Some Perspectives of the Major Biogeochemical Cycles
Edited by Gene E. Likens

CHAPTER 5

Chemical Coupling of the Nitrogen, Sulphur, and Carbon Cycles in the Atmosphere

D. H. EHHALT

Institute of Atmospheric Chemistry, Kernforschungsanlage,
5170 Jülich, Federal Republic of Germany

ABSTRACT

The various atmospheric cycles of nitrogen, sulphur, and carbon are coupled through reactions between molecules belonging to the different cycles. It is argued from a simple tropospheric model that much of the coupling proceeds indirectly through the common dependence on the OH-radical which for most trace gases initiates the most efficient removal. In the case of the nitrogen- and carbon-cycles this coupling can be quite strong.

5.1 INTRODUCTION

Traditionally atmospheric trace gas cycles were treated separately. The mass balance was determined from the direct sources and from the direct sinks, disregarding the influence on the other trace gas cycles. The same was done in predictions of increased future concentrations due to man-made pollutants. Recently, however, our understanding of atmospheric chemistry has greatly improved. We have begun to recognize that there are a number of reactions between molecules from different trace gas cycles. As a result it has been realized that there are many more pathways of direct or indirect interaction than previously assumed, that at least some of the cycles cannot be treated independently, and that a much more complicated system analysis is required than hitherto practised. In the following I will try to investigate, if and how much the atmospheric cycles of S, N, and C are mutually coupled.

5.2 THE MAJOR TRACE GASES IN THE ATMOSPHERIC CYCLES OF N, S, AND C

The major source species by which reactive N, S, and C compounds are introduced into the atmosphere are listed in Table 5.1. The major carbon species listed in this

Table 5.1 The Reaction of Atmospheric Trace Gases containing C, N, and S with OH

Trace gas	Mixing ratio in the northern hemisphere (p.p.b.)*	Mean tropospheric lifetime	Contribution of OH-sink reaction (%)
CH_4	1600	5 yr	100
CO	250	60 days	100
Non-methane hydrocarbons (NMHC), C_2–C_5	2–10	1–100 days	50–100
SO_2	0.2	14 days	50
COS	0.5	1 yr	100
H_2S		4 days	100
$(CH_3)_2S$		1 day	50
NO, NO_2	0.1	1 day	100
NH_3	ca. 1	14 days	10
N_2O	310	100 yr	0

*Here b, billion, is 10^9

table are CH_4 and CO. The mixing ratios given refer to unpolluted, ground-level air in the northern hemisphere. CO_2 is not discussed, because, as far as tropospheric gas-phase chemistry is concerned, CO_2 is inert. The non-methane hydrocarbons, C_2 to C_5, are lumped together; the mixing ratio given refers to the total.

Among the sulphur species, SO_2 is considered the most important. Its background mixing ratio is only 0.2 p.p.b. although in polluted areas much higher values have been found. COS is a molecule whose presence in the atmosphere has been demonstrated only recently. It seems to be fairly uniformly distributed with a mixing ratio of about 0.5 p.p.b. which appears consistent with its rather long lifetime of one year. The remaining two S-species, H_2S and $(CH_3)_2S$–and I might have added other mercaptans–are known to be emitted into the atmosphere. However, their lifetimes are so short that their background concentrations are low, highly variable, and not reliably established. Except for the fact that their gas-phase oxidation is started by the reaction with the OH-radical, the homogeneous chemistry of atmospheric sulphur compounds is not well established; what is known has been summarized by Graedel (1977). The most recent scheme for SO_2 oxidation has been suggested by Davis *et al.* (1979). Rainout has been discussed by Gravenhorst *et al.* (1978).

The N-cycle also has several subcycles. Because of their multiple interactions, NO and NO_2 are most important chemically. They interconvert rapidly and their combined mixing ratio in background air is about 0.1 p.p.b. They are eventually oxidized to HNO_3 which is present at about 0.1 p.p.b. in the troposphere. NH_3 is present with a mixing ratio of the order of 1 p.p.b. Again, because of the short lifetimes, the mixing ratios of these N-compounds are highly variable and the average background concentration is not well established. Values for N_2O are given in Table 5.1 because of its prominence in the nitrogen group; however like CO_2 it is essentially chemically inert in the troposphere.

There are several features common to the trace gases in Table 5.1.

(i) The major sources are located at the earth's surface, i.e. external to the atmosphere. Therefore, as far as the atmosphere is concerned, they can be treated as independent boundary conditions. In other words, the production rates of these gases are not coupled. The only exception is CO a significant part of which is produced within the atmosphere from the oxidation of CH_4.

(ii) The major part of the cycles takes place within the troposphere (excepting N_2O).

(iii) Much of the chemical conversion into other species is initiated by the OH-radical. The fraction is given in the last column of Table 5.1. Most values lie between 50 and 100 per cent.

(iv) In the case of NO_x and the sulphur species, this conversion leads eventually to acidic and highly soluble species: HNO_3 and H_2SO_4. These reactions contribute greatly to the fact that all of the eventual atmospheric removal in the S-cycle and most of the removal in the N-cycle proceeds through dry and wet deposition.

5.3 THE COUPLING OF THE CYCLES

As indicated in Table 5.1, and as far as we know, reaction with OH provides most of the coupling between the cycles. This coupling is indirect because it proceeds through a perturbation of the OH concentration. Each of the cycles, but particularly the N-cycle and the C-cycle, exerts a certain control over the OH concentration. For example, an increase in the atmospheric concentration of NO_2 leads to an increase in the OH concentration. Since CH_4 or CO are destroyed by OH, their atmospheric concentrations will decrease in inverse proportion. As increase by a factor of two in OH will decrease the atmospheric steady-state concentration of CH_4 by a factor of two.

There are of course other reactions which lead to direct coupling of the cycles. I shall briefly consider two of them. One is provided by reactions of the NH_2 radical with NO and NO_2 as outlined by the reaction scheme of Table 5.2. These data suggest the interesting possibility of a destruction of NH_3 and NO within the troposphere to form N_2 and N_2O as final products. This possibility very much depends on the rate constant of reaction (2), for which so far only an upper limit of 10^{-18} cm^3 $molecule^{-1}$ s^{-1} exists for the effective second order rate constant (Lesclaux and Demissy, 1977). If reaction (2) is much slower than that, reaction (3) and (4) will be the significant removal paths of NH_2 leading to a considerable production of N_2O, up to 6×10^{12} g yr^{-1}, within the troposphere.

Another coupling proceeds through the rainout of soluble gases. Solution of NH_3 in cloud droplets will increase the pH of these droplets and allow more rapid solution of SO_2. Thus the respective wet removal rates are coupled to a small extent.

Table 5.2 Reactions and Reaction Rate Constants of NH_3 and NH_2

Reaction				Rate constant at 298 °K and 1 atm (cm^3 $molecule^{-1}$ s^{-1})
(1)	$NH_3 + OH$	→	$NH_2 + H_2O$	1.6×10^{-13}
(2)	$NH_2 + O_2 + M$	→	$NH_2O_2 + M$	$< 10^{-18}$
(3)	$NH_2 + NO$	→	$N_2 + H_2O$	1.2×10^{-11}
(4)	$NH_2 + NO_2$	→	$N_2O + H_2O$	1.2×10^{-11}

(1) Smith and Zellner, 1975; (2) Lesclaux and Demissy, 1977; (3) Hack *et al.*, 1978; (4) Hack *et al.*, 1978.

First estimates indicate, however, that on a global scale these and other conceivable couplings are small compared to that provided by the OH-radical. Therefore the following discussion will focus on the latter.

The coupling of the N, S, and C cycles through OH is by no means fully understood. Nevertheless a sufficient number of reaction paths have been identified to present a rather complicated picture. To simplify matters, the OH-reaction scheme shown in Figure 5.1 has been reduced to the most important reactions and contains only one major representative of each cycle. It applies to background conditions as most of the calculations published so far refer to the background atmosphere. The concentrations, reactions, and reaction rate constants involved are given in Tables 5.3 and 5.4.

As indicated in Figure 5.1, the primary production of radicals proceeds via the photolysis of O_3. At wavelengths below 310 nm O_3 is photolysed to give an excited oxygen atom, O^1D, which partly reacts with H_2O to form OH. OH rapidly reacts with a large number of molecules, it is so to speak the major 'cleansing agent' of the atmosphere. During its reaction it interconverts to other radical species. Through the reaction with O_3, in which O_3 is converted to O_2, OH is converted to HO_2. The attack on CH_4 by OH entails a whole sequence of reactions symbolized by the circle around CH_4 (Figure 5.1), in which CH_4 is decomposed first to H_2CO then to CO and H_2, whereas OH is eventually converted to HO_2. (The reaction of H_2CO with OH is included in the conversion rate given in the arrow; there is slightly more HO_2 produced than OH used, as indicated by the factor α. In the lower troposphere $\alpha \approx 1$.) The fastest conversion of OH, however, is the reaction with CO. The products are CO_2 and atomic H. The H atom reacts so quickly with O_2 to form HO_2 that the H concentration remains very low. The HO_2 formed is less reactive than OH. The back reactions from HO_2 to OH have smaller rate constants and the HO_2 concentration builds up to higher values. The back reactions with O_3 and NO lead directly to OH. HO_2 also reacts with itself to form H_2O_2 which photolyses to form OH. H_2O_2 can also be removed by rainout, heterogeneous reactions or reaction with OH, which leads to a net loss of radicals. Note that interconversion

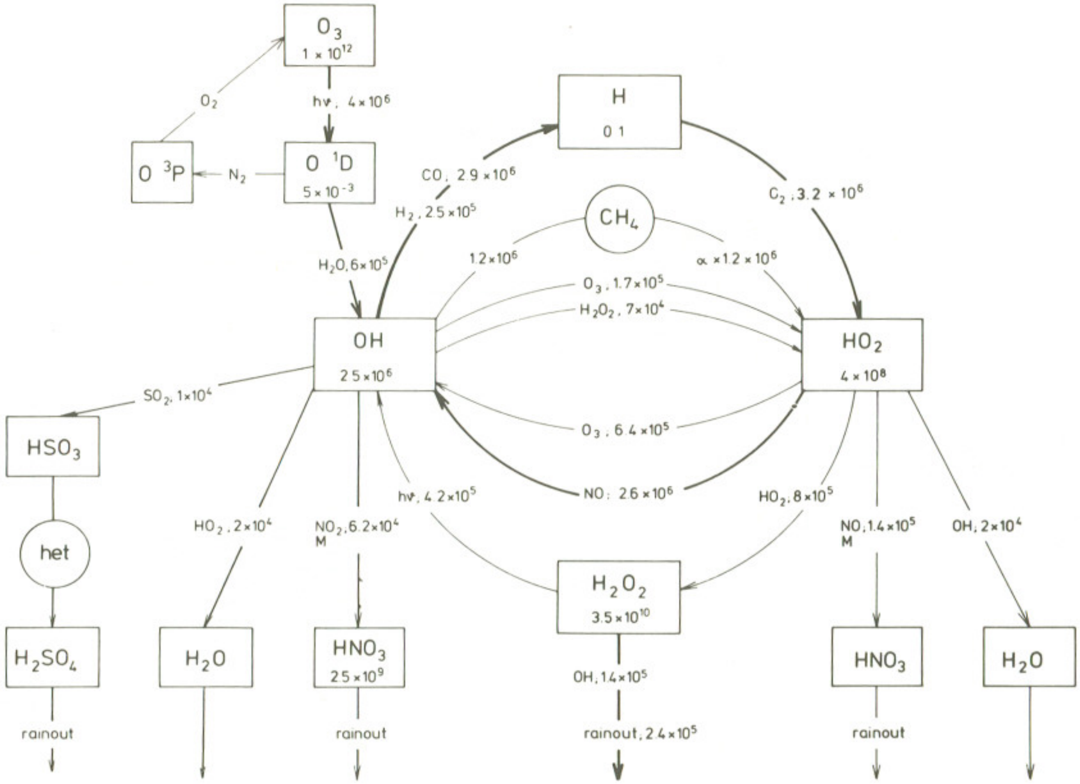

Figure 5.1 Reaction cycle of hydrogen radicals. The numbers in the boxes indicate the concentrations (cm^3), the numbers in the arrows the radical conversion rates ($cm^3\ s^{-1}$). Concentrations and reaction rates were calculated for surface level background air on a sunny summer day at mid-latitudes. ${}^3P$ and ${}^1D$ are different oxygen electronic states and 'het' represents heterogeneous reaction

Table 5.3 Average Daytime Concentrations used to derive Figure 5.1

Molecule	Concentration (molecule/cm^3)	Mixing ratio (p.p.b.)
NO	0.8×10^9	0.33×10^{-2}
NO_2	1.7×10^9	0.66×10^{-2}
HNO_3	2.5×10^9	0.1
SO_2	5.0×10^9	0.2
O_3	1.0×10^{12}	40
CO	3.7×10^{12}	150
H_2	13.8×10^{12}	550
CH_4	4×10^{13}	1600
H_2O	2.5×10^{17}	10^7

Table 5.4 Reactions and Reaction Rate Constants* used to derive Figure 5.1

Reaction			Reaction constants (298 °K, 1 atm)
$O^1D + N_2$	→	$O^3 + N_2$	3×10^{-11} cm^3 molecule^{-1} s^{-1}
$O^1D + H_2O$	→	$OH + OH$	2.3×10^{-10} cm^3 molecule^{-1} s^{-1}
$OH + H_2$	→	$H_2O + H$	7.5×10^{-15} cm^3 molecule^{-1} s^{-1}
$OH + CO$	→	$CO_2 + H$	3×10^{-13} cm^3 molecule^{-1} s^{-1} †
$OH + CH_4$	→	$CH_3 + H_2O$	7.7×10^{-15} cm^3 molecule^{-1} s^{-1}
$OH + O_3$	→	$HO_2 + O_2$	6.8×10^{-14} cm^3 molecule^{-1} s^{-1}
$OH + NO_2 + M$	→	$HNO_3 + M$	1.45×10^{-11} cm^3 molecule^{-1} s^{-1}
$OH + HNO_3$	→	$H_2O + NO_3$	8.5×10^{-14} cm^3 molecule^{-1} s^{-1}
$OH + H_2O$	→	$H_2O + O_2$	4.0×10^{-11} cm^3 molecule^{-1} s^{-1}
$OH + SO_2 + M$	→	$HSO_3 + M$	8×10^{-13} cm^3 molecule^{-1} s^{-1}
$OH + H_2O_2$	→	$HO_2 + H_2O$	8.1×10^{-13} cm^3 molecule^{-1} s^{-1}
$H + O_2 + M$	→	$HO_2 + M$	1.4×10^{-12} cm^3 molecule^{-1} s^{-1}
$HO_2 + HO_2$	→	$H_2O_2 + O_2$	2.5×10^{-12} cm^3 molecule^{-1} s^{-1}
$HO_2 + O_3$	→	$OH + O_2 + O_2$	1.6×10^{-15} cm^3 molecule^{-1} s^{-1}
$HO_2 + NO$	→	$OH + NO_2$	8×10^{-12} cm^3 molecule^{-1} s^{-1} ‡
$HO_2 + NO + M$	→	$HNO_3 + M$	1.4×10^{-13} cm^3 molecule^{-1} s^{-1}
$O_3 + h\nu$	→	$O_2 + O^1D$	4×10^{-6} s^{-1}
$H_2O_2 + h\nu$	→	$OH + OH$	6×10^{-6} s^{-1}
H_2O_2	→	rainout, heterogeneous reactions	3.4×10^{-6} s^{-1}

*Unless otherwise stated the rate constants are taken from the compilation of DeMore *et al.*, 1979; †includes three body reaction; ‡Cox, 1975.

does not mean a net loss of radicals; OH is only temporarily stored as HO_2, which is eventually recycled to OH. Net radical losses are only maintained by the arrows pointing downward and out of the cycle. The loss via H_2O_2 was already mentioned. HO_2 also reacts with OH to form H_2O. In addition, Figure 5.1 shows a not well-established reaction of HO_2 with NO to form HNO_3. This reaction is included because it has been used by Hameed *et al.* (1979) to calculate the curves shown in Figures 5.2 and 5.3. Another important radical loss is the reaction of OH with NO_2 which yields HNO_3. Finally the reaction of SO_2 with OH is important, because it removes about 50 per cent of the SO_2 from the atmosphere by reaction to HSO_3 followed by heterogeneous reaction to H_2SO_4 and finally by rainout. Owing to the small radical flux, however, it is of very limited influence on the OH balance.

Adding up all the flux values in the arrows, it is seen that the recycling of OH is about 10 times faster than the net loss through the removal reactions, and that OH takes about 0.5 s to pass through one such cycle.

Now I shall identify the coupling points, where the radicals react with the N-, C-, and S-species. Most easily understood is the reaction with SO_2. It leads to a net loss of OH. The loss is small, however, at least in the background atmosphere. There, SO_2 accounts for about one per cent of the net radical loss. Even doubling of the SO_2 concentration would have little impact on the OH concentration and hardly any influence on the C and N cycle.

For the carbon species CO and CH_4 the coupling is more important but also more complicated. Especially, the concentration of CO, whose radical conversion is quite fast, has a large impact on the OH concentration. This impact, however, since it takes place within the interconversion loop, depends also on the rate of the back reaction which is mediated mainly by NO. Thus the impact of CO will also depend on the NO concentration. If the NO concentration is low, the back reaction of HO_2 to OH is slow. An increase in the CO concentration will accelerate the reaction of OH to HO_2 and decrease the OH concentration. If NO concentrations are large, the following feedback comes into play. In the reaction of HO_2 with NO the latter is oxidized to NO_2. NO_2 is then photolysed by solar ultraviolet radiation to give O-atoms which in turn react to form O_3. The O_3 concentration increases, and with it the primary production of OH. This counterbalances the increased conversion rate of OH due to the increased CO concentration. Even more complicated is the situation with respect to NO and NO_2, because they enter into the interconversion, into the net loss of HO_2 and OH, and into the primary production through the feedback via O_3 as just shown. All I can say from the analysis of Figure 5.1 is that an increase of NO_x will increase significantly the net losses, and thus decrease the sum of OH and HO_2. To obtain a more quantitative understanding it is necessary to turn to model calculations of atmospheric chemistry. As an example I shall discuss the recent calculations by Hameed *et al.* (1979). These calculations were made with a steady-state, zero-dimensional model of the global troposphere. This means that the data I will use to quantify the coupling between the cycles through OH still come from a rather simplified model and do not warrant far-reaching conclusions. The changes of the OH, HO_2, and HO_x concentrations following a change in the global NO_2 concentration are illustrated in Figure 5.2. All

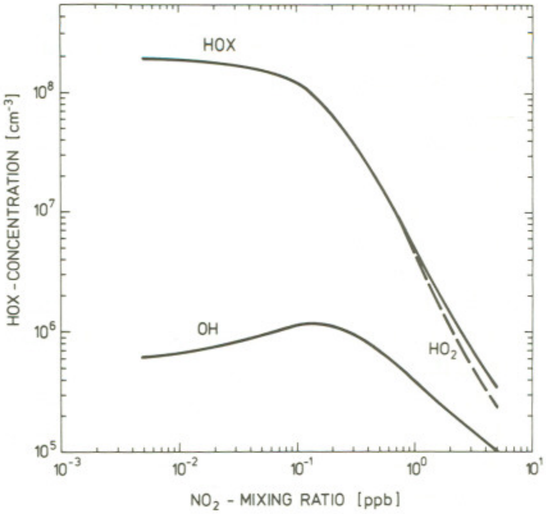

Figure 5.2 The concentration of OH, HO_2, and their sum, HO_x, as a function of the NO_2 mixing ratio calculated from a zero-dimensional, steady-state model of the troposphere (Hameed *et al.*, 1979)

other input parameters remain fixed. For very small initial NO_2 concentrations, 10^{-2} to 10^{-1} p.p.b., the sum of OH and HO_2, HO_x, decreases little with increasing NO_2. In this range the other net losses of radicals, mainly formation and rainout of H_2O_2, apparently still dominate. Only above a NO_2 concentration of about 0.1 p.p.b., do reactions of OH with NO_2, and HO_2 with NO become the dominant net loss terms and the decrease of HO_x with further increase of NO_2 becomes very marked. It can also be seen that over much of the NO_2 range shown in Figure 5.2 the HO_x decrease is essentially due to a decrease of HO_2. In fact, at low NO_2 concentrations OH increases with increased NO_2 concentration. Below about 0.1 p.p.b. NO_2, the OH response to an increased NO_2 concentration is dominated by faster conversion from HO_2 to OH via NO which is in rapid equilibrium with NO_2 and not by the slight increase in the net losses of odd hydrogen radicals from reaction with NO and NO_2. Only above 0.1 p.p.b. NO_2, when the external radical loss due to NO and NO_2 starts to dominate the other external loss reactions, does OH also begin to decrease with increasing NO_2, despite the increased conversion rate of HO_2 to OH.

Obviously the OH response of the system considered depends strongly on the initial NO_2 concentration. In the background troposphere with relatively low NO_2 concentrations (below 0.1 p.p.b.) the response to an increase in NO_2 should be relatively small judging from the flat slope of the OH curve around that concentration. In polluted areas with already high NO_2 concentrations a strong decrease in OH might be expected with further increase in NO_2.

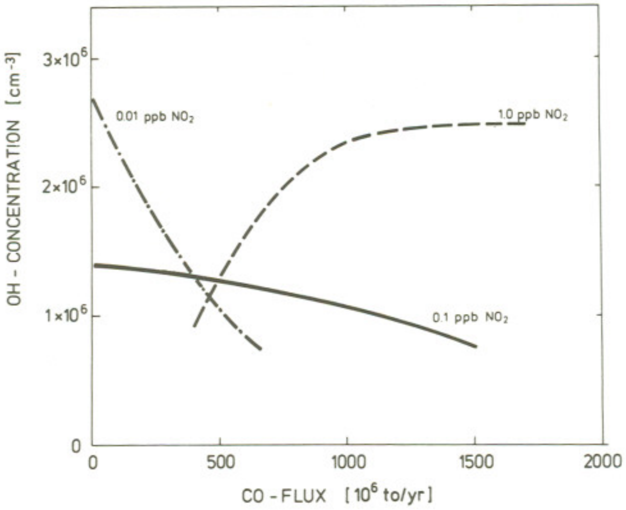

Figure 5.3 The concentration of OH as a function of the CO emission into the troposphere for various mixing ratios of NO_2 (adapted from Hameed *et al.*, 1979)

The change of OH concentration with change in CO emission is shown in Figure 5.3. This change is calculated from the CH_4 response curves given by Hameed *et al.* (1979) assuming that the only loss for CH_4 is the reaction with OH and that the CH_4 input flux is fixed. Clearly the OH response to an increased CO flux depends on the NO_2 concentration. OH drops rapidly with increasing CO flux for very small NO_2 concentrations, say 0.01 p.p.b., as pointed out in the discussion of Figure 5.1. The response curve for 0.1 p.p.b. NO_2 is much weaker but still decreasing. For large concentrations of NO_2, say 1 p.p.b., an increased emission of CO leads to more OH. This change in the response can be traced to the faster cycling between OH and HO_2: the forward reaction of OH to HO_2 is accelerated by increased CO concentration; the back reaction of HO_2 to OH is accelerated by the increased NO concentration. Since in its reaction with HO_2, NO is oxidized to NO_2 which in turn is rapidly photolysed to NO and O atoms, the faster cycling leads to an increased production of O atoms. The O atoms combine with O_2 to give O_3, and the increased levels of O_3 lead to an increased primary production of OH.

Incidentally, the present anthropogenic emission of CO is about 500×10^6 ton yr^{-1} which gives an OH concentration of about 10^6 OH cm^{-3} for all three curves. Nevertheless a change of OH due to a change in CO could be fairly substantial. It depends on the initial concentrations of CO as well as the NO_2 present in the atmosphere.

These findings are summarized in Table 5.5 and show the relative change in the global concentration due to a change in CO emission or in NO_2 and SO_2 concentration. The numerical value of -1.1 means that the global OH concentration would decrease by 11 per cent if the global CO emission increased by 10 per cent. Obviously,

Table 5.5 Relative Change of OH Concentration with Change in CO, NO_2, and SO_2 Concentrations as a Function of the NO_2 Concentration

Relative change	NO₂ concentration (p.p.b.) 0.01	0.1	1.0	Remarks
$\frac{\Delta OH}{OH} \quad \frac{\Delta CO}{CO}$	−1.1	−0.13	+1.42	change of CO flux around 500×10^6 ton yr^{-1} after Hameed *et al.*, 1979
$\frac{\Delta OH}{OH} \quad \frac{\Delta NO_2}{NO_2}$	+0.11	+0.22	−0.92	change of NO_2 concentration, after Hameed *et al.*, 1979
$\frac{\Delta OH}{OH} \quad \frac{\Delta SO_2}{SO_2}$	−0.01	−0.01	−0.01	change of SO_2 concentration around 0.2 p.p.b., estimated from Figure 5.1

depending on the NO_2 concentration, the OH changes due to perturbations of CO or NO_2 can be fairly large. For SO_2 the influence on OH concentrations is small in any case. The middle column for 0.1 p.p.b. NO_2 probably represents the closest estimate of today's global conditions. Fortuitously, the present global response of OH to a perturbation of CO and NO_2, should be relatively small that is, about two per cent for a 10 per cent change in NO_x.

The conclusion from these model calculations then is: Yes, the atmospheric trace gas cycles should be coupled through the OH radical. As man or nature change the carbon or nitrogen cycle, the global OH concentration will change also. The resulting OH change is a complicated function of initial conditions and size of the perturbation. Since reaction with OH is the major sink mechanism for most trace gases, their chemical lifetime in the atmosphere will adjust accordingly. A change in one trace gas cycle, however, will not influence the overall mass balance of the atmospheric cycles of the other trace gases. The mass balance is fixed by the production of the trace gases which except for CO occurs outside the atmosphere and thus to a first approximation remains unaffected. What will change is the atmospheric concentration and global distribution of the other trace gases. It seems, however, judging from Table 5.5, that on a global scale and in the near future the effects due to coupling through OH should be relatively small.

Regional pollution is a different matter. Man introduces and concentrates a large part of the pollutant trace gases in industrial areas. There the perturbation of the local chemical system may become severe and coupling via the OH-radical may be quite important. (Other, direct coupling mechanisms could begin to play a role too.) As Figures 5.2 and 5.3 show, it is conceivable that in such a situation–given the proper mix of pollutants–the local OH concentration could decrease with higher emissions in the future. In that case the self cleansing ability of the local atmosphere would become overloaded. As a result an increasing fraction of the pollutants would spill over into the background atmosphere. In this way regional coupling of the trace gas cycles may produce a global impact. The simple model data presented here can only identify the questions, they do not provide a final answer. In fact much future research needs to be done before the extent of chemical coupling in the atmosphere is understood in reasonable detail.

5.4 REFERENCES

Cox, R. A. (1975) The photolysis of gaseous nitrous acid–a technique for obtaining kinetic data on atmospheric photo-oxidation reactions, *Int. J. Chem. Kinetics,* Symp. 1, 379–398.

Davis, D. D., Ravishankara, A. R. and Fischer, S. (1979) SO_2 oxidation via the hydroxyl radical: Atmospheric fate of HSO_x radicals, *Geophys. Res. Lett.,* **6**, 113–116.

DeMore, W. B., Stief, L. J., Kaufman, F., Golden, D. M., Hampson, R. F., Kurylo, M. J., Margitan, J. J., Molina, M. J. and Watson, R. T. (1979) *Chemical Kinetic and Photochemical Data for use in Stratospheric Modelling,* Eval. 2, NASA Panel for Data Evaluation, JPL Publication 7/9–27.

Graedel, T. E. (1977) The homogeneous chemistry of atmospheric sulfur, *Rev. Geophys. and Space Phys.,* **15**, 421–428.

Gravenhorst, G., Janssen-Schmidt, Th. and Ehhalt, D. H. (1978) The influence of clouds and rain on the vertical distribution of sulfur dioxide in a one-dimensional steady-state model, *Atmospheric Environment,* **12**, 691–698.

Hack, W., Schacke, H., Schröter, M. and Wagner, H. G. (1978) *Reaction Rates of NH_2-radicals with NO, NO_2, C_2H_2, C_2H_4 and Other Hydrocarbons,* Report Max-Planck-Institute für Strömungsforschung, Göttingen.

Hameed, S., Pinto, J. P. and Stewart, R. W. (1979) Sensitivity of the predicted CO-OH-CH_4 perturbation to tropospheric NO_x concentrations, *J. Geophys. Res.,* **84**, 763–768.

Lesclaux, R. and Demissy, M. (1977) On the reaction of NH_2 radical with oxygen, *Nouv. J. de Chimie,* **1**, 443–444.

Smith, I. W. N. and Zellner, R. (1975) Rate measurements of OH by resonance absorption, IV, Reactions of OH with NH_3 and HNO_3, *Int. J. Chem. Kinetics,* Symp., 1, 1–351.