

Review Articles

Global Tropospheric Ozone Dynamics

Part II: Numerical Modelling of Tropospheric Ozone Variability

Part I: Tropospheric Ozone Precursors [ESPR 8 (1) 57 – 62 (2001)]

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Abstract (Part II). Various causes of tropospheric changes have been considered in Part I in connection with the analysis of observation data. It is clear however, that the principal instrument for understanding numerous and often interacting causes of ozone changes is numerical modelling. A review of the current status of the numerical modelling has been made for the variability of the ozone concentration in the troposphere. Observation data on tropospheric ozone and relevant numerical modelling results show that a necessity exists to get more adequate global observational data.

Keywords: Chemical-transport models; greenhouse gases; photochemistry of troposphere

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Abstract (Part I). An overview of the tropospheric ozone changes is presented focussing mainly on the tropospheric ozone precursors. The complexity of the problem is shown through the consideration of a great number of relevant substances, like nitrogen compounds, volatile organic compounds, peroxyacetyl nitrate, hydroxyl radical, carbon monoxide, alkyl nitrates. The up-to-date knowledge on the relevant numerical modelling is presented in Part II.

Keywords: Ozone precursors; photochemical smog; solar radiation; tropospheric chemical composition

Part II

Introduction

Tropospheric ozone (which amounts to about 10% of the total ozone content-TOZ) is a significant greenhouse gas (GHG). Stratospheric and tropospheric ozone changes contribute differently to climate changes as well as having different effects on humans and ecosystems. An important, specific phenomenon relevant to tropospheric ozone changes is photochemical smog formation. Specific functions of stratospheric and tropospheric ozone have given certain grounds to consider stratospheric ozone as *good* ozone, while tropospheric ozone is *bad* (Low, 1998).

The increase of ozone in the troposphere since pre-industrial times is estimated to have contributed to 10% to 20% of the warming due to the increase in long-lived greenhouse gases during the same period.

Problems of tropospheric ozone changes have recently attracted much more attention than before, especially in the field of numerical modelling (observations still remain inadequate). Important success has been achieved in the interactive simulation of the troposphere dynamics and ozone changes (HOV, 1997; ISAKSEN, 1988). Impacts of both stratospheric and tropospheric ozone on climate have been studied (Ozone Depletion, Greenhouse Gases and Climate Change, 1989; KONDRATYEV and VAROTSOS, Part I and II 1996; KONDRATYEV and VAROTSOS, 2000; KONDRATYEV and VAROTSOS,

1997). Special attention has been paid to heterogeneous chemical reactions on surfaces of aerosol particles in the stratosphere (especially in cases of polar stratospheric clouds) and troposphere (KONDRATYEV, 1989, 1998; KULMALA and WAGNER, 1996; SEINFELD and PANDIS, 1998).

Nevertheless, there is a necessity for a more comprehensive and integrative consideration of all ozone problems in their full complexity, and this is precisely the principal purpose of this survey.

This paper is the second part of the review article "Global Tropospheric Ozone Dynamics" dealing with the field of numerical modelling related with the problems of tropospheric ozone changes (KONDRATYEV and VAROTSOS, Part I)

1 Discussion and Results

1.1 Impact of tropospheric ozone from surface emission changes

To assess impacts of increased emissions in Asia on tropospheric ozone and climate, Berntsen et al. (1996) have used a global 3-D chemical transport model (CTM) developed at NASA Goddard Institute for Space Studies (GISS). An extended set of chemical compounds (including such principal ozone precursors as hydrocarbons, nitrogen oxides, carbon monoxide), 25 of which are transported, has been taken into account in the model.

Three model experiments have been conducted to study the impact of tropospheric ozone from surface emission changes:

- (1) A reference run (R) with global emissions of NO_x and hydrocarbons representative for 1980,
- (2) Two additional experiments with increased emissions (E_{A2} , E_{A4}): the anthropogenic sources have been increased by factors of 2 and 4, respectively. New emissions applied in the Asian region are then defined by equations:

$$E_{A2} = 2 \times F_a \times E_R + (1 - F_a) \times E_R$$

$$E_{A4} = 4 \times F_a \times E_R + (1 - F_a) \times E_R$$

where F_a defines the fraction of the emissions assumed to be of anthropogenic origin for each component. The factor F_a gives the fraction of the emissions which are perturbed in the runs with increased emissions relative to the reference run (A2 and A4).

Berntsen et al. (1996) have pointed out that:

- 1) The reference results lead to surface NO_x concentrations in the Asian region with maxima over Japan and north-east China of about 1 ppbv as a monthly averaged concentration in August. This level is about 45% and 30% of the corresponding levels predicted over the eastern United States and Central Europe, respectively. Over south-east Asia and India, the NO_x concentrations in the model are significantly lower (300 pptv or less).

It is important that enhanced short-term ozone values during episodes are becoming more pronounced in the cases with high emissions. Significant ozone increases have also been obtained in the upper troposphere due to efficient convective transport. A doubling of NO_x emissions results in ozone increases up to 30% in the upper troposphere. Estimates of the regionally positive radiative forcing due to the increases of tropospheric ozone give values up to 0.5 W/m^2 , which is 30-50% of the negative RF due to the direct effect of sulphate aerosols in the region. The averaged RF values for the Northern hemisphere, the Southern hemisphere and total are calculated to be 0.13, 0.016, and 0.073 W/m^2 , respectively. The long-wave RF dominates the total RF which is highly inhomogeneous. These conclusions are a very important demonstration of the role of tropospheric ozone as a greenhouse gas (WANG and ISAKSEN, 1995).

- 2) With a sustained economic growth in the Asian region with increased use of coal as the primary source of energy, local pollution effects from sulphur emissions will probably lead to emission controls on sulphur emissions. The emissions of NO_x , CO and hydrocarbons leading to ozone production, are more difficult to control and will probably continue to increase. The net effect of anthropogenic emissions of sulphur dioxide and ozone precursors on the radiation budget over Asia is therefore likely to become positive in the future.

1.2 The photochemistry of troposphere

Flato et al. (1996) have applied a 3-D Mesoscale Chemistry Transport (MCT) model to show that: (1) Physical processes, especially convection, may dominate in the vertical

distribution of ozone in the free troposphere; (2) sinking air which compensates for convective updrafts is important for the tropospheric ozone budget; and (3) transport of ozone precursors from the boundary layer into the free troposphere by convection enhances the rate of O_3 photochemical production significantly.

Flato et al. (1996) have emphasised the necessity of a further improvement in the model as well as more thorough comparisons with observation data. Future modelling will include a study of how far North American tracer emissions of NO_x , NH_3 , SO_2 , and VOCs (volatile organic compounds), and the secondary products formed, can be identified, and in what chemical form. In addition, the chemical impact of subsonic aircraft emissions of NO_x over the North Atlantic on the upper tropospheric NO_x and ozone budgets will be calculated. New assessments will be obtained of how the flux of stratospheric ozone into the troposphere in tropopause folding events can influence the oxidation of NO_x and VOCs.

Mauzerall et al. (1996) have quantified the tropospheric ozone budget over remote, high northern latitudes in summer using chemical and meteorological measurements between 0 and 6-km made during the summer of 1990 Arctic Boundary Layer Expedition (ABLE 3B). The observations and 1-D photochemical modelling indicate that regional photochemical production and loss in the 0-6 km column are approximately equal. Therefore, the net photochemical production is near zero. The influx of stratospheric ozone is of secondary importance (27%), the long-range transport of pollution ozone makes a small contribution (9%), and the photochemical production of ozone within biomass wildfire plumes is a relatively negligible term (2%) in the budget. Mauzerall et al. (1996) have found that in situ photochemistry within the 0-6km column accounts for nearly 90% of the ozone mixing ratio within the boundary layer, while above 5km it accounts for only 40%.

With the purpose of assessing the level of agreement between observed ratios of NO_2 to NO and photochemical modelling, Crawford et al. (1996) have accomplished a comparison of measurements made during the NASA Global Tropospheric Experiment (GTE) Pacific Exploratory Mission-West A (PEM-West A) with photostationary state model calculations. The results indicate that the value of the ratio $(\text{NO}_2)_{\text{expt}} / (\text{NO}_2)_{\text{calc}}$ showed a general trend of increasing magnitude with increasing altitude and decreasing latitude. In order to understand causes of discrepancies, various assumptions have been made concerning different components of the atmospheric chemical composition. The general conclusion is that incompleteness in the model's chemistry was unlikely to be the major cause of the discrepancy. Measurement errors were probably the major cause, which implies a necessity to further develop measurement techniques for NO_2 .

The most recent development of simulation modelling has been marked by an outstanding progress in substantiation and application of global 3-D photochemical tracer transport models (CTM) to analyse causes and potential future changes of tropospheric ozone (BERNTSEN et al., 1998; HAUGLUSTAINÉ et al., 1998; WANG et al., 1998a, b).

Berntsen and Isaksen (1997) have emphasised that:

- 1) In view of the strong non-linearities in the photochemistry of the troposphere, it has become increasingly evident that a 3-D resolution of the atmosphere is crucial in models aimed at studies of the distribution of ozone and its precursors. The chemical scheme includes 49 components, 85 chemical reactions, and 16 photolytic reactions.
- 2) Their model simulates the lower tropospheric distribution of key species like carbon monoxide, NMHCs, and ozone very well and
- 3) net ozone production takes place in the boundary layer and in the upper troposphere, but there is generally a loss of ozone in the middle troposphere except for in the European and North American regions. Globally, the net loss in the middle, free troposphere is of the same magnitude as the net production in the boundary layer.

1.3 Ozone Chemical-Transport models

A new fundamental effort to develop and apply a global 3-D chemical-transport model (MOZART, version 1) has been undertaken by Brasseur et al. (1998 a, b) and Hauglustaine et al. (1998).

Hauglustaine et al. (1998) have discussed in detail the application of a MOZART model to simulate global distributions of tropospheric ozone and its precursors. The general conclusion is that the model is able to simulate the distribution of species in the troposphere with fair agreement. MOZART reproduces accurately important transport-chemistry processes, including the ventilation of the planetary boundary layer, convective transport and the Walker circulation in the tropics, the impact of monsoon circulation on chemical tracers, and the vertical and seasonal gradients of ozone and nitrogen species in the vicinity of the tropopause. The model simulates the distribution of methane, NMHCs, and CO successfully enough. However, the model evaluation in the tropics stresses the need for a better representation of biomass burning emissions in order to evaluate the budget of carbon monoxide, nitrogen species, and ozone with more accuracy in these regions. MOZART reproduces the NO observations in most parts of the troposphere. Nitric acid, however, is overestimated over the Pacific by up to a factor of 10 and over continental regions by a factor of 2-3. The seasonal cycle of ozone in the troposphere is generally well reproduced by the model in comparison with ozone soundings. MOZART, however, tends to underestimate O₃ at higher latitudes, and specifically above 300hPa. The global mean OH concentration is probably underestimated by 10% in the model. The distribution of radicals (OH, RO₂, HO₂ / RO₂) are generally consistent with available measurements. This is an important positive feature of the model because recent studies stressed the significant role played by aldehydes, peroxides, and acetone as potential sources of radicals in the upper stratosphere (PRATHER and JACOB, 1997). Hauglustaine et al. (1998) have underlined that the global budget of nitrogen species in the troposphere is still an important area for future model improvement.

Now, we shall consider some of the results in more detail. Hauglustaine et al. (1998) have emphasised that:

- 1) The importance of CO is connected with the fact that the reaction of carbon monoxide with the hydroxyl radical provides the major sink of OH in the free troposphere and leads to ozone photochemical production in the presence of NO_x. The most important source is direct emission from incomplete fossil fuel and biomass burning combustion. In addition, carbon monoxide is produced from the oxidation of methane and NMHCs. The calculations of CO global distribution indicate the presence of the highest concentrations resulting from anthropogenic activities over the industrial regions of Europe, Asia and North America. The CO mixing ratios over these areas are typically 300-400 ppb during winter and 200-300 ppb during summer. The effect of biomass burning over the African and South American continents is also visible, with CO surface concentrations of typically 200-300 ppb (biomass burning is the most intense during the dry season).

The analysis of model data on nitrogen species made by Hauglustaine et al. (1998) indicates the large impact of atmospheric sources in the boundary layer in the Northern hemisphere. The contribution of biomass burning in the tropics is visible. Maximum NO_x concentrations (its lifetime is on the order of a few days or less in the boundary layer) were found over the industrial and urbanised regions of the eastern United States, California, western and central Europe, China, and Japan. Typical mixing ratios in these regions are in the range of 1-5 ppb (due to Horowitz et al. (1998) this is in the higher range of observations).

- 2) The simulated total ozone distribution is characterised by low tropical values (typically about 250 DU) and high polar values, particularly in the winter hemisphere (on the order of 380-450 DU in the Northern hemisphere and 280-320 DU in the Southern hemisphere during January), in agreement with observations.

The global ozone photochemical production is 3018 Tg/yr (the NH contribution dominates). Stratospheric ozone intrusion (391 Tg/yr) contributes for 11% to the global source of ozone in the troposphere (8% and 11% for the NH and SH, respectively). The photochemical destruction is 2511 Tg/yr. Dry deposition at the surface (898 Tg/yr) contributes for 26% to the global sink of tropospheric ozone (about 30% and 20% in the NH and SH, respectively). This data obviously demonstrates that the budget of tropospheric ozone is dominated by photochemistry. A typical situation takes place: The net photochemical production (production-destruction) is a small difference between two large terms. The calculations have shown that the net tropospheric ozone production exhibits a strong seasonal cycle, varying from about 200 Tg/yr in January to 600-700 Tg/yr in June-September. A strong seasonal variability also takes place in case of the ozone influx from the stratosphere across the 250 hPa upper boundary, with an annual maximum of about 1200 Tg/yr in March-April. The dry deposition is characterised by a strong seasonal cycle in the Northern hemisphere associated with larger vegetation uptake during summer. Approximately 60% of the global tropospheric burden (163 Tg) is found in the Northern hemisphere. The calculated lifetime of ozone is about 1 month in global and

annual average. When surface dry deposition is considered, the global lifetime decreases for about 20 days. This lifetime exhibits a strong seasonal and geographical variability. In the Northern hemisphere the lifetimes range from 15 days in summer to about 30 days in winter on the average.

- 3) The background tropospheric columns calculated by Hauglustaine et al. (1998) are typically 15-25 DU. Enhanced TrOZ values are calculated as a result of anthropogenic activities, including fossil fuel combustion in the Northern hemisphere and biomass burning emissions in the tropics. The following basic features of TrOZ global distribution are in agreement with the observational data considered by Fishman and Brackett (1997): NH high ozone values; evidence of plume structure emanating from North America, Asia, Europe, and Africa; relatively lower TrOZ over the Rockies, Himalayas, and Andes due to surface elevation; low ozone amount over the tropical Pacific Ocean where convective transport is dominant, and high TrOZ values over the tropical South Pacific associated with biomass burning in Africa and South America. During the September-October period, for example, the calculated TrOZ values reach a maximum of 40 DU in the Northern hemisphere plumes, 35 DU over the tropical Atlantic, 30-35 DU in the southern part of Australia (African plume), and a minimum of less than 20 DU in the central Pacific. At mid-latitudes the observed TrOZ values reach 30-35 DU, whereas MOZART produces values of only 15-20 DU (the disagreement may partly be due to differences in the definition of the tropopause height).
- 4) Although many of the results provided by MOZART are encouraging, the model will continuously require improved formulations and parameterisations of physical and photochemical processes. A principal aspect of future research is obtaining more adequate observation data which is very important for both the improvement and validation of global models (KRITZ et al., 1998; STOCKWELL et al., 1998). More complete and precise laboratory data on various reaction rates is also necessary.

One of the important phenomena which may be used for model verification purposes is surface ozone depletion at polar sunrise fuelled by sea-salt halogens. Barrie et al. (1998 a,b) have pointed out that the Arctic troposphere (0 to ~8 km) at polar sunrise becomes a unique chemical reactor influenced by human activity and the Arctic Ocean. At this time, a relatively high abundance of photochemically reactive compounds and aerosols is found in the troposphere which results in O₃ depletion in the surface-based inversion layer over the Arctic Ocean (a similar phenomenon develops probably in the Antarctica as well). During the period of mid-March to the end of May when sunlight is present and the Arctic Ocean is still frozen, ground-based O₃ mixing ratios decrease from a mid-winter mean of 30 to 40 ppb to <1 ppb («surface ozone hole» is formed). It may be assumed that the involvement in a polar rise chemistry of BrO/Br, ClO/Cl and possibly IO/I acting individually or in combination, as well as the important role of heterogeneous reactions on ice or acid aerosols, is responsible for the observed O₃ destruction. In contrast to stratospheric O₃ depletion, Br atoms rather than Cl are responsible for most of the O₃ destruction. Strong evidence is now emerging to show that atmospheric reac-

tions involving oxidants lead to the autocatalytic liberation of reactive bromine from sea-salt. In this context, the ARC Troposphere O₃ Chemistry (ARC-TOC) project was organised by European scientists.

Klonecky and Levy (1997) have used a photochemical box model with CO-CH₄-NO_y-H₂O chemistry to calculate the diurnally averaged net photochemical rate of change of ozone (which is called the chemical ozone tendency) in the troposphere for different values of parameters: NO_x and ozone concentration, temperature, humidity, CO concentration, and surface albedo. The relevant sensitivity studies indicate that the magnitude of the tendency decreases rapidly with height mostly as a result of lower absolute humidity and temperature. In the upper troposphere (at 190 hPa), the maximum tendencies are below 2 ppbv/day. Lower temperature and specific humidity cause a shift in the value of NO_x values. In the upper troposphere the net tendency is at least as sensitive to variations in H₂O concentration as to NO_x. The latter conclusion made by Klonecky and Levy (1997) suggests a possible synergism between direct NO_x pollution by aircraft and the indirect modification of H₂O by climate change.

Tie and Hess (1997) have used a GCTM to study ozone mass exchange between the stratosphere and troposphere under conditions of background and volcanic sulphur aerosol in the northern and southern extratropical, lowermost stratosphere and in the tropical, upper troposphere. The calculations have shown that the stratospheric ozone mass flux into the troposphere is highest during the spring months in both hemispheres, but higher in the NH than in the SH. During background aerosol conditions, the net modelled stratospheric flux of ozone to the troposphere is 792 Tg/yr. The results obtained indicate a significant impact on the ozone mass flux across the tropopause of the heterogeneous chemical reactions occurring on the surface of sulfate aerosols, leading to a possible 15% reduction in the annual global ozone mass transported from the stratosphere to the troposphere after a large volcanic eruption. Most of the reduction in ozone mass flux occurs in the Northern hemisphere. In the Southern hemisphere during the winter and spring, the ozone concentration is already significantly perturbed by the heterogeneous reactions occurring on the surface of polar stratospheric cloud particles over Antarctica.

1.4 Improvements of tropospheric chemistry modelling

A number of recent studies have been devoted to improvements of various aspects of tropospheric chemistry modelling. Kindler et al. (1998) have pointed out that one of the substantial uncertainties in the simulation and prediction of minor species changes is a poor mechanistic understanding of the role of advective and subgrid-scale transport in the redistribution of key species. This requires a further improvement of GCTMs with the aim to accurately simulate current distributions of all major atmospheric species. In this context, Kindler et al. (1998) have undertaken an evaluation using ¹⁴C and N₂O simulations of 3-D transport driven by U.K. Met. Office and Goddard Space Flight Center assimilated winds. Their principal conclusion is that, because of the significant discrepancies between the model simula-

tions, using either one of the wind field sets, and the observations, it is necessary to be careful in using these assimilated winds for long-term model studies.

Brunner et al. (1998) have used aircraft observation data over the Northern hemisphere to examine the role of large-scale nitrogen oxide plumes in the tropopause region for ozone. It has been found out that the upper tropospheric, nitrogen oxide distribution is strongly influenced by large scale plumes extending about 100 to 1300 km along flight tracks. Because the plumes were frequently observed downwind of thunderstorms and frontal systems, it may be assumed that they were formed due to the upward transport of polluted air from the continental boundary layer. Some contribution may also belong to nitrogen oxide production by lightning strokes.

The origin of NO_x in the upper troposphere over the central United States has been studied by Jaegle et al. (1998) using aircraft observations obtained during the SUCCESS campaign in April-May of 1996. They have discovered correlations between NO_y and CO at 8-12 km altitude which indicates that NO_x originates primarily from the convective transport of polluted, boundary layer air. Due to Jaegle et al. (1998a), lighting and aircraft emissions appear to be only minor sources of NO_x . The principal conclusion is that the NO_x/NO_y ratio is maintained above chemical steady state by frequent convective injections of fresh NO_x from the polluted boundary layer and by the long lifetime of NO_x in the upper troposphere (5-10 days). In contrast to previous studies, no evidence for fast heterogeneous recycling from HNO_3 to NO_x in the upper troposphere was found.

Using observation data obtained during the same SUCCESS aircraft campaign in April-May 1996, Jaegle et al. (1998 b) have assessed the sources of NO_x (out of peroxy radicals) and the associated production of ozone at 8-12 km over the United States by examining modelled observation data of OH, HO_2 , NO and other species. The results indicate that the HO_x concentrations were up to a factor of 3 times higher than can be calculated from the oxidation of water vapour and photolysis of acetone. The highest discrepancy was found in the outflow of a convective storm. It has been shown that the convective injection of peroxides (CH_3COOH and H_2O_2) and formaldehyde (CH_2O) from the boundary layer to the upper troposphere could resolve this discrepancy. A general conclusion is that, in the case considered local, convection was a major source of HO_x and NO_x to the upper troposphere. An average net ozone production of 2 ppbv/day between 8 and 12 km over the continental United States was found in the spring. This ozone production was NO_x -limited. The high levels of HO_x present in the upper troposphere stimulate ozone production and increase the sensitivity of ozone to NO_x emissions from aircraft and other sources.

In view of the important role of non-methane hydrocarbons (NMHC) in global scale tropospheric chemistry, Houweling et al. (1998) have suggested a new chemical scheme (for NMHC's impact parameterisation). Results of the global Tracer Model 3 (TM3) runs with and without NMHC chemistry (compared with observations) illustrate the effects of NMHC on key compounds of tropospheric photochemistry such as ozone, the hydroxyl radical, carbon monoxide, and

NO_x . It has been shown, in particular, that the simulation of ozone over a polluted region improves when NMHC chemistry is taken into account. Globally, the contribution of NMHC to net photochemical ozone production has been estimated at about 40%, leading to a 17% increase of the tropospheric ozone column. OH is depleted over the continents owing to reactions with NMHC, which is most evident in regions with strong biogenic emissions. Although NMHC significantly influence the global OH distribution, their effect on its total tropospheric content appears to be marginal.

Results of sensitivity calculations with and without organic peroxy nitrates show that this N reservoir may significantly change the global NO_x distribution, leading to a NO_x increase over the oceans on the order of 50%. Although the results obtained by Houweling et al. (1998) reproduce the NMHC impact on the main features of tropospheric chemistry, some large discrepancies with observations still remain.

Using a 3-D continental-scale model of tropospheric O_3 - NO_x -NMHC chemistry for the conditions of North America in summer, Horowitz et al. (1998) have demonstrated that the global influence on tropospheric chemistry of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) emitted by fossil fuel combustion may be strongly modulated by non-methane hydrocarbon chemistry taking place in the continental boundary layer. A specific feature of the model is the consideration of an isoprene oxidation mechanism. The chemical mechanism used in the model includes detailed photooxidation schemes for four NMHCs: Propane, butane, propene and isoprene (butane is considered as a surrogate for all alkanes $\geq \text{C}_4$, while propene is used to represent all alkenes $\geq \text{C}_3$). Model calculations have been compared with observations for ozone, reactive nitrogen species, and photochemical tracers at a number of sites in North America. The principal objective of the simulation modelling was the improvement of understanding of the export of NO_x and its reservoirs out of the continental boundary layer over the United States in summer (the US accounts for about 30% of the global NO_x source from fossil fuel combustion).

A budget analysis for the United States accomplished by Horowitz et al. (1998) indicates that 9% of NO_x emitted from fossil fuel combustion is exported out of the continental boundary layer as NO_x , 3.5% is exported as peroxyacetyl nitrate (PAN), and 3.7% is exported as another organic nitrate. Isoprene is the principal NMHC responsible for the formation and export of organic nitrate, which eventually decomposes to provide a source of NO_x in the remote troposphere. It has been shown that the export of NO_x and organic nitrates from the US boundary layer is a major source of NO_x on the scale of the Northern hemisphere troposphere and on the scale of the upper troposphere at northern midlatitudes. Therefore, an adequate representation of isoprene chemistry in the continental boundary layer is important for simulation of NO_x in global tropospheric chemistry models.

Liang et al. (1998) have applied the same 3-D continental scale photochemical model to investigate seasonal budgets of O_3 and NO_y species (including NO_x and its oxidant products) in the boundary layer of the United States to assess the export of these species from the US boundary layer to the global atmosphere. Model results have been verified through a comparison with year-round observations for O_3 , CO and NO_y spe-

cies at non-urban sites. The model solves the 3-D continuity equations for 21 chemical tracers over a domain including North America and large portions of the neighbouring oceans.

The lumping of organic compounds is done on a per carbon basis. Uniform concentrations of 1.7 ppmv CH₄ and 1.2 ppbv C₂H₆ are assumed over the model domain.

According to Liang et al. (1998) calculations, formation of hydroxy organic nitrates during oxidation of isoprene, followed by decomposition of these nitrates to HNO₃, is estimated to account for 30% of the chemical sink for NO_x in the US boundary layer in the summer. Model results indicate that PANs are most abundant in spring (25% of total NO_y), reflecting a combination of active photochemistry and low temperature. About 20% of the NO_x emitted from fossil fuel combustion in the US is exported out of the US boundary layer as NO_x or PANs (15% in summer, 25% in winter). All quantities are 3-month averages for the U.S. boundary layer extending horizontally over the area mentioned and vertically to the top of model layer 3 (about 740 hPa). The budgets are for NO_y emitted by fossil fuel combustion within the region, as determined by subtracting the background NO_y concentrations and fluxes from the zero-NO_x simulation. PANs includes PAN, PMN, and PPN; RNO₃ includes isoprene nitrates and alkylnitrates. HNO₃ (I) denotes HNO₃ of inorganic origin, namely formed from oxidation of NO₂ by OH and hydrolysis of N₂O₅ in aerosols; HNO₃ (O) denotes HNO₃ produced by the decomposition of hydroxy organic nitrates (mainly isoprene nitrates). Aerosol nitrate is lumped with HNO₃ in the model. Lifetimes are defined as the concentrations divided by the sum of chemical and deposition loss rates.

A very important and rapidly developing branch of environmental numerical modelling is the simulation of urban environmental dynamics including tropospheric ozone dynamics in a polluted atmosphere. Without having an intention to consider this special subject here we shall limit ourselves by mentioning a number of recent publications.

Ziomas et al. (1998 a,b) have discussed the results of the Mediterranean Campaign of Photochemical Tracers - Transport and Chemical Evolution (MEDCAPHOT-TRACE) experiment conducted in the Athens area in 1994-1995 - in a thematic issue on the "Atmospheric Environment". One of the important results of this project has been the development of the Urban Airshed Model to apply it for the simulation of environmental dynamics of the Greater Athens Area, including the assessment of ozone episode formation. The effect on ozone was studied for 36 scenarios of possible VOC and NO_x reductions of the entire area-wide emission. A comparison of model results with observations has proven the adequacy of the model. It has been shown that ozone abatement strategy should focus mostly on VOC emission controls rather than controlling NO_x. The VOC reduction should be on the order of 30-40% to effectively reduce the ozone levels at the northern part of the greater Athens, down to the European Union's limit of 90 ppb.

Similar studies have been recently accomplished by a number of other research groups (BERKOWITZ et al., 1998; CALBO et al., 1998; DUNCAN and CHAMEIDES, 1998; JACOBSON 1998), although it must be pointed out that some earlier results are still very important, such as devoted to the analysis of sensi-

tivity of urban / regional chemistry to climate change (GERY et al., 1989; WUEBBLES and PENNER, 1988).

To adequately plan measures to reduce surface ozone concentration, it is necessary to assess the sensitivity of ozone concentration to various perturbations. Summarising relevant results, Lu and Chang (1998) have pointed out, first of all, that the dependence of ozone formation on the change in concentrations of precursors (VOC and NO_x) is highly non-linear. Since comparable ozone levels can be associated with diverse combinations of VOC and NO_x concentrations, the ozone level by itself is not sufficient to foretell its sensitivity to precursor change.

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