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Aerosol formation pathways from aviation emissions

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Abstract

Aviation emissions are responsible for an estimated 24,000 premature mortalities annually and 3.5% of anthropogenic radiative forcing (RF). Emissions of nitrogen and sulfur oxides (NO_x and SO_x) contribute to these impacts. However, the relative contributions and mechanisms linking these emissions to formation and impacts of secondary aerosols (as opposed to direct aerosol emissions) have not been quantified, including how short-lived aerosol precursors at altitude can increase surface-level aerosol concentrations. We apply global chemistry transport modeling to identify and quantify the different chemical pathways to aerosol formation from aviation emissions, including the resulting impact on radiative forcing. We estimate a net aerosol radiative forcing of –8.3 mWm^{-2}, of which –0.67 and –7.8 mWm^{-2} result from nitrate and sulfate aerosols respectively. We find that aviation NO_x causes –1.7 mWm^{-2} through nitrate aerosol forcing but also –1.6 mWm^{-2} of sulfate aerosol forcing by promoting oxidation of SO_2 to sulfate aerosol. This accounts for 21% of the total sulfate forcing, and oxidation of SO_2 due to aviation NO_x is responsible for 47% of the net aviation NO_x attributable RF. Aviation NO_x emissions in turn account for 41% of net aviation-aerosol-attributable RF (non-contrail). This is due to ozone-mediated oxidation of background sulfur and the 'nitrate bounce-back' effect, which reduces the net impact of sulfur emissions. The ozone-mediated mechanism also explains the ability of cruise aviation emissions to significantly affect surface aerosol concentrations. We find that aviation NO_x emissions cause 72% of aviation-attributable, near-surface aerosol loading by mass, compared to 27% from aviation SO_x emissions and less than 0.1% from direct emission of black carbon. We conclude that aviation NO_x and SO_x emissions are the dominant cause of aviation-attributable secondary inorganic aerosol radiative forcing, and that conversion of background aerosol precursors at all altitudes is amplified by enhanced production of aviation attributable oxidants at cruise altitudes.

1. Introduction

Aviation emissions have an impact on both climate [1] and surface air quality [2, 3]. It is estimated that commercial aviation is responsible for ~3.5% (80.4 mWm^{-2}) of all anthropogenic effective radiative forcing (RF) [4], and ~24,000 premature mortalities each year [5] due to degraded air quality. The most important RF components from a climate perspective have been identified to be due to carbon dioxide (CO_2), oxides of nitrogen (NO_x), water vapor (H_2O), aerosol (soot, sulfates, nitrates), and condensation trails (contrails) [6].

The time scales associated with the different components of aviation attributable radiative forcing range from several hours (contrails) to hundreds of years (CO_2). CO_2 and contrails are a consequence of burning hydrocarbon fuels which results in the direct emission of CO_2 as well as the emission of soot and water vapor. Technological limitations of alternative energy carriers (such as the low specific energy of electric batteries relative to jet fuel) for aviation make it likely that commercial aviation will continue to be mostly fueled by liquid hydrocarbons for the next few decades. Given the ~4% annual rate of growth of the aviation industry [7] and the ~3% increase in aviation CO_2 emissions annually [8] the mitigation strategies for reducing aviation CO_2 related radiative forcing in the near term are therefore mostly limited to use of sustainable aviation fuels, improving aircraft and engine efficiency, increasing operational efficiency and offsets. Aviation emissions of NO_x and SO_x, however may be amenable to reduction through other means—low sulfur fuel, combustor design modifications or the use of post-combustion emissions control technology [5] and therefore present a more immediate need to be characterized and quantified so that mitigation strategies can be appropriately formulated and analyzed.

Aviation NO_x and SO_x have an indirect impact on the atmosphere through the formation of ozone and function as precursors for secondary inorganic aerosol. The relative contribution and mechanisms of secondary aerosols formation are poorly understood, including how short-lived precursor species such as NO_x alter surface aerosol loading. An improved quantitative understanding of the pathways along with the interaction of aviation and non-aviation emissions is needed to develop relevant policies for reducing aviation's impact on the environment. Although reduction of aviation emissions of NO_x and SO_x are also important from an air quality perspective, the radiative forcing resulting from aviation NO_x and SO_x emissions will be the focus of this paper as outlined in sections 1.1 and 1.2 below.

1.1. Aviation NO_x attributable climate impacts

Aviation NO_x emissions are understood to have two mechanisms by which they directly perturb the climate [4]. The first is through ozone formation. Upper tropospheric NO_x emissions result in ozone production (short term, positive RF). This then results in tropospheric methane depletion (long term, negative RF), which in turn reduces tropospheric ozone production (long term, negative RF) and reduces a source of stratospheric water vapor (long term, negative RF). The second mechanism is through the local formation of nitrate aerosols, which can scatter incoming solar radiation and provide a short-term, negative RF [4, 6, 9, 10].

The ozone resulting from high altitude NO_x emissions [11] can promote the oxidation of aerosol precursors, including non-aviation NO_x and SO_x which can lead to the formation of secondary inorganic aerosols. These additional climate perturbation pathways through reactions with background species have not been quantified in the literature relative to the more direct nitrate pathway. The low solubility of ozone compared to the higher solubility of aerosol precursors such as HNO_3 (which might form directly from NO_x emissions) results in the formation of secondary inorganic aerosol over inter-hemispherical length scales. The existence of this mechanism also implies that cruise-altitude aviation NO_x emissions can cause changes in near-surface particulate matter.

While the role of aviation NO_x emissions in ozone production has been documented in the literature [3, 9, 10], the pathways through which this aviation-attributable ozone affects the formation of secondary inorganic aerosols have not been characterized or quantified.

Since the majority (~92%) of aviation fuel burn and emissions occur during cruise and ~56% of the total fuel burn occurs [12] at altitudes between 10–12 km, the impacts of non-CO_2 emissions from aviation are unique relative to other anthropogenic combustion emissions. Dahlmann *et al* [13] showed that aviation NO_x emissions have about twice the ozone production efficiency relative to road transport primarily due to the altitude of emissions. This higher ozone production efficiency [11, 13] of aviation NO_x coupled with the 4% annual growth rate [7] of the industry implies a need to further understand the pathways and impact of aviation NO_x attributable RF. Furthermore, recent work by Skowron *et al* [14] has shown that a reduction in background emission might reduce the net radiative impact of aviation NO_x emissions, but may also increase the short term ozone response. This further emphasizes the need to understand the aerosol formation pathways that are promoted by the short term production of ozone by aviation NO_x.

1.2. Aviation SO_x attributable climate impacts

Aviation SO_x emissions affect the climate through the direct formation of sulfate aerosol which scatter incoming solar radiation and result in a short-term, negative RF [4, 6]. Lee *et al* [4] reported a sulfate aerosol cooling of $-7.4\ \mathrm{mWm^{-2}}$ due to aviation emissions in 2018, while the Federal Aviation Administration's (FAA) Aviation Climate Change Research Initiative (ACCRI) [15] reported a RF range of -3 to $-7\ \mathrm{mWm^{-2}}$ in 2006. The sulfate related RF in these reports have however been limited to the direct RF due to sulfate aerosol.

Sulfate aerosols in the UTLS also have an effect on tropospheric and stratospheric ozone concentration. Solomon *et al* [16] showed that aerosol from volcanic eruptions can lead to ozone depletion in the atmosphere by the conversion of NO_x to reservoir species, in turn enhancing halogen catalyzed ozone destruction. Work done in the area of solar radiation management through sulfate injection in the stratosphere arrived at similar conclusions regarding the effect of stratospheric sulfate injection on the tropospheric ozone concentration [17–20].

Table 1. Emissions inventories used in GEOS-Chem simulations, relevant species, and the year to which the inventory corresponds. GEOS-Chem uses the latest available data year for years outside the inventory's available years. *Emissions calculated online using meteorological data for that year; however, they also use a mix of other historical data. **Emissions are a climatology and reflect multiple years of observations.

Region	Inventory	Year	Species
Global	EDGARv4 [28]	2010	NO_x, SO_x, SO_4, CO, NH_3
Global	BOND [29]	2000	BC. OC
Global	RETRO [30]	2000	NMVOCs, except C_2H_6 and C_3H_8
Global	SHIP [31] and ParaNOx [32]	2013	NO_x, SO_4, CO, O_3, HNO_3
Global	C2H6_2010 [33]	2010	C_2H_6
Global	POET [34]	2000	C_2H_5OH
Global	VOLCANO	2009	SO_2
Global	Lightning [35]	2015*	NO
Global	Soil NOx [36]	2015*	NO
Global	BROMOCARB [37]	**	$CHBr_3$, CH_2Br_2
Global	IODOCARB [38]	**	CH_3I, CH_2I_2, CH_2ICl, CH_2IBr
Global	MEGAN [39]	2015*	Biogenic NMVOCs
Asia	MIX [40]	2010	NO_x, SO_2, CO, BC, OC, NMVOCs, NH_3
US	NEI2011 [41] (scaled to 2013)	2013	NO_x, SO_2, CO, BC, OC, NMVOCs, NH_3
Canada	APEI [42]	2014	NO_x, SO_2, CO, BC, OC, NMVOCs, NH_3
Mexico	BRAVO [43]	1999	NO_x, SO_2, CO
Europe	EMEP [44]	2012	NO_x, SO_2, CO

Furthermore, sulfate and nitrate aerosol formation are coupled by the dynamics of the nitrate-sulfate-ammonium system [21]. Aviation SO_x emissions increase competition for available ammonia due to the preferential reaction [21] of ammonia with SO_x to form ammonium sulfate, which can displace nitrate aerosol.

As outlined in sections 1.1 and 1.2 above, aviation emissions of NO_x and SO_x have multiple pathways through which they perturb the climate and this work is the first to separate out and quantify the impact that each of these pathways have on the concentrations and corresponding RF of the resulting ozone and secondary inorganic aerosols. These findings will be relevant from a policy perspective as they will provide scientific understanding of how aviation NO_x and SO_x emissions affect aerosol and ozone related RF.

2. Methods

This section outlines the computational methods used to evaluate the impact that aviation NO_x and SO_x have on secondary inorganic aerosol and ozone. The changes in radiative forcing and atmospheric composition are calculated using the global chemistry-transport model GEOS-Chem. The pathways and impacts are attributed to aviation emissions by performing multiple simulations and calculating differences in atmospheric composition and RF.

2.1. Chemistry-transport modeling

We use the GEOS-Chem global atmospheric chemistry-transport model (version 12.0.2) [22, 23] to calculate chemistry and transport of chemical species in the atmosphere. We use the standard mechanism, including unified tropospheric and stratospheric chemistry and physics [24]. Meteorological data is taken from the NASA Global Modeling and Assimilation Office's Modern Era Retrospective analysis for Research and Applications v2 (MERRA-2) [25]. We perform all simulations on a $4^\circ \times 5^\circ$ (latitude by longitude) global grid, with 72 vertical layers from sea-level to a pressure of 1 Pa. One-year simulations are run for all scenarios considered (with a one-year model spin up period). Table 1 summarizes the emissions inventories used in this work. Previous studies have compared observations of cruise-altitude conditions, in particular ozone concentrations, against GEOS-Chem simulations and found reasonable agreement [26, 27]. A comparison of cruise altitude ozone from GEOS-Chem version 12.0.2 against aircraft observational data is provided in the supplementary information (SI, available online at stacks.iop.org/ERC/4/021002/mmedia) and shows that GEOS-Chem agrees well with observed ozone at cruise altitude but may underestimate ozone mixing ratios at high northern latitudes. Since the pathways identified in this work (see section 3) are mediated by atmospheric oxidants such as ozone and OH, an underestimate in the ozone mixing ratios at high northern latitudes may result in an underestimate of the RF due to sulfates and nitrates. Furthermore, as seen in Figures S1 and S3 (available online at stacks.iop.org/ERC/4/021002/mmedia) simulated ozone mass mixing ratios at high northern latitudes exhibit lower variability and a low bias compared to aircraft campaign data from IAGOS. The implications for radiative forcing due to aircraft emissions is unclear and depends on the source of this bias. If the bias is due to an underestimate of local ozone

Table 2. Aviation emissions from the Aviation Environmental Design Tool (AEDT) for the year 2015.

	Quantities in Tg/yr
Fuel Burn	240
NO_x emissions (Tg NO_2)	3.60
SO_x emissions (Tg S)	0.144

Table 3. Aviation emissions scenarios used to calculate the impact of specific aviation emissions by species. The columns indicate whether the particular species is emitted by aviation.

Aviation emissions:	NO_x	SO_x	BC
Baseline aviation	Yes	Yes	Yes
Background	No	No	No
noNOx	No	Yes	Yes
noSOx	Yes	No	Yes
noBC	Yes	Yes	No
noNOxSOx	No	No	Yes

production, aviation-induced radiative forcing may also be underestimated. However, Hu *et al* [27] suggest that this low bias may instead be due to insufficient simulated troposphere-stratosphere air exchange.

Baseline aviation emissions used are from the Aviation Environmental Design Tool [12] (AEDT) for the year 2015 as shown in table 2. The total annual fuel burn in this inventory is 240 Tg (cf. 188 Tg in 2006). The landing and take-off cycle (altitudes below 3000 ft) accounts for approximately 8% of the total annual aviation fuel burn, and ~56% of the fuel is burned between 10 and 12 km. A fuel sulfur content of 600 ppm by mass and a direct sulfate conversion efficiency of 0.02 (with the rest emitted as SO_2) are assumed. A black carbon (BC) emission index of 40 mg kg^{-1} is assumed as calculated by the SCOPE11 method outlined in reference [45]. Sensitivity of BC related RF to the emissions index of BC is estimated to be 19 mWm^{-2}/g-BC/kg-fuel as shown in the supplementary material.

2.2. Radiative forcing calculations

Radiative forcing (RF) calculations are carried out by the Rapid Radiative Transfer Model (Global) (RRTMG) [46] module in GEOS-Chem. RRTMG is called by GEOS-Chem in 3 h intervals and calculates the longwave and shortwave instantaneous radiative fluxes. The RRTMG module also calculates the radiative fluxes associated with specific species (ozone, methane, sulfates, nitrates, ammonium, black carbon, organic carbon, sea salt, dust, total particulate matter). We do not quantify the effects of methane feedback which may affect the aerosol RF. All RF are calculated based on the flux at the tropopause, as outlined by the Intergovernmental Panel on Climate Change (IPCC) and the National Research Council [47, 48]. All RFs are instantaneous, without stratospheric adjustments.

2.3. Identifying impact pathways

The impact of aviation emissions on the global atmospheric composition and RF is estimated by calculating the difference in atmospheric composition and RF between two model simulations, one with aviation emissions (called the baseline aviation scenario) and one without aviation emissions (called the background scenario). Table 3 shows the various scenarios we simulate. A similar method is applied to isolate the impact of aviation NO_x emissions on secondary inorganic aerosols and ozone. The difference between the baseline aviation scenario and the 'no aviation NO_x emissions' scenario (noNOx in table 3) provides an estimate of the impact that aviation NO_x emissions have on the global RF and atmospheric composition. Similarly, the impact of aviation SO_x and the combined effect of aviation NO_x and SO_x is determined by performing additional simulations and calculating the change in quantities of interest from the baseline aviation scenario: (Baseline–noSOx) and (Baseline–noNOxSOx) respectively.

3. Results and discussion

As described in section 1, aviation NO_x and SO_x emissions have multiple pathways through which they perturb the climate. We find that aviation emissions are responsible for 34% of Northern Hemispheric, cruise-level

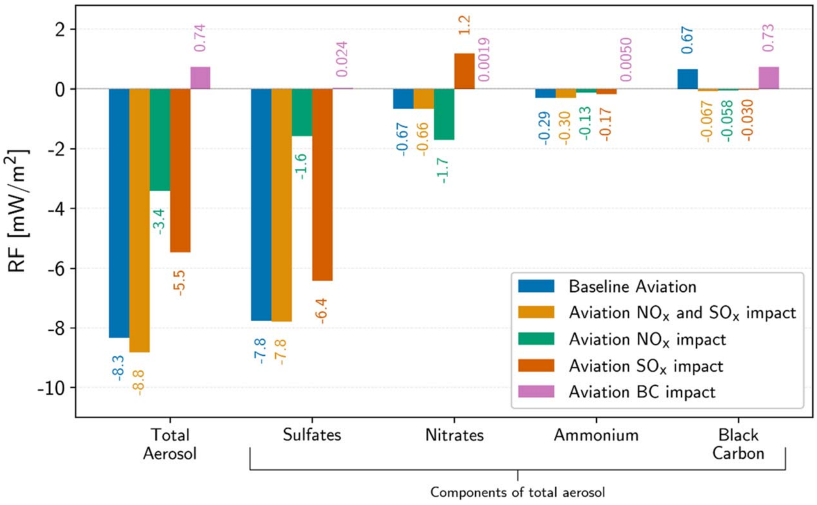

Figure 1. Aviation-attributable radiative forcing (in mW/m^2) due to aerosol species (total aerosol and its components—sulfates, nitrates, ammonium, black carbon). Total tropospheric aerosol includes the RF due to other aerosols such as organic and black carbon.

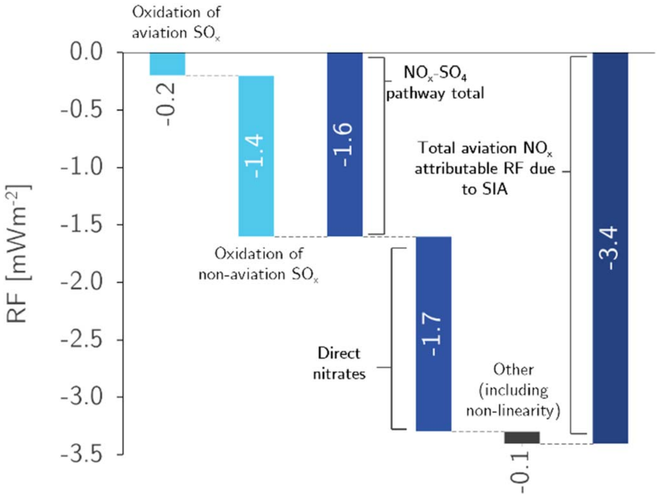

Figure 2. Aviation NO_x attributable RF due to secondary inorganic aerosol, broken down by the aerosol formation pathways. The light blue bars show indicate the absolute contribution of NO_x attributable sulfate formation through the oxidation of aviation and non-aviation SO_x. All values shown are in mWm^{-2}.

(10–12 km) NO_x mixing ratios on an annual average basis (i.e. zonally mass weighted average of NO_x mixing ratios across the Northern Hemisphere at the typical cruise altitudes). This increases to 49% at cruise altitudes during the Northern Hemisphere winter and 31% during the Northern Hemisphere summer. Further details on the contribution of aviation emissions to the NO_x budget can be found in the supplementary material of reference [5].

Aviation-attributable SO_x accounts for ~5.0% of the total annual average atmospheric SO_x mixing ratios at cruise altitudes. The contribution of aviation emissions to SO_x mixing ratios increases to 17% at Northern Hemisphere cruise altitudes during the Northern Hemisphere winter and ~1.8% during Northern Hemisphere summer.

3.1. Aviation-attributable radiative forcing

The global annual average aviation-attributable RF from various aerosol species in 2015 is shown in figure 1. We find that the aviation-attributable RF from ozone is ~51 mWm^{-2}, the RF due to aerosol is −8.3 mWm^{-2}. As shown in figure 1 aviation NO_x and SO_x emissions are together responsible for −8.8 mWm^{-2} of aviation-attributable aerosol RF, while BC emissions from aviation result in an RF of 0.74 mWm^{-2} (the sum of the fractional RF components from NO_x, SO_x and BC does not equal 1 due to non-linear interactions). The RF reported in this work is within the range reported by prior work [4, 6, 15]. Recent work by Grewe *et al* [49]

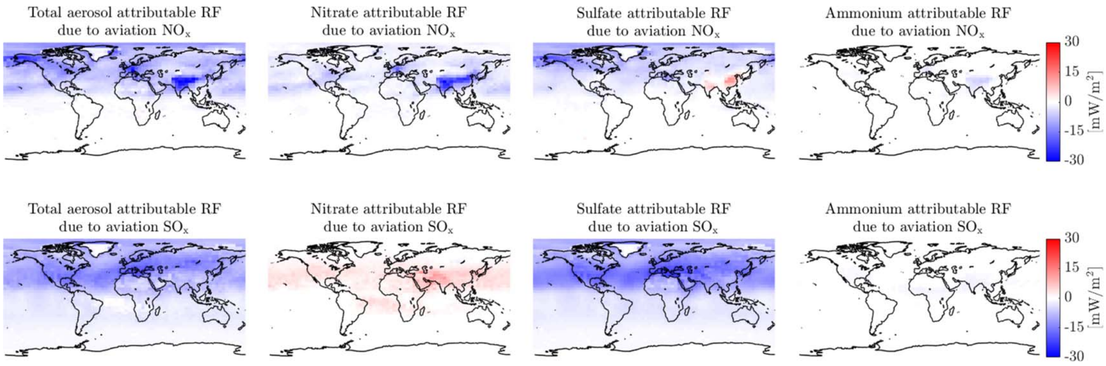

Figure 3. Aviation NO_x attributable impact on secondary inorganic aerosol related radiative forcing. Radiative forcing is calculated at the tropopause.

Table 4. Aviation-attributable radiative forcing (in mW/m^2) due to ozone and aerosol species (sulfates, nitrates, ammonium, black carbon, total aerosol).

	Ozone (mWm^{-2})	Total Aerosol (mWm^{-2})	Sulfates (mWm^{-2})	Nitrates (mWm^{-2})	Ammonium (mWm^{-2})	Black Carbon (mWm^{-2})
Baseline aviation	51	−8.3	−7.8	−0.67	−0.30	0.67
NO_x attributable RF	51	−3.4	−1.6	−1.7	−0.13	−0.058
SO_x attributable RF	0.14	−5.5	−6.4	1.2	−0.17	−0.031
BC attributable RF	−0.032	0.74	0.024	0.0019	0.0050	0.73

Table 5. Speciated aviation-attributable radiative forcing normalized by mass of emissions.

	Sulfates	Nitrates	Black carbon
Aviation-attributable RF (mWm^{-2} per Tg fuel burn)	−0.032	−0.0028	0.0028
NO_x attributable RF (mWm^{-2} per Tg N)	−1.4	−1.6	−0.052
SO_x attributable RF (mWm^{-2} per Tg S)	-1.8×10^3	3.3×10^2	−8.5
BC attributable RF (mWm^{-2} per Tg BC)	3.3	0.27	1.0×10^2

suggests that perturbation methods, as used in this study, may underestimate the impact of NO_x emissions on ozone concentrations, resulting in the ozone RF also being underestimated by a factor of 1.6. While the focus of this paper is on the aerosol attributable RF impacts from aviation, almost all of the pathways to aerosol formation we explore are mediated by ozone and may therefore also be underestimated. Further comparison of the RF reported in this work to prior estimates in the literature are provided in the supplementary information. Table 4 also shows that aviation ozone related RF is dominated by aviation NO_x emissions (~51 mWm^{-2}). The sulfate, nitrate and ammonium aerosols have contributions from aviation NO_x and SO_x as discussed in the following sections. Table 5 shows that aviation SO_x emissions have the largest magnitude of both nitrate and sulfate RF impact per unit mass of emissions (0.33 Wm^{-2} and −1.8 Wm^{-2} per Tg S emitted), while aviation emissions of BC are responsible for ~100 mWm^{-2} of BC related warming per Tg of BC emitted. The remainder of this paper will focus on the radiative impacts from ozone and the nitrate-sulfate-ammonium system.

3.2. Aviation NO_x attributable impacts

We estimate that aviation NO_x emissions result in an ozone related warming of 51 mWm^{-2} and an aerosol related cooling of −3.4 mWm^{-2}. Aviation NO_x is also responsible for ~72% of aviation attributable near surface aerosol loading. The impact of aviation NO_x emissions on the production of ozone is well documented in the literature [2, 3] from an air quality perspective and will not be addressed further in this paper. There are several pathways through which aviation emissions of NO_x results in the formation of secondary inorganic aerosol. As shown in figure 2 the two dominant pathways are the formation of nitrate (−1.7 mWm^{-2}) and sulfate aerosol (−1.6 mWm^{-2}) from oxidation of both aviation and non-aviation NO_x and SO_x. The latter is discussed in detail in section 3.2.3 below.

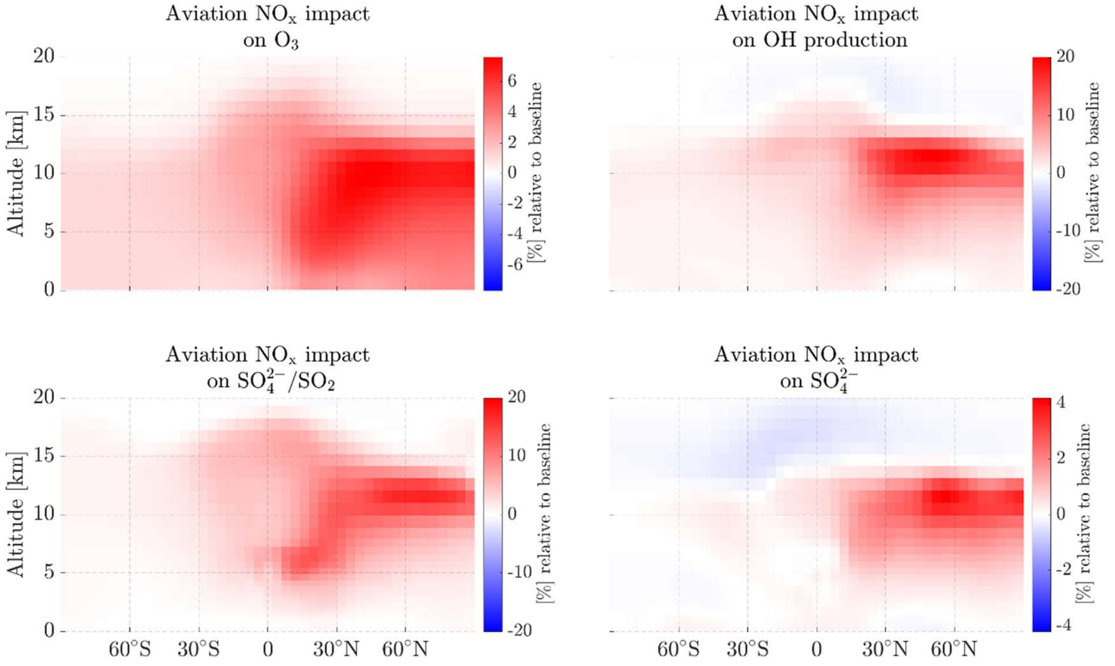

Figure 4. Effect of aviation NO_x on the oxidation of SO_x to sulfates.

3.2.1. NO_x—NO_3 pathway

The impact that aviation NO_x has on aviation attributable nitrate, sulfate, and ammonium RF is shown in the top row of figure 3 below. The RF attributable to each of these species is obtained by first calculating the RF due to the sulfate-nitrate-ammonium-water system and apportioning the RF based on the mass fractions of the comprising species. The peak nitrate (cooling) RF values, particularly over northern India and parts of China, and the corresponding peak in ammonium attributable RF over the same region are due to higher concentrations of free ammonia that is available for the formation of nitrates (see supplementary material). Aviation attributable ozone derived from aviation NO_x emissions results in the conversion of background NO_x to HNO_3 in the troposphere [21], which then reacts with ammonia to produce ammonium nitrate. This agrees with previous studies that estimated aviation attributable particulate matter from an air quality perspective [2, 3]. The nitrate cooling seen in figure 3 is a combination of direct formation from aviation NO_x and oxidation of non-aviation NO_x by aviation attributable ozone. The loss of sulfate cooling over parts of Asia is due to the effect of aviation NO_x on the lifetime of background SO_x as described in section 3.2.3.

3.2.2. Impacts of aviation NO_x on aviation SO_x

In addition to promoting the formation of nitrate aerosols, aviation NO_x emissions are also responsible for 21% of the aviation-attributable RF from sulfate aerosols. This is because the ozone formed as a consequence of aviation NO_x emissions results in an increase in upper tropospheric OH, as shown in figure 4. The top two panels show that aviation NO_x emissions increase ozone mixing ratios in the northern hemisphere by ~5% and increase OH mixing ratios in upper troposphere and lower stratosphere by up to 20%. This increase in ozone and OH promotes the oxidation of gas phase SO_2 to SO_4^{2-}. Sulfate aerosol mixing ratios are increased by approximately 4% in the northern hemisphere UTLS, as shown in the bottom two panels of figure 4. We also find that aviation emissions increase the global annual average surface ozone mixing ratio by ~2.3%. This is consistent with the increases of 0.3%–1.9% reported by Cameron *et al* [50] based on a 2006 AEDT aviation emissions inventory, which included ~30% less aviation fuel burn than our 2015 inventory.

This demonstrates that in addition to the formation of nitrates, aviation NO_x emissions impact secondary aerosol formation by increasing the concentration of aviation attributable oxidants in the atmosphere that oxidize background NO_x and SO_x to nitrates and sulfates. Prior studies such as that by Pitari *et al* [51] noted a similar effect of aviation NO_x attributable OH on the oxidation of SO_2 to sulfate aerosol but report a smaller sulfate radiative forcing of -0.2 mWm^{-2}. Three possible sources for the greater radiative forcing of -1.6 mWm^{-2} in this work are as follows. Firstly, the aviation emissions in this work (from the AEDT 2015 inventory, table 2) include NO_x emissions which are 55% greater than the total from the 2006 FAST inventory used by Pitari *et al.*, implying greater ozone production. Similarly, the SO_2 emissions used in this work are 50% greater than the 2006 FAST inventory resulting in more aviation SO_x available to be oxidized to sulfates. Secondly, as

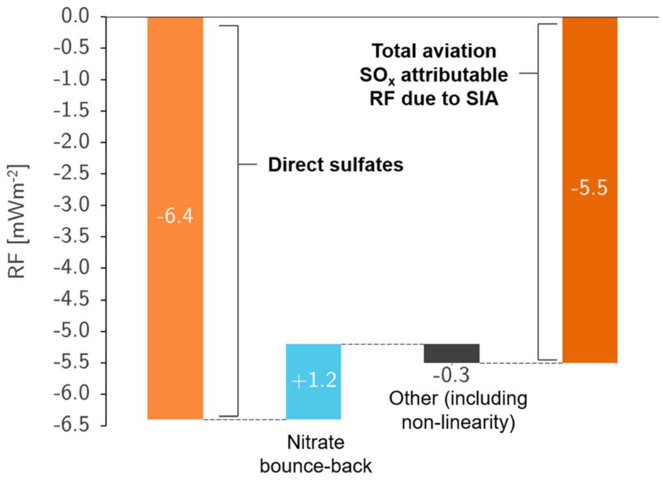

Figure 5. Aviation SO_x attributable RF due to secondary inorganic aerosol broken down to show the various pathways. Aviation emissions of SO_x result in a direct sulfate cooling of 6.4 mWm^{-2} and a nitrate bounce-back of $+1.2$ mWm^{-2}. All values are in mWm^{-2}.

outlined in the following section, the sulfate attributable RF is dependent on the emissions of aviation and non-aviation SO_x and therefore is dependent on the background emissions considered. Greater emissions of non-aviation SO_x will therefore result in a larger sulfate attributable RF resulting from aviation emissions. Finally, the two models show different sensitivities of ozone production per unit of NO_x emitted. The models used by Pitari *et al* estimate an increase in column ozone per unit of aviation NO_x emitted which is 27%–45% lower than estimated by the version of GEOS-Chem used in this study. Further details are presented in the SI.

3.2.3. Impacts of aviation NO_x on background SO_x

The lifetime of sulfur species in the troposphere is primarily determined by the rate of wet deposition of sulfates [21, 52]. This sulfate removal process is enhanced by aviation NO_x since it promotes the conversion of background (non-aviation) SO_x to sulfates as described in the previous section. This reduces the lifetime of sulfates around regions of higher background SO_x emissions. This is observed in figure 3 where aviation NO_x results in a loss of cooling (positive RF) from sulfates over regions of India and eastern China, where there is a high concentration of SO_2 emissions from coal fired power plants.

Furthermore, as shown in figure 1 aviation NO_x is responsible for a global sulfate RF of -1.6 mWm^{-2}. Repeating this experiment in a scenario where the fuel is already desulfurized still yields a sulfate RF of -1.4 mWm^{-2} attributable to aviation NO_x emissions, ~88% of the previous value. Given that the total sulfate aerosol RF due to aviation is -7.8 mWm^{-2}, 18% of the total sulfate aerosol forcing resulting from aviation is not the result of aviation sulfur. Instead, aviation NO_x emissions are taking part in chemical mechanisms which promote the oxidation of ambient, mostly non-aviation sulfur to form sulfate aerosol.

3.3. Aviation SO_x attributable impacts

Aviation SO_x emissions are estimated to result in an ozone related warming of 0.14 mWm^{-2} and an aerosol related cooling of -5.5 mWm^{-2} as seen in figure 1, which accounts for ~65% of aviation attributable aerosol related RF. Aviation SO_x emissions are also responsible for ~27% of near surface aerosol loading. The following sections will focus on the aerosol contribution to aviation attributable RF resulting from aviation SO_x emissions.

3.3.1. Aviation SO_x impact on nitrate aerosol related RF

Nitrates and sulfates in the troposphere compete to react with ammonia to form ammonium nitrate and ammoniated sulfate compounds respectively. The ammonia in the troposphere preferentially reacts with the available sulfates, therefore ammonium nitrate is typically formed only in regions where the molar concentration of total ammonia exceeds that required to neutralize the available sulfates [21]. Figure 1 shows that aviation NO_x contributes a nitrate related cooling of -1.7 mWm^{-2} while the net nitrate cooling due to all aviation emissions is only -0.67 mWm^{-2}. This is because aviation SO_x emissions result in a decrease in nitrate cooling as they preferentially react with the free ammonia thereby reducing the nitrate concentrations. We estimate the degree of this 'nitrate RF bounce back' due to aviation SO_x emissions to be ~70% ($+1.2$ mWm^{-2}) of the nitrate cooling due to NO_x as shown in figure 5. Use of ultra-low sulfur fuel (<15ppm mass of sulfur) will therefore lead to an increase in nitrate cooling due to NO_x.

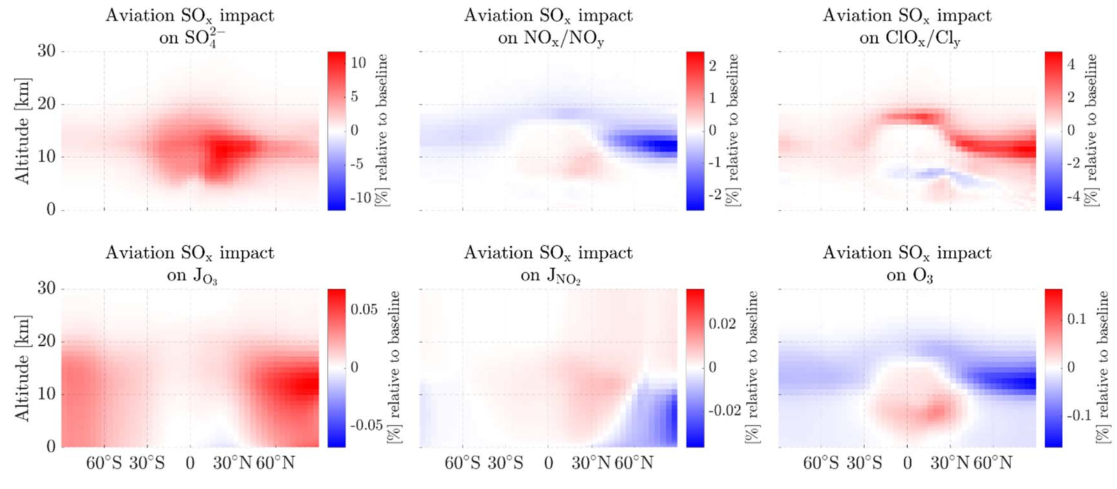

Figure 6. Impact of aviation SO_x emissions on the atmosphere. All plots shown are the percentage change in the zonally averaged annual average quantities.

3.3.2. Aviation SO_x attributable ozone depletion in the stratosphere

Aviation SO_x emissions results in the formation of sulfate aerosol as seen in figure 6. The increase in sulfate aerosol promotes the heterogenous hydrolysis of N_2O_5 to HNO_3 on the aerosol surface. The HNO_3 thus formed is likely to be in the gas phase as the lower stratosphere is not saturated with respect to HNO_3 [21]. The conversion of a N_2O_5 to relatively stable HNO_3 serves to remove active NO_x and therefore decrease the NO_x/NO_y ratio as seen in figure 6. The reduction of NO_2 additionally increases the ClO_x/Cl_y ratio by reducing the formation of $ClONO_2$. The increase in active chlorine species increases the halogen catalyzed destruction of ozone through the enhanced ClO_x cycles. The reduction in NO_2 has a competing effect by reducing the effectiveness of ozone removal by the NO_x cycle. However at typical cruise altitudes (10–12 km) it is known that the halogen cycles are the dominant loss mechanism of ozone [17, 19, 20] therefore the net effect of aviation SO_x at cruise altitudes is to deplete ozone by up to 0.1% as shown in the bottom right panel of figure 6. The role of atmospheric halogen species in this pathway implies that this effect will be diminished in the future as the burden of anthropogenic halogens in the atmosphere reduces.

3.3.3. Aviation SO_x attributable ozone in the troposphere

Depletion of ozone in the lower stratosphere leads to an increase in ultra-violet radiation (UV) in the troposphere which results in an increase the photolysis rate (J_{O_3}) of the ozone in reaction 1 and a decrease in the photolysis rate of NO_2 (J_{NO_2}) in reaction 3 (as shown below) in the high latitudes. Similar findings have been reported in the context of solar geoengineering by high altitude sulfate injection [17, 20]. There are regions where there is an increase in J_{NO_2} in the tropics, which leads to a local increase in ozone production in the troposphere as seen in the bottom right panel of figure 6.

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \quad \text{(R1)}$$

$$O(^1D) + H_2O \rightarrow 2OH \quad \text{(R2)}$$

$$NO_2 + h\nu \rightarrow NO + O \quad \text{(R3)}$$

$$O + O_2 + M \rightarrow O_3 + M \quad \text{(R4)}$$

The decrease in ozone production rates in the troposphere combined with lower ozone mixing ratios in stratospheric air masses entering the troposphere lead to a decrease in ozone mixing ratios in the mid to high latitudes. However, the effect of stratospheric—tropospheric exchange is less pronounced in the tropics as the Hadley cell leads to strong upwelling of well mixed tropospheric air masses in the inter-tropical convergence zone (ITCZ). Additional details of the ozone RF response to aviation SO_x at different latitudes is provided in the supplementary material.

4. Conclusions

Aviation emissions are known to impact air quality and the climate. Current regulatory standards for NO_x and SO_x emissions are largely motivated by near-airport air quality concerns and the detailed pathways by which aviation NO_x and SO_x perturb the climate have not been previously characterized and quantified. Better scientific understanding of these pathways plays a role in informing aviation environmental policy. This is the first work to separate out the mechanisms by which aviation NO_x and SO_x impact concentrations of ozone and secondary inorganic aerosol and quantify their impact in terms of RF using a detailed radiative transfer scheme (RRTMG) coupled to a global chemistry-transport model (GEOS-Chem).

We find that, at cruise altitudes, aviation is responsible for ∼30%–50% of NO_x mixing ratios and ∼2%–16% of SO_x mixing ratios depending on the season. Aviation NO_x emissions are estimated to result in an ozone related RF of $+51$ mWm^{-2} and an aerosol RF of -3.4 mWm^{-2}. Aviation NO_x is the primary driver for aviation attributable ozone formation accounting for over 99% of the total aviation attributable ozone. Aviation NO_x is also responsible for -1.6 mWm^{-2} of sulfate related RF through the NO_x-SO_4 pathway where aviation attributable oxidants derived from aviation NO_x emissions result in the oxidation of SO_x emissions to sulfate aerosol. We also find that 88% of this sulfate related RF through the NO_x-SO_4 pathway is due to the oxidation of non-aviation SO_x. Therefore, sulfate formation through the NO_x-SO_4 pathway due to aviation NO_x emissions accounts for almost half (47%) of the aviation NO_x attributable RF.

Aviation SO_x emissions are responsible for -5.5 mWm^{-2} of the aerosol RF and is the dominant source of aviation attributable aerosol RF in the stratosphere. Furthermore, we find that aviation SO_x emissions result in ozone depletion in the upper troposphere and lower stratosphere by promoting the heterogeneous hydrolysis of N_2O_5 and the subsequent enhancement of the halogen catalytic cycles. We estimate that aviation SO_x emissions have only a small impact on ozone depletion (∼0.1%).

Further work is required to quantify the impact that the above pathways have on aviation air quality impacts by using surface concentrations of ozone and particulate matter together with epidemiological studies that relate the risk of premature mortality to increase in population exposure to these pollutants. For example, the impact that aviation SO_x emissions have on surface ozone implies that a future scenario with desulfurized jet fuel can have a negative air quality impact through the aviation SO_x—ozone pathway in addition which needs to be quantified. The role of background conditions must be quantified to better understand how future non-aviation emissions changes will affect aviation's environmental impacts. Localized impacts can also be studied by performing GEOS-Chem simulations at a finer spatial resolution, which would also help to quantify potential errors due to excessive numerical diffusion on coarse spatial grids. This work supplements the current literature to improve our understanding of the impacts that specific aviation emissions (NO_x and SO_x) have on the aviation attributable climate perturbation.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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