Atmospheric Environment 44 (2010) 2434–2442

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Sea salt concentrations across the European continent

A.M.M. Manders [a,*], M. Schaap [a], X. Querol [b], M.F.M.A. Albert [a], J. Vercauteren [c], T.A.J. Kuhlbusch [d], R. Hoogerbrugge [e]

[a] TNO, Business unit Environment, Health and Safety, P.O. Box 80015, 3508 TA Utrecht, The Netherlands
[b] Institute of Environmental Assessment and Water Research, IDÆA, CSIC, C/Jordi Girona 11, Barcelona 08028, Spain
[c] Flemish Environment Agency (VMM), A. Van de Maelestraat 96, 9320 Erembodegem, Belgium
[d] IUTA e.V., Air Quality & Sustainable Nanotechnology Unit, D-47229 Duisburg, Germany
[e] National Institute for Public Health and the Environment (RIVM), P.O. Box 1, 3720 BA Bilthoven, The Netherlands

ARTICLE INFO

Article history:
Received 6 January 2010
Received in revised form
19 March 2010
Accepted 22 March 2010

Keywords:
Sodium
Sea salt
Regional modelling
PM10

ABSTRACT

The oceans are a major source for particles that play an important role in many atmospheric processes. In Europe sea salt may contribute significantly to particulate matter concentrations. We have compiled sodium concentration data as a tracer for sea salt for 89 sites in Europe to provide more insight in the distribution of sea salt across Europe. The annual average sea salt concentrations above land were estimated to range between 0.3 and almost 13 μg m^{-3}. Maximum concentrations are found at the Irish coast. At coastal sites along the Atlantic and North Sea coast concentrations tend to be around 5 μg m^{-3}. More inland locations up to about 300 km away from the coast tend to show concentrations between 2 and 5 μg m^{-3}, whereas sites further away from the coast are characterized by lower concentrations. An analysis of the representativity of the data with respect to a long term average showed that the long average is associated with a standard deviation of around 15%. The compilation of observations provides an improved overview of sea salt concentrations in Europe as well as an improved basis for model validation. Verification of the results of the LOTOS-EUROS model learned that the model represents well the spatial variability of the observed sea salt concentrations very well. However, the absolute concentrations are significantly overestimated due to large uncertainties in the emission and dry deposition parameterizations. Using the high explained variability in the gradients across Europe, the bias-corrected modelled distribution serves as a best estimate of the sea salt distribution across Europe for 2005.

1. Introduction

The oceans are a major source for atmospheric particles. In coastal regions sea salt may contribute tens of percents to the annual mean particulate mass, e.g. PM10 (e.g. Putaud et al., 2004). Furthermore, sea salt plays an important role in a number of physical and chemical atmospheric processes. The reaction of sea salt particles with nitric acid forms sodium nitrate, which is in contrast to ammonium nitrate not semi-volatile and needs to be accounted for in the (particulate) nitrogen budget (Tamm and Schulz, 2003). The halogens released by the reaction of acidic gases with sea salt contribute to ozone destruction (Finlayson-Pitts, 2003; Knipping and Dabdub, 2003). Sea salt contributes to the deposition of base cat-ions and its deposition flux needs to be accounted for to assess the total acid deposition to vulnerable ecosystems (Van Loon et al., 2005). Also, sea salt contributes to corrosion in coastal regions (Muster and Cole, 2005). Finally, sea salt aerosols are an important contributor to cloud condensation nuclei (CCN) in marine air masses (Yoon and Brimblecombe, 2002). Hence, sea salt aerosols are essential components of atmospheric models at urban, regional and global scales (Gong et al., 1997).

In recent years, a large number of studies have been dedicated to the modelling of atmospheric particles in general and sea salt particles in particular. Many studies of marine aerosols and their role in the climate system were performed on the global scale (e.g. Gong et al., 1997, 2003; Guelle et al., 2001; Stier et al., 2005). For air quality assessment, it is important to resolve the large gradients in sea salt levels and a number of regional models includes a description of sea salt (e.g. Foltescu et al., 2005; Bessagnet et al., 2004; Langmann et al., 2008; Schaap et al., 2008). The verification of these models is severely hampered by the number of available measurements. For example, Foltescu et al. (2005) compared their regional model results against measurements from eight monitoring stations in two

* Corresponding author at: TNO Environment and Geosciences, Unit Environment, Health and Safety, P.O. Box 80015, 3508 TA Utrecht, The Netherlands. Tel.: +31 (0) 88 8662260; fax: +31 (0) 88 8662044.
E-mail address: astrid.manders@tno.nl (A.M.M. Manders).

1352-2310/$ – see front matter © 2010 Published by Elsevier Ltd.
doi:10.1016/j.atmosenv.2010.03.028

countries in Europe. The model evaluations show in general a reasonable agreement between modelled and observed temporal variation but large systematic biases. Because of the limited number of validation data, an integrated picture was not available.

We present a compilation of existing data on sodium, that have (mostly) become available from PM mass closure studies, to provide more insight in the distribution of sea salt in PM10 across Europe, As such the observational basis for model verification for Europe is expanded. These data are then used verify the calculated sea salt distributions from the chemistry transport model (CTM) LOTOS-EUROS. Since 2005 had about average weather conditions and a reasonable amount of observations was available to validate the model, this year is chosen as the model year. Finally, a best estimate of the sea salt distribution based on the model to measurement comparison is provided.

2. Methodology

2.1. Compilation of observations

Sea salt aerosol consists mainly of chloride (Cl, 55.1% by weight) and sodium (Na, 30.6% by weight) (Millero, 2004), which may both be used as a tracer for sea salt. However, since reactions between chloride and acidic gases such as nitric acid may cause a chloride loss (in the form of HCl) (McInnes et al., 1994), both in the atmosphere and on a filter substrate (Slanina et al., 2001), chloride is not a conserved tracer for sea salt aerosol. Sodium, on the other hand, is a conserved tracer and has only minor non-marine sources (White, 2008). Therefore, it is a robust tracer for sea salt and we have restricted ourselves to the use of sodium data. To calculate the total sea salt concentration from the observed sodium concentration, the sodium concentration has to be multiplied by $100/30.6 = 3.26$ (Millero, 2004).

A comprehensive literature search for available data sets on atmospheric sodium in PM10 was performed. These data points were added to the data available through the EMEP network (www.emep.int). Many short-term campaign observations are available, but due to the high temporal variability of sea salt concentrations these are often not representative for a longer period. Therefore, only studies that are representative for at least a year were included, but without the restriction to daily sampling. Furthermore, we have restricted ourselves to data for which the measurement methodology was retraceable. To avoid the inclusion of stations (partly) representative for the free troposphere, mountain sites (above 700 m a.s.l.) were excluded from the analysis. For 2005, daily measurements were collected for a number of stations to verify the model results.

The comprehensive compilation of sodium observations yielded data for 89 stations throughout Europe. The sites, measurement periods and average sodium concentrations are listed in Table 1. For a number of countries data are obtained through the EMEP program, e.g. Denmark, Norway, Spain and Ireland. For other countries such as the Netherlands, Belgium and Austria the data stem from national programs or research stations. The data from national programs often cover about 60–90 measurement days spread through a year, whereas sites within the EMEP program normally have daily coverage. Since sea salt aerosol concentrations are larger near the coast, the number of sites is slightly biased towards locations not too far from the coast. In (south) eastern Europe hardly any observations are available.

2.2. The LOTOS-EUROS model

The regional air quality model LOTOS-EUROS (Schaap et al., 2008) is used to simulate the sea salt distribution across Europe. The LOTOS-EUROS model is a 3D chemistry transport model aimed to simulate air pollution in the lower troposphere. The model has been used for the assessment of particulate air pollution in a number of studies of total PM10 (Denby et al., 2008; Manders et al., 2009a), secondary inorganic components (Schaap et al., 2004a; Barbu et al., 2009) and primary carbonaceous components (Schaap et al., 2004b). The model has participated frequently in international model comparisons addressing ozone (van Loon et al., 2005; Hass et al., 1997) and particulate matter (Cuvelier et al., 2007; Hass et al., 2003; Stern et al., 2008).

The model incorporated four sea salt particle 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 sub-micron particles (0.14–1 μm) the emission function by Mårtensson et al. (2003) was used. For the other modes Monahan et al. (1986) are followed. Both parameterizations use a whitecap cover as function of the wind speed, whereas Mårtensson et al. (2003) also included sea water temperature as an explanatory variable. The surf zone contributes locally to the additional generation of aerosol, depending on wind velocity and fetch (De Leeuw et al., 2000). However, since this process is very local (an area of a few hundred meters width along the coast) its contribution to the total sea salt aerosol production is likely to be small and only noticeable in the immediate vicinity of the coast. Thus, open-sea conditions are also applied to the surf zone. All sea salt aerosol is generated within the model domain, no initial or boundary conditions from other models were used.

The generation functions are generally valid for open ocean conditions with a salinity of around 35‰. But within our domain the salinity of the Baltic Sea (7‰) is much lower than that of the open ocean, leading to an overestimation of the emission flux when using open ocean conditions. Therefore, a crude approach for the Baltic Sea (between 54 and 66°N, 14–32°E) was used, in which the abovementioned emission parameterizations were applied and resulting emission strength was divided by 10. This factor is based on the experimental data presented by Mårtensson et al. (2003), as the impact of the low salinity on the emission strength is not well understood (Lewis and Schwartz, 2004).

The model applies a dry deposition scheme based on Zhang et al. (2001), with constant roughness length. Wet deposition is treated using simple scavenging coefficients.

The model was applied to a domain that ranges from 30°W to 40°E, 35°–70°N, with a normal 0.5° × 0.25° longitude–latitude resolution. The domain was extended further to the west compared to its normal set-up to incorporate a reasonable fetch west of Ireland and the Iberian Peninsula. Therefore, the analysis or the results was restricted to 20°W–30°E, 35°–70°N (Fig. 1). The model is forced using 3-hourly meteorological fields from ECMWF and calculates hourly concentrations of all sea salt modes.

3. Results

3.1. Compilation of particulate sodium data

Measured average sodium concentrations (Table 1, Fig. 1) range between 0.1 and almost 4 μg m^{-3}. As expected, the highest concentrations are generally found near the coast, and concentrations rapidly decrease with increasing distance from the coast. At coastal sites, concentrations tend to be between 1 and 1.5 μg m^{-3}. Higher values are only found for stations located at the Atlantic coast of Ireland, whereas lower values are found at the Baltic coast. More inland locations up to about 300 km away from the coast tend to show concentrations between 0.5 and 1 μg m^{-3}, whereas remote continental sites are characterized by concentrations below 0.5 μg m^{-3}.

The data provided above are based on measurements for different meteorological years. As the inter-annual variability in meteorology may affect the extent to which the presented concentration data represent a long term average, an analysis on the