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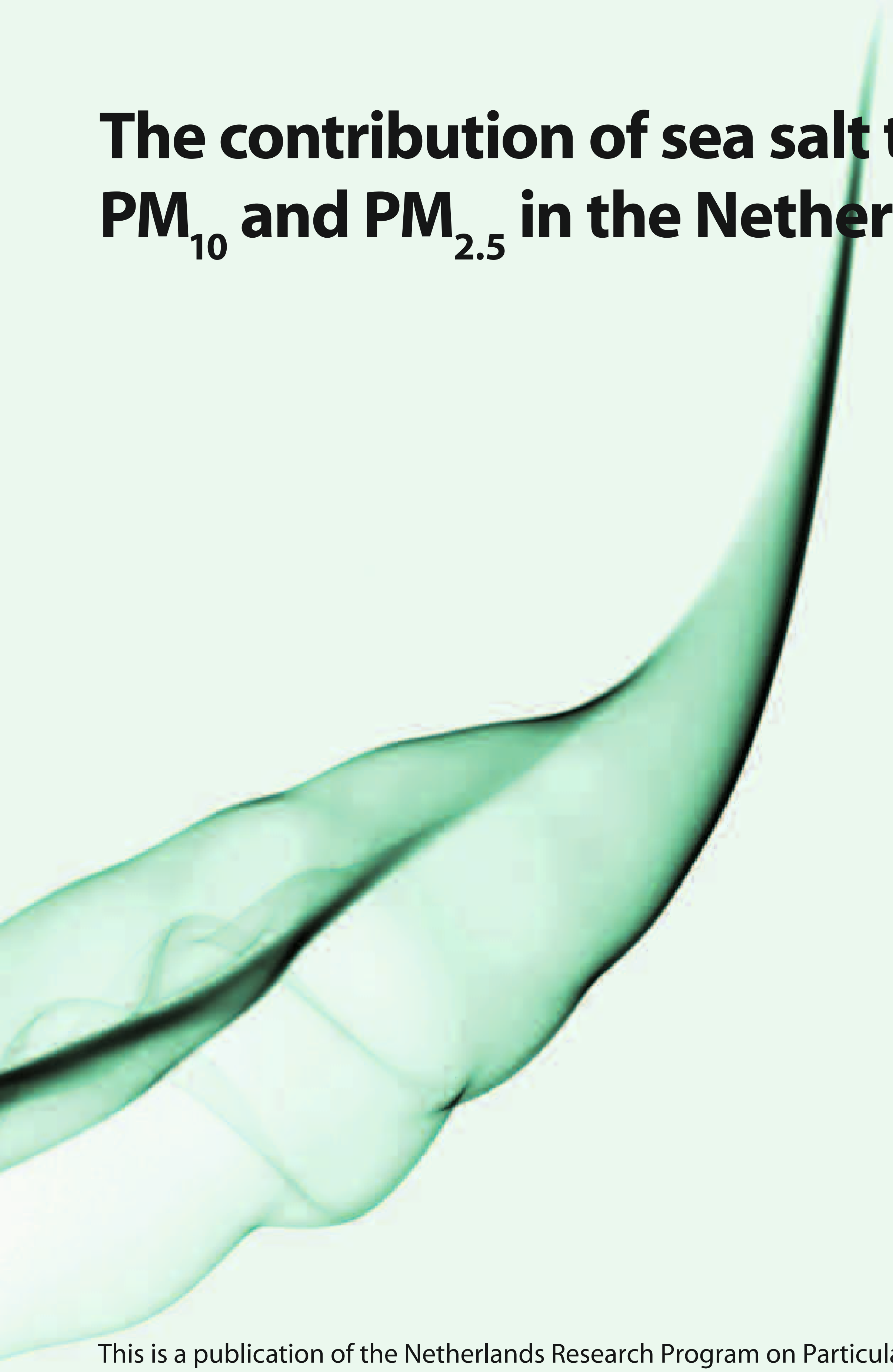

This is a publication of the Netherlands Research Program on Particulate Matter

Netherlands Environmental Assessment Agency
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BOP report

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ECN Energy research Centre of the Netherlands
PBL Netherlands Environmental Assessment Agency
TNO Built Environment and Geosciences
RIVM National Institute for Public Health and the Environment

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Summary

Sea salt aerosol makes a natural contribution to particulate matter (PM_{10}), and cannot be influenced by abatement strategies. The report improved the so-far limited knowledge on sea salt and its contribution to PM_{10} and $PM_{2.5}$ in the Netherlands. We focused on one year of measurements of sodium, which is a good indicator for sea salt, and combined these with results of the LOTOS-EUROS model, which describes the generation and transport of sea salt aerosol.

The average concentration over the observation period varied from 4 µg/m³ in Rotterdam, close to the coast, to 2 µg/m³ in Vredepeel, land inwards. Daily average concentrations were sometimes much higher or smaller. When the European limit vale of 50 µg/m³ for PM_{10} was exceeded, the contribution of sea salt aerosol to PM_{10} was, in general, less than the annual average concentration. Because the contribution of sea salt to PM_{10} and $PM_{2.5}$ varies strongly from day to day and also from year to year, our conclusions on the observation period of about one year can not straightforwardly be extrapolated to other years. Therefore, it is recommended to extend the current analysis with routine sodium measurements, which recently have started in the National Air quality Monitoring Network, in combination with model calculations.

Rapport in het kort

Zeezoutaerosol vormt een natuurlijke bijdrage aan fijn stof (PM_{10}), die niet door beleidsmaatregelen beïnvloed kan worden. Dit rapport draagt bij aan een verbetering van de tot nu toe beperkte kennis rond zeezout en de bijdrage er van aan PM_{10} en $PM_{2.5}$ in Nederland. De nadruk lag op de meetresultaten van een jaar, met natrium als goede indicator voor zeezout, en op resultaten van het LOTOS-EUROS model, dat de aanmaak en het transport van zeezoutaerosol beschrijft.

De concentratie van zeezoutaerosol gemiddeld over de meetperiode varieerde van 4 µg/m³ in Rotterdam, niet ver van de kust, tot 2 µg/m³ in Vredepeel, landinwaarts. Daggemiddeld was de bijdrage soms veel hoger of juist lager. Op dagen met hoge fijnstofconcentraties, wanneer de Europese limietwaarde van 50 µg/m³overschreden werd, was de bijdrage van zeezout meestal lager dan het jaargemiddelde. Omdat de bijdrage van zeezout aan PM_{10} en $PM_{2.5}$ sterk per dag en ook van jaar tot jaar varieert, kunnen de conclusies over de onderzochte periode niet zonder meer worden vertaald naar andere jaren. Daarom bevelen we aan om de analyse voort te zetten op basis van natriummetingen die recentelijk zijn gestart in het Landelijk Meetnet Luchtkwaliteit, gecombineerd met modelberekeningen.

Contents

Abstract

Particulate matter (PM) is known to cause adverse health effects. Therefore, legislation has imposed limit values for PM_{10} concentrations. In the Netherlands, sea salt aerosol can contribute significantly to the total PM_{10} concentrations, but the amount and the variability in time and space remain rather uncertain. Since sea salt is thought to be harmless, and cannot be influenced by abatement measures as it is a natural contribution to PM_{10}, the current Dutch practice is to subtract the sea salt contribution from total PM_{10} when assessing its compliance with regulation.

The present report aims to improve the knowledge on absolute sea salt concentrations in the Netherlands, and the relative contribution of sea salt to PM_{10} and $PM_{2.5}$ concentrations. Previously, chloride measurements were used to assess the sea salt concentration, but these measurements were not very accurate. New measurements of sodium – a more reliable tracer for sea salt – were collected from August 2007 to September 2008. These included daily average concentrations from filter analysis at six sites, and a few months of hourly measurements at three sites. Two of the sites with hourly measurements coincided with filter measurement sites. These measurements were interpreted and compared to observations in other European countries. Concentrations in the Netherlands were comparable with those in other countries bordering the North Sea.

These results were also compared to results from the chemical transport model LOTOS-EUROS. In this way, LOTOS-EUROS was validated, leading to the conclusion that LOTOS-EUROS, in general, has a correct timing of events with high or low concentrations and has a realistic gradient from the coast to land inwards, but that it overestimated the observed concentrations. After the determination and application of an appropriate scaling factor to correct this overestimation, the results from LOTOS-EUROS were used to complete the observations by filling in the gaps in space and time.

In the Netherlands, we found annual average sea salt concentrations with a north-west to south-east gradient, ranging from about 4 µg/m^3 in Rotterdam (and somewhat higher, immediately at the coast) to about 2 µg/m^3 in Vredepeel, in the southeast of the country. Sea salt concentrations are highly variable as they directly depend on weather conditions. Daily average concentrations reached values of up to 16 µg/m^3 in Rotterdam, and up to 10 µg/m^3 in Vredepeel. About 35% of the sea salt in PM_{10} was in the $PM_{2.5}$ fraction. For days with continental winds, the gradient over the country was weaker or absent.

Sea salt concentrations were negatively correlated to total PM_{10} concentrations. High sea salt concentrations occurred during westerly winds, transporting relatively clean air, whereas high total PM_{10} concentrations occurred during weak and continental winds. The contribution of sea salt to total PM_{10} concentrations on days when the limit value was exceeded, was 2 µg/m^3 or less, and in the considered year, the number of days with exceedances was hardly affected by subtraction of the measured sea salt contribution. Subtraction of the sea salt contribution reduced the number of those days, for Rotterdam, by two or three, and by one, for Breda, depending on the method. For the other measurement locations, no reduction in the number of days with exceedances was found.

The observations used in this study cover only one year. Because of the year-to-year variability in the weather, sea salt contributions will also vary, with relative differences in annual average sea salt concentrations of up to 40%. The concentration levels in the period concerned in this study were believed to be representative for the long-term average. But considering the large inter-annual variability, it is recommended to assess sea salt contributions for each individual year and location, instead of using an average for all years. Consequently, when sea salt is to be subtracted from total PM_{10}, it would also be better to determine the reduction in the number of PM_{10} limit-value exceedances after subtraction of sea salt aerosol from total PM_{10} concentrations, for each individual year and location.

For prognostic PM_{10} levels, a better approach would link the reduction in the number of days with PM_{10} limit-value exceedances to the estimated levels of future PM_{10} concentrations.

This is not only because of the variability in sea salt concentrations, but also because of the variability in the number of PM_{10} limit-value exceedances itself. Whether and how such improvements could be made operational for national compliance checking is subject to further assessment.

1

Introduction

1.1 The importance of sea salt aerosol

Sea salt aerosol plays an important role in atmospheric chemistry and physics. It is important for climate issues, since it influences the radiative balance of the atmosphere (Murphy *et al*. 1998) and cloud formation (Pierce and Adams 2006). Furthermore, sea salt constituents interact with other chemical substances, contributing to the halogen and sulphur chemistry, and have a corrosive effect (e.g. Anwar Hossain *et al.*, 2009). Global sea salt emissions are estimated at 5 to 10 petagram per year, depending on the method (Lewis and Schwartz, 2004), and are larger than other single aerosol emission sources, by a factor of 10 to 100.

Since sea salt aerosol is generated above the sea, and has a short lifetime (of around one day), the highest concentrations are found over open sea. Still, in coastal areas, sea salt can contribute substantially, with daily average values of up to 8 µg/m³ (Genoa, Italy, Marenco *et al.* 2007), and, occasionally, even 100 µg/m³ (Erdemli, Turkey, Koçaka *et al.*, 2007). Annual average concentrations, however, are substantially lower. For the Netherlands, previous estimates of the annual average varied from 7 µg/m³ near the coast, to less than 3 µg/m³ in the south-east (Hoogerbrugge *et al.*, 2005, Matthijsen and Visser, 2006) with a clear gradient from north-west to south-east.

1.2 The contribution of sea salt aerosol to PM

Sea salt aerosol can be a substantial fraction of particulate matter for locations close to the coast. Particulate matter (PM) is a mixture of particulate and liquid material from different sources, for example, secondary inorganic salts, carbonaceous material, crustal matter, and sea salt. PM is associated with adverse health effects. Some of its constituents are generally believed to be harmless, like sea salt. But epidemiological studies on health effects were generally done on the basis of the ambient mixture of constituents (e.g. Brunekreef and Forsberg 2005). Furthermore, the combination of constituents may influence the toxicity of the individual substances, and a correlation between sea salt and mortality was found, albeit with a substantial time lag (Mar *et al.*, 2006). In this report, we will not discuss health effects of sea salt but restrict ourselves to the absolute sea salt concentrations and the contribution of sea salt to total PM_{10} and $PM_{2.5}$.

The European Union has introduced legislation to limit the adverse effects of air pollution on health and ecosystems. As part of the EU legislation to improve air quality, the EU air quality directive 2008/50/EC was issued, setting limit values and target values for PM_{10} and $PM_{2.5}$ concentrations in ambient air. Annual average PM_{10} concentrations should not exceed 40 µg/m³ and daily averages should not exceed 50 µg/m³, on more than 35 days per year. For $PM_{2.5}$ there is a target value for the annual average concentration, by 2010 (25 µg/m³), which becomes the limit value by 2015, and an exposure concentration obligation of 20 µg/m³ by 2015 (a limit value for the national average city background concentration). When limit values are exceeded, Member States have to take action by making plans and programmes with adequate abatement measures. However, sea salt and desert dust concentrations will not be affected by abatement measures, since they originate from natural processes.

In the assessment of a Member State's compliance with limit values, the EU Air Quality Directive allows subtraction of the natural contribution from the PM concentration , provided that it can be determined with sufficient certainty, and if the limit values are exceeded – fully or partly – because of these natural contributions. A Member State has to provide evidence of the contribution from natural sources to these exceedances, and be able to quantify the contribution. Subtraction of sea salt from PM_{10} concentrations when assessing compliance with PM_{10} limit values, de facto, relaxes these limit values with the subtracted amount.

In the Netherlands, the EU Air Quality Directive is implemented in national legislation in such a way that it provides the possibility of subtracting sea salt from PM_{10} when assessing compliance with the PM_{10} limit values. National regulations on this subject are described in the Regulation on Air Quality Assessment (*Regeling beoordeling luchtkwaliteit*,Staatscourant, 2007). This regulation was based on a map of sodium depositions (1998, see Matthijsen and Visser, 2006), combined with a second assessment of the contribution of sea salt to PM_{10} in the Netherlands, based on chloride (Hoogerbrugge *et al.*, 2005). In this second assessment, the contribution during days when average daily PM_{10} concentrations exceeded 50 µg/m³, was also investigated. A best estimate for subtracting the sea salt from the total number of exceedance days for average daily PM_{10} concentrations provided a reduction of 6 days. This number was uniform for the whole country. One should note that when PM levels are high, sea salt contributions are generally low, since in the Netherlands, high PM concentrations are associated with weak and southerly or easterly winds, whereas high sea salt contributions occur during strong westerly and northerly winds. The sea salt contribution to the average annual PM_{10} concentration varies from west to east. Highest sea salt concentrations occur along the west coast and decrease towards the eastern part of the Netherlands. Therefore, the Regulation on Air Quality Assessment provides location-dependent estimates for subtracting sea salt from the average annual PM_{10} concentrations.

So far, estimates of sea salt contributions to PM_{10} and $PM_{2.5}$, made by means of modelling and measurements, have been limited by large uncertainties. In models, the uncertainties are easily a factor two. On the measurement side, the use of chloride measurements in the Netherlands was subject to uncertainties regarding the precise sampled fraction and losses of chloride, because of chemical reactions. The present study aims to improve the knowledge on the contribution of sea salt to daily and annual average PM_{10} and $PM_{2.5}$ concentrations in the Netherlands. This study is part of the BOP national programme on PM_{10} and $PM_{2.5}$ (see text box). The study addresses the following questions.

1.3 Main questions

How large is the contribution of sea salt to PM_{10} and $PM_{2.5}$ in the Netherlands?

We assessed the variability from day to day and from year to year, minimum and maximum concentrations, the gradient from coastal to inland areas, and the relative contribution of sea salt to total PM_{10} and $PM_{2.5}$. This last assessment was relevant for answering the underlying question of how much sea salt contributes to exceedances of the standard for daily average PM_{10} concentrations of 50 µg/m³. The composition of PM_{10} and $PM_{2.5}$ was analysed at six stations, for a full calendar year. Sodium was part of the elemental analysis and served as a tracer for sea salt. Also, model results were used to complete the picture. The observations and modelling of the contribution of sea salt to PM in the Netherlands, were compared to observations of sea salt concentrations in other European countries.

How should we use a chemical transport model for to assessing the temporal and spatial behaviour of sea salt in the Netherlands?

Since observations are restricted within space and time, the use of a model is recommended by the European Air Quality Directive (2008/50/EC). For this study, the LOTOS-EUROS model was used. This is a chemistry-transport model, the type of model that is generally used for air quality assessments. We compare the results from the LOTOS-EUROS model with observations, and use the model to study spatial gradients and temporal variability in detail. The model description, and a validation of the overall performance of the LOTOS-EUROS model for different PM constituents, are described in the technical background report by Schaap *et al.* (2009). The uncertainties and sensitivity in the LOTOS-EUROS model results will be discussed briefly, and some attention will also be paid to an alternative model, based on trajectories.

How do the new findings relate to the present Regulation on Air Quality Assessment, with regard to sea salt?

In particular, what are the average sea salt concentrations in PM_{10} and $PM_{2.5}$, and what are the contributions on days when PM_{10} concentrations exceed 50 µg/m³? We compared the present findings to estimates by Hoogerbrugge *et al.* (2005), ultimately followed by conclusions and recommendations.

Structure of the report

In Chapter 2, the observation strategy and the observations, themselves, are presented and interpreted. Also, the two observation methods that were used, are compared. In Chapter 3, the LOTOS-EUROS model is described and model results are compared with observations. The contribution of sea salt on days with exceedances of the PM_{10} limit value is assessed in Chapter 4, by using both observations and model results. Finally, in Chapter 5, the conclusions are presented.

Netherlands Research Program on Particulate Matter (BOP)

This study was conducted under the auspices of the Netherlands Research Program on Particulate Matter (BOP), a national programme on PM_{10} and $PM_{2.5}$, funded by the Netherlands Ministry of Housing, Spatial Planning and the Environment (VROM). The programme is a framework of cooperation, involving four Dutch institutes: the Energy Research Centre of the Netherlands (ECN), the Netherlands Environmental Assessment Agency (PBL), the Environment and Safety Division of the National Institute for Public Health and the Environment (RIVM), and TNO Built Environment and Geosciences.

The goal of BOP is to reduce uncertainties about particulate matter (PM) and the number of policy dilemmas, which complicate development and implementation of adequate policy measures. Uncertainties concerning health aspects of PM are not explicitly addressed.

The approach for dealing with these objectives is through the integration of mass and composition measurements of PM_{10} and $PM_{2.5}$, emission studies and model development. In addition, dedicated measurement campaigns were conducted to research specific PM topics.

The results from the BOP research programme are being published in a special series of reports. The subjects in this series, in general terms, are: sea salt (this report), mineral dust, secondary inorganic aerosol, elemental and organic carbon (EC/OC), and mass closure and source apportionment. Some BOP reports concern specific PM topics: urban background, PM trend, shipping emissions, EC and OC emissions from traffic, and attainability of $PM_{2.5}$ standards. Technical details of the research programme will be condensed in two background documents; one on measurements and one on model developments. In addition, all results will be combined in a special summary for policymakers.

2

Observations

The purpose of the observations was to get a better idea of the sea salt concentrations in the Netherlands. We were not only interested in annual averages, but also in variations on different time scales: interannual, seasonal, day to day, and hourly. Particularly relevant were the concentrations on days on which limit values for PM_{10} were exceeded. Also, spatial gradients of sea salt concentrations within in the Netherlands were examined. We investigated the representativeness of the observations, obtained during the BOP measurement campaign, for average annual sea salt concentrations, and, therefore, we also explored the interannual variability in concentrations of sea salt tracers. The observations were compared with observations of sea salt in PM from previous studies, and from other European countries.

2.1 Sea salt tracers

Sea salt consists of a mixture of ions (Table 2.1). Chloride (Cl) contributes most in weight, closely followed by sodium (Na). The latter is a better tracer for sea salt, since it is not subject to chemical losses, contrary to chloride (e.g. Dasgupta *et al.*, 2007). This issue is addressed further below. For the Netherlands, sea salt can also contribute to the sulphate concentration. The sulphate fraction in sea salt is only 7%, but since sulphate concentrations in the Netherlands are relatively low, the contribution of sea salt may not be negligible. The sulphate concentrations in the Netherlands, also measured in the framework of the BOP programme, are addressed in a report on secondary inorganic aerosols (Weijers *et al.*, 2009).

2.1.1 Sodium measurements versus chloride measurements

In this study, sodium was used as the main tracer for sea salt. Earlier assessments of sea salt in PM, in the Netherlands, were largely based on a long time series of chloride observations in the Dutch Air Quality Monitoring Network (LML, 2009), at six rural locations in the Netherlands. Chloride observations have a large margin of uncertainty for several reasons:

1. High detection limit, corresponding with 1.14 µg/m³. This detection limit is reached rather often, so many chloride measurements are not well quantified.
2. The cut-off size of the PM measurements for which chloride was analysed was not well defined. It was estimated to around 3 µm. Most of the sea salt is present in the coarse PM fraction (2.5-10 µm). Hoogerbrugge *et al.* (2005) estimated a correction factor of 2 to 4 to extrapolate the measurements to PM_{10}.
3. Chloride can be removed from sea salt aerosol by the following reactions

   $$NaCl + HNO_3 \leftrightarrow NaNO_3 + HCl$$
   $$2NaCl + H_2SO_4 \leftrightarrow Na_2SO_4 + 2HCl$$

   Then the gaseous HCl is no longer part of the PM mixture, but the solid $NaNO_3$ and Na_2SO_4 still are. Therefore, sodium is a better tracer for sea salt than chloride, when analysing the PM composition. Hoogerbrugge *et al.*, 2005 estimated the degree of volatilisation of chloride at 10%, 20% (average), or 30%, which render a correction factor of 1,1, 1.25 (average), or 1.4, respectively.

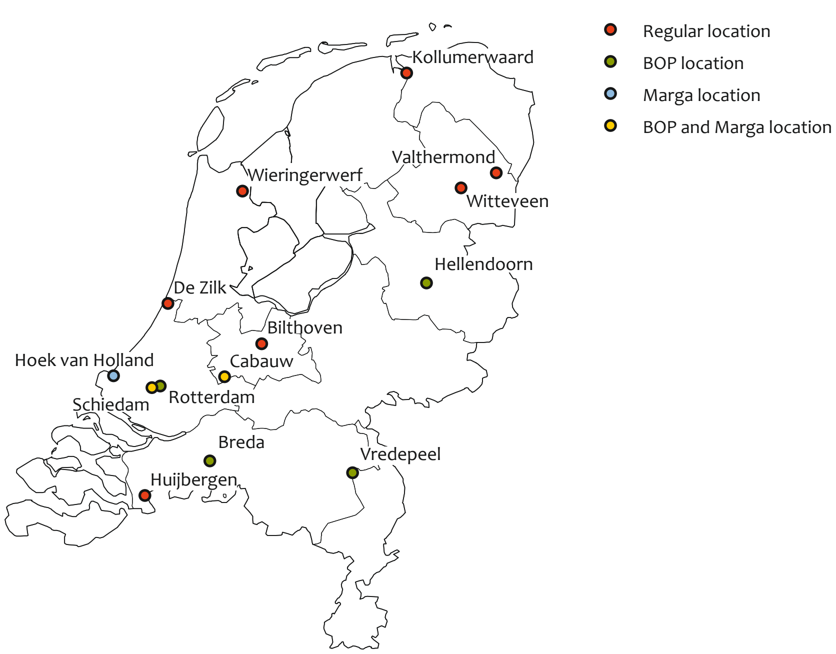
Before the BOP campaign was held, such chloride measurements were the only available routine tracer measurements for sea salt. To investigate how accurate these measurements were, we compared the chloride and sodium measurements for those time frames for which both were available. Details can be found in appendix A. In this comparison, the correlation between the standard chloride measurements and the BOP sodium measurements was poor, possibly due to the crude cut-off estimate. For the MARGA (Monitoring instrument for AeRosols and GAses) measurements, which had

Elemental composition of sea salt **Table 2.1**

Element	Percent by weight
Cl	55.04
Na	30.61
SO4-	7.68
Mg	3.69
Ca	1.16
K	1.1

Composition of sea salt, based on the composition of sea water (Seinfeld and Pandis 1998), for components that contribute more than 1% to the sea salt mass.

Overview of regular and BOP measurement locations **Figure 2.1**



Overview of regular and BOP measurement locations.

sampled sodium and chloride at the same time, the correlation was good (R=0.85-0.90), and a correction factor for the depletion could be estimated for each station (of the order of 20%). This means that the *LML* chloride measurements, with an appropriate correction factor (Hoogerbrugge *et al.*, 2005), probably give the right order of magnitude for annual average values, but because of the combined uncertainties in cut-off size, chemical losses, and the high detection limit, they were less suitable for assessing day-to-day variability.

2.2 Sea salt from the BOP measurement campaign: measurement locations and sampling strategy

Within the BOP research programme on PM_{10} and $PM_{2.5}$, the composition of particulate matter was determined at a number of sites, in the Netherlands, between August 2007 and September 2008. For this purpose, PM samples were collected using filters, which were subsequently analysed for their sodium content. These samples were collected every second or fourth day, depending on the location. In addition, at selected locations, continuous observations on an hourly time resolution were made by the MARGA instrument. Below, we briefly introduce the measurement strategy and methodology. Special attention was given to the assessment of the consistency of data obtained with the two different measurement methods. For a detailed overview of the measurement methodologies employed here, we refer to Van Arkel *et al.* (2009). Figure 2.1 indicates the observation locations.

2.2.1 Filter measurements: average daily concentrations

During the BOP measurement campaign, the composition of both PM_{10} and $PM_{2.5}$ was measured at six locations (see Table 2.2). The locations include three regional sites (Cabauw, Hellendoorn, Vredepeel), and three urban sites (Rotterdam, Schiedam and Breda (in Breda, only PM_{10} was measured). The classic differentiation between regional background, urban, or traffic locations, was not relevant to the assessment of the sea salt contribution to PM, because the sea is, by far, the most important source of atmospheric sodium in the Netherlands. Therefore, the six locations provided good coverage of the southern part of the Netherlands, with locations at different distances from the coast.

Samples were collected every other day, from all stations. The twenty-four-hour sampling was performed by using a Leckel SEQ47/50 sequential, low-volume system (LVS), at a constant flow rate of 2.3 m^3/hr. A Teflon filter was used to collect samples for the analysis of the elemental composition, including sodium. For other analysing purposes, parallel sampling on quartz filters was used.

A full chemical analysis was performed for half of the filters, that is, for every fourth day. The regular analyses were supplemented with a number of analyses of days that provided interesting cases. The total number of valid analyses, per station, is specified in Table 2.2. The sodium content of the samples was determined by extraction of the filters using nitric acid, followed by ICP-MS analysis. The procedures followed the standard operational procedures of the *LML*. The recovery of sodium in the ICP-MS analysis was not well determined. Analysis of a test sample indicated a recovery of only 65%. The true recovery rate would probably be much higher, since the test sample was representative for sodium in soil, and we expect that sodium could be extracted from sea salt more easily. A second indication of the recovery was

Location and sampling period for all 6 sites employing filter measurements Table 2.2

Location	Classification	Fraction	sampling period	#used samples
Breda	Urban	PM$_{10}$	1.9.07-8.9.08	97
Cabauw	Rural	PM$_{2,5}$ & PM$_{10}$	23.09.07-8.9.08	76 81
Hellendoorn	Rural	PM$_{2,5}$ & PM$_{10}$	16.10.09-8.9.08	63 72
Rotterdam	Kerbside	PM$_{2,5}$ & PM$_{10}$	08.9.07-8.9.08	100 117
Schiedam	Urban	PM$_{2,5}$ & PM$_{10}$	08.9.07-8.9.08	72 76
Vredepeel	Rural	PM$_{2,5}$ & PM$_{10}$	1.9.07-8.9.08	105 109

Location and sampling period of MARGA instruments Table 2.3

Location	Classification	Fraction	sampling period	#days
Hoek van Holland	Industrial	PM$_{10}$	1.09.07-28.10.07	37
Cabauw	Rural	PM$_{10}$	1.08.07-27.02.08	141
Schiedam	Urban background	PM$_{10}$	1.08.07-22.02.08	96

a comparison of concentrations from filter analyses and from MARGA observations, which are provided further on.

2.2.2 MARGA measurements: hourly concentrations

At three locations, the hourly concentrations of sodium in PM$_{10}$ were monitored with the MARGA (Monitoring instrument for AeRosols and GAses) instrument (Slanina *et al.*, 2001; see also http://www.applikon-analyzers.com/applikonanalyzer/images/pdf/marga-leaflet2.pdf)). At two locations (Schiedam and Cabauw) MARGA measurements were performed in parallel with filter measurements. In this way, a high-resolution data set was obtained, partially overlapping the filter data, as the MARGA also provided data for days without filter measurements. The labour-intensive MARGA measurements were carried out for seven months; from August 2007 to February 2008, in Schiedam and Cabauw. A third system was operated at Hoek van Holland, for two months, and provided a data point at only 1.5 km from the coast. Table 2.3 summarises the observation strategy.

The MARGA instrument consists of two boxes: a sampling unit and an analytical unit. A mass flow controlled air pump draws 1 m^3 ambient air per hour through the sampling box. During the campaign, a URG PM$_{10}$ head impactor was positioned as inlet, at a four-metre height. The sampler unit has a Wet Rotating Denuder (WRD) for gas sampling and a Steam Jet Aerosol Collector (SJAC) (Khlystov *et al*, 1995). Gases are dissolved in the water which forms a thin film on the inner wall of the WRD. Aerosols are collected in the SJAC. These have a slow diffusion speed, and, therefore, do not dissolve in the WRD. The air, stripped from water-soluble gases, is drawn through a glass mixing chamber and, subsequently, a 2-micron cut-off glass cyclone. In the mixing chamber, a water supersaturated condition is created by means of steam injection, forcing a water vapour condensation process. Through condensational growth, aerosols are quantitatively separated in the cyclone.

The solutions, containing the stripped gases and the aerosols, are separated and analysed using ion chromatography based on the ion exchange mechanism and conductimetric detection. The continuous sampling provides hourly concentrations of

- sulphate, nitrate and chloride in aerosols
- ammonium and sodium in aerosols
- nitric acid, nitrous acid, sulphur dioxide, ammonia, and hydrochloric acid in gas phase.

From these components, the aerosol sodium data were used in this report. The detection limit for sodium is 0.08 µg/m^3, and the accuracy (closeness to true value) and precision (reproducibility) are 7% and 5%, respectively.

2.3 Representativeness

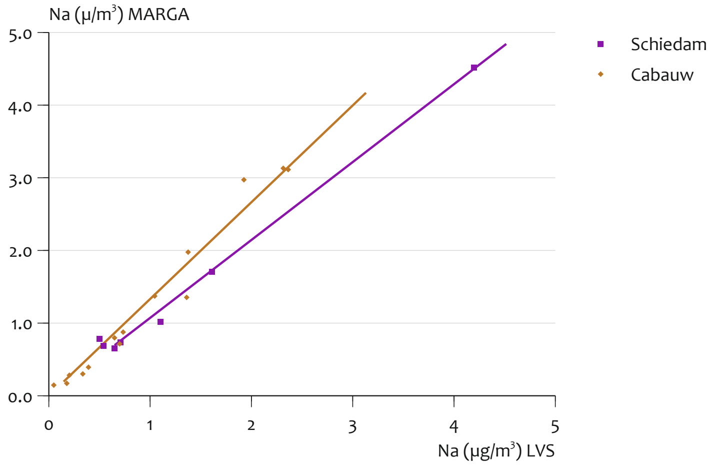
2.3.1 MARGA versus filter measurements

Daily average concentrations from MARGA measurements and filter measurements were compared for Cabauw and Schiedam, in Figure 2.2. Unfortunately, the number of days on which both measurements were available was very limited (14 observations for Cabauw, 9 for Schiedam; and we have omitted two outliers in Schiedam for which the sodium concentrations from the filter analysis were substantially higher than from the MARGA sodium measurements). Nevertheless, the linear relationship between MARGA and filter measurements was evident, and the correlation between them was very good at both locations, except for two measurements at Schiedam. We fitted a straight line through the correlation plot with LVS observations on the horizontal axis, and daily average MARGA observations on the vertical axis, and forced the line to the origin. The resulting line estimates are:

Cabauw: ConcMarga=1.33 ConcLVS, R2=0.97
Schiedam: ConcMarga=0.98 ConcLVS, R2=0.91
ConcMarga=1.07 ConcLVS, R2=0.99 (two observations omitted)

For Cabauw, concentrations observed by MARGA were always higher than those in the filter measurements. For Schiedam, MARGA observations were only marginally higher than filter measurements. Measurements at Cabauw

Correlation between observed and modelled sodium concentrations **Figure 2.2**



Correlation plot of daily average sodium concentrations, from MARGA measurements and LVS filter analyses. The two deviating measurements in Schiedam were omitted.

indicated a recovery of 75% for the LVS sodium analyses, and measurements at Schiedam indicated a nearly 100% recovery.

2.3.2 Sodium versus chloride measurements

The BOP data set enabled a direct comparison between chloride and sodium measurements. This intercomparison can be found in Appendix A. The main findings were:

- intercomparison of simultaneous MARGA chloride and sodium observations showed that chloride and sodium were well correlated. Chloride was depleted with respect to sodium, on average by about 20%. For high sea salt concentrations the depletion was slightly less (fresh aerosol), for low concentrations (aged aerosol) chloride was slightly more depleted, as expected. This is in line with the estimate by Hoogerbrugge *et al*. (2005).
- intercomparison of the traditional LVS PM_3 chloride measurements in 2007, and the present sodium filter measurements were not very conclusive, because of a very limited time overlap and very poor correlation. Earlier observations, from April 2005, showed a rather good correlation, which was not found in the present BOP observations. The multiplication factor for translating chloride to total sea salt depended on the station; in 2005, varying between 2.2 for Bilthoven and 3.5 for Kollumerwaard. The latter is in agreement with the factor used for the assessment of sea salt concentrations by Hoogerbrugge *et al.* (2005). Further verification with additional chloride observations would be needed to draw firm conclusions.

2.4 Sea salt climatology

Sea salt concentration levels are closely linked to meteorological conditions, because generation processes, removal, and dispersion, are determined mainly by meteorological parameters. Generation of sea salt particles is determined by local wind speed and sea surface temperature, and transport is determined by wind speed and direction. Also, removal through deposition depends on the weather, directly depending on the wetness of the surface, and on wash-out through rain and cloud processes. On a slower time scale, it also depends on seasonal variation in vegetation properties and snow cover, which have an effect on deposition velocities. This report presents both annual average concentrations and the variability on different scales, as well as the spatial gradient.

2.4.1 Annual average concentrations

Contribution to PM_{10} and $PM_{2.5}$

Table 2.4 gives the average sodium concentration over the observation period for the PM_{10} fraction, and Table 2.5 for the $PM_{2.5}$ fraction. The average values indicated a gradient, with higher concentrations near the coast and lower concentrations inland. It must be stressed that the full year was not covered in all locations, which may partly have obscured true regional differences. For example, for the period that it was operating, Hoek van Holland had the highest concentrations of all stations, but it did not function for the whole year, and missed the episodes with the highest concentrations. Schiedam had the highest annual average concentrations, closely followed by Rotterdam. Breda had a somewhat lower concentration, and, at Cabauw, the concentration was about half of that in Rotterdam. The concentration in Vredepeel was much lower. The lowest concentrations were observed in Hellendoorn, but, generally, the concentrations in Hellendoorn were close to those in Vredepeel.

Concentrations were highly variable, as could be seen from the standard deviation, which had a value close to the average value, and from the minimum and maximum concentrations.

When interpreting these results, one should keep in mind that the annual averages, by themselves, are a very crude summary of the results. On individual days, not only the absolute values would be different, but so would the gradient over the country, with more pronounced gradients when the wind would be coming from sea, and less pronounced or even with

Observed sodium concentrations in PM_{10}

Table 2.4

	Average (µg/m³)	stdev (µg/m³)	min (µg/m³)	max (µg/m³)
Breda (LVS)	0.85	0.78	0.08	3.33
Cabauw (LVS)	0.76	0.63	0.05	2.84
Cabauw (M)	1.00	0.81	0.10	5.08
Hellendoorn (LVS)	0.52	0.53	0.03	2.34
Rotterdam (LVS)	1.09	0.99	0.02	4.89
Schiedam (LVS)	1.21	1.09	0.10	5.54
Schiedam (M)	1.33	0.97	0.29	4.83
Vredepeel (LVS)	0.70	0.63	0.00	3.02
Hoek van Holland (M)	1.23	0.82	0.17	3.50

Climatology of observed sodium concentrations in the PM_{10} fraction: average, standard deviation, minimum and maximum. Note that MARGA observations at Schiedam and Cabauw only cover the first half year, and at Hoek van Holland only two months. MARGA results were first translated to twenty-four-hour averages

Observed sodium concentrations in $PM_{2.5}$

Table 2.5

	Average (µg/m³)	stdev (µg/m³)	min (µg/m³)	max (µg/m³)
Cabauw (LVS)	0.26	0.24	0.03	1.24
Hellendoorn (LVS)	0.18	0.20	0.01	1.19
Rotterdam (LVS)	0.26	0.28	0.02	1.69
Schiedam (LVS)	0.35	0.31	0.04	1.77
Vredepeel (LVS)	0.21	0.21	0.00	1.25

Climatology of observed sodium concentrations in the $PM_{2.5}$ fraction: average, standard deviation, minimum and maximum.

Ratio of observed sodium concentrations in $PM_{2.5}$ and in PM_{10}

Table 2.6

	ratio annual averages	average ratio	stdev average ratio	correlation R
Cabauw	0.34	0.38	0.16	0.94
Hellendoorn	0.35	0.43	0.33	0.77
Rotterdam	0.24	0.32	0.17	0.81
Schiedam	0.29	0.36	0.33	0.93
Vredepeel	0.30	0.35	0.18	0.93

Climatology of the ratio of sodium in $PM_{2.5}$ and sodium in PM_{10}: ratio of annual averages, annual average of ratios, standard deviation of ratios, and correlation between sodium in $PM_{2.5}$ and PM_{10}.

reversed gradients during continental winds. In Chapter 4, the effect of wind on concentrations is addressed in more detail.

Relative contribution of sodium in $PM_{2.5}$ to sodium in PM_{10}

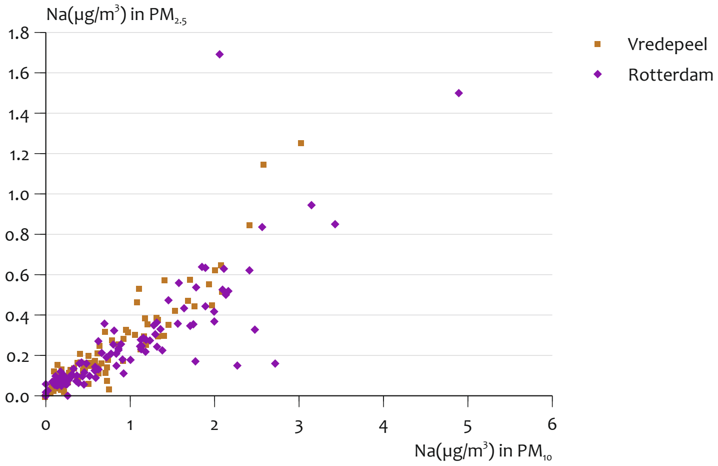
Table 2.6 and Figure 2.3 illustrate the relative contribution of sodium in $PM_{2.5}$ to sodium in PM_{10}. For Rotterdam, there were some incidental, relatively low sodium values for the $PM_{2.5}$ fraction, and one exceptionally high value, which caused the lower correlation and lower ratio. Also for Hellendoorn, there are some suspiciously low values for sodium in $PM_{2.5}$, and the number of observations was smaller, too. Only for very small and very large concentrations, the relative contribution seemed somewhat larger. One would expect a change in ratio from the coast to stations more land inwards. The ratio seemed somewhat smaller for the stations near the coast, than for Cabauw. For Vredepeel, however, the ratio was close to that of Schiedam. So, we had to conclude that the ratio was rather constant across the whole country. The sodium concentrations in PM_{10} and in $PM_{2.5}$ were well correlated. In general, the ratio also appeared rather constant over the full range of concentrations. We concluded that around 30 to 40% of the sodium, present in the PM_{10} fraction, was in the $PM_{2.5}$ fraction.

2.4.2 Day-to-day variability

Figure 2.4 shows observed sodium concentrations at Cabauw, to illustrate the variability in the concentrations. Concentrations were based on daily averages of the MARGA observations, including only those days with more than 12 hours of observations. There were several episodes with high concentrations, such as around 6 November, alternated by episodes of low concentrations, such as around 16 November. Concentrations may rise or drop significantly within one day.

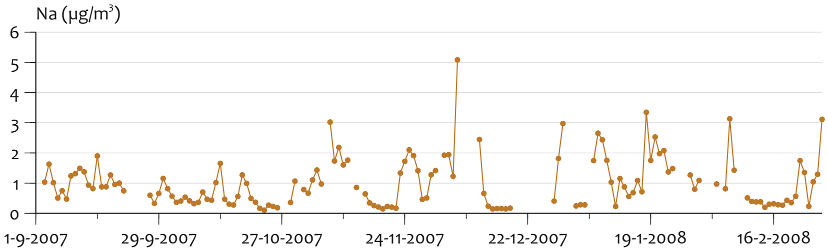
For other locations, the overall picture was the same, but since the LVS samples were not taken daily, the variability was more difficult to see. Large variabilities could also be observed from the minimum and maximum values and the standard deviation in Tables 2.4 and 2.5. The standard deviation had a value close to the average value. From Tables 2.5 and 2.6 followed that the behaviour of sodium in $PM_{2.5}$ (not shown) was similar to that in PM_{10}.

Correlation between sodium contribution in PM $_{2.5}$ and sodium contribution PM $_{10}$ **Figure 2.3**



Sodium concentrations in PM$_{2.5}$ versus those in PM$_{10}$ at the measurement locations Vredepeel (in land) and Rotterdam (coastal).

Daily average MARGA sodium concentration at Cabauw **Figure 2.4**



Daily average MARGA sodium concentrations at Cabauw. Only days with valid measurements for more 12 hours were included.

2.4.3 Hour-to-hour variability

The MARGA measurements in Figure 2.5 show that the hour-to-hour variability in the sodium concentration was very high, with fluctuations from less than 1 to more than 3 µg/m³ within one day. The reason for this is that sea salt concentrations are directly dependent on meteorology, which may also vary significantly, on an hourly basis. This holds both for the generation of sea salt, with storms typically lasting for (part of) one day at any specific location, and for sea salt deposition; especially wet deposition (rain) is a highly efficient discrete phenomenon. Sea salt typically has a lifetime of around one day. The hourly observations showed concentrations up to 10 µg/m³ (see Table 3.4), but because of the high variability, average daily concentrations were much lower.

The correlation between the three stations was high (R2 around 0.8). This indicates that generation and transport were large-scale phenomena, even on this time scale, with an overall decrease in concentration due to deposition, as the distance from the sea increased.

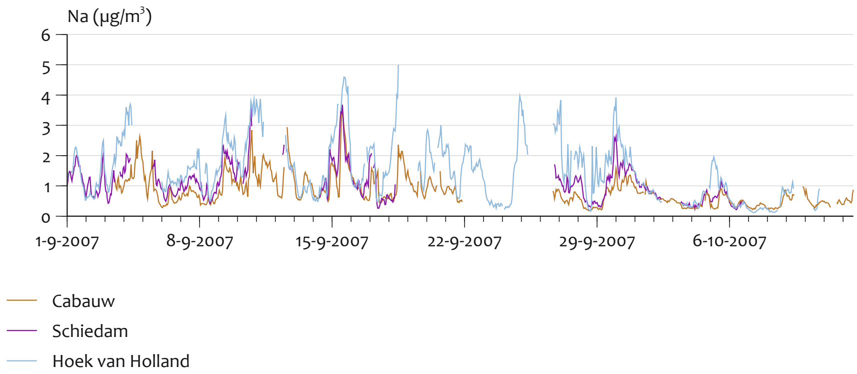
For the time frame shown, Hoek van Holland had the highest sodium concentrations, for most of the time, followed by Schiedam, with the lowest concentrations in Cabauw. This was consistent with the increasing distance from the coast. Only when the sodium concentrations were very low (end of September and in October), concentration levels were similar for all three stations. The low concentrations and small gradients over the country coincided with episodes of weak and continental winds.

2.4.4 Seasonal variability

Figure 2.6 illustrates the seasonal variability in sodium, by showing the monthly averages for Rotterdam and Vredepeel. Despite the variability, it is clear that concentrations were highest in autumn and winter, the relatively windy seasons, with large low pressure systems over the Atlantic Ocean and the North Sea. PM$_{10}$ sodium concentrations in Vredepeel were significantly lower, except during months when concentrations were very low (October, May). PM$_{2.5}$ did not show clear seasonal variability, and concentrations in Vredepeel were even somewhat higher than in Rotterdam. This behaviour was not expected, based on the generally good correlation between sodium in PM$_{10}$ and PM$_{2.5}$. For Rotterdam, PM$_{2.5}$ sodium values in January seemed unrealistically low, therefore, these values were omitted. Although on some other individual days, some of these values were suspiciously

Hourly average MARGA sodium observations

Figure 2.5

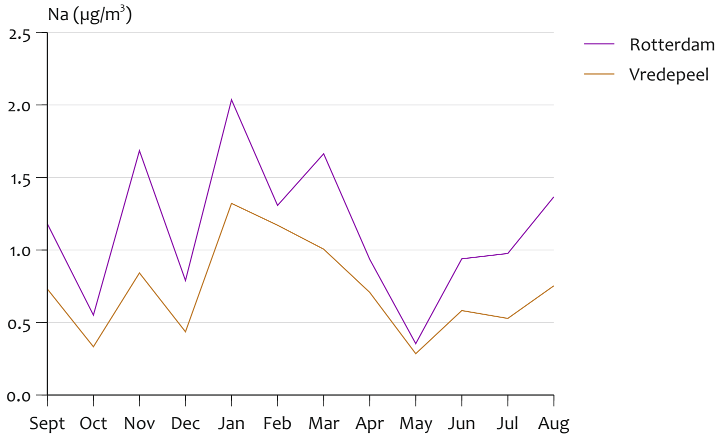


MARGA hourly observations. Only one time frame of the observations is shown to better illustrate the variability within one day, the good correlation between the stations, and the decrease in concentrations with increasing distance from the coast.

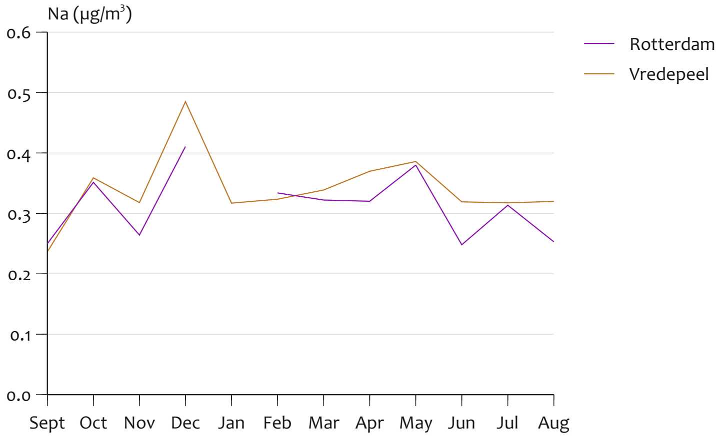
Monthly average sodium contribution (September 2007-August 2008)

Figure 2.6

in PM_{10}



in $PM_{2.5}$



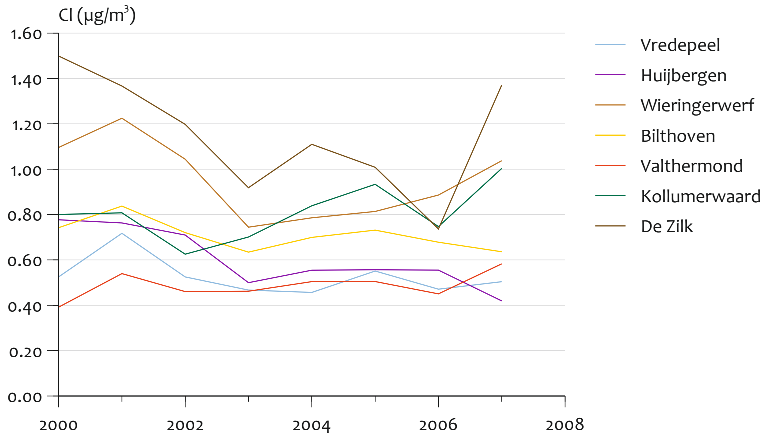
Monthly average concentrations in Rotterdam and Vredepeel, sodium in PM_{10} and in $PM_{2.5}$.

low, they were included. Something that also played a role, was that sodium in both $PM_{2.5}$ and PM_{10} was not always measured on the same days, so that a different subset of days was made. Given the high day-to-day variability, this may have caused differences in the observed seasonal patterns between sodium in PM_{10} and in $PM_{2.5}$ in the monthly average

Overview of historical sodium measurements in the Netherlands and in Duisburg Germany **Table 2.7**

	Period	Na	Reference
Speuld	Jan-Dec'95	0.79	Erisman, *et al.* (1996)
Cabauw (200m)	Nov'00-Mar'01	0.84	Weijers *et al.* (2002)
Cabauw (20m)	Nov'00-Mar'01	0.78	Weijers *et al.* (2002)
Duisburg	Feb'02-Mar'03	0.66	Quass *et al.* (2004)
Bilthoven	April 2005	0.50	Pre-BOP
Biest-Houtakker	April 2005	0.37	Pre-BOP
Kollumerwaard	April 2005	0.69	Pre-BOP
Vlaardingen	April 2005	0.70	Pre-BOP

Annual mean concentrations of chloride based on the LML-PM$_3$ measurements **Figure 2.7**



Annual average concentrations of chloride, based on LML PM$_3$ measurements.

data. For the annual average, the PM$_{2.5}$ concentration in Rotterdam was indeed higher than in Vredepeel.

2.4.5 Interannual variability

For the Netherlands, we had only one year of sodium observations. To obtain an indication of the interannual variability, the average annual values of the traditional LVS chloride measurements were used. For the calculation of the annual averages, the chloride values below the detection limit (1.14 µg/m³) were set to a small value (to 0.2 µg/m³, which is slightly below the lowest reported regular concentrations, to include the correction for the filter blank analysis) instead of being discarded, Otherwise, the average concentration would have been too high. Figure 2.7 shows these annual average values, and indicates that the values between years may differ by up to 40%. One should note that the relative maxima and minima of the different time series did not coincide. This could have been the result of inaccurate measurements, but could also have been due to a difference in transport: during westerly winds, the sodium concentrations may have been higher in De Zilk than in Kollumerwaard, and during more northerly winds, the opposite may have been true.

2.4.6 Comparison with other Dutch and European observations

There are a few studies in which sodium concentrations in the Netherlands were measured. The corresponding data have been summarised in Table 2.7. During 1995, an average annual sodium concentration of 0.79 µg/m³ was measured at Speuld (Erisman *et al.*, 1996), and during the winter of 2000 to 2001, Weijers *et al.* (2002) obtained sodium concentrations of about 0.8 µg/m³ at Cabauw. These concentrations were similar to the levels obtained during the BOP campaign. A full year of data from the Ruhr area, in Germany, showed a sodium concentration of 0.66 µg/m³, which is comparable to the concentration at Vredepeel. Also, a month of observations of four locations in the Netherlands in 2005 was included. To put the sea salt concentrations in the Netherlands in a European perspective, the comparison between sea salt concentrations from BOP and those from foreign data was extended and is reported here.

To compare the observed sodium concentrations with data in other European countries, a compilation of data was made. A literature search revealed a host of measuring stations with data on sodium. For our comparison, we selected only those stations that had at least one year of data. Many of these stations did not contain data on daily resolutions, but each data set represented 80 days of measurements or more. For the comparison, we focussed on sodium in PM$_{10}$. Because of possible chemical losses, chloride data were not taken into account. It should be kept in mind that not all data stemmed from the same year, however, we expected the overall picture to represent the main features of the sodium concentrations in Europe. Table 2.8 indicates the interannual variability, with some stations showing higher concentrations in 2005, and others in 2006. The variability was up to 40%, which

Observed average annual sodium concentrations, 2005 and 2006 and ratio

Table 2.8

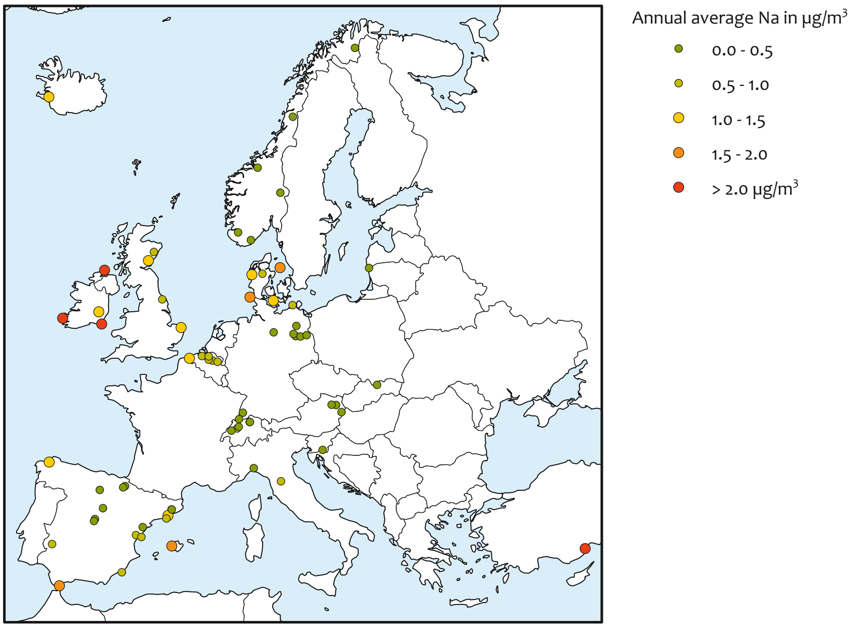
Station	Country	2005	2006	%
Illmitz	AUT	0.07	0.10	138
Westerland	DEU	2.14	1.56	73
Langenbrügge	DEU	0.39	0.39	102
Schauinsland	DEU	0.14	0.14	101
Neuglobsow	DEU	0.41	0.38	91
Zingst	DEU	0.77	0.58	75
Melpitz	DEU	0.27	0.26	97
Tange	DNK	1.11	0.98	88
Keldsnor	DNK	1.07	1.11	103
Anholt	DNK	1.85	1.53	82
Ulborg	DNK	1.51	1.31	87
Campisabalos	ESP	0.50	0.23	46
Montseny	ESP	0.26	0.36	138
Valentia Observatory	IRL	1.73	2.08	120
Oak Park	IRL	0.71	1.01	141
Malin Head	IRL	2.44	2.44	100
Carnsore Point	IRL	2.86	3.67	128
Rucava	LVA	0.22	0.23	106
Birkenes	NOR	0.46	0.35	78
Tustervatn	NOR	0.28	0.29	106
Kårvatn	NOR	0.18	0.17	90
Spitsbergen, Zeppelinfjell	NOR	0.27	0.23	85
Karasjok	NOR	0.21	0.22	102

Observed average annual sodium concentrations (µg/m^3) for 2005 and 2006, and ratio (%) of the 2005 and 2006 concentrations.

Sodium concentration in Europe

Figure 2.8

Annual average



Sodium concentrations in Europe (in µg/m^3).

corresponded with the variability that was deduced from the Dutch chloride measurements.

Figure 2.8 presents the data set, in the form of a geographical map. At a first glance, it is obvious that sea salt concentrations trail off from coastal areas to inland areas. The observations from Belgium, Denmark, Great Britain, Ireland, and other coastal regions were very similar to the concentrations observed in the Netherlands. In these countries, the sodium concentrations were between 0.6 and 1.3 µg/m³, depending on the distance from the coast. It appeared that coastal regions bordering on the Atlantic Ocean (Ireland, Spain) had higher sea salt levels than those bordering on the North Sea.

2.4.7 Contribution from road salting

In winter, if temperatures are expected to drop below zero degrees Celsius, main roads are salted to prevent the formation of ice. In principle, this salt could become part of the measured PM_{10} concentration. The chemical composition of this salt is different from fresh sea salt: the sodium and magnesium ratios are different. But sodium and magnesium are not unique to sea salt; a correlation with calcium must be studied to obtain a better indication of their origin. Therefore, in the filter analysis, the concentrations of calcium and magnesium were determined. The scatter of the ratios for these elements was so large that we could not identify any days with a significant change in the ratio of these elements. We also could not identify days with high sodium concentrations on street locations only, not even on cold winter days with southerly or easterly winds. One should note that the winter of 2007 to 2008 was not a cold winter, therefore, it was impossible to estimate the contribution from road salting to PM_{10} on individual days, on the basis of the observation set at hand. An average annual contribution of less than 1 µg/m³ was estimated by Denier van der Gon (personal communication), and this contribution was assumed to be a local effect.

3

Model

Observations are restricted in space and time. Modelled concentrations can be used to complete the picture that is outlined by the observations, provided that the modelled values are in good agreement with the observations. Here, we investigated the possibility of using the LOTOS-EUROS model for an assessment of the sea salt concentrations in the Netherlands. LOTOS-EUROS is a state-of-the-art Eulerian transport model, developed by the Netherlands Organisation for Applied Scientific Research (TNO) and the National Institute for Public Health and the Environment (RIVM). For reasons of completeness, we provide a brief description of this model. Detailed information can be found in the technical background report (Schaap *et al*., 2009) and in background documentation on the model (Schaap *et al.*, 2008). We compared the model results with the observations and with a Dutch trajectory model, OPS-KT (Van Jaarsveld and Klimov, 2009), which was also used for modelling sea salt concentrations in the Netherlands. The OPS-KT model is described in Appendix B.

Following the model description, the results are presented and compared to observations, with respect to absolute values and variability in space and time. In this way, we investigated whether the model would be suitable for assessing sea salt concentrations in the Netherlands

3.1 Model description

LOTOS-EUROS is a Eulerian chemistry-transport model (CTM), on a European scale. The domain ranges between 10 W-60 E, and 35 -70 N, with a regular 0.5 x 0.25 longitude/latitude grid. It includes nesting and zoom options. In the vertical, the model covers the lower 3.5 kilometres of the atmosphere, divided into three dynamical vertical layers and a boundary layer of 25 metres. ECMWF analysis fields are used as the meteorology that is driving the transport. The model is used for several gases and aerosols, and photochemistry with the CBM-IV scheme can be included. The model yields output of hourly concentrations. The full model is described in Schaap *et al.* (2008). In the framework of the present study, LOTOS-EUROS was adapted to state-of-the-art parameterisations regarding the source function of sea salt and the deposition of aerosols. The development and model validation are laid down in the technical background report by Schaap *et al.* (2009). Here, we briefly point out the main characteristics.

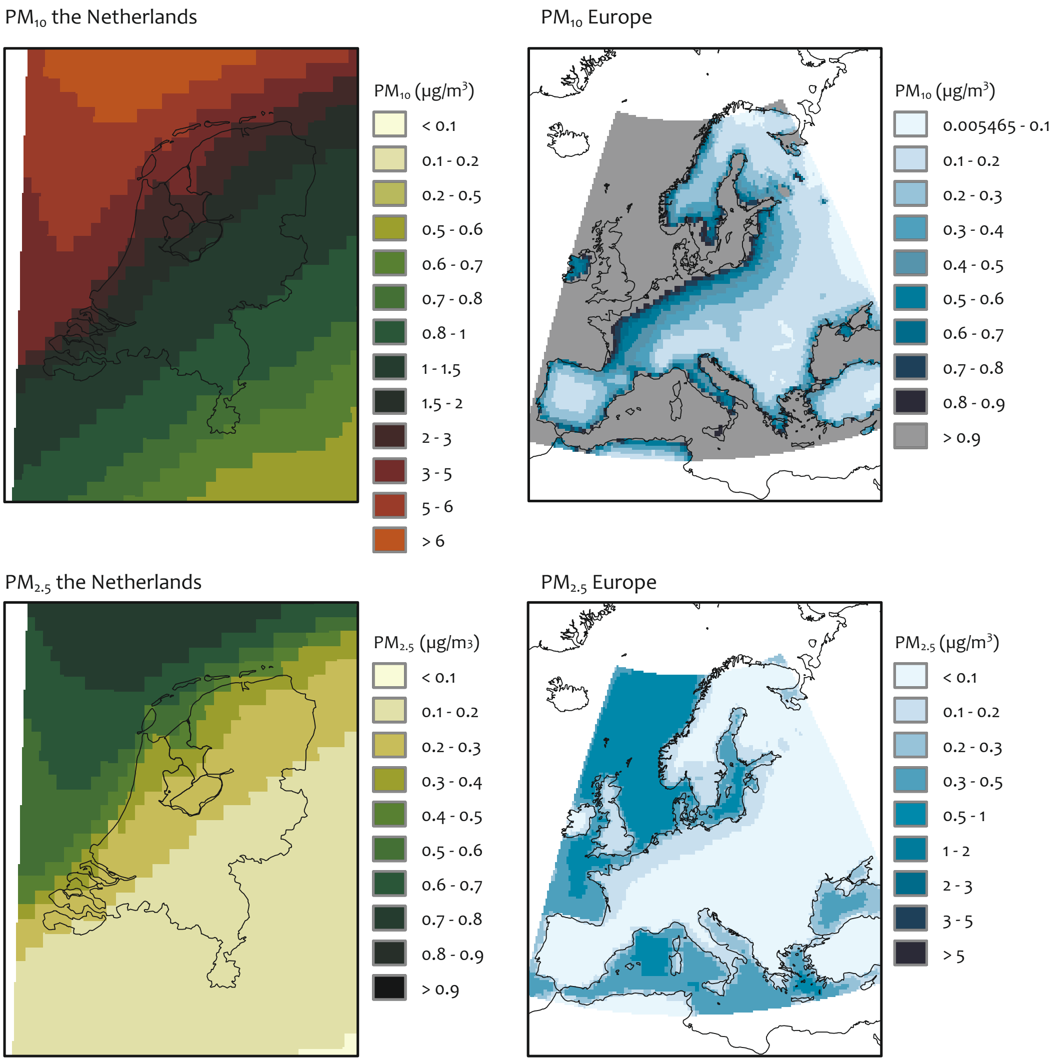
For sea salt aerosol, four particle size classes were used: 0.14-1, 1-2.5, 2.5-5, and 5-10 μm wet diameter (at 80% relative humidity). This choice enabled a reasonable size-dependent treatment of the size-dependent generation and deposition processes. Especially the dry deposition velocity of the larger particles depends strongly on the particle size. The dry deposition scheme was based on Zhang (2001), with a constant roughness length over sea.

Sea salt is generated at the interface of water and air, and the amount of aerosol formed depends on whitecap ratio and, probably, on the wave field characteristics; in essence, both are dependent on wind speed. The fundamental processes are known, but only empirically determined generation functions exist to quantify the amount of generation. For the generation of the smallest particles, the generation function by Mårtensson *et al.* (2003) was used, and for the larger fraction, the Monahan *et al.* (1986) parameterisation was used. Both parameterisations use a whitecap ratio, based on wind speed; Mårtensson also included sea water temperature. These generation functions still have a considerable uncertainty (by a factor of 3 to 7, depending on wind speed, Lewis and Schwartz, 2004), and for large wind speeds, whitecap ratio may be overestimated and aerosol production may be too high (Witek *et al*., 2007). However, both parameterisations are among the most established methods in their size class. Aerosol production within the surf zone was not taken into account, which may have resulted in an underestimation very close to the coast.

In the technical model report, the model was validated against observations in Denmark, Spain, Germany and Ireland. Correlations in time and space were good, but the model overestimated the observed annual average concentrations by about a factor of 2. This had to be taken into account when using the model for assessing the sea salt concentrations. Whether this factor would also hold for the Netherlands, was determined for this report by comparing the model results to the observations.

For this report, the model was run from 25 August 2007 to 15 September 2008, with a restart on 1 January 2008, leading to the loss of the first four days in January due to model spin-up. Two sets of runs were made: one on the 0.5° lon x 0.25° lat grid of the full model domain, and one nested run over the Netherlands, from 3 to 9° E and 49 to 55° N, on a 0.125° lon x 0.0625° lat grid.

Modelled annual average sodium concentrations **Figure 3.1**



Modelled annual average sodium concentrations (BOP period, September 2007 to August2008) in the Netherlands (left) and Europe (right), for PM_{10} (upper panels) and $PM_{2.5}$ (lower panels). The legend is in µg/m^3, note the differences between the panels.

3.2 Model verification

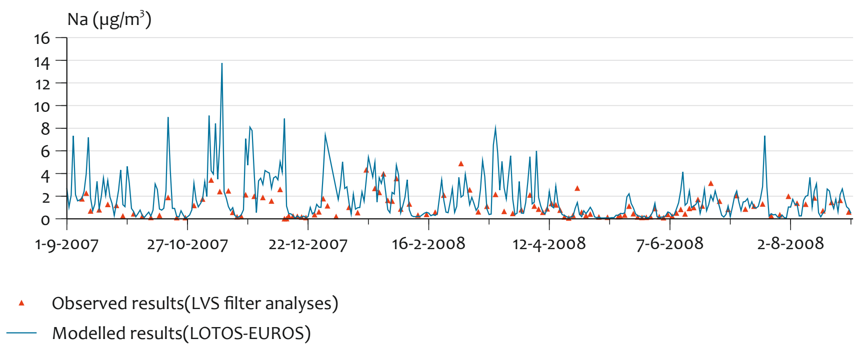
3.2.1 Annual average

Figure 3.1 shows the average annual concentration of sodium in the Netherlands and Europe. The figure clearly shows the strong gradients, with high values above the sea surface. Above land, concentrations decreased rapidly with increasing distance from the coast. One should note that, in the Baltic sea, the salinity is much lower than was assumed for the sea salt source function, resulting in an overestimation of the concentrations for that region, by a factor of 4.

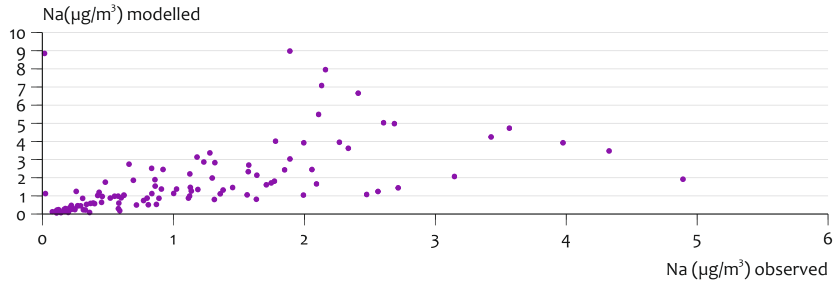
Figures 3.2 and 3.3 show the correlation between LOTOS-EUROS results and observations for sodium, from PM_{10} filter measurements and average twenty-four-hour MARGA measurements, in Rotterdam. The grid-cell value in LOTOS-EUROS for the corresponding station was taken, and no interpolation was applied. The general correlation was evident – high values on days with high concentrations, low values on days with low concentrations – although, for most days, there was a systematic overestimation. The correlation between model and observations was reasonable, but not very good. For the MARGA observations, the correlation was somewhat better, but a shorter time period was covered. Again, episodes with higher and lower concentrations were modelled at the right time, but the absolute values could differ, substantially.

Table 3.1 shows the average annual model output for the measurement locations. Two values are given: one for the average over all model days, and one for the average over the days of observation. There was a difference between the results, the largest for the stations with fewer observations. Because of the high day-to-day variability in concentrations, it does matter on which days the samples were taken. For both Rotterdam and Vredepeel, having many samples available, the difference was only 10%, for Hellendoorn, however, the difference was more than 30%. It is noticeable that, in all cases, the annual averages were higher. This effect must be

Sodium concentrations in PM_{10} in Rotterdam — Figure 3.2

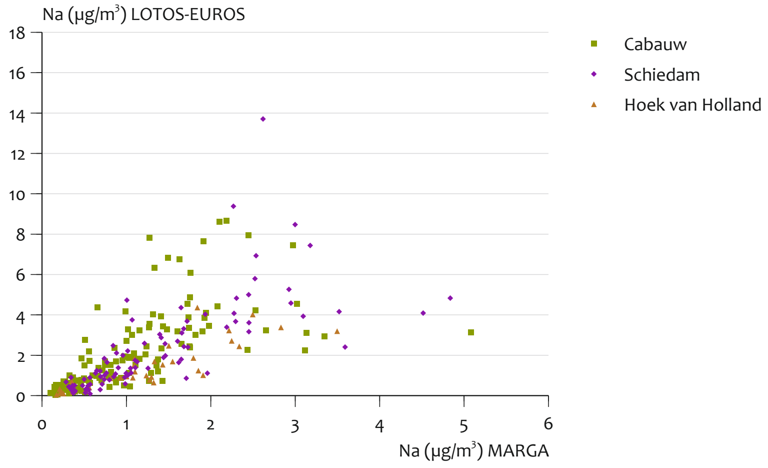

Daily average

Correlation between modelled and observed sodium daily average concentrations



Modelled and observed daily average sodium concentrations in PM_{10} in Rotterdam. Upper panel: time series, lower panel correlation plot.

Correlation between modelled and observed sodium concentrations — Figure 3.3



Observed and modelled daily average sodium concentrations.

taken into account when interpreting the observations, and it shows the added value of using a model.

The spatial gradient over the country was well represented, with systematic overestimations of the annual average concentrations, as follows from comparison between Table 2.4 and Table 3.1. The average scaling factor to translate modelled annual average concentrations to observations, was 0.70. This factor is used in Chapter 4.

3.2.2 Contribution of sea salt to $PM_{2.5}$

The sodium concentrations in $PM_{2.5}$ were also investigated. Figure 3.1 indicates the annual average values. As for sodium in PM_{10}, concentrations in $PM_{2.5}$ were highest above the sea and decreased land inwards, and the relative variability was also comparable with that of PM_{10}. However, concentrations were substantially lower than for PM_{10}, and gradients were less pronounced. In contrast to the sodium concentrations in PM_{10}, comparison between the observed concentrations (Table 2.5) and the modelled concentrations (Table 3.2) indi-

Modelled sodium concentrations in PM$_{10}$ at measurement locations

Table 3.1

	correlation R	average µg/m^3	stdev µg/m^3	min µg/m^3	max µg/m^3
Breda		1.28	1.51	0.02	19.98
	0.61	1.05	1.16	0.03	6.93
Cabauw		1.62	1.82	0.03	13.94
	0.57	1.24	1.36	0.06	7.59
Hellendoorn		1.29	1.52	0.02	10.62
	0.49	0.86	0.86	0.02	4.81
Rotterdam		1.79	1.91	0.05	13.75
	0.56	1.68	1.83	0.06	8.98
Schiedam		1.90	1.98	0.04	13.71
	0.64	1.45	1.39	0.07	8.15
Vredepeel		1.00	1.25	0.02	8.67
	0.62	0.92	1.12	0.03	5.24

Climatology of modelled sodium concentrations in PM$_{10}$ at measurement locations. Average values represent the average over the full modelled period (first line per station) and over the modelled period on days with observations only (second line per station).

Modelled sodium concentrations in PM$_{2.5}$ at measurement locations

Table 3.2

	correlation R	Average µg/m^3	stdev µg/m^3	min µg/m^3	max µg/m^3
Breda		0.20	0.22	0.006	1.62
Cabauw (LVS)		0.24	0.26	0.007	1.92
	0.54	0.18	0.20	0.012	1.00
Hellendoorn (LVS)		0.20	0.24	0.006	1.75
	0.34	0.14	0.16	0.007	0.96
Rotterdam (LVS)		0.26	0.28	0.008	1.89
	0.46	0.21	0.22	0.010	1.22
Schiedam (LVS)		0.27	0.29	0.008	1.89
	0.52	0.21	0.20	0.013	1.01
Vredepeel (LVS)		0.16	0.19	0.005	1.55
	0.43	0.15	0.16	0.006	0.75

Climatology of modelled sodium concentrations in PM$_{2.5}$ at measurement locations. Average values represent the average over the full modelled period (first line per station) and over the modelled period on days with observations only (second line per station).

Ratio of modelled sodium concentrations in PM$_{2.5}$ and in PM$_{10}$ at measurement locations

Table 3.3

	ratio annual averages	average ratio	stdev average ratio	correlation R
Breda	0.15	0.18	0.06	0.95
Cabauw	0.14	0.16	0.05	0.96
Hellendoorn	0.16	0.18	0.06	0.95
Rotterdam	0.15	0.16	0.04	0.97
Schiedam	0.15	0.16	0.04	0.97
Vredepeel	0.16	0.19	0.08	0.95

Climatology of the ratio of sodium in modelled PM$_{2.5}$ and PM$_{10}$: ratio of annual averages, annual averages of ratios, standard deviation of ratios, and correlation between sodium in PM$_{2.5}$ and PM$_{10}$

cates that the modelled sodium concentrations in PM$_{2.5}$ were slightly lower than the observed concentrations. This results in a too low ratio of sodium in PM$_{2.5}$ and sodium in PM$_{10}$ (Table 3.3 compared to Table 2.6), From the modelling perspective, the fact that this ratio was too low implied that some processes for smaller and larger particles were modelled differently. This provided an indication for further model improvement, as is discussed at the end of this chapter.

3.2.3 Hour-to-hour variability

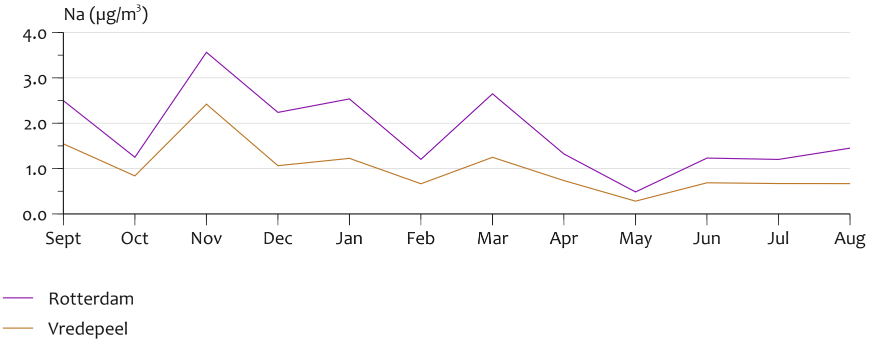
Table 3.4 compares the hourly modelled sodium concentrations with the hourly average concentrations measured with the MARGA instrument. The behaviour was much the same as for the daily average concentrations, with clear overestimations. However, the good correlation between hourly concentrations indicated that the concentrations in LOTOS-EUROS varied in a realistic way. The average scaling factor (0.55), going from LOTOS-EUROS averages for sodium in PM$_{10}$

Hourly observed and modelled sodium concentrations in PM_{10} **Table 3.4**

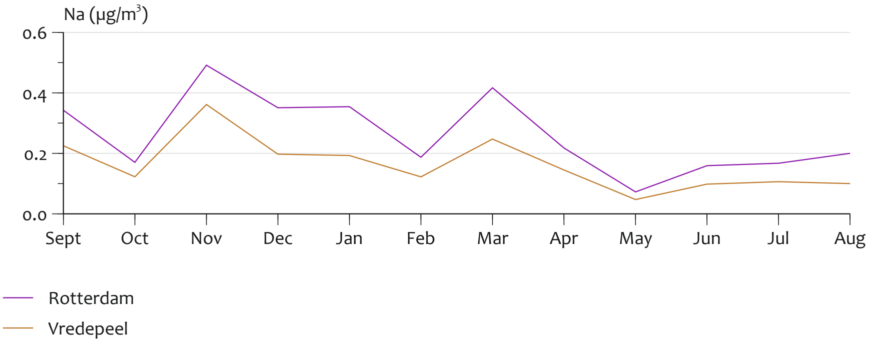
	observed (µg/m³)			modelled (µg/m³)			correlation R
	average	min	max	average	min	max	
Cabauw	0.96	0.00	6.50	2.03	0.02	23.45	0.58
Schiedam	1.38	0.01	10.50	2.34	0.04	23.03	0.54
Hoek van Holland	1.29	0.00	5.00	2.13	0.03	20.44	0.69

Modelled monthly average sodium concentrations (LE) in Particulate Matter **Figure 3.4**

in PM_{10}



in $PM_{2.5}$



Modelled monthly average sodium in PM_{10} (upper panel) and $PM_{2.5}$ (lower panel), for Rotterdam and Vredepeel, the stations with relatively high and low sodium concentrations.

to observed MARGA sodium concentrations, was a little lower than for the filter measurements, implying a somewhat larger overestimation by the model. This could have been due to the different observation period used by the MARGA instrument, compared to that used for the filter measurements, with more observations but restricted to the first half year of the BOP period, from September 2007 until the end of February 2008.

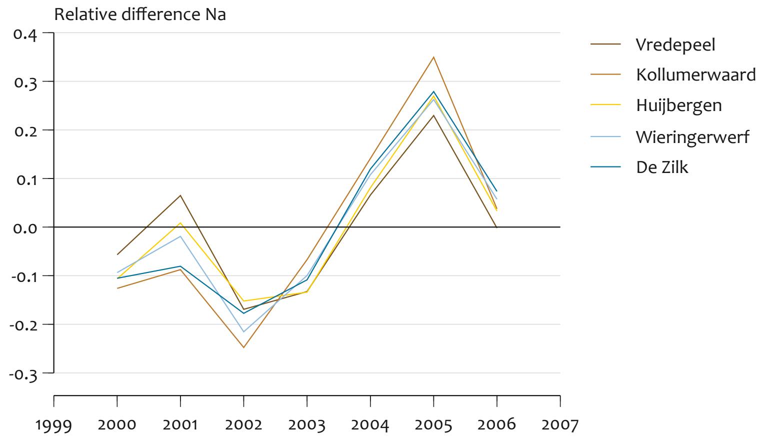
3.2.4 Seasonal variability

Figure 3.4 shows the monthly averages in modelled concentrations at two measurement locations. When averages were taken only for the days with observations, the correspondence with Figure 2.6 became even slightly better, although for the observations, the highest values were still for January instead of November. Furthermore, the modelled values were always higher than the observations. The figure clearly shows the seasonal variability with high values in autumn and low values in summer. The autumn and early winter are the seasons with the most storms at sea, generating and transporting sea salt to the continent. The relative difference for sodium in PM_{10} and $PM_{2.5}$ between Vredepeel and Rotterdam was similar, whereas in the observations the sodium concentrations in $PM_{2.5}$ were nearly equal for both locations.

3.2.5 Interannual variability

To study the interannual variability, LOTOS-EUROS runs were studied for the years 2000 to 2006. These runs were done with the basic version of LOTOS-EUROS, without including the new developments for sea salt (Schaap *et al.*, 2009). The year-to-year variability for sodium was up to 40%, which was in agreement with the chloride observations and the European sodium observations. In contrast with the chloride observations, the maximum and minimum concentrations of the different locations were clearly correlated. The patterns for Kollumerwaard and Vredepeel did resemble the pattern of the chloride measurements; for the other locations this was not the case.

Relative difference between modelled and observed sodium concentrations **Figure 3.5**



Relative difference between modelled sodium concentration and the average concentrations of 2000 to 2006.

The modelled annual average concentrations, for the BOP period, were compared with the results from the modelled annual average concentration in 2005, for which runs were available in the old and the new model version. The results from the BOP year, on average, were 25% lower than those for 2005. The year 2005 had relatively high concentrations; for the BOP year, the concentrations were about average. This indicated that the BOP year is representative for the long-term average sodium concentrations in the Netherlands.

3.2.6 Comparison with other models

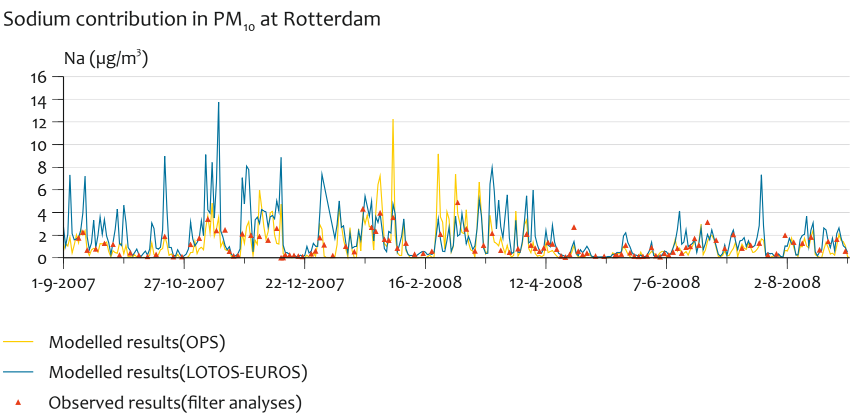
In the international modelling community, many CTMs are used to model sea salt emissions and concentrations. Differences between model results are large due to the uncertainties in emission and deposition (e.g. Lewis and Schwartz, 2004). Foltescu *et al.* (2005) found a good agreement between model results and observations for Denmark, when using the MATCH model, albeit with an overestimation of the highest \daily average concentrations. Within the range of model uncertainties, results are comparable with the LOTOS-EUROS results. Witek *et al.* (2007b) used a global model to investigate sea salt aerosol concentrations above open sea, and compared them with observations. They also arrived at an overestimation by the model, by about a factor of 1.6. In the NATAIR project (Grice *et al.*, 2009), only emissions were modelled for the European area for several years, with an interannual variability of up to 40%, for some areas. This is in line with our findings in this report. We can conclude that our model is up to the same standards as other models.

In the Netherlands, the OPS-KT model has also been used for modelling sea salt concentrations. This model is based on trajectories (Lagrangian approach). It is not to be confused with the OPS long-term model, which is used for modelling annual average concentrations and deposition in the Netherlands. In Appendix B, the OPS-KT model is briefly described. A more complete description can be found in Klimov (2006), and a discussion on the model can be found in Van Jaarsveld and Klimov (2009). Below, Figure 3.6 and Table 3.5 show model results for the BOP measurement period. With a few exceptions, OPS-KT did not overestimate the measurements as much as LOTOS-EUROS, and the correlation was slightly better. However, its correlation with LOTOS-EUROS was somewhat lower than between LOTOS-EUROS and the observations. OPS-KT captured the gradient over the country, with high concentrations near the coast (Rotterdam, Schiedam), and lower concentrations inland (Vredepeel, Hellendoorn).

The annual average concentrations which were determined by OPS-KT, were closer to the observations than those from LOTOS-EUROS, but the variability was still larger than for the observations. The high concentrations between 15 January and 15 March 2008 were remarkable. Only during this time frame, concentrations from OPS-KT were higher than from LOTOS-EUROS, and much higher than the observed concentrations. A notable difference between the models is that LOTOS-EUROS can take into account the actual wind speed at sea, and the free path length of the wind (fetch), since the wind above sea is included. For OPS, the wind above sea is an extrapolation of the observed wind over the Netherlands and over a platform at 10 km from the coast. Since the emission of sea salt is very sensitive to actual wind speed, this can explain part of the differences between LOTOS-EUROS and OPS. In Chapter 4, the effect of wind on sodium concentrations is illustrated in more detail.

As the uncertainty in the emission strength is very large (deviating at least by a factor of 2 to 3, as indicated above), the absolute correspondence between modelled and measured values could not be interpreted in relation to model quality. Any combination of ‘state-of-the-art’ emission and deposition modules in a CTM, that yields concentrations that are not more than two or three times larger or smaller than the observations, is as likely to be sound as any other. In the case of our comparison, the different behaviour of OPS-KT should be investigated by determining the modelled sea salt emission over the North Sea, to investigate the effects of the meteorology used in both models. In addition, the effect of the different model domains, that is the fetch, and deposition schemes have to be considered.

Comparison of modelled time series to filter measurements **Figure 3.6**



Sodium contribution in PM_{10} at Rotterdam

Comparison between daily average sodium in PM_{10} from modelled time series (OPS-KT and LOTOS-EUROS) and filter measurements at Rotterdam.

Modelled (OPS-KT) sodium concentrations in PM_{10} at measurement locations **Table 3.5**

	correlation R	average (µg/m³)	stdev (µg/m³)	min (µg/m³)	max (µg/m³)
Breda		0.84	1.25	0	10.75
	0.67	0.82	1.44	0	10.75
Cabauw		0.96	1.38	0	11.72
	0.76	0.80	1.14	0	6.12
Hellendoorn		0.82	1.27	0	10.50
	0.57	0.64	1.37	0	10.50
Rotterdam		1.08	1.47	0	12.24
	0.70	1.08	1.67	0	12.25
Schiedam		1.11	1.50	0	12.34
	0.69	1.11	1.82	0	12.34
Vredepeel		0.69	1.07	0	9.09
	0.65	0.72	1.22	0	9.09

Climatology of modelled (OPS-KT) sodium concentrations in the PM_{10} fraction: average, standard deviation, minimum and maximum.

3.2.7 Model uncertainties and sensitivity

The LOTOS-EUROS model performed quite well, it represented the spatial gradient of the observations well, and the timing of episodes with high sodium concentrations was good. The time correlation with the measurements was reasonable, although the absolute values of the modelled sodium concentrations in PM_{10} were often too large, especially for days with high sodium concentrations. For sodium in $PM_{2.5}$, the concentrations were underestimated. This resulted in a too low ratio of sea salt in $PM_{2.5}$ and PM_{10}. The general behaviour of the model was realistic, but in the parameterisations that were used in LOTOS-EUROS, there were several uncertainties which may have caused the discrepancies with the observations. These uncertainties are discussed here.

The most important uncertainty concerned the source function. An uncertainty in the emission strength would cause a corresponding uncertainty in the sea salt aerosol concentration,which made the model very sensitive to the source function. Unfortunately, all source functions are empirical functions based on observations in the laboratory and at sea, and are valid under a limited range of conditions. The source functions by Mårtensson *et al.* (2003) and Monahan *et al.* (1986), which are used here, are well established, but are uncertain by a factor of 10 (Lewis and Schwartz, 2004). Especially for high wind speeds, they may overestimate the source strength (Witek *et al.*, 2007a). In a sensitivity analysis, we put a maximum on the source function by cutting off the effective wind speed at 12.5 and 15 m/s. This indeed gave a reduction for high concentrations, but the effect was rather small, and not all episodes were affected. Clearly, not only the effect of wind speed on generation plays a role, but fetch and wind direction also had effects on totals and transport.

Further uncertainties are introduced by the parameterisation of dry deposition. Various parameterisations are used, according to literature, for different types of vegetation, and also the used parameters themselves are not universal. Here we do not elaborate on the uncertainty in the parameterisation itself: comparisons between the Zhang parameterisation and other parameterizations and observations can be found in Zhang *et al.* (2001) and Petroff (2005). The parameter values that we used were within the range of parameter values used in other models, except for the roughness length for sea water. A constant roughness length was assumed, whereas, in fact, this depends on wind speed and wave conditions. At larger wind speeds, the sea becomes rougher, thereby increasing the roughness length which would enhance deposition. Since more sea salt aerosol is generated at large wind speeds, not having taken the enhanced deposition for these conditions into account may have contributed to overestimation of the high concentrations.

In LOTOS-EUROS, the effect of relative humidity on particle size and density was not taken into account. This will have affected the correlation between modelled and observed hourly and daily concentrations, but its effect on monthly and annual averages was small. The effect will have been largest for the deposition of the largest particles, for which the deposition velocity is most sensitive to size and density, because of the relatively large contribution from the gravitational settling process. For smaller particles, deposition is dominated by other processes.

Finally, wet deposition is generally underestimated in LOTOS-EUROS. Only below-cloud scavenging is taken into account, in-cloud processing is neglected. This could also contribute to too high concentrations. Furthermore, for wet deposition fine and coarse particles are treated as two classes (0.14-2.5 and 2.5-10 µm). This could have led to an additional underestimation of scavenging for large particles and an overestimation for smaller particles, leading to an overestimation and an underestimation of their concentrations, respectively.

In conclusion, the large uncertainties in the source function made it difficult to constrain the other uncertainties. But the good spatial and reasonable temporal resolution justified the use of LOTOS-EUROS, with an appropriate scaling factor for the assessment of sea salt concentrations. The low ratio of sea salt in $PM_{2.5}$ and PM_{10} indicates that this model could be improved by further investigating the modelling of the size-dependent processes. Given the model uncertainties, it would be premature to judge OPS-KT to be a better model for sea salt modelling in the Netherlands than LOTOS-EUROS, based on the agreement between model results and observations, only.

Contribution of sea salt to total PM_{10} and $PM_{2.5}$

4

Here, we integrated all results for the contribution of sea salt to total PM_{10} and $PM_{2.5}$ in the Netherlands, and compared the new findings to the Dutch guideline for subtraction of sea salt concentrations from the total PM_{10} concentration. First, the effect of wind on the sea salt concentration was investigated, for the observations and both models. Then the sea salt concentrations were related to total PM_{10} and $PM_{2.5}$ concentrations. This resulted in an estimate of the number of days on which subtraction of the sea salt contribution would have brought the PM_{10} concentration below the limit value of 50 µg/m³. This chapter also presents the best estimate of the average annual sea salt concentration. Finally, it discusses the implications of the present findings for the Dutch guideline for the subtraction of sea salt from total PM_{10}.

4.1 The effect of wind on sodium concentrations

Wind plays a major role in the formation and transport of sea salt aerosol. We briefly investigated the correlation between wind direction, wind speed and sodium concentrations.

Figure 4.1 and 4.2 show the observed and modelled concentrations, set against wind direction and wind speed for sodium in PM_{10}. The observed wind speed and direction in De Bilt were used. De Bilt is located near the geographical centre of the Netherlands. Despite the considerable scatter, there was a clear relationship between concentration and wind direction. In the Netherlands, high sodium concentrations are found when the wind comes from the sea, whereas during continental winds (southerly or easterly), concentrations are very low. There was a small difference in behaviour between the observations and the models. The observations indicated that the highest sodium concentrations were reached during south-westerly to westerly winds. LOTOS-EUROS modelled the highest concentrations during north-westerly winds, whereas the observations and OPS indicated that the highest concentrations were reached during westerly winds. Both models overestimated the highest concentrations.

The observed sodium concentrations in PM_{10} and wind speed were positively correlated. For LOTOS-EUROS, the scatter was remarkably large, with part of the correlation plot well within the observed range, but with a substantial overestimation for intermediate wind speeds, on many days. The highest concentrations were not necessarily reached during the highest wind speeds. A possible explanation for this behaviour would be that local wind speeds are not representative of those above open sea, at the distance where generation takes place.

We also investigated the behaviour of sodium concentrations in $PM_{2.5}$, versus wind conditions. The results are shown in Figures 4.3 and 4.4. The relation with wind direction was similar to that for sodium in PM_{10}, for both observations and model, with the same discrepancy for the wind direction at which maximum concentrations were reached, but with better absolute model values. Also, the general increase in sodium concentrations with increasing wind speeds, as we saw for sodium in PM_{10}, was obvious and similar in both observations and model results. The difference in behaviour between model results and observations was less pronounced than for sodium in PM_{10}.

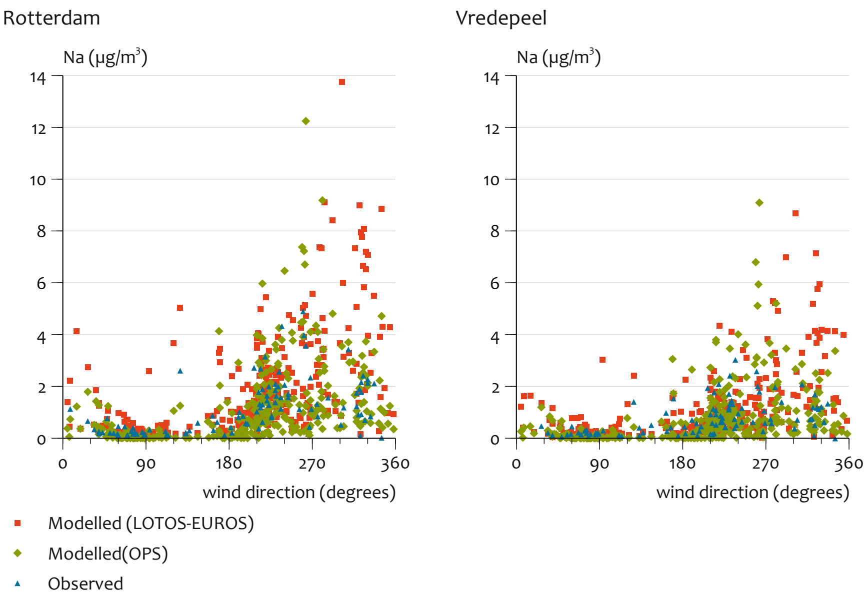
For sodium in $PM_{2.5}$ and in PM_{10}, both observations and model results showed that the gradient over the country was more pronounced when the wind was coming from the sea, than from the land.

4.2 Relative contribution of sea salt to PM_{10} and $PM_{2.5}$

The behaviour of sea salt concentrations, with respect to wind direction and wind speed, was opposite to that of total PM_{10}, which reached high values during weak winds from the south and east. This would have had its impact on the relative contribution of sea salt to PM_{10}. Figure 4.5 shows the observed and modelled sea salt concentration, versus the total PM_{10} concentration in Rotterdam. In Rotterdam, relatively high PM_{10} concentrations were observed, since this is a traffic-oriented location. Furthermore, Rotterdam is relatively close to the coast, thus, relatively high sea salt contributions were present. We calculated total sea salt from observations by multiplying sodium concentrations by 3.26 (mass fraction 0.306, Table 2.1), for the model results the factor 0.7*3.26 was used to compensate for the overestimation in the model. We must remark that this correction factor of 0.7 was based on annual average concentrations and may not apply to individual days.

Behavior of sodium concentrations in PM_{10} versus wind direction

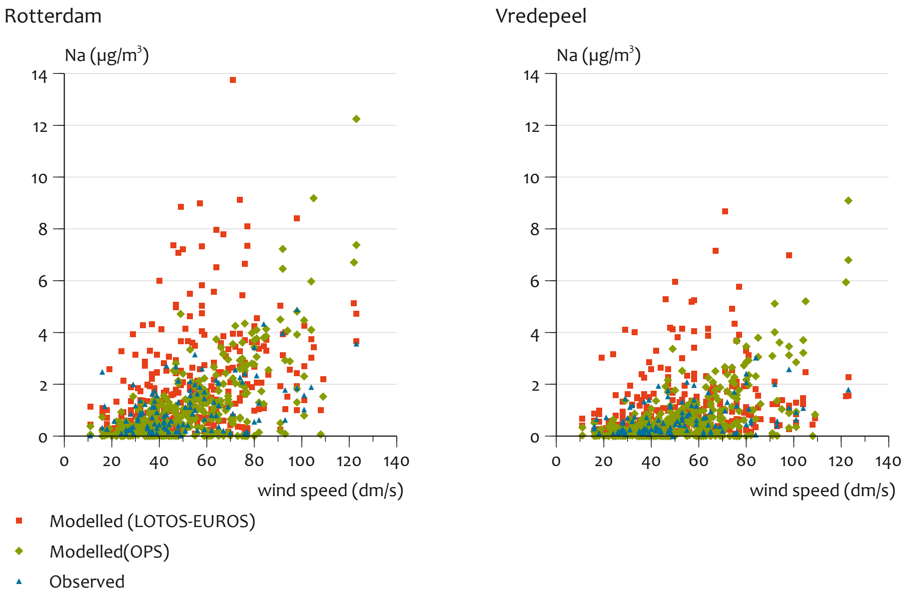
Figure 4.1



Observed and modelled sodium concentrations in PM_{10} for Rotterdam and Vredepeel, versus the observed wind direction in De Bilt.

Behavior of sodium concentrations in PM_{10} versus wind speed

Figure 4.2

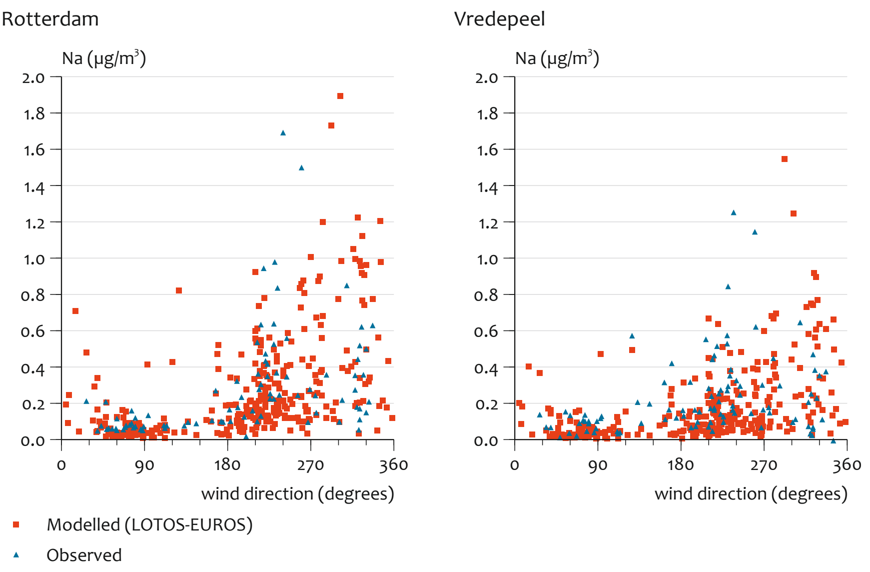


Observed and modelled sodium concentrations in PM_{10} for Rotterdam and Vredepeel, versus wind speed in De Bilt.

Sea salt may contribute significantly to PM_{10}, especially to low to intermediate PM_{10} concentrations. Sodium observations revealed that sodium contributed up to 5 µg/m³ to the daily average PM_{10} concentration in Rotterdam, which corresponded to a sea salt contribution of up to16 µg/m³. At very short distances from the coast (Hoek van Holland), the concentration could even be up to twice as high, occurring only on days with very high sea salt concentrations, as followed from the MARGA results. However, for days with high daily average PM_{10} concentrations, the contribution of sodium turned out to be small, less than 0.6 µg/m³, which corresponded to sea salt contributions of less than 2 µg/m³. The BOP measurement campaign rendered a limited number of sodium observations on days with high PM_{10} concentrations. Nevertheless, the phenomenon that high average daily PM_{10} concentrations coincide with low sea salt concentrations is in line with the earlier assessment of sea salt (Hoogerbrugge et

Behavior of sodium concentrations in PM$_{2.5}$ versus wind direction

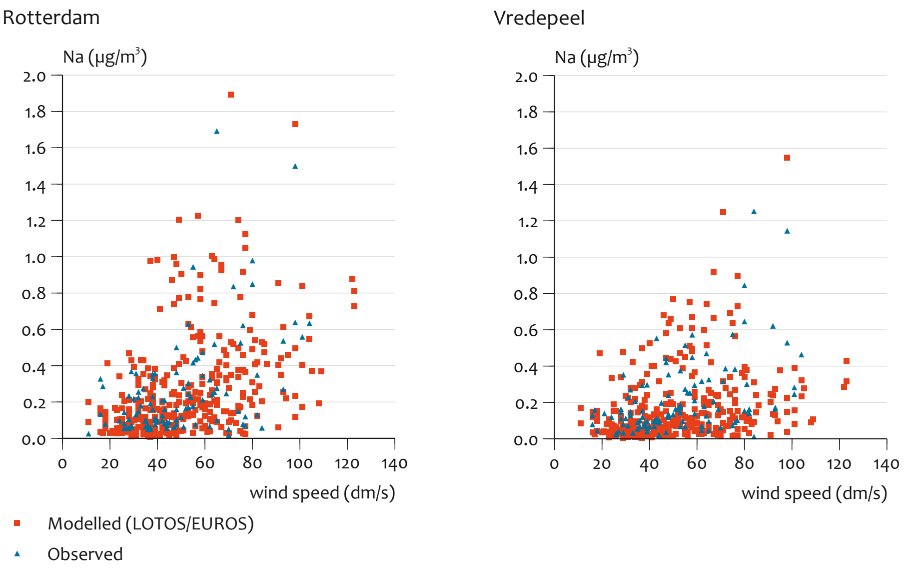
Figure 4.3



Observed and modelled sodium concentrations in PM$_{2.5}$ for Rotterdam and Vredepeel, versus wind direction in De Bilt.

Behavior of sodium concentrations in PM$_{2.5}$ versus wind speed

Figure 4.4



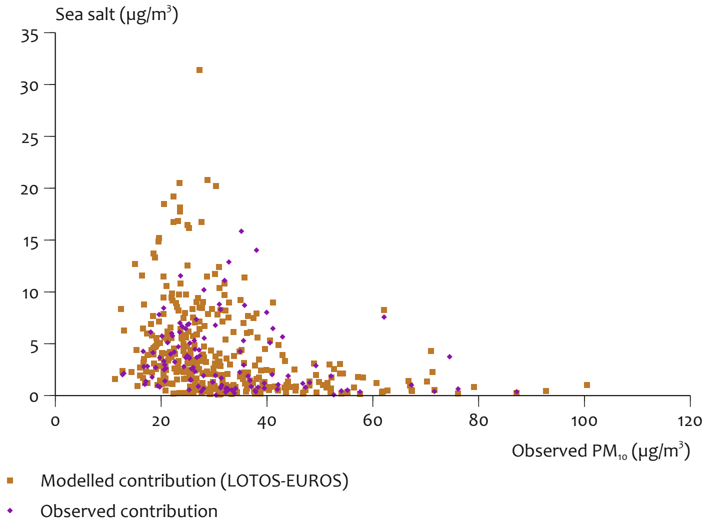
Observed and modelled sodium concentrations in PM$_{2.5}$ for Rotterdam and Vredepeel, versus wind speed in De Bilt.

al., 2005) and international studies on sea salt (e.g. Quass et al., 2004; Spindler et al., 2003).

For the measurement location Vredepeel, situated more inland and not shown here, the situation was similar, but with less high maximum daily average contributions of sea salt (up to 10 µg/m³), occurring during periods with low to moderate PM$_{10}$ concentrations. For high PM$_{10}$ concentrations, the contribution of sea salt was again low, but not lower than in Rotterdam. During easterly winds, the gradient over the country, in general, was smaller than during westerly winds, both in the observations and in the model results.

The relative contribution of sea salt to daily average PM$_{10}$ varied between 5 and 50%. Sea salt concentrations and total PM$_{10}$ concentrations were negatively correlated. In periods with strong winds from the sea, relatively clean air with higher sea salt concentrations was transported to the Neth-

Relative contribution of modelled and observed sea salt to PM_{10} in Rotterdam **Figure 4.5**



Modelled and observed sea salt concentrations in PM_{10}, versus observed PM_{10} concentrations in Rotterdam.

erlands, whereas weak and continental winds with hardly any sea salt carried air with other PM_{10} components, such as dust, combustion products, and secondary aerosols. In the latter case, the gradient in sea salt concentration over the country was also smaller.

About 30% of the sea salt in PM_{10} was present in the $PM_{2.5}$ fraction which implied that 70% was in the coarser part of PM_{10}. For the different measurement locations, there were small differences, but no clear gradient in the ratio between the sodium concentrations in the two size fractions. Absolute contributions of sea salt to $PM_{2.5}$ varied between less than 1% to more than 50%. The sea salt contribution decreased with increasing $PM_{2.5}$ concentrations, similar to the contribution of sea salt to PM_{10}.

4.3 Contribution of sea salt on days with PM_{10}>50ug/m³

We calculated total PM_{10}, as observed in the *LML* minus the sea salt concentration, to determine whether subtraction of the sea salt concentrations would reduce the number of days with PM_{10} concentrations larger than 50 µg/m³. We did not use the more accurate PM_{10} filter mass, since these measurements were not always available, and the routine observations have been used for air quality assessments over the past years, which, therefore, represent the current practice.

When we subtracted salt concentrations derived from sodium analysis on filter material, this did not cause any day with a PM_{10} concentration of over 50 µg/m³ to fall below this limit value. The sea salt concentrations on exceedance days varied between 0.5 and 2 µg/m³, with exceptionally some higher values. But the number of observations was limited. The LOTOS-EUROS results yielded two days for Rotterdam and one day for Breda, on which PM_{10} concentrations exceeded the limit value, out of a total of 27 and 38 days, respectively.

The same exercise was done with OPS. This resulted in three days for Rotterdam and one day for Breda (see Table 4.1)

4.4 Comparison with the Regulation on Air Quality Assessment with respect to subtraction of sea salt

The guideline for subtraction of sea salt as laid down in the Regulation on Air Quality Assessment (Staatscourant, 2007) was based on Hoogerbrugge *et al.* (2005). Their estimates were based on chloride measurements, which, as we have demonstrated, may have their limitations. Here, we compare our results with their findings.

Figure 4.6a shows a map with the annual average sea salt concentration for the BOP period. This was based on the LOTOS-EUROS sodium results, scaled by a factor of 0.70, which followed from comparison with observations, and being multiplied by 3.26 (Table 1) to obtain total sea salt instead of sodium. Figure 4.6b shows a map, based on several years of chloride data. Both maps exhibit the same features, with a gradient from north-west to south-east. However, the absolute values in the scaled LOTOS-EUROS map and in the observations are nearly twice as low as in the chloride-based map, and the gradient at the coast is steeper. Note, that the present findings are within the uncertainties of the chloride-based method, as indicated by Hoogerbrugge *et al.* (2005). In the previous chapter, we saw that the annual average sea salt concentrations in the BOP year were in about the same range as those in other years. Although the BOP period only covered one year, the new results indicate that the annual average concentrations used in the guideline may be too high. These results need to be further substantiated by means of ongoing routine sodium measurements within the *LML*.

In the guideline, the number of days on which the average daily PM_{10} concentration exceed 50 µg/m³ because of the

Number of daily limit-value exceedances for PM_{10} and reduction after sea salt subtraction

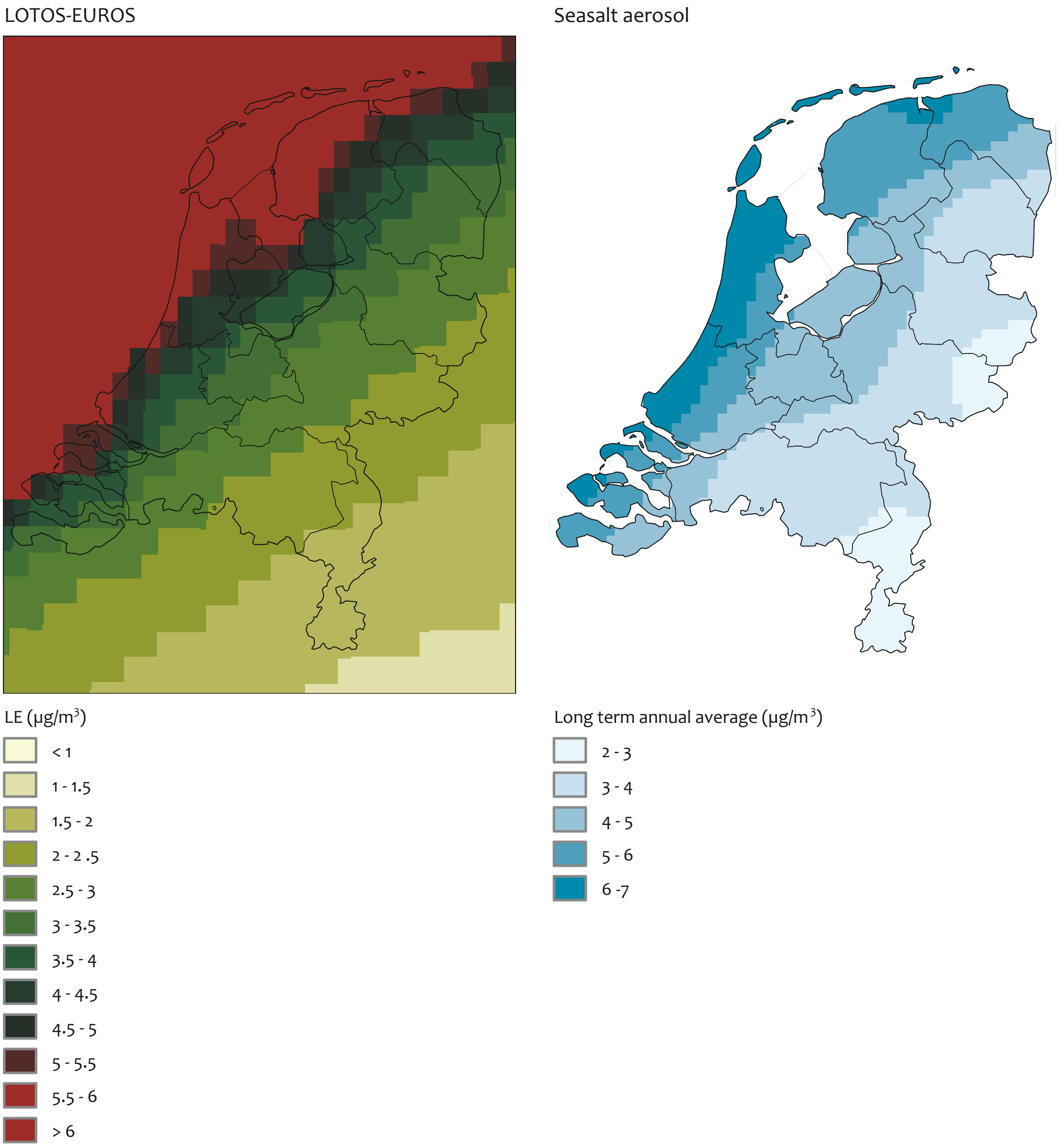
Table 4.1

	Number of exceedances	Reduction after subtraction of sea salt
Breda	25	1
Rotterdam	36	2
Hellendoorn	7	0

BOP period, number of limit-value exceedances for PM_{10} *and the number of exceedances that could be subtracted when the sea salt aerosol concentrations were subtracted from the total* PM_{10} *concentration.*

Annual average sea salt concentration

Figure 4.6



Left (4.6a): annual average sea salt concentration for BOP year, based on scaled model results. Right (4.6b): annual average sea salt concentrations, based on several years of chloride observations and interpolation of the results (e.g. Matthijsen and Visser, 2006).

contribution of sea salt, was set to six. Hoogerbrugge *et al.* recognised that a constant-value approach might be too simple. But they considered the margin of uncertainty associated with the chloride data, and its conversion to total sea salt concentration, too high to be more specific. This idea was substantiated by the assumption that on days with exceedances, the winds were generally weak, southerly or easterly, causing the sea salt concentrations to be low and the gradient over the country to be small. This assumption appears to be valid, according to our observations.

Number of daily limit-value exceedances for PM_{10} at measurement locations

Table 4.2

	2000	2001	2002	2003	2004	2005	2006	2007
Vredepeel	46	37	45	65	25	16	16	21
De Zilk	25	19	31	52	22	11	17	14
Wieringerwerf	22	11	22	56	13	8	7	7
Den Haag	34	30	37	51				
Valthermond	8	21	34	47	24	15	23	10
Kollumerwaard				24	15	21	18	14
Huijbergen				40	28	34	19	23
Utrecht					28	47	43	36

Reduction of daily limit-value exceedances for PM_{10} after sea salt subtraction

Table 4.3

	2000	2001	2002	2003	2004	2005	2006	2007
Vredepeel	3	6	4	5	3	1	0	0
De Zilk	4	3	2	4	5	1	2	3
Wieringerwerf	4	0	3	5	3	2	1	2
Den Haag	7	6	3	2				
Valthermond	2	0	0	2	0	0	0	0
Kollumerwaard				2	0	2	4	0
Huijbergen				1	4	4	2	3
Utrecht					2	5	5	2

Number of limit value exceedances that can be subtracted from those in Table 4.1, when the sea salt aerosol concentration is subtracted from the total PM_{10} concentration

In the present assessment, we arrived at a lower number of days with PM_{10} concentrations being brought under the 50 µg/m³ as a consequence of accounting for sea salt. For Rotterdam, a reduction of 2 to 3 days was found, for Breda this was only 1 day, and for other stations there were none. We must, however, be careful in extrapolating these results to other years, because of the small amount of data points for the single year investigated.

Nevertheless, the method as used by Hoogerbrugge *et al.* (2005) does not seem inconsistent with our findings. For days with high sea salt concentrations, the conversion factors for chloride to total sea salt were in line with our data (see Annex A). However, especially the low chloride concentrations may not have been very accurate (Annex A), mainly because of the high detection limit and more chloride depletion. Consequently, the concentrations on days with high total PM_{10} concentrations were more uncertain.

Although the uncertainty in chloride was relatively high, we feel that the decrease in the number of observed exceedances plays a large role in explaining the low number of days with PM_{10} concentrations below the limit value after subtraction of sea salt. We found that, during the period on which the assessment of Hoogerbrugge *.et al* was based, the number of days with PM concentrations >50 µg/m³ was much higher than in recent years. Table 4.2 lists the number of these days for six regional stations, from 2000 to 2007. For example, at Vredepeel, a large reduction from about 50 to 16 was observed. This implied that, between 2000 and 2003, the number of days with concentrations of just above 50 µg/m³ (the levels at which subtraction of a few micrograms of sea salt has impact) was higher than in recent years. This is illustrated in Table 4.3, which shows the reduction in the number of exceedance days caused by the subtraction of sea salt, based on the method of Hoogerbrugge *et al.* (2005). For this purpose, we used the chloride data from the period of 2000 to 2007 (2008 was not available yet). The number of exceedance days due to sea salt is decreasing; in Vredepeel, for example, this number fluctuated from 6 in 2001, to 0 in 2006 and 2007. The efficiency of the reductions seemed related to the sea salt concentrations, which were higher near the coast, and to the number of exceedances. Furthermore, the variability between the years was large. Therefore, subtraction of a uniform number of exceedance days, if any subtraction should be applied, appeared not to be the best approach. In short, we have strong indications that the number of days subtracted for sea salt, in the current national guideline, may be too large, and assuming a constant number of days may be unrealistic.

A year-specific number of days to be subtracted, has the disadvantage that it would be more difficult to handled in policy support applications, such as scenario studies and legislation. Therefore, we also tested a simple rule of thumb of subtracting all days with PM_{10} concentrations between 50 and 52 µg/m³. However, this approach caused a significantly higher number of days being subtracted, than in the explicit methods used above.

A variable sea salt contribution may seem problematic for policy-making. But, for the assessment of air quality in future years, for example, one could use model results for both total PM_{10} concentrations and sea salt concentrations, and determine the relative contribution of sea salt for a particular year, by using emissions and meteorological fields that are thought representative for that specific year.

5

Conclusions

The aim of this report within the BOP project was to investigate the contribution of sea salt aerosol to PM$_{2.5}$ and PM$_{10}$ concentrations in the Netherlands. To this end, new observations were used, both from filter analysis at six locations (daily averages, one year of observations), and from hourly observations (MARGA instrument, three locations, one with two months and two with six months of observations). These were compared with modelling results from LOTOS-EUROS and OPS-KT. After this validation, model results could be used to complete the picture in space and time. The present results are an improvement, compared to previous assessments based on chloride observations, since the presented data are more accurate, and, therefore, also are better suited for model validation. The major limitation of this new data set is that it only covers one year. Below, the main questions are addressed, which were raised in the introduction.

What is the contribution of sea salt to PM$_{10}$ and PM$_{2.5}$ in the Netherlands?

The annual average sea salt concentration in PM$_{10}$ showed a maximum near the coast and trailed off as the distance from the coast increased. The monitoring data indicated a gradient from 4 µg/m³ in Rotterdam, to about 2.3 µg/m³ in Vredepeel. The measurements indicated that about 35% of the sea salt mass in PM$_{10}$ was in the PM$_{2.5}$ fraction.

Daily average sea salt concentrations were very variable, depending on wind direction, with the highest concentrations arriving in the Netherlands from the westerly sectors. The observed maximum in daily average concentrations declined from around 16 µg/m³ in Rotterdam, to around 10 µg/m³ in Vredepeel and Hellendoorn, in the east of the country. For sea salt in PM$_{2.5}$, a similar pattern was found, but with values that were 65% lower.

In a relative sense, sea salt contributed between 5 and 50% to PM$_{10}$, and between 1 and 60% to PM$_{2.5}$, on individual days. Because of the different source region of sea salt, compared to anthropogenically derived PM, the sea salt contribution to PM declined with increasing anthropogenic contribution, and, thus, with total PM$_{10}$. At days with PM$_{10}$ concentrations above the daily limit value, sea salt contributed less than 2 µg/m³ to the total mass.

The measurements during the BOP campaign represented conditions with about average sea salt concentrations. For years with different conditions, concentrations may vary by up to ±40%. The sea salt concentrations in the Netherlands were similar to those in other countries or coastal regions bordering on the North Sea, for example, Belgium, Denmark, and the United Kingdom, in terms of absolute concentrations and concentration gradients from the coast to about 200 km inland.

How should we use a chemical transport model for assessing the temporal and spatial behaviour of sea salt in the Netherlands?

We compared results from LOTOS-EUROS and OPS-KT with present observations, to validate them. For both models, the time correlation of events with high and low concentrations was reasonable to good, and the spatial gradients were well represented. The major shortcoming was in the modelling of the absolute value of the sodium concentration. Especially high concentrations were overestimated. But, since the correlations were good, we were able to scale the annual average concentration field towards the measured levels. This resulted in a map of annual average sea salt concentrations, for the Netherlands and for Europe, filling the gaps between the observations.

How do the new findings relate to the present Regulation on Air Quality Assessment with regard to sea salt?

We have compared the new insights into the sea salt concentrations in the Netherlands to the results of a first assessment by Hoogerbrugge *et al*. (2005). That study was used in the Regulation on Air Quality Assessment with regard to sea salt (*Regeling beoordeling luchtkwaliteit*, Staatscourant, 2007). The *Regeling beoordeling luchtkwaliteit* gives a fixed number of six days with PM$_{10}$ limit-value exceedances to be subtracted due to the presence of sea salt. However, the new findings indicated that this number is probably not constant, but more likely dependent on the PM$_{10}$ concentration and it appears to vary in time and space. The *Regeling beoordeling luchtkwaliteit* would need to be revised with regard to sea salt in order to take these new findings properly into account. Before that, however, the new findings need to be further substantiated.

In more detail:

- Our findings are not inconsistent with the assumptions made to determine the contribution of sea salt by Hoogerbrugge et al. (2005). Nevertheless, the average annual sea salt concentration derived from model results and observations for the BOP observation period, were nearly twice as low as the concentrations laid down in the *Regeling beoordeling luchtkwaliteit*. The observed as well as the modelled estimate are believed to represent concentrations under long-term average conditions. The underlying results need to be further substantiated by routine sodium measurements, which recently have started within the Nationals Air Quality Monitoring Network.

- We found that sea salt concentrations are strongly determined by meteorological conditions, resulting in a substantial inter annual variability. Therefore, subtraction of long term average sea salt concentrations from average PM_{10} concentrations of a specific year in the past, as laid down in the *Regeling beoordeling luchtkwaliteit* is considered not appropriate when year-specific data are available. It would be better to determine an average annual concentration for each individual year, based on observations and model results.
- The study also indicated that the reduction in the number of days with limit-value exceedances – after subtraction of sea salt from total PM_{10} – is not constant over the country, in contrast to what is laid down in the *Regeling beoordeling luchtkwaliteit.* In addition, we found that the number of days subtracted for sea salt, six under the present national guidelines, may be too large at the present ambient PM_{10} concentration levels. We estimated this to be between one and three days for the traffic-oriented stations in Rotterdam and Breda, being close to the coast and with relatively high PM_{10} concentrations, and none for the inland stations Hellendoorn and Vredepeel.
- The decrease in the number of observed exceedances over the past decade largely explained the lower number of days for which the PM_{10} concentration reduced to less than 50 µg/m^3, after the subtraction of sea salt. Theoretically, the number of days to be subtracted due to the presence of a fixed amount of sea salt depends on the average annual PM_{10} concentration level at a specific location. A preliminary analysis based on PM_{10} observations confirms this principle. For prognostic modelling of PM_{10}, to check future compliance, the *Regeling beoordeling luchtkwaliteit* provides subtraction based on long term average sea salt concentrations. This practice seemed appropriate in 2005; however, a more suitable approach would provide a number of days with exceedances due to sea salt which should vary according to the estimated levels of future PM_{10} concentrations.
- As for the estimation of the average annual sea salt concentration, it would be better to determine this for each location and each year, individually, using the support of model results and sodium observations for the year under consideration. Whether and how such an approach could be made operational for national compliance checking is subject to further assessment.

5.1 Recommendations

The present report has enabled a thorough assessment of the sea salt concentrations in the Netherlands, through a wealth of new observations combined with model development and model results.

In general, the observations were of good quality, with the drawback of not accurately knowing the recovery of sodium from the filter measurements. We assumed a 100% recovery, so there may have been a slight underestimation of true concentrations. The recovery could be investigated further, by using test filters with known concentrations of table salt (NaCl). This would be useful for the interpretation of present and future results, since sodium concentrations will also be analysed on a regular basis in the National Air Quality Monitoring Network.

The combination of observations and model results revealed that their general behaviour was consistent, and that the results completed each other, with the constraint of having to scale the model results. This is feasible for annual average concentrations, but would be more difficult for individual concentrations, since this would require good knowledge of the processes, such as generation and deposition. A major issue is the uncertainty in the source function for sea salt, which depends critically on wind speeds. The too low values modelled for sodium in $PM_{2.5,}$ compared to the too large values modelled for sodium in $PM_{10,}$ indicated that the size-dependent processes in generation and deposition should be investigated further, to improve the model. In addition, the source characteristics of OPS-KT should be compared to those of LOTOS-EUROS, to explain the differences in behaviour.

The conclusions of this report were based on a data set for one year, with measurements taken every two to four days. In addition, the BOP campaign does not cover the northern half of the country. Most findings appeared robust, but nevertheless, we recommend to consolidate the present findings with a larger dataset. In 2007, the Dutch Air Quality Monitoring Network started measuring sodium concentrations in PM_{10} Since 2008, the sodium content of PM_{10} is being measured regularly, within this network. Several years of these data should be used to validate the results from our report. Unfortunately, data for 2008 were not yet available at the time of this study.

Appendix A
Chloride measurements

In the past, chloride measurements were used to assess the sea salt concentrations in the Netherlands. Since chloride in the aerosol can be depleted due to reaction of the sea salt aerosol with other components (HNO_3, H_2SO_4), part of the sea salt aerosol was missed.

In our study, first, we investigated this depletion, by studying the ratio of sodium and chloride in the MARGA measurements. This investigation is followed by a comparison between the sodium filter analyses and the chloride from filter measurements, as collected by the RIVM in their regular network.

MARGA measurements

The MARGA instrument was able to measure the chloride and sodium concentrations simultaneously. Therefore, these measurements were excellent for studying the effect of depletion. Figure A1 shows the sea salt observations as derived from sodium (SS=3.24*[Na]) and chloride (SS=1.8*[Cl]) observations, at Cabauw. The slopes of the linear fits and the correlation coefficient for the three stations were

Hoek van Holland	SS_Cl=0.82 x SS_Na, R^2=0.91
Schiedam	SS_Cl=0.83 x SS_Na, R^2=0.86
Cabauw	SS_Cl=0.80 x SS_Na, R^2=0.85

The correlation was good for all three stations. Figure A1 illustrates the good general correlation for Cabauw, but also shows that, for high concentrations, the depletion was less (values above the trend line), and for low concentrations, the chloride was more depleted with a rather large spread. This behaviour was also found for Hoek van Holland, but to a lesser extent for Schiedam. This fits in with the idea that high concentrations are related to strong winds bringing more sea salt aerosol, which did not have the time to deplete because of the rapid transport and eventually cleaner air. In contrast, during weak and southerly or easterly winds, less sea salt aerosol is present, and it has had the time to react with other components.

Therefore, we concluded from the MARGA measurements that, in theory, chloride measurements could be used for assessing average concentrations.

Filter measurements

The MARGA measurements showed a good correspondence between sodium and chloride. However, in the traditional Dutch filter measurements, not the full PM_{10} fraction was sampled, but rather PM_3, causing a combined effect of depletion and a missing size fraction. Two sets of measurements are available: that of a short period in April 2005, with sodium measurements taken every second day, and the BOP data set for 2007. For 2008, chloride measurements were not yet available. For the chloride data, there is a rather high detection limit (1.14 μg/m^3); when the analysis is below the detection limit, the value is reported, without subtracting the blank value. Therefore, the data below the detection limit were set to 0.2 ug/m^3, slightly below the lowest valid measurements. Simultaneous chloride and sodium measurements were taken at only three stations.

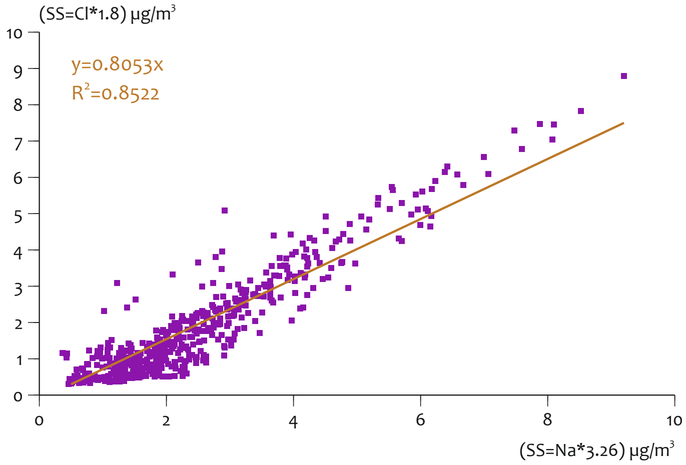
Figure A2 shows scatter plots for 2005, and Figure A3 for 2007. For the short period in 2005, the correlation was rather good. For 2007, this correlation was less evident. Especially for Vredepeel, the correlation was very poor, with many chloride values below the detection threshold. The wide range of sodium measurements, coupled to the detection threshold values, indicated that the approximation with the value 0.2 ug/m^3 may not have been accurate. For the other stations, the approximation seemed reasonable. For Rotterdam, the results were compared with the chloride observations in De Zilk, which is closer to the coast an further to the north. This led to a much smaller slope than for Kollumerwaard and Bilthoven, since the sea salt aerosol concentrations in De Zilk were expected to be higher than in Rotterdam. Nevertheless, the figure shows a weak correlation between the two sets of measurements.

We conclude from these measurements that those of Cl were correlated with the sea salt concentrations. We cannot exclude that the correlation depended on the season. Furthermore, the multiplication factor may have depended on the station. For Kollumerwaard, with a relatively large amount of coarse sea salt aerosol, the effect of missing the fraction larger than PM_3 may have been larger than for Vredepeel. The factors for Kollumerwaard (3.48) and Vredepeel (3.57) were slightly lower than the factor that was used in Hoogerbrugge *et al.* 2005. For Bilthoven, the factor was much lower, but was based on only a few observations. The factors for Kollumerwaard and Vredepeel did fit in with the estimate of 20% depletion, and sampling roughly 30% of the total PM_{10}.

Correlation between sea salt concentrations derived from sodium and chloride, 2007-2008

Figure A.1

Cabauw



Sea salt derived from simultaneous MARGA observations of sodium and chloride, at Cabauw.

Line fit parameters for sea salt concentration estimates of PM_{10} sodium versus PM3

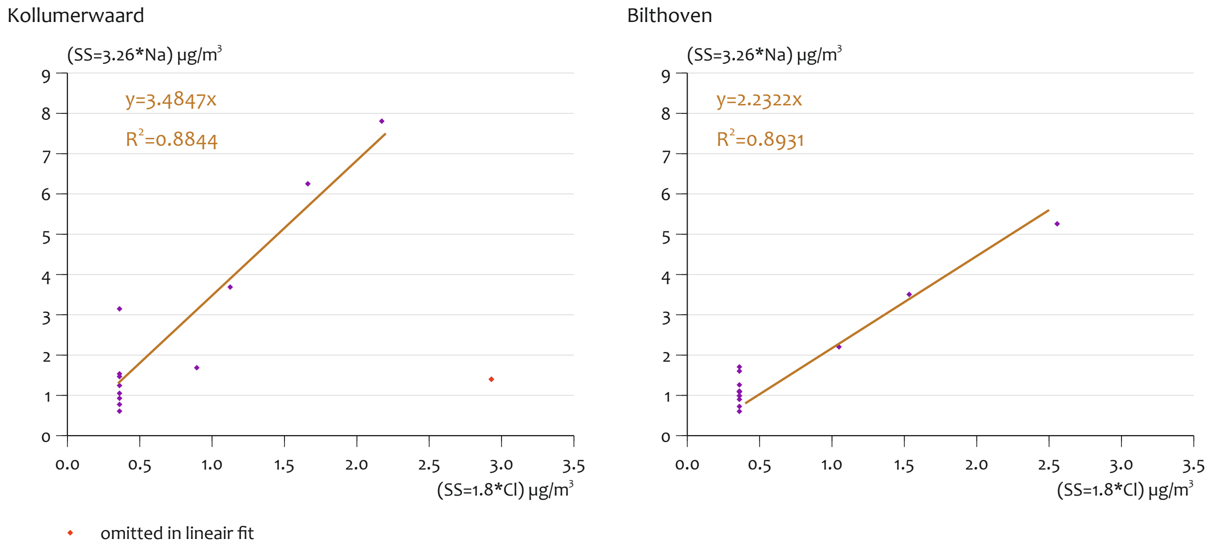
Table A.1

	SS_Na=a*SS_Cl	R^2
Kollumerwaard 2005	3.48	0.88
Bilthoven 2005	2.23	0.89
Vredepeel 2007	3.52	0.18
Rotterdam 2007	0.88	-0.04

Line fit parameters for sea salt concentration estimates of PM_{10} sodium versus PM_3 chloride observations. The line was forced through the origin.

Correlation between sea salt concentrations derived from sodium and chloride, 2005

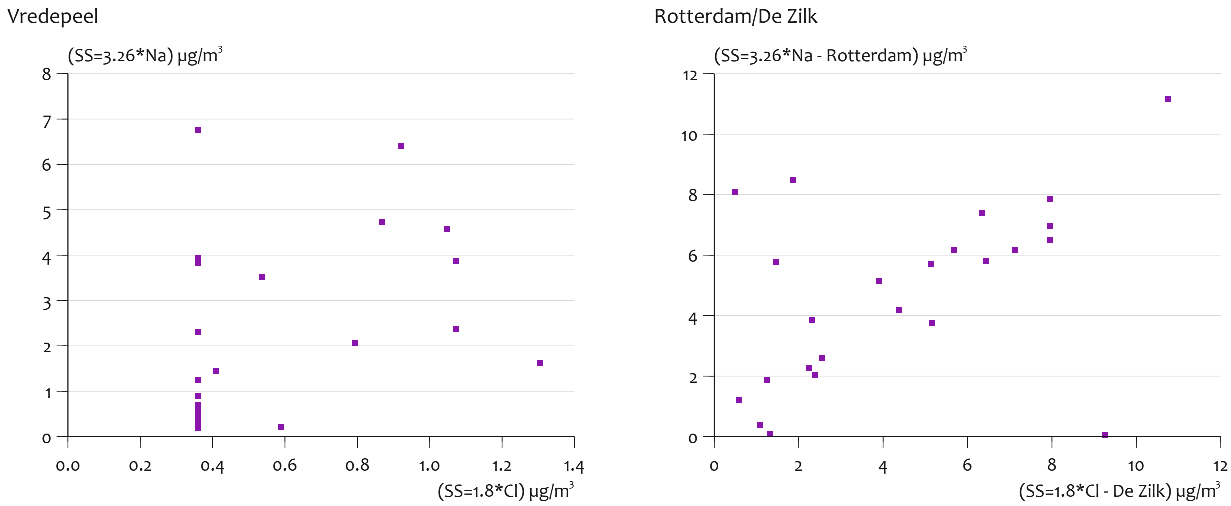
Figure A.2



Scatter plots for Kollumerwaard and Bilthoven, April 2005. One data point (pink) was omitted for Kollumerwaard.

Correlation between sea salt concentrations derived from sodium and chloride, 2007

Figure A.3



Scatter plots for Vredepeel and Rotterdam, September to December 2007. For Rotterdam, the chloride observations stem from De Zilk, a station closer to the coast.

Appendix B
Trajectory model OPS-KT

Another model that has been used for studying sea salt in, the Netherlands, is the trajectory model OPS-KT (Klimov 2006, Van Jaarsveld and Klimov 2009). It acts as a Gaussian plume model for local situations. This research model is not to be confused with the OPS model from which it is derived, since the OPS long-term model is aimed at long-term averages and, therefore, uses different parameterisations.

OPS-KT uses the Mårtensson source function for particles smaller than 1 µm dry diameter, and that of Monahan for particles up to 10 µm. Dry deposition velocities are modelled on the basis of the models of Slinn & Slinn (1980) and Williams (1982). To take into account the different properties of the particles within the size spectrum, the model uses up to 20 bins; here, five size bins were used for the PM_{10} fraction. In case of calculating wet deposition, also very large particles (10 µm < Dp < 200 µm) can be dealt with. The effect of relative humidity on the growth of particles is parameterised using the parameterisation of Gerber (1985) and the effect on the density is accounted for by using the empirical relation by Tang *et al.* (1997).

Furthermore, the effect of sedimentation on plume and transport height is taken into account. The model is driven by a set of hourly meteorological parameters taken from 14 stations of the network of the Royal Netherlands Meteorological Institute (KNMI). For our study, also observations from a North Sea platform (approx. 10 km from the coastline) were included. The domain was from 6° W to 10° E, and 50° to 58° N, so that the North Sea would be included; the grid of 50x50 km^2 was refined to 5x5 km^2 along the coast line, and to 1x1 km^2 around a monitoring location close to the coast.

The capability of the OPS model (from which OPS-KT was derived) to simulate local dispersion, has been tested against well known datasets, such as the Kincaid (Bowne and Londergan, 1983) and Prairie grass data sets (Barad, 1958). For larger scale transport of gases, such as SO_2, NO_x and NH_3, the model has successfully been compared with results from the Dutch National Air Quality Monitoring Network. Furthermore, the model has been subjected to several model intercomparison studies (e.g. Derwent *et al*, 1989).

References

Anwar Hossain , K.M. Easa, S.M. and Lachemi, M. (2009). Evaluation of the effect of marine salts on urban built infrastructure, Building and Environment 44 713–722

Barad, M.L. editor (1958), Project Prairie grass, a filed program in diffusion, Volume1 Geophysics Research Paper no 59. Geophysics Research Directorate, Air Force Cambridge Research Center, Cambridge MA, USA

Bowne,N.E. Londergan, R.J. (1983). Overview, results and conclusions for EPRI Plume Model Validation and Development Project: Plains site, APRI, Palo Alto, Calofornia 94304

Brunekreef, B, Forsberg, B. (2005). Epidemiological evidence of the effects of coarse particulate matter on health. Eur. Respir. J. 26, 309-318

Dasgupta. P.K., Campbell, S.W., Al-Horr, R.S., Ullah, S.M. R., Li, J., Amalfitano, C., Poor, N.D. (2007). Conversion of sea salt aerosol to NaNO3 and the production of HCl: Analysis of temporal behavior of aerosol chloride/nitrate and gaseous HCl/HNO3 concentrations with AIM, Atm. Envir. 41

De Leeuw, G., Neele, F.P., Hill, M, Smith, M.H., Vignati, E., (2000). Production of sea spray aerosol in the surf zone, J. Geophys. Res. 105.

Derwent, R.G., Hov, Ø., Asman, W.A.H., Jaarsveld, J.A. van, Leeuw, F.A.A.M. de, (1989). An intercomparison of long-term atmospheric transport models ; the budgets of acidifying species for The Netherlands, Atmos. Envir. 23

Erisman, J.W. et al. (1996). Towards development of a deposition monitoring network for air pollution in Europe. RIVM report 722108014, RIVM, Bilthoven, The Netherlands.

EU, 21 May 2008. Directive 2008/50/EC of the European Parliament and of the Council on ambient air quality and cleaner air for Europe.

Gerber, H.E., (1985), Relative-humidity parameterization of the Navy aerosol model (NAM), NRL Rep. 8956, Natl. Res. Lab., Washington DC

Grice, S.; Sturman, J.; Dore, Ch. and Woodfield, M. (2008). Modelling emissions of marine aerosol from the ocean at a European scale, Atm. Environment, in press

Hoogerbrugge, R. Matthijsen, J., van Jaarsveld, H., Schaap, M., Denier van der Gon, H. (14 July 2005) Recommendation for a preliminary guideline for the correction of PM_{10} concentrations for the sea salt contribution (Aanbeveling voor een voorlopige regeling voor de correctie van fijn stof (PM_{10}) concentraties voor de bijdrage van zeezout, in Dutch), www.rivm.nl/milieuportaal/dossier/fijnstof/bronnen

Khlystov, A., Wyers, G.P., Slanina, J., (1995). The steam-jet aerosol collector, Atm. Environment, 29

Klimov, D. (2006). Contribution of sea-salt aerosol to PM_{10} concentrations in the Netherlands on the basis of a mechanistic approach, Master's Thesis Free University Amsterdam

Koçaka, M., Mihalopoulosb, N., Kubilaya, N., (2007). Contributions of natural sources to high PM_{10} and PM2:5 events in the eastern Mediterranean, Atmospheric Environment 41

Lewis, E.R. and Schwartz, S.E. (2004). Sea Salt Aerosol production. AGU, Washington DC, 2004.

LML, (2009). Data from the Dutch National Air Quality Monitoring Network, Landelijk Meetnet Luchtkwaliteit. (http://www.lml.rivm.nl)

Mar, T.F., Ito, K., Koenig, J.Q., Larson T.V., Eatough, D.J., Henry, R.C., Kim, E., Laden, F., Lall, R., Neas, L.h, Stölzel, M., Paatero, P.j, Hopke, P.K.,Thurston G.D. (2006). PM source apportionment and health effects. 3. Investigation of inter-method variations in associations between estimated source contributions of $PM_{2.5}$ and daily mortality in Phoenix, AZ, J. Expos. Sci. and Environ. Epidemiology, 16.

Marenco, F., Mazzei, F., Prati, P., Gatti, M. (2007). Aerosol advection and sea salt events in Genoa, Italy, during the second half of 2005, Science of the Total Environment 377, 396–406

Mårtensson, E.M, Nilsson, E.D.,de Leeuw, G., Cohen, L. H., Hansson , H.-C. (2003). Laboratory simulations and parameterization of the primary marine aerosol production. J.Geophys. Res. 108.

Matthijsen, J, en H. Visser, H. (2006). PM_{10} in the Netherlands (PM_{10} in Nederland. Rekenmethodiek, concentraties en onzekerheden, in Dutch) MNP report 500093005/2006, MNP, Bilthoven, the Netherlands. (http://www.rivm.nl/bibliotheek/rapporten/500093005.pdf)

Murphy, D.M., Anderson, J.R., Quinn, P.K., McInnes, L.M., Brechtel, F.J., Kreidenweis, S.M., Middlebrook, A.M., Posfai., M., Thomson, D.S., Buseck, P.R. (1998). Influence of sea-salt on aerosol radiative properties in the Southern Ocean marine boundary layer. Nature 392, 62-65

Monahan, E.C., Spiel, D.E., Davidson, K.L. (1986). A model of marine aerosol generation via whitecaps and wave disruption. In Oceanic Whitecaps and Their Role in Air-Sea exchange, eds. E.C. Monahan and G. Mac Niocaill.

Pierce, J.R., and Adams, P.J., (2006). Global evaluation of CCN formation by direct emission of sea salt and growth of ultrafine sea salt. J. Geophys. Res. 111

Quass, U., T. Kuhlbusch and M. Koch (2004). Identification of source groups for fine dust, IUTA report LP 15/2004 (in German), IUTA, Duisburg, Duitsland

Staatscourant, (2007). Regulation on air quality assessment 2007 (in Dutch): Regeling van de Minister van Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer van 8 november 2007, nr. LMV 2007.109578, houdende regels met betrekking tot het beoordelen van de luchtkwaliteit, Staatscourant,13 november 2007, nr. 220 / pag. 21. (http://www.infomil.nl/contents/pages/22907/regelingbeoordeling_publicatieinclusieftoelichting.pdf).

Schaap, M., Manders, A.M.M., Hendriks, E.C.J., Cnossen, J, Segers, A.J.S., Denier van der Gon, H.A.C., Jozwicka, M., Velder, G., Matthijsen, J., Builtjes, P.J.H., (2009). Regional modelling of PM_{10} over the Netherlands, technical background report, BOP report 500099008, Netherlands Environmental Assessment Agency, Bilthoven. (http://www.mnp.nl/bibliotheek/rapporten/500099008.pdf)

Seinfeld, J.H. and Pandis, S.N., (1998). Atmospheric chemistry and physics, Wiley, 1998

Slanina, J., ten Brink, H.M., Otjes, R.P., Even, A., Jongejan, P., Khlystov, A., Waijers-IJpelaan, A., Hu, M., and Lu, Y. (2001).Continuous analysis of nitrate and ammonium in aerosols by the Steam Jet Aerosol Collector (SJAC): extension and validation of the methodology, Atmos Envir. 35, pp. 2319–2330.

Slinn, S.A., Slinn, W.G.N., (1980). Predictions for particle deposition on natural waters, Atmos. Environ., 14, pp 1013–1016.

Spindler, G., K. Müller, E. Brüggemann, T. Gnauk and H. Herrmann (2003). Long-term size-segregated characterization of PM_{10}, $PM_{2.5}$, and PM1 at the IfT research station Melpitz downwind of Leipzig (Germany) using high and low-volume filter samplers, Atmos. Environ., 38, 5333–5347.

Stalpers, S.I.P. (2003). Modeling the sea salt fraction of particulate matter with the atmospheric transport model EUROS, Reports Environmental Studies nr 229, Katholieke Universiteit Nijmegen.

Van Jaarsveld, J.A. and Klimov, D. (2009). Modelling the impact of sea-salt particles on the exceedances of daily PM_{10} air quality standards in the Netherlands. Int. J. Environment and Pollution, in press.

Van Arkel, F.Th, Voogt, M., Weijers, E.P. (2009). Measurements in the BOP national programme on PM_{10} and $PM_{2.5}$: a technical background document, BOP report 500099009, Netherlands Environmental Assessment Agency, Bilthoven. (http://www.mnp.nl/bibliotheek/rapporten/500099009.pdf)

Weijers, E.P. et al. (2002). Concentrations, size and origin of particulate matter in the Netherlands, ECN report ECN-CX--02-010, ECN, Petten, Nederland

Weijers , E.P. et al., (2009). Secondary inorganic aerosol in the Netherlands, BOP report 500099006, Netherlands Environmental Assessment Agency, Bilthoven.

Witek, M.L., Flatau, P.J. , Teixeira, J. ,. Westphal, D.L (2007a). Coupling an ocean wave model with a global aerosol transport model: A sea salt aerosol parameterization perspective, Geophys.res let. 34

Witek, M.L., Flatau, P.J. , Quinn, P., J. ,. Westphal, D.L (2007b). Global sea-salt modelling: Results and validation against multicampaign shipboard measurements., J.Geophys. Res. 112.

Zhang, L., Gong, S., Padro, J., and Barrie, L., (2001). A size-segregated particle dry deposition scheme for an atmospheric aerosol module Atmos. Env.35 549-560

Zhang, K.M., Knipping, E.M., Wexler, A.S., Bhave, P.V., Tonnesen, G.S. (2005). Size distribution of sea-salt emissions as a function of relative humidity. Atmos Env. 39, pp 3373–3379.

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Sea salt aerosol makes a natural contribution to particulate matter (PM_{10}), and cannot be influenced by abatement strategies. The report improved the so-far limited knowledge on sea salt and its contribution to PM_{10} and $PM_{2.5}$ in the Netherlands. We focused on one year of measurements of sodium, which is a good indicator for sea salt, and combined these with results of the LOTOS EUROS model, which describes the generation and transport of sea salt aerosol.

The average concentration over the observation period varied from 4 µg/m^3 in Rotterdam, close to the coast, to 2 µg/m^3 in Vredepeel, land inwards. Daily average concentrations were sometimes much higher or smaller. When the European limit vale of 50 µg/m^3 for PM_{10} was exceeded, the contribution of sea salt aerosol to PM_{10} was, in general, less than the annual average concentration. Because the contribution of sea salt to PM_{10} and $PM_{2.5}$ varies strongly from day to day and also from year to year, our conclusions on the observation period of about one year can not straigthforwardly be extrapolated to other years. Therefore, it is recommended to extend the current analysis with routine sodium measurements, which recently have started in the National Air quality Monitoring Network, in combination with model calculations.

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