

GLOBAL ATMOSPHERIC CHEMISTRY AND IMPACTS FROM AVIATION

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Abstract

The atmosphere contains a large number of chemical trace compounds among which complex chemical processes take place. These processes form an important part of the natural global biogeochemical cycles. Anthropogenic emissions of chemically active pollutants can interfere in the natural chemical processes and result in impacts on the climate system or lead to the accumulation of substances hazardous to ecosystems. This article outlines the most important chemical processes taking place in the atmosphere with a view to the global scale and to an extent as they are of relevance to chemical interference caused by aircraft engine emissions. The effects caused by emissions of nitrogen oxides, sulphur compounds and water vapour from subsonic aviation are discussed and placed into context with global atmospheric chemistry.

1 Introduction

In the natural atmosphere a large number of chemical processes take place. Mostly they involve reactions between atmospheric trace gases — gaseous compounds that exist in small concentrations relative to the main constituents of air, nitrogen and oxygen. The part of the atmosphere extending from the surface to approximately 10 km altitude is called the troposphere and its chemistry forms an important part of the global biogeochemical cycles. Its processes occur on a wide range of scales in space and time. As a result of human activities the composition of the atmosphere is altered to an increasing extent by emitting pollutants and by transforming the land surface.

The combustion of fossil fuel in aircraft engines leads to emissions of a range of pollutants. Some of these substances interfere with the natural chemical processes in the atmosphere. These chemical changes due to aircraft engine emissions can be loosely grouped into three categories: First, the chemistry of plume processes describes the rapid interactions and chemical transformation of substances in the wake of an aircraft that occurs within few minutes after emission (*Hayman and Markiewicz, 1996; Meijer et al., 1997; Kraabøl et al., 2000*). Second, local air quality deals with pollution near the ground due to air traffic activity. This describes an issue of regional scale which usually applies to the vicinity of airports. Third, global atmospheric chemistry deals with the impact of aircraft emissions on chemical processes that occur over large spatial scales and over time periods from weeks to many

decades. In this context the impact of aircraft emissions on the abundance of greenhouse gases and their subsequent impact on the climate system are of relevance. This article deals with the third aspect of global atmospheric chemistry and related changes due to emissions from global aviation. The other two aspects are dealt with elsewhere. Here global atmospheric chemistry processes are outlined as far as they are relevant for chemistry involving aircraft engine emissions. More comprehensive descriptions of atmospheric chemistry can be found in textbooks such as *Jacob (1999)*, *Finnlayson-Pitts & Pitts (2000)* or *Seinfeld and Pandis (2006)*.

The impact of aviation on atmospheric composition was investigated first in the early 1970s when concerns were raised about stratospheric ozone depletion due to the prospect of a large fleet of supersonic passenger aircraft (*Johnston, 1971*). While the envisaged fleet of high-speed civil transports eventually did not become a reality, it was acknowledged that an accurate quantification of the impact of aircraft emissions on atmospheric chemistry was limited by the large uncertainties associated with the knowledge of the global distribution of key chemical compounds, primarily of the tropospheric budget of nitrogen oxides. Since the 1950s global air traffic has consistently grown and this is expected to continue for the foreseeable future during the 21st century. It has therefore become essential to understand the present and potential future impact from global air traffic on atmospheric chemistry in the context of global environmental change. In the 1990s assessment reports and reviews were published based on research programmes in the United States (*Friedl, 1997*) and Europe (*Schumann et al., 1997; Brasseur et al., 1998*) with a focus on chemical and other environmental impacts from aircraft emissions. The Intergovernmental Panel on Climate Change published a Special Report on Aviation and the Global Atmosphere at the end of the previous century (*IPCC, 1999*). Since then further advances in atmospheric modelling and in the understanding of atmospheric chemistry has led to the continuing publication of updated reviews such as *Lee et al. (2010)*.

2 Emissions

In order to determine the impacts of aviation on global atmospheric chemistry detailed knowledge on the nature of aircraft engine emissions, specifically about their local composition and global geographical distribution, is required. Global data on aircraft engine emissions are compiled into emissions inventories which serve as input into numerical models capable of simulating chemical processes in the atmosphere. These inventories contain emissions flux data in gridded format, with the spatial grid typically having a horizontal resolution of the order of 1 degree in longitude and latitude and a vertical resolution of approximately 1,000 feet. Seasonal variability in the emissions is mostly expressed in form of monthly totals for each emitted species at each grid point. Recent inventories that represent contemporary emissions from global aviation are, for example, available from the EU-funded project REACT4C (*Grewe et al., 2014*), as well as from the U.S. Federal Aviation Administration's AEDT (*Roof et al., 2007; Olsen et al., 2013*). Some of these inventories also include emissions forecasts for the near future (e.g. 2025) or emissions scenarios for the more distant future (e.g. 2050). Aircraft emissions consist mainly of water vapour (H₂O, 232 Tg per year) and carbon dioxide (CO₂, 594 Tg per year). They further contain oxides of nitrogen (NO_x, 0.81 Tg (N) per year), carbon monoxide (CO, 0.68 Tg per year), oxides of sulphur (SO_x, 0.12 Gg (S) per year), unburned hydrocarbons (HC, 94 Gg per year), and particulate matter (PM). All annual total emission values are taken from AEDT 2006 (*Olsen et al., 2013*).

Globally the largest proportion of emissions is released at cruise altitude (9–13 km) which contains parts of the upper troposphere (UT) and lower stratosphere (LS). The release of aircraft emissions within the troposphere or stratosphere is of relevance as these atmospheric regions differ with regard to their dynamical and chemical properties. The part of emissions placed inside the stratosphere is estimated to be within the range of 20–60% (*Hoinka et al.*, 1993; *Forster et al.*, 2003). The boundary between the troposphere and the stratosphere is the tropopause and its location is highly variable, depending e.g. on the geographical location, season and local weather patterns, which complicates the chemical impact assessment of aircraft emissions.

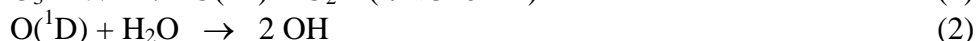
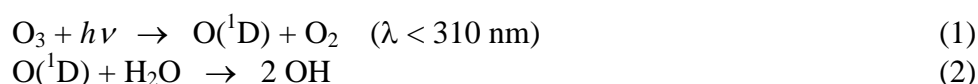
3 Chemical Processes in the Troposphere

The troposphere is strongly influenced by exchange processes of energy and matter with the Earth's surface. It is characterised by short transport time scales leading to efficient mixing and rapid overturning of air. This results in the uplift of emitted chemical compounds from the surface into the free troposphere and their transport by the global atmospheric circulation. Atmospheric concentrations of chemically active trace constituents are controlled to a large extent by natural biogeochemical cycles and increasingly by human influence (*IPCC*, 2013). Substances that are not destroyed either through chemical or physical processes can gradually enter the stratosphere over a time scale of several years.

3.1 Oxidation of Organic Compounds

Photochemical processes are the principal driver of radical-chain reactions in the troposphere. The spectrum of available solar radiation is however limited to wavelengths longer than 280 nm due to the filtering effect of stratospheric ozone. O₃ and NO₂ are two of the most important species that are photolysed at these wavelengths. One of the most important chemical processes in the troposphere is the oxidation of organic substances (hydrocarbons) and carbon monoxide to H₂O and CO₂. This natural photochemical process constitutes in essence a low-temperature combustion system and is dominated by the hydroxyl radical (OH), a highly reactive substance which exists in only very small quantities in the troposphere (*Jacob*, 1999). During the absence of sunlight at night time the nitrate radical (NO₃) plays a similar role in the tropospheric oxidation process; the reactions at night are however less efficient and will only be considered briefly later when the impact of sulphate aerosol is discussed. Figure 1 shows a schematic of the tropospheric oxidation reactions. It illustrates the interactions between the key chemical compounds for carbon monoxide oxidation and the production of ozone. In the following the radical-chain reactions at day time will be described using the oxidation of CO and CH₄ as an example.

At wavelengths λ of less than 310 nm the photolysis of O₃ can produce an excited-state oxygen atom, O(¹D). This high-energy oxygen atom can overcome the stability of the H₂O molecule and, upon reaction with water vapour, result in the formation of OH.



Reactions (1) and (2) constitute an important sink for O₃ and a principal source for OH. Further sources of OH exist, for instance, through the photolysis of acetone and formaldehyde in the atmosphere.

In the troposphere the OH radical converts rapidly into HO₂ (the hydroperoxy radical). One possible and common reaction chain for this process involves O₃ and CO.



This conversion results in the destruction of ozone and in the oxidation of carbon monoxide to carbon dioxide. The additional molecule M required for reaction (4) is usually molecular nitrogen. The reactions between OH and HO₂ occur on very short time scales such that the two species are usually in chemical steady state and are together referred to as the HO_x chemical family.

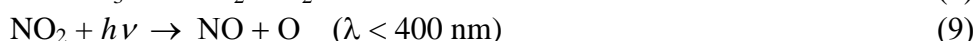
The OH radical is capable of oxidising a large number of atmospheric trace gases, most importantly CO, as shown above, and other organic compounds such as methane (CH₄).



Reactions (3), (4), (6), and (7) result in the formation of water vapour, carbon dioxide, and most importantly a peroxy radical (RO₂) species, in this case hydroperoxy and methylperoxy radicals. The fate of the peroxy radicals is crucially important for whether the reaction chains result in either the net chemical production or the net loss of ozone. A possible termination of these reaction chains is the reaction of HO₂ with itself to form hydrogen peroxide (H₂O₂) or with CH₃O₂ to form methyl hydroperoxide (CH₃OOH).

3.2 The Importance of Nitrogen Oxides

The compounds nitric oxide (NO) and nitrogen dioxide (NO₂), when available in sufficiently large concentrations, have the ability to interfere in the above described reaction process. During day time atmospheric NO rapidly inter-converts with NO₂ in the presence of ozone such that both species usually are in chemical steady state and are together referred to as the NO_x chemical family (nitrogen oxides).



Natural sources of NO_x in the troposphere include emissions from soil, burning biomass (e.g. wildfires), the fixation of atmospheric nitrogen by lightning, and the downward transport of NO_x from the stratosphere where it is produced through oxidation of nitrous oxide (N₂O). The largest amount of tropospheric NO_x however is produced by the combustion of fossil fuel and therefore of anthropogenic origin (*IPCC*, 2001). Nitrogen oxides are typically removed from the atmosphere through the formation of nitric acid (HNO₃) and its subsequent rainout or deposition at the surface. The atmospheric lifetime of NO_x increases with altitude in the troposphere. In the upper troposphere and above, where precipitation is less frequent or does not occur at all, NO_x can be stored in either HNO₃ or various other reservoir gases for several weeks and transported potentially over long distances. NO_x can then be restored from nitric acid either through photolysis or through the reaction with OH (e.g., *Logan*, 1983).

In an atmospheric environment where concentrations of nitrogen oxides are very low, such as in remote marine areas far from the continents, the peroxy radicals can form peroxides which can be photolysed back into HO_x radicals or dissolved in water and removed from the atmosphere through precipitation. In most regions in the troposphere however the

concentrations of nitrogen oxides are much larger. When the abundance of NO_x is higher the peroxy radicals, formed in reactions (4) and (7), will begin to react with NO.



Reactions (11) and (12) take place in addition to reaction (8) and result in the formation of further NO_2 without destroying O_3 . Subsequent photolysis of NO_2 and recombination with molecular oxygen, as shown in reactions (9) and (10), leads to the formation of ozone. The threshold level for the abundance of NO_x required for the chemical O_3 production to exceed the O_3 loss is dependent on various factors, such as temperature, humidity, and O_3 background concentrations (*Reeves et al.*, 2002).

When NO_x concentrations continue to increase to even higher levels, such as they are typically found in polluted regions within the atmospheric boundary layer near the surface, OH radicals begin to react with NO_2 to form HNO_3 .



This reaction represents a sink for peroxy radicals and nitrogen oxides. As a consequence the rates of reactions (11) and (12) as well as the ozone production rate begin to decrease.

The net chemical ozone production rate in the troposphere is the balance between the chemical reactions responsible for ozone production (reactions 9 and 10) and those responsible for ozone loss (mainly reaction 5). This rate is a non-linear function of the concentration of NO_x which depends on the availability of organic hydrocarbon compounds (Figure 2).

3.3 Sulphur Compounds and Aerosol Effects

Atmospheric sulphur compounds are released into the atmosphere through a range of natural and anthropogenic processes. The natural sources include emissions from volcanoes, biomass burning, oceans (marine plankton), and soil. Their emissions consist partly of reduced sulphur compounds, such as H_2S , OCS, CS_2 , and CH_3SCH_3 (dimethyl sulphide, abbreviated as DMS), which eventually are oxidised into SO_2 . The largest amount of sulphur compounds however is emitted directly as SO_2 with most of it attributable to human activities, in particular from fossil fuel combustion.

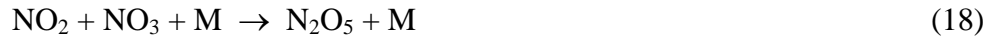
SO_2 is oxidised in the atmosphere both in the gas phase as well as in the liquid phase and produces sulphuric acid (H_2SO_4) as an end product. In the gas phase the reactions involve the hydrolysis of SO_3 with water vapour:



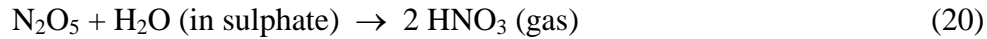
Sulphuric acid has an extremely low saturated vapour pressure and as a consequence it deposits onto solid or liquid surfaces or condenses with ambient water vapour to form sulphate aerosol particles.

Sulphate aerosol affect the Earth's radiative balance either directly by scattering of radiation or indirectly by affecting the formation of clouds and by altering their physical properties. Sulphate aerosol however also influences atmospheric chemistry through heterogeneous surface reactions. N_2O_5 is an important night-time reservoir species for NO_x . Its hydrolysis on sulphate aerosol results in the conversion of NO_x to HNO_3 which has a longer atmospheric

lifetime than N_2O_5 . As a consequence sulphate aerosol leads to a more efficient conversion of NO_x into HNO_3 and hence an enhanced removal of reactive nitrogen oxides from the atmosphere (*Dentener and Crutzen, 1993; Tie et al., 2003*). This results then in a decrease in the chemical ozone production rate. At night-time the process begins with the formation of N_2O_5 .



At low temperatures and during night N_2O_5 is a stable compound in the atmosphere. The hydrolysis of N_2O_5 on sulphate aerosol can then take place.



During day-time N_2O_5 is quickly photolysed and reaction (18) slows down. Reaction (13) represents then the dominant but slower process that converts NO_x to HNO_3 .

4 Chemical Processes in the Stratosphere

The stratosphere is characterised by its stable stratification with temperatures increasing with altitude due to photochemical ozone formation – the "ozone layer" (*WMO, 2014*). This stability results in vertical transport processes to be much slower compared with the troposphere, typically on a time scale of several years (*Hall and Plumb, 1994*).

4.1 Ozone Formation

Chemically the composition of the stratosphere is characterised by in-situ formation of ozone and by low abundance of water vapour. Our current understanding of the formation of stratospheric ozone is based on a theory developed first by Sydney Chapman (*Chapman, 1930*). Ozone is produced through the photolysis of molecular oxygen which requires solar radiation at wavelengths below 240 nm. The atomic oxygen recombines then with molecular oxygen to form an O_3 molecule. The bonds in the O_3 molecule are weaker than those in O_2 and hence O_3 is photolysed at wavelengths below 320 nm. Ozone loss occurs through the reaction of atomic oxygen with O_3 .



Reactions (10) and (22) form a rapid inter-conversion of O and O_3 , together referred to as "odd oxygen", and can be assumed to be in steady state. As such they do not produce or destroy any odd oxygen but rather determine the ratio of concentrations between atomic oxygen and ozone. The stratospheric ozone layer formed through the Chapman mechanism is essential for life on the surface as it filters out the near-ultraviolet spectrum of the solar radiation with wavelengths below 280 nm. For this reason ozone cannot be produced through the Chapman mechanism in the troposphere.

4.2 Catalytic Cycles

A faster sink processes for stratospheric ozone than reaction (23) exists in form of catalytic reaction cycles. Two dominant families of species for these cycles are HO_x and NO_x . In the

stratosphere HO_x is created from water vapour (reaction 2) which is either transported into the stratosphere from the troposphere below or is produced chemically by oxidation of CH_4 .



This cycle inter-converts the HO_x species OH and HO_2 and in the process converts two O_3 molecules into three oxygen molecules. HO_x is conserved and acts as a catalyst, capable of destroying a large number of O_3 molecules. The termination for this catalytic cycle requires the loss of HO_x , e.g. through reaction (25).



The catalytic cycle shown in reactions (24) and (5) is most effective in the stratosphere above 40 km altitude and plays no important role in the troposphere as reaction (3) between OH and CO in the troposphere is faster than reaction (24) and reaction (11) between HO_2 and NO competes with reaction (5).

NO_x is produced chemically in the stratosphere through photolysis of N_2O (nitrous oxide). N_2O is transported into the stratosphere from the troposphere where it is chemically inert. The catalytic cycle that inter-converts NO and NO_2 while destroying ozone in the process is described in reactions (8) and (26).



The net effect is identical to that of reaction (23) and constitutes a loss of odd oxygen. The important step in this cycle, which is most effective at altitudes between 20 and 40 km, is reaction (26) which competes with reaction (9). The termination of this cycle involves the loss of NO_x , for instance through the formation of HNO_3 at day time (reaction 13) or of N_2O_5 at night time (reactions 17 to 19).

In addition to the two catalytic cycles shown here other similar cycles exist, most notably involving halogen species, but they are beyond the scope of this article and therefore not further discussed.

5 Impacts of Aircraft Emissions

The impact of the emissions of chemical compounds by aircraft engines can now be seen in context with the chemical processes occurring in the natural troposphere and stratosphere as outlined above. The changes in atmospheric chemistry due to aircraft emissions are investigated through the use of numerical models, such as atmospheric chemistry transport models or chemistry-climate models. These models can reproduce the atmospheric transport of aircraft emissions by air motion and their influence on the natural chemical processes together with the impacts from other (non-aviation related) emission sources. A direct observation through measurements of the global scale chemical impacts from aircraft engine emissions is generally not possible as the natural daily, seasonal or inter-annual variability, for instance in nitrogen oxides and ozone, masks the changes in atmospheric concentrations caused by aircraft emissions. Uncertainty in the assessment of the chemical impacts can be due to limitations in the understanding of the natural atmospheric background conditions, associated chemical processes and their interactions. Further uncertainties arise from limitations in the ability of contemporary atmospheric models to reproduce atmospheric

processes accurately. The compilation of global aircraft emission inventories, which serve as input for atmospheric models, usually requires further abstractions and simplifications both regarding the location of emissions as well as in the emissions flux. In spite of these inherent uncertainties research in impact assessment studies, carried out since the 1990s, has shown a rather consistent picture of the atmospheric effects from aircraft emissions, chemical or otherwise, and has been documented in various publications such as *Brasseur et al.* (1998), *IPCC* (1999), and *Lee et al.* (2010).

5.1 Water Vapour and Carbon Dioxide

Water vapour and carbon dioxide are the principal emitted species produced by the combustion of kerosene or other fossil fuels. Both chemical species are efficient greenhouse gases and changes in their atmospheric abundance affect the radiative balance of the Earth-Atmosphere system. Emissions of water vapour into the troposphere have no real significance, both chemically and radiatively, due to the high natural background concentrations and due to the fact that the atmospheric abundance of water vapour is mainly controlled through physical processes (temperature) rather than by chemical reactions. Water vapour emissions that are released inside the much drier stratosphere however will result in an increase in HO_x concentrations and therefore add to O₃ destruction through catalytic cycles as outlined in Section 4.2. Cruise altitudes of present-day subsonic commercial aircraft extend into the lower stratosphere. Their impact of water vapour emissions was estimated to be near negligible (*IPCC*, 1999). The impact of potential future commercial supersonic transports flying at significantly higher cruise altitudes was shown to have a potentially much larger impact on stratospheric ozone loss by catalytic cycles (*Grewe et al.*, 2007).

Emissions of carbon dioxide are chemically inert in the atmosphere, however they take part in the global carbon cycle, interacting with the biosphere and the hydrosphere, with an estimated atmospheric lifetime that exceeds 100 years. Over time the CO₂ emissions from aviation therefore accumulate, are distributed globally, and eventually become indistinguishable from CO₂ emissions from other sources.

5.2 Effects of Nitrogen Oxides

Emissions of NO_x interfere in chemical processes of the troposphere and stratosphere, influencing the abundance of the greenhouse gases ozone and methane. The atmospheric lifetime of NO_x increases in the troposphere with altitude and as such does its ozone production potential. Other than NO_x emissions from other transport modes the largest amounts of NO_x from aviation are emitted at cruise altitudes near the tropopause. There, at low ambient temperatures, NO_x is easily converted into other compounds, sometimes referred to as NO_x reservoir species, such as HNO₃, N₂O₅ or PAN (peroxyacetyl nitrate). As such the relative importance of NO_x from aviation, compared with emissions from other sectors released at the surface, is greater. Other sources of NO_x in the upper troposphere are the influx from the stratosphere above, the uplift from the lower troposphere by convective activity and in-situ chemical production from lightning (*Berntsen and Isaksen*, 1999). Current estimates indicate that the stratospheric flux is comparable in size with that from global aviation. Emissions from lightning however are estimated to be five times larger than those from air traffic (*Schumann and Huntrieser*, 2007; *Lee et al.*, 2010). Both sources are difficult to quantify which is to a large part responsible for the uncertainty associated with the present understanding of the tropospheric reactive nitrogen budget.

Due to the difficulty in constraining atmospheric background concentrations of NO_x there remain significant uncertainties in the magnitude of the chemical impact from aircraft NO_x emissions. The range of model results has been reviewed by *Holmes et al.* (2011). As an illustrative example from the published literature, Figure 3 shows the change in atmospheric ozone volume mixing ratios due to present-day's aircraft NO_x emissions, calculated independently by two models. The figure represents a latitude-altitude cross section through the atmosphere with contour lines indicating the annual and zonal mean O_3 changes, i.e. they are averaged over all longitudes. The model in panel (a) simulates atmospheric chemistry and transport in the troposphere and lower stratosphere (from the surface to 30 km altitude). Values are positive all over the troposphere, indicating an increase in atmospheric O_3 due to aircraft emissions. The location of the largest O_3 increase is found in the northern hemispheric upper troposphere overlapping with the location of the emissions maximum. The maximum increase here is 5–6 ppb (parts per billion). This represents an increase in O_3 mixing ratios by approximately 5%. The natural O_3 background amounts to approximately 40–100 ppb in the troposphere and 100–150 ppb near the tropopause. The ozone produced by aircraft emissions has a lifetime of several weeks which is much shorter than time scales for inter-hemispheric transport of air. Therefore the ozone impact is much larger in the northern hemisphere where the quantity of aircraft emissions is higher. The model in panel a) does not simulate the full extent of the stratosphere and hence stratospheric ozone loss through catalytic cycles is underestimated. The model in panel (b) simulates atmospheric chemistry and transport in the stratosphere between approximately 15 and 60 km altitude (omitting the troposphere). Here the gradual uplift of aircraft NO_x into the middle stratosphere is simulated after an integration time of six model years. NO_x emissions transported into the middle stratosphere, typically in form of HNO_3 or other reservoir species are capable of contributing there to O_3 loss via catalytic cycles. Typically between 20 and 30 km altitude, depending on latitude, a "cross-over" point can be identified where the effect of additional NO_x from aircraft emissions changes from net ozone production to net ozone loss. Model studies investigating the efficiency of the upward transport of NO_x emissions from present-day cruise altitudes into the middle stratosphere reveal significant differences (*Rogers et al.*, 2002). The impact of emissions from subsonic commercial aircraft to stratospheric ozone loss has however been found negligibly small compared to the natural background concentrations (approximately 10^5 ppb) at this altitude (*IPCC*, 1999; *Lee et al.*, 2010).

The increase in ozone from aircraft NO_x is largest in the UTLS region. Some of this additionally produced ozone is transported to lower altitudes where it is photolysed and contributes to the formation of additional HO_x radicals. These HO_x radicals lead to a more efficient oxidation of methane and carbon monoxide. As a consequence of the emissions of NO_x from aviation, ozone levels are increased throughout the troposphere and in the UTLS region, whereas levels of CH_4 and CO are globally reduced. The reduction of CO due to these chemical processes outweighs by far the emitted amounts of CO from kerosene combustion in aircraft engines. The increase in O_3 and HO_x enhances the oxidising capacity of the atmosphere and as a consequence organic compounds, such as methane, are more efficiently destroyed through chemical reactions. Model calculations estimate that the atmospheric lifetime of CH_4 is reduced by up to 3% due to global aircraft NO_x emissions (*Köhler et al.*, 2008). A further degree of complexity in the chemical interactions is introduced by another effect. The reduction in CH_4 and CO results in a partial off-setting of the ozone increase caused by the NO_x emissions, as a reduction in hydrocarbons and carbon monoxide impacts directly on ozone formation through equations (3) and (6).

5.3 Effects of Sulphur Oxides

Aircraft emissions affect the abundance of sulphate aerosol mainly by the release of SO_2 . Aerosol is of chemical importance as it represents a surface on which heterogeneous reaction processes can take place. An increase in the regional surface area density of aerosol by formation of H_2SO_4 will result in the enhanced loss of reactive nitrogen from the atmosphere, as outlined above in Section 3.3. As a consequence this loss of reactive nitrogen will contribute to a reduction of the ozone increase caused by emissions of nitrogen oxides. A further effect due to the loss of reactive nitrogen is the reduced potential of forming halogen nitrate compounds near the tropopause in higher latitude regions. Halogen nitrates are reservoir species for atmospheric chlorine and bromine and their reduced abundance will result in an increase in halogens capable of depleting O_3 via catalytic cycles. Model studies in *Pitari et al.* (2002) have shown at high latitudes a reduction in lower stratospheric O_3 levels by -4 to -6 ppb due to aerosol effects, and subsequent downward transport of the ozone depleted air into the troposphere resulted there in an off-set of the O_3 increase caused by NO_x emissions by about 2 ppb.

6 Conclusions

In the context of emissions from global aviation and their effects on the Earth's climate a distinction is often made between CO_2 and non- CO_2 effects. Emissions of CO_2 are linearly related to fuel usage. They are distributed globally due to their long atmospheric lifetime and have no impact on atmospheric chemistry. A particular characteristic of aviation emissions, however, is their numerous non- CO_2 impacts. Their atmospheric lifetime is much shorter which makes their effects more regional. Moreover, the magnitude of their atmospheric impact is often very dependent on the local atmospheric conditions and not linearly related to the emissions. All of this makes the non- CO_2 effects more difficult to quantify. In this article the non- CO_2 effects that have an influence on global atmospheric chemistry have been described. In the atmosphere a large range of chemical processes takes place between individual trace constituents. The nature of these processes depends on factors such as the location (in particular the altitude), the availability of sunlight, and the atmospheric composition. The release of nitrogen oxides, sulphur compounds and water vapour from aircraft engines into the atmosphere results in their interference in the natural chemical cycles of the atmosphere. The magnitude of these impacts is heavily dependent on the location of the emissions and hence an accurate quantification requires their simulation in numerical models capable of reproducing three-dimensionally atmospheric chemistry and transport processes. Emitted nitrogen oxides affect the chemically active greenhouse gases ozone and methane throughout the lower atmosphere up to an altitude of 25 km. Water vapour emissions inside the stratosphere can interfere with chemical HO_x cycles and lead to ozone destruction. Emissions of sulphur compounds play a significant role in the formation of aerosol which affects heterogeneous chemical processes such as the removal of reservoir species for nitrogen oxides. Aviation emissions of these compounds are therefore capable of interfering in atmospheric chemistry and result in a large range of complex environmental impacts. Their impact on global chemistry occurs through a multitude of pathways and is difficult to quantify separately due to the numerous interdependencies. In these instances where the abundance of radiatively active substances is affected, such as greenhouse gases or aerosol, aircraft emissions have an impact on the global climate system.

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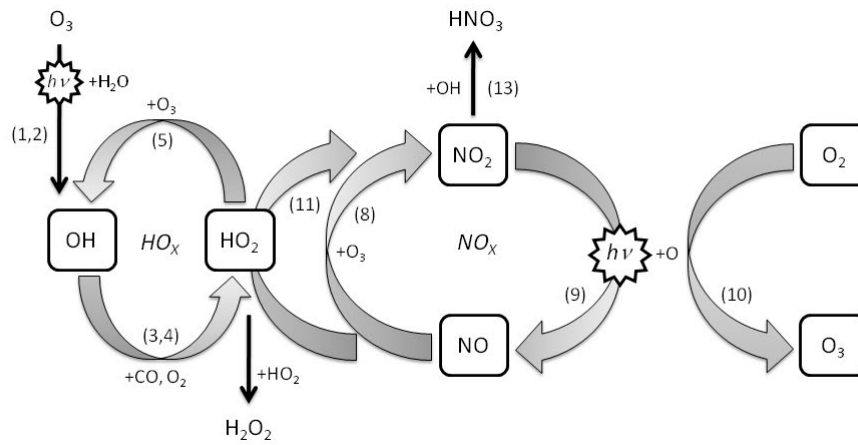


Figure 1: Schematic of the mechanism for O_3 - HO_x - NO_x -CO chemistry in the troposphere. The numbers in parentheses refer to the equation number used in the text for the corresponding chemical reaction.

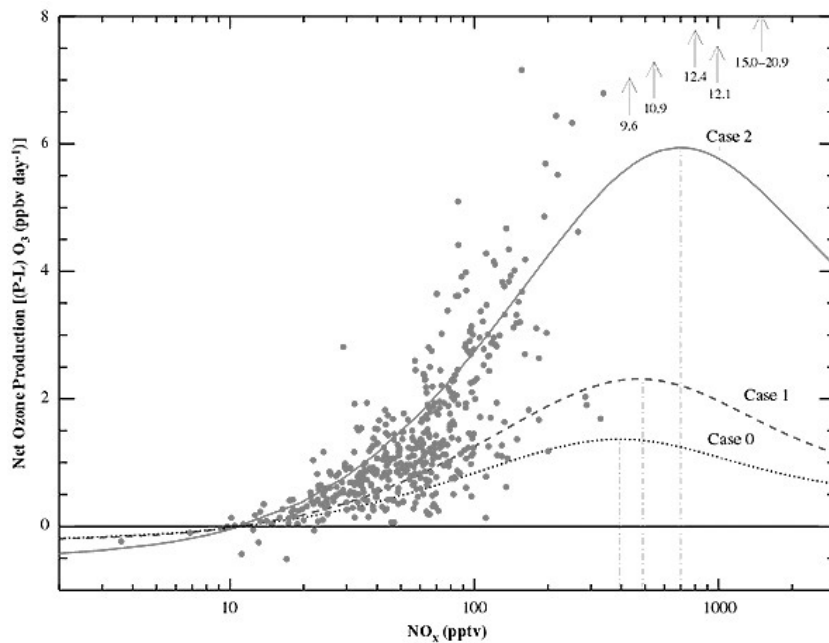


Figure 2: Net ozone production (24-hr average) as a function of NO_x in the upper troposphere. Data points are obtained from the NASA-sponsored SUCCESS campaign, defining the rate of chemical ozone production. Also shown in this figure are three calculations of for average tropospheric conditions experienced above 11 km in SUCCESS (Figure 2-1 from IPCC, 1999).

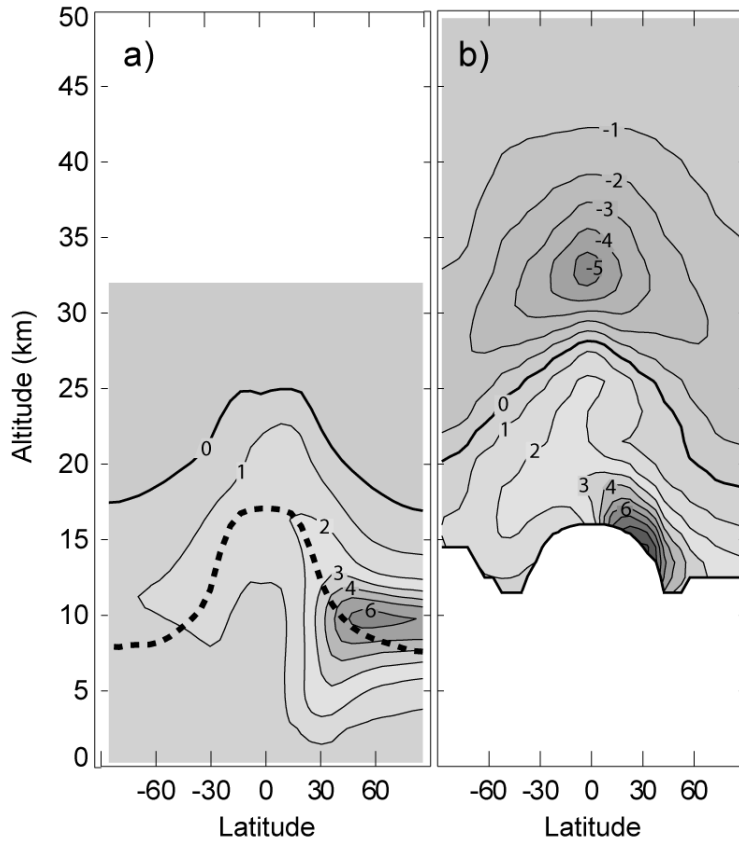


Figure 3: Change in O₃ due to aircraft NO_x emissions calculated by two independent chemistry transport models. Values are shown as zonal and annual mean volume mixing ratios in parts per billion (ppb), relative to an atmosphere without aircraft emissions. The vertical domain of model (a) includes the troposphere and the lower stratosphere. The dashed line is the location of the tropopause. Model (b) calculates changes in the stratosphere only. The zero contour line marks the cross-over point between net O₃ increase to net O₃ loss due to aircraft NO_x. Modified after Köhler *et al.* (2008).