H14-160
MODELLING EMISSION, CONCENTRATION AND DEPOSITION OF SODIUM FOR POLAND

Małgorzata Werner[1], Maciej Kryza[1], Anthony J. Dore[2], Stephen Hallsworth[2], Marek Błaś[1]

[1]Wroclaw University, Department of Climatology and Atmosphere Protection, Poland
[2]Centre for Ecology and Hydrology, Edinburgh, UK

Abstract: The main source of sodium (Na^+) in the atmosphere is a sea surface. Depending on the distance from the sea to a considered area of deposition, the emission's contribution of sea and land sources differs remarkably. The interest of Na^+ emission, concentration and deposition results from its role in the natural environment. Na^+ particles through their alkaline properties impact on ecosystems and regional air quality. Here, the estimation of natural and anthropogenic sodium emissions for Poland for year 2007 was performed. Sea salt aerosol (SSA) from the Baltic Sea was calculated with the parameterisations proposed by Gong (2003) for ultrafine particles, Monahan et al. (1986) for fine particles and Smith and Harisson (1998) for coarse particles. Estimation of natural land production of Na^+ was based on wind blown dust (WBD) PM_{10} emission from the NatAir project and Geochemical Atlas for Europe. Na^+ anthropogenic emission was calculated using PM_{10} inventory and activity factors reported for Poland. Emissions estimates were used as an input data to the Fine Resolution Atmospheric Multi-pollutant Exchange (FRAME) model, and annual average concentration and total deposition of Na^+ were calculated. Comparison of the FRAME modelled wet deposition results with available measurements values indicates that the model is capable of simulating sodium distribution in Poland.

Key words: sodium, FRAME, emission, deposition, Poland.

INTRODUCTION
Sea salt aerosols (SSA) are salt water droplets ejected from the ocean to the atmosphere. Experiments show that the oceanic aerosols are present in the continental environment (Teinila et al. 2000) and also continental aerosols in the ocean environment (Heintzenberg et al. 2000). SSA dominates the particulate mass concentrations in unpolluted marine air and contributes significantly to the global aerosol load on mass basis (Lewis and Schwartz 2004, Seinfeld and Pandis 2006, Vignati et al. 2010). In coastal regions SSA may contribute tens of percents to the annual mean particulate mass e.g. PM_{10} (Putaud et al. 2004). Marine aerosols influence the Earth's radiative budget, scattering the incoming solar radiation and modifying cloud properties and their interaction with the solar radiation (Behnke et al. 1997, O'Dowed and de Leeuw 2007). Because of its role in radiative transfer SSA is important in a large number of applications related to global climate change (Haywood and Boucher 2000). SSA particles have also a significant impact on air quality which makes them important components of atmospheric models at urban, regional and global scales (Gong et al. 1997).

Sodium)Na^*, as well as chlorine and magnesium, is a major component of SSA. Sodium, as a base cation, changes the surface pH when deposited, causing an increase in alkalinity and neutralizing the effects of acidity generated by sulphur and nitrogen deposition (Gong et al. 1997). Besides SSA, sodium also originates from land sources, both anthropogenic and natural. On average, the most significant anthropogenic contribution to sodium emission is from combustion in the manufacturing industry, sinter production in iron production as also domestic and power station coal burning (NAEI, www.naei.org.pl). Natural land emission mainly comes from soil surface erosion – wind blown dust (WBD). WBD emission is caused by the wind blowing above dry and sparsely vegetated soils where particles with a diameter of ten to hundreds of μm are present (Mahowald et al. 2005). Particles are moved by the wind and bounce on the surface causing the dislodgement of smaller particles that can be lifted into the atmosphere and travel long distance (Korcz et al. 2009).

The sea spray source functions describe the amount (number, volume, mass) of sea spray aerosol produced at the sea surface per unit time and area as a function of environmental conditions and particle size. The most important factor responsible for SSA emission is wind speed, but also temperature plays a significant role (e.g. Maårtensson et al. 2003). SSA is produced by wind induced wave breaking and subsequent evaporation mechanism (Fitzgerald 1991, Schwartz and Lewis 2004). Sea spray production parameterisations have been developed by Monahan et al. (1986), Andreas (1992), Smith and Harisson (1998), Maårtenson et al. (2003) and Gong (2003) among others. 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. Most of these studies were performed on the global scale (e.g. Gong et al. 1997, 2003, Guelle et al. 2001, Witek et al. 2007). There are also some regional models which includes a description of sea salt (e.g. Foltescu et al. 2005, Schaap et al. 2008). One of the largest problems is the number of available measurements, which are needed for verification of the models results. For example Foltescu et al. (2005) compared their regional model results against measurements from eight monitoring stations in two European countries. Similarly, Manders et al. (2010) verified sodium concentrations in Europe using nine stations for the year 2005. Werner et al. (2011) compared FRAME model results of Na^+, Mg^{2+} and Ca^{2+} concentrations and deposition for the UK against measurements for the year 2006 from more than 20 sites. According to authors' knowledge there are no studies of modeling the sodium emissions, concentrations and deposition for the Central Europe and Poland.

Here we present the results of Na^+ emission estimations both anthropogenic and natural for Poland for the year 2007. SSA emission from the Baltic Sea was calculated using selected parameterisation schemes (Monahan et al. 1986, Smith and Harrison 1998, Gong 2003), supported with the WRF modelled wind speed. To calculate natural emission of Na^+ from soil erosion, the estimations of PM_{10} wind blown dust from the NatAir project and concentrations of Na^+ in topsoil were used. A spatial distribution of anthropogenic emission of Na^+ was prepared using PM_{10} point sources and area emission for the year 2007 and activity and emission coefficients dependent on SNAP sector and type of burnt material. The calculated maps of Na^+ emissions were used in the Fine Resolution Atmospheric Multi-pollutant Exchange model to obtain mean annual

concentrations and wet deposition at the 5km x 5km spatial resolution for Poland. The modelled results were compared with measurements of wet deposition from the National Monitoring Network.

DATA AND METHODS

Calculation of the sea salt aerosol emission

For all formulae applied, radius in relative humidity equal 80% (r_{80}) is used. For the smallest particles ($r_{80}<0.8\mu m$) parameterisation of Monahan et al. (1986), modified by Gong (2003), was used. For larger particles ($0.8<r_{80}<4.0$ μm) Monahan et al. (1986) was used, and for particles of $r_{80}>4.0$ μm, the formula of Smith and Harrison (1998). SSA particles are in the large size range. Lewis and Schwartz 2004 suggest that their diameter can range from 0.1 μm to more than 500 μm. It is also assumed that in the long range transport the particles up to 10 μm of dry diameter are important (Foltescu et al. 2005, Manders et al. 2010).The selected functions are presented below:

Monahan et al. (1986), modified by Gong (2003), for the smallest particles:

$$\frac{\Delta F_i}{\Delta r_i} = 1.373 |v_{h,10}|^{3.41} \left(1 + 0.057 r_i^{3.45}\right) 10^{1.19 e^{-B^2}} r_i^{-A} \tag{1}$$

$$A = 4.7(1 + \theta r_i)^{-0.017 r_i^{-1.44}} \tag{2}$$

$$B = (0.433 - log_{10} r_i)/0.433 \tag{3}$$

Monahan et al. (1986), for the particles of size $0.8<r_{80}<4.0$ μm:

$$\frac{\Delta F_i}{\Delta r_i} = 1.373 |v_{h,10}|^{3.41} \left(1 + 0.057 r_i^{1.05}\right) 10^{1.19 e^{-B^2}} r_i^{-3} \tag{4}$$

$$B = (0.38 - log_{10} r_i)/0.65 \tag{5}$$

Smith and Harrison (1998), for the largest particles with $r_{80}>4.0$ μm

$$\frac{\Delta F_i}{\Delta r_i} = 0.2 |v_{h,10}|^{3.5} e^{1.5 ln\left(\frac{r_i}{3}\right)^2} + 0.0068 |v_{h,10}|^3 e^{-ln\left(\frac{r_i}{30}\right)^2} \tag{6}$$

F_i – particle flux (m^{-2} s^{-1})
$V_{h,10}$ – mean horizontal wind speed at 10m height (m s^{-1})
r_i – droplet radius (μm) at a reference relative humidity of 80%

All functions describe the surface flux at 10m above the ocean of sea-spray aerosol, i.e. the number of droplets produced per unit surface area and per unit time. Being hygroscopic, SSA changes size as the ambient relative humidity changes. The equilibrium droplet size equation is presented in: Gerber (1985), Gong et al. (1999). As a rule of thumb eq. 7 is used after O'Dowed and de Leeuw (2007):

$$r_0 = 2r_{80} = 4r_{dry} \tag{7}$$

where,
r_{dry} – radius in relative humidity equal 0%
r_0 – radius in relative humidity equal 97%

A detailed description of SSA production mechanism and used parameterization is provided by Werner et al. (2011). The main input data indispensable to calculate the emissions is wind speed information at a 10m altitude above the sea surface. This data was calculated with the WRF (Weather Research Forecast, www.wrf-model.org) model, at a 10 km×10 km grid square resolution for Baltic Sea and 50 km x 50 km for the rest of European ocean area, with a 3-hour time step.

The calculations of SSA production were done with a 0.1 μm radius size step for particles. It was assumed that at formation, the density of particles is the same as the density of sea water at 15ºC and 3.5% salinity and the particles have the same ion composition as the sea water. Composition of SSA at RH80% was calculated assuming that only water evaporates and sea salt particles remain. Size changes with relative humidity are considered according to equation 7. To calculate the mass of sea salt particles it is assumed that they are spherical in shape. To get the dry mass of SSA the total mass of the particles (ions, other species contained in the sea water, and water) is multiplied by the percentage content of ions (salinity in RH=80%).

Land emission

For Poland, there is no spatial information of Na$^+$ emission for anthropogenic or natural sources. To prepare a spatial distribution of anthropogenic Na$^+$ emission, methodology similar to EMEP and NAEI was used (van Loon et al. 2005, www.naei.org.pl). Na$^+$anthropogenic emission was calculated using PM$_{10}$emission inventory and activity factors reported by the Polish Chief Inspectorate of Environmental Protection (CIEP). Emission and activity factors for calculations were dependent on the SNAP sectors and type of burnt fuel. To calculate natural emission of Na$^+$ from soil erosion, the estimation of PM$_{10}$ wind blown dust emission from NatAir project (Imroving and Applying Methods for Calculation of Natural and

Biogenic Emissions and Assesment of Impacts on Air Quality, Korcz et al. 2009) and concentration of Na^+ in topsoil were used. NatAir data is provided for all Europe with a one hour time step and 10 km x 10 km spatial resolution for years 1997, 2000, 2001 and 2003. An average estimation of PM_{10}emission from available years was taken for calculations of Na^+. Detailed data on Na^+ concentration in topsoil was taken from the Geochemical Atlas of Europe (www.gsf.fi/publ/foregsatlas/), which contains data from more than 2000 measurement points from 26 European countries. To get continuous information about topsoil, point data was interpolated in the resolution of 10 km x 10 km. The uncertainty related with WBD estimations is large. The largest is caused by the factor which change the horizontal emission to vertical emission. Van Harmelan et al. (2004) show that local models of WBD emission involvecalculations with uncertaintyof 50%, but for the mesoscale model the uncertainty could be higher.

FRAME model description
The atmospheric transport model, FRAME provides information on the annual mean deposition and concentrations of atmospheric pollutants. A detailed description of the FRAME model is provided by Singles et al. (1998), Fournier et al. (2002, 2004), Dore et al. (2006) and Vieno et al. (2010). Originally FRAME was working for nitrogen, sulphur and primary particulate matter. Recently FRAME was further developed to allow sea salt and base cation modelling, with the aim to develop a complex tool supporting environmental policy in both the UK and Poland. Details on model configuration for the base cations are provided by Werner et al. (2011). FRAME is a Lagrangian model with a grid resolution of 5 km x 5 km and grid dimension of 160 x 160 cells for Poland (Kryza et al. 2010). Aerosol concentrations at the boundary of the model domain are calculated with FRAME-Europe model. FRAME-Europe is a similar model to FRAME, but runs for the entire Europe on the EMEP grid at 50 x 50 km resolution. The FRAME model was run with emission information prepared according to the methodology described above and meteorology data for the year 2007. Because there are no measurements of Na^+ air concentrations in Poland, FRAME modelled wet deposition was compared with measurements gained at 25 stations of the Polish Chief Inspectorate of Environmental Protection (CIEP).

RESULTS
The highest values of marine Na^+ emissionsare noted for regions with the highest wind speed. For the central areas of the Baltic Sea, Na^+ emission exceeds 90 kg ha^{-1} $year^{-1}$.Lower values are evident in bays and in general near the coastline. In case of Na^+ wind blown dust emisison over the land, increased values correspond to the high emission of PM_{10} (Marshland, Lower Silesia, Lubelska Upland). The land anthropogenic emission, WBD emission and import from the Baltic Sea and North Atlantic Ocean contribute to 3.5 Gg, 0.19 Gg and 720 Gg of the annual total emission in he model domain, respectively.

Spatial information on Na^+ deposition and concentration, calculated with FRAME, is presented in Fig. 1. The concentrations are particularly high over the source Baltic Sea region. A gradient in concentration is observed from the coastal region towards S and SE over land. An average yearly concentration of sodium amounts to 1.9 μg m^{-3} for the entire domain, with the maximum exceeding 20 μg m^{-3} over the the north – west region. Similarly, the highest value of wet deposition is on the north – west Poland, where amounts of 20 kg ha^{-1} $year^{-1}$ and locally 30 kg ha^{-1} $year^{-1}$are reached. Additionally, higher concentrations on the west could be also related to the predominant westerly wind directions bringing air masses formed over the North Atlantic. Increased wet deposition is also calculated for Sudety Mountains in the south. For the centralareas of the country, deposition is significantly lower, and mean value amounts to 1 - 3 kg ha^{-1} $year^{-1}$.
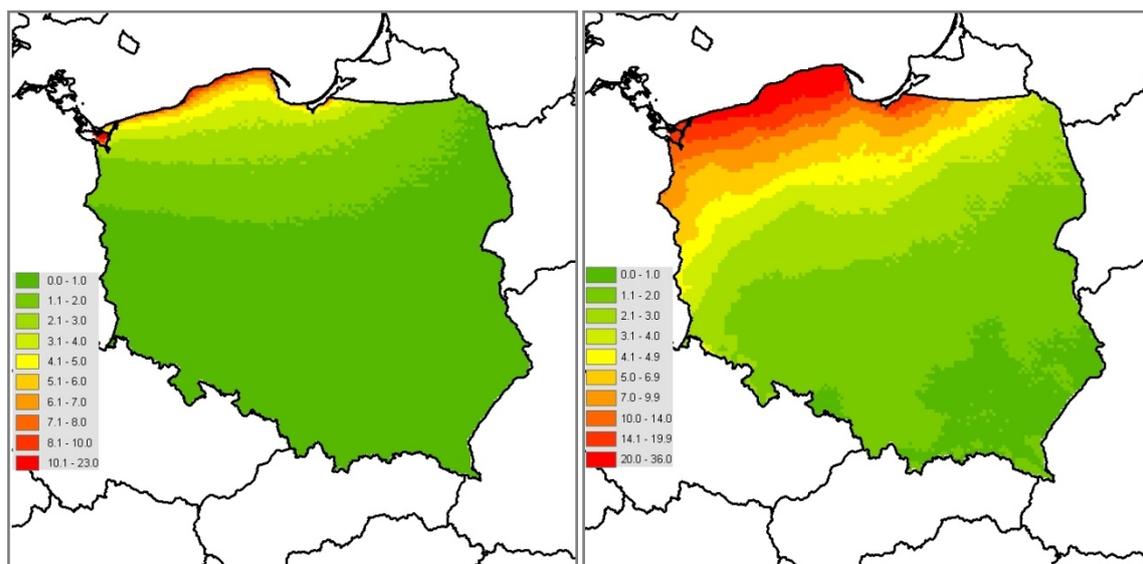

Figure 32. Spatial distribution of Na^+ concentrations (left) and deposition (right) for year 2007.

The comparison of the FRAME modelled and measured values of wet deposition is presented in Fig. 2. There is no general tendency for underestimation or overestimation by the model. In general the agreement between modelled and measured values is reasonable, with correlation coefficient equal 0.7 and mean absolute error equal 2.6 kg ha $year^{-1}$. The highest overestimation appears for one out of three coastal stations – Łeba, whereas the highest underestimationis for mountainous stations –Kasprowy Wierch and Śnieżka.
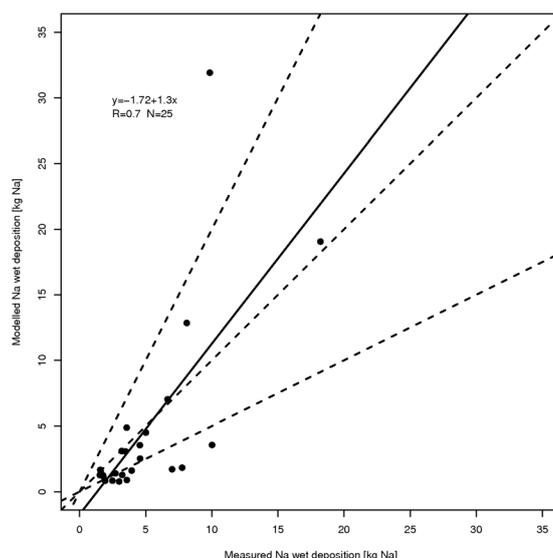
Figure 2. Model – measurements comparison of Na^+ wet deposition for Poland for 2007.

SUMMARY AND CONCLUSIONS

Although Poland is not a typical coastal country, the main source of sodium is the aerosol produced from the sea surface both from the Baltic Sea and Atlantic Ocean. There is a very low contribution of natural land emission. This estimation was based on PM_{10} WBD emission calculated by the NatAir project which is characterised by large uncertainty. Further work is needed to improve estimations of natural land emission.

Spatial patterns of Na^+ air concentrations, modelled with FRAME and presented here, show the gradient from the coastal region towards low concentrations over land. The wet deposition gradient from the north west to the east is related with the dominant westerly wind directions bringing oceanic masses of air. Locally, an increase in wet deposition also appears in the Sudety Mountains. As this is an area of special environmental protection, increased deposition is of special importance for ecosystems conservation. The comparison of FRAME results with measurements showed that the model was capable of predicting the spatial distribution of sodium. The model result of Na^+ wet deposition was found to be in reasonable agreement with measured wet deposition. The highest overestimation was noticed in Łeba, but for the others coastal stations overestimation did not appear. Further work will concern modelling remaining elements of base cations (Mg^{2+}, Ca^{2+}, K^+), for which greater contributions are from anthropogenic and natural land emission.

REFERENCES

Andreas, E. L,1992: Sea spray and turbulent air-sea heat fluxes. *J. Geophys. Res*., **97 (C7)**, 11429-11441.

Behnke, W, G. C.,V. Sheer, C. Zetzsch, 1997: Production and decay of ClNO2 from the reaction of gaseous N2O5 with NaCl solution: bulk and aerosol experiments. *J. Geophys. Res*., **102**, 3795–3804.

Bieser, J, A. Aulinger, V. Matthias, M. Quante, P. Builtjes, 2011: SMOKE for Europe – adaptation, modification and evaluation of a comprehensive emission model for Europe. *Geoscientific Model Development*, **4**, 47-68.

Dore, A. J, M. Vieno, N. Fournier, K. Weston, M. A. Sutton, 2006: Development of a new wind-rose for the British Isles using radiosonde data, and application to an atmospheric transport model. Q. J. R. Meteorol. Soc, **132**, 2769-2784.

Fitzgerald J. W., 1991: Marine aerosols: a review. *Atmos Environ. ZSA*, 533-546.

Foltescu, V.L, S. C. Pryor, C. Bennet, 2005: Sea salt generation, dispersion and removal on the regional scale, *Atmos Environ.*, **39**, 2123–2133.

Fournier, N, V. A. Pais, M. A. Sutton, K. J. Weston, U. Dragosits, S.Y. Tang, J. Aherne, 2002: Parallelisation and application of an atmospheric transport model simulating dispersion and deposition of ammonia over the British Isles. *Environmental Pollution*, **116 (1)**, 95 - 107.

Fournier, N, A. J. Dore, M. Vieno, K.J. Weston, U. Dragosits, M.A. Sutton, 2004: Modelling the deposition of atmospheric oxidized nitrogen and sulphur to the UK using a multi-layer long-range transport model. *Atmos Environ.*, **38**, 683–694.

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

Gong, S. L, L.A. Bartie, J.P. Blanchet, 1997: Modeling sea-salt aerosols in the atmosphere. Model development. *J. Geophys. Res.*, **102**, 3805–3818.

Gong, S. L, 2003: A paramterization of sea-salt aerosol source function for sub- and super-micron particles. *J. Geophys. Res*, **17**, 1097.

Guelle, W, M. Schulz, Y. Balkanski, and F. Dentener, 2001: Influence of the source formulation on modeling the atmospheric global distribution of sea salt aerosol. *J. Geophys. Res.*, **106(D21)**, 27509-27524.

Haywood, J and O. Boucher, 2000: Estimates of the direct and indirect radiative forcing due to tropospheric aerosols: A review. *Review of Geophysics,***38**, 513–543.

Heintzenberg, J, D. C. Covert, R. Van Dingenen, 2000: Size distribution and chemical composition of marine aerosols: a compilation and review. *Tellus,***52B**, 1104–1122.

Korcz, M, J. Fudala, C. Klis, 2009: Estimation of wind blown dust emissions in Europe and its vicinity. *Atmos Environ*., **43**, 1410-1420.

Lewis, E. R. and S. A. Schwartz, 2004: Sea salt aerosol production. Mechanisms, methods, measurements, and models. Washington, DC: American Geophysical Union, 413 pp.

Kryza, M., Werner M., Blas M., Dore A. J., Sobik M., 2010: The Effect of Emission form Coal Combustion In Nonindustrial Sources on Deposition of Sulfur and Oxidized Nitrogen In Poland. J. Air. Waste.Ma., **60 (7)**, 856-866, DOI: **10.3155/1047-3289.60.7.856**

Mahowald, N, A. Baker, G. Bergametti, N. Brooks, R. Duce, T. Jickells, N. Kubilay, J. Prospero, I. Tegen, 2005: Atmospheric global dust cycle and iron inputs to the ocean Global Biogeochem. *Cycles*, **19 (4)**, GB4025,10.1029/2004GB002402.

Manders,A. M. M,M. Schaap, X. Querol, M.F.M.A. Albert, J. Vercauteren, T.A.J. Kuhlbusch and R. Hoogerbrugge, 2010:Sea salt concentrations across the European continent. *Atmos Environ*., 44 **(20)**, 2434-2442.

Maårtensson, E. M, E.D.Nilsson, G. de Leeuw, L.H. Cohen, H.C. Hansson, 2003: Laboratory simulations and parameterization of the primary marine aerosol production. *J. Geophys. Res.*, **108 (D9),** 4297.

Monahan, E.C, D.E. Spiel, K.L. Davidson In: Monahan, E.C., Mac Niocaill, G. (Eds.), 1986: Oceanic Whitecaps., Riedel, Norwell, MA, 167–174 pp.

O'Dowd, C.D. and G. de Leeuw, 2007: Marine aerosol production: a review of the current knowledge. *Phil. Trans. R. Soc*, **365**, 1753-1774.

Schaap, M, R. M. A. Timmermans, F. J. Sauter, M. Roemer, G. J. M. Velders, G. A. C Boersen, J. P. Beck and P. J. H. Builtjes, 2008: The LOTOS-EUROS model: description, validation and latest developments. *Int. J. of Environ. and Pollution***32** (No. 2), 270–290.

Seinfeld, J. H. and S.N. Pandis, 2006: Atmospheric Chemistry and Physics, from Air Pollution to Climate Change, Wiley, New York, 1326 pp.

Singles, R. J, M. A. Sutton, K. J. Weston, 1998: A multi-layer model to describe the atmospheric transport and deposition of ammonia in Great Britain. *Atmos Environ*, **32**, 393–399.

Smith, M. H, N. M. Harrison, 1998: The sea spray generation function. *J. Aerosol Science*, **29 (Suppl. 1)**, 189–190.

Vignati, E, M. C. Facchini, M. Rinaldi, C. Scannell, D. Ceburnis, J. Sciare, M. Kanakidou, S. Myriokefalitakis, F. Dentener, C. D. O'Dowd , 2010: Global scale emission and distribution of sea spray aerosol: sea-salt and organic enrichment. *Atmos. Environ.*, doi: 10.1016/j.atmosenv.2009.11.013, 2010.

Putaud, J. P, F. Raes, R. Van Dingenen, J. P. U. Baltensperger, E. Brüggemann, M. C. Facchini, S. Decesari, S. Fuzzi, R. Gehrig, H. C. Hansson, C, P. Hüglin, P. Laj, G. Lorbeer, W. Maenhaut, N. Mihalopoulos, K. Müller, X. Querol, S. Rodriguez, J. Schneider, G. Spindler, H. ten Brink, K. Třrseth, B. Wehner and A. Wiedensohler, 2004: A European Aerosol Phenomenology. 2: chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe. *Atmos. Environ*., **38**, 2579-2595.

Smith, M. H, N. M. Harrison, 1998: The sea spray generation function. *J. Aerosol Science*, **29 (Suppl. 1)**, 189–190.

K. Teinila, V.M. Kerminen R. Hillamo, 2000: A study of size-segregated aerosol chemistry in the Antarctic atmosphere. *J. Geophys. Res,* **105**, 3893–3904.

van Harmelen, A. K., H. A. C. Denier van der Gon, H. J. G. Kok, W. J. Appelman, A. J. H Visschedjik, J. H. Hulskotte, 2004: Particulate Matter in Dutch Pollutant Emission Register: State of Affairs. TNO-report, **428**, 82pp.

Van Loon, M, L. Tarrason, M. Posch, 2005: Modelling Base Cations in Europe. EMEP/MSC-W & CCE Note 2/2005, Norwegian Meteorological Institute, Oslo, Norway, 47 pp.

Vieno, M, A. J. Dore, W. J. Bealey, D. S. Stevenson, M. A. Sutton, 2010: The importance of source configuration in quantifying footprints of regional atmospheric sulphur deposition. *Science of the total environment*, **408**, 985-995.

Werner, M, M. Kryza, A. J. Dore, M. Błaś, S. Hallsworth, M. Vieno, Y. S. Tang, R. I. Smith, 2011: Modelling of marine base cation emissions, concentrations and deposition in the UK. *Atmos. Chem. Phys.*, **11**, 1023–1037.

Witek, M. L, P. J. Flatau, P. K. Quinn, and D. L. Westphal, 2007: Global sea-salt modeling: Results and validation against multicampaign shipboard measurements. *J. Geophys. Res*.,, **112**, D08215, doi:10.1029/2006JD007779.