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Special Paper on the Possible Contents of Annexes and/or Protocols to the Draft Convention for the Protection of the Ozone Layer

List of Substances capable of modifying Stratospheric Ozone

DRAFT TEXT SUBMITTED BY THE
DELEGATION OF
THE UNITED STATES OF AMERICA

ANNEX III

LIST OF SUBSTANCES CAPABLE OF MODIFYING STRATOSPHERIC OZONE

1. Recognizing that certain chemical substances may be capable of modifying the spatial and temporal distribution and abundance of stratospheric ozone, the Contracting Parties agree to support, as appropriate, individually and collectively, research and monitoring as outlined in Annex I on the substances which are listed below.

2. This annex is a compilation of chemical substances of natural and anthropogenic origin released at the earth's surface or directly in the upper atmosphere which are thought to have the potential to modify the chemical, physical or radiative properties of the earth's atmosphere. This list is primarily devoted to substances presently (1983) being released to the atmosphere in quantities believed sufficient to cause changes in the chemical composition or the physical properties of the atmosphere.

3. [The major scientific issues associated with continued stratospheric pollution revolve around, (a) modification

of the total column content of ozone which would result in a change in the amount of solar UV-B radiation that reaches the earth's surface with potential consequences for human health and ecological organisms and systems, and (b) modification of the vertical distribution of ozone which would change the temperature structure of the stratosphere with potential consequences for weather and climate. In addition there could be direct modification of the thermal structure of the atmosphere due to the addition of gases that absorb infrared radiation, e.g. carbon dioxide, CO_2; methane, CH_4; nitrous oxide N_2O; chloroflurormethanes, CFM's; and tropospheric ozone.]

4. The chemical subtances are discussed by family, i.e. carbon, nitrogen, chlorine, bromine, etc.

4.1. Carbon Substances.

4.1.1. Carbon Monoxide (CO).

CO has significant natural sources (oxidation of naturally-occurring hydrocarbons and combustion of vegetation biomass) and anthropogenic sources (fossil fuel burning and the oxidation of anthropogenic hydrocarbons). While CO is not believed to play a significant role in stratospheric ozone photochemistry, it is thought to play a major role in tropospheric photochemistry by controlling the hydroxyl radical (OH) and ozone concentrations. Reaction with CO is believed to be the dominant loss mechanism for OH. The OH radical reacts with and thereby limits the atmospheric residence times of numerous species, e.g. methane, CH_4; methyl chloride, CH_3Cl; methyl chloroform, CH_3CCl_3; methyl bromide, CH_3Br; non-methane hydrocarbons, NMHC; hydrogen sulphide, H_2S; dimethyl sulphide, $(CH_3)_2S$; sulfur dioxide, SO_2; etc. Therefore, any significant increase in the atmospheric concentration of CO, which would reduce the OH radical concentration, could influence stratospheric ozone by increasing the flux of those tropospheric species into the stratosphere.

4.1.2 Carbon Dioxide (CO_2)

Carbon dioxide has significant natural and anthropogenic (fossil fuel burning and deforestation) sources. Atmospheric CO_2 is currently increasing at a rate of about 1ppm yr^{-1} ($3x10^{15}$gm yr^{-1}). CO_2 does not influence stratospheric ozone through direct chemical reactions, but increasing concentrations of CO_2 should decrease the temperature of the stratosphere, altering rates for several key reactions, resulting in a change in ozone.

4.1.3. Methane (CH_4)

The sources of methane are believed to be both natural (wetlands, animal enteric fermentation, and oceans), and anthropogenic (domestic animal enteric fermentation). These sources need to be quantified in order to understand the global atmospheric budget of CH_4. There is strong evidence that the concentration of atmospheric CH_4 has risen over the past decade (1-2% per yr) and some debatable evidence for an increase dating back to the sixteenth century. However, the cause for the increase is unknown. CH_4 has a relatively long photochemical lifetime ($\sim$10 years, governed by tropospheric OH) and is important to stratospheric photochemistry. It affects stratospheric ozone because it limits the catalytic efficiency of chlorine by the reaction of atomic chlorine with methane and contributes to the HO_x radical and water vapor concentrations through its oxidation products.

4.1.4 Non-Methane Hydrocarbon species (NMHC)

NMHC's include alkanes (e.g. C_2H_6); alkenes (e.g. C_2H_4); alkynes (e.g. C_2H_2); aldehydes (e.g. CH_2O); peroxyacetyl nitrate ($CH_3C(O)OONO_2$); isoprene; and terpenes. Alkanes, alkenes and alkynes have both natural (natural gas) and anthropogenic sources, while isoprene and terpenes are emitted from vegetation. The remaining NMHC atmospheric species result from the chemical transformations of these emitted species. The photochemical lifetimes of NMHC species are normally short due to their reactivity with the OH radical which limits the flux of these species into the stratosphere. Consequently, NMHC species play a vital role in tropospheric photochemistry but their direct impact on stratospheric processes is relatively minor.

4.2 Nitrogen Substances

4.2.1 Nitrous Oxide (N_2O)

The dominant source of N_2O is natural (nitrification and denitrification) but there may be increasingly important anthropogenic contributions (combustion and agricultural fertilization). The atmospheric concentration is currently increasing at a rate of ~0.2% per year, but the exact sources are still open to question. N_2O has no known removal mechanisms in the troposphere. It is the primary source of stratospheric NO_x (i.e. $NO + NO_2$) which plays a vital role in controlling the abundance of stratospheric ozone (4.2.2). Increased levels of N_2O are currently believed to decrease the concentration of ozone in the stratosphere.

4.2.2. Nitrogen Oxides (NO_x)

NO_x denotes the nitrogen oxides NO and NO_2. The magnitudes of the natural (including lightening and soil microbial processes) and anthropogenic (combustion, biomass burning, aircraft exhaust and atmospheric nuclear explosions sources are poorly defined. Stratospheric NO_x is well recognized for its pivotal role in controlling both the distribution and abundance of stratospheric ozone. Ground level sources of tropospheric NO_x do not contribute to the stratospheric budget of NO_x due to heterogeneous removal of inorganic nitrogen species (HNO_3; HNO_2; NO_2; NO; N_2O_5; HO_2NO_2) in the troposphere (i.e. by rain-out processes). Consequently, there is no direct influence of ground level sources of tropospheric NO_x on stratospheric O_3. However, NO_x plays a vital role in tropospheric photochemical processes which control the concentrations of OH and O_3. Therefore, ground level sources of tropospheric NO_x may have an important indirect influence on stratospheric photochemistry.

Injection of NO_x in the upper troposphere and stratosphere by aircraft exhaust or by atmospheric explosion of nuclear weapons can directly lead to a change in stratospheric and upper tropospheric ozone levels.

4.3. Chlorine Substances

4.3.1. Fully Halogenated Alkanes (e.g. CCl_4, $CFCl_3$, CF_2Cl_2, etc.)

The source of the fully halogenated alkanes is solely anthropogenic. The atmospheric concentrations of carbon tetrachloride, CCl_4; fluorocarbon 11, $CFCl_3$; and fluorocarbon 12, CF_2Cl_2 are such that they are presently the greatest anthropogenic contributors to the stratospheric ClO_x concentration, where ClO_x denotes Cl and ClO. The stratospheric ClO_x concentration is currently increasing primarily due to continued releases of $CFCl_3$ and CF_2Cl_2 because of the long atmospheric lifetimes of these species. There are no known tropospheric removal mechanisms for these species. Stratospheric ClO_x plays a vital role in ozone photochemistry, especially in the 30-50km altitude region. Increasing levels of stratospheric ClO_x are currently believed to decrease the concentration of ozone in the stratosphere.

4.3.2 Partially Halogenated Alkanes (e.g. CH_3Cl, CHF_2Cl, CH_3CCl_3).

The source of CH_3Cl is not quantitatively well understood but it is thought to be primarily due to biospheric processes arising in the tropical oceans. CH_3Cl has a relatively short atmospheric lifetime due to reaction with OH in the troposphere. It is presently the single greatest natural contributor to the stratospheric ClO_x concentration. Other partially halogenated alkanes (e.g. CHF_2Cl and CH_3CCl_3) are anthropogenic in origin. The flux of these gases to the stratosphere is determined by their source strengths and their atmospheric lifetimes which are largely controlled by reaction with tropospheric OH.

4.3.3 Halogenated Alkenes (e.g. C_2HCl_3, C_2Cl_4)

These gases are anthropogenic in origin but their flux to the stratosphere is relatively unimportant due to their very short tropospheric lifetimes. Again like the partially halogenated alkanes their lifetimes are controlled by reaction with tropospheric OH.

4.3.4. Hydrogen Chloride (HCl)

HCl has both anthropogenic and natural (release from sea salt) sources. However, tropospheric sources of HCl do not significantly contribute to stratospheric ClO_x due to rain-out in the troposphere.

4.4. Bromine Substances

4.4.1. Fully Halogenated Alkanes (e.g. CF_3Br)

The source of these gases is anthropogenic, there are no known tropospheric removal mechanisms for these species. BrO_x is currently believed to be at least as efficient as ClO_x, on a molecular basis, in controlling the concentration of stratospheric ozone. However, the source strengths are thought to be much smaller (several orders of magnitude lower) than their chlorine analogs.

4.4.2. Partially Halogenated Alkanes (e.g. CH_3Br)

The only substance in this class observed in the atmosphere is CH_3Br which is natural in orgin. The source strength is unknown. The flux of CH_3Br, or any substance in this class, to the stratosphere is limited by its reaction with OH in the troposphere.