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The Essential Role for Laboratory Studies in Atmospheric Chemistry

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84 **Abstract**

85 Laboratory studies of atmospheric chemistry characterize the nature of atmospherically relevant
86 processes down to the molecular level, providing fundamental information used to assess how
87 human activities drive environmental phenomena such as climate change, urban air pollution,
88 ecosystem health, indoor air quality, and stratospheric ozone depletion. Laboratory studies have
89 a central role in addressing the incomplete fundamental knowledge of atmospheric chemistry.
90 This article highlights the evolving science needs for this community and emphasizes how our
91 knowledge is far from complete, hindering our ability to predict the future state of our
92 atmosphere and to respond to emerging global environmental change issues. Laboratory studies
93 provide rich opportunities to expand our understanding of the atmosphere via collaborative
94 research with the modeling and field measurement communities, and with neighbouring
95 disciplines.

96 **Introduction**

97 Atmospheric chemistry is the study of the chemical processes that affect the composition of the
98 atmosphere, encompassing societally important issues such as air pollution and its related health
99 and ecosystem effects, as well as climate (see Figure 1). This field unifies the evaluation of both
100 natural and anthropogenic emissions, measurements of atmospheric composition across a range
101 of temporal and spatial scales, and assessment of deposition processes that ultimately remove
102 chemical compounds from the air. All of these processes are impacted by, or may feedback on,
103 climate change. At the heart of atmospheric chemistry are chemical transformations, often
104 initiated by sunlight. Molecules absorb solar radiation, leading to a cascade of catalytic and
105 oxidative reactions. Our molecular-level understanding of atmospheric chemistry has

106 successfully provided the foundations of air quality forecasts including those related to acid
107 rain,¹ the basis upon which the chemicals responsible for the formation of the Ozone Hole were
108 banned under the Montreal Protocol and its amendments,² and connections between human
109 impact on atmospheric composition and climate change.³ The evaluation of geoengineering as an
110 option to offset global warming also requires a detailed understanding of the underlying
111 chemistry.⁴

112 Simplified parameterizations of this detailed chemistry developed from well-controlled
113 laboratory studies, alongside representations of emissions, transport and deposition processes,
114 are incorporated into computer models to predict atmospheric composition across appropriate
115 temporal and spatial (local, regional, and global) scales. Comparisons with measurements from
116 the field are often used to evaluate model predictions or to help identify poorly represented
117 chemistry. Laboratory studies are an essential bridge between field measurements and models
118 and provide the basic (or fundamental) physics and chemistry of the underlying mechanisms of
119 phenomena observed in the field, which is the basis for generating physically meaningful
120 parameterizations for use in models. This interplay between laboratory studies of chemical,
121 photochemical, and physical processes, atmospheric modeling, and field measurements has
122 propelled the field of atmospheric chemistry forward to achieve remarkable success in
123 understanding the details of stratospheric ozone depletion, acid rain, urban air quality, and the
124 chemistry of climate-forcing agents, and in informing environmental policies (see Figure 2).

125 The increased emphasis by funding agencies on solutions-driven research, as opposed to
126 fundamental research of the atmosphere in general, inherently demotivates the development of a
127 comprehensive understanding of the core processes occurring in the atmosphere. In particular,
128 attention and resources are funneled into important but highly specific sub-fields, such as

129 detailed studies of the atmospheric impacts of different energy source activities including light
130 oil extraction, hydraulic fracturing or bitumen extraction.⁵ Laboratory studies, together with
131 field and modeling studies, constitute the long-standing “three-legged stool” of atmospheric
132 chemistry. The fundamental science aspect of this "three-legged stool" is overshadowed when
133 the science is solutions-driven, lessening our ability to not only address known environmental
134 issues such as the relationship of air quality to human health but also our readiness to respond to
135 unforeseen future environmental threats. Moreover, the complexity of the environment demands
136 avenues both for discovery-based science and for developing and testing hypotheses under well
137 controlled and relevant conditions. Despite the successes mentioned above, the atmosphere is far
138 from being fully understood with regard to changes in composition and the complex interplay of
139 chemical and physical processes, and thus predictive capabilities are limited. The importance of
140 fundamental understanding has been stressed previously,⁶ most recently in the recent report on
141 the Future of Atmospheric Chemistry Research prepared for the National Academy of Science in
142 the United States.⁷

143 This article highlights the significant role of laboratory-based atmospheric chemistry research,
144 pointing out that our ability to respond to a changing environment and to accurately inform
145 policy development hinges upon a fundamental molecular-level understanding of these
146 processes. Additionally, a commitment from universities, research centers, and governmental
147 agencies to support such research activities in a meaningful way and to promote innovative and
148 interdisciplinary research is needed at this time of a rapidly changing atmospheric composition.
149 Several key challenges and opportunities facing the laboratory community are presented in this
150 article.

151 **Emerging Topics for Future Laboratory Studies in Atmospheric Chemistry**

152 The atmospheric chemistry community has traditionally relied on laboratory studies to determine
153 the rates and mechanisms of key gas-phase reactions. For example, these processes have been
154 shown to be important for better understanding ozone depletion in the stratosphere and the
155 coupled processes of tropospheric oxidant production and organic oxidation that control the
156 abundance of key climate forcing agents such as methane (CH₄) and dimethyl sulfide (DMS).^{2,8}
157 There is currently considerable focus on the chemistry that occurs within or on aerosol particles
158 and cloud droplets, and increasingly on the interface of the atmosphere with the oceans,
159 biosphere, cryosphere, and indoor environments.⁹⁻¹³

160 Recent advances that highlight how far we have come in this field but, more importantly, how
161 much further we have to go to develop sufficiently accurate and predictive models of the
162 atmosphere are presented below. The examples below demonstrate that chemistry is central to
163 our understanding of the field and that we once thought to be understood, such as volatile
164 organic carbon (VOC) oxidation mechanisms, is much more varied and complex than described
165 by current mechanisms and included in models.

166 i. Do we understand how organic molecules are oxidized in the atmosphere?

167 Our conceptual view of organic oxidation mechanisms (see Figure 3), central to our
168 understanding of smog formation, the lifetime of greenhouse gases such as ozone (O₃) and
169 methane, and the climate effects of aerosol particles, has been transformed in the past few years.
170 An example of such a transformation is illustrated by recent studies of the chemistry of key
171 biogenic hydrocarbons, isoprene and the monoterpenes, that are emitted from vegetation.
172 Although isoprene is the largest source of organic carbon to the atmosphere and even a
173 component of exhaled human breath, our understanding of how it is oxidized under appropriate

174 radical concentration conditions is still incomplete.¹⁴ Only a short time ago, it was not known
175 whether it could contribute to aerosol formation, but recent advances now indicate it is an
176 important aerosol precursor (Figure 3).^{15, 16} In particular, when the OH radical adds to one of
177 isoprene's carbon-carbon double bonds a variety of highly oxidized products form.¹⁷ The radical
178 intermediates are reactive, and can isomerize leading to efficient autocatalytic oxidation and
179 multi-functionalised compounds that may form aerosol particles.¹⁸ Similarly, α -pinene, a
180 monoterpene, is converted into "highly oxidized molecules (HOMs)" (or "extremely low
181 volatility organic compounds", ELVOCs) under atmospheric conditions on timescales of seconds
182 to minutes, with up to 10 oxygen atoms being introduced onto the terpene backbone.¹⁹ These are
183 all new findings.

184 Major uncertainties in the oxidation mechanisms of VOCs, particularly biogenic VOCs, still
185 remain. In particular, there is a need to fully establish how much recycling of the OH radical
186 occurs from isoprene oxidation under different atmospheric conditions. This is especially true in
187 environments with significant input of molecules from biogenic sources, where the impact of OH
188 recycling on oxidant levels may be significant.²⁰ Also important toward understanding the
189 impacts of VOC oxidation are the roles of epoxides and the HOM compounds in the formation of
190 biogenic secondary organic aerosol (SOA), new particles,²¹ and the potential health effects of
191 particles containing these highly oxidized species. Indeed, the recognition that such organics
192 may play a major role in atmospheric particle nucleation and growth processes nicely illustrates
193 another connection between fundamental physical chemistry processes and atmospheric
194 behavior.

195 Little is known about the chemistry of these highly oxidized multifunctional reaction products
196 with respect to subsequent gas-phase and condensed-phase reactivity, photochemistry and light-

197 absorbing properties, hygroscopicity, and volatility. Further complexity arises through the
198 addition of nitrogen-based functional groups to the molecule via reactions involving nitrogen
199 oxide radicals, amines, or ammonia. Light-absorbing compounds can result that contribute to the
200 colored particles collectively referred to as brown carbon aerosol and known to arise from
201 burning processes. This has implications for climate change given that biomass burning and
202 wildfire emission sources are expected to increase in the future.²²

203 Our framework for understanding the multiphase chemistry of when these oxidized products
204 partition from the gas phase to cloud water or an aerosol particle is in its infancy. Questions that
205 arise include: How important are radical processes compared to non-radical
206 nucleophilic/electrophilic, hydrolytic, and addition/condensation reactions?²³ How important are
207 non-ideal solution effects and how can they best be treated to help interpret field investigations
208 and improve representations in models?²⁴ These issues can be addressed with focused laboratory
209 studies coming out of the coupled atmospheric-physical-analytical chemistry laboratory
210 communities.

211 ii. What controls the major oxidants in the atmosphere?

212 The chemistry of reactive chemical intermediates – usually radicals – is at the heart of
213 atmospheric chemistry (see Figure 4). Although our understanding of reaction mechanisms
214 initiated by conventional oxidants (OH, Cl, O₃) is extensive, it is not complete and the
215 importance of new classes of reactive intermediates, e.g. Criegee intermediates, is now being
216 recognized and studied. For example, although the rapid cycling of OH and HO₂ radicals helps
217 to drive the chemistry that forms multifunctional organic compounds, the field still does not yet
218 have closure between measured and modeled OH concentrations in clean environments.^{20, 25}

219 Beyond gas-phase OH, there has been a recent surge of activity in the chemistry of other reactive
220 intermediates, notably nitrate radicals,²⁶ halogen oxide radicals, Criegee intermediates, and
221 compounds active as photosensitizers,²⁷ but our understanding of these processes remains largely
222 insufficient. The Criegee intermediates present a compelling story, having recently been
223 observed for the first time via advanced mass spectrometry techniques.^{28, 29} These reactive
224 species are formed when ozone reacts in the gas phase with carbon-carbon double bonds, and
225 their involvement in the oxidation of key molecules, such as SO₂, thus affecting new particle
226 formation, is now being studied.

227 iii. What is the atmospheric importance of multiphase chemistry?

228 Some of the largest uncertainties in our field arise from the chemistry and photochemistry that
229 takes place involving different interfaces and media, such as aerosol particles and cloud droplets,
230 that interact with gas phase constituents. Collectively, this is referred to as multiphase chemistry
231 (see Figure 5).³⁰

232 The organic aerosol medium represents a poorly characterized component of particle chemistry
233 that can affect partitioning of gas-phase organics and can promote chemistry distinctly different
234 from that which occurs in other chemical environments. Aqueous phase droplets and particles
235 can enhance the formation of organic aerosol by promoting soluble organic partitioning and
236 subsequent reactions.³¹ Constraining advances in the field of organic particle and mixed organic-
237 inorganic particle chemistry is our lack of detailed knowledge of the bulk composition, phase
238 state, morphology, transport properties, interfacial composition, and photochemistry within these
239 particles under environmental conditions.^{27, 32} The development of new methodologies, such as
240 spectroscopic and mass spectrometric approaches, that are able to better characterize these

241 properties at the individual particle level is a key challenge. In addition, limitations currently
242 exist in our ability to prepare appropriately complex model substances in the laboratory that
243 realistically resemble those present in the environment.

244 Since particles can indirectly modify climate by acting as cloud condensation nuclei (CCN) and
245 ice nuclei (IN) an important area of multiphase chemistry involves studies of the hygroscopicity
246 of atmospheric particles.³³ Although much has been learned about the relationship of aerosol
247 particle composition to hygroscopicity and CCN activity, the roles of interfacial processes and
248 organic substituents are still being resolved.^{34, 35} Our understanding of the IN activity of aerosol
249 particles is even less refined because we lack a first-principles model that can accurately predict
250 the rates of heterogeneous ice nucleation as a function of aerosol type and composition.³⁶

251 The atmosphere interacts with the surfaces of the oceans, vegetation, soil, and indoor
252 environments. To illustrate such interactions, a long-standing uncertainty in atmospheric
253 chemistry has been related to non-gas phase sources of HONO, a photolytic source of the OH
254 radical. To explain measured levels within many boundary layer environments, it is known that
255 during the day there is a source that forms HONO much faster than the traditional gas-phase
256 formation route.^{37, 38} A variety of mechanisms have been proposed, all involving interfacial
257 chemistry.^{39, 40, 41, 42}

258 A highly interdisciplinary frontier lies with the impacts of atmospheric particles on human
259 health. Reactive oxygen species (ROS), such as hydrogen peroxide or organic hydroperoxides,
260 are a class of molecules that can give rise to oxidative stress, the state where the human body's
261 oxidant and anti-oxidant balance is disrupted.⁴³ Also important to oxidative stress are molecules
262 with labile oxidation states and metals that promote the formation of ROS species, either in

263 inhaled atmospheric particles or the body.⁴⁴⁻⁴⁶ A key question is the degree to which these
264 molecules drive oxidative stress in the body and whether their sources are endogenous or
265 exogenous. Moving ahead in this field requires the collaboration of atmospheric chemists and
266 toxicologists.

267 **Challenges and Opportunities in Laboratory Atmospheric Chemistry Research**

268 i. Complexity

269 The atmosphere has many chemical constituents and processes interacting in a non-linear
270 manner. The complexity that arises in the system has typically been addressed by a reductionist
271 approach where every relevant rate constant and photochemical property is measured. For
272 example, this approach is used to predict the non-linear response of urban ozone to changing
273 NO_x emissions, a relationship now well-recognized in the air pollution control community and
274 with connections to climate change.^{8,47} But other complex interactions are less well understood.
275 For example, how do chemical interactions with aerosol particles affect the aerosols' ability to
276 nucleate liquid water and ice clouds? How does the liquid-like layer that exists at the surface of
277 snow affect the likelihood of molecules being sorbed from the gas phase?⁴⁸ How does biology
278 affect the indoor microbiome and its ability to change VOC levels?¹³ And, what is the interplay
279 between biology and chemistry in controlling the fluxes of climatically-active gases such as
280 DMS and isoprene to the atmosphere from the ocean and vegetation.^{9,12}

281 A reductionist approach is necessary to arrive at the understanding required for confidence in
282 model predictions of air quality and climate. Nevertheless, it is also fruitful to work with top-
283 down methods where observations from laboratory experiments conducted under conditions
284 close to those in the environment can be parameterized for inclusion in models. For example, it

285 is now possible to measure the rate of loss of a gas-phase reactant to ambient aerosol under real-
286 world conditions.⁴⁹ The goal of such experiments is to obtain quantitative closure between the
287 bottom-up and top-down approaches for assessing the rates of this chemistry.

288 ii. Collaboration and Interdisciplinary Research

289 In addition to the value of single-investigator science, atmospheric chemistry has also long
290 benefited from collaboration. A number of schemes can enhance opportunities for collaboration.
291 In particular, there is an advantage to incorporating laboratory projects into the funding of large
292 field campaigns, to facilitate exchange of ideas and experimental techniques from one
293 community to another. Another approach is for a small number of research teams to work
294 together to simultaneously study the chemistry in one facility, to examine the nature of complex
295 processes.⁵⁰ Recent advances in theoretical methods mean that quantum chemical calculations
296 can significantly enhance knowledge gained from laboratory investigations. In addition,
297 collaborations between laboratory scientists and atmospheric modelers are required to enable
298 both direct impact-testing of laboratory data and identify areas of research for which remaining
299 uncertainty has significant repercussions.

300 New interdisciplinary opportunities are continuing to arise at the interfaces of atmospheric
301 chemistry. For example, dedicated lab experiments under controlled conditions will inform us
302 regarding the nature of biosphere-atmosphere interactions.⁵¹ This, in turn, will help us to better
303 understand how ecosystem health is affected via atmospheric exposures and will aid in
304 determining the detailed mechanisms by which vegetation removes oxidants from the
305 atmosphere. Another example is the chemistry involving atmospheric constituents and the lung-
306 air interface. Experiments conducted jointly by atmospheric chemists and toxicologists will

307 better establish how airborne particles contribute to increased levels of oxidative stress, a
308 common hypothesis invoked to explain the epidemiological connections between increased
309 particulate loadings and negative health outcomes.⁵² There is also considerable scope for new
310 explorations in indoor environments where we spend most of our time and receive most of our
311 pollutant exposure.¹³ Indoor surface-area-to-volume ratios are high, suggestive of the importance
312 of surface chemistry, and many cleaning and personal care products whose constituents partition
313 between the gas phase and indoor surfaces are prevalent.⁵³ Furthermore, the desire to reduce
314 energy consumption in some modern buildings may lead to less ventilated indoor environments,
315 and requires better understanding of indoor air chemistry to ensure that such green buildings are
316 also healthy buildings.

317 For all these opportunities, there is the need for science funding agencies to recognize that such
318 interdisciplinary research often falls between the cracks of funding programs that are better tuned
319 to promote the value of disciplinary research.

320

321 iii. The interplay of laboratory experiments with computational and atmospheric modeling
322 scientists

323 Connecting laboratory experiments to chemical theory remains crucial to the atmospheric
324 chemistry field. At the molecular level, as computational methods allow for increasingly
325 complex chemistry to be studied on a computer,⁵⁴ interactions between laboratory and
326 computational chemists are expected to become more common.

327 Individual gas-phase rate or photochemical parameters may be easily incorporated into chemical
328 transport models and their impact evaluated. However, the challenge of transferring laboratory

329 results from complex systems is not as straightforward. The evaluation of physical and chemical
330 laboratory data as provided by the NASA JPL (<http://jpldataeval.jpl.nasa.gov/>) and IUPAC
331 (<http://iupac.pole-ether.fr/>) panels is a particularly important task that supports feedback between
332 modelers and experimentalists in both directions.^{55, 56} Collaborative efforts between laboratory
333 scientists and process-level atmospheric modelers can ensure accurate parameterizations of
334 complex chemistry are incorporated into models, and the integrating nature of the models can
335 provide information about which conditions or timescales need further experimental constraints.
336 Such collaborations can occur as part of research grants, information collaborations, or special
337 sessions at international conferences that emphasize the integration of modeling and laboratory
338 results.

339 iv. The interplay of laboratory experiments with field measurements

340 Many advanced analytical technologies have been developed in the past decade that can be
341 applied to atmospheric chemistry research, with increasingly sensitive and multiplexing
342 instruments deployed in both the lab and atmosphere. In order to understand new field
343 observations the laboratory community is pushed to develop a better understanding of the
344 associated chemistry and its possible environmental impacts. For example, recent progress has
345 arisen from the advent of advanced mass-spectrometric techniques that now allow for the
346 identification and quantification of species present in complex chemical mixtures.^{57, 58} Such
347 instrumentation has been used extensively in new studies of particle nucleation and growth
348 processes.²¹ With a strong demand for sensitive and reliable measurement technologies, the
349 atmospheric chemistry field fosters developments in advanced measurement technologies. These
350 advances have led to a recent growth in experimental studies where the relevant chemistry is
351 studied on genuine atmospheric materials (such as atmospheric aerosol particles) commonly

352 referred to as “field-in-the-lab” or “lab-in-the-field” methods.⁴⁹ These approaches are attractive
353 to test the applicability of laboratory model materials and to provide top-down results that
354 fundamental-based bottom-up approaches aspire to match.

355 **Conclusions**

356 The scientific uncertainties illustrated above are associated with some of the most central
357 questions in atmospheric chemistry: How are atmospheric molecules transformed, and by what
358 mechanisms? In what phase does this chemistry occur and on what timescale? How does this
359 chemistry affect air quality and climate? How do ecosystems affect atmospheric chemistry and
360 vice versa? How does this chemistry affect the interaction of the atmosphere with other parts of
361 the environment? These issues and others highlight the ongoing central role for laboratory
362 studies and a molecular-level understanding of atmospheric chemistry that enable the
363 development of informed environmental policy.

364 The laboratory studies community is adapting to address far greater scientific complexity than
365 was apparent only a decade ago, needing to embrace an interdisciplinary and collaborative
366 research approach while at the same time continuing to focus on the measurement of
367 fundamental properties of atmospherically relevant molecules and processes. These aspects of
368 the field are highly attractive to early career scientists who are looking for research experiences
369 outside of traditional disciplines. Funding agencies can facilitate these efforts, by supporting
370 fundamental laboratory science and by promoting interdisciplinary and collaborative research
371 and the interplay between laboratory studies and associated modeling, and field measurement
372 activities.

373

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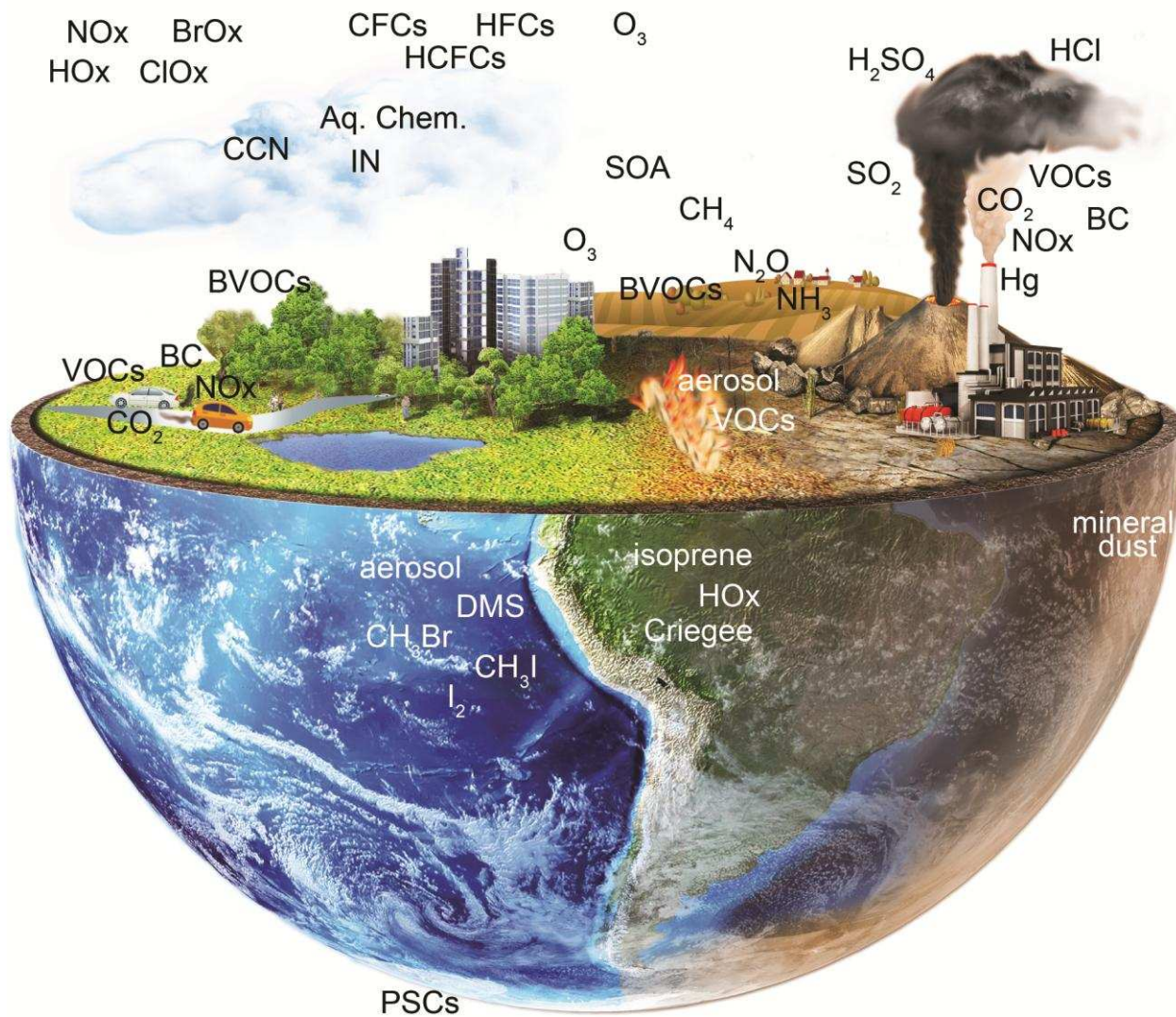
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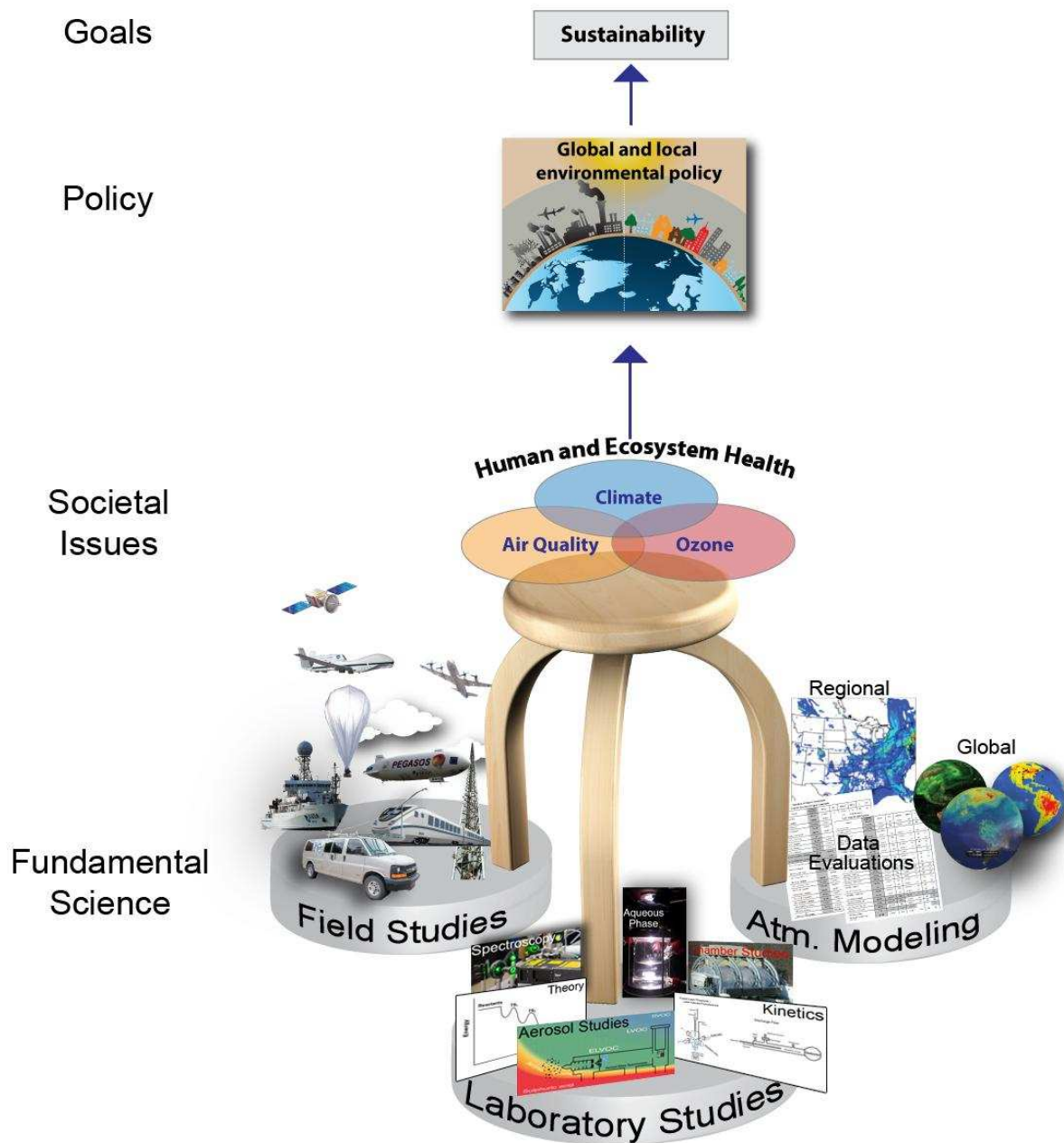
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540 **Figure 1:** A chemical view of the atmosphere highlighting biogenic and anthropogenic
 541 emissions sources and key atmospheric species.

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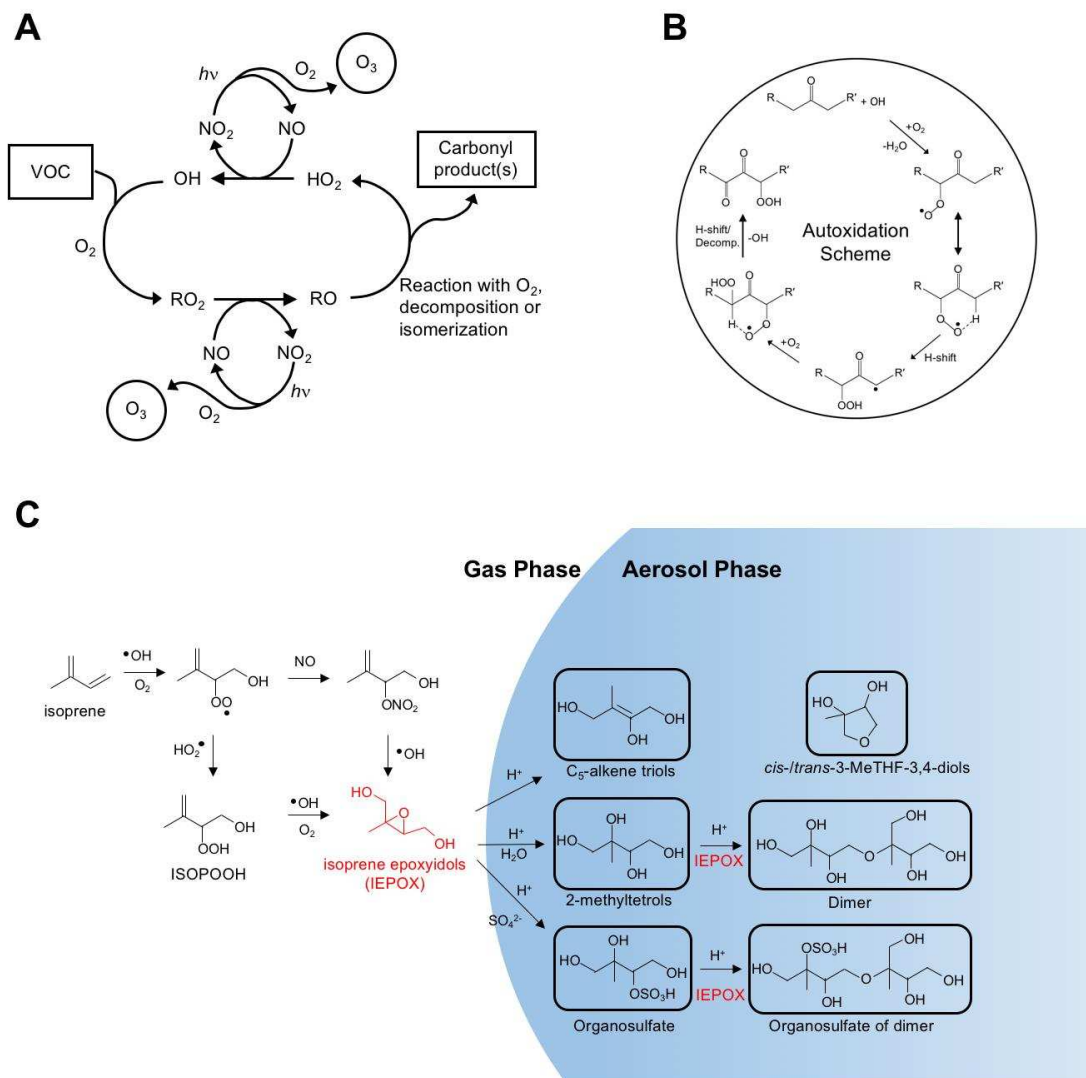
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546 **Figure 2:** The three-legged stool connecting atmospheric chemistry to sustainable policy.

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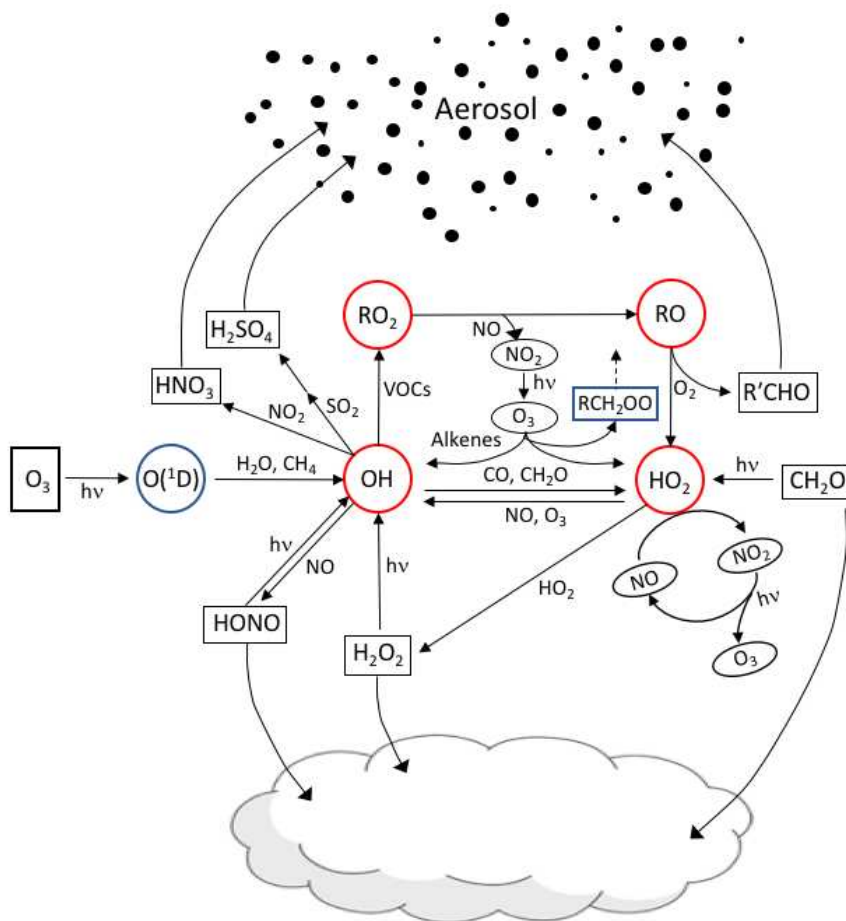


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550 **Figure 3:** Examples of volatile organic compound (VOC) oxidation mechanisms. A.
 551 Formation of ozone coupled to VOC oxidation in the presence of NO_x , B. VOC
 552 autoxidation scheme adapted from Crouse et al.,¹⁸ C. Isoprene oxidation mechanism
 553 emphasizing the interplay between chemistry occurring in both the gas and condensed
 554 phases.

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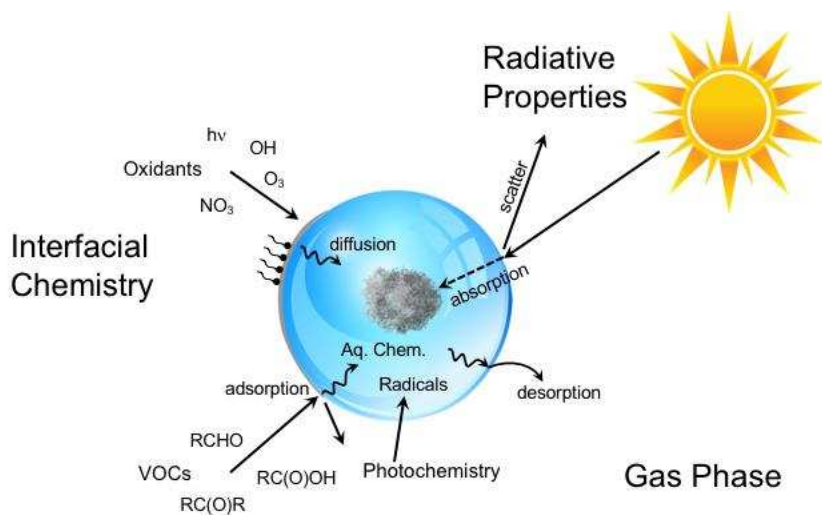
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559 **Figure 4:** Examples of radical formation, cycling, formation of stable products, and
560 contributions to aerosol and cloud chemistry. Note that radical chemistry also occurs in cloud
561 droplets and aerosol particles but is not shown.

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567 **Figure 5:** Representation of multiphase processes and radiative properties for a particle or
568 droplet containing a solid core. Note that other particle morphologies are possible.

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