

1 **Opinion: Atmospheric Multiphase Chemistry: Past, Present,**
2 **and Future**

3 Jonathan P.D. Abbatt¹, Akkihebbal R. Ravishankara²

4 ¹Department of Chemistry, University of Toronto, Toronto, ON, Canada M5S 3H6; jonathan.abbatt@utoronto.ca

5 ²Departments of Chemistry and Atmospheric Science, Colorado State University, Fort Collins, CO, USA 80523;
6 a.r.ravishankara@colostate.edu

7

8 **Abstract**

9 Multiphase chemistry occurs between chemicals in different atmospheric phases, typically involving gas-solid and
10 gas-liquid interactions. The importance of atmospheric multiphase chemistry has long been recognized. Its central
11 role extends from acid precipitation and stratospheric ozone depletion, to its impact on the oxidizing capacity of the
12 troposphere, and to the roles that aerosol particles play in driving chemistry-climate interactions and affecting
13 human health. This opinion article briefly introduces the subject of multiphase chemistry and tracks its development
14 before and after the start of *Atmospheric Chemistry and Physics*. Most of the article focuses on research
15 opportunities and challenges in the field. Central themes are that a fundamental understanding of the chemistry at
16 the molecular level underpins the ability of atmospheric chemistry to accurately predict environmental change, and
17 that the discipline of multiphase chemistry is strongest when tightly connected to atmospheric modeling and field
18 observations.

19

20

21

22

23

24

25

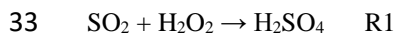
26

27

28

29 **1 Introduction**

30 When *Atmospheric Chemistry and Physics* was launched over two decades ago, Abbatt was invited to submit an
31 article to the inaugural issue, which addressed the kinetics of the multiphase reaction between SO₂ and H₂O₂ on ice
32 surfaces (Clegg and Abbatt, 2001):



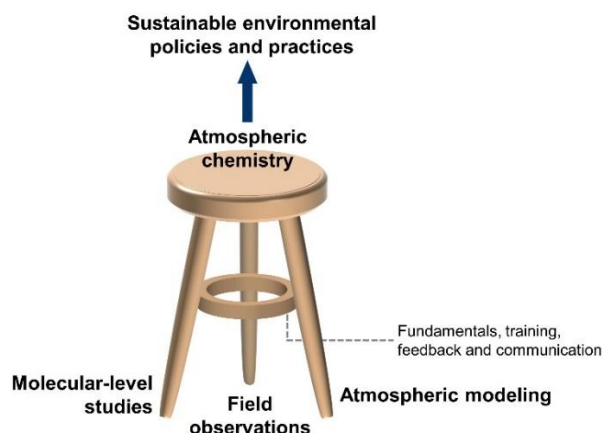
34 This contribution built upon concepts described in a review article published a few years earlier by Ravishankara,
35 which presented a conceptual view of tropospheric heterogeneous and multiphase chemistry (Ravishankara, 1997).
36 As part of the Special Issue entitled *20 Years of Atmospheric Chemistry and Physics*, both authors value the current
37 opportunity to contribute to the overall goal of the special issue “to reflect on the developments of the field of
38 atmospheric chemistry and physics in the last 20 years and point to exciting directions for the future” by addressing
39 the evolution of the field of atmospheric multiphase chemistry. Specifically, this paper will briefly describe
40 multiphase chemistry, its origins, and the progress made in the past twenty years since the inauguration of
41 *Atmospheric Chemistry and Physics*. It then focuses in depth on future research opportunities and associated
42 challenges. For the sake of brevity, the citations in this paper are illustrative and not comprehensive. And so, the
43 reader is directed to in-depth reviews on specific aspects of multiphase chemistry (Ravishankara, 1997; Jacob, 2000;
44 Rudich, 2003; Usher et al., 2003; Finlayson-Pitts, 2003; Rudich et al., 2007; Kolb et al., 2010; George and Abbatt,
45 2010; Abbatt et al., 2012; McNeill et al., 2012; Poschl and Shiraiwa, 2015; Herrmann et al., 2015; McNeill, 2015;
46 Burkholder et al., 2017; Pye et al., 2020; Tilgner et al., 2021).

47 In the 1997 paper, Ravishankara distinguished between heterogeneous and multiphase chemistry based on the extent
48 of diffusion into the bulk. At that time, the term “heterogeneous chemistry” was in vogue to describe ozone hole
49 chemistry. Over the years, it has become clear that diffusion depths vary continuously from solid-like substrates to
50 dilute water solutions. Therefore, in this article, we use the term “multiphase chemistry” to refer to all chemistry that
51 involves more than one phase. Interfacial chemistry falls under this umbrella, with interfaces invariably present
52 when more than one phase is present. We note that “heterogeneous chemistry” is a useful term to describe
53 exclusively interfacial processes (Svehla, 1993), such as for the reactions of gas phase molecules and atoms on solid
54 material such as metallic or mineral catalysts. Similarly, “bulk chemistry” refers to chemistry that occurs mainly in
55 only one phase. In this article, our focus is primarily on processes involving the gas phase interacting with
56 atmospheric condensed phases, so we do not describe in-depth advances in the associated chemistry that takes place
57 in the bulk phase.

58 One underlying theme in the paper is that understanding multiphase processes at the molecular level improves our
59 ability to accurately predict atmospheric change, which in turn aids in developing sustainable environmental policy
60 and practices. Positive impacts arise across multiple fields, from climate and air quality to human health and
61 ecology. Another theme is that multiphase chemistry studies are most impactful when closely connected to the
62 entire atmospheric science field, noting the interrelated nature of fundamental chemistry, field measurements, and
63 atmospheric modeling that together constitutes the “three-legged stool” model of our field (see Figure 1) (Abbatt et

64 al., 2014). Multiphase chemistry studies should be conducted to guide, interpret, and encourage field observations,
65 and to quantitatively inform atmospheric models.

66



67

68 **Figure 1:** The atmospheric chemistry three-legged stool, where the legs are: i) atmospheric modeling, ii) field
69 observations, and iii) molecular-level studies via experimental and theoretical investigations of gas- and multiphase
70 chemistry. The support ring represents the value arising from collaboration, training, and feedback that occurs
71 across the field, along with the need to focus on fundamental science throughout. (Figure credit: Zilin Zhou)

72 **2 What is atmospheric multiphase chemistry?**

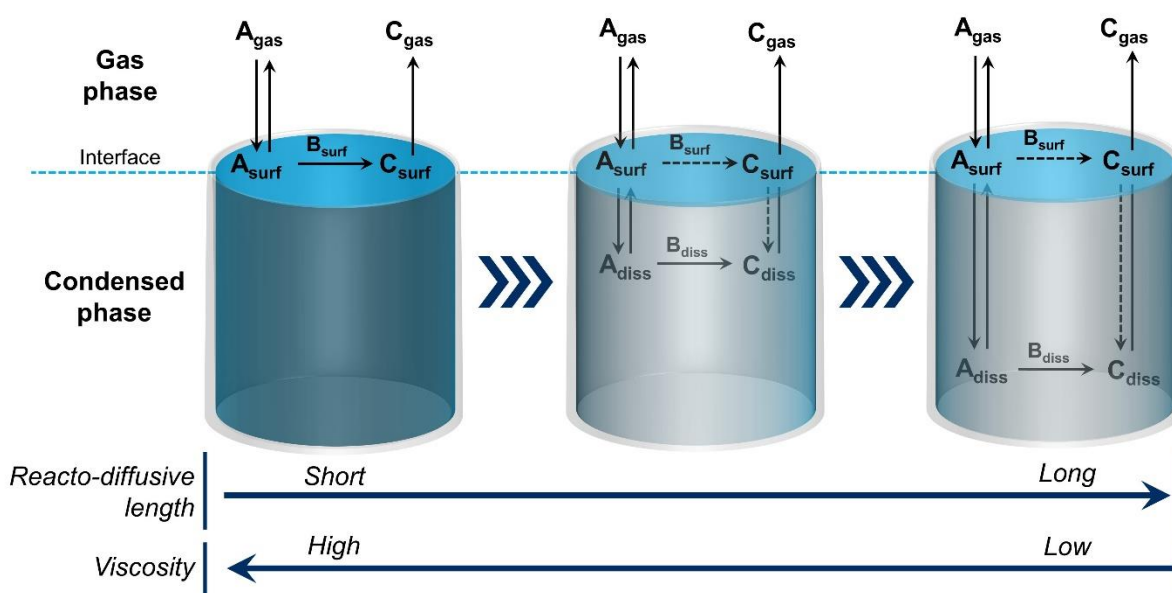
73 Multiphase chemistry involves interactions of chemical species present in two or more atmospheric phases,
74 including gas-solid, gas-liquid, and liquid-solid processes. These interactions typically require both chemical
75 reactions and mass transfer, i.e., the movement of a molecule within a phase or from one phase to another. Also
76 important are processes in the interfacial regions, which are the thin transition zones from one phase to another.

77 To illustrate a multiphase process, consider R1, a key reaction leading to acid precipitation. Gas-phase reactants
78 must first partition to the condensed phase, such as an aerosol particle, cloud water droplet, or ice crystal. Once
79 molecules collide with the interface, intermolecular forces promote adsorption for a short period, during which they
80 can diffuse and react via an interfacial process (see Figure 2). If diffusion into the bulk is sufficiently fast, they can
81 also react in the bulk. In the case of R1 in liquid water, dissolved SO_2 forms HSO_3^- , which can be oxidized by
82 dissolved H_2O_2 and O_3 to form sulfate (Hoffmann and Edwards, 1975; Penkett et al., 1979). When the substrate is
83 ice instead of liquid water, the reaction proceeds either at the gas-solid ice interface or within a thin, liquid-like layer
84 prevalent on the ice's surface below its melting point (Girardet and Toubin, 2001; Abbatt, 2003).

85 The interface is involved in all multiphase processes, participating in mass transfer and reactivity. For a low-
86 volatility material, such as a bare mineral or metal, there is a step function drop in the density moving from the

87 condensed phase to the gas phase. A solid's interface, roughly one molecule (or atom) deep, can promote
 88 heterogeneous chemistry that occurs in a two-dimensional space (Tabazadeh and Turco, 1993). However, solid
 89 particles in the atmosphere, such as soot or mineral dust, frequently have mobile, semi-volatile molecules, such as
 90 water, sulfuric acid, and organics, deposited as multilayer-thick films or islands. In these cases, the multiphase
 91 chemistry is likely occurring in a three-dimensional space involving chemical interactions with not only the solid
 92 substrate but also the liquid coatings (Worsnop et al., 2002; Poschl et al., 2007). For cloud droplets and liquid
 93 aerosol particles, which are very dynamic with large fluxes of substrate molecules being rapidly exchanged between
 94 the phases, the interfacial region is also thicker than it is for a pure solid (Gopalakrishnan et al., 2005). When the
 95 underlying substrate is a liquid, the depth to which a molecule diffuses from the interface into the bulk before
 96 reacting is called the reacto-diffusive length, which can be very short for species reacting close to the interface and
 97 extending to the size of an aerosol particle for reactions that are aerosol-volume limited (see Figure 2) (Hanson et
 98 al., 1994). It is not easy to determine whether a reaction is occurring exclusively in a two-dimensional manner at an
 99 interface, where the concept of reacto-diffusive depth breaks down because of different energetics and solvation
 100 than in the bulk phase. For particle chemistry, the reaction kinetics dependence on particle size and reactant
 101 concentration can provide some information. Nevertheless, even in reactions which exhibit Langmuir-Hinshelwood
 102 kinetics (Poschl et al., 2001), the depth of the reactive region at the surface of a particle is not clear for liquids or
 103 coated solids.

104
 105



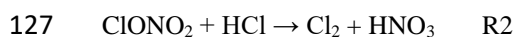
106

107 **Figure 2:** Multiphase reactions occur at the interface and within the bulk of condensed phase materials. Bare solids
108 undergo heterogeneous chemical reactions at the interface. High-viscosity liquids may have sufficiently short
109 reacto-diffusive lengths to restrict reactivity to the surface of the particle. As the viscosity lessens and the reacto-
110 diffusive length deepens, multiphase chemistry can occur deeper into the bulk phase. For reactions that proceed in
111 the bulk, some component of the reaction may also simultaneously occur at the interface (as indicated by the dashed
112 reaction arrow). As noted in the text, the concept of the reacto-diffusive length, which is formally calculated from
113 the bulk diffusion and rate constants, may break down in the interface region. (Figure credit: Zilin Zhou)

114 **3 How does multiphase chemistry differ from gas-phase chemistry?**

115 Although thermodynamically allowed, reactions between neutral closed-shell molecules are slow in the gas phase
116 because of large reaction barriers. However, the rates of multiphase reactions involving the same reactants (or
117 suitably altered versions in the condensed phase) can be larger than in the gas phase, either because the free energy
118 barrier to reaction is lowered or because the concentrations of reactants are enhanced in the condensed phase. To
119 illustrate, SO₂ and H₂O₂ do not react efficiently in the gas phase, but oxidation with dissolved H₂O₂ can proceed
120 once SO₂ dissolves in water and forms HSO₃⁻. Moreover, the gas phase H₂O₂ is efficiently scavenged in clouds,
121 enhancing its concentration for reaction.

122 Another example is the set of reactions that drive polar stratospheric ozone depletion (Solomon, 1999). Chlorine
123 reservoir compounds such as ClONO₂ and HCl do not react rapidly in the gas phase. However, HCl partitions
124 strongly to polar stratospheric clouds by either adsorbing to their surfaces or dissolving within them. For example, it
125 is likely that both adsorbed and dissolved HCl dissociates on/in ice to form chloride ions, which are reactive with
126 ClONO₂:



128 leading to the formation of Cl₂, which is then released to the gas phase and is readily photolyzed, forming radicals
129 that catalyze gas phase ozone destruction in the Antarctic ozone hole. Also, ClONO₂ can be protonated in strongly
130 acidic cloud droplets, or it may dissociate to form Cl⁺ and NO₃⁻ (although there is no direct experimental evidence
131 yet for forming Cl⁺ as an independently solvated species). Other possible mechanisms include a concerted reaction
132 between Cl⁻ and ClONO₂ to produce Cl₂ (Bianco and Hynes, 1999). It is unclear if such a reaction is truly an SN2-
133 type process or if it can occur in a cage in the condensed phase.

134 Another distinguishing feature of multiphase chemistry is that it can lead to the formation of products that do not
135 arise in the gas phase. Consider the acid-catalyzed nucleophilic reactions between sulfate and isoprene-derived
136 epoxydiols that form organo-sulfate molecules and secondary organic aerosol (SOA) (Riva et al., 2019). Water
137 molecules lower the transition state energies of such reactions. The solvent shell, which confines reactant partners
138 via the so-called cage effect, can also promote novel products. For example, the formation of biologically-active
139 secondary ozonides is facile in the condensed-phase ozonolysis of unsaturated fatty esters and triglycerides, arising
140 from reactions of Criegee and carbonyl intermediates that form in the same solvent shell after dissociation of a
141 primary ozonide (Zhou et al., 2019b, 2022). In the gas phase, the solvent shell is essentially absent (except for some

142 specific cases, such as cluster formation with H₂O), so the carbonyl and Criegee intermediates fly apart, and
143 secondary ozonides do not form so readily.

144 Lastly, some multiphase reactants, such as transition metal ions, are absent in the gas phase. More generally, ion-ion
145 and ion-molecule regions play a much greater role in condensed phase chemistry than in tropospheric and
146 stratospheric gas phase chemistry, leading to a wide variety of novel reaction pathways, with R1 being an excellent
147 example.

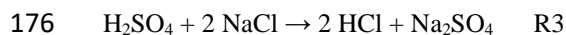
148 **4 Early studies of atmospheric multiphase chemistry**

149 Studies of aerosol and cloud chemistry have proceeded in concert with the development of the wider atmospheric
150 chemistry field with many of the concepts of coupled reactivity and mass transfer initially developed by the process-
151 oriented chemical engineering community (Dankwerts, 1970). Interest in multiphase reactions arose via the
152 profound ways these sparse aerosol particles and cloud droplets can alter gas phase composition. Also, as described
153 in more detail below, it is now evident that the reverse is important, i.e., the gas phase alters the condensed media
154 with important environmental consequences. Many aerosol and multiphase reaction studies were initially performed
155 to develop parameterizations for atmospheric modeling. Even though this is still a major goal, much more effort is
156 now given to understand the physico-chemical processes, which is essential for predictive capabilities.

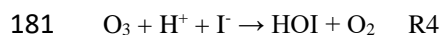
157 The idea of reactive chemistry in hydrometeors goes back to the late 1960s and 1970s and possibly earlier. As in
158 much of science, it is hard to pinpoint a specific paper that expounded this idea. The expectation that the SO₂
159 pollutant can be oxidized to sulfuric acid in the water droplets in the atmosphere spurred many studies, hypotheses,
160 and definitive results. Early studies examined the potential oxidation of SO₂ in the liquid phase via a variety of
161 oxidants, including O₃, H₂O₂, and NO₂ (Hoffmann and Edwards, 1975; Erickson et al., 1977; Schroeder and Urone,
162 1978; Penkett et al., 1979). As well, modeling studies showed the feasibility of such oxidation reactions occurring in
163 the atmosphere (Jacob and Hoffmann, 1983; and references therein). The Great Dun Fell experiment observationally
164 established that SO₂ is indeed oxidized in the troposphere via reactions in cloud droplets (Choularton et al., 1997).

165 Similar multiphase reactions in the stratosphere were sometimes evoked but never pursued with great vigor until the
166 spectacular occurrence and subsequent explanation of the ozone hole (Solomon, 1999) and a multitude of laboratory
167 studies showing that indeed there can be chlorine activation (Molina et al., 1987; Tolbert et al., 1988; Leu, 1988;
168 Hanson and Ravishankara, 1992; and many others).

169 Additional pioneering atmospheric multiphase chemistry studies arose from aerosol composition measurements
170 conducted over a half-century ago. Specifically, continental aerosol particles always contain a measurable quantity
171 of ammonium, indicating the uptake of gas-phase ammonia to acidic particles (Lee and Patterson, 1969; Kadowaki,
172 1976). Furthermore, particulate chloride levels in the marine aerosol are depleted relative to their seawater
173 abundance, replaced by sulfate or nitrate (Junge, 1956; Martens et al., 1973). This process was long thought to be
174 the major source of gas-phase chlorine, whereby gaseous HCl is displaced from NaCl particles via the uptake of gas-
175 phase strong acids :



177 Another early example of halogen chemistry demonstrated that volatile iodine species are released when dissolved
178 oceanic iodide is exposed to either ultraviolet light or ozone (Miyake and Tsunogai, 1963; Garland et al., 1980).
179 This multiphase chemistry is important for the dry deposition of ozone and the release of iodine into the atmosphere
180 (Carpenter et al., 2013):



183 After these early studies, many additional important tropospheric multiphase chemical processes were identified
184 prior to the launch of *Atmospheric Chemistry and Physics*. Some examples, which all address gas-particle and cloud
185 droplet interactions, include: i) the formation of reactive halogen species in the boundary layer (Finlayson-Pitts,
186 2003; Simpson et al., 2015), ii) the uptake of tropospheric gases by mineral dust, especially nitric acid (Hanisch and
187 Crowley, 2001; Usher et al., 2003), iii) the scavenging of trace gases, such as nitric acid and small oxygenated
188 VOCs, by snow and ice crystals in the free and upper troposphere (Abbatt, 2003), iv) the impact of aqueous cloud
189 and aerosol chemistry on gas phase HO_x levels (Chameides and Davis, 1982; Calvert et al., 1985; Jacob, 1986;
190 Lelieveld and Crutzen, 1991), v) conversion of N_2O_5 to HNO_3 on tropospheric aerosol, with impacts on the NO_x
191 budget (Dentener and Crutzen, 1993), vi) uptake of HO_2 to aerosol (Mozurkewich et al., 1987; Martin et al., 2003),
192 and vii) multiphase conversion of NO_2 to HONO (Finlayson-Pitts et al., 2003). A critical point is that each of these
193 multiphase processes affects the oxidizing capacity of the troposphere, frequently through modification of radical
194 budgets and occurring via gas-aerosol or gas-droplet interactions. For example, these processes initiate oxidation in
195 urban atmospheres through HONO photolysis, drive Arctic boundary layer ozone and mercury depletion via gas-
196 phase halogen chemistry, and modulate the global oxidizing capacity via N_2O_5 or HO_2 loss on aerosol particles.
197 Additional work in the multiphase world at this time involved a wide variety of condensed-phase photochemistry
198 studies, for example involving the interactions of light with nitrate (Zepp et al., 1987), which can lead to the release
199 of NO_x to the gas phase, and with transition metal ion complexes (Faust and Zepp, 1993).

200 **5 Progress in the past twenty years**

201 Two major developments profoundly influenced multiphase chemistry. First was the recognition of the importance
202 of aerosol particles in changing the radiative balance of the Earth system, with impacts on climate. The second was
203 the continued recognition of the deleterious effects of particulate matter on human, animal, and ecosystem health.
204 These two fields, climate change and air quality, have provided the impetus (and resources) for the development of
205 the field. As a result, additional research emphasis in the multiphase chemistry community was given at the turn of
206 the 21st century to assess the impacts that arise on the composition of the particles.

207 Once inhaled, particles harm human health (Landrigan et al., 2018; Murray et al., 2020), with recent studies
208 implicating the secondary component of the particles in negative health outcomes (Pye et al., 2021). Research in the
209 past two decades has focused strongly on the formation of SOA (Kroll and Seinfeld, 2008; Hallquist et al., 2009;

210 Ziemann and Atkinson, 2012; Shrivastava et al., 2017b). SOA formation has required better knowledge of the
211 kinetics and mechanisms of gas phase oxidation of SOA precursors (Crouse et al., 2013; Ehn et al., 2014). It has
212 also needed a more complete understanding of gas-particle nucleation processes (Kulmala et al., 2014; Trostl et al.,
213 2016; Xiao et al., 2021), volatility (Pankow, 1994; Donahue et al., 2011), and condensed-phase reactions that occur
214 within aerosol particles. Specifically, volatility and multiphase reactivity can be coupled, as illustrated by the
215 formation of high molecular weight, low volatility species within particles (Kalberer et al., 2004). While such
216 oligomers and highly oxygenated species may also form in the gas phase (Bianchi et al., 2019), they arise via a
217 variety of reactions involving pairs of organic reactants, frequently forming esters and acetals/hemiacetals in the
218 condensed phase (Tobias and Ziemann, 2000; Surratt et al., 2006; DeVault and Ziemann, 2021). These reactions
219 may be acid-catalyzed (Jang et al., 2002). Also, multiphase oxidation by gas-phase oxidants can increase the average
220 oxidation state of organic aerosol particles (Kroll et al., 2011) via a series of reactions that initially functionalize and
221 eventually fragment the component molecules (Moise and Rudich, 2000; Molina et al., 2004; George et al., 2007;
222 Kroll et al., 2009). Oxidation leads to a more soluble particle that increases its rate of wet deposition. In addition to
223 forming organic aerosol via gas-to-particle conversion, they are produced from the evaporation of cloud droplets.
224 Oxidation processes occur within cloud droplets (Herrmann et al., 2015), producing more oxidized organics that
225 yield oxygenated aerosol upon evaporation. Similar reactions, proceeding at much higher organic reactant
226 concentrations, can also occur within the aqueous component of tropospheric aerosol (Blando and Turpin, 2000).

227 Tightly connected to SOA formation and modification processes are the condensed phase viscosity and phase state,
228 which set mixing times within particles and are dependent on relative humidity and temperature (Virtanen et al.,
229 2010; Koop et al., 2011; Renbaum-Wolff et al., 2013). Organic particles are likely glasses in the cold free
230 troposphere (Shiraiwa et al., 2017b), which may affect SOA formation and growth, and restricts the degree to which
231 heterogeneous oxidation can affect the aerosol composition. The particles are liquids in warm, wet boundary layers,
232 with the full particle volume involved in partitioning with gas phase molecules. The large variation in molecular
233 diffusion coefficients and associated mobility determines where chemical reactions are important in the particles,
234 from two-dimensional processes that occur solely at the gas-particle interface to three-dimensional chemistry with
235 reactivity at the interface and deeper in the bulk (see Figure 2). Overall, diffusion is a key parameter for determining
236 whether a reaction is surface-area-limited or volume-limited (Hanson et al., 1994).

237 Multiphase chemistry also leads to the formation of secondary inorganic aerosol. For example, the hydrolysis of
238 N_2O_5 converts NO_x to HNO_3 ; the gas-particle partitioning of HNO_3 is then controlled by temperature, relative
239 humidity, and ammonia levels. Also, particulate sulfate is rapidly formed in polluted environments through
240 multiphase aqueous chemistry, acting as the major formation mechanism in cloud-free settings (Cheng et al., 2016;
241 Wang et al., 2016). Potential routes for fast sulfate formation in deliquesced particles include: the role of ionic
242 strength in accelerating the rates of specific processes (Liu et al., 2020), fast interfacial chemistry (Liu and Abbatt,
243 2021), formation of condensed-phase oxidants through the photolysis of particulate nitrate (Zheng et al., 2020; see
244 also Section 6.5), and the role of specific particle-phase reactants, such as organic hydroperoxides (Wang et al.,
245 2019), hydroxymethanesulfonate (Song et al., 2019), and dissolved transition metal ions (Li et al., 2020b). An

246 accurate quantitative assessment of these and other reaction pathways is still developing but far from complete (Liu
247 et al., 2021b).

248 As noted earlier, the need to better understand aerosol-climate interactions has also motivated multiphase chemistry
249 research in the past twenty years. Atmospheric processing leads to the formation of water-soluble condensed-phase
250 products, such as sulfate or highly oxygenated organic molecules (Jimenez et al., 2009), enhancing the abilities of
251 tropospheric aerosol particles to act as cloud condensation nuclei (CCN) and affecting their ability to scatter light
252 (Cappa et al., 2011; Moise et al., 2015). As well, the optical properties of the fraction of organic aerosol that
253 absorbs near ultraviolet and visible light (i.e., atmospheric ‘brown carbon’ particles) are subject to change via
254 multiphase oxidation and condensed phase photochemistry (Laskin et al., 2015; Li et al., 2020a; Hems et al., 2021;
255 Schnitzler et al., 2022), potentially involving transition metals (Al-Abadleh and Nizkorodov, 2021). Although the
256 rates of optical property changes remain uncertain, primary brown carbon particles, as formed in wildfires, tend to
257 become less absorbing in the near UV and visible parts of the spectrum on the timescale of days via a variety of
258 multiphase aging mechanisms (Laskin et al., 2015; Hems et al., 2021), i.e., they are ‘bleached.’ The diminution of
259 light absorption is in accord with field observations (Forrister et al., 2015).

260 Multiphase chemistry can also affect the properties of ice nucleating particles (INPs) by both gas-solid and liquid-
261 solid interactions, noting that INPs can act in the deposition mode where water vapor forms ice directly on solid
262 substrates and in the immersion mode where a solid particle immersed in supercooled water leads to nucleation
263 (Kanji et al., 2017). For example, mineral dust can have its IN activity decreased by condensation of involatile
264 materials, such as sulfate or by cloud processing (Sullivan et al., 2010b; Kilchhofer et al., 2021), and strong acids
265 can react with carbonate-containing minerals, leading to particles that are less IN-active in the deposition mode but
266 more active in the immersion mode (Sullivan et al., 2010a). Such effects can also arise when different gas and
267 liquid species are exposed to volcanic ashes (Maters et al., 2020; Fahy et al., 2022). Oxidation reactions can also
268 occur so that efficient biological INPs, such as pollen fragments, lose activity upon oxidation by OH radicals,
269 probably by morphological changes of surface proteins and carbohydrates (Gute and Abbatt, 2018). The
270 mechanisms involving all these interactions are very complex. In the case of mineral dusts, immersion INP activity
271 can be changed by surface modification, ion exchange, adsorption of solutes such as ammonium, and acid
272 dissolution (Sihvonen et al., 2014; Kumar et al., 2019; Yun et al., 2021).

273 **6 The future of atmospheric multiphase chemistry studies**

274 **6.1 Multiphase chemistry at the interfaces of the atmosphere**

275 There are exciting opportunities for applying the conceptual, instrumental, and modeling tools developed for
276 multiphase chemistry to understand chemistry occurring at the interfaces of the atmosphere with other
277 environmental domains.

278 Consider the interface of the atmosphere and the ocean, where the sea-surface microlayer (SML) is a thin layer of
279 ocean water that has enhanced concentrations of biological detritus, surface-active compounds, and gel-like

280 substances (Cunliffe et al., 2013). Recognizing that individual molecule surrogates of the SML only capture specific
281 aspects of the chemistry, experimental designs now involve either genuine seawater or water samples with
282 significant biological components (Prather et al., 2013; Schneider et al., 2019). While we know that the SML can
283 affect the composition of primary marine aerosol, an open question is the degree of chemical processing by
284 photosensitization in the SML or by gas-surface heterogeneous oxidation, yielding volatile species that contribute to
285 marine SOA formation (Donaldson and George, 2012; Rossignol et al., 2016; Mungall et al., 2017; Croft et al.,
286 2019).

287 Another key role of multiphase reactions is in dry deposition processes on the ocean (e.g., see R4 and R5),
288 vegetation, the built environment, and land surfaces (Garland et al., 1980; Fowler et al., 2009; Kavassalis and
289 Murphy, 2017; Tuite et al., 2021). Deposition is a critical step that controls removing chemicals from the
290 atmosphere. Yet, this process is a parameterization in models. Deposition in many environments needs to be
291 predictive, which demands molecular-level understanding and quantification. This process is essentially a
292 multiphase process that should be broken down into physico-chemical steps, which can be independently measured
293 and understood.

294 Indoor environments, with their vast surface area-to-volume ratios, are another example of poorly explored
295 multiphase processes (Morrison, 2008; Abbatt and Wang, 2020; Ault et al., 2020). Contrary to the outdoor
296 environment, where aerosol particles may remain suspended for days to weeks, the indoor air-exchange timescale is
297 on the order of an hour or two. While this lessens the potential for gas-particle chemistry, multiphase chemistry
298 occurs over much longer timescales on fixed indoor surfaces. For example, O₃ is efficiently lost via dry deposition
299 so that its mixing ratios are considerably lower indoors than outdoors (Weschler, 2000). This produces VOCs
300 (Wisthaler and Weschler, 2009) and modifies the composition of sorbed molecules, in some cases forming species
301 more toxic than their precursors (Pitts et al., 1978, 1980; Zhou et al., 2017). It can also lead to the formation of gas-
302 phase OH radicals (Zannoni et al., 2022). This source of OH from alkene ozonolysis is in addition to the generation
303 of OH from photolysis of HONO (Gomez Alvarez et al., 2013), which is partly formed by multiphase chemistry on
304 indoor surfaces. Indoor surfaces are a chemically complex, poorly understood environment, with input from building
305 materials, commercial products, humans, and cooking and cleaning activities. This chemistry is important because
306 humans obtain most of their chemical exposure indoors, not only via inhalation but also through direct dermal
307 uptake and by ingesting dust and contaminated foodstuffs (Li et al., 2019b). Lastly, the light environment indoors
308 can be substantially different than outside, bringing a new twist to multiphase photochemistry (Young et al., 2019).

309 **6.2 Multiphase chemistry and human health**

310 Epidemiological studies have conclusively shown that aerosol particle inhalation harms human health (Pope et al.,
311 2009; Landrigan et al., 2018). For example, it is well-recognized that inflammation occurs upon particle exposure
312 (Brook et al., 2003). The current epidemiology (empirical evidence) does not readily distinguish the specific
313 molecules in the particles and their formation pathways that lead to negative health outcomes, nor the toxicity
314 mechanism at the molecular level. Studies are currently examining oxidative stress, e.g., the reactive oxygen species
315 (ROS) and reactive nitrogen species (RNS), as a mechanism for negative impacts (Shiraiwa et al., 2017a). Although

316 there is debate over whether oxidants are largely endogenous or exogenous (Fang et al., 2022), one hypothesis is that
317 the biochemical balance between oxidants and antioxidants is upset by inhaling harmful species (Miller, 2020). To
318 contribute to this debate, the multiphase chemistry community needs to better describe the chemistry that occurs at
319 the lung-air interface and the composition of respirable aerosol particles, especially the biologically active
320 components that contain reactive functional groups (e.g., epoxides, hydroperoxides), redox-active materials (e.g.,
321 quinones), and reactive oxygen species (e.g., peroxides, HO₂/O₂[•]). Many of these species are formed by multiphase
322 oxidation processes.

323
324 An associated issue is how ultrafine particles influence health. These particles have been shown to be taken directly
325 to the bloodstream and even move to the brain (Oberdorster et al., 2004; Maher et al., 2016). Though the chemistry
326 involved is not the multiphase chemistry discussed here, the interactions of the particle in the liquid phase (i.e.,
327 impacting biological systems) are likely important. Many of the lessons learned from studies of multiphase
328 processes are likely applicable to understanding such issues.

329 Largely unexplored until the recent COVID-19 pandemic is the impact of the atmosphere on airborne and surface-
330 deposited biological pathogens, including bacteria and viruses. Early work in this area included the multiphase
331 chemistry between NO₂ and proteinaceous material, motivated by its potential to drive an allergenic response
332 (Franze et al., 2005; Shiraiwa et al., 2012). Gas phase O₃ has also been examined for its ability to affect the viability
333 of bacteriophages, i.e., microorganisms with a lipid envelope and RNA core similar to the structure of SARS-CoV-
334 2, deposited on surfaces (Tseng and Li, 2008). With the pandemic, research has accelerated into the impact of
335 hygroscopic growth and water content on viral viability within respiratory particle surrogates that consist of viruses
336 embedded in saline droplets containing surfactants, proteins, and carbohydrates. It is important to understand the
337 changes in the acidity of these particles, the mass transfer within them, and the precipitation of salts as the particle
338 water content changes (Lin et al., 2020; Oswin et al., 2022; Huynh et al., 2022).

339 The recent pandemic led to an emphasis on cleaning surfaces to reduce the potential for infection by fomites, i.e., via
340 contact with contaminated surfaces. While cleaning agents such as chlorine bleach have well-established anti-
341 microbial activity, their multiphase chemistry can release gases and particles that are deleterious to human health
342 (Wong et al., 2017; Mattila et al., 2020). Understanding the multiphase chemistry associated with these cleaning
343 activities and the outcomes of using air cleaners (Collins and Farmer, 2021), is essential for establishing healthy
344 indoor environments.

345 Lastly, the pandemic prompted a re-examination of an overlooked aspect of our atmosphere that it has an as-yet-
346 unidentified germicidal component referred to as the Open Air Factor (Cox et al., 2021). In particular, it was shown
347 many decades ago that fresh air led to better outcomes for tuberculosis patients and injured World War I soldiers
348 than indoor air. Historically, sending sick people to pristine environments (e.g., the seaside) was a common medical
349 recommendation. It is crucial to determine whether these effects are related in some way to multiphase chemistry
350 occurring between reactive species in the gas phase interacting with biological molecules at the surface of the
351 wounds and lungs.

352 Each of the above topics provides exciting opportunities for atmospheric chemists to collaborate with the
353 environmental health, medical, and toxicological communities.

354 **6.3 Chemistry of the free troposphere and lower stratosphere**

355 Although the upper troposphere – lower stratosphere region was the focus of much attention in the 1980s and 1990s
356 to understand the changes in ozone levels in these regions, most multiphase chemistry studies are currently
357 conducted at room temperature. There is considerable motivation to re-explore chemistry at colder temperatures,
358 given past work that illustrated the atmospheric impacts of a strongly non-linear dependence of multiphase reactions
359 rates on temperature (Murphy and Ravishankara, 1994) and extensive new observations from the Atom campaigns
360 (Thompson, 2022) that sampled from the boundary layer to the upper troposphere over many latitudes and seasons.
361 As well, there is emerging evidence for organic aerosol in the lower stratosphere, likely arising from wildfire
362 injection, with potential influence on stratospheric ozone (Solomon et al., 2022; Strahan et al., 2022).

363 Organic aerosol viscosity and phase state depend on the environmental conditions (Koop et al., 2011), with semi-
364 solid and glassy organic particles predicted throughout much of the free troposphere (Shiraiwa et al., 2017b). Aside
365 from those at the gas-particle interface, molecules in highly viscous organic particles are protected from
366 heterogeneous oxidation (Shiraiwa et al., 2011; Zhou et al., 2012; Shrivastava et al., 2017a). Such protection
367 increases the lifetimes of pollutants, e.g., brown carbon chromophores (Schnitzler et al., 2022), and lengthens
368 particles' oxidation timescale and wet deposition lifetime.

369 In addition to continuing to address the fundamentals of cloud chemistry oxidation processes, the associated
370 chemistry of transition metals, and the production of oxidants within cloud water and via uptake from the gas phase
371 (Herrmann et al., 2015), there is a particular need to also study such processes at cold temperatures, including under
372 supercooled water conditions. When supercooled water is frozen, solutes are excluded from the ice crystals and
373 become highly concentrated at grain boundaries and in liquid and liquid-like layers at the surface, potentially leading
374 to enhanced rates of aqueous phase chemistry. As well, the Reynolds-Workman potential (Workman and Reynolds,
375 1950), arising at the ice-water interface, can drive chemistry.

376 A key factor affected by temperature is the solubility of various atmospheric constituents. Simple Henry's law
377 constants and further equilibration steps that determine the overall solubilities are poorly known, especially below
378 room temperature. Most of the data on the solubilities in organics goes back to chemical engineering literature that
379 is more than half a century old. Also, since solubilities vary according to Henry's law equilibria that vary
380 exponentially with temperature, the accurate temperature dependence of solubilities is essential. Acid dissociation
381 constants in organic acids and organic substrates are poorly known, and they determine the overall solubility of a
382 chemical.

383 **6.4 Reactive transformations of organic chemical contaminants**

384 Over forty years ago, it was recognized that multiphase oxidation of chemical contaminants leads to the rapid loss of
385 surface-bound PAHs and the formation of more toxic and potentially carcinogenic products such as nitro-PAHs and
386 oxygenated PAHs (Pitts et al., 1978, 1980). These reactions occur on a variety of surfaces with light, ozone, and
387 NO₂ reactants, some via Langmuir-Hinshelwood mechanisms (Poschl et al., 2001; Mmereki and Donaldson, 2003;
388 Kwamena et al., 2004). Buried PAHs are protected from heterogeneous loss by a crust of unreactive products that
389 accumulates upon them and, when present, within viscous organic aerosol (Zhou et al., 2013, 2019a), enabling the
390 potential for long-range atmospheric transport (Mu et al., 2018). The chemistry of other organic contaminants,
391 including smoking products such as nicotine (Destailats et al., 2006) and tetrahydrocannabinol (Yeh et al., 2022), a
392 few pesticides (Segal-Rosenheimer and Dubowski, 2007; Finlayson-Pitts et al., 2022), and organophosphate esters
393 (Liu et al., 2021a), has also been recently explored.

394 However, these are largely exceptions, and the multiphase fate of most chemical contaminants, especially thousands
395 of commercial products, has not been examined. Indeed, the atmospheric chemistry and chemical contaminant
396 communities have traditionally not strongly interacted. Although assessment of the gas phase OH reactivity is
397 customarily performed in environmental fate analyses (Li et al., 2019b), many commercial products have
398 sufficiently low volatility such that they reside primarily on surfaces or within particles. It is important to establish
399 whether organic contaminants traditionally viewed as persistent are indeed unreactive with respect to multiphase
400 transformation.

401 **6.5 Understanding the role of light**

402 Many condensed-phase photochemical reactions proceed via indirect mechanisms where a photosensitizing
403 molecule absorbs light, forming reactive species such as HO₂/O₂⁻ or ¹O₂ (George et al., 2015). Such chemistry, first
404 identified for natural waters (Canonica et al., 1995), has been implicated in the daytime formation of HONO
405 (George et al., 2005), the photoreactions of brown carbon aerosol (Laskin et al., 2015; Hems et al., 2021), the
406 formation of active halogens (Reeser et al., 2009), and reactivity of black carbon (Monge et al., 2010; Li et al.,
407 2019c). This chemistry has been illustrated using efficient photosensitizing agents, but quantitative assessments of
408 atmospheric importance remain uncertain largely because the character and quantity of atmospheric photosensitizers
409 are not well established. Developing a tighter quantitative connection to the atmosphere will require using more
410 representative photosensitizers, as now being done using marine aerosol components (Ciuraru et al., 2015; Garcia et
411 al., 2021). The wavelengths of interest for the troposphere are in the near UV and visible part of the solar flux.

412 In addition to indirect sensitization, light can also lead to direct photochemistry. An important finding was that
413 photolysis on ice and snow surfaces was demonstrated to form NO_x in midlatitudes and polar regions (Honrath et al.,
414 1999; Wolff et al., 2002; Domine and Shepson, 2002). This process, which likely proceeds in a wide range of
415 environments, is now referred to as “re-noxification” as it releases NO_x from HNO₃ that has deposited from the
416 atmosphere. Other condensed-phase chemical processes of importance include the formation of oxidants from
417 nitrate and nitrite photolysis (Zepp et al., 1987), photolysis of condensed-phase organic hydroperoxides and other
418 highly oxygenated organics, and the photochemical activity of many transition metal ion complexes (Faust and
419 Zepp, 1993; Weller et al., 2013). It is important to recognize that the absorption spectra and product quantum yields

420 of dissolved species can be different than those in the gas phase (George et al., 2015), with aqueous nitrate a prime
421 example (Benedict et al., 2017). The variable viscosity of organic aerosol matrices can affect photolysis rates,
422 products, and their temperature dependence (Lignell et al., 2014).

423 **6.6 Developments in Field Observational Capabilities**

424 Our ability to characterize atmospheric composition continues to push the field of atmospheric chemistry forward.
425 For multiphase chemistry, advances in analytical mass spectrometry have been transformative. Within the last
426 twenty years, online characterization of aerosol composition has become commonplace (Canagaratna et al., 2007),
427 studies of single particle composition allow us to observe the variability in mixing state and chemical diversity
428 (Zelenyuk and Imre, 2005; Murphy et al., 2006; Prather et al., 2008), and offline filter sampling has progressed from
429 the characterization of a few targeted species to non-targeted analyses using a range of mass spectral ionization
430 methods (Papazian et al., 2022; Ditto et al., 2022). Identifying specific molecular "markers" for organics and
431 functional groups is still somewhat uncertain; developing such identification would be very helpful.

432 The continued development of analytical techniques will enable increasingly sophisticated characterization of
433 aerosol particles and environmental surfaces, with the opportunity to deploy the same tools in both lab and field
434 settings. However, challenges are arising as well. Despite the rapid development of low-cost sensors, affordable
435 instrumentation for the long-term characterization of aerosol composition in many locations is still lacking. The
436 increasing sophistication of analytical instrumentation also continues to unveil the high degree of chemical
437 complexity present. Whereas high-resolution mass spectrometry yields chemical formulae in real-time, there is
438 often the need to identify chemical structures. This suggests that we should increasingly deploy separation
439 techniques (e.g., chromatography, ion mobility) as front ends to our increasingly sophisticated mass spectrometric
440 techniques (Krechmer et al., 2016; Claflin et al., 2021). There is also value to the expanded use of other classical
441 chemical speciation methods, such as infrared (Russell, 2003) and NMR (Decesari et al., 2007) characterization of
442 aerosol composition collected by filters. While these techniques have low time resolution, they provide
443 complementary quantitative and functional group information and can be inexpensively deployed for long-term
444 analyses in a wide range of environments. Such analyses will also help with the source apportionment of the
445 aerosols.

446 Aerosol characteristics related to multiphase chemistry can be studied with increasingly sophisticated remote
447 sensing techniques. These approaches have been applied for many years to polar stratospheric clouds, whose
448 composition and phase (via the degree of depolarization of a lidar probe) have been studied (Tritscher et al., 2021).
449 Another example comes from satellite measurements of solid ammonium nitrate particles in the upper troposphere,
450 driven by the Asian monsoon that uplifts ammonia-rich continental air (Hopfner et al., 2019). It is important to
451 determine the role of these particles in ice nucleation and multiphase chemistry.

452 **6.7 Developments in Laboratory and Molecular Modeling Techniques**

453 In addition to our ability to conduct field observations, a revolution has occurred in the laboratory's analytical
454 methods. This is most widely apparent in applying sophisticated mass spectrometric techniques, increasingly

455 involving high mass resolution and a range of ionization schemes (Laskin et al., 2013). When coupled with other
456 analytical methods, we can now determine the physico-chemical properties of individual molecules and their
457 mixtures in extreme detail. For example, this approach has been taken to characterize the optical properties of
458 brown carbon aerosol materials (Fleming et al., 2020), the viscosity of organic aerosol (DeRieux et al., 2018), and
459 the structural isomers of complex organic mixtures (Krechmer et al., 2016). There are significant opportunities for
460 additional adoption of techniques from neighboring disciplines. As well, the use of a number of these analytical
461 techniques in both the laboratory and the field will enhance our ability to connect the lab to the field.

462 Molecular-level chemical models increasingly provide valuable insights into complex multiphase processes. For
463 example, important insights into the nature of the chemistry occurring on polar stratospheric cloud materials were
464 obtained from molecular dynamics modeling (Wang and Clary, 1996; Bianco and Hynes, 2006) and more recent
465 studies have addressed gas-surface interactions and the roles of solvent molecules in small molecular clusters
466 (Gerber et al., 2015; Fang et al., 2019; Yang et al., 2019). Whereas past computational methods only included a few
467 solvent molecules, current dynamics models using state-of-the-art force fields can realistically simulate partitioning,
468 surface adsorption constants, diffusion constants, and vapor pressures, representing an important point of contact to
469 the physical chemistry and chemical physics communities (Tobias et al., 2013). We also note that machine-learning
470 techniques are very recently being applied to molecular dynamics simulations, for example, to describe the
471 interactions of N_2O_5 with liquid water (Galib and Limmer, 2021) and the dissociation of strong acids at aqueous
472 interfaces (de la Puente et al., 2022). For establishing fundamental parameters that are experimentally challenging to
473 measure, such as the likelihood that a collision of a molecule with a particle leads to uptake by the condensed phase
474 (i.e., a mass accommodation coefficient), theoretical methods may be preferable to experiment in some situations.

475 **6.8 Grappling with chemical complexity**

476 Atmospheric aerosol particles and surfaces are morphologically and compositionally complex. This complexity can
477 be enticing from a fundamental chemistry perspective as we disentangle mass transfer, phase separation, and
478 reactivity. However, it can impede the development of an accurate, quantitative description required to inform an
479 atmospheric model. It can also be constraining if we study the detailed chemistry and lose sight of its overall impact
480 on climate, air quality, or ecosystem health.

481 With enough care, the rate constant for a gas-phase, radical-molecule reaction can be measured with 10-20%
482 accuracy (Cox, 2012). Atmospheric modelers rely upon this confidence level as they assess their predictions. It is
483 humbling to consider the accuracy of the available multiphase kinetics data for the modeling community. Take for
484 example the reaction of N_2O_5 with tropospheric aerosol, which has been long known to impact NO_x/NO_y and active
485 chlorine levels, with a secondary influence on OH, O_3 , and CH_4 (Dentener and Crutzen, 1993). Although studies
486 started in the 1980s, new mechanistic insights on N_2O_5 heterogeneous reactivity are still arising (Sobyra et al., 2019;
487 Karimova et al., 2020). Laboratory reactive uptake coefficients for the hydrolysis of N_2O_5 vary over one-to-two
488 orders of magnitude, with larger values reported for aqueous particles composed of sulfate or soluble organics, and
489 lower values for particles with less soluble organics and nitrate (Burkholder et al., 2020). Likewise, uptake
490 coefficients inferred from field measurements or with genuine ambient particles vary by roughly an order of

491 magnitude compared to those measured with laboratory surrogates (Brown et al., 2006; Bertram et al., 2009; Abbatt
492 et al., 2012; Phillips et al., 2016; Tham et al., 2018). The discrepancies between field and lab studies are
493 undoubtedly due to complex and variable particle composition and phase state. Simply put, unlike the case with gas
494 phase reactions, one of the "reactants" in this gas-particle reaction is highly variable. This complexity is exacerbated
495 by the changes in the composition (including acidity), mixing state, and water content of the particle as it resides in
496 the atmosphere. Added complexity arises from the differences in composition that occur in the bulk of particles and
497 droplets compared to their interfacial composition (Wingen and Finlayson-Pitts, 2019).

498 Likewise, HO_x loss on tropospheric aerosol may significantly impact ozone in high-NO_x atmospheric regimes, as in
499 East Asia. As particulate levels drop in such regions, HO_x abundance and ozone mixing ratios will both rise (Martin
500 et al., 2003; Li et al., 2019a; Ivatt et al., 2022). However, reported HO₂ uptake coefficients vary widely, from
501 research group to research group and from the lab to the field (Burkholder et al., 2020), making modeling
502 predictions highly uncertain.

503 Both bottom-up and top-down approaches can address chemical complexity. In the traditional bottom-up approach,
504 the effects on the reaction system of step-by-step additions of chemical complexity are evaluated. This leads to a
505 better understanding of the fundamental chemistry needed to develop our predictive abilities. Top-down approaches
506 involve studying chemistry on ambient aerosol particles. This has been done for N₂O₅ and HO₂ aerosol uptake
507 (Bertram et al., 2009; Zhou et al., 2021), for heterogeneous OH oxidation (George et al., 2008), and to characterize
508 SOA formation by using mobile reaction chambers (Jorga et al., 2021). Another top-down method constrains the
509 rates of multiphase chemistry using detailed, simultaneous measurements of gas-phase composition under a range of
510 environmental conditions (Brown et al., 2006). Combining top-down and bottom-up approaches enhances our
511 understanding of the fundamental science while ensuring that parameterizations for atmospheric modeling are
512 accurate.

513 Models working over a wide range of spatial and temporal scales can help address issues in chemical complexity. As
514 mentioned in the previous section, molecular dynamics calculations are becoming increasingly sophisticated. So too
515 are multiphase kinetics models that can incorporate insights gained at the molecular level into modelling
516 frameworks that aim to couple the gas phase and condensed phases, including bulk reaction kinetics, mass transfer
517 and interfacial processes (Poschl et al., 2007; Tilgner et al., 2013; Woo and McNeill, 2015). A challenge is to couple
518 bulk and interfacial processes correctly. As computing capabilities grow, the complexity of the multiphase and
519 detailed molecular mechanism models that can be incorporated into chemical transport models will also increase.
520 Also, Lagrangian-type models increasingly can model specific field observations (Zaveri et al., 2010). We note that
521 a successful hierarchical approach has arisen in the indoor chemistry community where modeling groups using a
522 wide range of tools, from molecular dynamics to large-scale computational fluid dynamics, interact closely with
523 each other and with experimental scientists (Shiraiwa et al., 2019).

524 **7 Concluding thoughts**

- 525 • Multiphase chemistry has evolved alongside the wider field of atmospheric chemistry. While initial studies
526 focused on its impacts on the gas phase, the field now addresses how chemistry affects particles. Although
527 modification of aerosol composition has direct relevance to climate and human health, we should not lose sight
528 of the connection of multiphase chemistry to the gas phase composition of the atmosphere.
- 529 • We need to understand chemical processes at the molecular level to improve our ability to interpret field
530 observations and predict the nature of a changing atmosphere. Reinforcing an approach based on physico-
531 chemical understanding is necessary for detailed predictions of environmental change.
- 532 • There are significant research opportunities for the characterization of the chemistry that occurs at the interface
533 of the atmosphere with the rest of the environment, such as studies of ocean-atmosphere interactions, indoor air,
534 aerosol health effects, atmosphere-cryosphere chemistry from the stratosphere all the way to the snowpack, and
535 pathogen-air interactions.
- 536 • With increasingly sophisticated experimental and theoretical tools, atmospheric chemical complexity becomes
537 more apparent. While exciting, this presents challenges and constraints. We should emphasize not only highly
538 detailed, molecular-level measurements but also more widespread and more prolonged aerosol characterization
539 that has less chemical specificity but nevertheless provides valuable insights; there is also a role for both remote
540 sensing measurements and classical analytical techniques in this regard. This is akin to a need to understand and
541 quantify thermal gas phase reactions while also understanding and quantifying microcanonical reactivity.
- 542 • Measurements of many fundamental physico-chemical parameters such as solubility, diffusion coefficients, and
543 liquid/solid phase reactivities are sorely needed.
- 544 • Multiphase chemistry studies conducted under conditions that match those in the atmosphere, including those of
545 the free troposphere and lower stratosphere, are needed.
- 546 • Using the atmosphere as a laboratory to quantify rates of multiphase processes holds promise, with
547 simultaneous measurements of many chemicals and other external parameters becoming more feasible through
548 coordinated field measurements. Designing field studies with an eye toward quantification of the multiphase
549 reactions is beneficial.
- 550 • The field of atmospheric chemistry is healthiest when there is extensive communication and feedback between
551 the fundamental chemistry, modeling, and field observation communities (see Figure 1). To keep the three-
552 legged stool balanced and strong, multiphase chemists should interact widely with not only other atmospheric
553 scientists, but also scientists in related fields such as meteorology, climate dynamics, ecology, and human
554 health. This can be accomplished by participation in conferences and seminars that involve science from
555 different legs of the stool, students exploring short-term training opportunities in diverse research groups, and
556 collaborative grants that bring together laboratory and theory, modeling, and field measurement scientists.

557

558 **Author Contributions**

559 Both authors contributed to writing the manuscript.

560 **Competing Interests**

561 The authors declare they have no conflict of interest.

562 **Acknowledgements**

563 Thank you to Hind Al-Abadleh, Len Barrie, and Will Fahy for their comments on the manuscript, and to Zilin Zhou
564 for crafting the figures.

565

566 **References**

567 Abbatt, J. and Wang, C.: The atmospheric chemistry of indoor environments, *Env. Sci. Proc. Impacts*, 22,
568 25–48, <https://doi.org/10.1039/c9em00386j>, 2020.

569 Abbatt, J., George, C., Melamed, M., Monks, P., Pandis, S., and Rudich, Y.: New Directions: Fundamentals
570 of atmospheric chemistry: Keeping a three-legged stool balanced, *Atmos. Environ.*, 84, 390–391,
571 <https://doi.org/10.1016/j.atmosenv.2013.10.025>, 2014.

572 Abbatt, J. P. D.: Interactions of atmospheric trace gases with ice surfaces: Adsorption and reaction,
573 *Chem. Rev.*, 103, 4783–4800, <https://doi.org/10.1021/cr0206418>, 2003.

574 Abbatt, J. P. D., Lee, A. K. Y., and Thornton, J. A.: Quantifying trace gas uptake to tropospheric aerosol:
575 recent advances and remaining challenges, *Chem. Soc. Rev.*, 41, 6555–6581,
576 <https://doi.org/10.1039/c2cs35052a>, 2012.

577 Al-Abadleh, H. and Nizkorodov, S.: Open questions on transition metals driving secondary thermal
578 processes in atmospheric aerosols, *Commun. Chem.*, 4, <https://doi.org/10.1038/s42004-021-00616-w>,
579 2021.

580 Ault, A., Grassian, V., Carslaw, N., Collins, D., Destailats, H., Donaldson, D., Farmer, D., Jimenez, J.,
581 McNeill, V., Morrison, G., O'Brien, R., Shiraiwa, M., Vance, M., Wells, J., and Xiong, W.: Indoor Surface
582 Chemistry: Developing a Molecular Picture of Reactions on Indoor Interfaces, *Chem*, 6, 3203–3218,
583 <https://doi.org/10.1016/j.chempr.2020.08.023>, 2020.

584 Benedict, K., McFall, A., and Anastasio, C.: Quantum Yield of Nitrite from the Photolysis of Aqueous
585 Nitrate above 300 nm, *Environ. Sci. Technol.*, 51, 4387–4395, <https://doi.org/10.1021/acs.est.6b06370>,
586 2017.

587 Bertram, T. H., Thornton, J. A., Riedel, T. P., Middlebrook, A. M., Bahreini, R., Bates, T. S., Quinn, P. K.,
588 and Coffman, D. J.: Direct observations of N₂O₅ reactivity on ambient aerosol particles, *Geophys. Res.
589 Lett.*, 36, 5, <https://doi.org/10.1029/2009gl040248>, 2009.

590 Bianchi, F., Kurten, T., Riva, M., Mohr, C., Rissanen, M., Roldin, P., Berndt, T., Crouse, J., Wennberg, P.,
591 Mentel, T., Wildt, J., Junninen, H., Jokinen, T., Kulmala, M., Worsnop, D., Thornton, J., Donahue, N.,
592 Kjaergaard, H., and Ehn, M.: Highly Oxygenated Organic Molecules (HOM) from Gas-Phase Autoxidation
593 Involving Peroxy Radicals: A Key Contributor to Atmospheric Aerosol, *Chem. Rev.*, 119, 3472–3509,
594 <https://doi.org/10.1021/acs.chemrev.8b00395>, 2019.

595 Bianco, R. and Hynes, J.: A theoretical study of the reaction of ClONO₂ with HCl on ice, *J. Phys. Chem. A*,
596 103, 3797–3801, <https://doi.org/10.1021/jp990471b>, 1999.

597 Bianco, R. and Hynes, J. T.: Heterogeneous reactions important in atmospheric ozone depletion: A
598 theoretical perspective, *Acc. Chem. Res.*, 39, 159–165, <https://doi.org/10.1021/ar040197q>, 2006.

599 Blando, J. D. and Turpin, B. J.: Secondary organic aerosol formation in cloud and fog droplets: a literature
600 evaluation of plausibility, *Atmos. Environ.*, 34, 1623–1632, <https://doi.org/10.1016/S1352->
601 2310(99)00392-1, 2000.

602 Brook, R., Brook, J., and Rajagopalan, S.: Air pollution: The “heart” of the problem, *Curr. Hypertens.*
603 *Rep.*, 5, 32–39, <https://doi.org/10.1007/s11906-003-0008-y>, 2003.

604 Brown, S. S., Ryerson, T. B., Wollny, A. G., Brock, C. A., Peltier, R., Sullivan, A. P., Weber, R. J., Dube, W.
605 P., Trainer, M., Meagher, J. F., Fehsenfeld, F. C., and Ravishankara, A. R.: Variability in nocturnal nitrogen
606 oxide processing and its role in regional air quality, *Science*, 311, 67–70,
607 <https://doi.org/10.1126/science.1120120>, 2006.

608 Burkholder, J. B., Abbatt, J. P. D., Barnes, I., Roberts, J. M., Melamed, M. L., Ammann, M., Bertram, A. K.,
609 Cappa, C. D., Carlton, A. G., Carpenter, L. J., Crowley, J. N., Dubowski, Y., George, C., Heard, D. E.,
610 Herrmann, H., Keutsch, F. N., Kroll, J. H., McNeill, V. F., Ng, N. L., Nizkorodov, S. A., Orlando, J. J., Percival,
611 C. J., Picquet-Varrault, B., Rudich, Y., Seakins, P. W., Surratt, J. D., Tanimoto, H., Thornton, J. A., Tong, Z.,
612 Tyndall, G. S., Wahner, A., Weschler, C. J., Wilson, K. R., and Ziemann, P. J.: The Essential Role for
613 Laboratory Studies in Atmospheric Chemistry, *Environ. Sci. Technol.*, 51, 2519–2528,
614 <https://doi.org/10.1021/acs.est.6b04947>, 2017.

615 Burkholder, J. B., Abbatt, J. P. D., Cappa, C. D., Dibble, T. S., Kolb, C. E., Orkin, V. L., Wilmouth, D. M.,
616 Sander, S. P., Barker, J. R., Crouse, J. D., Huie, R. E., Kurylo, M. J., Percival, C. J., and Wine, P. H.:
617 Chemical kinetics and photochemical data for use in atmospheric studies, NASA - JPL, Pasadena, CA,
618 2020.

619 Calvert, J., Lazrus, A., Kok, G., Heikes, B., Walega, J., Lind, J., and Cantrell, C.: Chemical mechanisms of
620 acid generation in the troposphere, *Nature*, 317, 27–35, <https://doi.org/10.1038/317027a0>, 1985.

621 Canagaratna, M. R., Jayne, J. T., Jimenez, J. L., Allan, J. D., Alfarra, M. R., Zhang, Q., Onasch, T. B.,
622 Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L. R., Trimborn, A. M., Northway, M. J.,
623 DeCarlo, P. F., Kolb, C. E., Davidovits, P., and Worsnop, D. R.: Chemical and microphysical
624 characterization of ambient aerosols with the Aerodyne aerosol mass spectrometer, *Mass Spec. Rev.*, 26,
625 185–222, 2007.

626 Canonica, S., Jans, U., Stemmler, K., and Hoigne, J.: Transformation kinetics of phenols in water -
627 photosensitization by dissolved natural organic matter and aromatic ketones, *Environ. Sci. Technol.*, 29,
628 1822–1831, <https://doi.org/10.1021/es00007a020>, 1995.

629 Cappa, C. D., Che, D. L., Kessler, S. H., Kroll, J. H., and Wilson, K. R.: Variations in organic aerosol optical
630 and hygroscopic properties upon heterogeneous OH oxidation, *J. Geophys. Res.-Atmospheres*, 116, 12,
631 <https://doi.org/D15204> 10.1029/2011jd015918, 2011.

632 Carpenter, L., MacDonald, S., Shaw, M., Kumar, R., Saunders, R., Parthipan, R., Wilson, J., and Plane, J.:
633 Atmospheric iodine levels influenced by sea surface emissions of inorganic iodine, *Nat. Geosci.*, 6, 108–
634 111, <https://doi.org/10.1038/NGEO1687>, 2013.

635 Chameides, W. and Davis, D.: The free-radical chemistry of cloud droplets and its impact upon the
636 composition of rain, *J. Geophys. Res.*, 87, 4863–4877, <https://doi.org/10.1029/JC087iC07p04863>, 1982.

637 Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., Gao, M., Zhang, Q., He, K., Carmichael, G.,
638 Poschl, U., and Su, H.: Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze
639 events in China, *Sci. Adv.*, 2, <https://doi.org/10.1126/sciadv.1601530>, 2016.

640 Choulaton, T., Colvile, R., Bower, K., Gallagher, M., Wells, M., Beswick, K., Arends, B., Mols, J., Kos, G.,
641 Fuzzi, S., Lind, J., Orsi, G., Facchini, M., Laj, P., Gieray, R., Wieser, P., Engelhardt, T., Berner, A., Krusiz, C.,
642 Moller, D., Acker, K., Wieprecht, W., Luttke, J., Levsen, K., Bizjak, M., Hansson, H., Cederfelt, S., Frank, G.,
643 Mentes, B., Martinsson, B., Orsini, D., Svenningsson, B., Swietlicki, E., Wiedensohler, A., Noone, K., Pahl,
644 S., Winkler, P., Seyffer, E., Helas, G., Jaeschke, W., Georgii, H., Wobrock, W., Preiss, M., Maser, R., Schell,
645 D., Dollard, G., Jones, B., Davies, T., Sedlak, D., David, M., Wendisch, M., Cape, J., Hargreaves, K., Sutton,
646 M., StoretonWest, R., Fowler, D., Hallberg, A., Harrison, R., and Peak, J.: The Great Dun Fell Cloud
647 Experiment 1993: An overview, *Atmos. Environ.*, 31, 2393–2405, [https://doi.org/10.1016/S1352-2310\(96\)00316-0](https://doi.org/10.1016/S1352-2310(96)00316-0), 1997.

649 Ciuraru, R., Fine, L., van Pinxteren, M., D’Anna, B., Herrmann, H., and George, C.: Photosensitized
650 production of functionalized and unsaturated organic compounds at the air-sea interface, *Sci. Rep.*, 5,
651 <https://doi.org/10.1038/srep12741>, 2015.

652 Claflin, M., Pagonis, D., Finewax, Z., Handschy, A., Day, D., Brown, W., Jayne, J., Worsnop, D., Jimenez, J.,
653 Ziemann, P., de Gouw, J., and Lerner, B.: An in situ gas chromatograph with automatic detector
654 switching between PTR- and EI-TOF-MS: isomer-resolved measurements of indoor air, *Atmos. Meas.*
655 *Tech.*, 14, 133–152, <https://doi.org/10.5194/amt-14-133-2021>, 2021.

656 Clegg, S. M. and Abbatt, J. P. D.: Oxidation of SO₂ by H₂O₂ on ice surfaces at 228 K: a sink for SO₂ in ice
657 clouds, *Atmos. Chem. Phys.*, 1, 73–78, 2001.

658 Collins, D. and Farmer, D.: Unintended Consequences of Air Cleaning Chemistry, *Environ. Sci. Technol.*,
659 55, 12172–12179, <https://doi.org/10.1021/acs.est.1c02582>, 2021.

660 Cox, R., Ammann, M., Crowley, J., Griffiths, P., Herrmann, H., Hoffmann, E., Jenkin, M., McNeill, V.,
661 Mellouki, A., Penkett, C., Tilgner, A., and Wallington, T.: Opinion: The germicidal effect of ambient air
662 (open-air factor) revisited, *Atmos. Chem. Phys.*, 21, 13011–13018, <https://doi.org/10.5194/acp-21-13011-2021>, 2021.

664 Cox, R. A.: Evaluation of laboratory kinetics and photochemical data for atmospheric chemistry
665 applications, *Chem. Soc. Rev.*, 41, 6231–6246, <https://doi.org/10.1039/c2cs35092k>, 2012.

666 Croft, B., Martin, R., Leaitch, W., Burkart, J., Chang, R., Collins, D., Hayes, P., Hodshire, A., Huang, L.,
667 Kodros, J., Moravek, A., Mungall, E., Murphy, J., Sharma, S., Tremblay, S., Wentworth, G., Willis, M.,
668 Abbate, J., and Pierce, J.: Arctic marine secondary organic aerosol contributes significantly to
669 summertime particle size distributions in the Canadian Arctic Archipelago, *Atmos. Chem. Phys.*, 19,
670 2787–2812, <https://doi.org/10.5194/acp-19-2787-2019>, 2019.

671 Crouse, J. D., Nielsen, L. B., Jorgensen, S., Kjaergaard, H. G., and Wennberg, P. O.: Autoxidation of
672 Organic Compounds in the Atmosphere, *J. Phys. Chem. Lett.*, 4, 3513–3520,
673 <https://doi.org/10.1021/jz4019207>, 2013.

674 Cunliffe, M., Engel, A., Frka, S., Gašparović, B., Guitart, C., Murrell, J. C., Salter, M., Stolle, C., Upstill-
675 Goddard, R., and Wurl, O.: Sea surface microlayers: A unified physicochemical and biological perspective
676 of the air–ocean interface, *Prog. Oceanogr.*, 109, 104–116,
677 <https://doi.org/10.1016/j.pocean.2012.08.004>, 2013.

678 Dankwerts, P. V.: *Gas-Liquid Reactions*, McGraw-Hill, 1970.

679 Decesari, S., Mircea, M., Cavalli, F., Fuzzi, S., Moretti, F., Tagliavini, E., and Facchini, M.: Source
680 attribution of water-soluble organic aerosol by nuclear magnetic resonance spectroscopy, *Environ. Sci.*
681 *Technol.*, 41, 2479–2484, <https://doi.org/10.1021/es061711l>, 2007.

682 Dentener, F. J. and Crutzen, P. J.: Reaction of N₂O₅ on tropospheric aerosols - Impact on the global
683 distributions of NO_x, O₃, and OH, *J. Geophys. Res.-Atmospheres*, 98, 7149–7163,
684 <https://doi.org/10.1029/92jd02979>, 1993.

685 DeRieux, W.-S., Li, Y., Lin, P., Laskin, J., Laskin, A., Bertram, A. K., Nizkorodov, S. A., and Shiraiwa, M.:
686 Predicting the glass transition temperature and viscosity of secondary organic material using molecular
687 composition, *Atmos Chem Phys*, 18, 6331–6351, <https://doi.org/10.5194/acp-18-6331-2018>, 2018.

688 Destailats, H., Singer, B. C., Lee, S. K., and Gundel, L. A.: Effect of ozone on nicotine desorption from
689 model surfaces: Evidence for heterogeneous chemistry, *Environ. Sci. Technol.*, 40, 1799–1805,
690 <https://doi.org/10.1021/es050914r>, 2006.

691 DeVault, M. and Ziemann, P.: Gas- and Particle-Phase Products and Their Mechanisms of Formation
692 from the Reaction of Delta-3-Carene with NO₃ Radicals, *J. Phys. Chem. A*, 125, 10207–10222,
693 <https://doi.org/10.1021/acs.jpca.1c07763>, 2021.

694 Ditto, J., Machesky, J., and Gentner, D.: Analysis of reduced and oxidized nitrogen-containing organic
695 compounds at a coastal site in summer and winter, *Atmos. Chem. Phys.*, 22, 3045–3065,
696 <https://doi.org/10.5194/acp-22-3045-2022>, 2022.

697 Domine, F. and Shepson, P. B.: Air-snow interactions and atmospheric chemistry, *Science*, 297, 1506–
698 1510, 2002.

699 Donahue, N. M., Epstein, S. A., Pandis, S. N., and Robinson, A. L.: A two-dimensional volatility basis set:
700 1. organic-aerosol mixing thermodynamics, *Atmos. Chem. Phys.*, 11, 3303–3318,
701 <https://doi.org/10.5194/acp-11-3303-2011>, 2011.

702 Donaldson, D. and George, C.: Sea-Surface Chemistry and Its Impact on the Marine Boundary Layer,
703 *Environ. Sci. Technol.*, 46, 10385–10389, <https://doi.org/10.1021/es301651m>, 2012.

704 Ehn, M., Thornton, J. A., Kleist, E., Sipila, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann,
705 R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I. H., Rissanen, M., Jokinen, T., Schobesberger, S.,
706 Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurten, T., Nielsen, L. B., Jorgensen, S., Kjaergaard, H. G.,
707 Canagaratna, M., Dal Maso, M., Berndt, T., Petaja, T., Wahner, A., Kerminen, V. M., Kulmala, M.,

708 Worsnop, D. R., Wildt, J., and Mentel, T. F.: A large source of low-volatility secondary organic aerosol,
709 Nature, 506, 476–480, <https://doi.org/10.1038/nature13032>, 2014.

710 Erickson, R., Yates, L., Clark, R., and McEwen, D.: Reaction of sulfur dioxide with ozone in water and its
711 possible atmospheric significance, Atmos. Environ., 11, 813–817, [https://doi.org/10.1016/0004-
712 6981\(77\)90043-9](https://doi.org/10.1016/0004-6981(77)90043-9), 1977.

713 Fahy, W., Maters, E., Miranda, R., Adams, M., Jahn, L., Sullivan, R., and Murray, B.: Volcanic ash ice
714 nucleation activity is variably reduced by aging in water and sulfuric acid: the effects of leaching,
715 dissolution, and precipitation, Env. Sci. - Atmospheres, 2, 85–99, <https://doi.org/10.1039/d1ea00071c>,
716 2022.

717 Fang, T., Huang, Y., Wei, J., Mena, J., Lakey, P., Kleinman, M., Digman, M., and Shiraiwa, M.: Superoxide
718 Release by Macrophages through NADPH Oxidase Activation Dominating Chemistry by Isoprene
719 Secondary Organic Aerosols and Quinones to Cause Oxidative Damage on Membranes, Environ. Sci.
720 Technol., <https://doi.org/10.1021/acs.est.2c03987>, 2022.

721 Fang, Y., Lakey, P. S. J., Riahi, S., McDonald, A. T., Shrestha, M., Tobias, D. J., Shiraiwa, M., and Grassian,
722 V. H.: A molecular picture of surface interactions of organic compounds on prevalent indoor surfaces:
723 limonene adsorption on SiO₂, Chem. Sci., 10, 2906–2914, <https://doi.org/10.1039/c8sc05560b>, 2019.

724 Faust, B. and Zepp, R.: Photochemistry of aqueous iron(III) polycarboxylate complexes - roles in the
725 chemistry of atmospheric and surface waters, Environ. Sci. Technol., 27, 2517–2522,
726 <https://doi.org/10.1021/es00048a032>, 1993.

727 Finlayson-Pitts, B., Wingen, L., Sumner, A., Syomin, D., and Ramazan, K.: The heterogeneous hydrolysis
728 of NO₂ in laboratory systems and in outdoor and indoor atmospheres: An integrated mechanism, Phys.
729 Chem. Chem. Phys., 5, 223–242, <https://doi.org/10.1039/b208564j>, 2003.

730 Finlayson-Pitts, B., Anderson, A., Lakey, P., Wang, W., Ezell, M., Wang, X., Wingen, L., Perraud, V., and
731 Shiraiwa, M.: Oxidation of solid thin films of neonicotinoid pesticides by gas phase hydroxyl radicals, Env.
732 Sci. Atmos., <https://doi.org/10.1039/d2ea00134a>, 2022.

733 Finlayson-Pitts, B. J.: The tropospheric chemistry of sea salt: A molecular-level view of the chemistry of
734 NaCl and NaBr, Chem. Rev., 103, 4801–4822, 2003.

735 Fleming, L. T., Lin, P., Roberts, J. M., Selimovic, V., Yokelson, R., Laskin, J., Laskin, A., and Nizkorodov, S.
736 A.: Molecular composition and photochemical lifetimes of brown carbon chromophores in biomass
737 burning organic aerosol, Atmos Chem Phys, 20, 1105–1129, <https://doi.org/10.5194/acp-20-1105-2020>,
738 2020.

739 Forrister, H., Liu, J., Scheuer, E., Dibb, J., Ziemba, L., Thornhill, K. L., Anderson, B., Diskin, G., Perring, A.
740 E., Schwarz, J. P., Campuzano-Jost, P., Day, D. A., Palm, B. B., Jimenez, J. L., Nenes, A., and Weber, R. J.:
741 Evolution of brown carbon in wildfire plumes, Geophys. Res. Lett., 42, 4623–4630,
742 <https://doi.org/10.1002/2015gl063897>, 2015.

743 Fowler, D., Pilegaard, K., Sutton, M., Ambus, P., Raivonen, M., Duyzer, J., Simpson, D., Fagerli, H., Fuzzi,
744 S., Schjoerring, J., Granier, C., Neftel, A., Isaksen, I., Laj, P., Maione, M., Monks, P., Burkhardt, J.,
745 Daemmgen, U., Neiryneck, J., Personne, E., Wichink-Kruit, R., Butterbach-Bahl, K., Flechard, C., Tuovinen,

746 J., Coyle, M., Gerosa, G., Loubet, B., Altimir, N., Gruenhage, L., Ammann, C., Cieslik, S., Paoletti, E.,
747 Mikkelsen, T., Ro-Poulsen, H., Cellier, P., Cape, J., Horvath, L., Loreto, F., Niinemets, U., Palmer, P., Rinne,
748 J., Misztal, P., Nemitz, E., Nilsson, D., Pryor, S., Gallagher, M., Vesala, T., Skiba, U., Brüeggemann, N.,
749 Zechmeister-Boltenstern, S., Williams, J., O'Dowd, C., Facchini, M., de Leeuw, G., Flossman, A.,
750 Chaumerliac, N., and Erisman, J.: Atmospheric composition change: Ecosystems-Atmosphere
751 interactions, *Atmos. Environ.*, 43, 5193–5267, <https://doi.org/10.1016/j.atmosenv.2009.07.068>, 2009.

752 Franze, T., Weller, M., Niessner, R., and Poschl, U.: Protein nitration by polluted air, *Environ. Sci.*
753 *Technol.*, 39, 1673–1678, <https://doi.org/10.1021/es0488737>, 2005.

754 Galib, M. and Limmer, D.: Reactive uptake of N₂O₅ by atmospheric aerosol is dominated by interfacial
755 processes, *Science*, 371, 921–924, <https://doi.org/10.1126/science.abd7716>, 2021.

756 Garcia, S., Pandit, S., Navea, J., and Grassian, V.: Nitrous Acid (HONO) Formation from the Irradiation of
757 Aqueous Nitrate Solutions in the Presence of Marine Chromophoric Dissolved Organic Matter:
758 Comparison to Other Organic Photosensitizers, *ACS Earth Space Chem.*, 5, 3056–3064,
759 <https://doi.org/10.1021/acsearthspacechem.1c00292>, 2021.

760 Garland, J., Elzerman, A., and Penkett, S.: The mechanism for dry deposition of ozone to seawater
761 surfaces, *J. Geophys. Res. Oceans*, 85, 7488–7492, <https://doi.org/10.1029/JC085iC12p07488>, 1980.

762 George, C., Streckowski, R. S., Kleffmann, J., Stemmler, K., and Ammann, M.: Photoenhanced uptake of
763 gaseous NO₂ on solid-organic compounds: a photochemical source of HONO?, *Faraday Discuss.*, 130,
764 195–210, <https://doi.org/10.1039/b417888m>, 2005.

765 George, C., Ammann, M., D'Anna, B., Donaldson, D. J., and Nizkorodov, S. A.: Heterogeneous
766 Photochemistry in the Atmosphere, *Chem Rev*, 115, 4218–4258, <https://doi.org/10.1021/cr500648z>,
767 2015.

768 George, I. J. and Abbatt, J. P. D.: Heterogeneous oxidation of atmospheric aerosol particles by gas-phase
769 radicals, *Nat. Chem.*, 2, 713–722, <https://doi.org/10.1038/nchem.806>, 2010.

770 George, I. J., Vlasenko, A., Slowik, J. G., Broekhuizen, K., and Abbatt, J. P. D.: Heterogeneous oxidation of
771 saturated organic aerosols by hydroxyl radicals: uptake kinetics, condensed-phase products, and particle
772 size change, *Atmos. Chem. Phys.*, 7, 4187–4201, <https://doi.org/10.5194/acp-7-4187-2007>, 2007.

773 George, I. J., Slowik, J., and Abbatt, J. P. D.: Chemical aging of ambient organic aerosol from
774 heterogeneous reaction with hydroxyl radicals, *Geophys. Res. Lett.*, 35,
775 <https://doi.org/10.1029/2008GL033884>, 2008.

776 Gerber, R., Varner, M., Hammerich, A., Riikonen, S., Murdachaew, G., Shemesh, D., and Finlayson-Pitts,
777 B.: Computational Studies of Atmospherically-Relevant Chemical Reactions in Water Clusters and on
778 Liquid Water and Ice Surfaces, *Acc. Chem. Res.*, 48, 399–406, <https://doi.org/10.1021/ar500431g>, 2015.

779 Girardet, C. and Toubin, C.: Molecular atmospheric pollutant adsorption on ice: a theoretical survey,
780 *Surf. Sci. Rep.*, 44, 163–238, 2001.

781 Gomez Alvarez, E., Amedro, D., Afif, C., Gligorovski, S., Schoemaeker, C., Fittschen, C., Doussin, J.-F.,
782 and Wortham, H.: Unexpectedly high indoor hydroxyl radical concentrations associated with nitrous
783 acid, *Proc. Natl. Acad. Sci. U. S. A.*, 110, 13294–13299, <https://doi.org/10.1073/pnas.1308310110>, 2013.

784 Gopalakrishnan, S., Jungwirth, P., Tobias, D., and Allen, H.: Air-liquid interfaces of aqueous solutions
785 containing ammonium and sulfate: Spectroscopic and molecular dynamics studies, *J. Phys. Chem. B*, 109,
786 8861–8872, <https://doi.org/10.1021/jp0500236>, 2005.

787 Gute, E. and Abbatt, J. P. D.: Oxidative Processing Lowers the Ice Nucleation Activity of Birch and Alder
788 Pollen, *Geophys. Res. Lett.*, 45, 1647–1653, <https://doi.org/10.1002/2017GL076357>, 2018.

789 Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue,
790 N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M.,
791 Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A.,
792 Prevot, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and
793 impact of secondary organic aerosol: current and emerging issues, *Atmos. Chem. Phys.*, 9, 5155–5236,
794 2009.

795 Hanisch, F. and Crowley, J.: The heterogeneous reactivity of gaseous nitric acid on authentic mineral
796 dust samples, and on individual mineral and clay mineral components, *Phys. Chem. Chem. Phys.*, 3,
797 2474–2482, <https://doi.org/10.1039/b101700o>, 2001.

798 Hanson, D. R. and Ravishankara, A. R.: Investigation of the reactive and nonreactive processes involving
799 ClONO₂ and HCl on water and nitric acid doped ice, *J. Phys. Chem.*, 96, 2682–2691,
800 <https://doi.org/10.1021/j100185a052>, 1992.

801 Hanson, D. R., Ravishankara, A. R., and Solomon, S.: Heterogeneous reactions in sulfuric acid aerosols - A
802 framework for model calculations, *J. Geophys. Res. Atmos.*, 99, 3615–3629,
803 <https://doi.org/10.1029/93jd02932>, 1994.

804 Hems, R. F., Schnitzler, E. G., Liu-Kang, C., Cappa, C. D., and Abbatt, J. P. D.: Aging of Atmospheric Brown
805 Carbon Aerosol, *ACS Earth Space Chem*, 5, 722–748, 2021.

806 Herrmann, H., Schaefer, T., Tilgner, A., Styler, S. A., Weller, C., Teich, M., and Otto, T.: Tropospheric
807 Aqueous-Phase Chemistry: Kinetics, Mechanisms, and Its Coupling to a Changing Gas Phase, *Chem. Rev.*,
808 115, 4259–4334, <https://doi.org/10.1021/cr500447k>, 2015.

809 Hoffmann, M. and Edwards, J.: Kinetics of oxidation of sulfite by hydrogen peroxide in acidic solution, *J.*
810 *Phys. Chem.*, 79, 2096–2098, <https://doi.org/10.1021/j100587a005>, 1975.

811 Honrath, R. E., Peterson, M. C., Guo, S., Dibb, J. E., Shepson, P. B., and Campbell, B.: Evidence of NO_x
812 production within or upon ice particles in the Greenland snowpack, *Geophys. Res. Lett.*, 26, 695–698,
813 <https://doi.org/10.1029/1999gl900077>, 1999.

814 Hopfner, M., Ungerer, J., Borrmann, S., Wagner, R., Spang, R., Riese, M., Stiller, G., Appel, O.,
815 Batenburg, A., Bucci, S., Cairo, F., Dragoneas, A., Friedl-Vallon, F., Hunig, A., Johansson, S., Krasauskas, L.,
816 Legras, B., Leisner, T., Mahnke, C., Mohler, O., Molleker, S., Muller, R., Neubert, T., Orphal, J., Preusse,
817 P., Rex, M., Saathoff, H., Stroh, F., Weigel, R., and Wohltmann, I.: Ammonium nitrate particles formed in

818 upper troposphere from ground ammonia sources during Asian monsoons, *Nat. Geosci.*, 12, 608–613,
819 <https://doi.org/10.1038/s41561-019-0385-8>, 2019.

820 Huynh, E., Olinger, A., Woolley, D., Kohli, R., Choczynski, J., Davies, J., Lin, K., Marr, L., and Davis, R.:
821 Evidence for a semisolid phase state of aerosols and droplets relevant to the airborne and surface
822 survival of pathogens, *Proc. Natl. Acad. Sci. U. S. A.*, 119, <https://doi.org/10.1073/pnas.2109750119>,
823 2022.

824 Ivatt, P., Evans, M., and Lewis, A.: Suppression of surface ozone by an aerosol-inhibited photochemical
825 ozone regime, *Nature Geosci.*, 15, 536–540, <https://doi.org/10.1038/s41561-022-00972-9>, 2022.

826 Jacob, D.: Chemistry of OH in Remove Clouds and Its Role in the Production of Formic-Acid
827 Peroxymonosulfate, *J. Geophys. Res.-Atmospheres*, 9807–9826, 1986.

828 Jacob, D.: Heterogeneous chemistry and tropospheric ozone, *Atmos. Environ.*, 34, 2131–2159,
829 [https://doi.org/10.1016/S1352-2310\(99\)00462-8](https://doi.org/10.1016/S1352-2310(99)00462-8), 2000.

830 Jacob, D. J. and Hoffmann, M. R.: A dynamic model for the production of H⁺, NO₃⁻, and SO₄²⁻ in urban fog,
831 *J. Geophys. Res.-Oceans Atmospheres*, 88, 6611–6621, <https://doi.org/10.1029/JC088iC11p06611>, 1983.

832 Jang, M. S., Czoschke, N. M., Lee, S., and Kamens, R. M.: Heterogeneous atmospheric aerosol production
833 by acid-catalyzed particle-phase reactions, *Science*, 298, 814–817,
834 <https://doi.org/10.1126/science.1075798>, 2002.

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

845 Jorga, S., Florou, K., Kaltsonoudis, C., Kodros, J., Vasilakopoulou, C., Cirtog, M., Fouqueau, A., Picquet-
846 Varrault, B., Nenes, A., and Pandis, S.: Nighttime chemistry of biomass burning emissions in urban areas:
847 A dual mobile chamber study, *Atmos. Chem. Phys.*, 21, 15337–15349, <https://doi.org/10.5194/acp-21-15337-2021>, 2021.

849 Junge, C.: Recent investigations in air chemistry, *Tellus*, 8, 127–139, 1956.

850 Kadowaki, S.: Size distribution of atmospheric total aerosols, sulfate, ammonium and nitrate in Nagoya
851 area, *Atmos. Environ.*, 10, 39–43, [https://doi.org/10.1016/0004-6981\(76\)90257-2](https://doi.org/10.1016/0004-6981(76)90257-2), 1976.

852 Kalberer, M., Paulsen, D., Sax, M., Steinbacher, M., Dommen, J., Prevot, A. S. H., Fisseha, R.,
853 Weingartner, E., Frankevich, V., Zenobi, R., and Baltensperger, U.: Identification of polymers as major
854 components of atmospheric organic aerosols, *Science*, 303, 1659–1662,
855 <https://doi.org/10.1126/science.1092185>, 2004.

856 Kanji, Z., Ladino, L., Wex, H., Boose, Y., Burkert-Kohn, M., Cziczo, D., and Kramer, M.: Overview of Ice
857 Nucleating Particles, in: *Ice Formation and Evolution in Clouds and Precipitation: Measurement and
858 modeling challenges*, vol. 58, edited by: Baumgardner, D., McFarquhar, G., and Heymsfield, A.,
859 <https://doi.org/10.1175/AMSMONOGRAPHS-D-16-0006.1>, 2017.

860 Karimova, N., Chen, J., Gord, J., Staudt, S., Bertram, T., Nathanson, G., and Gerber, R.: SN2 Reactions of
861 N₂O₅ with Ions in Water: Microscopic Mechanisms, Intermediates, and Products, *J. Phys. Chem. A*, 124,
862 711–720, <https://doi.org/10.1021/acs.jpca.9b09095>, 2020.

863 Kavassalis, S. and Murphy, J.: Understanding ozone-meteorology correlations: A role for dry deposition,
864 *Geophys. Res. Lett.*, 44, 2922–2931, <https://doi.org/10.1002/2016GL071791>, 2017.

865 Kilchhofer, K., Mahrt, F., and Kanji, Z.: The Role of Cloud Processing for the Ice Nucleating Ability of
866 Organic Aerosol and Coal Fly Ash Particles, *J. Geophys. Res. - Atmospheres*, 126,
867 <https://doi.org/10.1029/2020JD033338>, 2021.

868 Kolb, C. E., Cox, R. A., Abbatt, J. P. D., Ammann, M., Davis, E. J., Donaldson, D. J., Garrett, B. C., George,
869 C., Griffiths, P. T., Hanson, D. R., Kulmala, M., McFiggans, G., Poschl, U., Riipinen, I., Rossi, M. J., Rudich,
870 Y., Wagner, P. E., Winkler, P. M., Worsnop, D. R., and O' Dowd, C. D.: An overview of current issues in
871 the uptake of atmospheric trace gases by aerosols and clouds, *Atmos. Chem. Phys.*, 10, 10561–10605,
872 <https://doi.org/10.5194/acp-10-10561-2010>, 2010.

873 Koop, T., Bookhold, J., Shiraiwa, M., and Poschl, U.: Glass transition and phase state of organic
874 compounds: dependency on molecular properties and implications for secondary organic aerosols in the
875 atmosphere, *Phys. Chem. Chem. Phys.*, 13, 19238–19255, <https://doi.org/10.1039/c1cp22617g>, 2011.

876 Krechmer, J., Groessl, M., Zhang, X., Junninen, H., Massoli, P., Lambe, A., Kimmel, J., Cubison, M., Graf,
877 S., Lin, Y., Budisulistiorini, S., Zhang, H., Surratt, J., Knochenmuss, R., Jayne, J., Worsnop, D., Jimenez, J.,
878 and Canagaratna, M.: Ion mobility spectrometry-mass spectrometry (IMS-MS) for on- and offline
879 analysis of atmospheric gas and aerosol species, *Atmos. Meas. Tech.*, 9, 3245–3262,
880 <https://doi.org/10.5194/amt-9-3245-2016>, 2016.

881 Kroll, J. H. and Seinfeld, J. H.: Chemistry of secondary organic aerosol: Formation and evolution of low-
882 volatility organics in the atmosphere, *Atmos. Environ.*, 42, 3593–3624, 2008.

883 Kroll, J. H., Smith, J. D., Che, D. L., Kessler, S. H., Worsnop, D. R., and Wilson, K. R.: Measurement of
884 fragmentation and functionalization pathways in the heterogeneous oxidation of oxidized organic
885 aerosol, *Phys. Chem. Chem. Phys.*, 11, 8005–8014, <https://doi.org/10.1039/b905289e>, 2009.

886 Kroll, J. H., Donahue, N. M., Jimenez, J. L., Kessler, S. H., Canagaratna, M. R., Wilson, K. R., Altieri, K. E.,
887 Mazzoleni, L. R., Wozniak, A. S., Bluhm, H., Mysak, E. R., Smith, J. D., Kolb, C. E., and Worsnop, D. R.:
888 Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol, *Nat.*
889 *Chem.*, 3, 133–139, <https://doi.org/10.1038/nchem.948>, 2011.

890 Kulmala, M., Petaja, T., Ehn, M., Thornton, J., Sipila, M., Worsnop, D., and Kerminen, V.: Chemistry of
891 Atmospheric Nucleation: On the Recent Advances on Precursor Characterization and Atmospheric
892 Cluster Composition in Connection with Atmospheric New Particle Formation, in: *Annual Review of
893 Physical Chemistry*, vol. 65, edited by: Johnson, M. and Martinez, T., 21–37,
894 <https://doi.org/10.1146/annurev-physchem-040412-110014>, 2014.

895 Kumar, A., Marcolli, C., and Peter, T.: Ice nucleation activity of silicates and aluminosilicates in pure
896 water and aqueous solutions - Part 3: Aluminosilicates, *Atmos. Chem. Phys.*, 19, 6059–6084,
897 <https://doi.org/10.5194/acp-19-6059-2019>, 2019.

898 Kwamena, N., Thornton, J., and Abbatt, J.: Kinetics of surface-bound benzo[a]pyrene and ozone on solid
899 organic and salt aerosols, *J. Phys. Chem. A*, 108, 11626–11634, <https://doi.org/10.1021/jp046161x>,
900 2004.

901 Landrigan, P., Fuller, R., Acosta, N., Adeyi, O., Arnold, R., Basu, N., Balde, A., Bertollini, R., Bose-O'Reilly,
902 S., Boufford, J., Breyse, P., Chiles, T., Mahidol, C., Coll-Seck, A., Cropper, M., Fobil, J., Fuster, V.,
903 Greenstone, M., Haines, A., Hanrahan, D., Hunter, D., Khare, M., Krupnick, A., Lanphear, B., Lohani, B.,
904 Martin, K., Mathiasen, K., McTeer, M., Murray, C., Ndahimananjara, J., Perera, F., Potocnik, J., Preker, A.,
905 Ramesh, J., Rockstrom, J., Salinas, C., Samson, L., Sandilya, K., Sly, P., Smith, K., Steiner, A., Stewart, R.,
906 Suk, W., van Schayck, O., Yadama, G., Yumkella, K., and Zhong, M.: The Lancet Commission on pollution
907 and health, *Lancet*, 391, 462–512, [https://doi.org/10.1016/S0140-6736\(17\)32345-0](https://doi.org/10.1016/S0140-6736(17)32345-0), 2018.

908 Laskin, A., Laskin, J., and Nizkorodov, S. A.: Chemistry of Atmospheric Brown Carbon, *Chem. Rev.*, 115,
909 4335–4382, <https://doi.org/10.1021/cr5006167>, 2015.

910 Laskin, J., Laskin, A., and Nizkorodov, S. A.: New mass spectrometry techniques for studying physical
911 chemistry of atmospheric heterogeneous processes, *Int. Rev. Phys. Chem.*, 32, 128–170,
912 <https://doi.org/10.1080/0144235x.2012.752904>, 2013.

913 Lee, R. and Patterson, R.: Size determination of atmospheric phosphate, nitrate, chloride and
914 ammonium particulate in several urban areas, *Atmos. Environ.*, 3, 249–261, 1969.

915 Lelieveld, J. and Crutzen, P.: The Role of Clouds in Tropospheric Photochemistry, *J. Atmos. Chem.*, 12,
916 229–267, <https://doi.org/10.1007/BF00048075>, 1991.

917 Leu, M. T.: Heterogeneous reactions of N₂O₅ with H₂O and HCl on ice surfaces - Implications for Antarctic
918 ozone depletion, *Geophys. Res. Lett.*, 15, 851–854, <https://doi.org/10.1029/GL015i008p00851>, 1988.

919 Li, C., He, Q., Fang, Z., Brown, S. S., Laskin, A., Cohen, S. R., and Rudich, Y.: Laboratory Insights into the
920 Diel Cycle of Optical and Chemical Transformations of Biomass Burning Brown Carbon Aerosols, *Environ.*
921 *Sci. Technol.*, <https://doi.org/10.1021/acs.est.0c04310>, 2020a.

922 Li, J., Zhang, Y., Cao, F., Zhang, W., Fan, M., Lee, X., and Michalski, G.: Stable Sulfur Isotopes Revealed a
923 Major Role of Transition-Metal Ion-Catalyzed SO₂ Oxidation in Haze Episodes, *Environ. Sci. Technol.*, 54,
924 2626–2634, <https://doi.org/10.1021/acs.est.9b07150>, 2020b.

925 Li, K., Jacob, D., Liao, H., Zhu, J., Shah, V., Shen, L., Bates, K., Zhang, Q., and Zhai, S.: A two-pollutant
926 strategy for improving ozone and particulate air quality in China, *Nature Geosci.*, 12, 906–911,
927 <https://doi.org/10.1038/s41561-019-0464-x>, 2019a.

928 Li, L., Arnot, J., and Wania, F.: How are Humans Exposed to Organic Chemicals Released to Indoor Air?,
929 *Environ. Sci. Technol.*, 53, 11276–11284, <https://doi.org/10.1021/acs.est.9b02036>, 2019b.

930 Li, M., Bao, F., Zhang, Y., Sheng, H., Chen, C., and Zhao, J.: Photochemical Aging of Soot in the Aqueous
931 Phase: Release of Dissolved Black Carbon and the Formation of $^1\text{O}_2$, *Environ. Sci. Technol.*, 53, 12311–
932 12319, <https://doi.org/10.1021/acs.est.9b02773>, 2019c.

933 Lignell, H., Hinks, M. L., and Nizkorodov, S. A.: Exploring matrix effects on photochemistry of organic
934 aerosols, *Proc. Natl. Acad. Sci.*, 111, 13780–13785, <https://doi.org/10.1073/pnas.1322106111>, 2014.

935 Lin, K., Schulte, C., and Marr, L.: Survival of MS2 and phi 6 viruses in droplets as a function of relative
936 humidity, pH, and salt, protein, and surfactant concentrations, *PLOS ONE*, 15,
937 <https://doi.org/10.1371/journal.pone.0243505>, 2020.

938 Liu, Q., Li, L., Zhang, X., Saini, A., Li, W., Hung, H., Hao, C., Li, K., Lee, P., Wentzell, J., Huo, C., Li, S.,
939 Harner, T., and Liggio, J.: Uncovering global-scale risks from commercial chemicals in air, *Nature*, 600,
940 456–459, <https://doi.org/10.1038/s41586-021-04134-6>, 2021a.

941 Liu, T. and Abbatt, J. P. D.: Oxidation of sulfur dioxide by nitrogen dioxide accelerated at the interface of
942 deliquesced aerosol particles, *Nat. Chem*, 13, 1173–1177, 2021.

943 Liu, T., Clegg, S., and Abbatt, J.: Fast oxidation of sulfur dioxide by hydrogen peroxide in deliquesced
944 aerosol particles, *Proc. Natl. Acad. Sci. U. S. A.*, 117, 1354–1359,
945 <https://doi.org/10.1073/pnas.1916401117>, 2020.

946 Liu, T., Chan, A. W. H., and Abbatt, J. P. D.: Multiphase Oxidation of Sulfur Dioxide in Aerosol Particles:
947 Implications for Sulfate Formation in Polluted Environments, *Env Sci Technol*, 55, 4227–4242, 2021b.

948 Maher, B., Ahmed, I., Karloukovski, V., MacLaren, D., Foulds, P., Allsop, D., Mann, D., Torres-Jardon, R.,
949 and Calderon-Garciduenas, L.: Magnetite pollution nanoparticles in the human brain, *Proc. Natl. Acad.*
950 *Sci. U. S. A.*, 113, 10797–10801, <https://doi.org/10.1073/pnas.1605941113>, 2016.

951 Martens, C., Wesolowski, J., Harriss, R., and Kaifer, R.: Chlorine loss from Puerto Rican and San Francisco
952 Pay Area Marine Aerosols, *J. Geophys. Res.*, 78, 8778–8792, <https://doi.org/10.1029/JC078i036p08778>,
953 1973.

954 Martin, R. V., Jacob, D. J., Yantosca, R. M., Chin, M., and Ginoux, P.: Global and regional decreases in
955 tropospheric oxidants from photochemical effects of aerosols, *J. Geophys. Res.-Atmospheres*, 108, 19,
956 <https://doi.org/10.1029/2002jd002622>, 2003.

957 Maters, E., Cimarelli, C., Casas, A., Dingwell, D., and Murray, B.: Volcanic ash ice-nucleating activity can
958 be enhanced or depressed by ash-gas interaction in the eruption plume, *Earth Planet. Sci. Lett.*, 551,
959 <https://doi.org/10.1016/j.epsl.2020.116587>, 2020.

960 Mattila, J., Lakey, P., Shiraiwa, M., Wang, C., Abbatt, J., Arata, C., Goldstein, A., Ampollini, L., Katz, E.,
961 DeCarlo, P., Zhou, S., Kahan, T., Cardoso-Saldana, F., Hildebrandt Ruiz, L., Abeleira, A., Boedicker, E.,
962 Vance, M., and Farmer, D.: Multiphase Chemistry Controls Inorganic Chlorinated and Nitrogenated
963 Compounds in Indoor Air during Bleach Cleaning, *Environ. Sci. Technol.*, 54, 1730–1739,
964 <https://doi.org/10.1021/acs.est.9b05767>, 2020.

965 McNeill, V. F.: Aqueous Organic Chemistry in the Atmosphere: Sources and Chemical Processing of
966 Organic Aerosols, *Environ. Sci. Technol.*, 49, 1237–1244, <https://doi.org/10.1021/es5043707>, 2015.

967 McNeill, V. F., Grannas, A. M., Abbatt, J. P. D., Ammann, M., Ariya, P., Bartels-Rausch, T., Domine, F.,
968 Donaldson, D. J., Guzman, M. I., Heger, D., Kahan, T. F., Klán, P., Masclin, S., Toubin, C., and Voisin, D.:
969 Organics in environmental ices: sources, chemistry, and impacts, *Atmospheric Chem. Phys.*, 12, 9653–
970 9678, <https://doi.org/10.5194/acp-12-9653-2012>, 2012.

971 Miller, M.: Oxidative stress and the cardiovascular effects of air pollution, *Free Radic. Biol. Med.*, 151,
972 69–87, <https://doi.org/10.1016/j.freeradbiomed.2020.01.004>, 2020.

973 Miyake, Y. and Tsunogai, S.: Evaporation of iodine from ocean, *J. Geophys. Res.*, 68, 3989–3993,
974 <https://doi.org/10.1029/JZ068i013p03989>, 1963.

975 Mmereki, B. T. and Donaldson, D. J.: Direct observation of the kinetics of an atmospherically important
976 reaction at the air-aqueous interface, *J. Phys. Chem. A*, 107, 11038–11042,
977 <https://doi.org/10.1021/jp036119m>, 2003.

978 Moise, T. and Rudich, Y.: Reactive uptake of ozone by proxies for organic aerosols: Surface versus bulk
979 processes, *J. Geophys. Res.-Atmospheres*, 105, 14667–14676, <https://doi.org/10.1029/2000jd900071>,
980 2000.

981 Moise, T., Flores, J., and Rudich, Y.: Optical Properties of Secondary Organic Aerosols and Their Changes
982 by Chemical Processes, *Chem. Rev.*, 115, 4400–4439, <https://doi.org/10.1021/cr5005259>, 2015.

983 Molina, M., Tso, T., Molina, L., and Fang, F.: Antarctic stratospheric chemistry of chlorine nitrate,
984 hydrogen chloride and ice - release of active chlorine, *Science*, 238, 1253–1257,
985 <https://doi.org/10.1126/science.238.4831.1253>, 1987.

986 Molina, M. J., Ivanov, A. V., Trakhtenberg, S., and Molina, L. T.: Atmospheric evolution of organic
987 aerosol, *Geophys Res Lett*, 31, L22104, 2004.

988 Monge, M. E., D’Anna, B., Mazri, L., Giroir-Fendler, A., Ammann, M., Donaldson, D. J., and George, C.:
989 Light changes the atmospheric reactivity of soot, *Proc. Natl. Acad. Sci.*, 107, 6605–6609,
990 <https://doi.org/10.1073/pnas.0908341107>, 2010.

991 Morrison, G.: Interfacial chemistry in indoor environments, *Environ. Sci. Technol.*, 42, 3494–3499, 2008.

992 Mozurkewich, M., McMurry, P. H., Gupta, A., and Calvert, J. G.: Mass Accommodation for HO₂ Radicals
993 on Aqueous Particles, *J. Geophys. Res.-Atmospheres*, 92, 4163–4170, 1987.

994 Mu, Q., Shiraiwa, M., Octaviani, M., Ma, N., Ding, A., Su, H., Lammel, G., Poschl, U., and Cheng, Y.:
995 Temperature effect on phase state and reactivity controls atmospheric multiphase chemistry and
996 transport of PAHs, *Sci. Adv.*, 4, <https://doi.org/10.1126/sciadv.aap7314>, 2018.

997 Mungall, E. L., Abbatt, J. P. D., Wentzell, J. J. B., Lee, A. K. Y., Thomas, J. L., Blais, M., Gosselin, M., Miller,
998 L. A., Papakyriakou, T., Willis, M. D., and Liggio, J.: Microlayer source of oxygenated volatile organic
999 compounds in the summertime marine Arctic boundary layer, *Proc. Natl. Acad. Sci.*, 114, 6203,
1000 <https://doi.org/10.1073/pnas.1620571114>, 2017.

1001 Murphy, D. and Ravishankara, A.: Temperature averages and rates of stratospheric reactions, *Geophys.*
1002 *Res. Lett.*, 21, 2471–2474, <https://doi.org/10.1029/94GL02287>, 1994.

- 1003 Murphy, D., Cziczko, D., Froyd, K., Hudson, P., Matthew, B., Middlebrook, A., Peltier, R., Sullivan, A.,
1004 Thomson, D., and Weber, R.: Single-particle mass spectrometry of tropospheric aerosol particles, *J.*
1005 *Geophys. Res. - Atmospheres*, 111, <https://doi.org/10.1029/2006JD007340>, 2006.
- 1006 Murray, C., Aravkin, A., Zheng, P., Abbafati, C., Abbas, K., Abbasi-Kangevari, M., Abd-Allah, F., Abdelalim,
1007 A., Abdollahi, M., Abdollahpour, I., Abegaz, K., Abolhassani, H., Aboyans, V., Abreu, L., Abrigo, M.,
1008 Abualhasan, A., Abu-Raddad, L., Abushouk, A., Adabi, M., Adekanmbi, V., Adeoye, A., Adetokunboh, O.,
1009 Adham, D., Advani, S., Agarwal, G., Aghamir, S., Agrawal, A., Ahmad, T., Ahmadi, K., Ahmadi, M.,
1010 Ahmadi, H., Ahmed, M., Akalu, T., Akinyemi, R., Akinyemiju, T., Akombi, B., Akunna, C., Alahdab, F., Al-
1011 Aly, Z., Alam, K., Alam, S., Alam, T., Alanezi, F., Alanzi, T., Alemu, B., Alhabib, K., Ali, M., Ali, S., Alicandro,
1012 G., Alinia, C., Alipour, V., Alizade, H., Aljunid, S., Alla, F., Allebeck, P., Almasi-Hashiani, A., Al-Mekhlafi, H.,
1013 Alonso, J., Altirkawi, K., Amini-Rarani, M., Amiri, F., Amugsi, D., Ancuceanu, R., Anderlini, D., Anderson,
1014 J., Andrei, C., Andrei, T., Angus, C., Anjomshoa, M., Ansari, F., Ansari-Moghaddam, A., Antonazzo, I.,
1015 Antonio, C., Antony, C., Antriyandarti, E., Anvari, D., Anwer, R., Appiah, S., Arabloo, J., Arab-Zozani, M.,
1016 Ariani, F., Armoon, B., Arnlov, J., Arzani, A., Asadi-Aliabadi, M., Asadi-Pooya, A., Ashbaugh, C., Assmus,
1017 M., Atafar, Z., Atnafu, D., Atout, M., Ausloos, F., Ausloos, M., Quintanilla, B., Ayano, G., Ayanore, M.,
1018 Azari, S., Azarian, G., Azene, Z., et al.: Global burden of 87 risk factors in 204 countries and territories,
1019 1990-2019: a systematic analysis for the Global Burden of Disease Study 2019, *Lancet*, 396, 1223–1249,
1020 [https://doi.org/10.1016/S0140-6736\(20\)30752-2](https://doi.org/10.1016/S0140-6736(20)30752-2), 2020.
- 1021 Oberdorster, G., Sharp, Z., Atudorei, V., Elder, A., Gelein, R., Kreyling, W., and Cox, C.: Translocation of
1022 inhaled ultrafine particles to the brain, *Inhal. Toxicol.*, 16, 437–445,
1023 <https://doi.org/10.1080/08958370490439597>, 2004.
- 1024 Oswin, H., Haddrell, A., Otero-Fernandez, M., Mann, J., Cogan, T., Hilditch, T., Tian, J., Hardy, D., Hill, D.,
1025 Finn, A., Davidson, A., and Reid, J.: The dynamics of SARS-CoV-2 infectivity with changes in aerosol
1026 microenvironment, *Proc. Natl. Acad. Sci. U. S. A.*, 119, <https://doi.org/10.1073/pnas.2200109119>, 2022.
- 1027 Pankow, J. F.: An Absorption Model of the Gas/Aerosol Partitioning Involved in the Formation of
1028 Secondary Organic Aerosol, *Atmos. Environ.*, 28, 189–193, 1994.
- 1029 Papazian, S., D’Agostino, L., Sadiktsis, I., Froment, J., Bonnefille, B., Sdougkou, K., Xie, H., Athanassiadis,
1030 I., Budhavant, K., Dasari, S., Andersson, A., Gustafsson, O., and Martin, J.: Nontarget mass spectrometry
1031 and in silico molecular characterization of air pollution from the Indian subcontinent, *Comm Earth*
1032 *Environ.*, 3, <https://doi.org/10.1038/s43247-022-00365-1>, 2022.
- 1033 Penkett, S., Jones, B., Brice, K., and Eggleton, A.: Importance of atmospheric ozone and hydrogen
1034 peroxide in oxidizing sulfur dioxide in cloud and rainwater, *Atmos. Environ.*, 13, 123–137,
1035 [https://doi.org/10.1016/0004-6981\(79\)90251-8](https://doi.org/10.1016/0004-6981(79)90251-8), 1979.
- 1036 Phillips, G., Thieser, J., Tang, M., Sobanski, N., Schuster, G., Fachinger, J., Drewnick, F., Borrmann, S.,
1037 Bingemer, H., Lelieveld, J., and Crowley, J.: Estimating N₂O₅ uptake coefficients using ambient
1038 measurements of NO₃, N₂O₅, ClNO₂ and particle-phase nitrate, *Atmos. Chem. Phys.*, 16, 13231–13249,
1039 <https://doi.org/10.5194/acp-16-13231-2016>, 2016.
- 1040 Pitts, J., Van Cauwenbergh, K., Grosjean, D., SCHMID, J., Fitz, D., Belsler, W., Knudson, G., and Hynds, P.:
1041 Atmospheric reactions of polycyclic aromatic hydrocarbons - Facile formation of mutagenic nitro-
1042 derivatives, *Science*, 202, 515–519, <https://doi.org/10.1126/science.705341>, 1978.

- 1043 Pitts, J., Lokensgard, D., Ripley, P., Van Cauwenberghe, K., Van Vaeck, L., Shaffer, S., Thill, A., and Belser,
1044 W.: Atmospheric epoxidation of benzo[a]pyrene by ozone - Formation of the metabolite
1045 benzo[a]pyrene-4,5-oxide, *Science*, 210, 1347–1349, <https://doi.org/10.1126/science.210.4476.1347>,
1046 1980.
- 1047 Pope, C. A., Ezzati, M., and Dockery, D. W.: Fine-Particulate Air Pollution and Life Expectancy in the
1048 United States, *N. Engl. J. Med.*, 360, 376–386, 2009.
- 1049 Poschl, U. and Shiraiwa, M.: Multiphase Chemistry at the Atmosphere-Biosphere Interface Influencing
1050 Climate and Public Health in the Anthropocene, *Chem. Rev.*, 115, 4440–4475,
1051 <https://doi.org/10.1021/cr500487s>, 2015.
- 1052 Poschl, U., Letzel, T., Schauer, C., and Niessner, R.: Interaction of ozone and water vapor with spark
1053 discharge soot aerosol particles coated with benzo[a]pyrene: O₃ and H₂O adsorption, benzo[a]pyrene
1054 degradation, and atmospheric implications, *J. Phys. Chem. A*, 105, 4029–4041, 2001.
- 1055 Poschl, U., Rudich, Y., and Ammann, M.: Kinetic model framework for aerosol and cloud surface
1056 chemistry and gas-particle interactions - Part 1: General equations, parameters, and terminology, *Atmos
1057 Chem Phys*, 7, 5989–6023, 2007.
- 1058 Prather, K., Bertram, T., Grassian, V., Deane, G., Stokes, M., DeMott, P., Aluwihare, L., Palenik, B., Azam,
1059 F., Seinfeld, J., Moffet, R., Molina, M., Cappa, C., Geiger, F., Roberts, G., Russell, L., Ault, A., Baltrusaitis,
1060 J., Collins, D., Corrigan, C., Cuadra-Rodriguez, L., Ebben, C., Forestieri, S., Guasco, T., Hersey, S., Kim, M.,
1061 Lambert, W., Modini, R., Mui, W., Pedler, B., Ruppel, M., Ryder, O., Schoepp, N., Sullivan, R., and Zhao,
1062 D.: Bringing the ocean into the laboratory to probe the chemical complexity of sea spray aerosol, *Proc.
1063 Natl. Acad. Sci. U. S. A.*, 110, 7550–7555, <https://doi.org/10.1073/pnas.1300262110>, 2013.
- 1064 Prather, K. A., Hatch, C. D., and Grassian, V. H.: Analysis of Atmospheric Aerosols, *Annu. Rev. Anal.
1065 Chem.*, 1, 485–514, <https://doi.org/10.1146/annurev.anchem.1.031207.113030>, 2008.
- 1066 de la Puente, M., David, R., Gomez, A., and Laage, D.: Acids at the Edge: Why Nitric and Formic Acid
1067 Dissociations at Air-Water Interfaces Depend on Depth and on Interface Specific Area, *J. Am. Chem. Soc.*,
1068 144, 10524–10529, <https://doi.org/10.1021/jacs.2c03099>, 2022.
- 1069 Pye, H., Ward-Caviness, C., Murphy, B., Appel, K., and Seltzer, K.: Secondary organic aerosol association
1070 with cardiorespiratory disease mortality in the United States, *Nat. Commun.*, 12,
1071 <https://doi.org/10.1038/s41467-021-27484-1>, 2021.
- 1072 Pye, H. O. T., Nenes, A., Alexander, B., Ault, A. P., Barth, M. C., Clegg, S. L., Collett Jr., J. L., Fahey, K. M.,
1073 Hennigan, C. J., Herrmann, H., Kanakidou, M., Kelly, J. T., Ku, I.-T., McNeill, V. F., Riemer, N., Schaefer, T.,
1074 Shi, G., Tilgner, A., Walker, J. T., Wang, T., Weber, R., Xing, J., Zaveri, R. A., and Zuend, A.: The acidity of
1075 atmospheric particles and clouds, *Atmos Chem Phys*, 20, 4809–4888, <https://doi.org/10.5194/acp-20-4809-2020>, 2020.
- 1077 Ravishankara, A. R.: Heterogeneous and multiphase chemistry in the troposphere, *Science*, 276, 1058–
1078 1065, <https://doi.org/10.1126/science.276.5315.1058>, 1997.
- 1079 Reeser, D. I., George, C., and Donaldson, D. J.: Photooxidation of Halides by Chlorophyll at the Air-Salt
1080 Water Interface, *J. Phys. Chem. A*, 113, 8591–8595, <https://doi.org/10.1021/jp903657j>, 2009.

1081 Renbaum-Wolff, L., Grayson, J. W., Bateman, A. P., Kuwata, M., Sellier, M., Murray, B. J., Shilling, J. E.,
1082 Martin, S. T., and Bertram, A. K.: Viscosity of α -pinene secondary organic material and implications for
1083 particle growth and reactivity, *Proc. Natl. Acad. Sci.*, 110, 8014–8019,
1084 <https://doi.org/10.1073/pnas.1219548110>, 2013.

1085 Riva, M., Chen, Y., Zhang, Y., Lei, Z., Olson, N., Boyer, H., Narayan, S., Yee, L., Green, H., Cui, T., Zhang, Z.,
1086 Baumann, K., Fort, M., Edgerton, E., Budisulistiorini, S., Rose, C., Ribeiro, I., Oliveira, R., dos Santos, E.,
1087 Machado, C., Szopa, S., Zhao, Y., Alves, E., de Sa, S., Hu, W., Knipping, E., Shaw, S., Duvoisin, S., de Souza,
1088 R., Palm, B., Jimenez, J., Glasius, M., Goldstein, A., Pye, H., Gold, A., Turpin, B., Vizuete, W., Martin, S.,
1089 Thornton, J., Dutcher, C., Ault, A., and Surratt, J.: Increasing Isoprene Epoxydiol-to-Inorganic Sulfate
1090 Aerosol Ratio Results in Extensive Conversion of Inorganic Sulfate to Organosulfur Forms: Implications
1091 for Aerosol Physicochemical Properties, *Environ. Sci. Technol.*, 53, 8682–8694,
1092 <https://doi.org/10.1021/acs.est.9b01019>, 2019.

1093 Rossignol, S., Tinel, L., Bianco, A., Passananti, M., Brigante, M., Donaldson, D. J., and George, C.:
1094 Atmospheric photochemistry at a fatty acid-coated air-water interface, *Science*, 353, 699–702,
1095 <https://doi.org/10.1126/science.aaf3617>, 2016.

1096 Rudich, Y.: Laboratory perspectives on the chemical transformations of organic matter in atmospheric
1097 particles, *Chem. Rev.*, 103, 5097–5124, <https://doi.org/10.1021/cr020508f>, 2003.

1098 Rudich, Y., Donahue, N. M., and Mentel, T. F.: Aging of Organic Aerosol: Bridging the Gap Between
1099 Laboratory and Field Studies, *Annu. Rev. Phys. Chem.*, 58, 321–352,
1100 <https://doi.org/10.1146/annurev.physchem.58.032806.104432>, 2007.

1101 Russell, L.: Aerosol organic-mass-to-organic-carbon ratio measurements, *Environ. Sci. Technol.*, 37,
1102 2982–2987, <https://doi.org/10.1021/es026123w>, 2003.

1103 Schneider, S. R., Collins, D. B., Lim, C. Y., Zhu, L., and Abbatt, J. P. D.: Formation of Secondary Organic
1104 Aerosol from the Heterogeneous Oxidation by Ozone of a Phytoplankton Culture, *ACS Earth Space*
1105 *Chem.*, 3, 2298–2306, <https://doi.org/10.1021/acsearthspacechem.9b00201>, 2019.

1106 Schnitzler, E., Gerrebos, N., Carter, T., Huang, Y., Heald, C., Bertram, A., and Abbatt, J.: Rate of
1107 atmospheric brown carbon whitening governed by environmental conditions, *Proc. Natl. Acad. Sci. U. S.*
1108 *A.*, 119, <https://doi.org/10.1073/pnas.2205610119>, 2022.

1109 Schroeder, W. H. and Urone, P.: Isolation and identification of nitrosium hydrogen sulfate as a
1110 photochemical reaction product in air containing sulfur dioxide and nitrogen dioxide, *Environ. Sci.*
1111 *Technol.*, 12, 545–550, <https://doi.org/10.1021/es60141a016>, 1978.

1112 Segal-Rosenheimer, M. and Dubowski, Y.: Heterogeneous ozonolysis of cypermethrin using real-time
1113 monitoring FTIR techniques, *J. Phys. Chem. C*, 111, 11682–11691, 2007.

1114 Shiraiwa, M., Ammann, M., Koop, T., and Poeschl, U.: Gas-uptake and chemical aging of semisolid
1115 organic aerosol particles, *Proc. Nat. Acad. Sci. U.S.A.*, 108, 11003–11008, 2011.

1116 Shiraiwa, M., Selzle, K., Yang, H., Sosedova, Y., Ammann, M., and Poeschl, U.: Multiphase Chemical
1117 Kinetics of the Nitration of Aerosolized Protein by Ozone and Nitrogen Dioxide, *Environ. Sci. Technol.*,
1118 46, 6672–6680, <https://doi.org/10.1021/es300871b>, 2012.

- 1119 Shiraiwa, M., Ueda, K., Pozzer, A., Lammel, G., Kampf, C., Fushimi, A., Enami, S., Arangio, A., Frohlich-
1120 Nowoisky, J., Fujitani, Y., Furuyama, A., Lakey, P., Lelieveld, J., Lucas, K., Morino, Y., Poschl, U.,
1121 Takaharna, S., Takami, A., Tong, H., Weber, B., Yoshino, A., and Sato, K.: Aerosol Health Effects from
1122 Molecular to Global Scales, *Environ. Sci. Technol.*, 51, 13545–13567,
1123 <https://doi.org/10.1021/acs.est.7b04417>, 2017a.
- 1124 Shiraiwa, M., Li, Y., Tsimpidi, A., Karydis, V., Berkemeier, T., Pandis, S., Lelieveld, J., Koop, T., and Poschl,
1125 U.: Global distribution of particle phase state in atmospheric secondary organic aerosols, *Nat. Commun.*,
1126 8, <https://doi.org/10.1038/ncomms15002>, 2017b.
- 1127 Shiraiwa, M., Carslaw, N., Tobias, D. J., Waring, M. S., Rim, D., Morrison, G., Lakey, P. S. J., Kruza, M., von
1128 Domaros, M., Cummings, B. E., and Won, Y.: Modelling consortium for chemistry of indoor
1129 environments (MOCCIE): integrating chemical processes from molecular to room scales, *Env. Sci*
1130 *Process. Impacts*, 21, 1240–1254, <https://doi.org/10.1039/C9EM00123A>, 2019.
- 1131 Shrivastava, M., Lou, S., Zelenyuk, A., Easter, R., Corley, R., Thrall, B., Rasch, P., Fast, J., Simonich, S.,
1132 Shen, H., and Tao, S.: Global long-range transport and lung cancer risk from polycyclic aromatic
1133 hydrocarbons shielded by coatings of organic aerosol, *Proc. Natl. Acad. Sci. U. S. A.*, 114, 1246–1251,
1134 <https://doi.org/10.1073/pnas.1618475114>, 2017a.
- 1135 Shrivastava, M., Cappa, C., Fan, J., Goldstein, A., Guenther, A., Jimenez, J., Kuang, C., Laskin, A., Martin,
1136 S., Ng, N., Petaja, T., Pierce, J., Rasch, P., Roldin, P., Seinfeld, J., Shilling, J., Smith, J., Thornton, J.,
1137 Volkamer, R., Wang, J., Worsnop, D., Zaveri, R., Zelenyuk, A., and Zhang, Q.: Recent advances in
1138 understanding secondary organic aerosol: Implications for global climate forcing, *Rev. Geophys.*, 55,
1139 509–559, <https://doi.org/10.1002/2016RG000540>, 2017b.
- 1140 Sihvonen, S., Schill, G., Lykтей, N., Veghte, D., Tolbert, M., and Freedman, M.: Chemical and Physical
1141 Transformations of Aluminosilicate Clay Minerals Due to Acid Treatment and Consequences for
1142 Heterogeneous Ice Nucleation, *J. Phys. Chem. A*, 118, 8787–8796, <https://doi.org/10.1021/jp504846g>,
1143 2014.
- 1144 Simpson, W. R., Brown, S. S., Saiz-Lopez, A., Thornton, J. A., and von Glasow, R.: Tropospheric Halogen
1145 Chemistry: Sources, Cycling, and Impacts, *Chem. Rev.*, 115, 4035–4062,
1146 <https://doi.org/10.1021/cr5006638>, 2015.
- 1147 Sobyra, T., Pliszka, H., Bertram, T., and Nathanson, G.: Production of Br₂ from N₂O₅ and Bromide in Salty
1148 and Surfactant-Coated Water Microjets, *J. Phys. Chem. A*, 123, 8942–8953,
1149 <https://doi.org/10.1021/acs.jpca.9b04225>, 2019.
- 1150 Solomon, S.: Stratospheric ozone depletion: A review of concepts and history, *Rev. Geophys.*, 37, 275–
1151 316, 1999.
- 1152 Solomon, S., Dube, K., Stone, K., Yu, P., Kinnison, D., Toon, O., Strahan, S., Rosenlof, K., Portmann, R.,
1153 Davis, S., Randel, W., Bernath, P., Boone, C., Bardeen, C., Bourassa, A., Zawada, D., and Degenstein, D.:
1154 On the stratospheric chemistry of midlatitude wildfire smoke, *Proc. Natl. Acad. Sci. U. S. A.*, 119,
1155 <https://doi.org/10.1073/pnas.2117325119>, 2022.
- 1156 Song, S., Gao, M., Xu, W., Sun, Y., Worsnop, D., Jayne, J., Zhang, Y., Zhu, L., Li, M., Zhou, Z., Cheng, C., Lv,
1157 Y., Wang, Y., Peng, W., Xu, X., Lin, N., Wang, Y., Wang, S., Munger, J., Jacob, D., and McElroy, M.:

- 1158 Possible heterogeneous chemistry of hydroxymethanesulfonate (HMS) in northern China winter haze,
1159 *Atmos. Chem. Phys.*, 19, 1357–1371, <https://doi.org/10.5194/acp-19-1357-2019>, 2019.
- 1160 Strahan, S., Smale, D., Solomon, S., Taha, G., Damon, M., Steenrod, S., Jones, N., Liley, B., Querel, R., and
1161 Robinson, J.: Unexpected Repartitioning of Stratospheric Inorganic Chlorine After the 2020 Australian
1162 Wildfires, *Geophys. Res. Lett.*, 49, <https://doi.org/10.1029/2022GL098290>, 2022.
- 1163 Sullivan, R., Minambres, L., DeMott, P., Prenni, A., Carrico, C., Levin, E., and Kreidenweis, S.: Chemical
1164 processing does not always impair heterogeneous ice nucleation of mineral dust particles, *Geophys. Res.
1165 Lett.*, 37, <https://doi.org/10.1029/2010GL045540>, 2010a.
- 1166 Sullivan, R., Petters, M., DeMott, P., Kreidenweis, S., Wex, H., Niedermeier, D., Hartmann, S., Clauss, T.,
1167 Stratmann, F., Reitz, P., Schneider, J., and Sierau, B.: Irreversible loss of ice nucleation active sites in
1168 mineral dust particles caused by sulphuric acid condensation, *Atmos. Chem. Phys.*, 10, 11471–11487,
1169 <https://doi.org/10.5194/acp-10-11471-2010>, 2010b.
- 1170 Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A., Szmigielski, R.,
1171 Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Chemical Composition of
1172 Secondary Organic Aerosol Formed from the Photooxidation of Isoprene, *J. Phys. Chem. A*, 110, 9665–
1173 9690, <https://doi.org/10.1021/jp061734m>, 2006.
- 1174 Svehla, G.: Nomenclature of kinetic methods of analysis, *Pure and Applied Chem.*, 65, 2291–2298,
1175 <https://doi.org/10.1351/pac199365102291>, 1993.
- 1176 Tabazadeh, A. and Turco, R.: A model for heterogeneous chemical processes on the surfaces of ice and
1177 nitric acid trihydrate particles, *J. Geophys. Res. - Atmos.*, 98, 12727–12740,
1178 <https://doi.org/10.1029/93JD00947>, 1993.
- 1179 Tham, Y., Wang, Z., Li, Q., Wang, W., Wang, X., Lu, K., Ma, N., Yan, C., Kecorius, S., Wiedensohler, A.,
1180 Zhang, Y., and Wang, T.: Heterogeneous N₂O₅ uptake coefficient and production yield of ClNO₂ in
1181 polluted northern China: roles of aerosol water content and chemical composition, *Atmos. Chem. Phys.*,
1182 18, 13155–13171, <https://doi.org/10.5194/acp-18-13155-2018>, 2018.
- 1183 Thompson, C.: The NASA Atmospheric Tomography (ATom) Mission: Imaging the Chemistry of the
1184 Global Atmosphere, *Bull. Amer. Meteor. Soc.*, E761-790, <https://doi.org/10.1175/BAMS-D-20-0315.1>,
1185 2022.
- 1186 Tilgner, A., Brauer, P., Wolke, R., and Herrmann, H.: Modelling multiphase chemistry in deliquescent
1187 aerosols and clouds using CAPRAM3.0i, *J Atmos Chem*, 70, 221–256, [https://doi.org/10.1007/s10874-
1188 013-9267-4](https://doi.org/10.1007/s10874-013-9267-4), 2013.
- 1189 Tilgner, A., Schaefer, T., Alexander, B., Barth, M., Collett, J., Fahey, K., Nenes, A., Pye, H., Herrmann, H.,
1190 and McNeill, V.: Acidity and the multiphase chemistry of atmospheric aqueous particles and clouds,
1191 *Atmos Chem Phys*, 21, 13483–13536, <https://doi.org/10.5194/acp-21-13483-2021>, 2021.
- 1192 Tobias, D., Stern, A., Baer, M., Levin, Y., and Mundy, C.: Simulation and Theory of Ions at Atmospherically
1193 Relevant Aqueous Liquid-Air Interfaces, in: *Annual Review of Physical Chemistry*, vol. 64, edited by:
1194 Johnson, M. and Martinez, T., 339–359, <https://doi.org/10.1146/annurev-physchem-040412-110049>,
1195 2013.

- 1196 Tobias, H. and Ziemann, P.: Thermal desorption mass spectrometric analysis of organic aerosol formed
 1197 from reactions of 1-tetradecene and O₃ in the presence of alcohols and carboxylic acids, *Environ. Sci.*
 1198 *Technol.*, 34, 2105–2115, <https://doi.org/10.1021/es9907156>, 2000.
- 1199 Tolbert, M. A., Rossi, M. J., and Golden, D. M.: Antarctic ozone depletion chemistry - Reactions of N₂O₅
 1200 with H₂O and HCl on ice surfaces, *Science*, 240, 1018–1021,
 1201 <https://doi.org/10.1126/science.240.4855.1018>, 1988.
- 1202 Tritscher, I., Pitts, M., Poole, L., Alexander, S., Cairo, F., Chipperfield, M., Grooss, J., Hopfner, M.,
 1203 Lambert, A., Luo, B., Molleker, S., Orr, A., Salawitch, R., Snels, M., Spang, R., Woiwode, W., and Peter, T.:
 1204 Polar Stratospheric Clouds: Satellite Observations, Processes, and Role in Ozone Depletion, *Rev.*
 1205 *Geophys.*, 59, <https://doi.org/10.1029/2020RG000702>, 2021.
- 1206 Trostl, J., Chuang, W. K., Gordon, H., Heinritzi, M., Yan, C., Molteni, U., Ahlm, L., Frege, C., Bianchi, F.,
 1207 Wagner, R., Simon, M., Lehtipalo, K., Williamson, C., Craven, J. S., Duplissy, J., Adamov, A., Almeida, J.,
 1208 Bernhammer, A. K., Breitenlechner, M., Brilke, S., Dias, A., Ehrhart, S., Flagan, R. C., Franchin, A., Fuchs,
 1209 C., Guida, R., Gysel, M., Hansel, A., Hoyle, C. R., Jokinen, T., Junninen, H., Kangasluoma, J., Keskinen, H.,
 1210 Kim, J., Krapf, M., Kurten, A., Laaksonen, A., Lawler, M., Leiminger, M., Mathot, S., Mohler, O., Nieminen,
 1211 T., Onnela, A., Petaja, T., Piel, F. M., Miettinen, P., Rissanen, M. P., Rondo, L., Sarnela, N., Schobesberger,
 1212 S., Sengupta, K., Sipilaa, M., Smith, J. N., Steiner, G., Tome, A., Virtanen, A., Wagner, A. C., Weingartner,
 1213 E., Wimmer, D., Winkler, P. M., Ye, P. L., Carslaw, K. S., Curtius, J., Dommen, J., Kirkby, J., Kulmala, M.,
 1214 Riipinen, I., Worsnop, D. R., Donahue, N. M., and Baltensperger, U.: The role of low-volatility organic
 1215 compounds in initial particle growth in the atmosphere, *Nature*, 533, 527–530,
 1216 <https://doi.org/10.1038/nature18271>, 2016.
- 1217 Tseng, C. and Li, C.: Inactivation of surface viruses by gaseous Ozone, *J. Environ. Health*, 70, 56–62, 2008.
- 1218 Tuite, K., Thomas, J., Veres, P., Roberts, J., Stevens, P., Griffith, S., Dusanter, S., Flynn, J., Ahmed, S.,
 1219 Emmons, L., Kim, S., Washenfelder, R., Young, C., Tsai, C., Pikelnaya, O., and Stutz, J.: Quantifying Nitrous
 1220 Acid Formation Mechanisms Using Measured Vertical Profiles During the CalNex 2010 Campaign and 1D
 1221 Column Modeling, *J. Geophys. Res. - Atmospheres*, 126, <https://doi.org/10.1029/2021JD034689>, 2021.
- 1222 Usher, C. R., Michel, A. E., and Grassian, V. H.: Reactions on mineral dust, *Chem. Rev.*, 103, 4883–4939,
 1223 <https://doi.org/10.1021/cr020657y>, 2003.
- 1224 Virtanen, A., Joutsensaari, J., Koop, T., Kannosto, J., Yli-Pirila, P., Leskinen, J., Makela, J. M., Holopainen,
 1225 J. K., Poschl, U., Kulmala, M., Worsnop, D. R., and Laaksonen, A.: An amorphous solid state of biogenic
 1226 secondary organic aerosol particles, *Nature*, 467, 824–827, <https://doi.org/10.1038/nature09455>, 2010.
- 1227 Wang, G., Zhang, R., Gomez, M., Yang, L., Zamora, M., Hu, M., Lin, Y., Peng, J., Guo, S., Meng, J., Li, J.,
 1228 Cheng, C., Hu, T., Ren, Y., Wang, Y., Gao, J., Cao, J., An, Z., Zhou, W., Li, G., Wang, J., Tian, P., Marrero-
 1229 Ortiz, W., Secrest, J., Du, Z., Zheng, J., Shang, D., Zeng, L., Shao, M., Wang, W., Huang, Y., Wang, Y., Zhu,
 1230 Y., Li, Y., Hu, J., Pan, B., Cai, L., Cheng, Y., Ji, Y., Zhang, F., Rosenfeld, D., Liss, P., Duce, R., Kolb, C., and
 1231 Molina, M.: Persistent sulfate formation from London Fog to Chinese haze, *Proc. Natl. Acad. Sci. U. S. A.*,
 1232 113, 13630–13635, <https://doi.org/10.1073/pnas.1616540113>, 2016.
- 1233 Wang, L. and Clary, D.: Time-dependent wave-packet studies on the sticking of HCl to an ice surface, *J.*
 1234 *Chem. Phys.*, 104, 5663–5673, <https://doi.org/10.1063/1.471772>, 1996.

- 1235 Wang, S., Zhou, S., Tao, Y., Tsui, W. G., Ye, J., Yu, J. Z., Murphy, J. G., McNeill, V. F., Abbatt, J. P. D., and
 1236 Chan, A. W. H.: Organic Peroxides and Sulfur Dioxide in Aerosol: Source of Particulate Sulfate, *Environ.*
 1237 *Sci. Technol.*, 53, 10695–10704, <https://doi.org/10.1021/acs.est.9b02591>, 2019.
- 1238 Weller, C., Horn, S., and Herrmann, H.: Effects of Fe(III)-concentration, speciation, excitation-wavelength
 1239 and light intensity on the quantum yield of iron(III)-oxalato complex photolysis, *J. Photochem. Photobiol.*
 1240 *-Chem.*, 255, 41–49, <https://doi.org/10.1016/j.jphotochem.2013.01.014>, 2013.
- 1241 Weschler, C.: Ozone in indoor environments: Concentration and chemistry, *Indoor Air*, 10, 269–288,
 1242 <https://doi.org/10.1034/j.1600-0668.2000.010004269.x>, 2000.
- 1243 Wingen, L. and Finlayson-Pitts, B.: Probing surfaces of atmospherically relevant organic particles by easy
 1244 ambient sonic-spray ionization mass spectrometry (EASI-MS), *Chem. Sci.*, 10, 884–897,
 1245 <https://doi.org/10.1039/c8sc03851a>, 2019.
- 1246 Wisthaler, A. and Weschler, C. J.: Reactions of ozone with human skin lipids: Sources of carbonyls,
 1247 dicarbonyls, and hydroxycarbonyls in indoor air, *Proc. Natl. Acad. Sci. U. S. A.*, 107, 6568–6575,
 1248 <https://doi.org/10.1073/pnas.0904498106>, 2009.
- 1249 Wolff, E., Jones, A., Martin, T., and Grenfell, T.: Modelling photochemical NO_x production and nitrate
 1250 loss in the upper snowpack of Antarctica, *Geophys. Res. Lett.*, 29,
 1251 <https://doi.org/10.1029/2002GL015823>, 2002.
- 1252 Wong, J. P. S., Carslaw, N., Zhao, R., Zhou, S., and Abbatt, J. P. D.: Observations and impacts of bleach
 1253 washing on indoor chlorine chemistry, *Indoor Air*, 27, 1082–1090, <https://doi.org/10.1111/ina.12402>,
 1254 2017.
- 1255 Woo, J. and McNeill, V.: simpleGAMMA v1.0-a reduced model of secondary organic aerosol formation in
 1256 the aqueous aerosol phase (aaSOA), *Geos Model Dev*, 8, 1821–1829, [https://doi.org/10.5194/gmd-8-](https://doi.org/10.5194/gmd-8-1821-2015)
 1257 [1821-2015](https://doi.org/10.5194/gmd-8-1821-2015), 2015.
- 1258 Workman, E. J. and Reynolds, S. E.: Electrical Phenomena Occurring during the Freezing of Dilute
 1259 Aqueous Solutions and Their Possible Relationship to Thundrstorm Electricity, *Phys Rev*, 78, 254–259,
 1260 1950.
- 1261 Worsnop, D. R., Morris, J. W., Shi, Q., Davidovits, P., and Kolb, C. E.: A chemical kinetic model for reactive
 1262 transformations of aerosol particles, *Geophys. Res. Lett.*, 29, 4, <https://doi.org/10.1029/2002gl015542>,
 1263 2002.
- 1264 Xiao, M., Hoyle, C., Dada, L., Stolzenburg, D., Kurten, A., Wang, M., Lamkaddam, H., Garmash, O.,
 1265 Mentler, B., Molteni, U., Baccharini, A., Simon, M., He, X., Lehtipalo, K., Ahonen, L., Baalbaki, R., Bauer, P.,
 1266 Beck, L., Bell, D., Bianchi, F., Brilke, S., Chen, D., Chiu, R., Dias, A., Duplissy, J., Finkenzeller, H., Gordon,
 1267 H., Hofbauer, V., Kim, C., Koenig, T., Lampilahti, J., Lee, C., Li, Z., Mai, H., Makhmutov, V., Manninen, H.,
 1268 Marten, R., Mathot, S., Mauldin, R., Nie, W., Onnela, A., Partoll, E., Petaja, T., Pfeifer, J., Pospisilova, V.,
 1269 Quelever, L., Rissanen, M., Schobesberger, S., Schuchmann, S., Stozhkov, Y., Tauber, C., Tham, Y., Tome,
 1270 A., Vazquez-Pufleau, M., Wagner, A., Wagner, R., Wang, Y., Weitz, L., Wimmer, D., Wu, Y., Yan, C., Ye, P.,
 1271 Ye, Q., Zha, Q., Zhou, X., Amorim, A., Carslaw, K., Curtius, J., Hansel, A., Volkamer, R., Winkler, P., Flagan,
 1272 R., Kulmala, M., Worsnop, D., Kirkby, J., Donahue, N., Baltensperger, U., El Haddad, I., and Dommen, J.:

- 1273 The driving factors of new particle formation and growth in the polluted boundary layer, *Atmos. Chem. Phys.*, 21, 14275–14291, <https://doi.org/10.5194/acp-21-14275-2021>, 2021.
- 1274
- 1275 Yang, J., Li, L., Wang, S., Li, H., Francisco, J., Zeng, X., and Gao, Y.: Unraveling a New Chemical Mechanism
1276 of Missing Sulfate Formation in Aerosol Haze: Gaseous NO₂ with Aqueous HSO₃⁻/SO₃²⁻, *J. Am. Chem. Soc.*,
1277 141, 19312–19320, <https://doi.org/10.1021/jacs.9b08503>, 2019.
- 1278 Yeh, K., Ditto, J., and Abbatt, J.: Ozonolysis Lifetime of Tetrahydrocannabinol in Thirdhand Cannabis
1279 Smoke, *Environ. Sci. Technol. Lett.*, <https://doi.org/10.1021/acs.estlett.2c00311>, 2022.
- 1280 Young, C. J., Zhou, S., Siegel, J. A., and Kahan, T. F.: Illuminating the dark side of indoor oxidants, *Env. Sci*
1281 *Process. Impacts*, 21, 1229–1239, <https://doi.org/10.1039/C9EM00111E>, 2019.
- 1282 Yun, J., Kumar, A., Removski, N., Shchukarev, A., Link, N., Boily, J., and Bertram, A.: Effects of Inorganic
1283 Acids and Organic Solutes on the Ice Nucleating Ability and Surface Properties of Potassium-Rich
1284 Feldspar, *ACS Earth Space Chem.*, 5, 1212–1222, <https://doi.org/10.1021/acsearthspacechem.1c00034>,
1285 2021.
- 1286 Zannoni, N., Lakey, P., Won, Y., Shiraiwa, M., Rim, D., Weschler, C., Wang, N., Ernle, L., Li, M., Beko, G.,
1287 Wargocki, P., and Williams, J.: The human oxidation field, *Science*, 377, 1071–1076,
1288 <https://doi.org/10.1126/science.abn0340>, 2022.
- 1289 Zaveri, R., Barnard, J., Easter, R., Riemer, N., and West, M.: Particle-resolved simulation of aerosol size,
1290 composition, mixing state, and the associated optical and cloud condensation nuclei activation
1291 properties in an evolving urban plume, *J Geophys Res - Atmos*, 115,
1292 <https://doi.org/10.1029/2009JD013616>, 2010.
- 1293 Zelenyuk, A. and Imre, D.: Single particle laser ablation time-of-flight mass spectrometer: An
1294 introduction to SPLAT, *Aerosol Sci Tech*, 39, 554–568, <https://doi.org/10.1080/027868291009242>, 2005.
- 1295 Zepp, R. G., Hoigne, J., and Bader, H.: Nitrate-induced photooxidation of trace organic chemicals in
1296 water, *Environ. Sci. Technol.*, 21, 443–450, <https://doi.org/10.1021/es00159a004>, 1987.
- 1297 Zheng, H., Song, S., Sarwar, G., Gen, M., Wang, S., Ding, D., Chang, X., Zhang, S., Xing, J., Sun, Y., Ji, D.,
1298 Chan, C., Gao, J., and McElroy, M.: Contribution of Particulate Nitrate Photolysis to Heterogeneous
1299 Sulfate Formation for Winter Haze in China, *Environ. Sci. Technol. Lett.*, 7, 632–638,
1300 <https://doi.org/10.1021/acs.estlett.0c00368>, 2020.
- 1301 Zhou, J., Sato, K., Bai, Y., Fukusaki, Y., Kousa, Y., Ramasamy, S., Takami, A., Yoshino, A., Nakayama, T.,
1302 Sadanaga, Y., Nakashima, Y., Li, J., Murano, K., Kohno, N., Sakamoto, Y., and Kajii, Y.: Kinetics and
1303 impacting factors of HO₂ uptake onto submicron atmospheric aerosols during the 2019 Air Quality Study
1304 (AQUAS) in Yokohama, Japan, *Atmos. Chem. Phys.*, 21, 12243–12260, <https://doi.org/10.5194/acp-21-12243-2021>, 2021.
- 1305
- 1306 Zhou, S., Lee, A. K. Y., McWhinney, R. D., and Abbatt, J. P. D.: Burial Effects of Organic Coatings on the
1307 Heterogeneous Reactivity of Particle-Borne Benzo[a]pyrene (BaP) toward Ozone, *J. Phys. Chem. A*, 116,
1308 7050–7056, <https://doi.org/10.1021/jp3030705>, 2012.

- 1309 Zhou, S., Yeung, L. W. Y., Forbes, M. W., Mabury, S., and Abbatt, J. P. D.: Epoxide formation from
1310 heterogeneous oxidation of benzo[a]pyrene with gas-phase ozone and indoor air, *Environ. Sci. Process.*
1311 *Impacts*, 19, 1292–1299, <https://doi.org/10.1039/C7EM00181A>, 2017.
- 1312 Zhou, S., Hwang, B. C. H., Lakey, P. S. J., Zuend, A., Abbatt, J. P. D., and Shiraiwa, M.: Multiphase
1313 reactivity of polycyclic aromatic hydrocarbons is driven by phase separation and diffusion limitations,
1314 *Proc. Natl. Acad. Sci. U. S. A.*, 116, 11658–11663, <https://doi.org/10.1073/pnas.1902517116>, 2019a.
- 1315 Zhou, S. M., Shiraiwa, M., McWhinney, R. D., Poschl, U., and Abbatt, J. P. D.: Kinetic limitations in gas-
1316 particle reactions arising from slow diffusion in secondary organic aerosol, *Faraday Discuss.*, 165, 391–
1317 406, <https://doi.org/10.1039/c3fd00030c>, 2013.
- 1318 Zhou, Z., Zhou, S., and Abbatt, J. P. D.: Kinetics and Condensed-Phase Products in Multiphase Ozonolysis
1319 of an Unsaturated Triglyceride, *Environ. Sci. Technol.*, 53, 12467–12475,
1320 <https://doi.org/10.1021/acs.est.9b04460>, 2019b.
- 1321 Zhou, Z., Lakey, P., von Domaros, M., Wise, N., Tobias, D., Shiraiwa, M., and Abbatt, J.: Multiphase
1322 Ozonolysis of Oleic Acid-Based Lipids: Quantitation of Major Products and Kinetic Multilayer Modeling,
1323 *Environ. Sci. Technol.*, 56, 7716–7728, <https://doi.org/10.1021/acs.est.2c01163>, 2022.
- 1324 Ziemann, P. J. and Atkinson, R.: Kinetics, products, and mechanisms of secondary organic aerosol
1325 formation, *Chem. Soc. Rev.*, 41, 6582–6605, <https://doi.org/10.1039/c2cs35122f>, 2012.
- 1326