Opinion: Papers that shaped Tropospheric Chemistry

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Abstract

Which published papers have transformed our understanding of the chemical processes in the troposphere, and shaped the field of atmospheric chemistry? By way of expert solicitation and interactive peer-review, this paper explores the influence of the ideas in peer-reviewed articles based on the input from our community of atmospheric scientists. We explore how these papers have shaped the development of the field of atmospheric chemistry, and identify the major landmarks in the field of atmospheric chemistry through the lens of those papers’ impact on science, legislation and environmental events. We also explore the ways in which one can identify the papers that have most impacted the field and discuss the advantages and disadvantages of the various approaches.
1. Introduction

Air quality and anthropogenic climate change are two environmental issues of current importance to society. Atmospheric composition is central to both these issues. The atmosphere, and its components, supports life on Earth. In turn, the atmosphere is affected by human population growth and industrialization, as well as all the consequences of those changes. The changes in atmospheric composition also influence the ecosystem on which humans rely.

Air pollution (née composition) and its impacts have a history stretching back to antiquity – see for example the expositions in (Brimblecombe, 1987; Fuller, 2018; Jacobson, 2002; Stern, 1968; Sportisse, 2010; Preining and Davis, 1999; Fowler et al., 2020) and others. Changes in atmospheric composition, with their negative impact particularly on human health (Lelieveld et al., 2015), ecosystems (Fowler et al., 2009) and latterly links to their climate (see for example, (Fiore et al., 2012; von Schneidemesser et al., 2015)), have become primary global concerns during the 20th century. As an academic subject, air pollution has mostly been systematically studied only since the mid-late 20th Century. There have been several recent reviews, (e.g., (Brasseur et al., 2003; Monks et al., 2009; Ravishankara et al., 2015; Ravishankara, 2003)), which have mapped the growth of atmospheric chemistry, but it is not only peer-reviewed papers that provide relevant overviews. It is important to note that when dealing with the development of this subject (or any scientific subject for that matter), much of the baseline knowledge is embodied in textbooks, which for many are the entry point to and the primary reference for the topic (e.g. (Jacob, 1999; Wayne, 2000; Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 2006; Brasseur et al., 1999).

Figure 1 shows the number of peer-reviewed by year that mentioned the phrase “atmospheric chemistry” in the text, as catalogued by the Scopus bibliographic database (https://www.scopus.com/). It shows a growth in the later 70s from around a hundred papers a year to approximately 4,000 a year currently, with a large increase especially over the past two decades. Of course, many more papers discuss atmospheric chemistry, or are relevant to it, without explicitly mentioning these words!
This paper aims to recognize and highlight some of the most influential peer-reviewed articles that have shaped this field. There were many pivotal scientific discoveries and there were many papers that spurred action and further research. What were the significant discoveries that shaped the atmospheric chemistry of today? And how do we narrow down the list contributions to highlight the most impactful ones?

There are many ways to choose the papers that described discoveries and influenced atmospheric composition and chemistry. Here we have assembled an initial\(^1\) compilation of influential articles. Our goal is not to show what makes a ‘great’ paper, which depends not only on the science, but also the quality of the writing, readability, and structure of the written work – all criteria that are highly subjective. Nor are we aiming only for those papers that led to policy and management actions. Instead, we try to reflect on the papers’ science and content and the influence of the ideas in those papers on our community of scientists and on the field’s development. Our approach is to present our thoughts – informed by the solicitation for input from colleagues in the field – and share what we think are the fundamental discoveries and developments, start a discussion, and allow others to build on, reinforce or critique our work.

In addition to peer-reviewed papers, and the above mentioned textbooks, we have of course other mediums through which we communicate (have communicated) with our peers. These include scientific reports, conferences, and meetings. In addition, we have scientific assessments and evaluations, which often get more scrutiny and reviews than the peer-reviewed papers they include. These days, other communication media, such as social media, have also become prevalent as formats for exchange both within the scientific community and with a broader audience. However, the entire community cannot attend all conferences and meetings, the scientific reports are not always accessible and often not peer-reviewed, and the assessments are often driven more by policy needs

\(^{1}\) Initial as it is intended to be informed by the community through an open review process as outlined later.
rather than by scientific discoveries. Publishing peer-reviewed papers is the closest we come to reaching the whole community. We do note that, despite its known issues, peer-reviewed literature is still considered the gold standard for quality and reliability. For these reasons, we discuss only peer-reviewed papers here, although we aim to communicate the overarching scientific advances that shaped the field.

1.1. How were the papers selected?

Easily measurable criteria, like the number of citations, are one metric. However, this approach favours papers of a particular vintage and not necessarily the earlier or later papers. Besides, there are several drawbacks to these simple and objective criteria. Citations tend to go down when something is assumed to be common knowledge and makes it into textbooks or compilations. For example, nobody cites Priestley for discovering oxygen or Schönbein for discovering ozone, whenever atmospheric composition is mentioned. Indeed, some of the central concepts of atmospheric chemistry and physics are considered to be common knowledge, and their origins are taken for granted. The number of citations will also be influenced by the journal in which a paper is published, and quite often (we hate to say this) also depends on who else cited them and in which journal they were cited. Citations also depend on how many people are otherwise researching a particular subject. Furthermore, critical assessments and expert data evaluations suppress the citation of the original papers. This is particularly the case, for example, for papers on chemical kinetics and photochemistry, whereby people tend to simply cite the data evaluations such as NASA/JPL (https://jpldataeval.jpl.nasa.gov/) or IUPAC (http://iupac.pole-ether.fr/) panel reports. Similarly, people often cite the quadrennial ozone layer depletion and IPCC assessments, thereby obfuscating the underlying original papers. Other types of papers, such as reviews, tend to get an excessive number of citations (for understandable reasons). Lastly, we cannot overlook the influence of journal availability in different parts of the world. This availability is exacerbated when journal costs go up, and not everybody can access new papers. Nevertheless, there is still a relevance to the number of citations of a paper. We show, for example, the 10 most-cited papers if we were to search on the combination of words “atmospheric and chemistry” in Table 2.

For all the above reasons, we decided to use a different approach here. We solicited the scientific community to obtain input from the experts in the field. To accomplish this, we put out a call through the International Global Atmospheric Chemistry (IGAC) (Melamed et al., 2015) project to its contacts and thereby engaged a broad audience. Despite the broad audience of IGAC, the vast majority of responses came from scientists in North America and Europe. An initial list of influential papers was established by combining the replies received from the expert solicitation to evaluate the most nominated papers. In addition, a variety of perspectives were assembled for the writing team, including different career stages, nationalities, and genders. Despite all these efforts, the selection methods will still inevitably create bias that cannot be escaped. Therefore, in many respects, the chosen papers are not supposed to be a definitive list, but rather a compilation that allows researchers to discuss and reflect on what makes impactful science, and maybe ponder on the landmarks in our subject. Furthermore, we hope that the end product can provide an interesting history and context to those who are joining the community and document the current “perception” of what are the most important papers.

We have noted the drawbacks in our methodology simply to present upfront some of the limitations of what we did in this paper. However, we hope that others will find this work relevant and engaging, and actively participate during the peer-review process, so that we can obtain the perspective of a
broader community more reflective of the global composition of the field. To facilitate this, we submitted the paper in an open-access and interactive review that includes a public comment period. We hope that this approach will overcome some of the limitations and reservations we expressed earlier. We invite and encourage you, the reader, to weigh in on the choices and help determine the final shape of this overview. We shall seek to reflect this discussion in the final version.

1.2. Scope of work

As with the selection method, one can debate the scope and the methodology for a work such as this. Still, the boundaries we have drawn encompass studies that have shaped our understanding of the atmosphere and the underlying chemical and physical processes, focusing mostly on the troposphere. This includes modelling, field measurements, remote sensing, and laboratory studies (Abbatt et al., 2014). We have also included atmospheric interactions with the biosphere, cryosphere, and hydrosphere.

We selected 2010 as the cut-off year. Our rationale is that for a paper to have been influential in the whole field it must be at least ten years old and thus had time to accrue recognition. We recognize that important papers in newer areas of endeavour are disadvantaged by this criterion. Examples include the subjects of SOA formation (Ehn et al., 2014; Crounse et al., 2013), the chemistry of Criegee intermediates (Welz et al., 2012), galactic rays induced aerosol nucleation (Kirkby et al., 2011), and air pollution-climate connections (Shindell et al., 2012). Influential assessments such as bounding black-carbon (Bond et al., 2013) are also missed. However, these areas will undoubtedly be recognized in the coming decades. The ten-year window also allows the scientific community to have had extensive input on a paper’s validity, i.e., meeting the criterion of “standing the test of time.”

The papers have been grouped into the following general categories and are presented as such in Section 2.

1. Foundations
2. Aerosols and Clouds
3. Secondary Organic Aerosols
4. Chemical Kinetics, Laboratory Data and Chemical Mechanisms
5. Heterogeneous and Multiphase Chemistry
6. Chemical Models
7. Tropospheric Ozone
8. Nitrogen Chemistry
9. HOx Chemistry
10. Nighttime Chemistry
11. Halogen Chemistry
12. Volatile Organic Compounds
13. Biogenic Emissions & Chemistry
14. Biomass Burning
15. Emissions and Deposition
16. Chemical Transport
17. Satellites and the Troposphere
18. Stratospheric Chemistry
19. Other issues that influenced tropospheric chemistry
The groups were chosen to reflect the main areas of research or endeavour, recognizing that this division could be done in several different ways. There is no assumed equivalence in these groups regarding their perceived or real importance or impacts. In the following, we discuss the papers in each group to show why they have been nominated and to put them in the historical context of the development of atmospheric chemistry as a discipline.
2. Survey of Areas

2.1. Foundations

Atmospheric chemistry has some long-standing and deep roots. However, it blossomed in the second half of the 20th century following concerns about the ozone layer depletion and various forms of tropospheric pollutions, including such as Los Angeles smog, London smog and acid precipitation (Table 1). Many note John Dalton’s early contributions on the proportion of gases in the atmosphere (Dalton, 1805) and John Tyndall’s Bakerian lecture on radiation and gases (Tyndall, 1861) as among the first studies in this field. The work of Arrhenius “On the Influence of Carbonic Acid in the Air upon the Temperature of the Ground” (Arrhenius, 1896) and the subsequent paper of Callendar, “The artificial production of carbon dioxide and its influence on temperature” (Callendar, 1938), laid the groundwork for the linkage between atmospheric chemistry and climate. Concerning aerosols, the seminal work of John Aitken (Aitken, 1888) “On the number of dust particles in the atmosphere” details early work to count the number per cubic centimeter in various indoor and outdoor environments. It is interesting to note that physiologists looking at the number of live germs in the air stimulated Aitken’s work. The later work of Köhler (Köhler, 1936) which explored cloud droplet nucleation remains the basis for later work (see the Aerosols and Clouds section). The start of atmospheric chemistry as a distinct discipline probably arrived with Chapman’s chemical theory of the stratospheric ozone layer in 1930 (Chapman, 1930), which will be further discussed in the Stratospheric Chemistry section. This study heralded the importance of atmospheric chemistry on a global scale.

In analyzing the influential papers on atmospheric composition, one cannot help but note the relationship between these papers and the most significant contemporary environmental issues (Table 1). The first of these was the Los Angeles smog, which had its European counterpart, the London “Pea-Soup” (Brimblecombe, 1987). The two events, which in chemical terms have no equivalence, had comparable impacts on public health and opinion. The oft recognized work of Haagen-Smit (Haagen-Smit and Fox, 1954; Haagen-Smit, 1952; Haagen-Smit et al., 1953) in the early 1950s on the Los Angeles smog was the first to coin the term “air pollution” in the modern era. Haagen-Smit showed that automobile exhaust gases can form ozone in the air and should, therefore, be considered a definite source of smog. Figure 2, redrawn from Haagen-Smit (1952), shows a schematic presentation of the reactions in polluted air leading to smog. Notably, the basic features of tropospheric chemical processes, as we understand them today, were already recognized in these early papers, and they already showed how ozone could be chemically produced in the troposphere.

It is widely recognized that both Crutzen (Crutzen, 1973a; Crutzen, 1973b) and Chameides and Walker (1973) found that similar “smog reactions” oxidize methane and carbon monoxide to produce substantial amounts of ozone in remote regions of the atmosphere. They estimated chemically produced ozone to be much greater than that transported from the stratosphere, which was believed to be the primary source of this chemical in the troposphere at that point. A few years earlier, in 1970, Hiram Levy II had suggested that the hydroxyl radical, which provides the dominant oxidation mechanism in the troposphere, was formed in unpolluted air by the same mechanism that had been described as occurring in polluted air (Levy, 1971). This paper by Levy (1971) is recognized by many as the first description of the chemistry of the lower atmosphere involving hydroxyl radical reactions of
methane and carbon monoxide, hydroperoxyl radicals, and the photolysis of ozone and formaldehyde as radical sources. In particular, he recognized that the very short-lived electronically excited oxygen atom (O(1D)) is a possible source of the OH radical, an idea now well established.

Around the same time, Weinstock (1969) explained how cosmic rays lead to the production of radiocarbon dioxide (14CO2), which is incorporated into living plants. This process requires a rapid turnover of radiocarbon monoxide (14CO), which was unexpected because the lower atmosphere was thought to be a “chemical desert”. Instead, carbon monoxide appeared to have a turnover time of about one-tenth of a year, primarily driven by hydroxyl radical oxidation. To some, this paper kicked off the research which led to our present understanding of the atmospheric chemistry of the lower atmosphere.

It has been claimed that “acid rain was one of the most important environmental issues during the last decades of the twentieth century” (Grennfelt et al., 2019) (see Table 1). One of the reasons is that acid rain first demonstrated that air quality was not merely a local issue but a regional issue and showed that the atmosphere has no definite boundaries (Fowler et al., 2020). Although the case of acid rain and its effects had been noted and reported by some earlier papers e.g., Odén (1968), for some, it is the paper by Likens and Bormann (1974) that made this issue known to the science community at large. Other early papers (for example, from Urone and Schroeder (1969) and Penkett et al. (1979)) also recognized the vital role of liquid-phase oxidation of SO2 by oxidants such as H2O2 and O3. Current estimates suggest that roughly 50% of the SO2 oxidation in the lower troposphere occurs through liquid-phase reactions.

There is little doubt that one of the most impactful series of papers is that of the eponymous curve by Keeling (Keeling, 1960;Keeling et al., 1979;Pales and Keeling, 1965), showing the steady rise in CO2 measured at Mauna Loa observatory (this work has continued uninterrupted by NOAA/ESRL/CML over the past few decades). Keeling’s work was built on the previously mentioned work of Callendar (1938) who compared measurements of CO2 at Kew, UK (1891-1901) with those in the Eastern USA (1936-1938) and noted an increase in concentration. Although the gas in question is CO2, which is often seen only as climate gas, changes in its levels reflect the changing composition of the atmosphere and the
effects that it can have, and shows that the two subjects cannot be easily separated. Furthermore, the increase in CO₂ is of immense importance to ocean acidification, a topic not touched upon here but nevertheless very important. The seminal paper by Ramanathan et al. (1985) that highlighted the role of methane, chlorofluorocarbons, and N₂O for climate strengthened the case for the inclusion of chemistry in the climate issue. In many respects, this close-coupling between atmospheric chemistry and climate change was brought to the forefront with the 1995 Nobel prize being awarded to Paul Crutzen, Mario Molina and F. Sherwood Rowland “for their work in atmospheric chemistry, particularly concerning the formation and decomposition on ozone”² (see Stratospheric Chemistry section) and, later, with the Nobel prize to the Intergovernmental Panel on Climate Change, IPCC.

2.2. Aerosols and Clouds

Aerosols in the atmosphere greatly influence both air quality and climate change; they are also a significant media for composition change in the atmosphere. In this section we discuss three main areas of aerosol related research: (1) Understanding the mechanisms and atmospheric chemistry processes that influence aerosol formation, nucleation, and growth, and how aerosols affect composition; (2) The role of aerosols as cloud condensation nuclei and the influence that this process has on climate; and (3) The impact of particulate matter on human health. These areas are however, related and there is not always a clear division. Secondary Organic Aerosols (SOA) and Heterogeneous and Multiphase Chemistry are discussed in the corresponding sections (2.3 and 2.5).

The roots of modern aerosol science lie, as previously discussed (see the 2.1. Foundations section), in the works of Aitken (1888) and Köhler in 1936 (Köhler, 1936) on the cloud droplet. Twenty years after Köhler’s research, Junge (1955) provided the power-law describing aerosol number and identified the stratospheric aerosol layer, now dubbed the ‘Junge layer’. Junge concluded: “A real step forward in the understanding of the basic processes in air chemistry can be gained only if aerosol and gases are measured simultaneously but separately, and if the aerosols, in turn, are separated according to size.” This suggestion has been a clarion call for atmospheric scientists ever since.

In 1958, Junge and Ryan (1958) attempted to elucidate the formation of particles from gas-phase reactants, particularly SO₂ and NH₃, while Fitzgerald (1974) investigated the variation in aerosol composition with particle size. They showed that cloud droplet size distribution was insensitive to the specific soluble constituents. Twomey (Twomey, 1977, 1974) suggested that air pollution gives rise to the whitening of clouds and influences the planet’s radiative balance. He also indicated that there is a connection between pollution aerosols and cloud reflectance (albedo). This concept is now often referred to as the “Twomey effect.” Twomey (1977) expanded on the 1974 work, exploring the balance between the scattering vs. absorption effect on the incoming solar radiation. It is on this basis that much of the current research on the role of aerosols via their direct and indirect effect on climate has been built. Bolin and Charlson (1976) estimated that anthropogenic sulfate aerosol from the US and Europe would lead to a global temperature decrease of 0.03-0.06 °C. They recognized early on that “we are already approaching the time when the magnitude of the indirect effects of increasing use of fossil fuel may be comparable to the natural changes of the climate over decades and centuries.”

In the early 1970s, Whitby and Knutson developed an instrument to measure particle size distribution in the nm to µm range (Knutson and Whitby, 1975) – the well-known aerosol mobility analyser. They used the measurements from this instrument to introduce a new formulation of the formation and growth of atmospheric particles and aerosol size modes – the Whitby diagram which is now a common textbook figure and is shown in Figure 3. The outcomes of this work show the importance and influence of the development of new instruments that probe the atmosphere.

The CLAW hypothesis (the acronym taken from the surnames of the proposers Charlson, Lovelock, Andreae, and Warren) (Charlson et al., 1987) further connected aerosol science to gas-phase chemistry, specifically focused on the feedback loop between ocean ecosystems and Earth’s climate. Although the conclusions of the paper have been questioned (Quinn and Bates, 2011), this paper highlighted the interconnections within atmospheric sciences, and environmental sciences in general. The work of Friedlander and co-workers (Stelson et al., 1979) further highlighted the role of liquid-phase chemistry leading to aerosol particles. A key milestone in our understanding of sulfate formation was the recognition that the reaction of HOSO2 with O2 is exothermic (Calvert et al., 1978) and leads to gas-phase SO3, contrary to what was accepted at the time. Prior to this finding, there were major difficulties in understanding the formation of gas-phase H2SO4 formation (Davis et al., 1979).
from SO₂ oxidation, an essential step for the nucleation of new particles from the gas-phase in the atmosphere.

This area of research was further developed by Robbin and Damschen (1981) who investigated the role of peroxide in the liquid-phase in oxidising SO₂ which was key to understanding the phenomenon of acid rain. Graedel and Weschler (1981) reviewed the chemical transformations in atmospheric aerosols and raindrops and extended the idea of Martin and Damschen. Stelson and Seinfeld (1982) evaluated the thermodynamics of ammonium, nitrate, and sulfate aerosols, which was a significant step in understanding particle formation and growth. Pankow’s 1994 work (Pankow, 1994b, a) on the absorption model of gas/particle partitioning of organic compounds in the atmosphere is of fundamental importance for models to calculate the amounts of PM formed and their growth in the urban and regional air, and in the global atmosphere.

Charlson et al. (Charlson et al., 1990; Charlson et al., 1991) produced the first global estimate of the direct aerosol effect that subsequently had a large impact on climate modelling. The role that aerosols would have on CCN and cloud albedo was also acknowledged, concluding that it may be substantial. How substantial, however, was not quantified at that point because of a lack of knowledge on the relationships involved. A few years later, Boucher and Lohmann (1995) provided an estimate of the indirect effect of anthropogenic aerosols on climate. After many additional years of study based on these foundations and analyses of radiative balance, the total radiative forcing by anthropogenic aerosol is now estimated to be roughly -1.1 W/m², thereby solidifying the importance of aerosols in climate change.

Building on the work of Whitby, Mäkelä et al. (1997) conducted continuous monitoring of particles at a forest site in Finland. Beyond confirming the existence of 3 submicron particle size modes (the nucleation, Aitken, and accumulation modes, see also Covert et al. (1996)), they also observed new particle formation events. These events have been subsequently observed by others and are often depicted in the literature using the famous “banana plots” (Figure 4).
Figure 4 - Contour plots of particle formation event occurring in the morning, followed by a subsequent growing process of the nucleation mode during the afternoon. a) February 21st 1996, b) March 13th 1996 and c) April 13th 1996 (Mäkelä et al., 1997). Thought to be the origin of the “banana plot.”

There has been ample recognition for the research on process representations, such as the mole-fraction-based thermodynamic models (Clegg et al., 1998b, a) and one-parameter model for hygroscopic growth and CCN activity (Petters and Kreidenweis (2007)). Facchini et al. (1999) presented experimental work aimed at understanding the role of surface tension in droplet growth and the subsequent effect on cloud albedo and radiative forcing (RF), while Knipping et al. (2000) used a simplified experiment to investigate the role of reactions of gases with ions at the air-water interface.
More specifically, the role of organics in the formation and growth of aerosols particles has been a significant area of research (Kulmala et al., 2000). In addition to the natural hydrocarbons noted above, it has become clear that anthropogenic hydrocarbons such as aromatic compounds are also involved in new particle formation and their growth (Odum et al. (1997).

2.3. Secondary Organic Aerosols

Since the mid-2000s, secondary organic aerosols (SOA) have been the focus of much research, addressing their abundance, sources, and production pathways. One of the foundational works in this area is the recognition of the role of natural and anthropogenic hydrocarbons, and in particular isoprene chemistry in the formation of SOA (Claeys et al., 2004).

The chemical composition of SOA across the globe is still poorly understood (Zhang et al., 2007), although ways to describe the growth of SOA have advanced significantly (Kalberer et al., 2004). Donahue et al. (2006) developed an approach based on the volatility of organics, a concept termed “volatility basis set.” This concept has been extended to a host of volatilities and their classifications. For example, as shown in Figure 5, Robinson et al. (2007) postulated that a large amount of SOA mass is unexplained by current models, and methods used to estimate SOA production do not capture what is measured/observed in the field.

Jaenicke (2005) was the first to suggest that biological particles are an important fraction of atmospheric aerosol. This paper prompted the development of a new and exciting field within atmospheric sciences.

![Figure 5 - Results from the photochemical oxidation of diesel exhaust in an environmental chamber. The grey area indicates the primary aerosol (POA + other species). The red area shows the upper-bound estimate of the contribution of known SOA precursors to the suspended aerosol mass leaving behind a large fraction that is not accounted for (blue area) (Robinson et al., 2007).](https://doi.org/10.5194/acp-2020-1266)
The introduction of the aerosol mass spectrometer (AMS) by Worsnop and colleagues (Canagaratna et al., 2007) along with the pioneering instruments of Prather (Gard et al., 1997) and Murphy et al. (2006) have established that organic compounds are ubiquitous in aerosols. Zhang et al. (2007) and later Jimenez et al. (2009) explored the chemical composition of PM at different sites across a part of the globe, and their work has been extended by a large number of groups.

Aimed at addressing some of the ‘missing urban SOA’ in models, Surratt et al. (2010) investigated SOA production from isoprene and Virtanen et al. (2010) showed the amorphous solid state of biogenic secondary organic aerosol particles, challenging the traditional views of the kinetics and thermodynamics of SOA formation and transformation.

Figure 6 - Total mass concentration (in micrograms per cubic meter) and mass fractions of nonrefractory inorganic species and organic components in submicrometer aerosols measured with the AMS at multiple surface locations in the Northern Hemisphere at mid-latitudes. The organic components were obtained with FA-AMS methods (Zhang et al., 2007). In some studies, the FA-AMS methods identified one OOA factor, whereas in other locations, two types, SV-OOA and LV-OOA, were identified. HOA is a surrogate for urban primary OA, and Other OA includes primary OAs other than HOA that have been identified in several studies, including BBOA. Inset: distributions of O:C for the OA components identified at the different sites (Jimenez et al., 2009).
2.4. Chemical Kinetics, Laboratory Data and Chemical Mechanisms

Chemical kinetics is one of the foundations of atmospheric chemistry (Abbatt et al. (2014)). This includes a number of different areas: investigation of individual chemical reactions; theoretical understanding of elementary reactions; evaluations and compilation of kinetics data; development and compilation of chemical mechanisms for use in models (see the 2.6. Chemical Models section); testing and simplification of the models for use in numerical models. Demerjian et al. (1974) is considered by many in the community to be one of the cornerstones of chemical mechanism development and it has been influential in a number of other research areas as well. This paper provided an explicit chemical mechanism for the troposphere in which all the chemical reactions were written as numerically integrated stoichiometric equations to predict photochemical ozone production rates. Previously, all chemical mechanisms had been highly “reduced” (into simple mechanisms) and/or parameterised, with non-stoichiometric equations. Using Demerjian’s approach, many explicit atmospheric chemical mechanisms have been derived, including one of the most widely used, the Master Chemical Mechanism (MCM, Figure 7) (Jenkin et al., 1997; Jenkin et al., 2003).

Currently, there are a variety of tropospheric chemistry mechanisms that capture the scope of chemical reactions that are used in a number of models including the 1990 Carter mechanism (Carter, 1990), RADM/RACM (Stockwell et al., 1997; Stockwell et al., 1990), SAPRC-07 (Carter, 2010) and the aqueous-phase mechanism CAPRAM (Ervens et al., 2003).

There is no doubt that the chemical kinetic data compilations have been the backbone of providing much needed experimental data to all chemical mechanisms and models (see the 2.6. Chemical Models section). The comprehensive reviews of Atkinson starting around 1986 (Atkinson (1986)) and followed by many others, provided a consistent description of the reaction pathways of the alkyl, peroxy and alkoxy radicals produced by the reactions of hydroxyl radicals with a wide range of organic compounds. These papers led the way for the compilation of the IUPAC and JPL chemical kinetic data evaluation of tropospheric reactions (Atkinson et al., 1989; Crowley et al., 2010; Atkinson et al., 1992; Atkinson et al., 2004; Atkinson et al., 2006; DeMore et al., 1997; Burkholder et al., 2020). (Note that compilation of kinetics data for stratospheric reactions dates back to mid-1970s (Hudson and Reed, 1979)) These works have been the foundation for the development of all chemical mechanisms and have led to the standardisation and improvement of condensed chemical mechanisms used in all chemical models.
The recognition of reactions with negative activation energies and the role of weakly bound adducts were other steps in improving our understanding of chemical kinetics. When the adduct is strong, we term it an association reaction, which exhibits negative activation energies and pressure dependence. Understanding and representing these type of reactions in atmospheric chemistry has been a major step. In particular, the pioneering work of Troe and coworkers have enabled realistic and simpler representation of these reactions based on the Rice-Ramsperger-Kassel-Marcus (RRKM) theory (Troe, 1979, 1994).

Atmospheric chemistry is often termed atmospheric photochemistry since the initiator for many of the reactions is the production of free radicals, which are directly or indirectly the result of solar radiation. Over the decades, the representation of photochemical processes has been well established. A key element is the calculation of the “j-value” (i.e. the photolysis rate) for a photochemical process, which depends on radiative transfer to obtain the solar flux and laboratory measurements of absorption cross sections and quantum yields. The pioneering works on methods for quickly and accurately calculating j-values are those of Madronich and Flocke (1999) and of Prather and colleagues (Wild et al., 2000).

Moving towards individual reactions, the work of Howard and Evenson (Howard and Evenson, 1977) on the reaction between HO$_2$ + NO has been recognised as a scrupulously careful study that overturned conventional wisdom on this key reaction in photochemical smog/ozone formation (and in stratospheric chemistry).

Three papers nearly a decade apart address the fundamental importance of robust laboratory measurements to underpin model-led interpretation of experimental data. The seminal work demonstrating the long-wavelength tail on the ozone photodissociation quantum yield (Ball et al., 1993; Ravishankara et al., 1998) and the related work on the O$_1D + N_2/O_2$ reactions (Ravishankara et al.,...
al., 2002), key processes in the formation of OH radicals in the troposphere. Prompted by the findings
of Lelieveld et al. (2008) (see the 2.13. Biogenic Emissions & Chemistry section), a pair of laboratory
papers published in 2009, about HO₂ radical regeneration in the oxidation of isoprene (Peeters et al.,
2009) and unexpected epoxide formation in the gas-phase photooxidation of isoprene (Paulot et al.,
2009) have changed the way we understand the gas and aerosol products and impacts of isoprene
chemistry (Kleindienst, 2009).

2.5. Heterogeneous and Multiphase Chemistry

Earth’s atmosphere contains various amounts of condensed matter suspended in air. The most visible
condensed matter is, of course, clouds. One can also see aerosols when their concentrations are large;
examples include smog, wildfires, and volcanic eruptions. In addition to clouds, snow and ice provide
different mediums that can alter chemistry. Many chemical reactions occur on the surfaces of particles suspended in air, ice/snow on the ground, and within liquid drops. In general, these processes catalyse reactions that would be very slow in the
gas-phase, such as those between closed-shell molecules, and/or can produce products that do not
form in the gas-phase. For these reasons, heterogeneous and multiphase reactions are of immense
interest, although distinction between heterogeneous and multiphase chemistry is not always clear
(cut (Ravishankara, 1997).

The unique contribution of reactions in/on condensed matter burst into the limelight due to their role
in stratospheric ozone depletion (Solomon et al., 1986). However, such reactions had been recognized
to be important before the ozone hole research, in the oxidation of SO₂ (Urone and Schroeder (1969)
and Penkett et al. (1979)). Since the 1990s, the roles of heterogeneous and multiphase reactions have
been highlighted in many tropospheric processes, as noted here in various sections (see for instance

Chameides and Davis (1982) studied the free radical chemistry of cloud droplets and its impact upon
the composition of rain showing that the radical chemistry in water droplets could drive peroxides
production, which has the ability to rapidly oxidise sulphur species – a strong link to acid rain. Akimoto
et al. (1987) work on the photoenhancement of nitrous acid formation in the surface reaction of
nitrogen dioxide and water vapour demonstrated the existence of an additional radical source in smog
chamber experiments and challenged our understanding of the role of such heterogeneous reactions
in the atmosphere. The work of Mozurkewich et al. (1987), Hanson et al. (1992) and subsequently
Thornton and Abbatt (2005), on the measurements of HO₂ uptake to aqueous aerosol was highly
influential in the debate on the aerosol loss of HO₂, a question that has vexed many modelling studies.

A pioneering paper in tropospheric cloud chemistry is the study by Jacob et al. (1986) in the San
Joaquin valley that used a multiphase measurements and modelling approach to study the formation
of acid fog. Two further papers have brought heterogeneous chemistry to the fore: Dentener et al.
(1996) in their original paper on the role of mineral aerosol as a reactive surface in the global
troposphere showed the potential role of mineral dust on the SO₂, NO₂, and O₃ chemistry, and Jacob
(2000) who reviewed in more detail at heterogeneous chemistry and ozone via HO₂ and NO₂ chemistry
in relation to aerosols and cloud droplets producing a highly cited series of recommendations for
future studies.
Another similar area is the role of chemical reactions on/in snow and ice. Such reactions were highlighted by Barrie et al. (1988), specifically with regard to the role of halogens at the surface layer in the troposphere, and hinting at the role of the cryosphere as a source of chemical species to the atmosphere (see the 2.11 Halogen Chemistry section). Given the extent of the cryosphere and in particular of snow (Grannas et al., 2007), results in the late 1990s demonstrated its role in promoting heterogeneous reactions as a significant source of unusual and unexpected chemical species to the atmosphere. One of the most nominated works in this area was that by Honrath et al. (1999) investigating NO\textsubscript{x} production from the illuminated snowpack. Davis et al. (2001) pioneering work on the unexpected production of NO\textsubscript{x} in the pristine Antarctica is also worthy of note.

2.6. Chemical Models

Chemical models are the conduit to represent our knowledge of the chemical and physical processes in the atmosphere within a mathematical framework that allows prediction and testing against laboratory and field studies. They also help explain atmospheric observations and predict what could happen under different conditions. Early, simple chemical models (with no chemical transport) were useful tools to elucidate and test the basic theory of photochemical ozone formation (Levy, 1971). The recognition that one cannot treat the chemical transformation without considering atmospheric transport came early. The original simple 1-D models, often designed with a parameterized vertical transport in terms of an “Eddy Diffusion” concept, were superseded by 2-dimensional models and have now been largely replaced by complex 3-D models. Also, chemical transport models (CTMs), which use analysed winds, are often used to separate transport from chemistry. Now, free-running on-line 3-D models, which include chemistry, have been implemented, and the continued enhancements in computing capabilities have greatly improved our modelling capabilities. Logan and co-authors are recognised by many contributors as providing the basic model description of global tropospheric chemistry (Logan et al., 1981).

A series of three papers from the Seinfeld group (Reynolds et al., 1973; Reynolds et al., 1974; Roth et al., 1974) provided the earliest complete descriptions of an air quality policy model. They linked together emission inventories, meteorological data, chemical mechanisms and air quality network data to evaluate model performance. All subsequent air quality policy models have followed the same general approach and basic formulation.

One of the earliest detailed chemical modelling studies that integrated highly instrumented intensive field campaigns data was that of Harriss (1988) for the ABLE 1A campaign in the Amazon Boundary Layer. Bey et al. (2001) first detailed GEOS-Chem, a global, three-dimensional, tropospheric, chemical transport model. Though not the only global tropospheric model, as an open-source model with a large user community and flexibility, it has become a very influential global model. In recent years WRF-Chem has also been used extensively (Grell et al., 2005). Earlier stratospheric chemical transport models were advanced by for example, Chipperfield and Pyle (1988).

Multi-model ensembles of the troposphere as epitomised by Stevenson et al. (2006) and Fiore et al. (2009) (see the 2.16 Chemical Transport section) are a powerful tool for generalising the model “understanding” of the atmosphere. This modelling approach makes use of many different models to achieve a more accurate representation of the observations than it would be possible by using only
one model, thus producing more reliable outcomes for assessments and policies on a global scale. In addition, multiple runs of the same models with slightly different initial conditions are used to examine the range of outcomes. This approach is akin to the use of multiple models and model runs in weather predictions.

2.7. Tropospheric Ozone

Ozone is one of the central molecules of atmospheric chemistry and runs through much of the foundations of the discipline, from its role in the stratosphere as UV shield, to its role as a major greenhouse gas, to its pivotal part in the troposphere as the start and end-product of oxidation chemistry, and its detrimental influence as an air pollutant harmful to human health and ecosystems. Much of the early thinking on ozone was focused on the question of whether tropospheric ozone was a small subset of stratospheric ozone, see for example Galbally (1968) and Fabian and Pruchniewicz (1977). The latter paper showed the value of observational networks based on standardised instrumentation and calibration techniques, together with consistent siting criteria, and raised the issue of seasonal variations in tropospheric ozone and the nature of the processes that drive them. The vertical structure of a layer of high O₃ concentrations in the stratosphere, where O₂ could be directly photolyzed to make oxygen atoms and hence ozone, and declining concentration in the troposphere was indicative of a stratospheric source and a tropospheric sink and was the prevalent theory prior to late 1970s (see also the 2.18. Stratospheric Chemistry section). A major breakthrough were the two papers by Chameides and Walker, and Crutzen (Chameides and Walker, 1973; Crutzen, 1973b) that showed that ozone can be photochemically made across the troposphere, just like it is made in smog via the reactions involving hydrocarbons and nitrogen oxides.

The importance of ozone as a radiative gas has been known for a long time, with a significant fraction of heating in the stratosphere coming from ozone photolysis followed by its reformation and thus converting sunlight to heat. Fishman in 1979, (Fishman et al., 1979) identified that tropospheric ozone is also a greenhouse gas. Hence, a change in tropospheric ozone will perturb the radiative energy budget of the Earth-atmosphere system which will in turn perturb the climate system. Ozone thus became the second trace gas after carbon dioxide to be implicated in global warming and climate change.

Large scale mapping of global tropospheric ozone was first undertaken by Logan (Logan, 1985) who looked at seasonal behaviour and trends with a view to understanding anthropogenic influence. This was later complemented by a paper exploring the photochemical origins of tropospheric, rather than stratospheric, ozone in the rural United States (Logan, 1989). As the understanding of the photochemistry of ozone developed, measurements at Niwot Ridge, Colorado (Liu, 1987) aimed to quantify the elements of the ozone budget by season, bringing forward the concept of ozone production efficiency. Lin et al. (1988) explored the non-linearity of tropospheric ozone production with respect to NMHCs and NOx. Though this chemistry had been outlined much earlier – e.g. Demerjian et al. (1974) – this work explored it in the background atmosphere with models and measurements. A powerful demonstration of the low-NOx ozone destruction chemistry came from measurements made at Cape Grim, Australia, a background station, where Ayers and Penkett (Ayers
et al., 1992) and their team(s) used measurements of ozone and peroxides (Figure 8) to show further experimental proof for the photochemical control of ozone in remote locations.

Figure 8 – Average diurnal cycles of peroxide (orange line) and ozone (blue lime) in baseline (low NOx) air at Cape Grim (Tasmania, Australia) for January 1992. Adapted from Ayers et al. (1992).

Measurements have always been a critical driver in tropospheric chemistry, and the idea to use in-service commercial aircraft as a platform for programs such as MOZAIC/IAGOS (Thouret et al., 1998) has been recognised for the enormous amount of high quality data, which would otherwise be difficult to regularly obtain from the upper troposphere and lower stratosphere. Using such measurements Newell et al. (1999) combined dynamical and chemical tracers to further delineate ozone origin and budgets. In the same year, Logan published a synthesis of ozone sonde data (Logan, 1999) which gave an unprecedented look at the seasonal and vertical distribution of ozone and became a reference point for the subject. A year later, Thompson et al. (2000) used a combination of shipboard and satellite views of a tropospheric ozone maximum to suggest the occurrence of a tropical Atlantic ozone “paradox”. The “Atlantic paradox” refers to a greater tropospheric ozone column amount over the South Atlantic than the North Atlantic during the West African biomass burning season. This phenomena was further explored using an expanded network of ozonesondes in the southern hemisphere (SHADOZ) (Thompson et al., 2003). In combination with the earlier work of Logan these became the basis for the measurement description of ozone in the troposphere.

A decades worth of knowledge on the relationship between ozone and its precursors was pulled together by Sillman (Sillman, 1999), cementing the concepts of NOx- and VOC-sensitive (or NOx saturated) chemical regimes. The paper introduced a generation of researchers to isopleth diagrams (the famous Sillman plot Figure 9) and ozone production efficiencies (OPEs).
Figure 9. Ozone isopleths (ppb) as a function of the average emission rate for NO\textsubscript{x} and VOC (10\textsuperscript{12} molec. cm\textsuperscript{-2}s\textsuperscript{-1}) in 0-D calculations. The isopleths (solid green lines) represent conditions during the afternoon following 3-day calculations with a constant emission rate, at the hour corresponding to maximum O\textsubscript{3}. The short blue dashed line represents the transition from VOC-sensitive to NO\textsubscript{x}-sensitive conditions. Adapted from Sillman and He (2002).

The power of models to explore global tropospheric ozone distributions, budgets and radiative forcing was fully demonstrated in the study by Stevenson et al. (2006), that brought together 26 atmospheric chemistry models to explore both the air quality and climate roles of ozone (see also the 2.6. Chemical Models section). As discussed in the 2.16. Chemical Transport section, a similar approach was used by Fiore et al. (2009) to explore the relationship between inter-continental transport and ozone.

2.8. Nitrogen Chemistry

Nitrogen oxides are an integral part of tropospheric processes. Nitrogen oxides are released into the troposphere from a variety of biogenic and anthropogenic sources including fossil-fuel combustion, biomass burning, microbial activity in soils and lightning. The concept of the Leighton photostationary state (Leighton, 1961) between NO, NO\textsubscript{2}, and O\textsubscript{3} was well established by mid-1990s, and early work from Singh and Hanst (1981) highlighted the potential role of peroxyacetyl nitrate (PAN) to be a reservoir for NO\textsubscript{x} in the unpolluted atmosphere. A landmark paper in the area of nitrogen chemistry was that of Logan (1983) that brought together global and regional budgets for the nitrogen oxides (Table 3). Later, a paper that focused more narrowly on a specific source of NO\textsubscript{x} was that of Yienger and Levy II (1995) who produced an empirical model of global soil-biogenic NO\textsubscript{x} emissions. Higher up in the atmosphere, the work on sources and chemistry of NO\textsubscript{x} by Jaeglé et al. (1998) is recognised for its contribution to the understanding of the NO\textsubscript{x} cycle in the upper troposphere.

These works were complemented by a more holistic view of the nitrogen cycle and in particular the concept of reactive nitrogen (Nr) from Galloway et al. (2004) that clearly showed the linkages between the terrestrial ecosystem and the atmosphere and how the nitrogen budget had and would change.
In more recent times, extensive work on vehicle NOx sources from exhaust remote sensing data, as epitomised in Carslaw (2005) should be highlighted. This paper pointed out the trends that can be said to have led to the denouement of the Volkswagen emissions scandal.

### 2.9. HOx Chemistry

There is no doubt that the chemistry of OH and HO2 (known together as HOx) has a central role in the atmosphere as well as holding a certain fascination to atmospheric scientists owing to the significant challenges involved in measurement and understanding its impact locally to globally. Much of the history of the measurements of OH and HO2 is covered in the review of Heard and Pilling (2003). As they wrote “clearly, OH plays a central role in tropospheric chemistry. The in situ measurement of its concentration has long been a goal, but its short lifetime and consequently low concentration provide a serious challenge.”

In order to assess the global impact of OH chemistry in the absence of direct measurements, reactive proxies have been used. Singh (Singh, 1977) used methyl chloroform to estimate OH abundance since methyl chloroform is exclusively anthropogenic and its emissions are known. This type of work provided a comprehensive picture of the global distribution of OH and, hence, a first overall look at the oxidative capacity of the atmosphere. It was followed, using halocarbon measurements by the AGAGE network, by a global OH determination while also introducing the atmospheric chemistry community to formal inverse modelling (Prinn et al., 1995). Spivakovsky and co-workers expanded on this work to derive 3-D distributions of OH and used this information to assess the wider impact on the lifetimes of halocarbons, which have implications for stratospheric ozone (Spivakovsky et al., 2000). Thanks to the availability of long term observations of halocarbons from the AGAGE and NOAA Networks, later work using a similar approach found evidence for substantial variations of atmospheric hydroxyl radicals in the previous two decades (Prinn et al., 2001), thus providing a broad overview not only of the global distribution but also of the temporal variability of this crucial species. Such estimates allowed for the quantification of the lifetime of important chemicals such as methane and HCFCs.

The in-situ OH detection in the troposphere has proven elusive for a long time. The use of laser-induced fluorescence provided some of the first clues to its atmosphere concentrations in the 1970s and early 1980s (Davis et al., 1976; Wang et al., 1975), but any of these early measurements were found to have significant artefacts. The study by Eisele (1994) at the Fritz Peak Observatory in Colorado, was the first intercomparison experiment of different measurement techniques and provided much needed confidence in the observations of this key molecule. Stevens et al. (1994) developed the low-pressure laser-induced-fluorescence (LIF) instrument, which quickly became one of the most successful and widely used techniques for ambient measurements of OH and HO2. As ambient observations of HOx became available, they were found useful to test our understanding of the tropospheric chemical processes, by comparing them with the results of chemical models (see the 2.6. Chemical Models section). Recognised as a foundational paper in this area, Ehhalt (1999) explained with clarity the role of radicals in tropospheric oxidation and what controls their concentrations, using both ambient measurements and calculated concentrations of OH. The OH radical is particularly suited to test our understanding of chemical processes and this was clearly demonstrated in 2009, when the discrepancies between observed and calculated OH and HO2 in the
A polluted region of Southern China led Hofzumahaus and co-workers to propose a regeneration pathway for OH, which does not involve NOx and thus does not produce O₃ (Hofzumahaus et al., 2009). This, in turn, prompted a major reassessment of the isoprene oxidation mechanism by Peeters et al. (2009) who suggested that isomerisation of hydroxyperoxy radicals from isoprene oxidation could be fast enough to regenerate HOx in highly forested, low NOx environments (see the 2.4. Chemical Kinetics, Laboratory Data and Chemical Mechanisms section) and led to a major revision of isoprene chemistry and its role in the troposphere (see the 2.13. Biogenic Emissions & Chemistry section).

The sources and sinks of HOx radicals have always been a major research focus (Finlayson and Pitts, 1976) and the work of Paulson and Orlando (1996) on the reactions of ozone with alkenes as a source of HOx in the boundary layer is widely recognised. Radical chemistry is highly sensitive to the levels of NO and NO₂ and Kleinman’s modelling work on hydrogen peroxide (H₂O₂) concentrations in the boundary layer is recognised for its simple elegance in describing how the HOx cycle chemistry is influenced by NOx and in giving insight into the differing fates of OH/HO₂ radicals under different NOx regimes (Kleinman, 1991) (Figure 10).

The first direct measurements of OH lifetime (Di Carlo et al., 2004) provided evidence of missing reactivity, i.e. that not all sinks of the OH radical are known, which relates to earlier work by Lewis et al. (2000) on unmeasured volatile organic compounds (see the 2.12. Volatile Organic Compounds section).

Nighttime Chemistry

There is widespread recognition that the atmosphere’s oxidative chemistry is active during the night as well during the day. Evidence of nighttime chemistry driven by the nitrate radical (NO₃) as well as by ozone was first observed in the (polluted) troposphere in 1980 by Platt and co-workers (Platt et al., 1980). Much of the early NO₃ work, including laboratory and field studies, is summarised in Wayne’s
seminal review (Wayne et al., 1991). Platt and colleagues and Plane and colleagues’ groundbreaking work based on long-path absorption had indicated the importance of NO$_3$ in the troposphere (Allan et al., 1999; Platt et al., 1979).

Two papers that have been highly influential in shaping our view of nocturnal chemistry are “Nitrogen oxides in the nocturnal boundary layer: Simultaneous in situ measurements of NO$_3$” (Brown et al., 2003) and “Variability in Nocturnal Nitrogen Oxide Processing and Its Role in Regional Air Quality” (Brown et al., 2006). Both these papers showed the power of state of the art measurements coupled with models to assess the impact of nocturnal and heterogeneous chemistry on regional air quality. In particular, the paper by Brown et al. (2006) was a powerful demonstration of the role of heterogeneous chemistry and aerosol composition in controlling N$_2$O$_5$ and, therefore NO$_3$, concentrations (Figure 11).

![Figure 11 – Measurements during a flight of the NOAA research aircraft P3 for 9 and 10 August 2004, showing the relationship between NO$_3$ and N$_2$O$_5$ concentration and aerosol composition (Brown et al., 2006).](https://doi.org/10.5194/acp-2020-1266)
In comparison to the atmospheric chemistry in the stratosphere, where halogen chemistry has been well known and characterized for a long time (see the 2.18. Stratospheric Chemistry section), the recognition of the role of halogen species in the oxidative chemistry of the troposphere occurred much later. Reviews of the earlier work can be found in Platt and Hönninger (2003), Monks (2005) and the extensive review by von Glasow and Crutzen (von Glasow and Crutzen, 2007).

The role of halogens in the troposphere has been discussed going back to the 1970s (e.g. (Graedel, 1979)). The potential importance of iodine in the troposphere was highlighted by a seminal paper by Chameides and Davis in 1980 (Chameides and Davis, 1980). An important early paper is that from Barrie in 1988 (Barrie et al., 1988) that demonstrated the dramatic impact of bromine chemistry on Arctic boundary layer ozone (Figure 12). The occurrence of ozone depletion events in the polar boundary layer suggested that halogens could have a significant impact on atmospheric chemistry at low altitudes and not just in the stratosphere. This work brought together halogen and heterogeneous chemistry and led to the discovery of bromine catalyzed ozone depletion on ice-covered surfaces. (see 2.5. Heterogeneous and Multiphase Chemistry).

One of the foundational papers in the area of halogen chemistry is the modelling study by Vogt et al. (1996) which set the theoretical framework for the sea-salt activation mechanism for halogen release and linked halogen chemistry with the sulphur cycle. While the initial research focus was on chlorine and bromine, Alicke et al. (1999) reported the first iodine oxide observations in the marine boundary layer at Mace Head, Ireland, and proved that iodine can also be an important player in the chemistry of the troposphere. Further investigation found evidence that biogenic iodine species can be responsible for the formation of marine aerosol and cloud condensation nuclei (O’Dowd et al., 2002) recognizing the potential for wide scale impact of iodine chemistry in particle formation. Finlayson-Pitts and her colleagues had suggested the importance of chlorine in tropospheric chemistry based...
on laboratory data (Finlayson Pitts, Nature 1989), but it wasn’t until 2008 that Ostoff and co-workers (Osthoff et al., 2008) – and the related comment “When air pollution meets sea salt” by von Glasow (2008) – brought attention to the potential for nitryl chloride (ClNO₂) chemistry to impact ozone formation, nitrogen recycling and VOC oxidation, with the first ambient observations of this molecule. Also in 2008, the work from Read et al. (2008) clearly showed the global importance of halogens on tropospheric ozone using long-term observations of iodine and bromine oxides (IO, BrO) made at the Cape Verde Observatory.

2.12. **Volatile Organic Compounds**

Volatile organic compounds (VOC) embrace a wide variety of species emitted from man-made and natural sources. In many respects VOC are the fuel of the oxidative chemistry in the atmosphere, involved in many gas- and particle-phase processes.

Ehhalt (1974) brought together the details of the methane sources and sinks and put them into a consistent framework that described the life cycle of methane. This conceptual framework has subsequently been developed for a wide range of trace organic gases. The original understanding of the life cycle of methane has remained largely unchanged over the subsequent 40 years and has formed the basis of the IPCC science assessments on the role of methane in global warming and climate change. Methane itself has been long recognised as important for tropospheric chemistry, but also for climate change as a greenhouse gas. Specifically, the work of Blake and Rowland (1986) documented the global increase in methane and its implications for climate change.

The large differences in reactivity among the individual VOC have always been a feature of their chemistry. Darnall et al. (1976) produced a reactivity scale for atmospheric hydrocarbons based on their reaction with the hydroxyl radical, an idea that is still influential to the present day. The concept was further advanced by Carter and Atkinson (1989) who looked at incremental hydrocarbon reactivity, where knowledge of the reactivities of organics with respect to ozone formation in the atmosphere can provide a useful basis for developing appropriate control strategies to reduce ambient ozone levels. It was the beginning of an approach that is often now used in regulation to determine which organic compounds would have the greatest effect in reducing ozone.

VOC transformation can be important in a number of different atmospheric processes. One highly cited early example is the work of Pitts et al. (1978) on the atmospheric reactions of polycyclic aromatic hydrocarbons and their ability to form mutagenic nitro derivatives under typical atmospheric conditions.

While measurement techniques rarely seem to get a mention as being influential, the discipline relies on observations as a critical part of the oeuvre. Already mentioned was the huge impact that accurate techniques to measure the OH radicals had on the development of the field (see the sections 2.9. HOx chemistry). Another example is the development of Proton-Transfer Reaction Mass-Spectrometry, which has revolutionised the measurement, in particular, of VOCs (Lindinger et al., 1998).

Research is ongoing as to how many VOCs there are in the atmosphere and what the consequences are of not being able to measure them all. The work of Lewis et al. (2000) used novel VOC measurements (GC x GC) to find that there was a larger pool of ozone-forming carbon compounds in urban atmospheres than previously posited (Figure 13). The later paper by Goldstein and Galbally

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(2007) expanded on this work hypothesizing that thousands of VOCs are still unmeasured and unknown, with potentially huge consequences for the carbon budget of the atmosphere.

Continuing work in this area, de Gouw et al. (2005) produced a landmark study that combined analysis of organic carbon in both the gas- and particle-phase in the polluted atmosphere as part of the New England Air Quality study by looking at the evolution of VOCs from their emission sources. The study showed that most of the organic carbon in the particle-phase was formed by secondary anthropogenic processes and that an increasing fraction of the total organic mass was constituted by oxygenated VOCs as a result of the air masses being processed/aged.

Figure 13 - Comprehensive (right) and one-dimensional (left) separations of volatile organic compounds in urban air demonstrating a greater variety and number of VOCs (Lewis et al., 2000)

2.13. Biogenic Emissions & Chemistry

Although it has been known for a long time that plants emit organic compounds, the relevance of biogenic VOC for atmospheric chemical processes was not immediately recognized. Detection of isoprene and α-pinene in forested environments was first reported in the 1960s-1970s (Rasmussen and Went, 1964; Rasmussen, 1970; Went, 1960). One of the first studies, a paper from Went (1960) hypothesised that “volatilisation of terpenes and other plant products results in the production of, first, blue haze, then veil clouds ... “. The biological mechanisms that control the release of organic
compounds from vegetation were investigated by Baldwin and Schultz (1983) and many others that followed. Before the late 1980s, it was largely assumed that all reactive volatile organic compounds in the atmosphere came from pollution sources and that biogenic sources were trivial and inconsequential. The fundamental work by Chameides and co-workers (Chameides et al., 1988) was one of the first to show the ubiquity of biogenic VOCs and their role in ozone formation even in urban areas. Later, Fehsenfeld et al. (1992) extensively reviewed the state of the knowledge of sources and biochemical processes of VOCs, bringing the subject to the attention of the wider atmospheric chemistry community and opening a new branch of atmospheric chemistry. Another influential review of biogenic VOC emissions, including the physiology of plants, was that by Kesselmeier and Staudt (1999). These studies were pivotal for major policy formulations to abate ozone pollution.

Based on this work, relatively simple functions to predict the emissions of biogenic VOC were developed early on by Guenther et al. (1993) and soon evolved into more sophisticated high resolution global models (Guenther et al., 2000; Guenther et al., 1995), allowing for the emissions of biogenic compounds to be included in atmospheric chemistry models across all scales, and is still used in modern Earth system models today. Eventually, this work took the form of the widely used MEGAN model (Model of Emissions of Gases and Aerosols from Nature) (Guenther et al., 2006) (Table 2 and Figure 14).
Figure 14 - Global distribution of isoprene emission rate estimates (g C m\(^{-2}\) month\(^{-1}\)) for (top) January and (bottom) July (from Guenther et al. (1995)).

Terrestrial vegetation is not the only source of biogenic emissions. Aneja et al. (1979) discussed the importance of biogenic sulphur compounds and their role in stratospheric chemistry, while Charlson et al. (1987) connected marine biology, atmospheric chemistry and climate into the already mentioned CLAW hypothesis (see the 2.2. Aerosols and Clouds section).

Marine aerosol formation was thought for a long time to be dominated by inorganic components, mainly sea-salt and non-sea salt sulphate, but O’Dowd and co-workers (O’Dowd et al., 2004) showed that biological activity of plankton blooms can enhance the concentration of cloud condensation nuclei (CCN), a key aspect of the chemistry-climate feedback mechanism. A similar mechanism is also active in relation to biogenic halogen compounds (O’Dowd et al., 2002) which also affect aerosol formation as well as the ozone, nitrogen and sulphur cycles, as discussed in the Aerosols and Clouds section.
A paper that has been defined as “controversial but set off a huge amount of activity” is “Atmospheric oxidation capacity sustained by a tropical forest” by Lelieveld et al. (2008). In their work, the authors proposed a new chemical mechanism for low NOx, high VOC regions (such as tropical forests), based on modelling studies of a field dataset. Although further studies contradicted this hypothesis, Lelieveld et al. (2008) was instrumental in prompting a large amount of laboratory and theoretical studies in the past 10 years; these studies resulted in a major revision of our understanding of biogenic VOC chemistry, as discussed in the HOx chemistry section.

2.14. Biomass Burning

Biomass burning, particularly in the tropics, affects terrestrial vegetation dynamics, soil erosion, movement of organic carbon, hemispheric atmospheric composition, air quality and more broadly the radiative forcing via emissions of trace gases and aerosols (Monks et al., 2009). Crutzen (Crutzen et al., 1979) was the first to highlight biomass burning in the tropics as an important source of atmospheric gases, such as CO, H2, N2O, NO, CH3Cl and COS. The importance of biomass burning, based on the observations of a small set of fires, and the appreciation of its potential role was a major step in our understanding of the role of biomass burning in air quality, climate change, and the composition of the troposphere. It is, however, the later paper “Biomass Burning in the Tropics: Impact on Atmospheric Chemistry and Biogeochemical Cycles” by Crutzen and Andrea (Crutzen and Andreae, 1990) – one of the top 10 most cited Atmospheric Chemistry paper (Table 2) – that has had the greatest impact on this research area. Hao and Liu (1994) made a further step forward, looking at where and when biomass burning and thereby the related emissions occur. They developed an improved database of the amount of biomass burned owing to deforestation, shifting cultivation, savannah fires, fuel wood use, and clearing of agricultural residues, focused on tropical America, Africa and Asia during the late 1970s.

Simoneit et al. (1999) introduced the important concept that “the monosaccharide derivatives (e.g. levoglucosan) are proposed as specific indicators for cellulose in biomass burning emissions.” They showed that levoglucosan is emitted at such high concentrations that it can be detected in air pollution filter samples at considerable distances from the original combustion source, allowing for source apportionment.

The 2001 paper “Emission of trace gases and aerosols from biomass burning” by Andreae and Merlet (2001), which is also one of the top 10 most cited paper (Table 2 and Figure 15), pulled together emission factors for a large variety of species emitted from biomass fires and is considered a key reference for biomass burning emission factors. Further work in the biomass burning area was later presented by Reid et al. (2005) in a review paper where they looked at measurements of smoke particle size, chemistry, thermodynamic properties, and emission factors from a variety of sources, including laboratory burns, in-situ experiments, remote sensing and modelling. They brought together information from the ‘milieu of small pieces of the biomass-burning puzzle’ and showed that there are large differences in measured particle properties and particle carbon budgets across the literature.

van der Werf et al. (2006) investigated interannual variability and the underlying mechanisms regulating variability at continental to global scales using a time series of 8 years of satellite and model data. Total carbon emissions was driven by burning in forested areas, while the amount of burned
area was driven by savannah fires, which are influenced by different environmental and human factors than forest fires.

![Figure 15 - Vertical profiles of O₃ in the tropical troposphere.](https://doi.org/10.5194/acp-2020-1266)

Figure 15 - Vertical profiles of O₃ in the tropical troposphere. The profile over the equatorial Pacific shows no influence from biomass burning, whereas the profile over the Pacific off South America suggests O₃ enhancement due to long-range transport from the tropical continents. The O₃ profiles over Brazil and the Congo show high O₃ concentrations at altitudes between 1 and 4 km due to photochemical production in biomass burning plumes. At higher altitudes, O₃ concentrations are also substantially enhanced, possibly also because of O₃ production by reactions in the emissions of biomass burning (Crutzen and Andreae, 1990).

2.15. Emissions and Deposition

Non-chemical sources and sinks of various species are critical components of atmospheric processes and therefore are particularly essential for global and regional models. An early advocate for such was the work of Olivier and the team that created the EDGAR (Emission Database for Global Atmospheric Research) database (Olivier et al., 1994). Emissions from vehicles and power plants have always been an essential aspect of air quality related policies, and therefore an area where more focused inventory work was needed and done. This approach was pioneered in California in the early 1990s, and the studies by Calvert et al. (1993), Lawson (1993) and Singer and Harley (1996) helped define and verify the California Smog Control Program, providing a solid scientific basis with reliable emissions data. Techniques such as the remote monitoring of traffic generated carbon monoxide (Chaney, 1983) are also essential to recognise the role they played in understanding vehicle emissions.

The deposition of gases and aerosol to the surface is another critical process in the atmosphere. Chamberlain (1966) is credited with the first exposition of the resistance network approach to describe the uptake of gases on surfaces and the identification of transport through the atmospheric boundary.
layer, through the surface layer, and through the stomata on plants, as important elements of surface
uptake. Building upon this work, a comprehensive and widely adopted, parametrization of the dry
deposition process for regional and global models was presented in the late 1980s by Wesely (1989).
Currently, there has been renewed interest in quantifying and understanding deposition process. Yet,
a systematic description based on fundamental independently measureable physico-chemical
parameters are lacking.

### 2.16. **Chemical Transport**

Transport is an integral part of atmospheric processes and influence atmospheric composition across
a range of spatial scales. As early as 1975, Junge (1975) pointed out the importance of atmospheric
residence time of a constituent with respect to global transport and dispersion. Prather’s work
(Prather, 1994, 1996) provided new insights onto timescales for atmospheric oxidation chemistry.

Stratospheric-tropospheric exchange (STE) has always been recognised as a key mechanism in
determining tropospheric composition. Early chemical dynamics were demonstrated by Danielsen
(1968) that laid the foundations for 3-dimensional modelling of chemical transport looking at
stratosphere-troposphere exchange based on radioactivity, ozone, and potential vorticity. Later,
Holton and co-authors (Holton et al., 1995) proposed an approach that placed stratosphere-
troposphere exchange in the framework of the general circulation and helped clarify the roles of the
different mechanisms involved and the interplay between large and small scales, by the use of
dynamical tracers and potential vorticity. This work is recognised as a big step forward for the
understanding of the tropospheric ozone budget. While the regional nature of air pollution has always
been recognised, that is less the case for the impact of trans-continental emissions on air quality. Jacob
et al. (1999) showed that there was a need for a global outlook for understanding regional air quality
and meeting pollution reduction objectives. This perspective spawned a decade of intense work on
intercontinental air pollution and transport. Recognised in this area is the work by Stohl and colleagues
(Stohl et al., 2002) who mapped out the pathways and timescale of intercontinental air pollution
transport and brought life to the subjects of atmospheric dynamics and transport of air pollution
(Figure 16).
The study Moody et al. (1998) explored atmospheric transport history using back trajectories for the Harvard Forest experiment demonstrating the power of trajectory methods at the regional scale. Stohl and colleagues (Stohl et al., 2003) brought together what has been viewed by many as the authoritative work on stratosphere-troposphere exchange. Key tools in the development of this area were the HYSPLIT (Draxler and Hess, 1998) a forerunner of various particle trajectory and dispersion models, which developed into a widely used particle dispersion model, and the FLEXPART model, a Lagrangian particle dispersion model designed for calculating the long-range and mesoscale dispersion of air pollutants (Stohl et al., 2005).

The ideas of intercontinental source-receptor relationships as embodied in the aforementioned earlier works by Jacob et al. (1999) and Stohl et al. (2002). The concept was developed in an effort to explore the source-transport relationships that drive ozone in regions farther away from the emission regions (Fiore et al., 2009) (see the 2.6. Chemical Models section). This large community collaboration provided valuable insights into the sensitivities of the hemispheric regional background of ozone and how this is controlled by emissions from continental source regions.

Another critical area for atmospheric chemistry is boundary layer dynamics and meteorology. This is particularly important since most emissions are emitted in the boundary layer. Atmospheric dynamics in this important region has been mostly expressed as parameterizations in numerical models (Stull, 1988). The spatial and temporal scales involved in the processes in this region range over a very wide range. The understanding of this region has been mostly based on meteorological and energy/water vapour balance points of view. However, the chemical transformation and
dispersion in this region are crucial for how much chemicals actually get out of this region to influence the regional and global atmosphere. Furthermore, the process of dry deposition, a critical loss process for chemicals, is mostly limited to the boundary layer.

2.17. Satellites and the Troposphere

The importance of satellites on the discipline of atmospheric chemistry centres on the ability to give a self-consistent global view of a selected set of tropospheric trace species. The beginning and first demonstration of the effective application of these attributes for the troposphere were the data and the retrievals from the GOME instrument (Burrows et al., 1999) on ERS-2 and SCIAMACHY on Envisat (Bovensmann et al., 1999). Historically, the roots of these early instruments are in stratospheric chemistry, with GOME being deployed to be able to track stratospheric ozone and its key controlling chemical species.

The most nominated paper in this area, and one that demonstrated the power of such observations for tropospheric composition research, was “Increase in tropospheric nitrogen dioxide over China observed from space” by Richter et al. (2005), which showed the capability of the satellites to track the build-up of air pollution over vast regions from space (Figure 17). The importance of the work lead by Palmer and co-workers in establishing a method to convert satellite observations to vertical columns for comparison with e.g. models was also widely recognised (Palmer et al., 2001).

Figure 17 - The mean annual NO\(_2\) column amount normalized to that in 1996 for the geographical regions USA, Central East Coast USA, Western Europe, Poland, Japan, East Central China, and Hong Kong showing a marked increase in NO\(_2\) over China and decrease over Europe (Richter et al., 2005).

Satellite-based instrumentation can measure not only gas-phase trace species but also dust and aerosols; the combination of SEAWIFS and TOMS to track Asian dust events (Husar et al., 2001) and the development of the MODIS aerosol algorithm (Remer et al., 2005) provided convincing
demonstrations of this capability. A step-change in this area was made with the paper “Estimating
ground-level PM2.5 using aerosol optical depth determined from satellite remote sensing” by van
Donkelaar et al. (2006) which was the first description of the derivation of surface PM2.5 from satellite
AOD, and which has been extensively used to estimate the global impact of particulate matter (both
PM2.5 and PM10) on health.

2.18. Stratospheric Chemistry

Tropospheric chemistry has always been influenced by the study of stratospheric chemistry. As
mentioned earlier (see the 2.1. Foundations section), the basis of stratospheric ozone chemistry were
laid in the 1930s (Chapman, 1930), whereas tropospheric chemistry followed a couple of decades
later. Interest in stratospheric ozone chemistry increased substantially following the works of
Johnston and Crutzen on the role of nitrogen oxides in the stratosphere (Crutzen, 1970; Johnston,
1971). The impact of supersonic transport (Johnston, 1971) and of CFCs (Molina and Rowland, 1974)
were important events for stratospheric ozone chemistry. While Crutzen (1970) showed that the
nitrogen oxides in the stratosphere come from the nitrous oxides from the ground, Johnson suggested
that a fleet of supersonic aircraft could release large amounts of nitrogen oxides into the lower
stratosphere causing substantial ozone loss (Johnston, 1971). The potential threat of supersonic
transport highlighted the importance of gas-phase catalysis in the atmosphere and, in particular, of
the catalytic ozone destruction by HO2 and NOx. These works opened the world’s eyes to the potential
for global environmental change from human activities. Soon after, Lovelock (1974) identified CFCs in
the troposphere and showed that practically all the CFCs emitted to date were still in the atmosphere.
The significant contributions of Hampson, Crutzen, and Johnston, and the recognition of chlorine-
catalysed ozone destruction by Stolarski and Cicerone (1974), paved the way for the seminal work of
Molina and Rowland (Molina and Rowland, 1974) linking chlorofluorocarbons to ozone layer
depletion. The recognition that bromine compounds can also destroy stratospheric ozone (McElroy et
al., 1986) further refining the story. The potential role of iodine in the stratospheric ozone depletion
has been raised (Solomon et al. 1994), but it is still somewhat unsettled.

The ozone hole (Farman et al., 1985) was an unanticipated shock that awoke the world to the global
nature of ozone layer depletion. In an historic set of studies over a relatively short five-year period,
the cause of the ozone hole was understood. First was the insightful and seminal work of Solomon et
al. (1986) that showed that chlorofluorocarbons and other ozone-depleting gases were the key
anthropogenic ingredient for the ozone hole. The confluence of cold temperatures that lead to the
formation of polar stratospheric clouds (PSCs) and the winter vortex formation over Antarctica
provided the opportunity for the massive ozone depletion that resulted in the ozone hole. This work
confirmed the suggestion of Farman that the ozone hole was due to the increasing abundances of
CFCs. In particular, Solomon and co-workers (Solomon et al., 1986) recognized that stable molecules
such as ClONO2 and HCl could react on solid (and indeed liquid). Along the way, during this intense
investigative period, the detection and quantification of the role of ClO as a catalyst by Anderson et
al. (1991), as well as De Zafra et al. (1988), was the “smoking gun” that linked the CFCs with the ozone
hole. The entire set of field measurements, from the ground, aircraft, and balloons, solidified this
linkage.
Less heralded, but equally important, were the laboratory studies that showed that chlorine nitrate (ClONO₂) and HCl did indeed react on PSCs (Hanson and Ravishankara, 1994; Tolbert et al., 1987; Leu, 1988; Molina, 1991; Molina et al., 1987) and determined the critical rate coefficients for the self-reaction of ClO, the rate-limiting step in the unique catalytic cycles in Antarctica (Cox and Hayman, 1988; Sander et al., 1989; Trolier et al., 1990). Much was learned in later years by studying the Arctic and from the continued observations over the Antarctic. It should be noted that the termolecular reaction of ClO was suggested to be important for high chlorine chemistry by Molina and Molina, and the history of this reaction goes back to Norrish’s work at Cambridge (Norrish and Neville, 1934). One of the lessons from this episode is that natural factors, in this case the formation of a vortex and the occurrence of polar stratospheric clouds, can lead to unexpected consequences when an anthropogenic ingredient (ozone-depleting chemicals) is added to the mix.

The numerical modelling of the stratosphere was an important ingredient for the success of mitigating polar ozone loss, along with the theories of the ozone layer depletion and the ozone hole, the laboratory studies of key processes, and the measurements in the atmosphere. Over the years, these models have enabled a great deal of understanding of the coupling between chemistry and climate. The development of stratospheric chemical transport models (Chipperfield and Pyle, 1988) was a pivotal advancement that enabled quantitative understanding of the ozone layer depletion, including the ozone hole (see the 2.6. Chemical Models section).

The weight of science led to the Vienna convention, the Montreal Protocol, and the Protocol’s many amendments and adjustments that have, by now, phased out the ozone-depleting gases. The Montreal Protocol is the first international treaty on an environmental issue to be universally ratified and is regarded as one of the most successful. That said, the ozone layer depletion story is not complete. For example, the recognition that nitrous oxide is the remaining major ozone-depleting gas emission (Ravishankara et al. 2009) has connected food production (tropospheric nitrogen cycles) to ozone layer depletion and highlighted the importance of a holistic approach to environmental issues.

### 2.19 Other issues that influence tropospheric chemistry

Atmospheric chemistry advances have been advanced by growth in other areas. The importance of anthropogenic climate change has been instrumental in invigorating atmospheric chemistry studies because many of the major climate forcing agents are chemically active and climate change, in turn, influence tropospheric chemistry (von Schneidemesser et al., 2015). This issue was noted earlier. In addition to climate change, other adjacent discoveries and findings have influenced tropospheric chemistry studies.

The global atmospheric and climatic consequences of nuclear war were investigated by both Crutzen and Birks (1982) and Turco et al. (1983). Using models developed for looking at the impact of volcanic eruptions, Turco et al. (1983) concluded that “enhancement of solar ultraviolet radiation due to ozone depletion, long-term exposure to cold, dark, and radioactivity could pose a serious threat to human survivors and to other species.” Similarly (Crutzen and Birks, 1982) concluded that “the screening of sunlight by the fire-produced aerosol over extended periods during the growing season would eliminate much of the food production in the Northern Hemisphere”.

Air quality has an obvious direct impact on people, and this connection was recognized very early (it was in fact the primary motivation behind the fundamental work of Haagen-Smit). In 1993, Dockery et al. (1993) presented a study of six US cities showing a direct association between air pollution and...
mortality rates. This paper a great example of an adjacent field influences another, in this case atmospheric chemistry and public health. Though association between air pollution and health stretch back to the Los Angeles and London smog, the ‘Six Cities Study’ was a landmark as it demonstrated the association between air pollution and mortality extended to much lower concentrations than those observed in the smog days.

3. Discussion and Summary

A mixture of the history of the discipline and its the landmark ideas emerges in this exercise of asking the community to point to what they consider has shaped their research field. Table 1 seeks to bring these elements together to look at the evolution of the leading scientific concepts, their relevance to the environmental legislation (in this sense, we acknowledge an Euro-/US-centric bias, which the community can perhaps correct during the discussion of this paper), and the most notable environmental events that have shaped the discipline. Atmospheric science often sits at an interesting intersection between the societal outcomes (e.g., acid precipitation, air quality, ozone layer depletion, and climate) and its scientific venture. Monks and Williams (2020) have recently explored how environmental events in air quality drive policy and how a scientific and societal paradigm shift occurs once the emergency phase has passed.

From an overview of all the nominated papers, several general features are apparent. Ambient measurements are one of the cornerstones of atmospheric science (Abbatt et al., 2014). It is clear that the atmosphere is under-sampled but over time we have found many ingenious ways to build different measurement strategies from the ground, airborne, balloon, sonde and space. With a focus on chemistry, it is clear that one needs to be able to measure with surety, specificity and speed in the troposphere. Many of the nominated papers reflect the importance of instrument developments. Examples include the electrostatic sizers in aerosol science (Knutson and Whitby, 1975), various techniques to measure the hydroxyl radical (Eisele, 1994;Stevens et al., 1994;Perner et al., 1976), the development of chemical ionization mass spectrometry (Lindinger et al., 1998), and the application of the GCxGC-MS technique (Lewis et al., 2000), and aerosol mass-spectrometry measurements, e.g., Zhang et al. (2007). Often, the science underlying the development of these instruments, such as ion-molecule chemistry, is not necessarily acknowledged.

Another common theme is the critical importance and impact of long-term observations, often termed monitoring, of key atmospheric components, from CO₂ (the “Keeling” curve) to chemically active molecules such halocarbons (the Antarctic ozone hole, ozone layer depletion and climate change), methane (the changes in the global OH field, background ozone production), and NOₓ (catalyst for tropospheric ozone production, vehicle emissions and acid precipitation). On the other hand, many breakthroughs in understanding the observations emerged because of basic laboratory information on kinetics and photochemistry (e.g., the reaction of HO₂ + NO, the determination of O(¹D) quantum yields, and the reactions of CIONO₂ and HCl on PSCs.) It is noteworthy that both laboratory studies and long-term observations are currently under funding stress, a situation that is already worrying the community (see, for example, the discussion in Burkholder et al. (2017)).

There is no doubt that atmospheric chemistry is an integrative science: one of the recurring themes in the papers discussed here is the tight relationship between ambient observations, laboratory experiments, and modelling. The integrative power of models has been recognised from the early
studies by Levy (1971) to the development of highly sophisticated global transport models by Chipperfield and Pyle (1988) and Bey et al. (2001) up to the more recent demonstrations of the power of model ensembles (Stevenson et al., 2006; Fiore et al., 2009). Much of this progress has parallels in stratospheric chemistry. It is evident in the community that models are a powerful tool to map, test, and predict the atmosphere’s past, present, and future. The predictions and projections from these models play essential roles in policy, planning, and management of environmental issues.

Another form of integrative or meta-analysis brings together a range of individual studies to produce a more significant outcome, such as new insights or models. There are some notable examples of this approach in the works on biomass burning by Crutzen and Andreae (1990) and more recently, by van der Werf et al. (2010). Similarly, the work to produce isoprene emissions models brought together several global isoprene flux measurements (Guenther et al., 1995; Guenther et al., 2006). Other examples include the work of Zhang et al. (2007) and Jimenez et al. (2009) who integrated various sets of AMS observations to give insight into land distributions of SOA.

There have been developments in fields adjacent to atmospheric chemistry that have shaped atmospheric chemistry progress. Examples include developments in epidemiology (e.g., the Six Cities Study by Dockery et al., 1993), atmospheric dynamics (the role of transport in determining chemical composition, the role of the Antarctic vortex), in ocean science (pertaining to deposition to the ocean surface and emissions from the oceans) and in biospheric/plant science (e.g., Kesselmeier and Staudt, 1999)). Integrating atmospheric chemistry with these adjacent fields is not only essential but also fruitful and was for many years embodied in the IGBP (Seitzinger et al., 2015), World Climate Research Program (WCRP), and Earth-system science programs (now Future Earth). Wider contexts such as paleoclimate has allowed an understanding of climate and atmospheric history over the 100,000 year timescales (e.g., Petit et al., 1999)). That work set the understanding that the present-day atmospheric burdens of carbon dioxide and methane as important greenhouse gases are unprecedented during the past 420,000 years. They also allow us to estimate the composition of the troposphere in those ancient times.

Similarly, there are concepts that have their roots in tropospheric chemistry that have gone onto have wider impact. The concept of the Anthropocene, first proposed by Crutzen and Stroemer in 2000, indicates that we are in a new geological epoch driven by human activities. The idea was more fully expounded in Crutzen (2002) the geology of mankind. There is little doubt that this has been a key idea that has influenced much thinking as well as wider work beyond atmospheric science (Table 1).

As discussed in detail in the introductory text, we opted here to assemble this compilation of papers by reaching out to the community for nominations, rather than using the number of citations as a primary measure. We will not go into the details again here, suffice it to say that there are inherent advantages and drawbacks to any method one might consider for such a work. In that sense, we would re-iterate our call for input during the open peer-review phase for this manuscript.

The papers highlighted capture a substantial scope of the atmospheric research endeavour over the last 60 years. The challenge now for you, the reader, is to reflect on this preliminary version of included papers, critique the choice and the reasoning, and propose other suggestions. Again we request you to engage in this discussion and help shape the final compilation of papers to make it a truly community effort.
4. Author Contributions

PSM developed the concept and led the writing, PSM, ARR, RS, and EvS solicited input, ARR, RS, EvS contributed to writing and editing.
Table 1 – Science, Regulatory and Environmental Landmarks of the 20th and early 21st Centuries

<table>
<thead>
<tr>
<th>Decade</th>
<th>Science Landmark</th>
<th>Regulatory Landmarks</th>
<th>Environmental Events</th>
</tr>
</thead>
<tbody>
<tr>
<td>1930</td>
<td>Chapman Cycles and Stratospheric Chemistry</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1940</td>
<td>Air Pollution</td>
<td>1943 – LA Smog</td>
<td></td>
</tr>
<tr>
<td>1950</td>
<td>Air Pollution</td>
<td>1956 - UK Clean Air Act</td>
<td>1952 – Great Smog of London</td>
</tr>
<tr>
<td>1960</td>
<td></td>
<td>1963 - US Clean Air Act</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>SOA Concept of Anthropocene</td>
<td>2001 - NEC Directive (EU)</td>
<td></td>
</tr>
<tr>
<td>2010</td>
<td>Air Pollution and Climate</td>
<td>2015 - Dieselgate</td>
<td></td>
</tr>
<tr>
<td>2020</td>
<td></td>
<td>2020 - COVID 19</td>
<td></td>
</tr>
</tbody>
</table>

¹ For more details on the UK/EU perspective see (Williams, 2004; Maynard and Williams, 2018) and for the USA perspective see (Jacobson, 2002); see also (Monks and Williams, 2020).
Table 2 – Top 10 Cited Atmospheric Chemistry Papers (Atmospheric+Chemistry)
(Scopus, 27/3/20)

<table>
<thead>
<tr>
<th>#</th>
<th>Paper</th>
<th>Title</th>
<th>Citations</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Guenther et al. (1995)</td>
<td>A global model of natural volatile organic compound emissions</td>
<td>2760</td>
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<tr>
<td>2</td>
<td>Andreae and Merlet (2001)</td>
<td>Emission of trace gases and aerosols from biomass burning</td>
<td>2350</td>
</tr>
<tr>
<td>5</td>
<td>Atkinson (2000)</td>
<td>Atmospheric chemistry of VOCs and NOx</td>
<td>1773</td>
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<tr>
<td>6</td>
<td>Crutzen and Andreae (1990)</td>
<td>Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles</td>
<td>1686</td>
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<tr>
<td>7</td>
<td>van der Werf et al. (2010)</td>
<td>Global fire emissions and the contribution of deforestation, savanna, forest, agricultural, and peat fires (1997-2009)</td>
<td>1578</td>
</tr>
<tr>
<td>9</td>
<td>Grell et al. (2005)</td>
<td>Fully coupled “online” chemistry within the WRF model</td>
<td>1436</td>
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<tr>
<td>10</td>
<td>Lelieveld et al. (2015)</td>
<td>The contribution of outdoor air pollution sources to premature mortality on a global scale</td>
<td>1425</td>
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(Web of Science, 27/3/20)

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<tr>
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<th>Paper</th>
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<th>Citations</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>Ramanathan et al. (2001)</td>
<td>Atmosphere - Aerosols, climate, and the hydrological cycle</td>
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<td>2</td>
<td>Andreae and Merlet (2001)</td>
<td>Emission of trace gases and aerosols from biomass burning</td>
<td>2168</td>
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<td>4</td>
<td>Jimenez et al. (2009)</td>
<td>Evolution of organic aerosols in the atmosphere</td>
<td>1844</td>
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<tr>
<td>5</td>
<td>Crutzen and Andreae (1990)</td>
<td>Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles</td>
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<td>The contribution of outdoor air pollution sources to premature mortality on a global scale</td>
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<tr>
<td>10</td>
<td>Bey et al. (2001)</td>
<td>Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation</td>
<td>1212</td>
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</table>

1107

1108
Table 3 - A global budget for NOx (Logan, 1983)

<table>
<thead>
<tr>
<th>Source</th>
<th>10^12 gm N yr⁻¹</th>
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<tr>
<td>Fossil fuel combustion</td>
<td>21 (14-28)</td>
</tr>
<tr>
<td>Biomass Burning</td>
<td>12 (4-24)</td>
</tr>
<tr>
<td>Lightning</td>
<td>8 (8-20)</td>
</tr>
<tr>
<td>Microbial activity in soils</td>
<td>8 (4-16)</td>
</tr>
<tr>
<td>Oxidation of ammonia</td>
<td>1-10</td>
</tr>
<tr>
<td>Photolytic or biological processes in the ocean</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Input from the Stratosphere</td>
<td>≈ 0.5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>25-99</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sink</th>
<th>10^12 gm N yr⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation</td>
<td>12-42</td>
</tr>
<tr>
<td>Dry Deposition</td>
<td>12-22</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>24-64</strong></td>
</tr>
</tbody>
</table>
Appendix 1

Documents per year by source

Documents by country or territory
### Appendix 2 - Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABLE</td>
<td>Amazon Boundary-Layer Experiment</td>
</tr>
<tr>
<td>AGAGE</td>
<td>Advanced Global Atmospheric Gases Experiment</td>
</tr>
<tr>
<td>AMS</td>
<td>Aerosol Optical Depth</td>
</tr>
<tr>
<td>BBOA</td>
<td>Biomass-Burning Organic Aerosol</td>
</tr>
<tr>
<td>CAPRAM</td>
<td>Chemical Aqueous Phase Radical Mechanism</td>
</tr>
<tr>
<td>CCN</td>
<td>Cloud Condensation Nuclei</td>
</tr>
<tr>
<td>CFC</td>
<td>Chlorofluorocarbon</td>
</tr>
<tr>
<td>CLAW</td>
<td>Charlson-Lovelock-Andreae-Warren</td>
</tr>
<tr>
<td>CTM</td>
<td>Chemical Transport Model</td>
</tr>
<tr>
<td>EDGAR</td>
<td>Emission Database for Global Atmospheric Research</td>
</tr>
<tr>
<td>FA-AMS</td>
<td>Factor Analysis of Aerosol Mass Spectrometry</td>
</tr>
<tr>
<td>FLEXPART</td>
<td>FLEXible PARTicle dispersion model</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas Chromatography-Mass Spectrometry</td>
</tr>
<tr>
<td>GEOS-Chem</td>
<td>Goddard Earth Observing System - Chemical Transport Model</td>
</tr>
<tr>
<td>GOME</td>
<td>Global Ozone Monitoring Experiment</td>
</tr>
<tr>
<td>HCFC</td>
<td>Hydrochlorofluorocarbon</td>
</tr>
<tr>
<td>HOA</td>
<td>Hydrocarbon-like Organic Aerosol</td>
</tr>
<tr>
<td>HYSPLIT</td>
<td>Hybrid Single-Particle Lagrangian Integrated Trajectory model</td>
</tr>
<tr>
<td>IAGOS</td>
<td>In-service Aircraft for a Global Observing System</td>
</tr>
<tr>
<td>IGAC</td>
<td>International Global Atmospheric Chemistry</td>
</tr>
<tr>
<td>IGBP</td>
<td>International Geosphere-Biosphere Programme</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>JPL</td>
<td>NASA Jet Propulsion Laboratory</td>
</tr>
<tr>
<td>LIF</td>
<td>Laser Induced Fluorescence</td>
</tr>
<tr>
<td>LV-OOA</td>
<td>Low-volatility Oxygenated Organic Aerosol</td>
</tr>
<tr>
<td>MCM</td>
<td>Master Chemical Mechanism</td>
</tr>
<tr>
<td>MEGAN</td>
<td>Model of Emissions of Gases and Aerosols from Nature</td>
</tr>
<tr>
<td>MODIS</td>
<td>Moderate Resolution Imaging Spectroradiometer</td>
</tr>
<tr>
<td>MOZAIC</td>
<td>Measurements of OZone and water vapour by in-service Airbus airCraft</td>
</tr>
<tr>
<td>NASA</td>
<td>National Aeronautics and Space Administration</td>
</tr>
<tr>
<td>NMHC</td>
<td>Non-Methane Hydrocarbon</td>
</tr>
<tr>
<td>NOAA</td>
<td>National Oceanic and Atmospheric Administration</td>
</tr>
<tr>
<td>OA</td>
<td>Organic Aerosol</td>
</tr>
<tr>
<td>OOA</td>
<td>Oxygenated Organic Aerosol</td>
</tr>
<tr>
<td>OPE</td>
<td>Ozone Production Efficiency</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>PAN</td>
<td>Peroxyacetyl Nitrate</td>
</tr>
<tr>
<td>PM</td>
<td>Particulate Matter</td>
</tr>
<tr>
<td>POA</td>
<td>Primary Organic Aerosol</td>
</tr>
<tr>
<td>PSC</td>
<td>Polar Stratospheric Clouds</td>
</tr>
<tr>
<td>RACM</td>
<td>Regional Atmospheric Chemistry Mechanism</td>
</tr>
<tr>
<td>RADM</td>
<td>Regional Acid Deposition Model</td>
</tr>
<tr>
<td>RF</td>
<td>Radiative Forcing</td>
</tr>
<tr>
<td>RRKM</td>
<td>Rice-Ramsperger-Kassel-Marcus</td>
</tr>
<tr>
<td>SAPRC</td>
<td>Statewide Air Pollution Research Center</td>
</tr>
<tr>
<td>SCIAMACHY</td>
<td>SCanning Imaging Absorption spectroMeter for Atmospheric CartograpHY</td>
</tr>
<tr>
<td>SeaWIFS</td>
<td>Sea-Viewing Wide Field-of-View Sensor</td>
</tr>
<tr>
<td>SHADOZ</td>
<td>Southern Hemisphere ADDitional OZonesondes</td>
</tr>
<tr>
<td>SOA</td>
<td>Secondary Organic Aerosol</td>
</tr>
<tr>
<td>STE</td>
<td>Stratospheric-Tropospheric Exchange</td>
</tr>
<tr>
<td>SV-OOA</td>
<td>Semi-volatile Oxygenated Organic Aerosol</td>
</tr>
<tr>
<td>TOMS</td>
<td>Total Ozone Mapping Spectrometer</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compound</td>
</tr>
<tr>
<td>WCRP</td>
<td>World Climate Research Program</td>
</tr>
<tr>
<td>WRF-Chem</td>
<td>Weather Research and Forecasting model coupled to Chemistry</td>
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