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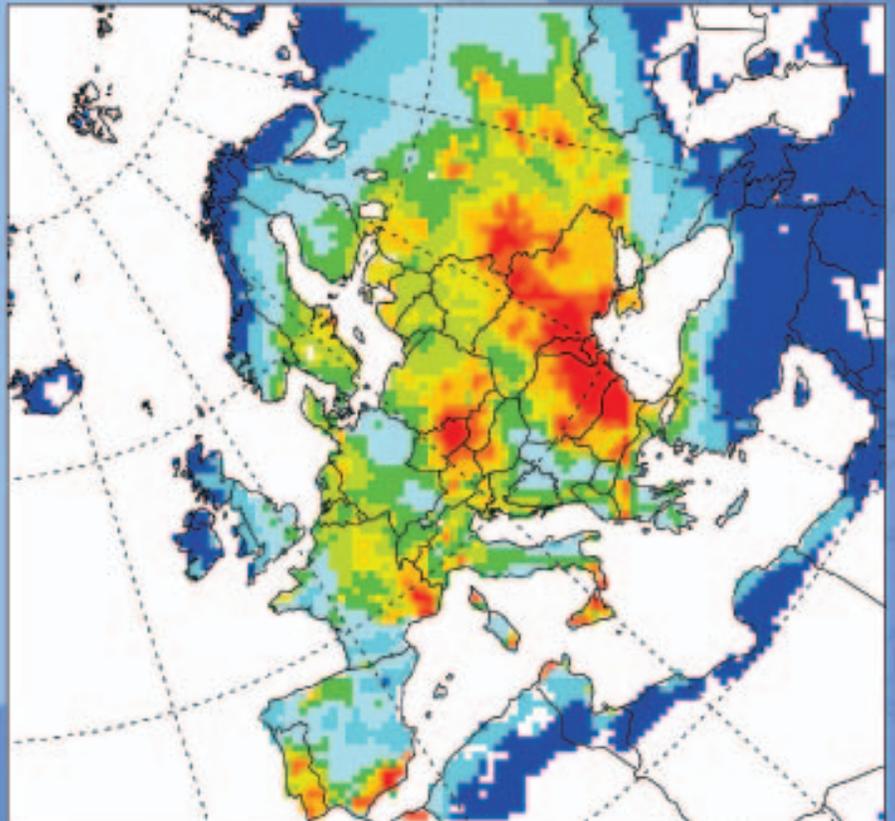
*Co-operative programme for monitoring  
and evaluation of the long-range  
transmission of air pollutants in Europe*

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## Modelling Base Cations in Europe

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## Executive Summary

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Base cation deposition is an important factor affecting the critical loads of acidity and the recovery of ecosystems affected by acidification. Up to present, most estimates of base cation depositions over Europe used to calculate the critical loads of acidity have been based on empirical approaches. The estimates used by the national experts largely vary from each other, depending on the quality of the used observations of base cation content in precipitation and on the empirical assumptions made to derive dry deposition fluxes. On request from the Working Group on Effects, EMEP/MSC-W has carried out this first co-operative attempt to derive a generalized model approach to derive base cation depositions over Europe.

The results presented here are initial estimates of the base cation total deposition of calcium (Ca), magnesium (Mg), potassium (K) and sodium (Na) based on the Unified EMEP chemical transport model. The estimates are valid for year 2000 and include both natural and anthropogenic sources of base cations. They provide a generalized approach over Europe and are intended for use by the Working Group on Effects as input for their calculations of critical loads of acidity over Europe.

In order to include base cations, the Unified EMEP model has been extended. The most important additions to the model are related to the calculation of sources of base cations. Once their sources are determined, the transport and deposition of base cations in the atmosphere is straight forward since base cations can be considered in the same way as primary particles. However, the determination of sources of base cations has required considerable effort and the estimates presented here should be considered only as a first step. Future efforts should be directed to the further development and validation of sources of base cations.

Anthropogenic emissions of Ca, Mg, K and Na from combustion and industrial processes have been derived based on a detailed disaggregation of sector emissions of primary particles (PM) and available information on the chemical composition of the particles. The new estimates are 424 ktonnes for Ca, 54 ktonnes for Mg, 91 ktonnes for K and 49 ktonnes for Na and are considered to be valid for year 2000. In the

case of calcium, the new estimates are considerably lower than previous estimates of Lee and Pacyna (1999), valid for 1990. However, the new estimates are based on a robust methodology and, although further information of the base cation content in PM would be desirable, the new estimates seem to be appropriate for the emissions around the year 2000.

Natural sources of base cations from sea salt and wind blown dust have been estimated in this work. Base cations from sea salt production have been parameterized following the Unified EMEP modelled PM<sub>10</sub> production from sea salt and the chemical composition of sea salt. For wind blown dust emissions, a new subroutine has been developed to describe both saltation and sandblasting processes. The study distinguishes the origin of wind blown dust from three different classes: wind blown dust from agricultural soils, Saharan dust emissions inside the EMEP domain and Saharan dust emissions entering the EMEP domain as boundary conditions. For all these cases, the composition of soils needs to be determined and a first estimate has been elaborated in co-operation with the Working Group on Effects to secure consistency within the LRTAP Convention.

It is shown that natural wind blown dust sources are by far dominating the deposition of calcium and potassium. Sodium and magnesium depositions and air concentrations originate primarily from sea salt, their occurrence being mostly confined to coastal areas. The anthropogenic contribution to base cation deposition is largest for Ca and K but is usually below 15%, except over Scandinavia and Russia, where anthropogenic emissions can contribute up to 20-25%. The contribution of wind blown dust is also largely different for Southern and Northern Europe. In Southern Europe, Saharan dust can contribute up to 70-80% of the calcium deposition. In Northern Europe, wind blown dust from agricultural soils is dominating, and can contribute up to 40-50% to the total calcium depositions.

Initial comparisons with observations of wet deposition fluxes of base cations compiled at the EMEP and ICP-Forest networks show encouraging results, in particular for Ca. The model reproduces well the distribution of the base cation depositions over Europe, with spatial correlations up to 0.70. For calcium, the model shows the best performance, with a slight tendency to underestimate wet deposition fluxes (bias of -15%). The underestimation of wet deposition fluxes for potassium is more significant, and is probably related to the fact that the present version of the model does not totally account for wind blown dust sources of K since the potassium content in soils is not available for all areas. For Na and Mg, the present model calculations considerably underestimate the observed values. This is related to the sea salt production of base cations and requires further attention in the near future. It is intended to continue the development and validation of the EMEP model calculations for base cations, in particular as more information on air concentrations become available following the implementation of the new EMEP Monitoring Strategy.

Comparison of the present EMEP model estimates with previous empirical values of base cation depositions shows differences of  $\pm 25-50\%$  in different European areas. For the meteorological conditions in 2000, the new estimates show larger depositions

along the coast of the Benelux countries and smaller depositions in Germany, Poland and the UK. This will undoubtedly affect the calculation of critical loads in these areas with exceedances. Given the initial good agreement with available observations and the extent of the differences with previous approaches, it is recommended that the ICP on Modelling & Mapping evaluates the consequences of using this generalized approach for dynamic modelling and in their critical load calculations.



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# CHAPTER 1

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## Introduction

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### 1.1 The need for base cation deposition

Base cations such as calcium (Ca), magnesium (Mg) and potassium (K) are important plant nutrients and their associated anions as well as sodium (Na) may reduce the acidity of air and precipitation and increase soil base saturation. Part of the acid input to the soils may therefore be counteracted by deposition of base cations. For some regions it is estimated that more than 50% of the acid input is neutralized by base cations (Draaijers et al. (1997)). Thus, base cations play an important role in determining the critical load of acidity. Even though all over Europe significant emission reductions of acidifying compounds (in particular of  $SO_x$ ) have been achieved over the past two decades and as a consequence acid input to ecosystems has substantially decreased, for large parts of Europe still exceedances of critical loads for acidity are computed, see the EMEP MSC-W Status Report for 2004, Tarrasón et al. (2004). As can be seen from Figure 1.1 these exceedances occur mostly at latitudes between 40 and 60 degrees. In addition, there are clear indications that the base cation deposition has decreased over the last decades. This means that the amount of acid input to the soil that is neutralised by base cation input has decreased. As a result, the overall decrease in acid input is relatively less than the decrease in emission of acidifying compounds and the critical levels for acid input will decrease. Hedin et al. (1994) show a dramatic decline in concentrations of non sea-salt Ca, Mg and K in precipitation over North America and Europa. Similar findings were reported by Lee et al. (1999) for the period 1974-1993 and by Tørseth et al. (1999) for the period 1986-1996. The latter study is restricted to Norway, but in addition to concentrations in precipitation also air concentrations are taken into account, as the Norwegian monitoring network is one of the few networks that provide such data since the mid 1980s.

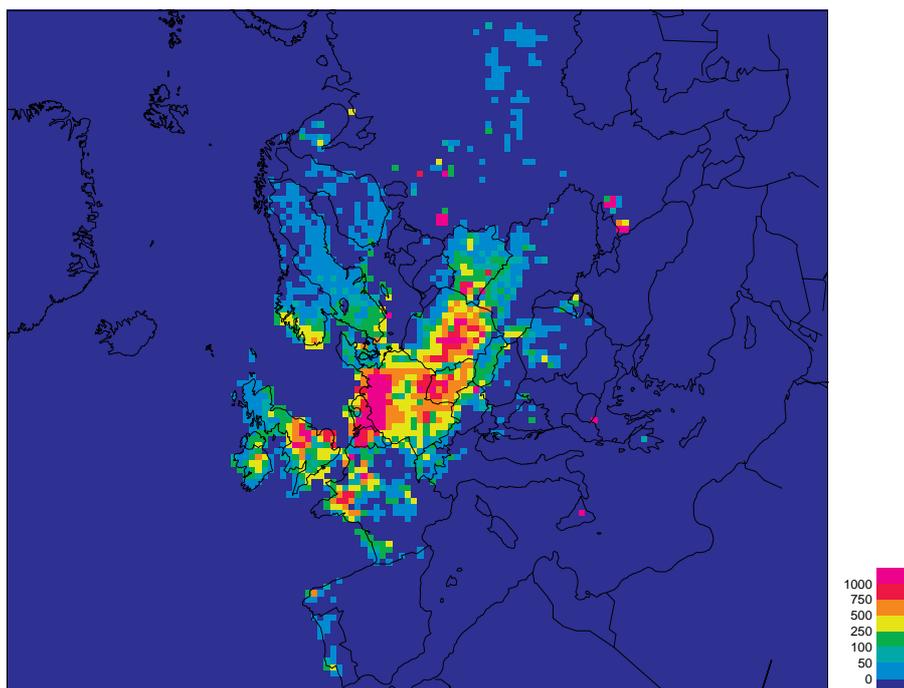


Figure 1.1: Calculated exceedances (in eq/ha/yr) for critical loads for acidification (Fig. 5.19 in Tarrasón et al. (2004)).

The apparent general decline in base cations concentrations, both in air and in precipitation, points in the direction of decreased anthropogenic emissions. However, there are important natural sources of base cations, namely those related to wind blown dust and sea salt emissions, where trends are not so clear. Given the role of base cations in the critical load of acidity, it is important to quantify their sources and subsequently estimate the transport and deposition of base cations.

## 1.2 Current estimates of base cation deposition

Until recently, there have been few attempts to model base cations concentrations in air and depositions, despite the fact that their role in critical load modelling has been widely acknowledged. Most estimates of base cation depositions used in critical load calculations have been based on measurements of wet deposition fluxes. The total deposition of base cations has been calculated as the sum of the observed wet deposition fluxes and a rough estimate of the dry deposition fluxes, which are empirically derived as a percentage of the wet fluxes, see van Leeuwen et al. (1995, 1996), Spranger (2004). This empirical approach, however, is not generalized over Europe and has the important drawback of not being able to determine the origin of the different sources of base cations. For source allocation purposes, it is necessary to model the transport and deposition of base cations. This involves among other things an estimation of their

anthropogenic and natural sources. In Lee and Pacyna (1999) an attempt is made to estimate the anthropogenic calcium emissions from industrial sources. Their estimate for anthropogenic calcium emissions in Europe for the base year 1990 is 745-802 ktonnes Ca yr<sup>-1</sup>, of which point sources are responsible for about 256-314 ktonnes Ca yr<sup>-1</sup>. In a companion paper (Lee et al. (1999)), the Ca emissions database is used together with an estimate of the natural Ca emissions from arid regions in order to model Ca deposition over Europe. Model results are then evaluated against measurements in the United Kingdom. The evaluation shows a large gap between modelled Ca total deposition fluxes in the UK and those estimated from measurements: 30 ktonnes yr<sup>-1</sup> versus 103 ktonnes yr<sup>-1</sup>. This large difference is attributed by Lee et al. (1999) to the fact that wind blown dust emissions from agricultural soils were not taken into account in their model calculations. According to their conclusions, the contribution from wind blown dust from agricultural sources to the calcium deposition in the United Kingdom would represent about 70% of the total. This percentage may be rather high, especially because the authors seem to be underestimating the contribution from the Sahara, but it still indicates the need to include agricultural wind blown dust emissions in base cation deposition calculations.

Concerning Saharan dust, several publications report Saharan dust outbreaks in large areas of Europe, the largest contributions being reported in southern Europe, see for example Rodríguez et al. (2002b,a, 2001). Consequently, modelling of base cation deposition in Europe needs to take into account Saharan dust emissions.

### 1.3 This work

This work is a first attempt to model the deposition of base cations in the EMEP area. Yearly total depositions of calcium (Ca), magnesium (Mg), potassium (K) and sodium (Na) are presented for the year 2000. The calculations have been performed using an extended version of the Unified EMEP model. The advantage of using a chemical transport model for the calculation of base cations in Europe is that it provides a physical description of the wet and dry deposition fluxes. The model results provide a common approach and are intended for use by the Working Group on Effects (WGE) as input for their calculations of critical loads over Europe.

A first attempt has also been made to quantify four different sources of base cations: anthropogenic sources, Saharan dust emissions, emissions from wind blown dust from agricultural soils and sea salt. The first results indicate a large contribution from wind blown dust sources, both from the Sahara and from agricultural soils. However, the results are subject to a number of uncertainties, especially concerning the parametrisation of wind blown dust sources and the sea salt contribution.

Initial comparisons with observations of wet deposition fluxes from the EMEP and ICP Forest networks show encouraging results. The comparisons have to be extended to measurements of dry deposition fluxes and air concentrations which are currently not available, but which are envisaged to be compiled under the new EMEP monitoring

strategy. Given the initial good agreement with available observations and the differences with previous approaches, it is recommended that the ICP Modelling & Mapping evaluates the consequences of using this generalized approach for dynamic modelling and in their critical load calculations.

## CHAPTER 2

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### Anthropogenic Emissions

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The main anthropogenic sources of base cations are: a) combustion processes using coal and wood fuels and b) industrial processes, such as cement production, iron- and steel industry. Emissions of base cations from these anthropogenic processes are relatively small compared to emissions to natural sources. Of the considered base cations, emissions of calcium from these processes are by far the largest.

#### 2.1 Methodology

At present, few data are available on emissions for base cations. Emissions from anthropogenic sources in the Nordic countries have been inventoried to a limited extent (Lövblad (1987), Antilla (1990), Kindbom et al. (1993)). At European level, only calcium emissions have been inventoried with sufficient level of detail to allow atmospheric transport modelling of such sources (Lee and Pacyna, 1999). However, base cation emission information can be derived from emission data of particulate matter if described per sector. Such information is available through different initiatives like the CEPMEIP project, the PM information reported to UNECE/EMEP (Vestreng and Klein (2002)) and recently also the new estimates of PM sector emissions made by IIASA under the CAFE Baseline project.

We briefly outline the methodology we have followed in order to derive estimates of the anthropogenic base cation emissions for the year 2000. This year has been chosen because of the availability of rather large amount of observational data (see Chapter 5) and well validated emission estimates for PM (IIASA estimates, Klimont (2004)).

Base cations are emitted in the form of particles. Depending on the emissions processes, the emitted particles have different speciations, thus determining the emissions

of base cations. We have determined the base cation content of primary PM particles for different emission sectors based on the following available data:

- Detailed country-wise sector data from IIASA on PM<sub>10</sub> and PM<sub>2.5</sub> emissions. The data correspond to the CAFE Baseline (version August 2004, Klimont (2004)) and include a total of 44 countries/areas. Where applicable, the data include information on fuel type which is of relevance because within the same emission sector very different base cation contents may apply depending on the fuel type.
- Emission data on base cations for the UK from Goodwin (2004). These data include about 50 different source sector for base cations in the form of percentages in total PM<sub>10</sub>. Also the sector totals for the UK are available. The dataset provides data for each year in the period 1990-2001.
- Estimates of base cation content in PM are available for Nordic Countries from Kindbom (2004) and Antilla (1990).
- Estimates of calcium emissions for Europe from Lee and Pacyna (1999).

For use in EMEP modelling, base cation emissions have been derived per SNAP level 1 sector. The following three steps methodology has been applied.

- Firstly, we identified the sectors within the data from IIASA that have non-zero base cation fractions according to the above mentioned references. These fractions are given in Table 2.1.
- Secondly, we multiplied these fractions by the corresponding PM sector emissions provided by IIASA to obtain base cation emissions.
- Thirdly, we aggregated the base cation emissions in the IIASA sectors given in Table 2.1 into SNAP level 1 sectors.

For use in modelling base cation emissions need to be spatially distributed by country, per sector and for two different size fractions (fine and coarse). All this information is necessary, because it affects the transport and deposition conditions of base cations. In order to derive the necessary emission information, given the limitations of the available data, we made a number of assumptions. A first, maybe trivial but necessary, assumption is that the sources included in Table 2.1 represent the bulk of the total anthropogenic base cations sources. For combustion sources the same base cation fractions have been assumed for all different coal types. This is because for this study no information was available to distinguish between different coal types. The same holds for all different fuel types. For residential/commercial combustion wood has been taken as fuel type whenever "Other solid-low S (biomass, waste, wood)" was specified as fuel in the IIASA data. It appears that most of the PM emissions in this category originate from fire places which can indeed be assumed to be the result of

snap	category	description	fuel type	Ca	Mg	K	Na	reference
1	Fuel prod. and conversion	Combustion	all coal types	4.65	1.25	1.48	1.51	UK, A1990, SE
1	Fuel prod. and conversion	Combustion	other fuel types	0.29	0	0	0.19	UK
1	Power plants: combustion	Power plants & district heat plants	all coal types	4.65	1.25	1.48	1.51	UK, A1990, SE
1	Power plants: combustion	Power plants & district heat plants	other fuel types	0.92	0	0	0.61	UK
1	Industrial processes	Briquettes production	n.a.	4.65	1.25	1.48	1.51	UK, A1990, SE
2	Residential-Commercial	Combustion: fi re places	wood	30	3	8	0.5	A1990, SE
2	Residential-Commercial	Combustion: boilers	coal	4.65	1.25	1.48	1.51	UK, A1990, SE
2	Residential-Commercial	Combustion: boilers	wood	30	3	8	0.5	A1990, SE
2	Residential-Commercial	Combustion: stove	coal	4.65	1.25	1.48	1.51	UK, A1990, SE
2	Residential-Commercial	Combustion: stove	wood	30	3	8	0.5	A1990, SE
2	Residential-Commercial	Combustion: other	other fuel types	0.29	0	0	0.19	UK
3	Industry	Combustion in boilers	coal	4.65	1.25	1.48	1.51	UK, A1990, SE
3	Industry	Combustion in boilers	other fuel types	0.29	0	0	0.19	UK
3	Industry	Other combustion	coal	4.65	1.25	1.48	1.51	UK, A1990, SE
3	Industry	Other combustion	other fuel types	3	2	1	2	UK
3	Industrial processes	Secondary aluminium production	n.a.	0.29	0	0	0.19	UK
3	Industrial processes	Cast iron	n.a.	4.65	1.25	1.48	1.51	UK, A1990, SE
3	Industrial processes	Cement production	n.a.	30	1	1	1	UK, SE, LP
3	Industrial processes	Glass production	n.a.	7.51	1.2	0.75	9.65	UK
3	Industrial processes	Lime production	n.a.	32	0	1	0	UK, SE
3	Industrial processes	Other non-ferrous metals production	n.a.	0.29	0	0	0.19	UK
3	Industrial processes	Pellets plants	n.a.	0.29	0	0	0.19	UK
3	Industrial processes	Sinter plants	n.a.	3.6	0.6	0.1	0.1	UK, SE
4	Industrial processes	Primary aluminium production	n.a.	1	1	1	1	UK
4	Industrial processes	Basic oxygen furnace	n.a.	7.86	1.09	0.17	0.37	UK
4	Industrial processes	Coke oven	n.a.	4.65	1.25	1.48	1.51	UK
4	Industrial processes	Electric arc furnace	n.a.	7.51	1.81	1.2	1.3	UK, SE
4	Industrial processes	Open hearth furnace	n.a.	1	1	1	1	UK
4	Industrial processes	Pig iron, blast furnace	n.a.	3.57	0.69	0.5	0.25	UK, SE
4	Industrial processes	Small industrial and business facilities - fugitive	n.a.	0	0	0	7.36	UK
4	Mining	Bauxite, copper, zinc ore ore, manganese ore, other	n.a.	1	1	1	1	UK
4	Storage and handling	Cement, bauxite and coke	n.a.	28.6	0	2	0	UK, SE, LP
7	Road Transport	All road transport	medium destillates (diesel and light fuel oil)	0.29	0	0	0.19	UK
8	Other Mobile sources	Other transport	medium destillates and heavy fuel oil	0.29	0	0	0.19	UK
8	Other Mobile sources	Other transport	hard coal	4.65	1.25	1.48	1.51	UK, A1990, SE

Table 2.1: Percent base cations in primary PM emissions from literature as used in this study

Note: UK refers to data obtained from Goodwin (2004), SE refers to data from Kindbom (2004), A1990 refers to Antilla (1990) and LP to Lee and Pacyna (1999).

wood burning. In certain cases, however, this assumption may lead to an overestimation of in particular the calcium emissions in this sector, since 30% of the resulting PM emissions are assumed to be in the form of Ca in case of wood burning (see Table 2.1). More detailed information would be necessary to refine the emission estimates at this point. The base cation content for the different sectors has been assumed to be the same for all countries/areas. This could be improved if country specific information would become available. For countries/areas for which no sector information was available from IIASA an average base cation content per SNAP level 1 sector was applied. The base cation content has been assumed to be same for  $PM_{coarse}$  and  $PM_{fine}$ . And finally, the spatial distribution of the base cation emissions follows the existing gridding for each of the SNAP level 1 sectors.

## 2.2 Calculated emissions and comparison with other estimates

The calculated emission totals for each of the countries/areas in the IIASA data are listed in Table 2.2 and the corresponding percentages in Table 2.3. As it can be seen from those tables, the content of base cations in PM changes from country to country. It can also be seen that the base cation content in the same country can be different for the coarse and fine fraction. This is because the relative importance of the different sectors and the fuel types used within the sectors changes from country to country. The same explanation applies for the size fractions. Therefore, it is not possible to derive base cation emissions directly from aggregated PM emissions and a bottom-up approach as the one proposed here is needed in order to derive base cation emissions.

The spatial distributions of the emissions are given in Figure 2.1. Anthropogenic emissions of Ca are generally larger than the emission of any of the other components. For all components, the higher emissions are, as expected, in the mid-latitudes and local peaks in the distribution along the Spanish and Portuguese coast are seen.

The total annual emissions for the year 2000 in the EMEP area are calculated to be about 424 ktonnes calcium, 54 ktonnes magnesium, 91 ktonnes potassium and 49 ktonnes sodium. Only for the UK we have national information on base cation emissions available for comparison for the year 2000 (Goodwin (2004)). For Ca our estimate for the UK, 6544 ton/year, is about 20% lower than the estimate from Goodwin (2004). For Mg the two estimates compare quite well, for K our estimate is about 30% higher and for Na about 8% lower. Though our numbers compare relatively well with Goodwin (2004), it is not clear at this stage whether the two methodologies are actually independent.

Our estimate for anthropogenic calcium emissions for the year 2000 is 424 ktonnes, which is almost a factor of two lower than earlier estimates from Lee and Pacyna (1999) for the year 1990. One could speculate that this difference may be explained by the general decrease in emissions during the 90s. And indeed the data from Goodwin

country	fine				coarse			
	Ca	Mg	K	Na	Ca	Mg	K	Na
AL	783	82	195	44	116	17	27	41
AT	3482	347	854	138	275	27	48	70
ATL	100	0	0	65	6	0	0	4
BA	854	211	249	273	1248	328	388	427
BAS	61	0	0	40	3	0	0	2
BE	2521	282	423	261	919	100	113	178
BLS	21	0	0	14	1	0	0	1
BUL	4345	669	949	600	1903	345	409	456
BY	1891	237	390	238	802	122	158	222
CH	823	71	155	67	70	6	10	69
CY	109	4	4	11	16	1	1	7
CZ	4029	795	1091	885	1648	377	459	517
DE	8756	903	1591	987	2047	159	277	701
DK	2672	266	674	109	158	18	35	62
ES	18715	1577	3335	1009	3314	263	362	605
EST	2581	357	713	235	946	238	293	290
FI	5088	514	1311	146	257	28	56	50
FR	44636	4481	11387	1401	2528	297	556	713
GB	4961	771	1089	1028	1936	392	472	842
GR	5209	543	1172	341	755	101	150	204
HR	1703	181	333	168	575	86	112	135
HU	4782	593	866	442	1337	209	238	305
IE	619	80	126	100	239	27	41	63
IT	31234	2755	6515	1227	3727	258	408	704
LT	3207	327	846	88	171	20	41	37
LU	233	26	34	22	54	4	5	7
LV	716	85	190	48	86	15	22	32
MD	878	226	247	276	723	189	221	259
MED	313	0	0	205	17	0	0	11
MK	452	80	93	106	499	119	141	159
MT	2	0	0	3	1	0	0	3
NL	1824	176	399	165	214	16	29	150
NO	3635	367	939	111	247	25	50	46
NOR	116	0	0	76	6	0	0	4
PL	24293	3076	6024	2135	3843	660	877	987
PT	7361	632	1553	253	800	59	96	136
RO	12098	1424	2676	888	3220	446	558	644
RUS	59960	9066	11589	8193	25067	4560	5363	5947
SE	15757	1581	4120	338	656	71	156	89
SI	1645	198	426	111	282	58	77	79
SK	695	123	135	162	367	74	88	123
TR	43150	4611	8761	2719	9839	1133	1377	1659
UA	13894	2573	2371	2619	8708	1748	1935	2318
YU	1852	356	409	482	2089	490	582	673
Total	342055	40644	74235	28831	81717	13086	16231	20034

Table 2.2: Estimated base cations emissions in ton/year

country	fine				coarse			
	%Ca	%Mg	%K	%Na	%Ca	%Mg	%K	%Na
AL	11.94	1.25	2.98	0.67	4.51	0.67	1.06	1.59
AT	9.42	0.94	2.31	0.37	2.24	0.22	0.39	0.57
ATL	0.29	0	0	0.19	0.29	0	0	0.19
BA	4.21	1.04	1.22	1.35	4.48	1.18	1.39	1.53
BAS	0.29	0	0	0.19	0.29	0	0	0.19
BE	5.63	0.63	0.95	0.58	3.48	0.38	0.43	0.67
BLS	0.29	0	0	0.19	0.29	0	0	0.19
BUL	7.41	1.14	1.62	1.02	5.4	0.98	1.16	1.29
BY	4.42	0.55	0.91	0.56	3.82	0.58	0.75	1.06
CH	8.1	0.7	1.52	0.66	1.41	0.13	0.19	1.39
CY	4.4	0.15	0.17	0.44	2.18	0.12	0.13	0.94
CZ	5.27	1.04	1.43	1.16	4.03	0.92	1.12	1.26
DE	5.11	0.53	0.93	0.58	2.31	0.18	0.31	0.79
DK	11.93	1.19	3.01	0.49	1.52	0.17	0.34	0.6
ES	11.06	0.93	1.97	0.6	5.14	0.41	0.56	0.94
EST	11.79	1.63	3.25	1.07	4.71	1.18	1.46	1.44
FI	15.44	1.56	3.98	0.44	3.51	0.39	0.77	0.69
FR	15.97	1.6	4.08	0.5	3.17	0.37	0.7	0.89
GB	3.67	0.57	0.81	0.76	2.53	0.51	0.62	1.1
GR	10.56	1.1	2.38	0.69	4.51	0.6	0.89	1.22
HR	8.64	0.92	1.69	0.85	5.7	0.85	1.11	1.34
HU	7.95	0.99	1.44	0.74	5.06	0.79	0.9	1.16
IE	4.34	0.56	0.88	0.7	3.22	0.37	0.55	0.85
IT	13.86	1.22	2.89	0.54	5.62	0.39	0.62	1.06
LT	18.34	1.87	4.84	0.51	4.94	0.58	1.2	1.07
LU	7.19	0.79	1.05	0.69	5.81	0.4	0.57	0.78
LV	9.57	1.14	2.53	0.64	3.15	0.57	0.81	1.18
MD	3.84	0.99	1.08	1.21	4.04	1.05	1.23	1.45
MED	0.29	0	0	0.19	0.29	0	0	0.19
MK	4.76	0.84	0.98	1.11	4.37	1.04	1.23	1.39
MT	0.4	0	0	0.49	0.32	0	0	1.36
NL	5.05	0.49	1.11	0.46	1	0.08	0.13	0.7
NO	12.68	1.28	3.27	0.39	4.03	0.4	0.82	0.75
NOR	0.29	0	0	0.19	0.29	0	0	0.19
PL	11.3	1.43	2.8	0.99	4.26	0.73	0.97	1.09
PT	15.74	1.35	3.32	0.54	6.32	0.47	0.76	1.08
RO	10.49	1.23	2.32	0.77	5.83	0.81	1.01	1.17
RUS	6.67	1.01	1.29	0.91	4.98	0.91	1.07	1.18
SE	22.38	2.25	5.85	0.48	5.58	0.6	1.33	0.76
SI	12.64	1.52	3.27	0.85	4.74	0.98	1.29	1.33
SK	3.77	0.67	0.73	0.88	3.48	0.7	0.84	1.16
TR	14.28	1.53	2.9	0.9	8.8	1.01	1.23	1.48
UA	4.35	0.81	0.74	0.82	4.27	0.86	0.95	1.14
YU	4.13	0.79	0.91	1.07	4.4	1.03	1.23	1.42
Average	8.81	1.05	1.91	0.74	4.6	0.74	0.91	1.13

Table 2.3: Percentage base cations in PM

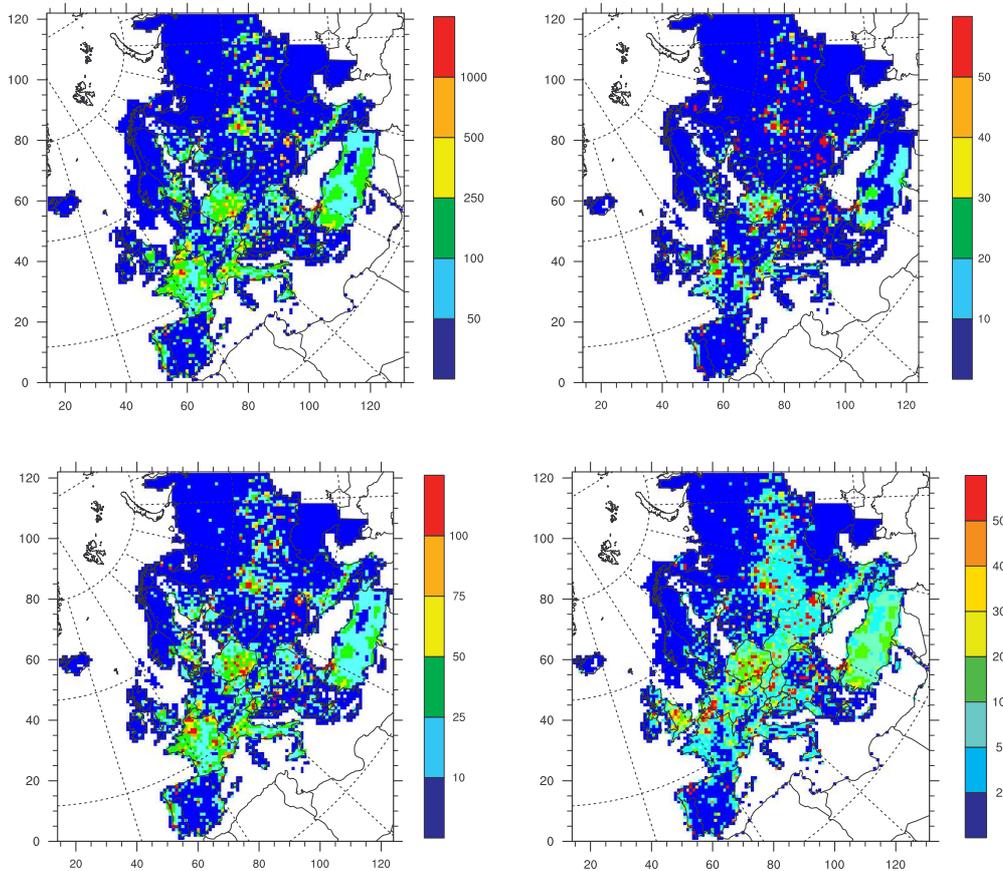


Figure 2.1: Estimated anthropogenic emissions in the year 2000 in ton/cell for Ca (upper left) and Mg (upper right), K (lower left) and Na (lower right). Note the different scales.

(2004) suggest a decline in base cation emissions in the UK by a factor of two from 1990 to 2000. However, it is difficult to establish to what degree the UK emission trends are valid in other parts of Europe and a closer look at the data shows larger inconsistencies between the Lee and Pacyna (1999) estimates and those presented here. In the first place, Lee and Pacyna (1999) do not seem to include wood combustion, whereas in our estimates, wood combustion is included and contributes significantly to the emissions totals for Ca. If we take away this contribution, differences between our estimates and those from Lee and Pacyna (1999) are even larger. In the second place, Lee and Pacyna (1999) attribute more than 75% of the calcium emissions to power generation from pulverised coal boilers (small). These emissions appear to be extremely large: Lee and Pacyna (1999) derived them using a 2% Ca content in the PM emissions from these small boilers. Calculating PM emissions from their Ca emission estimates results into PM emissions that only for this sector are already an order of magnitude higher than reported total  $PM_{10}$  emissions in 2000. For other sectors, Lee

and Pacyna (1999) seem to be in good agreement with the UK national estimate for 1990, Goodwin (2004). Therefore we believe that the earlier Ca emission estimates from Lee and Pacyna (1999) considerably overestimate the actual emissions of Ca over Europe.

In conclusion, based on this initial analysis, the present approach leads to reasonable estimates of the anthropogenic base cation emissions in Europe for the year 2000. However, there are recognized limitations in the availability of the data necessary for this approach and the present estimates should be considered as preliminary.

## CHAPTER 3

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### Natural Emissions

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#### 3.1 Introduction

As has been pointed out in Chapter 1, large part of base cations in air and precipitation originates from natural sources. Whereas for total PM the contribution of wind blown dust is reported to be relatively low, for base cations the natural contribution is expected to exceed by far the anthropogenic contribution. The natural sources included in this work are sea salt and wind blown dust. Within wind blown dust we distinguish two different sources: Saharan dust and dust emissions from agricultural soils.

##### Sea salt

Sea salt aerosol is considered to be the largest source of sodium concentrations and depositions (Tørseth et al. (1999)). It is also an important source of magnesium and to a lesser degree of potassium and calcium. The generation of sea salt aerosol over oceans is driven by the surface wind. There are two main mechanisms for sea salt aerosol generation: bubble bursting during whitecap formation (indirect) and through spume drops under the wave breaking (direct). The first mechanism is believed to determine the production of sea salt particles smaller than 10  $\mu\text{m}$  and therefore is presently included in the EMEP model parametrization of PM mass (Simpson et al. (2003)).

The extension of this parametrization of sea salt emissions to include base cation emissions in the EMEP model is described below in Section 3.2.

##### Saharan dust

In the past decade, there has been an steadily increasing interest in dust emissions from

deserts, after their role in the earth's climate has been acknowledged. Despite the fact that many studies have tried to estimate source strengths and provide source functions, current estimates show large differences, ranging from 500-5000 Tg  $yr^{-1}$  (Grini et al. (2004)).

It is also widely reported that Saharan dust contributes episodically to the PM concentrations in Europe. The highest contributions occur in southern Europe and in Spain for example concentrations of PM<sub>10</sub> up to 100  $\mu\text{g}/\text{m}^3$  are recorded during Saharan dust outbreaks (Rodríguez et al. (2002b,a, 2001)). The base cation content in Saharan dust is typically in the order of a few percent. Therefore, especially in southern Europe, Saharan dust is believed to have a substantial contribution to base cation concentration and deposition.

Saharan dust originating from outside the model domain is taken into account through boundary conditions, as described in section 4.2. However, the EMEP model domain also contains parts of the Sahara, for which dust emissions need to be modelled.

#### Emissions from agricultural soils.

Dust emissions from agricultural soils not have received much attention in climate and air quality research. The main focus of the research performed in this direction is on estimating the losses of plant nutrients due to wind erosion, but to our knowledge the coupling with continental scale air quality models is usually not made. Except in southern Europe, wind blown dust emission from agricultural and other soils could be the largest source of base cations in certain parts of Europe. There are also indications that this source locally contributes to a non-negligible extent to the PM concentrations.

Modelling of emissions from agricultural soils is a much more complex process than modelling of Saharan dust emissions. Whereas dust emissions in the Sahara are mostly dependent on surface wind velocity, dust emissions from agricultural soils vary also depending on the surface wetness, the surface morphology and the crop height. In addition, human activities like tillage may change the surface morphology, thus affecting the dust emissions. This imposes a series of challenges to the parametrization of dust emissions from agricultural soils.

The proposed parametrization of wind blown dust emissions from the Sahara and agricultural soils within the EMEP model domain is described below in Section 3.3.

### **3.2 Base cation emission from sea salt**

The sea salt contribution to base cations is taken into account by using the present parametrization for sea salt and assigning fractions to each of the base cations. The composition of sea salt is assumed to be: 30.83% Na, 55.44% Cl, 1.17% Ca, 1.11% K and 3.70% Mg. The remaining part that is not taken into account in the base cation

simulations is composed of Cl (55.44%) and SO<sub>4</sub> (7.75%).

Sea salt generation by bubble bursting is parametrized in the Unified EMEP Model following two different parameterizations depending on the size distribution of the aerosol (Simpson et al. (2003)).

The first parameterization is for sea salt aerosol larger than  $r_w = 0.8 \mu\text{m}$  (or particles with dry diameters exceeding ca. 1-2  $\mu\text{m}$ ), according to the empirical expression from Monahan et al. (1986):

$$\frac{dF}{dr_w} = 1.373 \cdot U_{10}^{3.41} r_w^{-3} (1 + 0.057r_w^{1.05}) \cdot 10^{1.19 \exp(-B^2)} \quad (3.1)$$

where  $dF/dr_w$  is the rate of sea salt droplet generation per unit area of sea surface and per increment of droplet “wet” radius,  $r_w$  is the aerosol wet radius at 80% relative humidity,  $U_{10}$  is the wind speed at 10m, and  $B = (0.380 - \log r_w)/0.650$ .

The second parameterization for the generation of sea salt aerosols with dry diameters smaller than 1-2  $\mu\text{m}$  is from the work by Mårtensson et al. (2003).

$$\frac{dF}{d(\log D_d)} = 3.84 \cdot 10^{-6} (A_k T_w + B_k) \cdot U_{10}^{3.41} \quad (3.2)$$

where  $dF/d(\log D_d)$  is the flux of sea salt particle per unit area of the whitecap cover and per increment of  $\log D_d$ ,  $D_d$  is the dry diameter,  $T_w$  is the temperature of sea water (constant  $T_w = 280 \text{ K}$  was used for now), and  $A_k$  and  $B_k$  are defined as in Mårtensson et al. (2003).

An initial comparison of sea salt modelled results with observations of Na in air can be found in Tørseth (2004). The initial comparison showed a general underestimation by the EMEP model of the observed concentration of Na in air by 52 and 54% in year 2001 and 2002, respectively. Under this study, the evaluation of sea salt generation was extended to compare modelled wet deposition fluxes with observations.

### 3.2.1 Correction of sea salt contribution used in this study

As has been mentioned above, the air concentrations and depositions of Na and Mg are most likely to be almost completely determined by sea salt. This is in particular the case for Na. We compared the model calculated Na concentrations in precipitation with wet flux observations from the EMEP and the ICP Forest networks. The comparison shows a systematic underestimation of the wet deposition fluxes calculated by the model, generally by a factor of 8! This underestimation is quite consistent throughout Europe, as illustrated by Figure 3.1 where the modelled annual wet deposition fluxes are multiplied by a factor of 8 and compared to the observed wet fluxes. Note that the x-axis in Figure 3.1 corresponds to the different stations measuring wet deposition fluxes of Na over Europe.

The model underestimation of wet deposition fluxes is larger than the underestimation of air concentrations. While the underestimation of air concentrations is about a factor of two, wet fluxes are generally underestimated by about a factor of eight. It is a

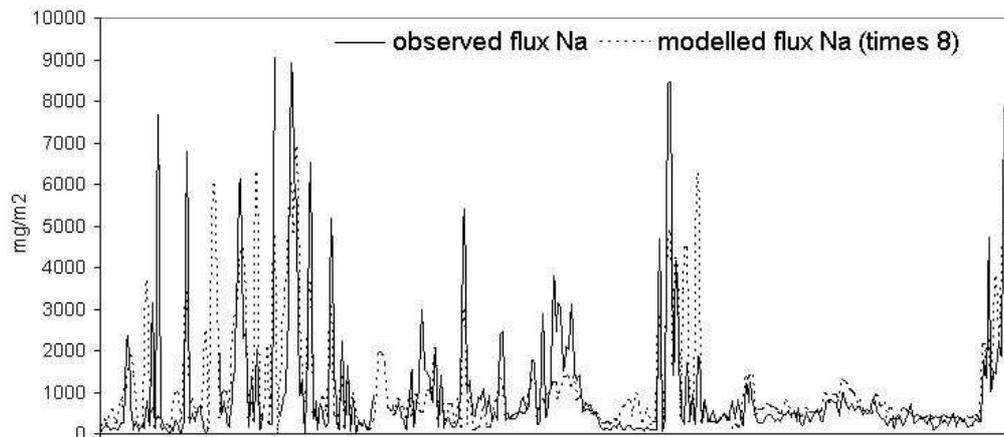


Figure 3.1: Observed total wet fluxes of Na versus modelled wet fluxes of Na arising from sea salt, multiplied by eight.

general feature in most chemical transport models, and also the Unified EMEP model, that they perform more poorly for wet deposition than for concentrations in air. This is related to the limitations inherent to the representation of precipitation processes in most meteorological drivers. However, the underestimation of Na, and consequently also of Mg, from sea salt generation in the model is much larger than for other chemical compounds, like sulphur. It is difficult to explain at the moment the reason for this very large underestimation for sea salt generated components.

As illustrated in Figure 3.1, the spatial correlation between modelled and observed fluxes is quite good (0.73). This is an indication that the production and transport of sea salt is done properly in the model, but it does not explain why the underestimation in concentrations in precipitation is much larger than the underestimation in air concentrations. One possible explanation for the different extent of underestimation could be that in precipitation also particles larger than  $10\mu\text{m}$  are caught. These particles are not taken into account by the model which originally aimed at modelling  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  only. For the modelling of air concentrations of  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  this is of course correct, but will lead to an (additional) underestimation when comparing concentrations in precipitation. It seems, however, unlikely that this can explain the difference completely. Given the short residence time of particles larger than  $10\mu\text{m}$  it is not to be expected that they contribute largely to the total contribution from sea salt outside coastal areas.

For the purpose of this study, an initial correction of sea salt generation has been applied. The modelled base cation wet and dry deposition fluxes originating from sea salt have been multiplied by a factor of eighth following the comparison with observations. This is only for the purpose of allocating base cations from sea salt. We are aware that this is not a physical approach and that the model needs to be revised to improve the parametrization of sea salt generation, including also direct generation

of aerosol from wave breaking. The parametrization of sea salt generation requires further attention within EMEP and the present results can only be considered as a preliminary estimate of the contribution of sea salt generation to the deposition of base cations.

### 3.3 Parametrization of wind blown dust

The same parametrization is applied for dust emissions from the Sahara and from agricultural soils and is based on the Dust Prediction Model (DPM) described in Gomes et al. (2003a,b), Rajot et al. (2003), Marticorena et al. (1997) and Alfaro et al. (2004). However, the approach described by these authors requires very specific input data on soil characteristics that is insufficiently available at European scale. Therefore we had to make assumptions and simplifications on the input soil characteristics. Once the dust emissions are estimated with a simplified version of the DPM, the base cation content of the soil is used to determine the actual base cation emissions associated with wind blown dust. This adds an additional uncertainty to the results as several assumptions have also been made to determine the base cation content in the soil. In the following the main processes and assumptions are described.

#### 3.3.1 Saltation and sandblasting processes

In soils, particles with diameter smaller than 10  $\mu\text{m}$  are not found in free state, but are embedded in soil aggregates of larger size, ranging from 30  $\mu\text{m}$  up to several centimeters. Because of their weight, the largest of these aggregates cannot be set into motion by wind. Under usual condition only soil particles up to 840  $\mu\text{m}$  can be lifted by the wind and set into motion. From a physical point of view, mobilization of a particle is controlled by the forces acting on the particle: gravity, interparticle cohesion forces and wind shear stress. The latter depends on the transfer of wind momentum to the erodible surface, that in turn is controlled by the presence of roughness elements on the surface. The corresponding critical stress value can thus be characterized by means of a threshold friction velocity  $u_*^t$ . When  $u_*$  is larger than  $u_*^t$ , soil aggregates are set into an essentially horizontal motion in a layer close to the surface. This process is called *saltation*. The horizontal flux  $F_h$  (in  $g\ m^{-1}\ s^{-1}$ ) is defined as the integrated amount of saltating mass over a 'door' with infinite height and width unity perpendicular to the average wind direction. For the horizontal flux, the following parametrization is employed (Gomes et al. (2003a))

$$F_h = \begin{cases} K_{lim}\rho_a/gu_*^3(1-R)(1+R)^2, & u_* > u_*^t, \\ 0 & \text{otherwise,} \end{cases} \quad (3.3)$$

where  $K_{lim}$  is a dimensionless parameter, representing the supply of soil aggregates,  $\rho_a$  the air density,  $g$  the gravitational constant and  $R = u_*^t/u_*$ .

The factor  $K_{lim}$  reflects the possibility of a limited supply of soil aggregates. Following Gomes et al. (2003a)  $K_{lim} = 1$  is taken for wind blown dust from the Sahara, whereas  $K_{lim} = 0.02$  is taken for wind blown dust emissions from agricultural soils. Apart from real desert areas (Sahara and desert areas in the south-eastern part of the EMEP modelling domain), in the current land use data base the land use class "desert" is used for bare soils, dunes etc. as well. For these areas  $K_{lim}$  is arbitrarily taken to be equal to 0.1.

$$K_{lim} = \begin{cases} 1, & \text{desert,} \\ 0.02, & \text{agricultural soils,} \\ 0.1, & \text{other bare soils.} \end{cases}$$

The threshold friction velocity  $u_*^t$  is defined as:

$$u_*^t = u_{*,uncor}^t \cdot \frac{f_w}{f_{eff}}. \quad (3.4)$$

where  $u_{*,uncor}^t$  is the uncorrected threshold friction velocity,  $f_w$  is a correction factor for the soil moisture and  $f_{eff}$  accounts for the fraction of the total wind shear that acts on the erodible surface. In the original DPM parametrization the uncorrected threshold friction velocity depends on the size of the soil aggregates (Marticorena et al. (1997)). Since insufficient information was available on the size of the soil aggregates an averaged value of  $u_{*,uncor}^t = 0.25$  m/s was taken in this parametrization, using the formulations in Marticorena et al. (1997).

The correction factor for soil moisture  $f_w$  is defined as (Fécan et al. (1999))

$$f_w = \begin{cases} 1 & w \leq w_t, \\ (1 + 1.21(100(w - w_t)))^{0.68} & w > w_t, \end{cases} \quad (3.5)$$

where  $w_t = 0.1$  kg/kg is the threshold soil moisture content (Fécan et al. (1999)). The actual soil moisture  $w$  is available from the meteorological input to the model.

Following Marticorena et al. (1997)  $f_{eff}$  is defined as

$$f_{eff} = 1 - \frac{\ln(Z_0/z_{0s})}{\ln(0.35(0.1/z_{0s})^{0.8})}, \quad (3.6)$$

where  $Z_0$  is the aerodynamic roughness length and  $z_{0s}$  is an additional parameter representing the roughness of the erodible surface. Following Marticorena et al. (1997)  $z_{0s}$  is taken to be  $10^{-5}$  m. Note that the aerodynamic roughness length for agricultural soils changes during the growing season: with increasing crop height obviously less and less momentum will be transferred to the erodible surface, which is reflected also in equation 3.6.

When the saltating soil aggregates hit the ground, relatively fine particles (with diameter  $< 20 \mu\text{m}$ ) can be released from these aggregates themselves or from the soil on which they impact. This process is called *sandblasting*. The mass of the fine

particles released in this way is called the vertical flux  $F_v$  and is usually related to the horizontal flux  $F_h$  by the ratio  $\alpha$

$$\alpha = F_v/F_h. \quad (3.7)$$

For different soil types, values of  $\alpha$  may differ orders of magnitudes from each others. Measured values of  $\alpha$  are in the range  $10^{-7} - 10^{-4} \cdot m^{-1}$ . In the present set-up, however,  $\alpha$  is given a constant value of  $5 \cdot 10^{-5}$ .

The modelled dust emissions have to be assigned to the models fine and coarse fraction. According to Alfaro and Gomes (2001), this is a function of  $u_*$  and the characteristics of the soil aggregates. The mass percentages given in Alfaro and Gomes (2001) for various soil types have been averaged, resulting in the percentages given in Table 3.1.

	$u_*$			
	0.35	0.40	0.55	0.80
Fine	2	4	26	35
Coarse	9	11	30	11

Table 3.1: Percentage of the wind blown dust emissions attributed to the fine and coarse fraction.

Finally, some rules are needed that specify conditions that allow or do not allow wind blown dust emission. We have assumed that no dust emissions can take place when the air temperature (at 2m) is below  $0^\circ C$ , in case of snow cover and during precipitation. In addition it is required that there has been no precipitation for the last 48 hours. Small precipitation amounts ( $< 0.1\text{mm}$  in the 3h intervals considered in the model) were ignored when computing the accumulated rain amounts. The chosen time interval is rather arbitrary, but such a condition is necessary in order to prevent unrealistic dust events immediately after rainfall when the soil is still wet. Ideally, the time interval should be space dependent, based on meteorological parameters.

### 3.3.2 The base cation content of the soil

To estimate the amount of base actions due to wind erosion, the element content in the top soils of Europe and adjacent regions has to be known. For calcium, Lee et al. (1999) provided a table with Ca-contents in the top 30cm layer of 106 soil types according to the FAO classification, based on work by Batjes (2002). Since this table does not cover all soil types occurring in Europe, the Ca-content of 19 missing soils has been estimated for this work with the help of soil scientists. Overlaying a soil map covering Europe, composed of a 1:1,000,000 soil map for Europe except the former Soviet Union (Eurosoil (1999)) and a 1:5,000,000 soil map for the former Soviet Union (FAO (1981)) with the landcover map used in the Unified EMEP Model, the area and

Ca content for every landcover/soil combination within each 50x50 km<sup>2</sup> EMEP grid cell was determined. For use in wind blown dust modelling only landcover classes associated with agriculture were used. These data are restricted to Europe and do for example not contain information on Ca fractions of the Sahara soils. Therefore, additional gridded data from Batjes (2002) were used, kindly provided by W. Winiwarter (IIASA). Nevertheless, for a number of grid cells outside Europe still no estimate for the Ca content in the top soil is available, as can be seen in Figure 3.2, where the estimated Ca fractions (in %) in the top soil are shown.

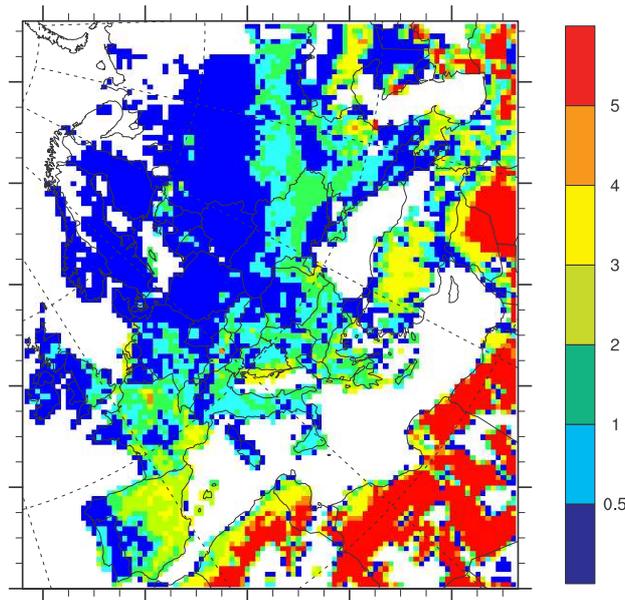


Figure 3.2: Estimated Ca fractions (in %) in the top soil.

Unfortunately, no comparable information for the other base cations (Mg, K and Na) was found in the literature. However, estimates of these contents have been made by computing the average base cation contents in the top soil for 53 soil types (members of 17 soil groups) from measurements made at ICP Forest Level-I sites (van Mechelen et al. (1997)). If a soil type on the map was none of the 53, it was assigned the average value of its corresponding group. If the soil belonged to a group not among the 17, it was assigned zero Mg, K and Na contents.

Since wind blown dust is expected to be the most important source of base cations in large parts of the modelling domain, future efforts should be directed at obtaining better estimates for the base cation contents in soils, especially for Mg, K and Na. Also the spatial coverage on the fringes of the modelling domain, especially in North Africa, should be improved. Since the element contents for those areas have been set to zero, we expect an underestimation of the computed contributions from wind-blown dust.

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### Modelling transport and deposition of base cations

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#### 4.1 Introduction

The Unified EMEP model is used as the basis for the present base cations calculations. The model has been extended to explicitly include calcium, magnesium, potassium and sodium. These base cations are treated in the model in the same way as primary particles. This means that they are considered as passive tracers, i.e. chemically inert. They share with primary particles the same transport and deposition processes. Since both dry and wet deposition of primary particles are parametrized for two different size classes, ranging up to  $2.5\mu\text{m}$  and from  $2.5$  to  $10\mu\text{m}$ , the same classes have been defined for base cations. These classes are usually called the *fine mode* and the *coarse mode* respectively. There are four base cations components in the fine mode and also four in the coarse mode, hence eight additional prognostic variables have been added to the model.

As the EMEP model has been fully documented in Simpson et al. (2003), here only an overview is given of the changes made in order to model base cations. The main additions to the Unified EMEP model are:

- the calculation of new estimates of anthropogenic emissions of base cations (as described in Chapter 2)
- the inclusion of a new subroutine to evaluate natural emissions of wind blown dust (as described in Chapter 3).
- the extension of the sea salt generation routines to include base cations (as described in Chapter 3).

- the extension of the boundary condition subroutine to include transport of Saharan dust.

In this chapter we describe the extension of the boundary condition subroutine in more detail.

## 4.2 Boundary conditions

A rather large part of the concentrations and depositions of base cations is expected to originate from the Sahara, in particular in Southern Europe. Part of this contribution will arise from source regions within the EMEP model domain. Hence, contributions from these regions are taken care of by the parametrization described in Chapter 3. In order to account for emissions from outside the model domain boundary conditions are specified. These are derived from model calculations performed by the University of Oslo (courtesy: A. Grini) with the global Oslo CTM model. A description of the dust parametrization at the Oslo CTM model can be found in Zender et al. (2003), Grini et al. (2004). For use as boundary conditions in the Unified EMEP model, size resolved fields of  $PM_{10}$  with monthly averages were obtained and interpolated to the EMEP grid as  $PM_{fine}$  and  $PM_{coarse}$ . Further it was assumed that the dust  $PM_{10}$  concentrations are composed of 4% Ca, 2% Mg, 2% K and 2% Na.

The figures 4.1 and 4.2 show the average  $PM_{10}$  concentrations for the years 1997 and 2000, respectively, as computed with the Oslo CTM model. Both years show very similar average concentrations. Note that up to about  $50^{\circ}N$  the annual average contribution from the Sahara to the  $PM_{10}$  concentrations is still in the order of  $1-2\mu g/m^3$ , although this may be partly due to numerical diffusion as a result of the coarse horizontal resolution of the global model (Grini (2004)). Note that assuming a 4% Ca content of Sahara dust, a contribution of  $1\mu g/m^3$   $PM_{10}$  corresponds to  $0.04\mu g/m^3$  Ca. This is just 30% lower than the yearly average observed at Kolummerwaard (EMEP code NL09), the only EMEP station in this region that reports Ca concentrations in air. The other EMEP stations providing Ca in air are all located in Norway, hence no information is available from regions that are more exposed to Sahara dust. The observed 4-day average Ca concentrations in the year 2000 in the station NL09 are shown in Figure 4.3. Some clear peaks are visible in the observed concentrations and can possibly be associated with Sahara dust. For that reason also the simulated time series of  $PM_{10}$  from the the Oslo CTM model (from 3-hourly model output) is plotted. Four-day averaged  $PM_{10}$  concentrations up to  $10\mu g/m^3$  are modelled a few times in the year 2000 in the grid cell containing the station NL09. The  $PM_{10}$  measurements at a close-by location in the same cell do not show clear peaks on these occasions, but on some of them the (4 day averaged) observed Ca concentrations in NL09 do. For example, around the 21th of June, the Oslo CTM computes a 4-day averaged contribution to  $PM_{10}$  of about  $10\mu g/m^3$ . Ca concentrations on the same period peak up to  $0.48\mu g/m^3$ Ca. These values correspond well with modelled PM values, assuming

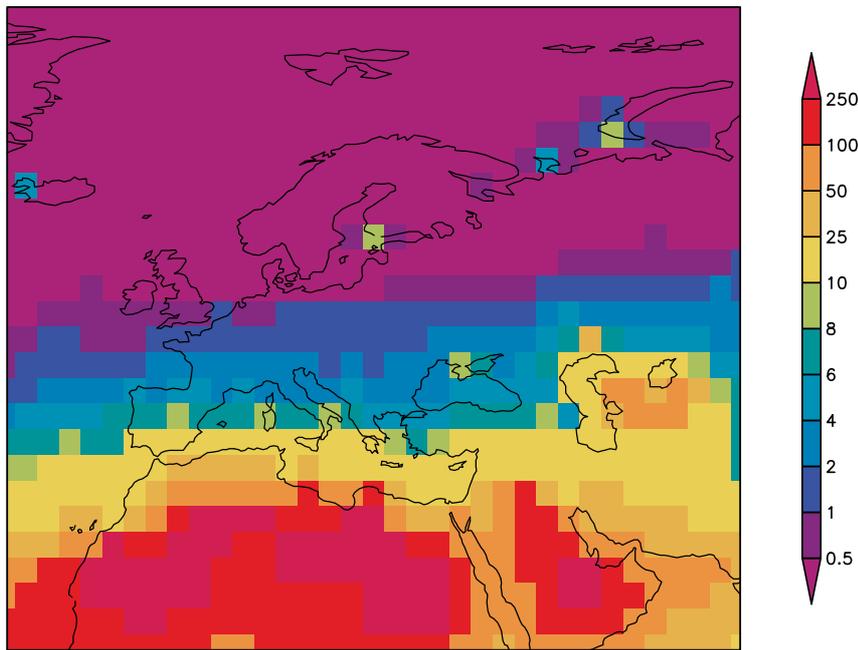


Figure 4.1: Averaged dust concentrations (PM<sub>10</sub>) in µg/m<sup>3</sup> from the Oslo CTM model for the year 1997.

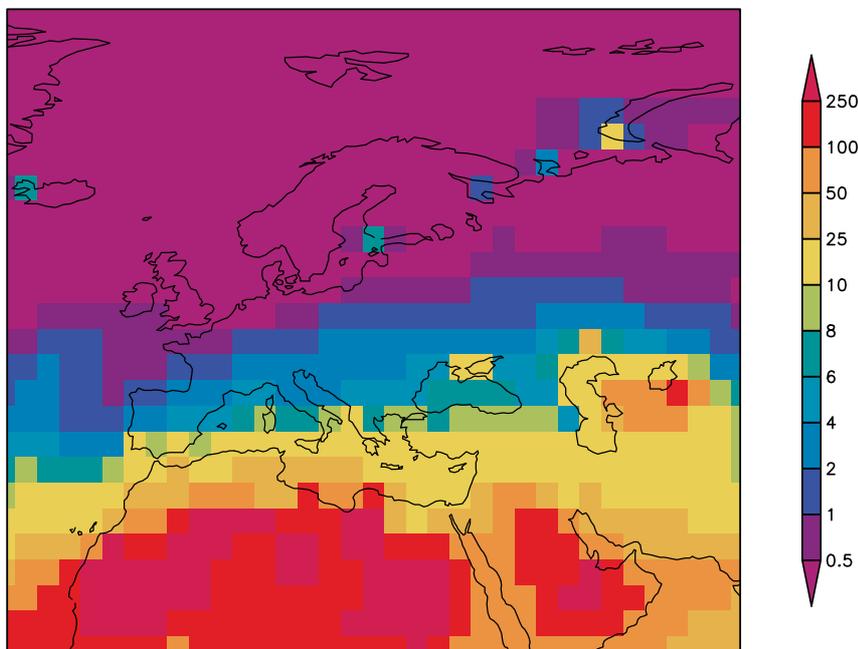


Figure 4.2: Averaged dust concentrations (PM<sub>10</sub>) in µg/m<sup>3</sup> from the Oslo CTM model for the year 2000.

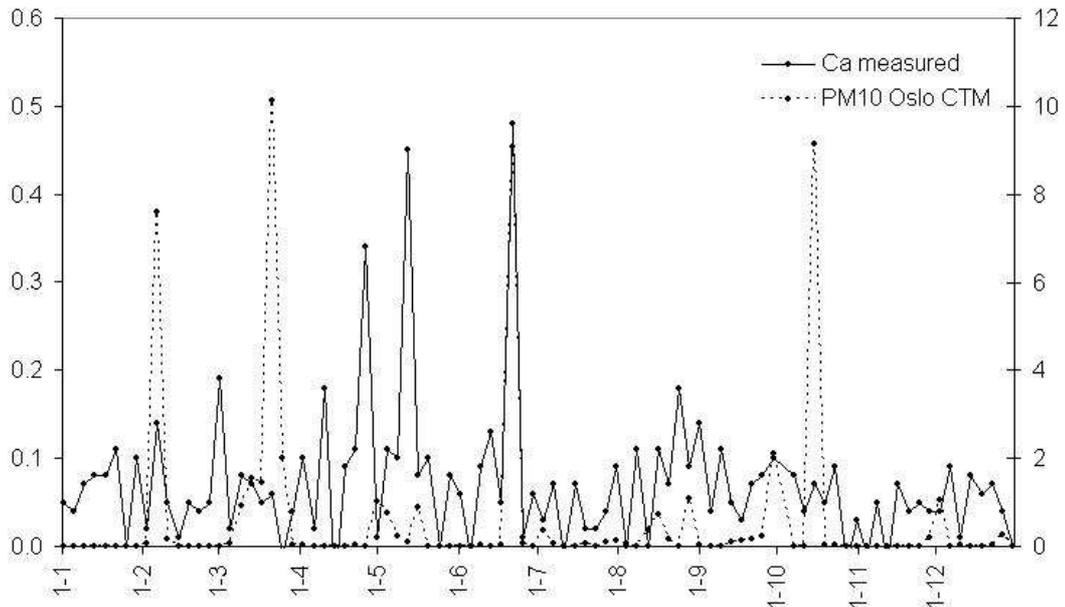


Figure 4.3: Observed 4 day averaged Ca concentrations in air  $\mu\text{g}/\text{m}^3$  at Kolummerwaard (NL09) in the year 2000 and simulated  $\text{PM}_{10}$  concentrations from the Oslo CTM model (right axis).

a 4% Ca content in the Sahara dust. This is an indication that there probably is an important contribution from Sahara dust to the concentrations and depositions of base cations also at higher latitudes.

Not all of the modelled peaks in  $\text{PM}_{10}$  correspond with enhanced observed Ca concentrations. It should be noted, however, that the Ca content in Saharan dust is dependent on the area of origin in the desert so that some of the modelled peaks in  $\text{PM}_{10}$  from the Sahara could originate from areas with low Ca content.

It should also be noted that not all peaks in observed Ca concentrations are necessarily related to Saharan dust. Some of them could well be associated with local agricultural dust sources that are present in the surrounding of the station NL09.

## CHAPTER 5

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### Results

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In this chapter the results of a first computation for base cations are presented. As has been pointed out earlier, the modelled fields should be considered as a first attempt, even though the comparison with observations in Section 5.3 is encouraging.

In order to be able to analyze the origins of the depositions, separate simulations have been performed:

- Applying only anthropogenic emissions with zero boundary conditions (ANTH).
- Applying only sea salt emissions with zero boundary conditions. Recall that the sea salt contributions have been multiplied by eight in the results presented in this chapter, see Section 3.2.1 for an explanation (SeaSalt).
- Applying only wind blown dust emissions with zero boundary conditions (WBD).
- Applying only wind blown dust in a limited area with latitude larger than  $37^{\circ}\text{N}$  and longitude less than  $40^{\circ}\text{E}$  (WBD-Europe)
- Applying only boundary conditions with zero emissions (Bound.Cond)

The boundary condition run (Bound.Cond) identifies the contribution from wind blown dust from areas in the Sahara outside the EMEP model domain. The WBD-Europe run identifies the contribution from wind blown dust from European agricultural soils. The difference between WBD and WBD-Europe (hereafter denoted as WBD-rest) enables us to distinguish between the contribution from the wind blown dust from areas in the Sahara inside the EMEP domain.

By performing separate simulations using only one of the emissions sources at a time, individual contributions of each of these sources are computed. Note that in the model there is no chemical interaction between the base cations themselves nor

with any other components and that deposition velocities of particles have predefined values and are not depending on the actual concentration nor on the composition of the aerosol. This means that the deposition amounts to each individual grid cell can be calculated as a sum of the computed separate contributions. This sum should be equal to the amounts computed by one simulation taking into account all emission sources at once. Only numerical diffusion will lead to very small differences in space and time, but are negligible when considering averages over time, as has been shown in Tarrasón et al. (2002). The results presented in Tarrasón et al. (2002) show that for components least affected by chemical nonlinearities these differences arise up to at most a few percent. In the case of base cations we can assume that this is an upper bound, because they are unaffected by chemical nonlinearities. When averaging also over space the differences become even smaller.

## 5.1 Modelled deposition

The computed total deposition fluxes for the year 2000 for Ca, Mg, K and Na are shown in Figure 5.1. Figure 5.2 shows the computed wet deposition fluxes for the year 2000 for Ca, Mg, K and Na. The amount of dry deposition expressed in percent of the total is plotted in Figure 5.3

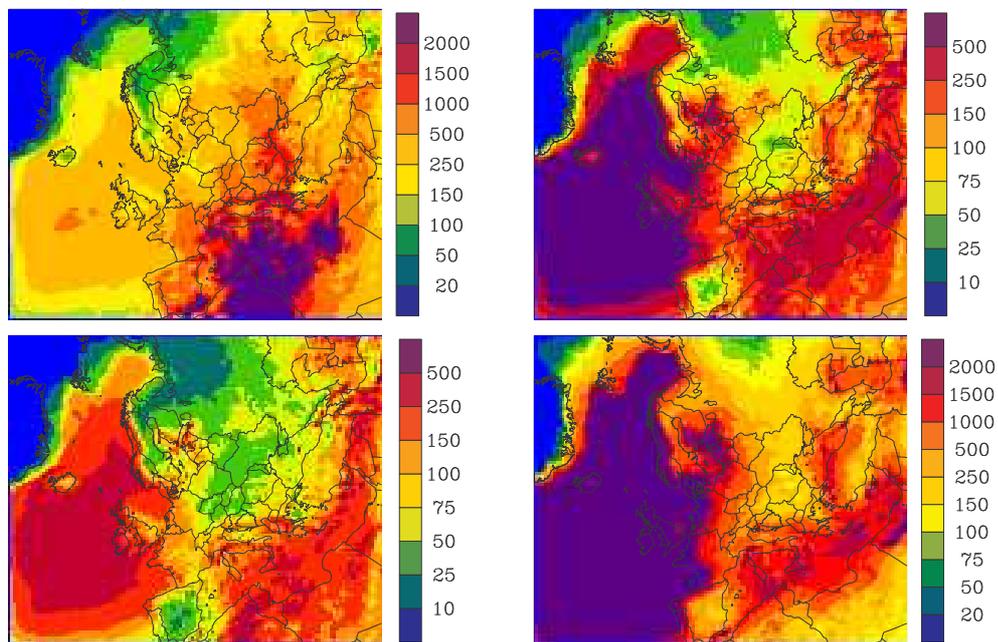


Figure 5.1: Modelled total deposition for the year 2000. Ca (upper left) and Mg (upper right), K (lower left) and Na (lower right). Units:  $\text{mg}/\text{m}^2$ .

It can be seen that wet deposition dominates the total deposition of base cations for all components. For forest areas the relative contribution of dry deposition is expected

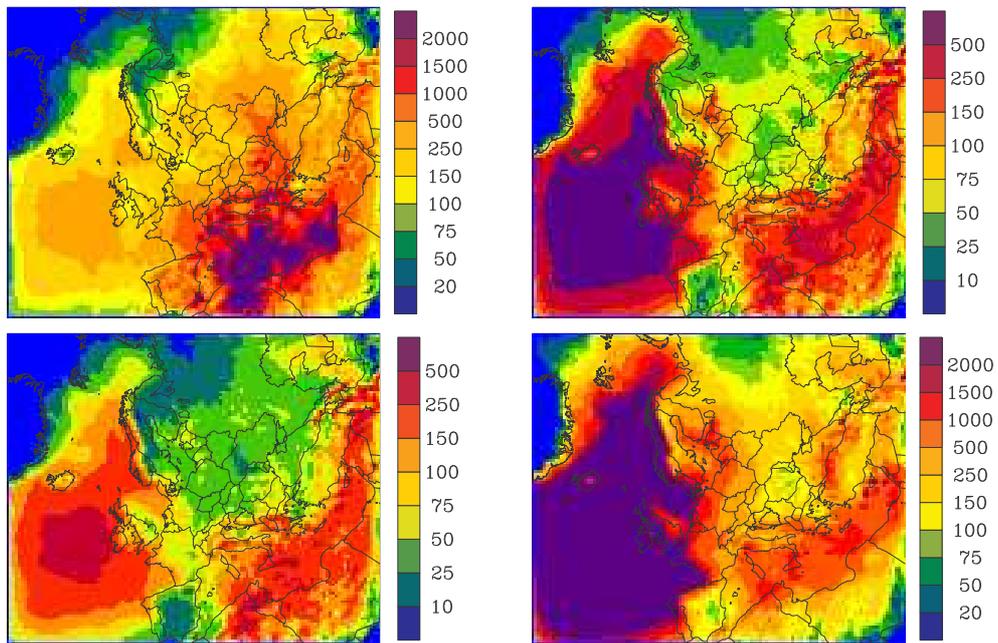


Figure 5.2: Modelled wet deposition for the year 2000. Ca (upper left) and Mg (upper right), K (lower left) and Na (lower right). Units:  $\text{mg}/\text{m}^2$ .

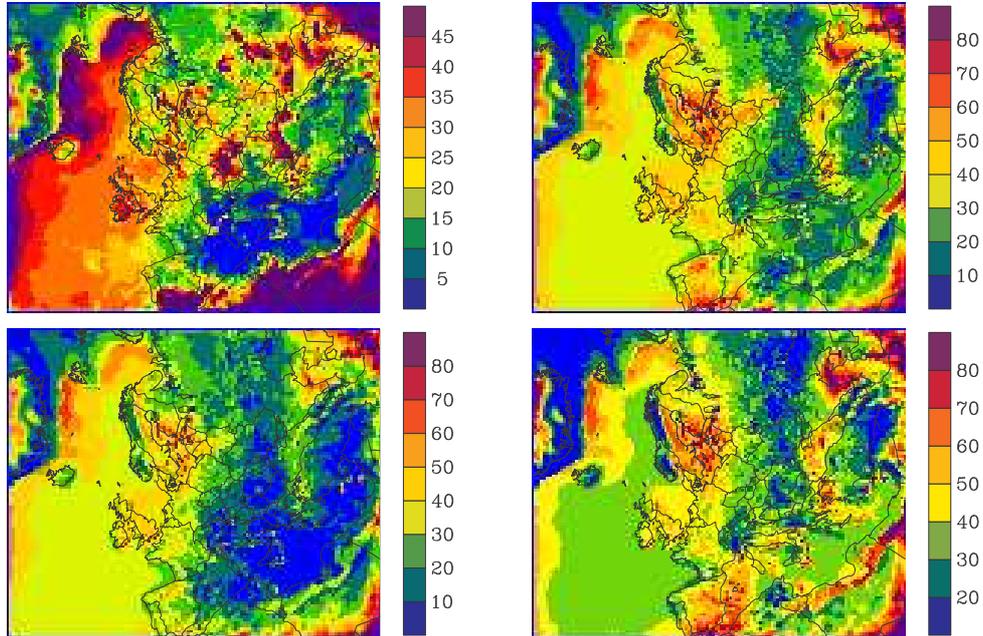


Figure 5.3: Modelled dry deposition for the year 2000 as percent of the total modelled deposition. Ca (upper left) and Mg (upper right), K (lower left) and Na (lower right). Units: %.

to be higher than the contributions shown in Figure 5.3, since dry deposition velocities to forests are generally larger than to other land use categories. This implies that the total modelled deposition estimates to forests will be higher than the values presented in Figure 5.1. Deposition to forests will be further discussed in section 5.4, where the modelled estimates of deposition to forests are compared to earlier estimates. The EMEP modelled fields of wet and total deposition have been distributed in electronic form for use by the ICP Modelling & Mapping.

## 5.2 Origin of the depositions

Figure 5.4 shows the modelled wet and dry deposition in the simulations performed as a sum over the whole model domain. Only land areas are considered because otherwise unproportionally large deposition of sea salt to sea areas would be included. For similar reasons desert areas are excluded. A first conclusion from Figure 5.4 is the low contributions from anthropogenic sources. Even though they locally seem to be largely determining the modelled air concentrations of for example Ca, their contribution to the total deposition is at most only a few percent for all four compounds. This means that the total modelled deposition in the model domain originates mostly from natural sources. As expected, for Ca, the contribution from the Sahara dominates, especially from areas inside the EMEP model domain. Note that for potassium and magnesium there is no calculated contribution from the Sahara inside the EMEP domain (WBD-rest). This is simply because we do not have at present a characterization of K and Mg content in desert soils. The relative contributions of the different sources to K and Mg is expected to change significantly when wind blown sources from the Sahara desert are treated consistently. For calcium and sodium we do not expect significant changes in the relative contribution of the sources, presented in Figure 5.4.

Even though the *total deposition* over the whole EMEP domain (excluding sea and desert areas) may be largely determined by natural emissions, this does not necessarily need to be the case everywhere in the model domain. This is illustrated by the Figures 5.5 and 5.6 where the various estimated contributions to the total Ca deposition are shown as absolute values and as percent of the total Ca deposition. Though in most areas the anthropogenic contribution is well below 15%, it is clear that above a latitude of about 45°N the anthropogenic contribution is still substantial, in particular for parts of Russia and Scandinavia. An implication of this observation is that, in particular in these areas, further though moderate reductions in base cation depositions can be expected when anthropogenic PM emissions are further reduced, whereas outside these areas only very small reductions can be expected.

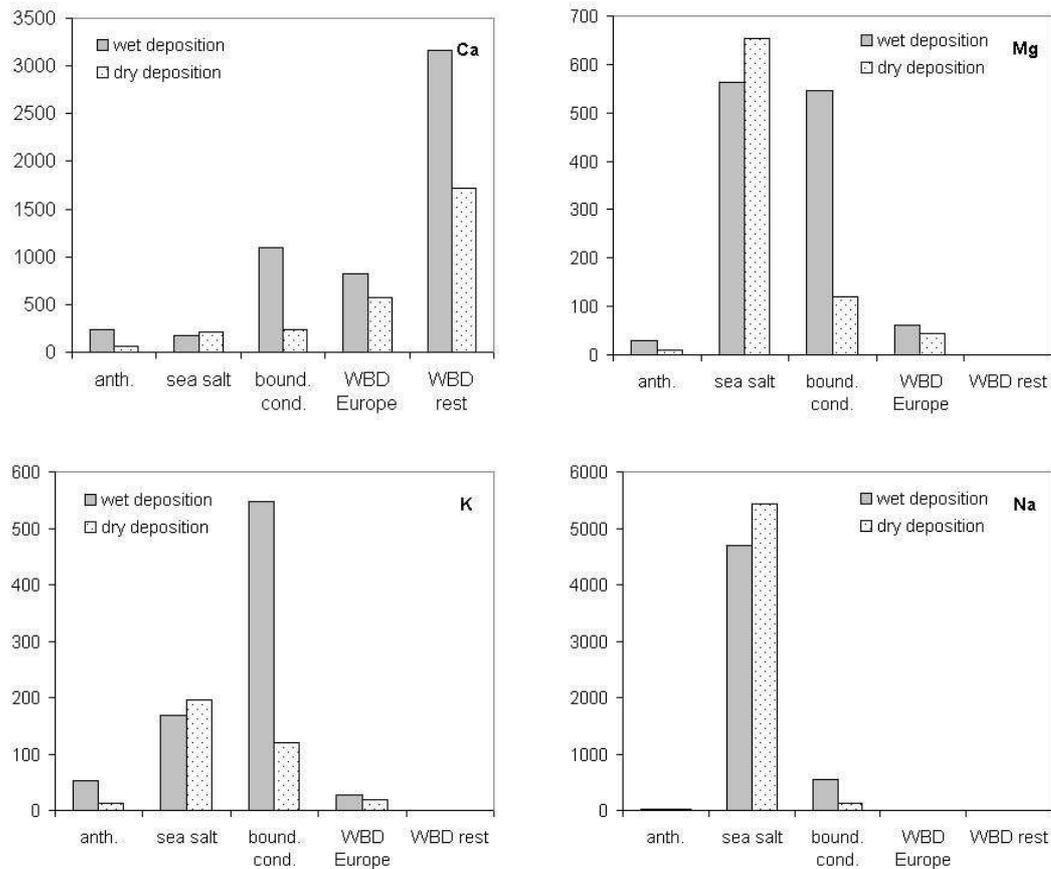


Figure 5.4: Modelled wet and dry fluxes in the year 2000 to main land areas in the EMEP domain for the sources considered, see text for further explanation. Unit: ktonnes.

## 5.3 Comparison with measurements

### 5.3.1 Wet deposition fluxes

Data on concentrations in precipitation have been obtained from a number of stations from the EMEP network (104) and the ICP forest network (243). Most of the EMEP sites have daily wet only measurements while ICP Forest have longer sampling periods (often monthly) and usually bulk collector is used. These measurements are more influenced by dry deposition and contaminated by e.g. fallen leaves and wind blown dust. The original data from ICP Forest have been cleaned by Aas and Hjellbrekke (2004) for inconsistent data, i.e. data set with very poor ion balance or obviously not regional representative measurements.

The observed and modelled average concentrations in precipitation for the year 2000 are plotted in the Figures 5.7 - 5.10 for the different components.

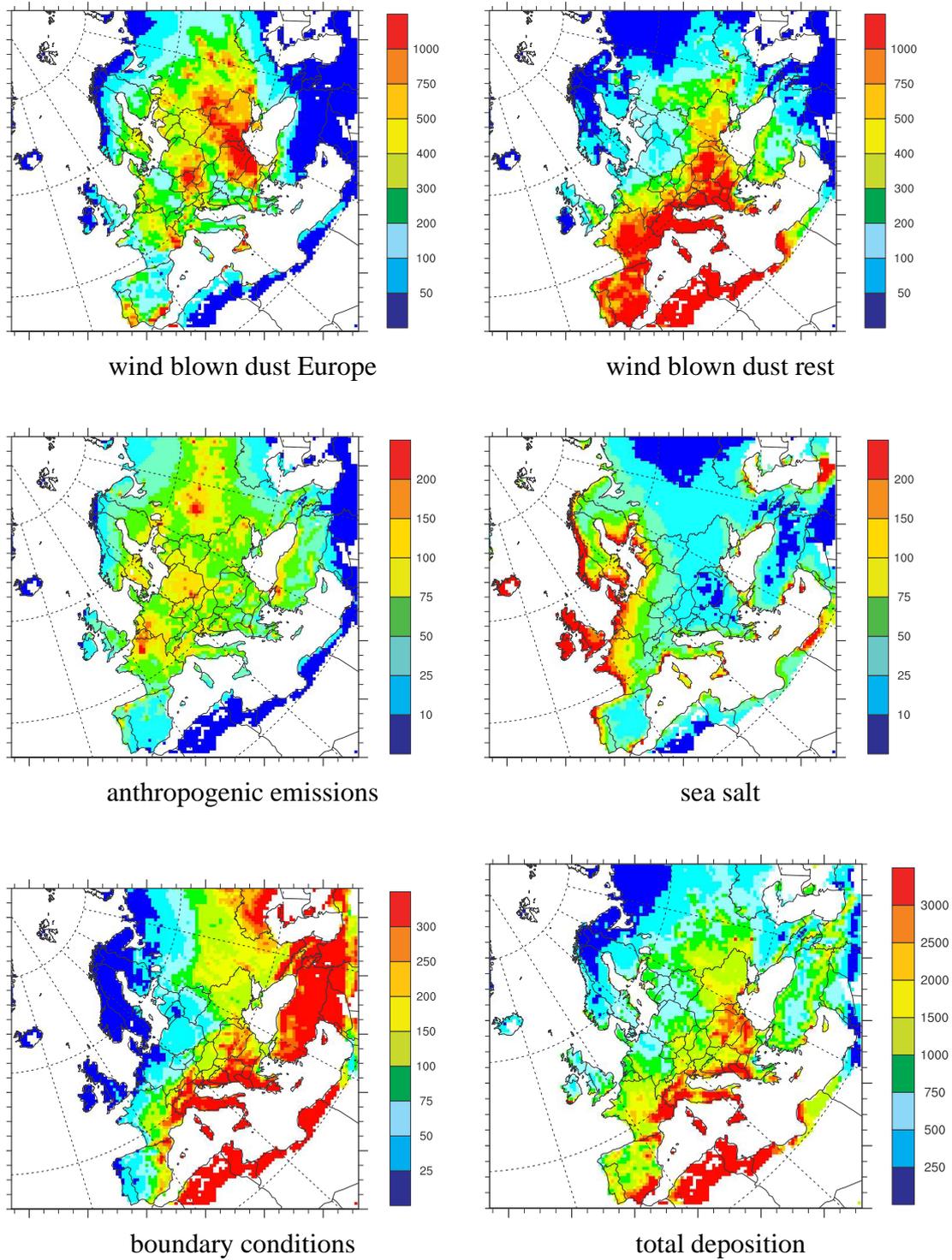


Figure 5.5: Sum of dry and wet deposition of Ca to land area in tonnes/cell in the year 2000 for the five different simulations and the total.

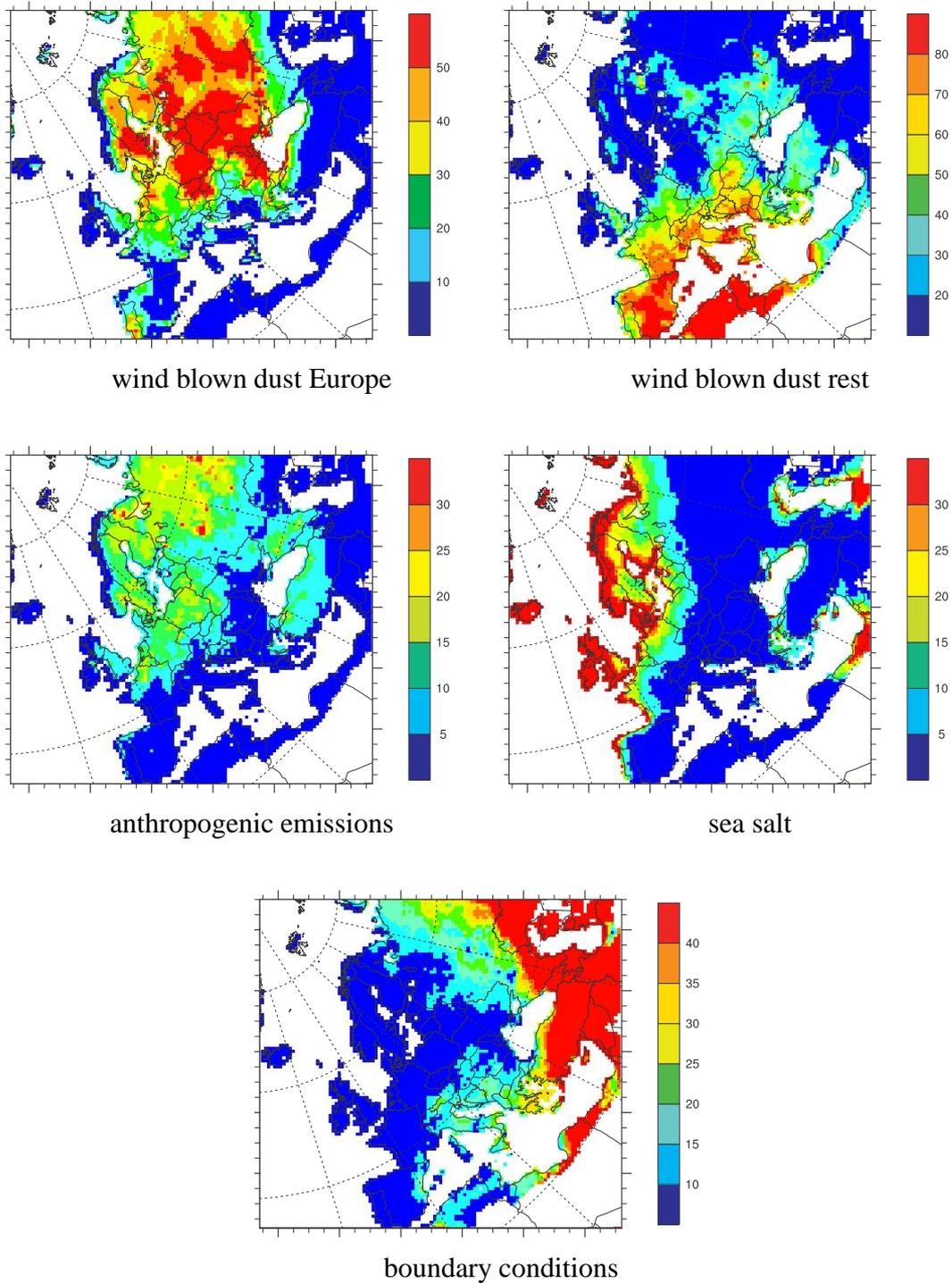


Figure 5.6: Sum of dry and wet deposition of Ca to land area in the year 2000 for the five different simulations, expressed as percent of total deposition.

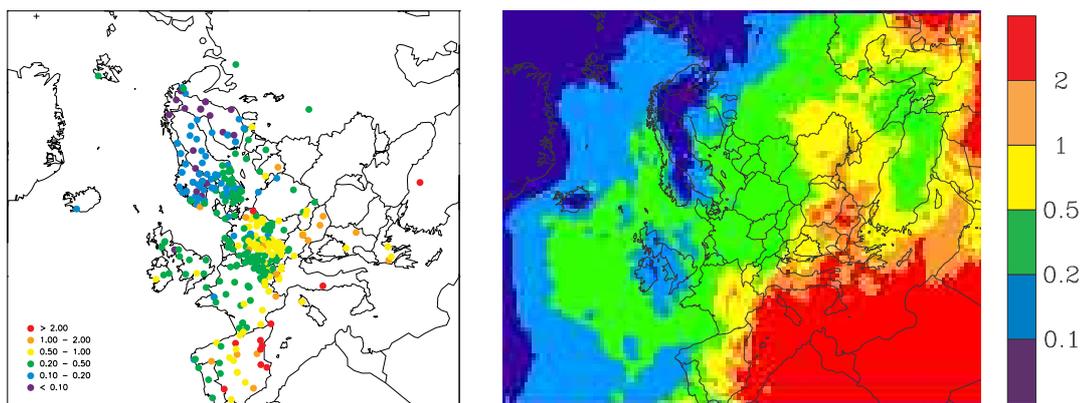


Figure 5.7: Observed (left) and modelled (right) average concentrations in precipitation of Ca in the year 2000 (mg/l).

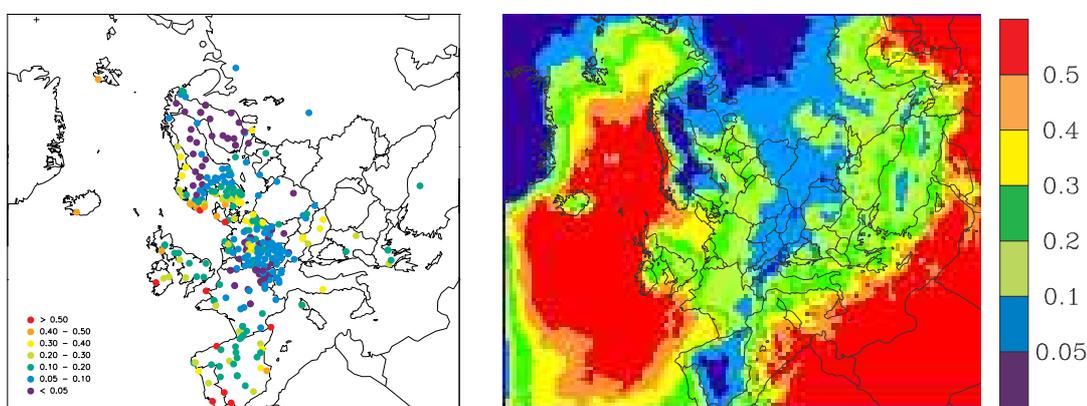


Figure 5.8: Observed (left) and modelled (right) average concentrations in precipitation of Mg in the year 2000 (mg/l).

Both the observations and the model results show the highest calcium concentrations in Southern Europe, in particular in Spain, pointing at a large influence of dust from the Sahara. For sodium and magnesium the influence of sea salt is clearly seen in the observations, with the highest concentrations of these compounds in the (near) coastal stations. This is also reflected in the modelled fields, but we have to keep in mind that in the figures the computed sea salt contributions have been multiplied by eight for source allocation purposes for all four components. For potassium both in the observations and in the modelled fields a mixed picture arises, suggesting no dominant source but rather a mix of contributions of similar magnitude. For this component the spatial correlation between observations and modelled values are lowest, as indicated by Table 5.1 where the spatial correlation coefficients as well as the observed and modelled means are given for the wet fluxes. Table 5.1 shows quite satisfactorily performance of the EMEP model, both in terms of spatial correlation and modelled concentrations levels. The spatial correlation of the modelled and observed wet deposition is also shown in the Figures 5.11 and 5.12 for all base cation components.

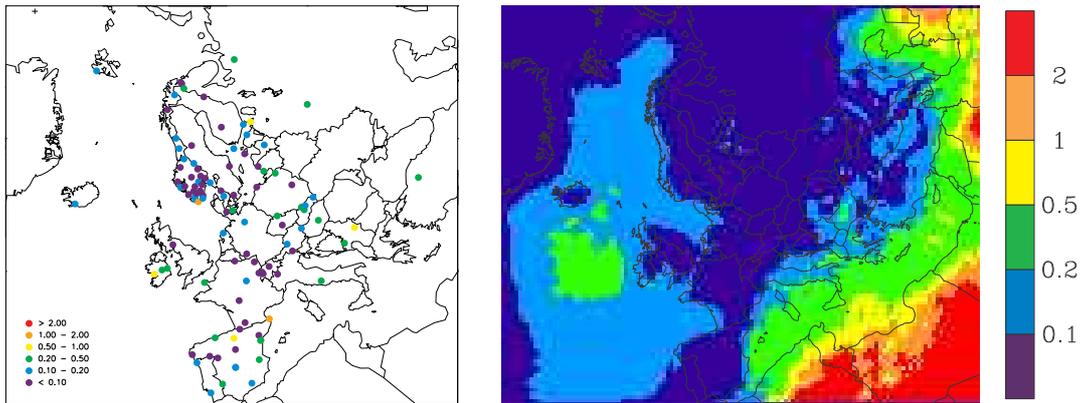


Figure 5.9: Observed (left) and modelled (right) average concentrations in precipitation of K in the year 2000 (mg/l).

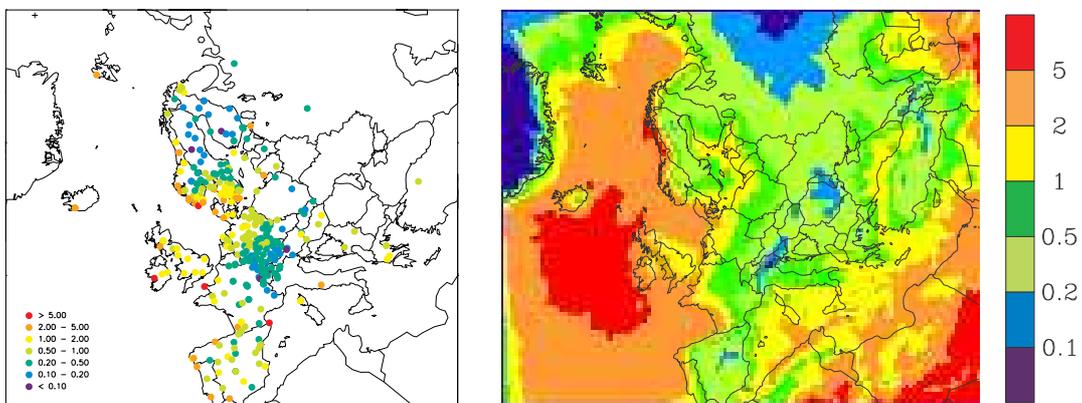


Figure 5.10: Observed (left) and modelled (right) average concentrations in precipitation of Na in the year 2000 (mg/l).

Averaged over the stations it can be concluded that the modelled amounts of wet deposition of Mg and Na quite well match the observed values. This is no surprise since these contributions mainly arise from sea salt and the modelled depositions have

	correlation			mean flux		
	all	EMEP	ICP-forest	obs.	model	bias
Ca	0.73	0.78	0.73	427	362	-15%
Mg	0.72	0.72	0.73	152	145	-5%
K	0.53	0.53	n.a.	124	72	-42%
Na	0.73	0.72	0.73	1005	984	-2%

Table 5.1: Spatial correlation coefficients and average modelled and observed wet fluxes ( $\text{mg}/\text{m}^2$ ) for the year 2000. Sea salt correction has been applied to the values in the table.

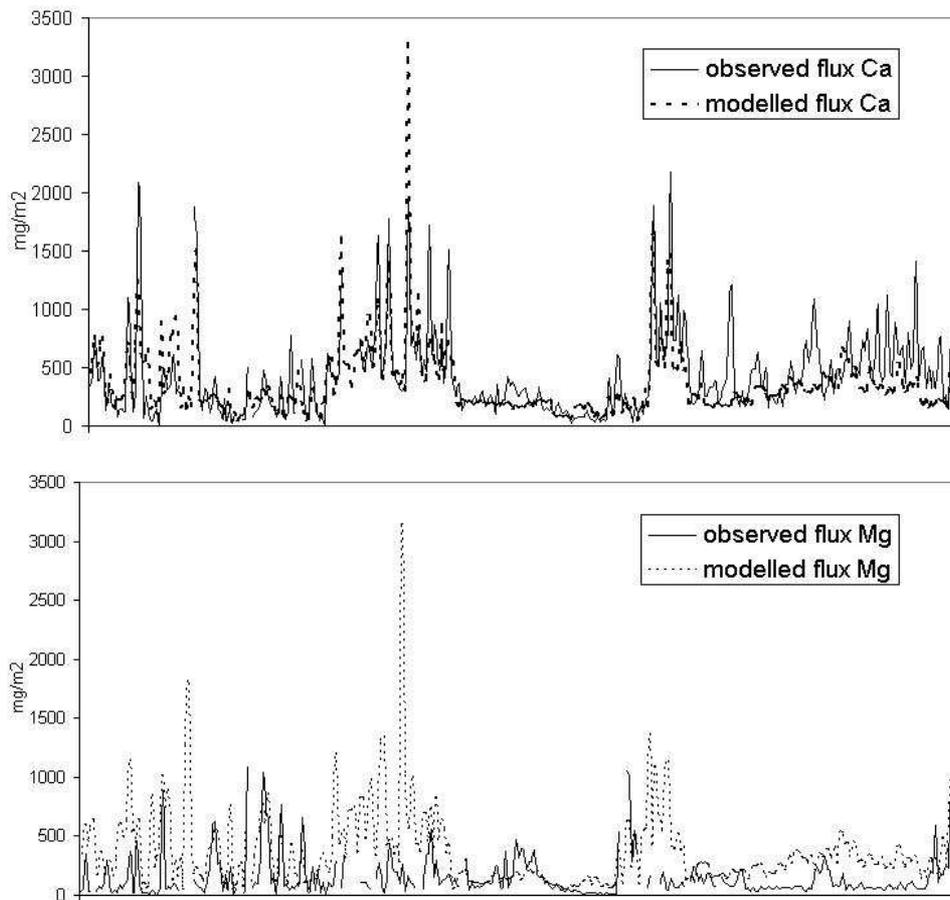


Figure 5.11: Modelled versus observed total annual wet fluxes of Ca and Mg at the observational sites (x-axis) for the year 2000. Units:  $\text{mg}/\text{m}^2$ .

been multiplied by a factor of eight in order to get the absolute values right. For Ca a 15% underestimation is seen on average which is mainly due to underestimation at stations with higher deposition values, as can be seen in Figure 5.11. For K only half of the deposited mass is modelled on average, but this is to some extent due to missing information on the soil mineralogy, causing a relatively low contribution from wind blown dust (see Section 5.2). For this component the spatial correlation is lower than for the other compounds. We have tried to add various fractions of the modelled Ca deposition due to wind blown dust as a proxy for the deposition of K due to wind blown dust, but this did not result into better spatial correlation. This indicates that, as could be expected, the ratio between the content of K and of Ca in soils is varying. If it had been relatively constant, an improvement in correlation could have been expected.

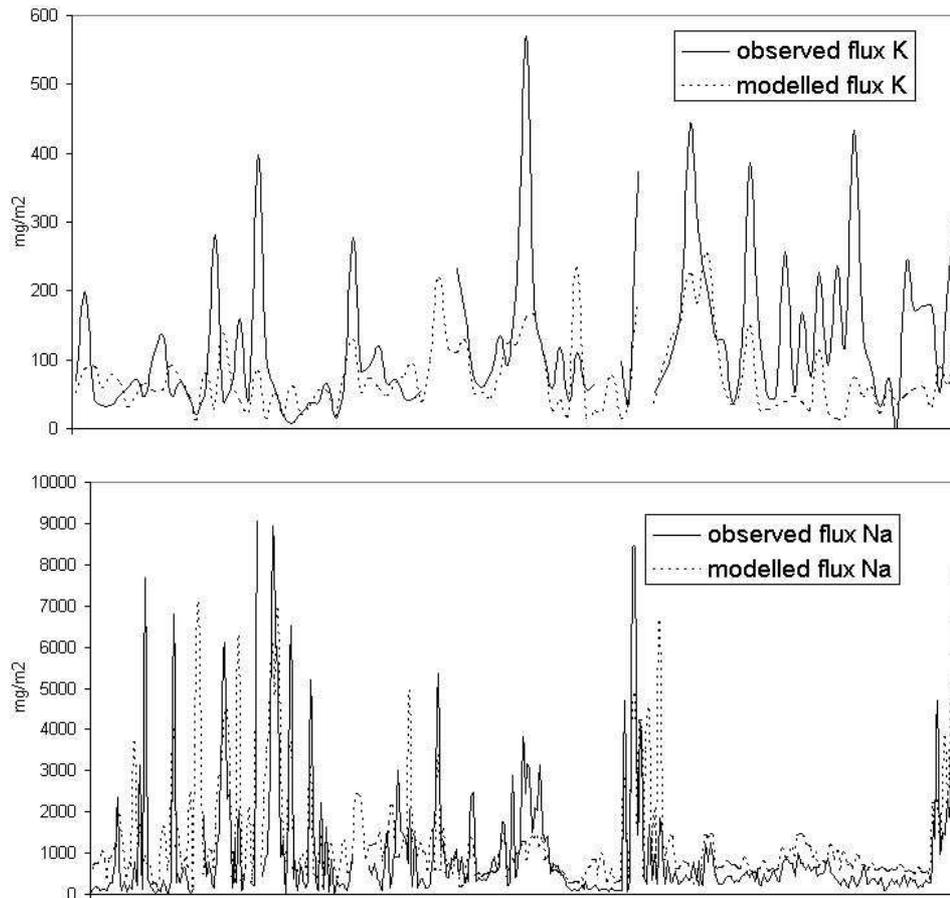


Figure 5.12: Modelled versus observed total annual wet fluxes of K and Na at the observational sites (x-axis) for the year 2000. Units:  $\text{mg}/\text{m}^2$ .

### 5.3.2 Air concentrations

Unfortunately, there are presently very few stations that measure base cations in air. These are mostly Nordic stations: some few Norwegians (all four compounds considered) and three Danish stations (Na only), and one Dutch station (Ca only). Thus, a comparison with concentrations of base cations in air is only possible to a limited extent.

For calcium, the model seems to generally overestimate the observed concentrations. However, the observed Ca concentrations at these stations are quite low, with annual averages less than  $0.1 \mu\text{g}/\text{m}^3$ . Since no measurements are available of concentrations in air in regions where higher concentrations can be expected, it is difficult to draw more specific conclusions.

Whereas the model considerably underestimates the wet deposition of Na and Mg, this underestimation is significantly lower for air concentrations. Although at the lo-

cations considered Na concentrations both in air and in precipitation are almost completely determined by sea salt, there is a difference between the modelled and measured ratio between concentrations in air and in precipitation. Part of the difference could be explained by the fact that the measured air concentrations only deal with particles  $< 10\mu m$  whereas in precipitation in principle all particles sizes are captured (though not with the same efficiency). This is not taken into account by the present model, but additional efforts need to be done within EMEP to better characterize the production of base cations by sea salt.

The comparison with the limited amount of available measurements of air concentrations suggest a general underestimation by the model of Mg, K and Na, which can be partly attributed to the fact that are still missing contributions from wind blown dust sources for these components. The overestimation of Ca needs to be further analyzed for different years and with better data coverage in order to assess the appropriateness of the present wind blown dust parametrizations.

## 5.4 Comparison with previous estimates

Base cation depositions that are presently used as input to the critical load computations are different from country to country. Most estimates are empirically derived and vary depending on the quality of the used observations of base cation content in precipitation and on the empirical assumptions made to derive dry deposition fluxes. For countries that do not deliver own estimates, CCE employs background values for the total base cation deposition. The background CCE estimates are based on measurements of wet deposition averaged over 5 years (1991-1995) from EMEP/CCC monitoring stations in Europe. The number of stations varies from 89 to 96, depending on the ion. The measurement data is extended to cover the whole of Europe, using an inverse distance interpolation technique taking into account the five nearest measurement stations according to

$$X_i = \frac{\sum_{j=1}^5 X_{meas,j}/r_{i,j}}{\sum_{j=1}^5 1/r_{i,j}}, \quad \text{with } X = \text{Ca, Mg, K, Na,} \quad (5.1)$$

where  $X_i$  and  $X_{meas,j}$  represent the wet (bulk) deposition of ion  $X$  in grid cell  $i$  and at station  $j$ , respectively and  $r_{i,j}$  is the distance of the center of grid cell  $i$  to station  $j$ .

Total deposition to forests is obtained by multiplying the wet deposition totals by 1.8 for coniferous forest and 1.4 for deciduous forests. These factors were derived from Forest level II measurements (de Vries et al. (1999)).

Figure 5.13 compares the background CCE estimates with the new EMEP model fields of total deposition for Ca. The background CCE estimates distinguish between coniferous and deciduous forests. The EMEP modelled depositions for particles have in practice only one land use category for forests. The EMEP modelled depositions presented earlier in this chapter were grid averages, while in Figure 5.13 forest-specific

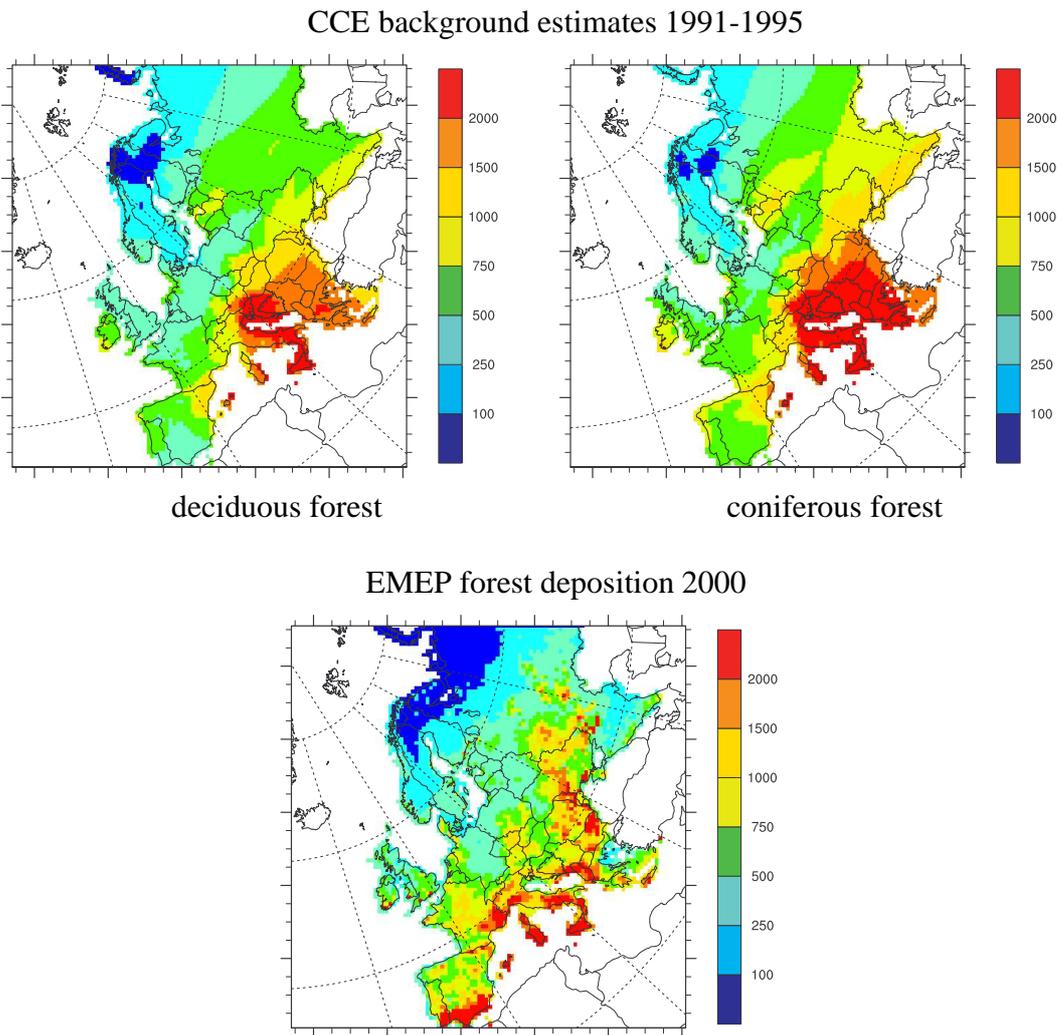


Figure 5.13: Background CCE estimates of total Ca deposition ( $\text{mg}/\text{m}^2/\text{year}$ ) for the period 1991-1995 for coniferous and deciduous forests (upper panels) versus EMEP modelled total Ca deposition in forests for the year 2000 (lower panel).

values are shown. Note that deposition fluxes to forest areas are usually larger than the grid averaged values. Since the background CCE estimates are averaged fields over the period 1991-1995, it is difficult to directly compare these fields with modelled fields for the year 2000. However, a first comparison shows similar deposition values and similar north-south gradients in Figure 5.13. Significant differences are seen in Spain and Portugal, where the modelled EMEP fields show high values, mainly due to the Saharan contribution in the southern part of the Iberian Peninsula which are not seen in the background CCE estimates. This is probably due to the fact that an insufficient amount of observations from that area were available for the period 1991-1995. As a result, observed values further north largely determine the kriged concentrations in the

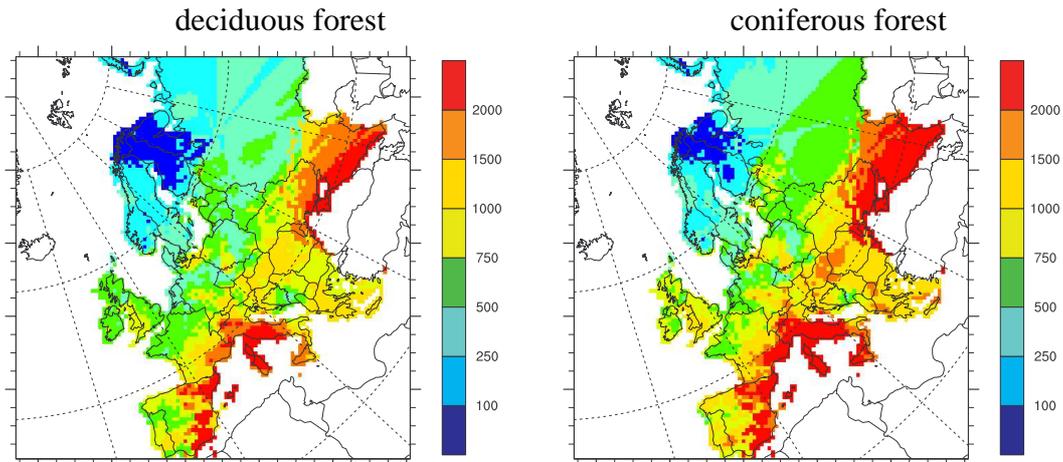


Figure 5.14: Empirically derived total Ca deposition ( $\text{mg}/\text{m}^2/\text{year}$ ) for the year 2000 for deciduous and coniferous forests.

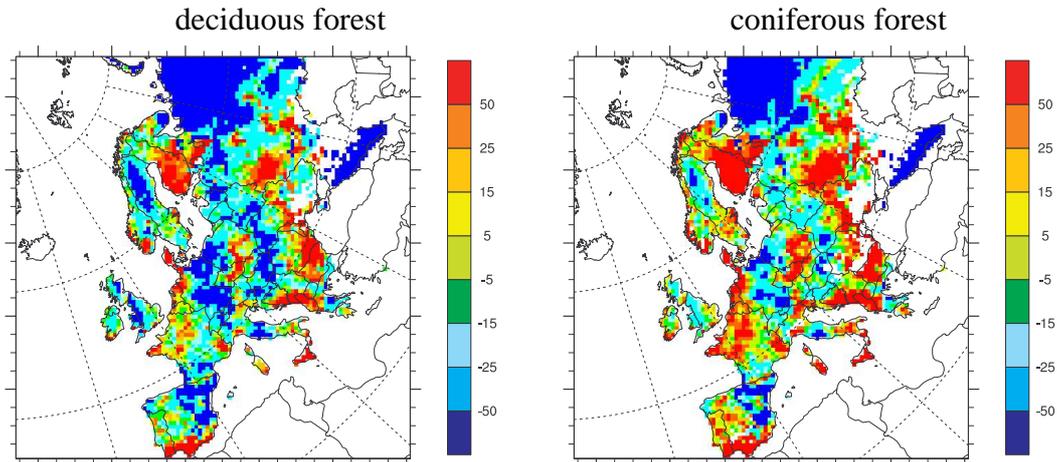


Figure 5.15: Percentage difference of total Ca deposition for the year 2000 between the EMEP model estimates and the empirical estimates. Unit: %

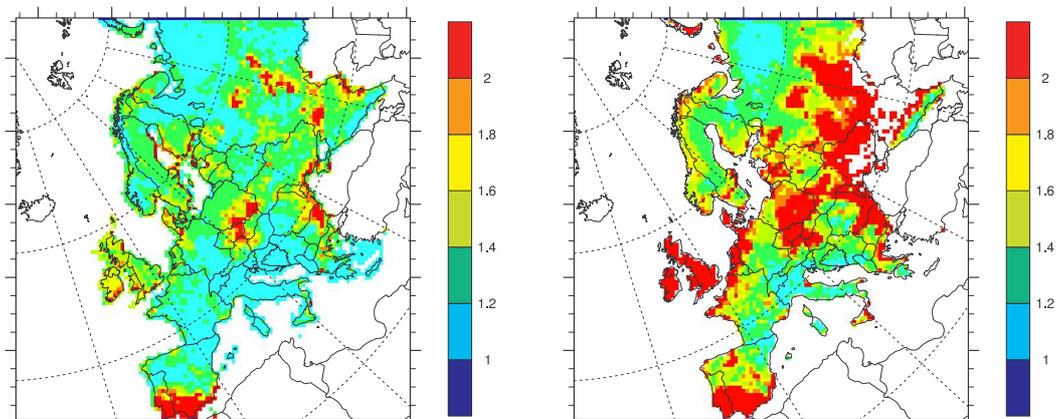


Figure 5.16: Modelled ratio between total deposition and wet deposition of Ca for grid averages (left panel) and for forests (right panel).

south of Spain and Portugal. Another significant difference is seen in the Balkan area, where the background CCE estimates are higher than the EMEP modelled ones. Apart from meteorological variability, a possible explanation could be a lower anthropogenic contribution in 2000 compared to the period 1991-1995.

In order to provide a more direct comparison, we have constructed empirical background estimates for the year 2000 following the same procedure as CCE (described above), based on the available measurements described earlier in this chapter. The resulting fields are given in Figure 5.14. Note that the empirical estimates for the year 2000 derived here are closer to the EMEP modelled fields in south-western Europe than to the CCE background estimates for 1991-1995. This indicates that the differences in south-western Europe mentioned above are probably due to inter-annual meteorological variability and differences in available measurement data. Still, differences between the empirical estimates and the EMEP model estimates are significant. Figure 5.15 shows that the use of the new EMEP model estimates will impose a change total deposition of calcium by 25-50% in many areas. Positive differences will probably result in less exceedances of critical loads, while negative differences, mostly over Germany, Poland and the UK, may lead to higher exceedances. The CCE background estimates assume a ratio between total and wet deposition of 1.4 for deciduous and 1.8 for coniferous forests uniformly for all forest areas in Europe. This is a reasonable assumption for some places as is indicated by Figure 5.16, but especially over eastern Europe, southern Spain and the British Isles the EMEP model estimates tend to provide higher ratios. In these areas the EMEP model estimates higher dry deposition values than wet deposition values for the meteorological conditions of the year 2000. Given the relatively large differences between the total deposition estimated by the EMEP model and previous methodologies used, it is recommended to investigate further the effect of the present base cation estimates on the calculation of critical loads of acidity.



## CHAPTER 6

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### Conclusions & Recommendations

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A first, successful attempt has been made to model base cation depositions to the EMEP model domain. Considering the limitations of the present parametrizations, the comparison with measurements from the EMEP and ICP Forest networks for the year 2000 showed an encouragingly good model performance both in terms of absolute level of modelled deposition amounts and spatial patterns.

A comparison of the EMEP modelled total deposition of calcium with previous empirical estimates showed relatively large differences by 25-50% in many areas. The EMEP estimates will probably result in less exceedances of critical loads over the coast of the Benelux countries while over Germany, Poland and the UK, they may lead to higher exceedances. This is the case for the year 2000, but differences due to inter-annual meteorological variability can be expected, especially because natural sources dominate the base cation deposition and are very dependent on the meteorological conditions. Further studies on the effect of meteorological variability on base cation deposition will be undertaken. Still, it is strongly recommended to investigate first the effect of the present base cation estimates on dynamic modelling and on the calculation of critical loads of acidity.

It turned out that wind blown dust contributes significantly to the deposition of base cations, except for Na, which is largely determined by sea salt. To a lesser extent this holds also for Mg. Particularly Ca depositions seem to be controlled largely by wind blown dust. For K this probably also the case, but the interpretation of the results is hampered by incomplete data on the base cation content of the soil. Given the large contribution from wind blown dust, further work on the verification of the present model approach is highly recommended. This applies both to the proper derivation of maps of the base cation content of the soil and to the revision and further development of the wind blown dust model parametrization.

The revision of the parametrization of wind blown dust sources is currently in

progress in relation with further PM modelling activities within EMEP. This project revealed the need for proper input data regarding surface characteristics and soil pedology, i.e. spatial information on the sizes of the soil aggregates, since they determine the actual vertical dust flux and its size distribution. This concerns especially the characterization of desert soils as Saharan dust is identified as a main source. Also within Europe various land use classes are aggregated into the category 'desert', while further disaggregation of this land use class is necessary in order to distinguish between erodible and non-erodible soils. The soil characterization involves not only a chemical speciation of the top soil, but also additional information on the erodibility of the soil and on the sizes of the soil aggregates. Therefore it is recommended that an attempt is made to refine the land use database at this point. In addition, the dust flux formulation is very sensitive to the choice of parameters like  $u_*$ . Further refinement of the methodology to compute the sub-grid  $u_*$  for desert areas and agricultural soils is recommended.

This initial study has also shown limitations in the present parametrization of sea salt production. For Na and Mg, the model calculations considerably underestimate the observed values and the parametrization of sea salt requires further attention in the near future. It is intended to continue the development and validation of the EMEP model calculations for base cations, in particular as more information on air concentrations becomes available following the implementation of the new EMEP Monitoring Strategy.

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## APPENDIX A

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### Unit conversions for base cations

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Here we present the factors needed to convert deposition of base cations (and chloride) from  $\text{mg/m}^2$  (as used in this report) to  $\text{eq/ha}$  (as used in critical load data submissions). We use the term 'equivalents' (eq) instead of the more official 'moles of charge' ( $\text{mol}_c$ ) for convenience.

If  $X$  is an ion with molecular weight  $M$  and charge  $z$ , one has:

$$1 \text{ g } X = \frac{1}{M} \text{ mol } X = \frac{|z|}{M} \text{ eq } X,$$

where the vertical bars mean that the absolute value has to be taken. From this follows immediately:

$$1 \text{ mg/m}^2 X = 10 \cdot \frac{|z|}{M} \text{ eq/ha } X$$

The charges, molecular weights and conversion factors from  $\text{mg/m}^2$  to  $\text{eq/ha}$  for base cations and chloride are given in the following Table:

Ion	Charge of ion	Molecular weight of ion (g/mol)	To convert 1 $\text{mg/m}^2$ to $\text{eq/ha}$ multiply with:
Ca	+2	40.078	0.499
Mg	+2	24.305	0.823
K	+1	39.098	0.256
Na	+1	22.990	0.435
Cl	-1	35.453	0.282