Quantifying the impact of aviation emissions
on global nitrogen deposition

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by

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Preface

This report is the final product of my thesis work undertaken over the last eight months, and was written with the aim to obtain my master's degree in Aerospace Engineering at the Delft University of Technology. It was through circumstance that I ended up performing my thesis work at the Aircraft Noise and Climate Effects department, however I could not have found a more welcoming and enthusiastic department to work with. My thesis focuses on the aviation effects on nitrogen deposition, a very relevant topic in the current political scene, especially in the Netherlands, which has been a great motivator for this research.

I would like to express my sincerest gratitude to Professor Dedoussi for her daily supervision throughout my thesis work. I have learned a lot from our discussions and it was a pleasure to work with and learn from you. I would also like to thank Flavio for his help in supervision, and especially his help with the modelling side of my research. Finally I would like to thank my family, and friends, who have always had my back and have been incredibly supportive throughout my entire thesis work, and without whom I would never have made it this far. Thank you!

Marijn van Loo
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Executive Summary

Excessive nitrogen deposition from anthropogenic emissions has a global impact on natural biodiversity. While aviation emissions have been studied in the context of climate change and air quality, this is not true for nitrogen deposition. Meanwhile the growth of the aviation industry is likely to increase the relative contribution of aviation emissions to nitrogen deposition. Current regulatory policies aiming to mitigate nitrogen deposition are limited to local scale, and are inadequately applicable to the global nature of the aviation industry.

In this research the impact of aviation emissions from both landing and take-off (LTO) and non-landing and take-off (non-LTO) emissions are studied by perturbing emission scenarios in the GEOS-Chem chemistry transport model for 2005. The total nitrogen deposition from all sources was compared to both other model results as well as deposition measurements to evaluate the performance of the GEOS-chem model. Subsequently the aviation attributable nitrogen results were analysed for its spatial distribution, species make-up, and relative contribution to total nitrogen deposition from all sources. This was done for full-flight emissions, as well as for separate LTO and non-LTO contributions.

The model evaluation showed adequate results for total wet deposition when comparing relevant performance indicators, both compared to other models as well as measured values. The dry deposition showed a large deviation from both model and measurement values, replicating findings in literature, and reinforcing the fact that there are still challenges in the modelling and measurement of dry deposition.

Aviation attributable nitrogen deposition results show that the aviation industry is responsible for 0.71% of total nitrogen deposition worldwide. While the aviation attributable nitrogen deposition is highest in Europe, East Asia and the Easter United states, spatial distribution patterns show a large amount of spread, leading to increased nitrogen deposition globally, but especially in the northern hemisphere. An evaluation of the land cover that aviation emissions deposit on further reinforce this notion, showing that a tendency to deposit over open seas as well as oceans. While regionally contributing up to 30%, on average only 7.7% of aviation attributable nitrogen deposition is attributable to landing and take-off emissions globally , indicating that local regulatory policies do not take into account upwards of 70% of aviation attributable nitrogen deposition.

The results in this report provide a basic understanding of the global impact of aviation emissions on nitrogen deposition, giving a base for the development of global policies supporting a sustainable future for the aviation industry.

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Abbreviations

$PM_{2.5}$	Fine Particulate Matter (> 2.5 microns)
AAND	Aviation-Attributable Nitrogen Deposition
AEIC	Aviation Emissions Inventory Code
BNF	Biological Nitrogen Fixation
CEDS	Community Emissions Data System
CTM	Chemistry Transport Model
FAC2	Fraction of measured values which fall within a factor 2 of observed values
FB	Fractional Bias
GC	GEOS-Chem
LTO	Landing & Take-Off
LTOAND	LTO-Attributable Nitrogen Deposition
MERRA	Modern-Era Retrospective analysis for Research and Applications
NMB	Normalised Mean Bias
NMSE	Normalized Mean Squared Error
non-LTOAND	non-LTO-Attributable Nitrogen Deposition

Symbols

τ	Lifetime of species within atmosphere
$C(z)$	Local concentration of species at altitude z
F	Dry deposition flux
k_i	First order removal coefficient for process i
P_i	Summation of atmospheric sources for species i
Q_i	Total mass of species i within a volume of air
R	Summation of atmospheric sinks for species i
r_a	Aerodynamic resistance
r_b	Boundary layer resistance
r_c	Canopy resistance
r_t	Total resistance to dry deposition
v_d	Dry deposition velocity
Ar	Argon

BC	Black Carbon
CH_4	Methane
CO_2	Carbon Dionoxide
CO	Carbon Monoxide
H_2O	Water
HNO_3	Nitric Acid
N_2O_5	Dinitrogen Pentoxide
N_2O	Nitrogen Oxide
N_2	Nitrogen
NH_3	Ammonia
NH_4	Ammonium
NO_2	Nitrogen Dioxide
NO_3	Nitrate
NO_x	Collective term for nitrogen oxides (NO_2 + NO)
O_2	Oxygen
O_3	Ozone
OH^-	Hydroxide
SO_2	Sulphur Dioxide

1

Introduction

In this chapter the topic of this research is introduced, including the relevance of the subject, the research questions and scope for the project. The motivation for this research project is given in Section 1.1. The research goals and research questions are presented in Section 1.2. Finally the structure of the report is given in Section 1.3.

1.1. Motivation

Reactive nitrogen is an essential element both as a plant nutrient in many ecosystems, and as an ingredient in many industrially useful compounds. It is naturally produced by bacteria in the soil and oceans. However, anthropogenic creation of reactive nitrogen has more than doubled its presence in the atmosphere [19]. The use of artificial fertilizers containing reactive nitrogen is the only way to provide the food needed to support the current human population on earth [19]. Furthermore the growth of industry and transportation sectors including aviation have also increased the amounts of reactive nitrogen being emitted into the atmosphere. This increased amount of reactive nitrogen present in the atmosphere is resulting in global increases in nitrogen deposition [1, 47].

Elevated levels of nitrogen deposition have a detrimental effect on the environment due to over-enrichment and acidification of the soil [5, 37], leading to loss of biodiversity in a wide range of ecosystems [10, 40]. Policies are in place to limit the deposition of nitrogen over vulnerable ecosystems by regulating emissions of (agricultural) industry and traffic sectors [16, 17], as well as disallowing infrastructure projects in the vicinity of these protected areas that have a negative impact [15].

Of these transportation sectors, aviation is currently the most rapidly growing [27]. While Covid-19 temporarily halted this advance, recovery scenarios predict a return to 2019 levels within the next two to six years, and predict continued growth in the years to follow [14]. Even with improvements in both engine filter technologies and improved air traffic infrastructure use, NO_x emissions from aircraft are expected to at least double in the coming 25 years [9].

Aviation emissions have been shown to contribute to climate change [30, 20], and have detrimental effects on human health [8] and air quality [35, 39] on a global scale. However the exact extent and impact of aviation emissions on nitrogen deposition have not been extensively investigated. In view of future growth expectations it seems even more prudent to make sure that the consequences of aviation emissions are fully understood.

Global regulations regarding the standards on aviation emissions by ICAO [26] only cover the standard landing and take-off (LTO) cycle operations, which can be considered rather local. ICAO regulations do not include non-LTO emissions, even though these make up over 90% of all aviation emissions [44]. The local nature of regulatory policies regarding emissions is difficult to rhyme with the global scale of the aviation industry. Unfortunately, there is only limited research into the non-LTO effects of aviation emissions. Tarrason et al. [45] conducted a study on regional air quality over Europe due to non-LTO emissions, and found that the effects of non-LTO emissions are considerably larger than those from LTO emissions. They also concluded that European airspace emissions accounted for only half the total impact of non-LTO emissions, further reinforcing the necessity to evaluate these effects on a global scale.

In a bid to better understand the full extent of the environmental impact of aviation emissions, and to get a clearer picture of the different effects of LTO and non-TLO emissions, this study will investigate the global effects of aviation emissions on nitrogen deposition, with the ultimate goal of supporting the development of global policies enabling a sustainable future for the aviation industry.

1.2. Research goals and questions

As is evident, a more thorough understanding of the relation between aviation emissions and nitrogen deposition is needed to fully understand the environmental effects of aviation emissions, as well as to aid in the limitation of nitrogen deposition to vulnerable ecosystems. Without this knowledge, it is difficult to apply local and regional regulation to the aviation sector, and hard to develop mitigation measures on a global scale. Therefore the aim of this thesis is stated as follows:

Research Aim: *To evaluate the impact of aircraft emissions (LTO & non-LTO) on global nitrogen deposition, by perturbing aircraft emission in the GEOS-chem atmospheric chemistry model and analyzing the resulting wet and dry nitrogen deposition values on a global scale.*

In order to achieve this aim, the following research goals have been established:

- **Research Goal 1:** *To quantify the contribution of aviation emissions to nitrogen deposition.*
- **Research Goal 2:** *To evaluate the difference between LTO & non-LTO aircraft emission impacts on nitrogen deposition.*
- **Research Goal 3:** *To quantify the deposition of aviation attributable nitrogen deposition to specific land cover types.*

Research questions:

The main research question that needs to be answered to achieve the research goals is set as follows:

- **Main:** *What are the effects of LTO & non-LTO aircraft emissions on global nitrogen deposition?*

To help fully answer this question and in order to satisfy all the research goals set above, the following sub-questions have been set up:

- **SQ1:** *What are the effects of aircraft emissions on global nitrogen deposition?*
    1.1 *Which nitrogen depositing species are (most) sensitive to aircraft emissions, and to what extent?*
    1.2 *What is the contribution of aircraft emissions to total nitrogen deposition?*
    1.3 *Is there any seasonal and/or regional variation to these effects?*
- **SQ2:** *What are the separate contributions of LTO and non-LTO emissions to changes in global nitrogen deposition?*
    2.1 *Which nitrogen depositing species are the main contributors for both cases?*
    2.2 *How do these contributions compare to each other, and to total effects?*
    2.3 *Is there any seasonal and/or regional variation to these effects?*
- **SQ3:** *Where does aviation attributable nitrogen deposit?*

1.3. Research structure

In the following report, Chapter 2 presents the background and context necessary for this research. Chapter 3 defines the methodology employed to obtain the results. An extensive evaluation of the GEOS-Chem model is conducted and presented in Chapter 4. The modelled results describing the behaviour of aviation attributable nitrogen deposition are given in Chapter 5. Finally Chapter 6 discusses the conclusions and recommendations that can be drawn from these results.

2

Background & Research Context

In this chapter the background context for the thesis is presented. Section 2.1 gives some background in atmospheric chemistry, and Section 2.2 describes the destiny of nitrogen containing compounds within the atmosphere, from source to deposition and back. Finally Section 2.3 how the current state of knowledge with respect to the environmental impact of aviation emissions.

2.1. Tropospheric chemistry

The majority of the following section is summarised from the excellent book on atmospheric chemistry by Seinfield and Pandis [42], which will therefore not be cited repeatedly. Chemical species are subject to a myriad of different effects during their presence in the atmosphere from emission to deposition. The lowest level of the earths' atmosphere is known as the troposphere, where the temperature and pressure slowly decrease (from $15 \deg c$ down to $-51 \deg C$, and from 1000 mb to 200 mb respectively) as the altitude increases, up to the boundary layer with the stratosphere, where this temperature flux changes. This boundary layer is known as the tropopause. Its altitude is variable depending on latitude and conditions, but is usually located between 12-16 km altitude. Since cruise flight takes place at around 11km altitude, it is within the troposphere therefore that aviation emissions have their greatest influence.

The main constituents of dry air in the troposphere are nitrogen (78%), oxygen (21%) and argon (1%), followed by an assortment of trace constituents in much smaller concentrations. An overview of these constituents is given in Table 2.1, by volume mixing ratio. Also the respective estimated lifetimes of the species are given. Especially of interest is the lifetime of nitrogen oxides in the troposphere, which can be seen to be increasing as the altitude increases.

Lifetime of species

The greater the concentration of a chemical in the atmosphere, the faster it is removed [42]. This holds true for both wet and dry deposition mechanisms. In other words the species concentration over time differs linearly with the first-order removal coefficient k. The different removal pathways each have their own removal coefficient that show their influence on a species over time. They can be used to estimate species lifetime in the troposphere using Equation 2.1.

$$\frac{1}{\tau} = k_1 + k_2 \tag{2.1}$$

The change of a species' presence in the atmosphere for a certain volume of air (dQ_i/dt) is computed through Equation 2.2, as the conservation of mass within the volume is required. In this equation P is a summation of source terms for the species i, and consists of sources from natural emissions

Table 2.1: Tropospheric makeup division per species, including mean volume mean mixing ratio and average lifetime in the troposphere [6].

Species	Formula	Volume mixing ratio	Lifetime
Nitrogen	N_2	0.781	$1.5\text{x}10^7$ yr
Oxygen	O_2	0.209	40,000 yr
Water vapour	H_2O (surface)	0.01	days
	H_2O (tropopause)	10 ppmv	weeks
Argon	Ar	$9.3\text{x}10^{-3}$	accumulates
Carbon dioxide	CO_2	360 ppmv	50-200 yr
Methane	CH_4	1.73 ppmv	9 yr
Nitrous oxide	N_2O	313 ppbv	130 yr
Ozone	O_3 (surface)	5-50 ppbv	weeks
	O_3 (tropopause)	100 ppbv	months
Carbon monoxide	CO (surface)	50-200 ppbv	60 days
	CO (tropopause)	50-100 ppbv	0.05 yr
Nitrogen oxides	NO_x (surface)	0.01-1 ppbv	days
	NO_x (tropopause)	0.05-0.5 ppbv	weeks
Sulphur dioxide	SO_2 (surface)	0.01-1 ppbv	days
	SO_2 (tropopause)	10-50 pptv	weeks

(P_i^n), anthropogenic emissions (P_i^a), and chemical reactions (P_i^c). R_i is the summation of sink rates for species i, and consists of the dry deposition (R_i^d), wet deposition (R_i^w), chemical reactions (R_i^c), and transport (R_i^t) to the stratosphere. The loss processes are generally represented as first order coefficients k_i, so that it becomes Equation 2.3.

$$\frac{dQ_i}{dt} = P_i - R_i \tag{2.2}$$

$$\frac{dQ_i}{dt} = P_i^n + P_i^a + P_i^c - (k_i^d + k_i^w + k_i^c + k_i^t)Q_i \tag{2.3}$$

Transport of species through the atmosphere

Before a chemical species is removed, it is subject to a range of chemical transformations and transport mechanisms. The transport mechanisms will be described briefly, while the chemical reactions taking place will be discussed for nitrogen specifically in the next section. There is a manner of both vertical and horizontal circulation and mixing throughout the entire atmosphere, but the processes take place slightly differently. Due to the large temperature differences within the troposphere, the air is subject to rapid vertical exchange of energy and mass due to convection. This is therefore also the most tumultuous part of the atmosphere, constantly changing due to cloud formation, precipitation, prevailing wind patterns and pressure fronts.

Differences in absorption of solar radiation, and therefore differences in temperature, are the main driver of global circulation. The lower part of the troposphere heats up faster than the upper parts, causing the less dense warm air to rise, and denser, cooler air to fall to the surface. Furthermore the equatorial region of Earth is subject to a net energy gain due to solar radiation. The opposite is true for the poles which experience a net energy loss. This causes massive scale circulation attempting to balance this energy inequality. Due to the Coriolis force caused by the rotation of the Earth, this global circulation is split into multiple cells, as shown in Figure 2.1.

In the equatorial regions, warm air converging from both hemispheres rises and causes large amounts of precipitation to form, furthering the speed of convection to the upper troposphere. This causes large low pressure zones characterised by large amounts of cloud formation and rainfall. At around $30 \deg N$ air currents converge in the upper troposphere as they are cooling, causing large high pressure zones characterized by clear skies and low winds.

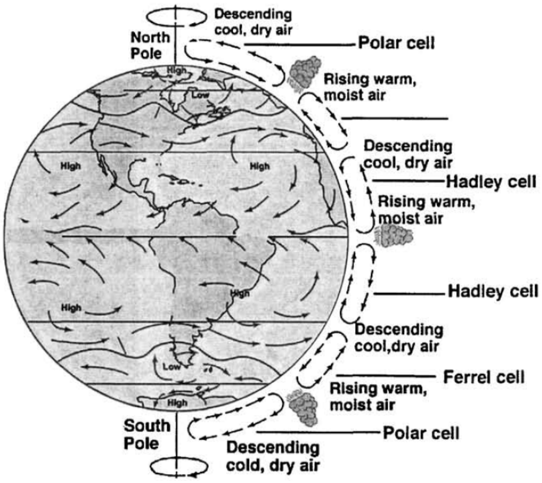

Figure 2.1: Three-cell representation of global atmospheric circulation [42]

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The stratosphere is only well-mixed for species which have a lifetime there that exceeds the rate at which global weather patterns can mix it. Again, these are different for different directions. The characteristic mixing rate for vertical mixing in the troposphere is about one week, whereas the characteristic horizontal mixing time is about on year. For nitrous oxides at the surface, this means the troposphere is not well mixed in any direction. Even for nitrous oxides in the upper regions of the troposphere, the lifetime is too short to be considered well mixed in either direction, but may be considered partially mixed vertically.

Deposition

The removal pathway for trace constituents of the atmosphere can be grouped into two types: wet deposition, and dry deposition. Wet deposition includes any pathway in which the species reaches the surface through precipitation. This may be either because they are absorbed into droplets, because droplets condense around particles, or because droplets collide with particles on the way down. The dry deposition is any pathway in which the species transfers into the Earth's surface without any interference of precipitation, which can happen either as a particle or a gas. Close to the ground, the settling of particles through dry deposition is generally the main deposition pathway for species, but from the altitude of about 100m, wet deposition generally becomes more dominant [42].

An overview of the processes contributing to the wet deposition of a species is given in Figure 2.2. As can be seen there are many different processes simultaneously happening both within and below clouds. The two main pathways towards deposition are either because species are scavenged within the cloud, which is called rain-out deposition, or when species collide with precipitation on the way to the surface, which is referred to as wash-out. The amount of wet deposition therefore depends strongly on the amount and location of precipitation, and therefore highly dependent on the weather. The challenge in modelling wet deposition lies not only in the large amounts of processes, but also that the species involved can be in many different phases (gas, aerosol, aqueous), as can the form of precipitation (as rain, fog, snow, hail, etc.). Furthermore the processes involved scale from the molecular level of chemical interactions all the way up to weather fronts stretching hundreds of kilometers.

Wet deposition is measured through the use of collector vessels. By collecting precipitation over an extended period of time and analyzing the resulting concentrations of the water collected the wet deposition in an area may be estimated. However measurements may be affected by conversion of nitrogen in the collector, dry deposition onto the collector vessel or contamination with organic matter [4].

During dry deposition gases and particles in the atmosphere are directly deposited onto the earths

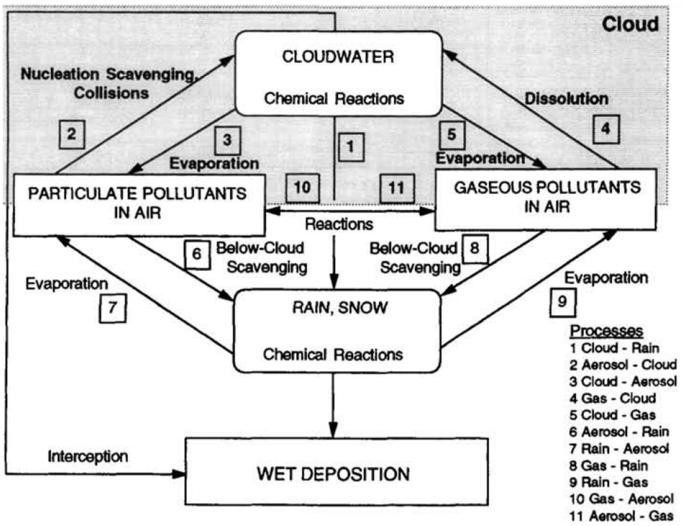


Figure 2.2: Overview of the processes contributing to wet deposition in and below clouds [42].

surface, either onto the soil, vegetation or buildings. The deposition flux is greatly dependent on the concentration of the species within the air, the amount of air movement or turbulence in the boundary layer with the surface, as well as the efficacy of the surface to capture present species. The dry deposition flux of a species can be described by Equation 2.4, as a function of the dry deposition velocity v_d at height z, as well as the species concentration C. In this formula, it is assumed that the flux is directly proportional to the local concentration C of the deposition species.

$$F = -v_d(z)C(z) \tag{2.4}$$

The dry deposition velocity v_d is often modelled as a big leaf model, which is an analogy to the electrical resistances in series. In the case of dry deposition, these resistances consist of the aerodynamic resistance r_a, the boundary layer resistance r_b and the surface resistance r_c (c for canopy). The dry deposition velocity can then be computed according to Equation 2.5. Representing the dry deposition by its velocity is advantageous for modelling deposition, as it captures all affecting processes into a single parameter. However this is also its downside, as it may be hard to determine an accurate value. Its sensitivity to weather conditions and surface conditions means that it is also constantly changing.

$$v_d = \frac{1}{r_t} = \frac{1}{r_a + r_b + r_c} \tag{2.5}$$

r_a and r_b are determined by wind speed, vegetation height, leaf size, and atmospheric stability. In general the greater the movement of the air and the larger the receiving surface area (taller trees, bigger leaves), the lower the resistance and therefore the higher the deposition velocity. r_c behaves a bit differently depending on whether the species is in gaseous or particle form. In gaseous for r_c is mostly dependant on the solubility and reactivity of the species, whereas for particles the biggest factor is the particle size. For instance HNO_3 and NH_3 are highly soluble and reactive species, and therefore their deposition is rapid and irreversible on almost any surface.

The dry deposition velocity considers the dry deposition as one directional, only down onto the earths surface. However nitrogen-containing species are also emitted from the soil, and there is an exchange of nitrogen-containing species going on [23]. This may influence both dry deposition measurements as well as modelling if it is not accounted for properly.

Measuring dry deposition involves measuring species concentrations in both upward and downward mass flow at several altitude levels above the ground, as well as knowledge of very local meteorological parameters. It cannot be measured directly, but must be inferred from concentration measurements in the air. Due to the minute differences in concentrations at different levels that need to be registered, the required accuracy for the equipment is very high in order to determine realistic dry deposition fluxes. From the measured concentrations, models are used to determine the deposition flux at that location. However, the resulting deposition velocity is greatly dependant on which model is used, and can differ up to a factor of 2-3 [41].

2.2. The nitrogen cycle through the atmosphere

Nitrogen makes up 78% of the atmosphere around us. Most of this nitrogen is contained in elemental nitrogen N_2, which has an extremely strong triple bond keeping the two nitrogen atoms tied together. Nitrogen is an essential element both as nutrients for plants and animals many ecosystems, and as an ingredient in many industrially useful compounds. Unfortunately this strong triple bond causes great difficulty in making single nitrogen atoms available for these purposes.

The conversion of nitrogen to a usable form is referred to as fixing nitrogen. These single nitrogen atoms contained in chemical compounds are referred to as reactive nitrogen, or ”fixed” nitrogen. Therefore it is important to make the distinction between nitrogen and reactive nitrogen. For the rest of this report when discussing nitrogen and nitrogen deposition, it will be implicit that reactive nitrogen is being discussed.

For the following overview of current estimates of global nitrogen fixation, we refer to Fowler et al. [19]. Natural nitrogen fixation is estimated to introduce about $203\ TgNyr^{-1}$ into the nitrogen cycle. The vast majority of reactive nitrogen is through biological nitrogen fixation (BNF). Whilst the mechanism is not completely understood, it is generally accepted that this nitrogen takes places through micro-organisms and bacteria, either in the soil or in the oceans. The total contributions of each are estimated at $58\ TgNyr^{-1}$ in the soil, and $140\ TgNyr^{-1}$ in the marine environment. A secondary natural source of reactive nitrogen is lightning, though much smaller in magnitude at just $5\ TgNyr^{-1}$. Omitting anthropogenic activities these two processes would be the only sources of reactive nitrogen.

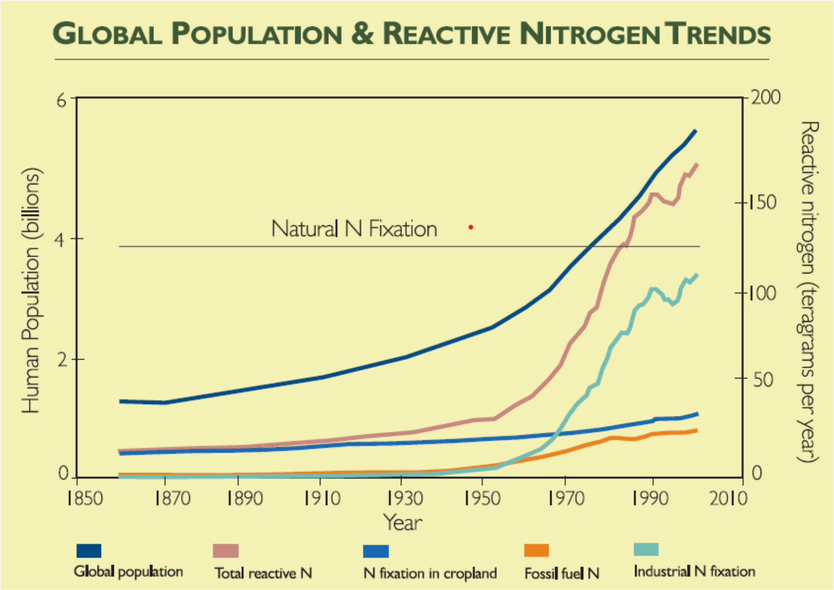


Figure 2.3: Reactive nitrogen availability vs global population[18].

Reactive nitrogen is a key component in determining the earth’s food supply on a global scale. Without anthropogenic influences, the amount of natural reactive nitrogen on Earth is only enough to support a human population of around 2 billion people [18]. As shown in Figure 2.3, the global population growth past this number was supported by vast amounts of anthropogenic nitrogen fixation, mostly through the use of fertilizer to increase crop yield. The nitrogen cycle has been greatly affected in order to make this happen. As shown, anthropogenic nitrogen fixation has by now surpassed natural nitrogen fixation. Fowler et al. [19] estimate the total amount at $180(\pm20)TgNyr^{-1}$ of reduced nitrogen mainly in the form of NH_3.

Nitrogen pathways from emission to deposition

Figure 2.4 shows the main pathways of anthropogenic reactive nitrogen through the atmosphere, as well as their main method of deposition. The main source of anthropogenic nitrogen is through fixation by the Haber-Bosch process [12]. It combines H_2 and N_2 at high temperatures to produce NH_3, of which the vast majority is used a agricultural fertilizer. This is referred to as reduced nitrogen. Over $120\ TgNyr^{-1}$ of reduced nitrogen is produced this way. Through its use in industry it partly finds its way into the atmosphere. About another $60\ TgNyr^{-1}$ is produced by cultivating nitrogen fixating crops NH_3 mostly dry deposits as particles close to its source [4]. The other main pathway is through chemical reaction to form NH_4 containing aerosols, which mostly wet deposit. Reduced nitrogen accounts for about 85% of anthropogenic nitrogen fixation [19].

$$NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^- \tag{2.6}$$

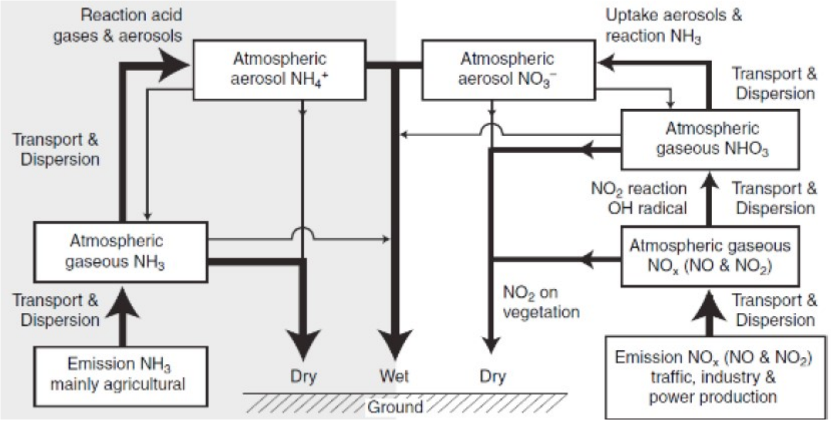


Figure 2.4: Main pathways of anthropogenic sourced reactive nitrogen in the atmosphere from source to deposition[23].

The other big contribution to anthropogenic nitrogen fixation is through the formation of oxidized nitrogen (NO_x) in incomplete combustion, through emissions from transportation and industry. Estimates for the year 2000 show approximately $40\ TgNyr^{-1}$, of which 30 from fossil fuel combustion, 5 from biomass combustion, and 5 from soil NO emissions [50]. Together with reduced nitrogen this places the estimated total anthropogenic contribution to nitrogen fixation at around $220-240\ TgNyr^{-1}$.

The nitrogen from emissions partially dry deposits directly as NO_x, however by far the greater part of it reacts with other species to end up as HNO_3, which is extremely water soluble [42]. This happens during the day through reactions 2.7-2.8, and at night through reactions 2.9-2.11.

$$NO + O_3 \longleftrightarrow NO_2 + O_2 \tag{2.7}$$
$$NO_2 + OH \longrightarrow HNO_3 \tag{2.8}$$

During the night the upper reaction does not take place because the balance of reaction 2.7 is governed by intensity of UV radiation from the sun. HNO_3 either wet and dry deposits directly, but it also combines with NH_3 to form the ammonium nitrate aerosol NH_4NO_3.

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \tag{2.9}$$
$$NO_3 + NO_2 \longleftrightarrow N_2O_5 \tag{2.10}$$
$$N_2O_5 + H_2O \longrightarrow 2\,HNO_3 \tag{2.11}$$

In general the deposition of nitrogen is slightly higher in summer, owing to the increased activity in both the agricultural as well as transportation industries. For the seasonal variation of dry deposition, gaseous HNO_3 and particulate NO_3- were higher in winter and autumn, but lower in spring and summer. In contrast, gaseous NH_3 and particulate NH_4^+ were higher in spring and summer, but lower in winter and autumn.

Effects of excessive nitrogen presence and deposition

The growing amounts of reactive nitrogen present both in the atmosphere and in the soil has detrimental effects to th natural environment. Emissions of NO_x into the troposphere can lead to the increased generation of ozone (O_3) both in the troposphere and stratosphere, having a warming effect on the earth and leading to climate change. However by changing the concentration of OH^- radicals, the CH_4 concentration is also reduced by increasing levels of NO_x, leading to negative radiative forcing and cooling [20]. Background levels of ozone also lead to detrimental effects on human health [8] and nature [13].

The vast increases in reactive nitrogen emissions by anthropogenic activity have also led to global increases in nitrogen deposition [47][1]. Many of the worlds ecosystems are limited by nitrogen availability, and so the increase of deposition can lead to the enrichment of the soil (eutrophication) and therefore increased ecosystem productivity. This can result in the excessive growth of invasive species and the decrease of biodiversity [5].

In marine environments, excessive nitrogen deposition also cause eutrophication and acidification of fresh and coastal waters, leading to the enhanced emissions of N_2O, a greenhouse gas, as well as excessive algae bloom and devastation of fish populations [40].

Because each ecosystem is balanced at a different level of reactive nitrogen availability, it makes sense to attempt to identify critical loads for each of these ecosystems separately. There are three main approaches for assessing critical loads; empirical, steady state mass balance and dynamic modelling. Critical load estimations have been carried out explicitly for Europe [5] and North America [37]. 11% of the worlds land based ecosystems are estimated to receive nitrogen deposition in excess of these critical loads [10], with the most affected areas are in Europe, Asia and the United States.

2.3. Environmental effects of aviation emissions

The aviation sector is the fastest growing transportation sector worldwide, and therefore so is the amount of aviation emissions [27]. Emissions from other sectors, both from industry and transportation, are steadily decreasing due to advancements in technology and the increasing regulation of allowed emissions. There is no viable replacement of aviation transport available at the moment, in terms of combined transportation speed and global coverage. It is for this reason that the growth of the aviation industry is expected to keep going for a considerable amount of time into the future [27].

In the study of the environmental effects of aviation emissions. The three main aspects that have garnered the most attention are the effects are climate change, air quality and noise pollution. Being interested the results of changing atmospheric composition, only the first two will be discussed.

The climate effects of aircraft emissions are mainly attributable to the (long term) effects of CO_2 emissions, and the (more immediate) effects of non-CO_2 emissions, including NO_x, water vapour and soot particles. The aviation emission contribution to anthropogenic climate change is estimated to be in the range of $1.3\% - 10\%$, and slightly greater if the effects of cirrus cloud enhancements are also considered. Future scenario's indicate that future radiative forcing due to aviation emissions may increase by a factor 3-4 within the next 30 years [30].

Formation of NO during incomplete combustion happens mainly due to the Zel'dovich mechanism as shown in Equations 2.12-2.13. NO_x formed in this way is referred to as thermal NO_x, and is the primary anthropogenic source of NO_x in the atmosphere. The formation of NO_x during combustion is greatly dependent on the fuel-air mix, and is highest at full thrust settings, which mostly occur during take-off.

$$N_2 + O \longrightarrow NO + N \tag{2.12}$$

$$N + O_2 \longrightarrow NO + O \tag{2.13}$$

Air quality effects of aircraft emissions are attributable to the formation of secondary fine particulate matter $PM_{2.5}$ as well as O_3 produced from the emission of NO_x [35]. Increased air pollution leads to adverse human health effects. Yim et al. [53] conducted a study into the health impacts of civil aviation, and concluded that aviation emissions cause around 16,000 premature deaths of which 25% are attributable to LTO emission. A global societal cost analysis estimated this to be in the same order of magnitude as climate effects of aviation.

The study of nitrogen deposition effects of aviation emissions has been limited, and only on a local scale. Leung et al. [31] conducted a study regarding the effect of aviation emissions in Swedish airspace to nitrogen deposition. They concluded that contributions to deposition (in Sweden) are in the order of less than 1%. They show that LTO emissions have the greatest effect locally, however they also conclude that emissions from above Swedish airspace can be traced to well beyond the Swedish borders. High cruise emissions are shown to have insignificant contributions to local deposition in Sweden.

Tarrason et al. [45] investigated regional air quality over Europe due to non-LTO emissions, and showed that in general the effect of non-LTO NO_x emissions is an order of magnitude larger than from LTO emissions. They attributed it to the predominance of non-LTO emissions, and estimate that non-LTO NO_x emissions contribute with about $2\% - 3\%$ to the deposition of oxidised nitrogen over Europe.

3

Methodology

This chapter covers the methodology used for answering the research questions posed in section 1.2. First, section 3.1 describes the numerical model used to simulate the atmosphere. Section 3.2 describes the aviation emission database used as input. Then section 3.3 carefully describes the settings for each model run, as well as the different scenarios that were performed.Sections 3.4 and 3.5 show how the data produced in these scenarios are used to come to the results which are presented in the following chapters. Finally section 3.6 clarifies the scope of the project.

3.1. GEOS-Chem model description

The GEOS-Chem chemistry transport model will be used to evaluate nitrogen deposition as a result of aviation emission perturbations. Measurements can only give us the current state of the atmosphere at any given time, while laboratory experiments can only target our understanding of specific processes taking place in the atmosphere. In order to aid in the full understanding of the workings of our atmosphere, our understanding of these individual processes are combined in mathematical models.

The three main parts of any model are the input emissions, the transport mechanisms through the atmosphere and the transformations that occur both physically and chemically. An overview of the key components of any atmospheric chemical transport model can be seen in Figure 3.1. The sources include databases of species emissions, both natural and anthropogenic. A weather database input is also needed, in order to be able to evaluate all the parameters needed for the transport part of the model.

For this thesis the atmospheric modelling was carried out using GEOS-Chem (GC) version 12.6.1. (GEOS-Chem user community, http://acmg.seas.harvard.edu/geos/, original paper by Bey et al. [3]) The model was run on the Dutch national supercomputer Cartesius, with the support of the SURF Cooperative. GC is a Eulerian type model, which means that the air parcels it simulates are fixed in space, and the species enter and leave through its sides, assessing the concentration of each species at every time step. With air parcels in a three dimensional grid the entire atmosphere is simulated as a function of space and time.

The wet deposition scheme in GC is described by Liu et al. [33] for water-soluble aerosols and by Amos et al. [2] for gases. Dry deposition is based on the resistance-in-series scheme implemented by Y. Wang et al. [51]. Aerosol deposition is from Zhang et al. [54]. Cold-temperature HNO_3 deposition is from Jaegle et al. [28]. Recent developments relevant to this thesis and updated in the 12.6.0 version of GC include the reactive uptake of NO_2, NO_3, and N_2O_5 by aerosols, as described by Holmes et al. [25], and reactive uptake coefficients for N_2O_5 on sulfate-nitrate-ammonium-organic aerosol from McDuffie et al. [36].

Several databases are used as model inputs. The meteorological input data is from the MERRA-2 reanalysis product from NASA/GMAO [21], at a native resolution of $0.5°$ x $0.625°$. The main global

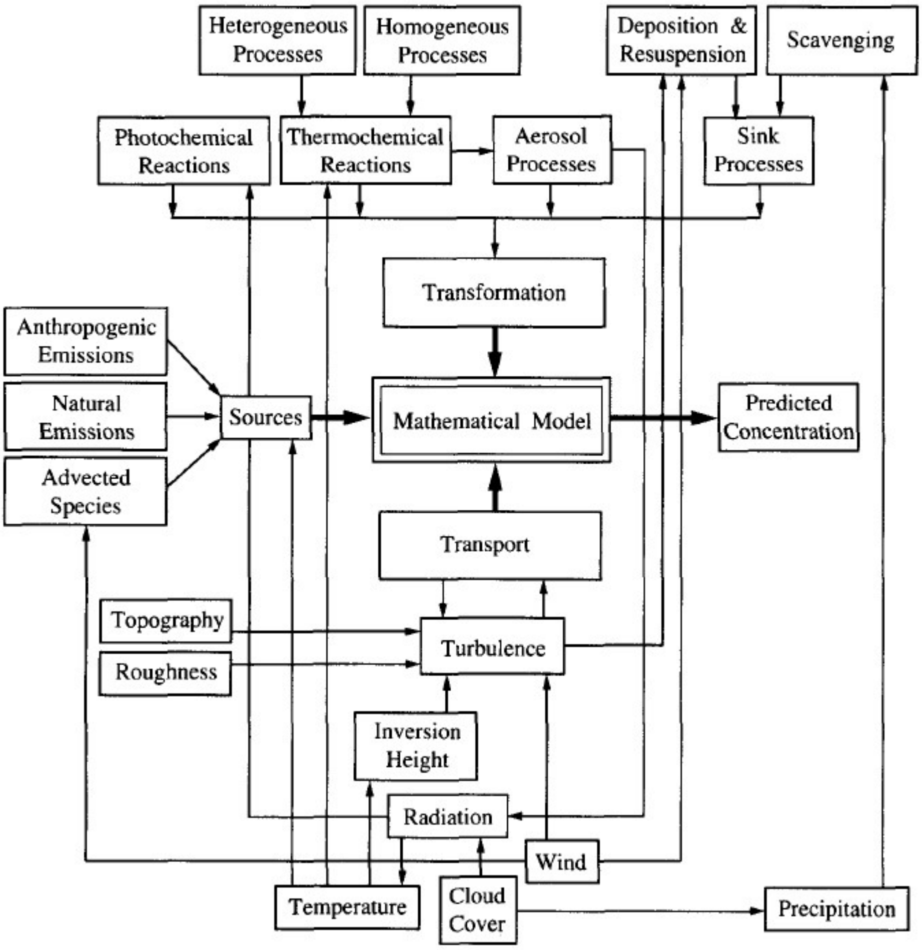


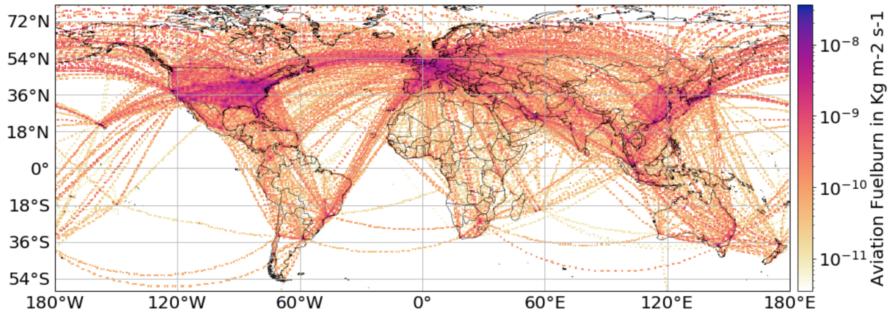
Figure 3.1: Overview of elements of a chemical transport model for the atmosphere [42].

anthropogenic emissions input is from the Community Emissions Data System (CEDS) [24], extended with regional inputs from DICE-Africa [34], MIX-Asia [32], NEI2011 [46] (USA) and APEI (Canada) [11].

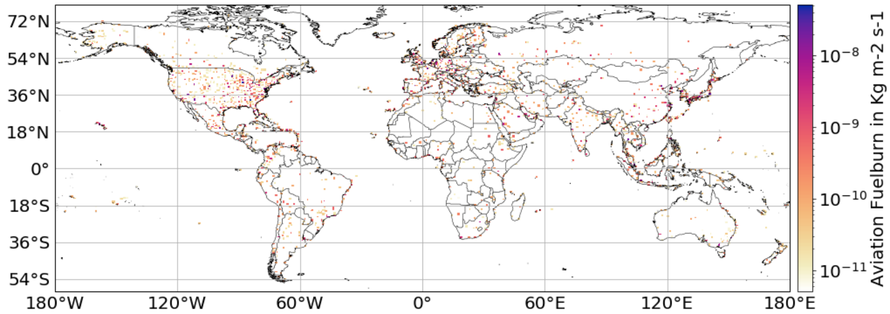
3.2. AEIC aviation emissions

The full flight aviation emissions used in this research are from the AEIC database [44]. This database includes full flight aviation emissions for the year 2005, at a 1° x 1° degree grid resolution. All emission databases are loaded and assembled in the HEMCO module described by Keller et al. [29], before being input to GC.

During this study, the distinction will be made between emissions take place in Landing and Take-Off (LTO) operations and non-LTO operations, or cruise flight. The spatial distributions for LTO and non-LTO emissions within the database are plotted in Figure 3.2. As can be seen, the vast majority of flight traffic takes place on the northern hemisphere, but is distributed globally. Owing to this, emissions are slightly higher in the northern hemisphere summer, coinciding mostly with the increase in passenger transport due to the holiday period. The LTO emissions only take place in grid cells containing airports, and show no flight paths owing to the quick climbing time of commercial aircraft. According to AEIC data, of all the emissions, 8.9% of all fuelburn, and 7.4% of NO_X emissions take place during LTO operations.



(a) non-LTO fuelburn



(b) % LTO fuelburn

Figure 3.2: Global spatial distributions of non-LTO and LTO fuelburn from AEIC data for 2005 [44].

3.3. Simulation scenarios

Four simulation scenarios were run in order to be able to asses the effects of aviation emissions and subsets thereof. The initial state of the atmosphere for each of the scenarios was determined by performing a 21 month spin-up simulation of the GEOS-Chem model. Each scenario has an individual spin-up period of 3 months during which the aviation emissions are already adjusted, up to the end of 2004. Subsequently the scenario is run for the full 12 months of 2005. The results are analyzed for 2005 only. An overview of all the simulations performed is given in Table 3.1.

Table 3.1: Overview of simulation scenarios ran on GEOS-Chem, and the respective aviation emissions and grid resolutions used.

Scenario	**Aviation emissions input**	**Grid resolution**
1	None	4°×5°, 2°×2.5°
2	All	4°×5°, 2°×2.5°
3	LTO only	4°×5°, 2°×2.5°
4	non-LTO only	4°×5°

For every scenario two model runs were performed, one at a coarse grid at $4°$ x $5°$, and one at a finer grid at $2°$ x $2.5°$. Each grid has 72 simulations levels of altitude, starting at the surface level, up to $0.01\ hPa$. All 72 levels were included in the simulation runs. For transportation and convection the time step was set to 600 seconds. For the chemistry and emissions part of the model the time step was set to 1200 seconds. This base run, or scenario 1, is used to determine total global nitrogen deposition values from non-aviation sources, and will be subtracted from all following scenarios.

All subsequent scenarios were performed at the same model settings as the base run, with the only variation being the input emissions from the AEIC database. In the second scenario, all aircraft emissions are included as inputs to GC. Subtracting the base run from this scenario allows the assessment of full aviation emission effects on nitrogen deposition.

In the third scenario the AEIC database was partially masked in order to input only emissions taking place during LTO stages of flight. In keeping with literature, the emission level cutoff between LTO and non-LTO emissions was set to 1km altitude. This altitude range for LTO emissions is equivalent to the first 8 levels in GC. Again subtracting the base run from this scenario allows for the assessment of LTO effects on nitrogen deposition.

In the fourth scenario the inverse mask used on the AEIC database in order to input only emissions taking place during non-LTO, or mostly cruise flight. Again subtracting the base run from this scenario allows for the assessment of non-LTO effects on nitrogen deposition.

3.4. Nitrogen deposition output from GEOS-Chem

In general the key output of every chemistry transport model is the atmospheric composition at each location at each time step (as seen in Figure 3.1), which contains concentrations of all relevant species of interest. However for this research the key parameters are actually sink processes within the model which are of interest. In particular, the deposition process which includes dry deposition, and the scavenging process which results in wet deposition of species.

For each of the simulations three diagnostic collections of GC were used as output in order to determine the total nitrogen deposition data. For the wet deposition scheme in GC, there are two relevant diagnostics, the species loss at each time step due to convective uptake, and the species loss at each time step due to rainout and washout in precipitation. To determine the total wet deposition of a species, the contributions of both convective and rainout/washout species loss were summed over the entire atmospheric column, consistent with the methodology of Ackerman et al. [1]. The species considered for wet deposition of nitrogen included NH_3,NH_4,HNO_3, and NO_3^-. Both wet deposition diagnostics were set to output a daily mean value of the species loss, given in kg/s. Using the mass of nitrogen per species, and the equivalent area of each grid cell in GC, the resulting deposition values were converted to a deposition flux in $kg\ N/km^2/yr$.

For the dry deposition the relevant diagnostic is the species lost due to dry deposition at surface level. The species considered for dry deposition of nitrogen included NH_3,NH_4,HNO_3, NO_3^-,NO_2, and N_2O_5. Similar to the wet deposition, this diagnostic was set to output a daily mean value per species, this time given in $molec/cm^2/s$. Using Avogadro's constant, the molar mass of nitrogen per species and the equivalent area of each grid cell, the dry deposition values were also converted to a deposition flux in $kg\ N/km^2/yr$.

After these conversions the nitrogen deposition data was saved both as a total deposition flux, as well as separated into dry and wet deposition constituents, with individual values per grid cell, per month of the year and per contributing species.

By looking at the difference between the no-emissions scenario and the other three scenarios, these results can be used to determine the changes caused by aviation emissions, both from full emissions as well as separated into LTO and non-LTO constituents.

3.5. Assessment of aviation contribution to nitrogen deposition per land cover type

In addition to being interested in the relation between aviation emissions and nitrogen deposition, we are also interested in where this nitrogen deposition occurs. Knowing the aviation attributable nitrogen deposition per grid cell, we can use a land cover database in order to assess this. Therefore the nitrogen deposition results from the previous section will be compared to the global land cover database from Copernicus Global Land Cover (CLC) [7].

The discrete classification dataset is used, which is a raster based dataset, prepared in a rectangular latitude-longitude grid so that it can easily be re-gridded and directly compared to simulation results. The grid resolution is about 100m at the equator, decreasing slightly with changing latitude. Figure 3.3 shows the contents of the CLC for the Netherlands. Very distinct are the large areas of cropland in pink, the urban and built up areas in red, as well as some of the larger forested areas in green. A full legend for the 23 land cover types and their description can be found in Appendix A.

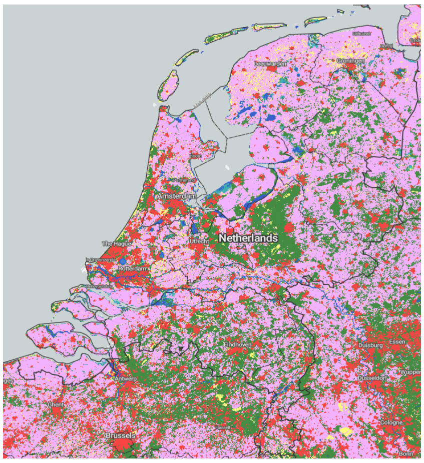


Figure 3.3: Example section of the discrete land cover database (Netherlands) [7]

The coverage area of the dataset ranges from longitudes $180°E$ to $180°W$, and from latitudes $60°S$ to $80°N$. So there is near global coverage of habitable classified areas, but it omits the inclusion of both polar regions. As the $2°$ x $2.5°$ grid contains grid cells with grid centers at exactly the limiting latitudes of the land cover data set, the grid cells at these latitudes are only covered for 50%. In the results section a quantification will be given of how much nitrogen deposition is omitted by not including the polar regions in the comparison.

For each (partially) covered grid cell in the GC simulations a land cover percentage was calculated based on the land cover database, as well as total percentage covers for all forest types and all other vegetation types. Together with the nitrogen deposition results these cover percentages will be able to give an idea on what type of land cover aviation attributable nitrogen deposition is likely to deposit on, and whether this differs from nitrogen deposition from other sources.

3.6. Research scope

This study is limited to the effect of aviation emissions on nitrogen deposition to the surface. As such any analysis done is purely discussed in relation to deposition. Any other effects nitrogen containing species have by their increased or decreased concentrations in the atmosphere, such as radiative forcing leading to climate change, or surface air quality due to particulate matter formation, will not be addressed within this study.

The perturbations made to aviation emissions within GEOS-Chem are done by altering the full emission data, which also includes the emissions of CH_4, CO and Black Carbon (BC). Their interaction with and effect on nitrogen containing species and deposition, though limited, is therefore present in results found.

Owing to the global scale of the GEOS-Chem model being run, as well as the coarse grid resolution employed, the results presented are limited to a similar scale, and no attempt will be made to analyse results on anything smaller than continental scale. Local and regional fluctuations from these macro-scale patterns are not only likely, but are expected, and finer resolution modelling is needed to analyse them.

4

GEOS-Chem Model Evaluation

In this chapter the model evaluation of the GEOS-Chem model will be discussed. First, in section 4.1 the methodology applied in the evaluation is described. Section 4.2 will compare the base run simulation total nitrogen deposition to each other and to literature, in order to assess the effect of grid size on model results. In section 4.3 the simulation data will compared to other GC model results. Then in section 4.4 the full simulation results will be compared with measurement data in order to assess the validity of the model. Finally, in Section 4.5 will discuss the result of the evaluation, and compare the findings to existing literature.

4.1. Model evaluation methodology

In order to be able to assess the effectiveness of GEOS-Chem at calculating nitrogen deposition results, a model evaluation was carried out. The full nitrogen deposition results from scenario 2 were used, which includes all aviation emissions. First, the results from both the 4° x 5° and the $2^\circ \times 2.5^\circ$ grid resolutions are compared. Second, the $2^\circ \times 2.5^\circ$ grid resolution results are compared first to the 2005 deposition results modeled by Ackerman et al. [1]. The 2005 data from Ackerman include both wet, dry and total nitrogen deposition values, at the same $2^\circ \times 2.5^\circ$ resolution, thereby allowing a direct comparison of deposition results. Finally, the same scenario 2 results are compared to measured nitrogen deposition from a range of measuring networks, compiled in a single data set by Vet et al. [47].

In accordance with a multi-model evaluation study performed by Vivanco et al. [49], several statistical performance indicators are used in order to evaluate the model performance. This is done by comparing the Observed (O) model values, to the Measured (M) values of the comparison data set. These include the normalized mean squared error (NMSE), the fractional bais (FB), and the fraction of model estimates which fall between a factor two of the observed values (FAC2). The NMSE is a measure of scatter of the data, and the fractional bias is a measure of consistent bias in either direction. The Normalised Mean Bias is not part of the evaluation criteria, but is used to get a sense of the bias in the observed model values. An overview of the performance indicators used is given in Table 4.1, as well as the criteria they are required to meet. Owing to the fact that the resolution of GC grid, similar to other global atmospheric models, is coarse, the acceptability criteria for these performance statistics is quite broad. A model is deemed to perform acceptably when two of the three criteria (NMSE, FB, FAC2) are met.

In addition to these criteria, scatter plots of each comparison show the measure of correlation between the observed and measured values. These show the slope of the linear interpolation, the correlation coefficient r, as well as the Normalised Mean Bias (NMB). Together with the above performance indicators, they allow us to evaluate the validity of the GC model results.

Throughout this section, it is important to differentiate clearly between this study's GEOS-Chem

Table 4.1: Overview of statistic performance indicators used for model evaluations together with their acceptability criteria.

Statistic	Calculation	Criterion
NMSE	$\frac{\overline{(O-M)^2}}{\bar{O}\bar{M}}$	≤ 1.5
FB	$\frac{2(\bar{M}-\bar{O})}{(\bar{O}+\bar{M})}$	≤ 0.3
FAC2	$0.5 \leq \frac{M}{O} \leq 2.0$	≥ 50%
NMB	$\frac{\sum_{i=1}^{N}(M_i-O_i)}{\sum_{i=1}^{N}O_i}$	(-)

model results, Ackerman et al. [1] their GEOS-Chem model results, and the Vet et al. [47] measurement data set. Therefore for the rest of this chapter, this study's results will be referred to as GC results, whilst the Ackerman model results will be referred to as Ackerman results.

4.2. Model run grid size comparison

In order to evaluate the difference between the two global resolution grids, GEOS-Chem was run using scenario two, including all aviation emissions, at both resolutions. The runtime for the $4°$ x $5°$ grid resolution was about 65 hours (2.7 days) for the 15 months of a simulation run. Specifically lowering output frequency, allowing the model to average output over longer periods of time, did not decrease this runtime. The runtime for the $2°$ x $2.5°$ resolution run was around 325 hours, but due to the maximum runtime restrictions of Cartesius at 72 hours this took about 15 days (360 hours) to complete due to having to manually restart the simulation.

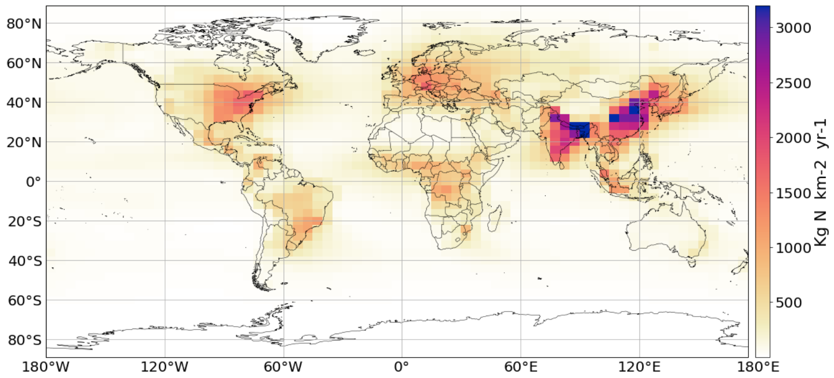
The spatial distribution of the two simulation runs can be seen in Figure 4.1. Because every grid cell has a different area depending on its latitude, the nitrogen deposition per grid cell was converted to a value per km^2, as this is a more accurate representation when displaying these results spatially. As can be seen, the general deposition patterns show similar patterns for both grid resolutions, as expected. Very high values of deposition are found in India and parts of China. Of course at a the greater resolution, there is a degree of improved spatial accuracy.

The deposition per species, and per type of deposition, of these simulations can be viewed in Table 4.2. The main depositing pathways for nitrogen deposition agree with literature (see Section 2.2), being through NH_3, NH_4 and HNO_3. Per grid resolution, together they make up 92.6% and 92.0% of all nitrogen deposition respectively. There is slightly more wet deposition than dry deposition at both resolutions. The further analysis of specific species contributions is left to the results section.

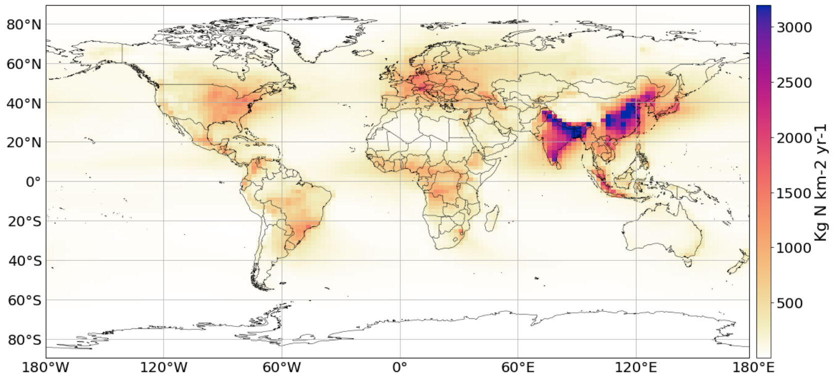
When looking at the differences between the two simulation results, we do see some differences in the makeup of the total deposition. The coarse resolution finds 2% less deposition than its counterpart. This is mostly due the lower amount of dry deposition. The biggest differences occur in the species which make up a smaller amount of the total nitrogen deposition (NO_3, NO_2 and N_2O_5). The cause of any of these species specific differences between the two resolutions is unclear. No comparison to other speciated results from GC was done, as these were not available.

Table 4.2: Full nitrogen deposition results for both $4°$ ×$5°$ and $2°$ ×$2.5°$ grid resolution, separated by species and wet/dry/total deposition. Depositions are in Tg N yr^{-1}, except for the contribution percentages per species.

	$4°$ x $5°$	**in Tg N yr-1**				$2°$ x $2.5°$	**in Tg N yr-1**		
Species	**Dry**	**Wet**	**Total**	**(%)**	**Species**	**Dry**	**Wet**	**Total**	**(%)**
NH_3	20.23	13.03	33.26	28.87	**NH_3**	19.71	12.74	32.44	28.67
NH_4	3.99	21.39	25.38	22.02	**NH_4**	3.79	22.89	26.67	23.57
NO_3	1.39	4.66	6.04	5.25	**NO_3**	1.28	5.39	6.68	5.90
HNO_3	25.92	22.14	48.06	41.71	**HNO_3**	23.90	21.13	45.03	39.79
NO_2	2.23	(-)	2.23	1.94	**NO_2**	2.07	(-)	2.07	1.83
N_2O_5	0.25	(-)	0.25	0.22	**N_2O_5**	0.27	(-)	0.27	0.24
Total	54.01	61.22	115.23		**Total**	51.02	62.15	113.16	



(a) 4° ×5°



(b) 2° ×2.5°

Figure 4.1: Total nitrogen deposition for both grid resolutions.

Due to the large difference in runtime between model resolutions, some preliminary results were produced for all scenarios at a 4° x 5° resolution in order to get an idea of what these results would look like. One of the main findings of this preliminary investigation is the linearity in GC deposition results. The results for LTO-attributable nitrogen deposition and non-LTO-attributable nitrogen deposition, produced separately by altering the emissions data, add up to exactly the same results as those for full aviation emission attributable nitrogen deposition.

This shows that while there are many non-linear processes at work within GC, there is no interaction between the LTO and non-LTO emissions, and the resulting nitrogen deposition found, given the model set up used. It also shows that there are no interfering effects taking place in the model between the effects of LTO and non-LTO emissions, even around the boundary altitude between the two at 1km. As was shown in Section 2.1, modelling deposition is first-order dependent on the concentration within the atmosphere, so while there may be non-linear processes influencing the determination of the removal coefficients for each species, these do not change with the perturbations to the model by this study.

Concluding the grid size comparison, it was determined to use the 2° x 2.5° grid resolution simulation as the baseline resolution for both the model evaluation and all results following later in this study, as there is only a small difference of 2% between the two grid sizes. This difference is not directly attributable to anything to do with the aviation emission input or anything else traceable, and the difference in results from different grid resolutions can therefore not be used to give additional meaning to any following results. The greater resolution due to its greater spatial accuracy is therefore the better candidate to use for determining model results.

Furthermore due to the conclusions of linearity within the model for the 4° x 5° resolution, as well as the runtime duration for the smaller grid resolution, it was determined to not run the final scenario of the 2° x 2.5° resolution, but to use the linearity to deduce these results from the difference between scenario 2 and scenario 3.

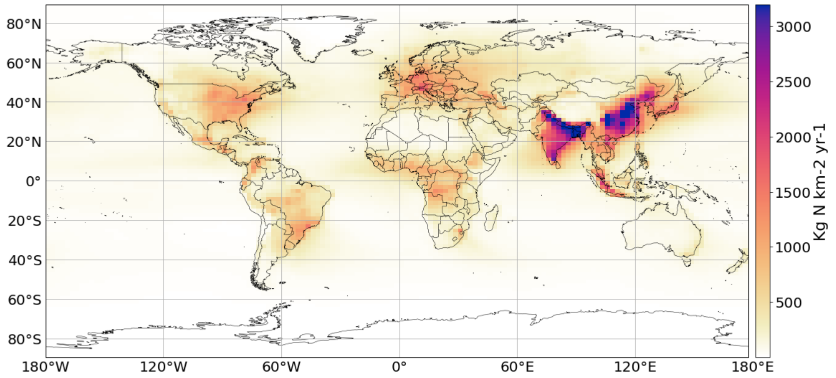
4.3. Simulated nitrogen deposition validation versus other simulations

In this section the $2^\circ \times 2.5^\circ$ resolution results are compared to those found by Ackerman et al [1]. Ackerman et al use a previous version of GEOS-Chem (V11-01) to study total nitrogen deposition trends across four decades, simulating 3 years within each decade including our reference year 2005. In this evaluation their 2005 deposition data for dry, wet and total deposition was used to evaluate GC results. Table 4.3 shows the dry, wet, and total deposition determined by each simulation. As can be seen the wet deposition agrees quite strongly, however there are large differences in the dry deposition at both grid resolutions. Due to the fact that the data by Ackerman did not publish speciated deposition values, it was unfortunately not possible to use their results to validate species-specific results of the GC model. The total nitrogen deposition results agree more strongly with the 106.3 Tg N found by Vet et al. for 2001 [47].

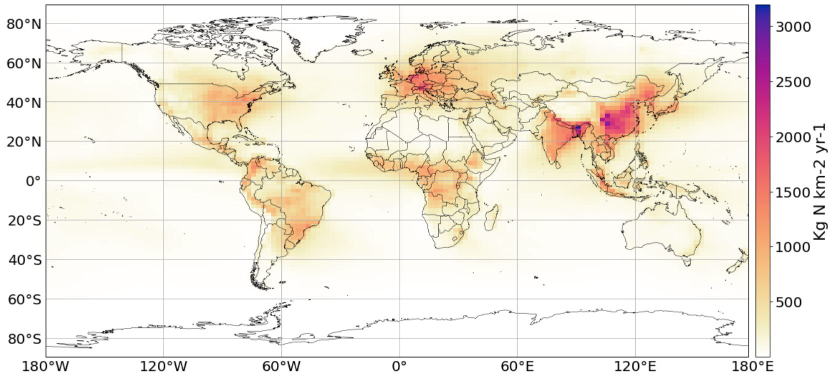
Table 4.3: Total nitrogen deposition in 2005, in Tg N, for both grid resolutions as well as Ackerman results.

Simulation	**Dry**	**Wet**	**Total**
4x5	54.01	61.22	115.23
2x2.5	51.02	62.15	113.16
Ackerman	32.68	63.41	96.09

The spatial distribution of the 2° x 2.5° results compared to the Ackerman data is shown in Figure 4.2. Both depositions are plotted at exactly the same grid resolutions, so as to highlight the differences better. As can be seen the general deposition patterns appear to match strongly, however in the GC results there are large deposition peaks in Asia which are not found in the Ackerman results.



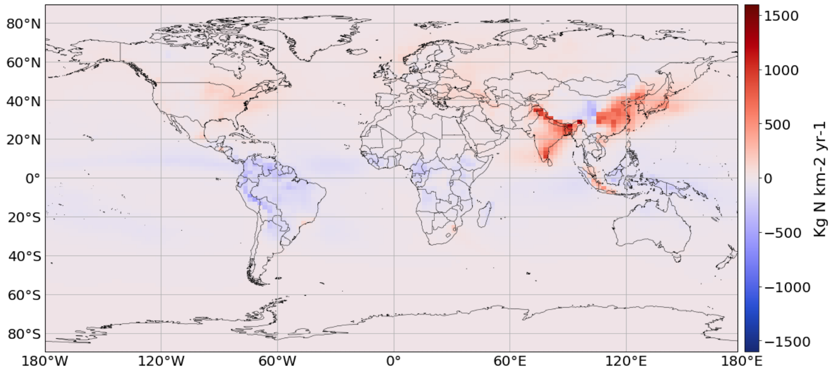
(a) This study



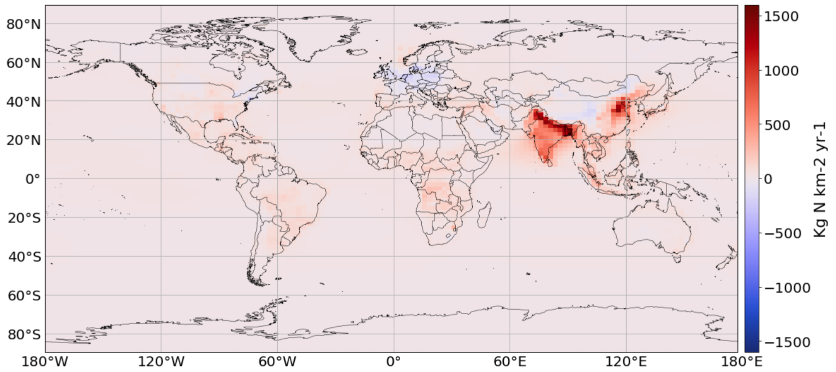
(b) Ackerman

Figure 4.2: Total nitrogen deposition comparison vs. Ackerman data, at 2° x 2.5°.

To highlight the differences between the two spatially, it was plotted in Figure 4.3. As can be seen for the dry deposition, GC results were higher almost globally, with large peaks in northern India, Nepal and China regions. Again the dry deposition is much larger in GC results. For the wet deposition however, there are some differences in both directions, indicating a stronger agreement between model results.



(a) Wet deposition difference



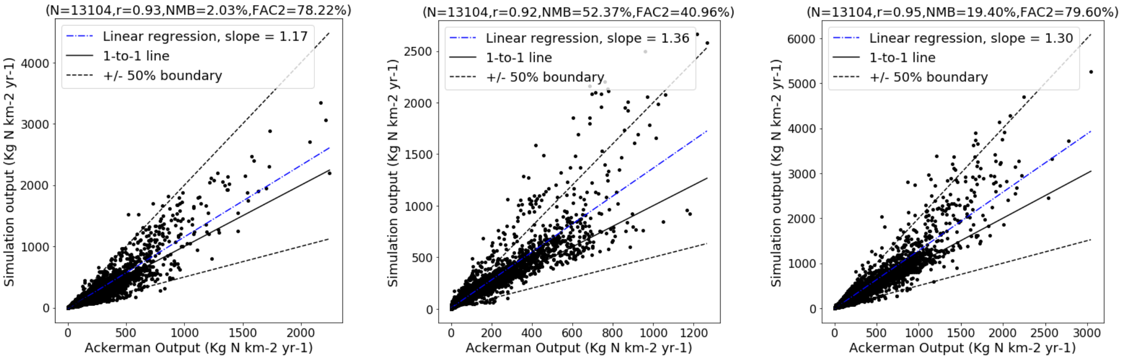
(b) Dry deposition difference

Figure 4.3: Difference in wet and dry nitrogen deposition between Ackerman results and own GC results, positive values indicate higher deposition in 2° x 2.5° model results.

However these spatial visualisations do not tell the full picture. Following the methodology from Section 4.1, the two datasets were compared statistically. The results of this comparison can be seen in Figure 4.4 and in Table 4.4. It can be see that there is a strong correlation between the two data sets, in both wet and dry nitrogen deposition. In all cases the GC results appear higher than the Ackerman results. The large difference found in the dry deposition spatially is also apparent from this comparison. Looking at the bottom three statistics, which are used as acceptability criteria, it can be seen that the wet deposition meets all three criteria, whereas the dry deposition meets none of them. However the combination of the two and owing to the fact that wet deposition makes up a slightly large portion of the total deposition, the combined deposition again meets all three acceptability criteria.

The cause of this large difference in dry deposition is unclear. The input of GC model parameters used as well as the nitrogen-containing species included in the analysis, was exactly the same for both data sets as far as could be determined from their paper. However the anthropogenic emissions data sets were slightly different. Where the current study uses the updated CEDS data set as input, Ackerman et al. used the slightly older EDGAR emissions data.

An attempt was made to replicate Ackerman results by changing anthropogenic input emissions to the EDGAR data. However GC results still showed the same large discrepancies in the dry nitrogen deposition. Other tweaking to input parameters, such as timestep differences or output frequency, made no difference to the results found, as was expected. The only other difference is the difference in versions of GEOS-Chem used to perform the simulation (v12.6.1 vs v11-01), but no updates in the changelog could directly be linked to causing such a large change in dry deposition. Dentener et al.



(a) wet deposition (b) dry deposition (c) total deposition

Figure 4.4: Scatter plots for GC results vs Ackerman data.

[10] found a similar large bias in East Asia, and attributed it to either highly uncertain NH_3 emissions, or the underestimation of NH_4 measured values.

In conclusion, no singular cause could be identified for the differences between results coming from the same model. It is likely that either an update to the emission inventories, or some of the mechanisms related to the calculation of dry deposition fluxes in GC is responsible, but this could not be verified.

Table 4.4: Comparison statistics for GC simulation vs Ackerman data.

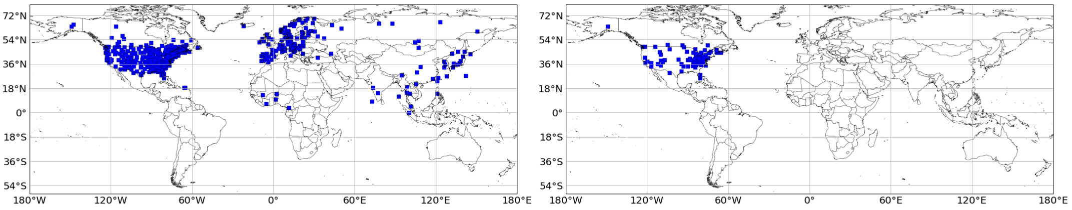
Statistic (crit)	**Wet**	**Dry**	**Tot**
r	0.93	0.92	0.95
slope	1.17	1.36	1.3
NMB	2.03%	52.37%	19.40%
|FB| (≤ 0.3)	0.02	0.41	0.18
NMSE (≤ 1.5)	0.58	1.73	0.74
FAC2 ($\geq 50\%$)	78.22%	40.96%	79.60%

4.4. Simulated nitrogen deposition validation versus measured data

In this section the 2° x 2.5° results are compared to the global measurement set compiled by Vet et al. [47]. The majority of wet deposition sites come from measurement networks in Europe (EMEP), North America (NADP) and Asia (EANET). The vast majority of dry deposition sites come from the American CASTNET, with a few additional sites also in North America being supplied by the Canadian CAPMoN network. A full list of measurement networks and references can be found in the addendum to the paper by Vet et al. [48]. The locations of all measurement stations for which acceptable quality data (as assessed by Vet et Al.) was available are shown in Figure 4.5. These were also the only sites used in the evaluation of GC results.

As can be seen the majority of wet deposition measurement sites are located in North America and Europe, with only 30 measurement sites (6.5%) outside these regions. For dry deposition the only available measurement sites are all located in North America. This means that it is not possible to directly validate GC results for other regions. In choosing sites included in the database, care was taken to only include sites in rural and remote locations, to ensure that measurements taken from that site are regionally representative [48]. As such any sites situated close (>50km) to urban or industrial hotspots were explicitly excluded from the database.

Similar to the previous section, the spatial distributions were plotted against each other for both data sets in order to get an idea for the emerging patterns, starting with wet deposition. Figure 4.6 shows the spatial distribution of the wet deposition measurement stations as well as their measured nitrogen deposition, plotted against the background of GC results. Cut-outs of both Europe and North America

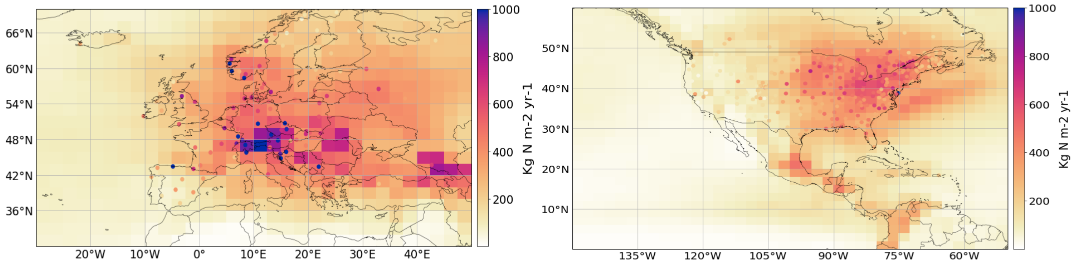


(a) wet deposition (463 sites)

(b) dry deposition (71 sites)

Figure 4.5: Acceptable measurement site locations for 2005 from Vet et al. dataset [47].

are shown, as this is where the vast majority of measuring sites are located. The wet deposition sites for North America seems to match quite well, as can been seen from the fact that the measuring sites seem to blend in well with the background. In Europe this seems to be the case as well, but to a lesser extent, with some measuring stations showing very clear deviation from the GC deposition. It could be that due to the more compact nature of built up area in Europe, it is harder to place representative sites, and a higher resolution is needed to capture deposition patterns at this local scale.



(a) Europe

(b) North America

Figure 4.6: Wet deposition GC model results in the background, versus Vet et al measurements values per site for a) Europe and b) North America.

Figure 4.7 shows the same, but only for the dry deposition measurement stations in North America. It is very clear at first glance that again there is a large discrepancy between the simulated GC deposition and the dry deposition measured at these sites, with the GC simulations showing much higher deposition values.

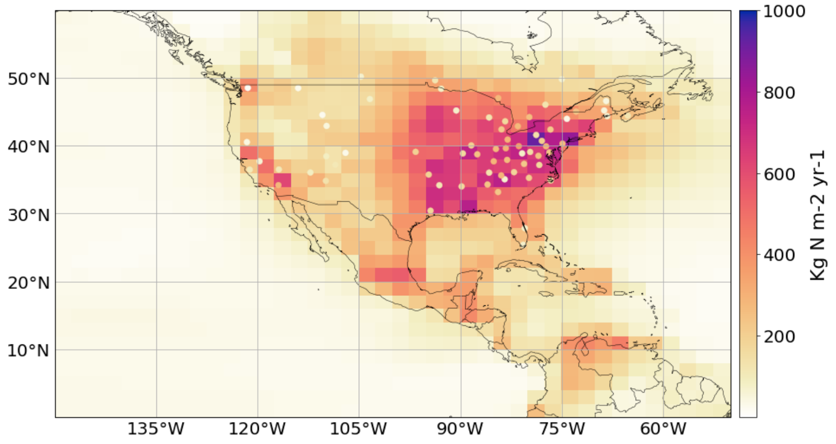
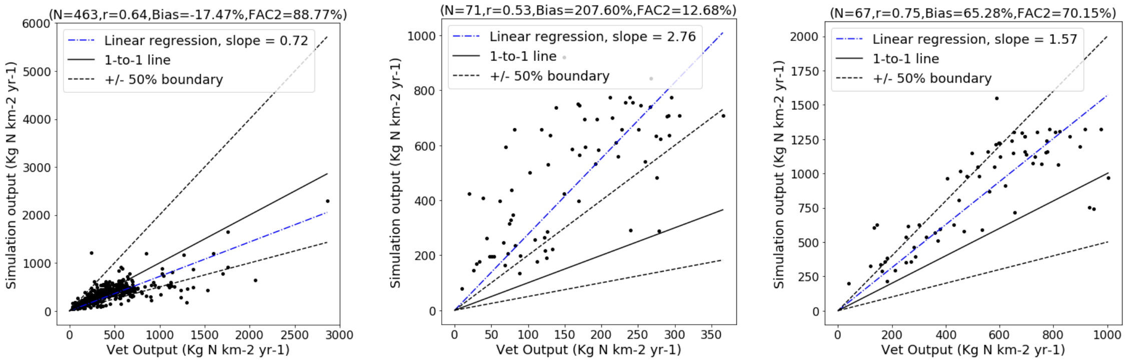


Figure 4.7: Dry deposition GC model results in the background, versus Vet et al measurements values per site.

Similar to the Ackerman comparison, the observed values from the GC results were compared to the measured values from the Vet et al. dataset. The resulting scatter plots can be seen in Figure

4.8, and the statistic results can be viewed on the left side of Table 4.5. Looking at the scatter plots in Figure 4.8 we see there is a strong correlation in the wet deposition values found by GC. GC even slightly underestimates the dry deposition globally, having a slightly negative bias. However looking at the dry deposition plot, again it is obvious that while there is some measure of correlation, the deposition values are greatly overestimated by GC.

Dentener et al. [10] used a multimodel evaluation of 26 atmospheric chemistry models to evaluate future trends in nitrogen deposition. They compared the mean model value against the larger networks in the Vet et al. data, finding a FAC2 of around $70 - 80\%$. The GC model results agree with this evaluation of wet deposition with a FAC2 of 88.8%.



(a) wet deposition (b) dry deposition (c) total deposition

Figure 4.8: Scatter plots for GC simulated values vs Vet measurement data.

When looking at the acceptability criteria for GC model results, we see that they are all being met for the wet deposition, and none of them are being met for the dry deposition. Similar to the Ackerman comparison, GC results model much higher values of dry deposition, however here they are even more extreme (dry deposition bias of 207.6% vs 53.4%). When the measurements are combined to a total measurement, we can see that criteria for both NMSE and FAC2 are being met, but the FB is not. According to the acceptability criteria as set by Vivanco et al [49], strictly speaking the GC model is performing acceptably in determining total nitrogen deposition. However we note the already wide margins of these criteria and how close the parameters are to the limits of these criteria. Nonetheless it is clear that the largest discrepancy is in the dry deposition, and that GC performs more than adequately for wet deposition.

In order to determine whether this discrepancy was only the case for this study's GC model results, the same comparison was made for the Ackerman data from 2005. The results for this can be found in the right side of Table 4.5. The discussion of these results largely match the GC model results, however due to the lower deposition in general it seems that the wet deposition is underestimated, and the bias and error in the dry deposition is slightly lower than the GC model results. In fact, for the wet deposition the acceptability criteria are only just met, indicating that our own GC model run is doing a better job of modelling global wet deposition. Ackerman's results do a slightly better job at modelling dry deposition, however their model is also far from meeting the acceptability criteria set.

4.5. Discussion of GEOS-Chem model evaluation

The model evaluation has proven the validity of the wet nitrogen deposition results produced by GC. However, it has also indicated the discrepancies between the modelled dry deposition and the measurements in North America. These findings will be discussed, as well as how the bias found will be dealt with in the results presented in the next chapter. Comparing results from Ackerman's study who also use GC, it is shown that the found bias is also prevalent in their study, even though the total deposition values are lower than those found in this study. This indicates that this may be an issue that is inherent to the GEOS-Chem model.

Table 4.5: Comparison statistics for GC results versus Vet measurement data and Ackerman data versus Vet measurement data (2005).

Statistic	GC Wet	GC Dry	GC Tot	Ack Wet	Ack Dry	Ack Tot
r	0.64	0.53	0.75	0.63	0.65	0.77
slope	0.72	2.76	1.57	0.64	2.58	1.33
NMB	-17.47%	207.60%	65.28%	-26.45%	180.42%	38.86%
|FB|(≤ 0.3)	0.19	1.02	0.49	0.3	0.95	0.33
NMSE(≤ 1.5)	0.32	1.81	0.36	0.42	1.61	0.2
FAC2($\geq 50\%$)	88.77%	12.68%	70.15%	87.69%	16.90%	86.60%

There may be several reasons why there is a large discrepancy in the dry deposition. The first is that it is hard to model dry deposition, especially on the global scale that is being used in GC. GC uses a big leaf resistance-in-series model (see dry deposition in Section 2.2), where dry deposition flux of species disappearing from the lowest model layer is a function of multiple resistances. These are for the majority dependent on meteorological conditions and local surface cover. Furthermore, nitrogen exchange with the surface of both NO_x and NH_x particles is two-directional, meaning that trace amounts of these substances are being emitted by the soil. GC treats these phenomena as completely decoupled, where the additional nitrogen containing species being emitted are treated as emissions and are not taken into account when determining the dry deposition within a timestep. So therefore by only looking at the dry deposition diagnostic in GC the dry deposition might be overestimated.

There are several other studies which have used GC to look at nitrogen containing species, looking not only at the deposition but also species concentrations within the lower levels of the atmosphere. There is a general agreement that there is an overestimation of especially nitrate (NO_3) concentrations [55] and nitric acid (HNO_3) deposition in GC.

Heald et al. [22] conduct an extensive discussion of the nitrate bias in GC, a brief summary of which is given here. They show that neither the effects of excessive HNO_3 formation through N_2O_5 hydrolysis, nor an excessively oxidizing environment, nor the insufficient uptake of HNO_3 on coarse dust and salt is strong enough the be the sole cause of the bias encountered. Suggestions that excessive nitrate levels in GEOS-Chem are associated with biases in the emission inventories used are similarly debunked. In conclusion, no single process or uncertainty is singularly responsible for the bias found in GC. Heald et Al. [22] show that artificially reducing the modelled concentrations of HNO_3 to 75% before the thermodynamic gas-particle partitioning step in GC seems to improve model performance greatly when compared to measurement sites in the US. However this correction would influence both dry and wet deposition values for nitrate.

Pye et al. [38] attribute an underestimate of nitrate aerosol in GC to an overestimation of dry deposition velocities over the western united states (up to 88%) , especially of HNO_3. This indicates a strong positive bias within GC dry deposition. However, a sensitivity analysis wherein the dry deposition of HNO_3 was capped did not significantly improve their model results.

The second reason that there might be a large discrepancy in the dry deposition is that it is very difficult to measure dry deposition accurately [52]. As explained in Section 2.2, dry deposition is not measured directly, but inferred from a deposition resistance model using differences between species concentrations in the air close to ground level. While these resistance modelling schemes of dry deposition perform adequately during daytime over flat terrain, more complex conditions can cause large differences between measured and modelled values.

The only measurement campaigns available to validate dry deposition measurements was situated in North America. However when looking at the spatial distribution of the total deposition in Figure 4.2, the largest difference between the two data sets is obviously located in Asia. Combined with the knowledge that the largest difference between the two sets of results is in the dry deposition, it is clear that measurement data from North America is not enough to validate either set of model results.

Even when having perfect measuring equipment, the fact remains that local measurements are considered representative and are being compared modelled average values of grid cells covering over $2500km^2$. Dry deposition fluxes may change greatly even locally, and it is considered ”extremely difficult to establish a representative flux value for more extended regions from measurements at a single site” [42]. Whilst care is being taken in positioning these sites such that they are representative of a larger area, this ”larger area” refers to an area less than 100km in diameter. With GC results having a grid resolution of $2°$ x $2.5°$, each grid cell has an area of over $2500\ km^2$. It is obvious that this difference in grid sizes is hard to overcome, and hard for the global model to say anything at a local scale. Therefore the global model can only be used to identify macro trends in nitrogen deposition, as much more local models are going to be needed and validated to draw local conclusions.

In conclusion to this evaluation, dry deposition is both hard to measure as well as hard to model, meaning that the validation of GC performance with regards to dry deposition is very difficult. However the results found are in line with other studies performed using GC. The bias found may originate both in the observed model values (due to the manner of modelling as well as atmospheric phenomena not accounted for in the model) as well as in the measured values. Due to this, much of the research dedicated to identifying global trends in nitrogen deposition choose to forgo the analysis of their modelled dry deposition values altogether.

The final issue that remains is how to deal with the bias in model results. Because it is uncertain which is closer to the truth and there is uncertainty in both the model and the measurement, it is also unclear what measure might be undertaken to remove the bias from these results. Following the methodology as described in Chapter 3, the final results for aviation attributable nitrogen deposition are based upon the linear difference between the four scenario runs. All comparisons that will be made with these results will be to total nitrogen results from own simulation data. Therefore the bias found in this simulation data will be present in all results, and trying to remove bias from the data would only change the magnitude of the total deposition values, but would have no effect on the relative comparisons that are made in terms of percentage contributions. Therefore the choice was made to keep full model results in their original form and use these to generate the results for the next chapter, whilst acknowledging that there is a strong bias in the dry deposition produced by GC.

5

Results

Where the results in the previous chapter were analysing total nitrogen deposition produced by GC, the following chapter will only be looking at nitrogen deposition that is caused by aviation emissions. Results will be separated between full-flight emissions results, and those found for landing and take-off (LTO) emissions, and non-LTO emissions. During this chapter, the distinction therein will be made between aviation attributable nitrogen deposition, LTO attributable nitrogen deposition and non-LTO attributable nitrogen deposition. The $2^\circ \times 2.5^\circ$ resolution grid results from GC were used to generate these results.

First, Section 5.1 will describe the results found for aviation attributable nitrogen deposition from full-flight emissions. Then, Section 5.2 will divide these results further into LTO attributable and non-LTO attributable nitrogen deposition, and look at the differences between the two. Finally Section 5.3 will describe where this aviation attributable nitrogen deposition is being deposited.

5.1. Aviation attributable nitrogen deposition

The results for aviation attributable nitrogen deposition were determined by looking at the difference between scenarios 1 and 2, where the only difference between the two GC runs was in the input of the full-flight aviation emissions for 2005. Table 5.1 shows the speciated results found for aviation attributable nitrogen deposition, as well as the relative contribution of each species to the change in deposition, and the percentage change to total nitrogen deposition. As can be seen aviation emissions caused an additional $0.80 Tg\ N\ yr^{-1}$ of nitrogen deposition. This amounts to 0.71% of the total amount of deposition. Of this amount of deposition, the vast majority deposited as wet deposition, consisting of 71.56% of the deposition, where dry deposition was only 28.44%. This deviates from the about 50/50 split found for total deposition (see Section 4.2), indicating that aviation contributes more to wet deposition than to dry deposition.

Table 5.1: Aviation attributable nitrogen deposition in (1) Tg N yr-1, (2) % contribution to deposition change and (3) % change to baseline nitrogen deposition.

Species	**Dry**	**Wet**	**Total**	**Dry**	**Wet**	**Total**	**Dry**	**Wet**	**Total**
NH_3	-0.04	-0.03	-0.07	-4.58%	-4.39%	-8.97%	-0.18%	-0.27%	-0.22%
NH_4	0.01	0.06	0.07	1.83%	7.09%	8.92%	0.39%	0.25%	0.27%
NO_3	0.01	0.04	0.05	1.77%	4.75%	6.51%	1.11%	0.71%	0.78%
HNO_3	0.23	0.51	0.74	29.23%	64.11%	93.34%	0.98%	2.47%	1.68%
NO_2	0.00	(-)	0.00	-0.62%	(-)	-0.62%	-0.24%	(-)	-0.24%
N_2O_5	0.01	(-)	0.01	0.81%	(-)	0.81%	2.40%	(-)	2.40%
Total	0.23	0.57	0.80	28.44%	71.56%	100.00%	0.45%	0.92%	0.71%

That the greater percentage of aviation attributable nitrogen deposition is wet deposition is likely to be cause by the greater emission altitude of aviation emissions. NO_x species have a longer lifetime in the upper atmosphere, in the order of 1-2 weeks at altitude, instead of in the order of 1-2 days closer to the surface [42]. So these species have a much larger path to the ground, meaning it will take much longer for them to deposit, and greatly increasing the chance that they are caught up in precipitation. Furthermore increased lifetime in the atmosphere increases the likelihood that NO_x reacts with other species, and deposits as a product of these reactions.

Taking a close look at the speciated results, we can see that the main deposition pathway for aviation attributable nitrogen deposition is through the wet deposition of HNO_3, which logically follows as this is the main deposition pathway of any NO_x species in the atmosphere (see Section 2.2). Also interesting to note is that none of the NO_x emitted actually makes it to the ground as such, and all of it reacts within the atmosphere. There is even a slight decrease in NO_2 deposition. Next the the nitric acid however, directly related species of nitrate and N_2O_5 form the rest of the increase in nitrogen deposition.

Furthermore it can be seen that aviation attributable nitrogen deposition has almost equal but opposite effects on the deposition of ammonia and ammonium. The balance between these two substances in the atmosphere is regulated according to the balance of Reaction 5.1, which can go both ways. It is most likely that due to increased presence of NO_x in the atmosphere the oxidization of NO_x to form HNO_3 is also increased. This either takes preference over the ammonia / ammonium balance, or this happens at altitude before OH^- radicals have a chance to react with the ammonium at lower altitudes. Therefore this balance shifts in the favour of increased levels of ammonium that we see in the results.

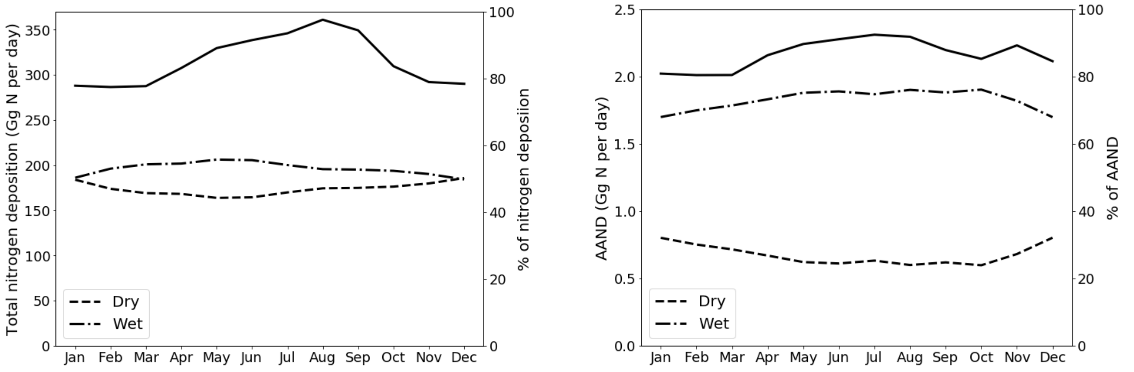
$$NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^- \tag{5.1}$$

Figure 5.1 shows the average daily nitrogen deposition per month for both total nitrogen deposition from all sources, as well aviation attributable nitrogen deposition. As can be seen in Figure 5.1a, the general seasonal trend for nitrogen deposition is that there is an increase in deposition throughout the northern hemisphere summer months, with a peak in August. This matches the seasonal trends for nitrogen deposition found in literature as described in Section 2.2. The aviation attributable nitrogen deposition in Figure 5.1b appears to match this seasonal trend, also peaking in the summer months, although the trend is not quite as pronounced. This trend is likely to be correlated to the increase in flight traffic and therefore emissions during the norther hemisphere summer months, coinciding with the general holiday period from July to September.

Looking at the division of the average deposition between wet and dry deposition, we can see that for total nitrogen deposition both values hover around 50%, with slightly more wet deposition than dry deposition, increasing in difference throughout the northern hemisphere summer. The average yearly dry deposition amounts to 46.9% of all deposition, with the other 53.1% being wet deposition. For aviation attributable nitrogen deposition, these figures show a much greater degree of wet deposition than dry deposition, as previously described. However in general still showing the same seasonality trend as for total nitrogen deposition. The averages hover around their yearly averages of 28.4% for dry and 71.6% for wet deposition respectively.

Knowing that there is a great bias in the dry deposition in GC, the relative contribution of wet deposition to aviation attributable nitrogen deposition might even be understated by these results. However knowing that the majority of aviation attributable nitrogen deposition is made up of wet deposition improves the confidence in these results, considering there is a greater confidence in the GC wet deposition values than in the dry deposition values.

Figure 5.2 shows the spatial distribution of aviation attributable nitrogen deposition. It can be seen that aviation attributable nitrogen deposition is greatest around the worlds largest aviation hubs, focusing on Europe, South-East Asia and the Eastern United States. Comparing the spatial distribution to the global fuel burn distribution presented in Section 2.3, it is clear that like the fuelburn, most aviation attributable nitrogen deposition takes place in the northern hemisphere. However the spatial distribution also clearly shows that there is global dispersion of aviation attributable nitrogen deposition. This dispersion was likely expected, with the majority of emissions taking place in the upper troposphere and being subject to an array of global circulation patterns and weather effects before they find their



(a) Total nitrogen deposition

(b) Aviation attributable nitrogen deposition

Figure 5.1: Average daily nitrogen deposition values per month (solid line) for total nitrogen deposition and aviation attributable nitrogen deposition, as well as the relative contributions of wet and dry deposition (dashed lines).

way down to the ground.

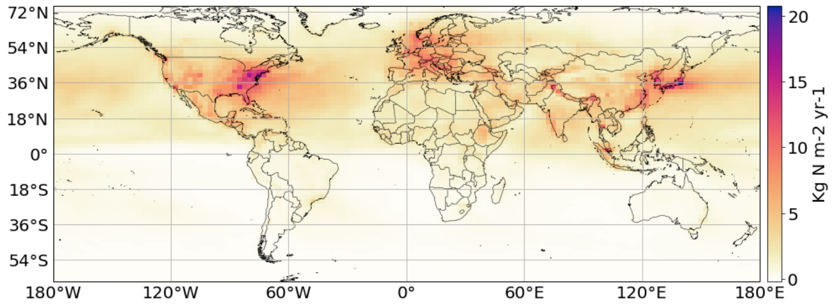


Figure 5.2: Spatial distribution of aviation attributable nitrogen deposition.

Also of interest is in which area's of the globe aviation attributable nitrogen deposition has the most effect on total nitrogen deposition. As shown before the global average increase in nitrogen deposition due to aviation attributable nitrogen deposition is 0.71%. Figure 5.3 shows the relative contribution of aviation attributable nitrogen deposition to total nitrogen deposition per grid cell. It clearly shows that in more industrialized and urban areas, aviation emissions only contribute for a very small part to the nitrogen deposition taking place in these areas. This is not the case for the more remote regions of the globe, such as the Pacific and Atlantic ocean, as well as the North Pole and the Sahara desert. In these areas, aviation emissions are a much larger source of nitrogen deposition, locally up to 5.4%. This could partially be attributable to the fact that aviation emissions in these areas are one of very few anthropogenic emission sources and thus have a much greater impact. It could also be partially attributable to the increased amount of dispersion of emissions due to the high emissions altitude.

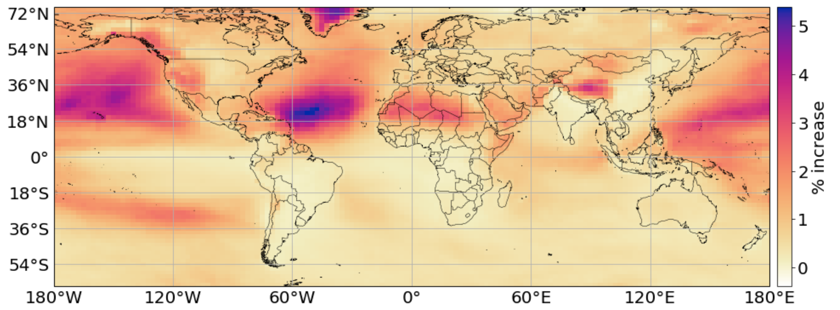


Figure 5.3: Relative contribution of aviation attributable nitrogen deposition to total nitrogen deposition.

5.2. LTO and non-LTO attributable nitrogen deposition

The following section will look at and compare the results from scenarios 3 and 4 to the baseline scenario containing no aviation emissions, thereby comparing the nitrogen deposition changes caused by only LTO emissions, or only non-LTO emissions.

Table 5.2: Fuelburn % (from AEIC [44]) versus contribution to aviation attributable nitrogen deposition for LTO and non-LTO emissions.

	% Fuelburn	% of AAND
LTO	8.90%	7.70%
non-LTO	91.10%	92.30%

Before looking at speciated results and the breakdown, Table 5.2 shows the division of both fuelburn and aviation attributable nitrogen deposition between LTO emissions and non-LTO emissions. Where LTO fuelburn comprises almost 9% of global fuelburn for 2005, the percentage of LTO attributable deposition is slightly lower at 7.7%. This suggests that fuelburn average is slightly higher during landing and take off. This seems logical as thrust settings are highest during take-off, an incidentally also cause the most production of NO_x. Apparently these increased thrust settings overcompensate for reduced thrust settings during approach and landing.

Due to the fact that 92.3% of aviation attributable nitrogen deposition is attributable to non-LTO emissions, it follows logically that all results found for non-LTO attributable nitrogen deposition are similar to those for total aviation attributable nitrogen deposition. For the sake of brevity these will therefore not be discussed in great detail, except where there are striking differences. The main focus of this section will therefore be on the differences found in the results for LTO attributable nitrogen deposition.

Table 5.3 and Table 5.4 show the speciated results found, the relative contribution of each species to the change in deposition, and the percentage change to total nitrogen deposition for LTO attributable nitrogen deposition and non-LTO attributable nitrogen deposition respectively. Focusing on non-LTO attributable nitrogen deposition first, it can be seen that non-LTO emissions are responsible for causing $0.734Tg\ N\ yr^{-1}$, or an increase of 0.65% of total nitrogen deposition. The main deposition pathways and likely mechanisms at play in the atmosphere are similar to those described for aviation attributable nitrogen deposition, and will not be repeated here.

Table 5.3: LTO attributable nitrogen deposition in (1) Tg N yr-1, (2) % contribution to deposition change and (3) % change to baseline nitrogen deposition.

Species	Dry	Wet	Total	Dry	Wet	Total	Dry	Wet	Total
NH_3	-0.003	-0.003	-0.006	-4.70%	-4.42%	-9.12%	-0.01%	-0.02%	-0.02%
NH_4	0.001	0.004	0.006	1.86%	7.25%	9.11%	0.03%	0.02%	0.02%
NO_3	0.001	0.004	0.005	1.64%	6.27%	7.91%	0.08%	0.07%	0.07%
HNO_3	0.029	0.025	0.054	47.46%	40.22%	87.68%	0.12%	0.12%	0.12%
NO_2	0.002	(-)	0.002	3.64%	(-)	3.64%	0.11%	(-)	0.11%
N_2O_5	0.000	(-)	0.000	0.77%	(-)	0.77%	0.18%	(-)	0.18%
Total	0.031	0.030	0.062	50.68%	49.32%	100.00%	0.06%	0.05%	0.05%

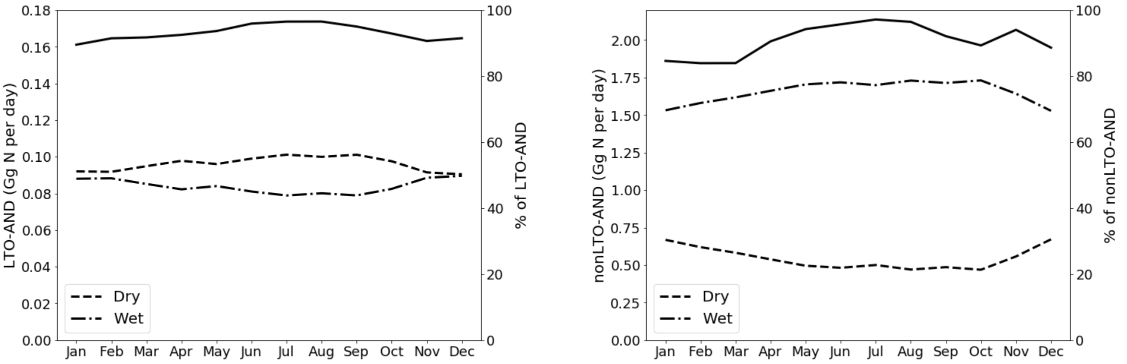
The LTO attributable nitrogen deposition results presented in Table 5.3 show that LTO emissions are responsible for causing $0.062Tg\ N\ yr^{-1}$ of nitrogen deposition, or an increase of 0.05%. Looking at the species distribution, we can see that results differ significantly from the aviation attributable nitrogen deposition results. While the same mechanism seems to be at play in changing the balance between ammonium and ammonia, it seems to be slightly stronger for LTO, likely due to the larger presence of these species at lower altitudes. Furthermore the most noticeable change is the relative importance of dry deposition, which more than 50% of LTO attributable nitrogen deposition. HNO_3 remains the main deposition pathway for nitrogen from LTO emissions, however in the surrounding species we see that

Table 5.4: non-LTO attributable nitrogen deposition in (1) Tg N yr-1, (2) % contribution to deposition change and (3) % change to baseline nitrogen deposition.

Species	**Dry**	**Wet**	**Total**	**Dry**	**Wet**	**Total**	**Dry**	**Wet**	**Total**
NH_3	-0.034	-0.032	-0.066	-4.57%	-4.38%	-8.95%	-0.17%	-0.25%	-0.20%
NH_4	0.013	0.052	0.065	1.83%	7.07%	8.91%	0.36%	0.23%	0.25%
NO_3	0.013	0.034	0.047	1.78%	4.62%	6.40%	1.03%	0.63%	0.71%
HNO_3	0.203	0.485	0.689	27.69%	66.12%	93.82%	0.86%	2.35%	1.56%
NO_2	-0.007	(-)	-0.007	-0.98%	(-)	-0.98%	-0.34%	(-)	-0.34%
N_2O_5	0.006	(-)	0.006	0.81%	(-)	0.81%	2.22%	(-)	2.22%
Total	0.195	0.539	0.734	26.57%	73.43%	100.00%	0.38%	0.88%	0.65%

the relative contributions of NO_3 and NO_2 play a larger part in the deposition. NO_3 deposition increased by a couple of percentage points, from 6.5% to 7.9%. NO_2 contribution, which was negative for aviation attributable nitrogen deposition is actually positive for LTO attributable nitrogen deposition, showing that some NO_x does make it to the surface without reacting.

Figure 5.4 shows the average daily deposition for both LTO attributable nitrogen deposition and non-LTO attributable nitrogen deposition. The LTO-attributable nitrogen deposition daily deposition follows the same seasonality pattern as the total deposition. However the division between dry and wet deposition seems reversed, with dry deposition increasing in the northern hemisphere summer, and the wet deposition decreasing there. This matches their averages though. where dry deposition makes up 50.7% of the yearly deposition, and wet deposition 49.3%. It also seems to be missing the slight elevation of daily average in November that aviation attributable nitrogen deposition did have. The results for non-LTO attributable nitrogen deposition show similar patterns to aviation attributable nitrogen deposition, both in terms of daily deposition average per month, as well as the division between wet and dry deposition.



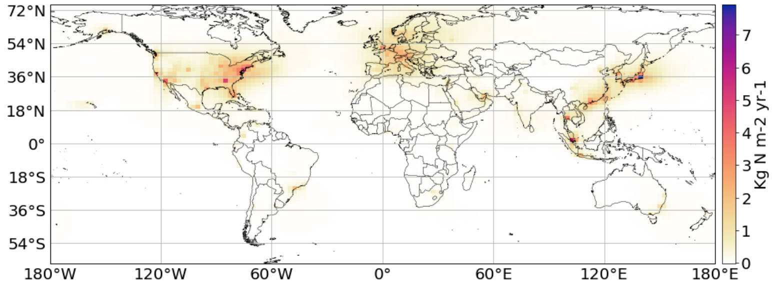
(a) LTO attributable nitrogen deposition

(b) non-LTO attributable nitrogen deposition

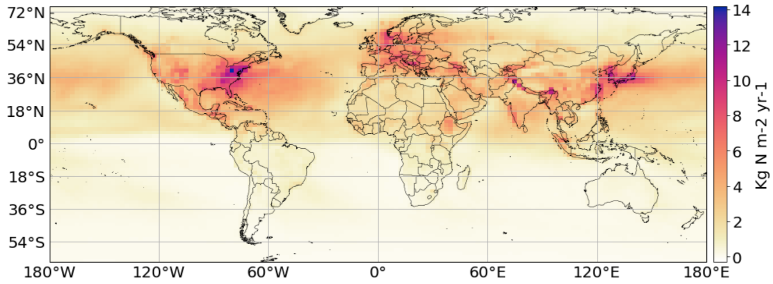
Figure 5.4: Average daily nitrogen deposition values per month for LTO attributable nitrogen deposition and non-LTO attributable nitrogen deposition (solid line), as well as the relative contributions of wet and dry deposition (dashed lines).

The spatial distribution patterns for LTO attributable nitrogen deposition and non-LTO attributable nitrogen deposition are shown in Figure 5.5. Even though LTO emissions are extremely localised around airports and major hubs, Figure 5.5a shows that nitrogen containing species from LTO emissions disperse for hundreds of kilometers before depositing. However it also shows that this deposition does take place regionally, and does not disperse globally. Again the non-LTO attributable nitrogen deposition results show no significant difference from aviation attributable nitrogen deposition results.

As presented, LTO emissions on average account for only about 7% of aviation attributable nitrogen deposition. However, we are more interested in local contributions of LTO emissions to aviation attributable nitrogen deposition. Therefore, Figure 5.6 shows relative importance of LTO attributable deposition (showing only areas more than the average of 7%). The poles have been omitted from



(a) LTO attributable nitrogen deposition



(b) non-LTO attributable nitrogen deposition

Figure 5.5: Spatial distributions of LTO versus non-LTO attributable nitrogen deposition.

this images for clarity, because the tiny amounts of nitrogen deposition taking place there cause some anomalies in presenting the results in this manner. The significance of this figure is twofold; first of all it clearly shows that LTO emissions locally contribute to up to 28% of aviation attributable nitrogen deposition, especially in the more inhabited parts of the globe. Secondly, similar to the spatial distribution it shows that while LTO emissions do mostly deposit locally, there is still regional transport and distribution, however not on an intercontinental scale. For instance LTO emissions cause LTO attributable nitrogen deposition which account for between 15-20% of the coastal waters.

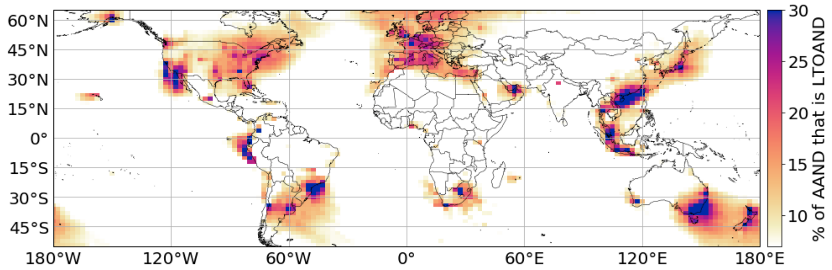


Figure 5.6: Spatial distribution of where the relative contribution of LTO-attributable nitrogen deposition to aviation attributable nitrogen deposition is higher than its 7% average.

5.3. Aviation attributable nitrogen deposition distribution per land cover type

Using the methodology as described in Section 3.5, nitrogen deposition results were compared to the land cover database from Copernicus Global Land Service [7]. While the land cover data does not have global coverage, it can be determined that of the total nitrogen deposition, only 0.3% deposits outside the latitudes covered by the dataset. For aviation attributable nitrogen deposition, only 0.2% of the deposition deposits outside this range. Therefore for the following section it can be assumed that the results found are representative for both total nitrogen deposition as well as aviation attributable nitrogen deposition.

Table 5.5 shows the difference in deposition over land vs that over water. Whereas land takes up just under 29% of the landcover in the data set, 58.81% of total nitrogen deposition deposits on land. This values matches closely with the 55.6% deposition over land found by Vet et al. [47]. This makes sense as most anthropogenic emissions sources such as agriculture and industrial emissions are land based (over 70%). Even the most prevalent natural source of NO_x in the atmosphere, lightning, occurs mostly above land [43].

Table 5.5: Land cover percentage and nitrogen deposition percentage for land and water.

	% Landcover	% Total N. Dep	% AAND	% LTOAND	% nonLTOAND
Water	70.89	41.19	57.27	47.69	58.08
Land	28.68	58.81	42.72	52.30	41.91

Compared to the total nitrogen deposition, aviation attributable nitrogen deposition shows a much stronger tendency to deposit above water than above land, with 57.27% of the deposition taking place above the water. Non-LTO attributable nitrogen deposition shows a similar and slightly stronger tendency. However the LTO attributable nitrogen deposition behaves a little more like the total deposition, and deposits more above land than above water. The tendency of aviation attributable nitrogen deposition to deposit more above water is logical, as aviation emissions take place above water and oceans much more frequently than any other anthropogenic or natural emission sources, except of course ships. However LTO emissions happening in the vicinity of airports also deposit more locally than non-LTO emissions, and therefore their increased deposition above land is also to be expected.

In the interest of protecting natural areas from nitrogen deposition, we are especially interested in where aviation attributable nitrogen deposition reaches the ground. Considering the coarse resolution of the GEOS-Chem model, the best way to achieve this was to compare the aviation attributable nitrogen deposition results to a global land cover database, to see if there are any large discrepancies between deposition resulting from aviation emissions versus other anthropogenic emission sources. Table 5.6 shows the result of this analysis. The first column shows the percentage of land area covered by this type of land cover as determined by the Copernicus land cover database [7]. So water area is omitted in this entire table. The same holds for the deposition columns. The other columns show the relative percentages of total deposition, aviation attributable nitrogen deposition, LTO attributable nitrogen deposition and non-LTO attributable nitrogen deposition depositing in each of the different land cover types. They add up to 100% of that type of deposition depositing on land.

Compared to total nitrogen deposition, aviation attributable nitrogen deposition shows an increased tendency to deposit over vegetation, however this is almost completely attributable to the increased deposition over deserts and areas of sparse vegetation. This agrees with earlier findings earlier in these results showing that aviation attributable nitrogen deposition has a greater contribution to deposition over remote areas. This is relevant however, because these sparse deserts are some of the most nitrogen starved areas of the planet, and therefore their estimated critical loads are also almost factor 5 lower in these areas [37][5].

Removing deserts from the summation, it can be seen that for all the rest of vegetation land cover types, there is no strong difference between aviation attributable nitrogen deposition and total nitrogen deposition in the total, however that there is slightly less deposition over forests, and slightly higher deposition over other types of vegetation. For non-natural land cover types, aviation attributable nitrogen

Table 5.6: Land cover percentage and nitrogen deposition percentage per land cover type.

Name	**% land cover**	**% total N. dep.**	**% AAND**	**% LTO-AND**	**% nonLTO-AND**
Closed forest, evergreen, needle leaf	6.41	5.19	7.72	10.36	7.44
Closed forest, deciduous, needle leaf	8.25	15.21	8.64	7.96	8.71
Closed forest, evergreen, broad leaf	3.16	0.79	1.05	0.37	1.12
Closed forest, deciduous, broad leaf	4.41	7.37	7.17	9.88	6.89
Closed forest, mixed	1.60	1.52	2.24	3.27	2.14
Closed forest, unknown	4.05	3.34	3.33	4.48	3.21
Open forest, evergreen, needle leaf	0.50	0.33	0.62	0.75	0.61
Open forest, deciduous, needle leaf	0.38	1.31	0.70	0.90	0.68
Open forest, evergreen, broad leaf	0.03	0.01	0.01	0.00	0.01
Open forest, deciduous, broad leaf	1.51	1.59	0.98	0.59	1.02
Open forest, mixed	0.13	0.20	0.26	0.45	0.24
Open forest, unknown	6.74	8.81	8.08	9.95	7.88
Subtotal forest	37.18	45.68	40.80	48.97	39.94
Shrubs	7.55	5.45	6.46	5.45	6.56
Herbaceous vegetation	23.23	14.75	17.25	12.94	17.70
Herbaceous wetland	2.35	1.41	1.31	1.31	1.31
Moss and lichen	2.17	0.13	0.31	0.18	0.32
Bare / sparse vegetation (Desert)	13.08	5.67	14.43	7.79	15.10
Subtotal other vegetation	48.37	27.41	39.75	27.67	40.99
Total vegetation	85.56	73.09	80.56	76.64	80.93
Total vegetation (excluding desert)	72.48	67.42	66.13	68.85	65.83
Cultivated and managed vegetation / agriculture	10.30	24.26	16.80	19.45	16.50
Urban / Built-up	0.82	2.38	1.97	3.56	1.80
Permanent snow and ice	3.33	0.27	0.68	0.36	0.71
Total non-vegetation	14.44	26.91	19.44	23.36	19.01

deposition shows a lower tendency to deposit here than other emission sources. Owing to the often remote location of emissions this makes sense.

Comparing the LTO attributable nitrogen deposition results to total nitrogen, we can clearly see that LTO emissions have a slightly higher tendency to deposit over forested regions, and slightly lower over other types of vegetation. Above deserts, it has an only slightly higher deposition percentage that other emission sources, clearly showing the tendency to deposit more locally rather than dispersing over very great distances. Instead, LTO attributable nitrogen deposition deposits more often on land used for agricultural purposes as well as urban environments.

Similar to all previous results the non-LTO attributable nitrogen deposition results look very much like the aviation attributable nitrogen deposition results and for the sake of brevity will not be individually discussed.

It has been shown that in a similar vein to eutrophication and nitrification of the soil, excessive nitrogen deposition can have similar detrimental effects to marine ecosystems. Especially considering the fact that 57.27% of aviation attributable nitrogen deposition deposits on water it would have been interesting to do an analysis in a similar vein as land deposition. However different types of marine ecosystems are not extensively identified by the Copernicus land cover database, instead classified generally under the name of either permanent water body or open sea. Instead all that can be stated is that aviation emissions is likely to have a bigger influence on marine ecosystems than other emissions types, relative to their emission magnitude.

6

Conclusions & Recommendations

6.1. Conclusions

Excessive nitrogen deposition from anthropogenic emissions has a global impact on natural biodiversity. While aviation emissions have been studied in the context of climate change and air quality, this is not true for nitrogen deposition. Meanwhile the growth of the aviation industry is likely to increase the relative contribution of aviation emission to nitrogen deposition in the years to come. Current regulatory policies aiming to mitigate nitrogen deposition are limited to local and regional scale, and are inadequately applicable to the global nature of the aviation industry.

In a bid to better understand the full extent of the environmental impact of aviation emissions, and to get a clearer picture of the different effects of LTO and non-TLO emissions, this study investigated the global effects of aviation emissions on nitrogen deposition. This was done by evaluating total nitrogen deposition results from the GEOS-Chem atmospheric transport model for the year 2005. The model results are derived from the comparison of four different simulation scenarios, each of which is subject to a different perturbation of aviation emissions input.

Overall it can be concluded that the GEOS-Chem model showed adequate performance for wet nitrogen deposition; there is was strong correlation to both other models ($r = 0.93$,Bias$= 2\%$) and measured values ($r = 0.64$,Bias$= -17.5\%$), both in spatial and seasonal patterns. The dry deposition showed a large deviation from both model ($r = 0.92$,Bias$= 52\%$) and measurement ($r = 0.35$,Bias$= 208\%$) values which, though while consistent with literature, shows there are challenges in modelling method as well as measurement accuracy, making a robust evaluation difficult.

Aviation emissions were calculated to be responsible for 0.8 Tg N or $+0.71\%$ of total nitrogen deposition per year globally, of which 71.6% through wet deposition, and 28.4% through dry deposition. The main deposition pathway is through the formation of HNO_3 from NO_x. Aviation attributable nitrogen deposition is highest in the Eastern United States, East Asia and Central Europe. However, spatial nitrogen deposition patterns show increased nitrogen deposition across the entire northern hemisphere.

LTO and non-LTO specific emissions are responsible for 0.06 Tg N $(+0.05\%)$ and 0.73 Tg N $(+0.65\%)$ of total nitrogen deposition respectively. LTO specific results show a much greater degree of dry deposition, as well as a tendency to deposit much more locally than non-LTO emissions. While regionally contributing up to 30%, on average only 7.7% of aviation attributable nitrogen deposition is attributable to LTO emissions globally.

Evaluating the land cover type that aviation deposits on further reinforces the notion that non-LTO emission caused widely dispersed deposition, showing a strong tendency to deposit both over open seas, as well as a tendency to deposit over remote desert areas when compared to other emissions. LTO-emissions do not share this tendency, and are only distinguishable from other emission sources by a greater deposition over urban areas. Excluding deserts, non-LTO emissions show a very slight tendency to deposit less over natural vegetation than other emissions sources do.

The results presented provide a basic understanding of the impact of aviation emissions on global nitrogen deposition, as was the aim of this study. The global spread and large impact of non-LTO emissions especially illustrate the challenges in attempting to regulate aviation attributable nitrogen deposition impact on a local scale, and require a coordinated international effort to mitigate the environmental effects. The findings presented in this study can form the scientific basis for global policies supporting a sustainable future for the aviation industry.

6.2. Recommendations

With regards to nitrogen deposition modelling, it is clear there is a need to improve the accuracy of dry deposition modelling. The many factors that influence the dry deposition modelling require a more careful analysis before they can be applied to the global scale used in this report. It is likely beneficial to attempt this on a more local scale first. Furthermore, a greater coverage of regionally representative dry deposition measuring sites is needed in order to adequately validate dry deposition values and patterns on any scale.

With regards to aviation attributable nitrogen deposition, it would be interesting to repeat a similar analysis with emissions data for a more recent year. Both the growth of the aviation industry as well as policies and technological advancements limiting the emissions from other sectors are likely to have increased the relative contribution of the aviation sector. It would also be interesting to apply partial perturbation scenarios to a global nitrogen deposition measurements, where one area is perturbed at a time, in order to be able to quantify the intercontinental transport of aviation emissions.

However, even doubling the impact of aviation emissions means aviation still causes just 1.5% of total nitrogen deposition. Care has to be taken that mitigation measures in relative weight to its total contribution mean that very stringent and short terms measures on aviation emissions would have a limited effect, while having large consequences for the aviation sector.

Given the results we now know that by applying local policies to LTO-only operations of the aviation industry we are not accounting for upwards of 70% of resulting deposition. However given the global spread from non-LTO emissions it is not possible to connect nitrogen deposition to a single local source.

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A

Copernicus Global Land Cover legend

Map Code	UN LCCS level	Land Cover Class	UN-LCCS Description
0	(-)	No input data available	(-)
111	A12A3A10B2D2E1	Closed forest, evergreen, needle leaf	tree canopy >70 %, almost all needle leaf trees remain green all year. Canopy is never without green foliage
113	A12A3A10B2D2E2	Closed forest, deciduous, needle leaf	tree canopy >70 %, consists of seasonal needle leaf tree communities with an annual cycle of leaf-on and leaf-off periods
112	A12A3A10B2D1E1	Closed forest, evergreen, broad leaf	tree canopy >70 %, almost all broadleaf trees remain green year round. Canopy is never without green foliage.
114	A12A3A10B2D1E2	Closed forest, deciduous, broad leaf	tree canopy >70 %, consists of seasonal broadleaf tree communities with an annual cycle of leaf-on and leaf-off periods.
115	A12A3A10	Closed forest, mixed	Closed forest, mix of types
116	A12A3A10	Closed forest, unknown	Closed forest, not matching any of the other definitions
121	A12A3A11B2D2E1	Open forest, evergreen, needle leaf	top layer- trees 15-70 % and second layermixed of shrubs and grassland, almost all needle leaf trees remain green all year. Canopy is never without green foliage
123	A12A3A11B2D2E2	Open forest, deciduous, needle leaf	top layer- trees 15-70 % and second layermixed of shrubs and grassland, consists of seasonal needle leaf tree communities with an annual cycle of leaf-on and leaf-off periods
122	A12A3A11B2D1E1	Open forest, evergreen, broad leaf	top layer- trees 15-70 % and second layermixed of shrubs and grassland, almost all broadleaf trees remain green year round. Canopy is never without green foliage.
124	A12A3A11B2D1E2	Open forest, deciduous, broad leaf	top layer- trees 15-70 % and second layermixed of shrubs and grassland, consists of seasonal broadleaf tree communities with an annual cycle of leaf-on and leaf-off periods.
125	A12A3A12	Open forest, mixed	Open forest, mix of types
126	A12A3A12	Open forest, unknown	Open forest, not matching any of the other definitions
20	A12A4A20B3(B9)	Shrubs	These are woody perennial plants with persistent and woody stems and without any defined main stem being less than 5 m tall. The shrub foliage can be either evergreen or deciduous.
30	A12A2(A6)A20B4	Herbaceous vegetation	Plants without persistent stem or shoots above ground and lacking definite firm structure. Tree and shrub cover is less than 10 %.
90	A24A2A20	Herbaceous wetland	Lands with a permanent mixture of water and herbaceous or woody vegetation. The vegetation can be present in either salt, brackish, or fresh water.
100	A12A7	Moss and lichen	Moss and lichen
60	B16A1(A2)	Bare / sparse vegetation (Desert)	Lands with exposed soil, sand, or rocks and never has more than 10 % vegetated cover during any time of the year
40	A11A3	Cultivated and managed vegetation / agriculture(cropland)	Lands covered with temporary crops followed by harvest and a bare soil period (e.g., single and multiple cropping systems). Note that perennial woody crops will be classified as the appropriate forest or shrub land cover type.
50	B15A1	Urban / Built-up	Land covered by buildings and other manmade structures
70	B28A2(A3)	Permanent snow and ice	Lands under snow or ice cover throughout the year.
80	B28A1B1	Permanent water bodies	Lakes, reservoirs, and rivers. Can be either fresh or salt-water bodies.
100	B28A1B1	Open Sea	Oceans, seas. Can be either fresh or saltwater bodies.