Summertime tropospheric ozone over China simulated with a regional chemical transport model

2. Source contributions and budget

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[1] A regional three-dimensional chemical transport model is used to simulate the contributions of various sources to the NO_x and O_3 distributions in the troposphere over China during a summertime period. O_3 tracers are added in the model to simulate the distribution of O_3 that originates from stratosphere-troposphere exchange (STE), lateral boundary import (LBI) and in situ photochemistry via NO , respectively. Tracers for reactive nitrogen species are further incorporated into the model to simulate the distributions of NO_x that originate from surface emissions, aviation, lightning, STE and LBI, respectively. Meanwhile, the O_3 formed by chemical reactions via the NO tracer originating from these sources is also tagged. The model results indicate that surface emissions are the dominant contributor to the NO_x and hence O_3 concentrations in the polluted boundary layer of eastern China. At higher altitudes the O_3 produced via surface-emitted NO_x accounts for 10–20% of the O_3 concentrations over these polluted regions. The impact of aircraft NO_x emissions on tropospheric O_3 over China is small, contributing up to 2% of the O_3 concentrations at cruise altitudes. The net O_3 production via surface-emitted NO_x over the region is estimated to be 132 Gg d^{-1} in the boundary layer and 33 Gg d^{-1} in the free troposphere. Because there is much more O_3 transported into than out of the region and high relative humidity, in situ photochemistry acts as a sink for O_3 in the troposphere over the region.

INDEX TERMS: 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305);

KEYWORDS: tropospheric ozone, modeling, nitrogen oxides, tagging procedure, ozone budget, China

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1. Introduction

[2] In a companion paper [Ma *et al.*, 2002b], we described a regional three-dimensional chemical transport model for the simulation of tropospheric ozone chemistry over China, and evaluated the model by comparing simulated distributions of tropospheric ozone (O_3) and its precursors with available observations and other model results for summertime. In this paper, we use the model to analyze the factors that control tropospheric ozone over China during the summertime period and quantify the contributions of various sources to the concentrations of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) and O_3 in the troposphere over the region.

[3] The source turning on and off method has been widely used in model studies of tropospheric O_3 , particularly its perturbation by human activities. The method is very efficient in evaluate the impact of current (or future) pollutant emissions on the pristine (or present) “background” atmosphere. However, the turning on and off method is not so efficient in the study of various processes in a specific atmosphere. For instance, if one investigates the significance of stratospheric O_3 intrusions to the source of tropospheric O_3 using turning on and off method, it would be difficult to quantify the relevant contribution, since the concept of the atmosphere with stratospheric O_3 source being turned off is not clear. For this case, the tagging (or tracing) procedure provides a different and more efficient measure of the relative importance of different sources to tropospheric NO_x and O_3 levels, as the chemical characteristic of the simulated atmosphere keeps the same while adding a tracer. Lamarque *et al.* [1996]

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estimated the relative contributions of the different NO_x sources in the troposphere. Wang *et al.* [1998] quantified the contributions to tropospheric O_3 concentrations from production in the stratosphere, the upper troposphere, the polluted continental boundary layer, as well as the middle troposphere and the marine boundary layer. Horowitz and Jacob [1999] evaluated the global impact of fossil fuel combustion on tropospheric NO_x , with a focus on the importance of emissions from United States and China. Roelofs and Lelieveld [1997], Kentarchos *et al.* [1999] and Lelieveld and Dentener [2000] studied the effect of stratosphere-troposphere exchange (STE) on tropospheric O_3 levels in different regions.

[4] In the present study, we investigate the contributions of various sources to the NO_x and O_3 concentrations in the troposphere over China using a regional chemical model with the tagging procedure incorporated. First, we trace the O_3 that originate from STE, lateral boundary import (LBI), and in situ photochemistry via NO (CHEM). Then, we trace the reactive nitrogen species from the individual source of surface emission, aviation, lightning, STE and LBI. At the same time, the O_3 formed by chemical reactions via the different NO tracers from these sources are also traced. Finally, the budget of tropospheric O_3 over the region is analyzed. As in the companion paper [Ma *et al.*, 2002b], our simulations have been performed for a summertime period July 1–15 of 1995, and the results of the last six days are analyzed considering that the initial conditions of chemical species can decay away after a 9-day simulation.

2. Ozone Transported to and Formed Within the Region

[5] From a global point of view, tropospheric O_3 arises from two processes: stratosphere-troposphere exchange (STE), and in situ photochemical production from the oxidation of hydrocarbons and CO in the presence of NO_x (CHEM). Ozone is removed from the troposphere by in situ chemistry and by uptake at the Earth's surface. Tropospheric O_3 has a lifetime of several weeks, and can be transported on a global scale. Therefore, from a regional point of view, tropospheric O_3 over a specific region may also come from lateral boundary import (LBI). We added an O_3 tracer, O_3^T , in the model to investigate these ozone sources over China for the simulated period. The tracer O_3^T , which is assigned to come from a specific source, has the same chemical and physical removal processes as “regular” O_3 . Only one O_3 source was traced for each model simulation, although theoretically several tracers could be added to account for different sources in a model simulation. We tagged the STE O_3^T by imposing the same tropopause concentration as for regular O_3 , the LBI O_3^T by assuming the same lateral boundary condition as for regular O_3 , and the CHEM O_3^T by using chemical reactions via NO, while the otherwise sources were switched off. For instance, the vertical upper boundaries for the LBI and CHEM O_3^T and the lateral boundaries for the STE and CHEM O_3^T were assumed to be zero. In this way, each source of the regional O_3 was taken into account and not calculated repeatedly.

[6] From a dynamic point of view, O_3 in the troposphere has a short lifetime against the reaction

However, O_3 is reformed rapidly in sunlight by the reactions

Reactions (R1)–(R3) represents a null cycle for ozone production and loss since no change in the O_3 abundance results at steady state. Therefore, the reaction (R1) is not considered as a loss of the tracer O_3^T . This treatment may under estimate the loss of O_3 tracers at night especially when NO_x levels are relatively high. The limitation of the tagging technique used will be discussed below. The photodissociation of O_3 molecules at ultraviolet wavelengths

followed by the reaction with water vapor

act as a sink for O_3 . In addition, ozone loss through the HO_x ($= \text{OH} + \text{HO}_2$) catalytic cycle

and addition reaction with olefins (alkenes), OL, are included for the loss of the tracer O_3^T .

Other loss processes involved by odd oxygen, for instance,

are not taken into account in the loss term for the STE O_3^T and LBI O_3^T , since these reactions are much less important than the reactions (R4)–(R7). NO_2 , as an odd oxygen species, may attribute either STE O_3^T , or LBI O_3^T , or CHEM O_3^T , and it is not traced in the present study. In order to avoid repeated calculations, only for CHEM O_3^T is the reaction (R9) taken into account, considering that this reaction is relatively import in the polluted regions where NO_x levels are high.

[7] O_3 is dynamically formed via the reaction (R3) in the troposphere, and the reaction (R2) provides a main source of odd oxygen atom $\text{O}(^3\text{P})$. However, as discussed above, the production of O_3 via the reaction (R2)–(R3) is balanced by its destruction via the reaction (R1). On the other hand, peroxy radicals HO_2 and RO_2 (where R refers to organic groupings), which are produced through the oxidation of

Figure 1. Calculated percent contributions to O_3 concentrations at the surface (1), 500 mbar (2) and 250 mbar (3) from stratospheric O_3 intrusion (a), lateral O_3 import (b), and chemical production within the region (c) for July 10–15, 1995. Contour levels are 10, 30, 50, 70 and 90 for solid lines, and 20, 40, 60 and 80 for dashed lines.

Figure 2. Calculated source attribution of mean diurnal cycles of surface O_3 over the period July 10–15, 1995 at the WMO/GAW stations of Waliguan (a), Lin'an (b) and Longfeng (c). Dotted lines stand for stratospheric O_3 intrusion (STE), dashed lines for lateral O_3 import (LBI), and solid lines for chemical production within the region (CHEM). See Table 3 and Figure 6 of *Ma et al.* [2002b] for an introduction of the three WMO/GAW stations in China.

CO and hydrocarbons, can also efficiently oxidize NO to NO_2 by reactions

Thus, the reaction (R10) and (R11) are considered as the rate-determining steps for the effective formation of the CHEM O_3^T in the present study. The loss term of the CHEM

O_3^T is the same as that of the STE O_3^T and LBI O_3^T , except that the reaction (R9) is included for the CHEM O_3^T . So far, one can see that factually it is odd oxygen, O_x ($O_x = O_3 + O(^3P) + O(^1D) + NO_2$), instead of O_3 molecule itself, that has been traced as STE O_3^T , LBI O_3^T , and CHEM O_3^T , respectively, in the present study.

[8] After 15-days integration, the sum in the tropospheric burden of STE, LBI and CHEM O_3 tracers was calculated to be 10% more than the tropospheric burden of “regular” O_3 (13.8 Tg) over the region. The lack of additivity of the tagged tracers used cannot be due to the boundary conditions assumed, since the boundary conditions are additive for all the sources. It may come from inappropriate assumptions of what constitutes chemical loss of a tagged O_3 tracer. It may also arise from the assumptions of what constitutes formation of a tagged O_3 tracer. Therefore, it should be admitted that the tagging technique is at best approximate for O_3 , and that it provides an estimate of contributions with an error of approximately 10%. Since odd oxygen is tagged in all the cases, it is expected that discrepancies will affect different tracers in the same direction, although the magnitude may be quite different. Hence, the deviation in the calculated relative contribution of a tracer to the regular O_3 will be smaller than 10% with respect to its theoretical relative contribution.

[9] Figure 1 presents the calculated percent contributions of different O_3 tracers to the O_3 concentration at the surface, 500 mbar and 250 mbar, respectively. The calculated concentrations in the absolute sense are not shown, as the similar distributions of O_3 and other trace gases have been given in a companion paper [*Ma et al.*, 2002b]. As shown in Figure 1, through STE stratospheric O_3 contributes considerably to the O_3 concentration in the troposphere, even down to the surface over some remote areas. STE is a dominant source of O_3 in the upper troposphere of most northern parts of the model domain. It is noted that to the south of the Tibetan plateau, where the latitude is lower (20–30°N), the signature of stratospheric O_3 can also be found with a contribution of 30–40%, due to strong deep convection. *Lelieveld and Dentener* [2000] also showed that STE significantly contributes to O_3 in regions where the photochemistry is quiescent. LBI contributes significantly to tropospheric O_3 over the region, especially in northwestern and southeastern parts of the region. These imported O_3 can originally come from both STE and photochemical formation in the troposphere outside the region, and their attribution can be quantified with a global chemical transport model. The contribution of photochemistry occurring within the region to the O_3 concentration is dominant in the polluted boundary layer and, in the free troposphere, it is still considerable (20–40%) in downstream regions of polluted sources. In addition to eastern China, India looks like an important polluting source for the region that cannot be neglected.

[10] Figure 2 shows calculated source attribution of mean diurnal cycles of surface O_3 at the three WMO/GAW stations in China (the reader is referred to *Ma et al.*, [2002b] for a description of these three WMO/GAW stations in China). There is no significant daily variation in the contribution from CHEM at the Waliguan station. The contribution to the O_3 concentration from LBI, STE and CHEM is about 36, 16, and 5 ppbv, respectively. So ozone at Waliguan is dynamically controlled. At the Lin'an station, the daily variation in the source contribution of CHEM is

Figure 3. Calculated percent contributions to NO_x concentrations at the surface (1), 500 mbar (2) and 250 mbar (3) from various reactive nitrogen sources including surface emission (a), aviation (b), lightning (c), stratospheric intrusion (d), and lateral import (e) for July 10–15, 1995. Contour levels are 10, 30, 50, 70 and 90 for solid lines, and 20, 40, 60 and 80 for dashed lines.

considerable, indicating that local photochemistry is active. The contribution of LBI is comparable to and at night even larger than the contribution of CHEM. At the Longfeng station, CHEM plays a predominant factor controlling the surface O_3 as well as its diurnal variation, while the small

effect of STE and LBI is simulated. The simulated daily variation in surface O_3 is approximately three times larger at the Longfeng station than at the Lin'an station. While high levels of CHEM O_3 during the daytime indicate very active photochemistry occurring locally, high levels of CHEM O_3

Figure 3. (continued)

at the nighttime may implicate high ozone formation in a large scale, especially its upstream regions.

3. Ozone Formed Within the Region via Various Reactive Nitrogen Sources

[11] We have shown in the above section that chemistry can significantly affect the O_3 level in the troposphere over the region. In this section, we investigate the source attribution of photochemically produced O_3 by tracing nitrogen-containing species from various sources, with more concern about the perturbation of tropospheric O_3

by human activities such as fossil fuel composition and biomass burning. We tagged reactive nitrogen ($NO_y = NO + NO_2 + NO_3 + N_2O_5 + HNO_4 + HNO_3 + PAN$) from a specific source, including surface emission, aviation, lightning, STE and LBI, by adding tracers $N^T O$, $N^T O_2$, $N^T O_3$, $N^T O_5$, $N^T NO_5$, $HN^T O_4$, $HN^T O_3$ and PAN^T in the model. These tracers were assigned to have the same physical and chemical behavior as corresponding “regular” nitrogen-containing species in the model simulation. The reactions involving dinitrogen species $N_2^T O_5$ and $N^T NO_5$ were decomposed with the same procedure as used by Horowitz and Jacob [1999]. We also added a tracer, O_3^T , which was

Figure 3. (continued)

assumed to be produced via $\text{N}^{\text{T}}\text{O}$ traced above. The photochemical formation and loss of the tracer O_3^{T} from tagged N species are identical to those of $\text{CHEM-O}_3^{\text{T}}$. Consequently, the CHEM-O_3 formation was broken down into ozone formation for each specific N-source in a fully additive fashion. Results for the source attribution of the NO_x and O_3 concentrations are discussed below.

[12] Figure 3 presents the calculated percent contributions of various reactive nitrogen sources to the NO_x concentration at the surface, 500 mbar and 250 mbar,

respectively. Surface NO_x emissions contribute predominantly to the NO_x at ground levels in most of China, especially in polluted areas where more than 90% of NO_x are attributed to the surface source. In remote areas of the Tibetan plateau, the contributions to surface NO_x concentrations from (western) LBI and, to a lesser extent, from the lightning source are considerable. At 500 mbar, the contribution from surface emissions is still dominant over eastern China (more than 50%), while the lightning source is significant in some tropical parts and STE becomes more important over northern areas. At 250 mbar, surface emissions contribute to NO_x concentrations still significantly in the downstream of polluted areas (approximately 30–50%). The lightning contributes dominantly over the Tibetan plateau and its south in the tropics, and STE does over northern areas. The contribution of LBI is limited to some southeastern and western areas. It is noted that at this altitude, where maximum aircraft emissions occur, the contribution of aviation to the NO_x is considerable (20–30%) in the flight corridors as well as downstream regions over southeastern China. However, the signature of aviation NO_x is not so significant at 250 mbar over the northern China close to Beijing, where the “background” NO_x is high mainly due to surface emissions. By “tagging” the fossil fuel NO_x emitted by China in a global model simulation, Horowitz and Jacob [1999] estimated that at higher altitudes over southern and eastern China, the contribution of emissions from China is 10–40% of the total. In the latitude range 0–40°N, emissions from China account for 10–20% of the NO_x present over the western North Pacific through most of the depth of the troposphere. Our results are generally in agreement with those of Horowitz and Jacob [1999].

[13] Figure 4 presents the calculated percent contributions of the O_3 tracers produced via the individual NO_x tracers from various sources (surface, aviation, lightning, STE and LBI) to the O_3 concentration at the surface, 500 mbar and 250 mbar, respectively. The O_3 produced via surface-emitted NO_x is the dominant contributor to the O_3 in the polluted boundary layer, while the contributions via all other NO_x sources are relatively small. At higher altitudes over and downstream of these polluted areas, the contribution of the O_3 produced via surface-emitted NO_x is still highest among other NO_x sources, accounting up to 20% and 10% of the total O_3 concentrations in the middle and upper troposphere, respectively. The O_3 produced via lateral imported NO_x provides an important chemical contribution to the O_3 in the free troposphere. The contributions of the NO_x sources from lightning and STE are still considerable in some regions of the free troposphere. It is noted that the maximum contribution to the O_3 from a source of NO_x may not coincide with the maximum contribution to the NO_x from this source (Figure 3). For instance, the STE NO_x contributes predominantly to the NO_x in the upper troposphere over northern areas, while the contribution of the O_3 produced via the STE NO_x is negligent, since O_3 in these regions are dynamically controlled (Figure 1). The contribution of the O_3 produced via aircraft emitted NO_x is relatively small, about 2% at the cruise altitude downstream of main flight routes. The maximum concentration of O_3 produced via aircraft emitted NO_x is nearly 1 ppbv over southeastern China (not shown). The concentration of O_3

Figure 4. Calculated percent contributions to O_3 concentrations at the surface (1), 500 mbar (2) and 250 mbar (3) from O_3 tracers formed via various reactive nitrogen sources including surface emission (a), aviation (b), lightning (c), stratospheric intrusion (d), and lateral import (e) for July 10–15, 1995. Different contour intervals are used, with 5 for panels a1–a2 and b3–e3, 20 for panel a3, 1 for panels b1–b2, and 2 for panels c1–e1 and c2–e2.

produced via surface-emitted NO_x is calculated to reach its highest values of approximately 10 ppbv in the middle troposphere and 5 ppbv in the upper troposphere.

4. Regional Ozone Budget

[14] Table 1 presents the calculated daily-averaged tropospheric O_3 budget over China for July 10–15, 1995. Tropo-

spheric O_3 over China is simulated to come mainly from two large sources: transport from the western boundary (1412 Gg d^{-1}) and photochemical formation via NO_x (947 Gg d^{-1}) within the region. The other two sources are transport from the southern boundary (293 Gg d^{-1}) and STE (87 Gg d^{-1}). Tropospheric O_3 over China is simulated to lose mainly by two quantitatively comparable sinks: photochemical destruction within the region (1186 Gg d^{-1}) and

Figure 4. (continued)

transport to the eastern boundary (899 Gg d^{-1}). The other two sinks are deposition on surface (237 Gg d^{-1}) and transport to the northern boundary (55 Gg d^{-1}). Photochemical destruction of O_3 is larger than its photochemical formation, leading to a net destruction of O_3 (238 Gg d^{-1}) in the troposphere of the region. There is an imbalance (751 Gg d^{-1}) between the amounts of O_3 transported into and out of the region in the horizontal, with the former being much larger than the latter. This imbalance in O_3 transport for the region is due to the convergence of air masses over the region [see, Ma *et al.*, 2002b, Figure 1]. In addition, water vapor is high during this period, and hence O_3 is net destroyed over the region. We did

two sensitivity runs: one with a 20% reduction in the western boundary concentration of O_3 , the other with a 20% reduction in the mixing ratio of water vapor over the region. The photochemical formation and destruction of O_3 changes by factors of 1.07 and 0.86 in the former case, and by factors of 1.00 and 0.48 in the latter case, respectively. As a result, the net O_3 production changes to -6 Gg d^{-1} with a 20% reduction in the western boundary concentration of O_3 , and to 378 Gg d^{-1} with a 20% reduction in the mixing ratio of water vapor over the region. The importance of water vapor in the photochemical budget of O_3 was also revealed in the study of Ma *et al.* [2002a] for the Waliguan station. The

Figure 4. (continued)

amount of transported O₃ at the northern boundary and at the tropopause varies significantly from day to day, and in some cases can change the sign, i.e., to different directions. This may affect the regional O₃ budget greatly. On the other hand, day-to-day variations in formation, destruction and deposition of O₃ are quite small, with only a few percent. The total O₃ tendency over the region is 363 Gg d⁻¹, and varies day-to-day by as much as $\pm 140\%$. This variability is caused mainly by the changes in the O₃ flux during the simulation period, which is in turn determined by the O₃ concentration and wind. While the O₃ concentration is fixed in the upper boundary and varied much less in the lateral boundaries,

Table 1. Calculated Daily-Averaged Tropospheric O₃ Budget Over the Model Domain for the Period July 10–15, 1995

Process	Budget ^a , Gg d ⁻¹
Stratosphere-troposphere exchange ^b	87 $\pm$ 110
Net lateral boundary transport ^b	751 $\pm$ 445
North	-55 $\pm$ 520
East	-899 $\pm$ 241
South	293 $\pm$ 162
West	1412 $\pm$ 190
Net photochemical production ^c	-238 $\pm$ 31
Formation	947 $\pm$ 36
Destruction	1186 $\pm$ 9
Deposition on the surface	237 $\pm$ 10
Total Tendency ^d	363 $\pm$ 514

^a Expressed in the form of means $\pm$ standard deviations.

^b Positive sign means transport in, and negative sign transport out.

^c Positive sign means net production, and negative sign net destruction.

^d Sum of stratosphere-troposphere exchange, net lateral boundary transport, net photochemical production, and deposition on the surface.

the wind in the boundaries may fluctuate significantly and sometimes change to the opposite direction, leading to day-to-day variations in the amount of O₃ transported into and out of the region. However, due to the large model domain used, the total O₃ tendency only accounts for 2–3% of the total O₃ burden (13758 Gg) in the troposphere over the region.

[15] Table 2 shows the calculated daily-averaged photochemical budget for O₃ formed in the troposphere over China via various NO_x sources for July 10–15, 1995. Surface NO_x emissions are the most important photochemical source of O₃ in the boundary layer (BL) of the region (171 Gg d⁻¹), accounting for half of the total O₃ formation in this region. In addition, LBI-originated NO_x contributes 40% of the photochemical source of O₃ in BL of the region (136 Gg d⁻¹). In the free troposphere (FT), photochemical O₃ formation via the LBI-originated NO_x (predominantly from the western and southern boundaries) is significant (375 Gg d⁻¹), which contributes about 60% of the total O₃ formation in FT. The contribution of the STE-originated NO_x to the total O₃ formation in FT is also considerable (103 Gg d⁻¹) with a value of nearly 20%. The contributions from surface, aviation and lightning NO_x sources to the O₃ photochemical formation in FT are comparable, each less than 10%. The total destruction of O₃ that are formed via the NO_x-controlled photochemistry (100 + 86 = 186 Gg d⁻¹) is much smaller than the O₃ destruction given in Table 1

Table 2. Calculated Photochemical Budget and Deposition for Tropospheric O₃ Formed via Various NO_x Sources over the Model Domain for the Period July 10–15, 1995^a

Source	Formation		Destruction		Net Production		Deposition
	FT	BL	FT	BL	FT	BL	
Surface	53	171	20	39	33	132	38
Aviation	23	5	8	4	15	1	4
Lightning	55	16	14	8	41	8	8
STE	103	11	20	10	83	1	8
LBI	375	136	38	25	337	111	15
Total	609	339	100	86	509	253	73

^a Units are Gg/day. FT refers to the free troposphere and BL the boundary layer.

(1186 Gg d⁻¹). The deficit (1186 - 186 = 1000 Gg d⁻¹) is attributed to the destruction part of the O₃ that has been transported from outside due to STE and LBI. The deposition part of those transported O₃ can also be estimated (237 - 73 = 164 Gg d⁻¹). The net BL production of O₃ from LBI NO_x sources (111 Gg d⁻¹) is very similar in magnitude to the one from surface NO_x sources (132 Gg d⁻¹). Moreover, the net FT production of O₃ from LBI NO_x sources (337 Gg d⁻¹) is 10 times larger than that from surface NO_x sources (33 Gg d⁻¹). On the other hand, Figure 4 (panels a1–a3 and e1–e3) shows that the contribution of O₃ concentration associated with surface NO_x sources predominates over that associated with LBI NO_x sources in both BL and FT. This is partly due to the fact that O₃ from LBI NO_x sources is mostly formed in the regions where the O₃ concentration is large [see Ma *et al.*, 2002b, Figure 11 (panels a1–a3)] but not controlled by in situ photochemistry within the domain (Figure 1). It is also partly due to the fact that O₃ formed from LBI NO_x sources is spread out more uniformly over the model domain. It is implicated that while the photochemical production of O₃ due to long-range transport of O₃ precursors is significant in the regional and global scales, its verification by field experiments will be difficult, as its signals have become too weak due to smoothing.

5. Conclusions

[16] We have investigated, by using a tagging procedure in the model simulation, the contributions of various sources to the NO_x and O₃ concentrations in the troposphere over China, and estimated the regional O₃ budget for the summertime period. We have traced O₃ originating from stratosphere-troposphere exchange (STE), lateral boundary import (LBI), and formation by in situ photochemistry via NO. Furthermore, we have also traced nitrogen species from surface emission, aviation, lightning, STE and LBI, as well as O₃ formed by chemical reactions via the corresponding NO from these sources.

[17] The contribution of photochemistry occurring with the region is shown to be a dominant source of O₃ in the polluted boundary layer (BL) of eastern China and, in the free troposphere (FT), it still contributes 20–40% of the O₃ concentration in downstream regions of polluted sources. Surface emissions are the dominant contributor to NO_x and hence O₃ concentrations in the polluted BL, while at higher altitudes the O₃ produced via surface-emitted NO_x accounts for 10–20% of the total O₃ concentrations over these polluted regions. In the upper troposphere, the O₃ produced via surface-emitted NO_x is simulated to reach its highest values of about 5 ppbv over the polluted region. The contribution of aviation to NO_x and O₃ concentrations is found to be small relatively even at its cruise altitudes, where the absolute O₃ produced via aircraft emitted NO_x is simulated nearly to 1 ppbv in the flight corridors and downstream regions.

[18] STE is simulated to contribute considerably to the O₃ concentration in the upper troposphere, especially over northern parts of the region where STE is very active. Even down to the surface, the O₃ from STE contributes 30–40% of the O₃ concentration on the Tibetan Plateau. However, the contribution of the O₃ produced via NO_x from STE to tropospheric O₃ over the region is much small relatively,

since photochemistry is not so active in those regions. For the same reason, the contribution of the O₃ produced via lightning NO_x to tropospheric O₃ is also limited over the region during the investigated period. We have found that LBI contributes predominantly to tropospheric O₃ in most regions, except for the polluted BL of eastern China and the upper troposphere of northeastern region. This contribution comes mainly from import of O₃ itself and, to a smaller extent, from in situ photochemistry via imported NO_x.

[19] Our regional budget analysis indicates that an imbalance between O₃ transported in and out of the region exists, due to the convergence of air masses during the simulation period. The photochemistry in the troposphere over the region acts as a sink for O₃ during the simulated period. Our sensitivity studies show that water vapor is an important factor that influences the photochemical budget of O₃ over the region. Photochemical formation of O₃ in BL is predominantly via surface-emitted NO_x, and O₃ formation in FT is predominantly via LBI-originated NO_x. The net FT production of O₃ from LBI NO_x sources is calculated to be 10 times larger than that from surface NO_x sources. However, its signals are weaker according to our tracer-tagging simulations, since O₃ formed from LBI NO_x sources is spread out more uniformly over the model domain. O₃ formation in BL via surface-emitted NO_x (171 Gg d⁻¹) cannot completely be balanced by chemical destruction (39 Gg d⁻¹) and deposition (38 Gg d⁻¹) in BL. This implies that more than half of produced O₃ (up to 94 Gg d⁻¹) can be transported out of BL of the region.

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