Development of a Meteorological Research Institute Chemistry-Climate Model version 2 for the Study of Tropospheric and Stratospheric Chemistry

by

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Abstract

We present a new three-dimensional chemistry-climate model (CCM) called the “Meteorological Research Institute (MRI) Chemistry-Climate Model, version 2” (MRI-CCM2). The model treats chemical and physical processes interactively from the surface to the stratosphere to simulate the global distribution and evolution of ozone and other trace gases with a framework similar to that of version 1 (MRI-CCM1), which was a stratospheric model. We have added detailed tropospheric chemistry to Version 1 in order to seamlessly treat ozone chemistry in both the troposphere and stratosphere. The chemistry module of Version 2 includes 90 chemical species with 172 gas-phase reactions, 59 photolysis reactions and 16 heterogeneous reactions; includes improved grid-scale transport with a semi-Lagrangian scheme, sub grid-scale convective transport and turbulent diffusion, dry and wet deposition, and emissions of trace gases from various sources. We conducted a free run and an assimilated run towards observed atmospheric fields over 11 years, to reproduce the 1990s distribution of chemical constituents. The simulated seasonal cycle and geographical distribution of ozone below the middle troposphere are generally in good agreement with ozonesonde observations, although ozone was underestimated in the lower troposphere in the south polar region, and extratropical ozone was overestimated in the upper troposphere and lower stratosphere. Version 2 also reproduces realistic characteristics for other species such as carbon monoxide (CO), nitric oxide (NO), and the hydroxyl radical (OH): The model reproduces the observed seasonal cycle of CO well, although it overestimates CO by about 15 ppbv in the southern high latitudes; the vertical profiles of NO captures the observed features; and finally, distribution of the OH radical is similar to that simulated by other recent CCMs.

1. Introduction

One of the most important issues in atmospheric chemistry has been to determine the impacts of human activities on the atmosphere, especially on air quality and the climate itself. Human activities have greatly influenced the chemical composition of the global atmosphere in the industrial age of the last 200 years. In that time carbon dioxide (CO₂) and other well-mixed greenhouse gases have increased nearly 40%, and ozone precursors have increased dramatically in the troposphere, primarily due to anthropogenic (human) emissions (Volz and Kley, 1988; Marengo *et al.*, 1994). The main ozone precursors include carbon monoxide (CO), hydro-

carbons, and nitrogen oxides (NO_x), all of them pollutants. The rapid growth of these precursors has driven the increase of tropospheric ozone (O₃), because ozone is produced in the troposphere when CO and hydrocarbons are photo-oxidized in the presence of nitrogen oxides (Seinfeld and Pandis, 1998).

Tropospheric ozone damages human health (World Health Organization, 2003), crop yields, and ecosystems, and causes serious air pollution near the surface. The recent increase in ozone in the troposphere affects the chemical balance in the atmosphere, because ozone controls the oxidizing capacity of the atmosphere and affects the residence times of many pollutants and trace gases that are radiatively important. The photolysis of ozone in the presence of water vapor (H₂O) forms hydroxyl (OH) radicals, called “scavengers”, which break down many other trace gases, because of the strong oxidizing ability of OH radicals (Logan *et al.*, 1981).

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For example, the simultaneous increase of tropospheric ozone and OH radicals decreases the lifetime of methane (CH_4), which is removed from the troposphere when it is oxidized by OH radicals (Johnson *et al.*, 1999).

Ozone in the troposphere is a very important term in the atmospheric radiation budget. The Intergovernmental Panel on Climate Change (IPCC) estimated radiative forcing by tropospheric ozone to be about $+0.35 \text{ W m}^{-2}$ for ozone changes from 1750 to 2005, which makes ozone the third most important greenhouse gas after CO_2 and CH_4 (IPCC, 2007). The radiative forcing caused by ozone changes depends strongly on location and altitude (Forster and Shine, 1997; Hansen *et al.*, 1997; Gauss *et al.*, 2006).

Unlike the situation in the troposphere, ozone has been greatly depleted in the lower stratosphere over Arctic and Antarctic latitudes in during the past 30 years (WMO/UNEP, 2007). Above all, the dramatic ozone depletion high over the Antarctic during late winter and spring, a phenomenon called the “ozone hole,” has continued every year since it was discovered in the early 1980s (Chubachi, 1984; Farman *et al.*, 1985). Emissions of man-made halogen compounds, including chlorofluorocarbons and halons, cause these depletions (Solomon *et al.*, 1986). In the presence of solar ultraviolet (UV) radiation, these halogen compounds release chlorine and bromine atoms that participate in a catalytic cycle that efficiently destroys ozone. In the lower stratosphere of the southern middle latitudes, ozone had also been significantly depleted in all seasons during the past 30 years (WMO/UNEP, 2003, 2007).

Ozone depletion in the lower stratosphere has been a critical environmental concern, because it leads to an increase in the intensity of the UV-B portion of the solar irradiance (wavelengths from 280 to 315 nm) that reaches ground level (WMO/UNEP, 2003, 2007). While oxygen, ozone, and nitrogen molecules in the upper atmosphere absorb the entire UV-C portion (wavelength $< 280 \text{ nm}$) of the solar spectrum, the UV-B portion is not completely absorbed by stratospheric ozone. And after some further absorption and scattering by tropospheric ozone and aerosols, the rest of the UV-B reaches the surface. The surface UV-B has enough energy to break chemical bonds in DNA molecules, which elevates the skin cancer risk for humans (WMO/UNEP, 2007). From long-term measurements at Thessaloniki, Zerefos (2002) relates the increase of surface UV-B irradiance to the reduction of column ozone concentration (WMO/UNEP, 2007).

Another important scientific issue is that stratospheric ozone changes can affect the climate (*e.g.* Thompson and Solomon, 2002; Son *et al.*, 2008). Over several decades, the poleward side of the westerly jet in the southern hemisphere troposphere has been accelerating, which causes an increase in the index of the Southern Annular Mode. Son *et al.* (2008) attribute this acceleration to the combined anthropogenic effects of increasing greenhouse gases and decreasing stratospheric ozone. The radiative forcing caused by declining

stratospheric ozone is in a delicate balance and estimated to be about -0.05 W m^{-2} , for the decline from 1750 to 2005 (IPCC, 2007).

Global three-dimensional (3-D) chemistry-transport models (CTMs) and chemistry-climate models (CCMs) can be invaluable tools for addressing the above mentioned environmental issues (Murazaki and Hess, 2006; Gauss *et al.*, 2006; Eyring *et al.*, 2006, 2007). CTMs can predict the distribution, budgets and evolution of chemical constituents under imposed or calculated atmospheric fields in 3-D, and CCMs can evaluate how changes in chemical composition affect atmospheric climate by considering the radiative feedbacks of chemical constituents. In the last decades, various CTM and CCM models have been developed for the study of tropospheric chemistry (Levy *et al.*, 1985; Müller and Brasseur, 1995; Roelofs and Lelieveld, 1995; Brasseur *et al.*, 1998; Lawrence *et al.*, 1999; Sudo *et al.*, 2002a, 2002b; Horowitz *et al.*, 2003) and for the study of stratospheric chemistry (*e.g.* Chipperfield *et al.*, 1993; Lefevre *et al.*, 1994; Rasch *et al.*, 1995; Akiyoshi, 2000; Nagashima *et al.*, 2002; Shibata *et al.*, 2005). These models focus on either the troposphere or the middle atmosphere, partially due to computational constraints. However, a better understanding of interactions between the troposphere and the middle atmosphere, such as stratosphere-troposphere exchanges (STE), will improve the simulations of atmospheric chemistry and dynamics. Thus, CCMs targeting both regions have been developed in recent years (Rotman *et al.*, 2004; Jöckel *et al.*, 2006; Kinnison *et al.*, 2007). They can calculate dynamical fields and chemical compositions in the middle atmosphere and troposphere in a seamless and more consistent manner, even though the models are more complex. Using one such CCM, Pan *et al.* (2007) evaluated the representation of chemical transport processes in the upper troposphere and lower stratosphere (UTLS) region of the extratropics; the results qualitatively agree with observations for the location of the chemical transition across the tropopause.

In this paper, we introduce a new global chemistry-climate model developed at the Meteorological Research Institute (MRI), called *MRI-CCM2* (or simply “Version 2” here), which can simulate atmospheric chemistry and dynamics throughout the troposphere and the stratosphere. The principal objective of *MRI-CCM2* is to study the global behavior of ozone and related chemical species and their impacts on climate. Version 2 is an extension of the stratospheric CCM developed at MRI, known as *MRI-CCM1* (Shibata *et al.*, 2005) or “Version 1” here. Version 1 has been used in the operational system for forecasting UV-B radiation at the Japan Meteorological Agency (JMA). In addition, Version 2 is designed to support one part of an operational air-quality forecast, which is to predict the distribution of photochemical oxidants near the surface. In this paper, we provide a detailed description of Version 2 and evaluate its performance primarily by focusing on tropospheric ozone and its precursors, CO

and NO_x . The model configurations and performance of MRI-CCM1 have already been presented in several papers (Shibata *et al.*, 2005; Eyring *et al.*, 2006, 2010; Shibata and Deushi, 2008a, b). For the evaluation of Version 2, we compare the model results with several observational data sets that have been compiled from aircraft campaigns, and ozonesonde and surface measurements.

2. Model Description

The MRI-CCM2 model (henceforth *Version 2*) is a global CCM that simulates the distribution and evolution of ozone and other related chemical species in the troposphere and the stratosphere in three dimensions. The model consists of chemistry and dynamics modules, which can be coupled interactively. We have updated and markedly improved the chemistry module of Version 1 to incorporate detailed ozone chemistry in the troposphere. We have also added more chemical reactions to better simulate stratospheric ozone chemistry. The general circulation model of Shibata *et al.*, 1999 (abbreviated MJ98) is used as the dynamics module that provides the dynamical fields such as temperature, horizontal and vertical wind, and surface pressure for the chemistry

module in a way similar to Version 1. The chemistry module can feed back to the dynamics module by incorporating and considering the radiative effects of certain chemical tracers, such as O_3 , CH_4 , CO_2 , water vapor and nitrous oxide (N_2O), predicted in the chemistry module. We can also use Version 2 as a CTM when the radiative feedbacks from the chemistry module are not considered.

2.1 Chemistry module

The chemistry module handles 64 long-lived chemical species (which are transported in the model), seven long-lived chemical families, and 26 short-lived chemical species (which are not transported) as the prognostic variables. Table 1 identifies the long-lived and the short-lived species, and the long-lived families. The chemistry module has two processes: chemistry and transport. The chemistry process consists of four distinct sub-processes: chemical reactions (gas-phase, photolysis and heterogeneous reactions), wet and dry deposition, emissions of trace gases and their boundary conditions, and the formation and sedimentation of polar stratospheric clouds (PSCs). We do not describe the parameterization of the formation and sedimentation of these clouds in this paper, because they are identical to the treatment in Version 1, de-

Table 1. Names of chemical species

Long-lived species		
01... N_2O	02... CH_4	03... H_2O
04... NO_y	05... HNO_3	06... N_2O_5
07... Cl_y	08... O_x	09... CO
10... OCIO	11... CO_2	12...Passive tracer
13... HCl	14... ClONO_2	15... HOCl
16... Cl_2	17... H_2O_2	18... ClONO_2
19... HBr	20... BrONO_2	21... NO_x
22... HO_2NO_2	23... ClO_x	24... BrO_x
25... Cl_2O_2	26... HOBr	27... CCl_4 (CFC-10)
28... CFCl_3 (CFC-11)	29... CF_2Cl_2 (CFC-12)	30... Br_y
31... CH_3Cl	32... CH_3Br	33... CF_2ClBr (Halon-1211)
34... CF_3Br (Halon-1301)	35... COF_2	36... HF
37... CH_2O	38... CH_3OOH	39... C_2H_6
40... CH_3CHO	41... $\text{C}_2\text{H}_5\text{OOH}$	42...PAN ($\text{CH}_3\text{C}(\text{O})\text{OONO}_2$)
43... $\text{CH}_3\text{C}(\text{O})\text{OOH}$	44... C_3H_8	45...ACET ($\text{CH}_3\text{C}(\text{O})\text{CH}_3$)
46... $\text{C}_3\text{H}_7\text{OOH}$	47...HACET ($\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OH}$)	48...MGly ($\text{CH}_3\text{C}(\text{O})\text{CHO}$)
49... C_2H_4	50...GLY ALD (HOCH_2CHO)	51...GPAN ($\text{HOCH}_2\text{C}(\text{O})\text{OONO}_2$)
52... $\text{GC}(\text{O})\text{OOH}$ ($\text{HOCH}_2\text{C}(\text{O})\text{OOH}$)	53... C_3H_6	54...ONIT ($\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{ONO}_2$)
55... POOH ($\text{HOC}_3\text{H}_6\text{OOH}$)	56... C_4H_{10} ^a	57... C_5H_8 (isoprene)
58...MACR ^b	59...ISON ^c	60...ISOPOOH ^d
61...NALD ^e	62...MACROOH ^f	63...MPAN ^g
64... $\text{C}_{10}\text{H}_{16}$ (terpenes)		

^a C_4H_{10} ... a surrogate for all hydrocarbons with four more carbons, excluding isoprene and terpenes

^a MACR ... methacrolein, methylvinylketone and C_4 carbonyls

^b ISON ... β -hydroxy alkyl nitrates from $\text{ISOPO}_2 + \text{NO}$ and alkyl nitrates from $\text{C}_5\text{H}_8 + \text{NO}_3$

^c ISOPOOH ... β -hydroxy hydro-peroxides from $\text{ISOPO}_2 + \text{NO}_2$

^d NALD ... nitrooxy acetaldehyde

^e MACROOH ... hydro-peroxides from $\text{MACRO}_2 + \text{HO}_2$

^f MPAN ... peroxy methacryloyl nitrate and higher peroxy nitrates

The underlined gas phase reactions are included into MRI-CCM2, but were not treated in MRI-CCM1 (Shibata *et al.*, 2005).

Table 1. (continued)

Short-lived species			
01...O(¹ D)	02...OH	03...Cl	04...O(³ P)
05...O ₃	06...HO ₂	07...NO ₂	08...NO
09...Br	10...N	11...ClO	12...BrO
13...NO ₃	14...BrCl	15...H	<u>16...CH₃O₂</u>
<u>17...C₂H₅O₂</u>	<u>18...CH₃C(O)O₂</u>	<u>19...C₃H₇O₂</u>	<u>20...ACETO₂ (CH₃C(O)CH₂O₂)</u>
<u>21...EO₂ (HOC₂H₄O₂)</u>	<u>22...EO (HOC₂H₄O)</u>	<u>23...GC(O)O₂ (HOCH₂C(O)O₂)</u>	<u>24... PO₂ (HOC₃H₆O₂)</u>
<u>25...ISOPO₂^a</u>	<u>26...MACRO₂^b</u>		

^a ISOPO₂...peroxy radical from C₅H₈ + OH

^b MACRO₂...peroxy radical from MACR + OH

The underlined short-lived species are newly included into MRI-CCM2, but not treated in MRI-CCM1 (Shibata *et al.*, 2005).

Chemical families	
O _x	= O ₃ + O(³ P) + O(¹ D)
ClO _x	= Cl + ClO
Cl _y	= ClO _x + OCIO + 2Cl ₂ O ₂ + HCl + ClONO ₂ + HOCl + 2Cl ₂ + ClNO ₂ + BrCl
NO _x	= NO + NO ₂ + NO ₃
NO _y	= NO _x + N + HNO ₃ + 2N ₂ O ₅ + HO ₂ NO ₂ + ClONO ₂ + ClNO ₂ + BrONO ₂ + PAN + GPAN + ONIT + ISON + NALD + MPAN
BrO _x	= Br + BrO + BrCl
Br _y	= BrO _x + HBr + HOBr + BrONO ₂

scribed by Shibata *et al.* (2005).

The transport process includes two sub-processes: grid-scale transport, and parameterization of vertical transports due to moist convection and turbulent vertical mixing in the planetary boundary layer. We calculate the grid-scale transport with a hybrid semi-Lagrangian scheme (Shibata *et al.*, 2005; Shibata and Deushi, 2008b). The transport process computes the displacement of all the long-lived species except water vapor. Because water vapor is essentially treated in the dynamics module, it is subject only to chemical transformations in the chemistry module, and the rate of change of concentration of water vapor due to the chemical transformations is carried over to the computation of specific humidity in the dynamics module.

2.1.1 Chemical reactions

The chemistry module considers 172 gas-phase reactions (Table 2), 59 photolysis reactions (Table 3), and 16 heterogeneous reactions (Table 4), in predicting the detailed chemistry in the stratosphere and troposphere as other sophisticated CCMs do (Rotman *et al.*, 2004; Jöckel *et al.*, 2006; Kinnison *et al.*, 2007). Besides the major reactions for ozone chemistry in the stratosphere, an additional 88 gas-phase reactions, 21 photolysis reactions and 7 heterogeneous reactions are newly incorporated in Version 2 to depict detailed chemical reactions of ozone and its precursors in the troposphere. As a result, the new chemistry module can represent the more elaborate photochemistry of HO_x-NO_x-CH₄-CO, and a nearly explicit mechanism for degradation of the following non-methane hydrocarbons (NMHCs): ethane (C₂H₆), propane (C₃H₈), ethene (C₂H₄), propene (C₃H₆), iso-

prene (C₅H₈), a-pinene (C₁₀H₁₆)¹, and n-butane (C₄H₁₀)². The degradation mechanisms of the last two species, which are surrogate species, are described by their oxidation reactions, following Horowitz *et al.* (2003). The highly detailed Master Chemical Mechanism (MCM), Version 2.0 (Jenkin *et al.*, 1997) provides the base mechanism for acetone chemistry and propane oxidation. We adopted the condensed isoprene oxidation scheme of Pöschl *et al.* (2000), which is a reduction of the MCM, for computational efficiency. Isoprene oxidation mechanisms are not thoroughly understood, as observations and models disagree on the recycling efficiency of OH radicals (Lelieveld *et al.*, 2008). Although some new schemes (Butler *et al.*, 2008; Taraborrelli *et al.*, 2009) have been proposed to resolve the disagreements, there is a great deal of uncertainty about the current isoprene oxidation schemes in atmospheric chemistry models. In the future, Version 2 will need more updates of the isoprene oxidation scheme.

For the gas-phase reactions, we have generally taken kinetic reaction rates from the Jet Propulsion Laboratory (JPL) database compiled by Sander *et al.* (2006) (the JPL06-2 database), and from the recommendations of the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry (Atkinson *et al.*, 2004, 2006). In a few cases we employed values of Horowitz *et al.* (2003), Pöschl *et al.* (2000), Jenkin *et al.* (1997), Shibata *et al.* (2005), and the references therein. The JPL06-2 database also gave the absorption cross sections and quantum yields needed for

¹ A-pinene is defined as a surrogate variable for all terpenes, as was done in MOZART-2 (Horowitz *et al.*, 2003).

² N-butane is similarly defined as a surrogate for all hydrocarbons with four or more carbons (excluding isoprene and terpenes).

Table 2. Gas Phase Reactions

No.	Reactions	No.	Reactions
Oxygen reactions		a _{23c}	H + HO ₂ → H ₂ O + O
hk ₁	O + O + M → O ₂ + M	a ₂₄	H ₂ + O → OH + H
hk ₂	O + O ₂ + M → O ₃ + M	a ₂₆	HO ₂ + NO → NO ₂ + OH
hk ₃	O + O ₃ → 2O ₂	a ₂₇	HO ₂ + HO ₂ → H ₂ O ₂ + O ₂
hk ₄	O ^{1D} + N ₂ → O + N ₂	a ₃₀	OH + H ₂ O ₂ → H ₂ O + HO ₂
hk ₅	O ^{1D} + O ₂ → O + O ₂	a ₃₆	OH + CO → CO ₂ + HO ₂
Odd hydrogen reactions		Odd nitrogen reactions	
a ₁	H + O ₂ + M → HO ₂ + M	b ₃	NO ₂ + O → NO + O ₂
a _{1et}	O ^{1D} + H ₂ O → 2OH	b ₄	NO + O ₃ → NO ₂ + O ₂
a ₂	H + O ₃ → OH + O ₂	b ₆	N + NO → N ₂ + O
a _{2et}	O ^{1D} + CH ₄ → 0.75CH ₃ O ₂ + 0.25CH ₂ O + 0.75OH + 0.4HO ₂ + 0.05H ₂	b ₇	N + O ₂ → NO + O
a _{3et}	O ^{1D} + H ₂ → OH + H	b ₉	NO ₂ + O ₃ → NO ₃ + O ₂
a ₅	OH + O → H + O ₂	b ₁₂	NO ₂ + NO ₃ + M → N ₂ O ₅ + M
a ₆	OH + O ₃ → HO ₂ + O ₂	b ₂₂	NO ₂ + OH + M → HNO ₃ + M
a _{6b}	HO ₂ + O ₃ → OH + 2O ₂	b ₂₃	NO ₂ + HO ₂ + M → HO ₂ NO ₂ + M
a ₇	HO ₂ + O → OH + O ₂	b ₂₄	HO ₂ NO ₂ + M → HO ₂ + NO ₂ + M
a ₈	OH + OH → H ₂ O + O	b ₂₇	HNO ₃ + OH → H ₂ O + NO ₃
a ₉	OH + OH + M → H ₂ O ₂ + M	b ₂₈	HO ₂ NO ₂ + OH → H ₂ O + NO ₂ + O ₂
a ₁₀	H ₂ O ₂ + O → OH + HO ₂	b ₃₂	N ₂ O ₅ + M → NO ₂ + NO ₃ + M
a ₁₇	OH + HO ₂ → H ₂ O + O ₂	b ₃₈	N ₂ O + O ^{1D} → N ₂ + O ₂
a ₁₉	OH + H ₂ → H ₂ O + H	b ₃₉	N ₂ O + O ^{1D} → 2NO
a _{23a}	H + HO ₂ → 2OH	b ₅₁	NO ₃ + NO → 2NO ₂
a _{23b}	H + HO ₂ → H ₂ + O ₂	b ₅₂	NO ₃ + HO ₂ → OH + NO ₂ + O ₂
		b ₅₃	N ₂ O ₅ + H ₂ O → 2HNO ₃

The underlined gas phase reactions are newly included into MRI-CCM2, but not treated in MRI-CCM1 (Shibata *et al.*, 2005).

No.	Reactions
Carbon reactions	
— CH ₄ oxidation —	
c ₂	CH ₄ + OH → CH ₃ O ₂ + H ₂ O
c ₃	CH ₃ O ₂ + NO → CH ₂ O + NO ₂ + HO ₂
c ₄	CH ₃ O ₂ + CH ₃ O ₂ → 2CH ₂ O + 2HO ₂ + O ₂
c ₅	CH ₃ O ₂ + CH ₃ O ₂ → CH ₂ O + O ₂ (+CH ₃ OH)
c ₆	CH ₃ O ₂ + HO ₂ → CH ₃ OOH + O ₂
c ₇	CH ₃ OOH + OH → 0.7CH ₃ O ₂ + 0.3CH ₂ O + 0.3OH + H ₂ O
c ₈	CH ₂ O + OH → CO + HO ₂ + H ₂ O
c ₉	CH ₂ O + NO ₃ → CO + HO ₂ + HNO ₃
— C ₂ H ₆ oxidation and Acetaldehyde degradation —	
c ₁₀	C ₂ H ₆ + OH → C ₂ H ₅ O ₂ + H ₂ O
c ₁₁	C ₂ H ₅ O ₂ + NO → CH ₃ CHO + NO ₂ + HO ₂
c ₁₂	C ₂ H ₅ O ₂ + HO ₂ → C ₂ H ₅ OOH + O ₂
c ₁₃	C ₂ H ₅ O ₂ + CH ₃ O ₂ → 0.8CH ₃ CHO + 1.4CO ₂ + 0.6HO ₂
c ₁₄	C ₂ H ₅ O ₂ + C ₂ H ₅ O ₂ → 1.6CH ₃ CHO + 1.2HO ₂ (+ 0.4C ₂ H ₅ OH)
c ₁₅	C ₂ H ₅ OOH + OH → 0.286C ₂ H ₅ O ₂ + 0.714CH ₃ CHO + 0.714OH + H ₂ O
c ₁₆	CH ₃ CHO + OH → CH ₃ C(O)O ₂ + H ₂ O
c ₁₇	CH ₃ CHO + NO ₃ → CH ₃ C(O)O ₂ + HNO ₃
c ₁₈	CH ₃ C(O)O ₂ + NO → CH ₃ O ₂ + CO ₂ + NO ₂
c ₁₉	CH ₃ C(O)O ₂ + NO ₂ + M → PAN + M
c ₂₀	PAN + M → CH ₃ C(O)O ₂ + NO ₂ + M
c ₂₁	CH ₃ C(O)O ₂ + HO ₂ → CH ₃ C(O)OOH + O ₂
c ₂₂	CH ₃ C(O)O ₂ + HO ₂ → O ₃ (+CH ₃ COOH)
c ₂₃	CH ₃ C(O)OOH + OH → CH ₃ C(O)O ₂ + H ₂ O
c ₂₄	CH ₃ C(O)O ₂ + CH ₃ O ₂ → CH ₃ O ₂ + CH ₂ O + CO ₂ + HO ₂ + O ₂
c ₂₅	CH ₃ C(O)O ₂ + CH ₃ O ₂ → CH ₂ O + O ₂ (+ CH ₃ COOH)
c ₂₆	CH ₃ C(O)O ₂ + CH ₃ C(O)O ₂ → 2CH ₃ O ₂ + 2CO ₂ + O ₂
c ₇₃	PAN + OH → CH ₂ O + CO ₂ + NO ₃

Table 2. (continued)

No.	Reactions
— C ₃ H ₈ oxidation —	
<u>c₂₇</u>	C ₃ H ₈ + OH → C ₃ H ₇ O ₂ + H ₂ O
<u>c₂₈</u>	C ₃ H ₇ O ₂ + NO → 0.24C ₂ H ₅ O ₂ + 0.09CH ₃ CHO + 0.18CO + 0.7ACET + 0.6CO ₂ + NO ₂ + HO ₂
<u>c₂₉</u>	C ₃ H ₇ O ₂ + HO ₂ → C ₃ H ₇ OOH + O ₂
<u>c₃₀</u>	C ₃ H ₇ O ₂ + CH ₃ O ₂ → 0.8C ₂ H ₅ O ₂ + 0.3CH ₃ CHO + 0.2ACET + 0.6CO + 0.6CO ₂ + HO ₂
<u>c₃₁</u>	C ₃ H ₇ OOH + OH → 0.667ACET + 0.157C ₃ H ₇ O ₂ + 0.053CH ₃ CHO + 0.142C ₂ H ₅ O ₂ + 0.106CO + 0.035CO ₂ + 0.843OH + 0.157H ₂ O
<u>c₃₂</u>	ACET + OH → ACETO ₂ + H ₂ O
<u>c₃₃</u>	ACETO ₂ + NO → CH ₃ C(O)O ₂ + CH ₂ O + NO ₂
<u>c₃₄</u>	ACETO ₂ + HO ₂ → HACET + O ₂
<u>c₃₅</u>	ACETO ₂ + CH ₃ O ₂ → 0.2HACET + 0.5MGLY + 0.3CH ₃ C(O)O ₂ + 0.8CH ₂ O + 0.3HO ₂ + O ₂ (+ 0.5CH ₃ OH)
<u>c₃₆</u>	MGLY + OH → CH ₃ C(O)O ₂ + CO
<u>c₃₇</u>	MGLY + NO ₃ → CH ₃ C(O)O ₂ + CO + HNO ₃
<u>c₃₈</u>	HACET + OH → 0.323ACETO ₂ + 0.677MGLY + 0.677OH
<u>c₇₁</u>	C ₃ H ₇ O ₂ + C ₃ H ₇ O ₂ → 2.4CH ₃ CHO + 1.2HO ₂ + O ₂ (+ 0.4C ₃ H ₇ OH)
<u>c₇₄</u>	ACETO ₂ + ACETO ₂ → 0.37MGLY + 1.26CH ₃ C(O)O ₂ + 1.26CH ₂ O + O ₂ (+ CH ₃ C(O)CH ₂ OH)
— C ₂ H ₄ oxidation —	
<u>c₃₉</u>	C ₂ H ₄ + OH + M → 0.75EO ₂ + 0.5CH ₂ O + 0.25HO ₂ + M
<u>c₄₀</u>	EO ₂ + NO → EO + NO ₂
<u>c₄₁</u>	EO + O ₂ → GLY ALD + HO ₂
<u>c₄₂</u>	EO → 2CH ₂ O + HO ₂
<u>c₄₃</u>	C ₂ H ₄ + O ₃ → CH ₂ O + 0.5CO + 0.12HO ₂ + 0.12OH
<u>c₄₄</u>	GLY ALD + OH → 0.8GC(O)O ₂ + 0.4CO + 0.2HO ₂ + 0.2H ₂
<u>c₄₅</u>	GC(O)O ₂ + NO ₂ + M → GPAN + M
<u>c₄₆</u>	GPAN + M → GC(O)O ₂ + NO ₂ + M
<u>c₄₇</u>	GC(O)O ₂ + NO → CH ₂ O + CO ₂ + HO ₂ + NO ₂
<u>c₄₈</u>	GC(O)O ₂ + HO ₂ → 0.7GC(O)O ₂ H + 0.3O ₃ (+ 0.3CH ₃ COOH)
<u>c₄₉</u>	GC(O)O ₂ + CH ₃ O ₂ → 2CH ₂ O + CO ₂ + 2HO ₂
<u>c₅₀</u>	GC(O)O ₂ + CH ₃ O ₂ → CH ₂ O (+ CH ₃ COOH)
<u>c₅₁</u>	GC(O)O ₂ + GC(O)O ₂ → 2CH ₂ O + 2CO ₂ + 2HO ₂
<u>c₅₂</u>	GC(O)O ₂ H + OH → 0.5GC(O)O ₂ + 0.5CH ₂ O + 0.5CO ₂ + 0.5OH
<u>c₇₀</u>	EO ₂ + EO ₂ → EO + 0.5GLY ALD + O ₂ (+ 0.5HOC ₂ H ₄ OH)
— C ₃ H ₆ oxidation —	
<u>c₅₃</u>	C ₃ H ₆ + OH + M → PO ₂ + M
<u>c₅₄</u>	C ₃ H ₆ + O ₃ → 0.08CH ₄ + 0.5CH ₃ CHO + 0.31CH ₃ O ₂ + 0.54CH ₂ O + 0.56CO + 0.19HO ₂ + 0.33OH (+ 0.25CH ₃ COOH)
<u>c₅₅</u>	C ₃ H ₆ + NO ₃ → ONIT
<u>c₅₆</u>	PO ₂ + NO → CH ₃ CHO + CH ₂ O + HO ₂ + NO ₂
<u>c₅₇</u>	PO ₂ + HO ₂ → POOH + O ₂
<u>c₅₈</u>	POOH + OH → 0.5PO ₂ + 0.5HACET + 0.5OH + H ₂ O
<u>c₆₀</u>	ONIT + OH → MGLY + NO ₂
<u>c₆₁</u>	EO ₂ + HO ₂ → 0.667POOH + O ₂
<u>c₇₂</u>	PO ₂ + PO ₂ → 0.75GLY ALD + CH ₃ CHO + CH ₂ O + HO ₂ (+ 0.5HOC ₃ H ₆ OH)
— C ₄ H ₁₀ oxidation —	
<u>c₆₂</u>	C ₄ H ₁₀ + OH → 0.468ISOPO ₂ + 0.02C ₃ H ₇ O ₂ + 0.3C ₂ H ₅ O ₂ + CH ₂ O + HO ₂ + H ₂ O
— Isoprene oxidation —	
<u>i₁</u>	C ₅ H ₈ + O ₃ → 0.65MACR + 0.1MACRO ₂ + 0.58CH ₂ O + 0.1CH ₃ C(O)O ₂ + 0.08CH ₃ O ₂ + 0.14CO + 0.09H ₂ O ₂ + 0.25HO ₂ + 0.25OH (+ 0.28HCOOH)
<u>i₂</u>	C ₅ H ₈ + OH → ISOPO ₂
<u>i₃</u>	C ₅ H ₈ + NO ₃ → ISON
<u>i₄</u>	ISOPO ₂ + NO → 0.044ISON + 0.956MACR + 0.956CH ₂ O + 0.956HO ₂ + 0.956NO ₂
<u>i₅</u>	ISOPO ₂ + HO ₂ → ISOPOOH
<u>i₆</u>	ISOPO ₂ + ISOPO ₂ → 2MACR + CH ₂ O + CO ₂ + HO ₂
<u>i₇</u>	ISOPOOH + OH → MACR + CO ₂ + OH
<u>i₈</u>	ISON + OH → NALD + 0.2MGLY + 0.1CH ₃ C(O)O ₂ + 0.1CH ₂ O + 2.1CO ₂ + 0.1HO ₂
<u>i₉</u>	MACR + OH → MACRO ₂
<u>i₁₀</u>	MACR + O ₃ → 0.9MGLY + 0.1CH ₃ C(O)O ₂ + 0.22CO + 0.43CO ₂ + 0.32HO ₂ + 0.19OH (+ 0.45HCOOH)

Table 2. (continued)

Table 2. (continued)			
No.		Reactions	
i_{11}	MACR + NO	$\rightarrow 0.5\text{MGLY} + 0.25\text{HACET} + 0.25\text{CH}_3\text{C}(\text{O})\text{O}_2 + 0.75\text{CH}_2\text{O} + 0.25\text{CO} + 0.25\text{CO}_2 + 0.75\text{HO}_2 + 0.19\text{OH} + \text{NO}_2$	
i_{12}	MACRO ₂ + HO ₂	$\rightarrow \text{MACROOH}$	
i_{13}	MACRO ₂ + MACRO ₂	$\rightarrow \text{HACET} + \text{MGLY} + 0.5\text{CH}_2\text{O} + 0.5\text{CO} + 0.5\text{CO}_2$	
i_{14}	MACRO ₂ + NO ₂ + M	$\rightarrow \text{MPAN} + \text{M}$	
i_{15}	MPAN + M	$\rightarrow \text{MACRO}_2 + \text{NO}_2 + \text{M}$	
i_{16}	MPAN + OH	$\rightarrow 0.2\text{MGLY} + 0.1\text{CH}_3\text{C}(\text{O})\text{O}_2 + 0.1\text{CH}_2\text{O} + 3.1\text{CO}_2 + 0.1\text{HO}_2 + \text{NO}_2$	
i_{17}	MACROOH + OH	$\rightarrow \text{MACRO}_2 + \text{H}_2\text{O}$	
i_{18}	NALD + OH	$\rightarrow \text{CH}_2\text{O} + \text{CO} + \text{NO}_2$	
— Terpenes oxidation —			
t_1	C ₁₀ H ₁₆ + OH	$\rightarrow 1.3\text{ISOPO}_2 + 0.6\text{ACET} + 1.7\text{CO}_2$	
t_2	C ₁₀ H ₁₆ + O ₃	$\rightarrow 1.3\text{MACR} + 0.2\text{MACRO}_2 + 0.2\text{CH}_3\text{C}(\text{O})\text{O}_2 + 0.16\text{CH}_3\text{O}_2 + 0.18\text{H}_2\text{O}_2 + 1.16\text{CH}_2\text{O} + 0.5\text{OH} + 0.28\text{CO} + 0.5\text{HO}_2 + 1.44\text{CO}_2 (+ 0.56\text{HCOOH})$	
t_3	C ₁₀ H ₁₆ + NO ₃	$\rightarrow 1.2\text{ISOPO}_2 + 4\text{CO}_2 + \text{NO}_2$	

No.		Reactions		No.		Reactions	
Chlorine reactions				d_{64}	OCIO + O	$\rightarrow \text{ClO} + \text{O}_2$	
d_0	CH ₃ Cl + OH	$\rightarrow \text{Cl} + \text{H}_2\text{O} (+ \text{products})$		d_{65}	OCIO + NO	$\rightarrow \text{ClO} + \text{NO}_2$	
d_2	Cl + O ₃	$\rightarrow \text{ClO} + \text{O}_2$		d_{101}	CCl ₄ + O ^{1D}	$\rightarrow 4\text{Cl} (+ \text{products})$	
d_3	ClO + O	$\rightarrow \text{Cl} + \text{O}_2$		d_{102}	CFCl ₃ + O ^{1D}	$\rightarrow 3\text{Cl} + \text{HF} (+ \text{products})$	
d_4	ClO + NO	$\rightarrow \text{Cl} + \text{NO}_2$		d_{103}	CF ₂ Cl ₂ + O ^{1D}	$\rightarrow 2\text{Cl} + \text{COF}_2 (+ \text{products})$	
d_5	Cl + CH ₄	$\rightarrow \text{HCl} + \text{CH}_3\text{O}_2$		d_{110}	COF ₂ + O ^{1D}	$\rightarrow 2\text{HF} (+ \text{products})$	
d_6	Cl + H ₂	$\rightarrow \text{HCl} + \text{H}$		Bromine reactions			
d_7	Cl + HO ₂	$\rightarrow \text{HCl} + \text{O}_2$		e_2	Br + O ₃	$\rightarrow \text{BrO} + \text{O}_2$	
d_8	ClO + OH	$\rightarrow \text{Cl} + \text{HO}_2$		e_3	BrO + O	$\rightarrow \text{Br} + \text{O}_2$	
d_9	ClO + OH	$\rightarrow \text{HCl} + \text{O}_2$		e_4	BrO + NO	$\rightarrow \text{NO}_2 + \text{Br}$	
d_{11}	HCl + OH	$\rightarrow \text{Cl} + \text{H}_2\text{O}$		e_{5a}	BrO + ClO	$\rightarrow \text{OCIO} + \text{Br}$	
d_{31}	ClO + NO ₂ + M	$\rightarrow \text{ClONO}_2 + \text{M}$		e_{5b}	BrO + ClO	$\rightarrow \text{Br} + \text{Cl} + \text{O}_2$	
d_{32}	ClONO ₂ + O	$\rightarrow \text{ClO} + \text{NO}_3$		e_{5c}	BrO + ClO	$\rightarrow \text{BrCl} + \text{O}_2$	
d_{33}	ClO + HO ₂	$\rightarrow \text{HOCl} + \text{O}_2$		e_6	BrO + BrO	$\rightarrow 2\text{Br} + \text{O}_2$	
d_{34}	HOCl + OH	$\rightarrow \text{H}_2\text{O} + \text{ClO}$		e_7	Br + HO ₂	$\rightarrow \text{HBr} + \text{O}_2$	
d_{35}	HOCl + O	$\rightarrow \text{OH} + \text{ClO}$		e_8	Br + OCIO	$\rightarrow \text{BrO} + \text{ClO}$	
d_{36}	Cl + NO ₂ + M	$\rightarrow \text{ClNO}_2 + \text{M}$		e_{11}	HBr + OH	$\rightarrow \text{H}_2\text{O} + \text{Br}$	
d_{37}	HOCl + Cl	$\rightarrow \text{OH} + \text{Cl}_2$		e_{13}	BrO + NO ₂ + M	$\rightarrow \text{BrONO}_2 + \text{M}$	
d_{60}	ClO + ClO + M	$\rightarrow \text{Cl}_2\text{O}_2 + \text{M}$		e_{15}	BrO + HO ₂	$\rightarrow \text{HOBr} + \text{O}_2$	
d_{61}	Cl ₂ O ₂ + M	$\rightarrow \text{ClO} + \text{ClO} + \text{M}$		e_{91}	CF ₃ Br + O ^{1D}	$\rightarrow \text{Br} + \text{COF}_2 + \text{HF} (+ \text{products})$	
d_{62}	OCIO + OH	$\rightarrow \text{HOCl} + \text{O}_2$		e_{92}	CF ₂ ClBr + O ^{1D}	$\rightarrow \text{Br} + \text{Cl} + \text{COF}_2 (+ \text{products})$	
d_{63}	OCIO + Cl	$\rightarrow \text{ClO} + \text{ClO}$		e_{93}	CH ₃ Br + O ^{1D}	$\rightarrow \text{Br} (+ \text{products})$	
d_{64}	OCIO + O	$\rightarrow \text{ClO} + \text{O}_2$					

computations of photolysis reactions, although some of these are identical with those used in Version 1.

Version 2 computes the photolysis frequencies in basically in the same way that Version 1 does: with a pre-calculated multivariate interpolation table derived from a two-stream radiative-transfer model (Huang *et al.*, 1998). However, in Version 2 we added two improvements. First, the interpolation table now treats the dependence of the photolysis frequencies on the surface albedo. Thus, the rates of photolysis (J_{table}) are tabulated at 90 pressure levels, 5 values of the ozone column, 10 solar zenith angles, 5 values of temperature, and 5 values of surface albedo. Whereas we employed the temperature dependency table for 22 photolysis reactions (marked with + in Table 3), we employed the sur-

face albedo table only for those 5 photolysis reactions (marked with *) in which the chemical species strongly absorb visible radiation. Second, Version 2 considers effects of clouds on the photolysis rates: we use the cloudiness and surface albedo at each level to compute an effective albedo and a cloud-correction factor (Horowitz *et al.*, 2003). If no cloud exists below, the effective albedo E_{alb} at level k is identical with the surface albedo S_{alb} below. Otherwise, it is adjusted by clouds below the level k as

$$E_{\text{alb}}(k) = S_{\text{alb}} + f_c(k_s, k) \cdot (1 - t_r(k_s, k)) \cdot (1 - S_{\text{alb}}), \quad (1)$$

where $t_r(k_s, k)$ is the total transmissivity between the lowest level k_s and k , and $f_c(k_s, k)$ is the vertically averaged cloud cover fraction between the levels k_s and k . The transmissivity

Table 3. Photochemical Reactions

No.	Reactions	No.	Reactions
01	$O_2 + h\nu \rightarrow 2O$	31*	$CF_2ClBr + h\nu \rightarrow Br + Cl + COF_2 (+ \text{products})$
02* ^o	$O_3 + h\nu \rightarrow O + O_2$	32*	$CF_3Br + h\nu \rightarrow Br + COF_2 + HF (+ \text{products})$
03	$H_2O + h\nu \rightarrow H + OH$	33*	$ClONO_2 + h\nu \rightarrow ClO + NO_2$
04*	$N_2O + h\nu \rightarrow N_2 + O^{1D}$	34	$BrONO_2 + h\nu \rightarrow BrO + NO_2$
05	$CH_4 + h\nu \rightarrow CH_3O_2 + HO_2$	<u>35</u>	$COF_2 + h\nu \rightarrow 2HF (+ \text{products})$
06* ^o	$NO_2 + h\nu \rightarrow NO + O$	36	$CH_3OOH + h\nu \rightarrow CH_2O + HO_2 + OH$
07*	$HNO_3 + h\nu \rightarrow NO_2 + OH$	37*	$CH_2O + h\nu \rightarrow CO + 2HO_2$
08	$HOCl + h\nu \rightarrow Cl + OH$	38*	$CH_2O + h\nu \rightarrow CO + H_2$
09	$HO_2NO_2 + h\nu \rightarrow HO_2 + NO_2$	39*	$PAN + h\nu \rightarrow CH_3C(O)O_2 + NO_2$
10*	$ClONO_2 + h\nu \rightarrow Cl + NO_3$	40*	$PAN + h\nu \rightarrow CH_3O_2 + CO_2 + NO_3$
11*	$N_2O_5 + h\nu \rightarrow NO_3 + NO_2$	41	$C_2H_5OOH + h\nu \rightarrow CH_3CHO + OH + HO_2$
12*	$O_3 + h\nu \rightarrow O^{1D} + O_2$	42	$CH_3C(O)OOH + h\nu \rightarrow CH_3O_2 + CO_2 + OH$
13*	$H_2O_2 + h\nu \rightarrow 2OH$	43	$CH_3CHO + h\nu \rightarrow CH_3O_2 + CO + HO_2$
14	$OCIO + h\nu \rightarrow O + ClO$	44	$CH_3CHO + h\nu \rightarrow CH_4 + CO$
15	$Cl_2O_2 + h\nu \rightarrow 2Cl + O_2$	45	$C_3H_7OOH + h\nu \rightarrow 0.7ACET + 0.24C_2H_5O_2 + 0.09CH_3CHO + 0.18CO + OH + HO_2$
16	$HCl + h\nu \rightarrow H + Cl$	46*	$ACET + h\nu \rightarrow CH_3C(O)O_2 + CH_3O_2$
17	$Cl_2 + h\nu \rightarrow 2Cl$	47*	$ACET + h\nu \rightarrow 2CH_3O_2 + CO$
18	$CO_2 + h\nu \rightarrow CO + O$	48	$HACET + h\nu \rightarrow CH_3C(O)O_2 + CH_2O + HO_2$
19	$ClNO_2 + h\nu \rightarrow Cl + NO_2$	49 ^o	$MGLY + h\nu \rightarrow CH_3C(O)O_2 + CO + HO_2$
20	$BrONO_2 + h\nu \rightarrow Br + NO_3$	50	$GLY ALD + h\nu \rightarrow CH_2O + CO + 2HO_2$
21	$BrCl + h\nu \rightarrow Br + Cl$	51	$GLY ALD + h\nu \rightarrow CO (+CH_3OH)$
22	$HOBr + h\nu \rightarrow Br + OH$	52	$GC(O)OOH + h\nu \rightarrow CH_2O + CO_2 + OH + HO_2$
23	$NO + h\nu \rightarrow N + O$	53	$POOH + h\nu \rightarrow CH_3CHO + CH_2O + OH + HO_2$
24 ^o	$NO_3 + h\nu \rightarrow NO_2 + O$	54	$ISOPOOH + h\nu \rightarrow MACR + CH_2O + OH + HO_2$
25 ^o	$NO_3 + h\nu \rightarrow NO + O_2$	55*	$ISON + h\nu \rightarrow MACR + CH_2O + HO_2 + NO_2$
26*	$CCl_4 + h\nu \rightarrow 4Cl (+ \text{products})$	56	$MACR + h\nu \rightarrow CH_3C(O)O_2 + CH_2O + CO + HO_2$
27*	$CFCl_3 + h\nu \rightarrow 3Cl + HF (+ \text{products})$	57*	$MPAN + h\nu \rightarrow MACRO_2 + NO_2$
28*	$CF_2Cl_2 + h\nu \rightarrow 2Cl + COF_2 (+ \text{products})$	58	$MACROOH + h\nu \rightarrow 0.5HACET + 0.5MGLY + 0.5CH_2O + 0.5CO + OH + HO_2$
29*	$CH_3Cl + h\nu \rightarrow Cl (+ \text{products})$	59	$NALD + h\nu \rightarrow CH_2O + CO + HO_2 + NO_2$
30*	$CH_3Br + h\nu \rightarrow Br (+ \text{products})$		

*: temperature dependency is taken into account.

°: effective albedo is taken into account.

The underlined photochemical reactions are newly included into MRI-CCM2, but not treated in MRI-CCM1 (Shibata *et al.*, 2005).

Table 4. Heterogeneous Reactions

No.	Reactions
On sulfate, sea salt, tropospheric cloud particles	
g1	$ClONO_2 + (H_2O)_l \rightarrow HOCl + HNO_3$
g2	$N_2O_5 + (H_2O)_l \rightarrow 2HNO_3$
g3	$BrONO_2 + (H_2O)_l \rightarrow HOBr + HNO_3$
g4	$HO_2 + (H_2O)_l \rightarrow 0.5H_2O_2 + 0.5O_2$
<u>g5</u>	$EO_2 + (H_2O)_l \rightarrow (2/3)POOH$
<u>g6</u>	$PO_2 + (H_2O)_l \rightarrow POOH$
<u>g7</u>	$ISOPO_2 + (H_2O)_l \rightarrow ISOPOOH$
<u>g8</u>	$MACRO_2 + (H_2O)_l \rightarrow MACROOH$
<u>g9</u>	$CH_3COO_2 + (H_2O)_l \rightarrow HO_2 (+ CH_3COOH)$
<u>g10</u>	$NO_2 + (H_2O)_l \rightarrow 0.5NO_2 + 0.5HNO_3$
On polar stratospheric cloud particles	
het1	$ClONO_2 + (H_2O)_s \rightarrow HOCl + (HNO_3)_s$
het2	$ClONO_2 + (HCl)_s \rightarrow Cl_2 + (HNO_3)_s$
het3	$N_2O_5 + (H_2O)_s \rightarrow (2HNO_3)_s$
het4	$N_2O_5 + (HCl)_s \rightarrow ClNO_2 + (HNO_3)_s$
het5	$HOCl + (HCl)_s \rightarrow Cl_2 + (H_2O)_s$
het6	$HOBr + (HCl)_s \rightarrow BrCl + (H_2O)_s$

The underlined heterogeneous reactions are newly included into MRI-CCM2, but not treated in MRI-CCM1 (Shibata *et al.*, 2005). t_r between levels k_1 and k_2 is calculated according to

$$t_r(k_1, k_2) = 11.905 / (9.524 + \tau(k_1, k_2)), \quad (2)$$

where τ is the cloud optical depth, which is calculated from the liquid water path LWP (g water/g air) and the cloud fraction f_c (Slingo, 1989; Hack *et al.*, 1993)

$$\tau(k_1, k_2) = [(A + B/r_e)/g] \cdot \int LWP(k) \cdot f_c(k)^{1.5} dp, \quad (3)$$

where g is the gravitational acceleration, $A = 280 \text{ cm}^2 \text{ g}^{-1}$, $B = 13000 \text{ } \mu\text{m cm}^2 \text{ g}^{-1}$, and r_e is the effective cloud droplet radius, assumed to be $10 \text{ } \mu\text{m}$. The distribution of LWP and f_c are predicted in the dynamics module.

The derived photolysis rates (J_{table}) are further modified by the cloud-correction factors F within and above the level k . According to Chang *et al.* (1987), these factors F are parameterized and modify J_{table} in the following way:

$$J_{cld}(k) = J_{table}(k) \cdot (1 + F_{in}(k) + F_{above}(k)), \quad (4)$$

where J_{cld} is the cloud-corrected photolysis rate, and F_{in} and F_{above} are the cloud-correction factors within and above the

level k , respectively

$$F_{in}(k) = (1.4 \cos \chi - 1.0) \cdot f_c(k), \quad (5)$$

$$F_{above}(k) = (1.6 \cos \chi t_r(k, k_{top}) - 1.0) \cdot f_c(k, k_{top}), \quad (6)$$

where χ is the local zenith angle and k_{top} is the top level of the model. Note that the correction factors at $\chi > 60^\circ$ are equal to the values at $\chi = 60^\circ$.

Because heterogeneous reactions on aerosols and cloud particles play a key role in ozone chemistry in the troposphere and stratosphere (Jacob, 2000; Sander *et al.*, 2006), ten heterogeneous reactions on aqueous aerosol particles and liquid cloud droplets are considered in addition to six reactions on PSCs (Table 4). The current version does not bother with reactions on particles of tropospheric ice clouds and solid aerosols such as mineral dust. The heterogeneous reactions that are now included handle NO_2 , HO_2 radicals and some peroxy (RO_2) radicals from unsaturated hydrocarbons like isoprene (Jacob, 2000; Sudo and Akimoto, 2007). Note that the reaction of NO_2 is not considered in liquid clouds because the reaction rate in liquid clouds may be unrealistically fast in the model (Zhang *et al.*, 2004). The reaction of N_2O_5 in aqueous aerosols is important for both stratospheric and tropospheric chemistry (Dentener and Crutzen, 1993), because its reaction near the surface can reduce NO_x levels in polluted areas and thus less ozone is produced.

In the chemistry module, we have parameterized the heterogeneous reactions by a simple approach using reaction probability γ (Jacob, 2000). Following his recommendation, we have not adopted a more detailed approach. The simple approach assumes that the reactive uptake of a gas by aerosols or cloud particles is an irreversible loss process. The first-order rate constant θ (s^{-1}) for the reactive uptake of a gas species by a single-sized (mono-disperse) aerosols or cloud particles is given by

$$B = (a/D_g + 4/\gamma)^{-1} \cdot A, \quad (7)$$

where a (cm) is the particle radius of the aerosols or cloud particles, D_g is the gaseous mass transfer coefficient ($\text{cm}^2 \text{s}^{-1}$) of the gas species in air, v is the mean molecular speed (cm s^{-1}) of the species in air, γ is the reaction probability that a gas molecule impacting the surface of an aerosol (cloud) particle will undergo reaction, and A is the surface area density ($\text{cm}^2 \text{cm}^{-3}$) of the aerosols or cloud particles. The approach is generalized to poly-dispersed aerosols or cloud particles by integrating over the size distribution. Each uptake coefficient γ is adopted from Jacob (2000).

Sulfate and sea-salt aerosols are the two aqueous aerosols considered in the above heterogeneous reactions. While sea salt aerosols have their greatest influence on the chemistry of the marine boundary layer, sulfate aerosols affect ozone chemistry throughout the troposphere and stratosphere. Their effects are quite pronounced in polluted areas near the surface. In Version 2, climatological (monthly averaged) data

dictates the distribution of sulfate and sea-salt aerosols. The surface area densities of the stratospheric sulfate aerosols are specified by the satellite-observed zonal-mean distribution (Eyring *et al.*, 2006), but those of the tropospheric aerosols are calculated from a 3-D climatology of dry aerosol concentrations in a global aerosol model (Tanaka *et al.*, 2003). The tropospheric sulfate and dry sea-salt aerosol concentrations are converted to surface area densities by integrating over the size distribution, after considering hygroscopic growth that depends on relative humidity (Chin *et al.*, 2002). In liquid water clouds, the surface area densities are derived from cloud water content and cloud cover fraction, both computed in the dynamics module (we assume that the cloud droplets have a single size with an effective radius of $10 \mu\text{m}$).

When the chemical reactions in the chemistry module are computed, the model diagnoses a concentration of each chemical species at a grid point and moment in time. The chemical ordinary differential equations (ODEs) of the long-lived species are solved by using the multistep implicit-explicit (MIE) scheme (Jacobson, 1999), as in Version 1. The MIE scheme is an iterative method that draws two major advantages from the forward and backward Euler methods: conservation of mass, and stability. The form of an ODE for each long-lived species differs from day to night for computational efficiency (Appendix I). During nighttime, all the photolysis rates are zero and the mixing ratios by volume of the following short-lived species are set to a very small value (1×10^{-30}): $\text{O}(^1\text{D})$, OH , Cl , $\text{O}(^3\text{P})$, HO_2 , Br , N , H , $\text{C}_2\text{H}_5\text{O}_2$, $\text{C}_3\text{H}_7\text{O}_2$, ACETO_2 , EO_2 , EO and PO_2 .

RO_2 radicals are integrated in time by the Euler Backward Iterative (EBI) method based on Hertel *et al.* (1993), while the other short-lived species are diagnosed at each time step. The EBI method uses an analytical formulation for a group of strongly coupled chemical species, and these formulations are solved by using the Euler backward method. The analytical solutions improve the computational efficiency when compared to the well-known Quasi-steady State Approximation (QSSA) method of Hertel *et al.*, 1993. The EBI method performs better than the QSSA method, especially for long time steps under extreme conditions (Hertel *et al.*, 1993), and it has the advantage of conserving mass because it uses only linear operators. Appendix II gives the details of the application of the EBI method to computing the chemical reactions in Version 2. The following two diagnostic methods are used for the other short-lived species: a reduced Jacobian method (Sandilands and McConnel, 1997) for members of the O_x , NO_x , ClO_x and BrO_x chemical families; and a chemical equilibrium method for members of the HO_x family (*i.e.* H , OH and HO_2), N and EO . The latter can be assumed to be instantaneously in chemical equilibrium. These two diagnostic methods are identical to those used in Version 1 (see Appendix II for details).

Chemical equations for all the long-lived and short-lived species are solved iteratively every 10 min. The number

of iterations is set to 10 in the surface boundary layer, 7 in the free troposphere and 5 in the middle atmosphere, with a smooth transition.

2.1.2 Emissions of trace gases and boundary conditions

In the chemistry module, the following atmospheric gases are either assigned specified concentrations or they are specified by emission rates. Throughout the model domain, concentrations of nitrogen (N_2), oxygen (O_2) and hydrogen (H_2) are fixed at uniform mixing ratios of 0.8, 0.2 and 0.5×10^{-6} by volume, respectively. Uniform concentrations for other long-lived species are specified at the surface, for CH_4 , N_2O , CO_2 and the halogenated gases. The global mean values in the 1990s are used to set the uniform concentrations in this study.

On the other hand, emissions of CO , NO_x , and NMHCs (which includes CH_2O , C_2H_6 , C_3H_8 , C_2H_4 , C_3H_6 , C_4H_{10} , ACET, C_5H_{10} , and $C_{10}H_{16}$) are imposed at the surface, except for emissions from aircraft, burning of biomass, and lightning, which are specified at some height above ground. We used the same emission data that was used for the 1990s simulation of MOZART-2 (Horowitz *et al.*, 2003), except for NO emission by lightning. Trace gas emissions are simulated for the following anthropogenic and natural sources: burning of fossil fuels in industrial activities and aircraft, burning of biomass, and natural emissions from vegetation, soils, and the ocean. The anthropogenic emission data is taken from the inventory in the Emission Database for Global Atmospheric Research (EDGAR) v2.0 (Olivier *et al.*, 1996) modified by the seasonal adjustments of Müller (1992). Vegetative emission of isoprene and terpenes is taken from the Global Emissions Inventory Activity (GEIA) (Guenther *et al.*, 1995), and vegetative emissions of other hydrocarbons and NO from Müller (1992). Emission of NO from soils is taken from Yienger and Levy (1995); emission of CO and N_2O from soils, from Müller (1992). Emission of CO , CH_4 , and NMHCs from the ocean is based on Brasseur *et al.* (1998) with the modifications of Horowitz *et al.* (2003). Emissions due to biomass burning are from Andreae and Merlet (2001), but the quantity of biomass burned is based on Hao and Liu (1994) and Müller (1992). Emission of trace gases from burning biomass depends on the height above ground, based on description of EDGAR 32FT2000(v8) ([http://www.rivm.nl/edgar/Images/Description_of_EDGAR_32FT2000\(v8\)_tcm32-22222.pdf](http://www.rivm.nl/edgar/Images/Description_of_EDGAR_32FT2000(v8)_tcm32-22222.pdf)). We may choose a recent inventory of emissions in Asia (Regional Emission inventory in ASia (REAS), Version 1.1) (Ohara *et al.*, 2007) in Version 2, though it was not used here. In the future, even newer inventories of historical emission data such as RETRO (Schultz *et al.*, 2008) might be worthwhile.

Emission of NO by lightning is diagnosed at 6-h intervals. The amount of NO emissions from lightning depends on both lightning flash frequency and the production of NO per flash. The global flash frequency is calculated following

the parameterization of Price and Rind (1992, 1994), who empirically formulated the flash frequencies (flashes/min) per 5 km square (LF_{5km}) for continental and marine convective clouds using cloud height data (Rossow *et al.*, 1996) from the International Satellite Cloud Climatology Project (ISCCP), as

$$LF_{5km} = 3.44 \times 10^{-5} H^{4.9} \quad (\text{in continental convective clouds}), \quad (8)$$

$$LF_{5km} = 6.40 \times 10^{-4} H^{1.73} \quad (\text{in marine convective clouds}), \quad (9)$$

where H is the cloud-top height (km) averaged over a 5 km square. In the model, the cloud-top height H is calculated by using the upward mass flux and detrainment in the convective scheme, and a calibration factor multiplies the flash frequency LF_{5km} in order to adjust for spatial resolution differences.

The NO production rates in each cloud-to-ground (CG) flash and intra-cloud (IC) flash are assumed to be 6.7×10^{26} and 6.7×10^{25} molecules/flash in the column (Price *et al.*, 1997a; 1997b), respectively. The ratio of CG flashes to IC flashes (CG/IC) is calculated empirically as a function of cold-cloud thickness, defined as the depth of a layer from the freezing level up to the cloud top (Price and Rind, 1994; Price *et al.*, 1997a). The diagnosed production rate of NO in the column is then redistributed to each vertical layer, by assuming the C-shaped vertical profiles of Pickering *et al.* (1998).

Actually, the magnitude of global emissions of NO from lightning is still uncertain. Recent model intercomparison studies coordinated by the European Union project “Atmospheric Composition Change: the European Network of Excellence” (ACCENT) (Stevenson *et al.*, 2006) indicate that the global emissions of NO from lightning vary a lot, from 3 to 8 TgN yr⁻¹ in simulations. In this study, the global emission is set to be 5 TgN yr⁻¹. In Version 2, the simulated production of NO by lightning is realistically high over the land in the summer hemisphere where convective activity is intense (Fig. 1). This computed global distribution is similar to that of the estimation from the ISCCP cloud height data (Price *et al.*, 1997a). In January the simulated emission of NO by lightning is large over South America, Central and Southern Africa, the Indonesian maritime continent, and North Australia, while in July it is large over Central and North America, Central and North Africa, East and South Asia, and again, the Indonesian maritime continent.

2.1.3 Deposition

Wet and dry deposition is the path by which some trace gases are ultimately removed from the atmosphere; thus, deposition strongly affects the budget and distribution of atmospheric chemical species. Version 2 implements upgraded parameterization schemes for both wet and dry deposition processes compared to Version 1.

Fig. 1 Simulated emission of NO by lightning in the atmospheric column (in units of $10^{-13} \text{ kg N m}^{-2} \text{ s}^{-1}$) for January (left) and July (right). Ten-year averages of the FREE-run are shown.

2.1.3.1 Dry deposition

Dry deposition is applied for O_3 , HNO_3 , CO , H_2O_2 , NO_2 , HO_2NO_2 , CH_2O , ACET , HACET , MGLY , GLYALD , GCOO_2H , MACR , peroxides like CH_3OOH , and organic nitrates like PAN . We have adopted a resistance series parameterization to calculate dry deposition velocities, largely based on Seinfeld and Pandis (1998) and Zhang *et al.* (2002, 2003). In this parameterization, the dry deposition velocity V_d is defined to be the inverse of the total resistance

$$V_d = 1/(R_a + R_b + R_s), \quad (10)$$

where R_a is the aerodynamic resistance, R_b is the quasi-laminar layer resistance, and R_s is the surface resistance (Seinfeld and Pandis, 1998). The aerodynamic resistance R_a is determined by the amount of turbulent transport in the surface layer (the constant-flux layer), to which gradient-transport theory and mass-transfer or momentum-transfer similarity is applied. Following Jacobson (1999), R_a is given by

$$R_a = \int_{z_0}^{z_r} \varphi_h dz / (\kappa u^* z), \quad (11)$$

where κ is the von Kaman's constant, u^* is the friction velocity derived from the dynamics module, z_0 is the surface roughness length, φ_h is the dimensionless potential temperature gradient which is a function of the Monin-Obukhov length, and Z_r is the reference height set to 10 m. The quasi-laminar layer resistance R_b for a gas is determined by the molecular diffusion through a laminar layer having thickness of 0.1 to 0.01 cm. The layer resistance R_b is given by

$$R_b = 5 S_c^{2/3} / u^*, \quad (12)$$

where S_c is the Schmidt number calculated with the kinematic viscosity of air and the diffusive coefficient for the gas (Seinfeld and Pandis, 1998).

The surface resistance R_s , which has almost the largest effect of the three resistances over land, is determined by chemical, biological, and physical interactions of gases

with the surface, following Zhang *et al.* (2002, 2003). R_s is parameterized as a set of two parallel resistances: stomatal resistance (R_{st}) plus a mesophyll resistance (R_m), and non-stomatal resistance (R_{ns}), as

$$1/R_s = (1 - W_{st})/(R_{st} + R_m) + 1/R_{ns}, \quad (13)$$

where W_{st} is the fraction of stomatal closure, which depends on solar radiation and the canopy wet conditions. R_{st} has a finite value only during daytime, when it is calculated from a “sunlit/shade big-leaf” (SSBL) model (Zhang *et al.*, 2002, 2003) described below. R_m is set to constant values: 100 (s m^{-1}) for the chemical species of low solubility and small oxidizing capacity; 0 (s m^{-1}) for others.

In the sunlit and shade big-leaf model, R_{st} is expressed by

$$R_{st} = 1/(G_{st}(PAR) \cdot f(T) \cdot f(D) \cdot f(\Psi) \cdot D_i/D_v), \quad (14)$$

where D_v and D_i are the respective molecular diffusivities for water vapor and the trace gas, G_{st} is the unstressed canopy stomatal conductance which is a function of photosynthetically active radiation (PAR). The dimensionless functions $f(T)$, $f(D)$, and $f(\Psi)$ represent the effects of reducing leaf stomatal conductance by air temperature T , water vapor deficit D , and water stress Ψ , respectively. Since the canopy is divided into the sunlit big-leaf portion and the shaded portion, G_{st} is expressed as the sum of sunlit and shaded unstressed leaf stomatal conductances $1/r_{st}$ weighted by the respective total leaf area index F

$$G_{st}(PAR) = F_{sun}/r_{st}(PAR_{sun}) + F_{shade}/r_{st}(PAR_{shade}), \quad (15)$$

and resistance r_{st} is expressed by

$$r_{st}(PAR) = r_{stmin} \cdot (1 + b_{rs}/PAR), \quad (16)$$

where r_{stmin} is the minimum leaf stomatal resistance, and b_{rs} is an empirical constant.

There are also two parallel contributions to the non-stomatal resistance R_{ns} : the first is the soil uptake resistance (the

in-canopy aerodynamic resistance (R_{ac}) plus the subsequent ground resistance (R_g), and the cuticle uptake resistance (R_{cut})

$$1/R_{ns} = 1/(R_{ac} + R_g) + 1/R_{cut}. \quad (17)$$

R_{ac} is formulated by

$$R_{ac} = R_{ac0} \cdot LAI^{1/4}/u^{*2}, \quad (18)$$

where the reference value R_{ac0} is dependent on canopy type, season, and leaf area index.

R_g and R_{cut} are evaluated for sulfur dioxide (SO_2) and O_3 at first, and then scaled for other gaseous species by using scaling parameters based on their solubility and half-redox reactivity. R_g is tabulated for many land use categories including snow covered soil, and modified for the cases of rain and/or dew. The conditions of rain or dew are determined by surface precipitation, specific humidity, and temperature calculated in the dynamics module at each time step, following Brook *et al.* (1999). R_{cut} is evaluated whenever an atmospheric condition of dry air, or dew (or) rain occurs. If it is below $-1^\circ C$ and is dry, R_g and R_{cut} increase with temperature by an upper limit of 2 times their original values for the term $e^{0.2(-1-T)}$. Because R_{st} , R_m , R_{ac} and R_{cut} only apply over surfaces with leaf canopies, R_m and R_{ac} (R_{st} and R_{cut}) are set to token values of zero (an impossibly large value) over regions without leaf canopies (sea, sea ice, bare soil, and perennial land ice).

Because the surface resistance calculations of CO and CH_4 are not treated in Zhang *et al.* (2002, 2003), their surface resistances are calculated as a function of net primary production (NPP), in the case of CO, and of constants specific to land-use categories, in the case of CH_4 , following the formulation of Müller and Brasseur *et al.* (1995).

The simulated dry deposition velocities ($cm\ s^{-1}$) of O_x (Fig. 2) capture general features of the observed global distribution with realistic seasonal variability. The deposition velocities are less than $0.1\ cm\ s^{-1}$ over the high latitudes in winter, because the surface is nearly all covered with snow or ice, and solar insolation is small or zero. In the tropical rain forest, on the other hand, they have high values ($> 0.7\ cm\ s^{-1}$)

throughout the year. In the northern mid-latitudes in summer, they range from 0.2 to $0.5\ cm\ s^{-1}$ over land surfaces, in good agreement with the observations (Padro, 1996; Massman *et al.*, 1994).

2.1.3.2 Wet deposition

Version 2 has two wet deposition processes: scavenging in the cloud (“rain-out”) and scavenging below the cloud (“wash-out”). Whether a trace gas undergoes wet deposition depends on its solubility in cloud or rain droplets, and is determined by the effective Henry’s law constant (H_s) at standard pressure and temperature (Sudo *et al.*, 2002a). The scavenging in the cloud is used for moderately and highly soluble species ($H_s > 10^2\ M\ atm^{-1}$) (HNO_3 , H_2O_2 , HO_2NO_2 , HCl , HBr , COF_2 , HF , CH_2O , CH_3CO_3H , $HACET$, $MGLY$, $GLYALD$, $GCOO_2H$, $ISON$, and peroxides like CH_3OOH), while scavenging below the cloud is used for highly soluble gases ($H_s > 10^4\ M\ atm^{-1}$) such as HNO_3 , H_2O_2 , HCl , HBr , and H_2O_2 . The rain-out and wash-out scavenging processes are represented as a first-order loss process by Giorgi and Chameides (1985), and solved implicitly:

$$q^{t+\Delta t} - q^t (\Delta q) = -\beta q^{t+\Delta t}/(1 + \beta \Delta t), \quad (19)$$

where Δt is the time step (s), q^t and $q^{t+\Delta t}$ are mixing ratios (vol/vol) of species q at time $t = t$ and $t + \Delta t$, and β is loss rate (s^{-1}) due to wet deposition. Because Δq due to in-cloud and below-cloud scavenging (Δq_{in} and Δq_{below}) are evaluated within the cloudy and rainy part of a model grid box respectively, the total loss (Δq_{total}) in the model grid box is expressed by

$$\Delta q_{total} = FC_c \cdot \Delta q_{in,c} + FC_l \cdot \Delta q_{in,l} \quad (\text{for moderately soluble species}), \quad (20)$$

$$\Delta q_{total} = FC_c \cdot \Delta q_{in,c} + FC_l \cdot \Delta q_{in,l} + FR_c \cdot \Delta q_{below,c} + FR_l \cdot \Delta q_{below,l} \quad (\text{for highly soluble species}), \quad (21)$$

where the subscripts “c” and “l” mean convective and large-scale condensation, respectively. FC and FR are the cloud fraction and rain fraction in a grid box, respectively; FC_l is

Fig. 2 Simulated dry deposition velocities (in $cm\ s^{-1}$) of O_x at the surface for (left) January and (right) July. Ten-year averages of the FREE-run are shown.

obtained from the dynamics module at each time step; FR_i is estimated from FC_i under the assumption of maximum-random overlap; FC_c and FR_c are uniformly set to 0.05.

For in-cloud scavenging, the loss rate β_{in} (s^{-1}) is expressed by

$$\beta_{in} = P_r / (Q_L + d_{H_2O} / HRT), \quad (22)$$

where P_r is the precipitation rate ($kg\ m^{-3}\ s^{-1}$), Q_L is the liquid water content ($kg\ m^{-3}$), d_{H_2O} is the density of liquid water ($= 10^3\ kg\ m^{-3}$), R is the gas constant ($= 0.08205\ atm\ M^{-1}\ K^{-1}$), T is the temperature of ambient air (K), and H is the effective Henry's law constant ($M\ atm^{-1}$) of the soluble gas which is a function of T and pH of the cloud droplets. The pH of cloud droplets is uniformly set to 5.0. P_r and Q_L due to convective and large-scale condensation are diagnosed or predicted in the dynamics module.

In the case of below-cloud scavenging, we assume the gas dissolves irreversibly in raindrops. That is, the return flux of gas out of the raindrops back to the ambient air is neglected. The loss rate due to below-cloud scavenging is approximated by

$$\beta_{below} \simeq 6\ K_g\ L_p / (d_{H_2O}\ Dp), \quad (23)$$

where D_p is the effective raindrop diameter (m), from Mason (1971) and Roelofs and Lelieveld (1995), and L_p is the raindrop density ($g\ cm^{-3}$) determined from the rain water flux entering the model level concerned (Roelofs and Lelieveld, 1995). K_g is the mass transfer coefficient of a gaseous molecule to a spherical raindrop, and calculated by the empirical relation (Seinfeld and Pandis, 1998):

$$K_g = D_g / D_p \cdot (2.0 + 0.6\ Re^{1/2} Sc^{1/3}), \quad (24)$$

where D_g is the molecular diffusion coefficient of the gas, Sc is the Schmidt number, and Re is the Reynolds number. Below $0^\circ C$, we assume deposition of gas only on supercooled water drops, and not onto ice particles. Wet deposition below $0^\circ C$ is so simplified that the loss rate due to wet deposition is decreased by multiplying it with a temperature dependency factor; it is set to zero below $-25^\circ C$ at which all the cloud droplets are assumed to be frozen. The temperature dependency factor changes linearly with temperature from 0 at $-25^\circ C$ to 1 at $0^\circ C$.

The simulated annual-mean rate of loss (day^{-1}) of HNO_3 due to wet deposition is shown in Fig. 3. In the tropics and mid-latitudes HNO_3 is efficiently removed from the lower and the middle troposphere, with the lifetime of 1–2 days. It is associated with activity of cyclones in the mid-latitudes, and intense convective activity in the tropics.

2.1.4 Transport

We use a semi-Lagrangian scheme to simulate grid-scale transport of the long-lived gas species. The scheme has different forms for the horizontal and vertical directions. The horizontal form is an ordinary semi-Lagrangian scheme,

Fig. 3 Simulated annual mean wet deposition loss rate of HNO_3 (in day^{-1}). Ten-year average of the FREE-run is shown. Contour interval is $0.2\ day^{-1}$; contours of 0.1 and $0.01\ day^{-1}$ are also indicated. Values above $0.4\ day^{-1}$ are shaded.

in which departure point locations are calculated following the method of Bates *et al.* (1990). The vertical form, on the other hand, is a mass-conserving flux form in which pressure coordinates are transformed and specified by the vertical velocity. In the current version, the interpolation calculations at departure points are improved very much (Shibata and Deushi, 2008b). In the previous version, a cubic interpolation method was used to interpolate neighboring concentrations in the horizontal directions and to calculate whole column concentrations at the grid point. Instead, the current version employs a quintic interpolation in the horizontal, and a piecewise rational method (Xiao and Peng, 2004) in the vertical which uses a rational function that can be integrated analytically to reconstruct in-cell profiles from cell-averaged values. These improvements clearly reduce the numerical diffusion of transport, which is an artifact. Thus the present model can realistically reproduce an age-of-air distribution in the stratosphere (Eyring *et al.*, 2010) and a clear “tape-recorder signal” of water vapor described by Mote *et al.* (1996) in the tropical stratosphere; both result in substantially less positive bias of ozone concentrations in the lower stratosphere (not shown). Details of the new transport scheme are described by Shibata and Deushi (2008b).

2.1.5 Sub-grid vertical mixing and transport

The vertical turbulent mixing, which mainly occurs in the boundary layer, is expressed by the same diffusion equation as in the dynamics module; its formulation is given by

$$\rho\ \partial q / \partial t = -\rho\ \partial (K_d (\partial q / \partial z)) / \partial z, \quad (25)$$

where ρ is the density of air ($kg\ m^{-3}$), q is the mixing ratio of the long-lived species ($vol\ vol^{-1}$), and K_d is the vertical eddy diffusion coefficient ($m^2\ s^{-1}$) from the level-2 closure scheme of Mellor and Yamada (1974) in the dynamics module.

Eq.(25) is solved implicitly using zero flux condition at the surface for simplicity, even if there is surface emission or deposition. On the other hand, non-zero surface emissions, if there are any, are solved together with the chemical tendency. Then the deposition processes are evaluated.

In addition to the turbulent mixing, vertical transport due to cumulus convection is calculated for the long-lived species by using upward mass flux (UMF) in cumulus clouds, downdraft mass flux (DMF) below the clouds, entrainment (E) into the clouds, and detrainment (D) out of the clouds. The four variables (*i.e.* UMF , DMF , E and D) are predicted at first by a prognostic Arakawa-Schubert (A-S) cumulus parameterization (Arakawa and Schubert, 1974; Shibata *et al.*, 1999) in the dynamics module. However, they are modified for a simplified cumulus transport scheme in the chemistry module. The A-S scheme presupposes various types and stages of cumulus clouds in a grid box, and considers clouds (cloud sub-ensembles) uniquely defined by the respective cloud top heights.

In the chemistry module, one assumes there is a single effective cumulus cloud in the grid box. The cloud is derived from a grand ensemble of all the clouds in the box. Within the effective cloud, an effective UMF and D are defined as the sums of UMF and D in each cloud, and similarly for DMF . The effective entrainment E can be easily derived at each layer, assuming mass continuity between the effective UMF (or DMF), D , and E . The vertical differential equation for a chemical tracer concentration within the effective cumulus cloud (q_c) is expressed as a flux form

$$\partial (UMF \cdot q_c) / \partial z = E \cdot q - D \cdot q_c, \quad (26)$$

where q is rigorously the mean concentration of the chemical tracer in the cloud-free area, but actually equals the overall grid mean concentration. Eq.(26) is sequentially solved to compute q_c from the cloud base at which q_c is assumed equal to the grid mean value.

To derive q , another condition is required that an equivalent subsidence ($-UMF$) is induced within the grid to compensate the effective UMF . Then, the following differential equation can be formulated:

$$\partial (\rho q) / \partial t = \partial (UMF \cdot q_c - UMF \cdot q) / \partial z. \quad (27)$$

Eq.(27) is computed downward from the cloud top to the cloud base. Below the cumulus clouds, formulations similar to Eqs.(26) and (27) are also applied using the effective DMF instead of the effective UMF , and they are calculated in an opposite fashion.

2.2 Dynamics module

The present general circulation model MJ98 has some improvements, although in large part it is identical with that of Version 1. MJ98 is a full primitive equation spectral model with an η -pressure vertical coordinate (Simmons and Burridge, 1981), and includes the major physical parameter-

izations in both the troposphere and the middle atmosphere such as convection, planetary boundary layer turbulence, ground hydrology, radiation, and gravity wave drag. Time integration is achieved with the semi-implicit method (Hoskins and Simmons, 1975) using a weak time filter (Asselin, 1972). The Courant-Friedrich-Lewy (CFL) condition is preserved by automatically determining the time step.

We use the prognostic A-S mass flux convective scheme to simulate deep cumulus convection: updrafts in cumulus clouds are balanced by nearby subsidence having equivalent mass within a grid box; downdrafts below cloud base are similarly balanced by nearby updrafts. The level-2 turbulence closure scheme by Mellor and Yamada (1974) is used for the vertical diffusion with the mixing length of Blackadar (1962), in which surface flux is represented by the bulk method and the drag coefficients are based on those of Louis *et al.* (1982). The radiation scheme uses a multi-parameter random model for terrestrial (infrared) radiation, has four spectral intervals (20–550, 550–800, 800–1200 and 1200–2200 cm^{-1}) and handles radiative absorption by five gases (H_2O , CO_2 , O_3 , N_2O and CH_4) (Shibata and Aoki, 1989). For solar radiation, we employ the delta-two-stream discrete ordinate method (Shibata and Uchiyama, 1992) using the k-distribution and absorption cross section data from Briegleb (1992), in which ozone is taken into account in the ultraviolet and visible light regions (8 intervals in 0.2–0.7 μm), and so is water vapor in the near-infrared region (7 intervals in 0.5–5.0 μm), carbon dioxide at two wavelengths (2.7 and 4.3 μm), and oxygen in two (A and B) bands. In the current version, the non-orographic gravity wave drag (GWD) scheme of Hines (1997) is incorporated, in addition to the orographic GWD scheme developed by Iwasaki *et al.* (1989). The non-orographic GWD scheme with a weakened biharmonic (∇^4) horizontal diffusion and a relatively fine vertical grid spacing in the middle atmosphere enabled the MJ98 model to reproduce the spontaneous quasi-biennial oscillation in the tropical stratosphere (Shibata and Deushi, 2005).

An optional but useful forcing feature may be added to the model. In order to reproduce an observed atmospheric field for a specified period, or to diminish the systematic biases of this model, forcing of the temperature field or the horizontal wind field towards the observed field, by using Newtonian relaxation, can be optionally added as a nudging term in the dynamics module for temperature or zonal or meridional winds. However, the temperature forcing term is not used at present because it can induce artificial meridional circulations through additional diabatic heating (Miyazaki *et al.*, 2005).

3. Model Results

3.1 Properties of the simulations

The results presented here are from a free-running simulation of Version 2 (the “FREE-run”) for 11 years with full

stratospheric and tropospheric photochemistry, but without any relaxation forcing by the nudging term, described above in Section 2.2. The simulation was conducted to represent the climatology of the decade of the 1990s. In addition, an assimilation run (“NUDGING-run”) was also conducted for the period 1989–1999, in which the horizontal wind fields were nudged toward the European Centre for Medium-Range Weather Forecasting 40-year reanalysis (ERA40) fields (Simmons and Gibson, 2000). The two runs used identical boundary and initial data.

The 1990s climatological data of HADISST1 (Rayner *et al.*, 2003) were used for the sea-surface temperatures and sea ice. The dynamics module also used the concentrations of well-mixed greenhouse gases (N_2O , CH_4 , and CO_2) and ozone (O_3) from the 1990s, as in Shibata *et al.* (2005). Note that the radiative feedbacks from the chemistry module to the dynamics module were not considered in the two runs. To obtain the boundary data for the chemistry module, we used the emission inventories and surface concentrations described in Section 2.1.2. Initial data for the dynamics module were taken from other climatological runs which had been sufficiently stabilized for the mid-1990s. However, the initial concentrations of chemical species were not fully stabilized at the beginning of these runs, so the transient concentrations during an initial one year of the runs were discarded and then the stabilized ones during the last ten years were analyzed.

The horizontal resolution for the two runs of the model was a triangular truncation at the maximum wavenumber 42 (T42), corresponding to a grid resolution of about 2.8° in longitude and latitude. In the vertical, the model had 68 layers (L68) extending from the surface to the mesopause (~ 0.01 hPa) (Fig. 4). The layer thickness is about 500 m from 100 up to 10 hPa in order to simulate the stratospheric quasi-biennial oscillation (Shibata and Deushi, 2005).

3.2 Ozone

3.2.1 Stratospheric Ozone

The observed and simulated zonal-mean volume mixing ratios for ozone are plotted from 100 up to 0.1 hPa for January and July in Fig. 5. The simulations are 10-year averages of the FREE-run. The observations are from the extended standard ozone data set in the UARS-HALOE O_3 observations, version 18 (Brühl *et al.*, 1996), which covers the middle atmosphere from 100 up to about 0.3 hPa. The observed data set was compiled in the same way that Randel *et al.* (1998) did: a baseline period of observations (April 1992 to March 1993), then a period of extended sampling to March 1999. In January and July, our model reproduces the location and extension of the ozone core region in the equatorial upper stratosphere centered at roughly 10 hPa, although the peak concentration in the model is about 0.5 ppmv lower than the observed maximum value of 9–10 ppmv, and its core region is slightly smaller than the observed core. For the first time the MRI chemistry-climate model includes the

Fig. 4 The 68 model levels defined by the η -pressure vertical coordinates. From 100 to 10 hPa in the altitude range shown by the vertical arrow, the vertical spacing is about 500 m.

gas-phase reaction [$\text{d9: ClO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2$], which has improved the upper-stratospheric distribution of chlorine monoxide (ClO) in the model, and lessened the underprediction of ozone in the upper stratosphere to some extent. This version also captures an observed seasonal migration of the peak ozone region from north to south, from July to January.

The seasonal cycle of the (zonal mean) total ozone abundance simulated by the new version is compared with satellite observations in Fig. 6. These observations are a blend of data from the total ozone mapping spectrometer (TOMS) instrument and the solar backscattered ultraviolet (SBUV) instrument³ for 1990–1999, while the simulations are 10-year averages of the FREE-run. The simulated total ozone abundance has little bias throughout the year and reproduces the seasonal cycle well in the northern extratropics where a high latitude maximum of total ozone occurs in the late winter and early spring. In the tropics, although the simulated total ozone is slightly positively biased, it does capture well the observed seasonal cycle. Positive biases of about 20 Dobson units are also seen in the southern middle latitudes. Over the Antarctic during late winter and spring, the “ozone hole” is realistically reproduced by the model, although the simulated hole persists by about one month longer than in the observed data, because the dynamics module simulates a stronger Antarctic vortex.

³ The merged total and profile ozone data sets (from TOMS and SBUV) are based on the version 8 retrieval algorithm; see http://code916.gsfc.nasa.gov/Data_services/merged.

Fig. 5 Latitude-pressure cross sections of ozone mixing ratios (in ppm by volume), from 100 to 0.1 hPa, in January (left) and July (right), for the observations (upper sections) and a 10-year simulation of the Free-run (lower sections). Contour interval is 0.5 ppmv. Values from 6 to 8 ppm (above 8 ppmv) are lightly (darkly) shaded; values below 2 ppmv are heavily shaded.

Fig. 6 Time-latitude cross sections of 10-year averages of the zonal-mean total ozone abundance (in Dobson Units) for the FREE-run simulation (left) and satellite observations (right) from 1990 to 1999.

3.2.2 Tropospheric ozone near the surface

Simulated monthly mean ozone mixing ratios near the surface are shown in Fig. 7 for four seasons. Chemical production of O_x near the surface is similarly shown in Fig. 8. Note that although O_x is defined as the total concentration of species in the odd oxygen family, *i.e.* O_3 , $O(^1D)$ and $O(^3P)$, the abundance and budget of O_x near the surface are almost identical to those of O_3 . Tropospheric O_x is photochemically produced via photolysis of NO_2 , whose main atmospheric source is the reaction of NO with HO_2 radicals or RO_2 radicals. The main loss reactions of O_x are those of $O(^1D)$ radicals with H_2O and O_3 with OH radicals, HO_2 radicals, and hydrocarbons.

Simulated ozone concentrations near the surface have strong seasonal variability (Fig. 7). In July, high ozone levels (> 55 ppbv) are simulated over northern continental regions including North America, Asia, and the Mediterranean Sea region, probably due to the large net chemical production of O_x (> 10 ppbv day^{-1}) over these regions (Fig. 8). This is related to the high abundance of ozone precursors including NO_x , CO and NMHCs that originate in emissions from fossil-fuel combustion and that undergo enhanced photochemical reactions under intense summer sunlight. Low ozone levels (< 20 ppbv) are simulated over the summer-season extratropical

oceans where O_x is rapidly lost at the surface compared to the other seasons (Fig. 8). In the summer, the strong solar radiation and the low abundance of NO_x and hydrocarbons over the oceans facilitates the photolysis of ozone and the subsequent reaction of $O(^1D)$ with H_2O . In addition, the short lifetime of O_x in the summer does not permit long range transport of ozone from the industrialized continental areas to the remote marine atmosphere (*e.g.* Hauglustaine *et al.*, 1998).

Over the southern extratropical oceans, the longer lifetime of ozone in the winter clearly helps to raise the background level of ozone abundance (20–30 ppbv) in July, compared to the other seasons. In the southern tropical continents, two local maxima of ozone abundance are found over Central Africa and South America, where large sources of ozone precursors from biomass burning are found. Over Africa and South America, the seasonal cycle of biomass burning strongly affects the seasonal variation of surface ozone concentrations.

In January, high ozone levels (~ 50 ppbv) are seen over regionally limited areas in India and Central Africa. The ozone mixing ratios in the northern extratropical continents are generally less than 40 ppbv, and the net production of O_x is positive but becomes considerably smaller than in July,

Fig. 7 Simulated mean ozone volume mixing ratios (in ppbv) in the surface layer of about 500 m thickness for (upper left) January, (upper right) April, (lower left) July and (lower right) October. Ten-year averages of the FREE-run are shown.

Fig. 8 Same as Fig. 7 but for net chemical production of O_x (in ppbv day^{-1}).

synchronous with the intensity of solar radiation. Over the North Pacific and North Atlantic Oceans, on the other hand, a relatively high ozone belt where concentrations range from 30 to 40 ppbv is evident in January as well as April, in contrast with the low ozone concentrations (10–15 ppbv) over the southern extratropical ocean. This is caused by the effective long-range transport of ozone and its precursors in winter from the major polluted areas over the continents, in addition to some stratospheric ozone transport (Sudo and Akimoto, 2007). Chemical production of O_x is also slightly positive ($0\text{--}2 \text{ ppbv day}^{-1}$) over the northern extratropical oceans downstream of the continents, because of the effective long-range transport of ozone precursors in winter (Fig. 8). The simulated seasonal cycle of the ozone mixing ratio at 800 hPa reproduces the observed seasonal cycle at each of 9 measurement stations (Fig. 9). At the Naha station in the East China Sea the model captures well the observed summertime minimum due to the evolution of a continental air mass to a maritime one, which implies that the chemical destruction of O_x in the summer maritime air mass is adequately simulated. The observed summer minimum at the Hilo, Hawaii station in the middle of the North Pacific Ocean is also reasonably simulated by the model, although the model produces from 5 to 10 ppbv lower ozone levels than what is observed in the summer. At Hohenpeissenberg in Central Europe and

at Boulder in the Central US, where anthropogenic surface emissions are large, the observed summer maximum abundance of ozone is reasonably reproduced by the model in its magnitude and seasonal timing. However, at the Lauder and Marambio stations in the southern middle and high latitudes, respectively, the simulated ozone abundances are underestimated by up to 10 ppbv compared to the observations, especially in the austral winter.

3.2.3 Vertical distribution of tropospheric ozone

Both the FREE-run and NUDGING-run simulations capture the general features of the observed annual-mean ozone distribution in the vertical (Fig. 10), as other sophisticated CTMs also do (Stevenson *et al.*, 2006). In the figure, the zonal- and annual-mean observed ozone distribution is shown on a latitude-height cross-section, along with results of both simulations. Because measurements at only a few sites are available over the south polar region, the observed distribution is extrapolated over this region. Both runs underestimate the ozone mixing ratios in the lower troposphere over southern high latitudes (see also the comparisons at Lauder and Marambio stations in Fig. 9). In the tropics, intense convective activity, seen in the observations, extends the zone of low ozone mixing ratios from near the surface far upward into the upper troposphere; although the simulated vertical

Fig. 9 Annual cycle of observed ozone mixing ratios (in ppb by volume) (open circles) with standard deviations (error bars) at each station for the 800 hPa level, and the simulated mixing ratios (red line) of the FREE-run averaged over 10 years at the corresponding locations. The station names and locations are given above each plot. The observations are ozonesonde measurements (Logan, 1999).

Fig. 10 Annual-mean zonally-averaged simulated ozone volume mixing ratios (in ppbv) of (left) the FREE-run and (middle) the NUDGING-run averaged for 10 years, along with (right) observed ozone climatology (Logan, 1999).

distribution of the NUDGING-run has negative deviation (*i.e.* difference from observation) by up to 10 ppbv from about 700 to 200 hPa. The observed distribution in both northern and southern extratropical latitudes suggests that ozone-rich

air is brought down from the stratosphere and elevates the concentration of ozone in the middle and upper troposphere, and the sharp vertical gradient of ozone isopleths in the extratropical UTLS region approximately parallels the tropopause.

Both runs reproduce these features qualitatively.

In Fig. 11, seasonally averaged vertical profiles of ozone mixing ratios from both simulations are plotted with comparable ozonesonde observations (Logan, 1999) at 10 selected stations from north to south. Each station provided observations in a period from 5 to over 10 years in the 1980s and 1990s, from which the 3-month mean and the standard deviation at each station are computed from individual measurements for the corresponding season, while the curves for the two runs were calculated from the daily mean ozone concentrations at the geographically corresponding model grid box.

The simulated ozone profiles generally agree with the observations at all seasons and locations with some specific exceptions. The simulated vertical profiles at tropical and subtropical stations (Naha, Natal and Samoa) are clearly different between the FREE-run and NUDGING-run in the upper troposphere; the FREE-run overestimates ozone abundances while the NUDGING-run underestimates them. The respective biases may result from convective vertical transports in the model; the FREE-run may underestimate the magnitude of its upward transport, while the NUDGING-run may overestimate them. This can be attributed to various causes associated with the prognostic A–S convective scheme or the ERA40 reanalysis data, and the simplified convective transport scheme in the chemistry module. In addition, because NO_x emissions by lightning are diagnosed by using the physical variables from the prognostic A–S convective scheme, the estimates of NO emission by lightning might also add errors to the simulated ozone abundance in the tropical upper troposphere.

At the northern mid- and high-latitude stations (Alert, Resolute, Churchill, Hohenpeissenberg and Kagoshima), the observed ozone mixing ratios sharply increase upward from the upper troposphere into the lower stratosphere, with large variances according to day-to-day and year-to-year variations in the dynamical flow. The simulated ozone concentrations generally agree well with the observations in the low-to-mid-troposphere, but not so well in the upper troposphere-to-lower stratosphere (UTLS). At these five stations the vertical profiles of the NUDGING-run are positively biased compared to the observations in the UTLS, whereas those of the FREE-run agree relatively better with them (except at Kagoshima). In the southern mid- and high-latitude stations (Laverton and Syowa), both runs show positive biases in the UTLS through most of the year. This tendency for the model to generate a positive bias in the extratropical UTLS regions may result from the inadequate vertical and horizontal model resolution through the tropopause, where vertical gradients of dynamical quantities such as static stability, and abundances of chemical species change abruptly. Calculation of trace gas transports such as O_3 from the stratosphere may be overestimated because the inadequate model resolution leads to excessive numerical diffusion. It may be just as important to

dampen the numerical diffusion which is inevitably generated in the process of calculating grid-scale transports, as it is to use accurate inputs of atmospheric fields.

3.3 Carbon monoxide

The major sink of carbon monoxide (CO) in the troposphere is its reaction with OH radicals. The reaction of CO with OH radicals accounts for a large loss of tropospheric OH radicals, which induces photochemical production of ozone when NO_x is present. Thus, this reaction plays an important role in the budgets of ozone and OH abundances in the troposphere. The major sources of CO are chemical production via oxidation of methane (CH_4) and NMHCs, as well as surface emissions, primarily anthropogenic combustion of fossil fuels and biofuels in vehicles, and biomass burning (Seinfeld and Pandis, 1998).

At the surface high concentrations of CO are simulated by the FREE-run at all seasons over the northern industrial regions of the eastern United States, Europe, and Eastern Asia (Fig. 12), where anthropogenic fossil fuel and biofuel combustion are large sources, with clear seasonal variation: minimum in summer and maximum in winter. For example, in Europe CO mixing ratios in January are higher than those in July by 40–70 ppbv, and similar seasonal variations are found over other northern industrial regions. This seasonality strongly depends on concentrations of the OH radical: lower abundances of OH in winter are primarily caused by less solar UV radiation, which slows down the chemical loss of CO and lengthens its lifetime. Just the opposite happens in summer. In addition, over continents the stable boundary layer in winter confines the CO-rich air to the surface layer, which raises the CO concentration at the surface during winter. Finally, because its lifetime is longer in winter, CO emitted over industrial areas is effectively transported to remote regions, so that the background level is raised over the whole hemisphere by several tens of parts per billion.

Biomass burning emits large amount of CO over Africa and South America in the dry season from December to April in the northern tropics, and from July to October in the southern tropics. The simulated CO concentrations over these areas strongly reflect the seasonality of biomass burning (see Fig. 12). To be specific, the maximum CO emission occurs during September and October over Africa and South America in the SH, and thus the background CO mixing ratio is highest, exceeding 75 ppbv, during these months (Fig. 12).

The CO distribution over the northern and southern extratropics becomes more zonal at 500 hPa (Fig. 13) compared to the surface (Fig. 12). In northern winter and spring, steep meridional gradients of CO concentration occur in the mid-latitudes where strong jets exist; high CO mixing ratios (> 140 ppbv) in the northern high-latitudes are a sign that the CO is effectively transported to higher latitudes. As a result, in the northern extratropics, the CO abundance in winter and spring exceeds that in summer and autumn by several tens

Fig. 11 Vertical profiles of observed (open circles) 3-month mean ozone mixing ratios (in ppbv) at several stations for MAM (1st column), JJA (2nd column), SON (3rd column), and DJF (4th column), along with simulated mixing ratios of the FREE-run (red solid line) and the NUDGING-run (blue solid line) averaged for 10 years at corresponding geographical points. In addition, standard deviations of the observations (horizontal lines) and the simulations (dashed lines) are indicated, respectively. The observations are taken from ozonesonde measurements (Logan, 1999). The station names and locations are given above each plot.

Fig. 11 (continued)

Fig. 12 Simulated CO volume mixing ratios (in ppbv) at the surface for (upper left) January, (upper right) April, (lower left) July, and (lower right) October. Ten-year averages of the FREE-run are shown.

Fig. 13 Same as Fig. 12 but for the 500 hPa level.

of parts per billion at the 500 hPa level. In the low latitudes, on the other hand, two CO peaks are apparent over South America and Africa throughout the year, which reflects the effective upward transport from the surface where biomass is burned, and where NMHCs are oxidized and produce CO (*e.g.* Sudo *et al.*, 2002b).

Simulated seasonal cycles of CO mixing ratios at the surface are compared with the observations at nine selected sites from north to south, from the NOAA/CMDL measurement network (Novelli *et al.*, 1998). The model captures the observed concentrations and their seasonal variations at several observation sites. In the northern hemisphere (NH) the simulated CO abundances are in good agreement with the observations at the low- and mid-latitude stations (Macehead, Bermuda, Mauna Loa and Guam), but in the high-latitudes (*i.e.* Alert, Barrow and Iceland) the model underestimates them during late winter and spring and overestimates them in summer, by up to 20 ppbv. At Syowa station located in the

Antarctic, where local emission of CO and NMHCs are negligible, the simulation has an almost constant positive bias of about 15 ppbv at all seasons. The chemical loss of CO by OH radicals may be underestimated in the model, or the surface emissions of CO may be overestimated in remote source regions such as Australia and South Africa.

3.4 Nitrogen Oxides

The abundance of nitrogen oxides (NO_x) is critically important in oxidation chain reactions of hydrocarbons in which tropospheric ozone is photochemically produced. At the present time, surface emissions from fossil-fuel combustion account for a large fraction of the tropospheric sources of NO_x . Emissions from the soil (both natural and anthropogenic) and from biomass burning are important secondary sources (*e.g.* Seinfeld and Pandis, 1998). As a source in the free troposphere, lightning emissions also affect the distribution of NO_x , especially in the low latitudes (Pickering *et al.*,

Fig. 14 Annual cycle of observed (open circles) surface CO volume mixing ratios (in ppbv) and standard deviations (error bars) at each station, along with simulated mixing ratios (red line) of the FREE-run averaged for 10 years at corresponding geographical points. The observations are taken from the NOAA/CMDL measurement network (Novelli *et al.*, 1998). The station names and locations are given above each plot.

1998).

The simulated NO_x mixing ratios at the surface (Fig. 15, bottom charts) are noticeably different in the continental source regions and the remote oceans: the difference is three orders of magnitude or more. Because the lifetime of NO_x near the surface is generally less than a few days (Hauglustaine *et al.*, 1998), transport of NO_x from continental source regions to the remote regions is weak. This contributes greatly to the regional difference in NO_x abundances. In January, high NO_x concentrations (> 6 ppbv) are simulated over the eastern United States, Europe and East Asia where emissions from fossil fuel combustion are large. The mixing ratios over the ocean in the northern extratropics are higher in January than July because NO_x has a longer lifetime during winter and so more of it is transported from the continents to the oceans. In July, on the other hand, concentrations over the oceans are generally less than 10 pptv, because NO_x is rapidly lost in reactions with OH radicals, so its lifetime is a day or less. In addition, the local maxima of NO_x mixing ratios found over the continental industrial regions are reduced by 30–60% in July, compared to January. Over Africa and South America, high concentrations of NO_x (1–3 ppbv) are associated with biomass burning emissions and exhibit strong seasonal variations.

Surface emission of NO_x , NO emission by lightning, and chemical conversion of reservoir species (such as HNO_3 , PAN, and other organic nitrates) to NO_x (Horowitz *et al.*, 2003) all affect the distribution of NO_x in the middle troposphere. At 500 hPa (Fig. 15, upper charts) the background mixing ratios of NO_x in the northern high latitudes are higher than 10 pptv in July, but they become generally lower than 10 pptv in January. In the southern high latitudes, the background concentrations are generally less than 10 pptv in all seasons. In July local maxima of NO_x mixing ratios (60–100 pptv) are located over continents, the southeastern United States, central Europe, and southern and western Asia, while another NO_x mixing ratio peak appears (60–80 pptv) over the Atlantic ocean in January.

We evaluated vertical profiles of the simulated nitric oxide (NO) mixing ratios by comparing (Fig. 16) them with observational data compiled by Emmons *et al.* (2000). The observational data set is based on measurements during the NASA Global Tropospheric Experiment (GTE) aircraft campaigns (Table 5), and is used for evaluation of many other models, including MOZART (Emmons *et al.*, 2000; Horowitz *et al.*, 2003), CHASER (Sudo *et al.*, 2002b) and UMD-CTM (Park *et al.*, 2004). Because the NO observations are more reliable than those of nitrogen oxides (NO_x)

Fig. 15 Simulated NO_x volume mixing ratios (in ppbv) at (upper) 500 hPa and (lower) the surface for (left) January and (right) July. Ten-year averages of the FREE-run are shown.

Fig. 16 Regional vertical profiles of NO mixing ratios (in pptv): Observed (box-whisker), and simulated (solid and dotted lines). The observations are taken from aircraft field campaigns (Table 5, as compiled by Emmons *et al.*, 2000). The region and field campaign names are given above each plot. The observed values are shown as the mean (circle), median (diamond), interquartile range (open box), and central 90% of the data (horizontal line); the simulated values of the NUDGING-run are shown as a mean (solid line) and $\pm$ one standard deviation (dotted lines).

Table 5. Regions and Dates for Vertical Profiles of NASA GTE Campaigns

Expedition	Dates	Region name	Latitudes	Longitudes
PEM-Tropics-A	Aug. 15 to Oct. 5, 1996	Hawaii	10N–30N	190E–210E
		Chris.-Island	0–10N	200E–220E
		Tahiti	20S–0	200E–230E
		Fiji	30S–10S	170E–190E
		Easter-Island	40S–20S	240E–260E
PEM-Tropics-B	Mar. 6 to Apr. 18, 1999	Hawaii	10N–30N	190E–210E
		Chris.-Island	0–10N	200E–220E
		Tahiti	20S–0	200E–230E
		Fiji	30S–10S	170E–190E
		Easter-Island	40S–20S	240E–260E
SONEX	Oct. 7 to Nov. 12, 1997	E-Atlantic	35N–45N	35W–15W
		Newfoundland	45N–55N	290E–310E

(Bradshaw *et al.*, 2000), we compared the NO observations with the simulated ones, as did UMD-CTM (Park *et al.*, 2004). Simulation results of the NUDGING-run, which reproduced the dynamical fields at specific dates, were used for this comparison, although we used emission data that did not take into account day-to-day variations. The simulation results were averaged over the corresponding regions and dates of the GTE campaigns. The averages were not done over 24 h, but only in daytime (when the solar zenith angle $< 90^\circ$) because measurements were taken only in daytime. Note that concentrations measured by a flight campaign may not be representative, because they were taken only in scattered areas and for fragmentary periods of time.

Simulated NO vertical profiles generally agree with the observed ones, considering the large space and time variability of NO distribution. Over the remote tropical Pacific regions (PEM Tropics-A and -B), the simulated NO mixing ratios show a monotonic increase with altitude in accordance with the longer lifetime of NO_x with altitude, as seen in the observations. In the upper troposphere, NO mixing ratios also increase due to migration of NO_y family species from the stratosphere and NO emission by lightning (*e.g.* Sudo *et al.*, 2002b). Still, the calculated and observed vertical profiles during the PEM Tropics-A and -B show discrepancies in the upper troposphere. In Hawaii, the model underestimates the mixing ratios in the upper troposphere, whereas in Tahiti it overestimates them. As Sudo *et al.* (2002b) noted, the discrepancies may result from misrepresenting NO emission from three sources: lightning, biomass burning, and influx of stratospheric species in the NO_y family.

3.5 Hydroxyl radical

Because hydroxyl (OH) radicals have strong oxidizing power, they react strongly with many trace gases and remove them from the troposphere. Therefore, the abundance of OH radicals determines the atmospheric concentrations of these other chemical constituents. The concentration of OH radicals in the troposphere varies greatly and depends on complex, closely coupled photochemical reactions that involve H_2O ,

O_3 , NO_x and hydrocarbons (Brasseur *et al.*, 1998). The model simulates very low concentrations of OH radicals ($< 10^5$ molecules cm^{-3}) poleward of about 45° latitude in the winter hemisphere, due to weak or no UV radiation (Fig. 17). As many other global chemistry models have calculated (Hauglustaine *et al.*, 1998; Sudo *et al.*, 2002b; Horowitz *et al.*, 2003; Rotman *et al.*, 2004), the peak concentration of OH radicals in the lower troposphere shifts to the summer hemisphere because the intense UV radiation and the increased abundance of water vapor in summer favor the photolysis of ozone (O_3). Version 2 also simulates the maximum concentration in the lower troposphere in the summer hemisphere. In January the peak concentration ($> 15 \times 10^5$ molecules cm^{-3}) is located over the southern low latitudes (10° – 20°S), and shifts to the northern mid-latitudes (30° – 40°N) in July, where the maximum value is more than 20×10^5 molecules cm^{-3} . The higher maximum value in the NH summer can be attributed to the higher ozone and NO_x concentrations there (Hauglustaine *et al.*, 1998). Although the simulated maximum concentrations appear to be 15–30% lower than those of other recent chemistry model simulations (Hauglustaine *et al.*, 1998; Sudo *et al.*, 2002b; Horowitz *et al.*, 2003; Rotman *et al.*, 2004), Version 2 agrees reasonably well with these other recent models with regard to the simulated global distribution and seasonal cycle of tropospheric OH radicals.

4. Conclusions

We have developed a global chemistry–climate model (CCM), called the “Meteorological Research Institute (MRI) Chemistry-Climate Model, version 2” (*MRI-CCM2* or *Version 2*), to simulate the distribution and evolution of ozone and related chemical species from the surface up through the stratosphere. The *MRI-CCM2* is an extension of the stratospheric CCM developed at MRI (*MRI-CCM1* or *Version 1*), and incorporates for the first time an elaborate mechanism for the photochemistry of the four species HO_x , NO_x , CH_4 , and CO ; a mechanism for degradation of non-methane hydrocarbons (NMHCs); and tropospheric heterogeneous reactions

Fig. 17 Zonal-mean concentrations of the OH radical (in units of 10^5 molecules cm^{-3}) for the months of January (left) and July (right). Ten-year averages of the FREE-run are shown.

in aerosols and clouds, in order to simulate a detailed ozone chemistry in the troposphere. We have also introduced some important updates and improvements for the semi-Lagrangian transport scheme, the sub-grid vertical transports due to convection and turbulent diffusion, the dry and wet deposition processes, and the calculation of photolysis rates.

We performed a free run, and an assimilated run nudged to the dynamical fields of the ERA40 reanalysis for 11 years, to reproduce the climatological distribution of the important chemical constituents in the 1990s. We then evaluated the two runs by comparing the results with several observational data sets, with more emphasis on the chemistry of the troposphere. The horizontal resolution of Version 2 was set to T42, corresponding to a grid resolution of about 2.8° in longitude and latitude, and its vertical resolution was 68 layers (L68) with the highest model level at 0.01 hPa (~ 80 km). Emissions of NO_x , CO and NMHCs from the surface in the model were identical with those used for the 1990s simulation of MOZART-2 by Horowitz *et al.* (2003), including emission sources from combustion of fossil fuels, biofuels and biomass, and from other soil and biogenic sources and the ocean. The model diagnosed NO emissions from lightning every 6 h and global amounts were set to about 5 TgN yr^{-1} .

In general, Version 2 reproduces reasonably well the observed distribution of the key species in tropospheric chemistry, including ozone and its precursors, CO and NO_x . This model version exhibits less bias in the abundance of upper stratospheric ozone than the previous version of this model did, because we included a second path of the gas-phase reaction of ClO with OH radicals. The simulated distribution of ozone near the surface has clear seasonal variability that reflects the seasonal variability of solar radiation and surface emissions from sources such as biomass burning. The model simulates large net production of ozone over polluted continental areas and considerable net destruction over

remote ocean areas throughout the year, near the surface. In the lower troposphere, the seasonal cycles of the simulated ozone concentrations at each measurement station generally agree well with observations, except at high latitude southern stations, where the model underestimates ozone, especially in summer. In the tropical upper troposphere, the abundance of ozone is quite different between the free-run and the nudging-run, probably because the convective vertical transports are different in the two runs. In the low and middle troposphere of the northern extratropics, the simulated vertical profiles of ozone abundance are consistent with the observed profiles, but some positive biases are found in the upper troposphere/lower stratosphere (UTLS). These may be caused by the coarse resolution of the model through the tropopause, which generates excessive numerical diffusion in the calculation of transports.

Although the simulated abundance of carbon monoxide (CO) has some positive bias in the southern high latitudes, its seasonal cycle and geographical distribution in the lower troposphere are well simulated. The positive bias in that region might be due to underestimation of its breakdown by OH radicals there, or overestimation of biomass burning emissions in Australia and South Africa. The model captures the observed features of the vertical profiles of nitric oxide (NO), though its concentration in the upper troposphere was underestimated in Hawaii and overestimated in Tahiti during field campaigns. The simulated geographical distributions and seasonal cycle of OH radicals in the troposphere are essentially similar to results from other recent chemistry models, although the maximum concentrations in the lower troposphere of the summer hemisphere appear to be underestimated in the new Version.

The model will require continuous improvement to address several remaining problems that appeared in these two simulations. Among the improvements, we contemplate

a new wet deposition scheme in ice clouds, more elaborate simulations of heterogeneous reactions in various types of aerosols, and a new scheme for the oxidation of isoprene.

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Appendix I: Formulation of long-lived species

Prognostic equations for long-lived species are described here, with the different forms for daytime and nighttime. The same notation is used as in the text except for that $O^{1D} = O(1D)$.

I-1 Daytime

$$\frac{d[N_2O]}{dt} = -\{tj_4 + (b_{38} + b_{39})[O^{1D}]\}[N_2O]$$

$$\begin{aligned} \frac{d[CH_4]}{dt} &= 0.08c_{34}[C_3H_6][O_3] + tj_{44}[CH_3CHO] \\ &\quad - \{a_{2er}[O^{1D}] + c_2[OH] + d_5[Cl] + tj_5\}[CH_4] \end{aligned}$$

$$\begin{aligned} \frac{d[H_2O]}{dt} &= a_8[OH][OH] + a_{23c}[H][HO_2] + a_{17}[HO_2][OH] \\ &\quad + a_{19}[H_2][OH] + a_{30}[H_2O_2][OH] + b_{27}[HNO_3][OH] \\ &\quad + b_{28}[HO_2NO_2][OH] + d_0[CH_3Cl][OH] + d_{11}[HCl][OH] \\ &\quad + d_{34}[HOCl][OH] + e_{11}[HBr][OH] + c_2[CH_4][OH] \\ &\quad + c_7[CH_3OOH][OH] + c_8[CH_2O][OH] + c_{10}[C_2H_6][OH] \\ &\quad + c_{15}[C_2H_5OOH][OH] + c_{16}[CH_3CHO][OH] \\ &\quad + c_{23}[CH_3C(O)OOH][OH] + c_{27}[C_3H_8][OH] \\ &\quad + 0.157c_{31}[C_3H_7OOH][OH] + c_{32}[ACET][OH] \\ &\quad + c_{58}[POOH][OH] + c_{62}[C_4H_{10}][OH] + i_{17}[MACROOH][OH] \\ &\quad - \{a_{1er}[O^{1D}] + b_{53}[N_2O_5] + tj_3\}[H_2O] \end{aligned}$$

$$\begin{aligned} \frac{d[NO_y]}{dt} &= 2b_{39}[O^{1D}][N_2O] \\ &\quad - \{2b_6[N][NO] + (het_1 + het_2)[ClONO_2] \\ &\quad \quad + (2het_3 + het_4)[N_2O_5]\} \end{aligned}$$

$$\begin{aligned} \frac{d[HNO_3]}{dt} &= b_{22}[OH][NO_2][M] + 2b_{53}[N_2O_5][H_2O] + c_9[CH_2O][NO_3] \\ &\quad + c_{17}[CH_3CHO][NO_3] + c_{37}[MGLY][NO_3] + g_1[ClONO_2] \\ &\quad + 2g_2[N_2O_5] + g_3[BrONO_2] + 0.5g_{10}[NO_2] \\ &\quad - \{b_{27}[OH] + tj_7\}[HNO_3] \end{aligned}$$

$$\begin{aligned} \frac{d[N_2O_5]}{dt} &= b_{12}[NO_3][NO_2][M] \\ &\quad - \{b_{32}[M] + b_{53}[H_2O] + tj_{11} + het_3 + het_4 + g_2\}[N_2O_5] \end{aligned}$$

$$\begin{aligned} \frac{d[Cl_y]}{dt} &= 4(tj_{26} + d_{101}[O^{1D}])[CCl_4] + 3(tj_{27} + d_{102}[O^{1D}])[CFCl_3] \\ &\quad + 2(tj_{28} + d_{103}[O^{1D}])[CF_2Cl_2] + (tj_{29} + d_0[OH])[CH_3Cl] \\ &\quad + (tj_{31} + e_{92}[O^{1D}])[CF_2ClBr] + het_2[ClONO_2] + het_4[N_2O_5] \\ &\quad + het_5[HOCl] + het_6[HOBr] \end{aligned}$$

$$\begin{aligned} \frac{d[O_x]}{dt} &= a_8[OH][OH] + a_{23c}[H][HO_2] + b_6[N][NO] + b_7[N][O_2] \\ &\quad + c_{22}[CH_3C(O)O_2][HO_2] + 0.3c_{48}[GC(O)O_2][HO_2] \\ &\quad + 2tj_1[O_2] + tj_4[N_2O] + tj_6[NO_2] + tj_{14}[OCIO] + tj_{18}[CO_2] \\ &\quad + tj_{23}[NO] + tj_{24}[NO_3] \\ &\quad + \{(a_{1er}[H_2O] + a_{2er}[CH_4] + a_{3er}[H_2] + (b_{38} + b_{39})[N_2O] \\ &\quad \quad + d_{101}[CCl_4] + d_{102}[CFCl_3] + d_{103}[CF_2Cl_2] + d_{110}[COF_2] \\ &\quad \quad + e_{91}[CF_3Br] + e_{92}[CF_2ClBr] + e_{93}[CH_3Br])[O^{1D}] \\ &\quad \quad + (2hk_1[O][M] + 2hk_3[O_3] + a_5[OH] + a_7[HO_2] \\ &\quad \quad + a_{24}[H_2] + b_3[NO_2] + d_3[ClO] + d_{32}[ClONO_2] \\ &\quad \quad + d_{35}[HOCl] + d_{64}[OCIO] + e_3[BrO])[O] \\ &\quad \quad + (a_2[H] + a_6[OH] + a_{66}[HO_2] + b_4[NO] + b_9[NO_2] \\ &\quad \quad + c_{43}[C_2H_4] + c_{54}[C_3H_6] + i_1[C_5H_8] + i_{10}[MACR] \\ &\quad \quad + t_2[C_{10}H_{16}] + d_2[Cl] + e_2[Br])[O_3]\} \end{aligned}$$

$$\begin{aligned} \frac{d[CO]}{dt} &= c_8[CH_2O][OH] + c_9[CH_2O][NO_3] + 0.18c_{28}[C_3H_7O_2] \\ &\quad + 0.6c_{30}[C_3H_7O_2][CH_3O_2] + 0.106c_{31}[C_3H_7OOH][OH] \\ &\quad + c_{36}[MGLY][OH] + c_{37}[MGLY][NO_3] + 0.5c_{43}[C_2H_4][O_3] \\ &\quad + 0.4c_{44}[GLYALD][OH] + 0.56c_{54}[C_3H_6][O_3] \\ &\quad + 0.14i_1[C_5H_8][O_3] + 0.22i_{10}[MACR][O_3] \\ &\quad + 0.25i_{11}[MACRO_2][NO] + 0.5i_{13}[MACRO_2][MACRO_2] \\ &\quad + 0.28t_2[C_{10}H_{16}][O_3] + tj_{18}[CO_2] + (tj_{37} + tj_{38})[CH_2O] \\ &\quad + (tj_{43} + tj_{44})[CH_3CHO] + 0.18tj_{45}[C_3H_7OOH] + tj_{47}[ACET] \\ &\quad + tj_{49}[MGLY] + (tj_{50} + tj_{51})[GLYALD] + tj_{56}[MACR] \\ &\quad + 0.5tj_{58}[MACROOH] + tj_{59}[NALD] - \{a_{36}[OH]\}[CO] \end{aligned}$$

$$\begin{aligned} \frac{d[OCIO]}{dt} &= e_{5a}[BrO][ClO] \\ &\quad - \{d_{62}[OH] + d_{63}[Cl] + d_{64}[O] \\ &\quad \quad + d_{65}[NO] + e_8[Br] + tj_{14}\}[OCIO] \end{aligned}$$

$$\begin{aligned} \frac{d[CO_2]}{dt} &= a_{36}[CO][OH] + 1.4c_{13}[C_2H_5O_2][CH_3O_2] \\ &\quad + c_{18}[CH_3C(O)O_2][NO] + c_{24}[CH_3C(O)O_2][CH_3O_2] \\ &\quad + 2c_{26}[CH_3C(O)O_2][CH_3C(O)O_2] + 0.06c_{28}[C_3H_7O_2][NO] \\ &\quad + 0.6c_{30}[C_3H_7O_2][CH_3O_2] + 0.035c_{31}[C_3H_7OOH][OH] \\ &\quad + c_{47}[GC(O)O_2][NO] + c_{49}[GC(O)O_2][CH_3O_2] \end{aligned}$$

$$\begin{aligned}
& + 2c_{51}[\text{GC}(\text{O})\text{O}_2][\text{GC}(\text{O})\text{O}_2] + 0.5c_{52}[\text{GC}(\text{O})\text{OOH}][\text{OH}] \\
& + c_{73}[\text{PAN}][\text{OH}] + 0.72i_1[\text{C}_5\text{H}_8][\text{O}_3] + i_6[\text{ISOPO}_2][\text{ISOPO}_2] \\
& + i_7[\text{ISOPOOH}][\text{OH}] + 2.1i_8[\text{ISON}][\text{OH}] \\
& + 0.43i_{10}[\text{MACR}][\text{O}_3] + 0.25i_{11}[\text{MACRO}_2][\text{NO}] \\
& + i_{13}[\text{MACRO}_2][\text{MACRO}_2] + 3.1i_{16}[\text{MPAN}][\text{OH}] \\
& + 1.7t_1[\text{C}_{10}\text{H}_{16}][\text{OH}] + 1.44t_2[\text{C}_{10}\text{H}_{16}][\text{O}_3] + 4t_3[\text{C}_{10}\text{H}_{16}][\text{NO}_3] \\
& + tj_{40}[\text{PAN}] + tj_{42}[\text{CH}_3\text{C}(\text{O})\text{OOH}] + 0.06tj_{45}[\text{C}_3\text{H}_7\text{OOH}] \\
& + tj_{52}[\text{GC}(\text{O})\text{OOH}] - \{tj_{18}\}[\text{CO}_2]
\end{aligned}$$

$$\begin{aligned}
\frac{d[\text{HCl}]}{dt} &= d_5[\text{CH}_4][\text{Cl}] + d_6[\text{H}_2][\text{Cl}] + d_7[\text{HO}_2][\text{Cl}] \\
&+ d_9[\text{OH}][\text{ClO}] - \{d_{11}[\text{OH}] + tj_{16}\}[\text{HCl}]
\end{aligned}$$

$$\begin{aligned}
\frac{d[\text{ClONO}_2]}{dt} &= d_{31}[\text{NO}_2][\text{ClO}][\text{M}] \\
&- \{d_{32}[\text{O}] + tj_{10} + tj_{33} + \text{het}_1 + \text{het}_2 + g_1\}[\text{ClONO}_2]
\end{aligned}$$

$$\begin{aligned}
\frac{d[\text{HOCl}]}{dt} &= d_{33}[\text{HO}_2][\text{ClO}] + d_{62}[\text{OCIO}][\text{OH}] + (\text{het}_1 + g_1)[\text{ClONO}_2] \\
&- \{d_{34}[\text{OH}] + d_{35}[\text{O}] + d_{37}[\text{Cl}] + tj_8 + \text{het}_5\}[\text{HOCl}]
\end{aligned}$$

$$\begin{aligned}
\frac{d[\text{Cl}_2]}{dt} &= d_{37}[\text{Cl}][\text{HOCl}] + \text{het}_2[\text{ClONO}_2] + \text{het}_5[\text{HOCl}] \\
&- \{tj_{17}\}[\text{Cl}_2]
\end{aligned}$$

$$\begin{aligned}
\frac{d[\text{H}_2\text{O}_2]}{dt} &= a_9[\text{OH}][\text{OH}] + a_{27}[\text{HO}_2][\text{HO}_2] + 0.09i_1[\text{C}_5\text{H}_8][\text{O}_3] \\
&+ 0.18t_2[\text{C}_{10}\text{H}_{16}][\text{O}_3] + 0.5g_4[\text{HO}_2] - \{a_{30}[\text{OH}] + tj_{13}\}[\text{H}_2\text{O}_2]
\end{aligned}$$

$$\frac{d[\text{ClNO}_2]}{dt} = d_{36}[\text{Cl}][\text{NO}_2][\text{M}] + \text{het}_4[\text{N}_2\text{O}_5] - \{tj_{19}\}[\text{ClNO}_2]$$

$$\frac{d[\text{HBr}]}{dt} = e_7[\text{HO}_2][\text{Br}] - \{e_{11}[\text{OH}]\}[\text{HBr}]$$

$$\frac{d[\text{BrONO}_2]}{dt} = e_{13}[\text{BrO}][\text{NO}_2][\text{M}] - \{tj_{20} + tj_{34} + g_3\}[\text{BrONO}_2]$$

$$\begin{aligned}
\frac{d[\text{NO}_x]}{dt} &= b_7[\text{N}][\text{O}_2] + b_{24}[\text{HO}_2\text{NO}_2][\text{M}] + b_{27}[\text{HNO}_3][\text{OH}] \\
&+ b_{28}[\text{HO}_2\text{NO}_2][\text{OH}] + 2b_{32}[\text{N}_2\text{O}_5][\text{M}] + 2b_{39}[\text{N}_2\text{O}][\text{O}^{\text{ID}}] \\
&+ c_{20}[\text{PAN}][\text{M}] + c_{46}[\text{GPAN}][\text{M}] + c_{60}[\text{ONIT}][\text{OH}] \\
&+ c_{73}[\text{PAN}][\text{OH}] + i_{15}[\text{MPAN}][\text{M}] + i_{16}[\text{MPAN}][\text{OH}] \\
&+ i_{18}[\text{NALD}][\text{OH}] + d_{32}[\text{O}][\text{ClONO}_2] + tj_7[\text{HNO}_3] \\
&+ tj_9[\text{HO}_2\text{NO}_2] + 2tj_{11}[\text{N}_2\text{O}_5] + tj_{19}[\text{ClNO}_2] \\
&+ (tj_{10} + tj_{33})[\text{ClONO}_2] + (tj_{20} + tj_{34})[\text{BrONO}_2] \\
&+ (tj_{39} + tj_{40})[\text{PAN}] + tj_{55}[\text{ISON}] + tj_{57}[\text{MPAN}] + tj_{59}[\text{NALD}] \\
&- \{(b_6[\text{N}] + 0.044i_4[\text{ISOPO}_2] + tj_{23})[\text{NO}] \\
&+ (2b_{12}[\text{NO}_3][\text{M}] + b_{22}[\text{OH}][\text{M}] + b_{23}[\text{HO}_2][\text{M}] \\
&+ d_{31}[\text{ClO}][\text{M}] + d_{36}[\text{Cl}][\text{M}] + e_{13}[\text{BrO}][\text{M}] \\
&+ c_{19}[\text{CH}_3\text{C}(\text{O})\text{O}_2][\text{M}] + c_{45}[\text{GC}(\text{O})\text{O}_2][\text{M}] \\
&+ i_{14}[\text{MACRO}_2][\text{M}] + 0.5g_{10}[\text{NO}_2]\}
\end{aligned}$$

$$\begin{aligned}
& + (c_9[\text{CH}_2\text{O}] + c_{17}[\text{CH}_3\text{CHO}] + c_{37}[\text{MGLY}] \\
& + c_{55}[\text{C}_3\text{H}_6] + i_3[\text{C}_5\text{H}_8])[\text{NO}_3\}
\end{aligned}$$

$$\begin{aligned}
\frac{d[\text{HO}_2\text{NO}_2]}{dt} &= b_{23}[\text{HO}_2][\text{NO}_2][\text{M}] \\
&- \{b_{24}[\text{M}] + b_{28}[\text{OH}] + tj_9\}[\text{HO}_2\text{NO}_2]
\end{aligned}$$

$$\begin{aligned}
\frac{d[\text{ClO}_x]}{dt} &= d_0[\text{CH}_3\text{Cl}][\text{OH}] + d_{11}[\text{OH}][\text{HCl}] + d_{32}[\text{ClONO}_2][\text{O}] \\
&+ d_{34}[\text{HOCl}][\text{OH}] + d_{35}[\text{HOCl}][\text{O}] + 2d_{61}[\text{Cl}_2\text{O}_2][\text{M}] \\
&+ d_{63}[\text{OCIO}][\text{Cl}] + d_{64}[\text{OCIO}][\text{O}] + d_{65}[\text{OCIO}][\text{NO}] \\
&+ e_8[\text{OCIO}][\text{Br}] + e_{92}[\text{CF}_2\text{ClBr}][\text{O}^{\text{ID}}] + tj_8[\text{HOCl}] \\
&+ tj_{10}[\text{ClONO}_2] + tj_{14}[\text{OCIO}] + 2tj_{15}[\text{Cl}_2\text{O}_2] + tj_{16}[\text{HCl}] \\
&+ 2tj_{17}[\text{Cl}_2] + tj_{19}[\text{ClNO}_2] + tj_{21}[\text{BrCl}] + tj_{29}[\text{CH}_3\text{Cl}] \\
&+ tj_{31}[\text{CF}_2\text{ClBr}] + tj_{33}[\text{ClONO}_2] + 4(tj_{26} + d_{101}[\text{O}^{\text{ID}}])[\text{CCl}_4] \\
&+ 3(tj_{27} + d_{102}[\text{O}^{\text{ID}}])[\text{CFCl}_3] + 2(tj_{28} + d_{103}[\text{O}^{\text{ID}}])[\text{CF}_2\text{Cl}_2] \\
&- \{(d_9[\text{OH}] + d_{31}[\text{NO}_2][\text{M}] + d_{33}[\text{HO}_2] \\
&+ 2d_{60}[\text{ClO}][\text{M}] + (e_{5a} + e_{5c})[\text{BrO}][\text{ClO}] \\
&+ (d_5[\text{CH}_4] + d_6[\text{H}_2] + d_7[\text{HO}_2] \\
&+ d_{36}[\text{NO}_2][\text{M}] + d_{37}[\text{HOCl}][\text{Cl}])\}
\end{aligned}$$

$$\begin{aligned}
\frac{d[\text{BrO}_x]}{dt} &= e_{11}[\text{OH}][\text{HBr}] + (e_{91}[\text{O}^{\text{ID}}] + tj_{32})[\text{CF}_3\text{Br}] \\
&+ (e_{92}[\text{O}^{\text{ID}}] + tj_{31})[\text{CF}_2\text{ClBr}] + (e_{93}[\text{O}^{\text{ID}}] + tj_{30})[\text{CH}_3\text{Br}] \\
&+ (\text{het}_6 + tj_{22})[\text{HOBr}] + (tj_{20} + tj_{34})[\text{BrONO}_2] \\
&- \{(e_7[\text{HO}_2])[\text{Br}] + (e_{13}[\text{NO}_2][\text{M}] + e_{15}[\text{HO}_2])[\text{BrO}]\}
\end{aligned}$$

$$\frac{d[\text{Cl}_2\text{O}_2]}{dt} = d_{60}[\text{ClO}][\text{ClO}][\text{M}] - \{d_{61}[\text{M}] + tj_{15}\}[\text{Cl}_2\text{O}_2]$$

$$\begin{aligned}
\frac{d[\text{HOBr}]}{dt} &= e_{15}[\text{BrO}][\text{HO}_2] + g_3[\text{BrONO}_2] \\
&- \{tj_{22} + \text{het}_6\}[\text{HOBr}]
\end{aligned}$$

$$\frac{d[\text{CCl}_4]}{dt} = -\{d_{101}[\text{O}^{\text{ID}}] + tj_{26}\}[\text{CCl}_4]$$

$$\frac{d[\text{CFCl}_3]}{dt} = -\{d_{102}[\text{O}^{\text{ID}}] + tj_{27}\}[\text{CFCl}_3]$$

$$\frac{d[\text{CF}_2\text{Cl}_3]}{dt} = -\{d_{103}[\text{O}^{\text{ID}}] + tj_{28}\}[\text{CF}_2\text{Cl}_2]$$

$$\begin{aligned}
\frac{d[\text{Br}_y]}{dt} &= (e_{91}[\text{O}^{\text{ID}}] + tj_{32})[\text{CF}_3\text{Br}] + (e_{92}[\text{O}^{\text{ID}}] + tj_{31})[\text{CF}_2\text{ClBr}] \\
&+ (e_{93}[\text{O}^{\text{ID}}] + tj_{30})[\text{CH}_3\text{Br}]
\end{aligned}$$

$$\frac{d[\text{CH}_3\text{Cl}]}{dt} = -\{d_0[\text{OH}] + tj_{29}\}[\text{CH}_3\text{Cl}]$$

$$\frac{d[\text{CH}_3\text{Br}]}{dt} = -\{e_{93}[\text{O}^{\text{ID}}] + tj_{30}\}[\text{CH}_3\text{Br}]$$

$$\frac{d[\text{CF}_2\text{ClBr}]}{dt} = -\{e_{92}[\text{O}^{\text{ID}}] + tj_{31}\}[\text{CH}_2\text{ClBr}]$$

$$\frac{d[\text{CF}_3\text{Cl}]}{dt} = -\{e_{91}[\text{O}^{\text{ID}}] + tj_{32}\}[\text{CF}_3\text{Cl}]$$

$$\begin{aligned} \frac{d[\text{COF}_2]}{dt} &= (d_{103}[\text{O}^{\text{ID}}] + tj_{28})[\text{CF}_2\text{Cl}_2] + (e_{92}[\text{O}^{\text{ID}}] + tj_{31})[\text{CF}_2\text{ClBr}] \\ &+ (e_{91}[\text{O}^{\text{ID}}] + tj_{32})[\text{CF}_3\text{Br}] - \{d_{110}[\text{O}^{\text{ID}}] + tj_{35}\}[\text{COF}_2] \end{aligned}$$

$$\begin{aligned} \frac{d[\text{HF}]}{dt} &= (d_{102}[\text{O}^{\text{ID}}] + tj_{27})[\text{CFCI}_3] + 2(d_{110}[\text{O}^{\text{ID}}] + tj_{35})[\text{COF}_2] \\ &+ (e_{91}[\text{O}^{\text{ID}}] + tj_{32})[\text{CF}_3\text{Br}] \end{aligned}$$

$$\begin{aligned} \frac{d[\text{CH}_2\text{O}]}{dt} &= 0.25a_{2et}[\text{CH}_4][\text{O}^{\text{ID}}] + c_3[\text{CH}_3\text{O}_2][\text{NO}] \\ &+ (2c_4 + c_5)[\text{CH}_3\text{O}_2][\text{CH}_3\text{O}_2] + 0.3c_7[\text{CH}_3\text{OOH}][\text{OH}] \\ &+ (c_{24} + c_{25})[\text{CH}_3\text{C(O)O}_2][\text{CH}_3\text{O}_2] + c_{33}[\text{ACETO}_2][\text{NO}] \\ &+ 0.8c_{35}[\text{ACETO}_2][\text{CH}_3\text{O}_2] + 0.5c_{39}[\text{C}_2\text{H}_4][\text{OH}][\text{M}] \\ &+ 2c_{42}[\text{EO}] + c_{43}[\text{C}_2\text{H}_4][\text{O}_3] + c_{47}[\text{GC(O)O}_2][\text{NO}] \\ &+ (2c_{49} + c_{50})[\text{GC(O)O}_2][\text{CH}_3\text{O}_2] \\ &+ 2c_{51}[\text{GC(O)O}_2][\text{GC(O)O}_2] + 0.5c_{52}[\text{GC(O)OOH}][\text{OH}] \\ &+ 0.54c_{54}[\text{C}_3\text{H}_6][\text{O}_3] + c_{56}[\text{PO}_2][\text{NO}] + c_{62}[\text{C}_4\text{H}_{10}][\text{OH}] \\ &+ c_{72}[\text{PO}_2][\text{PO}_2] + c_{73}[\text{PAN}][\text{OH}] \\ &+ 1.26c_{74}[\text{ACETO}_2][\text{ACETO}_2] + 0.58i_1[\text{C}_5\text{H}_8][\text{O}_3] \\ &+ 0.956i_4[\text{ISOPO}_2][\text{NO}] + i_6[\text{ISOPO}_2][\text{ISOPO}_2] \\ &+ 0.1i_8[\text{ISON}][\text{OH}] + 0.75i_{11}[\text{MACRO}_2][\text{NO}] \\ &+ 0.5i_{13}[\text{MACRO}_2][\text{MACRO}_2] + 0.1i_{16}[\text{MPAN}][\text{OH}] \\ &+ i_{18}[\text{NALD}][\text{OH}] + 1.16t_2[\text{C}_{10}\text{H}_{16}][\text{O}_3] + tj_{36}[\text{CH}_3\text{OOH}] \\ &+ tj_{48}[\text{HACET}] + tj_{50}[\text{GLYALD}] + tj_{52}[\text{GC(O)OOH}] \\ &+ tj_{53}[\text{POOH}] + tj_{54}[\text{ISOPOOH}] + tj_{55}[\text{ISON}] \\ &+ tj_{56}[\text{MACR}] + 0.5tj_{58}[\text{MACROOH}] + tj_{59}[\text{NALD}] \\ &- \{c_8[\text{OH}] + c_9[\text{NO}_3] + tj_{37} + tj_{38}\}[\text{CH}_2\text{O}] \end{aligned}$$

$$\frac{d[\text{CH}_3\text{OOH}]}{dt} = c_6[\text{CH}_3\text{O}_2][\text{HO}_2] - \{c_7[\text{OH}] + tj_{36}\}[\text{CH}_3\text{OOH}]$$

$$\frac{d[\text{C}_2\text{H}_6]}{dt} = -\{c_{10}[\text{OH}]\}[\text{C}_2\text{H}_6]$$

$$\begin{aligned} \frac{d[\text{CH}_3\text{CHO}]}{dt} &= c_{11}[\text{C}_2\text{H}_5\text{O}_2][\text{NO}] + 0.8c_{13}[\text{C}_2\text{H}_5\text{O}_2][\text{CH}_3\text{O}_2] \\ &+ 1.6c_{14}[\text{C}_2\text{H}_5\text{O}_2][\text{C}_2\text{H}_5\text{O}_2] + 0.714c_{15}[\text{C}_2\text{H}_5\text{OOH}][\text{OH}] \\ &+ 0.09c_{28}[\text{C}_3\text{H}_7\text{O}_2][\text{NO}] + 2.4c_{71}[\text{C}_3\text{H}_7\text{O}_2][\text{C}_3\text{H}_7\text{O}_2] \\ &+ 0.3c_{30}[\text{C}_3\text{H}_7\text{O}_2][\text{CH}_3\text{O}_2] + 0.053c_{31}[\text{C}_3\text{H}_7\text{OOH}][\text{OH}] \\ &+ 0.5c_{54}[\text{C}_3\text{H}_6][\text{O}_3] + c_{56}[\text{PO}_2][\text{NO}] + c_{72}[\text{PO}_2][\text{PO}_2] \\ &+ tj_{41}[\text{C}_2\text{H}_5\text{OOH}] + 0.09tj_{45}[\text{C}_3\text{H}_7\text{OOH}] + tj_{53}[\text{POOH}] \\ &- \{c_{16}[\text{OH}] + c_{17}[\text{NO}_3] + tj_{43} + tj_{44}\}[\text{CH}_3\text{CHO}] \end{aligned}$$

$$\begin{aligned} \frac{d[\text{C}_2\text{H}_5\text{OOH}]}{dt} &= c_{12}[\text{C}_2\text{H}_5\text{O}_2][\text{HO}_2] \\ &- \{c_{15}[\text{OH}] + tj_{41}\}[\text{C}_2\text{H}_5\text{OOH}] \end{aligned}$$

$$\begin{aligned} \frac{d[\text{PAN}]}{dt} &= c_{19}[\text{CH}_3\text{C(O)O}_2][\text{NO}_2][\text{M}] \\ &- \{c_{20}[\text{M}] + c_{73}[\text{OH}] + tj_{39} + tj_{40}\}[\text{PAN}] \end{aligned}$$

$$\begin{aligned} \frac{d[\text{CH}_3\text{C(O)OOH}]}{dt} &= c_{21}[\text{CH}_3\text{C(O)O}_2][\text{HO}_2] \\ &- \{c_{23}[\text{OH}] + tj_{42}\}[\text{CH}_3\text{C(O)OOH}] \end{aligned}$$

$$\frac{d[\text{C}_3\text{H}_8]}{dt} = -\{c_{27}[\text{OH}]\}[\text{C}_3\text{H}_8]$$

$$\begin{aligned} \frac{d[\text{ACET}]}{dt} &= 0.7c_{28}[\text{C}_3\text{H}_7\text{O}_2][\text{NO}] + 0.2c_{30}[\text{C}_3\text{H}_7\text{O}_2][\text{CH}_3\text{O}_2] \\ &+ 0.666c_{31}[\text{C}_3\text{H}_7\text{OOH}][\text{OH}] + 0.6t_1[\text{C}_{10}\text{H}_{16}][\text{OH}] \\ &+ 0.7tj_{45}[\text{C}_3\text{H}_7\text{OOH}] - \{c_{32}[\text{OH}] + tj_{46} + tj_{47}\}[\text{ACET}] \end{aligned}$$

$$\begin{aligned} \frac{d[\text{C}_3\text{H}_7\text{OOH}]}{dt} &= c_{29}[\text{C}_3\text{H}_7\text{O}_2][\text{HO}_2] \\ &- \{c_{31}[\text{OH}] + tj_{45}\}[\text{C}_3\text{H}_7\text{OOH}] \end{aligned}$$

$$\begin{aligned} \frac{d[\text{HACET}]}{dt} &= c_{34}[\text{ACETO}_2][\text{HO}_2] + 0.2c_{35}[\text{ACETO}_2][\text{CH}_3\text{O}_2] \\ &+ 0.5c_{58}[\text{POOH}][\text{OH}] + 0.25i_{11}[\text{MACRO}_2][\text{NO}] \\ &+ i_{13}[\text{MACRO}_2][\text{MACRO}_2] + 0.5tj_{58}[\text{MACROOH}] \\ &- \{c_{38}[\text{OH}] + tj_{48}\}[\text{HACET}] \end{aligned}$$

$$\begin{aligned} \frac{d[\text{MGLY}]}{dt} &= 0.5c_{35}[\text{ACETO}_2][\text{CH}_3\text{O}_2] + 0.677c_{38}[\text{HACET}][\text{OH}] \\ &+ c_{60}[\text{ONIT}][\text{OH}] + 0.37c_{74}[\text{ACETO}_2][\text{ACETO}_2] \\ &+ 0.2i_8[\text{ISON}][\text{OH}] + 0.9i_{10}[\text{MACR}][\text{O}_3] \\ &+ 0.5i_{11}[\text{MACRO}_2][\text{NO}] + i_{13}[\text{MACRO}_2][\text{MACRO}_2] \\ &+ 0.2i_{16}[\text{MPAN}][\text{OH}] + 0.5tj_{58}[\text{MACROOH}] \\ &- \{c_{36}[\text{OH}] + c_{37}[\text{NO}_3] + tj_{49}\}[\text{MGLY}] \end{aligned}$$

$$\frac{d[\text{C}_2\text{H}_4]}{dt} = -\{c_{39}[\text{OH}][\text{M}] + c_{43}[\text{O}_3]\}[\text{C}_2\text{H}_4]$$

$$\begin{aligned} \frac{d[\text{GLYALD}]}{dt} &= c_{41}[\text{EO}][\text{O}_2] + 0.5c_{70}[\text{EO}_2][\text{EO}_2] \\ &+ 0.75c_{72}[\text{PO}_2][\text{PO}_2] - \{c_{44}[\text{OH}] + tj_{50} + tj_{51}\}[\text{GLYALD}] \end{aligned}$$

$$\frac{d[\text{GPAN}]}{dt} = c_{45}[\text{GC(O)O}_2][\text{NO}_2][\text{M}] - \{c_{46}[\text{M}]\}[\text{GPAN}]$$

$$\begin{aligned} \frac{d[\text{GC(O)OOH}]}{dt} &= 0.7c_{48}[\text{GC(O)O}_2][\text{HO}_2] \\ &- \{c_{52}[\text{OH}] + tj_{52}\}[\text{GC(O)OOH}] \end{aligned}$$

$$\frac{d[\text{C}_3\text{H}_6]}{dt} = -\{c_{53}[\text{OH}][\text{M}] + c_{54}[\text{O}_3] + c_{55}[\text{NO}_3]\}[\text{C}_3\text{H}_6]$$

$$\frac{d[\text{ONIT}]}{dt} = c_{55}[\text{C}_3\text{H}_6][\text{NO}_3] - \{c_{60}[\text{OH}]\}[\text{ONIT}]$$

$$\begin{aligned} \frac{d[\text{POOH}]}{dt} &= c_{57}[\text{PO}_2][\text{HO}_2] + 0.667c_{61}[\text{EO}_2][\text{HO}_2] + 0.667g_5[\text{EO}_2] \\ &\quad + g_6[\text{PO}_2] - \{c_{58}[\text{OH}] + tj_{53}\}[\text{POOH}] \end{aligned}$$

$$\frac{d[\text{C}_4\text{H}_{10}]}{dt} = -\{c_{62}[\text{OH}]\}[\text{C}_4\text{H}_{10}]$$

$$\frac{d[\text{C}_5\text{H}_8]}{dt} = -\{i_1[\text{O}_3] + i_2[\text{OH}] + i_3[\text{NO}_3]\}[\text{C}_5\text{H}_8]$$

$$\begin{aligned} \frac{d[\text{MACR}]}{dt} &= 0.65i_1[\text{C}_5\text{H}_8][\text{O}_3] + 0.956i_4[\text{ISOPO}_2][\text{NO}] \\ &\quad + 2i_6[\text{ISOPO}_2][\text{ISOPO}_2] + i_7[\text{ISOPOOH}][\text{OH}] \\ &\quad + 1.3t_2[\text{C}_{10}\text{H}_{16}][\text{O}_3] + tj_{54}[\text{ISOPOOH}] + tj_{55}[\text{ISON}] \\ &\quad - \{i_9[\text{OH}] + i_{10}[\text{O}_3] + tj_{56}\}[\text{MACR}] \end{aligned}$$

$$\begin{aligned} \frac{d[\text{ISON}]}{dt} &= i_3[\text{C}_5\text{H}_8][\text{NO}_3] + 0.044i_4[\text{ISOPO}_2][\text{NO}] \\ &\quad - \{i_8[\text{OH}] + tj_{55}\}[\text{ISON}] \end{aligned}$$

$$\begin{aligned} \frac{d[\text{ISOPOOH}]}{dt} &= i_5[\text{ISOPO}_2][\text{HO}_2] + g_7[\text{ISOPO}_2] \\ &\quad - \{i_7[\text{OH}] + tj_{54}\}[\text{ISOPOOH}] \end{aligned}$$

$$\frac{d[\text{NALD}]}{dt} = i_8[\text{ISON}][\text{OH}] - \{i_{18}[\text{OH}] + tj_{59}\}[\text{NALD}]$$

$$\begin{aligned} \frac{d[\text{MACROOH}]}{dt} &= i_{12}[\text{MACRO}_2][\text{HO}_2] + g_8[\text{MACRO}_2] \\ &\quad - \{i_{17}[\text{OH}] + tj_{58}\}[\text{MACROOH}] \end{aligned}$$

$$\begin{aligned} \frac{d[\text{MPAN}]}{dt} &= i_{14}[\text{MACRO}_2][\text{NO}_2][\text{M}] \\ &\quad - \{i_{15}[\text{M}] + i_{16}[\text{OH}] + tj_{57}\}[\text{MPAN}] \end{aligned}$$

$$\frac{d[\text{C}_{10}\text{H}_{16}]}{dt} = -\{t_1[\text{OH}] + t_2[\text{O}_3] + t_3[\text{NO}_3]\}[\text{C}_{10}\text{H}_{16}]$$

$$\frac{d[\text{HNO}_3]_{(s)}}{dt} = (\text{het}_1 + \text{het}_2)[\text{ClONO}_2] + (2\text{het}_3 + \text{het}_4)[\text{N}_2\text{O}_5]$$

$$\begin{aligned} \frac{d[\text{H}_2\text{O}]_{(s)}}{dt} &= \text{het}_5[\text{HOCl}] + \text{het}_6[\text{HOBr}] \\ &\quad - \{\text{het}_1[\text{ClONO}_2] + \text{het}_3[\text{N}_2\text{O}_5]\} \end{aligned}$$

$$\begin{aligned} \frac{d[\text{HCl}]_{(s)}}{dt} &= -\{\text{het}_2[\text{ClONO}_2] + \text{het}_4[\text{N}_2\text{O}_5] \\ &\quad + \text{het}_5[\text{HOCl}] + \text{het}_6[\text{HOBr}]\} \end{aligned}$$

I-2 Nighttime

The prognostic equations for long-lived species can be written as simple forms during nighttime because all photolysis rates are zero, and because concentrations of some short-lived species are set to zero for the nighttime calculation.

$$\frac{d[\text{N}_2\text{O}]}{dt} = 0$$

$$\frac{d[\text{CH}_4]}{dt} = 0.08c_{54}[\text{C}_3\text{H}_6][\text{O}_3]$$

$$\frac{d[\text{H}_2\text{O}]}{dt} = -\{b_{53}[\text{N}_2\text{O}_5]\}[\text{H}_2\text{O}]$$

$$\frac{d[\text{NO}_y]}{dt} = -\{(\text{het}_1 + \text{het}_2)[\text{ClONO}_2] + (2\text{het}_3 + \text{het}_4)[\text{N}_2\text{O}_5]\}$$

$$\begin{aligned} \frac{d[\text{HNO}_3]}{dt} &= 2b_{53}[\text{N}_2\text{O}_5][\text{H}_2\text{O}] + c_9[\text{CH}_2\text{O}][\text{NO}_3] + c_{17}[\text{CH}_3\text{CHO}][\text{NO}_3] \\ &\quad + c_{37}[\text{MGly}][\text{NO}_3] + g_1[\text{ClONO}_2] + 2g_2[\text{N}_2\text{O}_5] \\ &\quad + g_3[\text{BrONO}_2] + 0.5g_{10}[\text{NO}_2] \end{aligned}$$

$$\begin{aligned} \frac{d[\text{N}_2\text{O}_5]}{dt} &= b_{12}[\text{NO}_3][\text{NO}_2][\text{M}] \\ &\quad - \{b_{32}[\text{M}] + b_{53}[\text{H}_2\text{O}] + \text{het}_3 + \text{het}_4 + g_2\}[\text{N}_2\text{O}_5] \end{aligned}$$

$$\begin{aligned} \frac{d[\text{Cl}_y]}{dt} &= \text{het}_2[\text{ClONO}_2] + \text{het}_4[\text{N}_2\text{O}_5] \\ &\quad + \text{het}_5[\text{HOCl}] + \text{het}_6[\text{HOBr}] \end{aligned}$$

$$\begin{aligned} \frac{d[\text{O}_x]}{dt} &= -\{b_4[\text{NO}] + b_9[\text{NO}_2] + c_{43}[\text{C}_2\text{H}_4] + c_{54}[\text{C}_3\text{H}_6] \\ &\quad + i_1[\text{C}_5\text{H}_8] + i_{10}[\text{MACR}] + t_2[\text{C}_{10}\text{H}_{16}]\}[\text{O}_3] \end{aligned}$$

$$\begin{aligned} \frac{d[\text{CO}]}{dt} &= c_9[\text{CH}_2\text{O}][\text{NO}_3] + c_{37}[\text{MGly}][\text{NO}_3] + 0.5c_{43}[\text{C}_2\text{H}_4][\text{O}_3] \\ &\quad + 0.56c_{54}[\text{C}_3\text{H}_6][\text{O}_3] + 0.14i_1[\text{C}_5\text{H}_8][\text{O}_3] \\ &\quad + 0.22i_{10}[\text{MACR}][\text{O}_3] + 0.25i_{11}[\text{MACRO}_2][\text{NO}] \\ &\quad + 0.5i_{13}[\text{MACRO}_2][\text{MACRO}_2] + 0.28t_2[\text{C}_{10}\text{H}_{16}][\text{O}_3] \end{aligned}$$

$$\frac{d[\text{OCIO}]}{dt} = e_{5a}[\text{BrO}][\text{ClO}] - \{d_{65}[\text{NO}]\}[\text{OCIO}]$$

$$\begin{aligned} \frac{d[\text{CO}_2]}{dt} &= c_{18}[\text{CH}_3\text{C(O)O}_2][\text{NO}] + c_{24}[\text{CH}_3\text{C(O)O}_2][\text{CH}_3\text{O}_2] \\ &\quad + 2c_{26}[\text{CH}_3\text{C(O)O}_2][\text{CH}_3\text{C(O)O}_2] + c_{47}[\text{GC(O)O}_2][\text{NO}] \\ &\quad + c_{49}[\text{GC(O)O}_2][\text{CH}_3\text{O}_2] + 2c_{51}[\text{GC(O)O}_2][\text{GC(O)O}_2] \\ &\quad + 0.72i_1[\text{C}_5\text{H}_8][\text{O}_3] + i_6[\text{ISOPO}_2][\text{ISOPO}_2] \\ &\quad + 0.43i_{10}[\text{MACR}][\text{O}_3] + 0.25i_{11}[\text{MACRO}_2][\text{NO}] \\ &\quad + i_{13}[\text{MACRO}_2][\text{MACRO}_2] + 1.44t_2[\text{C}_{10}\text{H}_{16}][\text{O}_3] \\ &\quad + 4t_3[\text{C}_{10}\text{H}_{16}][\text{NO}_3] \end{aligned}$$

$$\frac{d[\text{HCl}]}{dt} = 0$$

$$\begin{aligned} \frac{d[\text{ClONO}_2]}{dt} &= d_{31}[\text{NO}_2][\text{ClO}][\text{M}] \\ &\quad - \{\text{het}_1 + \text{het}_2 + g_1\}[\text{ClONO}_2] \end{aligned}$$

$$\frac{d[\text{HOCl}]}{dt} = (\text{het}_1 + g_1)[\text{ClONO}_2] - \{\text{het}_5\}[\text{HOCl}]$$

$$\frac{d[\text{Cl}_2]}{dt} = \text{het}_2[\text{ClONO}_2] + \text{het}_5[\text{HOCl}]$$

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = 0.09i_1[\text{C}_5\text{H}_8][\text{O}_3] + 0.18t_2[\text{C}_{10}\text{H}_{16}][\text{O}_3]$$

$$\frac{d[\text{ClONO}_2]}{dt} = \text{het}_4[\text{N}_2\text{O}_5]$$

$$\frac{d[\text{HBr}]}{dt} = 0$$

$$\frac{d[\text{BrONO}_2]}{dt} = e_{13}[\text{BrO}][\text{NO}_2][\text{M}] - \{g_3\}[\text{BrONO}_2]$$

$$\begin{aligned} \frac{d[\text{NO}_x]}{dt} &= b_{24}[\text{HO}_2\text{NO}_2][\text{M}] + 2b_{32}[\text{N}_2\text{O}_5][\text{M}] + c_{20}[\text{PAN}][\text{M}] \\ &+ c_{46}[\text{GPAN}][\text{M}] + i_{15}[\text{MPAN}][\text{M}] \\ &- \{+(0.044i_4[\text{ISOPO}_2])[\text{NO}] \\ &+ (b_{12}[\text{NO}_3][\text{M}] + d_{31}[\text{ClO}][\text{M}] + e_{13}[\text{BrO}][\text{M}] \\ &+ c_{19}[\text{CH}_3\text{C}(\text{O})\text{O}_2][\text{M}] + c_{45}[\text{GC}(\text{O})\text{O}_2] \\ &+ i_{14}[\text{MACRO}_2][\text{M}] + 0.5g_{10})[\text{NO}_2] \\ &+ (c_9[\text{CH}_2\text{O}] + c_{17}[\text{CH}_3\text{CHO}] + c_{37}[\text{MGLY}] \\ &+ c_{55}[\text{C}_3\text{H}_6] + i_3[\text{C}_5\text{H}_8])[\text{NO}_3]\} \end{aligned}$$

$$\frac{d[\text{HO}_2\text{NO}_2]}{dt} = -\{b_{24}[\text{M}]\}[\text{HO}_2\text{NO}_2]$$

$$\begin{aligned} \frac{d[\text{ClO}_x]}{dt} &= 2d_{61}[\text{Cl}_2\text{O}_2][\text{M}] + d_{65}[\text{OCIO}][\text{NO}] \\ &- \{(d_{31}[\text{NO}_2][\text{M}] + 2d_{60}[\text{ClO}][\text{M}] + (e_{5a} + e_{5c})[\text{BrO}])[\text{ClO}]\} \end{aligned}$$

$$\frac{d[\text{BrO}_x]}{dt} = \text{het}_6[\text{HOBr}] - \{(e_{13}[\text{NO}_2][\text{M}])[\text{BrO}]\}$$

$$\frac{d[\text{Cl}_2\text{O}_2]}{dt} = d_{60}[\text{ClO}][\text{ClO}][\text{M}] - \{d_{61}[\text{M}]\}[\text{Cl}_2\text{O}_2]$$

$$\frac{d[\text{HOBr}]}{dt} = g_3[\text{BrONO}_2] - \{\text{het}_6\}[\text{HOBr}]$$

$$\frac{d[\text{CCl}_4]}{dt} = 0$$

$$\frac{d[\text{CFCl}_3]}{dt} = 0$$

$$\frac{d[\text{CF}_2\text{Cl}_3]}{dt} = 0$$

$$\frac{d[\text{Br}_y]}{dt} = 0$$

$$\frac{d[\text{CH}_3\text{Cl}]}{dt} = 0$$

$$\frac{d[\text{CH}_3\text{Br}]}{dt} = 0$$

$$\frac{d[\text{CH}_2\text{ClBr}]}{dt} = 0$$

$$\frac{d[\text{CF}_3\text{Cl}]}{dt} = 0$$

$$\frac{d[\text{COF}_2]}{dt} = 0$$

$$\frac{d[\text{HF}]}{dt} = 0$$

$$\begin{aligned} \frac{d[\text{CH}_2\text{O}]}{dt} &= c_3[\text{CH}_3\text{O}_2][\text{NO}] + (2c_4 + c_5)[\text{CH}_3\text{O}_2][\text{CH}_3\text{O}_2] \\ &+ (c_{24} + c_{25})[\text{CH}_3\text{C}(\text{O})\text{O}_2][\text{CH}_3\text{O}_2] + c_{43}[\text{C}_2\text{H}_4][\text{O}_3] \\ &+ c_{47}[\text{GC}(\text{O})\text{O}_2][\text{NO}] + (2c_{49} + c_{50})[\text{GC}(\text{O})\text{O}_2][\text{CH}_3\text{O}_2] \\ &+ 2c_{51}[\text{GC}(\text{O})\text{O}_2][\text{GC}(\text{O})\text{O}_2] + 0.54c_{54}[\text{C}_3\text{H}_6][\text{O}_3] \\ &+ 0.58i_1[\text{C}_5\text{H}_8][\text{O}_3] + 0.956i_4[\text{ISOPO}_2][\text{NO}] \\ &+ i_6[\text{ISOPO}_2][\text{ISOPO}_2] + 0.75i_{11}[\text{MACRO}_2][\text{NO}] \\ &+ 0.5i_{13}[\text{MACRO}_2][\text{MACRO}_2] + 1.16t_2[\text{C}_{10}\text{H}_{16}][\text{O}_3] \\ &- \{c_9[\text{NO}_3]\}[\text{CH}_2\text{O}] \end{aligned}$$

$$\frac{d[\text{CH}_3\text{OOH}]}{dt} = 0$$

$$\frac{d[\text{C}_2\text{H}_6]}{dt} = 0$$

$$\frac{d[\text{CH}_3\text{CHO}]}{dt} = 0.5c_{54}[\text{C}_3\text{H}_6][\text{O}_3] - \{c_{17}[\text{NO}_3]\}[\text{CH}_3\text{CHO}]$$

$$\frac{d[\text{C}_2\text{H}_5\text{OOH}]}{dt} = 0$$

$$\frac{d[\text{PAN}]}{dt} = c_{19}[\text{CH}_3\text{C}(\text{O})\text{O}_2][\text{NO}_2][\text{M}] - \{c_{20}[\text{M}]\}[\text{PAN}]$$

$$\frac{d[\text{CH}_3\text{C}(\text{O})\text{OOH}]}{dt} = 0$$

$$\frac{d[\text{C}_3\text{H}_8]}{dt} = 0$$

$$\frac{d[\text{ACET}]}{dt} = 0$$

$$\frac{d[\text{C}_3\text{H}_7\text{OOH}]}{dt} = 0$$

$$\begin{aligned} \frac{d[\text{HACET}]}{dt} &= 0.25i_{11}[\text{MACRO}_2][\text{NO}] \\ &+ i_{13}[\text{MACRO}_2][\text{MACRO}_2] \end{aligned}$$

$$\begin{aligned} \frac{d[\text{MGLY}]}{dt} &= 0.9i_{10}[\text{MACR}][\text{O}_3] + 0.5i_{11}[\text{MACRO}_2][\text{NO}] \\ &+ i_{13}[\text{MACRO}_2][\text{MACRO}_2] - \{c_{37}[\text{NO}_3]\}[\text{MGLY}] \end{aligned}$$

$$\frac{d[\text{C}_2\text{H}_4]}{dt} = -\{c_{43}[\text{O}_3]\}[\text{C}_2\text{H}_4]$$

$$\frac{d[\text{GLYALD}]}{dt} = 0$$

$$\frac{d[\text{GPAN}]}{dt} = c_{45}[\text{GC}(\text{O})\text{O}_2][\text{NO}_2][\text{M}] - \{c_{46}[\text{M}]\}[\text{GPAN}]$$

$$\frac{d[\text{GC}(\text{O})\text{OOH}]}{dt} = 0$$

$$\frac{d[\text{C}_3\text{H}_6]}{dt} = -\{c_{54}[\text{O}_3] + c_{55}[\text{NO}_3]\}[\text{C}_3\text{H}_6]$$

$$\frac{d[\text{ONIT}]}{dt} = c_{55}[\text{C}_3\text{H}_6][\text{NO}_3]$$

$$\frac{d[\text{POOH}]}{dt} = 0$$

$$\frac{d[\text{C}_4\text{H}_{10}]}{dt} = 0$$

$$\frac{d[\text{C}_5\text{H}_8]}{dt} = -\{i_1[\text{O}_3] + i_3[\text{NO}_3]\}[\text{C}_5\text{H}_8]$$

$$\begin{aligned} \frac{d[\text{MACR}]}{dt} = & 0.65i_1[\text{C}_5\text{H}_8][\text{O}_3] + 0.956i_4[\text{ISOPO}_2][\text{NO}] \\ & + 2i_6[\text{ISOPO}_2][\text{ISOPO}_2] + 1.3t_2[\text{C}_{10}\text{H}_{16}][\text{O}_3] \\ & - \{i_{10}[\text{O}_3]\}[\text{MACR}] \end{aligned}$$

$$\frac{d[\text{ISON}]}{dt} = i_3[\text{C}_5\text{H}_8][\text{NO}_3] + 0.044i_4[\text{ISOPO}_2][\text{NO}]$$

$$\frac{d[\text{ISOPOOH}]}{dt} = g_7[\text{ISOPO}_2]$$

$$\frac{d[\text{NALD}]}{dt} = 0$$

$$\frac{d[\text{MACROOH}]}{dt} = g_8[\text{MACRO}_2]$$

$$\frac{d[\text{MPAN}]}{dt} = i_{14}[\text{MACRO}_2][\text{NO}_2][\text{M}] - \{i_{15}[\text{M}]\}[\text{MPAN}]$$

$$\frac{d[\text{C}_{10}\text{H}_{16}]}{dt} = -\{t_2[\text{O}_3] + t_3[\text{NO}_3]\}[\text{C}_{10}\text{H}_{16}]$$

$$\frac{d[\text{HNO}_3]_{(s)}}{dt} = (\text{het}_1 + \text{het}_2)[\text{ClONO}_2] + (2\text{het}_3 + \text{het}_4)[\text{N}_2\text{O}_5]$$

$$\begin{aligned} \frac{d[\text{H}_2\text{O}]_{(s)}}{dt} = & \text{het}_5[\text{HOCl}] + \text{het}_6[\text{HOBr}] \\ & - \{\text{het}_1[\text{ClONO}_2] + \text{het}_3[\text{N}_2\text{O}_5]\} \end{aligned}$$

$$\begin{aligned} \frac{d[\text{HCl}]_{(s)}}{dt} = & -\{\text{het}_2[\text{ClONO}_2] + \text{het}_4[\text{N}_2\text{O}_5] \\ & + \text{het}_5[\text{HOCl}] + \text{het}_6[\text{HOBr}]\} \end{aligned}$$

Appendix II: Formulation of short-lived species

Prognostic or diagnostic equations for short-lived species are described here, with the different forms for daytime and nighttime.

II-1. Daytime

II-1-1 HO_x family, N and EO

Instantaneous chemical equilibrium is assumed for HO_x ($\equiv \text{H} + \text{OH} + \text{HO}_2$) and its members. Then, the change rate of [HO_x] can be set to zero

$$\begin{aligned} \frac{d[\text{HO}_x]}{dt} = & 2a_{1et}[\text{O}^{\text{ID}}][\text{H}_2\text{O}] + 1.15a_{2et}[\text{O}^{\text{ID}}][\text{CH}_4] + 2a_{3et}[\text{O}^{\text{ID}}][\text{H}_2] \\ & - 2(a_8 + a_9)[\text{OH}][\text{OH}] - 2a_{17}[\text{HO}_2][\text{OH}] - 2a_{23b}[\text{H}][\text{HO}_2] \\ & - 2a_{23c}[\text{H}][\text{HO}_2] + 2a_{24}[\text{H}_2][\text{O}] - 2a_{27}[\text{HO}_2][\text{HO}_2] \\ & - b_{22}[\text{NO}_2][\text{OH}][\text{M}] - b_{23}[\text{NO}_2][\text{HO}_2][\text{M}] + b_{24}[\text{HO}_2\text{NO}_2][\text{M}] \\ & - b_{27}[\text{HNO}_3][\text{OH}] - b_{28}[\text{HO}_2\text{NO}_2][\text{OH}] - d_0[\text{CH}_3\text{Cl}][\text{OH}] \\ & + d_6[\text{Cl}][\text{H}_2] - d_7[\text{Cl}][\text{HO}_2] - d_9[\text{ClO}][\text{OH}] - d_{11}[\text{HCl}][\text{OH}] \\ & - d_{33}[\text{ClO}][\text{HO}_2] - d_{34}[\text{HOCl}][\text{OH}] + d_{35}[\text{HOCl}][\text{O}] \\ & + d_{37}[\text{HOCl}][\text{Cl}] - d_{62}[\text{OCIO}][\text{OH}] - e_7[\text{Br}][\text{HO}_2] \\ & - e_{11}[\text{HBr}][\text{OH}] - e_{15}[\text{BrO}][\text{HO}_2] - c_2[\text{CH}_4][\text{OH}] \\ & + c_3[\text{CH}_3\text{O}_2][\text{NO}] + 2c_4[\text{CH}_3\text{O}_2][\text{CH}_3\text{O}_2] - c_6[\text{CH}_3\text{O}_2][\text{HO}_2] \\ & - 0.7c_7[\text{CH}_3\text{OOH}][\text{OH}] + c_9[\text{CH}_2\text{O}][\text{NO}_3] \\ & - c_{10}[\text{C}_2\text{H}_6][\text{OH}] + c_{11}[\text{C}_2\text{H}_5\text{O}_2][\text{NO}] - c_{12}[\text{C}_2\text{H}_5\text{O}_2][\text{HO}_2] \\ & + 0.6c_{13}[\text{C}_2\text{H}_5\text{O}_2][\text{CH}_3\text{O}_2] + 1.2c_{14}[\text{C}_2\text{H}_5\text{O}_2][\text{C}_2\text{H}_5\text{O}_2] \\ & - 0.286c_{15}[\text{C}_2\text{H}_5\text{OOH}][\text{OH}] - c_{16}[\text{CH}_3\text{CHO}][\text{OH}] \\ & - (c_{21} + c_{22})[\text{CH}_3\text{COO}_2][\text{HO}_2] - c_{23}[\text{CH}_3\text{C}(\text{O})\text{OOH}][\text{OH}] \\ & + c_{24}[\text{CH}_3\text{C}(\text{O})\text{O}_2][\text{CH}_3\text{O}_2] - c_{27}[\text{C}_3\text{H}_8][\text{OH}] \\ & + c_{28}[\text{C}_3\text{H}_7\text{O}_2][\text{NO}] - c_{29}[\text{C}_3\text{H}_7\text{O}_2][\text{HO}_2] \\ & + c_{30}[\text{C}_3\text{H}_7\text{O}_2][\text{CH}_3\text{O}_2] - 0.157c_{31}[\text{C}_3\text{H}_7\text{OOH}][\text{OH}] \\ & - c_{32}[\text{ACET}][\text{OH}] - c_{34}[\text{ACETO}_2][\text{HO}_2] \\ & + 0.3c_{35}[\text{ACETO}_2][\text{CH}_3\text{O}_2] - c_{36}[\text{MGly}][\text{OH}] \\ & - 0.323c_{38}[\text{HACET}][\text{OH}] - 0.75c_{39}[\text{C}_2\text{H}_4][\text{OH}][\text{M}] \\ & + c_{41}[\text{EO}][\text{O}_2] + c_{42}[\text{EO}] + 0.24c_{43}[\text{C}_2\text{H}_4][\text{O}_3] \\ & - 0.8c_{44}[\text{GLYALD}][\text{OH}] + c_{47}[\text{GC}(\text{O})\text{O}_2][\text{NO}] \\ & - c_{48}[\text{GC}(\text{O})\text{O}_2][\text{HO}_2] + 2c_{49}[\text{GC}(\text{O})\text{O}_2][\text{CH}_3\text{O}_2] \\ & + 2c_{51}[\text{GC}(\text{O})\text{O}_2][\text{GC}(\text{O})\text{O}_2] - 0.5c_{52}[\text{GC}(\text{O})\text{O}_2\text{H}][\text{OH}] \\ & - c_{53}[\text{C}_3\text{H}_6][\text{OH}][\text{M}] + 0.52c_{54}[\text{C}_3\text{H}_6][\text{O}_3] + c_{56}[\text{PO}_2][\text{NO}] \\ & - c_{57}[\text{PO}_2][\text{HO}_2] - 0.5c_{58}[\text{POOH}][\text{OH}] - c_{60}[\text{ONIT}][\text{OH}] \\ & - c_{61}[\text{EO}_2][\text{HO}_2] + 1.2c_{71}[\text{C}_3\text{H}_7\text{O}_2][\text{C}_3\text{H}_7\text{O}_2] + c_{72}[\text{PO}_2][\text{PO}_2] \\ & - c_{73}[\text{PAN}][\text{OH}] + 0.5i_1[\text{C}_5\text{H}_8][\text{O}_3] - i_2[\text{C}_5\text{H}_8][\text{OH}] \\ & + 0.956i_4[\text{ISOPO}_2][\text{NO}] - i_5[\text{ISOPO}_2][\text{HO}_2] \\ & + i_6[\text{ISOPO}_2][\text{ISOPO}_2] - 0.9i_8[\text{ISON}][\text{OH}] - i_9[\text{MACR}][\text{OH}] \\ & + 0.51i_{10}[\text{MACR}][\text{O}_3] + 0.75i_{11}[\text{MACRO}_2][\text{NO}] \\ & - i_{12}[\text{MACRO}_2][\text{HO}_2] - 0.9i_{16}[\text{MPAN}][\text{OH}] \\ & - i_{17}[\text{MACROOH}][\text{OH}] - i_{18}[\text{NALD}][\text{OH}] - t_1[\text{C}_{10}\text{H}_{16}][\text{OH}] \\ & + t_2[\text{C}_{10}\text{H}_{16}][\text{O}_3] + 2t_3[\text{H}_2\text{O}] + t_5[\text{CH}_4] + t_7[\text{HNO}_3] \\ & + t_8[\text{HOCl}] + t_9[\text{HO}_2\text{NO}_2] + 2t_{13}[\text{H}_2\text{O}_2] + t_{16}[\text{HCl}] \end{aligned}$$

$$\begin{aligned}
& + t_{j22}[\text{HOBr}] + 2t_{j36}[\text{CH}_3\text{OOH}] + 2t_{j37}[\text{CH}_2\text{O}] \\
& + 2t_{j41}[\text{C}_2\text{H}_5\text{OOH}] + t_{j42}[\text{CH}_3\text{C}(\text{O})\text{O}_2\text{H}] + t_{j43}[\text{CH}_3\text{CHO}] \\
& + 2t_{j45}[\text{C}_3\text{H}_7\text{OOH}] + t_{j48}[\text{HACET}] + t_{j49}[\text{MGLY}] \\
& + 2t_{j50}[\text{GLYALD}] + 2t_{j52}[\text{GC}(\text{O})\text{OOH}] + 2t_{j53}[\text{POOH}] \\
& + 2t_{j54}[\text{ISOPOOH}] + t_{j55}[\text{ISON}] + t_{j56}[\text{MACR}] \\
& + 2t_{j58}[\text{MACROOH}] + t_{j59}[\text{NALD}] - g_4[\text{HO}_2] \\
& + g_9[\text{CH}_3\text{C}(\text{O})\text{O}_2] \\
& = 0
\end{aligned} \tag{II.1}$$

Arranging Eq.(II.1) with the use of $[\text{H}]/[\text{OH}]$ and $[\text{HO}_2]/[\text{OH}]$, we get a quadratic function of $[\text{OH}]$

$$\begin{aligned}
& \frac{d[\text{HO}_x]}{dt} \\
& = -2 \left\{ a_8 + a_9 + a_{17} \frac{[\text{HO}_2]}{[\text{OH}]} + a_{23b} \frac{[\text{H}]}{[\text{OH}]} \frac{[\text{HO}_2]}{[\text{OH}]} \right. \\
& \quad \left. + a_{23c} \frac{[\text{H}]}{[\text{OH}]} \frac{[\text{HO}_2]}{[\text{OH}]} + a_{27} \frac{[\text{HO}_2]}{[\text{OH}]} \frac{[\text{HO}_2]}{[\text{OH}]} \right\} [\text{OH}]^2 \\
& - \left\{ b_{22}[\text{NO}_2][\text{M}] + b_{23}[\text{NO}_2][\text{M}] \frac{[\text{HO}_2]}{[\text{OH}]} + b_{27}[\text{HNO}_3] \right. \\
& \quad + b_{28}[\text{HO}_2\text{NO}_2] + d_0[\text{CH}_3\text{Cl}] + d_7[\text{Cl}] \frac{[\text{HO}_2]}{[\text{OH}]} + d_9[\text{ClO}] \\
& \quad + d_{11}[\text{HCl}] + d_{33}[\text{ClO}] \frac{[\text{HO}_2]}{[\text{OH}]} + d_{34}[\text{HOCl}] + d_{62}[\text{OCIO}] \\
& \quad + e_7[\text{Br}] \frac{[\text{HO}_2]}{[\text{OH}]} + e_{11}[\text{HBr}] + e_{15}[\text{BrO}] \frac{[\text{HO}_2]}{[\text{OH}]} + c_2[\text{CH}_4] \\
& \quad + c_6[\text{CH}_3\text{O}_2] \frac{[\text{HO}_2]}{[\text{OH}]} + 0.7c_7[\text{CH}_3\text{OOH}] + c_{10}[\text{C}_2\text{H}_6] \\
& \quad + c_{12}[\text{C}_2\text{H}_5\text{O}_2] \frac{[\text{HO}_2]}{[\text{OH}]} + 0.286c_{15}[\text{C}_2\text{H}_5\text{OOH}] \\
& \quad + c_{16}[\text{CH}_3\text{CHO}] + (c_{21} + c_{22})[\text{CH}_3\text{COO}_2] \frac{[\text{HO}_2]}{[\text{OH}]} \\
& \quad + c_{23}[\text{CH}_3\text{C}(\text{O})\text{OOH}] + c_{27}[\text{C}_3\text{H}_8] + c_{29}[\text{C}_3\text{H}_7\text{O}_2] \frac{[\text{HO}_2]}{[\text{OH}]} \\
& \quad + 0.157c_{31}[\text{C}_3\text{H}_7\text{OOH}] + c_{32}[\text{ACET}] \\
& \quad + c_{34}[\text{ACETO}_2] \frac{[\text{HO}_2]}{[\text{OH}]} + c_{36}[\text{MGLY}] + 0.323c_{38}[\text{HACET}] \\
& \quad + 0.75c_{39}[\text{C}_2\text{H}_4][\text{M}] + 0.8c_{44}[\text{GLYALD}] \\
& \quad + c_{48}[\text{GC}(\text{O})\text{O}_2] \frac{[\text{HO}_2]}{[\text{OH}]} + 0.5c_{52}[\text{GC}(\text{O})\text{O}_2\text{H}] \\
& \quad + c_{53}[\text{C}_3\text{H}_6][\text{M}] + c_{57}[\text{PO}_2] \frac{[\text{HO}_2]}{[\text{OH}]} + 0.5c_{58}[\text{POOH}] \\
& \quad + c_{60}[\text{ONIT}] + c_{61}[\text{EO}_2] \frac{[\text{HO}_2]}{[\text{OH}]} + c_{73}[\text{PAN}] + i_2[\text{C}_5\text{H}_8] \\
& \quad + i_5[\text{ISOPO}_2] \frac{[\text{HO}_2]}{[\text{OH}]} + 0.9i_8[\text{ISON}] + i_9[\text{MACR}] \\
& \quad + i_{12}[\text{MACRO}_2] \frac{[\text{HO}_2]}{[\text{OH}]} + 0.9i_{16}[\text{MPAN}] + i_{17}[\text{MACROOH}] \\
& \quad + i_{18}[\text{NALD}] + t_1[\text{C}_{10}\text{H}_{16}] + g_4 \frac{[\text{HO}_2]}{[\text{OH}]} \left. \right\} [\text{OH}]
\end{aligned}$$

$$\begin{aligned}
& + \{ 2a_{1el}[\text{O}^{\text{ID}}][\text{H}_2\text{O}] + 1.15a_{2el}[\text{O}^{\text{ID}}][\text{CH}_4] + 2a_{10}[\text{H}_2\text{O}_2][\text{O}] \\
& \quad + 2a_{3el}[\text{O}^{\text{ID}}][\text{H}_2] + 2a_{24}[\text{H}_2][\text{O}] + b_{24}[\text{HO}_2\text{NO}_2][\text{M}] \\
& \quad + d_6[\text{Cl}][\text{H}_2] + d_{35}[\text{HOCl}][\text{O}] + d_{37}[\text{HOCl}][\text{Cl}] \\
& \quad + c_3[\text{CH}_3\text{O}_2][\text{NO}] + 2c_4[\text{CH}_3\text{O}_2][\text{CH}_3\text{O}_2] + c_9[\text{CH}_2\text{O}][\text{NO}_3] \\
& \quad + c_{11}[\text{C}_2\text{H}_5\text{O}_2][\text{NO}] + 0.6c_{13}[\text{C}_2\text{H}_5\text{O}_2][\text{CH}_3\text{O}_2] \\
& \quad + 1.2c_{14}[\text{C}_2\text{H}_5\text{O}_2][\text{C}_2\text{H}_5\text{O}_2] + c_{24}[\text{CH}_3\text{C}(\text{O})\text{O}_2][\text{CH}_3\text{O}_2] \\
& \quad + c_{28}[\text{C}_3\text{H}_7\text{O}_2][\text{NO}] + 1.2c_{71}[\text{C}_3\text{H}_7\text{O}_2][\text{C}_3\text{H}_7\text{O}_2] \\
& \quad + c_{30}[\text{C}_3\text{H}_7\text{O}_2][\text{CH}_3\text{O}_2] + 0.3c_{35}[\text{ACETO}_2][\text{CH}_3\text{O}_2] \\
& \quad + c_{41}[\text{EO}][\text{O}_2] + c_{42}[\text{EO}] + 0.24c_{43}[\text{C}_2\text{H}_4][\text{O}_3] \\
& \quad + c_{47}[\text{GC}(\text{O})\text{O}_2][\text{NO}] + 2c_{49}[\text{GC}(\text{O})\text{O}_2][\text{CH}_3\text{O}_2] \\
& \quad + 2c_{51}[\text{GC}(\text{O})\text{O}_2][\text{GC}(\text{O})\text{O}_2] + 0.52c_{54}[\text{C}_3\text{H}_6][\text{O}_3] \\
& \quad + c_{56}[\text{PO}_2][\text{NO}] + c_{72}[\text{PO}_2][\text{PO}_2] + 0.5i_1[\text{C}_5\text{H}_8][\text{O}_3] \\
& \quad + 0.956i_4[\text{ISOPO}_2][\text{NO}] + i_6[\text{ISOPO}_2][\text{ISOPO}_2] \\
& \quad + 0.51i_{10}[\text{MACR}][\text{O}_3] + 0.75i_{11}[\text{MACRO}_2][\text{NO}] \\
& \quad + t_2[\text{C}_{10}\text{H}_{16}][\text{O}_3] + 2t_3[\text{H}_2\text{O}] + t_5[\text{CH}_4] + t_7[\text{HNO}_3] \\
& \quad + t_8[\text{HOCl}] + t_9[\text{HO}_2\text{NO}_2] + 2t_{13}[\text{H}_2\text{O}_2] + t_{16}[\text{HCl}] \\
& \quad + t_{j22}[\text{HOBr}] + 2t_{j36}[\text{CH}_3\text{OOH}] + 2t_{j37}[\text{CH}_2\text{O}] \\
& \quad + 2t_{j41}[\text{C}_2\text{H}_5\text{OOH}] + t_{j42}[\text{CH}_3\text{C}(\text{O})\text{O}_2\text{H}] + t_{j43}[\text{CH}_3\text{CHO}] \\
& \quad + 2t_{j45}[\text{C}_3\text{H}_7\text{OOH}] + t_{j48}[\text{HACET}] + t_{j49}[\text{MGLY}] \\
& \quad + 2t_{j50}[\text{GLYALD}] + 2t_{j52}[\text{GC}(\text{O})\text{OOH}] + 2t_{j53}[\text{POOH}] \\
& \quad + 2t_{j54}[\text{ISOPOOH}] + t_{j55}[\text{ISON}] + t_{j56}[\text{MACR}] \\
& \quad + 2t_{j58}[\text{MACROOH}] + t_{j59}[\text{NALD}] + g_9[\text{CH}_3\text{C}(\text{O})\text{O}_2] \} \\
& = 0.
\end{aligned} \tag{II.2}$$

The change rates of $[\text{HO}_2]$ and $[\text{H}]$ are also equal to zero

$$\begin{aligned}
& \frac{d[\text{HO}_2]}{dt} \\
& = -2a_{27}[\text{HO}_2]^2 \\
& - \{ (a_{23a} + a_{23b} + a_{23c})[\text{H}] + a_{6b}[\text{O}_3] + a_7[\text{O}] + a_{17}[\text{OH}] \\
& \quad + a_{26}[\text{NO}] + b_{23}[\text{NO}_2][\text{M}] + b_{52}[\text{NO}_3] + d_7[\text{Cl}] + d_{33}[\text{ClO}] \\
& \quad + e_7[\text{Br}] + e_{15}[\text{BrO}] + c_6[\text{CH}_3\text{O}_2] + c_{12}[\text{C}_2\text{H}_5\text{O}_2] \\
& \quad + (c_{21} + c_{22})[\text{CH}_3\text{C}(\text{O})\text{O}_2] + c_{29}[\text{C}_3\text{H}_7\text{O}_2] + c_{34}[\text{ACETO}_2] \\
& \quad + c_{48}[\text{GC}(\text{O})\text{O}_2] + c_{57}[\text{PO}_2] + c_{61}[\text{EO}_2] + i_5[\text{ISOPO}_2] \\
& \quad + i_{12}[\text{MACRO}_2] + g_4 \} [\text{HO}_2] \\
& + \{ a_1[\text{H}][\text{O}_2][\text{M}] + 0.4a_{2el}[\text{CH}_4][\text{O}^{\text{ID}}] + a_6[\text{O}_3][\text{OH}] \\
& \quad + a_{10}[\text{H}_2\text{O}_2][\text{O}] + a_{30}[\text{H}_2\text{O}_2][\text{OH}] + a_{36}[\text{CO}][\text{OH}] \\
& \quad + b_{24}[\text{HO}_2\text{NO}_2][\text{M}] + d_8[\text{ClO}][\text{OH}] + c_3[\text{CH}_3\text{O}_2][\text{NO}] \\
& \quad + 2c_4[\text{CH}_3\text{O}_2][\text{CH}_3\text{O}_2] + c_8[\text{CH}_2\text{O}][\text{OH}] + c_9[\text{CH}_2\text{O}][\text{NO}_3] \\
& \quad + c_{11}[\text{C}_2\text{H}_5\text{O}_2][\text{NO}] + 0.6c_{13}[\text{C}_2\text{H}_5\text{O}_2][\text{CH}_3\text{O}_2] \\
& \quad + 1.2c_{14}[\text{C}_2\text{H}_5\text{O}_2][\text{C}_2\text{H}_5\text{O}_2] + c_{24}[\text{CH}_3\text{C}(\text{O})\text{O}_2][\text{CH}_3\text{O}_2] \\
& \quad + c_{28}[\text{C}_3\text{H}_7\text{O}_2][\text{NO}] + 0.25c_{39}[\text{C}_2\text{H}_4][\text{OH}][\text{M}] \\
& \quad + 0.2c_{44}[\text{GLYALD}][\text{OH}] + c_{62}[\text{C}_4\text{H}_{10}][\text{OH}] \\
& \quad + 1.2c_{71}[\text{C}_3\text{H}_7\text{O}_2][\text{C}_3\text{H}_7\text{O}_2] + c_{30}[\text{C}_3\text{H}_7\text{O}_2][\text{CH}_3\text{O}_2] \\
& \quad + 0.3c_{35}[\text{ACETO}_2][\text{CH}_3\text{O}_2] + c_{41}[\text{EO}][\text{O}_2] + c_{42}[\text{EO}] \\
& \quad + 0.12c_{43}[\text{C}_2\text{H}_4][\text{O}_3] + c_{47}[\text{GC}(\text{O})\text{O}_2][\text{NO}] \\
& \quad + 2c_{49}[\text{GC}(\text{O})\text{O}_2][\text{CH}_3\text{O}_2] + 2c_{51}[\text{GC}(\text{O})\text{O}_2][\text{GC}(\text{O})\text{O}_2] \\
& \quad + 0.19c_{54}[\text{C}_3\text{H}_6][\text{O}_3] + c_{56}[\text{PO}_2][\text{NO}] + c_{72}[\text{PO}_2][\text{PO}_2] \\
& \quad + 0.25i_1[\text{C}_5\text{H}_8][\text{O}_3] + 0.956i_4[\text{ISOPO}_2][\text{NO}] \\
& \quad + i_6[\text{ISOPO}_2][\text{ISOPO}_2] + 0.1i_8[\text{ISON}][\text{OH}] \}
\end{aligned}$$

$$\begin{aligned}
& + 0.1i_{16}[\text{MPAN}][\text{OH}] + 0.32i_{10}[\text{MACR}][\text{O}_3] \\
& + 0.75i_{11}[\text{MACRO}_2][\text{NO}] + 0.5t_2[\text{C}_{10}\text{H}_{16}][\text{O}_3] + t_{j_5}[\text{CH}_4] \\
& + t_{j_9}[\text{HO}_2\text{NO}_2] + t_{j_{36}}[\text{CH}_3\text{OOH}] + 2t_{j_{37}}[\text{CH}_2\text{O}] \\
& + t_{j_{41}}[\text{C}_2\text{H}_5\text{OOH}] + t_{j_{43}}[\text{CH}_3\text{CHO}] + t_{j_{45}}[\text{C}_3\text{H}_7\text{OOH}] \\
& + t_{j_{48}}[\text{HACET}] + t_{j_{49}}[\text{MGLY}] + 2t_{j_{50}}[\text{GLYALD}] \\
& + t_{j_{52}}[\text{GC(O)O}_2\text{H}] + t_{j_{53}}[\text{POOH}] + t_{j_{54}}[\text{ISOPOOH}] \\
& + t_{j_{55}}[\text{ISON}] + t_{j_{56}}[\text{MACR}] + t_{j_{58}}[\text{MACROOH}] \\
& + t_{j_{59}}[\text{NALD}] + g_9[\text{CH}_3\text{C(O)O}_2] \} \\
= 0,
\end{aligned} \tag{II.3}$$

$$\begin{aligned}
& \frac{d[\text{H}]}{dt} \\
& = -\{a_1[\text{O}_2][\text{M}] + a_2[\text{O}_3] + (a_{23a} + a_{23b} + a_{23c})[\text{HO}_2]\}[\text{H}] \\
& + \{a_{3er}[\text{O}^{\text{ID}}][\text{H}_2] + a_5[\text{OH}][\text{O}] + a_{19}[\text{OH}][\text{H}_2] + a_{24}[\text{H}_2][\text{O}] \\
& + d_6[\text{Cl}][\text{H}_2] + t_{j_3}[\text{H}_2\text{O}] + t_{j_{16}}[\text{HCl}]\} \\
& = 0.
\end{aligned} \tag{II.4}$$

The equations of (II.3) and (II.4) are solved to derive $[\text{HO}_2]$ and $[\text{H}]$, respectively. From the two equations we also get

$$\begin{aligned}
& \frac{[\text{HO}_2]}{[\text{OH}]} \\
& = \{a_1[\text{H}][\text{O}_2][\text{M}] + 0.4a_{2er}[\text{CH}_4][\text{O}^{\text{ID}}] + a_6[\text{O}_3][\text{OH}] \\
& + a_{30}[\text{H}_2\text{O}_2][\text{OH}] + a_{36}[\text{CO}][\text{OH}] + b_{24}[\text{HO}_2\text{NO}_2][\text{M}] \\
& + d_8[\text{ClO}][\text{OH}] + c_3[\text{CH}_3\text{O}_2][\text{NO}] + 2c_4[\text{CH}_3\text{O}_2][\text{CH}_3\text{O}_2] \\
& + c_8[\text{CH}_2\text{O}][\text{OH}] + c_9[\text{CH}_2\text{O}][\text{NO}_3] + c_{11}[\text{C}_2\text{H}_5\text{O}_2][\text{NO}] \\
& + 0.6c_{13}[\text{C}_2\text{H}_5\text{O}_2][\text{CH}_3\text{O}_2] + 1.2c_{14}[\text{C}_2\text{H}_5\text{O}_2][\text{C}_2\text{H}_5\text{O}_2] \\
& + c_{24}[\text{CH}_3\text{C(O)O}_2][\text{CH}_3\text{O}_2] + c_{28}[\text{C}_3\text{H}_7\text{O}_2][\text{NO}] \\
& + 0.25c_{39}[\text{C}_2\text{H}_4][\text{OH}][\text{M}] + 0.2c_{44}[\text{GLYALD}][\text{OH}] \\
& + c_{62}[\text{C}_4\text{H}_{10}][\text{OH}] + 1.2c_{71}[\text{C}_3\text{H}_7\text{O}_2][\text{C}_3\text{H}_7\text{O}_2] \\
& + c_{30}[\text{C}_3\text{H}_7\text{O}_2][\text{CH}_3\text{O}_2] + 0.3c_{35}[\text{ACETO}_2][\text{CH}_3\text{O}_2] \\
& + c_{41}[\text{EO}][\text{O}_2] + c_{42}[\text{EO}] + 0.12c_{43}[\text{C}_2\text{H}_4][\text{O}_3] \\
& + c_{47}[\text{GC(O)O}_2][\text{NO}] + 2c_{49}[\text{GC(O)O}_2][\text{CH}_3\text{O}_2] \\
& + 2c_{51}[\text{GC(O)O}_2][\text{GC(O)O}_2] + 0.19c_{54}[\text{C}_3\text{H}_6][\text{O}_3] \\
& + c_{56}[\text{PO}_2][\text{NO}] + c_{72}[\text{PO}_2][\text{PO}_2] + 0.25i_1[\text{C}_5\text{H}_8][\text{O}_3] \\
& + 0.956i_4[\text{ISOPO}_2][\text{NO}] + i_6[\text{ISOPO}_2][\text{ISOPO}_2] \\
& + 0.1i_8[\text{ISON}][\text{OH}] + 0.1i_{16}[\text{MPAN}][\text{OH}] \\
& + 0.32i_{10}[\text{MACR}][\text{O}_3] + 0.75i_{11}[\text{MACRO}_2][\text{NO}] \\
& + 0.5t_2[\text{C}_{10}\text{H}_{16}][\text{O}_3] + t_{j_5}[\text{CH}_4] + t_{j_9}[\text{HO}_2\text{NO}_2] \\
& + t_{j_{36}}[\text{CH}_3\text{OOH}] + 2t_{j_{37}}[\text{CH}_2\text{O}] + t_{j_{41}}[\text{C}_2\text{H}_5\text{OOH}] \\
& + t_{j_{43}}[\text{CH}_3\text{CHO}] + t_{j_{45}}[\text{C}_3\text{H}_7\text{OOH}] + t_{j_{48}}[\text{HACET}] \\
& + t_{j_{49}}[\text{MGLY}] + 2t_{j_{50}}[\text{GLYALD}] + t_{j_{52}}[\text{GC(O)O}_2\text{H}] \\
& + t_{j_{53}}[\text{POOH}] + t_{j_{54}}[\text{ISOPOOH}] + t_{j_{55}}[\text{ISON}] + t_{j_{56}}[\text{MACR}] \\
& + t_{j_{58}}[\text{MACROOH}] + t_{j_{59}}[\text{NALD}] + g_9[\text{CH}_3\text{C(O)O}_2] \} \\
& / \{((a_{23a} + a_{23b} + a_{23c})[\text{H}] + a_{66}[\text{O}_3] + a_7[\text{O}] + a_{17}[\text{OH}] \\
& + a_{26}[\text{NO}] + 2a_{27}[\text{HO}_2] + b_{23}[\text{NO}_2][\text{M}] + b_{52}[\text{NO}_3] \\
& + d_7[\text{Cl}] + d_{33}[\text{ClO}] + e_7[\text{Br}] + e_{15}[\text{BrO}] + c_6[\text{CH}_3\text{O}_2] \\
& + c_{12}[\text{C}_2\text{H}_5\text{O}_2] + (c_{21} + c_{22})[\text{CH}_3\text{C(O)O}_2] + c_{29}[\text{C}_3\text{H}_7\text{O}_2] \\
& + c_{34}[\text{ACETO}_2] + c_{48}[\text{GC(O)O}_2] + c_{57}[\text{PO}_2] + c_{61}[\text{EO}_2] \\
& + i_5[\text{ISOPO}_2] + i_{12}[\text{MACRO}_2] + g_4[\text{OH}]\} \},
\end{aligned} \tag{II.5}$$

$$\begin{aligned}
& \frac{[\text{H}]}{[\text{OH}]} \\
& = \{a_{3er}[\text{O}^{\text{ID}}][\text{H}_2] + a_5[\text{OH}][\text{O}] + a_{19}[\text{OH}][\text{H}_2] + a_{24}[\text{H}_2][\text{O}] \\
& + d_6[\text{Cl}][\text{H}_2] + t_{j_3}[\text{H}_2\text{O}] + t_{j_{16}}[\text{HCl}]\} \\
& / \{(a_1[\text{O}_2][\text{M}] + a_2[\text{O}_3] + (a_{23a} + a_{23b} + a_{23c})[\text{HO}_2])[\text{OH}]\}.
\end{aligned} \tag{II.6}$$

When Eqs.(II.5) and (II.6) are calculated, all the coefficients of Eq.(II.2) are then given. The quadratic equation of (II.2) thus can be solved to derive $[\text{OH}]$.

Instantaneous equilibrium is also assumed for N and EO, and thus their respective change rates are expressed by

$$\frac{d[\text{N}]}{dt} = t_{j_{23}}[\text{NO}] - b_6[\text{N}][\text{NO}] - b_7[\text{N}][\text{O}_2] = 0, \tag{II.7}$$

$$\begin{aligned}
& \frac{d[\text{EO}]}{dt} \\
& = c_{40}[\text{EO}_2][\text{NO}] + c_{70}[\text{EO}_2][\text{EO}_2] - c_{41}[\text{O}_2][\text{EO}] - c_{42}[\text{EO}] \\
& = 0.
\end{aligned} \tag{II.8}$$

Then,

$$[\text{N}] = \frac{t_{j_{23}}[\text{NO}]}{b_6[\text{NO}] + b_7[\text{O}_2]}, \tag{II.9}$$

$$[\text{EO}] = \frac{c_{40}[\text{EO}_2][\text{NO}] + c_{70}[\text{EO}_2][\text{EO}_2]}{c_{41}[\text{O}_2] + c_{42}}. \tag{II.10}$$

II-1-2 NO_x family

The reduced-Jacobian method is used for NO_x family. The change rates of all the members are formulated to be linear for the values at $t + \Delta t$

$$\begin{aligned}
& \frac{[\text{NO}]^{t+\Delta t} - [\text{NO}]^t}{\Delta t} \\
& = \{-a_{26}[\text{HO}_2] - b_4[\text{O}_3] - b_6[\text{N}] - 0.5b_{51}[\text{NO}_3] - d_4[\text{ClO}] \\
& - d_{65}[\text{OCIO}] - e_4[\text{BrO}] - c_3[\text{CH}_3\text{O}_2] - c_{11}[\text{C}_2\text{H}_5\text{O}_2] \\
& - c_{18}[\text{CH}_3\text{C(O)O}_2] - c_{28}[\text{C}_3\text{H}_7\text{O}_2] - c_{33}[\text{ACETO}_2] \\
& - c_{40}[\text{EO}_2] - c_{47}[\text{GC(O)O}_2] - c_{56}[\text{PO}_2] - i_4[\text{ISOPO}_2] \\
& - i_{11}[\text{MACRO}_2] - t_{j_{23}}\} [\text{NO}]^{t+\Delta t} \\
& + \{b_3[\text{O}] + t_{j_6}\} [\text{NO}_2]^{t+\Delta t} \\
& + \{-0.5b_{51}[\text{NO}] + t_{j_{25}}\} [\text{NO}_3]^{t+\Delta t} \\
& + \{b_7[\text{N}][\text{O}_2] + 2b_{39}[\text{N}_2\text{O}][\text{O}^{\text{ID}}]\},
\end{aligned} \tag{II.11a}$$

$$\begin{aligned}
& \frac{[\text{NO}_2]^{t+\Delta t} - [\text{NO}_2]^t}{\Delta t} \\
& = \{a_{26}[\text{HO}_2] + b_4[\text{O}_3] + b_{51}[\text{NO}_3] + d_4[\text{ClO}] + d_{65}[\text{OCIO}] \\
& + e_4[\text{BrO}] + c_3[\text{CH}_3\text{O}_2] + c_{11}[\text{C}_2\text{H}_5\text{O}_2] + c_{18}[\text{CH}_3\text{C(O)O}_2] \\
& + c_{28}[\text{C}_3\text{H}_7\text{O}_2] + c_{33}[\text{ACETO}_2] + c_{40}[\text{EO}_2] + c_{47}[\text{GC(O)O}_2] \\
& + c_{56}[\text{PO}_2] + i_4[\text{ISOPO}_2] + i_{11}[\text{MACRO}_2]\} [\text{NO}]^{t+\Delta t} \\
& + \{-b_3[\text{O}] - b_9[\text{O}_3] - 0.5b_{12}[\text{NO}_3][\text{M}] - b_{22}[\text{OH}][\text{M}] \\
& - b_{23}[\text{HO}_2][\text{M}] - d_{31}[\text{ClO}][\text{M}] - d_{36}[\text{Cl}] - e_{13}[\text{BrO}][\text{M}] \\
& - c_{19}[\text{CH}_3\text{C(O)O}_2][\text{M}] - c_{45}[\text{GC(O)O}_2][\text{M}] \\
& - i_{14}[\text{MACRO}_2][\text{M}] - t_{j_6} - 0.5g_{10}\} [\text{NO}_2]^{t+\Delta t}
\end{aligned}$$

$$\begin{aligned}
& + \{-0.5b_{12}[\text{NO}_2] + b_{31}[\text{NO}] + b_{52}[\text{HO}_2] + t_3[\text{C}_{10}\text{H}_{16}] + t_{24}\} \\
& \quad [\text{NO}_3]^{t+\Delta t} \\
& + \{(b_{24}[\text{M}] + b_{28}[\text{OH}])[\text{HO}_2\text{NO}_2] + b_{32}[\text{N}_2\text{O}_5][\text{M}] \\
& \quad + c_{20}[\text{PAN}][\text{M}] + c_{46}[\text{GPAN}][\text{M}] + c_{60}[\text{ONIT}][\text{OH}] \\
& \quad + i_{15}[\text{MPAN}][\text{M}] + i_{16}[\text{MPAN}][\text{OH}] + i_{18}[\text{NALD}][\text{OH}] \\
& \quad + t_{j7}[\text{HNO}_3] + t_{j9}[\text{HO}_2\text{NO}_2] + t_{j11}[\text{N}_2\text{O}_5] + t_{j19}[\text{ClONO}_2] \\
& \quad + t_{j33}[\text{ClONO}_2] + t_{j34}[\text{BrONO}_2] + t_{j39}[\text{PAN}] + t_{j55}[\text{ISON}] \\
& \quad + t_{j57}[\text{MPAN}] + t_{j59}[\text{NALD}]\}, \quad (\text{II.11b})
\end{aligned}$$

$$\begin{aligned}
& \frac{[\text{NO}_3]^{t+\Delta t} - [\text{NO}_3]^t}{\Delta t} \\
& = \{-0.5b_{31}[\text{NO}_3]\} \quad [\text{NO}]^{t+\Delta t} \\
& \quad + \{b_9[\text{O}_3] - 0.5b_{12}[\text{NO}_3]\} \quad [\text{NO}_2]^{t+\Delta t} \\
& \quad + \{-0.5b_{12}[\text{NO}_2] - 0.5b_{31}[\text{NO}] - b_{52}[\text{HO}_2] - c_9[\text{CH}_2\text{O}] \\
& \quad - c_{17}[\text{CH}_3\text{CHO}] - c_{37}[\text{MGLY}] - c_{55}[\text{C}_3\text{H}_6] - i_3[\text{C}_5\text{H}_8] \\
& \quad - t_3[\text{C}_{10}\text{H}_{16}] - t_{j24} - t_{j25}\} \quad [\text{NO}_3]^{t+\Delta t} \\
& \quad + \{b_{27}[\text{HNO}_3][\text{OH}] + b_{32}[\text{N}_2\text{O}_5][\text{M}] + c_{73}[\text{PAN}][\text{OH}] \\
& \quad + d_{32}[\text{ClONO}_2][\text{O}] + t_{j10}[\text{ClONO}_2] + t_{j11}[\text{N}_2\text{O}_5] \\
& \quad + t_{j20}[\text{BrONO}_2] + t_{j40}[\text{PAN}]\}. \quad (\text{II.11c})
\end{aligned}$$

Eqs.(II.11a, b, c) can be formally written as a matrix equation of 3×3

$$\begin{aligned}
& \frac{[\text{NO}]^{t+\Delta t} - [\text{NO}]^t}{\Delta t} = A_{11}[\text{NO}]^{t+\Delta t} + A_{12}[\text{NO}_2]^{t+\Delta t} \\
& \quad + A_{13}[\text{NO}_3]^{t+\Delta t} + A_{14}, \\
& \frac{[\text{NO}_2]^{t+\Delta t} - [\text{NO}_2]^t}{\Delta t} = A_{21}[\text{NO}]^{t+\Delta t} + A_{22}[\text{NO}_2]^{t+\Delta t} \\
& \quad + A_{23}[\text{NO}_3]^{t+\Delta t} + A_{24}, \\
& \frac{[\text{NO}_3]^{t+\Delta t} - [\text{NO}_3]^t}{\Delta t} = A_{31}[\text{NO}]^{t+\Delta t} + A_{32}[\text{NO}_2]^{t+\Delta t} \\
& \quad + A_{33}[\text{NO}_3]^{t+\Delta t} + A_{34},
\end{aligned}$$

or equivalently,

$$(\delta_{ij} - A_{ij}\Delta t) \begin{pmatrix} \text{NO} \\ \text{NO}_2 \\ \text{NO}_3 \end{pmatrix}^{t+\Delta t} = \begin{pmatrix} \text{NO} \\ \text{NO}_2 \\ \text{NO}_3 \end{pmatrix}^t + \begin{pmatrix} A_{14}\Delta t \\ A_{24}\Delta t \\ A_{34}\Delta t \end{pmatrix} \quad (\text{II.12})$$

where δ_{ij} is Kronecker's delta. It is straightforward to obtain the ratios at $t + \Delta t$, for example $\left(\frac{[\text{NO}]}{[\text{NO}_2]}\right)^{t+\Delta t}$ and $\left(\frac{[\text{NO}_3]}{[\text{NO}_2]}\right)^{t+\Delta t}$, by solving Eq.(II.12). The final form of the members are then

$$[\text{NO}_2]^{t+\Delta t} = \frac{[\text{NO}_2]^t}{1 + \left(\frac{[\text{NO}]}{[\text{NO}_2]}\right)^{t+\Delta t} + \left(\frac{[\text{NO}_3]}{[\text{NO}_2]}\right)^{t+\Delta t}}, \quad (\text{II.13a})$$

$$[\text{NO}]^{t+\Delta t} = \left(\frac{[\text{NO}]}{[\text{NO}_2]}\right)^{t+\Delta t} [\text{NO}_2]^{t+\Delta t}, \quad (\text{II.13b})$$

$$[\text{NO}_3]^{t+\Delta t} = \left(\frac{[\text{NO}_3]}{[\text{NO}_2]}\right)^{t+\Delta t} [\text{NO}_2]^{t+\Delta t}. \quad (\text{II.13c})$$

As for O_x , ClO_x and BrO_x , their change rate equations are

expressed by similar matrix equations as given below, and thereby the solutions can be readily calculated as Eqs.(II.13a, b, c).

II-1-3 O_x family

$$\begin{aligned}
& \frac{[\text{O}_3]^{t+\Delta t} - [\text{O}_3]^t}{\Delta t} \\
& = \{-0.5hk_3[\text{O}] - a_2[\text{H}] - a_6[\text{OH}] - a_{6b}[\text{HO}_2] - b_4[\text{NO}] \\
& \quad - b_9[\text{NO}_2] - d_2[\text{Cl}] - e_2[\text{Br}] - c_{43}[\text{C}_2\text{H}_4] - c_{54}[\text{C}_3\text{H}_6] \\
& \quad - i_1[\text{C}_5\text{H}_8] - i_{10}[\text{MACR}] - t_2[\text{C}_{10}\text{H}_{16}] - t_{j2} - t_{j12}\} \quad [\text{O}_3]^{t+\Delta t} \\
& \quad + \{hk_2[\text{O}_2][\text{M}] - 0.5hk_3[\text{O}_3]\} \quad [\text{O}]^{t+\Delta t} \\
& \quad + \{0\} \quad [\text{O}^{1D}]^{t+\Delta t} \\
& \quad + \{c_{22}[\text{CH}_3\text{C}(\text{O})\text{O}_2][\text{HO}_2] + 0.3c_{48}[\text{GC}(\text{O})\text{O}_2][\text{HO}_2]\}, \quad (\text{II.14a})
\end{aligned}$$

$$\begin{aligned}
& \frac{[\text{O}]^{t+\Delta t} - [\text{O}]^t}{\Delta t} \\
& = \{-0.5hk_3[\text{O}] + t_{j2}\} \quad [\text{O}_3]^{t+\Delta t} \\
& \quad + \{-2hk_1[\text{O}][\text{M}] - hk_2[\text{O}_2][\text{M}] - 0.5hk_3[\text{O}_3] - a_{10}[\text{H}_2\text{O}_2] \\
& \quad - a_5[\text{OH}] - a_7[\text{HO}_2] - a_{24}[\text{H}_2] - b_3[\text{NO}_2] - d_3[\text{ClO}] \\
& \quad - d_{32}[\text{ClONO}_2] - d_{35}[\text{HOCl}] - d_{64}[\text{OCIO}] - e_3[\text{BrO}]\} \\
& \quad [\text{O}]^{t+\Delta t} \\
& \quad + \{hk_4[\text{N}_2] + hk_5[\text{O}_2]\} \quad [\text{O}^{1D}]^{t+\Delta t} \\
& \quad + \{a_8[\text{OH}][\text{OH}] + a_{23c}[\text{H}][\text{HO}_2] + b_6[\text{N}][\text{NO}] + b_7[\text{N}][\text{O}_2] \\
& \quad + 2t_{j1}[\text{O}_2] + t_{j6}[\text{NO}_2] + t_{j14}[\text{OCIO}] + t_{j18}[\text{CO}_2] + t_{j23}[\text{NO}] \\
& \quad + t_{j24}[\text{NO}_3]\}, \quad (\text{II.14b})
\end{aligned}$$

$$\begin{aligned}
& \frac{[\text{O}^{1D}]^{t+\Delta t} - [\text{O}^{1D}]^t}{\Delta t} \\
& = \{t_{j12}\} \quad [\text{O}_3]^{t+\Delta t} \\
& \quad + \{0\} \quad [\text{O}]^{t+\Delta t} \\
& \quad + \{-hk_4[\text{N}_2] - hk_5[\text{O}_2] - a_{1et}[\text{H}_2\text{O}] - a_{2et}[\text{CH}_4] - a_{3et}[\text{H}_2] \\
& \quad - (b_{38} + b_{39})[\text{N}_2\text{O}] - d_{101}[\text{CCl}_4] - d_{102}[\text{CFCl}_3] \\
& \quad - d_{103}[\text{CF}_2\text{Cl}_2] - d_{110}[\text{COF}_2] - e_{91}[\text{CF}_3\text{Br}] \\
& \quad - e_{92}[\text{CF}_2\text{ClBr}] - e_{93}[\text{CH}_3\text{Br}]\} \quad [\text{O}^{1D}]^{t+\Delta t} \\
& \quad + \{t_{j4}[\text{N}_2\text{O}]\}. \quad (\text{II.14c})
\end{aligned}$$

II-1-4 ClO_x family

$$\begin{aligned}
& \frac{[\text{Cl}]^{t+\Delta t} - [\text{Cl}]^t}{\Delta t} \\
& = \{-d_2[\text{O}_3] - d_5[\text{CH}_4] - d_6[\text{H}_2] - d_7[\text{HO}_2] \\
& \quad - d_{36}[\text{NO}_2][\text{M}] - d_{37}[\text{HOCl}] - d_{63}[\text{OCIO}]\} \quad [\text{Cl}]^{t+\Delta t} \\
& \quad + \{d_3[\text{O}] + d_4[\text{NO}] + d_8[\text{OH}] + e_{5b}[\text{BrO}]\} \quad [\text{ClO}]^{t+\Delta t} \\
& \quad + \{(d_0[\text{CH}_3\text{Cl}] + d_{11}[\text{HCl}])[\text{OH}] \\
& \quad + (4d_{101}[\text{CCl}_4] + 3d_{102}[\text{CFCl}_3] \\
& \quad + 2d_{103}[\text{CF}_2\text{Cl}_2] + e_{92}[\text{CF}_2\text{ClBr}])[\text{O}^{1D}] \\
& \quad + t_{j8}[\text{HOCl}] + t_{j10}[\text{ClONO}_2] + 2t_{j15}[\text{Cl}_2\text{O}_2] + t_{j16}[\text{HCl}] \\
& \quad + 2t_{j17}[\text{Cl}_2] + t_{j19}[\text{ClONO}_2] + t_{j21}[\text{BrCl}] + 4t_{j26}[\text{CCl}_4] \\
& \quad + 3t_{j27}[\text{CFCl}_3] + 2t_{j28}[\text{CF}_2\text{Cl}_2] + t_{j29}[\text{CH}_3\text{Cl}] \\
& \quad + t_{j31}[\text{CF}_2\text{ClBr}]\}, \quad (\text{II.15a})
\end{aligned}$$

$$\begin{aligned}
& \frac{[\text{ClO}]^{t+\Delta t} - [\text{ClO}]^t}{\Delta t} \\
&= \{d_2[\text{O}_3] + 2d_{63}[\text{OCIO}]\} [\text{Cl}]^{t+\Delta t} \\
&+ \{-d_3[\text{O}] - d_4[\text{NO}] - d_8[\text{OH}] - d_9[\text{OH}] \\
&- d_{31}[\text{NO}_2][\text{M}] - d_{33}[\text{HO}_2] - 2d_{60}[\text{ClO}] \\
&- (e_{5a} + e_{5b} + e_{5c})[\text{BrO}]\} [\text{ClO}]^{t+\Delta t} \\
&+ \{d_{32}[\text{ClONO}_2][\text{O}] + d_{34}[\text{HOCl}][\text{OH}] + d_{35}[\text{HOCl}][\text{O}] \\
&+ 2d_{61}[\text{M}][\text{Cl}_2\text{O}_2] + d_{64}[\text{OCIO}][\text{O}] + d_{65}[\text{OCIO}][\text{NO}] \\
&+ e_8[\text{Br}][\text{OCIO}] + t_{33}[\text{ClONO}_2] + t_{14}[\text{OCIO}]\}, \quad (\text{II.15b})
\end{aligned}$$

II-1-5 BrO_x family

$$\begin{aligned}
& \frac{[\text{Br}]^{t+\Delta t} - [\text{Br}]^t}{\Delta t} \\
&= \{-e_2[\text{O}_3] - e_7[\text{HO}_2] - e_8[\text{OCIO}]\} [\text{Br}]^{t+\Delta t} \\
&+ \{e_3[\text{O}] + e_4[\text{NO}] + (e_{5a} + e_{5b})[\text{ClO}] + 2e_6[\text{BrO}]\} [\text{BrO}]^{t+\Delta t} \\
&+ \{t_{21}\} [\text{BrCl}]^{t+\Delta t} \\
&+ \{e_{11}[\text{HBr}][\text{OH}] \\
&+ (e_{91}[\text{CF}_3\text{Br}] + e_{92}[\text{CF}_2\text{ClBr}] + e_{93}[\text{CH}_3\text{Br}])[\text{O}^{1\text{D}}] \\
&+ t_{20}[\text{BrONO}_2] + t_{22}[\text{HOBr}] + t_{31}[\text{CF}_2\text{ClBr}] \\
&+ t_{32}[\text{CH}_3\text{Br}]\}, \quad (\text{II.16a})
\end{aligned}$$

$$\begin{aligned}
& \frac{[\text{BrO}]^{t+\Delta t} - [\text{BrO}]^t}{\Delta t} \\
&= \{e_2[\text{O}_3] + e_8[\text{OCIO}]\} [\text{Br}]^{t+\Delta t} \\
&+ \{-e_3[\text{O}] - e_4[\text{NO}] - (e_{5a} + e_{5b} + e_{5c})[\text{ClO}] \\
&- 2e_6[\text{BrO}] - e_{13}[\text{NO}_2][\text{M}] - e_{15}[\text{HO}_2]\} [\text{BrO}]^{t+\Delta t} \\
&+ \{0\} [\text{BrCl}]^{t+\Delta t} \\
&+ \{t_{34}[\text{BrONO}_2]\}, \quad (\text{II.16b})
\end{aligned}$$

$$\begin{aligned}
& \frac{[\text{BrCl}]^{t+\Delta t} - [\text{BrCl}]^t}{\Delta t} \\
&= \{0\} [\text{Br}]^{t+\Delta t} \\
&+ \{e_{5c}[\text{ClO}]\} [\text{BrO}]^{t+\Delta t} \\
&+ \{-t_{21}\} [\text{BrCl}]^{t+\Delta t} \\
&+ \{het_6[\text{HOBr}]\}. \quad (\text{II.16c})
\end{aligned}$$

II-1-6 Peroxy radicals

The Euler Backward Iterative (EBI) method of Hertel *et al.* (1993) is used to time-integrate concentrations of peroxy radicals except HO₂. In the EBI method, chemical ODEs are analytically formulated for strongly coupled chemical species, and discretized by using the backward Euler formula. For example, two chemical ODEs for the strongly coupled pair of CH₃O₂ and CH₃OOH are constructed as

$$\begin{aligned}
[\text{CH}_3\text{O}_2]^{t+\Delta t} &= [\text{CH}_3\text{O}_2]^t + P_1\Delta t + r_{12}\Delta t[\text{CH}_3\text{OOH}]^{t+\Delta t} \\
&- 2r_{11}\Delta t([\text{CH}_3\text{O}_2]^{t+\Delta t})^2 - L_1\Delta t[\text{CH}_3\text{O}_2]^{t+\Delta t}, \quad (\text{II.17a})
\end{aligned}$$

$$\begin{aligned}
[\text{CH}_3\text{OOH}]^{t+\Delta t} &= [\text{CH}_3\text{OOH}]^t + r_{21}\Delta t[\text{CH}_3\text{O}_2]^{t+\Delta t} \\
&- L_2\Delta t[\text{CH}_3\text{OOH}]^{t+\Delta t}, \quad (\text{II.17b})
\end{aligned}$$

where,

$$\begin{aligned}
P_1 &= 0.75a_{2et}[\text{CH}_4][\text{O}^{1\text{D}}] + c_2[\text{CH}_4][\text{OH}] \\
&+ c_{18}[\text{CH}_3\text{C}(\text{O})\text{O}_2][\text{NO}] + 2c_{26}[\text{CH}_3\text{C}(\text{O})\text{O}_2][\text{CH}_3\text{C}(\text{O})\text{O}_2] \\
&+ 0.31c_{54}[\text{C}_3\text{H}_6][\text{O}_3] + 0.08t_i[\text{C}_3\text{H}_8][\text{O}_3] \\
&+ 0.16t_2[\text{C}_{10}\text{H}_{16}][\text{O}_3] + d_5[\text{CH}_4][\text{Cl}] + t_{15}[\text{CH}_4] \\
&+ t_{40}[\text{PAN}] + t_{42}[\text{CH}_3\text{C}(\text{O})\text{O}_2\text{H}] + t_{43}[\text{CH}_3\text{CHO}] \\
&+ (t_{46} + 2t_{47})[\text{ACET}],
\end{aligned}$$

$$\begin{aligned}
L_1 &= c_3[\text{NO}] + c_6[\text{HO}_2] + c_{13}[\text{C}_2\text{H}_5\text{O}_2] + c_{25}[\text{CH}_3\text{C}(\text{O})\text{O}_2] \\
&+ c_{30}[\text{C}_3\text{H}_7\text{O}_2] + c_{35}[\text{ACETO}_2] + (c_{49} + c_{50})[\text{GC}(\text{O})\text{O}_2],
\end{aligned}$$

$$L_2 = c_7[\text{OH}] + t_{36},$$

$$r_{11} = c_4 + c_5,$$

$$r_{12} = 0.7c_7[\text{OH}],$$

$$r_{21} = c_6[\text{HO}_2].$$

Substituting Eq.(II.17b) for Eq.(II.17a), we get a quadratic equation of $[\text{CH}_3\text{O}_2]^{t+\Delta t}$ as

$$\begin{aligned}
& 2r_{11}\Delta t([\text{CH}_3\text{O}_2]^{t+\Delta t})^2 + \left\{ (1 + L_1\Delta t) - \frac{r_{12}r_{21}\Delta t^2}{1 + L_2\Delta t} \right\} [\text{CH}_3\text{O}_2]^{t+\Delta t} \\
& - \left\{ ([\text{CH}_3\text{O}_2]^t + P_1\Delta t) + \frac{r_{12}\Delta t}{1 + L_2\Delta t} [\text{CH}_3\text{OOH}]^t \right\} \\
& = 0. \quad (\text{II.17c})
\end{aligned}$$

Eq.(II.17c) is solved to derive $[\text{CH}_3\text{O}_2]^{t+\Delta t}$.

Similar chemical ODEs are constructed for the pair of C₂H₅O₂ and C₂H₅OOH, and a quadratic equation of $[\text{C}_2\text{H}_5\text{O}_2]^{t+\Delta t}$ is derived from the ODEs as

$$\begin{aligned}
& 2r_{11}\Delta t([\text{C}_2\text{H}_5\text{O}_2]^{t+\Delta t})^2 + \left\{ (1 + L_1\Delta t) - \frac{r_{12}r_{21}\Delta t^2}{1 + L_2\Delta t} \right\} [\text{C}_2\text{H}_5\text{O}_2]^{t+\Delta t} \\
& - \left\{ ([\text{C}_2\text{H}_5\text{O}_2]^t + P_1\Delta t) + \frac{r_{12}\Delta t}{1 + L_2\Delta t} [\text{C}_2\text{H}_5\text{OOH}]^t \right\} \\
& = 0, \quad (\text{II.18})
\end{aligned}$$

where,

$$\begin{aligned}
P_1 &= c_{10}[\text{C}_2\text{H}_6][\text{OH}] + 0.24c_{28}[\text{C}_3\text{H}_7\text{O}_2][\text{NO}] \\
&+ 0.8c_{30}[\text{C}_3\text{H}_7\text{O}_2][\text{CH}_3\text{O}_2] + 0.142c_{31}[\text{C}_3\text{H}_7\text{OOH}][\text{OH}] \\
&+ 0.3c_{62}[\text{C}_4\text{H}_{10}][\text{OH}] + 0.24t_{45}[\text{C}_3\text{H}_7\text{OOH}],
\end{aligned}$$

$$L_1 = c_{11}[\text{NO}] + c_{12}[\text{HO}_2] + c_{13}[\text{CH}_3\text{O}_2],$$

$$L_2 = c_{15}[\text{OH}] + t_{41},$$

$$r_{11} = c_{14},$$

$$r_{12} = 0.286c_{15}[\text{OH}],$$

$$r_{21} = c_{12}[\text{HO}_2].$$

A quadratic equation of $[\text{CH}_3\text{C}(\text{O})\text{O}_2]^{t+\Delta t}$ is similarly derived from a set of chemical ODEs for CH₃C(O)O₂, PAN and CH₃C(O)OOH as

$$\begin{aligned}
& 2r_{11}\Delta t([\text{CH}_3\text{C}(\text{O})\text{O}_2]^{t+\Delta t})^2 \\
& + \left\{ (1 + L_1\Delta t) - \frac{r_{12}r_{21}\Delta t^2}{1 + L_2\Delta t} - \frac{r_{13}r_{31}\Delta t^2}{1 + L_3\Delta t} \right\} [\text{CH}_3\text{C}(\text{O})\text{O}_2]^{t+\Delta t}
\end{aligned}$$

$$\begin{aligned}
& - \left\{ ([\text{CH}_3\text{C}(\text{O})\text{O}_2]') + P_1\Delta t + \frac{r_{12}\Delta t}{1+L_2\Delta t} [\text{PAN}]' \right. \\
& \quad \left. + \frac{r_{13}\Delta t}{1+L_3\Delta t} [\text{CH}_3\text{C}(\text{O})\text{OOH}]' \right\} \\
& = 0,
\end{aligned} \tag{II.19}$$

where,

$$\begin{aligned}
P_1 &= c_{16}[\text{CH}_3\text{CHO}][\text{OH}] + c_{17}[\text{CH}_3\text{CHO}][\text{NO}_3] \\
& \quad + c_{33}[\text{ACETO}_2][\text{NO}] + 0.3c_{35}[\text{ACETO}_2][\text{CH}_3\text{O}_2] \\
& \quad + c_{36}[\text{MGLY}][\text{OH}] + c_{37}[\text{MGLY}][\text{NO}_3] \\
& \quad + 1.26c_{74}[\text{ACETO}_2][\text{ACETO}_2] + 0.1i_1[\text{C}_5\text{H}_8][\text{O}_3] \\
& \quad + 0.1i_{10}[\text{MACR}][\text{O}_3] + 0.25i_{11}[\text{MACRO}_2][\text{NO}] \\
& \quad + 0.1i_8[\text{ISON}][\text{OH}] + 0.1i_{16}[\text{MPAN}][\text{OH}] \\
& \quad + 0.2t_2[\text{C}_{10}\text{H}_{16}][\text{O}_3] + tj_{46}[\text{ACET}] + tj_{48}[\text{HACET}] \\
& \quad + tj_{49}[\text{MGLY}] + tj_{56}[\text{MACR}], \\
L_1 &= c_{18}[\text{NO}] + c_{19}[\text{NO}_2][\text{M}] + (c_{21} + c_{22})[\text{HO}_2] \\
& \quad + (c_{24} + c_{25})[\text{CH}_3\text{O}_2] + g_9, \\
L_2 &= c_{20}[\text{M}] + c_{73}[\text{OH}] + tj_{39} + tj_{40}, \\
L_3 &= c_{23}[\text{OH}] + tj_{42}, \\
r_{11} &= c_{26}, \\
r_{12} &= c_{20}[\text{M}] + tj_{39}, \\
r_{13} &= c_{23}[\text{OH}], \\
r_{21} &= c_{19}[\text{NO}_2][\text{M}], \\
r_{31} &= c_{21}[\text{HO}_2].
\end{aligned}$$

A quadratic equation of $[\text{C}_3\text{H}_7\text{O}_2]^{t+\Delta t}$ is similarly derived from a set of chemical ODEs for $\text{C}_3\text{H}_7\text{O}_2$ and $\text{C}_3\text{H}_7\text{OOH}$ as

$$\begin{aligned}
& 2r_{11}\Delta t([\text{C}_3\text{H}_7\text{O}_2]^{t+\Delta t})^2 + \left\{ (1+L_1\Delta t) - \frac{r_{12}r_{21}\Delta t^2}{1+L_2\Delta t} \right\} [\text{C}_3\text{H}_7\text{O}_2]^{t+\Delta t} \\
& - \left\{ ([\text{C}_3\text{H}_7\text{O}_2]') + P_1\Delta t + \frac{r_{12}\Delta t}{1+L_2\Delta t} [\text{C}_3\text{H}_7\text{OOH}]' \right\} \\
& = 0,
\end{aligned} \tag{II.20}$$

where,

$$\begin{aligned}
P_1 &= c_{27}[\text{C}_3\text{H}_8][\text{OH}] + 0.02c_{62}[\text{C}_4\text{H}_{10}][\text{OH}], \\
L_1 &= c_{28}[\text{NO}] + c_{29}[\text{HO}_2] + c_{30}[\text{CH}_3\text{O}_2], \\
L_2 &= c_{31}[\text{OH}] + tj_{45}, \\
r_{11} &= c_{71}, \\
r_{12} &= 0.157c_{31}[\text{OH}], \\
r_{21} &= c_{29}[\text{HO}_2].
\end{aligned}$$

A quadratic equation of $[\text{ACETO}_2]^{t+\Delta t}$ is similarly derived from a set of chemical ODEs for ACETO_2 and HACET as

$$\begin{aligned}
& 2r_{11}\Delta t([\text{ACETO}_2]^{t+\Delta t})^2 + \left\{ (1+L_1\Delta t) - \frac{r_{12}r_{21}\Delta t^2}{1+L_2\Delta t} \right\} [\text{ACETO}_2]^{t+\Delta t} \\
& - \left\{ ([\text{ACETO}_2]') + P_1\Delta t + \frac{r_{12}\Delta t}{1+L_2\Delta t} ([\text{HACET}]' + P_2\Delta t) \right\} \\
& = 0,
\end{aligned} \tag{II.21}$$

where,

$$\begin{aligned}
P_1 &= c_{32}[\text{ACET}][\text{OH}], \\
L_1 &= c_{33}[\text{ACETO}_2][\text{NO}] + c_{34}[\text{ACETO}_2][\text{HO}_2] \\
& \quad + c_{35}[\text{ACETO}_2][\text{CH}_3\text{O}_2], \\
P_2 &= 0.5c_{58}[\text{POOH}][\text{OH}] + 0.25i_{11}[\text{MACRO}_2][\text{NO}] \\
& \quad + i_{13}[\text{MACRO}_2][\text{MACRO}_2] + 0.5tj_{58}[\text{MACROOH}], \\
L_2 &= c_{38}[\text{OH}] + tj_{48}, \\
r_{11} &= c_{74}, \\
r_{12} &= 0.323c_{38}[\text{OH}], \\
r_{21} &= c_{34}[\text{HO}_2] + 0.2c_{35}[\text{CH}_3\text{O}_2].
\end{aligned}$$

A quadratic equation of $[\text{EO}_2]^{t+\Delta t}$ is similarly derived as

$$\begin{aligned}
& 2r_{11}\Delta t([\text{EO}_2]^{t+\Delta t})^2 + \{1 + L_1\Delta t\} [\text{EO}_2]^{t+\Delta t} \\
& - \{[\text{EO}_2] + P_1\Delta t\} = 0,
\end{aligned} \tag{II.22}$$

where,

$$\begin{aligned}
P_1 &= 0.75c_{39}[\text{C}_2\text{H}_4][\text{OH}][\text{M}], \\
L_1 &= c_{40}[\text{NO}] + c_{61}[\text{HO}_2] + g_5, \\
r_{11} &= c_{70}.
\end{aligned}$$

A quadratic equation of $[\text{GC}(\text{O})\text{O}_2]^{t+\Delta t}$ is similarly derived from a set of chemical ODEs for $\text{GC}(\text{O})\text{O}_2$, GPAN and $\text{GC}(\text{O})\text{OOH}$ as

$$\begin{aligned}
& 2r_{11}\Delta t([\text{GC}(\text{O})\text{O}_2]^{t+\Delta t})^2 \\
& + \left\{ (1+L_1\Delta t) - \frac{r_{12}r_{21}\Delta t^2}{1+L_2\Delta t} - \frac{r_{13}r_{31}\Delta t^2}{1+L_3\Delta t} \right\} [\text{GC}(\text{O})\text{O}_2]^{t+\Delta t} \\
& - \left\{ ([\text{GC}(\text{O})\text{O}_2]') + P_1\Delta t + \frac{r_{12}\Delta t}{1+L_2\Delta t} [\text{GPAN}]' \right. \\
& \quad \left. + \frac{r_{13}\Delta t}{1+L_3\Delta t} [\text{GC}(\text{O})\text{OOH}]' \right\} \\
& = 0,
\end{aligned} \tag{II.23}$$

where,

$$\begin{aligned}
P_1 &= 0.8c_{44}[\text{GLYALD}][\text{OH}], \\
L_1 &= c_{45}[\text{NO}_2][\text{M}] + c_{47}[\text{NO}] + c_{48}[\text{HO}_2] + (c_{49} + c_{50})[\text{CH}_3\text{O}_2], \\
L_2 &= c_{46}[\text{M}], \\
L_3 &= c_{52}[\text{OH}] + tj_{52}, \\
r_{11} &= c_{51}, \\
r_{12} &= c_{46}[\text{M}], \\
r_{13} &= 0.5c_{52}[\text{OH}], \\
r_{21} &= c_{45}[\text{NO}_2][\text{M}], \\
r_{31} &= 0.7c_{48}[\text{HO}_2].
\end{aligned}$$

A quadratic equation of $[\text{PO}_2]^{t+\Delta t}$ is similarly derived from a set of chemical ODEs for PO_2 and POOH as

$$\begin{aligned}
& 2r_{11}\Delta t([\text{PO}_2]^{t+\Delta t})^2 + \left\{ (1+L_1\Delta t) - \frac{r_{12}r_{21}\Delta t^2}{1+L_2\Delta t} \right\} [\text{PO}_2]^{t+\Delta t} \\
& - \left\{ ([\text{PO}_2]') + P_1\Delta t + \frac{r_{12}\Delta t}{1+L_2\Delta t} ([\text{POOH}]' + P_2\Delta t) \right\} \\
& = 0,
\end{aligned} \tag{II.24}$$

where,

$$\begin{aligned} P_1 &= c_{53}[\text{C}_3\text{H}_6][\text{OH}][\text{M}], \\ L_1 &= c_{56}[\text{NO}] + c_{57}[\text{HO}_2] + g_6, \\ P_2 &= 0.667c_{61}[\text{EO}_2][\text{HO}_2] + 0.667g_5[\text{EO}_2], \\ L_2 &= c_{58}[\text{OH}] + t_{53}, \\ r_{11} &= c_{72}, \\ r_{12} &= 0.5c_{58}[\text{OH}], \\ r_{21} &= c_{57}[\text{HO}_2] + g_6. \end{aligned}$$

A quadratic equation of $[\text{ISOPO}_2]^{t+\Delta t}$ is similarly derived as

$$2r_{11}\Delta t([\text{ISOPO}_2]^{t+\Delta t})^2 + \{1 + L_1\Delta t\}[\text{ISOPO}_2]^{t+\Delta t} - \{[\text{ISOPO}_2]^t + P_1\Delta t\} = 0, \quad (\text{II.25})$$

where,

$$\begin{aligned} P_1 &= 0.468c_{62}[\text{C}_4\text{H}_{10}][\text{OH}] + i_2[\text{C}_5\text{H}_8][\text{OH}] \\ &\quad + 1.3t_1[\text{C}_{10}\text{H}_{16}][\text{OH}] + 1.2t_3[\text{C}_{10}\text{H}_{16}][\text{NO}_3], \\ L_1 &= i_4[\text{NO}] + i_5[\text{HO}_2] + g_7, \\ r_{11} &= i_6. \end{aligned}$$

A quadratic equation of $[\text{MACRO}_2]^{t+\Delta t}$ is similarly derived from a set of chemical ODEs for MACRO₂, MPAN and MACROOH as

$$\begin{aligned} &2r_{11}\Delta t([\text{MACRO}_2]^{t+\Delta t})^2 \\ &+ \left\{ (1 + L_1\Delta t) - \frac{r_{12}r_{21}\Delta t^2}{1 + L_2\Delta t} - \frac{r_{13}r_{31}\Delta t^2}{1 + L_3\Delta t} \right\} [\text{MACRO}_2]^{t+\Delta t} \\ &- \left\{ ([\text{MACRO}_2]^t + P_1\Delta t) + \frac{r_{12}\Delta t}{1 + L_2\Delta t} [\text{MPAN}]^t \right. \\ &\quad \left. + \frac{r_{13}\Delta t}{1 + L_3\Delta t} [\text{MACROOH}]^t \right\} \\ &= 0, \quad (\text{II.26}) \end{aligned}$$

where,

$$\begin{aligned} P_1 &= 0.1i_1[\text{C}_5\text{H}_8][\text{O}_3] + i_9[\text{MACR}][\text{OH}] + 0.2t_2[\text{C}_{10}\text{H}_{16}][\text{O}_3], \\ L_1 &= i_{11}[\text{NO}] + i_{12}[\text{HO}_2] + i_{14}[\text{NO}_2][\text{M}] + g_8, \\ L_2 &= i_{15}[\text{M}] + i_{16}[\text{OH}] + t_{57}, \\ L_3 &= i_{17}[\text{OH}] + t_{58}, \\ r_{11} &= i_{13}, \\ r_{12} &= i_{15}[\text{M}] + t_{57}, \\ r_{13} &= i_{17}[\text{OH}], \\ r_{21} &= i_{14}[\text{NO}_2][\text{M}], \\ r_{31} &= i_{12}[\text{HO}_2] + g_8. \end{aligned}$$

II-2 Nighttime

During nighttime, only chemical families of (NO, NO₂, NO₃) and (BrO, BrCl) are solved with the reduced-Jacobian method. Peroxy radicals, CH₃O₂, CH₃C(O)O₂, GC(O)O₂, ISOPO₂ and MACRO₂, are solved with the EBI method.

II-2-1 NO_x family

(NO, NO₂, NO₃) is represented by a 3 × 3 matrix.

$$\begin{aligned} &\frac{[\text{NO}]^{t+\Delta t} - [\text{NO}]^t}{\Delta t} \\ &= \{-b_4[\text{O}_3] - 0.5b_{51}[\text{NO}_3] - d_{65}[\text{OCIO}] - c_3[\text{CH}_3\text{O}_2] \\ &\quad - c_{18}[\text{CH}_3\text{C(O)O}_2] - c_{47}[\text{GC(O)O}_2] - i_4[\text{ISOPO}_2] \\ &\quad - i_{11}[\text{MACRO}_2]\} [\text{NO}]^{t+\Delta t} \\ &+ \{0\} [\text{NO}_2]^{t+\Delta t} \\ &+ \{-0.5b_{51}[\text{NO}]\} [\text{NO}_3]^{t+\Delta t} \\ &+ \{0\}, \quad (\text{II.27a}) \end{aligned}$$

$$\begin{aligned} &\frac{[\text{NO}_2]^{t+\Delta t} - [\text{NO}_2]^t}{\Delta t} \\ &= \{b_4[\text{O}_3] + b_{51}[\text{NO}_3] + d_{65}[\text{OCIO}] + c_3[\text{CH}_3\text{O}_2] \\ &\quad + c_{18}[\text{CH}_3\text{C(O)O}_2] + c_{47}[\text{GC(O)O}_2] + i_4[\text{ISOPO}_2] \\ &\quad + i_{11}[\text{MACRO}_2]\} [\text{NO}]^{t+\Delta t} \\ &+ \{-b_5[\text{O}_3] - 0.5b_{12}[\text{NO}_3][\text{M}] - d_{31}[\text{ClO}][\text{M}] - e_{13}[\text{BrO}][\text{M}] \\ &\quad - c_{19}[\text{CH}_3\text{C(O)O}_2][\text{M}] - c_{45}[\text{GC(O)O}_2][\text{M}] \\ &\quad - i_{14}[\text{MACRO}_2][\text{M}] - 0.5g_{10}\} [\text{NO}_2]^{t+\Delta t} \\ &+ \{-0.5b_{12}[\text{NO}_2] + b_{51}[\text{NO}] + t_3[\text{C}_{10}\text{H}_{16}]\} [\text{NO}_3]^{t+\Delta t} \\ &+ \{b_{24}[\text{M}][\text{HO}_2\text{NO}_2] + b_{32}[\text{N}_2\text{O}_5][\text{M}] + c_{20}[\text{PAN}][\text{M}] \\ &\quad + c_{46}[\text{GPAN}][\text{M}] + i_{15}[\text{MPAN}][\text{M}]\}, \quad (\text{II.27b}) \end{aligned}$$

$$\begin{aligned} &\frac{[\text{NO}_3]^{t+\Delta t} - [\text{NO}_3]^t}{\Delta t} \\ &= \{-0.5b_{51}[\text{NO}_3]\} [\text{NO}]^{t+\Delta t} \\ &+ \{b_5[\text{O}_3] - 0.5b_{12}[\text{NO}_3]\} [\text{NO}_2]^{t+\Delta t} \\ &+ \{-0.5b_{12}[\text{NO}_2] - 0.5b_{51}[\text{NO}] - c_9[\text{CH}_2\text{O}] \\ &\quad - c_{17}[\text{CH}_3\text{CHO}] - c_{37}[\text{MGLY}] - c_{55}[\text{C}_3\text{H}_6] \\ &\quad - i_3[\text{C}_5\text{H}_8] - t_3[\text{C}_{10}\text{H}_{16}]\} [\text{NO}_3]^{t+\Delta t} \\ &+ \{b_{32}[\text{N}_2\text{O}_5][\text{M}]\}. \quad (\text{II.27c}) \end{aligned}$$

II-2-2 BrO_x family

(BrO, BrCl) is represented by a 2 × 2 matrix.

$$\begin{aligned} &\frac{[\text{BrO}]^{t+\Delta t} - [\text{BrO}]^t}{\Delta t} \\ &= \{-(e_{5a} + e_{5b} + e_{5c})[\text{ClO}] \\ &\quad - 2e_6[\text{BrO}] - e_{13}[\text{NO}_2][\text{M}]\} [\text{BrO}]^{t+\Delta t} \\ &+ \{0\} [\text{BrCl}]^{t+\Delta t} \\ &+ \{0\}, \quad (\text{II.28a}) \end{aligned}$$

$$\begin{aligned} &\frac{[\text{BrCl}]^{t+\Delta t} - [\text{BrCl}]^t}{\Delta t} \\ &= \{e_{5c}[\text{ClO}]\} [\text{BrO}]^{t+\Delta t} \\ &+ \{0\} [\text{BrCl}]^{t+\Delta t} \\ &+ \{het_6[\text{HOBr}]\}. \quad (\text{II.28b}) \end{aligned}$$

II-2-3 Peroxy radicals

Using the EBI method, a quadratic equation of $[\text{CH}_3\text{O}_2]^{t+\Delta t}$ is derived as

$$2r_{11}\Delta t([\text{CH}_3\text{O}_2]^{t+\Delta t})^2 + \{1 + L_1\Delta t\}[\text{CH}_3\text{O}_2]^{t+\Delta t} - \{[\text{CH}_3\text{O}_2]^t + P_1\Delta t\} = 0, \quad (\text{II.29})$$

where,

$$\begin{aligned} P_1 &= c_{18}[\text{CH}_3\text{C(O)O}_2][\text{NO}] + 2c_{26}[\text{CH}_3\text{C(O)O}_2][\text{CH}_3\text{C(O)O}_2] \\ &\quad + 0.31c_{54}[\text{C}_3\text{H}_6][\text{O}_3] + 0.08i_1[\text{C}_5\text{H}_8][\text{O}_3] \\ &\quad + 0.16t_2[\text{C}_{10}\text{H}_{16}][\text{O}_3], \\ L_1 &= c_3[\text{NO}] + c_{25}[\text{CH}_3\text{C(O)O}_2] + (c_{49} + c_{50})[\text{GC(O)O}_2], \\ r_{11} &= c_4 + c_5. \end{aligned}$$

A quadratic equation of $[\text{CH}_3\text{C(O)O}_2]^{t+\Delta t}$ is similarly derived from a set of chemical ODEs for $\text{CH}_3\text{C(O)O}_2$ and PAN as

$$\begin{aligned} 2r_{11}\Delta t([\text{CH}_3\text{C(O)O}_2]^{t+\Delta t})^2 &+ \left\{ (1 + L_1\Delta t) - \frac{r_{12}r_{21}\Delta t^2}{1 + L_2\Delta t} \right\} [\text{CH}_3\text{C(O)O}_2]^{t+\Delta t} \\ &- \left\{ ([\text{CH}_3\text{C(O)O}_2]^t + P_1\Delta t) + \frac{r_{12}\Delta t}{1 + L_2\Delta t} [\text{PAN}]^t \right\} \\ &= 0, \end{aligned} \quad (\text{II.30})$$

where,

$$\begin{aligned} P_1 &= c_{17}[\text{CH}_3\text{CHO}][\text{NO}_3] + c_{37}[\text{MGLY}][\text{NO}_3] \\ &\quad + 0.1i_1[\text{C}_5\text{H}_8][\text{O}_3] + 0.1i_{10}[\text{MACR}][\text{O}_3] \\ &\quad + 0.25i_{11}[\text{MACRO}_2][\text{NO}] + 0.2t_2[\text{C}_{10}\text{H}_{16}][\text{O}_3], \\ L_1 &= c_{18}[\text{NO}] + c_{19}[\text{NO}_2][\text{M}] + (c_{24} + c_{25})[\text{CH}_3\text{O}_2] + g_9, \\ L_2 &= c_{20}[\text{M}], \\ r_{11} &= c_{26}, \\ r_{12} &= c_{20}[\text{M}], \\ r_{21} &= c_{19}[\text{NO}_2][\text{M}]. \end{aligned}$$

A quadratic equation of $[\text{GC(O)O}_2]^{t+\Delta t}$ is similarly derived from a set of chemical ODEs for GC(O)O_2 and GPAN as

$$\begin{aligned} 2r_{11}\Delta t([\text{GC(O)O}_2]^{t+\Delta t})^2 &+ \left\{ (1 + L_1\Delta t) - \frac{r_{12}r_{21}\Delta t^2}{1 + L_2\Delta t} \right\} [\text{GC(O)O}_2]^{t+\Delta t} \\ &- \left\{ ([\text{GC(O)O}_2]^t \Delta t) + \frac{r_{12}\Delta t}{1 + L_2\Delta t} [\text{GPAN}]^t \right\} \\ &= 0, \end{aligned} \quad (\text{II.31})$$

where,

$$\begin{aligned} L_1 &= c_{45}[\text{NO}_2][\text{M}] + c_{47}[\text{NO}] + (c_{49} + c_{50})[\text{CH}_3\text{O}_2], \\ L_2 &= c_{46}[\text{M}], \\ r_{11} &= c_{51}, \\ r_{12} &= c_{46}[\text{M}], \\ r_{21} &= c_{45}[\text{NO}_2][\text{M}]. \end{aligned}$$

A quadratic equation of $[\text{ISOPO}_2]^{t+\Delta t}$ is similarly derived as

$$2r_{11}\Delta t([\text{ISOPO}_2]^{t+\Delta t})^2 + \{1 + L_1\Delta t\}[\text{ISOPO}_2]^{t+\Delta t} - \{[\text{ISOPO}_2]^t + P_1\Delta t\} = 0, \quad (\text{II.32})$$

where,

$$\begin{aligned} P_1 &= 1.2t_3[\text{C}_{10}\text{H}_{16}][\text{NO}_3], \\ L_1 &= i_4[\text{NO}] + g_7, \\ r_{11} &= i_6. \end{aligned}$$

A quadratic equation of $[\text{MACRO}_2]^{t+\Delta t}$ is similarly derived from a set of chemical ODEs for MACRO_2 and MPAN as

$$\begin{aligned} 2r_{11}\Delta t([\text{MACRO}_2]^{t+\Delta t})^2 &+ \left\{ (1 + L_1\Delta t) - \frac{r_{12}r_{21}\Delta t^2}{1 + L_2\Delta t} \right\} [\text{MACRO}_2]^{t+\Delta t} \\ &- \left\{ ([\text{MACRO}_2]^t + P_1\Delta t) + \frac{r_{12}\Delta t}{1 + L_2\Delta t} [\text{MPAN}]^t \right\} \\ &= 0, \end{aligned} \quad (\text{II.33})$$

where,

$$\begin{aligned} P_1 &= 0.1i_1[\text{C}_5\text{H}_8][\text{O}_3] + 0.2t_2[\text{C}_{10}\text{H}_{16}][\text{O}_3], \\ L_1 &= i_{11}[\text{NO}] + i_{14}[\text{NO}_2][\text{M}] + g_8, \\ L_2 &= i_{15}[\text{M}], \\ r_{11} &= i_{13}, \\ r_{12} &= i_{15}[\text{M}], \\ r_{21} &= i_{14}[\text{NO}_2][\text{M}]. \end{aligned}$$

II-2-3 The other short-lived species

The other short-lived species are set to zero or a certain very small, virtually zero, value ε .

$$\begin{aligned} [\text{H}] &= 0, \\ [\text{OH}] &= \varepsilon, \\ [\text{HO}_2] &= \varepsilon, \\ [\text{N}] &= \varepsilon, \\ [\text{O}^{1\text{D}}] &= \varepsilon, \\ [\text{O}^{3\text{P}}] &= \varepsilon, \\ [\text{O}_3] &= O_x - 2\varepsilon, \\ [\text{Cl}] &= \varepsilon, \\ [\text{ClO}] &= [\text{ClO}_x] - \varepsilon, \\ [\text{Br}] &= \varepsilon, \\ [\text{C}_2\text{H}_5\text{O}_2] &= \varepsilon, \\ [\text{C}_3\text{H}_7\text{O}_2] &= \varepsilon, \\ [\text{ACETO}_2] &= \varepsilon, \\ [\text{EO}_2] &= \varepsilon, \\ [\text{EO}] &= \varepsilon, \\ [\text{PO}_2] &= \varepsilon. \end{aligned}$$

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気象研究所対流圏-成層圏化学気候モデルの開発について

出牛 真、柴田清孝（環境・応用気象研究部）

本論文では、気象研究所で新たに開発した全球化学気候モデル（気象研究所化学気候モデル バージョン2）について記述する。バージョン2（MRI-CCM2）は、バージョン1（MRI-CCM1）と同様のフレームワークをもち、地上から成層圏までのオゾンおよび他の大気微量成分の時空間濃度分布を計算するために必要な化学・物理プロセスをその相互作用とともに考慮している。詳細な対流圏化学過程を新たに組み込んだことで、対流圏と成層圏におけるオゾン化学過程をバージョン2では統一に取り扱っている。バージョン2の化学モジュールにおいては、90の化学種・172の気相反応・59の光解離反応・16の不均一反応に加えて、改良されたセミ・ラグランジュスキームをもちいた格子スケールの輸送計算、サブ格子スケールの積雲鉛直輸送・乱流鉛直輸送、乾性・湿性沈着、さまざまな起源からの微量成分のエミッション、の各プロセスを取り扱っている。このバージョン2を用いて数値積分を11年間行い、1990年代の微量成分濃度分布の再現実験を行った。数値積分は、大気場の同化を行った場合と行わない場合の2通りについて行った。この数値積分結果においては、南半球極域の下部対流圏におけるオゾン濃度の過小評価および上部対流圏・下部成層圏の中高緯度における過大評価がみられるものの、中・下部対流圏におけるオゾン濃度の地理的な分布や季節変動はオゾンゾンデの観測とおおむね良く一致した。また、一酸化炭素（CO）・一酸化窒素（NO）・ヒドロキシルラジカル（OH）などの濃度分布の特徴もバージョン2は現実的に再現した。南半球高緯度においてCO濃度を約15 ppbv 過大評価したものの、バージョン2は観測されたCO濃度の季節変動をおおむね良く再現し、観測されたNO濃度の鉛直分布の特徴を捉え、またOHラジカルの濃度分布は最近の他の化学気候モデルが再現した濃度分布と同様の特徴を示した。