreini et al., 2009). Alternative methods to estimate ambient CE for ambient particles are of interest.

2.3 Quantification of OS/AS using Literature Methods

Two methods have been proposed to quantify OS contribution to total sulfate using AMS sulfate ion fragment fractions. The first method uses different sulfate ions to attribute measured

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

total sulfate to either OS, AS, or methanesulfonic acid (MSA). Due to the structure of OS, only non-hydrogenated sulfate ions, i.e., SO^+, SO_2^+ and SO_3^+, are produced in the AMS for OS. AS does produce hydrogenated sulfate ions, i.e., $H_2SO_4^+$ and HSO_3^+, as well as the same non-hydrogenated sulfate ions produced by OS. Chen et al. (2019) proposed a "triangle method" to estimate these two species and MSA, based on the observed fragments. Note that mineral sulfates such as sodium sulfate fragment similarly to OS, and thus these methods need to be interpreted differently in regions with significant submicron mineral sulfates. MSA calibrations show variability for the fragments (Chen et al., 2019), and were not performed for all the studies in this work. Since MSA can be quantified without using the sulfate fragments, here we apply this method to estimate the fractions of OS and AS by using a one dimensional version of the triangle (i.e. just the hypotenuse connecting pure OS to pure AS). An alternative method is based on the same assumptions, but uses different equations to quantify the relative concentration of OS (Song et al., 2019).

Both literature methods for deconvolving sulfate as OS and AS assume that the main factor impacting sulfate fragmentation in the AMS is sulfate structure (OS, AS, or MSA). Chen et al. (2019) briefly mention that acidity can impact sulfate fragmentation, but this effect has not been studied and quantified. In addition, Chen et al. (2019) used pure standards to quantify the AMS fragmentation of different species, but did not explore potential matrix effects in AMS fragments which could impact internally mixed ambient particles.

2.4 Quantification of the AMS Sulfate Fragment Ratios

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

Atmospheric Measurement Techniques Discussions

To compare our field data to that analyzed in Chen et al. (2019) we use the variables defined in that study, $fH_2SO_4^+$ and $fHSO_3^+$ and define the normalized $nfH_2SO_4^+$ and $nfHSO_3^+$ (normalized to the values of $fH_2SO_4^+$ and $fHSO_3^+$ for pure AS) :

$$fH_2SO_4^+ = \frac{[H_2SO_4^+]}{[H_2SO_4^+]+[HSO_3^+]+[SO_3^+]+[SO_2^+]+[SO^+]} \quad \text{Eq. 1}$$

$$nfH_2SO_4^+ = \frac{fH_2SO_4^+}{fH_2SO_4^+\,(pure\ AS)} \quad \text{Eq. 2}$$

$$fHSO_3^+ = \frac{[HSO_3^+]}{[H_2SO_4^+]+[HSO_3^+]+[SO_3^+]+[SO_2^+]+[SO^+]} \quad \text{Eq. 3}$$

$$nfHSO_3^+ = \frac{fHSO_3^+}{fHSO_3^+\,(pure\ AS)} \quad \text{Eq. 4}$$

It should be noted that while that study includes methanesulfonic acid (MSA) data, the impact of MSA on $fH_2SO_4^+$ and $fHSO_3^+$ is minimal for the ATom campaigns (see Fig. S2). Additionally, one study over the Western United States (representing a rural, continental region) observed MSA concentrations of ~50 ng m^{-3} (Sorooshian et al., 2015), which results in a very small deviation in the Chen triangle and can hence be neglected for the purposes of this work. All

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

261 variables were normalized to the values of the same variables for pure AS calibrations
262 (conducted during each field experiment) in order to eliminate some of the spread in the sulfate
263 ions that is likely due to instrument-to-instrument or instrument-in-time variability (Fry et al.,
264 2013; Chen et al., 2019) (Fig. S3) . We also define a new AMS sulfate ion ratio, $H_ySO_x^+/SO_x^+$, as
265 and create the normalized $nH_ySO_x^+/SO_x^+$ to reduce the influence of instrument-instrument
266 variability:

$$H_ySO_x^+/SO_x^+ = \frac{[HySO_x^+]}{[SO_x^+]} = \frac{[H_2SO_4^+]+[HSO_3^+]}{[SO_3^+]+[SO_2^+]+[SO^+]} \quad \text{Eq. 5}$$

267

$$n\,H_ySO_x^+/SO_x^+ = \frac{H_ySO_x^+/SO_x^+}{H_ySO_x^+/SO_x^+\,(pure\ AS)} \quad \text{Eq. 6}$$

268

269 The submicron aerosol molar Ammonium Balance (NH_{4_bal}) is calculated as:
270

$$NH_{4\_bal} = \frac{[NH_4]/18}{([SO_4]/48)+([NO_3]/62)+([Chl]/35)} \quad \text{Eq. 7}$$

271

272 The concentration of non-refractory chloride is only included for non-remote campaigns
273 (KORUS-AQ, WINTER, and SEAC^{4}RS), since it was negligible for others and strongly
274 impacted by seasalt in the marine boundary layer. The fraction of ammonium nitrate in the
275 particle phase (ammonium nitrate mass fraction, AN_f) (by mass):

$$AN_f = \frac{(80\div62)\times[Inorganic\ NO_3]}{[NO_3]+[SO_4]+[NH_4]+[Chl]+[Org]} \quad \text{Eq. 8}$$

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

Atmospheric Measurement Techniques Discussions

276

277 The fraction of total AMS aerosol mass comprised of OA (OA_f) is:

$$OA_f = \frac{[Org]}{[NO_3]+[SO_4]+[NH_4]+[Chl]+[Org]} \quad \text{Eq. 9}$$

278

279 The sulfate equivalent concentration of OS in the Song et al. (2019) paper is calculated as:

$$C_{OS} = M_{SO_4^{2-}}\left[\frac{SO_{obs}^{+} - R_{cd,SO^{+}/H_ySO_x^{+}} \cdot H_ySO_{x,obs}^{+}}{M_{SO^{+}}} + \frac{SO_{2,obs}^{+} - R_{cd,SO_2^{+}/H_ySO_x^{+}} \cdot H_ySO_{x,obs}^{+}}{M_{SO_2^{+}}}\right] \quad \text{Eq. 10}$$

280

281 where "cd" stands for "clean and dry". Clean and dry conditions are defined in Song et al. (2019)
282 as ambient data points where PM_1 = 10 µg m^{-3} and RH = 30%. Clean and dry conditions are
283 assumed to represent nearly pure AS. M is for the molar mass of the different sulfate ions, and
284 "obs" represents the ambient data for specific sulfate fragments. $H_ySO_x^+$ is defined in Song et al.
285 (2019) as (SO_3^++HSO_3^++$H_2SO_4^+$). For the Chen method, the C_{OS} is defined based on the AS
286 normalized $nfH_2SO_4^+$ values:

287

$$C_{OS} = [SO_4] - nfH_2SO_4^+ * [SO_4] \quad \text{Eq. 11}$$

288

289 OS_f, the fraction of OS:total sulfate is defined as:

290

$$OS_f = \frac{C_{OS}}{[SO_4]} \quad \text{Eq. 12}$$

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

Where C_{OS} is calculated from Eq. (10) or Eq. (11).

2.5 Laboratory Experiments

As ambient aerosols contain mixtures of chemical species, we investigated if matrix effects may impact the fragmentation of sulfate species. Different solution mixtures, composed of various amounts of AS (Certified ACS, 99.7% purity) and ammonium nitrate (AN) (Certified ACS, 99.9% purity) in water (Milli-Q grade (R > 19 MOhms)) were atomized to generate particles and size selected using a Differential Mobility Analyzer (DMA) (TSI Model 3081), analyzed with a Condensation Particle Counter (CPC) (Model 3775), and electrostatic classifier (Model 3080), for mobility diameters between 350-400 nm. We investigated AS/AN mixtures, ranging from AN_f = 0% to 95%.

In order to assess effects on the sulfate fragmentation from mixing with OA, chamber experiments, where different types of SOA were formed by gas-phase reactions and condensation onto AS seeds, were investigated. SOA was formed from alkanol and toluene photooxidation under high-NO_x conditions (Liu et al., 2019), as well as Δ-3-carene and α-pinene reactions with nitrate radicals (Kang et al., 2016) Experiments were initiated with 100% AS in a dry chamber (RH < 5%; ~ 298 K) followed by either rapid, gradual, or stepwise increases of SOA until a maximum OA/(OA+AS) ratio of ~ 70% was reached. Aerosol composition was monitored by AMS and size distributions were monitored with a scanning mobility particle sizer (SMPS, TSI). RIE of sulfate was directly calibrated with pure ammonium sulfate, while RIE * CE of the SOA produced was estimated by comparison to the SMPS integrated volume, together with OA density estimated from the AMS-derived elemental ratios per Kuwata et al. (2012)), in

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

order to accurately quantify OA/(OA+AS). Humid experiments were not considered here due to the potential of forming organosulfates.

2.6 E-AIM Thermodynamic Model for pH Estimation

Aerosol pH was estimated using the Extended Aerosol Inorganic Model (E-AIM) Model IV (Clegg et al., 1998b; Massucci et al., 1999; Wexler and Clegg, 2002). We input into the model the total nitrate (gas and particle phase), particle phase ammonium and sulfate, and ambient T and RH to calculate aerosol liquid water and aerosol pH. Model IV is not run with chloride ions, as their concentrations were very low, and including chloride limits the model to temperatures $\geq$ 263 K (Friese and Ebel, 2010), which would greatly limit the analysis of pH for WINTER, ATom-1, and ATom-2. Also, including chloride precludes running the model under supersaturated solution conditions, which is a closer approximation of ambient aerosol (Pye et al., 2019). The model was run in the "forward mode," meaning that total nitrate (gas-phase HNO_3 plus particle-phase total NO_3^-), sulfate, ammonium, relative humidity (calculated according to the parameterization of Murphy and Koop (2005) which is critical for upper tropospheric conditions), and temperature were input into the model. All aerosol mass concentrations were from the CU AMS. HNO_3(g) was measured by the California Institute of Technology chemical ionization mass spectrometer (CIT-CIMS) (Crounse et al., 2006), which was flown in all of these missions (excluding WINTER, where the UW-CIMS was used for the HNO3 measurements) (Lee et al., 2014, 2018). Results are generally similar when using the SAGA mist chamber measurement for total nitrate (Nault et al., 2020). The forward mode is less sensitive to uncertainties in measurements than the "reverse mode," which only uses particle

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

composition and T/RH as inputs (Hennigan et al., 2015). Also, due to lack of NH_3(g) measurements, the model was run iteratively until convergence in modeled NH_3 occurred, similar to Guo et al. (2016). Performance for modeled pH was investigated by comparing model-calculated HNO_3 and NO_3^- to measurements, as the partitioning of nitrate between gas- and particle-phase is sensitive to pH under acidic conditions (Guo et al., 2016). For all campaigns included herein (DC3, WINTER, SEAC^{4}RS, KORUS-AQ, ATom-1, and ATom-2), the slopes of HNO_3 (measured vs. predicted) are within the uncertainty of the measurements; with good correlations (SI Fig. S4). For NO_3^-, the slopes are within the measurement uncertainty for five of the six campaigns. For ATom-2, the NO_3^- slopes were low; however, for this campaign, the measured NO_3^- mass concentrations were extremely low (mean = 0.02 μg sm^{-3}), and the pH was also very low (mean = - 0.5), leading to very little NO_3^- in the aerosol phase (see SI Fig. S4).

In addition, other bases present in the atmosphere (such as amines) were examined. Prior studies have shown that amines were less than a maximum concentration of 30 ng m^{-3} at the ocean surface (Gibb et al., 1999; Facchini et al., 2008; Müller et al., 2009; Frossard et al., 2014; van Pinxteren et al., 2015; Youn et al., 2015). Another study found that amine mass concentration dropped off quickly with altitude to concentrations less than 10 ng m^{-3} at the altitude that the DC-8 flew over marine surfaces (Sorooshian et al., 2009). As the one minute detection limit for the AMS data for amines is typically 10 ng m^{-3}, we expect the amine signal to generally be below the limit of detection, and thus outside of our quantification capabilities. This was observed for AMS data from the ATom campaigns, using characteristic ions identified in past studies (Murphy et al., 2007; Ge et al., 2014). It was found that amine ions cannot be

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

distinguished from background for many ATom flights. Only during one flight in ATom-1, we observed an amine signal ($C_2H_6N^+$ m/z = 44) above the background (see SI Fig. S5). During this flight, amines (from the contribution of CH_4N, C_2H_6N, and C_3H_8N) only accounted for 0.7 ng $m^{-3}$of aerosol, whereas ammonium accounted for 19 ng m^{-3}. Amines can produce the same fragments as ammonium, but this is only the case for a few percent of the amine fragments (Ge et al., 2014). In this case, the ammonium concentration is 25 times that of the amines. Since amines were even lower during other flights, we assume the effect of amines to the pH calculation is very small and can be ignored for E-AIM calculations.

2.7 GEOS-Chem Model

We used a global chemical transport model (GEOS-Chem 12.6.1, doi:10.5281/zenodo.3520966; (Bey et al., 2001)) to investigate modeled global distributions of ammonium nitrate mass fraction (AN_f) and aerosol pH across different regions. GEOS-Chem was driven by assimilated meteorological fields from the Modern-Era Retrospective analysis for Research and Applications version 2 (MERRA2) (Gelaro et al., 2017) for the year of 2010. The simulation was conducted at 2˚ (latitude) × 2.5 (longitude) with 47 vertical layers up to 0.01 hPa and ~30 layers under 200 hPa. We used the Community Emissions Data System (CEDS) inventory for global anthropogenic emissions (Hoesly et al., 2018) and the global fire emissions database version 4 (GFED4) for biomass burning emissions (Giglio et al., 2013). Aerosol pH and gas-particle partitioning of inorganic aerosols were calculated online using the ISORROPIA-II model within GEOS-Chem (Fountoukis and Nenes, 2007; Pye et al., 2009). Similar to Jo et al., (2019) sea salt aerosol was excluded from pH calculations based on a better agreement with the

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

observationally-constrained pH values as suggested by Nault et al. (2020). GEOS-Chem includes sea salt aerosol in ISORROPIA calculation but we excluded sea salt aerosol based on Nault et al. (2020). Oceanic NH_x emissions were also included in this model based on recent work (Paulot et al., 2015; Nault et al., 2020).

3 Results and Discussion

3.1 Lab quantification of AMS data

Application of the one dimensional Chen method to laboratory data is shown in Fig. 1. Data are expected to lie inside the triangular region, and be apportioned depending on the relative distance to the three vertices. For example, data lying at [0.5,0.5] on the line between the OS and AS points would represent a sample with ~50% OS and ~50% AS. If data clusters around the [1,1] point where pure AS resides, all of the sulfate is attributed to AS.

The effect of internally mixed ammonium nitrate (AN) is shown in Fig. 1A. For mixtures containing AN_f < 50%, data centers around the pure AS point in the Chen triangle. When AN_f is increased past 0.50, there is an increase in both $nfH_ySO_x^+$ ions. For example, an aerosol with AN_f = 0.75 results in OS_f = - 11% with the Chen method, which is nonsensical. When AN_f = 0.90, OS_f =-33%, and when AN_f = 0.95, OS_f = - 50%. This indicates that in a sample containing some mixture of OS, AS, and AN, the total sulfate would need to be 50% OS and 50% AS (at AN_f = 0.95) to give a non-negative OS_f. Thus for laboratory data, the Chen method should not be used on mixtures containing AN_f > 0.50.

The effect of OA internally mixed with AS on the sulfate fragmentation pattern was also explored with toluene, alkanol, and monoterpene SOA. For the alkanol SOA experiments we

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

found that the presence of even a small coating of alkanol SOA (which is thought to be liquid (Liu et al., 2019)) shifts the normalized AS [1,1] point to ~[1.08,1.08], but increases in the fraction of OA (OA_f) from 0.1 to 0.3 lead to no further changes in $nfH_ySO_x^+$ (Fig. 1B). This means that for a sample containing a mixture of AS and alkanol SOA, the calculated OS_f would be ~15% (Chen). In contrast, toluene SOA, which spans $0 < OA_f < 0.5$, shows no clear change in the $nfH_ySO_x^+$ ions, indicating that OA_f would not bias the Chen method for this example. The monoterpene SOA, from two different experimental datasets using different AMSs, show more varied results than the previous two studies. Overall, in the OA_f range 0-0.50, the 2015 monoterpene data shows a consistent and constant 10-20% increase in $nfH_ySO_x^+$ compared to the pure AS calibration point (similarly to the alkanol SOA). However, when OA_f is in the range of $0.50<OA_f<0.70$, 30-40% increases are observed. This result is only applicable to a few of the experiments (see Fig. S6), potentially due to very high SOA loadings (up to 300 µg m^{-3}). These high OA concentrations could potentially lead to a change of the particle phase due to condensation of more volatile and liquid species, potentially altering the interactions of the particles and the vaporizer surfaces.

These experiments collectively suggest that a "pure" AS calibration point of [1.15,1.15] may be more appropriate when applying the Chen et al. method to some mixed aerosol at typical OA concentrations observed in the atmosphere.

Chen et al. briefly discussed the potential impact of acidity on their OS quantification method. This is explored here with pure sulfuric acid lab calibrations (Fig. 1C). Pure sulfuric acid shows a large deviation from the pure AS triangle point (similar to increasing AN_f), nearly

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

doubling the values for the $nfH_ySO_x^+$ ions. This implies that a particle containing sulfuric acid would produce a strong negative bias on the estimate of OS by the Chen method.

3.2 Physical Interpretation of the Sulfate Fragmentation Trends

It is useful to provide a physical interpretation of the trends that are likely driving the observed sulfate fragmentation changes, based on the physicochemical details of the AMS detection and those of the particles being sampled. In Fig. 2A, a simplified diagram of the AMS detection process is shown, highlighting important details that are thought to give rise to the observed trends.

Ambient particles containing AS, OS, and other species are sampled into the AMS through a focusing lens. Following a series of differential pumping steps through the instrument, the particles impact on a porous tungsten standard vaporizer. The time spent under vacuum from sampling to detection is of the order of 15 ms. A fraction of the more viscous particles may bounce from the vaporizer without detection. Non-refractory species in the particles that stick to the vaporizer (such as OS and AS) are heated by heat transfer from the vaporizer surface. Some species may evaporate in the form in which they are present in the particle, while others may thermally decompose to other species, which then evaporate. For example, ammonium sulfate may evaporate to $H_2SO_4(g)$ and $NH_3(g)$, but it may also thermally decompose to $SO_2(g)$, $SO_3(g)$ and $H_2O(g)$ (Hu et al., 2017b). Finally, these gaseous thermal decomposition products undergo electron ionization to become positively charged species. Since the electrons used in EI have far more energy (70 eV) than typical bonds in a molecule (~6 eV for S=O), the initial ions may fragment into smaller ions if the ionization process results in absorption of > 6 eV of internal

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

444 energy by the molecule, beyond the ionization energy (Lambert, 1998). Some of the evaporated
445 $H_2SO_4(g)$ may remain as $H_2SO_4^+$ after ionization, or it may fragment to HSO_3^+ or SO_x^+ ions.
446 $SO_2(g)$ can only produce SO_x^+ ions. Thus the mixture of fragments observed will retain some
447 memory of the species that evaporated from the particles. If the mixture of evaporating species is
448 influenced by the particle composition (e.g. pH, AN, OA, or OS_f) then it may be possible to
449 calibrate the observed relationship to estimate a particle intensive chemical property.
450 Fig. 2A also shows a schematic close-up of the SV surface, which is the main point in the
451 instrument that controls ammonium sulfate fragmentation. In this diagram, we show a
452 non-smooth surface with pores, consistent with the fabrication of the vaporizer by sintering 50
453 μm tungsten spheres. The interaction of a particle with this porous surface is dependent on the
454 particle phase / viscosity. The red particles represent rigid (more solid-like) particles. These rigid
455 particles can simply bounce off of the vaporizer, leading to no detection. AS-dominated particles
456 are likely to be rigid (due to the solid phase of pure AS), thus increasing bounce and lowering the
457 AMS CE (Matthew et al., 2008; Middlebrook et al., 2012). AS particles can also become trapped
458 in the porous surface. When trapped, they are heated by conduction from the vaporizer surface
459 and by radiation from surrounding surfaces. They reach higher temperatures that lead to more
460 thermal decomposition, and a lower $H_2SO_4(g)/SO_x(g)$ ratio. In addition, molecules that evaporate
461 as $H_2SO_4(g)$ from these trapped particles are likely to collide with tungsten surfaces on their way
462 out to the ionization region, leading to additional thermal decomposition (Hu et al., 2017b) and
463 further reducing the $H_2SO_4(g)/SO_x(g)$ ratio for the gases reaching the EI region, and thus the
464 $H_ySO_x^+/SO_x^+$ ion ratio.

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

The second case (blue particle) represents the situation where the particle is less rigid/viscous or liquid. Acidic sulfate particles (with a lower fraction of the sulfate ions neutralized by NH_4^+), particles with high AN_f, or particles coated with a large water or liquid organic layer are more likely to deform upon impact and not bounce. This leads to an increased CE (Matthew et al., 2008; Middlebrook et al., 2012; Hu et al., 2017a). There are several effects that will lead to a higher $H_2SO_4(g)/SO_x(g)$ ratio reaching the ionization region in this situation: (a) evaporated H_2SO_4(g) from particles that impact the front of the vaporizer and do not bounce can now escape without further collisions with the tungsten surface; (b) the increased surface area from impact deformation and the lower viscosity allow more $H_2SO_4(g)$ molecules to escape the particle before those molecules are heated to temperatures that would lead to thermal decomposition.

In Fig. 2B, we show a conceptual model of the impact of these phenomena on the Chen triangle. For very acidic sulfate (approx. pH < 0), the liquid character of the particles leads to less bounce in the vaporizer. It also leads to faster evaporation, which reduces the internal temperature for the particles and that of the evaporated molecules, leading to less fragmentation. In this regime OS_f cannot be estimated, but pH may be, as long as it can be assumed (or shown by additional measurements from the AMS or other instruments) that OS_f and non-volatile cations are small. As an air mass becomes more neutralized by NH_4^+, the particles become less acidic and more rigid/viscous, leading to more thermal decomposition of the evaporated species, and the fragmentation of ammonium sulfate occurs at the upper vertex of the triangle. In this regime methods such as Chen et al. (2019) may be applicable to estimate OS_f, as long as there are no other effects that interfere with the sulfate fragments detected (such as substantial

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

non-volatile cations or variations in possible OA effects). As more ammonia is added to an airmass, the acidity of the particles decreases and the higher pH favors the partitioning of $HNO_3(g)$ to the particle phase, forming ammonium nitrate. If AN_f becomes high enough (> 0.3), the particles again become less rigid/viscous and the fragmentation shifts again outside the Chen triangle for the same reasons discussed for the acidic particles. Finally, Fig. 2C shows the differences in the detection process and the fragments produced in the AMS for OS and/or AS/H_2SO_4.

3.3 Evaluation of the Chen Method with Aircraft Field studies

The results of applying the Chen et al. (2019) method to five aircraft campaigns are shown in Fig. 1D. The effect of internally mixed ammonium nitrate (AN) was explored in Fig. 1A and Sect. 3.1 (for laboratory studies). Here we explore the effect for field data from KORUS-AQ (near Seoul, South Korea) where AN was often a major aerosol component; average $AN_f \sim 0.18$). As discussed in Sect. 3.1, as the percent of AN in laboratory mixtures of AS/AN increases, so do the $nfH_ySO_x^+$, ions. The same effect is observed for the KORUS-AQ campaign, although the departure from the AS vertex is observed at substantially lower AN fractions for the field data ($AN_f \sim 0.30$). When field data is affected by AN, the Chen method might be applicable for situations with $AN_f < 0.30$. At higher fractions, a correction could potentially be developed, but with increased resulting uncertainty.

In Fig. 1D, average values for each campaign in less acidic (pH > 0) and lower AN_f(< 0.3) conditions are shown. In the absence of acidity, OS, or AN_f effects, it is expected that the data would fall on top of the [1,1] pure AS point in the 1D triangle plot, but this is not observed.

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

509 This shift suggests that there are other factors (such as the presence of organics) that affect the
510 location of the pure AS point. In addition, the average values for the different campaigns vary
511 substantially, so it is unlikely that a "corrected" pure AS point can be used for all campaign
512 and/or lab data.

513 To further look into the potential effect of acidity, we consider the ATom campaigns in
514 Fig. 1C. ATom focused on remote oceanic air, with very low AN_f (< 0.008). This is expected as
515 AN is semivolatile (DeCarlo et al., 2008; Hennigan et al., 2008; Nault et al., 2018) and for the
516 very low pH conditions during ATom (~ -1 to 1, average of -0.6), most of the nitrate will be in
517 the form of HNO_3(g) (Guo et al., 2016). The PALMS instrument independently reports OS_f ~ 0.3
518 - 0.7% for ATom (depending on the pH). The results for ATom span the range between pure AS
519 and pure H_2SO_4, following a monotonic trend as acidity increases, consistent with the laboratory
520 results and the results from the WINTER campaign in Chen et al. (2019). We hypothesize that
521 high acidity is leading to the observed departure from the Chen triangle. Hence, the ATom results
522 suggest that all of the sulfate sampled is inorganic and if the Chen method is applied OS_f = -26%
523 to +4%. Thus the Chen method is insufficient to describe the trends observed for very acidic
524 aerosols, until pH increases to ~ 0 (where the ATom data starts to converge onto the pure AS data
525 point). For campaigns containing particles of pH > 0, the Chen method might be applicable.

526 To further illustrate that the ATom and KORUS-AQ campaigns are representative of the
527 range of airmasses in the troposphere, Fig. 1D shows results for two additional campaigns that
528 focused on the continental US. SEAC^{4}RS and WINTER represent chemical regimes that are not
529 extremely acidic (average pH SEAC^{4}RS ~ -0.2, WINTER pH ~ 1.2). SEAC^{4}RS had low AN_f (~
530 0.04), while WINTER had high AN_f (~ 0.25). It is observed that every single campaign average

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

falls outside of the triangle (for the full campaign and non-acidic, low AN_f averages), indicating that the Chen et al. method, as proposed, breaks down for many regions of the atmosphere. Average AN_f, OA_f, and pH values for different campaigns are shown in table S1.

3.4 Specification of aerosol chemical regimes for feasibility of OS_f quantification

In Fig. 3A, we introduce a plot of AN_f vs. pH that can be used to evaluate the applicability of the OS_f methods to different datasets. Data for five different campaigns (those with AS calibrations, labelled "C" in Table 1) are shown, along with the campaign averages. Regime I ("highly acidic, low AN") occupies the bottom left quadrant, where $AN_f < 0.3$ and pH < 0. Campaigns sampling the more remote atmosphere (e.g. ATom-1, 89% of datapoints; ATom-2, 80%), and a fraction of the data from continental campaigns (SEAC^{4}RS, 13% ; DC3 , 40%) fall in this regime. For remote regions, emissions (such as NH_3 and NO_x) are generally low. Remote oceanic regions are relatively isolated from the major continental ammonia sources (Paulot et al., 2015). Therefore, less ammonia is available to balance the hydronium ions from H_2SO_4, leading to high acidity (Quinn et al., 1988; Keene, 2002; Nault et al., 2020). Highly acidic aerosols and lack of NH_3 shift HNO_3 to the gas phase, so low AN_f is observed. In contrast, for sampling in polluted source regions with strong HNO_3 formation and substantial NH_3 emissions, a much smaller fraction of the data falls in this regime (e.g. only 4% for KORUS-AQ). In Sect. 3.5 we discuss the potential to estimate pH from AMS data in regime I.

Regime II (lower right) involves less acidic conditions (pH > 0) and lower AN_f (< 0.3). In this region sulfate fragmentation in the AMS is not strongly impacted by either AN_f or acidity. In principle, in this regime the recently proposed sulfate deconvolution methods can be used. The

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

553 geographical regions studied in Chen et al. (2019) and Song et al. (2019) generally fall in this
554 regime, and this explains the lack of large negative OS_f values in those studies, in contrast to our
555 observations for other regions. About half of our campaign data is located in this regime, more
556 so for the continental campaigns and much less for the remote campaigns. Specifically, 65% of
557 KORUS-AQ, 60% of DC3, 87% of SEAC^{4}RS, 11% of ATom-1 and 20% of ATom-2 fall in this
558 regime. We have applied the 1D version of the Chen method to each field campaign after
559 filtering it by the AN_f and pH constraints for regime II. OS_f is nominally slightly greater than
560 zero for ATom-1 (OS_f~ 3%, greater than the 0.3% estimate in regime II from PALMS (for
561 ATom-1 and ATom-2, estimated by only considering the sulfate moiety from the IEPOX or
562 glycolic acid sulfate (GAS) OS, neither of which was detected in the supermicron aerosol (Froyd
563 et al., 2009, 2019; Liao et al., 2015)) but still small, (see Fig. S7) much less than zero for
564 ATom-2 (OS_f~ -23%) and KORUS-AQ (OS_f~ -26%). This shows that even when pH and AN
565 are not major influences on the sulfate fragmentation, estimating OS with sulfate ions may be
566 susceptible to inaccuracies in AS calibrations, noise present in the ambient data, or other factors.
567 We also show results from applying the Song et al. (2019) method in regime II (which is
568 based on similar principles to the Chen method) in Fig. S8. Similarly to the Chen method, we see
569 that most OS_f values are predicted to be less than zero. For the entire atmosphere, shown in Fig.
570 S9, the distribution for% OS looks similar to Fig. S8.
571 Regime III is characterized by high AN_f (> 0.3) and lower acidity (pH > 0). This
572 chemical regime primarily exists in polluted continental regions near large source regions such
573 as megacities and agricultural regions, as high NO_x and NH_3 emissions can lead to increased
574 particulate AN and an increase in aerosol pH (Pye et al., 2019). In this regime, there are strong

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

575 variations in the AMS sulfate fragments that are driven by AN_f. OS_f cannot be estimated with the
576 AMS sulfate fragmentation methods proposed so far, unless they are further modified to account
577 for the AN_f effect. ~ 31% of KORUS-AQ data falls in this regime, but almost none of the data
578 from the rural / remote campaigns falls in this region, as AN typically evaporates as the air is
579 diluted during advection away from polluted regions (DeCarlo et al., 2008).

580 Finally, regime IV in the top left quadrant has high AN (AN_f > 0.3) and high acidity (pH
581 < 0). This chemical regime is unlikely to be observed in the real atmosphere, and indeed there
582 are very few points in that region for our campaigns. Sulfate is ubiquitous (Zhang et al., 2007b;
583 Hodzic et al., 2020), and nitrate is not thermodynamically stable in the aerosol phase together
584 with acidic sulfate for pH < 0 (Guo et. al., 2016). For all campaigns we observe ~ 0% of points
585 occupying this regime. Very unusual datapoints can be observed when ammonium
586 nitrate-containing particles are externally mixed with acidic sulfate containing particles in an
587 airmass.

588 Since the field studies analyzed here targeted large regions but did not sample many
589 others, it is of interest to evaluate the fraction of the troposphere located in each one of the
590 chemical regimes. The results of the GEOS-Chem v12 model are used for this purpose in Fig. 3B
591 and shown as a global map in Fig. 4 and Fig. S10. ~ 67% of the model troposphere exists in
592 regime I (pH < 0). In addition, ~ 33% of the global troposphere exists in regime II where it may
593 be feasible to estimate OS_f from AMS fragments. Less than 1% of the modeled atmosphere
594 exists in regime III (upper right quadrant) where ammonium nitrate strongly influences sulfate
595 fragmentation, consistent with the relatively small very polluted geographical regions with very
596 large AN_f. Finally, none of the data fell in regime IV, consistent with aerosols being assumed to

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

be internally mixed in GEOS-Chem. At the surface during December, January, and February (DJF) (Fig. 4A), most of the remote oceans fall in regime I (pH < 0 and AN_f < 0.3), while regime II (pH > 0 and AN_f < 0.3) is dominant over continental regions. At the surface in June, July, and August (JJA) (Fig. 4C), most of the globe is in regime II. Very little of the data falls in regime III, except parts of Asia, regardless of season. A similar pattern is observed in the free troposphere (Fig. 4B and 4D) with some geographical differences. Regime III (pH > 0 and AN_f > 0.3), which represents pollution hotspots, is observed in a large region in Asia during the Summer months, whereas the Winter months are dominated by regime I (low pH). The Summer months in the free troposphere are also mostly in regime II, especially over continental regions. Due to averaging of an entire year, as well as the limited spatial resolution of the GEOS-Chem model, locations and periods of high AN_f hotspots are not as prominent in these results, even when the data is divided by season.

3.5 Potential pH estimation from AMS measurements

3.5.1 Estimation of pH from AMS sulfate fragments

In Sect. 3.4, we introduced chemical regime I with low pH and low AN_f. In this regime, which encompasses about half of the campaign data and ⅔ of the modeled global troposphere, PALMS data shows that the overwhelming majority of the sulfate is inorganic, with OS_f contributing ~ 0.7% to total sulfate by mass during ATom-1 and ATom-2 when pH < 0 (see Fig. S7, in regime I). This removes sulfate fragmentation changes caused by AN and sulfate type (OS vs. AS), indicating that sulfate fragmentation is almost exclusively controlled by the acidity of the aerosol. Fig. 1C shows that $fH_2SO_4^+$ and $fHSO_3^+$, i.e. the amount of sulfate fragments

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

retaining one or two hydrogens ($H_2SO_4^+$ and HSO_3^+) relative to the sulfate fragments without a hydrogen atom (SO_3^+, SO_2^+, SO^+) increases as pH decreases.

In Fig. 5 we show the relationship between $H_ySO_x^+/SO_x^+$ and aerosol pH. As the relationship is noisy for individual data points, we show the results for 5% quantiles of the data. $H_ySO_x^+/SO_x^+$ appears to show a proportional relationship with decreasing pH for the ATom campaigns, for which much of the data is in regime I. The KORUS-AQ data, of which very little falls in the regime I, does not show a relationship between these variables, as expected. A fitted equation to the ATom relationship may allow the real-time estimation of pH for different air masses for campaigns in regime I as:

$$pH = -1.3\ (\pm 0.06) + 6.0(\pm 1.2) \times e^{-1.3(\pm 0.18)\times \frac{H_ySO_x^+}{SO_x^+}} \quad \text{Eq. 13}$$

As shown in the histogram in Fig. 5B, this relationship is applicable to a substantial fraction of ambient observations. This estimation equation likely needs to be calibrated for each instrument (e.g. by sampling sulfate particles with different acidities), since the sulfate fragmentation does vary with instrument (Chen et al., 2019) (and potentially also in time for a given instrument).

Although an estimation equation that apparently works for only one unit of pH may seem of limited value, two caveats apply: first, it is of high value to know that pH < 0 for a certain air mass (as opposed to e.g. pH = 2 or 3 that are frequently encountered). Second, the range of pH below 0 is limited here due to not considering the activity coefficient. If that coefficient was included, the predicted pH range in this regime would be ~ -4 to 0.

3.5.2 Estimation of pH from Ammonium Balance

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

640 Ammonium balance (NH_{4_bal}) (Eq. (7)) is often used as a qualitative indicator of acidity.
641 (Zhang et al., 2007a) showed that pH under constant temperature and RH was well correlated
642 with ammonium balance, but much more scatter was observed when the instantaneous T and RH
643 were used. Several studies have argued that ammonium balance cannot be used to estimate
644 ambient pH (e.g., (Guo et al., 2015, 2016; Hennigan et al., 2015; Weber et al., 2016); however,
645 those studies were all performed at continental ground sites that were in the less-acidic chemical
646 regimes (II and III), and where daily temperature and humidity changes were strong. As shown
647 in Fig. 6, NH_{4_bal} and pH for the aircraft studies show a strong and consistent relationship in
648 regime I (pH < 0), providing another potential method for estimating pH. As ammonium balance
649 increases, so does pH across the six campaigns studied. These data are generally outside of the
650 continental boundary layer, where temperature and RH change less in a diurnal cycle, reducing
651 the impact of those changes on pH. For data in regimes II-III (pH > 0) some proportionality of
652 pH and NH_{4_bal} is still observed on average, but with more dispersion across campaigns. Given
653 the similarity of the results for regime I, the fitting equation of pH vs. ammonium balance may
654 be used to provide a near real-time estimate of pH (for $NH_{4\_bal} < 0.65$).

$$pH = -1.1(\pm 0.031) + 1.7(\pm 0.089) * NH_{4\_bal} \quad \text{Eq. 14}$$

655

656 As shown in the histogram in Fig 6B-6D, this relationship is also applicable to a
657 substantial fraction of ambient regions. This estimation equation should be tested with other
658 studies. An advantage of this relationship (vs. the one based on $H_ySO_x^+/SO_x^+$) is that it is likely to
659 be less instrument-dependent, as long as careful calibrations of RIE_{NH4} and RIE_{SO4} have been
660 performed. Conditions where non-volatile cations (e.g. Na^+, K^+, Ca^{2+}) are important for

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

submicron particles could lead to deviations from this relationship (Guo et al., 2020). However, such conditions are infrequent in remote air (Nault et al., 2020) and can be diagnosed by concurrent supermicron or filter measurements.

3.5.3 Application of pH estimation methods to ambient data

As discussed above, ammonium balance and $H_ySO_x^+/SO_x^+$ are two measurements that may be used to estimate aerosol acidity in parts of the atmosphere. In Fig. 7 these two methods are applied to one flight during ATom-1 and an SO_2 plume sampled during WINTER. In Fig. 7A, both $H_ySO_x^+/SO_x^+$ and NH_{4_bal} follow the trend for E-AIM calculated pH during most periods when pH < 0, even at one minute time resolution.

As expected from Fig. 6, NH_{4_bal} is a less noisy, more robust metric for estimating pH at one minute time resolution. Unlike $H_ySO_x^+/SO_x^+$, NH_{4_bal} appears to be able to capture basic pH trends at the full range of pH values observed during this flight in ATom-1. NH_{4_bal} also matches the E-AIM predicted pH well for the WINTER power plant plume. For RF01 in ATom-1 (WINTER), NH_{4_bal} predicted pH has an $R^2 \sim 0.6$ (0.9) for pH<0 (Fig. 7C-D).This shows that in the remote atmosphere (like in ATom) or in an SO_2 plume, NH_{4_bal} has the potential to allow fast estimation of pH, even under relatively low sulfate concentrations, albeit not perfectly. More scatter is observed for the estimate based on $H_ySO_x^+/SO_x^+$, indicating that longer averages are needed for this method. The error is typically within +/- 0.5 pH units, which is thought to be the accuracy of thermodynamic pH estimation models.

3.6 Possibility of Estimating CE from Sulfate Fragmentation

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

From the previous discussion it is clear that sulfate fragmentation changes due to some of the same factors (acidity, AN_f) that influence ambient AMS CE. It is of interest to explore whether a quantitative estimate of ambient particle CE could be derived from the measured sulfate fragments, at least under some conditions, as it could provide a complementary characterization to the CE estimates from the Middlebrook et al. (2012) parameterization. In Fig. 8 we show the CE estimated from Middlebrook et al. (2012) vs. $H_ySO_x^+/SO_x^+$ for ATom and KORUS-AQ. CE does show some relationship with $H_ySO_x^+/SO_x^+$, with most sensitivity around CE ~ 0.8-0.9. A substantial level of noise is observed on the high-time resolution data, and the trend varies between the two campaigns (where variations in CE are controlled by two different effects, acidity vs AN_f). Further research would be necessary to evaluate whether this method could be used to estimate CE.

Conclusions

The presence of organosulfates in particles is a topic of much recent interest, but there is a lack of online methods to quantify them. Two methods have been proposed to use widely available AMS data to quantify OS_f (Chen et al., 2019; Song et al., 2019). However, these methods have only been applied to ground continental datasets, to our knowledge. We show using both laboratory and field data that both high acidity (chemical regime I in this work) and high AN_f (regime III) result in major changes in sulfate fragmentation, which often produce nonsensical results for the OS_f methods. Regime I accounts for ~ ⅔ of the global troposphere , while regime III can be important in polluted regions (e.g. Seoul region), and thus it is critical to avoid applying the proposed OS_f estimation methods in these regimes. In regime II, with lower

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020


Atmospheric Measurement Techniques Discussions

acidity and lower nitrate (pH > 0, $AN_f < 0.3$) OS_f estimation methods may be applicable, if no other effects (e.g. significant non-volatile cations or variations in OA effects) confound the sulfate fragmentation. For reasons not fully understood, fragmentation of the sulfate ions in the lab vs. ambient data differ at times.

We investigated two different methods to estimate pH in real-time in regime I (pH < 0 and $AN_f < 0.3$), based on the AMS $H_ySO_x^+/SO_x^+$ fragment ratio and the ammonium balance, respectively, without the need to run a thermodynamic model, and without the need for gas-phase NH_3 or HNO_3 measurements. Low OS_f and non-volatile cations need to be assumed or confirmed from AMS and other measurements. The ammonium balance method shows better performance. These *in-situ* and direct pH estimation methods should be applicable in the remote atmosphere (oceanic regions, and often the continental free troposphere when not recently impacted by surface sources). Both the OS_f and pH estimations require careful instrument calibration for a given campaign, and the methods based on sulfate fragments are expected to be instrument-dependent, including for the same instrument in time when filaments or the vaporizer are replaced, or when the instrument is re-tuned. Both methods should be further evaluated with data from other studies.

We propose a conceptual model to explain the observed sulfate fragmentation changes with changing particle chemical composition. As particles become more acidic or higher in AN, a higher fraction of $H_2SO_4(g)$ can reach the ionization region, leading to changes in the observed ion population. Since AMS CE is thought to be controlled by the same effects, we explore whether it can be estimated from the observed sulfate fragmentation, and find that while changes in $H_ySO_x^+/SO_x^+$ do correlate to changes in CE, the relationship is not the same across different

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

campaigns. Further investigation of this relationship, especially when direct CE measurements are available via internal AMS light scattering, would be of interest.

Acknowledgements

This work was supported by NASA grants NNX15AH33A & 80NSSC19K0124, and a CIRES IRP project. We thank the members of the Jimenez group, the AMS users community, Weiwei Hu, Amber Ortega, and Patrick Hayes for help with data acquisition during SEAC^{4}RS and DC-3; Jason St. Clair, Alex Teng, Michelle Kim, John Crounse, and Paul Wennberg for providing CIT-CIMS HNO_3 data; Joel Thornton, Felipe Lopez-Hilfiker, and Ben Lee for providing UW-CIMS HNO_3 data during WINTER; Karl Froyd, Gregory P. Schill, and Daniel Murphy for providing PALMS organosulfate data for ATom campaigns; and Glenn Diskin for providing DLH H_2O data.

Data Availability

DC3 data available at DOI: 10.5067/Aircraft/DC3/DC8/Aerosol-TraceGas, last accessed on 9 September, 2018. SEAC^{4}RS data available at http://doi.org/10.5067/Aircraft/SEAC4RS/Aerosol-TraceGas-Cloud, last accessed on 27 April, 2020. WINTER data available at https://data.eol.ucar.edu/master_lists/generated/winter/, last accessed 27 April 2020. KORUS-AQ data available at DOI: 10.5067/Suborbital/KORUSAQ/DATA01, last accessed 14 June, 2018. ATom-1 and ATom-2 data available at https://doi.org/10.3334/ORNLDAAC/158, last accessed 27 April 2020.

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

Atmospheric Measurement Techniques Discussions

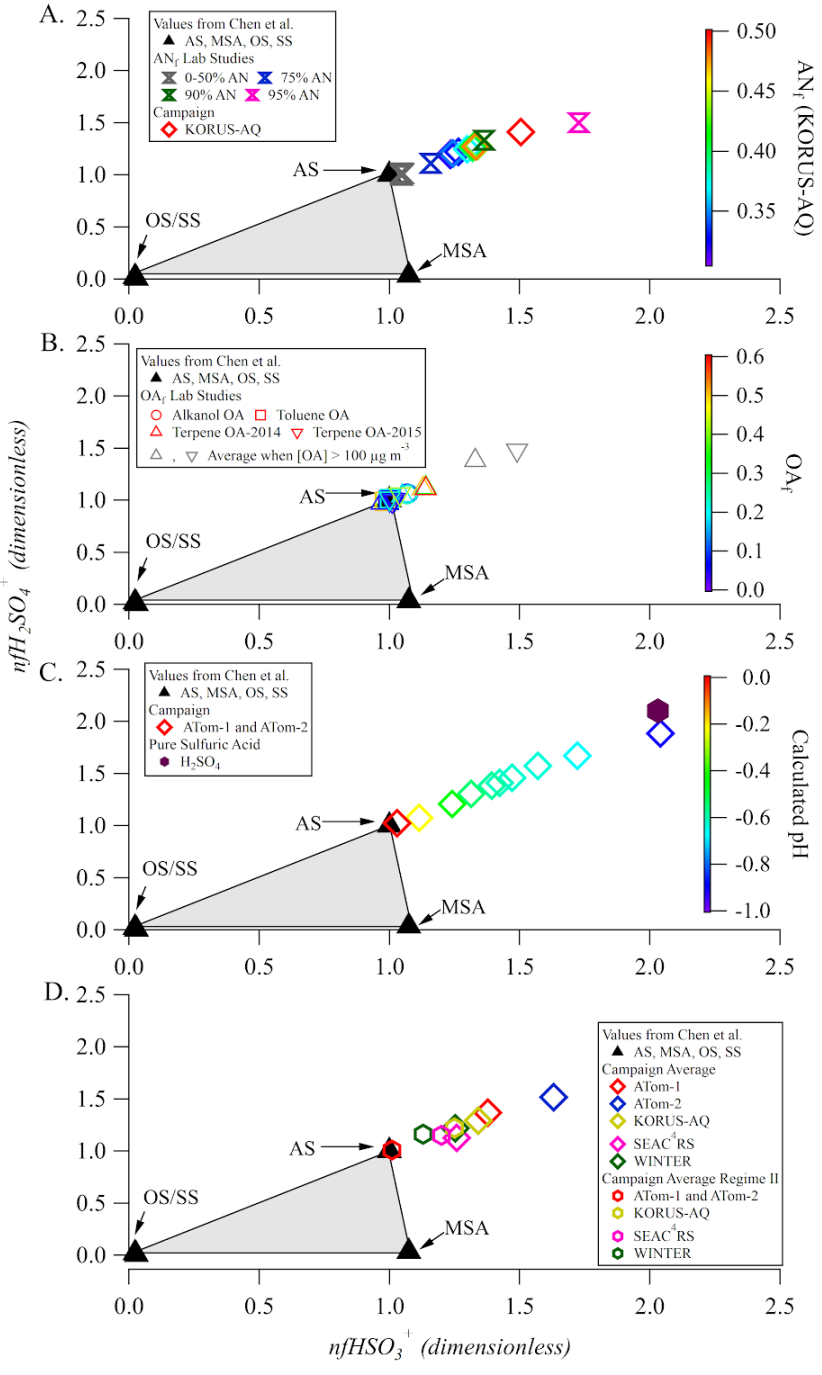
Tables

Table 1. Summary of the campaigns used in this study. See SI Fig. S1 for flight paths. Reference label refers to the type of data used for each campaign throughout this paper, depending on the quality and completeness of the data, for the purposes of a specific analysis. A : ammonium balance, f: SO_4 campaign-averaged fragments, F: SO_4 campaign-average and time-resolved fragments , and C: pure AS calibration data reliable and used.

Campaign	Location	Season/Year	References	Reference Label
DC3: Deep Convective Clouds and Chemistry	Mid-Latitude Continental United States	May-June 2012	Barth et al. , 2015	A
SEAC^{4}RS: Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys	Continental United States	Summer 2013	Wagner et al., 2015; Toon et al., 2016	A, f, C
WINTER: Wintertime Investigation of Transport, Emissions, and Reactivity	Eastern United States, continental and marine	Winter 2015	Schroder et al., 2018; Shah et al., 2018	A, f, C
KORUS-AQ: Korean United States Air Quality	South Korean Peninsula and Yellow Sea	Spring 2016	Nault et al., 2018	A, F, C
ATom-1: Atmospheric Tomography Mission 1	Remote Pacific and Atlantic Basins	Boreal Summer 2016	Hodzic et al., 2020; Brock et al., 2019; Hodshire et al., 2019	A, F, C
ATom-2: Atmospheric Tomography Mission 2	Remote Pacific and Atlantic Basins	Boreal Winter 2017	Hodzic et al., 2020	A, F, C

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

Atmospheric Measurement Techniques Discussions



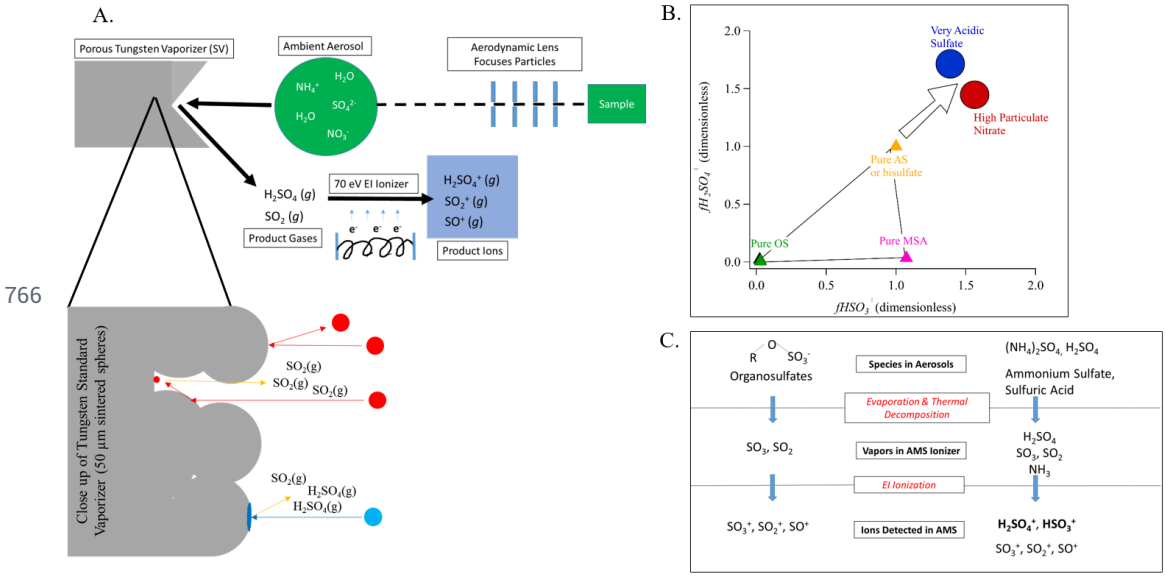
https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

Atmospheric Measurement Techniques Discussions

Fig. 1. Laboratory and field data for sulfate fragmentation shown in the triangle diagram proposed by Chen et al. (2019). (A) Data split into 10 quantiles of AN_f value for the full KORUS-AQ campaign, as well as for different laboratory internal mixtures of AS and AN . (B) Data from two chamber experiments, split into 5 quantiles of OA_f. Data with very high OA (>100 µg m^{-3}) are shown as grey triangles. Two separate datasets of monoterpene SOA chamber experiments are labelled as "2014" and "2015". (C) Data split into 10 quantiles by pH for ATom-1 and 2, colored by pH from E-AIM. (D) Averages for 5 aircraft campaigns for the full campaign and a subset of each campaign where pH<0 and AN_f <0.3.

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

Atmospheric Measurement Techniques Discussions



766

767 Fig. 2. (A) Simplified schematic of the AMS detection process, including a close up of the
768 tungsten standard vaporizer surface and the different species produced by AS and OS. (B)
769 Conceptual model of the position of particles of different compositions in the Chen et al. (2019)
770 triangle plot. As particles become more acidic or higher in particulate nitrate, the ratio of the
771 AMS hydrogenated to total sulfate fragments increases. When sulfate is present as AS (or
772 mixtures of AS and ammonium bisulfate), the sulfate fragmentation is mainly impacted by OS
773 vs. AS vs. MSA relative concentrations inside the Chen triangle. (C) Schematic of the
774 transformations during the AMS detection process for OS and AS.

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

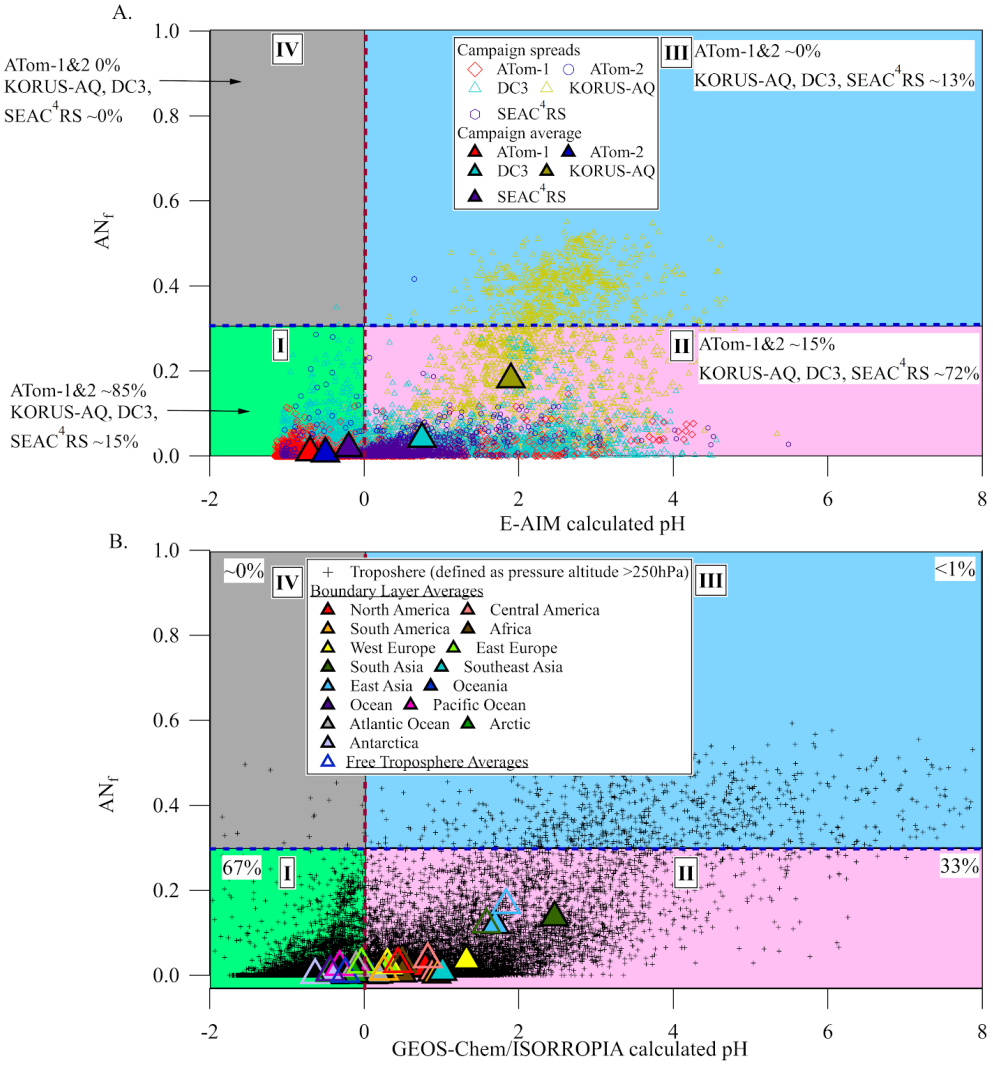
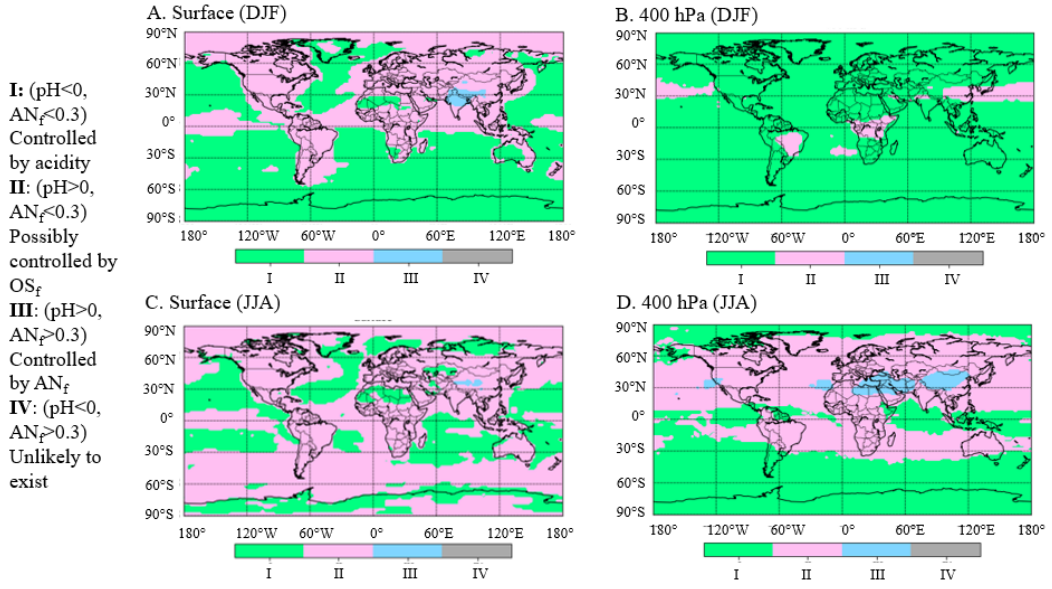


Fig. 3. (A) location of the aircraft campaign 1-minute data points on the chemical regimes defined in this paper (AN_f, from AMS measurements) vs. E-AIM pH. SEAC^{4}RS, WINTER, and KORUS-AQ are averaged to one value, for brevity, but defined individually in Sect. 3.4. (B) Location of global GEOS-Chem v12 results in the chemical-regimes diagram. Yearlong averages shown as large triangles.

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020



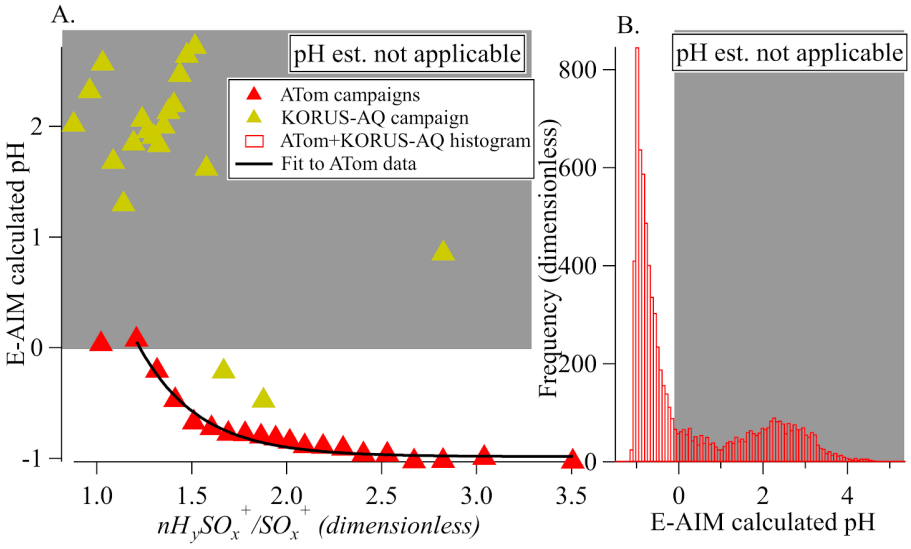
782

783 Fig. 4. Areas characterized by different chemical regimes according to results from
784 GEOS-Chem v12. (A) Surface for December, January, and February (DJF), (B) 400 hPa for DJF,
785 (C) Surface for June, July, and August (JJA), (D) 400 hPa for JJA. Roman numerals correspond
786 to regimes in Fig. 3.
787

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

Atmospheric Measurement Techniques Discussions

788



789

790 Fig. 5. (A) pH vs. sulfate fragmentation indicator ($H_ySO_x^+/SO_x^+$) for the ATom and KORUS-AQ
791 campaigns, and binned by $nH_ySO_x^+/SO_x^+$. The black line is an exponential fit to ATom data (see
792 text). (B) histogram of the calculated pH for the 1-minute datapoints from the ATom-1,2 and
793 KORUS-AQ datasets. In both panels, the white (gray) area shows the regime where pH can
794 (cannot) be estimated from the sulfate fragmentation.
795

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

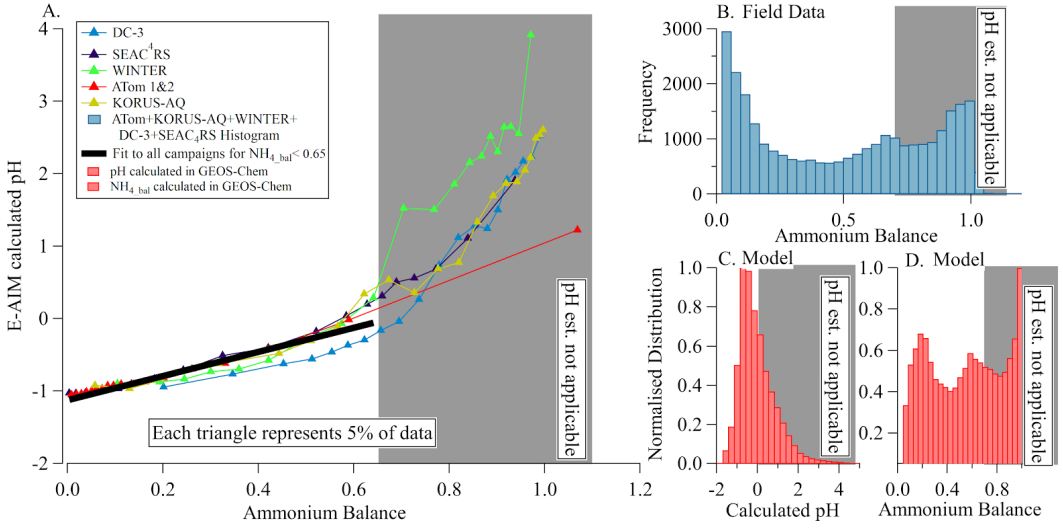
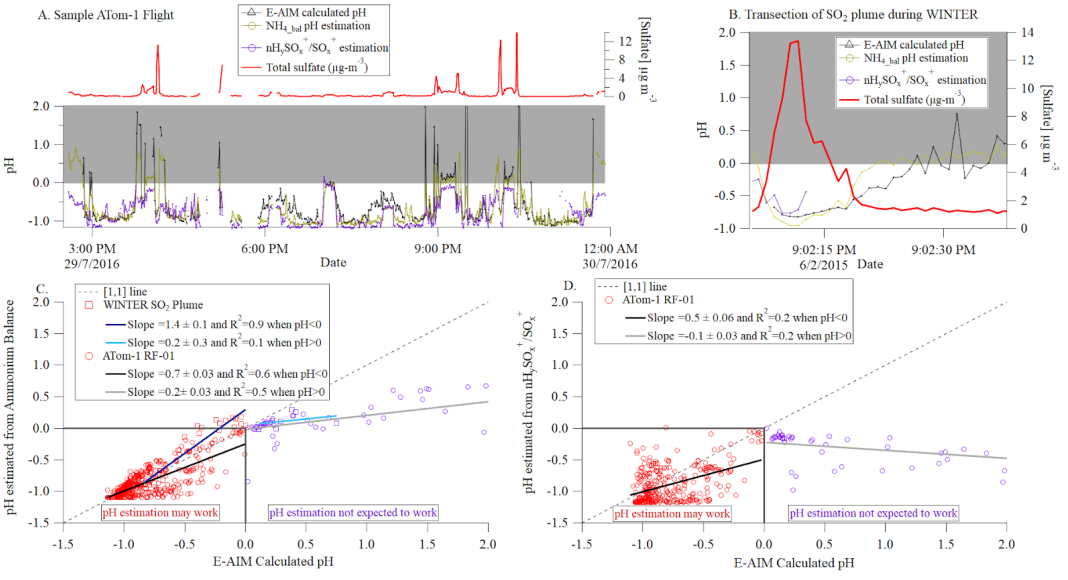


Fig 6. (A) calculated pH vs. ammonium balance for multiple campaigns. Quantiles of the data are used to reduce the impact of noise. The black line is an orthogonal distance regression (ODR) fit to the campaign data for values with $NH_{4\_Bal} < 0.65$. B) Histogram of measured ammonium balance for the 6 campaigns. (C) and (D), pH and ammonium balance from GEOS-Chem (pH calculated with ISORROPIA). In all panels the white (grey) areas encompass the data points for which pH can (cannot) be estimated from the measured ammonium balance.

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

Atmospheric Measurement Techniques Discussions

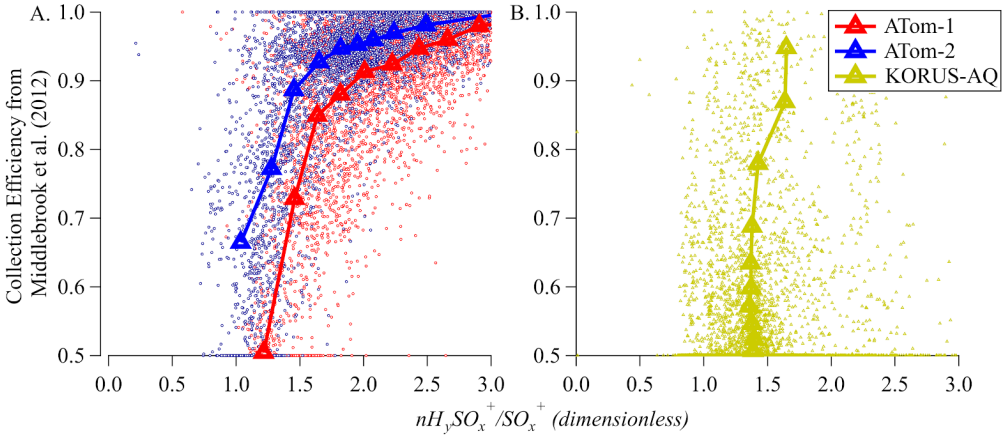
804



805

806 Fig. 7. (A) Time series of sulfate, pH calculated from E-AIM and estimated from $H_ySO_x^+/SO_x^+$,
807 and NH_{4_Bal} for one flight during ATom-1 (at 1 min. resolution, filtered to remove points where
808 sulfate was less than 3 times its detection limit). (B) Time series of sulfate and pH for a large
809 power plant plume sampled during WINTER. (C) Scatterplot of pH predicted from NH_{4_Bal} vs.
810 E-AIM pH for the data above. (D) Scatterplot of pH predicted from $H_ySO_x^+/SO_x^+$ vs. E-AIM pH
811 for the ATom flight.

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020



812

813 Fig. 8. (A) Collection efficiency parameterization vs. $H_ySO_x^+/SO_x^+$ for two ATom campaigns, and
814 (B) the KORUS-AQ campaign.
815

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

References

Ackendorf, J. M., Ippolito, M. G. and Galloway, M. M.: pH Dependence of the Imidazole-2-carboxaldehyde Hydration Equilibrium: Implications for Atmospheric Light Absorbance, Environ. Sci. Technol. Lett., 4(12), 551–555, doi:10.1021/acs.estlett.7b00486, 2017.

Alfarra, M. R., Coe, H., Allan, J. D., Bower, K. N., Boudries, H., Canagaratna, M. R., Jimenez, J. L., Jayne, J. T., Garforth, A. A., Li, S.-M. and Worsnop, D. R.: Characterization of urban and rural organic particulate in the Lower Fraser Valley using two Aerodyne Aerosol Mass Spectrometers, Atmos. Environ., 38(34), 5745–5758, doi:10.1016/j.atmosenv.2004.01.054, 2004.

Anon: Atmospheric chemistry and physics: from air pollution to climate change, Choice Reviews Online, 44(08), 44–4512–44–4512, doi:10.5860/CHOICE.44-4512, 2007.

Bahreini, R., Dunlea, E. J., Matthew, B. M., Simons, C., Docherty, K. S., DeCarlo, P. F., Jimenez, J. L., Brock, C. A. and Middlebrook, A. M.: Design and Operation of a Pressure-Controlled Inlet for Airborne Sampling with an Aerodynamic Aerosol Lens, Aerosol Sci. Technol., 42(6), 465–471, doi:10.1080/02786820802178514, 2008.

Bahreini, R., Ervens, B., Middlebrook, A. M., Warneke, C., de Gouw, J. A., DeCarlo, P. F., Jimenez, J. L., Brock, C. A., Neuman, J. A., Ryerson, T. B., Stark, H., Atlas, E., Brioude, J., Fried, A., Holloway, J. S., Peischl, J., Richter, D., Walega, J., Weibring, P., Wollny, A. G. and Fehsenfeld, F. C.: Organic aerosol formation in urban and industrial plumes near Houston and Dallas, Texas, J. Geophys. Res., 114, 1185, doi:10.1029/2008JD011493, 2009.

Barth, M. C., Cantrell, C. A., Brune, W. H., Rutledge, S. A., Crawford, J. H., Huntrieser, H., Carey, L. D., MacGorman, D., Weisman, M., Pickering, K. E., Bruning, E., Anderson, B., Apel, E., Biggerstaff, M., Campos, T., Campuzano-Jost, P., Cohen, R., Crounse, J., Day, D. A., Diskin, G., Flocke, F., Fried, A., Garland, C., Heikes, B., Honomichl, S., Hornbrook, R., Huey, L. G., Jimenez, J. L., Lang, T., Lichtenstern, M., Mikoviny, T., Nault, B., O'Sullivan, D., Pan, L. L., Peischl, J., Pollack, I., Richter, D., Riemer, D., Ryerson, T., Schlager, H., St. Clair, J., Walega, J., Weibring, P., Weinheimer, A., Wennberg, P., Wisthaler, A., Wooldridge, P. J. and Ziegler, C.: The Deep Convective Clouds and Chemistry (DC3) Field Campaign, Bull. Am. Meteorol. Soc., 96(8), 1281–1309, doi:10.1175/BAMS-D-13-00290.1, 2015.

Bertram, T. H. and Thornton, J. A.: Toward a general parameterization of N_2O_5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride, Atmos. Chem. Phys., 9(21), 8351–8363, 2009.

Bey, I., Jacob, D. J., Yantosca, R. M., Logan, J. A., Field, B. D., Fiore, A. M., Li, Q., Liu, H. Y., Mickley, L. J. and Schultz, M. G.: Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation, J. Geophys. Res., 106(D19), 23073–23095, doi:10.1029/2001JD000807, 2001.

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

853 Canagaratna, M. R., Jayne, J. T., Jimenez, J. L., Allan, J. D., Alfarra, M. R., Zhang, Q., Onasch,
854 T. B., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L. R., Trimborn, A. M.,
855 Northway, M. J., DeCarlo, P. F., Kolb, C. E., Davidovits, P. and Worsnop, D. R.: Chemical and
856 microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer,
857 Mass Spectrom. Rev., 26(2), 185–222, doi:10.1002/mas.20115, 2007.

858 Carlton, A. G., de Gouw, J., Jimenez, J. L., Ambrose, J. L., Attwood, A. R., Brown, S., Baker, K.
859 R., Brock, C., Cohen, R. C., Edgerton, S., Farkas, C. M., Farmer, D., Goldstein, A. H., Gratz, L.,
860 Guenther, A., Hunt, S., Jaeglé, L., Jaffe, D. A., Mak, J., McClure, C., Nenes, A., Nguyen, T. K.,
861 Pierce, J. R., de Sa, S., Selin, N. E., Shah, V., Shaw, S., Shepson, P. B., Song, S., Stutz, J.,
862 Surratt, J. D., Turpin, B. J., Warneke, C., Washenfelder, R. A., Wennberg, P. O. and Zhou, X.:
863 Synthesis of the Southeast Atmosphere Studies: Investigating Fundamental Atmospheric
864 Chemistry Questions, Bull. Am. Meteorol. Soc., 99(3), 547–567,
865 doi:10.1175/BAMS-D-16-0048.1, 2018.

866 Chen, Y., Xu, L., Humphry, T., Hettiyadura, A. P. S., Ovadnevaite, J., Huang, S., Poulain, L.,
867 Schroder, J. C., Campuzano-Jost, P., Jimenez, J. L., Herrmann, H., O'Dowd, C., Stone, E. A. and
868 Ng, N. L.: Response of the Aerodyne Aerosol Mass Spectrometer to Inorganic Sulfates and
869 Organosulfur Compounds: Applications in Field and Laboratory Measurements, Environ. Sci.
870 Technol., 53(9), 5176–5186, doi:10.1021/acs.est.9b00884, 2019.

871 Clegg, S. L., Brimblecombe, P. and Wexler, A. S.: Thermodynamic Model of the System H +
872 -NH 4 + -SO 42- -NO 3 - -H 2 O at Tropospheric Temperatures, , 5639(3), 2137–2154, 1998a.

873 Clegg, S. L., Brimblecombe, P. and Wexler, A. S.: Thermodynamic Model of the System H
874 −NH4 −SO42-−NO3-−H2O at Tropospheric Temperatures, The Journal of Physical Chemistry
875 A, 102(12), 2137–2154, doi:10.1021/jp973042r, 1998b.

876 Clegg, S. L., Seinfeld, J. H. and Edney, E. O.: Thermodynamic modelling of aqueous aerosols
877 containing electrolytes and dissolved organic compounds. II. An extended
878 Zdanovskii–Stokes–Robinson approach, J. Aerosol Sci., 34(6), 667–690,
879 doi:10.1016/S0021-8502(03)00019-3, 2003.

880 Craig, R. L., Peterson, P. K., Nandy, L., Lei, Z., Hossain, M. A., Camarena, S., Dodson, R. A.,
881 Cook, R. D., Dutcher, C. S. and Ault, A. P.: Direct Determination of Aerosol pH: Size-Resolved
882 Measurements of Submicrometer and Supermicrometer Aqueous Particles, Anal. Chem., 90(19),
883 11232–11239, doi:10.1021/acs.analchem.8b00586, 2018.

884 Crounse, J. D., McKinney, K. A., Kwan, A. J. and Wennberg, P. O.: Measurement of gas-phase
885 hydroperoxides by chemical ionization mass spectrometry, Anal. Chem., 78(19), 6726–6732,
886 doi:10.1021/ac0604235, 2006.

887 Cubison, M. J., Ortega, A. M., Hayes, P. L., Farmer, D. K., Day, D., Lechner, M. J., Brune, W.
888 H., Apel, E., Diskin, G. S., Fisher, J. A. and Others: Effects of aging on organic aerosol from
889 open biomass burning smoke in aircraft and laboratory studies, Atmos. Chem. Phys., 11(23),
890 12049–12064 [online] Available from:

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

https://www.atmos-chem-phys.net/11/12049/2011/acp-11-12049-2011.pdf, 2011.

DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R. and Jimenez, J. L.: Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer, Anal. Chem., 78(24), 8281–8289, doi:10.1021/ac061249n, 2006.

DeCarlo, P. F., Dunlea, E. J., Kimmel, J. R., Aiken, A. C., Sueper, D., Crounse, J., Wennberg, P. O., Emmons, L., Shinozuka, Y., Clarke, A. and Others: Fast airborne aerosol size and chemistry measurements above Mexico City and Central Mexico during the MILAGRO campaign, 1foldr Import 2019-10-08 Batch 1 [online] Available from: https://oaktrust.library.tamu.edu/bitstream/handle/1969.1/178622/document-2.pdf?sequence=2, 2008.

Dentener, F. J. and Crutzen, P. J.: A three-dimensional model of the global ammonia cycle, J. Atmos. Chem., 19(4), 331–369, doi:10.1007/BF00694492, 1994.

Docherty, K. S., Lewandowski, M. and Jimenez, J. L.: Effect of Vaporizer Temperature on Ambient Non-Refractory Submicron Aerosol Composition and Mass Spectra Measured by the Aerosol Mass Spectrometer, Aerosol Sci. Technol., 49(7), 485–494, doi:10.1080/02786826.2015.1042100, 2015.

Dockery, D. W., Cunningham, J., Damokosh, A. I., Neas, L. M., Spengler, J. D., Koutrakis, P., Ware, J. H., Raizenne, M. and Speizer, F. E.: Health effects of acid aerosols on North American children: respiratory symptoms, Environ. Health Perspect., 104(5), 500–505, doi:10.1289/ehp.96104500, 1996.

Dovrou, E., Lim, C. Y., Canagaratna, M. R., Kroll, J. H., Worsnop, D. R. and Keutsch, F. N.: Measurement techniques for identifying and quantifying hydroxymethanesulfonate (HMS) in an aqueous matrix and particulate matter using aerosol mass spectrometry and ion chromatography, Atmospheric Measurement Techniques, 12(10), 5303–5315, doi:10.5194/amt-12-5303-2019, 2019.

Dunlea, E. J., DeCarlo, P. F., Aiken, A. C., Kimmel, J. R., Peltier, R. E., Weber, R. J., Tomlinson, J., Collins, D. R., Shinozuka, Y., McNaughton, C. S. and Others: Evolution of Asian aerosols during transpacific transport in INTEX-B, Atmos. Chem. Phys., 9(19), 7257–7287 [online] Available from: https://www.atmos-chem-phys.net/9/7257/2009/acp-9-7257-2009.pdf, 2009.

Facchini, M. C., Decesari, S., Rinaldi, M., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Moretti, F., Tagliavini, E., Ceburnis, D. and O'Dowd, C. D.: Important source of marine secondary organic aerosol from biogenic amines, Environ. Sci. Technol., 42(24), 9116–9121, doi:10.1021/es8018385, 2008.

Farmer, D. K., Matsunaga, A., Docherty, K. S., Surratt, J. D., Seinfeld, J. H., Ziemann, P. J. and Jimenez, J. L.: Response of an aerosol mass spectrometer to organonitrates and organosulfates and implications for atmospheric chemistry, Proc. Natl. Acad. Sci. U. S. A., 107(15), 6670–6675,

928 doi:10.1073/pnas.0912340107, 2010.

929 Fountoukis, C. and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic
930 equilibrium model for K^+–Ca^{2+}–Mg^{2+}–NH_4^+–Na^+–SO_4^{2-}–NO_3^-–Cl^-–H_2O aero, Atmos. Chem.
931 Phys., 7(17), 4639–4659, doi:10.5194/acp-7-4639-2007, 2007.

932 Friese, E. and Ebel, A.: Temperature Dependent Thermodynamic Model of the System H −NH4
933 −Na −SO42−−NO3−−Cl−−H2O, The Journal of Physical Chemistry A, 114(43), 11595–11631,
934 doi:10.1021/jp101041j, 2010.

935 Frossard, A. a., Russell, L. M., Burrows, S. M., Elliott, S. M., Bates, T. S. and Quinn, P. K.:
936 Sources and Composition of Submicron Organic Mass in Marine Aerosol Particles, J. Geophys.
937 Res. D: Atmos., doi:10.1002/2014JD021913, 2014.

938 Froyd, K. D., Murphy, D. M., Sanford, T. J., Thomson, D. S., Wilson, J. C., Pfister, L. and Lait,
939 L.: Aerosol composition of the tropical upper troposphere, Atmos. Chem. Phys., 9(13),
940 4363–4385, doi:10.5194/acp-9-4363-2009, 2009.

941 Froyd, K. D., Murphy, D. M., Brock, C. A., Campuzano-Jost, P., Dibb, J. E., Jimenez, J.-L.,
942 Kupc, A., Middlebrook, A. M., Schill, G. P., Thornhill, K. L., Williamson, C. J., Wilson, J. C.
943 and Ziemba, L. D.: A new method to quantify mineral dust and other aerosol species from
944 aircraft platforms using single-particle mass spectrometry, Atmospheric Measurement
945 Techniques, 12(11), 6209–6239, doi:10.5194/amt-12-6209-2019, 2019.

946 Fry, J. L., Draper, D. C., Zarzana, K. J., Campuzano-Jost, P., Day, D. A., Jimenez, J. L., Brown,
947 S. S., Cohen, R. C., Kaser, L., Hansel, A., Cappellin, L., Karl, T., Hodzic Roux, A., Turnipseed,
948 A., Cantrell, C., Lefer, B. L. and Grossberg, N.: Observations of gas- and aerosol-phase organic
949 nitrates at BEACHON-RoMBAS 2011, Atmospheric Chemistry and Physics, 13(17),
950 8585–8605, doi:10.5194/acp-13-8585-2013, 2013.

951 Gaston, C. J., Riedel, T. P., Zhang, Z., Gold, A., Surratt, J. D. and Thornton, J. A.: Reactive
952 Uptake of an Isoprene-Derived Epoxydiol to Submicron Aerosol Particles, ,
953 doi:10.1021/es5034266, 2014.

954 Gelaro, R., McCarty, W., Suárez, M. J., Todling, R., Molod, A., Takacs, L., Randles, C. A.,
955 Darmenov, A., Bosilovich, M. G., Reichle, R., Wargan, K., Coy, L., Cullather, R., Draper, C.,
956 Akella, S., Buchard, V., Conaty, A., da Silva, A. M., Gu, W., Kim, G.-K., Koster, R., Lucchesi,
957 R., Merkova, D., Nielsen, J. E., Partyka, G., Pawson, S., Putman, W., Rienecker, M., Schubert, S.
958 D., Sienkiewicz, M. and Zhao, B.: The Modern-Era Retrospective Analysis for Research and
959 Applications, Version 2 (MERRA-2), J. Clim., 30(14), 5419–5454,
960 doi:10.1175/JCLI-D-16-0758.1, 2017.

961 Ge, X., Shaw, S. L. and Zhang, Q.: Toward Understanding Amines and Their Degradation
962 Products from Postcombustion CO2 Capture Processes with Aerosol Mass Spectrometry,
963 Environ. Sci. Technol. [online] Available from: http://pubs.acs.org/doi/abs/10.1021/es4056966,
964 2014.

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

965 Gibb, S. W., Mantoura, R. F. C. and Liss, P. S.: Ocean-atmosphere exchange and atmospheric
966 speciation of ammonia and methylamines in the region of the NW Arabian Sea, Global
967 Biogeochemical Cycles, 13(1), 161–178, doi:10.1029/98gb00743, 1999.

968 Giglio, L., Randerson, J. T. and van der Werf, G. R.: Analysis of daily, monthly, and annual
969 burned area using the fourth-generation global fire emissions database (GFED4), Journal of
970 Geophysical Research: Biogeosciences, 118(1), 317–328 [online] Available from:
971 https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1002/jgrg.20042, 2013.

972 Guo, H., Xu, L., Bougiatioti, A., Cerully, K. M., Capps, S. L., Hite, J. R., Jr, Carlton, A. G., Lee,
973 S.-H., Bergin, M. H., Ng, N. L. and Others: Fine-particle water and pH in the southeastern
974 United States, Atmospheric Chemistry & Physics, 15(9) [online] Available from:
975 https://www.researchgate.net/profile/Kate_Cerully/publication/276206260_Fine-particle_water_
976 and_pH_in_the_southeastern_United_States/links/55f6fc8508aeba1d9eee4213.pdf, 2015.

977 Guo, H., Sullivan, A. P., Campuzano-Jost, P., Schroder, J. C., Lopez-Hilfiker, F. D., Dibb, J. E.,
978 Jimenez, J. L., Thornton, J. A., Brown, S. S., Nenes, A. and Others: Fine particle pH and the
979 partitioning of nitric acid during winter in the northeastern United States, J. Geophys. Res. D:
980 Atmos., 121(17), 10–355 [online] Available from:
981 https://onlinelibrary.wiley.com/doi/pdf/10.1002/2016JD025311, 2016.

982 Guo, H., Liu, J., Froyd, K. D., Roberts, J. M., Veres, P. R., Hayes, P. L., Jimenez, J. L., Nenes, A.
983 and Weber, R. J.: Fine particle pH and gas–particle phase partitioning of inorganic species in
984 Pasadena, California, during the 2010 CalNex campaign, Atmospheric Chemistry and Physics,
985 17(9), 5703–5719, doi:10.5194/acp-17-5703-2017, 2017.

986 Guo, H., Campuzano-Jost, P., Nault, B. A., Day, D. A., Schroder, J. C., Dibb, J. E., Dollner, M.,
987 Weinzierl, B. and Jimenez, J. L.: The Importance of Size Ranges in Aerosol Instrument
988 Intercomparisons: A Case Study for the ATom Mission, , doi:10.5194/amt-2020-224, 2020.

989 Hennigan, C. J., Sullivan, A. P., Fountoukis, C. I., Nenes, A., Hecobian, A., Vargas, O., Hanks,
990 A. T. C., Huey, L. G., Lefer, B. L., Russell, A. G. and Others: On the volatility and production
991 mechanisms of newly formed nitrate and water soluble organic aerosol in Mexico City, [online]
992 Available from: https://hal.archives-ouvertes.fr/hal-00304021/, 2008.

993 Hennigan, C. J., Izumi, J., Sullivan, A. P., Weber, R. J. and Nenes, A.: A critical evaluation of
994 proxy methods used to estimate the acidity of atmospheric particles, Atmos. Chem. Phys., 15(5),
995 2775 [online] Available from:
996 https://pdfs.semanticscholar.org/18b0/f81231da34dbf1e29d753ae7c5e111cbd7fb.pdf, 2015.

997 Hodshire, A. L., Campuzano-Jost, P., Kodros, J. K., Croft, B., Nault, B. A., Schroder, J. C.,
998 Jimenez, J. L. and Pierce, J. R.: The potential role of methanesulfonic acid (MSA) in aerosol
999 formation and growth and the associated radiative forcings, Atmos. Chem. Phys., 19(5),
1000 3137–3160, doi:10.5194/acp-19-3137-2019, 2019.

1001 Hodzic, A., Campuzano-Jost, P., Bian, H., Chin, M., Colarco, P. R., Day, D. A., Froyd, K. D.,

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

Heinold, B., Jo, D. S., Katich, J. M. and Others: Characterization of Organic Aerosol across the Global Remote Troposphere: A comparison of ATom measurements and global chemistry models, Atmos. Chem. Phys., 2020.

Hoesly, R. M., Smith, S. J., Feng, L., Klimont, Z., Janssens-Maenhout, G., Pitkanen, T., Seibert, J. J., Vu, L., Andres, R. J., Bolt, R. M. and Others: Historical (1750--2014) anthropogenic emissions of reactive gases and aerosols from the Community Emissions Data System (CEDS), Geoscientific Model Development (Online), 11(PNNL-SA-123932) [online] Available from: https://www.osti.gov/biblio/1421326, 2018.

Huang, S., Poulain, L., van Pinxteren, D., van Pinxteren, M., Wu, Z., Herrmann, H. and Wiedensohler, A.: Latitudinal and Seasonal Distribution of Particulate MSA over the Atlantic using a Validated Quantification Method with HR-ToF-AMS, Environ. Sci. Technol., 51(1), 418–426, doi:10.1021/acs.est.6b03186, 2017.

Huffman, J. A., Jayne, J. T., Drewnick, F., Aiken, A. C., Onasch, T., Worsnop, D. R. and Jimenez, J. L.: Design, Modeling, Optimization, and Experimental Tests of a Particle Beam Width Probe for the Aerodyne Aerosol Mass Spectrometer, Aerosol Sci. Technol., 39(12), 1143–1163, doi:10.1080/02786820500423782, 2005.

Hu, W., Campuzano-Jost, P., Day, D. A., Croteau, P., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R. and Jimenez, J. L.: Evaluation of the new capture vaporizer for aerosol mass spectrometers (AMS) through field studies of inorganic species, Aerosol Sci. Technol., 51(6), 735–754, doi:10.1080/02786826.2017.1296104, 2017a.

Hu, W., Campuzano-Jost, P., Day, D. A., Croteau, P., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R. and Jimenez, J. L.: Evaluation of the new capture vapourizer for aerosol mass spectrometers (AMS) through laboratory studies of inorganic species, Atmospheric Measurement Techniques, 10(8), doi:10.5194/amt-10-2897-2017, 2017b.

Hu, W., Campuzano-Jost, P., Day, D. A., Nault, B., Park, T., Lee, T., Pajunoja, A., Virtanen, A., Croteau, P. L., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R. and Jimenez, J. L.: Ambient quantification and size distributions for organic aerosol (OA) in aerosol mass spectrometer (AMS) instruments with the new capture vaporizer (CV), ACS Earth and Space Chemistry, doi:10.1021/acsearthspacechem.9b00310, 2020.

Hu, W. W., Campuzano-Jost, P., Palm, B. B., Day, D. A., Ortega, A. M., Hayes, P. L., Krechmer, J. E., Chen, Q., Kuwata, M., Liu, Y. J. and Others: Characterization of a real-time tracer for isoprene epoxydiols-derived secondary organic aerosol (IEPOX-SOA) from aerosol mass spectrometer measurements, Atmos. Chem. Phys., 15(20), 11807–11833 [online] Available from: https://www.atmos-chem-phys.net/15/11807/2015/acp-15-11807-2015.html, 2015.

IPCC: IPCC 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, edited by T. F. Stocker, D. Qin, G. K. Plattner, M. Tignor, S. K. Allen, V. Bex, and P. M. Midgley, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.,

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

2013.

Jang, M., Czoschke, N. M., Lee, S. and Kamens, R. M.: Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions, Science, 298(5594), 814–817, doi:10.1126/science.1075798, 2002.

Jayne, J. T., Leard, D. C., Zhang, X., Davidovits, P., Smith, K. A., Kolb, C. E. and Worsnop, D. R.: Development of an Aerosol Mass Spectrometer for Size and Composition Analysis of Submicron Particles, Aerosol Sci. Technol., 33(1-2), 49–70, doi:10.1080/027868200410840, 2000.

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U. and Worsnop, D. R.: Evolution of organic aerosols in the atmosphere, Science, 326(5959), 1525–1529, doi:10.1126/science.1180353, 2009.

Jo, D. S., Hodzic, A., Emmons, L. K., Marais, E. A., Peng, Z., Nault, B. A., Hu, W., Campuzano-Jost, P. and Jimenez, J. L.: A simplified parameterization of isoprene-epoxydiol-derived secondary organic aerosol (IEPOX-SOA) for global chemistry and climate models: a case study with GEOS-Chem v11-02-rc, Geoscientific Model Development, 12(7), 2983–3000, doi:10.5194/gmd-12-2983-2019, 2019.

Johnson, K. S., Laskin, A., Jimenez, J. L., Shutthanandan, V., Molina, L. T., Salcedo, D., Dzepina, K. and Molina, M. J.: Comparative analysis of urban atmospheric aerosol by particle-induced X-ray emission (PIXE), proton elastic scattering analysis (PESA), and aerosol mass spectrometry (AMS), Environ. Sci. Technol., 42(17), 6619–6624, doi:10.1021/es800393e, 2008.

Kang et al.: Secondary organic aerosol mass yields from the dark NO3 oxidation of α-pinene and Δ-carene: effect of RO2 radical fate, 2016.

Keene, W. C.: Variation of marine aerosol acidity with particle size, Geophys. Res. Lett., 29(7), 20,565, doi:10.1029/2001GL013881, 2002.

Lambert, J. B.: Organic structural spectroscopy, Pearson College Division., 1998.

Lee, B. H., Lopez-Hilfiker, F. D., Mohr, C., Kurtén, T., Worsnop, D. R. and Thornton, J. a.: An iodide-adduct high-resolution time-of-flight chemical-ionization mass spectrometer: application to atmospheric inorganic and organic compounds, Environ. Sci. Technol., 48(11), 6309–6317,

1077 doi:10.1021/es500362a, 2014.

1078 Lee, B. H., Lopez-Hilfiker, F. D., Veres, P. R., McDuffie, E. E., Fibiger, D. L., Sparks, T. L.,
1079 Ebben, C. J., Green, J. R., Schroder, J. C., Campuzano-Jost, P. and Others: Flight deployment of
1080 a high-resolution time-of-flight chemical ionization mass spectrometer: Observations of reactive
1081 halogen and nitrogen oxide species, J. Geophys. Res. D: Atmos., 123(14), 7670–7686 [online]
1082 Available from:
1083 https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2017JD028082@10.1002/(ISSN)2169-
1084 8996.WINTER1, 2018.

1085 Lee, T., Sullivan, A. P., Mack, L., Jimenez, J. L., Kreidenweis, S. M., Onasch, T. B., Worsnop, D.
1086 R., Malm, W., Wold, C. E., Hao, W. M. and Collett, J. L.: Chemical Smoke Marker Emissions
1087 During Flaming and Smoldering Phases of Laboratory Open Burning of Wildland Fuels, Aerosol
1088 Sci. Technol., 44(9), i–v, doi:10.1080/02786826.2010.499884, 2010.

1089 Liao, J., Froyd, K. D., Murphy, D. M., Keutsch, F. N., Yu, G., Wennberg, P. O., Clair, J. M. S.,
1090 Crounse, J. D., Wisthaler, A., Mikoviny, T. and Others: Airborne measurements of
1091 organosulfates over the continental US, J. Geophys. Res. D: Atmos., 120(7), 2990–3005 [online]
1092 Available from:
1093 https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1002/2014JD022378%4010.1002/%28ISSN
1094 %292169-8996.SEAFOURC1, 2015.

1095 Li, G., Bei, N., Cao, J., Huang, R., Wu, J., Feng, T., Wang, Y., Liu, S., Zhang, Q., Tie, X. and
1096 Molina, L. T.: A possible pathway for rapid growth of sulfate during haze days in China, ,
1097 3301–3316 [online] Available from: https://dspace.mit.edu/handle/1721.1/109728?show=full
1098 (Accessed 2 August 2019), 2017.

1099 Lighty, J. S., Veranth, J. M. and Sarofim, A. F.: Combustion aerosols: factors governing their size
1100 and composition and implications to human health, J. Air Waste Manag. Assoc., 50(9),
1101 1565–618; discussion 1619–22 [online] Available from:
1102 https://www.ncbi.nlm.nih.gov/pubmed/11055157, 2000.

1103 Liu, P., Ziemann, P. J., Kittelson, D. B. and McMurry, P. H.: Generating Particle Beams of
1104 Controlled Dimensions and Divergence: II. Experimental Evaluation of Particle Motion in
1105 Aerodynamic Lenses and Nozzle Expansions, Aerosol Sci. Technol., 22(3), 314–324,
1106 doi:10.1080/02786829408959749, 1995.

1107 Liu, X., Day, D. A., Krechmer, J. E., Brown, W., Peng, Z., Ziemann, P. J. and Jimenez, J. L.:
1108 Direct measurements of semi-volatile organic compound dynamics show near-unity mass
1109 accommodation coefficients for diverse aerosols, Communications Chemistry, 2(1), 1–9,
1110 doi:10.1038/s42004-019-0200-x, 2019.

1111 Lohmann, U., Broekhuizen, K., Leaitch, R., Shantz, N. and Abbatt, J.: How efficient is cloud
1112 droplet formation of organic aerosols?, Geophys. Res. Lett., 31(5), 2004.

1113 Losey, D. J., Ott, E.-J. E. and Freedman, M. A.: Effects of High Acidity on Phase Transitions of

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

an Organic Aerosol, J. Phys. Chem. A, 122(15), 3819–3828, doi:10.1021/acs.jpca.8b00399, 2018.

Massucci, M., Clegg, S. L. and Brimblecombe, P.: Equilibrium Partial Pressures, Thermodynamic Properties of Aqueous and Solid Phases, and Cl2 Production from Aqueous HCl and HNO3 and Their Mixtures, J. Phys. Chem. A, 103(21), 4209–4226, doi:10.1021/jp9847179, 1999.

Matthew, B. M., Middlebrook, A. M. and Onasch, T. B.: Collection Efficiencies in an Aerodyne Aerosol Mass Spectrometer as a Function of Particle Phase for Laboratory Generated Aerosols, Aerosol Sci. Technol., 42(11), 884–898, doi:10.1080/02786820802356797, 2008.

Meskhidze, N., Chameides, W. L., Nenes, A. and Chen, G.: Iron mobilization in mineral dust: Can anthropogenic SO2 emissions affect ocean productivity?, Geophys. Res. Lett., 30(21) [online] Available from: https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2003GL018035, 2003.

Middlebrook, A. M., Bahreini, R., Jimenez, J. L. and Canagaratna, M. R.: Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data, Aerosol Sci. Technol., 46(3), 258–271, doi:10.1080/02786826.2011.620041, 2012.

Müller, C., Iinuma, Y., Karstensen, J., Van Pinxteren, D., Lehmann, S., Gnauk, T. and Herrmann, H.: Seasonal variation of aliphatic amines in marine sub-micrometer particles at the Cape Verde islands, [online] Available from: https://oar.tib.eu/jspui/handle/123456789/261, 2009.

Murphy, S. M., Sorooshian, A., Kroll, J. H., Ng, N. L., Chhabra, P., Tong, C., Surratt, J. D., Knipping, E., Flagan, R. C. and Seinfeld, J. H.: Secondary aerosol formation from atmospheric reactions of aliphatic amines, Atmospheric Chemistry and Physics Discussions, 7(1), 289–349, doi:10.5194/acpd-7-289-2007, 2007.

Nault, B. A., Campuzano-Jost, P., Day, D. A., Schroder, J. C., Anderson, B., Beyersdorf, A. J., Blake, D. R., Brune, W. H., Choi, Y., Corr, C. A., Gouw, J. A. de, Dibb, J., DiGangi, J. P., Diskin, G. S., Fried, A., Huey, L. G., Kim, M. J., Knote, C. J., Lamb, K. D., Lee, T., Park, T., Pusede, S. E., Scheuer, E., Thornhill, K. L., Woo, J.-H. and Jimenez, J. L.: Secondary organic aerosol production from local emissions dominates the organic aerosol budget over Seoul, South Korea, during KORUS-AQ, Atmos. Chem. Phys., 18(24), 17769–17800, doi:10.5194/acp-18-17769-2018, 2018.

Nault, B. A., Campuzano-Jost, P., Jo, D., Day, D., Bahreini, R., Bian, H., Chin, M., Clegg, S., Colarco, P., Kodros, J., Lopez-Hilfiker, F., Marais, E., Middlebrook, A., Neuman, A., Nowak, J., Pierce, J., Thornton, J., Tsigaridis, K., Jimenez, J. and ATom Science Team: Global Survey of Aerosol Acidity from Polluted to Remote Locations: Measurements and Comparisons with Global Models, display, doi:10.5194/egusphere-egu2020-11366, 2020.

Nenes, A., Pandis, S. N. and Pilinis, C.: Continued development and testing of a new

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

thermodynamic aerosol module for urban and regional air quality models, Atmos. Environ., 33(10), 1553–1560, doi:10.1016/S1352-2310(98)00352-5, 1999.

Ng, N. L., Herndon, S. C., Trimborn, A., Canagaratna, M. R., Croteau, P. L., Onasch, T. B., Sueper, D., Worsnop, D. R., Zhang, Q., Sun, Y. L. and Jayne, J. T.: An Aerosol Chemical Speciation Monitor (ACSM) for Routine Monitoring of the Composition and Mass Concentrations of Ambient Aerosol, Aerosol Sci. Technol., 45(7), 780–794, doi:10.1080/02786826.2011.560211, 2011a.

Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Chhabra, P. S., Seinfeld, J. H. and Worsnop, D. R.: Changes in organic aerosol composition with aging inferred from aerosol mass spectra, Atmos. Chem. Phys., 11(13), 6465 [online] Available from: http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.388.4858&rep=rep1&type=pdf, 2011b.

Ovadnevaite, J., Ceburnis, D., Canagaratna, M., Berresheim, H., Bialek, J., Martucci, G., Worsnop, D. R. and O'Dowd, C.: On the effect of wind speed on submicron sea salt mass concentrations and source fluxes, J. Geophys. Res. D: Atmos., 117(D16) [online] Available from: https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2011JD017379, 2012.

Paulot, F., Jacob, D. J., Johnson, M. T., Bell, T. G., Baker, A. R., Keene, W. C., Lima, I. D., Doney, S. C. and Stock, C. A.: Global oceanic emission of ammonia: Constraints from seawater and atmospheric observations, Global Biogeochem. Cycles, 29(8), 1165–1178, doi:10.1002/2015GB005106, 2015.

Phinney, L., Richard Leaitch, W., Lohmann, U., Boudries, H., Worsnop, D. R., Jayne, J. T., Toom-Sauntry, D., Wadleigh, M., Sharma, S. and Shantz, N.: Characterization of the aerosol over the sub-arctic north east Pacific Ocean, Deep Sea Res. Part 2 Top. Stud. Oceanogr., 53(20), 2410–2433, doi:10.1016/j.dsr2.2006.05.044, 2006.

van Pinxteren, M., Fiedler, B., van Pinxteren, D., Iinuma, Y., Körtzinger, A. and Herrmann, H.: Chemical characterization of sub-micrometer aerosol particles in the tropical Atlantic Ocean: marine and biomass burning influences, J. Atmos. Chem., 72(2), 105–125, doi:10.1007/s10874-015-9307-3, 2015.

Pye, H. O. T., Liao, H., Wu, S., Mickley, L. J., Jacob, D. J., Henze, D. K. and Seinfeld, J. H.: Effect of changes in climate and emissions on future sulfate-nitrate-ammonium aerosol levels in the United States, J. Geophys. Res. D: Atmos., 114(D1) [online] Available from: https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2008JD010701, 2009.

Pye, H. O. T., Nenes, A., Alexander, B., Ault, A. P., Barth, M. C., Clegg, S. L., Collett, J. L., Jr, Fahey, K. M., Hennigan, C. J., Herrmann, H. and Others: The Acidity of Atmospheric Particles and Clouds, UMBC Faculty Collection [online] Available from: https://www.atmos-chem-phys-discuss.net/acp-2019-889/acp-2019-889.pdf, 2019.

Quinn, P. K., Charlson, R. J. and Bates, T. S.: Simultaneous observations of ammonia in the

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

atmosphere and ocean, Nature, 335(6188), 336–338, doi:10.1038/335336a0, 1988.

Quinn, P. K., Bates, T. S., Coffman, D., Onasch, T. B., Worsnop, D., Baynard, T., De Gouw, J. A., Goldan, P. D., Kuster, W. C., Williams, E. and Others: Impacts of sources and aging on submicrometer aerosol properties in the marine boundary layer across the Gulf of Maine, J. Geophys. Res. D: Atmos., 111(D23) [online] Available from: https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2006JD007582, 2006.

Raizenne, M., Neas, L. M., Damokosh, A. I., Dockery, D. W., Spengler, J. D., Koutrakis, P., Ware, J. H. and Speizer, F. E.: Health effects of acid aerosols on North American children: pulmonary function, Environ. Health Perspect., 104(5), 506–514, doi:10.1289/ehp.96104506, 1996.

Rindelaub, J. D., Craig, R. L., Nandy, L., Bondy, A. L., Dutcher, C. S., Shepson, P. B. and Ault, A. P.: Direct Measurement of pH in Individual Particles via Raman Microspectroscopy and Variation in Acidity with Relative Humidity, J. Phys. Chem. A, 120(6), 911–917, doi:10.1021/acs.jpca.5b12699, 2016.

Riva, M., Budisulistiorini, S. H., Chen, Y., Zhang, Z., D'Ambro, E. L., Zhang, X., Gold, A., Turpin, B. J., Thornton, J. A., Canagaratna, M. R. and Surratt, J. D.: Chemical Characterization of Secondary Organic Aerosol from Oxidation of Isoprene Hydroxyhydroperoxides, Environ. Sci. Technol., acs.est.6b02511–acs.est.6b02511, doi:10.1021/acs.est.6b02511, 2016.

Riva, M., Rantala, P., Krechmer, J. E., Peräkylä, O., Zhang, Y., Heikkinen, L., Garmash, O., Yan, C., Kulmala, M., Worsnop, D. and Ehn, M.: Evaluating the performance of five different chemical ionization techniques for detecting gaseous oxygenated organic species, Atmospheric Measurement Techniques Discussions, 12(4), 2403–2421, doi:10.5194/amt-12-2403-2019, 2019a.

Riva, M., Chen, Y., Zhang, Y., Lei, Z., Olson, N. E., Boyer, H. C., Narayan, S., Yee, L. D., Green, H. S., Cui, T., Zhang, Z., Baumann, K., Fort, M., Edgerton, E., Budisulistiorini, S. H., Rose, C. A., Ribeiro, I. O., E Oliveira, R. L., Dos Santos, E. O., Machado, C. M. D., Szopa, S., Zhao, Y., Alves, E. G., de Sá, S. S., Hu, W., Knipping, E. M., Shaw, S. L., Duvoisin Junior, S., de Souza, R. A. F., Palm, B. B., Jimenez, J.-L., Glasius, M., Goldstein, A. H., Pye, H. O. T., Gold, A., Turpin, B. J., Vizuete, W., Martin, S. T., Thornton, J. A., Dutcher, C. S., Ault, A. P. and Surratt, J. D.: Increasing Isoprene Epoxydiol-to-Inorganic Sulfate Aerosol Ratio Results in Extensive Conversion of Inorganic Sulfate to Organosulfur Forms: Implications for Aerosol Physicochemical Properties, Environ. Sci. Technol., 53(15), 8682–8694, doi:10.1021/acs.est.9b01019, 2019b.

Salcedo, D., Onasch, T. B., Aiken, a. C., Williams, L. R., de Foy, B., Cubison, M. J., Worsnop, D. R., Molina, L. T. and Jimenez, J. L.: Determination of particulate lead using aerosol mass spectrometry: MILAGRO/MCMA-2006 observations, Atmos. Chem. Phys., 10(12), 5371–5389, doi:10.5194/acp-10-5371-2010, 2010.

Schindler, D. W.: Effects of Acid rain on freshwater ecosystems, Science, 239(4836), 149–157,

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

doi:10.1126/science.239.4836.149, 1988.

Schroder, J. C., Campuzano-Jost, P., Day, D. A., Shah, V., Larson, K., Sommers, J. M., Sullivan, A. P., Campos, T., Reeves, J. M., Hills, A., Hornbrook, R. S., Blake, N. J., Scheuer, E., Guo, H., Fibiger, D. L., McDuffie, E. E., Hayes, P. L., Weber, R. J., Dibb, J. E., Apel, E. C., Jaeglé, L., Brown, S. S., Thornton, J. A. and Jimenez, J. L.: Sources and Secondary Production of Organic Aerosols in the Northeastern United States during WINTER, J. Geophys. Res. D: Atmos., 42, 4478, doi:10.1029/2018JD028475, 2018.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics, 2nd ed., John Wiley & Sons, Inc., New York., 2006.

Song, S., Gao, M., Xu, W., Shao, J., Shi, G., Wang, S., Wang, Y., Sun, Y. and McElroy, M. B.: Fine-particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models, Atmos. Chem. Phys., 18(10), 7423–7438, doi:10.5194/acp-18-7423-2018, 2018.

Song, S., Gao, M., Xu, W., Sun, Y., Worsnop, D. R., Jayne, J. T., Zhang, Y., Zhu, L., Li, M., Zhou, Z. and Others: Possible heterogeneous chemistry of hydroxymethanesulfonate (HMS) in northern China winter haze, Atmos. Chem. Phys., 19(2), 1357–1371 [online] Available from: https://www.atmos-chem-phys.net/19/1357/2019/acp-19-1357-2019.pdf, 2019.

Sorooshian, A., Padró, L. T., Nenes, A., Feingold, G., McComiskey, A., Hersey, S. P., Gates, H., Jonsson, H. H., Miller, S. D., Stephens, G. L. and Others: On the link between ocean biota emissions, aerosol, and maritime clouds: Airborne, ground, and satellite measurements off the coast of California, Global Biogeochem. Cycles, 23(4) [online] Available from: https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2009GB003464, 2009.

Sorooshian, A., Crosbie, E., Maudlin, L. C., Youn, J.-S., Wang, Z., Shingler, T., Ortega, A. M., Hersey, S. and Woods, R. K.: Surface and airborne measurements of organosulfur and methanesulfonate over the western United States and coastal areas, J. Geophys. Res. D: Atmos., 120(16), 8535–8548, doi:10.1002/2015JD023822, 2015.

Stith, J. L., Ramanathan, V., Cooper, W. A., Roberts, G. C., DeMott, P. J., Carmichael, G., Hatch, C. D., Adhikary, B., Twohy, C. H., Rogers, D. C., Baumgardner, D., Prenni, A. J., Campos, T., Gao, R., Anderson, J. and Feng, Y.: An overview of aircraft observations from the Pacific Dust Experiment campaign, J. Geophys. Res., 114(D5), 833, doi:10.1029/2008JD010924, 2009.

Sueper, D.: ToF-AMS Data Analysis Software Webpage, [online] Available from: http://cires1.colorado.edu/jimenez-group/wiki/index.php/ ToF-AMS_Analysis_Software (Accessed 4 January 2017), 2018.

Surratt, J. D., Kroll, J. H., Kleindienst, T. E., Edney, E. O., Claeys, M., Sorooshian, A., Ng, N. L., Offenberg, J. H., Lewandowski, M., Jaoui, M., Flagan, R. C. and Seinfeld, J. H.: Evidence for organosulfates in secondary organic aerosol, Environ. Sci. Technol., 41(2), 517–527, doi:10.1021/es062081q, 2007.

Surratt, J. D., Gómez-González, Y., Chan, A. W. H., Vermeylen, R., Shahgholi, M., Kleindienst,

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

T. E., Edney, E. O., Offenberg, J. H., Lewandowski, M., Jaoui, M., Maenhaut, W., Claeys, M., Flagan, R. C. and Seinfeld, J. H.: Organosulfate formation in biogenic secondary organic aerosol, J. Phys. Chem. A, 112(36), 8345–8378, doi:10.1021/jp802310p, 2008.

Thornton, J. A., Jaeglé, L. and McNeill, V. F.: Assessing known pathways for HO2 loss in aqueous atmospheric aerosols: Regional and global impacts on tropospheric oxidants, J. Geophys. Res. D: Atmos., 113(D5) [online] Available from: https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2007JD009236, 2008.

Tolocka, M. P. and Turpin, B.: Contribution of organosulfur compounds to organic aerosol mass, Environ. Sci. Technol., 46(15), 7978–7983, doi:10.1021/es300651v, 2012.

Toon, O. B., Maring, H., Dibb, J., Ferrare, R., Jacob, D. J., Jensen, E. J., Luo, Z. J., Mace, G. G., Pan, L. L., Pfister, L. and Others: Planning, implementation, and scientific goals of the Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (SEAC4RS) field mission, J. Geophys. Res. D: Atmos., 121(9), 4967–5009 [online] Available from: https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1002/2015JD024297%4010.1002/%28ISSN%292169-8996.SEAFOURC1, 2016.

Wang, Y., Zhang, Q., Jiang, J., Zhou, W., Wang, B., He, K., Duan, F., Zhang, Q., Philip, S. and Xie, Y.: Enhanced sulfate formation during China's severe winter haze episode in January 2013 missing from current models, J. Geophys. Res. D: Atmos., 119(17), 10–425 [online] Available from: https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1002/2013JD021426, 2014.

Weber, R. J., Guo, H., Russell, A. G. and Nenes, A.: High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years, Nat. Geosci., 9, 282, doi:10.1038/ngeo2665, 2016.

Wexler, A. S. and Clegg, S. L.: Atmospheric aerosol models for systems including the ions H+, NH4+, Na+, SO42-, NO3-, Cl-, Br-, and H2O, J. Geophys. Res. D: Atmos., 107(D14), ACH–14 [online] Available from: https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2001JD000451, 2002.

Youn, J.-S., Crosbie, E., Maudlin, L. C., Wang, Z. and Sorooshian, A.: Dimethylamine as a major alkyl amine species in particles and cloud water: Observations in semi-arid and coastal regions, Atmos. Environ. , 122, 250–258, doi:10.1016/j.atmosenv.2015.09.061, 2015.

Zhang, Q., Stanier, C. O., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., Pandis, S. N. and Jimenez, J. L.: Insights into the chemistry of new particle formation and growth events in Pittsburgh based on aerosol mass spectrometry, Environ. Sci. Technol., 38(18), 4797–4809, doi:10.1021/es035417u, 2004a.

Zhang, Q., Jimenez, J. L., Worsnop, D. R. and Canagaratna, M.: A case study of urban particle acidity and its influence on secondary organic aerosol, Environ. Sci. Technol., 41(9), 3213–3219, doi:10.1021/Es061812j, 2007a.

https://doi.org/10.5194/amt-2020-339
Preprint. Discussion started: 31 August 2020

1300 Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M. R.,
1301 Takami, A., Middlebrook, A. M., Sun, Y. L. and Others: Ubiquity and dominance of oxygenated
1302 species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes,
1303 Geophys. Res. Lett., 34(13) [online] Available from:
1304 https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2007GL029979%4010.1002/%28ISSN
1305 %291944-8007.GRL40, 2007b.

1306 Zhang, X., Smith, K. A., Worsnop, D. R., Jimenez, J. L., Jayne, J. T., Kolb, C. E., Morris, J. and
1307 Davidovits, P.: Numerical Characterization of Particle Beam Collimation: Part II Integrated
1308 Aerodynamic-Lens–Nozzle System, Aerosol Sci. Technol., 38(6), 619–638,
1309 doi:10.1080/02786820490479833, 2004b.

1310 Zheng, B., Zhang, Q., Zhang, Y., He, K. B., Wang, K., Zheng, G. J., Duan, F. K., Ma, Y. L. and
1311 Kimoto, T.: Heterogeneous chemistry: a mechanism missing in current models to explain
1312 secondary inorganic aerosol formation during the January 2013 haze episode in North China,
1313 Atmospheric Chemistry and Physics Discussions, 14(11), 16731–16776,
1314 doi:10.5194/acpd-14-16731-2014, 2014.

1315 Zheng, Y., Cheng, X., Liao, K., Li, Y., Li, Y., Huang, R.-J., Hu, W., Liu, Y., Zhu, T., Chen, S. and
1316 Others: Characterization of Anthropogenic Organic Aerosols by TOF-ACSM with the New
1317 Capture Vaporizer, Atmospheric Measurement Techniques [online] Available from:
1318 https://www.atmos-meas-tech-discuss.net/amt-2019-449/amt-2019-449.pdf, 2020.

1319 Zorn, S. R., Drewnick, F., Schott, M., Hoffmann, T. and Borrmann, S.: Characterization of the
1320 South Atlantic marine boundary layer aerosol using an aerodyne aerosol mass spectrometer,
1321 [online] Available from: https://hal.archives-ouvertes.fr/hal-00304023/, 2008.

1322