The term “Anthropocene” was coined by Professor Paul Crutzen in 2000 to describe an unprecedented era in which anthropogenic activities are impacting planet Earth on a global scale. Greatly increased emissions into the atmosphere, reflecting the advent of the Industrial Revolution, have caused significant changes in both the lower and upper atmosphere. Atmospheric reactions of the anthropogenic emissions and of those with biogenic compounds have significant impacts on human health, visibility, climate and weather. Two activities that have had particularly large impacts on the troposphere are fossil fuel combustion and agriculture, both associated with a burgeoning population. Emissions are also changing due to alterations in land use. This paper describes some of the tropospheric chemistry associated with the Anthropocene, with emphasis on areas having large uncertainties. These include heterogeneous chemistry such as those of oxides of nitrogen and the neonicotinoid pesticides, reactions at liquid interfaces, organic oxidations and particle formation, the role of sulfur compounds in the Anthropocene and biogenic–anthropogenic interactions. A clear and quantitative understanding of the connections between emissions, reactions, deposition and atmospheric composition is central to developing appropriate cost-effective strategies for minimizing the impacts of anthropogenic activities. The evolving nature of emissions in the Anthropocene places atmospheric chemistry at the fulcrum of determining human health and welfare in the future.

Introduction

The term “Anthropocene”, proposed in 2000 by atmospheric scientist and Nobel Laureate Paul Crutzen, describes the era when humans began to have a global impact on our environment. Providing the basic human needs of food, water, and shelter requires both agriculture and energy, the latter provided to date primarily by fossil fuel combustion. While emissions from such human activities have been known to impact air quality for at least 1000 years, the recognition of global impacts is a relatively recent phenomenon.
The Anthropocene is generally accepted to begin with the Industrial Revolution around 1750–1800 (ref. 3–10) (although some arguments have been made that it started with agricultural activities around the beginning of the Holocene 11 600 years ago,11 with others arguing for much later times, the late 1940’s and early 1950’s12). Fig. 1 shows some indicators of this period of industrialization.13,14 While population and fossil fuel use increased at the beginning of the Industrial Revolution, there was a clear acceleration in all of the indicators after World War II. This recent period has been dubbed the “Great Acceleration”.8

The atmosphere is intimately linked to the biosphere through exchanges involving both emissions from, and deposition to, the land and oceans (Fig. 2).15 Terrestrial emissions include both anthropogenic as well as biogenic sources which are closely intertwined through changes in land use.16,17 Ocean–atmosphere interactions are also very important as oceans not only act as a source (e.g., of halogens and organics) but also as a sink for gases and particles.18–20 Thus, a key part of the atmosphere–biosphere interaction is deposition. This is central to ecosystem functioning and health as well as productivity that supports human existence through the production of food and other ecosystem services.21 However, deposition can also lead to deleterious effects on impacted media. One example is uptake of carbon dioxide (CO₂) by the oceans, which has already resulted in a 26% increase in the hydrogen ion concentration.22 Another example is increased nitrogen deposition which can alter the uptake and emissions of other gases such as CO₂ and nitrous oxide (N₂O), and impact biological diversity and processes both on land and in the oceans.23–25

Combustion of coal, oil and natural gas have provided most of the energy needed for essentially all facets of life as we know it today. Associated with this are emissions of highly reactive NOₓ (=NO + NO₂), sulfur dioxide (SO₂) and organic compounds, as well as particles and toxic metals such as mercury.26 Reactions of the direct (primary) emissions lead to formation of secondary pollutants, yielding a very complex mixture of gases and particles in the atmosphere. Indeed, the
troposphere would have a drastically different composition if not for the (photo) chemical conversion of primary emissions to secondary pollutants.

Fig. 3 summarizes some overall reaction sequences beginning with the conversion of nitric oxide (NO) to nitrogen dioxide (NO$_2$) by alkylperoxy free radicals (RO$_2$) arising from the oxidation of volatile organic compounds (VOC) in air.$^{27-30}$ Species that initiate the oxidation of VOC include the hydroxyl (OH) and nitrate (NO$_3$) free radicals as well as ozone (O$_3$). There is increasing evidence for a contribution from chlorine atoms$^{31}$ and from bromine atoms reacting with
some species such as aldehydes.\textsuperscript{18,19,32} The formation and photolysis of NO$_2$ serves as the sole significant source of anthropogenically produced O$_3$ in the troposphere. Ozone data (Fig. 4) from non-urban areas in Europe from 1876 to 1983 (ref. 33) and more recent global data\textsuperscript{34} show increases in many locations in the Northern Hemisphere by as much as a factor of five from pre-industrial times to the present, which has been attributed to increased NO$_x$ emissions.\textsuperscript{33} This rise in O$_3$ is a dramatic demonstration of the impact of photo- and secondary chemistry on global atmospheric composition.

Emissions of NO$_x$ and SO$_2$ from fossil fuel combustion lead to nitric (HNO$_3$) and sulfuric (H$_2$SO$_4$) acids in air, which are significant contributors to atmospheric particles (Fig. 5).\textsuperscript{27,35} Organics are also a major component, and their source is largely oxidation of gas phase organic precursors to form low volatility products, giving rise to secondary organic aerosol (SOA).\textsuperscript{36} As discussed in more detail below, there are both natural and anthropogenic sources of organic precursors to SOA. This is also the case for ammonia (NH$_3$) and amines that play important roles in particle formation. Thus, anthropogenic and natural processes are inextricably intertwined.

Direct and immediate consequences of fossil fuel use include deleterious impacts on human health. Children are particularly susceptible\textsuperscript{37–39} due to a combination of factors, including time spent outdoors and more rapid breathing; their metabolic, immune, and lung systems are also not as well developed. Health effects associated with the criteria pollutants such as O$_3$, NO$_2$, carbon monoxide (CO) and SO$_2$ are well documented,\textsuperscript{40–44} and include a variety of pulmonary and cardiovascular effects. Ozone is especially toxic to humans and stringent air quality standards are set for this secondary pollutant; for example, the World Health Organization guideline for O$_3$ is 50 ppb (100 \textmu g m$^{-3}$ for 8 h mean exposure time).\textsuperscript{45} Ozone also plays a major role in particle formation in air.
and is a greenhouse gas, one of the short-lived climate forcers (SLCF)\textsuperscript{16,46–49} whose lifetimes are less than that of CO\textsubscript{2} that yet still make significant contributions to climate change.\textsuperscript{50}

Relatively less is known about the health impacts of particulate matter (PM), especially ultrafine particles (<100 nm), although there is increasing evidence that they have a wide range of systemic effects which are summarized in Fig. 6.\textsuperscript{51} Overall, particulate matter has been linked to an increased risk of asthma, cardiopulmonary disease and pulmonary effects including lung cancer, as well as

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**Fig. 5** Composition of non-refractory (volatile at \(\leq 600 \, ^{\circ}C\)) portion of particles measured by Aerosol Mass Spectrometry (AMS) at different locations around the world. Adapted from ref. 35.

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**Fig. 6** Some health impacts associated with inhalation of fine and ultrafine particles. Adapted from ref. 51.
increased mortality and reduced life expectancy.\textsuperscript{52–67} Still in their infancy are studies of the potential effects of PM\textsubscript{2.5} (particulate matter less than 2.5 \textmu m in diameter) on diseases associated with the reproductive system (premature births, low birth weight, fetal growth and sperm quality)\textsuperscript{37,68–73} and with the brain (neurodegenerative diseases such as Alzheimer’s and Parkinson’s disease,\textsuperscript{74–78} strokes,\textsuperscript{79,80} autism,\textsuperscript{81,82} anxiety,\textsuperscript{83} and dementia\textsuperscript{84}). A mechanistic basis for the effects of PM may be translocation of particles to the brain.\textsuperscript{75,84–86} Interestingly, cognitive deficits due to air pollution were suggested around the year 1200, when the philosopher Maimonides attributed “dullness of understanding, failure of intelligence and defect of memory” to air pollution.\textsuperscript{2} A recent study\textsuperscript{87} linked outdoor air pollution, primarily particles, to 3.3 million premature deaths worldwide per year.

Fossil fuel combustion also intimately links air quality problems to climate change,\textsuperscript{49,88–91} and is largely responsible for the dramatic rise in atmospheric CO\textsubscript{2} to \textgreater400 ppm today.\textsuperscript{92} Other human activities have led to increases in climate-active methane (CH\textsubscript{4}), N\textsubscript{2}O, chlorofluorocarbons (CFCs) and stratospheric water vapor,\textsuperscript{93} particles and SLCF such as O\textsubscript{3} and hydrofluorocarbons (HCFCs).\textsuperscript{16,34,46–49} Particles play a significant role in climate change, but in much more complex ways because of their diverse and changing compositions. All particles scatter light, and a subset act as nuclei for the formation of both liquid and ice clouds.\textsuperscript{34} The ability of particles to scatter light and participate in cloud formation has partly masked the warming effects of greenhouse gases.\textsuperscript{34} However, soot/black carbon and some organics known as “brown carbon”\textsuperscript{94} are strong light absorbers and contribute to warming.

In addition to fossil fuel combustion, the Anthropocene is characterized by increasing agricultural activities.\textsuperscript{95,96} This impacts land use and involves application of chemicals such as fertilizers and pesticides, causing changes in emissions which influence both air quality and climate.\textsuperscript{95,96} The interrelationships can be quite complex. For example, the conversion of forests to croplands and grasslands changes biological volatile organic emissions, which influences the formation of O\textsubscript{3}, particles and the oxidation capacity of the atmosphere\textsuperscript{16,17} and hence the lifetime of gases such as CH\textsubscript{4}; these impacts of land-use change on emissions and atmospheric chemistry can have impacts on climate that are similar in magnitude to the well-recognized associated changes in surface albedo and carbon release.\textsuperscript{17} Conversion to croplands can also result in loss of soil carbon which would normally be sequestered. For example, Fig. 7 shows model-predicted percentage change in soil organic carbon per acre for U.S. croplands over a 30 year period;\textsuperscript{97} about three quarters of the cropland in the U.S. is estimated to have suffered loss of soil organic carbon.

The costs associated with impacts of air pollution and climate change are difficult to accurately assess, but are clearly substantial.\textsuperscript{98–105} For example, in addition to harming human health and impacting climate change, air pollutants may also alter weather, for example, through increased probabilities of heat waves, droughts, changes in rainfall and impacts on clouds and cloud dynamics that affect damaging storms and extreme weather events such as hurricanes and floods.\textsuperscript{106–115} Air pollutants damage crops and forests and diminish gross primary productivity and crop yields.\textsuperscript{116–119} It is noteworthy that changes in diffuse radiation from light scattering by particles can change gross primary productivity (GPP)
of forests and of croplands and grasslands, and impact emissions and uptake as well.\textsuperscript{120–122}

In short, the changes in the atmosphere and its chemical processes during the Anthropocene are enormous. Thus the topics treated here will of necessity be selective, and the citations representative rather than comprehensive. For example, some key areas such as stratospheric ozone and its relationship to climate change are not addressed; the author apologizes in advance for omissions that have resulted. To narrow the scope of this article, the focus is on the atmospheric chemistry primarily associated with fossil fuel combustion and agriculture, and their impacts on air quality and climate. Atmospheric chemistry is at the core of understanding these linkages and thus provides the basis for the development of effective control strategies directed to protecting human health and welfare.

**Tropospheric NO\textsubscript{x} chemistry**

A distinctive feature of the Anthropocene is increased emissions of NO\textsubscript{x} which forms O\textsubscript{3} as discussed earlier. However, NO\textsubscript{x} is also associated with the formation of other highly reactive compounds in the troposphere. An important example is the formation of nitrous acid (HONO) which is commonly found to be the major source of OH in the early morning hours, and often the dominant source when averaged over 24 h:\textsuperscript{123–126}

\[
\text{HONO} + \text{hv} (\lambda < 400 \text{ nm}) \rightarrow \text{OH} + \text{NO}
\]  

(1)
Chemistry involving active oxides of nitrogen, including HONO,\textsuperscript{130–133} has also been documented in the Arctic and Antarctic snowpack,\textsuperscript{134–136} and more recently in mid-latitude snowpacks.\textsuperscript{137} HONO is also believed to play a role in indoor air chemistry.\textsuperscript{129,138–144} Despite this, the relative importance of sources of atmospheric HONO are not yet well defined or quantified.\textsuperscript{145} There are direct emissions of HONO from combustion,\textsuperscript{146–153} and the reaction of OH with NO also generates a small steady-state HONO concentration during the day (since HONO photolyzes rapidly back to OH + NO).

While NO\textsubscript{2} does not react at a significant rate in the gas phase with water, it is known to react on surfaces to form HONO and HNO\textsubscript{3} \textsuperscript{154–163}

\[
2 \text{NO}_2 + \text{H}_2\text{O} \xrightarrow{\text{surface}} \text{HONO} + \text{HNO}_3
\]  

However, the mechanism and kinetics on different surfaces remain uncertain, which precludes accurate representation in atmospheric models. One possible mechanism involves the asymmetric form of the NO\textsubscript{2} dimer, ONONO\textsubscript{2}, which can autoionize in the presence of water to form NO\textsuperscript{+}NO\textsubscript{3}\textsuperscript{−}; subsequent reaction of the ion pair with surface-adsorbed water generates HONO and HNO\textsubscript{3}.\textsuperscript{164–169} In the troposphere there are widely varying amounts of water vapor, which typically form different structures on surfaces, ranging from islands at low relative humidity (RH) to multi-layer films at high RH.\textsuperscript{170} It is likely that the details of the water structure affect its interactions with gases such as NO\textsubscript{2}, or the dimer N\textsubscript{2}O\textsubscript{4}, as well as the nature of the surface-bound species. For example, theoretical treatment of N\textsubscript{2}O\textsubscript{4} on a thin water film carried out using \textit{ab initio} molecular dynamics simulations show that a water film can stabilize the asymmetric form of the dimer, ONONO\textsubscript{2} so it is available for reaction. This also activates it towards nucleophilic attack (\textit{e.g.}, by chloride ions, see the section on biogenic–anthropogenic interactions below).\textsuperscript{171} The presence of inorganic ions\textsuperscript{172} or organic surfactants\textsuperscript{173} has been shown to affect the kinetics of conversion of NO\textsubscript{2} to HONO at the interface of aqueous microjets, and presumably may also do so on surface-bound water.

Other potential sources of HONO in the atmosphere include NO\textsubscript{2} dark reactions with soot\textsuperscript{174–186} and with organics,\textsuperscript{187–190} photoenhanced interactions of NO\textsubscript{2} on both inorganic and organic surfaces,\textsuperscript{191–207} and photolysis of \textit{o}-nitrophenols.\textsuperscript{201,208} Photocatalysis by TiO\textsubscript{2} and components of mineral dust and building materials has also been shown to cause the conversion of NO\textsubscript{2} to HONO.\textsuperscript{209–218}

Despite this large body of research on the formation of HONO, significant discrepancies remain between the results of laboratory studies and many atmospheric measurements of HONO,\textsuperscript{128,219–224} leading to the possibility that there are still unidentified sources. If nitrification processes are responsible, increased fertilizer use since about 1950 (Fig. 1) is expected to lead to increased HONO emissions and hence increased oxidative capacity of the atmosphere. Recent studies\textsuperscript{225} confirm an earlier report\textsuperscript{226} that there is a source in soils. Soil-associated sources include ammonia-oxidizing bacteria\textsuperscript{227,228} and direct emissions from biological soil crusts which contain lichens, mosses, algae, cyanobacteria, heterotrophic bacteria, fungi and archaea.\textsuperscript{229} Nitrification converts ammonium to
nitrite (NO$_2^-$) and then nitrate (NO$_3^-$). Under sufficiently acidic conditions, NO$_2^-$ is released as HONO to the gas phase$^{225,230,231}$ as depicted in Fig. 8a. However, it has been shown that the nature of the surface, and particularly surface charge, plays an important role in the uptake and release of HONO from soils.$^{232}$ For example, as shown in Fig. 8b, soil surface components such as aluminum and iron oxides/hydroxides are present in a number of different forms such as MO$^-$, M–OH and MOH$_2^+$ (M = metal) which interact with oxides of nitrogen, changing the pH at which HONO is released to more basic conditions compared to pure water by as much as several pH units.$^{232}$

The relative importance of these HONO sources will depend on location, the nature and chemical composition of the surfaces, and atmospheric conditions such as solar intensity and the amount of water as indicated by the relative humidity (RH). Although HONO is ultimately derived from NO$_x$, it does not always trend with measured NO$_2$ concentrations.$^{152,220,235}$ While model-predicted contributions of various sources to HONO suggest that processes involving NO$_2$ conversion on the ground (both dark and photoenhanced) are important,$^{152,220,235}$ the identity and reactivity of the key surface intermediates that generate HONO after the exposure of surfaces to oxides of nitrogen, water vapor and/or light remain controversial.$^{160,196,236}$ As described above, theory predicts the formation and chemistry of intermediates such as the asymmetric N$_2$O$_4$ dimer and NO$^+$NO$_3^-$.$^{164-169}$ It is likely that similar intermediates are involved at ice interfaces.$^{167,206}$ Other surface-bound species may include nitric acid or nitrate.$^{194,195,237,238}$ The absorption cross sections for HNO$_3$ on surfaces have been

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Fig. 8 (a) Effect of pH on partitioning of HONO between the bulk aqueous and gas phase in aqueous solution and (b) schematic of speciation and partitioning of HONO on model soil surfaces. Adapted from ref. 232.
reported to be larger than in the gas phase,\textsuperscript{239} which may reflect interactions with other, as yet unidentified, species on the surface. This is consistent with the much higher than expected photolysis rates of surface-bound nitrate species in “urban grime”.\textsuperscript{240–242} For example, while one might expect the surface HNO\textsubscript{3} to be dissociated in the presence of water, there is evidence that a large fraction is actually in the form of nitric acid hydrates and even the nitric acid dimer.\textsuperscript{243} There is also indirect evidence for a rich and reactive surface-bound “soup” of different species in concentrated nitric acid,\textsuperscript{241,244} which might bear some similarity to the surface-bound acid concentrated in urban surface films. Finally, reactions between NO\textsubscript{x} surface species can occur, such as that of adsorbed HNO\textsubscript{3} with NO to generate NO\textsubscript{2} and some HONO, which was hypothesized to react further with surface HNO\textsubscript{3}.\textsuperscript{245,246} These heterogeneous reactions not only demonstrate the importance of deposition, but also show that a mechanism is available for NO\textsubscript{x} to re-enter the gas phase and contribute to further O\textsubscript{3} formation and other secondary chemistry.

Along with HONO, a small yield of N\textsubscript{2}O from the surface hydrolysis of NO\textsubscript{2} has been reported.\textsuperscript{159,160,247,248} Nitrous oxide is a strong greenhouse gas\textsuperscript{34} and is a significant source of nitrogen oxides to the stratosphere\textsuperscript{249} as originally proposed by Crutzen in his Nobel prize-winning work.\textsuperscript{250} Despite the knowledge that N\textsubscript{2}O is generated by the NO\textsubscript{2} heterogeneous reaction with water on surfaces, the mechanisms involved remain obscure.

There are also new sources which have been identified recently, which add to direct emissions of N\textsubscript{2}O.\textsuperscript{249,251} For example, N\textsubscript{2}O can be generated from the photolysis of ammonium nitrate (NH\textsubscript{4}NO\textsubscript{3}) on surfaces at room temperature\textsuperscript{252} as well as at low temperatures.\textsuperscript{253} The ambient temperature photolysis was estimated to generate 9.3 Gg of N\textsubscript{2}O per year over North America.\textsuperscript{252} The Anthropocene not only ushered in greater use of fertilizers such as NH\textsubscript{4}NO\textsubscript{3}, which will contribute to N\textsubscript{2}O through biological processes in soils and photolysis as just described, but it has also given rise to increased use of pesticides. One category of pesticides is the neonicotinoids (NNs) shown in Fig. 9.\textsuperscript{254} These NNs came into use starting in 1991 and have largely supplanted the use of organophosphates and carbamates.\textsuperscript{255,256} Fig. 10 shows the increasing use of NNs and another insecticide, fipronil, as a function of year for several countries and the state of California in the U.S.\textsuperscript{256} A significant concern that has arisen with their use is the impact on pollinators such as bees. There are a number of factors\textsuperscript{257} potentially involved in the observed bee colony collapse disorder besides NNs, including parasites and pathogens, loss of habitat and its diversity, and climate change. In any event, restrictions have been placed on NN use in parts of Europe.

Imidacloprid (IMD) is the major NN in use on a worldwide basis, for example as a seed coating. Relatively little is known about its photochemistry and atmospheric reactions on surfaces such as seeds or soil. However, recent work in the author’s laboratory has shown that photolysis of IMD generates N\textsubscript{2}O with a yield of $\geq$50\% relative to the loss of the parent compound.\textsuperscript{258} Based on the estimated 20 000 tonnes worldwide production of IMD in 2010,\textsuperscript{256} $\sim$2 Gg of N\textsubscript{2}O could be produced from photolysis of IMD alone. While this is not significant compared to the estimated global increase of 20 Tg emitted per year as N\textsubscript{2}O (equivalent to 13 Tg N) from the terrestrial biosphere,\textsuperscript{251} it could contribute to measurements of concentrations and fluxes made over soils that contain NNs.
The solid phase products identified from IMD photolysis are the urea and desnitro derivatives shown in Fig. 11. Neither of these absorbs in the actinic region so once formed, they will be stable with respect to photolysis in the

Fig. 9 Structures of some neonicotinoids with the nitroguanidine structure and the years they were each introduced. The red circles indicate the nitroguanidines, the green the cyanamidines and the blue the nitromethylene. Adapted from ref. 254.

The solid phase products identified from IMD photolysis are the urea and desnitro derivatives shown in Fig. 11. Neither of these absorbs in the actinic region so once formed, they will be stable with respect to photolysis in the

Fig. 10 Trends in the use of neonicotinoids and fipronil in Japan (domestic shipments), Sweden (sales), Britain (agricultural use) and California (use) in annual tonnes of active ingredient. Adapted from ref. 256.
troposphere. Previous toxicology studies\textsuperscript{259} have shown that the desnitro derivative is more toxic than the parent imidacloprid. As is the case with malathion,\textsuperscript{260} this is an example of the importance of considering not only the toxicity of the parent compound, but also that of its products from chemistry and photochemistry in the atmosphere.

In short, activities associated with the Anthropocene have led to increased emissions of oxides of nitrogen and ammonia, as well as the use of newly developed chemicals such as pesticides that can also contribute to oxides of nitrogen chemistry in the atmosphere. While a great deal is known about the gas phase reactions, heterogeneous chemistry is much less understood. New experimental and theoretical approaches would be very helpful in probing the composition, chemistry and photochemistry of these surface reactions.

Reactions at liquid interfaces

While uptake and reactions on solid surfaces in the atmosphere have been recognized for many decades – but not well understood – there is now firm evidence that the composition and chemistry at liquid surfaces in the atmosphere is often different from the bulk,\textsuperscript{261-264} with potentially important implications for tropospheric chemistry.\textsuperscript{265-268} In the Anthropocene, the importance of reactions at liquid interfaces can be impacted as the distribution, lifetimes and properties of clouds, fogs and particles that provide an interfacial medium are changing.

Inorganics

An example of unique chemistry at interfaces is an initially surprising result from a combination of experiments, atmospheric modelling and molecular dynamics simulations which suggested that chloride ions are present at interfaces of aqueous salt solutions as models for sea salt particles.\textsuperscript{269} This enhanced surface availability of chloride ions resulted in oxidation by incoming gas phase OH that was different in terms of both kinetics and mechanisms from the bulk, generating gas phase Cl\(_2\) much more efficiently than expected from bulk phase chemistry.\textsuperscript{269} Subsequent experimental\textsuperscript{270-274} and theoretical\textsuperscript{275-277} work firmly established that larger and more polarizable halide ions are enhanced at the interface relative to the bulk. This means, for example, that bromide ion chemistry at interfaces is relatively more important than chloride ion chemistry, which may contribute in
part to the importance of bromine chemistry in the Arctic boundary layer at polar sunrise despite low bromide concentrations.\textsuperscript{19,278–283} Iodide ions are even more enhanced at the interface;\textsuperscript{275,284,285} while present in much smaller concentrations than chloride or bromide, iodine from various sources including organoiodine compounds can play a significant role in particle formation in coastal areas.\textsuperscript{18,286,287} The relative importance of interface chemistry may be altered in the Anthropocene by changes in OH or by altered sea salt particle and cloud/fog concentrations due to changes in meteorology and wave action.\textsuperscript{288}

Photochemistry at interfaces may also be enhanced due to a reduced solvent cage,\textsuperscript{289–293} and this effect can be altered by the presence of other species.\textsuperscript{294–299} For example, nitrate ion photolysis at interfaces is more efficient than in the bulk, and is influenced by the presence of halide ions.\textsuperscript{294–299} However, it should be noted that whether nitrate ions are enhanced at the interface in water is somewhat controversial,\textsuperscript{300–302} and could depend on cluster size, for example.\textsuperscript{303}

Organics

Interfacial organic surfactants are well known in laboratory and atmospheric systems.\textsuperscript{304–306} In the atmosphere, they can alter the exchange between the gas phase and clouds, fogs and particles,\textsuperscript{307–313} change the kinetics of reactions such as the hydrolysis of NO\textsubscript{2} (ref. 173) and the oxidation of organics,\textsuperscript{268,314,315} and alter ion composition and chemistry at the interface.\textsuperscript{316,317}

There is also evidence that mechanisms and kinetics of reactions of organics can be altered at the interface compared to the bulk. For example, organic surfactants can form quite densely packed monolayers at the air–water interface. In the event of free radical formation, e.g., by direct photolysis, OH reaction or H-transfer to a triplet photosensitizer, radical–radical reactions can compete with scavenging of the radical by O\textsubscript{2}.\textsuperscript{318–323} This leads to the formation of oligomers as well as a variety of reactive products. Fig. 12, for example, shows some proposed pathways for the reaction of nonanoic acid initiated by H-atom transfer from the triplet state of the photosensitizer 4-benzoylbenzoic acid, 4-BBA. There are a variety of potential photosensitizers in atmospheric particles, including humic acids and imidazoles formed from the ammonia and amine reactions involved in the “browning” of SOA. Interestingly, there is evidence for HO\textsubscript{2} radical production from the imidazole photosensitized reaction of citric acid.\textsuperscript{324} Reactions of organics at interfaces may also have biological relevance; for example, the formation of peptide bonds at the air–water interface in the presence of Cu\textsuperscript{2+} ions has been observed.\textsuperscript{325}

There remain a number of outstanding questions with respect to differences in organic reactions at interfaces under atmospheric conditions where, for example, the surface packing of a complex mixture of organics and the proximity of photosensitizers is ill-defined.

**Organic oxidations and particle formation in the Anthropocene**

Organics are a ubiquitous component of atmospheric particles (Fig. 5). A large fraction of SOA typically originates in the oxidation of biogenic VOCs (BVOCs), which results in a “modern” carbon \textsuperscript{14}C isotope signature.\textsuperscript{326–328} Biogenic
emissions are impacted by anthropogenic activities, for example by drought associated with climate change.\textsuperscript{329} However, accurate assessment of biogenic emissions is challenging due to their dependence on a large number of factors such as plant type, temperature, sunlight intensity, soil characteristics, and stressors such as attack by insects.\textsuperscript{330,331} Recent modelling efforts that include 147 individual species suggest that a relatively small number of compounds (about a dozen) are responsible for \textasciitilde80\% of the BVOC emissions, with isoprene and the monoterpenes dominating.\textsuperscript{332}

Ozone–alkene reactions

The reactions of biogenic alkenes with the increasing amounts of O\textsubscript{3} (Fig. 4) are particularly important in SOA formation. The first steps in alkene ozonolysis are well-known, involving the formation of a primary ozonide which decomposes to an aldehyde or ketone and a carbonyl oxide, known as a Criegee intermediate. Criegee intermediates (CI), were first proposed about 1950 by Rudolph Criegee,\textsuperscript{333} and can be formed in the reactions of O\textsubscript{2} not only with C\textsubscript{2}C, but also with C\textsubscript{2}N and C\textsubscript{2}P groups.\textsuperscript{334} The reaction is exothermic, and the resulting CI has excess energy through which isomerization (e.g. to a vinyl hydroperoxide, VHP) and decomposition reactions can occur, generating OH radicals\textsuperscript{335–337} which then attack the alkene. Depending on the nature of the CI and pressure, collisional deactivation can lead to the formation of stabilized Criegee intermediates (SCI). Reactions of SCI with atmospheric species such as water vapor dimer are believed...
to be important in air, and theoretical studies suggest that interface reactions of the CI with water could also occur.

However, SCI also react with organics to generate SOA, whose composition is sensitive to the structure of the SCI. For example, in the trans-3-hexene reaction with O$_3$, the SOA composition reflects sequential addition of Criegee intermediates to RO$_2$ radicals, which is also predicted theoretically for the CH$_2$OO Criegee intermediate. However, for larger alkenes of more complex structure such as α-pinene or α-cedrene, the chemistry of Criegee intermediates is clearly much more varied, resulting in SOA with very complex composition.

A major advance in understanding this chemistry has been the development of techniques to directly detect SCI in the gas phase and to generate them in a relatively clean manner, for example from the reaction of O$_2$ with α-iodoalkyl radicals CH$_2$I and CH$_3$CHI to form CH$_2$OO and both the syn- and anti- forms of the CH$_3$COO Criegee intermediate, respectively. While these are sufficiently stabilized to undergo bimolecular reactions, they may still contain some excess energy. The ability to generate SCI has facilitated studies of the spectroscopic properties and reactions of SCI with many different potential atmospheric species, and there has been an explosion of papers in this area (e.g., see recent reviews).

Alkyl peroxy radicals (RO$_2$) are formed in ozone–alkene reactions, either through the reactions of the Criegee intermediate or through the generation of OH radicals which then attack the alkene. There is now experimental evidence that some larger RO$_2$ radicals can undergo intramolecular isomerization and become increasingly oxidized through an autooxidation mechanism, as known for many years to occur in the condensed phase and predicted earlier for the gas phase. Structure plays a key role in determining the importance of this pathway, with endocyclic alkenes particularly exemplifying this chemistry. For example, Fig. 13 shows the initial steps in the ozonolysis of 1-methylcyclohexene, forming an RO$_2$ radical through the VHP channel of the Criegee intermediate; quantum chemical calculations support the occurrence of a 1,6-hydrogen transfer with an energy barrier of ~21 kcal mol$^{-1}$ and a rate constant of 0.27 s$^{-1}$ to form a hydroperoxide and a new alkyl radical. The autooxidation mechanism then continues to form highly oxygenated, extremely low volatility organic compounds (ELVOC). Measurements of highly oxidized RO$_2$ radicals in the ozonolysis of α-cedrene are consistent with an autooxidation mechanism in that case as well. It is interesting, however, that calculations for intermediates in the ozonolysis of α-pinene suggest analogous mechanisms are not as energetically favorable, despite the presence of a similar methycyclohexene structure. Alternative mechanisms that still involve autooxidation as initial steps, have been proposed to explain high molecular weight particle phase products, such as the formation and uptake of diacyl peroxides into particles followed by their decomposition.

SOA phase

Given the thousands of potential SOA precursors in air and the range of oxidation products they form, there are a wide range of structures and volatilities of species that could contribute to SOA. As seen in Fig. 14, these are often lumped into bins designated VOC, IVOC, SVOC, LVOC and ELVOC according to
their saturation vapor pressures (I = intermediate, S = semi-, L = low, EL = extremely low). Given their very low vapor pressures, ELVOC are believed to be important in the earliest stages of particle formation and growth in air, while somewhat higher volatility compounds contribute more to their subsequent growth. However, analysis of SOA composition in some field studies suggests that more volatile products can be found in SOA than expected based on their volatility. This may be related to the particle phase and growth mechanisms.

Fig. 13 Some initial steps in the 1-methylcyclohexene oxidation that lead to the formation of ELVOCs through an autooxidation mechanism for RO2 radicals. VHP = vinyl hydroperoxide. Adapted from ref. 371.

Fig. 14 One classification scheme for organic compounds by volatility. Adapted from ref. 379.
Understanding the phase of organic particles is important for quantifying exchange with the gas phase, understanding water uptake, describing the chemistry in the bulk and on the surface, and being able to predict the growth and composition of SOA in air. Phase also affects photochemistry in SOA. It had been assumed until relatively recently that SOA particles were oily liquids. Given particle diameters of the order of a few hundred nanometers and typical diffusion constants in liquids, diffusion of gases in and out of the particles should be quite rapid, on the order of ms for 100 nm particles; on the other hand, it can be as much as a year for high viscosity particles (Fig. 15). In this case, exchange with the gas phase is not sufficiently fast that quasi-equilibrium can be assumed (as has been the case in most atmospheric models) and a kinetically limited, condensation type mechanism must be considered. In the latter case, molecules that adsorb on the surface with a sufficient residence time become incorporated into the particle, and once this happens, it is essentially irreversible. Of course, there will be intermediate cases where diffusion is sufficiently slow that the quasi-equilibrium assumption is not valid, yet exchange with the gas phase can occur on similar timescales as removal of particles from the atmosphere.

For relatively simple systems, viscosity (\( \eta \), Pa s) and the diffusion coefficient (\( D \), \( \text{cm}^2 \text{s}^{-1} \)) are inversely related through the Stokes–Einstein (S–E) equation developed to describe the diffusion of large spherical molecules through a continuum of solvent that provides frictional resistance. Although the S–E equation provides a first-order approach to the relationship between viscosity and diffusion coefficients, its assumptions may not always be met for diffusion of species in SOA. For example, diffusion of water in sucrose solutions of well-defined viscosity and in SOA can differ from the S–E relationship by orders of magnitude.

Fig. 15 (a) Range of viscosities with some common examples, and corresponding estimated diffusion coefficients; (b) diffusion times in particles of different sizes for different viscosities and diffusion coefficients. Adapted from ref. 387 and 391.
magnitude under some conditions. A number of interesting experimental approaches to determining viscosity of SOA have been developed and applied recently.\(^{396-400}\)

One of the first indications that some SOA may not be liquid came from studies of particle bounce in impactors,\(^{401-404}\) a phenomenon recognized for many decades during atmospheric sampling.\(^{405-414}\) Fig. 16, for example, shows impaction patterns on a germanium attenuated total reflectance (ATR) crystal for dry and wet inorganic salts as well as for SOA formed from \(\alpha\)-pinene ozonolysis.\(^ {404}\) Liquid sodium sulfate (Na\(_2\)SO\(_4\)) particles form a series of “spots” immediately below the holes in the impactor, as expected for liquids which do not bounce, while dry solid Na\(_2\)SO\(_4\) or ammonium sulfate ((NH\(_4\))\(_2\)SO\(_4\)) form “clouds” due to bounce either along or perpendicular to the air flow. When grease is applied to the crystal, the bounce stops (Fig. 16b). The pattern for SOA is similar to that of the dry salts, indicating it does not behave like a liquid.

Since the initial discovery of semi-solid SOA particles, there have been many different studies and approaches to understanding the phase and related properties of these particles under different conditions of formation and of subsequent changes in exposure (e.g., to water vapor).\(^{404,414-421}\) Li et al.\(^ {416}\) summarized published studies of viscosity, diffusion coefficients and related phenomena such as evaporation of components from SOA, as well as chemical reactivity. In brief, there is not yet a coherent picture that provides a basis for predicting phase, viscosity and effects on reactivity etc. over a broad range of conditions. Variables include the nature and concentrations of the SOA precursors and the experimental conditions, e.g., temperature, whether water is present during or after SOA formation, the sampling collection and handling procedure, whether an OH scavenger is present in ozone–alkene reactions, the presence or absence of NO\(_x\), etc.

Despite the breadth of approaches, systems and experimental conditions studied to date, there are some common trends. First, viscosity decreases and diffusivity increases when RH is increased either during SOA formation or if SOA

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**Fig. 16** Impaction patterns from the impaction of particles of liquid Na\(_2\)SO\(_4\), dry Na\(_2\)SO\(_4\), dry (NH\(_4\))\(_2\)SO\(_4\) and dry SOA from \(\alpha\)-pinene ozonolysis. The ones marked “greased” have vacuum grease applied to the right half of the surface to prevent particle bounce; the impacted particles can be seen embedded in the center of the grease. The mechanisms leading to the patterns are shown schematically on the left. Adapted from ref. 404.
is formed under dry conditions and is subsequently exposed to increasing water vapor concentrations. Second, diffusivity depends on the nature of the diffusing molecule as expected, with water diffusing faster ($D \sim 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ at 280 K)\textsuperscript{395} than larger compounds like pyrene ($D = 2.5 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$)\textsuperscript{415} or pinonaldehyde and acetic acid ($D \sim 3 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ within a large, order of magnitude, error bar)\textsuperscript{382}. Third, SOA with smaller O : C ratios and those formed from larger precursors tend to remain semi-solid at higher RH\textsuperscript{416}.

Fig. 17 demonstrates the importance of having a full understanding of the phase of particles. These studies attempted to model particle formation and growth (so-called “banana plots”) in several different locations assuming that the particles were liquid and that quasi-equilibrium with the gas phase applied, or that some fraction was solid, for which a condensation mechanism applied. The best fit to the experimental observations required that at least 50% proceeded via a condensation mechanism characteristic of highly viscous SOA\textsuperscript{422}.

**SOA structure and composition**

Associated with the composition and phase of SOA is the issue of the 3-D structure of SOA particles. If particles are liquid, they should be well-mixed, while if they are semi-solids, this might not be the case. One illustrative example (albeit not directly atmospherically relevant), is the formation of organic particles on a surface from the ozonolysis of a terminal alkene covalently bound to a surface in the form of a self-assembled monolayer.\textsuperscript{423} A free radical reaction occurred that detached the chain from the surface and formed large organic aggregates that were detected by atomic force microscopy (AFM), scanning electron microscopy (SEM) and Auger electron spectroscopy. Single particle FTIR indicated that the

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**Fig. 17** Measured (a) and predicted particle formation and growth on April 15, 2007 in Hyytiäälä, Finland using the assumption of equilibrium partitioning, (b) 100% equilibrium partitioning; (c) 50% equilibrium partitioning and 50% condensation mechanism, and (d) 100% condensation mechanism.\textsuperscript{422} The more red the colors, the larger the particle number $(N)$ concentration expressed as $dN/d\log D_p$ where $D_p$ is the particle diameter. Adapted from ref. 422.
aggregates were highly oxidized (Fig. 18a). However, depth profiling using secondary ion mass spectrometry (nanoSIMS) showed that the O : C ratio was not uniform throughout, but rather increased from the surface into the interior (Fig. 18b). This suggests that during formation the aggregates self-assembled with oxygenated polar groups buried inside a hydrophobic shell (Fig. 18c). In this case, despite what is presumably a high oxygen content on average, one would not expect the aggregates to be efficient in taking up water. If this mechanism holds for some particles, they may not have the ability to serve as cloud condensation nuclei (CCN) and a correlation between water uptake and CCN activity with degree of oxidation or O : C ratio would not necessarily be expected. This is, in fact, observed in some cases.424,425 However, this is clearly an area that requires much more in-depth, molecular level understanding in order to define the implications for ambient air, particularly in a changing climate.

While aqueous phase chemistry of SO2 and NOx is reasonably well-established,27 less is known about the chemistry and photochemistry of organic compounds in the condensed phase. Atmospheric particles may be organic, aqueous, homogeneous or heterogeneous. For example, when particles contain significant amounts of some organics as well as an aqueous phase with dissolved electrolytes, liquid–liquid phase separation426–431 can occur, providing both organic and aqueous phases within one particle. The aqueous phase may be in the

![Fig. 18](image-url)
form of clouds and fogs, or aerosol particles. These media differ in liquid water content, from $\sim 10^{-6}$ to 0.1 cm$^3$ liquid water per m$^3$ of air from particles to clouds/fogs, and in concentrations of dissolved species as reflected, for example, in the ionic strength which can vary from 10 M or more to $10^{-4}$ M from particles to clouds and fogs. There is increasing evidence for rich chemistry and photochemistry of organic compounds in these condensed phases. Detailed treatment is beyond the scope of this paper, but there are a number of excellent discussions of this area since it was highlighted by Blando and Turpin.

Thermal reactions include accretion reactions such as aldol condensation reactions, acetal and hemiacetal formation and the formation of esters and oligomers, as well as reactions with non-photochemically derived species such as ozone and amines. For example, reactions of ammonia and amines, both associated in part with agricultural activities, with components of SOA form nitrogen-containing organics such as imidazoles that absorb light in the visible region, dubbed “brown carbon”. These compounds affect the optical properties of the particles and have also been proposed to act as photosensitizers to form more SOA. Thermal reactions involving uptake of carbonyl compounds such as glyoxal, followed by hydration and then reaction with sulfate ions are known to generate organosulfates. Reactions of epoxides, for example from isoprene oxidation in the atmosphere, also generate significant amounts of organosulfates via ring-opening reactions with sulfuric acid/sulfate. Photochemical reactions in the condensed phase include direct absorption and photochemistry by organics, photosensitized reactions induced by interactions with excited triplet states (e.g. ref. 306, 471 and 472) and reactions with species generated by photochemistry such as the OH radical and likely singlet oxygen, $O_2(1\Delta_g)$ as well.

Oxidation in the condensed phase has been increasingly recognized to be important not only for determining the chemical and physical properties of SOA but also potentially for their health effects, where oxidants can initiate inflammatory responses. The term reactive oxygen species (ROS) is defined in practice as any species that oxidizes a selected non-fluorescing organic to an oxidized, fluorescing form. It includes free radicals such as OH, HO$_2$ and organic free radicals, superoxide anion, peroxynitrites and H$_2$O$_2$ as well as organic peroxides. Uptake of some of these from the gas phase is one source of the non-ionic species, and photochemical reactions involving transition metals such as iron is another. Reactive oxygen species have also been reported to be generated in SOA formed from oxidation of small carbonyls such as methyglyoxal and from biogenic VOCs in solution as well as from the interaction of SOA with water. Understanding the role of ROS in health impacts is clearly an area of great interest.

In short, much remains to be learned about the chemistry and photochemistry of organics in the condensed phase under atmospheric conditions. This is especially challenging due to the complex mixtures involved, the presence of both organic and aqueous phases with a range of viscosities, and the wide range of concentrations that are found. Advances in both experimental and theoretical approaches have proven invaluable and their continuing integration is important for advancing our understanding of multiphase processes in the atmosphere and their impacts on human health, visibility, climate and weather.
Sulfur compounds in the Anthropocene

Sulfur dioxide from fossil fuel combustion is oxidized in air to sulfuric acid through a combination of gas and aqueous phase processes, with some contribution from heterogeneous reactions on surfaces.\textsuperscript{27} Sulfuric acid has been credited as the major source of new particle formation in air for many decades.\textsuperscript{489} For example, small clusters containing up to four sulfuric acid molecules have been observed to be correlated to nucleation events.\textsuperscript{490} However, the observed rate of new particle formation in air from water and sulfuric acid\textsuperscript{491} is typically many orders of magnitude larger than predicted by classical nucleation theory.\textsuperscript{489,492,493} A key discovery has been that amines, as well as ammonia, play a central role in new particle formation.\textsuperscript{489,491,494–506} There are many sources of these bases,\textsuperscript{451,452} including livestock operations,\textsuperscript{507} food processing and cooking, composting, sewage treatment, combustion and tobacco smoke.\textsuperscript{451} One source of amines that may increase in the future is carbon capture and storage that uses amines to capture CO\textsubscript{2}.\textsuperscript{508–512}

Although much less is known about the role of organics in new particle formation, there is increasing evidence that under many atmospheric conditions they may play a key role in stabilizing and growing small sulfuric acid–amine clusters (Fig. 19) to detectable particle sizes\textsuperscript{378,513–515} and ultimately to $\sim$100 nm where particles scatter light effectively and also serve as CCN.\textsuperscript{516,517} In addition, there are direct interactions of some organics with sulfuric acid to form/grow particles.\textsuperscript{518–523}

There have been significant reductions in anthropogenic SO\textsubscript{2} emissions since the 1970’s (Fig. 20).\textsuperscript{524} While this is expected to have a substantial influence on particle formation in air, SO\textsubscript{2} will continue to be formed from oxidation of organosulfur compounds\textsuperscript{525,526} such as dimethyl sulfide (DMS). These compounds have a wide variety of biogenic oceanic and terrestrial\textsuperscript{527–533} as well as anthropogenic sources including agricultural activities, landfills and municipal waste\textsuperscript{95,534–544} and even human breath.\textsuperscript{545,546} Thus, even in the absence of the combustion of sulfur in fossil fuels, some SO\textsubscript{2}, and hence sulfuric acid and sulfate particles, will be formed.

![Fig. 19](image)

Fig. 19 Schematic of the role of organics in new particle formation and growth from sulfuric acid and amines. Adapted from ref. 513.
Another product of the oxidation of organosulfur compounds is methanesulfonic acid, CH$_3$S(O)(O)OH (MSA). While initial studies suggested that MSA would not contribute to new particle formation in air due to its higher volatility compared to sulfuric acid,$^{547,548}$ subsequent studies have shown that like H$_2$SO$_4$, MSA does form particles in the presence of amines and water vapor.$^{549-552}$ However, the mechanism of MSA formation has not been entirely clear. As shown for DMS oxidation in Fig. 21, MSA can be formed via the generation of the free radical CH$_3$S(O)(O)O$^-$, followed by hydrogen abstraction. While abstraction from organics had been suggested, there was little direct experimental evidence for this.

This is again where quantum calculations prove very helpful.$^{553}$ As seen in Fig. 22, reaction of CH$_3$S(O)(O)O with HCHO is predicted to proceed via a submerged transition state in a barrierless reaction. While the radical reaction with CH$_4$ does have a barrier, other hydrocarbons such as those with weaker...
allylic C–H bonds may have smaller barriers and potentially also contribute to MSA formation. Modelling studies that include DMS oxidation as a potential source of particles in the South Coast Air Basin of Southern California show that MSA and H₂SO₄ could be comparable once fossil fuel sulfur emissions have been eliminated. However, note that in these studies NOₓ emissions were kept constant and as seen in Fig. 21, NOₓ plays a role in forming MSA, something which has been observed in laboratory studies. Supporting the potential role of NOₓ in the mechanism are observations in some field campaigns that MSA is correlated with NOₓ.

Biogenic–anthropogenic synergies in the Anthropocene

There are increasing numbers of examples of synergistic interactions between anthropogenic and natural emissions. These include the effect of NOₓ on the formation of MSA during the oxidation of DMS, and the role of biogenic oxidations by anthropogenically derived oxidants in SOA formation discussed above.

A third example is the interaction of oxides of nitrogen with sea salt particles. Dinitrogen pentoxide (N₂O₅) formed in the gas phase from the reaction of the NO₃ radical with NO₂ (ref. 27) undergoes rapid hydrolysis on surfaces and in particles to form HNO₃. This reaction has been shown in both laboratory and field studies to be impeded by the presence of nitrate ions. Organic coatings also appear to decrease N₂O₅ uptake on particles, although this may be sensitive to the relative amounts of water present (and hence relative humidity) as well as the viscosity of the organic coating. If chloride ions are present, there is a competing reaction to form nitryl chloride, ClNO₂. It is interesting that the chloride ion reaction occurs at the interface, while that with water occurs deeper into the bulk of the particle.

Field campaigns have documented the formation of ClNO₂ in coastal urban regions and other areas influenced by both sea salt particles and oxides of nitrogen, with ClNO₂ correlated to gas phase N₂O₅ as predicted from laboratory studies. A surprising observation is the formation of ClNO₂ at inland...
continental locations removed from sources of sea salt (Fig. 23).\textsuperscript{582–584} This has usually been attributed to the reaction of N\(_2\)O\(_5\) with particulate chloride, with the source of the latter possibly being uptake of HCl from the gas phase. Another potential source in cold climates is road salt.

The possible mechanism harks back to reactions of oxides of nitrogen on surfaces discussed earlier. For example, exposing silica surfaces to N\(_2\)O\(_5\) and gas phase HCl generates ClNO\(_2\),\textsuperscript{585} which was proposed to occur \textit{via} ionic forms of oxides of nitrogen (and possibly the HCl) stabilized on surfaces:

\begin{equation}
\text{NO}_2^+\text{NO}_3^- + \text{HCl} \rightarrow \text{ClNO}_2 + \text{HNO}_3
\end{equation}

Fig. 23  Measurements of N\(_2\)O\(_5\) and ClNO\(_2\) near Boulder, CO from February 11–25, 2009. Adapted from ref. 582.

(a) Infrared peak due to NO\(_2^+\) before and after the addition of gas phase HCl, and (b) quantum chemical calculations showing how water assists in the reaction, rather than competing. Adapted from ref. 585.
Indeed, NO$_2^+$ was observed on an ATR ZnSe crystal by infrared spectroscopy, and as seen in Fig. 24a, the peak disappeared on exposure to gas phase HCl. The yields of ClNO$_2$ increased with water vapor concentration up to the predicted maxima ($\Delta$ClNO$_2$/$\Delta$N$_2$O$_5$ = 1), which was surprising since water was expected to compete with the HCl reaction, forming HNO$_3$ instead:

$$\text{NO}_2^+\text{NO}_3^- + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$$

However, theory predicts that even one water molecule promotes the autoionization of N$_2$O$_5$ to NO$_2^+$, and the subsequent reaction with HCl is predicted to be barrierless in the presence of two water molecules (Fig. 24b). In addition, ab initio molecular dynamics simulations show that for water films on surfaces, N$_2$O$_5$ can be stabilized at the air–water interface in such a way that reaction with Cl$^-$ via an SN2 reaction can occur. Baergen et al. proposed that similar chemistry could occur in “urban grime” which contains both oxides of nitrogen and chloride ions, as well as a complex mixture of organics.

A fourth example involves SOA formation in areas that have large biogenic emissions. It has been noted that SOA concentrations in air are significantly larger in the southeastern U.S. than in the Amazon, despite the much larger sources and concentrations of biogenic precursors in the latter location. One mechanism suggested for SOA production is the reaction of smaller, soluble organics in the aqueous phase of particles to generate larger, low volatility products that remain in the condensed phase when the water evaporates. In this case, SOA will be impacted by the availability of water in particles and the composition of the aqueous phase, especially the pH, which is largely determined by the presence of hygroscopic anthropogenically derived species such as sulfate and nitrate. This is an example of how the interplay between biogenic and anthropogenic species can introduce new, unexpected chemical mechanisms that would occur only in the Anthropocene era.

**Summary**

Research over the last decades has led to a vastly increased understanding of anthropogenic emissions, their chemistry, their interactions with natural systems and the ultimate impacts of these processes. The spatial and temporal scales involved in different aspects of the problem are very challenging, and will require additional new approaches for laboratory and theoretical studies as well as field measurements and modelling. Although not addressed here in detail, there is a need to develop analytical techniques for a number of different purposes such as probing the molecular composition of particles layer-by-layer, elucidating the nature of surface-bound oxides of nitrogen, and measuring both gases and particles at scales appropriate to the problem at hand. For example, while relatively long-lived gases such as CH$_4$ do not generally need to be measured on small spatial scales, species that impact human health need data ideally at or close to the point of inhalation. The development of small, low-cost, robust analytical techniques that can be reliably calibrated as well as the widespread use of
instrument platforms such as unmanned aerial vehicles (UAVs, “drones”) will be needed to address these problems.

Clearly a number of research issues remain that need to be addressed in order to fully understand atmospheric chemistry in the Anthropocene, which in turn will provide a quantitative foundation for control strategies that minimize impacts on human health and welfare.

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