Air Chemistry and Terrestrial Gas Emissions: A Global Perspective [and Discussion]

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Air chemistry and terrestrial gas emissions: a global perspective

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The troposphere is that atmospheric region which occupies the lowest 8–13 km or so, between the Earth's surface and the tropopause, the boundary with the stratosphere. It contains the bulk of the trace gas burden of the atmosphere and has an active chemistry which removes many of the trace gases and pollutants emitted by both terrestrial processes and by human activities. The hydroxyl radical, OH, plays an important role in cleansing the troposphere by oxidizing trace gases to harmless products or to those more readily removed from the atmospheric circulation. The distribution of hydroxyl radicals defines the oxidizing capacity of the troposphere and is itself controlled by the trace gas composition and hence by terrestrial gas emissions. This review identifies the important roles played by the terrestrial source gases: methane, carbon monoxide, oxides of nitrogen and isoprene in controlling the fast photochemical balance and oxidizing capacity of the troposphere.

1. Introduction

The troposphere is that atmospheric region which occupies the lowest 8–13 km or so, between the Earth's surface and the tropopause, the boundary with the stratosphere. It contains 80–90% of the atmospheric mass, almost all of the water vapour and the bulk of the trace gas burden of the atmosphere. The composition of the troposphere was originally thought to be derived from volcanic emissions, outgassing from the oceans and transport down from the stratosphere. This rather inactive view (Junge 1963) of tropospheric chemistry was held until the 1970s when it was realized, in contrast, that the troposphere has a rather active chemistry (Levy 1971). The reactive free radical species, hydroxyl or OH, plays a central role in tropospheric chemistry by cleansing the atmosphere of most of the trace gases emitted by terrestrial processes and by human activities. This steady state concentration of hydroxyl radicals defines the oxidizing capacity of the troposphere and is itself controlled by the trace gas composition and hence terrestrial emissions.

In this review, the chemical and photochemical processes by which terrestrial gas emissions control the free radical chemistry of the troposphere are defined. To do this, the fast photochemical balance between free radical production and destruction is constructed and solved to fix the hydroxyl radical concentration. Two major types of information are required to complete this analysis: (i) chemical ki-

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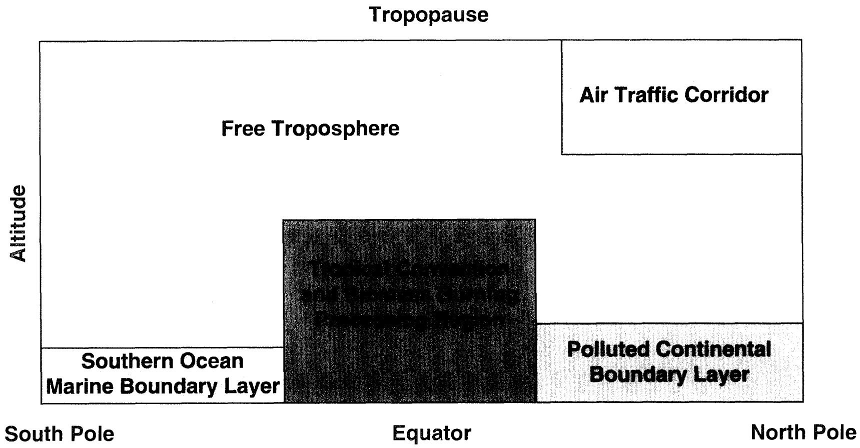

Figure 1. Diagrammatic representation of the major chemical processing regions of the troposphere.

netic data covering the individual elementary processes believed to be occurring, and (ii) concentration data for the trace gases involved.

The separate roles played by each synthetic and terrestrially derived trace gas are defined for the conditions appropriate to the polluted boundary layer of middle to high latitudes of the Northern Hemisphere. This important trace gas processing region is illustrated diagrammatically in figure 1.

2. The fast photochemical balance in the sunlit boundary layer troposphere

The fast photochemical balance in the sunlit troposphere of the polluted boundary layer at middle to high latitudes of the Northern Hemisphere is dominated by four processes: (1) photochemical reactions which generate the major free radicals, OH and HO_2; (2) chemical reactions which convert OH radicals to HO_2 radicals; (3) chemical reactions which convert HO_2 radicals to OH radicals; (4) chemical reactions which remove or recombine free radicals. The individual elementary chemical reactions which contribute to each of the above processes are characterized in the sections which follow.

(a) *Photochemical generation of* OH *and* HO_2 *radicals*

The chemistry of the troposphere is driven by the sunlight photochemical destruction of a whole range of labile molecules. The major trace constituents that absorb ultraviolet radiation to produce OH and HO_2 free radicals are ozone, formaldehyde, higher aldehydes, ketones, gaseous nitric acid, hydrogen peroxide and the higher peroxides. These are the photochemically labile species. In each case, the free radical production is obtained by multiplying together a photolysis coefficient (J-value, J) and the concentration of the photochemically labile trace gas. For example, the photolysis of gaseous nitric acid produces OH radicals through the photochemical reaction:

$$HNO_3 + \text{radiation} \quad (200\text{–}300\ \text{nm}) = OH + NO_2$$

Table 1. *Photochemical generation of* OH *and* HO_2 *radicals in the sunlit troposphere under conditions of the polluted continental Northern Hemisphere boundary layer at* 53° N, *1 July*

photochemical process	J value/s^{-1} (note a)	concentration of photochemically labile species (ppb)	reaction flux (molecule cm^{-3} s^{-1})
$O_3 = O^1D + O_2^b$	2.08×10^{-5}	$65^{b,c}$	6.1×10^6
$N_2O = N_2 + O^1D$	5.7×10^{-26}	310^d	0
$HNO_3 = OH + NO_2$	5.4×10^{-7}	10^e	1.4×10^5
$HCHO = H + HCO$	2.7×10^{-5}	2.3^e	3.1×10^6
$H_2O_2 = OH + OH$	6.6×10^{-6}	4.6^e	1.5×10^6
$HO_2NO_2 = HO_2 + NO_2$	6.5×10^{-6}	0.02^e	4.1×10^3
$CH_3OOH = CH_3O + OH$	3.6×10^{-6}	1.3^e	2.3×10^5
$CH_3CHO = CH_3 + HCO$	3.8×10^{-6}	0.8^e	1.4×10^5
$C_2H_5CHO = C_2H_5 + HCO$	1.6×10^{-5}	0.1^e	1.0×10^5
$CH_3COCH_3 = 2CH_3 + CO$	4.6×10^{-7}	1.0^e	2.4×10^4
$PAN = CH_3 + NO_2$	8.7×10^{-8}	2.1^e	4.7×10^3
total radical production rate, molecule cm^{-3} s^{-1}		1.13×10^7	

[a] Land albedo, solar zenith angle 30°, overhead ozone amount 350 Dobson Units, no clouds, 1 July, 500 m altitude (Hough 1988).

[b] Assumes that of all O^1D atoms produced, only 9% react with water vapour to produce two OH radicals, based upon $[H_2O] = 3.0 \times 10^{17}$ molecule cm^{-3}, $[N_2] = 1.9 \times 10^{19}$ molecule cm^{-3} and $[O_2] = 4.8 \times 10^{18}$ molecule cm^{-3}, with rate coefficients for O^1D reactions taken from Atkinson *et al.* (1992).

[c] UK PORG (1993).

[d] Simmonds *et al.* (1993).

[e] Photochemical model calculation, Germany–Ireland trajectory case (Derwent & Jenkin 1991).

with
$$\frac{d}{dt}[OH] = J[HNO_3].$$

J values are calculated by folding together the wavelength dependent solar actinic irradiance, the absorption cross-section of the photochemically labile species and the quantum yield for the particular process over a succession of discrete wavelength intervals. The solar actinic irradiance values (Peterson 1976) at each wavelength can be taken from observed data or from a model description of the transmission of ultraviolet and visible solar radiation through the atmosphere (Demerjian *et al.* 1980; Finlayson-Pitts & Pitts 1986; Hough 1988).

In the present study, quantum yields and absorption cross-section data have been taken from the evaluated chemical kinetic data compilation (Atkinson *et al.* 1992). Solar actinic irradiance data have been taken from a two-stream, sixth order calculation which takes into account the solar spectrum at the top of the atmosphere (WMO 1986) and allows for absorption by atmospheric oxygen and ozone, scattering from three height levels of cloud and scattering by the molecules of the atmosphere and by aerosol particles (Hough 1988).

Table 1 shows the J values for several important photochemical processes in the boundary layer for the solar actinic irradiance conditions of 1 July, midday, 53° N, land albedo, 350 Dobson units overhead ozone and no clouds. Concentrations of the photochemically labile species are tabulated for typical conditions of the polluted, continental, Northern Hemisphere boundary layer, PCNHBL over Europe. From the product of the J values and the species concentrations it is straightforward to estimate the rate of free radical production, whether OH or HO_2 or whatever. At this stage, it matters little which particular free radical is being generated since the aim is to calculate the rate at which new free radicals enter the free radical pool.

The most important free radical source by a significant margin is ozone photolysis. The total free radical production rate at midday, 1 July, 53° N in the PCNHBL is estimated to be about 1.1×10^7 molecule cm^{-3} s^{-1}.

(*b*) *Reactions which convert* OH *radicals into* HO_2 *radicals*

The hydroxyl radical is a highly reactive species, reacting rapidly with most atmospheric trace constituents. These reactions at first sight look like OH radical loss processes and if this is all that they are then the hydroxyl radical would be of little overall importance in tropospheric chemistry. It is important to look at the products of the hydroxyl radical reactions to see if any are reactive free radicals which can keep the reaction system going. In fact, many of the hydroxyl radical reactions go through highly reactive intermediates whose fates are to form hydrogen atoms, H, hydroperoxy radicals, or alkylperoxy radicals, RO_2. As a result, many of the hydroxyl radical reactions have the ability to form hydroperoxy radicals, ultimately. Hence such reactions are not considered hydroxyl radical loss processes but reactions which convert hydroxyl radicals into hydroperoxy radicals.

The simplest reactions which convert hydroxyl radicals into hydroperoxy radicals involve the inorganic atmospheric trace gas constituents, carbon monoxide, hydrogen, ozone and sulphur dioxide:

$$\begin{aligned} \mathrm{OH} + \mathrm{CO} &= \mathrm{H} + \mathrm{CO_2}, \\ \mathrm{H} + \mathrm{O_2} + \mathrm{M} &= \mathrm{HO_2} + \mathrm{M}, \\ \mathrm{OH} + \mathrm{H_2} &= \mathrm{H_2O} + \mathrm{H}, \\ \mathrm{OH} + \mathrm{O_3} &= \mathrm{HO_2} + \mathrm{O_2}, \\ \mathrm{OH} + \mathrm{SO_2} + \mathrm{M} &= \mathrm{HOSO_2} + \mathrm{M}, \\ \mathrm{HOSO_2} + \mathrm{O_2} &= \mathrm{HO_2} + \mathrm{SO_3}. \end{aligned}$$

The reactions with many organic trace constituents have the same result, they convert OH into HO_2, though the mechanisms are somewhat more complicated involving a cascade of organic free radicals and carbonyl species. The reaction system can be illustrated with methane, the simplest hydrocarbon and the most important organic species in the interconversion of OH to HO_2:

$$\begin{aligned} \mathrm{OH} + \mathrm{CH_4} &= \mathrm{CH_3} + \mathrm{H_2O}, \\ \mathrm{CH_3} + \mathrm{O_2} + \mathrm{M} &= \mathrm{CH_3O_2} + \mathrm{M}, \\ \mathrm{CH_3O_2} + \mathrm{NO} &= \mathrm{CH_3O} + \mathrm{NO_2}, \\ \mathrm{CH_3O} + \mathrm{O_2} &= \mathrm{HO_2} + \mathrm{HCHO}. \end{aligned}$$

In table 2, the rate coefficient and concentration data are collected for this important class of reactions for conditions appropriate to the PCNHBL over Europe.

Table 2. *The reactions which convert* OH *into* HO_2 *radicals in the sunlit troposphere under conditions of the polluted continental Northern Hemisphere boundary layer* 53° N, *1 July*

$OH + X$	rate coefficient for $OH + X$ (cm^3 $molecule^{-1}$ s^{-1})	[X] (ppb)	reaction loss coefficient/s^{-1}
CO	2.4×10^{-13}	200[b]	1.200
methane	6.7×10^{-15}	1900[c]	0.318
H_2	5.2×10^{-15}	550[d]	0.072
SO_2	1.5×10^{-12}	2.6[e]	0.098
O_3	5.9×10^{-14}	65[f]	0.096
HCHO	9.6×10^{-12}	2.3 [g]	0.552
H_2O_2	1.7×10^{-12}	4.6 [g]	0.196
i-butene	5.1×10^{-11}	0.269[h]	0.346
ethylene	8.5×10^{-12}	0.958[h]	0.204
isoprene	1.0×10^{-10}	0.064[i]	0.162
toluene	6.0×10^{-12}	0.741[h]	0.110
m-xylene	2.4×10^{-11}	0.179[h]	0.107
n-butane	2.5×10^{-12}	1.605[h]	0.100
propylene	2.6×10^{-11}	0.143[h]	0.094
i-pentane	3.9×10^{-12}	0.947[h]	0.092
o-xylene	1.4×10^{-11}	0.193[h]	0.066
p-xylene	1.4×10^{-11}	0.179[h]	0.064
n-hexane	5.6×10^{-12}	0.442[h]	0.062
2-methylpentane	5.6×10^{-12}	0.392[h]	0.055
trans but-2-ene	6.4×10^{-11}	0.033[i]	0.053
1-pentene	3.1×10^{-11}	0.063[i]	0.049
3-methylpentane	5.7×10^{-12}	0.349[h]	0.049
i-butane	2.3×10^{-12}	0.864[h]	0.049
total loss coefficient/s^{-1}		4.2	

[a] 288 K, 1 atm pressure.
[b] Mace Head data from Derwent *et al.* (1994).
[c] Mace Head data from Simmonds *et al.* (1993).
[d] Schmidt (1974).
[e] Mean value for 25 sites in rural U.K., June to August 1990.
[f] UK PORG (1993).
[g] Photochemical model calculation, Germany–Ireland trajectory case (Derwent & Jenkin 1991).
[h] Mean value for Harwell, Oxfordshire, June to August, 1986–90 , West Beckham, Norfolk and Great Dun Fell, Cumbria, June to August 1990.
[i] Mean value for West Beckham, Norfolk and Great Dun Fell, Cumbria, June to August 1990.

The interconversion of hydroxyl radicals to hydroperoxy radicals is thus seen to be dominated by its reaction with carbon monoxide. The total loss coefficient for hydroxyl radicals in table 2 is estimated to be $4.2\,s^{-1}$ which implies a time constant of about two tenths of a second for the hydroxyl radical.

Of the many trace gases in table 2, some are particularly associated with terrestrial emission sources. It is important to draw attention here to the role of the terrestrial emissions of methane, carbon monoxide and isoprene in the interconversion of hydroxyl to hydroperoxy radicals.

(*c*) *Reactions which convert* HO_2 *radicals into* OH *radicals*

In contrast with the hydroxyl radical, the hydroperoxy radical, HO_2, is much less reactive and then only with a limited range of trace gases. The two main reactions are with nitric oxide, NO, and ozone, O_3:

$$NO + HO_2 = NO_2 + OH,$$
$$O_3 + HO_2 = O_2 + O_2 + OH.$$

While ozone is relatively evenly distributed throughout the troposphere, this most certainly is not the case for nitric oxide and this causes considerable difficulties in quantifying the rate of HO_2 interconversion to OH. Nitric oxide is emitted by a wide range of human activities and by terrestrial processes in soils. Furthermore, its lifetime in the atmosphere is exceedingly short, 1–3 days, due to its reaction with ozone producing nitrogen dioxide and its subsequent reactions producing PAN, nitric acid and nitrate aerosol:

$$\begin{aligned} NO + O_3 &= NO_2 + O_2, \\ NO_2 + OH + M &= HNO_3 + M, \\ CH_3COO_2 + NO_2 &= PAN, \\ NO_2 + O_3 &= NO_3 + O_2, \\ NO_3 + NO_2 + M &= N_2O_5 + M, \\ N_2O_5 &= \text{nitrate aerosol}. \end{aligned}$$

Nitric oxide therefore has a typical transport distance scale of 500–1500 km and it tends to be found in significant concentration only over continental land masses and immediately downwind of source areas. The accurate representation of the competition between the above HO_2 reactions in coarse resolution chemistry-transport models is therefore difficult. Here, the importance of terrestrial emissions of nitric oxide from soils in continental areas remote from human activity is stressed.

In the PCNHBL, the nitric oxide reaction dominates over the ozone reaction, see table 3. The overall loss coefficient for hydroperoxy radicals is seen to be $0.22\ s^{-1}$ which implies a lifetime of 5 s. This is considerably longer than the corresponding lifetime for the hydroxy radical. The picture that emerges so far therefore is one of a few limited reactions which generate a steady state of reactive free radical species in the sunlit polluted boundary layer. Every 5 s the free radical species changes to the more reactive hydroxy radical for 0.2 s before converting back to the less reactive hydroperoxy radical for 5 s and so on.

(*d*) *Reactions which remove free radicals*

There is a final set of reactions which control the fast photochemical balance in the troposphere because they remove free radicals from the reaction system without recycling them. The two main processes involve the formation of nitric acid and hydrogen peroxide:

$$OH + NO_2 + M = HNO_3 + M,$$
$$HO_2 + HO_2 + M = H_2O_2 + M.$$

Table 3. *The reactions which convert* HO_2 *into* OH *radicals in the sunlit troposphere under conditions of the polluted continental Northern Hemisphere boundary layer at* 53° N, *1 July*

$HO_2 + X$	rate coefficient for $HO_2 + X$ (cm^3 $molecule^{-1}$ s^{-1})	[X] (ppb)	reaction loss coefficient/s^{-1}
NO	8.5×10^{-12}	1.0[a]	0.213
O_3	1.7×10^{-15}	65[b]	0.003
total loss coefficient/s^{-1}		0.216	

[a] 288 K.

[b] UK PORG (1993).

[c] Based on median summertime concentrations of 1.1 ppb and 0.9 ppb, respectively, at Ladybower and Lullington Heath, U.K. (Broughton *et al.* 1993).

The reaction products belong to an important class of tropospheric trace gases, called temporary reservoir species. This terminology implies that these species are not a permanent sink for free radical species. In the upper troposphere for example, nitric acid is photolysed back to release the hydroxyl radical:

$$HNO_3 + \text{radiation} = OH + NO_2.$$

In the polluted Northern Hemisphere continental boundary layer, this process can be effectively neglected and nitric acid formation is a complete sink for free radicals. Not all of the nitric acid is scavenged immediately by dry and wet deposition processes and some is recycled back to NO_x by reaction with hydroxyl radicals:

$$OH + HNO_3 = H_2O + NO_3,$$
$$NO_3 + \text{radiation} = NO_2 + O,$$

which when the initial nitric acid formation is taken into account is equivalent to an additional free radical loss mechanism:

$$OH + OH = H_2O + O$$

with the reaction rate determined by the flux through the $OH + HNO_3$ reaction. In the PCNHBL, nitric acid is the major loss process for free radical species.

Hydrogen peroxide behaves like a temporary reservoir in the boundary layer so its treatment requires a little more consideration. It has three main fates, as follows: deposition by wet or dry routes, photolysis back to free radicals and reaction with OH radicals. By consideration of each of these major fates in turn with the initial formation reaction, their contribution to the fast photochemical balance can be discerned.

Dry and wet removal of hydrogen peroxide act as a simple loss of free radicals and this is the dominant free radical loss process in the remote, clean troposphere. Hydrogen peroxide photolysis acts as an additional HO_2 to OH interconversion process in this region:

$$H_2O + HO_2 + M = H_2O_2 + M,$$
$$H_2O_2 + \text{radiation} = OH + OH.$$

Table 4. *The reactions which remove free radicals in the sunlit troposphere under conditions of the polluted continental Northern Hemisphere boundary layer at* 53° N, *1 July*

radical loss reaction	rate coefficient (cm^3 $molecule^{-1}$ s^{-1})	reaction flux ($molecule\ cm^{-3}$ s^{-1})
$HO_2 + HO_2 + M$ $= H_2O_2 + O_2 + M$	$(1.6 \times 10^{-12} + 5.2 \times 10^{-32}[N_2]$ $+4.5 \times 10^{-32}[O_2])$ $\times(1 + (1.4 \times 10^{-21} \exp(2200/T)[H_2O]))$	$9.4 \times 10^{-12}[HO_2]^2$
$OH + NO_2 + M = HNO_3 + M$	1.4×10^{-11}	$1.89[OH]$
$OH + HO_2 = H_2O + O_2$	1.1×10^{-10}	$1.1 \times 10^{-10}[OH][HO_2]$
total radical loss rate, molecule cm^{-3} s^{-1}	$9.4 \times 10^{-12}[HO_2]^2 + 1.89[OH]$ $+1.1 \times 10^{-10}[OH][HO_2]$	

[a] $[H_2O]$: 3.0×10^{17} molecule cm^{-3}.

[b] $[NO_2]$: 5.4 ppb based on median summertime concentrations at Ladybower and Lullington Heath of 6.2 ppb and 4.6 ppb, respectively.

Reaction of hydrogen peroxide with hydroxyl radicals is equivalent to an OH to HO_2 interconversion:

$$HO_2 + HO_2 + M = H_2O_2 + M,$$

$$OH + H_2O_2 = H_2O + HO_2.$$

The fate and behaviour of hydrogen peroxide is of crucial importance throughout the clean, remote sunlit troposphere.

Table 4 gathers together the information on the rate coefficients and concentration of the species involved in the free radical loss processes for conditions appropriate to the polluted Northern Hemisphere continental boundary layer. In this table, the detailed behaviour of hydrogen peroxide as a temporary reservoir can be neglected, for the present, for the polluted boundary layer conditions.

(*e*) *Construction of the fast photochemical balance*

The first step in the construction of the fast photochemical balance of the troposphere is to equate the rates of OH to HO_2 and of HO_2 to OH interconversions. This generates a relationship between the concentrations of the OH and HO_2 radicals:

$$4.2 \times [OH] = 0.22 \times [HO_2].$$

The second step is to equate the rates of free radical production and loss:

$$1.1 \times 10^7 = 1.9 \times [OH] + 1.1 \times 10^{-10} \times [OH][HO_2] + 9.4 \times 10^{-12} \times [HO_2]^2.$$

These two relationships can be solved to yield the instantaneous free radical concentrations when the fast photochemical balance is established:

$$[OH] = 6.0 \times 10^6 \text{ molecule cm}^{-3},$$

$$[HO_2] = 1.2 \times 10^8 \text{ molecule cm}^{-3}$$

for noon-time conditions in the sunlit continental Northern Hemisphere boundary layer over Europe. These concentrations are surprisingly close to those estimated

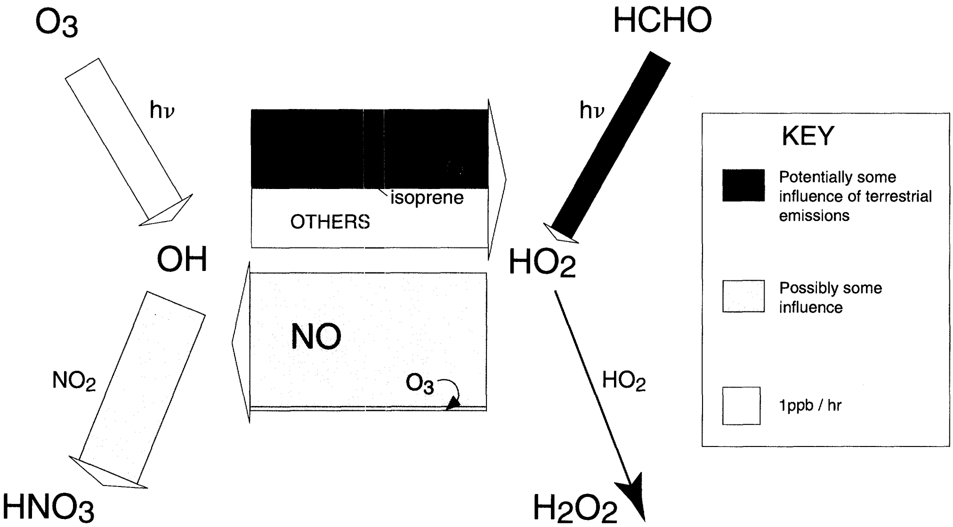

Figure 2. The fast photochemical balance in the polluted continental Northern Hemisphere boundary layer for the conditions of midday, 53° N.

in model calculations and lend some credence to the simple analysis of the roles of the chemical reactions outlined above.

When these concentrations are substituted back into tables 1–4 the reaction fluxes through the major processes can be calculated. These are illustrated diagrammatically in figure 2. This figure emphasizes the importance of the terrestrial emissions of methane, carbon monoxide, oxides of nitrogen and isoprene in controlling the fast photochemical balance of the sunlit polluted boundary layer.

3. The fast photochemical balance for the entire troposphere

Having illustrated the principal processes occurring in the sunlit boundary layer, the next stage is to extend the analysis to cover the entire troposphere. This is most conveniently performed in some form of computer model. Over the years since the pioneering work on tropospheric chemistry of Levy (1971), computer models have increased steadily in complexity through the development of one-dimensional models (Crutzen 1974), two-dimensional models (Crutzen & Gidel 1977; Derwent & Curtis 1977; Isaksen 1980: Isaksen & Hov 1987) and eventually three-dimensional models (Penner *et al.* 1991; Kasibhatla *et al.* 1993; Kanakidou & Crutzen 1993).

In solving the fast photochemical balance for the entire troposhere, there are basically two problems. The first is the meteorological problem which entails the description of the winds that transport the pollutants from their sources to their sinks, the temperature and humidities which set the background properties of the troposphere and the clouds which control the solar actinic irradiances. The second is the chemical problem which involves the description of the chemical development of the troposphere, the sources and sinks of the major trace gas constituents and how they are being influenced by human activities and terrestrial processes. These two problems are inextricably coupled together but the feedbacks between them have yet to be quantified accurately. These feedbacks arise because the chemistry affects the distribution of the radiatively active gases and generates additional radiatively active trace gases which have the potential to change the climate and hence the life cycles of the tropospheric source gases. The complete solution of the combined meteorological and chemical problems is currently beyond our ability. Furthermore, current computers do not have the capacity to handle all of the complexity and present understanding of the processes involved is necessarily limited. Simplifications and assumptions have therefore to be made to formulate a tractible problem and to make some progress towards understanding the nature of the processes involved and the likely influence of human activities upon them. Here a two-dimensional model (altitude and latitude) is used to examine the coupling between the life cycles of the major trace gases emitted by the biosphere and their role in the fast photochemical balance of the entire global troposphere.

The UK Meteorological Office two-dimensional model is used here to solve for the time dependence of the concentration, c_i, of species i, represented by the differential equation:

$$\mathrm{d}c_i/\mathrm{d}t + \nabla \cdot (c_i \boldsymbol{u}) = S_i + \nabla \cdot (KN\nabla(c_i/N)),$$

where $\boldsymbol{u}$ represents the zonally averaged wind field, S_i is the net source and sink term, K is an eddy diffusion tensor and N is the atmospheric molecular number density. The net source and sink term comprises the chemical and photochemical production and destruction of the constituent, i, emission from the surface and deposition or other removal processes. In principle, all the various terms in the above differential equation have been described for an extensive range of trace gases so that the system of coupled equations can be solved with useful resolution for a range of practical policy problems.

In this study, the UK Meteorological Office two-dimensional model is used to solve for the fast photochemical balance throughout the entire troposphere using the chemical mechanism detailed in table 5. The model uses 24 latitude bands pole-to-pole and 12 vertical levels covering 0–24 km. The chemistry of 56 species is described in 98 thermal reactions and 27 diurnally dependent photolytic processes. An emission inventory for 17 of the model species, including methane, carbon monoxide, nitric oxide and hydrocarbons, is provided, together with full treatment of the temporal and spatial variations of nine emission source categories. Both wet and dry removal processes are included for such species as ozone, nitrogen dioxide, PAN and nitric acid. Full details of the treament of each of these processes are given elsewhere (Hough & Derwent 1990; Hough 1991).

It is a straightforward matter to examine the chemical reaction fluxes through the entire 0–12 km, pole-to-pole model domain and the January–December time period. These reaction fluxes are compiled and illustrated in figure 3. There are many similarities between the two fast photochemical balances derived in this study for the polluted boundary layer and the entire troposphere. The reactions of $OH+CO$, $OH+CH_4$ and $OH+HCHO$ dominate the OH to HO_2 interconversions in both as do the $HO_2 + NO$ and $HO_2 + O_3$ reactions for the HO_2 to OH interconversions. Free radical production is dominated by ozone and formaldehyde photolysis in both, also.

The main differences between the fast photochemical balances in the polluted boundary layer and the entire troposphere lie in the free radical removal processes and the importance of the behaviour of hydrogen peroxide as a temporary reservoir species. Hydrogen peroxide reactions dominate free radical loss processes in

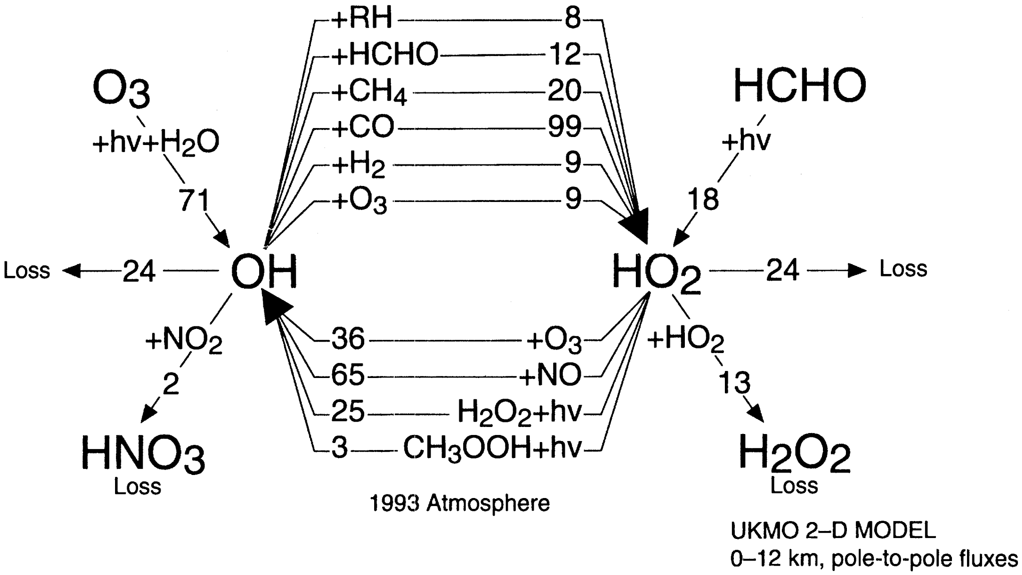

Figure 3. The total integrated reaction fluxes in moles per year from pole-to-pole, 1 January to 31 December, 0–12 km in the UK Meteorological Office two-dimensional tropospheric model.

the clean, remote troposphere whereas nitric acid formation dominates in the polluted boundary layer. In the fast photochemical balance of the entire troposphere, terrestrial emissions play an important role through their influence on the distributions of methane, carbon monoxide, oxides of nitrogen and formaldehyde. The main source of the latter compound being the photochemical oxidation of isoprene and methane.

The atmospheric lifetimes for a wide range of tropospheric trace gases are controlled by the distribution of tropospheric hydroxyl radicals generated in the fast photochemical balance which in turn is fixed by the distribution of the tropospheric source gases, their chemistry and hence terrestrial and synthetic emissions. Lifetimes range from a few hours for the natural hydrocarbons emitted by terrestrial processes to several years for the synthetic halocarbons. For the latter species, any halocarbons which survive tropospheric hydroxyl radical reactions have the potential to reach the stratosphere where they may be able to take part in stratospheric ozone depletion. In a real sense, then, terrestrial emissions help to define this oxidizing capacity.

4. Discussion and conclusions

Trace gases emitted by terrestrial processes play an important role in controlling the fast photochemical balance of the troposphere and hence in defining the oxidizing capacity of the troposphere. The main trace gases identified here as contributing to tropospheric chemistry and arising from terrestrial emissions are: (i) methane, (ii) carbon monoxide, (iii) oxides of nitrogen and (iv) isoprene.

Terrestrial emissions establish the baseline tropospheric abundances of these gases against which the relative impact of human activities can be compared. For some of these trace gases, emissions from human activities by far outweigh terrestrial emissions and this lays wide open the prospect of considerable human influence on the oxidizing capacity of the troposphere. This situation appears to be particularly true for methane and the oxides of nitrogen based on currently accepted global emissions (Houghton *et al.* 1990). As a result of the increasing emissions of methane and oxides of nitrogen from human activities, further increases in the tropospheric concentrations of the major radiatively active gases, methane and ozone are expected in the future (Derwent & Hough 1990). The projected increases in tropospheric burdens of these trace gases are likely to have radiative forcing consequences comparable to those of carbon dioxide over the next century.

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References

Atkinson, R. 1990 Gas-phase tropospheric chemistry of organic compounds: a review. *Atmos. Environ.* A **24**, 1–41.

Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, R. F., Kerr, J. A. & Troe, J. 1992 Evaluated kinetic and photochemical data for atmospheric chemistry. *J. Phys. Chem. Ref. Data* **21**, 1125–1568.

Broughton, G. F. J., *et al.* 1993 Air quality in the UK: a summary of results from instrumented air monitoring networks in 1991/92. Stevenage, Herts: Warren Spring Laboratory.

Crutzen, P. J. 1974 Photochemical reactions intiated by and influencing ozone in the unpolluted troposphere. *Tellus* **26**, 47–57.

Crutzen, P. J. & Gidel, L. T. 1983 A two-dimensional photochemical model of the atmosphere. 2. The tropospheric budgets of the anthropogenic chlorocarbons, CO, CH_4, CH_3Cl and the effect of various NO_x sources on tropospheric ozone. *J. geophys. Res.* **88**, 6641–6661.

Demerjian, K. L., Schere, K. L. & Peterson, J. T. 1980 Theoretical estimates of actinic (spherically integrated) flux and photolytic rate constants of atmospheric species in the lower atmosphere. *Adv. Environ. Sci. Technol.* **10**, 369–459.

Derwent, R. G. & Curtis, A. R. 1977 Two-dimensional model studies of some trace gases and free radicals in the troposphere. *AERE Rep.* R 8853. London: HMSO.

Derwent, R. G. & Jenkin, M. E. 1991 Long term measurements of ozone and other radiatively active gases at Mace Head in the Republic of Ireland. *Atmos. Environ.* A **25**, 1795–1808.

Derwent, R. G., Simmonds, P. G. & Collins, W. J. 1994 Ozone and carbon monoxide measurements at a remote maritime location, Mace Head, Ireland from 1990–1992. *Atmos. Environ.* **28**, 2623–2637.

Finlayson-Pitts, B. J. & Pitts, J. N. 1986 *Atmospheric chemistry: fundamentals and experimental techniques.* New York: Wiley.

Hough, A. M. 1988 The calculation of photolysis rates for use in global tropospheric modelling studies. *AERE Rep.* R 13259. Oxfordshire: Harwell Laboratory.

Hough, A. M. 1991 Development of a two-dimensional global tropospheric model: model chemistry. *J. geophys. Res.* **96**, 7325–7362.

Hough, A. M. & Derwent, R. G. 1990 Changes in the global concentration of tropospheric ozone due to human activities. *Nature, Lond.* **344**, 645–650.

Houghton, J. T., Jenkins, G. J. & Ephraums, J. J. 1990 *Climate change: the IPCC scientific assessment.* Cambridge University Press.

Isaksen, I. S. A. 1980 The tropospheric ozone budget and possible man-made effects. In *Proc. Quadrennial Ozone Symp.*, pp. 845–852. Boulder, CO: NCAR.

Isaksen, I. S. A. & Hov, O. 1987 Calculation of trends in the tropospheric concentration of O_3, OH, CO, CH_4 and NO_x. *Tellus* B **33**, 271–285.

Kanakidou, M. & Crutzen, P. J. 1993 Scale problems in global troposheric chemistry modelling: comparison of results obtained with a three-dimensional model, adopting longitudinally uniform and varying emissions of NO_x and NMHC. *Chemosphere* **26**, 787–801.

Kasibhatla, P. S., Levy, H., Moxim, W. J. & Chameides, W. L. 1991 The relative impact of stratospheric photochemical production on tropospheric NO_y levels: a model study. *J. geophys. Res.* **96**, 18 631–18 646.

Levy, H. 1971 Normal atmosphere: large radical and formaldehyde concentrations predicted. *Science, Wash.* **173**, 141–143.

Penner, J. E., Atherton, C. S., Dignon, J., Ghan, S. J., Walton, J. J. & Hameed, S. 1991 Tropospheric nitrogen: a three-dimensional study of sources, distributions and deposition. *J. geophys. Res.* **96**, 959–990.

Peterson, J. T. 1976 Calculated actinic fluxes (290–700 nm) for air pollution photochemistry applications. EPA-600/4-76-025. United States Environmental Protection Agency.

Schmidt, U. 1974 Molecular hydrogen in the atmosphere. *Tellus* **26**, 78–90.

Simmonds, P. G., Cunnold, D. M., Dollard, G. J., Davies, T. J., McCulloch, A. & Derwent, R. G. 1993 Evidence for the phase-out of CFC use in Europe over the period 1987–1990. *Atmos. Environ.* A **27**, 1397–1407.

UK PORG 1993 Ozone in the United Kingdom 1993 *Third report of the United Kingdom Photochemical Oxidants Review Group.* London: Department of the Environment.

WMO 1986 Atmospheric ozone 1985 – assessment of our understanding of the processes controlling its present distribution and change. Report 16. Geneva, Switzerland: World Meteorological Office.

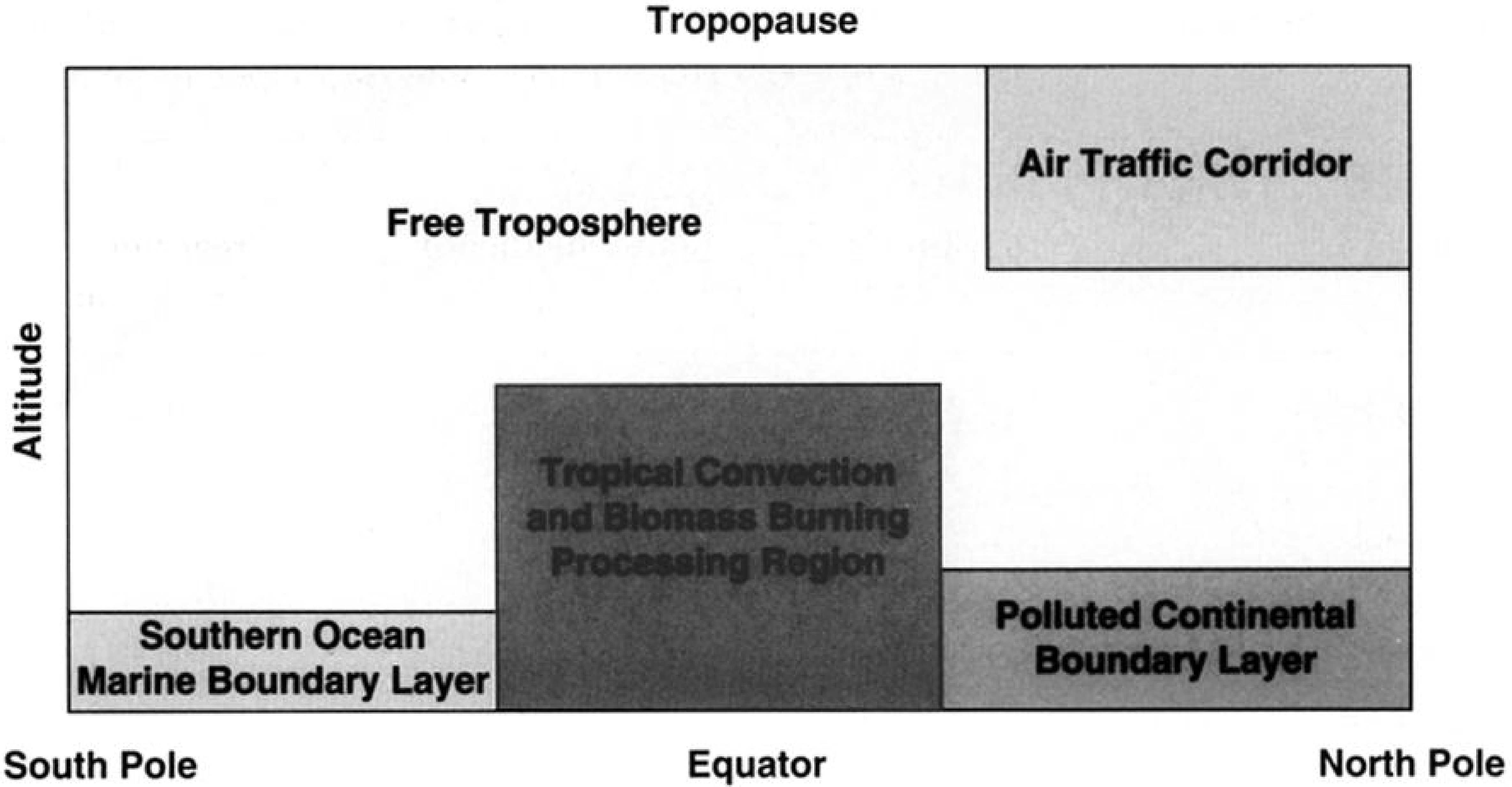
Discussion

D. S. Powlson (*Rothamsted Experimental Station, Harpenden, U.K.*). Do the current projections for future methane concentrations in the atmosphere take account of changes in the terrestrial sink for CH_4 – the oxidation of CH_4 to CO_2? Although this sink is relatively small compared to atmospheric sinks, it is one that is greatly influenced by human activity such as changes in land use and agricultural practice.

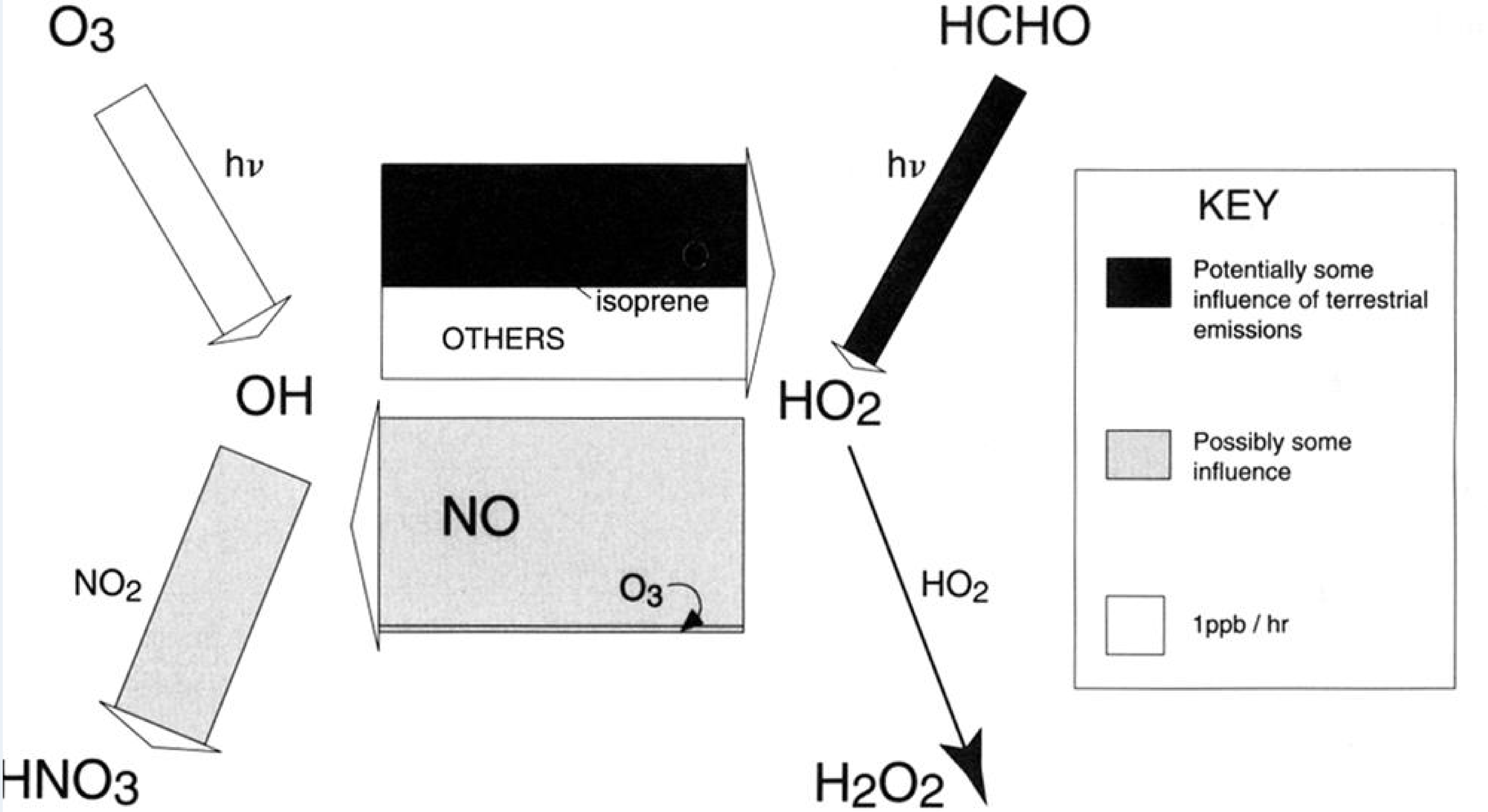
R. G. Derwent. Currently, models assume a terrestrial methane sink strength of about 15–45 $Tg(CH_4)\,a^{-1}$ compared to a total of 430–660 $Tg(CH_4)\,a^{-1}$. No impact of human activity on the terrestrial sink strength is generally taken into account.

R. Conrad (*Max Planck Institute, Marburg, Germany*). How could the production of HNO_3 contribute to the production of N_2O?

R. G. Derwent. In some rural areas, terrestrial ecosystems may receive substantial inputs through the deposition of synthetic oxidized and reduced nitrogen compounds which could conceivably stimulate increased nitrous oxide emissions.



gure 1. Diagrammatic representation of the major chemical processing regions of the troposphere.



igure 2. The fast photochemical balance in the polluted continental Northern Hemisphere boundary layer for the conditions of midday, 53° N.