draw the conclusion that the NO\textsubscript{2} flux close to the shuttle tiles is considerably enhanced over that near the bulkhead. Assuming that the conditions for the two flights are the same (mass spectrometer data from flight 41-B and glow data from flight 41-D), and that the glow intensity of the shuttle tiles is the same as that of Si-coated Z302, we deduce that $\Phi(\text{NO}_2^+)/\Phi(\text{NO}_2) = 0.01-0.1$. Thus the mass spectrometer data indicate that NO\textsubscript{2} desorbed from the surface is present in sufficient amount to further consider NO\textsubscript{2} a viable candidate for causing the glow.

To pursue this analysis, let us assume that NO is present on the surfaces of the space shuttle (from the ambient, from surface reaction between N and O (ref. 16), from chemical reaction of fast O with the shuttle materials, or from contamination caused by attitude thruster firings\textsuperscript{3}), and that O atoms striking the surface recombine with the adsorbed NO to yield NO\textsubscript{2}:

$$\text{NO (adsorbed) + O (fast) } \rightarrow \text{NO}_2^+ \text{ (fast)}$$  

(1)

This is an example of the Eley–Rideal mechanism in catalysis (see ref. 17 for a discussion of this and the Langmuir–Hinshelwood mechanism). In this mechanism, the desorbed molecule is expected to carry the evolved heat of the reaction as rotational, vibrational, electronic or kinetic energy (or a mix of all these). A summary of work relevant to the shuttle glow problem is given in ref. 18. For the case under discussion, reaction (1), the excess energy is enormous: kinetic energy of O (4.5 eV, corresponding to a velocity of 7.3 km s\textsuperscript{-1}) + $D_{\text{NO}}$(NO–O) (3.1 eV), or a total of 7.6 eV. The short wavelength cutoff of the glow is $\sim 430$ nm (ref. 7), corresponding to 2.9 eV in the form of electronic excitation. The desorbed NO\textsubscript{2} has a kinetic energy of 1.5 eV, as has been suggested\textsuperscript{13} then the remainder (3.2 eV, or $\sim 40\%$ of the excess energy) must be partitioned between vibrational/rotational excitation of NO\textsubscript{2} and surface deposition of the excess energy. Results from beam experiments\textsuperscript{14} and theoretical calculations\textsuperscript{15} indicate that the amount of energy deposited into the surface is quite small. For example, in a theoretical study of the reaction of O with adsorbed carbon on platinum at 0 and 500 K, it was found that $>90\%$ of the energy released in the reaction appears in the product, CO. If the case of O + NO\textsubscript{ads} is analogous, then most of the remaining energy would appear in vibrational/rotational excitation of NO\textsubscript{2} ($\sim 2.5$ eV); $\sim 5\%$ of the excess energy would be deposited in the surface ($\sim 0.4$ eV). The implication of this argument is that the glow cannot be emitted below 7 cm and is more intense in the infrared than in the visible. The problem becomes even more serious if the velocity of the desorbed NO\textsubscript{2} is less than that used above. In any case, the prediction from this mechanism is that the rate of desorption of NO\textsubscript{2} will increase with increasing [O], until a plateau is reached.

Another model is provided by the Langmuir–Hinshelwood mechanism, whereby fast O atoms are thermalized on the surface and then react with adsorbed NO to form NO\textsubscript{2}:

$$\text{NO (adsorbed) + O (adsorbed) } \rightarrow \text{NO}_2^+ \text{ or NO}_2^-$$  

(2)

Again, the NO\textsubscript{2} or NO\textsubscript{2}\textsuperscript{-} would be expected to contain the excess energy, which is now considerably smaller than in the Eley–Rideal mechanism, namely only $D_{\text{NO}}$(NO–O), 3.1 eV. Since the short-wavelength threshold is $\sim 430$ nm (2.9 eV), the remainder, 0.2 eV, is kinetic energy; this corresponds to a velocity of 0.9 km s\textsuperscript{-1} for the desorbed NO\textsubscript{2}. If we again use a radiative lifetime of 80 $\mu$s, then the e-folding distance becomes $\sim 7$ cm, which is not far from the observed distance. If both NO and O are strongly adsorbed on the surface and if the adsorption energies are comparable, then the rate of reaction (2), and therefore the glow intensity, will go through a maximum as [O] is increased. If, on the other hand, both NO and O are weakly bound to the surface, then the reaction will be second-order in [O] (ref. 17). We cannot yet choose between the two mechanisms, although the Langmuir–Hinshelwood mechanism seems easier to reconcile with the observations. Finally, the energies and lifetimes used above represent most probable values. In reality, there will be a distribution (perhaps Maxwellian) of interaction energies, which will in turn, lead to a distribution of excitation energies in the products. For the qualitative nature of this discussion, however, it is sufficient to consider the most probable values.

The question of the origin of the surface NO merits some discussion. The four sources mentioned above are all possible, and all can provide the required [NO]. We note that, for example, semi-empirical models of the thermosphere\textsuperscript{20} predict ambient densities [O] and [N] of 5.3 x $10^5$ cm\textsuperscript{-3} and 6.5 x $10^5$ cm\textsuperscript{-3}, respectively, during our observational period. Hence, fluxes of ambient species onto the cabin bulkhead have been $\Phi(\text{O}) = 3.4 \times 10^{14}$ cm\textsuperscript{-2} s\textsuperscript{-1} and $\Phi(\text{N}) = 4.1 \times 10^{13}$ cm\textsuperscript{-2} s\textsuperscript{-1}. $\Phi(\text{N})$ seems only just able to balance $\Phi(\text{NO}_2^+)$, however, due to local-time and latitudinal/seasonal variations in the global N distribution, $\Phi(\text{N})$ went through a local minimum at the location and time of our observation and the orbital average of $\Phi(\text{N})$ is considerably higher.

The data reported here are consistent with a glow hypothesis based on NO\textsubscript{2} emission. However, they do not prove this hypothesis, and a number of questions remain, concerning NO\textsubscript{2} as the source of the radiation.

We thank E. Wulf for support and I. Kofsky for helpful comments. This work was supported by the German Bundesministerium für Forschung und Technologie under grant 01 QV 239.

Received 29 October 1983; accepted 4 March 1986.


**Atmospheric CH\textsubscript{4}, CO and OH from 1860 to 1985**

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Atmospheric methane, CO and the gaseous OH radical are interdependent: if CH\textsubscript{4}, CO or OH is perturbed, background concentrations of the other two constituents are affected. Perturbations to OH alter photo-oxidation rates of numerous natural and anthropogenic trace gases and affect lifetimes of those species that pass from the Earth’s surface to the free troposphere and stratosphere. It is now known that global atmospheric methane con-
concentrations are increasing1–4; less definite data suggest that carbon monoxide is also increasing5–9. Even before the measurements of refs 1–5 were made, modelling studies of CH4–CO–OH coupling had led to predictions10–12 of future temporal increases of CH4 and CO. Here we look backwards in time, using a photochemical model to simulate the trace-gas composition of the unpolluted troposphere at the start of the industrial era (taken as 1860), and at intervals up to 1985. We find that the OH concentration in the background troposphere has decreased significantly and O3 has increased due to increases of CH4 and CO; calculated changes depend on temporal trends of NOx (NOx = NO + NO2), for which no historical data are available. The calculations allow recent trace-gas trends affecting background chemistry and climate to be viewed in a longer-term context.

In modelling the photochemistry of the pre-industrial atmosphere it is essential to specify past concentrations of NOx and the most stable species CH4 and CO. Before 1860, few ambient measurements were made of these trace species, so the input to our model is based on current mixing ratios or source flux estimates extrapolated backwards in time. A summary of key species follows.

CH4 and CO. We take two extreme methane cases: one with a minimum difference in CH4 mixing ratio between 1860 and 1985 and one with a maximum difference. Similarly, we assume minimum and maximum temporal changes in CO and combine alternate sets of CH4 and CO constraints to obtain four model types (Table 1). Models 1 and 2 assume a uniform CH4 flux (constant sources) at all times, yielding 1.2–1.3 p.p.m.v. (parts per 10^6 by volume) in 1860 and 1.60 p.p.m.v. in 1985 in the models. Models 3 and 4 are based on the assumption that large differences between modern CH4 and that extracted from ice cores13–15 represent real changes in atmospheric composition over the past hundred years, rather than diffusive losses of trapped gases5. This is consistent with recently published spectroscopic measurements of past CH4 (ref. 6). Thus, in models 3 and 4, CH4 is present at a concentration of only 0.82 p.p.m.v. at ground level in 1860.

Choosing model input for CO is complicated because ground-level CO concentrations vary greatly, owing to the short lifetime of CO and uneven geographical distribution of CO sources7,8. We take 120 p.p.b.v. (parts per 10^9 by volume) CO at ground level as typical for the 1985 mid-latitude Northern Hemisphere; Southern Hemisphere CO concentrations are lower because there are fewer local sources6,11,12. Uncertainties in CO sources are treated by parameterizing two components in the model representation of the total source, $S^{\text{total}}_{\text{CO}}$: $S_0$, a surrogate for the oxidation of non-methane hydrocarbons besides CH4, and $\Phi_{\text{CO}}$, representing directly injected surface sources. Both $S_0$ and $\Phi_{\text{CO}}$ include natural and anthropogenic contributions as described in Table 1. In ascribing 82% of present-day $S_0$ to natural hydrocarbon sources, we follow Logan et al.17, recognizing that this apportionment is still uncertain. Model runs for years before 1985 assume that natural sources contributing to $S_0$ and $\Phi_{\text{CO}}$ are unchanged and anthropogenic ones scale with population or fossil-fuel usage18. Thus, $S_0$ changes little in time and $\Phi_{\text{CO}}$ is strongly time-dependent.

Table 1: Model characteristics

<table>
<thead>
<tr>
<th>Input</th>
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<th>Model 1</th>
<th>Model 2</th>
<th>Model 3</th>
<th>Model 4</th>
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<tbody>
<tr>
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<tr>
<td>1860 CH4</td>
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Type 1-CO: 35% of $S^{\text{total}}_{\text{CO}}$ (1985) is $\Phi_{\text{CO}}$; type 2-CO: 65% of $S^{\text{total}}_{\text{CO}}$ (1985) is $S_0$. The total CO source in year $t$ is:

$$S^{\text{total}}_{\text{CO}}(t) = S_0(t) + \Phi_{\text{CO}}(t)$$

where $S_0(t)$, the in situ photochemical formation from CH4 and CH3OH oxidation, is derived from the model $[S_0(t), t]$, integrated from $t = 0$ to 15 km; $S_0$ (also column-integrated) explicitly represents photo-oxidation of non-methane hydrocarbons (NMHC) besides CH4.

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O₃. Ozone concentrations vary so much in time and space, even on a short timescale, that a realistic determination of tropospheric O₃ in 1860 is impossible. For simplicity we assume identical boundary conditions for O₃ in current and past-year models: these conditions are fixed stratospheric input and fixed deposition velocity.¹⁹

H₂O, NOₓ. These species and other model parameters, for example ultraviolet and visible radiation and rainout rates, are critical in determining O₂ and OH concentrations. Water vapour, radiation fluxes and rainout rates for soluble species are fixed at constant levels¹⁹ in all model runs. Boundary conditions for odd nitrogen (NOₓ) are assumed to be uniform at all times; a stratospheric odd-nitrogen source controls NOₓ in the upper and mid-troposphere and a small upward flux of NO gives 20-25 p.p.t.v. (parts per 10¹⁵ by volume) NOₓ in the boundary layer. Although NOₓ sources include a large anthropogenic component that has increased during the past century, it seems reasonable to suppose that the low levels of NOₓ that determine O₂ and OH in the background troposphere are supplied by non-anthropogenic sources,²⁰,²¹ (for example, stratospheric injection, lightning, weak oceanic and soil fluxes of NO) which have not changed appreciably with time.

Details of the model used in the present paper and profiles of tropospheric O₃, NOₓ and OH are reported in ref. 19. The model solves for a standard complement of odd O, H, N species; CO, CH₄ and species derived from CH₄ and C₂H₄ oxidation, including peroxyacetylnitrate (PAN). Simulations are performed with a steady-state model at 10-30-yr intervals. CH₄ and CO can exhibit slower transients than would be predicted from their respective 10-yr and 2-month lifetimes,¹³ depending on the mix of CO sources.

Figure 1 shows ground-level CH₄ and CO mixing ratios and changes in column-integrated OH (0–15 km) from 1860 to 1985. Figure 1a shows results assuming minimum CH₄ change between 1860 and 1985 (models 1 and 2), and Fig. 1b assumes maximum CH₄ change (models 3 and 4). Tropospheric OH decreases as CO and CH₄ increase, with the greatest change occurring when both CO and CH₄ undergo maximum change (model 4). In that case CH₄, CO and fractional OH increases in 1950 (relative to 1860) are similar to those presented by Levine et al.,²² although our NOₓ level is much lower. When we calculate perturbed CH₄, CO-OH cycles at higher NOₓ levels (1 p.p.t.v. at 0 km), we find that increased CH₄ and CO cause near-surface OH to increase, but total tropospheric OH decreases as in Fig. 1 (although by only half as much).

Changes in atmospheric lifetimes of hundreds of trace gases, for example, reactive hydrocarbons, sulphur and nitrogen compounds, may have occurred since 1860 as a consequence of OH perturbations. Figure 1a (models 1 and 2), for which no change in surface CH₄ emissions is assumed, shows that CO increases and OH decreases could have caused background-level CH₄ to increase by 24–37% from 1860 to 1985. Figure 1b, however, implies that CH₄ doubling since 1860 requires a change in CH₄ fluxes as well as altered background OH in response to CO changes.

Changes in CO-CH₄-OH chemistry affect climate because O₂, CH₄ and CO₂ (to which CO converts by OH oxidation) are 'greenhouse' gases. Increases in CH₄ and CO cause tropospheric ozone to increase because CH₄ and CO contribute to photochemical O₃ production.²³,²⁴ The temporal changes shown in Fig. 1 imply an 8–18% tropospheric O₃ increase from 1860 to the present (Table 1); observations point to a recent temporal increase in tropospheric O₃ (refs 26, 27). O₃ perturbations instantaneously alter the Earth's infrared radiative forcing. If there has been sufficient time for a temperature response, this could have caused a small rise in global temperature, depending on the altitude profile of the O₃ increase.²⁵ Atmospheric CO increases affect radiative by supplying CO₂ (provided that OH remains at adequate levels), and by suppressing OH and allowing O₂ and CH₄ to accumulate, even if CH₄ emissions do not increase. For example, atmospheric CO₂ formed from the reaction OH + CO in 1860 (8-16 × 10¹⁰ molecules cm⁻² s⁻¹, integrated through the troposphere) exceeded the direct fossil-fuel source of CO₂, that is, 2.6 × 10¹⁰ molecules cm⁻² s⁻¹ (ref. 18). Approximately 75% of this CO was natural in origin (Table 1).

A.M.T. acknowledges partial support from the NASA Tropospheric Chemistry Office. The National Center for Atmospheric Research is supported by NSF.

Received 25 November 1985; accepted 17 February 1986.

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**Spreadings in the central South China Sea**

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*Recent work,**²⁺ indicated that the South China Sea is an ‘Atlantic-type’ marginal basin of late Tertiary age. Magnetic anomalies in the eastern part of the sea are consistent with seafloor spreading directed approximately north–south²⁺. We present here a new morphostructural study based on coupled seabed mapping and single-channel seismic reflection profiling, which reveals dominant normal fault scarps, striking N50°E between 113 and 119°E longitude near the axis of this basin. Such a structural fabric implies a NW–SE spreading direction, at least in the 150–200-km-wide axial region of the South China Sea, and places new constraints on geodynamic models for the formation of this basin in the tectonic and paleogeographic framework of South-East Asia and the South-West Pacific.

The South China Sea (Namhai), largest of the marginal basins of the western Pacific, is bounded by the continental margins