

# The Importance of Tropical Atmospheric Chemistry in Global Change Research: The Need for Strongly Enhanced Research Efforts in the Developing Tropics and Subtropics

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## Introduction

The main permanent atmospheric gases N<sub>2</sub>, O<sub>2</sub> and Ar together make up more than 99.9 volume % of the atmosphere. Nevertheless, Earth's climate and the chemistry of the atmosphere are mainly determined by the remaining minor constituents, which because of their relatively low abundance are significantly affected by emissions from various human activities, in particular fossil fuel and biomass burning, chemical manufacturing, agriculture and land use changes (see Table 1). Most abundant among these rest gases is carbon dioxide (CO<sub>2</sub>), which plays essential roles both as the source of carbon in the photosynthesis of plant matter and as a so-called "greenhouse gas" (GHG) for Earth's climate. CO<sub>2</sub> does, however, not play any significant direct role in the chemistry of the atmosphere. Among the chemically active gases, methane (CH<sub>4</sub>) is most abundant with a volume-mixing ratio of about 1.7 ppmv (parts per million by volume), compared to a pre-industrial value of only about 0.7 ppmv. Its concentration in the atmosphere is still growing, although now at a slower rate (about 0.5%/year) than in and before the 1980's. Methane plays important roles both in the chemistry of the troposphere and the stratosphere. It too is a GHG. The next most abundant gas of chemical and climatic importance is nitrous oxide (N<sub>2</sub>O). Chemically almost inert in the troposphere, N<sub>2</sub>O is removed from the atmosphere by photochemical processes in the stratosphere. A fraction of the nitrous oxide is thereby oxidized to nitric oxide (NO), which, together with NO<sub>2</sub>, acts as a catalyst in an ozone-destroying cycle of reactions. Under natural conditions, the production of ozone (O<sub>3</sub>) by the photodissociation of O<sub>2</sub> in the stratosphere is largely balanced by its catalytic destruction of NO<sub>x</sub> (= NO + NO<sub>2</sub>). Because the abundance of N<sub>2</sub>O is increasing by 0.2 – 0.3%/year, partially due to the increased production of N<sub>2</sub>O in soils as a consequence of the rapidly growing application of N-fertilizer, there is a growing anthropogenic effect on stratospheric ozone. The most important anthropogenic impact on stratospheric ozone has been due to the emissions of a series of entirely manmade chlorine- (and bromine) containing compounds, in particular CFCb, CF<sub>2</sub>Cl<sub>2</sub>, the so-called CFC's, and CCl<sub>4</sub>. As N<sub>2</sub>O, these gases are only removed from the atmosphere by photodissociation in the stratosphere, thereby producing Cl and ClO radicals, which, even more efficiently than NO<sub>x</sub>, can break down ozone by catalytic reactions (see Figure 1). Most surprisingly, the strongest depletions in stratospheric ozone have occurred over Antarctica during the springtime months of September and October. Exactly in the height region (14-21 km) where naturally, and until about 2 decades ago, a maximum in O<sub>3</sub> concentrations over Antarctica was found, during the past twenty years and for decades to come, during each spring, ozone concentrations have been and will be reduced to zero, resulting in major depletions by factors of 2-3 in the total ozone abundance and causing major increases in the fluxes of biologically damaging ultraviolet radiation at the Earth surface during spring.

## Environmental Surprise

The possibility of such a catastrophic loss of ozone was not predicted and came as a total surprise to the scientific community, which had, up to the discovery of the "ozone hole",

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considered ozone in this altitude and high latitude region to be conservative. However, due to the input of large amounts of industrial CFC gases and the development of special meteorological and physicochemical conditions (temperatures below about  $-80^{\circ}\text{C}$ , leading to polar stratospheric cloud formation, followed by production of the ozone-destroying catalysts Cl and ClO by reaction on the surface of the cloud particles) rapid ozone destruction takes place. Because of the long residence times of the CFC gases in the atmosphere (50 – 100 years) the ozone hole will first be closed by the middle of this new century, despite the fact that the production of the CFC's in the industrial, developed world has stopped since the beginning of 1996. The totally unexpected appearance of the ozone hole in a part of the globe, the furthest away from the CFC release regions, should be a warning. Precisely where the complex web of interacting processes in the global environment may be most sensitive to anthropogenic disturbances may be very hard to predict and surprises can not be excluded. Stresses on the environment should, therefore, be kept to a minimum.

Ozone in the atmosphere serves many functions. It acts as a filter against solar ultraviolet radiation, thereby protecting the biosphere from a large fraction of the biologically active, solar UV-B radiation of wavelengths less than about 310 nm. About 90% of all ozone are located in the stratosphere and 10 % in the troposphere. Both are substantially affected by human activities. Contrary to what has happened in the stratosphere, ozone concentrations in the troposphere have increased, not only in urban and suburban regions during photochemical smog episodes, but also more generally in regions that are influenced by anthropogenic emissions of the ozone precursors hydrocarbons, carbon monoxide (CO) and nitric oxide (NO). Affected is not only the mid-latitude zone of the Northern Hemisphere, but also the continental tropics and subtropics as a consequence of extensive biomass burning during the dry season. Ozone is deleterious to the biosphere, affecting human health and plant growth, including agricultural productivity. It is estimated that between 2000-5000 million tons of biomass is burned each year in the tropics and subtropics during the dry season, resulting in high emissions of light absorbing smoke particles and ozone precursors (see Table 2). As a consequence, during the dry season high concentrations of ozone are produced in the rural areas of the tropics and subtropics (note that the so-called photochemical smog in the industrial regions is mostly an urban/suburban, ozone production in the tropics a rural phenomenon). In future, rapid population growth and enhanced agricultural and industrial activities in the developing world will lead to strong increases of air pollution, causing effects on health and climate parameters. The large potential for vastly increased pollutant loadings follows for instance from the projected increase in the emissions of NO from 1.1 million tons in 1990 to 7 million tons N in 2020 in the Indian subcontinent (van Aardenne et al., Atmospheric Environment, 33, 633-646, 1999). Similar developments can be expected in other parts of the developing world.

If their levels are not too high, the role of ozone and UV-B radiation in the troposphere is, however, not only negative. In fact, they fulfil an essential function in “keeping the atmosphere clean” due to their indirect role in the removal of almost all gases that are emitted into the atmosphere by nature and mankind. The latter occurs mainly through reactions with hydroxyl (OH) radicals. These are largely formed by the absorption of solar UV-B radiation by ozone, leading to the production of excited O atoms which have enough energy to react with water vapour to produce hydroxyl (HO) radicals, the “detergents of the atmosphere”. Despite very low tropospheric concentrations, globally averaging as little as  $4 \times 10^{-14}$  by volume, it is highly reactive hydroxyl, and not abundant (21%) molecular oxygen ( $\text{O}_2$ ), which is responsible for cleaning the atmosphere. Because of maximum abundance of

UV-B radiation and water vapour, the concentrations of hydroxyl, and thus the removal of many gases from the atmosphere, occurs predominately in the tropics and subtropics (see Figure 2). A quantitative understanding of the chemistry of the atmosphere requires, therefore, good knowledge of the chemistry of the tropics and subtropics.

### **Focussing in the Tropics and Sub-Tropics**

Exactly regarding the tropics and subtropics there exist major gaps in knowledge and observations of many key species in tropospheric chemistry, in the first place of ozone, but also of those species which determine the self-cleaning (or oxidizing) efficiency (largely determined by OH concentrations) of the atmosphere, such as CO, hydrocarbons and NO<sub>x</sub>. It is not known whether the self-cleaning efficiency of the atmosphere will increase or decrease in the future. This will be largely determined by developments in the tropics. The continental tropics and subtropics are already substantially affected by mostly human-caused biomass burning. In future, agricultural and industrial activities will particularly strongly grow in these regions. The study of their influence on atmospheric chemistry (especially ozone and hydroxyl concentrations) and climate is an important task for the atmospheric chemistry community. This requires much enhanced research in the tropical world which must involve the participation of researchers from developing world nations.

The present state of quantitative knowledge about particulate matter in the troposphere is even in worse shape than that of the gas phase. The role of aerosol is manifold:

1. Particulate matter influence the chemistry of the atmosphere by providing surfaces and liquid media for chemical reactions, which can not take place in the gas phase.
2. By the scattering and absorption of solar radiation, particulate matter plays a substantial role in the radiative properties of the atmosphere and, therefore, in Earth climate.
3. This influence is emphasized by the fact that atmospheric particles can serve as condensation and/or ice forming nuclei. Recent studies have indicated the possibility that climate warming due to increasing levels of the greenhouse gases can have been substantially counteracted by the backscattering to space of solar radiation, both directly from the aerosol or indirectly by the increased albedo of clouds. It appears indeed that calculated and observed temperature trends agree better with each other when optical aerosol effects are included in global climate models, thus adding some credence to the significance of the aerosol-climate feedback. However, such conclusions are still based on rather weak grounds, again largely because of lack of knowledge about the physiochemical properties and distributions of atmospheric aerosol. In particular, most climate model runs were performed only considering sulfate aerosol, which are strongly derived from coal and oil burning. However, several additional types of aerosol, which can likewise be influenced by human activities, are emitted to the atmosphere, such as
  - smoke particles , mostly from tropical and subtropical biomass burning
  - soil dust, largely from the subtropical deserts.
  - organic aerosol, resulting from gaseous organic precursor emissions from vegetation, with large contributions from tropical forests.
  - seasalt particles.

Clouds can provide major pathways for the chemical processing of natural and anthropogenic emissions. While this chemical cloud effect has been studied for a few major pollutants such as SO<sub>2</sub>, there are many other soluble and reactive atmospheric constituents whose cloud processing is largely unknown.

The lack of knowledge also concerns the interactions of gas phase species with the aerosol. As an example, in all climate simulations the calculated distributions of sulfate aerosols have been calculated, neglecting potential reactions of anthropogenic SO<sub>2</sub> with the various types of aerosol. This may well mean that much of the sulfur, which is emitted into the atmosphere, may be deposited on pre-existing aerosol, such as soil dust and seasalt particles instead of nucleating to new sulfate particles. If so, little additional sulfate particle formation could take place in regions with high emissions of pre-existing particles, implying that the sulfate cooling effect probably has been overestimated in most models. Neither the quantities of emissions nor the global distribution of the aerosol are even approximately known. However, one thing is clear: All types of aerosol play important roles for climate and the chemistry of the atmosphere. And again, also here the main gaps in knowledge are in the tropics and subtropics. What is needed most are measurements of the emissions and global distributions of the various kinds of aerosol, again especially in the tropics and subtropics.

Closely connected to the climate and atmospheric chemistry aspects of global change, are biosphere/atmosphere interactions, as many of the chemically and climatologically important trace gases are to a substantial degree emitted into, or removed from, the atmosphere by the biosphere. Besides CO<sub>2</sub> and N<sub>2</sub>O, we mention especially NO, CH<sub>4</sub>, and reactive hydrocarbons which together have a substantial impact on O<sub>3</sub> and OH concentrations and the ozone layer. They are increasingly impacted by human activities.

## **Conclusions**

I urge, therefore, that in future “Global Change” research efforts substantially more attention is given to the tropics and subtropics. This also requires the involvement and training of local scientists to participate in joint field programmes: A strong scientific basis in this part of the world will in future not only benefit progress in science, but will also lead to greatly improved scientific inputs in political decision making.

Figure 1. As  $\text{N}_2\text{O}$ , these gases are only removed from the atmosphere by photodissociation in the stratosphere, thereby producing Cl and ClO radicals, which, even more efficiently than  $\text{NO}_x$ , can break down ozone by catalytic reactions

Figure 2. Because of maximum abundance of UV-B radiation and water vapour, the concentrations of hydroxyl, and thus the removal of many gases from the atmosphere, occurs predominately in the tropics and subtropics.

Table 1. Earth's climate and the chemistry of the atmosphere are mainly determined by the remaining minor constituents, which because of their relatively low abundance are significantly affected by emissions from various human activities, in particular fossil fuel and biomass burning, chemical manufacturing, agriculture and land use changes.

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

<b><i>Slash and Burn Agriculture</i></b>	<b><i>0.5 – 1.0</i></b>
<b>Forest Clearing</b>	<b>0.2 – 0.7</b>
<b>Savanna Grass Fires</b>	<b>0.3 – 1.6</b>
<b>Wood Burning</b>	<b>0.3 – 0.6</b>
<b>Agricultural Wastes</b>	<b>0.5 – 0.8</b>
S	<b>1.8 – 4.7</b>

Table 2: Estimated rates of biomass burning in the tropics and subtropics. Due to this burning large quantities of pollutant gases and particles are created which even affect global atmospheric chemistry and climate.