

Sensitivity Analysis of O₃ and Photochemical Indicators Using a Mixed-Phase Chemistry Box Model and Automatic Differentiation Technology

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Introduction

Air pollution models have provided the most effective means to quantify the impact of human activities on the atmosphere and to develop balanced and cost-effective emission control strategies for toxic air pollutants such as tropospheric O₃ during the last several decades. The effectiveness of these abatement strategies depends on the reliability of model predictions, which is further built upon the accurate understanding and appropriate parameterization of a variety of atmospheric processes in modeling systems. Sensitivity analysis of these models provides valuable diagnostic tools capable of identifying the most influential parameters and predicting the responses to arbitrary perturbations. Previous studies on chemical mechanisms and their sensitivity using 0-3D models have largely focused on either gas-phase or aqueous-phase chemistry only. Heterogeneous atmospheric processes involving two or more phases, however, have recently begun to gain considerable attention because of their importance in global biogeochemical cycles. Recent studies show that clouds may decrease the gas-phase concentrations of NO_x, O₃, OH, HO₂ and HCHO by 10-85 % [1]. Aerosols may act as an effective scavenger for trace gas species and radicals under a variety of atmospheric environments [2, 3]. There are few models capable of realistically simulating these processes because of the nebulous mechanisms and many uncertain parameters and pathways associated with these processes. For the same reasons, the rigorous sensitivity analysis for mixed-phase chemical mechanisms has been seldom quantified.

We have performed a comprehensive sensitivity analysis of overall model predictions for a mixed-phase chemical mechanism [4]. The sensitivities of individual species and photochemical indicators with respect to (w.r.t.) a variety of model parameters are calculated using the novel Automatic Differentiation (AD) technology implemented as Automatic Differentiation of FORtran (ADIFOR) [5]. In this paper, the sensitivity of O₃ and indicators is presented and analyzed, with a particular focus on the evaluation of clear air chemistry and aerosol surface uptake that affect tropospheric O₃ formation and O₃-precursor relations. The sensitivity analysis of the coupled gas and cloud chemistry is presented elsewhere [6].

Methodology of Sensitivity Analysis

Multi-phase Chemistry Box Model

A time-dependent Mass Transfer with Chemical Reactions Box Model (MaTChM) has been developed to explore the effects of heterogeneous processes on tropospheric chemistry [4]. In MaTChM, emission, dilution, transport and deposition processes are neglected. The model treats gas and aqueous phase chemistry, as well as the interphase mass transfer, in a homogeneous parcel of air in an atmosphere where it may encounter various surfaces such as clouds and aerosols. It simulates 57, 58, and 29 species

in the gas, aqueous and aerosol phases, respectively. 125 gas-phase reactions, 160 aqueous-phase reactions, and 29 aerosol surface reactions are included. This mechanism is designed to be applicable to various atmospheric conditions. The mixed-phase chemistry is based on the modified Carbon Bond Mechanism IV [7], the dimethyl sulfide chemistry of Yin et al. [8] and the full aqueous-phase chemistry of Pandis and Seinfeld [9]. The mass transfer between gases and clouds is simulated based on the two-resistance theory [10]. Lognormal size distributions are used to characterize multi-mode aerosols with diameter ranging from 0.001 to 100 μm . The rate of heterogeneous uptake of gases on aerosol surface is calculated as a pseudo first-order rate [11]. Table 1, 2 and 3 list the simulated gas-phase species, aerosol-phase species and gas-phase reactions that are related to this paper. The uptake coefficients of individual species on aerosols are also given in Table 2. Detailed description of the model can be found elsewhere [4, 6]. Five typical atmospheric conditions were simulated: heavily-polluted (Heavypoll), polluted (Urban), moderately-polluted (Rural), marine (Marine) and remote marine (Remote) conditions, as shown in Table 4. Two scenarios: clear air conditions (Gas) and conditions with pre-existing aerosols (Aerosol) were further studied for each conditions. All simulations began at local noon and were run for 2 hours. A constant temperature of 280 K and a relative humidity of 80% were used.

Sensitivity Calculations

AD is a new promising technique for computation of derivatives. The ADIFOR co-developed by Argonne National Laboratory uses the forward mode to calculate the derivatives of intermediate variables w.r.t. the independent variables, and the reverse mode to propagate derivatives of the dependent variable w.r.t. the intermediate variables. Combining merits of both forward and reverse modes of AD, this approach is superior to finite difference approximation of the derivatives because of the guaranteed accuracy and the computational efficiency [12]. Using ADIFOR, the dimensionless sensitivities (i.e., normalized local sensitivities) of species concentrations C_i w.r.t parameter q_j are calculated as $S_{i,j} = (q_j / C_i) (\bullet C_i / \bullet q_j) = \bullet \ln C_i / \bullet \ln q_j$. The sign of the sensitivities reflects responses of C_i upon the relative variation of q_j . The positive values indicate that C_i increases with an increasing q_j , and the negative values mean a reversed change in C_i when q_j increases.

Given the sensitivities of individual species, the sensitivity of the ratio of the concentrations of two species w.r.t. an arbitrary parameter can be easily derived as the difference of the two individual sensitivities. The sensitivity of lumped concentrations of the two (or more) species can also be calculated as the sum of products of the concentration fraction and the sensitivity of each species. We have calculated the sensitivities of several lumped species (defined in Table 1) and photochemical indicators such as odd hydrogen (R_xO_y), nitrogen oxides (NO_x), reactive nitrogen (NO_y and NO_z), and O_3/NO_z w.r.t. all model parameters. Sensitivities during the last hour simulation are averaged and analyzed. The results are given and discussed below.

Results and Discussions

Clear Air Conditions

Effect of Gas-Phase Reaction Rate Constants

The 25 most influential reactions for O_3 concentrations under the five conditions are ranked along with the sensitivities of O_3 to these reactions in Table 5. These reactions could have either positive or negative influence depending on the signs of their sensitivities. O_3 predictions are more sensitive (by a factor of a few to several hundreds) to reaction rate constants under various polluted conditions (i.e., Rural, Urban and Heavypoll) than relatively clean conditions (Marine and Remote) for one unit change in rate constants. For example, when the rate constant of R1 doubles, the predicted O_3 concentration will increase by 1.86%, 4.13% and 27.7 % under Remote, Rural and Heavypoll conditions, respectively. This is because O_3 formation rate is proportional to the total oxidizing capacity (TOC), which is much higher under polluted conditions. Correspondingly, sensitivities are higher, reflecting larger responses on uncertainties in rate constants.

Under the Remote and Marine conditions, the most important reactions contributing to O₃ production are NO+HO₂ (R28), NO₂+hν (R1), CH₄+OH (R116), NO+CH₃O₂ (R117), H₂O₂+hν (R34), CO+OH (R36), HCHO+hν (R38), C₂O₃ + NO (R46), O₃+hν (R9) and the subsequent reaction of O(¹D)+H₂O (R11). R28 and R117 are major pathways for conversion of NO to NO₂. Followed by R1, they generate O(³p), which directly produces O₃. The photolysis of H₂O₂ (R34), HCHO (R38) and O₃ (R9) are the major sources of OH and HO₂ radicals. An increase in the rate constant of R9 decreases O₃ but increases O(¹D), which contributes to O₃ production through generation of OH radicals (R11). The increase in O₃ via R11 compensates the decrease in O₃ via R9. Thus, R9 has a net positive impact on O₃ formation. OH radicals can be converted to HO₂ and CH₃O₂ radicals through reactions with CO (R36) and CH₄ (R116), respectively. These radicals then convert NO to NO₂ followed by R28, R117 and R46. The generation and inter-conversion of these radicals thus help increase O₃ production by increasing the TOC. Compared to the Remote conditions, the O₃ photochemistry near the coast is more affected by R38 by one order of magnitude, due to a much higher concentrations of HCHO initially present under the Marine conditions. The reactions contributing to the destruction of O₃ include NO+O₃ (R3), HO₂+CH₃O₂ (R118), NO₂+OH (R26), 2HO₂+H₂O (R33), HO₂+HO₂ (R32), O(¹D)->O(³p) (R10), O₃+HO₂ (R13), O₃+OH (R12), ALD₂ +OH (R43), and C₂O₃ + NO₂ (R47). R3 is the predominant destruction pathway for O₃. R10 reduces O₃ through reducing concentrations of O(¹D), a major source of OH radicals. Representing the major sink for OH, HO₂, and CH₃O₂ radicals, the formation of peroxides (R118, R33 and R32), nitric acid (R26) and PAN (R47 following R43) reduces the TOC thus decreases O₃ formation. O₃ can also be directly destroyed by OH (R12) and HO₂ (R13) radicals.

Under various polluted conditions, R28, R32, R33, R116-118 become less important or unimportant because of the relatively lower levels of HO₂ and CH₃O₂. O₃ predictions are highly sensitive to chemistry of various reactive organic gases (ROG). R38 becomes the first and the second positively-influential reaction under both conditions, respectively. The ranks of ALD₂+OH (R43), NO+C₂O₃ (R46), NO₂+C₂O₃ (R47) and OLE+OH (R57) are also higher. Other positively-influential ROG reactions include photolysis of ALD₂ and MGLY (R45 and R74), OLE+O₃ (R58), NO+TO₂ (R64) and reactions of HCHO, PAR, ETH, TOL, and XYL with OH (R37, R52, R61, R63, and R69). A higher rate constant of R58 directly decreases O₃ but simultaneously increases concentrations of odd hydrogen R_xO_y and O₃ precursors HCHO and ALD₂, which eventually give rise to O₃ through R1 and R2. The increase in O₃ due to these pathways suppresses the direct decrease, thus R58 shows a net positive impact. Other ROG reactions (i.e., R37, R45-R47, R57, R61, R63, R64, R69, and R74) contribute to O₃ formation by producing HCHO, ALD₂, HO₂ and RO₂ radicals. R43 and R47 are dominant negatively-influential ROG reactions. R39 also contributes to O₃ destruction by competing with the positively-influential reaction R38 and consuming HCHO. These results are in good agreement with other sensitivity analyses of various gas-phase chemical mechanisms such as RADM2 and STEM-II [15, 16].

Various photochemical indicators such as NO_y, O₃/NO_z and H₂O₂/HNO₃, have recently been used to determine the O₃-NO_x-ROG sensitivity in order to effectively control O₃ at O₃ non-attainment regions [13, 14]. For example, ROG-sensitivity chemistry has been linked to afternoon conditions with 10 ppb <NO_y<25 ppb, O₃/NO_z < 7, HCHO/NO_y < 0.28, and H₂O₂/HNO₃ < 0.4, lower NO_y and higher ratios correspond to NO_x-sensitive chemistry [13, 14]. The indicators calculated from MaTChM show that O₃ is ROG-sensitive under the Heavypoll conditions and NO_x-sensitive under the moderately polluted conditions. O₃ chemistry exhibits a transition between the two regimes under the Urban conditions,

with $\text{NO}_y > 10$ ppb but values of other indicators higher than threshold values. These are consistent with the calculated O_3 sensitivity shown in Table 5 (and Figure 2 (a), see below).

Since indicators are mainly discovered based on theoretical rational and 3-D photochemistry models, their application involves large uncertainties based on model assumptions or omissions. Our sensitivity analysis shows that the indicator NO_y is relatively insensitive ($S_{i,j} < 0.01$) or less sensitive to changes in many model parameters, whereas other indicators involving either H_2O_2 or HNO_3 or HCHO or NO_z exhibit higher sensitivities. Figure 1 show the sensitivities of O_3/NO_z and $\text{H}_2\text{O}_2/\text{HNO}_3$ w.r.t. reaction rate constants under various polluted conditions. While the most influential reactions for the indicators are the same as those for O_3 , their relative impacts are different both in signs and amplitudes. For example, R38 has a positive influence on O_3 formation, but a negative impact on O_3/NO_z and $\text{H}_2\text{O}_2/\text{HNO}_3$. While a higher rate constant of R38 increases O_3 and H_2O_2 formation via generation of HO_2 , it also increases the denominator NO_z and HNO_3 . The net effect is a decrease in both indicators. Similar to sensitivity of O_3 , the indicators generally exhibit higher sensitivities on basic $\text{O}_3\text{-NO}_x\text{-CO}$ reactions (R9-R11, R26, R28, R29, R32-34, and R36) under the Rural conditions, and relatively higher sensitivities on ROG reactions (R38, R39, R43, R45-R47, R52, R57, R58, R61, R69, and R74) under more polluted conditions. Sensitivities of indicators to ROG reactions under the Urban and Heavypoll conditions are a factor of a few to several tenths bigger than those under the Rural conditions, coinciding with their nature as a good marker for the $\text{O}_3\text{-NO}_x\text{-ROG}$ sensitivity. For instance, the sensitivities of O_3/NO_z and O_3 to R38, R45 and R58 under the Heavypoll conditions are higher than those under the Rural conditions by a factor of 4.0, 16, and 29, and a factor of 18, 68, and 168, respectively, indicating that ROG chemistry is dominant under the Heavypoll conditions. Lower sensitivities to ROG reactions and higher sensitivities to $\text{O}_3\text{-NO}_x\text{-CO}$ reactions indicate a NO_x -dominant chemistry.

Effect of Species Initial Concentrations

Figure 2 (a) shows the sensitivity of O_3 w.r.t initial concentrations of various species under the five conditions. The initial concentration of O_3 always has the predominant positive impact on the predicted O_3 under all conditions. The O_3 -precursor relations are different at various conditions. Under relatively clean conditions (Remote and Marine), O_3 production increases with increasing NO_x but is insensitive to ROG (except for HCHO and ALD_2 under the Marine conditions, see below). At various polluted conditions (Rural, Urban and Heavypoll), O_3 formation increases rapidly with increasing ROG (except for ALD_2 , see below), and decreases with increasing NO_x . The sensitivities of O_3 w.r.t. positively-influential ROG species increase as the air becomes increasingly polluted. Other O_3 precursors such as H_2O_2 , CO , and CH_4 have relatively large impact on O_3 production under the Remote, Marine and Rural conditions. Being a major source of OH radicals, H_2O_2 helps produce O_3 under these conditions. CO and CH_4 always tend to increase O_3 production through R36 and R116 followed by R28, R1 and R2.

Since the rate of O_3 production is proportional to reactions of ROG with OH radicals under most atmospheric conditions [14], the different O_3 -precursor relations at various conditions can be interpreted by relative importance of odd hydrogen reactions, as shown in Table 6. The important sink and inter-conversion reactions for OH and HO_2 radicals are $\text{NO}_2 + \text{OH}$ (R26), $\text{NO} + \text{HO}_2$ (R28), $\text{HO}_2 + \text{HO}_2$ (R32), $2\text{HO}_2 + \text{H}_2\text{O}$ (R33), $\text{CO} + \text{OH}$ (R36) and $\text{HCHO} + \text{OH}$ (R37). The analogous reactions for RO_2 radicals in the presence of CH_4 and other NMHCs are $\text{CH}_4 + \text{OH}$ (R117) and $\text{HO}_2 + \text{CH}_3\text{O}_2$ (R118). Under the Remote and Marine conditions, formation of peroxides via R32, 33 and R118 are the major sinks for R_xO_y . The fate of OH is mainly governed by the inter-conversion of OH, HO_2 , and CH_3O_2 (R28, R117, R36, and R37). OH decreases with a higher HCHO (due to R37) under the Remote conditions and other ROG species (due to R37, R43, R47, R51, R52, R57 and R61) under the Marine conditions. Thus, O_3

production is insensitive to most ROG (HCHO only under the Remote conditions), because increases in ROG coincide with decreases in OH. Under the Marine conditions, generation of OH radicals increases with an increasing HCHO and a decreasing ALD₂. O₃ production to initial concentrations of HCHO and ALD₂ shows larger sensitivities than other ROG species due to its higher sensitivities to R38 and R43. As a predominant pathway for O₃ productions under the Remote and Marine conditions, the conversion of NO by HO₂ (R28) results in a higher O₃ followed by R1 and R2, as shown in Table 5. NO+HO₂ (R28) and NO₂+hν (R1) compete with NO+O₃ (R3) and NO₂+OH (R26), with less NO and NO₂ available for the latter reactions. In addition, the OH increases with increasing NO_x (due to R28). Thus a higher NO_x will always causes a higher O₃ under both conditions.

Under various polluted conditions, reactions of NO₂+hν (R1), NO+O₃ (R3), NO₂+OH (R26), HCHO+hν (R38), ALD₂+OH (R43), and NO₂+C₂O₃ (R47) are the overwhelming pathways affecting O₃ production. An increase in NO consumes more O₃ (R3), and a higher NO₂ increases its denitrification via R26 and R47. In addition, R28 and R26 are the predominant pathways for R_xO_y. OH concentrations always decrease with increasing NO_x (due to R26). Thus, an increasing NO_x leads to a lower O₃. Increases in individual ROG species either increase or decrease OH, but the net effect of a higher ROG is a slight increase in OH, reflecting ROG reactions could be a source of R_xO_y. Thus, O₃ increases with increases in most ROG. When present, ALD₂ always has a negative influence on O₃ formation because it acts as a sink for NO_x via R43 and R47. While R43 consumes OH and lowers the TOC, R47 depletes NO₂ under various polluted atmospheres, as shown in Table 5.

Figure 2 (b) and (c) show the sensitivities of O₃/NO_z and H₂O₂/HNO₃ to species initial concentrations under various polluted conditions. Both indicators are affected in a variety of ways. O₃/NO_z is anti-correlated to initial H₂O₂, NO, HCHO, ALD₂, TOL, XYL and ISOP, and positively-correlated with initial O₃, PAR, CO and CH₄. The impacts of NO₂, OLE, and ETH are complicated and can be either way. For H₂O₂/HNO₃, the positively-influential species include H₂O₂, ALD₂, PAR, CO and CH₄, and the negatively-influential species are O₃, NO_x, HCHO, and XYL. The impacts of OLE, ETH and TOL can be either negative or positive. These relations are much more complicated relative to O₃-precursor relations. The interpretation requires an understanding of the chemical behaviors of the both individual indicator species. For example, although an increase in various ROG species (other than ALD₂) can always increase O₃ production, only a few of them (e.g., PAR under polluted conditions) can sometimes increase O₃/NO_z. Most ROG species negatively affect the indicator because they simultaneously increase the denominator NO_z. Whether the species have positive or negative impacts depends on the relative importance of their reactions and the signs of the predominant reactions. For instance, R1, R26 and R28 are important reactions for NO₂. Under the Rural and Urban conditions R26 and R28 are the predominant reaction and have a negative sign. Under the heavily-polluted conditions, R1 is predominant and has a positive sign. Correspondingly, O₃/NO_z and NO₂ are positively-correlated under the heavily-polluted conditions but anti-correlated under the Rural and Urban conditions.

Conditions with Pre-existing Aerosols

Important Surface Uptake Processes

The predicted species concentrations are sensitive to uptake coefficients of individual species in the presence of aerosols. For those species that are assumed to be directly scavenged to aerosol surface, their predicted concentrations are always anti-correlated with their own uptake coefficients because higher uptake coefficients deplete more gas molecules onto aerosol surface. For instance, a higher uptake coefficient of O₃ always decreases gas-phase concentrations of O₃. Reactive species are also

found to be affected by surface uptake of other species. The most influential aerosol surface reactions to overall model predictions include uptake of HCHO, O₃, HO₂, HNO₂, HNO₃, NO, NO₂, N₂O₅, PAN, H₂O₂, and SO₂. Table 7 shows the sensitivity of O₃ to uptake coefficients of the most influential species under various conditions. The predicted O₃ becomes more sensitive to changes in uptake coefficients when the pre-existing atmospheric conditions become more polluted (i.e., more aerosol surface available). For example, doubling uptake coefficient of HCHO has no effect on predicted O₃ under the Remote conditions, but it decreases the predicted O₃ by 6.3% under the Heavypoll conditions. An increase in uptake coefficients of other species such as HCHO, NO₂, and HO₂ also decreases O₃ because these surface uptake processes reduce rate of O₃-producing reactions (e.g., R1, R28, R38, R57, R61, and R69). On the contrary, higher uptake coefficients of NO and SO₂ tend to increase O₃ because their surface reactions compete with their corresponding gas-phase reactions, and decrease the rates of the gaseous reactions that contribute to O₃ destruction (e.g., R3, R22, and R115).

Since some NO_y species such as N₂O₅ and HNO₃ and R_xO_y species such as H₂O₂ and CH₃OOH are highly sensitive to changes in uptake coefficients, the indicators involving these species are expected to respond to these changes. Table 8 shows the sensitivities of O₃/NO_z and H₂O₂/HNO₃ to uptake coefficients of the most influential species under the Urban and Heavypoll conditions. The sensitivities of the indicators are much higher, as compared to that of individual species. O₃/NO_z is sensitive to uptake of HNO₃, HCHO, HNO₂, HO₂, H₂O₂, CH₃O₂, NO_x, PAN and O₃. Similar to the effect on O₃, an increase in uptake coefficients of O₃ always causes a decrease in O₃/NO_z. The impacts of HCHO, HNO₂, HO₂, H₂O₂, CH₃O₂, NO, and SO₂ on O₃/NO_z, however, are just the opposite as compared to those on O₃. In addition, O₃/NO_z becomes sensitive to changes in uptake coefficients of HNO₃ and PAN, which have little effect on O₃ formation. An increase in uptake coefficients of NO₂ and N₂O₅ (under the Heavypoll conditions), and SO₂ decreases O₃/NO_z through reducing gaseous concentrations of O₃-precursors and thus O₃. Higher uptake rates of other species increase O₃/NO_z, via either directly reducing gaseous NO_z (e.g., HNO₃ and PAN) or decreasing the concentrations of HCHO, HO₂ and H₂O₂. Since R38 is the dominant positively-influential reaction for both NO_z and O₃, a decrease in gaseous HCHO concentration reduces the photolytic rate of HCHO, thus decreasing NO_z and O₃. Similarly, decreases in H₂O₂ and HO₂ tend to decrease OH and O₃ concentrations. But they also decrease NO_z concentrations by reducing the formation rates of NO₃, N₂O₅, HNO₃ and PAN through reactions with OH. Therefore, the net effect of decreases in HCHO, HO₂, and H₂O₂ is an increase in O₃/NO_z. The responses of H₂O₂/HNO₃ are even more significant because both H₂O₂ and HNO₃ are highly sensitive to changes in their own uptake coefficients. While an increase in the uptake coefficient of H₂O₂ greatly decreases gaseous H₂O₂ thus reduces the indicator, an increase in HNO₃ uptake coefficients decreases gaseous HNO₃ thus causes an increase in the indicator. In addition, this indicator is also sensitive to uptake of HCHO, HO₂, O₃, NO_x, N₂O₅, and HNO₂.

Effect of Aerosols on O₃-Precursor Relations

The presence of aerosols not only changes concentrations of O₃ and its precursors, but also their relations provided that the available aerosol surface areas are sufficiently large (i.e., > 1000 μm² cm⁻³, under the Urban and Heavypoll conditions). Figure 3 (a) shows the comparison of the sensitivities of O₃ concentrations to species initial concentrations after 2-hr simulation in the absence and presence of aerosols under the Heavypoll conditions. O₃ increases with an increase in NO₂ in the presence of aerosols, which is just the opposite to that in clear air. Under both clear air and aerosol conditions, the photolysis of NO₂ (R1), the formation of HNO₃ (R26) and PAN (R47) through oxidation of NO₂ by OH and C₂O₃ radicals are major sinks for NO₂. The effect of NO₂ on O₃ production is determined by

relative importance of these sinks. Under clear air conditions, R26 and R47 are predominant reactions. An increase in NO_2 results in a lower OH concentration, thus a lower O_3 . When there are sufficient aerosol surface areas, concentrations of OH and C_2O_3 radicals are significantly reduced (~20-48%) due to much lower concentrations of their precursors such as H_2O_2 , HCHO and ALD₂ and the direct surface uptake of OH. As a result, R1 becomes the overwhelming sink for NO_2 and leads to O_3 formation followed R2, while OH radicals still decrease with increasing NO_2 due to R26. In addition to the change in O_3 - NO_2 relations, O_3 becomes more sensitive to NO and less sensitive to initial O_3 and various hydrocarbon species such as HCHO and ALD₂. For example, for doubled concentrations of HCHO, the predicted O_3 concentrations only increase by 1.8% in air with aerosols, as compared to 21.1% in clear air. Higher sensitivity of O_3 to initial NO is due to a higher sensitivity to the rate constant of the reaction $\text{NO}+\text{O}_3$ (R3), and O_3 sensitivities to various ROG are lower because the TOC is reduced and O_3 sensitivities to most ROG reactions such as R38 and R43 are appreciably lower.

Effect of Aerosols on Sensitivity of Indicators

Significant changes are found in sensitivities of indicators to both reaction rate constants and initial concentrations due to the surface uptake processes. Figure 4 compares the sensitivities of O_3/NO_z and $\text{H}_2\text{O}_2/\text{HNO}_3$ to reaction rate constants with and without aerosol uptake under the Heavypoll conditions. O_3/NO_z becomes more sensitive to R9-R11, R43-47, R58, R69, R74, and R76, and less sensitive to R1, R3, R38, R39, R52, and R57. The most significant change is that the sign of the sensitivity of O_3/NO_z to the reaction rate constant of NO_2+OH (R26) changes from negative to positive. Under clear air conditions, HNO_3 produced via R26 remains in the gas-phase and largely increases the denominator, NO_z , thus an increase in the rate constant of R26 actually decreases the indicator. When there are sufficient aerosol surface areas, HNO_3 can be quickly taken onto aerosol surface once produced in the gas-phase. In the meanwhile, other NO_z species such as NO_3 , N_2O_5 and PAN can undergo similar surface uptake, therefore decrease NO_z in the gas-phase. This decrease is larger than simultaneous decrease in O_3 due to the surface uptake. As a result, the indicator increases with an increasing rate constant of R26. The sensitivities of $\text{H}_2\text{O}_2/\text{HNO}_3$ to almost all reaction rate constants in the presence of aerosols significantly enhance because both H_2O_2 and HNO_3 can be effectively scavenged onto aerosol surface, and these surface uptake become the predominant pathways for H_2O_2 and HNO_3 .

The changes in these sensitivities cause substantial changes in the sensitivities of the indicators to initial species concentrations, as shown in Figure 3 (b) and (c). O_3/NO_z becomes more sensitive to initial NO_2 , ALD₂, OLE, TOL, XYL and ISOP and less sensitive to initial O_3 , NO, HCHO, PAR, and ETH. The changes in sensitivities of $\text{H}_2\text{O}_2/\text{HNO}_3$ are even larger. $\text{H}_2\text{O}_2/\text{HNO}_3$ becomes extremely sensitive to initial NO, NO_2 , O_3 , and OLE and almost insensitive to H_2O_2 . In addition, the impact of initial concentrations of O_3 , HCHO, OLE, ETH, TOL, XYL and ISOP on $\text{H}_2\text{O}_2/\text{HNO}_3$ changes from negative under clear air conditions to positive under aerosol conditions. Aerosol surface uptake processes cause significant changes in dominant reactions of H_2O_2 . H_2O_2 is no longer a reservoir for OH and HO_2 (due to R34 and R35). Once produced, H_2O_2 can be rapidly scavenged onto aerosol surface. The gaseous H_2O_2 and OH and HO_2 radicals are substantially lower. While higher NO_2 increases the concentration of HNO_3 via R26, it also causes further decreases in concentrations of OH radicals (due to R26), thus a lower H_2O_2 and a subsequent significant decrease in the indicator. The extremely high sensitivity to initial NO, NO_2 , and OLE is caused by the much higher sensitivities to their corresponding reactions (i.e., R26, R28 and R57), as shown in Figure 4 (b). Similarly, the opposite effect of initial O_3 , HCHO, OLE, ETH, TOL, XYL and ISOP is due to the corresponding changes in sensitivities to their dominant reactions (i.e., R9-11, R38, R57, R58, R61, R63, R69 and R76), as shown in Figure 4(b).

Summary

O₃-precursor relations and their interactions with heterogeneous surface uptake are analyzed through a sensitivity study using AD technology. The most influential gas-phase reactions and aerosol surface uptake processes under a variety of atmospheric conditions have been identified. The most influential gas-phase reactions can be grouped into four categories: (1) the photolytic reactions of NO₂, O₃, H₂O₂, HCHO, ALD₂ and MGLY, i.e., R1, R9, R34, R38, R39 (under all conditions), R45 and R74 (under polluted conditions); (2) the conversion of NO to NO₂, i.e., R3, R28 (under all conditions), R117 (under relatively clean conditions), R46 and R15 (under polluted conditions); (3) generation and inter-conversion of radicals such as R10-R11, R36, R37 (under all conditions), R12, R13, R116 (under relatively clean conditions), R43, R52, R54, R57, R58, R61, R63, R69 and R76 (under polluted conditions); (4) the formation and dissociation of oxidant and acid, such as HNO₃, HNO₄, PAN, H₂O₂, and CH₃OOH, i.e., R26, R29, R30 (under all conditions), R32, R33, R118 (under relatively clean conditions), and R47 (under polluted conditions). Photochemical indicators such as O₃/NO_z and H₂O₂/HNO₃ are sensitive to changes in reaction rate constants, initial species concentrations, and uptake coefficients. These indicators are found to have higher sensitivities for ROG reactions and lower sensitivities for NO_x reactions under polluted conditions as compared to less polluted conditions. Aerosol surface uptake is important when the total surface area is larger than 1000 μm² cm⁻³, i.e., under the Urban and Heavypoll conditions. The identified important heterogeneous processes include aerosol surface uptake of HCHO, O₃, HO₂, HNO₂, HNO₃, NO, NO₂, N₂O₅, PAN, H₂O₂, CH₃O₂ and SO₂. These uptake processes can affect not only O₃ formation and its sensitivity, but also O₃-precursor relations and sensitivities of indicators.

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References

1. Lelieveld, J.; Crutzen, P.J. *Nature* 1990, 343(18), 227-233.
2. Dentener, F.J.; Carmichael, G.R.; Zhang Y.; Lelieveld J.; Cruzen, P.J. *J. Geophys. Res.* 1996, 101(D17), 22869-22889.
3. Pakkanen, T.A.; Kerminen, V.-M.; Hillamo, R.E.; Makinen, M.; Makela, T.; Virkkula, A. *J. Atmos. Chem.* 1996, 24, 189-205.
4. Zhang, Y.; Saylor, R.D.; Easter, R.C.; Chapman, E.G. In *Proceedings of the 89th Annual Meeting & Exhibition*, Air & Waste management Association, 1996; No. 96-FA130B.02, pp. 1-16.
5. Bischof, C.; Carle, A.; Corliss, G.; Griewank, A.; Hovland, P. *Scientific Programming* 1992, 1(1), 11-29.
6. Zhang, Y.; Bischof, C.; Easter, R.C.; Wu, P.-T. *J. Geophys. Res.* 1996, in preparation.
7. Gery, M.W.; Whitten, G.Z.; Killus, J.P.; Dodge, M.C. *J. Geophys. Res.* 1989, 94 (D10), 12925-12956.
8. Yin, F.; Grosjean, D.; Seinfeld, J.H. *J. Atmos. Chem.* 1990, 11, 309-364.
9. Pandis, S.N.; Seinfeld, J.H., *J. Geophys. Res.* 1989, 94(D1), 1105-1126.
10. Astarita, G. *Mass Transfer with Chemical Reaction*, Elsevier, New York, 1967.
11. Heikes, B.G.; Thompson, A.M. *J. Geophys. Res.* 1983, 88(C15), 10883-10895.
12. Griewank, A.; Gorliss, G., *Automatic Differentiation of Algorithms: Theory, Implementation, and Application*, SIAM, Philadelphia, PA, 1991.

13. Milford, J.B.; Gao, D.; Sillman, S.; Blossey, Peter; Russell, A.G. *J. Geophys. Res.* 1994, 99(D2), 3533-3542.
14. Sillman, S. *J. Geophys. Res.* 1995, 100(D7), 14175-14188.
15. Gao, D.; Stockwell, W.R.; Milford, J.B. *J. Geophys. Res.* 1995, 100(D11), 23153-23166.
16. Carmichael, G.R.; Sandu, A.; Potra, F.A. *Atmos. Environ.* 1997, 31(3), 475-489.

Table 1. Gas-phase species in MaTChM and lumped species used in sensitivity analysis.

No.	Species Name	Representation	No.	Species Name	Representation
1	Nitric oxide	NO	32	Isoprene	ISOP
2	Nitrogen dioxide	NO2	33	unknown organic oxidation product of nitrogen species	NTR
3	Nitrogen trioxide (nitrate radical)	NO3	34	Dimethyl sulfide, (CH3)2S	DMS
4	Dinitrogen pentoxide	N2O5	35	Methyl sulfonyl radical	CH3SO2
5	Nitrous acid	HONO	36	Methyl sulfonic radical	CH3SO3
6	Nitric acid	HNO3	37	Methane sulfonic acid (CH3SO3H)	MSA
7	Peroxynitric acid (HO2NO2)	PNA	38	Dimethyl sulfoxide (CH3)2SO	DMSO
8	Oxygen atom (singlet)	O(1D)	39	Dimethyl sulfone (CH3)2SO2	DMSO2
9	Oxygen atom (triplet)	O(3P)	40	Methyl sulfonyl acid	CH3SO2H
10	Hydroxyl radical	OH	41	Methyl sulfonyl peroxy radical	CH3S(O)2OO
11	Ozone	O3	42	Dimethyl sulfide peroxy radical	CH3SCH2OO
12	Hydroperoxy radical	HO2	43	Dimethyl sulfonyl peroxy radical	CH3S(O)2CH2OO
13	Hydrogen peroxide	H2O2	44	Sulfur dioxide	SO2
14	Formaldehyde (CH2=O)	HCHO	45	Sulfuric acid	H2SO4
15	Carbon monoxide	CO	46	Unkown oxidation product of sulfur species	SULF
16	High molecular weight aldehydes (RCHO, R>H)	ALD2	47	Methane	CH4
17	Peroxyacyl radical (CH3C(O)OO·)	C2O3	48	Ethane	C2H6
18	Peroxyacyl nitrate(CH3C(O)OONO2)	PAN	49	Methyl peroxy radical	CH3O2
19	NO-toNO2 operation	XO2	50	Ethyl peroxy radical	ETHP
20	Paraffin carbon bond (C-C)	PAR	51	Methyl peroxide	CH3OOH
21	Secondary organic oxy radical	ROR	52	Acetic acid	CH3COOH
22	NO-to-nitrate operation	XO2N	53	Formic acid	HCOOH
23	Olefinic carbon bond (C=C)	OLE	54	Methane alcohol	CH3OH
24	Ethene(CH2=CH2)	ETH	55	Carbon dioxide	CO2
25	Toluene(C6H5-CH3)	TOL	56	Ammonium	NH3
26	Cresol and higher molecular weight phenols	CRES	57	Hydrogen chloride	HCl
27	Toluene-hydroxyl radical adduct	TO2	Lumped species		
28	Methylphenoxy radical	CRO	58	Nitrogen oxides =NO+NO2	NOx
29	High molecular weight aromatic oxidation ring fragment	OPEN	59	Total reactive nitrogen =NO+NO2+NO3+N2O5+HNO3+PAN+NTR	NOy
30	Xylene(C6H4-(CH3)2)	XYL	60	Total non-NOx reactive nitrogen =NOy-NOx	NOz
31	Methylglyoxal (CH3C(O)C(O)H)	MGLY	61	Odd hydrogen =OH + HO2 +CH3O2+ETHP+C2O3+ROR+TO2+CRO	RxOy

Table 2. Aerosol-phase species and their uptake coefficients on aerosol surfaces.

No.	Species	γ	No.	Species	γ	No.	Species	γ
1	HNO3	1.0E-2	11	NH3	9.7E-3	21	CH3O2	5.0E-3
2	HNO2	5.0E-3	12	HO2	1.0E-2	22	CH3OH	3.4E-3
3	SO2	2.4E-3	13	H2O2	4.5E-2	23	DMS	7.4E-3
4	H2SO4	2.0E-3	14	HCHO	1.0E-3	24	DMSO	7.4E-3
5	HCl	1.0E-2	15	NO2	6.3E-5	25	DMSO2	7.9E-3
6	Cl	3.0E-5	16	NO	1.0E-6	26	CH3OOH	2.9E-3
7	HCOOH	4.7E-3	17	NO3	1.0E-3	27	CH3COOOH	2.9E-3
8	CH3COOH	4.7E-3	18	PAN	1.0E-4	28	N2O5	5.0E-3
9	CO2	1.0E-5	19	O3	5.3E-5	29	NTR	1.0E-7
10	MSA	9.0E-3	20	OH	3.5E-3			

Table 3. Gas-phase photooxidation mechanism in MaTChM.

No.	Reaction	Rate constant, cm ³ molecule ⁻¹ s ⁻¹	No.	Reaction	Rate constant, cm ³ molecule ⁻¹ s ⁻¹
<u>Inorganic Reactions</u>					
1.	NO ₂ + hν → NO + O(³ P)	Radiation Dependent	34.	H ₂ O ₂ + hν → 2OH	Radiation Dependent
2.	O(³ P) $\xrightarrow{\nu^2, M}$ O ₃	1.4E+03 exp(1175/T)	35.	OH + H ₂ O ₂ → HO ₂	3.1E-12 exp(-187/T)
3.	O ₃ + NO → NO ₂	1.8E-12 exp(-1370/T)	36.	CO + OH $\xrightarrow{\nu^2}$ HO ₂	2.2E-13
4.	O(³ P) + NO ₂ → NO	9.3E-12	<u>Formaldehyde Reactions</u>		
5.	O(³ P) + NO ₂ \xrightarrow{M} NO ₃	1.6E-13 exp(687/T)	37.	FORM + OH $\xrightarrow{\nu^2}$ HO ₂ + CO	1.0E-11
6.	O(³ P) + NO \xrightarrow{M} NO ₂	2.2E-13 exp(602/T)	38.	FORM + hν $\xrightarrow{2\nu^2}$ 2HO ₂ + CO	Radiation Dependent
7.	O ₃ + NO ₂ → NO ₃	1.2E-13 exp(-2450/T)	39.	FORM + hν → CO	Radiation Dependent
8.	O ₃ + hν → O(³ P)	Radiation Dependent	40.	FORM + O(³ P) → OH + HO ₂ + CO	3.0E-11 exp(-1550/T)
9.	O ₃ + hν → O(¹ D)	Radiation Dependent	41.	FORM + NO ₃ $\xrightarrow{\nu^2}$ HNO ₃ + HO ₂ + CO	6.3E-16
10.	O(¹ D) \xrightarrow{M} O(³ P)	1.19E+08 exp(390/T)	<u>Higher Molecular Weight Aldehyde Reactions</u>		
11.	O(¹ D) + H ₂ O → 2OH	2.2E-10	42.	ALD2 + O(³ P) $\xrightarrow{\nu^2}$ C2O3 + OH	1.2E-11 exp(-986/T)
12.	O ₃ + OH → HO ₂	1.6E-12 exp(-940/T)	43.	ALD2 + OH → C2O3	7.0E-12 exp(250/T)
13.	O ₃ + HO ₂ → OH	1.4E-14 exp(-580/T)	44.	ALD2 + NO ₃ $\xrightarrow{\nu^2}$ C2O3 + HNO ₃	2.5E-15
14.	NO ₃ + hν → .89NO ₂ + .11NO	Radiation Dependent	45.	ALD2 + hν $\xrightarrow{2\nu^2}$ CH ₃ O ₂ + HO ₂ + CO	Radiation dependent
15.	NO ₃ + NO → 2NO ₂	1.3E-11 exp(250/T)	46.	C2O3 + NO $\xrightarrow{\nu^2}$ CH ₃ O ₂ + NO ₂	5.4E-12 exp(250/T)
16.	NO ₃ + NO ₂ → NO + NO ₂	2.5E-14 exp(-1230)	47.	C2O3 + NO ₂ → PAN	8.0E-20 exp(5500/T)
17.	NO ₃ + NO ₂ \xrightarrow{M} N ₂ O ₅	5.3E-13 exp(256/T)	48.	PAN → C2O3 + NO ₂	9.4E+16 exp(-14000/T)
18.	N ₂ O ₅ + H ₂ O → 2HNO ₃	1.3E-21	49.	C2O3 + C2O3 → 2CH ₃ O ₂ + O ₂	2.0E-12
19.	N ₂ O ₅ \xrightarrow{M} NO ₃ + NO ₂	3.5E+14 exp(-10897/T)	50.	C2O3 + HO ₂ → .79CH ₃ O ₂ + .79OH	6.5E-12
20.	NO + NO $\xrightarrow{\nu^2}$ 2NO ₂	1.8E-20 exp(530/T)	<u>Alkane Reactions</u>		
21.	NO + NO ₂ + H ₂ O → 2HONO	4.4E-40	51.	C2H6 + OH → ETHP	T ² 1.37E-17 exp(-444/T)
22.	OH + NO \xrightarrow{M} HONO	4.5E-13 exp(806/T)	52.	PAR + OH → .87XO ₂ + .13XO ₂ N + .11HO ₂	8.1E-13
23.	HONO + hν → OH + NO	Radiation Dependent	+ .11ALD2 + .76ROR - .11PAR		
24.	OH + HONO → NO ₂	6.6E-12	53.	ROR → 1.1ALD2 + .96XO ₂ + .94HO ₂	1.0E+15 exp(-8000/T)
25.	HONO + HONO → NO + NO ₂	1.0E-20	+ .04XO ₂ N + .02ROR - 2.1PAR		
26.	OH + NO ₂ \xrightarrow{M} HNO ₃	1.0E-12 exp(713/T)	54.	ROR → HO ₂	1.6E+3
27.	OH + HNO ₃ \xrightarrow{M} NO ₃	5.1E-15 exp(1000/T)	55.	ROR + NO ₂ → NITRATES	1.5E-11
28.	HO ₂ + NO → OH + NO ₂	3.7E-12 exp(240/T)	<u>Alkene Reactions</u>		
29.	HO ₂ + NO ₂ \xrightarrow{M} PNA	1.2E-13 exp(749/T)	56.	OLE + O(³ P) → .63ALD2 + .38HO ₂ + .28XO ₂ + .3CO	1.2E-11 exp(-324/T)
30.	PNA \xrightarrow{M} HO ₂ + NO ₂	4.8E+13 exp(-10121/T)	+ .2HCHO + .02XO ₂ N + .22PAR + .2OH		
31.	OH + PNA → NO ₂	1.3E-12 exp(380/T)	57.	OLE + OH → CH ₃ O ₂ + ALD2 - PAR	5.2E-12 exp(504/T)
32.	HO ₂ + HO ₂ → H ₂ O ₂	5.9E-14 exp(1150/T)	58.	OLE + O ₃ → .5ALD2 + .524HCHO + .33CO + .228HO ₂	1.4E-14 exp(-2105/T)
33.	HO ₂ + HO ₂ + H ₂ O → H ₂ O ₂	2.2E-38 exp(5800/T)	+ .1OH + .216CH ₃ O ₂ - PAR		
			59.	OLE + NO ₃ → 91XO ₂ + HCHO + ALD2 + .09XO ₂ N + NO ₂ - PAR	7.7E-15
			60.	ETH + O(³ P) → .3HCHO + .7CH ₃ O ₂ + CO + HO ₂ + .3OH	1.0E-11 exp(-792/T)
			61.	ETH + OH → XO ₂ + 1.56HCHO + HO ₂ + .22ALD2	2.0E-12 exp(411/T)

Read 1.4E+03 exp(1175/T) as 1.4 x 10³ e^{1175/T}.

Table 3. Continued.

No.	Reaction	Rate constant, cm ³ molecule ⁻¹ s ⁻¹	No.	Reaction	Rate constant, cm ³ molecule ⁻¹ s ⁻¹
62.	ETH + O ₃ ⇌ HCHO + .42CO + .12HO ₂	1.3E-14 exp(-2633/T)	93.	CH ₃ S(O) ₂ CH ₂ OO+HO ₂ ⇌CH ₃ S(O) ₂ CH ₂ OOH+O ₂	1.5E-12
	<u>Aromatic Reactions</u>		94.	CH ₃ SO ₂ H + HO ₂ ⇌ CH ₃ SO ₂ + H ₂ O ₂	1.0E-15
63.	TOL + OH ⇌ .08XO ₂ + .36CRES + .44HO ₂ + .56TO ₂	2.1E-12 exp(322/T)	95.	CH ₃ SO ₂ H + NO ₃ ⇌ CH ₃ SO ₂ + HNO ₃	1.0E-13
64.	TO ₂ + NO ⇌ .9NO ₂ + .9OPEN + .9HO ₂	8.1E-12	96.	CH ₃ SO ₂ H + CH ₃ O ₂ ⇌ CH ₃ SO ₂ + CH ₃ OOH	1.0E-15
65.	TO ₂ ⇌ CRES	4.2	97.	CH ₃ SO ₂ H + OH ⇌ CH ₃ SO ₂ + H ₂ O	1.6E-11
66.	CRES + OH ⇌ .4CRO + .6XO ₂ + .6HO ₂ + .3OPEN	4.1E-11	98.	CH ₃ SO ₂ H + CH ₃ SO ₃ ⇌ CH ₃ SO ₂ + MSA	1.0E-13
67.	CRES + NO ₃ ⇌ CRO + HNO ₃	2.2E-11	99.	CH ₃ SO ₂ \xrightarrow{M} SO ₂ + CH ₃ O ₂	4.53E+13exp(-8656/T)
68.	CRO + NO ₂ ⇌ NITRATES	1.4E-11	100.	CH ₃ SO ₂ + NO ₂ ⇌ CH ₃ SO ₃ + NO	1.0E-14
69.	XYL + OH ⇌ .7OH + .5XO ₂ + .2CRES + .8MGLY + 1.1PAR + .3TO ₂	1.7E-11 exp(116/T)	101.	CH ₃ SO ₂ + O ₃ ⇌ CH ₃ SO ₃ + O ₂	5.0E-15
70.	OPEN + OH ⇌ XO ₂ + C ₂ O ₃ + 2HO ₂ + 2CO + HCHO	3.0E-11	102.	CH ₃ SO ₂ + HO ₂ ⇌ CH ₃ SO ₃ + OH	2.5E-13
71.	OPEN + hv ⇌ C ₂ O ₃ + CO + HO ₂	Radiation dependent	103.	CH ₃ SO ₂ + CH ₃ O ₂ ⇌CH ₃ SO ₃ +CH ₃ O+ O ₂	2.5E-13
72.	OPEN + O ₃ ⇌ .03ALD ₂ + .62C ₂ O ₃ + .7HCHO+ .03XO ₂ + .69CO + .08OH + .76HO ₂ + .2MGLY	5.4E-17exp(-500/T)	104.	CH ₃ SO ₂ + OH ⇌ MSA	5.0E-11
73.	MGLY + OH ⇌ XO ₂ + C ₂ O ₃	1.7E-11	105.	CH ₃ SO ₂ + O ₂ \xrightarrow{M} CH ₃ S(O) ₂ OO	2.6E-18
74.	MGLY + hv ⇌ C ₂ O ₃ + CO + HO ₂	Radiation dependent	106.	CH ₃ S(O) ₂ OO \xrightarrow{M} CH ₃ SO ₂ + O ₂	3.3
	<u>Isoprene Reactions</u>		107.	CH ₃ S(O) ₂ OO + NO ⇌ CH ₃ SO ₃ + NO ₂	1.0E-11
75.	ISOP + O(³ P) ⇌ .6HO ₂ + .8ALD ₂ + .55OLE + .5XO ₂ + .5CO + .45ETH + .9PAR	1.8E-11	108.	CH ₃ S(O) ₂ OO+CH ₃ O ₂ ⇌CH ₃ SO ₃ +CH ₃ O+O ₂	5.5E-12
76.	ISOP + OH ⇌ HCHO + XO ₂ + .67HO ₂ + .4MGLY + .2C ₂ O ₃ + ETH + .2ALD ₂ + .13XO ₂ N	9.6E-11	109.	CH ₃ S(O) ₂ OO+HO ₂ ⇌CH ₃ S(O) ₂ OOH+O ₂	2.0E-12
77.	ISOP + O ₃ ⇌ HCHO + .4ALD ₂ + .55ETH + .2MGLY + .06CO + .1PAR + .44HO ₂ + .1OH	1.2E-17	110.	CH ₃ SO ₃ \xrightarrow{M} H ₂ SO ₄ + CH ₃ O ₂	1.6E-1
78.	ISOP + NO ₃ ⇌ XO ₂ N + NITRATES	3.2E-13	111.	CH ₃ SO ₃ + NO ₂ ⇌ MSA + HNO ₃	3.0E-15
	<u>Operator Reactions</u>		112.	CH ₃ SO ₃ + NO ⇌ MSA + HNO ₂	3.0E-15
79.	XO ₂ + NO ⇌ NO ₂	8.1E-12	113.	CH ₃ SO ₃ + HO ₂ ⇌ MSA + O ₂	5.0E-11
80.	XO ₂ + XO ₂ ⇌ Products	1.7E-14 exp(1300/T)	114.	CH ₃ SO ₃ + HCHO $\xrightarrow{a^2}$ MSA+HO ₂ +CO	1.6E-15
81.	XO ₂ N + NO ⇌ NITRATES	6.8E-13	115.	SO ₂ + OH \xrightarrow{M} H ₂ SO ₄ + HO ₂	Troe expression
	<u>Condensed DMS Chemistry</u>			<u>Methane and Methylperoxyl Radical Reactions</u>	
82.	DMS + OH ⇌ CH ₃ SCH ₂ OO + H ₂ O	9.64E-12 exp(-234/T)	116.	CH ₄ + OH $\xrightarrow{a^2}$ CH ₃ O ₂	T ² 6.95E-18exp(-1280/T)
83.	DMS + NO ₃ ⇌ CH ₃ SCH ₂ OO + HNO ₃	1.40E-13 exp(500/T)	117.	CH ₃ O ₂ + NO ⇌ HCHO + HO ₂ + NO ₂	4.2E-12 exp(180/T)
84.	DMS + O(³ P) ⇌ CH ₃ SO ₂ + CH ₃ O ₂	1.26E-11 exp(409/T)	118.	CH ₃ O ₂ + HO ₂ ⇌ CH ₃ OOH	7.7E-14 exp(1300/T)
85.	DMS + OH ⇌ aCH ₃ SO ₂ + aCH ₃ O ₂ + (1-a)DMSO + (1-a)HO ₂	1.7E-12 (see note)	119.	CH ₃ O ₂ + CH ₃ O ₂ ⇌ 1.5HCHO + HO ₂	1.9E-13 exp(220/T)
86.	CH ₃ SCH ₂ OO + NO ⇌ CH ₃ SO ₂ + HCHO + NO ₂	8.0E-12	120.	CH ₃ O ₂ + C ₂ O ₃ ⇌ HCHO + .5HO ₂ + .5CH ₃ O ₂ + CH ₃ OOH	9.6E-13 exp(220/T)
87.	CH ₃ SCH ₂ OO + CH ₃ O ₂ ⇌ CH ₃ SO ₂ + CH ₃ O + HCHO	1.8E-13	121.	CH ₃ OOH + hv ⇌ HCHO + HO ₂ + OH	5.57E-06
88.	CH ₃ SCH ₂ OO + HO ₂ ⇌ CH ₃ SCH ₂ OOH	1.5E-12	122.	CH ₃ OOH+OH⇌.5CH ₃ O ₂ + .5HCHO+ .5OH	1.0E-11
89.	DMSO+OH⇌bCH ₃ SO ₂ H+bCH ₃ O ₂ +(1-b)DMSO ₂ + (1-b)HO ₂	5.8E-11 (see note)	123.	ETHP + NO ⇌ ALD ₂ + HO ₂ + NO ₂	4.2E-12 exp(180/T)
90.	DMSO ₂ + OH ⇌ CH ₃ S(O) ₂ CH ₂ OO + H ₂ O	1.0E-14	124.	ETHP + HO ₂ ⇌ Products	7.7E-14 exp(1300/T)
91.	CH ₃ S(O) ₂ CH ₂ OO + NO ⇌ CH ₃ SO ₂ + HCHO + NO ₂	5.0E-12	125.	ETHP + C ₂ O ₃ ⇌ ALD ₂ + .5HO ₂ + .5CH ₃ O ₂ + .5CH ₃ COOH	3.4E-13 exp(220/T)
92.	CH ₃ S(O) ₂ CH ₂ OO + CH ₃ O ₂ ⇌ CH ₃ SO ₂ + HCHO + CH ₃ O	1.8E-13		Note: a = 5E+5/(5E+5 + [O ₂] X 3E-12); b = 1.5E+7/(1.5E+7 + [O ₂] X 1.2E-12)	

Table 4. Initial gas-phase concentrations (in ppb) and pre-existing aerosol data in the model simulations.

Species	Remote	Marine	Rural	Urban	Heavypoll
O3	20.0	30.0	40.0	60.0	80.0
H2O2	1.0	1.0	1.0	1.0	1.0
NO	7.5×10^{-2}	7.5×10^{-1}	1.5	10.0	55.0
NO2	2.5×10^{-2}	2.5×10^{-1}	0.5	1.0	55.0
SO2	0.6	0.6	2.0	5.0	10.0
DMS	4.0×10^{-2}	4.0×10^{-2}	0.0	0.0	0.0
HCHO	0.2	1.8	0.2	8.3	27.5
ALD2	0.0	0.0	8.3×10^{-2}	11.7	39.0
C2H6	0.0	1.9	1.58	9.08	30.3
PAR	0.0	3.1	9.8	177.9	593.1
OLE	0.0	5.6×10^{-1}	0.3	13.2	44.0
ETH	0.0	1.9×10^{-1}	0.6	11.6	38.5
TOL	0.0	3.6×10^{-2}	5.3×10^{-1}	6.0	19.9
XYL	0.0	0.0	7.5×10^{-2}	3.2	10.5
ISOP	0.0	0.0	2.4×10^{-1}	0.5	2.0
CO	80.0	100.0	120.0	150.0	300.0
CH4	1.7×10^3	1.7×10^3	1.6×10^3	1.7×10^3	1.7×10^3
CO2	3.4×10^5	3.4×10^5	3.4×10^5	3.4×10^5	3.4×10^5
NH3	0.1	0.5	0.5	0.5	0.5
HCl	0.5	0.5	0.1	0.0	0.0
Aerosol number (cm ⁻³)	1.50×10^2	4.03×10^2	8.78×10^3	1.38×10^5	2.15×10^6
Aerosol surface (μm ² cm ⁻³)	1.39×10^1	2.93×10^1	1.36×10^2	1.13×10^3	3.27×10^3

Table 5. 1-hr averaged sensitivities of O3 w.r.t. reaction rate constants under clear air conditions.

Rank	Remote		Marine		Rural		Urban		Heavypoll	
	Rxn. #	Sensitivity	Rxn. #	Sensitivity	Rxn. #	Sensitivity	Rxn. #	Sensitivity	Rxn. #	Sensitivity
1	28	2.01E-2	1	6.03E-2	11	4.67E-2	38	1.20E-1	3	-2.58E-1
2	1	1.86E-2	3	-4.92E-2	10	-4.67E-2	43	-1.14E-1	1	2.77E-1
3	3	-1.29E-2	28	4.40E-2	9	4.47E-2	1	1.10E-1	38	1.85E-1
4	116	6.44E-3	26	-3.25E-2	1	4.13E-2	3	-1.06E-1	26	-1.75E-1
5	117	4.38E-3	11	2.26E-2	26	-4.10E-2	57	8.06E-2	57	1.23E-1
6	118	-4.05E-3	10	-2.26E-2	3	-3.87E-2	26	-6.34E-2	43	-8.70E-2
7	26	-3.94E-3	9	2.17E-2	36	1.54E-2	11	5.10E-2	45	5.07E-2
8	33	-3.33E-3	38	2.10E-2	116	1.50E-2	10	-5.10E-2	47	-4.11E-2
9	32	-2.81E-3	116	1.97E-2	28	1.32E-2	9	4.88E-2	46	4.11E-2
10	13	-2.62E-3	36	1.46E-2	38	1.04E-2	47	-4.60E-2	58	4.01E-2
11	34	2.29E-3	43	-9.41E-3	61	8.65E-3	46	4.60E-2	61	3.93E-2
12	12	-1.50E-3	33	-8.24E-3	34	8.48E-3	61	3.31E-2	69	3.79E-2
13	36	1.33E-3	32	-6.95E-3	47	-7.96E-3	45	2.98E-2	52	3.38E-2
14	38	1.12E-3	47	-6.72E-3	46	7.94E-3	69	2.82E-2	39	-2.74E-2
15	29	-7.65E-4	46	6.61E-3	43	-6.15E-3	28	2.35E-2	11	2.61E-2
16	30	7.48E-4	117	6.29E-3	52	6.14E-3	52	2.22E-2	10	-2.61E-2
17	97	-5.59E-4	34	6.03E-3	74	5.21E-3	58	2.08E-2	9	2.49E-2
18	89	-5.58E-4	118	-5.64E-3	57	3.72E-3	74	1.74E-2	74	1.71E-2
19	11	5.36E-4	37	4.84E-3	76	3.52E-3	39	-1.68E-2	28	1.50E-2
20	10	-5.36E-4	39	-3.72E-3	29	-3.20E-3	29	-1.47E-2	29	-1.46E-2
21	85	3.70E-4	29	-3.58E-3	30	3.12E-3	30	1.42E-2	30	1.44E-2
22	9	3.07E-4	30	3.43E-3	63	2.26E-3	37	6.26E-3	4	-1.42E-2
23	122	-2.55E-4	13	-3.04E-3	37	2.05E-3	34	6.12E-3	63	1.11E-2
24	22	-2.25E-4	57	2.88E-3	22	-1.99E-3	63	5.53E-3	76	9.99E-3
25	23	1.88E-4	61	2.55E-3	69	1.90E-3	36	4.17E-3	2	8.87E-3

Read 2.01E-2 as 2.01×10^{-2} .

Table 6. Sensitivities of odd hydrogen w.r.t. reaction rate constants under clear air conditions.

Rank	Remote		Marine		Rural		Urban		Heavypoll	
	Rxn. #	Sij	Rxn. #	Sij	Rxn. #	Sij	Rxn. #	Sij	Rxn. #	Sij
1	9	3.65E-1	9	5.16E-1	11	1.03E+0	38	8.42E-1	38	7.17E-1
2	11	3.52E-1	11	5.05E-1	10	-1.03E+0	28	-5.80E-1	28	-6.53E-1
3	10	-3.52E-1	10	-5.05E-1	9	1.03E+0	43	-5.69E-1	26	-6.21E-1
4	118	-1.80E-1	38	2.90E-1	28	-4.99E-1	11	4.03E-1	57	4.48E-1
5	33	-1.62E-1	116	1.72E-1	26	-4.27E-1	10	-4.03E-1	43	-3.21E-1
6	116	1.49E-1	33	-1.61E-1	116	2.54E-1	9	4.02E-1	117	-2.54E-1
7	32	-1.37E-1	32	-1.36E-1	38	2.46E-1	57	3.60E-1	58	2.34E-1
8	34	1.28E-1	117	-1.09E-1	36	2.02E-1	1	-3.20E-1	3	2.34E-1
9	117	-1.22E-1	34	1.06E-1	34	1.63E-1	3	2.88E-1	1	-2.28E-1
10	28	8.71E-2	118	-9.78E-2	1	-1.61E-1	26	-2.77E-1	45	2.09E-1
11	36	-6.94E-2	37	-8.74E-2	3	1.41E-1	117	-2.48E-1	69	1.72E-1
12	38	5.26E-2	39	-6.87E-2	117	-1.38E-1	47	-2.45E-1	39	-1.65E-1
13	37	-1.95E-2	26	-6.81E-2	74	1.12E-1	69	2.26E-1	47	-1.57E-1
14	1	-1.50E-2	47	-5.06E-2	47	-1.06E-1	46	2.24E-1	46	1.42E-1
15	35	-1.26E-2	36	4.16E-2	46	9.31E-2	45	2.10E-1	9	1.23E-1

Table 7. Sensitivities of O₃ and indicators w.r.t. uptake coefficients of individual species. Only those sensitivities greater than 1.0E-4 are shown.

(a) O₃

	Remote		Marine		Rural		Urban		Heavypoll	
	Species	Sij	Species	Sij	Species	Sij	Species	Sij	Species	Sij
Sij>0	--	--	--	--	--	--	NO	3.46E-4	NO	7.51E-3
							SO2	2.08E-4	SO2	1.98E-4
Sij<0	O3	-6.55E-4	O3	-1.31E-3	O3	-6.30E-3	O3	-4.67E-2	O3	-1.04E-1
			H2O2	-2.76E-4	HO2	-2.13E-3	HCHO	-2.49E-2	HCHO	-6.34E-2
			HO2	-2.54E-4	H2O2	-1.74E-3	HO2	-1.28E-2	NO2	-8.06E-3
					HCHO	-3.59E-4	H2O2	-1.43E-3	HO2	-3.47E-3
							CH3O2	-3.56E-4	N2O5	-2.15E-3
							NO2	-2.98E-4	HNO2	-1.28E-3
							N2O5	-2.96E-4	H2O2	-2.79E-4
							HNO2	-2.23E-4		

(b) O₃/NO_z and H₂O₂/HNO₃

	Urban				Heavypoll			
	O3/NOz		H2O2/HNO3		O3/NOz		H2O2/HNO3	
	Species	Sij	Species	Sij	Species	Sij	Species	Sij
Sij>0	HNO3	8.18E-2	HNO3	4.63E-1	HNO3	2.22E-1	HNO3	9.01E-1
	HCHO	7.71E-2	NO2	1.59E-2	HCHO	1.76E-1	NO2	8.37E-2
	HO2	4.53E-2	N2O5	8.05E-3	PAN	2.96E-2	NO	3.09E-2
	PAN	1.11E-2	NO	4.21E-3	HO2	1.01E-2	N2O5	1.07E-2
	H2O2	6.10E-3	HNO2	5.31E-4	HNO2	6.96E-3	SO2	9.14E-4
	HNO2	1.22E-3	SO2	2.80E-4	NO	4.73E-3		
	CH3O2	1.03E-3			H2O2	9.61E-4		
	N2O5	8.94E-4			CH3O2	2.01E-4		
	NO	3.25E-4						
Sij<0	O3	3.73E-2	H2O2	-3.46E+0	O3	-8.08E-2	H2O2	-2.99E+0
	SO2	9.12E-4	HCHO	-6.19E-2	NO2	-1.03E-2	HCHO	-3.44E-1
			HO2	-1.64E-2	SO2	-9.29E-4	O3	-1.13E-1
			O3	-9.60E-3	N2O5	-2.60E-4	HO2	-1.75E-2
			CH3O2	-3.90E-4			HNO2	-3.93E-3
							PAN	-4.97E-4
							CH3O2	-4.06E-4