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Evaluation of NARCM using aircraft observation from NARE

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science.

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Abstract

The Northern Aerosol Regional Climate Model (NARCM) is being developed in order to better understand how aerosols affect the Canadian climate. NARCM uses microphysical and chemical parameterizations that enable it to predict the evolution of the aerosol spectrum using the concentration and composition in 12 size-segregated bins as prognostic variables. In this study, two aerosol species are considered as prognostic variables within NARCM: sulphate and sea-salt. The sulphur species concentrations and aerosol distributions simulated by NARCM are evaluated against clear-sky in-situ aircraft measurement taken off the coast of Nova Scotia during the North Atlantic Regional Experiment (NARE). NARCM demonstrates skill at predicting the column burdens of the sulphur species concentrations at the NARE site throughout the NARE period. Simulations of the average column burdens of sulphur dioxide and sulphate showed differences of 57% and 28% respectively from the observed values. The accumulation mode in the aerosol distributions simulated by NARCM has a tendency to be smaller than the measured mode. There is evidence that the absence of other aerosol species may account for the too small sizes of the simulated aerosol when sulphate volumes are small.
Résumé

Le projet de Modèle Régional Climatique Aérosol de la region Nord (NARCM) est en cours de développement afin de mieux comprendre dans quelle mesure les aérosols interviennent dans le climat canadien. Le modèle NARCM utilise des paramètres chimiques et microphysiques qui permettent de prédire l'évolution spectrale des aérosols en considérant comme variables de sortie leur concentration et leur composition chimique en douze tailles différentes. Dans cette étude, les deux types d’aérosols étudiés en sortie du modèle NARCM sont le sulfate et le sel de mer. Les concentrations des composés de sulfate et les distributions d’aérosols, simulées par le NARCM, sont comparées aux mesures in situ effectuées en avion par temps clair au large de la côte de la Nouvelle-Écosse lors de l’Expérience Régionale Nord Atlantique (NARE). Le NARCM montre une certaine fiabilité lors de la simulation de l’intégration verticale des concentrations des composés de sulfate lors de l’expérience NARE. Les intégrations verticales moyennes cumulées d’acide sulfurique et de sulfate présentent des différences respectives de 57% et 28% comparativement aux valeurs observées lors des mesures. Dans la distribution simulée des aérosols, le mode d’accumulation tend à être moins important que le mode mesuré. Cela tend à montrer que l’absence d’autres types d’aérosols peut ne pas être négligeable dans les simulations du NARCM quand les volumes de sulfate ne sont pas suffisamment grands.
Acknowledgements

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Chapter 1

Introduction

Section 1.1: *General introduction*

Increases in global greenhouse gas concentration since the dawn of the industrial revolution is a growing concern in the public’s eye due to the possible implications for climatic change. This increase in greenhouse gas concentration is estimated to contribute a perturbation in longwave radiative forcing of $+2.4 \pm 0.2 \text{ Wm}^{-2}$ [Intergovernmental Panel on Climate Change, 2001] relative to pre-industrial values. Alongside this increase in greenhouse gas concentration, there was also an increase in the anthropogenic emission of aerosols. These aerosols also have a significant impact on climate and climatic variability on a global, regional and local scale.

For instance, aerosols are known to absorb and backscatter solar and infrared radiation [Intergovernmental Panel on Climate Change, 2001] thereby modifying the radiation budget at the surface of the Earth. The direct influence of these aerosols on the radiation budget is known as the direct effect of aerosol radiative forcing. It has been estimated that the direct effect of sulphate aerosols contributes a radiative forcing of about $-0.3 \text{ Wm}^{-2}$ to $-0.9 \text{ Wm}^{-2}$ [Jones et al., 1994, Haywood et al., 1997, Chuang et al., 1997]. The Intergovernmental Panel on Climate Change estimates the direct effect of sulphate aerosol in changing the
radiation budget at the surface to be \(-0.4 \text{ Wm}^{-2}\). The uncertainty associated with the direct effect is due mostly to the uncertainties in the amount of sulphate produced by the oxidation of sulphur dioxide, the uncertainty in the residency time (of the order of a week for tropospheric aerosols [Schwartz, 1996]), and the ambient relative humidity [Pan et al., 1997].

In addition, aerosols can also have numerous interactions with clouds by modifying the available concentration of cloud condensation nuclei. The change in the radiation budget resulting from changes in cloud properties is known as the indirect effect of aerosols. In 1974, Twomey hypothesised that an increase in the concentration of cloud condensation nuclei would lead to higher cloud albedo. Convincing evidence for this hypothesis was demonstrated by correlating bright streaks in clouds with the emissions from passing ships using satellite imagery [Twomey et al. 1984, Coakley et al., 1987, Radke et al., 1989, Hindman and Bodowski, 1996, Noone et al., 1998]. Furthermore, increases in cloud condensation nuclei can lead to increases in the lifetime of [Albrecht, 1989] and to the thickening of clouds [Pincus and Baker, 1994].

The indirect effect has been shown to have a more profound effect on the albedo of maritime clouds due to their low cloud droplet number concentrations [Twomey et al., 1984, Charlson et al., 1987]. In addition, the indirect radiative forcing of aerosols is more pronounced in regions downwind of major urban centres where anthropogenic sources of aerosols are the strongest [Charlson et al.,
1992]. This translates into a large regional variability in the susceptibility of clouds to anthropogenic aerosol loading. Kogan et al. [1996] depicted that the perturbation in the shortwave radiation incident on the Earth’s surface due to the indirect effect varied regionally from -0.08 Wm\(^{-2}\) near the equator up to -5 Wm\(^{-2}\) near major anthropogenic sources. For instance, over eastern North America, Leaitch et al. [1992] estimated the strength of the indirect effect to be between -2 Wm\(^{-2}\) to -3 Wm\(^{-2}\) based on the analysis of data collected from aircraft.

Several studies have estimated the global impact of the indirect effect on the shortwave radiation budget. One approach of these studies was to use empirically derived relationships to estimate the cloud condensation nucleus concentration and cloud properties. These empirical relationships were either functions of the mass of sulphate aerosols or of the aerosol number concentration. The studies of Jones et al. [1994] (-1.3 Wm\(^{-2}\)), Boucher and Lohmann [1995] (-0.5 Wm\(^{-2}\)), Kogan et al. [1996] (-1.1 Wm\(^{-2}\)) and Chuang et al. [1997] (-0.4 Wm\(^{-2}\) to -1.1 Wm\(^{-2}\)) coupled aerosol-cloud schemes using these empirical methods with general circulation models (hereafter referred as GCMs). Later, the simulations of Feichter et al. [1997] involving the coupling of a cloud microphysics scheme with a sulphur cycle model estimated the indirect aerosol effect to be -0.76 Wm\(^{-2}\). Still, these studies have all required that an increase in sulphate mass must correspond in a specified way to an increase in the cloud droplet number concentration. This simple assumption cannot account for all the dependencies of
aerosol activation such as the presence of other soluble aerosol species, updraft speed, or the shape of the aerosol size distribution.

Lohmann et al. [1999] included a prognostic equation for cloud droplet number concentration into their GCM simulations coupled to a sulphur and carbon cycle model. To calculate the cloud droplet number concentration they assumed that the aerosol size distributions for marine and continental air masses had a specified volumetric mean radius before the addition of anthropogenic sulphate mass to these distributions. The aerosol concentrations can then be calculated based on the aerosol mass present in a region and the density of those aerosols. The aerosols over the continent were composed of black carbon, organic carbon, and soil dust. The marine aerosol was composed of sea-salt and sulphate produced from dimethyl sulphide. In the calculation of the number of nucleated droplets, these distributions (for this discussion, loosely termed background aerosol distributions) are adjusted for the addition of sulphate mass using a parameter $\alpha$ to take into account the shape and composition of the aerosol size spectrum [Chuang and Penner, 1995]. The resulting number of nucleated cloud droplets is the based on the total aerosol number (sulphate + background), the parameter $\alpha$ and the updraft speed. The assumption of a single prescribed volumetric mean radius for marine and continental regions implies that concentrations are not subject to modification of the size spectrum of the aerosol by clouds or precipitation. Additionally, the assumption of a constant volumetric mean radius does not
account for the effect that varying aerosol composition may have on the size spectrum of these aerosols.

As an extension of the mechanistic approach of simulating the indirect effect of aerosols taken by Lohmann et al., the Northern Aerosol Regional Climate Model (NARCM) project was initiated in order to better understand how aerosols are affecting the Canadian climate. NARCM is unique amongst climate models, including those stated above, in that it has microphysical and chemical parameterizations that enable it to predict the evolution of the aerosol spectrum using the concentration and composition in 12 size-segregated bins as prognostic variables. This approach, after benefiting from a high-resolution framework in the NARCM model for its testing and development, will eventually be incorporated into a global climate model for use in sensitivity studies. These sensitivity studies are intended to investigate the impact of changing anthropogenic emissions on the global climate and to estimate the strength of the non-linear feedback that aerosols have on climate.

The rationale of NARCM is to incorporate the major tropospheric aerosol types, including sulphate, sea-salt, black carbon, organic carbon, soil dust, and aerosols from volcanoes and biomass burning. All of these aerosol types were not incorporated into the initial version of the model. In the first version of NARCM (termed NARCM-1) only sea-salt and sulphate aerosols were incorporated. This ensured that adequate testing of the model's capabilities could be done with a
simpler version. Recently, a newer version of NARCM has been developed which includes black carbon and organic carbon.

This study will evaluate the performance of NARCM-1 in a 3-dimensional simulation of the period of the North Atlantic Regional Experiment [NARE]. The NARE data set used in this study consists primarily of a series of continuous measurements obtained along the flight paths of the Canadian National Research Council NRC DHC-6 Twin Otter aircraft, which flew 48 flights off the coast on Nova Scotia, Canada during late summer of 1993. These flights were limited to within 50 km of Yarmouth, Nova Scotia and measured a variety of meteorological, chemical and microphysical variables. A comparison of average vertical profiles obtained from these measurements with those simulated by NARCM will be used to comment on how NARCM simulated the average aerosol size and volume distributions and the sulphur budget for this period. The evaluation of NARCM using the flight data taken during NARE is intended to compliment the previous comparisons of NARCM-1 with observations done by Von Salzen et al. [2000] and verification of the sea-salt parameterizations done by Gong and Barrie [1997] and Gong et al. [1997]. Unlike the simulation of the NARE period, the earlier studies made evaluations of NARCM's performance by comparing modelled values to observations with limited vertical extent over larger aerial extents. More details of the studies made by Von Salzen and Gong are presented in the next section.
Section 1.2: *Previous studies involving the evaluation of NARCM*

Gong and Barrie [1997] coupled a sea-salt aerosol model with the time-variant column version (FIZ-C) [Therrien, 1993] of the Canadian General Circulation model GCMII to demonstrate that the parameterizations of sea-salt aerosol used could produce realistic results. The sea-salt aerosol model included parameterizations for the generation of sea-salt as a function of the surface wind speed, the vertical transport by turbulence and convection, the dry deposition and gravitational settling of aerosol and the wet removal of aerosols by in-cloud and below-cloud scavenging. A 90-day simulation of a GCMII grid box in the North Atlantic (61.2 degrees North and 7.5 degrees West) by this coupled model showed that the predicted sea-salt aerosol size distributions, particle number densities and wind dependence were in very good agreement with observational data from that region. In that study, the parameterization for the production of sea-salt aerosols described by Monahan et al. [1986] as a function of wind speed at 10m above sea level was used. This source function for sea-salt was shown to give reasonable emission rates for particles larger than 0.1 μm dry radius, but overestimated the production rate of sea-salt aerosols below that size.

Gong et al. [1997] compared the simulated atmospheric sea-salt aerosols concentrations from this coupled model with long-term observations of Na⁺ at seven different stations around the world. A five-year simulation by the above
model reproduced nicely the sea-salt concentrations and their seasonal variability at the 5 coastal stations in that study. The other two stations were inland in Arctic regions. The over-prediction of sea-salt aerosol concentrations at these sites was believed to be caused by the absence of removal processes in the model over the snow during the transport to these sites.

The two preceding studies have validated the suitability of the sea-salt parameterizations and justified their incorporation into the 3-dimensional framework of NARCM. In addition to sea-salt, NARCM currently contains a treatment of sulphur species that includes emissions, nucleation, condensation, clear sky and in-cloud oxidation, wet and dry deposition. NARCM treats its sea-salt and sulphate aerosol as being internally mixed.

Von Salzen et al. [2000] estimated the seasonal variability in the sulphate aerosol distributions over North America while evaluating the model’s performance for a two-week period in July and a two-week period in December 1994. They concluded that the mass mean diameters of sulphate aerosols simulated by NARCM were strongly dependant on the relative humidity, clouds and the presence of seasalt in a region. The majority of the seasonal differences in observed and simulated mass mean diameters were attributed to differences in the relative humidity and cloud amounts.
Von Salzen et al. [2000] also described the sensitivity of aerosol size distributions and CCN concentrations over North America to reduced SO$_x$ emissions and increased hydrogen peroxide background concentrations for these periods. Sulphate concentrations for both periods decreased linearly due to a reduction of in-cloud production of sulphate with decrease in sulphur dioxide concentrations. The response of sulphate concentrations to increased hydrogen peroxide concentrations was smaller due to sulphur dioxide limitation effects in both simulated summer and winter conditions.

For the summer period simulated by Von Salzen et al., the meteorological conditions were reasonably well simulated, with the exception of too low relative humidity and precipitation over south-eastern North America. They attributed the under-prediction of relative humidity and precipitation in part to insufficient spin-up of the model leading to an underestimation in soil moisture. Furthermore, this study showed that NARCM under-predicted the mean sulphate concentration for this period over eastern North America at ground-level. An average difference of about 13% was found when compared to 6.3 $\mu$g m$^{-3}$ mean that was measured by the Clean Air Status and Trends Network (CASTNet) and the Canadian Air and Precipitation Monitoring Network (CAPMoN). The mean wet-deposition of sulphate over Eastern North America was also lower by 23% in the model compared to observations measured by these networks. In contrast, compared to the concentrations measured at the ground by the CASTNet network sulphur dioxide was over-predicted by NARCM, on average by 185%. This substantial
difference was attributed to excessive vertical diffusion potentially due to insufficient model resolution near the source region.

Unfortunately due to lack of observations of particle sizes during the summer of 1994, Von Salzen et al. used the combined measurements from three field studies from other years, namely the PRECP V Experiment from June 2 to 23, 1987 over Ohio [Kleinman and Daum, 1991], the New York City (NYC) Urban Plume Experiment from July 1 to 28, 1996 over New York [Kleinman et al., 2000] and the Southern Oxidants Study (SOS) from June 24 to July 20, 1995 over Tennessee [Hubler et al., 1998] to evaluate the simulated size distributions. They showed that the aerosol mass mean diameter simulated by NARCM for the size range 0.12 \( \mu m \) to 1.24 \( \mu m \) compared reasonably well with the observed values. At levels below 850 hPa, the modelled mass mean diameter (0.238 \( \mu m \)) was 10% less than the observed value (0.263 \( \mu m \)). Above this level, the bias increased to between 15 to 21%. Von Salzen et al. suggested that these differences, at least in part, were due to the absence of additional aerosol compounds in an internal mixture with sulphate.
1.3 Thesis outline

This study intends to improve on previous evaluations of NARCM's capabilities at simulating the sulphur cycle and aerosol size distributions by comparing simulated values directly with detailed in-situ measurements obtained from Twin Otter aircraft flights over the period of a month off the coast of Nova Scotia. This evaluation will view NARCM's performance in the vertical for a region that is away from the source region of anthropogenic aerosol in the eastern United States to compliment the mainly surface analysis done by von Salzen. Additionally, the aerosol size and volume distributions modelled by NARCM have not yet been directly compared to observed values for the same period as simulated. Therefore, this study is better able to draw links between how changes in the sulphur budget affect the simulated aerosol size distribution. The following is a description of the up-coming chapters.

Chapter 2 will give an overview of the observational experiment, NARE, which will be used later to evaluate NARCM. The details and methodologies of the instrumentation relevant to this study will be discussed. Additionally, an inter-comparison of modelling studies of NARE will be described.

Chapter 3 includes a general description of the NARCM model, and a reasonably detailed look at the aerosol parameterizations used in version I of NARCM and presents the methodology associated with this study.
Chapter 4 begins by showing the improvement made to the simulated wind fields when a nudging technique is used. Afterwards, Chapter 4 portrays the average meteorological conditions for two runs of the NARCM model. The two runs represent a sensitivity test into how changes in the aerosol processes resulting from an increase in initial soil moisture affect the comparison of modelled vertical profiles of sulphur species concentrations and the aerosol size and volume distributions simulated by NARCM. These concentrations for both runs will be contrasted with aircraft observations taken at the NARE site in order to make a useful evaluation of the NARCM model.
Chapter 2

The NARE study

Section 2.1: A general description of the NARE study

The North Atlantic Regional Experiment (NARE) was an intensive field study that took place from August 6th to September 8th, 1993 [Fehsenfeld et al., 1996]. The intent of NARE was to estimate the contribution of the anthropogenic emissions from the eastern North America to the tropospheric ozone budget over the North Atlantic. A secondary goal was to study the chemistry and microphysics of marine clouds over the North Atlantic.

As part of this study, a NRC DHC-6 Twin Otter aircraft was equipped with an array of instrumentation for the measurement of various meteorological, microphysical and chemical variables. In total, 48 separate flights of the Twin Otter aircraft were made during the observational period. A typical flight lasted on average for a little over a couple of hours. The majority of these flights sampled the environment within 50 km of Yarmouth (approximately 43.3° N, 66° W) with regular passes over the North Atlantic and inland to the Kejimkujik National Park, Nova Scotia (approximately 44.3° N, 65.5° W). The exception was a series of sampling runs to and around Saint John, New Brunswick on September 4th and 5th.
Section 2.2: NARE instrumentation relevant to this study

The Particle Measuring Systems (PMS) Passive Cavity Aerosol Spectrometer Probe (PCASP –100X) was used to obtain dry aerosol size distributions averaged in 10 second time intervals for aerosol diameters between 0.125 μm to 3.0 μm. The PCASP – 100X counter was equipped with a diffuser nozzle to decelerate the aerosols before sampling. The air was heated to ensure that the aerosol sampled in clear conditions would be dry. The cloud liquid water content (LWC) was measured using a PMS King hot wire probe. The uncertainty associated with this LWC probe for a 1 second measurements is ± (10% of measurement + 0.02) g m⁻³ [Cober et al., 1995]. The size spectrum of cloud droplets was also measured in ten-second samples over the size range 2-35 μm by a PMS forward scattering spectrometer probe (FSSP-100).

Trace gas measurements were obtained every second during the Twin Otter aircraft flights. These measurements include the mixing ratio of SO₂, which was obtained by a TECO-43S analyzer and the mixing ratio of ozone obtained with a TECO-49 UV absorption analyzer that has an uncertainty of ± (5 ppbv + 10%). The detection limit of the TECO-43S is 0.2 ppbv and with an uncertainty in SO₂ values of ± 0.1 ppbv + 30% of the measurement value [Banic et al., 1996]. The hydrogen peroxide concentration was measured using the Kok method with Fenton reagent chemistry. This method has a detection limit of 0.1 ppbv with an uncertainty of ± 5% [Weinstien-Lloyd et al., 1996].
The sulphate concentrations were determined by using ion chromatography on aerosols sampled by Teflon filters that were exposed during the Twin Otter flights and also near the surface at Cheboque Point, Nova Scotia (43°50'N, 66°7'W). These filters were used sporadically during the NARE period. Table 2.1, presents a summary of the numbers of filters that were exposed along the Twin Otter flight trajectories.

The total period during which these filters were exposed represents only a fraction of the total aircraft flight times and therefore provides only a discontinuous data set for the mass concentration of SO₄. However, a high correlation between the number concentration of aerosols in the seventh channel of the PCASP -100X (diameters of 0.31 μm to 0.4 μm) and the mass concentration of SO₄ measured during the NARE experiment was shown by Banic et al. [1996]. This correlation was later represented by Lohmann et al. [2001] as a fourth order polynomial fit constrained to pass through the origin of the correlation plot (Figure 2.1). In order to avoid the effect of local sources, the filter measurements that were used to determine the above relationship were limited to periods when the winds at Cheboque Point were from 270 degrees to 90 degrees [Lohmann et al., 2001]. The filter exposed during Twin Otter flight 22 was excluded from the analysis due to high concentration of black carbon associated with a forest fire in the Northwest Territories [Kleinman et al., 1996]. An independent testing of this relationship to all clear-sky filters (except flight 22) for all wind directions will be
presented with the results in Chapter 4. The consistency of this empirical relationship and hence the usefulness of PCASP data as surrogate for the mass concentration of \( \text{SO}_4 \) along a flight’s trajectory is discussed there.

**Table 2.1:** A list of Twin Otter flights with exposed filters

<table>
<thead>
<tr>
<th>Date</th>
<th>Month</th>
<th>Flights with filters</th>
<th># of filters</th>
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<tr>
<td>10</td>
<td>8</td>
<td>5</td>
<td>1</td>
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<td>14</td>
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<td>8</td>
<td>9</td>
<td>48</td>
<td>2</td>
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</table>
More details on the instrumentation used during NARE are given in Banic et al., 1996, and Daum et al., 1996.

Section 2.3: Some results from previous studies of NARE

Merrill and Moody [1996] presented an overview of the synoptic meteorology and transport that occurred during NARE. Their analysis revealed that the anticyclonic “Bermuda-Azores” high was relatively inefficient in transporting pollutants northeastwardly to Nova Scotia since the flow around the high is weak. They instead associated the most intense transport of pollutants to the coast of Nova Scotia with the development of frontal systems. In further investigating the transport of ozone and sulphur during NARE, Banic et al. [1996] showed that eighty percent of sulphate and 50% of sulphur dioxide that were transported was at altitudes above 1 kilometer. Strong transport events resulted in plumes of anthropogenic pollution from the United States that were observed over Nova Scotia as isolated layers between heights of 0.3 km and 2 km with depths of up to 1000 m.

The analysis of the chemical composition of aerosols transported from the United States and collected by the Teflon filters at the Cheboque Point site revealed a strong association between $\text{NH}_4^+$ and $\text{nssSO}_4^{\text{aq}}$ [Liu et al., 1996]. Liu et al. further suggested that sulphates were mostly present in the form of acid-salt mixtures, such as ammonium sulphate and ammonium bisulphate. They found that $\text{nssSO}_4^{\text{aq}}$
and NH$_4^+$ comprised from 15% to 80% and 6% to 31% of the sub-micron total aerosol mass respectfully with median proportions of 49% and 12% respectfully. Additionally, the mass fraction of total measured organic material was between 2% to 15% with a median value of 7%. The micron-sized aerosols were mostly associated with sodium nitrate and sea-salt.

Section 2.4: Previous simulations of NARE

Lohmann et al. [2001] described an inter-comparison of eleven large-scale atmospheric models (Table 2.2) in simulating the vertical distributions of sulphur species during NARE (hereafter, COSAM). These models fall into two classes, namely chemical transport model that are driven by observed winds and general circulation models that simulated their wind fields themselves. However, none of these models include explicit size-segregated aerosols as NARCM does. In chapter 4, the modelled sulphur species column burdens from NARCM will be compared with the results from these simulations.
Table 2.2: COSAM model names and references

<table>
<thead>
<tr>
<th>Model Name</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>GISS</td>
<td>Koch et al. [1999]</td>
</tr>
<tr>
<td>ECHAM4-UU</td>
<td>Roelofs et al. [1998]</td>
</tr>
<tr>
<td>CCCma</td>
<td>Lohmann et al. [1999]</td>
</tr>
<tr>
<td>ECHAM4-MPI</td>
<td>Feichter and Lohmann [1999]</td>
</tr>
<tr>
<td>TOMCAT</td>
<td>Law et al. [1998], Giannakopoulos et al. [1999]</td>
</tr>
<tr>
<td>KNMI/IMAU</td>
<td>Dentener et al. [1999]</td>
</tr>
<tr>
<td>MIRAGE</td>
<td>Saylor et al. [1999]</td>
</tr>
<tr>
<td>IMPACT</td>
<td>Penner et al. [1998]</td>
</tr>
<tr>
<td>GOCART</td>
<td>Chin et al. [2000]</td>
</tr>
<tr>
<td>NCAR</td>
<td>Rasch et al. [2000]</td>
</tr>
<tr>
<td>DEHM</td>
<td>Christensen [1997]</td>
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</tbody>
</table>
**Figure 2.1.** Correlation plot of the mass concentration of sulphate measured by filters against the number concentration of aerosols in the seventh channel of the PCASP - 100X averaged over the filters exposure time.
Chapter 3

NARCM model description

Section 3.1: General NARCM description

The NARCM model is a non-hydrostatic limited area model, which is driven by the dynamics kernel of the CRCM (Canadian Regional Climate model, version2) [Laprise et al., 1997; Caya et al., 1995], with a prognostic treatment of aerosol processes. NARCM's domain is defined on a polar-stereographic grid and uses Gal-Chan terrain following vertical coordinates with a staggered C-grid structure. The boundary and initial conditions supplied by the Canadian GCM [McFarlane et al., 1992] coupled with the CLASS land-surface scheme [Verseghy et al., 1993] force the meteorological fields within the domain. In addition, a sponge layer at the top and at the edges of the domain is used to ensure a smooth forcing of these fields [von Salzen et al., 2000].

The version of NARCM used in this study (version 1) considers the effects of two aerosols types, namely sea-salt and sulphate aerosols. The model assumes that these aerosol types are internally mixed. The dry aerosol size distributions in this study are described using 12 size bins (or sections). The size-segregated multi-component aerosol distribution of the NARCM model allows it to treat processes of emission, transport-diffusion, chemical/physical transformation, wet and dry
deposition, as well as radiative coupling which are all dependant on both the size and composition of the aerosols.

Section 3.2: *Details of the aerosol processes in NARCM*

The evolution of aerosol size distributions within NARCM is determined by the rate of production of new aerosols, by the removal rates of aerosols, and by the processes that influence the sizes of pre-existing aerosols, namely, condensation, clear and in-cloud oxidation and coagulation. The following sections describe the model’s treatment of these processes.

Section 3.2.1: *Sources of aerosols*

Sulphate aerosols are introduced directly into the domain by weak emissions at the surface, but more importantly through the oxidation of S(IV) on two fronts. The first mechanism of sulphate production is the in-cloud chemical conversion of S(IV) into S(VI) with hydrogen peroxide and ozone as oxidants. These reactions are described by von Salzen’s aqueous chemistry scheme [von Salzen et al., 2000] and are shown in Table 3.1.
Table 3.1: The reactions included in von Salzen’s aqueous S(IV) oxidation scheme

<table>
<thead>
<tr>
<th>Reaction</th>
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<tbody>
<tr>
<td>$\text{CO}_2 (g) \leftrightarrow \text{CO}_2 (aq)$</td>
</tr>
<tr>
<td>$\text{CO}_2 (aq) + \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HCO}_3^-$</td>
</tr>
<tr>
<td>$\text{SO}_2 (g) \leftrightarrow \text{SO}_2 (aq)$</td>
</tr>
<tr>
<td>$\text{SO}_2 (aq) + \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HSO}_3^-$</td>
</tr>
<tr>
<td>$\text{HSO}_3^- \leftrightarrow \text{H}^+ + \text{SO}_3^{2-}$</td>
</tr>
<tr>
<td>$\text{NH}_3 (g) \leftrightarrow \text{NH}_3 (aq)$</td>
</tr>
<tr>
<td>$\text{NH}_3 (aq) + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^-$</td>
</tr>
<tr>
<td>$\text{HNO}_3 (g) \leftrightarrow \text{HNO}_3 (aq)$</td>
</tr>
<tr>
<td>$\text{HNO}_3 (aq) \leftrightarrow \text{H}^+ + \text{NO}_3^-$</td>
</tr>
<tr>
<td>$\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$</td>
</tr>
<tr>
<td>$\text{S(IV)} + \text{H}_2\text{O}_2 (aq) \rightarrow \text{S(VI)} + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{S(IV)} + \text{O}_3 (aq) \rightarrow \text{S(VI)} + \text{O}_2 (aq)$</td>
</tr>
</tbody>
</table>

These above reactions are the basis of NARCM’s bulk approach to the oxidation of S(IV), which calculates the rate of change of the total (dissolved plus gaseous) S(IV). The bulk rate constant, $F$, given in equation (3.1), describes the in-cloud production of sulphate. The total concentration of S(IV) is represented by the variable $C_{S(IV)}$ in equation (3.1). The constants $F_1$ and $F_2$ are expressed in terms of
the appropriate rate constants and the partitioning of the reacting species between the gaseous and aqueous phases (von Salzen et al., 2000).

\[
F = \left| \frac{1}{C_{S(IV)}} \frac{dC_{S(IV)}}{dt} \right| = F_1 C_{O_3} + F_2 C_{H_2O_2} \tag{3.1}
\]

An individual constant, \( F_i \), for each bin, \( i \), can be calculated by using the bulk constant in equation (3.1) to determine the rate of mass addition to aerosols within a given bin. The individual constant, \( F_i \), is expressed in terms of \( F \) and the wet aerosol volume activated in bin \( i \) (von Salzen et al., 2000).

The background concentrations of the non-sulphur chemical species present in the reactions described in Table 3.1 are supplied by the monthly averages from the NCAR MOZART model [Brasseur et al., 1998], which are linearly interpolated to daily values and then held fixed at this prescribed daily concentration. The exception is hydrogen peroxide, the concentration of which is explicitly included in von Salzen’s parameterizations [2000]. The concentration of hydrogen peroxide, which decreases due to oxidation of S(IV), is relaxed back to its background value with a prescribed time constant of 30 min [von Salzen et al., 2000].

The other mechanism for sulphate production is the clear-sky oxidation of sulphur dioxide. This process is parameterized as a production rate that is dependant on the available concentration of \( \text{SO}_2 \) and the prescribed concentration of hydroxyl
radicals [Stockwell and Calvert, 1983]. This process is represented by the first term in equation (3.2). The rate constant $k_{SO_2}$ shown in equation (3.2) is based on the calculations of DeMore et al. [1992].

The production of $H_2SO_4$ by clear-sky oxidation is balanced by the subsequent addition of this mass to the aerosol distribution by condensation of mass onto pre-existing aerosols, or by homogenous binary nucleation of $H_2SO_4$ (g) and $H_2O$ (g) forming new sulphuric acid droplets. Equation (3.2) describes the mass balance equation for $H_2SO_4$ (g) where:

$$\frac{dC_{H_2SO_4}}{dt} = k_{SO_2} C_{OH} C_{SO_2} - C_{H_2SO_4} \sum_i k_{cond}^i - g \epsilon k_{nuc} (C_{H_2SO_4})^i$$ (3.2)

The second term on the right hand side of equation (3.2) represents the summation of the condensation rate over all size bins of the model, and the third term represents the rate of nucleation of new aerosols in the smallest size bin of the aerosol distribution. Further details of these terms can be found in von Salzen et al. [2000].

The ocean surface is a source of sea-salt aerosols within NARCM. The emission rate of sea-salt aerosols is approximated using a semi-empirical relationship [Monahan et al.1986] between the wind speed at the ocean surface and the rate of production of sea-salt aerosol of various sizes. Model results using this
relationship have been shown to give results in good agreement with observations [Gong et al., 1997].

Section 3.2.2: Coagulation

Coagulation is the process of aerosols colliding and combining to form particles of larger sizes. This process tends to be dominant for smaller aerosols whose number concentrations are much greater, which increases the probability of collisions between the aerosols. NARCM uses a semi-implicit numerical technique devised by Jacobson et al. [1994] to solve for the binary collection and coalescence of aerosols in a discretised aerosol distribution. This numerical scheme essentially solves the general coagulation equation described by Seinfeld and Pandis [1998],

$$\frac{dN_i}{dt} = \frac{1}{2} \sum_{j=1}^{m-1} K_{i,j} N_j N_{i-j} - N_i \sum_{j=1}^{m} K_{i,j} N_j$$  \hspace{1cm} (3.3)

where $N_i$ is the number concentration in bin $i$ and $m$ is the size bin of the largest aerosol. The first term on the right hand side calculates the rate of binary collisions that result in aerosols within size bin $i$. The second term is the collision rate of particles within size bin $i$ with any other aerosols, which would result in a particle larger than those of size bin $i$. The Jacobson scheme considers collisions due to four factors, namely Brownian motion, laminar shear, turbulence and gravitational settling. The coagulation coefficient $K$, which represents a probability of binary collision, depends on the mechanism responsible for the
collision. One is referred to Seinfeld and Pandis [1998] for details of the different collision mechanisms.

Section 3.2.3: Removal of aerosols

Removal of aerosol mass is accomplished by dry and wet deposition in the model. Dry deposition represents the downward diffusion of aerosols or gaseous species, which interact with the surface. The dry deposition rate of aerosols is parameterized as a function of particle size, surface drag, as well as the surface and aerosol type [Zhang et al., 2000]. An area-weighted average deposition rate is used for grid boxes whose terrain properties have subgrid variability.

The wet removal of aerosols is accomplished initially by the activation of aerosols to form cloud, which can be converted into rain through the auto-conversion and accretion of cloud droplets (rainout). The rain falling from clouds can also act to scavenge aerosols below cloud base (washout). The below-cloud scavenging is described using an approximate expression for the rain scavenging rate by Slinn [1984] and a detailed discussions on the below-cloud scavenging is given by Gong et al. [1997].
Section 3.3: *Modelling parameters and domain for this study*

The atmospheric sulphur chemistry over the coast of Nova Scotia, which is the location for NARE, can be influenced by various sources spread over Eastern North America. In order to include all of the major source terms for anthropogenic emissions, a large domain size was needed for the simulation of NARE. This domain centered at 43° N and 73° W extends in latitude from Florida to the top of Labrador and longitudinally from the mid United States to the mid Atlantic Ocean (Fig. 3.1). The anthropogenic emission rates of the SO₂ and SO₄²⁻ are supplied by the 1985 1-B GEIA inventory [Benkovitz et al., 1996] adjusted regionally to approximate the 1994 emission rates [Von Salzen et al., 2000]. As for natural emissions of H₂S and DMS, their emission rates are deduced at 1° x 1° resolution based on the surface inventories of Bates et al. [1992] and Kettle et al. [1995], respectively.

The NARCM was run for the period of August 1st to September 8th, 1993 including a spin up of 8 days before comparing to observations. The horizontal resolution was set to be 120 km at 60° N with 51 grid points in longitude and 41 grid points in latitude. 22 Gal-Chen levels were used for the description of the vertical coordinates between the surface and 14 hPa, while the dynamic time step was set to 20 minutes.
The meteorological parameters are driven by the boundary conditions that are updated every 12 hours. Additionally, the winds throughout the domain are nudged at every timestep towards the NMC/NCEP analysed wind fields [Kalnay et al., 1996] in order to improve the transport of the chemical constituents. The concentrations of these chemical constituents were constrained to be zero at the boundaries for the duration of the simulation, and were initially set to zero throughout the domain. This is a reasonable assumption due to the relatively low concentrations at the boundaries of the domain compared to those found in the major sources regions of the eastern United States.
Figure 3.1. NARCM domain used in this study.
Chapter 4

NARCM’s simulation of NARE

Section 4.1: *The use of nudged winds to improve transport*

The observations taken during the NARE study period were localized to a reasonably small area off the coast of Nova Scotia, away from the major source regions for anthropogenic aerosols in the eastern United States and Canada. The distance from the source regions of anthropogenic aerosols means that the concentrations of sulphur species at the NARE site are largely determined by the rate of advection into this region. Since the focus of this study was more to evaluate the physical and chemical processes affecting sulphur species concentrations and aerosol properties at the NARE location rather than the accuracy of transport by NARCM, the model winds were nudged using the NMC/NCEP reanalysis.

The improvement made to NARCM's wind field through nudging is shown in Fig. 4.1. The figure illustrates the differences between the simulated and analyzed 1000 hPa wind and geopotential fields for the synoptic events occurring on August 21st at 00Z using nudged and un-nudged winds in the simulation. For this period, the NCEP reanalysis geopotential and wind fields show a surface trough extending well into the mid-Atlantic coast from northern Labrador. This system was associated with an event of significant westerly transport of ozone into the
NARE region [Merrill and Moody, 1996]. This sharp increase in westerly flow in the NARE region can be seen clearly by the transitions between the NCEP reanalysis wind fields from 00Z on Aug 20\textsuperscript{th} to 00Z on August 21\textsuperscript{st} (figure 4.1a, and b respectively). The simulated 1000 hPa wind fields are better correlated with the NCEP reanalysis (figure 4.1b) when nudged (figure 4.1d) than those when not nudged (figure 4.1c). For example, the winds and geopotential heights in the simulation that was not nudged did not accurately reproduce the depth of the trough or the winds speeds and directions associated with this system.

Section 4.2: \textit{The meteorological performance of NARCM}

On average the 1000 hPa, 850 hPa, and 700 hPa geopotential height and wind fields simulated by NARCM for the period of August 9\textsuperscript{th} to September 8\textsuperscript{th}, 1993 using nudged winds (Figure 4.2 a, b, c) compare well to mean conditions from the NMC/NCEP reanalysis (Figure 4.2 d, e, and f). The largest differences can be seen at 1000 hPa where the simulated and observed geopotential heights differ and a slightly more cyclonic flow has developed south of Newfoundland in the simulated wind fields. At higher levels, the pattern of geopotential heights improve and errors in simulated wind fields can only be seen as a small shift southward in the westerly jet over Nova Scotia. It is expected that these errors in these mean conditions will not greatly affect the average concentrations of aerosols predicted by NARCM for this period.
Figure 4.3 shows the poor agreement of simulated 1000 hPa, 850 hPa and 700 hPa (Fig. 4.3 a-c) mean relative humidity fields for the NARE period against those of the NMC/NCEP reanalysis (Fig. 4.3 d-f). The differences in the mean relative humidity are most prominent near the surface where 70-80% errors can be seen over the eastern United States. Large errors of 25-40% are still persistent above the boundary layer. The under-prediction of the average relative humidity during this simulation cannot be explained by differences in the temperature fields between the simulation and NCEP reanalysis (compare Figure 4.4 a, and b). Rather, the poor agreement of the relative humidity fields over the continent indicates a likely problem with the water budget for our simulation.

It was concluded upon further investigation that the initialized soil moisture field at the onset of the simulation was inappropriate. In this simulation (now referred to as INIT_SOIL), the soil moisture field was set by default to an estimated climatological mean for January that was used to initialise the GCM model for long simulations. Another consequence of the low initial soil moisture is the under-prediction of the average precipitation amount over much of Eastern North America when compared to the mean precipitation from the NCEP reanalysis for the NARE period (Figure 4.5 a, and c). It should be noted that the lower density of observing stations over the ocean and Canada results in less reliable precipitation data from the NCEP reanalysis in these regions.
Section 4.3: *Adjustment of initial soil moisture*

In order to improve the atmospheric water budget seen in the INIT_SOIL run, a new model run with artificially increased soil moisture was initiated. The new run (hereafter called MOIST SOIL) will be used to test the sensitivity of the sulphur budgets and aerosol size distributions to an increase in atmospheric relative humidity. The soil moisture initially for the MOIST_SOIL run was set to 100% throughout the domain, allowing the CLASS land surface scheme to adjust to the maximum value for each soil type (i.e. the porosity of soil filled to capacity with water) after the first time step. The resulting difference between the average moisture fields for the period of August 9\textsuperscript{th} to September 8\textsuperscript{th} in the INIT_SOIL run and MOIST_SOIL run for the three soil levels can be seen in Figure 4.6.

The atmospheric water budget for the NARE period was improved with the increase in soil moisture between the two runs. Figure 4.7 (a-f) shows the average relative humidity fields from the MOIST_SOIL run are now in better agreement with the NCEP fields. Although the 1000 hPa relative humidity is now higher in general than that of the NCEP reanalysis especially over the Western United States, the relative humidity fields at 850 hPa are much closer to those observed. The values at 700 hPa for the MOIST_SOIL run are still too dry, but they have improved compared to those in the INIT_SOIL run.
The pattern and intensity of precipitation has also improved in the MOIST_SOIL run (Fig. 4.5 b, and c). For example, the precipitation rates over the north-eastern United States are higher and they extend into the Canadian Atlantic provinces in a similar manner as shown in the NCEP reanalysis. The regions where the simulated precipitation is most improved in the MOIST_SOIL run seem to be those where the relative humidity had the worst agreement in the INIT_SOIL run. Some precipitation feature, such as the high precipitations rates over Florida still have not been simulated with the increase in soil moisture and these errors may be due to the proximity of the domain edge. Furthermore, the average column integrated liquid water content has increased between the MOIST_SOIL and INIT_SOIL runs (Fig. 4.8 a and b). A difference field between the MOIST_SOIL and the INIT_SOIL fields shows that the cloud amount over the mid-eastern United States through to south-eastern Canada also showed a significant increase in the second simulation.

In the following sections, the result from the MOIST_SOIL run will used to evaluate the model performance in simulating the sulphur species concentrations and aerosol distributions measured at the NARE site. The differences between the INIT_SOIL run and MOIST_SOIL run will be used to assess the sensitivity of sulphur species concentrations to a change in ambient meteorological conditions and how the modification of the sulphur budget consequently affects the aerosol distributions predicted by NARCM.
Section 4.4: *Spatial distribution of sulphur species concentration and influencing factors on the sulphur budget.*

The effect of changing the initial soil moisture had the ramification of modifying the sulphur species concentration throughout the domain and hence also at the NARE site. An assessment of these changes will be presented in this section and sulphur budget over a limited domain will be used to ascertain what physical processes were responsible for these changes. This will set the stage for the assessment of these fields with the observations taken over Nova Scotia during the North Atlantic Regional Experiment.

The mean column integrated sulphur dioxide and sulphate concentrations of the NARE period simulated by NARCM are shown in Fig. 4.9 for the INIT_SOIL run (a and d, respectfully) and MOIST_SOIL run (b and e, respectfully). The difference fields between the INIT_SOIL run and the MOIST_SOIL run quantify the considerable decreases in the column-integrated concentrations of sulphur species in the MOIST_SOIL run. In order to investigate the physical process responsible for the differences in the column burdens seen in Fig. 4.9, the production, removal and transport rates over a limited domain (Fig. 4.10) of sulphur dioxide (Fig. 4.11) and sulphate (Fig. 4.12) are described for both the INIT_SOIL and the MOIST_SOIL runs. These figures show the balance of sources and sinks of sulphur species concentrations, which determine the
tendencies of their average concentrations over this domain in time. The most notable differences seen in these figures is the increased role taken by in-cloud production in the oxidation of sulphur dioxide, the significant increase in the wet removal of sulphate, and a reduction in the clear sky oxidation rate in the MOIST_SOIL run. An additional note is that the time series of in-cloud production, wet removal, and net horizontal transport are more correlated with one another in the MOIST_SOIL run.

A direct impact of the soil moisture on the aerosol distribution simulated by NARCM can be seen in the nucleation rates of aerosols. The reduction of clear air oxidation in the MOIST_SOIL means that less H₂SO₄ (g) is available to be depleted by the nucleation of new sulphate particles or by the condensation onto pre-existing aerosols. However the reduction in availability of H₂SO₄ in the MOIST_SOIL run coincided actually with a rather large increase in the nucleation rates in the source regions for anthropogenic sulphate aerosols (Figure 4.13).

Section 4.5: Independent evaluation of PCASP counts as surrogate for sulphate mass.

As mentioned in Chapter 2, a fourth degree polynomial fit of the average PCASP counts in the size range of 0.31 \(\mu\text{m}\) to 0.40 \(\mu\text{m}\) in diameter have been used as a surrogate for mass concentration of SO₄ along the Twin Otter flight trajectories [Lohmann, 2001]. Figure 4.14 shows the comparison of the mass concentrations
of sulphate predicted by the application of this polynomial fit to the counts in the seventh channel of the PCASP counter averaged over the time period of the exposure of teflon filters with the mass concentrations measured by ion chromatography of the corresponding Teflon filters.

The filters used in the development of the fourth degree polynomial fit have been differentiated on this figure so as to demonstrate the consistency of this relationship for cases beyond the conditions used for its development. Unfortunately, the concentrations measured by the filters exposed when the winds were from a northerly direction (which were omitted in the original fitting process) do not extend over the full range of sulphate measurement observed by all the filters. Therefore the empirical relationship cannot be verified with independent data over its full range of values. All that can be said is that the filters exposed when the winds were northerly show a similar scatter to the other filters and hence do not contradict this empirical relationship.

Section 4.6: *Methodology for calculating clear sky vertical profiles*

The relationship that was used to deduce sulphate concentrations from the PCASP measurements was inferred from measurements in clear skies. Therefore, comparisons of model sulphate concentrations and aerosol size distributions in the following sections are only made with observations in cloud-free conditions. The removal of the cloudy data from the NARE data set was accomplished in two
steps. The first was to exclude all measurements made when the PMS FSSP-100 counter showed droplet concentrations larger than 5 cm$^{-3}$ within the size range of 2 $\mu$m to 35 $\mu$m in diameter. Any droplet concentrations above this limit are assumed not to occur outside clouds. Secondly, if the liquid water content measured using the PMS King hot wire probe was greater than zero within a corresponding model grid box, the grid box was excluded and not used for comparisons of simulated and observed chemical concentrations. This method is certainly an overly conservative approach for selecting clear sky pixels.

After this filtering process, the average clear-sky vertical profiles of concentrations from individual flights and for the entire NARE period can be obtained by averaging all observations within height intervals that correspond to the pressure levels of the NARCM model. The trace gas concentrations below the detection limit of the particular measurement devices were not set to zero for the averaging process and if the resulting average for a grid box was negative, it was then adjusted to be zero. The corresponding simulated vertical profiles that will be evaluated in the upcoming sections are generated in following manner. The model values are linear interpolated in height to correspond to the average flight altitude in each sampled grid box and then are horizontally averaged, based on how many clear-sky observations were made within them.
Section 4.7: Comparison of prescribed oxidant concentrations

As a precursor to the comparison of modelled and observed concentrations of sulphur species for the NARE period, the following section will highlight any bias present between the prescribed background concentrations of oxidants used in sulphur chemistry of NARCM described in Chapter 3 and the observed values measured by Twin Otter aircraft during NARE. The concentrations of hydrogen peroxide and ozone were not significantly altered between the INIT_SOIL run and MOIST_SOIL run. For this reason, the following discussion will only show the results from the INIT_SOIL run.

The Figure 4.15a shows that the average prescribed background ozone concentration predicted by NARCM was less than the average observed value obtained by in-situ flight measurements. The model ozone concentrations near the surface are reasonably well reproduced compared to the consistent differences of about 8 ppbv present above 1 km. The high acidity of the cloud water in the NARE region makes hydrogen peroxide the more influential oxidant for in-cloud sulphur chemistry [Lohmann et al., 2001]. Therefore, the errors in the ozone concentrations will have less impact on the oxidation rates than those of hydrogen peroxide.
NARCM's average hydrogen peroxide profile for the NARE period (Fig. 4.15b) shows reasonable agreement with observed concentrations. The concentration of hydrogen peroxide on average near the surface was under-predicted by about 0.5 ppbv. This bias decreases with height till about 1 km and then reverses so that above 2 km the NARCM is over-predicting the flight's concentration of hydrogen peroxide by approximately 0.5 ppbv.

Section 4.8:  *Comparison of the observed and modelled profiles of sulphur species concentration during the NARE study:*

In this section, the average sulphur species concentrations throughout the NARCM domain presented in section 4.4 are now evaluated through comparisons with in-situ observations taken during the North Atlantic Regional Experiment. For clear sky conditions, the average sulphur dioxide, sulphate, and total sulphur concentrations measured during NARE were calculated and compared in height to the corresponding modelled values from the INIT_SOIL and the MOIST_SOIL runs (figure 4.16 a, b and, figure 4.17 a). Figures 4.16 a, b, and 4.17 a show that the concentrations of sulphur dioxide, sulphate, and total sulphur are in much better agreement with the in-situ observations for the MOIST_SOIL run. In the INIT_SOIL run both the sulphur dioxide and sulphate profiles were overestimated, on average by at least factors of 2 at all heights. In the MOIST_SOIL run a clear improvement, both in the shape of the sulphur species profiles and in the average column burden can be seen. The most notable
improvement in the MOIST_SOIL was associated with the modelled sulphur dioxide profile. The errors in the sulphur dioxide concentration are now reduced to the order of 50% or less. A much better agreement in the modelled sulphate concentration above 1.5 kilometers is also seen in the MOIST_SOIL run.

Figure 4.17b shows fraction of sulphur that is in the form of sulphur dioxide. The fraction at the highest level is connected with a dashed line, because the low concentration of total sulphur makes this result unreliable. The best agreement in the relative composition of sulphur is seen in both runs near the surface. The MOIST_SOIL run has a higher a percentage of sulphate than the INIT_SOIL at all heights. The translates as a better agreement with the observed sulphur ratios in the MOIST_SOIL run for heights away from the surface. The consistency in the modelled sulphur fraction for both runs is attributed to the similar shape between the predicted profiles of sulphur dioxide and sulphate.

The progress made in simulating the sulphur species profiles between INIT_SOIL and MOIST_SOIL was not just limited to simulating mean conditions that were more consistent with the observations of the NARE period. The improvement realized in the MOIST_SOIL was the result of a consistent reduction of errors in the simulated sulphur dioxide, and in part, sulphate column burdens for nearly all of the individual flights. This is shown in Figure 4.18 (a, b, and c) which has the column integrated concentration of sulphur dioxide, sulphate and, total sulphur (respectively) plotted in a time series for all the flights. It should be noted that
some of the flight-to-flight variability in column-integrated values is due to different ranges of sampling heights for different flights and due to the removal of cloudy grid boxes from this comparison. It can be seen from these figures that simulated sulphur species concentrations of the MOIST_SOIL run are much better correlated with the observations than the INIT_SOIL.

The observed and simulated column burdens of the average sulphur species below 5 km averaged over all flights are presented in Table 4.1. The average column burdens produced by the MOIST_SOIL run are in better agreement with the NARE data. The MOIST_SOIL column burdens of sulphur dioxide, sulphate and total sulphur show percentage difference from observations of 57%, 28%, and 37% respectively.

**Table 4.1.** Observed and simulated column burdens below 5 km at NARE site (µg m⁻² of S).

<table>
<thead>
<tr>
<th></th>
<th>SO₂</th>
<th>SO₄⁻</th>
<th>SO₂ + SO₄⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>NARE</td>
<td>1645</td>
<td>3740</td>
<td>5385</td>
</tr>
<tr>
<td>INIT_SOIL</td>
<td>7867</td>
<td>6550</td>
<td>14417</td>
</tr>
<tr>
<td>MOIST_SOIL</td>
<td>2590</td>
<td>4790</td>
<td>7380</td>
</tr>
</tbody>
</table>

The performance of NARCM in predicting the column burdens of sulphur species concentrations for both runs are also compared in Table 4.2 to the column burdens reported for the simulations for the COSAM study of the NARE period discussed...
in chapter 2. It is important to note that the column burdens of the NARE measurements calculated in this study differ from those present in COSAM by approximately 25%. These differences are attributed to the exclusion of more data in the filtering of clear and cloudy conditions and due to the differences in which height is assigned to represent the average value of a grid box. In this study, the average value within a grid box was assumed to be representative of time-averaged altitude at which the plane was flying within a particular grid box. While in the COSAM study, the average value was assigned to the pressure center of the particular grid box. In order for this bias not to interfere with a comparison of the models used in the COSAM paper, the performance of those models should only be compared to NARE column burdens from the COSAM study and not to the NARE column burdens obtained in this study.
Table 4.2. Column burdens below 3.8 km from this study in comparison to those simulated by 10 models in the COSAM study (µg m⁻² of S)

<table>
<thead>
<tr>
<th>Model Name</th>
<th>SO₂</th>
<th>SO₄⁻</th>
<th>SO₂ + SO₄⁻</th>
<th>SO₂/(SO₂ + SO₄⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NARE (obs from this study)</td>
<td>1602</td>
<td>3593</td>
<td>5195</td>
<td>0.31</td>
</tr>
<tr>
<td>NARCM (INIT_SOIL)</td>
<td>6230</td>
<td>7330</td>
<td>1356</td>
<td>0.46</td>
</tr>
<tr>
<td>NARCM (MOIST_SOIL)</td>
<td>2550</td>
<td>4700</td>
<td>7250</td>
<td>0.32</td>
</tr>
<tr>
<td>NARE (obs. From COSAM)</td>
<td>1110-</td>
<td>3005-</td>
<td>4130-4255</td>
<td>0.27-0.29</td>
</tr>
<tr>
<td>GISS</td>
<td>830</td>
<td>2530</td>
<td>3360</td>
<td>0.25</td>
</tr>
<tr>
<td>ECHAM4-UU</td>
<td>780</td>
<td>3390</td>
<td>4170</td>
<td>0.19</td>
</tr>
<tr>
<td>CCCma</td>
<td>2700</td>
<td>5830</td>
<td>8530</td>
<td>0.32</td>
</tr>
<tr>
<td>ECHAM4-MPI</td>
<td>2850</td>
<td>6050</td>
<td>8900</td>
<td>0.32</td>
</tr>
<tr>
<td>TOMCAT</td>
<td>3920</td>
<td>5770</td>
<td>9690</td>
<td>0.40</td>
</tr>
<tr>
<td>KNMI/IMAU</td>
<td>1380</td>
<td>4340</td>
<td>5720</td>
<td>0.24</td>
</tr>
<tr>
<td>IMPACT</td>
<td>1820</td>
<td>4270</td>
<td>6090</td>
<td>0.30</td>
</tr>
<tr>
<td>GOCART</td>
<td>1930</td>
<td>1460</td>
<td>3390</td>
<td>0.57</td>
</tr>
<tr>
<td>NCAR</td>
<td>170</td>
<td>1370</td>
<td>1540</td>
<td>0.11</td>
</tr>
<tr>
<td>DEHM</td>
<td>1840</td>
<td>2350</td>
<td>4190</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Table 4.2 shows the INIT_SOIL had a much worse column burden for the NARE period than models that participated in the COSAM study. However, the MOIST_SOIL run ranked quite well at reproducing the mean sulphur burden and sulphur dioxide ratios below an altitude of 3.8 kilometers.
Section 4.9: A comparison of mean aerosol size and volume distributions and their variability in height.

The sensitivity study of our results to an increase in initial soil moisture has so far shown a quite substantial improvement in sulphur species concentrations with the higher initial soil moisture. Figure 4.19 describes the sensitivity of the simulated average aerosol size and volume distributions over the NARE period to the increased soil moisture. The aerosol mass in both the INIT_SOIL and the MOIST_SOIL runs is concentrated at lower sizes than the average values seen in the Twin Otter flights. This can be seen in Figure 4.19a, where there is a strong indication of much higher concentrations of small particles than actually exist, and in the much smaller size of the simulated accumulation mode (0.1 \( \mu m \) diameter) compared to the observed mode (0.25 \( \mu m \) diameter).

Over the actual size range of aerosols measured by the PCASP counter, the vertical profile of total aerosol number concentration for both simulations seems to be in the right order of magnitude (figure 4.20a). The aerosol number concentrations for the MOIST_SOIL run exhibit errors of less than 50% over the observed height range and are on average closer to the observed aerosol number vertical profile than those from the INIT_SOIL run. Nevertheless, the aerosols simulated in both runs were on average too small (Figure 4.20 b and c) compared to those observed. The aerosol mean volume diameters \( (D_v) \) (equation 4.1) simulated within the size range 0.125 \( \mu m \) to 3.0 \( \mu m \) were under-predicted in both
runs on average by 18% to 32%, with an exception in the upper levels of the MOIST_SOIL run where the bias is less than 10%.

\[ D_v = \left( \frac{6}{\pi} \left[ V(D) dD \right] \right)^{\frac{1}{3}} \]  

(4.1)

Where \( V(D) \) and \( N(D) \) are the volume and number of aerosols of a given diameter \( D \) within a sample of air, respectively. Figure 4.19b shows however that it is only the tail of the modelled average aerosol volume distribution that overlaps with the observed size range of the PCASP counter. This means that the comparisons made over the limited size range above are not representative of the majority of the aerosol mass simulated by NARCM for both the INIT_SOIL and MOIST_SOIL runs.

In order to compare the observations to the aerosol volume distribution simulated by NARCM over a larger size range, the observed aerosol size distribution is extrapolated to sizes below the detection limit of the PCASP. The aerosol number distribution was extended by a linear extrapolation in figure 4.19a of the best-fit line through concentrations in size bins 2 through 8. As a measure of the sensitivity of this procedure, lines with double and half the slope are also shown. The corresponding extrapolated volume distributions are shown in figure 4.19b. The conclusion is that for the range of extrapolations considered, the contribution of small aerosol particles to the actual volume distribution is very small. The mean diameter of the volume distribution \( \langle D^* \rangle \) (equation 4.2) is calculated under
the assumption that the volume of aerosols with sizes above the PCASP detection limit is zero.

\[ D_v = \left( \frac{\left[ (D \times V(D))dD \right]}{\int V(D)dD} \right)^{\frac{1}{3}} \]  

(4.2)

Where \( V(D) \) is the volume of aerosols within a given sample of air. The advantage of describing the aerosol volume distributions by using \( D^* \) instead of by the mean volume diameter \( D_v \) is that \( D^* \) is much less sensitive to the number of small aerosols deduced from the extrapolation of the aerosol size distribution below the detection limit of the PCASP. The sensitivity in \( D^* \) for a particular flight and height level to a doubling or to a reduction of 50% in the slope used for the extrapolation was on average about \( \pm 3\% \).

Section 4.10: *Trends in the mean diameter of the modelled and observed aerosol volume distributions.*

The greatest perturbation to the average sulphate concentration caused by the increased soil moisture occurred at heights above one kilometer. Above this height sea-salt aerosols are found in lower concentration and hence have a diminished effect on determining the mean diameter of the aerosol volume distribution (\( D^* \)). Furthermore, above this level the assumption that there is negligible aerosol mass at sizes greater than the detection range of the PCASP counter (greater than 3.0 \( \mu m \)) is more valid. Comparison of figure 4.21a and 4.19a shows reduced concentration of aerosols with sizes greater than 0.5 \( \mu m \) at
altitudes above 1 kilometer. The average aerosol volume distribution for heights above 1 km presented in Figure 4.21a shows the discussed reduction in aerosol concentration for sizes greater than 0.5 μm. The mean of the aerosol volume distribution (D*) above 1km is primarily determined by the distribution of sulphate aerosols in the NARCM simulation. The sea-salt in the modelled distributions above 1 km only contributes significantly to the position of the mean when the concentrations of sulphate are small.

For model vertical levels above 1 kilometer, the means of the simulated aerosol volume distributions (D*) for each flight during NARE can be seen to increase in a manner similar to the trend of the observed D* as a function of the sulphate volume present in the distribution (Figure 4.21 b, and c). In the INIT_SOIL run, a clear bias between the modelled and observed D* is present over all volumes of sulphate. There was more scatter in the means from the MOIST_SOIL run, but these results still have a trend with sulphate amount that is similar to that from the INIT_SOIL run. However, it is clear that in some cases the MOIST_SOIL run produced values of D* larger than those seen in the INIT_SOIL run. Presumably, the increased in-cloud production of sulphate has increased the aerosol sizes. However, D* tends to be still significantly under-predicted for all sulphate volumes, and errors are largest when the sulphate volume is low (Figure 4.19).

From the total aerosol volume and the volume of sulphate, the fraction of non-sulphate can be obtained as a function of sulphate amount (figure 4.22). Since the
aerosols are assumed to be internally mixed, this relationship (deduced from observations) can be used to estimate the missing volume due to non-sulphate in the simulated aerosol volume distribution and then to estimate the increase in $D^*$ that could be expected if non-sulphate species were included. In fact, from the additional volume and the aerosol concentration the quantity that is obtained is the change in $D_v$ not the change in $D^*$.

\[ D_{v, \text{scaled}} = D_v \times \left( \frac{V_t}{V_s} \right)^{\frac{1}{3}} = D_v \times \left( \frac{1}{1 - a V_s - b} \right)^{\frac{1}{3}} \]  

(4.3)

Where $D_{v, \text{scaled}}$ and $D_v$ are the final and initial mean volume diameters respectively. The total aerosol volume ($V_t$) estimated applying the correction factor from the flights, and the volume of sulphate ($V_s$) present within a simulated distribution determine the strength of the correction factor. The symbols $a$ and $b$ represent the slope and intercept respectively of the fit parameter presented in figure 4.22 for three different size ranges of sulphate volume.

The change in $D^*$ will depend on the details of how the non-sulphate mass is distributed over the sulphate size distribution. To first order we assume that the change in $D^*$ is also given by equation 4.1. Figure 4.23 shows that the adjusted values of $D^*$ increased considerably at low sulphate volumes where the percentage of non-sulphate is highest. There is now considerable overlap between the simulated and observed values of $D^*$ when the sulphate concentration are low.
However, the adjustment of $D^*$ for the absence of non-sulphate species rapidly became ineffective as the sulphate volume increase and $D^*$ for sulphate concentrations above approximately 3 or 4 $\mu m^3cm^{-3}$ remains unchanged.

Obviously a better test of how the mean of the distribution will react to the addition of other aerosol species in NARCM is to add these aerosol species as prognostic variables within NARCM rather than from the coarse estimate of their effect in a post-processing analysis. These new simulations would also account for impacts of changes in microphysical and chemical processes (that depend on the aerosol sizes and composition) on the aerosol size distribution.
Figure 4.1. NCEP analysis of 1000 hPa height and wind field (a) on August 20th at 00Z and b) on August 21st at 00Z, and simulated fields on August 21st at 00Z using (c) un-nudged and (d) nudged winds.
Figure 4.2. Comparison of average simulated (left column) and observed (right column) geopotential height (in m) and wind (in m s\(^{-1}\)) fields for August 9 to September 8 1993. Figures (a) and (d) are at 1000 hPa, (b) and (e) at 850 hPa, (c) and (f) at 700 hPa.
Figure 4.3. Comparison of average simulated (left column) and observed (right column) relative humidity fields (in %) from August 9 to September 8 1993. Figures (a) and (d) are at 1000 hPa, (b) and (e) at 850 hPa, (c) and (f) at 700 hPa.
Figure 4.4. Comparison average 1000 hPa temperatures (K) fields (a) simulated by NARCM and (b) the observed fields from the NCEP reanalysis for the period of August 9th to September 8th, 1993.
Figure 4.5. Comparison of the average precipitation (in mm/day) for the period of August 9th to September 8th, 1993 simulated by (a) the INIT_SOIL run, and (b) the MOIST_SOIL run to (c) the observed average precipitation for this period by NCEP reanalysis.
Figure 4.6. Comparison of INIT_SOIL (left column) and MOIST_SOIL (right column) average soil moisture fields (in % by volume) for the period of August 9 to September 8 1993. Figures (a) and (d) are at a depth of 0 to 1 meter, (b) and (e) at 1 to 35 meters, (c) and (f) at 35 to 410 meters.
Figure 4.7. Comparison of average MOIST_SOIL (left column) and the NCEP reanalysis (left column) relative humidity fields (in %) from August 9th to September 8th, 1993. Figures (a) and (d) are at 1000 hPa, (b) and (e) at 850 hPa, (c) and (f) at 700 hPa.
Figure 4.8. Comparison of the average vertically integrated liquid water content (kg/m²) from August 9th to September 8th, 1993 from (a) the INIT_SOIL and (b) the MOIST_SOIL field. Figure (c) is the difference field of INIT_SOIL field subtracted from MOIST_SOIL field, the hatched zones indicates negative values.
Figure 4.9. Comparison of average vertically integrated SO$_2$ (left column) and SO$_4$ (right) amount (mg m$^{-2}$) for the period of August 9$^{th}$ to September 8$^{th}$, 1993. The top row is results from INIT_SOIL, the middle row is the simulated values for MOIST_SOIL run. The bottom row shows the difference fields of INIT_SOIL minus MOIST_SOIL results.
Figure 4.10. Selected domain used for sulphur budget calculations.
Figure 4.11. Sulphur dioxide budgets for the INIT_SOIL run (top) and MOIST_SOIL run (bottom) for the period of August 9th to September 8th, 1993.
Figure 4.12. Sulphate budgets for the INIT_SOIL run (top) and the MOIST_SOIL run (bottom).
Figure 4.13. Comparison of MOIST_SOIL and INIT_SOIL vertically integrated nucleation of sulphate (microgram hour$^{-1}$) from August 9 to September 8 1993. Figure (a) is the INIT_SOIL field, MOIST_SOIL field is represented in figure (b). Figure (c) is the difference field of INIT_SOIL field subtracted from MOIST_SOIL field, the hatched zones indicates negative values.
Figure 4.14. Correlation of sulphate concentration predicted by empirical relationship for the filters exposure times against the measured values by the filters. The data points that are filled are those used in the development of the empirical relationship and the other represent the values during the exposure of the remaining filters. The linear regression shown is the best fit through the filled data points and is constrained to pass through the origin.
Figure 4.15. The vertical profiles of modelled and observed ozone (top) and hydrogen peroxide (bottom).
Figure 4.16. The average vertical profiles of sulphur dioxide (top) and sulphate (bottom) for the period of August 9th to September 8th.
Figure 4.17. The average vertical profiles of total sulphur (top) and ratio of sulphur in the form of sulphur dioxide (bottom) for the period of August 9th to September 8th. The observed ratio is marked by a dashed line at the highest level (where low concentrations of total sulphur make the results unreliable).
Figure 4.18. The timelines of the column integrated sulphur dioxide (top), sulphate (middle) and total sulphur (bottom).
Figure 4.19. The aerosol size (top) and volume distributions (bottom) averaged for the period of August 9th to September 8th. The flight observations extrapolated below the detection limit of the PCASP-100X counter are marked with a thin line and hollowed squares. The two thin lines adjacent to this extrapolation line represent the values if the extrapolation slope used was doubled or halved.
Figure 4.20. The average vertical profiles of aerosol number concentration (top), mean aerosol diameter (middle) and volumetric mean diameter (bottom) for the observations size range of 0.125 to 3.0 micrograms.
Figure 4.21. The average aerosol volume distributions above 1 km (top) and the variability of the mean diameter ($D^*$) for all aerosol volume distributions measured above 1 km during NARE with the volume of sulphate present within that distribution for (b) the INIT_SOIL run, and (c) the MOIST_SOIL run.
Figure 4.22. The percentage of the volume of the observed aerosol volume above 1 km taken up by species other than sulphate plotted against the volume of sulphate present within the aerosols. The negative values in the percentage of non-sulphate are most likely associated with the uncertainty of the sulphate concentration produced by the empirical relationship. Three linear regression lines were used to fit the data over the ranges of sulphate volume 0 to 0.2, 0.2 to 4, and greater than 4 respectively.
Figure 4.23. The mean diameters of the modelled aerosol volume distributions (D*) above 1 km of the MOIST_SOIL run weighted to larger sizes using a scaling factor based on the difference in aerosol composition between the flight observations and simulated distributions.
Chapter 5

Discussion and Conclusions

The sulphur species concentrations simulated in the MOIST_SOIL run compared reasonably well on average with the observed values taken during the NARE study. The average column burdens of sulphur dioxide and sulphate differed from the observations by approximately 57% and 28% respectively and compared favourably against the results of the eleven models used in the COSAM study. With the exception of a few flights, NARCM demonstrated skill in simulating the column burdens of sulphur species throughout the NARE period. Furthermore, the simulated fraction of sulphur in the form of sulphur dioxide based in the above column burdens compared well with observations. The average vertical distribution of both the SO$_2$ and the SO$_4$ concentrations predicted in the MOIST_SOIL run peaked around 600 meters in height and then decayed with height. This resulted in the uniformity of the simulated fraction of sulphur in the form of sulphur dioxide as a function of height compared to the observed fraction whose average sulphur dioxide and sulphate profiles peak at different heights.

Aerosol size distributions in this study were not modelled as well as the sulphur species concentrations. The predicted aerosol size distributions contained an excessive number of small particles, which led to an underestimation of the location of the accumulation mode in the aerosol size spectrum. In fact, only the tail of the average simulated aerosol distribution overlapped with the size range of
aerosols measured using the PMS PCASP-100X counter (0.125 \( \mu m \) to 3.0 \( \mu m \)). Although this led to predictions of the mean volume diameters for this size range that were on average only 10% to 35% smaller than the observed values, these comparisons are considered to be unrepresentative of the errors in NARCM’s modelling of the aerosol volume distribution during NARE due to small overlap of the total distributions. To account for this, the observed aerosol size distribution was extrapolated to sizes below the detection limit of the PCASP counter and the mean diameter \( (D^*) \) of the volume distribution over the full aerosol size range modelled by NARCM (0.01 \( \mu m \) to 40.96 \( \mu m \) in diameter) was calculated. A sensitivity study showed that this estimated value of \( D^* \) from the observations was insensitive to the choice of the slope used for the linear extrapolation. Nevertheless, a degree of uncertainty still remains due to the absence of measurements of the small particles.

The values of \( D^* \) for distributions at altitudes above 1 km simulated by NARCM in the MOIST_SOIL run were for substantially smaller than the observed values. However, they did show a similar tendency to increase as a function of sulphate volume as the observations. A rough estimate used to account for the absence of missing non-sulphate aerosol species demonstrated that the large difference in \( D^* \) at low sulphate volume may have been due to the absence of other species in the model. However, there was no indication that the absence of other species could account for the differences seen in the aerosol volume distribution at sulphate volumes above 3 or 4 \( \mu m^3 cm^{-3} \). However, since the addition of these missing
aerosol species may significantly modify the aerosol processes, which in turn modify the aerosol size distribution, before the aerosol reaches the NARE site, we cannot infer their full effect on the values of $D^*$ without including them explicitly as prognostic variables within NARCM. The under-prediction of $D^*$ may possibly be due to the production of too many small particles through emission and nucleation or to the lack of coagulation. Any of these would mean that the sulphate mass added to a distribution would be spread over too many particles so that each particle would grow by a smaller amount. The likelihood that nucleation rates are the problem is small since the nucleation rates in the source region were dramatically increased on average in the MOIST_SOIL run compared to the INIT_SOIL run and yet the aerosol size distributions were more responsive to the addition of sulphate in the MOIST_SOIL run.

The simulation of the meteorology in this study is a major source of uncertainty in the above results. The improper initialisation of soil moisture at the onset of the simulation of the NARE period in the INIT_SOIL run has enabled us to investigate the impacts of a change in the atmospheric water budget on the predicted sulphur species concentrations and aerosol distributions at the NARE site. The modification of the relative humidity, column integrated liquid water content and precipitation fields associated with the increased soil moisture in the MOIST_SOIL run had profound consequences on the sulphur budget in the modelled domain. The overall oxidation rates, for example, rose due to the increase in importance of the in-cloud oxidation of sulphur dioxide. This increase
resulted in improved skill at forecasting the column burdens of sulphur dioxide in the MOIST_SOIL run. Additionally, a large increase in the wet deposition rate of sulphate also resulted in a marked improvement in the total sulphur burdens throughout the NARE period.

Although there were the substantial changes in the sulphur budget in response to the increased soil moisture, the effect on the shape of the simulated aerosol distribution was small. The values of $D^*$ were generally slightly larger in the MOIST_SOIL run, but the values of $D^*$ were still too small. The increase in the values of $D^*$ is attributed to an increase in in-cloud oxidation as a pathway for sulphate production.

The sensitivity of aerosol processes to the water budget in NARCM is a concerning limitation for this study and for future evaluations of the model. Although improved in the MOIST_SOIL run, the relative humidity and precipitation fields are still far from exact. Moreover, it is very difficult to verify the total cloud amount within the NARCM domain throughout the NARE period. It is also difficult to determine how the remaining errors in the water budget will impact the simulated sulphur species profiles and aerosol distributions at the NARE site. Another concern in this study is the accuracy of the empirical relationship that is used to estimate the sulphate concentrations from the particle concentrations in the seventh channel of the PCASP-100X. Although these errors
are probably reasonably small on average throughout the period, the error in the estimated sulphate amount for particular flights might be very significant.

In terms of future work for this study and for the NARCM project, it would be beneficial to obtain a better general understanding on how the limitations in simulating the atmospheric water budget can create uncertainties in the modelled sulphur concentrations and aerosol distributions. This could be investigated in selected case studies where the model's performance at simulating sulphur species column burdens at the NARE site was poor. Additionally, a better representation of the aerosol processes and of the sulphur budgets might be obtained by using increased spatial resolution over at least a part of the domain used for this study. Additional data set such as the Clean Air Status and Trends Network (CASTNet) and the Canadian Air and Precipitation Monitoring Network (CAPMoN) should be used in conjunction with the NARE data set to evaluate the predicted surface sulphate concentrations and wet deposition rates of sulphate that occur between the source regions of anthropogenic aerosols and Nova Scotia. An integration of a version of NARCM including non-sulphate aerosol species as prognostic variables for the NARE period will permit an evaluation of the importance of other aerosols such as organic aerosols relative to sulphate and sea-salt at sites downwind from major anthropogenic sources.
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