Air pollution impacts and trade-offs of ammonia as a road transportation fuel

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by

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List of Acronyms

Acronym	Full Name
ACS	American Cancer Society
AOC	Ammonia Oxidation Catalyst
CAL	California
CARB	California Air Resources Board
CFR	Cooperative Fuel Research
CRF	Concentration Response Function
CI	Confidence Interval
CIg	Compression Ignited
CONUS	Contiguous United States
CRF	Concentration-Response Function
DME	Dimethyl Ether
DMVO	DME Vehicle Operation
DIVO	Diesel Vehicle Operation
EGR	Exhaust Gas Recirculation
EPA	Environmental Protection Agency
FC	Feull Cell
FHWA	Federal Highway Administration
GAVO	Ammonia-Gasoline Vehicle Operation
GMAO	Global Modelling and Assimilation Office
GHG	Greenhouse gas
GEOS	Goddard Earth Observing System
ICE	Internal Combustion Engine
I/M	Inspection and Maintenance
LBV	Laminar Burning Velocity
LDV	Light Duty Vehicles
LNG	Liquid Natural Gas
LPG	Liquefied Petroleum Gas
MOVES	MOtor Vehicle Emission Simulator
NEI	National Emissions Inventory
NOx	Nitrogen Oxides
PCTM	Post-Combustion Treatment Methods
PC	Passenger Cars
RPD	Rate Per Distance
RPV	Rate Per Vehicle
RF	Radiative Forcing
SCC	Source Classification Code
SCR	Selective Catalytic Reduction
SI	Spark-Ignited
SMOKE	Sparse Matrix Operator Kerner Emissions
SOA	Secondary Organic Aerosol
TWC	Three-Way Catalyst
VMT	Vehicle Miles Travelled
VOC	Volatile Organic Compounds
VPOP	Vehicle Population
VSL	Value of Statistical Life
WRF-Chem	Weather Research and Forecasting and Chemistry

List of Symbols

Symbol	Description
BC	Black Carbon
CH_4	Methane
CO	Carbon Monoxide
CO_2	Carbon Dioxide
HCHO	Formaldehyde
N_2O	Nitrous Oxide
NH_3	Ammonia
NO_x	Nitrogen Oxides
SO_2	Sulfur Dioxide
OC	Organic Carbon
$PM_{2.5}$	Fine Particulate Matter (> 2.5 microns)
TiO_2	Titanium dioxide
V_2O_5	Vanadium oxide
WO_3	Tungsten oxide
VOC	Volatile Organic Compounds

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1
Introduction

This chapter serves as an introduction to the thesis work. It begins by discussing the motivation behind the research and identifying the existing knowledge gap in the literature in section 1. Next, the research objective and main research questions are clearly defined in section 2. Finally, an overview of the report's structure is provided in section 3.

1. Motivation

In an effort to decarbonize the road transportation sector and decrease its climate change impact, there is increased research activity surrounding the applications of alternative renewable fuels. An example of such a fuel is ('greenly' generated) ammonia producing no CO_2 greenhouse gas during combustion.

Ammonia is considered a promising fuel due to its relative ease of storage (resulting in 26 to 30 times lower storage costs than hydrogen (David et al., 2020)) and could be rapidly implemented using the already existing infrastructure (currently in use by the agriculture sector). In addition to the advantages of ammonia, it is important to highlight the toxicity and the high volatility of the molecule which could cause a large health and safety hazard if mishandled (Valera-Medina et al., 2021, 2018).

The application of ammonia as a fuel has been researched in the marine, road transportation and aviation sectors. In fact, the first application of ammonia for road transportation was recorded in 1933, when a pick-up truck was converted to be powered by ammonia. During WWII the fuel was also used in buses due to petrol shortages (Koch, 1945). Later on, research activities began to intensify again in the 1960s (Pearsall and Garabedian, 1967; Gray Jr et al., 1967) and in recent years anew, as researchers strive to innovate towards achieving the net-zero carbon goals by 2050.

Although the implementation of ammonia as a fuel could help in decarbonizing the transportation sector, the products of ammonia combustion (mainly unburned ammonia and nitrogen oxides) contribute to air pollution. The aim of this work is to quantify the emissions and evaluate the impacts of an ammonia-fueled road transportation fleet. This will be achieved by modelling air pollution resulting from emissions of the ammonia-fueled sector.

In preparation for this thesis work, a comprehensive literature review has been carried out. This review focused on key areas relevant to our research and helped to identify gaps in the state-of-the-art literature where further research is needed.

The literature review reveals that a significant number of studies have primarily focused on evaluating the performance characteristics of ammonia-fueled internal combustion engines (ICEs) running on different fuel compositions and operating conditions (Kobayashi et al., 2019; Duynslaegher, 2011; Frigo and Gentili, 2013). These studies also often quantify the emissions produced by such engines. The findings have highlighted a substantial discrepancy in emissions associated with ammonia-fueled engines (Valera-Medina and Banares-Alcantara, 2020).

On the other hand, there are studies focused on evaluating the health and environmental impacts of $PM_{2.5}$ and ozone formation, due to emissions from various sectors including the conventional petroleum-based road transportation sector (Barrett et al., 2015; Dedoussi et al., 2020).

Furthermore, there has been a growing interest in evaluating the potential of using ammonia as a fuel in recent years. Several reviews and life cycle analyses have been conducted to assess the feasibility and potential benefits of ammonia as a transportation fuel. These studies have considered multiple factors such as the synthesis process of ammonia, safety considerations, economic aspects, and comprehensive environmental assessments (Valera-Medina et al., 2021; Boero et al., 2023; Elbaz et al., 2022; Angeles et al., 2017). These evaluations provide valuable insights into the advantages and challenges associated with the utilization of ammonia as a fuel, which can contribute to the overall understanding of its viability as an alternative in the road transportation sector.

No previous studies have however integrated the aspects of air quality modeling, human health impact assessments, and emissions from ammonia-fueled vehicles to evaluate the future potential of ammonia as a fuel in terms of air quality impacts. This research aims to bridge this gap.

By evaluating emissions from ammonia-fueled vehicles and using them for air quality modeling and human health impact assessments, this work intends to provide evidence supporting the viability of ammonia as a clean fuel alternative for the current road transportation sector. Specifically, the focus is on reducing population exposure to particulate matter , which ($PM_{2.5}$) is a significant air pollutant with adverse health effects.

Additionally, this research focuses on evaluating the air quality trade-offs resulting from the application of ammonia as a fuel. These trade-offs are explored using an emission factor tradespace, which allows for the rapid assessment of air quality impacts associated with various emission factors (for specific engine designs for example). As a result, the emission factor tradespace can serve as a valuable tool for providing engine design recommendations and facilitating policy assessments for a potential ammonia-fueled road transportation sector.

2. Research objective and questions

Given the motivations of this thesis work, the research objective and research (sub)questions were formulated for this thesis.

The main research objective of this thesis is:

> “To investigate the impacts of an ammonia-fueled road transportation fleet by evaluating the emissions from state-of the-art ICEs in an atmospheric chemistry transport model to quantify the resulting air pollution, in terms of population exposure to $PM_{2.5}$.”

The main research question of this thesis is:

> “What would be the resulting $PM_{2.5}$ population exposure impact from the introduction of an ammonia-fueled road transportation fleet of passenger cars?”

The main research question has been divided into the following sub-questions:

SQ 1: What are the developments and the measured emissions for state-of-the-science ICEs running on varying ammonia fuel compositions?

SQ 2: How do emissions from ammonia-fueled ICEs (of varying fuel compositions) translate into air pollution and more specifically $PM_{2.5}$ particulate formation?

SQ 3: What is the population exposure impact of introducing an ammonia-fueled road transportation fleet and what are the underlying trade-offs?

SQ 4: What are the limitations and uncertainties associated with modelling ammonia-fueled fleet emissions to estimate their impact on $PM_{2.5}$ population exposure in the USA?

3. Outline

This thesis report is organized as follows. chapter 2 is dedicated to the scientific paper. Here, the methodology, results and conclusions of the research article are discussed. Next, the conclusions of the thesis work and the recommendations that follow are presented in chapter 3. Finally, Appendix A contains the appendices of the thesis paper and the supporting work to show a more comprehensive picture of the applications of ammonia as a fuel for road transport.

2
Journal Article

Air pollution impacts and trade-offs of ammonia as a road transportation fuel

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Abstract

In an effort to decarbonize the road transportation sector, ammonia has emerged as a potential fuel. This study investigates the air quality and human health trade-offs associated with potential emissions from ammonia-fueled passenger cars, based on the impacts from emissions of the current road transportation fleet.

We firstly develop a simplified emissions tool that spatially maps emissions from distinct vehicle and fuel categories for both conventional and ammonia-fueled fleets. By separately integrating emission factors from ammonia engine configurations into the tool, we account for the variability in emission factor data, providing insight into the range of emissions from potential fleets powered by state-of-the-art ammonia engines.

Analysis of the annual aggregated emissions shows that NH_3 emissions from all ammonia-fueled engine configurations are generally higher than those from conventional transport, but can be significantly reduced through Post-Combustion Treatment Methods (PCTM) like Selective Catalytic Reduction (SCR). NO_x emissions from gasoline-fueled passenger cars, however, fall within the range of NO_x emissions from potential ammonia-fueled fleets.

Once the spatially resolved emissions from both the conventional and ammonia-fueled sectors are obtained, we utilize the GEOS-Chem adjoint model to assess air quality and human health impacts, in terms of $PM_{2.5}$ exposure and premature mortality rates, respectively. The results indicate that total impacts from ammonia transportation in the United States surpass those from conventional passenger car road transport. The range of premature mortalities attributed to ammonia transportation is ~ 5 100 (95% CI: 3400 - 6800) to 250 000 (95% CI: 167 000 - 333 000), while conventional transport contributes ~ 4 850 premature mortalities (95% CI: 3230 - 6470) in 2011.

State-level analysis reveals variations in impacts, with densely populated states New York or with additionally high agriculture activity like California, experiencing greater sensitivities to emissions, leading to increased air quality impacts. On the other hand, states with low sensitivities to emissions, such as North Dakota in the Great Plains, exhibit considerably lower impacts of emissions compared to the rest of the country. In fact, in those states, the magnitude of the impact of ammonia fleet emissions is equivalent to that of the conventional sector.

Considering these findings, a potential fleet of ammonia-fueled vehicles may be better suited for heavy trucks due to their long-distance routes through rural areas, minimizing air quality impacts compared to passenger cars.

Finally, we construct an emission factor tradespace that enables rapid estimation of human health impacts associated with emission factors from ammonia-fueled engines at national or state-level. This tool highlights the importance of reducing NH_3 emissions relative to NO_x emissions to mitigate air quality and human health impacts, providing insights for future ammonia engine developments. It also aids in evaluating the emission standards for potential policy assessments, necessary in the decarbonization of the road transportation sector.

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1. Introduction

Climate change concerns, driven by rising global temperatures and sea levels, have prompted ambitious goals to reduce worldwide greenhouse gas (GHG) emissions by 45% by 2030 and achieve net-zero emissions by 2050. Within the GHG-emitting sectors, the transportation industry stands out as a significant contributor, accounting for approximately 29% of total GHG emissions in the United States in 2019 (EPA). Consequently, there has been increased research interest in enhancing engine fuel efficiency and exploring carbon-free fuel alternatives, such as hydrogen and ammonia, in order to mitigate the climate and environmental impact of transportation.

Ammonia is considered a promising fuel for the transportation sector primarily because it is carbon-free and its adoption could therefore offer reductions in the CO_2 emissions of the sector (Elbaz et al., 2022). The fuel can either be directly combusted in internal combustion engines (ICEs) or used in fuel cells (FC).

In ICE vehicles, ammonia's properties (slow chemistry and low reactivity) can be enhanced by dual-fuel combustion with more reactive fuels (Elbaz et al., 2022). Some of the more reactive fuels proposed in research are gasoline, diesel, acetylene, butane, liquid natural gas (LNG), liquefied petroleum gas (LPG), Dimethyl ether (DME) and hydrogen (Reiter and Kong, 2011; Ryu et al., 2014; Gross and Kong, 2013; Frigo and Gentili, 2013).

However, mixing ammonia with more reactive fuels may result in potential carbon emissions (in case of carbon-based fuels) or increased levels of (unburned) ammonia (NH_3) and nitrogen oxides (NO_x) due to the presence of additional reactive nitrogen.

It is important to study emissions from ammonia vehicles since NH_3 and NO_x react with sulfur dioxide (SO_2) and volatile organic compounds (VOCs) in the air, to form secondary $PM_{2.5}$. Fine particulate matter ($PM_{2.5}$) is a crucial air quality indicator that contributes to air pollution and adverse human health effects (US Environmental Protection Agency, 2011; Joint et al., 2006; Turner et al., 2015), among other environmental effects (Valera-Medina et al., 2021). The formation of secondary $PM_{2.5}$ is non-linear, as it is dependent on the competition between NO_3 and SO_4 for NH_3 (Holt et al., 2015; Pinder et al., 2007; Woody et al., 2011). However, in addition to being dependent on emission precursor concentrations, the formation of $PM_{2.5}$ is influenced by atmospheric composition, temperature, relative humidity (RH), and atmospheric conditions (Ansari and Pandis, 1998; Dedoussi, 2018; Tai et al., 2010). These factors highlight the necessity to evaluate spatial distributions of NH_3 and NO_x emissions because $PM_{2.5}$ formation, and therefore human health impacts, display a highly temporal and spatial variability.

Previous studies have quantified the $PM_{2.5}$ exposure and the human health impacts resulting from emissions of various sectors (Dedoussi and Barrett, 2014; Dedoussi et al., 2020), or specifically from road transportation (Barrett et al., 2015) or aviation (Quadros et al., 2020; Ashok et al., 2013). The US Environmental Protection Agency (EPA) estimated that $PM_{2.5}$ exposure caused approximately 160 000 premature deaths in 2010 in the USA (US Environmental Protection Agency, 2011). Specifically for the road transportation sector, estimates range from 52 800 (90% CI: 23 600 to 95 300) early deaths in 2005 (Caiazzo et al., 2013) to 30 800 (CI: 21 800 - 39 800) deaths in 2011 (Dedoussi et al., 2020). The results emphasize the magnitude of human health impacts of emissions from road transportation and therefore the importance of emission regulation.

In the USA, NO_x, PM, CO, HCHO and SO_2 vehicle emissions are regulated by federal acts such as the Clean Air Act and EPA's Tier 2 and 3 emission standards. The NH_3 emissions from road transportation are currently unregulated in the USA, despite being identified as having the largest $PM_{2.5}$ reduction potential (Ansari and Pandis, 1998; Pinder et al., 2007; Lee et al., 2015).

This study aims to investigate the air quality and human health trade-offs associated with potential emissions from ammonia-fueled road transportation fleets of passenger cars, based on the impacts of spatially distributed emissions from the current road transportation sector. In this work, we specifically model air quality and human health impacts in the USA for the year 2011. This is due to the significant contribution of the USA to global GHG emissions, ranking as the second-largest emitter worldwide and responsible for 16% of global CO_2 emissions from fossil fuels and industry in 2011 (Friedlingstein et al., 2022). Furthermore, the availability of adjoint spatial sensitivities, for the USA for the year 2011, enables the characterization of long-term pollution exposure and health effects, making it an ideal case for this research.

Additionally, this work provides a tool for rapidly evaluating the human health impacts of NO_x and NH_3 vehicle emission factors at the total US and state levels. To the author's knowledge, no prior studies have combined air quality modeling and ammonia engine research through the assessment of trade-offs between air quality, thus human health impacts, and emissions from ammonia-fueled vehicles.

The article is structured as follows. Section 2 discussed the modelling framework of compiling spatially disaggregated emissions and impacts from the conventional and ammonia road transportation sectors. Section 3 presents the air quality impacts and trade-offs of NO_x and NH_3 emission species for both sectors. Section 4 summarizes the conclusions and limitations of this work, highlighting important insights derived from the study's results.

2. Methodology

This section outlines the methods employed to compile spatial emissions from the conventional and ammonia-fueled road transportation sectors for investigating their associated impacts and trade-offs. In subsection 2.1, we present a methodology for obtaining spatially-mapped road transportation emissions, disaggregated per vehicle and fuel type. Subsequently, we apply the spatial sensitivities derived from the adjoint of the GEOS-Chem chemical-transport model to assess population exposure to $PM_{2.5}$ and estimate the resulting human health impacts of emissions from both sectors, as detailed in subsection 2.2.

2.1. Road transportation emissions

2.1.1 Conventional road transportation sector emissions

In this study, we develop a simplified emissions modelling tool, based on the framework used to compile the US EPA's National Emissions Inventory (NEI). This tool is capable of spatially mapping emissions for distinct vehicle and fuel categories. The flowchart of the methodology used to compile the spatial emission maps is presented in Figure 2.1, followed by an explanation of the main components of the process.

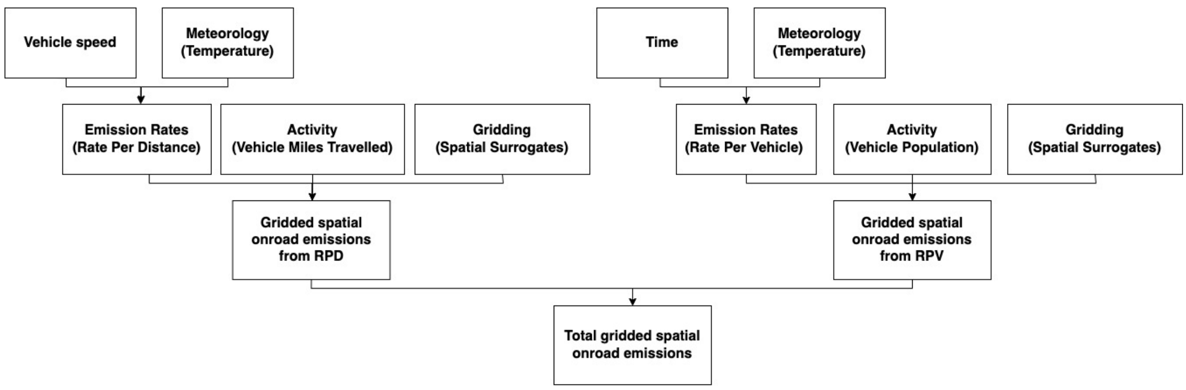

Figure 2.1: Flowchart of the emissions modelling tool used to map total annual gridded onroad emissions

Emission rates: The modelling tool estimates the total annual gridded emissions from on-roadway (e.g. driving) and off-network (e.g. parking) processes by utilizing Rate Per Distance (RPD) and Rate Per Vehicle (RPV) emission rate tables obtained from the EPA's MOtor Vehicle Emission Simulator (MOVES). The RPD table stores vehicle emission factors during driving, while the RPV table represents the emission factors during parking. A comprehensive description of the emission processes included in the tables can be found in Table A.1.

To optimize the computation time for calculating spatially disaggregated emissions, the RPD and RPV tables are specified for a set of reference counties and fuel months. Reference counties are selected to represent a group of counties with similar characteristics such as meteorological conditions, fuel parameters, fleet age distribution and inspection and maintenance (I/M) programs (EPA, 2017). Each group of counties is therefore characterized by the same emission rates for a given speed and temperature. Similarly, reference fuel months represent months with common fuel properties and temperatures, with January as the reference fuel month for winter and July for summer.

The emission rates in the look-up tables are categorized according to source classification codes (SCC), which indicate the vehicle fuel type, vehicle category, road type, and corresponding emission processes. This allows us to compile separate emission maps for each category included in the SCC, as well as the aggregate emissions of the full road transportation sector. Additional information on the SCC can be found in EPA (2017).

The emission factors stored in the RPD tables are provided in grams per kilometer (g/km). The mean value of the monthly temperature and the average monthly speed data are used as look-up fields to find the corresponding emission factor (for each representative county).

The emission factors from the RPV table are stored in grams per vehicle per hour ($g/vehicle/hr$), with temperature and hour of the day (weekday or weekend hours) as look-up fields. The mean value of the monthly temperature is used and is assumed constant throughout the hours of the day, which is considered adequate for compiling annual emissions.

Activity: The activity data for RPD emission factors consists of county total monthly values of Vehicle Miles Travelled (VMT) per road type, vehicle category and fuel type. This allows for easy matching of RPD emission rates to the corresponding activity data.

For RPV emission factors, county total annual values of Vehicle Population (VPOP) for each vehicle category are used. The VMT and the VPOP databases are obtained from state and local agencies, providing county-level inputs for MOVES.

Combining the emission rates with the activity data yields emission values in grams per county. To map emission data to grid cells, it is necessary to spatially disaggregate these values.

Gridding: The EPA provides spatial surrogates, used to spatially allocate county-total vehicle emissions to grid cells with a 4 km × 4 km grid resolution and Lambert-Conformal projection. On-network emissions are allocated to specific road types (unrestricted, restricted, urban, rural), while off-network emissions are allocated to population, where parked vehicle emissions occur (Eyth and Vukovich, 2016).

By combining emission rates, activity and spatial surrogates, annual gridded spatial emissions from on-network and off-road processes are compiled for the conventional road transportation sector in the US, or for distinct vehicle and fuel categories. The next subsection describes the methodology for mapping emissions from the ammonia-fueled sector.

2.1.2 Ammonia-fueled road transportation sector emissions

To compile a spatially disaggregated map of emissions from the ammonia-fueled transportation sector, we followed a similar approach as shown in Figure 2.1. However, there are some key differences. In this research, the ammonia sector is represented by on-road emissions from passenger cars, as there is limited data available for ammonia-fueled engines. By compiling annual US gridded spatial emissions for each ammonia-fueled engine configuration, characterized by distinct emission rates in (g/km), we accounted for the variability in emission factors found in the literature and captured the range of emissions from potential ammonia-fueled sectors. Below, we describe the emission rates obtained from state-of-the-art research.

Emission rates: Boero et al. (2023) investigated nine ammonia-fueled Light Duty Vehicle (LDV) engine model configurations, documenting the direct engine-out emissions and the emissions after the PCTM. The configurations vary in terms of equivalence ratios, exhaust gas recirculation rates (EGR), gearbox optimization criterions and PCTM. The PCTM consists of an oxide catalyst, a selective catalytic reduction (SCR) systems and an ammonia oxidation catalyst (AOC). Three different SCR configurations were employed, each with different levels of NH_3 slip and N_2O formation.

Moreover, Angeles et al. (2017) presented ammonia emission factors for three different engine types: Compression Ignited (CIg) engine using dual ammonia diesel fuel (DIVO) and CIg direct-injection ammonia-DME mixture (DMVO) as well as a Spark Ignited (SI) engine with gaseous ammonia direct injection and gasoline (GAVO). The emission factors for each engine configuration were applied to passenger car vehicle transport to estimate the corresponding emissions from the ammonia vehicle category.

The predominant emissions from ammonia engines are NO_x and NH_3, however, traces of N_2O GHG are also present. For engines running on ammonia fuel-mixtures, additional CO_2 and CH_4 emissions are measured at the exhaust.

In our analyses, we focus on quantifying the NO_x and NH_3 emissions resulting from the application of ammonia-fueled engines in the passenger car fleet. Figure 2.2 shows a logarithmic plot of the NO_x and NH_3 emission factors extracted from state-of-the-art literature, which are used to characterize ammonia-fueled vehicles.

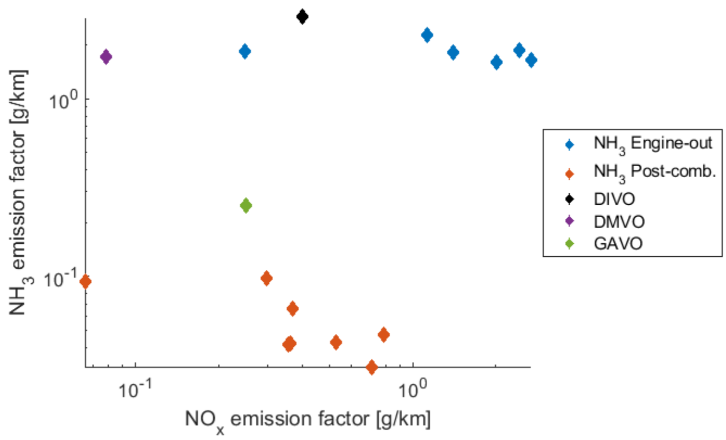

Figure 2.2: Logarithmic representation of emission factors for ammonia-fueled vehicles

Activity and Gridding: To enable the comparison between the conventional and ammonia-fueled sectors, we assume that the activity (VMT) and spatial allocation of emissions are the same for both sectors. This modelling approach assumes a linear relationship between the emission factors and the vehicle emissions.

Following the methodology described in subsubsection 2.1.1, we combine the emission rates, activity and spatial surrogates to compile annual US gridded spatial emissions for ammonia-fueled vehicles at a 4 km × 4 km resolution. The spatial mapping of emissions is important because air quality impacts are dependent on the location of emissions. To use the emission maps for further air quality modelling, the emissions are regridded to the 0.5° × 0.666° (latitude × longitude) grid of the nested GEOS-Chem adjoint model. The process of estimating the air quality impacts of emissions, utilizing the acquired spatial emission maps, is described in subsection 2.2.

2.2. Air quality modelling and human health impacts assessment

We use the previously obtained spatially gridded emission maps to quantify the corresponding air quality impacts in terms of population exposure to $PM_{2.5}$.

We employ the adjoint of the GEOS-Chem model, developed by Henze et al. (2007), to calculate the sensitivities of population exposure to $PM_{2.5}$ resulting from road transportation emissions. This method has been previously used by Koo et al. (2013); Lee et al. (2015); Barrett et al. (2015).

The adjoint sensitivity, denoted as S, quantifies how a perturbation of a unit of emission species w, emitted in grid cell location (i, j, k) at timestep t, influences the aggregated population exposure to $PM_{2.5}$ at the US or state level (represented by the objective function J), see Equation 2.1.

$$S^w_{ijkt} = \frac{\partial J}{\partial E^w_{ijkt}} \tag{2.1}$$

The sensitivities are computed for the 48 contiguous US (CONUS) states on a 3D grid which focuses on North America, spanning from 140 W to 40 W longitude and 10 N to 70 N latitude. The grid has a horizontal resolution of 0.5° × 0.666° (approximately 55 km × 55 km, latitude × longitude) with 47 vertical levels until 80 km. Although this horizontal resolution is suitable for analyzing state-wide impacts (Thompson et al., 2014; Li et al., 2016; Arunachalam et al., 2011), it does not provide information at a sub-state level (Dedoussi, 2018).

An annual simulation for the state-wide $PM_{2.5}$ exposure levels for the year 2011 resulted in 48 adjoint simulations using the meteorological data from the Global Modelling and Assimilation Office (GMAO) at the NASA Goddard Space Flight Center, following the approach described in Dedoussi and Barrett (2014).

To determine the population exposure to $PM_{2.5}$, we calculate the inner product of the spatial adjoint sensitivities and the spatially distributed road transportation emissions, see Equation 2.2. We can use this approach to calculate the population exposure to $PM_{2.5}$ for each vehicle and fuel category on a state-level, or to obtain total aggregate impacts for the entire USA.

$$\begin{aligned} &\frac{\partial \mathrm{PM}_{2.5}\ (\text{total})}{\partial \mathrm{NO_x}\ (\text{anywhere})} \times \Delta \mathrm{E}\,(\mathrm{NO_x})_{\text{road transportation}} \rightarrow \mathrm{IMPACT}_{\mathrm{NO_x}} \\ &\frac{\partial \mathrm{PM}_{2.5}\ (\text{total})}{\partial \mathrm{NH_3}\ (\text{anywhere})} \times \Delta \mathrm{E}\,(\mathrm{NH_3})_{\text{road transportation}} \rightarrow \mathrm{IMPACT}_{\mathrm{NH_3}} \end{aligned} \tag{2.2}$$

Quantifying the population exposure to $PM_{2.5}$ is important as it can cause adverse health effects, including ischemic heart disease, lung cancer, chronic obstructive pulmonary disease, and respiratory infections (Kurvits and Marta, 1998). Fine particulate matter, such as $PM_{2.5}$, can easily diffuse through skin and lungs to reach organs and bloodstreams. Prolonged exposure to $PM_{2.5}$ can even lead to premature mortality, which makes it a suitable metric for assessing the human health impact of emissions (Apte et al., 2018). The approach for evaluating the health impacts associated with emissions from both the conventional and ammonia-fueled road transportation sectors is shown in Figure 2.3.

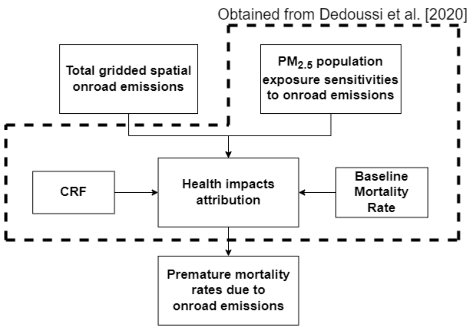

Figure 2.3: Flowchart of the approach to estimate human health impacts from road transportation emissions

The relationship between human exposure to $PM_{2.5}$ and the risk of premature deaths has been quantified using epidemiologically derived concentration–response functions (CRF). It is noted that the estimated health impacts from road transportation emissions are highly influenced by the choice of CRF.

In this study, we apply the all-cause CRF derived from the American Cancer Society cohort study. The CRF estimates a 6% increased risk of mortality (with a range of 4–8%) associated with a 10 $\mu g m^3$ increase in annually averaged exposure to $PM_{2.5}$ (Krewski et al., 2009). It is important to mention that this estimate is derived for adults over the age of 30 and has been widely used in various air quality studies (Anenberg et al., 2010; Evans et al., 2013; Wolfe et al., 2019).

3. Results

This section presents the results obtained from the methods described earlier, which involve compiling spatially disaggregated emissions and their air quality impacts. The comparison between total and distinct vehicle category emissions from the conventional and ammonia sectors is presented in subsection 3.1. The corresponding air quality impacts of both sectors are the discussed in subsection 3.2. Furthermore, the relationship between NO_x and NH_3 emission factors and their corresponding human health impacts is investigated by means of emission tradespaces, see subsection 3.3.

3.1. Emissions of the conventional and ammonia-fueled sectors

3.1.1 Conventional road transportation sector

In the USA in 2011, the most significant annual emissions for the conventional road transportation sector were NO_x emissions estimated at 3.28 Tg. Black Carbon (BC) and NH_3 emissions were of similar order of magnitude, at 0.10 Tg and 0.11 Tg respectively, while SO_2 emissions were the lowest out of these four at 0.03 Tg. Maps presenting the spatially disaggregated annual emissions of NO_x, BC, NH_3 and SO_2 for the conventional road transportation sector are provided in Figure A.1.

The total NO_x and NH_3 road transportation emissions in the USA compare well with existing literature. Specifically, for the conventional road transportation sector, the annual emissions of NO_x and NH_3 are 6% and 2.6% lower respectively compared to the values reported in Dedoussi et al. (2020) (refer to Table A.2).

Given that the total annual emission values align closely with those reported in the literature, we utilized the same simplified emissions modelling tool to compile annual road transportation emissions for each vehicle category. This allowed us to assess the emissions specific to motorcycles, passenger cars, buses, lighter trucks, heavy trucks, and motor homes (see Figure 2.4). The results indicate that heavy trucks contribute the highest share of NO_x (41%) and BC (66%) emissions. Moreover, passenger cars are the largest source of NH_3 emissions (49%), followed by passenger trucks (45%), while heavy trucks account for only approximately 5% of NH_3 emissions.

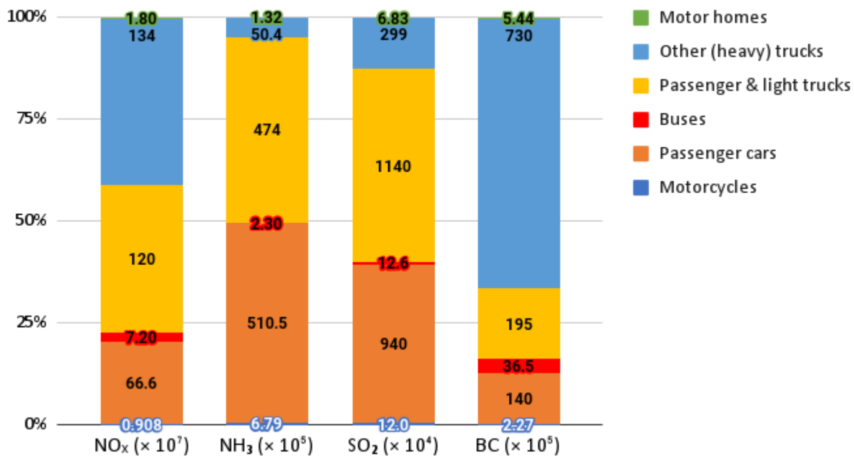

Figure 2.4: Breakdown of annual emissions per vehicle category from the conventional road transportation sector [in kg] (2011)

The presence of NH_3 emissions in the road transportation sector is primarily attributed to combustion after-treatment technologies, such as SCR in diesel-fueled vehicles (Desrochers, 2013), and Three-Way Catalysts (TWC) used in gasoline vehicles (Bishop and Stedman, 2015; Granger and Parvulescu, 2011). These catalysts are implemented to reduce tailpipe NO_x emissions. However, an important drawback is the potential for ammonia leakage, known as ammonia slip, if the optimal reductant proportions or temperature are not achieved (Lenaers and Van Poppel, 2004; Roe et al., 2004) . Consequently, there exists a crucial trade-off in engine design between NO_x and NH_3 exhaust emissions. With this trade-off identified, further analyses of emissions and impacts will focus on investigating the relationship between these two emission species.

The spatial distribution of annual NO_x and NH_3 emissions from passenger cars and heavy trucks is presented in Figure 2.5. The mapped emissions show that passenger vehicle emissions are more concentrated in densely populated urban centers. On the other hand, emissions from heavy trucks are more widespread across the US, particularly in the East, mapping the network of inter-state highways where heavy truck activity is more prevalent. This distribution of vehicle activity per road type is confirmed by the annual highway statistics published by the Federal Highway Administration (FHWA) (Office of Highway Policy Information, 2011).

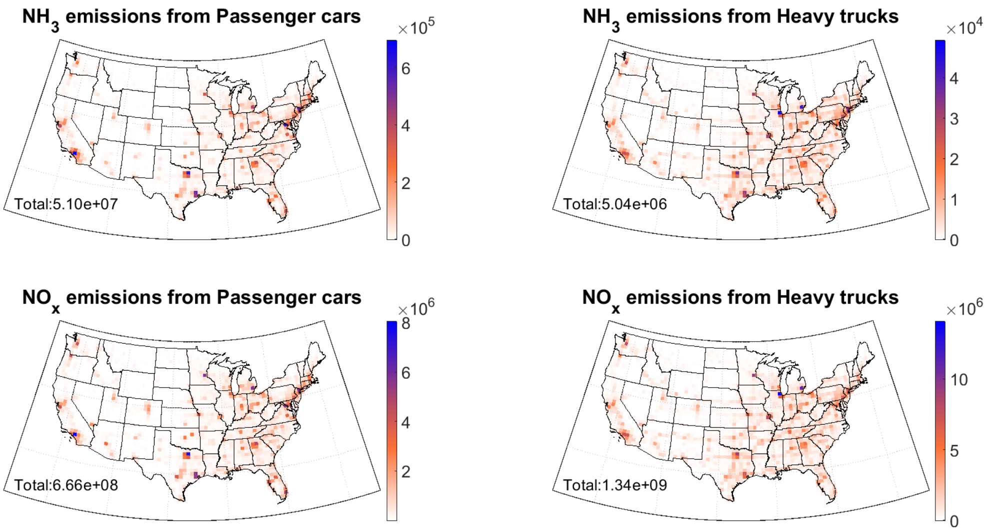

Figure 2.5: Spatial distribution of annual NO_x and NH_3 emissions from passenger cars and heavy trucks of the conventional road transportation sector (2011) [in kg]

3.1.2 *Ammonia-fueled passenger cars*

As stated earlier, NO_x and NH_3 emissions are one of the most important species to consider when evaluating the emissions from the ammonia sector.

Figure 2.6 presents the NO_x and NH_3 emissions resulting from the implementation of different ammonia-fueled engine configurations in passenger cars. It also includes the total emissions from diesel and gasoline counterparts in the conventional road transportation sector.

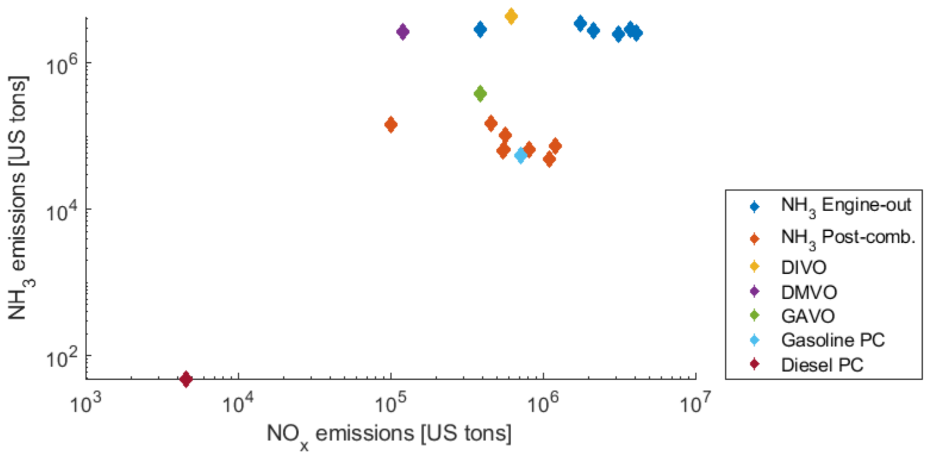

Figure 2.6: Logarithmic representation of annual NO_x and NH_3 emissions from the ammonia and conventionally-fueled road transportation sector (represented by Gasoline and Diesel Passenger Cars (PC)) (2011)

As shown in Figure 2.2, there is a significant variability in the emission factors of ammonia engine configurations. This variability is reflected in the magnitudes of both NO_x and NH_3 emissions from ammonia-fueled vehicles in Figure 2.6. The NO_x emissions range from 100 000 to 4 100 000 US tons, while the NH_3 emissions range from 48 000 to 4 500 000 US tons. This wide range highlights the variability in emissions that can be anticipated as a result of implementing ammonia-fueled engines into the road transportation sector.

In general, Figure 2.6 demonstrates that engine-out emissions from ammonia-fueled vehicles are characterized by high levels of NO_x and NH_3 emissions. On the other hand, engine configurations equipped with PCTM have proven to be effective in reducing both emission species. When road transportation vehicles are fueled with ammonia mixtures, the gasoline-ammonia engine exhibits lower NH_3 emissions compared to the DIVO and DMVO fueled engines, making it the preferable alternative to non-treated tailpipe emissions of ammonia-fueled engines in terms of NH_3.

When comparing the conventional and ammonia-fueled sectors, the NO_x emissions are similar for both, except for diesel-fueled vehicles. The NO_x and NH_3 emissions from diesel-fueled passenger cars are considerably lower compared to gasoline and ammonia-fueled fleets. This is due to the fact that diesel-fueled passenger cars only account for 0.5% of the total passenger car fleet, while gasoline-fueled vehicles make up the vast majority (97%) as of 2011.

Studying NH_3 emissions, these are also lowest for diesel and gasoline passenger vehicles, with the exception of an ammonia engine configuration operating at a lower equivalence ratio with a PCTM. Therefore, there is potential for achieving lower NO_x and NH_3 emissions with ammonia engines. However, based on state-of-the-art engine research, there is currently no existing configuration for an ammonia-fueled engine that, when implemented in the passenger car fleet, can simultaneously achieve lower NO_x and NH_3 emissions compared to gasoline and diesel vehicles.

Having compared the emissions of the two road transportation sectors, subsection 3.2 will now demonstrate the air quality impact of these spatially distributed emissions.

3.2. Air quality impacts of conventional and ammonia-fueled sectors

3.2.1 Aggregate US Impacts

The annual aggregate US human health impacts per vehicle category are presented in Figure 2.7. We observe that the emissions (presented in Figure 2.4) and impacts, here shown, are not directly proportional.

For example, heavy trucks account for 41% of the total NO_x emissions from road transport but cause 38% of premature mortalities due to NO_x. Similarly, passenger cars contribute 49% of the total NH_3 emissions from road transport, yet they are responsible for 51% of premature mortalities due to NH_3.

This occurs because air quality impacts are significantly influenced by the location of emissions and therefore the activity of the various vehicle categories. Considering this, we can estimate the sensitivities to a perturbation of a unit (kg) of emissions by examining the ratio of the human health impact to the corresponding emissions. The resulting table of sensitivities per vehicle type is presented in Table 2.1.

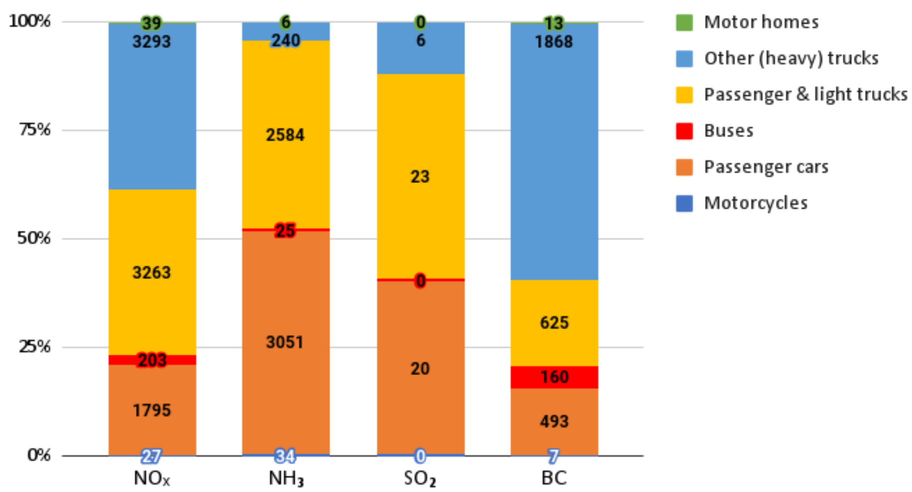

Figure 2.7: Breakdown of total annual health impacts of NO_x, NH_3, SO_2 and BC emissions from conventional road transport disaggregated per vehicle category (2011) [in premature mortalities]

Table 2.1: Sensitivities of human health impacts due to emissions for different vehicle categories in the US assuming an equal toxicity for each of the $PM_{2.5}$ constituents (2011) [in premature mortalities/kg]

Vehicle category	Emission species (premature mortalities/kg of emission)			
	NO_x (10^{-6})	NH_3 (10^{-5})	SO_2 (10^{-6})	BC (10^{-5})
Motorcycles	2.94	5.03	2.00	3.04
Passenger cars	2.70	5.98	2.11	3.51
Buses	2.82	10.9	2.22	4.40
Passenger & light trucks	2.73	5.45	2.05	3.20
Other (heavy) trucks	2.46	4.76	1.98	2.56
Motor homes	2.15	4.79	1.79	2.44
All vehicle average	2.61	5.68	2.06	2.85

The relative importance of BC and NH_3 in the formation of $PM_{2.5}$ in comparison with NO_x and SO_2, is evident in Table 2.1. Overall, passenger cars show a higher sensitivity to the perturbation of a unit of emissions compared to heavy trucks, with approximately 1.1 and 1.25 times higher sensitivities for a unit of NO_x and NH_3, respectively. Buses demonstrate the largest sensitivity to emission species, with an exception for NO_x emissions which demonstrate the highest sensitivity for motorcycles.

From an engine design perspective, the relative benefit of reducing a kilogram of NH_3 emissions for passenger cars is approximately 8 times higher than reducing a kilogram of NO_x emissions, per unit mass. For heavy trucks and buses the relative benefit is equivalent to 7 and 14, respectively. The results show that reducing NH_3 emissions for each vehicle category is beneficial because of the higher values of the total US premature mortality per unit mass of emissions.

The analysis in subsubsection 3.2.1 considered the total US premature mortality impacts. However, to account for the spatial variation of emissions and therefore impacts further studies will be conducted on the sensitivities of emissions at the state-level.

3.2.2 State-level sensitivity to emissions

We will now examine how the sensitivities to emissions vary at the state level and identify the factors that drive this variation. Figure 2.8 presents the state-level human health response to a unit of NO_x and NH_3 emissions from passenger cars and heavy trucks. The highest sensitivities to a unit of NH_3 emissions are observed in the state of New York for both heavy trucks and passenger cars. Similarly, for a unit of NO_x emissions, the largest impact is attributed to the state of California for both vehicle categories. Both California and New York are characterized by high population density areas. Additionally, California experiences significant background NH_3 emissions due to its extensive agricultural activity.

As mentioned previously, the formation of $PM_{2.5}$ is influenced by the competition between precursor emissions of NO_x and SO2 for free ammonia in the atmosphere. In California, where NH_3 emissions are abundant, the limiting species for $PM_{2.5}$ formation is NO_x, as indicated by the gas ratio map in Dedoussi (2018). Another region where agricultural activity is prominent, and the availability of nitric acid (formed from NO_x) limits the formation of $PM_{2.5}$, is the Great Plains. In this region, the sensitivity to NO_x is slightly higher than the sensitivity to NH_3, as shown in Figure 2.8.

Conversely, the lowest impacts of emissions for both vehicle categories can be seen in the regions of Rocky Mountains and the Great Plains. Therefore, ammonia-fueled vehicles could be suitable for long-distance travel routes, away from densely populated areas, to minimize human health impacts. Additionally, passenger cars demonstrate a slightly larger impact per unit of emissions compared to trucks, for both NO_x and NH_3, suggesting that trucks should be prioritized as a potential category for ammonia-fueled vehicles.

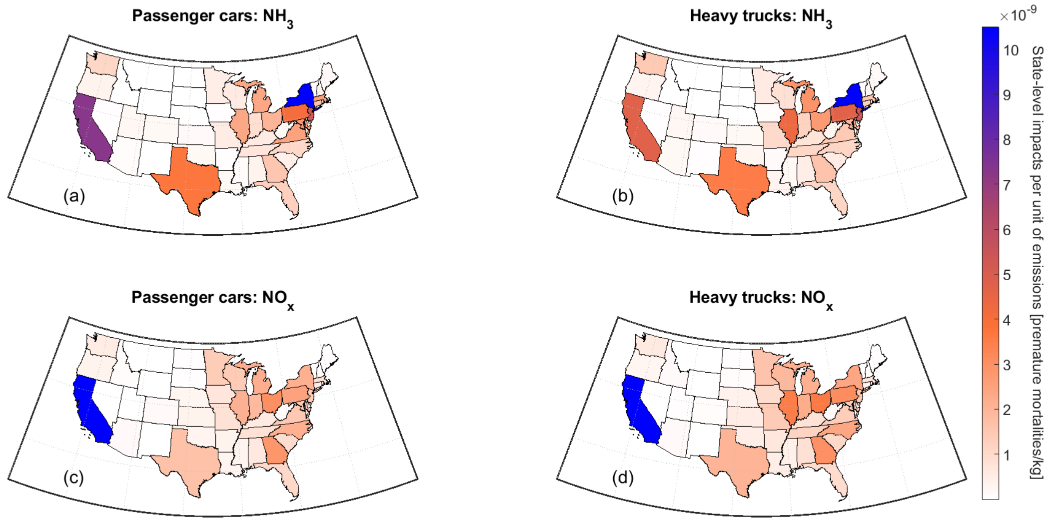

Figure 2.8: Annual state-level impacts per unit of NO_x and NH_3 emission perturbation for passenger cars and heavy trucks (2011) [premature mortalities/kg of emissions]

By applying the state-level sensitivities, we can calculate the total impacts of emissions for both the conventional and ammonia-fueled road transportation sectors on a state-level. Figure A.2 presents a comparison of those impacts, of NH_3 and NO_x emissions combined, for both sectors. The results show that total impacts for the ammonia-fueled sector are higher than those for the conventional sector. Specifically, in the states of New York, California, and Texas, the ammonia sector exhibits significantly higher impacts compared to the conventional sector, as illustrated in Figure A.2. This indicates that introducing an ammonia-fueled fleet would have a much greater impact in areas with a high population density compared to the conventional sector.

Furthermore, it is important to compare the state-level impacts of implementing ammonia engines with PCTM to the impacts of conventional transport on a state-level. As shown in Figure A.4, in regions characterized by low population density and vehicle emissions, the impact of the ammonia-fueled sector is found to be equally significant as that of the current sector.

3.3. Trade-off between emissions and their corresponding impacts

With the quantified emissions and their associated human health impacts, our aim is to integrate this data, by means of a trade-off study, to facilitate a rapid assessment of the total US human health impacts and state-wide impacts of emissions. This analysis takes into account various factors, including vehicle categories (passenger cars and heavy trucks), the location of emissions (at the state level), and different fuel compositions (gasoline, diesel, ammonia, and other fuel mixtures).

To carry out this trade-off an emission factor tradespace is constructed showing the relationship between NH_3 and NO_x emission factors and their effect on air quality in terms of premature mortalities for passenger cars and heavy trucks, as shown in Figure 2.9. This emission factor tradespace contains a pareto front which delineates the total US impact caused by the gasoline and diesel (combined) NO_x and NH_3 emissions for both passenger cars and heavy trucks. The area below the pareto front shows all the combinations of engine emission factors which would, if implemented into the road transportation fleet, have lower total US premature mortality impacts than gasoline/diesel emissions.

The emission tradespace shows that the gradients of the color map are more gradual for the NO_x emission factors compared to the NH_3 emission factors. This indicates that the impact of NO_x emissions on total US impacts is relatively smaller in comparison to NH_3 emissions. In fact, the total US impact attributed to NH_3 emission factors is approximately an order of magnitude larger than that of NO_x emissions.

Furthermore, the concave shape of the pareto front further emphasizes the relative importance of minimizing NH_3 emissions and NH_3 emission factors. This shape suggests that achieving significant reductions in total US impacts requires a more substantial reduction in NH_3 emissions compared to NO_x emissions. By prioritizing the reduction of NH_3 emissions by minimizing NH_3 emission factors, we can effectively mitigate the adverse health effects associated with road transportation emissions.

Figure 2.9(a) also demonstrates the total US impacts from different engine configurations. The emissions from ammonia engines, DIVO, DMVO and GAVO engines all cause significantly higher total impacts than conventional passenger cars. Ammonia-fueled engines with PCTM can achieve air quality impacts closest to those of gasoline vehicles. However, future engine developments focused on minimizing the NH_3 emission factor are necessary for an ammonia fleet to match the impact of the conventional sector in the USA.

Currently, there are no studies quantifying the emission factors (in g/km) for ammonia-fueled heavy trucks. Once this data becomes available in the future, Figure 2.9(b) can be used to rapidly estimate the corresponding air quality impacts. In order to fully utilize the potential of ammonia as a fuel for heavy trucks, it is important to develop engine designs with emission factors leading to lower air quality impacts as compared to the diesel vehicle pareto front.

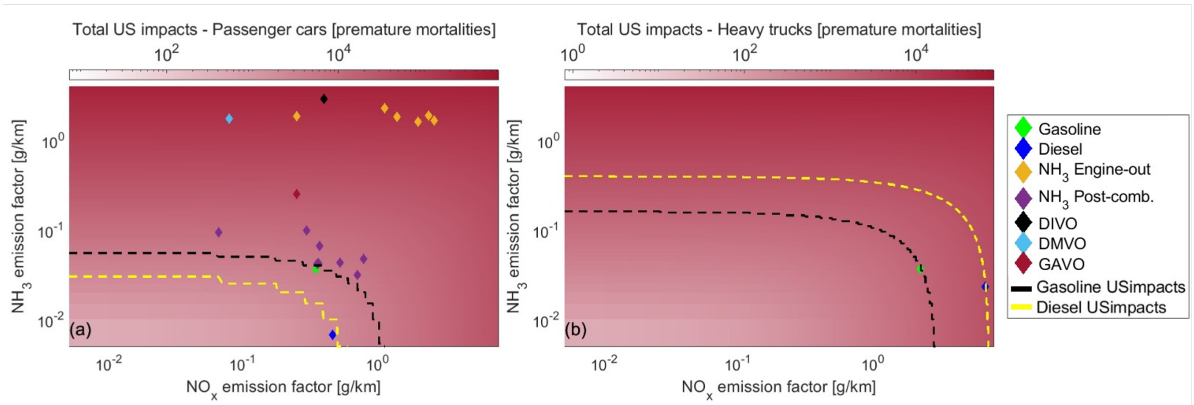

Figure 2.9: Total annual US impacts due to NO_x and NH_3 emissions a a function of vehicle emission factors for passenger cars (a) and heavy trucks (b) (2011)

To account for the location-specific impacts of emissions, the trade-offs are also evaluated at a state level in Figure 2.10 which compares states with varying air quality impacts for different vehicle categories. The state-level impacts for the emission factors from passenger car vehicles are studied for New York (a) and North Dakota (b), representing states with the highest and lowest total US air quality impacts, respectively. In the case of New York, the ammonia engine configuration with PCTM and the lowest NH_3 emission factor has a lower total state impact than the current gasoline vehicles. Conversely, for North Dakota, there are more ammonia-fueled engine configurations expected to yield lower or comparable total state impacts to the current gasoline and diesel equivalents.

Figure 2.10 (c) and (d) provide an emission tradespace for heavy trucks in New York and North Dakota. The magnitude of the impacts for heavy trucks is slightly lower for both states, than the impact of the passenger car counterpart. This emission tradespace could be useful when there is more research on engines for ammonia-fueled heavy trucks, and specifically more emission factor data.

In addition, we conducted a trade-off analysis of emission factors specifically for passenger cars and heavy trucks in the state of California. This was done because California, as well as having high air pollution levels, has its own regulatory body, the California Air Resources Board (CARB), which sets emissions standards at the state level. The emission tradespace tool shows that the current state-of-the-art ammonia engines should not be utilized in California, since the impacts of the resulting NO_x and NH_3 emissions would surpass those of the gasoline and diesel-fueled sectors.

Currently, the state-level trade-off analysis depicted in Figure 2.10 illustrates that the total air quality impacts associated with the current emission factors of ammonia engines in passenger vehicles exceed those of gasoline and diesel-fueled road transportation. However, these emission tradespaces could be useful for rapidly assessing the human health impacts of future advancements in ammonia engine technology. The tool can also help in policy assessments, allowing the development of state-specific emission standards.

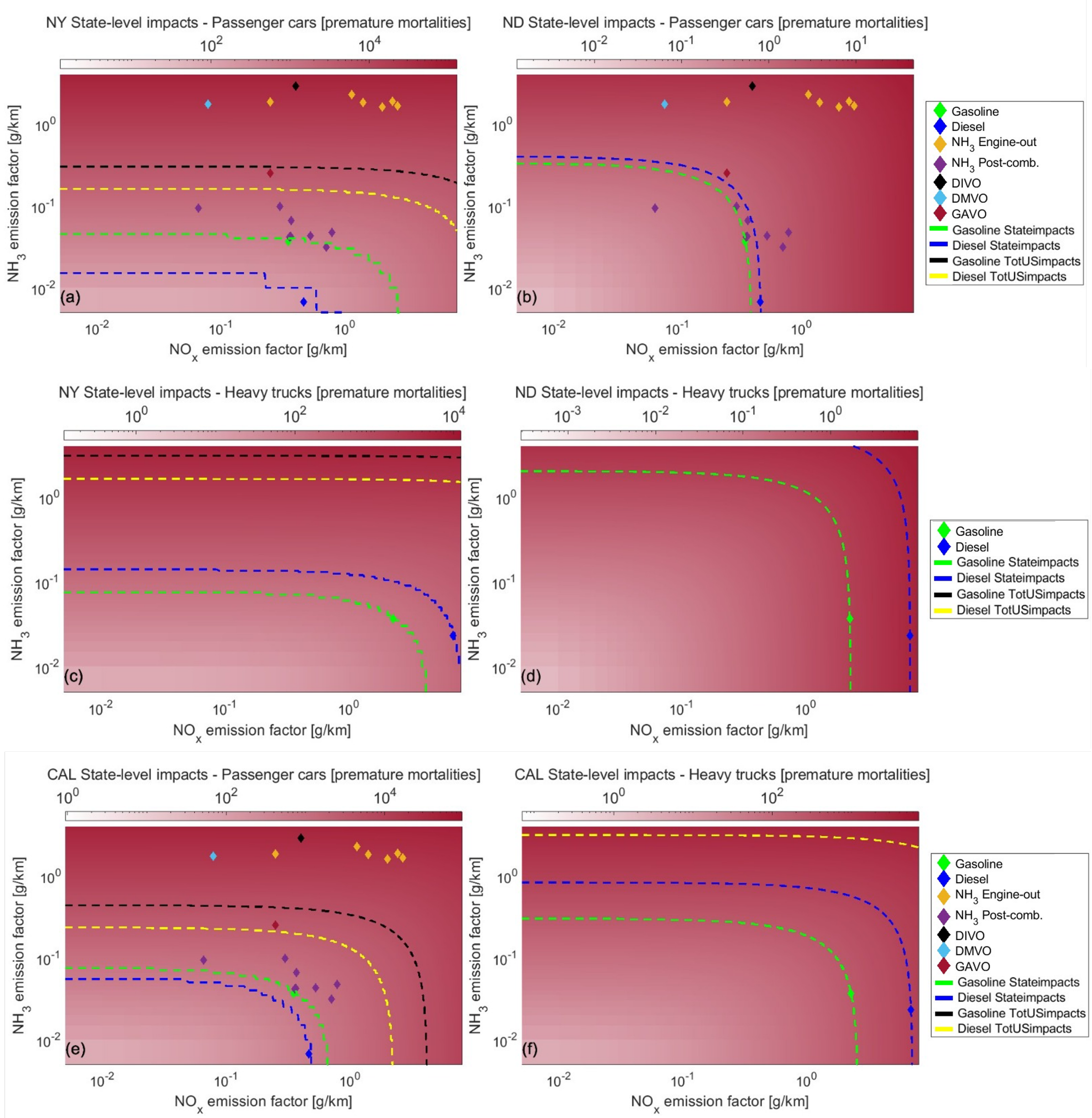

Figure 2.10: Annual state-level impacts due to NO_x and NH_3 emissions for various states (NY, ND and CAL) and vehicle categories (passenger cars and heavy trucks) (2011)

4. Conclusions

4.1. Results

In this study, we quantified the human health impacts (in terms of premature mortalities) for both the conventional and ammonia-fueled road transportation sectors. The aim was to evaluate the potential of using ammonia as a fuel from an air quality perspective. We also investigated trade-offs between the exhaust emissions of ammonia vehicles: NO_x and NH_3 and their corresponding impacts to better inform future ammonia-fueled engine designs and applications.

The results indicate that passenger cars have a higher impact per unit of NH_3 and NO_x emissions compared to heavy trucks. NH_3 emissions were found to have a significant contribution to $PM_{2.5}$ formation, highlighting the importance of minimizing NH_3 emissions in ammonia engine design, particularly for passenger cars.

We also observed that the states with high population density, such as New York and California (where agricultural activity is prevalent), had the highest air quality impacts per unit of emissions. Conversely, regions with low population density, like the Rocky Mountains and Plains, exhibited the lowest impacts. In these areas of low population density, equivalent air quality impacts were found for both ammonia and conventional-fueled sectors. However, in other regions, the introduction of ammonia as a fuel using current ammonia engine technology would lead to increased air quality impacts compared to the 2011 conventional road transportation sector. The results also highlighted the significance of PCTM in reducing both NO_x and NH_3 emissions.

Based on these observations, it would most beneficial, in terms of air quality impacts, to introduce ammonia-fueled trucks for long distance transportation, far away from highly densely populated areas. However, it is not possible to quantify the air quality impact of ammonia-fueled trucks since no applicable emission factors exist to this date. More research is also needed focused on engines for applications in passenger vehicles. The current ammonia engines with PCTM could prove to be a good alternative to gasoline vehicles, also for operation outside densely populated areas (in states with lower sensitivities to air quality impacts).

The trade-off graphs and emission tradespace generated in this study can serve as valuable tools for engine design optimization and policy assessment as they enable rapid assessments of premature mortalities in the USA based on engine emission factors.

4.2. Limitations

Our methodology and results are applicable for the investigation of air quality impacts due to ammonia-fueled passenger vehicles, however, they have some uncertainties and limitations.

In literature, there is a lot of variability in emission and impacts results, as well as in approaches taken for atmospheric chemistry-transport modelling and for the assessment of health impacts. This highlights the scientific uncertainty in estimating the impact of emissions. The methodology of approximating the emissions, used in this study, is based on EPA's NEI. Previous studies have found, however, that the 2011 NEI NO_x emissions from road transportation are overestimated by approximately 50% in the southeast and nationally (Anderson et al., 2014; Travis et al., 2016). More recent studies have also suggested that the NEI NH_3 onroad emissions are underestimated (Cao et al., 2021) and are, in reality, twice as high (Sun et al., 2017; Fenn et al., 2018). The uncertainties in emission inventories carry further onto the calculation of $PM_{2.5}$ population exposure levels (Dedoussi, 2018; Heald et al., 2012) which will therefore affect the air quality impact obtained for conventional vehicles. Dedoussi et al. (2020) has quantified that the NEI values of NO_x road transportation emissions have led to an overestimation of premature mortalities by approximately 7 500 annual deaths (95% CI: 5 200–9 700).

In this study, some simplifications were made in the approach taken to obtain the spatially-disaggregated emissions. For example, an average monthly speed and an average monthly temperature per county per vehicle category and road type were specified. This was assumed to be sufficient for capturing the annual onroad emissions. However, in reality, emissions and their impacts are strongly dependent on the vehicle speed and the meteorology. In future analysis, a more detailed approach could be used by using speed and temperature profiles.

The emissions and impacts of emissions are evaluated on an annual aggregated basis (due to the annual adjoint spatial sensitivity values). This does not take into account the seasonal variation of emissions and impacts. Dedoussi and Barrett (2014) found that the sensitivity of NH_3 emissions to population exposure to $PM_{2.5}$ has a strong seasonal variation, where it is lowest in the summer months. The impact of NH_3 emissions follows a similar annual trend. For the NO_x emissions, however, the highest impact is in the summer months. Studying the impact of ammonia vehicles on a monthly basis, could give more insights on the relationship between NH_3 and NO_x in the formation of secondary $PM_{2.5}$.

The emissions from the ammonia-fueled passenger car transportation fleet are primarily governed by the emission factors specific to an engine configuration/type, fuel composition and PCTM (as mentioned in subsubsection 2.1.2). However, in reality, emission factors are also dependent on vehicle age, road grade, temperature and operating conditions (Cao et al., 2021; Sun et al., 2016). The latter factors are not taken into account but may cause some minor variations in the emission and therefore premature mortality results.

Due to the limited availability of emission factor data (in units of (g/km)), this study focuses on the quantification of impacts of emissions from ammonia passenger vehicles. The evaluation of impacts from heavy trucks and buses would complete the analysis, making more comparisons of the transportation sector possible. However, passenger vehicles and heavy trucks have different engines, uses and characteristics that make the scaling of emission factors not possible.

This study is limited to computing emissions from ammonia vehicles from driving. In addition, there may be significant ammonia leakages when handling the fuel or resulting from car accidents, which will pose a lot of safety and environmental concerns due to its toxicity. To assess the viability of using ammonia as a fuel, it is crucial to conduct a thorough investigation of potential safety risks. Ammonia fuel leakages can have significant consequences on air quality and the environment. These consequences include the acidification of ecosystems due to the eutrophication caused by NH_x and N deposition (Vestreng and Støren, 2000; Krupa, 2003). By thoroughly examining these risks, we can better understand the air quality and environmental impact of using ammonia as a fuel and take appropriate measures to mitigate any associated risks.

3
Conclusions and Recommendations

This chapter covers the conclusions of the thesis work, answering the main research question. Consequently, a number of recommendations are offered to gain more scientific understanding in the field of air quality impacts and human health trade-offs of using ammonia as a road transportation fuel.

1. Conclusions

The aim of this research was to quantify the air quality impacts (in terms of premature mortalities) of the conventional and ammonia-fueled road transportation sector in order to evaluate the potential of using ammonia as a fuel. The main research questions were formulated in order to achieve this goal. This section provides answers to the main research question by referring to the main findings from the scientific article presented in chapter 2.

The main research question was the following: "what would be the resulting $PM_{2.5}$ population exposure impact from the introduction of an ammonia-fueled road transportation fleet of passenger cars?"

To answer this research question, firstly, ammonia engine developments were investigated to understand the underlying trade-offs and emission reduction methods. Next, emission factors for ammonia-fueled passenger vehicles were extracted from literature in order to create spatially disaggregated emission maps for the private transport sector. With the full range of emission factors from ammonia vehicles, the resulting NO_x emissions for total USA were estimated to be from 100 000 to 4 100 000 US tons, and 48 000 to 4 500 000 US tons for NH_3. The petroleum-based road transportation sector was disaggregated into vehicle categories in order to study the emissions and the corresponding air quality impacts of each vehicle category separately. For the petroleum-based passenger vehicles, the emissions varied from approximately 0.14 to 5.6 times the NO_x and 0.85 to 79 times the NH_3 emissions. Next, the population exposure impacts were quantified by taking the inner product of the sensitivity matrix with the spatially resolved emission maps for both emission species. This operation resulted in aggregate US air quality impacts attributable to NO_x and NH_3 emissions resulting from private road transport based on ammonia. The population exposure to $PM_{2.5}$ from NO_x and NH_3 emissions from ammonia-fueled passenger vehicles has been estimated at approximately 23 000 to 250 000 premature mortalities and 5 100 to 9 700 premature mortalities for ammonia engines without and with SCR post-combustion techniques, respectively. This clearly shows the potential of SCR to substantially decrease both the NO_x and NH_3 emissions, and therefore air quality impacts.

However, in general, the values are significantly higher than the 4 850 (95% CI: [3400 - 6800]) estimation for the current petroleum-based passenger car fleet (of the year 2011 in the USA). Therefore, it can be concluded that, the current developments in ammonia-fueled engines cause a significantly higher total $PM_{2.5}$ population exposure impact in the US than the petroleum-based equivalent of the road transportation sector.

Furthermore, since the air quality impacts are dependent on the location of emissions, the $PM_{2.5}$ population exposure impact from the introduction of ammonia-fueled vehicles will be the largest in the states of New York and California, where there is a high population density in urban areas. Conversely, in states with a significant amount of rural areas with low population density, the impacts of both sectors will be similar, demonstrating potential for ammonia-fueled vehicles.

2. Recommendations

During this thesis, a number of interesting ideas and additional tasks have been identified that were left unexplored. This section briefly describes points for future research.

- **Estimating air quality impacts for ammonia vehicles for present day use**
  Firstly, it is interesting to extend this research to obtain more recent air quality impacts to give a more accurate estimation of the potential of using ammonia as a fuel. The factors influencing sensitivities (specifically US population, background emissions and meteorology) have considerably changed since 2011.

  This can be done using scaling/projection factors, as was done in Dedoussi et al. (2020), or running the adjoint of GEOS-Chem for more recent values of adjoint sensitivities.

  In Dedoussi et al. (2020), the 2011 response was used to calculate total impacts for 2018 by using the US population growth. The results showed a significant decrease in the impacts of the onroad sector from 2011 to 2018, with decreasing mortalities due to NO_x and SO_2 but increasing mortalities due to NH_3 emissions. Taking these trends into account, the importance of minimizing the NH_3 emission factor, as compared to NO_x, has significantly increased since 2011. This demonstrates the significance of studying the air quality impacts for present-day atmospheric conditions and make projections for the impacts measured in future years because ammonia as a fuel could be more harmful than we envision.

- **Incorporating emissions resulting from future ammonia engine developments**
  Furthermore, research on ammonia engine developments is continuously advancing. This study could be extended when more values of ammonia engine emission factors (also for different vehicle categories such as buses or heavy trucks) are available. Conducting this analysis for other vehicle categories could confirm the hypothesis that there is a high potential for using ammonia for long-distance travel routes for heavy trucks.

- **Studying the monetary cost of introducing ammonia as a fuel for road transportation**
  This study can also be extended with calculating the monetary cost associated with introducing an ammonia-fueled fleet. For example, in Barrett et al. (2015) the increase in premature mortalities is monetized using the value of statistical life (VSL) which is an estimate of monetary value of changes in mortality risk. As well as this, the cost of introducing an ammonia-fleet could be included to give a bigger picture of the investment that an ammonia-fueled sector would encompass.

- **Studying air quality and health impacts in Europe**
  Moreover, this study focuses on the USA, because there is readily available spatial adjoint sensitivities for this area, taken from Dedoussi et al. (2020). However, it would also be interesting to evaluate the impact of using ammonia as a fuel for vehicles in Europe since a unit of emissions has different health impacts with respect to the emission location. In Europe, a unit of emissions has a higher global health impacts compared to a unit of fuel burn mass over North America (Quadros et al., 2020). Moreover, there is a number of differences between the USA and European continents (vehicle population, activity, population distribution and density, other anthropogenic activity, air quality emission limits). It is interesting to note that there are currently no emission standards regulating NH_3 vehicle emissions except for Euro VI standards for heavy duty diesel vehicles (Suarez-Bertoa et al., 2014). The emissions and the corresponding impact of using ammonia-fueled vehicles in Europe and the USA can be compared. The emissions from replacing conventional vehicles with their ammonia-equivalent can be used to check the compliance of Euro VI standards with ammonia fueled heavy trucks. New policy recommendations for ammonia emissions (for other vehicle categories) for Europe could also be an interesting extension of this study.

- **Extending the trade-off study by incorporating more factors**
  In the future, the trade-off study can be expanded to include additional parameters related to engine and fuel characteristics. For example, we could set up emission tradespace tools to assess the emissions resulting from varying percentages of ammonia in the fuel, engine power ratings, and specific fuel consumption, and trade those parameters off against the air quality impacts in the United States.

  Furthermore, the trade-off study could also be extended by estimating the radiative forcing (RF) associated with non-CO_2 emissions from ammonia-fueled engines or CO_2 emissions from dual fuel ammonia configurations. This would enable the evaluation of climate benefits in relation to the air quality impacts of using ammonia as a fuel in road transportation, based on the optimization conducted for aviation in Grobler et al. (2019). By considering these factors, a more comprehensive ammonia engine design map could be created to optimize the reduction of air quality impacts from emissions and further explore the potential of using ammonia as a fuel.

A
Appendix

This chapter serves as a the appendix to the journal article presented in chapter 2. It includes important supporting materials that were not included in the article but are necessary for a comprehensive understanding of the research.

1. Emission rate look-up tables

The U.S. Environmental Protection Agency (EPA) uses the SMOKE-MOVES modelling framework for regional air quality modelling. The EPA's MOtor Vehicle Emission Simulator (MOVES) model generates emission rate ("look-up") tables for a number of emission processes, vehicle types, road types, temperatures, speeds, hour of day etc. The RPD and RPV look-up tables are used in this analysis and the emission processes included in the emission factors are described in Table A.1. For more information on the data stored in the look-up tables see EPA (2017).

Table A.1: Overview of emission processes for MOVES look-up tables (EPA, 2017)

MOVES Lookup Table	Emissions Process	Units
RatePerDistance (RPD)	Running Exhaust Crankcase Running Exhaust Tire Wear Brake Wear On-road Evaporative Permeation On-road Evaporative Fuel Leaks On-road Evaporative Fuel Vapor Venting	grams/mile
RatePerVehicle (RPV)	Start Exhaust Crankcase Start Exhaust Off-network Evaporative Permeation Off-network Evaporative Fuel Leaks Crankcase Extended Idle Exhaust Extended Idle Exhaust	grams/vehicle/hour

2. Additional emissions and air quality impact results

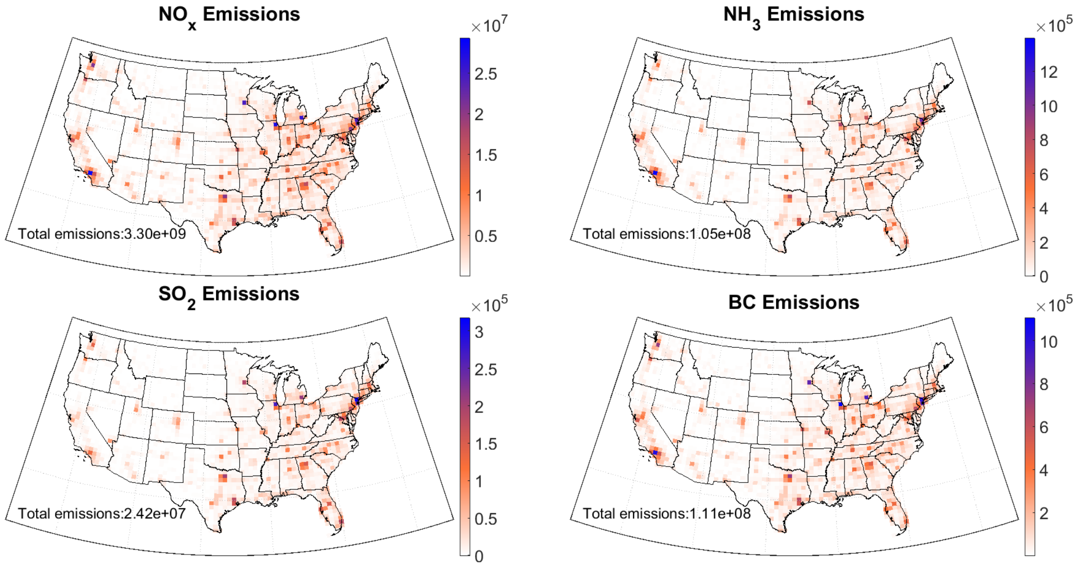

Figure A.1: Total annual NO_x, NH_3, SO_2 and BC emissions from conventional road transport (2011) [in kg]

Table A.2: Emissions and impacts results

Metric	Source	NO_x	NH_3	SO_2	BC
Emissions [Tg]	This study	3.28	0.10	0.02	0.11
	Dedoussi et al (2020)	3.49	0.11	0.03	0.12
	%	94.0	97.4	95.1	88.9
Impacts [premature mortalities]	This study	8547	5951	50	3140

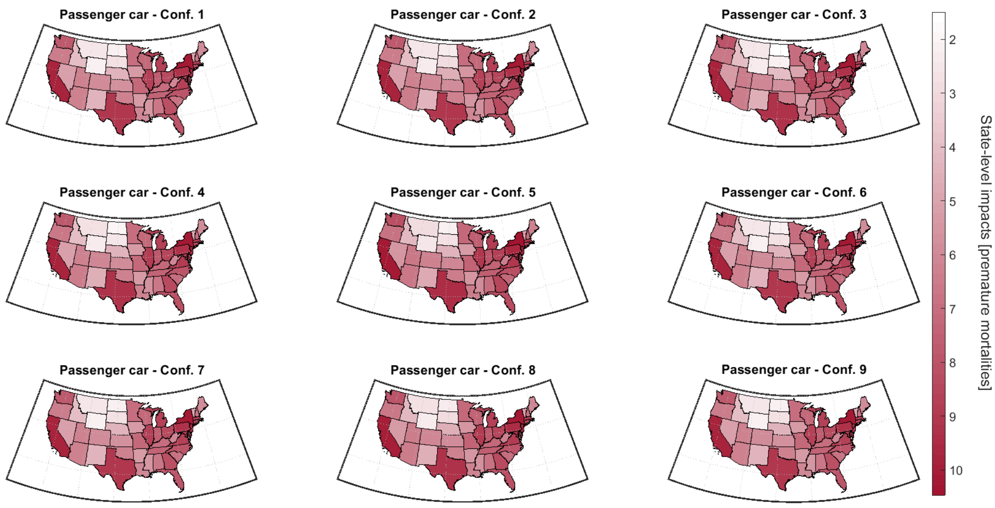

Figure A.2: Logarithmic representation of annual total impacts from NO_x and NH_3 emissions: comparison between conventional private road transport and the ammonia-fueled equivalent (based on 9 configurations from (Boero et al., 2023)) for 2011. Impacts expressed in premature mortalities

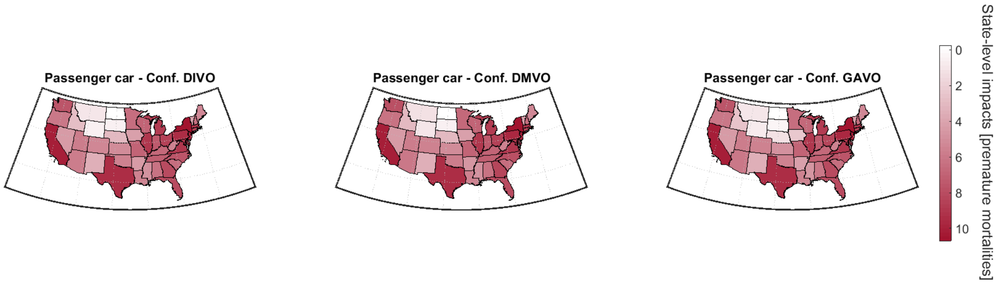

Figure A.3: Logarithmic representation of annual total impacts from NO_x and NH_3 emissions: comparison between conventional private road transport and the ammonia-fueled equivalent (based on 3 different fuel composition configurations from Angeles et al. (2017)) for 2011. Impacts expressed in premature mortalities

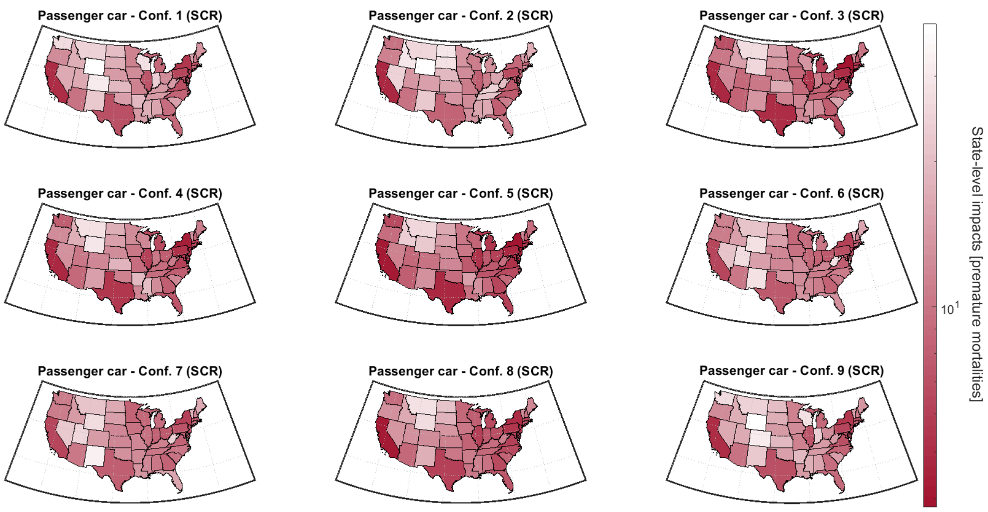

Figure A.4: Logarithmic representation of annual total impacts from NO_x and NH_3 emissions: comparison between conventional private road transport and the ammonia-fueled equivalent with SCR technology (based on 9 configurations from Boero et al. (2023)) for 2011. Impacts expressed in premature mortalities

B

Supporting Materials

This appendix includes supplementary materials that may not directly contribute to the research findings but are considered important to be included. These materials provide additional context and information related to the study, enhancing the overall understanding of the topic.

1. Ammonia engine developments

The properties and most recent developments in ammonia engine technology are discussed in this section.

1.1. Ammonia properties

Ammonia is a suitable fuel for road transport as it can be directly combusted in internal combustion engine (ICE) vehicles or applied in fuel cell (FC) vehicles. Pure ammonia has a narrow flammability range and a low laminar burning velocity (LBV) (as demonstrated in Table B.1), the combined effect of which, can lead to incomplete combustion in ICEs.

Table B.1: Comparison table of ammonia and other fuel properties

Fuel	Ammonia (NH_3)	Hydrogen (H_2)	Methane (CH_4)	Gasoline (C_8H_{18})
Density [kg/m^3]	603	71	162	698 (Reiter and Kong, 2011)
Volumetric energy density [MJ/L]	11.5	4.8	9.7	32.0 (?)
Lower heating value [MJ/kg]	18.80	120.00	50.05	42.5 (Linstrom and Mallard, 2001)
Adiabatic flame temperature [K]	1850	2483	2223	2411 (Linstrom and Mallard, 2001)
Laminar burning velocity [m/s]	0.07	3.51	0.38	0.34 (?)
Auto-ignition temperature [K]	930	773-850	859	573 (Zamfirescu and Dincer, 2009)
Minimum ignition energy [mJ]	8.000	0.011	0.28	0.8 (Kobayashi et al., 2019)

To improve the combustion performance of ammonia it can be used as a component of dual-fuel mixes with more reactive fuels such as gasoline, diesel, acetylene, butane, liquefied natural gas (LNG), liquefied petroleum gas (LPG), Dimethyl ether (DME) and hydrogen (Reiter and Kong, 2011; Ryu et al., 2014; Gross and Kong, 2013; Frigo and Gentili, 2013).

1.2. Emissions from ammonia engines

Mixing ammonia with more reactive fuels could result in carbon emissions (in case of carbon-based fuels) or increased (unburned) ammonia (NH_3), and nitrogen oxides $(NO)_x$ due to the presence of additional reactive nitrogen. Research shows a large variability in NO_x and NH_3 engine-out emissions for different power ratings, fuel compositions and engine types, see Figure B.1 and Figure B.2.

Engine tests are mainly concerned with studying the underlying chemistry of ammonia combustion technology and optimizing combustion performance, therefore, they are carried out in various operating conditions and experimental set-ups. The results from engine tests are documented with varying units and levels of detail, with some emission species results not measured or not mentioned in research papers. Moreover, most tests are carried out on Cooperative Fuel Research (CFR) engines or on laboratory engine benches with stable thermal conditions (Mounaïm-Rousselle and Brequigny, 2020). This makes it easier to compare results from experiments but it is not very representative of the on-road conditions for real-life vehicles which would therefore have different emissions.

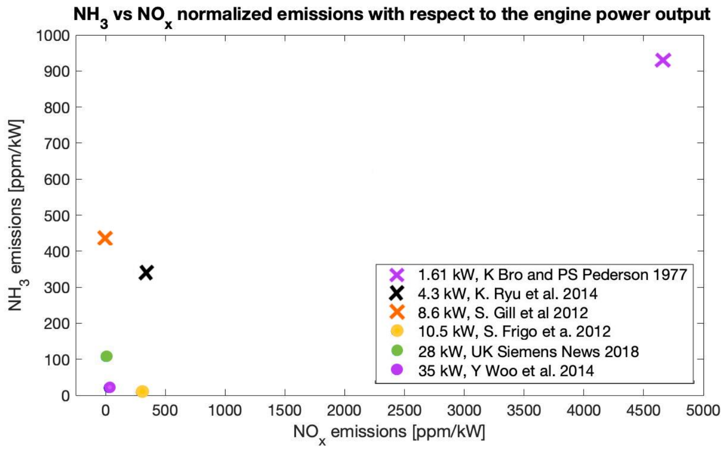

Figure B.1: NH_3 vs NO_x emissions per unit of power output for SI engines (circles) and CI engines (crosses)

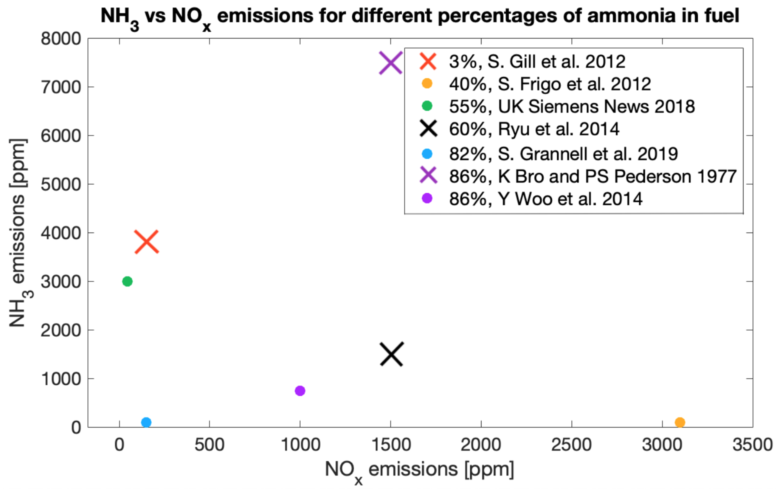

Figure B.2: NH_3 vs NO_x emissions for different ammonia fuel contents for SI engines (circles) and CI engines (crosses)

There is a lot of ongoing work on ammonia engine combustion performance therefore we expect to see the emergence of new emission factors (in g/km) as the ammonia engine technology further matures (for example for applications in different vehicle categories). The main conclusion from engine research is that NO_x and NH_3 emission species follow opposite trends with respect to combustion parameters such as operating temperature and equivalence ratios (Valera-Medina et al., 2021). This highlights the necessity to trade-off NO_x and NH_3 emissions, taking into account the air quality impacts of both these emission species which has been the focus of the thesis work. An important role in the trade-off of emissions is played by post-combustion treatment technologies which modify engine-out emissions, potentially contributing to the reduction in human health impacts.

1.3. Methods of reducing exhaust emissions

As was previously described, ammonia-fueled vehicles mainly produce NO_x emissions and unburned ammonia. However, various post-combustion technologies exist that reduce harmful exhaust emissions from road transportation vehicles which could also be applied to ammonia-fueled engines (currently no dedicated post-combustion system exists for ammonia combustion).

In practice, most of the post-combustion technologies focus on reducing NO_x emissions, and by doing so, produce ammonia. Ammonia emissions mainly originate from diesel vehicles equipped with a selective catalytic reduction system (SCR) (Desrochers, 2013) and gasoline vehicles equipped with a three-way catalyst (TWC) (Bishop and Stedman, 2015; Granger and Parvulescu, 2011). In engines with TWC the maximum NO_x reductions occur at slightly rich air-fuel ratios, which are also the conditions for the highest ammonia emissions in TWC (Thiruvengadam et al., 2016). This highlights the need to trade-off emission species, even when using post-combustion techniques.

So far for ammonia engines, Westlye et al. (2013) proposed to utilize a SCR catalyst for an ammonia-hydrogen dual fuel SI engine to reduce the resulting exhaust NO_x emissions. As well as this, the emission reduction potential of ammonia engines with V-based catalysts (V_2O_5,WO_3,TiO_2), Fe-exchanged zeolites and Cu-exchanged zeolites was investigated in Boero et al. (2023). The results showed that the after-treatment systems have a high effect on reducing the NO_x and NH_3 emissions, on average approximately -97% and -75%, respectively. For some engine configurations, however, higher N_2O emissions were observed with the use of SCR technology.

It is therefore interesting to take into account the effects of emission reducing mechanisms when trading off exhaust emissions from ammonia engines.

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