Response to the Reviewer

Below is a point by point response to the reviewer's comments. The majority of the suggested changes have been accepted and included in the revised manuscript.

On behalf of the authors,

Małgorzata Werner

1. **One of the general comments is that despite of the title and the aim stated in the Abstract, i.e. modelling of base cations, several parts of the manuscript give an impression that the sea salt modelling is largely in focus. For example, the whole Introduction is dedicated to description of sea spray production (parameterizations); section 3.1 states that "The main purpose of the work is to calculate BC emissions from sea salt…", and it is clearly seen in the results and illustrative figures. Also, in Summary a considerable attention is paid to sea salt production. The authors should decide firmly what the manuscript is about and be more consistent and balanced in presenting the work**.

The authors agree that the base cations of sea salt origin (emissions, concentrations and deposition modelling) are largely in focus and that the title and the aims stated in the abstract and introduction should be more precise. At the first stage, presenting in the paper, land anthropogenic and natural emissions were added in order to make preliminary validation of the model with measurements; to verify the model results.

To meet the reviewers comment, the title has been modified to:

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

Please also see the Reply to Specific comments below.

2. Connected to the first comment, rather limited details are given regarding BC emissions from anthropogenic sources and soil, i.e. their temporal and spatial distribution, relative contribution to the total emission amount (the emission numbers for anthropogenic BC are difficult to compare with sea spray contribution, and no numbers at all are mentioned for natural BC emissions). Also, it'd useful to indicate the uncertainties if available.

We agree with this comment. The title of the paper has been modified, to put more focus on the base cations of maritime origin. Because land emissions were also included in modelling, as this was necessary to compare the FRAME results with measurements, information on land emissions (total mass of emission) are also provided. The emission section was largely modified following the reviewer's comments, and information on emission uncertainties were provided where available. Also, description of temporal and spatial distribution of emission from land sources was included. A map of land emission of calcium was added (see Fig. 1, 2). Emissions of base cation is now summarized in new Table 1, where information on mass emitted from land sources and import from sea region into the land is included. A direct comparison between emissions from land and from sea is not straightforward due to the very different areas concerned and non-finite extent of the Atlantic Ocean.

Table 1. Emissions of base cation from land sources and import from sea region advected into the land (average for 2003 and 2006) [Gg].

Species	**Import from sea region to UK**	**Land anthropogenic**	**Land natural**
Na	1133.2	0.59	-
Mg	123.3	0.64	-
Ca	44.3	2.34	0.15

The following paragraphs have been added or rewritten to meet the reviewer comment:

Introduction, PP. 21991

Base cations enter the atmosphere from natural and anthropogenic sources. Sodium and magnesium originate mainly from sea salt, whereas an important source of calcium is wind blown dust from land areas. In Northern Europe wind blown dust from agricultural soils can contribute up to 40% of total calcium deposition. On average the anthropogenic contribution to base cations deposition in Europe is usually below 15% and is the largest for calcium (van Loon and Tarrasón, 2005).

Introduction, PP. 21993

Soil emission of calcium was calculated using wind blown PM_{10} emissions provided by the NatAir project supported with information on percentage content of calcium in various types of soil. Anthropogenic land emissions were taken directly from the National Atmospheric Emissions Inventory.

Emission section, PP. 21996

According to the NAEI, inventories for base cations have been significantly revised since the first version of calculations, but the estimates are still subject to significant uncertainty. This is because they are based on emission estimates for PM_{10} (which are themselves uncertain), coupled with estimates of the chemical composition of the PM_{10} which add further uncertainty (www.naei.org.uk). The smallest uncertainty is expected for magnesium (-40% to +80%) and the highest for calcium (-50% to +100%).

Estimation of natural land emission of calcium (Fig. 2) was based on PM_{10} wind blown dust emission calculated in the frame of the NatAir project (Korcz et al., 2009; natair.ier.uni-stuttgart.de), and information about Ca^{2+} content in different types of soil. Wind blown dust is estimated with high uncertainty, because it is determined by number of factors, including wind speed, surface wetness and roughness (van Loon and Tarrason, 2005). Uncertainty related with NatAir PM_{10} emission inventory is about 50% (Van Harmelen et al. 2004, after Korcz et al. 2009). NatAir provides data with spatial resolution of 10 km x 10 km and temporal resolution of 1 h. The data was prepared for four years: 1997, 2000, 2001 and 2003. The spatial pattern of the emission for different years is very similar, and changes are due to meteorological condition. The content of Ca^{2+} in the Earth's crust is 3.6%, but in soils the mineral composition is different because of the process of soil formation (Lee et al., 1999). The information on Ca content in soils was taken from Lee et al. (1999) for 106 soil types according to the FAO classification (Batjes et al., 2009, http://www.iiasa.ac.at/Research/LUC/External-World-soil-database), and multiplied by an average PM_{10} wind driven dust emission for the years 1997, 2000, 2001 and 2003. An average for the 4 years, UK wind blown dust emission of Ca amounts 148 Mg $year^{-1}$. The highest is for the year 2003 – 210 Mg, which is the driest year for the last period.

Emission section, PP. 21997

Foltescu et al. (2005) recommend the Monahan and Smith parameterisation, as discussed above, but for the smallest particles (below 0.8 µm radius) suggest use of Mårtensson 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 µm radius. Formulations comparison of a representative expression for the "whitecap method", made by Clarke et al. (2006), show that they lie within, approximately, a factor of 2.

3. As to data for evaluation of model calculated BC, it is advisable to provide (in a form of table or a map) details about measurement sites, especially because the differences in model performance for coastal and inland sites are discussed. Also some more relevant details can be given about the CBED measurements-interpolation technique. These would contribute to get a better insight in possible uncertainties in CBED estimates and help in interpreting comparison between those data with model calculations.

We agree with the comment. Measuring sites have been added on maps with base cation concentrations and deposition. For each site and both years (2003 and 2006) the differences between FRAME estimates and measurements have been calculated and marked on the maps to give the insight on spatial distribution of the model errors and meet the reviewer's comment (see figures 4 and 5).

The description of the CBED interpolation based method was extended (see section Model evaluation), and the references were provided:

CBED (Concentration Based Estimated Deposition) wet deposition data were calculated from measurements gathered at the national monitoring networks of gas concentrations in air and ion concentrations in precipitation (Smith et al. 2000, 2001). The wet deposition model predicted deposition from the mapped actual annual rainfall (based on measurements interpolated from the UK Met Office precipitation monitoring network), estimated orographic rainfall, ion concentration in orographic rain and the feeder rainfall enhancement factor. The rain ion concentrations in seeder rainfall were interpolated over the country to estimate a value for each 5 km grid square. The interpolation from the annual rainfall-weighted mean concentration data at the sites uses kriging with an expotential variogram, a zero nugget and a sill and range determined from the individual year's observations. The feeder rainfall enhancement factor was assumed to have a value of 2 across the country. Dry deposition was calculated using a ‘big leaf’ canopy resistance model combined with interpolation of measurements of base cation concentrations in air (Smith et al. 2000).

4. Furthermore, model results for BC concentrations and depositions would benefit from more in-depth discussion, including e.g. the relative importance of different emission sources (including anthropogenic and soil), main uncertainties in calculated BC due to input data (emissions, meteorology) and model formulations, which could give better understanding of discrepancies between calculations and measurements.

More details have been given regarding BC emissions from anthropogenic and soil sources.
(See also point 2 above). The comments in section “FRAME model evaluation” were
expanded to meet this comment:

Base cations import from the sea areas to land calculated with FRAME amount to 1148 Mg for Na^+, 124 Mg for Mg^{2+}, and 44 Mg for Ca^{2+}, for the year 2006. These values are dominant when compared with the contribution from land emissions (natural and anthropogenic sources), especially for sodium and magnesium. FRAME calculates that base cation emissions from the land sources contribute to 0.4% of total (land and sea) deposition for magnesium and 10% for calcium. According to CBED estimations, land sources also contribute to 0.4% of total Mg^{2+} deposition but more than 50% of Ca^{2+}. According to EMEP, wind blown dust in Northern Europe contributes up to 40% of total calcium deposition.

The comments in section “Summary & Conclusions” were extended, following the reviewer’s suggestion:

FRAME calculates that base cation emissions from the land sources contribute to 0.4% of total (land and sea) deposition for magnesium and 10% for calcium. There is reasonable agreement with the CBED estimations in case of magnesium, where land sources are also estimated to deliver 0.4%, but for calcium this estimation amounts to 50%. According to EMEP, wind blown dust contributes up to 40% of total calcium deposition. This suggests that the soil emission calculated here with NatAir estimations and Ca^{2+} content in the top 30 cm layer soil types is significantly underestimated.

All emissions estimates are subject to uncertainty. Uncertainties related with NatAir estimations of PM_{10} amount to 50% but, additionally, it is necessary to include the uncertainty related to the content of Ca^{2+} in the different types of soil and quality of soil map. In case of anthropogenic emission, the highest uncertainties are reported for Ca^{2+}.

Summary and conclusion section, PP. 22006

Both for concentrations and wet deposition, worse results are obtained for calcium than for remaining chemical components. As the largest contribution of land sources in total emission is reported for calcium, this suggests that land emission of calcium is significantly underestimated, but more work is needed here. Future work should consider improvements to calculations of calcium land emissions and representation of the particle removal processes from the atmosphere in the FRAME model. This would concern both wet and dry removal processes, and especially detailed consideration of particle size influence effects.

Specific comments:

P.21991

Line 1: Introduction talks basically exclusively about sea spray/sea salt

Introduction has been modified to meet this and previous comments (please see the reply to comment 1 above), and the following is added:

In this paper, selected parameterisations schemes (Mårtensson et al. 2003, Monahan et al. 1986 and Smith and Harisson 1998) have been used to calculate marine base cation emissions (Na^+, Mg^{2+}, and Ca^{2+}) for the UK domain for the years 2003 and 2006. In order to calculate base cation concentrations and deposition over UK, estimations of natural land emissions of calcium were made. These emissions were calculated using wind blown driven PM_{10} from the NatAir project and percentage content of calcium in different types of soil. Anthropogenic land emissions were taken directly from the National Atmospheric Emissions Inventory.

P.21992

Line 9: salt particles with radii smaller than 0.1 um also form

The statement has been clarified:

The radii of SSA particles range from below 0.1 µm to over 1000 µm (Lewis and Schwartz, 2004).

Line 11: The years 1986, 1987, 1992, etc. are not so recent:

The statement "In recent years" has been removed.

P. 21993 line 1:What do you mean by „also"?

Changed to "already".

Line 9: which physical properties are meant by „according to physical properties SSA"

The sentence changed:

Taking into account dehydration and chemical composition of marine aerosol, the mass of base cation compounds (Na^+, Mg^{2+}, Ca^{2+} and K^+) was calculated from the total mass of SSA.

P21995

Line 14-15: Are the"annual rainfall fields" used in model calculations? Or some temporal variation is imposed on them?

The sentence has been changed:

The data are used in the form of annual rainfall fields for the UK and Ireland, with a resolution of 5 km x 5 km, for the years 2003 and 2006.

P21996 Emissions: It would be quite useful to show maps of anthropogenic and soil BC emissions

The maps have been added (see Fig. 1, 2)

lines 18-23: it's worth describing more the natural Ca emission estimates, e.g. Spatial and temporal resolution, and also their inter-annual variability (since average emissions were used for the calculations).

Information on spatial and temporal resolution and inter-annual variability has been included. Please see the reply to point 2 in General comments above.

P 21998

line 5: why „particle-size distribution"

The sentence has been modified:

Sea-salt generation functions are usually given in the form of a continuous particle-size distribution (the amount of emitted particles is depended on particle radius) at a specific relative humidity (RH), e.g. RH = 80% denoted as r_{80} (Monahan et al., 1986; Smith and Harrison, 1998) or at formation, denoted as r_0 (de Leeuw et al., 2000).

line 13-14: I think it is quite right to state that „the emissions of drops from breaking wave whitecaps and sea foam is quite well known". The uncertainties are considerable.

We agree with this comment. The uncertainties related with estimation of sea spray emissions are considerable, and are now described in the Emission section. Please also see point 2 in General comment above.

Line 15-18: many repetitions; e.g. no need to say non-lineary if it was described as power-law function.

The sentence has been removed.

Line 19: somewhat slack formulation "sea salt aerosol production (PM10)"

The sentence changed:

In this project, to calculate the PM_{10} sea salt aerosol emission into the atmosphere, different parameterisations for three radius ranges were used.

Line 21: Which radius is referred to here, r80 or r0?

The sentence has been clarified:

For particles radius (r_{80}) below 0.8 µm the Mårtensson et al. (2003) parameterisation is applied.

P 22000

Line 5: what is the size range of calculated SSA? In particular, what is the upper size limit of sea salt particles used for describing PM10?

SSA emissions are calculated up to 10 µm of particles diameter.

Also, nothing is said about how SSA emissions were distributed between model vertical layer.

The information has been included in "FRAME model" section:

The emission from anthropogenic sources was inserted into the model according to the height of stack. The marine and wind blown dust emissions of base cations were injected in the surface layer (first layer of the FRAME model).

Line 28: what is meant by “two stations were eliminated because of monthly data”?

The sentence has been changed:

Data from two stations was removed due to insufficient monthly measurements following quality control.

P 22001

Line 4-8: Please elaborate a bit more regarding “large coefficient from Ca: what are plausible the reasons (e.g. large temporal variations due to windblown dust?) Or measurements artefacts?) and implication of this.

Currently, we cannot address this issue quantitatively, and more measurements are needed to find the reasons for this. The sentence has been removed from the manuscript.

Line 9: “not large change in number of stations”? from 10-12 to 30 in 2006

This large change concerns stations measuring concentrations of base cation but not wet deposition. The sentence has been changed for clarification:

There were no large changes between 2003 and 2006 in a total number of stations measuring wet deposition.

Line 19-20:what exactly was tested in those tests? And how the results of the tests were further used in the work, e.g. in interpretation of model calculations. I am not sure it is necessary to include these tests in the section about results (they only shift the focus even more to the issue of sea spray source function parameterizations).

We agree with this comment. The text has been modified for clarification and moved to the emission section.

PP 22000

Using WRF data, with high spatial and temporal resolution, has great influence on the results of base cation calculations, as the large amount of base cations is emitted during relatively short periods with strong wind. Figure 3 presents the number of particles (A) and the mass of particles (B) at definite size emitted per unit of time (1s) and unit area (1m^2) for different wind speeds (5, 10, 15 and 20 m s^{-1}). The number of emitted particles increases by more than 100 times when changing the wind speed from 5 to 20 m s^{-1}, and the emission mass will be greater more than 2*10^4.

22002

Lines 15-26: Unclear what results are discussed here? If those in fig. 2, references should be given here. I think it is a bit confusing that authors talk here about emissions from three individual sources functions. Have not they be combined in a single scheme in FRAME. As to the numbers given for emissions of ultra-fine , fine and coarse SSA, do they correspond to the same grid cell/area, or they describe just random grids?

Yes, the results refer to Fig. 2 (now Fig. 4). The text has been modified for clarification:

The highest values of total SSA emission are noted for regions with the highest wind speed, especially over the North Atlantic Ocean. For fine particles it is more than 2500 kg ha^{-1} year^{-1} (RH=80%), and about 900 kg ha^{-1} year^{-1} for particles larger than 4.0 µm (Fig. 4). The mass of ultra-fine particles for the whole area of the study domain is below 100 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 domain average emissions from the sea, for individual base cations are as follows: 129, 15, 4.9 and 4.7 kg ha^{-1} year^{-1} for 2003 and 145, 17, 5.5 and 5.3 kg ha^{-1} year^{-1} for 2006, for Na^+, Mg^{2+}, Ca^{2+}, K^+, respectively.

Line 24: what is meant by “the UK sea domain”? Any formal definition, e.g 100 or 200 nautical miles?

The domain was defined in the “FRAME model” section. The sea domain fits in the FRAME domain.

“The domain of FRAME covers the British Isles with a grid resolution of 5 km and grid dimensions of 172 x 244.”

P.22003

Line 4: Is the larger SSA production due to larger wind speeds in 2006 compared to 2003.

Yes, the increase of SSA production for the year 2006 is connected with larger wind speeds for this year.

The sentence has been modified for clarification:

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 caused by higher wind speed for 2006.

Line 14: Is that a map from the run with total (land+sea) emissions? It would be interesting to include a map showing the relative contribution of e.g. sea salt source; and for Ca2+ it would be useful to also see separate contributions from anthropogenic and soil dust sources.

Yes, the map presents results from the FRAME run with total (land+sea) emissions. To meet the reviewer’s comment, we have also added here a map showing Ca^{2+} concentration from anthropogenic and soil dust sources (see Fig. 5).

P.22005

Line 1-15: it would be worth discussing why the results for (only) Ca compares with measurements rather differently for 2003 and 2006; due to uncertainties in natural dust emissions? What was particular about 2006 in this respect, e.g. dry and windy? Or the anthropogenic emissions? Why Ca in precipitation is so underestimated, while Ca in air is

so much overestimated in 2006? The suggestion that the land emissions are underestimated does not explain the latter.

The text has been modified to meet this and previous comments. Please see also point 2 and 4 in General comments.

PP. 22005

In the case of calcium whilst the model – measurements comparison is poor, also there is a significant difference between this two years. For 2003, the concentrations are generally underestimated, but for 2006 the overestimation is evident. At the same time a significant decrease in wet deposition occurs. Because this state is evident only for calcium, and for other species the correlations are well presented, we conclude that the problem is not in marine emission. To explain the discrepancy for Ca between results for these two years, more work would be necessary concerning wind blown dust emission as well as removal processes in the FRAME model.

Line 3-4: how can we see that if none description of sites is provided.

The maps with model-measurements differences have been added (see Fig. 3).

Line 16: the authors write that it was "possible to compare model results with estimations of CBED budgets" to evaluate its performance despite acknowledging large uncertainties of in CBED calculations. Is it known how large those uncertainties could be and what kind of biases they could cause in the estimates? The comparison shows some rather severe disagreement between FRAME and CBED dry and wet deposition, but which of those two should we trust more.

There are discrepancies between CBED and FRAME results but there is good agreement of FRAME results with site measurements sites for Na^+ and Mg^{2+}. In case of Ca^{2+}, as it was mentioned above (ex. point 2 and 4 in General comments). Uncertainties exist in the FRAME estimates, as discussed. However large uncertainties with CBED estimates of deposition also occur due to interpolation of measurements from a limited number of points across the country. In particular, estimation of non-sea salt deposition by measurements is subject to large uncertainty as it involves calculating the difference between two numbers (the measured total Ca^{2+} and Mg^{2+} concentrations and the Ca^{2+} and Mg^{2+} sea salt concentrations which were inferred from measurement of the Na^+ concentration).

P.22006 Summary and conclusions

Again, much of the first paragraph is about sea salt implementation in the model, and nothing about other BC sources.

Yes, we agree with this comment. A modified text has been added to the summary:

PP. 22006, line1:

The main source of base cations, especially of sodium and magnesium, for the UK is the aerosol produced from the sea surface. For calcium, emission from wind blown dust and anthropogenic sources is also important. Anthropogenic emissions of base cation have decreased more than 70% for all analysed species for the period 1990-2006, and they amount to 585 Mg for Na^+, 616 Mg for Mg^{2+} and 2125 Mg for Ca^{2+} for the year 2006. According to the NatAir estimations, on average for one year, soil emission contributes 148 Mg of Ca^{2+} which represents about 7% of total (soil + anthropogenic) land emissions.

PP. 22006

SSA in air advected to the land 1148 kt of Na^+, 124 kt of Mg^{2+}, and 44 kt of Ca^{2+}, for the year 2006. FRAME calculations of contribution of land emission to total deposition are in close agreement with CBED estimations for magnesium, where both FRAME and CBED calculate 0.4%. In case of calcium, CBED estimates contribution of land sources to 50% and FRAME 10%.

All types of emissions are subject to uncertainty. Uncertainties related with NatAir estimations of PM_{10} amount to 50% but, additionally, it is necessary to include the uncertainty related to the content of Ca in the different types of soil and quality of soil map. In case of anthropogenic emission, the highest uncertainties are reported for Ca (-50% to +100%). As for Na and Mg, for which the contribution of marine base cations is much higher than for Ca, also the FRAME model results are in a better agreement with measurements and CBED estimations than for Ca.

Lines 10-11 say "Maps of base cation emissions (Na+, Mg2+, Ca2+, K+), extracted from the SSA, were used as the input data in the FRAME model". Are not sea salt is calculated online, along with the other BC components?

For the trajectory models like FRAME, emission data have to be prepared off line, output to the files of right format, which are then read in by the model. The following explanation was added to the Emission section (PP. 22000): Spatial information on emission, calculated with the presented parameterisations, were exported to the external files, and included off line to the FRAME model.

Line 20-21: "The larger scatter for calcium may be connected with underestimation of the land emission" – rather arguable statement; I'd say due to emission uncertainties. Could the authors say which of the land emissions (anthropogenic or natural) contribute most to calcium concentrations/depositions and their uncertainties?

The paragraphs concerning contribution of different sources of base cation in total amount have been added. Please see above: PP. 22006, point 2 in General comments.

Line 22-23: "It is also possible that measurements for Ca2+ have greater uncertainty" – please explain why? And what kind of artefacts (positive/negative) are expected?

The sentence has been removed from the 'Summary' section. More details concerning wet deposition measurements have been given in 'Model evaluation' section.

Measurements of Ca^{2+} and Mg^{2+} concentrations by ion chromatography have greater uncertainty than Na^{+} due to their lower concentrations in solution. Uncertainty in measurements of Na^{+} concentrations is estimated at approximately (+/-) 5% and for Ca^{2+} and Mg^{2+} (+/-) 15%. In addition it should be noted that the precipitation chemistry monitoring network uses bulk samplers and can be subject to some dry deposition on the collector surface, which may lead to over-estimates of 20% in ion concentrations in precipitation.