MODELLING THE IMPACT OF SEA-SALT PARTICLES ON THE EXCEEDANCES OF DAILY PM$_{10}$ AIR QUALITY STANDARDS IN THE NETHERLANDS

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INTRODUCTION

The European Commission (EC) has set standards for PM: yearly average values should not be higher than 40 µg/m^3 and daily average concentrations should not be higher 50 µg/m^3 with an allowed 35 exceedances per year. Despite the fact that there have been significant improvements in air quality during the past ten years, many EU members still violate the directives and exceed the standards. The EC thematic strategy on air pollution (*COM(2005) 446, Brussels, 21.9.2005*) provides a possibility to discount natural sources from air pollution levels for compliance purposes if determined with sufficient certainty. In a coastal country as the Netherlands sea-salt makes up a significant part of total PM$_{10}$ in ambient air and even more so in terms of human exposure if one considers that major cities are situated relatively close to the North Sea.

The contribution of sea-salt may be estimated on the basis of tracer elements such as sodium or chlorine but usually there is insufficient spatial coverage to produce reliable maps of sea-salt concentrations. An alternative approach is to simulate the production of aerosols at the sea surface together with the subsequent transport of the particles to the land, both as a function of meteorological parameters. This paper describes such a simulation approach in which measurements are used to validate simulation results while the spatial distribution is determined by the model.

RELEVANT ATMOSPHERIC PROCESSES

Sea-salt generation depends on several parameters such as sea surface wind speed, temperature and salinity (*Blanchard, 1983*). Several semi-empirical formulations were derived as a result of laboratory simulations, field experiments and observations. In all those formulations the main parameter is the wind speed, usually the flux is a function of $U10^{\,p}$ where *U10* is the wind speed at 10m above the sea surface and *p* is 3-3.5.

Sea water originating particles consist mainly of sodium-chloride (NaCl) which is highly hygroscopic. During transport from sea to the land the size (and mass) of the particle may change dramatically depending on the relative humidity of the ambient air. In terms of dry deposition the properties of the aerosol change also resulting in a changing atmospheric lifetime. Furthermore, under increasing moisture conditions a part of the particles may exceed the upper size limit of measurement systems (or the human respiratory system). This moisture dependency should therefore taken into account.

Model description

The Operational Priority Substances short term model (OPS-ST) was taken as the modelling platform for local-scale simulations of sea-salt aerosols transport and deposition. It is derived from the OPS long term model (*van Jaarsveld, 2004*) and is used for modelling of dispersion and deposition of pollutants for the Netherlands on both local and national scale. The model can be described as a Lagrangian (trajectory) model which act as a Gaussian plume model for local situations. Dry and wet deposition mechanisms are included as function of particle size

with some emphasis to the behaviour of large particles. Dry and wet deposition is taken into account as a function of particle size and density of the particles. Dry deposition velocities are modelled on the basis of the models of *Slinn & Slinn* (1980) and *Williams* (1982). In order to take into account the different properties of the particles within the size spectrum the model uses up to 20 bins. In case of calculating wet deposition also very large particles (10 µm < Dp < 200 µm) can be dealt with. Furthermore, the effect of sedimentation on plume and transport height is taken into account.

The model is driven by a set of hourly meteorological parameters taken from the network of the Royal Netherlands Meteorological Institute (KNMI). For the present purpose also observations from platforms at the North Sea are included.

Sea-salt emission and transport in the OPS model
In the present work semi empirical formulations for the generation of sea-salt aerosol. All these formulations describe a density function F defined as the number of sea-salt particles generated during one second per unit sea surface area and per increment of particle size. Following Gong et al.(2002) and *Foltescu et al.* (2005) we use three intervals each with specific generation functions: *Mårtensson et al.*(2003) for Dp = 1 µm, *Monahan et al.* (1986) for 1 < Dp < 5 µm and *Smith and Harrison* (1998) for Dp = 5 µm, where Dp is the particle size. We use an empirical relationship of *Gerber* (1985) to describe the actual size of the sea-salt particle as a function of relative humidity. The sea-salt emission of the North Sea is taken into account in an area between -6° and 10° longitude and between 50° and 58° latitude using grids of 50, 5 and 1 km resolution. The 5 km resolution is used along the coast line while the 1 km is applied only in the neighbourhood of a coastal monitoring location. For the translation of sea-salt mass to CL$^-$ mass we use a factor 0.556 according to *Millero* (1996).

COMPARISON WITH OBSERVATIONS
There are no direct measurements of sea-salt concentrations available. Since sea-salt consists mainly of NaCl we can use Na or Cl measurements as an indicator for sea-salt. Although Na$^+$ would be preferable above Cl because it is less involved in chemical reactions in the atmosphere and comes from less other sources we use Cl aerosol measurements because of their availability. Cl is measured in the Netherlands at 7 locations using Low Volume Sampler (LVS) systems. Unfortunately the cut-off size of the LVS system is not exactly known. Based on enquiries we selected 4 um in a range of 2-6 µm and investigated the effect of other cut-off sizes in a limited sensitivity test. Depletion of chloride from the aerosol by uptake of HNO_3 and H_2SO_4 (Ten Brink, 1998) is simulated using a first order conversion rate.
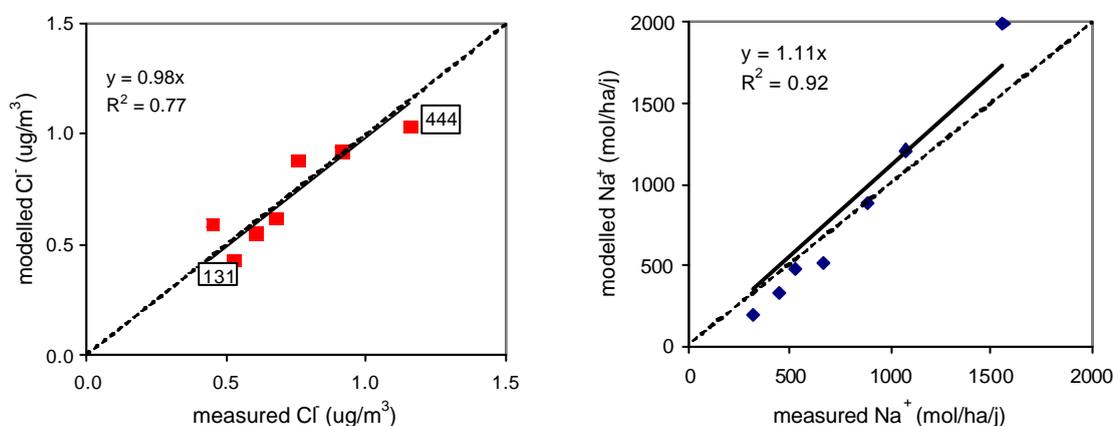

Fig. 1. Measured and modelled average concentrations and wet depositions over the period 2000-2004. Left: Cl$^-$ concentrations , Right: wet deposition of Na$^+$

Another indicator for levels of sea-salt in the atmosphere is wet deposition. Although wet deposition includes also the contribution of large particles, its spatial distribution and/or time behaviour is to a large extend representative for atmospheric concentrations of a PM_{10} subset as well. For the Netherlands there are 15 stations which measure wet deposition of Na^+ on a monthly basis.

In Figure 1 measured and modelled concentrations are compared showing the capability of the model to describe spatial differences. For this purpose a 5 year averaging is chosen. One can conclude that on this time scale 75 % of the spatial differences can be explained and in case of the wet deposition even more than 90%. A further conclusion is that the sets of modelled values are within 15 % of the measured values.

Comparison of model and measurements on the basis of time-series is carried out for two stations: De Zilk (code:444) which is a coastal station located 2.5 km from the shore line and Vredepeel (code:131) located in a rural area approx. 125 km from the North Sea coast in easterly direction (see also Figure 3). Daily variations in CL^- concentrations are explained for 50% typically for the coastal station and 24% typically for the land station with the lowest concentration. One reason for the inferior result at this station is that much more observations are below the detection limit.

The long term seasonal patterns of CL^- as measured and modelled for the 7 stations is given in Fig. 2. The overall agreement is good, however, for autumn the model under-predicts while for winter and early spring an over-prediction occurs. A possible explanation is the atmospheric stability above the sea water which depends on the sea-air temperature difference. This may influence both the efficiency of the particle generation mechanism and the vertical dispersion.
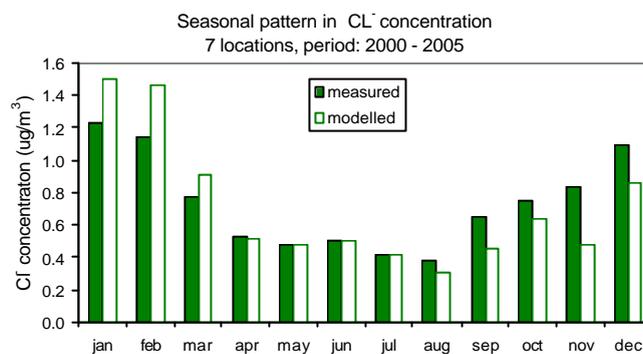

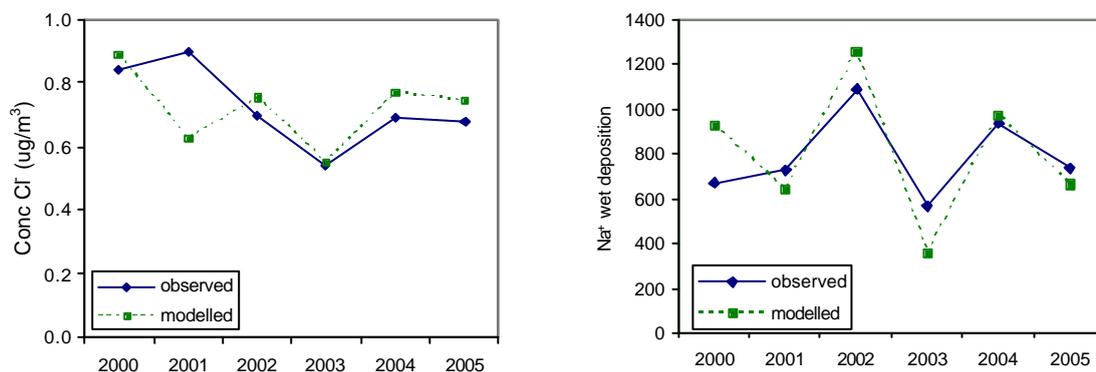*Fig 2. Average seasonal patterns in measured and modelled Cl^- concentrations*

Fig. 3. Trends in Cl^- concentration and Na^+ wet deposition. Values are averages of 7 stations

RESULTS AND DISCUSSION

In Table 1 measured PM_{10} levels are given and the number of exceedances of the 50 µg/m³ limit for daily mean PM_{10} concentrations. The calculated sea-salt contributions are in the order of 20 % of the measured PM_{10} values at the coastal station (De Zilk) and in the order of

10 % for the inland station. The influence of sea salt on the number of exceedances is examined by subtracting the modelled sea salt concentration from the measured PM_{10} concentration and see how many exceedances remain. The reduction is in the range of 0-5 days per year but typically less than 2 days. The influence of sea-salt on exceedance of the daily limit is much less than on the average concentrations. The reason is of course that daily peaks in sea-salt and PM_{10} concentrations are not or even negatively correlated. The spatial distribution of annual average sea-salt concentration (PM_{10} fraction) is shown in Figure 4. The east-west gradient is clearly visible.

Table 1. Modelled annual average sea-salt PM_{10} concentrations and the number of exceedance days due to the contribution of sea-salt aerosols

	Annual average			Number of exceedance days		
	PM_{10} ($\mu g/m^3$)	Sea-salt PM_{10} ($\mu g/m^3$)	Contribution to annual average	PM10	Due to sea-salt	Sea-salt contribution
	measured	modelled	%	measured	modelled	%
131- Vredepeel						
1999	31.6	2.35	7.4	34	1	2.9
2000	31.9	2.77	8.7	50	2	4.0
2001	32.5	2.00	6.1	39	1	2.6
2002	31.3	2.61	8.3	46	2	4.3
2003	40.9	1.84	4.5	98	4	4.1
2004	25.6	2.74	10.7	25	0	0.0
2005	24.8	2.69	10.8	16	0	0.0
average	**31.2**	**2.43**	**8.1**	**44**	**1.43**	**3.3**
444- De Zilk (coastal station)						
1999	27.2	5.21	19.2	20	3	15
2000	28.4	5.96	21.0	25	5	20
2001	26.3	4.83	18.4	19	0	0.0
2002	30.1	5.45	18.1	31	1	3.2
2003	33.8	4.19	12.4	58	4	6.9
2004	28.6	5.89	20.6	23	0	0.0
2005	25.1	5.53	22.0	11	0	0.0
average	**28.5**	**5.29**	**18.8**	**27**	**1.86**	**6.9**

A weakness of the current system is that the cut-off size of the Low Volume Sampler is not well known. The difference in calculated concentrations if we use a cut-off size of 3 µm instead of 4 µm is nearly 50 %! Another reference for the occurrence of sea-salt aerosols is the wet deposition of Na^+. The modelled wet deposition of Na^+ agrees very well with the measurements (see Figure 1 and 3). This supports the choice of the 4 µm cut-off limit for the LVS measurements. On the other hand one can argue that such a check is not decisive for the PM_{10} fraction since wet deposition of sea-salt is dominated by particles larger than 10 µm. A comparison of the current LVS method with a system using a specific PM_{10} inlet is therefore urgently needed.

CONCLUSIONS
Sea-salt contributes significantly to PM_{10} levels in the Netherlands. At a coastal location 2.5 km from the shoreline this contribution is 5.3 $\mu g/m^3$ at a mean PM_{10} concentration of 28.5 $\mu g/m^3$ (19%). At a station far from the sea the contribution is 2.4 $\mu g/m^3$ at a mean PM_{10} concentration of 31.2 $\mu g/m^3$ (8%). The contribution of sea-salt to PM_{10} concentration at days when the 50 $\mu g/m^3$ standard is exceeded is relatively low because of the different origins and

the fact that the generation of sea-salt is related to the occurrence of high wind speeds. Subtraction of sea-salt concentration from measured PM_{10} levels leads to a decrease of 0-5 exceedances of the 50 $\mu g/m^3$ daily standard in a year.

Measurements of chloride in aerosols have been used as a reference for modelled sea-salt concentrations. In general a good agreement, both in time and space, is obtained. Another reference for the occurrence of sea-salt aerosols is the wet deposition of Na^+ which is measured at 15 locations in the Netherlands. The modelled wet deposition of Na^+ agrees also very well with those measurements, although one can argue that such a check is not decisive for the PM_{10} fraction of sea-salt since wet deposition of sea-salt is dominated by particles larger than 10 μm. The largest uncertainty in the present calculations is probably formed by the ill-defined size characteristics of the LVS method.
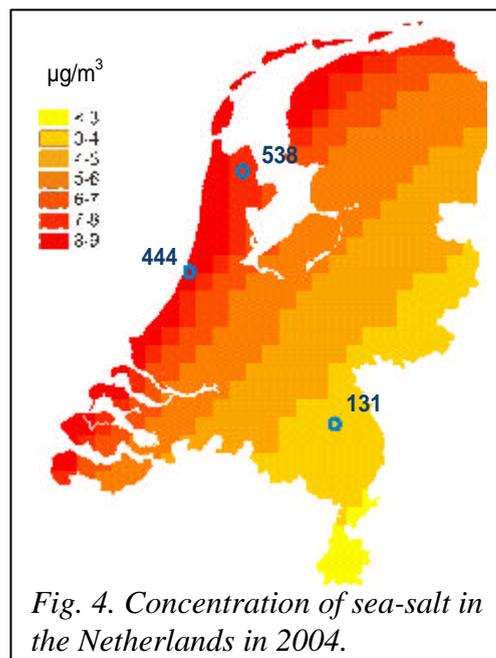

Fig. 4. Concentration of sea-salt in the Netherlands in 2004.

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