

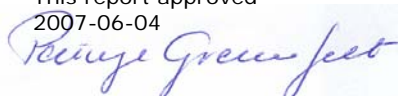
# Base cations deposition in Europe

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B1722  
June 2007



<b>Organization</b> IVL Swedish Environmental Research Institute Ltd.	<b>Report Summary</b>
<b>Address</b> P.O. Box 5302 SE-400 14 Göteborg	<b>Project title</b> Base cation deposition in Europe
<b>Telephone</b> +46 (0)31-725 62 00	<b>Project sponsor</b> The Nordic Council of Ministers, the Working Group for Air and Sea Pollution
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<b>Title and subtitle of the report</b> Base cations deposition in Europe	
<b>Summary</b> <p>The support from the Nordic Council of Ministers, the Working Group for Air and Sea Pollution, has significantly contributed to the development of unified calculations of base cation deposition across Europe with the EMEP model. Previous estimates of base cation deposition in Europe have mainly been based on empirical approaches of varying quality depending on country. The results of the model calculations will be used by CLRTAP and EU to assess the need for reduction of emissions of acidifying air pollutants in agreement with the Gothenburg protocol and NEC. The EMEP model has been extended to calculate the deposition of four base cations; calcium (Ca<sup>2+</sup>), magnesium (Mg<sup>2+</sup>), potassium (K<sup>+</sup>) and sodium (Na<sup>+</sup>). Natural emissions (from sea salt and wind blown dust) as well as anthropogenic emissions (from combustion and industrial processes) have been considered. Base cations are assumed to behave in a similar manner as primary particles in the atmosphere, and hence the transport and deposition of base cations are considered in the same way as primary particles in the EMEP model. The result of the EMEP modelling was compared with wet deposition fluxes derived from the EMEP and ICP-Forest network, and throughfall measurements from the ICP-Forest network, to assess the robustness of the model calculations. This comparison showed encouraging results. However, it was recognised that the EMEP model can be developed further, particularly regarding the estimates of base cation sources, to correctly quantify the base cation deposition in Europe. Furthermore, to provide a confident assessment of the results of the EMEP model, it is of great importance to further develop and improve the measurement methodologies and the methods applied to estimate dry deposition.</p>	
<b>Keyword</b> Base cations, deposition, acidification, critical loads, mapping	
<b>Bibliographic data</b> IVL Report B1722	
<b>The report can be ordered via</b> Homepage: <a href="http://www.ivl.se">www.ivl.se</a> , e-mail: <a href="mailto:publicationservice@ivl.se">publicationservice@ivl.se</a> , fax+46 (0)8-598 563 90, or via IVL, P.O. Box 21060, SE-100 31 Stockholm Sweden	

This report approved  
2007-06-04



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## Abstract

The deposition of base cations in Europe is important in the assessment of potential environmental impacts from acidification, as base cations affect the critical loads of acidity. Reliable data are necessary in integrated assessment modelling to develop abatement strategies for air pollutants across Europe. Previous estimates of base cation deposition in Europe have mainly been based on empirical approaches of varying quality depending on country. The current study has significantly contributed to the development of unified calculations of base cation deposition across Europe with the EMEP model. The results of the model calculations will be used by CLRTAP and EU to assess the need for reduction of emissions of acidifying air pollutants in agreement with the Gothenburg protocol and NEC.

The EMEP model has been extended to calculate the deposition of four base cations; calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), potassium ( $\text{K}^+$ ) and sodium ( $\text{Na}^+$ ). Considerable effort has been put in to estimating emissions of these four base cation species. Natural emissions (from sea salt and wind blown dust) as well as anthropogenic emissions (from combustion and industrial processes) have been considered. Base cations are assumed to behave in a similar manner as primary particles in the atmosphere, and hence the transport and deposition of base cations are considered in the same way as primary particles in the EMEP model.

The result of the EMEP modelling of the four base cations was compared with wet deposition fluxes derived from the EMEP and ICP-Forest network, to assess the robustness of the new model calculations. This comparison showed encouraging results. However, in order to assess also the dry deposition fraction, and to further assess the model outputs, the results were also compared with throughfall measurements from the ICP Forest Network. Throughfall data may be influenced by local sources, i.e. litterfall or resuspension of dust inside the forest floor. Furthermore, the canopy exchange, which for Mg, Ca and K may contribute to 10-80% of the total base cation flux (ICP-Forest, 2006), needs to be considered. Canopy exchange models therefore have to be applied in order to estimate the total deposition. These models are however associated with uncertainties and have a potential for improvements.

The comparison with throughfall measurements suggests that the EMEP model reproduces Ca values well, Mg and Na rather well, but for K the results are less encouraging. These results indicate that the EMEP model can be developed further, particularly regarding the estimates of base cation sources, to correctly quantify the base cation deposition in Europe. However, the discrepancies between the observed and modelled values are also due to uncertainties in the monitoring data. To provide a confident assessment of the results of the EMEP model, it is therefore of great importance to further develop and improve the measurement methodologies and the methods applied to estimate dry deposition.

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# 1 Introduction

## 1.1 Base cations and their role in acidification

The following four ions: calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), potassium ( $\text{K}^+$ ) and sodium ( $\text{Na}^+$ ) are referred to as base cations. These ions play an important role in the context of acidification in soil and water, because, together with weathering, base cation deposition adds ions for neutralising acids. Base cation deposition derives from anthropogenic emissions (from combustion and industrial processes) and from natural emissions (sea salt and wind blown dust). In most areas across Europe, the contribution from anthropogenic sources is small, however, in northern Europe, the contribution can be substantial. Currently, the emission trend for anthropogenic emissions of base cations points to reduced emissions, hence base cation deposition reductions can be expected in northern Europe. The emission trend for natural sources is not as evident; hence it is more difficult to predict future patterns of base cation depositions in central and southern Europe where natural sources of base cations are more important.

The deposition of acidifying pollutants has been reduced significantly in Europe, and when these pollutants have been reduced to the level where the acidification effect has ceased, the addition of base cations will contribute to ecosystem recovery. In the context of acidification, the importance of base cation deposition is of the same level of magnitude as the base cations weathering and the net uptake by vegetation. In many areas, the atmospheric deposition of base cations is enough to affect the critical loads and its exceedance to a considerable degree. However, so far the estimates of base cation deposition in many countries have only been based on wet deposition data, because dry deposition data has not been accessible, except for a few exceptions. Due to the importance of base cations in the context of acidification, deposition rates for base cations are essential in the calculation of exceedances of critical loads of acidity and other types of ecosystem effect assessments such as the calculation of ecosystem recovery (Westling and Lövblad, 2004). A correct quantification of the atmospheric deposition of base cations is therefore important for the calculations of Critical Loads for acidity and exceedance as a basis for emission reductions in Europe.

The mapping of deposition rates of total base cations can be carried out applying two different approaches;

- ❑ based on monitoring data in air and precipitation, and
- ❑ based on the emission distribution of base cations to air.

The first approach estimates base cation depositions based on observed wet deposition rates and a rough estimate of dry deposition, empirically derived either as a percentage of the wet deposition, or based on simple canopy exchange models together with throughfall measurements (Ulrich, 1983, van Leeuwen *et al.*, 1995; Westling *et al.*, 1995; van Leeuwen *et al.*, 1996). The advantage of this approach is that it includes the main part of all sources for base cations that occur, including those emissions that can be difficult to quantify, such as soil erosion. However, a disadvantage is that available monitoring data on levels of base cations in air and precipitation are scarce in many parts of Europe. Furthermore, although the methodology provides the overall picture of the deposition of base cations, it fails to distinguish between different sources. In most areas, only the contribution from sea salt can be distinguished in a simple way. However, links between the sources and

deposition can be derived to some extent applying source-receptor calculations using extensive monitoring data of the composition of the particles and in the deposition.

The second approach is based on dispersion- and deposition calculations with the EMEP chemical transport model. Applying this approach, the contribution from the different sources can be distinguished, as well as the contribution from long range transport and local sources. These aspects are important in the assessment of future levels of base cations through changes in anthropogenic emissions and potential changes in soil erosion, generation of sea salt etc., due to e.g. climate change. Up to now, there has not been a unified approach in Europe to calculate deposition rates of base cations. Most estimates across Europe have been based on empirical approaches of varying quality depending on the quality of the country specific data available.

## 1.2 The aim of this project

The aim of this project was to improve and assess a generalised model approach to derive base cation depositions over Europe based on the Unified EMEP chemical transport model. The project was initiated based on a request for European base cation deposition data from the Working Group on Effects (EMEP). An important basis for the project comprises of the conclusions from a workshop on base cations deposition in Gothenburg on the 26-28<sup>th</sup> of November 2003 (Westling and Lövblad, 2004), but also on the mapping of base cations for the Nordic countries within another NMR-project (Lövblad *et al.*, 2004).

The current project comprises four main activities:

- ❑ **Activity 1: Validating emission estimates for anthropogenic base cations** - The objective of this activity was to revise the accuracy and quality of the emission estimates applied in the EMEP model. Studies by Lee and Pacyna (1999) constitute an important basis in this validation process.
- ❑ **Activity 2: Assessment of the results of the EMEP model** - The objective of this activity was to assess the EMEP modelling results of the base cations deposition in Europe and the quality of the input data used in the model.
- ❑ **Activity 3: Assessment with throughfall measurements** - The objective of this activity was to compile and assess available data from throughfall measurements and canopy exchange modelling in Europe (ICP-Forest) to assess the results of the EMEP model considering dry deposition of base cations to forests.
- ❑ **Activity 4: Final report** - The final report presents the work from the activities above.

## 2 Emission inventory for base cations from anthropogenic sources

### 2.1 Introduction

The largest proportion of base cations in air and precipitation originates from natural sources, i.e. from sea salt and wind blown dust. Further information on these emissions and a more detailed description of the EMEP chemical transport model is provided in van Loon *et al.* (2005). Although emissions of base cations from anthropogenic processes are relatively small compared with natural

sources, anthropogenic emissions are still important in the context of modelling base cation deposition, particularly in northern Europe, where the contribution can be substantial.

The main sources of anthropogenic emissions of base cations are from combustion processes (coal and wood fuels) and from industrial processes (e.g. cement production, iron- and steel industry). However, few data are available on anthropogenic emissions of base cations at European level. In the Nordic countries, anthropogenic base cation sources have been inventoried to a limited extent (Lövblad, 1987; Antilla, 1990; Kindbom *et al.*, 1993; Lövblad *et al.*, 2004). At European level, only anthropogenic calcium emissions (Lee and Pacyna, 1999) have been inventoried with sufficient level of detail to allow for atmospheric transport modelling. In this study, an emission inventory of anthropogenic base cation emissions in Europe was therefore carried out. This inventory was then applied as input to the EMEP chemical transport model for base cations.

## 2.2 Methodology

The emission inventory for base cations from anthropogenic sources was based on available information from previous studies, and on expert opinion. Anthropogenic emissions of base cations can be derived from emission data of particulate matter if described per sector and the base cation content of primary PM particles for different emission sectors was therefore derived from detailed country-wise sector data from IIASA on PM<sub>10</sub> and PM<sub>2.5</sub>. Furthermore, data for the UK (Goodwin, 2004), the Nordic countries (Kindbom, 2004; Antilla, 1990) and estimates of calcium emissions for Europe (Lee and Pacyna, 1999) were also used.

From these sources, the base cation emissions for the year 2000 were derived per SNAP level 1 sector applying the following methodology: Firstly, the sectors within the data from IIASA that have non-zero base cation fractions (according to the data sources previously mentioned) were identified. These fractions were then multiplied by the corresponding PM sector emission provided by IIASA, to calculate the base cation emission. Finally, the emissions were aggregated into SNAP level 1 sectors, see Table 1. The base cations emissions were then spatially distributed by country, per sector and for PM<sub>fine</sub> and PM<sub>coarse</sub> respectively, applying the following assumptions: It was assumed that the sources in Table 1 constitute the bulk of the total anthropogenic base cation sources. No information was available to distinguish between different coal/fuel types, and therefore, the same base cation fractions have been assumed for all different coal/fuel types. When “Other solid-low S (biomass, waste, wood)” was specified as fuel in the IIASA data for residential/commercial combustion, wood was assumed as the fuel type. The base cation content for the different sectors was assumed to be the same for all countries/ areas, as no country specific information was available. For those countries where no sector information was available from IIASA, an average base cation content per SNAP level 1 sector was applied. The base cation content was assumed to be the same for PM<sub>coarse</sub> and PM<sub>fine</sub>. The spatial distribution of the base cation emissions follows the existing gridding for each of the SNAP level 1 sectors. Table 2 shows the calculated emission totals and the corresponding percentages for the two size fractions (fine and coarse) for each of the countries in the IIASA data.

The estimates of the anthropogenic base cations emission in Europe were applied in the EMEP model to calculate the spatial distribution of base cations from anthropogenic sources. van Loon *et al.* (2005) concluded that the present approach to estimate the anthropogenic base cations emission for year 2000 was considered to provide reasonable estimates for input to the EMEP model. However, the approach has some limitations regarding the availability of the data necessary, and the present estimates should therefore be considered as preliminary.

Table 1. Percent base cations in primary PM emissions derived from literature in this study (van Loon *et al.*, 2005).

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: fire 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 & business facilities – fugitive	n.a.	0	0	0	7.36	UK
4	Mining	Bauxite, copper, zinc 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 & light fuel oil)	0.29	0	0	0.19	UK
8	Other Mobile sources	Other transport	Medium destillates & 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

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



Table 2. Estimated base cations emissions in ton yr<sup>-1</sup> and percentage base cations in PM (van Loon *et al.*, 2005).

country	Fine								Coarse							
	Ca	Mg	K	Na	%Ca	%Mg	%K	%Na	Ca	Mg	K	Na	%Ca	%Mg	%K	%Na
AL	783	82	195	44	11.94	1.25	2.98	0.67	116	17	27	41	4.51	0.67	1.06	1.59
AT	3482	347	854	138	9.42	0.94	2.31	0.37	275	27	48	70	2.24	0.22	0.39	0.57
ATL	100	0	0	65	0.29	0	0	0.19	6	0	0	4	0.29	0	0	0.19
BA	854	211	249	273	4.21	1.04	1.22	1.35	1248	328	388	427	4.48	1.18	1.39	1.53
BAS	61	0	0	40	0.29	0	0	0.19	3	0	0	2	0.29	0	0	0.19
BE	2521	282	423	261	5.63	0.63	0.95	0.58	919	100	113	178	3.48	0.38	0.43	0.67
BLS	21	0	0	14	0.29	0	0	0.19	1	0	0	1	0.29	0	0	0.19
BUL	4345	669	949	600	7.41	1.14	1.62	1.02	1903	345	409	456	5.4	0.98	1.16	1.29
BY	1891	237	390	238	4.42	0.55	0.91	0.56	802	122	158	222	3.82	0.58	0.75	1.06
CH	823	71	155	67	8.1	0.7	1.52	0.66	70	6	10	69	1.41	0.13	0.19	1.39
CY	109	4	4	11	4.4	0.15	0.17	0.44	16	1	1	7	2.18	0.12	0.13	0.94
CZ	4029	795	1091	885	5.27	1.04	1.43	1.16	1648	377	459	517	4.03	0.92	1.12	1.26
DE	8756	903	1591	987	5.11	0.53	0.93	0.58	2047	159	277	701	2.31	0.18	0.31	0.79
DK	2672	266	674	109	11.93	1.19	3.01	0.49	158	18	35	62	1.52	0.17	0.34	0.6
ES	18715	1577	3335	1009	11.06	0.93	1.97	0.6	3314	263	362	605	5.14	0.41	0.56	0.94
EST	2581	357	713	235	11.79	1.63	3.25	1.07	946	238	293	290	4.71	1.18	1.46	1.44
FI	5088	514	1311	146	15.44	1.56	3.98	0.44	257	28	56	50	3.51	0.39	0.77	0.69
FR	44636	4481	11387	1401	15.97	1.6	4.08	0.5	2528	297	556	713	3.17	0.37	0.7	0.89
GB	4961	771	1089	1028	3.67	0.57	0.81	0.76	1936	392	472	842	2.53	0.51	0.62	1.1
GR	5209	543	1172	341	10.56	1.1	2.38	0.69	755	101	150	204	4.51	0.6	0.89	1.22
HR	1703	181	333	168	8.64	0.92	1.69	0.85	575	86	112	135	5.7	0.85	1.11	1.34
HU	4782	593	866	442	7.95	0.99	1.44	0.74	1337	209	238	305	5.06	0.79	0.9	1.16
IE	619	80	126	100	4.34	0.56	0.88	0.7	239	27	41	63	3.22	0.37	0.55	0.85
IT	31234	2755	6515	1227	13.86	1.22	2.89	0.54	3727	258	408	704	5.62	0.39	0.62	1.06
LT	3207	327	846	88	18.34	1.87	4.84	0.51	171	20	41	37	4.94	0.58	1.2	1.07
LU	233	26	34	22	7.19	0.79	1.05	0.69	54	4	5	7	5.81	0.4	0.57	0.78
LV	716	85	190	48	9.57	1.14	2.53	0.64	86	15	22	32	3.15	0.57	0.81	1.18
MD	878	226	247	276	3.84	0.99	1.08	1.21	723	189	221	259	4.04	1.05	1.23	1.45
MED	313	0	0	205	0.29	0	0	0.19	17	0	0	11	0.29	0	0	0.19
MK	452	80	93	106	4.76	0.84	0.98	1.11	499	119	141	159	4.37	1.04	1.23	1.39
MT	2	0	0	3	0.4	0	0	0.49	1	0	0	3	0.32	0	0	1.36
NL	1824	176	399	165	5.05	0.49	1.11	0.46	214	16	29	150	1	0.08	0.13	0.7
NO	3635	367	939	111	12.68	1.28	3.27	0.39	247	25	50	46	4.03	0.4	0.82	0.75
NOR	116	0	0	76	0.29	0	0	0.19	6	0	0	4	0.29	0	0	0.19
PL	24293	3076	6024	2135	11.3	1.43	2.8	0.99	3843	660	877	987	4.26	0.73	0.97	1.09
PT	7361	632	1553	253	15.74	1.35	3.32	0.54	800	59	96	136	6.32	0.47	0.76	1.08
RO	12098	1424	2676	888	10.49	1.23	2.32	0.77	3220	446	558	644	5.83	0.81	1.01	1.17
RUS	59960	9066	11589	8193	6.67	1.01	1.29	0.91	25067	4560	5363	5947	4.98	0.91	1.07	1.18
SE	15757	1581	4120	338	22.38	2.25	5.85	0.48	656	71	156	89	5.58	0.6	1.33	0.76
SI	1645	198	426	111	12.64	1.52	3.27	0.85	282	58	77	79	4.74	0.98	1.29	1.33
SK	695	123	135	162	3.77	0.67	0.73	0.88	367	74	88	123	3.48	0.7	0.84	1.16
TR	43150	4611	8761	2719	14.28	1.53	2.9	0.9	9839	1133	1377	1659	8.8	1.01	1.23	1.48
UA	13894	2573	2371	2619	4.35	0.81	0.74	0.82	8708	1748	1935	2318	4.27	0.86	0.95	1.14
YU	1852	356	409	482	4.13	0.79	0.91	1.07	2089	490	582	673	4.4	1.03	1.23	1.42
<b>Total</b>	<b>342055</b>	<b>40644</b>	<b>74235</b>	<b>28831</b>	<b>8.81</b>	<b>1.05</b>	<b>1.91</b>	<b>0.74</b>	<b>81717</b>	<b>13086</b>	<b>16231</b>	<b>20034</b>	<b>4.6</b>	<b>0.74</b>	<b>0.91</b>	<b>1.13</b>

### 3 Assessment of the results of the EMEP model

#### 3.1 Introduction

The deposition of base cations were modelled (van Loon, 2005), applying the EMEP chemical model, incorporating the inventory of anthropogenic emissions from this study, see Figure 1 to 3.

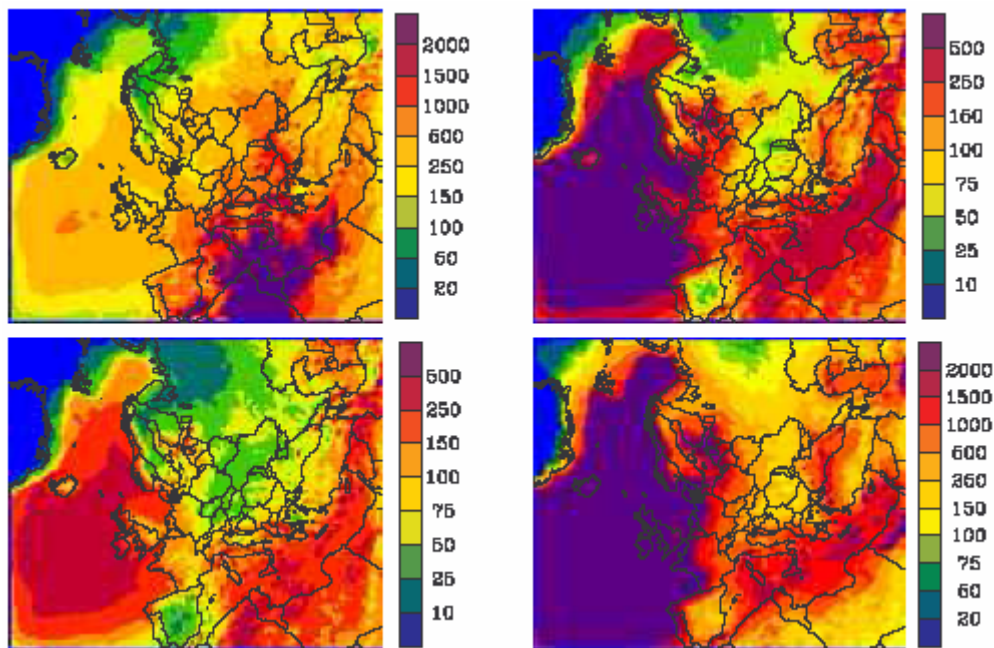


Figure 1. Modelled total deposition ( $\text{mg m}^{-2}$ ) of Ca (upper left), Mg (upper right), K (lower left) and Na (lower right) for the year 2000. Source: van Loon *et al.* (2005).

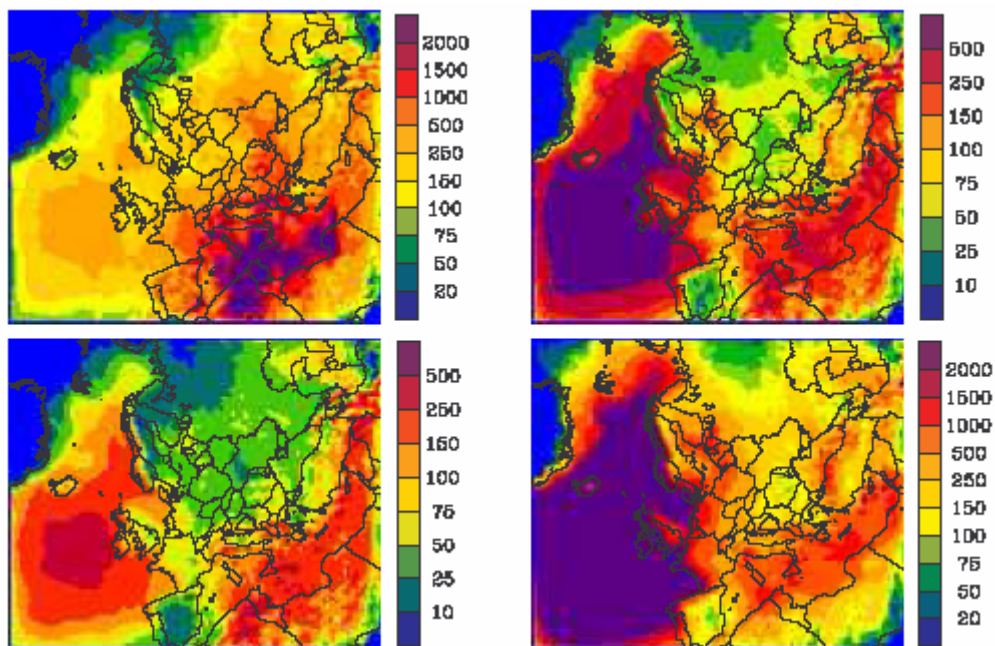


Figure 2. Modelled wet deposition ( $\text{mg m}^{-2}$ ) of Ca (upper left), Mg (upper right), K (lower left) and Na (lower right) for the year 2000. Source: van Loon *et al.* (2005).

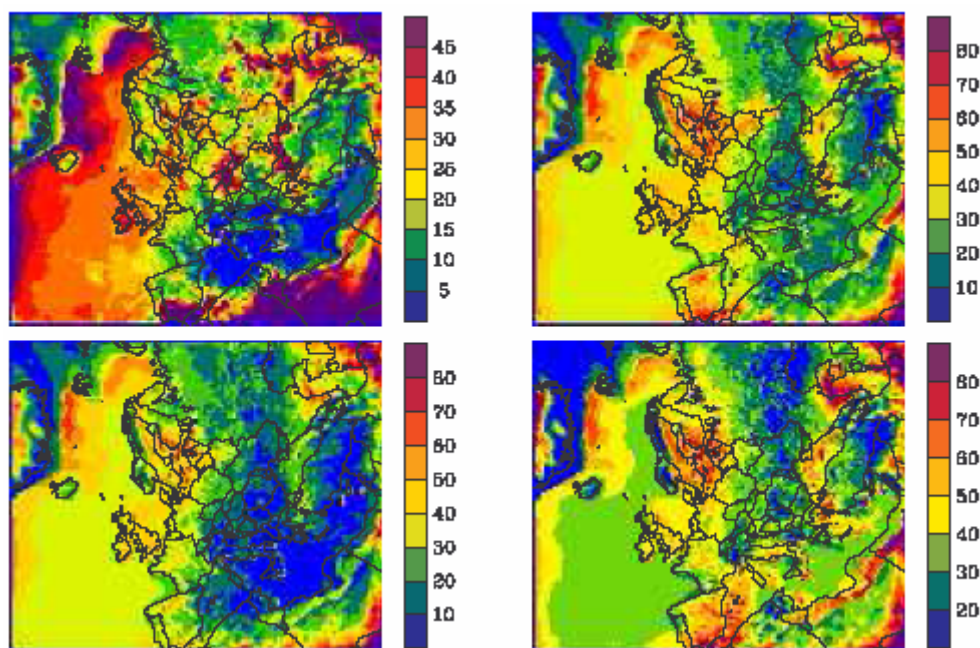


Figure 3. Modelled dry deposition ( $\text{mg m}^{-2}$ ) of Ca (upper left), Mg (upper right), K (lower left) and Na (lower right) for the year 2000. Source: van Loon *et al.* (2005).

The modelling results in Figure 1 to 3 were then compared with measurements to assess the robustness of the model. There are two different networks measuring wet deposition, EMEP and ICP Forest. In the EMEP network most of the countries use wet only collectors, except in the Nordic countries where daily or weekly bulk measurement are being used. In ICP Forest the main part of deposition rates is available as bulk deposition measurements on open field sites. Bulk measurements estimate wet deposition of various deposition species, however the bulk samplers can be contaminated, e.g. by leaves and bird excreta, and are also likely to capture an unknown part of the dry deposition in addition to the wet deposition. This is problematic, as the bulk collectors therefore neither represent the wet deposition, nor the total deposition. The influence of dry deposition depends on how dry the site is as well as the sampling frequency. In Norway, it has been shown that daily bulk sampling is very similar, less than 10% difference, to weekly wet only sampling (Aas, 2003). A study in Sweden, where bulk samplers were used in parallel with bulk samplers under roof at 11 sites to assess the dry deposition fraction of measured bulk deposition, suggest that the dry deposition fraction for base cations is about 10 - 20 % of the bulk measurement (Hellsten and Westling, 2006).

Throughfall measurements in forests can be used to estimate the total deposition of those ions that do not take part in the tree canopy internal circulation (such as uptake and leaching processes in the canopy), e.g. sulphate and sodium (Ulrich, 1983; Westling *et al.*, 1995).  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^{+}$  are affected by canopy exchange, and therefore, unlike  $\text{Na}^{+}$ , throughfall measurements are not a reliable indicator of total deposition for these base cations. Canopy exchange models have been proposed to assess total deposition rates, i.e. to separate between internal circulation and atmospheric deposition (Ulrich, 1983; Westling *et al.*, 1995), but the uncertainties in these models are relatively large.

## 3.2 Methodology

In this study, measurements from two monitoring networks were applied: the EMEP network and the ICP Forest Network. In addition, some extra data from the Norwegian and Swedish deposition network and from the ICP IM was used. The International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests, [www.icp-forests.org](http://www.icp-forests.org)) is an extensive monitoring system of forest sites in Europe. In contrast to the EMEP monitoring system, the ICP monitoring system provides throughfall measurements in addition to bulk measurements. Furthermore, ICP Forest consists of more monitoring sites, hence ICP Forest provides a better statistical basis for model evaluation. However, EMEP sites are usually situated in a more regional representative area. Furthermore, the problem with a dry deposition fraction in the sample is not as evident as for ICP, since the sampling frequency is higher and the method is usually wet only.

The results of the EMEP model (Figure 1 to 3) were evaluated by comparison with measurements. Two comparisons were carried out:

1. *Comparison with wet deposition fluxes from a number of stations from the EMEP- and the ICP Forest network (including data from the Norwegian deposition network and from the ICP IM).*
2. *Comparison with throughfall measurements from the ICP-Forest network (including data from the Swedish deposition network).*

### 3.2.1 Comparison with wet deposition fluxes

The wet deposition results of the EMEP model (Figure 2) were compared with observed average concentrations in precipitation from 104 stations from the EMEP network (Figure 4) and 243 stations from the ICP Forest network. Daily or weekly wet only measurements are carried out on most of the EMEP sites, while longer sampling periods (often monthly), usually using a bulk sampler, are more common for the ICP Forest sites. The ICP Forest measurements are therefore more sensitive to external factors, such as contamination and dry deposition. These data had therefore been checked, and inconsistent data (data with poor ion balance or obviously not regional representative measurements) had been removed from the dataset. The 347 monitoring values for 2000 for all four base cation species were compared with the corresponding values representative for the EMEP grid element (50 x 50 km) where the monitoring site is located.

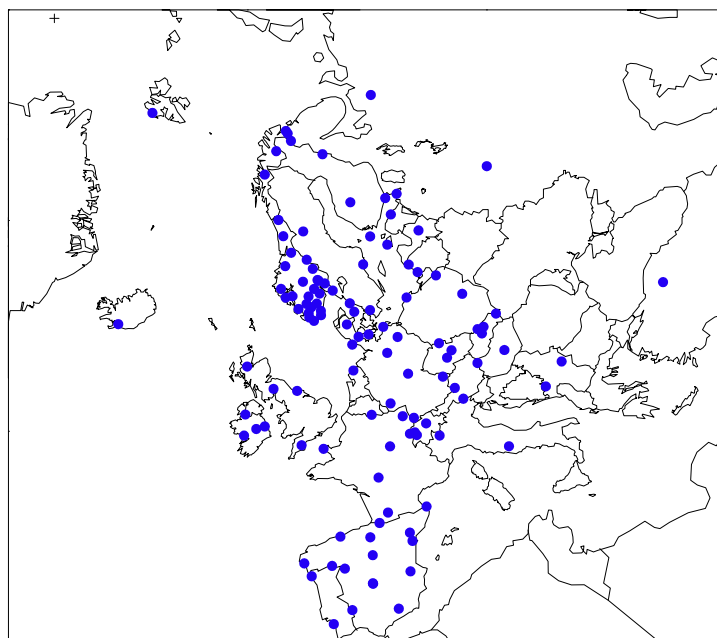


Figure 4. Location of the EMEP sites and some ICP IM used for measuring wet deposition. Some additional sites which are part of the Norwegian monitoring network have also been included.

### 3.2.2 Comparison with throughfall measurements

Although the evaluation of the modelling results with measurements of wet deposition fluxes provides an indication of the performance of the EMEP model, the comparison fails to assess the modelling results regarding dry deposition. Throughfall measurements from the ICP-Forest Network (and some additional Swedish sites) were therefore used to evaluate the results of the new EMEP model calculation for base cations total deposition.

ICP-Forest, Level II monitoring data from year 2000 were derived from the Forest Intensive Monitoring Coordinating Institute (FIMCI). These data had been quality assured, i.e. obviously contaminated or unrealistic values had been removed from the dataset. Sites with more than 50 days of missing data during a year were excluded from the study, to assure the data quality further.



In order to apply representative values for the whole year, values for those periods where data were missing, were estimated as the average values for the time period where monitoring data were available.

For elements that do not take part in canopy exchange, i.e.  $\text{Na}^{2+}$ , ideally the total deposition from throughfall in the forest should be larger than the wet deposition from the corresponding open field site. This is however not always the case. These types of discrepancies can be explained by uncertainties in the precipitation sampling, contamination of the sample, and/or the contribution of dry deposition to the open field collectors. In order to reduce uncertainties in the dataset, sites where the open field measurements for  $\text{Na}^{2+}$  showed higher values than the throughfall measurements, were excluded.

Data from only five European countries (France, Germany, Finland, Norway and Sweden) fulfilled the above requirements; giving 120 sites distributed over 107 EMEP grid elements (Figure 5). Although these 120 sites only represent a subset of the full ICP Forest data, these monitoring sites still provide data for a wide range of deposition levels. ICP Forest data had been collected at monthly intervals in Sweden and Finland, weekly in parts of Germany, and on an irregular basis in Norway and some German counties. France had collected data at 27 or 28 day intervals throughout the year (13 periods).

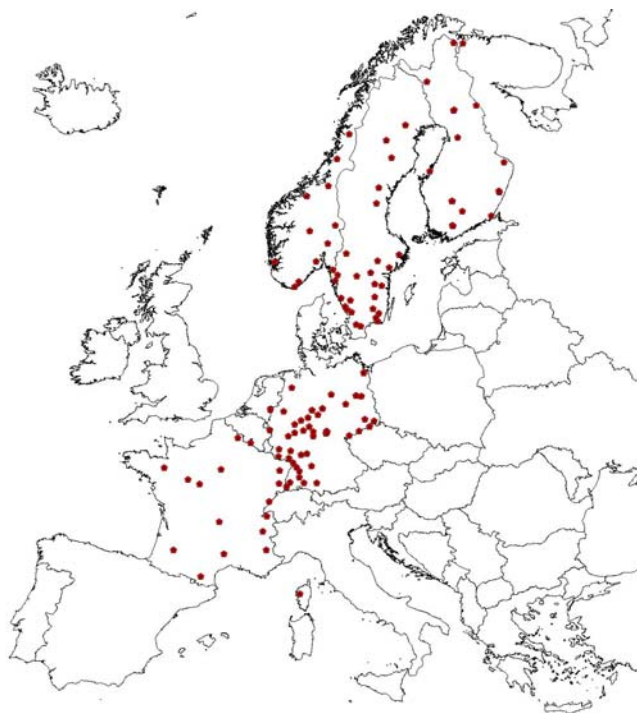


Figure 5. Location of the 120 ICP Forest sites (throughfall measurements) used in this study.

The 120 ICP Forest monitoring values for year 2000 for all four base cation species were compared with the corresponding EMEP grid cell (Table 3). Estimated wet deposition in the EMEP model was compared with the ICP Forest bulk measurements. Total deposition values could only be directly compared with throughfall measurements for Na, due to tree canopy internal circulation of Ca, Mg and K. The dry deposition fraction for Na was derived by subtracting the wet deposition

(bulk measurement) from the throughfall measurement. The ratio of Na in open field and in throughfall was applied to estimate the dry deposition proportion of Ca, Mg and K from the throughfall measurements (Ulrich, 1983), so that the EMEP dry deposition results could be assessed also for these base cation species. The deposition was further evaluated for Ca, Mg and K by subtracting the potential contribution from sea salt for both the modelled values representing dry deposition and the ICP dry deposition. The sea salt proportion was calculated from the Na contribution (assuming that all Na derives from sea salt). Concentration values for all four base cation species were also assessed. Volume weighted concentrations of Ca, Mg, K and Na were calculated for the ICP sites and the EMEP model based on the wet deposition/bulk measurements and precipitation for each site and grid cell respectively.

Table 3. Summary of the evaluated parameters at 120 sites in the comparison of modelled and observed data (ICP Forest) from 2000.

Parameter	Description
Wet deposition	EMEP modelled wet deposition was compared with ICP bulk measurements for all four base cation species.
Dry deposition	EMEP modelled dry deposition was compared with ICP values representing the dry deposition. For Na, dry deposition was derived as the difference between the bulk measurement and the throughfall measurement. For Ca, Mg and K, dry deposition was estimated from the throughfall measurements based on the ratio of Na in open field and in throughfall.
Total deposition	EMEP modelled total deposition was compared with ICP throughfall measurements for Na. For Ca, Mg and K, the calculated dry deposition was added to the bulk measurement to derive at a value representing the total deposition.
Non-marine total deposition	The potential sea salt contribution (estimated from Na) was subtracted from both the EMEP modelled total deposition and the value representing ICP Forest total deposition and compared.
Concentrations	Concentration values were calculated (based on wet deposition and precipitation) both for EMEP and ICP values and compared.

The 120 ICP Forest sites were divided into two subsets representing northern Europe (Norway, Sweden and Finland) and central Europe (Germany and France) to assess potential geographical differences in the EMEP model's performance. The two subsets comprised 56 sites (the northern European subset) and 64 sites (the central European subset), respectively. These areas are of interest since the sources and deposition rates of base cations varies between the two subsets, with generally higher contributions of anthropogenic sources and dry deposition in northern Europe compared with other parts of Europe. The EMEP model generated high dry deposition values in the eastern parts of the northern subset (Sweden and Finland), while wet deposition is important in southern, central and western Europe (see Figure 2 & 3). It would have been valuable also to evaluate the performance of the EMEP model in southern Europe where Saharan dust outbreaks is the largest contribution to the base cation deposition (Rodríguez *et al.*, 2001). However, due to limitations of reliable ICP Forest measurements of base cation deposition in southern Europe, the model evaluation was limited to central and northern Europe.

### 3.3 Results and discussion

The comparison is based on two datasets representing the deposition to forest sites derived from two completely different methods (measured data and modelled data). It is important to note that both these methods are associated with uncertainties, and no true values are available. The problem when comparing EMEP modelled data with ICP-forest measurements have been pointed out in other similar studies (Simpson *et al.*, 2006). Uncertainties in the EMEP model are to some extent discussed in van Loon *et al.* (2005). The data quality in the ICP Forest Network may vary between countries, due to the fact that there are several different sampling types in use, and that the sampling frequency varies. In addition to uncertainties associated with the sampling of throughfall and bulk measurements, the methods applied to derive the dry deposition fraction and the non-marine fraction, are associated with significant uncertainties. Furthermore, the forest sites may not be representative for a larger area, i.e. the EMEP grid cell in which they are located. The ICP data represent data from a forest plot of around 30 x 30 m, while the model calculation represents the average deposition to all landcover types in a corresponding grid square of size 50 x 50 km. Although the ICP datasets may not be representative for the EMEP grid square where they are located, an examination of the model results for a large number of sites should give a good indication of overall model biases and can still provide information about systematic differences and the causes and magnitude of uncertainties between measurements and the model calculation.

#### 3.3.1 Comparison with wet deposition fluxes

Observed and modelled average concentrations in precipitation for the different base cation species for the year 2000 are plotted in Figure 6 to 9. Figure 6 shows that the calcium concentration is highest in southern Europe, indicating that this area is significantly influenced by dust from the Sahara. The deposition pattern of magnesium (Figure 7) and sodium (Figure 9) show a different deposition pattern from calcium, with the highest concentration values in coastal areas, as these components are influenced by sea salt. Figure 8 suggests that the wet deposition pattern for potassium cannot be derived to any dominant source.

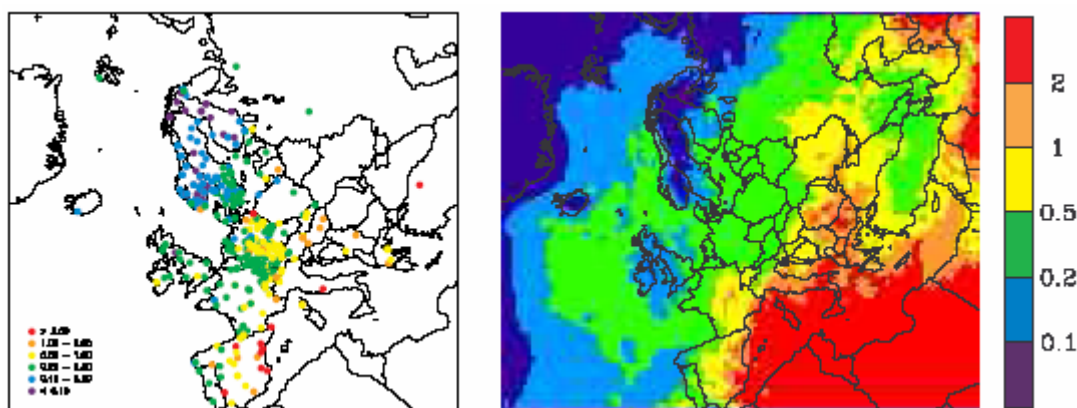


Figure 6. Observed (EMEP, ICP IM, ICP Forest) (left) and modelled (right) average wet deposition fluxes ( $\text{mg l}^{-1}$ ) for Ca in the year 2000. Source: van Loon *et al.* (2005).



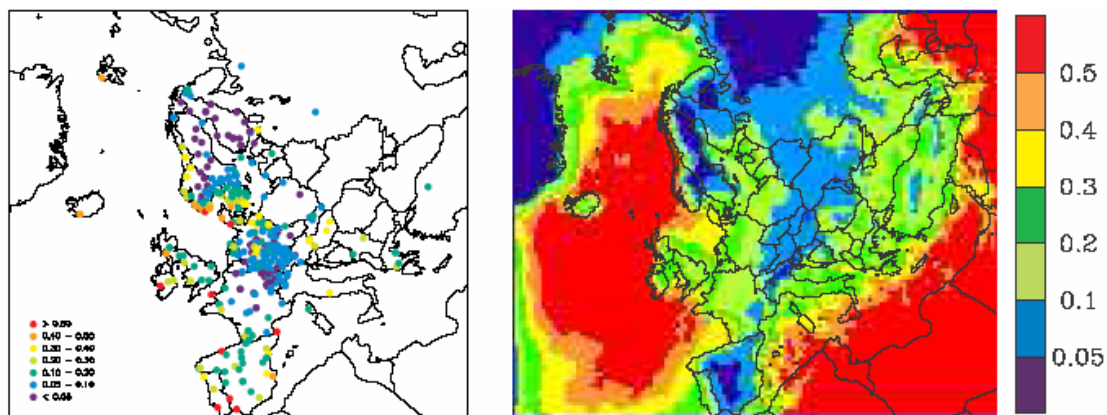


Figure 7. Observed (EMEP, ICP IM, ICP Forest) (left) and modelled (right) average wet deposition fluxes ( $\text{mg l}^{-1}$ ) for Mg in the year 2000. Source: van Loon *et al.* (2005).

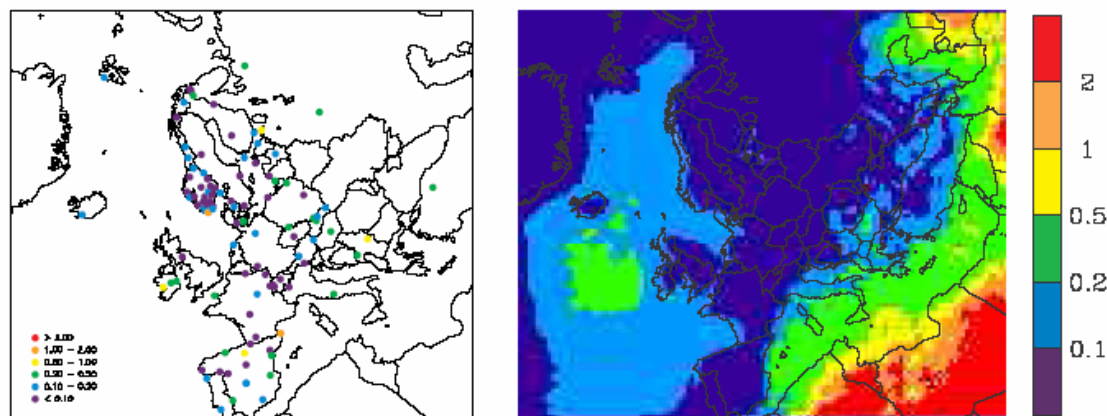


Figure 8. Observed (EMEP, ICP IM, ICP Forest) (left) and modelled (right) average wet deposition fluxes ( $\text{mg l}^{-1}$ ) for K in the year 2000. Source: van Loon *et al.* (2005).

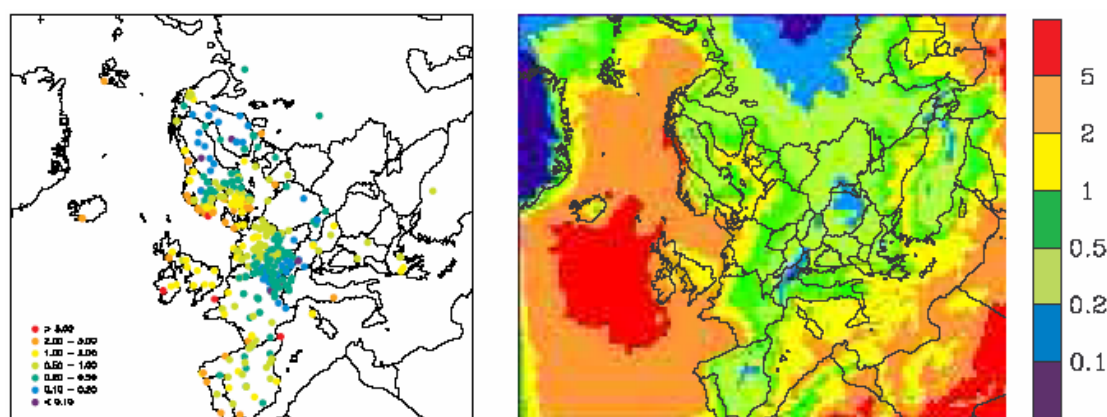


Figure 9. Observed (EMEP, ICP IM, ICP Forest) (left) and modelled (right) average wet deposition fluxes ( $\text{mg l}^{-1}$ ) for Na in the year 2000. Source: van Loon *et al.* (2005).

The spatial correlation between observed and modelled values for the four base cation species is shown in Table 4. The comparison suggests that the spatial correlation coefficient ( $r^2$ ) for Ca, Mg and Na is good ( $>0.7$ ). For K however, the spatial correlation was 0.53, suggesting that the model's performance for K is not as good as for the other base cation species. For K it was only possible to use the EMEP data since the ICP Forest measurements were influenced by local sources.

Table 4. Spatial correlation coefficients and average modelled and observed wet deposition fluxes ( $\text{mg m}^{-2}$ ) from the 347 sites (EMEP and ICP Forest) for the year 2000. (Sea salt correction has been applied)

	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 %

Comparing the observed and modelled means for the wet deposition fluxes (Table 4) suggests that the modelled wet deposition fluxes for Mg and Na match the observed values quite well. The good fit between the modelled and observed values can be mainly attributed to the fact that the main source of these two base cations are sea salt, and the modelled deposition values had been multiplied by eight to match the absolute values of the sea salt contribution. The sea salt contribution was scaled by a factor of eight as a comparison of initial model estimates with wet flux measurements showed a systematic underestimation of the wet deposition fluxes calculated by the model (van Loon, 2005).

Table 4 suggests that the model underestimates the wet deposition for Ca by 15 % on average. This underestimation is mainly evident at high deposition sites. K is underestimated by 42 %, and this underestimation is probably due to lack of data from the contribution of wind blown dust due to missing information on soil mineralogy. In the development of the EMEP model, an attempt to improve the spatial correlation for K had been carried out by scaling the proportion of wind blown dust from K to the modelled Ca deposition due to wind blown dust (van Loon *et al.*, 2005). This effort did however not improve the spatial correlation for K, hence indicating that the ratio between the content of K and Ca in soils is varying.

### 3.3.2 Comparison with throughfall measurements

The results of the comparison with throughfall measurements with the 120 ICP Forest sites in Figure 5 are summarised in Table 5. Spatial correlation coefficients and average modelled and observed values for year 2000 are shown for each parameter (wet-, dry-, total- and non-marine deposition and concentration) for the whole dataset (120 sites) and for the two subsets representing northern and central Europe.

## Wet deposition

In addition to the wet deposition comparison of 347 EMEP and ICP Forest sites in Section 3.3.1, wet deposition fluxes for the 120 ICP throughfall measurement sites were also assessed. This comparison suggested that the EMEP model reproduces wet deposition values rather well, with spatial correlations up to 0.60 (Table 5). However, the spatial correlation value for K was only 0.11. These spatial correlation values did not show as encouraging results as the initial comparison with wet deposition fluxes in Section 3.3.1, where the spatial correlation values were above 0.7 (except for K). This is probably because the monitoring sites and measurements applied in Section 3.3.1 are more representative and of better quality. In the initial comparison with measurements in Section 3.3.1 only the EMEP data were used for K, since the ICP forest measurements were considered to be influenced by local sources.

Table 5 suggests that the subset representing northern Europe show a better spatial correlation for wet deposition compared with central Europe for all base cation species, except Ca. No spatial correlation was evident for either Mg or K. Averaged over the sites, the modelled wet deposition for Ca, Mg and Na match the observed values quite well, with a tendency to underestimate the observed values (bias <10%). This underestimation was more evident in the subset representing northern Europe. The wet deposition for K was underestimated by a factor of almost 4 in both northern and central Europe. The systematic underestimation of wet deposition for all four base cation species may be explained by the contribution of dry deposition to the open field collectors in the bulk measurements, but could also, for Na and Mg be related to the sea salt production of base cations. The significant underestimation of wet deposition fluxes for potassium and the bad spatial correlation is probably related to the fact that the present version of the EMEP model fails to include all wind blown dust sources of K since the potassium content in soils is not available for all areas. However, there can be quite large local influence of K at the ICP Forest sites from resuspension of dust, litterfall etc, hence some underestimation of the model is expected.

Table 5. Spatial correlation coefficients and average observed and modelled values for the comparison with the 120 ICP Forest sites in Figure 5 for the year 2000. Dry and total deposition of Ca, Mg and K is calculated using a simple canopy budget model.

		All data				Northern Europe				Central Europe			
		Corr.	Obs.	Model	Bias	Corr.	Obs.	Model	Bias	Corr.	Obs.	Model	Bias
Wet deposition (mg m <sup>-2</sup> )	Ca	0.57	366	347	-5%	0.33	178	163	-8%	0.54	531	509	-4%
	Mg	0.54	129	118	-9%	0.65	161	125	-22%	0.05	101	111	10%
	K	0.11	189	53	-72%	0.50	166	47	-72%	0.02	210	59	-72%
	Na	0.60	800	754	-6%	0.61	1089	930	-15%	0.24	547	600	10%
Dry deposition (mg m <sup>-2</sup> )	Ca	0.004	220	210	-5%	0.03	103	242	135%	0.02	323	181	-44%
	Mg	0.024	86	359	317%	0.02	116	587	406%	0.07	60	160	167%
	K	0.008	110	117	6%	0.02	99	179	81%	0.02	119	62	-48%
	Na	0.025	586	2823	382%	0.02	841	4857	478%	0.15	363	1044	188%
Total deposition (mg m <sup>-2</sup> )	Ca	0.30	586	557	-5%	0.08	280	405	45%	0.32	854	690	-19%
	Mg	0.07	215	477	122%	0.05	277	712	157%	0.08	161	271	68%
	K	0.12	299	170	-43%	0.02	265	226	-15%	0.02	329	121	-63%
	Na	0.07	1385	3577	158%	0.05	1929	5786	200%	0.22	909	1644	81%
Non-marine (total) (mg m <sup>-2</sup> )	Ca	0.065	533	422	-21%	0.011	207	186	-10%	0.331	819	628	-23%
	Mg	0.005	48	46	-4%	0.023	44	15	-66%	0.015	51	73	43%
	K	0.006	249	41	-84%	0.001	195	18	-91%	0.044	296	61	-79%
Concentration (mg l <sup>-1</sup> )	Ca	0.32	0.34	0.35	3%								
	Mg	0.34	0.11	0.12	9%								
	K	0.004	0.19	0.06	-68%								
	Na	0.58	0.64	0.79	23%								

## Dry deposition

Table 5 suggests that there is no correlation between the datasets representing dry deposition. The significant level of scatter in the comparison of the dry deposition can to some extent be attributed to uncertainties in the deposition monitoring methods, and the methods applied to estimate the dry deposition fraction from throughfall. The dry deposition of Ca, Mg and K were estimated based on the ratio of Na in open field and in throughfall, and consequently, dry deposition for all base cations is sensitive to uncertainties in the measurement of Na. Although sites where the Na-ratio  $[Na_{\text{throughfall}} / Na_{\text{bulk}}] < 1$  had been removed from the calculation, as a dry deposition below zero is unrealistic, no “upper limit” of the Na-ratio was determined. Unrealistically high Na-ratios, due to for instance contaminated samples, will therefore influence the calculation of dry deposition for all four base cations.

It should be stressed that the contribution of dry deposition to forests is expected to be higher than to other landcover classes due to the aerodynamic properties of forests. Hence when comparing the EMEP modelling results (representing all landcover types) with ICP Forest sites, the modelled dry deposition values should be lower than the ICP estimates for dry deposition. However, averaged over the sites, the EMEP model overestimates dry deposition in northern Europe for all four base cations, particularly for Na and Mg. In central Europe, Ca and K were underestimated, but both Na and Mg were overestimated. Averaged over all the sites, the EMEP modelled dry deposition for Ca and K match the observer values well (bias <10%). Dry deposition values for Mg and Na on the other hand were overestimated by the model compared with the monitored values by a factor of up to 5. This overestimation was much higher in northern Europe compared with central Europe, mainly due to a few sites in northern Europe where the EMEP model give extremely high dry deposition rates that are not reflected in the ICP monitoring sites. These results suggest that the EMEP model provides too high dry deposition values in some parts of the subset representing northern Europe. In addition to the uncertainties mentioned above, these discrepancies can be due to an overestimation of the sea salt contribution from the Baltic Sea (which is brackish water).

## Total deposition

The total deposition (the sum of the wet and dry deposition) reflects the combined results of the wet- and dry- deposition comparison. The poor correlation for the total deposition in Table 5 is mainly a consequence of the poor correlation for dry deposition, see above. The spatial correlation for the total deposition is generally better in central Europe compared with the subset representing northern Europe for Ca, Mg and Na. For K, the spatial correlation was equally bad.

Averaged over the sites, the model values match the observed values for total deposition of Ca well (bias <10%). However, when looking at the two subsets, the picture is less encouraging. In northern Europe, Ca tends to be overestimated, while in central Europe, Ca is underestimated. For Na and Mg, averaged over all ICP sites, the model overestimates the total deposition compared with the deposition value for ICP by a factor of about 2 (mainly due to the overestimation of the dry deposition). This overestimation is more evident in the northern subset compared with central Europe. Considering the estimation of the non-marine Mg fraction (Table 5), the overestimation of Mg is probably mainly attributed to the marine fraction, i.e. uncertainties associated with sea salt production. As already mentioned, this overestimation could hence be due to an overestimation of the sea salt contribution from the Baltic Sea.

The total deposition for K is underestimated by a factor of almost 2, averaged over all the sites, mainly due to the underestimation of wet deposition of K. This underestimation was equally bad for the two subsets; hence no major differences between central and northern Europe were evident. The comparison of the non-marine fraction of K (Table 5) suggests that a significant proportion in the underestimation can be derived from the non-marine fraction of K.

Overall, Ca was the base cation ion where the EMEP model reproduced the observed values for total deposition in the ICP Forest Network the best. The encouraging results are probably due to the fact that the proportion of Ca emissions from anthropogenic emissions is high, and these emissions have been inventoried with a higher level of detail compared with the other anthropogenic emissions of base cations (Lee and Pacyna, 1999; van Loon *et al.*, 2005). For instance, the Ca content of the soil, which is an important parameter when modelling wind erosion, is rather well documented (Lee *et al.*, 1999; Batjes, 2002; van Loon *et al.*, 2005). For the other three base cations, the soil content at a European level is not as well known. In areas where wind blown dust is expected to be the most important source of base cations, lack of data regarding the Mg, Na and particularly the K content of the soil can therefore result in underestimates of these base cation species.

### **Non-marine total deposition**

The comparison of the non-marine fraction of the total deposition for Ca, Mg and K is associated with considerable scatter. This scatter is partly explained by uncertainties in the methodology to estimate the non-marine fraction of base cations. The spatial correlation between the two datasets was very poor for all three base cation species. Averaged over all the sites, the calculated non-marine deposition for Mg match the ICP data well, although the results suggest that the deposition is overestimated in central Europe and underestimated in northern Europe. For Ca the model tends to underestimate the deposition slightly in both subsets. However for K, the underestimation is significant (a factor of about 6), which suggests that a significant proportion of the underestimation of K can be derived from the non-marine fraction. This underestimation was greater in northern Europe compared with the subset representing central Europe.

## Concentration

When evaluating the volume weighted concentrations, uncertainties associated with the precipitation sampling adds to the overall uncertainties in the comparison. Figure 10 suggests that the EMEP model underestimates precipitation values compared with monitoring sites (bias of 12%).

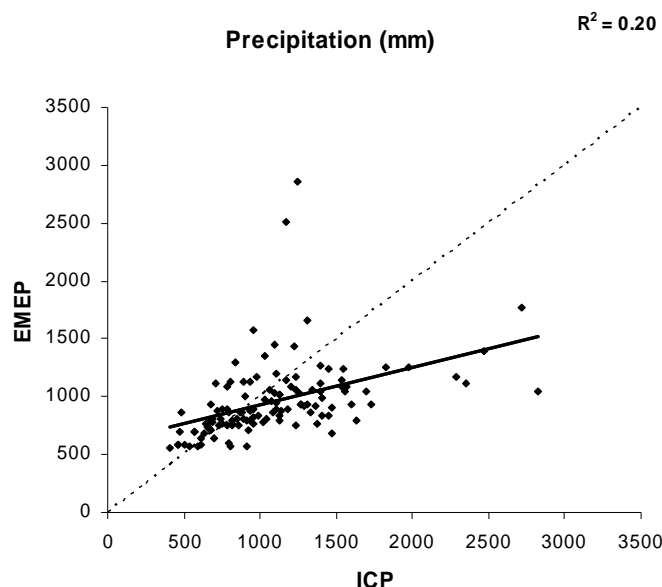


Figure 10. Precipitation (mm) during 2000, EMEP modelled vs. ICP bulk (open field).

The comparison of the volume weighted concentrations for the four base cations (Table 5) indicates that the spatial correlation for Na is rather good (0.58). The spatial correlation values for Ca and Mg are not quite as good (0.32 and 0.34 respectively), and for K there is no correlation between the two datasets. Overall, averaged modelled Ca values are in the same range as average ICP values. Na and Mg are slightly overestimated by the model, while K is significantly underestimated. The results are rather similar to those of wet deposition, however the underestimation of precipitation reduces some level of the underestimates evident in the wet deposition comparison.

## 4 Summary and conclusions

The EMEP model, and its predictions of base cations across Europe, plays a key role in the development of emission control strategies for Europe. Therefore it is important to improve and evaluate the EMEP model, and to test the model against observational data.

In this study, an emission inventory of anthropogenic base cation emissions was carried out, based on an approach where the emissions were derived from emission data of particulate matter. The base cation content of primary PM particles for different emission sectors was derived from detailed country-wise sector data from IISAS on PM<sub>10</sub> and PM<sub>2.5</sub>. The anthropogenic emission

inventory was incorporated in the EMEP chemical transport model to calculate deposition of base cations across Europe.

The estimated deposition of base cations for year 2000 was evaluated with measurements from the EMEP Network and the ICP Forest Network, in addition some extra data from the Norwegian and Swedish deposition network and from the ICP IM was used. Comparison with wet deposition fluxes from EMEP and ICP showed quite satisfactory performance of the EMEP model, both in terms of spatial correlation and modelled concentration levels. The EMEP measurement showed somewhat better correlation than the open field measurements in ICP Forest. This is expected since the EMEP sites are considered to be of better quality (wet only measurements with a higher sampling frequency) situated in more regional representative areas. The modelling results of total deposition were further evaluated with throughfall measurements from the ICP-Forest, level II, monitoring network.

It is important to point out that both measurement and modelling results are associated with uncertainties. The quality of the modelling results is very much related to the input data (representing the sources) and the dispersion methodology applied. The monitoring data are associated with uncertainties related to the sampling methodology, e.g. difficulties to exclude dry deposition in the bulk samplers, and also the methods applied to estimate the dry deposition proportion in throughfall and the non-marine contribution. Local contamination from e.g. resuspension of dust can be a problem at some sites. The measurements, especially for ICP Forest, may also not be representative for a larger area than the forest where the site is located. When evaluating a model where the results are calculated at a grid size of 50 x 50 km, it is always difficult to know how representative individual monitoring sites are of such large grid cells. When comparing single sites with grid data, scatter is therefore to be expected. Reducing uncertainties in the deposition monitoring of base cations and improving the quality control of the ICP data would have been useful for the evaluation process.

Data from the south of Europe are very scarce, and for ICP Forest data, data from this region have not been included in the evaluation process. It is of great importance to include monitoring data from all areas across Europe to evaluate the robustness of the EMEP model. The Mediterranean area is of particular interest since it is exposed to wind blown dust from the Sahara, an important source of base cation deposition. Furthermore, the base cation depositions in the south of Europe could be underestimated as the contribution of wind blown dust from some areas outside the modelling domain (northern Africa) have been excluded.

Ca and Na have been regarded to be modelled well with regards to the relative contribution of the sources (van Loon *et al.*, 2005). Although the EMEP model matches the observed values for Ca well, both regarding the wet- and dry deposition, Na values are overestimated by the model by a factor of >2 compared with the ICP sites, mainly due to an overestimation of the dry deposition of Na.

van Loon *et al.* (2005) suggest that Mg and K may have been underestimated, as the current model fails to incorporate K and Mg from the Sahara because there is no information available on the content of these base cations in desert soils. However, averaged over the sites, the comparison suggests that Mg values are overestimated, particularly in the subset representing northern Europe. K on the other hand, is underestimated by a factor of almost 2 averaged over all sites, suggesting that not all sources of K have been accounted for. The comparison for non-marine base cations (Ca, Mg and K) suggest that the spatial correlation is very poor. However, for Ca and Mg the modelled values reproduce the overall magnitude of the values well. For K, the underestimation is



significant (a factor of about 6), indicating that the non-marine sources of K (e.g. wind blown dust) significantly contribute to the underestimation of K.

The comparison of volume weighted concentration values suggests that the EMEP model underestimates precipitation amounts, hence, unlike for wet deposition, where all modelled values were underestimated, for concentrations, K is the only base cation species to be underestimated, but the measurement data may also be somewhat overestimated due to the influence of local sources.

Overall, the evaluation of the EMEP model reproduces Ca values well, Mg and Na rather well, but for K the results are less encouraging. These results indicate that the EMEP model can be developed further regarding the estimates of base cation sources, particularly for K, to correctly quantify the base cation deposition in Europe. However the discrepancies between the modelled and observed values also point to the need to further improve the monitoring methods and the methods applied to derive the dry deposition.

## 5 Acknowledgements

The authors would like to acknowledge the following scientists and organisations:

The support from the Nordic Council of Ministers, the Working Group for Air and Sea Pollution, has significantly contributed to the development of unified calculations of base cation deposition across Europe with the EMEP model.

We are thankful to EMEP and FIMCI (the Forest Intensive Monitoring Coordinating Institute) for the possibility of using data from EMEP and the ICP Forest Network.

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