Chemical Composition of the Atmosphere

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Abstract
Atmospheric trace gases have an important impact on Earth’s radiative budget, the oxidative or cleansing ability of the atmosphere, the formation, growth and properties of aerosols, air quality, and human health. During recent years, the coupling between atmospheric chemistry and climate has received particular attention. Therefore, research is now focused on the composition and processes in the upper troposphere and lower stratosphere, a key region in this respect. In this chapter the chemical composition of the atmosphere is addressed and selected examples of significant advances in this field are presented.

2.1 Introduction

Earth’s atmosphere is mainly composed of N₂, O₂, Ar, and H₂O (chemical formulas are explained in Table 2.1). In addition, it includes a multitude of trace gases with concentrations ranging from a few μmol/mol (see Box 2.1) to fmol/mol (Fig. 2.1). The atmospheric lifetime of the chemical compounds varies from a few seconds to
more than 1000 years. Most of the long-lived trace gases, including CO$_2$, CH$_4$, N$_2$O and halocarbons, are important greenhouse gases and have large effects on the radiation budget of the atmosphere. Many trace constituents are directly emitted into the atmosphere. Others, most importantly O$_3$, are chemically or photochemically

### Table 2.1 Molecular formulas and chemical compounds

<table>
<thead>
<tr>
<th>Formula</th>
<th>Compound</th>
<th>Formula</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>argon</td>
<td>NH$_3$</td>
<td>ammonia</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>methane</td>
<td>N$_2$O</td>
<td>dinitrogen oxide</td>
</tr>
<tr>
<td>(CH$_3$)$_2$CO</td>
<td>acetone</td>
<td>NO</td>
<td>nitric oxide</td>
</tr>
<tr>
<td>ClO</td>
<td>chlorine monoxide</td>
<td>NO$_2$</td>
<td>nitrogen dioxide</td>
</tr>
<tr>
<td>ClONO$_2$</td>
<td>chlorine nitrate</td>
<td>NO$_x$</td>
<td>nitrogen oxides</td>
</tr>
<tr>
<td>CO</td>
<td>carbon monoxide</td>
<td>NO$_y$</td>
<td>total reactive nitrogen</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>carbon dioxide</td>
<td>O$_2$</td>
<td>molecular oxygen</td>
</tr>
<tr>
<td>DMS</td>
<td>dimethyl sulfide</td>
<td>O$_3$</td>
<td>ozone</td>
</tr>
<tr>
<td>HCl</td>
<td>hydrogen chloride</td>
<td>OH</td>
<td>hydroxyl radical</td>
</tr>
<tr>
<td>HNO$_2$</td>
<td>nitrous acid</td>
<td>OCS</td>
<td>carbonyl sulfide</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>nitric acid</td>
<td>PAN</td>
<td>peroxyacetyl nitrate</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>water</td>
<td>PFC</td>
<td>perfluorocarbons</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>sulfuric acid</td>
<td>SO$_2$</td>
<td>sulfur dioxide</td>
</tr>
<tr>
<td>N$_2$</td>
<td>molecular nitrogen</td>
<td>VOC</td>
<td>volatile organic compounds</td>
</tr>
</tbody>
</table>

**Fig. 2.1** Range of concentrations for atmospheric trace gases. All denoted compounds are measured by the Institute of Atmospheric Physics (IPA) with airborne in situ instruments using a variety of techniques including thermo desorption gas chromatography (PFC is used for active tracer experiments because of the very low atmospheric concentrations), chemiluminescence (NO$_x$), chemical ionization mass spectrometry (OH, SO$_2$, HCl, HNO$_2$, HNO$_3$, PAN), ultraviolet (UV) absorption (O$_3$), UV fluorescence (CO), and cavity ring-down spectrometry (CH$_4$, CO$_2$)
produced from precursor gases. The short-lived chemical species are very reactive and control the so called oxidation capacity of the atmosphere, the ability of the atmosphere to oxidize chemical compounds to water-soluble gases which can be scavenged by precipitation. The most prominent oxidizing compound is the highly reactive hydroxyl radical (OH) with a typical atmospheric lifetime of less than one second, e.g. Brasseur et al. (2003).

Some trace gases also have an indirect impact on climate by destroying or generating species which are important for the radiative balance. Examples are chlorine- and bromine-containing gases causing ozone depletion, and aerosol precursor gases, e.g. sulfuric acid (H₂SO₄), which can form new particles in the atmosphere. Furthermore, some primary emitted gases or photochemically produced trace gases are toxic and thus have an impact on human health.

The regional and global distributions of trace gases are determined by a variety of factors including the distribution and strength of their sources and sinks, transport and mixing in the atmosphere, chemical reactions, and the interaction with radiation, aerosols and clouds. Major sources include fossil fuel combustion and biomass burning (important gas emissions: CO₂, SO₂, NOₓ, hydrocarbons), gas and oil production (CH₄, VOC), traffic (CO₂, NOₓ, CO), agriculture (CH₄, N₂O, NH₃), vegetation (volatile organic carbon compounds), volcanoes (SO₂, halogens), and oceans (N₂O, OCS, DMS, halocarbons). Important sinks of trace gases include oxidation by OH, photolysis, and wet removal.

Understanding the present and future distribution of trace gases and their impact on climate is one of the major objectives in atmospheric science. Research on the chemistry of the atmosphere started at the Institute of Atmospheric Physics (IPA) in the early 1980s with studies on the formation of O₃ from precursor pollutants near the surface during high pressure conditions in summer (Paffrath 1990). At the beginning of the 1990s, the impact of air traffic on the composition of the atmosphere became a major research topic at IPA. Therefore, experimental investigations and numerical model simulations were focused on the region of the upper troposphere and lower stratosphere (UTLS), extending from about 8–25 km altitude (depending on latitude). As a consequence, climate-chemistry model developments were enforced (Steil et al. 1998; Hein et al. 2001; Dameris et al. 2005) to better analyze processes in the UTLS. A schematic of processes affecting this region is depicted in Fig. 2.2, including the vertical distribution of the O₃ mixing ratio for September conditions, as simulated with the Chemistry-Climate Model EMAC (Jöckel et al. 2006). Further examples of trace gas distributions are shown in Fig. 2.3.

The upper troposphere and lower stratosphere are dynamically and chemically distinct regions. Characteristics of the lower stratosphere are slow vertical transport and a chemistry initiated by the photodissociation of O₂ into atomic oxygen by ultraviolet radiation at wavelengths less than 242 nm, e.g. Brasseur and Solomon (1984). The chemistry in the lower stratosphere is also dominated by catalytic ozone destruction cycles (Box 2.2). The largest production rates for ozone and reactive nitrogen are found in tropical regions, caused by a maximum in solar radiation. However, also ozone loss rates are largest in that region, leading to a very
short lifetime of ozone. Detailed modeling studies show that less than 50 % of the ozone found at high latitudes is actually produced at tropical latitudes and transported poleward by the large scale meridional circulation. The larger contribution arises from mid- and high-latitude ozone production (Grewe 2006). Water vapor is removed in the upper troposphere by condensation processes in the ascending air masses and at the cold tropopause. The descending air in the polar lower stratosphere stems from the tropical upper stratosphere after a transport time of a few years. Thus, this aged air is rich in ozone and NOy and poor in water vapor (see Fig. 2.3). In the winter polar vortex, ozone is significantly destroyed by chlorine and bromine chemistry in the presence of polar stratospheric clouds. Depletion of
Ozone in the lower stratosphere has a significant impact on the surface UV flux. The highest OH concentrations are present in the tropical middle stratosphere. There are also relatively high OH values in the TTL due to convective uplift of OH precursors. H2O and CO increases in the stratosphere above about 25 km due to their production by the oxidation of CH4. NOy increases in the stratosphere because of the reaction of N2O with excited oxygen atoms, a major source of nitrogen oxides.

In contrast, the upper troposphere is characterized by fast trace gas transport driven by weather systems and convection. The upper troposphere contains significantly lower O3, higher H2O and lower reactive nitrogen mixing ratios than the lower stratosphere. A key reaction in the upper troposphere is the photodissociation of NO2 into NO and O by visible radiation at wavelengths less than 400 nm. The latter immediately recombines with O2 and forms O3. In the upper troposphere, atomic oxygen cannot be formed by the photodissociation of O2 since the required UV radiation is shielded by the stratospheric ozone layer. The role of NOx as catalytic agent in tropospheric ozone formation is described in Box 2.3. During daytime NO and NO2 are in a chemical steady state involving the formation and destruction of NO2 by the reaction of NO with O3 and photolysis, respectively. Formation of NO2 by reactions of NO with peroxy radicals leads to O3 production. The O3 production rate depends on the NOx concentration in the atmosphere. Photodissociation of ozone in the upper troposphere may lead to hydroxyl radicals (OH), the main oxidizing species in the upper troposphere. They react with most trace gases in the troposphere and are therefore often called cleaning agents.

Instrument platforms used to measure the trace gas composition in the UTLS include research aircraft, in-service aircraft, balloons, and satellites and ground-based stations equipped with remote sensing instruments. Airborne measurements
are particularly well suited for studying the UTLS because of the high spatial resolution allowing the observation of small-scale horizontal and vertical structures in the trace gas distributions.

Satellite measurements are an important tool for monitoring the large scale distribution of chemical compounds in the atmosphere and their temporal evolution with global coverage. Important satellite instruments for chemical measurements during recent years were HALOE, GOME, MLS, MIPAS, SCIAMACHY, MOPITT, OMI, and IASI (Burrows et al. 2011). Observations of chemical species from space are discussed elsewhere in this book.

A range of models is used to describe the chemical and transport processes in the UTLS and the future evolution of the chemical composition including trajectory chemistry box models, Lagrangian particle dispersion models, chemistry-transport models, and climate-chemistry models. A recent activity at IPA combines all these model types in a consistent way, enabling an analysis from a box model to a chemistry-climate model using an efficient interface (Jöckel et al. 2006).

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**Box 2.1: Measure of atmospheric composition**

The principle measure of atmospheric composition is the **volume mixing ratio** (also called the mole fraction). It is defined as the number of moles of a trace gas per mole of air (unit mol/mol). It is equivalent to the number density of a trace gas per total number density of air at a given pressure. Volume mixing ratios are commonly given in the following units:

- \( \text{mmol/mmol} \times 10^{-3} \)
- \( \text{pmol/mmol} \times 10^{-12} \)
- \( \text{μmol/mmol} \times 10^{-6} \)
- \( \text{nmol/mmol} \times 10^{-9} \)

**Box 2.2: Ozone production and destruction in the stratosphere**

(a) Pure oxygen chemistry (**Chapman mechanism**):

\[
\begin{align*}
\text{O}_2 + \text{hv} & \rightarrow \text{O} + \text{O} \quad (\lambda < 242 \text{ nm}) \\
2(\text{O} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M}) \\
\text{Net:} \quad 3 \text{O}_2 + \text{hv} & \rightarrow 2 \text{O}_3 \quad \text{(ozone production)} \\
\text{O}_3 + \text{hv} & \rightarrow \text{O} + \text{O}_2 \quad (\lambda < 1200 \text{ nm}) \\
\text{O}_3 + \text{O} & \rightarrow \text{O}_2 + \text{O}_2 \\
\text{Net:} \quad 2 \text{O}_3 + \text{hv} & \rightarrow 3 \text{O}_2 \quad \text{(ozone destruction)}
\end{align*}
\]

(\( \text{hv} \) are photons with a wavelength \( \lambda \), \( \text{M} \) denotes a collision partner, e.g. \( \text{N}_2 \) or \( \text{O}_2 \))
(b) Gas-phase catalytic ozone destruction

\[
X + O_3 \rightarrow OX + O_2 \\
OX + O \rightarrow X + O_2
\]

Net: \( O_3 + O \rightarrow O_2 + O_2 \) (ozone destruction)

(X denotes a radical, e.g. Cl, Br, NO, OH)

(c) Heterogeneous ozone destruction (example)

\[
\text{ClONO}_2 + \text{HCl} (s) \rightarrow \text{HNO}_3(s) + \text{Cl}_2 \\
\text{Cl}_2 + h\nu \rightarrow \text{Cl} + \text{Cl} \\
2(\text{Cl} + O_3 \rightarrow \text{ClO} + O_2) \\
\text{ClO} + \text{ClO} + M \rightarrow \text{Cl}_2\text{O}_2 + M \\
\text{Cl}_2\text{O}_2 + h\nu \rightarrow \text{Cl} + \text{ClO}_2 \\
\text{ClO}_2 + M \rightarrow \text{Cl} + O_2 + M
\]

Net: \( 2 \text{O}_3 + h\nu \rightarrow 3 \text{O}_2 \) (ozone destruction)

(s denotes a compound in the solid state in polar stratospheric clouds)

Box 2.3: Ozone production and destruction in the troposphere

(a) Photostationary state between \( O_3, \text{NO} \) and \( \text{NO}_2 \)

\[
\text{NO} + O_3 \rightarrow \text{NO}_2 + O_2 \\
\text{NO}_2 + h\nu \rightarrow \text{NO} + O (\lambda < 400 \text{ nm}) \\
O + O_2 + M \rightarrow O_3 + M
\]

Net: no change in ozone

(b) Peroxy-radical-assisted ozone production

\[
\text{NO} + \text{RO}_2 \rightarrow \text{NO}_2 + \text{RO} \\
\text{NO}_2 + h\nu \rightarrow \text{NO} + O (\lambda < 400 \text{ nm}) \\
O + O_2 + M \rightarrow O_3 + M
\]

Net: ozone production

(\( \text{RO}_2 \) denotes a peroxy radical, e.g. HO\(_2\), CH\(_3\)O\(_2\); peroxy radicals are formed by reactions of OH with CO, CH\(_4\) and other hydrocarbons)
(c) Major ozone destruction reactions

\[ \text{O}_3 + \text{hv} \rightarrow \text{O}^1(\text{D}) + \text{O}_2(\lambda < 310 \text{ nm}) \]
\[ \text{O}^1(\text{D}) + \text{H}_2\text{O} \rightarrow 2 \text{OH} \]

These two reactions are an important sink of ozone and source of highly reactive OH radicals (O\(^1\)D denotes an oxygen atom in an excited state)

\[ \text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2 \]
\[ \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \]
\[ \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \]

This sequence of reactions constitutes another important sink of ozone in the troposphere.

2.2 Recent Achievements in Understanding the Chemical Composition of the Atmosphere

Important scientific issues relevant for a further understanding of the human impact on the chemical composition of the atmosphere include ozone loss in the lower stratosphere, quantification of important sources of reactive nitrogen including air traffic and lightning, vertical transport of pollution from surface sources by deep convection and frontal uplift, long-range transport, and exchange of trace gases between the upper troposphere and the lower stratosphere. Selected results on these topics with a focus on IPA investigations are presented in this section for polar, mid-latitude and tropical regions. These results were obtained in a variety of national and international projects which are addressed here and in other chapters of this book (Fig. 2.4). The main tools used by IPA were in situ and lidar measurements aboard the DLR research aircraft Falcon and the high-altitude research aircraft Geophysica, long-term measurements aboard an in-service Airbus 340 of Lufthansa in the frame of the CARIBIC project, and model simulations with microphysical chemical box models and global climate-chemistry models of the ECHAM family.

2.2.1 Advances in Understanding the Composition of the Polar Stratosphere and Troposphere

A recovery of the ozone hole in the winter polar stratosphere is expected for about the year 2050 when the anthropogenic chlorine loading in the stratosphere will have decreased to the same level as in the early 1980s. However, the recovery may be delayed because of the impact of climate change (Dameris et al. 1998a). These
predictions are still highly uncertain because some key processes important for the destruction of ozone are not yet fully understood, in particular for the Arctic region. The extent of ozone loss in the Arctic winter polar stratosphere depends, among other factors, on the degree of denitrification (removal of reactive nitrogen oxides). In denitrified air masses, ozone-destroying ClO molecules cannot be bound into nonreactive ClNO3 molecules by reaction with NO. It is now generally conceived that the denitrification in the winter Arctic polar stratosphere occurs mainly via a vertical redistribution of HNO3 by sedimentation of large nitric acid trihydrate (NAT: HNO3·3H2O) particles with diameters in the range 10–20 μm and number densities of 10^{-4}–10^{-3} cm^{-3} (so called NAT rocks). These NAT rocks may form at stratospheric temperatures below about 195 K (−78 °C) and distinctly differ from other typical polar stratospheric clouds (PSC) containing much smaller particles (< 6 μm) with a higher density (10^{-2} cm^{-3}). However, until recently there was only one single observation where these large HNO3 containing particles were detected in the Arctic (Fahey et al. 2001). Also, the formation mechanism for these particles is not yet understood.

The formation and distribution of NAT rocks and the denitrification in the Arctic vortex were key objectives of the projects EUPLEX and RECONCILE in the Arctic winters 2002/2003 and 2009/2010, respectively. Here, IPA performed measurements of NOy contained in the gas-phase and in ice particles aboard the Geophysica high altitude aircraft. During EUPLEX, for the first time NAT rocks could be detected in a very early state of formation at temperatures above the frost point. Thus, these particles did not form on ice but potentially on meteoritic condensation nuclei (Voigt et al. 2005).

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**Fig. 2.4** Aircraft campaigns including chemical measurements performed during the years 2000–2011 with coordination by or participation of IPA. Also included are campaigns foreseen in 2012/2013. The campaign acronyms are explained in Table 2.2
In winter 2010, the Geophysica successfully measured in polar stratospheric clouds. Figure 2.5 shows a photograph taken from the cockpit of the Geophysica during the approach of a PSC on 24 January 2010. The measured NO\textsubscript{y} concentrations within the PSC are depicted in Fig. 2.6. NAT rocks were observed embedded in PSC. During ascent and descent of the Geophysica, evaporating NAT rocks could also be detected below the PSC in the renitrification layer.

<table>
<thead>
<tr>
<th>Year</th>
<th>Campaign Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>EXPORT</td>
<td>European Export of Precursors and Ozone by Long-range Transport</td>
</tr>
<tr>
<td></td>
<td>INCA</td>
<td>Interhemispheric Differences in Cirrus Properties from Anthropogenic Emissions</td>
</tr>
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<td>2001</td>
<td>CONTRACE</td>
<td>Convective Transport of Trace Gases into the Middle and Upper Troposphere over Europe: Budget and Impact on Chemistry</td>
</tr>
<tr>
<td></td>
<td>MINOS</td>
<td>Mediterranean Intensive Oxidant Study</td>
</tr>
<tr>
<td>2003</td>
<td>EUPLEX</td>
<td>European Polar stratospheric cloud and Lee-wave Experiment</td>
</tr>
<tr>
<td>2004</td>
<td>TROCCINOX</td>
<td>Tropical Convection, Cirrus, and Nitrogen Oxides Experiment</td>
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<tr>
<td></td>
<td>ICARTT</td>
<td>International Consortium for Atmospheric Research on Transport and Transformation</td>
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<td>2005</td>
<td>SCOUT-O3</td>
<td>Stratospheric-Climate Links with Emphasis on the UT and LS</td>
</tr>
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<td>2006</td>
<td>AMMA</td>
<td>African Monsoon Multidisciplinary Analysis</td>
</tr>
<tr>
<td></td>
<td>INTEX</td>
<td>The Intercontinental Chemical Transport Experiment</td>
</tr>
<tr>
<td>2007</td>
<td>ASTAR</td>
<td>Arctic Study of Aerosol, Clouds and Radiation</td>
</tr>
<tr>
<td></td>
<td>QUANTIFY</td>
<td>Quantifying the Climate Impact of Global and European Transport Systems</td>
</tr>
<tr>
<td>2008</td>
<td>POLARCAT</td>
<td>Polar Study using Aircraft, Remote Sensing, Surface Measurements and Models, of Climate, Chemistry, Aerosols, and Transport</td>
</tr>
<tr>
<td></td>
<td>CONCERT</td>
<td>Contrail and Cirrus Experiment</td>
</tr>
<tr>
<td>2010</td>
<td>RECONCILE</td>
<td>Reconciliation of essential process parameters for an enhanced predictability of arctic stratospheric ozone loss and its climate interactions</td>
</tr>
<tr>
<td>2011</td>
<td>SHIVA</td>
<td>Stratospheric Ozone: Halogen Impacts in a Varying Atmosphere</td>
</tr>
<tr>
<td>2012</td>
<td>ACCESS</td>
<td>Arctic Climate Change, Economy and Society</td>
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<td></td>
<td>DC3</td>
<td>Deep Convective Clouds and Chemistry</td>
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<td>2013</td>
<td>ML-CIRRUS</td>
<td>Formation, Lifetime, Properties and Radiative/Chemical Impact of Mid-Latitude Cirrus Clouds</td>
</tr>
<tr>
<td></td>
<td>OMO</td>
<td>Oxidation Mechanism Observations</td>
</tr>
</tbody>
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Chemical fingerprints of human activities in the Arctic can also be found at lower altitudes. The Arctic troposphere is a receptor of anthropogenic pollution from North America and Eurasia. Import of emissions from boreal forest fires from North America and Siberia significantly increased during the last decade because of an increase in the frequency and area of the fires. Deposition of imported black carbon decreases the snow albedo and accelerates warming in the Arctic. This may cause unique regional responses including melting of ice sheets and permafrost. Import of pollution into the Arctic was studied during the ASTAR and POLARCAT campaigns in Spitzbergen and Greenland, respectively. The chemical composition in the Arctic during spring and summer was found to be significantly disturbed at altitudes from the lower troposphere to the tropopause region by emissions from forest fires in Canada and Siberia, and to a lesser extent by anthropogenic pollution originating in North America and Asia (Roiger 2011). A multitude of individual pollution plumes could be detected in the European sector of the Arctic during POLARCAT, as well as significantly enhanced background profiles of the pollution tracers PAN and CO (Fig. 2.7). Also, the import of East Asian pollution into the lower stratosphere could be detected for the first time (Roiger et al. 2011).

Fig. 2.5 Polar stratospheric clouds in the lower stratosphere south of Spitzbergen on 24 January 2010 as seen from the Geophysica during a RECONCILE mission flying southbound from Spitzbergen. The PSC layers (dark lines) above the bright horizon are marked with an arrow.

Fig. 2.6 Measurements of total (gas and condensed phase) reactive nitrogen (NO₃) from the Geophysica on 24 January 2010 in a polar stratospheric cloud (PSC). Four NAT rocks were detected during this flight sequence. The background signal is due to NO₃ contained in smaller PSC particles with higher number density.
2.2.2 Advances in Understanding the Composition at Mid-Latitudes

In order to understand the anthropogenic influence on the composition and chemistry of the UTLS over Europe, the impact of surface emissions from Europe and upstream continents, air traffic and lightning need to be quantified. The uplift of emissions from the boundary layer in Europe and Northern America to the upper troposphere by warm conveyor belts and convection was studied in a number of projects including CONTRACE, EXPORT, and ICARTT. Figure 2.8 shows an example of elevated pollution layers of different origin observed during EXPORT in the middle and upper troposphere over Germany (Schlager et al. 2003).

Depicted is a vertical profile of CO, a tracer of polluted boundary layer air, measured over Hanover. Three distinct pollution layers were observed at altitudes between 4 and 8 km originating from different European sources and uplifted either by local thunderstorms in the Hanover area or by a warm front between Geneva and Hanover. The CO mixing ratios measured in the outflow layers are very similar to the mixing ratios observed in the boundary layer near Hanover, indicating little dilution during the fast vertical transport. The pollution layer observed in the upper troposphere between 9.5 and 10.5 km was imported from the USA after being uplifted by a warm conveyor belt over the western North Atlantic.

The impact of aircraft emissions on the composition and chemistry of the UTLS was studied during the projects “Schadstoffe in der Luftfahrt” (“Pollutants from Air Traffic”) and POLINAT (Schumann et al. 2000). Emissions from air traffic are concentrated in major flight corridors over Europe, North America, and...
the North Atlantic at altitudes between 9 and 12 km. A series of Falcon campaigns was performed in the eastern North Atlantic flight corridor. The objective of these

**Fig. 2.8** Elevated pollution layers in the troposphere of various origins, measured with the DLR Falcon during EXPORT. Depicted is the volume mixing ratio of CO, a tracer of pollution from combustion sources at the surface (Schlager 2003)

**Fig. 2.9** Profiles of chemical species and condensation nuclei particles measured in the UTLS over the North Atlantic (composites of all measurements during the POLINAT Falcon campaigns in 1994, 1995 and 1997). Shown are individual measurements and mean values averaged over 1 km intervals (white dots) with standards deviations (Schumann et al. 2000)

the North Atlantic at altitudes between 9 and 12 km. A series of Falcon campaigns was performed in the eastern North Atlantic flight corridor. The objective of these
measurements was to determine the distribution of nitrogen oxides, ozone and tracer species for analysis of the air mass origin (Fig. 2.9). Distinct enhancements of primary and secondary gas emissions from air traffic (NO, NO₂, HNO₃, SO₂) and condensation nuclei (CN) particles could be detected in the flight corridor (Schlager et al. 1997; Schlager et al. 1999; Ziereis et al. 1999). Accompanying model simulations revealed that up to 60% of the NOₓ abundance in the upper troposphere is caused by aircraft emissions, depending on the time of the year and the meteorological situation (Sausen and Köhler 1994; Köhler et al. 1997; Dameris et al. 1998b; Grewe et al. 1999; Meijer et al. 2000; Schumann et al. 2000; Grewe et al. 2002; Grewe et al. 2001).

2.2.3 Advances in the Understanding of the Composition in the Tropics

The source of nitrogen oxides produced by lightning in the tropics represents an important uncertainty in the global budget of reactive nitrogen. According to model simulations, lightning-induced nitrogen oxides contribute about 70% to the NOₓ abundance in the tropical upper troposphere and is responsible for about 30% of the ozone in this region (Grewe 2004). In a series of aircraft campaigns in the tropics (TROCCINOX, SCOUT-O3, AMMA) IPA investigated the NOₓ production by electrified thunderstorms (Huntrieser et al. 2007; Schumann and Huntrieser 2007; Huntrieser et al. 2008; Huntrieser et al. 2009; Huntrieser et al. 2011). Measurements of nitrogen oxides and related chemical compounds were performed in anvils and in the vicinity of strong deep convective systems, as for

Fig. 2.10 An intense thunderstorm system (known as Hector) over the Tiwi Islands north of Darwin, Australia (picture taken from the Falcon during SCOUT-O3)
example the Hector thundercloud (Fig. 2.10). A combination of two or three aircraft with different maximum cruising altitudes were deployed during the tropical campaigns to cover the inflow and outflow regions as well as the top of the thunderclouds (Fig. 2.11).

A composite of all nitric oxide profiles measured with the Falcon and Geophysica aircraft during the TROCCINOX campaign in Brazil in 2005 is depicted in Fig. 2.12. Distinct signatures of fresh lightning-produced NOx were observed in the outflow region of deep convection at altitudes between 9 and 16 km. From these kinds of measurements and accompanying observations of lightning by ground- and space-based systems, a best estimate of the global
nitrogen mass source rate of 5 ± 3 Tg per year could be determined (Schumann and Huntrieser 2007). These measurements were also used to evaluate the simulation of lightning NO\textsubscript{x} in climate-chemistry simulations (Grewe 2009).

Another important trace gas, which has adverse effects on climate, is sulfur dioxide, e.g. Seinfeld and Pandis (1998). SO\textsubscript{2} may undergo conversion to sulfuric acid, a major aerosol precursor. However, observations of SO\textsubscript{2} distribution in the UTLS are very sparse. During recent years IPA performed extensive high-quality SO\textsubscript{2} measurements covering polar, mid-latitude and tropical regions (Fiedler 2007; Fiedler et al. 2009a, b) using chemical ionization mass spectrometry with on-line calibration employing isotopically labeled SO\textsubscript{2} (Speidel et al. 2007). Figure 2.13 shows mean and median SO\textsubscript{2} profiles measured during TROCCINOX, SCOUT-O3, and AMMA. The median mixing ratios are mostly constant in the free troposphere at the different measurement sites; however, the values observed in the tropics (70–90 nmol/mol) are interestingly higher than in Europe (30–40 nmol/mol). This indicates more effective vertical transport of SO\textsubscript{2} in the tropics by more frequent convection. These SO\textsubscript{2} measurements represent the most comprehensive SO\textsubscript{2} data set for the UTLS presently available.

2.3 Outlook

With the extended capabilities of the new research aircraft HALO in terms of payload and range, new opportunities will arise for airborne field studies on the composition of the UTLS. Chemical and particle measurement systems can be combined in one payload in a more comprehensive way than possible so far. Thereby, heterogeneous and multiphase processes involving ice and liquid particles that have the potential to influence the composition of the atmosphere can be investigated in future missions. The impact of large scale dynamic atmospheric features like the Asian monsoon can be studied during long-range flights. The air
composition in the Asian monsoon is affected by emissions from India and eastern China, regions with largely enhanced and increasing levels of anthropogenic pollutants. The transport of these emissions into the lower stratosphere may impact its composition on a global scale. Another important topic is understanding the ozone trends in the upper troposphere and, in this respect, the impact of NOx caused by aviation.

The present highly coupled 3D chemistry-climate models enable global simulations over decades at a resolution of roughly 300 km. Many processes are interactively coupled, like chemistry with radiation, clouds and transport. This complexity of the climate-chemistry model systems often hinders an interpretation of results. Future model developments will have to include specific diagnostics, enabling an analysis of causes and effects (Grewe et al. 2010; Jöckel et al. 2010; Garny et al. 2011). In addition, improvements are required, including a better representation of physical processes and the inclusion of other domains, such as the biosphere.

References


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