

SUBGRID SCALE INVESTIGATIONS OF FACTORS DETERMINING THE OCCURRENCE OF OZONE AND FINE PARTICLES (SUB-AERO)

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INTRODUCTION

The current work evaluates and assesses the physical, chemical and meteorological processes responsible for the spatial and temporal variability of photochemical pollutants and fine particles in subgrid scales (in the range from from hundred of meters to a few kilometers spatial resolution) (see e.g. Lesniewski and Friedlander, 1999) and their effect on long-range transport characteristics. An evaluation of the importance of mixing/transformation interactions, and the adequacy of existing modeling methods, for photochemical/fine particle air pollution systems, using extensive field data and modelling methods for gas and aerosol phase is performed.

METHODS

Two measurement campaigns were conducted at the Finokalia remote site on the island of Crete, Greece and on a research vessel (Aigaion) along selected tracks organised with respect to air mass transport patterns in the Mediterranean and the distance from the mainland (i.e. Greece). The summer campaign in Finokalia and the measurements using the research vessel were conducted during July 2000, whereas a winter campaign was performed in January 2001.

Semi continuous measurements of the accumulation and nucleation mode of the aerosol number size distribution were performed by a SMPS, (TSI), nephelometer, aethelometer and Las-X. Size distributions coarse and fine particulate mass concentration for selected inorganic species were determined by two Berner and one Andersen high volume Cascade Impactors. NO₂ and O₃ concentrations were measured by conventional chemiluminescence instruments and by a novel instrumentation. Nitrous and nitric acid collected by denuder filterpack systems and analysed by ion chromatography (IC) and were compared against the respective novel instrumentation. EC/OC analysis for the aerosol filter samples was also performed. Integrated gas and fine particulate species concentration measurements were conducted by means of annular denuders and filterpack systems sampling at the same time intervals as the cascade impactors. Analysis was performed by IC for the concentration of HCl, HNO₃, HONO, NO₂, SO₂, NO₃⁻, SO₄²⁻, Cl⁻, NH₄⁺ and H⁺. PIXE analysis was also used for the impactor samples. Measurements of black carbon (BC) from the boat Aigaion are presented in Figure 1.

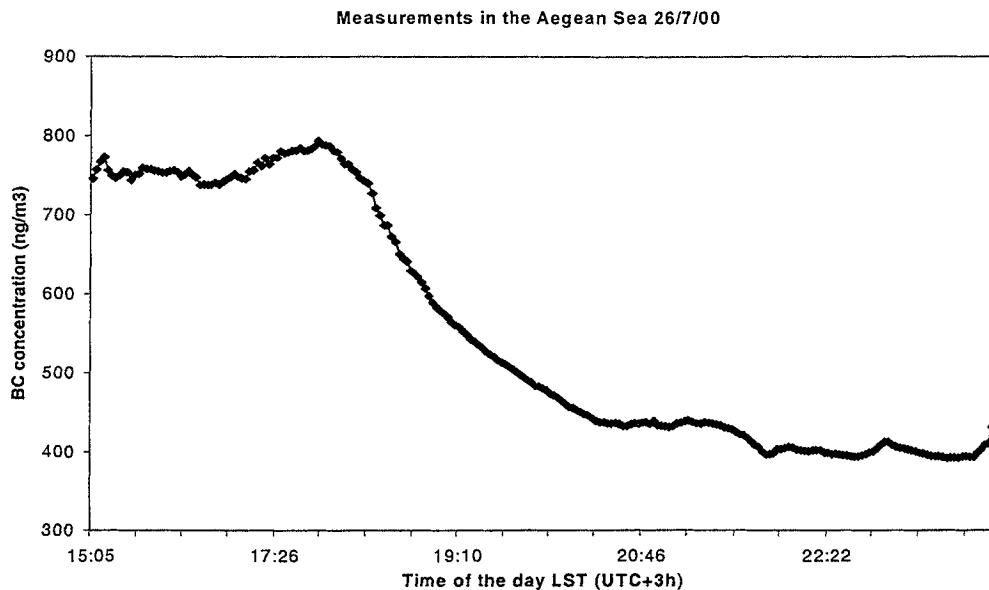


Figure 1: Black Carbon as tracer of anthropogenic emissions in the Mediterranean area.

Along with the experimental work a detailed modelling study is under progress using the UAM-AERO mesoscale air quality model (Lurmann et al., 1997) including state-of-the-art modules for photochemical oxidants and fine aerosols to study their transport/chemistry interactions in the Eastern Mediterranean area. Meteorological input data are prepared with the help of the RAMS model. The modelling domain includes the island of Crete, part of the Greek mainland and the Aegean Sea area between Crete and the Greek mainland.

RESULTS

An extensive set of chemical speciated data on aerosols in the eastern Mediterranean area was obtained and compared with modelling results. The physico-chemical characteristics of the aerosols and their photochemical precursors were evaluated and their sources were examined.

ACKNOWLEDGEMENTS

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MODIFICATION OF THE VISIBILITY BY SOOT AEROSOL ON THE REGIONAL SCALE - NUMERICAL SIMULATIONS

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Keywords: regional soot aerosol, aerosol dynamics and transport, visibility

INTRODUCTION

Soot particles are ubiquitous in the troposphere and participate in tropospheric chemistry, scatter and absorb light and affect human pulmonary health. While freshly emitted soot particles are hydrophobic their hygroscopic qualities can change due to coagulation with soluble aerosols and condensation processes. Hereby the growth of the particles in response to ambient relative humidity, the ability of being activated as cloud condensation nuclei and the optical properties are determined. This study focuses on the transformation of externally mixed soot into an internal mixture as it happens on the regional scale. We use an extended version of the aerosol module MADE (Ackermann *et al.*, 1998) which is fully coupled to the comprehensive mesoscale model system KAMM/DRAIS (Vogel *et al.*, 1995). This model configuration is applied to study the visibility degradation on the regional scale depending on the mixing state of the soot particles.

METHODS

The aerosol model MADE has been included in the comprehensive mesoscale model system KAMM/DRAIS in order to allow for a treatment of the aerosols in the regional scale. We extended the concept of MADE and introduced three additional modes in order to treat the transformation of soot from the external to the internal mixture. Modes i_f and j_f now describe the soot-free particles which contain sulfate, nitrate, ammonium and water in an internal mixture. Modes i_c and j_c contain the same species together with soot. Mode s is reserved for externally mixed, pure soot. To assess the optical properties of the aerosol population, the individual mixed particles are assumed to consist of an insoluble core and a soluble shell. Recent measurements of the refraction index of diesel soot made in the AIDA chamber are used (Kamm *et al.*, 1999, Schnaiter, 2001). The extinction coefficients of the soluble particles and the pure soot particles are calculated according to Binkowski (2001). For the mixed particles (soot and soluble material) a Mie code after Bohren and Huffman (1983) is used to determine the extinction coefficients. In order to investigate the relative importance of coagulation and condensation as the responsible aging processes for the soot particles, we carried out simulations using a 1-D version of the model system. Beyond this, a 3-D simulation for the region of the south-western part of Germany was carried out to study the effects of the mixing state of the soot particles on visibility.

RESULTS

Figures 1 to 3 present results of the 1-D simulations which were carried out to analyze the role of coagulation and condensation for the mixing process of soot. At first, only coagulation was considered whereas condensation was excluded. Figure 1 and Figure 2 show the diurnal development of the vertical profiles of the pure soot and the fraction of soot which is internally mixed under the assumption that only coagulation is responsible for the transfer of soot from the external into the internal mixture. In the

morning we find high soot concentrations near the ground because soot is emitted at this height and the vertical mixing is suppressed due to stable stratification. During the day, the concentration becomes almost constant with height caused by turbulent mixing. Comparing the soot mass of the pure soot mode and of the soot containing modes it results that after two days of simulation less than 50% of the soot is internally mixed. Figure 3 presents the fraction of soot which is internally mixed assuming that both coagulation and condensation account for the aging of soot. In this case pure soot can mainly be found close to the sources. During daytime over 80% of the soot is internally mixed.

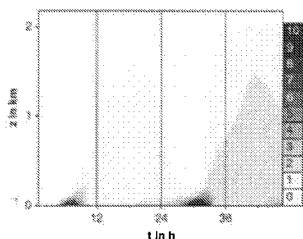


Fig. 1. Diurnal development of vertical profiles of mass of soot in $\mu\text{g m}^{-3}$.

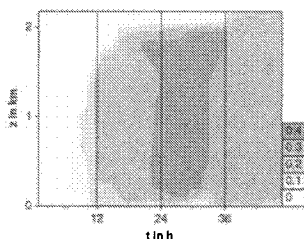


Fig. 2. Fraction of soot which is internally mixed (only coagulation).

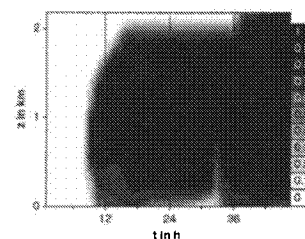


Fig. 3. Same as Fig. 2 but for coagulation and condensation.

With this model configuration we carried out a 3-D simulation for the region of South-West Germany. Figure 4 shows the topography and the wind field close to the surface at 9:00 CET. Figure 5 displays the corresponding horizontal distribution of the total particle number concentration. Due to the low wind speeds and the high emissions large number concentrations occur in the area of Stuttgart whereas in the mountainous regions only low number concentrations are reached. For this simulation the visibility reduction caused by aerosol particles will be presented.

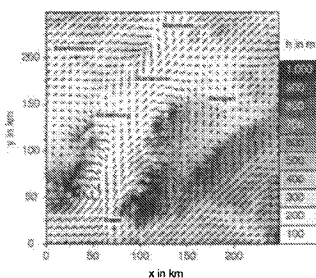


Fig. 4. Topography and the wind field close to the surface at 9:00 CET.

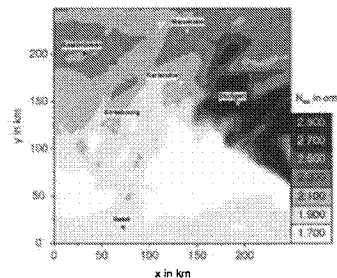


Fig. 5. Horizontal distribution of the total particle number concentration in cm^{-3} .

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DEVELOPMENT AND EVALUATION OF THE AEROSOL DYNAMICS MODEL MULTIMONO

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Keywords: aerosol dynamics, monodisperse box model

INTRUDUCTION

Due to the recognized impact of atmospheric aerosols on human health, particulate matter (PM) has recently become one of the central topics in the transboundary air pollution strategy in Europe. There is an ongoing debate on which properties of atmospheric aerosol, i.e. mass, number, surface area or chemical composition, are actually responsible for the human health damage.

The present EMEP¹ Eulerian transport model formulation allows only for a first estimate on aerosol mass and chemical composition distribution in Europe. In order to provide the necessary information for any other above-mentioned characteristics of the aerosol, an aerosol dynamics module is under implementation to the EMEP Eulerian model. The aerosol dynamic module is designed to allow for the interaction between different components of PM, formation of secondary aerosols and growth of particles by condensation and coagulation processes. The module is purposed to respond to policy needs on the source allocation of atmospheric particles and to facilitate the evaluation of the adverse health effects. It is aimed to provide revised long-term information on the mass and chemical composition of the aerosol and relevant information on the size and number distribution of atmospheric aerosols in Europe.

MODEL DESCRIPTION

The aerosol dynamics module to the EMEP Eulerian model is based on a multicomponent monodisperse model (MULTIMONO) developed at the University of Helsinki (Pirjola and Kulmala 2000) in a close co-operation with EMEP. The monodisperse model was shown to compare reasonably well with more sophisticated modal and sectional aerosol models (Pirjola et al, 1998). An essential for transboundary modelling purpose advantage of the monodisperse approach is that it limits the number of prognostic variables to two (i.e. mass M and number N) per mode, and thus, allows for computationally efficient source allocation calculations. MULTIMONO resolves aerosol size distribution with four modes: nucleation ($d_p < 0.02 \mu\text{m}$), Aitken ($0.02 < d_p < 0.1 \mu\text{m}$), accumulation ($0.1 < d_p < 2.5 \mu\text{m}$), and coarse ($d_p < 10.0 \mu\text{m}$). Concentrations of PM_{2.5} and PM₁₀, which the European air quality directives refer to, can be easily derived. The aerosol module is intended to treat seven chemical components: sulphate, nitrate, ammonium, organic carbon, elemental carbon, mineral dust, and sea salt. In a simplified version of MULTIMONO (henceforth referred to as MM32), all particles within each mode are assumed to have the same diameter and chemical composition (internal mixture). This yields totally 32 prognostic equations for number and mass concentrations. In fact, the number of prognostic equations will be further reduced, as each of those aerosols is present in all the modes.

SIMULATION OF AEROSOL DYNAMICS PROCESSES

MM32 has been compared with the original version of the Helsinki University MONO32 (Pirjola and Kulmala 2000) and as long as feasible with the sectional model AEROFOR2 (Pirjola and Kulmala, 2000). The only difference between the two former versions is that MONO32 applies a FORTRAN NAG-library to solve the differential equations, while MM32 uses a two-step integration scheme.

¹ Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe.

Results of simulations of particles formation and growth, as well as sensitivity tests of the effects of different parameters on aerosol dynamics processes will be presented. As expected, the experiments have shown a good agreement between MM32 and MONO32 for the large range of time steps from 1s to 10 min. The two-step integration scheme has been found to be computationally more efficient. Furthermore, MM32/MONO32 has been applied to study the influence of particles initial number and different concentrations of condensable vapour on particles size and number evolution (only sulphate aerosols have been considered in the present study).

Simulations with MM32 and MONO32 of new particle formation by binary $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ nucleation (Kulmala *et al.* 1998) have shown that the concentrations of H_2SO_4 exceeding 10^{10} molec cm^{-3} are needed at temperature $T=293\text{K}$ and relative humidity $Rh=50\%$ for a nucleation process to commence. Sensitivity studies have confirmed that lower temperatures and higher relative humidity favours the onset and intensity of nucleation events. The recently developed theory of ternary $\text{H}_2\text{SO}_4\text{-NH}_3\text{-H}_2\text{O}$ nucleation (Korhonen *et al.*, 1999) is able to predict formation of new particle by nucleation under typical tropospheric H_2SO_4 and NH_3 concentrations. A preliminary parameterization of ternary nucleation from the Helsinki University has been implemented in MULTIMONO. A simple scheme to account for the particle growth to larger modes has been tested here. All particles from the mode are moved to a larger one as the mean radius exceeds a threshold value. Simulated 5-day evolution of particles number concentrations, $\text{PM}_{2.5}$ and PM_{10} mass, including a ternary nucleation event, is given in Fig.1 The evaluation of MM32 and MONO32 with the MULTIMONO and AEROFOR2 models has shown their physically soundness, but further comparison and verification against measurement data is needed.

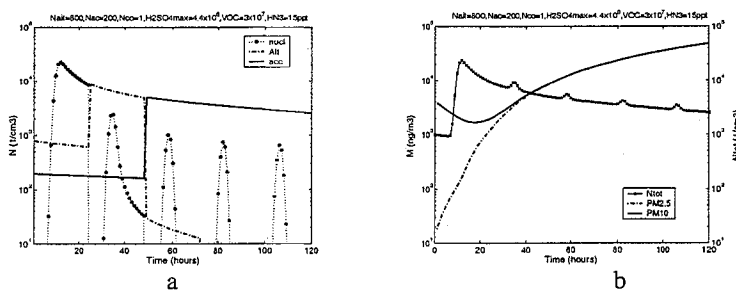


Figure 1. The evolution of particles modal number (a) and total number and mass of $\text{PM}_{2.5}$ and PM_{10} (b) in case of ternary nucleation (initial number is 800 m^{-3} in Aitken and 200 cm^{-3} in accumulation mode, sinusoidal pattern for H_2SO_4 with maximum of $4.4 \cdot 10^6 \text{ molec} \cdot \text{cm}^{-3}$, constant concentrations $\text{NH}=15 \text{ ppt}$, and $\text{VOC}=3 \cdot 10^7 \text{ molec} \cdot \text{cm}^{-3}$ (example taken from Kulmala *et al.* 2000)).

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INTERANNUAL VARIABILITY OF MINERAL DUST SIMULATED WITH A GENERAL CIRCULATION MODEL

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Keywords: Mineral Dust, Modelling, Climate.

INTRODUCTION

Mineral dust is an important aerosol component in the climate system. A determination of its climate impact requires knowledge about its sources function and its spatial and temporal distribution which is strongly dependent on meteorological conditions (wind speed, precipitation). Considerable uncertainty exist with regard to the interannual variability of the presence of dust and the reason for it.

Moulin *et al.* (1997) found the interannual variability in the dust transport over the North Atlantic Ocean and the Mediterranean Sea to be well correlated with the North Atlantic Oscillation index. It would be interesting to simulate such a variability in a climate model and investigate the reasons for the changes appearing from year to year. In the present study we will analyze multiannual climate model simulations of mineral dust. The climate model is operated for this purpose in both a climatological and a nudged mode.

METHODS

We use the Hamburg climate model ECHAM4 (surface up to 10 hPa) which is run with a spectral triangular truncation at wavenumber 30 (T30 resolution). Physical processes and nonlinear terms are calculated on a Gaussian longitude–latitude grid with a nominal resolution of $2.85^\circ \times 2.85^\circ$ (approx. 256 km x 256 km). The mineral dust is prescribed by 2 prognostic variables: mass and number concentration. For the source formulation we have used a function which has been developed by T. Claquin (1999). At the source the size distribution is imposed with a mode radius of $2.5 \mu\text{m}$ and a standard deviation of $\sigma=2$ according to observations and sensitivity studies (Schulz *et al.*, 1997). The calculation of the time evolution include: large scale scavenging, convective scavenging, sedimentation and turbulent deposition which determine the evolution of the size distribution and the dust cloud.

We performed three different experiments for several years, a climatological run, a model run with prescribed observed sea surface temperatures (SSTs) (1986-1991) and a nudged model run with prescribed SSTs, where the model is forced by ECMWF data of the particular years (1986-1991).

RESULTS

The model results show a considerably interannual and interseasonal variability with maximum optical depth in spring and summer and lowest values in autumn. The optical depth is however larger in the climatological run than in the nudged model run and is spread more over the Eurasian continent. Figure 1 shows the annual mean optical depth of the climatological runs for the first two years. Figure 2 in comparison shows the annual mean optical depth of 1990 and 1991. The climatological run has a tendency to produce more dust due to higher wind speeds, which result in higher global emission in this simulation. The importance of the "high-wind" tail of the wind speed distribution for the resulting mineral flux is evident.

It can also be seen in each figure that the two years of simulation from each mode of model operation (climatological or nudged) resemble each other. At the same time it makes a difference, whether the model is forced by ECMWF input or not. The dust cloud in the climatological simulations are positioned rather north and do not extend that much into the North Atlantic region. The reason for this different behaviour may be the position and the strength of the Azores high, which is different in the two modes. It appears that the mode of operation of the climate model seems to be as important as the interannual variability of the dust cloud by climate variations alone. This needs to be understood further.

The model results are in the process to be carefully compared with satellite observations from METEOSAT and POLDER. Special emphasis will be placed on the ability of the model to reflect the observed correlation with the North Atlantic oscillation. It will be in particular investigated whether the nudged model simulates the observed pattern from dust poor years (1986) and dust rich years (1989).

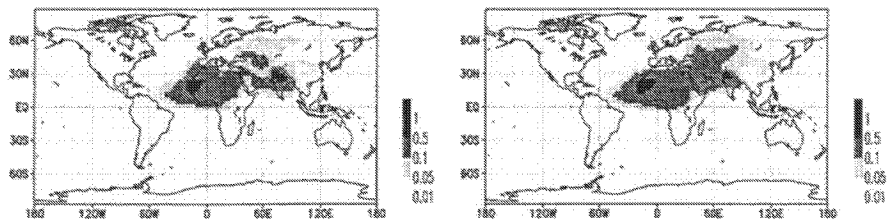


Figure 1: Annual mean of the optical depth at $\lambda = 0.55 \mu\text{m}$ for the first two years of the climatological run.

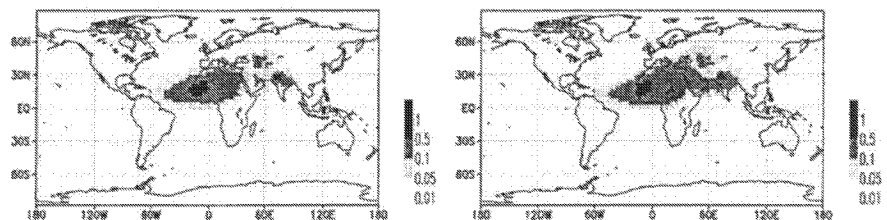


Figure 2: Annual mean of the optical depth at $\lambda = 0.55 \mu\text{m}$ in the nudged model run for 1990 (left panel) and 1991 (right panel).

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LONG RANGE AEROSOL TRANSPORT IN AND ABOVE THE PACIFIC MARINE BOUNDARY LAYER

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Keywords: AEROSOL, LONG RANGE TRANSPORT.

INTRODUCTION

Much of the progress in aerosol characterization came recently through extensive field campaigns of the last decade. Measurements have revealed numerous cases of plumes undergoing long range transport. These observations undermine the notion of “a global background aerosol”. Instead, a dynamic system of independent sources and sinks exists that tends to result in aerosol “rivers”, “layers” and “regions” in the troposphere with specific microphysical and chemical characteristics. It also became clear that the marine boundary layer, MBL, and the free troposphere, FT, aerosol are coupled through mixing and entrainment (Clarke, 1993; Clarke *et al.*, 1996; Clarke *et al.*, 2001, Moore *et al.*, 2001). There are many examples of continental aerosol detected over remote regions. However, there are few cases that illustrate transport mechanisms on global scales and over thousands of km. Here we will provide a two examples of transport active over 5,000 to 10,000km both in the MBL and in the FT followed by entrainment into the MBL that reveal the diverse ways such transport may occur.

MARINE BOUNDARY LAYER TRANSPORT

At low concentrations near “background” the presence of “natural variability” in measurements often makes it difficult to identify influences of continental emissions or to link them to model behavior. However, improvements in measurement sensitivity and model development are changing this situation. Here we show a case where small fluctuations in the aerosol light absorption coefficient and CO seen between two PEMT-B flights in the Equatorial Central Pacific can be linked to short period fluctuations in the meteorological transport of pollution occurring 10 days earlier in the vicinity of San Francisco. Fig. 1 (left) is a map of absorption coefficient measurements made in the boundary layer for all PEMT-B flights. Absorption usually indicates the presence of soot and enhancement is evident along the equator during flight 10 while other flights are the more typical “clean” condition.

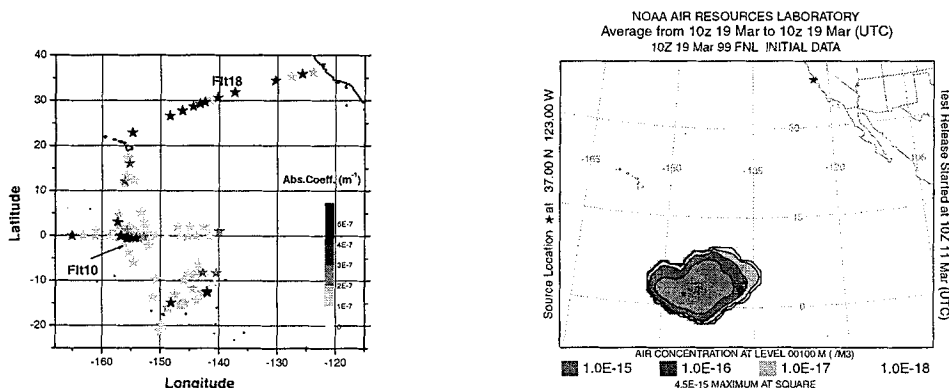


Figure 1. Near surface light absorption (left) and forward trajectory plume dispersion model after 8 days arrives at our flight 10 study region (right) on PEMT-B.

We have compared flight 10 (March 18, 1999) with a "clean" flight made 3 days apart at the equator. The 10 day back trajectories (HYSPLIT model) for these days lead back to near the coast of California with the cleaner case rising higher above the boundary layer and turning west and the flight 10 case (not shown) lying close to the surface near San Francisco (on March 8). Next we used a NOAA Air Resources Lab pollution dispersion model for both days initialized for San Francisco from 4 sites within a few hundred miles of San Francisco for the days (March 8 and 11) as determined by the back trajectory analysis. The "clean" forward plume trajectory diffused over the coast (not shown) but the flight 10 plume trajectory on March 11 heads directly from San Francisco south to our PEMT-B study region to arrive on the day we encountered pollution (Fig. 1 - right). Model results are consistent in time, space and predicted dilution with the small signatures detected in absorption and CO on the equatorial flights. The 12 days needed for transport in this case is far longer than the 3 days or so often estimated for aerosol lifetime in the MBL. This is reasonable however since the air mass traversed the MBL under a high pressure regions with only shallow non-precipitating MBL clouds that resulted in very little removal due to scavenging.

FT TRANSPORT AND ENTRAINMENT

In a separate study the vertical profiles of aerosol and gas phase species were measured on flights near Hawaii on April 10, 1999 during PEMT-B. These revealed physical, chemical and optical properties in extensive dust and pollution plumes with 10,000km trajectories back to sources in Asia. A new Chemical Transport Model (CTM) that includes meteorological fields, dynamics, gas and particle source emissions, a chemistry component (MATCH) and assimilated satellite data (Rasch et al, 2001) was used to predict aerosol and gas concentrations and optical effects along our flight path and provided in-situ validation of model behavior over global scale transport paths (Clarke et al., 2001). The most pronounced layer near 2km had high numbers of coarse and fine aerosol present at low relative humidity, (<10%) and consistent with our typical observations in dry "dust" layers aloft. However, below the inversion the highest number concentration of accumulation mode aerosol is evident near 1.2km with concentrations decreasing toward the surface, indicating that some of the pollution/dust layer above the inversion is being entrained and mixed into the MBL. These observations document the significance and complexity of long-range aerosol transport and highlight the potential of emerging CTM models to address related issues on global scales.

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**COUPLING QUASI-SPECTRAL MICROPHYSICS WITH MULTIPHASE CHEMISTRY :
A CASE STUDY OF A POLLUTED AIR MASS
AT THE TOP OF THE PUY DE DOME MOUNTAIN (FRANCE)**

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INTRODUCTION

In this paper, we present a new development of the model from Leriche et al. (2000) with the incorporation of the coupling between this fully explicit multiphase chemistry model and a quasi-spectral microphysics model based upon Berry and Reinhardt's parameterization (1974a, 1974b). This new coupled model is applied to the chemical conditions already described in Leriche et al. (2000) using a maritime air mass more or less precipitating. In this coupling, collection, evaporation and sedimentation processes are considered. The microphysical scheme considers two categories of particles (cloud drops and raindrops) and aerosol particles are not taken into account. The present study aims at evaluating the role of microphysical processes in redistributing reactive species among the different phases and to quantify the change in gas budgets when considering multiphase chemistry together with microphysical processes.

METHODS

The multiphase chemical box model is described in Leriche et al. (2000) for a more detailed description. The gas phase mechanism is the same than in the code of Madronich and Calvert (1990) and has been adapted to a rural environment, which includes 101 reactions and 48 gaseous species describing the chemistry of methane, sulfur, NO_y and ammonia.

This chemical mechanism is explicit and can be adapted to any environment in the troposphere. The initial model has been extended to include the exchange of chemical species between gas and aqueous phases of the cloud (Audiffren et al., 1998), which is parameterized by the mass transfer kinetic formulation developed by Schwartz (1986).

The chemical mechanism in the aqueous phase is fully explicit with detailed chemistry of HOx, of chlorine, of carbonate, of N-species, of organic species with one carbon atom and of S-species and is described in Leriche et al. (2000). 156 aqueous-phase reactions and 42 aqueous phase species are used in this mechanism based upon the work of Jacob (1986). It has been then updated with the latest kinetics and thermodynamic laboratory data available and with the work of Herrmann et al. (2000).

In order to better take into account the natural variability of the cloud as compared to the study of Leriche et al. (2000), we have chosen to parameterize the cloud evolution following Berry and Reinhardt (1974a, 1974b). In previous studies (Huret et al., 1994), it has been demonstrated that this parameterization is a good compromise between a simple bulk representation of the cloud and a fully spectral detailed scheme. The complete mathematical formulation of the microphysical rates are given for autoconversion of cloud into rain, for accretion of cloud droplets on larger drops, for self-collection of raindrops between themselves, for rain evaporation, and rain sedimentation. Condensation is treated in the same way than in Kessler's scheme.

Then, the set of equations developed in the multiphase chemistry model is extended in order to consider the two liquid phases of the cloud. Due to the quasi-spectral nature of the Berry and Reinhardt

parameterization, the microphysical model allows for two liquid categories (cloud and rain), plus for varying mean raindrop diameter. This is an interesting feature to study multiphase chemistry as a function of drop sizes. When the two forms of water are present (cloud and rain), the microphysical conversions of cloud water into rainwater interact with the aqueous phase chemistry and lead to a sink in cloud water and a source in rainwater due to collision/coalescence processes, and to a sink in rainwater due to sedimentation of rain.

CONCLUSIONS

Coupling chemistry and microphysics reveals two main effects that have been identified and separated:

- * a direct solubility effect through mass transfer and drop size dependency of the chemical species,
- * an indirect scavenging effect through microphysical conversions and redistribution of reactive soluble species among interstitial air, cloud droplets and raindrops.

The presence of clouds leads to a completely different fate for HO_x radicals due to the first effect. As a consequence of the indirect effect the microphysical conversions favor NO_x destruction through the nitric acid production enhancement by activation of the microphysical coalescence processes.

Coalescence of cloud drops to form rain transfers dissolved species into drops that are undersaturated compared to Henry's law equilibrium. The rain becomes a reservoir for these species, allowing aqueous chemistry to produce more acid than would be possible without the presence of rain.

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