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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., HNO₃, H₂CO, and H₂O₂) 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 NOₓ 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 HNO₃, CH₂O, 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 species 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:

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

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

| Altitude, km | Temperature, °K | Mixing Ratio (by volume) |
|-------------|-----------------|--------------------------|
|             | N2 cm⁻³ | O3 cm⁻³ | H2O | CH4* | CO* | H2* |
| 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          | 216.6    | 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) | 1.50 (−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) |
| 0.05        | 287.7    | 1.98 (19) | 5.30 (18) | 7.32 (−3) | 1.60 (−6) | 1.20 (−7) | 5.50 (−7) |
| 0.02        | 287.8    | 1.98 (19) | 5.32 (18) | 7.50 (−3) | 1.60 (−6) | 1.20 (−7) | 5.50 (−7) |
| 0.01        | 288.0    | 1.99 (19) | 5.33 (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, O3, 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 x 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(αP), NO, NO2, NO3, N2O3, HNO3, HNO4, H, OH, HO2, H2O2 and the hydrocarbons resulting from methane oxidation CH3, CH2O, CH3O2, CH2O3OH, and CH3O2. For convenience, reference is made to collective terms: odd oxygen, O3 = O + O(αP); odd nitrogen, NO = NO + NO2 + HNO3 + 2N2O3 + HNO4 + NO2; odd hydrogen, HO2 = H + OH + HO2; however, mixing ratios are always calculated for all the individuals, not the 'group' as a whole. We point out that NO3, 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 NO3 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(αD) are calculated from those of O3 using the tabulated extra-terrestrial solar flux [NASA, 1979], attenuated by ozone absorption and zero-order molecular scattering calculated from column densities ranging 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(αD) photolysis. The radiation calculation includes ozone absorption, surface reflection, and molecular scattering computed according to Luther's [1980] algorithm. Mid-latitude (30ø) 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 ranging 15-80 km: O3 = 8.33 x 10¹⁸ cm⁻²; total molecules 2.58 x 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...
| Reaction                        | Rate Constants |
|--------------------------------|----------------|
| $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$ | $k_1 = 5.58 \times 10^{-29}/T^2$ |
| $\text{O} + \text{O}_2 \rightarrow 2\text{O}_2$           | $k_2 = 1.5 \times 10^{-11} \exp(-2200/T)$ |
| $\text{O} + \text{M} + \text{O}_2 \rightarrow \text{M} + 2\text{O}_2$ | $k_3 = 4.26 \times 10^{-28}/T^2$ |
| $(\text{O})^+ + \text{N}_2 \rightarrow \text{O} + \text{N}_2$ | $k_4 = 1.8 \times 10^{-11} \exp(107/T)$ |
| $(\text{O})^+ + \text{O} \rightarrow \text{O}_2 + \text{O}$ | $k_5 = 3.2 \times 10^{-11} \exp(67/T)$ |
| $\text{NO} + \text{O}_2 \rightarrow \text{NO}_2 + \text{O}_2$ | $k_6 = 2.3 \times 10^{-12} \exp(-1450/T)$ |
| $\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$ | $k_7 = 9.3 \times 10^{-12}$ |
| $\text{NO}_2 + \text{O}_3 \rightarrow 2\text{NO}_2 + \text{O}_2$ | $k_{14} = 1.2 \times 10^{-13} \exp(-2450/T)$ |
| $\text{NO} + \text{NO}_2 \rightarrow 2\text{NO}_2$ | $k_8 = 2 \times 10^{-11}$ |
| $\text{NO} + \text{O} + \text{M} \rightarrow \text{NO}_2 + \text{O}_2$ | $k_9 = 3.45 \times 10^{-27}/T^6$; $k_a = 3 \times 10^{-11}$ |
| $\text{NO}_2 + \text{NO} + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}$ | $k_{17} = 9.0 \times 10^{-23}/T^6$; $k_a = 8 \times 10^{-13}$ |
| $\text{N}_2\text{O}_5 + \text{NO} + \text{M} \rightarrow \text{NO}_3 + \text{NO}_2 + \text{M}$ | $k_{18} = 6.1 \times 10^{-16} \exp(-9570/T)$; $k_a = 1.7 \times 10^{-13}$ |

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

*Third-order rate constant computed according to $k(M, T) = (k_o(T)/[M])^{-1} + k_a(T)/[M][k_0(T)]^{-1}$.

**See NASA [1981] for discussion of these rate constants. $k_{42}$ as given is the NASA recommendation. Standard value for $k_{45}$ is $7 \times 10^{-11}$; $k_a = 5 \times 10^{-7}/T^2$ is between high and low NASA limits. Value for $k_{46}$ is $2.3 \times 10^{-11}$ 

assumption that a single dense layer exists in the lower mid troposphere 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...
chemical reaction; \( n_s \) = total number of chemical species; \( n_p \) = 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\(_y\), HO\(_x\), is that short-lived radicals (e.g., O, OH, CH\(_2\)O, 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 \( \frac{dx}{dt} = 0 \). 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\(^6\) molec cm\(^{-2}\) s\(^{-1}\) | p.c.e. | \( v = 0.25 \) | \( v = 0.01 \) (10\(^{-4}\) – 10\(^{-2}\)) |
| \( (7.5 \times 10^7 - 1.5 \times 10^9) \) | \( (0.1 \text{ - } 1.0) \) | \( (0.1 \text{ - } 1.0) \) | \( (0.1 \text{ - } 1.0) \) |
| NO\(_2\) influx: | \( 7.5 \times 10^7 \text{ - } 1.5 \times 10^9 \) | fixed | \( v = 0.25 \) | \( v = 0.01 \) (10\(^{-4}\) – 10\(^{-1}\)) |
| \( v = 0.01 \) (0.001 – 0.5) | [same as 1] | \( v = 0.25 \) | \( v = 0.5 \) (0.005 – 0.5) |
| NO\(_3\) influx: | \( 7.5 \times 10^7 \text{ - } 1.5 \times 10^9 \) | same as 1 | \( v = 0.25 \) | \( v = 0.01 \) (10\(^{-4}\) – 10\(^{-1}\)) |
| \( v = 0.01 \) (0.005 – 0.5) | \( v = 0.25 \) | \( v = 0.5 \) (0.005 – 0.5) |
| HNO\(_4\) influx: | \( 7.5 \times 10^7 \text{ - } 1.5 \times 10^9 \) | same as 1 | \( v = 0.25 \) | \( v = 0.01 \) (10\(^{-4}\) – 10\(^{-1}\)) |
| \( v = 0.01 \) (0.005 – 0.5) | \( v = 0.25 \) | \( v = 0.5 \) (0.005 – 0.5) |
| HNO\(_3\) influx: | \( 7.5 \times 10^7 \text{ - } 1.5 \times 10^9 \) | same as 1 | \( v = 0.25 \) | \( v = 0.01 \) (10\(^{-4}\) – 10\(^{-1}\)) |
| \( v = 0.01 \) (0.005 – 0.5) | \( v = 0.25 \) | \( v = 0.5 \) (0.005 – 0.5) |

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: \( 5 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}\); O\(_2\): influx: \( 4 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}\) (value given is diurnally averaged and is one-half that used in time-dependent calculation); NO\(_y\) (=NO + NO\(_2\) + NO\(_3\) + HNO\(_3\) + HNO\(_4\) + 2N\(_2\)O\(_5\)): influx: \( 2.5 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}\) (2.2 – 2.8 \( \times \) 10\(^9\) cm\(^{-2}\) s\(^{-1}\)); CH\(_3\), CH\(_2\)O, CH\(_3\)OH, CH\(_2\)O\(_2\), H\(_2\)O\(_2\): p.c.e. (photochemical equilibrium); H, OH, HO\(_2\), H\(_2\)O\(_2\): p.c.e.

Lower boundary (0 km)—O\(_3\): \( v = 0.05 \) (\( v = \) surface removal rate or deposition velocity (cm s\(^{-1}\)); O\(_2\): \( v = 0.5 \) (value given is diurnally averaged and is one-half that used in time-dependent calculation); CH\(_3\), CH\(_2\)O, CH\(_3\)OH, CH\(_2\)O\(_2\), H\(_2\)O\(_2\): p.c.e. (photochemical equilibrium); CH\(_3\)OH, CH\(_2\)O, H\(_2\)O\(_2\): 1.0 (0.7 – 2); CH\(_2\)O: 0.3 (0.1 – 1); H\(_2\)O\(_2\): 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 (\( \Phi \), in mole cm\(^{-2} \) s\(^{-1} \)) or surface removal velocity (\( v_{\text{rem}} \) 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. 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], \( 5 \times 10^{10} \) cm\(^{-2} \) s\(^{-1} \) for O\(_3\) is the standard. For NO\(_x\), the reference influx, \( 2.5 \times 10^8 \) cm\(^{-2} \) s\(^{-1} \), represents a mean between Johnston’s [1979] evaluation of N\(_2\)O photooxidation in the stratosphere under spring-fall conditions (NO\(_x\) flux = \( 2.8 \times 10^8 \) cm\(^{-1} \) s\(^{-1} \)) and a minimum, \( 2.2 \times 10^8 \) cm\(^{-2} \) s\(^{-1} \) derived from the N\(_2\)O source less Logan’s estimate of NO loss through recombination with N (sink = \( 6 \times 10^7 \) cm\(^{-2} \) s\(^{-1} \) [Logan et al. 1981]). In estimating the stratospheric downflux of NO\(_x\) from N\(_2\)O photodissociation, we neglect other possible sources of upper atmospheric NO\(_x\) [see, e.g., Jackman et al., 1980]. The NO\(_x\) influx is divided among all odd nitrogen species in proportion to their photochemical equilibrium, so this is a ‘family-type’ boundary condition. At the lower boundary we considered several types of specifications for NO\(_x\) as shown in Table 3:

1. Model 1. NO source from the sea [Zafiriou and McFarland, 1981]; all odd nitrogen species subject to surface deposition.
2. Model 2. NO\(_2\) fixed at lower boundary, NO in photochemical equilibrium, all other NO\(_x\) removed at surface at a rate controlled by the species removal velocity \( v \).
3. Models 3 and 4. All NO\(_x\) 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\(_x\) species).

The standard parameterization for each model (Table 3) has been chosen to reproduce concentrations of ozone and NO\(_3\) consistent with the limited data available for the remote low- to mid-latitude marine boundary layer. These include measurements made as part of GAMETAG (Rothfert 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; Hdlas and Warneck, 1981; Noxon, 1981].

Removal at the sea surface is assumed for O\(_3\); O; the soluble gases H\(_2\)CO, HNO\(_3\), and HNO\(_4\); and the peroxides H\(_2\)O\(_2\) and CH\(_3\)OOH. 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\(_x\), 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\(_x\) and ozone are shown in Figure 2. Because NO\(_x\) 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\(_x\) and O\(_3\) to a 25% variation in the stratospheric NO\(_x\) input. Ozone varies in proportion to NO\(_x\) because injected NO contributes to the formation of ozone through the sequence of reactions:

\[
\begin{align*}
\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH} \\
\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}
\end{align*}
\]

The amount of ozone produced depends not only on the ratio of the NO\(_x\) flux relative to that of ozone [Liu et al., 1980] but also on the fraction of NO\(_x\) that is NO\(_3\). The positive correlation between O\(_3\) and scaling of the NO\(_x\) flux in the upper troposphere is the consequence of net ozone production in that region because ozone is also consumed by

\[
\begin{align*}
\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2 \\
\text{H} + \text{O}_2 \rightarrow \text{HO}_2 \\
\text{HO}_2 + \text{O}_3 \rightarrow 2\text{O}_2 + \text{OH} \\
\text{CO} + \text{O}_3 \rightarrow \text{O}_2 + \text{CO}_2
\end{align*}
\]
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 O₃ production, 5–15 km: 2.9 × 10¹⁰ cm⁻² s⁻¹, no cloud; 4.3 × 10¹⁰ cm⁻² s⁻¹, cloud.

The critical factor in determining the balance between the production cycle (reactions (3)–(5)) and loss (reactions (6)–(8)) is whether HO₂ attacks NO (reaction (3)) or O₃ (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 NO₃ 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 O₃ destruction. For the curve illustrated, the column-integrated net production above 5 km (without clouds) is 2.9 × 10¹⁰ cm⁻² s⁻¹ and net loss below 5 km is 4.5 × 10¹⁰ cm⁻² 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 O₃ to stratospheric NO 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 N₂O chemistry for the odd nitrogen budget of the lower troposphere.

Steady state distributions of the longer-lived soluble gases (HNO₃, HNO₄, CH₂O, CH₃OOH, and H₂O₂) are shown in Figure 4a. Since all of these compounds are produced by a sequence of reactions involving OH, they are directly proportional to O₃ (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 HNO₃ and H₂O₂ appear in Figure 4b.

Odd hydrogen, HOx, scales roughly with O₃. Distributions of HOx and H₂O₂ in Figure 5 were calculated from the reference NOx and O₃ 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 HOx chemistry [NASA, 1981]. Model runs performed with a set of minimum and maximum rate constants for the key HOx destruction reactions (39), (42), and (97) (Table 2) indicate the uncertainties in calculated HOx and H₂O₂ profiles (Figure 5) attributable solely to the HOx reaction rates. Because of its essential role in controlling ozone levels and because recent measurements of NOx in the marine boundary layer point to very low background levels (<0.1 ppb), we
have considered variations in the distribution of NO$_x$ members under different surface conditions but with a uniform stratospheric influx ($2.5 \times 10^8$ cm$^{-2}$ s$^{-1}$).

If there is no surface source of odd nitrogen and no rainout, the total amount of surface NO$_x$ and the fraction of each species depends only on the rates of surface removal. Low values of NO$_x$ and O$_3$ are compatible only with fairly rapid NO$_x$ deposition. For example, if a uniform removal velocity is specified for all NO$_x$ species (this is equivalent to a grouped or family approach), total NO$_x$ on the order of 50–60 pptv requires a transfer rate, $v = 0.20$ cm s$^{-1}$. In that case the NO$_x$ 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 [Helds 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 proportion of NO$_2$, but for a given total NO$_x$ there is only a small range over which NO$_y$/NO$_x$ 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$_x$ distributions calculated assuming a surface source of NO with surface deposition specified for the other NO$_x$ species (model 1 in Table 3). Figure 7a illustrates NO$_x$ 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$_x$ downflux ranges from 0.3 to 6. The solid-line profile corresponds to NO$_x$ = 26 ppt at the surface, which we have chosen as representative of clean surface marine air [McFarland et al., 1979; Helas and Warneck, 1981; Noxon, 1981].

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$_x$ 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$_x$ 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$_x$ 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. 6.** Distribution of major NO$_x$ 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$_x$ at lower boundary 50–60 ppt. Extremes calculated from HNO$_3$ surface removal rate = 0.2 cm s$^{-1}$ assuming standard surface removal rates (Table 3) and one-tenth standard rates for other NO$_x$ species.

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

**Fig. 7b.** Distribution of major odd nitrogen species (model 1) NO upflux is $7.5 \times 10^8$ cm$^{-2}$ s$^{-1}$ (diurnally averaged). Surface removal is specified for all other NO$_x$ 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 HNO₃ and NOₓ accumulation in middle to upper troposphere where eddy mixing coefficient, K(z), falls below 10⁵ cm² s⁻¹. Note large differences in lowest 10 m. Other soluble gases CH₃OOH, H₂O₂, CH₂O, HNO₄ follow pattern of NOₓ. NOₓ 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 NOₓ diurnal cycles at surface (model 1). Prescribed NO upflux is 1.5 × 10⁸ molec cm⁻² s⁻¹ (constant over day, 600-1800 hours) and zero at night. Surface removal rates for other NOₓ species are given in Table 3. Most of the sum N₂O₅ + NO is NO₃ since N₂O₅/NO₃ < 0.1 at all times. Diurnal patterns calculated in model 2 are identical except for NO₂ which is fixed at 23 ppt.

Fig. 9b. NOₓ diurnal cycles at surface (model 4-A, Table 3). Surface removal rate for HNO₃ (v = 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 NOₓ mixing ratios. In the case where NO is emitted from the surface (model 1-SBL), reduced transport keeps much of the NO (and also NO₂ since it is in near-photochemical equilibrium with NO) close to the surface. For the same lower boundary conditions a higher fraction of NOₓ is NOₓ within a few meters of the surface (Figure 8). A 25 ppt NOₓ mixing ratio in the surface boundary layer requires a NO flux of only 3.5 × 10⁸ cm⁻² s⁻¹ compared with 7.5 × 10⁸ cm⁻² 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 HNO₃ 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, H₂CO, H₂O₂, and CH₃OOH.) 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 HNO₃ 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 [NOₓ]/[HNO₃] 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 NOx, low O3) 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 NOx 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 NOx and in the majority constituent HNO3. The distribution of the various members is determined primarily by photochemistry: NO builds up during the day as a result of NO2 photolysis, NO2 is in balance among the photolysis, and conversion to HNO3 during the day and to NO3 at night (from which it reforms rapidly at sunrise). Fixing NO2 or prescribing a surface flux of NO (the two are nearly equivalent) introduces a 15–20% variation in total NOx, which is absorbed by a slow buildup of HNO3 during the day (Figure 9a). This effect is significant only below 3 km (i.e., in the region of effective NOx forcing (cf. model 1, Figure 7b)). We have also performed a model run with continuous NO upflux (7.5 × 108 cm–2 s–1 day and night). The only differences in NOx 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 NO2, which increases 15–20% in response to NO2 forcing at night, although only 5% on a diurnally averaged basis. The constant NO input also eliminates the small diurnal variation in total NOx (cf. Figure 9a).

We note that although our calculated NOx and HNO3 at surface are consistent with the data available, measurements of NO3 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+, NO3, and N2O5 suggested by reactions (17) and (18) (Table 2):

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

Platt et al. [1981] have noted that the value they deduce from measurements of NO2 and NOx suggests \( K_{ss} = 2–3 \times 10^{10} \) cm–3 at 100–15°C, which is 5–6 times higher than the laboratory experimental value [Connell and Johnston, 1979]. If we use our calculated mixing ratios for NO2, NOx, and N2O5 (as in Figure 9a where \([\text{N}_2\text{O}_3]/[\text{NO}_3] < 0.1 \) at all times) we compute \( K_{ss} = 1–2 \times 10^{10} \) 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 NO2 and N2O5 (0.5 cm s–1, Table 3), which suppresses near-surface NOx relative to NO2. This is equivalent to substantial heterogeneous removal, a likely cause for low NO3 [Thompson and Heikes, 1982]. Thus, our calculated NO3 may be fairly accurate for the background marine troposphere.

Figures 10a and 10b illustrate the diurnal cycles for surface OH, HO2, and H2O2. Mixing ratios of the soluble gases CH3OOH and H2CO at ground calculated from models
Fig. 11. CH$_2$O and CH$_3$OOH 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)

\[ \text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH} \]

and the elevated OH/HO$_2$ ratio means faster methane oxidation and a slight increase of H$_2$CO through the reactions

\[ \text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O} \]
\[ \text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M} \]
\[ \text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \]
\[ \text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2 \]

Above the planetary boundary layer (1–2 km) NO$_x$ species diurnal cycles are similar for all models, and away from surface influences the longer-lived soluble gases HNO$_3$, HNO$_4$, CH$_2$O, and the peroxydes 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$_x$ and the soluble gases. The magnitude of these changes turns out to depend strongly on the background NO$_x$ 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$_2$O$_2$, 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, NO$_2$, 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$_x$ 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$_2$O$_2$ 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.

Fig. 12. Effect of cloud on mixing ratios at ground: NO$_x$ and soluble gases HNO$_3$, H$_2$O$_2$, and CH$_2$O (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.
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 HNO₃, H₂O₂, HNO₄, H₂CO, and CH₃OOH. We parameterize species-specific wet removal constants (or scavenging coefficients, kₘᵣ) roughly according to solubility [Schwartz and White, 1981; Schwartz, 1980] relative to a value 2 × 10⁻⁴ s⁻¹ for HNO₃ 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 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

\[ k_{\text{wr}} \text{ event} = \frac{1}{T_{\text{event}}} \int_0^{T_{\text{event}}} k_{\text{wr}}(t) \, dt \] (9)

where \( T_{\text{event}} \) 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

\[ X = X_{t=0} \exp (-k_{\text{wr}} t) \] (10)

If we assume further that washout is irreversible and that saturation effects and evaporation of falling raindrops can be neglected, \( k_{\text{wr}} \) 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 (HNO₃), the total depletion at the end of a 4-hour shower is 90–95%, depending on the total NO boundary condition. The removal of other soluble gases, H₂CO and the peroxides, forms a similar pattern with the

**TABLE 4. Parameterizations of a Precipitation Episode**

| Species  | \( k_{\text{wr}} \) (s⁻¹) |
|----------|--------------------------|
| HNO₃     | 2 × 10⁻⁴                 |
| H₂O₂     | 2 × 10⁻⁴                 |
| HNO₄     | 5 × 10⁻⁵                 |
| CH₃OOH   | 5 × 10⁻⁵                 |

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

Cloud: \( J_{\text{cloud}} = 0.2 J_{\text{no cloud}} \text{ for } 0–2 \text{ km} \).

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

*Levine and Schwartz [1982].
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 HNO3 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, HNO3 is restored to 25% of its normal no-rain value; and at the end of a week, 90% of the original HNO3 level is achieved. When there is no NO input (Figure 15a), recovery of HNO3 from a 4-hour event is much slower. In both cases the NOx 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 HNO3 ~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 NOx 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 prerain 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 NOx and the soluble gases HNO3 and H2CO (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 HNO3 and

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Fig. 15a. Effect of cloud (model Cloud-1) and precipitation events (models Rain-1 and Rain-3) on HNO3 at the surface (model 4-A initial condition, see Figure 9b).

Fig. 15b. Effect of precipitation removal on surface HNO3 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: NOx, HNO3, and H2CO

| Model Initial Condition | Cloud/ Rain Model | Episode | 3 Days: [X] day 3/IX day 0 | 7 Days: [X] day 7/IX day 0 |
|-------------------------|------------------|---------|-----------------------------|----------------------------|
|                         |                  |         | X = NOx                      | X = NOx                     |
| 1 Cloud-1               | 3-day cloud; full NO flux | 1.22   | 0.92                        | 1.01                       |
| 1 Cloud-2               | 3-day cloud; NO flux/5 | 0.67   | 0.74                        | 0.98                       |
| 1 Rain-1                | 4 hour rain; day 0; full NO flux | 0.98   | 0.72                        | 0.99                       |
| 1 Rain-3                | 4 hour rain; day 0 and day 3 | same as Rain-1 | 0.98                       |
| 1 Rain-4                | 4 hour rain; day 0; NO flux/5; day 0 | 0.97   | 0.70                       | 0.99                       |
| 4A Cloud-1              | 3-day cloud      | 1.00   | 0.66                        | 0.98                       |
| 4A Rain-1               | 4 hour rain; day 0 | 1.00   | 0.66                        | 0.98                       |
| 4A Rain-3               | 4 hour rain; day 0 and day 3 | same as Rain-1 | 0.98                       |

negligible for H2CO and NOx. 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 third 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 NOx 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 NOy 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 reaction if transport is slow relative to chemistry the NO2/HNO3 ratio is given by the expression

\[
\frac{NO_2}{HNO_3} = \frac{J_4 + k_{37}[OH]}{k_{36}[OH]} \]

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

\[
\frac{NO_2}{HNO_3} = \frac{J_4 + k_{37}[OH] + k_{wr}}{k_{36}[OH]} \]

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

\[
HNO_3_{final} = HNO_3_{day=0} \exp (-k_{wr}T_{event}) \]

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 |
|---------|----------|-------|
| O3      | 2.75 (×8) | 3.38 (×8) |
| HNO3    | 4.51 (×10) | 4.46 (×11) |
| H2O     | 5.83 (×10) | 4.80 (×10) |
| CH3OOH  | 5.90 (×10) | 5.25 (×10) |
| H2CO    | 6.20 (×11) | 5.58 (×10) |

Model 4, diurnally averaged.

*2.75 (×8) signifies 2.75 × 10^-8 mixing ratio by volume.
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 HNO₃ and H₂CO 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 \( \dot{k}_{\text{ro}} \) to diurnally averaged photolysis and radical reaction terms for the soluble gases (e.g., for HNO₃):

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

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

\[
\dot{k}_{\text{ro}} = \frac{1}{T_{\text{period}}} \int_0^{T_{\text{event}}} k_{\text{wr}}(t) \, dt \quad (15)
\]

where \( T_{\text{period}} \) is the time between events. For a weekly rain shower lasting 4 hours with \( k_{\text{wr}} \) fixed over the course of the event, \( \dot{k}_{\text{ro}} = k_{\text{wr}}/42 \). 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 \( \dot{k}_{\text{ro}} \) or for species surface removal velocity. For example, if surface removal is the same in both models and \( \dot{k}_{\text{ro}} \) is parameterized by taking the inverse of the time period between events (e.g., for all species \( \dot{k}_{\text{ro}} = 1.65 \times 10^{-6} \, \text{s}^{-1} \) 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 \( k_{\text{wr}} \) 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 (\( \dot{k}_{\text{ro}} = 1.65 \times 10^{-6} \, \text{s}^{-1} \)) 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 (\( \dot{k}_{\text{ro}} = 3.3 \times 10^{-6} \, \text{s}^{-1} \)) 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 HNO₃ mixing ratio is 80% lower than the corresponding no-cloud, no-rain value. For HNO₃ mixing ratios calculated from steady state parameterizations of cloud cover and wet removal (model 1, Table 7) are shown in Figure 17.

![Fig. 17](image-url)

**Fig. 17.** HNO₃ 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\textsubscript{3} (\(\nu = 1\) cm s\textsuperscript{-1}) | H\textsubscript{2}O\textsubscript{2} (\(\nu = 1\)) | CH\textsubscript{3}OOH (\(\nu = 1\)) | H\textsubscript{2}CO (\(\nu = 0.3\)) |
|--------------------------|----------------|----------------|----------------|----------------|
| 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 \(k_{aw}\) | 2.3 (-11) | 5.1 (-10) | 5.3 (-10) | 8.6 (-11) |
| Steady state values 4 hour rain/week, no-cloud; species-specific \(k_{aw}\) = \(k_{aw,42}\), \((2 \times 10^{-4} \text{ s}^{-1})\) | 1.6 (-11) | 4.7 (-10) | 5.1 (-10) | 8.4 (-11) |
| Steady state values; one rain/week, \(k_{aw} = 1.65 \times 10^{-5} \text{ s}^{-1}\) for all species | 2.5 (-11) | 5.1 (-10) | 5.0 (-10) | 8.4 (-11) |
| Steady state values; one rain/week, constant cloud; \(k_{aw} = 1.65 \times 10^{-5} \text{ s}^{-1}\) for all species | 2.2 (-11) | 4.0 (-10) | 4.2 (-10) | 6.8 (-10) |
| Steady state values; two rains/week, constant cloud; \(k_{aw} = 3.3 \times 10^{-6} \text{ s}^{-1}\) 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\textsubscript{x}, 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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