
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 $\mu\text{mol/mol}$ (see Box 2.1) to fmol/mol (Fig. 2.1). The *atmospheric lifetime* of the chemical compounds varies from a few seconds to

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Table 2.1 Molecular formulas and chemical compounds

| Formula | Compound | Formula | Compound |
|------------------------------------|--------------------------|------------------|--------------------------------|
| Ar | argon | NH ₃ | ammonia |
| CH ₄ | <i>methane</i> | N ₂ O | <i>dinitrogen oxide</i> |
| (CH ₃) ₂ CO | <i>acetone</i> | NO | <i>nitric oxide</i> |
| ClO | <i>chlorine monoxide</i> | NO ₂ | <i>nitrogen dioxide</i> |
| ClONO ₂ | chlorine nitrate | NO _x | <i>nitrogen oxides</i> |
| CO | <i>carbon monoxide</i> | NO _y | <i>total reactive nitrogen</i> |
| CO ₂ | <i>carbon dioxide</i> | O ₂ | molecular oxygen |
| DMS | dimethyl sulfide | O ₃ | <i>ozone</i> |
| HCl | <i>hydrogen chloride</i> | OH | <i>hydroxyl radical</i> |
| HNO ₂ | <i>nitrous acid</i> | OCS | carbonyl sulfide |
| HNO ₃ | <i>nitric acid</i> | PAN | <i>peroxyacetyl nitrate</i> |
| H ₂ O | <i>water</i> | PFC | <i>perfluorocarbons</i> |
| H ₂ SO ₄ | <i>sulfuric acid</i> | SO ₂ | <i>sulfur dioxide</i> |
| N ₂ | molecular nitrogen | VOC | volatile organic compounds |

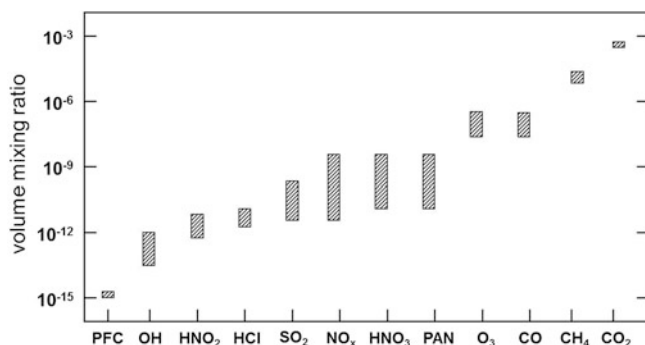


Fig. 2.1 Range of concentrations for atmospheric trace gases. All denoted compounds are measured by the Institute of Atmospheric Physics (IPA) with airborne *in situ* instruments using a variety of techniques including thermo desorption *gas chromatography* (PFC is used for active tracer experiments because of the very low atmospheric concentrations), *chemiluminescence* (NO_x), *chemical ionization mass spectrometry* (OH, SO₂, HCl, HNO₂, HNO₃, PAN), *ultraviolet (UV) absorption* (O₃), *UV fluorescence* (CO), and *cavity ring-down spectrometry* (CH₄, CO₂)

more than 1 000 years. Most of the long-lived trace gases, including CO₂, CH₄, N₂O 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 O₃, are chemically or *photochemically*

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 (H_2SO_4), 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: CO_2 , SO_2 , NO_x , hydrocarbons), gas and oil production (CH_4 , VOC), *traffic* (CO_2 , NO_x , CO), agriculture (CH_4 , N_2O , NH_3), *vegetation* (volatile organic carbon compounds), *volcanoes* (SO_2 , *halogens*), and *oceans* (N_2O , 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 O_3 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 O_3 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 O_2 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

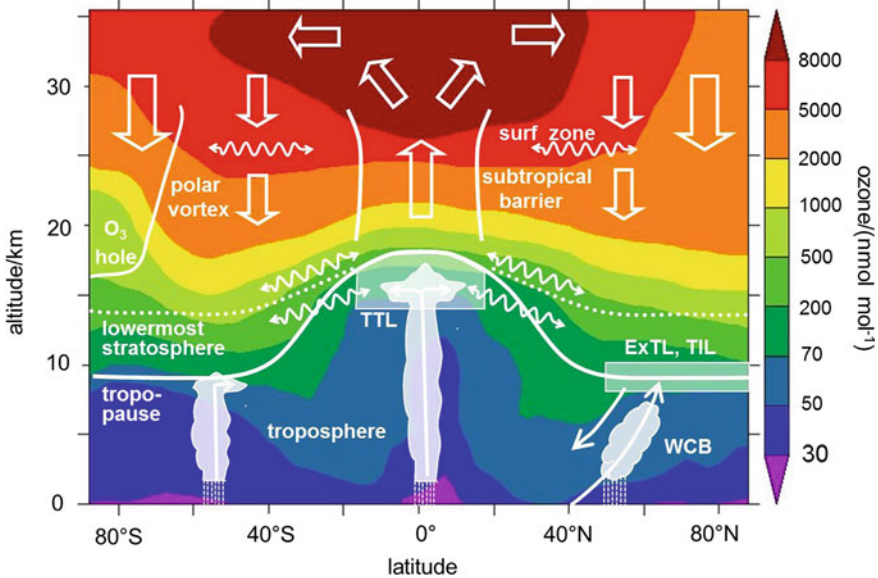


Fig. 2.2 Zonal (longitudinal) averaged ozone distribution for September (EMAC simulation) and schematic of distinct regions and important transport processes in the upper troposphere and lower stratosphere (UTLS). The mean tropopause (TP) is plotted (solid white curve). The region near the TP represents a transition layer (TTL—Tropical Transition Layer, ExTL—Extratropical Tropopause Layer) with characteristics intermediate to the UT and LS. The arrows indicate long-term mean transport pathways. In the lower stratosphere, slow downward transport occurs poleward of the subtropical barrier, while ascent of air masses occurs in the tropics. In the so called surf-zone, efficient horizontal exchange of air masses takes place. Fast upward transport of air from the Earth surface is caused by deep convective clouds in the tropics and mid-latitudes and by warm conveyor belts (WCB) associated with the warm fronts of mid-latitude cyclones. Quasi-horizontal air mass exchanges occur between the TTL and the LS. The stratosphere in the tropics and subtropics is a main ozone production region. The ozone concentration in the LS is higher in the spring hemisphere (here the southern hemisphere) due to air mass transport by the large-scale meridional circulation. However, in the polar vortex ozone is depleted due to anthropogenic ozone destruction (ozone hole in the Antarctic region). The lowest ozone concentrations are found in the atmospheric boundary layer in the tropics and mid/high latitudes in the southern hemisphere. Convective vertical transport in these regions also causes low ozone abundances in the UT and TTL.

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 NO_y 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

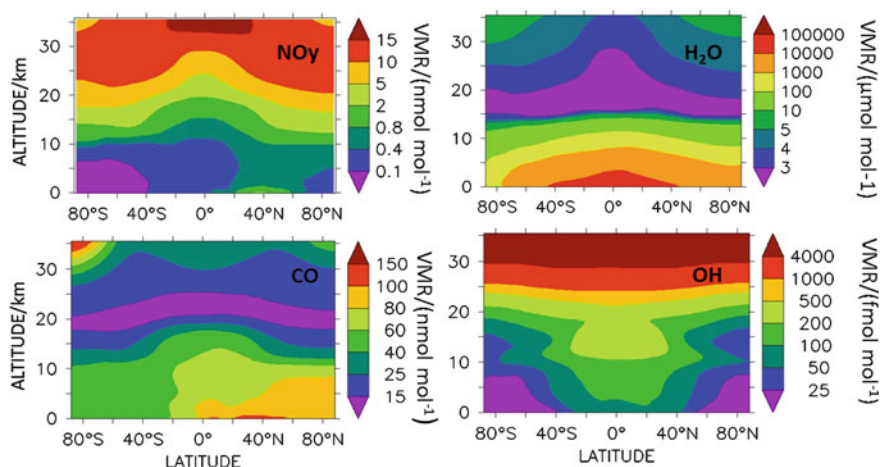


Fig. 2.3 Zonal and annual mean distributions of total reactive nitrogen (NO_y), CO, H_2O , and OH as calculated with the EMAC global chemistry-climate model of IPA. Note the nonlinearly distributed contour intervals

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. H_2O and CO increases in the stratosphere above about 25 km due to their production by the oxidation of CH_4 . NO_y increases in the stratosphere because of the reaction of N_2O 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 O_3 , higher H_2O and lower reactive nitrogen mixing ratios than the lower stratosphere. A key reaction in the upper troposphere is the photodissociation of NO_2 into NO and O by visible radiation at wavelengths less than 400 nm. The latter immediately recombines with O_2 and forms O_3 . In the upper troposphere, atomic oxygen cannot be formed by the photodissociation of O_2 since the required UV radiation is shielded by the stratospheric *ozone layer*. The role of NO_x as catalytic agent in tropospheric ozone formation is described in Box 2.3. During daytime NO and NO_2 are in a chemical steady state involving the formation and destruction of NO_2 by the reaction of NO with O_3 and photolysis, respectively. Formation of NO_2 by reactions of NO with peroxy radicals leads to O_3 production. The O_3 production rate depends on the NO_x 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).

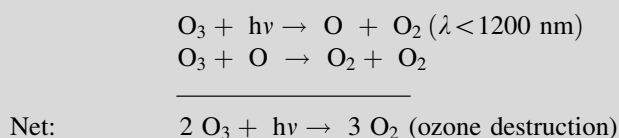
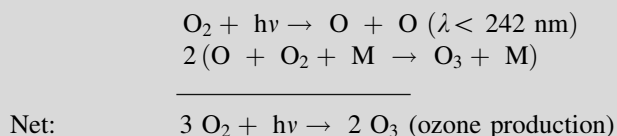
Box 2.1: Measure of atmospheric composition

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:

$$\begin{array}{ll} \text{mmol/mol } (10^{-3}) & \text{pmol/mol } (10^{-12}) \\ \mu\text{mol/mol } (10^{-6}) & \text{fmol/mol } (10^{-15}) \\ \text{nmol/mol } (10^{-9}) & \end{array}$$

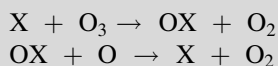
Box 2.2: Ozone production and destruction in the stratosphere

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



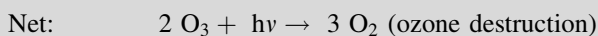
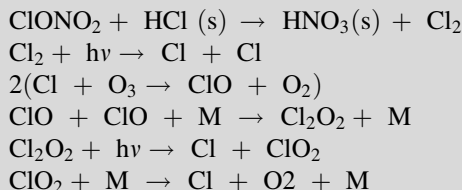
($h\nu$ are photons with a wavelength λ , M denotes a collision partner, e.g. N_2 or O_2)

(b) Gas-phase catalytic ozone destruction

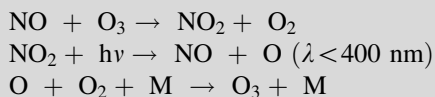


(X denotes a radical, e.g. Cl, Br, NO, OH)

(c) Heterogeneous ozone destruction (example)

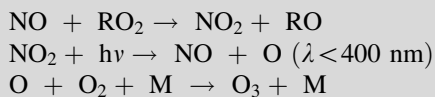


(s denotes a compound in the solid state in polar stratospheric clouds)

Box 2.3: Ozone production and destruction in the troposphere(a) Photostationary state between O_3 , NO and NO_2 

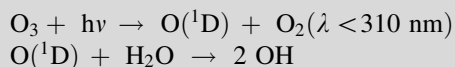
Net: no change in ozone

(b) Peroxy-radical-assisted ozone production

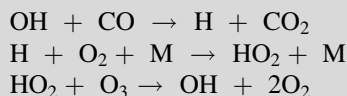


Net: ozone production

(RO_2 denotes a peroxy radical, e.g. HO_2 , CH_3O_2 ; peroxy radicals are formed by reactions of OH with CO, CH_4 and other hydrocarbons)

(c) Major *ozone destruction* reactions

These two reactions are an important sink of ozone and source of highly reactive OH radicals (O¹D denotes an oxygen atom in an excited state)



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



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

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 ClONO₂ 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, 3 H₂O) 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 NO_y 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).

Table 2.2 Airborne campaigns in the years 2000–2013 with chemical measurements involving IPA as coordinator or participant

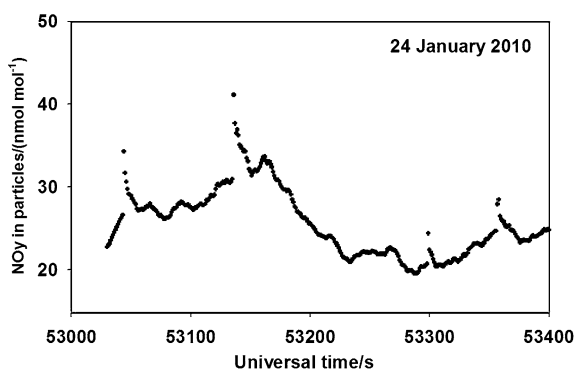
| | | |
|------|-----------|---|
| 2000 | EXPORT | European Export of Precursors and Ozone by Long-range Transport |
| | INCA | Interhemispheric Differences in Cirrus Properties from Anthropogenic Emissions |
| 2001 | CONTRACE | Convective Transport of Trace Gases into the Middle and Upper Troposphere over Europe: Budget and Impact on Chemistry |
| | MINOS | Mediterranean Intensive Oxidant Study |
| 2003 | EUPLEX | European Polar stratospheric cloud and Lee-wave Experiment |
| 2004 | TROCCINOX | Tropical Convection, Cirrus, and Nitrogen Oxides Experiment |
| | ICARTT | International Consortium for Atmospheric Research on Transport and Transformation |
| 2005 | SCOUT-O3 | Stratospheric-Climate Links with Emphasis on the UT and LS |
| 2006 | AMMA | African Monsoon Multidisciplinary Analysis |
| | INTEX | The Intercontinental Chemical Transport Experiment |
| 2007 | ASTAR | Arctic Study of Aerosol, Clouds and Radiation |
| | QUANTIFY | Quantifying the Climate Impact of Global and European Transport Systems |
| 2008 | POLARCAT | Polar Study using Aircraft, Remote Sensing, Surface Measurements and Models, of Climate, Chemistry, Aerosols, and Transport |
| | CONCERT | Contrail and Cirrus Experiment |
| 2010 | RECONCILE | Reconciliation of essential process parameters for an enhanced predictability of arctic stratospheric ozone loss and its climate interactions |
| 2011 | SHIVA | Stratospheric Ozone: Halogen Impacts in a Varying Atmosphere |
| 2012 | ACCESS | Arctic Climate Change, Economy and Society |
| | DC3 | Deep Convective Clouds and Chemistry |
| | TACTS | Transport and Composition in the UT/LMS |
| | ESMVal | Earth System Model Validation |
| 2013 | ML-CIRRUS | Formation, Lifetime, Properties and Radiative/Chemical Impact of Mid-Latitude Cirrus Clouds |
| | OMO | Oxidation Mechanism Observations |

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_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.



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 (NO_y) 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 NO_y contained in smaller PSC particles with higher number density



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).

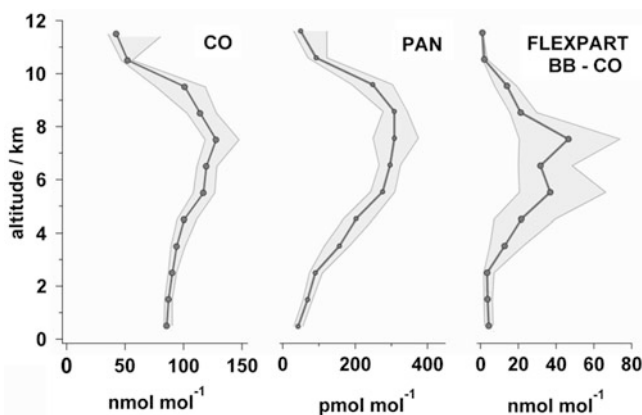


Fig. 2.7 Mean profiles of CO and PAN volume mixing ratios averaged over all Falcon flights in the European sector of the Arctic in summer 2008 during the POLARCAT campaign, including standard deviations (*shaded area*). Also shown are simulations with the FLEXPART model of a biomass burning (BB) CO tracer interpolated onto the Falcon flight tracks. The FLEXPART results indicate that the observed enhanced CO and PAN mixing ratios at altitudes between 4 and 10 km can be explained by the import of biomass burning emissions from Canada and Siberia (Roiger 2011)

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

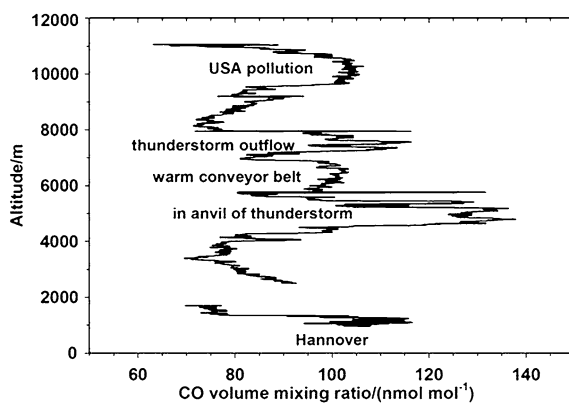


Fig. 2.8 Elevated pollution layers in the troposphere of various origins, measured with the DLR Falcon during EXPORT. Depicted is the volume mixing ratio of CO, a tracer of pollution from combustion sources at the surface (Schlager 2003)

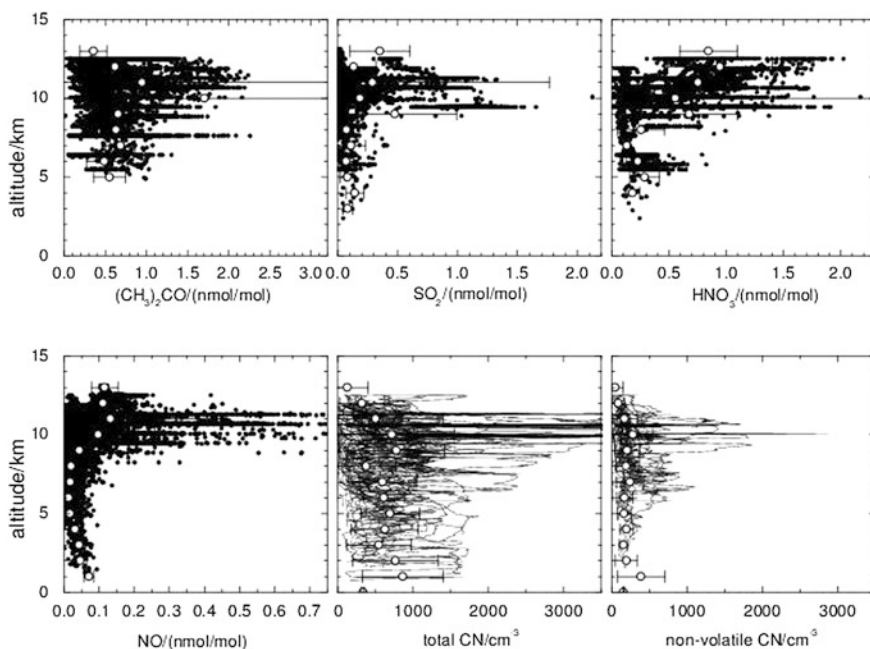


Fig. 2.9 Profiles of chemical species and condensation nuclei particles measured in the UTLS over the North Atlantic (composites of all measurements during the POLINAT Falcon campaigns in 1994, 1995 and 1997). Shown are individual measurements and mean values averaged over 1 km intervals (*white dots*)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



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)

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 , NO_y , HNO_3 , SO_2) 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 NO_x 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 NO_x 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 NO_x 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. 2.11 Research aircraft deployed during the second TROCCINOX campaign in Aracatuba, Brazil in 2005 (*left* DLR Falcon, *center* Geophysica of Myasishchev Design Bureau, Russia, *right* Bandeirante of Brazilian partners) and the campaign team

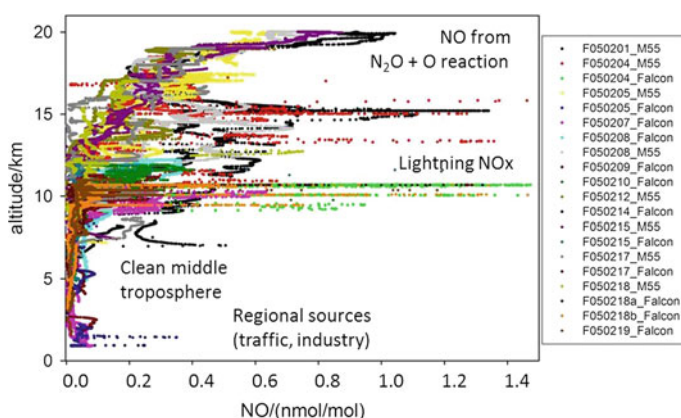


Fig. 2.12 Composite of all NO measurements aboard the Falcon and Geophysica M55 during the TROCCINOX campaign in 2005

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 NO_x 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

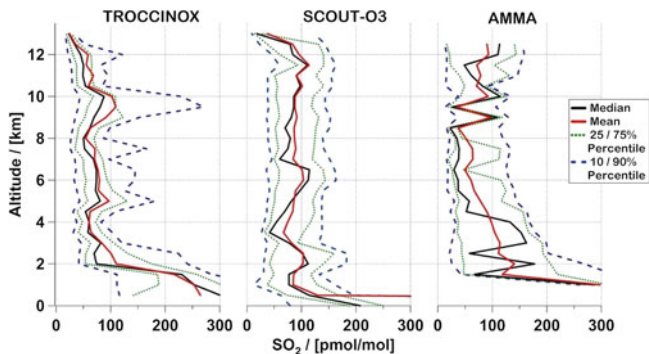


Fig. 2.13 Median (*black*) and mean (*red*) SO_2 volume mixing ratios from Falcon campaigns in the tropics. Also included are 10, 25, 75 and 90 % percentiles (Fiedler 2007)

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_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_2 may undergo conversion to sulfuric acid, a major aerosol precursor. However, observations of SO_2 distribution in the UTLS are very sparse. During recent years IPA performed extensive high-quality SO_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_2 (Speidel et al. 2007). Figure 2.13 shows mean and median SO_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_2 in the tropics by more frequent convection. These SO_2 measurements represent the most comprehensive SO_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 NO_x 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

- Brasseur, G., Solomon, S.: Aeronomy of the middle atmosphere. D. Reidel Publishing Company, Dordrecht (1984)
- Brasseur, G.P., Prinn, R.G., Pszenney, A.P. (eds.): Atmospheric chemistry in a changing world. Springer, Berlin (2003)
- Burrows, J.P., Platt, U., Borrell, P. (eds.): The remote sensing of tropospheric composition from space. Springer, Berlin (2011)
- Dameris, M., Grewe, V., Hein, R., Schnadt, C., Brühl, C., Steil, B.: Assessment of the future development of the ozone layer. Geophys. Res. Lett. **25**, 3579–3582 (1998a)
- Dameris, M., Grewe, V., Köhler, I., Sausen, R., Brühl, C., Grooß, J.-U., Steil, B.: Impact of aircraft NO_x -emissions on tropospheric and stratospheric ozone. Part II: 3-D model results. Atmos. Env. **32**, 3185–3200 (1998b)
- Dameris, M., Grewe, V., Ponater, M., Deckert, R., Eyring, V., Mager, F., Matthes, S., Schnadt, C., Stenke, A., Steil, B., et al.: Long-term changes and variability in a transient simulation with a chemistry-climate model employing realistic forcing. ACP **5**, 2121–2145 (2005)
- Fahey, D.W., Gao, R.S., Carslaw, K.S., et al.: The detection of large HNO_3 -containing particles in the winter Arctic stratosphere. Science **291**, 1026–1031 (2001)
- Fiedler, V.: Atmospheric SO_2 : global measurements using aircraft-based CIMS. Dissertation, DLR-Forschungsbericht, Ruprecht-Karls Universität Heidelberg, pp. 1434–8454 (2007)
- Fiedler, V., Arnold, F., Schlager, H., Dörnbrack, A., Pirjola, L., Stohl, A.: East Asian SO_2 pollution plume over Europe—Part 1: evolution and potential impact. Atmos. Chem. Phys. **9**, 4729–4745 (2009a). doi:[10.5194/acp-9-4729-2009](https://doi.org/10.5194/acp-9-4729-2009)
- Fiedler, V., Nau, R., Ludmann, S., Arnold, F., Schlager, H., Stohl, A.: East Asian SO_2 pollution plume over Europe—Part 2: Airborne trace gas measurements and source identification by particle dispersion model simulations. Atmos. Chem. Phys. **9**, 4717–4728 (2009b). doi:[10.5194/acp-9-4717-2009](https://doi.org/10.5194/acp-9-4717-2009)
- Garny, H., Grewe, V., Dameris, M., Bodeker, G.E., Stenke, A.: Attribution of ozone changes to dynamical and chemical processes in CCMs and CTMs. Geosci. Model Dev. **4**, 271–286 (2011). doi:[10.5194/gmd-4-271-2011](https://doi.org/10.5194/gmd-4-271-2011)
- Grewe, V.: The origin of ozone. Atmos. Chem. Phys. **6**, 1495–1511 (2006). doi:[10.5194/acp-6-1495-2006](https://doi.org/10.5194/acp-6-1495-2006)

- Grewe, V., Dameris, M., Hein, R., Köhler, I., Sausen, R.: Impact of future subsonic aircraft NO_x emissions on the atmospheric composition. *Geophys. Res. Lett.* **26**, 47–50 (1999). doi:[10.1029/1998GL900249](https://doi.org/10.1029/1998GL900249)
- Grewe, V., Dameris, M., Fichter, C., Sausen, R.: Impact of aircraft NO_x emissions. Part 1: Interactively coupled climate-chemistry simulations and sensitivities to climate-chemistry feedback, lightning and model resolution. *Meteor. Z.* **11**, 177–186 (2002)
- Grewe, V.: Technical note: A diagnostic for ozone contributions of various NO_x emissions in multi-decadal chemistry-climate model simulations. *Atmos. Chem. Phys.* **4**, 327–342 (2004)
- Grewe, V.: Impact of lightning on air chemistry and climate. In: Betz, H.D., Schumann, U., Laroche, P. (eds.) *Lightning: principles, instruments and applications review of modern lightning research*, pp. 524–551. Springer, Dordrecht (2009)
- Grewe, V., Tsati, E., Hoor, P.: On the attribution of contributions of atmospheric trace gases to emissions in atmospheric model applications. *Geosci. Model Dev.* **3**, 487–499 (2010)
- Grewe, V., Brunner, D., Dameris, M., Grenfell, J.L., Hein, R., Shindell, D., Staehelin, J.: Origin and variability of upper tropospheric nitrogen oxides and ozone at northern mid-latitudes. *Atmos. Env.* **35**, 3421–3433 (2001). doi:[10.1016/S1352-2310\(01\)00134-0](https://doi.org/10.1016/S1352-2310(01)00134-0)
- Hein, R., Dameris, M., Schnadt, C., Land, C., Grewe, V., Köhler, I., Ponater, M., Sausen, R., Steil, B., Landgraf, J., et al.: Results of an interactively coupled atmospheric chemistry-general circulation model: Comparison with observations. *Ann. Geophys.* **19**, 435–457 (2001)
- Huntrieser, H., Schlager, H., Roiger, A., Lichtenstern, M., Schumann, U., Kurz, C., Brunner, D., Schwierz, C., Richter, A., Stohl, A.: Lightning-produced NO_x over Brazil during TROCCI-NOX: airborne measurements in tropical and subtropical thunderstorms and the importance of mesoscale convective systems. *Atmos. Chem. Phys.* **7**, 2987–3013 (2007). doi:[10.5194/acp-7-2987-2007](https://doi.org/10.5194/acp-7-2987-2007)
- Huntrieser, H., Schumann, U., Schlager, H., Höller, H., Giez, A., Betz, H.-D., Brunner, D., Forster, C., Pinto Jr, O., Calheiros, R.: Lightning activity in Brazilian thunderstorms during TROCCINOX: implications for NO_x production. *Atmos. Chem. Phys.* **8**, 921–953 (2008). doi:[10.5194/acp-8-921-2008](https://doi.org/10.5194/acp-8-921-2008)
- Huntrieser, H., Schlager, H., Lichtenstern, M., Roiger, A., Stock, P., Minikin, A., Höller, H., Schmidt, K., Betz, H.-D., Allen, G., et al.: NO_x production by lightning in Hector: first airborne measurements during SCOUT- O_3 /ACTIVE. *Atmos. Chem. Phys.* **9**, 8377–8412 (2009). doi:[10.5194/acp-9-8377-2009](https://doi.org/10.5194/acp-9-8377-2009)
- Huntrieser, H., Schlager, H., Lichtenstern, M., Stock, P., Hamburger, T., Höller, H., Schmidt, K., Betz, H.-D., Ulanovsky, A., Ravegnani, F.: Mesoscale convective systems observed during AMMA and their impact on the NO_x and O_3 budget over West Africa. *Atmos. Chem. Phys.* **11**, 2503–2536 (2011). doi:[10.5194/acp-11-2503-2011](https://doi.org/10.5194/acp-11-2503-2011)
- Jöckel, P., Tost, H., Pozzer, A., Brühl, C., Buchholz, J., Ganzeveld, L., Hoor, P., Kerkweg, A., Lawrence, M., Sander, R., et al.: The atmospheric chemistry general circulation model ECHAM5/MESSy1: consistent simulation of ozone from the surface to the mesosphere. *Atmos. Chem. Phys.* **6**, 5067–5104 (2006). doi:[10.5194/acp-6-5067-2006](https://doi.org/10.5194/acp-6-5067-2006)
- Jöckel, P., Kerkweg, A., Pozzer, A., Sander, R., Tost, H., Riede, H., Baumgaertner, A., Gromov, S., Kern, B.: Development cycle 2 of the modular earth submodel system (MESSy2). *Geosci. Model Dev.* **3**, 717–752 (2010). doi:[10.5194/gmd-3-717-2010](https://doi.org/10.5194/gmd-3-717-2010)
- Köhler, I., Sausen, R., Reinberger, R.: Contributions of aircraft emissions to the atmospheric NO_x content. *Atmos. Environ.* **31**, 1801–1818 (1997)
- Meijer, E.W., van Velthoven, P.F.J., Thompson, A.M., Pfister, L., Schlager, H., Schulte, P., Kelder, H.: Model calculations of the impact of NO_x from air traffic, lightning, and surface emissions, compared with measurements. *J. Geophys. Res.* **105**, 3833–3850 (2000). doi:[10.1029/1999JD901052](https://doi.org/10.1029/1999JD901052)
- Paffrath, D.: Airborne chemistry measurements. In: *Proceedings of Remote Sensing and The Earth's Environment*, ESA, Alpbach Summer School, Alpbach, Austria, 26 July–4 August 1989, pp.43–49 (1990)

- Roiger, A.: Biomass burning pollution in the summer time Arctic atmosphere: development and deployment of a novel CI-ITMS instrument for PAN detection. Dissertation, Universität Heidelberg (2011)
- Roiger, A., Schlager, H., Schaeffler, A., Huntrieser, H., Scheibe, M., Aufmhoff, H., Cooper, O.R., Sodemann, H., Stohl, A., Burkhart, J.: In situ observation of Asian pollution transported into the Arctic lowermost stratosphere. *Atmos. Chem. Phys.* **11**, 10975–10994 (2011)
- Sausen, R., Köhler, I.: Simulating the global transport of nitrogen oxides emissions from aircraft. *Ann. Geophys.* **12**, 394–402 (1994)
- Schlager, H., Konopka, P., Schulte, P., Schumann, U., Ziereis, H., Arnold, F., Klemm, M., Hagen, D., Whitefield, P., Ovarlez, J.: In situ observations of air traffic emission signatures in the North Atlantic flight corridor. *J. Geophys. Res.* **102**, 10739–10750 (1997)
- Schlager, H., Schulte, P., Flato, F., Slemr, F., van Velthoven, P., Ziereis, H., Schumann, U.: Regional nitric oxide enhancements in the North Atlantic flight corridor observed and modeled during POLINAT 2—a case study. *Geophys. Res. Lett.* **26**, 3061–3064 (1999). doi:[10.1029/1999GL900349](https://doi.org/10.1029/1999GL900349)
- Schlager, H., Huntrieser, H., Heland, J., Ziereis, H.: Analysis of convective and long-range transport of reactive nitrogen species over Europe using aircraft observations. EXPORT-E2 Final Report, EUROTRAC-2 ISS, Penkett, S., Law, K.S., Platt, U., Volz-Thomas, A. (eds.) GSF—National Research Center for Environment and Health, Munich, Germany, pp.151–155 (2003)
- Schumann, U., Schlager, H., Arnold, F., Ovarlez, J., Kelder, H., Hov, Ø., Hayman, G., Isaksen, I.S.A., Staehelin, J., Whitefield, P.D.: Pollution from aircraft emissions in the North Atlantic flight corridor: Overview on the POLINAT projects. *J. Geophys. Res.* **105**, 3605–3631 (2000). doi:[10.1029/1999JD900941](https://doi.org/10.1029/1999JD900941)
- Schumann, U., Huntrieser, H.: The global lightning-induced nitrogen oxides source. *Atmos. Chem. Phys.* **7**, 3823–3907 (2007). doi:[10.5194/acp-7-3823-2007](https://doi.org/10.5194/acp-7-3823-2007)
- Seinfeld, J.H., Pandis, S.N.: Atmospheric chemistry and physics. Wiley, New York (1998)
- Speidel, M., Nau, R., Arnold, F., Schlager, H., Stohl, A.: Sulfur dioxide measurements in the lower, middle and upper troposphere: Deployment of an aircraft-based chemical ionization mass spectrometer with permanent in-flight calibration. *Atmos. Env.* **41**, 2427–2437 (2007). doi:[10.1016/j.atmosenv.2006.07.047](https://doi.org/10.1016/j.atmosenv.2006.07.047)
- Steil, B., Dameris, M., Brühl, C., Crutzen, P.J., Grewe, V., Ponater, M., Sausen, R.: Development of a chemistry module for GCMs: first results of a multiannual integration. *Ann. Geophys.* **16**, 205–228 (1998)
- Voigt, C., Schlager, H., Luo, B.P., Dörnbrack, A., Roiger, A., Stock, P., Curtius, J., Vössing, H., Borrmann, S., Davies, S., et al.: Nitric Acid Trihydrate (NAT) Formation at Low NAT Supersaturation in Polar Stratospheric Clouds (PSCs). *Atmos. Chem. Phys.* **5**, 1371–1380 (2005). doi:[10.5194/acp-10-9039-2010](https://doi.org/10.5194/acp-10-9039-2010)
- Ziereis, H., Schlager, H., Schulte, P., Köhler, I., Marquardt, R., Feigl, C.: In situ measurements of the NO_x distribution and variability over the eastern North Atlantic. *J. Geophys. Res.* **104**, 16021–16032 (1999). doi:[10.1029/1999JD900175](https://doi.org/10.1029/1999JD900175)

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