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Clouds and Wet Removal as Causes of Variability in the Trace-Gas Composition of the Marine Troposphere

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We describe a modeling study of the effects of clouds and wet removal on the chemistry of the remote marine troposphere. Using a time-dependent model with parameterized vertical transport to calculate trace-gas concentrations, we find that large variations in key species (e.g., HNO_3 , H_2CO , and H_2O_2) result from simulations of sporadic rainfall, changes in cloud cover, and external inputs such as surface NO sources. Depending on the frequency and intensity of an event, the effects of these perturbations may persist for several days, thereby invalidating assumptions of photochemical equilibrium in the interpretation of measurements. Long-term integrations with fixed boundary conditions and regularly occurring cloud and rain episodes demonstrate a strong sensitivity of the mean concentration of longer-lived soluble gases to precipitation frequency but also confirm the validity of using properly chosen parameterizations of wet removal in steady state calculations. The marine atmosphere is represented in our model by selecting boundary conditions such as oceanic albedo and lower background NO_x and hydrocarbons than observed over continents. The numerical model includes fairly complete gas-phase photochemistry, multiple scattering optics, and a simple parameterization of a marine boundary layer. Although a simple one-dimensional vertical transport is assumed, we demonstrate clearly that rainfall and cloud-cover changes contribute to species variability. Sensitivities to exchange rates of gases with the sea surface are also discussed.

1. INTRODUCTION

Trace gas photochemistry in the marine troposphere may be highly variable in both time and space. Spatial variability, for example, between remote marine and coastal regions, may be caused by differences in background meteorology and characteristic physical and chemical processes. Temporal variability within a given environment may result from changes in sea state, synoptic weather conditions, and episodic alterations in chemical inputs. Realistic modeling of marine boundary-layer chemistry, therefore, requires time-dependent chemical transport, rates of photolysis, and heterogeneous removal of trace gases. The latter is very complex and includes gas-particle and air-sea transfer, chemical transformations within aerosols, clouds, rainwater, and on the sea surface.

We report here the results of a modeling study that considers one aspect of the variability due to heterogeneous processes, namely, the influence of sporadic clouds and precipitation removal on trace gas distributions in the marine troposphere. Using a one-dimensional time-dependent transport-kinetics model to simulate these processes, we find that in a given air mass the concentrations of key species, particularly soluble gases such as HNO_3 , CH_2O , and the peroxides, may change by a factor of 5–10 in a few hours as a consequence of washout below a precipitating cloud. Further, depending on the mean cloud and precipitation frequency of a given environment, the spatial variability of these same compounds may also approach an order of magnitude. Even without wet removal an extended period of cloudiness may cause substantial changes in trace gas distributions.

These results are not simply of theoretical interest because to date measurements of trace species have been so few in

number and irregular in time and space that their interpretations depend on our understanding their allowable variations. It turns out, for example, that a short-lived perturbation may disrupt the photostationary relations among some gases for a number of days so that field measurements of these species are difficult to rationalize without a knowledge of the recent history of the air mass being sampled.

We first describe our model of the marine atmosphere (section 2) and some sensitivities of background level chemistry to various assumptions of chemical inputs (i.e., boundary conditions) (section 3). Sensitivities arise because one-dimensional transport restricts time-dependent calculations to a fairly uniform air mass and time-dependent simulations are always started from an initial condition with a fixed ozone profile and corresponding diurnal behavior for the other gases. In section 4 we consider two basic types of synoptic events, focusing on their effects on odd nitrogen and soluble gases. In section 5, assuming that certain synoptic episodes are regular events, we present the results of long-term integrations to look at effects on ozone and to test steady state assumptions of wet and dry removal of soluble gases.

2. MODEL

Chemical distributions of trace gases are determined as a function of altitude from a system of one-dimensional transport-kinetics equations where the time rate of change of species j is the sum of its chemical reaction rates and flux divergence, represented by eddy diffusion:

$$\frac{\partial}{\partial z} \left[K(z) N(z) \frac{\partial \chi_j(z, t)}{\partial z} \right] + P_j(z, t) - L_j(z, t) = \frac{\partial c_j(z, t)}{\partial t} \quad (1)$$

where z = altitude, t = time; $K(z)$ = eddy diffusion coefficient; $N(z)$ = molecular density (cm^{-3}) of background air; $\chi_j(z, t)$ = mixing ratio or mole fraction of species j , $c_j(z, t)$ is concentration (cm^{-3}); $P_j(z, t)$, $L_j(z, t)$ = production, loss rates ($\text{cm}^{-3} \text{ s}^{-1}$) for chemical reaction of species j .

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TABLE 1. Fixed Tropospheric Parameters

Altitude, km	Tem- pera- ture, °K	Mixing Ratio (by volume)					
		N ₂ , cm ⁻³	O ₂ , cm ⁻³	H ₂ O	CH ₄ *	CO*	H ₂ *
15	216.6	3.16 (18)†	8.48 (17)	3.10 (-6)	1.60 (-6)	4.00 (-8)	5.15 (-7)
14	216.6	3.70 (18)	9.93 (17)	3.50 (-6)	1.60 (-6)	4.85 (-8)	5.24 (-7)
13	216.6	4.33 (18)	1.16 (18)	4.00 (-6)	1.60 (-6)	5.49 (-8)	5.30 (-7)
12	216.6	5.07 (18)	1.36 (18)	4.80 (-6)	1.60 (-6)	6.04 (-8)	5.35 (-7)
11	216.8	5.93 (18)	1.59 (18)	7.00 (-6)	1.60 (-6)	6.54 (-8)	5.38 (-7)
10	223.3	6.72 (18)	1.80 (18)	1.20 (-5)	1.60 (-6)	7.02 (-8)	5.41 (-7)
9	229.7	7.58 (18)	2.03 (18)	3.30 (-5)	1.60 (-6)	7.47 (-8)	5.43 (-7)
8	236.2	8.51 (18)	2.28 (18)	8.00 (-5)	1.50 (-6)	7.94 (-8)	5.44 (-7)
7	242.7	9.60 (18)	2.58 (18)	3.00 (-4)	1.60 (-6)	8.42 (-8)	5.46 (-7)
6	249.2	1.07 (19)	2.87 (18)	8.86 (-4)	1.60 (-6)	8.94 (-8)	5.47 (-7)
5	255.7	1.19 (19)	3.20 (18)	1.37 (-3)	1.60 (-6)	9.51 (-8)	5.48 (-7)
4	262.2	1.33 (19)	3.56 (18)	2.03 (-3)	1.60 (-6)	1.01 (-7)	5.49 (-7)
3	268.7	1.48 (19)	3.96 (18)	3.25 (-3)	1.60 (-6)	1.08 (-7)	5.49 (-7)
2	275.2	1.63 (19)	4.38 (18)	4.55 (-3)	1.60 (-6)	1.14 (-7)	5.50 (-7)
1	281.7	1.80 (19)	4.84 (18)	5.92 (-3)	1.60 (-6)	1.18 (-7)	5.50 (-7)
0.50	284.9	1.90 (19)	5.09 (18)	6.66 (-3)	1.60 (-6)	1.19 (-7)	5.50 (-7)
0.20	286.9	1.95 (19)	5.24 (18)	6.82 (-3)	1.60 (-6)	1.20 (-7)	5.50 (-7)
0.10	287.5	1.97 (19)	5.29 (18)	7.15 (-3)	1.60 (-6)	1.20 (-7)	5.50 (-7)
7.5 (-2)	287.7	1.98 (19)	5.30 (18)	7.32 (-3)	1.60 (-6)	1.20 (-7)	5.50 (-7)
5.0 (-2)	287.8	1.98 (19)	5.32 (18)	7.50 (-3)	1.60 (-6)	1.20 (-7)	5.50 (-7)
2.5 (-2)	288.0	1.99 (19)	5.33 (18)	7.50 (-3)	1.60 (-6)	1.20 (-7)	5.50 (-7)
1.25 (-2)	288.1	1.99 (19)	5.34 (18)	7.50 (-3)	1.60 (-6)	1.20 (-7)	5.50 (-7)
6.25 (-3)	288.1	1.99 (19)	5.34 (18)	7.50 (-3)	1.60 (-6)	1.20 (-7)	5.50 (-7)
0.00	288.2	1.99 (19)	5.34 (18)	7.50 (-3)	1.60 (-6)	1.20 (-7)	5.50 (-7)

Profiles for temperature, O₂, N₂, and H₂O vapor taken from U.S. Standard Atmosphere (1976).

*Mixing ratios for CO, CH₄, and H₂ are fixed at 15 and 0 km and are calculated from a steady state code to initialize time-dependent calculations. Values shown correspond to model 4 (see Table 3). For all other model boundary conditions, mixing ratios for CO vary up to 15% of values given here but do not change for H₂ and CH₄.

†Number in parenthesis signifies exponent (e.g., 3.16 (18) = 3.16 × 10¹⁸).

We simulate the marine atmosphere by assuming fixed profiles for N₂, O₂, temperature, CH₄, CO, H₂, and H₂O (Table 1) and solve the system of continuity equations (1) for the volume mixing ratios of 17 gaseous species: O₃, O(³P), NO, NO₂, NO₃, N₂O₅, HNO₃, HNO₄, H, OH, HO₂, H₂O₂ and the hydrocarbons resulting from methane oxidation CH₃, CH₃O, CH₃O₂, CH₃OOH, and CH₂O. For convenience, reference is made to collective terms: odd oxygen, O_x = O₃ + O(³P); odd nitrogen, NO_y = NO + NO₂ + HNO₃ + 2N₂O₅ + HNO₄ + NO₃; odd hydrogen, HO_x = H + OH + HO₂; however, mixing ratios are always calculated for all the individuals, not the 'group' as a whole. We point out that NO_y as we define it does not include peroxyacetyl nitrate (PAN) which may be a major form of odd nitrogen in the mid-to-upper troposphere [Singh and Hanst, 1981]; our NO_y also excludes a contribution of approximately 200 ppt due to HCN from ground-level sources [Coffey et al., 1981; Cicero-ne, 1982]. Over 50 gas-phase radical reactions and photolyses describe the kinetics of free radicals and more stable molecules; these appear in Table 2, where most of the rates are taken from the recent NASA Panel Evaluation [NASA, 1981]. Concentrations of O(¹D) are calculated from those of O₃; reactions (4), (5), and (21) and photolysis reaction (1) determine [O(¹D)].

The upper boundary is at 15 km, appropriate for a low-latitude tropopause and the equations (1) are solved by finite differencing (see below) at 24 spatial grid points. Grid intervals are at 1 km except in the lowest kilometer where the spacing is refined, minimum Δz = 6.5 m (Table 1). This permits the inclusion of a rapidly diffusing planetary bound-

ary layer and a surface boundary layer. In the standard parameterization of eddy diffusion shown in Figure 1, it is assumed that the planetary boundary layer (PBL) (characteristic diffusion coefficients, $K = 10^5$ – 10^6 cm² s⁻¹) extends to the ground. A separate surface boundary layer (SBL), a region of reduced mixing between the ground and about 50 m altitude, is simulated with a value of $K(z)$, 2–3 orders of magnitude lower than in the planetary boundary layer and which increases with altitude. [see, e.g., Businger, 1973]. The shape of $K(z)$ was chosen to give a maximum value that corresponds to a mixing period of roughly 20 min in the several hundred meters above the surface boundary layer.

Photolysis rates at each altitude are calculated as a function of solar zenith angle by integrating over the wavelength range 250–750 nm with quantum yields and absorption cross sections taken from the NASA [1981] recommendation. A refined wavelength grid is used in the near-UV to ensure accurate calculation of O₃→O(¹D) photolysis. The radiation calculation includes ozone absorption, surface reflection, and molecular scattering computed according to Luther's [1980] algorithm. Mid-latitude (30°) equinox conditions are assumed. For radiation incident at the tropopause we take the tabulated extra-terrestrial solar flux [NASA, 1979], attenuated by ozone absorption and zero-order molecular scattering calculated from overhead column densities 15–80 km: O₃-8.33 × 10¹⁸ cm⁻²; total molecules 2.58 × 10²⁴ cm⁻² [Valley, 1964]. For clear sky conditions, surface albedos appropriate for the sea surface are specified as a function of solar zenith angle [Payne, 1972]. In certain specified model calculations we represent a simple cloud in the model by

TABLE 2. Reactions and Rate Constants

Reaction	Rate Constants
$O + O_2 + M \rightarrow O_3 + M$	$k_1 = 5.58 \times 10^{-29}/T^2$
$O + O_3 \rightarrow 2O_2$	$k_2 = 1.5 \times 10^{-11} \exp(-2200/T)$
$O + O + M \rightarrow O_2 + M$	$k_3 = 4.26 \times 10^{-28}/T^2$
$O(^1D) + N_2 \rightarrow O + N_2$	$k_4 = 1.8 \times 10^{-11} \exp(107/T)$
$O(^1D) + O_2 \rightarrow O + O_2$	$k_5 = 3.2 \times 10^{-11} \exp(67/T)$
$NO + O_3 \rightarrow NO_2 + O_2$	$k_{10} = 2.3 \times 10^{-12} \exp(-1450/T)$
$NO_2 + O \rightarrow NO + O_2$	$k_{11} = 9.3 \times 10^{-12}$
$NO_2 + O_3 \rightarrow NO_3 + O_2$	$k_{14} = 1.2 \times 10^{-13} \exp(-2450/T)$
$NO + NO_3 \rightarrow 2NO_2$	$k_{15} = 2 \times 10^{-11}$
$NO + O + M \rightarrow NO_2 + M$	$k_{16}^*: k_0 = 3.45 \times 10^{-27}/T^{1.8}; k_\infty = 3 \times 10^{-11}$
$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$	$k_{17}^*: k_0 = 1.21 \times 10^{-23}/T^{2.8}; k_\infty = 8 \times 10^{-13}$
$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$	$k_{18}^\dagger: k_0 = 6.1 \times 10^{-6} \exp(-9570/T) k_\infty = 1.7 \times 10^{17} \exp(-12450/T)$
$O(^1D) + H_2O \rightarrow 2OH$	$k_{21} = 2.2 \times 10^{-10}$
$O(^1D) + CH_4 \rightarrow OH + CH_3$	$k_{22} = 1.4 \times 10^{-10}$
$O(^1D) + CH_4 \rightarrow H_2 + H_2CO$	$k_{23} = 1.4 \times 10^{-11}$
$O(^1D) + H_2 \rightarrow OH + H$	$k_{24} = 9.9 \times 10^{-11}$
$H + O_3 \rightarrow OH + O_2$	$k_{25} = 1.4 \times 10^{-10} \exp(-470/T)$
$H + O_2 + M \rightarrow HO_2 + M$	$k_{26} = 1.62 \times 10^{-28}/T^{1.4}$
$OH + O_3 \rightarrow HO_2 + O_2$	$k_{27} = 1.6 \times 10^{-12} \exp(-940/T)$
$HO_2 + O_3 \rightarrow OH + 2O_2$	$k_{28} = 1.1 \times 10^{-14} \exp(-580/T)$
$OH + O \rightarrow H + O_2$	$k_{29} = 2.3 \times 10^{-11} \exp(110/T)$
$HO_2 + O \rightarrow OH + O_2$	$k_{30} = 4 \times 10^{-11}$
$H_2O_2 + O \rightarrow OH + HO_2$	$k_{31} = 2.8 \times 10^{-12} \exp(-2125/T)$
$OH + CH_4 \rightarrow H_2O + CH_3$	$k_{32} = 2.36 \times 10^{-12} \exp(-1710/T)$
$HO_2 + NO \rightarrow OH + NO_2$	$k_{33} = 3.5 \times 10^{-12} \exp(250/T)$
$OH + CO \rightarrow CO_2 + H$	$k_{34} = 1.35 \times 10^{-13} (1 + p_{atm})$
$OH + H_2 \rightarrow H_2O + H$	$k_{35} = 1.2 \times 10^{-11} \exp(-2220/T)$
$OH + NO_2 + M \rightarrow HNO_3 + M$	$k_{36}^*: k_0 = 3.97 \times 10^{-23}/T^{2.9}; k_\infty = 3.98 \times 10^{-8}/T^{1.3}$
$OH + HNO_3 \rightarrow H_2O + NO_3$	$k_{37} = 1.5 \times 10^{-14} \exp(650/T)$
$OH + H_2O_2 \rightarrow H_2O + HO_2$	$k_{38} = 2.7 \times 10^{-12} \exp(-145/T)$
$OH + HO_2 \rightarrow H_2O + O_2$	$k_{39}^\ddagger = 7 \times 10^{-11} (4 \times 10^{-11} - 1 \times 10^{-10})$
$OH + OH \rightarrow H_2O + O$	$k_{40} = 4.5 \times 10^{-12} \exp(-275/T)$
$OH + H_2CO \rightarrow H_2O + HCO$	$k_{41} = 1 \times 10^{-11}$
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$k_{42}^\ddagger = 2.3 \times 10^{-12} \exp(.15 \times z), z = 0 - 10 \text{ km}; 1 \times 10^{-11}, z = 11 - 15 \text{ km}$
$OH + OH + M \rightarrow H_2O_2 + M$	$k_{43}^*: k_0 = 2.4 \times 10^{-29}/T^{0.8}; k_\infty = 9 \times 10^{-9}/T$
$H + HO_2 \rightarrow H_2 + O_2$	$k_{44} = 4.2 \times 10^{-11} \exp(-350/T)$
$H + HO_2 \rightarrow H_2O + O$	$k_{45} = 8.3 \times 10^{-11} \exp(-500/T)$
$H + HO_2 \rightarrow 2OH$	$k_{46} = 4.2 \times 10^{-11} \exp(-950/T)$
$H_2CO + O \rightarrow OH + HCO$	$k_{47} = 3 \times 10^{-11} \exp(-1550/T)$
$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$	$k_{48}^*: k_0 = 7 \times 10^{-26}/T^{2.2}; k_\infty = 3.25 \times 10^{-8}/T^{1.7}$
$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	$k_{49} = 7.4 \times 10^{-12}$
$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$	$k_{50} = 7.7 \times 10^{-14} \exp(1300/T)$
$CH_3OOH + OH \rightarrow CH_3O_2 + H_2O$	$k_{51} = 2.1 \times 10^{-12} \exp(-145/T)$
$CH_3O + O_2 \rightarrow H_2CO + HO_2$	$k_{52} = 9.2 \times 10^{-13} \exp(-2200/T)$
$HCO + O_2 \rightarrow CO + HO_2$	$k_{53} = 5 \times 10^{-12}$
$HO_2 + NO_2 + M \rightarrow HNO_4 + M$	$k_{95}^*: k_0 = 5.1 \times 10^{-19}/T^5; k_\infty = 5.85 \times 10^{-7}/T^2$
$HNO_4 + M \rightarrow HO_2 + NO_2 + M$	$k_{96}^\S = 4.89 \times 10^{-6} \exp(-10000/T) (1 + 4.86 \times 10^{-12} [M]^{0.61})^{-1}$
$HNO_4 + OH \rightarrow H_2O + O_2 + NO_2$	$k_{97}^\ddagger = 2 \times 10^{-12} (8 \times 10^{-13} - 3.5 \times 10^{-12})$

Photolyses. J_1 : $O_3 + h\nu \rightarrow O_2 + O(^1D)$; J_2 : $O_3 + h\nu \rightarrow O_2 + O$; J_3 : $NO_2 + h\nu \rightarrow NO + O$; J_4 : $HNO_3 + h\nu \rightarrow OH + NO_2$; J_5 : $H_2O_2 + h\nu \rightarrow 2OH$; J_6 : $NO_3 + h\nu \rightarrow NO + O_2$; J_7 : $NO_3 + h\nu \rightarrow NO_2 + O$; J_8 : $H_2CO + h\nu \rightarrow H + CHO$; J_9 : $H_2CO + h\nu \rightarrow H_2 + CO$; J_{10} : $N_2O_5 + h\nu \rightarrow NO_2 + NO_3$; J_{11} : $CH_3OOH + h\nu \rightarrow CH_3O + OH$; J_{12} : $HNO_4 + h\nu \rightarrow HO_2 + NO_2$.

Note: Unless noted reactions and absorption cross sections are from NASA [1981]. Units for k are second-order $\text{cm}^3 (\text{molecule})^{-1} \text{s}^{-1}$.

*Third-order rate constant computed according to $k(M, T) = (k_0(T)[M]/1 + k_0(T)[M]/k_\infty(T))^{0.6(1 + [\log_{10}(k_0(T)[M]/k_\infty(T))])^{-1}}$.

† $k(M, T) = 2/[A + [A^2 + 22/(k_0 k_\infty [M])]^{1/2}]$; $A = (k_0[M])^{-1} + k_\infty^{-1}$ [Connell and Johnston, 1979].

‡See NASA [1981] for discussion of these rate constants. k_{42} as given is the NASA recommendation; standard value for $k_{39} = 7 \times 10^{-11}$ is between high and low NASA limits. Value for $k_{97} = 2 \times 10^{-12}$ is mean among NASA recommendation and higher values of Trevor *et al.* [1980] and H. S. Johnston (personal communication, 1981). Maximum HO_x destruction rates: $k_{39} = 1 \times 10^{-10}$; $k_{42} = 2 \times k_{42}$ as given; $k_{97} = 3.5 \times 10^{-12}$ [Trevor *et al.*, 1980]. Minimum HO_x destruction rates: $k_{39} = 4 \times 10^{-11}$; $k_{42} = 0.5 \times k_{42}$ as given; $k_{97} = 8 \times 10^{-13}$ [NASA, 1981].

§Graham *et al.* [1978].

assuming that a single dense layer exists in the lower midtroposphere and insert into the altitude grid a highly reflecting surface (albedo = 0.8 for all wavelengths) between 2 and 3 km. Details of the radiation calculation with and

without this simple cloud are described elsewhere [Thompson, 1980].

Numerical solutions to the transport-kinetics equations (1) are obtained by converting to a set of nonlinear algebraic

Fig. 1. Eddy diffusion coefficients. Dashed line represents parameterization of resistant surface boundary layer (SBL) below 100 m. Planetary boundary layer (PBL) is region of efficient mixing, ($K(z) \geq 2 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$). The most rapid mixing occurs just above the SBL.

expressions. Flux divergence at each altitude is approximated by a centered, second-order analog to the self-adjoint operator. We rewrite the equations (1) in this form:

$$\frac{d\bar{\chi}}{dt} = \bar{f}(\bar{\chi}, t)$$

$$\bar{\chi} = \chi_1^1, \chi_2^1, \chi_3^1 \cdots \chi_{ns}^1, \chi_1^2, \chi_2^2, \cdots \chi_{ns}^2, \cdots \chi_1^{np}, \chi_2^{np}, \chi_3^{np} \cdots \chi_{ns}^{np} \quad (2)$$

where χ_j^i = j th species mixing ratio at altitude grid point i ; $\bar{f}$ = forcing function, the sum of flux divergence, and rates of

chemical reaction; ns = total number of chemical species; np = total number of spatial grid points. The mixing ratios are obtained from integration of (2), using a second-order method based on the exponential fitting algorithm of Lininger and Willoughby [Lininger and Willoughby, 1970; Ehle, 1973; Iserles, 1979]. By maximizing use of vectorization on a CRAY1 computer, the system of equations for 1 day (17 chemical species, 24 altitudes, 37 times of day) can be solved in 2.3 s; calculation of the radiation field and photolysis rates accounts for 20% of that time.

A single diurnal cycle consists of 15 time steps at night and 22 daytime points (solar zenith angles), with the majority clustered around sunrise and sunset, minimum $\Delta t = 2$ min. One advantage to solving the full continuity equations (2) for individual species, rather than only for chemical 'families' like NO_x , HO_x , is that short-lived radicals (e.g., O , OH , CH_2O , NO) are always mathematically uncoupled from their longer-lived precursors. Similarly, highly soluble species like HNO_3 are mathematically uncoupled from less soluble species such as NO . Thus, we do not depend on assumptions of chemical equilibrium.

For sensitivity studies (e.g., to examine the effects of varying boundary conditions and reaction rates) a steady state version of the model is used to solve equations (2) for the case $d\bar{\chi}/dt = 0$. In the steady state model, diurnally averaged species concentrations are calculated according to the procedure of Turco and Whitten [1978]. Briefly, one multiplies each chemical rate constant by a factor that contains information on the diurnal behavior of the reactants. To compute these factors, the time-dependent code must be integrated until each species displays a 24-hour cycle and ozone (the most slowly varying of the chemical constituents) has converged to a fixed profile. In this manner, the steady state model calculates 24-hour averages for all species. The steady state and diurnally averaged time-dependent codes give results within 5% for all species at all altitudes.

Solution of the differential equations (1) requires specifica-

TABLE 3. Boundary Conditions for Marine Troposphere

	Model Type			
	1 and 1-SBL*	2	3	4 and 4-A†
NO	influx: $7.5 \times 10^8 \text{ molec cm}^{-2} \text{ s}^{-1}$ ($7.5 \times 10^7 - 1.5 \times 10^9$)	p.c.e.	$v = 0.25$ (0.1 - 1.0)	$v = 0.01$ ($10^{-4} - 10^{-2}$)
NO_2	$v = 0.01$ (0.001 - 0.5)	fixed (~25 ppt)	$v = 0.25$ (0.1 - 1.0)	$v = 0.01$ ($5 \times 10^{-4} - 5 \times 10^{-1}$)
NO_3	$v = 0.5$ (0.05 - 3)	same as 1	$v = 0.25$ (0.1 - 1.0)	$v = 0.5$ (0.005 - 0.5)
HNO_3	$v = 1$. (0.003 - 3)	same as 1	$v = 0.25$ (0.1 - 1.0)	$v = 0.20, 0.25$ (0.003 - 3)
HNO_4	$v = 1$. (0.25 - 2)	same as 1	$v = 0.25$ (0.1 - 1.0)	$v = 1.0$ (0.25 - 1)
N_2O_5	$v = 0.5$ (0.1 - 10)	same as 1	$v = 0.25$ (0.1 - 1.0)	$v = 0.5$ (0.001 - 1)

Where more than one value appears, boundary condition has been parameterized over range indicated parenthetically; standard value is given first.

Upper boundary (15 km) (models 1-4)— O_3 : influx: $5 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$; $\text{O}(^3\text{P})$: influx: $4 \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$ (value given is diurnally averaged and is one-half that used in time-dependent calculation); NO_x ($= \text{NO} + \text{NO}_2 + \text{NO}_3 + \text{HNO}_3 + \text{HNO}_4 + 2\text{N}_2\text{O}_5$): influx: $2.5 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ ($2.2 - 2.8 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$); CH_3 , CH_3O , CH_3O_2 , CH_3OOH , HC_2O : p.c.e. (photochemical equilibrium); H , OH , HO_2 , H_2O_2 : p.c.e.

Lower boundary (0 km)— O_3 : $v = 0.05$ (v = surface removal rate or deposition velocity (cm s^{-1})); $\text{O}(^3\text{P})$: $v = 0.5$ (value given is diurnally averaged and is one-half that used in time-dependent calculation); CH_3 , CH_3O , CH_3O_2 , H , OH , HO_2 : p.c.e. (photochemical equilibrium); CH_3OOH : $v = 1.0$ (0.7 - 2); H_2CO : $v = 0.3$ (0.1 - 1); H_2O_2 : $v = 1$ (0.15 - 3).

*Model 1 and Model 1-SBL standard boundary conditions are identical except that transport parameterization of Model 1-SBL includes resistant surface boundary layer below 100 m (Figure 1).

†Model 4-A and model 4 standard boundary conditions are identical except for HNO_3 : $v = 0.20$ (model 4) and $v = 0.25$ (model 4-A).

tion of values of each independent variable at the upper and lower boundaries (ground and 15 km) in our model troposphere. Three types of boundary conditions are used: (1) fixed concentration, (2) specified flux (Φ , in molec $\text{cm}^{-2} \text{s}^{-1}$) or surface removal velocity (v_{rem} in cm s^{-1}), and (3) photochemical equilibrium that can be assumed when the concentration of a short-lived radical is essentially independent of transport. The overall chemistry is very sensitive to the forcing from boundary conditions for the longer-lived gases. Ozone and NO_x ($=\text{NO} + \text{NO}_2$) are critical in this respect, but it is difficult to specify values with certainty because only a few isolated measurements of these species have been made in the marine troposphere, especially near the sea surface.

Table 3 summarizes the boundary condition choices. At the upper boundary we assume stratospheric injection of ozone and odd nitrogen. For odd oxygen the tracer-based estimate of *Mahlman et al.* [1980], $5 \times 10^{10} \text{ cm}^{-2} \text{s}^{-1}$ for O_3 is the standard. For NO_y the reference influx, $2.5 \times 10^8 \text{ cm}^{-2} \text{s}^{-1}$, represents a mean between *Johnston's* [1979] evaluation of N_2O photooxidation in the stratosphere under spring-fall conditions (NO_y flux $= 2.8 \times 10^8 \text{ cm}^{-2} \text{s}^{-1}$) and a minimum, $2.2 \times 10^8 \text{ cm}^{-2} \text{s}^{-1}$ derived from the N_2O source less Logan's estimate of NO loss through recombination with N (sink $= 6 \times 10^7 \text{ cm}^{-2} \text{s}^{-1}$ [Logan et al. 1981]). In estimating the stratospheric downflux of NO_y from N_2O photodissociation, we neglect other possible sources of upper atmospheric NO_y [see, e.g., *Jackman et al.*, 1980]. The NO_y influx is divided among all odd nitrogen species in proportion to photochemical equilibrium, so this is a 'family-type' boundary condition. At the lower boundary we considered several types of specifications for NO_y as shown in Table 3:

1. Model 1. NO source from the sea [Zafiriou and McFarland, 1981]; all other odd nitrogen species subject to surface deposition.
2. Model 2. NO_2 fixed at lower boundary, NO in photochemical equilibrium, all other NO_y removed at surface at a rate controlled by the species removal velocity v .
3. Models 3 and 4. All NO_y species removed at surface at a rate controlled by the species removal velocity v (i.e., no local odd nitrogen source or fixed value for any NO_y species).

Fig. 2. Diurnally averaged ozone and odd nitrogen (NO_y) calculated from model 4 (standard case, Table 3). Sensitivity to stratospheric NO_y influx is indicated by dashed lines.

The standard parameterization for each model (Table 3) has been chosen to reproduce concentrations of ozone and NO_y consistent with the limited data available for the remote low- to mid-latitude marine boundary layer. These include measurements made as part of GAMETAG (*Routhier et al.* [1980] for O_3 ; *Huebert and Lazrus* [1980] for HNO_3) and other recent determinations of odd nitrogen that suggest as a reasonable range of values at the surface 20–35 ppb O_3 and 20–60 ppt NO_x [Kley et al., 1981; Zafiriou et al., 1980; Zafiriou and McFarland, 1981; McFarland et al., 1979; Huebert, 1980; Hélas and Warneck, 1981; Noxon, 1981].

Removal at the sea surface is assumed for O_3 ; O ; the soluble gases H_2CO , HNO_3 , and HNO_4 ; and the peroxides H_2O_2 and CH_3OOH . For ozone the deposition rate (0.05 cm s^{-1} [Lenschow et al., 1981]) is based on measurements, but for the other species the rates are based on solubilities (as far as these are known) with highest values corresponding to the most soluble or reactive gases. It is assumed that diffusion through the sea-surface microlayer limits this transfer to 1 cm s^{-1} under calm conditions, but this rate may be exceeded for certain radicals that react on the surface [Garland et al., 1980; O. C. Zafiriou and A. M. Thompson, unpublished manuscript, 1980].

Because we simulate time-dependent perturbations that affect primarily boundary-layer chemistry, a number of calculations were performed to examine the sensitivity of NO_y , hydrocarbon, and ozone distributions to various assumptions of transport and chemical input and removal at the lower boundary. Chemical distributions were computed by using the eddy transport parameterization of a resistant surface layer (Figure 1) as well as the conventional scheme (model 1-SBL in Table 3).

3. RESULTS AND DISCUSSION: NO CLOUD, NO RAIN CONDITIONS

Typical diurnally averaged profiles for NO_y and ozone are shown in Figure 2. Because NO_y is injected from the stratosphere and removed at the surface, there is a positive gradient from ground toward the free troposphere. This is in accord with a number of measurements of NO_x and HNO_3 in remote environments [see the discussion by Kley et al., 1981; Levy et al., 1980]. The dashed lines indicate the sensitivity of NO_y and O_3 to a 25% variation in the stratospheric NO_y input. Ozone varies in proportion to NO_y because injected NO contributes to the formation of ozone through the sequence of reactions:

The amount of ozone produced depends not only on the ratio of the NO_y flux relative to that of ozone [Liu et al., 1980] but also on the fraction of NO_y that is NO_x . The positive correlation between O_3 and scaling of the NO_y flux in the upper troposphere is the consequence of net ozone production in that region because ozone is also consumed by

Fig. 3. Photochemical ozone production with and without cloud present at 2–3 km (24-hour average from model 4) versus altitude. Kink between 2 and 3 km in cloud case results from assumption of a single dense cloud layer. Column-integrated net O_3 production, 5–15 km: $2.9 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$, no cloud; $4.3 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$, cloud.

The critical factor in determining the balance between the production cycle (reactions (3)–(5)) and loss (reactions (6)–(8)) is whether HO_2 attacks NO (reaction (3)) or O_3 (reaction (8)). In Figure 3 the net photochemical production of ozone (i.e., the difference between formation and loss) is plotted as a function of altitude. The distribution is consistent with the corresponding NO_y pattern in Figure 2. In the upper troposphere close to the presumed stratospheric NO source, there is net photochemical production; near the surface where NO is only a few ppt, there is net O_3 destruction. For the curve illustrated, the column-integrated net production above 5 km (without clouds) is $2.9 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$ and net loss below 5 km is $4.5 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$. Hence, net loss dominates throughout the column from 0 to 15 km, but as other workers have pointed out [Crutzen, 1973; Chameides and Walker, 1973; Liu *et al.*, 1980], photochemical formation may account for a considerable fraction of total ozone in the upper troposphere. Details concerning the sensitivity of tropospheric O_3 to stratospheric NO_y inputs and to uncertainties in critical rate constants are found in Liu *et al.* [1980] and Fishman [1981] and in the work of Levy *et al.* [1980], who first pointed out the implications of stratospheric N_2O chemistry for the odd nitrogen budget of the lower troposphere.

Steady state distributions of the longer-lived soluble gases (HNO_3 , HNO_4 , CH_2O , CH_3OOH , and H_2O_2) are shown in

Fig. 4a. Soluble longer-lived gas mixing ratios (24-hour averages) calculated from model 4 (no rainout included). Corresponding O_3 and NO_y are solid profiles in Figure 2.

Fig. 4b. Sensitivity of soluble gas distributions to a five-fold variation in surface deposition velocity ($0.2 - 1 \text{ cm s}^{-1}$) for HNO_3 and H_2O_2 (all from model 4, 24-hour averages). CH_2O and CH_3OOH behavior are similar near the lower boundary. See also Figure 8.

Figure 4a. Since all of these compounds are produced by a sequence of reactions involving OH , they are directly proportional to O_3 (the OH precursor), which in the case illustrated is the solid profile of Figure 2. The boundary layer concentration of each soluble gas is very sensitive to its surface removal velocity. The effects of a five-fold variation in the assumed deposition rates for HNO_3 and H_2O_2 appear in Figure 4b.

Odd hydrogen, HO_x , scales roughly with O_3 . Distributions of HO_x and H_2O_2 in Figure 5 were calculated from the reference NO_y and O_3 columns of Figure 2 using the standard set of rate constants in Table 1. However, there is considerable uncertainty in several key rate constants governing HO_x chemistry [NASA, 1981]. Model runs performed with a set of minimum and maximum rate constants for the key HO_x destruction reactions (39), (42), and (97) (Table 2) indicate the uncertainties in calculated HO_x and H_2O_2 profiles (Figure 5) attributable solely to the HO_x reaction rates.

Because of its essential role in controlling ozone levels and because recent measurements of NO_x in the marine boundary layer point to very low background levels ($<0.1 \text{ ppb}$), we

Fig. 5. Odd hydrogen (HO_x) and H_2O_2 mixing ratios (model 4-A, noon; full diurnal cycle is in Figure 10). Sensitivity to key HO_x destruction rates is illustrated as described in text and Table 1: solid rule, mean rates; dashed-dotted, minimum rates; dotted, maximum rates.

have considered variations in the distribution of NO_y members under different surface conditions but with a uniform stratospheric influx ($2.5 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$).

If there is no surface source of odd nitrogen and no rainout, the total amount of surface NO_y and the fraction of each species depends only on the rates of surface removal. Low values of NO_y and O_3 are compatible only with fairly rapid NO_y deposition. For example, if a uniform removal velocity is specified for all NO_y species (this is equivalent to a grouped or family approach), total NO_y on the order of 50–60 pptv requires a transfer rate, $v = 0.20 \text{ cm s}^{-1}$. In that case the NO_y individuals, NO , NO_2 , NO_3 , etc., are in approximate photochemical equilibrium relative to one another, with calculated HNO_3 making up 80% of the total (Figure 6). An examination of recent marine data [Helás and Warneck, 1981; McFarland *et al.*, 1979; Huebert, 1980] implies that this fraction is too high and HNO_3/NO_x is probably closer to 1–3. By varying the deposition velocity for each species in turn it is possible to obtain a slightly greater porportion of NO_2 , but for a given total NO_y there is only a small range over which NO_x/NO_y can be changed by this approach. Thus, it is likely that near the surface odd nitrogen chemistry is dominated not by surface removal but by other processes in the boundary layer or even the free troposphere, for example, heterogeneous loss of HNO_3 [Fishman and Crutzen, 1977], nonstratospheric sources of NO_x such as lightning [Chameides *et al.*, 1977; Noxon, 1976], transport from continental areas [Chameides, 1978], or a local source [Zafiriou and McFarland, 1981]. In view of Zafiriou and McFarland's observations of photochemically induced NO formation near the sea surface, we examined NO_y distributions calculated assuming a surface source of NO with surface deposition specified for the other NO_y species (model 1 in Table 3). Figure 7a illustrates NO_y profiles based on a 20-fold range of NO flux and rapid mixing between the surface and the planetary boundary layer. The ratio NO upflux/stratospheric NO_y downflux ranges from 0.3 to 6. The solid-line profile corresponds to $\text{NO}_x = 26 \text{ ppt}$ at the surface, which we have chosen as representative of clean surface marine air [McFarland *et al.*, 1979; Helás and Warneck, 1981; Noxon, 1981].

Fig. 6. Distribution of major NO_y species (models 3 and 4, 24-hour averages). All species are removed by deposition at lower boundary. Shading represents range obtained by various parameterizations of surface removal velocities which give NO_y at lower boundary 50–60 ppt. Extremes calculated from HNO_3 surface removal rate $= 0.2 \text{ cm s}^{-1}$ assuming standard surface removal rates (Table 3) and one-tenth standard rates for other NO_y species.

Fig. 7a. Total odd nitrogen as function of surface NO flux (model 1, 24-hour averages). Stratospheric NO_y influx ($2.5 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$) is same in all cases and efficient mixing is assumed to the surface (see Figure 8).

Several observations should be made about the total odd nitrogen (NO_y) vertical profiles of Figure 7a. First, for every model considered here the importance of the stratospheric NO_y downflux is evident, as was proposed by Levy *et al.* [1980] and Kley *et al.* [1981]. Although we are simulating the marine atmosphere here, the situation can be similar in the middle and upper troposphere over continents if removal processes in the boundary layer and at the land surface remove much of the combustion-produced NO_x . Individual profiles of actual NO , can, of course, vary significantly from those shown in Figure 7a: Sporadic stratospheric injections and sporadic production of NO by lightning (not considered here) can produce very disturbed profiles.

Although total NO_y increases away from the surface, the corresponding NO and NO_2 distributions (Figure 7b) show a slight negative gradient as a consequence of the NO forcing at the boundary. The forcing also results in a smaller near-surface HNO_3/NO_x ratio than when there is no NO_x source (cf. Figures 6 and 7b), although these species redistributions are not significant above 5 km. Zafiriou and McFarland's [1981] estimated range of flux values for the Equatorial Pacific (very low NO [McFarland *et al.*, 1979]) falls near the lower end of the scale in Figure 7a.

Fig. 7b. Distribution of major odd nitrogen species (model 1) NO upflux is $7.5 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ (diurnally averaged). Surface removal is specified for all other NO_y species (Table 3).

Fig. 8. Effect of a resistant surface boundary layer (see Figure 1) on calculated odd nitrogen distributions. (Solid rule, model 1; dashed, model 1-SBL, 24-hour averages.) Mixing ratios in the refined grid below 100 m are shown as dots. Calculation with resistant boundary layer shows HNO_3 and NO_x accumulation in middle to upper troposphere where eddy mixing coefficient, $K(z)$ falls below $10^5 \text{ cm}^2 \text{ s}^{-1}$. Note large differences in lowest 10 m. Other soluble gases CH_3OOH , H_2O_2 , CH_2O , HNO_4 , follow pattern of HNO_3 .

NO_x distributions in the boundary layer are very sensitive to vertical transport. For example, for a very stable air mass with low wind (say, 3 m s^{-1} measured at 10 m) it may be inaccurate to assume that the rapidly mixed layer extends to the ground when diffusion at the lower boundary is limited

Fig. 9a. Individual NO_x diurnal cycles at surface (model 1). Prescribed NO upflux is $1.5 \times 10^9 \text{ molec cm}^{-2} \text{ s}^{-1}$ (constant over day, 600–1800 hours) and zero at night. Surface removal rates for other NO_x species are given in Table 3. Most of the sum $\text{N}_2\text{O}_5 + \text{NO}_3$ is NO_3 since $\text{N}_2\text{O}_5/\text{NO}_3 < 0.1$ at all times. Diurnal patterns calculated in model 2 are identical except for NO_2 which is fixed at 23 ppt.

Fig. 9b. NO_x diurnal cycles at surface (model 4-A, Table 3). Surface removal rate for HNO_3 ($\nu = 0.25$) was chosen to give mixing ratio ~ 35 ppt as in model 1.

by more nearly stagnant air and possibly by resistance to transfer through the sea surface microlayer. The inclusion of additional surface resistance (i.e., the eddy profile labeled SBL in Figure 1) has two effects on calculated NO_x mixing ratios. In the case where NO is emitted from the surface (model 1-SBL), reduced transport keeps much of the NO (and also NO_2 since it is in near-photochemical equilibrium with NO) close to the surface. For the same lower boundary conditions a higher fraction of NO_x is NO_x within a few meters of the surface (Figure 8). A 25 ppt NO_x mixing ratio in the surface boundary layer requires a NO flux of only $3.5 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ compared with $7.5 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ when efficient mixing extends to the ground. The second effect of a resistant surface boundary layer is to introduce a similar bottleneck into the surface deposition of the longer-lived soluble gases, causing them to accumulate in the planetary boundary layer. This phenomenon is depicted for HNO_3 in Figure 8 where the solid curve represents the mixing ratio calculated assuming efficient mixing to the ocean surface and the dashed one has been computed from reduced near-surface transport. (Although they are not illustrated here, a similar pattern applies to the other soluble gases, H_2CO , H_2O_2 , and CH_3OOH .) We would have to specify a very high surface removal velocity along with surface resistance (approximately 3 times greater than for the no-SBL case) to bring the dashed curve for HNO_3 into coincidence with the reference distribution in Figure 8. Providing that real-time determinations of a soluble gas are possible, the 'bottleneck effect' should be detectable when field measurements are made under conditions of reduced transport. If enhanced levels of these species are not observed, there is probably very effective destruction at the sea surface or heterogeneous removal by other processes in the boundary layer (e.g., removal to sea-salt particles or fog drops [Heikes and Thompson, 1981]). This simple example of chemical sensitivity to transport argues strongly for an accurate knowledge of dynamics when interpreting measured gas distributions. Note, for example, that the ratio $[\text{NO}_x]/[\text{HNO}_3]$ varies

strongly with altitude below 100 m in Figure 8. It may be that in a regime characterized by two or three layers of varying mean vertical diffusivity, there is a stratification of background chemistry, although horizontal transport could counteract these effects that have been simulated here only in one dimension.

In describing steady state results, we have tried to illustrate a few sensitivities of background level (low NO_y , low O_3) marine tropospheric chemistry which might be observed on a short time scale as chemical inputs and transport vary in a given air mass. These results might characterize a particular marine environment that has been stable over a long period of time.

4. TIME-DEPENDENT CALCULATIONS AND SHORT-TERM VARIABILITY

We performed time-dependent calculations for several reasons: to obtain proper diurnal average factors [Turco and Whitten, 1978] for the steady state calculations described above; to calculate full diurnal cycles (i.e., species concentrations at every time of day and night) for each species; and to simulate the time dependences induced by sporadic rain and cloud events. Pre-event (no cloud, no rain) diurnal cycles for NO_y at ground are illustrated in Figures 9a and 9b. In model type 4-A (Figure 9b) with a constant stratospheric input and surface removal for all species, there is no diurnal variation in NO_y and in the majority constituent HNO_3 . The distribution of the various members is determined primarily by photochemistry: NO builds up during the day as a result of NO_2 photolysis, NO_2 is in balance among the photolysis, and conversion to HNO_3 during the day and to NO_3 at night (from which it reforms rapidly at sunrise). Fixing NO_2 or prescribing a surface flux of NO (the two are nearly equivalent) introduces a 15–20% variation in total NO_y , which is absorbed by a slow buildup of HNO_3 during the day (Figure 9a). This effect is significant only below 3 km (i.e., in the region of effective NO_x forcing (cf. model 1, Figure 7b)). We

Fig. 10a. HO_2 , OH , and H_2O_2 diurnal cycles at surface (model 1); surface mixing ratio of O_3 is 34 ppb. Surface removal rate for H_2O_2 is 1 cm s^{-1} .

Fig. 10b. HO_2 , OH , and H_2O_2 diurnal cycles at surface (models 4 or 4-A); surface mixing ratio of O_3 is 27 ppb. Surface removal rate for H_2O_2 is 1 cm s^{-1} .

have also performed a model run with continuous NO upflux ($7.5 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ day and night). The only differences in NO_y mixing ratios between that run and model 1 are for NO itself (which instead of disappearing completely at night falls to a few percent of its daytime maximum) and for NO_2 , which increases 15–20% in response to NO forcing at night, although only 5% on a diurnally averaged basis. The constant NO input also eliminates the small diurnal variation in total NO_y (cf. Figure 9a).

We note that although our calculated NO_x and HNO_3 at surface are consistent with the data available, measurements of NO_3 in unpolluted air [Noxon *et al.*, 1980; Noxon, 1981; Platt *et al.*, 1981] are lower than calculated values based on the concept of a steady state relation among NO_2 , NO_3 , and N_2O_5 suggested by reactions (17) and (18) (Table 2):

$$\frac{[\text{NO}_2][\text{NO}_3]}{[\text{N}_2\text{O}_5]} = K_{ss}$$

Platt *et al.* [1981] have noted that the value they deduce from measurements of NO_2 and NO_3 suggests $K_{ss} = 2\text{--}3 \times 10^{10} \text{ cm}^{-3}$ at $10^\circ\text{--}15^\circ\text{C}$, which is 5–6 times higher than the laboratory experimental value [Connell and Johnston, 1979]. If we use our calculated mixing ratios for NO_2 , NO_3 , and N_2O_5 (as in Figure 9a where $[\text{N}_2\text{O}_5]/[\text{NO}_3] < 0.1$ at all times) we compute $K_{ss} = 1\text{--}2 \times 10^{10} \text{ cm}^{-3}$ nearly constant over the course of the night and not too far from Platt's value. The reason for this is the large deposition velocity assigned to NO_3 and N_2O_5 (0.5 cm s^{-1} , Table 3), which suppresses near-surface NO_3 relative to NO_2 . This is equivalent to substantial heterogeneous removal, a likely cause for low NO_3 [Thompson and Heikes, 1982]. Thus, our calculated NO_3 may be fairly accurate for the background marine troposphere.

Figures 10a and 10b illustrate the diurnal cycles for surface OH , HO_2 , and H_2O_2 . Mixing ratios of the soluble gases CH_3OOH and H_2CO at ground calculated from models

Fig. 11. CH_2O and CH_3OOH diurnal cycles at surface calculated from model 1 (solid rule) and model 4-A (dashed).

1 and 4-A are given in Figure 11; these species increase slightly over the course of a day as HO_x accumulates. In models 1 and 2, NO forcing consumes more HO_2 via reaction (33)

and the elevated OH/HO_2 ratio means faster methane oxidation and a slight increase of H_2CO through the reactions

Above the planetary boundary layer (1–2 km) NO_y species diurnal cycles are similar for all models, and away from surface influences the longer-lived soluble gases HNO_3 , HNO_4 , CH_2O , and the peroxides are nearly constant over the course of a day.

Two model types calculated with no clouds and or rain are chosen as starting points for calculating the short-term variability arising from synoptic weather changes. Time-dependent perturbations are parameterized to study effects on NO_y and the soluble gases. The magnitude of these changes turns out to depend strongly on the background NO_y distribution of the system and the two basic initial conditions (models 1 and 4-A) were selected to illustrate this sensitivity.

For simplicity we emphasize qualitative aspects of synoptic effects and restrict simulations to two prototypical events. In the first type a 3-day period of cloudiness is represented by including the simple cloud described above in the calculation of photolysis rates; this gives a measure of chemical sensitivity to changes in the radiation field. A second type of episode is a precipitation event in which the cloud effect on radiation is combined with below-cloud washout of soluble gases.

The effect of a 3-day cloud on the concentration of several soluble gases at the surface appears in Figure 12. Reduced photolysis below cloud decreases the concentration of the primary HO_x radicals, hence the rate of formation of HNO_3 , H_2O_2 , and the products of methane oxidation. The magnitude of the change is proportional to the radiation blockage (i.e., to cloud albedo, 0.8 in these simulations) and also depends on the lower boundary conditions. For example, when a NO upflux is assumed (model 1), at the end of 3 days the HNO_3 mixing ratio has declined 8% below its initial value, but with less conversion of NO_2 to HNO_3 , NO_x has increased 20%. One might suppose, however, that the NO upflux, which is derived from a photochemically driven source in the sea, is reduced during cloud cover in proportion to the decrease in radiation intensity at the surface (i.e., 80%). A 3-day cloud, combined with this altered boundary condition (model Cloud-2 in Figure 12), suppresses NO_x and HNO_3 until at the end of 3 days the latter has decreased to only 75% of its no-cloud value. For a system in which the initial distribution of NO_y species is already near photochemical equilibrium, cloud-induced effects are negligible for NO_x and HNO_3 (model 4-A, Figure 15a) but cause a 10–15% decrease in H_2O_2 and the hydrocarbons (Figure 13). In all cases illustrated here, the removal of the cloud at the end of 3 days along with the restoration of the original boundary conditions, gives rapid return toward initial values. This is evidence that although radiation effects may be significant,

Fig. 12. Effect of cloud on mixing ratios at ground: NO_x and soluble gases HNO_3 , H_2O_2 , and CH_2O (model 1). Solid line represents no-cloud (initial condition) diurnal behavior. Cloud layer at 2–3 km is assumed to persist for 3 days. Calculations for two values of NO surface flux are shown.

Fig. 13. Effect of cloud (model cloud-1) and combined cloud-and-rain events (models rain-1 and rain-3) on surface concentrations of H_2O_2 and H_2CO . Initial condition (model 4-A, see Figures 10 and 11) is indicated in each case by solid line. Cloud and rain models are described in text and in Tables 4 and 5. Beginning of model day is at sunrise.

they are probably not predominant influences in determining chemical distributions in the boundary layer.

Interactions between atmospheric gases and a precipitating system, both in-cloud and below-cloud, are very complex. We consider only the sensitivity of near-surface chemistry where the principal perturbations are likely to result from wet removal of soluble gases by falling rain droplets. The simplest representation of a precipitation event, therefore, consists of assuming uniform cloud cover in the calculation of photolysis rates (as in the cloud-only episodes) and adding a wet removal rate constant to the kinetic loss term for the most soluble species HNO_3 , H_2O_2 , HNO_4 , H_2CO , and CH_3OOH . We parameterize species-specific wet removal constants (or scavenging coefficients, k_{wr}) roughly according to solubility [Schwartz and White, 1981; Schwartz, 1980] relative to a value $2 \times 10^{-4} \text{ s}^{-1}$ for HNO_3 as estimated by Levine and Schwartz [1982] for below-cloud washout by a moderately intense shower (5 mm/hour) (Table 4). The assumptions of species-specificity and solubility-based parameterizations, while not essential to the overall results, seem reasonable in view of possible differences in the diffusion constants and sticking probabilities [Baldwin and

TABLE 4. Parameterizations of a Precipitation Episode

	k_{wr}
HNO_3^*	$2 \times 10^{-4} \text{ s}^{-1}$
H_2O_2	$1 \times 10^{-4} \text{ s}^{-1}$
H_2CO	$7 \times 10^{-5} \text{ s}^{-1}$
CH_3OOH	$5 \times 10^{-5} \text{ s}^{-1}$
HNO_4	$5 \times 10^{-5} \text{ s}^{-1}$

Rain: Wet removal rate constants (scavenging coefficients) 0–2 km.

Cloud: $J_{\text{cloud}}^{0-2 \text{ km}} \approx 0.2 \times J_{\text{no cloud}}^{0-2 \text{ km}}$.

Photolysis rates, J , calculated with cloud at 2–3 km, 0.8 reflectance (all wavelengths, solar zenith angles).

*Levine and Schwartz [1982].

Fig. 14a. Wet removal of HNO_3 during a precipitation event. Model 1 initial condition is assumed with full NO flux throughout (rain model-1). Solid line is profile at start of event; dashed lines show progressive loss due to scavenging after indicated number of hours. The 4-hour profile for model 4-A (similar starting point but no NO upflux) is also given (dashed-dotted line).

Golden, 1979] of the various compounds. The scavenging coefficients in Table 4 are probably uncertain to a factor of 2 or 3 and may change over the course of an event, but we are primarily interested in the total effect of an episode that depends on the time-integrated product

$$k_{wr}^{\text{event}} = \frac{1}{T_{\text{event}}} \int_0^{T_{\text{event}}} k_{wr}(t) dt \quad (9)$$

where T_{event} is the total duration of precipitation. For a constant removal rate the cumulative effect of removal is simply proportional to the time elapsed t since the start of the event. In a situation in which the local wet removal rate greatly exceeds local production and loss, the mixing ratio is given approximately by

$$X = X_{t=0} \exp(-k_{wr}t) \quad (10)$$

If we assume further that washout is irreversible and that saturation effects and evaporation of falling raindrops can be neglected, k_{wr} is independent of altitude below a cloud. Thus, a sequence of vertical profiles taken over the course of an event might appear as we have calculated in Figure 14a. For the species illustrated (HNO_3), the total depletion at the end of a 4-hour shower is 90–95%, depending on the total NO_y boundary condition. The removal of other soluble gases, H_2CO and the peroxides, forms a similar pattern with the

Fig. 14b. Wet removal of HNO_3 during a precipitation event (model 1-SBL initial condition). The parameterization of cloud and rain are as in Figure 14a (rain model-1); it is assumed further that increased turbulence during the event destroys surface resistance and restores near-surface diffusion to the no-SBL $K(0) = 6 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$.

Fig. 15a. Effect of cloud (model Cloud-1) and precipitation events (models Rain-1 and Rain-3) on HNO_3 at the surface (model 4-A initial condition, see Figure 9b).

magnitude of the change essentially proportional to the washout rate.

The assumption of irreversibility in precipitation scavenging is valid for species that react rapidly and essentially completely in solution (e.g., a strong acid):

Nitric acid is the only one of our scavenged gases for which this assumption is clearly justified. However, it seems reasonable to suppose that irreversible washout also applies to other species that react with water or another solute fast enough (typically $<10^2 - 10^3$ s) that the falling raindrop does not become saturated. For example, formaldehyde hydrates (H_2CO lifetime against hydration 0.1 s [Schecker and Schulz, 1969]) and the peroxides can be consumed as they oxidize HSO_3^- [Penkett et al., 1979; Heikes et al., 1982]. For species for which saturation effects in scavenging are significant, k_{wr} decreases with distance from the cloud, and the corresponding vertical profile sequence shows at all times a minimum mixing ratio just below cloud level where precipitation washout is most effective, 1–2 km in our simulations. These results assume that $K(z)$ does not change (i.e., transport is constant over the course of the event).

If the precipitation event begins from an initial condition based on the transport scheme of a resistant surface boundary layer (model 1-SBL; cf. Figure 8) the moving picture of a 4-hour episode for HNO_3 is shown in Figure 14b with the solid line representing the initial profile. It was pointed out (section 3) that only a very high rate of surface deposition or heterogeneous removal in the planetary boundary layer could bring the no-cloud, no-rain curve calculated with a surface boundary layer into coincidence with one computed assuming rapid mixing to the ground (dash-dotted line in Figure 14b). Precipitation washout can be an efficient mechanism for accomplishing this; with a wet removal coefficient $k_{\text{wr}} = 2 \times 10^{-4} \text{ s}^{-1}$, it takes less than an hour to reduce HNO_3 in the planetary boundary layer to the level of the no-SBL distribution.

The time dependence of soluble-gas mixing ratios at the surface during and after a precipitation event is illustrated in

Figures 15a and 15b. The no-cloud, no-rain reference diurnal cycle is the solid line near the top, and several variations of a simple cloud-and-rain perturbation are simulated (Table 5). Model Rain-1 consists of a single cloud-and-rain pulse lasting 4 hours, beginning at sunrise on model day 0. In Figure 15b this corresponds to a time in which HNO_3 is still increasing in its normal diurnal pattern under the influence of an NO upflux. If no further perturbation occurs and the same lower boundary condition is assumed, a damped diurnal pattern sets in as the original photochemistry and transport are reestablished. Within a few hours, HNO_3 is restored to 25% of its normal no-rain value; and at the end of a week, 90% of the original HNO_3 level is achieved. When there is no NO input (Figure 15a), recovery of HNO_3 from a 4-hour event is much slower. In both cases the NO_x diurnal patterns are virtually constant over the course of 7 days. In the simulation Rain-2 (Figure 15b), if the cloud cover of the storm produces a proportional reduction in the surface upflux of NO (80% loss), a 4-hour rain pulse reduces HNO_3 ~25% more than in Rain-1; after a day or two of integration, however, the concentration from models Rain-1 and -2 are virtually identical. A similar phenomenon is observed if the initial perturbation lasts 8 hours instead of 4; cf. Rain-1 and Rain-4 in Figure 15b. This demonstrates the dominant influence of the NO_x source (cf. Figure 12). In model Rain-3, a second 4-hour cloud-and-rain shower takes place on model day 3, greatly delaying restoration of soluble gas concentrations to their prerin levels (Figures 15a and 15b).

The sensitivity of surface chemistry to the various episodes that have been simulated here is summarized in Table 5, where for NO_x and the soluble gases HNO_3 and H_2CO (representing, maximum and minimum wet removal efficiency, respectively) we have computed the ratio of the mixing ratios on model days 3 and 7 to the initial value, day 0 (i.e., the fractional recovery from the start of the event). Models Cloud-1 and Cloud-2 refer to cloud-only perturbations that have maximum effect after 3 days; their effect 1 week after the start of the episode is relatively small for HNO_3 and

Fig. 15b. Effect of precipitation removal on surface HNO_3 mixing ratio (model 1 initial condition) rain models 1–4 are described in text and Table 5.

TABLE 5. Fractional Recovery of Surface Mixing Ratios: NO_x, HNO₃, and H₂CO

Model Initial Condition	Cloud/Rain Model	Episode	3 Days: [X] day 3/[X] day 0			7 Days: [X] day 7/[X] day 0		
			X = NO _x	X = HNO ₃	X = H ₂ CO	X = NO _x	X = HNO ₃	X = H ₂ CO
1	Cloud-1	3-day cloud; full NO flux	1.22	0.92	0.96	1.01	1.02	1.00
1	Cloud-2	3-day cloud; NO flux/5	0.67	0.74	0.77	0.98	0.91	0.98
1	Rain-1	4 hour rain; day 0; full NO flux	0.98	0.72	0.92	0.99	0.89	0.97
1	Rain-3	4 hour rain; day 0 and day 3	same as Rain-1			0.98	0.75	0.92
1	Rain-2	4 hour rain; day 0; NO flux/5;	0.97	0.70	0.91	0.99	0.89	0.97
1	Rain-4	8 hour rain; day 0	1.00	0.66	0.89	0.98	0.88	0.96
4-A	Cloud-1	3-day cloud	1.08	0.98	0.92	1.01	1.00	1.00
4-A	Rain-1	4 hour rain; day 0	0.82	0.50	0.84	0.84	0.71	0.91
4-A	Rain-3	4 hour rain; day 0 and day 3	same as Rain-1			0.74	0.47	0.82

negligible for H₂CO and NO_x. For the rain episodes, however, the situation is different for the most soluble gases. One week after a pulse of wet removal, HNO₃ levels are still 10–30% lower than the initial value; if a second shower occurred on day 3, they may be as much as 50% lower. For H₂CO, with only one third the wet removal rate of HNO₃, effects at the 3-day point are significant, but at the end of a week recovery is nearly complete. The critical dependence of these results on boundary conditions cannot be overemphasized. Except in specified NO_x in two model runs, a fixed set of boundary conditions has been maintained for a week of integration in all of these simulations. Hence, our results apply only to extremely stable meteorological conditions; and our numbers, especially for the recovery time of soluble gases, must be regarded as rough limits for what might be found in the atmosphere. Nonetheless, we believe we have made a good estimate of the magnitude of short-term variability which typical synoptic episodes might impose in the boundary layer while identifying other key sensitivities of background-level chemistry.

These model results have two practical implications for measurements of trace gases in the marine atmosphere.

First, if precipitation washout of a soluble gas reduces its concentration by a factor of 5–10 in just a few hours, the change should be detectable if the time scale of measurement is kept small and if offsetting effects of advection and convection are insignificant. Such washout has been observed in polluted air for H₂CO [Platt *et al.*, 1979], and recently for HNO₃ removal by snow at a clean continental site (B. J. Huebert, personal communication, 1981) but confirming data in the marine troposphere are lacking. Measurements of gas-phase HNO₃ in the Equatorial Pacific surface layer showed highest HNO₃ levels during a storm [Huebert, 1980]; it seems most probable that storm-induced convection introduced air enriched in NO_y into the area being sampled.

Second, the assumptions of photochemical equilibrium, which are sometimes used to interpret field data, are inadequate in the marine boundary layer (and probably over continents also) when applied to soluble or surface-active gases. For example, in the absence of heterogeneous reac-

tion if transport is slow relative to chemistry the NO₂/HNO₃ ratio is given by the expression

$$\frac{\text{NO}_2}{\text{HNO}_3} = \frac{J_4 + k_{37}[\text{OH}]}{k_{36}[\text{OH}]} \quad (11)$$

where J_4 is the photolysis rate of HNO₃, k_{36} is its bimolecular formation rate from reaction of NO₂ and OH, and k_{37} is the rate of its loss to reaction with OH. If surface HNO₃ changes 10 fold over the course of a cloud-and-rain episode (Figures 15a and 15b), during which time NO₂ is nearly constant, NO₂/HNO₃ may vary considerably, not just during the perturbation but for days afterward as the air mass carries a 'memory' of the event. The correct ratio at any one time during the event would be given by an expression that includes a correction for wet removal

$$\frac{\text{NO}_2}{\text{HNO}_3} = \frac{J_4 + k_{37}[\text{OH}] + k_{wr}}{k_{36}[\text{OH}]} \quad (12)$$

At the end of the event HNO₃ is a minimum with the mixing ratio given approximately by equation (10) with $t = T_{\text{event}}$:

$$\text{HNO}_{3,T_{\text{event}}} = \text{HNO}_{3,t=0} \exp(-k_{wr}T_{\text{event}}) \quad (13)$$

After the event, HNO₃ gradually increases (Figures 15a and 15b). Thus, if one were to measure HNO₃ and NO₂ simultaneously at some time after the event, the ratio NO₂/HNO₃ could not be interpreted without knowing something of the recent history of the air mass being sampled. Finally, the different surface reactivities of species such as NO₂ and HNO₃ can produce strong altitude gradients in the ratio of

TABLE 6. Effect of Continuous Cloud Cover on Surface Mixing Ratios

Species	No Cloud	Cloud
O ₃	2.75 (–8)	3.38 (–8)
HNO ₃	4.51 (–10)	4.46 (–11)
H ₂ O ₂	5.83 (–10)	4.80 (–10)
CH ₃ OOH	5.90 (–10)	5.25 (–10)
H ₂ CO	6.20 (–11)	5.58 (–10)

Model 4, diurnally averaged.

*2.75 (–8) signifies 2.75×10^{-8} mixing ratio by volume.

Fig. 16. Weekly cycle of HNO_3 and H_2CO at surface calculated from model 1 initial condition after integration assuming weekly 4-hour cloud-and-rain event (model rain-1). Seven-day mean mixing ratio for each species is also shown.

their concentrations in the surface boundary layer (see Figure 8).

5. TIME-DEPENDENT AND STEADY STATE SIMULATIONS: LONG-TERM VARIABILITY

Two long-term integrations have been performed assuming regular patterns of cloud and precipitation to determine effects on ozone and other longer-lived gases and to verify the validity of conventional parameterizations of precipitation removal.

We simulate the effects of prolonged cloud cover by continuing the integration begun with a 3-day cloud (model 4 initial condition) until a new steady state ozone profile is obtained. Below-cloud mixing ratios of the longer-lived soluble gases decline up to 20% with loss of radical formation depending on the compound and lower boundary condition (Table 6). Ozone increases ~20% throughout the troposphere; much of the increase is due to greater photochemical production in the upper troposphere (Figure 3) where radiation reflected from the cloud enhances net ozone production over the no-cloud starting point [Thompson, 1980]. Because of the long time required to achieve equilibrium, the ozone variation cannot be confirmed easily by observation, but the calculation may point to important differences in background chemistry between predominantly cloudy and cloudless environments.

A second long-term integration conducted from a no-cloud, no-rain initial condition (model 1) simulates the effect of periodic washout of soluble gases assuming that a 4-hour rain shower (model rain-1) occurs once a week beginning at sunrise. Slowly varying transients induced by periodic perturbation eventually produce a new converged ozone profile and a weekly cycle for each gas. Seven-day cycles are illustrated for HNO_3 and H_2CO in Figure 16; weekly mean surface mixing ratios, calculated for these species and the peroxides, appear in Table 7.

Mixing ratios are also calculated from the steady state

model by using the inadequate but standard practice of parameterizing wet removal by adding a constant removal rate $\bar{k}_{ro}$ to diurnally averaged photolysis and radical reaction terms for the soluble gases (e.g., for HNO_3)

$$\text{loss}_{\text{HNO}_3} = [\text{HNO}_3](J_4 + k_{37}[\text{OH}] + \bar{k}_{ro}) \quad (14)$$

The rainout constant is defined in analogy with equation (9)

$$\bar{k}_{ro} = \frac{1}{T_{\text{period}}} \int_0^{T_{\text{event}}} k_{wr}(t) dt \quad (15)$$

where T_{period} is the time between events. For a weekly rain shower lasting 4 hours with k_{wr} fixed over the course of the event, $\bar{k}_{ro} = k_{wr}/42$. A comparison of surface mixing ratios calculated by 7-day averaging and by steady state parameterization (Table 7) shows that weekly means for the soluble species are greater because surface removal, which is at all time proportional to the mixing ratio, is a relatively inefficient sink when surface material has been depleted by precipitation washout (Figure 15b). The steady state calculation gives better agreement when a smaller value is used for the rainout constant $\bar{k}_{ro}$ or for species surface removal velocity. For example, if surface removal is the same in both models and $\bar{k}_{ro}$ is parameterized by taking the inverse of the time period between events (e.g., for all species $\bar{k}_{ro} = 1.65 \times 10^{-6} \text{ s}^{-1}$ for a weekly shower), mixing ratios computed from the steady state and time-dependent models agree quite well (Table 7).

Depending on the magnitude of k_{wr} weekly rainout reduces mean soluble gas concentration at the surface 10–35% below those of a no-cloud, no-rain atmosphere (model 1, Table 7). From a steady state calculation with nominal once-a-week rainout ($\bar{k}_{ro} = 1.65 \times 10^{-6} \text{ s}^{-1}$) and photolysis rates computed assuming a cloud is present, we find that surface mixing ratios are reduced further, 10–25% below a weekly rain-only assumption (Table 7). Mean surface mixing ratios calculated with a cloud and twice-weekly rainout ($\bar{k}_{ro} = 3.3 \times 10^{-6} \text{ s}^{-1}$) are only 50–60% of what they would be in a dry, cloudless atmosphere. If a cloud and twice-weekly rainout are assumed for a model 4-type initial condition (no NO upflux at ground), the surface HNO_3 mixing ratio is 80% lower than the corresponding no-cloud, no-rain value. For HNO_3 mixing ratios calculated from steady state parameterizations of cloud cover and wet removal (model 1, Table 7) are shown in Figure 17.

Fig. 17. HNO_3 mixing ratio (model 1, 24-hour-average) versus altitude showing sensitivity to cloud-and-rain event frequency.

TABLE 7. Sensitivity of Soluble Gases (Surface Mixing Ratios) to Periodic Cloud-and-Rain Episodes (Model 1)

Episode Parameterization	HNO ₃ ($v = 1 \text{ cm s}^{-1}$)	H ₂ O ₂ ($v = 1$)	CH ₃ OOH ($v = 1$)	H ₂ CO ($v = 0.3$)
No cloud, no rain, steady state	3.7 (−11)	6.5 (−10)	6.5 (−10)	9.7 (−11)
7 day mean values time-dependent; 4 hour rain-and-cloud/week, species-specific k_{wr}	2.3 (−11)	5.1 (−10)	5.3 (−10)	8.6 (−11)
k_{wr}	($2 \times 10^{-4} \text{ s}^{-1}$)	($1 \times 10^{-4} \text{ s}^{-1}$)	($5 \times 10^{-5} \text{ s}^{-1}$)	($7 \times 10^{-5} \text{ s}^{-1}$)
Steady state values 4 hour rain/week, no-cloud; species-specific $k_{ro} = k_{wr}/42$,	1.6 (−11)	4.7 (−10)	5.1 (−10)	8.4 (−11)
k_{wr}	($2 \times 10^{-4} \text{ s}^{-1}$)	($1 \times 10^{-4} \text{ s}^{-1}$)	($5 \times 10^{-5} \text{ s}^{-1}$)	($7 \times 10^{-5} \text{ s}^{-1}$)
Steady state values; one rain/week, $k_{ro} = 1.65 \times 10^{-6} \text{ s}^{-1}$ for all species	2.5 (−11)	5.1 (−10)	5.0 (−10)	8.4 (−11)
Steady state values; one rain/week, constant cloud; $k_{ro} = 1.65 \times 10^{-6} \text{ s}^{-1}$ for all species	2.2 (−11)	4.0 (−10)	4.2 (−10)	6.8 (−10)
Steady state values; two rains/week, constant cloud; $k_{ro} = 3.3 \times 10^{-6} \text{ s}^{-1}$ for all species	1.7 (−11)	3.2 (−10)	3.3 (−10)	5.9 (−11)

6. SUMMARY AND CONCLUSION

A one-dimensional time-dependent chemical-transport model of the unpolluted marine atmosphere has been described along with some steady state results that illustrate principal sensitivities of boundary-layer chemistry to variations in surface NO_y, air-sea exchange rates, and near-surface transport. Simulations of sporadic clouds and rainfall superimposed on the background chemistry of a fixed air mass create large short-term changes (up to an order of magnitude) in the concentrations of soluble gases. As a consequence, the photochemical equilibrium of these compounds may be upset for a period of some days, an effect that cannot be neglected in trying to interpret measurements of these species. By choosing a few representative cases of regular cloud and precipitation removal we have tried to illustrate the sensitivity of lower troposphere chemistry to differences in average meteorology. Depending on the mean cloud and precipitation patterns of a given area, the spatial variability of soluble gases over a region of uniform background chemistry may also approach an order of magnitude.

In conclusion, we emphasize that although we have demonstrated a strong sensitivity of boundary-layer chemistry to typical synoptic episodes, the exact magnitude of such variations depends critically on dynamics and chemical inputs that have been simulated here in only one dimension neglecting cloud transport. Also, in focusing on precipitation washout as a primary mechanism for perturbing chemical equilibrium we have neglected other heterogeneous processes (e.g., diffusion of gases into fog, cloudwater, and aerosols) that may be more important in determining the chemistry of the marine troposphere.

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