The Effects of Industrial and Agricultural Practices on Atmospheric Chemistry During the Anthropocene with Emphasis on the Tropics[1]

Paul J. Crutzen*
Max-Planck-Institute for Chemistry, Mainz, Germany

INTRODUCTION

The gases that are most significant for atmospheric chemistry and for Earth's climate are not its main components - nitrogen (N_2), oxygen (O_2), and argon (Ar), which together with variable amounts of water vapor make up more than 99.9% of the mass of the Earth's atmosphere - but many gases that are found only in very low concentrations. Carbon dioxide (CO_2), which currently has a concentration of approximately 370 per million air molecules, is of crucial importance in that, together with water vapour and sunlight, it builds the organic molecules of living matter. As a so-called greenhouse gas, carbon dioxide is also significant for the Earth's climate. However, despite these important aspects, it plays no role in atmospheric chemistry.

The chemically active gases have much lower abundances in the atmosphere than CO_2. Among these, ozone (O_3) and water vapour are the most important drivers of the photochemistry of the atmosphere. Without ozone, the chemistry and chemical composition of the atmosphere would be totally different. Looking at the vertical distribution of ozone, an example of which is shown in Figure 1, we see that there is little ozone up to about 10 km altitude. In the stratosphere, above about 10 km, ozone concentrations rise quickly with altitude. Looking at the vertical distribution of temperatures, we also see that in the stratosphere they no longer decrease with altitude. Because of this temperature distribution, vertical mixing in the stratosphere is much suppressed.

Until about 20 years ago it was thought that the troposphere contained only ozone which had been transported down from the stratosphere and its enormous importance for the chemistry of the troposphere, as we will describe in this paper, was not recognized. Tropospheric ozone makes up only about 10% of the total ozone in the atmosphere, with an average mixing ratio of about 40 nmol mol^{-1} (nanomole per mole).

Figure 2. shows the altitude to which solar radiation penetrates into the atmosphere. Radiation with wavelengths shorter than 200 nm is to a large degree removed above 50 km. This happens primarily through absorption by N_2 and O_2. But absorption of solar radiation by these main atmospheric gases does not occur beyond about 240 nm. Fortunately, ozone strongly absorbs ultraviolet radiation in the wavelength range 200-310 nm. Were it not for atmospheric ozone, this radiation would penetrate uninterrupted to the Earth's surface. For the Earth's current biosphere, this would have catastrophic

---

[1] Keynote speech and dialogue at the Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand on 4 December, 2003.

*Professor Dr. Paul J. Crutzen is a Nobel Laureate for Chemistry in 1995.

consequences. It is worthwhile noting here that only during the last 20-25% of Earth's age its atmosphere may have contained about the current level of oxygen and ozone. The Earth was thus without the protective oxygen and ozone shields for most of its history. This must have forced primitive life to develop only in dark hideaways. The average mixing ratio of ozone in the atmosphere amounts to only about 0.3 per million air molecules. It is, nevertheless, sufficient to absorb the most part of the dangerous UV radiation. Beyond 300 nm the absorption ability of ozone becomes so weak that the UV radiation can penetrate to the Earth's surface. It is the radiation up to 340 nm, also called UVB radiation (B stands for biologically active), that still exerts a stress on the biosphere. We are all familiar with the fact that when we stay too long unprotected in the sun, we may get sunburnt. Plants can also be affected by this radiation.

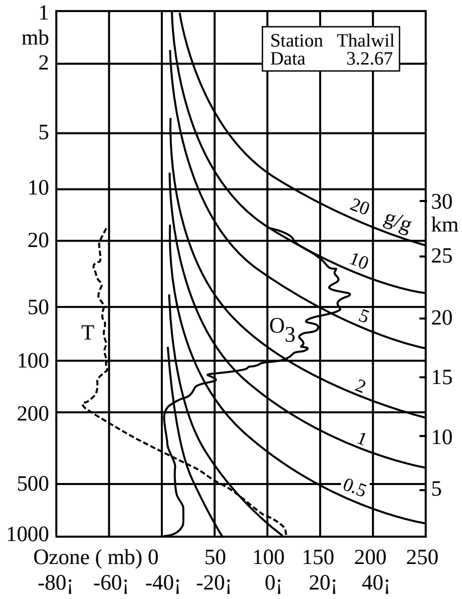


Figure 1. Measured ozone and temperature profiles over Thalwil, Switzerland, 1967.

On the other hand, we know from research conducted during the past 25 years (Levy, 1971) that this same radiation is also very important for keeping our atmospheric environment clean. The reason is the following: up to wavelengths of about 340 nm UV radiation is capable of splitting an ozone molecule into an oxygen molecule and an excited oxygen atom (O^*). The latter has enough energy to react with atmospheric water vapor to produce hydroxyl radicals, with the chemical formula OH (note: this is a neutral molecule and not the base ion OH-).

R1 $O_3 + hv \rightarrow O^* + O_2$
R2 $O^* + H_2O \rightarrow 2OH$

The OH radical, "the detergent of the atmosphere", reacts with almost all gases, of both natural and anthropogenic origin, thus removing them for the atmosphere.

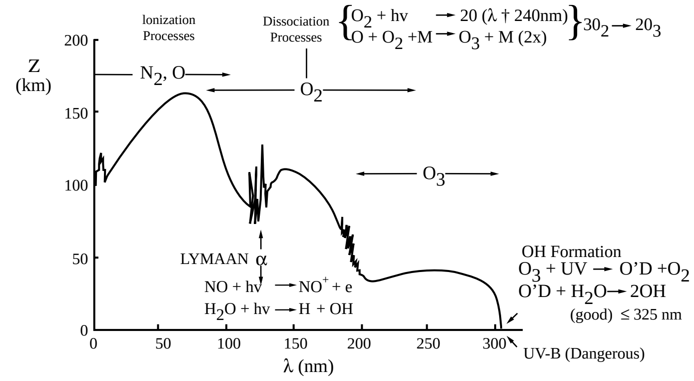
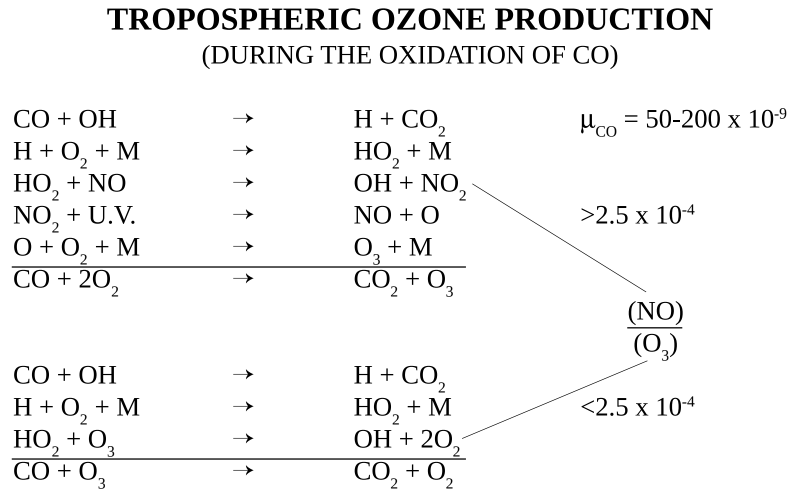


Figure 2. The altitude to which solar radiation penetrates the atmosphere is a function of the wavelength. Radiation shorter than 200 nm is absorbed above 50 km. The longer wavelength ultraviolet is mainly absorbed by ozone.

GLOBAL TROPOSPHERIC CHEMISTRY

There are three factors that are important for the formation of OH radicals: ozone, water vapor, and UV-B radiation. The average volume mixing ratio of OH amounts to only about 4 out of 10^{14} air molecules; negligibly few, one might say, but without this detergent the chemical composition of the atmosphere would be totally different. Molecular oxygen, which makes up almost 21% of the volume of the atmosphere, is not capable of oxidizing any of the gases that are released into the atmosphere. Through its role in the formation of OH, ozone in the troposphere is not the inert species it was taken for until about 25 years ago, but rather it plays a key role in atmospheric chemistry.

Ozone is created and also destroyed in the troposphere, e.g. by reactions R1 and R2. It also comes partly, although not principally, from the stratosphere. Through tropospheric reactions, the OH radical can initiate the formation or destruction of ozone, depending on the concentrations of reactive NO and NO_2 (Crutzen, 1973). For example, the oxidation of carbon monoxide (CO) begins with CO reacting with OH to form an H atom and CO_2 (Figure 3). The H atom then combines with an oxygen molecule to form HO_2. These HO_2 molecules can now react with NO or, in the case of too little NO, with either ozone or with another HO_2 radical, forming hydrogen peroxide (H_2O_2) in the latter case, a strong oxidizer in aqueous solution. The net result depends on the reaction branch and is in either case totally different. If HO_2 reacts with NO, NO_2 will be formed, which almost immediately will be split by UV radiation into NO and O, so that the NO previously lost is regenerated. The O atom combines with an oxygen molecule to form ozone. Thus the net result is the oxidation of CO to CO_2, with formation of ozone ($CO + 2O_2 \rightarrow CO_2 + O_3$) with NO and NO_2 acting as catalysts. On the other hand, if HO_2 reacts with ozone, CO is still oxidized to CO_2, but in the process ozone is lost ($CO + O_3 \rightarrow CO_2 + O_2$).



TROPOSPHERIC OZONE PRODUCTION

(DURING THE OXIDATION OF CO)

$$\begin{array}{lcll}
CO + OH & \rightarrow & H + CO_2 & \mu_{CO} = 50\text{-}200 \times 10^{-9} \\
H + O_2 + M & \rightarrow & HO_2 + M & \\
HO_2 + NO & \rightarrow & OH + NO_2 & \\
NO_2 + U.V. & \rightarrow & NO + O & >2.5 \times 10^{-4} \\
O + O_2 + M & \rightarrow & O_3 + M & \\
\hline
CO + 2O_2 & \rightarrow & CO_2 + O_3 & \\
 & & & \frac{(NO)}{(O_3)} \\
CO + OH & \rightarrow & H + CO_2 & \\
H + O_2 + M & \rightarrow & HO_2 + M & <2.5 \times 10^{-4} \\
HO_2 + O_3 & \rightarrow & OH + 2O_2 & \\
\hline
CO + O_3 & \rightarrow & CO_2 + O_2 &
\end{array}$$

Figure 3. The simplest photochemical smog reaction leading to ozone formation. Ozone is created when the concentration of NO is greater than about 10-11.

Which branch is more important, the one leading to ozone formation or to ozone destruction? The answer depends on the atmospheric concentrations of nitrogen oxides, NO_x ($NO + NO_2$). These come from a variety of natural and anthropogenic sources and have short atmospheric lifetimes of only a few days, largely due to the formation of nitric acid (HNO_3) by the reaction $NO_2 + OH + M \rightarrow HNO_3 + M$. One finds totally different concentrations of nitrogen oxides, in space and time. The regions in the world where ozone is formed in the troposphere are those with relatively high concentrations of NO, in particular areas where fossil fuels and dry plant materials are burned. Current estimates of the sources of NO are shown in Figure 4. The most important anthropogenic sources of NO include the burning of fossil fuels, approximately 21 million tons of N per year, and biomass burning, which takes place mainly during the dry season in the tropics and accounts for approximately 5-10 million ton N emitted to the atmosphere annually. Comparing this quantity with the estimated natural emissions from soils (5-20 million tons N per year, which could, in fact, also in part be anthropogenic by the use of N fertilizers in agriculture, and from lightning (2-15 million ton N/year) one recognizes that anthropogenic contributions to NO emissions are probably higher than the natural contributions.

TROPOSPHERIC SOURCES OF NO

(IN MILLIONS OF TONS N/YEAR)

NATURAL	
SOILS	5 - 20
LIGHTNING	2 - 15
STRATOSPHERE	0.5 (FROM $N_2O + O^1D \rightarrow 2NO$
Σ	7.5 - 35.5
ANTHROPOGENIC	
INDUSTRIAL BURNING	21
BIOMASS BURNING	5 - 10
AIRCRAFT	0.6
Σ	26.6 - 31.6

Figure 4. Estimates of sources of NO (million tons N year^{-1}).

The CO oxidation chain, is the simplest example of how ozone can be formed in the troposphere. If nitrogen oxides are present in significant quantities together with CO or methane (CH_4) or many, more reactive, hydrocarbons, ozone will be formed. During summertime high pressure weather conditions, which often combine plenty of solar UV radiation with stagnant air conditions, high concentrations of ozone can be produced over large areas, leading to so-called photochemical smog.

Almost all species found in the atmosphere, not including the main components (oxygen, nitrogen, argon, water vapor and carbon dioxide), react with the OH radical. Carbon monoxide is just one example. As shown in Figure 3, the OH radical is not lost during the oxidation of CO, but is rather reformed. The same goes for the HO_2, NO and NO_2 radicals.

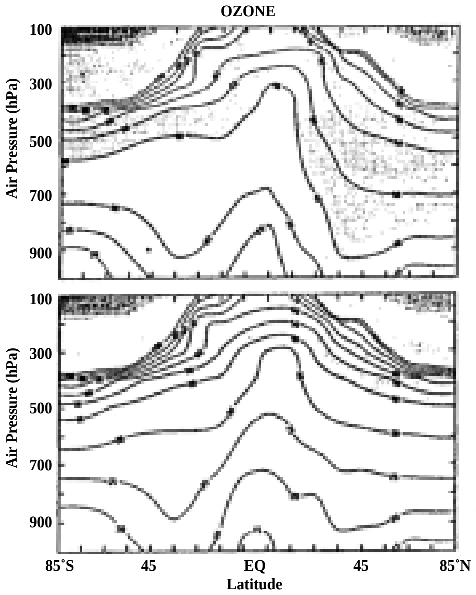


Figure 5. Calculations (Mainz model) of the average ozone concentration (nmol mol^{-1}) showing the latitude and altitude dependence in the month of July. The upper figure is for the present and the lower figure for the pre-industrial period. There is a clear increase in ozone concentration in the northern hemisphere.

Such, often lengthy, catalytic chains are typical in atmospheric chemistry. Besides the main, unreactive components of the atmosphere, there are several other important gases which do not react with OH, such as N_2O, and the chlorofluorocarbon ($CFCl_3$ and CF_2Cl_2) gases. Such gases are transported to the stratosphere where they are involved in ozone destruction by the formation of NO_x and ClO_x radicals.

While ozone is beneficial in that it provides the major source of OH radicals via reactions R1 and R2, it also is a strong air pollutant. In high concentrations, ozone can have damaging effects on human health and plants. Therefore, fortunately, the atmospheric lifetime of NO is only a few days. This means that nitrogen oxides produced near the earth's surface can not reach either the southern hemisphere or the stratosphere. At clean air locations, such as in the middle of the Pacific Ocean, one finds only very low concentrations of nitrogen oxides, possibly even fewer than one NO in 10^{12} (trillion) air molecules. In such regions it is clear that ozone decomposition will take place.

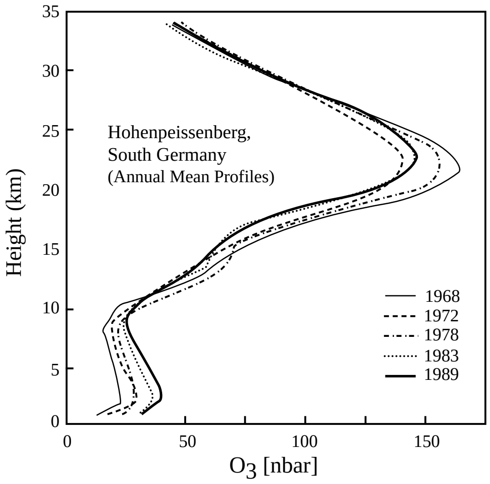


Figure 6. Annual average O_3 profiles measured at Hohenpeissenberg station in southern Germany.

Using mathematical models we can try to simulate the chemistry of today's atmosphere, including ozone concentrations, to that in the past, say for example 150 to 200 years ago. Unfortunately, there are no measurements of ozone before about 100 years ago as measurement techniques had not yet been developed. Because of its reactivity, ozone also is not preserved in ice cores. Theoretically, however, we can use model calculations to compare the modern conditions of the atmosphere to that before the agricultural/industrial revolution (for instance around 1800). This can be done by assigning for the corresponding periods, as input parameters, the sources and concentrations of NO_x, CH_4 and CO, which play important roles in O_3 formation. Figure 5 shows the calculated latitude/height distributions of the mixing ratios of ozone in the troposphere during July for these two time periods, showing a doubling of ozone concentrations in the Northern Hemisphere since pre-industrial times. In the Southern Hemisphere we see a much smaller increase.

Observations during this century at different locations in the Northern Hemisphere show a clear increase in tropospheric ozone. The clearest evidence comes from measurements made during the last 30 years at the Hohenpeissenberg station in Bavaria by scientists of the German Weather Service (Figure 6). These measurements show that, since 1968, the concentration of ozone in the troposphere has about doubled. The loss of stratosphere ozone, which is also shown, is caused by the emissions of chlorofluorocarbon (CFC) gases. Other northern hemisphere stations which are not located near industrial sources also show ozone increases. For example, results from Alaska where measurements have been made since the beginning of the 1970s by S. Oltmans and colleagues of the U.S. National Oceanographic and Atmospheric Administration, show that between June and November the ozone concentrations have been increasing at almost 1.4% per year. In comparison, during the winter almost no change in ozone concentrations has been observed. This is the pattern we expect as photochemical ozone formation is taking place primarily during the summer in the Northern Hemisphere. In the Southern Hemisphere no significant changes have occurred.

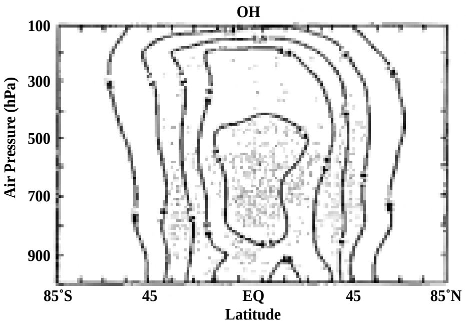


Figure 7. Zonally and annually averaged, 24 hour mean, OH concentrations in units of 10^6 molecules/cm^3, calculated with the Mainz model.

There are measurements by Albert Levi from the end of the last century which were made at the Montsouris Observatory, which at that time was located on the outskirts of Paris. The measurement method was well documented. The reliability of these early measurements verified by Professor Dieter Kley and his colleagues from the Forschungszentrum in Jülich. They show that during 1876-1896 ozone values near the ground were below 10 nmol/mol, less than a third of the values that are typically measured today.

THE IMPORTANCE OF THE TROPICS IN ATMOSPHERIC CHEMISTRY

The vertical column of ozone depends on latitude and season. Except for the “ozone hole” situation over Antarctica during springtime (September-November) minimum total ozone columns down to 250 Dobson units (corresponding to an atmospheric layer of 2.5 mm thickness if all ozone could be compressed to standard pressure and temperature conditions near the earth surface) are found over the tropics. Because of generally high sun angles and high concentrations of water vapour which favour production of OH radicals via reactions R1 and R2, maximum OH concentrations are calculated in the tropics. Figure 7 shows model calculated OH concentrations, averaged over 24 hours (at night the concentration drops to zero). Maximum concentrations amount to about 2.5 x 10^6 molecules per cm^3, corresponding to only one OH radical among 10^{13} air molecules. Towards higher latitudes the values decrease rapidly. Of course, the calculated OH concentration values in Figure 7 are not necessarily correct. Luckily, however, we have a way to check the gross features of the calculated OH distributions by comparing theoretical and calculated distributions of methylchloroform (CH_3CCl_3), a gas which was previously used in dry cleaning for instance. Through careful measurements we know how much of this gas is in the atmosphere. Because it has no natural sources and we know how much is produced by industry, the CH_3CCl_3 emissions to the atmosphere are known. By knowing its past emissions and current atmospheric concentrations, we can estimate how much methylchloroform is being decomposed by reaction with OH radicals, providing a measure of the global average OH concentration. In addition we can compare to what extent the model is able to reproduce measurements of methylchloroform at different locations. Figure 8 shows that model calculated values agree very well with the observations. Thus, the calculated OH radical concentrations, as shown in Figure 7, are largely confirmed, and although the method is indirect, it provides a good picture of the global distribution of the OH radical. With this knowledge we can also make estimates about the decomposition of other atmospheric trace gases, such as methane and carbon monoxide. In Figure 9 we can see that, in accord with the atmospheric distribution of OH, the destruction in tropical areas is much higher than at higher latitudes. Methane has a concentration that is now approaching 1.8 ppmv (parts per million by volume). Between 1978 and 1988 measurements recorded a steady increase of approximately 1% per year. This trend has weakened somewhat in the last 10 years, however, and is now less than 0.5% per year (Dlugokencky et al., 1998). Atmospheric concentrations of methane have been increasing for some time. Until approximately 200-300 years ago methane concentrations were almost constant at 0.7 ppmv, only about 40% of today's value (Craig and Chou, 1982). This information has been obtained from the analysis of air bubbles trapped in glaciers in Greenland and Antarctica. The reported increase is easy to explain. Mankind's activities, including agriculture and industry, have had a considerable influence on methane concentrations. Figure 10 shows the estimated CH_4 sinks and sources. The most important sink for atmospheric CH_4 is reaction with OH, which can be estimated from chemical model calculations. This can be done for present atmospheric conditions and those before the industrial era, representing anthropogenically perturbed and natural conditions, respectively. In this way we estimate that the total current CH_4 source is about 630 million tons per year and the sum of natural sources about 270 million tons per year, thus indicating 360 million tons of anthropogenic emissions. Major contributions stem from ruminants and animal manure decomposition, biomass burning, landfills, rice fields, coal mines, natural gas leaks, and venting at oil production sites.

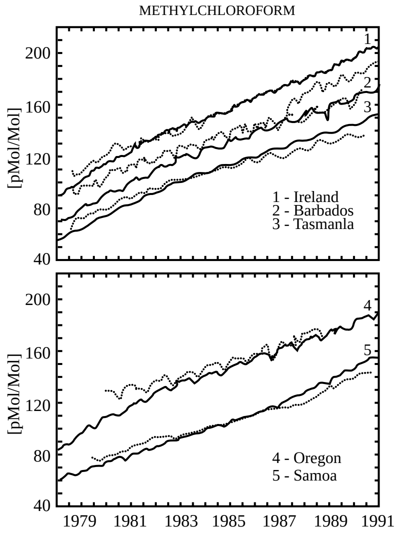


Figure 8. Calculated and modeled CH_3CCl_3 volume Mixing ratios at 5 stations between 1978 and 1991.

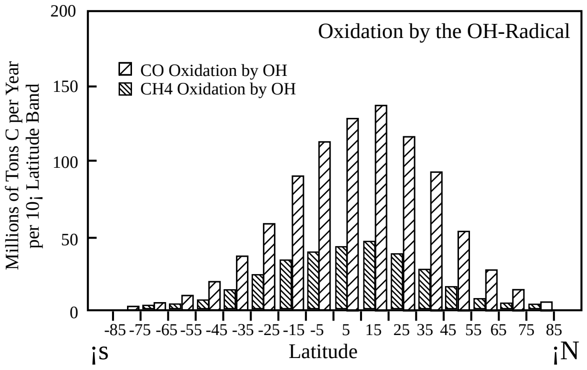


Figure 9. Oxidation rates of CO and CH_4 in millions of tons per year due to reaction with OH over 10˚ latitude bands

With an imbalance of less than 30 million tons per year, compared to a total anthropogenic input of 360 million tons per year, it is far from unrealistic to aim for a stabilization or even reduction of atmospheric CH_4 levels .

With so much photochemical activity in the tropics it is very unfortunate that we know very little about the atmospheric chemistry in these regions. Thus, an important goal for future research is to gain a better understanding about chemical processes in these areas. The tropics and subtropics, especially Asia, contain an increasing proportion of the world's population, which is under rapid development. The large changes in atmospheric chemistry and climate forcing during the coming decades will therefore largely come from these regions.

Methane (CH_4) Budget

(in millions of tons per year)

Methane Losses (1980-1990 Average values)	
Troposphere (OH)	530 ± 50
Stratosphere (OH, Cl, O^1D)	40
Soils	30 ± 10
Net Atmospheric Increase	**30**
Grand Total Sources (1980-1990 period)	**630 ± 60**
Methane Losses (pre-industrial)	
Troposphere (OH)	240
Stratosphere (OH, Cl, O^1D)	15
Soils	15
Grand Total Natural Sources	**270**

Sources (1980-1990 average)	
Natural	**270**
Anthropogenic	**630 - 270 = 360**
Ruminants	80 ± 20
Animal waste	20 ± 10
Biomass burning	40 ± 20
Natural gas leaks and oil production	65 ± 15
Coal mines	35 ± 10
Landfills	40 ± 20
Rice fields	80 ± 60

Figure 10. Natural and anthropogenic sources of CH_4 (in millions of tons = 10^{12}g).

Biomass Burning in the Tropics
(In Thousand Millions of Tons C/Year)

Slash and Burn Agriculture	**0.5 - 1.0**
Forest Clearing	**0.2 - 0.7**
Savanna Grass Fires	**0.3 - 1.6**
Wood Burning	**0.3 - 0.6**
Agricultural Wastes	**0.5 - 0.8**
$\sum$	**1.8 - 4.7**

Figure 11. Emissions of carbon (in thousand millions of tons per year) due to biomass burning.

Biomass burning produces the same gases as the burning of fossil fuels, but generally with higher pollutant emission ratios. During the dry season in the rural areas of the tropics, photochemical smog can develop, resulting in the accumulation of a considerable amount of tropical world. From satellite pictures we can very clearly see the influence that tropical biomass burning has on carbon monoxide and ozone, even outside the tropics. This is especially noted in the Southern Hemisphere. Contrary to what one might have thought before, the tropics and subtropics, and appreciable parts of the southern hemisphere are thus already strongly affected by mostly agricultural activities.

BIOMASS BURNING AS A POLLUTION SOURCE IN THE TROPICS

Biomass burning is presently the principle source of air pollution in the tropics. This takes place during the dry season, i.e., between December and April in the Northern Hemisphere and shifted by about 6 months in the Southern Hemisphere. There are several activities that involve biomass burning; for example, slash and burn agriculture and the establishment of permanent farms and cattle ranches, the clearing for which also involves the burning of large amounts of forest materials. Biomass is also burned in other practices. Every year in savanna regions, large amounts of dry grass are burned and wood is also burned for cooking and heating. Agricultural wastes are also frequently burned in the tropics. Figure 11 shows estimated quantities of burned biomaterial that Dr. M. O. Andreae and I have derived. According to our estimates 1.8-4.7 x 10^{15} g C of biomass are burned each year in the tropics. Unfortunately, better estimates cannot yet be made. In comparison, fossil fuel burning amounts to 5.5 x 10^{15} g C/year.

REFERENCES

Craig, H., and C.C. Chou. 1982. Geophysical Research Letters 9:1221

Crutzen, P.J. 1973. A discussion of the chemistry of some minor constituents in the stratosphere and troposphere. Pure and Applied Geophysics 106-108: 1385-1399.

Dlugokencky, E.J., K.A. Masarie, P.M. Lang, and P.P. Tans. 1998. Continuing decline in the growth rate of the atmospheric methane burden. Nature 393: 497-450.

Levy, H. 1971. Science 173: 141.