Environmental Consequences of Nuclear War Volume I:
Physical and Atmospheric Effects
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CHAPTER 6

Nuclear and Post-Nuclear Chemical Pollutants and Perturbations

6.1 INTRODUCTION

At the time of the 1975 NAS report on the long-term global effects of nuclear war, the major issue was the depletion of stratospheric ozone resulting from nitrogen oxides formed in fireballs and transported by them into the stratosphere (Foley and Ruderman, 1973; Johnston et al., 1973; Chang and Duewer, 1973; Hampson, 1974). The basis for consideration of this effect was growing theoretical understanding of the importance of nitrogen oxides in determining the stratospheric ozone abundance and concern for the environmental effects of the nitrogen oxides formed in the engines of aircraft flying in the lower stratosphere (Crutzen, 1970, 1971; Johnston, 1971). Recently, Crutzen and Birks (1982) suggested other potential impacts of nuclear war on large-scale atmospheric chemistry and estimated the quantities of smoke and gaseous emissions that could arise from fires ignited by nuclear explosions. They also suggested that the resulting fires would supply nitrogen oxides, hydrocarbons, and carbon monoxide to the lower 10 or 12 km of the atmosphere that could, under sunlit conditions, result in widespread ozone and oxidant production in the lower troposphere by the processes that are known to generate urban photochemical smog.

In this chapter, some estimates are presented of the quantities of gaseous and particulate effluents that could be emitted into the atmosphere by the fires ignited during a nuclear war, and the potential for developing harmful levels of these materials. The emission estimates are based on the nuclear fire properties described in Chapter 3. The changes in the concentrations of atmospheric species that may occur as a result of subsequent photochemical reactions are also considered. Perturbations to stratospheric and tropospheric chemistry are discussed separately, because of the independent nature of the chemical effects of stratospheric NO_x (produced by fireballs) and gaseous species emitted by fires into the troposphere. Chemical models of the unperturbed atmosphere are used to estimate these changes. The assessment could be carried out with greater confidence if the numbers and yields of weapon's detonations were precisely known and the potential effects of dust and smoke on atmospheric chemistry, dynamics and solar flux could be accurately calculated. As indicated in Chapter 5, however, such projections are extremely difficult to develop. Accordingly, for both the stratosphere and troposphere, there is a wide range of uncertainty in the estimates of photochemical effects. While some limited insight can be provided into what may occur in a perturbed atmosphere, better analyses will be needed in order to take into account the potentially significant changes in dynamics, temperature, and composition that could occur as a result of multiple nuclear explosions, fires, and smoke plumes.

Some of the major consequences of the predicted chemical changes arise from perturbations of the atmospheric ozone concentration. Stratospheric ozone depletion could, in the absence of thick smoke layers, lead to an increase in solar ultraviolet radiation at the Earth's surface sufficiently large to be noticeably harmful to man and the biosphere (NRC, 1984). High concentrations of ozone and other pollutants in the troposphere could be directly harmful to plants, and maybe humans as well. Both of these issues, and others related to the impact of more exotic atmospheric contaminants, are discussed below, and taken up again in Volume II.

6.2 EMISSIONS AND SHORT-TERM POLLUTANT CONCENTRATIONS FROM POST-NUCLEAR FIRES

During a nuclear war many chemical pollutants would be injected into the atmosphere. In Chapter 3, estimates were made of the potential areas of urban fires and quantities of combustible material that could burn as a result of several hundred megatons of nuclear explosions over urban and industrial centers. Although there are considerable uncertainties in estimating the quantities of materials that could burn under such circumstances, the studies by Turco et al. (1983a,b), Crutzen et al. (1984), and NRC (1985) indicate that they may amount to about 2000 to 5000 million tonne of cellulosic material and nearly 1000 million tonne of fossil fuels and fossil fuel-derived products. The flaming combustion of these materials could produce about 100 million tonne of sooty, absorbing smoke particles, which would cause substantial optical and meteorological perturbations in the global atmosphere, as described in Chapters 3, 4 and 5. Extensive smoldering of plastics and cellulosic materials could produce similar or even larger quantities of oily smoke particles that do not absorb sunlight as effectively. In addition, numerous gaseous pollutants could be created and dispersed by the fires. Nuclear explosions, in addition to forming nitrogen oxides as already noted, could disperse industrial chemicals directly into the environment from storage facilities. This section provides estimates of the potential releases of some of the gases that can play a role in the photochemistry of the atmosphere or that reach levels high enough to constitute a health hazard. For a discussion of potential health problems associated with the release of asbestos fibers into the atmosphere, the reader is referred to the NRC (1985) report and the more thorough discussion of Stephens and Birks (1985).

6.2.1 Smoke from Smoldering Combustion

The smoldering combustion of cellulosic materials can produce much more smoke than flaming combustion (McMahon and Tsoukalas, 1978; Bankston et al., 1981). Measured emission factors range between 3% and 20%. Various plastic materials likewise produce large concentrations of smoke by smoldering (Bankston et al., 1981). It is, therefore, clear that several hundred million tonne of smoke particles may be produced by smoldering combustion following nuclear attacks. This smoke would tend to stay at low altitudes, especially because it would be emitted well after the initial intense flaming phase, so that surface cooling and a stable near-surface temperature inversion might have been established. Some of the smoke particles would be in the supermicron range and would thus be deposited in the respiratory tracts of people. Gaseous byproducts and very fine aerosols would likewise be inhaled and absorbed by the lungs. The gaseous and condensed pollutants are likely to include potentially hazardous organic matter; for example, up to 100 ppm of polycyclic organic compounds (Hall and DeAngelis, 1980; McMahon and Tsoukalas, 1978).

6.2.2 Carbon Monoxide

A variety of measurements of the carbon monoxide yield from large fires in cellulosic materials, such as forest and other wildland fires (Crutzen et al., 1985; Greenberg et al., 1984), and also in real building fire situations (Treitman et al., 1980) indicate CO-to-CO_2 molar emission ratios of 12–15%. In the case of building fires, these ratios can be derived from the reported statistical distributions of elevated CO and CO_2 concentrations. Emission rates of about 100 g of CO per kg fuel have been determined by Muhlbaier (1981) for small-scale open biomass combustion, and by Quintière et al. (1982) in smoldering fires in closed compartments. Much higher CO emission ratios, however, are also possible for smoldering fires (Ives et al., 1972) and for the burning of damp forest fuels (Sandberg et al., 1975) and plastics (Terrill et al., 1978). Tewarson (1984) reports an average production from flaming burning of cellulosic materials of 6 g of CO per kg fuel for well-ventilated fires, increasing to 97 g of CO per kg fuel for mixed flaming/smoldering combustion. Here a yield of about 100 g of CO per kg fuel is adopted, after assigning the greatest weight to measurements taken in actual fire situations. This leads to a total emission of about 270 to 750 million tonne of CO from fires following a nuclear war, assuming that the total fuel consumed is within the range given by the Crutzen et al. (1984) value of 2700 million tonne and the NRC (1985) value of 7500 million tonne. With background atmospheric volume mixing ratios of CO varying between 50 ppv in the Southern Hemisphere and 150–200 ppbv at middle and high latitudes in the Northern Hemisphere (Seiler and Fishman, 1981), the total atmospheric mass of carbon monoxide is equal to about 500 million tonne, so that a substantial increase in ambient CO concentrations could occur, especially at middle latitudes of the Northern Hemisphere.

6.2.3 Hydrocarbons

Studies of the release of hydrocarbons from wildland fires (Crutzen et al., 1985; Greenberg et al., 1984) indicate methane to carbon dioxide release rate ratios of about 1%, or 5 g CH_4 per kg fuel. For nonmethane hydrocarbons, the average measured ratio was about 1.3%, or 6.5 g carbon per kg fuel. Both ratios are uncertain by about 30%. The composition of nonmethane hydrocarbons was about 45% alkenes (mostly C_2H_4), 25% alkanes (mainly C_2H_6 and C_3H_8), 13% aromatics (especially benzene and toluene), 6% acetylene, and the rest various oxygenated compounds. In a number of field fires in the U.S., total hydrocarbon emissions varied between 1.4% and 5.4% (7 to 27 g hydrocarbons per kg fuel) (McMahon, 1983). According to a compilation by the U.S. Environmental Protection Agency (EPA, 1972), methane production yields for various categories of fuels were as follows: municipal refuse 15, automobile components 15, horticultural refuse 10, and wood 2 g CH_4 per kg fuel. Wood-burning fireplaces produce only 1.5 g hydrocarbons per kg fuel (Muhlbaier, 1981). Fire tests performed with room furnishings produced typically 5–10 g unsaturated and 5–15 g saturated hydrocarbons per kg fuel (Ives et al., 1972). By assigning the greatest weight to those measurements which were made in large fires, emission factors of about 5–10 g CH_4 and 5–15 g nonmethane hydrocarbons per kg fuel may tentatively be adopted. This would lead to the emission of about 14 to 75 million tonne CH_4 and 14 to 110 million tonne nonmethane hydrocarbons, using the Crutzen et al. (1984) and NRC (1985) estimates of total fuel consumed.

The addition of this amount of methane to the atmosphere is negligible compared to the total of 5000 million tonne that is normally present in the atmosphere (Khalil and Rasmussen, 1983). The emissions of nonmethane hydrocarbons would, however, increase their atmospheric abundances by large factors. For instance, in the case of ethane (C_2H_6), which is currently present in the atmosphere at the ppb level, the global increase could be a factor of 2. For other more reactive compounds, the increase could be much larger, in some cases by orders of magnitude.

These emission estimates do not include the potentially large releases of hydrocarbons from explosions and fires in above ground fossil fuel deposits and natural gas distribution systems. It is also known that about 50% of spilled oil may volatilize within a few days (Jernelöv and Lindén, 1981). Such events may be rather common in a nuclear war, so that this volatilization could very well release on the order of 100 million tonne of reactive alkane hydrocarbons to the atmosphere. The effects of deliberate attacks on natural gas production wells, leading to blowouts, could be even more serious (Crutzen and Birks, 1982), but will not be taken into account in the following analyses.

6.2.4 Oxides of Nitrogen

It has been estimated that 10^{32} molecules of NO are formed per megaton explosion yield (Foley and Ruderman, 1973; Johnston et al, 1973). In a 6000 Mt nuclear war (Chapter 2), this mechanism would produce 30 million tonne of NO. Large-scale savanna fires (Crutzen et al., 1984) give NO-to-CO_2 molar emission rate ratios of about 2×10^{-3}. Laboratory experiments with various types of biofuels have given average molar ratios of 2.5×10^{-3} (Clements and McMahon, 1980). Similar or somewhat smaller values were compiled by EPA (1972) for the open burning of municipal refuse, automobile components, and horticultural refuse. Adopting an average NO_x-to-CO_2 molar emission rate of 2×10^{-3} (2 g NO per kg fuel), the production of NO from fires would be about 5 to 14 million tonne. The total amount of NO produced in the fireballs and in the urban and industrial fires would, therefore, add up to about 35 to 45 million tonne, which is roughly equal to the worldwide, annual production of NO from automotive and industrial combustion processes. This emission may be an underestimate, because it does not take into account the potential production of NO in hot mass fires.

6.2.5 Local Concentrations of Toxic Compounds

Emissions of CO, hydrocarbons, nitrogen oxides, and other primary emitted compounds, when distributed through large portions of the atmosphere, would not lead to concentrations that are lethal or hazardous to health. Of course, for survivors near local fire plumes, dangerous toxic levels may exist. Hazardous levels of primary pollutants might also be reached if, as a consequence of the absorption of sunlight high in the atmosphere, strong temperature inversions were to develop over the continents, particularly in river valleys and lowland areas, while smoldering combustion is still taking place. As an example, assume that strong temperature inversions can limit the vertical mixing of smoldering fire effluents to the lowest 200 m of the atmosphere; that smoke from smoldering fires over an area 5 km across mixes with background air flowing across the area at 5 m/s; and that the fires have a smoldering time of 3 days, an average fuel loading of about 10 kg/m^2, and a smoke yield of 50 g/kg fuel. In this case, the average smoke density in the air flowing out of the smoldering city beneath the inversion would be equal to about 10 mg/m^3 more than the smoke density in air flowing into the city. Such a high smoke density would limit visibilities to about 100 m (Middleton, 1952). Of course, close to the ground in the air immediately leaving the smoldering urban centers, the visibility could be appreciably less. Assuming an emission rate of 100 g CO per kg fuel, the air flowing out of the city could contain about 20 ppmv of carbon monoxide more than the air flowing into the city. Such concentrations would be too low to cause acute health effects. Treitman et al. (1980) estimate that much higher smoke densities of 1 g/m^3 are required to cause immediate respiratory distress and about ten times higher concentrations of CO are required to cause acute health effects (Woolley and Fardell, 1982). On the other hand, the pollutant concentrations calculated using this extremely simplified model are high enough to warrant further consideration of this issue. For instance, the effects of multiple city smoldering in densely populated regions was not considered. The duration of exposure to such pollutants could also be important. Furthermore, fuel loadings and emission yields of CO and smoke may be higher than assumed in these calculations, and the simultaneous presence of a variety of other toxins should also be considered. Inside or in the immediate surroundings of the burning areas low to the ground, CO concentrations could also be much higher than those estimated above.

In many fire environments, CO is the most hazardous gas (Terrill et al., 1978). If this is true in the case considered, other gaseous compounds produced by fires should generally constitute lesser health hazards on larger scales, but this has not yet been adequately studied. Besides CO, perhaps the most significant pyrotoxic gases are acrolein and hydrochloric acid (Terrill et al., 1978; Treitman et al., 1980; Woolley and Fardell, 1982). The same studies indicate much less concern for direct human health effects from HCN (hydrogen cyanide) and NO_x, depending on the conditions of exposure.

The simultaneous occurrence of health problems due to heavy air pollution cannot, therefore, become a matter of concern on continental scales. However, regionally and locally, acute health effects could be much more serious, especially in connection with the special meteorological conditions that may develop as a consequence of large scale nuclear war. Synergistic effects due to the presence of many gaseous and particulate air pollutants could also lower the thresholds for severe health effects considerably (Ives et al., 1972). Potential effects on plants are discussed in Volume II. It is clear that more thorough analysis of potential effects is required.

6.2.6 Other Emissions and Effects

If the $HC\ell$-to-CO_2 emission ratio of about 1%, measured by Treitman et al. (1980) in building fires, is extrapolated to global nuclear war conditions, the total emission of $HC\ell$ (hydrochloric acid) from the war itself could amount to about 30 million tonne. The release of about 1% sulfur from fossil fuel burning—a level consistent with current statistics (Bolin and Cook, 1983)—may lead to the production of about 14 million tonne of sulfur as H_2SO_4 (sulfuric acid). Further, if all oxides of nitrogen from the nuclear-induced fires were converted to HNO_3 (nitric acid), an injection of 5–14 million tonne of nitrogen as HNO_3 would result. These acids are removed naturally by precipitation. After a nuclear war, if the removal of the added acids occurred over one month of normal rainfall, the pH of precipitation over the northern mid-latitudes could be lower than 4 (i.e., almost ten times or more acidic than present polluted rain. The possible formation of cold acid fogs in a thermally stable atmosphere and its effects on the biosphere might be another consequence of the outcome of a nuclear war to be considered in future studies.

Chemical releases from the targeting of industries may lead to local pollution of the water, soil, and atmosphere (Turco et al., 1983a,b; NRC, 1985). As an example, consider the case of chlorine storage. In the United Kingdom, there are about 100 storage containers that can each hold between 20 and 50 tonne of chlorine. These containers are located at water treatment plants, large power stations, and various industrial plants. In addition, there are approximately 10 larger installations where greater quantities of chlorine are stored. These facilities hold between 250 and 2000 tons per site in tanks holding up to 350 tons. Any release of this heavy gas into the environment could create locally severe conditions. Chlorine container failures can, however, also trigger intense fires that could carry the chlorine to higher altitudes, thereby limiting toxic effects to the near vicinity of the accident (J.P.H. Shaw, personal communication). Thus, evaluating potential effects is not straightforward.

The release of numerous organic chlorine compounds may likewise be of concern in and downwind of targeted cities. Turco et al. (1983a,b) have reported the storage of more than 30 million tonne of PCBs (polychlorinated biphenyls) in electrical equipment in the U.S. Turco et al. (1983a,b) and Crutzen et al. (1984) point to the possible production of chlorinated dioxins and dibenzofurans from the smoldering combustion of such chlorine-containing substances. These compounds, and many others that are common in industry, are also persistent in the environment, and can be carcinogenic and mutagenic as well as toxic. Accordingly, long-term pollution effects need to be evaluated from the unprecedented chemical releases in a nuclear war.

6.2.7 Summary of Air Pollution Effects

In conclusion, chemical releases from attacks on industries and cities could cause hazardous pollution levels on local and perhaps regional scales, especially in low ventilation areas near smoldering fires, in water, soil and air affected by chemical spills, and in regions exposed to persistent toxins in the form of gases or combined with smoke. Most of the chemical releases would be likely to occur in or near densely populated areas. Obviously, a more detailed analysis of the release and effects of dangerous substances is needed.

6.3 STRATOSPHERIC CHEMISTRY

6.3.1 Impact of Fireball Nitrogen Oxides on Stratospheric Ozone

Although the current ambient integrated ozone column abundance varies substantially with latitude and season, assessments of the response of stratospheric ozone to perturbations have usually been based on models in which altitude is the single spatial dimension (NRC, 1984). The complexity of stratospheric transport is, in this case, reduced to a specification of characteristic times for vertical diffusion as a function of altitude in a hemispheric average sense. The result is a model that approximates mid-latitude or global average conditions based on the assumption that horizontal mixing is much more rapid than vertical mixing (i.e., that it is instantaneous) in the stratosphere. Recognizing this limitation, the one-dimensional models are useful for comparing the importance of chemical processes in the stratosphere and for estimating the general magnitude of stratospheric response to various perturbations. An observed mid-latitude ozone profile (WMO, 1982) and the altitude profile of ozone from a current model are shown in Figure 6.1. The nonuniform vertical distribution arises from the interaction of chemical processes, which are driven chiefly by solar ultraviolet radiation, and transport, which is most significant in the lower stratosphere where the ultraviolet flux has been reduced by absorption at higher altitudes. In the ambient atmosphere, production of ozone by ultraviolet photolysis of molecular oxygen is balanced by several chemical recombination processes (NRC, 1984). The two reactions involving NO_x ($NO + NO_2$):

$$\begin{aligned} NO + O_3 &\rightarrow NO_2 + O_2 \\ NO_2 + O &\rightarrow NO + O_2 \quad , \end{aligned}$$

are the most important (in current one-dimensional models) (e.g., Crutzen, 1970; NRC, 1984; Connell and Wuebbles, 1985). The remaining ozone destruction is distributed among processes involving chlorine radical species,

HO_x (= OH + HO_2) radical species, and, to a much lesser extent, transport to the troposphere.

Most of the ambient stratospheric NO_x is produced by the reaction of excited atomic oxygen with N_2O, which is emitted at the surface by various combustion processes and soil bacteria and transported into the stratosphere. The total abundance of NO_x in the present stratosphere is $0.5\text{–}1.5\times10^{11}$ moles (compared to 7×10^{13} moles of O_3). In a cooling nuclear fireball, NO_x production results when the equilibrium dissociation reaction, $N_2 + O_2 = 2NO$, is rapidly quenched from high initial temperatures (≥ 2000 K), such that a high non-equilibrium abundance of NO remains in the rising and expanding nuclear fireball. Theoretical estimates of the production of NO_x in this environment have been discussed by Gilmore (1975) and by the NRC committees (NAS, 1975 and NRC, 1985). Approximately 1×10^{32} molecules of NO (about 5000 tonne) are produced per megaton of nuclear energy release, with an uncertainty of perhaps a factor of 2. Hence, 400–900 Mt of nuclear explosions would double the existing stratospheric NO_x abundance. In 10000 Mt global nuclear war scenarios considered in the past (NAS, 1975; Turco et al., 1983b; Chang and Wuebbles, 1983), with the majority of the

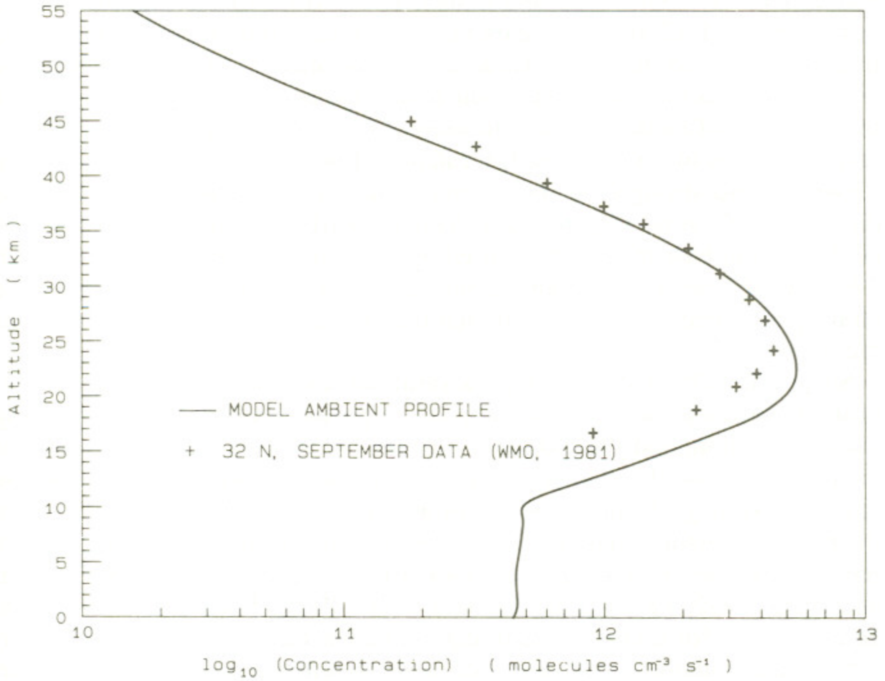

Figure 6.1. Observed vertical ozone concentration profile compared with that predicted by a one-dimensional model (Connell and Wuebbles, 1985)

explosive energy in weapons with individual yields ≥ 0.5 Mt, stratospheric NO_x would be increased by 15–20 times over the natural background. The more recent scenarios, especially NRC (1985) and Crutzen and Birks (1982) indicate stratospheric NO_x injections that are several times less. The 5000 Mt baseline scenario of Turco et al. (1983a), which included some of the larger weapons that still exist in the arsenals, resulted in an NO_x injection between the high and low cases just mentioned.

Because the various stratospheric chemical species interact with each other as well as with ozone, their net effect on ozone is not a simple sum of the effect of each species calculated independently. At each altitude, the overhead burden of ozone also affects the solar flux in the photolytically active ultraviolet region. Hence, the local change in the ozone abundance depends on the altitude distribution of injected NO_x and the resultant change in the ozone profile.

The ozone depletion depends on the heights of injection of NO_x, and therefore on the top and bottom altitudes of the stabilized nuclear clouds. These heights vary with the explosive yield, as discussed in Chapter 1. At middle latitudes, it is expected that weapons of about 0.4–0.5 Mt would loft substantial amounts of NO_x above 17 km (Peterson, 1970; Foley and Ruderman, 1973; Glasstone and Dolan, 1977; NRC, 1985). The tropopause lies at about 11–13 km, and weapons as small as ~100 kt would inject NO_x into the lower stratosphere. However, in the model, NO_x injected below ~17 km results in a small net *production* of ozone mainly as a byproduct of the oxidation of methane. The efficiency of this process increases with higher concentrations of NO_x. Thus, the calculated perturbations of stratospheric ozone depend strongly on the assumed nuclear detonation yields, but less directly on the total megatonnage. This is clearly demonstrated in the case of the Ambio baseline scenario (used by Crutzen and Birks, 1982) in which 5740 Mt of low-yield weapons produced essentially no net change in the stratospheric ozone column, although the vertical distribution of ozone was modified.

Since the 1975 NAS report, as a result of improving knowledge of relevant laboratory chemical kinetics, the importance of NO_x in calculating ozone depletion, and the crossover altitude between ozone production and ozone destruction, have varied. For massive injections of NO_x high into the stratosphere (e.g., from 10000 Mt in weapons of greater than 1 Mt each), the calculated ozone change has not been sensitive to the changes in kinetics parameters over the last decade (NAS, 1975; Duewer et al., 1978; Crutzen and Birks, 1982; Turco et al., 1983a,b; NRC, 1985). For smaller injections, and especially for scenarios assuming individual weapon yields smaller than 1 Mt, the calculated ozone depletion is more sensitive to chemical reaction rate coefficients whose measured values have varied with improvements in laboratory techniques. The simulations presented in this chapter were obtained with atmospheric models using current estimates of chemical reaction rates.

Even when an assumed scenario includes weapons of sufficient yield to penetrate the tropopause, the projected ozone depletion depends on the distribution of injection heights. A number of major factors come into play. First, since the ozone-dissociating ultraviolet solar flux intensity increases and air density decreases with altitude, the density of atomic oxygen—in steady state with respect to production by ozone photolysis and loss by combination with molecular oxygen—increases also. This increases the efficiency per NO_x molecule of the ozone-destroying NO_x chemical reactions by increasing the rate of the reaction of NO_2 with O, while NO_2 photolysis (an ozone neutral reaction) is unaffected. Second, about two-thirds of the stratospheric ozone column lies below about 25 km, so that large relative changes in the upper stratosphere can make a smaller contribution to the total change in the ozone column than smaller relative changes near the ozone maximum. Thirdly, methane oxidation reactions come into play that can increase ozone. Finally, if ozone is diminished above its concentration maximum at about 23 km, the subsequent increase in the ultraviolet flux at lower altitudes increases the rate of molecular oxygen photolysis and ozone production. Dissociation of oxygen by solar ultraviolet produces oxygen atoms and subsequently ozone, so the increase in oxygen photolysis can partially compensate for the decrease in the upper stratospheric ozone column.

Figure 6.2 shows the vertical distribution of NO_x injection that would result from three nuclear exchange scenarios. Since the distribution of injected NO_x is calculated from the yields of the individual weapons, widely different distributions can result from different scenarios involving the same total megatonnage. (See Chapter 2 for details of these scenarios.) The NRC 6500 Mt and the Ambio 5740 Mt scenarios are based on estimates of near-term nuclear arsenals assuming continuing trends to smaller warheads (however, see Chapter 2). The potential effect of including higher yield weapons, some of which may still be present in the arsenals, is illustrated by the Knox (1983) scenario, which included several 20 Mt warheads that would loft NO_x into the upper stratosphere. The NRC (1985) report also considered a case in which large yield weapons were assumed to be detonated over very "hard" targets. Although most of the larger warheads have been or are expected to be retired in the near future, some may remain and others could be added in the future.

While calculated ozone perturbations are very sensitive to the vertical distribution of NO_x injections, and therefore the assumed yields of individual weapons, smoke emissions are generally much less sensitive. Accordingly, calculated ozone changes may vary widely among scenarios estimated to produce roughly equivalent quantities of smoke. For the nuclear scenarios

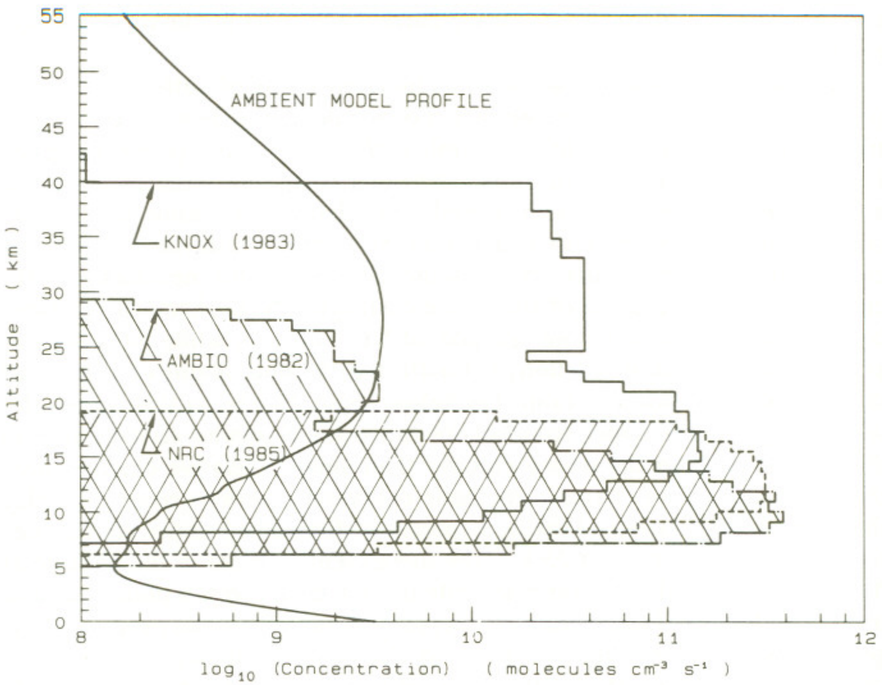

Figure 6.2. NO_x input from fireballs

described above, the predicted average hemispheric-scale ozone reductions are shown in Figure 6.3. The differences arise mainly from variations in the number of explosions with energy yields between 0.5 and 20 Mt (which deposit NO_x into the model stratosphere). The Knox (1983) scenario, which includes some high yield weapons, produces a maximum ozone column depletion of 44% after 6 months. The NRC 6500 Mt scenario excludes weapons larger than 1.5 Mt, but corresponds to a somewhat higher average injection height than the Ambio scenario, which contained many small weapons. The NRC scenario produced an ozone column decrease of about 17% and the Ambio scenario produced a 4% maximum decrease at a somewhat later time. The greater time delay in the Ambio case occurs because the injected NO_x is slowly transported and mixed upward to the region where it can affect the ozone. In general, maximum ozone depletions (in an atmosphere unperturbed by smoke) are found to range up to perhaps 50% for scenarios of ~5000 Mt including high yield weapons; the peak depletion is reached in 6 to 12 months, and a sustained depletion of 10% or more can persist for 3 to 6 years. On the other hand, with only low yield weapons, the peak ozone depletion may never reach even 10%. The 5000 Mt baseline model of Turco et al. (1983a,b) predicted peak ozone depletions of about 20–30%,

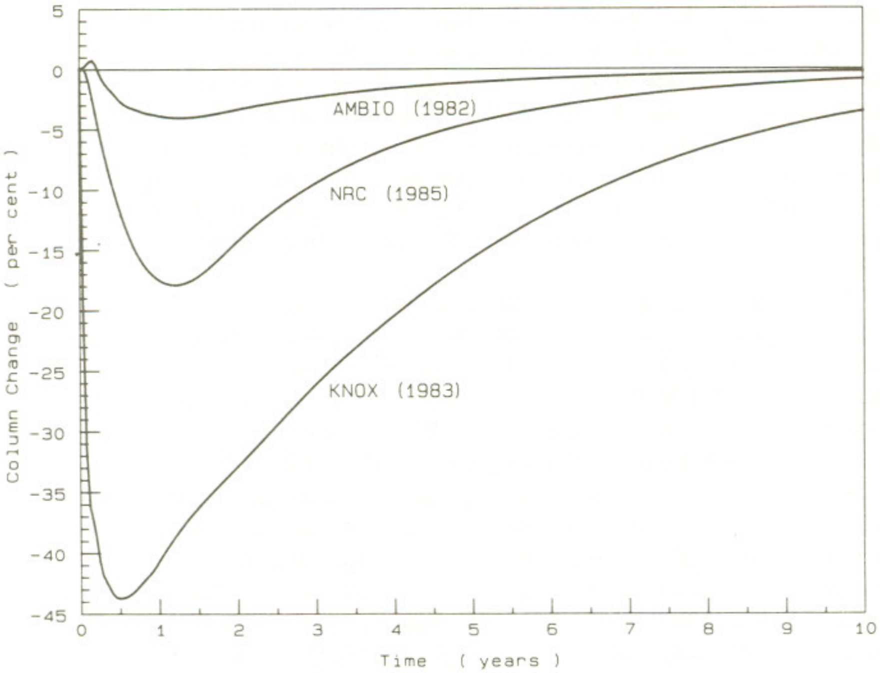

Figure 6.3. Total column ozone change vs time computed with the one-dimensional model, of Connell and Wuebbles (1985)

representing the impact of mixed high and low yield weapons. Izrael et al. (1983) have also considered the effects of nuclear-generated NO_x on stratospheric O_3, and estimated peak depletions of 30 to 50% consistent with the above discussion.

Several factors that can lead to much larger ozone depletions have not been considered in these studies, including the likely induced changes in atmospheric dynamics and temperature, and possible reactions of O_3 with injected aerosols. These will be discussed in more detail in the following section. Moreover, the instantaneous meridional and longitudinal spreading assumed in one-dimensional models very probably underestimates potential ozone reduction for the first few months in the northern mid-latitude zone, where the injected NO_x may tend to remain concentrated.

In addition to the problem of long-term hemispheric-scale ozone depletion, there may also be deep, transient, short-term regional-scale depletions. These could result from detonation of many large weapons within a confined area, such as an ICBM field, leading to a local NO_x concentration hundreds of times greater than the ambient value. Before dispersive processes dilute the injected NO_x, ozone in the affected region of the atmosphere could essentially be completely removed. Luther (1983) projected ozone column decreases of up to 70% after a few hours and persisting for several days—an "ozone hole"—assuming various numbers and sizes of weapons for areas characteristic of an attack by the U.S.S.R. on a U.S. ICBM field. These calculations ignored the effect of varying wind directions and velocities in different atmospheric layers (shear) that would tend to disperse the ozone hole as seen from the ground and also neglected the great mass of dust and water that would accompany the NO_x. Accordingly, the derived ozone depletion is probably an overestimate of what might occur for a given affected location.

The increases in ultraviolet radiation at the ground arising from reductions in total ozone depend on latitude and season (as well as on any absorption and scattering by intervening clouds of smoke, dust, and ice). The biological impacts of UV-B radiation (~280–320 nm) also depend on the action spectra (absorption times quantum yield) for various physiological responses to the radiation in individual organisms (NRC, 1984). For most organisms the responses are uncertain, although some effects on certain crops, insects and marine micro-organisms would be expected in light of recent laboratory studies (see Volume II and NRC, 1984). In humans, increased UV-B accumulated over many years can lead to a number of disorders, including skin cancer (NRC, 1984). While probably not a major health factor itself in the aftermath of a major nuclear exchange, enhanced UV-B radiation would be another factor degrading the post-war environmental state.

Nachtwey and Rundel (1982) have discussed the calculation of changes in biologically active ultraviolet radiation given a particular percentage reduction in total ozone. Based on that discussion, UV-B increases can be estimated for the scenarios discussed earlier. For a 40 to 50% ozone decrease at 30° N, a factor of five increase in biologically active, wavelength-integrated UV would result. At 30° with a 10% ozone decrease, biologically active UV would increase by about 25%. With all low yield weapons scenarios, a lower limit for the average change in surface UV-B radiation could essentially be zero (also see below). On the other hand, Luther (1983) calculated that a 70% ozone reduction in ozone holes would increase the surface flux of 300 nm radiation by about a factor of twelve. Accordingly, ultraviolet radiation intensities could be enhanced in some regions at certain times, by up to an order of magnitude, and over several years, on average, by up to a factor of around twice the estimated percentage ozone depletion.

6.3.2 Stratospheric Chemistry in an Atmosphere Perturbed by Smoke

The injection of nitrogen oxides from rising nuclear fireballs is only one of the potential influences of a nuclear war on the chemistry of the stratosphere, particularly on its ozone concentration. If nuclear explosions take place near the surface, substantial amounts of soil dust (and possibly soil carbon and water vapor) could be injected into the stratosphere (see Chapter 3). Reactions with dust could lower ozone concentrations. Smoke and gases generated in fires ignited by the nuclear exchange, particularly from very intense city fires, could also be lofted to stratospheric altitudes (see Chapters 3 and 4). In addition to direct injections into the stratosphere, perturbations of atmospheric temperatures and circulation could loft substantial quantities of smoke and debris from the troposphere to the stratosphere (see Crutzen et al., 1984, and Chapter 5) and could dynamically redistribute stratospheric ozone and other trace constituents. Other potential nuclear war induced perturbations include the introduction of additional compounds (e.g., soot, $HC\ell$ and H_2O) that affect chemical kinetics, changes in temperature that alter chemical reaction rates, and a lowering of the tropopause and changes in the dynamic coupling between the troposphere and stratosphere (via gravity and planetary waves) that determine stratospheric residence times.

There are two fundamental problems to be dealt with in order to calculate these effects. First, a reasonable estimate must be developed of what materials may be injected, and how the atmosphere could be perturbed. Second, since changes in the ozone concentration would induce temperature changes that in turn could alter the atmospheric response, the capability must be developed for interactively and simultaneously calculating the effects of all of these processes and perturbations as the atmosphere evolves following a nuclear conflict. Because neither of these problems has been completely solved, it is only possible to speculate on some of the possibilities. In doing so, it is assumed here that the smoke injection is relatively large and occurs in summer, thereby inducing a large perturbation to the atmospheric circulation (see Chapter 5). The effects of a winter war would likely be less dramatic, but could still be significant.

Smoke injected into the middle and upper troposphere could dramatically increase the normally slow vertical mixing in the stratospheric layers above the smoke and could lift the lower stratospheric air mass upward and towards the equator ahead of the warming smoke.The enhanced vertical mixing could bring ozone-destructive gases higher into the ozone layer than would otherwise occur, probably leading to deeper ozone reductions. The displacement of the ozone reservoir in the lower stratosphere to higher altitudes and toward the equator would also probably lead to further ozone depletions.

The strong upward air movement induced in regions of the Northern Hemisphere during the first weeks to months would be balanced by a large scale, slow downward motion in the Southern Hemisphere, which might well allow transport of stratospheric air having relatively high ozone concentrations to the surface (for example, under some current situations ozone concentration levels can occur briefly as a result of thunderstorm-induced downdrafts or other intense vertical mixing). Once the smoke spreads to the Southern Hemisphere, however, the Hadley circulation may become less intense (based on current GCM results, see Chapter 5), the upper troposphere may be stabilized and deepen the stratosphere, and stratospheric contributions to tropospheric ozone concentrations might decrease. The induced movement of air to the Southern Hemisphere may, however, also carry nitrogen oxides injected in the Northern Hemisphere, thereby leading to greater ozone reduction in equatorial and southern latitudes than would occur if the circulation were not perturbed. Although mixing of the NO_x into the Southern Hemisphere might somewhat reduce the ozone reduction in the Northern Hemisphere, this enhanced horizontal spreading of the NO_x is likely to lead to a greater average ozone reduction worldwide. Whether the surface flux of ultraviolet radiation would increase, however, would also depend on the concentrations of other radiative absorbers such as smoke particles.

Solar heating of the smoke lofted into the stratosphere by induced circulation changes could also produce substantial increases in stratospheric temperatures, in some cases by 20 to 50°C or more, depending on the season. Such temperature changes alone would cause substantial reductions in the ozone concentration. For example, when the NRC (1985) estimates of middle latitude temperature changes following a nuclear exchange are assumed (which basically create an isothermal lower stratosphere at a temperature of about 240 K) the vertical ozone column is found to be reduced by 18% in the absence of any other effects. However, note the concurrent presence of smoke, which would block a fraction of the enhanced solar UV-B radiation. On the other hand, the smoke would also lead to absorption of shorter wavelength UV radiation, which is active in producing ozone by molecular oxygen dissociation (Crutzen et al., 1984). This may be another important factor leading to ozone depletion. Warming of the stratosphere and upper troposphere by smoke is also projected to extend the atmospheric residence time of stratospheric constituents (see Chapter 5), thereby extending the recovery process from months to perhaps a few years.

In addition to absorbing UV radiation, ozone is an active constituent in determining the visible and infrared radiation balances of the atmosphere. Thus, changes in ozone can affect temperatures and circulation patterns (NRC, 1985). Solar absorption by ozone in the middle and upper stratosphere, for example, may provide a stable temperature inversion at 35–40 km, preventing smoke particles from rising beyond this level (Malone et al., 1985). Ozone infrared cooling of upper stratospheric air normally contributes to the wintertime descent of that air in polar regions; this sinking motion comprises one of the cleansing processes for the stratosphere. The infrared emission of smoke aerosols during the polar night may augment this cooling and thereby induce downward movement of the smoke to levels where it may be more subject to removal by precipitation scavenging.

Oxidation of smoke by ozone (and other reactive species, perhaps especially OH) may provide an important long-term removal mechanism for injected smoke particles. Oxidation of the nonabsorbing hydrocarbons comprising smoke at ozone levels typical of the unperturbed stratosphere could be relatively rapid, although at the temperatures expected in the perturbed stratosphere, and with depleted ozone, this possibility requires a more thorough review. The oxidation of light-absorbing graphitic soot should be even slower (R. Fristrom, private communication). At present, there is no quantitative evidence to suggest that the physical and optical properties of the injected smoke would be significantly altered over short periods as a result of chemical attack, but such an effect cannot be discounted.

This analysis of possible effects is certainly not complete and must be acknowledged as uncertain. It will require considerable research to answer the most important questions. Quite clearly, however, the changes in stratospheric chemistry that have been proposed could have important global influences; at this time, the effects cannot be accurately quantified. It should be recognized, however, that previous calculations of ozone reductions based on a smoke free atmosphere (as described in Section 6.3.1) probably do not represent the conditions likely to prevail after a nuclear war. Larger, longer lasting and more widespread reductions in stratospheric ozone would now seem to be a possibility.

6.4 TROPOSPHERIC EFFECTS

The chemistry of the troposphere is qualitatively different from that of the stratosphere. Most gaseous species emitted at the Earth's surface are removed from the air in a relatively short time by photochemical reactions and by a number of dry and wet physical scavenging and removal processes. The photochemistry of the troposphere is driven by chemical radicals, of which OH is most generally reactive. Ozone is produced as a byproduct of hydrocarbon decomposition via chain reaction mechanisms involving peroxy radicals and NO. Species that are relatively inert chemically, such as N_2O, CH_4, H_2O, COS and many fluorocarbons are transported upward through the tropopause in substantial quantities.

Crutzen and Birks (1982) and Birks and Staehelin (1985) have suggested a number of chemical changes that might occur in the troposphere as a result of nuclear war. Incorporating species emitted by fires into existing models of the atmosphere has been used to provide initial estimates of the expected perturbations. Major changes in atmospheric structure and climate caused by the smoke emissions could, of course alter current tropospheric processes and characteristics such as vertical mixing, temperature profile, and wet and dry deposition processes, and should eventually be factored into these studies. In such a perturbed state, atmospheric processes currently important, and therefore reasonably treated by models, might lose importance, while new processes not properly treated could be dominant. For example, the interaction of gaseous species with aerosols in a smoky atmosphere could control the overall composition of the troposphere, unlike present conditions (Birks and Staehelin, 1985).

The photochemical oxidation of hydrocarbons released to the troposphere by fires, in the presence of sunlight and sufficient quantities of NO would lead to the production of ozone. Crutzen and Birks (1982) have shown that the oxidation of one molecule of CO can yield one molecule of ozone, while the yield from ethane can be as much as six ozone molecules. The production of NO from nuclear explosions and fires is projected to be so large that the NO concentration should not be a limiting factor for ozone formation. The hydrocarbons and NO_x would also be mixed together in polluted air masses. By implication, the formation of a few hundred million tonne of tropospheric ozone from the oxidation of the hydrocarbon emissions discussed earlier could occur within a week or so. The average ambient mixing ratio of surface ozone is about 50 ppbv and the total tropospheric ozone burden is roughly four hundred million tonne. Therefore, in principle, the potential exists for noticeable ozone enhancements over large regions of the northern mid-latitudes. However, such an outcome requires sunlight sufficient to drive the necessary photochemical processes. The light intensity, in turn, depends on the optical properties, distribution, and residence time of the smoke injected by the fires. If a substantial quantity of smoke is not promptly removed, it is likely that NO and NO_2 would be transformed by reactions not requiring sunlight and deposited on particles or on the surface as follows:

$$
\begin{aligned}
NO + O_3 &\rightarrow NO_2 + O_2 \\
NO_2 + O_3 &\rightarrow NO_3 + O_2 \\
NO_3 + NO_2 + M &\rightarrow N_2O_5 + M \\
N_2O_5 + H_2O\ (aq) &\rightarrow 2HNO_3 \\
HNO_3 &\rightarrow \text{cloud droplets, aerosol} \\
\text{aerosol} &\rightarrow \text{deposition}
\end{aligned}
$$

Hence, photochemical ozone formation would be less likely to occur after the eventual removal of the smoke from the atmosphere.

A multi-dimensional model including coupled treatments of dynamics, radiation, and homogeneous and heterogeneous chemistry would be necessary to properly investigate this problem. Without such a model, and lacking the detailed experimental information needed to construct it, the potential tropospheric effects can only be sketched. An analysis of the problem has been carried out by Penner (1983), who concluded that large tropospheric ozone increases covering wide areas would be an unlikely outcome of a nuclear war. The surface ozone effects expected based on present calculations would be negligible against the direct effects of nuclear warfare, except perhaps in localized areas where enough pollutants and sunlight were present to generate large ozone concentrations.

Many natural and anthropogenic gases are removed from the atmosphere by reactions with hydroxyl radicals (OH), formed by photochemical processes. With large amounts of smoke in the atmosphere, the necessary sunlight to drive these reactions might not be available; the smoke itself could be a strong sink for hydroxyl radicals. Under these circumstances, there would likely be a buildup of undesirable gases that are now present in the atmosphere only at very low concentrations (Birks and Staehelin, 1985). No quantitative evaluation has, however, been presented and this problem may also turn out to be of secondary importance. For instance, the emission of H_2S (hydrogen sulfide) over the continents is about equal to 50 million tonne S per year under normal conditions. If this much H_2S were spread over the Northern Hemisphere mid-latitudes ($10^{14}\,m^2$) and mixed through a depth of a few kilometers, there could be a build-up of H_2S to about 10 ppbv over one month, assuming no removal. Although this level is quite high compared to normal, it is still probably not high enough to cause major health problems compared to the direct effects of a nuclear war.

6.5 SUMMARY

The potential impacts of a nuclear war on atmospheric chemistry have been investigated for more than a decade. During this period, a better recognition of the effects that may be most important has developed, although we have no assurances that all of the crucial issues have been investigated.

The potentially significant chemical consequences discussed in this chapter are summarized in Table 6.1. The impact of these changes on biological systems is discussed in Volume II. In the absence of fires and smoke emissions, the reduction in stratospheric ozone and consequent increases in surface ultraviolet radiation would likely be the most important effect of nitrogen oxides generated by nuclear explosions. With smoke in the stratosphere, changes in circulation and temperatures, as well as interactions between soot particles, solar UV radiation, and ozone, could lead to strongly enhanced ozone destruction. In the presence of large quantities of smoke particles, the variety of gaseous chemical emissions could also result in climatic changes through alterations of stratospheric composition (such changes have not yet been considered in the model studies reported in Chapter 5). These effects could delay the recovery of the atmosphere significantly. Further detailed analysis of these interactions is required. On the other hand, the formation of high ozone concentrations by photochemical reactions in the troposphere is not now considered to be an important problem.

On local and regional scales, the most important potential chemical effects

TABLE 6.1.
SUMMARY OF POTENTIALLY SIGNIFICANT ATMOSPHERIC CHEMISTRY EFFECTS

Time period after explosions	Spatial coverage	Effect
Hours to Days	Close to fires	High levels of CO and pyrotoxins Local releases of various hazardous pollutants from chemical factories and storage facilities
Days to Weeks	In unventilated areas such as river valleys and other low areas near smoldering fires; high values require strong temperature inversions	High particle and gas concentrations: Particles: 0.01–0.1 g/m^3 CO: 15–150 ppmv HCℓ: ≈1–10 ppmv Aldehydes: ≈0.1–1 ppmv
	In limited regions surrounding areas of many high yield explosions	Large increases in UV-B radiation in "ozone holes" if not shielded by smoke
Weeks	Northern Hemisphere mid-latitudes	Precipitation acidities with pH on the order of 4, assuming no change in other emissions Tropospheric ozone concentrations could increase at edges of smoke clouds, but unlikely to be very significant
Months	Northern Hemisphere	Several times increase in UV-B in smoke-free parts of atmosphere due to reductions in stratospheric ozone by up to 30% (or more as a result of changes in dynamics and presence of smoke in stratosphere)
Years		Unresolved (see text)

would include: the build-up of pollutants from smoldering fires, particularly in poorly ventilated, cooled air masses trapped in valleys and lowlands; spills and dispersal of highly toxic industrial chemicals and pyrototoxins; and, possibly, in very limited regions and for only a few days, severe stratospheric ozone depletion.

A nuclear war such as considered in this study could also lead to changes in atmospheric chemistry over months to decades after the initial releases of pollutants by the nuclear explosions and fires. Such alterations might be coupled to potential long-term changes in the biosphere that are described in Volume II. At the present level of knowledge, only a few of the possibilities deserving further study can be suggested. Although direct emissions of CO_2 from post-nuclear fires are roughly equivalent to only one year's emissions from current fossil fuel combustion (and are, therefore, climatically insignificant), the subsequent death of extensive plant communities, as suggested in Volume II, and release of CO_2 through decay and fires could, over a number of years, raise CO_2 levels by a few tens of percent if not balanced by regrowth of vegetation. Similarly, alteration of land and marine ecosystems over large areas could modify the production and release of trace gases such as methane, could alter air-sea gaseous exchange rates, and could affect the hydrological cycle. Uncertainties related to these and other longer term perturbations remain to be addressed.