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The effect of sub-grid scale clouds on sulphate production

A thesis submitted to the Faculty of Graduate Studies ad Research in partial fulfillment of the requirements of the degree of Masters of Science.

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Abstract

Clouds and aerosols impact on climate, both independently and through their interaction with one another. Thus, in climate models, it is important to make cloud schemes and in-cloud chemistry as realistic as possible. To this end, the UQÀM sub-grid scale cloud scheme was added to LCM11, a one-dimensional version of the Northern Aerosol Regional Climate Model (NARCM). The goal of this project is to assess whether it is necessary to complete parameterization of sub-grid scale processes in LCM11 by implementing sub-grid scale parcel chemistry.

Parallel runs of LCM11 with and without parcel chemistry were performed under various chemical scenarios. The production of sulphate, the main anthropogenic constituent of tropospheric aerosols, was compared within parallel runs. Sulphate production was not significantly changed by the implementation of parcel chemistry. Thus, for the scenarios assayed in this project, the addition of sub-grid scale parcel chemistry to LCM11 is deemed unnecessary.

Résumé

Les nuages et les aérosols, ensemble ou indépendamment l'un de l'autre, ont un impact sur le climat. Il est alors important d'incorporer dans les modèles climatiques des paramétrisations de nuages ainsi que la chimie des nuages qui soient aussi près que possible de la réalité. La paramétrisation de sous-maille de nuages de l'UQÀM a donc été incorporée au LCM11 dans ce but, le LCM11 étant une version unidimensionnelle du modèle NARCM (Northern Aerosol Regional Climate Model). L'objectif principal de ce projet est de déterminer s'il est nécessaire de compléter la paramétrisation des processus de sous-échelle dans le LCM11 en implémentant la chimie des particules de sous-maille.

Des simulations du modéle LCM11 avec et sans particules chimiques ont été effectuées avec divers scénarios chimiques.

La production de sulfate, le principal constituant des aérosols troposphériques, a été comparée pour différentes simulations. La production de sulfate n'a pas changé de façon significative avec l'implémentation des particules chimiques. Pour les scénarios testés dans ce projet, l'ajout des particules chimiques de sous-maille au modèle LCM11 n'est pas nécessaire.

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Acknowledgements

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Contributions to original knowledge

1. Adaptation of the von Salzen in-cloud chemistry scheme for implementation of sub-grid scale parcel chemistry with the UQAM sub-grid scale cloud scheme in the one-dimensional version of the Northern Aerosol Regional Climate Model, Local Climate Model version 11.

2. Investigation of the sensitivity of sulphate production modelling in LCM11 to the implementation of sub-grid scale parcel chemistry

3. Investigation of the reliance of this sensitivity on chemical conditions and vertical motion cap (or liquid water content profile)

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Chapter 1: Introduction

1.1 Purpose of study

The purpose of this study is to determine the sensitivity of model sulphate production to sub-grid scale cloud chemistry within the framework of the Northern Aerosol Regional Climate Model (NARCM). NARCM, as its name suggests, is a model designed to investigate the impact of aerosols on regional climate change at high latitudes. The main tool of this study is the Local Climate Model (LCM11), which is a one-dimensional version of NARCM.

NARCM currently uses a bulk microphysical cloud scheme. In such a scheme, a uniform slab of liquid water content and cloud cover occupies part of or the whole of a model grid square, thus model clouds are represented as homogeneous masses within a layer. These clouds also tend to "blink" on and off. It is reasonable to say that clouds in reality do not behave in this manner and it is important therefore to improve on this parameterization. A sub-grid scale cloud scheme was developed at the Université du Québec À Montréal (UQÀM) which subdivides the model grid into parcels generating a cloud with a spatial variation of liquid water content (LWC). This sub-grid scale parameterization aims to make the representation of clouds in NARCM more realistic and to improve the model's radiative budget calculations. This cloud scheme is currently written into the LCM11 where it has been tested. It has not yet been incorporated at the regional scale.

Clouds of course are not the only factor involved in modelling and understanding climate and climate change. Aerosols are amongst numerous entities whose impact on climate may be quite considerable and thus important. Aerosols not only impact on climate directly but they interact with clouds, and this interaction further contributes to influence climate, as illustrated by figure 1.1. A prime example of this is in the formation and processing of sulphate. Sulphate is the main anthropogenic constituent of tropospheric aerosols and it is formed primarily by in-cloud oxidation of dissolved sulphur dioxide. Climate researchers have associated a cooling effect to sulphate and its cloud chemistry (Seinfeld & Pandis, 1998; Harshvardhan, 1993; Hobbs, 1993b).

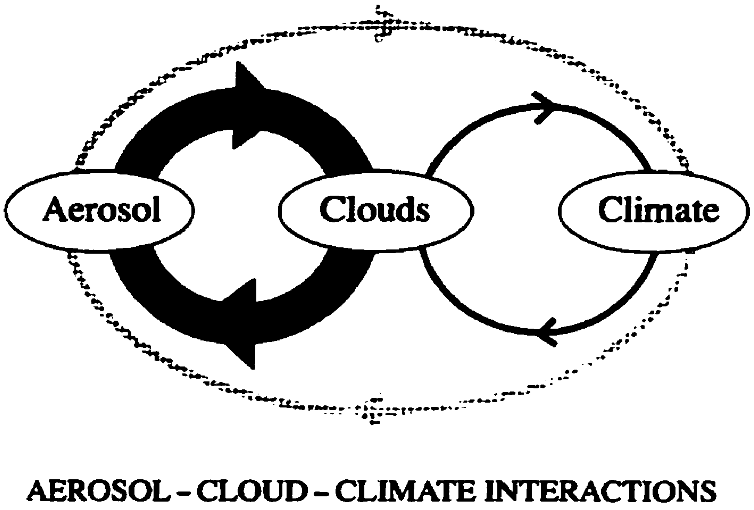


Figure 1.1: Aerosol-cloud-climate interactions (Hobbs, 1993a)

As cloud chemistry is an important component of climate modelling and thus of NARCM, one should like to determine how this chemistry is influenced by sub-grid scale cloud parameterization. Unfortunately, the UQÀM cloud scheme was not originally developed with chemistry in mind. Indeed, chemistry is not applied to each individual parcel of the UQÀM parameterization but to an averaged value of LWC instead (the implementation of sub-grid scale processes is in truth incomplete). In-cloud chemistry, such as the oxidation of sulphur dioxide is highly dependent on LWC and is a non-linear process. This raises an interesting question: if sub-grid scale processes were to be completed in LCM11, that is if one were to apply sub-grid scale parcel chemistry to the UQÀM clouds, would it significantly impact on the chemical processes modelled in LCM11?

The following project addresses this question by comparing sulphate production in parallel simulation runs of the LCM11 with and without sub-grid scale parcel chemistry. The in-cloud chemistry scheme has been adapted such that oxidation of sulphur dioxide can occur in each of the parcels of the sub-grid scale parameterization. Concentrations of sulphate within each parcel are summed and averaged over the layer. It is these layer mean concentrations that are compared to concentrations obtained when the adaptation is not employed, that is when the in-cloud chemistry is applied to the average LWC for the layer.

It is important to note that this study does not compare sulphate production between the bulk cloud scheme and the sub-grid scale UQÀM cloud scheme. Although the two schemes produce very similar cloud cover and LWC when averaged over a certain amount of time, on a day-to-day basis they differ too greatly for direct comparison. Any difference in sulphate production between the two schemes would reflect their differences in LWC rather than the implementation of sub-grid scale processes.

Before entering into the results of this project, the rest of chapter 1 offers a brief review of tropospheric aerosol and chemistry modelling, and chapter 2 provides a detailed description of the Local Climate Model.

1.2 Aerosols in climate and climate change

Interest in atmospheric chemistry, in particular in air pollution and in the chemistry of clouds and precipitation, began with the concern over acid deposition. According to Seinfeld & Pandis (1998) and Finlayson-Pitts & Pitts (1986), the phenomenon of acid rain appeared to be evident three centuries ago. Despite research as early as last century, the scope of the problem was not appreciated until the 1970's (Seinfeld & Pandis, 1998).

Rain tends to be slightly acidic naturally; as carbon dioxide gas dissolves and dissociates in water droplets, the hydrogen ions in the droplets reach an equilibrium with the ambient levels of carbon dioxide, about 350 ppm, at a pH ranging from 5.0 to 5.6 (Seinfeld & Pandis, 1998). Anthropogenic emissions can increase this acidity. Sulphur dioxide and oxides of nitrogen that are emitted from industrial areas are irreversibly converted in the atmosphere, by oxidation, to sulphate and nitrate. Sulphuric and nitric acids are strong acids, and when incorporated into cloud water and rainwater, they lower the pH. Precipitation with a pH less than 5.0 is considered as acid rain (Seinfeld & Pandis, 1998).

Acid deposition has several detrimental effects on the environment and on humans (for a description of these effects, please refer to Wayne, 1995, and Seinfeld & Pandis, 1998), and its precursors and components can be carried relatively long distances away from their source regions. Modelling the formation and transport of acidifying pollutants as well as their deposition, has been the focus of numerous studies. Hidy (1994) offers an overview of transport/deposition models for regional application used to determine source-receptor relationships. Among the many regional models described, the more interesting ones are the U.S. regional and deposition model (RADM) (Chang *et al.*, 1987; McHenry & Dennis, 1994), the Canadian/German acid deposition and oxidation model (ADOM) (Venkatram *et al.*, 1988; Karamchandani & Venkatram, 1992; Glazer & Leighton, 1994), and the U.S. sulphur transport eulerian model (STEM-II) (Carmichael *et al.*, 1991).

The acidification of rainwater is not the only consequence of the formation of sulphate and nitrate in the atmosphere. This additional mass changes the characteristics of the aerosol population and thus may affect climate. Sulphate and nitrate produced by clear air processes predominantly form small aerosols, thus increasing the number concentration of aerosols (to a lesser extent, they condense out onto pre-existing particles increasing their size). This increase in the number concentration of particles leads to a denser population that reflects more incoming solar radiation back to space. This impact on climate is known as the direct effect of aerosols and it lends a negative radiative forcing, cooling the earth as less solar radiation reaches the surface of the planet. (For a more detailed description of the direct effect of aerosols, refer to Seinfeld & Pandis, 1998, and Harshvardhan, 1993.)

In the case of sulphate, it is suggested that 40% to 95% of the sulphate formed in the atmosphere is produced not by clear air processes but by in-cloud aqueous-phase oxidation of sulphur dioxide (Liu *et al.*, 1993; Langner & Rodhe, 1991). If sulphate forms in cloud droplets, where the supersaturation is high, such as in convective clouds, the sulphate formed increases the size of the original cloud condensation nuclei as it dries upon evaporation. If, after evaporation, these larger aerosols are ingested into a stratiform cloud of lower supersaturation, the microphysical aspects and optical properties of this cloud may be altered. These larger particles become activated at the cloud's lower supersaturation, resulting in more droplets in the cloud. This leads to enhanced multiple scattering of light within the cloud and thus to an increase in the optical depth and albedo of the cloud. The aerial extent and cloud lifetime may also be increased. This, in a nutshell, is the accepted description of the indirect effect of aerosols on climate (for further information of this indirect effect of aerosols, refer to Seinfeld & Pandis, 1998, and Hobbs, 1993b). The indirect effect of aerosols, like the direct effect, is expected to contribute a negative forcing to the earth's radiative budget. There is however debate over this, as the description above, which is somewhat simplified, applies mainly to clouds with low supersaturation and liquid water content, and does not consider further cycling or processing of the aerosol either. It has been proposed that collision and coalescence of these droplets in an environment with a high liquid water content could lead to a decrease in the number concentration of droplets as larger droplets are formed, and thus to a decrease in the cloud albedo (Feingold, 1996).

1.3 Studying the impact of aerosols on climate: the laboratory, the field and the model

Regardless of debate, aerosols and their interaction with clouds are expected to play an important role in climate and climate change. It has been estimated that at the present time the combined direct and indirect cooling effect of anthropogenic aerosols may be as important as the warming which has resulted from the enhanced greenhouse effect (Langner & Rodhe, 1991; Feichter *et al.*, 1996; Pham *et al.*, 1996; Rodhe *et al.*, 1995; IPCC, 1996). The confidence level in this quantification however is quite low, see figure 1.2, due to uncertainties in atmospheric sulphate concentrations as well as a certain lacking in the understanding of all of the processes involved (Langner & Rodhe, 1991; Feichter *et al.*, 1996; Pham *et al.*, 1996; Rodhe *et al.*, 1995).

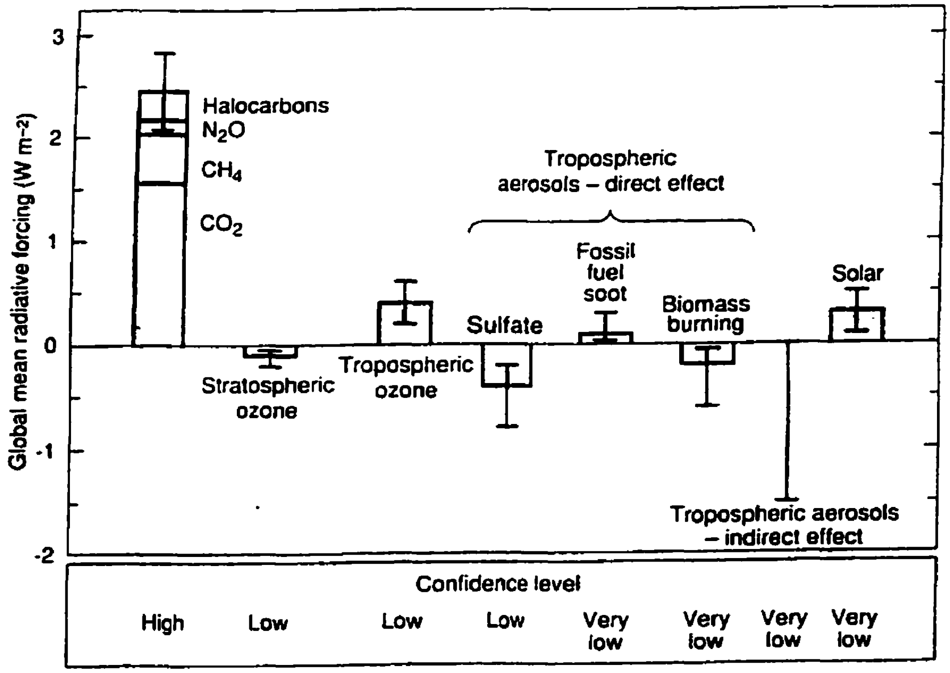


Figure 1.2: IPCC estimates of global-mean radiative forcing as of 1995 (IPCC, 1996).

To gather information and improve understanding, a wide variety of studies have explored the formation of sulphate in clouds, the tropospheric concentrations of sulphate as well as the climatic impact of the interaction between clouds and anthropogenic sulphate aerosols. Among these are laboratory experiments (Finlayson-Pitts & Pitts, 1986; Seinfeld and Pandis, 1998). Here chemical reaction rates and pathways are investigated under controlled circumstances using a variety of scenarios more or less likely to occur in the real atmosphere. Also important are the experimental field studies. Some are based around air-borne measurements (Liu *et al.*, 1993; Daum *et al.*, 1996). Others are ground-based field campaigns examining the processing in orographic clouds (Choularton *et al.*, 1997; Bower *et al.*, 1997; Laj *et al.*, 1997; Saxena *et al.*, 1996; Snider & Vali, 1994). Hill cap clouds offer unusual and unique opportunities as they are perfect "natural laboratories" (Choularton *et al.*, 1997; Saxena *et al.*, 1996) for studying gas scavenging and aerosol. Measurement of atmospheric compounds at various points before (upstream of), within, and following (downstream of) these semi-permanent clouds is feasible over extended periods of time. Also, the relatively well defined beginning and ending points of the clouds allow for the injection of reactive chemicals as well as the use of inert tracers (see Liu *et al.*, 1993, and references within). Some field studies have even used satellite measurements to relate in-cloud sulphate production to the short-wave albedo of clouds (Saxena *et al.*, 1996). Thus, laboratory and field experiments provide valuable information. These types of studies have limitations however. The conditions under which laboratory experiments are performed are often too specific, and in field experiments aeroplane flight paths can only span a certain radius around a point, likewise the experimental results obtained from a particular geographic location may not be representative of a larger area. Therefore, another tool, namely computer modelling, is necessary to explore sulphate in the atmosphere. Numerous three-dimensional models of atmospheric trace constituents exist. There are atmospheric chemical transport models which are used to investigate the chemical formation, physical transformation, and scavenging pathways of aerosols and involve chemistry models driven off-line by climate model generated or observed meteorological conditions. There are also climate/circulation models where aerosols are included as interactive constituents. In both modelling approaches the processes of trace constituent transport, transformation, and removal are parameterized with varying degrees of sophistication. Peters *et al.* (1995) offer a review of comprehensive tropospheric chemistry/transport models developed over the last two decades, in which they describe meso- and regional-scale models, as well as global-scale models. The more recent models described by Peters *et al.* employ extensive gas- and aqueous-phase chemical mechanisms and explicitly track numerous trace species concentrations. They also include a more detailed formulation of physical and chemical processes occurring within and below precipitating clouds (Peters *et al.*, 1995). The tropospheric sulphur cycle has been the focus of several studies including Langner & Rodhe (1991), Feichter *et al* (1996), Pham *et al.* (1996). Rodhe *et al.* (1995) review attempts that have been made to use three-dimensional tracer transport models to simulate the global distribution of sulphur and nitrogen compounds. There have also been studies on the effect of aerosol forcing on climate, for example Boucher & Lohmann (1995), Mitchell and Johns (1997), Feichter et al (1997),.

1.4 The impact of cloud scheme on modelled sulphate production

As mentioned earlier, the way in which clouds are parameterized can greatly impact on radiative processes and energy budgets in climate models. The interaction between clouds and aerosols likely constitutes a significant forcing of the earth's radiative budget. It follows therefore that the manner in which cloud LWC is resolved in a model can affect the chemical processes included in that model.

Two previous studies have looked into the effect of sub-grid scale cloud parameterizations on in-cloud chemistry and, of particular interest, on sulphur dioxide oxidation rates.

a) *Walcek & Brankov, 1994: The influence of entrainment-induced variability of cloud microphysics on the chemical composition of cloudwater.*

Walcek & Brankov present a preliminary assessment of the bias that may be implicit in models that "average-out" turbulent-scale features. They examine how entrainment influences cloud microphysics and thermodynamics structure, chemical composition of cloud water, and sulphur dioxide oxidation rates.

In order to investigate sulphur dioxide oxidation rates, Walcek & Brankov use a model representative cloud into which clean outside air is entrained. The amount of air entrained into the cloud is expressed by an entrainment fraction. The air entrained into the cloud is assumed to be relatively clean containing only hydrogen peroxide and ozone, while the air lifted from below cloud base is assumed to be polluted to some degree. They assess the bias in sulphur dioxide oxidation calculated over a range of hydrogen peroxide concentrations (from low to high) and over a range of ammonia, nitric acid, and sulphate concentrations varied together (from clean to highly polluted conditions). Sulphur dioxide concentration is kept constant at a relatively high value. They define as "true" oxidation rate, an average of the oxidation rates in 12 evenly spaced cloudy entrainment mixture fractions. This is compared to an "approximate" oxidation rate, which is more simply calculated from the mean of the meteorological and chemical conditions for the same 12 fractions. The ratio of the two rates is the bias, or error. Note, the temperature, water content, and pollutant concentrations are identical between both methods, however in the "true" method, the chemical and meteorological parameters are permitted to vary about the mean.

Walcek & Brankov find that the magnitude of the error is a function of the mean cloudwater pH and the relative importance of hydrogen peroxide and ozone oxidation in the cloud. Mean cloudwater pH values are mainly dependent on hydrogen peroxide, ammonia, nitric acid and sulphate as these compounds are considered highly soluble. Under very clean conditions, defined as very low concentrations of sulphate, the variation of acidity with water content and entrainment fraction is quite small, and the sulphur dioxide oxidation rate is a fairly uniform function of the amount of entrainment experienced at any point in the cloud. At high hydrogen peroxide concentrations, hydrogen peroxide is the dominant oxidant and its oxidation rate is a fairly linear function of the amount of entrainment experienced at any point in the cloud (the non-linear ozone oxidation rate is of minor importance under these conditions). Thus, for low sulphate or high hydrogen peroxide concentrations there is little error introduced by averaging the rate over the entrainment mixture fractions. Under highly polluted conditions and low hydrogen peroxide, the error can again be small as with increasing sulphate, and thus increasing acidity, hydrogen peroxide becomes the more important oxidant. Only under a restricted range of sulphate at very low hydrogen peroxide concentrations are significant errors, up to a factor of about 1.6, possible

The restricted conditions under which noticeable errors arise may not be the norm and one may be able to ignore small-scale variations. In order to relate how reasonable it is to neglect small-scale variation when modelling the real atmosphere, Walcek & Brankov assess how frequently errors might occur in the climatic conditions of the northeast US. They simulate the seasonal cycle of the parameters of interest using a simple model as well as measurements from a moderately polluted site. They find that errors are very small during summer months when the air is highly polluted and has high concentrations of hydrogen peroxide. During winter, there is little hydrogen peroxide so ozone is the dominant oxidant in clouds, however, the air is very clean during mid-winter, and with little sulphate in the clouds the oxidation rate by ozone is fairly linear with respect to the entrainment of clean air experienced by any point in the cloud. Highest errors (in the vicinity of 1.2, or 20% difference between "true" and "approximate" oxidation rates) are calculated to occur in spring and fall when ozone is the dominant sulphate production pathway and there is sufficient sulphate and nitrate present in the polluted air to cause the ozone mechanism to become non-linear. They also find that the ambient hydrogen peroxide concentration is a key factor when accounting for turbulent-scale effects.

Walcek & Brankov conclude that spring and fall, under certain chemical conditions, are the seasons in the year when it is most necessary to consider small-scale variations.

b) *Matthijsen et al., 1997: The effect of fractional cloudiness on the oxidation of SO_2.*

Matthijsen *et al.* present a study on the effects of fractional cloudiness on sulphur dioxide in the marine boundary layer. They investigate the difference between sulphur dioxide budgets calculated using an all-or-nothing approach to cloud amount versus a more realistic fractional cloudiness approach.

In a mesoscale model, in the case of an all-or-nothing approach, the grid cell has a cloud cover of either 1 or 0 and the amount of cloud water is calculated from the difference between total water content and saturation mixing ratio. Using this type of scheme, gas- and aqueous-phase chemistry can be easily described, however the calculated amount of sulphur dioxide oxidized may be seriously biased as the scheme doesn't account for fractional cloudiness conditions (Matthijsen *et al.* (1997)).

Matthijsen *et al.* examine the extent to which the all-or-nothing approach may be applied in the modelling of the sulphur dioxide budget, and under what conditions it is likely to be inappropriate.

They use a simple stationary state two-layer model with fixed cloud- and sub-cloud layers. Sulphur dioxide concentrations in both layers are assumed to be in quasi-stationary state such that chemical loss and production, deposition on seaspray and sea surface, and transport between cloudy and non-cloudy air are supposed to balance. The contribution of long range transport to the sulphur dioxide concentration is not included, nor is entrainment of free tropospheric air taken into account. For more details on the model and a description of the cloud scheme that Matthijsen *et al.* have used to conduct this study, refer to their paper and the references sited within.

Matthijsen *et al.* find that the sulphur dioxide concentration calculated using the sub-grid parameterization may deviate up to a factor of two as compared to that calculated using an all-or-nothing scheme. Using observed cases of fractional cloudiness from five different measurement campaigns to dictate the cloud parameters in their model. They find maximum deviations between –85% and +33%.

Matthijsen *et al.* conclude that taking fractional cloudiness into account in the simulation of cloud chemistry will greatly improve the quantification of the different formation and loss pathways of sulphur dioxide in the marine boundary layer cloud.

Chapter 2: Model description

2.1 The Northern Aerosol Regional Climate Model Project

NARCM is a model designed to investigate the impact of aerosols on regional climate at high latitudes. The NARCM project was initiated to meet an inadequacy in the Canadian General Circulation Model (CGCM) (McFarlane *et al.*, 1992), specifically that the CGCM does not treat aerosols as active constituents. The NARCM project aims to correct this, as well as to increase spatial and temporal resolution and improve parameterization of aerosol-associated processes. The long-term goal is to incorporate the aerosol algorithms developed within NARCM into the CGCM in order to perform aerosol climate feedback experiments in a global context.

The NARCM project is a collaborative Canadian climate research project involving several university and government research groups. This project is also linked to national and international research groups (for more information, refer to the NARCM website at http://www1.tor.ec.gc.ca/armp/NARCM/index.htm).

The Université du Québec À Montréal (UQÀM) regional climate model (Laprise *et al.*, 1998; Caya *et al.*, 1995) serves as the modelling framework of NARCM and is used on a moderate resolution domain centred on the North Pole and reaching to about 35° N latitude. Processes to be simulated with aerosols as active constituents include emissions, transport-diffusion, chemical/physical transformation, wet and dry removal, as well as radiative coupling, as illustrated in figure 2.1.1 (taken from the NARCM website).

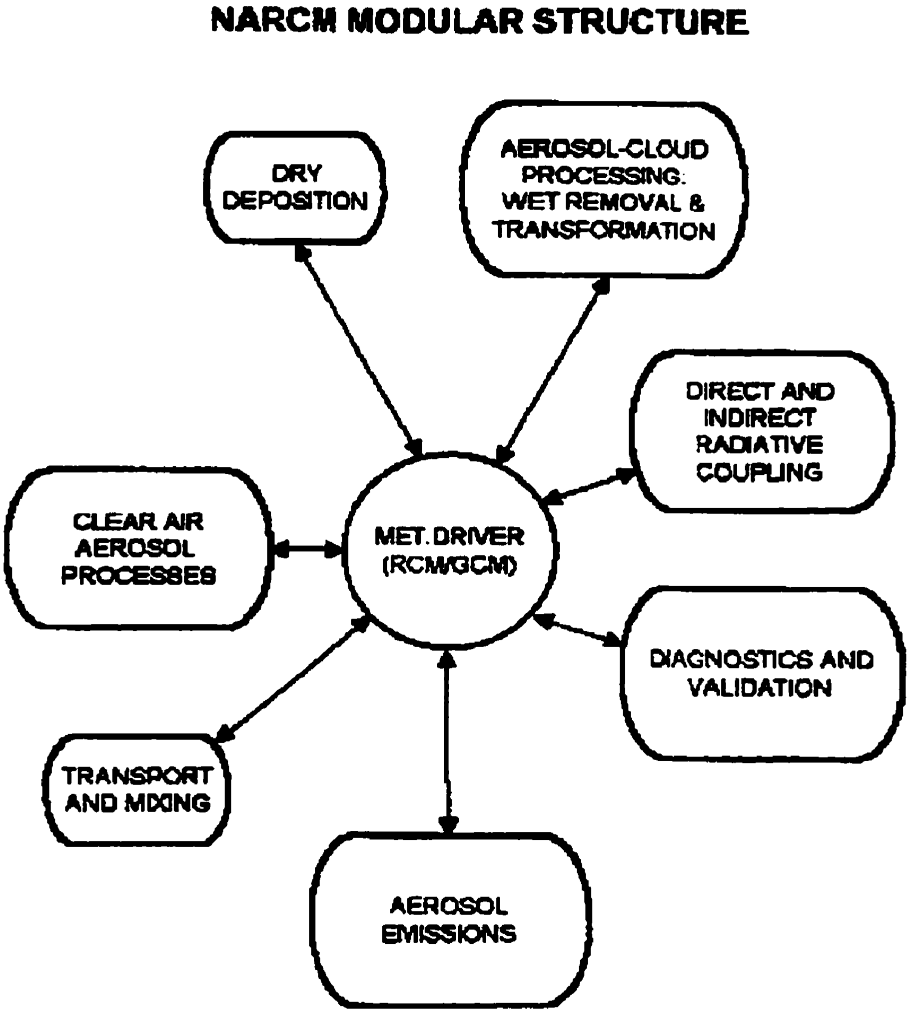


Figure 2.1.1: NARCM modular structure.

For a more detailed description of the current state of NARCM refer to von Salzen *et al.* (1999) and Spacek *et al.*(1999).

2.2 The Local Climate Model version 11

One-dimensional or column models are important tools for the development and testing of new parameterizations, for sensitivity studies, and to examine the relationship between processes because of their relatively inexpensive computational demands.

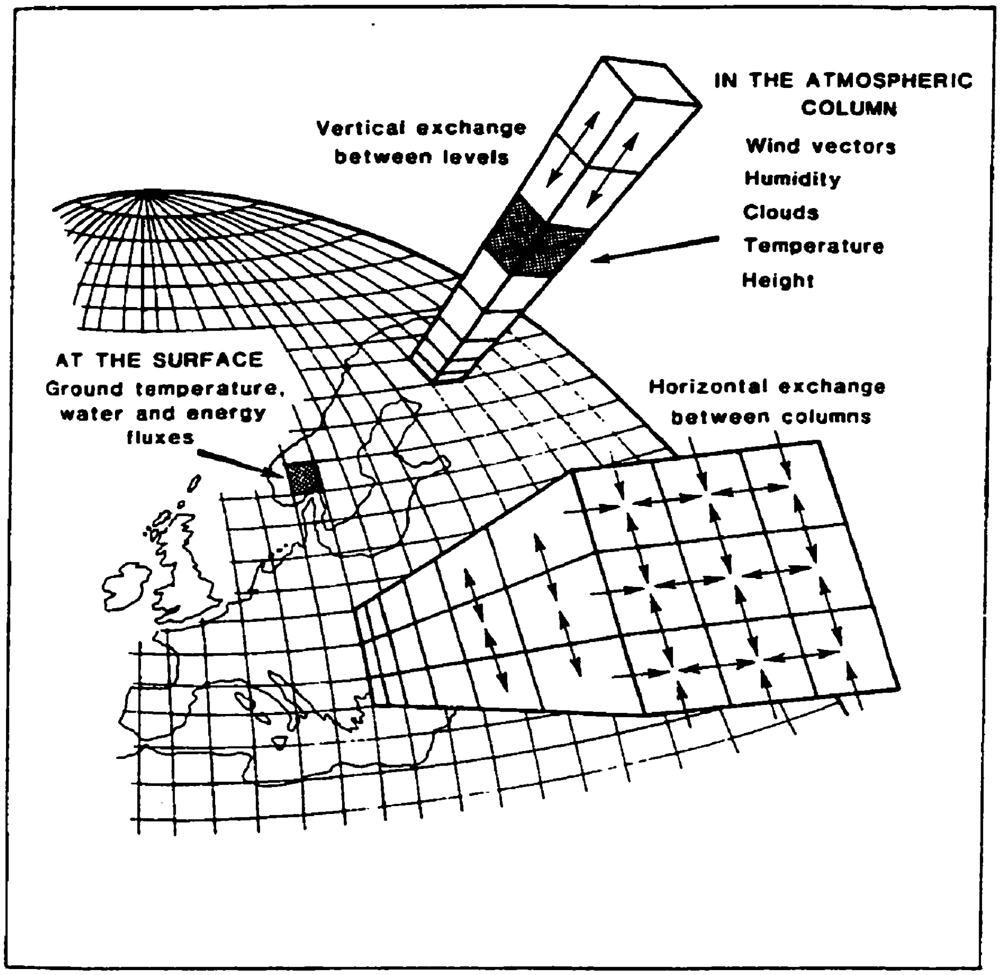


Figure 2.2.1: Illustration of the basic characteristics of a general circulation climate model (Henderson-Sellers & McGuffie, (1987)).

The main tool in this study is the Local Climate Model version 11 (LCM11), which is a one-dimensional column version of NARCM. LCM11 has the full Canadian Centre for Climate modelling and analysis (CCCma) second-generation general circulation model (gcmii) physics package developed by McFarlane *et al.* (1992) and is a semi-lagrangian, semi-implicit, semi-prognostic model of the atmosphere. This version of the model has 49 levels in the vertical and a 20-minute time step.

Like for other one-dimensional models, despite the small cost in computation time, there is a large requirement in terms of input data. The model must first be initialised with the site co-ordinates and ground characteristics. These characteristics are usually obtained from a global climatology file. In order to drive LCM11, surface pressure, profiles of zonal and meridional winds, temperature, and humidity, as well as the advection of heat and humidity into and out of the column for the entire simulation period are required. To fulfil this need, first data is extracted from hourly station surface observations, 12-hourly upper air soundings, and daily radiation and precipitation measurements to create 12-hourly physical tendencies. Next, since the local climate model column stands alone without adjoining columns with which it can communicate (contrary to a regional or global climate/circulation model, see figure 2.2.1), dynamic tendencies must be generated to perform a simulation run. Originally, this was accomplished by running a global climate model over the simulation period and extracting the dynamic tendencies for the site of interest. Unfortunately, this approach made the local climate model dependent on the global model, and no longer so inexpensive. In addition, dynamic tendencies generated were not necessarily concordant with the actual meteorology of the simulation period.

To solve this dilemma, in this project a procedure developed by Bourque (1998) is employed where by, using the physical tendencies the LCM11 is run iteratively in assimilation mode to extract the dynamic tendencies alone. It is important to remember that although the dynamic tendencies are closer to reality using this procedure, their quality is dependent on many inflexible factors such as the quality of the raw observations and the quality of the parameterizations in the model.

Once the site characteristics and the physical and dynamic tendencies have been assembled for the desired simulation period, the model can be driven to reproduce the meteorological events at that site. All physical processes, such as radiation, hydrology, convection, precipitation, sea-ice, heat fluxes, and surface energy balance are recalculated. The column model is expected to reproduce the atmosphere relatively well on average, however on a particular day, the simulation may not mirror the raw observations.

Two recent sophistications to the LCM11 are employed in this project: the sub-grid scale Université du Québec À Montréal (UQÀM) cloud scheme (Gagnon *et al.*, 1999; Jiang *et al.*, 1999) and von Salzen's S(IV) aqueous oxidation scheme (von Salzen *et al.*, 1999). These are described below.

2.3 Sub-grid scale clouds

The sub-grid scale UQAM cloud scheme (Gagnon *et al.*, 1999; Jiang *et al.*, 1999) was developed in an attempt to make NARCM's radiative budgets more reasonable by making the clouds less uniform and thus more realistic than the representation offered by the gcmii bulk cloud scheme.

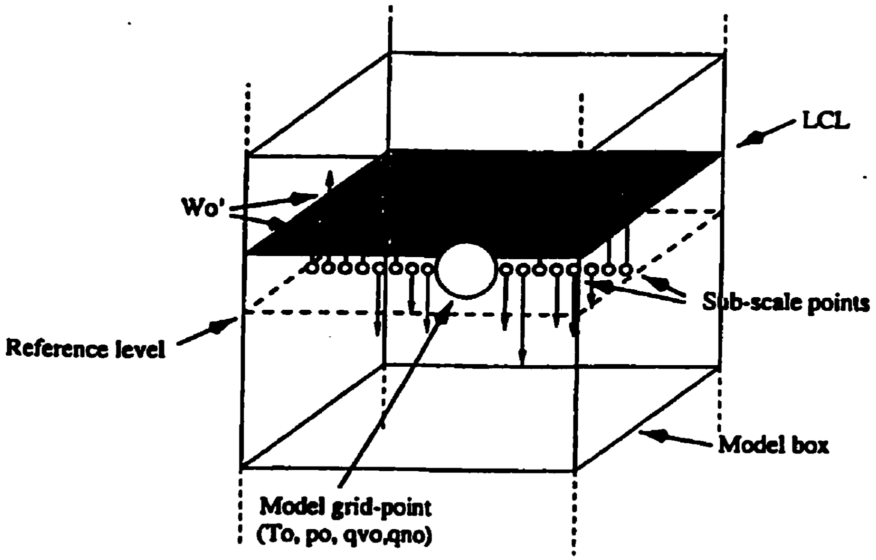


Figure 2.3.1: Three-dimensional representation of the numerical model grid box and of sub-grid scale calculation domain (Gagnon *et al.*, 1999)

This cloud parameterization involves subjecting sub-grid scale parcels along a transect to a spectrum of upward and downward vertical velocities at each vertical level. This leads to displacements of the parcels from their nominal level (Gagnon *et al.*, 1999). For those air parcels that ascend, they expand and cool. As the parcels reach their lifting condensation level (LCL), the water contained within them condenses out (refer to figure 2.3.1). The further the parcels travel upwards, the greater their LWC. Thus along the transect, there is generated a spatial variation of LWC, or in other words a cloud which is no longer uniform in density.

There are 256 sub-grid scale parcels along a transect. In the first version of the code Fast Fourier Transform (FFT) generated the vertical velocity spectra (Gagnon *et al.*, 1999). Parameters such as the lapse rate above and below the reference level, the Brunt-Väisälä frequency, and modulus of the wind determine whether the sub-grid scale motion falls within a turbulence regime or a gravity wave regime. Turbulence is representative of stronger winds and greater vertical development, while gravity waves occur in a more stable atmosphere where parcels oscillate up and down about their initial position. In this study, a more efficient computation scheme (Jiang *et al.*, 1999) is utilized instead of the original version of the UQÀM cloud scheme. Here, sets of "random look-up tables" are used for the vertical velocity spectra instead of generating them by FFT, as well as a sorting algorithm to bin the velocities in order to accelerate the computation (Jiang *et al.*, 1999). Figure 2.3.2a is an illustration of the upward and downward motion of the sub-grid scale parcels in time step 149, at 830 hPa, an arbitrarily chosen turbulent layer. This motion is expressed in terms of a relative spatial turbulence ratio. An amplitude, determined by the parameters listed above, such that each sub-grid scale parcel is subjected to an upward or downward velocity, multiplies the ratio. Figure 2.3.2b displays the velocities sorted into the bins; the velocity spectrum is quasi-gaussian. Due to the randomness of the distribution, some bins will receive no parcels. Figure 2.3.3c is an example of the resulting liquid water content distribution (relative frequency) over the bins and the average liquid water content over the cloudy portion of the grid.

Besides the distribution of vertical velocities on the sub-grid scale, the UQÀM cloud scheme differs from the gcmii bulk cloud scheme in that it treats LWC prognostically (in other words, as a tracer), and thus there is a feedback mechanism inherent in the parameterization. The gcmii bulk cloud scheme treats LWC diagnostically by recalculating it at every time step.

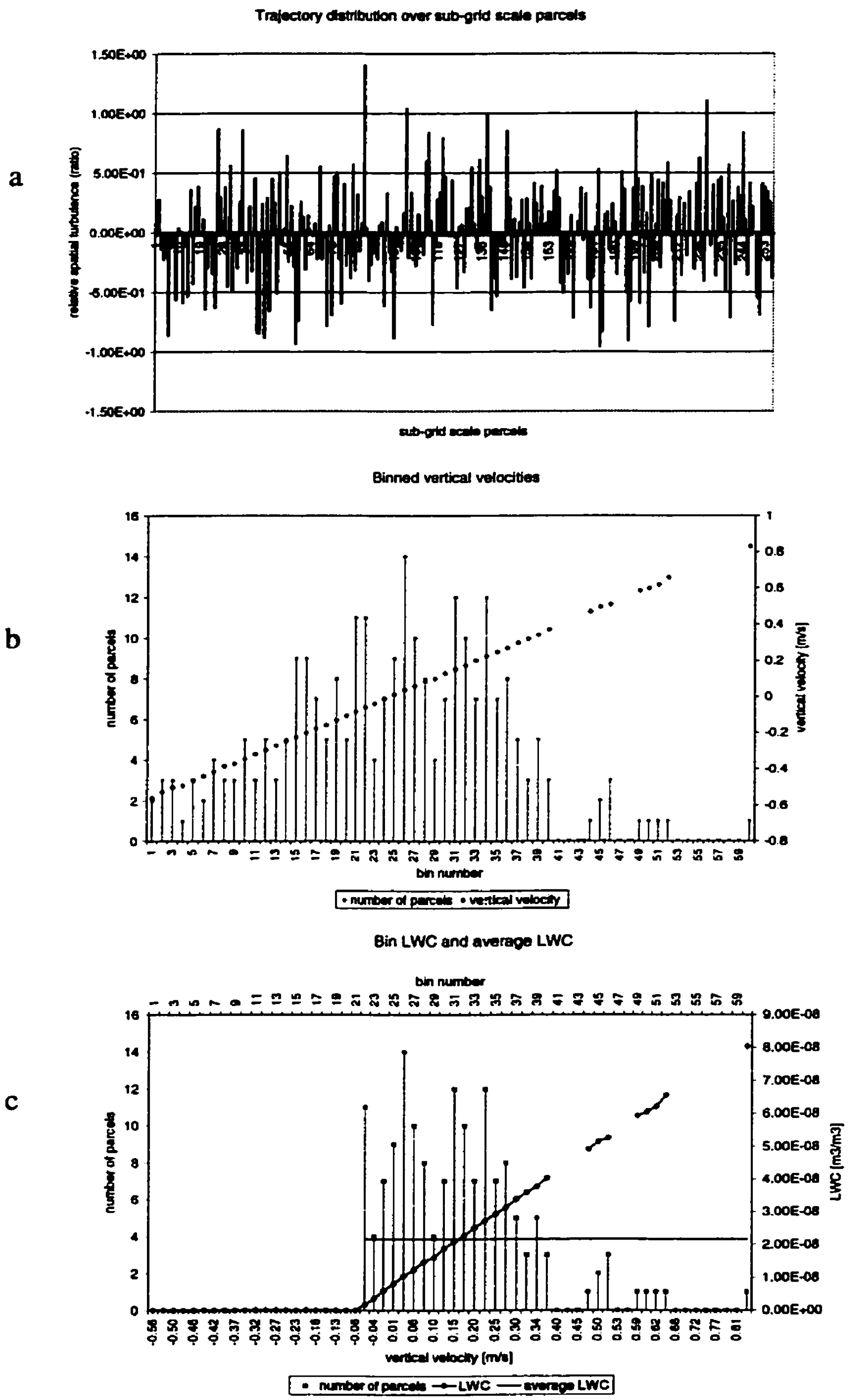


Figure 2.3.2 (a) Illustration of trajectory distribution over sub-grid scale parcel transect at 830 hPa in time step 149, this is a turbulent layer; (b) binned vertical velocities after sorting (velocity spectrum); (c) relative frequency of LWC and average LWC over the cloudy portion of the grid box.

2.4 Aqueous chemistry

The von Salzen's S(IV) oxidation scheme uses a bulk phase approach instead of a cloud-droplet size-dependent approach to cloud chemistry to increase model efficiency (von Salzen *et al.*, 1999). The two oxidants in this scheme are hydrogen peroxide and ozone; reactions with the hydroxyl radical catalyzed by ferrous oxide and other metal oxides are normally not important and so are not included here. The availability of sulphur dioxide and hydrogen peroxide is explicitly included in the parameterization (von Salzen *et al.*, 1999). In the real atmosphere, hydrogen peroxide is continuously produced by clear-air reactions, and sulphur dioxide is released from local sources and/or advected into the region of interest. Since these two processes are not reproducible in the one-dimensional model, the model concentrations relax back to the initial profiles of hydrogen peroxide and sulphur dioxide every 108 time steps (36 hours) such that ambient concentrations of these two compounds tend to be maintained during the simulation period. The impact of ammonia, nitric acid and carbon dioxide on in-cloud oxidation rates is also included (von Salzen *et al.*, 1999). Table 2.1 lists the reactions included in this scheme. The acidity of the cloud is calculated using the following equilibrium:

$$[H^+] + [NH_4^+] = [OH^-] + 2[SO_4^{2-}] + 2[SO_3^{2-}] + [HSO_3^-] + [NO_3^-] + [HCO_3^-] \qquad (2.4.1)$$

Note, in order to focus on in-cloud chemistry in this project, no clear air chemistry is included in the column model. Also, only oxidation occurring in stratiform and shallow convective clouds is considered, as the sub-grid scale UQÀM cloud scheme is not designed to simulate deeply convective clouds.

Table 2.1: Reactions included in the von Salzen's aqueous S(IV) oxidation scheme.

$CO_2(g) \leftrightarrow CO_2(aq)$
$CO_2(aq) + H_2O \leftrightarrow H^+ + HCO_3^-$

$SO_2(g) \leftrightarrow SO_2(aq)$
$SO_2(aq) + H_2O \leftrightarrow H^+ + HSO_3^-$
$HSO_3^- \leftrightarrow H^+ + SO_3^{2-}$

$NH_3(g) \leftrightarrow NH_3(aq)$
$NH_3(aq) + H_2O \leftrightarrow NH_4^+ + OH^-$

$HNO_3(g) \leftrightarrow HNO_3(aq)$
$HNO_3(aq) \leftrightarrow H^+ + NO_3^-$

$H_2O \leftrightarrow H^+ + OH^-$

$S(IV) + H_2O_2(aq) \rightarrow S(VI) + H_2O$
$S(IV) + O_3(aq) \rightarrow S(VI) + O_2(aq)$

Chapter 3: Experimental scenarios and model simulation runs

As discussed in chapter 1, it seems likely that cloud scheme will impact on the modelling of sulphate production. Indeed, two previous studies have shown this to be true under certain chemical scenarios. With the introduction of the UQÀM sub-grid cloud scheme into LCM11, it becomes important to assess whether the implementation of sub-grid scale parcel chemistry will significantly alter the modelling of sulphate in LCM11, and if so, under what chemical conditions. Here parallel simulation runs, with and without sub-grid scale parcel chemistry, are performed, and the modelled sulphate production is compared.

The model simulations are performed for Trout Lake, Ontario (53N 90W) (see figure 3.0.1), a site that can be considered somewhat remote. The simulation period is from June 1st to June 28th 1989, and spans 2088 20-minute model time steps.

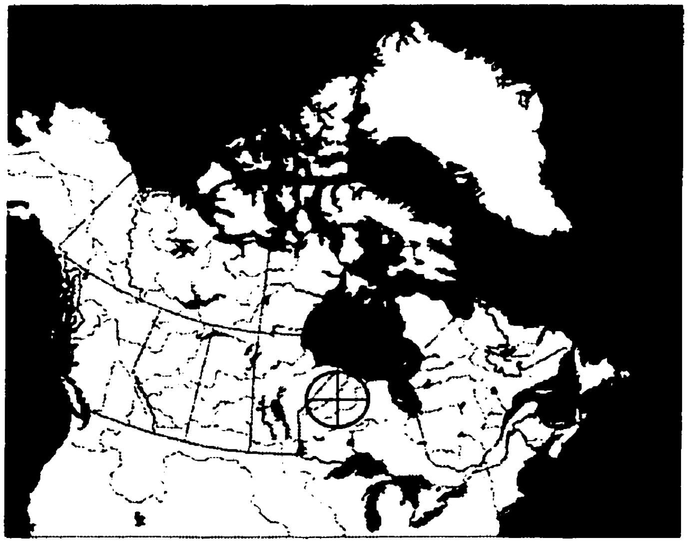


Figure 3.0.1 Position of Trout Lake, Ontario (53N 90W).

Simulation runs are conducted under different scenarios. For each scenario, arbitrary but realistic concentration profiles are assigned for the chemical compounds involved in the in-cloud production of sulphate. In consequence, simulation runs are only compared amongst themselves and not to real atmospheric observations.

The chemical vertical profiles that remain constant from one scenario to the next are described in section 3.1. Sections 3.2 to 3.5 present simulation runs under various chemical scenarios, differing concentrations of sulphur dioxide and hydrogen peroxide. Of note, this series of experiments illustrates the versatility of the local climate model and its usefulness for sensitivity studies: as concentration profiles can be set manually, it is possible to represent different conditions for the same site or simulation period.

In the LCM11 with the UQÀM cloud scheme, the sub-grid scale vertical motion has been restricted such that parcels are allowed to travel only up to one kilometre away from their reference level. The distance a parcel can travel from its reference level can be extended to two kilometres. In section 3.6, the effect of this extension allowing parcels to travel further and potentially acquire more LWC is investigated.

3.1 Sulphate, ozone, carbon dioxide, ammonia, and nitric acid profiles

As mentioned in section 2.4, the main focus of von Salzen's in-cloud chemistry scheme is the production of sulphate within the column. Since the interest of this study is to look at sulphate production and its dependence on sub-grid scale processes, this initial profile for sulphate in the column is set to zero for all simulation runs.

Ozone, carbon dioxide, ammonia, and nitric acid vertical concentration profiles are not changed from one simulation to another. Ozone, the second oxidant, is so abundant in the atmosphere (Seinfeld & Pandis, 1998), especially when compared to hydrogen peroxide, that its consumption during the oxidation process does not significantly alter its ambient concentration. In these simulations, it has a background concentration set constant with elevation at 30 ppb. This is representative of values at the lower end of the concentration range for ozone (Seinfeld & Pandis, 1998). Carbon dioxide is set at its global average concentration of 350 ppm, also constant with elevation. Nitric acid and ammonia (which usually behaves as a buffer to acidity) play a significant role in the determination of cloud pH, which in turn can affect in-cloud oxidation. It is therefore important to have realistic and fairly representative profiles for these two compounds. Figure 3.1.1a is the vertical profile for ammonia employed in this study, and it is an approximation of the zonal average concentration over 50N presented by Dentener & Crutzen (1994) in their general circulation model (gcm) study. The vertical profile for nitric acid is represented in figure 3.1.1b, and was obtained using Huebert & Lazrus' (1980) measurements of continental nitric acid as well as estimates referenced within their publication.

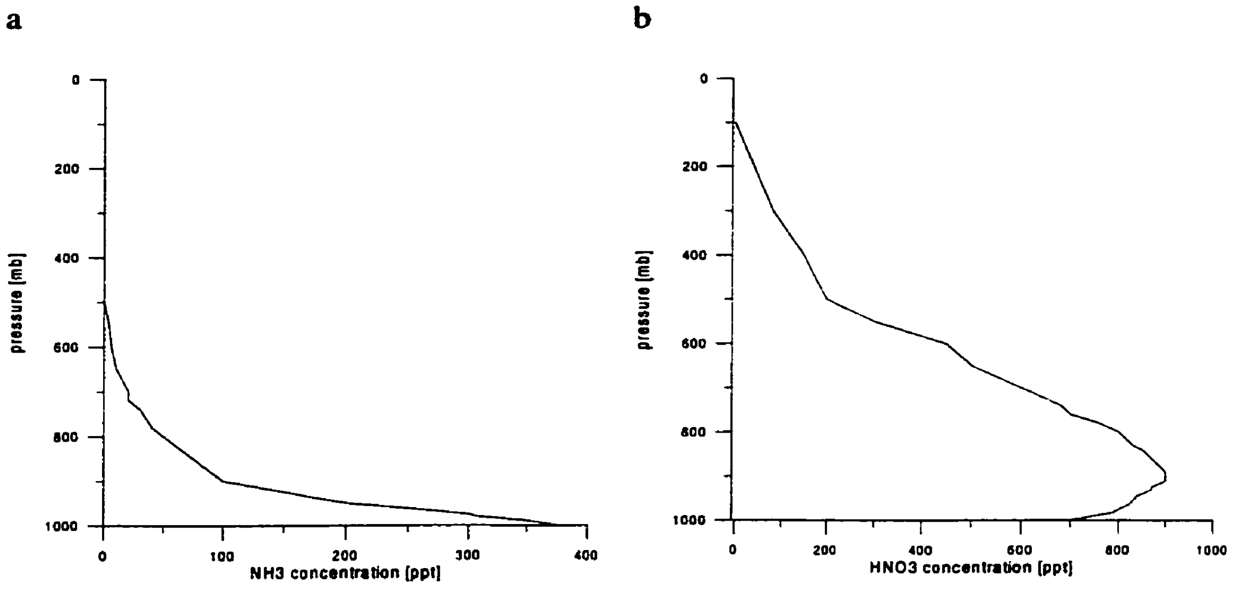


Figure 3.1.1 Background concentrations for (a) ammonia and (b) nitric acid, in ppt.

3.2 Base scenario

3.2.1 Chemical scenario

The first simulation is the base scenario run (BASE_V1). The chemical scenario uses initial concentrations which are characteristic of an average or non-polluted case.

The initial profile for sulphur dioxide is taken from Langner & Rodhe's (1991) global sulphur cycle gcm study, again approximating the global zonal average for 50N (figure 3.2.1).

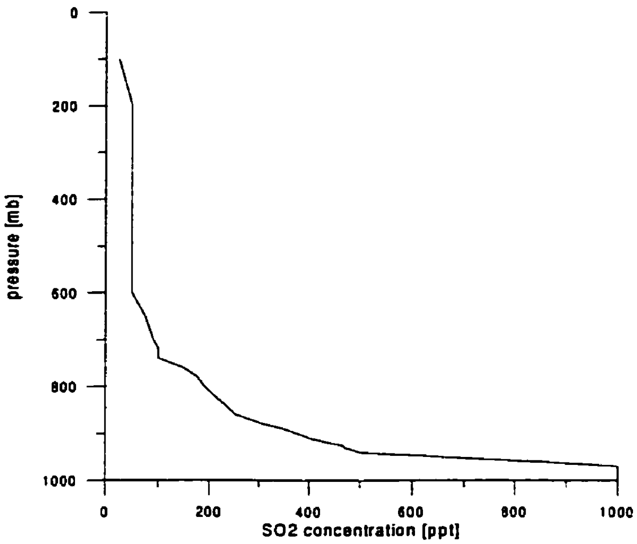


Figure 3.2.1 BASE_V1 sulphur dioxide initial concentration, in ppt.

The initial profile for hydrogen peroxide in BASE_V1 is a constant column set at 1 ppb. This value is quite close to what Isaac *et al.* (1992) found as a median profile for hydrogen peroxide in air masses originating from a non-polluted area for a site to the southeast of Trout Lake.

3.2.2 Simulation runs and comparisons

a) *Average LWC, cloud water and precipitation for BASE_V1*

Average LWC, cloud cover, and the amount of precipitation is the same for both the average chemistry simulation run and the sub-grid scale parcel chemistry run. This is important, as otherwise it would be difficult to compare sulphate production between runs and thus assess whether it is necessary to implement sub-grid scale parcel chemistry on sub-grid scale clouds in LCM11.

For the base runs and all subsequent runs with vertical motion cap equal to ±1 km, the average LWC (m^3/m^3), cloud cover (ranging from 0 to 1) and the amount of precipitation (kg/m^2) for the simulation period are depicted by figures 3.2.2 a, b and c, respectively. The shading employed is a hybrid between contour shading and gradient grey scale shading. The value of each contour line is denoted in the colour bar on the side of the panels where the shading itself grows smoothly from light to dark.

There are clouds during most of the simulation period, and these tend to be relatively low. In the few instances where there is greater vertical development, these clouds do not tend to have higher liquid water content than those which occur at a lower altitude. Since the majority of the clouds occur below 700 hPa, it is obvious that the in-cloud chemistry will be predominant in this region of the lower atmosphere.

Furthermore, since the sulphur dioxide concentration decreases with elevation (figure 3.2.1), the production of sulphate will be most interesting closer to the surface.

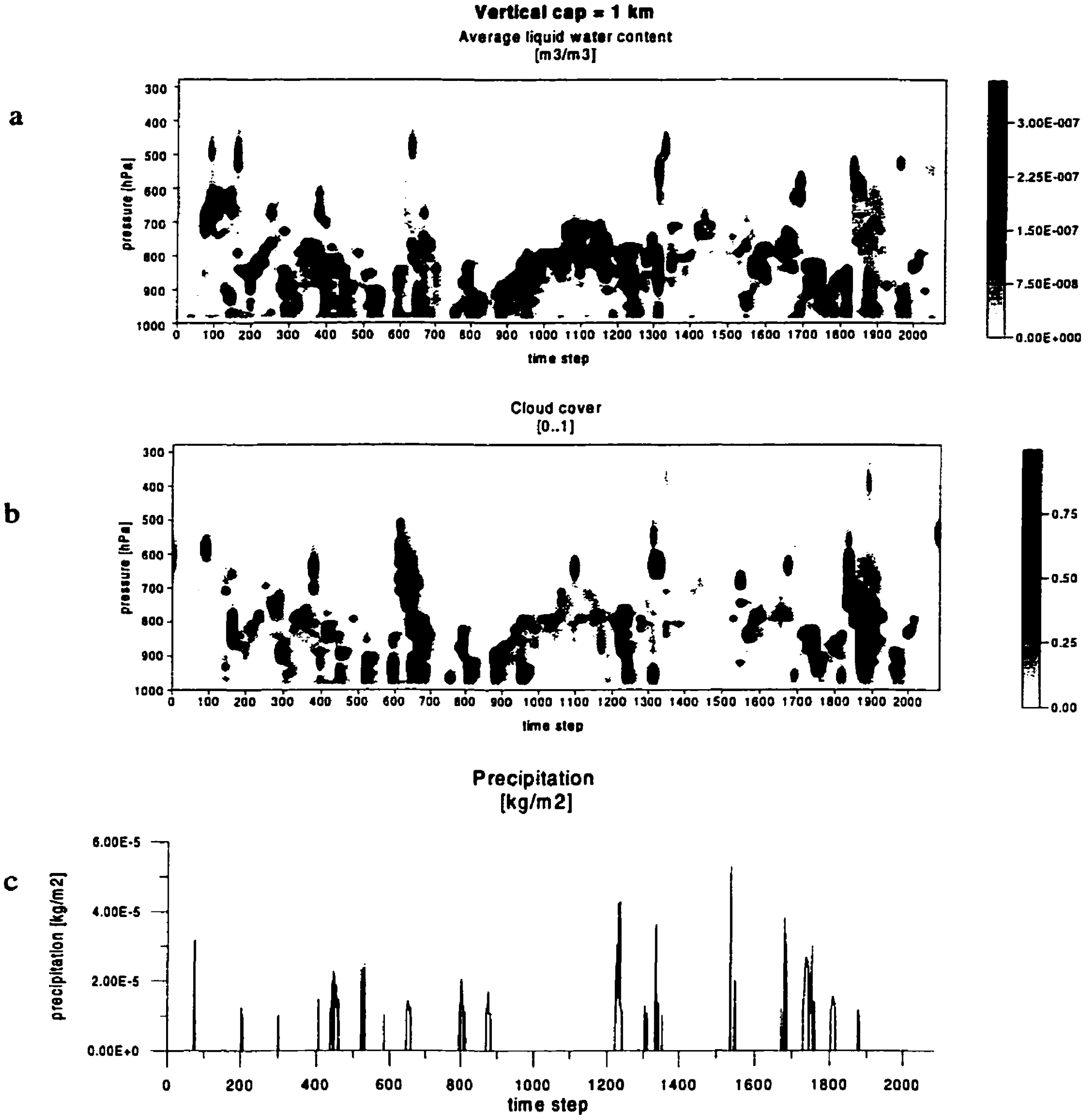


Figure 3.2.2 (a) Average liquid water content [m^3/m^3], (b) cloud cover and (c) precipitation [kg/m^2] for simulation runs with vertical cap equal to ±1 km, for the period from June 1st to June 28th, 1989 for Trout Lake, Ontario.

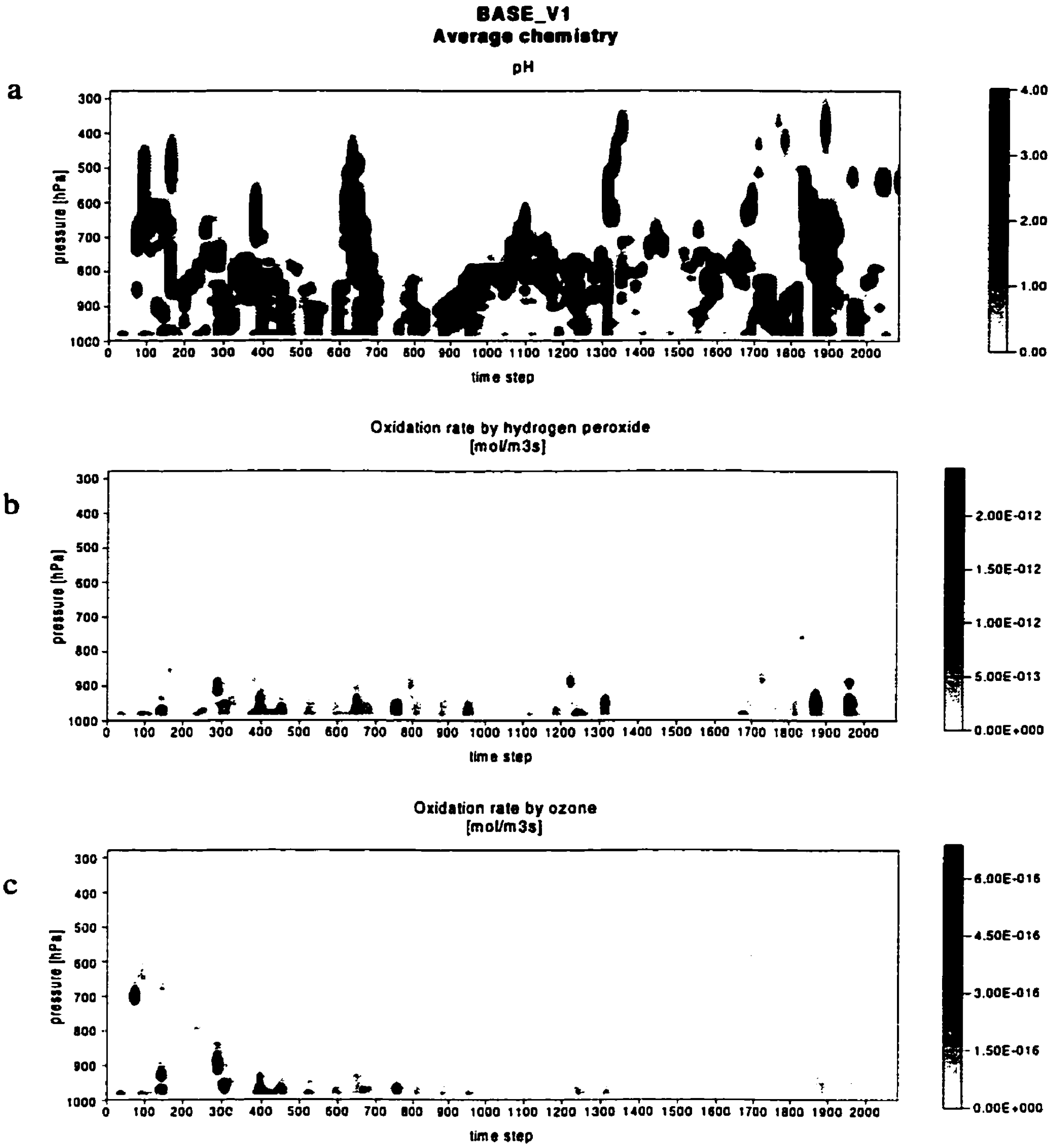


Figure 3.2.3 General characteristics of BASE_V1 average chemistry run.
(a) pH; rates of oxidation [mol/m^{3}s] by (b) hydrogen peroxide and (c) by ozone; concentrations of (d) hydrogen peroxide, (e) sulphur dioxide, and (f) sulphate [mol/m3].

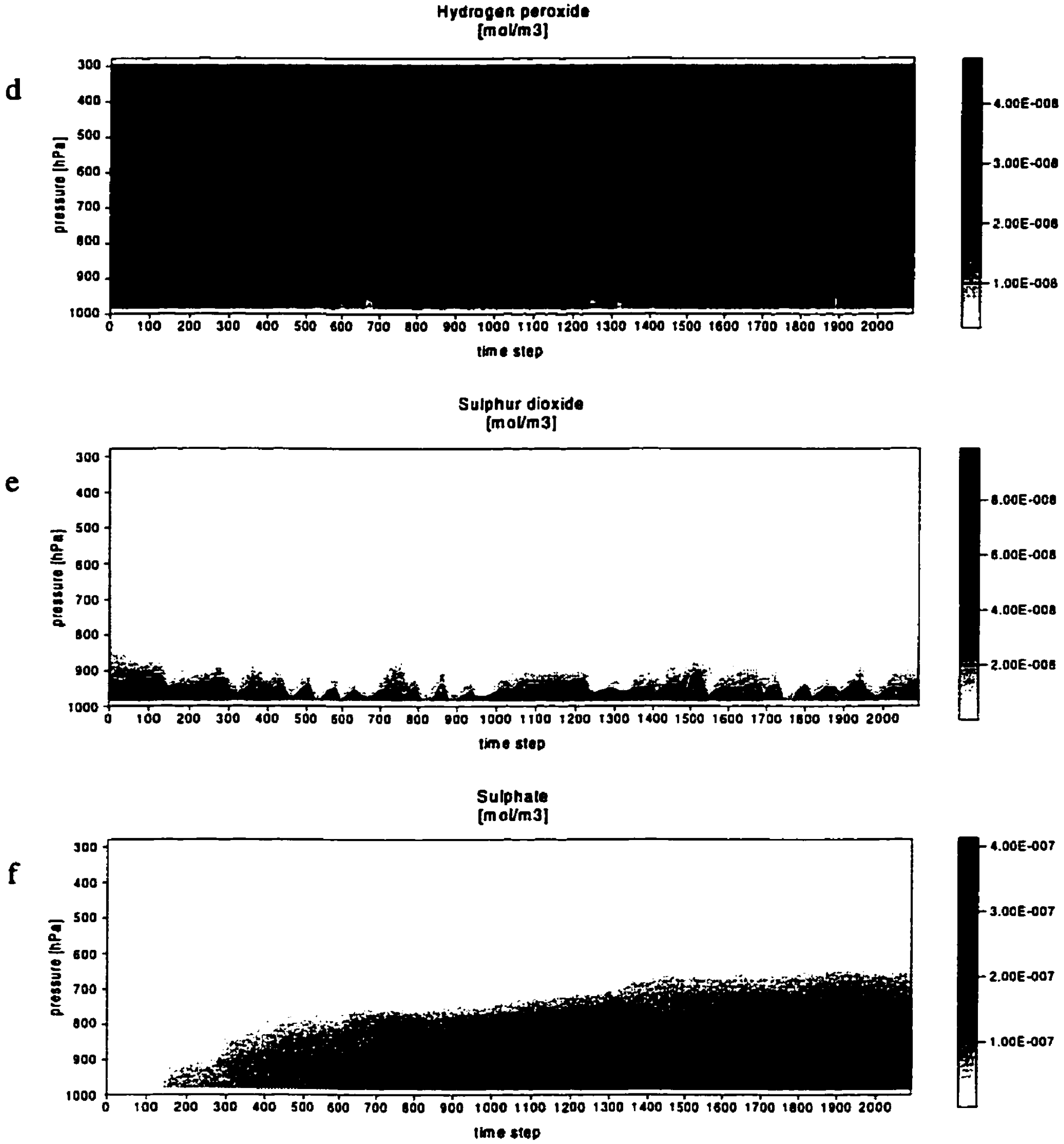


Figure 3.2.3 continued.

b) *General characteristics of the average chemistry run for BASE_V1*

The general characteristics of BASE_V1 with average chemistry are illustrated in figure 3.2.3, where the parameters of interest are pH, the oxidation rates in mol/m^{3}s, and sulphur dioxide, hydrogen peroxide, and sulphate concentrations in mol/m^3.

- *pH*

The clouds tend to be quite acidic in BASE_V1, with a pH around 3 or so for most of the simulation. Early in the simulation, the pH is around 4 and then decreases to a minimum of 2 near the surface by the end of the simulation period. Higher up the clouds tend to be slightly less acidic.

- *rates of oxidation by peroxide and ozone (mol/m^3 s)*

Hydrogen peroxide is the main oxidant. Its rate of oxidation is 1x 10^{-12} mol/m^{3}s on average reaching a peak near 2.4 x 10^{-12} mol/m^{3}s, with an efficiency of 3 to 4 orders of magnitude greater than that of ozone. The greatest conversion of sulphur dioxide to sulphate occurs near the surface.

- *hydrogen peroxide and sulphur dioxide (mol/m^3)*

The most noticeable feature in the plot of the hydrogen peroxide concentration is the forcing back to the initial concentration profile (refer to section 2.4). The wave pattern near the surface extends to almost 900 hPa and illustrates how the hydrogen peroxide is used up and/or washed-out and then is replenished according to the relaxing factor.

The sulphur dioxide concentration in the column over time mirrors its initial profile with high concentrations, at the surface, up to 10^{-7} mol/m^3 and an abrupt decrease in concentration with elevation. Here too, a wave pattern of depletion and replenishment is apparent especially just a little above the surface where the ambient sulphur dioxide concentrations are relatively small.

- *sulphate (mol/m^3)*

Sulphate accumulates in the column as the simulation progresses to reach a peak just above 4 x 10^{-07} mol/m^3 by the end of the simulation period.

- *relationships*

All of the parameters above are interrelated. Clearly a key parameter is the vertical profile of sulphur dioxide; it dictates which region of the troposphere will experience the greatest conversion of sulphur dioxide to sulphate. Cloud acidity is determined by the combined effect of all the compounds involved (see section 2.4). Sulphate adds to the acidity as it accumulates in the column. This accumulation is due to the forcing in the model to maintain the ambient concentration of the reagents and to the low frequency of washout by precipitation. The relative importance of the oxidants is pH dependent, and in this range of low pH values, ozone's contribution can be considered insignificant when compared to that of hydrogen peroxide.

c) *Comparison between parcel chemistry and average chemistry general characteristics for BASE_V1*

As it turns out, the general characteristics of the parcel chemistry run of BASE_V1 are almost identical to those of the average chemistry run. There are some small differences between the runs and to illustrate these, column integrated values are compared in one-to-one scatter plots in figure 3.2.4.

- *hydrogen ion (mol/m^2)*

Instead of comparing an average pH for the column, as this is difficult to interpret and somewhat misleading, the total amount of hydrogen ion in the column is used as a measure of acidity. The scatter plot and linear fit of the hydrogen ion concentration suggest that in the parcel chemistry run it is nearly identical to that in the average chemistry run.

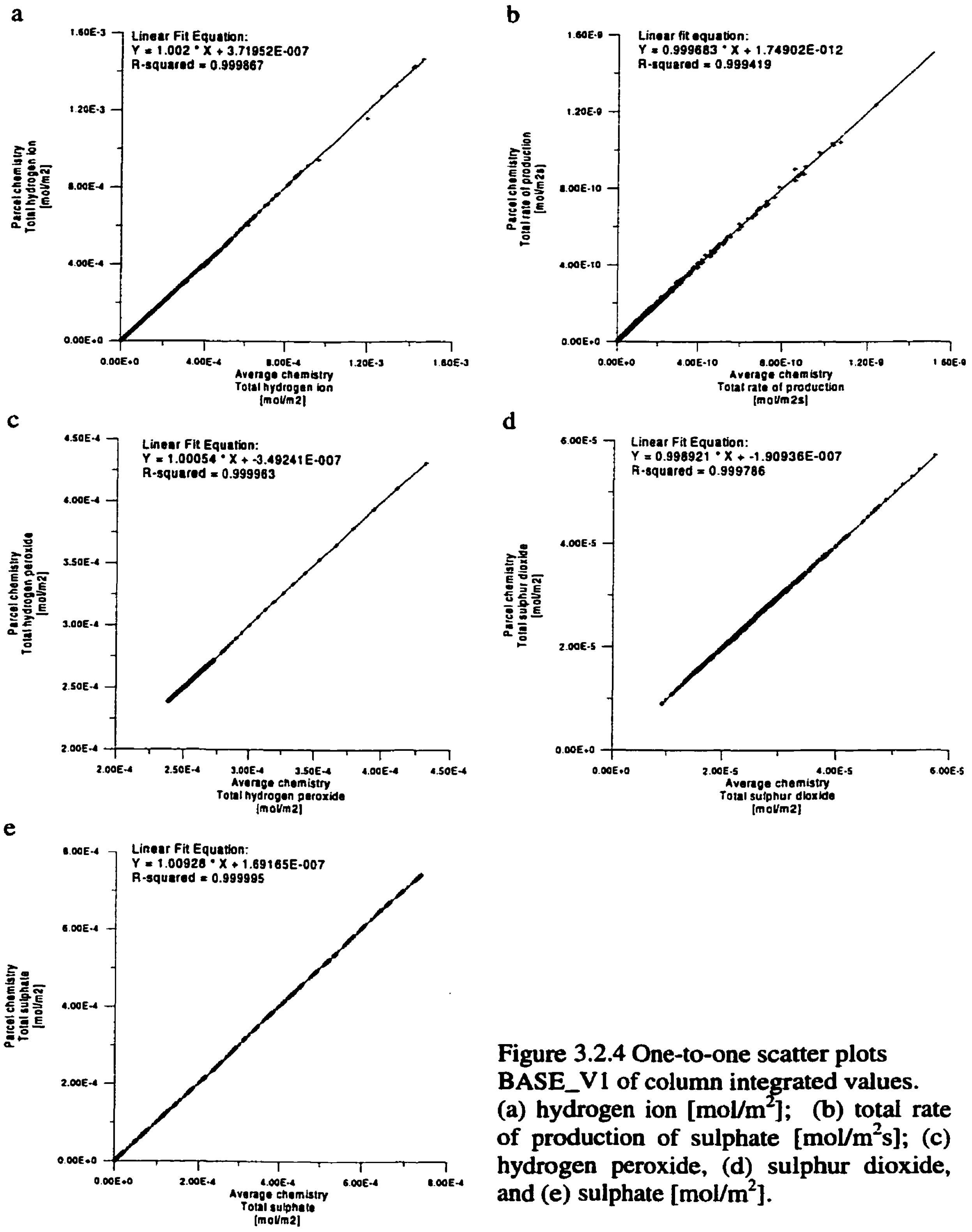


Figure 3.2.4 One-to-one scatter plots BASE_V1 of column integrated values. (a) hydrogen ion [mol/m^2]; (b) total rate of production of sulphate [mol/m^{2}s]; (c) hydrogen peroxide, (d) sulphur dioxide, and (e) sulphate [mol/m^2].

- *total rate of sulphate production (mol/m^2 s)*

The total rate of sulphate production is the sum of the rates of sulphur dioxide oxidation by hydrogen peroxide and by ozone. The scatter plot for the column total production rate displays very little change between the parcel chemistry run and the average chemistry run.

- *hydrogen peroxide and sulphur dioxide (mol/m^2)*

Again there is little variation in the concentrations of hydrogen peroxide and sulphur dioxide between the two methods of applying the in-cloud chemistry.

- *sulphate (mol /m^2)*

There is a very close match between the two applications of in-cloud chemistry as neither the scatter plot nor the linear fit (which is close to the one-to-one line) reveals significant variation.

- *relationships*

The differences found for the total rate of oxidation, the amount of hydrogen ion in the column and the concentrations of hydrogen peroxide, sulphur dioxide, and sulphate between the parcel chemistry and the average chemistry runs are too small to be significant.

To further illustrate the small differences in sulphate production between the average and parcel chemistry runs, figure 3.2.5 is the difference field for sulphate. The difference is defined as parcel chemistry minus average chemistry, so that when this difference is positive (negative) there is more (less) sulphate in the column in the parcel run.

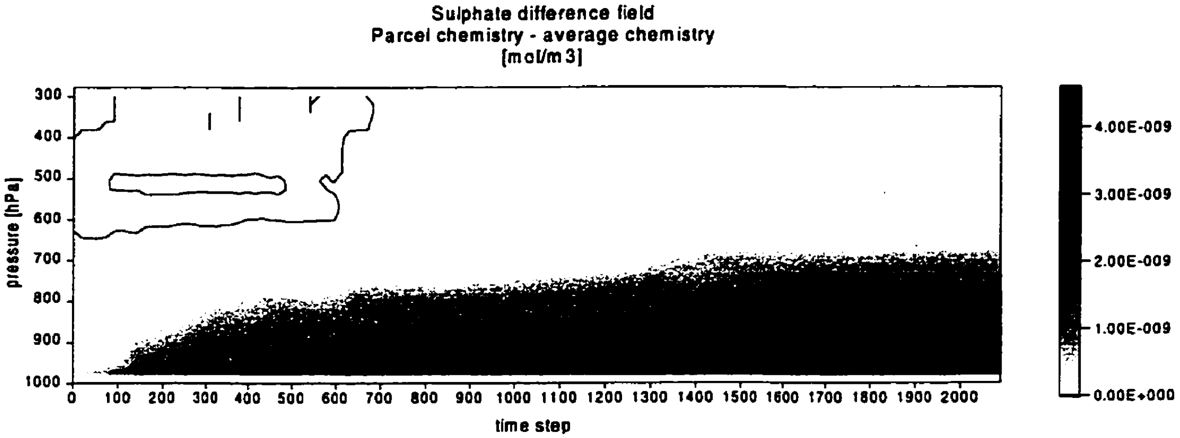


Figure 3.2.5 Difference field for sulphate in mol/m^3 for BASE_V1. The difference is defined as parcel chemistry concentration minus average chemistry concentration.

The difference field for sulphate in BASE_V1 shows positive values it suggests that sulphur dioxide is oxidized slightly more efficiently in the parcel chemistry. The difference reaches a maximum magnitude of 4.6 x 10^{-09} mol/m^3 by the end of the simulation period. Comparing the rise in sulphate concentration to the concentration of sulphate in the average chemistry run (panel f of figure 3.2.3), the change is in the range of only a few percent. This can be considered an insignificant change.

3.3 Doubled hydrogen peroxide run

3.3.1 Chemical scenario

In this second scenario, the initial concentration of hydrogen peroxide is doubled to 2 ppb while the other profiles remain unchanged, this scenario will be referred to as 2 x H_2O_2. This is a relatively hypothetical scenario selected to simulate conditions where the hydrogen peroxide concentrations are high in a somewhat non-polluted environment.

3.3.2 Simulation runs and comparisons

a) *General characteristics of the average chemistry run for 2 x* H_2O_2

Figure 3.3.1 describes the general characteristics of the average chemistry run for 2 x H_2O_2. In many ways, the features are very similar to that for BASE_V1. Differences with respect to BASE_V1 average chemistry run are highlighted below.

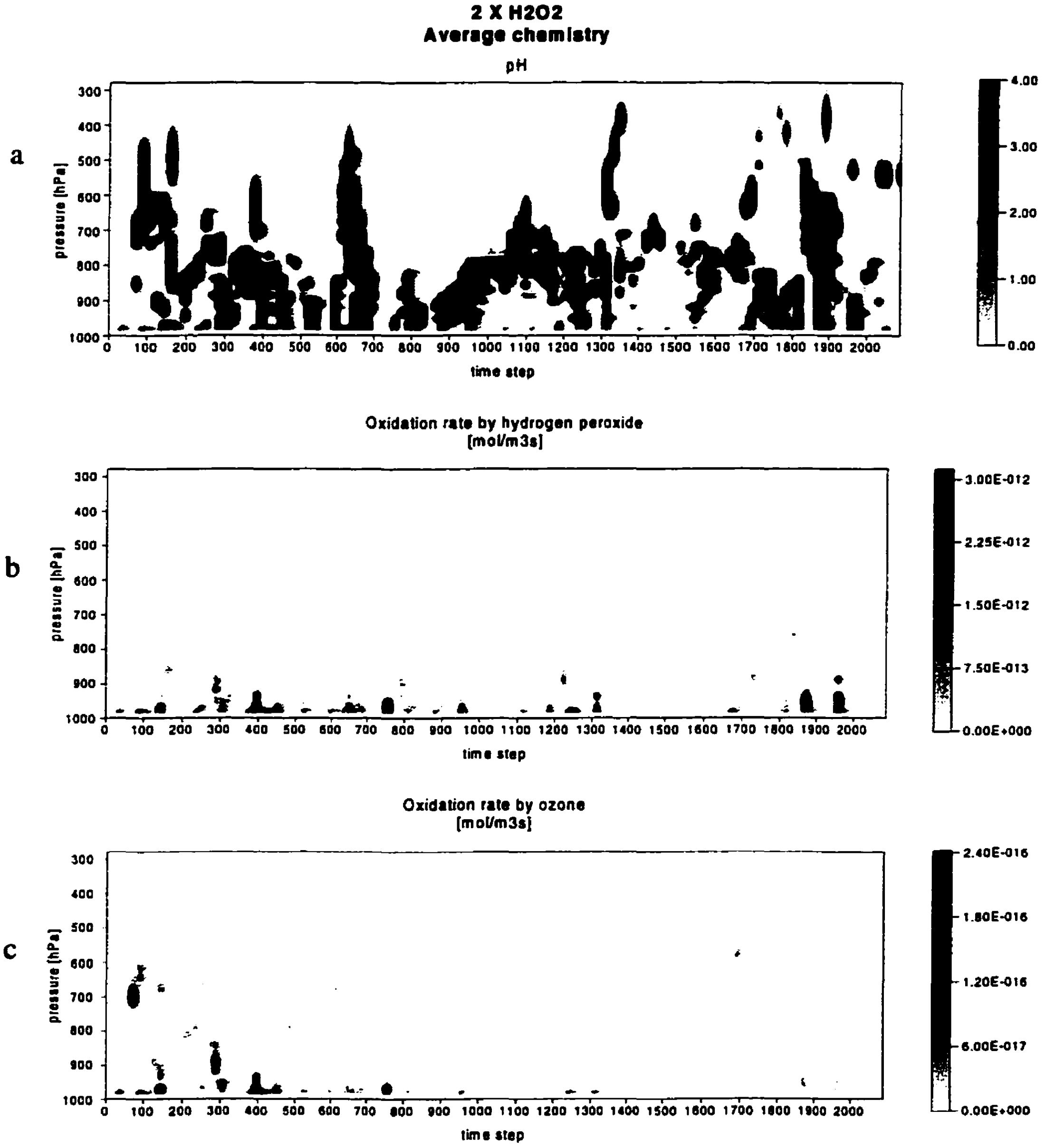
- *pH*

Overall acidity of the clouds has increased slightly, with pH values just below 3 for most of the simulation.

- *rates of oxidation by peroxide and ozone* (mol/m^3s)

Where oxidation takes place is the same as in BASE_V1, but the rate of oxidation by peroxide has increased to an average rate of 1.5 x 10^{-12} mol/m^3s and a peak of 3.1 x

10^{-12} mol/m^{3}s. Ozone's contribution to the production of sulphate is still insignificant compared to hydrogen peroxide, and its rate of oxidation has decreased by a factor of 2 compared to BASE_V1.


2 X H2O2
Average chemistry
pH

Oxidation rate by hydrogen peroxide [mol/m3s]

Oxidation rate by ozone [mol/m3s]

Figure 3.3.1 Same as figure 3.2.3 but for the 2 x H_2O_2 run.

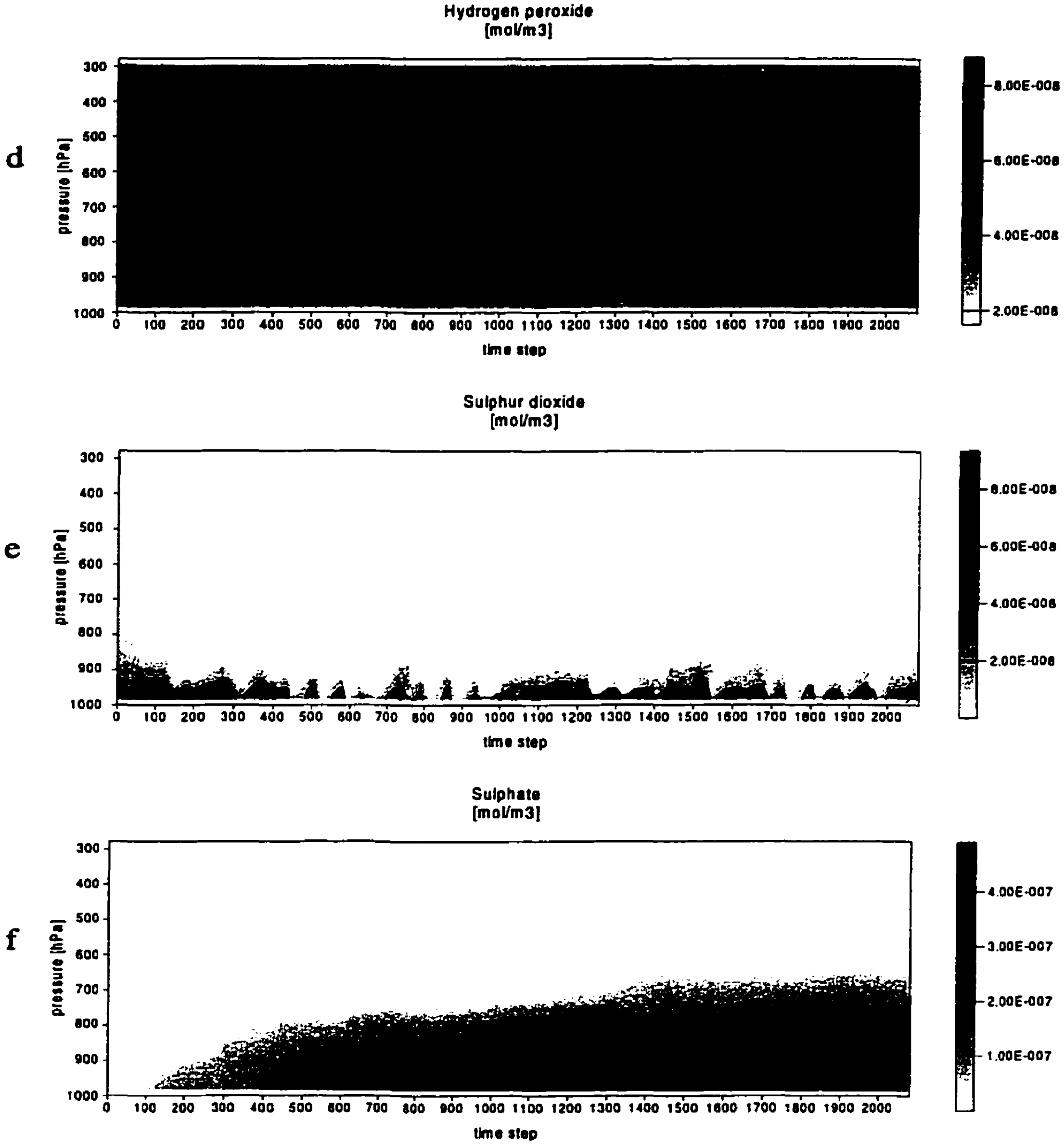


Figure 3.3.1 continued.

- *hydrogen peroxide and sulphur dioxide concentrations (mol/m^3)*

The wave pattern described in section 3.2.2 is evident here both for hydrogen peroxide and sulphur dioxide. Since the concentration of hydrogen peroxide is doubled for this scenario, it is not depleted to the same extent or up to the same elevation. The sulphur dioxide concentration is lower than in BASE_V1.

- *sulphate (mol/m^3)*

The way in which sulphate accumulates in the column as the simulation progresses in 2 x H_2O_2 is the same as for BASE_V1, but the concentrations are greater reaching a peak of 4.9 x 10^{-07} mol/m^3 by the end of the simulation.

- *relationships*

The relationships for 2 x H_2O_2 are similar to those of BASE_V1. The increased oxidation by the main oxidant results in a reduced concentration of sulphur dioxide and an increase in sulphate. Though the initial concentration of hydrogen peroxide is doubled, the rate of oxidation by peroxide is not doubled but increases by 1.2 to 1.5 times. The effect of doubling hydrogen peroxide levels is therefore non-linear. The acidity of the clouds in the 2 x H_2O_2 average chemistry run again limits ozone's efficiency. Ozone's rate is further reduced, compared to BASE_V1, because there is less sulphur dioxide available in the column.

b) *Comparison between parcel chemistry and average chemistry general characteristics for 2 x H_2O_2*

Comparisons of column integrated values by one-to-one scatter plots for 2 x H_2O_2 (figure 3.3.2) are qualitatively very similar to those for BASE_V1. The same conclusion may therefore be drawn as in BASE_V1, that applying in-cloud chemistry to the individual parcels of the sub-grid scale clouds does not significantly impact on sulphate production.

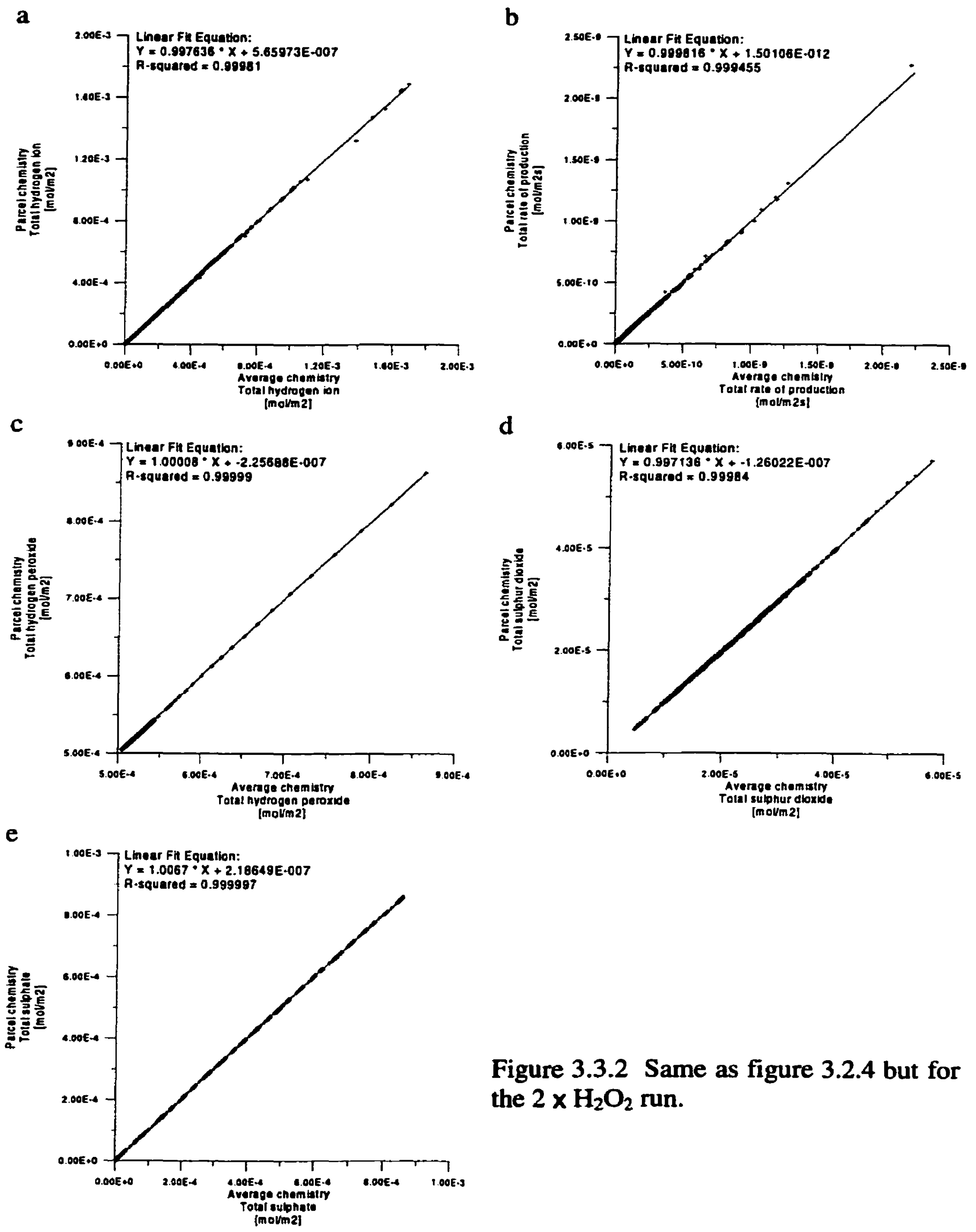


Figure 3.3.2 Same as figure 3.2.4 but for the 2 x H_2O_2 run.

3.4 Increased sulphur dioxide run

3.4.1 Chemical scenario

The third hypothetical scenario employs an increased sulphur dioxide profile which is representative of concentrations found in a polluted environment (Isaac *et al.*, 1992). All other chemical profiles, hydrogen peroxide included, are the same as in BASE_V1. This run will be referred to as INC_SO_2.

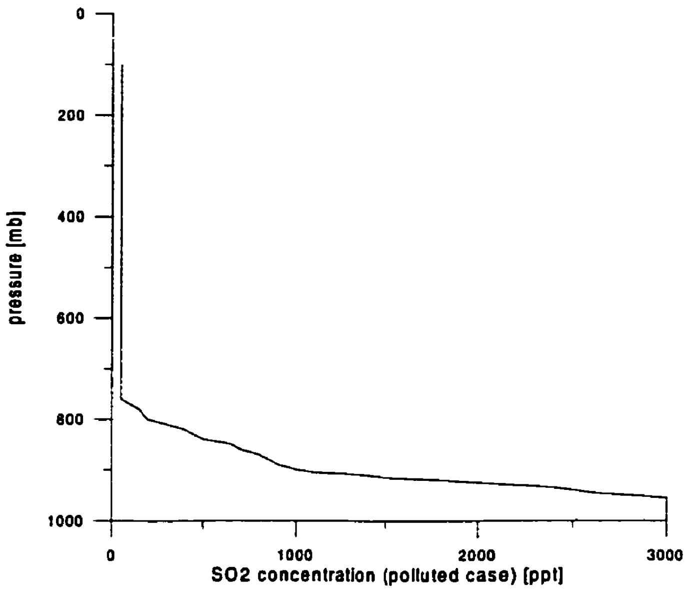


Figure 3.4.1 Concentration profile of sulphur dioxide representative of a polluted environment. This profile used for both INC_SO_2 and POLLUT runs.

3.4.2 Simulation runs and comparisons

a) *General characteristics of the average chemistry run for INC_SO$_2$*

Figure 3.4.2 displays the pH, rates of oxidation and concentration of the reagents and of sulphate, for the length of the simulation period applying average chemistry. The description that follows is in relation to BASE_V1.

- *pH*

The clouds tend to be more acidic overall, and noticeably so at higher elevations than in BASE_V1.

- *rates of oxidation by hydrogen peroxide and ozone (mol/m^{3}s)*

The rate of oxidation by peroxide is increased compared to BASE_V1, with an average value of around 1.5 x 10^{-12} mol/m^{3}s and a peak of 3.2 x 10^{-12} mol/m^{3}s. Hydrogen peroxide is still the main oxidant, with increased sulphur dioxide oxidation at higher altitudes than in BASE_V1 as well. The rate by ozone has increased by an order of magnitude compared to BASE_V1.

- *hydrogen peroxide and sulphur dioxide concentrations (mol/m^3)*

Hydrogen peroxide is consumed up to higher elevations than in BASE_V1. The wave pattern resulting for the relaxation back to the initial concentration profile is still evident. Sulphur dioxide also exhibits the wave pattern, but since its concentration is increased, especially near the surface, it is not depleted nearly to the same extent as in BASE_V1.

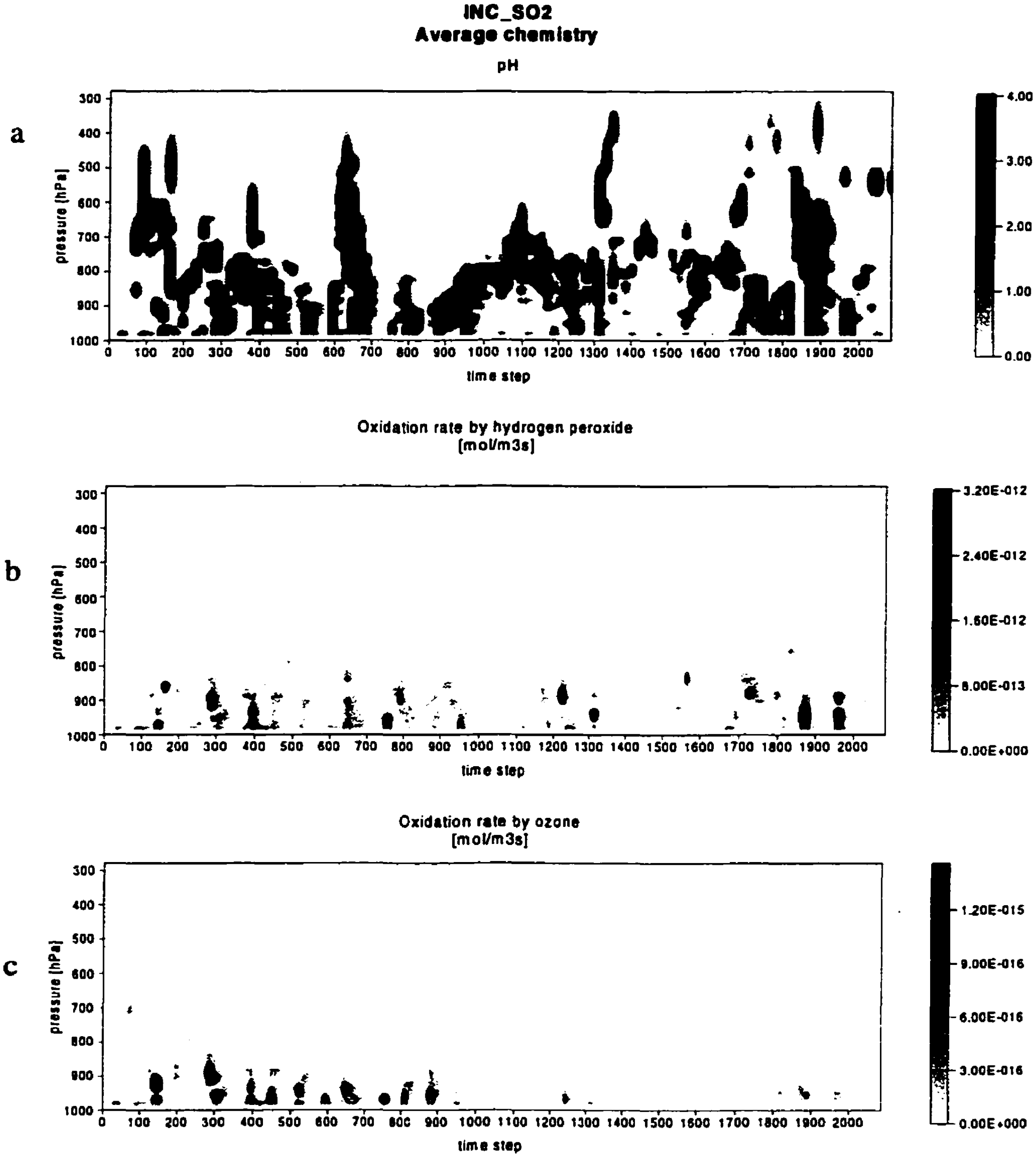


Figure 3.4.2 Same as figure 3.2.3 but for the INC_SO_2 run.

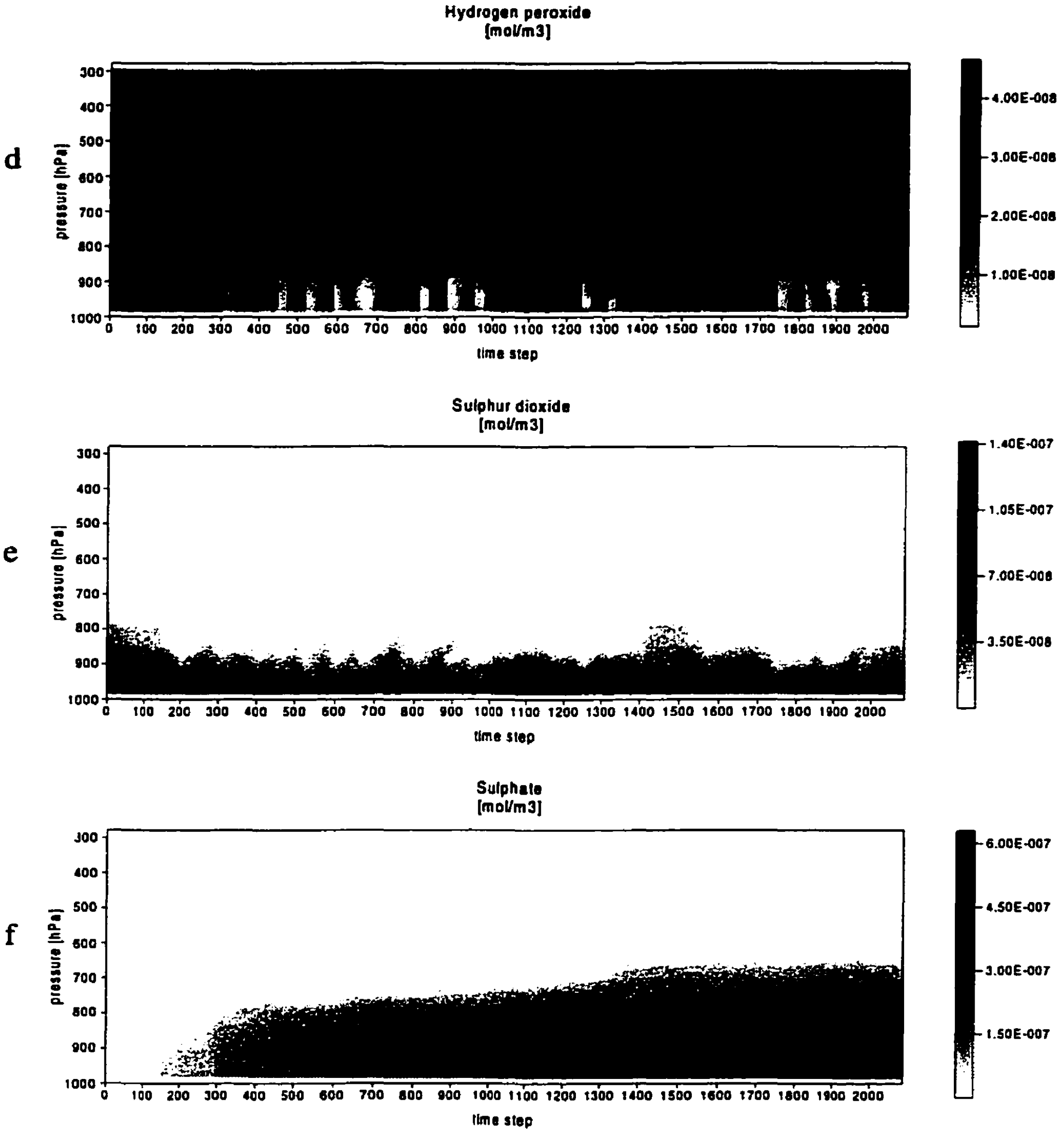


Figure 3.4.2 continued.

- *sulphate (mol/m^3)*

In accordance with the increase in the concentration of sulphur dioxide and rate of oxidation, there is more sulphate produced in relation to BASE_V1, reaching a maximum concentration of 6.3×10^{-7} mol/m^3.

- *relationships*

The increase in sulphur dioxide concentration in this scenario makes it more available for oxidation, thus increasing the oxidation rates by both hydrogen peroxide and ozone compared to BASE_V1. Hydrogen peroxide is still the dominant oxidant. The concentration of sulphate is even greater in this scenario than that found in $2xH_2O_2$ as more activity is occurring higher up in the column. The increased production of sulphate also increases the acidity in the clouds.

b) *Comparison between parcel chemistry and average chemistry general characteristics for INC_SO_2*

The one-to-one scatter plots comparing column integrated values for INC_SO_2 with average chemistry and with parcel chemistry are very similar to the plots in BASE_V1. Figure 3.4.3 shows the scatter plots and linear fits for INC_SO_2. It can be seen that the same conclusion can be drawn for this pair of simulation runs as for the previous two scenarios. The parcel chemistry does not influence sulphate chemistry in a significant manner.

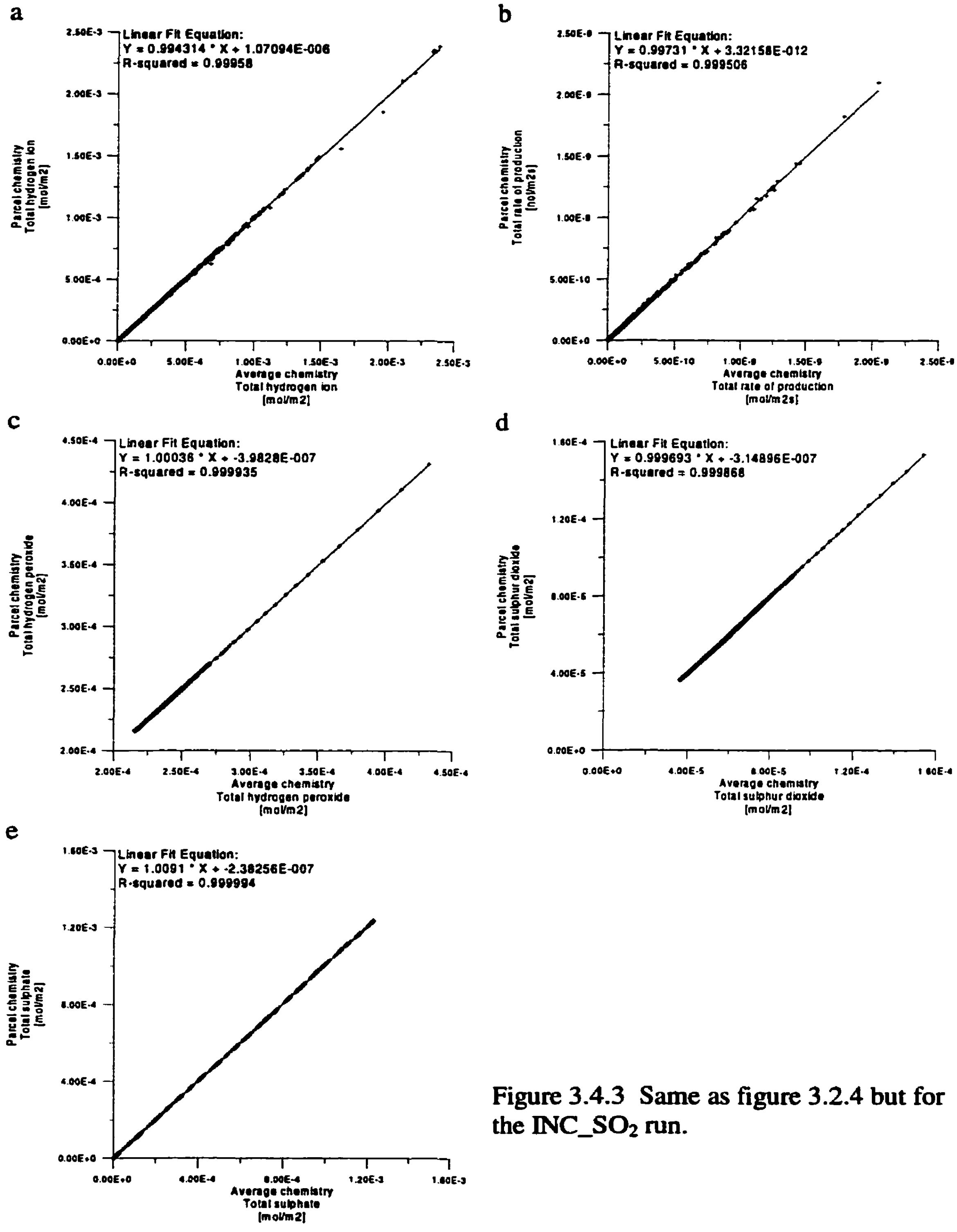


Figure 3.4.3 Same as figure 3.2.4 but for the INC_SO_2 run.

3.5 Polluted case

3.5.1 Chemical scenario

The last chemical scenario is the polluted case (POLLUT) where the doubled hydrogen peroxide and the increased sulphur dioxide profiles are employed in combination.

3.5.2 Simulation runs and comparisons

a) *General characteristics of the average chemistry run for POLLUT*

The general characteristics of POLLUT are illustrated in figure 3.5.1 and described below in relation to the average for all previous scenarios. They are very similar to both $2xH_2O_2$ and INC_SO_2.

- *pH*

Cloud acidity is greater than in BASE_V1 and INC_SO_2. Towards the end of the simulation period, near the surface, the pH is near 1.7 in the main body of the clouds.

- *rates of oxidation by peroxide and ozone (mol/m^3s)*

The rate of oxidation by hydrogen peroxide is about twice as large as it is in BASE_V1, at just about 2×10^{-12} mol/m^3s and a peak at 5.2×10^{-12} mol/m^3s. The rate for ozone is less than in BASE_V1 but greater than in $2 \times H_2O_2$.

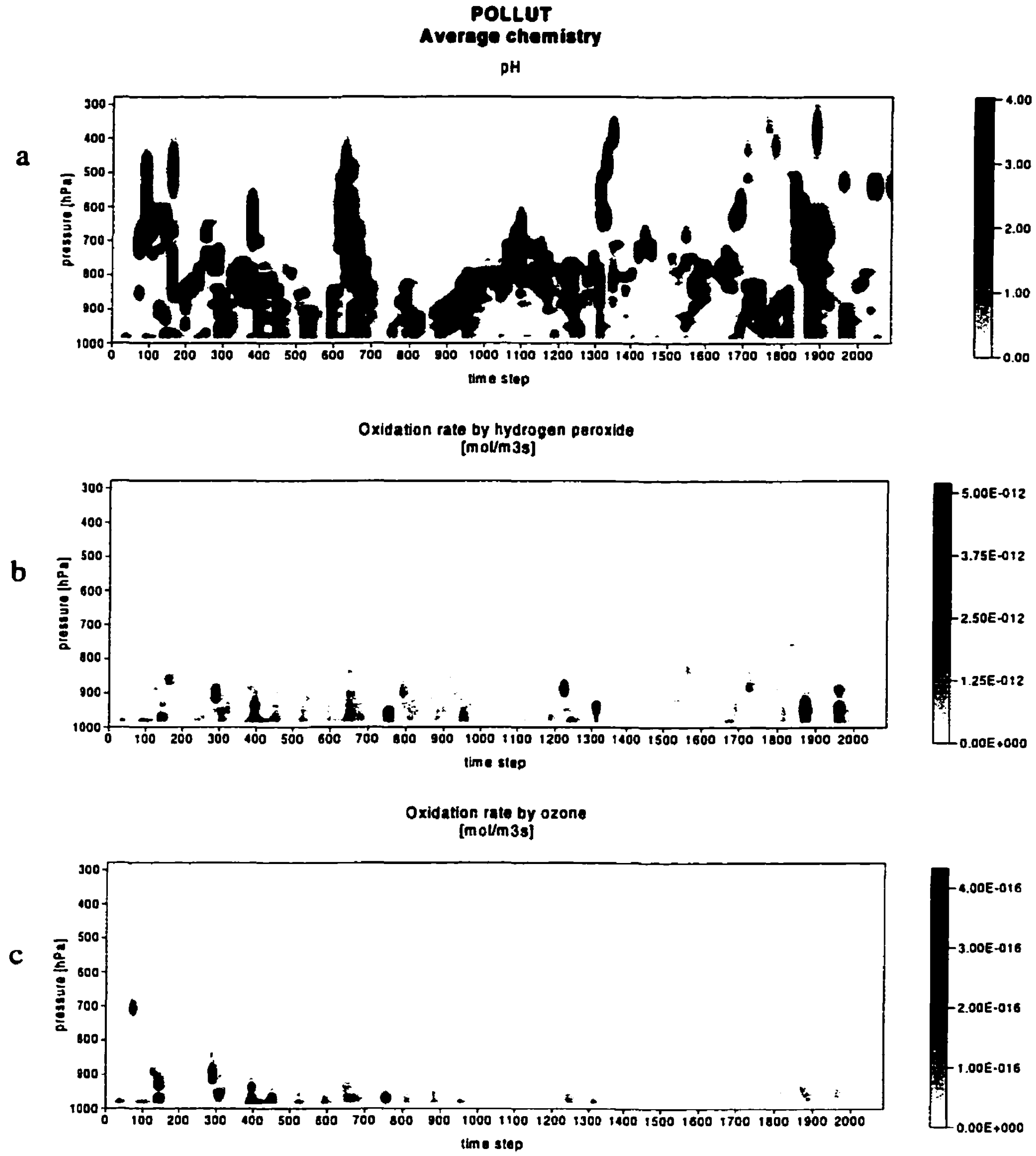


Figure 3.5.1 Same as figure 3.2.3 but for the POLLUT run.

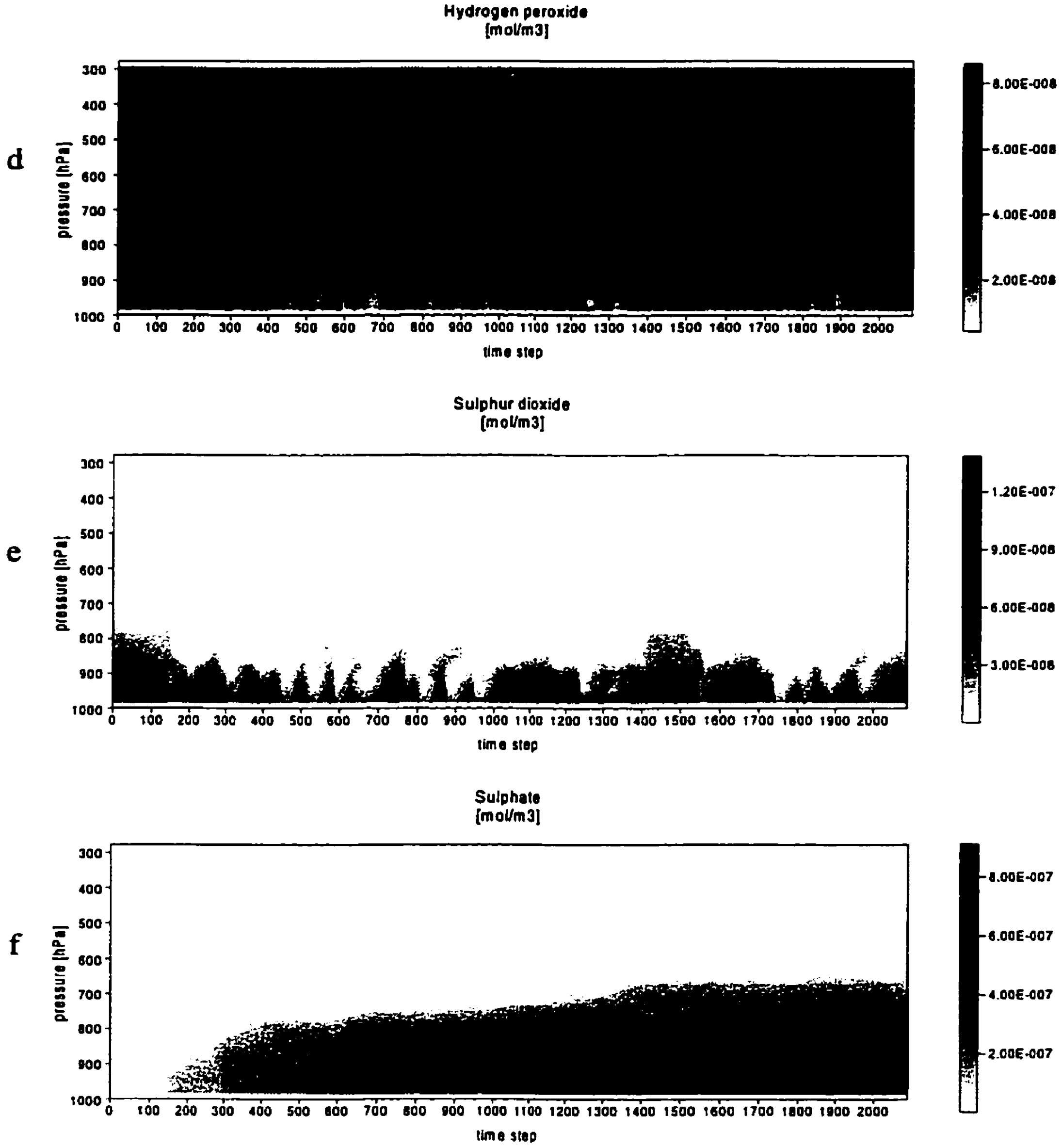


Figure 3.5.1 continued.

- *hydrogen peroxide and sulphur dioxide concentrations (mol/m^3)*

Although the concentration of hydrogen peroxide is the same as in 2xH_2O_2 in this simulation run, it is depleted up to a higher altitude. Similarly, sulphur dioxide is also depleted to a greater extent than in INC_SO_2. For both compounds, the wave pattern is still very evident.

- *sulphate (mol/m^3)*

The concentration of sulphate is doubled compared to BASE_V1 and is greater by 50% than in INC_SO_2. The accumulation of sulphate in the column builds to about 800 hPa.

- *relationships*

As in the previous scenarios, the relationships can be described in the same way as for BASE_V1. The vertical profile of sulphur dioxide determines where the most conversion takes place. Doubling the initial ambient concentration of hydrogen peroxide in addition to the increase in the sulphur dioxide leads to a doubling of the rate of oxidation by hydrogen peroxide. This in turn leads to a doubling in the sulphate concentration in the column and to an accumulation higher into the column. The forcing in the model to maintain ambient concentrations of the reagents, and the low frequency of removal from the column results in the accumulation of sulphate in the column. Ozone's efficiency is less in POLLUT than in BASE_V1 despite increased amounts of sulphur dioxide. This is likely because the greater concentration of hydrogen peroxide in the column allows this main oxidant to out-compete ozone.

b) *Comparison between parcel chemistry and average chemistry general characteristics for POLLUT*

The parcel chemistry run looks very much the same as for the average chemistry simulation run (figure 3.5.1). The resulting one-to-one scatter plots for POLLUT are also very similar to those of the BASE_V1 and other previous scenarios. Figure 3.5.2 displays the scatter plots as well as their linear fits. It can be concluded that, under the chemical conditions characteristic of POLLUT, parcel chemistry does not significantly alter the sulphate production in the sub-grid scale clouds of LCM11.

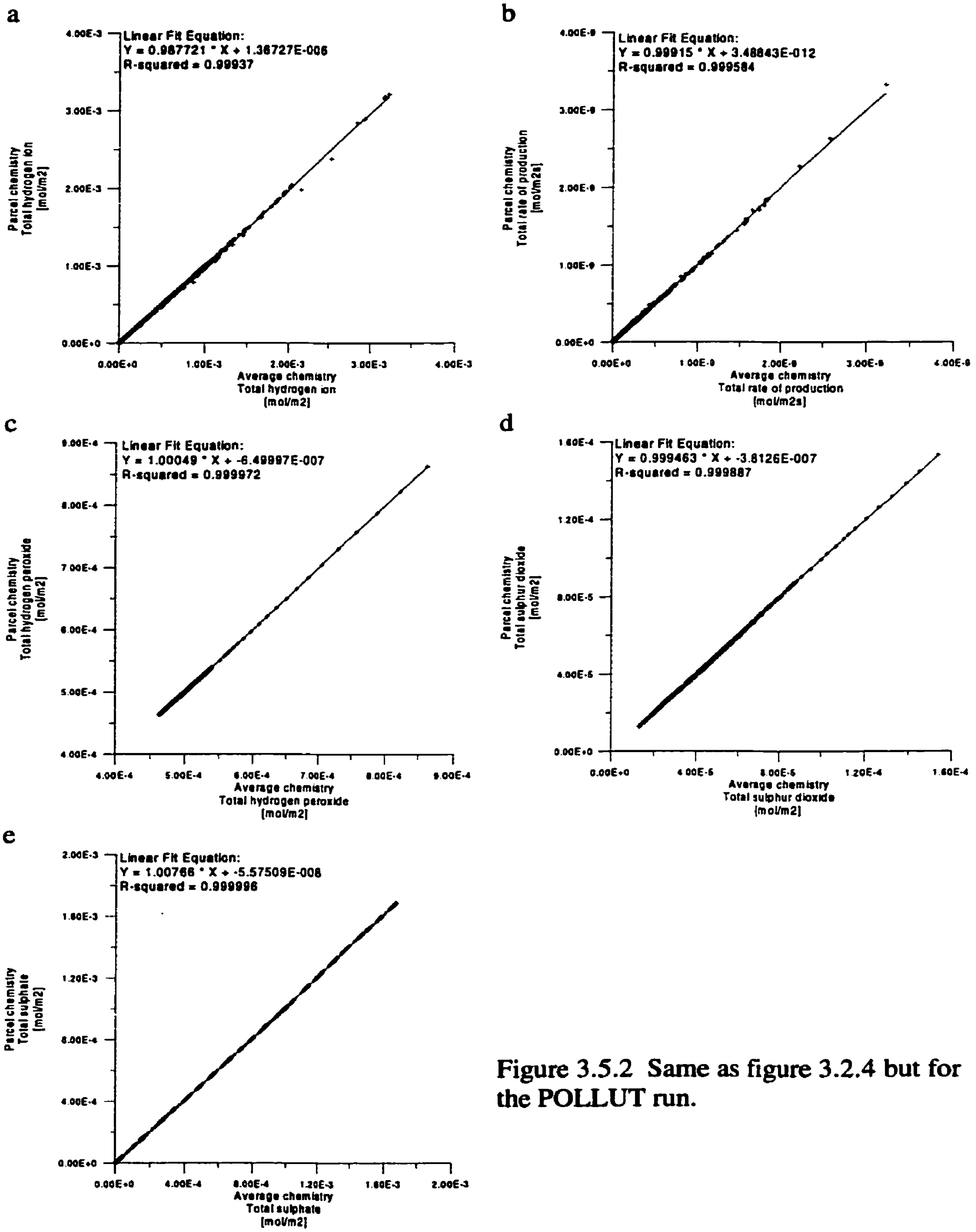


Figure 3.5.2 Same as figure 3.2.4 but for the POLLUT run.

3.6 Two kilometre vertical motion cap

As mentioned earlier, the sub-grid scale vertical motion in LCM11 is restricted. The scenarios addressed so far have used a one kilometre limit to vertical motion away from the reference level. This restriction however can be extended. It is expected that for parcels travelling upwards, this may lead to a greater LWC in the cloud and thus may influence the sulphate production in the cloud.

a) General characteristics of the average chemistry run for BASE_V2

The following simulation extends this vertical cap to two kilometres from the reference level. It is performed under the same chemical scenario as the base run BASE_V1 and so is called BASE_V2.

The general characteristics of the BASE_V2 simulation and the comparisons between average chemistry and parcel chemistry runs are analogous to those obtained for BASE_V1. The clouds are relatively acidic especially at the surface and near the end of the simulation period; hydrogen peroxide is the main oxidant as ozone's efficiency is limited by the low pH levels; sulphate accumulates in the column and increases the acidity of the clouds. Applying the parcel chemistry is found not to significantly modify sulphate production.

b) Comparison of LWC and sulphate production in BASE_V2 to BASE_V1

LWC and sulphate concentrations in BASE_V1 and BASE_V2 are compared in order to take a look at how the vertical motion restriction affects sulphate production. The average LWC for BASE_V2 and the difference field in LWC are presented in figure 3.6.1, where the difference is defined as BASE_V2 minus BASE_V1 such that a positive (negative) difference means that there is more (less) LWC in BASE_V2. In figure 3.6.2, the column integrated LWC are compared in a one-to-one scatter plot.

In BASE_V2, the LWC appears slightly increased in the lower part of the troposphere, while on the upper edge of some clouds, there is a little less LWC produced (figure 3.6.1b). The linear fit of the scatter plot (figure 3.6.2) also suggests an overall increase with a slope of 1.14 ($r^2 = 0.73$).

The difference field for sulphate is illustrated in figure 3.6.3, where the difference is again defined BASE_V2 minus BASE_V1 such that a positive (negative) difference means that there is more (less) sulphate in BASE_V2.

The sulphate concentration in BASE_V2 is slightly greater than in BASE_V1, by around 10 % in some instances as suggested by figure 3.6.3 (refer to figure 2.3.2 panel f). However in terms of total production, as demonstrated in the one-to-one scatter plot, there is little variation overall. Despite the trend towards more LWC where parcels are allowed to travel further from their reference level, there is only a small increase in sulphate production.

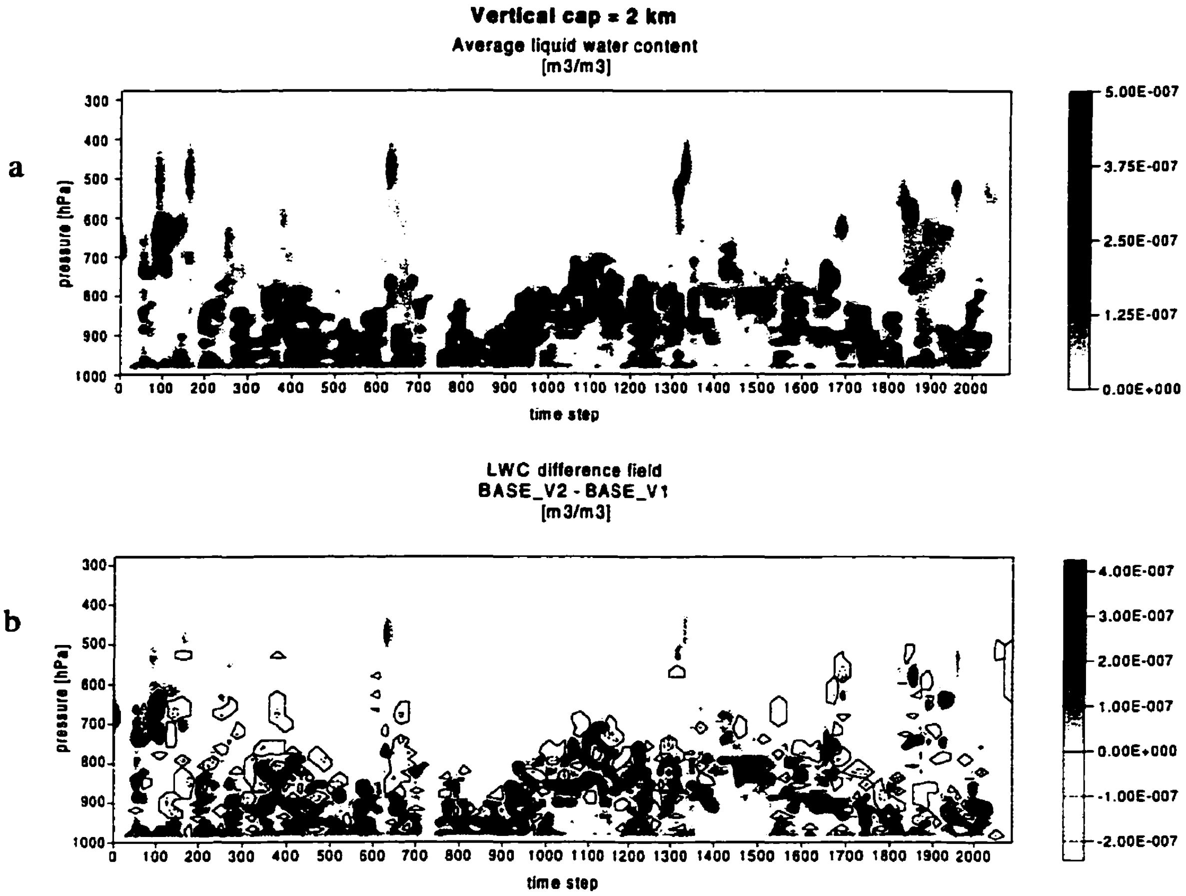


Figure 3.6.1 (a) The liquid water content for BASE_V2 where vertical cap = 2 km. Note that this is not to the same scale as figure 3.2.2a. (b) The difference field for LWC between simulation runs between BASE_V2 and BASE_V1, where the difference is BASE_V2 – BASE_V1.

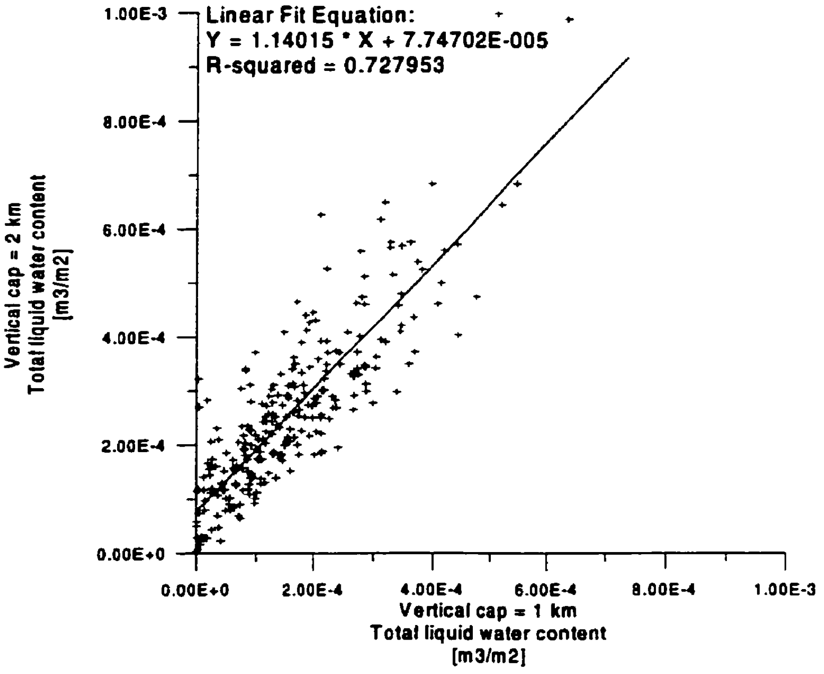


Figure 3.6.2 The one-to-one scatter plot and linear fit results for column integrated LWC for BASE_V2 versus BASE_V1.

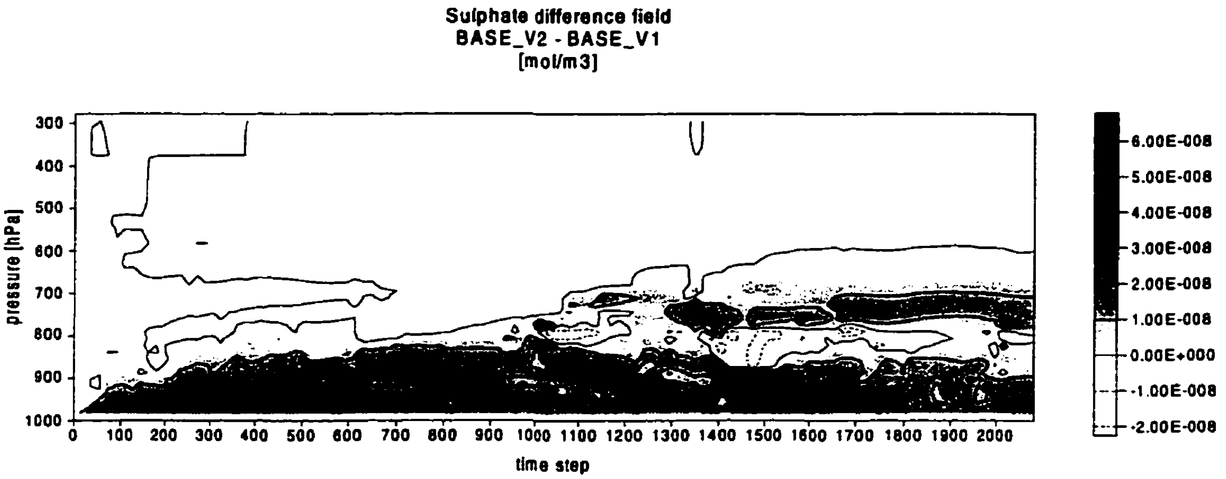


Figure 3.6.3. The difference field for sulphate concentration BASE_V2 – BASE_V1 in mol/m^3.

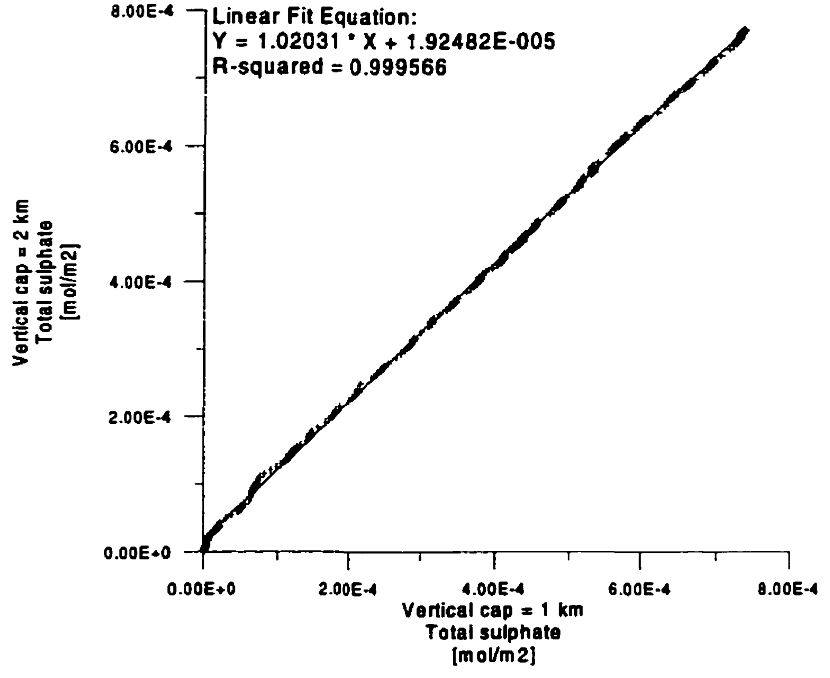


Figure 3.6.4 The one-to-one scatter plot and linear fit results for column integrated sulphate concentration [mol/m^2] for BASE_V2 versus BASE_V1.

Chapter 4: Discussion and conclusions

The objective of this study was to determine whether it is necessary to incorporate sub-grid scale parcel chemistry in NARCM's local climate model LCM11 when the UQÀM sub-grid scale cloud scheme is employed.

To answer this question, LCM11 was run in parallel simulation runs, with its in-cloud chemistry applied to average cloud parameters ("average chemistry") and with its in-cloud chemistry applied to each sub-grid scale parcel ("parcel chemistry"). The parallel runs were performed with data from Trout Lake, Ontario, for the month of June 1989 and were repeated for a number of hypothetical scenarios.

Total amount of hydrogen ion, column total rate of production of sulphate, and total hydrogen peroxide, sulphur dioxide and sulphate concentrations were compared within parallel runs in one-to-one scatter plots, and variations in these parameters were evaluated using linear fits, and in one instance, using a difference field.

4.1 Sub-grid scale parcel chemistry does not significantly alter sulphate production

- *Results for cases with vertical motion restriction equal to one kilometre*

Sulphate production, though slightly increased, is not significantly modified by the implementation of sub-grid scale parcel chemistry with sub-grid scale clouds. This conclusion is arrived at based on the considerable similarities within parallel runs in the general characteristics and column total rate of oxidation and the total concentrations of sulphur dioxide, hydrogen peroxide, and sulphate. These similarities within parallel runs were true of all chemical scenarios assayed, suggesting that the implementation of sub-grid scale parcel chemistry in LCM11 is inconsequential when modelling the climate of a continental somewhat remote site in unpolluted, high hydrogen peroxide, polluted and both polluted and high hydrogen peroxide conditions.

It can also be seen that the LCM11 reproduces results that are quite representative of the initial conditions. For instance, sulphate production is greatest when both sulphur dioxide and hydrogen peroxide concentrations are increased together. Also, although ozone is not nearly as efficient as hydrogen peroxide, the rate of oxidation by ozone increases when there is more sulphur dioxide available to ozone. This effect is illustrated when comparing the INC_SO_2 run to BASE_V1, where the rate of oxidation by ozone increases by an order of magnitude in response to the more polluted (high sulphur dioxide) conditions. The reverse is seen for 2xH_2O_2 as well as for POLLUT where the increased hydrogen peroxide reduces the amount of sulphur dioxide that is available to ozone.

- *Results for the case with vertical motion restriction equal to two kilometres*

The parallel runs in BASE_V2 yielded qualitatively the same results as BASE_V1. Again, the incorporation of sub-grid scale parcel chemistry did not alter sulphate production.

Since parcels are allowed to travel further in BASE_V2 than in BASE_V1, it was expected that the LWC would change between these runs and thus that the sulphate production would change. There was indeed a large variation in LWC and an increase denoted by the linear fit of the scatter plot for LWC between BASE_V2 and BASE_V1. There was also a small increase in sulphate. The changes in LWC were positive and negative depending which level of the column one examined, so one could argue that the changes in sulphate concentration due to these differences in LWC cancelled each other out upon summation. For this simulation period, increasing the distance that parcels may travel changed the amount of sulphate up to 10% in some instances but overall the total amount of sulphate produced changed little.

4.2 Why the impact of sub-grid scale parcel chemistry is small: a two-parcel analytical model

Dr. von Salzen, author of the in-cloud chemistry scheme for NARCM, has proposed an analytical model which may explain why the effect of sub-grid scale chemistry is small. This analytical model is very simple as it only considers two parcels with differing LWC.

First, it assumes that the concentration of sulphur dioxide in both parcels α and β decreases exponentially such that:

$$\frac{d[\mathrm{SO_2}]_\alpha}{dt} = -A \cdot LWC_\alpha \cdot [SO_2]_\alpha \ ; \tag{4.1}$$

$$\frac{d[\mathrm{SO_2}]_\beta}{dt} = -A \cdot LWC_\beta \cdot [SO_2]_\beta \ , \tag{4.2}$$

where $[SO_2]_n$ and LWC_n are the concentration of sulphur dioxide and liquid water content of parcel n, respectively. *A* is the rate of oxidation, therefore the rate of removal of sulphur dioxide in s^{-1} from the parcels. The rate of oxidation is assumed to be the same for both parcels.

Equations 4.1 and 4.2 lead to

$$[SO_2]_\alpha = [SO_2]_o \cdot \exp(-A \cdot LWC_\alpha \cdot t) \ ; \tag{4.3}$$

$$[SO_2]_\beta = [SO_2]_o \cdot \exp(-A \cdot LWC_\beta \cdot t) \ , \tag{4.4}$$

where $[SO_2]_0$ is the initial concentration in either parcel at time = t_0. Time t is set at 1200 seconds, which in LCM11 is the 20-minute time step. This can be illustrated by the following figure:

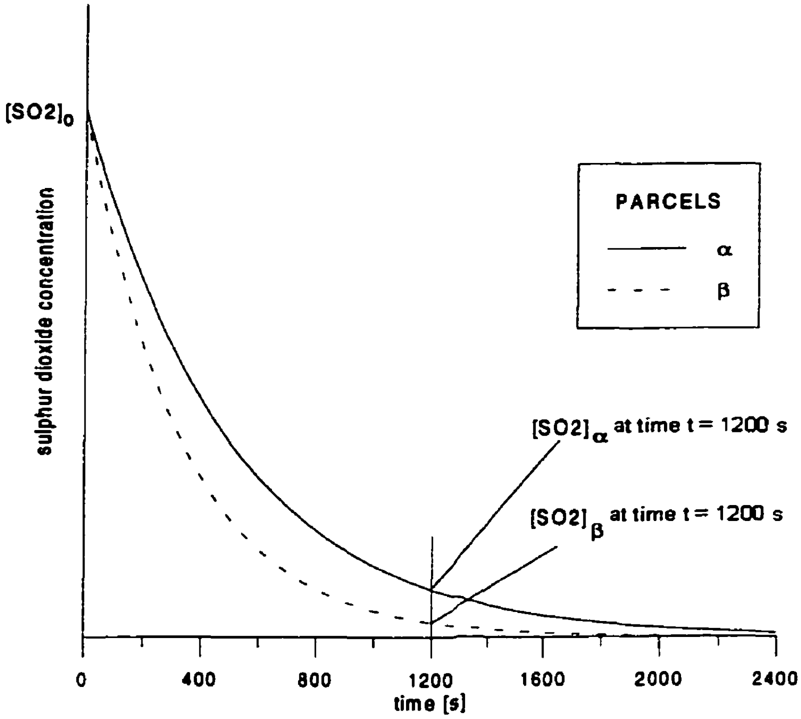


Figure 4.2.1: Example of exponential decrease of sulphur dioxide in parcels α and β.

If one were to calculate the concentration of sulphur dioxide at time t using an averaged liquid water content, denoted by $[SO_2]_{LWC}$, one would find:

$$[SO_2]_{LWC} = [SO_2]_o \cdot \exp(-A \cdot \frac{LWC_\alpha + LWC_\beta}{2} t) \ . \qquad (4.5)$$

If one were instead to take the concentration of sulphur dioxide for each parcel at time t and then average them, one would get $[SO_2]_P$:

$$[SO_2]_P = \frac{[SO_2]_\alpha + [SO_2]_\beta}{2} = \frac{[SO_2]_o}{2} \cdot \{\exp(-A \cdot LWC_\alpha \cdot t) + \exp(-A \cdot LWC_\beta \cdot t)\}. \quad (4.6)$$

The ratio between $[SO_2]_P$ and $[SO_2]_{LWC}$ is the variation in sulphur dioxide concentration between the two-parcel model using average chemistry and the two-parcel using parcel chemistry.

$$ratio = \frac{[SO_2]_P}{[SO_2]_{LWC}} = \frac{1}{2}\{\exp(B) + \exp(-B)\}, \text{ where } B = A \cdot \frac{(LWC_\alpha - LWC_\beta)}{2} \cdot t. \quad (4.7)$$

Where this ratio is greater than 1, sulphur dioxide is more concentrated in the model with parcel chemistry. More sulphur dioxide in the parcels means that less has been consumed and thus that less sulphate has been produced.

One can apply this analytical model to a hypothetical example of LWC distribution in the LCM11 sub-grid scale clouds scheme. Recall panel c of figure 2.3.2 where the LWC is distributed into the separate bins on the 830 hPa layer of time step 149 (which is an arbitrarily chosen turbulent level) and refer to figure 4.4.2 which is a continuation of figure 2.3.2. Using the two parcels from either extreme of the LWC distribution, LWC_α becomes 8 x 10^{-8} m^3/m^3 and LWC_β equals 2 x 10^{-9} m^3/m^3. An average for *A*, the rate of oxidation (here by hydrogen peroxide), is 7.55 x10^3 s^{-1}. Using the model time step of 1200 seconds, this gives a value of 0.35 for B. The ratio of $[SO_2]_P$ to $[SO_2]_{LWC}$ is 1.063. So this example of extreme LWC values in the LCM11 cloud scheme, the ratio reveals a difference in sulphur dioxide concentration of about 6%. Over many levels, this could add up to be quite significant.

It is important to remember that the assumptions stated above are not fully representative of the situation in LCM11. As can be seen in figure 4.4.2a, both LWC and the rate parameter vary considerably, in figure 4.4.2.b so does the pH; also, they are not independent of each other. The rate parameter is dependent on a number of factors, the inverse of the amount of hydrogen ion as well as the inverse of LWC being among them. Thus they appear anti-correlated and the product of the rate with LWC will not change much over the bins. Also, in figure 4.4.2b, the concentrations of sulphur dioxide and hydrogen peroxide do not vary much (concentrations in bins 1-21 are background concentrations in the non-cloudy part of the layer). The sulphate concentration plotted here is the amount that is produced in this example, and it does not change much either. Thus even when LWC varies considerably between LCM11 sub-grid scale parcels, implementation of sub-grid scale parcel chemistry does not significantly alter the production of sulphate in the sub-grid scale clouds.

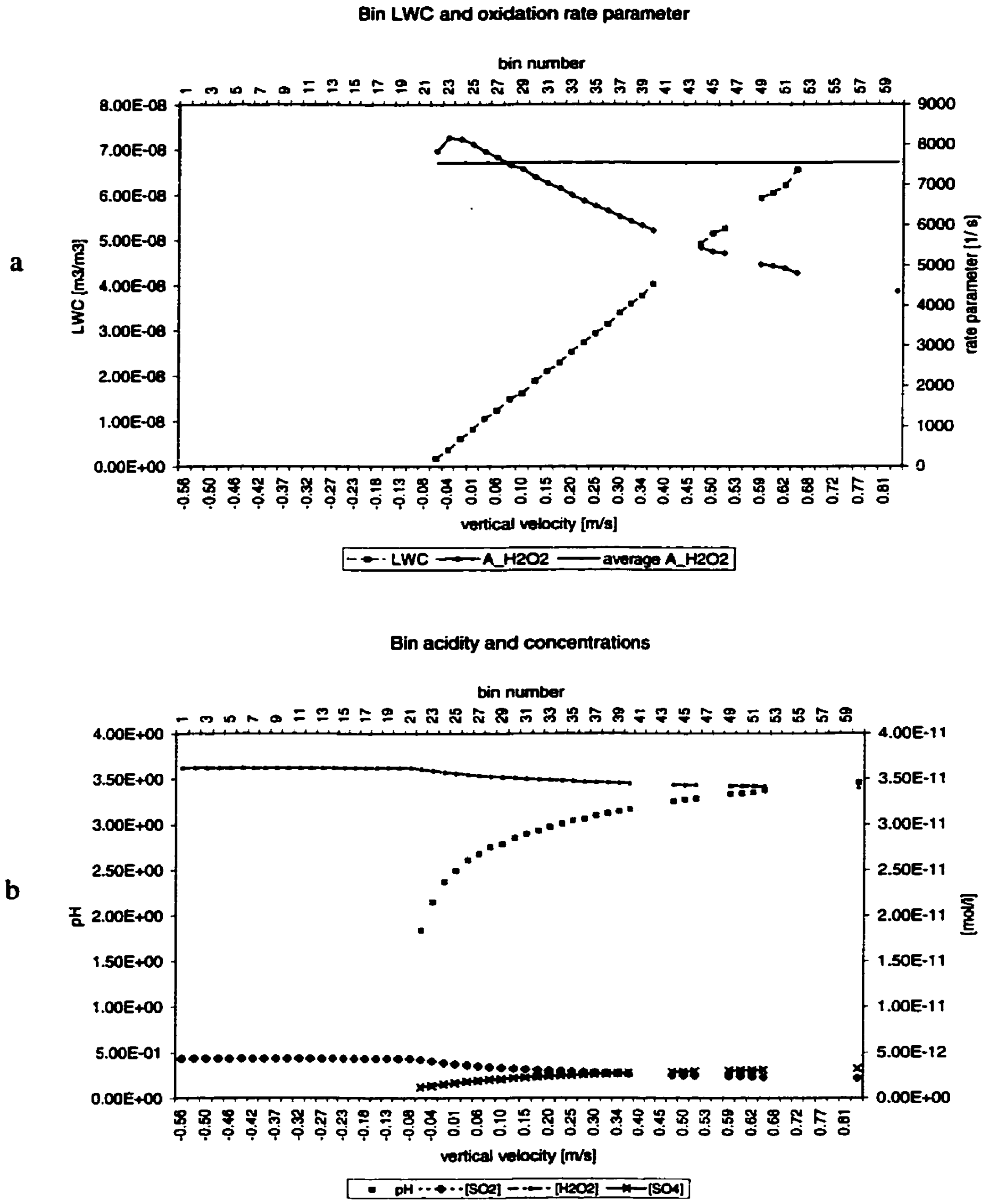


Figure 4.4.2 Continuation of example illustrated in figure 4.2.3.
(a) Bin LWC [m^3/m^3], hydrogen peroxide rate parameter A_H2O2 and average A_H2O2 [1/s]; (b) bin pH, and sulphur dioxide, hydrogen peroxide, and sulphate concentrations [mol/l].

4.3 This study in relation to previous work

As mentioned in the introduction, two previous studies have addressed the impact of sub-grid scale parameterization on chemistry modelling.

Walcek & Brankov (1994) used a model and assumptions that differed somewhat from the LCM11. Nevertheless, the low sensitivity of sulphate production to sub-grid scale parcel chemistry found for LCM11 is very similar to what Walcek & Brankov find in their simulation for summer conditions. They explained, "errors are calculated to be very small during summer months, primarily since there is so much sulphate in the air that clouds are fairly acidic, and with high concentrations of hydrogen peroxide, the non-linear ozone oxidation pathway is of minor importance", also "the oxidation rate is a fairly linear function of the amount of entrainment experienced by any point in a cloud, thus there is little error introduced by averaging the microstructure of the cloud" (Walcek & Brankov, 1994). The fact that the LCM11 simulation runs in this project were conducted with data from summer months may have contributed to the insensitivity of sulphate production to sub-grid scale parcel chemistry for the first reason quoted from Walcek & Brankov.

Matthijsen *et al.* (1997), presented results that differed from those obtained for the LCM11 runs. Their study is not truly comparable to the one performed for this project. The Matthijsen *et al.* study looks at sulphur dioxide budget in the marine boundary layer and not sulphate production in the atmosphere over the continent. The cloud scheme that they use to calculate fractional cloudiness is substantially different in approach from the UQÀM sub-grid scale cloud scheme. Their two-layer model includes production and loss mechanisms for sulphur dioxide that are not included in the LCM11. Furthermore, they are not concerned with the exact aqueous-phase chemical loss mechanisms of sulphur dioxide and employ an all over quasi-first order reaction rate constant which is not related to hydrogen peroxide and/or ozone, but instead is related to the hydroxyl radical. Since the focus and methodology of their study is notably different from that in this project, the results cannot be compared to those of the present study.

4.4 Limitations of this study and future work

It is important to realise that the findings of this project are only preliminary. While they are solid, they are only representative of one site, during one season. It would be inadvisable to generalise these results and say that sulphate production modelled by LCM11 for any data set will be insensitive to parcel chemistry.

To test the hypothesis more completely, additional work will be necessary. New chemical scenarios should be assayed. While the background concentration profiles for carbon dioxide, ammonia, nitric acid, and ozone were held constant between runs in this study, they could be varied once more is known of their typical concentrations under non-polluted and polluted conditions. The profiles employed in this study prescribed a limited range for pH values and the high acidity limited ozone's contribution to the production of sulphate. Thus it would be interesting to alter the profiles in order to produce a more basic environment such that ozone's efficiency is increased.

Since this study was performed for one particular site during a specific season, the runs are characterized by a certain range in LWC. Parallel simulation runs should be conducted for different environments with different predominant cloud types. Meteorological data for maritime, arctic, and other continental sites are probably readily available. Different times of year should also be explored; Walcek & Brankov

(1994) found larger differences between methods of calculating sulphate production in spring and fall. Indeed future work with the LCM11 might show that the sensitivity of sulphate production to parcel chemistry in sub-grid scale clouds is influenced by seasonal or geographic factors.

4.5 The future of sub-grid scale parcel chemistry in NARCM

Currently, NARCM does not employ the UQAM cloud scheme. This scheme, as mentioned in chapter 2, is only a recent addition to LCM11. Considering the results presented here, it is unlikely that sub-grid scale parcel chemistry has a future in the regional climate model in the modelling of sulphate production. However, if the future work suggested above should conclude contrary to this project, the impact of parcel chemistry would require careful consideration and examination before implementation into the larger model.

NARCM and its corresponding LCM are in constant development. When the next base version of the model is decided upon, it is quite possible that the chemistry scheme will have been expanded from its current state. If the UQÀM cloud scheme is fully implemented into NARCM, the question of incorporating parcel chemistry may arise again.

Appendix – List of abbreviations, symbols, and acronyms

ADOM	Canadian/German acid deposition and oxidation model
aq	aqueous phase
BASE_V1	base chemical scenario, non-polluted conditions, vertical cap = 1 km
BASE_V2	base chemical scenario, vertical cap = 2 km
CCCma	Canadian Centre for Climate modelling and analysis
CGCM	Canadian General Circulation Model
CO_2	carbon dioxide
CH_4	methane
FFT	Fast Fourier Transform
g	gaseous phase
gcmii	second-generation general circulation model
H^+	hydrogen ion
H_2O	water
H_2O_2	hydrogen peroxide
HCO_3^-	bicarbonate
HNO_3	nitric acid
HSO_3^-	bisulphite
INC_SO_2	increased sulphur dioxide chemical scenario
IPCC	Intergovernmental Panel on Climate Change
LCM11	Local Climate Model version 11, one-dimensional version of NARCM
LWC	liquid water content

NARCM	Northern Aerosol Regional Climate Model
N_2O	nitrous oxide
NH_3	ammonia
NH_4^+	ammonium
O_2	oxygen
O_3	ozone
OH^-	hydroxyl radical
pH	$-\log_{10}[H^+]$, measure of acidity
POLLUT	polluted chemical scenario
RADM	U.S. regional and deposition model
SO_2	sulphur dioxide
SO_3^{2-}	sulphite
SO_4^{2-}	sulphate
S(IV)	sulphur, valence IV, non-oxidized state
S(VI)	sulphur, valence VI, oxidized state
STEM-II	U.S. sulphur transport eulerian model
$2 \times H_2O_2$	doubled hydrogen peroxide chemical scenario

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