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

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- Metals
- Metalloids
- Non-metals
- Transition Metals
- Gases
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**Acid deposition** was recognized as a widespread problem in the 1970s.
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More recently, studies of the effects of trace chemical constituents in the atmosphere on the climate of the Earth have moved to centre stage.
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- 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.
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For a mixture of ideal gases like air the \textit{partial pressure} exerted by a gas is proportional to the \textit{mole fraction} of the gas in the mixture.

For example, if $\text{CO}_2$ occupies 0.03\% of the volume of air, the \textit{fraction of the total number of molecules} in air that are $\text{CO}_2$ (i.e., the mole fraction of $\text{CO}_2$) is 0.03\% and, if the total air pressure is 1 atm, the partial pressure exerted by $\text{CO}_2$ is 0.03\% of 1 atm (about 30 Pa).
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**Exercise:** N$_2$O occupies 310 ppbv of air. How many N$_2$O molecules are there in 1 m$^3$ of air at 1 atm and 0°C?
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Of prime importance is the photosynthesis reaction

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This removes carbon from the atmosphere and stores it in organic matter, and releases oxygen to the atmosphere.
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The most abundant halocarbon in the air, and the major natural source of chlorine (Cl) in the stratosphere, is methyl chloride (CH$_3$Cl), which derives, in part, from biological activity in seawater, wood molds and biomass burning.
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Terpenes are a class of hydrocarbons that evaporate from leaves. About 80% of these emissions oxidize to organic aerosols in about an hour.
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- chloroform — CHCl$_3$ (from combustion of petroleum, bleaching of woods, solvents).
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It has been estimated that on an annual basis biomass burning produces $\sim 38\%$ of the $\text{O}_3$, $\sim 32\%$ of the $\text{CO}$, $\sim 39\%$ of the particulate carbon, and more than $20\%$ of the $\text{H}_2$, $\text{NMHC}$, methyl chloride ($\text{CH}_3\text{Cl}$) and $\text{NO}_x$ in the troposphere.
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Biomass burning also produces $\sim 40\%$ 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.
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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.
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Biomass smoke can also be lofted into the middle and upper troposphere, where it can become a dominant source of $\text{HO}_x$ (where $x = 0, 1, \text{ or } 2$) and $\text{NO}_x$ and result in the production of $\text{O}_3$. 
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.
One **Dobson Unit** (DU) is the thickness, in hundredths of a millimeter, that the total $\text{O}_3$ column would occupy at $0^\circ\text{C}$ and 1 atm.
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**Exercise:** Calculate the partial pressure due to ozone, assuming the total column ozone to be 300 DU.
Volcanoes are the most important geochemical source of trace gases in the atmosphere. In addition to ash and copious small particles, volcanoes emit $\text{H}_2\text{O}$, $\text{CO}_2$, $\text{SO}_2$, $\text{H}_2\text{S}$, $\text{COS}$, $\text{HCl}$, $\text{HF}$ (hydrogen fluoride), $\text{HBr}$ (hydrogen bromide), $\text{CH}_4$, $\text{CH}_3\text{Cl}$, $\text{H}_2$, $\text{CO}$ and heavy metals.
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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 $\sim0.5^\circ\text{C}$ for two years and lowered ozone concentrations in the stratosphere.
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Argon has accumulated in air over aeons from the radioactive decay of potassium-$40$ in rocks.

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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., CaCO₃), 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 CO₂.
The oceans are a huge reservoir of those gases in the atmosphere that are soluble in water.
Sources: Oceanic

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

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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.
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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.
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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.
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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.
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Reference website: http://earthobservatory.nasa.gov/
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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.

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**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.
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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
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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 \( \text{O}_3 \) and other pollutants.
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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 ($O^*$)

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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 O₃ into molecular oxygen and energetically excited oxygen atoms (O*)

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Most of the O* atoms produced in this way dissipate their excess energy as heat and eventually recombine with O₂ to form O₃, which is a null cycle (i.e., has no net effect).

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

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However, a small fraction ($\sim1\%$) of the $O^*$ atoms reacts with water vapour to form two hydroxyl radicals

$$O^* + H_2O \rightarrow 2OH$$

The net effect of the two reactions is

$$O_3 + H_2O + h\nu \rightarrow O_2 + 2OH$$
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 N₂O and the chlorofluorocarbons (CFC)).
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For example, OH reacts with CO to form CO\textsubscript{2}, NO\textsubscript{2} to form HNO\textsubscript{3}, H\textsubscript{2}S to form SO\textsubscript{2}, SO\textsubscript{2} to form H\textsubscript{2}SO\textsubscript{4}, etc. (Figure below).
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For example, OH reacts with CO to form CO$_2$, NO$_2$ to form HNO$_3$, H$_2$S to form SO$_2$, SO$_2$ to form H$_2$SO$_4$, etc. (Figure below).

Because of its role in removing many pollutants, OH has been called the atmosphere’s detergents.
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$_2$O and the chlorofluorocarbons (CFC)).

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* * * * *

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$_5$H$_8$), 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

The oxides of nitrogen, NO (nitric oxide) and NO₂ (nitrogen dioxide), which together are referred to as NOₓ, play very important roles in atmospheric chemistry.
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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.
$\text{NO}_x$ is emitted into the troposphere primarily as NO, but during the day NO establishes a rapid equilibrium with NO$_2$. 
NO\textsubscript{x} is emitted into the troposphere primarily as NO, but during the day NO establishes a rapid equilibrium with NO\textsubscript{2}.

At night, NO\textsubscript{2} is oxidized by O\textsubscript{3} to NO\textsubscript{3}, the NO\textsubscript{3} then reacts with NO\textsubscript{2} to produce N\textsubscript{2}O\textsubscript{5}, and the N\textsubscript{2}O\textsubscript{5} reacts with water on particles to produce HNO\textsubscript{3}. 
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The nitric acid is removed in about 1 week by dry and wet deposition. The resulting residence time of NO\textsubscript{2} is \sim 1 day.
$\text{NO}_x$ 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$_2$O$_5$, and the N$_2$O$_5$ 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

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Ammonia neutralizes acid species by reactions of the form

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The primary removal mechanisms for $\text{NH}_3$ is its conversion to ammonium-containing aerosols which are then transported to the ground by wet and dry deposition.

The residence time of $\text{NH}_3$ in the troposphere is $\sim 10$ days.
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]
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Methane \((\text{CH}_4)\) is the most abundant hydrocarbon in the atmosphere, and it plays a central role in tropospheric chemistry. The present concentration of \(\text{CH}_4\) in the Northern Hemisphere is \(\sim 1.7\) ppmv.
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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.
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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$_3$. 
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Following water vapour and CO$_2$, CH$_4$ is the third most abundant greenhouse gas in the atmosphere.
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For example, alkanes (C\(_n\)H\(_{2n+2}\)), 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\(_6\)H\(_6\)) and toluene (C\(_7\)H\(_8\)).
Oxygenated Hydrocarbons
Oxygenated hydrocarbons, which contain one or more oxygen atoms, such as acetone (CH$_3$COCH$_3$), may provide an important source of HO$_x$ in the upper troposphere and thus influence O$_3$ chemistry in this region.
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* * *

**Exercise:** How much \(\text{CH}_3\text{–CH}_2\text{–OH}\) is in the atmosphere? What is it? Is it toxic or beneficial to humans?
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$_2$).
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The evaporation of solvents is the second largest source of VOCs worldwide. Biological processes are also important sources of VOCs.
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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 ($O_3$)
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.
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Ozone plays a controlling role in the oxidation capacity of the troposphere.
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Ozone reacts with hydrocarbons from automobile exhausts and evaporated gasoline to form secondary organic pollutants such as aldehydes and ketones.
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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 $\text{O}_3$ has occurred globally over the past century, from $\sim$10–15 ppbv in the pre-industrial era to $\sim$30–40 ppbv in 2000 in remote regions of the world. The increase is attributable to the increase in $\text{NO}_x$ emissions associated with the rapid increase in the use of fossil fuels since the Industrial Revolution.
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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 are the most important oxidants for many chemicals in the atmosphere, and are involved in the cycles of many chemical families. They include:
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water (H₂O), 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
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The most important sulfur gases in the atmosphere are $\text{SO}_2$, $\text{H}_2\text{S}$, dimethyl sulfide ($\text{CH}_3\text{SCH}_3$ or DMS for short), carbonyl sulfide ($\text{COS}$) and carbon disulfide ($\text{CS}_2$).
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The only significant sink for $\text{H}_2\text{S}$ is oxidation to $\text{SO}_2$. 
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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.

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