

**TNO report**

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**Establishing the origin of Particulate Matter concentrations in the Netherlands**

**Earth, Environmental and Life Sciences**

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## Summary

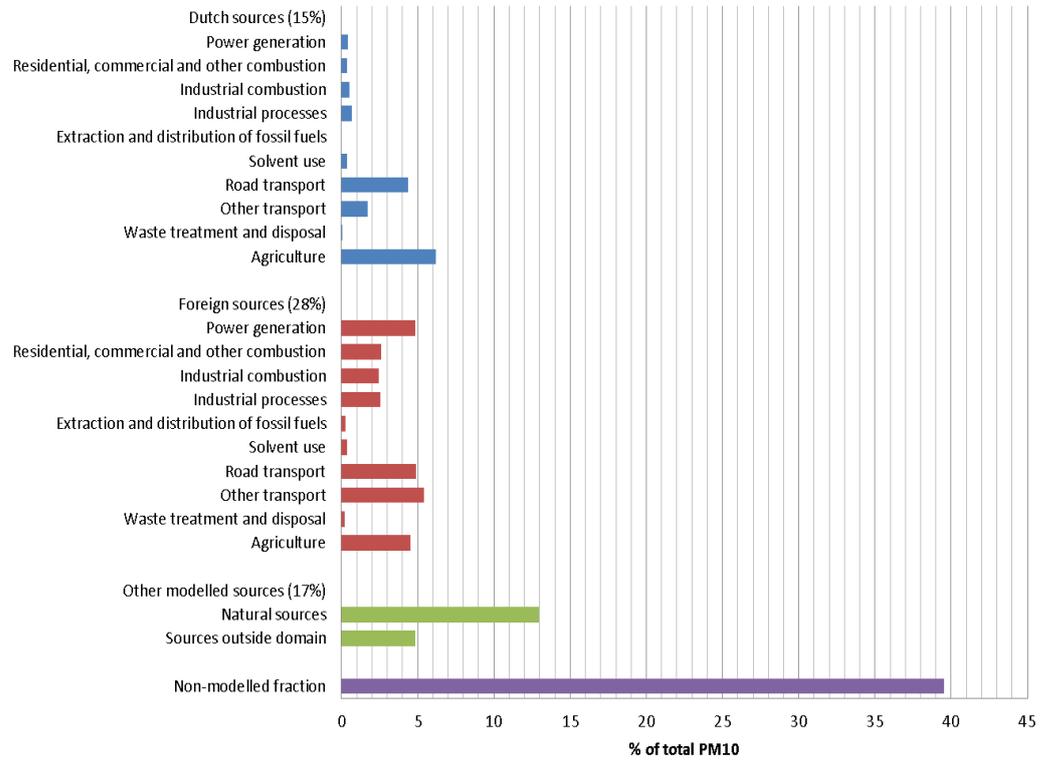
Air pollution, and more specifically particulate matter, still poses a significant threat to human health in Europe, including the Netherlands. To develop effective national and international mitigation strategies, the origin of particulate matter in the Netherlands needs to be established. Days with high PM concentrations are of particular interest, as the EU enforces a daily limit value which is still regularly exceeded.

The first Netherlands Research Program on Particulate Matter (BOP) was conducted to reduce the gaps in knowledge about composition, distribution and origin of particulate matter. While this study gained important insights in the concentrations and the chemical composition of PM<sub>10</sub> and PM<sub>2.5</sub>, only a limited attribution to source categories could be provided. To produce a more detailed view on the origin of PM, a source apportionment module was developed for the regional air quality model LOTOS-EUROS. The model was used in this study to establish the source attribution of PM<sub>10</sub> and PM<sub>2.5</sub> in the Netherlands for 2007 to 2009 at sector level, distinguishing between national and foreign sources. A priority was to establish if the source attribution varies with the PM concentration.

The averaged modelled PM<sub>10</sub> concentration for the years 2007-2009 in the Netherlands was 13 – 22 µg/m<sup>3</sup>, depending on location. A gradient from North (13 µg/m<sup>3</sup>) to South (18 µg/m<sup>3</sup>) was modelled, with higher concentrations in densely populated areas with large industrial activities. For PM<sub>2.5</sub>, the concentrations modelled were 9-11 µg/m<sup>3</sup>. The average observed concentrations for these years were 23-24 µg/m<sup>3</sup> for PM<sub>10</sub> and 14-15 µg/m<sup>3</sup> for PM<sub>2.5</sub>, which means that the non-modelled mass for both PM<sub>10</sub> and PM<sub>2.5</sub> is about 40%. The modelled PM mass consists for 60% of SIA components and 15% of carbonaceous particles. Sea salt and dust each contribute around 10% to the total modelled PM<sub>10</sub> mass. These shares change with location and air mass origin and thus with total PM concentration. Evaluation against observations showed that the non-modelled mass consists mainly of nitrate and carbonaceous matter.

Overall, this study confirms the previously established origin of particulate matter in the Netherlands, but explains a larger share of the observed PM mass with modelling and offers more detail on the source apportionment during high PM<sub>10</sub> episodes. Based on modelled PM, 70-80% of PM<sub>10</sub> and 80-95% of PM<sub>2.5</sub> in the Netherlands is anthropogenic. About 1/3 of anthropogenic PM<sub>10</sub> is of Dutch origin and 2/3 originates in foreign countries (Figure 1). Agriculture and transport (road and non-road) are the Dutch sectors with the largest contribution to total PM<sub>10</sub> mass in the Netherlands, together responsible for 85% of the total Dutch contribution. The foreign contribution is more equally apportioned to road transport, other transport, industry, power generation and agriculture. The remaining sectors combined account for 10% of the foreign contribution to modelled PM levels in the Netherlands.

### Origin of PM10 in the Netherlands



### Origin of PM2.5 in the Netherlands

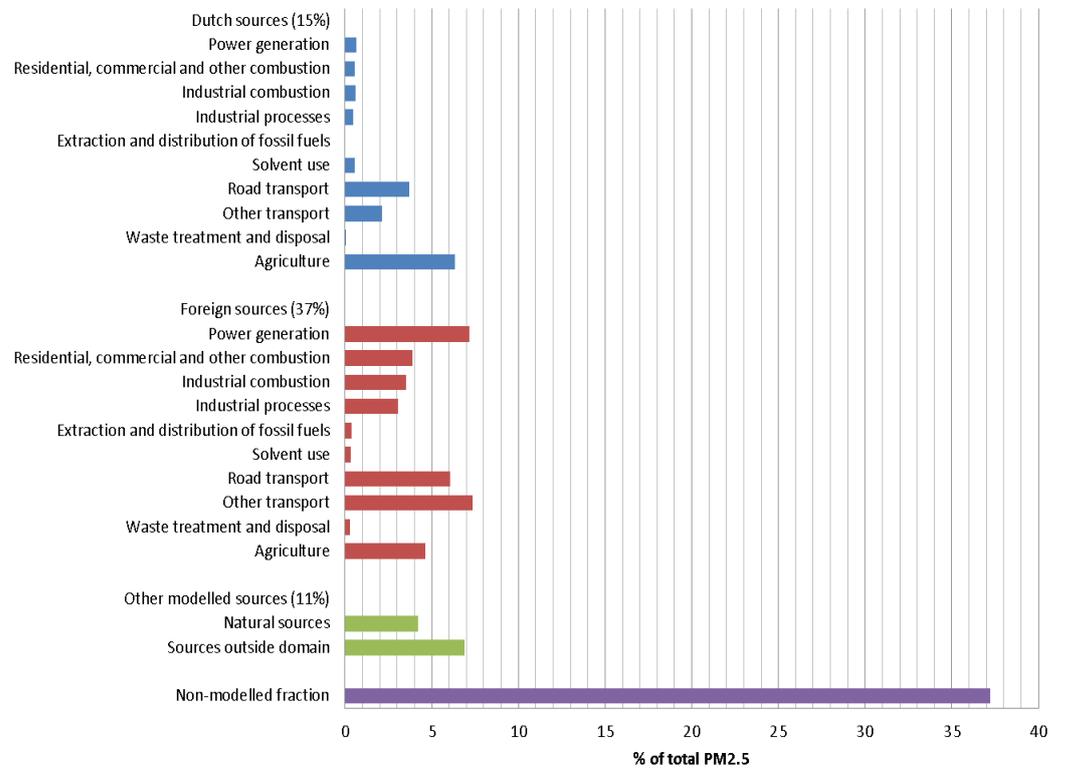


Figure 1 Origin of PM10 and PM2.5 in the Netherlands

The relative contribution of foreign sources to  $PM_{2.5}$  is larger than for  $PM_{10}$ , but the same source sectors are dominant. Because sea salt is found mainly in the coarse fraction, the natural contribution in  $PM_{2.5}$  is only 4% (13% for  $PM_{10}$ ). The source attribution of  $PM_{2.5}$  and  $PM_{10}$  changes with location, with higher foreign shares along the borders. The national contribution to PM levels is significantly higher in the Randstad area than for the country on average.

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

Given the importance of foreign emissions for PM concentrations in the Netherlands, international cooperation is recommended to develop effective strategies to reduce PM levels, especially during peak episodes. However, in the densely populated areas where population exposure to PM is largest, Dutch sources cause a relatively large share of total PM levels and domestic policy can achieve results as well. Reduction measures should focus on agriculture and transport. This would also be beneficial in reducing concentrations during peak episodes. For agriculture, the target substance would be ammonia, which is converted into aerosol in the atmosphere, whereas for transport, combustion, wear and resuspension emissions are important.

For the first time, a chemically consistent source apportionment for particulate matter was obtained for the Netherlands, that provides insight in the spatial and temporal variability of the source apportionment per sector. The information on the origin of particulate matter obtained in this study is valuable for policy discussions and scoping mitigation strategies. The developed tools can be used for policy support in e.g. visualization of the impact of measures. As the formation and fate of particulate matter is complicated, a full mass closure between model and measurements and source apportionment is not yet possible. Major improvements are expected by 1) a better representation of (secondary) organic aerosol in the LOTOS-EUROS model and the emission inventory; and 2) the inclusion of a plume-in-grid approach for a better representation of local gradients.



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# 1 Introduction

## 1.1 Background

Air pollution poses a significant threat to human health in many countries in Europe. Health effects of air pollution are dominated by particulate matter, both  $PM_{2.5}$  and  $PM_{10}$ . To reduce these adverse impacts of PM, the European Union adopted a new Directive (2008/50/EC) on ambient air quality and cleaner air for Europe (EU, 2008), establishing new air quality standards for  $PM_{2.5}$ . In the Netherlands, the daily limit value for  $PM_{10}$  is exceeded during high-PM episodes. Moreover, in years with unfavorable meteorological conditions (e.g. 2011) more than 35 exceedances are observed in large parts of the country. To develop effective mitigation strategies to reduce concentrations of both  $PM_{2.5}$  and  $PM_{10}$ , the origin of particulate matter in the Netherlands needs to be established.

The first assessment of the origin of particulate matter in the Netherlands was made in 2005 by Buijsman *et al.* (2005). These authors used the OPS model with a description of primary emissions and secondary inorganic aerosol (SIA) formation as a basis to calculate the origin of PM in the Netherlands (see Figure 1). They arrived at an estimated national contribution of 15% with a largest contribution from traffic and a 30% contribution from abroad with the largest contributions from industrial activities, power generation and traffic. The non-modelled part (55%) was attributed to sea salt (based on observations), northern hemispheric contribution and a semi-natural rest term (including soil dust).

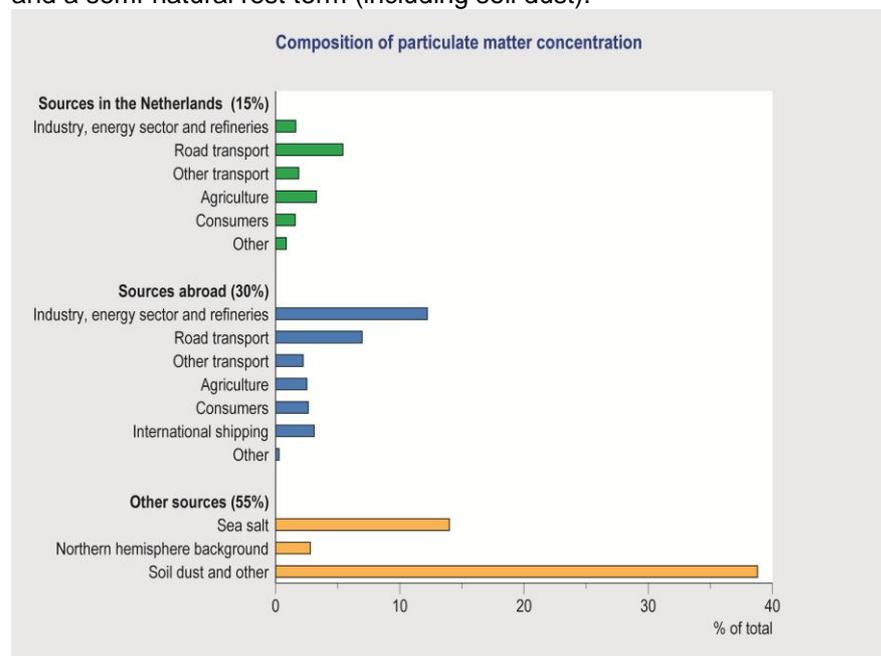


Figure 1 Source attribution of  $PM_{10}$  in the Netherlands as presented by Buijsman *et al.*, 2005

A number of issues can be raised with regard to the results from Buijsman *et al.* (2005).

- The large non-modelled fraction indicates that the picture is far from complete.
- Schaap and Denier van der Gon (2007) argued that the contribution from national sources for primary fine mode material, such as black carbon, is well

above 50% whereas the Buijsman *et al.* (2005) analysis shows a contribution lower than 50%.

- The observational data for PM composition that were used in the study were obtained in 1998-1999; an update of these data would be valuable.
- Buijsman *et al.* (2005) focused on PM<sub>10</sub> and no information on the fine mode is given.
- Knowledge in PM has increased significantly in recent years and an update of the results found by Buijsman *et al.* (2005) in which the extra information is included is valuable.

To reduce the gaps in knowledge about composition, distribution and origin of particulate matter the Netherlands Research Program on Particulate Matter (BOP) was conducted. The BOP study was facilitated by an intensive, one-year measurement campaign from August 2007 to August 2008. During this year, PM<sub>10</sub> and PM<sub>2.5</sub> were sampled, simultaneously, at five locations. Subsequently, the samples were chemically analysed to assess the composition of particulate matter. The chemically speciated PM data were used to address the origin of particulate matter using knowledge on existing markers for several sources as well as a statistical technique (PMF). Here, we give an overview of the most important findings and shortcomings considering the determination of the origin of PM.

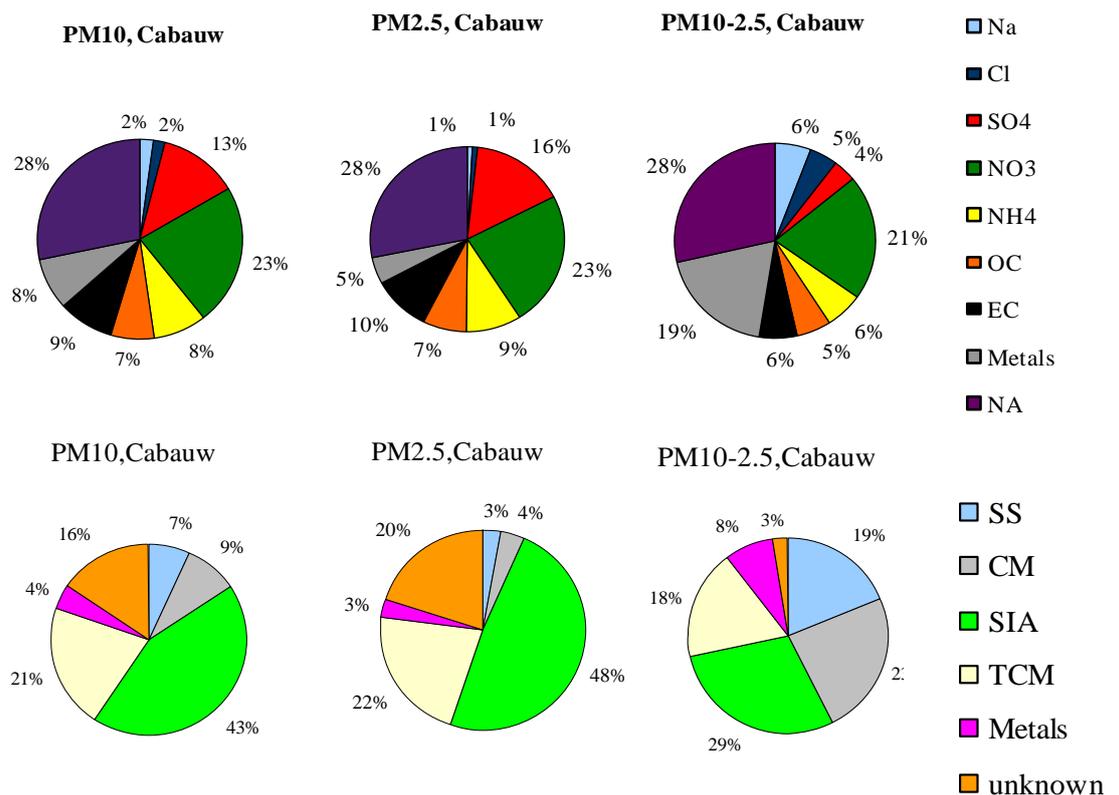


Figure 2 Average composition and mass closure for PM at Cabauw. Results are given for PM<sub>10</sub>, PM<sub>2.5</sub> and the coarse PM fraction. Data from Schaap *et al.* (2010)

BOP has provided a full characterisation of the PM<sub>10</sub>, PM<sub>2.5</sub> and the coarse fraction for its major components (see Figure 2). Using a mass closure approach 85 to 90%

of the  $PM_{10}$  mass was explained. Generally, there is considerable conformity in the chemical composition of PM in the Netherlands. From all the constituents that are part of  $PM_{10}$  the secondary inorganic aerosol – the sum of sulfate, nitrate and ammonium – was the most dominant. The second dominant contribution came from total carbonaceous matter (TCM). Sea salt, mineral dust and metals each comprised 10% of total  $PM_{10}$ . As sea salt (SS) and mineral dust (MD) are mainly found in the coarse mode, their contribution to the coarse fraction is higher than to  $PM_{10}$ . For TCM and SIA the contribution in the fine mode is larger.

Days with high  $PM_{10}$  concentrations are of particular interest, as the EU enforces a daily limit value. On days with high concentrations, all components, except sea salt, show higher concentrations. Sea salt maximizes in marine air masses associated with clean air conditions. Relatively speaking, the nitrate and undefined contributions increase most on these types of days, while the relative contribution of the remaining components is mostly stable as a function of PM concentration. From a literature study, the contribution from natural sources to PM was estimated to be one fourth for  $PM_{10}$  and one fifth for  $PM_{2.5}$ . Although this analysis was relatively pragmatic, it clearly illustrates that the majority of PM in the Netherlands is of anthropogenic origin.

To identify source categories and to apportion the observed PM concentrations to those categories, a statistical receptor model (Positive Matrix Factorization (PMF)) was applied to the data set. This technique groups the different components that behave similarly in time. Seven general source groups were identified, using this procedure. In order of decreasing mass contribution to  $PM_{2.5}$ , these were:

- 1) nitrate-rich secondary aerosol;
- 2) sulfate-rich secondary aerosol;
- 3) traffic and re-suspended road dust;
- 4) metals from industrial activity/incineration;
- 5) sea salt;
- 6) mineral dust; and
- 7) particles from residual oil combustion.

A disadvantage of this statistical procedure is that it cannot cope with non-linear components. Consequently, PMF does not provide detailed source information and is unable to differentiate sources for the secondary components. For the traditional PM components, such as SIA and primary material, it is recommended to perform a detailed source attribution with a chemistry transport model to identify source contributions at sector level, and to provide insight into national versus foreign contributions to ambient PM.

## 1.2 Goals

This study (BOP2) was set up to establish the source attribution of  $PM_{10}$  and  $PM_{2.5}$  in the Netherlands using the knowledge gained in the first BOP program (hereafter called BOP1), improving the modelling and reducing the non-modelled fraction of PM compared to Buijsman *et al.* (2005). The source apportionment was performed at sector level, i.e. SNAP level 1, distinguishing between national and foreign sources. A point of special attention was establishing whether the source attribution varies with the PM concentration, i.e. low versus high concentrations.

### 1.3 Approach

To meet the project goals the following approach is taken.

1. The study will use two sets of emission data:
  - The official Dutch Pollutant Release and Transfer Register (PRTR) for emissions in the Netherlands.
  - The European TNO-MACC emission dataset for the rest of Europe.
2. The two emission databases are used as input to perform model simulations of the air quality across the Netherlands. The model results are evaluated against observations.
3. The model simulations are coupled with a recently developed source apportionment routine to derive the different source contributions to PM concentrations in the Netherlands.
4. The simulation results will be analysed with special attention to annual distributions as well as situations with high PM levels.

The report is structured along these steps.

## 2 Emission data

To establish the sources of ambient particulate matter we have used the best available information on emissions. The official Dutch Pollutant Release & Transfer Register (PRTR) was used for the emissions in the Netherlands. This database contains information from many individual facilities (point sources) and typical information for the Netherlands concerning sources and distribution of emissions over the country. For the rest of the domain, the European TNO-MACC emission database (Kuenen *et al.*, 2011; Denier van der Gon *et al.*, 2010b) was used. The Dutch emission data in the European TNO-MACC database was replaced by the official PRTR emission dataset. The differences between both emission databases for the Netherlands are discussed in this chapter.

The Emission Registration ([www.emissieregistratie.nl](http://www.emissieregistratie.nl)) in the Netherlands is responsible for the annual assessment of emissions from all pollutants to air (both greenhouse gases and air pollutants). The calculation of the emissions is based on in-depth knowledge about specific sources for the Netherlands and a reporting system in which many individual companies are obliged to annually report their emissions. This system is also used for international reporting obligations, e.g. to the UNECE Convention on Long Range Transboundary Air Pollution (CLRTAP) and the United Nations Framework Convention on Climate Change (UNFCCC). The emissions have been obtained from RIVM (the responsible authority for the emission registration system) for the year 2008, on a highest available spatial resolution. The pollutants include NO<sub>x</sub>, SO<sub>2</sub>, NMVOC, CO, NH<sub>3</sub>, CH<sub>4</sub> and particulate matter (PM<sub>10</sub> and PM<sub>2.5</sub>). About 4000 point sources are included separately with their exact coordinates. The emissions are characterised by a source definition that has been translated to SNAP level 1 source categories which is the default in the existing TNO-MACC European emission database used as input to the LOTOS-EUROS model (Denier van der Gon *et al.*, 2010b). This database has been developed for the base year 2005 and has been scaled for the years 2003-2007 (Kuenen *et al.*, 2011). The impact of using national emissions for 2008 in contrast to 2007 data for the rest of the European domain is considered to be small as emissions change only slightly from year to year and emission changes are considerably smaller than the associated uncertainty as well as differences between different reportings.

The source definition in which the emissions have been obtained are specific source categories used in the Dutch Emission Registration (LED codes). These are given in Table 1 below (in aggregated form). The allocation to SNAP sectors has been made using existing link tables available from the Emission Registration, and additional TNO expert judgement. One of the main difficulties is the split between SNAP 3 and SNAP 4 for industrial sources, since the LED codes do not distinguish between industrial combustion and processes. On a per-pollutant basis the most suitable SNAP has been selected.

After this conversion step, the emissions have been converted and aggregated to 1/8° x 1/16° (longitude x latitude) (about 7x7 km), which is the zoom-resolution of LOTOS-EUROS that will be used over the Netherlands for this study.

Table 1 Link table between LED codes and SNAP level 1

LED code	LED Name	SNAP	Comments
1100	Industry – Food industry	3	SNAP 9 for CH <sub>4</sub> SNAP 4 for NH <sub>3</sub> /NMVOC
1200	Industry - Petroleum refining	1	SNAP 4 for CH <sub>4</sub> /NMVOC SNAP 5 for PM <sub>10</sub> /PM <sub>2.5</sub>
1300	Industry – Chemical industry	3	SNAP 4 for NH <sub>3</sub> SNAP 9 for CH <sub>4</sub>
1400	Industry – Building materials	3	SNAP 4 for CH <sub>4</sub> /NH <sub>3</sub> SNAP 3&4 split for PM
1500	Industry – Basic metals	3	SNAP 4 for CH <sub>4</sub> /NH <sub>3</sub> SNAP 3&4 split for PM
1700	Industry – Metal treatment	4	SNAP 3 for NO <sub>x</sub> /SO <sub>2</sub> /CO SNAP 6 for NMVOC
1800	Industry – Other	4	SNAP 3 for NO <sub>x</sub> /SO <sub>2</sub> /CO
2100	Energy – Production	1	
2200	Energy – Exploration and distribution	1	SNAP 5 for CH <sub>4</sub> /NMVOC
3100	Transport – Road transport	7	3160 allocated to SNAP 75; 3110-3150 to SNAP 71-74
3200	Transport – Mobile machinery	8	SNAP 5 partly for NMVOC
3600	Transport – Aviation	8	
3700	Transport – Rail	8	
3800	Transport – Navigation	8	SNAP 5 partly for NMVOC
4100	Agriculture – Animal husbandry	10	
4200	Agriculture – other/unknown	10	
4300	Agriculture – other/unknown	10	
4600	Agriculture – Other	2	SNAP 10 for NMVOC/ PM <sub>10</sub> /PM <sub>2.5</sub> ; SNAP 6 for NH <sub>3</sub>
5100	Waste treatment	1	SNAP 9 for CH <sub>4</sub> /NH <sub>3</sub> /NMVOC
6100	Services* – Sewage treatment plants	2	SNAP 9 for CH <sub>4</sub>
6200	Services* – Exploration and distribution	2	SNAP 9 for CH <sub>4</sub>
6300	Services* - Storage and handling	4	SNAP 5 for NMVOC
6400	Services* - Other	2	SNAP 5 for NMVOC SNAP 6 for NH <sub>3</sub>
7100	Building sector	3	SNAP 4 for PM <sub>10</sub> /PM <sub>2.5</sub> SNAP 6 for NMVOC
8100	Consumers/residents – Combustion	2	
8200	Consumers/residents – Other	6	SNAP 2 for NO <sub>x</sub> /SO <sub>2</sub> /CO SNAP 10 for NH <sub>3</sub>

\* Services: Trade, Services and Government (in Dutch: HDO = Handel, Diensten en Overheid)

Thereafter, the emissions from road transport allocated to SNAP 71-74 (see Table 1) are disaggregated to the actual SNAP codes 71 to 74. This has been done by using data from TREMOVE v2.7b regarding the share of gasoline, diesel and LPG in the emissions of each pollutant in the Netherlands. Thereafter, emissions from SNAP 74 (gasoline evaporation) are extracted from SNAP 71 by using a fixed ratio between SNAP 71 and SNAP 74 for the Netherlands, calculated from the Dutch total emissions in Denier van der Gon *et al.* (2010b). This yields the final emission database for the Netherlands for all relevant pollutants.

The primary reason to use the PRTR data for the Netherlands is the improved spatial distribution of the emissions as compared to the TNO-MACC database. Figure 5 and Figure 6 show the distributions of total NO<sub>x</sub> and total PM<sub>10</sub> emissions, respectively. For both figures, the distribution over the Netherlands as well as over the Dutch part of the North Sea (NCP) is updated in the European TNO-MACC 2007 inventory with the data from the Dutch Emission Registration. The revised distribution over the North Sea (which is not included in the analysis presented in Figure 3 and Figure 4) results in lower emissions for all pollutants in this area. Generally, the distributions for both components show a high level of correspondence between the PRTR and the European TNO-MACC database. However, both the NO<sub>x</sub> and PM<sub>10</sub> maps show an enhanced importance of the east-west transport route over the major waterways towards Germany and considerably lower emissions over the North Sea.

Since the PRTR uses detailed information on spatial distribution of emissions in the Netherlands, the spatial distribution is likely to be more accurate than the generic European distribution approach in the TNO-MACC 2007 inventory.

To check for consistency between the combined dataset and the TNO-MACC 2007 inventory, we have compared these two datasets in detail. Despite the fact that both are essentially based on the same dataset, limited differences do exist, highlighted in Figure 3.

The differences are related to a few issues:

- Different base years for the datasets (2007 vs. 2008).
- Version differences of the national emission inventory (a new national inventory is submitted each year for every year which can use updated/improved methodologies).
- The methodology used in the TNO-MACC 2007 inventory to scale emissions from 2005 to 2007 (Kuenen *et al.*, 2011).

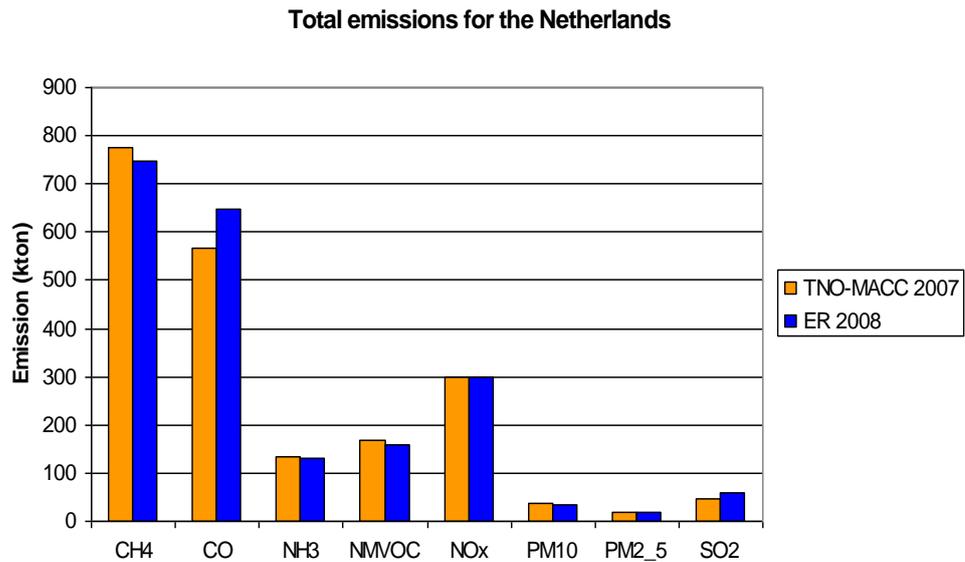


Figure 3 Emissions (kton) of each pollutant in the TNO-MACC 2007 inventory and the Emission Registration data for 2008

At the level of source sectors some larger differences exist due to the allocation of LED sectors to SNAP sectors which is not trivial, illustrated by the graph in Figure 4 for  $\text{NO}_x$  and  $\text{PM}_{10}$ . While national totals show good agreement, sectoral differences show more pronounced differences. For  $\text{NO}_x$ , smaller differences are found for most sectors, most pronounced in non-road transport (SNAP 8). For  $\text{PM}_{10}$ , more pronounced differences are seen in SNAP 3 and SNAP 4, which are both industrial sectors, highlighting a different division of combustion (SNAP 3) and process (SNAP 4) emissions for this sector.

Apart from the allocation problem between LED sectors and SNAP sectors and the year difference between the two datasets (2007 vs. 2008), differences are also partially due to version differences in the reported data and the methodology in which the TNO-MACC 2007 inventory was constructed (Kuenen *et al.*, 2011).

The annual total emissions are divided over the year using SNAP sector-specific monthly, daily and hourly factors reflecting the activity level at each time in each sector. For particulate matter, the emissions are divided among the PM species elemental carbon, organic matter (ec and pom, respectively), sodium and other minerals. The PM split differs per SNAP sector and country (Kuenen *et al.*, 2011).

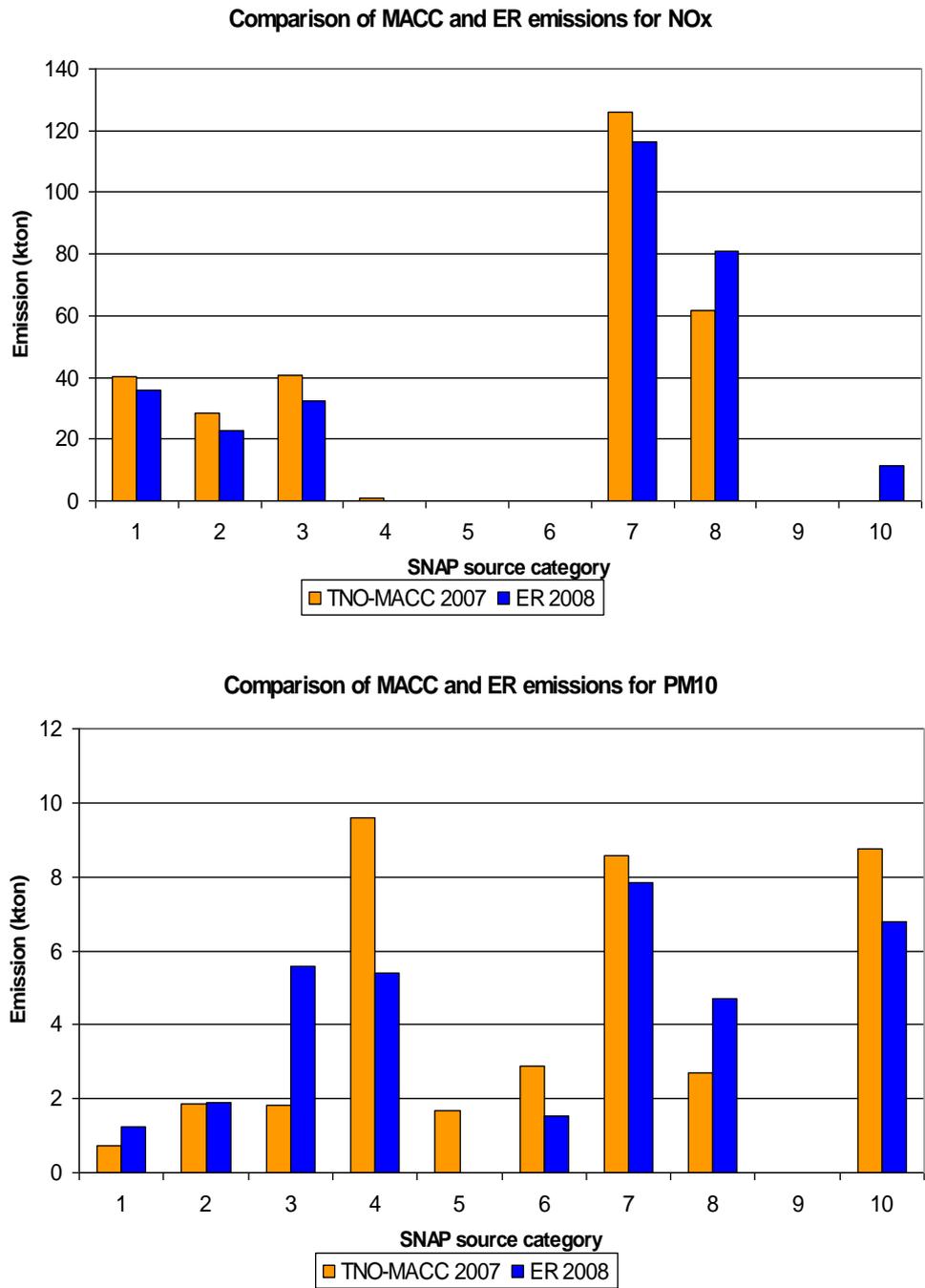


Figure 4 Comparison of emissions by SNAP source category for NO<sub>x</sub> (top panel) and PM<sub>10</sub> (bottom panel). SNAP 7 is shown here as a whole, being the sum of SNAP 71 to 75.

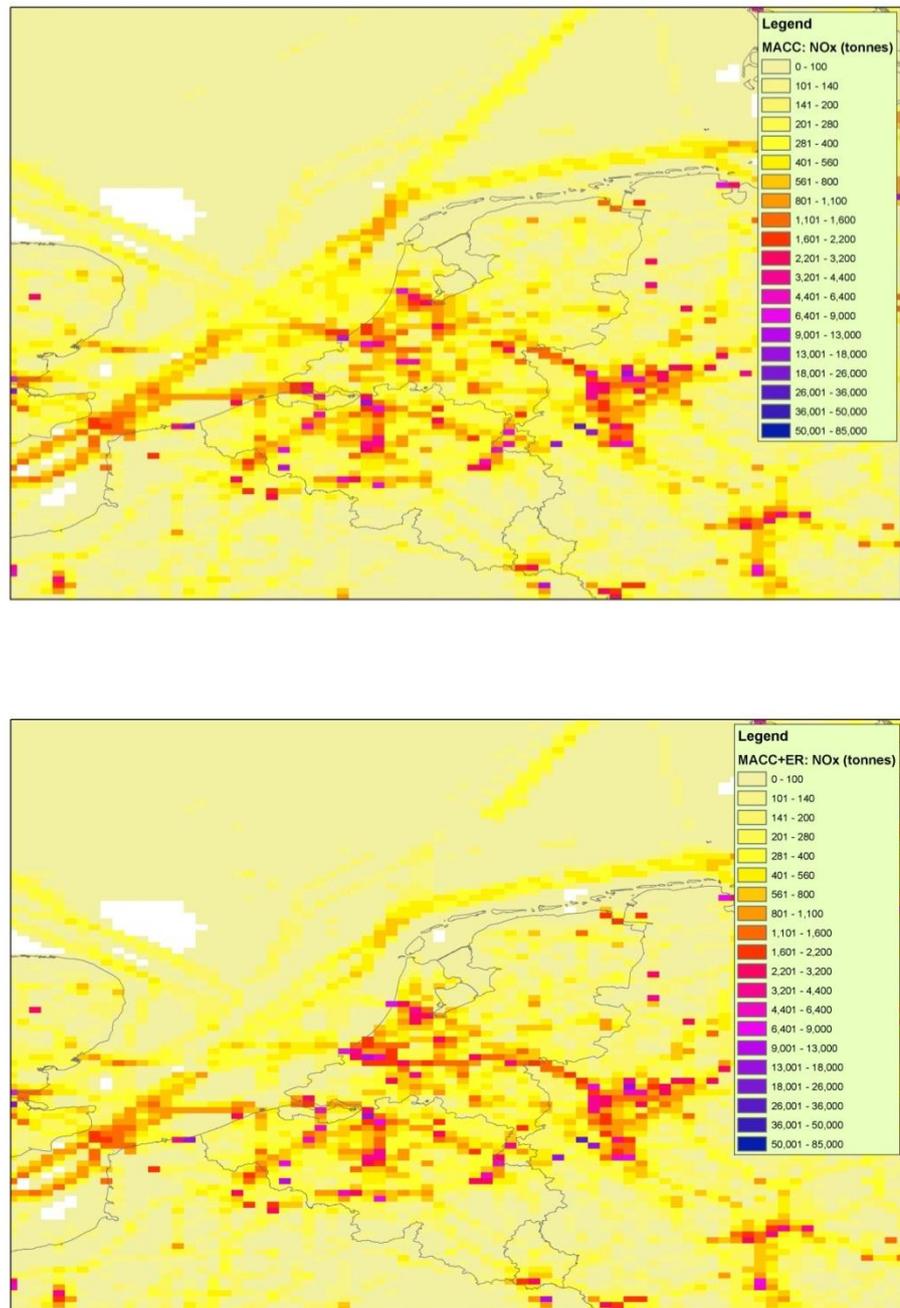


Figure 5 Comparison of spatial distribution of NOx emissions between TNO-MACC 2007 (top panel) and the Emission Registration data with TNO-MACC 2007 for the other countries (bottom panel)

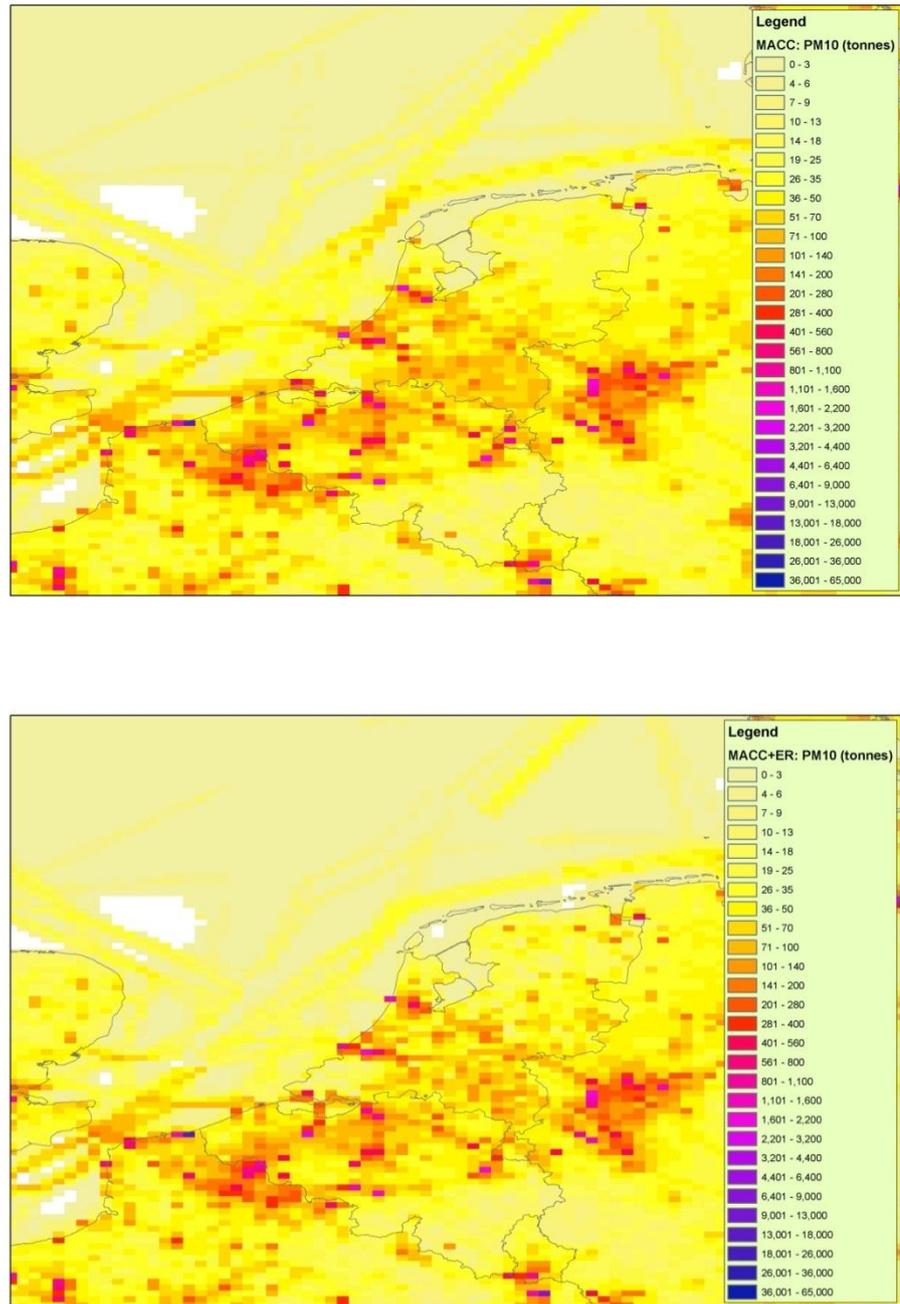


Figure 6 Comparison of spatial distribution of PM10 emissions between TNO-MACC 2007 (top panel) and the Emission Registration data with TNO-MACC 2007 for the other countries (bottom panel)



### 3 Model description

The model employed in this study is the 3D chemistry-transport model LOTOS-EUROS (Schaap *et al.*, 2008), which is aimed at simulating air pollution in the lower troposphere. The model is of intermediate complexity in the sense that the relevant processes are parameterized in such a way that the computational demands are modest enabling hour-by-hour calculations over extended periods of several years within acceptable CPU time.

The master domain of LOTOS-EUROS is bound at 35° and 70° North and 30° West, 60° East. The model projection is normal longitude-latitude and the standard grid resolution is 0.50° longitude × 0.25° latitude, approximately 25 × 25 km. The actual domain for a simulation can be set as long as it falls within the master domain. In addition, it is possible to increase or decrease the resolution up to a factor 8 or 2, respectively. In the vertical, there are three dynamic layers and a surface layer. The model extends in vertical direction 3.5 km above sea level. The lowest dynamic layer is the mixing layer, followed by two reservoir layers. The height of the mixing layer is obtained from the ECMWF meteorological input data used to drive the model. The height of the reservoir layers is determined by the difference between ceiling (3.5 km) and mixing layer height. Both layers are equally thick with a minimum of 50 m. In a few cases, when the mixing layer extends near or above 3500 m the top of the model exceeds the 3500 m according to the above-mentioned description. A surface layer with a fixed depth of 25 m is included in the model.

The advection in all directions is handled with the monotonic advection scheme developed by Walcek (2000). Gas phase chemistry is described using the TNO CBM-IV scheme, which is a condensed version of the original scheme by Whitten *et al.* (1980). Hydrolysis of N<sub>2</sub>O<sub>5</sub> is described following Schaap *et al.* (2004a). Aerosol chemistry is represented using ISORROPIA (Nenes *et al.*, 1999). The dry deposition in LOTOS-EUROS is parameterised following the well-known resistance approach following the EDACS system (Erisman *et al.*, 1994). The aerodynamic resistance is calculated for all land use types separately. Below cloud scavenging is described using simple scavenging coefficients for gases (Schaap *et al.*, 2004a) and particles (Simpson *et al.* 2003).

The emissions described in the previous chapter are used as input to drive the model. The temporal variation of the emissions is represented by time factors. For each source category a monthly factor breaks down the annual total into monthly values. This value is multiplied by a factor for the day of the week (i.e. Monday, Tuesday etc.) and finally by a factor for the hour of the day (local time). Sea salt emissions are described following Mårtensson *et al.* (2003) and Monahan *et al.* (1986) for fine and coarse mode sea salt, respectively. A first module for describing crustal matter emissions from wind erosion, traffic and agriculture was developed in BOP1 (Denier van der Gon *et al.*, 2010b) and is used here.

Scientific studies have been performed to address secondary inorganic aerosol (Schaap *et al.*, 2004a; Erisman and Schaap, 2004), black carbon (Schaap *et al.*, 2004b; Schaap and Denier van der Gon, 2007), sea salt (Manders *et al.*, 2010), PM (Manders *et al.*, 2009), and ozone (Vautard *et al.*, 2006). The model has

participated frequently in international model comparisons aimed at ozone (Solazzo *et al.*, 2011a; Van Loon *et al.*, 2007; Hass *et al.*, 2003), PM (Cuvelier *et al.*, 2007; Stern *et al.*, 2008) and source receptor matrices (Thunis *et al.*, 2008).

For total PM<sub>10</sub> the model shows an underestimation as compared to the observations. This bias is a common feature of CTMs (Stern *et al.*, 2008). Although the missing mass is largely associated with non-modelled components, most importantly organic material, an underestimation of the secondary inorganic components was also observed during BOP1. Within BOP2 an effort was made to improve the model description of the SIA components. The following developments were made:

- Adjustment of the height distribution for SO<sub>2</sub> emissions to better reflect the diurnal pattern in measured SO<sub>2</sub> concentrations.
- Implementation of a new module for dry deposition of gaseous species, DEPAC3.11. This module includes a compensation point for NH<sub>3</sub>, allowing NH<sub>3</sub> to be emitted by the surface under some atmospheric conditions. Another main difference with the old module is the improved SO<sub>2</sub> deposition modelling.
- Development of a routine to calculate the formation of coarse NO<sub>3</sub>.
- Including a new version of the thermodynamic equilibrium module ISORROPIA for aerosol formation.
- Development of a new cloud chemistry scheme with a better representation of the formation of sulfate aerosol.
- Implementation of the Zhang dry deposition scheme (Zhang *et al.*, 2001) for particles, decreasing the deposition velocity for PM<sub>10</sub>.
- Coupling of the sea roughness to wave height, increasing deposition of particles over sea.

The combined improvements were consolidated in an update of the LOTOS-EUROS base version. Version 1.8 is used to produce the results presented in this report. We evaluate the results of this version against measurements. For a detailed description of the improvements made in version 1.8 compared to earlier versions and their effect on the model performance for SIA and PM we refer to Wichink Kruit *et al.*, (2012). Also, we incorporated mineral dust emissions following Denier van der Gon *et al.* (2010b).

## 4 Simulation of particulate matter concentrations across the Netherlands

### 4.1 Simulation description

We have performed a set of simulations with LOTOS-EUROS version 1.8 using the combined TNO-MACC and PRTR emission database. First, a simulation on a European domain bound at 35° and 70° North and 15° West and 35° East was done. The grid resolution in this domain is 0.50° longitude x 0.25° latitude. The output from this run was used as boundary conditions for a simulation on a higher resolution (0.125° longitude x 0.0625° latitude) with a domain centred over the Netherlands (49-55° North, 3-9° East). The domains are depicted in Figure 7. Both simulations were performed for the years 2007 to 2009. By taking several years, year-to-year variations in the meteorology are averaged out and a more representative picture of the sources of PM in the Netherlands is obtained.

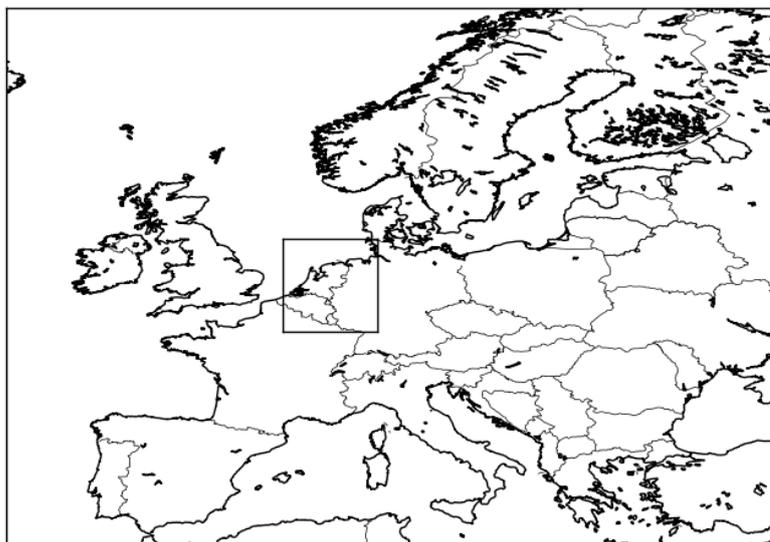


Figure 7 Domains used in this study

### 4.2 Results

Figure 8 displays the modelled PM<sub>10</sub> and PM<sub>2.5</sub> concentrations across the Netherlands averaged for the years 2007-2009. The average concentration for PM<sub>10</sub> ranges from 13 µg/m<sup>3</sup> for the northern and 18 µg/m<sup>3</sup> for the southern part of the country to 22 µg/m<sup>3</sup> for the Rotterdam area.

PM<sub>2.5</sub> average concentrations range from 9 µg/m<sup>3</sup> for Friesland and Groningen to 11 µg/m<sup>3</sup> along the main waterways and roads.

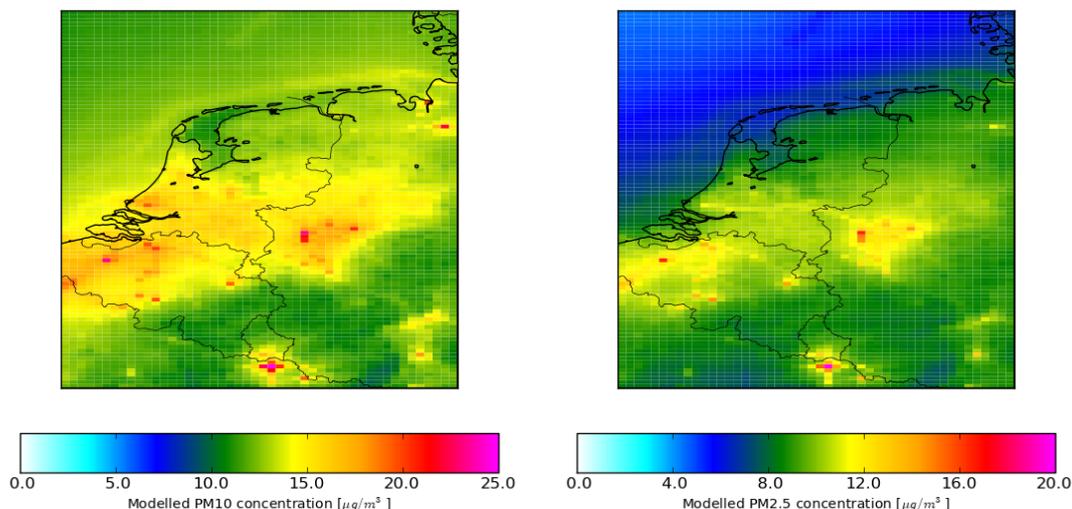


Figure 8 Average modelled concentrations of PM<sub>10</sub> (left) and PM<sub>2.5</sub> (right) for 2007-2009

Figure 9 displays the average modelled concentrations of the PM components elemental carbon (EC), primary organic matter (POM), crustal matter (or dust) and other primary particulate matter (PPM). Elemental carbon (EC) concentrations range from 0.4  $\mu\text{g}/\text{m}^3$  in Friesland and Groningen to 1.2  $\mu\text{g}/\text{m}^3$  in the Randstad. Especially along the main waterways and near areas with heavy industry, EC concentrations are high. EC contributes about 5% of the total modelled mass of PM<sub>10</sub> across the country. For organic material, two indicators for the total mass concentration are often used, organic carbon (OC) and organic matter (OM). The former consists only of the carbonaceous mass whereas the latter includes the mass of non-carbon atoms as well. Measurements usually yield OC data as most measurement techniques measure only the carbonaceous weight. In the emission database used here, OM is reported. Modelled primary organic matter (POM) concentrations are highest in the South-Eastern part of the country, with concentrations of 2 – 2.5  $\mu\text{g}/\text{m}^3$  in Noord-Brabant. In the North and West of the country, concentrations are 0.7 – 1.2  $\mu\text{g}/\text{m}^3$ , whereas the center of the Netherlands shows POM concentrations around 1.5  $\mu\text{g}/\text{m}^3$ . For dust, an increase in concentration from 1  $\mu\text{g}/\text{m}^3$  in the North to 3  $\mu\text{g}/\text{m}^3$  in the South is observed. PPM concentrations peak at 4  $\mu\text{g}/\text{m}^3$  in the Rotterdam area. In the rest of the country, the average modelled PPM concentration is 0.6 – 1.6  $\mu\text{g}/\text{m}^3$ , contributing around 10% to total PM<sub>10</sub>.

The modelled concentrations of secondary aerosol components Ammonium, Nitrate and Sulfate are shown in Figure 10, as well as sea salt concentrations. Note that the scale for all components in Figure 9 and Figure 10 (except for sea salt) is the same. In this way, the concentrations are easily comparable, but some detail in the gradients is lost. Ammonium (NH<sub>4</sub>) aerosol concentrations in the Netherlands range from 1.5  $\mu\text{g}/\text{m}^3$  in the North to 1.9  $\mu\text{g}/\text{m}^3$  in the South East, contributing around 15% to the total modelled PM concentration over the Netherlands. Sulfate concentrations increase from 1.7 to 2.3  $\mu\text{g}/\text{m}^3$  going from North to South. Nitrate contributions to total modelled PM range from 15% in the western part of the Netherlands to 25% in the northern and central parts, with concentrations of 2.6  $\mu\text{g}/\text{m}^3$  along the coast to 4  $\mu\text{g}/\text{m}^3$  in Noord-Brabant. On average, sea salt concentrations are 5  $\mu\text{g}/\text{m}^3$  near the

coastline, decreasing to  $2 \mu\text{g}/\text{m}^3$  in southern Limburg. On average, sea salt contributes 20-30% to the total modelled PM concentration.

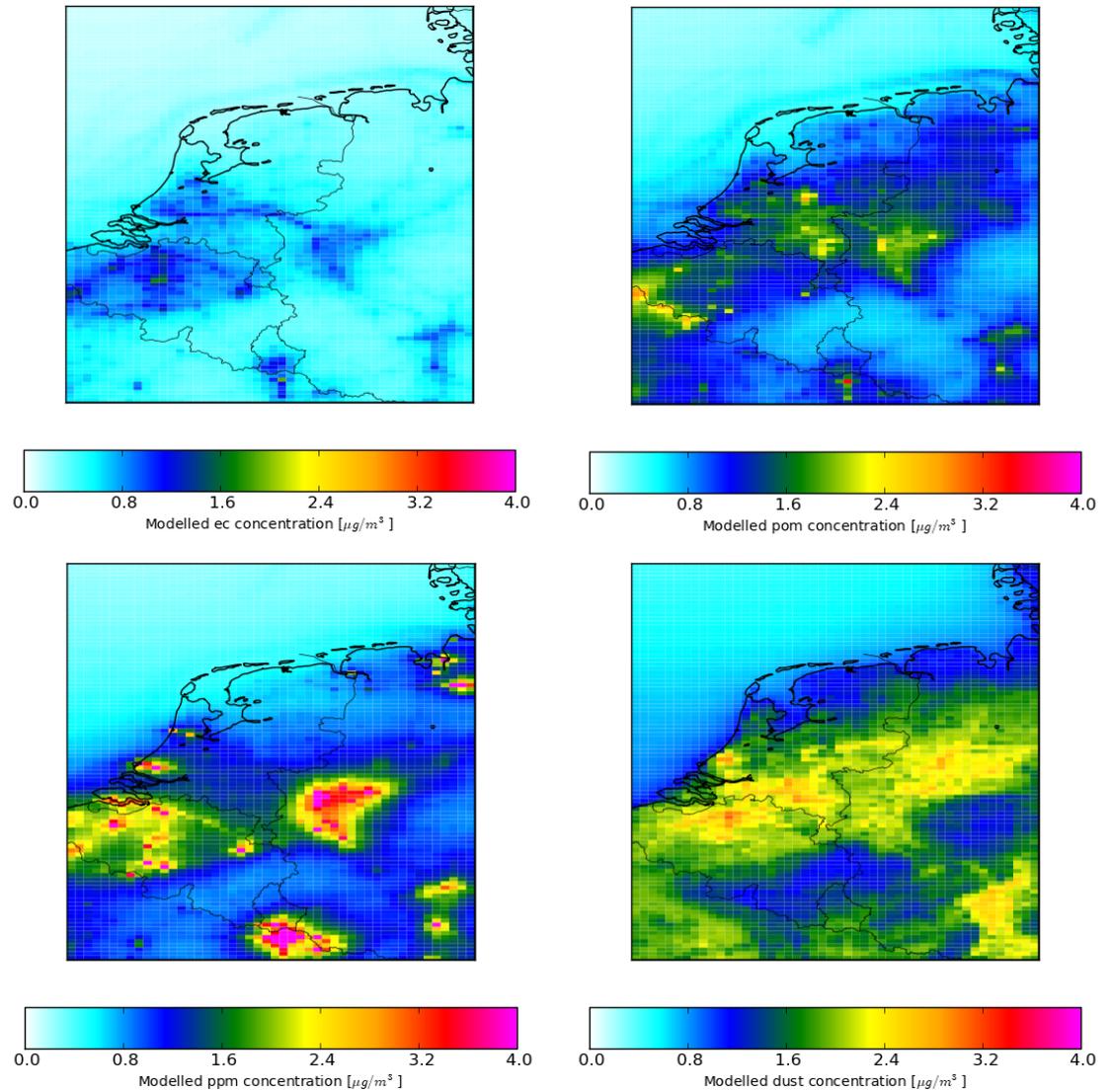


Figure 9 Average modelled concentrations of elemental carbon (top left), primary organic matter (top right), other primary particulate matter (bottom left) and dust (bottom right) for 2007-2009

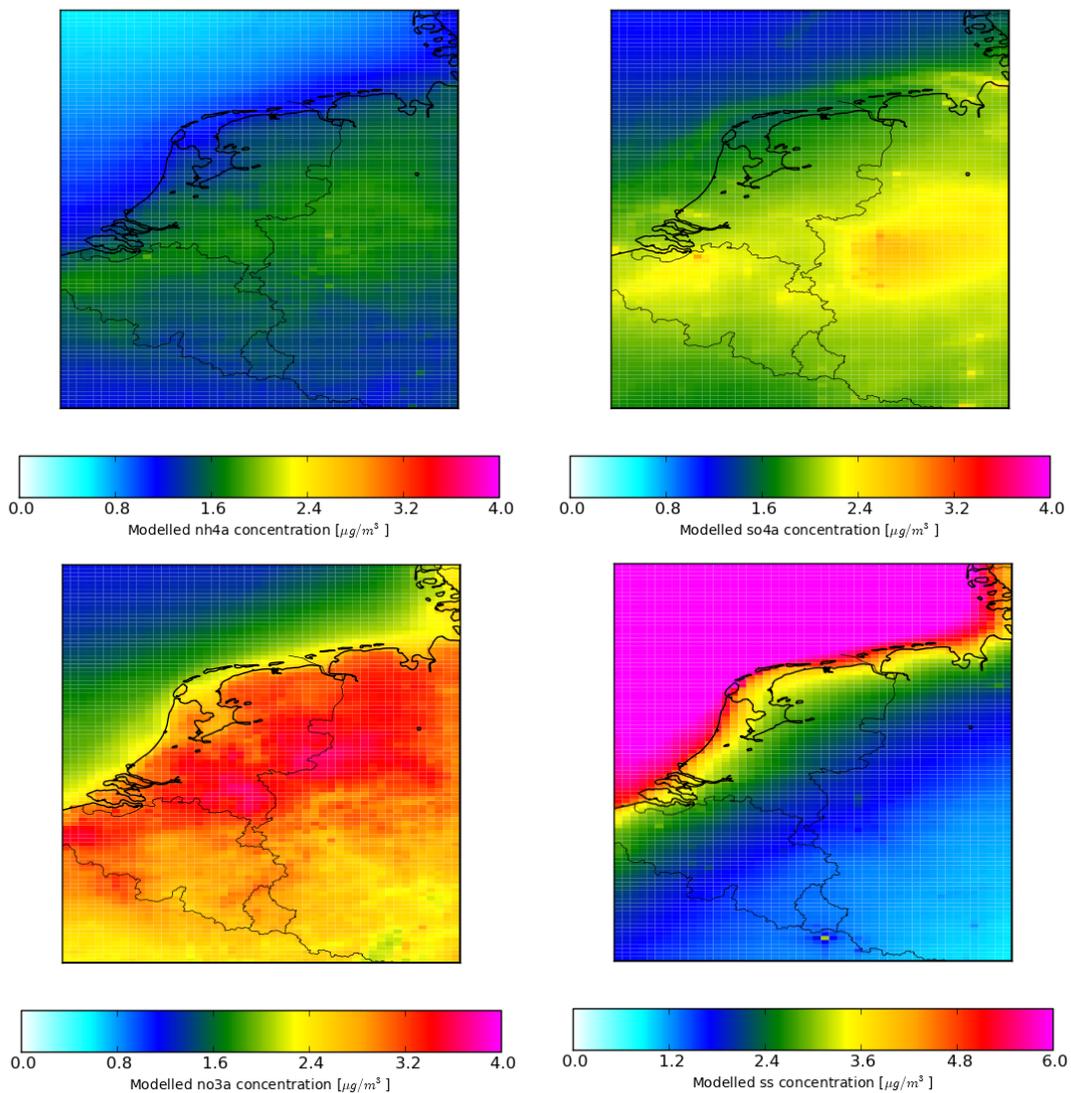


Figure 10 Average modelled concentrations of Ammonium (top left), Sulfate (top right), Nitrate (bottom left) and sea salt (bottom right) for 2007-2009

### 4.3 Model evaluation

The performance of the new version 1.8 of LOTOS-EUROS using the emission data described above is validated against measurements from the National Air Quality Monitoring Network (NAQMN) for the year 2009. First, we look at total  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  annual mean concentrations, as well as PM components and SIA precursors. For carbonaceous aerosol, data from the BOP measurement campaign (August 2007 – October 2008) were used, as these are not available in the NAQMN data. Additional to the evaluation of modelled annual mean concentrations, the extent to which the model correctly reproduces temporal variability in concentrations will be discussed as well.

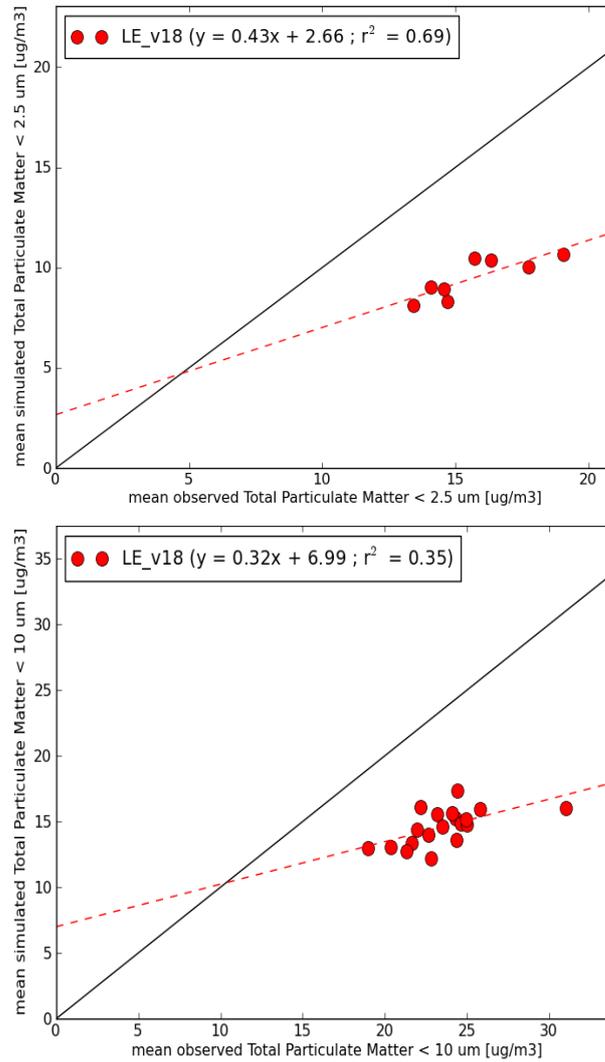
4.3.1  $PM_{10}$  and  $PM_{2.5}$ 

Figure 11 Mean observed vs modelled concentrations of  $PM_{2.5}$  (top) and  $PM_{10}$  (bottom). Observation data used are regional and suburban stations from the NAQMN, 2009

Figure 11 shows the comparison of modelled versus measured annual mean concentrations for  $PM_{2.5}$  (top) and  $PM_{10}$  (bottom) for the year 2009. LOTOS-EUROS underestimates both total and fine PM at all stations by about 40%. Time correlations ( $R^2$ ) around 0.50 were found (see as an example Figure 12: Vredepeel,  $R^2$  of 0.61 and 0.51 for  $PM_{2.5}$  and  $PM_{10}$ , respectively).

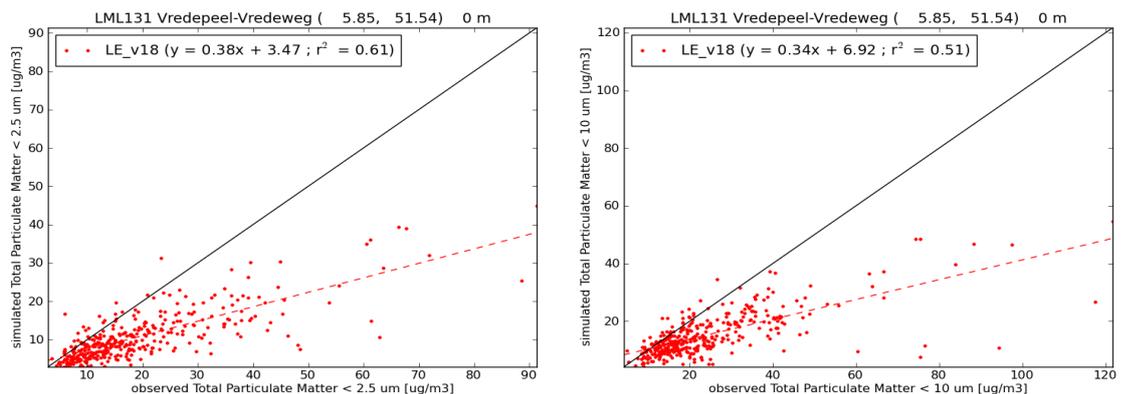


Figure 12 Daily mean observed vs modelled concentrations of  $PM_{2.5}$  (left) and  $PM_{10}$  (right) for LML station Vredepeel

#### 4.3.2 *PM components*

To address the composition of  $PM_{10}$  and  $PM_{2.5}$  and the cause of the underestimation of the total concentrations, we first look at the composition data available from the NAQMN. These provide data for Sulfate, Nitrate, Ammonium and Sodium. In Figure 13 we compare the annual mean modelled concentrations to those observed. Overall, the components do not show large systematic biases, except for nitrate. LOTOS-EUROS underestimates the measured nitrate concentrations by about 40%. Wichink Kruit *et al.* (2012) show that the formation of coarse mode nitrate in LOTOS-EUROS is underestimated, which is partly reality and partly due to filter artefacts (Weijers *et al.*, 2012). For Sulfate, Ammonium and Sodium, the annual modelled means are typically within 15% of the observed value. Moreover, the spatial gradients are well captured by the model as the spatial correlation coefficients vary between 60 and 90%. The temporal variation of  $NH_4$ ,  $NO_3$  and Na concentrations is reproduced by the model to the same degree as for total  $PM_{10}$ , whereas for  $SO_4$  20 - 55% of the temporal variation is captured. In the model Ammonium is bound to Sulfate and Nitrate. Hence, the close agreement between model and measurements for Ammonium in contrast to the (slight) underestimation for Nitrate and Sulfate may indicate that the missing Nitrate is associated with another cation, e.g. Sodium or Calcium.

Considering the relatively good agreement between measured and modelled concentrations for the SIA components when compared to total  $PM_{10}$  and  $PM_{2.5}$ , the underestimation of total PM cannot be explained by biases in the model results for the SIA components.

The agreement between the measured (during the BOP campaign, 2007-2008) and modelled primary PM components EC and POM, aggregated into total carbonaceous aerosol, is displayed in Figure 14 (left). This plot shows a marked underestimation of carbonaceous aerosol, of which the model captures about 40%. This underestimation is caused by both EC and POM. The extent to which the temporal variation is reproduced depends to a large extent on location, ranging from 19 % (Hellendoorn) to 52 % (Breda). As an example, the right panel of Figure 14 shows the daily mean concentrations for Vredepeel, with a temporal correlation factor of 0.38. Mineral dust concentrations are overestimated in the model by more than a factor of 2, but the temporal and geographical variation in the measurements are reproduced reasonably well (see Figure 15). A day with exceptionally high dust

concentrations at the end of January 2008 was reproduced by the model at the right day and – apart from Cabauw, where the modelled concentration far exceeds the measurements – the modelled concentration far exceeds the measurements – the right concentrations.

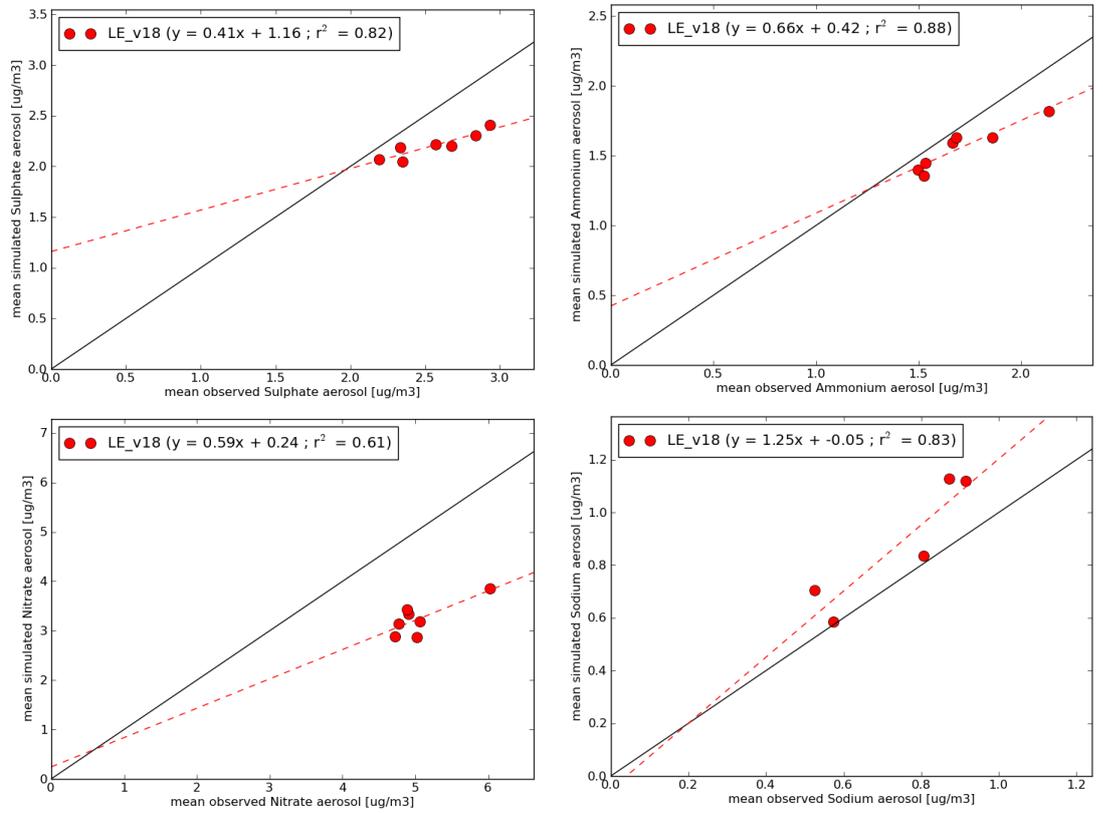


Figure 13 Annual mean observed vs modelled concentrations of Sulfate (top left), Ammonium (top right), Nitrate (bottom left) and Sodium (bottom right) aerosol for 2009

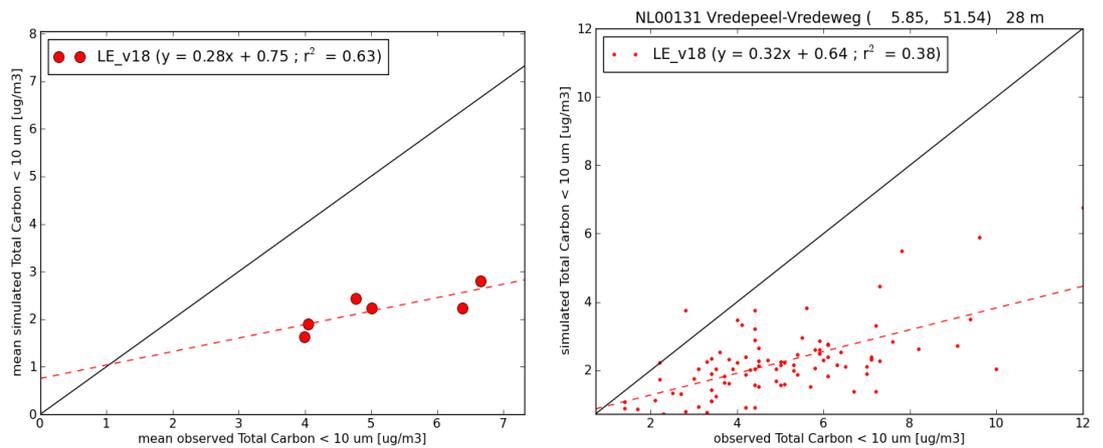


Figure 14 Observed vs modelled concentrations of carbonaceous aerosol for August 2007 – October 2008. Left: annual mean for all locations; Right: daily mean for Vredepeel

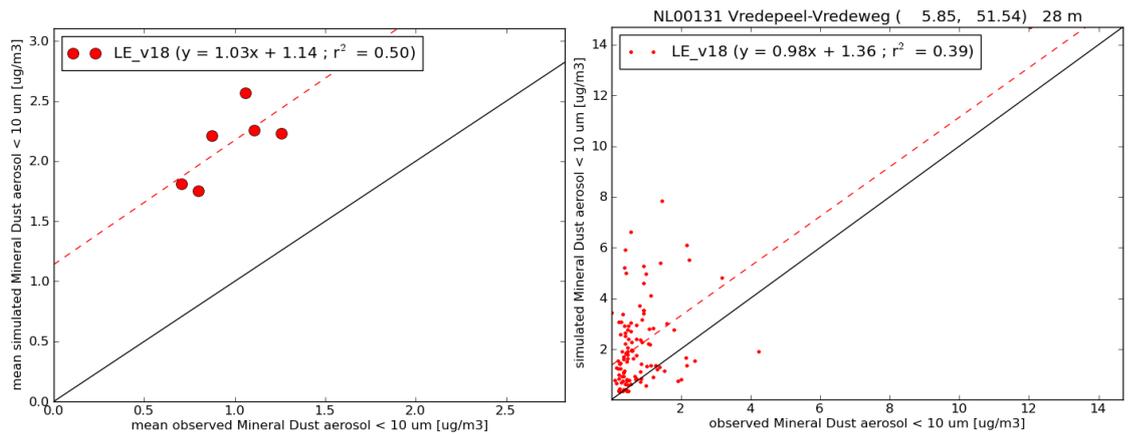


Figure 15 Observed vs modelled concentrations of mineral dust for August 2007 – October 2008. Left: annual means for all locations; Right: daily means for Vredepeel

#### 4.3.3 SIA precursors

Evaluation of the SIA precursors provides a means to build more confidence in the model performance for establishing the origin of the secondary components. Furthermore, evaluation of the primary components yields information on the quality of the emission distribution, the mixing and transport as well as the overall lifetime of the components. Hence, the degree of agreement between modelled and measured  $\text{SO}_2$  and  $\text{NO}_x$  concentrations can be used as indicator for the model performance of primary PM components like EC that are emitted along with these precursor gases, but for which less measurements are available.

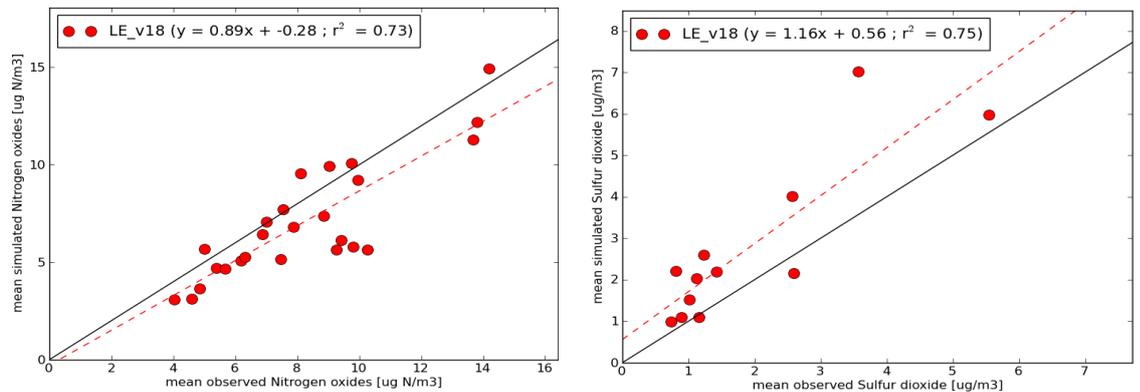


Figure 16 Annual mean observed vs modelled concentrations of  $\text{NO}_x$  (left) and  $\text{SO}_2$  (right) for 2009

Figure 16 compares modelled  $\text{NO}_x$  and  $\text{SO}_2$  concentrations to those observed.  $\text{NO}_x$  concentrations are on average underestimated by about 20%. The spatial correlation is 0.73, indicating that the general patterns are modelled reasonably well.  $\text{SO}_2$  concentrations are overestimated on most stations. Figure 17 shows the time correlation for  $\text{NO}_x$  and  $\text{SO}_2$  for Vredepeel, which is representative for the performance over all stations. The scatter around the linear fit for  $\text{SO}_2$  is larger than for the secondary components, which can be explained by the shorter lifetime and

higher dependence on the correctness of the emission distribution, model resolution and station representativeness.

For the evaluation of Ammonia we refer to Wichink Kruit *et al.* (2012). As the NAQMN stations are located in Ammonia source regions, they compared the Ammonia concentrations to observations in nature areas. Results showed that the model is able to capture the gradients across the Netherlands quite well and that the model slight overestimates Ammonia levels in nature areas whereas those in agricultural areas are underestimated.

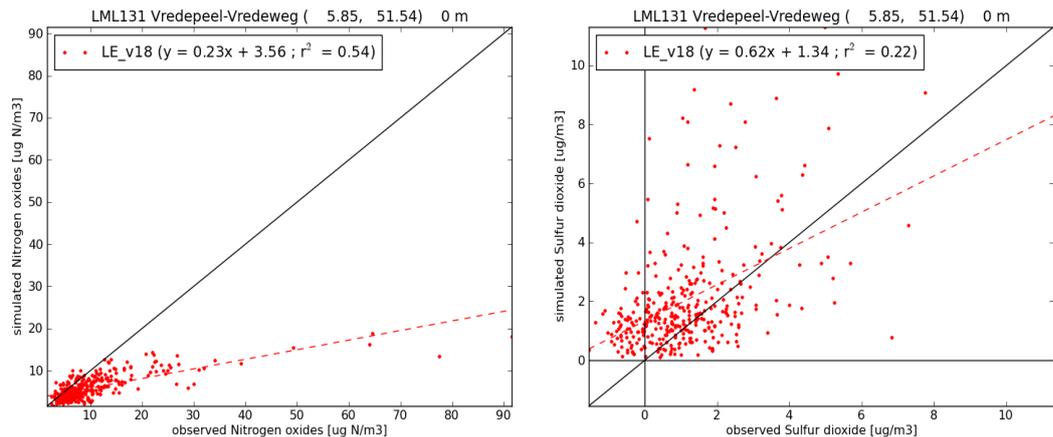


Figure 17 Daily mean observed vs modelled concentrations of NO<sub>x</sub> (left) and SO<sub>2</sub> (right) for LML station Vredepeel

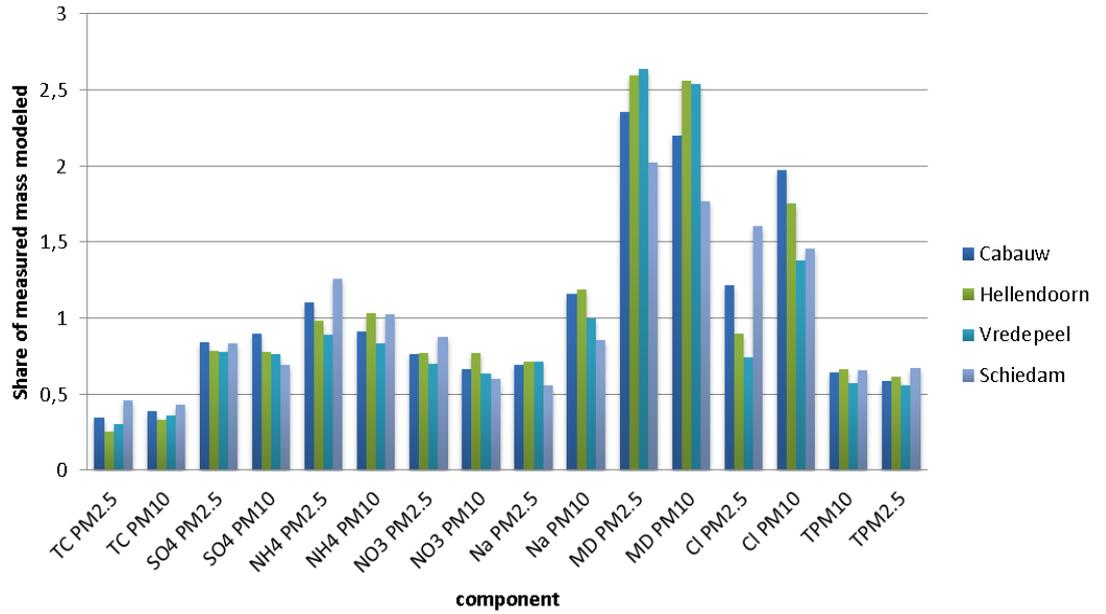
#### 4.3.4 Missing mass

To further investigate the origin of the missing mass in modelled PM<sub>2.5</sub> and PM<sub>10</sub>, data from the BOP1 measurement campaign (August 2007 – October 2008) is used. The comparison between measured and modelled average annual concentrations is summarized in Figure 18. Elemental and organic carbon are aggregated, as the measurements are more accurate for total carbon than for the separate components.

On average for the four stations, 63% of total PM<sub>10</sub> mass and 61% of PM<sub>2.5</sub> is modelled. For the SIA components, only 20% (for fine Nitrate) down to 5% (Ammonium aerosol) is missing, making a bias correction for these substances unnecessary. Figure 18 shows that the two components that contribute the most to total PM mass (TC and NO<sub>3</sub>) are the ones the model underestimates most. The underestimation of NO<sub>3</sub> is about equal for the fine and the coarse fraction, whereas for carbonaceous matter, almost all missing mass is associated with the fine fraction.

Although the modelled mineral dust levels are a factor 2.1-2.5 higher than the measured levels, the impact on total PM is limited because of the low absolute contribution of mineral dust.

### Share of measured mass modeled by LOTOS-EUROS



### Cabauw

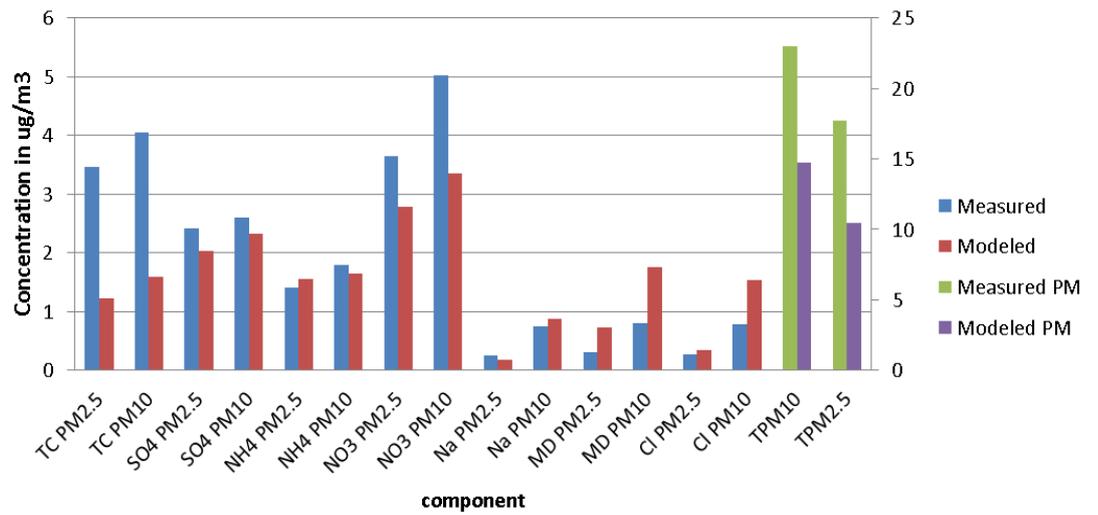


Figure 18 Comparison of modelled and measured concentrations of PM components for the BOP1 campaign period (Aug 2007 – Oct 2008). Top: share of measured mass captured by the model; bottom: measured and modelled concentrations for Cabauw (for total PM<sub>10</sub> and PM<sub>2.5</sub>, the right-hand y axis applies. A share of 1 means observed and modelled mass are equal

## 5 Source apportionment technique

### 5.1 Source apportionment module

In order to track the origin of the components of particulate matter, a source apportionment module for LOTOS-EUROS was developed. This module uses a labelling approach, which aims at tracking the source contribution of a set of sources through the model system. The emissions are categorized in different source categories (e.g. countries, sector, fuel) and labelled accordingly before the model is executed. The actual source allocation takes place when the emission data are processed each hour.

The source apportionment module works with fractions: the total concentration of each substance in each grid cell is modelled as before, but next to this the fractional contribution of each label to every substance is calculated. During or after each process, the new fractional contribution of each label is defined by calculating a weighted average of the fractions before the process and the concentration change during the process. Whereas this is rather straightforward for the linear processes in the model (such as vertical diffusion or deposition), it is more complicated for non-linear processes, most notably the atmospheric chemistry.

Due to the many feedbacks present in the chemistry of the atmosphere, it is impossible to provide an exact source attribution. Therefore, the choice was made to provide a source attribution that is valid for the current atmospheric conditions. Furthermore, the labelling routine is only implemented for chemically active tracers containing a C, N or S atom, as these are conserved and traceable. In order to trace components containing these atoms through the chemistry routine, it is necessary to know, for each component, the amount reacted as well as the amount and origin of the produced amount. The source allocation of the produced species will be calculated from the source allocations of the original species containing the N, C or S atoms involved in the reactions. Reactions that remove a substance from the atmosphere will not change the source apportionment of that substance, as each molecule of that substance has the same chance to react independent of its source.

In

Figure 19, a schematic overview of the application of the labelling module is given, for one time step. The adjust process is applied only once per hour while the other processes consist of smaller time steps.

For a more in-depth description of the source attribution module and the way the source contributions are tracked through the different model processes, we refer to Schaap *et al.* (2012).

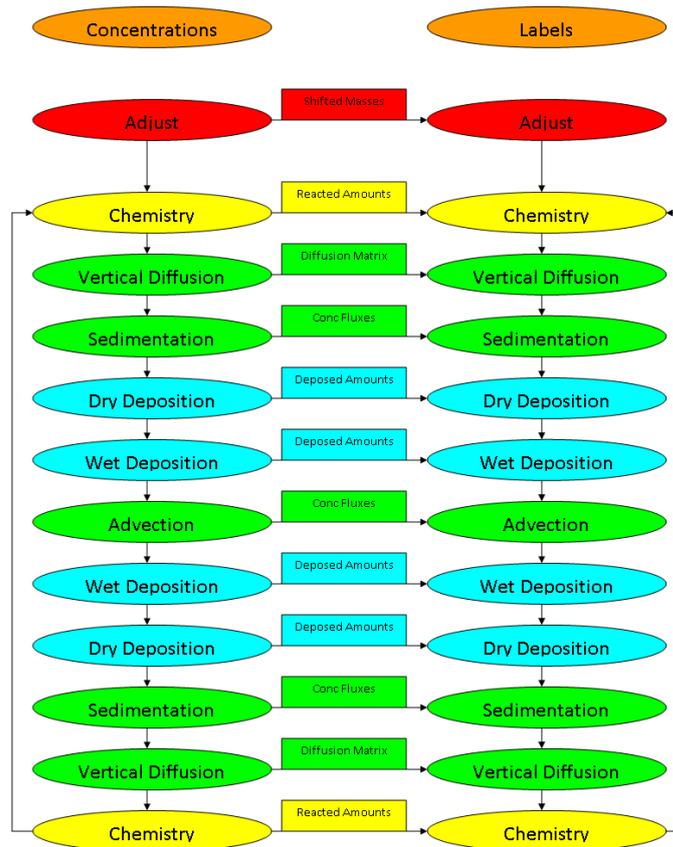


Figure 19 Schematic of LOTOS-EUROS including the labelling tool that keeps track of all source contributions based on the concentration changes and fluxes for each process

## 5.2 Performance evaluation

The performance evaluation of the source apportionment code was done with three dedicated experiments: one for the linear processes, one for the advection routine and another one for the chemistry.

To test the labelling technique for the linear processes, a model run was performed for the primary PM components. These include black carbon (BC), primary fine particulate matter ( $PPM_{2.5}$ ) and primary coarse particulate matter ( $PPM_c$ ). In the LOTOS-EUROS emission module, BC emissions are estimated as a percentage of the  $PPM_{2.5}$  emissions. Within this simulation the BC fraction of these components was labelled. Thus, the BC concentration was calculated twice: as a separate tracer and as the fraction of the  $PPM_{2.5}$  concentration tagged with the BC label. These two methods should yield the same BC concentration to prove that the labelling module functions correctly for the linear processes. Furthermore, the sum of all the labelled fractions must remain equal to 1.

Figure 20 shows the fraction of  $PPM_{2.5}$  with the label 'BC' plotted against the ratio of the tracer concentrations of BC and total  $PPM_{2.5}$  for the combination of the linear processes in the model emission, vertical diffusion and the adjustment of the

vertical layers. The left panel displays the results for January 2007 and shows that the fractions of label 'BC' for  $\text{PPM}_{2.5}$  are very close to the ratio between BC and  $\text{PPM}_{2.5}$ . The small deviations are caused by the adjust process at the first day. To illustrate that these small deviations are eliminated in time, the right panel of Figure 20 shows the comparison for the whole month except the first day. It is clear that the small errors caused by machine precision are eliminated and that the source allocation routine for these processes functions correctly.

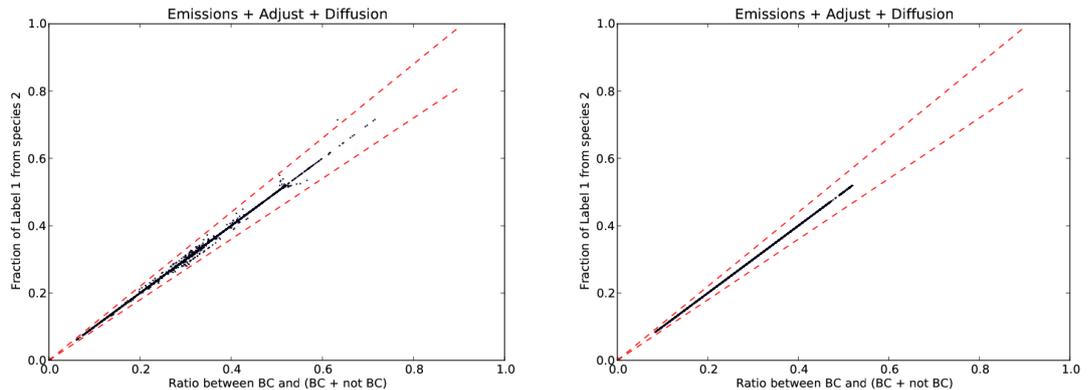


Figure 20 Ratio between BC and total  $\text{PPM}_{2.5}$  against the label fraction BC in  $\text{PPM}_{2.5}$  with emissions, the adjust process and the vertical diffusion involved in the model. Left for all hours in January 2007, right for January 2007 except the first day

To test the implementation of labelling in the advection routine, the primary aerosol components BC,  $\text{PPM}_{2.5}$  and  $\text{PPM}_c$  were used again. Two sets of model runs were performed for one year:

- A simulation with labels on Belgian, Dutch, German and other emissions;
- A set of simulations including only the Belgian, Dutch or German emissions, respectively.

Theoretically, the label fraction of each country multiplied with the total concentration (from the first simulation) should be equal to the concentration calculated with only the emission from that country in the second set of simulations.

Here we show the results for the Dutch contribution to BC. In the left panel of Figure 21, the annual mean concentrations BC with the label 'Dutch' are given. The right panel corresponds with the annual mean BC concentration from the model run with only Dutch emissions. The simulation with the Dutch only emissions differs by a few per cent from that using the labelling routine. These small differences occur because the Walcek advection algorithm, which is used in the model, is not linear. The effects are visible especially where large concentration gradients appear or are induced. When emissions from a country are removed from the model input, as is done here, large concentration gradients are introduced, resulting in an unnatural flux at the border cells. In a labelling simulation, these artificial gradients and associated change in fluxes do not occur. As such, one could argue that the labelling technique provides a more consistent approach.

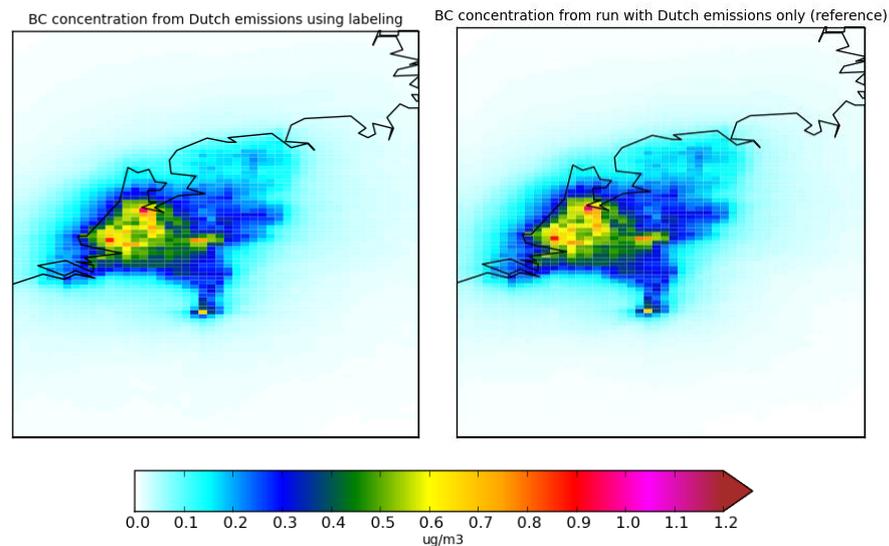


Figure 21 Left Annual mean concentration BC for the Dutch labelled emissions. Right: Annual mean concentration BC with only Dutch emissions involved in the model

For the test application for the chemistry module, three labels are defined:

- 5 % Dutch emissions
- 95 % Dutch emissions
- Other emissions

For comparison a simulation was made with a 5% reduction of the Dutch emissions. Note that for each source the emissions of the whole mix of emitted species is reduced. Theoretically, the results of both simulations will not give the same answer because the chemistry mechanism is not linear. Through interactions of the emitted species with the oxidant concentrations differences are induced between both simulations. Below, we discuss a reaction product from the degradation of non-methane volatile organic carbons (NMVOC), methylglyoxal (MGLY). This is a chemically very active substance with a short lifetime.

Figure 22 shows the 5% contribution of Dutch sources to MGLY for the labelling simulation and the reduction simulation. NMVOCs are derived from both natural and anthropogenic sources. The results indicate that anthropogenic emissions are not the dominant source for MGLY. However, the labelled 5% Dutch contribution is a factor 3 higher than the concentration difference due to a 5% reduction in all Dutch emissions. In addition, the patterns are not at all the same. It appears that the change in chemical regime due to the reduction of the full mixture has a large impact on the estimated contribution. To validate this assumption a second simulation was performed with only a 5% reduction on the Dutch NMVOC emissions, keeping all other emissions the same. The right panel of Figure 22 shows the concentration change for MGLY for this simulation. The results are much closer to the label simulation, both in magnitude and gradients. Differences are now at most 10% and occur in regions where anthropogenic emissions are largest and non-linearity in the chemistry and its impact on the solver is expected to be largest. These results clearly illustrate the difference between source apportionment based on scenarios versus a labelling technique, and that the labelling technique is more reliable, especially for reactive species.

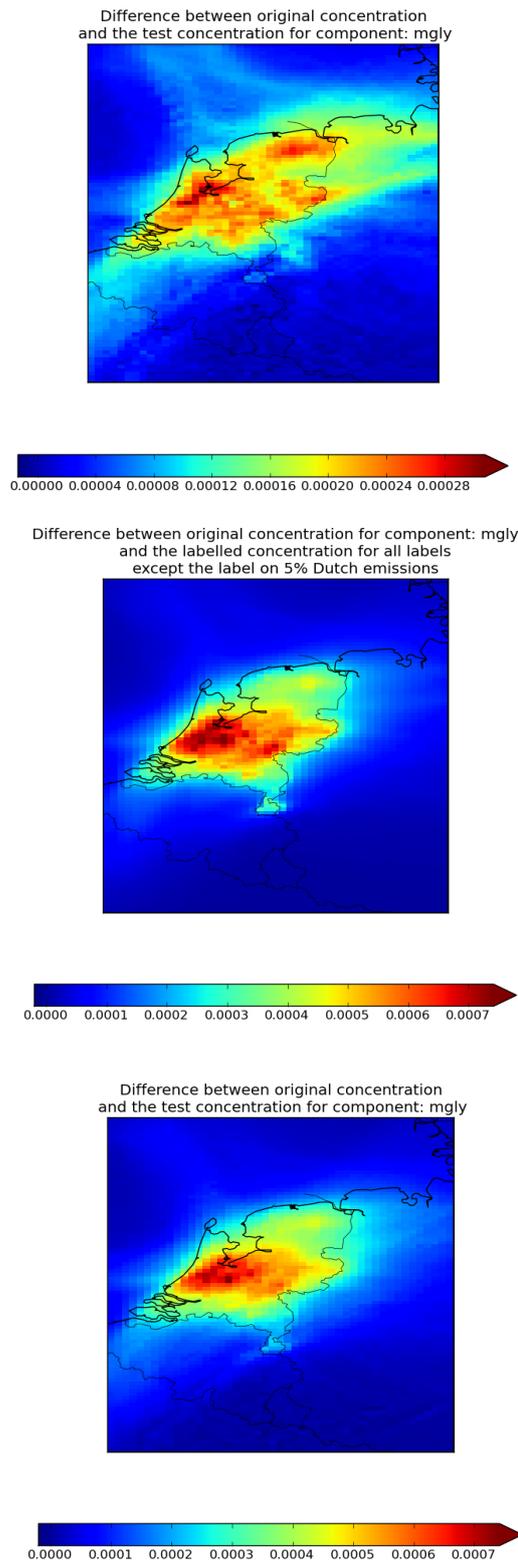


Figure 22 Comparison between a scenario result and labelling simulation for the 5% Dutch contribution to MGLY. Panels show the difference in MGLY concentration due to a decrease of all Dutch emissions by 5% (top), the labelled 5% contribution (middle) and the difference due to a decrease of Dutch VOC emissions by 5% (bottom)



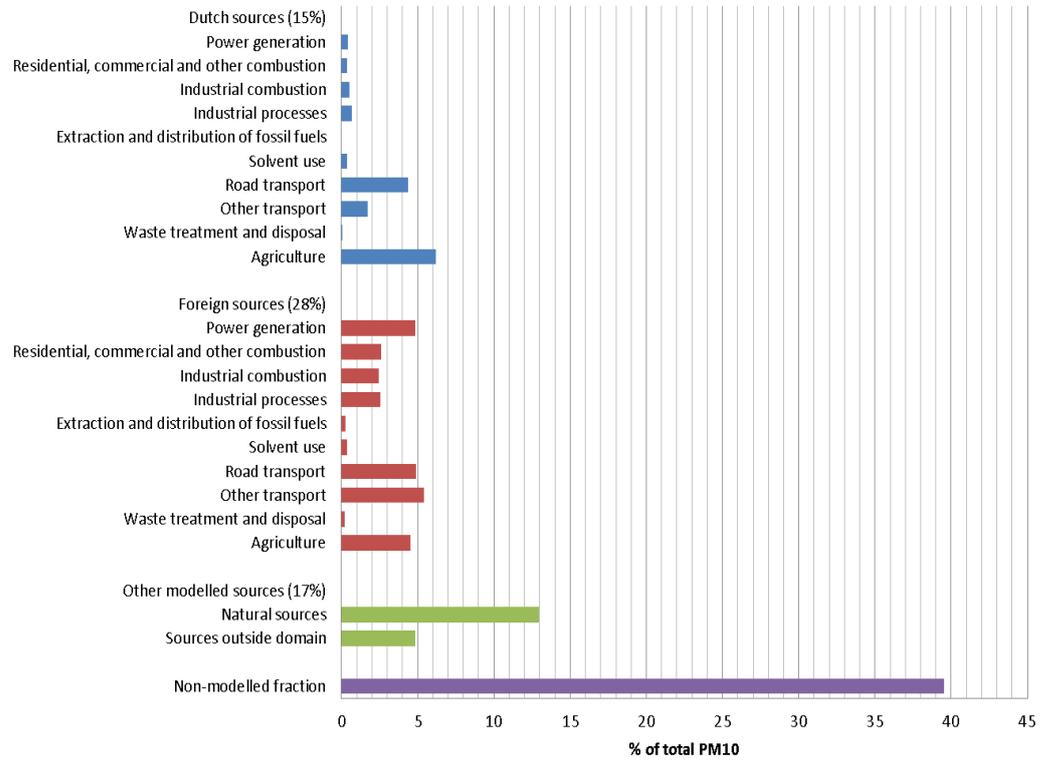
## 6 Source attribution of PM for the Netherlands

### 6.1 Origin of particulate matter in the Netherlands

Figure 23 summarizes the source attribution for particulate matter in the Netherlands for 2008, relating the source attribution found by LOTOS-EUROS to the total observed PM concentrations. The non-modelled fraction was defined by subtracting the modelled mass from the average measured PM concentration for 2008 from Velders *et al.* (2009),  $23.3 \mu\text{g}/\text{m}^3$  for  $\text{PM}_{10}$  and  $14.6 \mu\text{g}/\text{m}^3$  for  $\text{PM}_{2.5}$ . Of the modelled PM, representing 60% of the measured PM mass, 70-80% of  $\text{PM}_{10}$  and 80-95% of  $\text{PM}_{2.5}$  in the Netherlands is man-made. About 1/3 of anthropogenic  $\text{PM}_{10}$  is of Dutch origin and 2/3 originates in foreign countries. For  $\text{PM}_{2.5}$ , a domestic contribution of 30% was found. These figures change with location, with higher foreign shares along the eastern borders and higher domestic contributions in the densely populated western part of the country. The Dutch sectors with the largest contribution to total modelled  $\text{PM}_{10}$  mass in the Netherlands are agriculture and transport, together responsible for 85% of the total Dutch contribution. The foreign contribution is more equally divided over the different sectors. This is also true for  $\text{PM}_{2.5}$ .

The source apportionment is different for the different components of particulate matter. In general, the Dutch contribution to the concentration of primary species is larger than for secondary species. The sectoral origin for some substances is quite diffuse whereas for others, one or two sectors are dominant. Which sectors are important depends also on location and on total PM concentration. For the Netherlands as a whole, the foreign share grows as concentrations increase. These subjects are addressed in detail in the next sections.

### Origin of PM10 in the Netherlands



### Origin of PM2.5 in the Netherlands

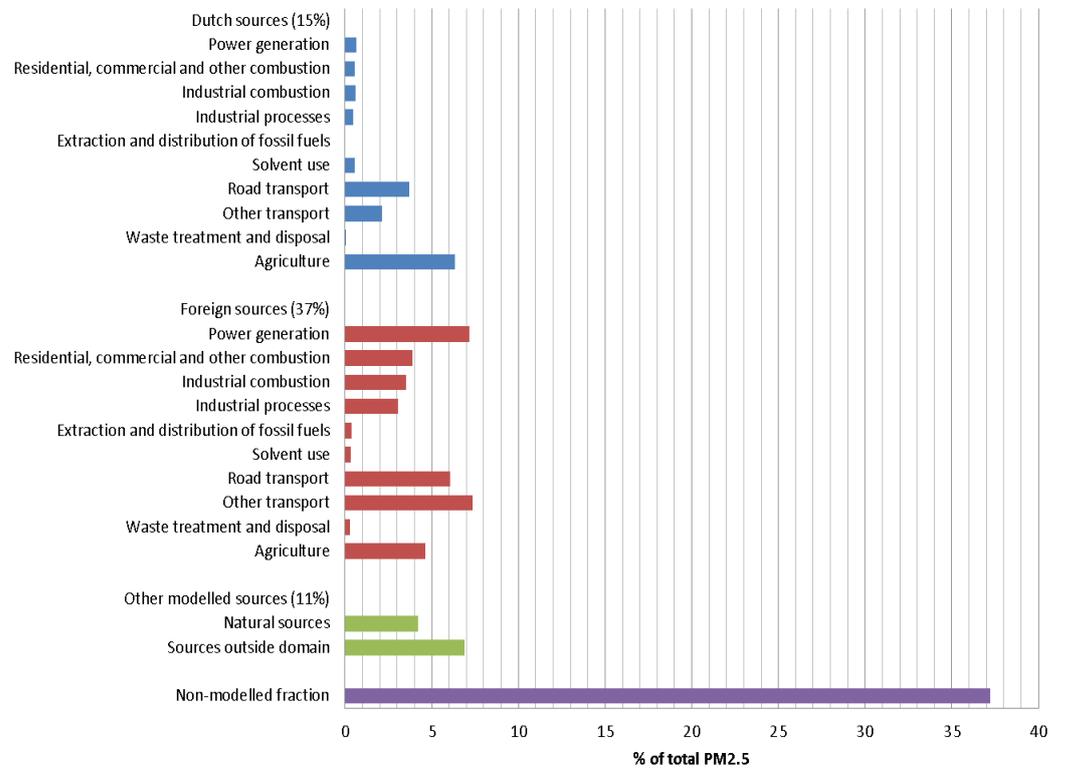


Figure 23 Origin of particulate matter in the Netherlands

## 6.2 Annual average distributions

### 6.2.1 National versus foreign contributions

In this section we first look at the modelled national versus foreign source contributions to total  $PM_{10}$  and  $PM_{2.5}$  across the Netherlands. The source attribution of the several primary and secondary PM components is discussed after that.

The national contribution to modelled  $PM_{10}$  ranges from 25 % near the border to 45% in the most populated and industrialised areas of the Netherlands. For the foreign emissions, the situation is reversed: the contribution to  $PM_{10}$  reaches 50% in the border regions and decreases to 35% near the western coast and in densely populated areas. These contributions are displayed in the lower panels of Figure 24. The remainder of the modelled  $PM_{10}$  is caused by natural emissions (i.e. sea salt), which contributes up to 35% of total modelled  $PM_{10}$  near the north western coastline and about 10% near the south eastern border. For modelled  $PM_{2.5}$ , the Dutch and foreign contribution are shown in the upper panels of this figure. The national contribution to  $PM_{2.5}$  levels in the Netherlands is comparable to that of  $PM_{10}$ . The foreign contribution is proportionally larger than for  $PM_{10}$ , ranging from 60% along the borders to 50% in the central and western provinces. This is explained by the fact that coarse particles deposit faster than fine particles, enabling transport of fine particles across larger distances. As sea salt particles are mostly found in the coarse PM fraction, the natural contribution to  $PM_{2.5}$  is smaller than for  $PM_{10}$ .

The modelled Dutch shares of the primary PM components are displayed in Figure 25. The top panels show the national contribution to the concentrations of the carbonaceous aerosols ec (left) and pom (right). For ec, this contribution ranges from 30% at the borders to 70% in the Randstad; For pom, the spatial gradient is smaller than for ec, with contributions ranging from 40 to 75 %. The higher contributions for pom than for ec are mainly caused by organic emissions from agriculture. The spatial distribution of pom looks like a combination of the distributions from ec (which originates mainly from combustion processes) and  $NH_4$ , which is mainly due to agricultural activities. The lower panel shows the Dutch contribution to other primary particulate matter, mainly minerals from industrial processes and wear. The Dutch contribution to the total modelled concentration peaks in the Randstad, especially the industrial Rotterdam and Amsterdam areas where the domestic share is 60-80%. In the rest of the country, Dutch emissions contribute 30 to 50% of the PPM concentration. As none of the primary PM components are associated with natural emissions and the boundary of the model domain is not important for these substances, the rest of the mass for the primary components comes from foreign countries. The lower right panel shows the Dutch share of dust concentrations, which ranges from 30 -45% in the North to 60-70 % in the rest of the country. The contribution from outside the model domain for dust is as high as 45 % in the North. This is associated with exceptionally high concentrations on a few days, possibly episodes of Saharan desert dust.

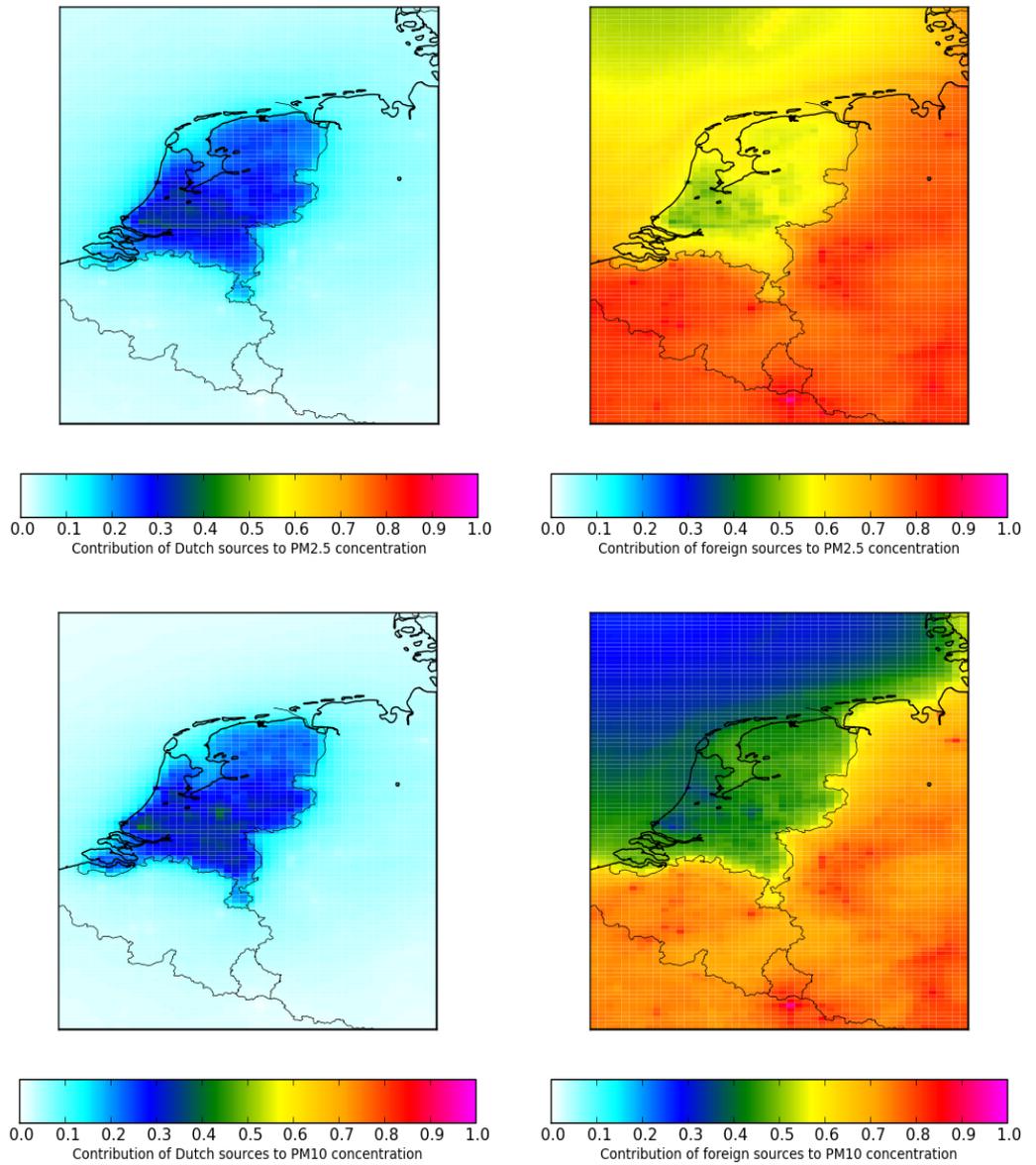


Figure 24 Dutch (left) and foreign (right) contributions to average PM<sub>2.5</sub> (top) and PM<sub>10</sub> (bottom) concentrations

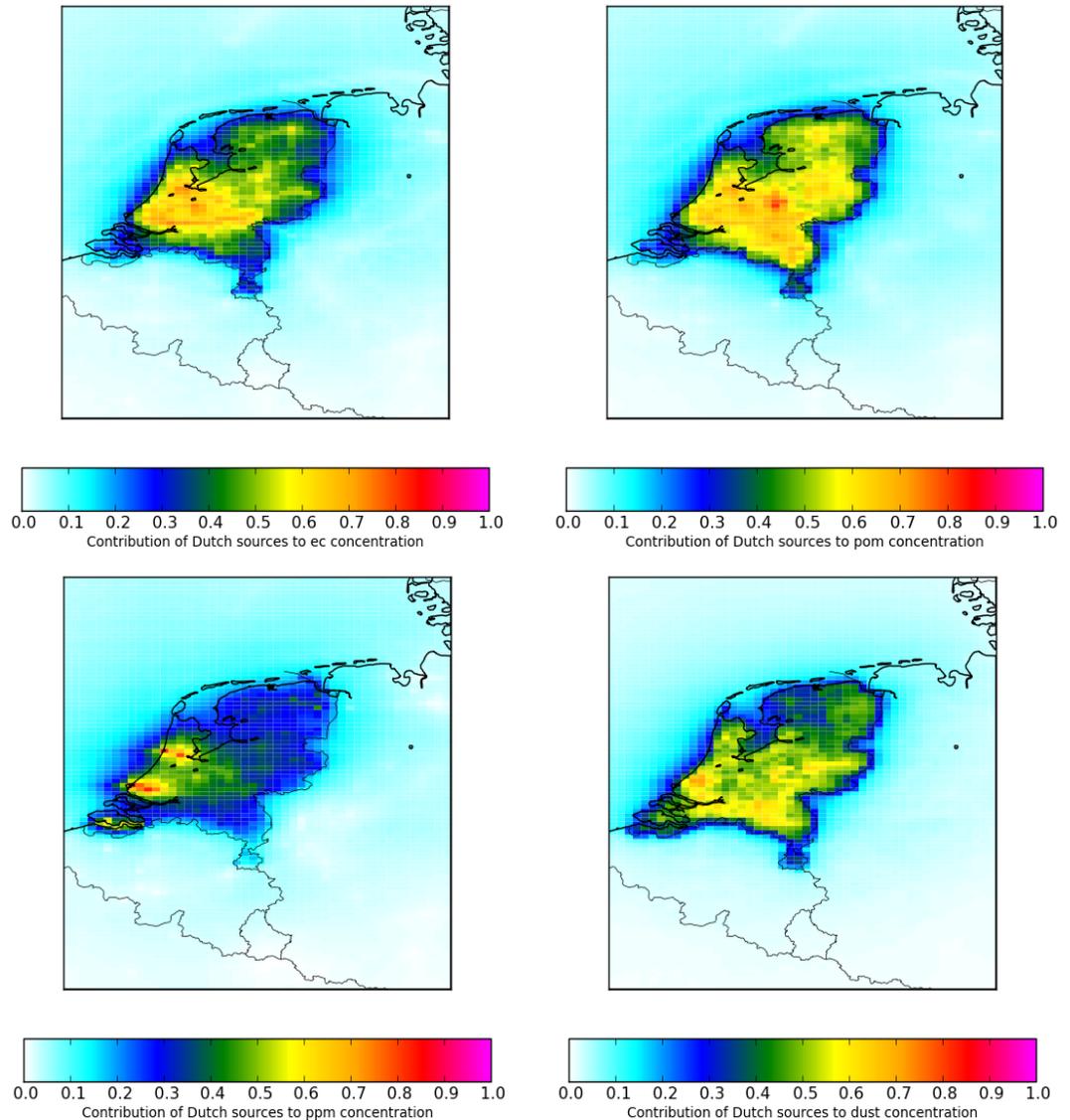


Figure 25 Dutch contribution to average ec (top left), pom (top right), ppm (bottom left) and dust (bottom right) concentrations

The contribution of Dutch sources to the modelled concentration of secondary PM species  $\text{SO}_4$ ,  $\text{NO}_3$  and  $\text{NH}_4$  is displayed in Figure 26. The domestic contribution to the concentrations of these secondary species is in general smaller than for the primary species. For  $\text{NO}_3$ , the domestic share to the total modelled PM concentration in the Netherlands is 10-20% and constant across the country. Around 10% of the  $\text{NO}_3$  concentration comes from the boundaries of the model domain, 75-80% originates from foreign sources. For  $\text{NH}_4$ , which originates from  $\text{NH}_3$ , domestic shares range from 50% in at the borders to 75% in Gelderland and Noord-Brabant, where intensive agricultural activities are located. Foreign sources are responsible for 25-35% of the total  $\text{NH}_4$  concentration in the Netherlands, with the highest shares along the borders. Note that for nitrogen-containing species, the source apportionment of  $\text{NH}_4$  is based fully on that of  $\text{NH}_3$ , whereas  $\text{NO}_3$  is attributed to sources emitting  $\text{NO}_x$ . The importance of this assumption and the

impacts of choosing another way of attributing  $\text{NH}_4$  and  $\text{NO}_3$  to the source sectors is discussed in Chapter 7.

The domestic share of modelled  $\text{SO}_4$  concentrations is very small, except for the Rotterdam harbour and the main waterways where the contribution of Dutch sources reaches a maximum of 20%. Across the Netherlands, foreign sources are contributing 65 – 75% of the total modelled  $\text{SO}_4$  concentrations and the remainder comes from outside the model domain. The origin of the secondary species discussed here is fully anthropogenic.

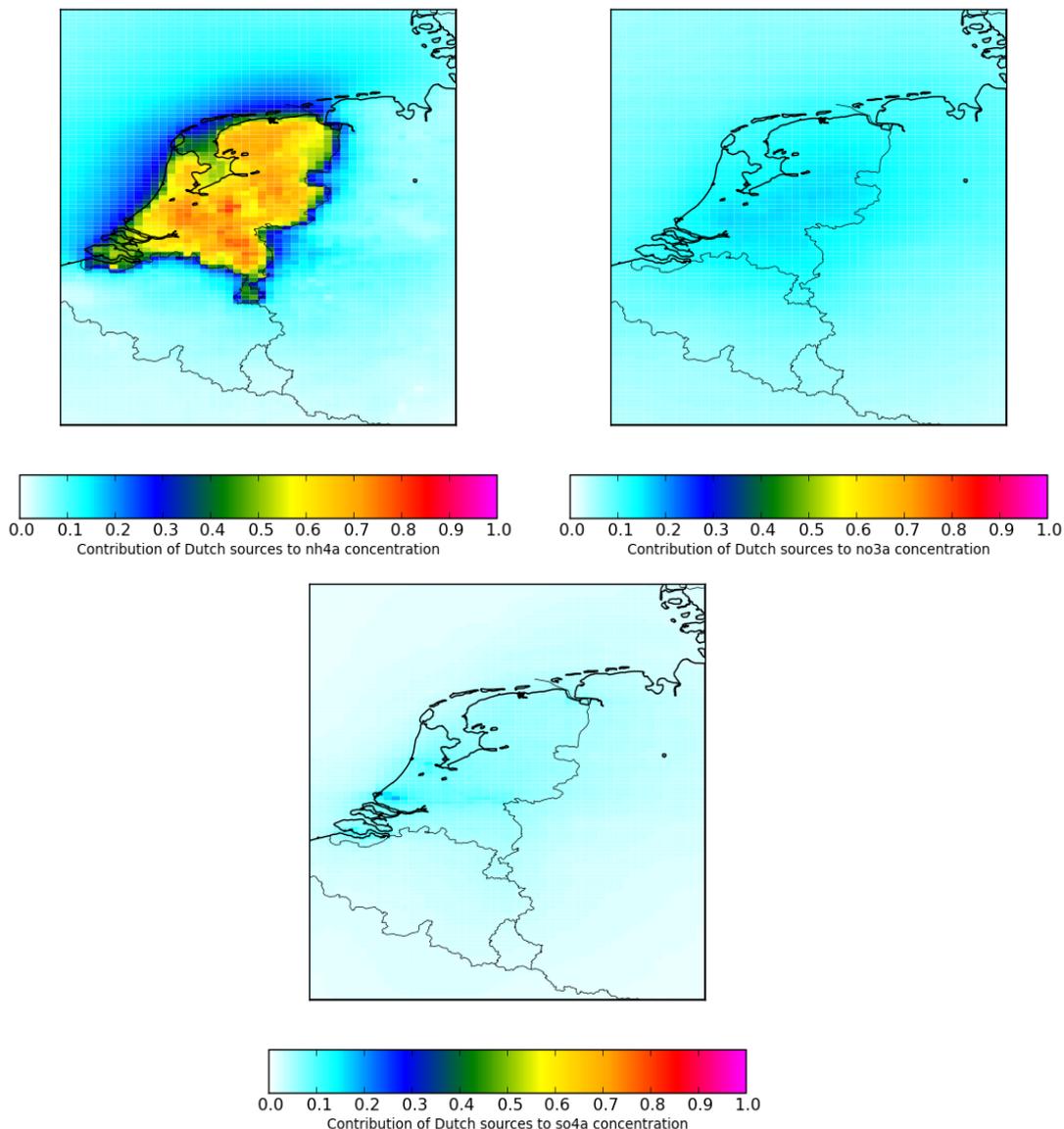


Figure 26 Dutch contribution to average  $\text{NH}_4$  (top left),  $\text{NO}_3$  (top right), and  $\text{SO}_4$ (bottom) concentrations

The average apportionment of modelled PM and its components in the Netherlands as a whole and at five BOP measurement locations (see Figure 27, the Schiedam and Rotterdam sites are combined) is displayed in Figure 28. For the Netherlands as a whole, the foreign contribution to total  $PM_{10}$  is larger than the domestic contribution (45 vs 25 % of total modelled  $PM_{10}$ ). PM labelled as natural contributes around 20%, whereas the label 'boundary of the model domain' contributes 10%. Looking at the BOP locations, we see that the foreign contribution to total  $PM_{10}$  concentrations is larger for Vredepeel, Hellendoorn and Breda, located relatively close to the German and Belgian borders. Rotterdam is the only BOP location for which the Dutch contribution exceeds the foreign. This is caused by slightly lower absolute concentrations originating from outside the Netherlands, but mainly by higher domestic concentrations. As many PM sources are located in the Rotterdam area, the higher Dutch contribution to PM levels in Rotterdam are mainly caused by sources in Rotterdam and its direct surroundings, which is supported by the lower amount of 'Dutch' PM in Cabauw. The natural contribution represents the sea salt gradient over the country: the absolute contribution is highest in Rotterdam and decreases going east. The concentrations with the label 'boundary of the model domain' are constant across the country.

The foreign contribution to modelled  $PM_{2.5}$  is on average for the Netherlands 58%, whereas the Dutch contribution is about 25% and natural sources contributes 5%. The differences in source apportionment between  $PM_{10}$  and  $PM_{2.5}$  can be explained by the fact that sea salt, the main natural component, is mainly coarse aerosol. As fine particles deposit slower than coarse particles, fine aerosol is transported over larger distances, explaining the higher foreign share.



Figure 27 Map of the BOP measurement locations and LOTOS-EUROS grid cells in which these stations are located. 1 = Schiedam, 2 = Rotterdam (traffic station), 3 = Vredepeel, 4 = Cabauw, 5 = Hellendoorn, 6 = Breda (traffic station)

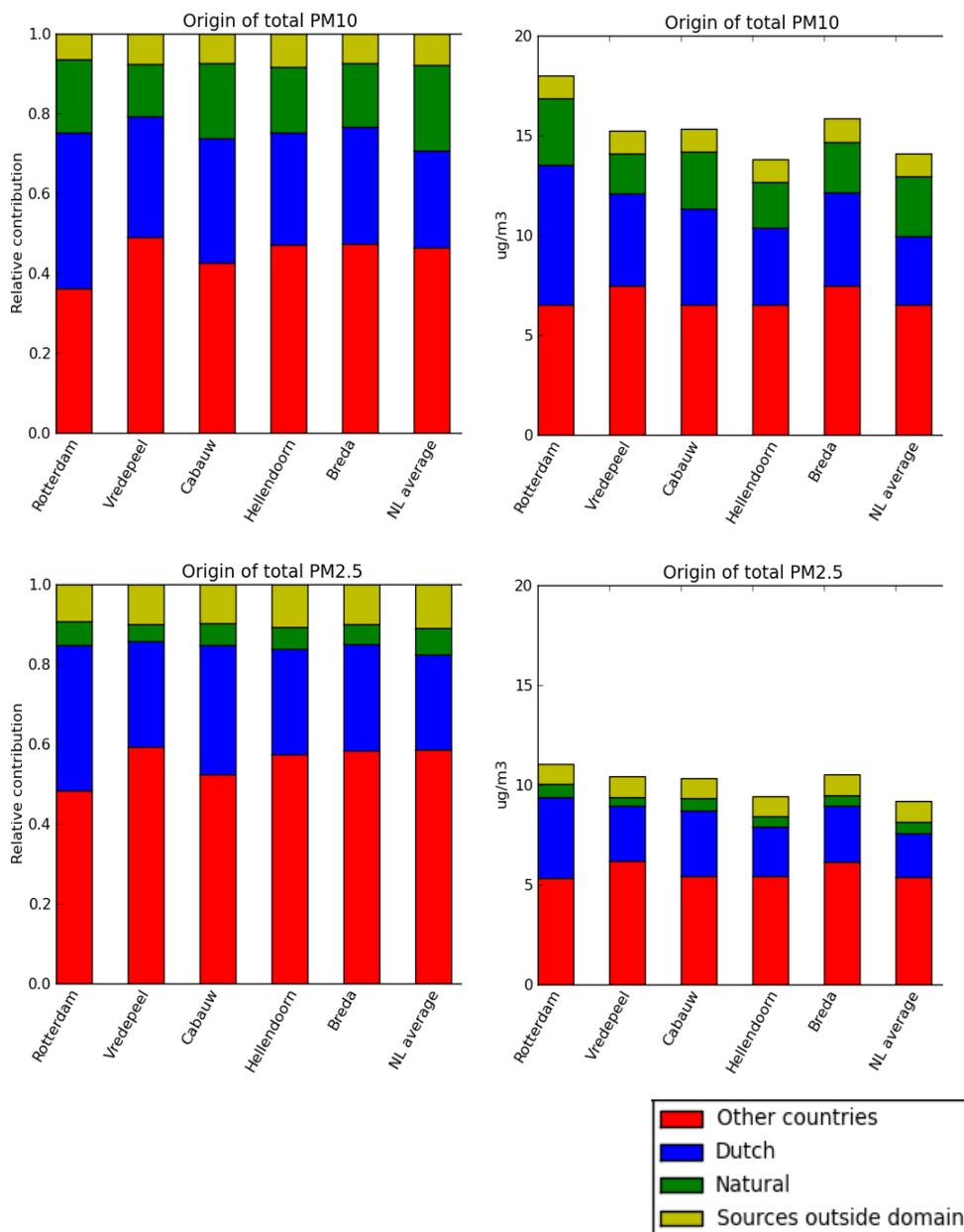


Figure 28 Relative (left) and absolute (right) modelled contributions of Dutch, foreign and natural emissions and emissions from the boundary of the model domain to the modelled total PM<sub>10</sub> (top) and PM<sub>2.5</sub> (bottom) concentrations at the BOP measurement locations and for the Netherlands as a whole

In short, we have seen that the national versus foreign contributions differ greatly between the components considered. They range from mostly national (carbonaceous aerosol, ammonium, dust) to mostly foreign (sulfate, nitrate) or natural (sea salt). Moreover, the origin shows a considerable spatial variation. The Randstad area, with a high population density and large industrial activities, shows a different signature than the more rural areas of the Netherlands.

### 6.2.2 Sectoral contributions

In this section, the contribution from the national and foreign source sectors (SNAP1 level) to modelled particulate matter concentrations in the Netherlands is presented.

Agriculture is the largest domestic source of PM<sub>10</sub>, causing 42 % of the national contribution to average total modelled PM<sub>10</sub> concentrations in the Netherlands. Transport causes another 42% of the domestic contribution to total PM<sub>10</sub> (30% from road transport, 12% from other transport). The remaining 15% is divided among (in decreasing order of importance) industrial processes and combustion, power generation, non-industrial combustion and solvent use. Emissions from extraction/distribution of fossil fuels and waste treatment and disposal do not contribute significantly to PM<sub>10</sub> concentrations over the Netherlands. An overview of the Dutch sectoral contributions to total PM<sub>10</sub> is given in Figure 29 (top left panel).

The sectoral origin of the foreign contribution to Dutch PM<sub>10</sub> concentrations (about 45% of total modelled PM<sub>10</sub>) is displayed in the lower left panel of Figure 29. The contributions are more equally divided among the sectors than for PM with Dutch origin. Road transport, other transport, agriculture, power generation and industrial combustion and processes each cause 15-20 % of the total foreign contribution. Residential heating is causing about 8% of the total foreign share of PM<sub>10</sub> in the Netherlands. The other sectors have marginal contributions.

The sectoral contributions change with location, especially for the Dutch sectors. To illustrate this, domestic and foreign contributions to annual average modelled PM<sub>10</sub> concentrations in the Netherlands at Rotterdam and Vredepeel are displayed in the central and right panel of Figure 29. At Vredepeel, located in an area with intensive agriculture (mainly pig breeding), agriculture is responsible for over half of the Dutch contribution. For Rotterdam, agriculture is less important than for the Netherlands on average, but road transport, other transport (shipping) and industry are more important. As the Rotterdam region combines a high population density with substantial industrial activities, this result is expected.

For some PM components, a few sectors are responsible for the major part of the concentration. Dutch agriculture, for example, is the most important source of NH<sub>4</sub>, responsible for about two-thirds of the total modelled NH<sub>4</sub> concentration in the Netherlands.

Dutch road transport is an important source of EC, contributing 25-40 % to the total modelled EC concentration over the western and central provinces.

For Nitrate aerosol, there is not one dominating sector, but several foreign sectors have significant contributions. Transport is an important source, responsible for more than half of the total modelled Nitrate concentration over the Netherlands. Another important source for Nitrate is power generation. For Sulfate, this sector is the highest contributor. Whereas the Dutch power generation sector is only important near power plants, foreign power generation causes about 25% of the total modelled SO<sub>4</sub> concentration in the Netherlands.

As an illustration, a selection of sectoral contributions to specific pollutants is displayed in Figure 30 (compare with Figure 9 and Figure 10 in Chapter 4). The contributions of all sectors to all PM components for 2008 are listed in Table 2.

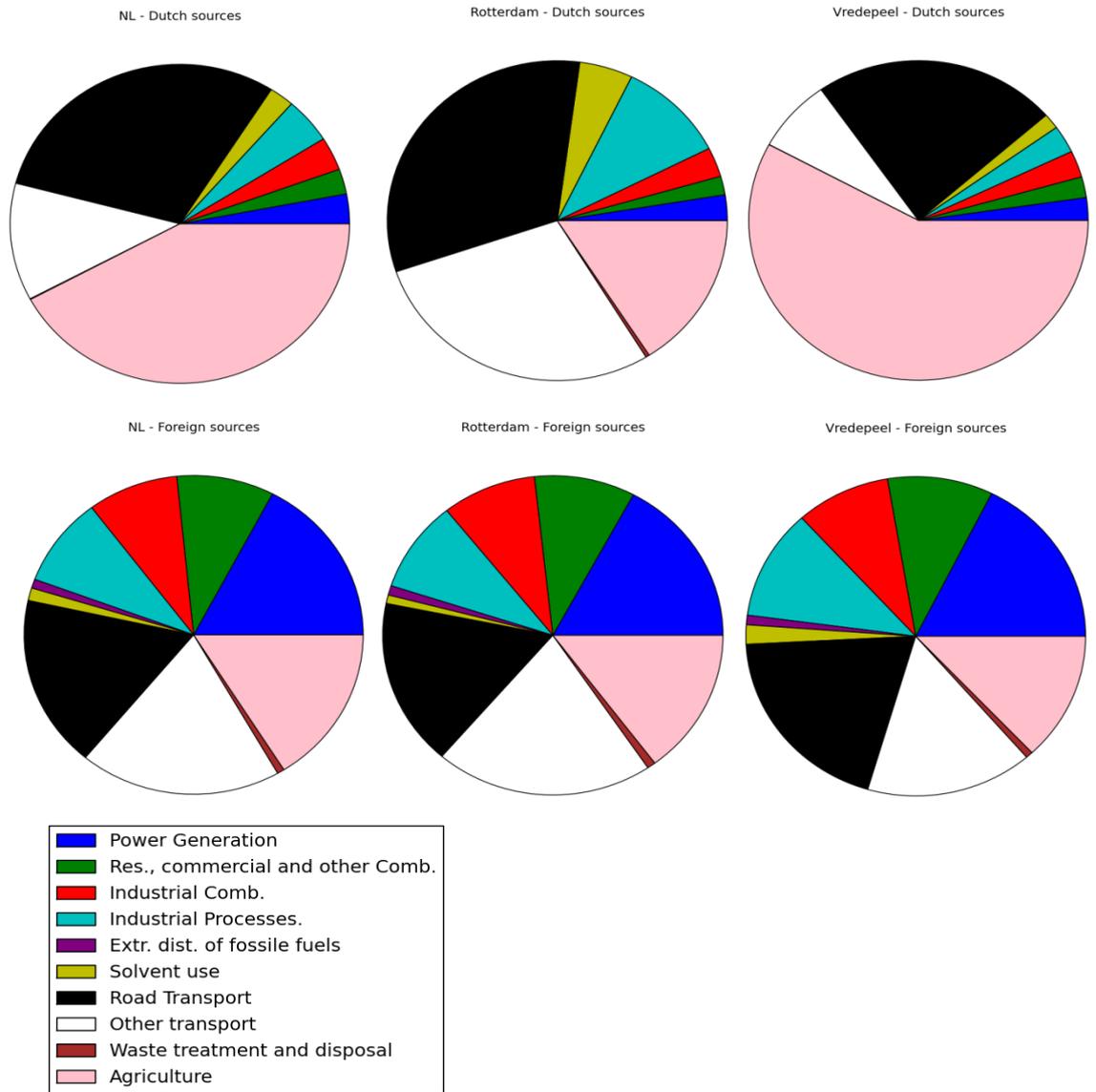


Figure 29 Modelled Dutch (top) and foreign (bottom) sectoral contributions to total modelled PM<sub>10</sub> in the Netherlands (left), Rotterdam (center) and Vredepeel (right)

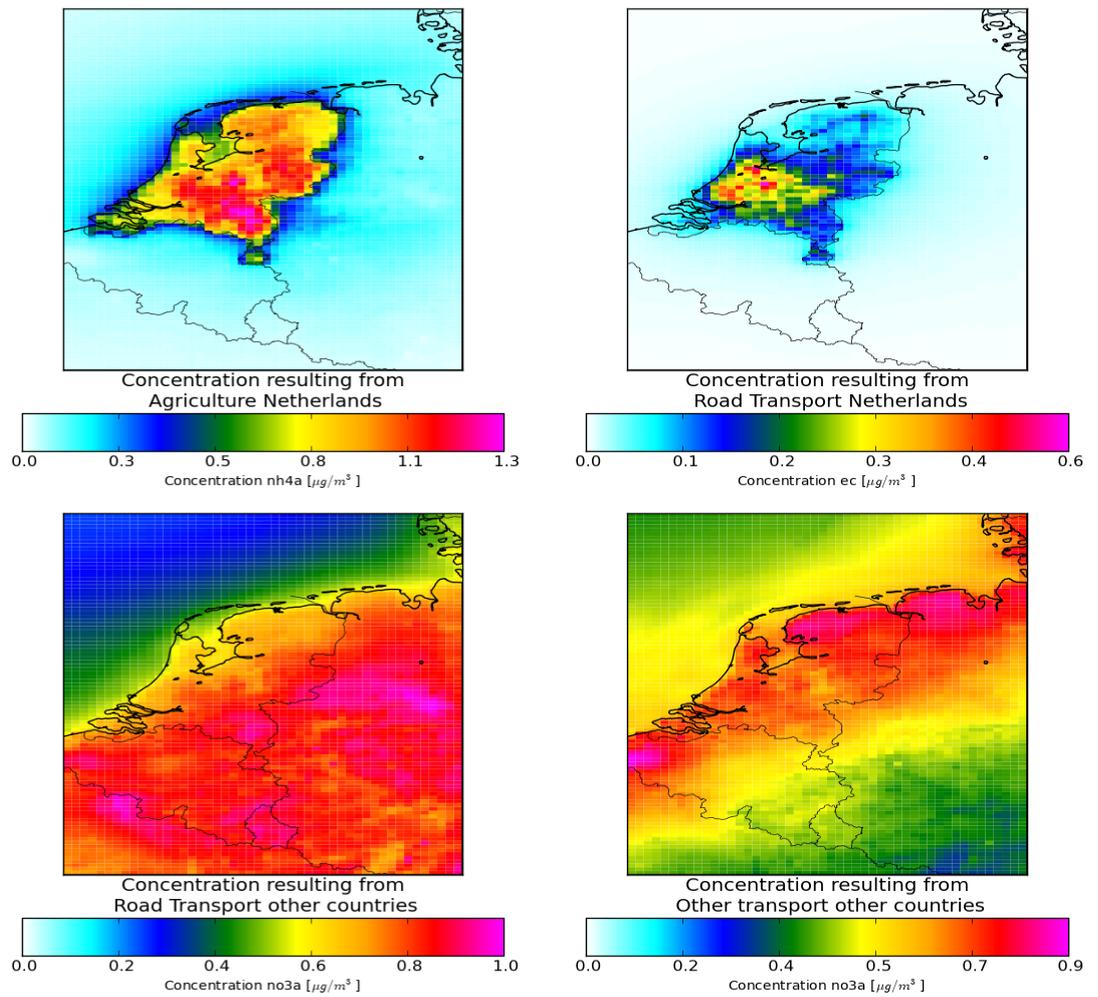


Figure 30 Top left:  $\text{NH}_4$  concentration caused by Dutch agriculture. Top right: EC concentration caused by Dutch road transport. Bottom:  $\text{NO}_3$  concentration caused by foreign road transport (left) and other transport(right)

Table 2 Modelled contributions of all sectors to all components in  $\mu\text{g}/\text{m}^3$  for 2008

Source	NO <sub>3</sub>	SO <sub>4</sub>	NH <sub>4</sub>	EC	POM	PPM	dust	sea salt	PM <sub>2.5</sub>	PM <sub>10</sub>
Dutch power generation	4,28E-02	4,90E-02	5,29E-04	1,20E-03	1,69E-03	7,29E-03	0	4,56E-04	<b>0,10</b>	<b>0,10</b>
Dutch residential, commercial and other combustion	3,86E-02	3,76E-03	0	8,93E-03	3,01E-02	4,18E-03	0	1,34E-03	<b>0,08</b>	<b>0,09</b>
Dutch industrial combustion	3,84E-02	2,66E-02	6,52E-03	6,08E-04	1,06E-03	4,12E-02	0	1,30E-03	<b>0,09</b>	<b>0,12</b>
Dutch industrial processes	0	0	5,64E-03	3,37E-03	6,00E-03	1,35E-01	0	7,35E-03	<b>0,07</b>	<b>0,16</b>
Dutch extraction and distribution of fossil fuels	0	0	0	0	0	0	0	0	<b>0,00</b>	<b>0,00</b>
Dutch solvent use	0	0	4,24E-03	3,87E-03	6,93E-02	3,80E-03	0	0	<b>0,08</b>	<b>0,08</b>
Dutch road transport	1,85E-01	1,72E-03	1,86E-02	1,50E-01	1,61E-01	6,14E-02	4,45E-01	3,71E-04	<b>0,54</b>	<b>1,02</b>
Dutch other transport	1,21E-01	4,64E-02	1,70E-04	7,00E-02	5,89E-02	1,08E-01	0	1,64E-03	<b>0,31</b>	<b>0,41</b>
Dutch waste treatment and disposal	0	0	2,49E-03	0	0	0	0	0	<b>0,00</b>	<b>0,00</b>
Dutch agriculture	1,75E-02	2,86E-04	8,27E-01	0	2,53E-01	2,73E-02	3,13E-01	0	<b>0,92</b>	<b>1,44</b>
Foreign power generation	4,52E-01	6,19E-01	1,91E-03	4,69E-03	2,70E-03	4,72E-02	0	2,56E-03	<b>1,05</b>	<b>1,13</b>
Foreign residential, commercial and other combustion	1,69E-01	1,55E-01	1,30E-03	5,21E-02	1,59E-01	6,45E-02	0	7,69E-03	<b>0,57</b>	<b>0,61</b>
Foreign industrial combustion	2,64E-01	2,38E-01	1,31E-03	2,73E-03	2,40E-03	5,82E-02	0	1,85E-03	<b>0,51</b>	<b>0,57</b>
Foreign industrial processes	7,12E-02	1,26E-01	9,81E-03	1,51E-02	3,88E-02	3,13E-01	0	1,77E-02	<b>0,45</b>	<b>0,59</b>
Foreign extraction and distribution of fossil fuels	4,58E-03	4,08E-02	3,27E-04	7,29E-03	1,45E-03	4,83E-03	0	2,30E-04	<b>0,05</b>	<b>0,06</b>
Foreign solvent use	7,43E-07	6,26E-05	1,03E-03	2,29E-03	4,12E-02	3,96E-02	0	0	<b>0,05</b>	<b>0,08</b>
Foreign road transport	7,30E-01	5,27E-03	1,03E-02	1,08E-01	5,84E-02	7,51E-02	1,53E-01	2,18E-04	<b>0,89</b>	<b>1,14</b>
Foreign other transport	6,88E-01	2,89E-01	4,22E-04	9,08E-02	1,12E-01	6,80E-02	0	1,27E-02	<b>1,08</b>	<b>1,26</b>
Foreign waste treatment and disposal	3,28E-03	2,91E-03	9,33E-03	7,38E-03	1,56E-02	6,22E-03	0	0	<b>0,04</b>	<b>0,04</b>
Foreign agriculture	4,67E-02	8,69E-05	5,28E-01	1,19E-03	1,38E-01	1,35E-02	3,22E-01	0	<b>0,68</b>	<b>1,05</b>
Natural	8,86E-04	1,82E-04	9,40E-04	5,00E-03	0	1,10E-02	1,46E-02	2,98E+00	<b>0,61</b>	<b>3,01</b>
Sources outside model domain	2,35E-01	3,51E-01	7,67E-02	7,95E-04	1,18E-04	1,98E-02	4,31E-01	8,53E-03	<b>1,00</b>	<b>1,12</b>
<b>Total</b>	<b>3,11</b>	<b>1,95</b>	<b>1,51</b>	<b>0,54</b>	<b>1,15</b>	<b>1,11</b>	<b>1,68</b>	<b>3,05</b>	<b>9,17</b>	<b>14,09</b>

### 6.3 Temporal variability

PM concentrations show episodic behaviour and since the daily limit values enforced by the EU are more stringent than the annual average limits, it is relevant to look at the differences in source attribution over time, with a focus on days with high PM concentrations. Figure 31 shows the source attribution for the spring of 2007 for Rotterdam (left) and Vredepeel (right). Note the different scaling for the two locations. In this period the PM concentrations show quite some dynamics. The timing of the high PM concentrations is the same for Vredepeel and Rotterdam, but the peak heights depend on location. Where the peak at the end of March is higher than the other peaks in Rotterdam, the peak in the first half of March is equally high in Vredepeel. This is mainly caused by extra domestic emissions from agriculture. Whereas this sector is important for Vredepeel, especially for the peak locations, it is less important in Rotterdam. There, both road transport and shipping are important during peak episodes. In general, at both locations, the relative contribution from Dutch emissions is higher during the peak episodes, reflecting the stable conditions under which local pollution builds up. Natural sources (i.e. sea salt) shows the highest contributions on days with low PM concentrations.

### 6.4 Variability with total mass concentration

To investigate the differences in source contributions between peak episodes and periods with lower total modelled PM concentrations, we look at it more systematically. All days were categorized based on the average modelled concentration of  $PM_{10}$ . The source attribution was calculated for each concentration bin separately for the BOP measurement locations and for the Netherlands as a whole. The results for the Netherlands, Rotterdam and Vredepeel are displayed in Figure 32. These plots show that the natural contribution is highest when the total modelled PM concentration is low. This can be explained by the fact that low concentrations are associated with westerly winds, which results in high transport of sea salt from the North Sea to the Netherlands. High PM concentrations are associated with easterly winds or stable conditions, during which the influx of sea salt from the sea is much smaller. For the Netherlands as a whole, the influence of both Dutch and foreign concentrations increases as the total modelled concentration goes up. However, for Rotterdam, which is surrounded by local sources, the domestic contribution grows faster with high total PM levels than the foreign contribution. For the Netherlands as a whole, the increase in concentrations going from low to high PM levels is proportional for most sectors, except natural sources (which decline, as explained above), and agriculture, which becomes more important mainly due to higher Ammonium (Nitrate) and dust concentrations. At Vredepeel, this pattern is more prominent than for the Netherlands on average, whereas at Rotterdam, agriculture grows less and especially transport (road transport and shipping) become more important as modelled PM concentrations increase.

Note that the concentration bins at both ends of the distribution represent only a few days, meaning that one day with an exceptional episode can make a large difference.

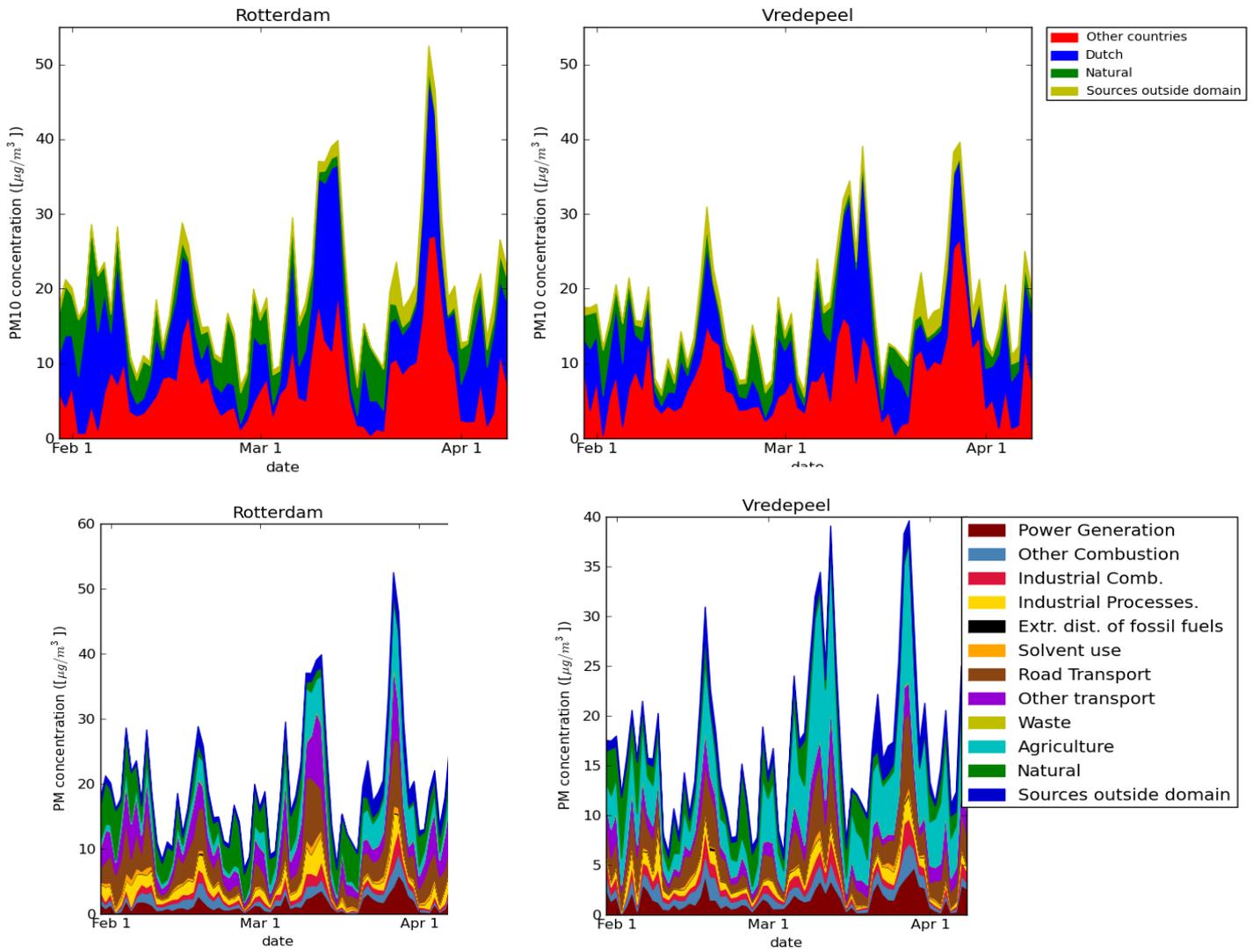


Figure 31 Time series of modelled PM<sub>10</sub> concentrations and its sources for February-April 2007 for Rotterdam and Vredepeel

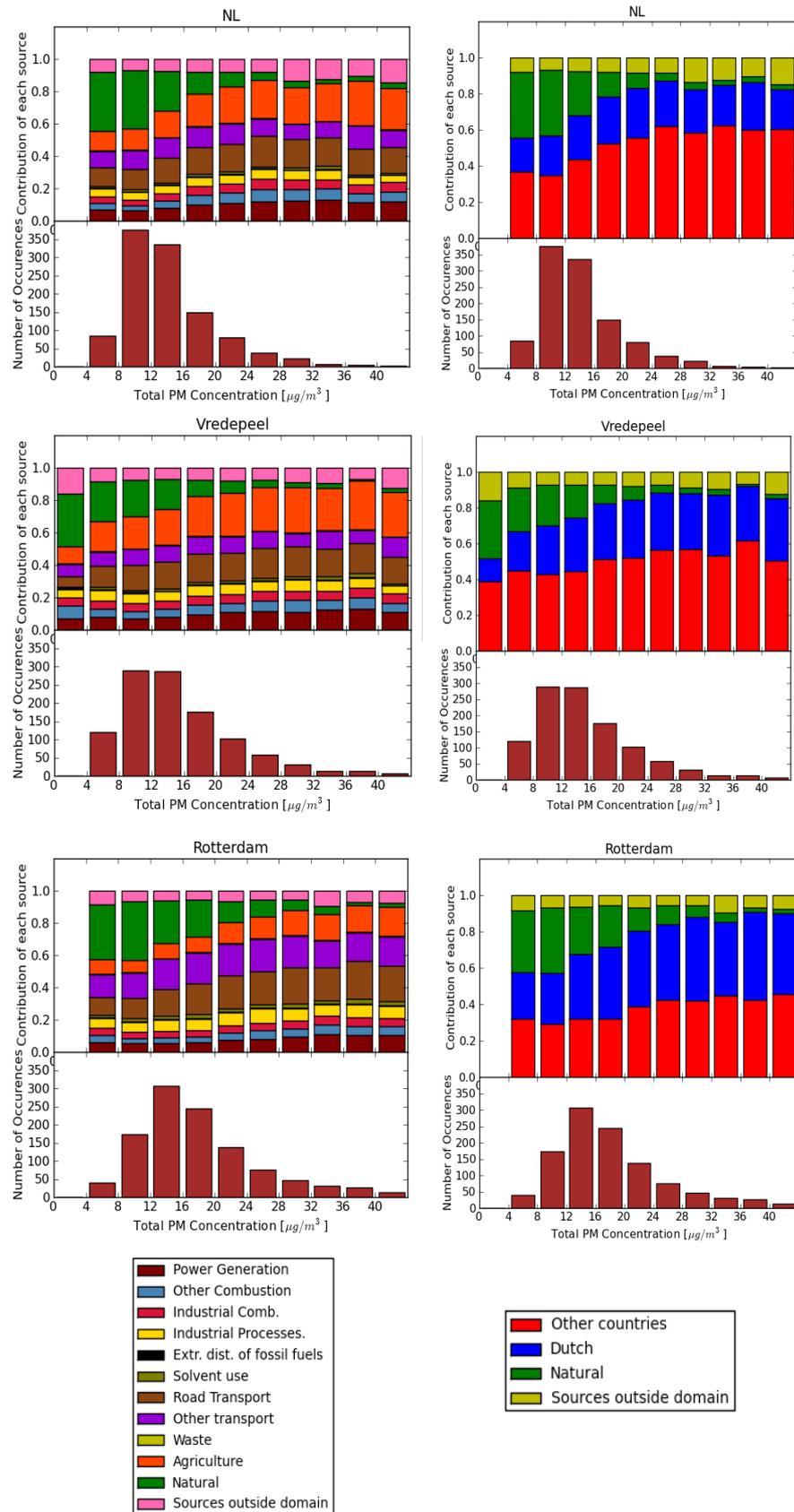


Figure 32 Source attribution of  $\text{PM}_{10}$  as a function of modelled total PM concentration



## 7 Discussion and conclusions

### 7.1 Explaining the non-modelled mass

In the model validation (section 4.3), it was shown that on average for the BOP1 stations about 40 % of total PM<sub>10</sub> and PM<sub>2.5</sub> is not explained by the model. As the SIA components, except NO<sub>3</sub>, are not underestimated, these components do not explain the missing mass. The components for which the largest share is missing in the modelled mass, are the carbonaceous aerosols (57%). Furthermore, mineral dust model results are associated with relatively large uncertainties. Below, we discuss the gaps in knowledge for carbonaceous aerosol, Nitrate and mineral dust.

#### 7.1.1 Carbonaceous matter

Uncertainties concerning carbonaceous matter exist both in the modelling framework and the measurement techniques.

A major issue in the chemical analysis procedure is the split between EC and OC, which is why up to this point in the report only total carbonaceous matter is considered in comparison to measurements. The different analysis procedures available correspond well for total carbon, but yield very different EC/OC ratios. During several available analysis procedures, a significant part of the OC may be converted to EC by charring (Ten Brink *et al.*, 2004). Most methods correct for the charring by monitoring the blackness of the filter during the analysis, using optical measurements. However, this is only successful to a limited extent.

For the EC and OC measurements that were performed during the BOP campaign (August 2007 – October 2008), the Cachier analysis procedure was used. With this method, refractory OC is not combusted in the first but in the second combustion step and is appointed to EC, thus providing an upper estimate for EC and a lower estimate for OC. In the BOP1 campaign, an EC/OC ratio of 1.25 was found, whereas analysis of the same filters with a different technique yielded an EC/OC ratio of 0.28 (Ten Brink *et al.*, 2009). Similar low ratios are reported for stations in the Netherlands by Schaap and Denier van der Gon (2007) using the SUNSET method. This implies that the EC concentrations as calculated by the model underestimate the atmospheric concentrations to a smaller extent than is suggested by the measurement data available, but that the model underestimation of OC concentrations is stronger. The share of the measured concentrations as analysed during the BOP campaign that is captured by the model is shown for four BOP measurement locations in Figure 33. If in reality the EC/OC ratio is closer to those reported by Ten Brink *et al.* (2009) and Schaap and Denier van der Gon (2007), the major part of the missing carbonaceous mass is organic carbon.

### Share of EC and POM captured by LOTOS-EUROS

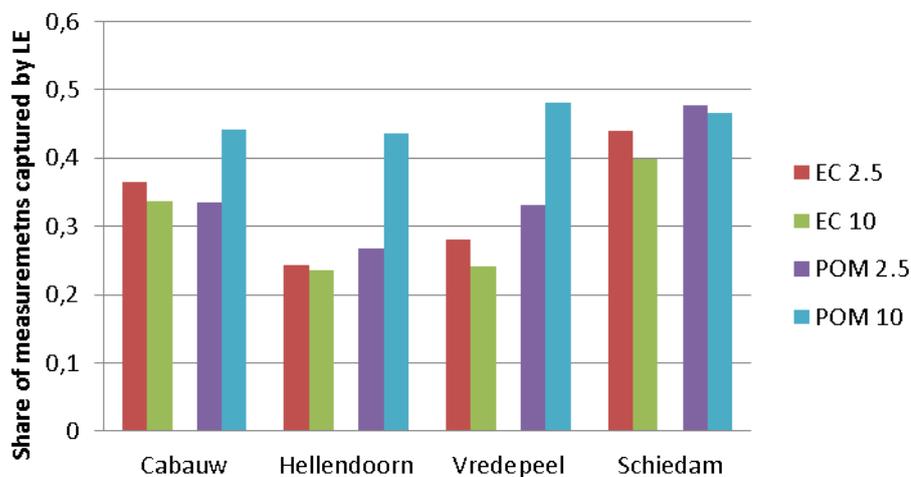


Figure 33 Share of the carbonaceous components captured by LOTOS-EUROS. A share of 1 means modelled and measured mass are equal

Besides sampling issues, the conversion factor from OC to organic matter is uncertain, with literature data varying between factors of 1.2 to 2. It is very well possible that this factor is spatially variable, showing lower values near sources and higher values after processing in aged air masses. In LOTOS-EUROS, OM is modelled, which is converted to OC in order to be able to compare with measurements using a factor 0.75, which corresponds to a OM/OC ratio of 1.33. In short, assuming no large bias in EC the model misses about 4-5  $\mu\text{g}/\text{m}^3$  of organic matter.

Organic matter is partly emitted as particles and partly as volatile condensable compounds that condensate after dilution and cooling to form particles or attach to existing particles. This condensable material is until now not or only partly included in the emission factors for particulate matter, but are also not covered in the emission data for volatile organic carbons (VOCs). Recent investigations to the emissions of wood heaters illustrated the potential importance of the condensable part. It was illustrated that the OM emission rate can be 2-4 times higher if condensables are properly included (Denier van der Gon et al., 2011). Incorporating these condensables in PM emission data results in significantly better air quality modelling for OM (Denier van der Gon et al., 2011). Note, that also the model formulation must be adapted so that semi-volatile organic material can be described. Furthermore, the formation of secondary organic aerosol (SOA) is not included in LOTOS-EUROS at the moment. Heavy (biogenic as well as anthropogenic) VOCs undergo oxidation reactions in the atmosphere and eventually condensate to form particles. Moreover, it is nowadays postulated that organics partition between the gas and aerosol phase and that the gaseous fraction can age to lower volatile species. This ageing shifts material with a high volatility to material with a lower volatility. One way to include the semi-volatile nature of organics and the ageing processes and to thereby improve the model performance for organic matter is to use a volatility basis set (VBS) for VOCs (Lane *et al*, 2008). This method categorizes all VOCs in terms of their volatility, after which chemistry and condensation processes are calculated for each volatility category.

With this method, no complete characterisation of all VOC emissions (which contain hundreds of different molecules) is necessary. Given the large missing mass for organic material the inclusion of this scheme is recommended.

### 7.1.2 *Mineral dust*

Modelled mineral dust concentrations exceed the measured concentrations by a factor 2 – 2.5. Mineral dust emissions from traffic re-suspension, agricultural practices and wind-blown dust events are included in the model. However, the emission functions are in general based on a limited experimental basis, which is not representative for the full range of European conditions (Schaap et al., 2009). The coupling of these emission factors with meteorological parameters (temperature, humidity) can be improved. For the agricultural sector, part of the emissions characterized as mineral dust may in reality be organic material, adding additional uncertainty to these figures. Hence, the range of uncertainty associated with the modelled concentrations is relatively large (overall uncertainty is estimated at a factor 2-3) (Denier van der Gon et al., 2010).

Another source of uncertainty is the quality of measurements of mineral dust concentrations. The BOP1 data for Dutch stations systematically report lower mineral dust concentrations compared to other measurement locations in Europe, at which the LOTOS-EUROS model in general underestimates mineral dust concentrations. Moreover, the BOP2 measurement data for Rotterdam are higher than those obtained during BOP1. Hence, more experimental data on mineral dust are needed to confirm its concentration and unravel its source contributions.

### 7.1.3 *Nitrate*

The Nitrate aerosol concentrations calculated by the model underestimate the measurements by 40%, whereas the concentrations of the other SIA components are much closer to the measurements. This study and Wichink Kruit *et al.* (2012) show that this underestimation of  $\text{NO}_3$  aerosol occurs both in the fine and the coarse mode. Nitrate formation is a complex process. In order to model it well, the fate and lifetime of precursor ( $\text{HNO}_3$ ,  $\text{NO}_x$ ) and reactant (mainly  $\text{NH}_3$ ) concentrations need to be correctly modelled including the time patterns. Also, the equilibrium between gas and particle phase needs to be estimated correctly as a function of temperature. A possible explanation for the underestimation of the fine mode  $\text{NO}_3$  is that the equilibrium module yields a too volatile Ammonium Nitrate during day time in summer. However, during the night and in winter the equilibrium was modelled to be too stable. Hence, it is unlikely to explain the bias over the full year. It was postulated that the equilibrium takes some time to establish (Aan de Brugh *et al.*, 2012). In that case meteorological conditions at a few hundred metres height would determine the equilibrium conditions. Using lower temperatures would force the gas-particle equilibrium to the particle phase and would consequently increase the  $\text{NO}_3$  concentrations, but also the  $\text{NH}_4$  concentrations. As the latter are modelled within 15% of the measurements, this approach may be beneficial for  $\text{NO}_3$  but may reduce the agreement between model and concentrations for  $\text{NH}_4$ . Other reasons for underestimation of  $\text{NO}_3$  aerosol may be associated with the incorrect timing of  $\text{NO}_x$  and especially the  $\text{NH}_3$  emissions, the impact of minerals and organics on the gas aerosol partitioning in the atmosphere and on uncertainties in dry deposition.

Nitrate aerosol is formed when  $\text{HNO}_3$  reacts with a alkaline component. In LOTOS-EUROS, only reactions with  $\text{NH}_4$  and Na are modelled. However, some components of mineral dust, mainly Calcium-containing components like  $\text{CaCO}_3$ ,

can also react with  $\text{HNO}_3$  to form coarse-mode Nitrate aerosol (Hodzic *et al.*, 2006; Berge, 2009). Including these reactions into the model would increase the coarse Nitrate concentrations.

Next to model imperfections, the measurements may also be biased. Weijers *et al.* (2012) argue that  $\text{NaNO}_3$  may be formed on the filter after the sampling when  $\text{NaCl}$  that is already collected on the filter substrate reacts with gaseous  $\text{HNO}_3$ , producing extra coarse nitrate. However, the total amount of nitrate found on the filter could still underestimate ambient Nitrate concentrations, caused by a loss through evaporation of fine  $\text{NH}_4\text{NO}_3$  when temperatures are high during summer (Schaap *et al.*, 2004; Vecchi *et al.*, 2009). More information about these measurement uncertainties is needed in order to know the exact mismatch between modelled and ambient concentrations of  $\text{NO}_3$  aerosol.

#### 7.1.4 Conclusion

The LOTOS-EUROS model underestimates the measured PM10 mass by about 40% or circa  $8 \mu\text{g}/\text{m}^3$ . Considering the information above and the comparison to the BOP data set in chapter 4 we can explain a large part of the gap. The model underestimates Nitrate by  $1.5 \mu\text{g}/\text{m}^3$ . Moreover, TC is underestimated by  $2.5 \mu\text{g}/\text{m}^3$ . This mass is largely attributed to organic matter and corresponds to 4-5  $\mu\text{g}/\text{m}^3$  of OM. Mineral dust validation is very uncertain and it may be overestimated up to  $1 \mu\text{g}/\text{m}^3$ , closing the gap by about  $5 \mu\text{g}/\text{m}^3$ . Considering that about 10% (about  $2 \mu\text{g}/\text{m}^3$ ) is unexplained in the mass closure exercise performed on the BOP experimental data (Weijers *et al.*, 2011), the gap is almost closed.

Note, that lowering the non-modelled fraction, largely consisting out of organic material and Nitrate, will impact the source allocation considerably when model improvements for these components are implemented in the future. As most of the organic mass and Nitrate is anthropogenic (Weijers *et al.*, 2011), the anthropogenic shares are anticipated to increase. The only natural component that is included in the missing fraction is biogenic secondary organic aerosol, that may have high concentrations in summer, whereas the model underestimates PM throughout the year.

## 7.2 Effects of changing source apportionment assumption for ammonium nitrate

For the chemically active species, the labelling module implemented in LOTOS-EUROS tracks the conserved atoms N, C and S. In case of nitrogen (N) the atoms in nitrogen oxides are traced separately from reduced nitrogen such as ammonia. For PM components with only one N or S atom, the attribution is straightforward. However, for ammonium nitrate, containing two nitrogen atoms of different classes, this is not the case and an assumption must be made. In this study, the choice was made to treat  $\text{NH}_4$  and  $\text{NO}_3$  as separate species for the labelling, attributing all  $\text{NH}_4$  to  $\text{NH}_3$  sources and all  $\text{NO}_3$  to  $\text{NO}_x$  sources. The advantage of this approach is that it makes the model implementation as well as the interpretation easier. As ammonia and nitric acid are both needed to form ammonium nitrate, an alternative is to attribute the mass of ammonium nitrate equally to the origin of ammonia and nitric acid. Here we investigate the consequences of changing the attribution procedure for ammonium nitrate for the source apportionment results.

To investigate the impact we have recalculated the origin of ammonium nitrate. We have defined  $\text{NH}_4\text{NO}_3$  as a single substance and appointed it one label, the

average of the fractional  $\text{NH}_4$  and  $\text{NO}_3$  source allocation. The remainder of  $\text{NH}_4$ , which is not bound completely to  $\text{NO}_3$ , was attributed to the  $\text{NH}_3$  emission sources. Because nitrate is heavier than ammonium, the net impact of treating  $\text{NH}_4\text{NO}_3$  as a single substance rather than as two separate ions is an increase of the importance of ammonia sources, i.e. agriculture. As an example, Figure 34 compares the nitrate concentration attributed to Dutch road transport using both approaches (top panels). The share of  $\text{NH}_4\text{NO}_3$  attributed to road transport, an important  $\text{NO}_x$  source, is smaller when  $\text{NH}_4\text{NO}_3$  is treated as a single substance and labelled accordingly. The bottom panels of Figure 34 show the concentration of  $\text{NO}_3$  and  $\text{NH}_4$  attributed to Dutch agriculture with the new assumption. Using the assumption that  $\text{NO}_3$  only comes from  $\text{NO}_x$  sources, the  $\text{NO}_3$  concentration attributed to agriculture was negligible. Using the 'one species' approach, about half of the nitrate mass is appointed to agriculture. For ammonium, significantly more than half of the mass remains agriculture as a large part of the mass is associated with sulfate. Note that we do not do a similar exercise for ammonium sulfate as this substance is not volatile and any sulphuric acid will condense to the particulate phase irrespectively of the available ammonia.

A change in approach that causes a shift in source attribution for PM components has consequences for the source apportionment for total  $\text{PM}_{10}$  as well. Figure 35 shows the source attribution for the Dutch sectors to total modelled  $\text{PM}_{10}$  in the Netherlands when  $\text{NH}_4\text{NO}_3$  is labelled as if it is a single substance rather than two separate ions. Comparing this figure to Figure 29 in section 6.1.2 shows that the mass associated with agriculture has become larger as explained above. Consequently, the mass originally assigned to  $\text{NO}_x$  source contributions (mostly transport) shrinks using this assumption. Finally, treating  $\text{NH}_4\text{NO}_3$  as one substance in the labelling, a higher contribution of the national activities to the total PM mass was found. The absolute modelled national contribution grows by 13 % to 17% of total  $\text{PM}_{10}$ , whereas the modelled foreign contributions decreases by 7% to 26% of total  $\text{PM}_{10}$  (see Figure 36), showing that assumptions made in the labelling approach can have significant impacts on the overall source apportionment result and should be made explicit.

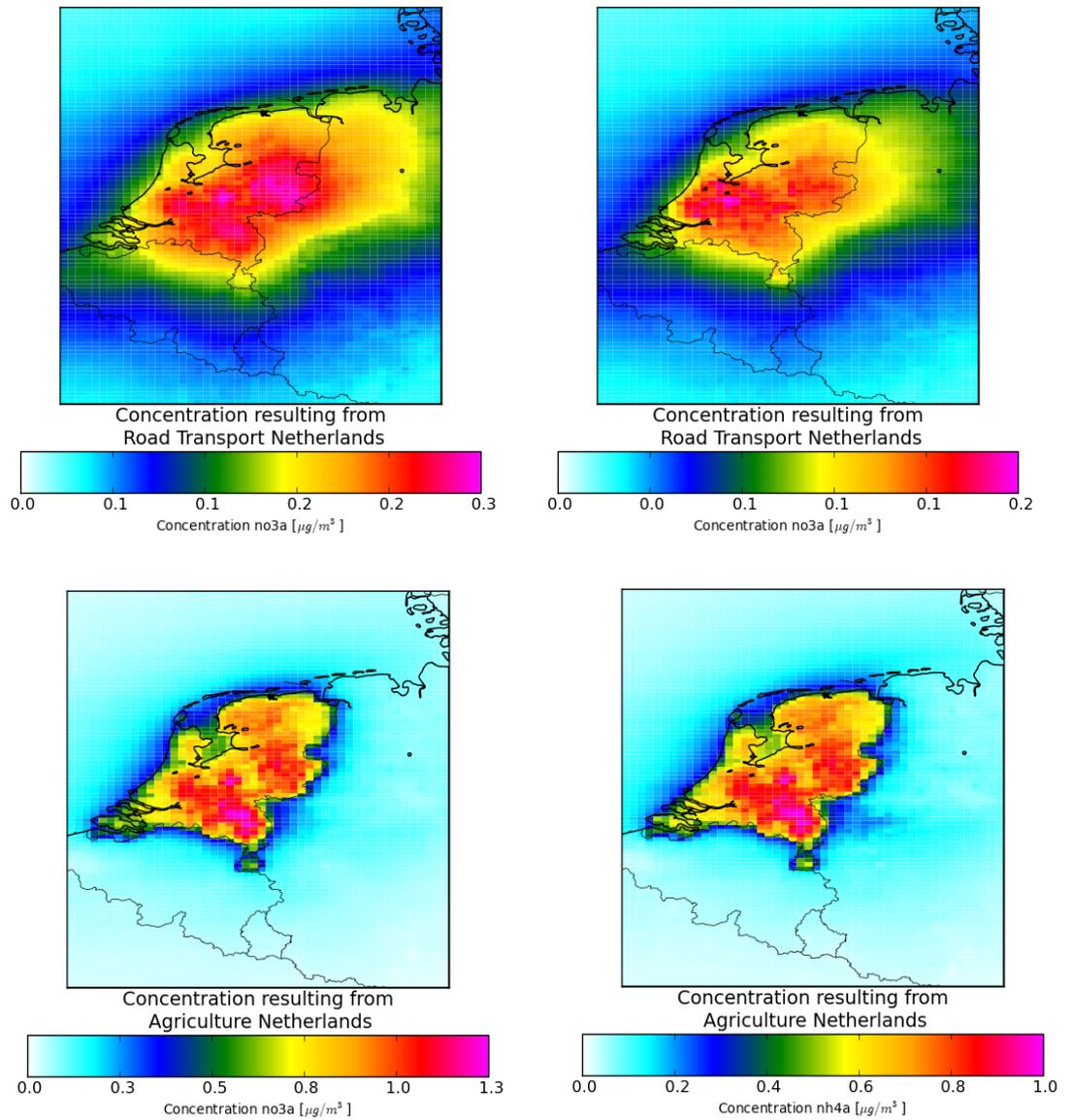


Figure 34 Concentration of  $\text{NO}_3$  attributed to Dutch road transport (top panel) when  $\text{NO}_3$  is attributed to  $\text{NO}_x$  and  $\text{NH}_4$  to  $\text{NH}_3$  sources (left) and when  $\text{NH}_4\text{NO}_3$  is treated as one substance with one source attribution (right). The bottom panel shows the concentration of  $\text{NO}_3$  (left) and  $\text{NH}_4$  (right) attributed to the agriculture sector in the Netherlands using the 'one-substance' assumption

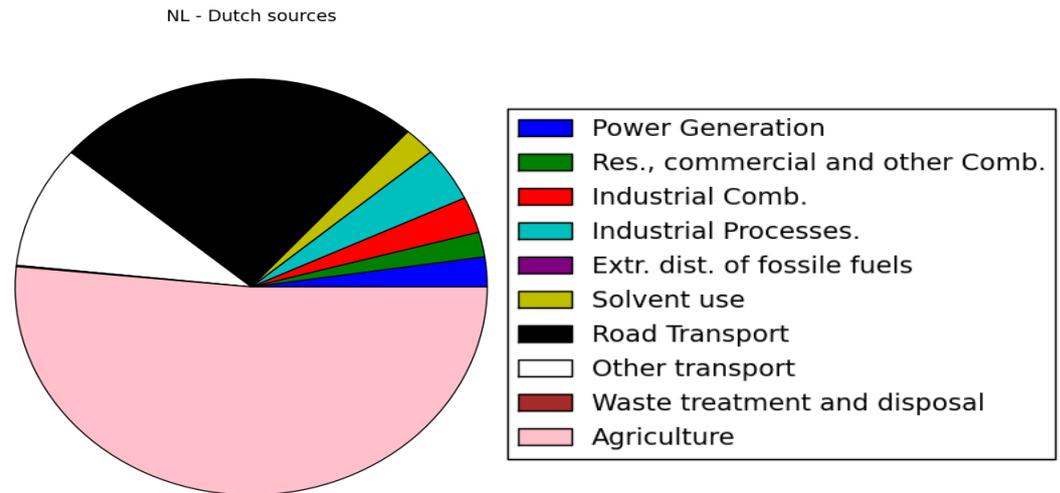


Figure 35 Modelled Dutch sectoral contributions to total PM<sub>10</sub> in the Netherlands, treating NH<sub>4</sub>NO<sub>3</sub> as one substance in the source attribution

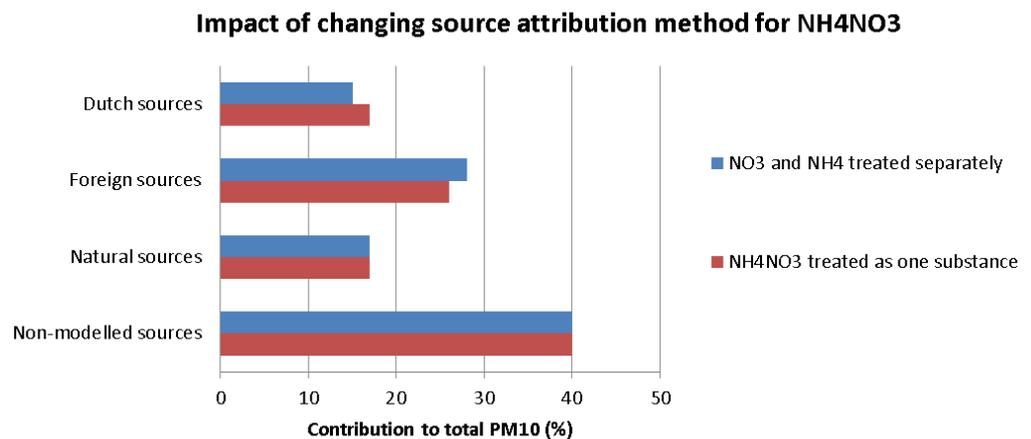


Figure 36 Impact of labelling assumption for NH<sub>4</sub>NO<sub>3</sub> on source attribution for total PM<sub>10</sub>

### 7.3 Comparison with other source apportionment studies for the Netherlands

Although the BOP2 project is the first project in which a labelling technique is used to investigate the source apportionment of particulate matter, it is not the first time an attempt is made to identify the origin of particulate matter in the Netherlands. In 2005, RIVM and MNP published 'Fijn stof nader bekeken' (Buijsman *et al.*, 2005), in which the origin of PM was assessed with the linear OPS model. The same model was used to produce a source apportionment estimate in Velders *et al.* (2011), where the model results were calibrated to measurements. The Convention on Long-range Transboundary Air Pollution uses the EMEP model to produce source receptor matrices for, among others, PM for a large number of countries including the Netherlands (Nyíri *et al.*, 2009 and 2010).

#### 7.3.1 Buijsman et al., (2005): Fijn stof nader bekeken

Before comparing the results between this study and those obtained by OPS one must realise that there are many differences between OPS and LOTOS-EUROS.

The first important difference is the ability of LOTOS-EUROS to model non-linear processes. The chemistry represented in OPS occurs using constant effective conversion rates between the precursor gases and the SIA components. Hence, SIA components are formed irreversibly. Because of this, the concentrations of the different SIA components are not in balance with each other. As Ammonium is bound either to Nitrate or Sulfate, the Ammonium concentration field should be a superposition of those of Nitrate and Sulfate. Schaap *et al.* (2009) showed that this is not the case for the concentrations calculated with OPS, while for LOTOS-EUROS this superposition is enforced through the equilibrium module. Furthermore, the deposition schemes used in the models are different for particles, with lower deposition velocities for LOTOS-EUROS, which is expected to give higher concentrations and longer-range transport due to the longer lifetime of PM components. LOTOS-EUROS includes more substances, such as mineral dust, and being a European model nested in global model results, it is able to calculate the hemispheric background contribution.

The smaller scale OPS model uses a higher resolution (1x1 km) than LOTOS-EUROS. Where LOTOS-EUROS is a eulerian grid model, the OPS model uses a plume description at short distances and a langrangian trajectory model for the larger scale, which enables the model to follow plumes from point sources more accurately. Hence, OPS is better able to model local differences in concentrations. In the LOTOS-EUROS model, a plume is directly averaged over the whole grid cell and the surface and mixing layer.

Surprisingly, the overall agreement between the source apportionment for PM<sub>10</sub> found by Buijsman *et al.* (2005) and the one derived in this study is large. Buijsman *et al.* (2005) attributed 15% of the total PM<sub>10</sub> mass to Dutch sources, 30% to foreign sources and 55% to non-modelled PM, including sea salt and mineral dust. In this study, we were able to reduce the non-modelled share substantially, arriving at 39.5% of non-modelled mass. The shares for Dutch (15%) and foreign sources (28%) to PM<sub>10</sub> found in this study are very close to those derived by Buijsman *et al.* (2005). The source attribution per sector shows large similarities between the two studies as well. The largest difference is found for Dutch agriculture, for which this study finds a contribution that is twice as large as the one found by Buijsman *et al.* (6 and 3 %, respectively). This is partly caused by the fact that in this study, mineral dust emissions are included, contributing about 25% of the total share of Dutch agriculture. Road transport and especially consumers are more important in the Buijsman *et al.* (2005) study.

Importantly, the understanding of the composition of the non-modelled share is much better due to knowledge developed in the BOP programme. The non-modelled fraction consists largely of primary and secondary organic material and nitrate. When model improvements for these components are implemented it will strongly impact the source allocation.

- 7.3.2 *Velders et al. (2011): Grootschalige concentratie- en depositiekaarten Nederland*  
 Velders *et al.* (2011) arrived at a total average PM<sub>10</sub> concentration of 23.5 µg/m<sup>3</sup> for the Netherlands in 2010, of which 3.7 µg/m<sup>3</sup> is of Dutch origin. Foreign emissions cause 6 µg/m<sup>3</sup> of PM<sub>10</sub> in the Netherlands, and sea salt is estimated to contribute 4.5 µg/m<sup>3</sup>. Non-modelled components, including mineral dust, add another 9.3 µg/m<sup>3</sup>. Comparing these values to (section 6.1) shows that the results are quite similar. We arrive at a total Dutch contribution to PM<sub>10</sub> of 3.4 µg/m<sup>3</sup> and a foreign

contribution of  $6.5 \mu\text{g}/\text{m}^3$  on average for the Netherlands in 2007 – 2009. (note that these numbers include mineral dust emissions). The unknown mass is equal for both studies, however it should be noted that Velders *et al.* (2011) include mineral dust in this number. This suggests that LOTOS-EUROS misses a larger part of the non-mineral dust mass compared to OPS. The relatively larger share for foreign sources found in this study can be explained by the lower deposition velocities of particles used by LOTOS-EUROS. The attribution of Dutch share of the average  $\text{PM}_{10}$  concentrations to sectors is also comparable for the two studies. Again, the largest differences are seen for the residential sector, where LOTOS-EUROS models  $0.09 \mu\text{g}/\text{m}^3$  and Velders *et al.* (2011) arrive at  $0.5 \mu\text{g}/\text{m}^3$ . The reason for this discrepancy needs to be addressed in the future.

Comparing the results of the two studies for  $\text{PM}_{2.5}$  gives roughly the same picture, although LOTOS-EUROS yields somewhat lower concentrations due to industry and transport compared to Velders *et al.* (2011). The total domestic contribution is  $2.9 \mu\text{g}/\text{m}^3$  (Velders *et al.*, 2011) vs.  $2.2 \mu\text{g}/\text{m}^3$  (this study), whereas the foreign contribution is almost equal ( $5.2$  vs.  $5.4 \mu\text{g}/\text{m}^3$ ), reflecting the results for  $\text{PM}_{10}$ . The agreement between these two studies is also seen at the more regional scale when the results from the Rotterdam/Dordrecht region from Velders *et al.* is compared to the results for Rotterdam from this study.

As mentioned before, we expected a higher modelled PM concentration for the LOTOS-EUROS model as compared to OPS as LOTOS-EUROS includes mineral dust and has a lower aerosol dry deposition velocity. Although many differences exist, e.g. in the chemistry, the higher concentrations of the national primary material in OPS hints at an important difference in the mixing and short range transport characteristics. Inspection of the modelled distributions shows that the impact of large urban areas and major highways is much more pronounced in the OPS distributions. Hence, it appears that the national emissions are associated with a systematically larger share of ground level primary PM due to the plume approach used in OPS. As emissions may be diluted too quickly in the grid model LOTOS-EUROS, incorporating a plume-in-grid approach in LOTOS-EUROS might be beneficial, since this would combine the benefits of using a non-linear regional CTM with the ability to model local concentrations better.

### 7.3.3 Nyíri *et al.* (2009; 2010): Transboundary air pollution by main pollutants ( $\text{S}$ , $\text{N}$ , $\text{O}_3$ ) and PM – Netherlands

Nyíri *et al.* (2009; 2010) give the main contributors to SIA and  $\text{PM}_{2.5}$ , arriving at Dutch contributions to modelled SIA of 16 and 11% for 2008 and 2009, respectively. For modelled total  $\text{PM}_{2.5}$ , the Dutch share was found to be highest: 27% for 2008 and 18% for 2009, illustrating that the year-to-year variation can be substantial. The average Dutch contribution to modelled SIA concentrations over the Netherlands for the years 2007-2009 as calculated in this study is 22%, whereas the national contribution to modelled  $\text{PM}_{2.5}$  was 24%. This last result is in agreement with the results from the EMEP study, but the domestic SIA contribution is markedly higher. As there are many differences between both studies (e.g. emission database used, model resolution, model parameters, the thermodynamic equilibrium module used), the reason for the different source attribution for SIA is unclear.

#### 7.3.4 *Schaap and Denier van der Gon (2007)*

Schaap and Denier van der Gon (2007) estimated a national contribution of 40-60% to Dutch EC concentrations, based on interpretation of measurements of EC and black smoke and on model results obtained with LOTOS-EUROS. The domestic share of modelled EC concentrations found in this study (on average 44% with a range from 35 – 75%) supports this estimate.

### 7.4 **Recommendations for improvement**

#### *Carbonaceous matter*

To improve the representation of carbonaceous matter in LOTOS-EUROS, incorporating condensable material into emission factors for PM as well as including secondary organic aerosol formation are recommended. We propose to do this with the earlier introduced VBS (volatility basis set) approach. A better representation of EC and especially OC in the model will improve the overall model performance and might therefore also be beneficial for the model performance during high PM episodes. Also, the conversion from OC to OM deserves further attention.

#### *Plume in grid approach*

Comparison of the results obtained with OPS hints at a systematically larger share of national primary PM at ground level due to the plume approach used in OPS. Such a systematic difference is highly policy relevant. As plumes may be diluted too quickly in the grid model LOTOS-EUROS, incorporating a plume in grid approach in LOTOS-EUROS might be beneficial, since this would combine the benefits of using a non-linear regional chemistry transport model with the ability to model local concentrations better.

#### *Consistency of emission database*

The emission database that was used for this study is where possible based on country reporting. Not all countries use exactly the same sector definitions, which did not raise a problem for air quality studies before. However, when a source attribution study such as this one is carried out, these inconsistencies make it difficult to compare the sector contributions from different countries. Hence, future improvements can be made by focussing on the consistency of the emission databases.

#### *Episodes and timing*

As especially peak concentrations and episodes are important from both the policy and the health perspective, an extra effort to improve the modelling of peak episodes is recommended. A detailed analysis of a limited number of episodes may increase our understanding and reveal important information on model performance and shortcomings. An improvement of the timing of emissions in the model could also have an impact on the representation of episodes, as well as a better understanding of mineral dust emission characteristics.

#### *Geographical origin of particulate matter*

In this study, the origin of particulate matter was investigated for Dutch and foreign sources on a sectoral basis. From an international policy point of view, however, it is interesting to look further into the contributions labelled as 'foreign'. Identifying the countries and/or regions that contribute most to Dutch particulate matter concentrations could indicate the importance of covenants with neighbouring

countries/regions compared to a European approach. From a scientific point of view, it is also valuable to learn more about the distances over which primary and secondary PM components are transported.

## 7.5 Synthesis

For the first time, a chemically consistent source apportionment for particulate matter was obtained for the Netherlands, that provides insight in the spatial and temporal variability of the source apportionment per sector. A dedicated source apportionment module was developed for the regional air quality model LOTOS-EUROS and successfully implemented. This module was used to establish the source attribution of PM<sub>10</sub> and PM<sub>2.5</sub> in the Netherlands for 2007 to 2009 at sector level, distinguishing between national and foreign sources. From a policy point of view, especially days with high PM levels are relevant. Therefore, special attention was given to the source attribution during peak episodes.

On average for the years 2007-2009, the modelled PM<sub>10</sub> concentration in the Netherlands was 13 – 22 µg/m<sup>3</sup>, depending on location. A gradient from North (13 µg/m<sup>3</sup>) to South (18 µg/m<sup>3</sup>) was modelled, with higher concentrations in densely populated areas with large industrial activities, like Rotterdam. For PM<sub>2.5</sub>, the concentration was 9-11 µg/m<sup>3</sup>, with the highest values along the Rotterdam – Nijmegen line. The average observed concentrations for these years were 23-24 µg/m<sup>3</sup> for PM<sub>10</sub> and 14-15 µg/m<sup>3</sup> for PM<sub>2.5</sub>. This leaves about 9 and 5 µg/m<sup>3</sup> of non-modelled mass for PM<sub>10</sub> and PM<sub>2.5</sub>, respectively. The most important substances in PM<sub>10</sub> are the SIA components, that make up about 60% of modelled PM mass. About 15% of modelled PM<sub>10</sub> is of carbonaceous origin, although the model misses a large fraction of this mass. Sea salt and dust each contribute around 10% to the total modelled PM<sub>10</sub> mass. The importance of the different species changes with location and with total PM concentration. For the Netherlands on average, the SIA contribution increases from 35% at total PM concentrations of 4-8 µg/m<sup>3</sup> to over 60% for PM levels over 32 µg/m<sup>3</sup>. Sea salt is an important specie at low concentrations (35% of total PM<sub>10</sub>) but its importance decreases rapidly with increasing PM levels.

Overall, this study confirms the previously established origin of particulate matter in the Netherlands, but captures more of the total PM mass with modelling and offers more detail. Based on modelled PM, 70-80% of PM<sub>10</sub> and 80-95% of PM<sub>2.5</sub> in the Netherlands is man-made. About 1/3 of anthropogenic PM<sub>10</sub> is of Dutch origin and 2/3 originates in foreign countries. Agriculture and transport are the Dutch sectors with the largest contribution to total PM<sub>10</sub> mass in the Netherlands, together responsible for 85% of the total Dutch contribution. The foreign contribution is more equally apportioned to road transport, other transport, industry, power generation and agriculture. The remaining sectors combined account for 10% of the foreign contribution to modelled PM levels in the Netherlands.

In general, the Dutch contribution to the concentration of primary aerosol is larger than for secondary aerosol species. The sectoral origin of the PM components changes per substance and is location and time dependent. During peak episodes, natural sources are less important than under normal conditions and especially road transport and agriculture become more important. For the Netherlands as a whole, the foreign share grows as concentrations increase. This can be explained by the

fact that peak episodes are usually associated with easterly winds or stable conditions, while the natural components (mainly sea salt) show the highest concentrations with westerly winds.

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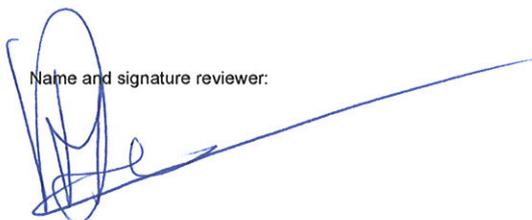
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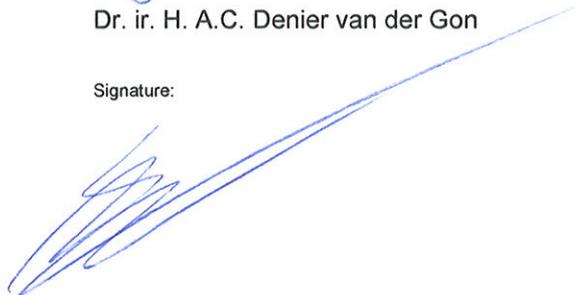
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