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THESIS PROJECT

Modelling secondary inorganic aerosol over the Netherlands during an episode of peak concentrations

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Abstract

Air pollution is one of the largest environmental health risks both worldwide as well as in the Netherlands. The main contribution to air pollution in the Netherlands comes from aerosol (particulate matter), which consists of fine solid or liquid particles suspended in the air. Secondary inorganic aerosol (SIA) makes up the largest part of particulate matter pollution. High particulate matter concentrations present a health risk as inhaled particles can penetrate deep into the lungs.

Aerosol chemistry is modelled here with the atmospheric chemistry and transport model WRF-Chem. This is done for high resolution domains focused on the Netherlands. A one month period between 10 January 2010 and 10 February 2010 with high observed peaks in SIA concentrations is studied. Boundary and initial conditions for meteorological and chemical parameters are taken from external data sets and models. Emissions of SIA precursor gases are based on data from the European Centre on Emission Inventories and Projections and the Dutch Pollutant Release and Transfer Register.

Results show that the WRF-Chem model underestimates SIA concentrations by 40 %, in line with results from other models. Modelled temporal variations in SIA concentrations generally match those found in the measurements. Two of the three peaks in SIA concentrations observed during the study period are also present in the model results. The other peak is strongly underestimated, likely due to an overestimation of modelled wind speeds at the time preventing the accumulation of pollutants in the air. Temporal variations in the nitrate and ammonium concentrations are better captured by the model than those in the sulfate concentrations. Sensitivity calculations show that reducing Dutch NO_x emissions is most effective towards reducing SIA concentrations, but reducing SO₂ or NH₃ emissions is also beneficial. Simulation of the European emission reductions for 2030 from the 2016 NEC Directive indicates that the goal of decreasing the negative health effects of particulate matter pollution by 50 % may be obtained for the SIA fraction of particulate matter.

Lay summary

Air pollution is one of the largest environmental health risks both worldwide as well as in the Netherlands. Each year, an estimated seven million people die as a consequence of breathing polluted air. The main contribution to air pollution in the Netherlands comes from fine particles floating in the air, known as aerosol (short for 'aero-solution'). These particles can originate directly from the ground (dust) or from the burning of materials (soot), but the particles can also be formed from gases present in the air. The aerosol particles formed in the air are the topic of this study. High particle concentrations in the air present a health risk as inhaled particles can penetrate deep into the lungs.

In this study an atmospheric chemistry and transport model is used with emissions from various sources, to calculate the formation of aerosol over the Netherlands for a period of one month in 2010.

The results show that too little aerosol is formed in the model simulations. Aerosol concentrations in the model are 40 % lower than measured concentrations. The day-today variations in the modelled aerosol concentrations however do match the variations found in the measurements. Two of the three peaks in air pollution observed during the study period are also present in the model results. The other peak is missing in the model, likely due to an overestimation of modelled wind speeds.

Simulations show that aerosol concentrations decrease significantly when nitrogen oxide emissions from the Netherlands are reduced by 50 %. Reductions in sulfur dioxide and ammonia emissions also reduce aerosol concentrations, but to a lesser extend.

Finally, the emission reductions planned towards 2030 by the European Union have been tested in the model. The goal of these reductions is to decrease the negative health effects of aerosol pollution by 50 %. Based on the model results it seems that this goal may be reached, if the emissions are indeed reduced as planned.

Acronyms

CBM-Z	Carbon Bond Mechanism version Z
CEIP	Centre on Emission Inventories and Projections (part of the Convention on Long-Range Transboundary Air Pollution)
DMS	DiMethyl Sulfide
EMEP	European Monitoring and Evaluation Programme (part of the Convention on Long-Range Transboundary Air Pollution)
EU	European Union
GFS	Global Forecast System
MBE	Mean Bias Error
MOSAIC	MOdel for Simulating Aerosol Interactions and Chemistry
MOZART	Model for OZone And Related chemical Tracers
NCEP	National Centers for Environmental Prediction
NCEP-FNL	National Centers for Environmental Prediction FiNaL reanalysis
NEC Directive	National Emission Ceilings Directive
NMBE	Normalized Mean Bias Error
NMGE	Normalized Mean Gross Error
NMVOC	Non-Methane Volatile Organic Compound
OPS	Operational Priority Substance
PM	Particulate Matter
RIVM	Dutch National Institute for Public Health and Environment
SIA	Secondary Inorganic Aerosol
SNAP	Selected Nomenclature for Air Pollution
WHO	World Health Organization
WRF	Weather Research & Forecasting model
WRF-Chem	Weather Research & Forecasting model with coupled online Chemistry

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1 Introduction

Air pollution is considered to be one of the largest environmental health risks worldwide. According to the World Health Organization (WHO), over 90 % of the world's population breaths air containing high levels of pollutants (WHO, 2019). Ambient (outdoor) air pollution accounts for an estimated 4.2 million deaths per year due to stroke, heart disease, lung cancer and chronic respiratory diseases (WHO, 2019). Most of these deaths can be attributed to exposure to excessively high particulate matter concentrations. Particulate matter consists of solid or liquid particles suspended in the air, that when breathed in can penetrate deep into the lungs and even enter the blood system through the lung barrier. Secondary inorganic aerosol (SIA) forms a major fraction (up to 50 %) of particulate matter mass in the Netherlands (Mooibroek et al., 2011; Weijers et al., 2010). SIA, consisting mostly of ammonium nitrate and ammonium sulfate, is produced in air, in droplets and on particles from precursor gases such as nitrogen oxides, sulfur dioxide and ammonia. Emission densities in the Netherlands of these precursor gases are among the highest in Europe (Centre on Emissions Inventories and Projections [CEIP], 2019). SIA is almost completely of anthropogenic origin, as its precursor gases are largely emitted by traffic, energy production and agriculture (Weijers et al., 2010). The European Commission (2016) has prescribed emission reductions towards 2030 in the National Emission Ceilings (NEC) Directive, in hopes of reducing the negative health effects of air pollution by 50 % compared to 2005.

This study uses the Weather Research and Forecast (WRF) model, coupled with 'online' chemistry (WRF-Chem) to investigate SIA over the Netherlands. SIA chemistry is relatively well understood, however modelling SIA has proven to be difficult. Models generally underestimate SIA concentrations in the Netherlands (Velders et al., 2018; Netherlands Organisation for Applied Scientific Research, 2012). Van der Swaluw et al. (2018) found that some peaks of high SIA concentrations are captured correctly in the model they used, but others are missed almost entirely. In early 2010, three SIA peaks occurred within a one month period, making it an interesting period to study. This study will therefore focus on the period between 10 January and 10 February 2010. As van der Swaluw et al. (2018) also modelled SIA concentrations for this period, results from this study can be compared to their results.

Gaining more insight into the chemistry and modelling of SIA concentrations, and high concentration peaks in particular, is valuable as a better understanding could help towards improving air quality and saving lives. To do so, the following research questions have been formulated:

- Is WRF-Chem able to reproduce measured SIA concentrations in the Netherlands?
- What caused the high SIA peaks in January/February 2010 in the Netherlands?
- Emission reductions of which precursor gas are the most effective towards lowering SIA concentrations in the Netherlands?
- How will the planned emission reductions for 2030, as laid down in the 2016 NEC Directive, affect Dutch SIA concentrations?

The answers to these questions should help provide insight into the chemistry and modelling of SIA, the usefulness of the WRF-Chem model as a tool for aerosol modelling, the origin of high SIA concentration peaks in the Netherlands and what the best ways are to limit SIA air pollution. In this report, first some background information is provided on aerosol chemistry and air pollution health risks and regulations (Chapter 2). Subsequently, the setup of the WRF-Chem model is described (Chapter 3). The following chapters (4 to 6) present the simulation results and finally the answers to the research questions are discussed in Chapter 7.

2 Air quality and aerosol

Air pollution is a large threat, killing an estimated seven million people each year (WHO, 2019). In Europe, it is considered to be the biggest environmental health risk (European Environment Agency, 2020). By far the largest contribution to this risk comes from aerosol (particulate matter). Especially aerosol particles smaller than 2.5 µm are harmful, as they can penetrate deep into the lungs. The life expectancy in the Netherlands is decreased by thirteen months due to air pollution, from which twelve months can be contributed to negative health effects of particulate matter (Dutch National Institute for Public Health and Environment [RIVM], 2013). In this chapter some background information is provided on aerosol chemistry, health risks of aerosol pollution and the limits and targets for particulate matter concentrations that are in place.

2.1 Secondary inorganic aerosol chemistry

Particulate matter in the Netherlands generally consists of several types of aerosol. The most abundant is the group that is called SIA. In the Netherlands, SIA makes up approximately 50 % of the particulate matter mass (Mooibroek et al., 2011; Weijers et al., 2010). Other smaller contributions come from elementary and organic carbon (25-30 %), sea salt, dirt and metals (RIVM, 2018). The 'Total' column in Figure 1 gives an overview of the composition of particulate matter in the Netherlands.



Origin of PM₁₀ in the Netherlands

Figure 1: Origin of particulate matter in the Netherlands in 2015. SIA compounds are split up in a domestic and a foreign anthropogenic contribution. Primary, natural and other compounds (mainly organic) are included only in the total column. The figure is based on data from Velders et al. (2020).

As SIA makes up the largest part of aerosol mass in the Netherlands, this study will exclusively focus on the modelling of SIA. This is advantageous also because inorganic aerosol chemistry is better understood than organic aerosol chemistry and emissions are better known. Moreover, strong air pollution events are usually largely due to increased SIA levels, meaning that more knowledge on SIA is highly relevant for a better understanding of why such events occur and how they can be avoided (RIVM, 2013). SIA is mainly anthropogenic in origin, with only 1-6 % of SIA mass coming from natural sources (RIVM, 2018). About two-thirds of the SIA mass in the Netherlands comes from anthropogenic emissions abroad (Figure 1), mainly from nearby European countries as only 10 % of Dutch SIA mass originates from outside of Europe (Velders et al.,

2020). These last factors indicate that air pollution in the Netherlands can potentially be drastically reduced by Dutch and/or European measures, as pollution comes from relatively nearby sources that are man-made.

SIA consists of inorganic particles that are formed by condensation of so called precursor gases in the atmosphere. The main precursor gases are nitrogen oxides (NO_x) , sulfur dioxide (SO_2) and ammonia (NH_3) , forming nitrate, sulfate and ammonium aerosol. The concentrations of these gases over the Netherlands and their origins are displayed in Figure 2. A short description of aerosol formation processes is given in the following subsections, as well as some information on the influence of meteorological conditions on SIA concentrations.



Origin of aerosol precursors in the Netherlands

Figure 2: Origin of SIA precursor gases in the Netherlands in 2015. The figure is based on data from Velders et al. (2020).

In addition to being grouped based on chemical characteristics, aerosol is generally grouped into categories based on particle size. The most commonly used categories are PM_{10} and $PM_{2.5}$, containing particulate matter with an aerodynamic diameter smaller than 10 µg and smaller than 2.5 µg respectively. SIA particles are mostly small enough to be part of both categories, although coarser particles may be formed especially when nitric acid reacts with sea salt to form sodium nitrate. SIA is removed from the atmosphere by dry and wet deposition, with wet deposition being the dominant sink for $PM_{2.5}$ and both sinks being equally important for PM_{10} (Wu et al., 2018).

2.1.1 Sulfate

Sulfate aerosol is a mixture of solid or liquid particles that include sulfuric acid (H_2SO_4) or sulfate salts. H_2SO_4 is formed by the oxidation of SO_2 , which therefore is one of the main precursor gases controlling the amount of SIA in the atmosphere. SO_2 is emitted mainly by combustion processes and shipping and by volcanoes (Figure 4). The conversion from SO_2 to H_2SO_4 dominantly takes place by reaction with the OH radical as follows:

$$SO_2 + OH + M \rightarrow HOSO_2 + M$$
 (1a)

$$HOSO_2 + O_2 \to HO_2 + SO_3 \tag{1b}$$

$$SO_3 + H_2O + M \rightarrow H_2SO_4 + M$$
 (1c)

This is the upper pathway displayed in Figure 3. These reactions and other chemical theory in this chapter are based on the books by Seinfeld & Pandis (2016) and Wayne (1991).



Heterogeneous reactions on sea salt, dust

Figure 3: Tropospheric oxidation of SO_2 to H_2SO_4 . The figure is based on chemical processes described by Seinfeld & Pandis (2016) and Wayne (1991).



Figure 4: Anthropogenic sources of SO_2 in the Netherlands in 2015. The figure is based on data from Velders et al. (2020).

Not all sulfate aerosol stems from SO_2 emissions. A major natural source of sulfur to the atmosphere is dimethyl sulfide (DMS). Large quantities are produced by algae in the oceans. Oceanic surface waters are super-saturated with DMS with respect to atmospheric concentrations, leading to a net flux to the atmosphere. In spring and summer up to 25 % of the H₂SO₄ burden carried in the atmosphere can come from the oxidation of DMS (Wayne, 1991). Oxidation of DMS and other organic sulfur compounds takes place by reaction with either OH or NO₃, leading eventually to the formation of SO₂. Other biogenic sulfur emissions come in the reduced forms of H₂S, CS₂ and COS. Oxidation of these biogenic compounds is driven by the hydroxyl radical. In each case SH radicals are formed, which are then further oxidized in the presence of O₂, O₃ or NO₂ to form SO₂ via the intermediate radicals SO and possibly HSO and S atoms. This SO₂ will then form H₂SO₄ via one of the routes displayed in Figure 3.

 H_2SO_4 is a strong acid, which is why excessive SO_2 emissions lead to acid rain. The preferred form of sulfate however, is solid or aqueous ammonium sulfate, where sulfuric acid has reacted with ammonia to form a salt. The ammonia thus neutralizes the acidity. In environments with low ammonia availability (ammonia/sulfuric acid ratio smaller than one) most sulfate is in the form of H_2SO_4 . If the ammonia/sulfuric acid molar ratio increases to between one and two, NH_4HSO_4 becomes the dominant aerosol component. For ratios of two and higher, the aerosol only consists of $(NH_4)_2SO_4$.

2.1.2 Nitrate



Figure 5: Tropospheric conversion between NO and NO₂ and the oxidation of NO₂ to HNO₃. Oxidation by OH mainly takes place during the day, oxidation via N_2O_5 at night. The figure is based on chemical processes described by Seinfeld & Pandis (2016) and Wayne (1991).

Nitrate aerosol consists of solid or liquid particles containing nitrate, mostly formed via nitric acid (HNO₃). The formation of nitrate aerosol is dependent on the emission of NO_x . The largest contributions to NO_x emissions come from fossil fuel combustion, biomass burning and lightning (Figure 6). NO_x consists of combined NO and NO_2 concentrations. These compounds are rapidly converted from one to the other via the photolysis of NO_2 and the reaction of NO with ozone. As mentioned before, the chemical theory described here and in the rest of the chapter is based on the books by Seinfeld & Pandis (2016) and Wayne (1991). The homogeneous pathway for the formation of nitrate aerosol leads via the oxidation of NO_2 to HNO_3 (Figure 5):

$$NO_2 + OH + M \rightarrow HNO_3 + M$$
 (2)

This reaction primarily takes place during the day, when hydroxyl radicals can be formed by photolysis. At night a different pathway of nitric acid formation is dominant:

$$NO_2 + O_3 \to NO_3 + O_2 \tag{3a}$$

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M \tag{3b}$$

$$[N_2O_5 + H_2O \rightarrow HNO_3 + HNO_3]_{aq}$$
(3c)

The gas-to-aqueous phase transfer of N_2O_5 is limited by gas-phase diffusion and transfer through the interface, while reaction 3c is so fast it can be considered instantaneous. The presence of clouds can therefore be very important for the formation of nitrate aerosol. Clouds furthermore affect nitrate aerosol formation as gaseous NO₃ radicals can be dissolved into cloud droplets, where they react rapidly with chloride ions to form dissolved nitrate ions.



Sources of NO_x

Figure 6: Anthropogenic sources of NO_x in the Netherlands in 2015. The figure is based on data from Velders et al. (2020).

Nitrate aerosol can be formed via multiple pathways. If the environment is ammonia rich and contains ammonia even after neutralization of all sulfuric acid, nitric acid will react with ammonia to form ammonium nitrate. This reaction can take place homogeneously or heterogeneously on the surface of pre-existing particles. Other heterogeneous pathways of nitrate aerosol formation also exist, for example the reaction of NO_2 or HNO_3 with sea salt particles (NaCl) to form NaNO₃.

2.1.3 Ammonium

Ammonium aerosol is formed by the reaction of ammonia with either sulfuric acid or nitric acid, see reactions 4 and 5. The reaction products are called ammonium sulfate and ammonium nitrate respectively. Ammonia is emitted by the soil, animals, sewage and in large amounts by agricultural processes (in particular the application of manure) (Figure 7).

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 \tag{4}$$

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$
 (5)

The reaction with sulfuric acid is faster, so that ammonium nitrate is only formed when all sulfuric acid has been neutralized (Seinfeld & Pandis, 2016). Therefore, two regimes can be identified:

- Ammonia poor: The atmosphere can be considered ammonia poor when the molar ratio between ammonia and sulfate is smaller than two. In this case there is insufficient ammonia to neutralize all available sulfate. Thus the aerosol phase will be acidic. Ammonia concentrations will be low, strongly limiting the formation of ammonium nitrate.
- Ammonia rich: The atmosphere can be considered ammonia rich when the molar ratio between ammonia and sulfate is larger than two. In this case there is excess ammonia, so all available sulfate can be neutralized. The ammonia that does not react with sulfate is available for reaction with nitrate to produce ammonium nitrate.

The Netherlands emits large amounts of ammonia, therefore the atmosphere can generally be assumed to be ammonia rich (Schaap et al., 2011).



Figure 7: Anthropogenic sources of NH_3 in the Netherlands in 2015. The figure is based on data from Velders et al. (2020).

2.1.4 Meteorology

Air pollution is not only dependent on the availability of chemical compounds. Meteorological factors can also play a large role, especially in inducing events of strong pollution. In the following paragraphs the roles of pressure, wind, temperature, relative humidity and clouds are shortly mentioned.

- **Pressure:** While pressure does not significantly influence air pollution directly, it does correlate with aerosol concentrations. High pressure systems usually come with weaker winds, allowing pollution levels to build up. Low pressure systems are characterized by wet and windy weather, causing pollutants to be dispersed and washed out of the atmosphere by rain.
- Wind: Local particulate matter pollution will depend largely on wind speed and direction. In the Netherlands for example, aerosol concentrations are usually high when winds are from the East and not very strong. In these conditions aerosol and aerosol precursors coming from continental Europe are blown into the country, where they mix with local emissions.
- **Temperature:** Aerosol nitrate is quite sensitive to temperature, with maximum concentrations of aerosol occurring when temperatures are at their minimum. This is because with higher temperatures more nitric acid remains in the gas phase as

nitric acid vapor. The temperature also influences the critical relative humidity, above which aerosol salts will take up water until they are dissolved. Generally the critical relative humidity decreases with temperature.

- **Relative humidity:** The availability of water vapour in the air is very important for aerosol formation processes. The oxidation of precursor gases via aqueous pathways increases with higher relative humidity (Zang et al., 2019). Additionally, aerosol hygroscopic growth increases with the larger availability of water, leading to larger and heavier aerosol particles. At higher relative humidities, more of the aerosol will be in the aqueous phase.
- Cloudiness: Photolysis rates in the troposphere are strongly influenced by the presence or absence of clouds. Beneath a thick layer of clouds photolysis is decreased, limiting the production of hydroxyl radicals and therefore the production of SIA. Underneath a clear sky photolysis rates are high, leading to increased hydroxyl radical concentrations and more oxidation of precursors gases and production of SIA.

2.2 Health risks

As already mentioned, aerosol pollution is a considerable health risk both worldwide as well as for the Netherlands. The European limit values (see section 2.3) are only occasionally exceeded in some locations in the Netherlands, but negative health effects are not limited to exceedances of particulate matter concentration limits. Most of these exceedances occur close to busy roads or large poultry farms, and in spring when ammonia emissions from manure spreading are high. The more strict guidelines on particulate matter pollution from the WHO (see section 2.3) are not met in 80 to 90 percent of European cities for PM_{10} and 90 to 94 percent for $PM_{2.5}$ (RIVM, 2013). Compared to other European countries the impact of air pollution in the Netherlands is slightly above average. Life expectancy is shortened by eleven months due to particulate matter in the Netherlands, while the average over Europe is nine months (European Environment Agency, 2019).

Measured PM_{10} concentrations in the Netherlands have been decreasing since 1993 when measurements started. PM_{10} concentrations in 2015 were about 50 % lower than in 1993 (Figure 8). Most of this decrease can be attributed to decreased primary aerosol emissions from diesel engines, due to the improvement and widespread implementation of soot filters. Particulate matter emissions from this source have decreased by over 50 % since 1990. Decreases in the emissions of SIA precursor gases have also contributed to the reduction of particulate matter pollution, albeit on a smaller scale (RIVM, 2013).

Even though the European limits are not often exceeded in the Netherlands and particulate matter concentrations have been decreasing, adverse health effects of air pollution should not be underestimated. There is no threshold level below which there are no negative effects of particulate matter pollution (WHO, 2019). Every year, thousands of people live days to months shorter due to air pollution (Velders et al., 2020; Fischer et al., 2020; Lelieveld et al., 2020). Especially elderly and people with cardiovascular and bronchial and lung diseases are at risk, as prolonged exposure to particulate matter can aggravate illnesses. Because there is no threshold level for adverse effects, meeting the European limits is not enough to prevent negative health effects. It is therefore important to note that striving for lower particulate matter concentrations will always remain beneficial to the public health.

2.3 Air pollution regulations

The European Union (EU) has imposed limit values on particulate matter concentrations since 1999 (European Commission, 1999). At first only for PM_{10} , but since 2008 also for $PM_{2.5}$ (European Commission, 2008). For PM_{10} , the following limits are have been formulated:

- Yearly average concentration should not be larger than $40 \ \mu g/m^3$.
- No more than 35 days with daily average concentrations above 50 μ g/m³.

The first limit targets the long term negative effects of air pollution, while the second limit targets the short term health risks due to episodes of very high concentrations.

For $PM_{2.5}$, the following limits have been formulated:

- A target value of $25 \ \mu g/m^3$ averaged over the year, starting from 2010.
- A limit value of 25 μ g/m³ averaged over the year, starting from 2015.
- An indicative limit value of 20 μ g/m³ averaged over the year, starting from 2020.
- A limit value of 20 $\mu g/m^3$ averaged over the year in urban background locations, starting from 2015.
- \bullet An exposure reduction of 15-20 % between 2010 and 2020 in urban background locations.

Contributions from natural sources do not have to be taken into account for exceedance of the limits. Therefore, a correction of 3-7 μ g/m² is applied to PM₁₀ concentrations, depending on the location. For the Netherlands this natural contribution mainly consists of sea salt, meaning that the largest corrections occur in the western and northern regions, while corrections are small in the southeastern part of the country (RIVM, 2013).

As mentioned before, particulate matter will still have negative health effects even if concentrations are below these limits. The WHO therefore has much stricter guidelines as to what levels of pollution are acceptable (WHO, 2005). They propose the following guideline values:

- PM_{10} : 20 µg/m³ annual mean concentration.
- $PM_{2.5}$: 10 µg/m³ annual mean concentration.

Meeting the guideline values according to the WHO should be an important target, as it would significantly reduce risks for acute and chronic effects from air pollution (WHO, 2005).



Figure 8: Measured average PM_{10} and $PM_{2.5}$ concentrations over the Netherlands. Data was retrieved from the website of the Dutch Environmental Data Compendium (2017, 2019).

As seen in Figure 8, average particulate matter concentrations in the Netherlands are currently well below the European limits and only slightly above the WHO guideline values. It is however important to consider that regional variations in concentrations can be large. An average around the WHO guideline value means that concentrations in many places will be above the guideline value.

To further limit air pollution, the EU in 2016 set national emission reduction commitments for important air pollutants including nitrogen oxides, sulfur dioxide and ammonia. These emission reductions are prescribed in the new NEC Directive, which entered into force on 31 December 2016 (European Commission, 2016). One of the goals of these emission reductions is to reduce the adverse effects of particulate matter by 50 % in 2030. The emission reductions for 2030 that have been specified to obtain this goal can be seen in Table 1. Reductions from the NEC Directive are set with respect to the 2005 emissions. These have been translated to reductions with respect to 2010 (using the CEIP (2020) emission database), as this study is focused on that year. In the Netherlands, 2030 emission goals are related to the Clean Air Agreement that was signed in 2020 (Ministry of Infrastructure and Water Management, 2020). This agreement was signed by the Minister of the Environment and Housing Department and 46 provinces and municipalities. The aim of the Clean Air Agreement is to reduce air pollution in the Netherlands in 2030 by 50 %, hoping to meet the WHO guidelines and prevent 4000 - 5000 premature deaths on an annual basis.

Table 1:	European	average	(EU)	and	Dutch	(NL)	emission	reductions	from	the	2016	NEC
Directive	(European	Commis	ssion,	2016).							

Compound	EU reduction 2005-2030	NL reduction 2005-2030
Compound	(2010-2030)	(2010-2030)
NO _x	63~%~(53~%)	61 % (52 %)
SO_2	79 % (62 %)	53 % (10 %)
NH ₃	19%(14%)	21 % (9 %)
NMVOC	40 % (28 %)	15 % (16 %)
$PM_{2.5}$	49%~(45%)	45%(27%)

3 Model setup

In this chapter, an overview is given of the application of the WRF-Chem model in this study. A description of the model is provided, as well as information on the choices made in the model setup. The study area, boundary and initial conditions and emission input data are presented. In the final section, the different simulations performed are listed.

3.1 Model description

This study uses version 3.8.1 of the mesoscale fully compressible non-hydrostatic WRF model, coupled with 'online' chemistry (WRF-Chem). Online in this context implies that meteorological and chemical components of the model are calculated simultaneously, leading to an interdependence of the meteorological and chemical processes. Examples of processes included in WRF-Chem are emission, transport, deposition, chemical transformation, aerosol interaction, radiation and photolysis. Transport is based on an Eulerian formulation of fluid transport processes. A complete description of the model is given by Grell et al. (2005). WRF-Chem can be used on different spatial and temporal scales and can produce simulations based on actual atmospheric or idealized conditions. As the model explicitly solves its meteorology instead of relying on prescribed fields, it is also applicable for use in real-time forecasting or future projections on both meteorology and air quality.

WRF-Chem includes many options for parameterization schemes for most of its physical and chemical processes. The main options chosen for this study are listed in Table 2. A more detailed description of the chemistry setup is provided in Section 3.2.

Process	Scheme	Namelist value	Reference
Microphysics	Morrison 2-mom	$mp_{-}physics = 10$	Morrison et al., 2009
Long-wave radiation	RRTM	$ra_lw_physics = 1$	Mlawer et al., 1997
Short-wave radiation	Dudhia	$ra_sw_physics = 1$	Dudhia, 1989
Cumulus physics	Grell 3D	$cu_physics = 5$	Grell, 1993
Planetary boundary layer	YSU	$bl_pbl_physics = 1$	Hong et al., 2006
Surface layer	Revised MM5	$sf_sfclay_physics = 1$	Jiménez et al., 2012
Land-surface	Unified Noah LSM	$sf_surface_physics = 2$	Tewari et al., 2004
Photolysis	Fast-J	$phot_opt = 2$	Wild et al., 2000
Gas-phase mechanism	CBM-Z	$chem_opt = 32$	Zaveri & Peters, 1999
Aerosol model	MOSAIC	$chem_opt = 32$	Zaveri et al., 2008

Table 2: WRF-Chem configuration summary.

3.2 Chemistry setup

As displayed in Table 2, the gas-phase chemistry is solved by the Carbon Bond Mechanism version Z (CBM-Z) scheme (Zaveri & Peters, 1999). This is a lumped structure mechanism, treating certain groups of organic species as one 'lump' according to the type of bond present. As these lumped species in reality do not all have the same reaction rates and products, this will lead to some inaccuracies. The advantage however is that the lumping of species is very computationally efficient. The CBM-Z scheme was chosen over for example the RADM2 mechanism as it can be coupled with the Model for Simulating Aerosol Interactions and Chemistry (MOSAIC) module, which according to Yang et al. (2018) produces the best results for simulating aerosol. The MOSAIC module includes nitrate, sulfate, ammonium, sodium, calcium, chloride, black carbon, primary organic mass, liquid water, and other inorganic mass. Particles are divided over four bins based on their size (Table 3). The module simulates major aerosol processes such as thermodynamic equilibrium, condensation, binary nucleation, and coagulation (Zaveri et al., 2008).

Table 3: Bins over which aerosol particles are divided in the MOSAIC module based on their size.

Bin number	Particle dry diameter (µm)
1	0.039 - 0.156
2	0.156 - 0.625
3	0.625 - 2.5
4	2.5 - 10

Dry deposition of gas and aerosol is parameterized using the Wesely scheme, which takes into account surface conditions (e.g. dew, surface moisture, temperature) and plant stomatal response to these environmental conditions (Wesely, 1989). Wet deposition is included in WRF-Chem as well, although it appears to be overpredicted by 25 % according to Karlický et al. (2017). This could potentially result in an underprediction of aerosol mass. Cloud chemistry in WRF-Chem is also activated.

3.3 Study area

This study focuses on SIA concentrations over the Netherlands, comparing simulation results to measurements at Dutch stations and investigating the impact of emission scenarios on SIA concentrations. Therefore WRF-Chem is set up with a focus on an area containing all of the Netherlands and parts of the neighbouring countries and sea. The model can be configured to use multiple domains, all having their separate spatial and temporal resolution as well as different settings for physical and chemical processes. In this case the choice was made to use the same settings over all the domains, only the resolution varies. The setup used in this study consists of four domains and is based on the setup used by van der Swaluw et al. (2018), who performed a similar study on modelling SIA using the European Monitoring and Evaluation Programme (EMEP) atmospheric chemistry and transport model and the Operational Priority Substances (OPS) model) (EMEP, 2020; RIVM, 2020). The four domains are shown in Figure 9.

The parent domain (domain 1) covers all of Europe and has a coarse resolution of 0.5×0.5 degree (approximately 34 km x 55.5 km over the Netherlands). At the boundaries of domain 1 external boundary conditions are applied, as described in Section 3.4. Nested within domain 1 is domain 2, with a resolution that is factor three higher (approximately 11 km x 18.5 km). This domain covers all of the Benelux region as well as the western half of Germany, the northernmost part of France, part of Denmark, a very small part of England and a large part of the North Sea. Boundary conditions for domain 2 come from domain 1. Within domain 2 is the third domain, which in turn contains domain 4. Both of these cover the Netherlands and only small parts of the neighbouring countries and the North Sea. The resolution again increases with a factor three for both domains, leading to resolutions of approximately 4 km x 6.2 km and 1.3 km x 2.1 km for domain 3 and 4 respectively. Domain 3 takes its boundary condition from domain 2, domain 4 is only run separately from to other domains and therefore also takes external boundary conditions as described in Section 3.4.



Figure 9: The four domains used in this study (domain 1 = yellow, domain 2 = blue, domain 3 = green, domain 4 = red).

Originally the plan was to use all four domains together, one parent domain with three nested child domains. This however turned out to be too computationally expensive, making it impossible to perform the desired simulations. Therefore the fourth domain, which due to its high resolution is the most time expensive, was cut from the nested setup. Instead, the fourth domain was run separately so as to compare it to the setup with the first three domains together. See Section 3.6 for more information on the performed simulations. Nesting in the simulations using domains 1, 2 and 3 goes both ways, with feedback from parent to child domains as well as the other way around.

3.4 Boundary and Initial conditions

The meteorological boundary and initial conditions are prescribed by the National Centers for Environmental Prediction (NCEP) FiNaL reanalysis (NCEP-FNL) (NCEP, 2000, updated daily). This data set has a horizontal resolution of 1-degree by 1-degree and is prepared operationally every six hours. NCEP-FNL is made with the same model which NCEP uses in the Global Forecast System (GFS), but is prepared an hour after the GFS is initialized so that more observational data can be used. The analyses are available on the surface, at 26 mandatory (and other) pressure levels from 1000 millibars to 10 millibars, in the surface boundary layer and at some sigma layers, the troppause and a few others. Parameters include surface pressure, sea level pressure, geopotential height, temperature, sea surface temperature, soil values, ice cover, relative humidity, uand v- winds, vertical motion, vorticity and ozone. For this study the initial conditions of meteorological variables for all four domains are set using the NCEP-FNL data set. In addition the boundary conditions for domain 1 are set every six hours based on the NCEP-FNL data set. The boundary conditions for domains 2 are 3 are derived from their respective parent domains 1 and 2. Domain 4 is run separately and therefore also takes boundary conditions from the NCEP-FNL data set every six hours.

Chemical initial and boundary conditions are taken from model output from the Model for OZone And Related chemical Tracers (MOZART)-4 (Emmons et al., 2010).

MOZART-4 data is provided on a 2.5-degree by 1.9-degree horizontal grid with 56 vertical levels. Output is provided every 6 hours. Species in the MOZART-4 output are not always identical to those in the CBM-Z chemical mechanism and MOSAIC aerosol module used in this study. The MOZART-4 variables are therefore mapped to the CBM-Z and MOSAIC speciation. This in done following the CBMZ-MOSAIC_4bins.inp file located in the EXAMPLES directory of the MOZBC utility used to write initial and boundary conditions to WRF-Chem input files (National Center for Atmospheric Research/Atmospheric Chemistry Observations & Modeling, 2019).

3.5 Emission data

Emissions of several compounds from a variety of sources are needed to correctly simulate aerosol chemistry using WRF-Chem. Parameterization schemes are used to determine to emissions from natural sources, while anthropogenic emissions are explicitly specified in NetCDF format input files read into WRF-Chem.

Natural emissions relevant to the formation of SIA in the Netherlands come in the form of biogenic, dust, sea salt and DMS emissions. Biogenic emissions include nonmethane volatile organic compounds (NMVOC) and nitrogen, and are parameterized in WRF-Chem by the Simple Guenther approach (bio_emiss_opt = 1). In this scheme the emissions are based on land use and depend on both temperature and photosynthetic active radiation (Guenther et al., 1994; Simpson et al., 1995). Dust emissions are calculated using the GOCART scheme with AFWA modifications (dust_opt = 3) (Jones et al., 2012). Sea salt emissions are determined using the MOSAIC or MADE/SORGAM sea salt scheme (seas_opt = 2) based on land cover and wind speed information. DMS emissions from the sea surface are based on the GOCART DMS emissions scheme (dm-semis_opt = 1). Emissions from biomass burning have not been included, as they are not thought to be a significant source of SIA in the Netherlands (Pandolfi et al., 2020).

Anthropogenic emissions on domains 1, 2, and 3 are taken from the 'Emissions as used in EMEP models' database from CEIP (2019). Emissions on domain 4 are a combination of data from CEIP, as well as higher resolution data from the Dutch Pollutant Release and Transfer Register (2019). The data from CEIP contains yearly emissions on a $0.1^{\circ}x \ 0.1^{\circ}grid$ for NO_X, SO_x, NH₃, NMVOC, CO, PM_{2.5}, PM₁₀ and PM_{coarse}. The emissions are based on reported gridded emissions. In areas with no grid reporting the emissions are based on gridded data from CAMS (CAMS-REG-APv2.2) and EDGAR, upgraded by point source information available under E-PRTR. International shipping emissions are based on FMI data from CAMS (CAMS-GLOB-SHIP). Emission data in the Emissions as used in EMEP models database from CEIP is divided over eleven Selected Nomenclature for Air Pollution (SNAP) categories. These categories represent different sectors from which emission can come. The sector names can be seen in Figure 13 and more information on the definition of the SNAP sectors can be found in Richardson (1999). The emission data from CEIP is regridded to the domains described in Section 3.3 and the compounds are mapped to those used in the CBM-Z and MOSAIC modules. The CEIP data is downsampled to the lower resolution on domain 1 and regridded to domains 2, 3 and 4 using linear interpolation. For domain 4 the Dutch and North Sea data is removed from the emission data from CEIP, and replaced by the higher resolution data (1 km x 1 km) from the Dutch Pollutant Release and Transfer Register. NO_x emissions are assumed to be 90 % NO and 10 % NO_2 . SO_x emissions are assumed to be exclusively in the form of SO_2 . NMVOC emission speciation is presented in Figure 32 in the appendix. All compounds are assumed to be emitted in the lowest model layer, which has a height of approximately 40 m.



Figure 10: Daily mean $\rm NO_x$ emission input for January/February 2010 on domains 1 (a), 3 (b) and 4 (c).



Figure 11: Daily mean SO₂ emission input for January/February 2010 on domains 1 (a), 3 (b) and 4 (c).



Figure 12: Daily mean NH_3 emission input for January/February 2010 on domains 1 (a), 3 (b) and 4 (c).

The emissions presented in figures 10, 11 and 12 are the daily mean values for January/February 2010. Emissions are very much time depended, with variations coming on several timescales. Firstly, emissions vary during one day, with most emissions being higher during daytime than nighttime. The hourly emission profiles used to scale the emissions from hour to hour are presented in Figure 13. The data on temporal variations in the emissions comes from Thunis et al. (2008). Different SNAP sectors have different hourly profiles. Agricultural emission for example have one peak during the day and are low at night. Road transport also has higher emissions during the day but it has two peaks, one in the early morning and one in the late afternoon. How much the emission of a compound varies thus depends on the SNAP sectors from which the emissions come. Based on the emissions per sector and the hourly emission profiles of the sectors, profiles can be calculated for the aerosol precursor gases NO_x , SO_2 and NH_3 . These profiles are presented in Figure 14. NO_x emissions for a large part come from Road transport (S7) and therefore have peaks in the morning and afternoon. SO₂ emissions peak in the morning and slowly decline the remainder of the day, following the profile of the Combustion in energy and transformation industries SNAP sector (S1), which emits a large amount of SO_2 . NH₃ is mostly emitted by the Agriculture (S10) and the Other sources and sinks (S11) sectors (which in this study represents the spreading of manure), and therefore has a strong peak during the day.



Figure 13: Hourly emission profiles per SNAP sector applied as a scaling factor to the daily emissions. Other sources and sinks (S11) in this case contains emissions related to the spreading of manure. The data on temporal variations in emissions comes from Thunis et al. (2008).



Figure 14: Hourly emission profiles per compound. These are calculated based on the hourly emission profiles per SNAP sector (Figure 13) and the distribution of the NO_x , SO_2 and NH_3 emissions over the SNAP sectors in the emission data for the Netherlands (CEIP, 2019).

Emissions do not only vary on an hourly timescale, but also on daily and monthly timescales. Variations between days are relatively minor and are therefore not applied in this study. Emissions mainly differ between week and weekend days, but these variations are smaller than those on hourly and monthly timescales. The monthly emission profiles per SNAP sector are shown in Figure 15. By far the largest variations are found for S2 and S11. S2 encompasses non-industrial combustion plants including residential heating, which is much more prominent in the winter than in the summer, leading to emissions peaking in winter. S11 in this study contains the spreading of manure, which largely takes place in early spring. As this study focuses only on the months January and February, an average of the factors for these two months was taken and applied to the emissions. This is advantageous for the amount of emission data that has to be supplied as input to WRF-Chem, as now the emissions only vary on an hourly timescale. The emission input files therefore only have to be defined for one period of 24 hours, as all days in the study period have identical emissions.



Figure 15: Monthly emission profiles per SNAP sector applied as a scaling factor to the annual emissions. Other sources and sinks (S11) in this case contains emissions related to the spreading of manure. The data on temporal variations in emissions comes from Thunis et al. (2008).

Uncertainties in the emissions of the aerosol precursor gases are significant. The Netherlands Organisation for Applied Scientific Research (2004) estimates the uncertainties in the annual Dutch emissions of NO_x , SO_2 and NH_3 to be $\pm 15 \%$, $\pm 6 \%$ and $\pm 17 \%$ respectively. Uncertainties for emissions from one specific source or location are in most cases larger. The more recent report on uncertainties in the CEIP emission database by Schindlbacher & Wankmüller (2019) finds numbers of the same order. Uncertainties in emissions from eastern Europe are larger than those in emissions from western Europe (Fagerli et al., 2019).

3.6 Model simulations

The WRF-Chem model, set up as described above, is used to perform eight simulations. Two simulations use only the fourth domain, the others use domains 1, 2, and 3. Other than this, the simulations only differ in the emission input. Meteorological and chemical boundary conditions are not changed and neither are the time period (10 January 2010 - 10 February 2010), spin-up time (nine days) or parameterizations. The eight simulations performed are listed below, including a short description of the used emissions for each simulation and the reason for performing the simulation.

- **2010**_**d123**: This simulation is performed on domains 1, 2, and 3. It uses the 2010 emissions from CEIP (2019), as described in section 3.5. The reason for doing this simulation is to see if the model is able to correctly simulate the SIA concentrations in early 2010. Results are compared to those from simulation 2010_d4, to determine which setup is best to use for further simulations. This simulation also serves as a reference for the simulations where emissions scenarios are applied.
- 2010_d4: This simulation is performed on domain 4. It uses 2010 emissions from CEIP (2019) combined with 2010 emissions from the Dutch Pollutant Release and Transfer Register (2019). Similar to simulation 2010_d123, the goal of this simulation is to see if the model can recreate to measured SIA concentrations from early 2010. Results are compared to those from simulation 2010_d123, to determine which setup is best to use for further simulations.
- Zero_NL_d123: This simulation is performed on domains 1, 2, and 3. Dutch emissions of NO_x, NH₃, SO₂, NMVOC, CO, PM2.5 and PM10 have been set to zero. Other emissions are equal to those in simulation 2010_d123. The aim of this simulation is to investigate contributions to Dutch air pollution from abroad, as well as seeing how the model reacts to changes in emissions. Results are compared to those from simulation Zero_NL_d4, to see if the behaviour of the two model setups is significantly different concerning changing Dutch emissions.
- Zero_NL_d4: This simulation is performed on domain 4. Dutch emissions of NO_x, NH₃, SO₂, NMVOC, CO, PM2.5 and PM10 have been set to zero. Other emissions are equal to those in simulation 2010_d4. The aim of this simulation is to investigate contributions to Dutch air pollution from abroad, as well as seeing how the model reacts to changes in emissions. Results are compared to those from simulation Zero_NL_d123, to see if the behaviour of the two model setups is significantly different concerning changing Dutch emissions.
- Half_NO_x_NL: This simulation is performed on domains 1, 2, and 3. Dutch NO_x emissions have been halved compared to the emissions used in simulation 2010_d123. The goal of this simulation is to investigate how effective reductions in NO_x emissions are when trying to limit air pollution by particulate matter.
- Half_NH₃_NL: This simulation is performed on domains 1, 2, and 3. Dutch NH₃ emissions have been halved compared to the emissions used in simulation 2010_d123. The goal of this simulation is to investigate how effective reductions in NH₃ emissions are when trying to limit air pollution by particulate matter.
- Half_SO₂_NL: This simulation is performed on domains 1, 2, and 3. Dutch SO₂ emissions have been halved compared to the emissions used in simulation 2010_d123. The goal of this simulation is to investigate how effective reductions in SO₂ emissions are when trying to limit air pollution by particulate matter.
- **2030_EU:** This simulation is performed on domains 1, 2, and 3. The 2010 emissions from CEIP (2019) have been modified to reflect the 2030 goals of the NEC Directive, entered into force on 31 December 2016 (European Commission, 2016). So, the emissions are those that we will have in 2030 if the emission reduction goals from the NEC Directive are met. For the Dutch emissions, the national emission reduction commitment for the Netherlands has been applied. For the rest of Europe, the European average has been applied. The aim of this simulation is to see how much these emission reductions help towards reducing the negative health effects of particulate matter and towards reaching the WHO guideline values for particulate matter pollution in 2030 in the Netherlands.

4 Model evaluation

This chapter presents the evaluation of the meteorology and chemistry simulated using the WRF-Chem model. This is done for simulations 2010_d123 and 2010_d4, which are the simulations with the unaltered 2010 emissions on domains 1, 2 and 3 and on domain 4, respectively. These should reproduce the measured 2010 SIA concentrations. Additionally, the simulations Zero_NL_d123 and Zero_NL_d4, where Dutch emissions are set to zero, are analyzed to see how the model reacts to changes in Dutch emissions and to investigate the contribution to air pollution in the Netherlands coming from emissions abroad. First, the observational data used for the evaluation is presented, as well as the used statistical methods. Thereafter, the results for meteorological variables are shown, followed by the results for chemical compounds. Finally, some conclusions are drawn about the quality of the model results and one domain configuration is selected for use in further simulations.

4.1 Evaluation data

The data that is used for the evaluation of meteorological variables comes from the NCEP-FNL reanalysis data set, see Section 3.4 for more information on this data set. Concentrations of chemical compounds are compared to measurements from the Dutch National Air Quality Monitoring Network (2019). This data set contains hourly measurements of the gases NO, NO₂, SO₂ and NH₃, as well as daily measurements of the aerosol compounds NO₃, SO₄ and NH₄. Measurements of the aerosol compounds have been performed at seven stations in the Netherlands. The locations of these stations are shown in Figure 16, with some details for each station in Table 4. Not all compounds are measured at each station, see Table 15 in the appendix for an overview of the compounds measured per station.



Figure 16: The geographical locations of the seven measurement stations in the Netherlands used for the evaluation of the model. Adapted from Williams et al. (2015). The station's names, latitudes and longitudes can be found in Table 4.

Station ID	Station name	Latitude (°N)	Longitude (°E)
131	Vredepeel	51.54	5.85
235	Huijbergen	51.43	4.36
444	De Zilk	52.30	4.51
538	Wieringerwerf	52.80	5.05
627	Bilthoven	52.12	5.19
929	Valthermond	52.88	6.93
934	Kollumerwaard	53.33	6.28

Table 4: Details of the measurement stations in the Netherlands used for the evaluation of the model. Station locations on the map are shown in Figure 16.

Uncertainties in the measured concentrations are considerable. In the tables below the 95 % confidence interval is included for the measurement data. For the SIA compound measurements the uncertainties are based on the standard deviations found in the measurements by Mooibroek et al. (2011). Standard deviations are given for five measurement stations in the Netherlands. The standard deviation of the average concentrations is calculated as the mean of the station standard deviations divided by the square root of the number of station. The 95 % confidence interval is calculated as twice the standard deviation. The uncertainty in the total SIA concentrations is found by summation in quadrature of the compound uncertainties. For NO, NO₂ and NH₃ the uncertainties are based on Wesseling et al. (2018) and for SO₂ the uncertainty comes from Velders et al. (2011). Wesseling et al. (2018) estimate an uncertainty of 15 % - 25 % in the yearly averaged concentrations of NO, NO₂ and NH₃ over the Netherlands. In this study the upper limit of 25 % will be used.

4.2 Evaluation methods

Statistical evaluation of the model performance with respect to observation data sets is based on the following metrics. The definitions of these metrics are taken from Yu et al., (2006).

• Pearson's correlation (r): also known just as the correlation coefficient, this measure provides an indication of the strength of the linear relationship between two variables. It is defined as the covariance of the variables divided by the product of their standard deviations. Values for r can range from -1 to 1. An r of -1 indicates a perfect negative linear relationship between variables, an r of 0 indicates no linear relationship between variables. Pearson's correlation can be calculated as follows:

$$\mathbf{r} = \frac{\sum_{i=1}^{n} (\mathbf{y}_{i} - \bar{\mathbf{y}})(\mathbf{x}_{i} - \bar{\mathbf{x}})}{\{\sum_{i=1}^{n} (\mathbf{y}_{i} - \bar{\mathbf{y}})^{2} \sum_{i=1}^{n} (\mathbf{x}_{i} - \bar{\mathbf{x}})^{2}\}^{1/2}}$$
(6)

where y is the model data and x the reference data set.

• Mean Bias Error (MBE): this measure is used to quantify the mean difference between the model results and the reference data set. It is in the same unit as the considered variable. The MBE can be calculated following Equation 7.

$$MBE = \frac{\sum_{i=1}^{n} (y_i - x_i)}{n}$$
(7)

• Normalized Mean Bias Error (NMBE): this measure is calculated by normalizing the MBE with the mean of the reference data (see Equation 8). In effect, it expresses the difference between the model and the reference in percentages. Note that care has to be taken when normalizing variables that can obtain negative values (in this case wind vectors). For such variables normalization should be performed by dividing by the mean of the magnitudes of the reference data. To prevent mistakes due to negative values, the absolute value of the reference data is taken in the denominator of Equation 8. The NMBE was chosen over the Mean Normalized Bias Error (MNBE) as it is less sensitive to disproportionately large errors from trivially low reference values.

$$NMBE = \frac{\sum_{i=1}^{n} (y_i - x_i)}{\sum_{i=1}^{n} |x_i|}$$
(8)

• Normalized Mean Gross Error (NMGE): while the NMBE is a good measure of the bias that is in the data, it does not provide information about the absolute magnitude of errors. The NMGE is introduced to indicate, in percentages, how much the model results on average deviate from the reference. Values are normalized using the reference data. The NMGE was chosen over the Root Mean Square Error because it can more easily be compared to the NMBE. The NMGE is calculated by dividing the sum of the absolute differences between the model and the reference by the sum of the absolute reference values (see Equation 9).

$$NMGE = \frac{\sum_{i=1}^{n} |y_i - x_i|}{\sum_{i=1}^{n} |x_i|}$$
(9)

4.3 Meteorology evaluation

Presented below is the meteorological output from the 2010 simulations on domains 1, 2 and 3 (2010_d123) and on only domain 4 (2010_d4). For simulation 2010_d123, statistics are calculated for domain 3 as well as domain 1. The table with the statistics for domain 1 can be found in the appendix (Table 16). For simulation 2010_d4, statistics are of course limited to only domain 4. Statistics of meteorological variables on domains 3 and 4 use daily means averaged over the Netherlands. Figures also use daily means averaged over the Netherlands. Figures also use daily means averaged over the Netherlands. Figures also use daily means averaged over the Netherlands and from domain 4 for 2010_d4. Figures of the daily mean 10-m zonal and meridional wind components are included here (Figures 17 a and b) as wind is thought to be the dominant meteorological determining variations in SIA concentrations in the Netherlands (RIVM, 2013). Figures of other meteorological variables can be found in the appendix (Figures 33 a, b, c and d) along with wind roses for 2010_d123, 2010_d4 and NCEP-FNL, providing more insight into dominant wind directions in the model and in the reanalysis data (Figures 34 a, b and c).



Figure 17: Daily mean 10-m zonal (a) and meridional (b) wind vectors between 10-01-2010 and 10-02-2010 for the modelled meteorology in the simulations on domains 1, 2 and 3 (2010_d123) and on domain 4 (2010_d4). Wind vectors from the NCEP-FNL reanalysis data are included as a reference. The wind vectors are averaged over the grid cells located over the Netherlands.

The zonal wind component (Figure 17a) during the study period was slightly negative on average, indicating winds from the East. Variations however are large. The meridional wind component (Figure 17b) was slightly positive on average, meaning winds from the South. The meridional wind was weaker than the zonal wind. This indicates that on average the wind came from the East-Southeast during the study period, so from eastern Europe towards the Netherlands. In general the model captures the wind components very well, although significant deviations can be found in the zonal wind. During the largest deviation, around 24 January, the zonal wind speed is overestimated by the model compared to the NCEP-FNL reanalysis data.

Table 5: Statistics of daily mean meteorological variables over the Netherlands for domain 3 from the 2010 simulation on domains 1, 2 and 3 (2010_d123). The NCEP-FNL reanalysis data serves as a reference for the modelled variables.

Variable	Mean ref*	Mean mod	r	MBE	NMBE (%)	NMGE (%)
Temperature (°C)	273.2	270.2	0.34	-3.0	-1.1	1.4
Sea-level pressure (hPa)	1014.6	1012.5	0.93	-2.1	-0.2	0.5
Relative humidity (%)	90.9	90.7	0.49	-0.2	-0.3	5.5
Wind speed (m/s)	4.1	4.1	0.40	0.0	-0.8	34.1
Zonal wind speed (m/s)	-0.9	-1.6	0.79	-0.8	-23.0	60.3
Meridional wind speed (m/s)	0.5	-0.2	0.69	-0.7	-39.3	77.0

*Mean ref = mean of the reference data, Mean mod = mean of the simulation data, r = correlation coefficient, MBE = Mean Bias Error, NMBE = Normalized Mean Bias Error, NMGE

⁼ Normalized Mean Gross Error.

Variable	Mean ref	Mean mod	r	MBE	NMBE (%)	NMGE (%)
Temperature (°C)	273.2	272.8	0.92	-0.5	-0.2	0.4
Sea-level pressure (hPa)	1014.6	1014.4	0.99	-0.2	0.0	0.1
Relative humidity (%)	90.9	91.8	0.67	0.9	1.0	3.9
Wind speed (m/s)	4.1	4.9	0.94	0.8	18.9	19.1
Zonal wind speed (m/s)	-0.9	-0.8	0.99	0.0	1.3	22.5
Meridional wind speed (m/s)	0.5	0.5	0.98	0.0	2.4	24.0

Table 6: Statistics of daily mean meteorological variables over the Netherlands for domain 4 from the 2010 simulation on domain 4 (2010_d4). The NCEP-FNL reanalysis data serves as a reference for the modelled variables.

From the statistics in Tables 5 and 6 it is clear that the meteorology is closest to the reanalysis data in simulation 2010_d4. This simulation uses one small domain and boundary conditions are set directly from the reanalysis data, so the meteorology calculated by the WRF-Chem model itself is tightly linked to that from the reanalysis. Wind speeds however are overestimated by 19 %. In simulation 2010_d123, correlations for domain 1 are high and normalized mean bias errors are small. Only for the relative humidity and the wind speed do we see significant deviations, with an overestimation of 7 % for the relative humidity and an overestimation of wind speeds of 24 %. Over the Netherlands on domain 3, correlations are weaker but normalized mean bias errors are smaller. Wind speeds are not systematically overestimated here. Differences in average temperature, pressure and relative humidity in neither of the simulations are large enough to significantly influence to formation of SIA (Seinfeld & Pandis, 2016). The differences in the wind components could affect concentrations, depending mostly on whether the simulated winds change the occurrences of strong pollution events (see Chapter 5 for a detailed analysis of the peaks in SIA concentrations).

4.4 Chemistry evaluation

As already described in Section 4.1, the results from the 2010 simulations on domains 1, 2 and 3 (2010_d123) and on domain 4 (2010_d4) are compared to the measurements of SIA compounds and precursors of SIA at the seven measurement locations of the RIVM in the Netherlands (Figure 16). In addition, results from a similar study performed by van der Swaluw et al. (2020) using the EMEP atmospheric chemistry transport model (EMEP, 2020) are also included in the figures under the label 'EMEP4NL'.



Figure 18: SIA concentrations from the 2010 simulations on domains 1, 2 and 3 (2010_d123) and on domain 4 (2010_d4) compared to measurements and EMEP4NL. Concentrations are averages over the seven measurement locations. Panel d shows the total SIA concentration, i.e. the sum of the concentrations in panels a, b and c. Uncertainty intervals for the measurements (grey shading) are based on Mooibroek et al. (2011), as described in Section 4.1.

Simulation 2010_d123 performs very similar to the EMEP4NL model, although slightly better capturing the SIA peaks around 15 January and 7 February (Figure 18). More details on the SIA peaks can be found in Chapter 5. SIA concentrations are underestimated by 41 % averaged over the study period, mainly due to the underestimation of peak concentrations (Table 7). In the periods between the peaks, the modelled SIA concentrations are actually very close to the measured concentrations. In general the temporal variations in SIA concentrations do seem to be captured by the model. The main exception on this is the peak around 25 January. Again, see Chapter 5 for more information. Out of the three main SIA compounds, SO₄ is captured the worst by the model, the peak in SO₄ concentrations around 25 January is missed completely. The correlation between the simulated and measured concentrations is lower than for NO_x and NH₃ and the NMBE is larger (Table 7).

Simulation 2010_d4 gives very different results, overestimating SIA concentrations by 64 % averaged over the study period (Table 8). This overestimation is mainly due to an overestimation of peak concentrations, as modelled SIA concentrations between the peaks are actually very close to the measured concentrations. All three SIA concentration peaks are captured by this simulation. Again variations in SO_4 concentration are the least well reconstructed by the model, as can be seen from the correlation coefficient that is lower for SO_4 than for NO_3 or NH_4 (Table 8).



Figure 19: SIA precursor concentrations from the 2010 simulations on domains 1, 2 and 3 (2010_d123) and on domain 4 (2010_d4) compared to measurements and EMEP4NL. Concentrations are averages over the seven measurement locations. Uncertainty intervals for the measurements (grey shading) are based on Wesseling et al. (2018) and Velders et al. (2011), as described in Section 4.1.

Looking at the SIA precursor gases (Figure 19) we find that simulations 2010_d123 and 2010_d4 perform much more similar than for the SIA concentrations. Simulated average concentrations over the study period of NO and NO₂ are close to the measured concentrations (within 15 % for NO and within 40 % for NO₂) (Tables 7 and 8). SO₂ and NH₃ concentrations on the other hand are much higher in the model than in the measurements (up to 360 % for SO₂ and up to 125 % for NH₃). The overestimation of SO₂ and NH₃ concentrations, indicating too little formation of ammonium sulfate, is in line with the underestimation of SIA concentrations in simulation 2010_d123. SIA concentrations in simulation 2010_d4 on the other hand are overestimated while the precursor gas concentrations are also overestimated. This would indicate that sources of SIA and SIA precursors are too large in this model setup.

Table 7: Statistics of daily mean chemical variables on domain 3 from the 2010 simulation on domains 1, 2 and 3 (2010_d123), averaged over the measurement locations. The results are compared to the average of the measurements from the seven stations.

Variable	Mean obs	Mean mod	r	MBE	NMBE	NMGE
	$(\mu g/m^3)$	$(\mu { m g}/{ m m}^3)$		$(\mu g/m^3)$	(%)	(%)
SIA	19.5 ± 3.6	11.5	0.56	-8.0	-41.1	52.3
NO ₃	9.9 ± 3.0	6.3	0.60	-3.7	-36.7	50.1
SO ₄	5.1 ± 1.6	2.4	0.23	-2.7	-52.5	74.5
NH ₄	4.5 ± 1.4	2.8	0.54	-1.7	-37.9	54.1
NO	4.4 ± 1.1	3.3	0.24	-1.2	-12.4	84.5
NO ₂	21.7 ± 5.4	26.6	0.51	4.9	23.2	49.3
SO_2	2.5 ± 1.0	8.0	0.25	5.4	195.7	240.7
NH ₃	2.0 ± 0.5	4.3	0.12	2.3	123.5	148.5

Table 8: Statistics of daily mean chemical variables on domain 4 from the 2010 simulation on domain 4 (2010_d4), averaged over the measurement locations. The results are compared to the average of the measurements from the seven stations.

Variable	Mean obs	Mean mod	r	MBE	NMBE	NMGE
	$(\mu g/m^3)$	$(\mu { m g}/{ m m}^3)$		$(\mu g/m^3)$	(%)	(%)
SIA	19.5 ± 3.6	32.0	0.73	12.5	63.8	74.6
NO ₃	9.9 ± 3.0	19.5	0.71	9.6	96.9	107.3
SO_4	5.1 ± 1.6	5.0	0.65	-0.1	-2.5	46.9
NH ₄	4.5 ± 1.4	7.6	0.71	3.0	66.6	77.8
NO	4.4 ± 1.1	4.5	0.54	0.0	6.5	72.3
NO ₂	21.7 ± 5.4	30.1	0.87	8.4	37.0	44.8
SO_2	2.5 ± 1.0	11.9	0.55	9.3	360.6	366.0
NH ₃	2.0 ± 0.5	3.1	0.48	1.1	71.9	100.0



Figure 20: Stack plots of the average composition of SIA over the seven measurement locations for the 2010 simulations on domains 1, 2 and 3 (2010_d123, panel a) and on domain 4 (2010_d4, panel b), the measurements (panel c) and EMEP4NL (panel d). Note that the vertical scale of the four figures is not identical.

Figure 20, showing the stacked concentrations of NO₃, SO₄ and NH₄ for the two 2010 simulations, the measurements and EMEP4NL, is useful for analyzing the composition of SIA during the study period. In the WRF-Chem simulations the relative contribution from SO₄ is lower compared to the measurements. An exception is the peak on 7 February where it is the NO₃ concentration that is underestimated in simulation 2010_d123. In EMEP4NL the relative contribution from NO₃ is lower than in the measurements or the WRF-Chem simulations. Based on the measurements it is clear that the concentrations of the three main SIA compounds are correlated. During peak events all three SIA compounds are abundant, while at low SIA concentrations all three components are depleted.



Figure 21: Stack plots of the average SIA concentration per bin over the seven measurement locations for the 2010 simulations on domains 1, 2 an 3 (2010_d123) and on domain 4 (2010_d4). The bins in the MOSAIC aerosol module are defined as follows: bin $1 = 0.039 \ \mu\text{m} - 0.156 \ \mu\text{m}$, bin $2 = 0.156 \ \mu\text{m} - 0.625 \ \mu\text{m}$, bin $3 = 0.625 \ \mu\text{m} - 2.5 \ \mu\text{m}$, bin $4 = 2.5 \ \mu\text{m} - 10 \ \mu\text{m}$. Note that the vertical scale of the two figures is not identical.

In Figure 21 the distribution of the SIA particles over the four bins (Table 3) is shown for both simulations. For simulation 2010_d123 almost all of the particles are in bin 2 $(0.156 \,\mu\text{m} - 0.625 \,\mu\text{m})$, with only some particles in bins 1 and 3 and almost none in bin 4. In simulation 2010_d4 a much larger part of the particles is in bin 3 $(0.625 \,\mu\text{m} - 2.5 \,\mu\text{m})$. A possible reason for this is that when setting the external boundary conditions, SIA mass is distributed equally over bins 2 and 3, with little mass going to bins 1 and 4. In simulation 2010_d4 the boundaries are close to the Dutch border and the distribution of SIA mass over the bins at the boundaries can therefore significantly influence the size distribution of SIA over the Netherlands. In simulation 2010_d123 external boundary conditions are only applied to the largest domain, covering all of Europe, meaning that the size of SIA particles over the Netherlands is not as strongly determined by the boundary conditions but more by the modelled chemistry. Ten Brink et al. (2007) measured SIA particle size in Cabauw in the center of the Netherlands. They found that about 70 % of the particles are smaller than $0.56\,\mu m$. The simulation results found here have either too small (simulation 2010_d123) or too large (simulation 2010_d4) particles compared to those measurements.

4.5 No Dutch emissions

This section looks at the results of simulations Zero_NL_d123 and Zero_NL_d4, where only Dutch emissions have been removed. Results are compared to the simulations with Dutch emissions included. This is done to see how the model reacts to changes in Dutch emissions. This information is useful for the evaluation of the model because it can provide insight into the origin of SIA in the model, which can be compared to the origin of SIA over the Netherlands found by other studies.

As WRF-Chem simulates meteorology and chemistry simultaneously, changing emissions can also affect the meteorology. In this case however, there is little change in meteorology due to the removal of Dutch emissions (Tables 17 and 18 in the appendix). For simulation Zero_NL_d4 the meteorology is exactly the same as in the 2010_d4 simulation, correlations between the meteorological variables from both simulations are equal to 1. For Zero_NL_d123 there are some slight differences compared to simulation

 $2010_d123,$ but correlations between meteorological variables from the two simulations are still around 0.9.



Figure 22: Average SIA concentrations over the Netherlands for simulations with (2010_d123, 2010_d4) and without (Zero_NL_d123, Zero_NL_d4) Dutch emissions.

SIA concentrations in the simulation on three domains without Dutch emissions (Zero_NL_d123) decrease by 18 % compared to the simulation with Dutch emissions (2010_d123) (Table 9). The concentrations closely follow those from simulation 2010_d123, except during the peak around 7 February where SIA concentrations are much more reduced than during the rest of the period. This indicates that Dutch emissions were crucial for the formation of SIA during that peak. Concentrations of all SIA precursor gases decrease, although only slightly for SO₂ (-10 %). NO, NO₂ and NH₃ concentrations decrease much more strongly (-62 %, -46 % and -75 % respectively).

SIA concentrations in the simulation on only domain 4 without Dutch emissions (Zero_NL_d4) decrease by 7 % compared to the simulation with Dutch emissions (2010_d4) (Table 10). Other than this the concentrations during the period progress identical to those from the simulation 2010_d4, correlations between SIA compounds from both simulations are equal to 1. Correlations between SIA precursor gases from both simulations are lower, especially for SO₂ (0.54). NO, NO₂ and NH₃ precursor concentrations are much more reduced than the SIA concentrations. SO₂ concentrations on the other hand have more than doubled, despite the removal of Dutch emissions.

Table 9: Statistics of daily mean chemical variables over the Netherlands on domain 3 from the simulation on three domains without Dutch emissions (Zero_NL_d123). The simulation on three domains with Dutch emissions (2010_d123) serves as a reference for the results.

Variable	Mean ref	Mean new	r	MBE	NMBE	NMGE
	$(\mu g/m^3)$	$(\mu g/m^3)$		$(\mu g/m^3)$	(%)	(%)
SIA	11.4	9.4	0.80	-2.0	-17.5	31.0
NO ₃	6.3	5.6	0.89	-0.6	-10.2	29.3
SO ₄	2.4	1.6	0.46	-0.8	-32.6	54.6
NH ₄	2.8	2.2	0.77	-0.6	-20.9	31.9
NO	4.7	1.8	0.39	-2.9	-62.4	69.5
NO ₂	30.6	16.5	0.49	-14.2	-46.3	47.7
SO_2	5.8	5.3	0.58	-0.6	-9.8	57.7
NH ₃	5.8	1.5	0.66	-4.4	-74.8	74.8

Table 10: Statistics of daily mean chemical variables over the Netherlands from the simulation on only domain 4 without Dutch emissions (Zero_NL_d4). The simulation on only domain 4 with Dutch emissions (2010_d4) serves as a reference for the results.

Variable	Mean ref	Mean new	r	MBE	NMBE	NMGE
	$(\mu g/m^3)$	$(\mu g/m^3)$		$(\mu g/m^3)$	(%)	(%)
SIA	32.7	30.6	1.0	-2.1	-6.5	6.5
NO ₃	19.9	18.8	1.0	-1.1	-5.6	5.7
SO_4	5.1	4.7	0.99	-0.4	-7.6	7.6
NH ₄	7.7	7.1	1.0	-0.6	-7.8	7.8
NO	5.8	2.4	0.93	-3.4	-58.7	58.7
NO_2 (33.2	22.2	0.97	-10.9	-32.9	32.9
SO_2	4.8	10.9	0.54	6.1	129.1	147.1
NH ₃	4.8	0.8	0.81	-4.0	-84.1	84.1

4.6 Model quality conclusions

Based on the results presented above, some qualitative conclusions are drawn about the model and a decision is made on which model setup to use for further simulations. The simulated period is not long enough for a more quantitative model evaluation to be of value. The period contains three high peaks in SIA concentrations and the correct or incorrect simulation of these peaks will largely dominate the calculated statistics. The qualitative conclusions drawn here are therefore only partly based on the statistics comparing the simulation results to the measurements. Also taken into account are the similarity of the results to those from other SIA modelling studies, the consistency of SIA and precursor concentrations with what can be expected based on chemical theory and the explicability of the simulation results.

Meteorology is well simulated in both the simulation on domains 1, 2 and 3 (2010_d123) as the simulation on only domain 4 (2010_d4), but in the latter is closer to the reanalysis data. The meteorological variable most important for the occurrence of high peaks in SIA concentrations in the Netherlands is thought to be the wind direction and speed. In simulation 2010_d123 there is one period around 24 January where zonal winds are overestimated, other than that the simulated wind vectors are very similar to the wind

vectors in the reanalysis data. Except for the period around 24 January the simulated meteorology is accurate enough that it is not expected to significantly influence modelled SIA concentrations. It will however remain important to carefully look at the simulated meteorology when analyzing SIA concentrations during a specific time period, as done in Chapter 5.

The SIA concentrations in the simulation with domains 1, 2 and 3 (2010_d123) and the simulation with only domain 4 (2010_d4) are very different. Simulation 2010_d123 underestimates SIA concentrations by 41 % averaged over the period, while 2010_d4 overestimates them by 64 % (Tables 7 and 8). Other modelling studies found an underestimation of SIA concentrations over the Netherlands, so the results from simulation 2010_d123 are more in line with what is expected (van der Swaluw et al., 2018; Netherlands Organisation for Applied Scientific Research, 2012). The composition of SIA in both simulations in similar, but particles in simulation 2010_d123 are smaller than in the measurements while particles in simulation 2010_d4 are larger than in the measurements (Figure 21). Yang et al. (2018) found that the formation of coarse SIA particles is poorly represented in most WRF-Chem aerosol schemes, this could explain the underestimation of particle size in simulation 2010_d123. The overestimation of particle size in simulation 2010_d4 is likely due to the distribution of SIA particles over the bin sizes when setting the boundary conditions. This has a large effect on particle size in simulation 2010_d4 because boundary conditions are applied directly to the relatively small domain 4. In simulation 2010_d123 boundaries are only set from the MOZART output for the large domain 1, meaning that particle size in the Netherlands is determined by the WRF-Chem chemistry and not by the distribution of SIA over the bins at the boundaries.

Correlations for SIA compounds in simulation 2010_d4 compared to measurements are better than for simulation 2010_d123, but due to the large overestimation of the height and duration of SIA peaks the confidence in the results from simulation 2010_d4 is low. The results from simulation 2010_d123 may have lower correlation coefficients for SIA compounds, but a large part of that is due to missing the SIA peak around 25 January, likely because of the overestimation of zonal wind speeds around that time (Chapter 5). Other peaks in measured SIA concentrations are also found in the model results and the underestimation of SIA concentration is somewhat expected based on the results from other modelling studies (van der Swaluw et al., 2018; Netherlands Organisation for Applied Scientific Research, 2012). The results from simulation 2010_d123 are very similar to those from EMEP4NL, although the peak SIA concentrations around 15 January and in particular 7 February are better captured by the WRF-Chem model simulation. Furthermore the concentrations of precursor gases in simulation 2010_d123 are in line with what can be expected based on the SIA concentrations. SO_2 and NH_3 are overestimated by the model, indicating that too little ammonium sulfate is formed, as also evidenced by the underestimation of sulfate aerosol. Precursor gas concentrations from simulation 2010_d4 on the other hand are overestimated just like the SIA concentrations, indicating that sources of pollution are far too large in this simulation. As emissions over the Netherlands are equal for the two simulations, the only source for this excess of SIA compounds and precursors can be at the boundaries of the domain. These are close to the Dutch border in simulation 2010_d4 and the chemical boundary conditions are based on relatively low resolution data from the MOZART-4 model.

The simulations without Dutch emissions confirm this interpretation as SIA concentrations in simulation Zero_NL_d4 are only marginally lower compared to those in simulation 2010_d4. Input from the boundaries is thus unrealistically large in the setup using only domain 4. This is even more pronounced in this scenario as boundary conditions remain the same without Dutch emissions, even though in reality concentrations in areas around the Netherlands would also change as a result of the omission of Dutch emissions. SIA concentrations in simulation Zero_NL_d123 do decrease more significantly compared to simulation 2010_d123. This is in line with what can be expected based on the knowledge that about one-third of Dutch SIA comes from Dutch sources.

Overall, confidence in the results from the simulations using 3 nested domains is higher than in the results from the simulations using only domain 4. This is mainly because the results from simulations 2010_d123 and Zero_NL_d123 are more in line with results expected based on literature and because in simulations 2010_d4 and Zero_NL_d4 the influence of the boundary conditions is too large for the simulations to give any sensible information on the modelled chemistry. Quantitatively, the modelled SIA concentrations in simulation 2010_d123 are in reasonable agreement with the measured concentrations during the study period between 10 January 2010 and 10 February 2010. The modelled concentrations are also in agreement with EMEP4NL model results for this period. Therefore, the rest of the simulations performed for this study are done using the setup with three nested domains. An additional advantage of this is that not only Dutch emissions can be altered, but other European emissions as well. This provides more possibilities for the application of emission scenarios.

The spatial distribution of SIA over the Netherlands has not been discussed much in this chapter, but now that the choice has been made to focus on the setup using three domains it seems appropriate to at least show how the SIA compounds are distributed over the Netherlands in the 2010 simulation using this setup. Therefore, maps of the SIA concentrations averaged over the study period in simulation 2010_d123 can be found in Figure 23. Maps of the SIA precursor concentrations can be found in Figure 36 in the appendix.



Figure 23: SIA concentrations from the 2010 simulation on domains 1, 2 and 3 (2010_d123). Concentrations are averaged over the study period.

5 SIA concentration peaks

Over the study period, three peaks in SIA concentrations occur (Figure 18 in Chapter 4). In the measurements there is one lower peak around 15 January where SIA concentrations reach close to $30 \ \mu\text{g/m}^3$ and two higher peaks around 25 January and 7 February where average SIA concentrations over the Netherlands reach about $50 \ \mu\text{g/m}^3$. For convenience these peaks will be called Peak 1, 2 and 3 respectively. Peak 1 is fairly well simulated in WRF-Chem simulation 2010_d123 and by the EMEP4NL model, Peak 2 is underestimated in both the WRF-Chem and EMEP4NL models and Peak 3 is only modelled accurately at some of the stations in simulation 2010_d123 (Figure 35 in the appendix). In this chapter the three peaks are discussed in more detail, with the aim of gaining insight into the cause of peaks in Dutch SIA concentrations and the reason why some peaks are modelled correctly and some are not.

For each of the three peaks, a figure is made of the backward trajectories of the air reaching the seven measurement station at the moment of the peak. These trajectories are plotted on a background map of the NH₃ concentrations, which are relatively high in the Netherlands and therefore very relevant to the formation of SIA (see Chapter 2 for more information on the role of NH_3 availability in the formation of SIA). The trajectories are calculated using the HYSPLIT model from the National Oceanic and Atmospheric Administration (NOAA, 2020). HYSPLIT can be configured to read meteorological variables from WRF output files and calculate trajectories to or from locations based on those variables. Output from HYSPLIT consists of times and coordinates, capturing to path of an air parcel towards a given location. This information can then be coupled with chemical variables in the WRF output to gain more information about the origin of the peaks in SIA concentrations. This is done for WRF output from domain 2 from the simulation on domains 1, 2 and 3 using the 2010 emissions (2010_d123), as that domain is large enough be able to make interesting trajectories and has a reasonably high resolution. The resolution of domain 1 $(0.5 \times 0.5 \text{ degree})$ is so low that making trajectories on the domain could lead to large errors. Therefore the length of all the trajectories in this study is limited by the boundaries of domain 2. Tables containing the concentrations of SIA compounds and precursors at the start and end of the trajectories are included in the appendix (Tables 19, 20 and 21).

5.1 Peak 1 (15 January 2010)

In Figure 24 the trajectories for Peak 1 are plotted. All of the trajectories show that the polluted air ending up at the seven measurement stations came from the East. SIA concentrations of the air entering the domain are already high and do not increase much along the trajectories. Concentrations in the south of the Netherlands are higher than in the north. This is pattern is not seen in the measurements, but other than that SIA concentrations are well simulated. The measured SIA concentration, averaged over the stations, is $27 \text{ }\mu\text{g/m}^3$, the simulated is $24 \text{ }\mu\text{g/m}^3$.



Figure 24: Backward trajectories from the seven measurement stations from 15-01-2010 00:00. Each dot represents one hour, the colour of the dot shows the SIA concentration at that time and location. The background NH_3 concentrations are averages over the 24 hours previous to the start time of the backward trajectories. The figure is created using the output data from domain 2 of the 2010 simulation on domains 1, 2 and 3 (2010_d123)

5.2 Peak 2 (25 January 2010)

For Peak 2, the trajectories again show that the polluted air is coming from the East (Figure 25). Like during Peak 1, SIA concentrations during Peak 2 do not increase along the trajectories. Simulated concentrations ($15 \ \mu g/m^3$ averaged over the stations) are much lower than the measured average over the stations of 50 $\ \mu g/m^3$. A possible explanation for this might be the overestimation of wind speeds in the simulation during this period, as seen in Figure 17 in Chapter 4.

This is further investigated in Figure 26, where the trajectories based on the wind vectors from simulation 2010_d123 are compared to trajectories based on the wind vectors in the NCEP-FNL reanalysis data. This shows that the general wind direction in the 2010_d123 simulation during this period was accurate, but the simulated wind speeds are much too large. The distance between yellow dots, representing the distance traveled by the air in one hour in the simulation, is two to four times larger than the distance between green dots representing the distance traveled by the air in one hour based on the NCEP-FNL reanalysis data. This overestimation of wind speeds means that pollution does not get time to build up in the air over western Germany and the Netherlands, as the air is rapidly blown away towards the North Sea. In reality wind speeds were lower, giving SIA concentrations time to increase over areas with large emissions of precursor gases like western Germany and the Netherlands.



Figure 25: Backward trajectories from the seven measurement stations from 25-01-2010 00:00. Each dot represents one hour, the colour of the dot shows the SIA concentration at that time and location. The background NH_3 concentrations are averages over the 24 hours previous to the start time of the backward trajectories. The figure is created using the output data from domain 2 of the 2010 simulation on domains 1, 2 and 3 (2010_d123)



Figure 26: Comparison of the trajectories from the seven measurements stations from 25-01-2010 00:00 using the wind vectors from domain 2 of the 2010 simulation on domains 1, 2 and 3 (2010_d123, yellow dots) or the wind vectors from the NCEP-FNL reanalysis data (green dots).

5.3 Peak 3 (7 February 2010)

As for the other two peaks, winds during Peak 3 come from the East (Figure 27). Unlike during Peak 2, the very high SIA concentrations measured during Peak 3 (around 50 $\mu g/m^3$) are also found in the results from simulation 2010_d123 (41 $\mu g/m^3$ averaged over the stations). The only station for which simulated SIA concentration are much lower than measured concentrations is Vredepeel in the southeast of the Netherlands. SIA concentration increase along the trajectories as soon as the air reaches areas with high NH₃ concentrations. The trajectory leading to Vredepeel misses the high NH₃ concentrations, explaining why SIA concentrations in the model are underestimated. The largest contribution to the high SIA concentrations during Peak 3 comes from sulfate. This is interesting as usually nitrate is the most found SIA compound in the Netherlands in the WRF-Chem simulations (Figure 20). Sulfate concentrations along the trajectories increase by 12.7 μ g/m³ (Table 21 in the appendix) while SO₂ concentrations strongly decrease by 13.7 μ g/m³ (-85 %). This decrease in SO₂ concentrations along the trajectories is also shown in Figure 28. The station where the highest SIA concentrations are found in the simulation is Valthermond (929). In Figure 28 we see that the SO_2 concentration of the air going to this station is also largest, as the SO_2 concentration along the trajectory has a pronounced peak while the air is already in the domain. The air probably picks up additional SO_2 as it moves over an area with industrial activity in Germany.



Figure 27: Backward trajectories from the seven measurement stations from 07-02-2010 00:00. Each dot represents one hour, the colour of the dot shows the SIA concentration at that time and location. The background NH_3 concentrations are averages over the 24 hours previous to the start time of the backward trajectories. The figure is created using the output data from domain 2 of the 2010 simulation on domains 1, 2 and 3 (2010_d123)

As seen in Figure 27, wind speeds decrease along the trajectories (dots are getting closer together) and are much lower over the Netherlands compared to during Peak 2. Using all of this information the peak in SIA concentrations on 7 February can be explained as follows: Air containing a large amount of SO_2 enters the domain from the East and travels towards the Netherlands. Over western Germany and the Netherlands

the air encounters high NH_3 concentrations and because the wind speeds are low there is sufficient time for the formation of large amounts of ammonium sulfate (and, to a lesser extent, ammonium nitrate). The air then reaches the stations and the high SIA concentrations are measured.



Figure 28: SO₂ concentrations along the backward trajectories displayed in Figure 27. Each line represents the concentration along the trajectory to the corresponding measurement station in the legend. 00:00 (at the right of the figure) is the time at which the air parcels reach the stations. The figure is created using the output data from domain 2 of the 2010 simulation on domains 1, 2 and 3 (2010_d123).

5.4 Conclusions on peaks in SIA concentrations

Based on the three peaks in SIA concentrations during the study period it can be concluded that SIA peaks in the Netherlands generally occur when winds are from the East. Apparently this wind direction means that the air reaching the Netherlands passes over regions with large emissions of precursor gases. Those regions include parts of eastern Europe outside of domain 2 that are not looked at here, but also western Germany where emissions from industry and agriculture are large. Important for the development of high SIA concentrations also seems to be whether the wind speed is low over the Netherlands. Lower wind speeds mean that pollution will build up in the air over a longer period, reaching higher concentrations. This is correctly simulated for Peak 3, and the overestimation of wind speeds in the model during Peak 2 is likely the reason for the underestimation of SIA concentrations. It is relevant to note that the source of SIA can differ per peak. For Peak 1 most of the SIA is already in the air when it enters domain 2, while for Peak 3 a significant part of the SIA is formed over western Germany and the Netherlands. This SIA is formed due to the combination of high SO₂ concentrations in the air entering the domain and high local NH₃ concentrations.

6 Emission scenarios

Several emission scenario simulations are performed to test the effectiveness of lowering SIA precursor gas emissions towards reducing air pollution. As described in Section 3.6, three simulations are performed in which the Dutch emissions of NO_x , SO_2 and NH_3 respectively are reduced by fifty percent (Half_ NO_x -NL, Half_ SO_2 -NL and Half_ NH_3 -NL). Additionally, a simulation is performed in which the emission reduction goals for 2030 from the 2016 NEC Directive are applied to the Netherlands and the rest of Europe (2030_EU). The 2010_d123 simulation, which uses the unaltered 2010 emissions, serves as a reference that the scenario simulations can be compared to. The results of the four scenario simulations are presented here.

In Figure 29 the SIA concentrations from the three simulations with halved emissions are plotted alongside the concentrations from simulation 2010_d123. The SIA concentrations decrease in all three scenario simulations compared to the reference simulation. The effectiveness of emission reductions varies over the study period. Halving NO_x emissions is more effective compared to halving SO_2 or NH_3 emissions for the SIA concentration peak around 25 January, but is the least effective for reducing SIA concentrations during the peak around 7 February. Halving SO_2 emissions is very effective during the peak around 7 February, but is not useful at all during the peak around 25 January. Halving NH_3 emissions has a somewhat more constant effect over the period, reducing concentrations during all three major peaks in SIA concentrations. The results are further discussed per simulation in the following sections.



Figure 29: Average SIA concentrations over the Netherlands from the simulations with halved Dutch NO_x (Half_ NO_x _NL), SO_2 (Half_ SO_2 _NL) and NH_3 (Half_ NH_3 _NL) emissions, compared to the simulation with the unaltered 2010 emissions on domains 1, 2, and 3 (2010_d123).

6.1 Halving Dutch NO_x emissions

Halving the Dutch NO_x emissions would take large efforts from mainly the transport sections, as the 'road transport' and 'other transport' sections in Figure 6 in Chapter 2 together are responsible for over 70 % of the NO_x emissions. The most direct method to reduce emissions would be to switch from the use of fossil fuels to power cars and

other transport methods to other forms of energy that do not emit NO_x , for example electricity from solar or wind power. Switching from coal-fired power plants to gas-fired power plants for the production of electricity also makes a large difference, as gas unlike coal contains little nitrogen. Additionally, the treatment of exhaust and chimney emissions can be optimized so that as little NO_x is emitted as possible.

In theory, halving the NO_x emissions should mainly lead to reduced formation of ammonium nitrate aerosol (Section 2.1). This is also what we see from the results of simulation Half_NO_x_NL in Table 11. SIA concentrations are reduced by 2.6 μ g/m³ largely due to reduced NO₃ (-1.8 μ g/m³) and NH₄ (-0.6 μ g/m³) concentrations. The SO₄ concentration does not change much (-0.2 μ g/m³). NO_x concentrations drop by over 20 %, as do SO₂ concentrations. NH₃ concentrations are not as much affected.

Table 11: Statistics for daily mean concentrations of SIA compounds and SIA precursors from the simulation with halved Dutch NO_x emissions (Half_ NO_x _NL, new) compared to the simulation with the unaltered 2010 emissions (2010_d123, ref). Statistics are averaged over Dutch grid cells on domain 3.

Variable	Mean ref	Mean new	r	MBE	NMBE	NMGE
	$(\mu g/m^3)$	$(\mu g/m^3)$		$(\mu g/m^3)$	(%)	(%)
SIA	11.4	8.8	0.64	-2.6	-23.1	46.3
NO ₃	6.3	4.5	0.40	-1.8	-28.8	55.7
SO_4	2.4	2.1	0.70	-0.2	-9.7	52.3
NH ₄	2.8	2.2	0.68	-0.6	-21.8	43.7
NO	4.7	3.6	0.44	-1.1	-24.1	61.9
NO ₂	30.6	24.1	0.51	-6.6	-21.4	32.5
SO_2	5.8	4.4	0.47	-1.5	-24.9	46.9
NH ₃	5.8	6.0	0.38	0.1	1.7	27.8

6.2 Halving Dutch SO₂ emissions

Reducing the SO₂ emissions would mainly depend on efforts from the Combustion in energy and transformation industries SNAP sector. Over 70 % of SO₂ emissions come from industry (Figure 4 in Chapter 2). As SO₂ is emitted mainly due to the use of fossil fuels, a transition to the use of cleaner energy sources is needed if we would want to drastically lower our emissions.

Theoretically, it can be expected that a reduction in SO₂ emissions would lead to less formation of ammonium sulfate and possibly more formation of ammonium nitrate. Less ammonia would be used for the formation of sulfate aerosol so that depending on the NO_x availability more ammonium nitrate could form (Section 2.1). In the results from simulation Half_SO₂_NL (Table 12) we see reductions in all three main SIA compounds, adding to a total SIA reduction of $2.1 \ \mu g/m^3$. Contributions from the three aerosol compounds to this reduction are similar, with a slightly lower reduction in NH_4 than in NO_3 and SO_4 concentrations. Note however that the reduction in SO_4 is clearly largest relative to the reference concentrations (-35 % for SO₄, compared to -12 % and -19 % for NO_3 and NH_4). Concentrations of aerosol precursor gases are not much affected, with a 13 % increase in NH₃ concentrations as the most notable change. An explanation for why the SO_2 concentrations do not change much, despite halving the SO_2 emissions, is that even with the high SO_2 emissions most SO_2 could efficiently be converted to SO_4 because of the high NH₃ concentrations in the Netherlands. Now that the SO_2 emissions are halved, less SO_4 is formed but the decrease in SO_2 emissions is not large enough to also affect the SO_2 concentration itself.

Table 12: Statistics for daily mean concentrations of SIA compounds and SIA precursors from the simulation with halved Dutch SO₂ emissions (Half_SO₂_NL, new) compared to the simulation with the unaltered 2010 emissions (2010_d123, ref). Statistics are averaged over Dutch grid cells on domain 3.

Variable	Mean ref	Mean new	r	MBE	NMBE	NMGE
	$(\mu g/m^3)$	$(\mu g/m^3)$		$(\mu g/m^3)$	(%)	(%)
SIA	11.4	9.3	0.53	-2.1	-18.4	45.6
NO ₃	6.3	5.5	0.73	-0.8	-12.0	43.9
SO ₄	2.4	1.5	0.14	-0.8	-34.6	68.5
NH ₄	2.8	2.3	0.49	-0.5	-19.3	45.1
NO	4.7	5.0	0.30	0.3	7.1	60.1
NO ₂	30.6	30.7	0.65	0.0	0.1	19.5
SO_2	5.8	5.6	0.51	-0.3	-4.6	58.8
NH ₃	5.8	6.6	0.52	0.7	12.6	27.5

6.3 Halving Dutch NH₃ emissions

Halving the NH₃ emissions would take large efforts from the agriculture sector, as that sector is responsible for almost 90 % of the emissions (Figure 7 in Chapter 2). Reductions could for example come in the form of decreased manure spreading or the use of cleaner fertilizing techniques.

In theory, reduced NH₃ emissions could lead to reductions in both ammonium nitrate and ammonium sulfate concentrations, but much depends on the state of the system. NH₃ emission reductions will be much more effective if the atmosphere is ammonia poor and ammonia availability is crucial for the formation of aerosol (Chapter 2). If the atmosphere is very rich in ammonia, reduced NH_3 emissions might not affect aerosol formation as much because there could potentially still be enough ammonia to neutralize all nitric and sulfuric acid. From the results of simulation Half_NH₃_NL in Table 13 we see that the modelled atmosphere is probably somewhere in between these extremes, as the SIA concentration does decrease but does so less strongly than for halved NO_x or SO_2 emissions. The decrease largely comes from a decrease in NO_3 concentrations, with a small contribution from decreasing NH_4 concentrations. SO_4 concentrations do not significantly change. This fits well with idea that the atmosphere in the Netherlands is ammonia rich, as in an ammonia rich regime a decrease in ammonia will first affect ammonium nitrate formation and will only affect ammonium sulfate formation when ammonia concentrations become so low that not all sulfate can be neutralized anymore. This result is similar to that found by Renner & Wolke (2010), who modelled a 50 %decrease in ammonia emissions over northern Germany. NO concentrations increase by 36%, while NO₂ concentrations do not change much. SO₂ concentrations drop slightly and NH_3 concentrations decrease by 40 %.

Table 13: Statistics for daily mean concentrations of SIA compounds and SIA precursors from the simulation with halved Dutch NH_3 emissions (Half_ NH_3 _NL, new) compared to the simulation with the unaltered 2010 emissions (2010_d123, ref). Statistics are averaged over Dutch grid cells on domain 3.

Variable	Mean ref	Mean new	r	MBE	NMBE	NMGE
	$(\mu g/m^3)$	$(\mu g/m^3)$		$(\mu g/m^3)$	(%)	(%)
SIA	11.4	9.8	0.82	-1.6	-13.8	30.9
NO ₃	6.3	5.0	0.78	-1.3	-20.8	40.0
SO ₄	2.4	2.4	0.57	0.1	3.7	62.1
NH ₄	2.8	2.4	0.82	-0.4	-12.8	29.3
NO	4.7	6.4	0.11	1.7	35.9	91.1
NO ₂	30.6	30.8	0.54	0.2	0.7	22.7
SO_2	5.8	5.0	0.55	-0.8	-14.0	40.0
NH ₃	5.8	3.5	0.76	-2.4	-40.2	41.7

6.4 Applying the NEC Directive emission reduction goals

In this scenario the emission reductions from the 2016 NEC Directive are applied. Dutch emissions of NO_x , SO_2 and NH_3 are reduced on average by 52 %, 10 % and 9 % respectively. European emissions of NO_x , SO_2 and NH_3 are reduced by 53 %, 62 % and 14 % respectively. The complete reductions for the Netherlands and Europe are displayed in Table 1 in Section 2.3. The goal of the emission reductions from the NEC Directive is to reduce the negative health effects of air pollution by 50 % in 2030 compared to 2005 (European Commission, 2016). The reductions should also make sure that pollutant concentrations get below the WHO guideline values. In the framework of this study it is not possible to fully test the effects of the emission reductions from the 2016 NEC Directive, as this study only looks at SIA compounds, uses 2010 as a reference instead of 2005 and only looks a time period of one month. In spite of these limitations it is still interesting to test the effect of the emission reductions on SIA concentrations in the context of this study.

In Figure 30 the SIA concentrations from simulation 2030_EU are compared to those from simulation 2010_d123. Concentrations are reduced significantly, especially during the peaks around 15 January and 7 February. As can be seen in Table 14, the concentrations of all three SIA compounds, and therefore the total SIA concentration, are decreased by close to 50 %. The largest absolute contribution to the decrease in SIA concentrations comes from a decrease in NO₃. This is in line with the large reduction in NO_x emissions. NO concentrations drastically decrease (-80 %), as do NO₂ (-52 %) and SO₂ (-61 %) concentrations. NH₃ concentrations on the other hand do not significantly change, in line with the small reductions required for NH₃ emissions by the NEC Directive.



Figure 30: SIA concentrations averaged over the grid cells over the Netherlands from the simulation with the emission reductions for 2030 from the 2016 NEC Directive applied (2030_EU), compared to the simulation with the unaltered 2010 emissions on domains 1, 2 and 3 (2010_d123)

The almost 50 % decrease in SIA concentrations is in line with the ambition of the NEC Directive to decrease the negative health effects of air pollution by 50 %. This simulation indicates that a 50 % decreases of aerosol pollution is a reasonable target, if the proposed emission reductions can be achieved. Also keep in mind that the decrease in SIA concentrations found in this study is for 2030 compared to 2010, while the NEC Directive aims for a 50 % reduction in 2030 compared to 2005. As emissions have already decreased between 2005 and 2010, some percentage of SIA reduction is likely to already have happened by 2010.

Testing whether this decrease in SIA concentrations is enough to meet the guideline values of the WHO in 2030 is harder, as these guidelines are only specified for annual mean PM_{10} and $PM_{2.5}$ concentrations. There are no specific guidelines for SIA concentrations. By making a few assumptions we can however give an estimate of how much the decrease in SIA concentration will help towards reaching the WHO guideline values. As almost all of the modelled SIA is part of the finer fraction of particulate matter $(PM_{2.5})$ (Figure 21), we will look at the guideline value for that fraction. This guideline value is an annual average $PM_{2.5}$ concentration of no more than 10 $\mu g/m^3$. In 2010 the measured average $PM_{2.5}$ concentration over the Netherlands was 17.3 $\mu g/m^3$ (Dutch Environmental Data Compendium, 2017). About 60 % of PM_{2.5} mass can be assumed to be SIA (Netherlands Environmental Assessment Agency, 2010). If we apply the model result of a 48.2 % SIA reduction to the SIA fraction of the measured $PM_{2.5}$, the resulting $PM_{2.5}$ concentration is 12.3 $\mu g/m^3$. Thus, other contributions to $PM_{2.5}$ would also have to decrease to meet the WHO guideline value of $10 \,\mu g/m^3$. Note however that a lot of assumption have been made to obtain this result, for example that the SIA reduction found for the modelled period over January and February is representative for the reduction of the annual mean SIA concentration.

Table 14: Statistics for daily mean concentrations of SIA compounds and SIA precursors from the simulation with the emission reductions for 2030 from the 2016 NEC Directive applied (2030_EU, new), compared to the simulation with the unaltered 2010 emissions (2010_d123, ref). Statistics are averaged over Dutch grid cells on domain 3.

Variable	Mean ref	Mean new	r	MBE	NMBE	NMGE
	$(\mu g/m^3)$	$(\mu g/m^3)$		$(\mu g/m^3)$	(%)	(%)
SIA	11.4	5.9	0.85	-5.5	-48.2	48.9
NO ₃	6.3	3.2	0.80	-3.1	-49.4	50.4
SO ₄	2.4	1.3	0.42	-1.1	-45.8	66.9
NH ₄	2.8	1.5	0.84	-1.3	-47.4	48.0
NO	4.7	0.9	0.61	-3.8	-80.4	80.4
NO ₂	30.6	14.7	0.75	-15.9	-52.0	52.0
SO_2	5.8	2.3	0.49	-3.6	-61.2	61.2
NH ₃	5.8	5.8	0.68	-0.1	-1.6	18.1

In Figure 31 maps are shown of the SIA concentrations in simulations 2010_d123 and 2030_EU. Noteworthy is the change in the spatial distribution of SIA concentrations over the Netherlands. Where for simulation 2010_d123 the highest concentrations are found in the south and the northeast of the country, the highest concentrations in simulation 2030_EU occur in the southwest in the area around the cities of Rotterdam and The Hague. It seems that in the 2010 situation the NH₃ emissions are dominant in determining the SIA concentrations, as high SIA concentrations are found over areas with high NH₃ emissions (Figure 12 in Chapter 3). In the 2030 situation however, SIA concentrations are high over areas with high NO_x and SO₂ emissions (Figures 10 and 11 in Chapter 3), indicating a dominant role for these compounds in the formation of SIA. This is likely due to the NO_x and SO₂ emissions being reduced more strongly than the NH₃ emissions, making the availability of NO_x and SO₂ crucial for the formation of SIA. Also important could be that Dutch SO₂ emissions are far less reduced in the NEC Directive than the average European SO₂ emissions (-10 % versus -62 %), making the Dutch SO₂ emissions relatively more important for the formation of SIA.



Figure 31: SIA concentrations over the Netherlands from the simulation with the unaltered 2010 emissions on domains 1, 2, and 3 (2010_d123, a) and the simulation with the emission reductions for 2030 from the 2016 NEC Directive applied (2030_EU, b). Concentrations are averaged over the study period. Note that the color scales are not identical.

6.5 Emission scenario conclusions

In conclusion, the scenario simulations with halved emissions show that reducing only the Dutch emissions does decrease SIA concentrations in the Netherlands. Reducing NO_x emissions seems to be the most effective in reducing peak concentrations, with a 50 % emission reduction leading to 23 % lower SIA concentrations. Halving the SO₂ or NH₃ emissions leads to 18 % or 14 % lower SIA concentrations respectively. Confidence in the quality of these results is increased by the fact that the changes in SIA compound and SIA precursor gas concentrations mostly follow what would be expected based on the known chemistry of aerosol.

In simulation 2030_EU the SIA concentrations over the Netherlands decreased by almost 50 %, even though Dutch emission reductions are only slightly larger than in the scenarios were emissions are halved. Certainly helping is the fact that the NEC directive emission reductions for the Netherlands focus on reducing NO_x emissions, which based on the halved emission scenarios is the most effective for decreasing SIA concentrations. The largest difference however is that in simulation 2030_EU emissions from other European countries are reduced as well. Keeping in mind that about two-third of SIA mass over the Netherlands is of foreign origin this is a very important factor.

Based on the modelled 50 % reduction in SIA concentrations it seems reasonable to conclude that the NEC Directive aim of a reduction of 50 % in negative health effects from air pollution could be attained, as long as the proposed emission reductions are achieved and other contributions to air pollution are also decreased by 50 %. It is also debatable if 50 % lower particulate matter concentrations are equal to 50 % less negative health effects. The goal of meeting the WHO guideline values for particulate matter concentrations also seems very reasonable, as based on the model results the SIA reduction alone lowers $PM_{2.5}$ concentrations to just above the guideline value. Assuming contributions to $PM_{2.5}$ from other compounds to decrease as well, it seems that meeting the WHO guidelines for particulate matter by 2030 could be possible. Again, this is based on the assumption that the proposed emission reductions are achieved.

7 Discussion & Conclusions

In this chapter a short overview is given of the performed research, the major results found in this study are discussed, shortcomings of the methods are pointed out and some ideas for further research are suggested.

In order to gain more insight into the chemistry and dynamics of SIA over the Netherlands, the WRF-Chem model has been used to simulate aerosol chemistry. Two domain configurations for WRF-Chem were tested: one with three nested domains with the outer domain spanning over Europe and the inner domain focused on the Netherlands and one with a single high resolution domain over the Netherlands. For both of these configurations, simulations were performed using the 2010 emissions of SIA precursor gases and using the 2010 emissions minus the Dutch emissions. Using the configuration with three domains, four more simulations were performed with altered emissions. Three simulations in which the NO_x, SO₂ and NH₃ emissions from the Netherlands were halved and one simulation where emissions were reduced following the emission reduction goals for 2030 from the 2016 NEC Directive. The results from all these simulations were used to answer the research questions formulated in the introduction. What follows is a discussion of the results found relating to each of the four research questions:

Is WRF-Chem able to reproduce measured SIA concentrations in the Netherlands?

In this study, two domain configurations have been tested for the WRF-Chem setup. The configuration using three domains performed better than the one using only one small, high resolution domain. The WRF-Chem setup with three domains was able to satisfactory reproduce SIA concentrations in the Netherlands, although with a strong negative bias. This negative bias in modelled SIA concentrations is also found by other studies modelling SIA over the Netherlands (van der Swaluw et al., 2018; Netherlands Organisation for Applied Scientific Research, 2012). Possible explanations for the underestimation of SIA concentrations in the model include an overestimation of wet deposition in WRF-Chem, as found by Karlicky et al. (2017), missing sources of precursor emissions or flaws in the used chemistry schemes. Variations in modelled SIA concentrations are very similar to those in the measurements. Two of the three major SIA peaks are well simulated, while the other peak is missing likely due to an overestimation of wind speeds in the model during that period.

What caused the high SIA peaks in January/February 2010 in the Netherlands?

Winds from the East seem to be the crucial factor initiating SIA peaks in the Netherlands, as they were found for all three cases of high SIA concentrations that occurred during the study period. These winds bring polluted air containing SIA and SO₂ from eastern Europe towards the Netherlands. Over the Netherlands and western Germany the SO₂ combines with NH₃ to form ammonium sulfate. If wind speeds are low the pollution builds up in the air over the Netherlands, but if wind speeds are higher the air is blown out over the North Sea and SIA concentrations do not increase as strongly. The importance of air stagnation for the formation of ammonium sulfate was also found by Long et al. (2014). Renner & Wolke (2010) found a similar result in their study for northern Germany, where ammonium sulfate concentrations also peaked during periods of weaker winds from the East. Note that three peaks is a rather small sample size and not all peaks have to be similar to these. It is interesting to see that WRF does model two of the peaks better than EMEP4NL and that the other is likely only missed by the model because of the incorrect wind speeds.

Emission reductions of which precursor gas are the most effective towards lowering SIA concentrations in the Netherlands?

Reducing Dutch emissions of NO_x by 50 % reduced modelled SIA peak concentrations the most, but decreasing SO_2 or NH_3 emissions was also effective. No hard conclusions about the effectiveness of emission reductions can be drawn from this, as the results may very well depend on the modelled period. The simulations show that for different SIA peaks, different emission reduction are most effective. The modelled period of one month, containing three SIA peaks, is likely not to be representative for the results over a longer time period. Note also that the result is specific for the Netherlands, results in other areas will likely differ because of the different origin of SIA concentrations. Despite the uncertainty in the relevance of these results over a longer time period, it is still interesting to see that reducing only Dutch emissions of one precursor gas can significantly alter SIA peak concentrations.

How will the planned emission reductions for 2030, as laid down in the 2016 NEC Directive, affect Dutch SIA concentrations?

Compared to the simulations with halved Dutch emissions of SIA precursor gases, the application of the European emission reductions planned for 2030 are much more effective towards decreasing SIA concentrations. Compared to 2010, modelled 2030 SIA concentrations in the Netherlands are almost 50 % lower averaged over the study period. The goal of decreasing the negative health effects of particulate matter pollution by 50 % therefore seems reasonable. That is of course assuming that a similar reduction can be achieved for organic and primary aerosol concentrations and assuming the proposed emission reductions are achieved.

WRF-Chem has proven to be a useful tool for modelling SIA pollution, as it is very versatile. The drawback of the wide range of settings that can be adjusted is that it is often hard to determine what the best configuration is. Some of the dynamics and chemistry settings are very complex and there are so many options that it can be difficult to find the most suitable combination for a particular simulation. One of the main shortcomings of the model setup used in this study is that the meteorology is not fixed. This opens up the possibility of feedback from the chemistry to the meteorology, but also leads to SIA concentrations that are different from those measured just because the meteorology is different. Peak 2 in this study is thought to be missed by the model because of an overestimation of wind speeds. The possible influence of errors in the simulated meteorology makes it harder to evaluate the model chemistry. Other shortcomings of this study are the short time period that had to be used due to how time expensive running WRF-Chem with aerosol chemistry is and the lack of hourly SIA measurements to compare the model results to. The fact that this study only looks at a one month period means that results are not likely to always be representative for what happens during the rest of the year.

Based on these shortcomings as well as on the results found in this study, a few ideas for further research are suggested. The first is to perform simulations with fixed meteorology and compare the results to the measurements and the results from the simulations performed here. Other ideas for running WRF-Chem with a setup similar to this study are to add deposition variables to the output, add chemistry schemes and emissions to also simulate primary and organic aerosol and to simulate a full year using a lower resolution. Adding deposition variables to the WRF-Chem output and comparing those to deposition measurements was originally also intended in this study, but this was not accomplished due to difficulties with recompiling the model after adding

variables to the registry. Aside from this it would be good to take a close look at the WRF-Chem aerosol schemes, to see where they differ from for example the EMEP4NL model. This is particularly interesting as the results found in this study suggest that some SIA peaks are better captured by WRF-Chem than by EMEP4NL. More in general, further research on the reason for the underestimation of SIA concentrations in the Netherlands by models would be valuable.

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Appendix

Model setup

CEIP]	CBM-Z
CH3OH	l•	E_CH3OH
(Methanol)	-	(Methanol)
C2H5OH]	E_C2H5OH
(Ethanol)	-	(Ethanol)
C2H6]	E_ETH
(Ethane)	-	(Ethane)
NC4H10	1	E_HC3
(n-Butane)	-	
		E_HC5
		E_HC8
C2H4	1	E_OL2
(Ethene)		(Ethene)
C3H6	l	E_OLT
(Propene)		(Terminal Alkenes)
	1	E_OLI
		(Internal Alkenes)
C5H8	1	E_ISO
(Isoprene)		(Isoprene)
		E_TOL
		(Toluene/less reactive
		aromatics)
OXYL		E_XYL
(o-Xylene)		(Xylene/reactive aromatics)
CH3CHO		E_ALD
(Acetaldehyde)		(Acetaldehyde/other higher
GLYOX	_	aldehydes)
(Glyoxal)	r	
MGLYOX		
(Methylglyoxal)		
HCHO	`	E_HCHO
(Formaldehyde)		(Formaldehyde)
MEK		E_KET
(Methyl Ethyl Ketone)	ĺ	(Ketones)
		E_ORA2
		(Acetic acid and other higher
		acids)

Figure 32: Mapping of NMVOC species from CEIP emission data to the CBM-Z module. The CBM-Z species marked in red do not receive any emissions.

Model evaluation

Table 15: Overview of the measured compounds per station used in this study. $*NH_3$ is measured at station 131, but it is not used in this study as this station is close to a farm, leading to measured NH₃ concentrations that are not representative for a larger area.

Station	NO	NO ₂	NH ₃	SO_2	NO ₃	NH ₄	SO_4
131	Х	Х	X*	Х	Х	Х	Х
235	Х	Х	Х	Х	Х	Х	Х
444	Х	Х	Х	Х	Х	Х	Х
538	Х	Х	Х		Х	Х	Х
627				Х	Х	Х	Х
929	Х	Х	Х	Х	Х	Х	X
934	Х	Х		Х	Х	Х	X



Figure 33: Daily mean sea-level pressure (a), 2-m temperature (b), 2-m relative humidity (c) and 10-m wind speed (d) between 10-01-2010 and 10-02-2010 for the modelled meteorology in the simulations on domains 1, 2 and 3 (2010_d123) and on domain 4 (2010_d4). Variables from the NCEP-FNL reanalysis data are included as a reference. The variables are averaged over the grid cell located over the Netherlands.



Figure 34: Wind roses of the daily mean wind averaged over the grid cells located over the Netherlands between 10-01-2010 and 10-02-2010 from the simulations on domains 1, 2 and 3 (2010_d123, b) and on domain 4 (2010_d4, c). The NCEP-FNL reanalysis data (a) serves as a reference.

Variable	Mean ref	Mean mod	\mathbf{r}	MBE	NMBE $(\%)$	NMGE $(\%)$
Temperature (°C)	275.2	275.0	0.76	-0.2	-0.1	0.7
Sea-level pressure (hPa)	1016.8	1013.4	0.94	-3.4	-0.3	0.4
Relative humidity (%)	81.1	86.3	0.64	5.2	7.1	10.0
Wind speed (m/s)	6.1	6.8	0.63	0.7	23.6	43.2
Zonal wind speed (m/s)	0.2	0.3	0.78	0.1	4.2	69.9
Meridional wind speed (m/s)	1.2	1.3	0.79	0.1	5.2	68.6

Table 16: Statistics of daily mean meteorological variables over domain 1 from the 2010 simulation on domains 1, 2 and 3 (2010_d123). The NCEP-FNL reanalysis data serves as a reference for the modelled variables.



SIA per measurement station

Figure 35: SIA concentrations per station for the 2010 simulations on domains 1, 2 and 3 (2010_d123) and on domain 4 (2010_d4) compared to measurements and EMEP4NL.

Table 17: Statistics of daily mean meteorological variables over the Netherlands on domain 3 from the simulation on three domains without Dutch emissions (Zero_NL_d123). The simulation on three domains with Dutch emissions (2010_d123) serves as a reference for the results.

Variable	Mean ref	Mean new	r	MBE	NMBE (%)	NMGE (%)
Temperature (°C)	270.2	271.1	0.89	0.9	0.3	0.6
Sea-level pressure (hPa)	1012.5	1011.4	0.98	-1.1	-0.1	0.2
Relative humidity (%)	90.7	91.8	0.94	1.1	1.2	2.6
Wind speed (m/s)	4.1	3.9	0.88	-0.2	-4.9	17.9
Zonal wind speed (m/s)	-1.6	-1.3	0.95	0.3	8.7	26.4
Meridional wind speed (m/s)	-0.2	-0.1	0.91	0.1	10.5	45.8

Table 18: Statistics of daily mean meteorological variables over the Netherlands from the simulation on only domain 4 (Zero_NL_d4). The simulation on only domain 4 with Dutch emissions (2010_d4) serves as a reference for the results.

Variable	Mean ref	Mean mod	r	MBE	NMBE (%)	NMGE (%)
Temperature (°C)	272.8	272.8	1.0	0.0	0.0	0.0
Sea-level pressure (hPa)	1014.4	1014.4	1.0	0.0	0.0	0.0
Relative humidity (%)	91.8	91.8	1.0	0.0	0.0	0.0
Wind speed (m/s)	4.9	4.9	1.0	0.0	0.0	0.0
Zonal wind speed (m/s)	-0.8	-0.8	1.0	0.0	-0.1	0.1
Meridional wind speed (m/s)	0.5	0.5	1.0	0.0	0.0	0.1



Figure 36: SIA precursor concentrations from the 2010 simulation on domains 1, 2 and 3 (2010_d123). Concentrations are averaged over the study period.

Peaks

Table 19: Concentrations of SIA compounds and SIA precursor gases at the start and end of the trajectories for Peak 1 displayed in Figure 24. Concentrations are averages over the seven trajectories.

Variable	Start ($\mu g/m^3$)	End ($\mu g/m^3$)	Change (%)
SIA	19.9	24.4	22.6
NO_3	13.2	15.9	20.5
SO_4	1.9	2.7	42.1
$\rm NH_4$	4.7	5.8	23.4
NO	1.5	6.4	326.7
NO_2	16.2	43.1	166.0
SO_2	15.5	20.1	19.7
NH ₃	2.6	9.6	269.2

Table 20: Concentrations of SIA compounds and SIA precursor gases at the start and end of the trajectories for Peak 2 displayed in Figure 25. Concentrations are averages over the seven trajectories.

Variable	Start ($\mu g/m^3$)	End ($\mu g/m^3$)	Change (%)
SIA	16.5	14.6	-11.5
NO ₃	11.8	10.5	-11.0
SO_4	0.9	0.7	-22.2
NH ₄	3.8	3.4	-10.5
NO	1.4	0.2	-85.7
NO ₂	16.5	20.6	24.8
SO_2	13.3	10.2	-23.3
NH ₃	4.3	5.3	23.3

Table 21: Concentrations of SIA compounds and SIA precursor gases at the start and end of the trajectories for Peak 3 displayed in Figure 27. Concentrations are averages over the seven trajectories.

Variable	Start ($\mu g/m^3$)	End ($\mu g/m^3$)	Change (%)
SIA	17.1	40.6	137.4
NO ₃	8.4	12.9	53.6
SO_4	4.6	17.3	276.1
NH ₄	4.2	10.4	147.6
NO	0.5	0.4	-20
NO ₂	15.7	30.4	93.6
SO_2	16.0	2.3	-85.6
NH ₃	0.1	4.4	4300