National Institute for Public Health
and the Environment
Ministry of Health, Welfare and Sport

Assessment of the level of sea salt in PM10

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Yearly average and exceedance days

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Colophon

R.Hoogerbrugge (Projectleader), RIVM
P.L.Nguyen, RIVM
J.Wesseling, RIVM
M.Schaap, TNO
R.J.Wichink Kruit, TNO
V.Kamphuis, TNO
A.M.M.Manders, TNO
E.P.Weijers, ECN

Contact:
R.Hoogerbrugge
Centre for Environmental Monitoring
Ronald.Hoogerbrugge@rivm.nl

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Abstract

Assessment of the level of sea salt in PM_{10} in the Netherlands
Effect on yearly average and exceedance days

The European air quality directive allows the subtraction of natural contributions from the levels of PM_{10}. In 2005 a regulation for sea salt was implemented in Dutch legislation. The sea salt levels in this regulation now appear to be too high and will be adjusted. This is the result of an evaluation on the basis of new measurement data on sea salt. Sea salt contributes to the level of particulate matter in the air.

Lower sea salt levels in The Netherlands
The new data on the estimated amount of sea salt in the air are based on measured concentrations of sodium. Sodium is a more reliable source of information than the chloride concentrations that are used in the current Dutch method. Measurements of sodium in PM_{10} reference samples indicate that sea salt concentrations are nearly 50% lower than the levels estimated in the current regulation. The new estimate is based on the reference method for the sampling of particulate matter (PM_{10}) and complies with the European regulations.

Adjustment of the correction
According to the directive the number of days with PM_{10} levels above 50 $\mu g/m^3$ may not be larger than 35. Due to the natural contribution this number of days may be corrected. Currently a flat number of six exceedance days can be discarded for the whole country. With the new assessment this number of days will be lower. Also allows the new assessment a differentiation over the various Dutch provinces. Near the coast the number of days, that can be discarded due to the amount of sea salt, will now be four instead of six. In the eastern part of the country the number of days reduces from six to two.

The effect of changing the method for sea salt reduction on the number of PM_{10} exceedances is presumably small. Measurement results in 2010 show no limit value exceedances even without sea salt correction. For 2011 some exceedances may be measured due to other weather conditions.

Keywords:
sea salt, PM_{10} ,particulate matter

Rapport in het kort

Schatting van de zeezoutconcentratie in PM_{10} in Nederland

Effect op het jaargemiddelde en het aantal overschrijdingsdagen

In de Europese luchtkwaliteit richtlijn staat dat natuurlijke bijdragen aan de concentraties van fijn stof (PM_{10}) mogen worden afgetrokken van de totale hoeveelheid fijn stof. In 2005 is in dat verband in de Nederlandse Regeling Beoordeling Luchtkwaliteit een methode voor de hoeveelheid zeezout vastgelegd. De 'zeezoutcorrectie' die daarmee werd bepaald, was echter te ruim en is nu bijgesteld. Dit blijkt uit een evaluatie van de methode door het RIVM, op basis van nieuwe meetgegevens over zeezout. Zeezout draagt bij aan de hoeveelheid fijnstofdeeltjes in de lucht.

Lagere zeezoutconcentratie in Nederland
De nieuwe gegevens van de geschatte hoeveelheid zeezout in de lucht zijn gebaseerd op gemeten concentraties natrium. Dit is een betrouwbaardere bron dan de chlorideconcentraties waarop de huidige zeezoutregeling is gebaseerd. Recente metingen van natrium in fijn stof (PM_{10}) geven aan dat de jaargemiddelde zeezoutconcentratie in Nederland bijna de helft lager is dan was geschat. Hierdoor kan de natuurlijke bijdrage eveneens lager worden ingeschat. De nieuwe schatting is gebaseerd op de referentiemethode voor de monsterneming van fijn stof (PM10) en voldoet aan de Europese eisen.

Correcties voor zeezout aangepast
De wet stelt een maximum aan het aantal dagen waarop PM_{10} boven de norm van 50 microgram per kubieke meter mag komen (35 dagen). Vanwege de natuurlijke bijdragen valt een aantal dagen af. Voor zeezout mochten in heel Nederland zes dagen worden afgetrokken. Met de nieuwe methode is dit aantal overschrijdingsdagen voor zeezout lager. Bovendien kan dat aantal op basis van de nieuwe data worden gedifferentieerd naar verschillende regio's van Nederland. Zo verandert de correctie voor het aantal normoverschrijdingsdagen in gebieden langs de kust van zes naar vier dagen. In het binnenland gaat deze correctie van zes naar twee dagen.

Naar verwachting zijn de beleidsmatige gevolgen van de voorgestelde methode gering. Zelfs zonder de zeezoutaftrek is op de Nederlandse meetpunten het aantal overschrijdingsdagen in 2010 namelijk niet overschreden. Voor 2011 worden, als gevolg van andere weersomstandigheden (droog voorjaar), wel overschrijdingen verwacht.

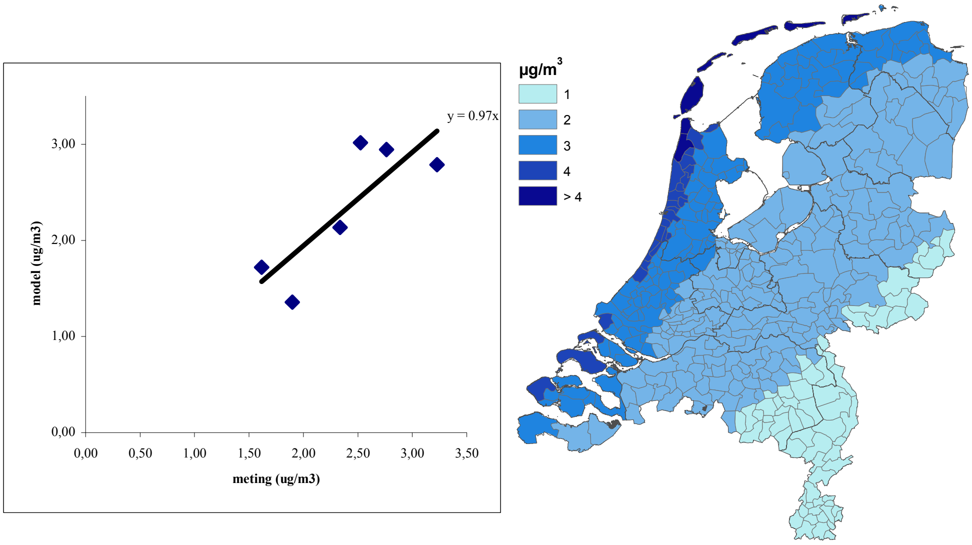
Trefwoorden:
zeezout, fijn stof, PM_{10}

Contents

Samenvatting

Inleiding

De Europese luchtkwaliteitrichtlijn biedt de mogelijkheid om bij de toetsing aan de luchtkwaliteitseis voor PM_{10} de bijdrage van natuurlijke componenten buiten beschouwing te laten. Dit maakt een onderbouwde schatting van de hoeveelheid zeezout in fijn stof (PM_{10}) van belang. In 2005 werd door RIVM, TNO en MNP een schatting gemaakt van de hoeveelheid zeezout in PM_{10}, zowel jaargemiddeld als op dagen met etmaaloverschrijdingen. Dit heeft er toe geleid dat in Nederland bij toetsing van de jaargemiddelde concentratie 3-7 µg/m^3 buiten beschouwing mag worden gelaten. Bij het toetsen op het aantal dagen boven de 50 µg/m^3 mogen in Nederland 6 dagen buiten beschouwing worden gelaten (regeling beoordeling luchtkwaliteit 2007). Deze schatting was gebaseerd op de toen beschikbare chloridemetingen van low volume samplers (LVS) filters. Het was bekend dat de onzekerheid in de schatting fors was (naar schatting 50%). Metingen van natrium geven een betere inschatting van de zeezoutconcentraties. Daarom wordt sinds het uitbrengen van de Regeling beoordeling luchtkwaliteit het natriumgehalte in PM_{10} gemeten. Deze meetinformatie is nu beschikbaar voor de jaren 2008-2010 en maakt het mogelijk de huidige regeling te evalueren en bij te stellen.



Figuur 1 Vergelijking tussen de berekende (model) en gemeten gemiddelde zeezoutconcentratie (2008-2010) op zes locaties (links) en de verdeling van de gemiddelde zeezoutconcentratie over Nederland (rechts).

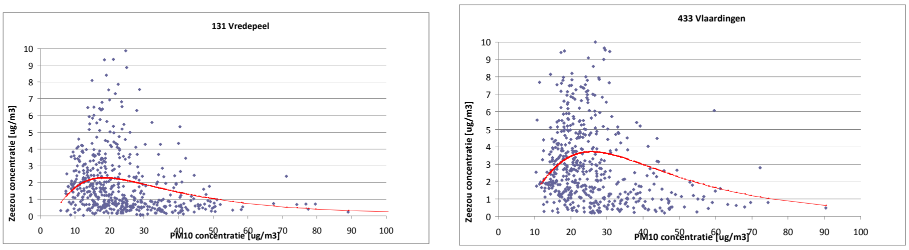
Definitie zeezout in PM_{10}

Zeezout in de lucht ontstaat door spetteren/vernevelen van kleine druppeltjes vanaf het oppervlak van de zee. De vorming van druppeltjes in de lucht is sterk afhankelijk van de windsnelheid; hoe harder de wind, hoe meer zeezoutdruppels. Voor het vaststellen van de hoeveelheid zeezout in de lucht wordt gebruikgemaakt van de verhouding van de diverse bestanddelen (natrium, chloride, magnesium …) in het zeewater. Omdat bij het transport van het zeezout door de lucht een deel van het chloride reageert, is natrium een geschiktere indicator voor de hoeveelheid zeezout. Daarbij komt dat er voor natrium in Nederland nauwelijks andere bronnen zijn. De hoeveelheid zeezout wordt dus geschat op basis van natrium en de verhoudingen van de chemische

elementen in de zee. Deze definitie is het eenvoudigst en ook consistent met de huidige regeling. Er zijn andere definities mogelijk op basis van zowel natrium als andere elementen waarvan sommige hoger en andere lager uitkomen. Bij deze definities zijn echter metingen van meer elementen nodig. Er dient dus een duurdere analyse plaats te vinden terwijl het onzeker is of dit een betere schatting van de zeezoutconcentratie oplevert. Ook is er meer proceskennis noodzakelijk om rekening te houden met de chemische reacties in de lucht en op het filter.

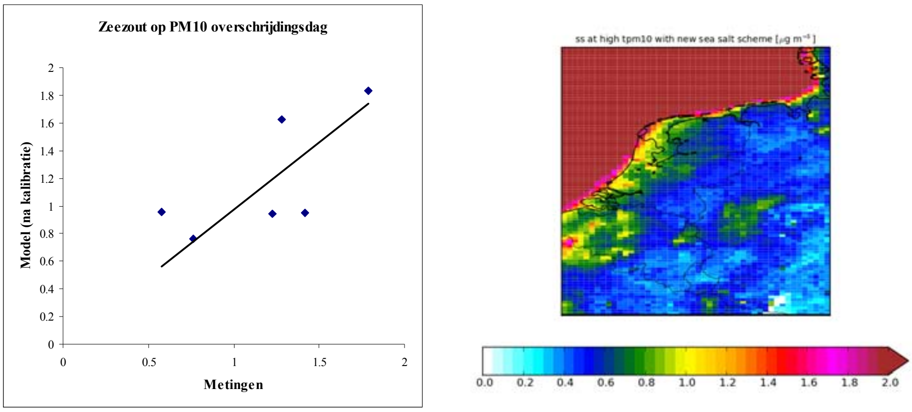
Bepaling van de jaargemiddelde zeezoutconcentratie
Er zijn diverse mogelijkheden om de vorming en verspreiding van zeezout wiskundig te beschrijven. Diverse mogelijkheden zijn toegepast in het LOTOS-EUROS (LE) luchtkwaliteitsmodel. Het bleek dat één combinatie van modelparameters de jaargemiddelde niveaus goed beschrijft, zowel in absolute waarde als ook in de verdeling over Nederland (zie Figuur 1). Op vergelijkbare wijze als in de huidige regeling voor zeezoutaftrek wordt de jaargemiddelde zeezoutconcentratie gepresenteerd per gemeente. De gradiënt loopt van 5 µg/m^3 op de Waddeneilanden tot 1 µg/m^3 in het zuidoosten van het land. Deze concentraties zijn systematisch lager dan in de huidige regeling. De hogere waarden in de huidige regeling kunnen worden verklaard doordat in 2005 de correctie voor de vangstkarakteristiek van de oude LVS-samplers te hoog is ingeschat.

Berekening van de zeezoutconcentratie bij overschrijdingsdagen
De hoeveelheid zeezout in PM$_{10}$ vertoont van dag tot dag grote variaties. Het zeezoutniveau blijkt een relatie te hebben met de niveaus van PM$_{10}$ (zie Figuur 2). Als voorbeeld zijn voor Vredepeel en Vlaardingen de niveaus zeezout (verticaal) tegen de niveaus PM$_{10}$ (horizontaal) uitgezet. De concentratie zeezout op een dag met een hoge PM$_{10}$-concentratie is duidelijk lager dan het jaargemiddelde. Daarom is het niet goed mogelijk om de jaargemiddelde zeezoutconcentratie te gebruiken voor de berekening van de zeezoutbijdrage op overschrijdingsdagen. Uit de vergelijking blijkt ook dat ook bij hoge PM$_{10}$-concentraties de hoeveelheid zeezout in kustprovincies (bijvoorbeeld Vlaardingen) hoger is dan verder landinwaarts (bijvoorbeeld Vredepeel).



Figuur 2 Zeezoutconcentratie uitgezet tegen de PM$_{10}$-concentratie voor de meetlocatie in Vredepeel (links) en Vlaardingen (rechts).

In de bestaande wettelijke regeling voor zeezoutaftrek mag overal hetzelfde aantal dagen buiten beschouwing worden gelaten. Op basis van de destijds beschikbare gegevens was het niet mogelijk om een gradiënt over Nederland vast te stellen voor de zeezoutconcentratie op overschrijdingsdagen. Op basis van de meetgegevens die nu beschikbaar zijn, is een gradiënt vastgesteld met behulp van een tweestapsbenadering. In de eerste stap wordt met het Lotos-Euros (LE)-model de gemiddelde zeezoutconcentratie berekend op de dagen met een PM$_{10}$-concentratie tussen de 40 en 70 µg/m^3. Dit gemiddelde, berekend over de periode 2008-2010 is weergeven in Figuur 3. In tegenstelling tot het jaargemiddelde blijkt de berekende zeezoutconcentratie bij hoge PM_{10}-dagwaarden lager te zijn dan de metingen. Voor een klein deel komt dit door de hoeveelheid natrium uit andere bronnen dat juist voor overschrijdingsdagen gemodelleerd wordt. Voor de resterende systematische onderschatting is gecorrigeerd.



Figuur 3 Berekende gemiddelde zeezoutconcentratie voor dagen met hoge PM_{10}-concentraties voor de periode 2008-2010 (rechts) en de relatie met de metingen (links).

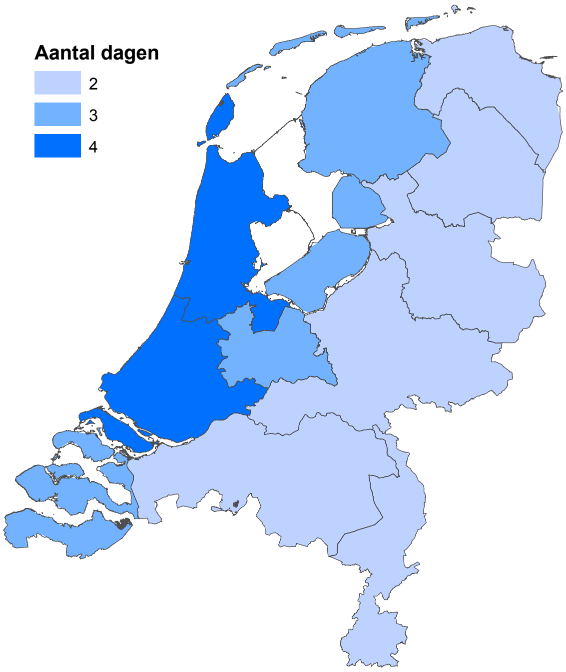
In Figuur 3 is net als bij het jaargemiddelde een gradiënt over Nederland van noordwest naar zuidoost zichtbaar. In de tweede stap wordt deze kaart vervolgens gebruikt om het effect van de zeezoutconcentratie op het aantal overschrijdingsdagen uit te rekenen. Bijvoorbeeld, als we weten dat op een bepaalde locatie gemiddeld 1 $\mu g/m^3$ zeezout aanwezig is op een overschrijdingsdag kan getoetst worden op een grenswaarde van 51 in plaats van op 50 $\mu g/m^3$. Bij het toetsen op een hogere grenswaarde vallen de dagen met een PM_{10}-concentratie tussen de 50 en de 51 $\mu g/m^3$ dan als overschrijdingsdag af. Het aantal dagen dat zo afvalt wordt berekend door gebruik te maken van de bekende / gemeten verdeling van PM_{10}-concentraties. Deze verdeling blijkt goed te kunnen worden beschreven met een log-normale statistische verdeling. Als deze verdeling wordt toegepast, blijkt dat er bij een verhoging van de jaargemiddelde toetswaarde tot 51 $\mu g/m^3$ gemiddeld ruim 2 PM_{10}-overschrijdingsdagen minder voorkomen. Bij een grotere hoeveelheid zeezout op overschrijdingsdagen wordt het aantal dagen dat buiten beschouwing kan worden gelaten groter. Op deze manier kan de kaart in Figuur 3 worden getransformeerd naar een kaart met het aantal overschrijdingsdagen dat vervalt. Op basis van de verdeling van zeezout over Nederland is het gemiddelde aantal afvallende overschrijdingsdagen per provincie uitgerekend. Het resultaat is:

- 4 dagen: Noord-Holland en Zuid-Holland
- 3 dagen: Friesland, Flevoland , Utrecht en Zeeland
- 2 dagen: Groningen, Drenthe, Overijssel, Gelderland, Noord-Brabant en Limburg

De beleidsmatige implicaties van de nieuwe methodiek voor zeezoutaftrek die hier wordt voorgesteld, zijn naar verwachting gering. Het risico op overschrijding van de dagnorm zal in het oosten iets toenemen ten gevolge van de nieuwe schattingsmethodiek, maar naar verwachting zal de invloed op het aantal knelpunten met normoverschrijding beperkt zijn.

Jaarlijks wisselende correcties voor zeezout versus één meerjaarsgemiddelde

De variatie in de jaargemiddelde zeezoutconcentratie is over de jaren 2008-2010 kleiner dan 10%. Dit geldt zowel voor de gemeten als de berekende resultaten. Er is, voor dit beperkte aantal jaren met bescheiden variaties, geen correlatie waargenomen tussen de gemeten en de berekende jaargemiddelde zeezoutconcentraties. Daarom is de meerwaarde van jaarlijks aangepaste correcties ten opzichte van één meerjaarsgemiddelde correctie op dit moment gering.



Figuur 4 Aantal dagen per provincie (links), dat vanwege de berekende bijdrage van zeezout, bij het toetsen aan de 35-dagennorm, buiten beschouwing mag worden gelaten.

Onzekerheden in de resultaten

De onzekerheid in de gepresenteerde jaargemiddelde zeezoutconcentraties wordt bepaald door de onzekerheid in de metingen en door de spreiding tussen de gemeten en de berekende concentraties. Het 95% -betrouwbaarheidsinterval voor de hoeveelheid zeezout wordt geschat op ongeveer 25-30%.
De onzekerheid in het aantal overschrijdingsdagen dat buiten beschouwing kan worden gelaten is groter vanwege het relatief kleine aantal dagen met een PM_{10}-concentratie rond de 50 µg/m^3 en wordt geschat op 40-50%. Beide onzekerheden zijn kleiner dan de geschatte onzekerheid in de huidige correctie.

Conclusie en Aanbevelingen

Op basis van recente metingen van natrium in PM_{10} is gebleken dat schatting van de hoeveelheid zeezout die ten grondslag ligt aan de huidige correctie te hoog is. De metingen geven aan dat er zowel bij het jaargemiddelde als bij zeezoutconcentraties bij hoge PM_{10}-concentraties een gradiënt van zeezout over Nederland is.

- Na verificatie van de modelresultaten op de beschikbare metingen is een onderbouwde jaargemiddelde zeezoutconcentratie vastgesteld van circa 5 µg/m^3 voor een aantal kustgemeenten tot 1 µg/m^3 in Limburg.

- Voor het aantal overschrijdingsdagen is de aanbeveling dat bij toetsing in Noord- en Zuid-Holland vier dagen buiten beschouwing kunnen worden gelaten tot twee dagen in de provincies meer landinwaarts.
- De onzekerheid in deze aanbeveling is geschat op 25-30% voor het jaargemiddelde en 40-50% voor het aantal overschrijdingsdagen.
- Vooral bij het effect op het aantal overschrijdingsdagen is de lengte van de meetreeks een kritische factor voor de onzekerheid. Daarom wordt aanbevolen om de natriummetingen in het Landelijk Meetnet Luchtkwaliteit te continueren. Daarmee kunnen over enkele jaren de hier vastgestelde concentraties worden geëvalueerd.
- De onderbouwing van deze aanbeveling is in lijn met de betreffende Internationale EU-Guideline voor ‘natural contributions’. Aanbevolen wordt om de Engelstalige onderbouwing in dit rapport als voorbeeld aan te bieden aan de FAIRMODE-werkgroep die de richtlijn over ‘natural contributions’ beheert.

1 Introduction

1.1 EU Directive on particulate matter PM_{10}

As part of the EU legislation to improve air quality, the EU air quality Directive 2008/50/EC has set target values and limit values for PM_{10} and $PM_{2.5}$ concentrations in ambient air. For PM_{10} there are 2 limit values: the annual average should not exceed 40 µg/m^3 and the daily averages should not exceed 50 µg/m^3 on more than 35 days per year. Measurements of the Dutch national air quality monitoring network showed no exceedance of the yearly limit. On the measurement locations exceedance of the daily limit with more than 35 times per year were not observed in recent years but can occur in years with less favourable weather conditions like 2011 appears until now.

Definition of PM_{10} (Directive 2008/50/EC)
PM_{10} shall mean particulate matter which passes through a size-selective inlet as defined in the reference method for the sampling and measurement of PM_{10}, EN 12341, with a 50% efficiency cut-off at 10 µm aerodynamic diameter

The EU directive allows subtraction of natural sources or winter-sanding or –salting of roads. In February 2011 a first version of the guideline for the demonstration and subtraction of natural sources has been issued (SEC, 2011).

Article 20 (Directive 2008/50/EC)
Contributions from natural sources
1. Member States shall transmit to the Commission, for a given year, lists of zones and agglomerations where exceedances of limit values for a given pollutant are attributable to natural sources.
Member States shall provide information on concentrations and sources and the evidence demonstrating that the exceedances are attributable to natural sources.
2. Where the Commission has been informed of an exceedance attributable to natural sources in accordance with paragraph 1, that exceedance shall not be considered as an exceedance for the purposes of this Directive.
3. The Commission shall by 11 June 2010 publish guidelines for demonstration and subtraction of exceedances attributable to natural sources.

Article 21
Exceedances attributable to winter-sanding or -salting of roads
4. Without prejudice to Article 20, in the case of zones and agglomerations referred to in paragraph 1 of this Article, Member States need to establish the air quality plan provided for in Article 23 only in so far as exceedances are attributable to PM_{10} sources other than winter-sanding or -salting of roads.

1.2 Current subtraction of sea salt in the Netherlands

In the Netherlands the contribution of sea salt may be discarded in the comparison of concentration levels with the critical levels (the Environmental Management Act (Wet milieubeheer in Dutch) 2007 article 5.19). The calculation procedure is described in the Regulation on air quality assessment 2007 (Regeling beoordeling luchtkwaliteit 2007(Rbl 2007) in Dutch). For the yearly average a table is included for each municipality. The correction is about 7 µg/m^3 along the coast and 3 µg/m^3 on the eastern border. The allowed subtraction of PM$_{10}$ exceedance days is 6 days for all locations in The Netherlands.

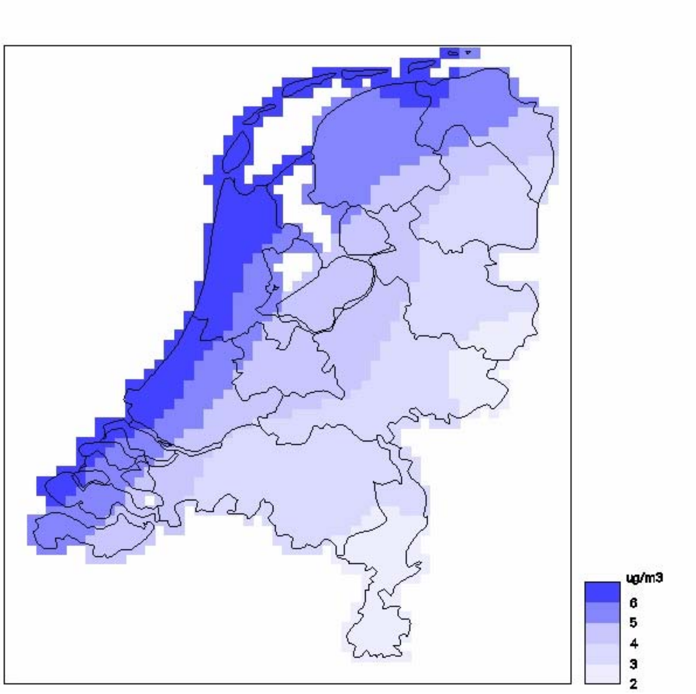


Figure 1.1 The annual average sea salt concentration in the current Dutch scheme.

The above estimate is the result of a study of the National Institute for Public Health and the Environment (RIVM), the Dutch Organization for Applied Research (TNO) and the Netherland Environmental Assessment Agency (MNP) (Hoogerbrugge et al., 2005). The study is based on a number of assumptions which result in a considerable overall uncertainty (50%). The major source of uncertainty was the fact that only chloride measurements were available from an instrument that was not compatible with current PM$_{10}$ reference instruments (Hafkenscheid et al.,2010). Since 2008, Na concentrations in PM$_{10}$ reference filters are determined on 6 locations in the Netherlands (every other day) within the Dutch national air quality network. This enables a more accurate sea salt assessment. In addition, sodium concentrations from a measurement campaign which was part of the Netherlands Policy Support Program on PM (BOP project; mid 2007-mid 2008) are available. Based on the results of this campaign a mismatch between the current scheme and the measured sea salt concentrations was identified (Manders et al., 2010). The new measured data 2007-2010 will be used to update the scheme to the latest insights.

Regeling beoordeling luchtkwaliteit 2007 (in Dutch)

Jaargemiddelde concentratie

Voor zwevende deeltjes (PM_{10}) geldt een grenswaarde van 40 microgram per m^3 als jaargemiddelde concentratie (bijlage 2, voorschrift 4.1, onder b, van de wet).

Het aandeel zeezout in de jaargemiddelde concentratie van zwevende deeltjes (PM_{10}) varieert van circa 7 µg/m^3 langs de westkust tot circa 3 µg/m^3 in het oostelijk deel van Nederland. Om een voor zeezout gecorrigeerde jaargemiddelde concentratie te bepalen, is een plaatsafhankelijke correctie nodig

Vierentwintiguurgemiddelde concentratie

Voor zwevende deeltjes (PM_{10}) geldt een grenswaarde van 50 microgram per m^3 als vierentwintiguurgemiddelde concentratie, waarbij geldt dat deze waarde maximaal vijfendertig maal per kalenderjaar mag worden overschreden Het blijkt dat de invloed van de in de buitenlucht aanwezige concentratie zeezout op het aantal dagen waarop de concentratie van zwevende deeltjes (PM_{10}) de waarde van 50 µg/m^3 overschrijdt, voor geheel Nederland nagenoeg gelijk is.

Uitgaande van de niet voor zeezout gecorrigeerde jaargemiddelde concentratie van zwevende deeltjes PM_{10}), wordt het voor zeezout gecorrigeerde aantal overschrijdingsdagen van de vierentwintiguurgemiddelde grenswaarde van 50 microgram per m^3 verkregen, door het op de gebruikelijke wijze bepaalde aantal overschrijdingsdagen met 6 dagen te verminderen.

1.3 Objectives of this report

This document has the following objectives:

- compare alternative methods for estimating the sea salt contribution to PM_{10};
- select the best methods;
- compare the newly derived results to the current approach;
- provide an update of the current approach;
- give input for the EU guidelines.

1.4 Effect of sea salt subtraction on health

There are many sources of particulate matter. The composition and the extent of these sources can be very different. Consequently, the composition of particulate matter shows spatial variations. Also seasonal variations and wind direction can have effect on particle sizes and chemical composition of particulate matter. Because of the wide variety of particle size and composition of particulate matter, the adverse health effects of individual sources cannot be determined easily. Toxicity studies show that not all components in particulate matter have the same adverse health effects. In combination with the concentration to which one is exposed, the contributions of individual components in particulate matter to health effects can be determined by studies like epidemiological research.

There are no studies showing that current sea salt levels in the Netherlands or anywhere in the world have significant health effects. It is therefore reasonable to assume that the contribution of sea salt to adverse health effects may be neglected compared to that of other components in particulate matter. The current limits do not distinguish the fractions of particulate matter; all components are assumed to be equally harmful. If non-harmful components with natural origin such as sea salt are not considered, exceedance will be reduced and limitation of spatial planning may be partly cancelled out. However the adverse health effects are not reduced; the problem will increase instead. The gap between the limit value and the reported concentrations may be filled with harmful substances which can have an adverse health effect.

2 Definition of sea salt in Particulate Matter

2.1 Introduction

This chapter describes possible approaches to determine the amount of sea salt in PM on the basis of tracer elements. For a useful definition the selectivity, to reduce possible interferences from other sources, and stability are important criteria.

Sea salt particles are emitted from the foam from breaking waves. The small air bubbles in sea water break and release small particles of sea salt. These droplets have the composition of sea water, therefore the dry salt has the same composition as sea salt. Sea salt consists of large mass fractions of sodium (Na = 30.8%) and chloride (Cl = 55%). Other contributions are provided by magnesium (Mg), sulphur (S) and other trace elements. Table 2.1 shows the main elements in fresh sea salt (Millero, 2004).

Table 2.1 Mass contribution (g/g) of selected elements in fresh sea salt

Element	**Contribution (%)**
Cl	55.4
Na	30.8
Mg	3.8
S	2.6
K	1.1
Ca	1.1
Other elements	5.2

To estimate the mass contribution of sea salt to the total particulate mass one needs to use one of the sea salt components as a tracer. For a component or combination of components to be a good tracer a number of constraints should hold:

- The tracer is easily attributable to the source of interest. Hence, there should be no other important sources of the tracer besides the source of interest.
- The tracer should be conserved. The tracer should not be subject to transformation processes that are not easily accounted for.
- The tracer should be measured reliably with sufficient accuracy.

Considering its composition, sodium and chloride are the key candidate tracers for sea salt. The total concentration of fresh sea salt can be derived from sodium or chloride or one of the other components, provided that there are no other significant sources of these elements. The concentration of fresh sea salt in air can be estimated by dividing the concentration of Na or Cl by the relative contribution of that trace element in sea salt (as given in Table 2.1). This leads to the following equations:

$$[\text{sea salt}] = 1/0.308\ [\text{Na}] \quad = 3.26 * [\text{Na}] \qquad [1]$$

$$[\text{sea salt}] = 1/0.554\ [\text{Cl}] \quad = 1.8 *[\text{Cl}] \qquad [2]$$

However, the estimation of the sea salt concentration in the atmosphere is complicated by the chemical interaction of acids with sea salt which causes a chloride loss (McInnes et al., 1994). The acids nitric acid and, to a lesser extent, sulphuric acid may react with NaCl. These reactions lead to the formation of sodium nitrate and sodium sulphate, respectively:

$NaCl + HNO_3 \rightarrow NaNO_3 + HCl$ [3]
$2\ NaCl + H_2SO_4 \rightarrow (Na)_2SO_4 + 2\ HCl$ [4]

Important in these reactions is the chloride replacement which is released in the form of gaseous HCl, removing particulate chloride from the atmosphere, which implies that the amount of chloride measured is always equal or smaller than the original amount in sea salt. The amount of chloride displacement by nitrate depends on the meteorological conditions (temperature, relative humidity), the residence time of the air mass over land and the availability of nitric acid and thus pollution level. Similarly, the same depletion through reaction 3 and 4 may occur on a filter substrate (Slanina et al., 2001). Hence, the extent of chloride depletion needs to be quantified for the Dutch situation to judge the credibility of chloride as a tracer for fresh sea salt.

To assess the suitability of chloride or sodium as a tracer for estimating sea salt concentrations, three main questions arise which will be discussed in this chapter:

1. Are there significant non-marine sources of the tracers sodium or chloride?
2. What is the importance of the chloride depletion in the Netherlands?
3. How important are reactions on filter substrates, what differences can be expected using different measurement instruments?

Based on the discussion of these questions, a method for the determining sea salt concentrations from measurements will be selected.

2.2 Other sources of atmospheric sodium and chloride

One of the key questions when it comes to estimating sea salt contributions is whether all the sodium and chloride that is measured in PM are originating from an emission of sea salt. There may be other important (anthropogenic or natural) emission sources of both sodium and chloride. This section discusses a model study that was performed to calculate source contributions for both anthropogenic sources and sea salt for the base cations (sodium, calcium, magnesium and potassium) using the LOTOS-EUROS model (Schaap et al., 2008), which is a 3D chemistry transport model which aims at simulating air pollution in the lower troposphere over Europe. Furthermore, we discuss in less detail the impact of suspended dust and road salt, as well as the potential contribution of anthropogenic HCl sources on particulate chloride.

2.2.1 Impact of anthropogenic emissions

Anthropogenic emissions

Base cations of Na, Ca, Mg and K are emitted by a host of anthropogenic sources and are part of the particulate matter emissions. To determine the absolute emissions of the base cations, the fractional mass contributions to PM emissions as proposed by Van Loon et al. (2005) have been used. For most sources the fraction of base cations in PM is only 1-2%, but exceptions are coal and wood combustion and glass production, where higher percentages of calcium and sodium, respectively, are released. These fractions are combined with the PM emissions in the TNO emission database (Visschedijk and Denier van der Gon, 2005) to calculate and distribute the base cation emission over Europe.

The calculated annual total emissions are 30 ktonnes for sodium, 218 ktonnes for calcium, 27 ktonnes for Magnesium, and 49 ktonnes for Potassium for the EU27 + Norway and Switzerland. Figure 2 shows the contribution of each of the 4 base cations to the anthropogenic emissions per SNAP code, which is a commonly used nomenclature relating the emission to its source. A detailed explanation of the SNAP codes is available from Visschedijk and Denier van der Gon (2005).Sodium emissions are found in industrial process emissions (SNAP 4) as well as combustion sources. The emissions of the other base cations are dominated by combustion processes (SNAP 1, 2 and 3), mainly by small combustion installations such as in households (SNAP 2). However, these emissions are particularly uncertain, especially with respect to wood combustion.

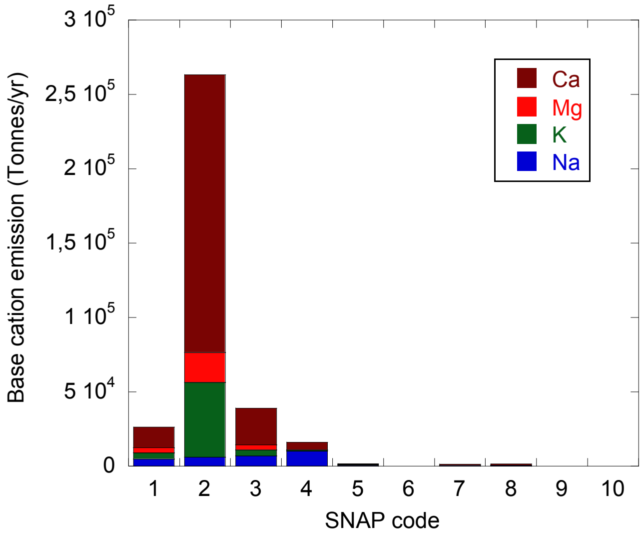


Figure 2.1 Base cation anthropogenic emissions (in tonnes) per SNAP category in the EU27 + Norway + Switzerland for the year 2000

Sea salt emissions

Sea salt emissions in the model are calculated using 4 different size classes (0.14-1, 1-2.5, 2.5-5 and 5-10 µm wet diameter at 80% relative humidity). For the generation of submicron and super micron particles, parameterizations of Mårtensson et al. (2003) and Monahan et al. (1986), respectively, are used. These emission functions provide the sea salt mass that is emitted to the atmosphere, which includes Na and Cl (see Table 2.1). For a detailed description of the sea salt emission module we refer to Manders et al. (2010). The simulations were performed with the Zhang deposition scheme (Zhang et al. , 2001).

Results

The modelled sodium distribution in Figure 2.2 shows the highest concentration over the open sea (Atlantic, Mediterranean), reflecting the sea salt emissions over the sea. Above the Atlantic, higher concentrations are reached than above the Mediterranean due to higher wind speeds. These high wind speeds are associated with westerly directions in Western Europe, and large quantities of sea salt can be transported inland during these conditions. Consequently, the concentrations gradually decrease from the Western European coastline to inland locations. The modelled annual mean concentrations are systematically larger than the observed concentrations. For 2005 (Figure 2.2), the European spatial correlation between model results and measurements is high, with an explained variability of 85%, but the model overestimates the absolute value by 60%. The model is able to capture the events in sodium concentrations, indicating that the variability in space and time of the generation as well as transport of sea salt are modelled realistically (Manders et al., 2010). The overestimation indicates that there are still significant biases and uncertainties in the source strength and life time of sea salt.

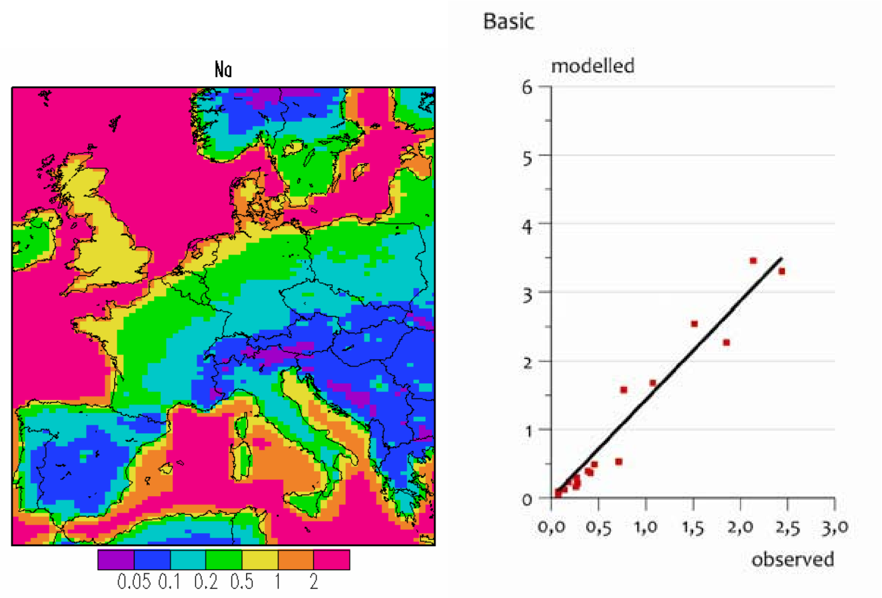


Figure 2.2 Modelled annual mean Na concentration ($\mu g/m^3$) with LOTOS-EUROS (left) and comparison between European modelled and measured annual mean sodium concentrations (right).

The modelled contribution of the different source groups for Na is given in Figure 2.3. Over coastal and remote regions sea salt is by far the dominating contributor to atmospheric sodium concentrations (top right panel). In these areas the sea contributes more than 95%. Over Central Europe and some smaller but densely populated areas the impact of anthropogenic emissions is larger, although the anthropogenic emissions of Na in these regions are still relatively small. Over most of Western Europe the contribution of the sea is still above 80%, including Germany. The top left panel shows that in the Po Valley and over large regions in Eastern Europe anthropogenic activities contribute 20-80%, illustrating that in these regions the assumption that all sodium derives from sea salt is not valid. Note that the absolute concentrations are small in these regions anyway (Figure 2.3).
For the Netherlands, the influence of anthropogenic emissions is generally below 5%. Only in the south-east of the country, the contribution of anthropogenic sources is slightly above 5%. Hence, in the Netherlands the annual average influence of anthropogenic emissions on the Na measurements may therefore be considered to be small. However, also the contribution of sodium on PM_{10} exceedance days is important. This subject is treated in more detail in section 5.2.

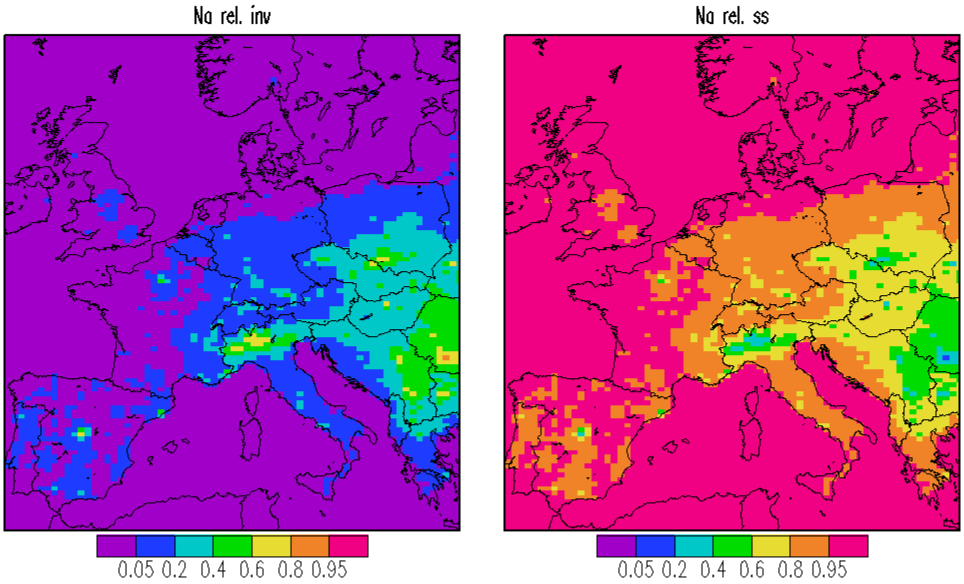


Figure 2.3 Modelled relative contributions of the emission inventory (inv) and sea salt (ss) to sodium concentrations.

2.2.2 *Suspended dust and road salt*

Two other sources of sodium that may have an occasional impact are the suspension of road salt and mineral dust from roads and other surfaces. Below we discuss the potential contributions of these sources.

Road salt

A different source, not taken into account in the model study described in this section, is the influence of road salt which is used in winter to de-ice roads. When this effect is important but not taken into account, the interpretation of measurements could potentially lead to significant overestimation of the sea salt contribution in PM.

To assess the importance of road salt on the concentrations of sodium in the atmosphere, two independent methods have been used:

- For a first indication of the possible amount of road salt a regression model is applied to the full dataset of available measurements. In this regression model the presence of an additional contribution of road salt is assumed to be visible:
    - if the minimum daily temperature is below zero; and
    - in the urban area around main roads where a large amount of road salt is applied.
- Another approach is to calculate the ratio Mg/Na for days with minimum temperature below zero and for other days. Information of Rijkswaterstaat (RWS) has shown that, for example, in the winter of 2009/2010 salt from various origins has been used as road salt: sea salt, coarse rock salt, ground salt. The compositions of these salts are not very different from sea salt. However, before being used, this salt is mixed with CaCl and/or MgCl to enhance the performance (dispersion and lowering the freezing point) of the salt. Because Ca is also contributed by other sources, the Ca concentration is less constant. Consequently Mg may be used as tracer for road salt.

Both these approaches do not show any significant indication that the interpretation of the data is affected by the presence of road salt (see Annex 1 for more details).

Sodium from suspended mineral dust
Apart from the anthropogenic and sea salt emissions, also emissions may occur from wind-blown dust emissions, resuspension from traffic and agriculture and from soils. We have performed a simulation with the sodium content of soil connected to the mineral dust distributions as provided by Denier van der Gon et al. (2010). It was shown that the contribution is very small and negligible. This can be easily understood considering that only a small part of the mineral dust consists of sodium. With average mineral dust concentrations of about 2 $\mu g/m^3$ (Weijers et al., 2011) the contribution of mineral dust to atmospheric sodium can therefore be neglected.

2.2.3 Non-marine chloride sources

Anthropogenic emissions of HCl mainly occur from the combustion of coal and other fossil fuels. According to the US EPA emission inventory for 2002 (US EPA, 2002), the two most important sources of HCl emissions are utility boilers (60%) and industrial/residential/institutional boilers and process heaters (33%). According to the AP42 chapter on hydrochloric acid production, the vast majority of the HCl is emitted from the combustion of coal. This situation is likely similar in the Netherlands, but has never been established.

HCl has a potentially important role in the formation of NH_4Cl in the atmosphere. Some campaigns in coastal regions indicate the presence of NH_4Cl measured by an Aerosol Mass Spectrometer (AMS) (Nemitz et al., 2011). This component is a semi-volatile component, with a higher volatility than ammonium nitrate. Hence, only in areas which are rich in ammonia and during cooler parts of the day/year a significant presence of NH_4Cl might be expected. An important effect of the volatility of this compound may be that it is easily lost from filter substrates, to a much greater extent than ammonium nitrate. At present there is little knowledge about the presence of ammonium chloride in the Netherlands. As the molar balance between ammonium and nitrate and sulphate hardly shows an excess of ammonium, the presence of this compound is expected to be small.

2.3 Depletion of chloride

One of the main uncertainties in relating chloride concentrations to its contribution from fresh sea salt is the depletion of chloride by reaction with HNO_3 and H_2SO_4 as explained in section 2.1. These reactions remove the particulate chloride from the atmosphere by the formation of gaseous HCl. Na particles are preserved due to the formation of $NaNO_3$ and Na_2SO_4, both in particulate form. Therefore the measured ratio of sodium and chloride in the atmosphere is less or equal to the ratio in sea water (= 1.8), unless other sources of Na or Cl become significant.

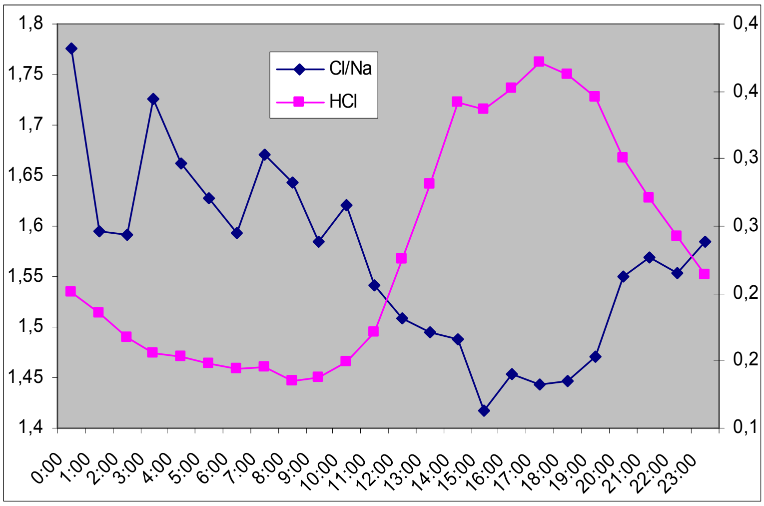


Figure 2.4 Daily cycles of Na/Cl and HCl measured by the Monitoring Instrument for AeRosols and GAses (MARGA) instrument at Schiedam Milieudienst Rijnmond (DCMR) station.

In the BOP project, both sodium and chloride have been measured using two different instruments (Weijers et al.,2010). Firstly, the PM was sampled with the reference method using quartz filters. In addition, a MARGA was used at Cabauw to monitor the hourly evolution of the inorganic aerosol composition. The advantage of the MARGA is that there is no collection step on a filter substrate that could be subject to additional artefacts. In Figure 2.4 the extent of chloride depletion in atmospheric aerosol based on the MARGA data as function of the time of the day is shown (Weijers et al., 2010). In fresh sea salt the Cl to Na ratio is 1.8. The measurements show that in the atmosphere a significant amount of chloride is displaced as the ratio varies between 1.4 and 1.8 (blue line). Furthermore, the depletion of chloride shows a diurnal cycle with lowest ratios and therefore highest chloride loss during the day. The degree of chloride displacement is correlated with the presence of nitric acid, which also shows a diurnal variation with a maximum during the day.

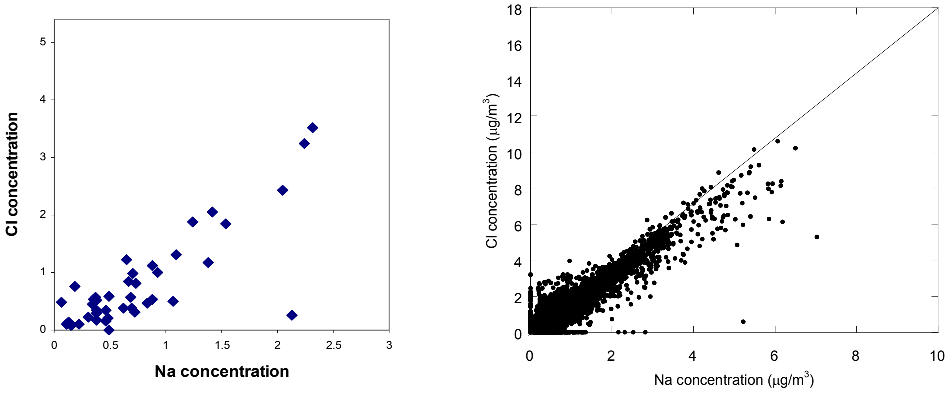


Figure 2.5 Measured ratio between sodium and chloride concentration measured at Cabauw during the BOP project, based on the filter measurements (left panel) and on the MARGA measurements (right panel).

Figure 2.5 shows the measured chloride concentrations as function of those of sodium for Cabauw using MARGA data (hourly basis) and the BOP filter measurements (daily basis). Both data sets show that chloride is lost compared to the expected amount of chloride from fresh sea salt. The linear fits through the data are:

[Cl] = 1.19 * [Na]; R^2 = 0.82   for the filter (one outlier removed at Na = 2.2 µg/m^3)
[Cl] = 1.50 * [Na]; R^2 = 0.86   for the MARGA

The R^2 correlation values for both fits are both above 0.8 and the Figure 2.5 clearly shows that the linear fit is in a fair agreement with the measurement data. Fitting the data without forcing the data through zero gives very similar explained variabilities. From these data one can estimate that the loss of chloride at the filters was on average 17% in the MARGA and 34% at the filters. From these data one cannot conclude that the filters were subject to higher depletion as the data in the figures are not paired in time and represent different days within the same period.
To analyze the difference between the filter and the MARGA in more detail, each day for which both MARGA and filter measurements are available has been plotted in Figure 2.6 for Na and Cl separately. The best fit through the data points shows that filter measurements result in lower concentrations than MARGA measurements both for Na and Cl. The sodium fit has a slope of 0.93, however there is quite some scattering and there appear to be a few outliers. Removing these outliers and fitting a linear trend (forced through zero) results in a slope of 0.99 which is basically unity. For chloride the slope is 0.77, but also here outliers are present. After removing them and forcing the fit through zero, the slope is 0.87 and therewith slightly lower than unity. Although the removal of the outliers is somewhat arbitrary, both with and without the removal an indication of a small effect of additional chloride depletion at the filter substrate is found. However, one could also interpret it as an indication of the uncertainty related to measurement of components of particulate matter.

From this analysis, it has been concluded that:

1. there is a significant atmospheric depletion of chloride in the order of 25%;
2. we cannot rule out the potential small effect of chloride depletion occurring at the filter itself.

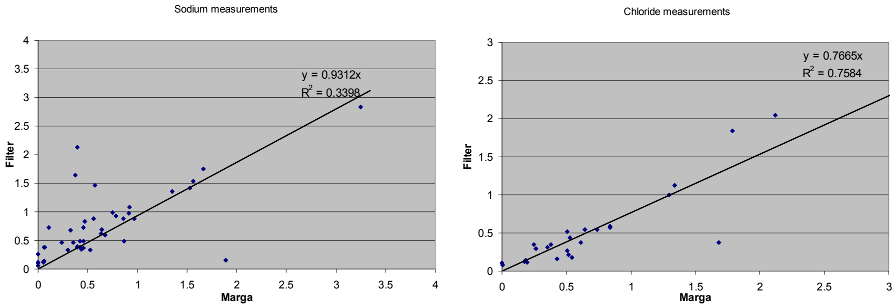


Figure 2.6 Plot of the measured concentrations of sodium (left panel) and chloride (right panel) using the filter method (vertical axis) and MARGA instrument (horizontal axis).

The loss of chloride in filter measurements will be further described in a BOP report by Weijers et al. (2012).

2.4 Available methods to estimate the concentration of sea salt

The measurements of Na and Cl form the basis for estimating the contribution of sea salt in particulate matter. Three options are available for calculating the sea salt concentrations from these measurements:

1. The first sea salt estimate uses the sea salt that is present in the sea. The change in composition after emission is ignored. It is only based on the concentration of sodium, which is the most conserved tracer. Hence, the sea salt concentration is calculated by using the sodium contribution in sea salt from Table 2.1:

   $$[seasalt]_{fresh} = \frac{[Na]}{0.308} = 3.26 \times [Na]$$

   This estimate can be interpreted as the **unaffected** sea salt estimate

2. The second estimate of the sea salt concentration accounts for chloride depletion and it calculates the actual sea salt contribution that is of pure marine origin. It contains two parts: the conserved non-chloride part (45%) (Millero, 2004) is estimated with Na as tracer and the remaining chloride concentration.

   $$[seasalt]_{pure} = (1-0.55) \times \frac{[Na]}{0.308} + [Cl] = 1.45 \times [Na] + [Cl]$$

   This estimate reflects the **pure residue** of the sea salt.

3. The third estimate of the sea salt concentration assesses the total particulate mass that would disappear if there is no source of sea salt. It uses the pure sea salt estimate, but includes an extra term to account for the added mass by displacement of chloride by nitrate. The nitrate contribution is calculated as the original Cl concentration (1.8 times the sodium concentration) minus the actual concentration of chloride (corrected for the additional mass by the replacement of Cl with NO_3).

   $$[seasalt]_{total} = [seasalt]_{pure} + (1.8 \times [Na] - [Cl]) \times \frac{62}{35} = 4.6 \times [Na] - 0.8 \times [Cl]$$

   This estimate reflects the **total** of sea salt induced PM_{10} .

Compared to the unaffected sea salt estimate, the pure residue sea salt method results in about 20% lower concentrations of sea salt, while the total sea salt estimate leads to an increase of about 15% compared to the unaffected sea salt method (taking only nitrate in consideration, when also sulphate is included the increase would be higher).

Sea salt is a hydroscopic component which implies that sea salt particles can consist for 10-20% of their weight of associated water. Obviously the multiplication factors should be increased by 10-20% to account for the weight of the associated water on the PM_{10} filters. The methods 1 and 2 are both described as options in the Guidance on the quantification of the contribution of natural sources (EU, 2011).

2.5 Selection of method to be used

To assess the suitability of chloride and sodium as a tracer for estimating sea salt concentrations, three main questions concerning the validity of the tracers were discussed in this chapter. It was shown that:

- Within the Netherlands, it is possible to use sodium as tracer for sea salt, since other potential sources of Na are generally small or even negligible.

- Non-marine sources of chloride include anthropogenic HCl sources, mainly originating from the combustion of coal.
- The depletion of Cl by reactions with HNO_3 and H_2SO_4 is a complication for using Cl.
- We cannot rule out the potential effect of depletion occurring at the filter.

The preceding section described three possible methods to determine the sea salt concentrations of the concentration of sodium and chloride. The selection of the most appropriate approach is not straightforward. The *pure residue* sea salt estimate obviously never overestimates the amount of PM_{10} originally arriving from the sea. However this approach has two disadvantages:

1. The estimate is sensitive for reactions on the filter, because Cl particles are removed from the filter by the reaction with HNO_3 as explained in section 2.1.
2. The method requires both the analysis of sodium and chloride which makes the assessment method more expensive in practice.

The *total* sea salt estimate obviously never underestimates the amount of PM_{10} related to sea salt. Using this method, the nitrate formed by the chloride displacement is added to the total sea salt mass. It is disputable whether this additional term is needed, since this NO_3 is not the actual sea salt anymore. On the other hand, without the presence of sea salt it would not have been formed at all. The total sea salt estimate presumably describes the PM_{10} concentrations that would be exist in a world without sea salt. The disadvantages are in the same line as for the pure estimate. The estimate is sensitive for reactions on the filter and the method requires both the analysis of sodium and chloride.
The *unaffected* sea salt estimate on the other hand does not require measurement of Cl and is therefore not sensitive to the removal reactions for NaCl in the atmosphere as well as on the filter. An additional advantage of the use of only Na particle measurements is the lower costs, since only one element is being measured. The disadvantage is that it is not the actual contribution of sea salt. On the other hand, when all anthropogenic emissions would be zero, the displacement would be negligible and the estimation based on sodium alone would be accurate. Thus one could conclude that the fresh mass is the marine mass that cannot be mitigated by policies. The *unaffected* sea salt estimate is consistent with the definition of sea salt which is used in the assessment of Hoogerbrugge et al. (2005) and was the basis for the current regulation.
Given the advantages of not including chloride measurements, the fresh sea salt method is found to be the most easily interpretable and, within its definition, the most accurate method available. Therefore, after discussions with the Dutch Ministry of Infrastructure and the Environment (I&M), it has been decided to use the fresh sea salt approach for calculating the sea salt concentrations in the Netherlands. Starting in chapter 4, this method will be used for determining the sea salt concentrations in the remainder of this report.

Conclusion

In this assessment the amount of sea salt is defined as 3.26 * Na. This definition ignores the amount of depletion of chloride and the amount of associated water. The definition is one of the options in the EU guidance (EU, 2011) and consistent with the definition used in the previous assessment. For the Netherlands the amount of sodium from other sources than the sea salt contribution is on average negligible. On exceedance days a correction for anthropogenic sodium may be necessary.

3 Evaluating the assumptions underlying the assessment of Hoogerbrugge et al (2005)

In 2005 the sea salt concentration in the Netherlands was estimated based on time series of chloride. These chloride concentrations were obtained from monitoring stations using an old LVS sampling device within the national air quality network. The cut-off for this device is not as sharp as a modern PM device and on average characterised as approximately 3-4 µm. Therefore, to estimate the sea salt concentration in PM_{10}, an estimate had to be made of the mass ratio (a) of PM_{10} to PM_3. Furthermore, there was a correction factor (b) to account for the replacement of chloride. Hence, the sea salt concentration in PM_{10} was estimated with the following formula:

$SS_{pm10} = 1.8 * Cl_{lvs} * a * b$

The values for the multiplication factor were estimated based on a small set of available data. The values estimated were a = 3 and b = 1.25. Hence, all chloride data were multiplied by a*b =3.75. This chapter discusses to what extent these values are still valid, taking into account the information obtained within the National Air Quality Monitoring Network (NAQMN) and the BOP study.

a. Particle size
The measurement data obtained since 2007 within the NAQMN and the BOP study allow for an evaluation of the factor (a) used by Hoogerbrugge et al. (2005). These new measurements indicate that the chloride content of PM_{10} using the reference method is about a factor of 1.7-1.8 higher than the concentrations measured with the LVS sampler (Hafkenscheid et al., 2010). Clearly, this factor is substantially lower than the factor a = 3 which was used previously. Within BOP the sodium content of both $PM_{2.5}$ and PM_{10} was measured at 5 locations in the Netherlands. Manders et al. (2009) found that the ratio between PM_{10} and $PM_{2.5}$ was 2.5-3.3 on average using the reference method. Thus, the LVS sampler measured considerably more chloride than present in $PM_{2.5}$, showing that the transmission of the LVS sampler for chloride is considerably larger than the 2.5 µm reference method.

b. Depletion of chloride
The BOP study also enabled to review the amount of chloride loss compared to freshly emitted sea salt. In section 1.3 the average chloride loss at Cabauw was estimated to be around 25% which would imply a factor b of 1.3. The latter is in line with the previously estimated value.

The value for b in Hoogerbrugge et al. (2005) was estimated from a literature survey on available data in and around the Netherlands, summarised in Table 3.1. At five locations the average chloride depletion varies between 15 and 24%. The lowest values tend to be for locations very close to the sea. From these values the authors estimated the average loss to be 20% which means that b would be 1.25.
The value for b was derived for the annual average situation and is a highly simplified factor for the correction of the chloride depletion. The justification is that the detailed information needed to correct for chloride depletion was not available.

Table 3.1 Literature survey of Na and Cl particle data in/around the Netherlands (from Hoogerbrugge et al., 2005)

Locatie	**Period**	**n**	**Na**	**Cl**	**Chloride depletion (%)**	**Bron**
Speuld	1995	~340	0.79	1.1	24	Erisman et al., 1996
Knokke	1999-2000	48	2.23	8.74	18	Eykmans et al., 2001
Eilsum	Fall, 1994	45	1.5	2.17	17	Behlen, 1996
Stralsund	1994	100	1.10	1.80	15	Behlen, 1996
Ruhr-area	1997-1998	97	0.66	0.92	23	Kuhlbush et al., 2000

The chloride depletion is a function of the availability of nitric acid and the residence time. Freshly emitted sea salt has not been subject to depletion, whereas in highly polluted air masses a major fraction of the chloride from the sea salt particles may have been depleted. Thus, chloride depletion is most important for days with low sea salt concentrations, whereas it is less important during high sea salt events. Hence, the average factor to account for the depletion may be too high for sea salt events and too low for continental air masses. In addition, chloride depletion is dependent on season. Gaseous nitric acid shows a large seasonal variation with low values in winter and high levels in summer. As a consequence, chloride depletion is low in winter and high in summer, which is nicely illustrated by Plate (2000) and was also found for the data in Table 3.1. Hence, the derived factor may be too high for winter and too low for summer. As exceedance days tend to be in winter with continental air masses with low sea salt content we implicitly assume that the underestimation due to the origin and overestimation due to season cancels out.

Conclusion

Based on the new knowledge the estimates of sea salt based on chloride measurements using the LVS method in Hoogerbrugge et al. (2005) have been at the high side. Based on the present insight in the size fractionation it is estimated that the previous estimate for the factor a was too high by 70%. Note that this number applies to the annual mean value.

The factor b is found to be correct (see also section 1.3), new measurements performed during the BOP project indicate a depletion factor which is in line with the previous estimate in Hoogerbrugge et al. (2005).

4 New approach

4.1 Method description

4.1.1 *Measurements*

In the Dutch national air quality monitoring network sodium and chloride concentrations in PM_{10} are measured at a number of locations. The sodium concentration is determined by extraction of the Teflon filter with HNO_3 solution, after which an ICP-MS P513 analysis follows. The standard uncertainty of the measurements is estimated as 5-10%.
Table 4.1 gives an overview of the locations at which sea salt components (Na and/or Cl) in PM_{10} fractions have been measured.

Table 4.1 Measurement stations on which sea salt components have been measured in PM_{10}

Station	Type	Station nr	Na measurement	Cl measurement
Vredepeel	Rural	131	X	X
Huijbergen	Rural	235		X
Breda	Traffic	240	X	X
Vlaardingen	Traffic	433	X	
De Zilk	Rural	444		X
Rotterdam	Traffic	448	X	X
Wieringerwerf	Rural	538	X	X
Cabauw	Rural	620	X	X
Bilthoven	Rural	627	X	X
Hellendoorn	Rural	807	X	X
Valthermond	Rural	929		X
Kollumerwaard	Rural	934	X	X
Schiedam (DCMR)	Urban	xxxx	X	X

As described in chapter 2 the sea salt concentration is estimated as:
sea salt= 3.26* Na. Therefore only the stations with Na measurements will be used. In Table 4.1 stations with a blue X mark a short series (< 100 samples). These samples originated from the BOP programme only (Manders et al., 2009). The other 6 stations have time series for more than 3 years and will be used in the assessment is this study.

4.2 Assessment of the annual limit value (40 µg/m^3)

In table 4.2 the estimated sea salt concentrations from measurements on a number of stations and the corresponding concentration of the current scheme are shown. The average concentrations are determined from all available measurement data (see columns 2 and 3 for the periods and the number of available data).

Table 4.2 Average sea salt concentration at measured locations and the sea salt concentration of the current regulation

Station	Measurement Period	N_data	Average sea salt measured $\mu g/m^3$	Sea salt conc. current scheme $\mu g/m^3$	Average sea salt/ current scheme
Vredepeel (131)	Aug07 - Dec10	528	1.9	3.0	0.62
Vlaardingen (433)	Jan08 - Dec10	533	3.2	5.9	0.55
Wieringerwerf (538)	Jan08 - Dec10	544	2.8	6.3	0.44
Bilthoven (627)	Jan08 - Dec10	539	2.3	4.3	0.54
Hellendoorn (807)	Feb08 - Dec10	451	1.6	3.4	0.48
Kollumerwaard (934)	Jan08 - Dec10	526	2.5	6.0	0.42
Average (6 stations)					0.51

As expected the highest sea salt concentrations have been measured on a station along the coast (Vlaardingen). On stations on the eastern border (Hellendoorn, Vredepeel) sea salt contribution is lower. The concentrations are also compared to the levels in the current scheme (regulation). For all locations the measured sea salt concentrations are lower than the sea salt concentrations in the current regulation. The same conclusions have also been found in a study conducted in the framework of the BOP project (Manders et al., 2009). On the whole data set the average measured sea salt concentration is nearly a factor of 2 lower than the current scheme.

In practice, the adjustment of the sea salt annual limit value will not have much consequences for the exceedances of the annual limit values since these exceedances have been rare for last few years . Even without correction in 2009 the annual limit value of PM_{10} has not been exceeded at any measuring station of the LML (Mooibroek et al.,2010).

Figure 4.1 Locations of the six continuous sodium measurement stations in the Netherlands.

4.2.1 *Determination of the influence on the number of exceedance days due to sea salt*

In principle, the number of exceedance days to be subtracted can be determined directly from the experimental data. In this *direct approach*, we need to determine the number of exceedance days (i.e. the number of days with PM_{10} concentration higher than 50 $\mu g/m^3$) and the amount of sea salt; then the amount of sea salt is subtracted from the PM_{10} concentration and the number of exceedance days is determined again. The difference is the number of days to be subtracted at that location. Because exceedances only occur occasionally, a very long measurement period is needed. Moreover, daily concentrations at many points are necessary. This direct approach however will be used as validation of the statistical approach (introduced below) in section 4.5.

To reduce the random uncertainties an alternative *statistical approach* is developed whereby the number of eliminated exceedance days is calculated in two steps.
In step 1, for each measurement station, we determine the sea salt contribution at a daily average PM_{10} concentration of 50 $\mu g/m^3$.
In step 2, the impact of the sea salt on the number of exceedance days is calculated. The latter uses the statistical relationship between the PM_{10} concentration, expressed as an annual average, and the number of days exceeding 50 $\mu g/m^3$ as shown in Figure 4.2. The form of the relationship is relatively generally applicable as demonstrated in a study on the majority of European countries (Wesseling et al., 2010). This relationship has a long tradition of application in the Netherlands since it has been used both in the calculation of background concentrations (Velders et al., 2010) and in the calculation of local concentrations in streets (Infomil, 2010).

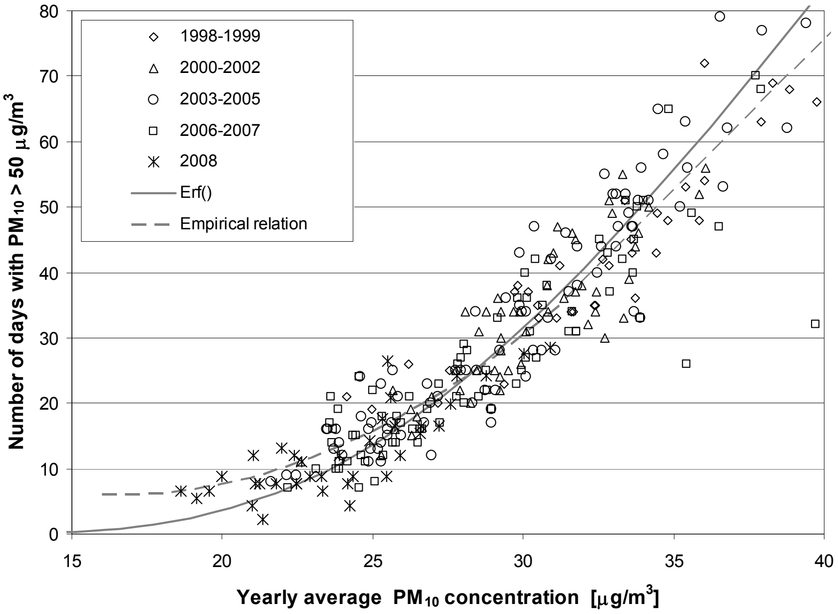


Figure 4.2 Number of exceedance days as a function of yearly average concentration of PM_{10}: data of LML stations in 2009 and the statistical relationship (Wesseling, 2010).

According to this relation, 35 exceedances of the daily limit of 50 µg/m^3 occur when the annual average concentration of PM_{10} is approximately 31 µg/m^3. Suppose the sea salt contribution on days with PM_{10}=50 µg/m^3 is 2 µg/m^3 (determined in step 1), the assumed daily limit for that station should be 52 µg/m^3. With this assumed daily limit, only 30 exceedances of the daily limit will occur when the annual average concentration of PM_{10} is 31 µg/m^3. The difference (5 days) is the number of exceedance days to be subtracted at that location.

This approach is demonstrated in Figure 4.3. In section 4.3 the results of this approach is shown.

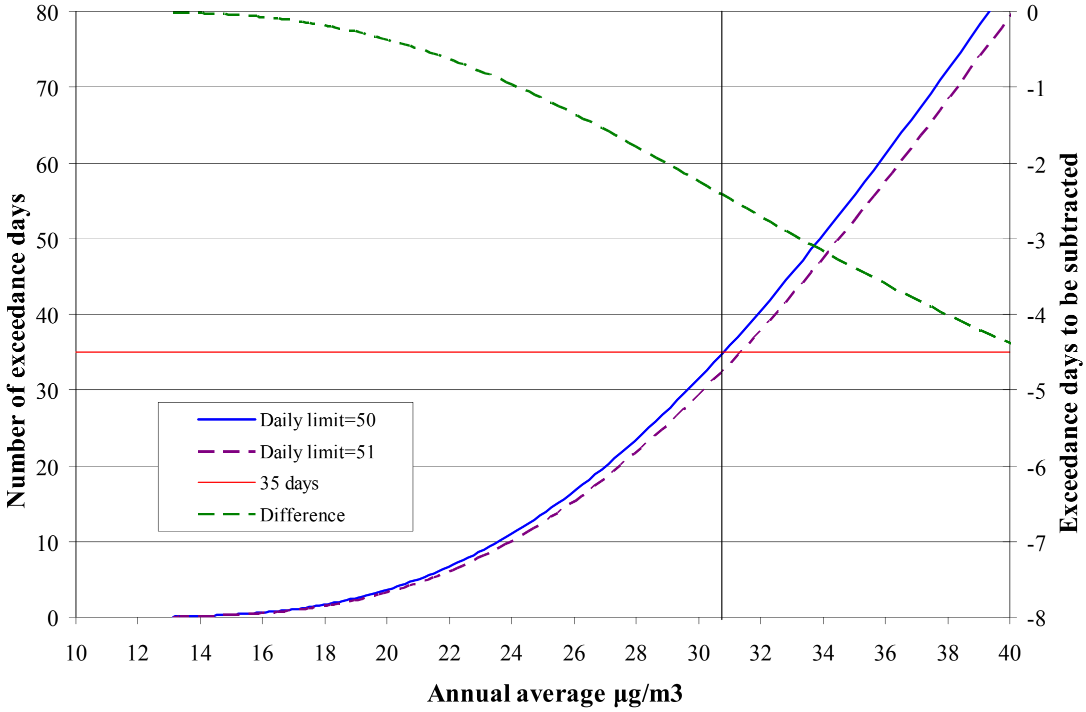


Figure 4.3 Relation between the number of exceedance days as a function of the yearly average PM_{10} concentration (blue line).

With, for example, a sea salt contribution of 1 µg/m^3, exceedances occur at PM_{10} > 51 µg/m^3 (purple line). The difference between both lines is the effect on the number of exceedance days (green line on right axis). For this location the new adjustment at the limit of 35 days/year is well over 2 days resulting in a sea salt corrected limit value of 37 days/year.

4.3 Result: Influence on daily limit value (50 µg/m^3) and exceedances

As described in section 4.1, the first step to determine the number of exceedance days to be subtracted for sea salt is the estimation of sea salt contribution at PM_{10}=50 µg/m^3. Figure 4.4 shows all measured sea salt concentrations at a site near the coast (Vlaardingen) and an inland site (Vredepeel). In both plots a log-normal distribution is fitted to the data.

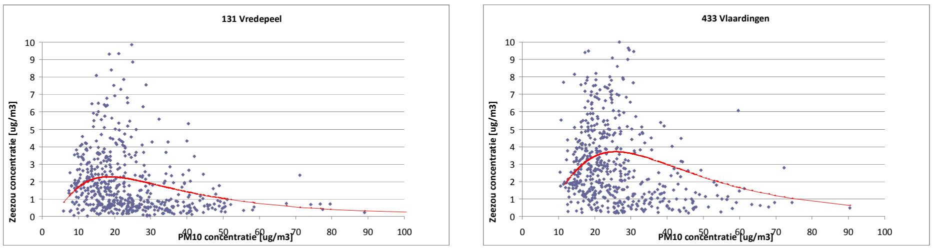


Figure 4.4 Sea salt concentration versus PM_{10} concentration for the measurement location at Vredepeel (left) and Vlaardingen (right). The fitted lognormal distribution is shown. At PM_{10}=50 the estimated concentration from the curve is 1 respectively 2.2 µg/m^3.

Figure 4.4 shows the difference in sea salt concentrations both for the bulk of the data and for the sea salt concentration on days with high PM_{10} concentrations. The plots also illustrate the considerable scatter around the curves. This influences the accuracy of the typical sea salt determination at PM_{10}

concentrations near 50 µg/m^3. To estimate the effect of the scatter 4 types of curves were fitted:

1) the lognormal distribution as shown (M1);
2) the lognormal distribution with a tenfold weight on $45 < PM_{10} < 65$ (M2);
3) the ax/(b+x)^3 distribution (M3);
4) the ax/(b+x)^3 distribution with a tenfold weight on $45 < PM_{10} < 65$ (M4).

The result is summarised in Table 4.3

*Table 4.3 Average sea salt concentration at PM_{10}=50 µg/m^3. The concentration estimated in this study by different methods (M1-M4). The sea salt concentration is estimated as 3.26*Na.*

Measurement station	N data pairs	Sea salt at PM_{10}=50 µg/m^3			
		M1	M2	M3	M4
Vredepeel (LML 131)	524	0.99	0.75	1.08	0.90
Vlaardingen (LML 433)	529	2.24	1.75	2.50	1.79
Wieringerwerf (LML 538)	538	1.50	1.28	1.75	1.39
Bilthoven (LML 627)	411	1.46	1.37	1.40	1.26
Hellendoorn (LML 807)	450	0.71	0.63	0.75	0.69
Kollumerwaard (LML 934)	523	1.82	1.28	1.68	1.36

Table 4.3 shows that, at an individual station, the estimated sea salt concentrations on days with PM_{10}=50 µg/m^3 can vary considerably, depending on the method of estimation. The results of M2 and M4 are more influenced by the few data points between 45 and 65 µg/m^3 but the probability for a systematic deviation due to the selection of the particular distribution is less. Methods M1 and M3 are less influenced by a few points but more dependent on the distribution. The correct curve is unknown, therefore the average of the four curves is used for further analysis. The difference between the curves is used in the overall uncertainty calculation.

5 Modelling sea salt over the Netherlands

To provide a background map that could be used to interpolate the annual mean concentrations as well as the sea salt concentrations at PM_{10} around 50 µg/m^3, we started with the BOP results from Manders et al. (2009). The authors ran the LOTOS-EUROS model v1.3 for a 7 year period (2000-2006) over Europe and a zoom domain over the Netherlands. Some results of these simulations are shown in chapter 2. The same model version has also been used to forecast PM_{10} levels over the Netherlands at an operational basis. Evaluation of these forecasts and the simulations above, however, showed that during storm conditions the sea salt contribution to PM_{10} was largely overestimated. Moreover, the land use data base of LOTOS-EUROS caused an effective emission strength from the IJsselmeer and Waddenzee. These shortcomings were improved within the EU-FP7 PASODOBLE project. Still, there is a large (systematic) uncertainty in the sea salt emissions as well as the dry deposition velocity, and modelled sea salt distributions normally show a systematic bias up to factor 2-3 (Manders et al., 2010). We have therefore designed a set of sensitivity simulations directed at the deposition rate at sea as well as those above land to select the model settings that give the best performance against the new observations. This approach is relatively pragmatic and allows model settings within the current range of the uncertainty of the model parameters. The selected model code is then used to evaluate the annual average concentration as well as the mass contribution at days with PM_{10} loads around the daily limit value.

5.1 Sensitivity simulations for the year 2009

Here, we describe the sensitivity simulations performed to illustrate the uncertainty in the modelled absolute concentrations as function of the deposition scheme and to select the best combination of settings for the definitive simulation. The simulations were aimed at:

1. Changing the deposition routine that describes the laminar layer resistance of the particles. To this end the IDEM-DEPAC routine (Erisman et al., 1994) was replaced by the scheme from Zhang (Zhang et al., 2001) assuming a diameter of 4 µm for coarse sea salt particles and 0.7 µm for fine sea salt particles. In addition, the model experiment with a diameter of 8 µm for coarse sea salt particles (Zhang8) was ran as this yields about the deposition velocity that is half way the Zhang and IDEM-DEPAC schemes.
2. Adding the dependency of the sea surface roughness to the wave height. Over grid cells with more than 90% water the wave height is calculated as function of ten metre wind speed:
    i. wave height = 0.0617 * u10 ** 1.52

   This function is a fit applicable for open water conditions The associated surface roughness is calculated as
    ii. z0 = wave height/30.

   Alternatively, a factor 300 was used in the latter calculation.
3. Assessing the combined impact.

In total, five simulations were performed for the full year of 2009 (see Table 5.1). The simulations were performed at the European domain as well as on the zoom domain for the Netherlands.

Table 5.1 Settings of the five sensitivity simulations

Base run	**settings**
base	IDEM_DEPAC z0 = constant
Experiment 1:	
Zhang	Zhang d = 4 μm
Zhang8	Zhang d = 8 μm
Experiment 2:	
z0	Zhang d = 4 μm z0 = h/300
z0b	Zhang d = 4 μm z0 = h/30 (z0b)
Experiment 3:	
Zhang8 + z0b	Zhang d = 8 μm z0 = h/30 (z0b)

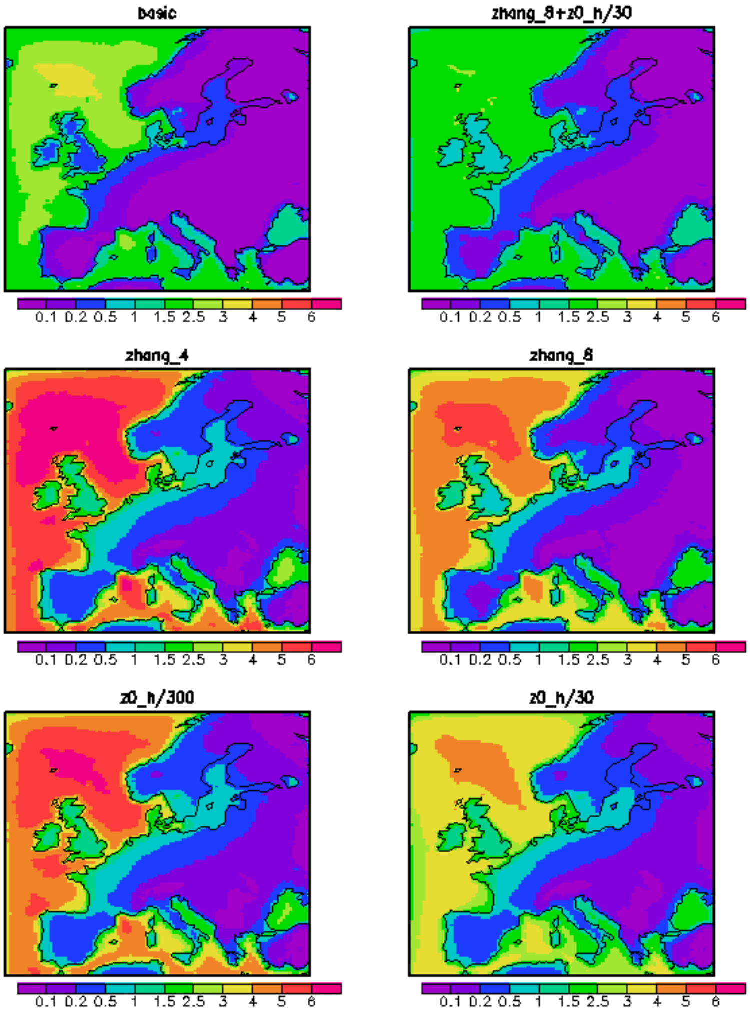


Figure 5.1 Annual average results for the set of simulations studies for Europe

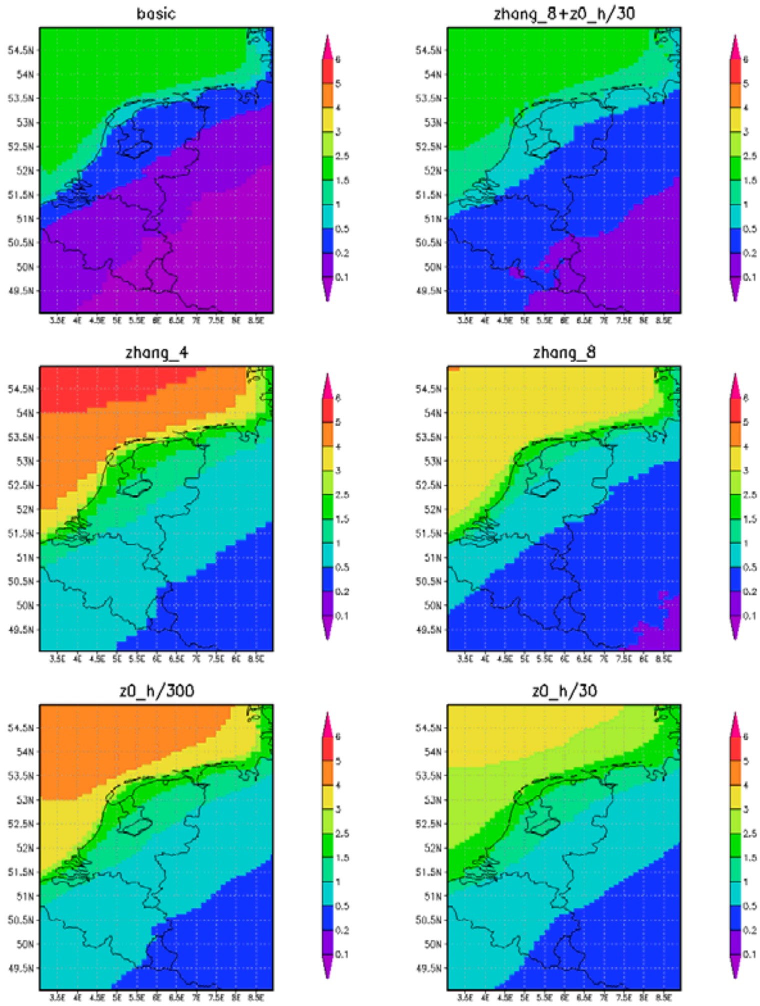


Figure 5.2 Annual average results for the set of simulations studies for the Netherlands

Model results and comparison with measurements

The replacement of the dry deposition scheme by that of Zhang (Zhang et al., 2001) yields considerably lower dry deposition rates for particles and modelled sodium concentrations increase by about a factor 3. Including a mass mean diameter of 8 µm yields a difference of a factor 2, illustrating the large model uncertainty concerning dry deposition. The choice of 8 µm reflects a fresh sea salt aerosol whereas a choice of 4 µm is much more an aged aerosol that has been subject to transport. The inclusion of the ocean surface roughness dependency on wind speed and wave height yields a lower atmospheric stability. High wind speed conditions cause high sea salt emissions, but also higher deposition rates due to the increased roughness. On average, including the wave height/30 option yields a decrease in the modelled sodium concentrations of about 30-40%.

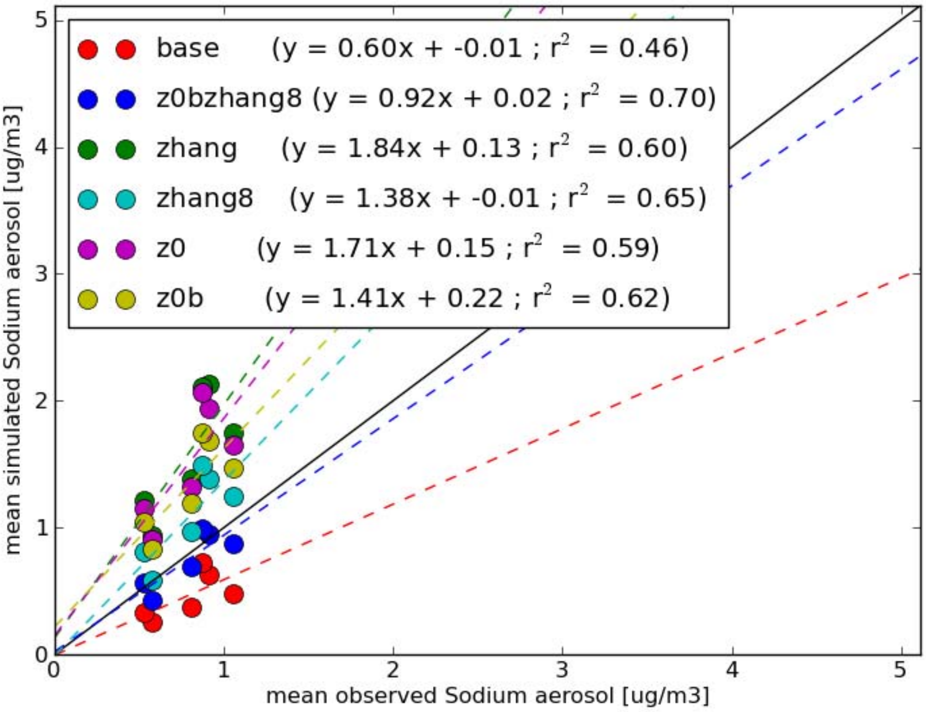


Figure 5.3 Scatter plot of the measured annual average sodium aerosol concentration versus the modelled annual average sodium aerosol concentration for six measuring stations in the Netherlands and for six model runs (represented by the different colours).

In Figure 5.3 the comparison of the different model runs with the measured sodium concentrations in 2009 (paired comparison) is shown. The different simulations show largely different mean concentrations. However, it must be noted that all give a similar gradient over the Netherlands. It is concluded that the sensitivity run with the Zhang deposition scheme with a representative particle diameter of 8 µm for coarse particles and a roughness length for the sea of wave height/30, gives best results. Not only the slope is close to 1 and the offset is nearly 0, but also the correlation coefficient R^2 is largest.

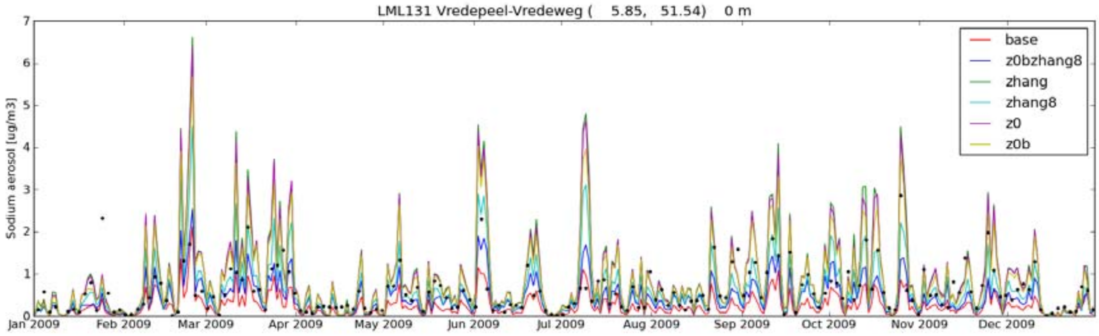


Figure 5.4 Time series of the measured (black dots) and modelled (different colours) sodium concentration for one station in the LML for the year 2009.

The time series from which the individual annual mean values Figure 5.4 were calculated, are shown in Figure 5.4. The time series show that especially the Zhang, z0, z0b and Zhang8 runs (i.e. the individual sensitivity tests) give extremely high peak values. A combination of the z0b and the Zhang8 test, however, produces much more realistic peak values for the sodium concentrations. Hence, also the day to day variability is captured best by this option. Finally, the fine-coarse ratio of this option is lower than in the base run and in better agreement with the observed ratio in BOP (Manders et al., 2010).

5.2 Modeling of the anthropogenic contribution to sodium concentrations

To assess the contribution of anthropogenic activities to the modelled sea salt distribution a simulation using the anthropogenic emission database was performed. In Figure 5.5 we compare the contributions in terms of sodium concentrations for the annual mean. The contribution of anthropogenic sodium over the Netherlands is small and below 0.1 μg/m^3, which corresponds to a few percent, i.e. 1-6%, of the total modelled sodium. Only over Limburg the contribution is slightly higher. This means that for the annual mean the anthropogenic contribution is negligible.

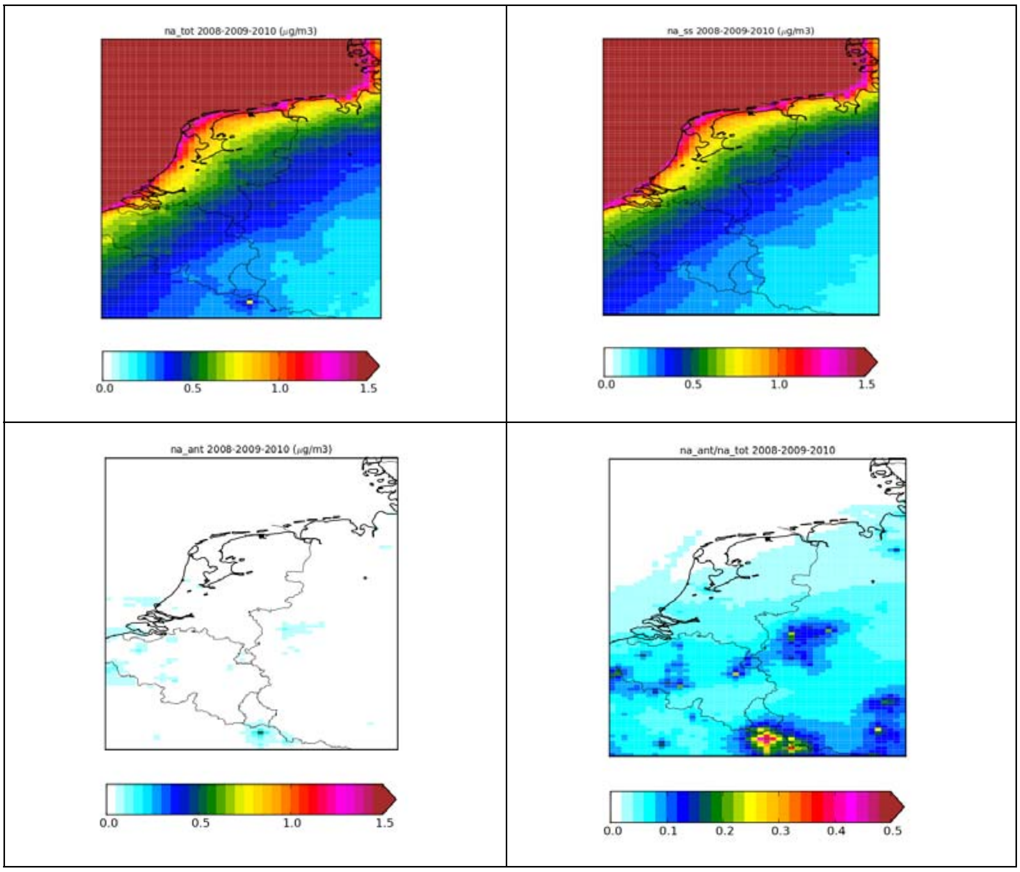


Figure 5.5 Annual mean concentration (μg/m^3) of total sodium (upper left), sea salt sodium (upper right) and anthropogenic sodium (lower left). In addition, the fractional contribution of anthropogenic sodium (lower right) is given.

The same simulations also enable us to investigate the anthropogenic contribution at high PM_{10} concentrations. As the sea salt concentrations are low under these conditions and the atmospheric conditions favor a buildup of anthropogenic pollutants, a higher contribution than in the annual average is expected. In Figure 5.6 is shown that the contribution of anthropogenic sources becomes visible in the total sodium distribution in the areas where the main sources of anthropogenic sodium are located, e.g. Ruhr area, southern Limburg and the coastal regions of the Netherlands and Belgium. Lowest contributions are found in Groningen, Friesland and Drenthe with about 12%. Contributions around and above 20% are found over the southern half of the country. Hence, the contribution of anthropogenic sources on days of high PM_{10} concentrations is not negligible. Note, that the anthropogenic contribution appears to be even more relevant for Belgium and the Ruhr area.

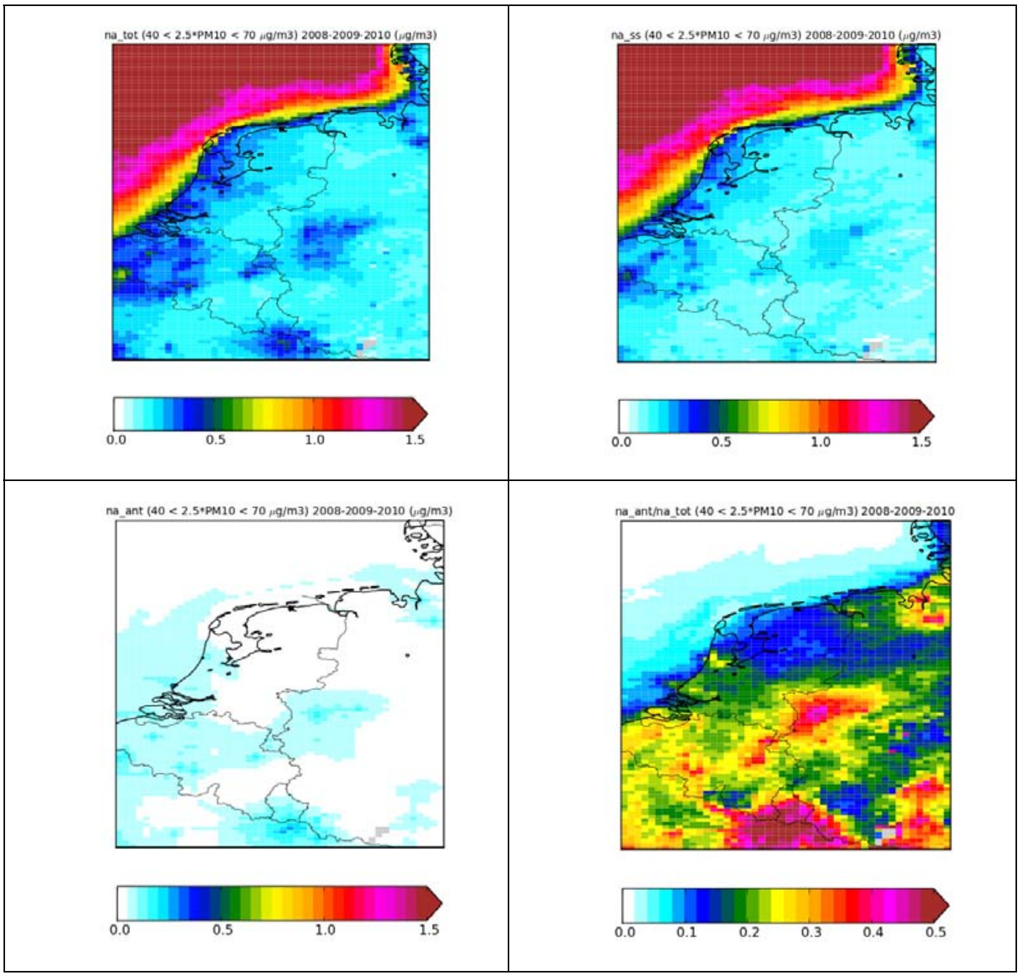


Figure 5.6 Concentration (μg/m^3) of total sodium (upper left), sea salt sodium (upper right) and anthropogenic sodium (lower left) at PM_{10} ~ 50 μg/m^3. In addition, the fractional contribution of anthropogenic sodium (lower right) is given.

Conclusion

In short, accepted modeling schemes of sea salt depend on the values of several parameters. The sensitivity of the resulting sea salt concentrations, within the physical acceptable parameter settings, were checked. The dry deposition in the base case appears to be too fast over land, whereas the deposition above sea may have been to low due to the neglected dependency of surface roughness with wind speed. The combination of the z0b and the Zhang8 schemes was selected for further use to pragmatically overcome the issues concerning the systematic biases in the model for the annual mean distribution.

The modelled anthropogenic concentration is on a yearly average basis negligible for the Netherlands. On PM_{10} exceeding days a correction (10-20%) is necessary.

6 Model calibration and validation

6.1 Annual average sea salt concentration

The previous chapter describes the selection of parameter settings based on the model and measurement results of 2009. Applying this set of parameters the three years 2008, 2009 and 2010 were calculated. Figure 6.1 shows the correlation with the average of the 2008-2010 measurements and the distribution over the Netherlands. As expected, the systematic deviation between measurement en model is negligible therefore no further calibration of the model results is applied.

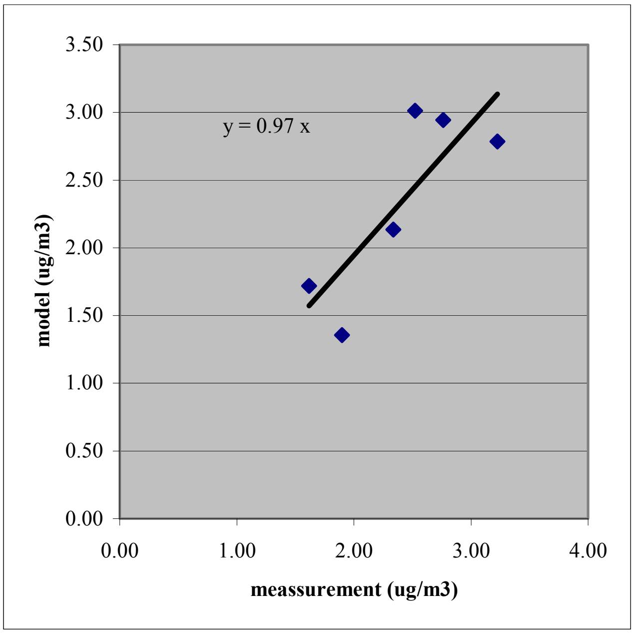


Figure 6.1 Comparison between the averaged measured (2008-2010) and modelled sea salt concentration on six locations in the Netherlands.

Figure 6.2 shows the modelled average sea salt concentrations for the period 2008-2010 for the Netherlands and some surrounding territory. The picture shows a clear gradient form the coast (6 μg/m^3) to the south eastern part of the country (1 μg/m^3).

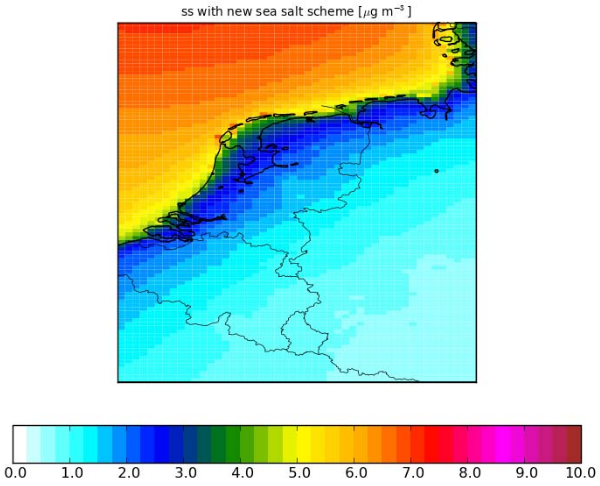


Figure 6.2 Modelled average sea salt concentration for the period 2008-2010.

To translate the spatial gradient in the sea salt concentrations the results from Figure 6.2 are geographically averaged over the municipalities. These municipality data enables the implementation in the Dutch air quality regulation. The result is shown in Figure 6.3.

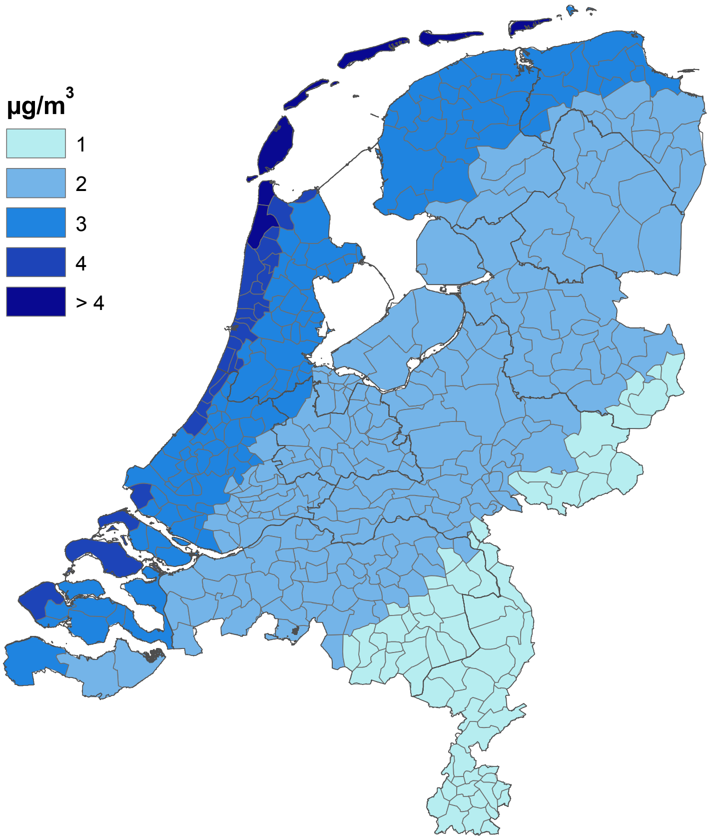


Figure 6.3 Modelled average sea salt concentration for the period 2008-2010. The results are geographically averaged for each municipality.

6.2 PM$_{10}$

To estimate sea salt levels on PM$_{10}$ exceedance days the model should generate unbiased PM$_{10}$ concentrations. Figure 6.1 shows that the average sea salt part of PM$_{10}$ now is correctly modelled; still the total amount of PM$_{10}$ is too low (as it is for most air quality models). This bias is resolved by calibration of the model results to the measurements by multiplying all other components (except sea salt) by a factor of 2.5.

6.3 Sea salt on exceedance days

The average sea salt concentration on relevant exceedance days is calculated for all grid cells for the period 2008-2010. In this calculation all days with $40<PM_{10}<70$ are included. The grid is shown in Figure 6.4. The average number of calculated days in the period 2008-2010 is above 40 for the largest part of the Netherlands. However, in the cleaner parts of the country in the north the number is slightly lower. The same applies to the clean areas outside the Netherlands such as the Eiffel and Ardennes. Modelled concentrations of sea salt at PM$_{10}$ ~ 50 range from 1 µg/m^3 at the coast to 0.4 in Limburg. Highest concentrations occur in those areas with the highest average PM$_{10}$ concentrations. These areas have more exceedances and more often include significant marine contributions. In the cleaner areas the exceedances are less frequent and more selective for continental air masses. As a result the model produces higher sea salt contributions on exceedance days in areas like the Randstad (Amsterdam, Rotterdam) as well as the city areas in Belgium and the Ruhr area. The behaviour reflects the theoretical basis outlined in chapter 4. The result is compared to the sea salt concentration at high PM$_{10}$ values from the measurements.

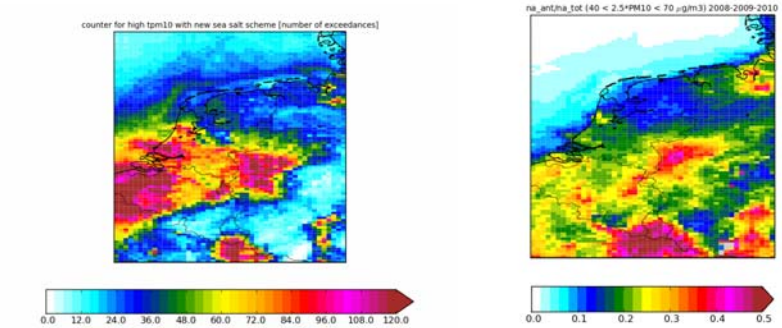


Figure 6.4 On the left the number of days with modelled PM$_{10}$ concentrations exceeding 50 µg/m^3 for the three year period 2008-2010. On the right the amount of sodium from other sources relative to the sea.

In this comparison we also evaluated the estimated sodium from sources other than sea salt for the period 2008-2010 on exceedance days. The result from this calculation is expressed relative to the total amount of sodium, which is also shown in Figure 6.4. The fraction of other sodium is reasonably small for the Netherlands (< 20%) however we considered this portion as too large to neglect. Therefore the measurement results were corrected for the calculated amount of anthropogenic sodium.

After this correction the amount of sea salt on exceedance days is still underestimated by a factor of 1.6. The bias can be explained by the settings chosen to optimise the annual mean distribution. During transport the sea salt mean size reduces as larger particles deposit faster. This is only partly incorporated in the model through the fine and coarse fraction. However, the shift within the coarse fraction is not. As sea salt concentrations are low during high PM_{10} episodes that are associated with continental air masses, the marine component is already quite old. Hence, the sensitivity to the deposition efficiency is quite large in the low sea salt range. A scaling by a factor 1.6 was applied to overcome this systematic difference. The resulting distribution is shown in Figure 6.5.

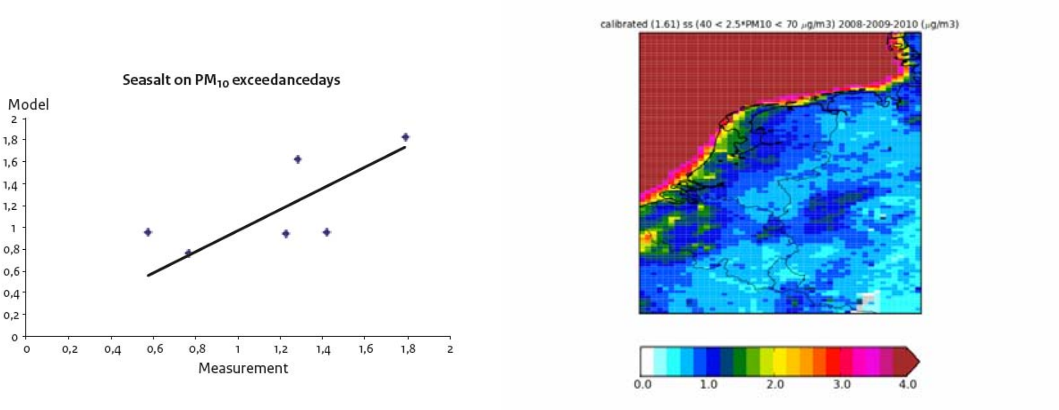


Figure 6.5 Average sea salt concentration for days with high PM_{10} concentrations for the period 2008-2010 (right) The left panel shows the relation between the calibrated model calculation and the corrected measurement results.

Compared to the average sea salt map there appears to be more local variation (islands with higher sea salt on exceedance days. This fine structure can partly be due to statistical noise. To reduce the effect of this noise the averaging of the results over larger area's (provinces) was applied. For the twelve Dutch provinces the number of exceedance days that can be eliminated summarises as:

- 4 days: Noord-Holland and Zuid-Holland;
- 3 days:, Friesland, Flevoland, Utrecht and Zeeland;
- 2 days: Groningen, Drenthe, Overijssel, Gelderland, Noord-Brabant and Limburg.

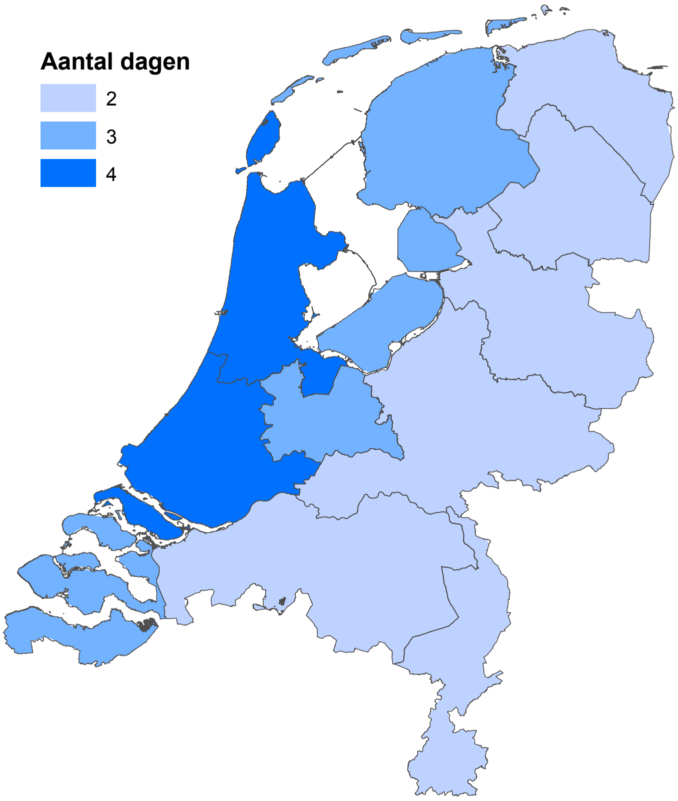


Figure 6.6 Number of exceedance days that can be excluded due to the contribution of sea salt. The number of days is geographically averaged for each province.

6.4 Uncertainty in the estimation of sea salt contribution

In this chapter the uncertainty of the several sea salt concentration estimates are discussed. Also the effect of the length of measurement period on the uncertainty is determined.

6.4.1 Contributions to the uncertainty in the estimates in this study

In this study both the average sea salt concentrations and the number of the sea salt induced exceedance days are estimated. For the yearly averaged sea salt concentration two contributions are identified:

i. systematic uncertainty in the chemical analysis of Na;
ii. variation in the ratio between modelled concentrations and the measurements for the various locations in the Netherlands.

Ad i) The systematic uncertainty, expressed as a relative standard deviation, in the analysis of Na is estimated as 5-10%.
Ad ii) The uncertainty in the calculated ratios is determined by the standard deviation between the stations. The average of all ratios is nearly 1 with a standard deviation of 0.13. Because 6 stations were used in the estimation, the relative standard error of the average ratio can be divided by the square root of 6 resulting in a relative standard error in the order of 6%.

Combining both uncertainties the standard uncertainty for the *annual average* is in the order of 8-12% and with a coverage factor of 2 (can be associated with 95% confidence interval) the expanded uncertainty is estimated as 20-25%.

For the number of days that can be eliminated due to the contribution of sea salt the following sources of uncertainty are addressed:

i. systematic uncertainty in the analysis of Na;
ii. variation in the ratio between modelled concentrations and the measurements for the various locations in the Netherlands;
iii. systematic uncertainty in the determination of PM_{10} concentration;
iv. uncertainty in the use of different distributions;
v. the uncertainty due to the curve of Figure 4.4;
vi. the uncertainty of the amount of anthropogenic sodium.

Ad i) The standard systematic uncertainty, expressed as a relative standard deviation, in the analysis of Na is estimated as 5-10%.
Ad ii) For each station the ratio between the measured and modelled sea salt concentration is calculated. As mentioned the average of these ratios is 1.6 and the standard deviation equals 0.4. The uncertainty in the calculated average ratio is then estimated as 10%.
Ad iii) The systematic uncertainty in the determination of PM_{10} is 8%. Figure 4.2 shows that this uncertainty results in an uncertainty of 10% in the Na estimate.[1]
Ad iv) The uncertainty due to the lack of knowledge on the shape of the relation between sea salt and PM_{10}. This standard uncertainty is estimated as 10%.
Ad v) The standard uncertainty due to the use of the relation in Figure 4.4 (average PM_{10} vs exceedance days) is estimated as 10%.
Ad vi) The standard uncertainty of the amount of anthropogenic sodium is estimated as 50% of its value which is only a small part (10-20%) of the measured value.

Combining all 6 uncertainties the standard uncertainty for the *number of days that can be eliminated* is in the order of 20-25% and with a coverage factor of 2 (can be associated with 95% confidence interval) the expanded uncertainty is estimated as 40-50%.

6.5 Effect of the length of measurement period

The yearly average sea salt concentrations for the 6 measurement stations are shown in Table 6.1. The standard deviation between the measured yearly averages is 8%.

Table 6.1 Yearly average sea salt concentrations (in µg/m^3) for the six measurement stations both by measurements and models.

Station	2008		2009		2010	
	Measurement	Model	Measurement	Model	Measurement	Model
131	2.10	1.42	1.87	1.38	1.72	1.27
433	2.99	2.95	3.45	2.83	3.24	2.58
538	2.38	3.10	2.97	3.05	2.94	2.69
807	1.54	1.76	1.71	1.79	1.60	1.60
934	2.04	3.00	2.83	3.05	2.70	2.99
627	2.10	2.23	2.64	2.23	2.27	1.94
	2.19	2.41	2.58	2.39	2.41	2.18

In Table 6.1 also the yearly averaged model values are shown. The standard deviation between the yearly averaged model values is 5%. Figure 6.7 shows the correlation between the measured and modelled averages.

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[1] Estimated as: $((Na(PM_{10}=46)- Na(PM_{10}=54))/(2*Na(PM_{10}=50)) = 10\%$.

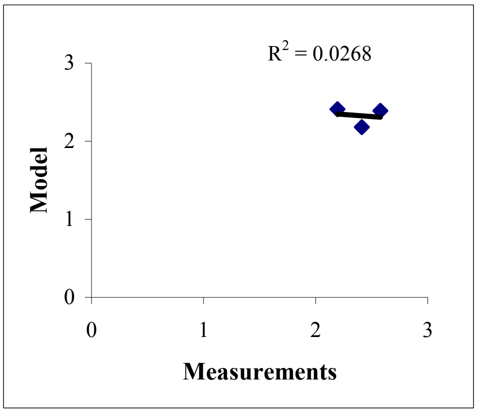

Figure 6.7 Yearly average sea salt concentration for the six measurement stations for each of the three years 2008, 2009 and 2010.

Conclusion
The variation in concentration in the three observed years is small in comparison with the various uncertainties. For these three years no correlation between the modelled and measured annual averages could be proven. Therefore the application of the yearly adjusted sea salt concentration presumably will not be more accurate the application of the multiple year average.

6.6 Comparing the new statistical approach to measurements (validation)

In order to compare the statistical method with the measurements the number of exceedance days has been determined by both methods. Per station the calculation is performed as follows:

- The yearly average PM_{10} concentration is determined for the dataset which has both PM_{10} and Na data.
- The number of exceedance days to be subtracted per year is determined by the statistical method (blue line in Figure 4.3). Then, taking into account the number of available data, the number of exceedance days at this station is calculated.
- Using the modelled sea salt concentration at PM_{10}=50 µg/m^3 (as used in the 'Gemeentekaart') the assumed limit value at this station is calculated (for example at Vredepeel the assumed limit value is 50.8 µg/m^3). Analogous to the above and using this assumed limit value, the number of exceedance days at this station after correction for sea salt is determined.
- This procedure has been applied for four datasets in 2007, 2008, 2009 and 2010. Then the total number of exceedances with and without sea salt correction over this period is determined.
- The difference is the number of exceedances due to sea salt according to the statistical method. This number has been compared to the measured number of exceedances due to sea salt which is determined by counting days with measured PM_{10} > 50 µg/m^3 and by counting days with PM_{10} > 50 µg/m^3 after subtraction of the measured sea salt concentration.

In Table 6.2 the results are shown.

Table 6.2 Number of exceedances over 2007-2010 before and after sea salt correction, determined by measurements and by the statistical method respectively.

Station nr.	Number of days with data (2007-2010)	Number of exceedances determined by measurements			Number of exceedances determined by the statistical scheme
		Before correction	After correction for measured sodium	Reduction due to measured sea salt	Reduction by statistical approach
131	524	17	14	3	1
433	529	21	20	1	4
538	538	13	13	0	1
627	411	12	10	2	1
807	450	13	12	1	1
934	523	10	8	2	1
total		86	77	9	8

Over this period the difference between these two methods is 1 day. Therefore we can conclude that, as far as can be determined, there is no indication that the statistical method either overestimates or underestimates the number of days to be subtracted. Please note that these measurement data are not corrected for the anthropogenic sodium contribution.

Table 6.2 shows a very limited number of exceedances at all measurement stations. Consequently the direct subtraction needs a very long measurement period.

6.7 Comparison with the guideline on the subtraction on natural contribution

The Guideline on the subtraction on natural contributions (SEC, 2011) describes several chemical definitions to estimate the amount of sea salt in PM_{10}. As described in section 2.5 the definition based on sodium has been selected both for simplicity and the consistency with the definition in the current Dutch regulation. The guideline gives a clear warning against the use of the annual average sea salt contribution in the estimation of the effect on exceedance days due to observed negative correlations between PM_{10} and sea salt concentrations. Our measurement results confirm these negative correlations. Because of these negative correlations the Guideline recommends the use of individual pairs of PM_{10} and sea salt concentrations to determine the best estimate for the subtraction. Section 6.6 shows that even for the quite substantial Dutch data set the statistical power of this approach is very limited. Therefore a representative sea salt concentration for days with high PM levels is used. This approach solves the problem of the negative correlation with improved statistical uncertainty. Despite the statistical uncertainties section 6.6 shows that for the current data set the results of both approaches are practically identical.

7 Conclusions and recommendations

The concentrations sodium in PM_{10} show that the sea salt estimates which support the current Dutch sea salt regulation are too high. Therefore a new assessment of the sea salt concentrations is made. The result shows a gradient in sea salt concentration over the Netherlands both for the yearly average sea salt concentration as for the amount of sea salt on exceedance days.

- The yearly averaged sea salt concentrations range from 5 $\mu g/m^3$ at some coastal municipalities to 1 $\mu g/m^3$ in Limburg.
- The number of exceedance days that can be discarded at compliance testing is recommended to range from 4 days for the Noord- and Zuid-Holland provinces to 2 days for the provinces further from the coast.
- The uncertainty in these recommendations is estimated as 25-30% for the yearly average contribution and 40-50% for the number of exceedance days.
- Especially the effect of the number of exceedance days is critically dependent on sufficient length of the measurement series. Therefore continuation of sodium concentration measurements and the national air quality network is recommended. These results can be used to evaluate the recommendations in this study.
- This assessment meets the proposals of the International EU-Guideline for ‘natural contributions’ [SEC, 2011]. This study will be sent to the FAIRMODE working group that maintains the guidance document on ‘natural contributions’.

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Annex 1 Determination of the contribution of road salt

Using a regression model
In building a regression model we want to study the presence of an additional contribution of road salt. We can assume that an additional contribution of road salt becomes visible
- if the minimum daily temperature is below zero; and
- in the urban area around main roads where a large amount of road salt is applied.

In order to distinguish this effect from the overall impact of the temperature itself, an additional term for temperature is added. In combination with the observed anti-correlation between PM_{10} and sea salt, the regression model then reads as follows:

$$SS_{ij} = C_i + \alpha \ln(PM_{ij}) + \beta\theta(T\min_j < 0) + \gamma\theta(T\min_j < 0)\theta(urban)$$

with:
SS_{ij} :sea salt concentration on location i en day j
PM_{ij} :PM_{10} concentration on location i en day j
$T\min_j$: minimum temperature on day j
$\theta(x)$: =1 if x is true and =0 if x is false
α,β,γ: regression coefficient

The coefficients in the above model are determined by minimizing the sum of squared differences between the modelled and measured sea salt concentrations. The results are the following values:
α = -0.6±0.2; β = -0.8±0.3; and γ = 0±0.5, with the following interpretation:

- The value of α shows for the total data set a clear anti-correlation between sea salt and total PM_{10} concentrations.
- The value of β shows that the measured sea salt concentrations at low minimum temperatures are lower than at higher temperatures. This clearly contradicts with expectation.
- The value γ shows that there is no indication that the sea salt concentrations in the city, at low temperatures, are higher than in the region. In conclusion, there is, on the basis of those results, no indication that the interpretation of the data is affected by the presence of road salt.

By determination of the Mg/Na ratios
The Mg/Na ratio at various LML stations on days with minimum temperature below zero and on other days are plotted below. The stations at Breda, Rotterdam and Vlaardingen are street stations, the station at Schiedam is an urban background station and the other are rural stations. The Figure 6.7 below shows that the effect of minimum temperature on the Mg/Na ratio is negligible (except at Schiedam). Because Schiedam has only 11 data at Tmin<0, this observation is less representative than most of the other stations which have a much more data.

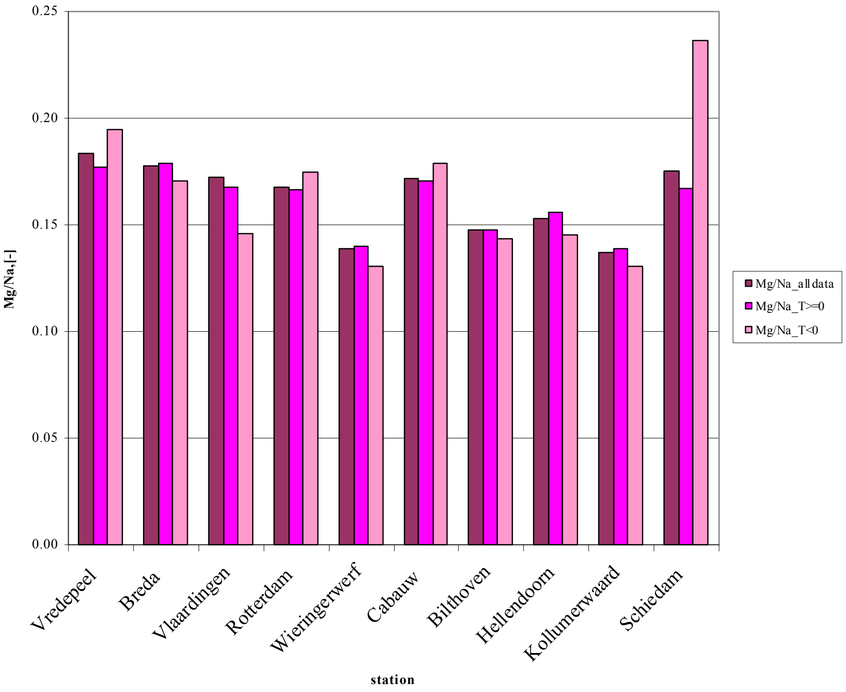

Figure Annex 1: Mg/Na ratio at various LML stations on days with minimum temperature below zero and on other days

Conclusion

The statistical evaluation shows no indication of an interfering contribution of road salt in urban locations. Also the ratio between sodium and magnesium shows no indication of a road salt interference.

**R. Hoogerbrugge | P.L. Nguyen | J. Wesseling |M. Schaap |
R.J. Wichink Kruit | V. Kamphuis | A.A.M. Manders |
E.P. Weijers**

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