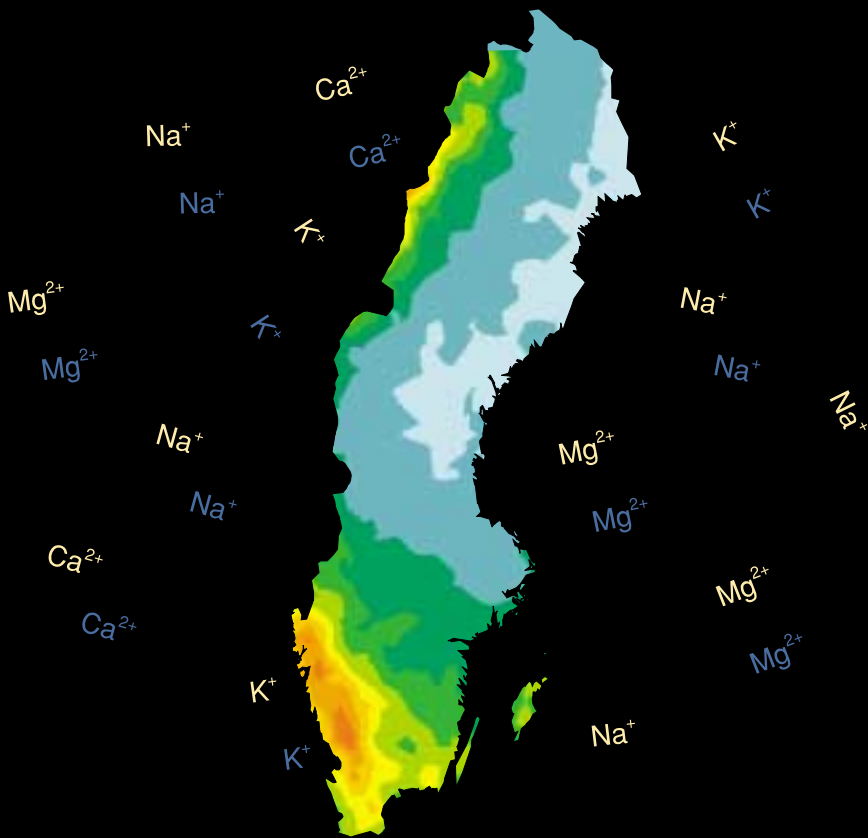


Deposition of Base Cations in Sweden

Gun Lövblad Christer Persson Elisabet Roos



*Deposition of
Base Cations in Sweden*

Gun Lövblad
Christer Persson
Elisabet Roos

Environmental Assessment Department
Environmental Impacts Section
Contact: Ulla Bertills, telephone +46 8 698 15 02

The authors assume sole responsibility for the contents of this report,
which therefore cannot be cited as representing the views of
the Swedish Environmental Protection Agency.
The report has been submitted to external referees for review.

Production: Margot Wallin
Cover: Johan Wihlke
Address for orders:
Swedish Environmental Protection Agency
Customer Services
SE-106 48 Stockholm, Sweden
Telephone: +46 8 698 12 00
Fax: +46 8 698 15 15
E-mail: kundtjanst@environ.se
Internet: <http://www.environ.se>
Bookstore: <http://www.miljobokhandeln.com>
isbn 91-620-5119-9
issn 0282-7298

© Swedish Environmental Protection Agency
Printed by: Berlings Skogs, Trelleborg, 2000
Edition: 1 000 copies

Preface

Base cations – calcium, magnesium, potassium and sodium – are present in forest soils where they are important nutrients for the forest trees. In the acidification process, base cations are leached from the soils as positive counter ions to sulphate and nitrate in soil water and thereby lost. One criteria used for determining the critical load is that the ratio between the concentration of (calcium+magnesium+potassium) and aluminum in the soil water should be ≥ 1 .

The atmospheric deposition is an important source of base cation input to the ecosystems. It is not easily estimated, since base cations are found on particles in different size ranges and of varying origin. They are naturally emitted and from anthropogenic sources, on which knowledge is poor, and base cations take part in the internal cycling of ions in the canopies. The report deals with different approaches for estimating the magnitude of base cation deposition in Sweden, the importance of different sources and deposition processes. The report is a basis for further work on estimating base cation deposition in the mapping of critical loads and its exceedance. The project was financially supported by the Swedish Environmental Protection Agency, mainly by the research programme Acidifying Substances and Tropospheric Ozone.

Gun Lövblad
Christer Persson and Elisabet Roos
Göteborg and Norrköping 2000

Contents

Preface

Summary 7

Svensk sammanfattning 10

1 Introduction 13

2 Methods used for estimating base cation deposition 19

2.1 The MATCH model 19

2.2 The Na-ratio method 27

2.3 The Scavenging ratio method by RIVM 28

2.4 Canopy budget modelling of throughfall data 29

2.5 Surrogate surface sampler 30

3 Results of deposition estimates 31

3.1 The MATCH model 31

3.2 The Na-ratio method 33

3.3 The RIVM model 37

3.4 The Surrogate surface method 39

4 Conclusions and recommendations 49

4.1 Wet, dry and total deposition 49

4.2 Sea salt and non-sea salt deposition 51

4.3 Swedish and long range transport contributions 51

4.4 Remaining uncertainties 52

4.5 Recommendations for future deposition estimates 52

Acknowledgement 55

References 57

Summary

Base cation deposition (potassium, K^+ , magnesium, Mg^{2+} , calcium, Ca^{2+} , and sodium, Na^+) is an essential parameter for quantifying critical loads and its exceedance, as well as for prognoses on the recovery of ecosystems from acidification. Base cations associated with carbonates and oxides act as a neutralising input of alkalinity to the ecosystems. The base cations are emitted to the atmosphere as particles via natural processes (soil erosion, sea salt etc.) as well as anthropogenic activities (combustion of fuels such as coal and wood, different industrial processes, agriculture etc.). Emissions occur as particles of different size distribution and composition. For several types of emissions the magnitude and character is not very well known.

In this study different approaches have been used to estimate base cation deposition and the results have been compared. The results have provided information on the magnitude of deposition over Sweden, the importance of different sources and deposition processes as well as the contribution from national sources in relation to long-range transport. Two of the methods used are based on monitoring data alone (Na-ratios in throughfall and wet deposition and surrogate surface in parallel with throughfall measurements), and two are based on monitoring data in combination with modelling (SMHI's MATCH-model and the RIVM-model). For the surrogate surface, monitoring data have been used for only one site.

The results show that total deposition of base cations is spatially and temporally variable, more variable than deposition of sulphur. In large parts of southern Sweden the total deposition of Na^+ including sea salt is 500–1100 mg/m^2 and year. The total deposition of Ca^{2+} , Mg^{2+} and K^+ is in the ranges 150–200 mg/m^2 , 75–150 and 100–150 mg/m^2 and year, respectively. The highest deposition is found at the west coast of Sweden, where also the strongest gradients are seen. Base cation deposition also shows a clear gradient with decreasing deposition from south to north.

The wet deposition depends to a large extent on precipitation amounts. However, there is a slight systematic deviation in wet deposition estimates based on different sets of monitoring data. This is unexpected, since the same type of equipment, the same sampling procedure and the same analytical laboratory is used. The deviations are thus suspected to be due to siting of sampling stations.

The dry deposition estimates for the two model-based methods represent a mixed land use. The other two, based on monitoring data, represent deposition to spruce forest only. As expected, these latter methods give larger dry deposition values than the model-calculated dry deposition representing mixed land use. The model-calculated deposition, however, in largely forested areas was lower than expected. The reason for this may be that emission input to the model is uncertain, and that the dry deposition process may be simulated in a way, which may underestimate the deposition.

The three methods used for the whole of Sweden show different decreasing gradients in total deposition amount from south to north, and different gradients in dry to wet deposition ratio. Monitoring data indicate that the dry deposition in the north is almost negligible. The two partly model-based methods indicate a certain dry deposition contribution also in the north. However, the uncertainties are large in the north due to less monitoring data available on air concentrations of base cations, and on base cations in throughfall. This also shows that it is not possible to estimate base cation deposition with the same accuracy all over Sweden.

The three methods used for Sweden show different gradients of the ratio between dry and total deposition. The Na-ratio method gives a dry deposition contribution of the magnitude 40% of the total deposition in southern Sweden. The importance of dry deposition decreases according to this method towards the north. The MATCH model results indicate that dry deposition is of less importance and that the differences over the country are less significant than is shown by the Na-ratio method. The RIVM method shows a dry deposition which is 60–70% of the total deposition for Na^+ , Ca^{2+} and Mg^{2+} in large parts of the country, while the dry deposition of K^+ is not more than approximately 40% of the total deposition. The RIVM method gives mainly the same relative dry deposition contribution over the country.

Sea salt deposition is a major contribution to the total deposition levels of Na^+ (in most areas >95%) and Mg^{2+} (50–80%). For Ca^{2+} and K^+ as little as 5–20% and 10–20% of the total deposition is sea salt. But there are large variations over the country. The sea salt contribution is largest on the west coast, where about 20–30% of the Ca^{2+} and K^+ wet deposition is sea salt. In parts of eastern and central Sweden the sea salt contribution is about 15% for K^+ and less than 10% for Ca^{2+} . For Mg^{2+} more than 85% is of sea salt origin in western Sweden, while in northern and eastern Sweden about 60% is sea salt.

The MATCH model results indicate that the Swedish contribution to the deposition of non-sea salt base cations is small, except locally around emission sources. For non-marine Ca^{2+} , Swedish sources contribute with up to 6–10% of the total deposition. In areas with extensive wood burning it reaches up to 15%. National anthropogenic Na^+ emissions are further found to account for less than 0.5% of the total deposition of Na^+ on the west coast. In most other areas the corresponding contributions are 1–7%, with the higher values locally on the coast in northern Sweden. This is in agreement with what can be estimated from monitoring data on Na^+ and Mg^{2+} in throughfall and wet deposition over the country.

Largely, there is an agreement between estimates of base cation deposition as regards the order of magnitude in southern Sweden. In northern Sweden, the deviations between methods are, relatively seen, larger than in the south. The different methods give sometimes contradicting results, however, as regards deposition gradients over the country and contribution from dry deposition and from sea salt deposition. A number of uncertainties involved in the methods used are defined. Many of these are due to lack of accurate data, for example for emission amounts and particle size ranges and for base cations in ambient air and in throughfall. To improve the estimates of base cation deposition more monitoring data are necessary. The lack of data is especially obvious in northern Sweden. Also, to improve the model-based estimate, an improved simulation of the dry deposition processes is necessary. This is not only necessary to improve the base cation deposition estimates, but also for estimating sulphur and nitrogen deposition.

For future deposition mapping, requirements have to be set for the need of details and accuracy of base cation deposition. The scale needed for the mapping is different in different areas. For example, the mapping of sea salt needs a special procedure, with a more detailed resolution, and taking into consideration the distance from the sea and local wind data. Use of new methods such as surrogate surfaces may contribute further to new knowledge. Such methods are now being used at approximately ten sites over Sweden and may add to the knowledge of deposition from particles and fog drops, and also to the relation between atmospheric deposition and canopy leaching in throughfall.

Svensk sammanfattning

Deposition av baskatjoner (kalium, K^+ , magnesium, Mg^{2+} , kalcium, Ca^{2+} , och natrium, Na^+) är en viktig parameter för att bestämma kritisk belastning och dess överskridande, samt för prognoser kring ekosystemens återhämtning från försurning. Baskatjoner som tillförts som karbonater och oxider ger ett tillskott av neutraliserande ämnen till ekosystemen. Baskatjoner emitteras till luft i partikelfas genom såväl naturliga processer (markererosion, havssalt, m fl) som antropogen verksamhet (förbränning av olika bränslen som kol och ved, olika industriella processer, jordbruk m m). Emissionerna sker via partiklar av olika kornstorleksfördelning och sammansättning. För flera typer av utsläpp är storlek och karaktär inte särskilt väl känd.

I denna studie har olika metoder använts för att uppskatta baskatjon-depositionen och resultaten har jämförts. Resultaten har gett information om storleksordningen på depositionen över Sverige, betydelsen av olika källor och olika depositionsprocesser samt bidraget från nationella källor i relation till långväga transport. Två av de metoder som använts baseras på enbart mätdata (Na-kvoter i krondropp och våtdeposition samt strängprovtagare parallellt med krondroppsmätningar) och två baseras på mätdata kombinerade med modellberäkningar (SMHI:s MATCH-modell och RIVM-modellen). För strängprovtagaren har enbart utnyttjats mätdata från en plats.

Resultaten visar att den totala depositionen av baskatjoner varierar både i rummet och i tiden, och variationerna är större än för svaveldepositionen. I stora delar av södra Sverige är totaldepositionen av natrium inklusive havssalter 500–1100 mg/m^2 och år. Den totala depositionen av kalcium, magnesium och kalium är vanligen i intervallen 150–200 mg/m^2 , 75–150 respektive 100–150 mg/m^2 och år. Den högsta depositionen återfinns på västkusten, där också de starkaste gradienterna observeras. Baskatjondepositionen visar också en tydlig gradient med minskande deposition från söder mot norr.

Våtdepositionen beror i hög grad av nederbörds mängderna. Det förekommer dock en systematisk skillnad i uppskattningarna av våtdeposition beroende på vilket mätdataset som används. Detta är inte förväntat, eftersom samma typ av utrustning, samma provtagningsförfarande och samma analyslaboratorium använts. Skillnaderna misstänks därför bero på lokaliseringen av mätstationer.

De uppskattningar av torrdeposition som erhålls med de två modellbaserade metoderna representerar blandad markanvändning. De två andra metoderna representerar deposition enbart till granskog. Som förväntat ger de senare större torrdeposition än den modellberäknade torrdepositionen till blandad markanvändning. Den modellberäknade depositionen till skogbevuxna områden är dock lägre än förväntat. Detta kan bero på att emissionsdata som används är osäkra och att simuleringen av torrdepositionen kan ha gjorts på ett sätt som kan underskatta depositionen.

Mätdata tyder på att torrdepositionen i norr är i det närmaste försumbar. De två delvis modellbaserade metoderna tyder på ett visst torrdepositionsbidrag även i norr. Men osäkerheterna är stora, beroende på att färre mätdata är tillgängliga för lufthalter av baskatjoner och för baskatjoner i krondropp. Detta visar att baskatjondepositionen inte kan bestämmas med samma noggrannhet över hela landet.

De tre metoder som använts för hela Sverige visar på olika gradienter i kvoten torr till total deposition. Na-kvotmetoden ger ett torrdepositionsbidrag som utgör ca 40 % av den totala depositionen i södra Sverige. Torrdepositionens betydelse minskar enligt denna metod mot norr. MATCH-modellens resultat tyder på att torrdepositionen är av mindre betydelse och att skillnaderna över landet inte är så stora som Na-kvot metoden indikerar. RIVM-metoden visar att torrdepositionen utgör ca 60–70 % av den totala depositionen för natrium, kalcium och magnesium i stora delar av landet, medan torrdepositionen av kalium endast utgör ca 40 % av den totala depositionen. RIVM-metoden visar att torrdepositionens andel av den totala depositionen är ungefär densamma över hela landet.

Havssaltet utgör ett dominerande bidrag till de totala depositionsnivåerna för natrium (i de flesta områden >95 %) och magnesium (50–80 %). För kalcium och kalium utgörs så lite som 5–20 % respektive 10–20 % av den totala depositionen av havssalt. Men stora variationer förekommer över landet. Havssaltsbidragen är störst på västkusten, där ca 20–30 % av våtdepositionen av kalcium och kalium är havssalt. I delar av östra och mellersta Sverige utgör havssaltsbidraget ca 15 % för kalium och mindre än 10 % för kalcium. För magnesium härrör mer än 85 % av den totala depositionen från havssalt i Västsverige, medan ca 60 % utgörs av havssalt i norra och östra Sverige.

Resultaten från MATCH-modellen tyder på att det svenska bidraget till icke havssaltsrelaterad baskatjondeposition är litet, utom lokalt runt vissa

utsläppskällor. För icke havssaltsrelaterat kalcium bidrar svenska källor med upp till 6–10 % av totaldepositionen. I områden med omfattande vedeldning kan det svenska bidraget uppgå till 15 %. Modellen uppskattar att nationella antropogena Na^+ -utsläpp bidrar till mindre än 0,5 % av totaldepositionen för Na^+ på västkusten. I de flesta andra områden är motsvarande bidrag 1–7 %, med högre värden lokalt längs kusten i norra Sverige. Detta överensstämmer med vad som kan uppskattas ur mätdata för natrium och magnesium i kronddropp och våtdeposition över landet.

I stort är det överensstämmelse mellan uppskattningarna av baskatjondeposition, vad gäller storleksordningen på depositionen i södra Sverige. I norra Sverige är avvikelserna mellan de olika metodernas resultat relativt sett större än i söder. Metoderna ger dock ibland motsägelsefulla resultat vad gäller gradienter över landet och bidrag från torrdeposition och havssalt. En rad osäkerheter i metoderna har definierats. Många av dessa beror på avsaknad av tillförlitliga mätdata, till exempel för emissioner och partikelstorleksfördelningar och för baskatjoner i luft och i kronddropp. För att förbättra uppskattningarna av baskatjondepositionen krävs mer mätdata. Bristen på mätdata är särskilt tydlig i norra Sverige. Förbättrade modellberäkningar kräver vidare en bättre simulering av torrdepositionsprocesserna. Detta är inte nödvändigt enbart för baskatjonerna, utan även för uppskattningarna av svavel och kvävedeposition.

För det framtida depositionsarteringsarbetet, behöver krav ställas på behovet av detaljering och noggrannhet. Den nödvändiga skalan för kartering är olika i olika områden. Till exempel kräver karteringen av havssaltsdeposition ett särskilt förfarande, med en mer detaljerad upplösning, och som tar hänsyn till avståndet till havet och till lokala vinddata. Användning av nya metoder som surrogatytor kan bidra ytterligare till ny kunskap. Sådana metoder används nu på ett tiotal platser i landet och kommer att kunna bidra till kunskaper om partikel- och dimdeposition och också till förhållandet mellan atmosfärsdeposition och interncirkulation i kronddropp.

Chapter 1.

Introduction

Base cation deposition (potassium, K^+ , magnesium, Mg^{2+} , calcium, Ca^{2+} , and sodium, Na^+) represents a major input to ecosystem nutrient pools and is a source for buffering acidic deposition. Base cations associated with carbonates and oxides represent an input of alkalinity with a capacity to neutralise acidic deposition. Neutralisation of acid deposition can occur via deposition of base cations from soil erosion or via alkaline base cation deposition originating from industrial processes and combustion emissions. Base cations are also important nutrients to forest trees. Uptake of base cations in stems and branches, which are removed from the ecosystems, may in some areas cause losses (Westling et al., 1997), which will further contribute to acidification. It therefore influences the reduction requirements for sulphur and nitrogen emissions.

A number of studies have estimated the base cation emission in Scandinavia (Lövblad, 1987; Anttila, 1990) and in Europe (Lee et al., 1999). Still, large uncertainties are connected with the estimated amounts of base cations from anthropogenic sources, as well as with the size ranges in which the base cation particles are emitted to the atmosphere. Also, considerable difficulties are involved in estimating natural base cation emissions.

The development of emission reduction policies for acidification in Europe, based on the critical loads approach, requires a detailed knowledge of ecosystem sensitivity and the deposition of both acidifying compounds and base cations. The input of base cations is, however, poorly known and dry deposition of base cations has not been directly measured anywhere in Europe. A number of different procedures for mapping of base cation deposition are suggested in the “mapping manual” (Task Force on Mapping, 1996) used for the European mapping activities. Some procedures are based on monitoring results, others on modelling. Traditional model estimates however, require emission data, which are only to some extent available with sufficient accuracy.

Estimates of base cation deposition have been made for the Nordic countries (Lövblad et al., 1992; Tørseth & Semb, 1997) and for Europe

(Draaijers et al., 1995; van Leeuwen et al., 1996; Draaijers et al., 1997a and b). The estimates are made using different methods and all include considerable uncertainties. The wet deposition contribution is relatively easily mapped from the large amount of wet deposition data available over Europe. For dry deposition, measurements, except for throughfall, are largely lacking, as well as input data for model calculations; emission data and air concentration data. The uncertainties in the base cation deposition estimates significantly influence the critical loads for acidity and its exceedance (Lövblad, 1996; Lövblad, 1997) as well as prognoses for ecosystem recovery from acidification.

Furthermore, the base cation deposition, as the sum of natural and anthropogenic contributions, is not constant over time. During the last few decades, changes in total emissions and in the spatial distribution of base cation deposition have taken place within Europe (Lövblad, 1987; Hedin et al., 1994; Ukonmaanaho et al., 1997; Kulmala et al., 1998). Monitoring results have shown that in Sweden, and also in other parts of Europe, base cations emissions and deposition has decreased markedly between 1970 and 1990. In other areas, mainly those influenced by emissions from former eastern Europe, there has been a decline in base cation deposition from 1990 (Spranger, Umweltbundesamt). These declines may to some extent have offset the positive impacts of the simultaneous decline in sulphur deposition.

The aim of this study is to estimate base cation deposition using different approaches available and to compare the results. A comparison of different methods is expected to provide information on the importance of different sources for base cations to the total deposition: anthropogenic sources and natural sources such as sea salt, biogenic material (pollen) and soil erosion dust (Table 1). It will also be possible to separate contributions from wet and dry deposition, and to separate local sources from long-range transport. Four different methods to estimate the base cation deposition over Sweden will be compared in this study. A fifth method which was applied at one site only, will also be included in the comparison.

Table 1. General overview of proceedings for estimating base cation deposition from different sources.

Contribution from	Scale of impact	Wet deposition	Dry deposition			
			Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
All sources	Local and regional	Can be estimated via monitoring or modelling. Wet deposition is usually estimated via data from an extensive monitoring net.	Can be estimated via monitoring (net through-fall) or modelling.	Can be estimated via modelling based on measured air concentrations or on emission data. Large uncertainties are involved.		
Swedish sources	Local and regional	Can be estimated only by modelling. Swedish emission data are necessary and available.				
Biogenic material (pollen)	Local and Regional	The contributions from other sources than sea salt are usually only determined as the sum of non-marine deposition. They can be determined separately via modelling, when emission data are available.	Dry deposition of base cation sources other than sea salt cannot be separated by approaches other than modelling. Emission data are necessary for the model calculation, but are usually not available.			
Industrial processes & combustion						
Soil erosion						
Sea salt	Relatively local	Sea salt contribution is estimated, assuming that all Na is from sea salt	All sodium is normally considered as sea salt	Sea salt contribution is estimated for K, Mg and Ca using Na as a tracer.		

1. Estimates of base cation deposition in Sweden using the Eulerian atmospheric transport modelling system MATCH.

The base cation deposition is estimated using emission inventory data for Swedish sources, detailed meteorological analyses and available air and precipitation base cation measurement data. This method will allow a tentative separation of wet and dry deposition, of Swedish and long-range origin, of sea salt and non-sea salt contribution, and of contributions from some different Swedish source types.

2. Estimates of potassium, magnesium and calcium deposition based on the sodium deposition in throughfall and wet deposition data.

The total deposition of base cations is estimated from the ratio of sodium in total and wet deposition. Sea salt contribution can be separated from non-marine sources, under the assumption that all Na is of sea salt origin.

3. Estimates of base cation deposition in Sweden as a part of the RIVM model calculation of European base cation deposition.

Wet deposition distribution over Europe is estimated from monitoring data. Air concentrations of base cations are estimated using the wet deposition observations and substance-specific scavenging factors as input data. Via inferential modelling, dry deposition of the base cations is estimated. Sea salt contribution is separated from non-marine sources, under the assumption that all Na is of sea salt origin.

4. Estimates of base cation deposition based on canopy budget modelling of throughfall.

A canopy budget modelling was tested but was not found to be applicable.

5. Estimates of base cation deposition using a surrogate surface

A passive sampler is used to collect fog and other particles on a surrogate surface resembling needles (nylon strings). The sampler collects airborne particles as dry deposition. The monitoring is made in parallel with throughfall and wet deposition measurements. Dry deposition is estimated from the ratio between different ions and sodium on the surrogate surface in relation to the net throughfall of sodium, which is assumed to be equal to the dry deposition of sodium. Sea salt contribution is possible to separate from non-marine sources under the assumption that all Na is of sea salt origin.

All five methods mentioned above are at least partly based on monitoring data from rural stations in the national and regional monitoring networks for air, precipitation and throughfall chemistry in Sweden.

A comparison of results is expected to indicate the importance of contributions from different deposition processes and to help in making priorities on the need for further work and for the need of accuracy in future estimates. The different approaches to estimate base cation deposition in Sweden are described in detail below. Base cation deposition was in this study mainly calculated for 1996. However, the RIVM data were not available for 1996, so in that case data for 1994 were used.

Methods used for estimating base cation deposition

2.1 Estimating base cation deposition using the MATCH model

The MATCH model system in this application consists of three parts:

- an objective analysis system for meteorological data,
- a regional atmospheric dispersion model, including modules for emission and deposition, and
- a system for data assimilation of concentrations in air and precipitation, which is combined with calculations of wet and dry deposition based on detailed meteorological and land use information.

2.1.1 Meteorological and physiographical data

The dispersion model requires meteorological data to calculate transport and deposition processes. For studies over Sweden an objective meteorological analysis system has been applied. The system makes use of routine meteorological observations to derive a number of parameters required by the dispersion model; wind fields, temperature, precipitation, friction velocity, sensible heat flux, Monin-Obukovs length and mixing height. For upper levels in the atmosphere, meteorological analyses from the operational weather prediction model, HIRLAM, are used. The analyses are performed at three hourly intervals and interpolated to hourly values within the MATCH model.

The precipitation analysis is given special attention. Data from about 800 stations measuring daily precipitation over Sweden are combined with precipitation and weather information from synoptic or automatic stations to give precipitation fields with three hourly time resolution and high horizontal resolution. Corrections for sampling losses and topographic effects are also applied.

A high-resolution data-base for topography and land use has been mapped to the 20 x 20 km horizontal grids, which are used in the dispersion model. The data-base provides topography, roughness length and land use information (fraction of forest, open field, water and urban areas within the

grid square). Also information about soil types is included, expressed as fraction of a specific soil type for each grid square in the dispersion model. The land-use and soil-type data-base is used for the meteorological analysis system, for estimates of soil emissions of base cations and for calculating the dry deposition.

2.1.2 Dispersion Model

MATCH (Multi-scale Atmospheric Transport and CHemistry) is a three dimensional Eulerian atmospheric dispersion model. It is a so called, “off-line”-model, meaning that it requires meteorological data from an external archive at regular time intervals (three hourly) in order to calculate transport and deposition. The MATCH model is presented in detail in Robertson et al., (1999). In the present study an earlier, somewhat simplified and less computer time demanding version of the MATCH model (Persson et al., 1996) has been applied. This model version has been in operational use for annual air pollution assessment studies of sulphur and nitrogen over Sweden since 1995. The applied model covers Sweden with a horizontal grid resolution of 20 km. The emitted base cations have been separated into five different particle-size classes according to Table 2 below. For the time being the hygroscopic particle growth is not considered in the model calculations.

2.1.3 Deposition processes

Wet scavenging of the different species in the atmosphere is proportional to the precipitation rate and a scavenging coefficient. In this study, we have assumed the same scavenging coefficient value for all five particle-size classes, which for the time being has been treated in a simplified way and put equal to $2.6 \cdot 10^{-4} \text{ (s}^{-1}\text{)}$ for Ca^{2+} , Mg^{2+} and Na^+ . This value is roughly twice that for sulphate. For K^+ half the value was used. These scavenging coefficient values are in good agreement with estimates based on measurements in Norway, presented by Semb et.al. (1995).

For the larger particle-size classes sedimentation velocities have been determined from Stoke’s Law and included in the model calculations. Dry deposition is proportional to the concentration and a dry deposition velocity at 1m height, which includes both turbulent exchange and sedimentation of coarse particles. Since the lowest model layer has a height of 75m, the turbulent part of the dry deposition flux calculation is transformed to the middle of that layer using standard similarity theory for the atmospheric

surface layer. Dry deposition velocities are specified for each particle-size and as a function of the surface characteristics (fraction of different landuse classes; forest, field etc). There are large uncertainties in the dry deposition values. Therefore we prefer, for the time being, not to include its dependence of e.g. friction velocity, u^* , or surface wetness, in order to make the interpretation of the results easier in relation to measurements. The deposition velocities applied are given in Table 2.

Table 2. Assumed deposition velocities, as a function of particle size (mean mass diameter), which have been used in the model calculations.

Size (μm)	Deposition velocity (cm/s)			
	Urban	Water	Field	Forest
0–2.5	0.2	0.15	0.2	0.6
2.5–6.0	0.4	0.3	0.4	0.8
6.0–10	0.8	0.7	0.8	1.1
10–15	1.4	1.3	1.4	1.8
>15	2.5	2.3	2.5	3.0

In literature very large differences in dry deposition velocities, v_d , occur for the particle sizes included in Table 2. Wind tunnel studies by Chamberlain (1960) and later studies show low v_d -values, while several field experiments, summarized by Gallagher et al. (1997) have shown much larger deposition rates. The values given in Table 2 are somewhere in between these extremes but can be regarded as low compared to some other recent performed model studies. The applied v_d -values are e.g. lower than used by Draaijers et.al. (1997a).

2.1.4 Emissions

Emissions of base cations derive mainly from four types of sources:

- industrial and combustion plants (anthropogenic)
- mechanical and wind erosion of soil particles from areas of uncovered soil and unpaved roads (natural and “semi-natural”)
- biogenic sources (pollen)
- sea salt.

Wind erosion affecting the base cation deposition over Europe in general would be dominated by emissions from arid regions of southern Europe and the Saharan region while soil emissions from Sweden, with a humid climate, must be very much smaller. In some agricultural regions of Sweden, with

sandy soil, the local soil emissions may, however, play a role and have therefore been included in our model calculations as well as the Swedish anthropogenic emissions. For the time being no estimates of biogenic emissions and no specific estimates of contributions of sea salt coming from the Swedish coasts, separated from the long-range transport, have been performed.

Industrial and combustion emissions

The anthropogenic base cation emission data for Sweden (1995/96) are based on updating of the data from Kindbom et al., (1993). They include point source data (pulp and paper mills, iron and steel works and cement industry) and area source data (burning of wood, other bio-fuels, oil and coal). Also the particle-size distribution of the emissions have been estimated. The area source emissions in each county were distributed into the 20 x 20 km model grid. Hence, the emissions from burning of wood were distributed proportional to the population living in forested areas, the emissions retrieved from burning of oil were distributed proportional to the population, and from burning of coal and bio-fuels, except wood proportional to the population living in urban areas. The emissions used in the present study are given in Table 3 and estimated particle-size distributions are briefly indicated in Table 4.

Table 3. Anthropogenic base cation emissions (tonnes/year) from Sweden 1995/96, separated into point and area sources according to the available emission inventory (updated data from Kindbom et al., 1993).

Source type	Calcium	Magnesium	Sodium	Potassium
Point sources				
Cement indust.	230	5	5	5
Forest industry	480	30	820	30
Steel industry	80	30	20	25
Area sources				
Wood/bio-fuel	2200	210	65	540
Oil	180	45	265	30
Coal	120	25	25	10

Table 4. Examples of estimated particle-size distribution (% per size-class) for some of the more important sources (data from emission monitoring archive, IVL).

Size (μm)	Burning of wood				Point sources			
	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
0–2.5	60	60	60	60	75	65	70	65
2.5–6.0	10	10	10	10	4	4	5	4
6.0–10	10	10	10	10	3	5	3	5
10–15	10	10	10	10	3	3	3	3
>15	10	10	10	10	15	23	19	23

The uncertainty of the data in Table 3 is estimated to be less than a factor of two except for wood burning, for which the uncertainty is much larger. The Swedish emissions could be as much as a factor of 5 larger than what is given in Table 3, according to Naturvårdsverket (1996) and Kindbom (pers.comm.). The contribution from sea salt is calculated only as long-range transport, see section 2.1.6, and thus not included in the emission inventory for Sweden.

Wind erosion emission

The present emission estimate includes only “natural” wind erosion from bare soils, while emissions caused by traffic on paved and unpaved roads as well as agricultural activities, for the time being, are excluded. Several empirical studies show that the amount of uplifted dust from bare soils is depending on the wind speed or the friction velocity, with a threshold wind velocity at which the erosion starts. Global modelling of the dust flux has been presented by i.e. Tegen and Fung (1994). Gillette and Passi (1988) have discussed a model for estimating the total dust production for the United States.

For the present application to Sweden the methods given by Marticorena and Bergametti (1995) have been used. The following equations were introduced into the MATCH model:

$$\text{Horizontal flux: } G = C u^3 (\rho_a / g) (1 + u_t^* / u^*) (1 - u_t^* / u^*)^2$$

where: C is a constant of proportionality with a value of 2.61,
 u^* = friction velocity,
 u_t^* = threshold friction velocity,
 ρ_a = air density and
 g = acceleration of gravity.

Vertical flux: $F = \alpha G$
 where: $\alpha = 10^{-2} - 10^{-4}$ (in SI-units) for arid and semiarid areas.

The vertical flux, which is describing the emission of dust particles available for long-range transport is thus put proportional to the horizontal flux. The horizontal flux calculations have been restricted to periods of dry weather, temperatures above zero and bare soil. For northern Europe very little information about the α -value is available. However, it is probably somewhat lower than for arid areas (Jönsson, 1994). In the present study α -values of $10^{-4} - 10^{-5}$ has been applied, and the results presented below are based on an α -value of $3.3 \cdot 10^{-5}$.

The friction velocities available in the MATCH system have been recalculated for the soil erosion estimates, using similarity theory, to represent wind-profiles over open fields with a roughness length of 0.5cm.

Soil types in southern Sweden, for which erosion damage on agricultural fields has been reported (Nihlen, 1990), have been selected as possible sources for soil erosion emissions in Sweden. The threshold friction velocities have been determined for these soil types in a rough way, mainly based on reported erosion and wind measurements in southern Sweden (Jönsson, 1994). The threshold friction velocities applied in the present model calculations are given in Table 5. Lack of quantitative measurements of the erosivity of the Swedish soils causes, however, substantial uncertainties.

Table 5. Soil types and threshold friction velocities applied in the calculations.

Soil type	Threshold friction velocity (m/s)
Sandy soils	0.43–0.90
Fluvial sediments	0.50–2.00

The number distribution of dust particles with regard to particle radius, r , was assumed to be described by $dN/d\log r \sim r^2$ (proportional to r^2). No direct information for Swedish conditions is available. The corresponding mass distribution follows $dM/d\log r \sim r$. This expression was then used to distribute the soil emissions into the different particle-size classes in the MATCH model. The assumptions of the base cation content in soil were based on information on the cation exchange capacity for agricultural soils in southern Sweden (Eriksson et al., 1997): 15 mg/100 g for Mg^{2+} , Na^+ , K^+ and 220 mg/100 g for Ca^{2+} . These values are used since they represent only

the chemically easy available base cations, in line with what is measured by air and precipitation monitoring programmes.

The estimated emissions in Table 6 are small, compared to the total anthropogenic emissions from Sweden. However, the soil erosion emissions occur from very small areas and only during a few episodes per year. During 1996, soil emissions were obtained only for the months April, May and to a small extent in September. The fact that the main emissions occur during spring, is in agreement with observations that bare and dry soil, earlier affected by frost, can cause large soil emissions in areas like northern Europe. Therefore, locally and during shorter periods the erosion can be of importance in Sweden. The model results presented below are based on the logarithmic mean for the Swedish soil emissions given in Table 6.

Table 6. Preliminary model estimates of base cation emissions (tonnes/year) from Sweden 1996 caused by wind erosion.

Calcium	Magnesium	Sodium	Potassium
20–200	1.5–15	1.5–15	1.5–15

2.1.5 Air and precipitation chemistry measurements

In the present study, data from a number of background air and precipitation chemistry stations have been utilised. Data was applied in the long-range transport calculations as discussed below. Daily base cation concentrations in precipitation, for the year 1996, were obtained from four Swedish, five Norwegian and three Finnish monitoring stations. In addition, monthly precipitation data from 24 Swedish stations were used. The available precipitation chemistry stations cover relatively homogeneously Sweden with surrounding areas. Concentrations in air, however, were only available from four stations in Southern and Central Sweden for the year 1994, which were used. Thus the information regarding observed air concentration of base cations over Sweden, included in this study, are rudimentary and involve large uncertainties. Norwegian data are available and has added to the knowledge of Scandinavian air concentrations of base cations (Semb et al., 1995; Tørseth et al., 1999).

2.1.6 Long-range transport

The dispersion model described above, using national emission estimates and meteorological data, provides daily estimates of concentrations in air and

precipitation as well as dry and wet deposition of base cations. These results refer to contributions from sources within Sweden. The contribution from sources outside Sweden and from marine sources were obtained by subtracting model calculated daily contributions from Swedish sources from observed daily values of concentration in air and precipitation at background locations on a point by point basis. Four stations in Sweden for air concentrations and about 36 stations for concentration in precipitation in and around Sweden are used. The residual is termed long-range transport contribution. These residuals are analyzed using an optimum interpolation method to give distributions of long-range transport contributions of concentrations in air and precipitation over the whole modelling domain.

The basic idea behind this method is that the long-range transport contributions to the concentrations can be expected to vary more smoothly in space, and therefore should be more suitable for interpolation than the total concentrations, which to some extent are affected by local sources. Long-range transport of wet deposition is then calculated by multiplying with the detailed observed precipitation field. Long-range transported dry deposition is calculated by running the long-range transport air concentrations through the dry deposition module of the dispersion model. Since we have no detailed measurements of particle size fractions for the long-range transport particles, we have only worked with one dry deposition velocity, v_d , for each compound and landuse class. For Ca^{2+} , Mg^{2+} and Na^+ v_d -values of 0.7 to 1.1 cm/s have been used depending on landuse class, while for K^+ v_d -values of 0.3 to 0.8 cm/s were assumed to be most relevant. These dry deposition values are however very uncertain and will be discussed further below. The chosen values are e.g. somewhat lower than used by Draaijers et al., (1997a).

The same calculation procedure for the long-range transport has earlier been applied with good results to assessment studies of sulphur and nitrogen over Sweden (Persson et al., 1996). For those compounds, a comprehensive set of measured data is available and considerable efforts have been spent on quality control. For base cations we still need more measured data for a reliable quality control.

The contribution from sea salt has been estimated as solely a long-range transport contributions, using measured sodium concentrations in precipitation and air assuming that sea salt is the only source of Na^+ in air and precipitation. The sea salt contribution to Mg^{2+} , Ca^{2+} and K^+ can then be expressed as a factor f_x of the $[\text{Na}^+]$ concentration, where f_x equals 0.113,

0.0218 and 0.212 respectively, on a molar basis. In all long-range transport deposition calculations, sodium is generally considered as 100% sea salt. The contribution of other sources for sodium over Sweden is discussed below.

2.2 Estimation of base cation deposition using the Na-ratio method

Total deposition of base cation is estimated using monitoring data on base cations in bulk deposition and throughfall. These estimates are produced in the same way as earlier for the critical loads mapping in Sweden (Lövblad et al., 1992; Ulrich, 1983). The base cation deposition is estimated by:

$$\text{Totdep}_i = \text{TF}_{\text{Na}} / \text{Wdep}_{\text{Na}} \times \text{Wdep}_i$$

where:

Totdep_i is total deposition of ion i Wdep_{Na} = wet deposition of ion Na^+
 TF_{Na} is throughfall of Na^+ Wdep_i = wet deposition of ion i

The following assumptions are made:

- Total deposition of Na^+ is well quantified via throughfall measurements. This assumption is generally accepted (Ivens 1990, and references therein).
- The wet deposition of all ions (Na^+ , K^+ , Mg^{2+} and Ca^{2+}) is quantified in the same way. Bulk deposition measurements are assumed to represent the wet deposition in lack of wet-only deposition data. This assumption involves only minor uncertainties (see Table 7 below) for Sweden.
- Base cations (Na^+ , K^+ , Mg^{2+} and Ca^{2+}) are deposited as particles. For our estimates they are – due to lack of data – assumed to be present in the atmosphere in the same particle size distribution. Measurements as well as literature data (Semb et al., 1995, Lee et al., 1999) indicate some differences, see below.

For accurate estimates of the dry deposition, wet deposition should be measured as wet-only deposition. Most measurements in Sweden are, however, made using open, so called bulk deposition samplers, which are subject to some contributions of dry deposition. The data from wet-only measurements are too few to provide a base for estimating base cation deposition. Bulk deposition data has therefore been used and been assumed to represent the true wet deposition. The importance of dry contributions

varies between regions and components. The difference between parallel wet and bulk deposition as a mean over five years for four rural stations in Sweden, is presented in Table 7 (Granat, 1988). The table indicates that the dry deposition contribution to the samplers is less than or approximately 10%.

Table 7. Comparison between parallel wet-only and bulk sampling at four rural sites during five years (Granat 1988). Ion concentrations are given in $\mu\text{eq l}^{-1}$ and precipitation amounts in mm.

Parameter	Average	Difference (bulk minus wet-only)	
		absolute	relative (%)
Precipitation amount	51	10	20
SO ₄ ²⁻	55	-0.7	-1
NO ₃ ⁻	27	-0.5	-2
NH ₄ ⁺	26	1.2	5
H ⁺	38	-1.0	-3
Na ⁺	13	1.5	12
Cl ⁻	17	1.2	7
Mg ²⁺	4	0.4	9
Ca ²⁺	8	-0.5	-6
K ⁺	2	(-0.4)	Not calculated

Few measurements of base cation concentrations in air are made in Sweden. Consequently, data are not available, neither on the total amount of base cations in air, nor on its distribution within different particle size ranges. Results from measurements in southern Norway (Semb et al., 1995; Tørseth et al., 1999) indicate similar size fractions for Ca²⁺ and Na⁺, while K⁺ seems to appear in somewhat smaller particles. Since base cations are of different origin, it seems reasonable to believe that they are present on different types and sizes of particles.

2.3 Estimation of base cation deposition using the scavenging ratio method by RIVM

Data on base cation deposition in Sweden were obtained from RIVM as a part of the data set calculated for the European critical loads mapping. The procedure is based on measured wet deposition of base cations. These data were collected from networks all over Europe (van Leeuwen et al., 1995; 1996, Draaijers et al., 1997 a och b). The major part of the monitored wet deposition data is consequently the same as for the other methods in this study. Annual mean bulk deposition was, however, corrected for estimated

dry deposition to the bulk samplers. Maps of base cation concentrations in precipitation have been produced using block-kriging interpolation technique with blocks of 50 x 50 km. The concentrations were multiplied with precipitation amounts to give the wet deposition flux. The precipitation chemistry data were further used to estimate ambient air concentrations of base cations using a model based on scavenging ratios. The dry deposition flux was then calculated as the product of dry deposition velocities and ambient air concentrations at a reference height of 50m. This is an inferential technique, based on Slinn's approach (Slinn, 1982) tested against micrometeorological measurements.

2.4 Estimation of base cation deposition using canopy budget modelling of throughfall data

Throughfall data cannot be used directly to estimate deposition of substances, which are taken up or leached in the canopy, such as nitrogen compounds and base cations. Consequently, there is a need for separating the internal cycling in the canopy from the influence of atmospheric deposition. A number of similar approaches, so called canopy budget models, have been tried (e.g Lovett & Lindberg, 1984; Van der Maas & Pape, 1991; Draaijers & Erisman, 1995, Hultberg & Ferm, 1995; Westling et al., 1995; Draaijers et al., 1996; Ferm & Hultberg, 1999).

These approaches, however, depend on reliable monitoring data and analyses of all major ions. The canopy budget model tested (Westling et al., 1995) did not produce reliable results based on the data set available. One factor is that most throughfall samples showed a deficit of anions. As an indication of the uncertainties, the deviation between measured cation and anions in the corresponding throughfall is in the range 50% of the estimated deposition of ($K^+ + Mg^{2+} + Ca^{2+}$) in southern to central Sweden. In the north, the anion deficit, are even larger, up to 150%.

It is not known to what extent this is due to the presence of compounds which are deposited or leached in the canopy, but not measured, or to what extent it is due to systematic errors in the analysis. In the throughfall samples collected at a large number of forest sites in Europe within the UN ECE Programme ICP Forests, it has been shown that poor ion balance is relatively frequent. It occurs even in cases where the analytical quality via laboratory intercomparisons has been found to be good.

The general conclusion is that the method tested is not suitable to use in this way, especially not in the northern areas, unless it is based on samples with improved ion balance, which is likely to include monitoring of additional parameters.

2.5 Estimation of base cation deposition using surrogate surface sampler

Particles and fog droplets are collected (dry deposition) on a surrogate surface resembling needles in parallel with throughfall and wet deposition measurements. The surrogate surface in this case is teflon strings (For further details on equipment and procedure, see Ferm & Hultberg, 1995; Ferm & Hultberg, 1999). The dry deposition of K^+ , Mg^{2+} and Ca^{2+} is estimated from the ratio between an ion i and sodium on the surrogate surface in relation to the net throughfall of sodium.

$$DD_i = NTF_{Na} \times SS_i / SS_{Na}$$

where:

DD = dry deposition, NTF = net throughfall,

SS_i = flux of ion i collected on the surrogate surface

SS_{Na} = flux of Na^+ collected on the surrogate surface

As for the Na-ratio and the RIVM method, this method assumes all base cations to be present in the same particle size ranges.

The method has been run and applied for some years, including 1996, within the Nitrex-project at the Gårdsjön monitoring site on the Swedish West Coast (Ferm & Hultberg, 1999). From 1997, the method has been applied also at a number other sites over Sweden (Ferm et al., to be published).

Chapter 3.

Results of deposition estimates

3.1 Estimated deposition using the MATCH model

It is a purpose of this study, as far as possible, to separate the deposition of different ions, to compare Swedish contribution with long-range transport contribution, as well as to compare sea salt contribution with non-sea salt contribution. Of course, also the total deposition is of interest. Therefore, different maps are presented and compared on the deposition of Ca^{2+} , Mg^{2+} , Na^+ and K^+ . Examples of model results for base cations over Sweden for 1996 are presented below in Figures 1–9, pp 40–48. It is important to observe the fact that different shading intervals are used for different maps. The results are still – to some extent – tentative, due to uncertainties in emission data, roughly estimated sink parameters and lack of air concentration measurements. For example, air concentration measurements had to be used for another year, 1994, and for only four stations, since no other measurements were available.

Figures 1–4 show comparisons between Swedish contributions, long-range transport and total wet+dry deposition of non-sea salt Ca^{2+} , Mg^{2+} , Na^+ and K^+ . For Na^+ also sea salt is included. The Swedish contribution of Ca^{2+} is estimated to be about 6–10% of the total deposition in most parts of southern Sweden and along the Eastern Coast (Figure 1). In areas with extensive wood burning the Swedish contributions may reach 15%. In northern Sweden, except for along the coast, the Swedish contributions are less than a few percent. The highest total deposition of non-sea salt Ca^{2+} is found in southeastern Sweden near the coasts.

Non-sea salt deposition of Na^+ is estimated to be approximately 1% or less in southern and central Sweden and may amount to as much as 3% of the total deposition in the north. For Ca^{2+} K^+ and Mg^{2+} 80–95%, 70–90% and 20–30%, respectively, is of other origin than sea salt. The largest deposition of sea salt (Na^+) occurs in southwest Sweden (Figure 3) and in the north-western mountains. However, since sea salt is only described through the long-range transport calculations, the number of monitoring sites for

atmospheric chemistry on the west coast is too small and the model resolution is too coarse to describe the local gradients of sea salt along the coast in detail. The sea salt deposition should have a maximum along the coast and decrease further inland, which in the present model version cannot be described without available measurements along the coast.

The non-sea salt depositions of Mg^{2+} and K^+ (Figure 2 and 4) are to a large extent dominated by the long-range transport. The largest total deposition values are found in southern Sweden, with values of 20–30 mg/m^2 for Mg^{2+} and 100–140 mg/m^2 for K^+ . In the very north of Sweden the values are around 10 mg/m^2 for Mg^{2+} and 50–60 mg/m^2 for K^+ .

Also for the other base cations the Swedish contributions are small. The calculations indicate e.g. that Swedish anthropogenic sources account for less than 1 % of the Na^+ -deposition on the Swedish west coast and in the westerly parts of the mountains in northern Sweden. On the eastern coast in northern Sweden the corresponding figures are 2–3 %. In small areas the anthropogenic sources may contribute with up to 7%. The non-sea salt contribution to Na^+ is here mainly caused by the forest industry. This means that for some areas on the Swedish east coast at least 2–7 % of what is normally estimated to be sea salt should not be regarded as such.

The calculated dry and wet deposition with and without sea salt for the different base cations are presented in Figures 5–8. All figures indicate larger deposition in southwest Sweden and low values in the very north. It is also obvious from these figures that the dry deposition, according to our present calculations, is much smaller than the wet deposition for all compounds. We can also see that for Ca^{2+} and K^+ , the non-sea salt wet deposition is a rather large part of the total deposition. For Mg^{2+} and, of course, for Na^+ the sea salt part dominates. In Table 8 average values for some different regions in Sweden are given. The selected regions are counties or groups of counties showing similar deposition patterns, see below. From our present tentative calculations, with large uncertainties in the deposition velocities, the dry deposition of Ca^{2+} accounts for about 10–20% of the total Ca^{2+} deposition, with the highest values in eastern Sweden where the precipitation amounts are smaller. For Mg^{2+} the corresponding dry deposition ratios are 20–40%, for Na^+ 20–50% and for K^+ about 10–15%. This might, however, be an underestimate of the dry deposition, especially in forested areas, since we have assumed rather small dry deposition velocities compared to what is indicated by e.g. Tørseth and Semb (1997).

Table 8. MATCH deposition estimates (incl. sea salt) as an average over different regions of Sweden, in meq/m² per year and % dry of total deposition.

Region*	Na ⁺	Na ⁺	Na ⁺	Ca ²⁺	Ca ²⁺	Ca ²⁺	Mg ²⁺	Mg ²⁺	Mg ²⁺	K ⁺	K ⁺	K ⁺
	Wet	Total	Dry in %	Wet	Total	Dry in %	Wet	Total	Dry in %	Wet	Total	Dry in %
K	22	27	21	9.0	10.0	10	6.7	8.3	21	3.2	3.6	12
D-H	14	22	25	7.0	8.0	13	4.6	6.1	24	2.3	2.7	14
O-P	34	44	21	7.5	8.8	13	9.2	11.3	20	2.7	3.1	13
R	16	22	28	5.3	6.3	17	4.8	6.7	28	2.1	2.4	14
A-C	8.3	12	32	4.5	5.5	17	3.6	4.2	28	1.8	2.1	14
U	7.8	12	36	5.5	6.5	15	3.6	4.2	28	2.0	2.3	12
W	8.7	14	38	5.3	6.0	13	2.7	4.2	36	1.9	2.2	12
AC/BD	4.1	8	49	3.4	3.8	11	1.4	2.3	37	1.6	1.8	10

* County codes: K = Blekinge, D-H = Södermanland to Kalmar, O-P = Bohuslän, Älvsborg, R = Skaraborg, A-C = Stockholm, Uppland, U = Västmanland, W = Kopparberg, AC/BD = Väster-/ Norrbotten

3.2 Estimated deposition to forests using the Na-ratio method

Estimated base cation deposition to spruce forest stands is presented per region in Table 9 below. The results are presented as wet and total deposition of K⁺, Mg²⁺ and Ca²⁺. The dry deposition (Table 9) and non-sea salt contributions are estimated (Table 10).

Table 9. Measured wet (bulk) deposition of base cations, throughfall of Na and estimated total deposition of K⁺+Mg²⁺+Ca²⁺ 1996 (meq/m²) per year in different regions (counties). The estimations are based on the ratio between throughfall and wet deposition for Na.

Region*	No of spruce sites	Meas. through-fall flux Na ⁺	Measured wet deposition				Estimated total deposition			Dry deposition % of total
			Na ⁺	Ca ²⁺	Mg ²⁺	K ⁺	Ca ²⁺	Mg ²⁺	K ⁺	
K	1	37	24	10	7.3	3.9	16	11.1	6.0	35
D-H	5	20	11	9.1	4.3	3.5	16	7.4	6.2	43
O-P	3	100	61	12	15	5.9	19	24	9.7	39
R	4	25	15	5.7	4.3	2.6	9.0	6.8	4.1	40
A-C	9	18	7.8	6.6	3.5	2.5	15	7.9	5.7	57
U	5	10	7.7	7.5	3.3	2.9	10	4.3	3.9	23
W	2	5.8	7.7	6.8	2.0	2.9	6.8	2.0	2.9	neg
AC/BD	2	4.8	7.4	6.5	2.1	3.5	6.5	2.1	3.5	neg

* Regions, see Table 8.

Dry deposition is estimated to contribute with approximately 40% of the total deposition in many parts of southern Sweden. Lower contributions, in some areas even negative contributions, are observed towards the north.

Table 10. Estimated non-sea salt deposition of different ions and the part of deposition which is possible to estimate in a relatively accurate way.

Region*	Estimated non-sea salt deposition in % of the total deposition				% of deposition which is possible to estimate in a relatively accurate way			
	Na ⁺	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	K ⁺
K	0	90	23	87	100	68	92	69
D-H	0	95	38	93	100	59	84	60
O-P	0	78	6	78	100	70	98	70
R	0	88	17	87	100	67	94	68
A-C	0	95	47	93	100	46	73	47
U	0	96	46	94	100	77	89	77
W	0	95	12	94	100	~100	~100	~100
AC/BD	0	95	18	95	100	~100	~100	~100

* Regions, see Table 8.

Negative values are assumed to be mainly an artefact due to uncertainties in the wet deposition estimates, to a large degree a consequence of difficulties in collecting representative samples, especially during wintertime.

The sea salt contribution is estimated from the assumption that all sodium is of sea salt origin. This assumption is only partly correct. In all areas, sea salt is the dominant source. In areas with a high sea salt deposition, other sources can largely be neglected. In other areas combustion and industrial sources may give a minor contribution of 10–20% at the most, except maybe very locally. This was estimated from throughfall data using the relation between Na⁺ and Mg²⁺ in throughfall and in sea salt. Also the MATCH model results indicate that only a small part (<10%) of the total Na⁺ deposition may be of other than sea salt origin. The Na-ratio method estimates indicate that K⁺ and Ca²⁺ to a large extent, >80–90%, of the total, is of other origin than sea salt. Between 15 and 50% Mg²⁺ is in many regions estimated to be of other origin than sea salt.

Table 10 also presents the part of the deposition, which is assumed to be possible to estimate in a relatively accurate way, i.e. the sum of total wet + dry sea salt deposition. For Mg²⁺ >75% is estimated to be “well known”. For Ca²⁺ and K⁺ the equivalent part varies between 50 and 70% in southern Sweden and almost all of the deposition is estimated as “well known” in the north.

The monitoring data for 1996 show a ratio between throughfall and wet deposition of Na⁺, varying over the country. Over the larger part of southern

Sweden the ratio is around 1.6. Higher ratios 1.8–2.3 are seen in the eastern parts of southeastern Sweden. The reasons for the geographical variation are not easily explained, especially since no data on base cations in the atmosphere are available. Both the air pollution levels, the deposition amounts, the precipitation frequency and the forest stand structure may be of importance. The ratio decreases towards the north. A similar decreasing gradient from south to north is seen also for the ratio between throughfall and wet deposition of sulphur.

In northern Sweden, even ratios <1 are obtained, indicating a larger wet deposition than throughfall deposition of sodium. This is seen also for sulphur and is assumed to be an artefact due to difficulties in correctly estimating the precipitation and wet deposition. The difficulties increase towards north due to long season with snow precipitation, which is extremely difficult to sample and to quantify correctly. Another factor, which may contribute to the uncertainties in the deposition estimate, is that at least one contributing process, stemflow, is not measured. Work is presently going on to separate the contribution to this uncertainty by different factors (Westling and Ferm, under preparation).

The monitoring results also indicate a difference between forest stands. The largest deposition is generally seen in spruce stands, and lower deposition is observed in pine and deciduous forests. This is obvious also for sulphur, nitrogen and base cation deposition. However, the monitoring data for other than spruce forests are too few to conclude generally and accurately on the dry deposition to these types of forests.

Comparisons between the MATCH model and the Na-ratio method results are made in Table 11. There is a tendency to higher wet deposition values using the Na-ratio method. For two regions, the west coast (O region) and northern Sweden (AC/BD region) the Na-ratio method gives considerably higher values. The west coast region is subject to high deposition due to influence from the sea. Precipitation amounts vary substantially within the region. The area is consequently subject to strong gradients, and the estimates of average deposition may be uncertain. In the north, the deposition levels are low and during winter, with snow precipitation, the wet deposition is especially difficult to estimate.

The Na-ratio method is expected to provide somewhat higher dry and total deposition, since it estimates deposition to spruce forests, while the MATCH results refer to mixed land use. This is also the case in most areas

in southern Sweden. Thus, the relative dry deposition contribution, estimated with the MATCH model in southern Sweden, is lower than that estimated with the Na-ratio method. In northern Sweden, the relative dry deposition contribution estimated by the Na-ratio method, decreases substantially, while it is increasing (especially for sea salt) or is constant in the MATCH estimates.

Further discussions and comparisons are given in chapter 4.

Table 11. Comparison between estimated deposition of Na⁺, Ca²⁺, Mg²⁺ and K⁺ by the MATCH model (MM) and the Na-ratio (NR) incl. sea salt (meq/m² per year) as wet and total deposition and dry deposition in % of total deposition.

Region*	Na ⁺						Ca ²⁺					
	wet dep		total dep		dry (%)		wet dep		total dep		dry (%)	
	MM	NR	MM	NR	MM	NR	MM	NR	MM	NR	MM	NR
K	22	24	27	37	21	35	9.0	10	10.0	16	10	35
D-H	14	11	22	20	25	43	7.0	9.1	8.0	16	13	43
O-P	34	61	44	100	21	39	7.5	12	8.8	19	13	39
R	16	15	22	25	28	40	5.3	5.7	6.3	9.0	17	40
A-C	8.3	7.8	12	18	32	57	4.5	6.6	5.5	15	17	57
U	7.8	7.7	12	10	36	23	5.5	7.5	6.5	10	15	23
<i>Average</i>	<i>17</i>	<i>21</i>	<i>23</i>	<i>35</i>	<i>26</i>	<i>40</i>	<i>6.5</i>	<i>8.5</i>	<i>7.5</i>	<i>14</i>	<i>13</i>	<i>39</i>
W	8.7	7.7	14	5.8	38	neg	5.3	6.8	6.0	6.8	13	neg
AC-BD	4.1	7.4	8	4.8	49	neg	3.4	6.5	3.8	6.5	11	neg
<i>Average</i>	<i>6.4</i>	<i>7.6</i>	<i>11</i>	<i>5.3</i>	<i>42</i>	<i>neg</i>	<i>4.4</i>	<i>6.7</i>	<i>4.9</i>	<i>6.7</i>	<i>11</i>	<i>neg</i>
Region*	Mg ²⁺						K ⁺					
	wet dep		total dep		dry (%)		wet dep		total dep		dry (%)	
	MM	NR	MM	NR	MM	NR	MM	NR	MM	NR	MM	NR
K	6.7	7.3	8.3	11.1	21	35	3.2	3.9	3.6	6.0	12	35
D-H	4.6	4.3	6.1	7.4	24	43	2.3	3.5	2.7	6.2	14	43
O-P	9.2	15	11.3	24	20	39	2.7	5.9	3.1	9.7	13	39
R	4.8	4.3	6.7	6.8	28	40	2.1	2.6	2.4	4.1	14	40
A-C	3.6	3.5	4.2	7.9	28	57	1.8	2.5	2.1	5.7	14	57
U	3.6	3.3	4.2	4.3	28	23	2.0	2.9	2.3	3.9	12	23
<i>Average</i>	<i>5.4</i>	<i>6.2</i>	<i>6.8</i>	<i>10.3</i>	<i>21</i>	<i>40</i>	<i>2.4</i>	<i>3.6</i>	<i>2.7</i>	<i>5.9</i>	<i>11</i>	<i>39</i>
W	2.7	2.0	4.2	2.0	36	neg	1.9	2.9	2.2	2.9	12	neg
AC-BD	1.4	2.1	2.3	2.1	37	neg	1.6	3.5	1.8	3.5	10	neg
<i>Average</i>	<i>2.1</i>	<i>2.1</i>	<i>3.3</i>	<i>2.1</i>	<i>36</i>	<i>neg</i>	<i>1.8</i>	<i>3.2</i>	<i>2.0</i>	<i>3.2</i>	<i>10</i>	<i>neg</i>

* County codes: K = Blekinge, D-H = Södermanland to Kalmar, O-P = Bohuslän, Älvsborg, R = Skaraborg, A-C = Stockholm, Uppland, U = Västmanland, W = Kopparberg, AC/BD = Väster-/ Norrbotten

3.3 Estimated deposition using the RIVM model

Data from RIVM were available only for the years 1991–1995, while the MATCH model estimates and most other data refer to the year 1996. However, estimates using the Na-ratio method are available also for 1994 and can be compared to the RIVM results. The years 1994 and 1996 are not comparable in detail due to e.g. differences in weather conditions. Thus, the RIVM data can only be compared in a rough way to the MATCH model results.

The RIVM data are mean deposition values, representative for grid-squares with mixed land use. This should be kept in mind when comparing the results. The deposition is generally significantly higher to forest stands than to open fields. The mean RIVM deposition is therefore expected to be lower than the forest deposition. The estimates for 1994 using the RIVM method are presented in Table 12 together with results for the Na-ratio method from the same year.

The total deposition of Na^+ and Mg^{2+} estimated with the RIVM method is largely in the same order of magnitude as deposition estimated with other methods. For Ca^{2+} and K^+ there are larger deviations, and the results vary over the country. Results from the RIVM method show a dominating dry deposition (60–70%) for all ions except for K^+ , for which it is approximately 40%. The relative dry deposition contribution is largely the same in all areas from south to north. The total deposition data, however, indicate a decreasing trend from south to north.

The wet and total deposition amounts estimated for southern Sweden with the RIVM method are largely in the same order of magnitude as those, estimated by Na-ratio method. One exception from the above is the west coast area (region O), where the Na-ratio method for all ions gives considerably higher deposition estimates than the RIVM method. Thus, the situation is similar to the comparison with the MATCH estimates. Large deposition gradients cause large uncertainties in the average values.

The results from both methods in Table 12 show a decreasing trend from south to north. In the north, however, the RIVM method seems to overestimate the total deposition for Na^+ , Ca^{2+} and Mg^{2+} in comparison to monitoring results. The RIVM method gives mainly the same relative dry deposition contribution over the country, while the Na-ratio method shows a decreasing dry deposition contribution towards north in relation to the total deposition.

Table 12. Comparison between estimated deposition of Na⁺, Ca²⁺, Mg²⁺ and K⁺ by the RIVM model (RI) and the Na-ratio (NR) incl. sea salt (meq/m²) per year as wet and total deposition and dry deposition in % of total deposition.

Region*	Na ⁺						Ca ²⁺					
	wet dep		total dep		dry (%)		wet dep		total dep		dry (%)	
	RI	NR	RI	NR	RI	NR	RI	NR	RI	NR	RI	NR
K	19	25	64	70	71	64	3.2	9.6	11	26	71	64
D-H	16	12	45	26	65	54	3.8	6.3	10	13	64	54
O-P	32	48	95	140	66	66	4.2	12	12	34	66	66
R	23	20	71	44	69	55	3.8	8.1	11	18	67	55
A-C	9.4	8.4	29	12	68	32	4.6	6.9	14	10	66	32
U	8.1	5.5	21	8.3	61	34	3.4	5.6	8.4	8.4	59	34
<i>Average</i>	<i>18</i>	<i>20</i>	<i>54</i>	<i>50</i>	<i>67</i>	<i>60</i>	<i>3.8</i>	<i>8.1</i>	<i>11</i>	<i>18</i>	<i>65</i>	<i>55</i>
W	6.5	3.9	15	4.7	57	17	2.4	3.9	7.2	4.7	54	17
AC/BD	5.9	2.4	15	2.7	61	11	1.8	1.9	4.2	2.1	59	11
<i>Average</i>	<i>6.2</i>	<i>3.2</i>	<i>15</i>	<i>3.7</i>	<i>59</i>	<i>17</i>	<i>2.1</i>	<i>2.9</i>	<i>5.7</i>	<i>3.4</i>	<i>63</i>	<i>15</i>

Region*	Mg ²⁺						K ⁺					
	wet dep		total dep		dry (%)		wet dep		total dep		dry (%)	
	RI	NR	RI	NR	RI	NR	RI	NR	RI	NR	RI	NR
K	6	6.0	22	17	73	64	3.5	3.3	6.6	8.9	47	64
D-H	4.6	4.1	14	8.7	68	54	2.5	2.6	4.3	5.5	42	54
O-P	6	14	20	39	70	66	2.6	4.0	4.6	12	43	66
R	4.2	4.9	15	11	72	55	2.3	2.7	4.2	6.0	45	55
A-C	2.6	5.9	8.6	8.7	70	32	1.7	2.3	3.1	3.5	44	32
U	2	2.8	5.4	4.2	64	34	1.5	2.6	2.4	3.9	37	34
<i>Average</i>	<i>4.2</i>	<i>6.3</i>	<i>14</i>	<i>15</i>	<i>70</i>	<i>58</i>	<i>2.4</i>	<i>2.9</i>	<i>4.2</i>	<i>6.6</i>	<i>43</i>	<i>56</i>
W	1.4	1.8	3.4	2.2	59	17	1.0	1.5	1.5	1.9	32	17
AC/BD	2.2	1.2	5.8	1.3	63	11	1.2	1.1	2.1	1.2	35	11
<i>Average</i>	<i>1.8</i>	<i>1.5</i>	<i>4.6</i>	<i>1.8</i>	<i>61</i>	<i>17</i>	<i>1.1</i>	<i>1.3</i>	<i>1.8</i>	<i>1.6</i>	<i>39</i>	<i>19</i>

* Regions, see Table 11.

There is less good agreement for wet deposition of Ca²⁺, for which the Na-ratio estimate in many areas in southern Sweden is a factor 2 higher. This might to some extent be due to corrections made in the RIVM method, for dry contribution to bulk collectors. According to available Swedish results, the dry deposition contribution of Ca²⁺ to bulk collectors is small and corrections are not considered necessary. No corrections are made in the Na-ratio method and in the MATCH model. Further discussions and comparisons are made in chapter 4.

3.4 Estimated deposition to forests using a Surrogate surface method

The results from 1996 are presented in Table 13 below. The dry deposition estimated by the surrogate surface method is in relatively good agreement with the estimate by the Na-ratio method.

Table 13. Estimated deposition (incl. sea salt) at the Gårdsjön site (in region O) 1996 (meq/m²) per year using the surrogate surface and Na-ratio based on throughfall data from the same site.

Estimate based on	Deposition estimated via the Surrogate surface				Deposition estimated using the Na-ratio method			
	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
Throughfall	95	27	23	27	95	27	24	27
Wet (bulk)deposition	48	5.3	7.4	11	48	5.3	7.4	11
Net throughfall	47	22	16	16	47	22	17	16
Surrogate surface deposition factor	1.00	0.05	0.15	0.26	-	-	-	-
Dry deposition from surrogate surface	47	2.2	7.1	12				
Internal cycling = Net throughfall – dry deposition	0	20	8.5	3.8				
Total deposition	95	7.5	14	23	95	10.5	15	22

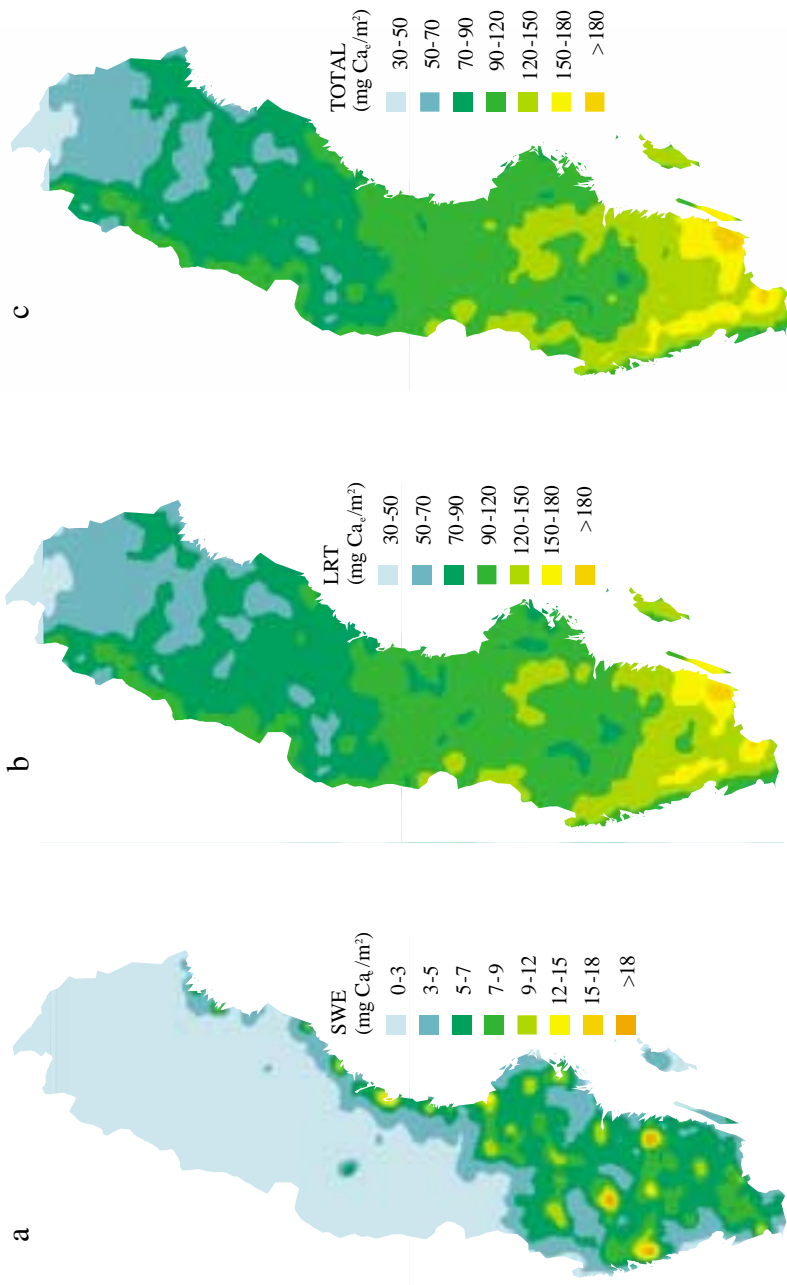
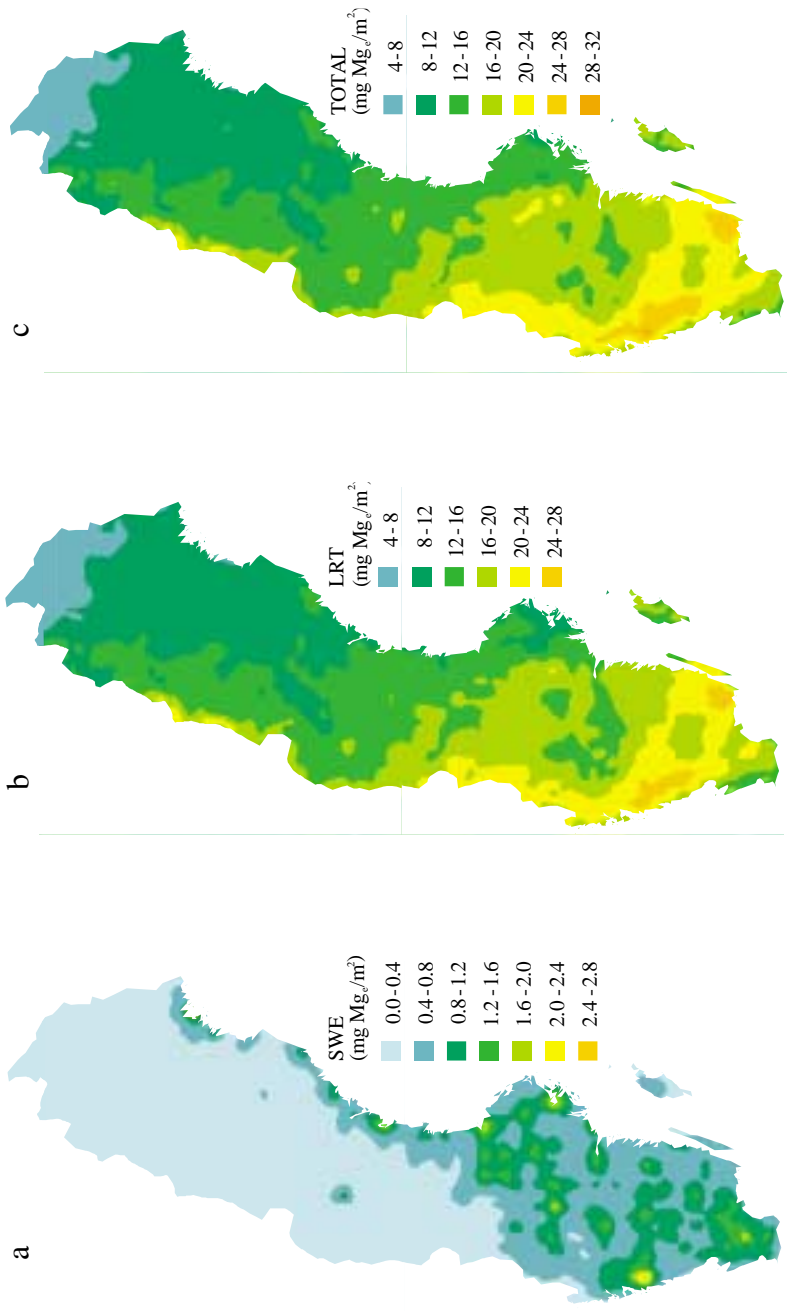


FIGURE 1. Calculated annual wet+dry deposition (mg/m²) of non-sea salt (excess) Ca²⁺ 1996: a) Swedish contribution, b) long-range transport and c) total.



FIGUR 2. Calculated annual wet+dry deposition (mg/m²) of non-sea salt (excess) Mg²⁺ 1996: a) Swedish contribution, b) long-range transport and c) total.

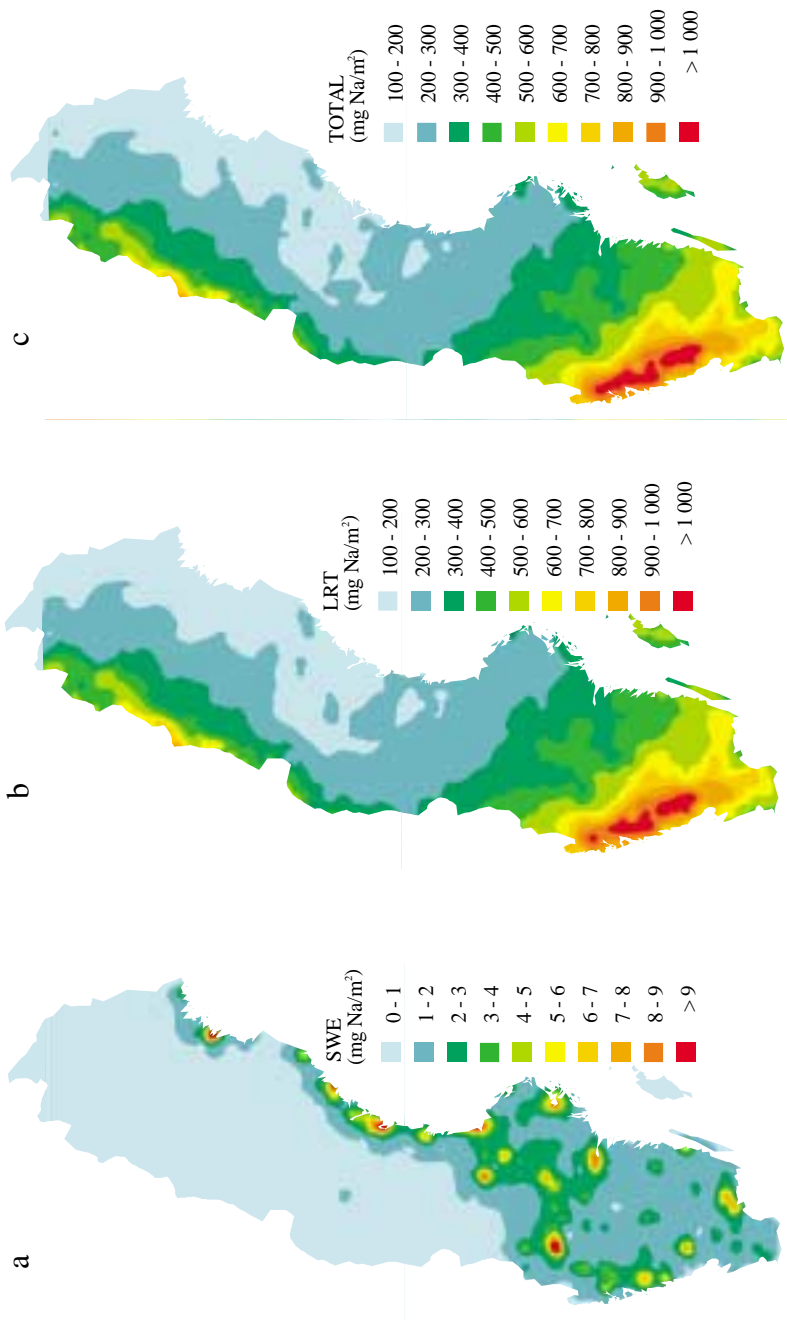
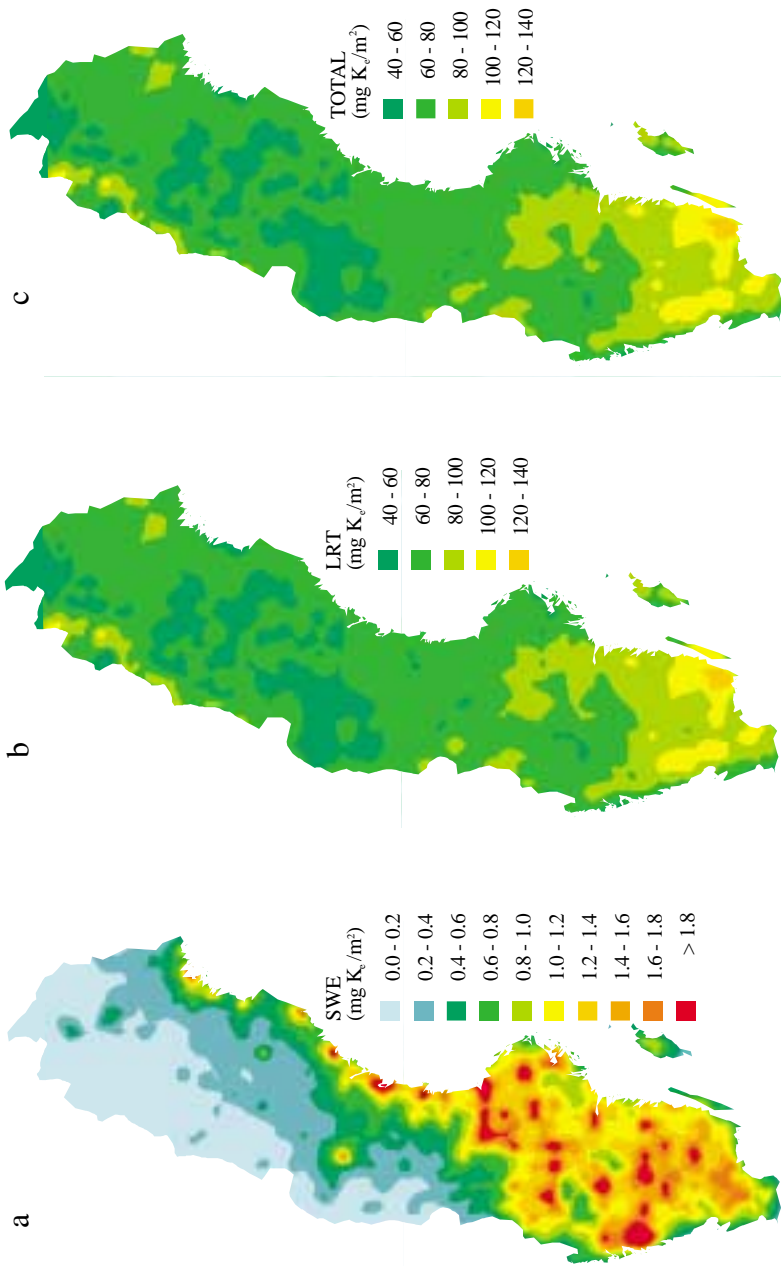
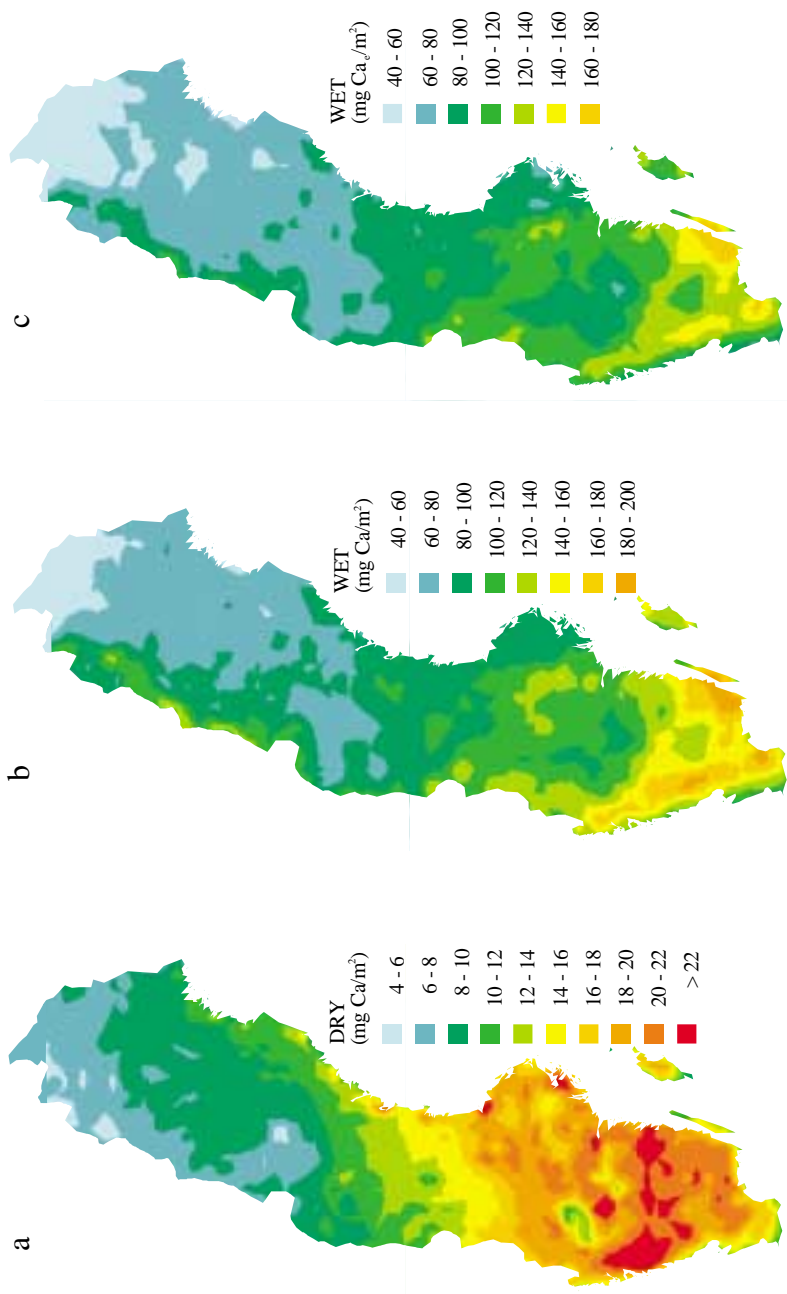


FIGURE 3. Calculated annual wet+dry deposition (mg/m²) of Na⁺ 1996: a) Swedish non-sea salt contribution, b) long-range transport (including sea salt) and c) total (including sea salt).



FIGUR 4. Calculated annual wet+dry deposition (mg/m²) of non-sea salt (excess) K⁺ 1996: a) Swedish contribution, b) long-range transport and c) total.



FIGUR 5. Calculated annual deposition (mg/m^2) of Ca^{2+} 1996: a) dry deposition including sea salt, b) wet deposition including sea salt and c) non-sea salt (excess) wet deposition.

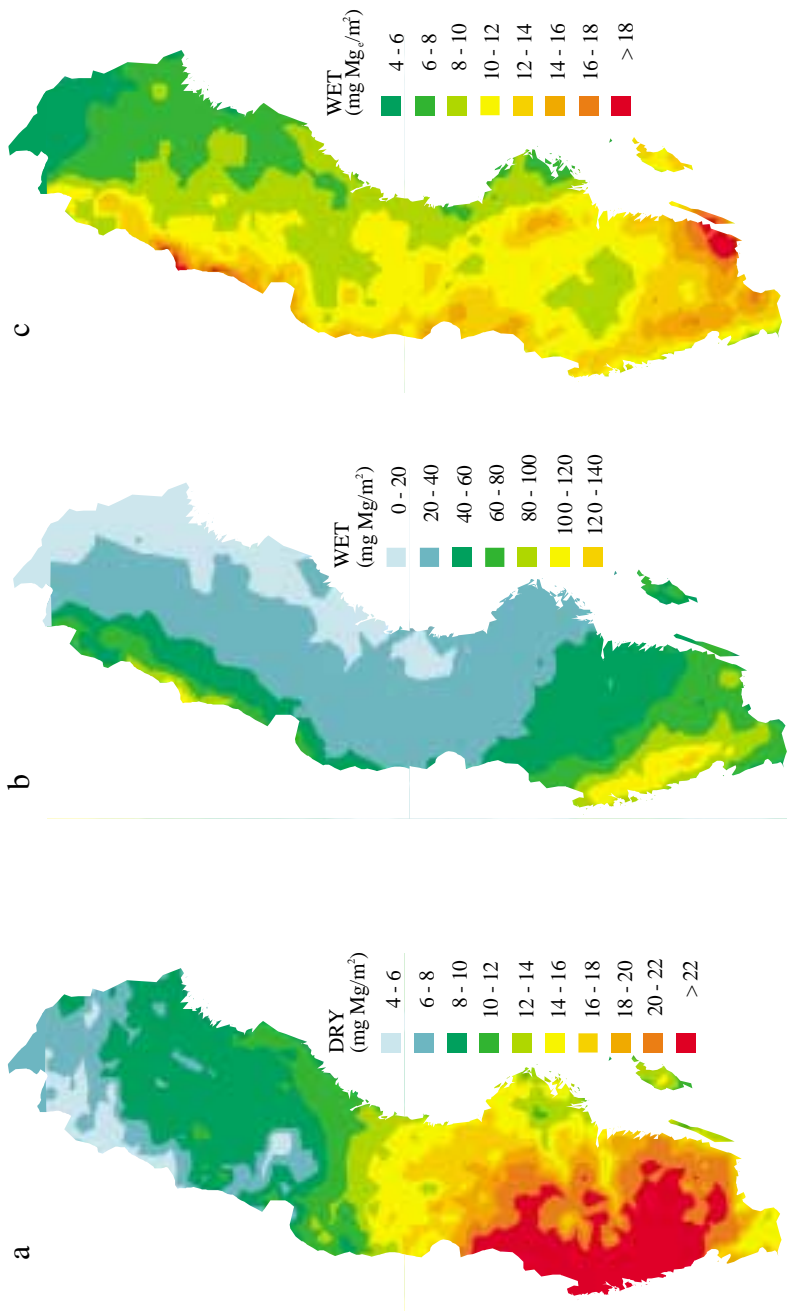
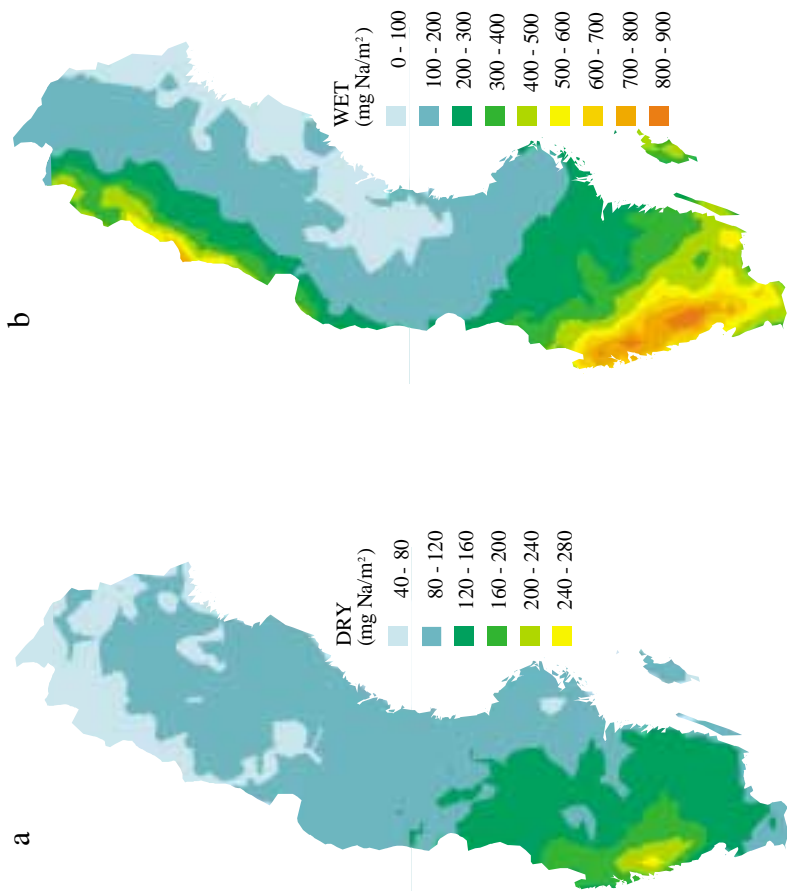


FIGURE 6. Calculated annual deposition (mg/m²) of Mg²⁺ 1996: a) dry deposition including sea salt, b) wet deposition including sea salt and c) non-sea salt (excess) wet deposition.



**FIGUR 7. Calculated annual deposition (mg/m²) of Na⁺ 1996: a) dry deposition including sea salt
b) wet deposition including sea salt.**

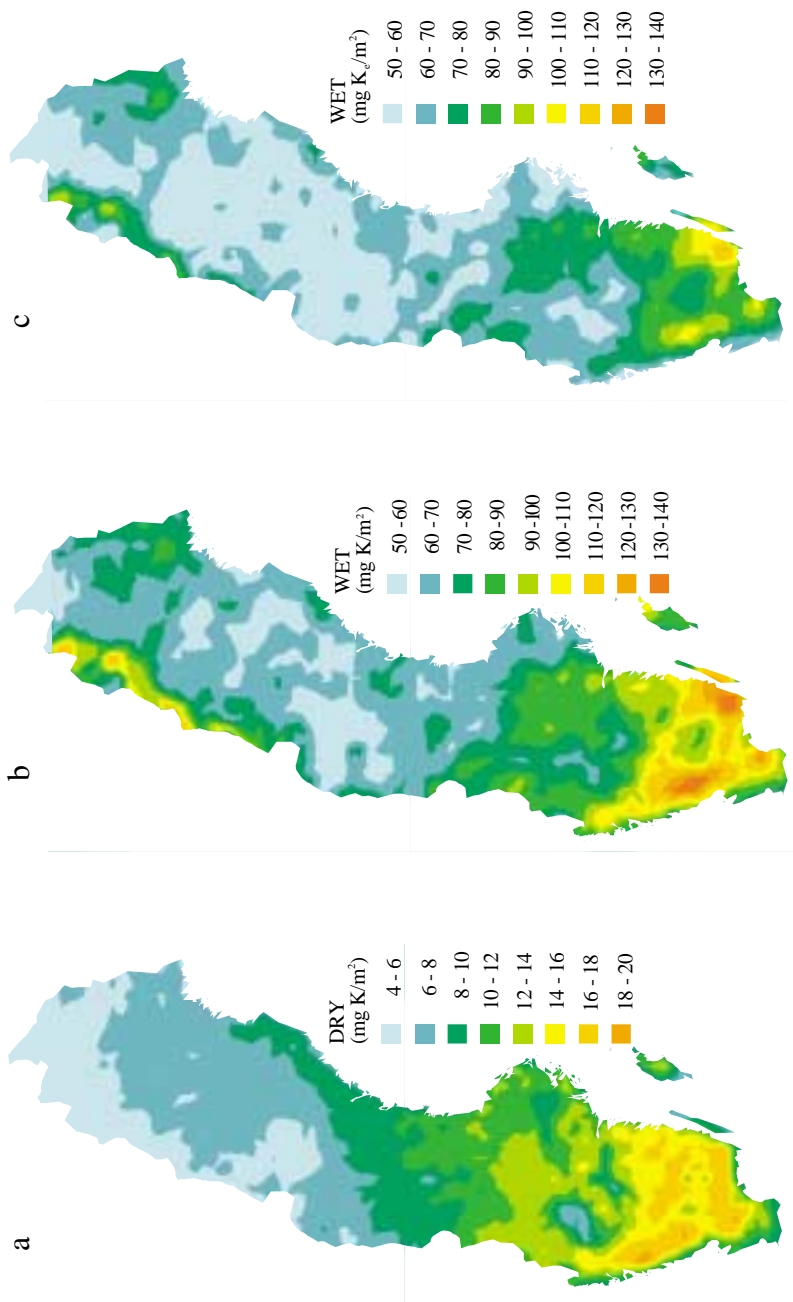
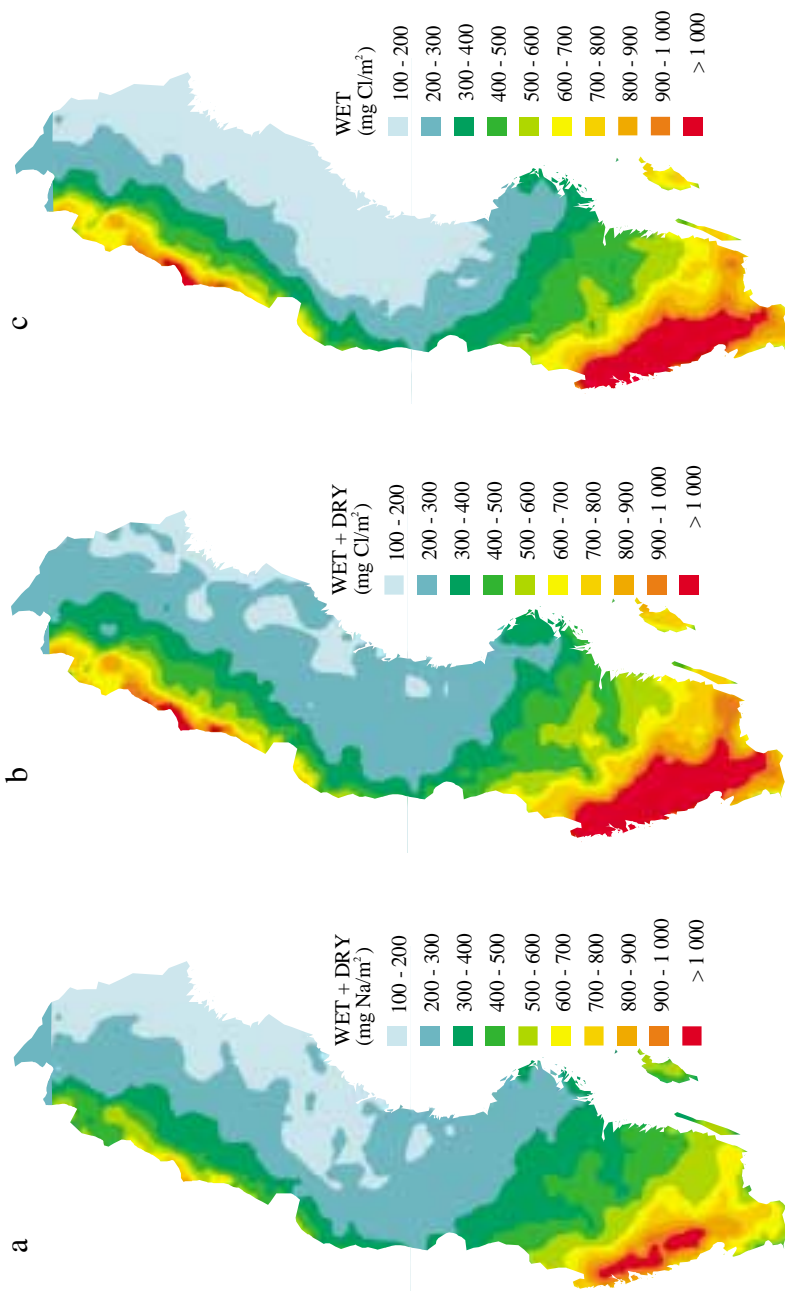


FIGURE 8. Calculated annual deposition (mg/m²) of K⁺ 1996: a) dry deposition including sea salt, b) wet deposition including sea salt and c) non-sea salt (excess) wet deposition.



FIGUR 9. Calculated annual deposition (mg/m²) of sea salt 1996: a) dry+wet deposition of Na⁺, b) dry+wet deposition of Cl⁻ and c) wet deposition of Cl⁻.

Chapter 4.

Conclusions and recommendations

Base cation deposition has been estimated using different approaches based on measurements alone, and on models where air- and precipitation chemistry measurements have been combined with modelling techniques. For some applications the differences are small, but the discrepancies between the results differ substantially depending on type of deposition, compound, type of land use and region of Sweden. This shows that it is not possible to estimate base cation deposition with the same accuracy all over Sweden.

4.1 Conclusions on wet, dry and total deposition

The wet deposition pattern depends to a large extent on precipitation amounts. In order to compare wet deposition for the years 1994 and 1996 we have to note that 1994 was a year with larger precipitation amounts in southern Sweden (110–130% of normal), while only about 80% of normal precipitation fell in the north. During 1996 the precipitation amounts were 80–90% of normal in most parts of Sweden, except for the northeast part of northern Sweden, where values up to 110% were obtained.

Considering the different precipitation amounts during the years 1994 and 1996, the wet deposition values for all three methods covering the whole of Sweden (MATCH, RIVM and Na-ratio) are in general in rather good agreement. However, there is a slight systematic deviation in wet deposition between the Na-ratio method on one side and MATCH and RIVM-modelling on the other side. This is to some extent unexpected, since all estimates should be based on partly the same monitoring data. However, the wet deposition estimates using Na-ratio are mainly based on the open field measurements near throughfall monitoring sites, while the MATCH and RIVM results are based only on data from the national precipitation chemistry network. When the two precipitation chemistry station networks are compared in detail a systematic difference can be seen. The wet deposition from the open field forest stations seems to be generally somewhat higher than that, from the national precipitation chemistry network. Besides

there are uncertainties in the measurements of precipitation amounts. These discrepancies, which must be due to influence of siting, since the same equipment is used and analyses are made at the same laboratory, are presently being subject to a special study. Part of the difference in wet deposition might also be caused by the fact that data used for Na-ratio and MATCH are not, like the RIVM estimates, corrected for dry deposition contributions to the bulk samplers.

When comparing the dry deposition estimates it is important to be aware of that MATCH and RIVM refer to a mixed land use, while Na-ratio estimates are made for spruce forest only. The Na-ratio method is therefore expected to give larger dry deposition values than the other methods. Comparisons for southern Sweden show that the Na-ratio and RIVM methods give similar and much larger dry deposition values than MATCH. Considering the differences in land use, RIVM actually indicates larger dry deposition values than Na-ratio. On the other hand, it is likely that the deposition velocities used in the MATCH calculations (see Table 2) are too small, especially to forest. For example, Tørseth & Semb (1997) and Fowler et al., (1998) have indicated somewhat larger deposition velocities. RIVM gives large dry deposition values also for northern Sweden, where the Na-ratio method gives very much less. The MATCH dry deposition in northern Sweden is larger than obtained from Na-ratio but much less than given by RIVM. The MATCH estimates for northern Sweden is, however, very uncertain due to lack of air concentration measurements of base cations for the northern half of Sweden. Also, the Na-ratio method gives uncertain results for the north, due to lack of data on base cations in throughfall.

The total deposition of base cations is spatially and temporally variable, more variable than deposition of sulphur. In southern Sweden the average total deposition including sea salt of Na^+ is 500–1100 mg/m² and year. The total deposition of Ca^{2+} , Mg^{2+} and K^+ is in the ranges 150–200, 75–150 and 100–150 mg/m² and year, respectively. The highest deposition is found on the west coast, where also strong gradients are seen.

Different estimates give different relative contributions of dry deposition to the total levels. The MATCH model, which may underestimate the dry deposition, estimates a relatively small dry contribution. For Na^+ it is in the range of 20–50% and for Ca^{2+} , Mg^{2+} and K^+ in the ranges 10–20%, 20–40% and 10–15%, respectively. The Na-ratio method, based on measurements in forests only, indicates a higher dry deposition contribution, approximately 40% in the southern part of the country. Due to the character of the method,

this value is valid for all ions. Thus, in the north, the dry deposition contribution, as observed by measurements of throughfall, is small. Consequently, the Na-ratio method gives a relative contribution, which strongly decreases towards the north. The MATCH model, however, gives decreasing total deposition towards the north, but equal or somewhat higher relative dry deposition contribution. This could be caused by lack of measurements of air concentration in the north. The RIVM method estimates a dominating dry deposition (60–70% of the total deposition for Na⁺, Ca²⁺ and Mg²⁺ and around 40% for K⁺) all over Sweden. The RIVM method seems to overestimate the deposition levels in the north, especially for Na⁺, Ca²⁺ and Mg²⁺.

The deposition estimates based on Na-ratio in throughfall and wet deposition, indicate that the part of the total deposition, which is possible to estimate in a relatively accurate way, i.e. the total wet deposition plus the dry sea salt deposition, is a dominating part of the estimated total deposition.

4.2 Conclusions on sea salt and non-sea salt deposition

Sea salt deposition is a major contribution to the total deposition levels of Na⁺ (in most areas >95%) and Mg²⁺ (50–80%). For Ca²⁺ and K⁺, as little as 5–20% and 10–20% of the total deposition is sea salt. There are large variations over the country. The sea salt contribution is largest on the west coast. Here about 20–30% of the Ca²⁺ and K⁺ wet deposition is caused by sea-salt. In parts of eastern and central Sweden the sea salt contribution is about 15% for K⁺ and less than 10% for Ca²⁺. For Mg²⁺ more than 85% is of sea salt origin in western Sweden, while for north eastern Sweden the value is about 60% sea salt.

4.3 Conclusions on Swedish and long range transport contributions

The MATCH model is the only method used for estimating deposition that can be used to provide data on the national contribution to the total deposition levels. The model indicates that the Swedish contribution to non-marine base cation deposition is small, except locally around emission sources. This is in agreement with Norwegian results, which indicated that nearly all non-marine K⁺ and Ca²⁺ are of long-range origin (Tørseth et al., 1999). For non-marine Ca²⁺, Swedish contribution values up to 6–10% of the total deposition are obtained. In areas with extensive wood burning it reaches up to 15%. The MATCH model estimates that national anthropogenic Na⁺ emissions account for <0.5% of the total deposition of Na⁺ on the west coast. In most other areas the corresponding contributions are 1–7%, with the

higher values in minor areas on the East Coast in northern Sweden. This is in agreement with what can be estimated from studying the Na^+ and Mg^{2+} fluxes in throughfall and wet deposition over the country.

4.4 Remaining uncertainties

Largely, there is an agreement between estimates of base cation deposition as regards the order of magnitude in southern Sweden. In northern Sweden, the deviations between methods is – relatively seen – larger than in the south. Different methods give sometimes contradicting results, however, as regards gradients over the country and contribution from dry deposition and from sea salt deposition.

There are a number of defined uncertainties involved in the methods used in this study. Many of these are due to lack of accurate data, for example for emission amounts and particle size ranges. Better estimates and measurements are needed for emission data.

Other uncertainties are due to insufficient information to improve and validate model approaches and model based mapping. For example, monitoring data are needed on air concentrations of base cations. Also monitoring data for different particle-size ranges, PM_{10} , $\text{PM}_{2.5}$ etc. would be of large importance.

Also, uncertainties involved in the measurements of wet deposition and throughfall complicates the estimation of base cation deposition.

4.5 Recommendations for future deposition estimates

A combination of air, precipitation and throughfall chemistry measurements and MATCH model applications is a useful tool for studies of base cation deposition in Sweden. The throughfall measurements carried out in Swedish forests only partly include base cation analyses. Especially in the north, where sea salt contribution is small, money has been saved by not analysing the base cations. However, it is necessary to base the estimates on extended monitoring data on base cations in throughfall and wet deposition all over the country.

Maybe also stemflow measurements and improved ion balance via analyses of other components, such as total organic carbon and organic nitrogen, at some sites would be of value for the future deposition estimates.

For the MATCH model validation, measurement data on airborne base cations are needed. To improve the model approach, better data are also

needed on deposition velocities for particles in the model. This is not only needed to improve the output for base cation deposition, but also for sulphur and nitrogen deposition. There are still large uncertainties in the deposition velocities to be used for particles. Large ranges are found in the literature. Sensitivity studies will show the influence on the estimates of deposition velocity and the uncertainties involved.

Data on leaf area index and its variation over Sweden is further expected to improve the model output. Model validation needs to be carried out using independent data sets on deposition and air concentrations. Base cation deposition estimates from throughfall may be used for validation, and to give indications on relevant deposition velocities.

Improved deposition velocities for particles and better information on leaf area indices will, as mentioned, be of value also for the estimate of sulphur and nitrogen deposition. The final aim is to provide deposition estimates in which ion balance is achieved. This includes model estimates of additional ions, such as H^+ and HCO_3^- .

Also, for the continued work, the requirements have to be set for the need of details and accuracy of base cation deposition. The scale needed for the mapping may be different in different areas. For example, the mapping of sea salt needs a special procedure, taking into consideration the distance from the sea and local wind data (Gustafsson, 1999). Such a mapping procedure may need extended measurements.

Recommendations are required on how to deal with the large local variations in base cation deposition as in deposition of sulphur and nitrogen. The local deposition is of importance on the short distance around emission sources and, if representative only for a minor area, it should be excluded from the large-scale mapping.

There are indications, that the wet deposition dataset from forest open field measurements gives generally and systematically somewhat higher deposition than the precipitation chemistry network. This may be due to differences in site selection strategy, as well as in the procedure for estimating precipitation amount, and needs to be studied further. Also the wet deposition sampling procedure has to be studied further to find out the reasons for the ratio <1 between throughfall and wet deposition at many sites in northern Sweden. Snow sampling is suspected to be an important part of the problem.

Use of new methods such as surrogate surfaces may contribute further to the knowledge. The surrogate surface sampler used at the Gårdsjön site is a method that now is being used more frequently in Sweden and which may

add to the knowledge of deposition from particles and fog drops, as well as to the relation between atmospheric deposition and canopy leaching in throughfall.

ACKNOWLEDGEMENT

The authors would like to thank all persons contributing to the work with data and other support, and who have made the study possible:

Karin Kindbom at IVL Göteborg updated the emission data from 1990 and collected available data on size ranges of emitted particles.

Olle Westling at IVL Aneboda provided the throughfall and wet deposition data for 1994 and 1996 from the regional network for forest deposition measurements.

Martin Ferm at IVL Göteborg provided data from the surrogate surface and throughfall monitoring at the Gårdsjön site.

Geert Draaijers, Erich van Leeuwen and Albert Bleeker sent us the Swedish part of the RIVM base cation deposition database for 1994.

Data to support the MATCH model has been obtained mainly from the Swedish National Environmental Monitoring from IVL. Precipitation chemistry data from background sites in Norway and Finland were given to us from the Norwegian Institute for Air Research (NILU) and the Finnish Meteorological Institute (FMI).

Ulla Bertills, Håkan Staaf and Lars Lindau at the Swedish Environmental Protection Agency have shown great interest for the work and have given valuable comments.

REFERENCES

- Antilla, P. (1990). Characteristics of alkaline emissions, atmospheric aerosols and deposition. In Kauppi, P., Anttila, P. and Kenttämies, K. (eds.) Acidification in Finland. Finnish Acidification Research Programme HAPRO 1985–1990. Springer Verlag, Berlin, pp. 111–134.
- Camberlain, A.C. (1960). Aspects of the deposition of radioactive and other gases and particles. *International Journal of Air Pollution* **3**, 63–88.
- Draaijers, G.P.J. and Erisman, J.W. (1995). A canopy budget model to assess atmospheric deposition from throughfall measurements. *Water, Soil and Air Pollution* **85**, 2253–2258.
- Draaijers, G.P.J., Erisman, J.W., Spranger, T. and Wyers, G.P. (1996). The Application of Throughfall Measurements for Atmospheric Deposition Monitoring. *Atmospheric Environment* **30** (19), 3349–3361.
- Draaijers, G.P.J., van Leeuwen, E.P., De Jong, P.G.H. and Erisman, J.W. (1997a). Base cation deposition in Europe – Part I. Model description, results and uncertainties. *Atmospheric Environment* **31** (24), 4139–4158.
- Draaijers, G.P.J., van Leeuwen, E.P., De Jong, P.G.H. and Erisman, J.W. (1997b). Base cation deposition in Europe – Part II. Acid neutralization capacity and contribution to forest nutrition. *Atmospheric Environment* **31** (24), 4159–4168.
- Eriksson, J., Andersson A. and Andersson, R. (1997). Tillståndet i svensk åkermark. Naturvårdsverket Rapport 4778 (In Swedish).
- Ferm, M. and Hultberg (1995). Method to estimate atmospheric deposition of base cations in coniferous throughfall. *Water, Air and Soil Pollution* **85**, 2229–2234.
- Ferm, M and Hultberg (1999). Dry deposition and internal circulation of nitrogen, sulphur and base cations to a coniferous forest. *Atmospheric Environment* **33**, 4421–4430.
- Ferm, M., Westling, O. and Hultberg, H. (2000). Atmospheric deposition of base cations, nitrogen and sulphur in coniferous forests in Sweden – a test of a new surrogate surface. *Boreal Environment Research* **5**: ? In press.
- Fowler, D., Cape, N.J., Coyle, M., Fletchard, C., Kuylenstierna, J., Hicks, K., Derwent, D., Johnson, C., and Stevenson, D. (1999). Global Exposure of Forests to Air Pollution. In: Proceedings from the IUFRO meeting in Edinburgh, Sept. 1998. *Water, Air and Soil Pollution*, **116**, 5–32.
- Gallagher, M.W., Beswick, K.M. Duyzer, J., Westrate, H., Choularton, T.W. and Hummelshøj, P. (1997). Measurement of aerosol fluxes to Speulder Forest using a micrometeorological technique. *Atmospheric Environment* **31**, 359–373.

- Gillette, D.A. and Passi, R. (1988). Modeling dust emission caused by wind erosion. *Journal of Geophysical Research* **93**, 14233–14242.
- Granat, L. (1988). Luft- och nederbördskemiska stationsnät inom PMK, Naturvårdsverket Rapport 3649 (In Swedish).
- Gustafsson, M. (1999). Marine Aerosols in southern Sweden. Earth Science Centre Göteborg University. A38. Thesis.
- Hedin, L.O., Granat, L., Likens, G.E., Buishand, T.A., Galloway, J.N., Butler, T.J. and Rodhe, H. (1994). Steep declines in atmospheric base cations in regions of Europe and North America. *Nature* **367**, 351–4.
- Hultberg, H. and Ferm, M. (1995). Measurements of atmospheric deposition and internal circulation of base cations to a forested catchment area. *Water, Air and Soil Pollution* **85**, 2235–2240.
- Ivens W.P.M.J (1990). Atmospheric deposition onto forests. Ph. D. Thesis. Faculty of Geographical Sciences, University of Utrecht, the Netherlands.
- Jönsson, P. (1994). Wind Climate During the Instrumental Period and Recent Wind Erosion in Southern Scandinavia. *Meddelanden från Lunds universitetes Geografiska Institutioner, avh. 121. Lund University Press.*
- Kindbom, K., Sjöberg, K. and Lövblad, G. (1993). Beräkning av ackumulerad syrabelastning från atmosfären. Delrapport 1: Emissioner av svavel, kväve och alkaliskt stoft i Sverige 1900–1990. IVL Rapport B 1109. (In Swedish).
- Kindbom, Karin, IVL Göteborg, pers. comm.
- Kulmala, A., Leihonen, L., Ruoho-Airola, T., Salmi, T., and Waldén, J. (1998). Air quality trends in Finland. Air Quality Measurements. Finnish Meteorological Institute, Helsinki. 91 p.
- Lee, D.S. and Pacyna, J.M. (1999). An industrial emissions inventory of calcium for Europe. *Atmospheric Environment* **33**, 1687–1697.
- Lovett, G.M. and Lindberg, S.E. (1984). Dry deposition and canopy exchange in a mixed oak forest as determined by analysis of throughfall. *Journal of Applied Ecology* **21**, 1013–1027.
- Lövblad, G. (1987). Utsläpp till luft av alkali. IVL Rapport B 858. Swedish Environmental Research Institute, Göteborg, Sweden. (In Swedish).
- Lövblad G., Andersen, B., Hovmand, M., Joffre, S., Pedersen, U., Reisell, A., (1992). Mapping deposition of sulphur, nitrogen and base cations in the Nordic Countries. IVL Report B 1055. Swedish Environmental Research Institute, Göteborg, Sweden.
- Lövblad, G. (1996). Importance of spatial deposition variations for critical loads Exceedances. Background paper presenterat vid UNECE Workshop i Wien 22–24 November 1995. *Spatial and Temporal Assessment of Air Pollution Impact on Ecosystems: Exceedances of Critical Loads and Levels.*
- Lövblad, G. (1997). Depositionsuppskattningens inverkan på överskridandet av kritisk belastning. IVL Rapport B 1276. Swedish Environmental Research Institute, Göteborg, Sweden. (In Swedish).

- Lövblad, G. and Persson, C. (1999). Base cation deposition in Sweden. Poster presented at the International Conference Air Quality in Europe for the 2000s, Venice Italy May 19-21, EI JRC, and others.
- Marticorena, B and Bergametti, G (1995). Modelling the atmospheric dust cycle: 1. Design of a soli-derived dust emission scheme. *Journal of Geophysical Research* **100** (D8), 16415–16430.
- Naturvårdsverket, (1996). Åtgärder för att minska utsläppen från småskalig vedeldning – Redovisning av ett regeringsuppdrag. Naturvårdsverket Rapport 4687 (In Swedish)
- Nihlen, T. (1990). Eolian Processes in Southern Scandinavia and the Mediterranean Area. *Meddelanden från Lunds universitets Geografiska Institutioner, avh. 110. Lund University Press.*
- Persson, C., Langner, J. and Robertson, L. (1996). Air pollution assessment studies for Sweden based on the MATCH model and air pollution measurements. *Air Pollution Modeling and Its Application*, Vol XI. (eds.) Gryning S-E and Schiermeier F.A., Plenum Press, New York and London.
- Persson, C., Lövblad, G. and Roos, E. (1999). Meso-scale modelling of base cation deposition. In: S-E. Gryning et al., (eds.) *Air Pollution Modeling and Its Application XIII*. NATO Conference, Plenum Publ., New York. (In print)
- Robertson, L., Langner J. and Engardt M. (1998). An Eulerian limited area atmospheric transport model. *Journal of Applied Meteorology* **38**, 190–210.
- Semb, A., Hanssen, J.E., Francois, F., Maenhaut, W. and Pacyna, J.M. (1995). Long-range transport and deposition of mineral matter as a source for base cations. *Water, Air and Soil Pollution* **85**: 1933–1940.
- Slinn W.G.N. (1982). Predictions for particle deposition to vegetative canopies. *Atmospheric Environment*, **16**, pp. 1785–1794
- Spranger, Till Umweltbundesamt, pers. comm.
- Task Force on Mapping. (1996). Manual on methodologies and criteria for Mapping Critical Loads/Levels. ISSN 0722–186X. Federal Environmental Agency, Berlin.
- Tegen, I. and Fung, I. (1994). Modelling of mineral dust in the atmosphere sources, transport, and optical thickness. *Journal of Geophysical Research* **99**, 22.897–22.914.
- Tørseth, K and Semb, A (1997). Deposition of major inorganic compounds in Norway 1992–1996. NILU rapport OR 67/97.
- Tørseth, K., Hanssen, J.E. and Semb, A. (1999). Temporal and spatial variations of airborne Mg, Cl, Na, Ca and K in rural areas of Norway. *The Science of the Total Environment* **234**, (1–3) 75–85.
- Ulrich, B. (1983). Interaction of forest canopies with atmospheric constituents: SO₂, alkali and earth alkali cations and chloride. Ulrich, B. and Pankrath, J. (eds.) *Effects of Accumulation of Air Pollutants in Forest Ecosystems*. (1983), pp. 33–45.

- Ukonmaanaho, L., Starr, M. and Ruoho-Airola, T. (1997). Trends in sulphate, base cations and hydrogen ion concentrations in bulk precipitation and throughfall at Integrated Monitoring areas in Finland 1989–1995. *Journal of Conference Abstracts* 2(2). 314. In: Bio. Geo. Mon. 3rd International Symposium on Ecosystem Behaviour, June 21–25 1997, Villanova USA.
- Van der Maas, M.P. and Pape Th, (1991). Hydrochemistry of two Douglas fir Ecosystems and a heather ecosystem in the Veluwe. The Netherlands Dutch Priority Programme on Acidification. Report no 102.1.01.
- Van Leeuwen, E.P. Potma, C.J.M., Draaijers, G.P.J., Erisman, J.W. and van Pul, W.A.J. (1995). European Wet Deposition Maps Based on Measurements. RIVM Report 722108006, National Institute for Public Health and the Environment, Bilthoven, the Netherlands.
- Van Leeuwen, E.P., Draaijers, G.P.J. and Erisman, J.W. (1996). Mapping Wet Deposition of Acidifying Components and Base Cations over Europe Using Measurements. *Atmospheric Environment*, **30** (14), 2495–2511.
- Westling, O., Hultberg, H. and Malm, G. (1995). Total deposition and tree canopy internal circulation of nutrients in a string acid gradient in Sweden, as reflected by throughfall fluxes. In: L.-O. Nilsson, R. Huttli & U.T. Johansson (eds.) Nutrient uptake and cycling in forest ecosystems. Kluwer Academic Publishers, Dordrecht pp. 639–647.
- Westling, O., Lång, L.-O. och Lövblad, G. (1997). Massbalansberäkningar i skogsmark i Göteborgs och Bohus län samt Älvsborgs län. Länsstyrelsen i Göteborgs och Bohus län, Miljöavdelningen 1997:16. (In Swedish).
- Westling, O. and Ferm, M. (to be published)

REPORT 5119

Deposition of Base Cations in Sweden

Atmospheric deposition of base cations, such as calcium, magnesium, potassium and sodium, is an important element in the process of acidification, recovery from acidification and for the calculations of critical loads.

Deposition of base cations is generally difficult to estimate, and varies widely from one site to another. In this study different methods have been used to estimate base cation deposition and the results have been compared. The study has provided new knowledge on the magnitude of deposition over Sweden, the importance of different sources and deposition processes and the contribution from national sources in relation to longrange transport.

The recommendations given in the report can serve as a basis for future work on estimating base cation deposition.



isbn 91-620-5119-9
issn 0282-7298