AN INSIGHT INTO AVIATION EMISSIONS AND THEIR IMPACT ON THE OXIDISING CAPACITY OF THE ATMOSPHERE

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1 Abstract

The industrial revolution brought about the mechanisation of transport, allowing humans to travel faster and further using machines such as cars, trains, powered boats and eventually aircraft. Aviation is the pinnacle of all transport systems as it has allowed humans to travel faster and further than ever before, accelerating globalisation and enhancing the prosperity of the global economy. However, the relentless growth of the aviation industry is contributing ever increasingly to the degradation of the environment on a local and global level. This is because aircraft are predominantly powered by hydrocarbons (fossil fuels) and the combustion of jet fuel generates a number of toxic emissions that impact the Earth-atmosphere system in a variety of ways, as reviewed in section 2.3. With the sector forecast to continue growing at a rapid rate, it is vital that these environmental implications are well understood so that action can be taken to mitigate against further warming.

This report identifies the aviation-induced climate impacts and explores the extent of the impact by measuring the change to the oxidising capacity, or the atmosphere's ability to cleanse itself of harmful pollutants, resulting from the release of flight emissions. This investigation is carried out for three frequently flown flight routes that are diverse in location, range and aircraft performance. The calculation process estimates the pollution emitted for each observed flight, which is overlaid onto the background pollution to analyse the effects induced by a single flight. Performing a local analysis of the climate impact of a single flight's emissions, as opposed to a global analysis of all aircraft emissions, allows one to determine more accurately the severity of the impact from that specific flight, so that a bespoke mitigation procedure can be proposed.

2 Introduction

2.1 The aircraft combustion process

2.1.1 The need for combustion

Conventional aircraft maintain their forward speed in flight by accelerating a mass of gas through a propulsion system, such as a jet engine, to provide the reaction force necessary to propel the aircraft and overcome aerodynamic drag. This reaction force is known as thrust. The magnitude of thrust depends on the mass of gas being accelerated and the difference in velocity of the gas through the propulsion system [1]. The forward speed generated by the propulsion system induces flow over the wings and the cambered nature of the wing geometry rotates the flow downwards, hence generating lift to counteract aircraft weight. This completes the force balance required for sustained flight.

From the 1930s onwards, gas turbine technology became the conventional propulsion method within aviation, powering the majority of all current commercial and military flights. Gas turbine engines work by taking in a mass flow of air, compressing it to high pressures (to increase the air's energy holding capacity), mixing with fuel and igniting to cause a combustion reaction, resulting in rapid expansion of the mass flow. This high temperature, high pressure fuel-air mix is then fed through a turbine which extracts energy from a relatively small part of the flow to drive the compressor, completing the engine cycle. The rest of the flow is then directed through an exhaust nozzle at the rear of the engine, exiting at a higher velocity than the oncoming flow, providing thrust.

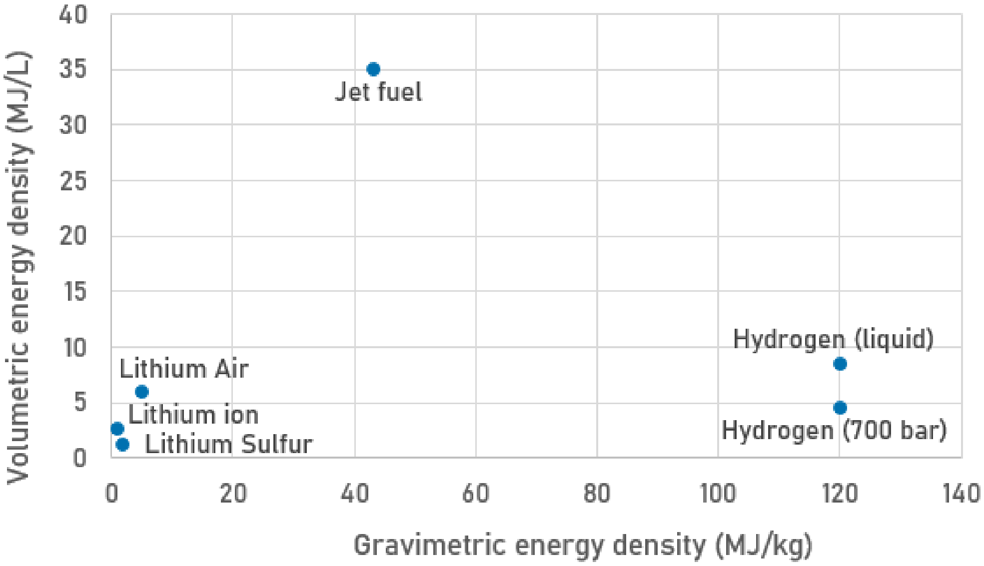

Figure 1: Energy densities for potential aviation fuels. (Adapted from 'Energy density', *Wikipedia* [2].)

Aviation uses a variety of hydrocarbon fuel types that depend on the specific aircraft purpose, such as jet fuel or avgas (aviation gasoline). Jet propelled aircraft, which are the primary focus of this report, currently use a variety of highly refined kerosene based fuels (jet fuels) as they provide a suitable compromise between volumetric and gravimetric energy densities, meaning they produce a relatively high amount of mechanical energy per unit mass and volume compared to alternative sources, as shown in figure 1. It is worth noting that Li-S and Li-Air are both nascent battery technologies which are still a number of years from commercialisation [3]. Additionally, conventional jet fuel provides a wider operating temperature range i.e. has a higher flash point and lower freezing point meaning it is less susceptible to accidental ignition and freezing compared to alternative fuels that would otherwise be fit for the same purpose [4].

2.1.2 The generation of emissions

The combustion reaction process of jet fuel generates emissions from the exhaust nozzle when the reaction mass is ejected. There are essentially two classes of emissions produced by aircraft:

- Emissions that are directly dependent on the the amount of fuel consumed in flight, i.e. carbon dioxide (CO_2), sulphur dioxides (SO_x) and water vapour (H_2O).
- Emissions that depend on the internal engine conditions throughout flight, as well as the amount of fuel consumed throughout flight, i.e. nitrous oxides (NO_x), carbon monoxide (CO) and unburned hydrocarbons (UHC) [5].

Figure 2 displays the products of the ideal aircraft combustion process, in which it can be assumed that the fuel is pure and completely combusted before exiting the exhaust nozzle. The actual combustion products are the complete combustion products plus the emissions that occur as a result of inefficiencies and/or impurities (or more simply, incomplete combustion products). Figure 3 refers to the proportion of constituents in the actual combustion process.

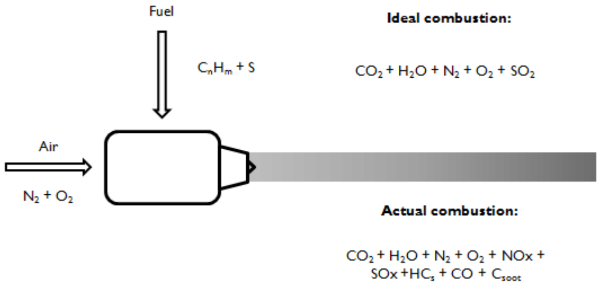

Figure 2: Ideal and actual combustion process [6].

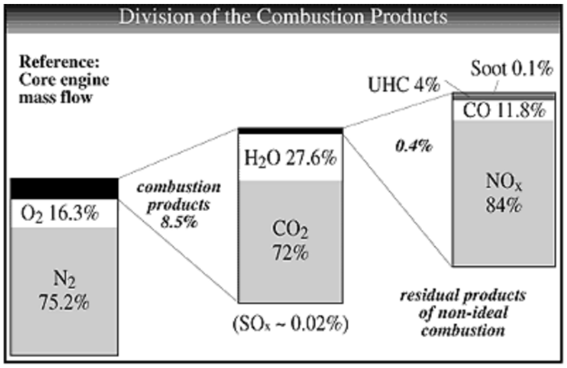

Figure 3: Constituents of the combustion process [6].

Each individual emission species gives rise to a unique phenomenon that can be detrimental to the environment in a variety of ways, depending on: atmospheric conditions (e.g. temperature, pressure, humidity) and aircraft/engine specification (e.g. thrust setting, combustor conditions, fuel flow rate). The severity of these impacts can be investigated by estimating the emissions released throughout a given flight mission and by carrying out observations of the atmospheric chemistry perturbations occurring as a result of release into the environment.

2.2 Impact of aviation emissions on the climate

2.2.1 Aviation CO_2 emissions

According to the International Air Traffic Association (IATA) Industry Statistics report 2018, aviation was responsible for emitting 905 million tonnes of CO_2, which correlates to approximately 2% of total man-made CO_2 emissions produced over the year [7]. Furthermore, the International Civil Aviation Organisation (ICAO) projected that international aviation fuel consumption will increase 2.2 to 3.1 times by 2045 compared to 2015 levels [8]. Figure 4 depicts the various CO_2 emissions pathways possible for the international aviation industry over the coming decades. It is clear that without monumental investment in aircraft emissions mitigation technologies – design improvements, improved Air Traffic Management (ATM) and implementation of Sustainable Aviation Fuels (SAFs) – sector emissions are expected to rise two to four fold in the next thirty years.

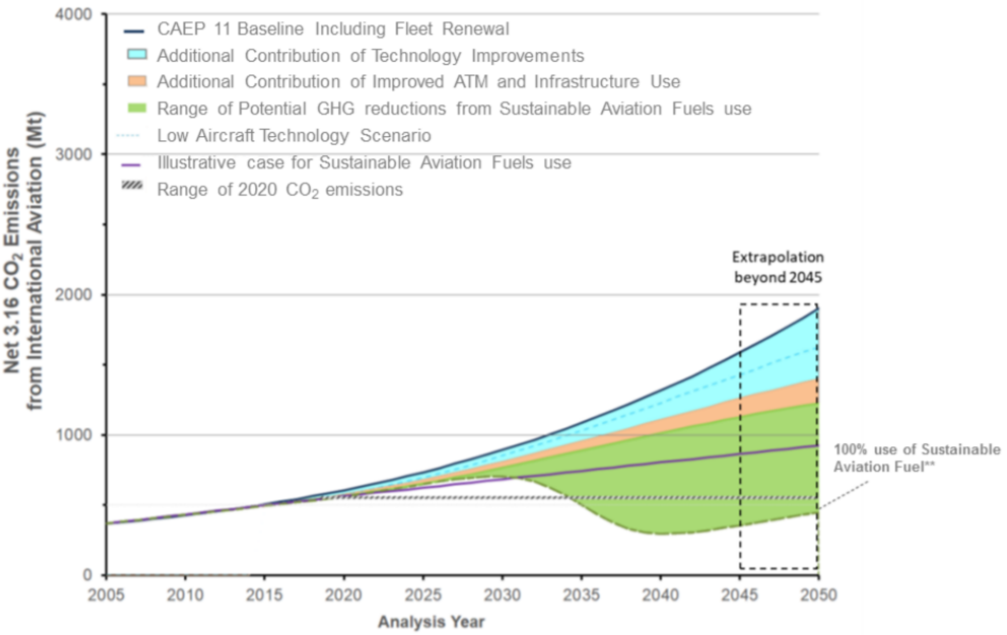

Figure 4: CO2 Emissions from International Aviation, 2005 to 2050, ICAO Working Paper (2019) [8].

2.2.2 Severity of non-CO_2 emissions

2% of current global CO_2 emissions does not however correlate with 2% of total man-made global warming. This is because there are a number of secondary warming effects that emerge as a result of non-CO_2 aviation emissions, so the combined radiative forcing[1] (RF) of aviation

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[1] Radiative forcing is defined as the change to the net energy balance of the Earth as a result of a potential climate change mechanism. So a positive RF results in warming and a negative RF results in cooling. Usually expressed in watts per square metre of the Earth's surface (W/m^2).

is actually closer to 5% of the total radiative forcing due to human-induced activities [9]. This discrepancy occurs due to the severity of non-CO_2 climate forcing mechanisms resulting from the combustion of jet fuel at high altitudes. Additionally, aircraft have large residence times at such altitudes which further augments the climate impact, as the radiative efficiency is higher (higher sunlight intensity) and background concentrations of trace gases are lower, allowing for the emissions to have a more prominent influence on the surroundings.

2.3 Aviation induced climate forcing mechanisms

Figure 5 displays the principal emission species released from aircraft, categorised by their unique influence on the surrounding atmosphere. It then categorises the climate impact of aviation into four climate forcing mechanisms: direct greenhouse gases (GHGs), indirect greenhouse gases, aerosol effects and aviation induced cloudiness.

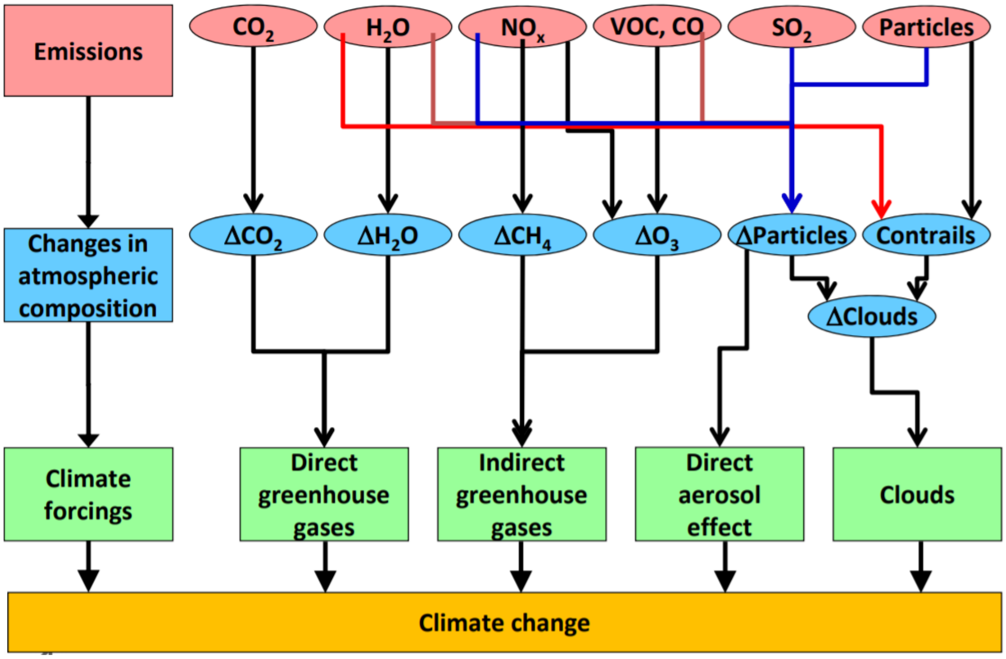

Figure 5: Atmospheric effects of aviation [9].

2.3.1 Direct GHG emissions

Direct GHGs are those which cause an immediate warming effect because aircraft CO_2 and water vapour emissions exhibit the greenhouse effect[2] directly. Therefore the impact can be quantified by measuring the amount of CO_2 and H_2O released throughout flight and determining the contribution to the global atmospheric composition.

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[2] The greenhouse effect is when so called 'greenhouse gases' such as carbon dioxide and methane absorb outbound infrared radiation and effectively trap heat within the atmosphere, causing average temperatures to rise.

2.3.2 Indirect GHG emissions

Emissions of NO_x, volatile organic compounds (VOCs) and CO do not directly exhibit the greenhouse effect, however they are in fact precursors to two potent greenhouse gases: methane and tropospheric ozone. At high altitudes, various reactions involving NO_x, VOCs and CO act to generate additional ozone (O_3) within the troposphere leading to a warming effect. On the contrary, other reactions involving NO_x act to deplete methane (CH_4) levels which leads to a cooling effect, slightly offsetting the warming from ozone generation. The net effect however is largely warming and therefore indirectly produced GHGs are considered another notable constituent of positive radiative forcing from aircraft. To determine the RF from indirect GHGs requires knowledge of the chemical reactions that are likely to occur, provided the internal engine conditions and the external ambient conditions are known. For this reason it is more difficult to measure the ΔO_3 and ΔCH_4 levels and therefore the influence on radiative forcing due to aviation is harder to quantify compared to that of direct GHG emissions.

2.3.3 Direct aerosol effects

An increase in particulates within the atmosphere due to aviation usually arises primarily from the emissions of SO_x, UHC and soot. These particulates produce a direct aerosol effect and the amount of warming induced by an emitted particle depends on its composition and colour. Brighter and more translucent particles such as SO_x tend to reflect sunlight back into space, producing a cooling effect whereas darker, more opaque particles such as UHC and soot absorb inbound solar radiation, leading to an increase in RF [10]. The total effect can be hard to quantify as it is difficult to determine the amount of particles emitted from an aircraft as a result of incomplete combustion of jet fuel.

2.3.4 Contrails and aviation induced cloudiness

The final aircraft-induced warming mechanism to mention is the formation of contrails which transition into cirrus clouds, otherwise known as aviation induced cloudiness (AIC). Contrails (condensation trails) are a phenomenon that occurs when the high temperature exhaust plume mixes with the sufficiently icy, moist conditions of the upper troposphere (threshold conditions for a contrail to form are above 8km altitude and below -40°C [11]), which result in the condensation of expelled water vapour and the formation of ice crystals in the aircraft's upper wake. If the relative humidity is high enough and the ambient temperature is low enough, the contrails will persist and may go on to generate additional cirrus clouds in the atmosphere. Contrail cirrus has the potential to spread >100km due to atmospheric disturbances and wind shear, creating vast regions of extra cloud cover. Contrarily, if the ambient conditions do not meet the cold, humid requirement, contrails are either relatively short lived, or do not form at all, resulting in a small warming effect compared to persistent contrails. Persistent contrails warm the atmosphere by trapping outbound terrestrial radiation more effectively than they reflect inbound solar radiation, leading to a net warming effect.

The radiative forcing of a contrail cirrus cloud depends on its optical properties, percentage of global cover and age. The uncertainty of these properties combined with the fact that it is difficult to differentiate AIC from natural occurring ice clouds in most instances leads to a significant uncertainty in their impact. This lack of scientific understanding has led to contrasting views on the relative impact of AIC over the last few decades, however recent literature such as Karcher, et al 2018 [11] has explicitly stated that previous reports that underpin the general scientific concensus around the impact of aviation on the climate (e.g. the IPCC special report: Aviation and the Global Atmosphere [12]) do not accurately account for the severity of contrail cirrus, and as a result, projections for the net RF of aviation have been limited in scope. Karcher states that "Since that report, climate model simulations have shown that RF due to contrail cirrus greatly exceeds that from persistent contrails, making contrail cirrus the most important contribution to AIC and to RF associated with aviation." Worse still, Burkhardt, Karcher (2011) [13] states that the net contrail effect contributed more to warming than the combined impact of all the CO_2 produced by aviation since the first powered flight of the Wright Brothers in 1903. Such a drastic level of uncertainty surrounding the impact of contrails points towards the necessity for better understanding of the contrail effect so that the net RF from aviation can be more accurately estimated. Figure 6 displays the projected RF contributions from aviation.

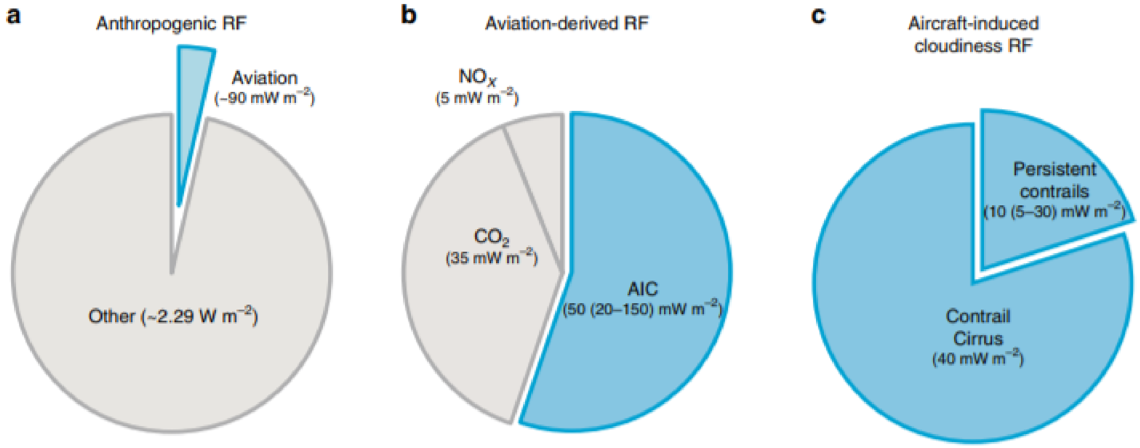

Figure 6: Comparison of radiative forcing due to aviation induced cloudiness [11].

2.4 Contextual atmospheric chemistry

2.4.1 The composition of the atmosphere

The Earth's atmosphere provides Earth with the habitable conditions to allow life to exist on it in abundance. It comprises a concoction of gases, or simply 'air', that creates pressure to allow liquid water to exist, retains heat through the greenhouse effect and facilitates the respiration of living organisms as it is inherently oxygen rich. Air is made up of approximately 78% nitrogen (N_2), 21% oxygen (O_2), <1% argon (Ar) and the remaining fraction is the group of so called atmospheric 'trace gases' which are a group of chemical species that exist in relatively small quantities within the atmosphere and are constantly changing in concentration due to both natural and artificial processes that contribute to their production and depletion [5]. The trace gases of most importance are greenhouse gases which retain heat and reduce the temperature extremes between day and night. Maintaining satisfactory concentrations of greenhouse gases is key in the survivability of the planet's living systems, as the greenhouse effect is a major factor in determining the Earth's net energy balance.

Natural biological, chemical and geological processes have kept trace species concentrations to safe levels since the dawn of life on Earth. However the industrialisation and globalisation of humanity since the 19th century has led to relentless growth in the consumption of energy and resources. The pollution emitted as a result of this has led to significant increases in greenhouse gas concentrations, triggering a stark rise in global temperatures and the breakdown of our climate.

Our new found desire for mass transport of people and goods since the industrial revolution has led air travel to become a primary source of transportation, as it is one of the fastest and most economical ways to do so. However, the toxic emissions released as a result of jet fuel combustion are having a profound influence on the environment on a local, regional and global scale. This report aims to quantify this impact by observing how flight emissions affect the atmospheric chemical composition. It will then explore the implications on the climate as a result of this changing chemistry.

2.4.2 Layers of the atmosphere

The atmosphere is made up of a number of layers with boundaries classified by temperature inversions, as can be seen in figure 7.

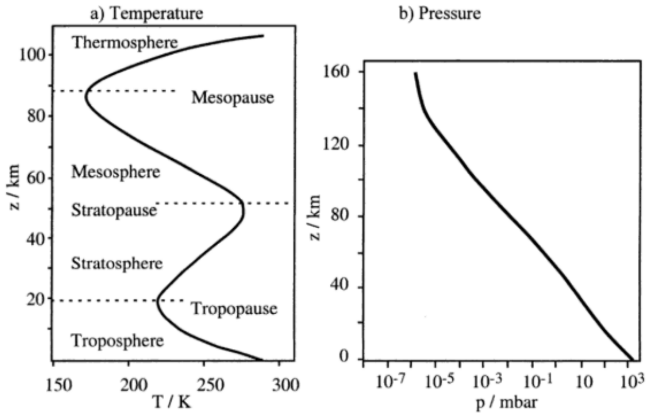

Figure 7: Layers of the atmosphere [14].

From the surface outwards, the layers are as follows: the troposphere, stratosphere, mesosphere, thermosphere and the exosphere. The layer closest to the Earth's surface is the troposphere. This is where the majority of life lives and about 75% of all air is contained [15]. It is the most dense due to the combined gravitational compression from all the other layers and almost all atmospheric water vapour is present here which leads to the occurrence of weather [16]. The temperature in this region reduces with altitude due to the main heat source being the emanation of heat from the Earth's surface which lessens the higher you go.

Above the troposphere lies the tropopause, the sub-layer between the troposphere and the stratosphere. The temperature here does not change with altitude, meaning mixing of substances between the troposphere and stratosphere is kept to a minimum as convection currents (i.e. molecular transfer of heat) are required to transport gases vertically [17].

The stratosphere is the region in which the ozone layer is present, an area where the concentration of ozone is significantly higher than anywhere else in the Earth's vicinity. The ozone layer absorbs and scatters inbound ultraviolet light from the sun, reducing the intensity of harmful UV radiation in the troposphere. Additionally, the temperature in the stratosphere increases with altitude due to absorption of UV light leading to increased temperatures. When analysing the impacts of pollution on the composition of the atmosphere, it is reasonable to assume that the troposphere and stratosphere account for the majority of reactions which alter trace gas concentrations, so the climatic effects of reactions that occur at altitudes beyond these two layers are negligible in comparison.

2.4.3 The oxidising capacity of the atmosphere

Despite the vast amounts of pollution emitted due to human activity daily, the atmosphere remains resilient to permanent damage by virtue of so called oxidation reactions[3]. The

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[3] Oxidation is the process involving the incorporation of an oxygen atom into a molecule e.g. the oxidation of iron results in rust formation.

oxidising capacity of the atmosphere is a measure of the atmosphere's ability to cleanse itself of harmful emissions, such as those released by aircraft combustion, and restore itself back to natural equilibrium. The prevailing sources of atmospheric oxidation are hydroxyl radicals (OH and HO_2, or collectively HO_x), nitrate radicals (NO_3) and tropospheric ozone (O_3), so measuring the concentration of each of these oxidants can help one to quantify the oxidising capacity of the atmosphere. Hydroxyl radicals dominate the oxidation process during the daytime as they are much more reactive than their counterparts, NO_3 and O_3. However, their reaction mechanism is initiated when ozone absorbs sunlight, through a process known as photolysis, meaning they are only produced when daylight is present and the levels of tropospheric ozone are sufficient. This means that during daytime, the concentration of OH is the most suitable indicator of the oxidising capacity of the atmosphere and will remain the focal point of this report when examining the warming impact of aviation.

Once produced, the hydroxyl radical has a tendency to react nearly immediately (< 1 second) with almost any nearby chemical compound, with the exception of chlorofluorocarbons (CFCs), nitrous oxide (N_2O) and carbon dioxide. This means that in highly polluted regions, such as an aircraft exhaust plume, where the density of potential reactants is much higher than usual, hydroxyl levels are diminished. This is due to OH consumption outweighing OH production, hence leading to a net loss over time.

Without sufficient levels of OH, more harmful chemicals are allowed to reside in the atmosphere for extended periods of time, which are capable of a far worse warming effect and are substantially more toxic to the surrounding environment than the compound it would be decomposed into if enough hydroxyl was present. An example of atmospheric oxidation is the decomposition of methane into carbon dioxide and water due to a reaction involving OH molecules. The warming potential of methane is approximately 28 times that of CO_2 over a 100 year timespan [18], so it is clear to see why an extended residence time of methane due to a lack of sustained OH concentrations can be a serious issue regarding increases in planetary radiative forcing and local environmental damage.

3 Project Aims

The purpose of this study is to highlight the negative repercussions associated with powering aircraft by fossil fuel combustion. It intends to draw a comparison between the warming impact of various flights along popular routes by analysing the levels of oxidising species prior to and after the release of emissions into the atmosphere as a result of these flights. The change in concentration of OH radicals, the predominant oxidising species, will allow for the relative impact of each flight to be deduced. The reasons for this are explained in section 1.3.3.

This project's first objective is to select three frequently flown aircraft routes, allowing for a diverse analysis of the impacts induced by flight routes around the globe. This will lead to a more thorough investigation into the impacts of global flights on the Earth's climate. Secondly, the emission species released and the general operational characteristics of each flight will be estimated using an aircraft performance modelling software, aptly known as the Aircraft Performance Model Implementation (APMI). Combined with positional data approximated for numerous discrete time-steps throughout flight, each mission's environmental impact will be estimated by modelling a simplified chemical mechanism that simulates key atmospheric reactions that have a profound impact on the concentration of atmospheric trace gases, hence allowing for the net production of hydroxyl to be estimated, enabling the oxidising capacity to be quantified. The purpose of this study is not to provide accurate estimates of the trace species compositions, as there are simply far too many influencing factors to account for that vary randomly day-to-day. Instead, this study will observe the relative changes in the concentrations of the oxidising species to compare the impacts of each flight route and to see how their net rate of production changes throughout the year.

4 Methodology

4.1 Aircraft route selection justification

The flight characteristics experienced by aircraft throughout flight alter depending on ambient conditions (i.e. temperature, pressure, air density, local wind etc.), aircraft/engine parameters, speed schedules, range and time of day. These variables all determine how much of each substance is released in the aircraft exhaust plume and also the extent to which these emissions influence the surrounding atmosphere. To ensure a rigorous study which adequately represents the diverse nature of flight, three popular flight corridors were decided upon for analysis:

3.2.1 London Heathrow (LHR) to New York JFK Int'l (JFK).
This long haul flight is the single most popular transatlantic flight to date and has proven to be the most lucrative for airliners, meaning airliners are likely to prioritise growth along this corridor in future. Furthermore, the departure and destination locations are both subject to fairly temperate climates with distinct seasonal variations, meaning the fluctuations in background chemistry will likely be significant.

3.2.2 Toronto Pearson Int'l (YYZ) to Vancouver Int'l (YVR).
This is a medium haul flight and is one of the more common domestic flight routes to remain over land at almost all times, experiencing the hot summer and harsh winter temperatures Canada is renowned for.

3.2.3 Kuala Lumpur Int’l (KUL) to Singapore Changi Int’l (SIN).

This is an extremely popular short haul domestic route in the hot and humid environment of Southeast Asia. The extremely short range means the chosen aircraft and the most common for this flight route, the Airbus A320 [19], is forced to fly at a sub-optimal cruise altitude and spends less than 50% of flight time in cruise, meaning a significant portion of the flight is dedicated to the climb phase in which the most fuel is burnt per kilometre. Also the climate is fairly constant through the seasons, so base case atmospheric composition is unlikely to alter much over the course of the flight, for all four times throughout the year.

The emissions impacts of these flights were considered for four times throughout the year: 1st January, 1st April, 1st July and 1st October. This was to capture the variations in background chemistry resulting from the change of seasons. Table 1 provides key information on the journey, daily temperatures for each month to be observed, a description of the climate in each location, aircraft data and journey specific data. This presents the distinctions between each flight for reference later in the study.

Table 1: Journey and aircraft data for each flight route.

	Departure	Destination	Departure	Destination	Departure	Destination
Journey	LHR	JFK	YYZ	YVR	KUL	SIN
Daily mean temperatures [°C] (Jan, Apr, Jul, Oct)	5.2, 9.9, 18.7, 12.0	0.4, 10.7, 24.4, 14.0	-6.3, 6.3, 20.8, 8.9	4.1, 9.4, 18.0, 10.3	27.7, 28.7, 28.1, 28.0	26.5, 28.0, 27.9, 27.6
Climate description	“Temperate oceanic climate, with warm summers and cool winters. The city annually has modest precipitation and large built up area creates an urban heat island effect.” [20].	“Warm, humid subtropical climate. Very cold winters and exceptionally warm and humid summers.” [21].	“Humid continental climate. Warm summers but very cold winters due to northerly latitude. Average winter snowfall is 108.5 cm.” [22].	“Moderate oceanic climate. Dry summers while the rest of the year is rainy, especially between October and March.” [23].	“Tropical rainforest climate, which is warm and sunny, along with abundant rainfall, especially during the northeast monsoon season from October to March. Temperatures tend to remain constant.” [24].	“Tropical rainforest climate, with no true distinct seasons. Uniform temperature and pressure, high humidity and abundant rainfall.” [25].
Aircraft	Boeing 747-400		Boeing 737-700		Airbus A320	
Seat capacity	416		128		180	
Great circle distance [km]	5540		3345		298	
Flight duration [min]	382.9 (Long haul)		252.4 (Medium haul)		36.8 (Short haul)	
Cruise altitude [km]	12.3		12.5		4.1	
Flights per week	226		134		360	

4.2 Estimating aircraft emissions using the APMI software

As section 1.2.2 explains, the emissions generation process depends on the amount of fuel burnt and the internal conditions of the engine throughout flight. In order to estimate emissions released throughout a given flight, it is necessary first to determine the mission data (distance flown, ambient conditions, cruise altitude etc.) and the aircraft data (engine and aerodynamic performance) in order to provide an estimate for fuel burn. Once fuel burn is approximated, the quantities of emitted substances that are only dependent on the amount of fuel burnt, such as CO_2, H_2O and SO_x can be directly calculated using a multiplication factor. The quantities of emissions that are dependent also on internal engine conditions, such as NO_x, CO and UHC can be ascertained through the knowledge of engine emissions data.

This study utilised a scientific Linux based software known as the Aircraft Performance Model Implementation (APMI) provided by Wasiuk, et al (2014) [5]. This software allowed for the estimation of emissions for each flight, following the previously explained process. This software determines the aircraft and engine performance at any stage of flight using the Base of Aircraft DAta (BADA) method. This method combines a database of current aircraft specifications with a mathematical aircraft performance model, known as the Total Energy Model [26], to calculate the in-flight aircraft performance for each stage of flight, thus allowing for the calculation of fuel burn throughout flight. The model then implements the so called Boeing Fuel Flow Method 2 (BFFM2) which couples the BADA method with 'ICAO engine emissions databanks' [27] to determine the approximate emissions released for a specific flight. The BADA method calculates fuel burn for various stages throughout flight and the ICAO engine emissions databanks provide the 'emissions indices' (how many grams of the emission species are released per kilogram of fuel burnt) of a given engine specification for four unique thrust settings: take-off, climb out, approach and idle. With knowledge of the emissions indices, the mass of each chemical species released throughout flight can be determined through the multiplication of emissions indices and fuel consumed, as shown in the primary output file (figure 8 for the LHR - JFK flight route. The input was 'B744 i 5400' which translates to a Boeing 747-400 travelling internationally for 5400km. The assumptions for this method include a constant cruise altitude, reserve fuel estimation, route follows great circle distance and so on. Greater detail on assumptions can be found in Wasiuk, et al. (2014) [5].

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                       ICAO CODE:                                       B744
                     ENGINE TYPE:                                        Jet
                          ENGINE:                                 CF6-80C2B4
    RATED OUTPUT (kN)/POWER (hp):                                        254
               NUMBER OF ENGINES:                                          4
                   DISTANCE (km):                                       5400
            CRUISE ALTITUDE (ft):                                      40500
    RESERVE CRUISE ALTITUDE (ft):                                      20000
                     DESTINATION:                              INTERNATIONAL
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                 PHASE BREAKDOWN:
-------------------------------------------------------------------------------------------------------------------------------------
                    DISTANCE (km)      TIME (m)     FUEL (kg)    CO2 (kg)     CO (kg)    H2O (kg)     HC (kg)    NOx (kg)    SOx (kg)
-------------------------------------------------------------------------------------------------------------------------------------
        TAXI OUT                -        19.000       916.560    2886.247      18.111    1127.369       1.457       4.290       0.770
           CLIMB          299.192        23.341      7808.554   24589.135       1.601    9604.521       0.590     209.487       6.559
          CRUISE         4883.031       328.348     44061.707  138750.317      25.307   54195.900       4.923    1201.710      37.012
         DESCENT          218.389        21.838      1267.294    3990.710      22.820    1558.772       1.945      11.541       1.065
         TAXI IN                -         7.000       337.680    1063.354       6.673     415.346       0.537       1.580       0.284
    TOTAL GROUND                -        26.000      1254.240    3949.602      24.784    1542.715       1.994       5.870       1.054
  TOTAL AIRBORNE         5400.613       373.528     53137.555  167330.161      49.728   65359.193       7.458    1422.738      44.636
-------------------------------------------------------------------------------------------------------------------------------------
   TOTAL MISSION         5400.613       399.528     54391.795  171279.763      74.512   66901.908       9.453    1428.608      45.689
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  RESERVE CRUISE                -        37.353      4698.900           -           -           -           -           -           -
 RESERVE MISSION          369.829             -      6885.621           -           -           -           -           -           -
    RESERVE HOLD                -        30.000      5282.893           -           -           -           -           -           -
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   TOTAL RESERVE                -             -     16867.414           -           -           -           -           -           -
-------------------------------------------------------------------------------------------------------------------------------------
           TOTAL         5400.613       399.528     71259.210  171279.763      74.512   66901.908       9.453    1428.608      45.689
-------------------------------------------------------------------------------------------------------------------------------------
              ALTITUDE BREAKDOWN:
-------------------------------------------------------------------------------------------------------------------------------------
   ALTITUDE (km)    DISTANCE (km)      TIME (m)     FUEL (kg)    CO2 (kg)     CO (kg)    H2O (kg)     HC (kg)    NOx (kg)    SOx (kg)
-------------------------------------------------------------------------------------------------------------------------------------
       0.0 - 1.0           37.529        33.749      3045.145    9589.163      27.774    3745.529       2.223      33.506       2.558
       1.0 - 2.0           32.754         4.275       749.319    2359.606       2.454     921.663       0.217      14.517       0.629
       2.0 - 3.0           27.851         3.207       549.487    1730.335       2.913     675.869       0.277      11.839       0.462
       3.0 - 4.2           39.881         3.479       692.773    2181.541       2.367     852.110       0.240      18.254       0.582
       4.2 - 5.6           45.772         3.699       805.616    2536.884       2.615     990.908       0.271      21.940       0.677
       5.6 - 7.2           65.251         4.879      1056.870    3328.082       3.150    1299.949       0.339      29.527       0.888
       7.2 - 9.2           94.231         6.409      1368.850    4310.510       3.461    1683.686       0.398      38.602       1.150
      9.2 - 11.8          135.529         8.910      1643.270    5174.659       3.721    2021.223       0.459      46.079       1.380
     11.8 - 16.2         4921.813       330.920     44480.465  140068.983      26.059   54710.972       5.027    1214.343      37.364
-------------------------------------------------------------------------------------------------------------------------------------
           TOTAL         5400.613       399.528     54391.795  171279.763      74.512   66901.908       9.453    1428.608      45.689
-------------------------------------------------------------------------------------------------------------------------------------
```

Figure 8: Sample APMI output file for LHR - JFK.

4.3 Simplifying the atmospheric reaction mechanism

In order to analyse the impact of flights on the surrounding atmosphere, it is necessary to compare two scenarios for each of the flight routes: the *base case* which represents the unperturbed atmosphere, free of the observed flight emissions (however still influenced by other emissions present in that region), and the *perturbation case* which is the scenario with the flight emissions present. As previously discussed, the climate impact of a flight can be gauged from the oxidising capacity of the atmosphere at the observed location in which the emissions are released. So to estimate the oxidising capacity, the concentration of OH radicals are calculated for both cases, allowing for the relative change in levels of these species to be determined and for a conclusion to be drawn on how these flights affect the environment relative to one another.

The atmosphere is in a state of constant flux due to varying meteorological conditions and changes to chemical composition. These variations are induced by, and are the cause of, the vast number of reactions that occur perpetually. This set of reactions is known as the chemical reaction mechanism. For the purpose of this project, a significantly reduced version of the atmospheric reaction mechanism is used to represent the Earth-atmosphere system, that focuses on the production and loss of OH radicals.

4.3.1 Determining a reduced reaction mechanism

Watson, Shallcross, et al. [28] suggests various reduction schemes and assesses the compromises to accuracy as a result. The reduction schemes are achieved through "systematic lumping" of chemical species and the removal of redundant species and their associated chemistry, in order to simplify the model considerably.

With guidance from Prof. D. Shallcross and the University of Bristol Atmospheric Chemistry Group, a reduced reaction mechanism optimised for the calculation of OH production was proposed (for prerequisite information on the constituting chemical species and reaction rate coefficients, see section A.2):

$$\mathrm{O_3 + hv \xrightarrow{J_1} O(^1D) + O_2} \tag{R1}$$

$$\mathrm{O(^1D) + O_2 \xrightarrow{k_2} O(^3P) + O_2} \tag{R2}$$

$$\mathrm{O(^1D) + N_2 \xrightarrow{k_3} O(^3P) + N_2} \tag{R3}$$

$$\mathrm{O(^1D) + H_2O \xrightarrow{k_4} OH + OH} \tag{R4}$$

$$\mathrm{OH + CO + O_2 \xrightarrow{k_5} HO_2 + CO_2} \tag{R5}$$

$$\mathrm{HO_2 + NO \xrightarrow{k_6} NO_2 + OH} \tag{R6}$$

$$\mathrm{HO_2 + O_3 \xrightarrow{k_7} OH + 2\,O_2} \tag{R7}$$

$$\mathrm{NO + O_3 \xrightarrow{k_8} NO_2 + O_2} \tag{R8}$$

$$\mathrm{NO_2 + hv + O_2 \xrightarrow{J_9} O_3 + NO} \tag{R9}$$

$$\mathrm{OH + NO \xrightarrow{k_{10}} HONO} \tag{R10}$$

$$\mathrm{NO_2 + OH \xrightarrow{k_{11}} HNO_3} \tag{R11}$$

$$\mathrm{HONO + hv \xrightarrow{J_{12}} OH + NO} \tag{R12}$$

$$\mathrm{HCHO + hv + 2\,O_2 \xrightarrow{J_{13}} 2\,HO_2 + CO} \tag{R13}$$

$$\mathrm{OH + O_3 \xrightarrow{k_{14}} HO_2 + O_2} \tag{R14}$$

The individual contribution to hydroxyl production and consumption of each reaction in the reduced mechanism is dependent on: the stoichiometry[4] of the reaction, the initial concentration of reactants and the rate at which the reaction happens. There are two types of reactions present in the reaction mechanism: photolysis reactions (initiated by sunlight energy which is denoted by 'hv' in equation form [29]) and gas-phase thermal reactions (initiated by temperature). The rate at which photolysis reactions happen is determined by the photolysis rate coefficient, J. The rate at which thermal reactions happen is determined by the complex rate coefficient, k.

4.3.2 Validation

This mechanism was derived using the same systematic lumping method as in [28], and when implementing the aforementioned method, it is stated that "reductions of up to 53% and 55% in the numbers of reactions display a degree of compromise in the ozone-forming ability of the VOC sub-categories, but retain a good level of overall performance". Knowledge of this provides a degree of validity to this study along with assurance from the University of Bristol Atmospheric Chemistry Research Group (ACRG).

4.4 Quantifying the climate impact from aviation emissions

4.4.1 Calculating the 'base case' atmospheric chemistry

The initial atmospheric compositions, temperatures and densities for the base case were derived from 1998 meteorological data, obtained from the ACRG, which served as the basis for all subsequent calculations. This included: temperature, air density and background concentrations of all substances present in the reduced reaction mechanism.

4.4.2 Calculating the 'perturbation case' atmospheric chemistry

The perturbed chemistry was calculated by summing the molecular densities from the base case scenario and the additional molecular densities of NO_X, CO and H_2O due to the release of aircraft emissions from the chosen flight. The additional density of each emitted substance is calculated assuming it disperses into the volume of the aircraft wake over the course of the flight. (For further information on how the increases in molecular densities due to aircraft emissions were calculated, refer to section A.1.) The sum of the base case concentrations and the additional concentrations due to aircraft emissions then constitutes the perturbation case.

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[4] Stoichiometry is a measure of the molar ratios of products and reactants in a reaction. Knowledge of this allows for the determination of how many molecules of product are produced for a given concentration of reactant.

The base case and perturbation case chemistry for each route was then analysed for each time-step throughout flight at the proposed four times throughout the year.

4.4.3 The hydroxyl production cycle

In the atmosphere, there are various reaction pathways available for the production of the hydroxyl radical. The most common is the photolysis of ozone to produce singlet oxygen (O) and oxygen (O_2), followed by the reaction of singlet oxygen with water vapour (H_2O) to produce two OH molecules (R1, R4). Other pathways include the photolysis of nitrous acid (HONO) (R12), the reaction of nitrogen oxide with hydroperoxyl radical (R6) and the reaction of hydroperoxyl with ozone (R7) [30].

The primary loss of OH is due to reactions with CH_4, CO and O_3. However in the reduced reaction mechanism used in this study, the reaction pathways that lead to OH destruction include (R5), (R10), (R11) and (R14).

The purpose of the simplified reaction mechanism is to estimate the net production of hydroxyl. To provide this metric in a clear and efficient manner, it was only necessary to include the emissions of NO_x, CO and H_2O for the following reasons: firstly the generation of ozone due to the NO_x cycle is a significant contributor to the creation and destruction of hydroxyl, so changes to NO and NO_2 in the perturbation case significantly alter the net production rate of the oxidant. Secondly the reaction of OH with CO in (R5) is also another important process in the oxidant's production cycle, so CO concentration changes are of relevance too. The reaction of singlet oxygen with water vapour is the most important production source of OH, so changes to H_2O concentrations are also important. Emissions of CO_2, SO_x and UHC are of less importance in this study as they are less likely to play a significant role in the hydroxyl production cycle, however they do of course impact the atmosphere in alternative ways as explained in section 1.2.

4.4.4 Using the steady state approximation

Due to its highly reactive nature, the hydroxyl radical is consumed almost immediately once generated. This means that the net production of OH can be determined using the steady state approximation method. This method assumes that the generation rate is equal to the consumption rate (every molecule produced is instantly consumed - a reasonable approximation for OH as it is highly reactive) hence deeming the concentrations of intermediate[5] substances effectively constant [31]. Applying this to the reduced reaction mechanism, the net production of OH, HO_2 and HONO are calculated and displayed in equations (2), (3)

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[5] An intermediate is a species that is neither a reactant or a product, and exists only during the course of the reaction.

and (4) where concentrations of chemical species are denoted by square brackets and reaction rates are denoted by ‘k’ (thermal reaction rate) or ‘J’ (photolysis reaction rate) coefficients.

$$f = \frac{k_4[H_2O]}{k_4[H_2O] + k_3[N_2] + k_2[O_2]} \tag{1}$$

$$[OH] = \frac{[OH_{Prod}]}{[OH_{Loss}]} = \frac{2fJ_1[O_3] + k_6[HO_2][NO] + k_7[HO_2][O_3] + J_{12}[HONO]}{k_5[CO] + k_{11}[NO_2] + k_{10}[NO] + k_{14}[O_3]} \tag{2}$$

$$[HO_2] = \frac{[HO_{2_{Prod}}]}{[HO_{2_{Loss}}]} = \frac{k_5[OH][CO] + 2J_{13}[HCHO] + k_{14}[OH][O_3]}{k_7[O_3] + k_6[NO]} \tag{3}$$

$$[HONO] = \frac{[HONO_{Prod}]}{[HONO_{Loss}]} = \frac{k_{10}[OH][NO]}{J_{12}} \tag{4}$$

Initially, the base case atmospheric composition was considered. The concentration of hydroxyl present at each time-step for the four times throughout the year were calculated by setting an initial arbitrary value and iterating around [OH], [HO_2] and [HONO] to find [OH]. The perturbation case then overlays the increased molecular densities due to the release of emissions and the same process is carried out to essentially find [OH] with and without the aircraft present. Once the base and perturbation values were obtained for each time-step, it was then necessary to carry out an analysis into how the hydroxyl levels change resulting from the combustion products reacting with the surrounding atmosphere.

4.5 Results

In order to obtain results that indicate the climate impact of each flight, the change in net OH production relative to the base case was measured. This represents the change in oxidising capacity - the atmosphere’s inherent ability to clean up harmful pollutants by decomposing them into something less harmful.

$$\Delta OH = \frac{[OH_{BC}]}{[OH_{PC}]} \tag{5}$$

ΔOH is the ratio between the OH concentration in the base case and the perturbation case, as seen in equation (5). This represents the loss of OH in the aircraft wake due to the release of emissions (more specifically CO, H_2O and NO_X) and therefore is indicative of the observed flight’s impact on the oxidising capacity. It was found for each time-step throughout flight and for each time of year being investigated. The results were then plotted on a surface plot to see if any trends occurred in the data, as seen in figures 9, 10 and 11. The major factors that play a part in the relative depletion of OH are:

- The amount of OH depleting substances released by the aircraft into that region.
- The background concentration of OH.

The amount of polluting substances released depends on the aircraft fuel burn and the internal engine conditions. Fuel burn however prevails as the most influential factor, which is highest in climb (highest thrust setting), intermediate in cruise (most efficient thrust setting) and lowest in descent (idle engine). For this reason, the oxidising capacity is affected by which phase of flight the aircraft is in.

The background concentration of OH depends on the chemical composition of the atmosphere, temperature, humidity and the intensity of sunlight. From equation (2), it is evident that higher [O_3], [H_2O], [HO_2], [NO] and [HONO] will lead to increased OH production. Furthermore, lower concentrations of the substances responsible for the loss of OH will also lead to higher hydroxyl concentrations in the atmosphere. The intensity of sunlight and temperature will affect the reaction rates as explained in section 4.3, which determine the production-consumption rate of hydroxyl. Humidity also plays a key role in OH production as water vapour is an important precursor to hydroxyl, as suggested by (R4) in the reduced reaction mechanism.

4.5.1 LHR to JFK

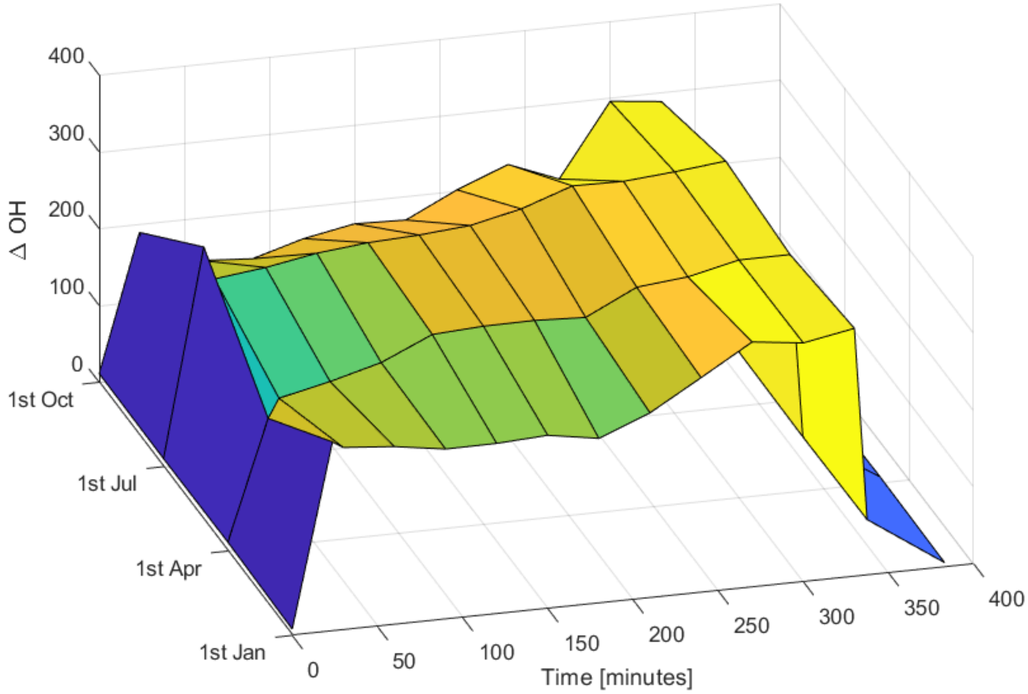

Figure 9: Variation in [OH] between base case and perturbation case (LHR to JFK).

From figure 9, it is evident that there is a spike in OH depletion at the top of the climb phase, which then dips again in cruise. Throughout cruise, the aircraft is gradually depleting more OH with every time-step, until descent phase is reached and the difference in OH production between base case and perturbation swiftly returns to zero.

The variation over the year appears to follow a trend of increasing up until 1st July, then decreasing again to levels similar to January. Throughout the cruise phase, 'ΔOH', or the depletion of OH concentration in the aircraft wake, reaches a factor of 140 to 320 times compared to the base case scenario.

4.5.2 YYZ to YVR

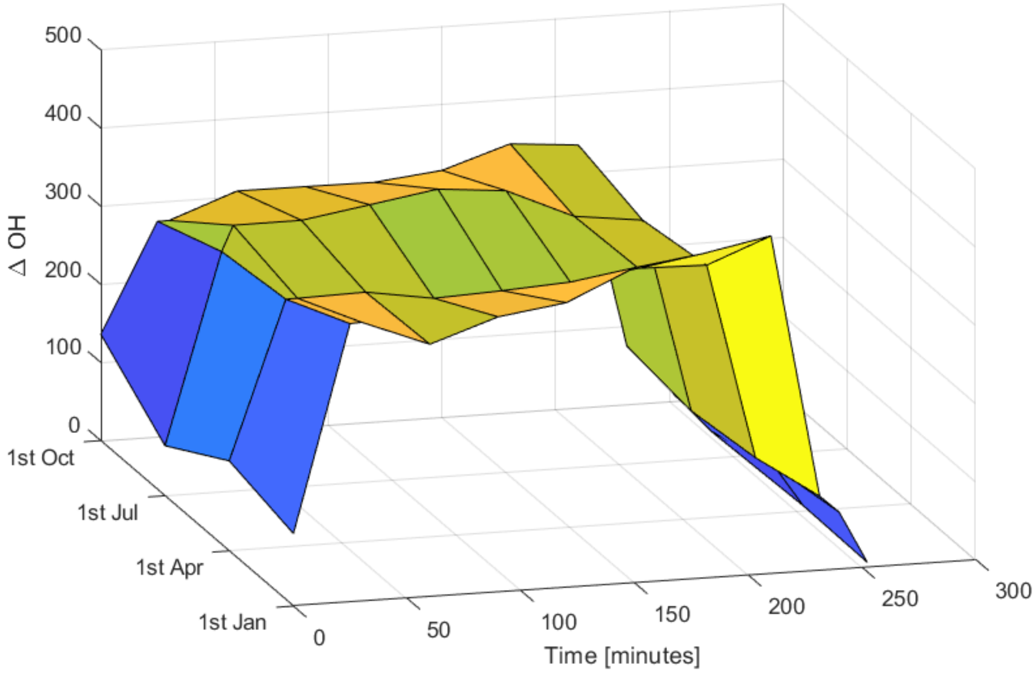

Figure 10: Variation in [OH] between base case and perturbation case (YYZ to YVR).

Figure 10 also displays large variations between time-step and time of year, following the same trend as LHR - JFK with a sharp increase throughout climb, maintaining similar levels in cruise then sharply decreasing in descent as expected.

The seasonal variation is also prevalent here and cruise sees depletion by a factor of 280 to 430. Despite similar cruise altitudes, there is significantly more hydroxyl depleted relative to the base case in this flight compared to LHR - JFK. This is likely due to the fact that YYZ - YVR is entirely over land, whereas a significant portion of the LHR - JFK flight is over water, meaning more water vapour is present and consequently there is a much higher production rate of hydroxyl.

4.5.3 KUL to SIN

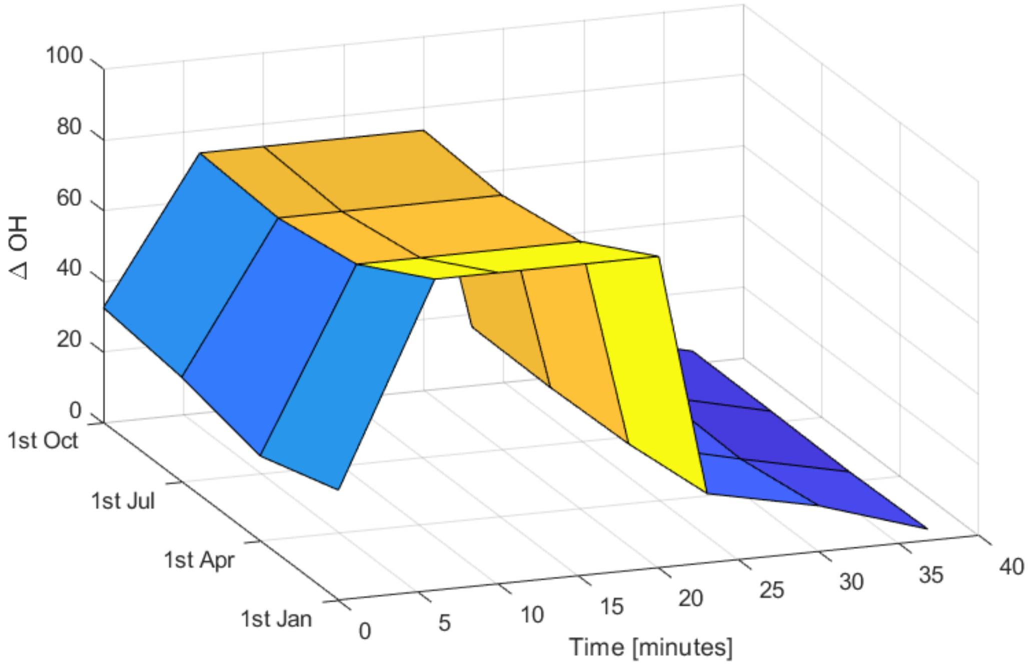

Figure 11: Variation in [OH] between base case and perturbation case (KUL to SIN).

This flight route is considerably shorter than the others, hence leading to much smaller fluctuations in atmospheric chemistry between departure and destination. The same trend holds throughout the duration of this flight, with a spike in variation in the climb phase, sustained levels in the cruise phase and decreases in the descent phase.

The seasonal variation is much smaller here also and there appears to be much more structure to the nature of OH over the course of this flight. In cruise, OH concentration is depleted by a factor of 72 to 88 compared to the base case. This is notably less than both other considered flight routes, most likely because the KUL - SIN flight has a much lower cruise altitude, meaning a higher density and it is hot and humid, so the thermal reaction rates are increased and water vapour levels are higher. These are all prime conditions for producing high levels of oxidising species and therefore releasing emissions into this region has a decreased effect on the oxidising capacity here.

5 Conclusion

The intrinsic link between anthropogenic emissions and climate breakdown is unmistakable, with aviation being a significant contributor to this. The emissions released as a result of the combustion of jet fuel have a considerable effect on the chemistry of the atmosphere and a variety of climate change mechanisms, such as the greenhouse effect and the contrail phenomenon, occur that contribute to the change in the Earth's net energy balance. The combined effect of all mechanisms produces a radiative forcing of around 5% of all anthropogenic RF, so it is vital to understand the source of each mechanism and quantify the impact, so that action can be taken to reduce it. This report focuses on how the sheer act of releasing emissions into the atmosphere exacerbates the impact of the associated climate mechanisms by consuming oxidants in the surrounding area. The reduction in oxidising capacity means that more harmful substances can linger in the atmosphere for longer, resulting in a more severe warming effect. This report investigated the depletion of OH, the most important oxidising species for three flight routes with diverse characteristics.

The emissions for each flight were estimated using the Aircraft Performance Model Implementation software and this provided the basis for determining the perturbed chemistry of the atmosphere as a result of flying. The *base case* and *perturbation case* were proposed, which outlined the nature of the atmospheric chemistry in the surrounding environment, with and without the aircraft. This allowed for observations on how the aircraft affected the local oxidising capacity, or the atmosphere's ability to cleanse itself of harmful pollutants. A reduced reaction mechanism was utilised to approximate the production and loss of oxidising species in order to gauge the changes to local oxidising capacity.

When observing the changes in oxidising capacity in the aircraft exhaust plume for each of the three flights, KUL - SIN was a good source of validity in proving that thrust setting has a profound impact on the depletion of OH; the fairly stagnant background chemistry meant that the overriding factor affecting levels of hydroxyl was the amount of emissions being released into the atmosphere. The medium haul flight, YYZ - YVR and long haul flight, LHR - JFK, both experienced vast fluctuations throughout flight and much higher levels of depletion occurred. The fluctuating OH depletion occurs because the flights are much longer, meaning the changes in chemical composition of the atmosphere are much larger. The levels of depletion are higher because the density is much lower at higher cruise altitudes, meaning the emitted species are more influential on the surrounding environment, hence impacting the chemistry more significantly.

6 Discussion and further work

This report largely builds on the study carried out in Wasiuk, et al. (2014) [5], which examined the global impact on the Earth's oxidising capacity by estimating the global rise in emissions due to aircraft movements between 2005 - 2011. The APMI was used to estimate emissions for all flights over this time, and it was assumed that the emitted gases from each flight instantaneously disperse into the surrounding 1km cube to estimate the increase in substance concentrations. This assumption allowed for a much more practical approach considering the vast number of flights and extensive time period being examined. However in reality, the diffusion of emissions into the atmosphere is a much more complex and gradual process and when considering individual flights, it is necessary to provide a higher degree of accuracy.

This report also analysed the change to local oxidising capacity, so to incorporate a higher degree of accuracy, it was deduced that the gases diffuse into the wake of the aircraft, as in reality, most gases will remain confined to this region. This approach provided a level of originality to this work and highlighted the detriment of aircraft emissions to the cleansing capability of the atmosphere for a range of singular flights, as opposed to observing the global picture like in Wasiuk, et al. [5]. Such data could be useful if one wants to investigate the impact of a chosen flight route and to take action to mitigate against this impact through changes in design of the aircraft and engine, alternative fuels and Air Traffic Management measures such as re-routing to avoid climate sensitive regions which are susceptible to depleting vast amounts of oxidants or producing persistent contrails and so on.

Further work could explore aviation's impacts on oxidising capacity in different regions and carry out sensitivity analyses to investigate how impactful a flight is on the local oxidising capacity when subject to more minor changes to a single determining factor, such as simulating the same flight and seeing how changes to cruise altitude affects the OH depletion differently, or how route changes can reduce the impact of contrails etc. Alternatively, one could analyse the difference in radiative forcing when flying the same aircraft on the same flight but instead it is powered by hybrid electric engines or consumes sustainable aviation fuel instead of conventional jet fuel.

A Appendix

A.1 Calculating the perturbed chemistry using the APMI software

In order to calculate the resulting increase in concentration of chemical substances, the substance's mass and the volume over which it was released had to be approximated. The

APMI software was used to estimate the mass of emissions released over each stage of flight: climb, cruise and descent. The software assumes a constant thrust setting over each stage, meaning the mass flow of emissions is constant throughout is effectively constant over each stage. This assumption of constant thrust throughout cruise could potentially be a source of inaccuracy because in reality, the aircraft is constantly burning fuel, which reduces aircraft weight, meaning lift and drag are reduced and hence thrust would decrease to maintain a constant speed. Unterstrasser et al. [32] investigates the behaviour of aircraft exhaust plumes and attempts to quantify their dimensions at various points post combustion. It is stated that after six minutes of release, the "aircraft-induced dynamical effects on plume spreading became negligible", meaning the diffusion process of exhaust gases is no longer dominated by the aircraft's wake behaviour. As a result of this, the emission species are then primarily dispersed by atmospheric turbulence beyond the six minute period, meaning the volume becomes much more difficult to estimate.

For this analysis, the volume of the wake at each time-step over the six minutes prior was calculated by taking the average cross-sectional areas from figure A.1 for zero and six minutes, then calculating the volume of the frustum that encapsulates the emissions species released over that period. This data is derived from [32] which involved an empirical study which observed the characteristics of a Boeing 747's wake under various atmospheric conditions.

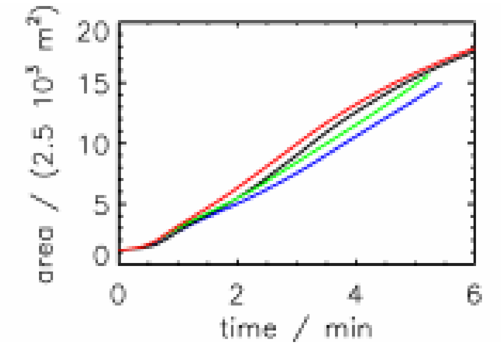

Figure A.1: Plume cross-sectional area, subject to various atmospheric fluctuations [32].

A.2 Reduced reaction mechanism prerequisite chemistry

This section is dedicated to the clarification of all terms and nomenclature mentioned in the reduced reaction mechanism.

A.2.1 Chemical nomenclature

The following chemical species were all involved in the reaction mechanism and therefore play a key role in determining the chemistry of the atmosphere. The nomenclature can be described as follows:

- O_3 : tropospheric ozone - a potent greenhouse gas usually derived from reactions involving NO_2 and is responsible for adverse impacts on the respiratory condition of living organisms and can cause inflammation of the airways.
- $O(^1D)$: singlet state oxygen - highly reactive oxygen atom with no unpaired electrons in the outer shell. Largely responsible for the conversion of tropospheric ozone into hydroxyl radicals (R1, R4).
- $O(^3P)$: triplet state oxygen - oxygen atom with two unpaired electrons in outer shell.
- O_2 : molecular oxygen - oxygen molecule that naturally occurs in the atmosphere.
- N_2 : molecular nitrogen - nitrogen molecule that naturally occurs in the atmosphere.
- H_2O : water vapour - naturally occurring greenhouse gas present in the atmosphere due to the water cycle and also a significant pollutant from the fuel combustion process.
- OH : hydroxyl radical - prevailing species responsible for oxidation of the atmosphere.
- HO_2 : hydroperoxyl radical - secondary species that aids the production of hydroxyl, however has less affect on the oxidising capacity of the atmosphere.
- CO : carbon monoxide - strong greenhouse gas that tends to play a role hydroxyl production cycle (R5).
- CO_2 : carbon dioxide - most common form of anthropogenic pollution and is largely responsible for global heating due to the greenhouse effect.
- HONO : nitrous acid - produced through the reaction of nitrogen oxide and water vapour.
- HNO_3 : nitric acid - resulting from the reaction of nitrogen oxide and hydroxyl radical (R11) and is a common source of wet deposition or acid rain.
- NO : nitrogen oxide - common product of the fuel combustion process. Highly reactive and plays a significant role in the hydroxyl cycle (R6, R10, R12).
- NO_2 : nitrogen dioxide - a reactive compound which is mainly sourced from the reaction of nitrogen oxide with oxygen (R6, R8). Also it is a primary precursor to tropospheric ozone (R9).
- HCHO : formaldehyde - this substance plays an important role in atmospheric photochemistry as it produces HO_2 through reactions involving sunlight energy, improving the oxidising capacity of the atmosphere.

A.2.2 Reaction types

The core reactions that appear in the reduced reaction mechanism can be divided into two categories, gas-phase thermal reactions and photolysis reactions.

A.2.3 Photolysis reactions

Photolysis is a reaction process that involves the splitting or decomposition of chemical compounds by means of light energy or photons. Equation (1) is the integral which describes the rate at which a particular photolysis reaction occurs, also known as the photolysis rate coefficient.

$$J = \int \sigma(\lambda)\ \phi(\lambda)\ F(\lambda)\ d\lambda \tag{6}$$

where J is the photolysis rate coefficient, λ is the wavelength of incident sunlight, $F(\lambda)$ is the solar actinic flux (intensity of sunlight), $\sigma(\lambda)$ is the absorption cross section (efficiency of sunlight absorption) and $\phi(\lambda)$ is the quantum yield (the probability that the absorption of a photon will result in reaction) [33].

Saunders et al. (2003) [34] assigns photolysis parameters to a core number of atmospheric reactions where the absorption cross section and quantum yield data has been optimised through empirical testing. This leads to a more computationally efficient method of calculating the photolysis rate coefficient, J, because equation (6) can be replaced with a simpler expression that calculates the rate of photolysis for a given reaction provided three optimised reaction constants, l, m and n and the solar zenith angle, χ:

$$J = l\ cos(\chi)^m\ exp(-n\ sec(\chi)) \tag{7}$$

In order to determine the zenith angle, χ for each time-step throughout flight, a simple script was written in MATLAB which determines the hour angle[6] for each time-step for every hour of the day at four times throughout the year; 1st January, 1st April, 1st July and 1st October. The photolysis reactions in the reaction mechanism are (R1), (R9) (R12) and (R13) and each one has a corresponding photolysis rate coefficient, J_1, J_9, J_{12} and J_{13}.

A.2.4 Thermal reactions

Another source of energy capable of initiating a chemical reaction is simply heat. The thermal reactions that commonly occur in the atmosphere are those which are initiated at the standard atmospheric temperature range: 150 - 300K. Reactions (R2), (R3), (R4), (R5), (R6), (R7), (R8), (R10), (R11) and (R14) all represent thermal reactions in the simplified atmospheric reaction mechanism, however these reactions are actually a condensed version of a more complex process, in which only the initial reactants and the final products are displayed and the intermediate steps are not shown.

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[6] The hour angle is effectively a measure of time quantified by the location of the sun.

This means that the rate at which these reaction processes happen involves an elaborate calculation process, as one has to take into account the rates at which each step of the reaction happens. The product of all the individual reaction rates that constitute the stoichiometry of each individual reaction is used to calculate the rate of the complex thermal equations seen in the reduced reaction mechanism, and is known as the complex rate coefficient. The complex rate coefficients for the reduced reaction mechanism (k_2, k_3, k_4, k_5, k_6, k_7, k_8, k_{10}, k_{11} and k_{14}) are derived from the Leeds University Master Chemical Mechanism V3.3.1 [35]. These reaction rates are dependent on the spatio-temporal temperature and molecular density, so the thermal chemistry at each timestep is simply dependent on the surrounding meteorological conditions.

Once the volume was calculated and the mass of each emission species was estimated over the six minute period, the molecular density of emissions was approximated. By adding the additional concentration of each gas to the base case composition, the perturbation case composition was then attained.

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