M.Sc. in Meteorology

Synoptic Meteorology

[MAPH P312]

Prof Peter Lynch

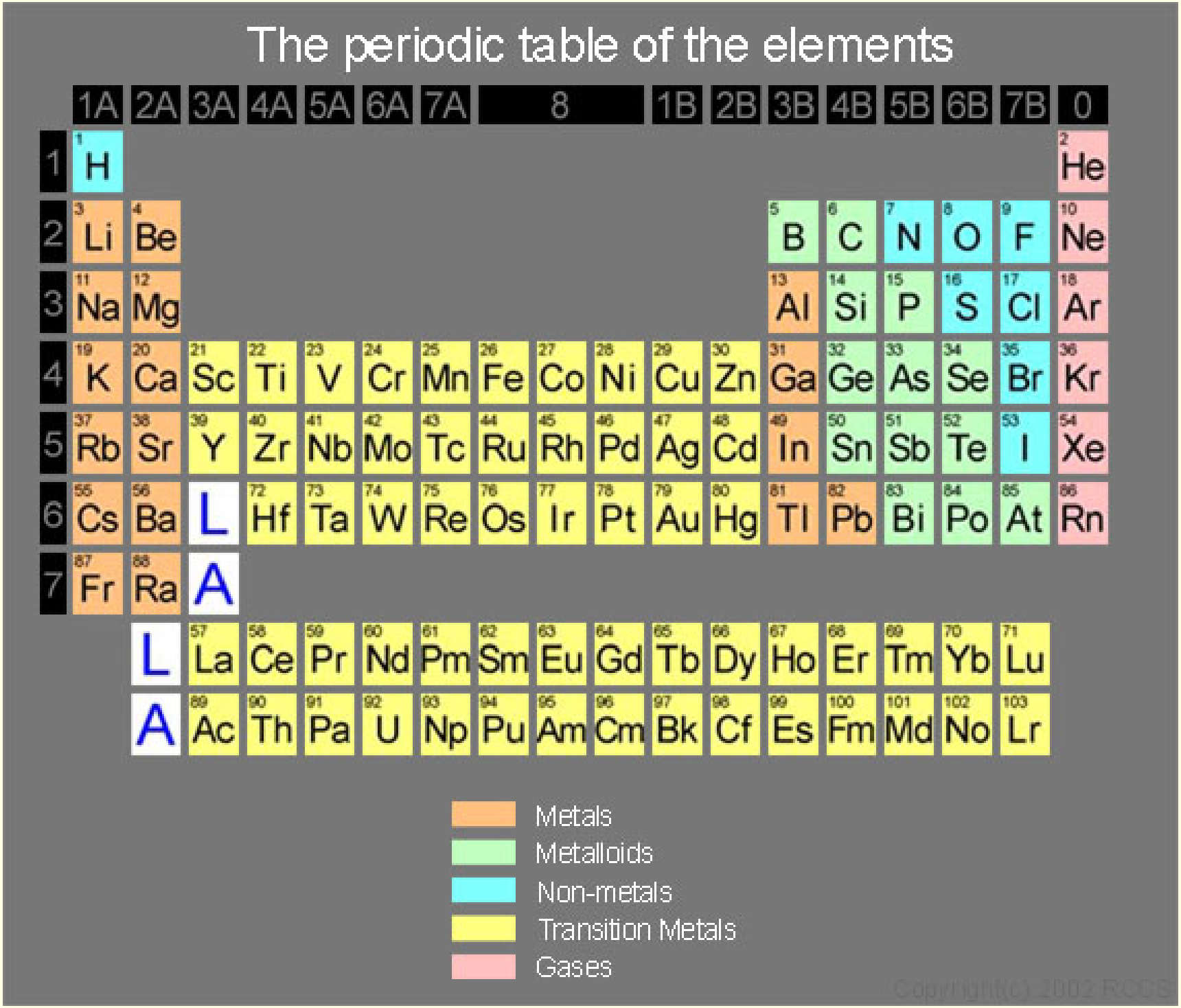
Second Semester, 2004–2005
Seminar Room

Dept. of Maths. Physics, UCD, Belfield.

Part 5

Atmospheric Chemistry

These lectures follow closely the text of *Wallace & Hobbs*.


The periodic table of the elements
1A 2A 3A 4A 5A 6A 7A 8 1B 2B 3B 4B 5B 6B 7B 0
1 H He
2 Li Be B C N O F Ne
3 Na Mg Al Si P S Cl Ar
4 K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
5 Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
6 Cs Ba L Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
7 Fr Ra A
L La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
A Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr
Metals
Metalloids
Non-metals
Transition Metals
Gases
Copyright(c) 2002 RCCB

Introduction

Introduction

- ***Atmospheric chemistry studies were originally concerned with determining the major gases in the Earth's atmosphere.***

Introduction

- ***Atmospheric chemistry studies were originally concerned with determining the major gases in the Earth's atmosphere.***
- ***In the latter half of the 1900s air pollution became an increasing problem.***

Introduction

- ***Atmospheric chemistry studies were originally concerned with determining the major gases in the Earth's atmosphere.***
- ***In the latter half of the 1900s air pollution became an increasing problem.***
- ***Acid deposition was recognized as a widespread problem in the 1970s.***

- *It became obvious that pollutants can be transported over large distances and undergo significant transformations as they move through the atmosphere.*

- *It became obvious that pollutants can be transported over large distances and undergo significant transformations as they move through the atmosphere.*
- *The identification in 1985 of significant depletion of ozone in the Antarctic stratosphere focussed attention on stratospheric chemistry.*

- *It became obvious that pollutants can be transported over large distances and undergo significant transformations as they move through the atmosphere.*
- *The identification in 1985 of significant depletion of ozone in the Antarctic stratosphere focussed attention on stratospheric chemistry.*
- *More recently, studies of the effects of trace chemical constituents in the atmosphere on the climate of the Earth have moved to centre stage.*

1. Composition of Tropospheric Air

1. Composition of Tropospheric Air

- **Oxygen occupies 21% by volume of dry air.**

1. Composition of Tropospheric Air

- **Oxygen occupies 21% by volume of dry air.**
- **Nitrogen occupies 78%.**

1. Composition of Tropospheric Air

- **Oxygen occupies 21% by volume of dry air.**
- **Nitrogen occupies 78%.**
- **The next two most abundant gases in air are argon (∼1%) and carbon dioxide (∼0.03%).**

1. Composition of Tropospheric Air

- **Oxygen occupies 21% by volume of dry air.**
- **Nitrogen occupies 78%.**
- **The next two most abundant gases in air are argon (∼1%) and carbon dioxide (∼0.03%).**
- **Together these four gases account for 99.99% of the volume of dry air.**

1. Composition of Tropospheric Air

- **Oxygen occupies 21% by volume of dry air.**
- **Nitrogen occupies 78%.**
- **The next two most abundant gases in air are argon (∼1%) and carbon dioxide (∼0.03%).**
- **Together these four gases account for 99.99% of the volume of dry air.**
- **Many of the remaining minute amounts of the many other gases in air are of prime importance in atmospheric chemistry because of their chemical reactivity.**

The most common unit for expressing the quantity of a gas in air is the fraction of the total volume of air that the gas occupies.

The most common unit for expressing the quantity of a gas in air is the fraction of the total volume of air that the gas occupies.

The volumes occupied by different gases at the same temperature and pressure are proportional to the numbers of molecules of the respective gases.

The most common unit for expressing the quantity of a gas in air is the fraction of the total volume of air that the gas occupies.

The volumes occupied by different gases at the same temperature and pressure are proportional to the numbers of molecules of the respective gases.

For a mixture of ideal gases like air the partial pressure exerted by a gas is proportional to the mole fraction of the gas in the mixture.

The most common unit for expressing the quantity of a gas in air is the fraction of the total volume of air that the gas occupies.

The volumes occupied by different gases at the same temperature and pressure are proportional to the numbers of molecules of the respective gases.

For a mixture of ideal gases like air the partial pressure exerted by a gas is proportional to the mole fraction of the gas in the mixture.

For example, if CO_2 occupies 0.03% of the volume of air, the fraction of the total number of molecules in air that are CO_2 (i.e., the mole fraction of CO_2) is 0.03% and, if the total air pressure is 1 atm, the partial pressure exerted by CO_2 is 0.03% of 1 atm (about 30 Pa).

The most common unit for expressing the quantity of a gas in air is the fraction of the total volume of air that the gas occupies.

The volumes occupied by different gases at the same temperature and pressure are proportional to the numbers of molecules of the respective gases.

For a mixture of ideal gases like air the partial pressure exerted by a gas is proportional to the mole fraction of the gas in the mixture.

For example, if CO_2 occupies 0.03% of the volume of air, the fraction of the total number of molecules in air that are CO_2 (i.e., the mole fraction of CO_2) is 0.03% and, if the total air pressure is 1 atm, the partial pressure exerted by CO_2 is 0.03% of 1 atm (about 30 Pa).

Exercise: N_2O occupies 310 ppbv of air. How many N_2O molecules are there in $1\,m^3$ of air at 1 atm and 0°C?

2. Sources of Trace Gases

2. Sources of Trace Gases

The major natural sources of gases in the troposphere are biogenic, the solid Earth, the oceans and *in situ* formation.

In addition, we must consider human or anthropogenic sources.

2. Sources of Trace Gases

The major natural sources of gases in the troposphere are biogenic, the solid Earth, the oceans and *in situ* formation.

In addition, we must consider human or anthropogenic sources.

Biogenic

The Earth's present atmosphere was formed by biological activity starting about 2 billion years ago.

2. Sources of Trace Gases

The major natural sources of gases in the troposphere are biogenic, the solid Earth, the oceans and *in situ* formation.

In addition, we must consider human or anthropogenic sources.

Biogenic

The Earth's present atmosphere was formed by biological activity starting about 2 billion years ago.

Of prime importance is the photosynthesis reaction

$$\mathbf{CO_2(g) + H_2O(l) + h\nu \rightarrow CH_2O(s) + O_2(g)}$$

2. Sources of Trace Gases

The major natural sources of gases in the troposphere are biogenic, the solid Earth, the oceans and *in situ* formation.

In addition, we must consider human or anthropogenic sources.

Biogenic

The Earth's present atmosphere was formed by biological activity starting about 2 billion years ago.

Of prime importance is the photosynthesis reaction

$$\mathbf{CO_2(g) + H_2O(l) + h\nu \rightarrow CH_2O(s) + O_2(g)}$$

This removes carbon from the atmosphere and stores it in organic matter, and releases oxygen to the atmosphere.

About 80% of the CH_4 in air derives from recent organic materials (as opposed to fossil fuels) through ruminant animals (cows, etc.), termites, rice paddies and wetlands.

About 80% of the CH_4 in air derives from recent organic materials (as opposed to fossil fuels) through ruminant animals (cows, etc.), termites, rice paddies and wetlands.

Biological processes (often by microbes) convert N_2 into NH_3 (primarily via animal urine and soils), N_2O (through nitrate respiration by bacteria in soils), and NO.

About 80% of the CH_4 in air derives from recent organic materials (as opposed to fossil fuels) through ruminant animals (cows, etc.), termites, rice paddies and wetlands.

Biological processes (often by microbes) convert N_2 into NH_3 (primarily via animal urine and soils), N_2O (through nitrate respiration by bacteria in soils), and NO.

Regions of the ocean with high organic content and biological productivity (e.g., upwelling regions, coastal waters and salt marshes) are a major source of carbon disulphide (CS_2) and carbonyl sulfide (COS).

About 80% of the CH_4 in air derives from recent organic materials (as opposed to fossil fuels) through ruminant animals (cows, etc.), termites, rice paddies and wetlands.

Biological processes (often by microbes) convert N_2 into NH_3 (primarily via animal urine and soils), N_2O (through nitrate respiration by bacteria in soils), and NO.

Regions of the ocean with high organic content and biological productivity (e.g., upwelling regions, coastal waters and salt marshes) are a major source of carbon disulphide (CS_2) and carbonyl sulfide (COS).

Phytoplankton are the major source of atmospheric dimethal sulphide (DMS) and dimethyldisulfide (CH_3SSCH_3). DMS is oxidized to SO_2 and then to sulfate aerosols. Microbial degradation of dead organic matter releases H_2S.

About 80% of the CH_4 in air derives from recent organic materials (as opposed to fossil fuels) through ruminant animals (cows, etc.), termites, rice paddies and wetlands.

Biological processes (often by microbes) convert N_2 into NH_3 (primarily via animal urine and soils), N_2O (through nitrate respiration by bacteria in soils), and NO.

Regions of the ocean with high organic content and biological productivity (e.g., upwelling regions, coastal waters and salt marshes) are a major source of carbon disulphide (CS_2) and carbonyl sulfide (COS).

Phytoplankton are the major source of atmospheric dimethal sulphide (DMS) and dimethyldisulfide (CH_3SSCH_3). DMS is oxidized to SO_2 and then to sulfate aerosols. Microbial degradation of dead organic matter releases H_2S.

The most abundant halocarbon in the air, and the major natural source of chlorine (Cl) in the stratosphere, is methyl chloride (CH_3Cl), which derives, in part, from biological activity in seawater, wood molds and biomass burning.

Halogen compounds (e.g., chlorine and bromine species) are also produced by biological activity in the oceans.

Halogen compounds (e.g., chlorine and bromine species) are also produced by biological activity in the oceans.

Volatile organic compounds (VOCs) are emitted by plants (and anthropogenic sources). Several thousand VOCs from biogenic sources have been identified. Some of the more important are **isoprene** (C_5H_8), **ethene** (C_2H_4) and **monoterpenes**.

Halogen compounds (e.g., chlorine and bromine species) are also produced by biological activity in the oceans.

Volatile organic compounds (VOCs) are emitted by plants (and anthropogenic sources). Several thousand VOCs from biogenic sources have been identified. Some of the more important are **isoprene** (C_5H_8), **ethene** (C_2H_4) and **monoterpenes**.

Isoprene accounts for 50% of the NMHC. The photooxidation of isoprene can produce compounds that have vapour pressures low enough for them to condense onto pre-existing particles. This could account for some 5–20% of the annual secondary organic aerosol from biogenic sources.

Halogen compounds (e.g., chlorine and bromine species) are also produced by biological activity in the oceans.

Volatile organic compounds (VOCs) are emitted by plants (and anthropogenic sources). Several thousand VOCs from biogenic sources have been identified. Some of the more important are isoprene (C_5H_8), ethene (C_2H_4) and monoterpenes.

Isoprene accounts for 50% of the NMHC. The photooxidation of isoprene can produce compounds that have vapour pressures low enough for them to condense onto pre-existing particles. This could account for some 5–20% of the annual secondary organic aerosol from biogenic sources.

Terpenes are a class of hydrocarbons that evaporate from leaves. About 80% of these emissions oxidize to organic aerosols in about an hour.

Emissions from vegetation are a significant source of hydrocarbons, which can react photochemically with NO and NO_2 to produce O_3, thereby playing a central role in atmospheric chemistry.

Emissions from vegetation are a significant source of hydrocarbons, which can react photochemically with NO and NO_2 to produce O_3, thereby playing a central role in atmospheric chemistry.

Use by humans of biological materials results in the emissions of many chemicals into the atmosphere, for example:

Emissions from vegetation are a significant source of hydrocarbons, which can react photochemically with NO and NO_2 to produce O_3, thereby playing a central role in atmospheric chemistry.

Use by humans of biological materials results in the emissions of many chemicals into the atmosphere, for example:

CO_2, CO, NO_x, N_2O, NH_3, SO_2 and HCl (from the combustion of oil, gas, coal and wood),

Emissions from vegetation are a significant source of hydrocarbons, which can react photochemically with NO and NO_2 to produce O_3, thereby playing a central role in atmospheric chemistry.

Use by humans of biological materials results in the emissions of many chemicals into the atmosphere, for example:

CO_2, CO, NO_x, N_2O, NH_3, SO_2 and HCl (from the combustion of oil, gas, coal and wood),

Hydrocarbons (automobiles, refineries, paints and solvents),

Emissions from vegetation are a significant source of hydrocarbons, which can react photochemically with NO and NO_2 to produce O_3, thereby playing a central role in atmospheric chemistry.

Use by humans of biological materials results in the emissions of many chemicals into the atmosphere, for example:

CO_2, CO, NO_x, N_2O, NH_3, SO_2 and HCl (from the combustion of oil, gas, coal and wood),

Hydrocarbons (automobiles, refineries, paints and solvents),

H_2S and DMS (from paper mills, and oil refineries),

Emissions from vegetation are a significant source of hydrocarbons, which can react photochemically with NO and NO_2 to produce O_3, thereby playing a central role in atmospheric chemistry.

Use by humans of biological materials results in the emissions of many chemicals into the atmosphere, for example:

CO_2, CO, NO_x, N_2O, NH_3, SO_2 and HCl (from the combustion of oil, gas, coal and wood),

Hydrocarbons (automobiles, refineries, paints and solvents),

H_2S and DMS (from paper mills, and oil refineries),

carbonyl sulfide — COS (from natural gas), and

Emissions from vegetation are a significant source of hydrocarbons, which can react photochemically with NO and NO_2 to produce O_3, thereby playing a central role in atmospheric chemistry.

Use by humans of biological materials results in the emissions of many chemicals into the atmosphere, for example:

CO_2, CO, NO_x, N_2O, NH_3, SO_2 and HCl (from the combustion of oil, gas, coal and wood),

Hydrocarbons (automobiles, refineries, paints and solvents),

H_2S and DMS (from paper mills, and oil refineries),

carbonyl sulfide — COS (from natural gas), and

chloroform — $CHCl_3$ (from combustion of petroleum, bleaching of woods, solvents).

Emissions from Biomass Burning

Emissions from Biomass Burning

About half a billion hectares (about half the area of Europe) of vegetation are burned globally each year, and the amount of burning is increasing.

Emissions from Biomass Burning

About half a billion hectares (about half the area of Europe) of vegetation are burned globally each year, and the amount of burning is increasing.

Most biomass burning is associated with deforestation (e.g., in the Amazon Basin), refertilization of soils and grazing (e.g., in the savannas of southern Africa), and with the use of wood for heating and cooking (e.g., in Africa, India, and SE Asia).

Emissions from Biomass Burning

About half a billion hectares (about half the area of Europe) of vegetation are burned globally each year, and the amount of burning is increasing.

Most biomass burning is associated with deforestation (e.g., in the Amazon Basin), refertilization of soils and grazing (e.g., in the savannas of southern Africa), and with the use of wood for heating and cooking (e.g., in Africa, India, and SE Asia).

It has been estimated that on an annual basis biomass burning produces ~38% of the O_3, ~32% of the CO, ~39% of the particulate carbon, and more than 20% of the H_2, NMHC, methyl chloride (CH_3Cl) and NO_x in the troposphere.

Emissions from Biomass Burning

About half a billion hectares (about half the area of Europe) of vegetation are burned globally each year, and the amount of burning is increasing.

Most biomass burning is associated with deforestation (e.g., in the Amazon Basin), refertilization of soils and grazing (e.g., in the savannas of southern Africa), and with the use of wood for heating and cooking (e.g., in Africa, India, and SE Asia).

It has been estimated that on an annual basis biomass burning produces ~38% of the O_3, ~32% of the CO, ~39% of the particulate carbon, and more than 20% of the H_2, NMHC, methyl chloride (CH_3Cl) and NO_x in the troposphere.

Biomass burning also produces ~40% of the world's annual production of CO_2, but this is largely offset by the uptake of CO_2 by young vegetation that sprouts quickly on burned areas.

Ozone is produced in the troposphere by photochemical reactions involving oxidation by OH of CO, CH_4 and NMHC in the presence of NO_X.

Ozone is produced in the troposphere by photochemical reactions involving oxidation by OH of CO, CH_4 and NMHC in the presence of NO_x.

Since all of these precursors are present in smoke from biomass burning, elevated O_3 concentrations are produced in biomass smoke as it disperses in the troposphere.

Ozone is produced in the troposphere by photochemical reactions involving oxidation by OH of CO, CH_4 and NMHC in the presence of NO_x.

Since all of these precursors are present in **smoke from biomass burning**, elevated O_3 concentrations are produced in biomass smoke as it disperses in the troposphere.

Many of the emissions from biomass burning are **carcinogens**, they cause significant degradation to air quality on local and regional scales, and they have global effects on atmospheric chemistry and climate.

Ozone is produced in the troposphere by photochemical reactions involving oxidation by OH of CO, CH_4 and NMHC in the presence of NO_x.

Since all of these precursors are present in smoke from biomass burning, elevated O_3 concentrations are produced in biomass smoke as it disperses in the troposphere.

Many of the emissions from biomass burning are carcinogens, they cause significant degradation to air quality on local and regional scales, and they have global effects on atmospheric chemistry and climate.

Biomass smoke, which contains high concentrations of CO, CH_4 and O_3, can be dispersed over large distances in the atmosphere.

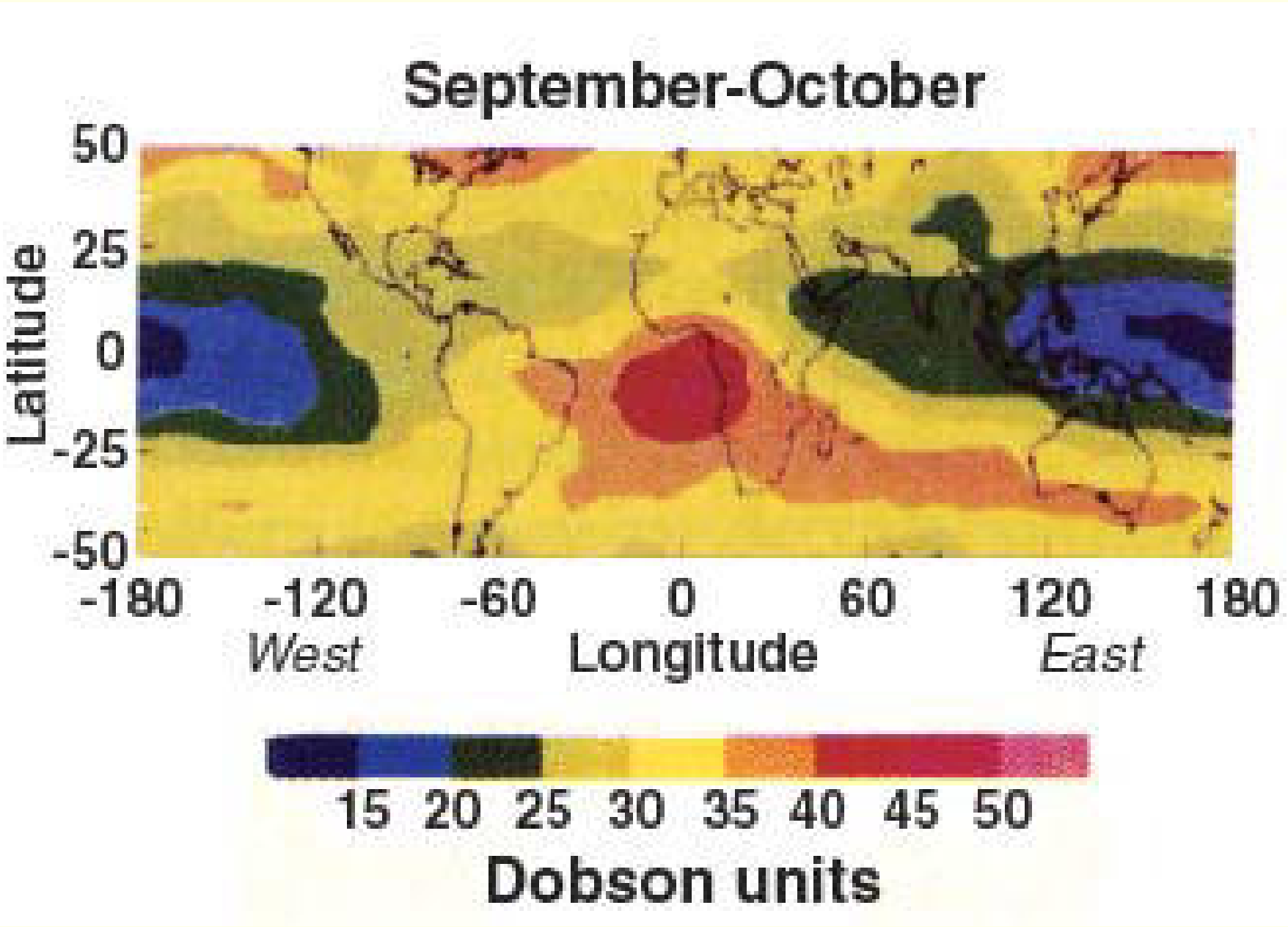
Ozone is produced in the troposphere by photochemical reactions involving oxidation by OH of CO, CH_4 and NMHC in the presence of NO_x.

Since all of these precursors are present in **smoke from biomass burning**, elevated O_3 concentrations are produced in biomass smoke as it disperses in the troposphere.

Many of the emissions from biomass burning are **carcinogens**, they cause significant degradation to air quality on local and regional scales, and they have global effects on atmospheric chemistry and climate.

Biomass smoke, which contains high concentrations of CO, CH_4 and O_3, can be **dispersed over large distances** in the atmosphere.

Not even the most **remote regions** of Earth are immune to pollution. For example, under appropriate wind conditions biomass smoke from Africa is dispersed across the South Atlantic Ocean and even to Australia (Figure below).



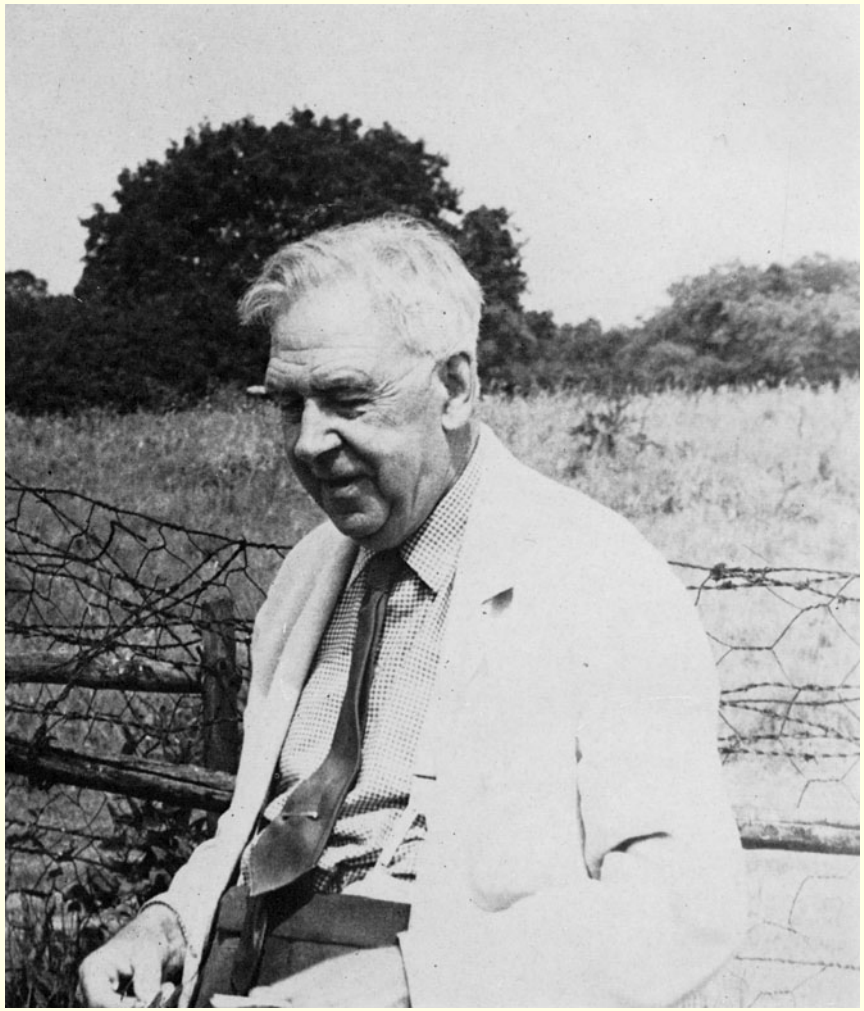
Satellite measurements of tropospheric ozone (in Dobson units) in September and October for the period 1979-1989.

The high column amounts of ozone (indicated by high Dobson units) over tropical and southern Africa (see Figure) are due to smoke from biomass burning. Depending on the winds, this smoke can be carried to the west or east.

The high column amounts of ozone (indicated by high Dobson units) over tropical and southern Africa (see Figure) are due to smoke from biomass burning. Depending on the winds, this smoke can be carried to the west or east.

Biomass smoke can also be lofted into the middle and upper troposphere, where it can become a dominant source of HO_X (where x = 0, 1, or 2) and NO_X and result in the production of O_3.

G. M. B. Dobson
(1889-1976)



was an English physicist and meteorologist. He made the first measurements of the variation of wind with height using pilot balloons (1913). In 1922 he discovered the presence of a warm layer of air at about 50 km, which he correctly attributed to the absorption of UV radiation by O_3. Dobson built a UV solar spectrograph for measuring the atmospheric O_3 column. He also obtained the first measurements of water vapour in the stratosphere.

The Dobson Unit

One Dobson Unit (DU) is the thickness, in hundredths of a millimeter, that the total O_3 column would occupy at $0^\circ C$ and 1 atm.

The Dobson Unit

One Dobson Unit (DU) is the thickness, in hundredths of a millimeter, that the total O_3 column would occupy at 0°C and 1 atm.

The Earth's total atmospheric O_3 column is ∼300 DU (i.e., if all the O_3 in the atmosphere were brought to 0°C and 1 atm, it would form a layer just about 3 mm deep).

The Dobson Unit

One Dobson Unit (DU) is the thickness, in hundredths of a millimeter, that the total O_3 column would occupy at 0°C and 1 atm.

The Earth's total atmospheric O_3 column is ∼300 DU (i.e., if all the O_3 in the atmosphere were brought to 0°C and 1 atm, it would form a layer just about 3 mm deep).

It is a remarkable fact that in the absence of such a small amount of O_3 life on Earth would have been impossible.

The Dobson Unit

One Dobson Unit (DU) is the thickness, in hundredths of a millimeter, that the total O_3 column would occupy at 0°C and 1 atm.

The Earth's total atmospheric O_3 column is ∼300 DU (i.e., if all the O_3 in the atmosphere were brought to 0°C and 1 atm, it would form a layer just about 3 mm deep).

It is a remarkable fact that in the absence of such a small amount of O_3 life on Earth would have been impossible.

Exercise: Calculate the partial pressure due to ozone, assuming the total column ozone to be 300 DU.

Sources: Solid Earth

Volcanoes are the most important geochemical source of trace gases in the atmosphere. In addition to ash and copious small particles, volcanoes emit H_2O, CO_2, SO_2, H_2S, COS, HCl, HF (hydrogen fluoride), HBr (hydrogen bromide), CH_4, CH_3Cl, H_2, CO and heavy metals.

Sources: Solid Earth

Volcanoes are the most important geochemical source of trace gases in the atmosphere. In addition to ash and copious small particles, volcanoes emit H_2O, CO_2, SO_2, H_2S, COS, HCl, HF (hydrogen fluoride), HBr (hydrogen bromide), CH_4, CH_3Cl, H_2, CO and heavy metals.

Emissions from violent volcanic eruptions can be blasted into the stratosphere, where they have long residence times and can therefore be dispersed around the globe.

Sources: Solid Earth

Volcanoes are the most important geochemical source of trace gases in the atmosphere. In addition to ash and copious small particles, volcanoes emit H_2O, CO_2, SO_2, H_2S, COS, HCl, HF (hydrogen fluoride), HBr (hydrogen bromide), CH_4, CH_3Cl, H_2, CO and heavy metals.

Emissions from violent volcanic eruptions can be blasted into the stratosphere, where they have long residence times and can therefore be dispersed around the globe.

The violent eruption in 1883 of the Indonesian volcano of Krakatau caused remarkable sunsets and lowered global temperatures at the Earth's surface by $\sim$0.5°C.

Sources: Solid Earth

Volcanoes are the most important geochemical source of trace gases in the atmosphere. In addition to ash and copious small particles, volcanoes emit H_2O, CO_2, SO_2, H_2S, COS, HCl, HF (hydrogen fluoride), HBr (hydrogen bromide), CH_4, CH_3Cl, H_2, CO and heavy metals.

Emissions from violent volcanic eruptions can be blasted into the stratosphere, where they have long residence times and can therefore be dispersed around the globe.

The violent eruption in 1883 of the Indonesian volcano of Krakatau caused remarkable sunsets and lowered global temperatures at the Earth's surface by $\sim$0.5°C.

The largest volcanic eruption in the 20^{th} century, in terms of its atmospheric effects, was Pinatubo in the Philippines in 1991. The emissions from this eruption produced a global average cooling of $\sim$0.5°C for two years and lowered ozone concentrations in the stratosphere.

Rocks are the major sources of He, Ar and Rn (radon) in the atmosphere.

Rocks are the major sources of He, Ar and Rn (radon) in the atmosphere.

Helium is produced by the radioactive decay of uranium-238 and thorium-232. It does not accumulate in the atmosphere because it is so light that it escapes from the exosphere.

Argon has accumulated in air over aeons from the radioactive decay of potassium-40 in rocks.

Radon-222 is a decay product of uranium in rocks; it has a half-life of only 3.8 days.

Rocks are the major sources of He, Ar and Rn (radon) in the atmosphere.

Helium is produced by the radioactive decay of uranium-238 and thorium-232. It does not accumulate in the atmosphere because it is so light that it escapes from the exosphere.

Argon has accumulated in air over aeons from the radioactive decay of potassium-40 in rocks.

Radon-222 is a decay product of uranium in rocks; it has a half-life of only 3.8 days.

Carbonate rocks, such as limestone (e.g., $CaCO_3$), contain about 20,000 times more carbon than the atmosphere, but most of this is sequestered. However, carbonate rocks and marine sediments are involved in a long-period cycle with atmospheric CO_2.

Sources: Oceanic

The oceans are a huge reservoir of those gases in the atmosphere that are soluble in water.

Sources: Oceanic

The oceans are a huge reservoir of those gases in the atmosphere that are soluble in water.

Thus, the oceans may serve as either a sink or a source for soluble gases.

Sources: Oceanic

The oceans are a huge reservoir of those gases in the atmosphere that are soluble in water.

Thus, the oceans may serve as either a sink or a source for soluble gases.

The oceans are an atmospheric source for many gases produced by biological activity, particularly sulfur-containing gases.

Other Sources

Other Sources

In situ formation

Trace gases emitted from the biosphere, solid Earth and oceans are generally in a reduced (low) oxidation state (e.g., carbon, nitrogen and sulfur).

They are oxidized (i.e., raised to a higher oxidation state) by *in situ* reactions in the atmosphere.

Other Sources

In situ formation

Trace gases emitted from the biosphere, solid Earth and oceans are generally in a reduced (low) oxidation state (e.g., carbon, nitrogen and sulfur).

They are oxidized (i.e., raised to a higher oxidation state) by *in situ* reactions in the atmosphere.

Anthropogenic sources

Anthropogenic sources play significant roles in the budgets of many important trace gases in the atmosphere.

As a result of increasing populations, anthropogenic emissions of a number of important trace gases have increased significantly over the past century.

The extent and effects of human influences on the atmosphere is one of the main themes of current research.

Transport

In the planetary boundary layer (PBL) the atmosphere interacts directly with the Earth's surface through turbulent mixing.

Transport

In the planetary boundary layer (PBL) the atmosphere interacts directly with the Earth's surface through turbulent mixing.

Consequently, during the day over land, chemicals in the PBL are generally well mixed up to a height of $\sim$1 km.

Transport

In the planetary boundary layer (PBL) the atmosphere interacts directly with the Earth's surface through turbulent mixing.

Consequently, during the day over land, chemicals in the PBL are generally well mixed up to a height of $\sim$1 km.

Turbulent mixing, and therefore the dilution of chemical compounds, is less efficient at night when the PBL may extend up to only a few hundred meters.

Transport

In the planetary boundary layer (PBL) the atmosphere interacts directly with the Earth's surface through turbulent mixing.

Consequently, during the day over land, chemicals in the PBL are generally well mixed up to a height of $\sim$1 km.

Turbulent mixing, and therefore the dilution of chemical compounds, is less efficient at night when the PBL may extend up to only a few hundred meters.

Over the oceans, the diurnal cycle is much less apparent.

If a chemical that originates from the Earth's surface is not returned to the surface or transformed by in situ reactions in the PBL, it will eventually pass into the free troposphere.

If a chemical that originates from the Earth's surface is not returned to the surface or transformed by in situ reactions in the PBL, it will eventually pass into the free troposphere.

Once in the free troposphere, and if the chemical has a long residence time, it will follow the global circulation pattern.

If a chemical that originates from the Earth's surface is not returned to the surface or transformed by in situ reactions in the PBL, it will eventually pass into the free troposphere.

Once in the free troposphere, and if the chemical has a long residence time, it will follow the global circulation pattern.

For example, in midlatitudes, where the winds are generally from west to east and have speeds of $\sim$10–30 $\mathrm{m\,s^{-1}}$, a chemical will be distributed fairly uniformly in longitude around the globe within a few months.

If a chemical that originates from the Earth's surface is not returned to the surface or transformed by in situ reactions in the PBL, it will eventually pass into the free troposphere.

Once in the free troposphere, and if the chemical has a long residence time, it will follow the global circulation pattern.

For example, in midlatitudes, where the winds are generally from west to east and have speeds of $\sim$10–30 $\mathrm{m\,s^{-1}}$, a chemical will be distributed fairly uniformly in longitude around the globe within a few months.

However, in the north-south direction, where wind speeds are much less, the distribution of chemicals will reflect more the latitudinal distribution of their sources.

If a chemical that originates from the Earth's surface is not returned to the surface or transformed by in situ reactions in the PBL, it will eventually pass into the free troposphere.

Once in the free troposphere, and if the chemical has a long residence time, it will follow the global circulation pattern.

For example, in midlatitudes, where the winds are generally from west to east and have speeds of $\sim$10–30 $\mathrm{m\,s^{-1}}$, a chemical will be distributed fairly uniformly in longitude around the globe within a few months.

However, in the north-south direction, where wind speeds are much less, the distribution of chemicals will reflect more the latitudinal distribution of their sources.

Since the transport of tropospheric air across the equator is relatively restricted, so is the transport of chemicals.

The main effect of this is that the chemistry of the troposphere in the northern hemisphere is affected by emissions from the use of fossil fuels much more than the southern hemisphere.

The main effect of this is that the chemistry of the troposphere in the northern hemisphere is affected by emissions from the use of fossil fuels much more than the southern hemisphere.

The chemistry of the southern hemisphere reflects more the effects of emissions from the oceans and from biomass burning.

The main effect of this is that the chemistry of the troposphere in the northern hemisphere is affected by emissions from the use of fossil fuels much more than the southern hemisphere.

The chemistry of the southern hemisphere reflects more the effects of emissions from the oceans and from biomass burning.

Transport is also restricted from the free troposphere into the stratosphere. Most of the upward transport is in the tropics, and the downward transport is in higher latitudes.

The main effect of this is that the chemistry of the troposphere in the northern hemisphere is affected by emissions from the use of fossil fuels much more than the southern hemisphere.

The chemistry of the southern hemisphere reflects more the effects of emissions from the oceans and from biomass burning.

Transport is also restricted from the free troposphere into the stratosphere. Most of the upward transport is in the tropics, and the downward transport is in higher latitudes.

Nevertheless, certain long-lived chemicals of anthropogenic origin can accumulate in the stratosphere, where they can have major effects.

Satellite observations provide strong evidence for the transport of tropospheric gases and particles.

Satellite observations provide strong evidence for the transport of tropospheric gases and particles.

For example, satellite observations reveal large plumes of particles off the east coasts of the U.S.A. and Asia, enormous dust plumes carried westward from the Sahara Desert over the Atlantic Ocean, and large smoke plumes from regions of biomass burning (above Figure).

Satellite observations provide strong evidence for the transport of tropospheric gases and particles.

For example, satellite observations reveal large plumes of particles off the east coasts of the U.S.A. and Asia, enormous dust plumes carried westward from the Sahara Desert over the Atlantic Ocean, and large smoke plumes from regions of biomass burning (above Figure).

During the winter monsoon (December through April), a plume of pollutants extends from the southwest coast of India over the Indian Ocean.

Satellite observations provide strong evidence for the transport of tropospheric gases and particles.

For example, satellite observations reveal large plumes of particles off the east coasts of the U.S.A. and Asia, enormous dust plumes carried westward from the Sahara Desert over the Atlantic Ocean, and large smoke plumes from regions of biomass burning (above Figure).

During the winter monsoon (December through April), a plume of pollutants extends from the southwest coast of India over the Indian Ocean.

In spring and summer, pollutants are transported from Europe to the North Atlantic Ocean.

Satellite observations provide strong evidence for the transport of tropospheric gases and particles.

For example, satellite observations reveal large plumes of particles off the east coasts of the U.S.A. and Asia, enormous dust plumes carried westward from the Sahara Desert over the Atlantic Ocean, and large smoke plumes from regions of biomass burning (above Figure).

During the winter monsoon (December through April), a plume of pollutants extends from the southwest coast of India over the Indian Ocean.

In spring and summer, pollutants are transported from Europe to the North Atlantic Ocean.

Reference website:

http://earthobservatory.nasa.gov/

Sinks of Trace Gases

The final stage in the life history of a chemical in the atmosphere is its removal. Sinks include transformations into other chemical species and gas-to-particle conversion.

Sinks of Trace Gases

The final stage in the life history of a chemical in the atmosphere is its removal. Sinks include transformations into other chemical species and gas-to-particle conversion.

The other important removal process for both gases and aerosols is deposition onto the Earth's surface.

Sinks of Trace Gases

The final stage in the life history of a chemical in the atmosphere is its removal. Sinks include transformations into other chemical species and gas-to-particle conversion.

The other important removal process for both gases and aerosols is deposition onto the Earth's surface.

Deposition is of two types, wet and dry:

Sinks of Trace Gases

The final stage in the life history of a chemical in the atmosphere is its removal. Sinks include transformations into other chemical species and gas-to-particle conversion.

The other important removal process for both gases and aerosols is deposition onto the Earth's surface.

Deposition is of two types, wet and dry:

Wet deposition: This involves the scavenging of gases and particles in the air by clouds and precipitation, and is one of the major mechanisms by which the atmosphere is cleansed.

Sinks of Trace Gases

The final stage in the life history of a chemical in the atmosphere is its removal. Sinks include transformations into other chemical species and gas-to-particle conversion.

The other important removal process for both gases and aerosols is deposition onto the Earth's surface.

Deposition is of two types, wet and dry:

Wet deposition: This involves the scavenging of gases and particles in the air by clouds and precipitation, and is one of the major mechanisms by which the atmosphere is cleansed.

Dry deposition: This involves the direct collection of gases and particles in the air by vegetation and the Earth's solid and liquid surfaces.

Sinks of Trace Gases

The final stage in the life history of a chemical in the atmosphere is its removal. Sinks include transformations into other chemical species and gas-to-particle conversion.

The other important removal process for both gases and aerosols is deposition onto the Earth's surface.

Deposition is of two types, wet and dry:

Wet deposition: This involves the scavenging of gases and particles in the air by clouds and precipitation, and is one of the major mechanisms by which the atmosphere is cleansed.

Dry deposition: This involves the direct collection of gases and particles in the air by vegetation and the Earth's solid and liquid surfaces.

Dry deposition is much slower than wet deposition, but it is continuous rather than episodic.

The oceans are important sinks for many trace gases.

The oceans are important sinks for many trace gases.

The flux of a gas to the ocean depends on how undersaturated the ocean is with respect to the gas.

The oceans are important sinks for many trace gases.

The flux of a gas to the ocean depends on how undersaturated the ocean is with respect to the gas.

If the surface layers of the ocean are supersaturated with a gas, then the flux is from the ocean to the atmosphere

The oceans are important sinks for many trace gases.

The flux of a gas to the ocean depends on how undersaturated the ocean is with respect to the gas.

If the surface layers of the ocean are supersaturated with a gas, then the flux is from the ocean to the atmosphere

For example, the estimated global flux of DMS from the ocean to the atmosphere is $\sim$25 Tg of sulfur per year.

3. Some Trace Tropospheric Gases

3. Some Trace Tropospheric Gases

Prior to the 1970s, photochemical reactions, and the oxidation of most trace gases, were thought to take place primarily in the stratosphere where the intensity of UV radiation is much greater than in the troposphere.

3. Some Trace Tropospheric Gases

Prior to the 1970s, photochemical reactions, and the oxidation of most trace gases, were thought to take place primarily in the stratosphere where the intensity of UV radiation is much greater than in the troposphere.

However, in the 1960s and 70s, it came to be realized that the very reactive hydroxyl radical OH can be produced by photochemistry in the troposphere.

3. Some Trace Tropospheric Gases

Prior to the 1970s, photochemical reactions, and the oxidation of most trace gases, were thought to take place primarily in the stratosphere where the intensity of UV radiation is much greater than in the troposphere.

However, in the 1960s and 70s, it came to be realized that the very reactive hydroxyl radical OH can be produced by photochemistry in the troposphere.

At about the same time, studies of photochemical smogs (such as those that occur in Los Angeles) began to reveal the roles of OH, nitrogen oxides and hydrocarbons in the formation of O_3 and other pollutants.

The Hydroxyl Radical

The Hydroxyl Radical

Because of its high reactivity with both inorganic and organic compounds, OH is one of the most important chemical species in the atmosphere.

The Hydroxyl Radical

Because of its high reactivity with both inorganic and organic compounds, OH is one of the most important chemical species in the atmosphere.

This is despite the fact that it is present in the troposphere in globally and diurnally averaged concentrations of just a few tenths of a pptv ($\sim 10^{12}$ OH molecules m^{-3}, or about 3 OH molecules per 10^{14} molecules in the air).

The Hydroxyl Radical

Because of its high reactivity with both inorganic and organic compounds, OH is one of the most important chemical species in the atmosphere.

This is despite the fact that it is present in the troposphere in globally and diurnally averaged concentrations of just a few tenths of a pptv ($\sim 10^{12}$ OH molecules m^{-3}, or about 3 OH molecules per 10^{14} molecules in the air).

Reaction with OH is the major sink for most atmospheric trace gases. Because it is so reactive, the average lifetime of an OH molecule in the atmosphere is only about 1 second.

Hydroxyl radicals are produced when UV radiation from the Sun decomposes O_3 into molecular oxygen and energetically excited oxygen atoms (O^*)

$$\mathbf{O_3} + h\nu \rightarrow \mathbf{O_2} + \mathbf{O}^*$$

Hydroxyl radicals are produced when UV radiation from the Sun decomposes O_3 into molecular oxygen and energetically excited oxygen atoms (O^*)

$$\mathbf{O_3} + h\nu \rightarrow \mathbf{O_2} + \mathbf{O}^*$$

Most of the O^* atoms produced in this way dissipate their excess energy as heat and eventually recombine with O_2 to form O_3, which is a null cycle (i.e., has no net effect).

Hydroxyl radicals are produced when UV radiation from the Sun decomposes O_3 into molecular oxygen and energetically excited oxygen atoms (O^*)

$$\mathbf{O_3} + h\nu \rightarrow \mathbf{O_2} + \mathbf{O}^*$$

Most of the O^* atoms produced in this way dissipate their excess energy as heat and eventually recombine with O_2 to form O_3, which is a null cycle (i.e., has no net effect).

However, a small fraction ($\sim$1%) of the O^* atoms reacts with water vapour to form two hydroxyl radicals

$$\mathbf{O}^* + \mathbf{H_2O} \rightarrow \mathbf{2OH}$$

Hydroxyl radicals are produced when UV radiation from the Sun decomposes O_3 into molecular oxygen and energetically excited oxygen atoms (O^*)

$$\mathbf{O_3} + h\nu \rightarrow \mathbf{O_2} + \mathbf{O}^*$$

Most of the O^* atoms produced in this way dissipate their excess energy as heat and eventually recombine with O_2 to form O_3, which is a null cycle (i.e., has no net effect).

However, a small fraction ($\sim$1%) of the O^* atoms reacts with water vapour to form two hydroxyl radicals

$$\mathbf{O}^* + \mathbf{H_2O} \rightarrow \mathbf{2OH}$$

The net effect of the two reactions is

$$\mathbf{O_3} + \mathbf{H_2O} + h\nu \rightarrow \mathbf{O_2} + \mathbf{2OH}$$

Once formed, the OH radical is a powerful oxidant that reacts quickly with almost all trace gases containing H, C, N, O and S and the halogens (except N_2O and the chlorofluorocarbons (CFC)).

Once formed, the OH radical is a powerful oxidant that reacts quickly with almost all trace gases containing H, C, N, O and S and the halogens (except N_2O and the chlorofluorocarbons (CFC)).

For example, OH reacts with CO to form CO_2, NO_2 to form HNO_3, H_2S to form SO_2, SO_2 to form H_2SO_4, etc. (Figure below).

Once formed, the OH radical is a powerful oxidant that reacts quickly with almost all trace gases containing H, C, N, O and S and the halogens (except N_2O and the chlorofluorocarbons (CFC)).

For example, OH reacts with CO to form CO_2, NO_2 to form HNO_3, H_2S to form SO_2, SO_2 to form H_2SO_4, etc. (Figure below).

Because of its role in removing many pollutants, OH has been called the atmosphere's detergent.

$\star$ $\star$ $\star$

Once formed, the OH radical is a powerful oxidant that reacts quickly with almost all trace gases containing H, C, N, O and S and the halogens (except N_2O and the chlorofluorocarbons (CFC)).

For example, OH reacts with CO to form CO_2, NO_2 to form HNO_3, H_2S to form SO_2, SO_2 to form H_2SO_4, etc. (Figure below).

Because of its role in removing many pollutants, OH has been called the atmosphere's detergent.

$\star \qquad \star \qquad \star$

The dominant sinks for OH in the global troposphere are oxidation by CO and CH_4, while reactions with NMHC dominate as a sink of OH over the continents.

In forests, the dominant reactant with OH is often isoprene (C_5H_8), which is emitted by deciduous trees.

The Atmosphere's Detergent

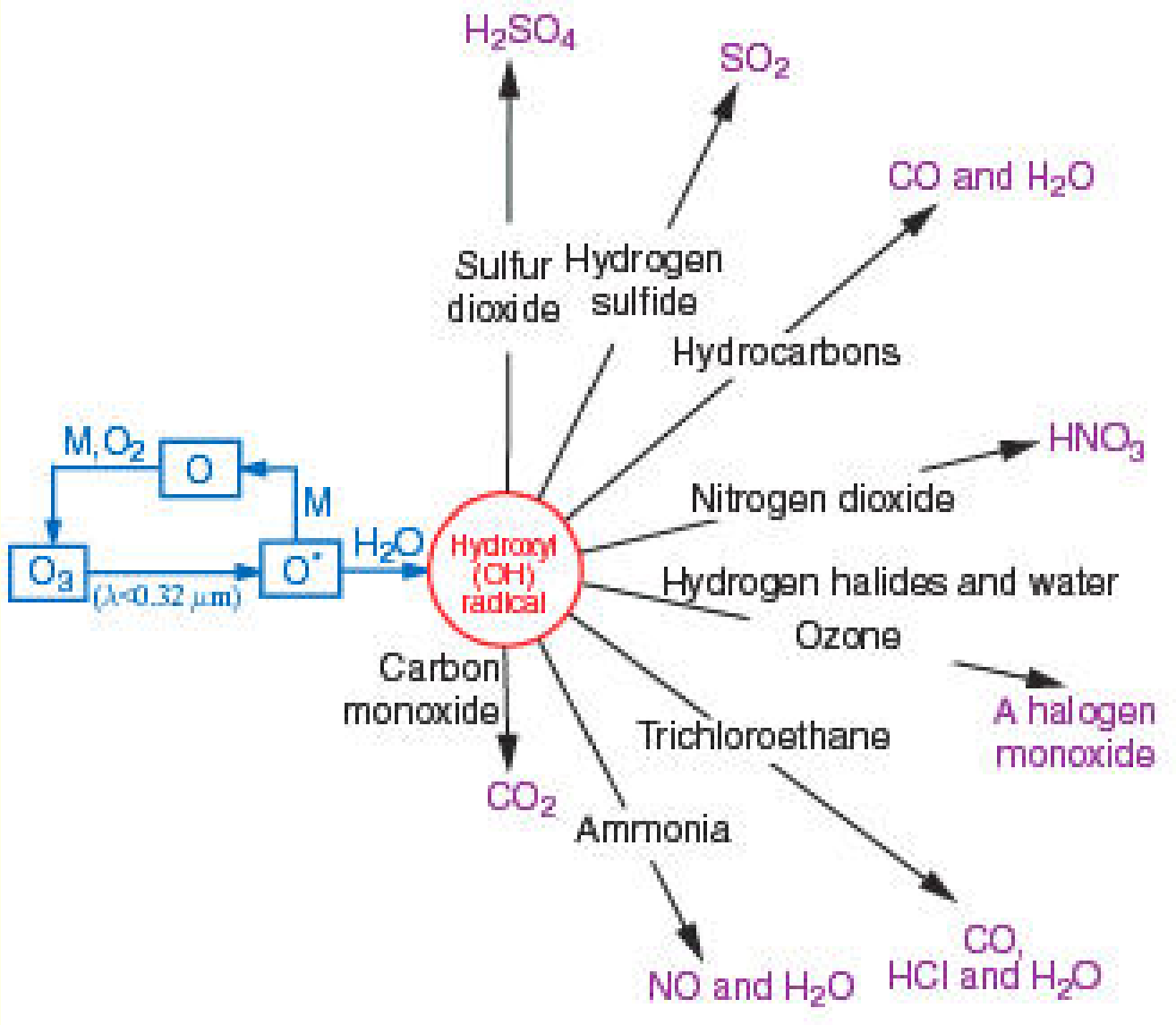


Illustration of the central role of the OH radical in the oxidation of tropospheric trace gases. Little escapes oxidation by OH.

Reactive Nitrogen Compounds

Reactive Nitrogen Compounds

The oxides of nitrogen, NO (nitric oxide) and NO_2 (nitrogen dioxide), which together are referred to as NO_x, play very important roles in atmospheric chemistry.

Reactive Nitrogen Compounds

The oxides of nitrogen, NO (nitric oxide) and NO_2 (nitrogen dioxide), which together are referred to as NO_x, play very important roles in atmospheric chemistry.

They are produced by:

- **Fossil fuel combustion**
- **Biomass burning**
- **From soils**
- **By lightning**
- **NH_3 oxidation**
- **Aircraft emissions**
- **Transport from the stratosphere.**

NO_x is emitted into the troposphere primarily as NO, but during the day NO establishes a rapid equilibrium with NO_2.

NO_x is emitted into the troposphere primarily as NO, but during the day NO establishes a rapid equilibrium with NO_2.

At night, NO_2 is oxidized by O_3 to NO_3, the NO_3 then reacts with NO_2 to produce N_2O_5, and the N_2O_5 reacts with water on particles to produce HNO_3.

NO_x is emitted into the troposphere primarily as NO, but during the day NO establishes a rapid equilibrium with NO_2.

At night, NO_2 is oxidized by O_3 to NO_3, the NO_3 then reacts with NO_2 to produce N_2O_5, and the N_2O_5 reacts with water on particles to produce HNO_3.

The nitric acid is removed in about 1 week by dry and wet deposition. The resulting residence time of NO_2 is $\sim$1 day.

NO_x is emitted into the troposphere primarily as NO, but during the day NO establishes a rapid equilibrium with NO_2.

At night, NO_2 is oxidized by O_3 to NO_3, the NO_3 then reacts with NO_2 to produce N_2O_5, and the N_2O_5 reacts with water on particles to produce HNO_3.

The nitric acid is removed in about 1 week by dry and wet deposition. The resulting residence time of NO_2 is $\sim$1 day.

Since OH is produced primarily by photochemical reactions and has a very short lifetime, it is present in the atmosphere only during the day.

At night, the nitrate radical NO_3 takes over from OH as the major reactive oxidant in the troposphere.

The nitrate radical is formed by

$$\mathbf{NO_2 + O_3 \rightarrow NO_3 + O_2}$$

The nitrate radical is formed by

$$\mathbf{NO_2 + O_3 \rightarrow NO_3 + O_2}$$

Although NO_3 is much less reactive than OH, it is present in much higher mean concentrations than OH.

$\star$ $\star$ $\star$

The nitrate radical is formed by

$$\mathbf{NO_2 + O_3 \rightarrow NO_3 + O_2}$$

Although NO_3 is much less reactive than OH, it is present in much higher mean concentrations than OH.

$\star \qquad \star \qquad \star$

Ammonia (NH_3) originates from soils, animal waste, fertilizers and industrial emissions. It is the principal basic gas in the atmosphere.

The nitrate radical is formed by

$$\mathbf{NO_2 + O_3 \rightarrow NO_3 + O_2}$$

Although NO_3 is much less reactive than OH, it is present in much higher mean concentrations than OH.

$\star \qquad \star \qquad \star$

Ammonia (NH_3) originates from soils, animal waste, fertilizers and industrial emissions. It is the principal basic gas in the atmosphere.

Ammonia neutralizes acid species by reactions of the form

$$\mathbf{2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4}$$

The nitrate radical is formed by

$$\mathbf{NO_2 + O_3 \rightarrow NO_3 + O_2}$$

Although NO_3 is much less reactive than OH, it is present in much higher mean concentrations than OH.

$\star \qquad \star \qquad \star$

Ammonia (NH_3) originates from soils, animal waste, fertilizers and industrial emissions. It is the principal basic gas in the atmosphere.

Ammonia neutralizes acid species by reactions of the form

$$\mathbf{2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4}$$

The primary removal mechanisms for NH_3 is its conversion to ammonium-containing aerosols which are then transported to the ground by wet and dry deposition.

The nitrate radical is formed by

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

Although NO_3 is much less reactive than OH, it is present in much higher mean concentrations than OH.

$\star \qquad \star \qquad \star$

Ammonia (NH_3) originates from soils, animal waste, fertilizers and industrial emissions. It is the principal basic gas in the atmosphere.

Ammonia neutralizes acid species by reactions of the form

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

The primary removal mechanisms for NH_3 is its conversion to ammonium-containing aerosols which are then transported to the ground by wet and dry deposition.

The residence time of NH_3 in the troposphere is $\sim$10 days.

Organic Compounds

Organic Compounds

Organic compounds contain carbon atoms.

The four electrons in the outer orbital of the carbon atom can form bonds with up to four other elements: hydrogen, oxygen, nitrogen, sulfur, halogens, etc. [HONC-link]

Organic Compounds

Organic compounds contain carbon atoms.

The four electrons in the outer orbital of the carbon atom can form bonds with up to four other elements: hydrogen, oxygen, nitrogen, sulfur, halogens, etc. [HONC-link]

Hydrocarbons are organics composed of carbon and hydrogen. There are large natural and anthropogenic sources of atmospheric hydrocarbons, and they play key roles in many aspects of the chemistry of the troposphere.

Organic Compounds

Organic compounds contain carbon atoms.

The four electrons in the outer orbital of the carbon atom can form bonds with up to four other elements: hydrogen, oxygen, nitrogen, sulfur, halogens, etc. [HONC-link]

Hydrocarbons are organics composed of carbon and hydrogen. There are large natural and anthropogenic sources of atmospheric hydrocarbons, and they play key roles in many aspects of the chemistry of the troposphere.

Methane (CH_4) is the most abundant hydrocarbon in the atmosphere, and it plays a central role in tropospheric chemistry. The present concentration of CH_4 in the Northern Hemisphere is $\sim$1.7 ppmv.

Organic Compounds

Organic compounds contain carbon atoms.

The four electrons in the outer orbital of the carbon atom can form bonds with up to four other elements: hydrogen, oxygen, nitrogen, sulfur, halogens, etc. [HONC-link]

Hydrocarbons are organics composed of carbon and hydrogen. There are large natural and anthropogenic sources of atmospheric hydrocarbons, and they play key roles in many aspects of the chemistry of the troposphere.

Methane (CH_4) is the most abundant hydrocarbon in the atmosphere, and it plays a central role in tropospheric chemistry. The present concentration of CH_4 in the Northern Hemisphere is $\sim$1.7 ppmv.

Methane has a residence time in the atmosphere of about 9 years.

Sources of CH_4 include wetlands, landfills, domestic animals, termites, biomass burning, leakages from natural gas lines, and coal mines.

Sources of CH_4 include wetlands, landfills, domestic animals, termites, biomass burning, leakages from natural gas lines, and coal mines.

The primary sink for tropospheric CH_4 is its oxidation by OH to form formaldehyde (HCHO); HCHO then photodissociates into CO. Also, in air with sufficient NO_x, OH oxidizes CO to produce O_3.

Sources of CH_4 include wetlands, landfills, domestic animals, termites, biomass burning, leakages from natural gas lines, and coal mines.

The primary sink for tropospheric CH_4 is its oxidation by OH to form formaldehyde (HCHO); HCHO then photodissociates into CO. Also, in air with sufficient NO_x, OH oxidizes CO to produce O_3.

Following water vapour and CO_2, CH_4 is the third most abundant greenhouse gas in the atmosphere.

NMHCs

Hydrocarbons other than CH_4 are referred to as non-methane hydrocarbons (NMHCs). They originate from fossil fuel combustion, biomass burning, forest vegetation, etc.

NMHCs

Hydrocarbons other than CH_4 are referred to as non-methane hydrocarbons (NMHCs). They originate from fossil fuel combustion, biomass burning, forest vegetation, etc.

The primary sink for most NMHC is oxidation by OH. Since NMHC are more reactive than CH_4, their atmospheric residence times are much shorter (hours to months).

NMHCs

Hydrocarbons other than CH_4 are referred to as non-methane hydrocarbons (NMHCs). They originate from fossil fuel combustion, biomass burning, forest vegetation, etc.

The primary sink for most NMHC is oxidation by OH. Since NMHC are more reactive than CH_4, their atmospheric residence times are much shorter (hours to months).

There are numerous NMHC, and many of them play important roles in tropospheric chemistry. Based on the molecular structures of NMHC they can be grouped into several classes.

NMHCs

Hydrocarbons other than CH_4 are referred to as non-methane hydrocarbons (NMHCs). They originate from fossil fuel combustion, biomass burning, forest vegetation, etc.

The primary sink for most NMHC is oxidation by OH. Since NMHC are more reactive than CH_4, their atmospheric residence times are much shorter (hours to months).

There are numerous NMHC, and many of them play important roles in tropospheric chemistry. Based on the molecular structures of NMHC they can be grouped into several classes.

For example, alkanes (C_nH_{2n+2}), which include ethane ($CH_3{-}CH_3$) and propane ($CH_3{-}CH_2{-}CH_3$); alkenes, which have a double bond, such as ethene ($CH_2{=}CH_2$) and propene ($CH_3{-}CH{=}CH_2$); and aromatics, such as benzene (C_6H_6) and toluene (C_7H_8).

Oxygenated Hydrocarbons

Oxygenated Hydrocarbons

Oxygenated hydrocarbons, which contain one or more oxygen atoms, such as acetone (CH_3COCH_3), may provide an important source of HO_X in the upper troposphere and thus influence O_3 chemistry in this region.

$\star$ $\star$ $\star$

Oxygenated Hydrocarbons

Oxygenated hydrocarbons, which contain one or more oxygen atoms, such as acetone (CH_3COCH_3), may provide an important source of HO_x in the upper troposphere and thus influence O_3 chemistry in this region.

$\star$ $\star$ $\star$

Exercise: How much CH_3–CH_2–OH is in the atmosphere? What is it? It it toxic or beneficial to humans?

Volatile Organic Compounds

Volatile Organic Compounds

Volatile organic compounds, which play a central role in atmospheric chemistry, refer to the entire set of vapour-phase organics in the atmosphere (except for CO and CO_2).

Volatile Organic Compounds

Volatile organic compounds, which play a central role in atmospheric chemistry, refer to the entire set of vapour-phase organics in the atmosphere (except for CO and CO_2).

Motor vehicles are the main source of VOCs in the USA; they are mainly in a form of hydrocarbons produced by the incomplete combustion of fuel and from the vapourization of fuel.

Volatile Organic Compounds

Volatile organic compounds, which play a central role in atmospheric chemistry, refer to the entire set of vapour-phase organics in the atmosphere (except for CO and CO_2).

Motor vehicles are the main source of VOCs in the USA; they are mainly in a form of hydrocarbons produced by the incomplete combustion of fuel and from the vapourization of fuel.

The evaporation of solvents is the second largest source of VOCs worldwide. Biological processes are also important sources of VOCs.

$\star \qquad \star \qquad \star$

Carbon Monoxide (CO)

Carbon Monoxide (CO)

Carbon monoxide (CO) is produced by the oxidation of CH_4 or a NMHC, such as isoprene.

Other important sources of CO are biomass burning and the combustion of fossil fuels.

Carbon Monoxide (CO)

Carbon monoxide (CO) is produced by the oxidation of CH_4 or a NMHC, such as isoprene.

Other important sources of CO are biomass burning and the combustion of fossil fuels.

The dominant sink of CO is oxidation by OH:

$$\mathbf{2CO + 2OH \rightarrow H_2 + 2CO_2}$$

Carbon Monoxide (CO)

Carbon monoxide (CO) is produced by the oxidation of CH_4 or a NMHC, such as isoprene.

Other important sources of CO are biomass burning and the combustion of fossil fuels.

The dominant sink of CO is oxidation by OH:

$$\mathbf{2CO + 2OH \rightarrow H_2 + 2CO_2}$$

An important feature of CO is its seasonal cycle: it accumulates in the atmosphere during winter when OH concentrations are low, but in spring CO is rapidly depleted due to the reaction above.

Ozone (O_3)

Ozone (O_3)

Since about 90% of the O_3 in the Earth's atmosphere is in the stratosphere, it was suggested in the middle of the 20^{th} century that the stratosphere was a primary source for tropospheric O_3, and that a balance existed between this source and surface sinks.

Ozone (O_3)

Since about 90% of the O_3 in the Earth's atmosphere is in the stratosphere, it was suggested in the middle of the 20^{th} century that the stratosphere was a primary source for tropospheric O_3, and that a balance existed between this source and surface sinks.

Subsequently, it was realized that trace gases, such as NO, CO and organic compounds, which are emitted by human activities, lead to the formation of O_3 through photochemical reactions.

Ozone (O_3)

Since about 90% of the O_3 in the Earth's atmosphere is in the stratosphere, it was suggested in the middle of the 20^{th} century that the stratosphere was a primary source for tropospheric O_3, and that a balance existed between this source and surface sinks.

Subsequently, it was realized that trace gases, such as NO, CO and organic compounds, which are emitted by human activities, lead to the formation of O_3 through photochemical reactions.

In addition, natural processes produce O_3 precursors (e.g., hydrocarbons from vegetation and NO from lightning). Much of the O_3 in the troposphere is produced by in situ homogeneous gas-phase reactions involving the oxidation of CO, CH_4 and NMHC by OH in the presence of NO_x.

Ozone (O_3)

Since about 90% of the O_3 in the Earth's atmosphere is in the stratosphere, it was suggested in the middle of the 20^{th} century that the stratosphere was a primary source for tropospheric O_3, and that a balance existed between this source and surface sinks.

Subsequently, it was realized that trace gases, such as NO, CO and organic compounds, which are emitted by human activities, lead to the formation of O_3 through photochemical reactions.

In addition, natural processes produce O_3 precursors (e.g., hydrocarbons from vegetation and NO from lightning). Much of the O_3 in the troposphere is produced by in situ homogeneous gas-phase reactions involving the oxidation of CO, CH_4 and NMHC by OH in the presence of NO_x.

Ozone plays a controlling role in the oxidation capacity of the troposphere.

Good Ozone and Bad Ozone

The German chemist Schönbein discovered ozone by its odour following an electrical discharge. He called it ozone, after the Greek word *ozein*, meaning to smell.

Good Ozone and Bad Ozone

The German chemist Schönbein discovered ozone by its odour following an electrical discharge. He called it ozone, after the Greek word *ozein*, meaning to smell.

Ozone is an irritating, pale blue gas that is toxic and explosive.

Good Ozone and Bad Ozone

The German chemist Schönbein discovered ozone by its odour following an electrical discharge. He called it ozone, after the Greek word *ozein*, meaning to smell.

Ozone is an irritating, pale blue gas that is toxic and explosive.

Because of its high reactivity ozone is an extremely powerful oxidizing agent that damages rubber and plastics, and is harmful to humans and plants even at low concentrations (∼several tens of ppbv).

Good Ozone and Bad Ozone

The German chemist Schönbein discovered ozone by its odour following an electrical discharge. He called it ozone, after the Greek word *ozein*, meaning to smell.

Ozone is an irritating, pale blue gas that is toxic and explosive.

Because of its high reactivity ozone is an extremely powerful oxidizing agent that damages rubber and plastics, and is harmful to humans and plants even at low concentrations (∼several tens of ppbv).

The Dutch scientist Haagen-Smit suggested that the formation of O_3 in cities is due to photochemical reactions involving nitrogen oxides and hydrocarbons released by cars and oil refineries.

Good Ozone and Bad Ozone

The German chemist Schönbein discovered ozone by its odour following an electrical discharge. He called it ozone, after the Greek word *ozein*, meaning to smell.

Ozone is an irritating, pale blue gas that is toxic and explosive.

Because of its high reactivity ozone is an extremely powerful oxidizing agent that damages rubber and plastics, and is harmful to humans and plants even at low concentrations (∼several tens of ppbv).

The Dutch scientist Haagen-Smit suggested that the formation of O_3 in cities is due to photochemical reactions involving nitrogen oxides and hydrocarbons released by cars and oil refineries.

Ozone reacts with hydrocarbons from automobile exhausts and evaporated gasoline to form secondary organic pollutants such as aldehydes and ketones.

Ozone produced in urban areas can be transported into rural areas far removed from industrial regions.

For example, during a summer heat wave in 1988 the Acadia National Park in Maine had dangerously high concentrations of O_3, which originated in New York City.

Ozone produced in urban areas can be transported into rural areas far removed from industrial regions.

For example, during a summer heat wave in 1988 the Acadia National Park in Maine had dangerously high concentrations of O_3, which originated in New York City.

Ozone alone, or in combination with SO_2 and NO_2, causes about 90% of the annual loss of crops due to air pollution in the United States.

$\star \qquad \star \qquad \star$

Ozone produced in urban areas can be transported into rural areas far removed from industrial regions.

For example, during a summer heat wave in 1988 the Acadia National Park in Maine had dangerously high concentrations of O_3, which originated in New York City.

Ozone alone, or in combination with SO_2 and NO_2, causes about 90% of the annual loss of crops due to air pollution in the United States.

$\star \qquad \star \qquad \star$

In contrast to the bad effects of O_3 in the troposphere, the much greater concentrations of O_3 in the stratosphere reduces the intensity of dangerous UV radiation from the Sun, which has allowed the development of life on Earth.

An increase in tropospheric O_3 has occurred globally over the past century, from ∼10–15 ppbv in the pre-industrial era to ∼30–40 ppbv in 2000 in remote regions of the world.

The increase is attributable to the increase in NO_X emissions associated with the rapid increase in the use of fossil fuels since the Industrial Revolution.

⋆ ⋆ ⋆

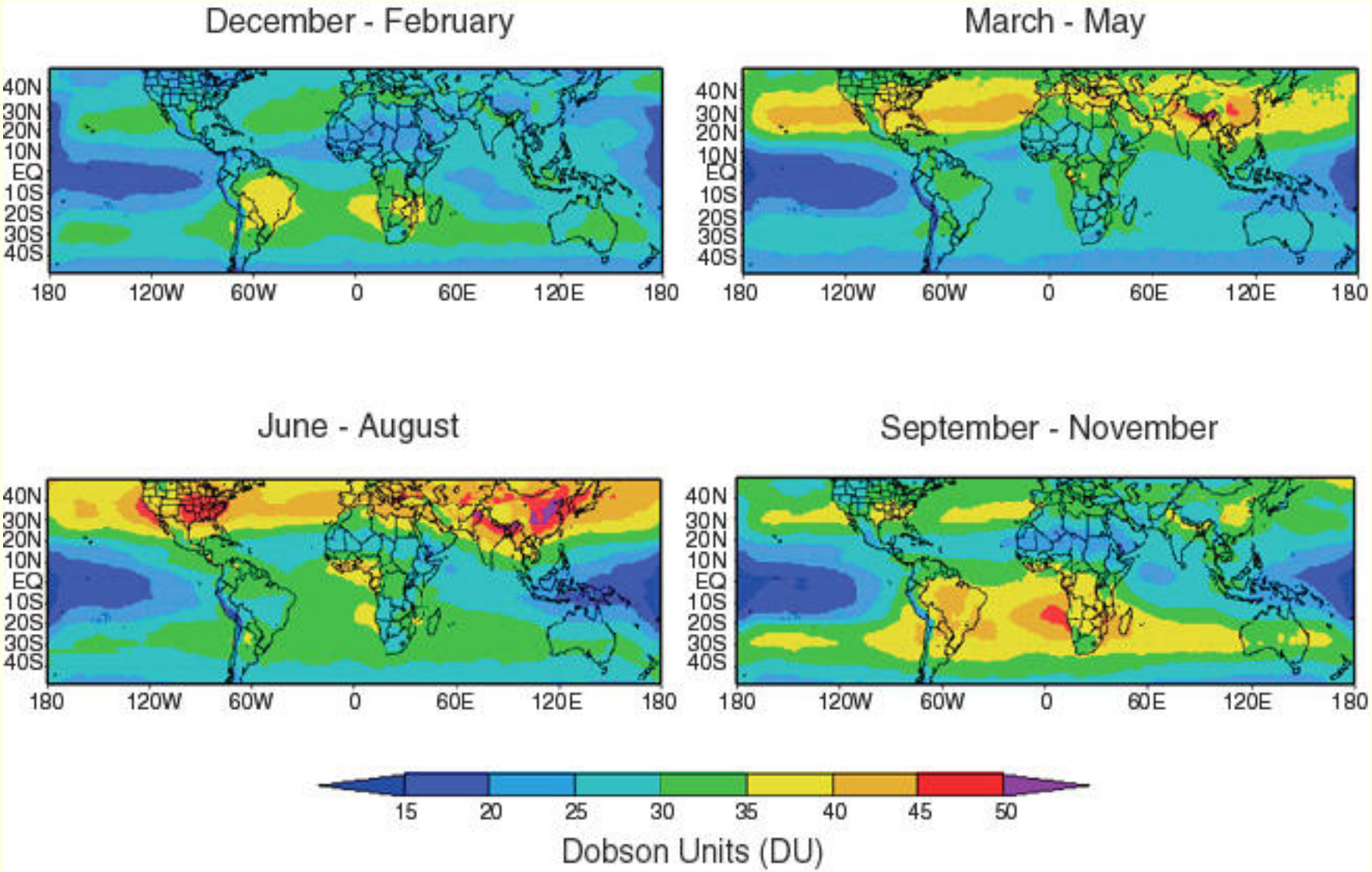
An increase in tropospheric O_3 has occurred globally over the past century, from ∼10–15 ppbv in the pre-industrial era to ∼30–40 ppbv in 2000 in remote regions of the world.

The increase is attributable to the increase in NO_x emissions associated with the rapid increase in the use of fossil fuels since the Industrial Revolution.

⋆ ⋆ ⋆

The following Figure shows the global distribution of O_3 in the troposphere obtained by subtracting satellite measurements of O_3 in the stratosphere from those in the stratosphere and troposphere.

It can be seen that O_3 is generally low over the tropical oceans. At midlatitudes it increases in spring in both hemispheres, and O_3 is high in the summer months over the industrialized regions of the northern hemisphere.



Composite seasonal distribution of the tropospheric ozone column (in Dobson units) determined from satellite measurements from 1979-2000.

Hydrogen Compounds

Hydrogen compounds are the most important oxidants for many chemicals in the atmosphere, and are involved in the cycles of many chemical families. They include:

Hydrogen Compounds

Hydrogen compounds are the most important oxidants for many chemicals in the atmosphere, and are involved in the cycles of many chemical families. They include:

- **atomic hydrogen (H), which quickly combines with O_2 to form the hydroperoxyl radical (HO_2)**

Hydrogen Compounds

Hydrogen compounds are the most important oxidants for many chemicals in the atmosphere, and are involved in the cycles of many chemical families. They include:

- **atomic hydrogen (H), which quickly combines with O_2 to form the hydroperoxyl radical (HO_2)**
- **molecular hydrogen (H_2), which, next to CH_4, is the most abundant reactive trace gas in the troposphere**

Hydrogen Compounds

Hydrogen compounds are the most important oxidants for many chemicals in the atmosphere, and are involved in the cycles of many chemical families. They include:

- **atomic hydrogen (H), which quickly combines with O_2 to form the hydroperoxyl radical (HO_2)**
- **molecular hydrogen (H_2), which, next to CH_4, is the most abundant reactive trace gas in the troposphere**
- **the hydroxyl radical, (OH)**

Hydrogen Compounds

Hydrogen compounds are the most important oxidants for many chemicals in the atmosphere, and are involved in the cycles of many chemical families. They include:

- **atomic hydrogen (H), which quickly combines with O_2 to form the hydroperoxyl radical (HO_2)**
- **molecular hydrogen (H_2), which, next to CH_4, is the most abundant reactive trace gas in the troposphere**
- **the hydroxyl radical, (OH)**
- **the hydroperoxyl radical, (HO_2)**

Hydrogen Compounds

Hydrogen compounds are the most important oxidants for many chemicals in the atmosphere, and are involved in the cycles of many chemical families. They include:

- **atomic hydrogen (H), which quickly combines with O_2 to form the hydroperoxyl radical (HO_2)**
- **molecular hydrogen (H_2), which, next to CH_4, is the most abundant reactive trace gas in the troposphere**
- **the hydroxyl radical, (OH)**
- **the hydroperoxyl radical, (HO_2)**
- **hydrogen peroxide (H_2O_2), which is formed by the reaction of HO_2 radicals and is an important oxidant for SO_2**

Hydrogen Compounds

Hydrogen compounds are the most important oxidants for many chemicals in the atmosphere, and are involved in the cycles of many chemical families. They include:

- **atomic hydrogen (H), which quickly combines with O_2 to form the hydroperoxyl radical (HO_2)**
- **molecular hydrogen (H_2), which, next to CH_4, is the most abundant reactive trace gas in the troposphere**
- **the hydroxyl radical, (OH)**
- **the hydroperoxyl radical, (HO_2)**
- **hydrogen peroxide (H_2O_2), which is formed by the reaction of HO_2 radicals and is an important oxidant for SO_2**
- **water (H_2O), which, in addition to its central role in the hydrological cycle and the radiative balance of the Earth, reacts with excited atomic oxygen to form OH.**

Sulfur Gases

Sulfur Gases

Sulfur is important to life on Earth. It is assimilated by living organisms, and released as an end-product of metabolism.

Sulfur Gases

Sulfur is important to life on Earth. It is assimilated by living organisms, and released as an end-product of metabolism.

The most important sulfur gases in the atmosphere are SO_2, H_2S, dimethyl sulfide (CH_3SCH_3 or DMS for short), carbonyl sulfide (COS) and carbon disulfide (CS_2).

Sulfur Gases

Sulfur is important to life on Earth. It is assimilated by living organisms, and released as an end-product of metabolism.

The most important sulfur gases in the atmosphere are SO_2, H_2S, dimethyl sulfide (CH_3SCH_3 or DMS for short), carbonyl sulfide (COS) and carbon disulfide (CS_2).

Volcanoes and biomass burning are also sources of atmospheric SO_2. However, the largest source of SO_2 is fossil fuel combustion.

Sulfur Gases

Sulfur is important to life on Earth. It is assimilated by living organisms, and released as an end-product of metabolism.

The most important sulfur gases in the atmosphere are SO_2, H_2S, dimethyl sulfide (CH_3SCH_3 or DMS for short), carbonyl sulfide (COS) and carbon disulfide (CS_2).

Volcanoes and biomass burning are also sources of atmospheric SO_2. However, the largest source of SO_2 is fossil fuel combustion.

The main sources of H_2S are emissions from soils, marshlands, oceans and volcanoes.

Sulfur Gases

Sulfur is important to life on Earth. It is assimilated by living organisms, and released as an end-product of metabolism.

The most important sulfur gases in the atmosphere are SO_2, H_2S, dimethyl sulfide (CH_3SCH_3 or DMS for short), carbonyl sulfide (COS) and carbon disulfide (CS_2).

Volcanoes and biomass burning are also sources of atmospheric SO_2. However, the largest source of SO_2 is fossil fuel combustion.

The main sources of H_2S are emissions from soils, marshlands, oceans and volcanoes.

The only significant sink for H_2S is oxidation to SO_2.

Biological reactions in the oceans involving phytoplankton emit several sulfur gases, of which DMS has the largest emission rate.

Biological reactions in the oceans involving phytoplankton emit several sulfur gases, of which DMS has the largest emission rate.

DMS is removed from the atmosphere primarily by its reaction with OH to produce SO_2.

Biological reactions in the oceans involving phytoplankton emit several sulfur gases, of which DMS has the largest emission rate.

DMS is removed from the atmosphere primarily by its reaction with OH to produce SO_2.

The sulfur gas with the largest concentration in the unpolluted atmosphere is carbonyl sulphide (COS) ($\sim$0.5 ppbv).

Biological reactions in the oceans involving phytoplankton emit several sulfur gases, of which DMS has the largest emission rate.

DMS is removed from the atmosphere primarily by its reaction with OH to produce SO_2.

The sulfur gas with the largest concentration in the unpolluted atmosphere is carbonyl sulphide (COS) ($\sim$0.5 ppbv).

The major sources of COS are biogenic and the oxidation of CS_2 by OH; the source of CS_2 is also biogenic.

Biological reactions in the oceans involving phytoplankton emit several sulfur gases, of which DMS has the largest emission rate.

DMS is removed from the atmosphere primarily by its reaction with OH to produce SO_2.

The sulfur gas with the largest concentration in the unpolluted atmosphere is carbonyl sulphide (COS) ($\sim$0.5 ppbv).

The major sources of COS are biogenic and the oxidation of CS_2 by OH; the source of CS_2 is also biogenic.

Because COS is very stable in the troposphere, it is eventually transported into the stratosphere where it is the dominant source of sulfate particles during volcanically quiescent periods.

$\star$ $\star$ $\star$