

# Clearing the air

Air quality modelling for policy support

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Clearing the air

– Air quality modelling for policy support

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# Clearing the air

Air quality modelling for policy support

## De lucht geklaard

(met een samenvatting in het Nederlands)

### PROEFSCHRIFT

ter verkrijging van de graad van doctor  
aan de Universiteit Utrecht  
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Prof.dr. M. Schaap

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## SUMMARY

**T**HE STUDIES PRESENTED in this thesis were performed to provide policy makers with more accurate information about the sources of air pollution and the possible consequences of future developments on air quality. This enables policy makers to make better informed decisions when formulating policies that have consequences for air quality.

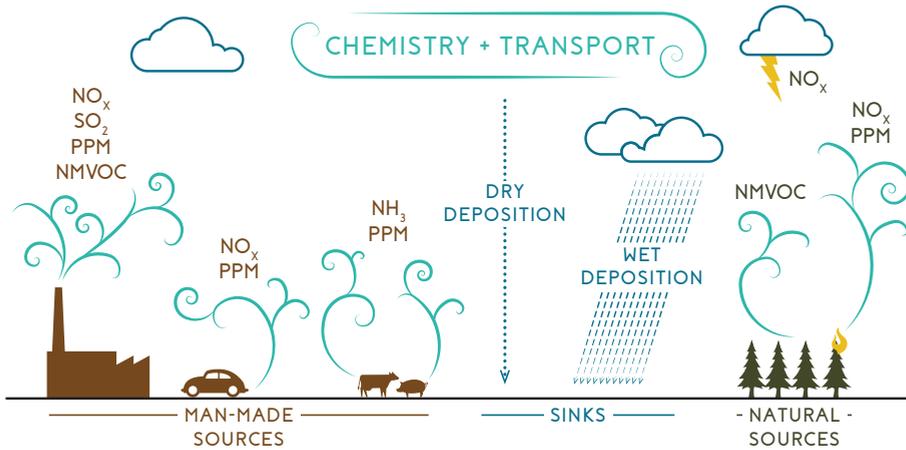
### Harmful effects and sources of air pollution

Exposure to outdoor air pollution is the most deadly environmental problem in the world, contributing to 3.7 million deaths each year globally<sup>†</sup>. This is caused by several different air pollutants, of which particulate matter (PM) is by far the most important. The gaseous substances nitrogen dioxide and ozone also cause widespread health damage. Ecosystem damage and biodiversity loss due to air pollution occur when excessive amounts of a substance are deposited on sensitive ecosystems. Ozone deposition causes damage to plants and deposition of substances containing nitrogen and sulphur makes soils less suitable for sensitive plants to grow on. In addition, ozone and particulate matter also play a role in climate change.

Considering the wide range of severe environmental problems caused by air pollution, there is plenty of reason to attempt to control and reduce (exposure to) it. To do this effectively, we need to know the sources, sinks and levels of air pollution. Important sources of air pollution are industry, transport, residential combustion and agriculture. Some sources (industry and traffic, for example) emit mostly nitrogen oxides (NO<sub>x</sub>) and primary particulate matter (PPM), while agriculture is the single largest source of ammonia (NH<sub>3</sub>) emissions. Once emitted, these substances undergo atmospheric transport and chemical reactions, forming other air pollutants. Ozone is not directly emitted but produced from nitrogen oxides and volatile organic compounds, of which traffic and industry are important sources. Nitrogen oxides and sulphur dioxide (SO<sub>2</sub>) can react with ammonia, forming particulates called secondary inorganic aerosol (SIA). Air pollutants are removed from the atmosphere by dry and wet deposition. A schematic representation of the most important sources and sinks of air pollutants is shown in figure [s1.1](#).

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<sup>†</sup>WHO, *Review of evidence on health aspects of air pollution – REVIHAAP project*, WHO Regional Office for Europe, Copenhagen, Denmark (2013).



**Figure s1.1:** Schematic representation of emission sources, atmospheric processes and sinks of air pollutants. The air concentration of a substance is a balance between its sources (emissions and chemical reactions) and sinks (chemical reactions and deposition). The three main factors determining the concentration of a substance are the emissions, the meteorology and land use. NMVOC is short for non-methane volatile organic compounds, PPM for primary particulate matter.

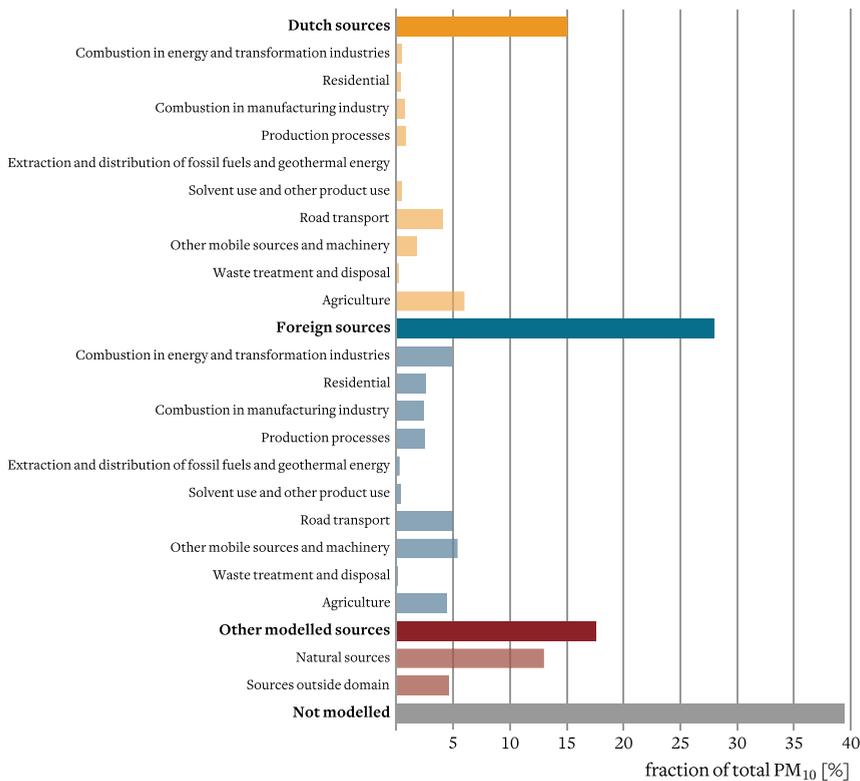
## Air quality research

Measurements of air pollutant concentrations, which can be ground-based or from a satellite, provide crucial information to monitor and research air quality. Computer models are another important tool to investigate air pollution, its sources and its sinks. Modelling of air quality at the national, regional and continental scale is often done using chemistry transport models. These models aim to calculate the complete range of processes that air pollutants undergo in the atmosphere. The air quality model LOTOS-EUROS is the instrument that I used in all my studies. Air quality models are the tool most suited to study possible future scenarios to assess for example the potential effects of a policy intervention or climate change on air quality.

## Air quality modelling for policy support

My thesis consists of four studies driven by policy questions. In chapter 2 I look into the origin of particulate matter concentrations in the Netherlands. I track emissions from the ten main economic sectors, separating Dutch and foreign sources, to arrive at a source attribution of particulate matter. Of the modelled  $\text{PM}_{10}$  in the Netherlands,

about 25 % comes from natural sources such as sea-salt and wind-blown dust. The remaining 75 % is of man-made origin, one third of which has sources inside the Netherlands. Transport (road and non-road) and agriculture are by far the two largest Dutch source sectors. The sector-specific source attribution of  $PM_{10}$  is shown in figure s1.2. During periods with high PM concentrations, the contribution of foreign sources becomes more important, emphasising the need for international cooperation in reduction strategies for PM. The source attribution is based on model results only, and LOTOS-EUROS captures only about 60 % of the measured concentrations. This is mainly caused by a strong underestimation of the concentration of organic carbon particles. Reducing the missing mass is an important step to improve the source attribution of PM.



**Figure s1.2:** Origin of  $PM_{10}$  in the Netherlands for 2007–2009 as modelled by LOTOS-EUROS. The contributions from Dutch and foreign sources are specified by economic sector.

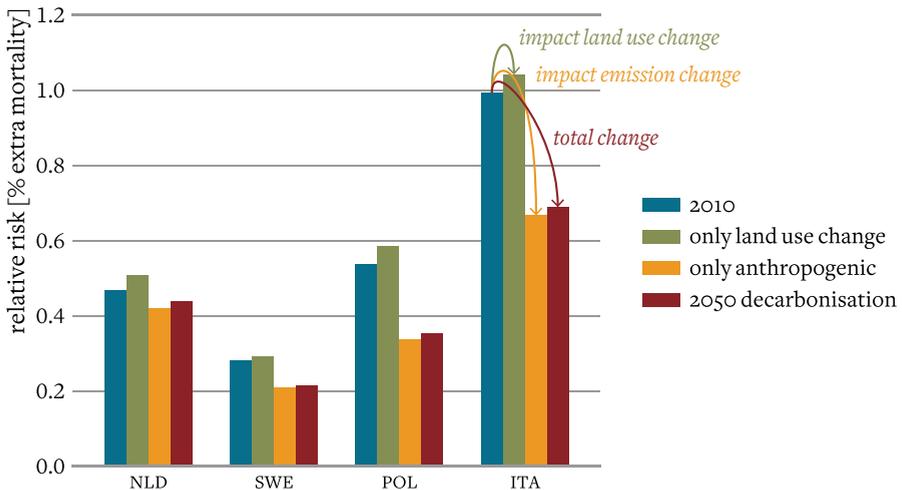
In chapter 3, ammonia in Flanders is in focus. Flanders has a large agricultural sector and therefore considerable ammonia emissions, which contribute to secondary inorganic aerosol formation. Emissions of ammonia are highly variable and weather-dependent, and their representation in LOTOS-EUROS did not reflect this well. I use ma-

nure transport data as a way to estimate the temporal variability of ammonia emission from manure application. I investigate whether using this approach in LOTOS-EUROS leads to an improvement in the modelling of ammonia and secondary inorganic aerosol. It turns out that this approach strongly improves the agreement between observations and model outcome for ammonia, but has no effect for secondary inorganic aerosol. In this study I also test whether restricting manure spreading shortly before and during a period with high particulate matter concentrations is an effective way to reduce particulate matter concentrations during these episodes. I conclude that this is not the case: the reduction in particulate matter concentration that is achieved by reducing ammonia emissions just before and during an episode is rather small compared to the total concentration during these episodes. This does not mean that reducing ammonia emissions is not important to bring down PM concentrations in spring. Rather, more long-term reductions over a larger region are probably needed.

Chapters 4 and 5 investigate possible consequences of energy transitions for air quality. During the envisaged energy transition from fossil fuels to renewable alternatives there is likely a phase in which fossil fuel energy production will be mainly used to provide backup capacity. This implies that the temporal variability of emissions from these power plants will change, which might have an impact on the concentrations of pollutants emitted by these power plants. The effect of this projected shift in emission timing on air pollutant concentrations is assessed in chapter 4. For all components of particulate matter that I consider, the air concentrations are higher than expected based on the emission change. This effect is found because the power plants are more likely to operate during stagnant weather conditions and during nighttime in this transition phase, as these are the times when solar and wind energy are not available. In stagnant weather, air pollution is much less effectively transported and diluted than under more dynamic conditions. The outcomes of this study show that emission timing is an important aspect to look into when trying to assess the impacts of system changes on air quality.

In chapter 5, I focus on ozone and how its concentrations and related damage to health and ecosystems will change under realistic future energy and air quality scenarios. Bio-energy is expected to become a more important energy source than it is today, which implies that the production of biomass for energy needs to be increased. This causes a change in land use. In this work the effects of land use change as well as changes in man-made emissions are taken into account. An increased production of biomass caused by EU energy policy is expected to cause an increase in ozone damage, but this effect turns out to be only marginal compared to the reduction of ozone damage because of reduced ozone precursor emissions in other sectors. The combined effect of land use change and emission reduction is a significant reduction in health damage due to ozone, especially in southern Europe. Figure s1.3 shows the effect of the different changes regarded

in this study on health damage due to ozone. The figure shows the risk of mortality due to ozone damage relative to all-cause mortality. It illustrates that changes in man-made emissions determine the final outcome more than land-use change. When I include the effects of a warming climate (2 to 5 °C warming across Europe in summer) modelled ozone concentrations increase, so much so that the health damage from ozone might actually *increase* towards 2050 despite the strong reduction in ozone precursor emissions.



**Figure s1.3:** Decomposition of relative risk of mortality from ozone health damage for a few example countries (the Netherlands (NLD), representative for north west Europe; Sweden (SWE), representative for Scandinavia; Poland (POL), representative for central Europe; Italy (ITA), representative for the Mediterranean region. Note that the impact of climate change on ozone health damage is not included in this figure.

## Outlook

Air pollution is truly a multi-faceted and transboundary problem that requires international cooperation to solve. Air quality modelling is a valuable tool to explore the effects of possible policy interventions to reduce air pollution, but also the unintended impacts of other developments. To provide effective policy advice it is important to couple model expertise with knowledge about emission processes and observations of air pollutants.

While there is still enough to be done in Europe to reduce the harmful impacts of air pol-

lution on humans and ecosystems, a much larger challenge lies in developing countries. In China and India for example, the fast economic development has caused immense problems with air quality leading to widespread health and ecosystem damage. While these countries can benefit from the experience in reducing harmful emissions obtained over the years in Europe and the United States, there are also new questions specific to each country. To address these effectively, more information about the rapidly changing emissions in developing countries is needed and observation networks need to be established or expanded to monitor air pollution. Deploying a network of ground-based observation sites with high-quality data can take a long time and is expensive. Satellite observations therefore become of great added value for emerging economies in the monitoring of emissions as well as ambient concentrations. Combining ground-based measurements, satellite observations and air quality modelling expertise with local knowledge about emission sources is crucial to enable more effective policy support in developing countries.

## SAMENVATTING

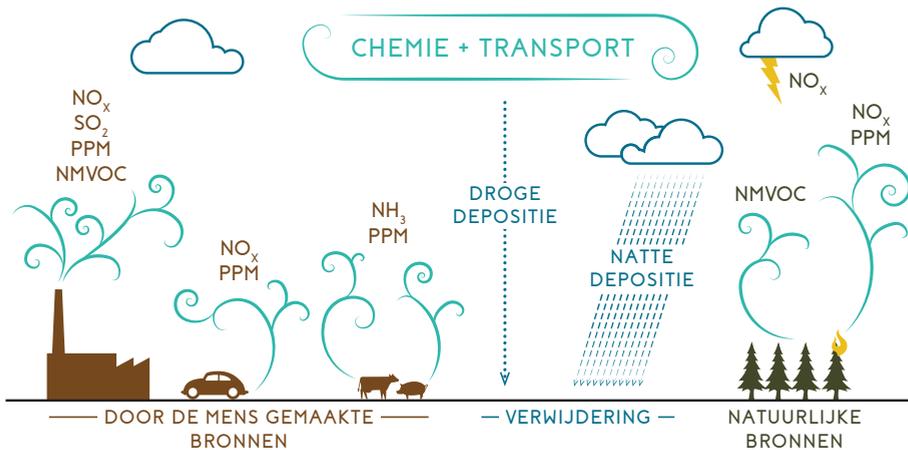
**D**IT PROEFSCHRIFT BEVAT onderzoek dat als doel heeft beleidsmakers te ondersteunen met betere informatie over de bronnen van luchtvervuiling en mogelijke toekomstige ontwikkelingen in luchtkwaliteit. Met dit soort informatie kan gerichter beleid geformuleerd worden om luchtvervuiling te verminderen of tegen te gaan.

### Waarom is luchtvervuiling een probleem?

Elk jaar sterven naar schatting 3,7 miljoen mensen ter wereld mede door blootstelling aan vervuilde buitenlucht<sup>†</sup>. Er zijn verschillende stoffen in de lucht die gezondheidsschade veroorzaken, waarvan fijnstof met afstand de dodelijkste is. Ook gasvormige luchtvervuiling zoals stikstofdioxide en ozon veroorzaakt gezondheidsschade. Vervuilende stoffen kunnen letterlijk uit de lucht komen vallen. Wanneer bepaalde vervuilende stoffen vanuit de lucht op gevoelige ecosystemen terecht komen, veroorzaakt dit schade aan het ecosysteem en vermindert het de biodiversiteit. Luchtvervuiling die stikstof of zwavel bevat, maar ook ozon, zorgt voor deze schadelijke depositie. Daarnaast spelen luchtvervuilende stoffen als ozon en fijnstof een rol in klimaatverandering.

Er is dus reden genoeg om een poging te doen luchtvervuiling te beteugelen en de blootstelling eraan te verminderen. Om dit effectief te doen, moeten we weten waar de vervuiling vandaan komt en wat ermee gebeurt als het eenmaal in de lucht zit. Belangrijke activiteiten die de uitstoot van luchtvervuilende stoffen veroorzaken, zijn bijvoorbeeld industrie, transport, landbouw en activiteit in huishoudens. Sommige sectoren (bijvoorbeeld industrie en transport) stoten voornamelijk stikstofdioxide ( $\text{NO}_x$ ) en fijnstof (PM) uit, terwijl bijvoorbeeld landbouw met afstand de grootste bron van ammoniak ( $\text{NH}_3$ ) in de lucht is. Als deze stoffen eenmaal in de lucht zijn aanbeland, worden ze door de lucht getransporteerd en kunnen ze reageren met andere stoffen in de atmosfeer. Hierbij kunnen andere typen luchtvervuilende stoffen ontstaan. Ozon is het belangrijkste voorbeeld van een stof die niet direct wordt uitgestoten, maar in de atmosfeer wordt gevormd door reacties van andere stoffen. Stikstofdioxide en zwaveldioxide ( $\text{SO}_2$ ), afkomstig uit bijvoorbeeld verkeer en energiecentrales, kunnen reageren met ammoniak uit landbouw, waarbij deeltjes gevormd worden die secundair inorganisch aerosol (SIA) genoemd worden. Dit is één van de componenten van fijnstof. Uiteindelijk komt alles wat naar de lucht wordt uitgestoten ook weer naar beneden in een proces dat we depositie noemen. Al deze processen zijn samengevat in figuur S2.1.

<sup>†</sup>WHO, *Review of evidence on health aspects of air pollution – REVIHAAP project*, WHO Regional Office for Europe, Copenhagen, Denemarken (2013).



**Figuur s2.1:** Schematische weergave van bronnen van luchtvervuiling, de atmosferische processen die de stoffen ondergaan en manieren waarop luchtvervuiling weer uit de lucht verdwijnt. De concentratie van een stof in de lucht is een evenwicht tussen de bronnen (uitstoot en chemische reacties) en verwijdering (chemische reacties en depositie). NMVOC staat voor vluchtige organische stoffen, exclusief methaan. PPM staat voor primair fijnstof.

## Onderzoek naar luchtkwaliteit

Zonder metingen van de concentratie van vervuilende stoffen in de lucht zouden we de luchtkwaliteit niet kunnen in de gaten kunnen houden en zouden we cruciale informatie missen die nodig is om onderzoek te doen naar luchtvervuiling. Zowel metingen van observatiestations op de grond als satellietobservaties geven belangrijke informatie. Computermodellen zijn ook belangrijke instrumenten in (beleidsgericht) onderzoek naar luchtvervuiling. Een veelgebruikt type model is het zogenaamde chemie-transportmodel, dat alle atmosferische processen doorrekent. Dit type computermodel is onder andere zeer geschikt om verschillende toekomstscenario's door te rekenen om te zien wat het effect van een beleidsmaatregel of bijvoorbeeld klimaatverandering op de hoeveelheid vervuiling in de lucht is. Voor al het onderzoek in dit proefschrift heb ik gebruik gemaakt van het chemie-transportmodel LOTOS-EUROS.

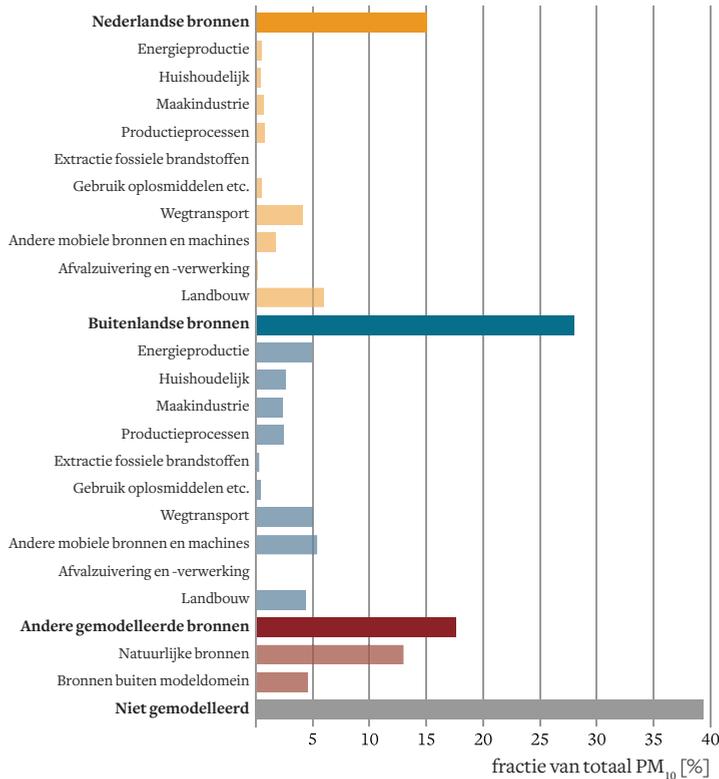
## Luchtkwaliteitsmodellering voor beleidstoepassingen

In dit proefschrift zijn vier onderzoeken gebundeld, die allen gedreven zijn door een beleidsvraag. In hoofdstuk 2 onderzoek ik de herkomst van fijnstof in Nederland. Met een speciale module in het LOTOS-EUROS-model volg ik emissies van de tien belangrijk-

ste economische sectoren door het model, waarbij ik ook Nederlandse en buitenlandse bronnen apart bekijk. Dit levert een beeld op van wat de belangrijkste bronnen van fijnstof zijn. Ongeveer een kwart van het gemodelleerde fijnstof in Nederland is afkomstig van natuurlijke bronnen, zoals zeezout en opwaaiend stof. De rest wordt veroorzaakt door uitstoot bij menselijke activiteiten en een derde hiervan komt uit Nederland. Transport (zowel wegverkeer als treinverkeer en scheepvaart) en landbouw zijn met afstand de belangrijkste twee bronnen van fijnstof in Nederland. De totale brontoekenning van fijnstof in Nederland is weergegeven in figuur s2.2. Wanneer het totale fijnstofniveau hoog is, wordt de bijdrage van buitenlandse bronnen relatief belangrijker. Dit laat zien dat internationale samenwerking belangrijk is in het terugdringen van te hoge fijnstofconcentraties. Deze brontoekenning is gebaseerd op de gemodelleerde fijnstofconcentraties, die de werkelijke concentraties sterk onderschatten. De belangrijkste reden hiervoor is dat het model de concentratie van organische koolstof bevattende deeltjes in de lucht sterk onderschat. De verbetering van het model zodat een groter deel van de fijnstofconcentratie daadwerkelijk gemodelleerd wordt, is een belangrijke stap om de kwaliteit en bruikbaarheid van dit soort brontoekenningstudies te vergroten.

In hoofdstuk 3 kijk ik naar ammoniak in Vlaanderen. In Vlaanderen is veel landbouwactiviteit en als gevolg hiervan een hoge ammoniakuitstoot. Ammoniak draagt bij aan de vorming van secundair fijnstof. Hoeveel ammoniak uitgestoten wordt, verandert sterk door de dag en het jaar, en er is een grote weersafhankelijkheid. In LOTOS-EUROS wordt deze variabiliteit echter niet goed weergegeven. In dit onderzoek gebruik ik gegevens van mesttransporten om de tijdsverdeling van ammoniakuitstoot als gevolg van het uitrijden van mest te benaderen. Het gebruik van deze tijdsverdeling in LOTOS-EUROS levert een grote verbetering in de modellering van ammoniakconcentraties op, maar de modellering van fijnstof verbetert niet. Ik heb ook getest of een verbod op het uitrijden van mest vlak voor een periode met hoge fijnstofniveaus een goede manier is om de fijnstofconcentraties in deze periodes te verlagen. Dat blijkt niet het geval: de fijnstofconcentraties dalen wel een beetje, maar niet genoeg om een relevante bijdrage te leveren aan het verminderen van de te hoge fijnstofconcentraties. Dit betekent niet dat het terugdringen van de ammoniakuitstoot niet leidt tot lagere fijnstofconcentraties in de lente, maar dat waarschijnlijk substantiëlere reducties over een langere tijd en een groter gebied nodig zijn om fijnstofniveaus serieus te verlagen.

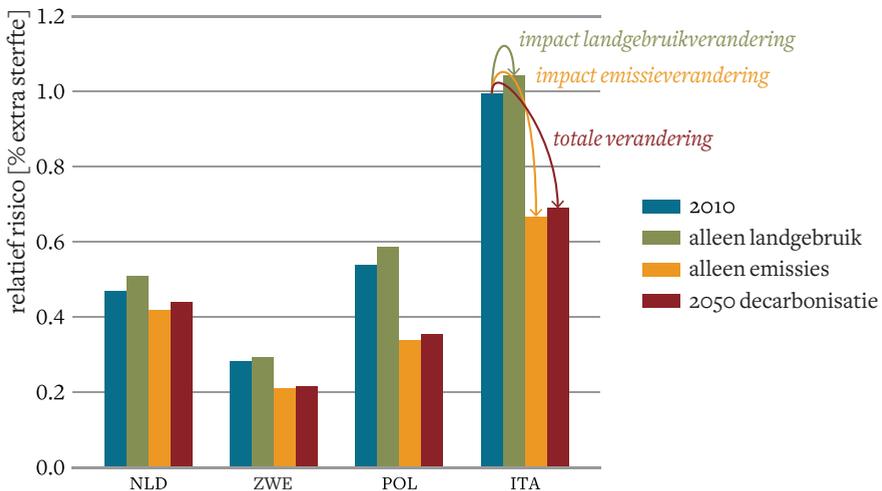
Hoofdstukken 4 en 5 behandelen mogelijke gevolgen van een energietransitie voor luchtvervuiling. In de overgangperiode van fossiele naar hernieuwbare bronnen van elektriciteit is er een fase dat beide elektriciteitsbronnen belangrijk zijn. In deze periode zullen fossiele energiecentrales niet meer zoals nu fluctueren met de energievraag, maar vooral actief zijn als er weinig zon en wind is om elektriciteit op te wekken. Dit betekent dat de momenten waarop deze sector verontreinigende stoffen uitstoot, zul-



**Figuur s2.2:** Herkomst van fijnstof in Nederland voor de jaren 2007–2009 gemodelleerd met LOTOS-EUROS. De bijdrages van Nederlandse en buitenlandse bronnen zijn uitgesplitst per economische sector.

len veranderen. Hierdoor kunnen de concentraties van vervuilende stoffen in de lucht veranderen. In hoofdstuk 4 bekijk ik hoe groot het effect van deze andere tijdsverdeling van de uitstoot kan zijn. Voor alle stoffen die ik bekijk in dit onderzoek, blijkt een verandering in tijdsverdeling invloed te hebben op de concentratie. De totale uitstoot door fossiele elektriciteitsproductie daalt (er is immers minder vraag naar elektriciteit uit fossiele bron), en ook de concentraties in de lucht gaan omlaag. De concentraties dalen echter niet zoveel als verwacht zou worden als je simpelweg kijkt naar de verandering in de totale uitstoot. Dit komt doordat de uitstoot vooral verschuift naar periodes waarin de atmosfeer stabiel is, zoals windstille winterdagen en zomernachten (momenten waarop geen zonne- of windenergie beschikbaar is). Dit soort omstandigheden zorgen ervoor dat vervuiling laag bij de grond blijft hangen en maar langzaam verdunt. Met dit onderzoek laat ik zien dat het belangrijk is aandacht te besteden aan een mogelijke verandering in de tijdsverdeling van uitstoot, wanneer men onderzoek doet naar de invloed van een structurele verandering in een sector op luchtvervuiling.

Ozon is het onderwerp van hoofdstuk 5. Ik bereken hoe de ozonniveaus en de bijbehorende gezondheids- en ecosysteemschade veranderen voor een paar realistische toekomstscenario's voor Europa. Hierbij focus ik op de effecten van luchtkwaliteits- en energiebeleid. Het EU-beleid gaat ervan uit dat er in de toekomst meer biomassa voor energieproductie gebruikt zal worden. Een deel van die biomassa zal in Europa zelf geteeld worden, wat een verandering in landgebruik zal veroorzaken (bijvoorbeeld: grasland wordt bomenplantage). Ik neem het effect van deze landgebruiksverandering en de verandering in uitstoot door andere bronnen mee in mijn berekening. Ik had verwacht dat de door EU-beleid veroorzaakte toename in het aantal biomassaplantages een grotere ozonschade zouden veroorzaken, maar dit effect blijkt verwaarloosbaar te zijn in vergelijking met de afname in ozonschade door de betere controle op uitstoot van andere sectoren. Deze twee effecten samen geven een sterke afname in gezondheidsschade door ozon, vooral in Zuid-Europa. Figuur s2.3 laat het effect van de verandering in landgebruik en emissieverandering op de relatieve sterfte (ten opzichte van totale sterfte) door ozonschade zien.



**Figuur s2.3:** Relatief sterfterisico als gevolg van hoge ozonconcentraties voor verschillende landen (Nederland (NLD), representatief voor Noordwest-Europa; Zweden (ZWE), representatief voor Scandinavië; Polen (POL), representatief voor Centraal-Europa; Italië (ITA), representatief voor de regio rond de Middellandse Zee). Het effect van klimaatverandering op ozonconcentraties is in deze figuur niet meegenomen.

Als ik echter ook het effect van een warmer klimaat meeneem in deze berekening (we liggen op koers voor een temperatuurstijging van 2 tot 5 °C in de zomer rond 2050) worden de gemodelleerde ozonconcentraties juist hoger. Dit effect is zo sterk dat het er-

voor kan zorgen dat de gezondheidsschade door ozon in 2050 zelfs hoger is dan op dit moment, ondanks de daling van de uitstoot van luchtvervuilende stoffen.

### **Wat brengt de toekomst?**

Luchtvervuiling is een veelkoppig monster met een letterlijk grensoverschrijdend karakter. Internationale samenwerking is dan ook nodig om de problemen rond luchtvervuiling op te lossen. Modelleren van de luchtkwaliteit is een belangrijk instrument om de effecten van mogelijke maatregelen om vervuiling terug te dringen te verkennen. Het beste beleidsadvies komt voort uit de verbinding van luchtkwaliteitsmodellen met kennis van de processen die de uitstoot bepalen en observaties van de luchtkwaliteit.

Hoewel er in Europa nog genoeg werk te doen is om de gezondheids- en ecosysteem-schade door luchtvervuiling terug te dringen, ligt de echte uitdaging in ontwikkelingslanden. In landen als China en India veroorzaakt de snelle economische groei enorme problemen met luchtvervuiling en daaraan gerelateerde sterfte. Voor een deel kunnen deze landen profiteren van de kennis die in Europa en de Verenigde Staten bestaat over hoe de uitstoot van vervuilende stoffen teruggedrongen kan worden, en hoe de voortgang bewaakt kan worden. Om echt effectief beleid te voeren in deze landen is echter ook lokale kennis cruciaal. Elk land heeft zijn eigen uitdagingen in termen van uitstootbronnen, die in snel ontwikkelende landen net zo vlug groeien als de economie. In deze landen is ook vaak een gebrek aan een dekkend netwerk van observatiestations voor luchtvervuiling dat nodig is om de voortgang te volgen. De opbouw van zo'n netwerk is een langdurige en prijzige aangelegenheid. Satellietobservaties kunnen dit gat voor een deel vullen, zowel op het gebied van het meten van de uitstoot in snel veranderende economieën als in het vaststellen van de concentraties luchtvervuilende stoffen. De combinatie van observaties vanaf de grond, het gebruik van satellietdata en luchtkwaliteitsmodelleren met lokale kennis over bronnen van luchtvervuiling is van groot belang voor de ondersteuning van luchtkwaliteitsbeleid in deze snel ontwikkelende landen.

# Introduction



**E**XPOSURE TO OUTDOOR air pollution is the fifth largest risk factor for premature death globally (Health Effects Institute, 2017), making it the most deadly environmental problem. The most important pollutants in terms of health damage are fine particulate matter, nitrogen dioxide and ozone. Apart from affecting human health, these and other substances also cause damage to ecosystems and play a role in climate change. Some air pollutants occur naturally in the atmosphere or are emitted from natural sources, but human activity is the main cause of air pollution. Which activities are the largest contributors to air pollution depends on the pollutant and impact under consideration. Many sources emit a variety of air pollutants and most pollutants have adverse effects in more than one way. All three impact categories mentioned before are affected by several pollutants.

Ground-based measurements of air pollutants, as well as satellite measurements, provide crucial information to monitor and research air quality. Air pollution, its sources and its sinks are also evaluated using computer models. Modelling of air quality at the national, regional and continental scale is often done using chemistry transport models (CTMs). These models explicitly calculate the complete range of processes – from emission via atmospheric transport and chemical conversions to dry deposition and rainout – for a range of air pollutants. One of the key benefits of modelling is that it can be used to explore future (policy) scenarios, providing valuable information on which policies could best be implemented to reduce air pollution. The air quality model LOTOS-EUROS is the instrument used to perform the research that is presented in this thesis. Two chapters focus on the improvement of knowledge on the sources of particulate matter: how much does each source contribute to the ground level concentration? The other two papers study the possible impact of energy transition scenarios on particulate matter and ozone; in the latter case, the influence of a changing climate is also assessed.

As an introduction to this thesis, the following section presents a historical overview of air pollution in Europe. This leads to a discussion on the adverse effects of air pollution that are at present the most relevant. After this, the most important sources and sinks of the different (precursors of) air pollutants are presented. This is followed by an introduction to current policy-relevant research on air quality, leading to my research questions.

## 1.1 History of air pollution in Europe

Problems with urban air pollution have existed since the development of large cities. In ancient Roman times, the burning of solid fuel for cooking and heating already caused unhealthy fumes with bad smell (Neumann, 1979). The city most known for its long history of air pollution however is London. This city experienced problems with air quality from the late Middle Ages onwards, as is clear from several (rather unsuccessful) attempts to ban mineral coal burning from 1273 onwards (Landsberg, 1981). By this time, Londoners were burning mineral coal instead of wood for heating and cooking, producing a lot of sulphurous smoke. Especially during stable and foggy conditions the fumes would not disperse, a phenomenon now known as winter smog. These problems persisted for centuries. However, because of the lack of another cheap fuel, bans on coal burning failed to make an impact. In 1661, John Evelyn wrote a pamphlet on ‘the Aer and Smoake of London’, in which he described the dangers of the fumes from coal burning including smell, health damage and the blackening and erosion of buildings (Landsberg, 1981). The industrial revolution kicking off in Britain only resulted in more coal burning, as it was the main fuel for factory furnaces and later for steam engines.

London was not the only city having trouble keeping its air clean. Similar problems with winter smog were common in Paris and, by the 1850s, in industrial cities like Manchester as well. The British Public Health Act of 1875 included legislation on industrial smoke but did nothing to curb the open coal hearths common in British households as this was perceived to limit the personal freedom of people (Brimblecombe, 2011). The number of severe smog episodes in Britain decreased because of the legislation targeting industry and because alternatives to coal became available for domestic heating. However, increasing urbanisation and industrialisation in Europe and the United States meant that urban air pollution problems started occurring in more and more cities.

It was clear that coal fumes could cause irritation of the eyes and throat, and the air during smog episodes was perceived as unhealthy. The toxicity of smog, however, was not understood well and it was perceived more a nuisance than a serious health risk. How dangerous air pollution could be only became clear from several serious incidents. In 1930, a sulphurous fog built up over the Meuse Valley in Belgium, widely causing respira-

tory problems and leading to over 60 deaths in three days (Nemery et al., 2001). In the United States, the so-called ‘killer smog’ episode in Donora in 1948 caused the deaths of nearly 40 people from asphyxiation, with about 6 000 of the 14 000 residents experiencing serious respiratory or cardiovascular problems (Schrenk et al., 1949). Steel and zinc industry close to the town caused toxic emissions. The 1948 episode was not caused by a toxic gas leak, it was just the ‘normal’ emission being trapped in the town because of unfavourable weather conditions.

In December 1952, an extreme cold spell hit London. This caused an increase of coal burning for heating coincident with very stable weather conditions, meaning that the pollution was not dispersed. The particulate matter (PM) and sulphur dioxide (SO<sub>2</sub>) levels increased to extreme levels, causing the deaths of over 4 000 people during and in the weeks after this episode (Brimblecombe, 2011). This episode strongly raised public and political awareness about the dangers of air pollution, leading to the first British Clean Air Act, which was put in place in 1956. This legislation included measures on domestic fuel burning as well as industrial pollution. In other countries, similar types of legislation were adopted. This was followed by a strong improvement of urban air quality, although whether the legislation is the main cause of the improvement is debated (Brimblecombe, 2011). Autonomous change in the fuel mix also contributed to a large extent to the reduction of air pollution.

In the 1950s and 1960s, air pollution shifted from an urban health problem to a large-scale environmental issue. An alarming decline of fish populations in Norwegian lakes was noticed in the 1950s, which was eventually linked to acid rain. While the phenomenon was already discovered in the 19<sup>th</sup> century, the large-scale effects of acid rain on terrestrial ecosystems and water bodies as well as buildings and statues only became clear in the second half of the 20<sup>th</sup> century (Gorham, 1998). Emissions of nitrogen and sulphur oxides (NO<sub>x</sub> and SO<sub>2</sub>, respectively) are oxidised in the atmosphere, forming nitric and sulphuric acid. These are removed from the atmosphere through dry and wet deposition, causing acidification of the receiving surfaces. In addition, deposition of ammonia and ammonium (NH<sub>3</sub> and NH<sub>4</sub>, respectively) also contributes to acidification because they are converted to nitric acid once they are in the soil.

The first EU Air Quality Directive was agreed on in 1980 and set limit values for ambient concentrations of smoke and SO<sub>2</sub> (EEC, 1980). The 1985 Helsinki Protocol on the Reduction of Sulphur Emissions was an international agreement to reduce sulphur emissions in order to protect vulnerable ecosystems from acid rain, and was followed by more ambitious reduction targets. Between 1980 and 2004, emissions of SO<sub>2</sub> in Europe were reduced by 73 %, and have been almost halved again since then (EEA, 2014c; Vestreng et al., 2007). Other large-scale environmental issues regarding air quality identified in the second half of the 20<sup>th</sup> century include depletion of the ozone layer (which was

addressed by the Montreal Protocol in 1987), ground level ozone and eutrophication of ecosystems because of nitrogen deposition.

In urban areas, meanwhile, the number of cars had been increasing steadily, resulting in new problems regarding air quality. The first issue to arise was that of lead, a toxic substance added to gasoline to reduce engine knock. Halfway the 1990s it was prohibited in Europe to sell gasoline containing lead. By the late 1980s a new smog phenomenon became more common in large cities with limited ventilation. This type of smog is caused by ozone formation due to high  $\text{NO}_x$  and non-methane volatile organic compound (NMVOC) levels, the main urban sources of which are traffic and solvent use. Since this reaction also requires sunlight, this pollution most often occurs in summer. It is therefore known as summer or photochemical smog. The 1999 Gothenburg Protocol on the abatement of acidification, eutrophication and ground level ozone was the first European effort to reduce problems regarding the latter two. In this protocol and the 2001 EU Emission Ceilings Directive (EC, 2001), emission ceilings for sulphur dioxide, nitrogen oxides, volatile organic compounds and ammonia were set. The current EU air quality legislation sets emission ceilings (EU (2016) is the update of the 2001 Directive) as well as limit values for the concentrations of a range of air pollutants (EC, 2008). The goal of this legislation is to reduce both adverse health and ecosystem impacts.

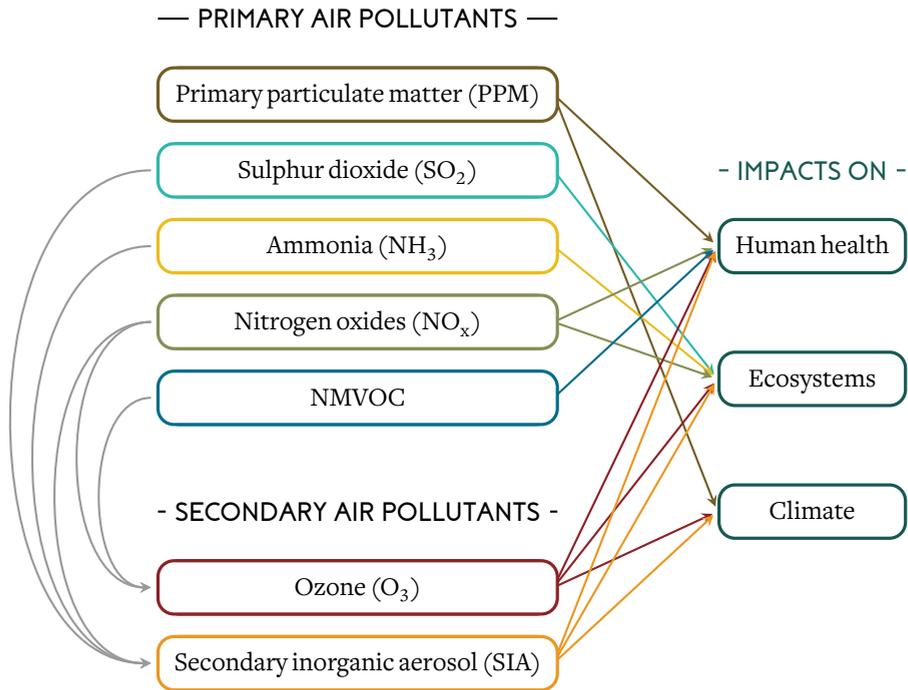
## 1.2 Present-day air quality problems

In Europe, periods like the London 1952 episode in which the air quality situation causes widespread acute health damage no longer occur. However, damage to human health from long-term exposure to air pollution is still one of the three main concerns regarding air quality. The adverse effects of air pollution on ecosystems and its role in climate change are the two other important themes. Figure 1.1 shows which air pollutants are the main contributors to human health damage, ecosystem damage and climate change. In this section I will discuss each of these impacts.

### 1.2.1 Damage to human health

In the 28 countries of the EU (EU28), about 491 thousand premature deaths each year are associated with air pollution. The large majority of these, roughly 403 thousand, are due to exposure to particulates with a diameter under  $2.5 \mu\text{m}$  ( $\text{PM}_{2.5}$ ) (EEA, 2015a). The remainder is attributed to exposure to nitrogen dioxide ( $\text{NO}_2$ ) and ozone ( $\text{O}_3$ ).

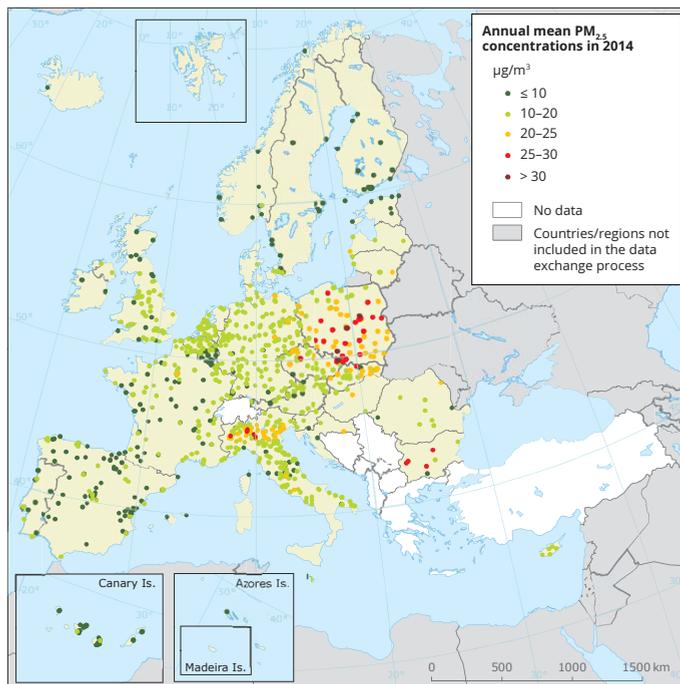
The adverse health effects of **particulate matter** occur when particulates enter the lungs. There is a higher prevalence of cardiac and respiratory problems in regions with high particulate matter concentration, which are mainly urban and industrialised areas. There is little evidence that a threshold below which no adverse health effects occur ex-



**Figure 1.1:** Schematic overview of air pollutants and their impacts. NMVOC is short for non-methane volatile organic compounds.

ists (WHO, 2006). Both short-term exposure to high levels of particulate matter as well as long-term exposure to lower levels cause harmful effects. In Europe, people in Italy and eastern countries such as Poland and Bulgaria are exposed to the highest levels of PM<sub>2.5</sub> (figure 1.2). The Po Valley in Italy is a region combining high emissions with low ventilation due to the surrounding mountain ranges, leading to often stable weather conditions. In eastern Europe, measures to reduce air pollution are not always implemented yet and combustion processes often use more polluting fuels than in western Europe (mainly coal instead of gas).

Particulate matter (PM, or *aerosol*) is a catch-all for many different substances that have in common that they exist in the atmosphere in a particulate form. Not all particulate matter components are thought to be equally harmful for human health. For example, soot particles are thought to have stronger adverse effects than sea salt or mineral dust particles. However, which components are the most harmful is difficult to establish because this research relies on epidemiological studies, and high levels of one particulate matter component often occur simultaneously with high levels of other components (and/or gaseous air pollutants). In general, smaller particulates are thought to be more



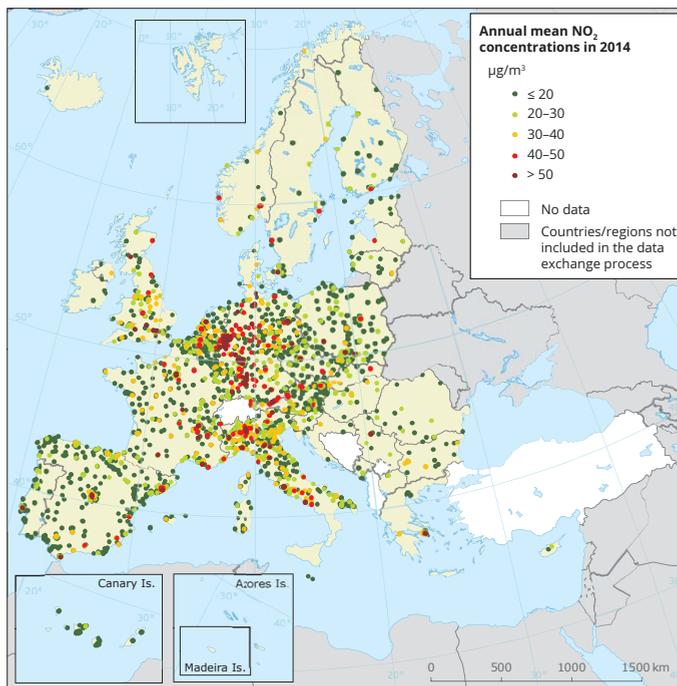
**Figure 1.2:** Annual mean  $PM_{2.5}$  concentrations at measurement locations in Europe in 2014 (EEA, 2016).

harmful than larger ones: the smaller the particulate, the further it can penetrate into the respiratory system. A distinction is therefore made between  $PM_{2.5}$ ,  $PM_{10}$  (particles with a diameter under  $10\ \mu\text{m}$ , which also contains  $PM_{2.5}$ ) and larger particles. In the EU, the annual average limit value for  $PM_{10}$  is set at  $40\ \mu\text{g m}^{-3}$ , for  $PM_{2.5}$  the limit value is  $25\ \mu\text{g m}^{-3}$ . If this limit value is exceeded, a country needs to take action to reduce concentrations. The WHO guidelines set stricter limits on particulate matter concentrations than the EU legislation. A comparison of the EU limit values and WHO guidelines for PM is presented in table 1.1.

**Table 1.1:** EU limit values and WHO guidelines for ground level particulate matter concentrations (EC, 2008; WHO, 2006)

	EU limit value [ $\mu\text{g m}^{-3}$ ]	WHO guideline [ $\mu\text{g m}^{-3}$ ]
$PM_{2.5}$ annual mean	25 (starting 2020: 20)	10
$PM_{2.5}$ 24-hour mean	-	25
$PM_{10}$ annual mean	40	20
$PM_{10}$ 24-hour mean	50 (max. 35 days per year)	50

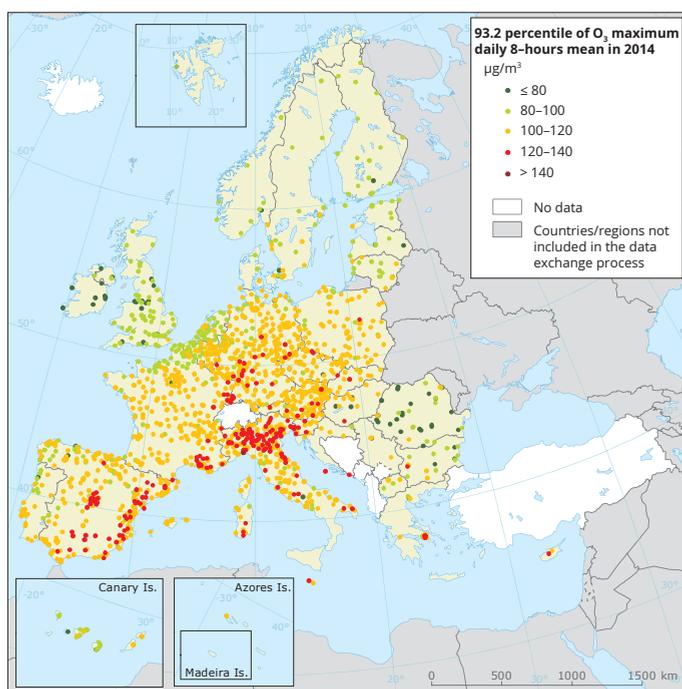
**Nitrogen dioxide** causes respiratory problems in humans because it inflames the lining of the lungs and can reduce immunity to lung infections. This risk becomes significant when short-term (hours to days) exposure to concentrations over  $200 \mu\text{g m}^{-3}$  (which is the WHO guideline and EU Air Quality Directive standard for the maximum 1-hour concentration) occurs or when long-term exposure to concentrations exceeding  $40 \mu\text{g m}^{-3}$  (the standard for maximum annual average concentration) takes place. If these high levels occur, it is almost always at locations close to intensively used roads. People living in cities in densely populated regions, especially those close to major and busy roads, are most exposed to high  $\text{NO}_2$  levels. Figure 1.3 gives an overview of annual average  $\text{NO}_2$  concentrations at observation stations in Europe in 2014. Exposure to  $\text{NO}_2$  leads to about 72 thousand premature deaths annually in the EU28 (EEA, 2015a).



**Figure 1.3:** Annual mean  $\text{NO}_2$  concentrations at measurement locations in Europe in 2014 (EEA, 2016).

**Ozone** has a strong oxidative capacity. Breathing in air with a high ozone concentration leads to damage to human lung tissue. If the 8-hour mean concentration of ozone exceeds  $240 \mu\text{g m}^{-3}$ , significant health effects are considered likely (WHO, 2006). Both healthy and asthmatic individuals are expected to suffer from significantly reduced lung function and airway inflammation at these concentrations. Respiratory morbidity in children is also increased at high ozone concentrations. Chronic exposure at the

WHO Air Quality Guideline of  $100 \mu\text{g m}^{-3}$  is associated with an estimated 1–2 % increase in mortality. In the EU28, 93–99 % of the population has been exposed to ozone levels exceeding the WHO guidelines each year in the period 2003–2012 (EEA, 2015b), leading to an estimated 16 thousand premature deaths annually (EEA, 2015a). Damage below the  $100 \mu\text{g m}^{-3}$  threshold may also occur, especially for sensitive individuals, but robust evidence is lacking. Annual average ozone concentrations as well as peak levels are generally highest in southern Europe, because the higher temperatures and availability of light enable more efficient ozone formation compared to the conditions at higher latitudes. This is illustrated in figure 1.4, which shows the 93.2 percentile, corresponding to the 26<sup>th</sup> highest value of daily 8-hour maxima at measurement stations in Europe for 2014. This is the relevant indicator in legislation terms, since the EU Air Quality Directive allows for exceedance of the limit value of  $120 \mu\text{g m}^{-3}$  on 25 days in a year.



**Figure 1.4:** 26<sup>th</sup> highest daily 8-hour maximum ozone concentrations at measurement locations in Europe in 2014 (EEA, 2016).

## 1.2.2 Damage to ecosystems and biodiversity loss

Ecosystem damage and biodiversity loss due to air pollution occur when excessive amounts of a substance are deposited on sensitive ecosystems. Ozone causes damage to plants when it is deposited on leaf surfaces and taken up by the stomata of plants.

Through its oxidative capacity, ozone damages the leaf surface and the stomata which can lead to visible leaf injury, reductions in plant growth and altered sensitivity to stresses. Figure 1.5 shows an example of plants affected by ozone. The damage on vegetation affects ecosystem resilience and biodiversity as well as agricultural crop yield, leading to a global crop production loss of 11 to 18 billion dollars annually (Avnery et al., 2011). The indicator used for vegetation damage is AOT40, (accumulated ozone exposure above a threshold concentration of 40 ppb for the period May – July). Following the EU Air Quality Directive (EC, 2008), AOT40 should not exceed 18 000  $\mu\text{g m}^{-3} \text{ h}$  averaged over 5 years. In 2013, this value was exceeded for 21 % of all agricultural land in the EU28 (EEA, 2014a). The United Nations Economic Commission for Europe’s Convention on Long-range Transboundary Air Pollution (UNECE CLRTAP) defined a critical load of 10 000  $\mu\text{g m}^{-3} \text{ h}$  not to be exceeded for forests (UNECE, 2011). In 2013, this value was exceeded for 68 % of the total forest area in the EU28 (EEA, 2014a). Just like for human health damage, exceedances of the critical load are mainly in Mediterranean countries. The AOT40 indicator is solely based on the ozone concentration. However, plants are less sensitive to ozone when their stomata are closed. This is the case under arid conditions when plants attempt to reduce water evaporation. By closing the stomata, the exchange of gas between the plant interior and ambient air is inhibited, severely limiting the uptake of ozone. These aspects of vegetation damage from ozone are taken into account in the ozone flux approach, which calculates the uptake of ozone by plant stomata. A commonly used indicator to quantify the ozone flux is the Phytotoxic Ozone Dose (POD), representing the accumulated stomatal flux above a certain threshold. For example,  $\text{POD}_1$  represents the accumulated ozone flux above 1  $\text{nmol m}^{-2} \text{ s}^{-1}$ .



**Figure 1.5:** Healthy plants (top row) and plants damaged by ozone exposure (bottom row) (NASA, 2016).

Deposition of gaseous and particulate substances containing nitrogen or oxidised sulphur causes acidification of soils, which is harmful for sensitive ecosystems. Nutrient availability and microbial activity, both important for ecosystem health, are reduced when the soil becomes too acidic. Acid soil also reduces root access to water and nutrients, especially in the subsurface. As discussed in section 1.1, acidification of surface waters causes increased mortality in fish. In western Europe, eutrophication caused by excessive input of oxidised and reduced nitrogen via deposition is a major issue in ecosystem conservation. Especially ecosystems that thrive on nutrient-poor soils are at risk. The European Environmental Agency estimated that 63 % of the total ecosystem area in the EU28 was at risk of eutrophication in 2010, and 7 % was at risk of acidification (EEA, 2014a). While the area exposed to risk of acidification has declined with 30 % since 2005, for eutrophication the decline is much smaller.

### 1.2.3 Climate change

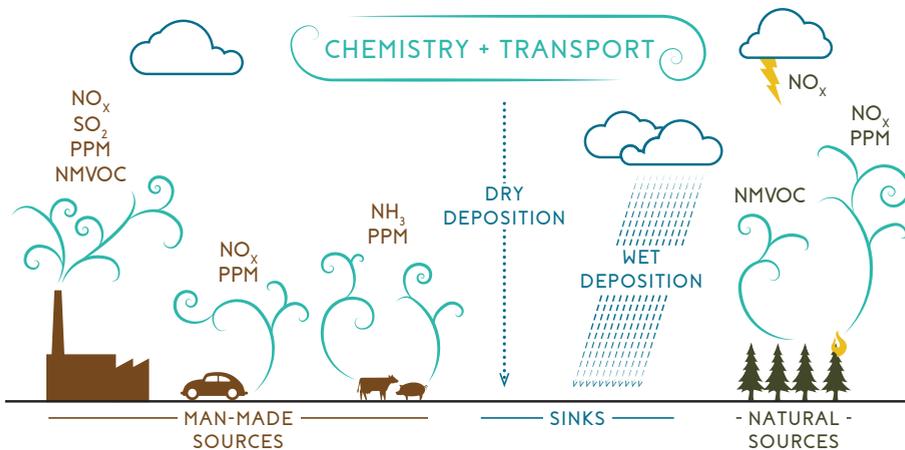
Like carbon dioxide, ozone absorbs infrared radiation that is radiating from the earth to the higher atmosphere, and releases it in all directions. This means that ozone is a greenhouse gas. The most recent report of the Intergovernmental Panel on Climate Change (Stocker et al., 2013) states that the increase of tropospheric ozone since 1750 causes a radiative forcing of  $0.40 \text{ W m}^{-2}$ ; this is 22 % of the warming effect caused by increased carbon dioxide concentrations.

A changing climate also impacts ozone concentrations: higher temperatures, an increase of drought events and blocked weather patterns are projected to cause an increase of up to  $8 \mu\text{g m}^{-3}$  in ozone concentrations in Europe by 2100 (EEA, 2015b). Chapter 5 in this thesis further explores the impact of climate change on ozone concentrations.

Particulates can absorb or scatter solar radiation. This means that particulate matter also plays a role in climate change. While black carbon (or soot) particles have a strong warming effect, organic carbon particles, mineral dust and inorganic particles have a cooling effect through their interaction with radiation. Black carbon particles also have a local warming effect when they deposit on snow and ice, increasing the capacity of these surfaces for absorption of radiation. Indirectly, aerosols also have an impact on climate change because of their interaction with clouds. The magnitude of the total climate impact from all the particulate matter substances and effects combined is still relatively uncertain compared to the effect of carbon dioxide. There is, however, a high confidence that overall, the particles in the atmosphere have a cooling effect (Stocker et al., 2013).

### 1.3 The many sources and components of air pollution

As explained in the previous sections, a range of gases and particles released into or formed in the atmosphere are considered air pollutants because of their adverse effects on human and ecosystem health. Once emitted, some substances undergo chemical reactions while others remain as they are. All air pollutants are transported through the air via diffusion and turbulent mixing and are taken with the wind. The emitted pollution eventually returns to the surface via dry or wet deposition (the latter is also called rainout). Because of the chemistry and transport in the atmosphere, the deposited substances can be different from those that were emitted, and air pollution may travel large distances before depositing again, depending on the atmospheric lifetime of the substance. A schematic overview of emission sources, atmospheric processes and removal processes of air pollutants is shown in figure 1.6. In the following I will discuss the sources, atmospheric processes and sinks of each of the major pollutants separately.



**Figure 1.6:** Schematic representation of emission sources, atmospheric processes and sinks of air pollutants. The air concentration of a substance is a balance between its sources (emissions and chemical reactions) and sinks (chemical reactions and deposition). The three main factors determining the concentration of a substance are the emissions, the meteorology (which drives transport and strongly influences chemical processes) and land use (the efficiency of dry deposition depends on the type of land use and vegetation). PPM stands for primary particulate matter, NMVOC for non-methane volatile organic compounds.

### 1.3.1 Nitrogen oxides

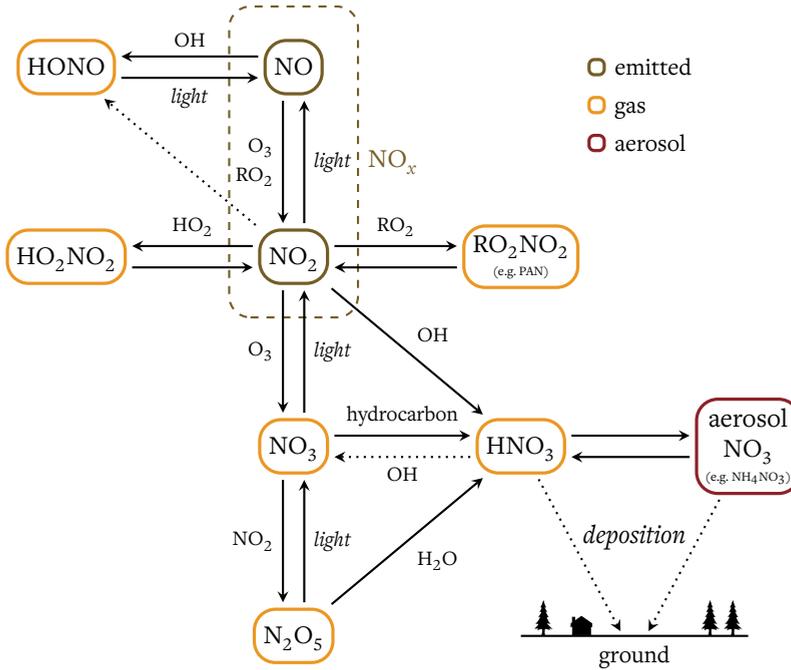
Nitrogen oxides (NO and NO<sub>2</sub>, together known as NO<sub>x</sub>) are released during high temperature combustion processes by oxidation of N<sub>2</sub> (which occurs naturally in air) such as the burning of fossil fuels. Transport and energy production are the main sources of NO<sub>x</sub> in Europe. Other important sources are industrial and residential combustion as well as air traffic and shipping. In addition, NO<sub>x</sub> is produced by soils, especially in areas with intensive fertilisation. Globally, biomass burning, whether in wildfires or controlled by humans, is also an important NO<sub>x</sub> source. Thunderstorms are an important natural source: the intense energy release during lightning strikes causes NO formation from N<sub>2</sub>. In the EU28, man-made NO<sub>x</sub> emissions in 2011 were 8.8 Mt, a 49 % decrease from 1990 levels (EEA, 2014b).

In the atmosphere, a quick cycling between NO and NO<sub>2</sub> takes place in the presence of light, ozone and oxygen molecules. This is why NO and NO<sub>2</sub> are often taken together as NO<sub>x</sub>. NO<sub>2</sub> can be oxidised to the NO<sub>3</sub> radical, which is an important oxidant during the night (when no OH is present). NO<sub>3</sub> radicals react with hydrocarbons such as formaldehyde (HCHO) to form HNO<sub>3</sub>. During the day, when OH is available, HNO<sub>3</sub> can also be formed directly from NO<sub>2</sub>. HNO<sub>3</sub> in turn reacts with ammonia (NH<sub>3</sub>), forming particulate ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>). This is one of the components of secondary inorganic aerosol (SIA) which is part of particulate matter. NO<sub>x</sub> can also be converted into some other species, such as HONO and peroxyacetyl nitrate (PAN). These species have a longer lifetime and can be transformed back into NO<sub>x</sub> and are therefore called reservoir species for NO<sub>x</sub>. Since NO<sub>x</sub> is hardly soluble in water, direct deposition of NO<sub>x</sub> itself is inefficient. The most important sink of NO<sub>x</sub> is therefore the chemical reaction to the water-soluble and efficiently deposited HNO<sub>3</sub> and particulate NO<sub>3</sub>. A schematic overview of the reactions NO<sub>x</sub> and its reaction products can undergo is shown in figure 1.7.

### 1.3.2 Sulphur dioxide

Sulphur dioxide (SO<sub>2</sub>) is a pollutant emitted mostly during the combustion of sulphur-containing fuels, the most important of which are coal and heavy fuel oil. In Europe the main sources are coal-based power plants, some industrial processes and residential burning of coal for residential heating. In the EU28, emissions of SO<sub>2</sub> in 2011 amounted to 4.6 Mt, a 82 % reduction compared to the 1990 emissions (EEA, 2014c). International shipping, which is powered by the combustion of heavy fuel or bunker oil, is also an important emission source of SO<sub>2</sub>. Shipping on European seas emits an estimated 2 Mt of SO<sub>2</sub> emissions annually (EEA, 2013), over 40 % of the land-based emissions in the EU28.

In the gas phase, SO<sub>2</sub> is oxidised by the OH radical to form H<sub>2</sub>SO<sub>4</sub>. A much faster reac-

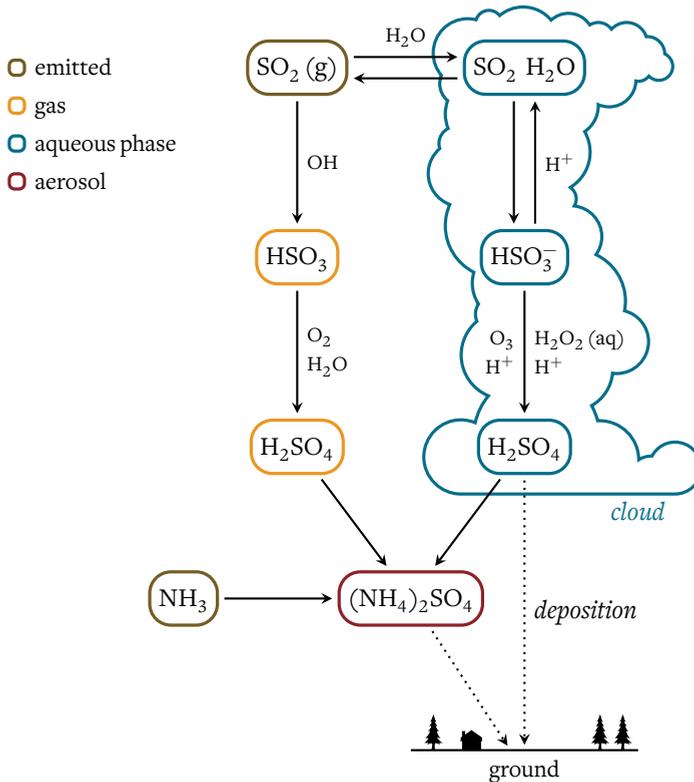


**Figure 1.7:** Schematic overview of  $\text{NO}_x$  atmospheric chemistry and sinks.

tion to form  $\text{H}_2\text{SO}_4$  takes place in cloud droplets where  $\text{SO}_2$  is oxidised by  $\text{H}_2\text{O}_2$  and  $\text{O}_3$ . Since the latter reaction is pH-dependent, it is influenced by how much ammonia is dissolved in the cloud droplet (ammonia is a base, increasing cloud pH). The oxidation of  $\text{SO}_2$  in cloud droplets is very efficient, which means that hardly any direct wet deposition of  $\text{SO}_2$  occurs. Its oxidation products, however, undergo efficient wet deposition.  $\text{H}_2\text{SO}_4$  can react with  $\text{NH}_3$  to ammonium sulphate via a fast and irreversible reaction. Ammonium sulphate is a component of SIA and is removed from the atmosphere through wet and dry deposition. A schematic of the reactions is shown in figure 1.8.

### 1.3.3 Ammonia

By far the largest emission source of ammonia ( $\text{NH}_3$ ) is agriculture, which causes over 90 % of the European emissions (Sutton et al., 2011). Animals excrete ureum via urine and manure, which in part reacts to  $\text{NH}_3$  and evaporates. The application of chemical fertiliser and manure on farmland causes  $\text{NH}_3$  to be released into the air from agricultural soils. About 1/3 of the  $\text{NH}_3$  emissions from agriculture come from fertiliser and manure application, the other 2/3 originate from all the aspects of manure management (livestock housing, manure storage and grazing cattle). Other (minor) sources of  $\text{NH}_3$  emissions are cars with a three-way catalyst system and some industrial processes such



**Figure 1.8:** Schematic overview of  $\text{SO}_2$  atmospheric chemistry and sinks.

as fertiliser production and coke manufacturing. The total emissions of ammonia in the EU28 in 2013 amounted to 3.6 Mt, a 30 % decrease from 1990 levels (Eurostat, 2015).

Since  $\text{NH}_3$  is a volatile substance that evaporates from manure faster in warm conditions, the emitted quantity increases with temperature. Because manure application is a strongly seasonal process (the moment of application depending on the growing season of the crop on the field), most emissions of  $\text{NH}_3$  occur in spring and summer, with a minimum of emissions in winter. The seasonality of the emissions can change from year to year, depending on weather: when spring is early, manure application will start earlier in the year than when the onset of spring is late. In chapter 3, information about manure transport is used to better include this temporal variability of ammonia emissions in a CTM.

$\text{NH}_3$  is effectively removed from the air by dry and wet deposition. As mentioned above, it can also react with sulphuric or nitric acid, forming SIA. SIA particles are effectively removed from the atmosphere via wet deposition.

### 1.3.4 NMVOC

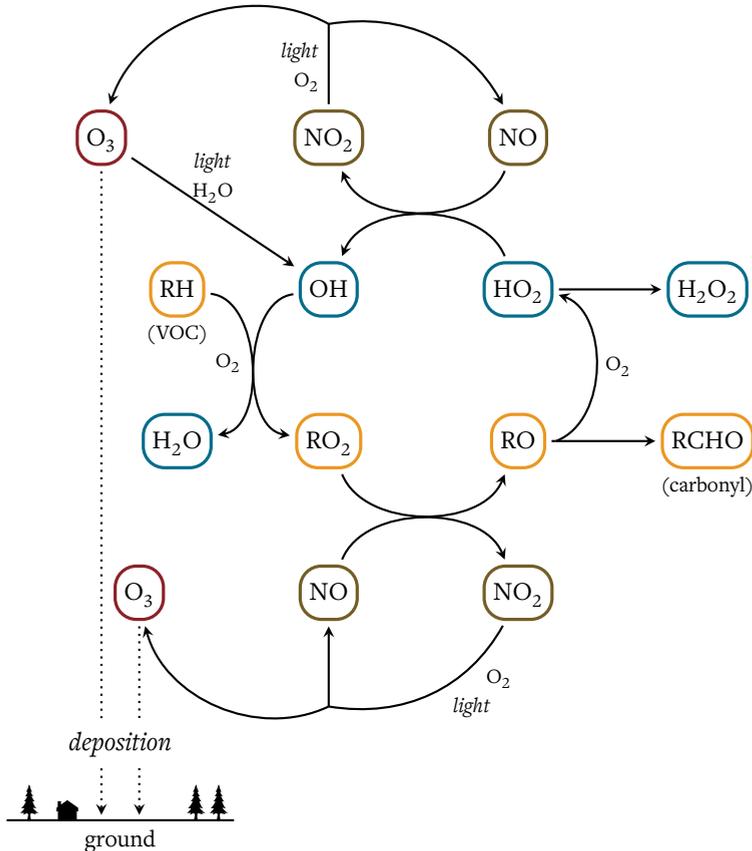
Volatile organic compounds (VOCs) are usually taken together as a group. The molecules in this group have in common that they contain one or more carbon atoms and have a boiling point below 250 °C. Methane ( $\text{CH}_4$ ) is often excluded from this group because of its long lifetime, its role in climate change and its specific sources, leaving the rest of the group to be called non-methane volatile organic compounds (NMVOCs). NMVOC emissions from human activity come from, among others, the extraction and use of fossil fuels, the use of solvents in paints and coatings and slow emission from building materials. Another important source is the biosphere. Almost all plants emit NMVOCs, especially isoprene (2-methyl-1,3-butadiene,  $\text{C}_5\text{H}_8$ ) and terpenes ( $(\text{C}_5\text{H}_8)_2$ ). Plants are the most important biogenic source of NMVOCs, but animals, fungi and microbes also excrete small quantities.

The emissions of NMVOCs from plants are species-dependent and driven by temperature and the availability of light. Therefore, the highest emissions of NMVOCs from plants occur in the tropics, with lower emissions at higher latitudes. Globally, biogenic sources make up about 90 % of the total annual emissions of NMVOCs, leaving a share of 10 % for man-made sources. In Europe, man-made and biogenic sources contribute equally to the total emissions, with high biogenic emissions in the summer period because of the higher temperatures and light availability. Most NMVOCs are quite reactive, leading to an atmospheric lifetime of hours to months. From an air quality perspective, the role of NMVOCs in the atmosphere is twofold: they can form organic particulates and play an important role in ozone formation.

### 1.3.5 Ozone

Ozone ( $\text{O}_3$ ) is a naturally occurring component of the atmosphere. In the stratosphere (about 10–50 km above the earth's surface), it plays a crucial role in preventing mutagenic uv radiation from reaching the earth's surface. This is the well-known *ozone layer*. Ozone also occurs in the troposphere (the lowest layer in the atmosphere, reaching up to 8–18 km with the higher altitudes occurring in the tropics) and has an important role to play here as well. Ozone produces OH radicals that oxidise and neutralise many (harmful) atmospheric contaminants. Free radicals have mutagenic properties and are therefore harmful to human health and ecosystems. Ozone is not directly emitted into the atmosphere, but is formed from ozone precursors  $\text{NO}_x$  and VOC (see schematic in figure 1.9; in this scheme, VOC is represented as RH, with R a hydrocarbon group). Overall, the reaction scheme shown in figure 1.9 consumes one VOC molecule and four oxygen molecules and yields one carbonyl compound, two ozone molecules and one water molecule. When  $\text{NO}_x$  concentrations are low compared to VOC concentrations (typical for clean environments), a change in VOC concentration does not have a large

impact on ozone levels, but a change in  $\text{NO}_x$  levels does. This is called the  *$\text{NO}_x$ -limited regime*. The opposed situation in which  $\text{NO}_x$  levels are high occurs mainly in urban areas and polluted regions. In this situation a change in VOC levels will impact ozone concentrations, but a reduction in  $\text{NO}_x$  levels will not significantly reduce ozone concentrations. This is called the *VOC-limited regime*.



**Figure 1.9:** Schematic overview of the production of ozone in the atmosphere. Ozone is formed from nitrogen oxides ( $\text{NO}$  and  $\text{NO}_2$ ) and VOC (shown as  $\text{RH}$  in this figure).

Ozone formation depends on light. Hence, ozone levels peak in the afternoon and reach a minimum during the night. Ozone is cycled back and forth to and from molecular oxygen ( $\text{O}_2$ ) and is removed from the atmosphere by dry deposition. Its average lifetime is of the order of a few weeks.

### 1.3.6 Primary particulates and condensables

Primary particulate matter (PPM) emissions come from a wide range of sources, including natural sources such as wind-blown dust, seas emitting sea salt and forest fires. The most important man-made sources of primary particulate matter in Europe are residential heating, traffic exhaust and industrial activities. Other sources are agricultural and building activities that cause resuspension of dust. Traffic not only causes PPM emissions from exhaust (mainly soot) but also from brake and tyre wear that cause a range of particulate matter emissions (e.g. copper, antimony and rubber). Incomplete combustion is the most important source of soot (or black carbon) particles. Particles are removed from the atmosphere via dry deposition, sedimentation and wet deposition.

Condensables are organic substances that are gaseous at the high temperatures of stack plumes but condense quickly once they enter the much colder atmosphere, forming particles of organic matter. These are particles that condense without undergoing a chemical reaction, which is why one could argue they should be included as primary particulates in emission databases. Presently, this is very rarely the case and condensables are not included in official reported emissions of primary particulates.

### 1.3.7 Secondary particulates

As described in several of the previous paragraphs, species that are emitted as gases can react in the atmosphere to form aerosols. This is true for both organic (VOC) and inorganic gases ( $\text{NO}_x$ ,  $\text{SO}_2$  and  $\text{NH}_3$ ). The particles formed from inorganic gases are called secondary inorganic aerosol (SIA). The base  $\text{NH}_3$  can react with sulphuric or nitric acid (that are formed from  $\text{SO}_2$  and  $\text{NO}_x$ , respectively) to form ammonium sulphate or ammonium nitrate. These are the main components of SIA. The irreversible reaction of ammonia with sulphuric acid to ammonium sulphate is favoured. When all sulphuric acid is consumed, the remaining ammonia will react with nitric acid to form ammonium nitrate in an equilibrium with the gas-phase reactants. The SIA components are essentially salts in which ammonium acts as the positive ion. This function can also be performed by some mineral species such as sodium or calcium, forming components like sodium nitrate and calcium sulphate that are also part of SIA. All SIA particles are effectively removed from the atmosphere via (especially wet) deposition. As long as there is no rain, SIA particles have quite a long lifetime in the atmosphere and can be transported over large distances.

Volatile organic compounds can be oxidised in the atmosphere. As explained above, these oxidation steps insert oxygen atoms into the molecules, (usually bound to a C atom with a stable double bond, i.e. a carbonyl group). The addition of such 'functional groups' to hydrocarbons lowers the volatility of the compound. The less volatile

a species is, the more prone it is to condense and leave the gas phase. After several oxidation steps (depending on the starting compound), these substances form particles called secondary organic aerosol.

## 1.4 Policy-supporting air quality research

We have seen that many air pollutants have multiple sources, and that emission sources often emit more than one type of pollutant. Most pollutants have adverse effects on several environmental impact categories (human health, ecosystem damage, climate change) and each impact category is influenced by several pollutants. This justifies the statement that air pollution is truly a multi-source, multi-component, multi-effect problem.

A variety of research fields is related to air pollution and its effects: knowledge of emissions and atmospheric processes is required to calculate and explain the atmospheric concentrations of the different air pollutants, epidemiological studies are needed to derive the damage to human health, and human and ecosystem biologists are crucial to determine the pathways via which air pollutants damage human and ecosystem health. Geophysics, ecosystem biology and economics are among the research fields that are important to assess the causes and effects of climate change. Since this thesis only presents research into the state of the atmosphere, I will only discuss that type of research here.

### 1.4.1 Observations

Observations of the concentration of pollutants in ambient air are essential to monitor whether legislation on air quality has the desired effects and whether countries meet the emission ceilings and limit values established by (inter)national laws or agreements. Apart from this monitoring function, air quality observations are also very important to improve scientific understanding of the processes and mechanisms determining air pollutant concentrations. In Europe, the EMEP (European Monitoring and Evaluation Programme) network is the main source of ground-based observations of air concentrations of pollutants such as  $O_3$ ,  $NO_x$ ,  $SO_2$ , and particulate matter. This network was set up to support the monitoring of the effectivity of international legislation aimed at reducing transboundary acidification, eutrophication and ozone damage. For this reason, observation stations are mainly located at rural background sites that are not influenced by local sources. The EMEP network is therefore mainly suitable to detect long-term trends in background concentrations.

However, the concentrations of many air pollutants are higher in urban environments and most population exposure also happens there. Therefore, every European country

or other responsible authority also has its own measurement network which not only performs observations of the rural background but also of the urban background and the street level. In Europe, many of these observations are collected in the Air Quality e-Reporting database (previously Airbase) (EEA, 2017). While observations of O<sub>3</sub>, NO<sub>x</sub>, SO<sub>2</sub> and PM are available for a large number of locations and at high time resolution, observations of PM composition are less common. Apart from observations of the ambient concentration, the EMEP and country networks also include observations of wet or total (bulk) deposition. Observations of dry deposition are very difficult and expensive and are therefore uncommon except for experimental research projects.

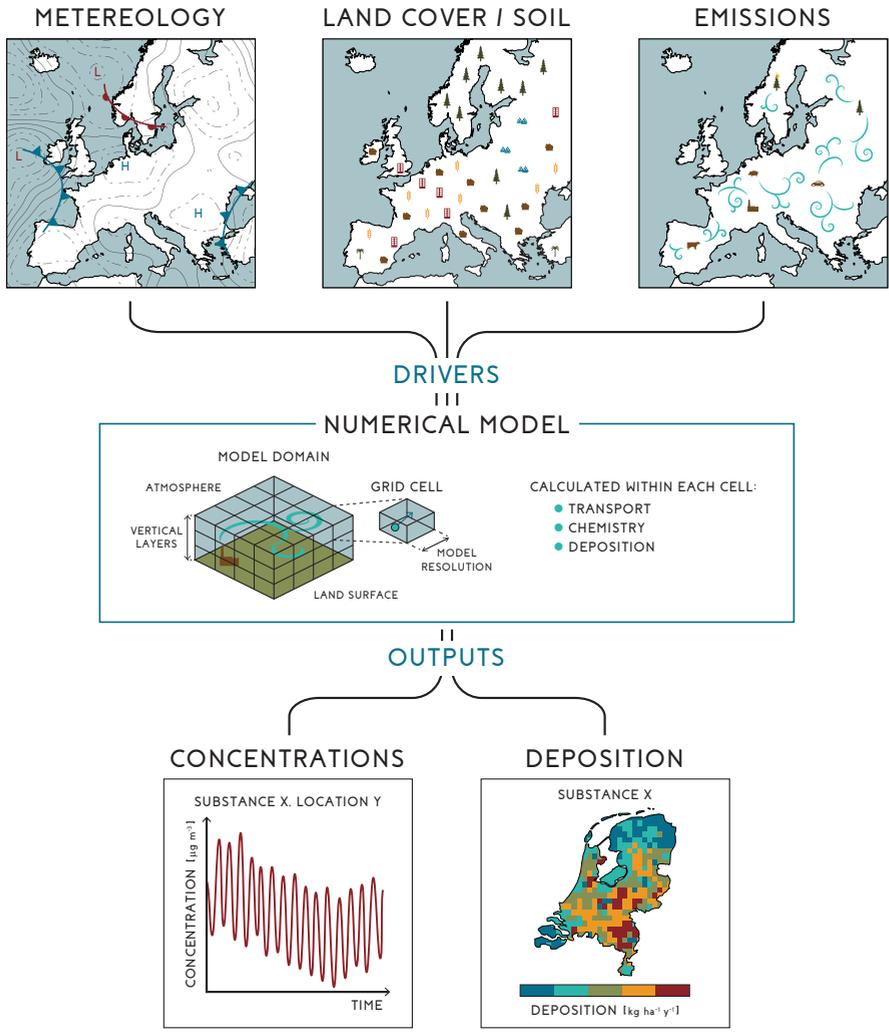
Ground-based observations have the great advantage of sampling at inhalation level and are thus crucial in monitoring ambient air quality and for the comparison with limit and target values. There are methods to derive the origin of air pollution from observation data. Some correlate meteorological data (mainly wind direction) with measured concentrations to determine the geographical origin of air pollution. Others (such as Positive Matrix Factorisation, PMF) use statistical receptor models to obtain source categories from observations. If observations of certain tracers (that are often only measured during dedicated campaigns) are available to link observed concentrations to source sectors, this method can be applied with more success (e.g. Waked et al., 2014). However, none of the observation-based source attribution methods are able to provide detailed information about the origin of ambient air pollution, especially for the secondary part.

An important disadvantage of ground-based measurements is their limited geographical coverage: it is impossible to sample the whole surface of a country using ground-based measurements, even though observation locations are chosen such that they are representative for a larger area. Satellite observations do not have this disadvantage, but can only sample the same area once or twice a day depending on the overpass times. Satellite observations naturally always look at the entire atmospheric column, and deriving ground concentrations from this is far from trivial. However, observations of column loads as well as ground concentrations using satellites have great potential for emission and concentration monitoring.

#### 1.4.2 Regional chemistry transport modelling

Another approach to learn more about air pollutant concentrations is the use of models. Different approaches are possible, each with its own strengths and weaknesses. One of the model types used in air quality research is the chemistry transport model (CTM). In this thesis, the CTM LOTOS-EUROS (Schaap et al., 2008) is used as the main instrument. A database containing information about the quantity, location and temporal distribution of emissions of air pollutants is an important input for these models, as are meteo-

rological data and information on land use. With this information, the model calculates horizontal and vertical transport and diffusion of the gases and particles emitted into the atmosphere, as well as the chemical reactions taking place in the air and in clouds, and removal through wet and dry deposition. A schematic representation of the CTM LOTOS-EUROS and its drivers and outputs is shown in figure 1.10.



**Figure 1.10:** Overview of the CTM LOTOS-EUROS, its main drivers and outputs.

Modelling of atmospheric processes requires and builds a comprehensive understanding of the drivers and mechanisms of these processes, contributing to a better fundamental knowledge base. One of the other great advantages of chemistry transport modelling is that modelling can provide a calculated concentration of every air pollutant

at every hour and every location. However, one should always treat model outcomes with care: the model is not reality, and the output of the model is as good as its inputs and process parametrisations. This is why validation of model outcomes using observations is always an essential part of any air quality assessment using model systems. Especially for particulate matter, some sources are difficult to quantify and chemistry transport models in general underestimate ambient air concentrations (Vautard et al., 2005).

Air quality models are the instrument most suited to study possible future scenarios to assess for example the potential effects of a policy intervention or climate change on air quality. In such scenario studies, the model inputs can be chosen such that they reflect the estimated future emissions, meteorological conditions and/or land use. The change in air pollutant concentrations or deposition caused by this scenario is calculated. In the past, many of the measures taken to reduce air pollution were so-called *end-of-pipe measures* such as the installation of filters on smoke stacks. These types of measures only reduce the amount of pollutant released but patterns in space and time remain the same. Policies aimed at structural change (shifting from a fossil fuel based to a renewable fuel based energy system, for example) lead to altogether different emission patterns in terms of the mix of emitted pollutants as well as the geographical and temporal characteristics. To evaluate this type of policy and to investigate the co-benefits between policies aimed to reduce climate change, biodiversity loss and air pollution, it is valuable to model the changes in emission totals and variability, land use change and the effect of climate change all at once. In this thesis, three scenario studies are described considering a reduction in emissions (chapters 3, 4 and 5), a change in the temporal variability of emissions (chapters 3 and 4) and/or changes in land use and climate (chapter 5).

The scenario approach in which emissions are changed can also be used to calculate from which sector(s) and region(s) air pollution originates. By performing a model run with for example the emissions from German road transport reduced by 15 % and calculating the difference with a base run, the effect of this emission reduction on ambient air quality can be calculated. However, this approach requires a model run for each source under consideration, and the relation between reduced emissions and reduced concentrations is assumed to be linear. In the LOTOS-EUROS model, a source labelling approach is used that tracks each emission of primary particulate matter and gases containing carbon, sulphur or nitrogen through the atmospheric transport and chemistry to its removal, while keeping track of what source emitted the substance in the first place (Kranenburg et al., 2013). This labelling method requires less computing power than running a separate simulation for each source and also accounts for non-linear effects. Either way, models can provide information on the origin of air pollution that cannot be derived from observations.

Of course, the distribution of air pollutants in a model, and therefore the resulting source attribution critically depends on the quality of the emission data used in the model. The total emissions, their location as well as their temporal variability are very important to accurately calculate the source attribution on an annual average basis or to assess which emission sources or regions are the most relevant during peak levels. Validation of source attribution results is difficult because observation-based techniques can only provide general source categories. Nevertheless, results from Positive Matrix Factorisation studies and the use of specific tracers for specific sources (for example, vanadium is a tracer for heavy fuel oil combustion) provide valuable information that can be compared to the modelled source attribution results.

Ground-based measurements, satellite observations and modelling all have strengths and weaknesses when it comes to policy-supporting air quality research. A combination of the three, using observations for validation as well as model assimilation, is very helpful in answering a range of policy questions. Monitoring of emissions and emission trends, assessment of limit value exceedances at ground level as well as exploring what future policies, climate and land use change could mean for air quality can all be done using a combination of these three tools.

## 1.5 Thesis outline

This thesis contains a collection of research driven by policy questions concerning the sources of particulate matter air pollution and the possible impact of different energy scenarios on air quality. Chapters 2 and 3 focus on the origin of particulate matter concentrations in the Netherlands and Flanders. Chapter 2 addresses the question: **What is the origin of particulate matter in the Netherlands?** To answer this question we tracked emissions from the ten main economic sectors (SNAP1 level), separating Dutch and foreign sources and taking natural sources and the non-modelled fraction of particulate matter into account.

In chapter 3, the focus is on the SIA-precursor ammonia. Flanders has a large agricultural sector with considerable ammonia emissions. These emissions peak in spring, when high particulate matter and ammonium nitrate concentrations are also common. To provide a reliable source attribution of particulate matter during these episodes, the temporal variability of ammonia emissions in the model was needed improvement. We used manure transport data as a proxy for ammonia emission from manure application. The questions addressed in this chapter are: **Can we improve the modelling of ammonia, SIA and particulate matter concentrations using manure transport data to model the temporal variability of ammonia emissions from manure?** and **Is restricting manure spreading shortly before and during a particulate matter episode effective to reduce particulate matter concentrations during episodes?**

Chapters 4 and 5 describe studies about energy transitions. The main question addressed in chapter 4 is: **What could be the impact of an increasing share of intermittent renewable electricity generation (wind and solar energy) on particulate matter concentrations over Europe?** During the energy transition from fossil fuels to renewable alternatives there is likely a phase in which fossil fuel energy production will be mainly used to provide backup capacity. This implies that the temporal variability of emissions from these power plants will change, which might have an impact on ambient concentrations. The effect of this projected shift in emission timing on total concentrations as well as on source-receptor relations which quantify the impact of a sector in one country on the air quality in other countries is assessed in this chapter.

In chapter 5, the central question is: **How will ozone concentrations and damage change under realistic future European energy and air quality scenarios?** Since bioenergy is expected to become a more important energy source than it is today, the effects of land use change as well as changes in man-made emissions are taken into account. We also explore the possible effects of climate change and changing hemispheric background concentrations on ozone concentrations towards 2050.

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# The origin of ambient particulate matter in the Netherlands



**P**ARTICULATE MATTER POSES a significant threat to human health. To be able to develop effective mitigation strategies, the origin of particulate matter needs to be established. The regional air quality model LOTOS-EUROS, equipped with a newly developed labelling routine, was used to establish the origin of PM<sub>10</sub> and PM<sub>2.5</sub> in the Netherlands for 2007 to 2009 at the source sector (SNAP1) level, distinguishing between national and foreign sources. The results suggest that 70–80 % of modelled PM<sub>10</sub> and 80–95 % of PM<sub>2.5</sub> in the Netherlands is of anthropogenic origin. About 1/3 of anthropogenic PM<sub>10</sub> is of Dutch origin and 2/3 originates in foreign countries. Agriculture and transport are the Dutch sectors with the largest contribution to PM<sub>10</sub> mass in the Netherlands, whereas the foreign contribution is more equally apportioned to road transport, other transport, industry, power generation and agriculture. For the PM<sub>2.5</sub> fraction, a larger share is apportioned to foreign and anthropogenic origin than for PM<sub>10</sub>, but the same source sectors are dominant. The national contribution to PM levels is significantly higher in the densely populated Randstad area than for the country on average and areas close to the borders. In general, the Dutch contribution to the concentration of primary aerosol is larger than for secondary species. The sectoral origin varies per component and is location and time dependent. During peak episodes, natural sources are less important than under normal conditions, whereas especially road transport and agriculture become more important.

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## 2.1 Introduction

Exposure to particulate matter (PM) in ambient air leads to human health problems (Dockery et al., 1993; Klemm et al., 2000). To limit the effects of PM pollution, efforts are made to reduce emissions of PM and its precursors. Legislation on maximum PM concentrations is put in place in e.g. the European Union (EC, 2008). Limit values for the annual average concentration ( $40 \mu\text{g m}^{-3}$ ) as well as the number of days (35) with concentrations above  $50 \mu\text{g m}^{-3}$  are enforced for  $\text{PM}_{10}$ , whereas for  $\text{PM}_{2.5}$  annual mean limit values as well as reduction targets must be met from 2015 onwards. Despite air quality regulation and emission reduction policies, the daily  $\text{PM}_{10}$  limit value is still exceeded in many areas in Europe. To design cost effective mitigation strategies, a thorough understanding of the sources of particulate matter is crucial. As PM consists of a host of components with different sources and atmospheric behaviour, establishing the origin of PM remains a challenge.

Experimental approaches to establish the origin of PM differ in complexity. Simple schemes have been applied to estimate local and urban contributions using a gradient approach (e.g. Lenschow et al., 2001). Composition and tracer data have often been used to interpret PM time series and origin. Chemical mass closure studies are reported for many regions (Putaud et al., 2010), including the Netherlands (Weijers et al., 2011). Moreover, detailed chemical speciation data sets enable the use of more elaborate statistical approaches, such as Positive Matrix Factorisation, to identify PM source origins (Kuhlbusch et al., 2009; Mooibroek et al., 2011). However, these methods are only able to distinguish between a limited number of broad source categories. Furthermore, they are typically not able to provide a source apportionment for secondary components. Moreover, the experimental approaches are expensive and do not yield information on the geographical origin of PM.

Complementary to experimental data, a chemical transport model (CTM) can be used to obtain a detailed source apportionment. The most straightforward procedure to do this is the *brute force* approach, in which impacts of emission sources are assessed by perturbing or removing them one-by-one and calculating the differences in pollutant concentrations (e.g. Lane et al., 2007). In previous studies on the origin of PM in the Netherlands, this approach was followed with the dispersion model OPS (Buijsman et al., 2005; Velders et al., 2011). Note that these studies quantify the effect of emission reductions rather than the actual origin of the current pollutant concentrations (Wagstrom et al., 2008). For pollutants involved in atmospheric chemistry, non-linear effects occur and perturbing emissions may impact atmospheric reaction rates that negatively impact the source apportionment results (Blanchard, 1999; Seinfeld and Pandis, 1998). Another drawback is that (small) negative differences between the base case and the perturbed simulation may occur due to numerical issues and non-linear chemistry. Finally, the brute-force method is computationally very demanding and therefore not

suitable for experiments with a large number of sources.

To avoid these disadvantages, several other modelling approaches were developed. The Tagged Species Engineering Model (McHenry et al., 1992) uses output from the Regional Acid Deposition Model to establish source-receptor relationships for sulphate particles, tracking five chemical species. The source-oriented external mixture (SOEM) method developed by Ying and Kleeman (2006) is capable of dealing with secondary species as well and accurately tracks source contributions of PM. However, because each PM component is divided into source-specific species that are tracked separately through the model, SOEM is computationally demanding. Wagstrom et al. (2008) presented the Particulate Source Apportionment Technology (PSAT) algorithm, combining the capability of accurately dealing with secondary species with limited CPU demand. The concentration of the substances is modelled as before, but next to this the fractional contribution of all sources is calculated for each process. To simplify the source attribution, all secondary PM components are linked directly to specific precursors. This implies that indirect effects from a change in atmospheric composition and chemical regime (e.g. an increase of nitrate concentrations due to a decrease of sulphate concentrations) are not accounted for.

The regional CTM LOTOS-EUROS (Schaap et al., 2008) is equipped with a source apportionment module based on the PSAT approach (Kranenburg et al., 2013). In this work, the model is used to establish the origin of ambient PM concentrations over the Netherlands for the years 2007–2009. Because episodes and regions with high PM levels are especially policy relevant, a priority was to establish the source attribution at different PM concentrations. Prior to presenting source apportionment results, model evaluation results are given. Results are presented for PM<sub>10</sub> as well as PM<sub>2.5</sub> and attention was given to geographical and temporal differences in source attribution.

## 2.2 Methods

### 2.2.1 The LOTOS-EUROS model

To study the source apportionment of particulate matter across the Netherlands, we used LOTOS-EUROS v1.8, a three dimensional regional CTM that simulates air pollution in the lower troposphere. Previous versions of the model have been used for the assessment of (particulate) air pollution (Barbu et al., 2009; Manders et al., 2009, 2010; Schaap et al., 2004a,b, 2009). For a detailed description of the model we refer to Schaap et al. (2008), Wichink Kruit et al. (2012a) and abovementioned studies. Here, we describe the most relevant model characteristics and the model simulation performed in this study. The model uses a normal longitude-latitude projection at a standard grid resolution of  $0.50^\circ \times 0.25^\circ$  (longitude  $\times$  latitude). The model top is placed at 3.5 km

above sea level and consists of three dynamical layers: a mixing layer and two reservoir layers on top. The height of the mixing layer at each time and position is extracted from ECMWF meteorological data used to drive the model. The height of the reservoir layers is set to the difference between ceiling (3.5 km) and mixing layer height. Both layers are equally thick with a minimum of 50 m. If the mixing layer is near or above 3500 m high, the top of the model exceeds 3500 m. A surface layer with a fixed depth of 25 m is included in the model to monitor ground level concentrations.

Advection in all directions is handled with the monotonic advection scheme developed by Walcek (2000). Gas phase chemistry is described using the TNO CBM-IV scheme (Schaap et al., 2009), which is a condensed version of the original scheme by Whitten et al. (1980). Hydrolysis of  $N_2O_5$  is described following Schaap et al. (2004a). Aerosol chemistry is represented with ISORROPIA2 (Fountoukis and Nenes, 2007). The pH dependent cloud chemistry scheme follows Banzhaf et al. (2012). Formation of coarse-mode nitrate is included in a dynamical approach (Wichink Kruit et al., 2012a). Dry deposition for gases is modelled using the DEPAC3.11 module, which includes canopy compensation points for ammonia deposition (Van Zanten et al., 2010). Deposition of particles is represented following Zhang et al. (2001). Stomatal resistance is described by the parametrisation of Emberson et al. (2000a,b) and the aerodynamic resistance is calculated for all land use types separately. Wet deposition of trace gases and aerosols is treated using simple scavenging coefficients for gases (Schaap et al., 2004a) and particles (Simpson et al., 2003). The model set-up used here does not contain secondary organic aerosol formation or a volatility basis set approach as we feel that the understanding of the processes as well as the source characterisation are too limited for the current application.

## 2.2.2 Emissions

For anthropogenic trace gas emissions we use the European TNO-MACC emission database for 2007 (Kuenen et al., 2014) and replaced the data for the Netherlands with the emissions reported by the official Dutch Pollutant Release and Transfer Register (PRTR, 2010) for 2008 as described by Hendriks et al. (2012). The temporal variation of the emissions is represented by monthly, daily and hourly time factors for each source category (Bultjes et al., 2003). The emission height distribution for all source sectors follows the Eurodelta approach (Cuvelier et al., 2007). Biogenic emissions of volatile organic compounds (VOC) (Schaap et al., 2009) are derived from a dataset with the distributions of 115 tree species as obtained from Köble and Seufert (2001). Mineral dust due to resuspension and agricultural activities (Denier van der Gon et al., 2010), sea salt particulates (following Mårtensson et al. (2003) and Monahan et al. (1986)) and fire emissions (Kaiser et al., 2009) are taken into account.

### 2.2.3 Source apportionment module

A source apportionment module for LOTOS-EUROS was developed to be able to track the origin of the components of particulate matter (Kranenburg et al., 2013). This module uses a labelling approach similar to the approach taken by Wagstrom et al. (2008), tracking the source contribution of a set of sources through the model system. The emissions can be categorised and labelled in several source categories (e.g. countries, sector, fuel type) before the model is executed. The total concentration of each substance in each grid cell is modelled as usual. However, next to this the fractional contribution of each label to the total concentration of every species is calculated. During or after each process, the new fractional contribution of each label is defined by calculating a weighted average of the fractions before the process and the concentration change during the process. Whereas this is rather straightforward for the linear processes in the model (such as vertical diffusion or deposition), it is more complicated for non-linear processes, most notably the atmospheric chemistry. The labelling routine is therefore only implemented for chemically active tracers containing a C, N (reduced and oxidised) or S atom, as these are conserved and traceable. For components with only one N or S atom, the attribution is straightforward. For ammonium nitrate, containing both oxidised and reduced nitrogen atoms, several approaches can be chosen. In this study,  $\text{NH}_4$  and  $\text{NO}_3$  are straightforwardly treated as separate species for the labelling, attributing all  $\text{NH}_4$  to  $\text{NH}_3$  sources and all  $\text{NO}_3$  to  $\text{NO}_x$  sources. As ammonia and nitric acid are both needed to form ammonium nitrate, an alternative is to attribute the mass of ammonium nitrate equally to the origin of ammonia and nitric acid. The latter would yield a higher contribution of the agricultural sector compared to the current approach as ammonium is lighter than nitrate. The full sensitivity is discussed in Hendriks et al. (2012). Since only substances containing C, S and N atoms are traced, this technique is not suitable to investigate the origin of e.g.  $\text{O}_3$  and  $\text{H}_2\text{O}_2$ . The source apportionment module for LOTOS-EUROS provides a source attribution valid for current atmospheric conditions as all chemical conversions occur under the same oxidant levels. For details and validation of this source apportionment module we refer to Kranenburg et al. (2013).

### 2.2.4 Simulation description

A simulation across Europe at  $0.5^\circ$  longitude  $\times$   $0.25^\circ$  latitude (about  $28 \times 28 \text{ km}^2$ ) resolution was performed, the results of which were used as boundary conditions for a simulation at a resolution of  $0.125^\circ$  longitude  $\times$   $0.0625^\circ$  latitude ( $7 \times 7 \text{ km}^2$ ) over the Netherlands (see figure 2.1). The simulations were performed for 2007, 2008 and 2009 to obtain a sufficiently large dataset for recent years. Labels were applied to distinguish Dutch and foreign emissions sources specified to SNAP (Selected Nomenclature for sources of Air Pollution) level 1, which uses ten main sectors:

1. Combustion in energy and transformation industries
2. Non-industrial combustion plants
3. Combustion in manufacturing industry
4. Production processes
5. Extraction and distribution of fossil fuels and geothermal energy
6. Solvent use and other product use
7. Road transport
8. Other mobile sources and machinery
9. Waste treatment and disposal
10. Agriculture

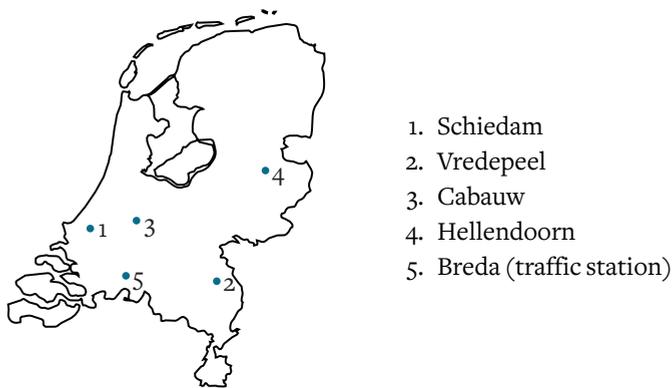


**Figure 2.1:** Domains used in this study. The full domain ( $15^{\circ}\text{W}$ – $30^{\circ}\text{E}$ ,  $35^{\circ}$ – $70^{\circ}\text{N}$ ) was simulated at a  $0.5^{\circ} \times 0.25^{\circ}$  scale, the zoom domain ( $3^{\circ}$ – $9^{\circ}\text{E}$ ,  $49^{\circ}$ – $55^{\circ}\text{N}$ ) at  $0.125^{\circ} \times 0.0625^{\circ}$ .

Natural emissions and PM originating from the initial conditions, aloft conditions and PM coming from regions outside the model domain were tracked as well, yielding a total of 24 labels. The model provides the source apportionment of the modelled mass. Analyses were performed on the spatial variability across the country as well as for the country average. Attention is given to the variability of the PM origin with increasing modelled PM concentrations. To assess the source attribution in relation to observed PM concentrations and determine the non-modelled fraction for the country average we follow the annual mean  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  concentrations for 2008 as estimated using measurements (Velders et al., 2009), respectively  $23.3$  and  $14.6 \mu\text{g m}^{-3}$ .

### 2.2.5 Validation data

To compare simulated and experimentally determined PM and PM component concentrations in the Netherlands, we use data from rural and suburban stations in the Dutch National Air Quality Monitoring Network (LML). Within the network, PM<sub>10</sub> mass and concentrations of sulphate, nitrate, ammonium and sodium were measured with Leckel low volume samplers since 2009. Data prior to 2009 were found to be unreliable, especially for the secondary inorganic aerosol components (Weijers et al., 2012). Therefore only NAQMN data for the year 2009 were used to evaluate the model performance. Data from a dedicated measurement campaign (August 2007 – October 2008; Weijers et al. (2011)) were used for a more detailed comparison including carbonaceous aerosol and mineral dust. This dataset contains detailed chemical speciation data covering a full year with samples at every 4<sup>th</sup> day and allows to evaluate the fine and coarse fractions of all PM components. The measurement locations are shown in figure 2.2. For an evaluation of modelled ammonia concentrations we refer to Wichink Kruit et al. (2012b).



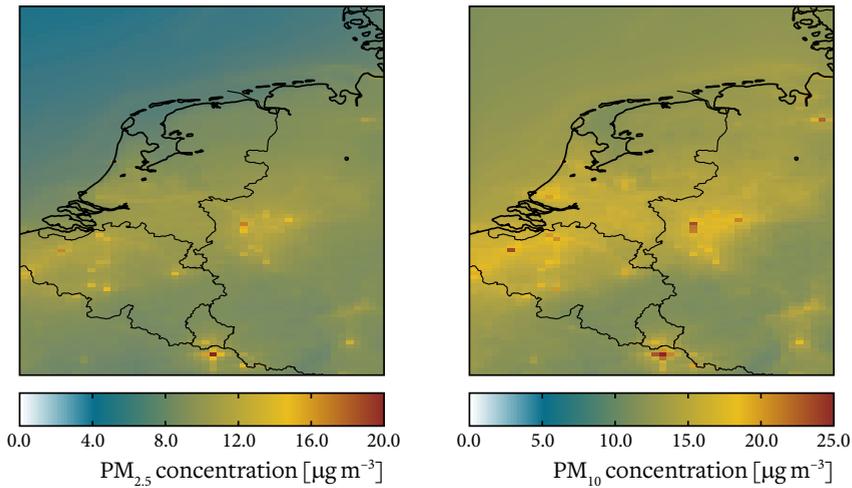
**Figure 2.2:** Map of the measurement locations used in this analysis to validate the chemical composition of PM (adapted from Weijers et al. (2011)).

## 2.3 Results

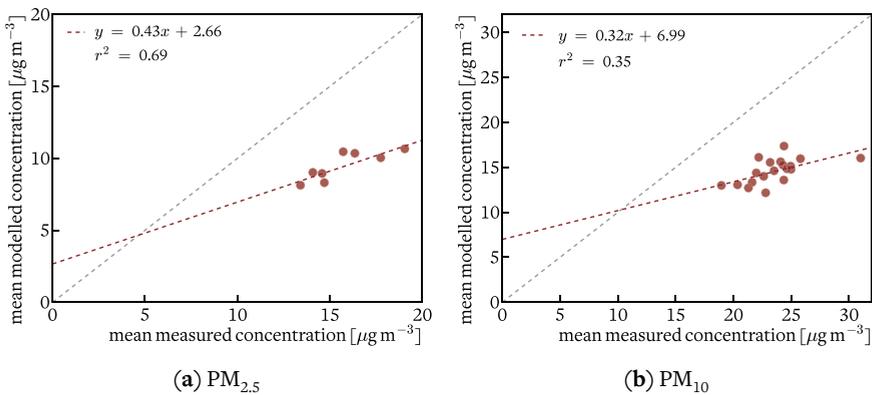
### 2.3.1 Average distributions and model validation

Figure 2.3 displays the modelled average PM<sub>10</sub> and PM<sub>2.5</sub> concentrations over the Netherlands for 2007–2009. For PM<sub>10</sub>, these range from 13  $\mu\text{g m}^{-3}$  in the north and 18  $\mu\text{g m}^{-3}$  in the south to 22  $\mu\text{g m}^{-3}$  in the densely populated and industrialised western part of the country. For PM<sub>2.5</sub>, average concentrations of 9  $\mu\text{g m}^{-3}$  in the north to 11  $\mu\text{g m}^{-3}$  in the centre are modelled. The highest concentrations are found along important transportation routes. Note that important source regions of PM and its precursors are located

east (Ruhr area, Germany) and south (Flanders, Belgium) of the country. Figure 2.4 shows the comparison of modelled annual mean concentrations for  $PM_{2.5}$  and  $PM_{10}$  for 2009 with measurements from NAQMN. LOTOS-EUROS underestimates both  $PM_{10}$  and  $PM_{2.5}$  at all stations by about 40 %. The coefficients of determination ( $r^2$ ) suggest that the model's representation of spatial gradients for  $PM_{2.5}$  is better than for  $PM_{10}$ , but the difference is at least partly due to the lower number of measurement stations for  $PM_{2.5}$ . If only the measurement stations for which both  $PM_{10}$  and  $PM_{2.5}$  are available are included in the analysis, the performance is equal for  $PM_{10}$  and  $PM_{2.5}$ .

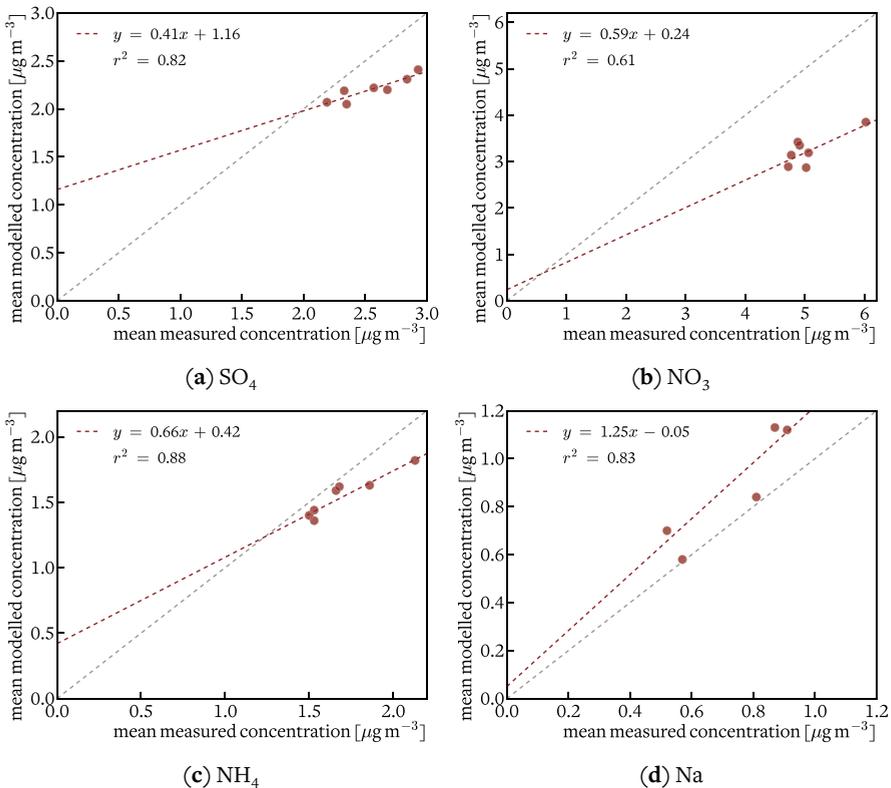


**Figure 2.3:** Average modelled concentration of  $PM_{2.5}$  (left) and  $PM_{10}$  (right) for 2007 to 2009.

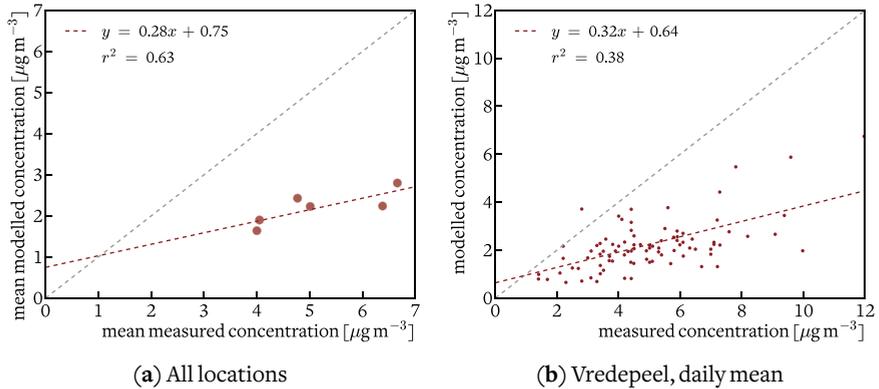


**Figure 2.4:** Mean measured versus modelled concentrations of particulate matter. Observation data used are regional and suburban stations from LML.

In figure 2.5 we compare the annual mean modelled concentrations sulphate, nitrate, ammonium and sodium to those observed in  $\text{PM}_{10}$ . Nitrate concentrations are underestimated by about 40 %. For sulphate, ammonium and sodium, the modelled annual means are typically within 15 % of the observed value. Coefficients of determination vary between 0.6 and 0.9. For ammonium (0.67), nitrate (0.62) and sodium (0.60), the temporal correlation ( $r^2$ ) is better than that of  $\text{PM}_{10}$  (0.51), whereas for sulphate 20–55 % of the temporal variation is reproduced. The lower performance for the sulphur components with respect to the spatial and temporal distributions is attributed to the dominant contribution of point sources instead of area sources as well as the uncertainties to cloud distributions and formation. Modelled carbonaceous aerosol is compared to measurements from the campaign (2007–2008) in figure 2.6, showing a 60 % underestimation by the model. LOTOS-EUROS reproduces 19–52 % of the temporal variation, depending on location. Although the spatial correlation indicates that the distribution of the main emission sources may be captured, the comparison shows that the representation of carbonaceous matter in the model needs to be improved.

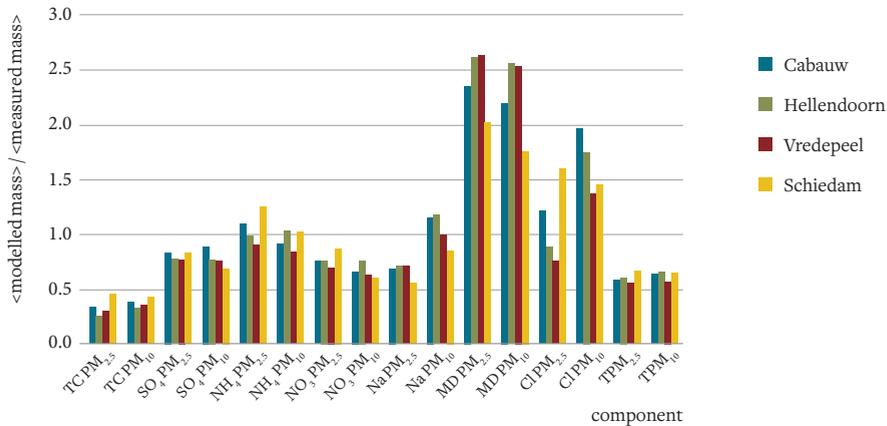


**Figure 2.5:** Annual mean measured versus modelled concentrations of PM components for 2009. The observations are from LML.



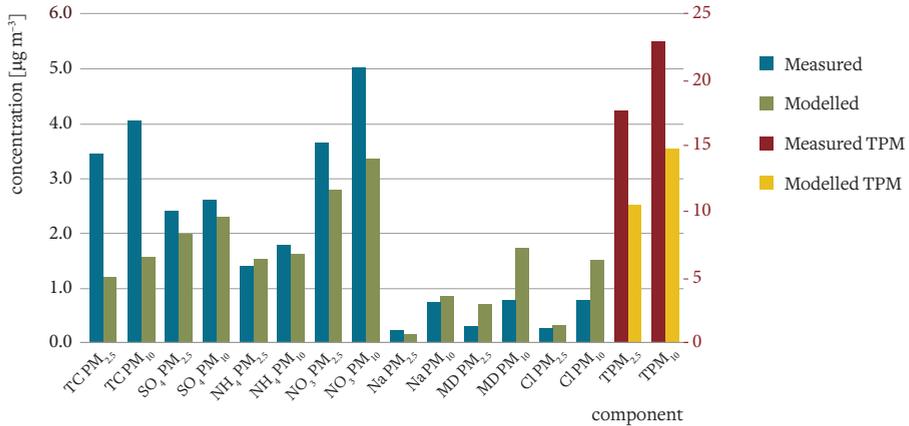
**Figure 2.6:** Measured versus modelled concentrations of carbonaceous aerosol for August 2007 – October 2008. The observations are from Weijers et al. (2011).

The comparison against PM<sub>10</sub> data confirms the findings presented above for 2009 and allows to investigate the nature of the gap between modelled and observed PM<sub>2,5</sub> and PM<sub>10</sub> (see figure 2.7). On average for the four background stations included in the analysis, 63 % of PM<sub>10</sub> mass and 61 % of PM<sub>2,5</sub> is modelled. For the SIA components, about 30 % of both fine and coarse nitrate and 15 % of sulphate is missing, whereas ammonium does not show a large bias. Mineral dust concentrations are overestimated by a factor 2, but the temporal and geographical variation in the measurements are reproduced reasonably well.



**Figure 2.7:** Share of mean measured mass captured by LOTOS-EUROS for PM and components, August 2007 – October 2008. A share of 1 means observed and modelled masses are equal. Observation data from Weijers et al. (2011). TC: total carbonaceous aerosol; MD: mineral dust; TPM: total PM.

Figure 2.8 shows that the two components that contribute the most to  $PM_{10}$  mass, carbonaceous aerosol and nitrate, are underestimated strongest by LOTOS-EUROS. The underestimation of nitrate is about equal for the fine and the coarse fraction, whereas for carbonaceous matter the missing mass is mainly associated with the fine fraction. Although LOTOS-EUROS strongly overestimates mineral dust levels in a relative sense, the impact on PM is limited because of the low absolute contribution of mineral dust.

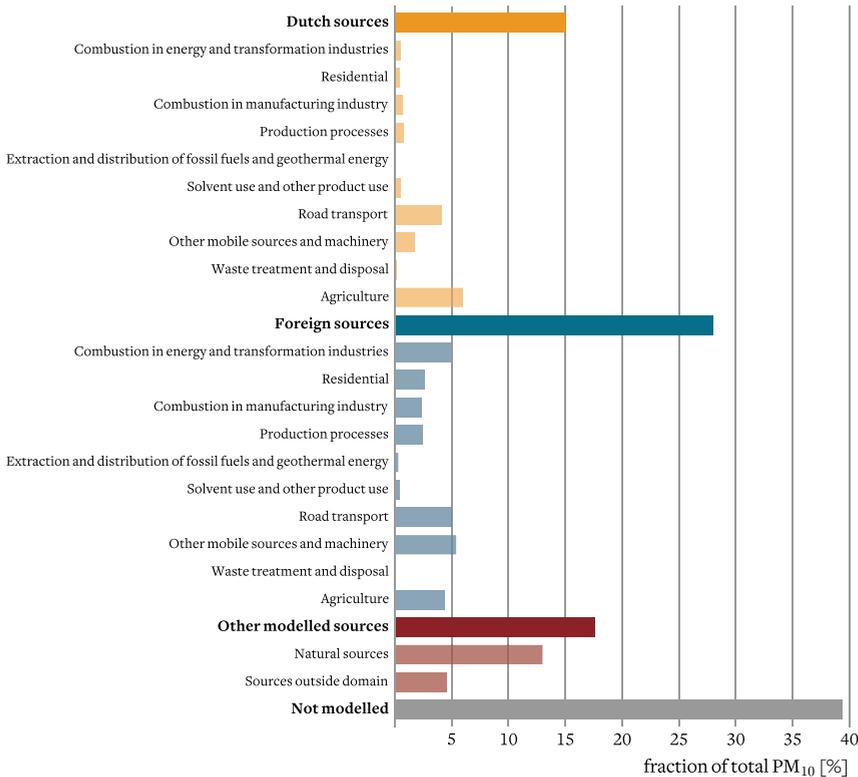


**Figure 2.8:** Mean measured and modelled concentrations for Cabauw (August 2007 – October 2008). TC: total carbonaceous aerosol; MD: mineral dust; TPM: total PM. For  $TPM_{10}$  and  $TPM_{2.5}$ , the right-hand vertical axis applies. Observation data from Weijers et al. (2011).

### 2.3.2 Source apportionment of particulate matter in the Netherlands

#### Annual average

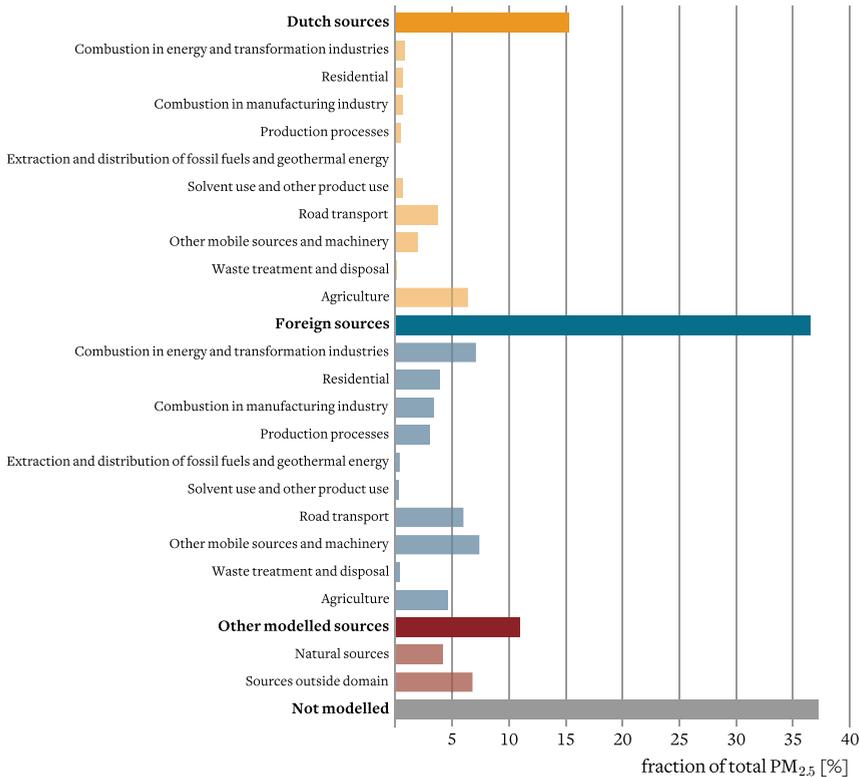
Figures 2.9 and 2.10 summarise the source attribution per sector for 2008 with respect to the measured mass concentrations of  $PM_{10}$  and  $PM_{2.5}$ , respectively. The analysis shows that foreign anthropogenic sources make a larger contribution (28%) than national anthropogenic sources (15%) and natural sources (17%) in case of  $PM_{10}$ . For  $PM_{2.5}$  the contribution of national anthropogenic sources is modelled to be the same, while the contribution of foreign anthropogenic sources (37%) is larger and that of natural sources is lower (11%) than for  $PM_{10}$ . Of the modelled part, 70–80% of  $PM_{10}$  and 80–95% of  $PM_{2.5}$  over the Netherlands is anthropogenic and about one third of these fractions is of Dutch origin. The largest difference in the contributions to  $PM_{10}$  and  $PM_{2.5}$  is found for the natural sources, i.e. sea salt, which can be explained by the lower importance of sea salt in  $PM_{2.5}$ . Because of the longer atmospheric lifetime of the fine PM fraction compared to the coarse mode, a higher contribution from long range transport for  $PM_{2.5}$  is found.



**Figure 2.9:** Origin of PM<sub>10</sub> in the Netherlands for 2007–2009 as modelled by LOTOS-EUROS.

The impact of the difference in lifetime is also clearly visible in the distributions of the national and foreign contributions to modelled PM<sub>10</sub> and PM<sub>2,5</sub> in figure 2.11. The shares of Dutch, foreign and natural sources are not constant across the country. The highest contribution from foreign countries is found along the eastern borders whereas the domestic share peaks in the densely populated western part of the country (see figure 2.11). The natural contribution trails off with distance to the coast and consists mainly of sea salt. For a detailed study on sea salt concentrations and gradients across the Netherlands, we refer to Hoogerbrugge et al. (2012).

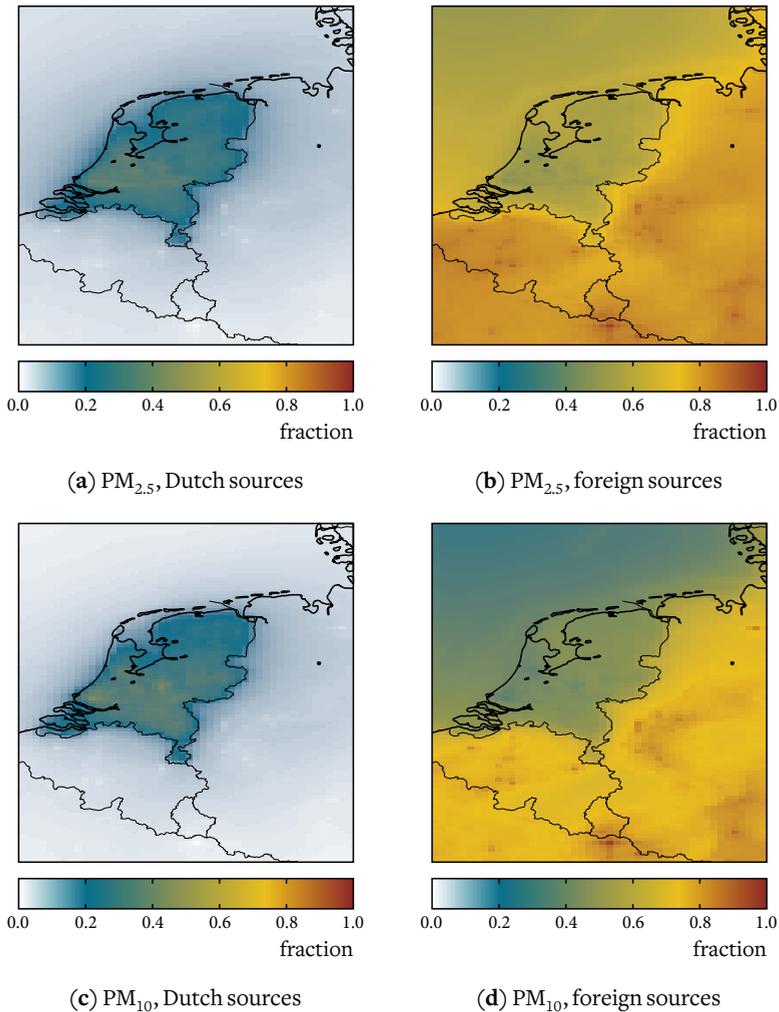
In figure 2.12 we take a closer look at the sector origin of modelled PM<sub>10</sub> from Dutch and foreign sources for the Netherlands as a whole and its variability within the country. To illustrate the latter, two locations are shown being Rotterdam, located at the coast in the densely populated Randstad area with large industrial and harbour activities, and Vredepeel, located in a region with intensive agriculture in the south-east of the country. The sectors with the largest national contribution to modelled PM<sub>10</sub>



**Figure 2.10:** Origin of PM<sub>2.5</sub> in the Netherlands for 2007–2009 as modelled by LOTOS-EUROS.

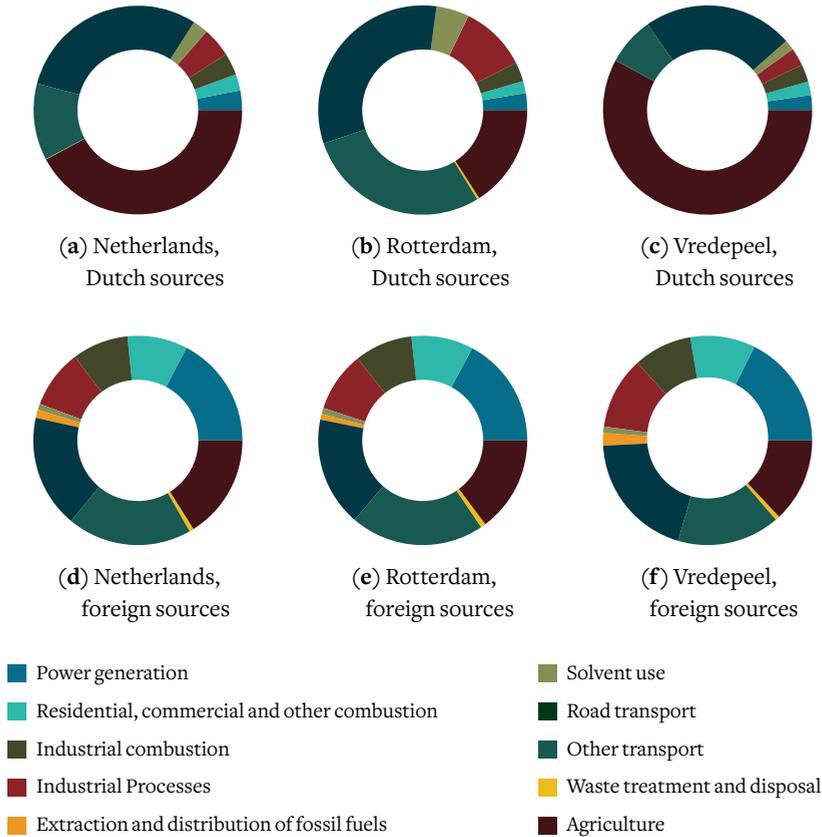
mass in the Netherlands are agriculture, road transport and other transport, together responsible for 85 % of the total Dutch contribution. Within the country the relative contributions of the major contributors vary. In Rotterdam, road transport and other transport, i.e. shipping, are the most important sources, whereas in Vredepeel agriculture causes over half of the Dutch contribution to modelled PM<sub>10</sub>. As expected, also the contributions of the other sectors vary as a function of proximity to their major source regions, as illustrated by the larger contribution of industrial process emissions for Rotterdam. For foreign anthropogenic PM<sub>10</sub>, the contributions show six sectors with comparable contributions being road transport, other transport, agriculture, power generation, residential combustion and industry. The variability across the country is small. The source attribution for PM<sub>2.5</sub> (not shown) strongly resembles the patterns found for PM<sub>10</sub>.

So far only total PM mass was considered, whereas the source apportionment is performed for each component. Figure 2.13(a) shows the source attribution per sector



**Figure 2.11:** Modelled fractional source contributions of PM in the Netherlands from Dutch and foreign sources for 2007 to 2009.

for the most important PM components. Some components are dominated by a few sectors. Agriculture is by far the most important source of ammonium, causing over 90% of the emissions and concentration of this substance in the Netherlands. The dust concentration in the Netherlands originates for about 25% outside the model domain. The remaining part is equally divided between agriculture and road transport. Nitrate, sulphate and elemental carbon (EC) concentrations originate mainly from sectors in which combustion is an important source (e.g. transport, industrial combustion and power generation). For the other components, the sector origin is more diffuse. The na-

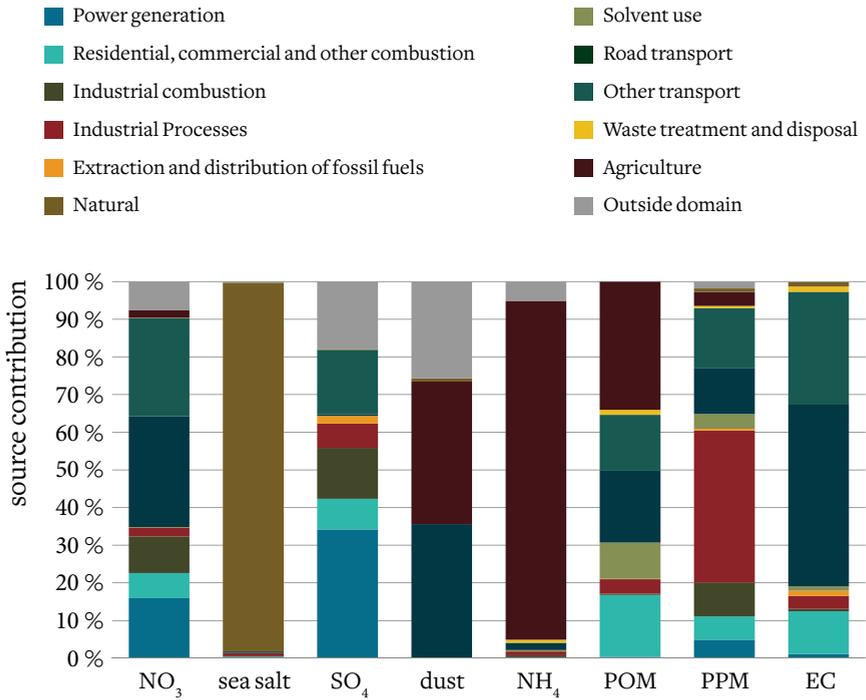


**Figure 2.12:** Modelled Dutch (*top*) and foreign (*bottom*) sectoral contributions to modelled  $PM_{10}$  in the Netherlands, Rotterdam and Vredepeel.

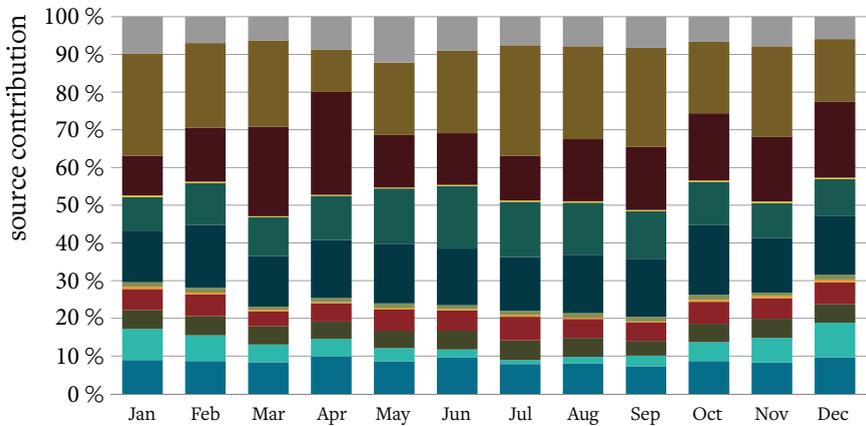
tional contribution to the concentration of primary PM components is larger than for secondary species. For instance, national contributions to EC range between 40 % in the north to 75–80 % in the densely populated west of the country, whereas the national contribution to sulphate is below 10 % everywhere (not shown).

The seasonal dependence of the origin of modelled  $PM_{10}$  is displayed in figure 2.13(b). Residential sources and the power sector, with a winter peak, and the agricultural sector, with a strong peak in spring, are the sectors with the strongest seasonal dependence. The contribution of natural sources also changes over the months, but a clear seasonal pattern cannot be discerned. Transport contributes relatively more to  $PM_{10}$  concentrations in summer, but this is mainly because concentrations coming from other sources are lower in this season.

THE ORIGIN OF AMBIENT PARTICULATE MATTER IN THE NETHERLANDS

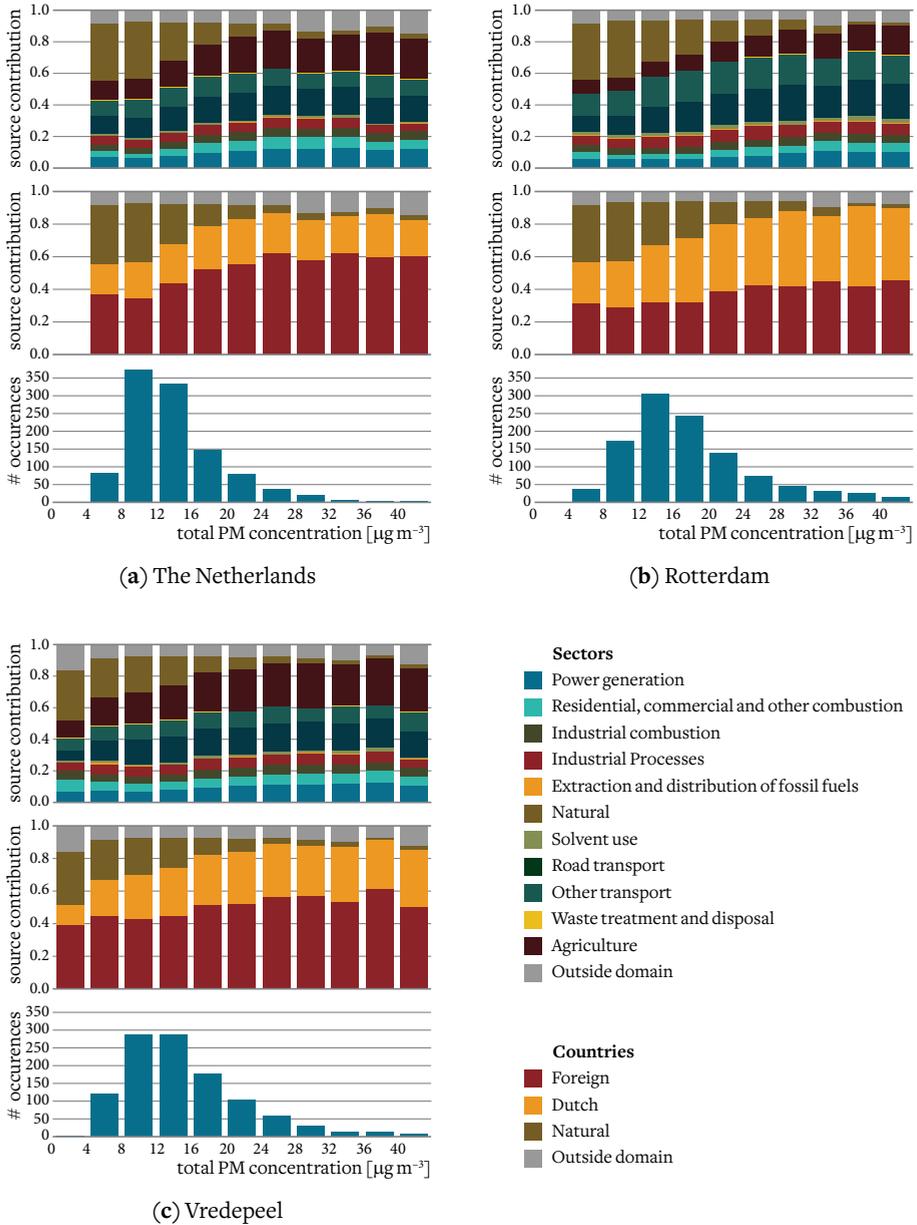


(a) Source contributions per component. Components are ordered from high (left) to low (right) contribution to PM<sub>10</sub>. POM stands for primary organic matter.



(b) Source contributions for each month.

**Figure 2.13:** Average origin of modelled PM<sub>10</sub> components in the Netherlands. The source sector labels represent both the Dutch and the foreign contribution of that sector to the concentration.



**Figure 2.14:** Source attribution of  $PM_{10}$  for different total  $PM_{10}$  concentration levels, categorised in  $4 \mu g m^{-3}$ -wide bins. For each subfigure, the *top* bars represent the sectoral source attribution, the *middle* bars the geographical origin and the *bottom* bars the number of times a concentration in that bin was modelled.

## Particulate matter episodes

The differences in source contributions between peak PM episodes and low PM episodes were investigated to find out if certain source categories contribute more during PM peak episodes. All days were categorised based on the average modelled concentration of  $PM_{10}$  after which the source attribution was calculated for concentration bins of  $4 \mu g m^{-3}$ . The results for the Netherlands as a whole as well as Rotterdam and Vredepeel are displayed in figure 2.14. With increasing ambient PM concentration the importance of natural sources rapidly declines. Low concentrations are associated with westerly winds, resulting in transport of sea salt from the North Sea and Atlantic Ocean to the Netherlands. High PM concentrations occur mainly with easterly winds or stagnant conditions, during which the influx of sea salt is much smaller. For the Netherlands as a whole, the influence of both Dutch and foreign concentration contributions increases with rising modelled PM levels. In the west of the country, as illustrated for Rotterdam, the domestic contribution grows faster with increasing  $PM_{10}$  concentration than the foreign contribution. For the Netherlands as a whole, the increase in concentrations going from low to high PM levels is proportional for most sectors, except for agriculture and transport, which become more important mainly due to higher ammonium (nitrate) and dust concentrations. At Vredepeel, this pattern is more prominent than for the Netherlands on average, whereas at Rotterdam, agriculture is less important and especially transport (road transport and shipping) becomes more important as modelled PM concentrations increase.

## 2.4 Discussion

### 2.4.1 Emission data

Providing an accurate source attribution of air pollution with a chemical transport model requires a consistent sector-specific emission database. The anthropogenic emission database used in this study is based on country reportings (Kuenen et al., 2014), which provide detailed sector-specific emissions but are not entirely consistent across countries. Kuenen et al. (2014) checked for completeness of source sector contributions, gap-filled the emission data and performed various consistency checks including removal and substitutions if country-reported data were deemed unreliable. For the countries in the immediate vicinity of the Netherlands, deviations between reported emissions and the final emission database at the source sector level are minor and the effect on the results presented above is assessed to be negligible. However, for source attribution studies differentiating more subsectors, a higher level of detail and consistency in emission data and source sector splits may be required. The spatial and temporal distribution of annual emission totals might also be improved by using more accurate time profiles instead of the same time profile for all countries. Coupling the

emissions of mineral dust and ammonia, but also emissions from e.g. residential heating to meteorological conditions is recommended. Using more realistic distributions of emissions over the year could improve the overall model performance and the source apportionment in episodes considerably (see below).

#### 2.4.2 Modelled versus observed PM

Comparison to observations showed that the modelled  $PM_{10}$  and  $PM_{2.5}$  mass by LOTOS-EUROS underestimates the measurements by 40 % on average. It is crucial to understand the reason for this underestimation and what type of sources or mechanisms are involved to make the final source apportionment robust and suitable for policy advice. The largest deviations were found for nitrate ( $1.5 \mu\text{g m}^{-3}$ ) and total carbon ( $2.5 \mu\text{g m}^{-3}$ ), both species coming mainly from anthropogenic sources. We did not make a comparison for EC and OC separately due to uncertainties in measurement techniques. The different procedures for analysis of the carbon content of PM samples correspond well for total carbon mass, but yield very different EC/OC ratios (Ten Brink et al., 2004). For the measurement campaign used for validation in this study, the Cachier analysis procedure (Cachier et al., 1989) was used, yielding an EC/OC ratio of 1.25. With this method, refractory OC is combusted in the second combustion step and is appointed to EC, giving an upper estimate for EC and a lower estimate for OC. Analysis of a subset of the filters with the SUNSET protocol yielded an EC/OC ratio of 0.28 (Ten Brink et al., 2009). The EC concentrations obtained by the Cachier protocol are three times higher than those modelled, whereas the model results are close to the concentrations obtained with the SUNSET protocol. Hence, we feel that the underestimation of total carbon is largely an underestimation of organic carbon. To convert the organic carbon contribution to a mass contribution one needs to account for the non-C atoms in organic material. In LOTOS-EUROS, primary OM is converted to OC using a OM/OC ratio of 1.33. However, literature values vary between 1.2 to 2.2 (e.g. Chen and Yu, 2007; El-Zanan et al., 2009), and Aiken et al. (2008) suggest that this factor is spatially variable, showing lower values near sources and higher values after processing in aged air masses. Hence, assuming the model bias for EC to be small, LOTOS-EUROS misses  $4\text{--}5 \mu\text{g m}^{-3}$  of organic matter, next to the earlier mentioned  $1.5 \mu\text{g m}^{-3}$  of nitrate. Given their importance these underestimated PM components are discussed in more detail below. Mineral dust emissions from re-suspension of road dust and agriculture were a novel source category included in the modelling and will also be briefly discussed.

Some of the scatter plots show quite skewed regression lines, indicating that the model underestimates the measurements more strongly at locations with higher concentrations and that spatial variability is underestimated. A possible reason for this could be that the vertical mixing near emission sources is too fast, causing a too strong dilution. Also, in contrast to reality anthropogenic emissions are not dependent on meteorological conditions.

logical variables which may induce more dilution than in reality. For example, heating emissions take place during conditions that are colder and more stable than average. Neglect of this dependency may cause the dilution to be overestimated on average causing lower gradients. Also, the spatial gradients in emissions might be underestimated as many smaller diffuse sources are allocated according to population. Note also that for  $PM_{10}$  mass the natural background consisting of sea salt at the low concentrations is rather well captured. The underestimation of the anthropogenic part than causes a skewed fit.

### Carbonaceous particulate matter

Particulate organic matter in the atmosphere derives from direct primary emissions and the formation of secondary organic aerosol (SOA). Regarding the primary OC emissions, it has recently been suggested that part of these emissions are not properly represented in the emission databases. For example in the case of wood combustion emissions, [Denier van der Gon et al. \(2015\)](#) argued that emission factors are used that are obtained from measurements in hot air directly after emission, while condensation may occur immediately when the emitted air is cooled down to ambient conditions, increasing the effective emissions. Revision of the emission model input through incorporating this immediate “condensable” PM, which consists entirely of OC, would increase the PM-OC emissions and thereby reduce the gap between modelled and observed OC. This hypothesis needs further study, but from our model perspective it would fit well with the underrepresentation of OC. From a modelling perspective improvements for the representation of organic aerosol can be made as well. Biogenic as well as anthropogenic VOCs undergo oxidation reactions in the atmosphere and eventually condensate to form particles. This SOA formation is not included in this version of LOTOS-EUROS. Furthermore, [Donahue et al. \(2009\)](#) postulated that primary and secondary organics partition between the gas and aerosol phase and that the gaseous fraction can age to lower volatile species. One possibility to include the semi-volatile nature of organics and ageing processes in LOTOS-EUROS, thereby improving the model performance for organic matter, is to use a volatility basis set (vbs) for VOCs ([Lane et al., 2008](#)). Concluding, the extension of the organic matter model description may significantly decrease the non-modelled mass and it is anticipated that the source attribution of PM could shift considerably.

### Particulate nitrate

LOTOS-EUROS underestimates observed nitrate concentrations by 40 %. In the Netherlands most of the nitrate is present in the form of ammonium nitrate ([Weijers et al., 2011](#)). The concentration of ammonium nitrate is sensitive to the sulphate concentration, concentrations of the precursor gases as well as the meteorological conditions.

This makes the diagnosis of the origin of an underestimation difficult as one needs to verify the source strengths of precursors, chemical production of sulphate and nitric acid, the equilibrium between ammonium nitrate and its gaseous counterparts as well as the sinks for all components involved. Major improvement may be expected from improved representation of the ammonia emissions as function of ambient conditions (Skjøth et al., 2011). Furthermore, the lifetime of the components is largely influenced by atmospheric stability and mixing, which may differ greatly between models and meteorological drivers (Stern et al., 2008). Recently, contradicting studies about the correctness of the equilibrium models have been published (Fisseha et al., 2006; Schaap et al., 2011; Yu et al., 2005) and it has been postulated that the time scales to reach chemical equilibrium may be in the order of minutes so that vertical mixing should be accounted for in the assessment of the equilibrium (Aan de Brugh et al., 2012; Morino et al., 2006). Moreover, the influence of organic compounds on gas-aerosol partitioning of nitrate should be investigated. Finally, the modelling of coarse mode nitrate remains a challenge (Berge, 2009; Hodzic et al., 2006). The current model set-up underestimates the amount of coarse nitrate, but evaluation is difficult as sodium chloride on the filter reacts with gaseous nitric acid yielding additional nitrate (Weijers et al., 2012). As sea salt is mainly present in the coarse mode, this artefact occurs predominantly in the PM<sub>10</sub> sampler and to a lesser extent in the PM<sub>2.5</sub> sampler. Hence, a substantial but unknown part of the difference between the samplers, and thus the coarse mode, may be artificial. More experimental work is needed to constrain the coarse mode nitrate concentrations in different environments.

### Mineral dust

An new addition to the input data were mineral dust emissions from sources inside the European domain (as opposed to boundary conditions that account for e.g. Sahara dust episodes). A first attempt has been made by Vautard et al. (2005), who focused on wind-blown dust. The mineral dust emission functions included in LOTOS-EUROS build on these studies and include additional functions for traffic re-suspension and agricultural practices (Schaap et al., 2009). The latter are based on a limited experimental basis, which may not be representative for the full range of European conditions. Moreover, the coupling of emission factors with meteorological parameters is very basic and needs to be improved. Denier van der Gon et al. (2010) estimated the overall uncertainty associated with the modelled concentrations of mineral dust to be a factor 2–3, which is in line with estimates by Vautard et al. (2005). Modelled mineral dust concentrations across the Netherlands exceed the measured concentrations by a factor 2. However, the Dutch campaign data (Weijers et al., 2011) are systematically on the low side compared to measurements at other locations in Europe, at which the LOTOS-EUROS model in general underestimates mineral dust concentrations (Denier van der Gon et al., 2010). New measurement data for Rotterdam give higher concentrations than those obtained

during the 2007–2008 campaign (Keuken et al., 2011). Hence, more experimental data on mineral dust concentrations and source characterisation are needed to confirm its concentration and unravel its origin.

In short, LOTOS-EUROS misses about 40 % ( $8 \mu\text{g m}^{-3}$ ) of the measured  $\text{PM}_{10}$  mass. It can be explained by an underestimation of nitrate by  $1.5 \mu\text{g m}^{-3}$  and organic matter by  $4\text{--}5 \mu\text{g m}^{-3}$ . Mineral dust concentrations may be overestimated up to  $1 \mu\text{g m}^{-3}$ . Considering that about 10 % (about  $2 \mu\text{g m}^{-3}$ ) is unexplained in the mass closure exercise performed on the experimental data (Weijers et al., 2011), the gap to the explained measured mass is only about  $1 \mu\text{g m}^{-3}$ .

If model improvements concerning nitrate and especially (secondary) organic matter are implemented, the anthropogenic contribution to  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  concentrations is expected to increase, as these substances mainly originate from man-made emissions. The domestic and the transport sector are expected to become more dominant, because anthropogenic VOC emissions occur mainly in those sectors.

#### 2.4.3 Comparison to other source apportionment studies for the Netherlands

Previous studies to assess the origin of PM in the Netherlands have used the OPS model (Buijsman et al., 2005; Velders et al., 2008, 2009, 2010, 2011). Substantial differences between the two models exist. LOTOS-EUROS is able to model non-linear processes, which OPS linearises. In OPS, formation of SIA components is irreversible, whereas LOTOS-EUROS uses an equilibrium module to make sure that the concentrations of the different SIA components are balanced. LOTOS-EUROS included more PM components, such as mineral dust, and uses lower deposition velocities than OPS. OPS runs on a  $1 \times 1 \text{ km}^2$  resolution and uses a plume description to model the transport of air pollution, whereas LOTOS-EUROS has a lower resolution ( $7 \times 7 \text{ km}^2$  in this study) and the model is Eulerian. Although these differences between the models might generate quite different model outcomes, this study largely confirms previous work with OPS. The shares for Dutch (15 %) and foreign sources (28 %) to  $\text{PM}_{10}$  found in this study are very close to those derived by Buijsman et al. (2005), respectively 15 and 30 %. Buijsman et al. (2005) arrived at a non-modelled fraction of 55 %, including sea salt and mineral dust. In this study, we were able to reduce the non-modelled share to 40 %.

The explanation of the missing mass is better in the present study than in Buijsman et al. (2005), who labelled most of it as ‘soil dust and other’ whereas we now show that it is not soil material but mostly organic aerosol from both anthropogenic and biogenic origin. A more recent application of OPS by Velders et al. (2008, 2009, 2010) attributes on average for the years 2007–2009  $3.7 \mu\text{g m}^{-3}$  of  $\text{PM}_{10}$  (in total  $23.5 \mu\text{g m}^{-3}$ ) to Dutch sources. Foreign emissions including international shipping cause  $7.2 \mu\text{g m}^{-3}$  of  $\text{PM}_{10}$

in the Netherlands, and sea salt is estimated to contribute  $4.5 \mu\text{g m}^{-3}$ . Non-modelled components, including mineral dust, add another  $8.4 \mu\text{g m}^{-3}$  on average. We arrive at a Dutch contribution to  $\text{PM}_{10}$  of  $3.4 \mu\text{g m}^{-3}$  and a foreign contribution of  $6.5 \mu\text{g m}^{-3}$  on average for the Netherlands in 2007–2009, including mineral dust. The relatively larger share for foreign sources found in this study compared to Velders et al. (2008, 2009, 2010) can be explained by the lower deposition velocity of particles in LOTOS-EUROS. The emission database used in both studies is almost the same and differences are minor. The attribution of the Dutch share of the average  $\text{PM}_{10}$  concentrations to sectors is comparable for the two studies, with the largest difference for the residential sector ( $0.09 \mu\text{g m}^{-3}$  for LOTOS-EUROS and  $0.5 \mu\text{g m}^{-3}$  for Velders et al. (2008, 2009, 2010)). The source attribution for  $\text{PM}_{2.5}$  is also similar for the two studies, although LOTOS-EUROS yields somewhat lower concentrations due to industry and transport compared to Velders et al. (2008, 2009, 2010).

The domestic contribution to  $\text{PM}_{2.5}$  is  $2.9 \mu\text{g m}^{-3}$  Velders et al. (2008, 2009, 2010) versus  $2.2 \mu\text{g m}^{-3}$  (this study), whereas the foreign contribution is again larger for the OPS studies ( $6.2$  versus  $5.4 \mu\text{g m}^{-3}$ ).

As LOTOS-EUROS includes mineral dust, which OPS does not, and uses a lower aerosol dry deposition velocity than OPS, a higher modelled PM concentration for the LOTOS-EUROS model was expected. This was not found, and since OPS models higher concentrations of national primary material this hints at an important difference in the mixing and short range transport characteristics. Inspection of the modelled distributions shows that the impact of large urban areas and major highways is much more pronounced for OPS. The higher resolution in combination with the plume approach used in OPS appears to result in a systematically larger share of ground level primary PM due to national emissions. As emissions may be diluted too quickly in the grid model LOTOS-EUROS, incorporating a plume-in-grid approach in LOTOS-EUROS might be beneficial as this would combine the benefits of using a non-linear regional CTM with the ability to model local concentrations more accurately.

## 2.5 Conclusions and outlook

For the first time, a chemically consistent source apportionment for particulate matter was obtained for the Netherlands, that provides insight in the spatial and temporal variability of the source apportionment per sector. A dedicated source apportionment module was developed for the regional air quality model LOTOS-EUROS and used to establish the source attribution of  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  in the Netherlands for 2007 to 2009 at sector level, distinguishing between national and foreign sources. Special attention was given to the source attribution during peak episodes. The quality of the source apportionment depends on the quality of the emission input data as well as the capability of

the model to capture the formation routes and fate of the components in a realistic way. The modelled  $PM_{10}$  concentrations miss about 40 % ( $8 \mu\text{g m}^{-3}$ ) of the measured  $PM_{10}$  mass. This is mostly explained by an underestimation of nitrate (about  $1.5 \mu\text{g m}^{-3}$ ) and organic matter (about  $4\text{--}5 \mu\text{g m}^{-3}$ ). Therefore, it is concluded that a better understanding and representation of emissions and atmospheric processes concerning primary and secondary organic aerosol and nitrate will reduce the non-modelled fraction considerably, significantly improve the presented source allocation and may change the source sector contributions (as not all source sectors will contribute equally to organic matter and nitrate). Furthermore, the results are sensitive to the assumption concerning the origin of ammonium nitrate, an important PM component in the Netherlands.

On average for the years 2007–2009, the modelled  $PM_{10}$  concentration in the Netherlands was  $13\text{--}22 \mu\text{g m}^{-3}$ , depending on location. A gradient from north ( $13 \mu\text{g m}^{-3}$ ) to south ( $18 \mu\text{g m}^{-3}$ ) was observed, with higher concentrations in densely populated areas with large industrial activities like Rotterdam. For  $PM_{2.5}$  the concentration was  $9\text{--}11 \mu\text{g m}^{-3}$ , with the highest values along the west-east line in the middle of the country. The annual average observed concentrations for these years were  $22.8\text{--}25.2 \mu\text{g m}^{-3}$  for  $PM_{10}$  and  $13.8\text{--}15.0 \mu\text{g m}^{-3}$  for  $PM_{2.5}$  (Velders et al., 2008, 2009, 2010). This leaves about 9 and  $5 \mu\text{g m}^{-3}$  of non-modelled mass for  $PM_{10}$  and  $PM_{2.5}$ , respectively.

Overall, this study confirms previous research on the origin of particulate matter in the Netherlands, but captures more of the PM mass with modelling and offers more detail. Based on modelled PM, 70–80 % of  $PM_{10}$  and 80–95 % of  $PM_{2.5}$  in the Netherlands is man-made. About 1/3 of anthropogenic  $PM_{10}$  is of Dutch origin and 2/3 originates in foreign countries. Agriculture and transport are the Dutch sectors with the largest contribution to  $PM_{10}$  mass in the Netherlands, together responsible for 85 % of the Dutch contribution. The foreign contribution is more equally apportioned to road transport, other transport, industry, power generation and agriculture, making up 90 % of the foreign contribution to PM in the Netherlands.

In general, the Dutch contribution to the concentration of primary aerosol is larger than for secondary species. The sectoral origin of the PM components changes per substance and is location and time dependent. During peak episodes, natural sources are less important than under normal conditions, whereas especially road transport and agriculture become more important. For the Netherlands as a whole, the foreign share is larger in the high concentration range. This can be explained by the fact that peak episodes are usually associated with easterly winds or stable conditions, while the natural components (mainly sea salt) show the highest concentrations with westerly winds.

To evaluate the model performance the model results were compared to mass concen-

tration measurements throughout the Netherlands. To gain further insight in the quality of the source apportionment a more specific model evaluation is needed. Comprehensive experimental data sets allow to identify and apportion observed PM concentrations to source categories using a statistical receptor model (e.g. Positive Matrix Factorisation (PMF)) or specific tracers (Viana et al., 2009). To optimally use specific tracers such as vanadium for heavy fuel oil combustion a redefinition of the apportionment in terms of fuels may be worthwhile.

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## Dynamic ammonia emission time profiles improve ammonia modelling



**A**CCURATE MODELLING OF mitigation measures for nitrogen deposition and secondary inorganic aerosol (SIA) episodes requires a detailed representation of emission patterns from agriculture. In this study the meteorological influence on the temporal variability of ammonia emissions from livestock housing and application of manure and fertiliser are included in the chemistry transport model LOTOS-EUROS. For manure application, manure transport data from Flanders (Belgium) were used as a proxy to derive the emission variability. Using improved ammonia emission variability strongly improves model performance for ammonia, mainly by a better representation of the spring maximum. The impact on model performance for SIA was negligible because ammonia is not a limiting factor for SIA formation in the ammonia-rich region in which the emission variability was updated. The contribution of Flemish agriculture to modelled annual mean ammonia and SIA concentrations in Flanders were quantified at respectively 7–8 and 1–2  $\mu\text{g m}^{-3}$ . A scenario study was performed to investigate the effects of reducing ammonia emissions from manure application during PM episodes by 75 %, yielding a maximum reduction in modelled SIA levels of 1–3  $\mu\text{g m}^{-3}$  during episodes. Year-to-year emission variability and a soil module to explicitly model the emission process from manure and fertiliser application are needed to further improve the modelling of the ammonia budget.

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### 3.1 Introduction

Ammonia ( $\text{NH}_3$ ) is the primary form of reactive nitrogen in the environment (Sutton et al., 2013).  $\text{NH}_3$  is lost to the environment at different stages of the nitrogen cascade: during and after application of fertiliser to land, from senescence of plants, animal excretion in housing systems, during grazing and after application of manure, in food processing, at industries using  $\text{NH}_3$  and as a byproduct from car exhausts equipped with a three-way catalyst (Erisman et al., 2007; Galloway et al., 2003). The atmospheric lifetime of ammonia is limited to several hours as it is effectively removed by dry and wet deposition. Once deposited, the reduced nitrogen components contribute to acidification and eutrophication of vulnerable terrestrial and aquatic ecosystems that can lead to reduced biodiversity (Bobbink et al., 1998; Krupa, 2003). Recently, also the role of reduced nitrogen in the fixation of carbon dioxide has emerged as a new research topic (Reay et al., 2008).

Ammonia readily reacts with sulphuric and nitric acid to form its particulate ammonium salts (Fowler et al., 2009). These particles play an important role in the radiation balance of the earth as they contribute effectively to light scattering and they alter the number, size and hygroscopic properties of cloud condensation nuclei (Xu and Penner, 2012). Moreover, particulate ammonium salts provide a means of long range transport of reduced nitrogen due to their longer atmospheric lifetime than ammonia. In terms of mass, ammonium salts contribute largely (40–50 %) to the levels of fine particulate matter (Putaud et al., 2004), which is thought to cause adverse health effects (Brunekreef and Holgate, 2002). Especially ammonium nitrate concentrations are increased during particulate matter episodes in Europe (Vercauteren et al., 2011; Weijers et al., 2011). The potential to mitigate particulate matter concentrations through ammonia emission reductions has been highlighted by several modelling studies (e.g. Banzhaf et al., 2013; Bessagnet et al., 2014; Erisman and Schaap, 2004). In comparison to mitigating emissions of sulphur dioxide and nitrogen oxides, taking measures aimed at reducing ammonia emissions is considered to be cost-effective (Pinder et al., 2007).

Despite its central role in many environmental threats, our knowledge about the ammonia budget is rather poor. Agriculture largely dominates the ammonia emissions to air in Europe, of which livestock excretion is the most important source (Eurostat, 2010). However, there are large uncertainties in the emission estimates for ammonia with errors over 50 % on the global emission budget and even higher uncertainties on regional/local scales (e.g. Galloway et al., 2008; Sutton et al., 2013). In north western Europe, livestock housing and manure application are the agricultural activities leading to the largest ammonia emissions (Velthof et al., 2015). Emissions from livestock housing in principle depend on the total inorganic nitrogen content of manure, the temperature and ventilation conditions as well as housing type (Groot Koerkamp et al., 1998). Manure and fertiliser application occurs mainly at the start of the growing season for

summer and winter crops, which occurs at different times in different climate zones and may differ between years (Geels et al., 2012). Besides, the timing of manure application depends on soil conditions such as soil water content and non-frozen conditions, as well as agricultural practice, crop type and legislative limitations (Hutchings et al., 2001; Webb et al., 2010). Although the annual emissions of manure application are lower than those from livestock housing, the limited time period of application causes these emissions to dominate during springtime in north western Europe.

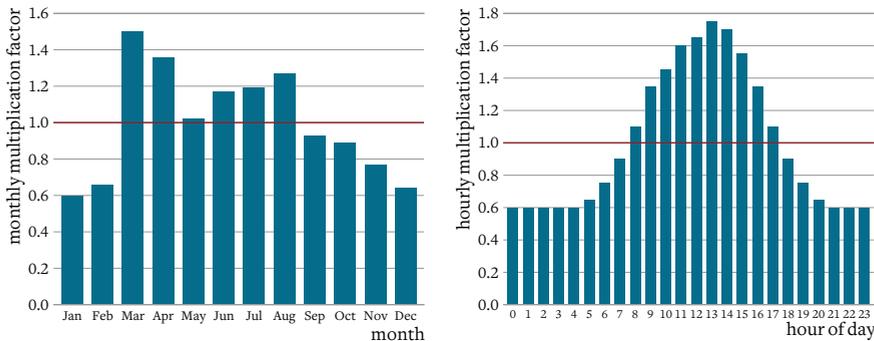
Designing mitigation strategies for particulate matter relies on the use of chemistry transport models (CTMs) (Kieseewetter et al., 2015; Simpson et al., 2012). The emission information used in CTMs consists of inventories obtained by combining activity data and activity-specific emission factors. In most CTMs, the annual total emission of ammonia is translated into hourly fluxes using relatively simple approaches (Hutchings et al., 2001; Pouliot et al., 2012). Hence, the intrinsic dependence of ammonia emissions on meteorological conditions is neglected, which may be a severe limitation (Sutton et al., 2013). Several validation studies have highlighted the underestimation of the temporal variability in ammonia concentrations in comparison to observations (Menuet and Bessagnet, 2010; Pouliot et al., 2012; Skjøth and Geels, 2013). Moreover, evaluation of seasonal cycles have highlighted that the month with maximum ammonia levels in spring is often not predicted correctly (e.g. Banzhaf et al., 2013). A first attempt to model NH<sub>3</sub> emissions dynamically has been presented for Denmark (Skjøth et al., 2011). Application of the emission model including temperature effects but neglecting impacts of soil conditions improved the CTM skill. A second study related agricultural cropping information and a process based description of the ammonia evaporation from soils after fertiliser application (Hamaoui-Laguel et al., 2014). This study showed that the more explicit approach affected the spatial distribution of the ammonia emissions in France. Moreover, they reported a systematic effect on modelled SIA concentrations for a three-month period in 2007. The temporal variability in manure application is not yet included in this study. Paulot et al. (2014) use an inverse modelling approach to establish ammonia emission timing characteristics from wet deposition flux measurements while Bash et al. (2013) use a process-based approach by coupling a CTM to an agroecosystem model. These recent efforts show that the need to improve the temporal variation of ammonia emissions is widely recognised.

For some countries with a large livestock farming sector, detailed data on manure production, transport and/or application are available in order to monitor and regulate the amount of manure applied to the land. This is for example the case for Flanders, where in 2013 82 % of ammonia emissions came from animal manure (VMM, 2014). In this study we examine the use of Flemish manure transportation data to model the temporal variability in ammonia emissions from manure application. Moreover, we assess if the modified temporal variability affects modelled ammonia and SIA concentrations

using the CTM LOTOS-EUROS. Using the updated variability, we investigate the impact of reducing emissions from manure application on PM levels during episodes.

### 3.2 Ammonia emission variability

The CTM LOTOS-EUROS uses sector-specific time profiles to model the temporal variation of anthropogenic emissions over the year. For ammonia from agriculture, the seasonal and hourly variation that is used is shown in figure 3.1. Standard practice in CTMs is to use these fixed time profiles for each year, independent of climatological variables (Flecharth et al., 2013). In reality, however, meteorological conditions have a large impact on emissions from agriculture. The start of the growing season and soil conditions determine when farmers work and fertilise their land. Also, emissions of volatile ammonia from manure and livestock housing increase with temperature. As the fate of reactive nitrogen after emission is also highly dependent on concurring meteorological conditions, it is important to use meteorological dependent time profiles for ammonia emissions in LOTOS-EUROS.



**Figure 3.1:** Standard time profiles for ammonia emissions from agriculture in LOTOS-EUROS (Schaap et al., 2004).

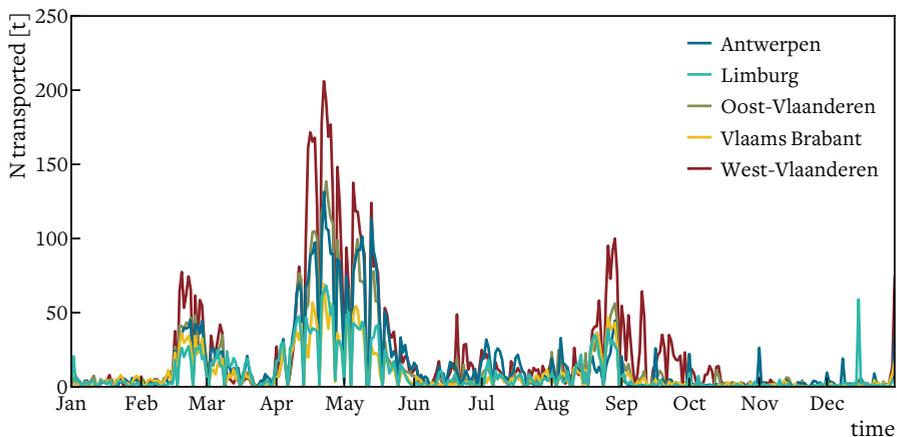
To investigate the importance of a correct representation of temporal variability in ammonia emissions, updated emission profiles for manure application, fertiliser application and emissions from livestock housing are used in this study. These time profiles are described in the following sections.

#### 3.2.1 Manure application

Manure transportation data were used as a proxy to estimate the variability in ammonia emissions from manure application in Flanders during year. The Flemish Landmaatschappij (VLM) provided manure transportation data for 2007–2011 comprising manure transports between farmers on a province basis. For these transports, the

provinces in which sending and receiving farmer reside and the amount of manure, including its nitrogen content, are reported. Two types of transport data were used. Daily data are available for manure transports across multiple municipality boundaries. For manure that is transported across less than two municipality boundaries, longer running contracts can be reported (these were not available for 2007). The VLM divides these evenly over the weeks in the contract period. For the years 2007 to 2011, daily reports of manure transport accounted for 70 % of the total nitrogen content of the manure, while the longer running contracts contributed only 30 %.

Figure 3.2 shows the amount of manure transport (in kg nitrogen) reported on a daily basis for each receiving province for 2008. In this year, manure transport peaked in early spring (February–March), late spring (April–May) and late summer (August–September). In April–May, the amount of transported manure is three times higher than in February–March, while the August–September peak is comparable to the latter. All provinces follow roughly the same pattern, both for the daily and longer-term transport data. These features are seen for each year in the 2007–2011 period, although for some years the two spring peaks overlap. This is for example the case in 2007 and 2011, in which temperatures were high in late winter and early spring, causing an early start of the growing season. In these years the second spring peak in manure transport occurs up to 20 days earlier than in 2008. On Sundays and public holidays, the quantity of transported manure is much lower than during the week. This is probably because although manure transport on these days is allowed, application of manure to the fields is prohibited.



**Figure 3.2:** Daily manure transport data for 2008 for the Flemish provinces.

In total, the manure transport data used in this study account for roughly one third of the amount of manure used in Flanders each year. The remaining two thirds consists of

manure that farmers apply on their own land. This is mainly manure from dairy cows applied on grass and maize fields. To which extent these data are representative for the manure application for which no manure transport documents are available, is difficult to say as no detailed data on this part of manure application is available. According to VLM experts (Dr. B. Fernagut, personal communication) it is valid to assume that the non-documented part of manure application follows the same temporal patterns. Especially for the day-to-day variation the same patterns are expected for both transported and non-transported manure. This variation is determined by weather conditions (e.g. frost, heavy rain) rather than the growth season of the specific crop on the field. The seasonal pattern of grassland fertilisation (which is largely not represented in the data) is different from crop fertilisation as manure spreading in summer is common for grasslands but not for crops. This could mean that using the manure transport data as proxy for all manure spreading causes an underestimation of ammonia emissions in summer.

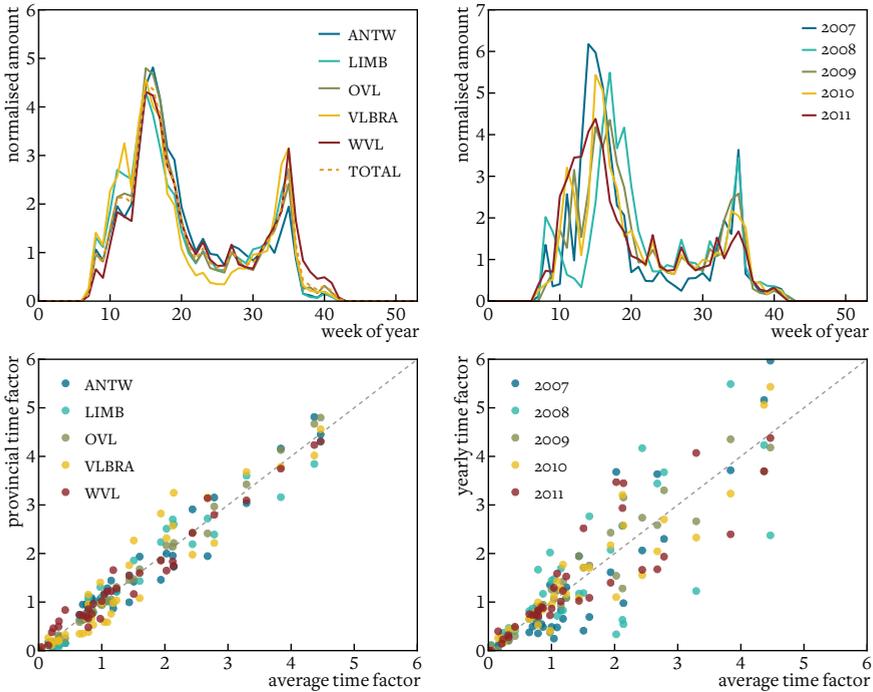
In this study, we use the pattern of manure transport as a proxy for the temporal pattern of ammonia emissions from manure application. This proxy is only valid under a number of important assumptions:

- Manure is applied to the fields on the day of transport, i.e. no storage occurs on the receiving farm. The fact that on Sundays and public holidays hardly any manure transport takes place supports this assumption.
- Ammonia emissions from manure application occur on the day of application.
- The amount of ammonia emitted is directly proportional to the amount of nitrogen applied on the field, i.e. effects of differences in application technique, soil type and condition and temperature are not taken into account in this study.

This implies that the time profile for ammonia emissions from manure in this study is a simplification of reality. However, given the  $7 \times 7 \text{ km}^2$  scale at which we calculate ammonia concentrations, variables like soil type and application technique that differ for each plot of land have to be aggregated anyway.

The transport data are converted into time profiles by dividing the weekly data over the days using the day-to-day variation emerging from the transport data on a daily basis. Also, for Sundays and public holidays, on which manure application is not allowed, the transported manure is assumed to be applied to the land on the days directly before and after the day(s) on which manure application is forbidden. For the period 16 October – 15 February, the time profile is set to zero as Flemish legislation prohibits manure application for the whole period. To convert this time profile to an hourly emission profile, the manure transport data are normalised and multiplied by the hourly profile shown in figure 3.1.

Weekly aggregated time profiles derived from the manure transport data are shown in figure 3.3. The left panel shows an average over all years for each of the five provinces, while the right panel shows the average for all provinces for each year. It is clear that the difference between years (caused by meteorological differences) is larger than the difference between provinces, with  $r^2$  values of 0.84 and 0.97, respectively. We therefore assume that an average profile for Flanders for each year can be used for all provinces.

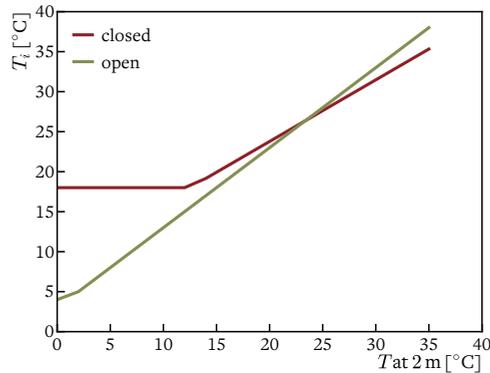


**Figure 3.3:** Upper panels: weekly time profile for ammonia emissions from manure application for the years 2007–2011 for each province (*left*) and an average for all provinces for each year (*right*). Lower panels: corresponding scatter plots comparing the variation in time profiles between provinces (*left*) and years (*right*) to the 5-year average time profile for Flanders as a whole. The provinces are West-Flanders (WVW), East-Flanders (OVL), Antwerp, (ANTW), Limburg (LIMB) and Flemish-Brabant (VLBRA).

### 3.2.2 Ammonia emissions from livestock housing and fertiliser application

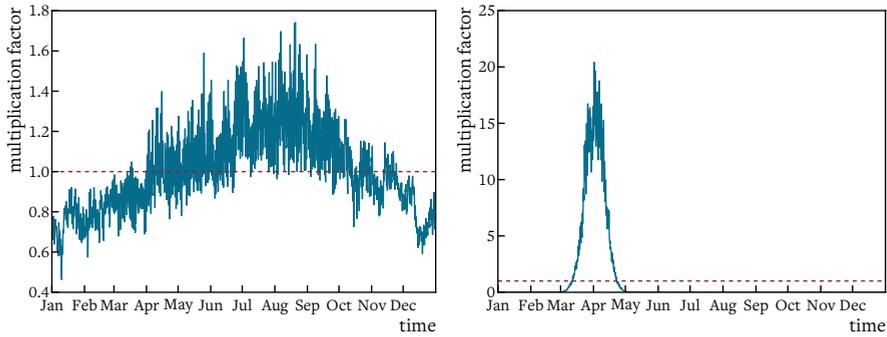
The variability of ammonia emissions from livestock housing over the year is adapted to better reflect the influence of temperature on emissions. With high temperatures, ammonia evaporates more efficiently from manure in livestock housing, especially for open livestock housing in which there is no barrier between the air inside and outside

the housing facility. We use the relation between  $T_i$  (temperature inside livestock housing) and 2-meter ambient temperature for open and closed livestock housing presented in Skjøth et al. (2004), which is displayed in figure 3.4. In this study we assumed that 50 % of the emissions from livestock housing comes from open facilities and 50 % from closed systems.



**Figure 3.4:** Relation between temperature inside livestock housing ( $T_i$ ) and ambient temperature at 2 m ( $T$ ) (Skjøth et al., 2004).

To represent the variability in ammonia emissions from application of chemical fertiliser, we use the Gaussian distributions with a correction factor to account for differences in ambient temperature for spring and summer fertiliser application as presented in Skjøth et al. (2004). The parametrisations for emissions from livestock housing and fertiliser application are applied on each grid cell in the model domain using temperature data from the European Centre for Medium-Range Weather Forecasts (ECMWF). After normalisation for each grid cell, this leads to hourly time factors. Figure 3.5 presents the time profiles for ammonia emissions from livestock housing and fertiliser application for Wingene in Flanders (51.06°N, 3.28°E). For livestock housing, the ammonia emissions during winter are about half of those during the summer months. On top of this seasonal variation, day-to-day and diurnal variations in temperature can cause another 25 % variability in emission factor. The time profile for ammonia emissions from chemical fertilisers shows a strong maximum in early March, with the complete annual budget being emitted between the beginning of February and mid-April. This means that, while this emission source causes only 10 % of the annual ammonia emissions from agriculture in Flanders, its contribution to ammonia concentrations in spring can be quite large. Daily variations in temperature can give rise to a 20 % deviation from the Gaussian distribution that describes the seasonal emission pattern.



**Figure 3.5:** Temporal variability of  $\text{NH}_3$  emissions from livestock housing (*left*) and fertiliser application (*right*) for Wingene (Flanders) in 2009, based on Skjøth et al. (2004).

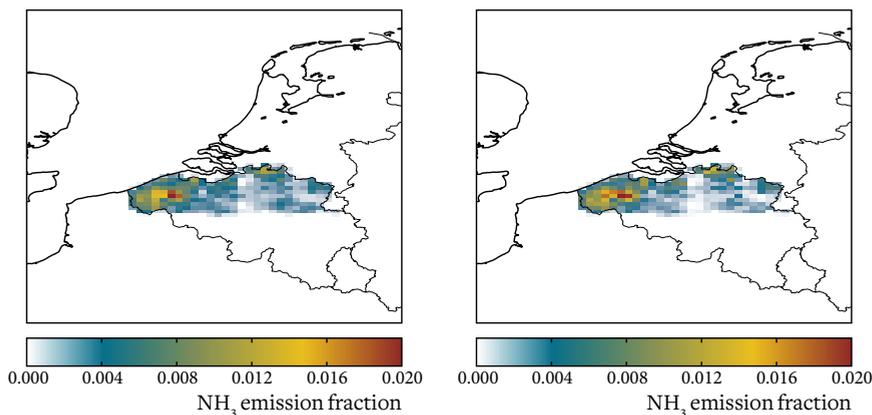
### 3.2.3 Emission inventory

For anthropogenic trace gas emissions we use the European JOAQUIN emission database (Denier van der Gon et al., 2015, pages 7–10) which is based on the TNO-MACC-II emission database (Kuenen et al., 2014). In the JOAQUIN set, emissions from the Netherlands, Flanders and the UK have been replaced with the countries' own high resolution gridded emission inventories which have been converted and aggregated to the  $1/8 \times 1/16$  degree grid. For Flanders the total  $\text{NH}_3$  emission from agriculture is 40 kt (28 % manure, 62 % livestock housing, 10 % chemical fertiliser) (VMM, 2014). The geographical distribution for these sources were taken from the emission mapping E-MAP model (Maes et al., 2008) and displayed in figure 3.6.

## 3.3 Chemistry transport simulation and validation

### 3.3.1 Model description LOTOS-EUROS

LOTOS-EUROS is a three dimensional chemistry transport model. The off-line Eulerian grid model simulates air pollution concentrations in the lower troposphere solving the advection-diffusion equation on a regular lat-lon-grid with variable resolution over Europe (see Schaap et al. (2008) for a detailed description of the model). The vertical transport and diffusion scheme accounts for atmospheric density variations in space and time and for all vertical flux components. The vertical grid is based on terrain following vertical coordinates and extends to 3.5 km above sea level. The model uses a dynamic mixing layer approach to determine the vertical structure, meaning that the vertical layers vary in space and time. The layer on top of a 25 m surface layer follows the mixing layer height, which is obtained from the ECMWF meteorological input data



**Figure 3.6:** Emission pattern of  $\text{NH}_3$  (fraction, summing to 1 for Flanders) from manure and fertiliser application (*left*) and livestock housing (*right*) in Flanders based on E-MAP (Maes et al., 2008) and used in this study.

that is used to force the model. The height of the two reservoir layers is determined by the difference between the model top at 3.5 km and the mixing layer height. Both layers are equally thick with a minimum of 50 m. When the mixing layer extends near or above 3.5 km, the top of the model exceeds 3.5 km according to the above-mentioned description. The horizontal advection of pollutants is calculated applying a monotonic advection scheme developed by Walcek (2000).

Gas-phase chemistry is simulated using the TNO CBM-IV scheme, which is a condensed version of the original scheme (Whitten et al., 1980). Hydrolysis of  $\text{N}_2\text{O}_5$  is explicitly described following Schaap et al. (2004). LOTOS-EUROS explicitly accounts for cloud chemistry computing sulphate formation as a function of cloud liquid water content and cloud droplet pH as described in Banzhaf et al. (2012). For aerosol chemistry LOTOS-EUROS features the thermodynamic equilibrium module ISORROPIA2 (Fountoukis and Nenes, 2007). Dry deposition fluxes are calculated using the resistance approach as implemented in the DEPAC (DEPosition of Acidifying Compounds) module (Erisman and Baldocchi, 1994; Van Zanten et al., 2010). Furthermore, a compensation point approach for ammonia is included in the dry deposition module (Wichink Kruit et al., 2012). The wet deposition module accounts for droplet saturation following Banzhaf et al. (2013). In LOTOS-EUROS, the temporal variation of the non-agricultural emissions is represented by monthly, daily and hourly time factors that break down the annual totals for each source category (Schaap et al., 2004). The biogenic emission routine is based on detailed information on tree species over Europe (Köble and Seufert, 2001). The emission algorithm is described in Schaap et al. (2009) and is very similar to the simultaneously developed routine by Steinbrecher et al. (2009). Sea salt emissions are

described using [Mårtensson et al. \(2003\)](#) for the fine mode and ([Monahan et al., 1986](#)) for the coarse mode. Dust emissions from agricultural activities and resuspension of particles from traffic are included following [Schaap et al. \(2009\)](#).

LOTOS-EUROS includes a source apportionment module, which enables tracking the origin of the modelled concentrations of tracers containing sulphur, carbon, oxidised or reduced nitrogen compounds and primary particulates. Using a labelling technique the module calculates the contribution of specified sources for all model grid cells and time steps. The contributions per label are calculated as fractions of the total tracer concentration. The source apportionment module is extensively described in [Kranenburg et al. \(2013\)](#).

### 3.3.2 Model simulations

In this study three simulations were performed to quantify the impact of the new approach to model the temporal variability of agricultural ammonia emissions. The first simulation, in which the default emission profiles are used, serves as the base case. In the following, this run is called *default*. Next, a simulation is performed in which the time profiles from manure, livestock housing and fertiliser application emissions are replaced by the improved approaches, called the *new* run. These simulations were run for the period 2007–2011. A third run was done for 2009 only, using the standard time profiles for emissions from manure application while using the updated ones for livestock housing and fertiliser application. This run is called *house-fert*. This enables us to quantify the influence of the change in emissions from manure on the model results and performance.

The three model runs described above were run for a domain centred over Belgium and the Netherlands (2°–9°E, 49°–55°N) on a  $0.125^\circ \times 0.0625^\circ$  lon-lat resolution (about  $8 \times 7 \text{ km}^2$ ). These high resolution simulations are nested (one way) into a single European scale simulation (15°W–30°E, 35°–70°N) at  $0.5^\circ \times 0.25^\circ$  lon-lat resolution. The lower resolution European simulation was performed using the default emission profiles, since extrapolation of the time profiles based on manure transport data to regions far away from Flanders is not warranted. This is due to shifts in climatological conditions and agricultural practices. Because the atmospheric lifetime of ammonia is in the order of a few hours, we feel that the impact of the boundary conditions is limited given the size of the zoom domain around the Netherlands and Belgium.

To track the contribution of emission sources to ammonia and SIA concentrations, the following sources were labelled in the model runs:

- Flemish livestock housing

- Flemish manure application
- Flemish fertiliser application
- Other Flemish agricultural activities
- Flemish transport
- Other sources in Flanders
- Sources from outside Flanders (including Wallonia and Brussels)
- Natural sources
- Sources outside domain boundaries.

In this way, the impact of the important ammonia emission sources in Flanders on ammonia and particulate matter concentrations can be quantified separately and the relative importance of the Flemish agricultural sector for PM levels can be compared to that of the transport sector.

### 3.3.3 Evaluation using observations

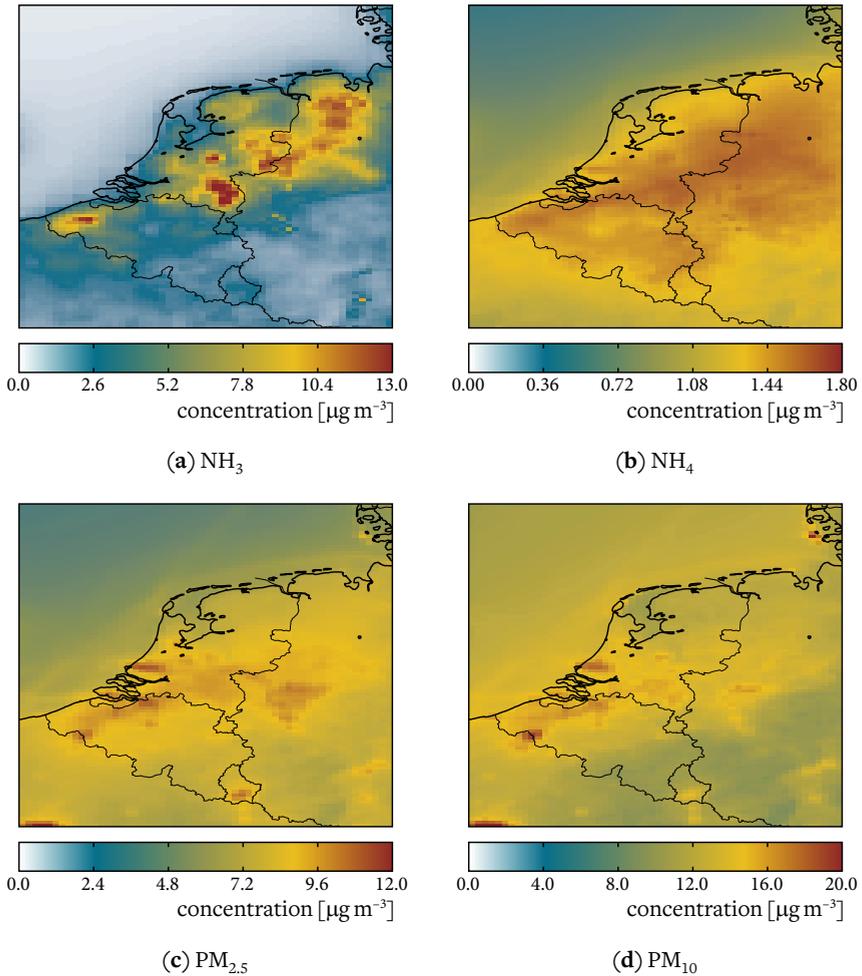
To evaluate the model performance for ammonia, a comparison of the model runs was made with measurements from the Flemish Environmental Agency (Bo van den Bril, personal communication). For the period 2007–2011 two-weekly passive sampler data are available for 20 measuring locations in Flanders, 8 of which have started in 2008 (VMM, 2013). To validate modelled PM<sub>10</sub> and SIA components NH<sub>4</sub>, NO<sub>3</sub> and SO<sub>4</sub>, measurement data from the second Chemkar campaign was used (VMM, 2010). Daily measurements of PM and its components are available from October 2008 to November 2009. Sampling occurred at every 6<sup>th</sup> day resulting in about 60 observations at each site. Note that the stations include three background sites (Moerkerke, Aarschot and Retie) and six sites in source areas. As the SIA levels are normally not enhanced at PM hotspot locations (e.g. Weijers et al., 2011) the evaluation for SIA is not expected to be affected by the location of the sites. However, for PM<sub>10</sub> we expect that the model severely underestimates concentrations at hotspots as local contributions are not captured using a regional model.

For the model validation time series of NH<sub>3</sub>, PM<sub>10</sub> and SIA components were evaluated as well as the annual average concentrations and root mean square error (RMSE) at all stations.

### 3.4 Results

#### 3.4.1 Mean geographical distributions

Figure 3.7 shows the average modelled concentrations of ammonia, ammonium,  $PM_{2.5}$  and  $PM_{10}$  for the period 2007–2011 from the *new* model run. For ammonia, the regions with intensive agriculture (the western part of Flanders, the eastern part of the Netherlands and Niedersachsen in Germany) show markedly higher concentrations ( $7\text{--}14\ \mu\text{g m}^{-3}$ ) compared to the rest of the domain ( $1\text{--}5\ \mu\text{g m}^{-3}$ ). The strong local gradients reflect the short atmospheric lifetime of ammonia.



**Figure 3.7:** 5-year average (2007–2011) modelled concentrations of  $NH_3$ ,  $NH_4$ ,  $PM_{2.5}$  and  $PM_{10}$ . Results from *new* model run.

The gradient for ammonium, for which ammonia is the only precursor, is smoother although an elevation in the source regions for ammonia is still visible. Modelled concentrations are between 1–1.65  $\mu\text{g m}^{-3}$ . For  $\text{PM}_{2.5}$ , a background annual average concentration of 7  $\mu\text{g m}^{-3}$  is modelled with concentrations in highly populated areas increasing to 9  $\mu\text{g m}^{-3}$ . For  $\text{PM}_{10}$ , the annual average background and hotspot modelled concentrations are 10–13 and 18  $\mu\text{g m}^{-3}$  respectively. For PM, gradients across the domain are dominated by other sources than agriculture, such as transport and industrial activities. In regions with high ammonia emissions such as the western part of Flanders, the contribution of ammonium to  $\text{PM}_{2.5}$  levels can be up to 20% (10% for  $\text{PM}_{10}$ ). For an overall discussion of particulate matter modelling with LOTOS-EUROS we refer to [Hendriks et al. \(2013\)](#) (chapter 2 of this thesis). Here we focus on the ammonia and SIA components.

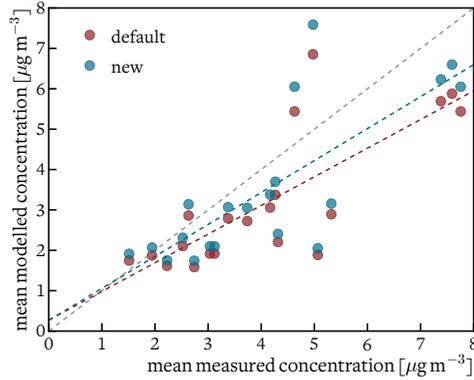
The differences in annual average modelled fields between the *default* run and the *new* run are small (not shown), both in geographical patterns and absolute levels.

### 3.4.2 Impact on ammonia modelling

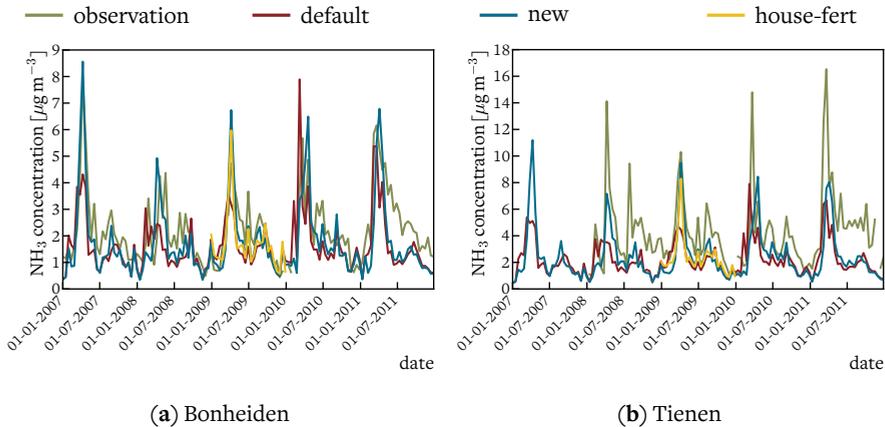
Figure 3.8 shows the average modelled ammonia concentrations for 2007–2011 for the *default* and *new* model runs compared to measured values at 20 measurement locations in Flanders. The modelled ammonia concentrations from the *new* run underestimate the measurements across Flanders by an average of 0.6  $\mu\text{g m}^{-3}$  with variations in bias ranging from  $-3$  to 2  $\mu\text{g m}^{-3}$ . All average modelled concentrations increase going from the *default* run, in which the average bias is  $-0.9 \mu\text{g m}^{-3}$ , to the *new* model run. The slight increase is explained by the higher emissions under fair weather conditions with lower removal through rainout. In general the geographical variability of modelled concentrations reflects that found in the observations.

Time series of modelled and measured  $\text{NH}_3$  concentrations for measurement sites Tienen and Bonheiden are displayed in figure 3.9. The measurements show a spring maximum in ammonia concentrations with less pronounced elevated values in summer. The general temporal pattern is captured by LOTOS-EUROS in the *default* run, although the spring maximum is strongly underestimated for most years. The *new* model run represents the spring maximum better but capturing the year-to-year and geographical variability in the magnitude of this peak remains difficult. Figure 3.10 displays the temporal correlation between the two model runs and the observations for the entire 2007–2011 period and for each measurement site, showing an improvement of 15–20% in correlation coefficient.

To distinguish the impact of updating the modelled temporal variability for ammonia emissions from manure application, livestock housing and fertiliser application, a run

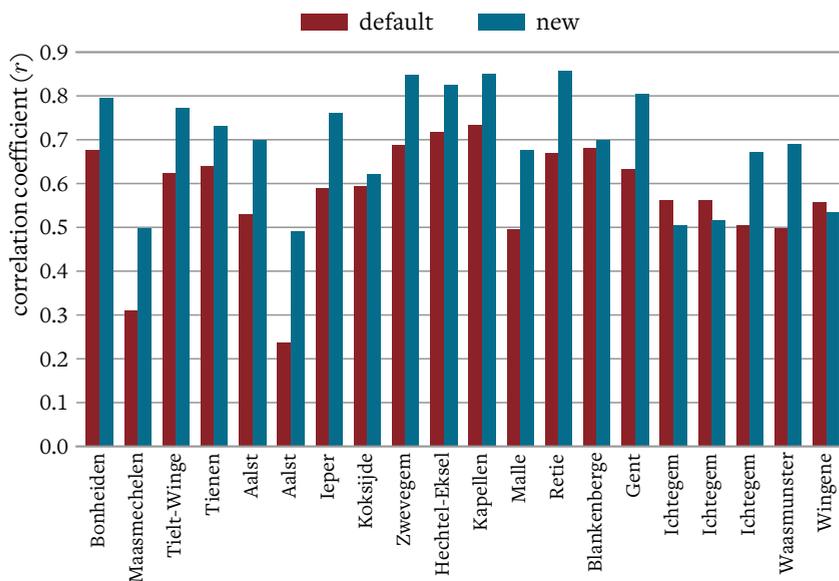


**Figure 3.8:** Measured versus modelled average  $\text{NH}_3$  concentrations for 20 measurement locations in Flanders for the *default* and *new* model runs.



**Figure 3.9:** Time series of measured and modelled ammonia concentrations at measurement locations Bonheiden and Tienen.

was done for 2009 in which only the temporal variability for the latter two were updated (run *house-fert*). For manure application the standard time profiles were used. The correlation coefficients and biases for all measurement sites for the three runs for 2009 are shown in table 3.1. For all sites, the model performance increases going from *default* via *house-fert* to the *new* settings. For most locations, updating the temporal variability for livestock housing and fertiliser application is responsible for the larger part of the improvement in correlation and bias going from the *default* to the *new* run. For some stations the update for manure application appears to be dominant. We can therefore conclude that both steps are important to improve ammonia modelling in LOTOS-EUROS.



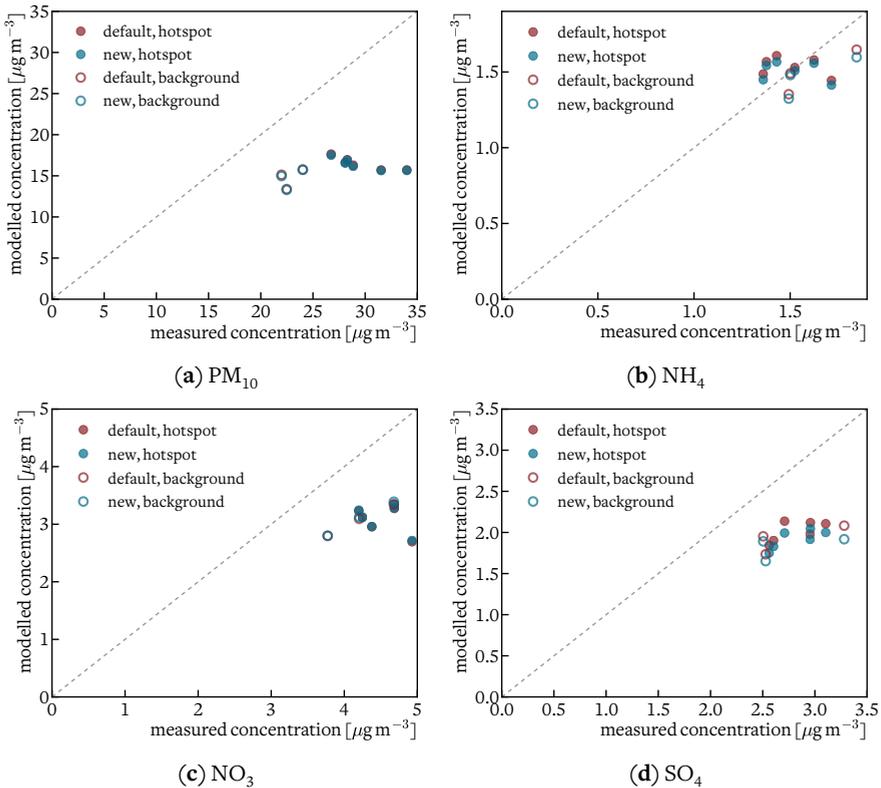
**Figure 3.10:** Correlation ( $r$ ) of *default* and *new* model runs with measurements for the period 2007–2011 for all locations.

### 3.4.3 Impact on inorganic aerosol modelling

Table 3.2 lists the bias, correlation and  $\text{RMSE}$  of the *default* and *new* model runs compared to Chemkar 2 measurement data for nine locations. This comparison shows that the performance of LOTOS-EUROS for SIA and PM changes only slightly when better temporal variability of  $\text{NH}_3$  emissions is included. For  $\text{NO}_3$  and  $\text{NH}_4$ , the *default* run even performs slightly better, although for some locations a small improvement is seen. The largest difference between the model runs is found for  $\text{SO}_4$ , for which the bias increases but the change in correlation and  $\text{RMSE}$  is in the direction of better model performance for the *new* model run. Model performance for total  $\text{PM}_{10}$  is slightly better for the *default* run.

As the model bias in table 3.2 and the plots of annual average measured and modelled values (figure 3.11) show, LOTOS-EUROS underestimates  $\text{PM}_{10}$  measurements by 30–50 %, depending on the location. The fact that the current operational LOTOS-EUROS version does not include secondary organic aerosol is thought to explain the largest part of this underestimation (Hendriks et al., 2013, chapter 2 of this thesis). The underestimation of  $\text{PM}_{10}$  concentrations is smaller for the background stations than for the hotspots, at which the contributions from local sources are not captured well by the regional LOTOS-EUROS model. SIA concentrations are underestimated about 25 % (for  $\text{NO}_3$  and  $\text{SO}_4$ ;

for  $\text{NH}_4$  no structural bias is observed). Figure 3.11 shows that the update of the time profiles for  $\text{NH}_3$  from agriculture only has a noticeable impact on modelled annual average levels of  $\text{NH}_4$  and  $\text{SO}_4$ , both of which show slightly lower modelled concentrations using the new time profiles. For these two components, LOTOS-EUROS underestimates the spatial variability of the observations in Flanders. The spatial variability of  $\text{SO}_4$  is difficult to capture in a regional model because of uncertainties in the representation of cloud chemistry. The underestimation of spatial  $\text{SO}_4$  variability causes the spatial variability of  $\text{NH}_4$  concentrations to be underestimated as well, since  $\text{NH}_4$  is bound to either  $\text{NO}_3$  or  $\text{SO}_4$ .



**Figure 3.11:** Average measured versus modelled concentrations of  $\text{PM}_{10}$ ,  $\text{NH}_4$ ,  $\text{NO}_3$  and  $\text{SO}_4$  for the *default* and *new* model run. Different symbols are used for background stations and hotspot stations. Observations taken from [VMM \(2010\)](#).

**Table 3.1:** Measured concentrations (obs), correlation (corr), bias and RMSE of *default*, *house-fert* and *new* model runs compared with two-weekly observations of ammonia in Flanders for 2009.

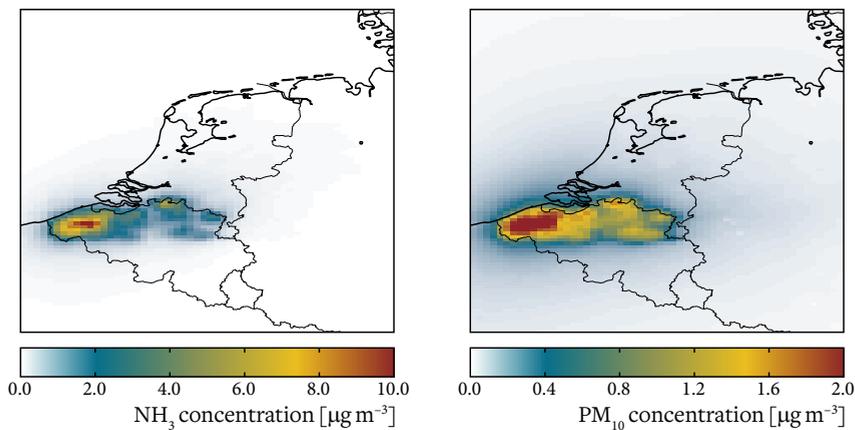
	default				house-fert				new				
	obs [ $\mu\text{g m}^{-3}$ ]	corr	bias [ $\mu\text{g m}^{-3}$ ]	RMSE	corr	bias [ $\mu\text{g m}^{-3}$ ]	RMSE	corr	bias [ $\mu\text{g m}^{-3}$ ]	RMSE	corr	bias [ $\mu\text{g m}^{-3}$ ]	RMSE
Bonheiden	2.02	0.64	-0.41	0.90	0.73	-0.28	0.76	0.83	-0.26	0.82	0.83	-0.26	0.82
Maasmechelen	2.31	0.24	-0.71	1.76	0.45	-0.56	1.55	0.50	-0.56	1.62	0.50	-0.56	1.62
Tielt-Winge	1.33	0.64	0.41	0.81	0.79	0.58	1.09	0.87	0.60	0.98	0.87	0.60	0.98
Tienen	4.00	0.80	-1.78	2.19	0.91	-1.60	1.71	0.92	-1.58	1.81	0.92	-1.58	1.81
Aalst	2.99	0.55	-0.39	1.58	0.74	-0.20	1.26	0.82	-0.19	1.32	0.82	-0.19	1.32
Ieper	7.54	0.50	-1.69	3.34	0.75	-1.20	2.22	0.85	-1.20	2.41	0.85	-1.20	2.41
Koksijde	2.71	0.43	0.24	1.49	0.60	0.55	1.98	0.66	0.62	1.68	0.66	0.62	1.68
Zwevegem	4.08	0.69	-0.63	1.70	0.88	-0.37	0.87	0.94	-0.34	1.17	0.94	-0.34	1.17
Hechtel-Eksel	1.88	0.72	-0.02	0.80	0.89	0.17	0.63	0.96	0.18	0.62	0.96	0.18	0.62
Kapellen	2.08	0.69	-0.01	0.96	0.87	0.15	0.78	0.88	0.21	0.69	0.88	0.21	0.69
Malle	4.10	0.42	-1.02	2.24	0.72	-0.73	1.51	0.80	-0.72	1.63	0.80	-0.72	1.63
Retic	3.48	0.61	-0.68	1.62	0.85	-0.39	0.88	0.91	-0.39	1.10	0.91	-0.39	1.10
Blankenberge	5.22	0.36	-3.29	3.81	0.54	-3.09	3.45	0.56	-3.05	3.54	0.56	-3.05	3.54
Gent	3.65	0.64	-0.88	1.61	0.84	-0.57	1.08	0.88	-0.54	1.14	0.88	-0.54	1.14
Ichtegem	5.31	0.56	1.77	3.25	0.68	2.50	3.67	0.72	2.53	3.19	0.72	2.53	3.19
Ichtegem	4.51	0.64	1.16	2.37	0.71	1.78	2.98	0.71	1.83	2.44	0.71	1.83	2.44
Ichtegem	8.22	0.44	-2.55	3.98	0.49	-1.93	3.45	0.58	-1.88	3.51	0.58	-1.88	3.51
Waasmunster	6.38	0.56	-3.43	5.11	0.69	-3.18	4.59	0.71	-3.16	4.79	0.71	-3.16	4.79
Wingene	7.68	0.53	-1.64	2.96	0.74	-0.88	2.51	0.77	-0.84	1.95	0.77	-0.84	1.95

**Table 3.2:** Comparison of *default* and *new* model runs with Chemkar 2 measurement data (daily measurements with 6-day intervals) from 9 locations (VMM, 2010). Stations marked with \* are background stations, the rest are hotspots.

		Moerkerke*	Rette*	Aarschot*	Borghout	Roeselare	Oostrozebeke	Zwevegem	Evergem	Zwijndrecht	
NO <sub>3</sub>	Underestimation [%]	default	28.42	25.85	45.32	28.74	30.11	26.45	23.08	32.48	
		new	27.53	25.75	44.83	28.56	29.95	26.70	22.74	32.35	
	R	default	0.65	0.79	0.77	0.90	0.70	0.69	0.75	0.68	0.83
		new	0.64	0.78	0.77	0.87	0.69	0.68	0.74	0.67	0.82
	RMSE	default	2.99	3.14	2.51	3.21	3.06	3.18	2.59	2.93	2.46
		new	3.01	3.17	2.52	3.32	3.07	3.21	2.63	2.96	2.49
NH <sub>4</sub>	Underestimation [%]	default	0.68	10.75	9.35	15.80	-13.90	2.74	-9.32	-12.42	-0.36
		new	1.43	13.46	11.30	17.57	-12.09	4.05	-6.55	-9.59	1.06
	R	default	0.76	0.89	0.89	0.87	0.77	0.77	0.83	0.80	0.86
		new	0.79	0.92	0.87	0.87	0.76	0.76	0.81	0.78	0.84
	RMSE	default	1.02	1.14	0.82	1.15	1.00	1.05	0.80	0.96	0.75
		new	0.95	1.14	0.87	1.18	1.01	1.05	0.82	0.97	0.82
SO <sub>4</sub>	Underestimation [%]	default	22.04	36.52	31.39	32.13	26.96	32.98	28.06	21.13	28.34
		new	24.49	41.53	34.69	35.56	29.74	35.15	31.66	26.42	30.82
	R	default	0.65	0.71	0.67	0.74	0.64	0.60	0.63	0.66	0.72
		new	0.74	0.80	0.68	0.79	0.64	0.62	0.64	0.68	0.75
	RMSE	default	1.80	2.35	1.63	1.81	1.92	2.08	1.69	1.87	1.84
		new	1.57	2.27	1.64	1.75	1.85	2.01	1.64	1.67	1.78
PM <sub>10</sub>	Underestimation [%]	default	34.38	31.16	40.44	40.01	50.14	53.74	34.00	43.49	40.80
		new	34.51	31.90	40.85	40.38	50.39	53.95	34.52	44.03	41.07
	R	default	0.62	0.89	0.78	0.74	0.56	0.54	0.54	0.65	0.76
		new	0.60	0.88	0.76	0.72	0.55	0.52	0.52	0.63	0.74
	RMSE	default	13.71	9.07	11.97	14.55	20.82	21.85	14.11	16.10	14.89
		new	13.88	9.39	12.20	14.78	20.98	21.96	14.35	16.37	15.10

### 3.4.4 Source apportionment

For the model run including meteorological dependent ammonia emissions from agriculture, a source attribution exercise was performed for the source categories presented in section 3.3.3. Figure 3.12 shows the modelled concentration of ammonia and  $\text{PM}_{10}$  attributed to emissions from agriculture in Flanders. The contribution of agricultural emission is highest in regions where intensive agriculture takes place, mainly the western part of Flanders. On average across Flanders, the contribution of Flemish agriculture to the 5-year average ammonia concentrations is 59 % with a maximum of 80 % ( $10 \mu\text{g m}^{-3}$ ) in the western source area. The contribution of Flemish agriculture to 5-year average  $\text{PM}_{10}$  concentrations is more evenly divided over the region and is on average 9 % (about  $1 \mu\text{g m}^{-3}$ ) going up to 15 % ( $2 \mu\text{g m}^{-3}$ ) for the western part of Flanders.



**Figure 3.12:** Modelled concentration (*new model run*) of  $\text{NH}_3$  (*left*) and  $\text{PM}_{10}$  (*right*) attributed to the agriculture sector in Flanders (average 2007–2011).

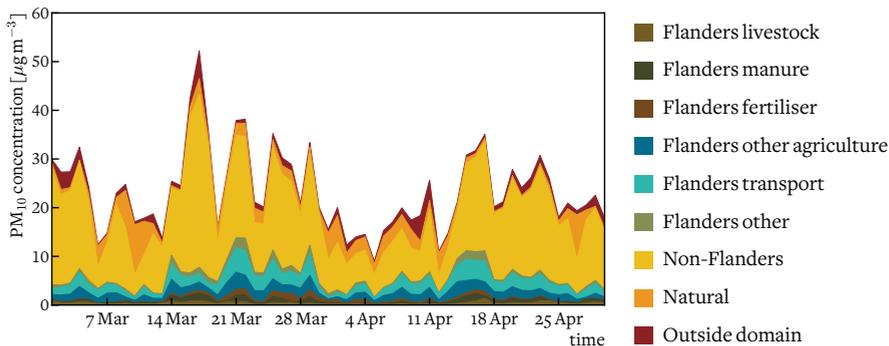
Table 3.3 shows the source attribution for all selected sectors for 5-year modelled concentrations of  $\text{NH}_3$ ,  $\text{NH}_4$  and  $\text{PM}_{10}$  for Flanders on average and for Roeselare, a village in the western part of Flanders. From this table, it is clear that the contribution of Flemish agriculture to average concentrations of  $\text{NH}_3$ ,  $\text{NH}_4$  and  $\text{PM}_{10}$  is larger in Roeselare than for Flanders on average. The contribution of Flemish agriculture to pollutant levels in Flanders is larger for  $\text{NH}_3$  than for  $\text{NH}_4$ , reflecting the strongly local character and short lifetime of  $\text{NH}_3$ , whereas  $\text{NH}_4$  can be transported across longer distances. Livestock housing is the largest contributing subsector of agriculture for all three pollutants, followed by manure application. This reflects the emission proportions.

**Table 3.3:** Source attribution percentage of  $\text{NH}_3$ ,  $\text{NH}_4$  and  $\text{PM}_{10}$  for Flanders and Roeselare (in the west of Flanders) for 2007–2011.

Source sector	Flanders			Roeselare		
	$\text{NH}_3$	$\text{NH}_4$	$\text{PM}_{10}$	$\text{NH}_3$	$\text{NH}_4$	$\text{PM}_{10}$
$\text{NH}_3$ from livestock housing Flanders	37.41	33.36	3.31	55.92	55.61	5.47
$\text{NH}_3$ from manure application Flanders	15.30	9.80	1.05	20.78	14.95	1.57
$\text{NH}_3$ from fertiliser application Flanders	5.92	3.84	0.43	4.71	3.34	0.39
Other agriculture Flanders	0.00	0.00	4.01	0.00	0.00	7.34
<b>Total Flemish agriculture</b>	<b>58.63</b>	<b>46.99</b>	<b>8.81</b>	<b>81.42</b>	<b>73.89</b>	<b>14.77</b>
Transport Flanders	0.85	1.14	11.98	0.42	0.48	9.90
Other sectors Flanders	2.86	4.25	3.31	2.97	3.74	3.17
Anthropogenic sources outside Flanders	35.52	44.19	51.31	13.97	20.05	46.84
Natural sources	0.07	0.08	18.96	0.03	0.04	20.09
Sources outside model domain	2.07	3.36	5.64	1.19	1.79	5.23

For Flanders on average the contribution of agriculture to  $\text{PM}_{10}$  is about 75 % of the contribution of Flemish road transport, about half of which stems from ammonia emissions. The remainder originates mainly from primary particulates emitted from livestock housing and during land cultivation. Agriculture and transport are the largest domestic contributors to  $\text{PM}_{10}$  in Flanders: together they cause 86 % of the domestic part of average modelled  $\text{PM}_{10}$  concentrations. Anthropogenic sources outside Flanders contribute about 50 %, whereas natural sources (mainly sea salt) contribute around 20 % depending on the distance from the coast.

The source attribution presented above looks at multi-year averages. During episodes the source attribution can be quite different. Figure 3.13 illustrates this, showing modelled  $\text{PM}_{10}$  concentrations for Flanders on average during the spring of 2011, in which PM episodes occurred from 28 February – 5 March, 15–18 March and 15–21 April. Measured concentrations during these episodes were well above  $50 \mu\text{g m}^{-3}$ . LOTOS-EUROS underestimates the measured concentrations by about 30–40 % but the source attribution information is still informative. Figure 3.13 shows that while the first two episodes have a largely regional character with a high contribution of PM from abroad, the last episode shows mainly elevated contributions from Flemish sources. During this episode, the modelled contribution of Flemish agriculture to  $\text{PM}_{10}$  roughly doubles from  $2\text{--}3 \mu\text{g m}^{-3}$  to about  $5 \mu\text{g m}^{-3}$ .



**Figure 3.13:** Source attribution of  $\text{PM}_{10}$  in Flanders during the spring of 2011.

### 3.4.5 Effect of reduction $\text{NH}_3$ emission from manure application on PM peaks

In north-western Europe, PM episodes in spring are quite common. In this period the largest share of manure and fertiliser is applied as well. If stable atmospheric conditions occur during the peak of manure application, emissions from these processes are hypothesised to contribute significantly to PM concentrations during episodes. To investigate whether shifting manure application to days before and after a PM episode can help reducing the amount of exceedance days (days at which the average  $\text{PM}_{10}$  ex-

ceeds  $50 \mu\text{g m}^{-3}$ ), a scenario study was performed in which 75 % of the ammonia emission from manure and fertiliser application of the day before and during episodes was shifted to the days before and after this period. This was done for the zoom domain described in section 3.3.2, nested in the European simulation with default time profiles. The effect of this emission reduction during PM episodes on modelled  $\text{PM}_{10}$  is shown in table 3.4. The impact on modelled  $\text{PM}_{10}$  is limited, the maximum modelled reduction is  $3.2 \mu\text{g m}^{-3}$ . The effect is largest for the episode during 15–21 April which is explained by the largely local character of this episode. During the episode 28 February – 5 March the maximum reduction in this scenario is  $0.9 \mu\text{g m}^{-3}$  illustrating the stronger regional influence (compare to figure 3.13).

**Table 3.4:** Modelled reduction in  $\text{NH}_4$  and  $\text{PM}_{10}$  concentrations in 2011 if 75 % of the emissions from manure and fertiliser application of the day before and during episodes was shifted to the days before and after this period.

Date	$\text{NH}_4$	$\text{PM}_{10}$
28 February	0.23	0.83
1 March	0.20	0.69
2 March	0.04	0.14
3 March	0.00	0.01
4 March	0.01	0.00
5 March	0.25	0.92
15 March	0.22	0.92
16 March	0.35	1.39
17 March	0.61	2.25
18 March	0.39	1.46
15 April	0.45	1.75
16 April	0.63	2.46
17 April	0.83	3.23
18 April	0.27	1.21
19 April	0.34	1.48
20 April	0.67	2.94
21 April	0.47	2.06

### 3.5 Discussion and conclusions

This study shows that using meteorological dependent temporal variability of ammonia emissions from agriculture strongly improves ammonia modelling. This is the first study in which manure transport data are used as a proxy for the temporal variability in ammonia emissions. Although the use of this proxy comes with quite large uncertain-

ties and simplifications, comparison with ambient ammonia concentration measurements show that for the  $7 \times 7 \text{ km}^2$  scale a considerable improvement over the use of standard time profiles is observed. Temporal correlation between modelled and measured ammonia concentrations increased on average 10 %. Incorporating temperature-dependent time profiles for emissions from livestock housing and chemical fertiliser application also improved the correlation with on average 15 % compared to the standard time profiles. The impact on modelled SIA and PM concentrations found in this study is limited. A correct representation of temporal variability of ammonia emissions is also important for source attribution studies that increase insight in the potential of mitigation measures during PM episodes. Also, emissions of ammonia from agriculture are the most important contributor to deposition of reduced nitrogen (Sutton et al., 2011). A better understanding of the temporal variability of this emission source will also improve nitrogen deposition modelling and allow for better informed mitigation policies.

Previous studies show a larger sensitivity of PM levels to ammonia emissions during SIA-dominated episodes (e.g. Banzhaf et al., 2013; Derwent et al., 2009; Tarrasón et al., 2003) compared to this study. The cited studies used scenarios in which annual emissions were reduced across large areas. In this work, the annual total emissions are kept the same and emissions variability is updated in a relatively small area (the zoom domain) only. This means that the high-ammonia conditions in the region are not changed, which can explain the small effect of a changed emission timing for ammonia on SIA levels. In Flanders and its surroundings more ammonia is available in the atmosphere than is needed for the reactions with sulphuric and nitric acid to form SIA components. A reduction in ammonia emissions from one source will therefore cause ammonia from another source to be transformed into ammonium more efficiently. Hence, we cannot exclude that the update of the emission variability across the European continent and in important upwind source areas for Flanders may impact modelled SIA and PM levels. Such an effect is supported by the abovementioned studies, in which the largest effects of ammonia emission reductions were found for areas with less ammonia availability.

The scenario simulations to investigate the reduction of ammonia emissions prior to PM episodes was motivated by the question if regional measures would be beneficial. The associated strong emission reductions from manure and fertiliser application over a short period of time did not dramatically change modelled PM concentrations during episodes. This is due to the relatively small importance of local  $\text{NH}_3$  emissions for SIA formation in the area (which in turn is caused by the small area covered by Flanders) and the background of ammonia due to livestock housing emissions. As figure 3.13 shows, the maximum modelled contribution of Flemish manure and fertiliser application is  $3\text{--}4 \mu\text{g m}^{-3}$ , so reductions in PM concentration beyond this cannot be expected.

This suggests that local and short-time measures to reduce  $\text{NH}_3$  emissions are not effective to reduce SIA and PM concentrations during episodes; an international effort would be more effective.

Another explanation for the small effect of reducing ammonia emissions on modelled PM levels during episodes is bi-directional exchange of ammonia (compensation point). Vegetation and soils are not only a sink of ammonia via deposition processes, but they can also emit ammonia if the concentration in stomata or in the top soil is high and air concentrations are low (e.g. [Denmead et al., 1978](#); [Flechard and Fowler, 1998](#); [Wichink Kruit et al., 2007](#)). This is exactly the situation that is created by strongly reducing ammonia emissions during a few days in a period that is otherwise characterised by strong ammonia emissions. This process of re-emission will moderate the reduction in ammonia concentration caused by the emission reduction, which also limits the PM reduction.

We have used manure transport statistics to model the temporal variability of the manure application emissions of ammonia. The emission of ammonia occurs mostly within 24 hours after manure application (e.g. [Huijsmans et al., 2001](#)). Hence, we feel that this approach is a major step forward with respect to the current practice. However, several factors such as soil pH, soil water content and atmospheric conditions influence the emitted fraction of the applied total ammoniacal nitrogen as well as the hour-to-hour emission profile ([Génermont and Cellier, 1997](#)). Using a fixed hour-to-hour profile, as done in this study, is an oversimplification of reality. A more mechanistic approach to model the emission variability after application is possible ([Hamaoui-Laguel et al., 2014](#)) and could give more temporal and spatial detail.

The ammonia emission per unit applied nitrogen in manure is highly dependent on the application technique. The factors range from 2 % for slurry injection into arable land to as much as 74 % for broadcast surface spreading on grassland ([Velthof et al., 2012](#)). Implicitly, we assume that the technology mix for manure spreading is equal throughout the total application period and throughout the model domain. This is unlikely to be true as the practices are dependent on the crop and thus on the growing season. As soil and crop type are not equally distributed, information on application technique will improve the representation of the temporal and the geographical variability in the model. Also, the assumption that manure transport data can be used as a proxy for all  $\text{NH}_3$  emissions from manure in Flanders does not hold completely. Especially for regions dominated by cattle breeding, in which grassland is the common use for arable land, the timing of manure spreading might be different. In these regions manure spreading in summer is probably more common than for regions dominated by crops that stand high on the field in summer.

We assumed a 50/50 distribution of open and closed livestock housing throughout the country. Especially for regions in which almost solely one type of animal is kept, this assumption is an oversimplification. Pigs are generally kept in closed livestock housing, whereas cattle is often kept in open housing. In summer (when emissions from open housing are larger than from closed housing) and winter (when the reverse is true, and  $\text{NH}_3$  emissions from other sources are small) our assumption could cause an underestimation in the spatial variability of ammonia emissions from livestock housing. Working with detailed information on which type of housing is located where would improve the geographical representation of emissions from livestock housing.

The use of detailed information on manure application customs (legislation, time of year, application technique, etc.) coupled with a geographically explicit soil module that calculates the total emission based on manure/fertiliser input, crop type, soil and weather conditions is an important next step in the modelling of ammonia emission from manure. However, detailed and high-resolution information about the temporal characteristics of manure application is not available for many regions or countries for multiple years. Skjøth et al. (2004, 2011) and Geels et al. (2012) have shown that using a parametrisation of the temporal variability of ammonia emissions from manure based on temperature sums and ambient temperature significantly improves the modelling of ambient ammonia concentrations in Europe. This approach is not dependent on availability of high-detail manure application data and therefore it is more straight-forward to apply for Europe. A disadvantage of this method is that local regulations (e.g. on the period during which manure application is allowed) and weather conditions other than temperature are not taken into account. A parametrisation of the temporal variability in manure application based on their approach combined with other meteorological variables (e.g. soil moisture) and local legislation calibrated for the Flemish manure transport data has been shown to improve the temporal performance of ammonia concentration modelling using a CTM (Schaap et al., *in prep.*). This approach can be extended to other regions based on very limited local information on legislation and growth season of the crops.

We showed here that manure transport data can be a valuable source of information on the temporal characteristics of manure application. The results of this study for Flanders should flow into a larger framework to detail the highly variable ammonia emissions from European agriculture based on regional patterns in agricultural practices and process descriptions. This framework will increase the knowledge basis for decisions about regulations for air pollution mitigation and nature conservation.

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## Energy transitions may change air quality source receptor matrices



**E**FFECTIVE AIR POLLUTION and short-lived climate forcer mitigation strategies can only be designed when the effect of emission reductions on pollutant concentrations and health and ecosystem impacts are quantified. Within integrated assessment modelling, source-receptor relationships (SRRS) based on chemistry transport modelling are used to this end. Currently, these SRRS are made using invariant emission time profiles. The LOTOS-EUROS model equipped with a source attribution module was used to test this assumption for renewable energy scenarios. Renewable energy availability and thereby fossil fuel backup are strongly dependent on meteorological conditions. We have used the spatially and temporally explicit energy model REMIX to derive time profiles for backup power generation. These time profiles were used in LOTOS-EUROS to investigate the effect of emission timing on air pollutant concentrations and SRRS. It is found that the effectiveness of emission reduction in the power sector is significantly lower when accounting for the shift in the way emissions are divided over the year and the correlation of emissions with synoptic situations. The source receptor relationships also changed significantly. This effect was found for both primary and secondary pollutants. Our results indicate that emission timing deserves explicit attention when assessing the impacts of system changes on air quality and climate forcing from short lived substances.

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## 4.1 Introduction

Global energy consumption has grown considerably over the last decades and is anticipated to grow further in the future (IEA, 2012). To date, a large share of the energy used originates from fossil fuels. To reduce the impact of energy use on climate, the European Commission has set goals to increase the share of renewable energies in Europe to 20 % by 2020 (EC, 2009). One of the major pathways leading to a sustainable energy system is electrification of transport and the building sector (Deng et al., 2012), in combination with using renewable energy sources for the electricity generation sector. According to the Roadmap towards a low carbon economy in 2050 in Europe, greenhouse gas emissions from the power sector should be reduced by 54–68 % in 2030 and 93–99 % in 2050 (EC, 2011). A major role in a sustainable power sector is often attributed to wind and especially solar (photovoltaic, PV) energy, since these are available in abundance throughout Europe and beyond (Deng et al., 2012; IEA, 2012). Bioenergy is also anticipated to become more important, but will mainly be used as direct fuel and not for electricity production.

Solar and wind based electricity systems are intermittent power sources, i.e., the electricity production depends on weather conditions and availability of sunlight. Consequently, electricity demand cannot be met at each hour of the day and night by PV and wind power alone. This could be accounted for by storing energy when it is abundantly available but this is relatively expensive and difficult to achieve (Ferreira et al., 2013; Østergaard, 2012; Twidell and Weir, 2015). As long as energy storage is not a viable option on the scale required, there is a need for backup electricity generation capacity that can be switched on and off quickly, to be used when the supply of electricity from renewable technologies is insufficient. In the coming decades, the backup capacity most likely consists of fossil fuel (especially natural gas) fired plants. However, considering that the price of coal is much lower than for natural gas, coal fired power plants may also be used (IEA, 2013). Hence, a solid environmental impact assessment for fossil fuel combustion remains necessary in the future.

Currently, power generation is an important contributor to atmospheric concentrations of air pollutants like sulphur dioxide (SO<sub>2</sub>), nitrogen dioxide (NO<sub>2</sub>) and particulate matter (PM) (EEA, 2013; Rafaj et al., 2014). Exposure to these pollutants is associated with adverse health effects (Deng et al., 2012; Pope III, 2007) and loss of biodiversity (Bobbink et al., 1998). Furthermore, these pollutants contribute to climate forcing through aerosols and ozone (Hansen and Sato, 2001; Solomon et al., 1999). As pollutant emissions from fossil fuel fired power plants will be reduced dramatically and emissions from renewable electricity generation are much smaller, a transition to renewable energy will have a significant impact on air quality (Cofala et al., 2007). Given the intermittent nature of renewables, there will also be a significant change in the temporal variability of the emissions. At the moment, as most power plants are fossil fuel

based, the highest emissions from power plants occur when the demand for electricity is highest. When renewables provide a large share of electricity demand, the highest emissions will occur when the gap between the renewable electricity production and electricity demand is largest. Air pollutant concentrations and fate are dependent on meteorological conditions and chemical regime and are thus impacted by seasonal and diurnal emission timing patterns (De Meij et al., 2006; Mues et al., 2013; Reis et al., 2011). A shift in the temporal variability of the emissions could therefore impact the relation between an emission from a certain source and its impact on air pollutant concentrations in a certain receptor region, also called source receptor relations (SRRS).

Source receptor relations are commonly used in integrated assessment models to assess the impact of emission reduction measures and design cost effective mitigation strategies (Amann et al., 2011; EMEP, 2013). These models are widely applied for policy support and political negotiations are informed by the outcome of integrated assessment modelling studies. In these models, the SRRS are assumed to be linear and constant, enabling fast calculations of the expected effect of mitigation measures. Currently, SRRS are calculated by reducing one by one the pollutant emission total (by a fixed relative amount) from each country in Europe (Tarrasón et al., 2003; EMEP, 2013). Except for the emission total all model parameters, including temporal emission patterns, are kept constant. Currently, integrated assessment models are extended to be able to assess co-benefits between air pollution and climate policies (Amann et al., 2011; Grambsch et al., 2009). Hence, for the application to energy transition scenarios the sensitivity of the SRRS to shifts in emission time profiles needs to be known.

In this study, we explore the impact of changing time profiles of emissions from the power sector on source receptor relations. We developed two simple renewable energy scenarios by assuming a certain share of wind and PV power in the electricity mix (section 4.2). The emission time profiles were developed by hourly matching of electricity production and consumption. The air quality impacts of these scenarios and the impacts on SRRS are assessed using the Chemistry Transport Model (CTM) LOTOS-EUROS (section 4.3). Results are provided in section 4.4 and discussed in section 4.5.

## 4.2 Scenario definition

In this study, four emission scenarios for Europe (in this study taken as the European Union plus Norway, Croatia, Turkey and Switzerland) were defined to investigate the effect of a shift in temporal variability associated with a high deployment of renewable electricity on air quality. For the *baseline* scenario, the current electricity mix is used, consisting of fossil fuels (55 % of the electricity generated in Europe), nuclear power (27 %) hydroelectric power (including pumped storage) (16 %), wind (2 %) and other sources, including solar energy (together adding up to 0.3 %) (Eurostat). Between

countries, large differences in the electricity mix exist. For example, France and Norway have much higher shares than average of nuclear and hydro power, respectively. In the scenarios with high renewable electricity production, the share of renewable electricity production (i.e. PV and wind power) is increased, replacing fossil fuel based electricity.

To keep the scenarios as simple as possible, storage and trade of electricity are not included in our scenarios. This means that for each hour and each country the electricity load should equal the sum of the electricity generation from all sources:

$$U_{\text{total}}(x, t) = U_{\text{nuclear,hydro}}(x) + U_{\text{PV}}(x, t) + U_{\text{wind(onshore)}}(x, t) + U_{\text{wind(offshore)}}(x, t) + U_{\text{fossil}}(x, t). \quad (4.1)$$

Here,  $U_{\text{total}}(x, t)$  is the electricity demand for country  $x$  at hour  $t$ .  $U_{\text{nuclear,hydro}}(x)$  is the contribution of hydroelectric and nuclear power. These sources are assumed to generate a constant power output each hour of the year, making  $U_{\text{nuclear,hydro}}$  time-independent.  $U_{\text{PV}}(x, t)$ ,  $U_{\text{wind(onshore)}}(x, t)$  and  $U_{\text{wind(offshore)}}(x, t)$  represent the electricity generated by the three renewable sources considered in this study, and  $U_{\text{fossil}(x,t)}$  is the remaining fossil fuel needed to fulfil the demand.

The production of renewable electricity for each hour is defined using the following equation:

$$U_{\text{renewable,total}}(x) = \sum_{\text{renewable types}} \left( \alpha_{\text{ren}}(x) \times \sum_{t=1}^{t=8760} P_{\text{ren}}(x, t) \right). \quad (4.2)$$

The potentials  $P_{\text{ren}}(x, t)$  represent the electricity generation from a renewable source that would be possible for country  $x$  at hour  $t$  if the maximum capacity for that source in country  $x$  would be installed, whereas  $\alpha$  represents the fraction of the maximum capacity that is installed in country  $x$  in a scenario. Hourly renewable electricity generation potentials  $P_{\text{ren}}(x, t)$  were calculated using the REMIX (Renewable Energy Mix for Sustainable Electricity Supply) model (Scholz, 2012). REMIX is an energy system model that calculates the hourly availability of renewable electricity based on meteorological conditions. The energy system model can also dimension power supply systems with high shares of renewable energy and calculate the least cost operation of the system components.

For the *baseline* scenario,  $\alpha_{\text{ren}}(x)$  are chosen such that over the whole year, the current contributions of PV and wind to the electricity mix of each country are obtained. In the first renewable energy scenario, hereafter referred to as the *50/50* scenario,  $\alpha_{\text{ren}}(x)$  are chosen such that over the whole year, the contributions of PV and wind to the electricity mix are approximately equal, together totalling 30 % of the electricity demand. In

the second scenario, the *high wind* scenario,  $\alpha_{\text{wind}}(x)$  is chosen such that wind energy produces 30 % of the electricity demand. Where the 30 % is not reached, PV power is used to fill the gap.

The determination of  $\alpha$  for all renewable technologies was done iteratively, starting by choosing  $\alpha$  such that  $U_{\text{renewable,total}}(x)$  meets the requested share of the total electricity generation. However, for some  $x, t$  combinations there is overproduction of electricity from renewables. Since no storage or trading is assumed, this electricity is ‘lost’ and the parameter  $\alpha$  needs to be increased to reach the envisaged contribution of renewables. This iterative procedure has been repeated until no further improvement was found. However, the 30 % contribution of renewables is not reached Europe-wide. This is due to the fact that in some countries (e.g. France and Norway) the power production from nuclear and/or hydro installations is so large that the share of PV and wind together cannot reach the 30 % by replacing only fossil fuel based energy. Therefore, in both scenarios with high renewable deployment, the renewable share in the whole region is around 25 %. The share of fossil fuels in the electricity mix is 57 % in the *baseline* scenario and 34 % for the *50/50* and *high wind* scenarios.

The assumption that hydroelectric power generation is constant throughout the year is an over-simplification as well: in reality it can be varied according to the demand. Therefore, the scenarios developed in this study should not be seen as realistic, but merely as a means to explore the impact of a shift in time profiles of emissions from power plants in Europe on air quality.

The annual total emissions for all sectors are taken from the TNO-MACC-II database (Kuenen et al., 2014). In all scenario runs except the *baseline*, the emissions of the power sector are reduced by the percentage of fossil fuels replaced by renewables. Therefore, in the scenarios assuming a high deployment of renewable electricity, the annual emissions from the European power sector are effectively reduced by 40 %. In this study, we have assumed that the emissions are reduced equally across all power plants. Also, it has been assumed that the shares of each fuel in the fossil fuel generated electricity remains constant. In the real world, some power plants would be shut down completely and others would remain fully operational and fuel shift is possible, but including this is beyond the scope of this study.

For all scenarios including the *baseline*, the annual total emissions from the power sector for each country were divided over the year assuming a linear relation to the fossil fuel based electricity generated:

$$E_i(x, t) = \frac{U_{\text{fossil}}(x, t)}{U_{\text{fossil,total}}(x)} E_i(x)_{\text{total}}. \quad (4.3)$$

Here,  $E_i(x, t)$  is the emission of substance  $i$  in country  $x$  at hour  $t$  and  $E_i(x)_{\text{total}}$  is the

annual emission of that substance in that country.

Additional to the *baseline*, *50/50* and *high wind* scenarios, a control scenario was defined to be able to distinguish the impact of the emission reduction and of the change in timing. This *low emission* scenario consists of the emission totals of the *50/50* scenario and the time profiles of the *baseline* scenario.

The distribution of the fossil fuel based electricity varies considerably between the scenarios (table 4.1). In the *50/50* scenario, the relative difference between summer and winter becomes larger due to the abundant availability of PV power in the summer months. The *high wind* scenario shows more fluctuations throughout the year because high wind speed conditions come in episodes. For the *50/50* scenario, these fluctuations are partly subdued by using two renewable sources, each with its own favourable weather conditions.

### 4.3 Model description

The scenarios described above were used as input to the chemistry transport model LOTOS-EUROS (Schaap et al., 2008) version 1.8 to calculate the effects of a high deployment of solar and wind energy on air pollutant concentrations. Four simulations (one for each scenario) were carried out for the European domain (13°E–35°W, 35°–70°N). The model top is placed at 3.5 km above sea level and consists of three dynamical layers: a mixing layer and two reservoir layers on top. The height of the mixing layer at each time and position is extracted from ECMWF meteorological data used to drive the model. The height of the reservoir layers is set to the difference between ceiling (3.5 km) and mixing layer height. Both layers are equally thick with a minimum of 50 m. If the mixing layer is near or above 3500 m high, the top of the model exceeds 3500 m. A surface layer with a fixed depth of 25 m is included in the model to monitor ground level concentrations. Advection in all directions is handled with the monotonic advection scheme developed by Walcek (2000). Gas phase chemistry is described using the TNO CBM-IV scheme (Schaap et al., 2009), which is based on Whitten et al. (1980). Hydrolysis of N<sub>2</sub>O<sub>5</sub> is described following Schaap et al. (2004b). Aerosol chemistry is represented with ISORROPIA2 (Fountoukis and Nenes, 2007). The pH dependent cloud chemistry scheme follows Banzhaf et al. (2012). Formation of coarse-mode nitrate is included in a dynamical approach (Wichink Kruit et al., 2012). Dry deposition for gases is modelled using the DEPAC3.11 module, which includes canopy compensation points for ammonia deposition (Van Zanten et al., 2010). Deposition of particles is represented following Zhang et al. (2001). Stomatal resistance is described by the parametrisation of (Emberston et al., 2000a,b) and the aerodynamic resistance is calculated for all land use types separately. Wet deposition is handled using simple scavenging coefficients for gases (Schaap et al., 2004a) and particles (Simpson et al., 2003). The CORINE land use dataset



(EEA, 2007) combined with the distributions of 115 tree species over Europe (Köble and Seufert, 2001) are used to calculate biogenic VOC emissions following Schaap et al. (2009), which is comparable to the approach of Steinbrecher et al. (2009). Emissions from wild fires and boundary conditions are taken from the global MACC service (Flemming et al., 2009). Anthropogenic emissions are taken from the TNO-MACC-II database (Kuenen et al., 2014). The treatment of the power sector is discussed in detail in the previous section. The temporal variation of the emissions from other sectors is represented by monthly, daily and hourly time factors for each source category (Bultjes et al., 2003). The emission height distribution for all source sectors follows the Eurodelta approach (Cuvelier et al., 2007). For all sectors, elemental carbon (EC) is calculated as a fraction of the primary particulate matter (PPM) emission. This fraction is country and sector dependent.

Previous versions of the model have been used for the assessment of (particulate) air pollution (Barbu et al., 2009; Manders et al., 2009, 2010; Schaap et al., 2004a,b, 2009). The model has participated frequently in international model comparisons aimed at ozone (Solazzo et al., 2012b; Van Loon et al., 2007), PM (Solazzo et al., 2012a; Stern et al., 2008) and source receptor matrices (Thunis et al., 2007). For a detailed description of the model we refer to Schaap et al. (2008), Wichink Kruit et al. (2012), Kranenburg et al. (2013) and abovementioned studies.

#### 4.3.1 Source apportionment module

A source apportionment module for LOTOS-EUROS was developed to be able to track the origin of  $\text{NO}_x$ ,  $\text{SO}_2$  and  $\text{PM}_{10}$  and its components (Kranenburg et al., 2013). This module uses a labelling approach similar to the approach taken by Wagstrom et al. (2008), tracking the source contribution of a set of sources through the model system. The emissions can be categorised and labelled in several source categories (e.g. countries, sector, fuel type) before the model is executed. The total concentration of each substance in each grid cell is modelled as usual. Additionally, the fractional contribution of each label to the total concentration of every species is calculated. During or after each process, the new fractional contribution of each label is defined by calculating a weighted average of the fractions before the process and the concentration change during the process. For details and validation of this source apportionment module we refer to Kranenburg et al. (2013). In this study, emissions from power plants were given a separate label to distinguish them from emissions from other sectors. Ten countries across Europe were selected and labelled separately in order to calculate the effect from emissions from these countries on the whole domain. This resulted in 24 labels, including labels for natural emissions and for influx from outside the model domain. The labels are listed in table 4.2.

**Table 4.2:** Overview of the labels used in all scenario runs.

Label	Country	Emission source
1	Spain	Power plants
2	Great Britain	Power plants
3	Germany	Power plants
4	France	Power plants
5	Italy	Power plants
6	Poland	Power plants
7	Czech Republic	Power plants
8	Belgium and Luxembourg	Power plants
9	The Netherlands	Power plants
10	Other countries	Power plants
11	Spain	Other sectors
12	Great Britain	Other sectors
13	Germany	Other sectors
14	France	Other sectors
15	Italy	Other sectors
16	Poland	Other sectors
17	Czech Republic	Other sectors
18	Belgium and Luxembourg	Other sectors
19	The Netherlands	Other sectors
20	Other countries	Other sectors
21	–	Natural sources
22, 23, 24	–	Sources outside model domain

#### 4.4 Results

To investigate the impacts of a change in the electricity generation system on air quality, we focus on sulphur dioxide ( $\text{SO}_2$ ), particulate sulphate ( $\text{SO}_4$ ), nitrogen dioxide ( $\text{NO}_2$ ), nitrate ( $\text{NO}_3$ ), total particulate matter ( $\text{PM}_{10}$ ) and elemental carbon (EC). All these pollutants ( $\text{NO}_x$ ,  $\text{SO}_2$ , EC, primary particulate matter (PPM), some  $\text{SO}_4$ ) and the precursors of secondary PM ( $\text{SO}_4$  and  $\text{NO}_3$ ) are emitted during combustion processes in power plants. While  $\text{NO}_x$  emissions are almost independent of fuel type,  $\text{SO}_2$  and  $\text{SO}_4$  are emitted mostly during coal combustion. Emissions of PM (including EC) and PM precursors also differ with fuel and technology. First, we validate model performance for these substances, after which the concentrations and contributions from the power sector for each scenario are presented.

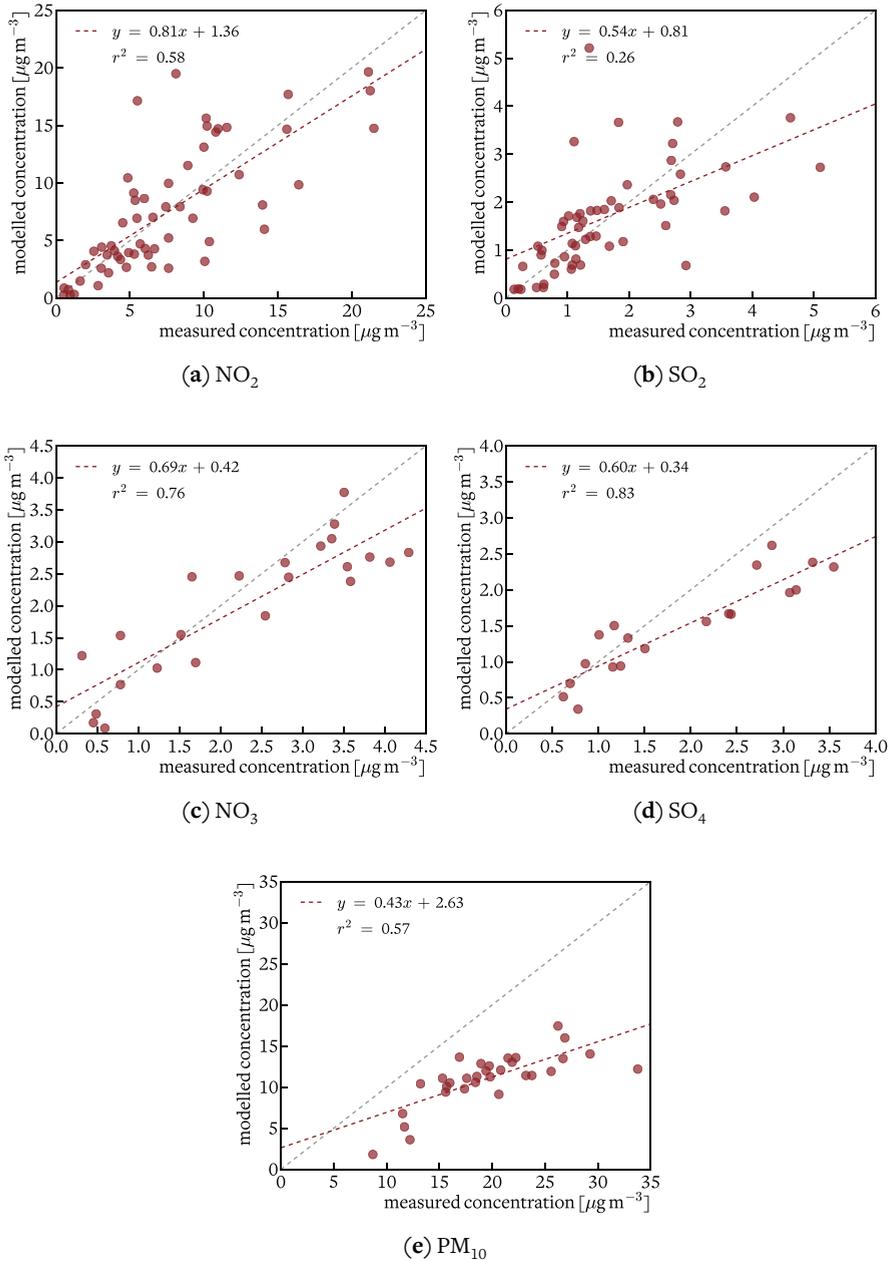
#### 4.4.1 Validation

The performance of version 1.8 of LOTOS-EUROS is validated against measurements from regional background stations of the EMEP network (Tørseth et al., 2012) for the year 2006. In figure 4.1 the annual mean modelled concentrations of SO<sub>2</sub>, SO<sub>4</sub>, NO<sub>2</sub>, NO<sub>3</sub> and PM<sub>10</sub> are compared to observations. In general the model shows skill in describing the spatial distributions of these pollutants. For the primary species SO<sub>2</sub> and NO<sub>2</sub> there is no indication for a systematic bias between the model and observations. The model strongly over- or underestimates observed concentrations for a few stations, causing a lower coefficient of determination for NO<sub>2</sub> ( $r^2 = 0.58$ ) and SO<sub>2</sub> ( $r^2 = 0.26$ ) in comparison to the secondary component sulphate and nitrate ( $r^2 = 0.83$  and  $0.76$ , respectively). For particulate sulphate and nitrate, observed concentrations at the stations with the highest levels are underestimated by LOTOS-EUROS by about 25 % and 33 %, respectively. Particulate matter concentrations are systematically underestimated by the model by about 40 % on average, with  $r^2 = 0.57$ . The reason for the underestimation of total PM<sub>10</sub> is that not all PM components, e.g. mineral dust and secondary organic aerosol, are included in the model system. On average for all stations, temporal correlations ( $r^2$ ) of daily averages for the four substances are between 0.43–0.57.

#### 4.4.2 Importance of the power sector for air pollutant concentrations

Table 4.3 shows the reduction in emissions from the power sector for the 50/50 scenario (the same emission totals were used in the *low emission* scenario) compared to the *baseline* scenario for NO<sub>x</sub>, primary PM<sub>10</sub> and SO<sub>2</sub>. This table shows that the share of emissions caused by the power sector differ greatly per substance and country. In general, SO<sub>2</sub> emissions have the highest contribution from power plants, especially in countries with many coal-fired power plants (Czech Republic, Poland). In the 50/50 scenario, emissions from power plants are lower for all countries and substances and take up a smaller share of the total emissions (note that emissions from other sectors were kept constant). The reduction in emissions is strongest for France, where relatively little electricity is produced from fossil fuels as France has many nuclear power plants. Installing a large share of renewables at the cost of fossil fuel power plants therefore causes a larger relative reduction in power plant emissions than for e.g. the Netherlands, where in the current electricity mix fossil fuels are much more dominant. For the *high wind* scenario, the trends in annual emissions are the same as for the 50/50 scenario.

Figure 4.2 shows the contribution of power plants to the annual average concentration of fine sulphate aerosol for all four simulations. This figure shows that a 40 % reduction of power plant emissions causes a reduction in ambient fine sulphate, mostly in Eastern

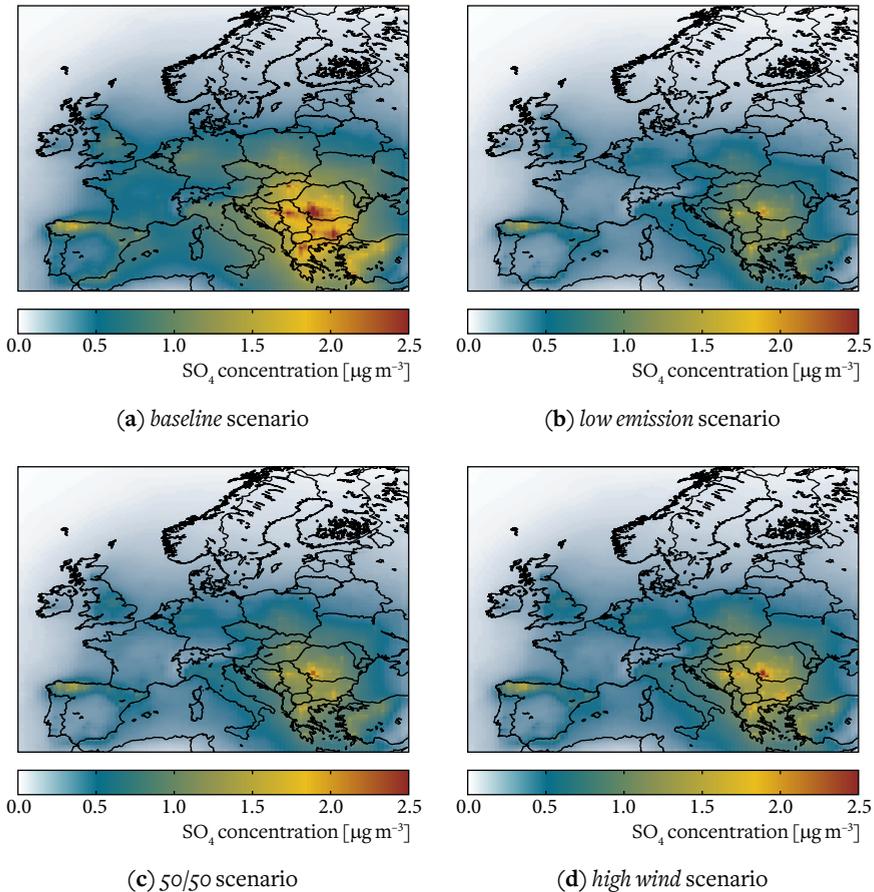


**Figure 4.1:** Comparison of modelled concentrations with observations from regional background stations in the EMEP monitoring network (Tørseth et al., 2012).

**Table 4.3:** Emissions from the power sector and their share of total emissions for a number of countries (Czech Republic (CZE), Germany (DEU), France (FRA), the Netherlands (NLD) and Poland (POL)) for the *baseline* and the *50/50* scenario (also emission totals for the *low emission* scenario).

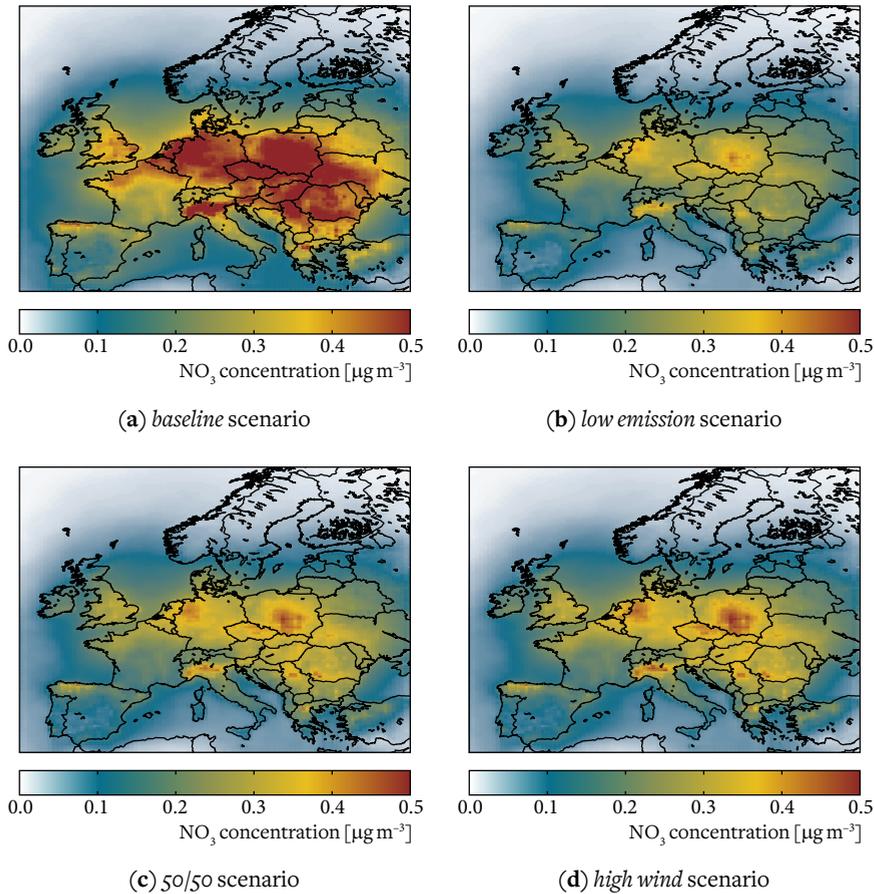
Country		NO <sub>x</sub>		PM <sub>10</sub>		PM <sub>2.5</sub>		SO <sub>2</sub>	
		baseline	50/50	baseline	50/50	baseline	50/50	baseline	50/50
CZE	emissions from power sector [kt]	94 387	45 997	4158	2026	2724	1327	137 352	66 935
	% of total emissions	34	17	12	6	13	6	63	31
DEU	emissions from power sector [kt]	241 796	156 499	10 527	6814	9385	6074	215 872	139 721
	% of total emissions	16	10	5	3	7	5	38	25
FRA	emissions from power sector [kt]	106 942	30 946	8626	2496	4442	1285	120 988	35 010
	% of total emissions	9	3	2	0	1	0	26	8
NLD	emissions from power sector [kt]	44 987	33 965	294	222	241	182	8454	6383
	% of total emissions	13	10	1	1	1	1	14	10
POL	emissions from power sector [kt]	289 493	176 242	25 800	15 707	8849	5388	644 469	392 350
	% of total emissions	40	24	9	5	6	4	53	32

Europe where coal is an important fuel for power plants. A 40 % reduction of power plant emissions reduces sulphate concentrations from the power sector in this region reduction by on average around 35 %. The effect of using more realistic time profiles for power plant emissions for the 50/50 case can be seen by comparing the panels for the 50/50 and *low emission* scenarios. This shows that part of the concentration reduction achieved by reducing the emissions is cancelled out by incorporating the shift in the temporal emission characteristics. When the more realistic time profiles are used, the annual average concentrations caused by the power sector are up to 20 % higher than using the default time profiles for power plants. Using the time profiles calculated for the *high wind* scenario, the effect of using realistic time profiles is even larger: half of the reduction in concentration because of the lower emissions from the power sector is cancelled when the time profiles are adapted.



**Figure 4.2:** Annual average concentration of sulphate particulate matter for the four scenarios.

Figure 4.3 shows that these trends are also observed for fine nitrate aerosol, displaying the contribution of power plants to the annual average concentration of this substance. Comparing figure 4.2 and figure 4.3 shows that power plants have an impact on fine nitrate concentrations across the continent, whereas fine sulphate concentrations due to (coal-fired) power plants are centred in eastern Europe and north-west Spain. This can be explained by the lower dependency of  $\text{NO}_x$  emissions on fuel mix used in a country.



**Figure 4.3:** Annual average concentration of nitrate particulate matter for the four scenarios.

#### 4.4.3 Source receptor relations

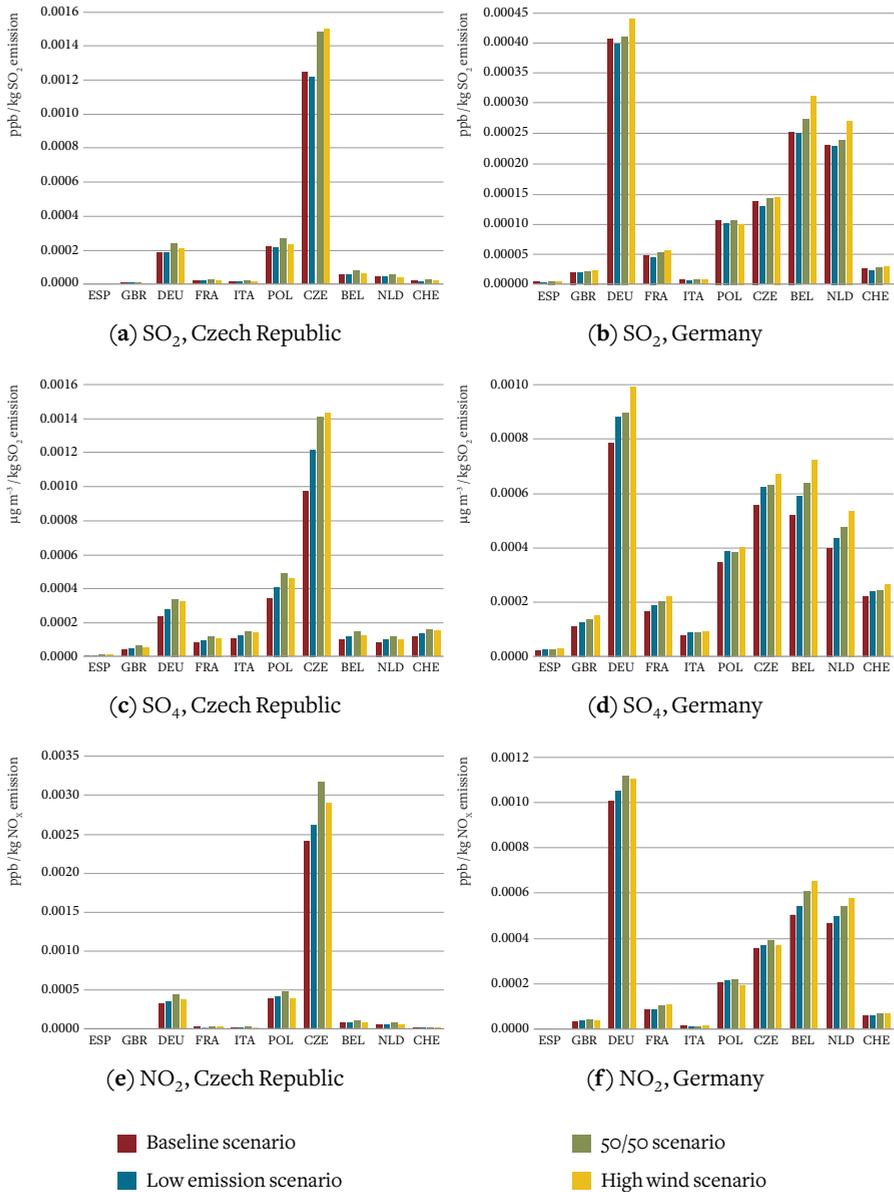
Next, the effect of timing of power plant emissions on source receptor relations is investigated. The source receptor relations used in this study are country-to-country relations. The impact of selected countries (table 4.2) was averaged for all the countries

in the exercise. For example, the concentrations due to the Netherlands in Germany were calculated as the mean over all cells that cover Germany. Cells containing borders were weighted according to the surface area of the countries in the cell.

Figure 4.4 shows the effect of  $\text{SO}_2$  and  $\text{NO}_2$  emissions from German and Czech power plants on the concentrations of  $\text{SO}_2$ , sulphate aerosol and  $\text{NO}_2$  for ten European countries. The figure shows the average concentration due to the German/Czech power sector to ten receptor countries, divided by the total emissions ( $\text{SO}_2$  for  $\text{SO}_2$  and  $\text{SO}_4$  concentrations;  $\text{NO}_x$  for  $\text{NO}_2$  concentrations) from Germany/Czech republic in each scenario. The result is a measure for the 'effectivity' of emissions in terms of resulting air pollution. As figure 4.4 illustrates, reducing  $\text{SO}_2$  emissions without changing the time profile yields slightly higher concentrations of  $\text{SO}_4$  per unit of  $\text{SO}_2$  emission and slightly lower  $\text{SO}_2$  concentrations per unit of  $\text{SO}_2$  emission in most receptor countries. This is an effect of the inherent non-linearity of the chemistry processes in the atmosphere. Looking at the effect of the change in time profile (compare the second and third bars for each country) shows that this increases the effectivity of  $\text{SO}_2$  emissions from German/Czech power plants for all receptor countries. This effect is strongest for countries close to the source country and can amount to 40 % of the original pollutant/emission ratio (e.g. for sulphate aerosol from Czech power plants). For the *high wind* scenario, the concentration per unit emission also increases compared to the *baseline* scenario. Note that the impact for certain receptor countries is larger than others, for example the change in impact of the German power sector is larger for the Netherlands than for Poland.

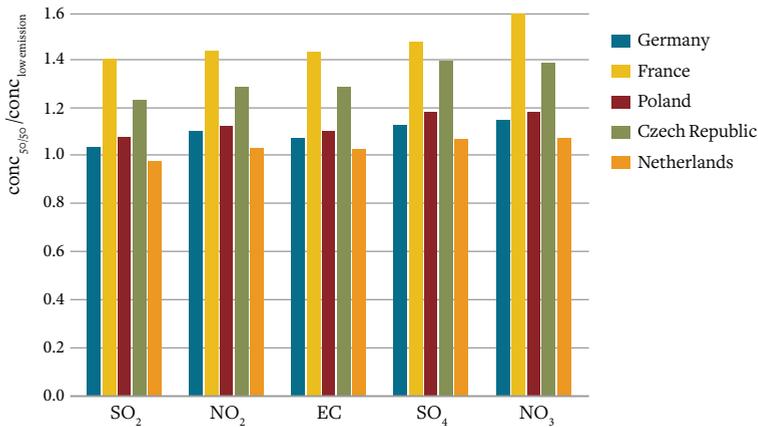
For  $\text{SO}_2$  emissions, the power sector can be quite dominant, especially in eastern Europe as  $\text{SO}_2$  is mainly emitted during coal combustion. For  $\text{NO}_x$ , other sectors like transport are also important emitters. The effect of the non-linear chemistry due to the emission reduction for  $\text{NO}_2$  'effectivity' is up to 8 %, while the effect of the change in emission timing causes up to 23 % higher  $\text{NO}_2$  concentrations per unit of  $\text{NO}_x$  emission from power plants. Overall, the increase in effectivity of power plant emissions for the high renewable scenarios is found for all substances and also for other countries, illustrating that the effect found here is systematic.

For a selection of countries, the ratio of concentrations across the domain for the *50/50* and the *low emission* scenarios weighed with the respective emissions of the substance or its precursor are shown in figure 4.5. The effect of the change in timing is larger for the secondary substances ( $\text{NO}_3$  and  $\text{SO}_4$ ) than for the primary substances. Secondary inorganic aerosols (SIA) in general have a longer lifetime than its precursors ( $\text{SO}_2$  and  $\text{NO}_2$  shown here) which are quickly removed via chemical reactions and might not be present long enough to accumulate in the atmosphere. The concentration of SIA components could therefore be more sensitive to weather conditions and e.g. mixing



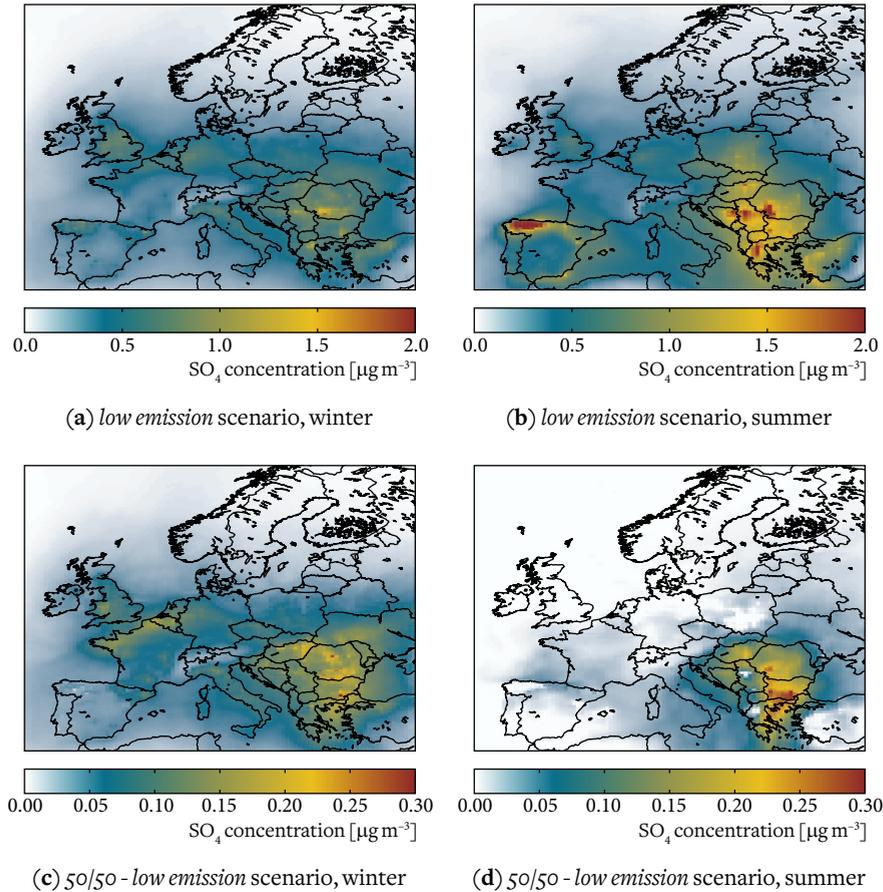
**Figure 4.4:** Effect of changing emission quantity and time patterns on SO<sub>2</sub>, SO<sub>4</sub>, and NO<sub>2</sub> concentration-to-emission ratios attributed to the Czech and German power sector for ten receptor countries (Spain (ESP), United Kingdom (GBR), Germany (DEU), France (FRA), Italy (ITA), Poland (POL), Czech Republic (CZE), Belgium (BEL), the Netherlands (NLD) and Switzerland (CHE)).

layer height. The impact of emission timing on average concentrations for France and the Czech Republic are more pronounced than for the other countries. The remaining emissions from fossil fuel combustion in the power sector for the renewable energy scenarios are very small for France because it has a large share of nuclear power (compare to table 4.1). Therefore the fluctuations in emissions from the power sector is larger than for countries for which fossil fuel power stations are also still needed for the base load. For the Czech Republic the same reasons apply, although the effect is less pronounced because nuclear energy is less important than in France. Although there are differences across species and countries, this figure illustrates that the effect is found everywhere.



**Figure 4.5:** Ratio of concentrations of air pollutants across the domain attributed to the power sector in Germany, France, Poland, Czech Republic and the Netherlands in the 50/50 and *low emission* scenarios

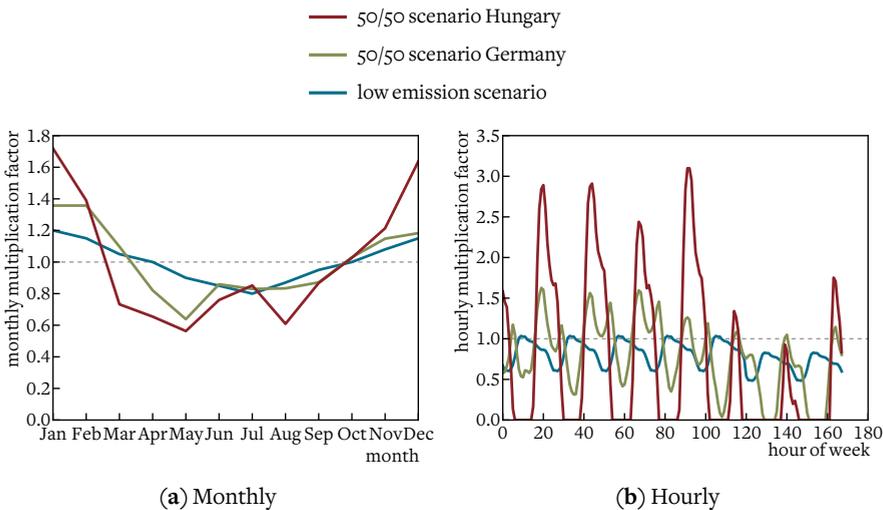
The top panels of figure 4.6 display the contribution of the power sector to sulphate concentrations in winter (*left*) and summer (*right*) for the *low emission* scenario. The sulphate concentrations due to fossil fuel combustion in power plants is higher in summer in the regions in which coal-fired power plants are commonly used (a factor 2 in south-eastern Europe and a factor 6 in northern Spain) whereas for the rest of Europe the sulphate levels due to the power sector are about the same for summer and winter. The effect of emission timing is shown in the bottom panels of figure 4.6, where the difference between the 50/50 scenario and the *low emission* scenario is shown. In the summer, concentrations due to power consumption are 10 % higher in south-eastern Europe because of the adjusted time profiles. In winter, this increase in concentration is 20 % in both south-eastern Europe and the Atlantic coastal region. The absolute difference between the two runs is slightly larger for the summer in south-eastern Europe, but for the Atlantic coast the difference is larger in winter.



**Figure 4.6:** Seasonal average concentration of sulphate aerosol from power plants in the *low emission* scenario, and the difference of the *50/50* scenario and the *low emission* scenario. Winter: December, January, February; summer: June, July, August.

Looking at the monthly average time profiles for the power sector (figure 4.7(a)) explains why the increase in concentrations is larger in winter than in summer: the seasonal variation in the default profile is much flatter than the time profiles in the *50/50* scenario, which shows a larger emission intensity in winter. Actually, when considering this figure the difference between the *low emission* and the *50/50* scenario in summer would be expected to be negligible, which is not the case. The increase in concentration can be explained by the distribution of emissions over the day (figure 4.7(b)). In the *low emission* scenario, the emissions peak when the demand is highest, i.e. around noon. For the *50/50* scenario, the emission timing is adjusted to take into account the hourly

production of renewable electricity and the emission peak from fossil fuel based power generation shifts to the night hours. During the day enough wind and especially solar energy is available to cover (the major part of) the demand. During the night there is of course no solar electricity (remember we did not include electricity storage) and wind speeds are generally lower than during the day, so fossil fuel based electricity is needed to meet the demand. As during the night the atmosphere is generally more stable (because of lower mixing layer height, lower wind speeds, sometimes inversion), the average concentration increases when a larger part of emissions is taking place during the night.



**Figure 4.7:** Temporal variability for power plant emissions for each month and for each hour in a summer week in Germany and Hungary. In the *low emission* scenario, all countries have identical time profiles.

## 4.5 Discussion and conclusions

This study explored for the first time the consequences for air quality of a shift in the temporal variability of fossil fuel combustion in the power sector induced by an increasing use of renewable energy resources. To isolate the impact of emission timing, one of the two high renewable energy scenarios was compared to a scenario which did not include the lower emissions but not the change in emission timing. The results showed that for all species considered the concentration per unit of emission from the power sector is larger when fossil fuel based power plants operate mainly as backup capacity in an energy system with a significant share of renewable electricity. The impact was found to be larger for secondary species than for primary components with increases of concentration-to-emission ratio of up to 40 % and 20 %, respectively. Hence, the

shift in the timing of emissions from the power sector during a transition to renewable energy might result in a smaller improvement in air quality than currently anticipated. The main reason for the observed behaviour is a larger seasonal variation in emission strength with maxima under winter time stagnant conditions. In addition, in summer emissions from the power sector shift from a day time maximum to a night maximum causing less dilution. The results of this study may have some important consequences and need to be verified with more detailed studies as discussed below.

It has been posed by several authors that the emission data used in CTMs are too static (Kukkonen et al., 2012; Mues et al., 2012). However, the impact of emission time profiles on modelled pollutant concentrations and model performance and results has been given little attention in the past. De Meij et al. (2006) found that in the global TM5 model the diurnal and day of the week profiles are only important for NO<sub>x</sub>, NH<sub>3</sub> and aerosol nitrate, whereas for all aerosol species (SO<sub>4</sub>, NH<sub>4</sub>, POM, BC) the seasonal emission variability was important. In line with these results, improved temporal variability for road transport has shown to improve model performance of NO<sub>2</sub> concerning diurnal and week cycles (Menut et al., 2012; Mues et al., 2013; Pierce et al., 2010). Hence, there are some strong indications that improving emission variability may improve model skill. The calculation of anthropogenic emissions in CTMs follows the same procedure since the early nineties. Annual emission totals are spatially distributed using proxy maps and point source information. These spatially distributed inventories are combined with static time profiles per sector to calculate the emission of air pollutant at each hour of the simulation. Skjøth et al. (2011) moved away from this practice for the agricultural sector and found an improvement in CTM performance by applying a dynamic ammonia emission model which accounts for local agriculture management and local climate. Mues et al. (2013) showed that temperature dependent emissions for domestic heating improves model performance. Based on our results we recommend to also build a detailed emission model of the energy sector to be able to assess impacts of an energy transition in detail, especially considering the anticipated electrification of the transport and industry sectors which will cause emissions from the power sector to be larger in both relative and absolute terms.

When assessing the impact of a shift in emission timing on air pollution levels, it is important to know how well a CTM explains variability in concentrations over time and space in the current situation. Many CTMs, including LOTOS-EUROS, underestimate the variability of air pollutant levels in general and specifically as a function of meteorology (Li et al., 2013; Solazzo et al., 2012b). The underestimation of variability in concentrations is mainly caused by the underestimation of concentration peaks (Mues et al., 2012; Stern et al., 2008). These peak episodes mainly occur during stagnant meteorological conditions, during which most fossil fuel power plant emissions remain in our scenarios. Therefore, assuming that the too simplistic representation of the tempo-

ral variability of emissions is not the main reason for the underestimation of the peak concentrations, the increase of concentration per unit of emission from power plants because of the change in emission timing might well be underestimated. Therefore, a reanalysis effort for the last 1–2 decades is necessary to determine the impact of a temporally explicit emission model (containing all sectors) to assess the sensitivity of the model results to the emission description.

Considerable shifts in the diurnal cycle of  $\text{NO}_x$  emissions may also impact ozone formation. Previous studies found a significant increase in model performance when considering emission profiles for the day-of-week and the diurnal cycle compared to a simulation with constant emissions (Castellanos et al., 2009). Inclusion of a day of the week emission profile led to successfully capturing the higher observed ozone concentrations in the weekend compared to weekdays by the CMAQ model (Pierce et al., 2010). The ozone formation potential per unit emission is dependent on the ratio between anthropogenic and biogenic VOCs and  $\text{NO}_x$  as well as meteorological conditions (Atkinson, 2000). Hence, the ozone formation potential per unit emission is likely to change considerably when emissions shift from day to night time due to the different fate of  $\text{NO}_x$  during day and night time chemistry (Crutzen, 1979). Unfortunately, our source apportionment module is not suited for tracing ozone origin, so we could not separate the impact of the power sector from the other important  $\text{NO}_x$  and VOC emitting sectors. Hence, for the assessment of the impact of the power sector on future ozone levels a dedicated scenario study remains to be performed.

The scenarios developed in this study were not meant to be a realistic representation of a possible future, but only as an instrument to explore the impact of a shift in the timing of emissions from power plants in Europe on air quality. Three important assumptions were made that impact the results of this study. First, no storage and trade of electricity was accounted for. Also, hydroelectricity production is assumed to be constant over the year, whereas in reality the electricity production from this source can be regulated almost instantly and water reservoirs can even be used to store excess electricity. Including these factors would partly counterbalance the intermittent character of wind and solar energy and balance the timing of fossil fuel combustion emissions through the year and throughout Europe. Secondly, the electricity demand was assumed not to change in quantity and time pattern. The electricity demand in Europe is anticipated to increase over the coming years, meaning that with the assumed amount of electricity production from renewable sources more fossil fuel based electricity will be needed than estimated here. When electrification of e.g. the transport sector is considered, the time pattern of electricity demand might change as well. This will not only impact the time and quantity of electricity production but will also increase the relative importance of the power sector in terms of emissions compared to other sectors. The third important assumption is that the fuel mix of power plants is not changed. In reality the

response to a decrease in fossil fuel electricity demand will be the shutdown of older power plants. Also, gas power plants can in general be switched on and off more quickly than coal fired plants. Therefore, the fuel mix is anticipated to change with varying electricity demand and meteorology. The latter is expected to be more relevant for emissions of sulphur dioxide than nitrogen oxides. Future scenario studies should test the importance of these major assumptions.

Within integrated assessment models such as GAINS (Amann et al., 2011) the SRRs are at the core of the development of cost effective mitigation strategies for climate change and air pollution. They are assumed to be linear in the optimisation simulations. Currently, SRRs are calculated by reducing one by one the pollutant emission total by 15 % for each country in Europe assuming no change in emission timing (Tarrasón et al., 2003). The assumption that the SRRs behave linearly is assumed to hold when the emission change is less than 15 % of the total annual emission (EMEP, 2013), as for larger changes non-linear effects in atmospheric chemistry cannot be neglected anymore. In our simulations, the impact of a shift in temporal variability is larger than the non-linear effect induced by a change in the chemical regime (by a 40 % reduction in power sector emissions). This may mean that for system changes that involve shifts in the temporal and geographical profile of emissions, SRRs may be non-linear for much smaller changes in the total emissions than currently assumed. Hence, in case our results are confirmed in more extensive studies, refined SRRs for assessing the impacts of an energy transition appear to be needed.

Recent research suggests that the co-benefits of climate change policy for air quality are much larger than vice versa (McCollum et al., 2013). An important consequence of our results is the implication that the estimated co-benefits from climate change policies for air quality might be too optimistic when impacts on emission timing are not considered. It should directly be noted that this is probably not important in case the projected power sector emissions are marginal compared to the current situation (e.g. a very large share of renewable electricity or very effective emission control). Our simulations are representative for the transition phase towards a renewable power sector. As a fully renewable energy system is at least a few decades away, the outcomes of this study are the most relevant for the next 20-40 years. Note that we have addressed the impact on ground level air quality concentrations only and our results therefore cannot be directly translated to an impact on radiative forcing. Particulate matter and ozone are important short lived climate forcers. We speculate that the impact we illustrated for secondary sulphate may also be relevant of future climate impacts of regional aerosol distributions, in Europe or elsewhere in the world. In short, to improve our capability to forecast the levels and impacts of air pollutants during a transition to a renewable energy system, the representation of fossil fuel combustion in CTMs needs to be more detailed.

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## Ozone projections for realistic climate and air quality scenarios



**G**ROUND LEVEL OZONE poses a significant threat to human health from air pollution in the European Union. Anthropogenic emissions of precursor gases ( $\text{NO}_x$ , NMVOC,  $\text{CH}_4$ ) are regulated by EU air quality legislation and will decrease further in the future. However, biogenic isoprene emissions may increase significantly in the coming decades if short-rotation coppice plantations are expanded strongly to meet the increased biofuel demand resulting from the EU decarbonisation targets. This study investigates the effects of anticipated trends in land use change, anthropogenic ozone precursor emissions and climate change on European ground level ozone concentrations and related health and environmental impacts until 2050. The work is based on a consistent set of energy consumption scenarios that underlie current EU climate and air quality policy proposals. Human and ecosystem health damage because of high ground level ozone concentrations are projected to decline significantly towards 2030 and 2050 under current climate conditions for both energy scenarios. The projected change in anthropogenic ozone precursor emissions is found to have a larger impact on ozone damage than land use change. The increasing effect of a warming climate on ozone concentrations and associated health damage, however, might be higher than the reduction achieved by cutting back European ozone precursor emissions. Global action to reduce air pollutant emissions is needed to make sure that ozone damage in Europe decreases towards the middle of this century.

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## 5.1 Introduction

Ozone is a natural component of the troposphere and necessary because of its cleansing role. However, since pre-industrial times concentrations have risen to levels harmful to human health, crops and ecosystems (Fowler et al., 2008). In the EU28, ground level ozone is associated with at least 16 thousand excess deaths each year, making it the third most important pollutant in terms of health damage after particulate matter and nitrogen dioxide (EEA, 2015). Ozone production is driven by emissions of the ozone precursor substances nitrogen oxides ( $\text{NO}_x$ ), methane ( $\text{CH}_4$ ), non-methane volatile organic compounds (NMVOC) and the availability of light. While  $\text{NO}_x$  has some natural sources, the vast majority of the emissions in Europe is of anthropogenic origin (Sutton et al., 2011). For NMVOCs, emissions from vegetation make up about 90 % of total emissions globally, whereas in Europe anthropogenic and biogenic emissions contribute about equally to the total (Guenther et al., 1995). Biogenic NMVOC emissions (of which isoprene and monoterpenes are the most important) are driven by the type and density of vegetation as well as temperature and light.

EU climate and energy policies promote renewable energy production and increased energy efficiency measures (EC, 2009). One expected effect of these policies is a significant expansion of commercial bioenergy crop production such as short-rotation coppice (SRC) plantations and an increasing use of forests (EC, 2014). Bioenergy crops and trees typically emit more isoprene than the crops or grassland they replace because of a higher isoprene emission factor as well as higher leaf density, whereas monoterpene emissions are equal or reduced since bioenergy species have generally low monoterpene emission factors (Benjamin and Winer, 1998; Steinbrecher et al., 2009). The increase in isoprene emissions could increase ground level ozone production and concentrations. Previous studies have explored the impact of a significant increase in SRC bioenergy plantations on ozone in Europe using chemistry transport models (CTMs) concluding that the increase in ground level ozone damage for human health and crop production could be significant (Ashworth et al., 2013; Beltman et al., 2013; Lathiere et al., 2006). While some of these studies used country-specific projections of future SRC plantation areas (Ashworth et al., 2013), most used general and/or extreme assumptions about the amount and location of SRC plantations and used a CTM at a coarse scale, limiting the extent to which regional ozone formation is resolved (Emery et al., 2012; Wild and Prather, 2006).

The EU air quality directive (EC, 2008) restricts emissions of air pollutants from anthropogenic sources, leading to a significant decrease in European  $\text{NO}_x$  and NMVOC emissions in the near future (Amann et al., 2014). Results of energy policies such as an increasing share of renewable sources in the energy mix or increasing use of electric vehicles could cause a further decline in emissions of  $\text{NO}_x$ , NMVOCs and methane from the energy and transport sector (Cofala et al., 2012). These trends in anthropogenic

emissions act towards a reduction in ground level ozone formation (Lacressonnière et al., 2014). Because some steps in the ground level ozone formation process are driven by absorption of light and/or proceed faster with higher temperatures, climate conditions influence ozone formation and ground level ozone concentrations could increase in future due to climate change nonetheless (Katragkou et al., 2011; Varotsos et al., 2013). The combined effect of increasing global ozone precursor emissions and climate change has been studied by Revell et al. (2015), who project a significant increase in ground level ozone concentrations and damage globally.

While the isolated impacts of changing land use and anthropogenic emissions on ozone levels have been investigated before (in- or excluding the possible impacts of a changing climate), the combined effect of these two correlated trends has not received a lot of attention so far. In this work, we investigate the change in ozone concentration and associated health and vegetation damage caused by the combined land use and emission changes projected by policy-relevant EU energy and emission scenarios. For this, we use the regional CTM LOTOS-EUROS at a  $0.5^\circ \times 0.25^\circ$  resolution (approx.  $28 \times 28 \text{ km}^2$ ) to model ground level ozone concentrations and damage indicators SOMO35 and POD<sub>1</sub> (a health and ecosystem damage indicator, respectively) based on consistent and policy-relevant emission and land use scenarios for the EU28. Also, we provide a decomposition of the total effect on ozone levels and explore the impact of the projected trend in hemispheric background concentrations as well as the possible effects of climate change.

## 5.2 Methods

### 5.2.1 The LOTOS-EUROS model

In this study, the three dimensional regional chemistry transport model (CTM) LOTOS-EUROS v.1.1.10 (Beltman et al., 2013) was used to assess the influence of EU climate and air quality policies on ground level ozone concentrations. Previous versions of the model have been used for air pollution assessments, some of which were aimed at ozone (e.g. Manders et al., 2012), NO<sub>x</sub> (Curier et al., 2014; Schaap et al., 2013), and scenario studies (Mues et al. (2013) and chapter 4 of this thesis). LOTOS-EUROS is used to provide operational forecasts of ozone, nitrogen dioxide and particulate matter within the CAMS (Copernicus Atmosphere Monitoring Service) ensemble (Curier et al., 2012; Marécal et al., 2015). Furthermore, LOTOS-EUROS has frequently participated in international model comparisons concerning ozone (Hass et al., 2003; Schaap et al., 2015; Solazzo et al., 2013; Van Loon et al., 2007). For a detailed model description we refer to Schaap et al. (2008) and Wichink Kruit et al. (2012). Here, only the most relevant aspects for the current study are presented.

The model uses a normal longitude–latitude projection and was run at a resolution of  $0.5^\circ \times 0.25^\circ$  over Europe ( $15^\circ\text{W}$ – $25^\circ\text{E}$ ,  $35^\circ$ – $70^\circ\text{N}$ ). For boundary conditions of  $\text{O}_3$  and  $\text{NO}_x$ , monthly climatological steady state values were used. The model top is placed at 3.5 km above sea level and consists of three dynamical layers: a mixing layer and two reservoir layers on top. The height of the mixing layer at each time and location is extracted from ECMWF meteorological data used to drive the model. The height of the reservoir layers is set to the difference between ceiling (3.5 km) and mixing layer height. Both layers are equally thick with a minimum of 50 m. If the mixing layer is near or above 3500 m high, the top of the model exceeds 3500 m. A surface layer with a fixed depth of 25 m is included in the model to monitor ground level concentrations. Advection in all directions is represented by the monotonic advection scheme developed by (Walcek, 2000). Gas phase chemistry is described using the TNO CBM-IV scheme (Schaap et al., 2008), which is based on Whitten et al. (1980). The isoprene chemistry description follows Adelman (1999) and  $\text{N}_2\text{O}_5$  hydrolysis is described in Schaap et al. (2004a). Dry deposition for gases is modelled using the DEPAC.11 module (Van Zanten et al., 2010), while the description of particle deposition follows (Zhang et al., 2001). Stomatal resistance is described by the parameterisation of Emberson et al. (2000a,b) and the aerodynamic resistance is calculated for all land use types separately. Wet deposition of trace gases and aerosols are treated using simple scavenging coefficients for gases (Schaap et al., 2004b) and particles (Simpson et al., 2003).

Biogenic NMVOC emissions are calculated based on detailed information on tree types in Europe because the biogenic emission factors are extremely variable between species. Therefore, the CORINE land use dataset (Büttner et al., 2012) is combined with the distribution of 115 tree species over Europe (Köble and Seufert, 2001). During each simulation time step, biogenic isoprene and monoterpene emissions are calculated as a function of the biomass density and standard emission factor of the species or land use class (Schaap et al., 2009), taking into account the growing season of deciduous trees and agricultural crops. The role of local temperature and photo-synthetically active radiation are taken into account in the biogenic emissions following the empirically designed algorithms described by Guenther et al. (1993) and Tingey et al. (1980). The implementation of biogenic NMVOC emissions is very similar to the approach by Steinbrecher et al. (2009).

Anthropogenic emissions per country and sector (SNAP1 level) for the EU28 for 2010 as well as country-specific  $\text{NO}/\text{NO}_2$  ratios for  $\text{NO}_x$  emissions from transport are taken from the Greenhouse Gas and Air Pollution Interactions and Synergies (GAINS) model (Amann et al., 2011). Sector and country totals for non-EU countries were taken from the TNO-MACC-III emission database (Kuenen et al., 2014). The sector and country emission totals were gridded following the allocation procedures representative for 2005 described in (Kuenen et al., 2014). Temporal variability is included using sector

specific monthly, daily and hourly factors (Bultjes et al., 2003) to divide the annual emissions over the year.

To evaluate the vegetation damage due to exposure to ozone, the indicator Phytotoxic Ozone Dose ( $POD_1$  or accumulated stomatal flux above a threshold of  $1 \text{ nmol m}^{-2} \text{ s}^{-1}$  (Emberson et al., 2000b)) is calculated within the LOTOS-EUROS model. Relative risk of mortality (based on overall mortality) is used as a human health indicator. This is calculated from  $sOMO_{35}$  (the sum of daily maximum 8-hour means over 35 ppb, or  $70 \mu\text{g m}^{-3}$ ) by multiplying  $sOMO_{35}$  (in  $\mu\text{g m}^{-3}$ ) by  $1.51 \times 10^{-6}$ , the WHO-recommended relation between  $sOMO_{35}$  and relative risk of mortality (WHO, 2013).

## 5.2.2 Scenario implementation and model setup

Two energy scenarios for the EU28 developed with the PRIMES energy model (Capros and Antoniou, 1999) were used as input to the GAINS model to generate air pollutant emissions for 2030 and 2050. In the first, EU energy policy does not put additional climate change mitigation targets beyond commitments implemented and adopted by spring 2012 (current legislation or *CLE* scenario in this study, ‘reference scenario’ in the original publication (EC, 2013)), while in the second a target of 40 % reduction in greenhouse gases (GHGs) is achieved in 2030 (and 80 % in 2050), including extra energy efficiency measures (hereafter called the *decarbonisation* scenario (EU, 2014)). For air quality policy, no further measures beyond current legislation were assumed in both scenarios.

The abovementioned energy scenarios (especially the demand for bioenergy) were also used to drive the Global Biosphere Model (GLOBIOM) (Havlík et al., 2014), that analyses the competition for land use between agriculture, forestry and bioenergy, providing land use change projections until 2050 for each EU28 member state. The land use maps used in LOTOS-EUROS for 2030 and 2050 for both energy scenarios were produced by taking the total area of natural land, grassland and cropland in each country that was converted into forest and short rotation coppice plantations by GLOBIOM. For each country, the land use change was divided proportionally over all grid cells containing natural, grassland or cropland. To calculate isoprene and monoterpene emissions from SRC plantations, they are assumed to consist of poplar trees, which is a representative tree species for SRC plantations in terms of isoprene emissions. Monoterpene emissions of tree species used in SRC plantations are small or negligible (Benjamin and Winer, 1998). CTM model runs for both energy scenarios were performed for 2030 and 2050. A run for 2010 was also performed to establish the current situation and to evaluate the CTM performance. For the scenario runs, two meteorological years were used to explore the possible impact of a warming climate on ground level ozone concentrations. Meteorological year 2010 (which had an average summer in terms of temperatures and

dominant weather patterns in Europe) was used to represent current climate, whereas the year 2003 was taken to represent a possible future climate situation. Temperatures in the European 2003 summer were significantly higher than the long-term average (2–5 °C depending on region and month, (Black et al., 2004)) and are in the range of what could be expected for Europe in 2050 (Kirtman et al., 2013).

To be able to distinguish the contributions of land use change and anthropogenic emission change to the total signal for the 2050 decarbonisation scenario, two additional runs were performed in which only the land use change or the anthropogenic emission scenario was used, while the other was kept at 2010 level.

Another factor that influences future ground level ozone concentrations are trends in hemispheric background ozone levels that are determined by global long-term trends of precursor emissions. To investigate the extent to which this will influence European ozone levels, a model run was carried out in which the boundary conditions were scaled to fit the 2050 ECLIPSE CLE emission scenario (Stohl et al., 2015; IIASA, 2015). This was done using monthly O<sub>3</sub> distributions from 14 independent CTMs and Global Circulation Models (GCMs) under 2001 meteorological conditions, along with the O<sub>3</sub> responses associated with 20 % changes in anthropogenic precursor emissions from 5 world regions, and in global CH<sub>4</sub> emissions. The responses were averaged over the 14 models and scaled by the actual changes in regional emissions (global for CH<sub>4</sub>) according to the ECLIPSE v5(a) CLE scenario, thus accounting for the non-linear response of O<sub>3</sub> to NO<sub>x</sub> and CH<sub>4</sub>. The general approach is documented in (Wild et al., 2012). For ozone, the impact on the boundary conditions is -5.0 to +4.4 µg m<sup>-3</sup> on average for the period April-September, depending on location. Changes in NO<sub>x</sub> are in the order of -3.5 to +3.5 µg m<sup>-3</sup>.

To explore to what extent emission reductions beyond CLE of O<sub>3</sub> precursors in the EU28 could contribute to a reduction in ground level ozone concentrations, a sensitivity run was performed in which the anthropogenic emissions of the 2050 decarbonisation scenario were replaced by those of a maximum technically feasible reduction (MTFR) scenario developed in the ECLIPSE project for 2050 developed with the GAINS model, while for the hemispheric background also the impacts of a global MTFR scenario were considered (IIASA, 2015).

In table 5.1 an overview of all the LOTOS-EUROS model runs performed in this study is presented. All scenarios were performed for the period April-September, because ozone pollution is mainly an issue during the summer and harmful concentrations of ozone in winter hardly occur.

**Table 5.1:** Overview of LOTOS-EUROS model runs performed for this study.

Model run	Meteorological year	GAINS scenario and year	Land use scenario and year	Boundary conditions
2010	2010	2010	standard LOTOS-EUROS	2010
CLE-2030	2010	CLE 2030	CLE 2030	2010
CLE-2050	2010	CLE 2050	CLE 2050	2010
decarb-2030	2010	decarbonisation 2030	decarbonisation 2030	2010
decarb-2050-cc	2010	decarbonisation 2050	decarbonisation 2050	2010
decarb-2050-fc	2003	decarbonisation 2050	decarbonisation 2050	2010
GAINS-only	2010	decarbonisation 2050	standard LOTOS-EUROS	2010
bound-2050	2010	decarbonisation 2050	decarbonisation 2050	ECLIPSE v5(a) 2050
landuse-only	2010	2010	decarbonisation 2050	2010
MTFR-cc	2010	MTFR 2050	decarbonisation 2050	MTFR
MTFR-fc	2003	MTFR 2050	decarbonisation 2050	MTFR

### 5.2.3 Validation approach

Modelled ground level ozone and nitrogen dioxide concentrations for the baseline run for April–September 2010 are compared with hourly measurements at EMEP rural background stations (Tørseth et al., 2012). Only stations below 700 m elevation were taken into account. For NO<sub>2</sub>, 25 measurement stations were available, 83 for ozone.

## 5.3 Results

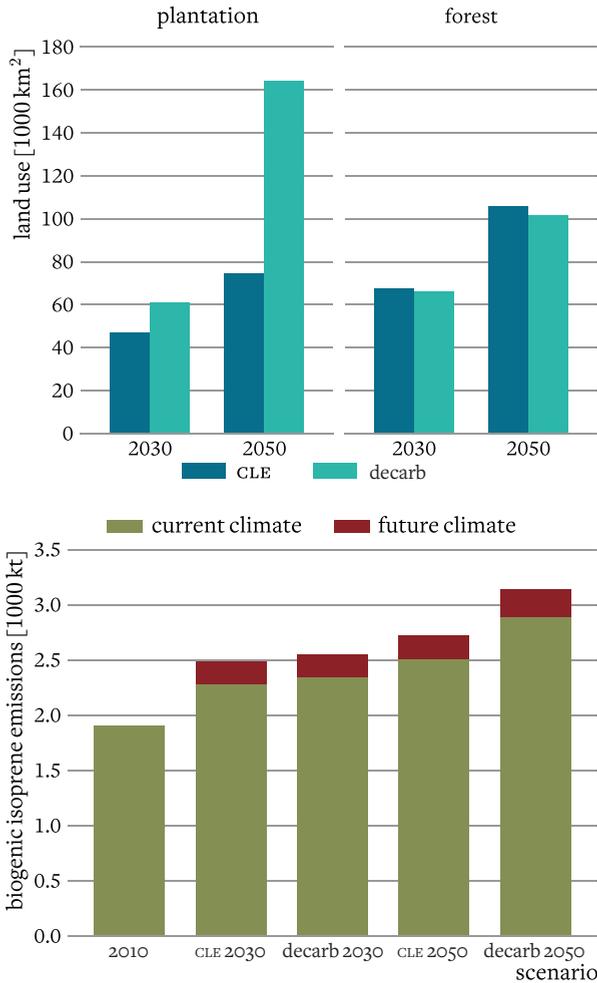
### 5.3.1 Anthropogenic and biogenic emissions

Total anthropogenic emissions in EU28-countries calculated with GAINS for 2010 and the scenarios studied are shown in table 5.2. NO<sub>x</sub>, NMVOC and CH<sub>4</sub> emissions are the most relevant in terms of ozone formation. Of these, both NO<sub>x</sub> and NMVOC emissions are projected to decline strongly (by 61–70 % and 38–48 %, respectively) until 2050 under both the CLE and the decarbonisation scenario. For CH<sub>4</sub>, emission reductions of 16–17 % are projected for 2050. For all species the largest reductions take place before 2030. Within the EU28, regional differences in emission trends occur. For example, in the decarbonisation scenario for 2050, methane emission for Cyprus are increased by 32 % compared to 2010 (mainly due to increased emissions from transport), while Hungary shows a reduction of 54 %. NMVOC emissions decrease in all countries in this scenario, ranging from –7 to –70 % (Ireland and Cyprus, respectively). For NO<sub>x</sub>, the smallest reduction relative to total emissions is seen for the Netherlands (44 %) whereas in Malta and Luxembourg less than 10 % of the 2010 NO<sub>x</sub> emissions remain. Differences in projected emission reductions also exist across economic sectors. Methane emissions from industry (which in 2010 are less than 1 % of the total CH<sub>4</sub> emissions) are projected to increase over fivefold while e.g. residential combustion and transport show strong declines in emissions going from 2010 to 2050 in the decarbonisation scenario. For NMVOC and NO<sub>x</sub>, emissions from road transport are projected to decrease by 80 % resp. 85 %, while those from agriculture increase by 15 % resp. 17 %.

GLOBIOM calculations project an increase in short rotation coppice and forests at the cost of (in this order) other natural land, grassland and cropland. Figure 5.1 displays the amount of land use change implemented in LOTOS-EUROS for each scenario and the effect of the land use change on biogenic isoprene emissions. The extra isoprene emissions produced in a hot summer (future climate, 2003 meteorology) is also shown. The growth of forest area is almost independent of the scenario used, because the modelled change in revenues from agricultural land or forests is small, leading to a fairly constant amount of afforestation and deforestation over time under both scenarios. The extra amount of biomass required in the decarbonisation scenario compared to the CLE case comes from plantations, a more intensive use of forests as well as the use of waste

**Table 5.2:** Anthropogenic emissions of air pollutants and their precursors (in kg) for the scenarios used in this study. CLE: current legislation, decarb: 40% decarbonisation by 2030 including energy efficiency measures, MTR: maximum technical feasible reduction for air pollutants.

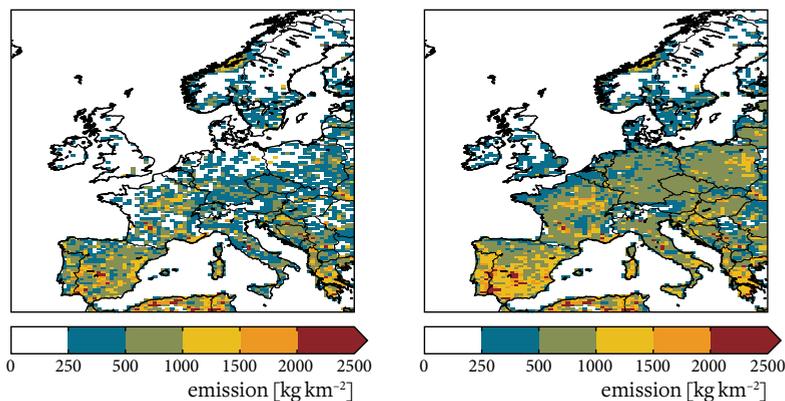
Emission scenario	CH <sub>4</sub>	CO	NH <sub>3</sub>	NMVOG	NO <sub>x</sub>	SO <sub>2</sub>	PM <sub>2.5</sub>	PM <sub>2.5-10</sub>
2010	19 659	24 377	3780	4010	7392	4688	1530	745
CLE-2030	15 759	17 454	3767	2661	3365	2228	1180	764
CLE-2050	16 334	16 068	3866	2475	2892	1843	1089	812
decarb-2030	16 597	11 587	3671	2486	3073	2046	1053	750
decarb-2050	16 572	9016	3760	2092	2193	1160	907	790
MTR-2050	16 572	5519	2477	1381	1583	700	507	614



**Figure 5.1:** *Top:* area of other natural land, grassland and cropland and replaced by short rotation coppice plantations and forests in EU28 for the CLE and decarbonisation scenario for 2050 as calculated by GLOBIOM. *Bottom:* corresponding effect on biogenic isoprene emissions calculated in LOTOS-EUROS, for current and future climate conditions.

streams and agricultural products. Especially for 2050, a large increase in biomass plantation area is seen for the decarbonisation scenario. This is directly driven by the need for bioenergy to reach the EU target of 80 % GHG emission reduction in 2050. Total isoprene emissions for the EU28 increase by 20–51 % depending on scenario and scenario year compared to 2010. For all scenarios, future climate conditions increase the total isoprene emissions by a further 9 %.

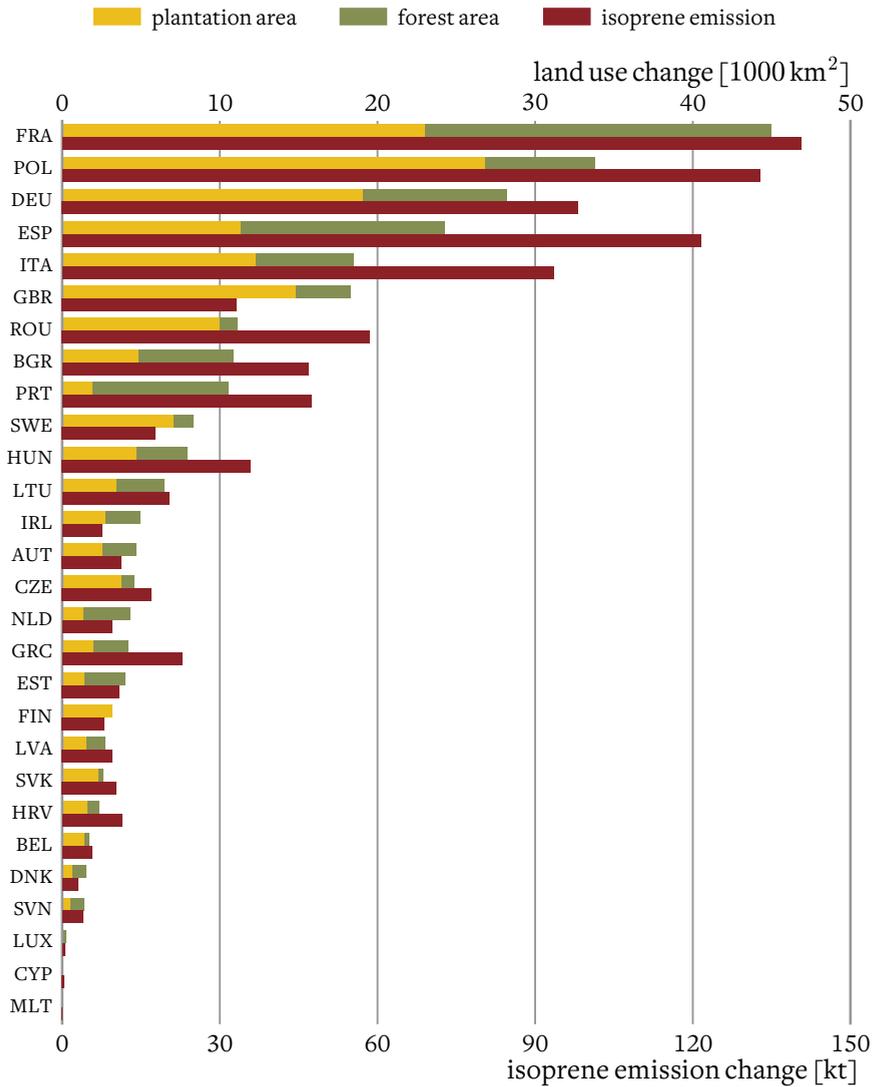
The highest isoprene emissions are seen for the *decarb-2050-fc* model run, which shows a 56 % increase compared to the 2010 *baseline* run. Figure 5.2 shows the geographical pattern of biogenic isoprene emissions across Europe. The countries with the largest increase in biomass plantations and forests in the scenarios are generally also the ones with the largest increase in emissions, as is shown in figure 5.3. Because isoprene emissions increase with temperature, the emission increase per added hectare of biomass production area is higher in southern Europe. Modelled isoprene emissions in North Africa could be overestimated due to uncertainties in the land use database underlying the model results in this area; the amount of agricultural land might be lower than what is recorded in the CORINE database for this part of the domain.



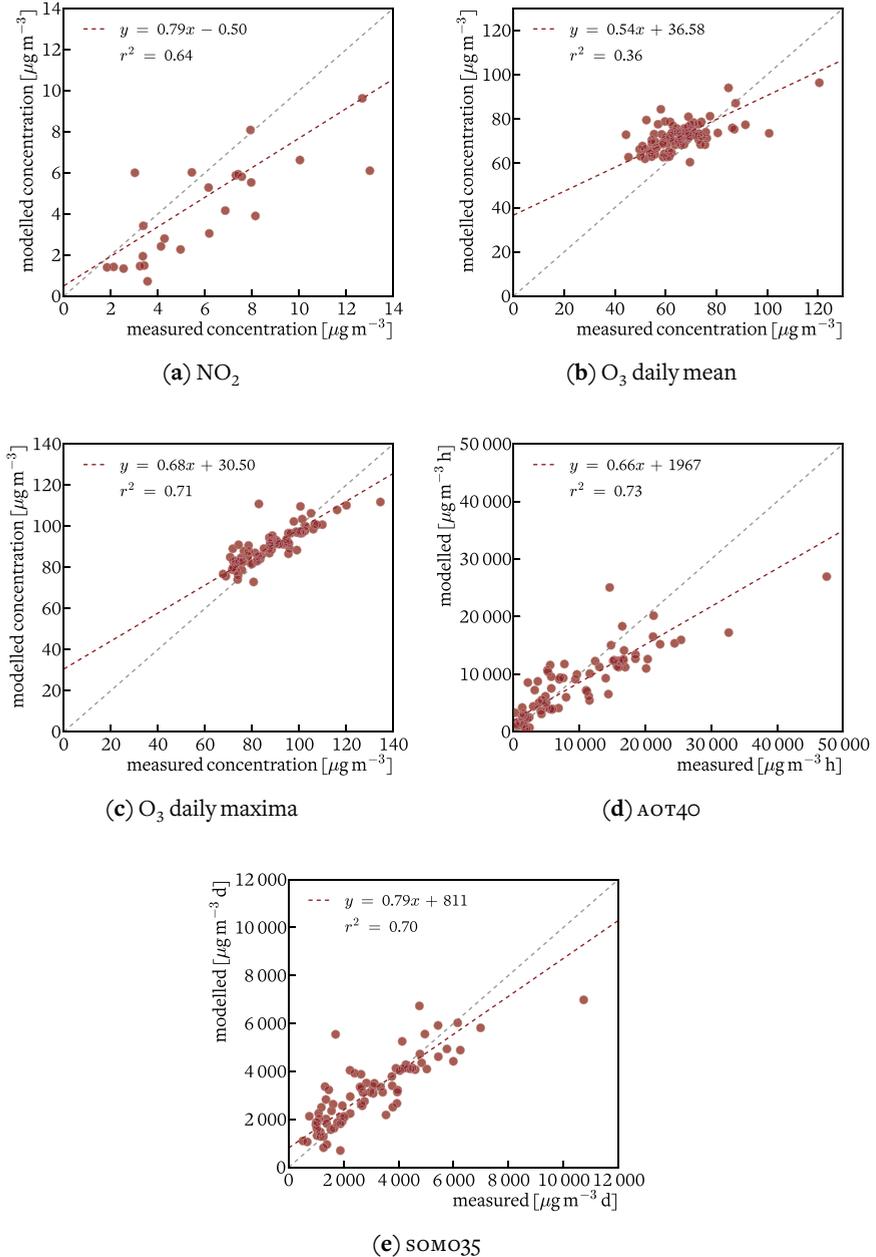
**Figure 5.2:** Biogenic isoprene emissions across Europe for 2010 (*left*) and for the *decarb-2050-cc* scenario (*right*).

### 5.3.2 LOTOS-EUROS validation

The comparison of average modelled and measured ground level concentrations of  $\text{NO}_2$  and  $\text{O}_3$  for the period April–September for EMEP rural background stations is shown in figure 5.4. LOTOS-EUROS captures the spatial variability of  $\text{NO}_2$  well ( $r^2 = 0.64$ ) but on average measurements are about 20 % underestimated. The average temporal correlation coefficient is 0.12; such low temporal correlations for hourly  $\text{NO}_2$  over Europe are seen for most CTMS (Vautard et al., 2009). The spatial variability of ozone concentrations is underestimated in the model and the average bias is about 10 % ( $6.3 \mu\text{g m}^{-3}$ ). Spatial and average temporal coefficient of determination ( $r^2$ ) are both 0.36. As health and vegetation damage mainly occur at high ozone concentrations, daily maximum concentrations for model and measurement are compared, as well as damage indicators  $\text{AOT}_{40}$  and  $\text{SOM}_{35}$ . Model performance for these indicators is higher than for hourly ozone concentrations, with  $r^2$  values between 0.7–0.73 and a bias of  $2.06 \mu\text{g m}^{-3}$  for daily maxima. Table 5.3 summarises the performance parameters.



**Figure 5.3:** Overview of land use change and corresponding change in isoprene emissions in the *decarb-2050-cc* scenario for each EU28 country (except Malta, for which no land use change was modelled). The countries are represented by their ISO3 codes.



**Figure 5.4:** Comparison of modelled and observed average concentrations and ozone indicators for April–September 2010 for EMEP rural background stations.

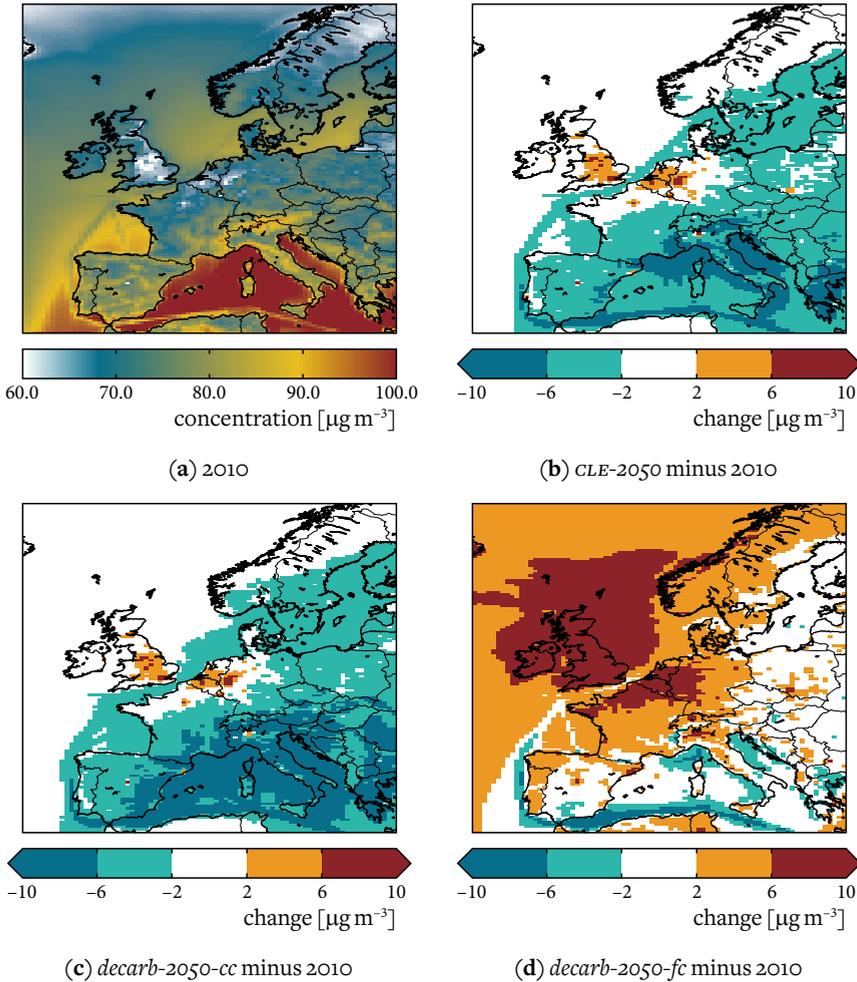
**Table 5.3:** LOTOS-EUROS performance for ozone concentrations and indicators and hourly NO<sub>2</sub> concentrations. Observed mean, bias and RMSE for NO<sub>2</sub> and O<sub>3</sub> hourly concentrations, daily maxima and maximum 8hr means are in  $\mu\text{g m}^{-3}$ , AOT40 in  $\mu\text{g m}^{-3} \text{ h}$  and SOMO35 in  $\mu\text{g m}^{-3} \text{ d}$ .

	obs mean	bias	RMSE	correlation ( <i>r</i> )	# stations
O <sub>3</sub> hourly	65.9	6.3	21.9	0.6	83
O <sub>3</sub> daymax	88.5	2.06	16.2	0.7	83
O <sub>3</sub> max8hrmean	82.9	3.8	15.6	0.7	83
AOT40	10 033	-1419	n.a.	n.a.	83
SOMO35	2962	186	n.a.	n.a.	83
NO <sub>2</sub> hourly	5.86	-1.75	5.13	0.35	25

### 5.3.3 Ozone concentrations and damage indicators

Figure 5.5 displays modelled average ozone concentrations over Europe for April–September 2010 (figure 5.5(a)) and the change in concentration compared to 2010 for the *CLE-2050* (figure 5.5(b)), *decarb-2050-cc* (figure 5.5(c)) and *decarb-2050-fc* (figure 5.5(d)) model runs. In densely populated areas such as central England, the Benelux and Ruhr area, modelled ozone summer mean concentrations are lowest (around  $60 \mu\text{g m}^{-3}$ ). In these regions ozone is titrated away at night during the conversion of NO to NO<sub>2</sub>. Across the rest of north-western Europe, concentrations are around  $70 \mu\text{g m}^{-3}$ , increasing toward southern Europe to  $80\text{--}85 \mu\text{g m}^{-3}$ . The highest values are seen over sea because ozone deposition, one of the most important loss processes, does not occur over water.

For the *CLE-2050* model run the average ozone levels increase by  $2\text{--}10 \mu\text{g m}^{-3}$  in the high-NO<sub>x</sub> regions in north-western Europe because night-time titration is reduced when NO<sub>x</sub> emissions are lowered. Reductions during the daytime are small, since these high-NO<sub>x</sub> regions are NMVOC-limited and ozone concentrations are not very sensitive to changes in NO<sub>x</sub> levels. Changes in NMVOC emissions in these regions are limited. Across the rest of Europe, ozone concentrations are lower compared to 2010 because of the lower precursor emissions (mainly NO<sub>x</sub>, as for large regions in Europe, O<sub>3</sub> formation is NO<sub>x</sub>-limited). Differences between the *CLE-2050* and *decarb-2050-cc* model runs are limited although average ozone concentrations are reduced more strongly in southern Europe for the *decarb-2050-cc* case. Results for both scenarios for 2030 (not shown) for each scenario are very similar to the 2050 concentrations, except for some Mediterranean shipping tracks. For the *decarb-2050-fc* run, we see an increase in average ozone concentration across the whole of Europe compared to the 2010 situation, except for the shipping tracks in the Mediterranean sea. The modelled increase is up

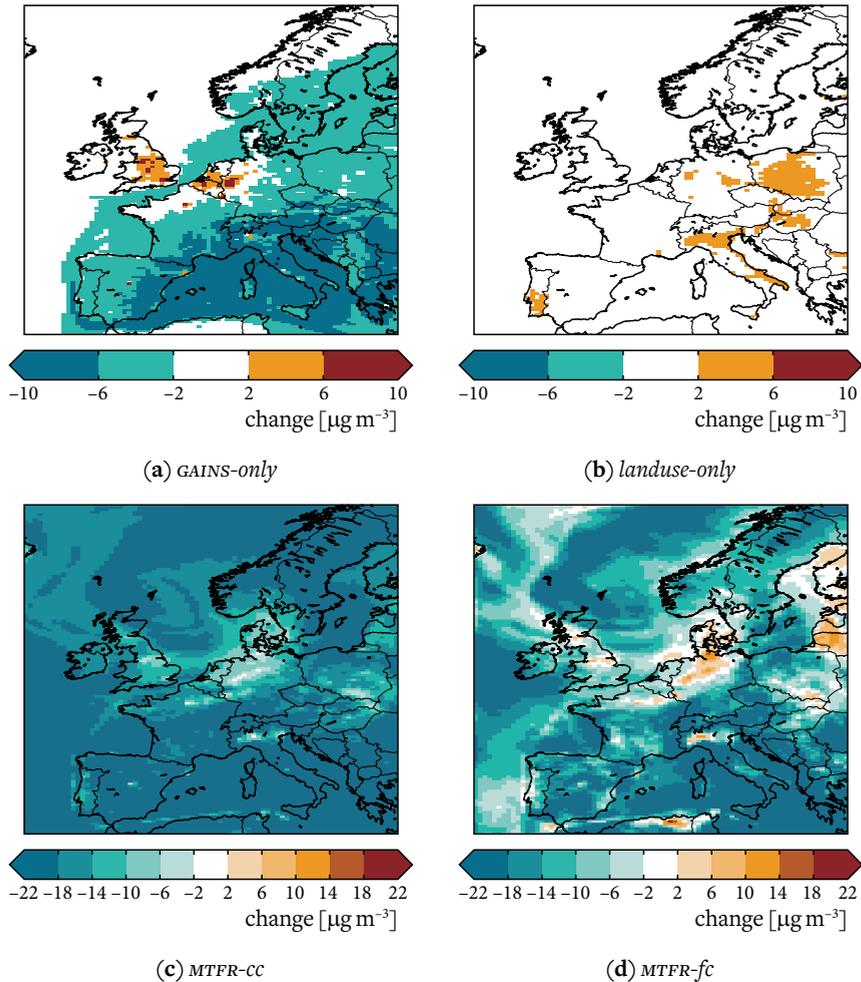


**Figure 5.5:** Modelled ozone concentrations for April–September for 2010 and the absolute difference of three scenarios for 2050 with the 2010 concentration.

to 20 % in some regions in north-western Europe. This suggests that the influence of climate change on average ozone levels may overcompensate the reduction achieved by emission reductions of ozone precursors.

A model run using anthropogenic emissions from 2010 but land use data from the 2050 decarbonisation scenario (*landuse-only*) as well as a run with 2010 land use but the 2050 decarbonisation emission data (*GAINS-only*) were performed to make a decomposition of the change observed in figure 5.5(c). Figure 5.6 shows the difference in average  $O_3$  concentration for *GAINS-only* (figure 5.6(a)) and *landuse-only* (figure 5.6(b)) runs with

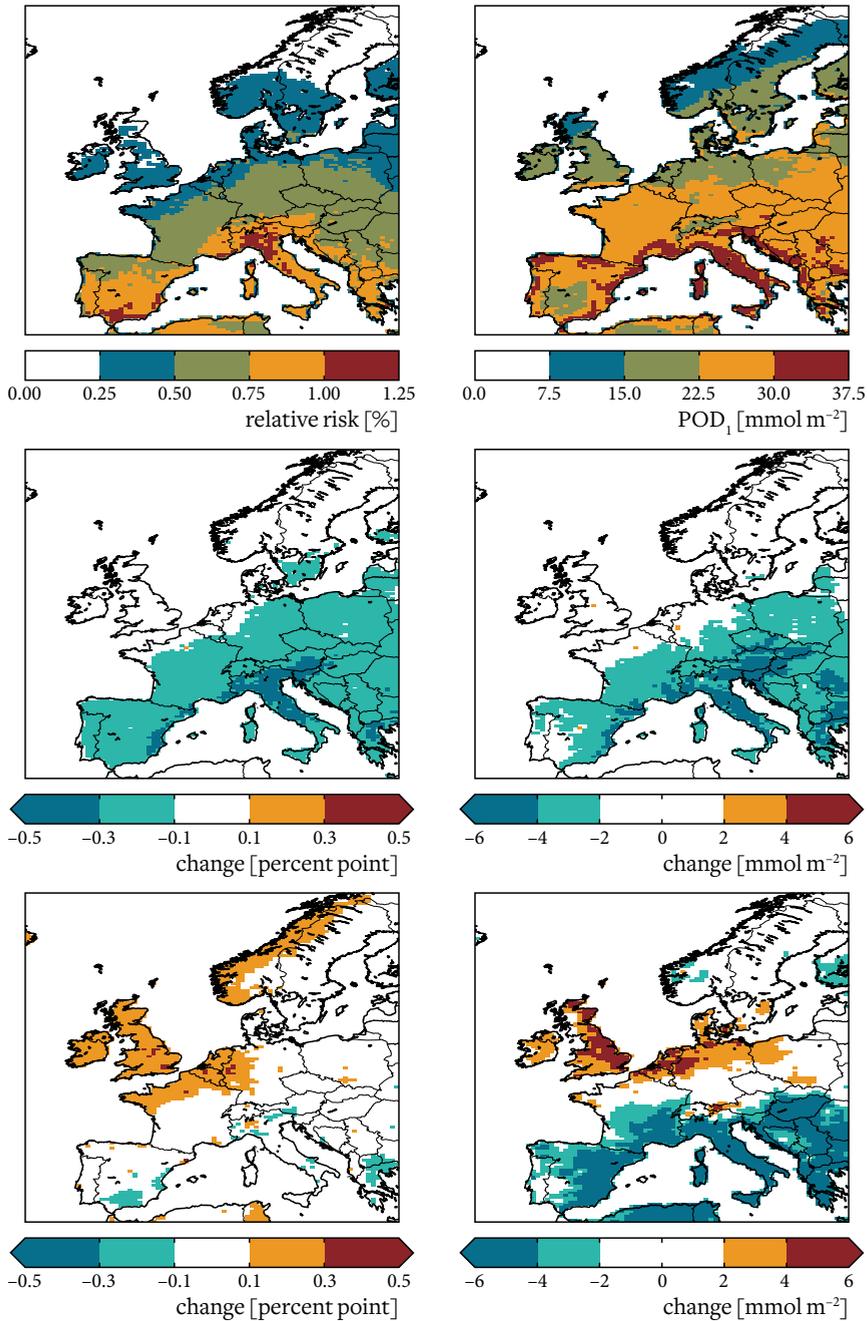
the 2010 reference run. This shows that because of land use change and the corresponding increase in biogenic isoprene emissions, ozone concentrations are increased by 2–6  $\mu\text{g m}^{-3}$  for a few regions in central and southern Europe whereas ozone levels in the rest of the domain show a response below 2  $\mu\text{g m}^{-3}$ . The anticipated decrease in  $\text{NO}_x$ , NMVOC and methane emissions from anthropogenic sources gives a much stronger signal: a decrease in average ozone concentrations of 2–10  $\mu\text{g m}^{-3}$  across the whole of Europe except for the  $\text{NO}_x$ -dominated regions in north-western Europe and metropolitan areas.



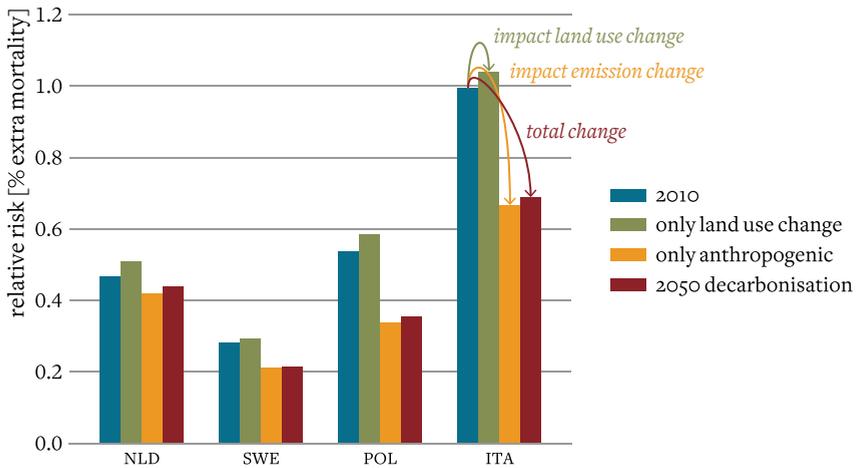
**Figure 5.6:** Change in average ground level ozone concentration for April–September compared to 2010 for four sensitivity scenarios. Note the different scales for panels (a),(b) and (c),(d).

Changes in the hemispheric background at the boundaries of our model domain under the global CLE scenario causes an increase of  $1\text{--}2\ \mu\text{g m}^{-3}$  for ozone levels across Europe. A sensitivity run for 2050 was performed in which the land use scenario for the decarbonisation case was combined with a maximum technically feasible reduction (MTFR) scenario for emissions of air pollutants for the EU28 (run *MTFR-CC*). This shows that there is additional potential for a reduction of ozone concentrations by about  $2\ \mu\text{g m}^{-3}$  across Europe when more stringent European air quality policies are adopted. If the rest of the world also adopts stringent air quality measures (represented by a global MTFR scenario), the hemispheric ozone background around Europe could decrease by 6 to  $20\ \mu\text{g m}^{-3}$  in 2050, following the methodology of Wild et al. (2012). Such a strong reduction in hemispheric background ozone concentrations could cause a further reduction of about  $10\ \mu\text{g m}^{-3}$  on average, highlighting the importance of global efforts to reduce ozone air pollution. The bottom panels of figure 5.6 show the change in average ozone concentration for the global and European MTFR scenario for current (figure 5.6(c)) and future (figure 5.6(d)) climate in 2050.

The effect of the emission and land use scenarios on modelled health indicator relative risk (in %, all-cause mortality) and vegetation damage indicator  $\text{POD}_1$  for damage to deciduous trees is shown in figure 5.7. The basis of relative risk as health impact indicator is  $\text{SO}_2$ . For both health and vegetation damage, the *decarb-2050-cc* model run shows a significant decrease in damage compared to 2010 over the whole domain: modelled health damage is halved for a large part of Europe. The  $\text{POD}_1$  values for the reference case calculated with LOTOS-EUROS (figure 5.7, top right) agree well with values calculated with the EMEP model (EMEP, 2015). The effect of the energy scenarios and climate change on  $\text{POD}_1$  values is smaller than the effect on relative risk. While for health damage the modelled values increase for the *decarb-2050-fc* run, this is not the case across the whole domain for  $\text{POD}_1$ . In southern Europe  $\text{POD}_1$  values are actually lower for the *decarb-2050-fc* run compared to the *decarb-2050-cc* run because plants under heat and water stress will close their stomata, thus limiting ozone uptake. For some example countries, the average relative risk is shown in figure 5.8. This figure illustrates the differences in impact of land use change and decreasing anthropogenic emissions between regions as well as the decomposition of the total effect into the solitary impacts of land use change and emission change. This shows clearly that the magnitude of the effects found are different for different regions, but that the impact of a decrease in emissions from anthropogenic sources exceeds that of land use change for all countries.



**Figure 5.7:** Relative risk (*left*) and  $POD_1$  (*right*) for 2010 (*top*), and the difference between the *decarb-2050-cc* (*middle*) and *decarb-2050-fc* (*bottom*) scenarios and 2010.



**Figure 5.8:** Decomposition of relative risk for a few example countries (the Netherlands (NLD), representative for north west Europe; Sweden (SWE), representative for Scandinavia; Poland (POL), representative for central Europe; Italy (ITA), representative for the Mediterranean region).

## 5.4 Discussion

Previous modelling studies focusing on the possible future impact of bioenergy plantations on isoprene emissions and  $O_3$  levels did not take changing emissions from other sources or climate change into account. [Beltman et al. \(2013\)](#), [Ashworth et al. \(2013\)](#) and [Lathiere et al. \(2006\)](#) use straightforward assumptions on the amount of land use change with no clear policy underpinning. [Beltman et al. \(2013\)](#) assumed a conversion of 5 % of agricultural and grassland into poplar plantations across Europe while [Ashworth et al. \(2013\)](#) converted 72 Mha (45 of which in EU28 countries) of agricultural land into bioenergy plantations. In the present work, in total 7 % (16 Mha) of agricultural and grassland in the EU28 is converted into poplar plantations and an additional 4 % (10 Mha) into forests (for the 2050 decarbonisation case). The increases in isoprene emissions and ozone levels found in the abovementioned studies are comparable with the impacts of land use change found in this study. [Ashworth et al. \(2013\)](#) and [Beltman et al. \(2013\)](#) find isoprene emission increases of 40 and 45 %, respectively, which agrees well with the increase of 50 % for the 2050 decarbonisation case found in this work, taking into account the differences in land use change assumptions and geographical area covered in these studies. The resulting impact on ozone concentrations and damage found by previous studies also correspond with our results. This indicates that different models agree on the responses in ozone levels because of an isoprene emission increase.

The connection between high temperatures and increased ground level ozone concentration is well established (Smith and Tirpak, 1989; Wakim, 1989; Wolff et al., 1988), although the exact relation is difficult to define because many other meteorological factors (e.g. wind, cloud cover, relative humidity) also play a role and the strength of the signal is also determined by atmospheric-chemical conditions. Katragkou et al. (2011) found the impact of projected climate change on ground level ozone concentrations to be below  $2 \mu\text{g m}^{-3}$  increase in the 2040s but up to  $6\text{--}10 \mu\text{g m}^{-3}$  towards the end of the century, for which an average temperature increase of  $2.7^\circ\text{C}$  was calculated in the climate scenario they used. This corresponds well with the response of ground level ozone concentrations to higher temperatures and lower cloud cover found in the present work, where we use the extreme summer of 2003 to represent 'future climate' rather than a climate scenario. Most Global Circulation Models agree that because of climate change, the occurrence of stagnant weather conditions over the northern mid-latitude regions will increase (Jacob and Winner, 2009). Since the 2003 summer featured significantly more stagnant weather than normal in the current climate and temperature increases correspond with what is expected around 2050 (Kirtman et al., 2013), taking the 2003 summer is a fair choice to explore the effects of climate change on air quality in 2050. LOTOS-EUROS underestimates the variability in the observations between 2003 and more 'average' summers in the period 2003–2008 (Mues et al., 2013), which means that the effect of climate change calculated in this study may be underestimating the real effect of more frequent occurrence of summer conditions like in 2003.

Varotsos et al. (2013) model an increase in 8-hour maximum ozone concentrations for north-western Europe because of climate change in 2050, but find a decrease in central and southern Europe which they attribute to increasing water vapour over sea and increased wind speeds in these regions. They also take a global scenario for future emissions of air pollutants into account, which shows increasing emissions of ozone precursors and corresponding increases in ozone levels. Lacressonnière et al. (2014) take a similar approach but use an emission scenario projecting significant reductions in anthropogenic emissions for Europe. Their results are comparable to those presented in this paper both in absolute increase/decrease of average ozone concentrations found and in the geographical patterns of the response.

This comparison to other studies investigating part of the effects included in this work shows that the responses in ozone concentrations to the separate effects of changes in land use, decreasing anthropogenic emissions and climate change correspond well with those found by other authors. This increases the confidence in the ozone response to the combined changes in land use, anthropogenic emissions and climate found in this study.

## 5.5 Conclusions

This study explores for the first time the combined impacts of changing land use and anthropogenic emissions on ground level ozone concentrations and damage for energy scenarios in Europe, using a consistent and policy-relevant combination of land use and emission datasets and taking into account the possible impacts of climate change as well. For both energy scenarios studied here, health damage because of high ground level ozone concentrations is projected to decline significantly towards 2030 and 2050, especially for central and southern Europe where health damage due to ozone might be halved in 2050. Damage to crops and ecosystems is also expected to decrease but to a smaller extent. The differences in ozone impact between the CLE and decarbonisation scenario were limited, indicating that the results presented here are robust for several possible European energy futures. The projected change in anthropogenic ozone precursor emissions, caused by current European air quality legislation rather than energy policies, was found to be a more important factor for resulting ozone levels than the projected land use change. Under an MTR scenario for air quality, even further reductions of ozone damage in Europe are possible. Hemispheric background concentrations of ozone are expected to increase in a CLE scenario which leads to an increase of a 2–4  $\mu\text{g m}^{-3}$  in European ozone levels and causes a small but relevant increase in relative risk and  $\text{POD}_1$  as well. The increasing effect of a warming climate (+2 to +5 °C across Europe in summer) on ozone concentrations and associated health damage might be higher than the reduction that is achieved by cutting back ozone precursor emissions; ambitious air quality measures close to the MTR scenario would be required to do that. However, if strong global action to reduce air pollutant emissions is taken, ozone damage in 2050 could be lower than at present.

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## Conclusion and outlook



**S**OURCE APPORTIONMENT STUDIES and scenario studies using chemistry transport models can be very valuable in policy support. The former can help policymakers to focus their efforts on the source sector(s) with the largest contribution to air pollution; the latter can identify possible future air quality problems, and investigate to what extent a candidate policy may improve air quality.

The previous four chapters describe research driven by policy questions concerning the sources of particulate matter air pollution and the possible impact of different energy scenarios on air quality. In the following section each of the research questions presented in the introduction will be answered. This is followed by a few general conclusions and an outlook in which I will discuss some knowledge gaps as well as current and emerging air quality policy issues.

### 6.1 Answers to research questions

#### **What is the origin of particulate matter in the Netherlands?**

Of the modelled  $PM_{10}$  in the Netherlands, about three quarters is of man-made origin. The remainder comes from natural sources such as sea-salt and wind-blown dust. Of the man-made part, two thirds of PM is of foreign origin and one third has sources inside the Netherlands. Transport (road and non-road) and agriculture are by far the two largest Dutch source sectors, together contributing over 80% of the total Dutch share. For particulate matter originating abroad, the contributions of the source sectors are more equally divided, with significant contributions from the energy sector and industry in addition to transport and agriculture. For  $PM_{2.5}$ , natural sources are less important than for  $PM_{10}$  while the contribution from abroad is larger. During periods with high PM concentrations, the contribution of foreign sources becomes more important while at the same time the share of natural PM is smaller than on average

over the whole period. It is important to note that this source attribution is based on model results only, and that LOTOS-EUROS captures only 60 % of the measured concentrations, mainly because of a strong underestimation of organic carbon concentrations. Reducing the missing mass is an important step to improve the source attribution of PM.

### **Can we improve the modelling of ammonia, secondary inorganic aerosol and particulate matter concentrations using manure transport data to model the temporal variability of ammonia emissions from manure?**

Modelling of the temporal variability of ammonia concentrations improves considerably when the temporal variability of ammonia emissions in the model is parametrised based on detailed manure transport data. The agreement of the model with measurements improved by 10–15 %, mainly because of an improvement of the representation of the spring maximum in ammonia concentrations. For SIA and total PM, no improvement was found. This may be due to the fact that Flanders is quite a small region with very intensive agriculture and correspondingly high ammonia emissions and concentrations. It could well be that for a region where the availability of ammonia is the limiting factor for SIA production, an improvement in the temporal variability representation of ammonia emissions would improve the quality of SIA and PM modelling.

### **Is restricting manure spreading shortly before and during a particulate matter episode effective to reduce concentrations during these episodes?**

The contribution of Flemish agriculture to modelled annual mean ammonia and SIA concentrations in Flanders are at 7–8 and 1–2  $\mu\text{g m}^{-3}$ , respectively. About 45 % of the contribution to particulate matter comes from primary particulates, the remainder comes from ammonia that reacts to form SIA. From the results of this model study, we conclude that the maximum reduction in particulate matter concentration achieved by prohibiting manure spreading on a (few) day(s) before and during a high PM episode is about 3  $\mu\text{g m}^{-3}$ . Considering that the exceedance of the limit value of 35  $\mu\text{g m}^{-3}$  is often much stronger than that (concentrations during episodes can be over 100  $\mu\text{g m}^{-3}$ ), this measure does not seem to be particularly effective in reducing the severity of particulate matter episodes. This does not mean that reducing ammonia emissions is not important to reduce PM concentrations in spring. Rather, more long-term reductions over a larger region are probably needed to achieve a significant reduction in PM episodes.

### **What could be the impact of an increasing share of intermittent renewable electricity generation (wind and solar energy) on particulate matter concentrations over Europe?**

During the energy transition from fossil fuels to renewable alternatives, there is likely

a phase in which fossil fuel energy production will be mainly used as backup capacity when there is no sun (mainly during winters and nights) and the wind speed is low. These are generally also stable weather conditions in which air pollution does not disperse quickly and a fast build-up of concentrations can occur. While the lower demand for fossil fuel based electricity causes the emissions from the energy sector to decline, the reduction in particulate matter concentration could be partly offset by a higher concentration-to-emission ratio. The model study shows that for all species considered, the concentration per unit of emission from the power sector is larger when fossil fuel based power plants operate mainly as backup capacity in an energy system with a significant share of renewable electricity. The impact was found to be larger for secondary species than for primary components with increases of concentration-to-emission ratio of up to 40 % and 20 %, respectively. The reason for the observed behaviour is a larger seasonal variation in emission strength with maxima under stagnant conditions in the winter time. In addition, in summer the power sector emission peaks shift from the day to the night, causing less dilution. This means that the effectiveness of emission reduction in the power sector is significantly lower when accounting for the shift in the way emissions are divided over the year and the correlation of emissions with synoptic situations. The source receptor relationships between countries also changed significantly. This effect was found for both primary and secondary pollutants. Our results indicate that emission timing deserves explicit attention when assessing the impacts of system changes on air quality.

### **How will ozone concentrations and damage change under realistic future European energy and air quality scenarios?**

Health damage because of high ground level ozone concentrations is projected to decline significantly towards 2030 and 2050 under current climate conditions, especially for central and southern Europe. Damage to crops and ecosystems is also expected to decrease but to a smaller extent. This reduction is mainly caused by the projected change in man-made emissions of ozone precursors, a consequence of current European air quality legislation rather than energy policies. An increased production of biomass caused by EU energy policy was expected to cause an increase in ozone damage, but this effect is only marginal compared to the reduction of ozone damage because of reduced ozone precursor emissions in other sectors. When we include the effects of a warming climate (2 to 5 °C warming across Europe in summer) modelled ozone concentrations increase, so much so that the health damage from ozone might actually *increase* towards 2050 despite the strong reduction in ozone precursor emissions. Policy makers should be aware that ozone air pollution is more difficult to reduce under a warming climate.

## 6.2 General conclusions

Air pollution is truly a multi-source, multi-component, multi-effect and multi-scale problem. Because air pollution can be transported over large distances, a city, region or country is unlikely to be able to solve its air quality problems by itself. While population exposure to NO<sub>2</sub> and PM can to some degree be reduced effectively by local measures, a large part of PM undergoes long-range transport and causes damage in a region far removed from the source area. The transboundary character of air pollution problems is even more pronounced for human health damage due to ozone, ecosystem damage caused by harmful deposition, and climate change. Therefore, international cooperation is crucial to effectively reduce concentrations of air pollutants and their negative impacts.

Since most of the simple end-of-pipe measures to reduce harmful emissions have been implemented in Europe, what remains are the more intricate and comprehensive measures. Assessment of the potential of these measures requires an integral approach in which changes in emission quantity, geographical and temporal emission variability as well as land use and climate change are considered. As I have shown in this thesis, all these aspects can be important drivers of changes in concentrations of air pollutants. The summer of 2003 has been used to explore the effect of future climate conditions for ozone (chapter 5 in this thesis) and PM (e.g. Mues et al., 2012). While this is a good approach to assess whether climate change impacts the effectivity of a policy in terms of air quality, a coupled climate – air quality model system would be better able to take the feedbacks between air quality and climate policy into account. A dynamic (emission) modelling system, which incorporates the impact of a changing climate on emission quantities and patterns as well as the changing climate's impact on atmospheric processes, is a very important tool to study possible policy impacts. The integral climate – air quality modelling approach will enhance the understanding of the interplay and feedbacks between air quality and weather. As such, it will improve the assessment of possible co-benefits between climate, energy, air and biodiversity policy and can also identify where a policy aimed at one of the themes has adverse effects on another theme.

Even a perfect air quality model (which will in all probability never exist) needs high-quality inputs to produce useful results. The emission data are often the most uncertain input factor for air quality models. For most substances and source sectors, the European emission databases (e.g. Kuenen et al., 2014) offer reliable information on the emission totals and locations. For some source sectors, however, the current information is lacking detail. Emissions from residential wood burning, for example, are probably underestimated in official emission databases (Denier van der Gon et al., 2015) and the geographical variability of agricultural emissions is difficult to parametrise correctly. The temporal variability of emissions also needs to be represented well in the

model. This is far from trivial, especially when the emissions are weather-dependent. While using static time profiles is still common, the use of dynamic temporal variability in emission modelling is increasing (e.g. [Mues et al., 2014](#); [Skjøth et al., 2011](#), and chapter 3 of this thesis). The correct representation of emissions in space, time and their quantity requires a constant effort for improvement and updates to keep up with changes in society.

### 6.3 Outlook

In Europe, large emission reductions have been achieved since the 1990s. However, problems with air quality still remain. The largest source of air pollution that has proven difficult to tackle effectively is agriculture. This is a sector with many diffuse emission sources rather than a few large point sources, making measures more complicated. While some emission reductions in this sector have been achieved, there is much potential for further reductions when best practices are improved and adopted across Europe. Residential combustion is another important remaining source of air pollution that is often underestimated by the public. Especially with increasing urbanisation and an increasing number of houses in which wood burning stoves or fireplaces are installed in western European cities, residential heating becomes an ever more relevant source of pollution for the urban population. For both agriculture and residential combustion, the temporal variability of emissions cannot be correctly parametrised in models using static time profiles. Emissions from these sources fluctuate strongly with weather conditions and this should be accounted for in air quality modelling. Transport is also an important remaining emission source, especially because a high share of emissions from transport takes place in urban environments where the population density is large, increasing its health impacts. Emissions of  $\text{NO}_x$  from road traffic are projected to decrease in the coming years, even when the difference between emissions during test conditions and real driving emissions is taken into account ([Boulter et al., 2013](#)). With reduced exhaust emissions, the emissions of particles from brake and tyre wear become relatively more important. So far, policies targeting brake and tyre wear have not been formulated.

In air quality policy in Europe, the focus is shifting from meeting the EU limit values to reducing health damage to the urban population from exposure to particulate matter and  $\text{NO}_x$ . In order to effectively support policy makers in this goal, correctly representing the background-urban-street level gradient is very important. This requires modelling at a high resolution (1 km or higher) and a coupling between regional models and local models that can calculate concentrations in street canyons in high detail. To support policy makers in their attempt to reduce exposure of the urban population to particulate matter, it is important to reduce the gap between observed and modelled PM values. The part of the PM concentration not explained by the model could

arise from underestimated or even unrepresented sources. The largest part of the gap between observations and model results in LOTOS-EUROS is caused by a strong underestimation of organic carbon (as seen in chapter 2 of this thesis). An improvement of emission estimates of organic matter from residential wood and coal burning reduces this underestimation. The inclusion or improvement of representation of secondary organic aerosol formation in CTMS is another important step.

Ecosystem damage from excessive nitrogen inputs will remain an issue in Europe in at least the coming decade. It is well-known that ammonia emission from agriculture and nitrogen oxide emission from transport and other combustion processes are the main causes of nitrogen deposition. However, which ecosystems are most at risk and which interventions are most effective to reduce damage to those ecosystems is a much more difficult question to answer. To determine this better, it would be valuable to include a biosphere model into CTMS, so both atmospheric and biological processes can be modelled explicitly in one framework. This would greatly improve the modelling of the nitrogen (and carbon) cycle. It would also enable much more reliable studies into the combined effects of air pollution and climate change on vegetation.

While improvement of air quality in Europe is still needed and possible, much larger challenges exist in large emerging economies. The WHO estimated that in 2012, ambient air pollution caused over one million deaths in China, and over 600 thousand deaths in India (versus 176 thousand in the EU28) (WHO, 2017). Globally, air pollution contributed to 5.4 % of deaths in that year. Air quality problems in rapidly developing economies have become more prominent over the last decade.  $PM_{2.5}$  concentrations in Chinese megacities regularly exceed  $900 \mu\text{g m}^{-3}$ , while the WHO guideline for short-term exposure is a maximum of  $25 \mu\text{g m}^{-3}$ . The problems China is experiencing now are also common in India, and other emerging economies could follow in their footsteps.

Partly, air pollution in emerging economies is foremost an issue of policy and priority: a lot of the measures taken in developed countries to reduce emissions of air pollutants could also be implemented in emerging economies without problems. Examples are the installation of filters on the smokestacks of power plants and large industrial facilities. Nevertheless, to effectively address the air quality problems in these rapidly developing economies, more research into characteristics specific to the region or country is needed. The fast development makes it difficult to produce up-to-date emission databases, the geographical and temporal variability of emissions is difficult to establish and most regional air quality models are for example not tailored to function well in the tropics or mountainous areas such as the Himalayas. Moreover, reliable observation networks to monitor air quality are often scarce or lacking completely in these countries. Observations are essential in assessing the severity of the problems, but also in the validation of emission databases and air quality models.

Building up a network of ground-based observation sites with high-quality data can take a long time and is expensive. Satellite observations therefore become of great added value for emerging economies in the monitoring of emissions as well as ambient concentrations. With the combination of ground-based observations (when available), satellite observations of the atmospheric column and air quality modelling, a great toolbox is available to further develop knowledge of the sources and necessary policy interventions to reduce health and ecosystem damage in countries like China and India. For all instruments in this toolbox, developments are required to be of maximum use in rapidly developing economies, especially in tropical regions. Ground-based observation networks need to be expanded and the quality of observations needs to be improved, and air quality models need adaptations to local customs and climate. These developments have great potential to increase scientific understanding and enable more effective policy support. Linking local knowledge with the expertise in air quality research and policy obtained over the past century is very important to achieve this.

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## ABOUT THE AUTHOR

Carlijn Hendriks was born on 26 April 1987 and grew up in Sint Anthonis, a small town in Noord-Brabant, the Netherlands, surrounded by pig farms. In 2005 she completed grammar school at the Elzendaalcollege in Boxmeer. Moving on to study Chemistry at the Radboud University in Nijmegen, she quickly started doing volunteer work in committees of the student association and was a member of its board from 2006 to 2008. In 2008, she received her bachelor's degree in Chemistry cum laude. She continued her studies with a master's programme in Energy Science at Utrecht University (MSc, 2010). For her research project she went back to Nijmegen. Here, she worked in the Environmental Science department on including short-lived climate forcers in life cycle assessment studies under the supervision of Mark Huijbregts. As part of this research she worked with data from the TM5 chemistry transport model under supervision of Frank Dentener.

It is this taste of air quality modelling that defined the next years of her career: in 2011, she started working at TNO in Utrecht as a researcher in air quality modelling. After writing her first scientific publication, Martijn Schaap encouraged her to pursue a PhD, of which this thesis is the result. In 2015, Carlijn was selected to participate in the Young Scientist Summer Program at IIASA (Laxenburg, Austria). During the three-month programme she worked with the Mitigation of Air Pollutants and Greenhouse Gases group at IIASA under the supervision of Wolfgang Schöpp and Gregor Kiesewetter. For her research on the impact of several policy scenarios on ozone levels in Europe, she received the Peccei Award for best applied research paper. In the air quality field, her main interests are (policy) scenario studies for particulate matter and nitrogen, source attribution studies and policy advice.



## LIST OF PUBLICATIONS

### Selection of journal articles

- C. Hendriks, N. Forsell, G. Kieseewetter, M. Schaap, W. Schöpp  
*Ozone concentrations and damage for realistic future European climate and air quality scenarios*  
[Atmos. Environ., 144 \(2016\) 208–219](#)
- C. Hendriks, R. Kranenburg, J.J.P. Kuenen, B. van den Bril, V. Verguts, M. Schaap  
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## Conference contributions

C. Hendriks, R. Timmermans, M. De Ruyter de Wildt, H. Eskes, D. Balis, E. Katragkou, M. Sofiev,

C. Talbot, H. Elbern, M. Schaap, T. Erbertseder

*PASODOBLE AIRSHEDS: Regional Operational Air Quality Forecasts*

ITM Conference, Utrecht, 2012 (oral)

C. Hendriks, R. Kranenburg, J.J.P. Kuenen, B. van den Bril, V. Verguts, M. Schaap

*Improved modelling of ammonia by using manure transport data*

Air Quality Conference, Milan, 2016 (oral)

C. Hendriks, N. Forsell, G. Kieseewetter, W. Schöpp

*Impact of EU climate and air quality policy on ozone damage in Europe*

Air Quality Conference, Milan, 2016 (poster)

*This presentation received the Best Poster Award for young scientists.*

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