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Modelling of base cation emissions, concentrations and deposition in the UK

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Abstract

Base cations exerts a large impact on various geochemical and geophysical processes both in the atmosphere and at the Earth surface. One of the essential roles of these compounds is impact on surface pH causing an increase in alkalinity and neutralizing the effects of acidity generated by sulphur and nitrogen deposition. During recent years anthropogenic emissions of base cations in the UK have decreased substantially, by about 70% for Na^+, 78% for Mg^{2+}, 75% for Ca^{2+} and about 48% for K^+ for the period 1990–2006. For the island regions, such as the is UK, the main source of base cation particles is the aerosol produced from the sea surface. Here, the sea salt aerosol (SSA) emissions are calculated with parameterisations proposed by Maårtensson et al. (2003); ultra fine particles, Monahan et al. (1986); fine particles and Smith and Harisson (1998); coarse particles continuously with a 0.1 µm size step using WRF-modelled wind speed data at a 5 km × 5 km grid square resolution with a 3 h time step for two selected years 2003 and 2006. SSA production has been converted into base cation emissions, with the assumption that the chemical composition of the particle emitted from the sea surface is equal to the chemical composition of sea water, and used as input data in the Fine Resolution Atmospheric Multi-pollutant Exchange Model (FRAME). FRAME model results, yearly mean concentrations and total wet deposition at a 5 km × 5 km grid resolution, are compared with concentrations in air and wet deposition from the National Monitoring Network and measurements based estimates of UK deposition budget. The correlation coefficient for wet deposition achieves high values for Na^+ and Mg^{2+}, and for Ca^{2+} there is significant scattering. Base cation concentration is also represented well, with some overestimations on the west coast and underestimations in the centre of the land.

1 Introduction

Because approximately two-thirds of the Earth's surface is covered by oceans, sea salt aerosol (SSA) particles are one of the most important natural aerosol systems globally. In coastal regions sea salt may contribute tens of percent to the annual mean particulate mass, e.g. PM_{10} (Putaud et al., 2004). Sea salt is also one of the major contributors to the mass of particulate matter injected into the atmosphere globally (Tegen et al., 1997; Penner et al., 2001). It is estimated that global emission of sea salt aerosols into the atmosphere comes to 5900 Tg year^{-1} (Tegen et al., 1997).

The SSA exerts a large impact on various geochemical and geophysical processes and on the Earth's climate. It modifies the Earth's radiative budget, biogeochemical cycling, impacts on ecosystems and regional air quality (O'Dowed and de Leeuw, 2007). SSA influence radiative transfer directly, by scattering solar radiation and also they are important as a source of cloud condensation nuclei (CCN) in the maritime environment and may be implicated in the regulation of global climate through their influence on the albedo of marine clouds and the global atmospheric sulphur cycle (Foltescu et al., 2005). Sea salt aerosol particles can also alter cloud properties and lifetime and provide media for chemical reactions (e.g. Gong et al., 1997; Murphy et al., 1998; Behnke et al., 1997). The primary marine aerosol is emitted from the water surface into the atmosphere directly as droplets with the composition of seawater enriched with chemical compounds, bacteria and viruses occurring in the upper water column and in the film covering the water surface. The reactions 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). Sea salt is the one of the most important sources of base cations in the atmosphere. SSA contributes to the deposition of base cation and its deposition flux should be accounted for in ion balance calculations to assessment of the exceedances of the acid critical loads (VanLoon et al., 2005). Base cations, such as Na^+, Mg^{2+}, Ca^{2+} and K^+ are important in the environment (NAEI, www.naei.org.uk)

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀| |▶
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

because deposition has an impact upon surface pH causing an increase in alkalinity and neutralizing the effects of acidity generated by sulphur and nitrogen deposition. Hence, sea salt aerosols are essential components of atmospheric models at urban, regional and global scales (Gong et al., 1997).

Sea spray forms when winds and waves force air bubbles to burst at the sea surface (Woodcock, 1953). Winds also tear off wave crests to form larger drops, but these drops fall back to the ocean quickly. At the time of production sea spray contains all the components of sea water (about 96.8% of the mass is water and the rest is the sea salt, Jacobson, 2005). The radii of SSA particles range from 0.1 µm to greater than 1000 µm (Lewis and Schwartz, 2004).

In recent years, a large number of studies have been dedicated to sea salt particle production. Sea spray production parameterisations have been developed by Monahan et al. (1986); Woolf et al. (1987); Andreas (1992); Wu (1992); Smith et al. (1993); Smith and Harisson (1998); de Leeuw et al. (2000); Maårtensson et al. (2003) and Gong (2003), among others. Existing models of drop emissions from the sea surface are based both on laboratory studies (e.g. Monahan et al., 1986; Monahan and Van Patten, 1989; Maårtensson et al., 2003) as well as measurements (Smith et al., 1993).

Commonly used formulations for sea salt aerosol generation are primarily based on the relation between whitecap coverage and wind speed, although other variables such as sea surface temperature and salinity may also influence the flux (Maårtensson et al., 2003). A whitecap method is based on combining the parameterization of the whitecap cover using field experimental data and the production of sea-spray aerosol per unit whitecap area determined from laboratory experiments (Monahan et al., 1986). Maårtensson et al. (2003) determined their source function from bubble-mediated laboratory studies to determine the flux as a function of whitecap coverage and then incorporated Monahan's wind speed and whitecap relationship to produce flux estimates. De Leeuw et al. (2000) based their parameterization on surf zone experiments while Reid et al. (2001) used a concentration build-up method using aircraft measurements in an evolving internal boundary layer.

SSA source functions have also been included in atmospheric models but most of these studies are on a global scale (e.g. Gong et al., 1997; Witek et al., 2007; Gong, 2003) and only a few refer to regional scale in high resolution (Foltescu et al., 2005). Because of the limited availability of measurements of the chemical composition of aerosol, there is also a major problem with verification of these models. For example Foltescu et al. (2005) compared their regional model results against measurements from eight monitoring stations in two European countries.

In this paper, selected parameterisations have been used to calculate the PM_{10} SSA production for the UK domain for the years 2003 and 2006. According to the physical and chemical properties of SSA, the mass of base cation compounds (Na^+, Mg^{2+}, Ca^{2+} and K^+) are calculated from the total mass of SSA. The calculated maps of base cation emissions were used in the Fine Resolution Atmospheric Multi-pollutant Exchange model to obtain mean annual concentrations and wet and dry deposition of Na^+, Mg^{2+}, Ca^{2+} and K^+ at a high resolution of 5 km × 5 km for the British Isles. The modelled results were compared with measurements of base cation wet deposition and air concentrations from the National Monitoring Network, using an increased number of stations for the year 2006.

2 Methodology

2.1 FRAME model

The atmospheric transport model, FRAME (Fine Resolution Atmospheric Multi-pollutant Exchange) is used to assess the long-term annual mean air pollutant concentrations and deposition of base cation: Na^+, Mg^{2+}, Ca^{2+} and K^+ over the UK. FRAME has been previously used to model sulphur and nitrogen compounds, heavy metals and particulate matter (e.g. Dore et al., 2007; Matejko et al., 2009; Kryza et al., 2010). Recently FRAME was further developed to allow sea salt and base cation modeling, with the aim to develop a complex tool supporting environmental policy in the UK. The fundamentals of the model are described by Singles et al. (1998), Fournier et al. (2004) Dore et al. (2007) and Vieno et al. (2010).

FRAME is a Lagrangian model which represents the main atmospheric processes taking place in a column of air moving along straight-line trajectories following specified wind directions. The model consists of 33 vertical layers of varying thickness ranging from 1 m at the surface and increasing to 100 m at the top of the domain (ApSimon et al., 1994; Singles et al., 1998). Vertical mixing is described using K-theory eddy diffusivity, and solved with Finite Volume Method (Vieno, 2006).

Dry removal rates are calculated separately for four groups of particle sizes using the geometric mean size, with the middle point of 1.25 µm, 3.75 µm, 6.25 µm and 8.75 µm. The higher deposition velocity applies to larger particles for which the gravitational settling is more efficient. This is set according to the values proposed by Ruigrok et al. (1995, 1997), Zhang et al. (2001), Nho-Kim et al. (2004), Seinfeld and Pandis (2006).

Wet deposition is calculated with a scavenging coefficient and constant drizzle approach, using precipitations rates calculated from a measurement-based map of average annual precipitation. The amount of material removed in a time period (Δt) is given by:

$$\Delta c_i = c_i \left(1 - e^{\lambda_i \Delta t}\right) \tag{1}$$

Δc_i – decrease in concentration of species “*i*” due to removal by precipitation
λ_i – scavenging coefficient
c_i – concentration of pollutants.

The wet deposition flux to the surface is the sum of wet removal from all volume elements aloft, assuming that scavenged material comes down as precipitation. There is no separation between in-cloud and below-cloud processes and an averaged value of scavenging ratio (Δ_i) is used in the model. To produce scavenging coefficient λ_i, Δ_i is combined with the precipitation rate and the depth of the mixing layer ΔH_{mix}:

$$\lambda_i = (\Delta_i P)/H_{\text{mix}} \tag{2}$$

An increased washout rate is assumed over hill areas due to the seeder-feeder effect. It is assumed that the washout rate for the orographic component of rainfall is twice that used for the non-orographic components (Dore et al., 1992).

The FRAME model domain covers the UK and the Republic of Ireland with a grid resolution of 5 km × 5 km and grid dimensions of 172 × 244 cells. Input pollutant concentrations at the boundary of the model domain are calculated with FRAME-Europe – a similar model which runs on the EMEP grid at 50 km × 50 km resolution. Trajectories are calculated with different starting angles at a 1 degree resolution, using directionally dependent wind speed and wind frequency roses. To create wind speed and wind frequency roses for FRAME radiosonde data are used (Dore et al., 2006).

2.2 Meteorology

The precipitation data used in FRAME comes from Meteorological Office national network (approximately 5000 stations). The data are in the form of annual rainfall fields for the UK and Ireland, with a resolution of 5 km × 5 km, for the years 2003 and 2006. A higher annual precipitation amount is apparent along the western cost and at higher altitudes. However during the wetter year (2006), annual precipitation above 2000 mm year^{-1} occurs over wider areas of the hill regions.

Wind speed and wind frequency data are prepared using the radiosonde information, separately for each year of interest. In order to sample data from different geographical locations, four stations were selected in the British Isles. The selection criteria for radiosonde data were the existence of a complete data set and geographical representation of the northern, southern, western and eastern limits of the British Isles. The stations meeting these criteria are: Camborne (South-West England), Hemsby (East Coast of England), Stornoway (North-West Scotland) and Valentia (on the East Coast of the Republic of Ireland. The highest wind speeds are observed from the south-west and lower from the east directions. The predominant wind directions for both years are from SW-W.

2.3 Emission

Emissions of base cations consist of land (anthropogenic and natural) and marine sources. Anthropogenic emissions of base cation are taken directly from the National Atmospheric Emissions Inventory (NAEI, www.naei.org.uk) for the years 2003 and 2006. The most significant anthropogenic contribution to base cation emission is from glass production, quarrying, cement and lime production industries. The main sources of calcium are combustion in the manufacturing industry sector and quarrying of limestone. For magnesium and potassium the main sources are emissions from fireworks and then quarrying of dolomite – for Mg^{2+} and iron and steel production or coal burning in power stations for K^{+}. Sodium is mainly emitted during combustion in the manufacturing industry, sinter production in iron production, domestic and power station coal burning.

During the last two decades anthropogenic emissions of base cations in the UK have decreased significantly. For the years 1990–2006 the decrease was from 2106 kg to 585 kg (595 kg in 2003) for Na^{+}, from 2800 kg to 616 kg (669 kg in 2003) for Mg^{2+}, from 8609 kg to 2125 kg (2559 kg in 2003) for Ca^{2+}, and from 2422 kg to 1249 kg (1490 kg in 2003) for K^{+}.

Natural land emission of calcium (wind driven dust emission) was prepared using PM_{10} natural emission from the NatAir project (Korcz et al., 2009; natair.ier.uni-stuttgart.de) for the years: 1997, 2000, 2001 and 2003. An average NatAir estimations of PM_{10}, from the available years: 1997, 2000, 2001 and 2003, were multiplied by the percentage content of calcium in different types of soil (Batjes et al., 2009; http://www.iiasa.ac.at/Research/LUC/External-World-soil-database).

Calculation of base cation emissions maps of Na^{+}, Mg^{2+}, Ca^{2+}, K^{+} from the sea surface is one of the aims of this paper. Sea spray droplets come in three varieties: film droplets, jet droplets and spume droplets. Film (0.5–5.0 µm) and jet droplets (3–50 µm) derive from the same process: the bursting of air-entrained bubbles from oceanic whitecaps formed during the breaking of wind-induced waves (Maårtensson et al., 2003;

Zhang et al., 2005). Spume droplets ($>20\,\mu$m) derive from wind shear which tears the droplets directly from the wave crests (Andreas, 1998). The continuous impact of the wind to the sea surface results in wave breaking. Breaking waves are visualized by oceanic whitecaps, covering a limited part of the sea surface, typically 10% for wind speeds of $10\,\mathrm{m\,s^{-1}}$ (Wu, 1979). The relationships between the concentrations of sea-salt aerosol mass in the air and whitecap cover and wind speed were discovered in the 1950s (Woodcock, 1953). This dependence is very commonly used in SSA production formulas. The empirical equation, which is used in SSA formulations, for the whitecap cover (W in percent) as a function of the wind speed is presented by Monahan and O'Muircheartaight (1980):

$$W = 3.84 \times 10^{-4} \left(U_{10}^{3.41}\right) \tag{3}$$

The equation is used directly in the form given above by Maårtensson et al. (2003) and in a modified form by other authors of SSA particle parameterisations.

The number of drops produced depends on the size of the bubble (Blanchard, 1963). The size of the jet drops is about 1/10 of the initial bubble diameter size which places the jet drops in the super-micrometer aerosol size range. Film drops appear as a sub-micrometer aerosol (Woolf et al., 1987) and they can be up to several hundred per bubble and increase in number with diameter size of the bubble (Blanchard, 1963).

De Leeuw et al. (2000) illustrate that the source function of Monahan et al. (1986) applies best to particles with diameters below $10\,\mu$m at formation, whereas the formulation proposed by Smith et al. (1993) gives better results for larger particles. Hoppel et al. (2002) also recommend a combined source function using Monahan et al. (1986) and a modified version of Smith et al. (1993). Foltescu et al. (2005) recommend the Monahan and Smith parameterisation, as discussed above, but for the smallest particles (below $0.8\,\mu$m radius) suggest use of Maårtensson et al. (2003). Gong (2003) modified Monahan's source function to account for the observed decrease in the particle concentration for particles smaller than $0.1\,\mu$m radius.

The primary SSA source function describes the surface flux (typically at 10 m 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. Sea-salt generation functions are usually given in the form of a continuous particle – size distribution at a specific relative humidity (RH), e.g. RH = 80%$-r_{80}$ (Monahan et al., 1986; Smith and Harrison, 1998) or at formation $-r_0$ (de Leeuw et al., 2000). Particle radius may also be presented as a dry particles when the relative humidity is zero $-r_{\mathrm{dry}}$. The formulation depends on the way the source function has been derived. The equilibrium droplet size equation is presented in Gong et al. (1997), after Gerber, 1985; Zhang et al. (2005). As a rule of thumb, the Eq. (4) is used (O'Dowed and de Leeuw, 2007):

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

The emissions of drops from breaking wave whitecaps and sea foam is quite well-known thanks to the laboratory studies of, e.g. Wu (1973) and Monahan et al. (1982). Mostly, the source functions are presented as power-law functions and hence, at higher wind speeds, the emission of sea spray increase in greater proportions than the wind speed increase. Thus the source function for bubble mediated sea spray is highly nonlinearly dependent on the surface wind (or friction velocity).

In this project, to calculate the sea salt aerosol production (PM$_{10}$) emitted into the atmosphere, different parameterizations for three radius range are used. For particles radius below 0.8 µm the Maårtensson et al. (2003) parameterisation is applied:

$$\frac{dF}{d\log D_{\mathrm{p}}} = 3.84 \times 10^{-6} {v_{\mathrm{h},10}}^{3.41} \left(A_k T_{\mathrm{w}} + B_k\right) \tag{5}$$

$$A_k = c_4 {D_{\mathrm{p}}}^4 + c_3 {D_{\mathrm{p}}}^3 + c_2 {D_{\mathrm{p}}}^2 + c_1 {D_{\mathrm{p}}}^1 + c_0 \tag{6}$$

$$B_k = d_4 {D_{\mathrm{p}}}^4 + d_3 {D_{\mathrm{p}}}^3 + d_2 {D_{\mathrm{p}}}^2 + d_1 {D_{\mathrm{p}}}^1 + d_0 \tag{7}$$

F – particle flux ($\mathrm{m^{-2}\,s^{-1}}$)
$V_{\mathrm{h},10}$ – mean horizontal wind speed at 10 m height ($\mathrm{m\,s^{-1}}$)
T_{w} – water temperature (K)
D_{p} – dry particle diameter (µm)
A_k, B_k – the polynomials for given size ranges with coefficients c_0 to c_4 and d_0 to d_4 reported in Maårtensson et al. (2003).

For larger particles ($0.8 < r_{80} < 4.0$) the sea salt generation function is taken from Monahan et al. (1986):

$$\frac{\Delta F_i^{\mathrm{spume}}}{\Delta r_i} = 1.373\left|V_{\mathrm{h},10}\right|^{3.41}\left(1+0.057 r_i^{1.05}\right)10^{1.19e^{-B^2}} r_i^{-3} \tag{8}$$

$$B = (0.38 - \log_{10} r_i)/0.65 \tag{9}$$

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

For particles larger than 4.0 µm radius at 80% humidity, the Smith and Harrison (1998) parameterisation is used:

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

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

The main input data indispensable to calculate the emissions are wind speed information at a 10 m altitude above the surface. These data were generated with WRF

(Weather Research Forecast, www.wrf-model.org) model, at a 5 km × 5 km grid square resolution, with a 3-h time step. The WRF set up is described in Vieno et al. (2010). As noted above, to calculate the sea salt aerosol production (PM_{10}) emitted into the atmosphere, different parameterizations for three radius range are used. All formulations are calculated with 0.1 µm radius size step for particles.

It is assumed that at formation, the density of particles is the same as density of sea water at 15 °C and 3.5% salinity and the particles have the same ion composition as ocean water. The particles are assumed to be water containing at salinity representative of the relevant sea. The Monahan (for fine particles) and also Smith and Harrison (for coarse particles) equations used in the present work (defined above) give results for 80% humidity. Therefore the chemical composition is recalculated with the assumption that water evaporates and that radius at 80% humidity is equal to half of the radius at formation Eq. (1). To calculate the mass of PM_{10} sea salt particles it is assumed that they are spherical in shape. To get the dry mass of base cation (Na^+, Mg^{2+}, Ca^{2+}, K^+) the total mass of PM_{10} particles (ions, other species contained in the sea water, and water) is multiplied by the percentage content of a given ion. The mass percentages in sea water contents of particular compounds are the following: Na – 1.05%, Mg – 0.125%, Ca – 0.0398%, K – 0.0386% (Seinfeld and Pandis, 2006).

2.4 Model evaluation

The model results for each year were evaluated by comparison with the measurements of air concentrations and wet deposition of Na^+, Mg^{2+}, and Ca^{2+}.The base cation measurements are undertaken as a part of the UK Eutrophying and Acidifying Pollutants Monitoring Network. The CEH DELTA (Denuder for Long-Term Atmospheric sampling) system, which was originally developed for long-term sampling of ammonia and ammonium (Sutton et al., 2001) was used. The system uses monthly sampling, with stable sampling rates of 0.3-0.4 $\mathrm{l\,min^{-1}}$ achieved using a piston air pump, with air volumes being measured by a high sensitivity dry gas meter. Data from 12 stations for Na^+, Mg^{2+} and 10 stations for Ca^{2+} concentrations (two stations were eliminated because of monthly data) are available for the year 2003. The Delta sampler monitoring network was expanded to 30 stations during 2006, but some of the additional sites did not have a complete data set for this year. Stations which had more than 2 months with no data were removed here from the analysis. It should also be emphasized that calcium air concentrations measurements characterize the largest value of coefficient of variation (CV) in comparison to other species, e.g. for 2006 for calcium there are six months where average for sites CV is higher than 100%, whereas for other species CV is lower than 50%.

There were not large changes in number of stations between 2003 and 2006, but some stations were closed and others established. Total mass of wet deposition was calculated using volume – weighted annual mean concentration (Na^{+}, Mg^{2+}, and Ca^{2+}) and amount of precipitation for each station. For the year 2006, the FRAME national budgets of Mg^{2+} and Ca^{2+} dry and wet deposition were compared with the CBED (Concentration Based Estimated Deposition) measurement-interpolation technique.

3 Results

3.1 Primary marine particles and base cation emissions

The main purpose of the work is to calculate base cation emissions from the sea in the vicinity of the UK domain for the years 2003 and 2006. Before calculating the total production of particles for the domain, some tests for unit area and unit time, concerning the relationship between the wind speed, the number of particles produced and the size of particles, have been done.

A number of particles at definite size emitted per unit of time (1 s) and unit area (1 m^2) have been calculated for different wind speeds: 5, 10, 15 and 20 $m\,s^{-1}$ (Fig. 1a). The largest number of particles is emitted for small size of particles and for the highest wind speeds. For the same wind e.g. 5 $m\,s^{-1}$, the number of particles decreases from about 94 000 for the radius 0.1 µm size to about 40 particles for 5 µm size. Analyzing different wind speeds e.g. $5\,\mathrm{m\,s^{-1}}$ and $20\,\mathrm{m\,s^{-1}}$ it is noticeable that the number of particles decreases by more than 100 times. Figure 1b shows the mass of the particles for the wind speed $10\,\mathrm{m\,s^{-1}}$ emitted for the individual particle sizes. The Monahan et al. (1986) formulation was run for all particles sizes, Måårtensson et al. (2003) for the smallest one, and Smith and Harrison (1998) for the largest particles. Characteristic mode is evident for a 2.5 µm radius. From comparison of different formulations for the same particle radii it is evident that there is quite good correlation for the smallest particles between the Monahan and Måårtensson approaches and the largest difference between Monahan et al. (1986) and Smith and Harrison (1998) results. To determine the influence of wind speed on an emission value, a run for the Monahan et al. (1986) formulation for different wind speeds has been conducted. In comparison to $5\,\mathrm{m\,s^{-1}}$, for $20\,\mathrm{m\,s^{-1}}$ wind speed the mass produced was more than 2×10^4 greater (Fig. 1c). This also means that the detailed information on wind speed, in spatial and temporal terms, is of special importance for sea spray emission calculations.

The highest values of total SSA emission are noted for regions with the highest wind speed, especially over the North Atlantic Ocean and it gives more than $2500\,\mathrm{kg\,ha^{-1}\,year^{-1}}$ (RH = 80%) for fine particles (Monahan et al., 1986 parameterisation), and about $900\,\mathrm{kg\,ha^{-1}\,year^{-1}}$ for particles larger than 4.0 µm (Smith and Harrison, 1998 parameterisation). The mass of ultra-fine particles calculated with the Måårtensson et al. (2003) formulation, for the whole area of the study domain is below $100\,\mathrm{kg\,ha^{-1}\,year^{-1}}$.The lowest mass is obtained close to the land, which is certainly connected to the wind friction and correspondingly lower wind speed. The calculated emissions results are converted to base cation mass according to the percentages given earlier. The average emissions for a grid square in the UK sea domain, for individual base cations are the following: 129, 15, 4.9 and $4.7\,\mathrm{kg\,ha^{-1}\,year^{-1}}$ for 2003 and 145, 17, 5.5 and $5.3\,\mathrm{kg\,ha^{-1}\,year^{-1}}$ for 2006, for $\mathrm{Na^+}$, $\mathrm{Mg^{2+}}$, $\mathrm{Ca^{2+}}$, $\mathrm{K^+}$, respectively.

Maps of the total SSA (RH = 80%) production in kg ha^{-1} for the year 2006 are shown in Fig. 2. There is no evident difference in spatial distribution between SSA production for the year 2003 and 2006, but there is a clear difference in total mass of emission. The mass is about 12% greater for the year 2006.

3.2 Base cation concentration and deposition

The base cation emissions maps for the UK domain described above were used to run the FRAME model for the years 2003 and 2006. Additionally for the year 2006 two more simulations were run to validate the FRAME model with CBED (Concentration Based Estimated Deposition using measurement-interpolation) estimations. In order to establish the relative contributions of sea-salt and land based emissions, the first simulation was performed with land emissions only and the second one with sea emissions only. As a result of each run the average spatial distribution of Na^+, Mg^{2+}, Ca^{2+} and K^+ concentrations and total deposition for a year was calculated.

The distribution of base cation concentration near the surface is presented in Fig. 3. The concentrations are particularly high over oceanic regions with high production of SSA. A gradient in concentration is observed from the coastal regions towards low concentrations over land.

Average yearly concentrations over the land domain were somewhat higher for 2006 than for 2003, and amount to: 2.17 µg m^{-3} of Na^+, 0.22 µg m^{-3} of Mg^{2+}, 0.08 µg m^{-3} of Ca^{2+} and 0.12 µg m^{-3} of K^+. For the year 2003 these values were respectively: 1.89, 0.19, 0.07 and 0.11 µg m^{-3}. Average yearly concentrations for measurement sites, which usually present conditions for the centre of the land but not for the coast area, are evidently lower than the average for the whole land area estimated by the FRAME model. For the year 2003 they amount to 0.80 µg m^{-3}, 0.06 µg m^{-3} and 0.05 µg m^{-3}, respectively for Na^+, Mg^{2+} and Ca^{2+}.

The highest values of FRAME base cation concentrations are noted close to the coastal zone, especially in the western part of UK, which is the result of predominant westerly circulation. In these regions, concentrations of Na^+, Mg^{2+}, and Ca^{2+} can even exceed 5 $\mu g\,m^{-3}$, 0.32 $\mu g\,m^{-3}$, 0.1 $\mu g\,m^{-3}$, respectively. For most areas of the UK the concentrations are in the range of 1.0 to 2.0 $\mu g\,m^{-3}$ for Na^+, 0.05 to 0.12 $\mu g\,m^{-3}$ for Mg^{2+}, and from 0.03 to 0.04 $\mu g\,m^{-3}$ for Ca^{2+}. Increased BC concentrations are also calculated for the centre of the land. This is especially evident for calcium in the region of Northern England and South-West England.

Wet deposition of BC reaches the highest values on the western coast, and over the mountainous regions, where deposition of Na^+, Mg^{2+} and Ca^{2+} exceeds 50 $kg\,ha^{-1}\,year^{-1}$, 6 $kg\,ha^{-1}\,year^{-1}$ and 2.5 $kg\,ha^{-1}\,year^{-1}$, respectively (Fig. 4). The substantial enhancement in wet deposition with altitude can be partially explained with the seeder-feeder enhancement mechanism, whereby rain falling from a higher level cloud (seeder cloud) layer passes through an orographically formed “cap cloud” (feeder cloud) over high terrain (Błaś et al., 1999). As it passes through the cap cloud, the rain scavenges cloud droplets, adding to the rainfall amount and ion content. The concentration is enhanced since cloud droplets are much smaller than rain drops and are thus far more concentrated for a given aerosol loading (e.g. Choularton et al., 1988; Dore et al., 1992; Inglis and Choularton, 2000). For the center part of the land, deposition is significantly lower, and mean value amounts to 14 $kg\,ha^{-1}\,year^{-1}$, 1.4 $kg\,ha^{-1}\,year^{-1}$ and 0.5 $kg\,ha^{-1}\,year^{-1}$ of Na^+, Mg^{2+}, Ca^{2+} respectively.

3.3 FRAME model evaluation

The model results for each considered year were evaluated by comparison of the modelled values with measurements of concentrations and wet deposition of Na^+, Mg^{2+}, and Ca^{2+}. For the year 2006, the FRAME national budget of Mg^{2+} and Ca^{2+} dry and wet deposition were compared with CBED estimations. Figure 5 illustrates the correlation with measurements of modelled Na^+, Mg^{2+} and Ca^{2+} concentrations in air for the years 2003 and 2006. For both years most points are located above/the 2:1 and below the 1:2 reference lines. The best fit is visible for sodium, with correlation coefficient at

0.6 for the year 2006, and the worst for Ca^{2+} for the same year. The spatial distribution of model-measurement errors for all base cation air concentrations is quite similar. The model overestimates concentrations on the western coast and in Scotland, whilst underestimating in the center of the land mass (England). This suggests that there is a general underestimate of transport distances for base cations in the model, which may be due to the simple meteorology and constant drizzle approximation adopted. For sodium overestimations on the west coast are lower and underestimations in England are slightly higher than for other species.

Modelled wet deposition is also compared with measurement data. Wet deposition is estimated by the FRAME model particularly well for sodium and magnesium, with correlation coefficient of 0.8 for both years (Fig. 6). Overestimation mostly occurs for higher values of deposition, which are measured on sites close to the western seaside, and the underestimation occurs in the hilly regions. Considerably larger scattering is evident for Ca^{2+} wet deposition. This could be connected with underestimation of calcium land emissions which are associated with greater uncertainty.

To evaluate the performance of FRAME it is also possible to compare model results with estimations of national budgets of dry and wet deposition of magnesium and calcium prepared by CBED for the year 2006 (Table 1). Both for Mg^{2+} and Ca^{2+} FRAME obtains lower deposition originating from land, with much lower values for calcium than CBED. The reason for this may be underestimation of both anthropogenic and natural emission from the land in the model. In the case of sea emission, lower values of wet deposition and higher values for dry deposition are evident with FRAME. It is interesting to note that underestimation in wet deposition is not visible from model comparison with – station measurements comparison (presented above). It should be noted that large uncertainties can also occur in the CBED calculation due to the subtraction process based on the Na^+ concentration used to separate the contributions from land and sea. Further tests with transport and removal processes from the atmosphere in the FRAME model will be undertaken in future work.

4 Summary and conclusions

The three formulations of Maårtensson et al. (2003); Monahan et al. (1986) and Smith and Harrison (1998) have been used to calculate the SSA production for the UK region. All are based on WRF-derived information on wind speed at 10 m a.s.l. Additionally the Maårtensson function takes into account the temperature effects on the amount of production. The WRF wind speed data at a 5 km × 5 km grid square resolution with a 3 h time step was used to calculate SSA emissions. The calculations were run with a 0.1 µm size step for two selected years: 2003 and 2006. There is no large variations in spatial distribution between the two years, but the mass of SSA production is higher by more than 10% for 2006. Maps of base cation emissions (Na^+, Mg^{2+}, Ca^{2+}, K^+), extracted from the SSA, were used as the input data in the FRAME model.

Spatial patterns of air concentrations of BC show the gradient from the coastal regions towards low concentrations over land. The wet deposition besides reaching high values close to the western coast, is also elevated in high rainfall hilly regions due to seeder-feeder mechanism. The comparison of FRAME results with measurements has shown that the model is capable of predicting base cation concentrations and depositions for the UK region. The model results were found to be in reasonable agreement with measured wet deposition. Unfortunately, there are no measurements available for evaluation of the modeled dry deposition flux. The correlation coefficient for wet deposition achieves high values for Na^+ and Mg^{2+} for both years. The larger scatter for calcium may be connected with underestimation of the land emission, in particular as the contribution of land emission is the highest just for Ca^{2+}. It is also possible that measurements for Ca^{2+} have greater uncertainty. Base cation concentration is also well represented by the model, with some overestimation on the west coast and underestimations in the centre of the land. Future work will consider improvements to representation of the particle removal processes from the atmosphere in the FRAME. This will concern both wet and dry removal processes, and especially detailed consideration of particle size influence effects.

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Table 1. The comparison of FRAME national budget (Gg) of sea salt and non sea salt base cation (Mg^{2+} and Ca^{2+}) with CBED estimations for the year 2006.

simulation	land emissions only		sea emissions only	
FRAME regional deposition budget (Gg)				
	Mg	Ca	Mg	Ca
dry	0.14	1.85	30.16	9.63
wet	0.37	2.55	99.39	31.75
CBED estimations (Gg)				
dry	0.14	9.66	12.0	4.24
wet	0.45	58.01	130.1	47.37

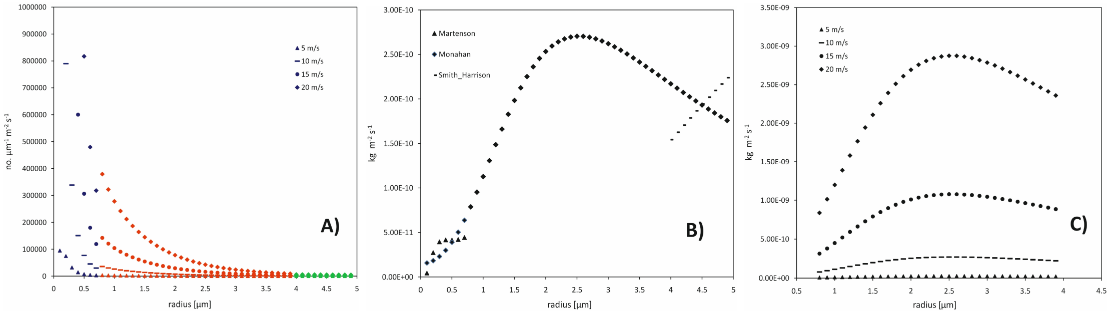

Fig. 1. Sea salt aerosol production: **(A)** number of particles for different wind speed for three parameterizations **(B)** mass emitted for different formulations **(C)** mass emitted for different wind speed for Monahan parameterisation.

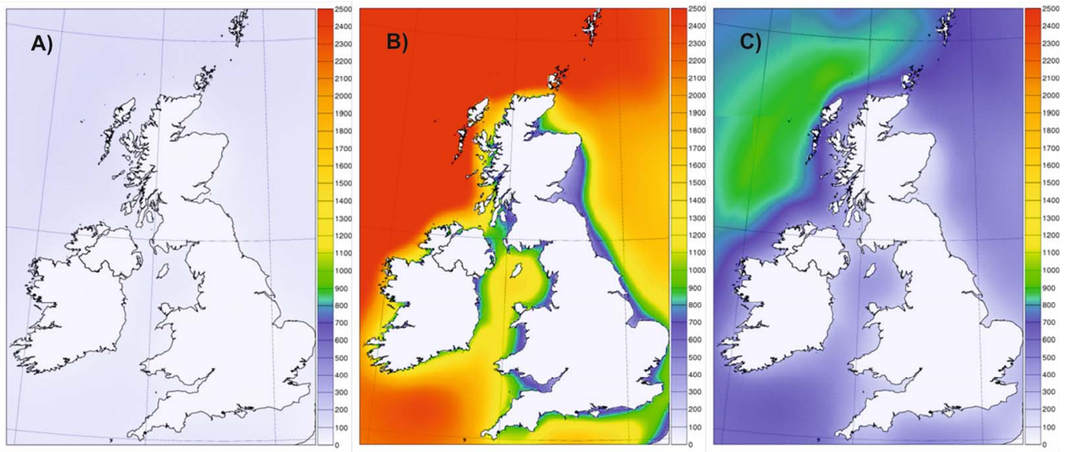

Fig. 2. Sea salt aerosol production of PM_{10} (RH = 80%) for the year 2006: **(A)** $r < 0.8\,\mu m$, **(B)** $0.8\,\mu m < r < 4.0\,\mu m$ **(C)** $r > 4.0\,\mu m$. Units: kg ha^{-1} year^{-1}.

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

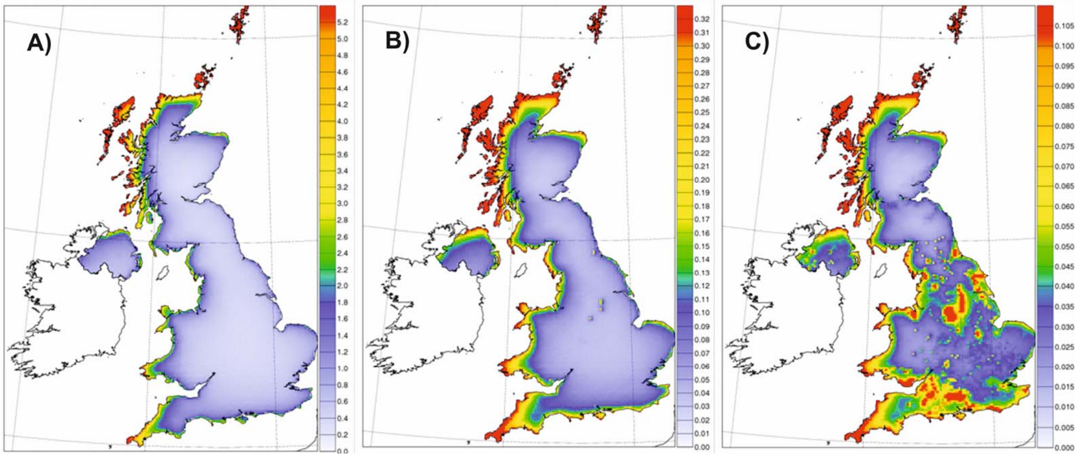

Fig. 3. Distribution of base cation concentrations for the year 2006: **(A)** Na^+, **(B)** Mg^{2+}, **(C)** Ca^{2+}. Units: $\mu g\,m^{-3}$.

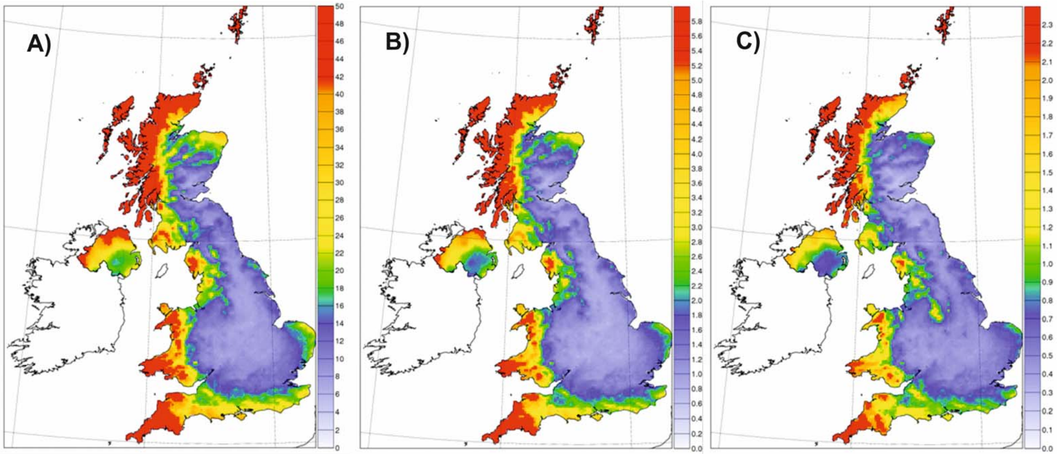

Fig. 4. Spatial distribution of base cation wet deposition for the year 2006: **(A)** Na^+, **(B)** Mg^{2+}, **(C)** Ca^{2+}. Units: $kg\,ha^{-1}\,year^{-1}$.

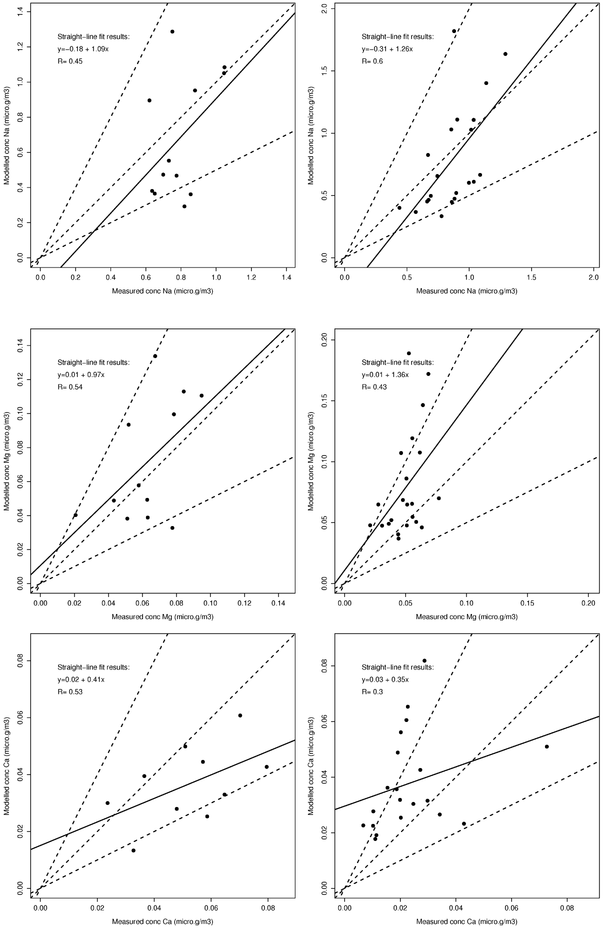

Fig. 5. Correlation of modelled and measured air concentrations of Na^+, Mg^{2+} and Ca^{2+} for the year 2003 (left) and 2006 (right).

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Modelling of base cation emissions, concentrations and deposition in the UK

M. Werner et al.

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
◀
▶
Back
Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

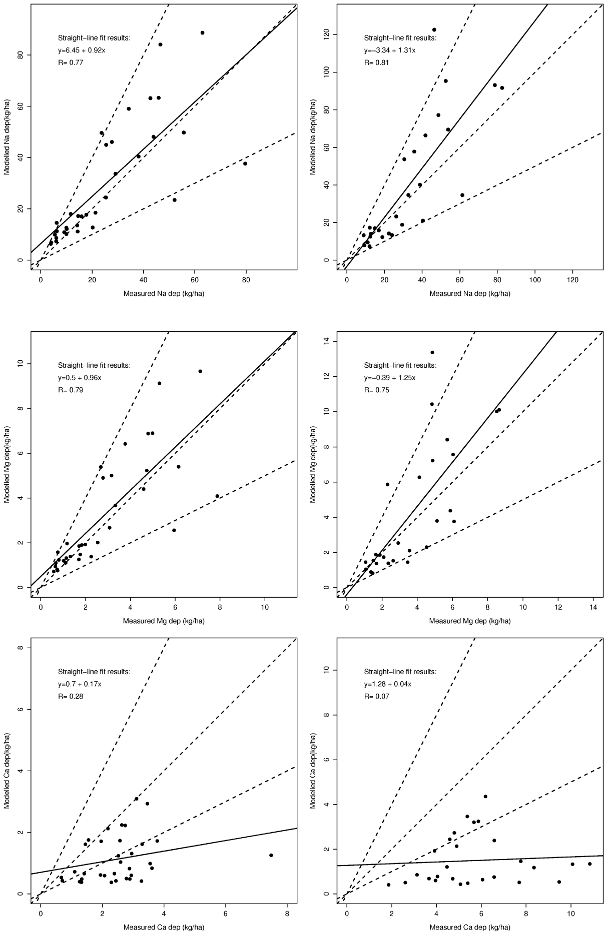

Fig. 6. Correlation of modelled and measured wet deposition of Na^+, Mg^{2+} and Ca^{2+} for the year 2003 (left) and 2006 (right).